Università degli Studi di Torino
Doctoral School of the University of Turin
Ph.D. Program in Innovation for the Circular Economy XXXIV Cycle

CIRCULAR ECONOMY AND SUSTAINABILITY ASSESSMENT AS STRATEGIES FOR MATERIALS SELECTION IN THE ENERGY SECTOR

Ph.D. candidate: **Nicole Mariotti**

Supervisor: Prof. **Claudia Barolo**

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ABBREVIATIONS

Amorphous silicon	α-Si
Balance of system	BoS
Building-integrated photovoltaics	BIPV
Carbon PayBackTime	CPBT
Chlorophyll	Chl
Cumulative Energy Demand	CED
Counter Electrode	CE
Critical Raw Material	CRM
Donor−π−Acceptor	D-π-A
Deep Eutectic Solvent	DES
Dye-Sensitized Solar Cell	DSSC
Ecotoxicity potential	ETP
Electron Transporting Layer	ETL
End-of-Life	EoL
Energy PayBackTime	EPBT
European Chemical Society	EuChemS
European Union	EU
Fill Factor	FF
Fluorine Tin Oxide	FTO
Greenhouse gas	GHG
Hole Transporting Material	HTM
Highest Occupied Molecular Orbital	
Human Toxicity Potential	HTP
Indene-C60 bis-adduct	ICBA
Indium Tin Oxide	ITO
International Energy Agency	IEA
Incident Photon-to-electron Conversion Efficiency	IPCE
International Renewable Energy Agency	IRENA
Short-circuit current density	J_{sc}
Life Cycle Assessment	LCA
Lowest Unoccupied Molecular Orbital	LUMO
Monocrystalline Silicon	m-Si
Open-Circuit Voltage	V_{oc}
Organic Photovoltaic	OPV
Oxygen Transmission Rate	OTR
Power Conversion Efficiency	PCE
Perovskite Solar Cell	PSC
Polylactic acid	PLA
Poly(3-hexylthiophene)	P3HT
Polyethylene Terephalate	PET

Poly(3,4-ethylenedioxythiophene)	PEDOT
Polyurethane	PU
Polyvinyl alcohol	PVA
Rare Earths	RE
Reactive Oxygen Species	ROS
Restriction of hazardous Substances Directive	RoHS
Room Temperature Ionic Liquid	RTIL
Sustainability assessment	SA
Sustainable Development Goal	SDG
Triple Bottom Line	TBL
Bis(trifluoromethanesulfonyl)imide	TFSI
Water Vapour Transmission Rate	WVTR
[6,6]-Phenyl C_{61} butyric acid methyl ester	PCBM
4,4-bis(2-ethylhexyl)-4Hsilolo[3,2-b:4,5-b′]dithiophene	DTS

1. Materials, circular economy, and sustainable development

The “green” and digital transitions are the two crucial revolutions our productive system is facing. In this context, materials have a pivotal role; the enabling technologies for these two revolutions currently depend on several materials (**Figure 1**) which are or will become new valuable resources as important as oil.[1] For instance, lithium and cobalt are key elements for battery production, while rare earths are present in our phones, laptops, and renewable energy technologies.[2]

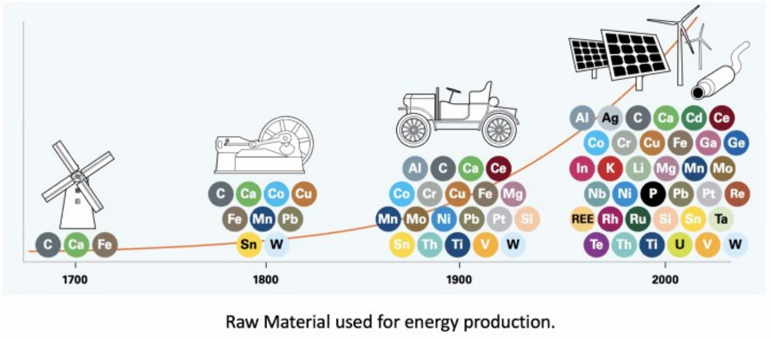


Figure 1 Elements used in energy technologies. Adapted from Zepf et al.[3]

The increasing importance of these materials is generating new commercial and geopolitical issues: monopolistic supply chains, price volatility, and supply disruption might threaten materials’ cost and reliability.[2]

For instance, in 2010, China was producing 97% of the world’s rare earths (RE) supply and between early 2010 and July 2011, the neodymium price increased from $25/kg to a peak value of $340/kg. In 2012, the Chinese government released two documents (“*Interim Measures for the Administration of RE Mandatory Production Plan*” and the “*Measures for the Administration of Total Mining Quota*”) to enhance the implementation of the production quota and control the total amount of RE products on the market. These choices led China to a dispute with the World Trade Organization: China canceled its export quota and export tax on RE products in 2015.[4] In

2021, during the Covid-19 pandemic, strong global market demand and rapid China's economic recovery lead the world to a shortage of many raw materials.[5]

It is obvious that strategic materials management is crucial to guarantee a secure supply. Moreover, nowadays, it is essential that this strategy should also comply with environmental conservation aspects.[6] Resource extraction and processing make up about half of the total global greenhouse gas (GHG) emissions and more than 90 percent of land- and water-related impacts (biodiversity loss and water stress).[7] Along with emissions, annual waste generation is projected to increase by 70% by 2050.[8]

Along with Green Economy and Bioeconomy, one of the suggested solutions to achieve a more secure and less impactful supply chain is the Circular Economy (CE).[9] All these strategies present a strong technical orientation (engineering, environmental sciences) in the research environment. Consequently, in the literature, there is often a call for 'more comprehensive and holistic approaches'.[10]

In particular, CE emphasizes the enhancement of the value embedded in material and energy and the importance of the system thinking in production-consumption processes. Concepts like reduction of material and low energy requirements; long-term maintenance and repair; sharing, reuse, refurbishing and remanufacturing, repurposing; recycling and reclassification of waste into inorganic and biological components; and renewability of energy sources are extremely important in a CE vision.[9–11] The literature, however, criticise CE for lacking of a societal and institutional restructuring perspective. The problem of how the incorporation of social and consumption-based issues may be achieved remains largely unresolved. When these complex socioeconomic factors are included, the environmental outcome of the circular economy becomes ambiguous. It turns out that simply closing material loops is not enough to guarantee environmental improvement.

Finally, it is worth mentioning CE rebounds[12] that are unintended consequences leading to negative sustainability outcomes that cannot be entirely ruled out. Such negative sustainability effects threaten the CE-sustainable development relationship.

1.1 Circular Economy and sustainability

Circular Economy is an antonym of linear economy. It is an economic paradigm aiming at better using resources and reducing waste and emissions than linear *take-make-dispose* system.[10] However, its definition is not obvious and circularity is not always a sufficient condition to achieve ameliorated environmental performances.[13]

In 2017, Kirchherr *et al.*[11] discussed the conceptualization of Circular Economy through the analysis of 114 definitions; hence, it is clear that its definition is blurred.[14] Even if Circular Economy has gained notoriety in the last years,[6] some of basic concepts have been already outlined many years ago. In 1966, the economist Kenneth Boulding wrote about "a stable, *closed-cycle*, high-level technology" in his seminal paper "The economics of the coming spaceship Earth".[15] Then, in the '70s, many practical developments have been suggested as the "*regenerative* design" concept proposed by John Lyle[16], the "*cradle-to-cradle*"[17] idea conceptualized by William McDonough and Michael Braungart and the "*extension* of goods *use-life*" promoted by Walter Stahel.[10] Finally, Pearce and Turner[18] formally reported the CE as an economic model for the first time, in 1990.

Despite the plethora of definitions, concepts and discussions on the CE, one of the most prominent Circular Economy definition[10,11,19] has been provided by Ellen MacArthur Foundation[6] which reads:

> *"[Circular Economy] an industrial system that is restorative or regenerative by intention and design. It replaces the 'end-of-life' concept with restoration, shifts towards the use of renewable energy, eliminates the use of toxic chemicals, which impair reuse,*

> *and aims for the elimination of waste through the superior design of materials, products, systems, and, within this, business models."*

Nowadays, Circular Economy is presented in many research projects and policy frameworks as a tool to achieve a sustainable development.[10,20,21] In this context, many researchers[10,22] investigated the differences between circular economy and sustainability. In 2017, Geissdoerfer *et al.*[10] published a paper titled "The Circular Economy – A new sustainability paradigm?" which reached more than 1900 citations in only five years. The authors[10] underline as the CE clearly seems to prioritise the economic system with primary benefits for the environment, and only implicit gains for social aspects. These aspects are still an important research questions for many researchers who aim at clarifying the main differences.[9,23]

The hierarchy between economy, environment and society does not completely match with the holistic view suggested by the Brundtland Report in 1987 in which sustainable development is presented as

> "*the development that meets the needs of the present without compromising the ability of future generations to meet their own needs*".[24]

Circularity itself does not ensure social, economic, and environmental performance (i.e., sustainability) and it has its own externalities.[25] Established that circularity is not a sufficient condition for sustainability, it is crucial to understand the importance to assess the sustainability of a material, process or service.[25] Hence, considering circularity as a strategy to achieve sustainability, it is essential to have a more holistic view about the sustainability of a system.

1.2 Sustainability assessment (SA)

Sustainable development is a balanced integration of economic performance, social inclusiveness and environmental resilience considering both present and future generations.[10] Dealing with sustainability means dealing with complex systems because many entities interacting between each other are involved (**Figure 2**).[26]

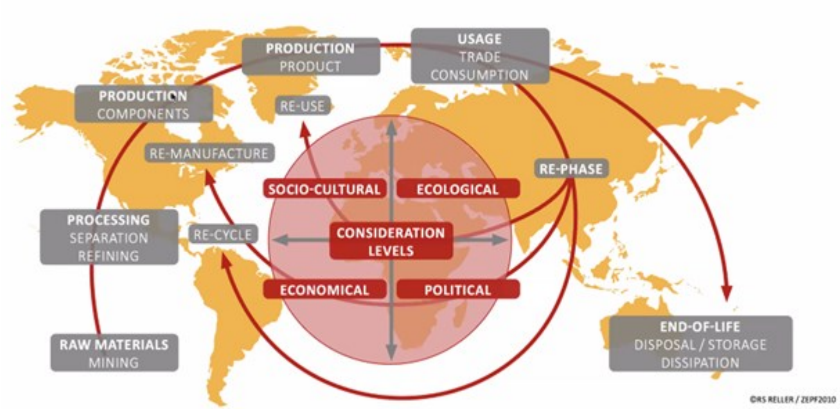


Figure 2 Consideration levels when assessing sustainability[27]

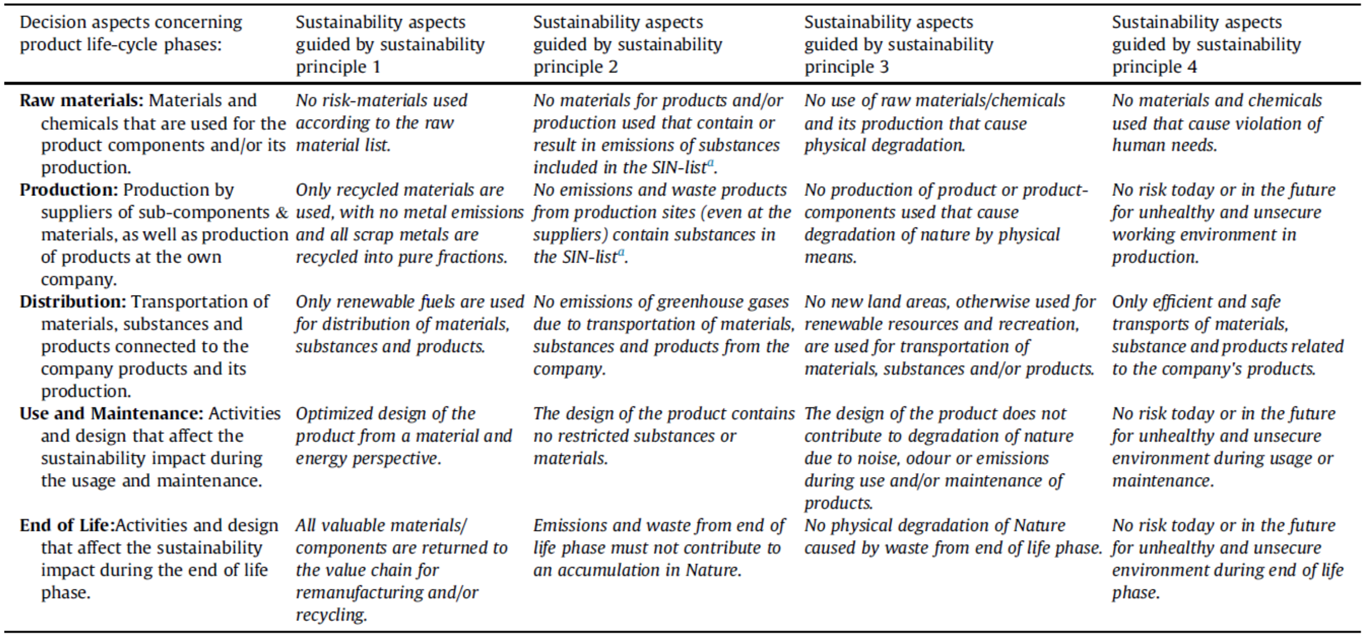
When an initiative is presented as sustainable, the actual benefits and the unintended consequences must be thoroughly investigated. In 2001, Mulder[28] referred to a contribution to the sustainable development, as an "***articulation***"[28], that is, an activity aiming at diminishing resource consumption, emission release and social inequity. For instance, bio-fuels and electric cars are two articulations aiming at decoupling the dependence from fossil-fuels and reducing emissions, respectively. However, it is important to highlight that these two examples have their own unintended consequences. The former can face competition with food production when renewable fuels are obtained with crops intended for food. The latter deal with the issue of critical materials dependence as cobalt and lithium are essential for batteries production. In 2008, van Lente and van Til[29] applied the concept of the articulation of sustainability to the nanocoatings field even if their definition does not completely match the one suggested by Mulder. Both the papers highlight the need of declared objectives, facts and data when claiming an initiative as sustainable.

To better understand if an activity is actually sustainable (or more sustainable), a ***Sustainability Assessment*** (SA) must be performed.[30] A SA is designed to "direct the planning and decision-making process toward achieving sustainable development"[31]. A SA helps to: anticipate and assess conditions and trends, provide early warning information to prevent economic, social and environmental damage, formulate strategies and communicate ideas and support decision-making. Envisioning the future from sustainability principles and asking which steps are necessary to reach it from where we are now is called *backcasting.*

The definition of SA, its framework and the approach to deal with it are matters of discussion.[32,33] One of the most prominent papers about this debate is the one authored by Pope *et al.*[30] In this work, the authors conceptualised the SA as "seeking to determine whether or not an initiative is actually sustainable". The research highlights the importance of deriving criteria from sustainability principles (*e.g.,* Rio Declaration) to avoid the limits of the "Triple Bottom Line" (TBL, environment, economy and society) approach.[34] In fact, according to the authors,[30] splitting the concept of sustainability into the well-known three pillars (*i.e.*, planet, profit and people)[34], tends to emphasise potentially competing interests rather than the linkages and interdependencies between them.[31,35,36] Furthermore, the TBL can be considered a reductionist approach toward sustainability; dividing the holistic concept of sustainability runs the risk of the sum of the parts being less than the whole.

An interesting example of SA methodology built on sustainability principles is the one presented by Hallsted.[37] In her work, life-cycle phases and sustainability principles are inter-crossed to formulate sustainability criteria of a sustainability matrix (**Table 1**).

Table 1 Sustainability criteria matrix by Hallstedt[37]



Decision aspects concerning product life-cycle phases:	Sustainability aspects guided by sustainability principle 1	Sustainability aspects guided by sustainability principle 2	Sustainability aspects guided by sustainability principle 3	Sustainability aspects guided by sustainability principle 4
Raw materials: Materials and chemicals that are used for the product components and/or its production.	*No risk-materials used according to the raw material list.*	*No materials for products and/or production used that contain or result in emissions of substances included in the SIN-list*[a].	*No use of raw materials/chemicals and its production that cause physical degradation.*	*No materials and chemicals used that cause violation of human needs.*
Production: Production by suppliers of sub-components & materials, as well as production of products at the own company.	*Only recycled materials are used, with no metal emissions and all scrap metals are recycled into pure fractions.*	*No emissions and waste products from production sites (even at the suppliers) contain substances in the SIN-list*[a].	*No production of product or product-components used that cause degradation of nature by physical means.*	*No risk today or in the future for unhealthy and unsecure working environment in production.*
Distribution: Transportation of materials, substances and products connected to the company products and its production.	*Only renewable fuels are used for distribution of materials, substances and products.*	*No emissions of greenhouse gases due to transportation of materials, substances and products from the company.*	*No new land areas, otherwise used for renewable resources and recreation, are used for transportation of materials, substances and/or products.*	*Only efficient and safe transports of materials, substance and products related to the company's products.*
Use and Maintenance: Activities and design that affect the sustainability impact during the usage and maintenance.	*Optimized design of the product from a material and energy perspective.*	*The design of the product contains no restricted substances or materials.*	*The design of the product does not contribute to degradation of nature due to noise, odour or emissions during use and/or maintenance of products.*	*No risk today or in the future for unhealthy and unsecure environment during usage or maintenance.*
End of Life: Activities and design that affect the sustainability impact during the end of life phase.	*All valuable materials/ components are returned to the value chain for remanufacturing and/or recycling.*	*Emissions and waste from end of life phase must not contribute to an accumulation in Nature.*	*No physical degradation of Nature caused by waste from end of life phase.*	*No risk today or in the future for unhealthy and unsecure environment during end of life phase.*

The matrix is then exploited to support decision at early-stages in product development.[37] In particular, it was tested to evaluate a pilot test of an electro-chemical milling in a company. Moreover, Hallstedt[37] pointed out that there is neither time, nor data available to analyse sustainability in a rigorous manner in the early stages of product development. Hence, there is a need to derive pragmatic approaches that account for a full socio-ecological sustainability perspective also in these restrained circumstances, without compromising the completeness of sustainability (**Figure 4**). In this thesis, an approach to assess the sustainability at the early stage of an emerging photovoltaic technology (*i.e.*, Dye Sensitised Solar Cell) development is presented. The approach and the matrix presented by Hallstedt played a pivotal role in building the new methodology. Furthermore, another interesting approach to assess sustainability is the one described by the Royal Society research professor emeritus of materials science and engineering, Michael F. Ashby.[26] In 2015, he published a book entitled "Materials and sustainable development" where he presents "a way of thinking about complex problems" called the *layering (or layered) approach* (**Figure 3**). In this book, the author borrowed the aforementioned "articulation" definition suggested by Mulder[28] and suggests his approach as a strategy to deal with the analysis of an articulation of sustainable development.

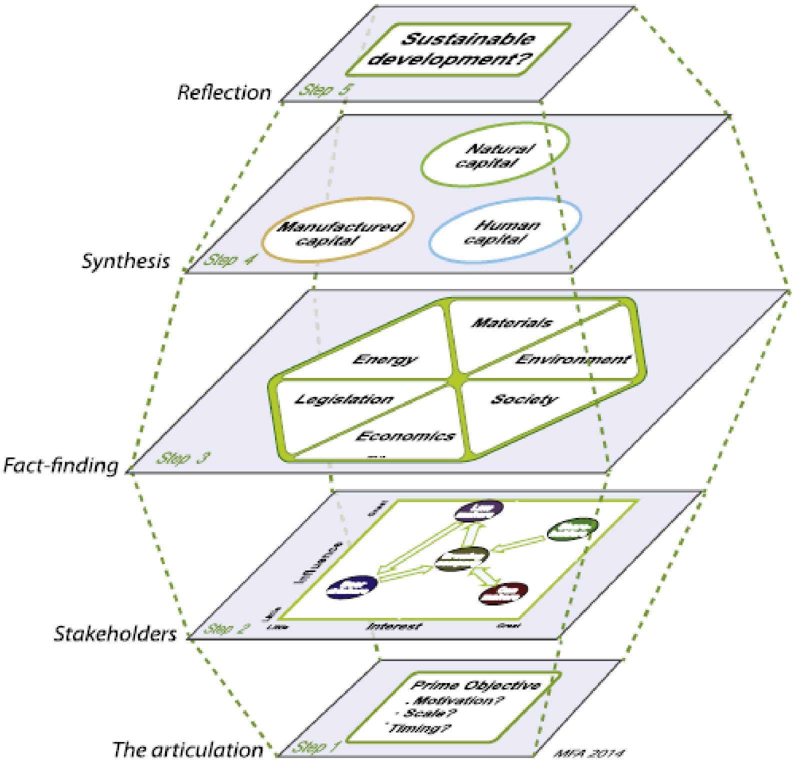


Figure 3 Layered approach by Ashby[26]

The approach consists of splitting a problem into five layers: (i) *the articulation* along with the definition of the problem (prime objective identification), (ii) *the stakeholder analysis* for a comprehensive consideration of the context, (iii) *the fact finding* to collect the relevant information about , (iv) the *synthesis* and debate implications, (v) policy or decision *reflection*. Ashby declares that:

> "*there is no "right" answer to assessing issues as complex as those of sustainable development. Instead, there is a thoughtful, well-researched response that accepts the complexity and seeks to work with it to reach a balanced, fair and defensible conclusion*".

The layered method merges different levels of factual uncertainty and complexity: the stakeholder analysis and fact-finding are objective and systematic, both characteristics of normal science-based reasoning. When the facts are not well known and the system complexity is wide, the study is included in the so called “post-normal” science (**Figure 4**).[38,39]

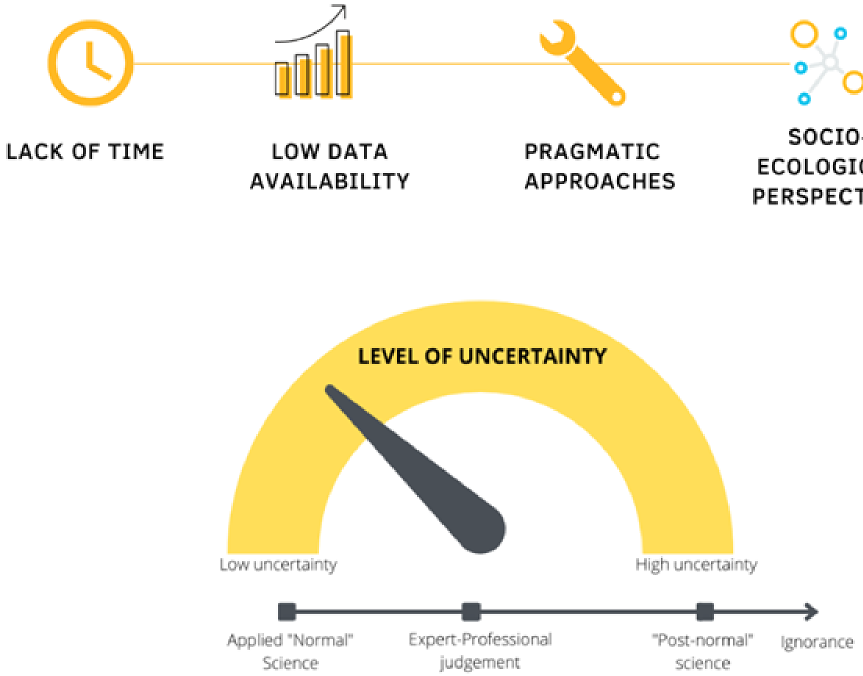


Figure 4 Characteristics of the SA at early stage of product development according to Hallstedt.[37]
The levels of uncertainty and methods of tackling them.[38]

Dealing with sustainability often means dealing with limited information availability and a certain degree of uncertainty. Hence, SA is a powerful tool to drive decisions towards sustainability highlighting positive and negative impacts but it should be used carefully to avoid either stifling innovation or unintended consequences.[40] Different SA can be developed in different stages: from basic research to market (**Figure 5**) as well from preliminary stage to industrialization.

The case studies presented by Hallstedt[37,41] and Ashby[26] involve new product development in companies, firms and governments. For instance, they investigated the sustainability of banning incandescent light bulbs, the achievability of 20% in carbon emissions by silicon solar panels alone and the pilot test of a low-pressure turbine component. All these cases involve either new product development in firms or products already in the market. On the other hand, interesting studies at preliminary stage (applied research and basic research)[40,42–44] are present. These works involves the SA for chemical process for both laboratory[40] and for process design[42] stages. Sugiyama *et al.*,[44] describe a decision framework for chemical process design including different stages of environmental, health, and safety assessment for 17 different MMA production processes. Their work has been selected as the starting point to build a SA of novel chemical processes at early stage by Patel *et al.*[40] to assess the methodology and examine the plausibility of the results, it has been applied to a biobased and a petrochemical but-1,3-diene production process. A further step in the chemical process design selection has been taken by Othman and co-workers[42] presenting a methodology for the biodiesel production processes.

All these studies highlight that there is a need for a tool that provides a rather quick but informative assessment that can aid in key decision-making at the laboratory stage of a process. For such an assessment, it is important to utilize both quantitative and qualitative information. The primary goal of these works is to identify bottlenecks and set research targets in process development. Rather, it should be used to guide innovation toward sustainability.[40] Finally, it is interesting to note that these studies[40,42–44] suggest inspiring methodologies for material production, while the final application is not considered.

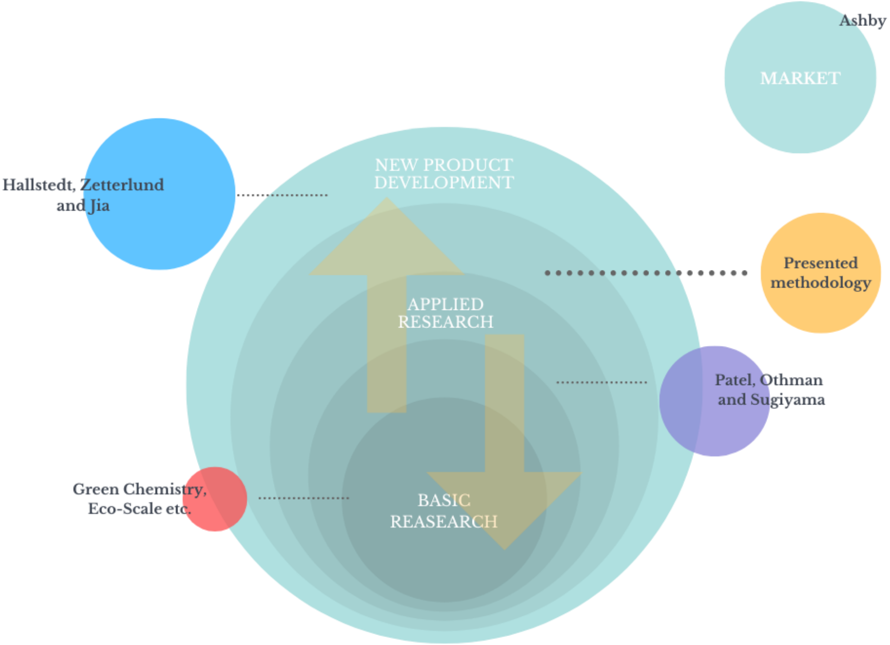


Figure 5 Classification of research[45] *and literature positioning*

2. Development of an early-stage SA for innovative materials for energy: a framework analysis

Throughout this thesis, a SA for materials from raw material selection to its application in device is proposed. This methodology merges the approaches presented by Ashby[26] and Hallsedt[37] with the ones suggested by Patel[40] and Othman.[42] The approach aims at building a bridge between the applied research and the new product development (**Figure 5**). The methodology is intended for materials produced at lab-scale for an intended application (i.e., renewable energy); hence, the considered aspects are related not only to the chemical process at lab-scale but also to the final product where the material is involved. Conversely, innovation in product design starts with materials. Developing successful commercial products requires a sound understanding of the materials; this methodology wants to facilitate a better knowledge of both material and product or device.[46]

Following the Pope's guideline of deriving sustainability criteria from sustainability principles,[30] the renewable energy framework has been analysed to identify the most suitable ones.

2.1 Sustainable renewable energy

The energy sector is accounting for around 60% of total global greenhouse gas (GHG) emissions.[47] Renewable-based energy systems are at the core of the energy transition aiming at getting clean energy to fight climate change.[48] Moreover, they also play a pivotal role in the circular systems development for their own regenerative nature.[6] However, a renewable resource[49] does not necessarily ensure a clean and sustainable energy output. Indeed, this purpose can be achieved only through efficient technologies, where their entire life cycle is not compromised by the toxicity and availability of materials and processes.

In 2015, the United Nations drew up 17 Sustainable Development Goals (SDG) that are at the core of the 2030 Agenda for Sustainable Development. Within this this list, the SDG7 is related to energy and it aims at ensuring access to affordable, reliable and secure, clean, sustainable and modern energy for all.[47] Actually, renewables along with energy efficiency have an enormous potential for the achievement to the “well below 2° C” target of Paris Agreement.[50] According to both the International Energy Agency (IEA) and the International Renewable Energy Agency (IRENA),[50] the target is technically possible (with a “66% 2°C scenario”: limiting the global mean temperature rise to below 2°C with a probability of 66%) but will require significant policy reforms, carbon pricing and additional technological innovation. Around 70% of the global energy supply mix in 2050 would need to be low-carbon.[2,51] The largest share of the emissions reduction potential up to 2050 comes from renewables and energy efficiency, but all low-carbon technologies, from solar panels to the carbon capture and storage, play a role. However, the efforts to have a cleaner energy (lower emissions) must also consider the security and the resiliency of energy systems. The achievement of the Paris Agreement target means to quadruple the whole mineral requirements for clean energy technologies (EVs, battery storage, grid lines, solar PV, hydropower, biomass and nuclear, hydrogen) by 2040; for this reason, concerns about price volatility and security of supply will be still urgent in an electrified, renewables-based energy system.[2] However, there are significant differences between oil security and mineral security, especially, in the impacts that any disruption may have. If an oil supply crisis occurs, all consumers driving gasoline cars or diesel trucks are affected by higher prices. By contrast, a shortage or spike in the price of a mineral affects only the supply of new electric vehicles or solar plants. Another positive aspect is that minerals have the potential to be recovered and recycled. Despite these differences, for the above discussion, diversification is of great importance to build a sustainable renewable energy system. In the energy transition scenario, wind and solar would become the largest source of electricity by 2030.[52] Considering solar energy, crystalline silicon modules dominate and are expected to continue to dominate the solar PV market. According to the Organization for Economic Co-operation and Development (OECD), IEA and IRENA, along with solar mature technologies, alternative and emerging PV technologies require to be spread out[51] as they exhibit a plethora of potential advantages:

i. Material differentiation
ii. Building Integrated Photovoltaics (BIPV) applications (outdoor and indoor)
iii. Excellent diffuse light efficiency
iv. Flexibility
v. High efficiency/weight ratio, less energy and mass requirement in the production
vi. Low-cost materials, easy manufacturing

Material differentiation (i) is well-related to the aforementioned material discussion and it becomes much more important when dealing with a critical raw material (CRM) as Silicon.[53] As a matter of fact, in 2014, the EU included the Silicon metal in the critical raw materials list for its economic importance especially in the context of the increasing production of solar panels. In the solar energy context, to date, land use (ii) is negligible compared to other human land uses (e.g., cultivation and housing). However, van de Ven *et al.*[54] analysed a largely decarbonized electricity system scenario pointing out the significant amounts of land to be occupied by solar power plants when high penetration rates of solar energy is required. Brownfields[55] and BIPV are two solutions to limit this unwanted consequence, while diffuse light efficiency (iii) and flexibility (iv) allow to explore new application for PV technologies (i.e., indoor and wearable devices). The lower weight along with lower energy and mass requirements

(v) allow to decrease emissions both during transportation and production, respectively.

The alternative technologies to silicon modules that are being studied and developed are the thin film solar cells and the third-generation (emerging) solar cells. Thin film technologies are based on cadmium tellurium (CdTe), copper indium gallium selenide (CIGS), or amorphous silicon (α-Si) considered as a cheaper alternative to crystalline silicon cells. They provide better mechanical properties, allowing for flexible usages at the risk of a lower efficiency.

Third generation photovoltaics include organic photovoltaics (OPV), dye-sensitized solar cells (DSSC) and, more recently, perovskite solar cells (PSC). Third-generation photovoltaics are also referred to as “emerging” because of their low market penetration, although some of them have been investigated for over 25 years.[56] This generation accounts for a broad spectrum of concepts, ranging from low-cost low-efficiency systems (dye-sensitized, organic solar cells) to high-cost high-efficiency systems (III–V multijunction). Considering efficiencies, it is worth highlighting that Silicon solar cells have almost reached their physical efficiency limit (Shockley-Queisser limit = 33.1%) in laboratory devices.[57] Researchers[2] have demonstrated perovskite/silicon tandem solar cells that reach laboratory efficiencies of up to 31%, outperforming both perovskite and silicon single-junction devices.

Not only emerging PVs allow to enhance the performance of traditional solar modules, but they also give the opportunity to investigate innovative materials for solar energy.

2.2 Emerging photovoltaics

In this section, emerging photovoltaics[58] are presented and a brief device description is provided. Some parts of this section have been already published in the book chapter entitled “Emerging Photovoltaic Technologies and Eco-Design—Criticisms and Potential Improvements”.[59]

2.2.1 Organic photovoltaics

OPV refers to a class of solar cells involving a molecular donor−acceptor heterojunction.[60] The research over the last decades has resulted in a library of donor and acceptor molecules and therefore in a progressive advancements in molecular design and cell performance. From their very beginning, the OPVs were simple, single-layer devices based on a Schottky diode structure, a pristine polymer and two electrodes, resulting in low photoconversion efficiency (PCE). The first relatively successful OPV was reported by Tang *et al.* in 1986, which was based on a double-layer structure of p-type copper phthalocyanine and n-type perylene diimide derivative.[61] This emerging technology exhibits a unique combination of attributes, such as low-cost solution processing, low material usage due to the ultrathin absorber films, and tunable optical absorption for harvesting a wide range of the solar spectrum. Together, this offers the perspective toward large-scale, low-cost PV with attractive properties such as semitransparency, flexibility, and ultralight-weight modules. Decades of research on OPVs has resulted in record power conversion efficiencies (PCEs) exceeding 18%,[62] with reported device lifetimes ranging from months to several years. However, despite the rapid development and interesting potential, OPV has not yet succeeded as a commercial technology on the large scale, especially for stability issues.[60,63]

Organic solar panels (**Figure 6**) are usually structured as follows:

- A flexible polyethylene terephthalate (PET) substrate on the light collecting side;

- A transparent conductive oxide (TCO), usually indium tin oxide (ITO) or fluorine-doped tin oxide (FTO), as electrode
- An active layer usually made of a [6,6]-phenyl-C61-butyric acid methyl ester:poly-3-hexyl-tiophene (PCBM:P3HT) mixture behaving as electron transport layer (ETL)
- A hole transport layer (HTM) usually based on a PEDOT:PSS system but also MoO_3 can be used
- An aluminium back electrode covered by a thin layer of lithium fluoride
- Sometimes, a second PET layer could be employed to cover (and straightforwardly protect) the entire device.
- Epoxy resins as encapsulant material
- Interconnections made of a silver paste

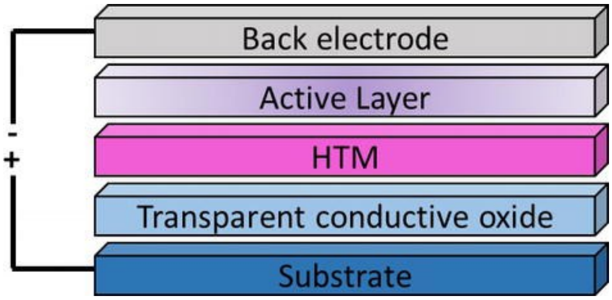


Figure 6 General structure of an OPV device

The configuration of the devices can be of two different types: the single- and multi-junction system. The former is a single p-n junction while the latter has more than one p-n junction leading to better efficiencies but requiring a higher amount of materials coupled to more elaborated production processes.

2.2.2 Perovskite Solar Cells

The name perovskite was firstly used for the calcium titanium oxide ($CaTiO_3$) mineral in 1839, named after the Russian mineralogist Lev Perovski. In

1957, Christian Møller discovered that caesium lead halides ($CsPbX_3$, X = Cl, Br or I) owned the same structure of $CaTiO_3$[64] and found out that they were photoconductive behaving as semiconductors. An important step towards the development of photovoltaics based on perovskites was made in 1978 by Weber who replaced caesium with methylammonium cations and obtaining in this way an organic-inorganic hybrid perovskites.[65] In particular, methylammonium lead iodide (general formula: $CH_3NH_3PbI_3$) is one of the most implemented materials in PSCs. It is a semiconducting pigment that can absorb light over the whole visible solar emission spectrum. Excitons produced in $CH_3NH_3PbI_3$ dissociates very rapidly into free carriers of different sign and exhibits high carrier mobilities for electrons and holes and also long carrier-diffusion lengths when coupled with efficient Electron Transport Layer (HTL) and Hole Transport Material (HTM), respectively. Hence, the choice of the different HTL and HTM should be thoughtfully made, because they should be inert towards the Perovskite layer but, on the other hand, they should assure a good energy levels matching.

A perovskite solar cell is usually composed of:

- A glass substrate
- An ITO or FTO layer
- A compact layer made of TiO_2 (SnO_2 and ZnO)
- A mesoporous TiO_2 layer as electron transporting layer (ETL) on the previous layer.
- Perovskite ($CH_3NH_3PbI_3$) layer
- A hole transport material (HTM) layer
- A gold or silver cathode

The most implemented technologies are the mesoporous and the planar structures: the former involves the use as electron transporting material of a compact and a mesoporous layer of TiO_2, while the latter is composed only of a compact layer (**Figure 7**) of TiO_2, SnO_2 or other semiconducting metal oxides.

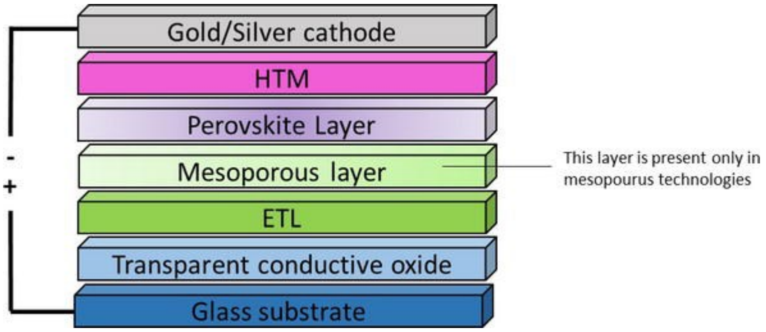


Figure 7 General structure of a perovskite solar cell.

The first studies on perovskite solar cells (PSCs) were carried out only in 2009[66] and since then different types of PSCs were developed as they are promising for their relatively low cost and high power conversion efficiency.

2.2.3 Dye-Sensitized Solar Cells

DSSCs were invented by O'Regan and Grätzel in 1991.[67] They were firstly designed aiming at reproducing the principle of photosynthesis occuring in plants' cells. DSSC photovoltaic technology can be compared to artificial photosynthesis since it mimics the way nature absorbs energy from sunlight. According to researchers in this field,[68] DSSCs are the closest concept we have to photosynthesis due to their greener, more flexible and eco-friendly features compared to the early-generation solar cells, which require much more energy to manufacture. These advantages are due to the use of a dye as the photosensitive material.

A DSSC basically consists of four major components, the anode, the photosensitizer (PS), the electrolyte and counter electrode (CE). A typical DSSC device (**Figure 8a**) consists of:

- A transparent anode made of glass coated with a TCO (usually ITO or FTO)
- A mesoporous TiO_2 layer
- A monolayer of dye adsorbed onto TiO_2
- An electrolyte

- A glass cathode coated with a catalyst (usually Pt)

This assembly is generally enclosed within a sandwiched structure of two conductive substrates made of fluorine-doped tin oxide (FTO)-coated glass at both the photoanode and the cathode.

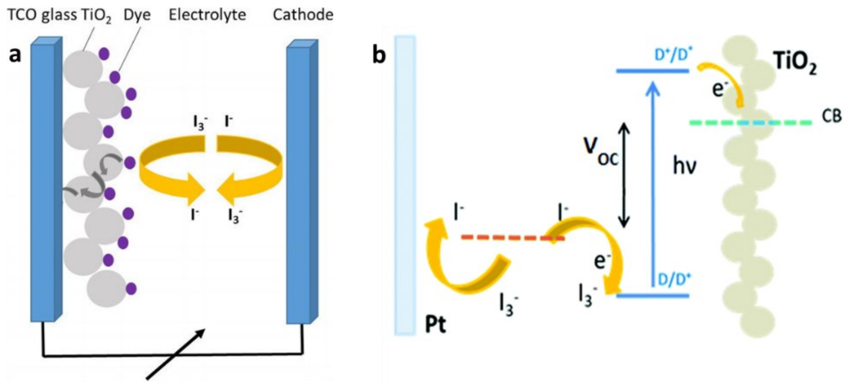


Figure 8 a) Schematic diagram of the dye-sensitised solar cells; b) main electronic processes occurring in a conventional DDSC

The working principle of DSSCs involves four fundamental processes (**Figure 8b**) to convert the electromagnetic radiation coming from the Sun (or any artificial source) into electrical energy: (i) the impingement of sunlight onto the dye provokes photoexcitation; (ii) the photogenerated electrons are then injected in the conduction band (CB) of the photoanode and, then, to the external circuit; (iii) the electrolyte supplies electrons to reduce the dye molecules, thus avoiding their decomposition, through the redox reaction of iodide into triiodide (this reaction has to be rapid to avoid the recombination of injected electrons with the oxidized dye molecules, which causes photovoltage reduction) and (iv) at the cathode, triiodide eventually recovers an electron coming from the external load to complete the electronic circuit.

2.3 Matrices for early-stage SA for innovative materials for energy at laboratory-scale

In the emerging PVs field, researchers aim at obtaining more efficient and/or more stable materials and devices. However, nowadays, efficiency and stability studies are not sufficient when developing a new product. The investigation of the main responsible factors threating the sustainability of a particular technology is of great importance. In the energy transition context, this is crucial to achieve renewable energy that can be indeed claimed as sustainable.[59,69]

To drive decisions towards sustainability, highlighting positive and negative impacts, a methodology for SA of materials for energy from raw materials selection to their application in a device is presented. The methodology is intended for the applied research. The final use is considered. The scale is the lab-scale. However, also the real application is considered pushing the user to consider all the life-cycle aspects.

Figure 9 aims at better visualize the scales of application. This visualization is inspired by the TRIZ method that forces a view of the system on different conceptual scales.[70]

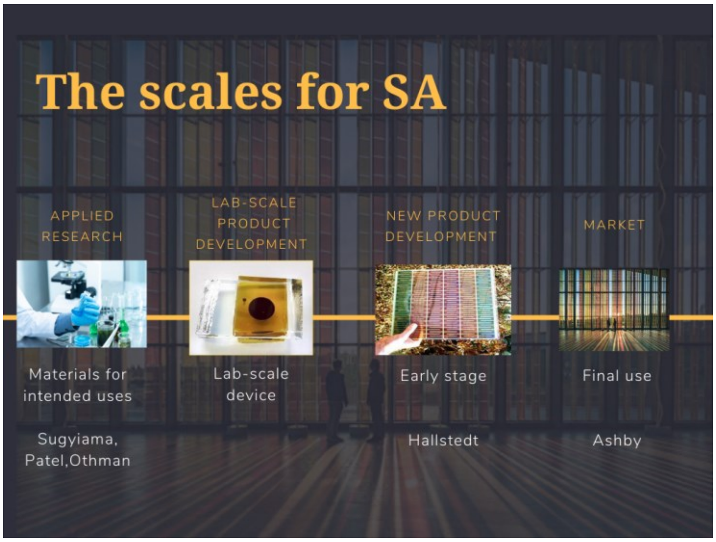


Figure 9 From the bottom to the top: materials; device at lab-scale; early-stage product development; real application of DSSCs

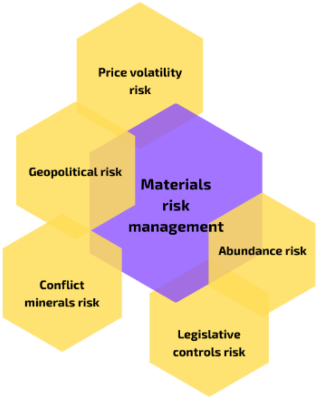
Following the Pope's guideline of deriving sustainability criteria from sustainability principles,[30] the SDG 7[47] has been selected as strategic principle towards sustainable energy. As presented in **Section 2**, the SDG7 is specifically related to energy and it aims at ensuring access to *reliable* and *secure, clean* and *affordable* energy for all.[47] These aspects have been exploited as building blocks for the development of a sustainability criteria matrix (**Table 2**) along with life-cycle phases following the methodology presented by Hallstedt (**Table 1**).[37] It is interesting to observe that the matrix tends to merge the *fact finding* with the *synthesis* steps presented by Ashby (**Figure 3**). Combining life-cycle phases with sustainability principles leads to the formulation of sustainability criteria. The criteria show long-term and strategic sustainability aspects to be considered and targets to achieve. The developed matrix differs from the Hallstedt's[37] one in two aspects: the materials are more deeply investigated through two phases (i.e., the raw materials selection and the materials production phase), while the Hallstedt's production phase is substituted by the device assembling phase. At laboratory-scale, the stakeholder analysis (suggested by both Ashby and Hallstedt)[26,37] has not been considered for the nature of the dimension (scale). However, this analysis has been carried out by the author on two different fields: soil regeneration in private-public partnership[71] and plastics recycling in Italy (**Appendix A**).[72]

Table 2 Sustainability criteria matrix for SA of materials for energy.

		SDG7 PRINCIPLES		
		RELIABLE AND SECURE	CLEAN	AFFORDABLE
LIFE-CYCLE PHASES	**RAW MATERIALS**	Raw materials should be available and non-toxic. The supply-chain should be safe from both political and social aspects.	Fossil-based or renewable sources. Raw materials extraction or production (if recycled) impacts should be considered.	High-cost raw materials (e.g., precious metals) should not be used.
	MATERIALS PRODUCTION	Synthesis should be safe (*e.g.*, toxic solvents, harsh conditions).	The synthesis should involve low impacts processes.	The production should exploit low-cost processes and low materials amount.
	DEVICE ASSEMBLING	Working conditions	Energy requirements and emissions for device assembling with a specific material should be considered.	The device assembling should exploit low-cost processes and lo materials amount
	DEVICE DISTRIBUTION	Efficient and safe transportation (*e.g.*, fragility).	Distance and fuels	Distribution costs
	USE AND MAINTAINANCE	Optimization for efficiency, durability and stability.	No leakages, noise or odour.	Efficiency
	EOL	Safe disposal	Easy to recovery. Waste and emissions minimization.	Low-cost processes.

2.4 Indexes and parameters for the sustainability tool matrix

The sustainability criteria matrix must be filled with both quantitative and qualitative information.[40] The parameters, indexes and tools to assess sustainability in emerging PVs are here introduced. Furthermore, at the end of this section, each box of the sustainability criteria matrix is filled with the desired information and data. This matrix is called sustainability tools matrix (**Table 4**).



When reliability and security must be assessed during the material selection process the so-called emerging material constraints should be considered. Price volatility risk, monopoly of supply and geopolitical risk, conflict risk, legislative limitations and abundance risk are crucial parameters.

In this context, the data provided by the Royal Society of Chemistry[73] (**Table 3**) were used to compare different elements according to the related risks.

Table 3 Supply risk data from RSC[74]

Supply risk data	
Relative supply risk	Reserve distribution
Crustal abundance	Recycling rate
Top 3 reserve holders	Top 3 reserve producers
Substitutability	Production concentration
Political stability of top producers	Political stability of top reserve holders

Relative supply risk is an integrated supply risk index from 1 (very low risk) to 10 (very high risk). This is calculated by combining the scores for crustal abundance, reserve distribution, production concentration, substitutability, recycling rate and political stability scores.

Crustal abundance (ppm) is the number of atoms of the element per 1 million atoms of the Earth's crust.

Recycling rate is the percentage of a commodity which is recycled. A higher recycling rate may reduce risk to supply.

Substitutability represents the availability of suitable substitutes for a given commodity (high=substitution not possible or very difficult; medium= substitution is possible but there may be an economic and/or performance impact; low=substitution is possible with little or no economic and/or performance impact).

Production concentration is the percentage of an element produced in the top producing country. The higher the value, the larger risk there is to supply.

Reserve distribution is the percentage of the world reserves located in the country with the largest reserves. The higher the value, the larger risk there is to supply.

Political stability of top producer is a percentile rank for the political stability of the top producing country, derived from World Bank governance indicators.

Political stability of top reserve holder is a percentile rank for the political stability of the country with the largest reserves, derived from World Bank governance indicators.

Moreover, the list of Critical Raw Materials (CRM) from the EU is a key source for criticality data.[75] Material criticality is assessed considering the economic importance and the supply risk of the material.

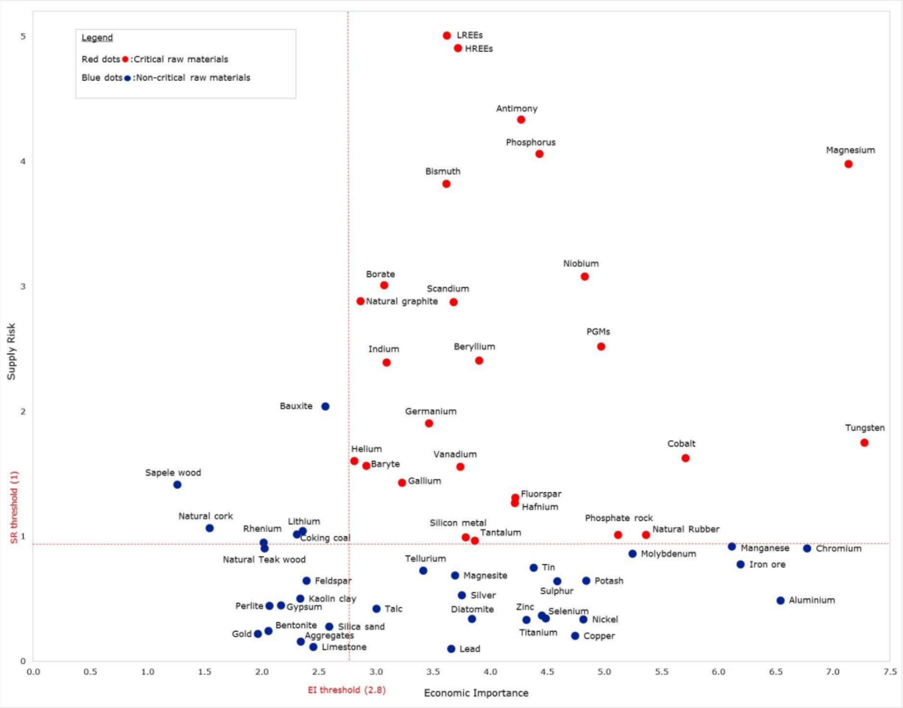


Figure 10 EU Critical Raw Materials: economic importance and supply risk of 2020 criticality assessment.

A powerful tool to examine the environmental sustainability of a product or service is the life cycle assessment (LCA, ISO 14040),[76] which allows the evaluation of its environmental impacts and the identification of the main contributors, namely "*hotspots*". LCA results are characterized by uncertainty levels, where the more the life cycle of a product is assessed, the lower the uncertainty.[77] In the case of emerging PVs, the large-scale production and the end-of-life (EoL) phase are not mature, which means that the accuracy of the presented results can be improved in the future when more data will be available, and the processes will be better defined. Moreover, many LCAs for emerging PVs have been studied in a "*cradle-to-gate*" way, where this approach considers the life cycle of panels from the extraction of raw materials to the production phase (the use phase and the EoL are not considered due to the lack of data for waste management).[78] Subsequently, the LCAs presented in literature deal with "*established architecture*", in which conventional (and high performing) materials are employed.[78–80] Therefore, the majority of the innovative materials presented throughout this review have not been investigated *via* an effective LCA; nevertheless, if LCA data are available, we critically analysed the preparation procedures of a specific material in dedicated paragraphs. On the other hand, when LCA data are not available, we evidenced eventual "*hotspots*" to be considered in a forthcoming assessment. Usually, in early technology development stage, an overestimation of the energy consumption is possible because laboratory instruments are not completely conceived for a specific synthesis or process. However, it has been recognised that 70% of a product's environmental impact is determined in the design and development stage.[81–83]

Additional indicators considered for PV energy systems are the cumulative energy demand (CED) and the energy payback time (EPBT). CED [equivalent of MJ of primary energy] is defined as an energetic indicator that quantifies the whole energy required during the life cycle of a product. It is obtained by summing both the direct energy (*e.g.*, electricity for manufacturing, and thermal energy) and the indirect energy (embodied energy of materials) contributions.[80,84] EPBT is an indicator, which is expressed in years. It represents the time required to generate the same amount of energy consumed during the production processes and can be considered a quantitative evaluation of the cost-effectiveness of a specific technology (and its constituent materials).[80,84] With regards to the DSSC system, the EPBT is the time (in years) in which the photovoltaic system produces the equivalent amount of energy that was consumed during the manufacturing and production phases.[85] The EPBT depends on the CED, the yearly energy output (YEO) and the electrical conversion factor (C), according to the following equation: $\mathrm{EPBT} = \mathrm{CED}\ \mathrm{YEO}^{-1}C^{-1}$. Both CED, and, more broadly, EPBT, are parameters readily neglected in the literature when innovative materials are proposed.

Green Chemistry principles and metrics have been taken into account for synthetic processes.

Information about human rights violation should be reported. Regulations and normatives (*e.g.,* REACH, SINList) have been also considered to detect potential phasing out or restrictions.

Finally, efficiency, durability and end-of-life considerations have also been provided.

The presented indexes and information have been entered in the box of the sustainability matrix to build a sustainability tools matrix (**Table 4**) which gives instructions of what is necessary to assess each phase according to each sustainability principle.

Table 4 Sustainability tool matrix

		SDG7 PRINCIPLES		
		RELIABLE AND SECURE	CLEAN	AFFORDABLE
LIFE-CYCLE PHASES	RAW MATERIALS	Supply risk data, CRMs list, REACH, SIN List, human rights and toxicity	Embodied energy (CED)	Costs of raw materials
	MATERIALS PRODUCTION	Human rights and toxicity	Green Chemistry principles and metrics Synthesis LCA	Materials and processes (energy) costs, quantities
	DEVICE ASSEMBLING	Human rights and risk exposure	Energy consumption and waste production	Energy, material quantities
	DEVICE DISTRIBUTION	Supply security *not considered*	Transportation emissions Weight	Distance *not considered*
	USE and MAINTAINANCE	Durability (lifetime), leakage	Leakage, soil consumption, BIPV	Refurbishment, efficiency
	EoL	Leakages	Disassembling, recovery, energy and materials requirements	Disposal costs

When assessing sustainability through a sustainability matrix, the positive or negative consequences can be highlighted as suggested by Ashby.[26] Information and data that has a generally positive influence is given a (+), one that has a generally negative influence is given a (-). The same fact can appear in more than one cell of the matrix. In addition to (+) and (-) suggested by Ashby,[26] a (0) is given when no information is available (and more research and investigation is necessary) or no particular concerns are to be reported.

The presented parameters have been exploited for a general sustainability and critical aspects analysis of emerging PVs (**Section 3**). Subsequently, DSSCs have been selected for a deep investigation (**Section 4**) and for sustainability matrix testing (**Section 5)**.

3. Third-generation photovoltaics critical aspects

In this section, a general analysis of the critical aspects of OPVs and PSCs will be presented to highlight weaknesses and failures and to identify the corrective measures to apply to build more sustainable PVs.[86] It is worth mentioning that the studies considered hereafter mainly concerns laboratory-scale device. Yet, the strategies highlighted could be feasibly extended on larger scale too.[86]

In **Section 4**, Dye-Sensitized Solar Cells will be deeply analysed and a SA for each component and alternatives will be provided.

3.1 OPVs environmental impacts and critical aspects

OPVs usually exhibit lower efficiency and shorter lifetime compared to silicon panels, but they always show lower cradle-to-gate life-cycle impacts;[63] OPV panels can save around one-sixth and one-fourth of the cradle-to-gate energy consumption compared to m-Si and a-Si (monocrystalline and amorphous silicon) panels, respectively.[87] Even if OPVs show higher environmental efficiency with respect to the more diffused silicon technologies, some failures have been determined. PET, that is used both as a substrate and encapsulant, is a non-biodegradable polymer under environmental conditions. Even if it is not considered to be directly toxic, PET can be dangerous for the environment and can show ecotoxic issues when it is broken into small particles (diameter smaller than 5 mm).[88] If so finely dispersed, it can reach organisms through the food chain. It has also been demonstrated that PET particles can sorb other persistent organic pollutants and, straightforwardly, these compounds can reach organisms more easily. Photo-degradation is another critical parameter considered in the literature:[89] the natural photo-degradation of PET leads to the formation of both monomer and dimer fragments. Thus, the employment of a stable substrate and enclosing system are essential to have a reasonable lifespan. Bio-plastics (such as PLA) have been considered to be adopted instead of PET, but even if they present a better LCA, their mechanical stability is not good enough. Straightforwardly, it is compulsory to design a configuration such as the persistent materials (not bio-degradable) can be easily recovered and then recycled.[89] In particular, PET recovery can be performed only through an efficient delamination process. In this context, it is necessary to identify the best encapsulant material that can be thermally or chemically separated from the substrate. It should have a different solubility or a melting point lower than the other device components. As far as we are aware, nowadays, researchers are focused on various features of an encapsulant such as chemical inertness, water vapour transmission rate (WVTR) and oxygen transmission rate (OTR), but recycling or recover perspective are not considered yet.[90] ITO, applied as conductive coating on the PET substrate, tends to etch by air and water becoming then a pneumo-toxic entity and a strong reactive oxygen species (ROS) producer when it is in its nanoparticulate form.[91] Further studies are still necessary to understand the fate aspects of ITO in the environment, but its behaviour should be more carefully investigated to highlight potential criticisms. The presence of indium, that is a CRM led to focus the attention on the recovery of this material. Alternatively, efforts should be made on the research of similar but more environmental friendly, for example, FTO.[63] Nevertheless, FTO is defined as a hotspot in a cradle-to-grave OPV LCA too.[92]

A meaningful focus on the active layers has been carried by different studies.[89,93,94] Zimmermann *et al.*[89] focused their attention on the degradation and the ecotoxicity of PCBM/P3HT active layer. The results show that P3HT is degraded by a radical building process. The formed compounds can be oxidised, and this reaction is found to be responsible for the degradation of the organic polymer layer. Although ecotoxicity data for P3HT are not available, they suggested to investigate the potential degradation in small pieces similarly to what happens with PET. The second component of the active layer is the fullerene derivative PCBM. Fullerenes' toxic effects have been thoroughly discussed in the literature:[95,96] they exhibit acute toxicity and can sorb pollutants making them more bioavailable. These studies focused on fullerenes and not on their derivatives, such as PCBM. Therefore, further critical analyses on these compounds are essential to assess their fate and their ecotoxicity.[89] Very interestingly, Tsang *et al.*[63] reported a comparison between the OPV based on PCBM/P3HT and completely polymeric OPV (i.e. changing PCBM with an n-type polymer) showing that the latter is slightly better for some impact factors than the former one. In particular, an all-polymer-based device exhibits a water depletion factor lower (−12%) compared to the counterpart based on PCBM/P3HT. The substitution of the fullerene derivative with an n-type polymer has been suggested from the results of previous studies that identified PCBM as an important factor in the increase of the Cumulative Energy Demand (CED) component.[92,97–99] CED is defined as an energetic indicator that quantifies the whole energy required during the life cycle of a product. It is obtained summing up both the direct energy (e.g., electricity) and the indirect energy (embodied energy of materials) contributions.[84] The investigation of 15 different materials implemented as active materials in OPVs showed that fullerenes and their derivatives (used as electron-acceptors) have the highest CED in a cradle-to-gate LCA.[93] On the other hand, electron donor materials, such as polymers or small molecules, affect less sensibly the total cradle-to-gate CED. A deeper analysis on fullerenes showed that functionalized ones have a higher CED than the native counterparts, while the indene-C60 bis-adduct (ICBA) derivatives present a CED 40% lower than C60-PCBM and C70-PCBM. This behaviour can be explained by the fact that ICBA derivatives have a simpler reaction scheme that results in a lower number of synthetic step; in this way, the purification steps and the use of solvents are decreased. Fullerenes in any case have an embodied energy one or two orders of magnitude higher than the common semiconducting polymers.[93] The semiconducting P3HT is the polymer with the lowest CED because the number of steps for its synthesis is relatively lower; generally, the doubling of the number of steps lead to a 10-fold increase in the CED. Block copolymers, such as PCDTB and PTB7, have a higher embodied energy but they show a lower CED with respect to fullerenes.

Interestingly, phthalocyanines and squaraines can be used in place of electron-donor polymers and have been thoroughly examined;[93] comparing these two classes of molecules, they show very similar CED except for the PdPc that has a higher embodied energy due to the Pd extraction. These small molecules compered to polymers showed a similar CED. The embodied energy of polymer-based devices is mainly due to the intrinsic energy of materials while for the small molecule-based cells to the processing conditions (e.g., fabrication step). For this reason, multi-junction small molecule-based devices are energetically convenient compared to mono-junction. Indeed, for small molecule-based devices, the process to build a multi-junction device requires almost the same energy compared to a mono-junction, and the increase in the amount of required material does not sensibly affect the CED. The hole transporting layer (HTL), usually made of a composite of PEDOT:PSS or MoO_3, contributes in a very minimal way to the overall CED. In particular, Anctil *et al.*[93] reported that, concerning PEDOT:PSS, the solvent used for the deposition is the main energy increasing factor. The interfacial layer can be also responsible for the device degradation. PEDOT:PSS is an hygroscopic material, and it is quite sensitive to oxidation reactions; this could cause an extremely fast degradation of the organic panels. PEDOT materials, in their particulate form, showed cytotoxicity, ROS production, apoptosis, and necrosis.[100] Such as for ITO, particular attention must be paid to a potential dispersion in water.

Finally, considerations about the use of silver must be done. Silver is one of the main responsible for resource depletion and freshwater eutrophication.[89] Espinosa *et al.*[101] carried out a cradle-to-grave (from the materials supply to the end-of-life) LCA of an organic solar park. They compared three different end-of-life scenarios: recycling, incineration and an average local mix. The results showed that the recycling scenario is favoured mainly because of PET and silver recovery.

Silver should be recovered or replaced by a non-metal electrode and bio-based electrode materials or production from waste should be considered. Alternative materials such as carbon, copper and aluminium have been studied, and the environmental impacts were proved to be the lowest for carbon-based modules.[102] The recovery of silver is of great importance also to avoid soil contamination. As a matter of fact, when a damaged panel is in contact with soil, the silver release is highly enhanced.[94] If the balance of system (BOS), consisting of mounting-structure, inverter and cables for electrical installation, is considered into the LCA of OPVs, the results showed that BOS is what affects more the apparatus impacts. On the other hand, the a-Si impacts depend more on the contribution from the panel itself. This shows that the eco-design should be more focused on the BOS improvement in OPV technologies. The contribution of BOS allowed to state that, generally, if the efficiency of the device decreases, the impact is higher; this relation depends on the increasing contribution of the background system.[63,101] Organic photovoltaics show many advantages not only for their functionalities but also for an environmental point of view. They generally show better environmental performances than Si-PV and also lower Energy PayBack Time (EPBT) and Carbon PayBack Time (CPBT) compared to m-Si.

The factor that usually affects the impacts in a negative way is the too short lifetime of these devices. Thus, the increase in the lifetime of the panels is a feasible strategy to decrease their impact.[63] It is worth remembering that PET, PEDOT:PSS and P3HT are not fully biodegradable. It could be interesting to re-think the OPV design to improve the recyclability and the biodegradability in environmental conditions of its components. The external apparatus should be resistant and durable during the use-phase and recyclable at its end of life; the internal materials that are often mixed or difficult to separate should be degradable when they reach the environment.

Obviously, this is necessary if the risk of leaks is present, otherwise they can be collected and degraded in the suitable plants with adequate conditions.

3.2 PSCs environmental impacts and critical aspects

The first studies on perovskite solar cells (PSCs) were carried out only in 2009[66] and since then different types of PSCs were developed as they are promising for their relatively low cost and high power conversion efficiency.[103] These advantages could be eclipsed by the potential toxicity of lead even if many studies revealed that the main environmental impacts are due to the presence of gold (as back contact) and the use of organic solvents throughout the fabrication process.[104–106]

The main point to consider regarding the environmental impact of PSCs is that ITO or FTO glass represents about the 97% of the total mass of the modules; for this reason, the substrate is the main contributor to the energy consumption due to the embedded energy of materials.

When gold is used as cathode, the energy consumption is mainly equally distributed between the substrate [ITO (FTO)-glass] and gold. The substitution of gold with silver can decrease not only the energy demand but also the environmental impact: gold is also mainly responsible for eutrophication, freshwater aquatic ecotoxicity, fresh water sediment ecotoxicity, human toxicity, land use, marine aquatic ecotoxicity, marine sediment ecotoxicity, depletion of abiotic resources, stratospheric ozone depletion, and terrestrial ecotoxicity.[106] Deposition of gold is also an important factor affecting the energy demand: its deposition and evaporation under vacuum is an intensive-energy process. Anyway, we have to consider all the issues belonging to silver already cited in the OPV section.

As we already said for the other technologies, ITO glass should be replaced with the FTO substrate since avoiding the use of precious metal (In) improves the environmental impacts of the modules.

Along with the TCO/glass and the gold cathode, solvents used to rinse the ITO (FTO) glass and to prepare the perovskite layer play an important role in the environmental impacts. Even if they could be partially recycled, solvents show negative impacts due to the electricity needed in the recycling process; in particular, the solvent recycling exhibits the worst environmental performances for the ozone depletion potential and for the global warming potential.[104] Straightforwardly, the use of solvents should be directly downgraded or greener solvents should be preferred.[107,108]

Since the lead toxicity is of really high concern,[109] many studies focused their attention on this element: the impacts of lead derivatives and disposal scenarios have been analysed in detail. Lead can cause irritability, difficulty in concentrating, headache, and anaemia and in higher concentrations (over 100 µg/dL) gives rise to seizures, delirium and even coma.[110] Lead toxicity is well documented, so regulation promoting the gradual phasing out of this substance has been promulgated by EU.[111] The Restriction of Hazardous Substances Directive (RoHS)[111] affirms that the maximum permitted concentrations are 0.1% or 1000 ppm by weight. The restrictions are on each homogeneous material in the product and understanding. If lead halide perovskites are considered homogeneous materials or not is a matter of study. If perovskites were considered homogeneous materials, they would not meet the regulatory restrictions. The regulation is not applied to PVs intended for a defined location (e.g. solar parks) but put limits on portable devices. In this case, where the regulation must be followed, PSCs would not match the 0.1% limit as lead is present in higher concentrations. Moreover, lead presence could affect consumers' choices as the public opinion owns a solid awareness of lead toxicity raised through historical facts such as Romans poisoning caused by lead present in drinking-water, Goya's and Van Gogh's mental disorder probably due to lead contained in their colours and Kabwe inhabitants poisoned by mining activities. Obviously, these cases are not comparable for the technology emissions.

In contrast to the high concern for lead toxicity, the results reported by Alberola-Borràs *et al.*,[112] Billen *et al.*[113] and Zhang *et al.*[104] deserve particular attention. They have demonstrated that the content of Pb in the perovskite contributes to the human toxicity cancer impact category 1–2 orders of magnitude less than the rest of the module components [Glass/ITO (FTO), ETM, HTM and back contact].[112] Furthermore, the energy used for the manufacturing of panels is the dominant contributor to lead emissions.[113] Zhang *et al.*[104] highlighted that lead contributes less than 1% to the Human Toxicity Potential (HTP) and Ecotoxicity Potential (ETP). It is possible to conclude that lead is not the factor of main concern for these parameters although the widespread belief.

Commercialization of PSCs is still far to be achieved. This technology presents short life-time, substantial stability issues and lacks scale-up processes and waste disposal strategies. To overcome these limits, researchers foresaw and analysed different emissions and disposal scenarios. Alberola-Borràs *et al.*[112] studied three disposal scenarios for both planar and mesoporous structures. The three considered disposal routes were: (i) inertization and residual landfill, (ii) re-use and residual landfill and (iii) reuse and recycling. For re-use, they mean regenerative cycles suggested from Kim *et al.* and Huang *et al.*[114,115] As largely expected, reuse strategies reduced the values of all impact category. Additionally, they found that the device with a mesoporous TiO_2 substrate is the one with the largest improvement in all impact categories. This highlights that the mesoporous TiO_2 reuse is of great importance to reduce the environmental impacts, while Pb derivatives recovery does not affect the performances in a significant way.

Billen *et al.*[113] considered potential lead emissions during the use phase and two different end-of-life scenarios. They proved that the lead emissions are dominated from those produced from the energy production for the manufacturing of the panel itself and of the BoS; indeed, the components that do not include the panel (BoS) are the main contributors. This study analysed a disposal scenario in which no lead release was supposed, and a second case in which lead is completely released in groundwater. They demonstrated that even in the worst case, the toxicity potential is smaller than that one calculated for an offset grid.[113]

Although lead toxicity potential concern is minimised by different research studies, aforementioned studies highlight the necessity to avoid incidental release, adopting proper encapsulating materials and maintenance measures, as well adequate disposal strategies. Encapsulant should be resistant and stable under environmental conditions but easily removable through solvent dissolution or by thermal decomposition without the production of toxic substances.[116] The recovery of TiO_2 and lead derivatives from the perovskite layer is necessary for an environmental benefit but it is not economically attracting for their relatively small contribution on the cost; specifically, TiO_2 can be substituted with SnO_2 and ZnO; Gong *et al.*[106] reported that the use of ZnO decreases almost every impact. These studies are performed on data obtained for cells and considered scalable to a module.

On the other hand, the recycling of the TCO/glass is convenient for both an economic and an environmental perspective.[117] Another important aspect to consider is that even if the lead emissions during the use-phase are unlikely (if a proper encapsulating strategy is adopted), the occupational exposure and the chronic exposure to lead must be considered.[118]

In light of an industrial development of the modules, electrodes made of noble metals will be not feasible:[119] carbon-based electrodes could be the best available solution. Furthermore, the slot-die coating will be preferred to the spin-coating as a perovskite deposition method as the slot-die coating allows material savings. The deposition methods are not analysed in this chapter because the attention has been focused on the materials to comply the extension of this chapter. In a recent study about PSC specifically tailored for a commercial purpose, Celik *et al.*[119] pointed out the fact the most commonly used organic HTM are very expensive and they do not exhibit a good stability. They suggested a copper-based semiconductor CuSCN as inorganic HTM suitable in an industrial outlook.

The results obtained through many LCA analyses[104,119] also suggest the importance of increasing the energy efficiency, (especially during the thermal deposition methods), of the PSCs manufacturing process as well the need of decrease the quantity of solvents used.

Substitution of lead with less toxic materials is one of the main challenging purposes for different reasons: (i) the elimination of a cause of concern due to the toxic metal, (ii) the facilitation of the market entry of this new technology also due to the consumer scepticism towards devices containing lead and (iii) the removal of administrative barriers built by the European Union (EU) regarding hazardous materials.

In this way, tin has been suggested as a solution. Nevertheless, it does not seem to be a promising solution. It exhibits ecotoxicity and global warming potential factors higher than lead impacts[120] and, additionally, it is a metal with a low substitution potential. Additionally, its low distribution in the world (Peru, Indonesia, China), which could lead to supply disruption, is dramatically remarkable. Tin is also more expensive than lead, so it could result in a less sustainable PV technology from an economic point of view. Moreover, this evidence is coupled with sensible lower photoconversion efficiency assured by tin-based PSC.[65]

Lead is considered an issue for its intrinsic toxicity, but many studies have demonstrated that lead present in PSCs is not the main contributor both for lead emission potential and toxicity potential. Once that the risk and the intensity (lead emission potential) of lead are proved to be admissible, R&D should invest in improve stability, energy efficiency in manufacturing and waste management strategies.

4. DSSC fact finding for sustainability assessment

According to different studies,[85,121,122] the critical factors for DSSCs are: (i) use of CRMs or noble metals, (ii) performance degradation due to electrolyte instability, (iii) high energy demanding TCO/glass, and (iv) sustainability concerns related to uncertain waste management.

Ruthenium, cobalt, silver and platinum are the most controversial elements in this context. It is worth mentioning that the impact of different materials (and the related procedures) strongly depends on their amount employed to build a complete device. Therefore, sensitizers will be less meaningful in a sustainability-driven analysis with respect to the counter-electrode and/or electrolyte.

Hereafter, the main sustainability issues are briefly presented, but will be more deeply investigated in dedicated sections. Historically, the most widely employed sensitizers are based on ruthenium, resulting in the highest certified efficiency for DSSCs (12.3%). Nonetheless, ruthenium is a scarce material and it has been included in the list of CRMs by the EU.[123] It is costly and its complexes require relatively sophisticated syntheses and solvent-demanding purification steps.[124] Thus, to address these issues, alternative dyes have been developed, such as metal-free organic and natural dyes,[124,125] which should be synthesised following the twelve principles of Green Chemistry,[126] thus allowing the lowest impacts on the lab-scale phase and the possible evaluation through the green chemistry metrics.[127]

The research on alternative electrolytes is important to overcome degradation issues and extend the lifetime of devices.[128] However, the lifetime of DSSCs is affected by different factors as follows: (i) leakage of electrolytes, (ii) corrosion of CE by the redox couple, (iii) electrolyte bleaching and (iv) removal of the adsorbed dye on the surface of TiO_2. To overcome the conventional iodine-based electrolyte-related issue, researchers have tried different routes.[86] For example, alternative redox couples to the traditional I^-/I_3^- have been suggested, which are less prone to evaporation;[129–131] among others, quasi-solid electrolytes in gelled forms and truly solid-state polymer-based electrolytes have been explored;[132,133] and even water,[134] room temperature ionic liquids (RTILs)[135] and deep eutectic solvents (DESs)[136] were proposed. Gel electrolytes guarantee the best trade-off between efficiency and durability,[137] while solid-electrolytes, despite providing lower efficiencies, have the remarkable advantages of being non-volatile and non-fluid, thus avoiding evaporation, leakage and related risks of toxic compound inhalation.[138] With respect to redox mediators, cobalt-based couples have been recently exploited as feasible and best performing alternatives to iodine-based couples.[139,140] Issues related to the use of cobalt include its toxicity, and mainly its supply since cobalt is primarily mined in the politically sensitive Democratic Republic of Congo. Its supply regulation is of great importance, as confirmed by the establishment of the Cobalt Institute, an organisation aimed at promoting “the sustainable and responsible use of cobalt in all forms”.[141]

The cost of a technology must be considered, not only for economic reasons, but also for complete compliance of the aforementioned sustainability principles (affordability). Platinum-based CEs are typically used in DSSCs, but Pt cost (about \$32 000 kg^{-1})[142] is extremely high due to the presence of a precious metal, which also requires high temperatures for its deposition. Platinum is also correlated with degradation/stability issues because of its electrocatalytic properties and its dissolution in the electrolyte.[121] The suggested alternatives are carbon-based,[143] such as activated carbon[144] and graphene,[145] transition metal-based[146] and composite electrodes.[147]

The energy consumption of a process must be considered when attempting to lower its impacts. In DSSCs, the coated glass is the most relevant component in almost all environmental impacts.[80,148,149] Actually, it is highly impactful in terms of high energy required for its production; in addition, it has a high impact in terms of weight with respect to total mass and overall cost, since glass accounts for 17% of the total device cost.[150] Accordingly, several LCA studies[80,148] have suggested the replacement of glass with plastic materials as a suitable solution because of their lighter weight and lower process temperatures required compared to sintering and glass lamination, which are time and energy consuming.[148] However, exploiting lower temperatures for material processing can lead to worse performances. For instance, it was observed that the TiO_2 sintering performed at lower temperatures over poly(ethylene terephthalate) (PET) resulted in lower efficiencies due to the different morphologies and sizes of TiO_2 particles compared to that obtained through sintering on glass substrates.[148,151] Additionally, electrode fabrication and glass-glass lamination are highly energy demanding processes.[152]

It is worth mentioning that photoanodes are not specifically reviewed here. Indeed, a sustainable alternative to the use of TiO_2 nanoparticles has not been proposed thus far since they exhibit a low recombination rate for hole–electron pairs, excellent absorption properties, high chemical and thermal stability, corrosion resistance, non-toxicity, large availability, biocompatibility and competitive cost.[153,154] However, it should be noted that some properties of TiO_2 are not ideal; for example, having a band gap of 3.2 eV (in its anatase phase) it absorbs ultraviolet radiation ($\lambda<380$ nm). This leads to the formation of highly reactive holes, which can degrade some device components. Accordingly, the employment of semiconductors with a wider band gap has been exploited, for example tin oxide, SnO_2, has a larger band gap (3.6 eV), but its more energetic conduction band leads to a sizeable decrease in photovoltage compared to classical devices.[155] On the other hand, zinc oxide, ZnO, has also attracted increasing attention to be employed as a photoelectrode material in DSSCs,[156–158] guaranteeing faster electron mobility compared to TiO_2.[159] However, it does not guarantee improved performances compared to traditional photoanodes, since the electron transport throughout the semiconductor is not a limiting factor for DSSCs under their operational conditions. In summary, alternative semiconducting oxides can operate as photoanodes in DSSCs, but, to the best of our knowledge, their performances have not surpassed that of TiO_2.

The main components of DSSCs along with the corresponding critical materials, related issues and envisaged solutions are summarized in (**Figure 11**).

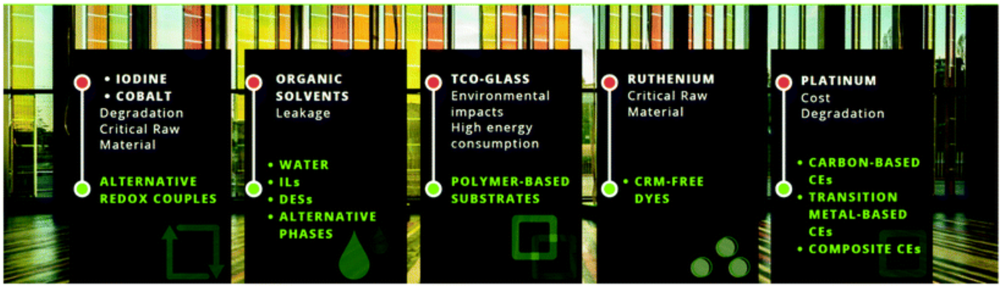


Figure 11 Main DSSC components, along with corresponding most critical materials, related issues and envisaged solutions.

Sealing and encapsulation is crucial for both cell stability and waste management,[121,160] where specific materials are used to guarantee perfect sealing (no leakage and/or contamination) of the device during its whole lifespan, but should also be easily removable upon disposal at the end of its operational life. Degradation and stability are two concepts directly bound to the lifetime of a product. Thus, preventing the production of waste is pivotal to prevent the correct functionality of the PV panel from jeopardizing its lifetime, and thus research on new materials that are stable upon operation and in contact with the other cell components is mandatory.

After product disposal, any device becomes waste, and thus must be correctly designed to become a new source of materials. The EoL of any PV device is a fundamental step to consider chiefly when aiming at producing truly sustainable technology. Nowadays, any industrial product must be designed from the initial step of its production process to be suitable for disassembling, thus allowing the recovery of the highest amount of materials as possible, especially precious and rare metals as well as CRMs.

DSSCs are not a fully mature technology. Research in this field is still at the laboratory or pre-industrial scale. This means that researchers are mainly focused on the investigation of the best materials using the standard assembly adopted for conventional PVs. Once efficient and stable materials are obtained, this technology may have structural improvements to increase its sustainability profile. Accordingly, for other PV technologies, delamination is one of the critical aspects in PV waste treatment since it is the first step performed to disassemble the device.[161] At a material level, as already mentioned above, it is worth highlighting the role of sealing in the perspective of dismantling the panel. From a sustainability viewpoint, scientists must consider numerous aspects in choosing the most suitable materials, where they should (i) be derived from available, widespread and fairly managed resources; (ii) be synthesized minimizing waste, avoiding the use of toxic materials and saving energy; and (iii) improve the product integrity and facilitate the waste recovery and disposal at the EoL.

The development of an ideal DSSC, which can establish its position in the market, should not function just on the best efficiency (where this and long-term stability are the key factors to break through the market), but should also consist of inexpensive sensitizers, non-toxic electrolytes, platinum-free CE and recyclable/reusable components/encapsulation systems, resulting in a PV device that can be fabricated by smart and sustainable procedures. The opportunity to use cheap, available and sustainable or waste-derived materials (*e.g.* waste from both the food and agriculture industries) for the conversion of solar energy, together with the smart use of nanomaterials and nanotechnology to replace precious (platinum) and rare (indium, component of indium-doped tin oxide – ITO layer) metals can favor the fabrication of next-generation solar cells that are much cheaper and simultaneously eco-friendly and sustainable, like the inspiring first idea of Grätzel aimed to achieve.

DSSCs (13.0%)[103] have not reached the efficiency of silicon-based photovoltaics yet. Anyway, their use in smart windows or their indoor application[162] gives the opportunity to this technology to enter the market, in particular in the building-integrated photovoltaics (BIPV).[163] The added value of DSSCs is that they are not only functional but they also have a pleasant aesthetics.

4.1 Dye

Historically, the most widely employed sensitizers are based on ruthenium, allowing highest certified efficiency for DSSCs (12.3%). Nonetheless, ruthenium is a scarce material and it has been included in the list of CRMs by the EU.[75,121,122,148] It is costly and its complexes require relatively sophisticated syntheses and solvent-demanding purification steps.[164] In order to address these issues, alternative dyes have been developed, such as metal-free organic and natural dyes,[125,164] which in addition should be synthesised following the Twelve Principles of Green Chemistry,[126] thus allowing the lowest impacts on the lab-scale phase and the possible evaluation through the green chemistry metrics.[127]

The dye (or photosensitizer) is one of the most important components of the DSSC, since it has the main role of absorbing photons from sunlight, supplying electrons to the semiconductor and, then, converting the absorbed sunlight into electrical energy.

To be considered as an efficient PS for DSSCs, a dye should possess several essential requirements, which include:[165] (i) a high molar extinction coefficient with panchromatic light absorption ability (from the visible - Vis - to the near-infrared - NIR - region); (ii) the ability to strongly bind to the semiconductor through an anchoring group (typically, a carboxylic or a hydroxyl group), so that electrons can be efficiently injected into the semiconductor CB; (iii) a good highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) energy alignment with respect to the redox couple and the CB level in the semiconductor, which allows an efficient charge injection into the semiconductor and, at the same time, an efficient regeneration of the oxidized dye; (iv) the electron transfer rate from the dye sensitizer to the semiconductor must be faster than the decay rate of the PS; (v) stability under solar light illumination and continuous light soaking. Thus, the specific function and the working mechanism of the sensitizers is closely related to both the photoelectrode and the redox mediator. Indeed, the design of an effective PS should not neglect the mutual interaction with both these components. Physically speaking, the adsorption of the PS onto the photoelectrode should lead to the highest surface coverage (to limit the back-transfer reaction between electrons in the CB of the semiconductor and the redox mediator) without giving rise to multilayered structures that promote the self-quenching of the excited state. Chemically speaking, the LUMO of the sensitizer should be delocalized as close as possible to the anchoring site to promote an effective charge injection into the semiconductor CB, whereas the opposite is valid for the HOMO that should be delocalized in the portion of the molecule facing the electrolyte to promote the regeneration process (**Figure 8b**).

Among the most efficient sensitizers, we can include three main classes of dyes: functionalized oligopyridine metal complexes, Zn-based dyes (Zn-porphyrins and Zn-phthalocyanines) and fully organic dyes. The major issues regarding mostly all of these PSs is the possible release of harmful chemicals as by-products, during the synthetic processes jeopardizing their sustainability. Moreover, in the case of metal-based molecules, where rare metals such as ruthenium and osmium are employed, the main concern is the use of CRMs, which makes the overall device production to be highly dependent on rare resources, thus non-sustainable and uneconomical from a large scale production viewpoint.[166] It should be pointed out that Ruthenium-based dyes are exhaustively reviewed in literature;[167–173] they have been widely investigated and have achieved some of the best PV properties with conversion efficiencies exceeding 11%.[174] According to different LCA[78,80,149] results, the dye contributes to the overall impacts in a very small part and the main reason for its environmental impacts is the high consumption of solvents and eluents during the synthesis. Indeed, the quantity of dye necessary for the sensitization of the semiconductor is very limited since normally the dye loading capacity of a DSSC is around $3{\cdot}10^{-7}$

mol/cm^2 which means that, in the case of N719 and a squaraine dye, 0.35 or 0.20 mg/cm^2 are needed, respectively.[175] From this calculation, it is clear that the overall impact in terms of costs of the whole device is not due to the PS, therefore its replacement with a more sustainable alternative is less urgent. Anyway, when it comes to consider Ru-based dyes, the metal centre results the most impactful component. It is interesting to observe that assessing the impacts of YD2-o-C8, D5 and N719 (Zn-porphyrin dye, organic metal-free dye and Ru-based dye respectively) the latter one results to be the less impactful as its synthesis is well optimized.[80] The optimization of the synthesis for Ru-based dyes is evident also from their availability on the market at very low price compared to organic dyes: 65 €/g for N719 versus 400 €/g for a squaraine based dyes.[176] In order to overcome the limitations on the use of sensitizers based on rare metal complexes, the scientific community has focused, in the last years, to replace them by other PSs with comparable efficiencies, which are briefly discussed in the following paragraphs. On the other side, the removal of critical elements is not the only one solution to achieve a more sustainable dye. This is why it is crucial to combine LCA and green metrics to appreciate the overall environmental impacts.[79]

4.1.1 CRM-free dyes

After DSSCs co-sensitized with two CRM-free organic dyes reached the highest efficiency of 14.3%,[177] CRM-free and fully organic dyes started to be considered the most promising alternatives to replace metal complexes. They have been extensively explored due to their numerous advantages:[164] optimal flexibility in molecular design, easy large-scale production and the possibility of simple synthetic pathway requiring few and economical purification steps. In addition, they show extremely high molar extinction coefficients (usually exceeding 2.50 10^4 M^{-1} cm^{-1} in the Vis region) of the charge transfer band compared to ruthenium(II) complexes with a tunable absorption,[178] from the Vis to the NIR. It would be impossible to gather all the

PSs proposed so far and only some examples will be analysed starting from the recent review by Boschloo.[179] Other reviews specifically focused on metal-free PSs can be found in literature.[171,172]

One of the first well performing porphyrin dyes is the YD-2 dye (**Figure 12**), bearing a diarylamino donor group and an ethynylbenzoic acid moiety acceptor group that reached a photoconversion efficiency (PCE) of 11% when used with iodide/triiodide-based electrolyte (**Table 5, entry 1**). The device exhibited a broad absorption from 400 to 750 nm with a peak maximum over 90% at 675 nm, a short-circuit current density (J_{SC}) of 18.6 mA cm^{-2} and an open-circuit voltage (V_{OC}) of 0.77 V.[180]

In 2011, Yella *et al.*[181] proposed a tailored variant of YD-2, *viz.* the donor−π−acceptor (D-π-A) Zn porphyrin dye YD2-o-C8 (**Figure 12**), which reached a PCE value as high as 11.9% using a cobalt(II/III) tris(bipyridyl)–based redox electrolyte, with a V_{OC} of 965 mV and a J_{SC} of 17.3 mA cm^{-2} under standard air mass (AM) 1.5 sunlight at 995 W m^{-2} intensity (**Table 5, entry 2**). The YD2-o-C8 absorbs light over the whole Vis range and bears two octyloxy groups in the ortho positions of each meso-phenyl ring, impairing interfacial back electron transfer reaction and leading to enhanced photo-induced charge separation in the DSSC. Moreover, this porphyrin dye reached a power conversion efficiency (PCE) of 12.3% under simulated AM1.5G sunlight when used in co-sensitization with the Y123 organic D-π-A dye (**Figure 12, Table 5, entry 3**). The corresponding cell showed remarkable panchromatic photocurrent response over the whole Vis range, with a limited 10 to 15% decrease of the overall efficiency after continuous (220 h) exposure to full sunlight at 30° C. The advantage of using a Zn-based PS instead of Ru can be also explained by the higher supply risk of this latter metal. In fact, the natural abundance of Zn in the Earth's crust is considerably higher (72 ppm versus 0.000037 ppm for Ru) and the political stability of top reserve holders make the Zn overall relative supply risk lower (4.8) compared to Ru (7.6).[182]

A further tailored modification on the zinc-porphyrin structure was proposed in 2014 by Mathew *et al.*,[140] who included a bulky bis(2′,4′-bis(hexyloxy)-[1,1′-biphenyl]-4-yl)amine donor group and proposed a novel benzothiadiazole group as acceptor. The panchromatic porphyrin sensitizer SM315 (**Figure 12**), together with a $[Co(bpy)_3]^{2+/3+}$ redox couple, showed an improved J_{SC} (18.1 mA cm $^{-2}$) with a record 13.0% PCE (**Table 5, entry 4**) at full sun illumination without the need of a co-sensitizer. The introduction of a novel cobalt(II/III) tris(phenanthroline)–based complex redox electrolyte along with the use of a novel metal-free sensitizing dye ADEKA-1 (a carbazole/alkyl-functionalized oligothiophene with an alkoxysilyl-anchor moiety, **Figure 12**) led to improved light-to-electric energy conversion efficiencies of over 12% (**Table 5, entry 5**).[183] The same dye demonstrated >14% PCE in the presence of the co-sensitizer LEG4 (a carboxy-anchor organic sensitizing dye, **Figure 12** and **Table 5, entries 6 and 7**).[177] Benzothiadiazole group was used as acceptor in the organic R6 dye (**Figure 12, Table 5 , entry 8**), which exhibited a polycyclic aromatic hydrocarbon core with a diarylamine electron donor[184] and a brilliant sapphire color when absorbed on TiO_2 film with a cobalt(II/III) tris-(bipyridyl)-based redox electrolyte. The resulting DSSC provided an impressive PCE of 12.6% with a remarkable photostability. Nevertheless, the employment of a cobalt-based electrolyte negatively influences the sustainability of the device, as thoroughly discussed in the following section.

In principle, all these reported PSs are sustainable as they do not present CRMs; however, high efficiency values reported so far are achieved especially in the presence of cobalt-based redox couples. Moreover the synthetic pathways of Zn-porphyrin dyes should be analyzed and further optimized in order to diminish the number of required synthetic steps (*i.e.* actually more than ten for SM315 from available starting materials), increase their yields and possibly remove the use of homogeneous noble metal catalysts (*i.e*. several steps required Pd-based complexes).[185] Indeed, the higher the number of synthetic step and the lower the reaction yield, the higher the CED of the process.

Examples of more sustainable DSSCs are those using CRM-free PSs coupled with CRM-free copper-based electrolytes, where the use of rare metals and cobalt is actually avoided. In 2017, Cao *et al.*[186] proposed the well-known Y123 dye using a blend of $[Cu(tmby)_2](TFSI)_2$ and $[Cu(tmby)_2](TFSI)$ as hole transporting material (HTM) and electrodeposited poly(3,4-ethylenedioxythiophene) (PEDOT) as the CE. In 2018 also thanks to the design of an enhanced DSSC architecture, the same group achieved an efficiency of 13.1% on a lab-scale (**Table 5, entry 9**).[187] A 26% improvement over the Y123 reference dye was achieved with WS-72 dye (**Figure 12**), always employing a $[Cu(tmby)_2]^{2+/+}$ liquid-junction redox electrolyte.[188] The solidification of the electrolyte for the champion device led a PCE of 11.7% (J_{SC} = 13.8 mA cm^{-2}, V_{OC} = 1.07 V), which is the highest efficiency reported so far for solid-state DSSCs (**Table 5, entry 10**).

Among fully organic dyes, Marder and his group proposed a 4,4-bis(2-ethylhexyl)-4Hsilolo[3,2-b:4,5-b′]dithiophene (DTS) covalently linked to a squaraine donor yielding an asymmetrical push−pull D−π−A structure that provided 8.9% with the triiodide/iodide redox couple (**Table 5, entry 11**).[189] The DTS-CA squaraine dye (**Figure 12**) bears two branched 2-ethylhexyl chains out-of-plane, being able to reduce dye aggregation with a considerable improvement over J_{SC}, incident photon-to-electron conversion efficiency (IPCE) and overall cell performance. Another well performing organic dye featuring more than 10% efficiency is C219 (**Figure 12**); it is an amphiphilic push-pull chromophore, which consists of a binary π-conjugated spacer, apart from the blocks of a lipophilic alkoxy-substituted triphenylamine electron-donor and a hydrophilic cyanoacrylic acid electron-acceptor. C219 dye demonstrated stable performance and high efficiency of 8.9% in lab-scale solvent-free ionic liquid cell (**Table 5, entry 12**).[190]

Anyway, even if these fully organic dyes do not bear CRMs, their synthetic procedure can often be non-sustainable. Dyes themselves as well as solvents and reagents used for their synthesis can be toxic, hazardous or expensive or by-products of the manufacturing process might be environmental pollutants. For every synthesis, the calculation of the CED should be undertaken. For example, synthesis of R6 consists of several time/energy consuming steps, including two-fold Suzuki-coupling, a double Grignard nucleophilic addition, an acid-catalyzed intra-molecular Friedel−Crafts cyclization, a Buchwald−Hartwig coupling, a monobromination, a Sonogashira−Hagihara reaction plus a final hydrolysis and acidification.[184] The organic dye C219 is achieved by seven synthetic steps requiring a certain amount of organic solvents and palladium catalysts.[190] The synthesis of the squaraine dye DTS-CA consists of an aldehyde protection step, a lithiation and stannylation followed by a Knoevenagel condensation.[189] All or most of all these synthetic steps require CRM-based catalysts and an overall large amount of organic solvents making the final dye non-sustainable at all, even if the final dye actually does not bear rare metals or CRMs.

An interesting approach to design simpler and more stable dyes that require only few synthetic steps and consequently a lower amount of energy (lower CED) was proposed by Abbotto *et al.*, designing di-branched di-anchoring sensitizers.[191] A similar idea was also proposed in the case of symmetrical far-RED-NIR sensitizers based on squaraine dyes (VG1-C8 and VG1-C10, **Figure 12**).[192,193] The authors were able to obtain a symmetric squaraine and its related non-symmetric structure with comparable efficiencies in DSSCs, but with undoubtedly advantages in the low cost and easiness of synthesis for the symmetrical structure. The latter approach was further implemented in the subsequent years improving the synthetic yields and lowering the energy request by performing all the synthetic steps within a microwave assisted oven.[194] Unfortunately, photovoltaic efficiencies that overcome the record Zn-porphyrins and/or metal-free organic dyes reported in **Table 5** have not been reached yet with this approach.

More recently a mass-based green metrics and life cycle assessment combined approach was applied to identify the best synthetic protocol for the preparation of an organic dye TTZ5 (**Figure 12**),[79] previously proposed as sensitizer.[195] New synthetic strategies have been compared with the previously reported synthesis. The procedures rely on two different approaches based on a C-H activation/Stille cross-coupling sequence or on a one-pot double C-H activation sequence and have been optimized to allow the production of TTZ5 in gram scale. Results highlight the contribution of direct energy consumption and purification operations in organic syntheses at lab scale. It becomes evident how both the new procedures allowed to complete the synthesis in a more sustainable way than the previous one, considering the inferior production of waste, the lower costs and a smaller environmental impact. Despite a higher number of steps, surprisingly the C-H/Stille route revealed to be more sustainable than the one-pot C-H activation one, even if the employment of toxic and/or flammable reagents such as n-butyllithium and tin-containing materials raised its Eco-scale value, while the application of LCA showed that the drawback of the one-pot C-H activation route procedure is represented by raw material inputs for the chromatography setup. Furthermore, this approach demonstrates the usefulness of the environmental multifaceted analytic tool and the power of LCA to overcome the intrinsic less comprehensive nature of green metrics for the evaluation of organic synthetic protocols.

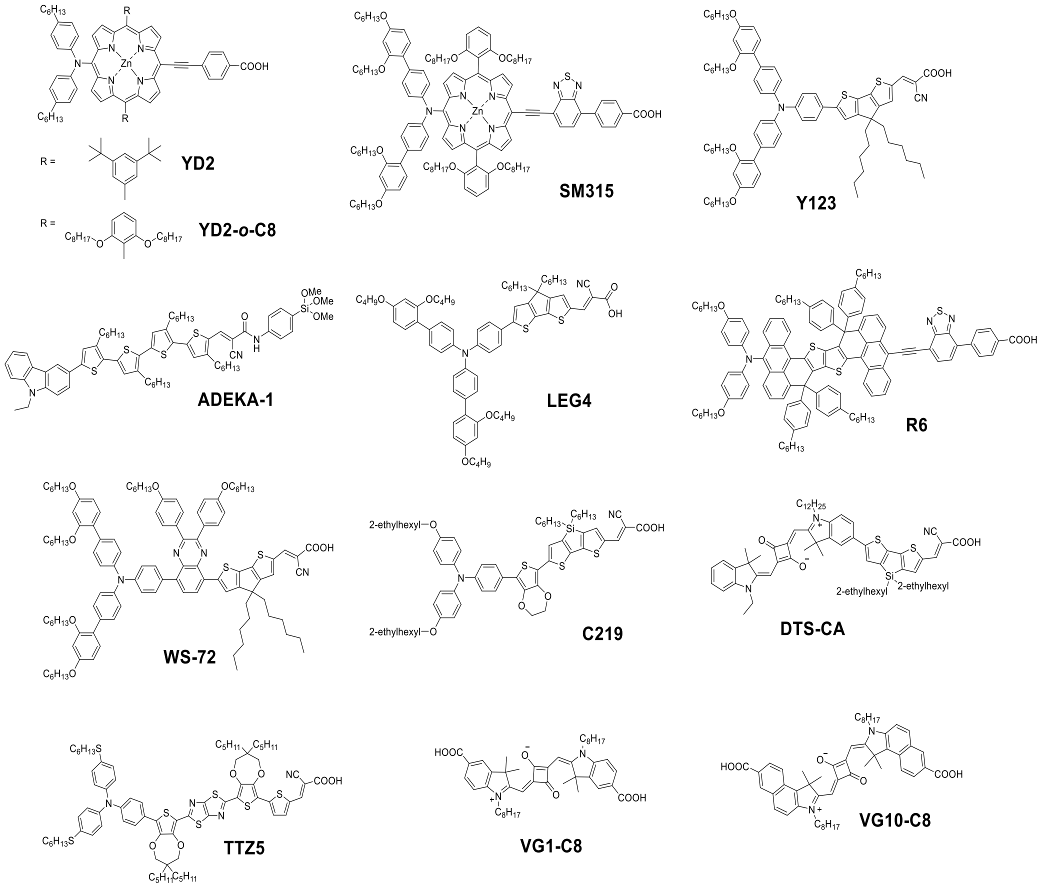


Figure 12 Structures of various CRM-free photosensitizer: Porphyrins (YD2 and YD2-o-C8) and fully organic dyes. All the molecules are made by ChemDraw 19.0.

4.1.2 Natural dyes

To overcome the limitations in the sustainability of using metal complexes and metal-free dyes, natural pigments and dyes found in plants have been proposed as good alternative PSs for DSSCs.[196–198] As initial statement of this paragraph, we would stress that an extremely precise analyses of the cost-effectiveness of natural dyes was not possible, no matter our efforts; in fact, the volume of solvents used for the extraction and the overall yield of this process are usually not reported in literature. The final costs of natural dyes are in many cases difficult to assess greatly depending on the availability of the natural sources and the impact of the extraction and purification method. The advantage is that, even if in some cases huge quantity of solvents are needed, they can be easily recovered (with a fixed energy request) downsizing the overall CED and environmental impact of the dye production process due to the minimization final costs and wastes.

Despite the limited performance that natural dyes have demonstrated so far, they have several beneficial features, which include, amongst others, high absorption coefficients, simple, low cost and energy saving production, low toxicity, complete biodegradability, ready availability, and, most importantly, high reduction of usage of noble metals and CRMs, thus negligible environmental impact at lower cost. With respect to the photoconversion efficiency, for all dyes and chiefly for natural ones, it is important to control the recombination with the electrolyte and with the oxidized dye since a relatively fast electron/dye cation recombination process has been evidenced.[199] It is therefore necessary the optimization of the interfaces to improve the V_{OC}, that is usually 200 mV lower compared to Ru complexes. Moreover, the IPCE can be affected by the electrolyte choice: Co-based complexes may greatly decrease it while a kinetically faster redox couple like iodine/iodide seems compulsory.

Natural pigments (*e.g.*, anthocyanin, carotenoid, aurone, chlorophyll, tannin, betalain and many others) may become cost effective (depending on their photovoltaic efficiency) when compared to manufactured dyes, as they can easily be extracted from fruits, flowers, leaves, seeds, roots, barks and various parts of plants utilizing simple extraction processes based on water and simple alcohols (i.e. methanol or ethanol) which are environmentally preferable solvents from an environmental perspective.[200] These dyes and pigments may not contain a solubilising group, which can be temporarily generated during the application.[201] On the other hand, the efficiency obtained using natural dyes as sensitizers is quite low because of their tendency to degrade and the lack of a panchromatic absorption, being limited from 400 to 700 nm.[202]

They can be grouped into four main families: flavonoids (**Figure 13a**), including anthocyanins, (**Figure 13b**), carotenoids (**Figure 13c**), betalains (**Figure 13d**) and chlorophylls (**Figure 13e**).[203] Flavonoids (**Figure 13a**) are important natural products belonging to a class of plant secondary metabolites having a polyphenolic structure; they are widely found in fruits, vegetables, grains, bark, roots, stems, flowers, tea and wine. Flavonoids act as unique ultraviolet (UV) filters, also protecting plants from different biotic and abiotic stresses.[204] From the structural viewpoint, they have a basic C6-C3-C6 skeleton and can be divided into four different classes, i.e. flavonoids or bioflavonoids, isoflavonoids and neoflavonoids. They contain a 15-carbon (C15)-based structure with two phenyl rings connected by three carbon bridges, forming a third ring. The degree of phenyl ring oxidation identifies their different colours.[202] They can be used as natural PSs for DSSC;[205] indeed, their adsorption to the mesoporous TiO_2 surface is fast, displacing an OH^- counter ion from the titanium sites able to combine with a proton coming from the flavonoid structure. Anthocyanins are the most abundant and widespread pigment of the flavonoid family. They exhibit a broad band in the Vis region of the spectrum, ascribed to charge transfer transitions, and their compounds can easily bind to the semiconductor by means of carbonyl and hydroxyl functional groups, through a chelation mechanism.[166] DSSCs sensitized by anthocyanin pigments show efficiencies below 1%, with the exception of few cases (**Table 5, entry 13**).[166,197,206,207] The generated IPCE does not exceed 20%, even if charge injection is usually very fast, due to problems connected to dye aggregation, electron recombination with the oxidized sensitizer and electron recapture by iodine/iodide electrolyte. In all of these examples, both efficiency and stability of lab-scale DSSCs are highly affected by the temperature of the extracting solvent, as well as its nature,[208,209] chiefly its polarity that influences the solubility of the pigments. Actually, acidic aqueous dye extracts greatly improved the coloration of the photoanodes for selected eggplant and red grapes extracts compared to photoanodes obtained from ethanolic solutions.

Carotenoids (**Figure 5c**) are an essential component of all photosynthetic organisms due to their eminent photoprotective and antioxidant properties.[210] We counted more than 600 known carotenoids that can be further categorized into two major classes: xanthophylls (containing oxygen) and carotenes (purely hydrocarbons without oxygen, like lycopene and carotene). Further classification is between primary (*i.e.*, required by plants for the photosynthetic process) and secondary (*i.e.*, localized in fruits and flowers) carotenoids. Normally, they are yellow, orange and red organic pigments, produced by plants and algae, as well as several bacteria and fungi. Carotenoids belong to the general family of isoprenoids, having a basic structure made up of eight isoprene units, which results in a C_{40} backbone, and allows them to absorb electromagnetic radiation of short wavelengths ranging from 380 to 550 nm. Their absorptive capability, together with their molar extinction coefficients exceeding 10^5, allows some kinds of carotenoids to be potential sensitizer materials in PV cells and other artificial photochemical devices. Usually, raw natural dyes are better than their purified or commercial analogues due to the presence of natural extracts, such as alcohols and organic acids, which can improve dye adsorption, prevent electrolyte recombination and decrease dye accumulation.[201,202]

Another promising research is the realization of natural, low cost and environmentally friendly DSSCs made from organic waste leading to a huge decrease of the overall CED. A good example has been proposed by Maiaugree *et al.* where both dye and counter electrode were prepared from waste mangosteen peel.[211] In particular, carbonized mangosteen peel film was used with mangosteen peel dye extract as a natural counter electrode and a natural photosensitizer, respectively, to obtain a 2.63% solar conversion efficiency in combination with an organic disulfide/thiolate mixture as the electrolyte (**Section 4.2.1**).

Different approaches using carotenoids demonstrated generation of photocurrents upon illumination (usually, around 2 nA cm $^{-2}$), but the resulting

IPCE was very low (<0.4%). The main issue consists in a kinetic limitation of efficient photo-injection and movement of electrons imposed by the short S_1 excited state lifetime (10–50 ps). This was partially solved by Gao *et al.* by directly coordinating a carotenoid, the 8’-apo-β-caroten-8’-oic acid substituted with a terminal carboxylate group, to the TiO_2 surface via formation of covalent bonds.[212] The resulting cell showed a J_{SC} of 4.6 mA cm^{-2} with an IPCE of 34% and a V_{OC} of 0.15 V, along with 1 h stability under continuous irradiation. In fact, carotenoids have not been thoroughly investigated as sensitizers for DSSCs because most of them do not have effective functional groups to bond with the hydroxylic groups of TiO_2; in addition, the strong steric hindrance of long alkyl chains prevents the dye molecules from arraying efficiently onto the TiO_2 film. Yamazaki *et al.*[213] proposed a comparison study between the different photosensitization behavior of two carotenoids, namely crocetin and crocin. Crocetin, a carotenoid bearing carboxylic groups, exhibited a high binding ability to the surface of the semiconductor film and its photoelectrochemical performance (0.56%) was three times or even higher than crocin (0.16%). These successful attempts promoted the use of carotenoids as potential new natural sensitizers. Thereafter, carotenoids have been used in DSSCs[214–216] reaching the highest efficiency of 2.6% with analogues of carotenoic acids (**Table 5, entry 14**),[217] the value increased up to 4.2% in combination with a chlorophyll derivative as the sensitizer (**Table 5, entry 15**).[218]

Chlorophylls (**Figure 13e**) are natural green pigments that are found in natural photosynthetic systems, like leaves of most of the plants, algae and bacteria.[219] Six different types of chlorophylls pigments exist. Chlorophylls a (Chl-a) and b (Chl-b) are the most common types and absorb light from red, blue and violet with an absorption maximum at 670 nm.[202] The basic molecular structure of chlorophyll includes a porphyrin ring, which is coordinated to the central atom, along with different side chains and a hydrocarbon tail. Chl-a and Chl-b differ only by a substituent being attached to the pyrrole ring on the porphyrin ring opposite to the phytol tail.[166] The absorption spectra of Chl-a and Chl-b are in the range of 400-700 nm and 450-650 nm, respectively, depending of the different side groups. Chlorophylls and their derivatives are therefore attractive as PSs in DSSCs because of their ability to absorb light over a broad region of the Vis spectrum.

The use of chlorophylls as PSs in DSSCs was recently reviewed.[197,207,220] The main disadvantage can be the presence of long chains leading to low-electron transferability due to steric hindrance and in some cases their very low adsorption ability on the semi-conductor caused by the absence of proper anchoring groups.[221] The most interesting examples utilize chlorophyll extracted from a species of the moss bryophyte in combination with a quasi-solid-state polyacrylonitrile (PAN)-based iodide electrolyte; it led to a 1.97% efficiency with J_{SC} of 5.78 mA cm^{-2} and V_{OC} of 0.60 V, covering quite a wide IPCE spectrum from 300 to about 550-600 nm.[222] A further increase (J_{SC} = 5.96 mA cm^{-2}, V_{OC} = 0.58 V with PCE = 2.00%) was obtained using chlorophyll, extracted from the bryophyte *Hyophila involuta*, and a gel electrolyte based on poly(vinyl alcohol) (PVA) and double salt (KI and tetrapropylammonium iodide). The use of chenodeoxycholic acid (CDCA) as anti-aggregation agent added to the chlorophyll led to a further increase of the light to electricity efficiency of 2.62% with J_{sc} of 8.44 mA cm^{-2} and V_{OC} of 0.54 V.[223] To our knowledge, chlorophyll c2 extracted from *Undaria pinnatifida*, isolated from a brown seaweed, demonstrated the highest efficiency ever recorded among chlorophyll-sensitized DSSCs.[224] Chlorophyll c (Chl-c) was isolated by removing Chl-a and carotenoids; then, the purified Chl-c was subjected to polyethylene column chromatography to isolate Chl-c1 and Chl-c2. Efficiencies of 3.4 and 4.6%, the highest recorded so far for a chlorophyll-based dye, were obtained from the Chl-c1 and Chl-c2 sensitized DSSCs, respectively, with liquid electrolyte (**Table 5, entries 16** and **17**).[224] On the other hand, the additional purification steps counterbalance the gain in efficiency. Moreover, a DSSC prepared by a cocktail dye (by chlorophyll extract of wormwood and anthocyanin extract of purple cabbage) achieved

PCE of 1.95%, V_{OC} of 0.765 V and J_{SC} of 5.83 mA cm^{-2}.[225] Even if Chlorophylls have been widely employed as natural sensitizers in DSSCs thanks to their efficient light-harvesting mechanism and electron-transfer reactions,[203] they lack stability and are highly dependent on the condition of leaves (whether fresh or dried) that could affect the device performance. Moreover, the absorption is greatly influenced by the solvent and the pH used during pigments extraction.[226]

Betalains (**Figure 13d**) are a small group of water-soluble and nitrogen-containing indole-derived glycoside pigments present in the vacuoles of cells of fruits, roots and flowers of plants of the order of *Caryophyllales*. They can be divided into betacyanins and betaxanthins. Red and violet tonalities result from different substitution patterns in betacyanins, while different amino acid or amine side chains determine the color of betaxanthins.[227] Betalains are aromatic indole derivatives and are an alternative to synthetic colorants, which absorb radiation in a Vis range between 476 and 600 nm; they show stability over a wide pH range and a high molar extinction coefficient, but they are generally unstable when exposed to light, heat and oxygen.[201] Although only few reports were published so far about betalain-based DSSCs, the presence of carboxylic functional groups favours their binding to the surface of TiO_2, which makes them promising PSs. Few published examples, reporting efficiencies around 0.5%[228,229] up to 2%,[230] are thoroughly reviewed by Bartolotta and Calogero,[203] who explained the limitations of using betalains in DSSCs due to their short S_1 lifetime. Güzel *et al.*[231] recently reported a betanidin extract, with a very broad absorption from 300 to 700 nm, which showed the highest PCE of 3.04% and excellent stability during solar irradiation when tested in lab-scale DSSCs (**Table 5, entry 18**). The low performances of betalain-based DSSC are due to a low V_{OC} as for other natural dyes and to an insufficient electron injection quantum yield. The short S1 lifetime is responsible of a rapid internal conversion process, so that the injection is highly affected.[232] Calogero *et al.*[199] observed that it is unlikely that charge injection can be the IPCE limiting process, but recombination losses can be responsible. Unfortunately, a detailed investigation is still missing.

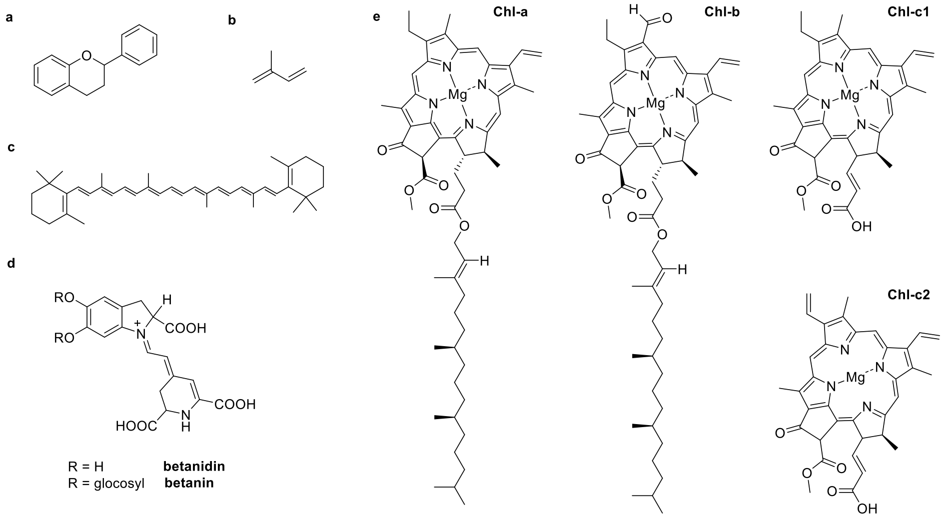


Figure 13 Chemical structures of natural dyes: a) basic flavonoid structure, b) basic structure of an isoprene unit, c) chemical structure of carotene, d) structure of betalain derivatives and e) chemical structures of various chlorophylls. All the molecules are made by ChemDraw 9.

The overall performances of DSSCs based on natural dyes and pigments are low when compared to other devices where organic or metal-organic dyes are employed as sensitizers. This is chiefly ascribable to the low interaction between dye sensitizers and the semiconductor surface due to the absence of specific anchoring groups and/or the presence of bulky groups on the dyes that result in a steric hindrance to form a strong bond with the oxide surface. The low efficiency is also determined by the low V_{OC}, coming from the inefficient reduction of the oxidized dye. It can be overcome by the use of additives and co-absorbers, but this could have a negative influence on the molar extinction coefficient and the absorption maximum since natural dyes are pH-sensitive.[203] Another important issue is the stability of these devices that is most often low and insufficient to meet the standard devices assembled using other classes of dyes. Other issues concern the source of the dyes and pigments, as well as the solvents employed for their extraction. From the examples reported so far, it is clear that the device performance depends upon the polarity and acidity of the solvent or on the extraction temperature;[208] actually, solvents used to extract these natural dyes must be carefully selected to achieve high effectiveness in extraction process, without hampering the sustainable features.[166]

4.1.3 Final remarks on dyes

Albeit the actual quantity of dye to be used in a DSSC device is very low, making the problem of cost-effectiveness less impactful, the sustainability of the photosensitizers could be substantially enhanced. Starting from the "classical" Ru-based dyes, different directions have been plumbed. The substitution of ruthenium with other metal that are not CRM (such as Zinc) had greatly improved the overall sustainability. A complementary approached consisted in the design of fully organic sensitizers. Yet, this elegant approach is usually not classifiable as sustainable being characterized by a sizeable number of synthetic step and the employment of harmful reactant, solvents and catalysts. Aiming at sustainability, natural dyes could be considered a valid alternative being environmental-friendly due to their natural occurrence from locally available resources, *i.e.* plants, flowers, fruits and roots. Unfortunately, their performances are lower with respect to synthetic dyes ones and they suffer degradation in the presence of sunlight radiation resulting in great stability problems in DSSC. Moreover, natural dyes show absorption mainly in the visible region (400–700 nm) of the solar spectrum losing a consistent energetic contribution from longer wavelength. For the above-mentioned reasons, even if the natural dye production is less expensive since it requires simple and direct chemical procedures, they are not cost-effective at all and synthetic dyes are still more successful and performing. Increasing the light absorption capacity by using co-sensitization is amongst the most effective possibilities to enhance the DSSC performances, because it promotes a synergistic effect in improving electron injection, light harvesting and limitation of electron recombination. This is actually critical already with synthetic dyes, which are in principle designed for this specific target, but it becomes much more critical when using natural dyes that may also bear impurities and functional groups that can affect the device functioning. Thus, from a chemical point of view, efforts can be done on the modification of the design and production of the synthetic dyes varying the overall synthetic approach rather than optimizing the single steps of the conventional protocol, lowering the environmental impact and reducing wastes.[233] The latter route could lead to performing, stable synthetic dyes and could be considered as the best trade-off between to obtain cost-effective but sustainable dyes.

Table 5 Different classes of dyes, along with name/acronym of the most representative ones, related advantages, most critical issues, highest recorded efficiency values and corresponding reference articles.

Class	***Dye***	***Pros***	***Issues****	***η (%)***	***Entry***[*Ref*]
n-porphyrin	YD2	• Iodide/triiodide electrolyte • Broad absorption	• Not meaningful	11.1	**1**[180]
	YD2-o-C8	• High PCE • High stability	• Cobalt-based electrolyte: $Co(bpy)_3^{3+/2+}$	11.9	**2**[181]
	YD2-o-C8 + Y123	• High PCE • High stability	• $Co(bpy)_3^{3+/2+}$	12.3	**3**[181]
	SM315	• Panchromatic absorption • No need of co-sensitization • Very high PCE	• $Co(bpy)_3^{3+/2+}$	13.0	**4**[140]
D-π-A	Adeka-1	• High PCE • High stability	• $[Co(Cl\text{-}phen)_3]^{3+/2+}$	12.5	**5**[183]
	Adeka-1 + LEG4	• Iodide/triiodide electrolyte	• Not meaningful	11.2	**6**[177]
	Adeka-1 + LEG4	• Record PCE	• $[Co^{2+}(phen)_3](PF_6^-)_2$	14.3	**7**[177]
	R6	• High PCE • High photostability	• $Co(bpy)_3^{3+/2+}$	12.6	**8**[184]
	Y123	• Copper-based electrolyte: $Cu(tmp)_2^{2+/+}\ TFSI$	• Not meaningful	13.1	**9**[187]
	WS72	• Copper-based electrolyte: $Cu(tmp)_2^{2+/+}\ HTM$	• Not meaningful	11.6	**10**[188]
	DTS-CA	• Iodide/triiodide electrolyte	• Not meaningful	8.9	**11**[189]
Organic squaraine dye	C219	• Iodide/triiodide electrolyte	• Not meaningful	10.1	**12**[190]
Flavonoids	Anthocyanin from *M. malabathricum*	• Natural PS • Extended π conjugation • • •	• Low stability • Low PCE • • •	1.1	**13**[206]

Class	***Dye***	***Pros***	***Issues****	***η (%)***	***Entry***^{Ref}
		•	•		
Carotenoids	MeO-φ-6-CA	• Natural PS	• Low stability • Low PCE	2.6	**14**[217]
	PPB + β-carotene	• Natural PS • Iodide/triiodide electrolyte	• Low stability • Co-sensitization with a chlorophyll derivative • Low PCE	4.2	**15**[218]
Chlorophylls	Chlorophyll c1 from *Undaria pinnatifida*	• Natural PS	• Low stability • Low PCE	3.4	**16**[224]
	Chlorophyll c2	• Natural PS	• Low stability • Low PCE	4.6	**17**[224]
Betalains	SPA	• Natural PS • Iodide/triiodide electrolyte	• Low stability • Low PCE	3.0	**18**[231]

* Issues related to the synthesis of the dyes are omitted for clarity purpose.

4.2 Sustainable electrolyte: beyond iodine, cobalt and organic solvents

As already mentioned in the introductory section, the electrolyte is amongst the key elements for a well-performing DSSC:[234] it is responsible for the dye regeneration after the injection of electrons or holes in *n*-type and *p*-type devices, respectively,[235,236] and ensures a good charge transfer through the cell, enabling proper device operation. The electrolyte should have high stability, appropriate redox potential with respect to the HOMO level of the sensitizer, high transparency in the Vis region to avoid competition for light absorption with the dye and low corrosiveness.[234] To further improve the practical application of DSSCs, at a large scale, it should also result from abundant, possibly renewable, raw materials. Historically, liquid electrolytes have been firstly exploited for application in DSSC, because of the high charge carrier diffusion assured and the possibility of effectively permeation of the photoelectrode porous structure. As discussed in detail below (**Section 4.2.3**), more recently quasi solid and solid electrolytes have been also investigated to minimize the critical issue of liquid-based device, typically linked to the solvent leakage. Throughout this chapter, we mainly focus on liquid (both organic, **4.2.1**, and aqueous, **4.2.2**) electrolytes being the more thoroughly investigated and considering that first industries entering in the market proposed DSSCs based this type of electrolytes. In this context, it should be pointed out that the improved stability assured by quasi-solid and solid electrolyte is not automatically a "*green light*" toward sustainability, but proper LCA analyses should be performed.

The most common redox couples of the electrolyte are based on iodine or cobalt. Iodine-based electrolytes are composed by the I^-/I_3^- redox couple, I_3^- being formed through the reaction $I_2 + I^- \leftrightarrows I_{3,}{}^-$ which offers several advantages, such as fast dye regeneration and charge mobility.[237] Additionally, being I^- a very small anion, it effectively permeates the mesoporous structure of sensitized photoelectrode assuring a almost quantitative sensitizer regeneration. On the other hand, this could also favor the recombination reaction with the electron injected in the VB of TiO_2, but this could be efficiently prevented by the insertion of a nanometric "blocking" layer.[238,239] However, I_2 often results corrosive for commonly used metals (both at lab-scale and module-scale levels);[240] in particular, when platinum is used as CE, iodate could be formed, with a depletion of the active species in the electrolyte.[234] This affects negatively the long-term durability of cells, which is also reduced by the volatility of I_2, even if this last issue was partially solved by the use of a quasi-solid electrolyte.[241,242] Moreover, I_2 is colored and absorbs part of the solar radiation, being in competition with the sensitizer.[240] This point is of crucial interest in the development of bifacial device to be applied in BIPV. In addition, it has a fixed, high redox potential, so the V_{OC} is limited between 0.6 and 0.8 V and cannot be tailored as desired.[243] Finally, this redox couple presents a complicated two-electron process, analytically described in some review articles.[236]

On the other hand, cobalt-based organometallic complexes offer the possibility of finely tuning the chemical and redox properties of the mediator, by varying the ligands on the metal center. However, they are usually sterically hindered molecules, and this entails a mass transportation issue, with slow charge transfer dynamics (*i.e.* for $10^{-6}\cdot cm^2\cdot s^{-1}$ in ACN, slower than the triiodide one, $\sim 2\cdot 10^{-5}\cdot cm^2\cdot s^{-1}$).[244,245] Cobalt is a CRM; its natural abundance of 0.003% in the Earth's crust and 8×10^{-9}% in the oceans[73] entails a high risk for its future supply according to a recent press release by the European Chemical Society (EuChemS). If the last three months of 2019 are considered, the cost of cobalt hydroxide increased by 55%.[246] Despite the high performance of its complexes as redox pairs, which allowed the highest efficiency values in the DSSC scenario (up to 14.3%),[177] it must be replaced with abundant and renewable raw materials for sustainability. Therefore, albeit in this context they are not detailly investigated, a recent review excellently summarized their application in DSSC.[247]

Owing to the disadvantages of iodine- and cobalt-based electrolytes, extensive research was focused in the recent years on the development of alternative redox pairs.[234] In the following subparagraphs, we will briefly review the most interesting developments in this respect, including major outcomes in the last five years, chiefly enlightening specific aspects related to circular economy of the DSSC market of tomorrow. We anticipate that we strongly believe that a fully sustainable DSSC should be based on innovative electrolytes and related components, arising from renewable sources and not be made up of CRMs, the supply of which could fail in the coming years and the use of which is also not justified in terms of overall gain in efficiency output of the device. To the best of our knowledge, we did not find literature reports of redox pairs obtained from renewable sources or waste-derived products, as conversely demonstrated for CE (*e.g.*, carbon-based cathodes coming from food industry waste, *vide infra*). However, we are quite confident that efficient redox pairs based on transition metal complexes might be obtained from waste recovery, as well as purely organic or sulfur-based shuttles might be readily obtained from biomasses or renewable sources.[248]

4.2.1 Alternative redox couple electrolytes

Pseudohalogens are amongst the first alternative redox couples reported in the literature.[249,250] In particular, the $SeCN^-/(SeCN)_2$ couple can be easily incorporated in a photo-reticulated polymer membrane, which may potentially enhance the long-term stability of devices (*i.e.* the trapping of the redox couple in a polymer matrix greatly reduces the evaporation of the electrolyte solvents), thus representing a step further forward towards their commercialization. Pseudohalogen-based redox couple allows *in-situ* free-radical polymerization, which is not possible with the traditional iodine-based redox couple due to its radical-quencher nature.[249] Free-radical polymerization is amongst the most useful and lucrative fields of chemistry ever discovered, is tolerant of diverse functionality and can be performed in a wide range of media. Particularly, UV and thermally induced methods are rapid, energy saving, solvent-free, thus cost-effective and sustainable, and already widely propelled to the commercial scale for the manufacturing of diverse polymers starting from oil derivatives. Furthermore, the chemical behavior of pseudohalogens is close to that of halide ions; the presence of heteroatoms and double bonds does not significantly influence their chemical properties.[249] They often show a more positive redox potential, *e.g.* the redox potential of $SeCN^-/(SeCN)_2$ shuttle is 0.19 V higher than that of I^-/I_3^-, leading to higher V_{OC}. It has also been reported that $SeCN^-/(SeCN)_2$ redox couple possesses good mass transport characteristics, at the level of iodine-based ones.[249] The application of $SeCN^-/(SeCN)_2$ in a UV-crosslinked polymer network was demonstrated, which led to a quasi-solid state system showing V_{OC} of 550 mV, J_{SC} of 6.68 mA cm^{-2}, fill factor (FF) of 0.53 and a PCE of 1.95% (**Table 6, entry1**). A selenium-based pseudohalogen redox couple was also reported by Lennert *et al.*,[250] who used a RTIL as the electrolyte medium. RTILs are salts in the liquid state at room temperature, which present several advantages, such as low volatility, high chemical and thermal stability, low flammability and rather easy structure tuning to increase the solubility of specific solutes.[251] As a result, they are potential candidates to replace the high-performing state-of-art organic solvents in DSSC electrolytes. However, despite RTILs offer a suitable solution for the replacement of volatile and flammable organic solvents, according to the green chemistry criteria their synthesis and final disposal at the EoL are still not sustainable[59] and extensive work has still to be done, in order to make them suitable alternatives. In the work by Lennert *et al.*, an alkyl-substituted RTIL was used with either selenocyanate or iodide counter anions. Remarkably, the PCE of the selenocyanate-based device was only slightly lower than its the iodide-based counterpart (5.00 *vs.* 5.60%, respectively, **Table 6, entry 2**) mainly due to slower ionic diffusion and a less efficient regeneration at the counter electrode, with respect to the iodine-based counterparts. Overall, despite these promising results, no other relevant work was done in the development of this redox couple, most likely because selenium is a pretty rare element in the Earth's crust (5×10^{-6} wt%)[73] and is toxic at high concentration.[252]

Iron-based redox couples were also investigated for the replacement of cobalt- and iodine-based electrolytes. Iron is one of the most abundant metals (6.3 wt% in the Earth's crust)[73] and its metal complexes ensure the possibility of tuning the redox potential with the use of different ligands. Unfortunately, most of the iron complexes are air sensitive and require dry glove-box confinement for the assembly of the device. This represents a hindrance for the scalability of the manufacturing process, particularly when easier processability is claimed for DSSC technology with respect to other PV devices. Noteworthy, Fe forms several complexes that are soluble in water, thus envisaging its use in green, aqueous-based DSSCs,[129,253] as will be discussed in the **Section 4.2.2**. One of the first devices based on iron complexes as redox mediators was reported by Daeneke *et al.,*[129] who demonstrated the use of a ferricyanide/ferrocyanide ($Fe(CN)_6^{4-/3-}$) redox couple, using water as the solvent and proposing this electrolyte as non-corrosive. This redox couple had a similar redox potential to that of I^-/I_3^-, thus it could be effectively coupled with already existing molecular dyes. A pH buffer and a surfactant were used to regulate the pH of the electrolyte and to allow the permeation of the electrolyte into the hydrophobic sensitized TiO_2; unfortunately, the PCE is the half of the Iodine-based reference (**Table 6, entry 3**). The same redox couple was adopted by Kokal *et al.*,[254] who reported an aqueous DSSC with an inexpensive magenta dye (New Fuchsin) and a platinum-free CE based on CoS deposited on carbon fabric. Here as well, a remarkable efficiency of 2.88% was reached (**Table 6, entry 4**), that could be considered, as a first approximation, cost-effective. $Fe(CN)_6]^{4-/3-}$ redox couple has some intrinsic problems that limited its application: having a lower redox potential, it less effectively regenerates commonly employed dyes and, straightforwardly, more pronounced TiO_2/dye recombination could be expected. In addition, it undergoes to photolysis and photodecomposition under UV and near UV radiation, loosing almost 80% of its initial efficiency just after 5 h of light soaking.[255]

Iron-based organometallic complexes were also exploited in *p*-type DSSCs.[256] Perera *et al.*[255] successfully employed Fe(*acac*)$_3^{0/-1}$ redox couple (*acac* = acetylacetonate) in a *p*-type DSSCs with NiO as photocathode. This redox couple showed a remarkably lower redox potential (-0.20 V *vs.* NHE) with respect to that of I^-/I_3^- (+0.32 V *vs.* NHE). Consequently, both the V_{OC} and the PCE were strongly improved (645 *vs.* 243 mV and +191%, respectively, **Table 6, entry 5**). Despite its higher abundance and ready availability with respect to cobalt, results with iron based redox couples are still unsatisfactory, which, added to their O_2-sensitiveness, severely limited a widespread exploitation on a large scale.

Copper is intrinsically less toxic,[73] more environmental friendly[243] and two times more abundant than cobalt in the Earth crust (0.003% *vs.* 0.0068%, respectively).[73] Its complexes are generally more stable in air than iron-based ones, which allows their assembly without using glove-box conditions. The most common copper-based redox couples are constituted by copper(II/I) organometallic complexes with distorted geometry (**Figure 14a**).[243,257–262] This kind of complexes shows negligible structural changes when switching from the oxidized to the reduced form, which means minimal energy losses and fast electron transfer.[254] Their usually more positive redox potential assures higher theoretical V_{OC} value compared to conventional redox mediator (iodine and cobalt), but, on the other hand, a less efficient dye regeneration could be expected due to the limited G of this process. However, transient absorption spectroscopy confirmed an almost quantitative dye regeneration yield.[259,261] Additionally, from a pure electrochemical point of view, copper-complexes have been proved to be relatively stable.[243]

The main drawback in the use of copper complexes is the presence of the phenanthroline-derived ligand, that requires harsh synthetic condition, despite allowing the realization of complexes with tunable features and low-reorganization energy.[263] Indeed, 2-substituted phenanthroline ligand is commonly produced by a nucleophilic aromatic substitution of the commercially available 1,10-phenanthroline, by using the proper lithium derivatives. These are produced by transmetallation reaction between the corresponding bromo-derivative and t-butyllithium in diethyl ether or pentane at -68° C. For the purification of the ligands, toluene is also used. Moreover, the synthesis of the copper complexes is carried out in dry ACN or toluene, under argon atmosphere.[257] As a result, despite the higher abundance of copper and its reduced toxicity compared to cobalt, the synthesis of copper complexes bearing the 2-substituted phenanthroline ligand is still a significant issue to be solved for the exploitation of this metal as sustainable redox mediator in DSSC.

In 2016, Magni *et al.*[243] reported on the preparation of [Cu(2-mesityl-4,7-dimethyl-1,10-phenanthroline)]$^{+/2+}$ complexes, used as effective redox mediator in ACN solution. They reached an efficiency of 4.4 and 4.1% with the organic G3 dye and platinum and PEDOT as CEs, respectively, proving that this couple could be effectively regenerated by carbon-based CEs too (**Table 6, entry 6**). In order to broaden the light harvesting capability, copper-based complexes were coupled with a Zn^{2+} porphyrin bearing the cyanoacrylic acid as anchoring group at the beta-pyrrolic position with an ethynylphenyl bridge. This structure was reported by Colombo *et al.* [258] to be more accessible with respect to that of the natural porphyrin dyes, allowing a deeper contact with the complexes.

The substituent in the 2-position of the phenanthroline ligands of the [Cu(2-mesityl-4,7-dimethyl-1,10-phenanthroline)]$^{+/2+}$ complexes plays an important role in keeping a distorted geometry and reducing the internal reorganization energy involved in the redox reaction. In 2018, Benazzi *et al.*[259] introduced different substituents in 2-position, such as tolyl, phenyl and *n*-butyl. For all of these complexes, the regeneration of the dye is effective and faster than interfacial recombination, as demonstrated by transient absorption spectroscopy measurements. No substantial differences were observed on the shape of the J-V curve of the corresponding devices, with efficiencies in the range of 4.9 to 6.0%, suggesting that all the proposed redox couples may be efficiently used as redox mediator (**Table 6, entry 7**). In a similar way, Karpacheva *et al.*[260] introduced different substituents in the phenanthroline ligands, such as methyl, methoxyl and bromophenyl in ortho and para positions. However, in this case, efficiency values were found to be rather low (**Table 6, entry 8**) with respect to those reported by Benazzi *et al.*.[259] In 2016, Freitag *et al.*[261] reported a copper complex bearing the dmp ligand (dmp = 2,9-dimethyl-1,10-phenanthroline). The diffusion coefficient of the $[Cu(dmp)]^{+/2+}$, determined by cyclic voltammetry, was found to be two times higher than that of the state-of-art $[Co(bpy)]^{2+/3+}$; furthermore, the dye regeneration was four times faster, as confirmed by transient absorption spectroscopy measurements. Consequently, the PCE was high (7.0%) and comparable to that of the best performing cobalt-based devices (**Table 6, entry 9**). Albeit the increase in device sustainability is clear, the cost-effectiveness of this redox mediator should be further investigated by means of specific LCA.

Among metal complexes proposed as redox mediators in DSSCs, oxovanadium-based ones are worth to be considered. Even if according to the European Commission, vanadium is envisaged as a CRM,[264] it is widely used in other energy fields, such as redox-flow batteries[265] and was proposed as valid alternative to cobalt due to its higher abundance in Earth's crust (0.019 *vs* 0.003%).[73] In addition, vanadium-based redox shuttles present fast electron transport, as confirmed by paramagnetic resonance spectroscopy and electrochemistry.[240] The first paper reporting the oxovanadium redox couple was published in 2013 by Oyaizu *et al.*[266] The oxovanadium (IV/V) redox couple has an efficient redox mechanism that involves bimolecular self-exchange reaction. In particular, the authors reported the complex $[VO(salen)]^{0/+}$ (where *salen* = N,N'-ethylenebis(salicylideneiminate)), being the latter highly soluble in ACN electrolyte solvent if compared to its homologous. From its crystal structure, it can be derived that the [VO(salen)]0/+ redox couple experienced just little changes during the redox reaction, highlighting a low rearrangement energy and fast electron exchange. The more positive redox potential with respect to iodine-based electrolyte accounts for the larger V_{OC} (0.74 V). Remarkably, J_{SC} and PCE were found to be 12.3 mA cm^{-2} and 5.4%, respectively (**Table 6, entry 10**). Two years later, Apostopoulou *et al.*[240] reported an oxovanadium complex bearing tetradentate hybeb ligand (hybeb = [1-(2-hydroxybenzamido)-2-(2-pyridinecarboxamido)benzenato]). Despite the rapidity of the charge exchange process, as demonstrated by electron paramagnetic resonance (EPR), the overall efficiency of the cell (**Table 6, entry 11**) was definitely low if compared to that reported by Oyaizu.[266]

Other two metals were exploited in the electrolyte of *p*-type solar cells, namely tungsten and molybdenum. Both of them have a rather low natural abundance of 0.00011% in the Earth crust, but only tungsten is considered a CRM.[53] Bakker *et al.*[267] reported about an excellent V_{OC} improvement by using two kinds of Lindqvist polyoxometalates (POMs), *viz.* $[TBA]_2Mo_6O_{19}$ and $[TBA]_2W_6O_{19}$ (where *TBA* = tetrabutylammonium), with redox potentials of -0.40 and -0.90 V, respectively (**Figure 14a**). These values were remarkably lower than those of I_3^-/I^- (+0.32 V) and $[Co(en)_3]^{3+/2+}$ (-0.03 V). In addition, the two POMs showed a negligible molar absorption in the Vis range, thus avoiding any competition for light harvesting with the dye. As expected, V_{OC} values were found to dramatically increase for both the molibdenum- and wolfranium-based electrolytes, with respect to iodine- and cobalt-based ones (100 and 80 mV, respectively). Unlikely, a sluggish diffusion caused a drop in the J_{SC}; therefore, the overall efficiencies of these devices were still unsatisfactory (0.13 and 0.11%, respectively, **Table 6, entry 12**). The development of alternative redox pairs comprised also the synthesis of fully organic electrolytes to completely overcome also the issues related to the use of metals, in particular cobalt, in complexes. However, the evaluation of impacts for each approach should be evaluated. In this respect, Parisi *et al.* observed that the electrolyte does not have a huge impact in the overall device.[80] However, the study highlights the larger impacts (ozone depletion) of the iodine-based couple compared to the cobalt-based one due to the higher requirement of organic solvents. They also suggest the opportunity to achieve lower impacts shifting towards solid electrolytes. It would be really interesting to evaluate the impacts of different electrolyte categories.

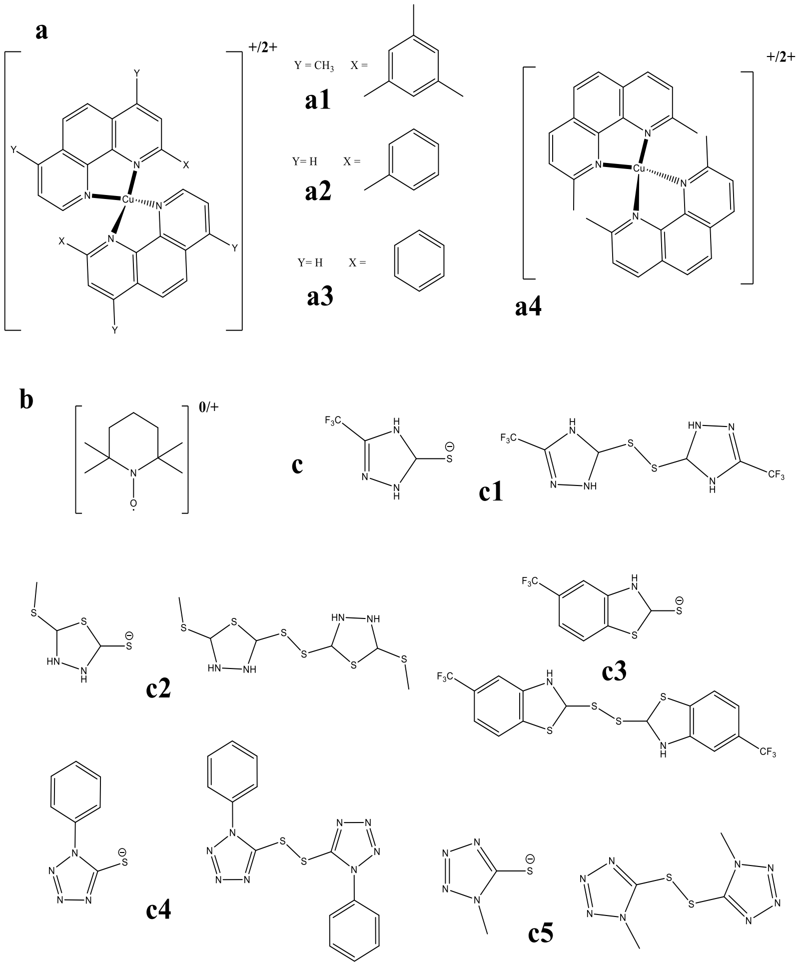


Figure 14. Chemical structures of various alternative redox couples: (a) copper-based complexes (a1: [Cu(2-mesityl-4,7-dimethyl-1,10-phenanthroline)]+/2+; a2: [Cu(2-tolyl-4,7-dimethyl-1,10-phenanthroline)2]+/2+; a3: [Cu(2-phenyl-4,7-dimethyl-1,10-phenanthroline)2]+/2+; a4: [Cu(2,9-dimethyl-1,10-phenanthroline)2]+/2+), b) TEMPO0/+ (2,2,6,6-tetramethyl-1-piperidinyloxy) and c) sulphur-based organic molecules: (c1: 2-methyl-5-trifluoromethyl-2H-[1,2,4]triazole-3-thiol and 3,3'-dithiobis(2-methyl-5-trifluoromethyl-2H-[1,2,4]triazole); c2: 5-(methylthio)-1,3,4-thiadiazolidine-2-thiolate and 1,2-bis(5-(methylthio)-1,3,4-thiadiazolidin-2-yl)disulfane; c3: 5-(trifluoromethyl)-2,3-dihydrobenzo[d]thiazole-2-thiolate and 1,2-bis(5-(trifluoromethyl)-2,3-dihydrobenzo[d]thiazol-2-yl)disulfane; c4: 1-phenyl-1H-tetrazole-5-thiolate and 1,2-bis(1-phenyl-1H-tetrazol-5-yl)disulfane; c5: 5-mercapto-1-methyl tetrazole and di-5-(1-methyltetrazoledisulfide)). All the molecules are made by ChemDraw 9.

Besides metal-based redox couples, pure organic ones could be a feasible choice to achieve sustainable, but efficient, DSSCs and to overcome the limitation displayed by the metal-based redox couples, namely low diffusion coefficient and complicated charge transfer kinetics (see above). An example of fully organic electrolytes is the TEMPO/TEMPO$^+$ (**Figure 14b**), a redox couple with good efficiency also in aqueous environment.[268,269] TEMPO (2,2,6,6-tetramethyl-1-piperidine-1-oxyl) is a commercially available and relatively (3.87 € g^{-1} by Merck) nitroxide radical molecule,[270] that can be easily oxidized to TEMPO$^+$. When used in DSSCs, TEMPO$^{0/+}$ redox couple offers several advantages, such as easy preparation, non-toxicity,[271] no light absorption in the Vis range, fast electron transfer process, rapid mass transport kinetics[272] and highly positive redox potential, which is necessary for achieving high V_{oc}.[268] In 2015, Yang *et al.* tested TEMPO$^{0/+}$ in ACN solution with two different dyes: D149 and LEG4.[271] Albeit TEMPO$^{0/+}$ presented a relatively low regeneration driving force (due to its highly positive redox potential), that brought the regeneration efficiency to a value of 68% and 87% (with D149 and LEG4 dyes, respectively), the authors were able to achieve a remarkable efficiency values of 3.29 and 4.70%, respectively (**Table 6, entry 13**). It shows diffusion coefficient comparable to that of cobalt complexes in ACN ($4.4*10^{-6}$ cm^{2}s^{-1}),[273] suggesting that mass transport be a limiting factor for the obtainment of high conversion efficiency. Additionally, TEMPO$^{0/+}$ has smaller electron lifetime, if compared with traditional cobalt and iodine-based electrolytes; therefore, some precautions, such as the employment of thinner electrodes should be taken in order to reduce the undesired charge recombination.

To the best of our knowledge, TEMPO$^{0/+}$ redox couple was applied for the first time in aqueous DSSCs by Yang *et al.*[268] in the same year. As expected, they obtained high V_{oc} (995 mV), J_{sc} (5.78 mA cm^{-2}), FF (0.75) and, consequently, rather high PCE of 4.14% (**Table 6, entry 14**). In an elegant work,[272] TEMPO redox couple was used in combination with ZnO photoanodes, thus avoiding the energy-consuming high-temperature thermal treatment of traditionally used TiO_2. ZnO was electrochemically deposited at low temperature; its morphology consisted of pillars grown vertically to the substrate. It ensured enhanced electron mobility and the resulting lab-scale cell demonstrated an efficiency of 3.92% (**Table 6, entry 15**). More recently, Kato *et al.*[274] reported a hydrophilic TEMPO derivative (4-hydrox-2,2,6,6-tetramethyl piperidine-1-oxyl, TEMPOL), which was successfully entrapped into a Nafion® polymeric matrix, using an aqueous solution to replace ACN. Nafion® is a good choice to immobilize electro-active cations: a Nafion®-coated electrode (NCE) was dipped in an aqueous TEMPOL solution, giving a PCE equal to 1.6%, that is several times higher than the Pt-counterpart (0.11%),(**Table 6, entry 16)**. It is worth mentioning that NCE is a CRM-free CE, even if its applicability is limited to Nafion-based polymeric electrolytes. 4-hydroxy-TEMPO is less expensive than TEMPO, because it is obtained from the cheaper precursor triacetonamine.[275] Overall, while TEMPO is sufficiently inexpensive to be exploited at a laboratory scale, it is rather to become not affordable on an industrial scale viewpoint. Conversely, structurally related analogues (*e.g.*, TEMPOL) could be much less expensive, since they are produced from acetone and ammonia, the latter being under serious consideration by the scientific community as an emerging solar fuel.[276] For its purification, selective adsorption onto a hydrophobic resin is highly effective, thus costly azeotropic distillation is avoided. For these reasons, it can be considered a more sustainable choice with respect to TEMPO. Concerning applications, it can be easily incorporated onto/into a solid support to achieve a heterogeneous material for catalysis or electrochemistry.

TEMPO$^{0/+}$ redox couple and its homologous are very cheap and commercially available materials. The matter of the cost of the redox couple should be carefully considered in design of sustainable, but cost-effective, DSSCs. In fact, in a conventional electrolyte the redox couple concentration is usually higher than 1 M and, albeit the modest volume of electrolyte employed in a conventional device, it could seriously hamper the cost-effectiveness of the complete device. In this context, TEMPO$^{0/+}$ and its derivatives could be considered as promising cost-effective redox couples in sustainable DSSCs.

Organic thiolate/disulfide couple and its derivatives offer several advantages when used as redox mediators in DSSCs (**Figure 14c**): easiness of preparation, non-corrosiveness, negligible light absorption in the Vis range and tunable redox potential. 5-mercapto-1-methyl tetrazole (T^-) with its dimer di-5-(1-methyltetrazoledisulphide) (T_2) was the first[277] and the most commonly exploited organic sulfur-based redox couple. Sulfur-based electrolyte cannot be used in combination with platinum CE, due to the formation of an irreversible S-Pt bond that contributes to the depletion of both redox active species of the electrolyte and active metal centers of the electrode.[278] Simultaneously, also transition metal compounds (TMCs) seems to be unexploitable in conjunction with these couples due to the likely formation of S-M bonds. As a result, alternative materials have to be developed, such as PEDOT or carbonaceous materials (section 2.3.1).[279] In 2015, two interesting papers were published using a composite TiC/carbon[280] and a full carbon CEs.[278] In particular, the TiC/carbon composite electrode was hydrothermally synthesized by using TiC and glucose as carbon source. When compared to platinum, bare TiC and carbon CEs,[280] TiC/carbon composite electrode generated the strongest reduction in current density among all the electrodes under testing, suggesting that it was able to effectively reduce T_2. PV parameters of the TiC/carbon-based cell were comparable to platinum-based ones (PCE = 3.59% vs. 3.84%, **Table 6, entry 17**). In the following example, the carbonaceous material used as CE was obtained by the pyrolysis at 850° C under inert atmosphere of a mangosteen peel (MP), an important source of natural phenolic antioxidants.[211] Even if the MP is obviously a green and sustainable scaffold, the very high pyrolysis temperature negatively impacts on a comprehensive sustainability-driven approach. Among all the electrode materials tested (platinum and PEDOT), MP ensured the lowest charge transfer resistance in symmetrical cell, using T^-/T_2 in ACN as electrolyte. Consequently, MP-based cells reached an average efficiency of 2.63%, remarkably higher than that of PEDOT:PSS-cells (0.60%) and almost twice that of the platinum counterpart (**Table 6, entry 18**). The promising prospects of carbon CE combined with T^-/T_2 were further confirmed by Tangtrakarn and co-workers in 2019,[278] who presented a comparison of the electrocatalytic behavior of an annealed carbon-based material, obtained by arc evaporation method, and platinum (**Table 6, entry 19**).

In 2012 Tian *et al.*[281] demonstrated that T^-/T_2 was effective also in aqueous electrolytes, in combination with two organic dyes, D45 and D51. The efficiency obtained with the aqueous electrolyte (2.6%) was even higher than that reached by using the corresponding ACN-based one (1.1%), likely ascribable to the enhanced solubility of the compounds and wettability of the hydrophobic dye-TiO_2 by using Triton X as surfactant. However, these efficiencies were still unsatisfactory if compared to that of the iodine-based device (**Table 6, entry 20**). As a matter of facts, the diffusion coefficient of DTT in pure water was much lower than that of triidiode one. Furthermore, the regeneration of D45 dye was found to be 4-time slower when using TT^-/DTT with respect to the iodine-based counterpart. In the successive years, the redox and chemical properties of the thiolate/disulfide redox couple were customized by the modification of substituents in the tetrazole ring.[282–284] The main goal was to increase the solubility of these sulfur-based compounds in organic solvents. In fact, the low solubility of T^-/T_2 still represents a sizeable issue in the use of organic sulfur-based redox mediators. In this context, it should be pointed out that to thoughtfully choose a redox couple, a benefits/costs analysis should be also considered: as example, we reported the case of T^-/T_2 redox mediator. They could be easily substituted with different alkyl moieties (e.g. butyl, hexyl, octyl,…) by following the same synthetic route and with almost quantitative yields.[282] Yet, the alkylthiocanates employed as precursors have different prices: 8 €/g, 5 €/g and 103 €/g for 1-butyl, 1-hexyl and 1-ocytl thiocyanate, respectively.

With the aim of increasing the redox potential and speeding up the reduction process, Rahman *et al.*[285] reported the easy preparation of 5-methylthio-1,3,4-thiadiazole-2-thiol (*MTDT*)/5-methylthio-1,3,4-thiadiazolium disulfide dication (*MTDD*$^{2+}$) as redox mediator (**Figure 14c**), which was then combined with PEDOT CE and indolenine D205 dye or CdS quantum dots (QDs) as sensitizers. The well-matched combination of the MTDT/MTDD^{2+} redox shuttle with PEDOT CE and favorable band alignment of the sensitizers with the redox potential led to efficiency values of 3.55 and 1.20% with D205 and CdS, respectively, still lower compared to the reference device (**Table 6, entry 21**): this was attributed to both ionic conductivity (0.52 S/m, four time lower) and diffusion issues (D of MTDD^{2+} in ACN is roughly two order of magnitude lower). Bhargava *et al.*[286] substituted the methyl group with a phenyl one (**Figure 14c**) in 5-mercaptotetrazole, which was used in combination with 20 μm-thick carbon CE. The different substituents on the tetrazole ring had a fundamental effect on the self-assembly properties of the electrolyte; more specifically, the 1-phenyl substituted redox couple formed a protective monolayer on the surface of the CE, which worked as a surface-passivating agent to limit corrosion and recombination phenomena at the interface. Under optimized condition, an overall efficiency of 4.6% was achieved (**Table 6, entry 22**) The dual effect of 1-phenyl-5-mercaptotetrazole and its dimeric form was also demonstrated in *p*-type DSSCs, with sensitized-NiO as photocathode (PCE = 0.51%).[287]

Concluding this section, several alternative redox mediators have been reported. Much work has still to be done in tuning the chemical, electrochemical and physical features of these compounds, considering also the sustainability of the raw materials and the processes involved. It should be pointed out that, a thoughtful development of redox mediator could not overlook the synergic behavior with both the sensitizer (that needs to be regenerated by the redox mediator) and the counter-electrode (thanks to which the redox mediator is back reduced). Additionally, the above-presented materials have been designed for a specific application in liquid (or at least quasi-solid) electrolytes, whereas a substantial different paradigm is required in light of an application in solid-state DSSCs (**4.2.3**).

Other two examples of the use of T^-/T_2 as redox mediator are worth to be reported,[288,289] in which the efforts of the authors were devoted to the replacement of organic solvents and to the realization of non-volatile, non-flammable and stable electrolytes. In the first case,[289] succinonitrile (SCN) was mixed with T^-/T_2 and used as quasi-solid electrolyte, having the positive characteristics of ensuring good contact with electrode materials, maintaining an acceptable ionic conductivity and, at the same time, avoiding the leakage of the electrolyte. More specifically, SCN is a solid non-ionic polymer, with high polarity, able to dissolve various kind of salts. Under optimized condition, a remarkable PCE of 3.52% was achieved (**Table 6, entry 23**).[289]

In the second example,[288] Tan and co-workers firstly demonstrated a crystalline DSSC electrolyte with the T^-/T_2 redox couple, which was obtained in the form of a smectic liquid crystal by mixing 1-dodecyl-3-methyl-1H-imidazol-3-ium, 1-methyl-1H-tetrazole-5-thiolate ($[C_{12}MIm][T]$) and di-5-(1-methyltetrazole) disulfide in the 2:1 ratio. The smectic liquid crystal allowed exploiting its highly mobile 2D pathways, resulting in remarkable PCE of 4.1% (**Table 6, entry 24**).

Table 6 Different classes of alternative redox couple electrolytes, along with constituting material(s), related advantages, most critical issues, highest recorded efficiency values vs. state-of-art and corresponding reference articles

Class	***Material***	***Pros***	***Issues***	***PCE vs reference***	***Entry***[Ref]
Pseudo-halogens	$SeCN^-/(SeCN)_2$ in ACN	• Integration in quasi-solid electrolytes	• Toxicity • Use of organic solvents • Low availability of Se	Not reported	**1**[249]
	$C_6SeCN/(SeCN)_2$ in alkyl-substituted ionic liquid	• Non-volatile solvent	• Slower regeneration of the dye • Low availability of Se	-10.7%	**2**[250]
Iron-based complexes	$K_4Fe(CN)_6/K_3Fe(CN)_6$ in water	• Water as solvent	• Use of surfactants	-50.6%	**3**[129]
	$K_4Fe(CN)_6/K_3Fe(CN)_6$ in water	• Water as solvent	• Low stability	+182% (but using a carbon fabric as CE and not optimizing the condition of I^-/I_3^- with this set up)	**4**[254]
	$Bu_4N[Fe(acac)_3]$/ $[Fe(acac)_3]$ in ACN	• Natural abundance	• N_2 atmosphere for electrolyte preparation • Use of organic solvent • Low stability	+191% p-type	**5**[255]
Copper-based complexes	$[Cu(2\text{-mesityl-4,7-dimethyl-1,10-phenanthroline})]^{2+/+}$ in ACN	• Low toxicity	• Organic solvent-based electrolyte • Use of t-butyllithium (-78° C under argon atmosphere in DMF) for the synthesis of the ligand	+2.32% (equimolar) -40.5% (concentrated)	**6**[243]
	$[Cu(2\text{-}\mathit{alkyl}\text{-1,10-phenanthroline})_2]^{2+/+}$	• Low toxicity	• Use of t-butyllithium, toluene • Argon condition for the synthesis of the ligand	+7.69% (mesityl) +15.4% (tolyl) -5.77% (phenyl) +9.62% (n-butyl)	**7**[259]

Class	*Material*	• *Pros*	• *Issues*	*PCE vs reference*	*Entry*[Ref]
Copper-based complexes	$[Cu(diimine)_2]^{2+/+}$ in ACN	• Low toxicity	• The synthesis of the ligands is not reported • Organic solvent-based electrolyte	-88.1% -79.3% -61.9%	**8**[260]
	$Cu(2\text{-mesityl-}1,10\text{-phenathroline})_2]^{2+/+}$ and $[Cu(2\text{-mesityl-}1,10\text{-phenathroline})_2]^{2+/+}$ in ACN	• Low toxicity • Comparable to Co-based electrolyte	• Use of t-butyllithium (-78° C under argon atmosphere in pentane) for the synthesis of the ligand • Use of toluene for purification • Organic solvent-based electrolyte	-4.8%	**9**[261]
Other metal-based redox couples	VO(salen) in ACN (the oxidized form of the redox couple is formed in situ through $NOBF_4$)	• Abundance of vanadium with respect to cobalt • Non corrosive	• Synthesis under strictly controlled conditions • Organic solvent-based electrolyte	Not reported	**10**[266]
	$(Ph_4P)[VO(hybeb)]$/ $Ph_4P[(VO(hybeb)]$ in ACN	• Abundance of vanadium with respect to cobalt • Non corrosive	• Synthesis of the ligand in anhydrous tetrahydrofuran under argon conditions	Not reported	**11**[240]
	$[TBA]_2Mo_6O_{19}$ and $[TBA]_2W_6O_{19}$ in ACN	• Air stable • Low temperature • Synthesis in water ($Mo_6O_{19}^{2-}$)	• Synthesis in acetic anhydride and DMF	+62.2% ($Mo_6O_{19}^{2-}$) -18.9% ($W_6O_{19}^{2-}$) in *p*-type DSSC	**12**[267]

Class	***Material***	• ***Pros***	• ***Issues***	***PCE vs reference***	***Entry^{Ref}***
TEMPO-based redox couples	TEMPO/$TEMPOBF_4$ in ACN	• Non toxicity • Easy synthesis • Low temperature	• Organic solvent-based electrolyte	-18.7% (*vs.* Co(II)/Co(III))	**13**[271]
	TEMPO/$TEMPOBF_4$ in water	• Non toxicity • Easy synthesis • Low temperature • Aqueous DSSC	• None relevant	Not reported	**14**[268]
	TEMPO/$TEMPOBF_4$ in ACN	• Non toxicity • Easy synthesis • Low temperature	• Organic solvent-based electrolyte	Not reported	**15**[272]
	TEMPOL/$TEMPOLBF_4$ in ACN	• Non toxicity • Easy synthesis • Low temperature • Low cost	• Organic solvent-based electrolyte	+1500 % (using a Nafion® membrane not optimized for organic electrolyte)	**16**[274]
Thiolate/disulfide-based redox couples	T^-/T_2 in ACN (T^- = 5-mercapto-1-methyltetrazole N-tetramethylammonium; T_2 = di-5-(1-methyltetrazole disulfide))	Room temperature	• Argon atmosphere Organic solvent-based electrolyte	Not reported	**17**[280]
	T^-/T_2 in ACN (T^- = 5-mercapto-1-methyltetrazole N-tetramethylammonium; T_2 = di-5-(1-methyltetrazole disulfide))	Room temperature	• Argon atmosphere Organic solvent-based electrolyte	-16% (CE: platinum) -31.8% (CE: PEDOT:PSS) +32.2% (CE: MP carbon)	**18**[211]

Class	*Material*	*Pros*	*Issues*	*PCE vs reference*	*Entry*[Ref]
Thiolate/disulfide-based redox couples	T^-/T_2 in ACN (T^- = 5-mercapto-1-methyltetrazole N-tetramethylammonium; T_2 = di-5-(1-methyltetrazole disulfide))	• Room temperature	• Argon atmosphere • Organic solvent-based electrolyte	-45.8%	**19**[278]
	T^-/T_2 in ACN(T^- = 1-ethyl-3-methyl-imidaziolium 4-methyl-1,2,4-triazole-3-thiolate; T_2 = 3,3'-dithiobis[4-methyl-(1,2,4)-triazole])	• Low temperature	• Organic solvent-based electrolyte	-53.6%	**20**[281]
	T^-/T_2 in DMSO/ACN (T^- = 5-methylthio-1,3,4-thiadiazole-2-thiol; T_2 is formed in situ through BF_4NO)	• In-situ generation of the oxidized form (T- commercial)	• Organic solvent-based electrolyte	-37.0%	**21**[285]
	$T_{ph}^-/(T_{ph})_2$ and $T_{me}^-/(T_{me})_2$ in ACN (T_{ph}^- = sodium 1-phenyl-1H-tetrzole-5-thiolate; $(T_{ph})_2$ = 5,5'-dithiobis(1-phenyl-1H-tetrazole; T_{me}^- = sodium 5-mercapto-1-methyltetrazole; $(T_{me})_2$ = di-5-(1-methyltetrazole)disulfide	• Room temperature	• Argon atmosphere • Organic solvent-based electrolyte	Not reported	**22**[286]
	T^-/T_2 in ACN (T^- = 5-mercapto-1-methyltetrazole N-tetramethylammonium; T_2 = di-5-(1-methyltetrazole disulfide))	• Low temperature	• Argon atmosphere • Organic solvent-based electrolyte	Not reported	**23**[289]
	$[C_{12}MIm][T]/[T_2]$ ($[C_{12}MIm][T]$ = 1-dodecyl-3-methyl-1H-imidazol-3-ium 1-methyl-1H-tetrazole-5-thiolate; T_2 = di-5-(1-methyl tetrazole)	• Room temperature • Ambient condition • Ionic liquid (non volatile solvents)	• Chloroform is involved during the synthesis	Not reported	**24**[288]

Notes: DMF = N,N-dimethylformamide; PSS = poly(styrenesulfonate); MWCNTs = multi-walled carbon nanotubes; DMSO = dimethyl sulfoxide.

4.2.2 On the use of water as alternative, sustainable electrolyte solvent

Traditional DSSC electrolytes are made of organic solvents, mainly nitrile-based, characterized by relevant drawbacks, which chiefly include toxicity and related severe environmental impact, as well as high vapor pressure and, in some cases, explosiveness; this issue affects safety and seriously limits their practical applications in DSSCs, especially if indoor applications are envisaged.[290] However, the DSSC community has historically considered water as a poison for cell stability, and this forced the design of robust encapsulation systems[121] and specifically conceived barrier materials.[134] Despite these precautions, water traces are always present in the mesopores of the photoanode layer as well as in the electrolytic solution; water contamination exponentially increases if plastic/flexible architectures are envisaged; actually, water permeation in these materials is rather high (*i.e.*, 0.01 g m^{-2} day^{-1}), which may account for a water content even exceeding 10 wt.% after one year of real outdoor use.[134,291] In this sense, aqueous DSSCs have been studied in order both to avoid all the negative effects of the organic solvents and to build a solar cell that is inherently thought to work in the presence of water moisture.[134] Instead of performing laborious processes to avoid water penetration, researchers tried to build partially or fully aqueous solar cells.[292,293] Water is considered to be the greenest solvent as it is safe, not-flammable and non-toxic but attention must be paid to a couple of aspects when water is considered. The first one is that fresh water is a limited resource;[294,295] as reported by Shiklomanov[296] and USGS[297], fresh water resources are just 2.5% of total water amount present in the world and only a small part is really available. As a matter of fact, since 2020, water is traded in the stock exchange.[298] The second significant point to stress is that any impurities or contaminants released in aqueous waste streams will, by their nature, readily find their way into aquifers, enhancing the risk of human exposure. The transition from an organic solvent to water, especially when organic molecules are involved, has its own barriers. Initially, chemists have put their efforts either in the optimization of aqueous DSSCs using traditional electrolytes and dyes or in the investigation of not-fully aqueous (mixture of water and organic solvents) electrolytes.[299] Nowadays, one of the major trend is to re-think completely the chemistry aiming to completely aqueous DSSCs, using, for instance, surfactants.[120] It is still worth highlighting that water displays many attractive features as a solvent, but it is not without its own set of problems though. Water is inherently a safe substance, but its precious value should be recognised.[6,300] Moreover, to obtain good photoconversion efficiency, ultrapure water is mandatory: this leads to a huge increase in the overall cost of the device, which in turn lowers its sustainability. Our group is actually involved in an LCA analyses on the economic impact of the employment of ultrapure water. Indeed, the production process of ultrapure water is highly energy-demanding affecting the impacts of the resulting devices. A more sustainable option could be the employment of wastewater or tap water, at least, but we did not find any report on this topic. Clearly, it is worth highlighting that water displays many attractive features as a solvent, but its use has its own barriers and own set of problems though,[59] especially when organic molecules are involved. Preliminary investigations towards aqueous DSSCs passed either through the use of traditional electrolytes and dyes or the investigation of non-fully aqueous electrolytes comprised of different ratios of water and organic solvents.[299] Nowadays, the trend is to re-think completely the chemistry aiming at fabricating fully aqueous DSSCs, by making use, for instance, of surfactants.[120]

The seminal paper by O'Regan *et al.* in 2010 placed water at the center of the research of new truly green DSSC and use it as main component of the electrolytes. It represented the turning point in the recent days of these photoelectrochemical cells.[301] The relative amounts of methoxypropionitrile (MPN) and water were varied when preparing different electrolytes (PMII 2.0 M, I_2 50 mM, GuSCN 0.10 M and TBP 0.5 M; PMII = 1-propyl-3-

methylimidazolium iodide; GuSCN = guanidinium thiocyanate; TBP = 4-tert-butylpyridine); besides this, a hydrophobic dye (TG6) was chosen and 1% Triton X-100 surfactant was introduced into the electrolyte to avoid phase separation. The basic functions of DSSCs (injection, regeneration and transport) worked properly at all water concentration levels; even at H_2O content as high as 80 vol%, lab-scale cells showed limited 7 and 8% losses in J_{SC} and V_{OC}, respectively, after 1000 h at 1 sun illumination (35° C with UV-filter).

In the last decade, the scientific community has spent considerable efforts aiming at using bare water as a solvent. In the context of green chemistry and circular economy milestones, DSSCs fabricated with water-based electrolytes are foreseen to guarantee reduced costs, non-flammability, lower volatility and improved environmental compatibility without neglecting the importance of water as a precious resource. This approach is however extremely challenging from both the chemical and materials science viewpoints, and an increasing number of electrodes, dyes and electrolyte components has already been proposed for operating in aqueous environment.[134] This also matches with the initial purpose of DSSC inventors, *viz.* the construction of an artificial photosynthetic system able to convert solar light into electricity: only using water as key component we will be close to photosynthesis, also paving the way to a widespread diffusion of sustainable PV cells in the market. Besides being inexpensive and inherently safe, aqueous DSSCs clearly do not suffer from water contamination issues, with the added value of easily solvating many potential redox mediators. In the recent years, photoanode modifications, selection of specifically conceived redox couples, introduction of novel additives and surfactants, preparation of suitable cathodes and jellification of electrolytes rapidly led to the assembly of 100% aqueous solar cells (see **Table 7**). Note that 100% aqueous solar cells means water as the only solvent. The wide variety of cell components clearly enlightens that a unique strategy to achieve good efficiencies in the presence of aqueous electrolytes is not yet available.

Indeed, TiO_2 electrode structure, dye molecules, redox pairs and related concentration, cathode type and cell thickness are all extremely variable and current efficiency records approaching 7% represent, in principle, a solid stone in view of future optimization in the field.[302]

Table 7 List of the most efficient 100% aqueous DSSCs, characterized under 1 sun irradiation (AM 1.5G), with their main components, advantages, drawbacks, highest recorded efficiencies and corresponding reference articles

Anode	***Dye***	***Electrolyte***	***Cathode***	***Pros***	***Issues***	***PCE (%)***	***Entry**[Ref]*
TiO_2 (4.5 µm) + $TiCl_4$	D149	GuI 8.0 M, I_2 20 mM and CDCA until saturation	Platinum	Cobalt-free	High iodide concentration required (8.0 M)	4.1	**1**[303]
BL + TiO_2 (1.3 µm *T* + 5 µm *SL*) + $TiCl_4$	MK-2	$K_4Fe(CN)_6$ 0.40 M, $K_3Fe(CN)_6$ 40 mM, KCl 0.10 M, Trizma-HCl buffer 50 mM (pH 8) and Tween 20 0.1%	Platinum mirror	Cheap formulation	Unstable, presence of cyanide	4.1	**2**[129]
TiO_2 (1 µm *T* + 3 µm *SL*)	MK-2	$[Co(bpy)_3]^{2+}$ 0.20 M, $[Co(bpy)_3]^{3+}$ 40 mM, NMBI 0.70 M and PEG 300 1%	Platinum	Simple photoanode fabrication	Cobalt-based	4.2	**3**[304]
TiO_2 (*BL* + 4 µm *T* + 4 µm *SL*) + $TiCl_4$	LEG4	TEMPO 0.15 M, $TEMPOBF_4$ 50 mM, $LiClO_4$ 0.10 M and NMBI 0.20 M	Platinum	Metal-free redox shuttle	Acute toxicity of NMBI	4.1	**4**[268]
$TiCl_4$ + TiO_2 (14 µm + 6 µm *SL*) + $TiCl_4$	T169	T^-/T_2 0.4/0.4 M, TritonX-100 0.1%, pH 5.0	PEDOT	Metal-free redox shuttle and cathode	25% PCE loss in 2000 h	4.5	**5**[305]
TiO_2 (9 µm *T* + 3 µm *SL*)	MD3	TEMPO 0.40 M, $NOBF_4$ 0.40 M, LiI 0.10 M, I_2 50 mM, DMPII 0.60 M, GuSCN 0.10 M and Tween 20 0.1%	Platinum	Metal-free redox shuttle	8 components in the electrolyte	5.0	**6**[306]
TiO_2 (1 µm *T* + 3 µm *SL*)	MK-2	$[Co(bpy)_3]^{2+}$ 0.20 M, $[Co(bpy)_3]^{3+}$ 40 mM, NMBI 0.70 M and PEG 300 1%	Platinum ITO	Lowering Pt amount by adding ITO	Cobalt-based	5.0	**7**[304]
TiO_2 (7 µm) + $TiCl_4$	D51	$[Co(bpy\text{-}pz)_3]Cl_2$ 0.13 M, $[Co(bpy\text{-}pz)_3]Cl_3$ 60 mM, NMBI 0.80 M	PEDOT	Improved solubility of the redox shuttle	Cobalt-based	5.5	**8**[307]
TiO_2 (1 µm *T* + 3 µm *SL*) + $TiCl_4$	MK-2	$[Co(bpy)_3](NO_3)_2$ 0.20 M, $[Co(bpy)_3](NO_3)_3$ 40 mM, NMBI 0.70 M and PEG 300 1 wt%	Platinum	Stability (0% PCE decrease in 500 h)	Cobalt-based	5.6	**9**[308]

Anode	***Dye***	***Electrolyte***	***Cathode***	***Pros***	***Issues***	***PCE (%)***	***Entry^{Ref}***
TiO_2 (10 μm)	EO3	JC-IL 0.40 M and $NOBF_4$ 0.40 M	Platinum	Dual metal-free redox couple	Stability not demonstrated	6.0	**10**[309]
TiO_2 (*BL* + 12.5 μm) + $TiCl_4$	D149	NaI 1.0 M and I_2 10 mM	cPEDOT	Metal-free redox shuttle, dye and cathode	Impact of D149 synthesis	7.0	**11**[302]

Notes: GuI = guanidinium iodide; BL = blocking layer; T = transparent layer; SL = scattering layer; PEG = poly(ethylene glycol); NMBI = N-methylbenzimidazole; DMPII = 1,2-dimethyl-3-propylimidazolium iodide; cPEDOT = cationic PEDOT.

Among these studies, two of them emerge in terms of sustainability-related aspects, namely the work by Fayad *et al.*[305] and Lin *et al.*[306] The article by Lin *et al.*[306] firstly showed a 100% water-based device bearing metal-free sensitizer and redox-shuttle. Anthracene/phenothiazine units were used as spacers for the MD3 dye; in the presence of CDCA, it was able to match the performance of N719 in standard lab-scale devices. In aqueous environment, a dual-TEMPO iodide electrolyte (JC-IL) was proposed and led to a 4.96% efficiency. Besides enhancing the V_{OC} up to 0.77 V, the TEMPO-based redox couple avoids the use of cobalt, thus appearing as a big step ahead in the sustainable path. However, TEMPO is toxic for aquatic life, it is highly persistent and can accumulate in the environment. Even if this is not widely known in the solar harvesting community, in other fields (*e.g.*, catalysis) researchers are spending huge efforts to allow reuse/recycling of TEMPO or its immobilization into polymeric matrixes.[310]

Sulfide/polysulfide couple is a valid alternative in aqueous environment. It was investigated by Fayad *et al.*[305] in combination with a zwitterionic and thiocyanate-free dye (namely, T169). Resulting solar cells demonstrated very high current densities (J_{SC} = 13.30 mA cm^{-2}) and a PCE of 4.5%, rather stable after 2000 h of aging test (limited 3.3% performance decay). The sustainability of this sulfur-based electrolyte should be fully understood starting from its precursor, *i.e.* 1-(2-hydroxyethyl)-5-mercaptotetrazole, the synthesis of which involves several steps. Even if a couple of LCA studies of DSSCs were published in the recent years, further efforts should be focused on the proper understanding of the concrete impact of these alternative redox shuttles. Actually, in some cases, issues related to the use of solvents and energy spent for the whole synthesis place these emerging systems not so far from the traditional ones based on cobalt or organic electrolytes.

Independently from the specific literature papers under analysis, some common aspects related to aqueous DSSCs emerge. First, platinum is still highly used within the aqueous DSSC community; in view of the practical widespread application of the devices on a large-scale, this represents an obstacle to be overcome soon due to cost-related reasons. Second, half of the proposed redox couples are based on cobalt, and this is even more critical as it adds safety as well as environmental issues. Third, a clear strategy to design molecular dyes is still scarce, since it requires the development of a photoanode showing good wettability, while concurrently preventing dye desorption by water. Last, but not less important, the analysis of solar cell parameters highlights J_{SC} values that are roughly half of those recorded by the corresponding organic electrolyte-based cells. The reason for the low current of water-based DSSCs is still rather unclear, being likely ascribed to the contributions of a weak electrolyte penetration in the whole electrode thickness and the fraction of recombination phenomena at the photoanode/electrolyte interface.

A further interesting strategy in the field of aqueous DSSC, deals with the preparation of hydrogel electrolytes, with the aim of increasing cell stability and facilitating device assembly with printing techniques. Noteworthy, the first examples of the kind involved the use of polymeric matrices obtained by non oil-derived sources.[311] Xian *et al.* and Zhang *et al.* prepared hydrogels by using gelatin, a widely available, non-toxic and biodegradable polypeptide made by hydrolytic degradation of collagen.[312,313] In a recent work, the use of cellulose gum, widely known as Carboxymethyl Cellulose (CMC),[241] allowed the development of homogenous gels with less than 10 wt% CMC in the aqueous electrolyte. The resulting lab-scale devices demonstrated remarkable 93% efficiency retention after one month of dark storage, and excellent stability when subjected to a further month of thermal aging at 60° C in an oven.

4.2.3 Beyond liquid-state electrolytes

When screening the DSSCs literature, it clearly emerges a progressive transition from studies focused on liquid electrolytes (during the first years after the 1991 seminal paper) to articles dealing with quasi-solid systems (*i.e.* physically or chemically gelled by means of polymers or nanoparticles);[314] subsequently, completely solid cells were proposed.[315] The rationale behind this evolution is clearly based on the stability issues, as well as on the difficulty of perfectly sealing a liquid electrolyte between two glasses. However, it is rarely discussed in DSSCs community how this is in contrast - to date - with the fact that the first industries entering in the market proposed DSSCs (conceived for architectural integration or portable electronics) based on liquid electrolytes.

As regards those aspects strictly related to sustainability, quasi-solid electrolytes do not represent a concrete step forward. In fact, they are usually made of the same salts, solvents and additives used for the preparation of traditional liquid electrolytes. Moreover, in most cases, a thermoplastic polymer derived from oil is used to jellify the system, negatively influencing the sustainability-driven trade-off. As regards the working mechanism, there is no any substantial difference between quasi-solid and liquid electrolytes: on one hand, the regeneration of the dye is always based on the electron injection from the redox potential of the mediator to the HOMO level of the dye; on the other, the mediator regeneration is always based on the mass diffusion of the redox mediator between the cell electrodes. The presence of a polymeric membrane could negatively influence the mediator diffusion throughout the electrolyte, but, at the same time, it could protect the latter from unwanted charge recombination at the TiO_2/electrolyte interface. Several reviews have been published on this issue so far,[316,317] from which a good step forward in terms of industrial stability and processability emerges (*e.g.*, through printing techniques), but this is overall accompanied by a step back in terms of device sustainability.

Replacing liquids-based systems with solid semiconducting materials started to be concretely possible in 1998, when Bach *et al.* demonstrated the hole-transporting ability of 2,2′,7,7′-tetrakis-(N,N-di-pmethoxyphenylamine)9,9′-spirobifluorene (Spiro-OMeTAD).[318] Right now, it represents one of the most attractive solid-state p-type charge transporting layer due to its adequate TiO_2 pore-filling capability and the very efficient light-induced charge carriers generation at the heterojunction. Spiro-OMeTAD completely chanced the working mechanism of DSSCs, passing from the diffusion of a redox shuttle to the hole hopping process through a very thin layer separating the electrodes. On the other hand, this solid-state compound led to poor interfacial contacts, making interface electrostatics become one of the limiting factors for well reproducible, efficient and stable devices.[319] However, the most important issues regarding Spiro-OMeTAD concern its relatively sensitivity to both moisture and oxygen and its high production costs, mainly due to its lengthy synthesis protocol, also being low yield and with a considerable impact in terms of solvents used for separation and purification steps.[320,321] Furthermore, it necessitates the addition of additives based on lithium and/or cobalt (a well-known CRM) to boost its conductivity and hole mobility, thus making this system far from the sustainability targets of the DSSCs scenario. Finding alternatives to Spiro-OMeTAD is now an urgent research topic, mainly in the PSCs field where the hole transporting material must be at the solid state.[322]

Plastic crystals, i.e. crystal consisting of weakly interacting molecules bearing some conformational or orientational degree of freedom, entered in the solid-state DSSCs scenario not many times. After some seminal studies on succinonitrile,[323] some groups proposed organic ionic plastic crystal utilizing pyrrolidinium, phosphonium or quaternary ammonium cations.[324] These systems are solid, show poor volatility and high ionic conductivity (that can be further increased by the addition of SiO_2 nanoparticles), targeting PCE close to 8%. They can be liquefied at mild temperature to allow cell filling and then become solid; indeed, the plastic crystal works as the solid solvent for the iodine-based redox shuttle. However, sustainability of such approach is poor (or, at least, not better that that of liquid organic electrolytes). Indeed, succinonitrile production passes through the addition of HCN to acrylonitrile, both of them strictly connected to impactful industrial preparation protocols.[325]

As a third type of solid DSSC, "zombie solar cells" emerged in the recent years when liquid DSSCs based on copper complexes, like $[Cu(tmby)_2]^{2+/+}$, were dried and the redox shuttle was able to work as a solid hole conducting species.[326] Up to date, this approach is able to give PCE values up to 11.7%, being the highest ever obtained for solid-state DSSCs.[188] Interestingly, photocurrent dynamics as a function of different irradiation intensities showed that J_{SC} depended linearly on the light power, thus clarifying the absence of mass transport limitations, that could instead be present in the case of copper complexes usually employed in liquid electrolytes. An LCA study of this approach would be crucial at this stage. In fact, being able to fabricate solid-state DSSCs based on copper could leads to the simultaneous achievement of sustainability, stability and high efficiencies.

4.2.4 Final remarks on electrolytes

As discussed above, many alternative redox couples have been proposed so far, which can be potentially derived from renewable sources or waste products. This would actually limit issues related to the use of CRMs and allow the electrolyte components to be sustainable. However, as reported in **Table 7**, in most cases the use of organic solvents in the electrolyte, having high energy-consuming synthetic procedures, threatens the sustainability of these alternative redox couples. As a result, extensive research still has to be focused on new materials and reliable procedures. In summary, several redox couples, alternative to traditional iodine and cobalt, have been here reported. When using metal-based redox couples, the natural abundancy, the availability and the eventual recovery must be considered and related to their effective properties. As an example, iron is an abundant metal in the Earth crust. However, its complexes, when used as redox mediators in DSSC, highlighted several problems, such as O_2^- sensitiveness, photodegradation and high recombination rate. On the other hand, copper complexes present several advantages, such as low light absorption in the visible region, high dye regeneration efficiency, efficient regeneration at the

CE, stability. However, the synthesis of specific ligand (based on phenanthroline) and of the complex is far to be “sustainable”, since it involves the use of toxic organic solvent and inert N_2 or Ar atmosphere. Parallelly to metal-based complexes, completely organic redox mediators, such as $TEMPO^-$ and sulphur-based ones, were considered as well. Concerning $TEMPO^{0/+}$ redox couple, the main issues are the smaller regeneration efficiency and electron lifetime, if compared to traditional cobalt and iodine. For these reasons, the use of thinner photoanodes must be considered, in order to reduce recombination losses and improving electron collection. Finally, sulphur-based compounds are the most investigated in the wide plethora of alternative redox couples. As a matter of facts, they offer several advantages, such as ease of preparation, non-corrosiveness, negligible light absorption in the visible region. They cannot be used in combination with traditional platinum CEs, but work well with alternative candidates, such as PEDOT or carbonaceous materials.

The choice of the redox pair must also be accompanied by the adequate replacement of the organic solvents (in the case of liquid-state DSSCs). Albeit the long-term stability of aqueous-DSSC is not unambiguously accepted, water would certainly represent a winning choice to this purpose, especially considering that commercial DSSCs are now assembled with liquid electrolytes and the introduction of water as a solvent would not require an invasive intervention on the production plants. Achieving a truly aqueous solar cell with high efficiency at the level of the organic-based electrolyte counterparts represents the *Holy Grail* for the DSSC community, which is strongly focused on the development of a sustainable, cheap and up scalable technology with unique features, especially if indoor and portable objects are envisaged. In this context, the issue related to the (ultra)purification of the water should be carefully evaluated to be classify aqueous DSSCs as a truly sustainable technology.

Beside the development of water-based DSSCs, the discovery of the remarkable performance assured by copper-based “Zombie-cell” has opened a new branch in the field of hole transporters. This strategy, which can offer efficiencies above 11% today, could became an unprecedent breakthrough in the realization of truly sustainable DSSCs if in-depth LCA studies will show adequate figures of merit. To date, this solution has already demonstrated the ability of bypassing the use of CRMs, such as cobalt, and offering, at the same time, high efficiency and stability.

4.3 Cost-effective and eco-sustainable counter-electrodes

Counter-electrode (CE) plays a key role in DSSCs,[327] as it catalyses the reduction (also known as regeneration) of the oxidized species of the redox shuttle. Beyond fast catalytic activity, CEs should exhibit wide thermal and (photo)chemical stability.[328] With regards to the regeneration mechanism, its kinetic is mainly dependent on the nature of the redox mediator and the physical status of the electrolyte more than on the CE material itself (*vide* **Section 6.2**). Indeed, the latter should present a wide surface area in order to expose a large number of catalytic sites. Straightforwardly, throughout this section, we mainly focus on the morphological features of the different classes of materials effectively employed as CEs without neglecting their electrochemical properties and relations with other device components. Specific attention is paid on greener and more sustainable synthetic and deposition approaches. Concerning liquid and quasi-solid electrolytes, the reduction of the redox mediator occurs in the three following steps: (i) the approaching and the absorption of the reduced species onto the CE surface; (ii) the regeneration reaction; (iii) the desorption of the oxidized species from the CE surface into the electrolyte solution.[329] Therefore, a good CE should avoid a strong chemisorption of the redox species in order to assure an efficient regeneration kinetic. To compare different type of CEs two main parameters should be analysed, namely the charge transfer resistance (R_{CT}) and the limiting current density (J_{lim}). The former, usually obtained from electrochemical impedance spectroscopy (EIS),[330] is a quantitative detector of the resistance experimented by an electron to be transferred from the CE to the oxidized species of the redox couple. The latter is the maximum current density value a CE could support. In order to have an efficient counter-electrode, low R_{CT} and high J_{lim} are required.

Historically, platinum is the CE of choice in DSSCs, yet the scientific community is searching for feasible alternative, sustainable materials, being cheaper and more readily available.[331–336] In addition, platinum tends to degrade when in contact with the standard I_3^-/I^- redox mediator, thus restricting its use on a large scale.[337–339] Finding and developing an alternative CE to replace platinum, with its superior characteristics of high electrical conductivity and electrocatalytic activity, is a significant challenge and huge demand in the community.[340]

Recently, several research works have been focused on the development of cost-effective platinum-free CEs. A plethora of different materials were explored such as carbon-based materials,[341] conducting polymers,[316,342] metal chalcogenides or oxides,[146,343,344] nitrides[345] and metal/carbon composites.[346] Among them, we will hereafter focus our attention on carbonaceous materials, metal-based compounds and composites, *viz.* the most effective in terms of sustainability and scalability. We decided not to discuss about polymeric films because, despite their good catalytic activity, they usually require rather time- and energy-demanding synthetic procedures and the employment of toxic solvents increasing the CED and lowering the sustainability of the corresponding devices.[347] The most sustainable approaches to obtain efficient CEs are briefly detailed in the followings. It is worth mentioning that a 100% green and sustainable approach is actually unpractical or, at least, it has not been already discovered, to our knowledge. Therefore, we referred to papers aiming at reducing the environmental impact in terms of CE production, which avoid the use of CRMs, hazardous solvents or chemicals and harsh procedures, while concurrently demonstrating PCE values close or even higher than those recorded with standard platinum-based reference devices.

Furthermore, due to the large number of reports on this topic we specifically focus on the most recent (*i.e.* last year) papers. Indeed, the purpose of this chapter is to evidence some useful approaches towards sustainable, futuristic cathode materials for DSSCs rather than give just a simple comprehensive overview. It should be pointed out that a definite verdict on the sustainability of a specific material could be drawn just after a specific LCA.

4.3.1 Carbon-based CEs

Among different carbonaceous materials,[348,349] graphite was firstly investigated mainly due to its large availability. However, natural graphite has been evaluated as critical material since 2011 by the EU.[350] This criticality assessment is based on economic importance, supply risk and on proven and readily available substitutes (both from a cost and performance perspective). Graphite results critical especially for its low *substitution potential* in refractories, in particular for steel production, and for its large commercial use as Li-ion battery anode. However, graphite is claimed as "green" material because of its simple, time/energy saving deposition procedure even at ambient conditions. Pristine graphite shows high electronic conductivity, but its catalytic ability toward triiodide reduction is quite poor. This is mainly ascribable to its limited surface (*i.e.*, few catalytic sites) and slow electron transfer on the z-axis, which results from the intrinsic plane-to-plane structure.[351,352] Owing to their high surface area-to-volume ratio and stability, the use of both carbon black[353,354] and carbon nanotubes[355] is very promising to obtain excellent performances. Unfortunately, the synthesis of carbon black usually implies to operate at very high temperature,[356,357] and high surface area CNTs are obtained by rather expensive and harsh templates.[358,359]

It is worth mentioning that even though the eco-friendliness of carbonaceous materials is widely accepted, their sustainability is tightly linked to both the source of precursors and the manufacturing approach and it should be considered in light of green metrics.[360] In this respect, chiefly the use of harsh solvents as well as the carbon dioxide production should be minimized. Moreover, the existing carbon-based CEs still demonstrate unsatisfactory features/performance and, overall, provide lower electrocatalytic activity compared to standard platinum electrode when classical redox couples are employed. As a result, further material design and innovation are required to boost the intrinsic electrocatalytic activity of carbonaceous materials. Moreover, it is worth to be noticed that using platinum-free CEs is not always cost-effective and environmentally friendly. Sometimes, the impact of the production process of tailored materials is referred to even exceed the one linked to the use of bare platinum. To reduce the environmental impact, a valuable approach is to use bio-derived wastes as carbon sources and reduce the number of production steps leading to lower CED. Recently, different biomasses/bio-wastes, including coffee waste,[361] corn straw,[362] leaves,[363] mangosteel peels,[211] potato peels and waste residues,[364] were exploited and transformed into biochar for CE application.

Very recently, Di and co-workers showed a carbon-based matrix obtained through humic acid pyrolysis at high temperature and under inert atmosphere.[365] The precursor was a sub-product of the microbial biodegradation of organic biomasses. Even though the process was relatively time consuming (1 day) and required high pyrolysis temperature (*i.e.*, 900° C), the use of a secondary raw material made this approach more environmentally sustainable in a circular economy viewpoint compared to those coming from virgin materials. The electrocatalytic properties (toward the triiodide reduction) of the newly synthesised material were lower than platinum. Nonetheless, by cell testing the authors recorded a remarkable PCE of 6.14%, which is only slightly lower than that of the platinum-based reference cell (7.1%), likely because of the lower current density assured by the carbonaceous matrix (**Table 8, entry 1**): suggested improvements include the functionalisation with cheap metal atoms (*i.e.*, nickel). The use of wastes derived from fruits and vegetables to produce valuable CE materials has been recently investigated. Balanay *et al.*[366] exploited orange peels as starting material to obtain performing carbonaceous CEs after grinding with $Co(NO_3)_2$ and following heat treatment at 200/300° C. The higher the sintering temperature, the better the catalytic performances of CEs (**Table 8, entry 2**), even though the slight amelioration did not justify the increased energy consumption. In a similar approach, Yun and co-workers reported on the employment of pomelo peels as raw material.[367] After washing with water to remove impurities and grinding to finely pulverise the precursor, the authors proposed three different methods to obtain bio-derived carbonaceous films with controllable morphologies. The first method simply consists of a chemical degradation process (to disrupt the macromolecular structure of pomelo peels) followed by microwave pyrolysis (500 W, 6 min); the so obtained powders showed insufficient Brunauer-Emmett-Teller (BET) specific surface area. To better control the morphologies and the surface area of the powders, the authors tested the effect of two consecutive carbonization processes (at 500 and 800° C, respectively). From the sustainability viewpoint, the enhancement of the catalytic properties of the materials after pyrolysis was counterbalanced by the improved energy consumption. The third approach aimed to reduce both the energy consumption and the use of chemicals: the macromolecular structure was hydrothermally disrupted avoiding the use of H_3PO_4 and the annealing process was limited to a single step at 500° C for 2 h. The latter method proved to be the best trade-off between good catalytic activity and improved sustainability. For final CE production (**Table 8, entry 3**), the powders (dispersed in isopropanol) were sprayed onto FTO and annealed at 400° C for 30 min.

As already mentioned, the use of carbonaceous material as CEs in DSSCs has been worldwide reported and investigated, but the sole use of carbon is not sufficient for the resulting CE to be considered truly “sustainable”. Indeed, various factors should be taken into consideration: i) the carbonaceous material under use should preferably come from waste or low-cost precursor; ii) the energy demand as well as the CO_2 emissions should be minimized during the carbonization process; iii) the final material should exhibit good catalytic properties. To exemplify this concept, it is worth reporting the approach by Kumar *et al.*,[368] who carbonized a commercial 2-methyl-8-hydroxy quinolinol under inert argon atmosphere. The starting material is relatively cheap (30 $ each 100 g), but the process required very high temperature (1200° C) and it produces more than 4 eq. of carbon dioxide. Moreover, the carbonaceous powders could not be directly deposited onto FTO, but require a pre-dispersion in polyvinylpyrrolidone (PVP) followed by doctor-blading. The use of PVP binder forced to an additional sintering step (450° C, 1 h) leading, in turn, to a lower PCE compared to Pt-based device (**Table 8, entry 4**). This is a clear example of green, CRMs-free material production, which is nonetheless hardly sustainable in our opinion; clearly, it should be evaluated after thorough LCA.

As already discussed early in this section, we decided not to tackle polymer-based CEs due to their hardly sustainable synthesis procedures and their poor solubility that prevents CE production through solution processing. However, compared to both carbonaceous materials and transition metal compounds, polymers are elastic, thus readily exploitable in flexible or wearable electronics. In this respect, amongst the plethora of works on this topic, one example of truly innovative and sustainable approach, as for the specific aim of this thesis, is the one recently proposed by the group of Ehrmann.[369] They coated a conductive liquid silicone rubber (Powersil® 466 A/B) layer, based on polydimethylsiloxane filled with carbon black and graphite, onto a viscose cotton woven fabric, which was employed as CE in lab-scale DSSCs after being sintered at 200° C. Even if PCE value was found to be rather low (**Table 8, entry 5**), this work could be effectively considered a first interesting step toward the development of sustainable textile-based DSSCs.

4.3.2 Transition metal-based CEs

The green characteristics of carbonaceous materials are somehow outshined by their issues in terms of instability towards corrosive iodine-based electrolyte.[370] As a result, different classes of materials were exploited as alternative, efficient CEs in DSSCs.[349] Among them, transition metal-based compounds actually represent the best trade-off between long-term stability, environmental impact and sustainability, assuring a good catalytic activity toward the most commonly employed redox couple, a remarkable chemical inertness and good electronic properties.

Among various transition-metal compounds, MoS_2 and more broadly sulphides[333] could be considered the most viable option to replace platinum due to their abundance, low cost and comparable electrocatalytic behaviour. Vikraman *et al.* described a chemical bath method to deposit MoS_2 directly onto FTO-coated glass.[371] Yet, the performances of the obtained device are strongly dependent on the film deposition time, being layer grown form less than 20 min. not able to support the current powered by the photoanode and resulting in very low FF. To enhance the PCE of pure MoS_2, a mixed cobalt/molibdenum sulphur composite was used. Qian *et al.* recently reported on the synthesis of pure MoS_2 and Co_3S_4/MoS_2 nanocubes by hydrothermal synthesis (200° C for 18 h) in autoclave.[372] They obtained PCE values similar or even better (mixed sulphur) compared to platinum-based devices (**Table 8, entry 6**) and EIS evidence slightly lower charge transfer resistance at the CE/electrolyte interface. Unfortunately, this approach could not be classified as "green", as it used DMF as the solvent. Moreover, due to requirements in terms of material crystallinity, a further annealing step (350° C for 1 h under argon atmosphere) was added that sensibly increased the overall energy demand of the whole process, thus lowering its sustainability. The (even partial) replacement of molybdenum with cobalt is somehow critical.[59] Unfortunately, the chemical approach for their preparation affects sustainability on a large-scale and also leads to extremely thick substrates, thus affecting DSSC transparency. To overcome both the issues in a single stage, Jeong and co-workers reported on an innovative approach consisting in the low-temperature (below 100° C) atomic layer deposition of nanometric films to be employed in bi-facial devices.[373] The so obtained films did not require any sintering step, which greatly reduced the total energy consumption for CEs production. Remarkably, this material also showed PCE values almost comparable (-8%) to control cells (**Table 8, entry 7**) due to relatively high J_{lim} and low R_{CT}. On the other hand, CoS nanostructures could be produced by means of simple and cost-effective procedures, with reduced number of synthetic steps.[374–377] In this context, Ashok Kumar *et al.* presented hierarchical CoS structures directly grown onto a FTO substrate by hydrothermal method[378] in which they mixed the reactants (*i.e.*, $CoCl_2$ and thiourea) on the top of an FTO substrate inside a sealed autoclave. The layout was heated at 180° C for 24 h, thus concurrently growing CoS structures that were tightly anchored onto the conducting film support avoiding any further deposition step. Then, they tested a specular approach to synthetize a plethora of binary and ternary sulphides, encompassing alternatively cobalt, nickel or zinc (**Table 8, entry 8** and **9**).[333] The best results were obtained with cobalt-containing ternary mixtures, whereas cobalt-free electrodes mainly suffer for slow triiodide regeneration reaction that minimize the current density output. To completely avoid the use of CRMs, Park and co-workers focused on crystalline pyrite (*i.e.*, FeS) nanoparticles synthetized by hot-injection moulding,[379] which requires moderate operating temperature of about 200° C).[380] FeS nanoparticles were then spin-coated onto FTO glass and used as CEs giving slightly lower PCE compared to platinum-based ones (**Table 8, entries 10** and **11**). To further improve the efficiency of the newly developed CEs, nanoparticles were supported onto amorphous carbon. Even though glucose carbon source could be considered “green”, the supplementary synthetic procedure was time and energy consuming (high temperature needed) and required a completely inert atmosphere, which actually overcame the overall sustainability of this approach.

To completely avoid the use of CoS, Li *et al.*[381] focused on the hydrothermal synthesis of Cu_7S_4/CuS nano-hollows that mimic the behaviour of platinum. The authors reported on the whole synthetic approach starting from a copper salt: the use of cheap and less hazardous precursors (*i.e.*, $Cu(NO_3)_2$, NaOH, ascorbic acid, ethylene glycol) to obtain Cu_2O, the avoiding of organic solvents, and the low-temperature solvothermal synthesis (using Na_2S as sulphur source) along with the good PCE values in lab-scale cell, accounted for the true sustainability of this proposed approach, even though it was not definitely confirmed by LCA. If supported on GO, it showed lower charge transfer resistance and higher limiting current density if compared to Pt. Yang and Chen[382] employed a low cost and scalable hydrothermal approach to synthetize $NiMoS_4$ compounds by using cheap, abundant and rather safe reactants (*i.e.*, nickel acetate, sodium molybdate and thiourea as nickel, molybdenum and sulphur source, respectively) using deionized water as solvent and relatively low temperature for heat treatment (200° C for 12 h). Once thoroughly washed and dried, an ethanol solution of the corresponding compound was spin-coated onto an FTO glass and then dried at 140° C. This approach confirms the possibility of obtaining resistant, cheap and catalytically active materials even at relative low temperature effectively avoiding the use of any organic solvent (**Table 8, entry 12**).

Titanium is an abundant and relatively cheap material, usually employed in photoconversion devices. Schmuki and co-workers reported on the use of TiS_2 as an efficient alternative to platinum.[383] A titanium thin layer (1 μm) was directly evaporated onto FTO glass and then anodized at room temperature in an EG:H_2O solution of NH_4F (60 V for 10 min; EG = ethylene glycol). The so obtained titanium oxide layer was thermally converted to anatase phase (450° C for 1 h) that showed very poor electrocatalytic properties. A further sulfidation step was then required, which was performed in a quartz tube under H_2S flow (500° C). The process took 2 h for completion and the resulting TiS_2@FTO showed catalytic activity comparable to platinum (**Table 8, entry 13**). If we just consider the final material, this approach might be surely classified as green, but the use of fluorinated compounds, high voltage and a sizeable amount of H_2S does not allow it to be considered truly sustainable.

One of the paradigms of sustainability is to reduce the amount of energy required for materials production, especially without a massive transition to renewables. In view of that, it could be very useful to avoid high temperature post-treatments, usually needed to obtain crystalline materials. Lee and co-workers reported on a direct solvothermal growth of CoS nanostructures onto FTO by using aniline as template, ethanol as solvent and $Co(NO_3)_2$ as cobalt precursor. These were mixed together in an autoclave containing cleaned FTO slides; then, thiourea was added as sulphur source and the sealed vessel was heated at 200° C for 12 h. The so obtained films were directly employed as CEs leading to similar results compared to control devices.

Selenium could be effectively used in place of sulphur in binary transition metal compounds due to the similar electronic structure and reactivity.[384] Among the different production methods to directly deposit the catalytic film onto a TCO substrate, Jiang and his group[385] focused their efforts on the use of electrodeposition, being the latter a relative cheap method that completely avoids the use of harsh solvents and/or toxic materials. Here, thiourea, selenium oxide, nickel chloride in water were used as sulphur, selenium and nickel sources, respectively. The so-obtained CEs showed outstanding catalytic properties leading to a PCE of 7.54% (20% higher than the control device, **Table 8, entry 14**) due to an increased J_{SC} and a lower charge-transfer resistance as proved by both J-V and EIS analyses. Due to the relatively high PCE coupled with easy and cheap synthetic path, these NiSe CEs could be considered as cost-effective. A specular approach was recently exploited by Ahn and co-workers to deposit $CoSe_2$ films.[386]

However, compared to previous work, notwithstanding the promising PCE, the use of cobalt in place of nickel reduces the sustainability of this route.

Green features of selenium-based material are undisputed, especially if coupled to inexpensive, abundant and hazardless cations, such as tin. However, their sustainability is still under debating. As an example, Kumar and co-workers[387] deposited SnSe films by manual screen-printing onto FTO glass and annealed them in an inert atmosphere at 900° C similarly to platinum-CEs (**Table 8, entry 15**). Even if avoiding the use of platinum looks like a great improvement in terms of sustainability of the devices, SnSe production is far to be really sustainable being the reaction carried out in a quartz tube at 900° C for 24 h (relatively high CED). As a matter of fact, the use of an extreme temperature seriously increases the energy consumption of the overall process undermining the sustainability of these SnSe films.

The *in-situ* hydrothermal growth method surely provides a feasible, even if hardly scalable, approach for the fabrication of MSe_x films, having good adhesion to FTO glass. Chen *et al.*[388] recently reported on an economic and scalable hot-injection approach to produce copper/iron mixed selenide nanocubes (**Table 8, entry 16**). The acetylacetonate precursor salts of both metals were mixed in oleylamine and heated at 150° C under controlled nitrogen atmosphere to avoid oxidation. Then, a selenium precursor solution was added, and the temperature increased up to 250° C. The excess of oleylamine was removed by ion exchange reaction and the surfactant-free $CuFeS_2$ nanocubes were drop casted onto FTO glass and dried at 60° C. In our opinion, the only drawback of this approach is the replacement of water (a green solvent) with oleylamine, which is still questionable in terms of environmental impact. The so-obtained film demonstrated lower charge transfer resistance and comparable limiting current density if compared to platinum, leading to almost identical PCE values.

An innovative approach was recently proposed by Ho and co-workers,[389] based on the use of VSe_2 as electrocatalytic material. Indeed, both vanadium and selenium as well as the resulting VSe_2 are not CRMs;

moreover, the synthetic procedure is relatively easy, it does not require very high temperature (*i.e.* 220° C), or even hazardous reactants or solvent. Noteworthy, crystalline materials were obtained without any treatment at high temperature. The only drawback of this approach is the high 13:1 ratio of moles of CO_2 per mole of VSe_2 being produced, starting from SeO_2, V_2O_5 and $C_2H_2O_4{\cdot}2H_2O$ precursors dissolved in deionized water (**Table 8, entry 17**). Therefore, alternative routes should be experimented aiming at reducing the amount of produced carbon dioxide without undermining the good catalytic properties of the material.

Compared to both selenides and sulphides, oxides are more stable and cheaper CEs to produce. Interestingly, Miclau and co-workers proposed a “full-copper” device: Cu_2O was used as both the photocathode and the CE,[390] into which some metallic copper nanoparticles were dispersed to enhance the catalytic activity toward the reduction of the redox shuttle. Authors simply employed copper acetate as starting material and the synthesis was conducted in autoclave (180° C for 24 h). Being both the electrodes made by a p-type semiconductor, the PCE was relatively low (**Table 8, entry 18**), but the simple and inexpensive synthetic route made this approach appealing in terms of sustainability of the final device. Alami and co-workers[391] attempted complementary approaches to obtain Cu_xO@Cu films. Among them, electrodeposition required the use of a strong oxidizing acid (*i.e.*, H_2SO_4), but a very short deposition time of 15 min. Chemical bath approach led to a mixed oxide/hydroxide, thus limiting the scalability of the procedure; however, the very low sintering temperature (60° C) sensibly reduced the overall energy consumption. Finally, they carried out chemical ageing (an ammonia-based water solution) for 24 h followed by baking at 250° C for 2 h. It should be pointed out that, even if the obtained PCE of the control device are very low mainly because of a non-optimized photoanode, the Cu-based device suffer for lower FF compared to Pt that could be ascribed to a poor charge transfer at the electrolyte/CE interface.

Li, Jin and co-workers presented a ternary oxide (*i.e.*, $La_{0.7}Ca_{0.3}MnO_3$ with a perovskite structure, as CE in DSSCs approaching the PCE of platinum-based device (**Table 8, entry 19**).[392] Authors claimed for the low-cost of their material, but the use of lanthanum, a rare-earth element, ethylenediaminetetraacetic acid (EDTA) as coordinating molecule and the high (900° C) calcination temperature seriously affected the sustainability of the proposed approach. Yun *et al.* recently explored the use of tantalum-based bimetallic oxides.[393] They mixed the $TaCl_5$ (tantalum precursor) with nitrate secondary metal precursor (*i.e.*, iron, cobalt or copper) in an ethanol solution, which was hydrothermally treated at 200° C for 18 h in autoclave. The so obtained precipitate was then annealed under nitrogen at 800° C for 3 h to obtain the corresponding oxides: $FeTa_2O_6$, $CoTa_2O_6$ and $CuTa_{10}O_{26}$ (**Table 8, entry 20**). The latter showed lower catalytic activity compared to Pt-based CEs as proved by electrochemical characterization. To improve their photocatalytic properties without significantly impairing the green characteristics of the approach, the oxides were supported onto a carbon matrix, which in turn was obtained from bio-sourced aloe peel waste (**Table 8, entry 21**).[394] Both the pristine and the carbon-based powders were simply dispersed in isopropanol and sprayed onto a heated FTO substrate and annealed at 400° C (at least 100° C lower than the annealing temperature for platinum-based CEs). The best efficiency was provided by the iron-modified supported oxide that outperformed the reference device, thus resulting a “green” and rather sustainable alternative to platinum.

2.3.3 Composite CEs

The use of composite materials is a valuable approach to concurrently exploit the positive characteristics of different materials.[395] It is known, however, that the complexity of a material affects negatively its recyclability.[396–398] In the DSSC field, this seminal approach was reported by Pang and co-workers,[399] who coupled the robustness and eco-friendly features of MoS_2 with the electronic properties of reduced graphene oxide (rGO): the composite electrode achieved 6.7% of PCE compared to 0.74% and 3.18%, for bare MoS_2 and rGO, respectively (**Table 8, entry 22**). Notwithstanding the better performance compared to Pt-device, the proposed materials suffered for relatively high series resistance (as proved by EIS) that is a warning light on the stable adhesion of the film onto the FTO substrate. As regards the synthetic approach, a MoS_2/GO film was hydrothermally synthetized (200° C for 12 h) starting from a DMF/water solution of GO, Na_2MoO_4 and L-cysteine. The resulting material was then deposited onto FTO through blade-coating. A meaningful step toward sustainability consisted in the use of a hydrogen flux (under moderate vacuum) to reduce GO to rGO, thus completely avoiding hazardous chemical reductants. The synthesis of composites is usually complicated, often requiring a number of different steps and high temperatures negatively impacting on the CED. Hydrothermal synthesis is amongst the less impactful methods due to the little amount of solvent required, the good control on the final material structural/morphological characteristics and the relatively low energy demand. Metal sulphides usually show high catalytic performance, but poor conductivity and structural instability.[400] To overcome this, they are coupled with carbonaceous material such as CNTs or graphene that greatly enhance the overall conductivity of the composite. Li *et al.* exploited a mixture of $Ni(NO_3)_2$, glucose, urea and cysteine to obtain carbon-supported Ni_3S_4 composites that showed catalytic features comparable to Pt (**Table 8entry 23**).[401] The synthetic procedure could be considered as a further improvement towards more sustainable DSSCs, even though the autoclave reaction (180° C, 20 h), and mainly the following sintering at 500° C under nitrogen somehow impair the green features of this approach. Authors also reported on the use of Ni_3S_4@C/CNTs CEs that outperformed the control device: this is mainly ascribable to an increase of both FF and J_{SC} assured by the combination of the electrochemical features of sulphur and carbon-based materials. Nonetheless, the claim for the real sustainability of this second approach should be verified after further details on the production of CNTs are provided.

Some very interesting results were reported by Oh and co-workers, who employed a perovskite-based material slightly doped with GO as very efficient CE (**Table 8, entries 24** and **25**).[402] Best device (4% GO doping) achieved remarkably high PCE (*i.e.*, 12.5%) even though the authors did not report the value of the reference platinum-based device. It is worth mentioning that GO sheets were synthetized by Hummers' method that could not be considered green as it makes use of concentrated H_2SO_4, $KMnO_4$, H_2O_2. On the other hand, the relatively small amount of GO used, also coupled with extremely good performance obtained, counterbalances the rather hazardous approach. Graphene-$La_2CdSnTiO_4$-WSe_2 (G-LCT-W) hybrids were prepared by hydrothermal method mixing LCT, graphene and WSe_2 followed by heating at 150° C for 15 h. The precipitate was washed and dried several times, and then dispersed in ethanol to obtain a slurry that was finally deposited on FTO trough doctor-blade at room temperature.

Rosei *et al.* presented a CuS/graphene composite that showed catalytic activity comparable to platinum (5.73 vs 5.78%, **Table 8, entry 25**).[403] The most valuable point of this approach consisted in the relatively low sintering temperature required (100° C for 15 min), even though complete LCA study must follow. Indeed, even if the CuS precursor (*i.e.*, thioacetamide and copper nitrate trihydrate) were actually "green", authors did not give any useful information about the synthesis of graphene. If this is produced by a sustainable approach, undoubtedly this work has to be considered as a meaningful milestone in the obtainment of 100% green and sustainable CEs. Very recently, Silambarasau and co-workers[404] reported on the synthesis of hierarchical NiO@NiS@G nanocomposites coupling the electrochemical ability of cheap NiO with the electronic properties of graphene, thus leading to the fabrication of more cost effective and CRM-free CEs, having similar efficiency values compared to platinum-based device. An innovative composite was recently proposed by Feng and co-workers[405] as effective CE

(**Table 8, entry 26**): a nickel-cobalt phosphide supported on CNTs, which was obtained by using cheap and green reactants and a sustainable synthetic hydrothermal approach. More in details, nickel and cobalt oxalates were dissolved in deionized water and added dropwise to a basic solution of CNTs, which was then heated at 100° C for 24 h in autoclave. The nickel/cobalt mixed hydroxide@CNTs precipitate was obtained by phosphorylation process through NaH_2PO_2 and, then, heat-treated at 300° C for 2 h. The performance of NiO@NiS-based device are partially jeopardized by a lower FF that could be ascribable to adsorption phenomena of both triiodide and iodide anions onto the NiO surface.[406] Even though the proposed approach avoids the use of critical materials and/or procedures (only cobalt-based issue remains), the sustainability of the approach is not clear because of the lack of information on the precursors as well as production process of CNTs. If their renewable source is confirmed, approach has to be included in the sustainable ways to obtain effective CEs outperforming platinum-based ones.

Table 8 Summary of the various materials implemented as most sustainable CEs in DSSCs.

Class	***Material***	***Pros***	***Issues***	***PCE vs. Platinum***	***Entry***^{Ref}
Carbonaceous	Humic acid	• Sub-product of biodegradation	• 1 day reaction • High temperature	-13%	**1**[365]
	Orange fiber	• Waste-derived	• Use of cobalt	n.a.	**2**[366]
	Pomelo peels	• Waste-derived • CRMs-free	• High temperature	Slightly better	**3**[367]
	2-methyl-8-hydroxy quinolinol	• Cheap source • CRMs-free	• Very high temperature • CO_2 emission • Binders	-27%	**4**[368]
	Silicon rubber	• Textile-based • Low temperature	• Poor PCE	Very low	**5**[369]
TM compounds	Co_3S_4/MoS_2	• Low temperature • (amorphous)	• Use of DMF • Use of cobalt • Argon atmosphere	Slightly better	**6**[372]
	MoS_2	• Low temperature • Bifacial device • No sintering	• None relevant	Slightly lower	**7**[373]
	CoS	• Direct growth • Low temperature • No sintering	• Use of cobalt • 1 day reaction	-11%	**8**[378]
	Ni/ZnS	• Direct growth • Low temperature • No sintering	• 1 day reaction • Slow I_3^- regeneration	Extremely lower	**9**[333]
	FeS	• CRMs-free • Moderate temperature	• Moderate PCE	Slightly lower	**10**[380]
	FeS@C	• CRMs-free • Glucose as carbon source	• Very high temperature • Long reaction • Argon atmosphere	Slightly better	**11**[380]
	$NiMoS_4$	• Cheap sources • Low temperature • Water-based	• Use of thiourea	Slightly better	**12**[382]
	TiS_2	• Direct growth	• High voltage • Use of NH_4F • Sulfidation step	Comparable	**13**[383]

Class	*Material*	*Pros*	*Issues*	*PCE vs. Platinum*	*Entry^{Ref}*
TM compounds	NiSe	• Direct growth • Electrodeposition • Water-based	• Use of thiourea	+ 20%	**14**[385]
	SnSe	• Direct growth • CRMs-free	• High temperature • Argon atmosphere	Extremely lower	**15**[387]
	Cu/FeSe	• Direct growth • Scalable	• Complexants • N_2 atmosphere • Use of oleylamine	Slightly better	**16**[388]
	VSe_2	• CRMs-free • Low temperature • (crystalline) • Water-based	• CO_2 emission	+ 10%	**17**[389]
	Cu_2O	• CRMs-free • Simple approach	• Low PCE	Lower	**18**[390]
	$La_{0.7}Ca_{0.3}MnO_3$	• CRMs-free	• Use of lantanium • Use of EDTA • High temperature	Lower	**19**[392]
	$FeTa_2O_6$	• CRMs-free • Moderate temperature	• Low surface area	Lower	**20**[393]
	$FeTa_2O_6$@C	• CRMs-free • Carbon from waste • Moderate temperature	• None relevant	Slightly better	**21**[394]

Class	*Material*	• *Pros*	• *Issues*	*PCE vs. Platinum*	*Entry[Ref]*
COMPOSITES	MoS_2/rGO	• Low temperature • Hydrogen as reductant • CRM-free	• Long time • Use of DMF	Slightly lower	**22**[399]
	Ni_3S_4@Carbon	• CRMs-free • Water-based • Carbon from glucose	• Nitrogen atmosphere	Comparable	**23**[401]
	Ni_3S_4@Carbon/CNFs	• CRMs-free • Water-based	• Nitrogen atmosphere • Unknown source of CNFs	Higher	**24**[401]
	CuS/Graphene	• Low temperature • Short time • CRMs-free	• Unknown source of graphene	Comparable	**25**[403]
	Ni/CoP_x@CNTs	• Low temperature • Green precursor	• Use of cobalt • Long time • Unknown source of CNTs	Higher	**26**[405]

4.3.3 Final remarks on CEs

Throughout this section, we discussed some feasible approaches to design and implement environmental-friendly, green and sustainable DSSC CEs, some of which are also shown in **Figure 15**. The most interesting and valuable ones have been summarized, chiefly focusing on the kind of approach and related sustainability than on the bare PCE, which is nonetheless a meaningful output in view of practical application. Considering the plethora of approaches and materials analysed, it is quite difficult to outline a homogenous and straightforward path, and only some general considerations can be drawn.

True understanding of which is the most sustainable CE material is questionable, since LCA studies are rarely performed. As rules of thumb: (i) the use of cobalt should be minimized as much as possible, most likely completely avoided; (ii) transition-metals based materials should be preferred over carbonaceous ones in terms of better stability even though the latter are more convenient if “waste-sourced”; (iii) oxides should be preferred over selenides and sulphides because of the reduced number of additional synthetic steps (*i.e.*, selenization or sulfidation); (iv) composites show the most promising prospects, particularly if the synthetic procedures will be substantially improved in the coming future. All these suggestions should be coupled with a thoughtful choice of the most suitable redox mediator (without neglecting the nature of the solvent and the presence of additives, if any) and, in order to better match with the electronic features of the state-of-art electrolyte (**Section 6.2**), a further engineering of the CE could be considered as well.

In terms of preparation procedures, among the different approaches, those allowing direct deposition of CE materials onto TCO glasses should be highly preferred, *viz.* electrodeposition and hydrothermal synthesis. Actually, these methods effectively avoid the rather energy demanding anchoring step. It is worth mentioning that a sintering step is always necessary to improve the catalytic performance and the stability of the material; obviously, the lower the sintering temperature, the higher the relevance and added value of the approach, as it will reduce the energy consumption and pave the way for the use of polymeric (and flexible) substrates. A wise development of synthesis and deposition procedures should not neglect a future industrialization and, straightforwardly, the proposed approaches should be scalable and easily implemented in existing pilot lines.

It is worth mentioning that the drafted conclusions here refer to standard systems in which iodide/triiodide in organic solvent and glass/FTO are the electrolyte couple and the CE substrate, respectively, being the latter the most exploited in large-scale devices. Nonetheless, our general considerations could be rather easily applied to alternative redox couples, greener solvents (*e.g.*, aqueous electrolytes) or innovative substrate (*e.g.*, flexible PET).

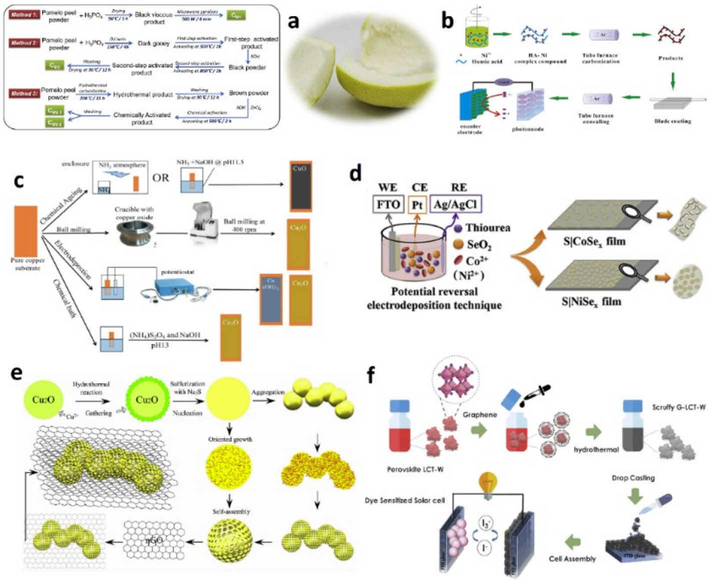


Figure 15. Some of the most interesting and sustainable approaches to produce green and cost-effective counter-electrodes based on (a,b) waste-derived carbonaceous materials, (c,d) transition metal compounds and (e,f) composites materials. The frame have been adapted from ref[365,381,385,391,407] *and* [402]*, respectively.*

4.4 The sustainability issue of TCO/glass substrates

Cradle-to-gate LCA identified TCO/glass substrate as one of the main responsible for the environmental impacts of DSSC modules,[80,408] which are easily ascribable to the following: (i) TCO/glass is the dominant component in terms of mass of a module and (ii) its production is highly energy demanding.

According to a cradle-to-gate LCA,[80] investigation of other substrates to assess the different impacts demonstrated that polymeric substrates, such as PET or PEN (polyethylene naphthalate), decrease the environmental impacts in all the indicators. Replacing glass with polymers results in enhanced performance also in terms of CED and global warming potential within 100 years (GWP100); moreover, the EPBT for DSSCs with polymeric substrates was calculated to be lower than the corresponding DSSCs with glass substrates, even accounting for the lower neat efficiency reachable with a polymeric substrate. Indeed, the trade-off between costs, efficiency, socio and environmental sustainability should be the final achievement of any process design.

Some representative configurations of polymeric substrates for DSSC are those reported by Yamaguchi and Hsu.[409,410] Both Yamaguchi's and Hsu's groups prepared a plastic substrate photoelectrode starting from ITO/PEN supplied by Oji-Tobi Co. and Pecce Technologies, Inc., respectively (PEN is more thermally stable than PET, but more expensive). Nowadays, the most implemented technology to obtain the conductive substrate is the direct magnetron sputtering. Usually, ITO/glass is annealed at 350° C after the deposition process, but this temperature is too high for plastic substrates. The lower temperature required by polymeric substrates leads to the investigation of alternative deposition techniques, such as pulsed laser deposition and gravure printing process, both proposed as low temperature treatment.[411]

Glass substrates are high temperature treated also for proper activation of TiO_2 through sintering. The traditional process for the preparation of electrodes involves the TiO_2 sintering at a temperature between 400-450° C, while the maximum operational temperature for a plastic substrate is around 150° C due to its moderate thermal resistance. Yet, low sintering temperatures do not allow the complete removal of both the binder and the solvent in the TiO_2 paste; it results in insufficient electronic connections between the TiO_2 active material nanoparticles with corresponding decrease of performance.[412]

Different processes or a combination of them were investigated to achieve high efficiencies with polymeric substrates too. To achieve a good adhesion onto the TCO/substrates and a good interconnection between the TiO_2 particles using low temperatures (lower than 200° C), alternative TiO_2 layer preparations were exploited,[151,412,413] which include the press method developed by Hagfeldt *et al.*,[413] the lift-off process investigated by Dürr *et al.*[414] and the combination of UV light exposition with a subsequent low temperature heating step by Longo and co-workers.[415] Miyasaka and co-workers explored the combination of electrophoretic deposition and chemical treatments[416] as well as the preparation of a binder-free paste for the low temperature coating process.[151] An in depth analysis of these approaches falls out of the scope of the present thesis, but we consider it worth mentioning that these processes exploit lower temperature compared to the traditional sintering, hence the energy requirement is lower even if the conditions and chemicals used in each process should be considered for environmental impact evaluation. For instance, Dürr *et al.*[414] exploited a gold layer for the lift-off process, which means that the sustainability as a whole might be impaired by the precious metal. It is clear that one of the most critical aspect to consider comparing glass and plastics is the employed temperature that hugely affects the final CED. However, manufacturing process, water influence, weight and fragility and the final application are important aspects to be considered while comparing the two substrates.

Roll-to-roll production is one of the most meaningful added values of the polymeric substrates as it allows a continuous production instead of the discontinuous one required for glass modules. Polymeric substrates are also superior in term of both light weight and flexibility: these two aspects allow to have a high efficiency to weight ratio, lower emission during transportation and reduced risks of breaking during transportation and stocking.[417,418] On the contrary, stability and permeability to water and other small molecules are issues for polymeric substrates: aqueous electrolytes as well as the exploitation of suitable encapsulants could actually avoid this drawback.

Several studies compare glass and plastics in different fields of application (*e.g.* bottles),[419–421] but a comprehensive study chiefly focused on DSSCs is still missing likely due to the lack of a thorough life-cycle knowledge. It should be pointed out that a proper glass recycling could decrease the overall impact of large-scale DSSC modules. Albeit considering pros and cons of each substrate is a valuable approach, the final application is always pivotal in the definitive choice and sustainability evaluation of a product or service. The future market for DSSCs is more addressed towards wearables, portables and indoor application due to the widespread diffusion of PSCs for outdoors and the high efficiency of DSSCs under weak and diffuse illumination.[422,423] However, envisaging the replacement of a traditional window with a DSSC module glass cannot be avoided. In this case, glass impacts are partially incorporated in those produced by window glass. Again, the best choice in terms of sustainability is a trade-off between many aspects: environmental impacts, thermal stability, efficiency, ease of manufacturing, weight, fragility and final use that should be carefully and thoughtfully evaluated.

4.5 Encapsulation

Stability and durability are still a major challenge in DSSC technologies (~6 years *vs.* 20-30 years of Si-based counterparts)[424] due to the moisture and oxidation stability of materials underneath the cells. In this context, a pivotal role in photovoltaics protection is played by encapsulants.[425] Actually, the second glass-substrate in DSSCs works as encapsulant when coupled with a proper sealant. Glass owns exceptional barrier properties toward both water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) up to 10^{-5} g m^{-2} day^{-1} and 10^{-4} cm^3 m^{-2} day^{-1} atm^{-1}, respectively; on the other hand, glass almost completely filters UV radiation.[426] Long-term stability is related both to the "reliability" and "clean" sustainability principles.[85,427] In particular, Parisi *et al.* declared that the decrease of environmental loads are particularly affected by lifetimes along with raw materials amounts and efficiency.[85] Furthermore, glass affects the overall weight of the device with subsequent higher emissions during transportation; furthermore, it leads to fragility-issues.[59]

A promising alternative to overcome the glass-related issues is the use of polymers[428] (as in the case of substrates) owning the advantages of low weight, low cost and tuneable properties; furthermore, polymers offer the opportunity to be flexible meeting the increasing demand for wearable and indoor photovoltaics. However, the advantages of polymers must comply with the properties required for encapsulants: high transparency, good barrier properties and good aging resistance. Among polymers, ethylene vinyl acetate, epoxy resins and polyurethanes are the most studied ones.[429] In **Section 6**, polyurethanes (PUs) are deeply discussed as encapsulants and the main sustainability issues related to their production are examined. Hence, a production pathway to overcome the presented concerns is presented.

5 Application of sustainability matrices for DSSCs' components

In this section, the information of some materials presented in **Section 4** are assessed as impacts in the sustainability matrices.

The matrices developed in **Section 2.3** are here tested. The (0) value is given when no information is available (and more research and investigation is necessary) or no particular concerns are to be reported. Hence, these matrices wants to be a starting point and/or a benchmarking tool to sistematically assess sustainability.

For each component, the traditional material and the one suggested as more sustainable have been screened to have a comparison.

The first assessed component is the dye, in particular N719 and YD2-o-C8.

Table 9 N719 sustainability matrix

N719 (Ru-based dye)	**RELIABLE AND SECURE**	**CLEAN**	**AFFORDABLE**
RAW MATERIALS	**(-)** Low abundance ($3.7 \cdot 10^{-5}$ ppm) **(-)** Ru is a CRM (High supply risk (7.6))	**(-)** High CED (41'100 MJ-eq Kg^{-1})[430]	**(-)** Ru is high-costly (USD $13'757 Kg^{-1})[431]
MATERIALS PRODUCTION	**(0)**	**(+)** Low impacts wrt Ru-free dyes (optimized synthesis)[80]	**(+)** Low price € 65 g^{-1} (full-organic € 410 g^{-1})[176]
DEVICE ASSEMBLING	**(0)**	**(-)** High metal depletion impact in module manufacturing	**(+)** Small quantities (0.35 mg cm^{-2})
DEVICE DISTRIBUTION	**(0)**	**(0)**	**(0)**
USE and MAINTAINANCE	**(-)** Iodine-based electrolyte's corrosiveness issues	**(0)**	**(+)** High PCE (11%)
END of LIFE	**(0)**	**(0)**	**(+)** Metal recycling opportunity

Table 10 Table 10 YD2-o-C8 sustainability matrix

Zn porphyrin dye YD2-o-C8	**RELIABLE AND SECURE**	**CLEAN**	**AFFORDABLE**
RAW MATERIALS	**(+)** Zinc is an abundant element (72 ppm) **(+)** Zinc has a low supply risk (4.8)	**(+)** Zinc low CED (52.9 MJ-eq Kg^{-1}) [430]	**(+)** Zinc is a low-cost element (USD $ 3.81 Kg^{-1})[431]
MATERIALS PRODUCTION	**(0)**	**(-)** High impacts wrt Ru-based N719 (no optimized synthesis)[80]	**(0)**
DEVICE ASSEMBLING	**(-)** Cobalt (CRM) based electrolyte	**(-)** High ozone depletion impact on the overall system	**(0)**
DEVICE DISTRIBUTION	**(0)**	**(0)**	**(0)**
USE and MAINTAINANCE	**(0)**	**(0)**	**(+)** High PCE (11%)
END of LIFE	**(0)**	**(0)**	**(+)** Metal recycling opportunity

From these two matrices it is evident that the removal of the CRM, that is the prime objective in the use of CRM-free dyes, is not achieved because of the use of Cobalt. On the other hands some data are still lacking or must be calculated as the material cost.

The second assessed component is the electrolyte. I^-/I_3^- redox couple and AY1 cobalt-based electrolyte are compared.

Table 11 Iodine-based electrolyte sustainability matrix

I^-/I_3^- electrolyte	**RELIABLE AND SECURE**	**CLEAN**	**AFFORDABLE**
RAW MATERIALS (Iodine)	**(+)** Political stability of top producer (67.5) **(-)** High Supply Risk (6.5)[432] **(-)** Difficult substitutability[433]	**(+)** Low CED (76.2 MJ-eq Kg^{-1}) (SimaPro 9.2, Ecoinvent v3.7.1)[434]	**(+)** USD $ 28 Kg^{-1}[433]
MATERIALS PRODUCTION	**(0)**	**(+)** Low overall impacts wrt the whole device[80] **(-)** High ozone depletion	**(+)** € 1.8 ml^{-1}
DEVICE ASSEMBLING	**(0)**	**(-)** Electrolyte injection has one of the highest impact of the manufacturing steps[85]	**(0)**
DEVICE DISTRIBUTION	**(-)** Leakages	**(0)**	**(0)**
USE and MAINTAINANCE	**(+)** Refilling[435] **(-)** Leakages **(-)** Short lifetime for electrolyte corrosiveness	**(+)** Refilling[435] **(-)** Leakages	**(+)** Refilling[435] **(+)** High PCE
END of LIFE	**(0)**	**(-)** Iodine can produce HI in pyrolytic recycling processes[436]	**(0)**

Table 12 Cobalt-based electrolyte

AY1[181] Cobalt-based electrolyte	**RELIABLE AND SECURE**	**CLEAN**	**AFFORDABLE**
RAW MATERIALS (Cobalt)	**(-)** Political stability of top producer (2.8) **(-)** CRM (High supply risk (7.6)) **(-)** Child labour exploitation	**(+)** Low CED (128 MJ-eq Kg^{-1})	**(-)** More expensive than Iodine (USD $ 82 Kg^{-1})[433]
MATERIALS PRODUCTION	**(0)**	**(+)** Low overall impacts wrt the whole device[80]	**(0)**
DEVICE ASSEMBLING	**(0)**	**(-)** Electrolyte injection has one of the highest impact of the manufacturing steps[85]	**(0)**
DEVICE DISTRIBUTION	**(0)**	**(0)**	**(0)**
USE and MAINTAINANCE	**(+)** Refilling[435] **(+)** High Efficiency **(+)** No corrosiveness **(-)** Leakages	**(+)** Refilling[435] **(-)** Leakages	**(+)** Refilling[435] **(+)** High efficiency
END of LIFE	**(0)**	**(0)**	**(0)**

One of the most interesting aspects is that beside iodine derives from more politically stable countries, its supply risk is high and its substitutability difficult. Hence, from the collected information the real disadvantage in the use of cobalt is the child labour exploitation. Costs should be evaluated both for the materials production and the device assembling phase; in this way, materials quantity are taken into account.

Considering the counter-electrode, Platinum and PEDOT:PSS have been chosen as reference material and sustainable alternative, respectively.
In this case, a cost-analysis have been performed to fill both the materials production and device assembling phases, taking into account quantities. These calculations have been published in the paper entitled "Poly(3,4-ethylenedioxythiophene) in Dye-Sensitized Solar Cells: Toward Solid-State and Platinum-Free Photovoltaics".[437]

Table 13 Platinum counter-electrode sustainability matrix

Platinum counter-electrode[85,437]	**RELIABLE AND SECURE**	**CLEAN**	**AFFORDABLE**
RAW MATERIALS	**(-)** CRM (High supply risk (7.6)) **(-)** Difficult substitutability	**(-)** Pt primary energy (190 000 MJ kg^{-1})	**(-)** Cost (USD $ 32′000 kg^{-1})[431]
MATERIALS PRODUCTION	**(0)**	**(+)**Low overall impacts wrt the whole device[80] [Silver shows worse impacts] **(-)** Metal depletion	**(-)** H_2PtCl_6 8 wt% in water € 72.8 g^{-1}
DEVICE ASSEMBLING	**(0)**	**(+)** Thickness 300 nm **(-)** High temperature Pt firing[85]	**(+)** Thickness 300 nm **(-)** More expensive than PEDOT:PSS Overall cost per area m€ 6.43 cm^{-2} (Only € 0.0012 more)
DEVICE DISTRIBUTION	**(0)**	**(0)**	**(0)**
USE and MAINTAINANCE	**(+)** High catalytic activity **(-)** Degradation and stability issues, especially when used with iodine-based electrolyte	**(0)**	**(+)** High catalytic activity
END of LIFE	**(0)**	**(0)**	**(+)** Opportunity to

			recover the precious metal

Table 14 PEDOT:PSS sustainability matrix437

PEDOT:PSS[438]	**RELIABLE AND SECURE**	**CLEAN**	**AFFORDABLE**
RAW MATERIALS	**(0)**	**(0)**	**(0)**
MATERIALS PRODUCTION	**(0)**	**(+)** PEDOT:PSS solution CED (159 MJ kg^{-1})	**(+)** PEDOT:PSS solution (1.3 wt% in water) € 8.96 g^{-1}
DEVICE ASSEMBLING	**(0)**	**(-)** Waste due to spin coating deposition **(-)** Thickness 300 nm	**(+)** Cheaper than Pt Overall cost per area m€ 5.23 cm^{-2} (Only € 0.0012 less)
DEVICE DISTRIBUTION	**(0)**	**(0)**	**(0)**
USE and MAINTAINANCE	**(+)** High catalytic activity **(-)** Charge transfer complexes between PEDOT and iodide	**(0)**	**(+)** High catalytic activity
END of LIFE	**(-)** Particulate PEDOT materials exhibit cytotoxic effects.[89]	**(-)** Multimaterials and composites are more complex to be recycled	**(0)**

PEDOT:PSS does not result much cheaper than Pt as expected as the amount of required material is much higher. Moreover, it might present a more challenging end-of-life than the metal as composite materials are more difficult to be recycled. The main advantage of using PEDOT:PSS is mainly related to the elimination of the precious metal (reliability) and lower CED.

The last example of matrix application is on the substrate. Glass and polymers are compared as substrates.

Table 15 Glass substrate sustainability matrix

GLASS SUBSTRATE	**RELIABLE AND SECURE**	**CLEAN**	**AFFORDABLE**
RAW MATERIALS	**(0)**	**(0)**	**(0)**
MATERIALS PRODUCTION	**(0)**	**(-)** High temperatures	**(0)**
DEVICE ASSEMBLING	**(0)**	**(-)** High environmental impacts in a life-to-gate evaluation[85]	**(-)** High cost component, 17% of total cost[121] solar glass (12.68%) represents the majority of the device mass.
DEVICE DISTRIBUTION	**(-)** Breaking issues, fragility	**(-)** Weight	**(0)**
USE and MAINTAINANCE	**(0)**	**(+)** Longer lifespan **(+)** Higher efficiency	**(+)** Longer lifespan **(+)** Higher efficiency
END of LIFE	**(0)**	**(-)** High temperatures **(+)** FTO glass[117] can be re-used	**(+)** FTO glass[117] can be re-used

Table 16 Polymeric substrates sustainability matrix

PET/PEN SUBSTRATE	**RELIABLE AND SECURE**	**CLEAN**	**AFFORDABLE**
RAW MATERIALS	**(-)** Mainly fossil based	**(0)**	**(0)**
MATERIALS PRODUCTION	**(0)**	**(+)** Low temperatures	**(+)** Low cost
DEVICE ASSEMBLING	**(0)**	**(+)** Low environmental impacts in a cradle-to-gate evaluation	**(+)** Low cost
DEVICE DISTRIBUTION	**(+)** Flexibility	**(+)** Light weight	**(0)**
USE and MAINTAINANCE	**(0)**	**(-)** Low efficiency **(-)** Low thermal stability	**(-)** Low efficiency **(-)** Low thermal stability
END of LIFE	**(0)**	**(+)** PET recycling process is a well-established one	**(0)**

The main aspect is that the substitution of glass with polymers leads to lower impacts in a cradle-to-gate LCA. However, the low efficiency obtained with polymers and the opportunity to re-use the FTO-glass could completely change the final impacts in a cradle-to-grave perspective.

6 Case-study: polyurethanes for glass replacement

The presented sustainability matrices (**Section 5**) are tools of paramount importance to drive decisions towards sustainability, highlighting positive or negative impacts. They can be used with an iterative approach and thus they are exploitable to always have an updated and complete sustainability framework.[439]

Considering the whole DSSC device, the glass substrate represents the majority of the device mass and the highest energy demanding component. Hence, it is an interesting component to focus the attention on for alternative materials investigation. **Section 4.4** illustrates the opportunity to replace glass with polymers; **Table 15** and **Table 16** show the positive and negative impacts of both materials.

In this context, polymers can be exploited in two different ways. The first approach is the substitution of the second glass-substrate that actually works as encapsulant along with a thermosetting polymer used as sealant; on the other hand, polymers can completely substitute glass, as substrate as well. This last approach does not only contribute at lowering weight and breaking concerns, but it allows the production of flexible devices.

An interesting class of polymers to study as glass substituents in DSSC are polyurethanes (PUs). In particular, PUs have been identified as promising encapsulants for their durability, corrosion and weather resistance.[440,441] Furthermore, they could be also exploited as substrates.

To ensure long-term stability and reliability, durable encapsulants are crucial to protect the active components of the DSSCs from external factors.[442] The typical reported degradation factors include intrusion of moisture and oxygen in the cell active area, electrolyte sensitivity towards UV light, electrolyte leakage and electrolyte solvent evaporation when subjected to stressful climatic and simulated environmental conditions.[442] To address such challenges, the encapsulant should provide strong mechanical support to resist external and internal strains that could damage the active components of the DSSCs (and also PSCs).

Looking at the sustainability matrices, it is clear how stability is related to the overall sustainability of the solar cell. For instance, corrosiveness issues and leakages mine reliability principle in different life-cycle phases especially in the device distribution and use and maintenance phases. Stability ensures longer lifetime and durability avoiding waste production and subsequent raw materials exploitation.[59,69,425]

In our research group,[426] thermosetting polyurethanes have been investigated as encapsulants for PSCs,[426] directly drop-casting the PU precursors to obtain the final film, in contrast with the traditional application of self-standing films sealed with specific glue which could induce degradation of the active film. The formulated polyurethane showed low or insignificant degradation after aging tests. Moreover, the encapsulated final devices exhibited worth-to-notice stability (over 2500 h) when stored in ambient condition, retaining more than 90% of their initial efficiency. The improved stability was ascribed to the good moisture and oxygen barrier properties ensured by the PU film that prevented the degradation of the perovskite film into PbI_2.

Despite good performance, PUs presents some issues during their application as encapsulants in outdoor testing. For instance, when coupled with glass, delamination at the PU/glass interface usually occurs due to the different expansion coefficients of the materials when exposed to temperature fluctuations.[443] Furthermore, problems with internal contacts are present between the copper tape and the printed silver electrodes, which have a tendency to detach.[443]

Moreover, PUs own their sustainability concerns belonging to their production. The traditional PUs synthesis involves a polycondensation between polyisocyanates and polyols (**Figure 16**).[444]

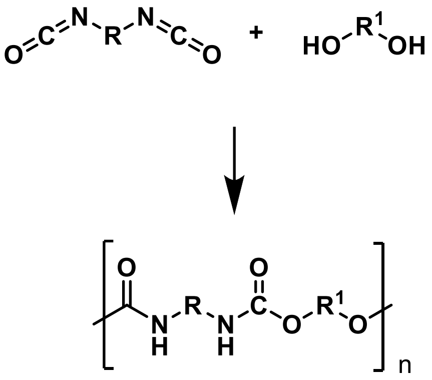


Figure 16 Traditional PUs synthetic pathway

Reagents for polyurethanes synthesis comes mainly from virgin, petroleum-based sources. Moreover, the use of di-isocyanates are traditionally obtained from phosgene, an aggressive and lethal gas, and the two most widely used di-isocyanates in PU industry, MDI (methylene diphenyl di-isocyanate) and TDI (toluene di-isocyanate), are classified as CMR (carcinogenic, mutagenic and repro toxic);[445]di-isocyanates are always considered responsible for occupational asthma.[445] Not only health-related but also environmental regulations limit or banish the use of some isocyanates.[445]

The catalyst choice is another critical aspect to consider in the PU synthetic process. The traditional catalysts used for the synthesis of polyurethanes are tertiary amines and metal complexes (**Figure 17**).

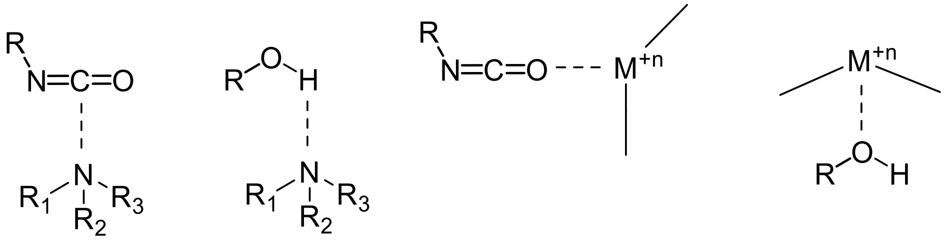


Figure 17 Example of mechanisms of catalysts action

In particular, catalysts based on tin and mercury show high reactivity and selectivity; however, toxicity-related issues are responsible of their phasing out.[446] Furthermore, in the EU, the use of mercury-containing catalysts in polyurethane production is prohibited since 1 January 2018 (Regulation (EU)

2017/852) and, globally, its adverse effect are controlled by the Minamata Convention.[447]

After the screening of the reagents for PUs production, the attention is now focused on their end-of-life. Due to their commercial success, a growing quantity of polyurethane waste is produced every year. Landfilling is still the most common way to process polyurethane waste;[448] for this reason, alternative PUs disposal needs to be implemented in a sustainability perspective. In fact, landfilling is the last option to be taken according to the waste hierarchy.[449–451] In the landfills, polyurethanes can hydrolyse leading to toxic amines. When incinerated, PUs are degraded and release isocyanates that decompose mainly in hydrogen cyanide (HCN).[452] It is clear that the implementation of recovery and recycling strategies are crucial to improve PUs sustainability.[453,454] In this context, many approaches have shown to be economically and ecologically beneficial; at the moment, mechanical recycling and glycolysis are the most important ones.[450,455]

All the relevant facts discussed above are reported in the following sustainability matrix (**Table 17**) which will be used for a comparison with the sustainability matrix (**Table 26**) presented in **Section 6.6**.

Table 17 Polyurethanes' traditional synthesis sustainability matrix

Polyurethanes	**RELIABLE AND SECURE**	**CLEAN**	**AFFORDABLE**
RAW MATERIALS	**(-)** Mainly fossil-based raw materials	**(0)**	**(0)**
MATERIALS PRODUCTION	**(-)** Toxic metal complexes as catalysts **(-)** Phosgene is a lethal gas **(-)** Diisocyanates are toxic	**(-)** Diisocyanates are environmentally harmful **(+)** Room temperature	**(+)** low cost
DEVICE ASSEMBLING	**(0)**	**(+)** It may lower CED value wrt glass	**(+)** Low cost wrt glass m^2 should be considered
DEVICE DISTRIBUTION	**(+)** Flexibility	**(+)** Low weight	**(0)**
USE and MAINTAINANCE	**(-)** shorter encapsulation time wrt glass	**(0)**	**(0)**
END of LIFE	**(-)** Leakages	**(-)** Leakages **(-)** It can require less energy wrt glass **(+)** Glycolysis is a quite mature recycling process	**(0)**

6.1 The progressive substitution approach and the Design of Experiment as efficient strategies for sustainable materials

The use of a polyurethane for glass replacement is not a straightforward process but an iterative one (**Figure 18**). In fact, one of the main purposes of a SA is to reveal the *unintended consequences.* From **Table 17**, it is clear that traditional PUs possess their own negative impacts especially in the raw material selection and in the production phase. Hence, the PU exploited for glass replacement should be designed to minimize the impacts presented in **Table 17**.

This is possible in two different ways:

1) Complete reagents substitution approach
2) Progressive reagents substitution approach

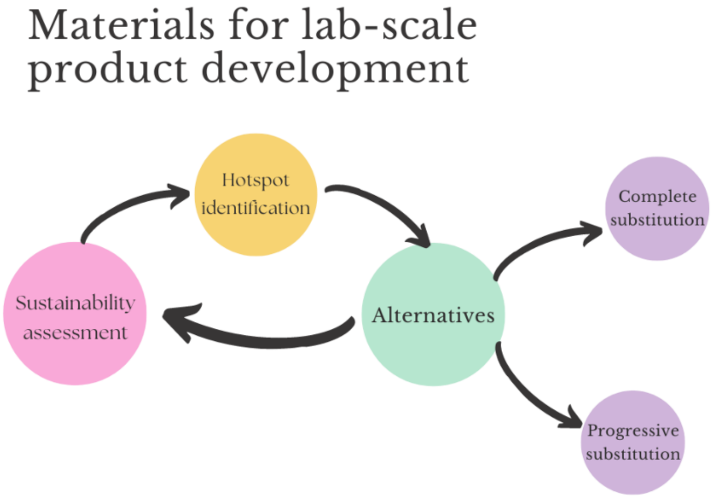


Figure 18 The iterative process for substitution for sustainability

The first approach involves the total substitution of all the traditional components at the same time; the second approach consists of the substitution step-by-step of the reagents of a traditional PU.

The first approach prioritizes the minimization of impacts; on the other hand, the progressive substitution approach can lead to a less radical substitution allowing, however, final properties monitoring. The latter approach is also easier from an industrial point of view as it is possible to achieve a new product for each substitution step.

For this case-study, the progressive substitution approach has been selected. In fact, the study involves the replacement of the reagents of a commercial PU already used for optoelectronics encapsulation for the formulation of a new PU. This approach has been selected because of the collaboration with a company (DEMAK POLYMERS srl) looking for a ready-to-market product and for the industrial nature of the PhD program.

Furthermore, to minimize the number of experiments and subsequently reduce costs and save time, the formulation optimization has been planned by the Design of Experiment (DoE). When a new formulation is investigated, there are many parameters (e.g., temperatures, time, components ratios etc.) to be considered and explored, along with their potential dependency. The opportunity to simultaneously study several experimental conditions (factors) would permit to effectively lead research towards well-defined paths supported by a solid mathematical/statistical justification. In this context, multivariate chemometrics, such as DoE, would represent a key-enabling method[456] against the traditional one-factor-at-a-time (OFAT) process. DoE shows an impressive wide range of applications from quality monitoring in food production to solar cell production.[457–459] Furthermore, this approach allows to reduce the number of the experiments without compromise the completeness of the investigation.

The substitution requires the use of materials selected according to different principles illustrated in the following Section along with some examples from the literature.

6.2 Screening and selection of alternative reagents towards circular and sustainable PUs for glass replacement

The progressive substitution starts from a screening and selection phase of alternative reagents and catalysts.

Polyols

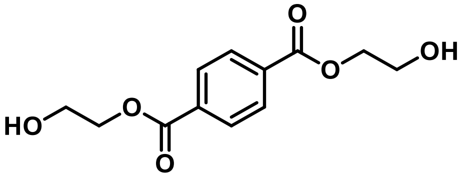
In this thesis, the first substitution step involves the replacement of the fossil-based polyol (LCR-540 RT) of the commercial PU with bio-based and waste-derived materials. The shift towards a Circular Economy and sustainable plastics is pushing both industries[460] and the academic research[452,454] to innovate the whole PUs life-cycle from the raw materials selection to the end-of-life.[453,454] A pivotal role in the pathway from linear to circular PUs - i.e., PUs from bio-based sources and/or secondary raw materials - is played by renewable sources and waste-derived materials aiming at reducing energy consumption and greenhouse gas emissions. Decoupling the industrial production from non-renewable sources allows to overcome the dependence from finite resources allowing to decrease energy consumption and greenhouse gas (GHG) emissions.[461,462] The environmental advantages of the utilization of bioresources involve the reduction of energy consumption during production and greenhouse gases emission along with the biodegradability improvement, especially when the bio-based polyester polyols are used.[462] On the other hand, attention to water consumption is fundamental as bio-based polyols can require 130 % more water than fossil-based ones. Moreover, the use of recycled materials instead of virgin raw ones meets the European Union commitment of creating a well-functioning market for secondary (from waste) raw materials.[20]

As reported by Miao *et al.*[463] and Hashimoto *et al.*[464] circular PUs can be obtained from soybean oil and alditol, respectively. On the other hand, Borrero-López *et al.*[465] and Cassales *et al.*[466] exploited castor oil and lignin. The former formulated a gel-like PU with a bio-based content up to 90% w/w in the total PU, the latter got a film with a bio-based content up to 74% w/w in the total PU (extrapolated data from original paper). Recently, Vijayan *et al.*[467] have obtained a bio-based PU for coatings from a cardanol derived diol achieving a transmittance higher than 98%.

In this thesis, two different bio-based polyols have been selected for PU production: castor oil and Sovermol®780. The former has been chosen for its widespread presence in the literature,[468] while the latter for its compatibility in the coating field.[469]

Albeit bio-based polyols have been widely studied in the synthesis of circular PUs, even waste-derived materials deserve attention. In this context, a pivotal role is played by plastic recycling products. It is clear that, in a plastic, single use-driven world, chemical recycling is one of the most valuable strategies to avoid waste accumulation.[72] In 2015, 33 million tons of polyethylene terephthalate (PET) were produced and, in the same year, 32 million tons were disposed.[470] Actually, mechanical recycling is the most implemented strategy for PET. However, recently, chemical recycling has been spreading as an approach to further valorise those PET components hard to recycle through mechanical recycling (*e.g.*, plasmix) and to obtain molecules to be exploited as new building blocks.[72] Chemical PET recycling (glycolysis) leads to the production of the bis-(2-hydroxyethyl) terephtalate (BHET) oligomer which can be directly re-used in the synthesis of rPET. As recycling should be necessarily coupled with the creation of a well-functioning secondary raw materials market,[20] it is of great importance not only to re-use BHET in a closed-loop (rPET) but also in different production routes to develop industrial symbioses. The two hydroxyl functionalities make BHET a promising candidate for the PU production industry, especially as chain extender. Actually, BHET has been already studied in PUs formulation by Li *et al.*[471] who produced PU foams showing promising flame retardant properties.[472,473] On the other hand, Maafi *et al.* synthesised a polyurethane film based on polycaprolactone and BHET as chain extender.[474]

For this thesis, BHET has been selected as potential secondary raw material to be tested in the PU production.



Bis(2-hydroxyethyl) terephthalate (BHET)
Chemical Formula: C12H14O6
Exact Mass: 254,08
Molecular Weight: 254,24
Melting point: 106°C

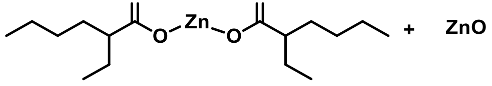
Figure 19 BHET structure.

Catalyst

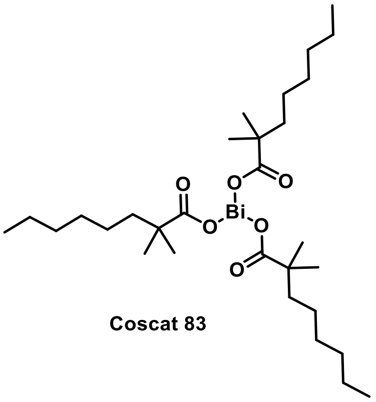
The Hg removal represents the second substitution step of this work.

As said before, mercury and tin organo-compounds have been widely used as catalysts in the fields of polyurethane synthesis and crosslinking due to their efficiency and selectivity towards the reaction between isocyanate and hydroxy moieties. Albeit mercury and tin-based systems remain two of the most exploited strategies, because of health and environmental concerns, they have slowly been replaced by other catalysts to provide more sustainable alternatives. Researchers and companies have made efforts in order to find alternative catalysts, either based on metals such as iron, copper, zinc, bismuth, titanium and cobalt, or strong organic bases such as 1,4-diazabicyclo[2.2.2]octane (DABCO), 2,2′-dimorpholinodiethylether (DMDEE), various guanidines and also organic acids.[475]

The toxicity of many of these compounds led to an increasing attention towards bismuth and zinc catalysts and a mixture of both;[476–478] in fact, mixtures of bismuth and zinc carboxylates represents a successful replacements of mercury or tin-containing catalysts.[477] Several cases have been reported in the literature. The 1965 Perry & Wild patent describes zinc carboxylates as compounds with low catalytic activity compared to other catalysts used for isocyanate and polyol catalysis. However, the inventors advocate the use of zinc compounds in a mixture with other catalysts. In fact, co-catalysis leads to reduced reaction times. There appears to be a synergy, as the mixture of catalysts is more active than the catalysts taken individually.[479] There is evidence that combinations of bismuth and zinc carboxylates can accelerate the drying time of polyurethane coating formulations even if the mechanisms are still under investigation.[476,480] Hence, Zinc 2-ethylhexanoate (**Figure 20**), marketed as Coscat Z-22 and Coscat 83 (**Figure 20**), a catalyst based on bismuth neodecanoate have been selected to co-catalyse the PU formation for their good performance in coatings applications (Technical Data Sheet, TDS).



Coscat Z-22



Coscat 83

Figure 20 Coscat Z-22 and Coscat 83 structures

Isocyanate

The third substitution step involves the replacement of the 100% fossil-based DK180HV with a bio-based polyisocyanate. Actually, the most critical and urgent concerns regarding isocyanates are their own inherent toxicity and their synthesis via phosgene. Even if at commercial-scale the amine phosgenation is the main isocyanate production pathway, it is worth mentioning two further mechanisms at lab-scale: the Curtius and Hoffman rearrangements. The former involves the rearrangement of acyl azide, while the latter of an amide group.[481]

A step forwarded by researchers to overcome the isocyanate related issues involves their total elimination leading to the synthesis of the so called NIPUs (Non-Isocyanates PUs). There are different synthetic protocols leading to NIPUs,[452] however, only the polyaddition between bicyclic carbonates and diamines, allows to prevent the utilization of toxic substances (phosgene, aziridines, azides, carboxamides, etc.) and the production of by-products. Moreover, the final products, NIPUs present pendant hydroxyl groups, that is the reason why this group of polyurethanes is also known as polyhydroxyurethanes (PHU).[481] Initially, due to the similarities in the chemical structure, NIPUs were thought to be used to directly replace conventional PUs. Actually, this replacement resulted to be more challenging to be achieved in practice. As a result, and in spite of the vast amount of academic research into this topic, the market size of NIPUs remains negligible.[482]

The first and most important aspect involves the curing conditions which require thermal treatments. In contrast, room or low temperature curing can be used for most conventional PUs. Recent studies have shown that combining PHU chemistry with complementary reactive groups can facilitate the curing improve the final properties. Nevertheless, even if some curing can now be done at room temperature, reaction times are still too long, which does not facilitate the implementation of the technology in the most relevant applications. When thermal curing can be tolerated, some of the previous systems are of great promise. Future research directions to overcome the slow curing process consists of the utilization of cyclic carbonates that can be more easily aminolyzed at room temperature or activated five-membered ones. Despite their greater reactivity, their production has to be optimized to furnish formulations that are cost-effective and price competitive with respect to conventional PUs. Indeed, cost is the second major limitation for the NIPUs utilization at the industrial scale. This is primarily the result of the limited availability of polycyclic carbonates. While many polyamines are commercially available at large scale and low cost, polycyclic carbonates are not available in large volume.

For these reasons, the complete elimination of isocyanates in favor of non-isocyanate route has not been the selected strategy due to some obstacles in the translation of the academic work on NIPUs to industrial products.

Nevertheless, the market offers bio-based isocyanates. Desmodur® eco N 7300 by Covestro® and Tolonate™ X FLO 100 by Vencorex® are among the main commercially available bio-based isocyanates (**Figure 21**).[468] Hence, these isocyanates do not overcome the phosgene issue but only (and partially) the source related one.

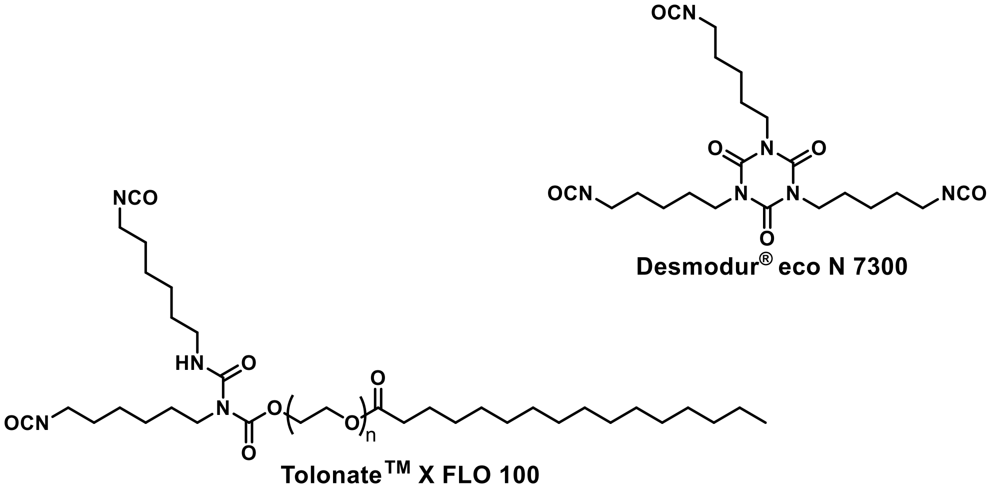


Figure 21 Chemical structures of the commercial partially bio-based isocyanates Desmodur and Tolonate.

Desmodur® eco N 7300 is a polyisocyanurate synthesized by the amination of glucose with ammonia, followed by reaction with phosgene to obtain pentamethylene-diisocianate (PDI). Subsequently, PDI is oligomerized with a catalyst such as tri-*n*-butylphosphine to yield PDI trimers, pentamers, heptamers, and higher molecular weight oligomers.[483]

The chemical structure of polyisocyanurates (PIR) improves the mechanical and insulation properties of the materials and makes them less flammable compared to PUs, without the use of halogens, making them attractive for many applications. Desmodur® eco N 7300 own bio-based carbons except those that come from phosgene (68% bio-based carbons according to TDS results).[484] Tolonate™ X FLO 100, on the other hand, contains only 25% of renewable material (TDS).

These two commercially available bio-based isocyanates have been compared (**Table 18**) to identify the best candidate for the new formulation.[468]

Table 18 Comparison between the two commercial bio-based polyisocyanates and DK180HV.

Characteristics	Tolonate™ X FLO 100	Desmodur® eco N 7300	DK180HV
Bio-based content [%]	25	68	0
NCO content	12.3	21.5	27
Viscosity [mPa·s]	140	9’500	690
Functionality	≈2	≈3.7	≈ 3

Desmodur® eco N 7300 have a much higher content compared to Tolonate™ X FLO 100; moreover, its NCO content and its functionality are closer to the DK180HV’s values. Hence, the hardener supplied by Covestro has been selected as the suitable one. Moreover a functionality higher than 2 allows to have thermosetting PU instead of thermoplastic ones.

6.3 Materials and Methods

6.3.1 Materials

LCR540RT was supplied by Demak Polymers. It is a 100% fossil-based polyol, trifunctionalized and it is mixed with UV absorbers for UV stabilization.[426,485] Castor oil was supplied by Thermo Fisher Scientific. Sovermol®780 was supplied by BASF®. This polyol is 65% bio-based and its functionality is equal to f=3. BHET was provided by Sigma Aldrich. DK180HV was supplied by Demak polymers. It is a polyisocyanate, prepolymerized, with high viscosity. The mercury-based catalyst was supplied by Demak Polymers s.r.l. Desmodur® eco N 7300 was supplied by Covestro®. It is a 68% bio-based polyisocyanurate with f=3. The Coscat Z-22 and Coscat C-83 have been supplied by Vertellus.

6.3.2 Formulation process

PU film preparation involves 4 steps: (i) polyols mixture preparation; (ii) degassing step; (iii) polyisocyanate addition; (iv) PU film deposition.

6 grams of polyols mixture (i) is prepared mixing Sovermol®780, LCR540RT, BHET and catalyst. BHET is to be considered as a potential waste-derived material. Hence, it is included in the calculation for circular inputs.

Working conditions are reported in the 3 DoE worksheets (**Table 20, Table 21** and **Table 22**). Polyols and catalysts are added in different ratios as indicated in DoE worksheets. The catalyst amount was evaluated keeping "% of catalyst by weight / active OH groups" ratio constant. The polyols mixture is heated and stirred by a plate, at a temperature and for a time as reported in **Table 20**. Then, it is degassed (ii) under vacuum for 10 minutes. After degassing, the polyisocyanate is added (iii) in a stoichiometric ratio (hydroxyl:isocyanate groups=1:1) to obtain 5 grams of the final PU formulation which is stirred in the conditions reported in DoE worksheets. Finally, the PU formulation is deposited (iv) on a polypropylene substrate and left to polymerize at room temperature for a week. Two replicates are made for each experimental condition.

6.3.3 Methods

The UV-Visible (UV-Vis) spectrophotometry was performed using Agilent Cary 300 Bio spectrophotometer. The wavelengths range was from 800 nm to 200 nm, with a scanning speed of 5 nm s^{-1}.

Thermogravimetric analysis (TGA) was performed using TA Instrument Q600. The samples (≈ 6mg) were placed in an alumina pan and heated from 25° C to 600° C (5° C/min) under a nitrogen atmosphere (100 ml/min).

Differential Scanning Calorimetry (DSC) was performed using TA Instruments Q200 with the RCS90 cooling system. The samples were placed in an aluminum pan and subjected to 3 cycles under a nitrogen atmosphere: 2 heating cycles from -80° C to 180 ° C (20° C/min), and a cooling cycle from 180 ° C to -80° C (10° C/min).

ATR-IR characterizations were performed using a spectrophotometer (Invenio, Bruker, Germany) equipped with a InGaAs detector and OPUS sofware.

Accelerated weathering tests (QUV-A TEST) were kindly performed by DEMAK polymers s.r.l. using an ultraviolet light accelerated weathering test cabinet. The samples were cyclically exposed to UV-light (340 nm) for 8 h at 70° C and kept in dark for 4h at 50° C with 100% air humidity, for 20 days.

The thermal aging test was performed heating the samples in an oven at 80° C for 50 days.

Swelling was studied monitoring the weight variation during time of the samples in different solvents. Each sample was placed in a vial with a solvent at 20° C. The measurements were carried out periodically for 5 hours. The swelling ratio percentage (%S) was calculated using eq.1:[466]

$$\%S = \frac{W - W_0}{W_0} \cdot 100$$

where W_0 is the weight at t=0 and W is the weights at different swelling time.

Gel time was measured as the time period from the deposition of the PU mixture until the time at which a rod immersed in the mixture is able to completely lift the sample.

6.4 DoE planning: identification of factors and responses

The progressive substitution has been planned by DoE to minimize the number of experiments saving time and reducing waste. The selection of the parameters for DoE setting requires clear objectives and screening analyses.

Clear objectives define the responses to monitor the final material properties. The objective of this study is to maximize the circular components into the PU formulation and remove the Hg-based catalyst. Simultaneously the maintenance or even the improvement of the commercial PU properties is monitored: the desired target is a transparent film, with good UV and thermal stability.[426,485] Hence, the obtained films were characterized by UV-Vis spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry analysis (DSC). Moreover, aging and swelling tests were performed to study long-term stability and crosslinking, respectively.

The screening analyses are crucial to identify the factors and the ranges within setting the DoE. For instance, BHET addition in a formulation is far to be straightforward due to its physical state. This chain extender (f=2) is a white solid powder, and its complete dissolution is crucial for its incorporation in the PU formulations. Hence, its dissolution has been tested through two different pathways.

The first approach involved the BHET dissolution in a solvent (*e.g.*, acetonitrile and THF) at room temperature and its subsequent incorporation in the polyol. Hence, the solvent was removed under vacuum evaporation. Although the good dissolution exhibited in some of the tested solvents, BHET re-precipitated after the vacuum evaporation step. For this reason, this approach was not furtherly investigated.

The second approach involved the direct dissolution of the BHET in the polyol. Dissolution tests were performed both in castor oil and in Sovermol®780 with 10%, 15% and 20% of BHET stirring at different temperatures (from r.t. to 85° C) up to 90 minutes. Both polyols could not dissolve BHET at r.t. Evaluating higher temperatures, Sovermol®780 resulted in a total BHET dissolution from 65° C, while castor oil was unable to completely dissolve BHET in any of the tested conditions. The total dissolution of 20% BHET was achieved only by Sovermol®780 at 85° C. However, the mixture was difficult to handle as the BHET immediately precipitated once the system cooled down. Hence, BHET concentration values higher than 20% were not examined. In general, Sovermol®780 showed better dissolution ability compared to castor oil and it was selected for further investigations.

Another interesting consideration on dissolution derives from the influence of LCR540RT. At 50° C, Sovermol®780 was not able to dissolve 10% BHET, but the combination with LCR540RT lead to better dissolution probably for its lower viscosity leading to a better stirring. For this reason, a small percentage of LCR540RT was kept within the polyols mixture.

After BHET dissolution tests, different PUs formulations have been tested for preliminary evaluations. It was observed that the replacement of LCR540RT with Sovermol®780 lowered the flexibility of the final PU narrowing the application versatility. Hence, the complete substitution of LCR540RT was avoided. Flexibility can be further modulated by the selection of a specific di-isocyanate precursor;[444] however, this falls outside the aim of this work.

Furthermore, the final PUs transparency resulted to be greatly affected by the mixing time and temperature of DK180 with the polyols mixture; low transparency was achieved when mixing is conducted at room temperature, whereas high temperatures lead to more transparent PUs as it allows to keep BHET completely dissolved.

From these screening analyses, it is clear that many parameters could affect the whole formulation process sizeably impacting on the final PU properties.

Hence, for the first substitution (polyol) 7 parameters have been selected as factors to plan formulation experiments by DoE. In particular, the DoE involved 3 formulative and 4 process factors and fixed ranges (**Table 19**).

Table 19 DoE formulative and process factors.

Factors	Abbreviation	Ranges	Units
BHET concentration	BHE	0.08- 0.2	*
Sovermol®780 concentration	sov	0.4-0.72	*
LCR540RT concentration	lcr	0.2-0.46	*
Polyols stirring time	tiPol	30-90	min
Polyols stirring temperature	TePol	50-70	° C
Polyurethanes mixing time	tiPU	2-6	min
Polyurethanes mixing temperature	TePU	40-70	° C

*Ratios are referred to the polyols mixture.

To understand the influence of the presented factors on the final PU properties, 4 process outputs, namely, (i) BHET dissolution, (ii) transmittance (%T_{555nm}), (iii) degradation temperature ($T_{5\%}$) and (iv) glass transition temperature (T_g) have been set as DoE responses.

BHET dissolution (i) was evaluated using a progressive and qualitative scale: 0 = no dissolution, 1 = partial dissolution, 2 = almost complete dissolution, 3 = complete dissolution. For the aforementioned reasons, the study has been conducted to find the best conditions for a complete dissolution.

Transmittance (ii) is fundamental for PU applied in the optoelectronic field. Values at 555 nm have been considered and compared to the standard's one aiming at achieving equal or higher transparency.

Degradation (iii) and glass transition (iv) temperatures are fundamental to evaluate the PU thermal stability.

Finally, after the factors and responses selection, *Screening* analysis method and *Linear D-optimal* model have been identified as suitable for DoE setting (MODDE® Pro software, v. 12.1). D-optimal models are particularly useful to constrain the experimental space achieving excellent results with the minimum number of experiments (runs).[486–488]

Table 20 shows the 18 experiments resulted from the first DoE along with the corresponding measured responses.

Table 20 DoE plan for fossil-based polyols substitution

Run	tiPol [min]	TePol [° C]	tiPU [min]	TePU [° C]	BHE	sov	lcr	BHET dissol	%T_{555nm}	$T_{5\%}$	T_g
1	90	50	2	40	0.20	0.40	0.40	1	75.2	277	48.5
2	60	60	4	55	0.14	0.52	0.34	2	83.5	273	49.2
3	90	70	6	40	0.20	0.60	0.20	2	19.5	283	51.8
4	90	70	2	40	0.08	0.46	0.46	3	81.4	285	45.5
5	30	50	6	70	0.08	0.72	0.20	2	84.4	276	55.3
6	30	50	2	40	0.20	0.60	0.20	1	57.7	274	54.0
7	90	70	6	70	0.08	0.46	0.46	3	82.9	280	46.8
8	90	70	2	70	0.20	0.60	0.20	2	84.4	281	54.9
9	60	60	4	55	0.14	0.52	0.34	2	80.7	270	49.0
10	90	50	2	40	0.08	0.72	0.20	2	87.5	267	53.3
11	30	70	2	40	0.20	0.40	0.40	2	2.3	276	49.5
12	30	70	6	40	0.08	0.72	0.20	3	85.8	267	52.0
13	30	70	2	70	0.08	0.72	0.20	3	91.2	270	55.0
14	30	70	6	70	0.20	0.40	0.40	2	79.2	277	49.8
15	90	50	6	70	0.20	0.60	0.20	1	67.8	270	52.6
16	30	50	6	40	0.08	0.46	0.46	2	85.0	271	45.1
17	30	50	2	70	0.08	0.46	0.46	2	90.1	276	41.8
18	60	60	4	55	0.14	0.52	0.34	2	84.2	274	48.7
Std	**/**	**/**	**1**	**20**	**0**	**0**	**1.00**	**/**	**88.0**	**270**	**35**

Data were collected 7 days after the deposition (except for BHET dissolution, obtained during the process).

The catalysts substitution requires the investigation of the influence of the two catalysts in the PU formulation. It has been explored through preliminary tests considering two different parameters:

(i) The ratio by weight between Coscat® 83 and Coscat® Z-22R called from now on $r_{Bi/Zn}$.

(ii) The catalyst amount into the polyol mixture, expressed as % by weight.

The influence on polymerization rate has been preliminarily monitored by gel time measurements. Hypothesizing a lower catalytic activity for the new catalysts,[453] a concentration higher than the Hg-based catalyst (0.43% w/w for the commercial PU) was tested. Hence, a first preliminary test was run with 1.5 % Coscat® 83, without the addition of the Zn-based co-catalyst. This formulation led to a PU with a sticky surface. Hence, the co-catalyst has been added and $r_{Bi/Zn}$=0.3 was tested; these conditions yielded to a too viscous PU mixture, hard to handle. On the other hand, keeping $r_{Bi/Zn}$=0.3 and lowering the catalyst concentration to 0.1% lead to a 3 hours gel time. Moreover, it was observed that higher $r_{Bi/Zn}$ led to PUs with higher bubbles amount. Bubbles are incorporated during PU mixing procedure and a quick polymerization threats their natural leak. To overcome this issue, the polyurethanes have been placed in a vacuum chamber to facilitate the bubbles removal. However, this technique was not successful for this intent. Another solution to the bubbles formation might be represented by an under vacuum continuous process which could not be possible to set up in the laboratory. It is worth highlighting that gel time monitor a phase transition and give an indication of the polymerization rate velocity, but it does not give any specific information about the curing state; on the other hand, curing can be monitored by IR spectroscopy.[465] It is important to notice that ATR-IR spectroscopy allows only a superficial analysis, measuring the superficial curing.

The polymerization of polyurethanes has been evaluated using the ATR-IR technique. There are different methods to monitor the polymerization process of polyurethanes. The urethane bonds generation can be observed through the formation of an absorption band at 3330 cm^{-1} (-NH stretching vibration) overlapped to the wide absorption band centred at 3400 cm^{-1} (-OH stretching vibration).[465,466] The occurrence of urethane groups can be also monitored by the band of stretching vibration of carbonyl groups in the range of 1745 to 1600 cm^{-1}.[465]

From the screening analyses on catalysts, the second DoE has been set to obtain a new set of Hg-free formulations. Both the catalysts concentration and ratio have been considered as factors; the ranges have been selected to allow an easy handling of the polymer mixture and a good control of bubbles formation. In this perspective, the concentration was set between 0.1% and 0.8%, while $r_{Bi/Zn}$ was set between 0.1 and 0.5. Bubbles, gel time and curing rate were selected as responses to investigate the influence of catalysts. Bubbles amount has been monitored by a qualitative scale: 0 = no bubbles,1 = minimum quantity of bubbles, 2 = moderate amount of bubbles, 3 = high amount of bubbles, 4 = very high amount of bubbles (almost 100% of the entire surface covered with bubbles).

The curing rate has been monitored by means of ATR-IR measurements through the disappearing of the band at 2270 cm^{-1}. In particular, the curing rate was expressed by the ratio between the intensity of the polyurethane free isocyanates absorption peaks and the peak of pure isocyanate (DK180HV or DESMODUR ECO N7300) after normalization. The normalization (Figure xx) can be carried out with the methylene absorption bands[465] at wavenumber values equal to 2850 cm^{-1} and 2950 cm^{-1} as they remain unaltered during the whole curing process.[489] In our case, only the band at 2950 cm^{-1} was selected to both allow a better normalization with DK180HV (having a more pronounced signal at 2950 cm^{-1}) and to avoid interference of the polyols' signals (**Figure 22**).

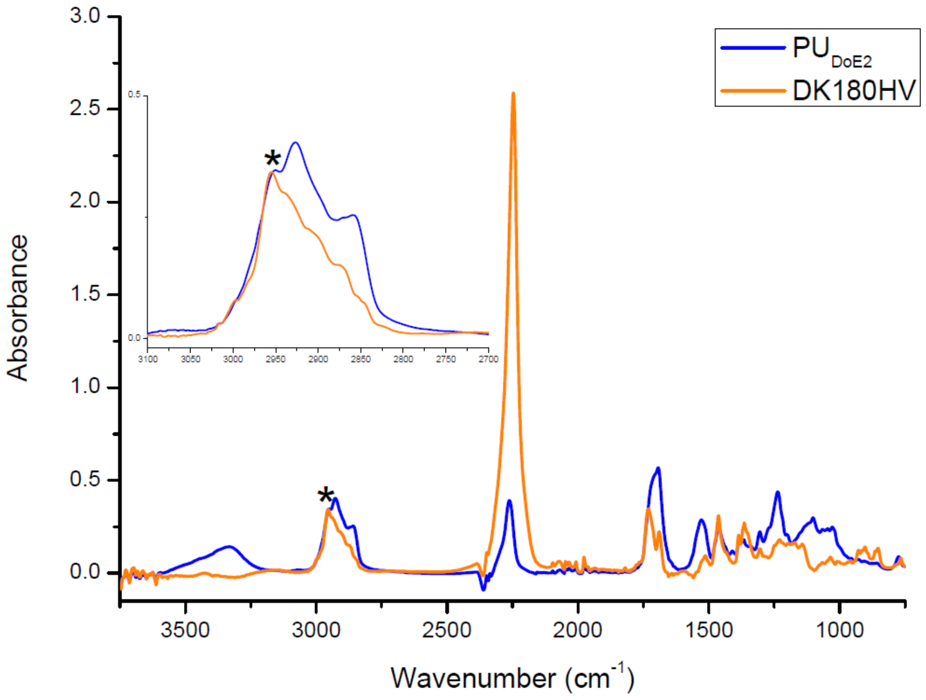


Figure 22 Example of ATR-IR spectrum of a polyurethane film from DoE2 (blue line) and pure isocyanate (DK180HV, orange line) normalized at 2950 cm^{-1} (*).

The ATR-IR measurements were performed after 1 day and after 10 days from the PU deposition.

To ensure the maintenance of the final properties required for encapsulation, transparency (%T_{555nm}) and glass transition temperature (T_g) were kept as responses (as in the first DoE). On the other hand, $T_{5\%}$ was not considered for the high uncertainty observed in the first model.

After the selection of factors and responses, the second DoE was set. A Response Surface Modeling[490] (RSM) design was chosen with a quadratic polynomial model to investigate in more detail how the factors influence the response. In particular, a Central Face Centered RSM was set **Table 21** shows the 11 experiments resulted from DoE along with the corresponding measured responses.

Table 21 Second DoE plan for Hg- free catalytic system optimization

Run	$r_{Bi/Zn}$	% cat	Gel time [min.]	IR_{1gg}	IR_{10gg}	Bubbles	$\%T_{555nm}$	T_g [° C]
1	0.3	0.10	180	0.150	0.045	1	89.6	56.2
2	0.5	0.80	3	0.136	0.031	4	23.2	62.7
3	0.3	0.45	37	0.152	0.037	2	86.5	63.1
4	0.1	0.45	59	0.168	0.042	1	88.9	61.2
5	0.5	0.10	135	0.184	0.042	1	89.4	63.0
6	0.3	0.45	40	0.156	0.021	2	88.2	63.3
7	0.3	0.80	7	0.122	0.025	3	77.4	58.4
8	0.1	0.80	15	0.138	0.032	2	86.1	57.4
9	0.5	0.45	7	0.138	0.028	2	86.0	64.0
10	0.3	0.45	38	0.145	0.001	2	88.8	57.2
11	0.1	0.10	265	0.173	0.002	1	90.3	51.6

The last DoE on polyisocyanate substitution, actually, is an investigation on the effect of the catalytic Bi-Zn system on the new PU formulation with Desmodur® eco N 7300. Hence, the DoE plan was set as the previous. **Table 22** shows the 11 experiments resulted from DoE along with the corresponding measured responses.

Table 22 Third DoE plan for Hg-free catalytic system optimization in polyisocyanate substitution

Run	$r_{Bi/Zn}$	% cat	Gel time [min.]	$\%T_{555nm}$	IR_{1gg}	IR_{10gg}	Bubbles	Tg [° C]
1	0.3	0.80	3	53.8	≈ 0	≈ 0	4	45.5
2	0.5	0.10	61	89.0	≈ 0	≈ 0	1	35.0
3	0.1	0.80	10	64.7	≈ 0	≈ 0	3	39.8
4	0.1	0.10	87	88.0	≈ 0	≈ 0	1	36.6
5	0.3	0.45	7	55.6	≈ 0	≈ 0	3	41.8
6	0.5	0.45	5	37.1	≈ 0	≈ 0	3	39.7
7	0.3	0.45	6	59.1	≈ 0	≈ 0	3	39.8
8	0.5	0.80	2	16.9	≈ 0	≈ 0	4	46.5
9	0.3	0.45	6	56.0	≈ 0	≈ 0	3	39.6
10	0.3	0.10	70	89.7	≈ 0	≈ 0	1	35.7
11	0.1	0.45	25	74.1	≈ 0	≈ 0	2	39.6

6.4.1 Polyol substitution DoE analysis

After DoE planning and selected data collection, the influence of the experimental conditions on the responses (presented above in **Table 20, Table 21** and **Table 22**) needs to be evaluated.

In the presented progressive substitution, the first evaluation regards the polyol substitution.

In this perspective, **Figure 23** shows the coefficient plot, a graphical representation of how the factors affect the responses. The green bars describe the influence of each factor on each response, while the black segments are the confidence intervals. For the purpose of the present work, this investigation was crucial not only to highlight the effect of experimental conditions on the final PU properties but, in particular, to focus the attention on the effect of raw materials substitution.

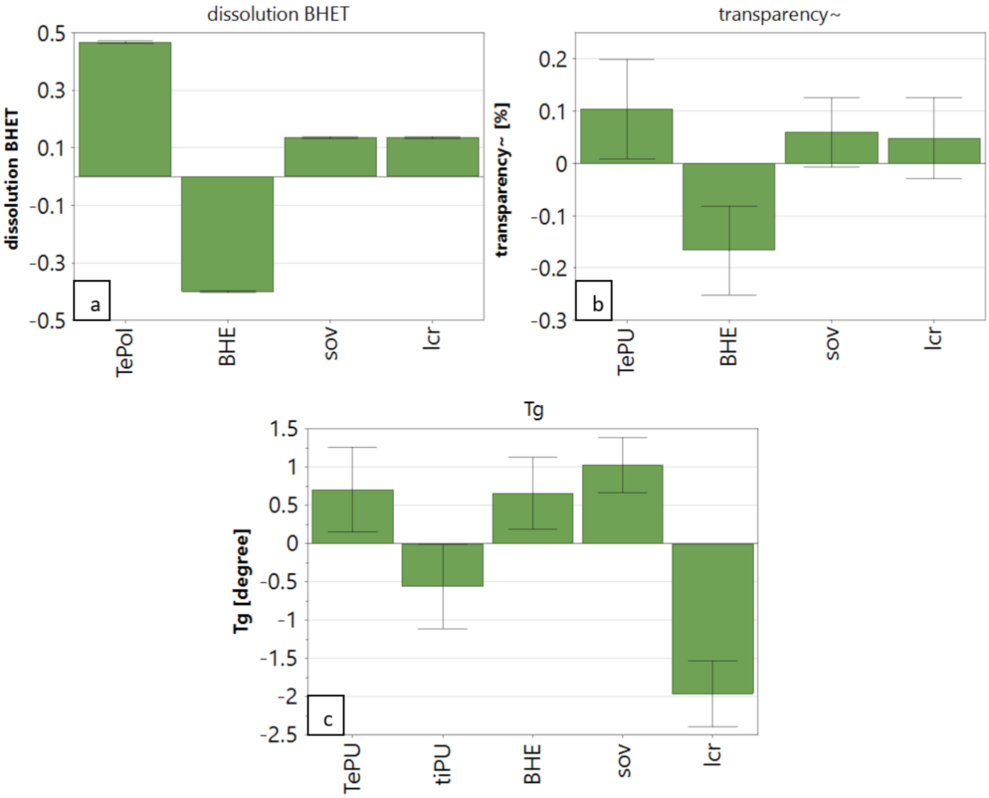


Figure 23 Evaluation of the most influential formulation and process factors. a)BHET dissolution coefficient plot, b)transparency coefficient plot, c)T_g coefficient plot, d)$T_{5\%}$ coefficient plot. Non-relevant factors are omitted for clarity.

The best BHET dissolution in the polyols' mixture was obtained for high TePol, as expected. None of the 18 experiments showed no BHET dissolution (0). No other process factors appear to significantly influence the dissolution of BHET (**Figure 23-a**). As shown in **Figure 23-a**, Sovermol®780 and LCR540-RT seem to affect the BHET solubility in the same way. Hence, the trend observed in preliminary screening tests, where LCR540RT seemed to have a better solubility ability, was not confirmed. It is worth highlighting the importance of the multivariate analysis for this evaluation.

The highest transmittance values were obtained for low BHET amounts and high PU mixing temperatures both ensuring a complete BHET dissolution (**Figure 23-b**). As expected, the most significant losses in $\%T_{555nm}$ were found for the samples in which BHET was not completely dissolved due to unavoidable scattering phenomena. An increase of %T_{555nm} values was obtained also with higher Sovermol®780 ratio (**Figure 23-b**); however, its influence is clearly lower than the BHET concentration factor. The other three process factors (tiPol; TePol and tiPU) do not substantially affect the transmittance values.

The T_g values range between 41.8° C and 55.3° C. The lowest T_g values were obtained with high LCR540RT concentrations and low quantities of Sovermol®780, confirming the flexibility trend highlighted in the preliminary screening experiments. Moreover, lower PU mixing temperature and longer PU mixing time lead to lower T_g values as shown in **Figure 23-c**. On the other hand, higher BHET concentration results in higher T_g.

The influence of the 7 factors on $T_{5\%}$ response was difficult to determine given the high uncertainty associated with the confidence intervals. However, obtained $T_{5\%}$ values do not show large variations compared to the commercial standard ($T_{5\%}$=270.3° C). The values range from 267° C to 285° C ensuring a good thermal stability; in fact, too low $T_{5\%}$ could compromise the final applicability. In general, the increase in BHET concentration leads to higher $T_{5\%}$ than the standard's one.

The LCR540RT substitution with Sovermol®780 and BHET lead to promising results. Specific formulative ratios and experimental conditions yield to PUs owning equal or even better properties compared to the commercial PU. Hence, it was worth to investigate the determination of the best formulative conditions to achieve the optimized PU with the required final characteristics. Selecting desired responses ranges, the software generates a *Sweet Spot Plot* (**Figure 24**), whose analysis leads to the optimized conditions identification.

6.4.2 Optimal formulation PU_{opt1} determination

The obtained results demonstrate the opportunity to formulate a circular PU with the required properties; hence, it is necessary to identify the optimal operating and formulation conditions. The optimization was performed through the Sweet Spot Plot (**Figure 24**) analysis; the graph was generated selecting specific process factors and desired responses.

The process factors choice has been made taking into account time requirements, circular content and energy consumption. The shortest times (tiPol=30 min. and tiPU=2min.) have been selected to obtain a rapid process. The highest temperatures (TePol= 70° C and TePU=70° C) allowed to increase as much as possible the BHET concentration. Moreover, shortest times and highest temperatures allowed to reduce energy consumption. This reduction was confirmed by wattmeter measurements. The stirring and heating of 6 g of polyol at 50° C for 90 minutes required 0.14kW/h (32.3 g CO_2-eq, EU-27 Greenhouse gas emission (GHG) intensity 2020), while stirring at 70° C for 30 minutes required 0.09kW/h (20.8 g CO_2-eq, EU-27 GHG intensity 2020).[491] In both cases the stirring was kept constant.

Regarding the desired responses, BHET dissolution ≥ 2.7 and $\%T_{555nm} \geq 88\%$ have been set to constrain the Sweet Spot Plot. On the other hand, T_g and $T_{5\%}$ were not limited. In fact, all the obtained T_g were acceptable for the final application in optoelectronics, while $T_{5\%}$ did not show any particular dependency from the selected factors.

The generated Sweet Spot Plot presents 2 different areas which define formulative combinations to achieve the required BHET dissolution and transparency criteria. The blue area (**Figure 24-b**) define the formulative conditions to achieve a complete BHET dissolution but not the desired transparency. The green area (**Figure 24-a**) represents the *sweet spot* where both the BHET dissolution and the transparency criteria are met at the same time. To verify the model reliability a validation procedure was followed. Two PUs was formulated under two different conditions extrapolated from the Sweet Spot Plot. The obtained responses fall within the confidence intervals provided by the software, validating the model.

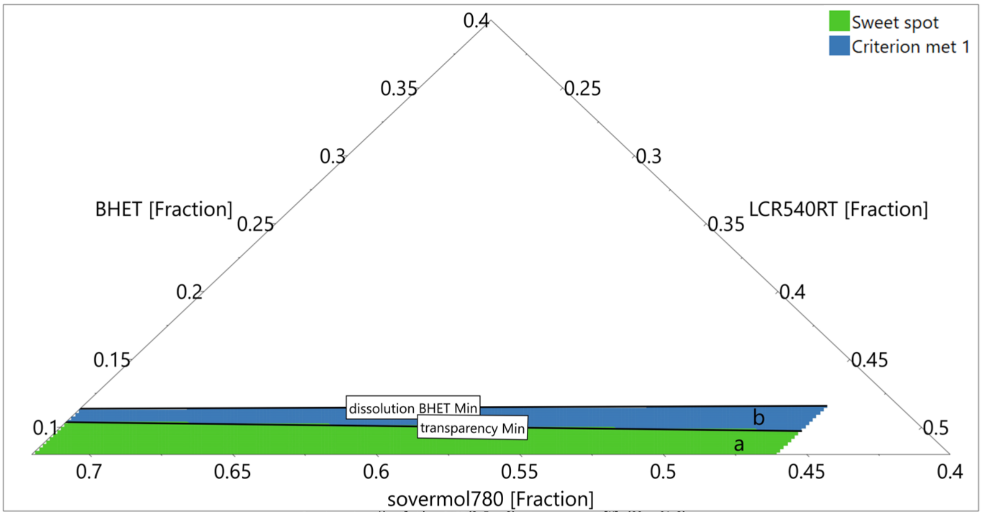


Figure 24 DoE 1 sweet spot plot. Green area (a): sweet spot. Blue area (b): only BHET dissolution criterion is met.

All the possible formulations in the sweet spot allow to achieve the desired properties. In our case, the formulation with the highest circular content was selected as the optimized one. It consists of a polyols blend formulated with 10% BHET, 70% Sovermol® 780 and 20% LCR540RT. A quantity of Hg-based catalyst equal to 0.215% by weight in the polyols mixture was used. The PU obtained with the optimized formulation in the aforementioned conditions will be referred as PU$_{opt1}$.

The total percentage of bio-based (considering 65% of bio-based components for Sovermol® 780) and recycled components within the polyol blend was 55.5% which translates into a percentage of 24.2% within the final polyurethane film. In particular, in the final PU$_{opt1}$, 4.4% is represented by BHET and 19.8% by the bio-based component of Sovermol® 780. PU$_{opt1}$ has been compared to the commercial standard. The measured %T$_{555nm}$ and T$_{5\%}$ were 87.6% and 270.0° C, respectively. Both the transparency and the degradation temperature match the standard's values (88.0% and 270.3° C). However, the transmittance profiles are not completely identical: Figure 26-a shows a drop at 370 nm for the PU$_{opt1}$ and at 340 for the standard PU. This difference is probably due to the presence of a greater amount of UV absorbers in the latter one.

Different profiles are also obtained by TGA analysis. At ≈ 330° C, the thermograms' slopes change (**Figure 26-b**). To understand which component affects the TGA profile, the $T_{5\%}$ of different PUs were measured: same BHET amounts lead to the same TGA profiles excluding the Sovermol®780 influence.

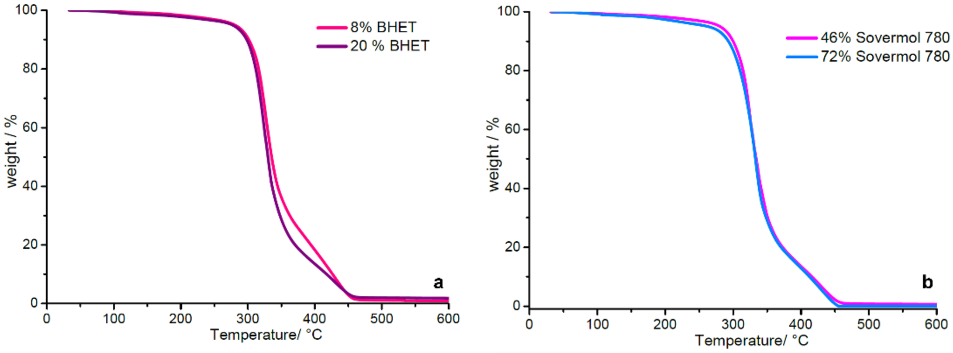


Figure 25 Effect of BHET and Sovermol®780 on the thermal stability of PU.

a) The increase in the amount of BHET determines an increase in the thermal stability of the final PU.

b) The differences in the amount of Sovermol®780 do not seem to determine any variation of the thermal stability of the final PU.

On the contrary, different BHET amounts lead to different TGA profiles. Hence, the change in slope is probably due to the BHET presence. Also the literature corroborates this hypothesis: for instance, T. Kousuke *et al.* reported on a slower weight loss in polypeptide thermal decomposition due to the addition of aromatic units.[492] Other examples in literature report on the better thermal stability of polymers with aromatic structures.[493,494]

The obtained T_g value (54.9° C) turns out to be the only one not in line with the standard (35° C) but suitable for the application in optoelectronics. Established that the PU should be as stable as possible during its application, T_g should not fall within the operating temperature. Hence, higher T_g guarantees thermal stability for a wider range of working conditions.

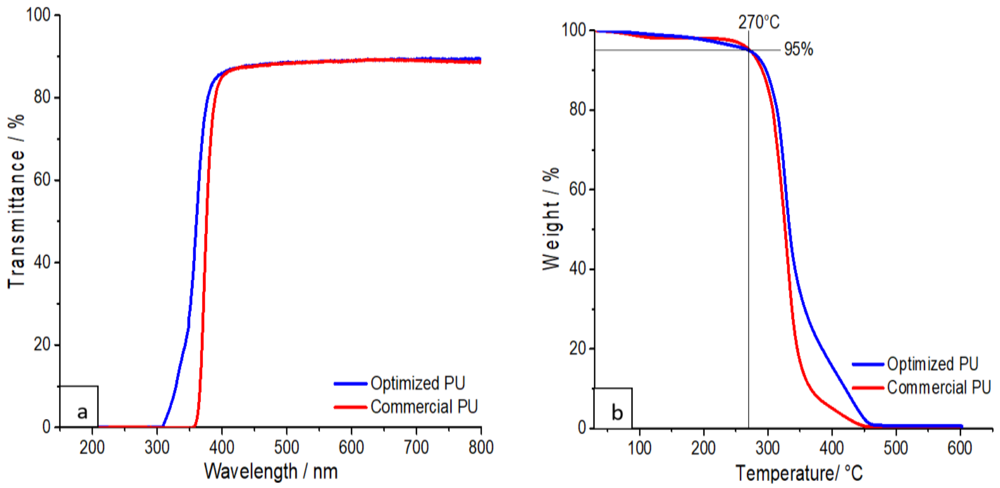


Figure 26 Comparison between standard and optimized PU. (a) UV-Vis spectra; (b) TGA analysis performed in N_2.

Cross-linkers and chain extenders are used to modify cross-linking and the packing of hard segment domains and the mechanical properties of polyurethanes.[495,496] Swelling allows to investigate the cross-linking level and the effects of different chain extender amounts inside the samples.[497,498] In particular, the chain extender addition is expected to increase the percentage weight variation due to the absorption of the solvent over time (%S),[497] as the cross-linking density decreases. In our study, BHET acts as a chain extender (f=2). To better understand the possible influences of BHET on films properties, two BHET-free polyurethanes were formulated with this polyol blends (polyisocyanate: DK180HV):

- $PU_{0\%BHET}$: 100% Sovermol 780
- $PU_{0\%BHET}$: 80 % Sovermol780 + 20 % LCR540RT.

First of all, the swelling percentage (S%) was evaluated in water (**Figure 27**). A good encapsulating material must guarantee both low water absorptivity and moisture permeability, depending on the final application.[31] To better evaluate the barrier properties of polyurethane films, water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) measurements would be necessary. However, these types of analysis require high costs and extremely long measurement times to obtain reliable results.[30] To overcome this obstacle, the degree of cross-linking of the different samples was taken into consideration as a first approximation of the barrier properties of the films through swelling.

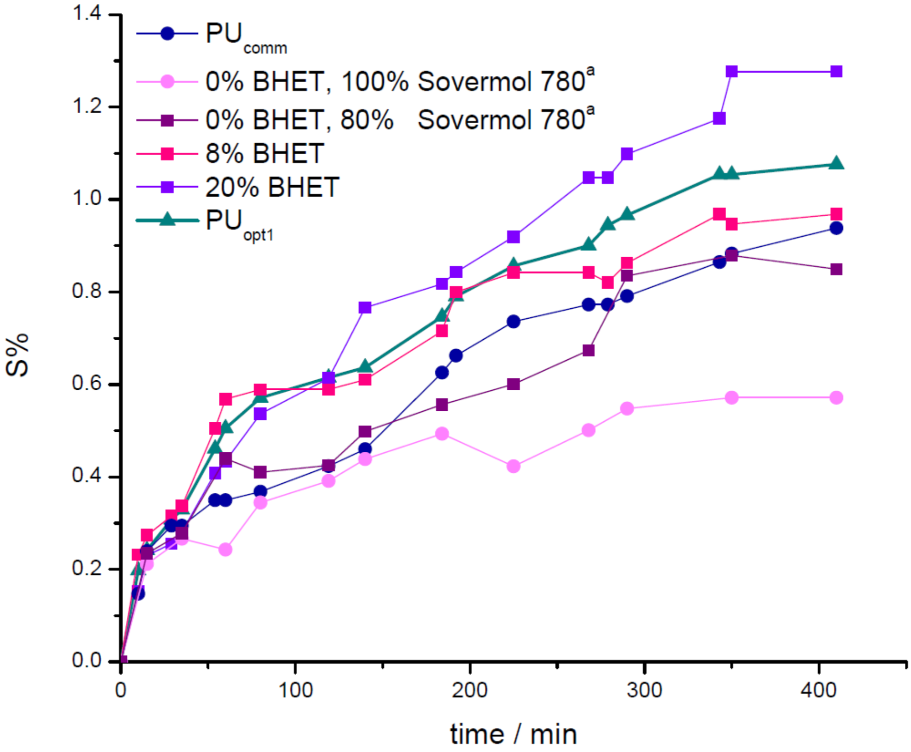


Figure 27 Swelling in H_2O. [a]Percentage referred to the polyol mixture.

All samples S% values lower than 1% after 7 hours. No relevant differences were found between the S% of the samples, proving a remarkable resistance of our PUs to water permeation. Thus, to verify a possible influence of the chain extender on swelling properties, methanol and acetonitrile have been taken into consideration. Unlike what was expected, PUs with a higher BHET amount exhibit a lower %S in both methanol and acetonitrile (**Figure 28**).

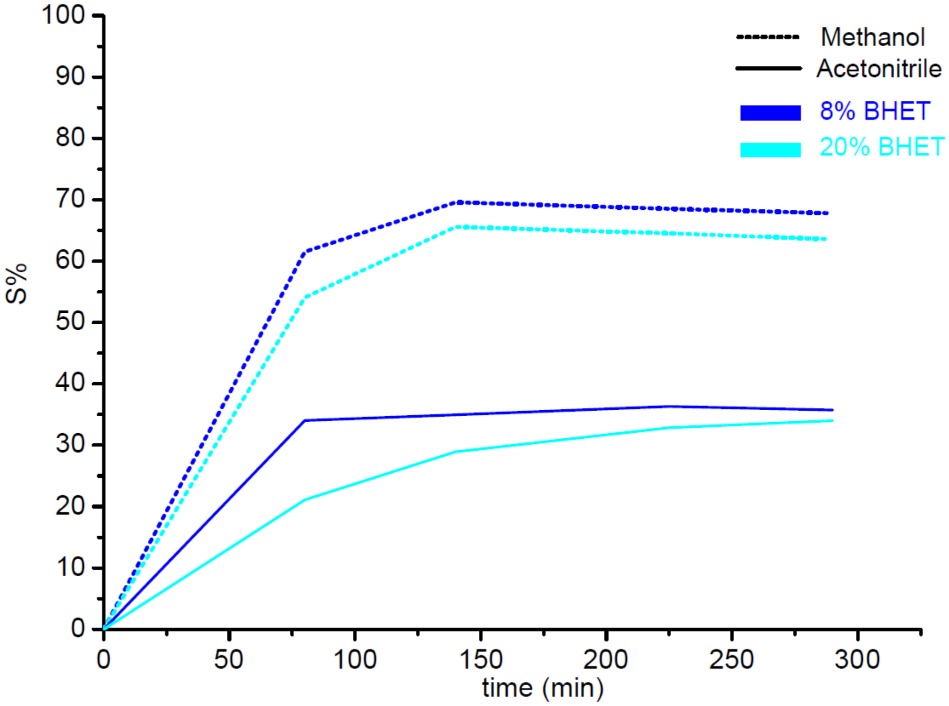


Figure 28 %S in methanol (dashed line) and acetonitrile (continuous line). The measurements were carried out after 2 months from the film deposition.

This unexpected trend might be explained by a double effect promoted by BHET addition: cross-linking decrease and packing increase. In fact, the BHET addition, with f=2, leads to the formation of more linear hard segments by the reaction with the isocyanate;[499] these linear domains guarantee a tighter packing of the chains.[500] A more packed structure can results in lower %S values[501] due to the decrease in the free volume available for absorption. From **Figure 28**, it can be assumed that BHET promotes the packing effect more than the cross-linking.

Further analyses should be carried out to confirm the BHET behavior in achieving tightly meshed PUs.

6.4.3 Catalytic system: second and third DoE analysis

The fossil-based polyol substitution is only the first step of the progressive raw materials substitution process. Although the first substitution led to the formulation of a 24.4% circular PU, the synthesis is still based on the Hg-based catalyst and the fossil-based isocyanate.

Both the catalyst and polyisocyanate substitutions result in the analysis of the influence of the catalytic system on the responses.

Figure 29 show the coefficient plots for all the responses of the catalyst substitution DoE (DoE 2).

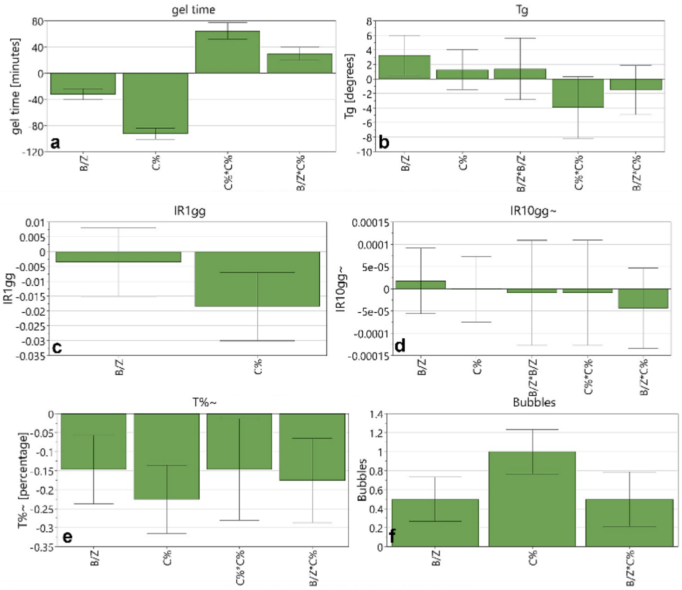


Figure 29 DoE 2 coefficient plots. Evaluation of the most influential catalysts related factors. a) Gel time; b)T_g; c) IR ratio after 1 day; d) IR ratio ater 10 days; e) %T_{555nm}; f) bubbles.

Gel time is mostly affected by the % catalyst (**Figure 29-a**), while T_g by $r_{Bi/Zn}$ (**Figure 29-b**). However, the model presents a high uncertainty for T_g values. From measurements replications, a high variance was observed. This is probably due to phase segregation during the mixing process.[502]

It is clear that the presence of bubbles into the PU matrix affects the final transparency. In particular, the bubbles increase when % catalyst increase (**Figure 29-f**). Subsequently, higher catalyst amount gives lower %T_{555nm} (**Figure 29-e**). The same trend is observed for high $r_{Bi/Zn}$.

To better highlight the opposite trend of bubbles and transparency also the contour plot is presented (**Figure 30**). The contour plot is a 3-dimensional surface that represents simultaneously the effect of two factors on the same response (iso-response values).[503] Moreover, this graph allows to visualize the values of the responses giving more detailed information than the coefficient plot but neglecting the uncertainty.

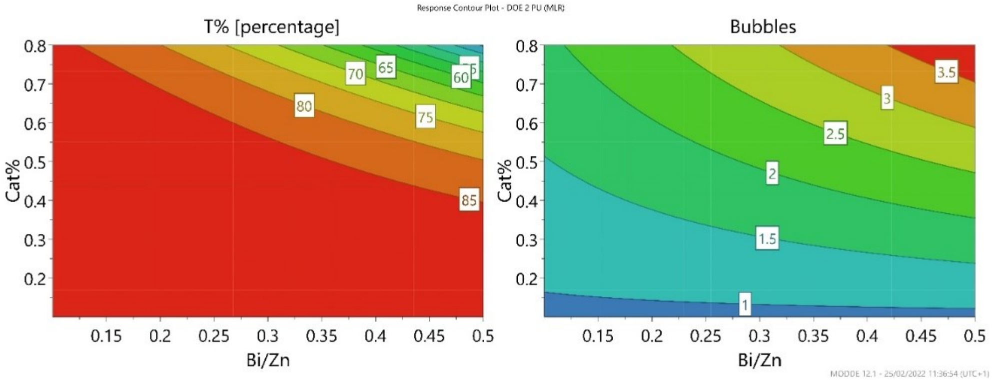


Figure 30 DoE 2 Contour Plot for %T_{555nm} and bubbles responses

All the 11 PUs formulated according to the **Table 21** resulted almost completely cured after 10 days (**Figure 31**); for this reason, IR_{10gg} does not show any dependency from both %cat and $r_{Bi/Zn}$. On the other hand, the coefficient plot show how IR_{1gg} strongly depends on the % catalyst. In particular, higher amounts of catalyst give lower IR_{1gg}, that is a faster polymerization rate.

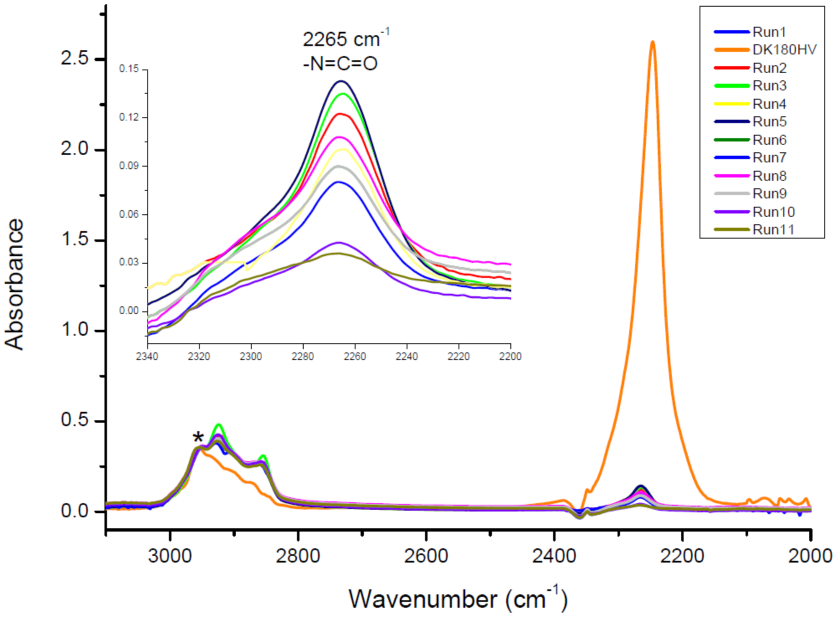


Figure 31 ATR-IR spectra of the 11 PUs formulated according DoE2 plan. Data were collected 10 days after the formulation. Peaks are normalized at 2950 cm^{-1} (*) with the pure isocyanate (DK180HV) peak

Similar considerations are those obtained from the study on the polyisocyanate substitution. **Figure 32** shows the coefficient plots.

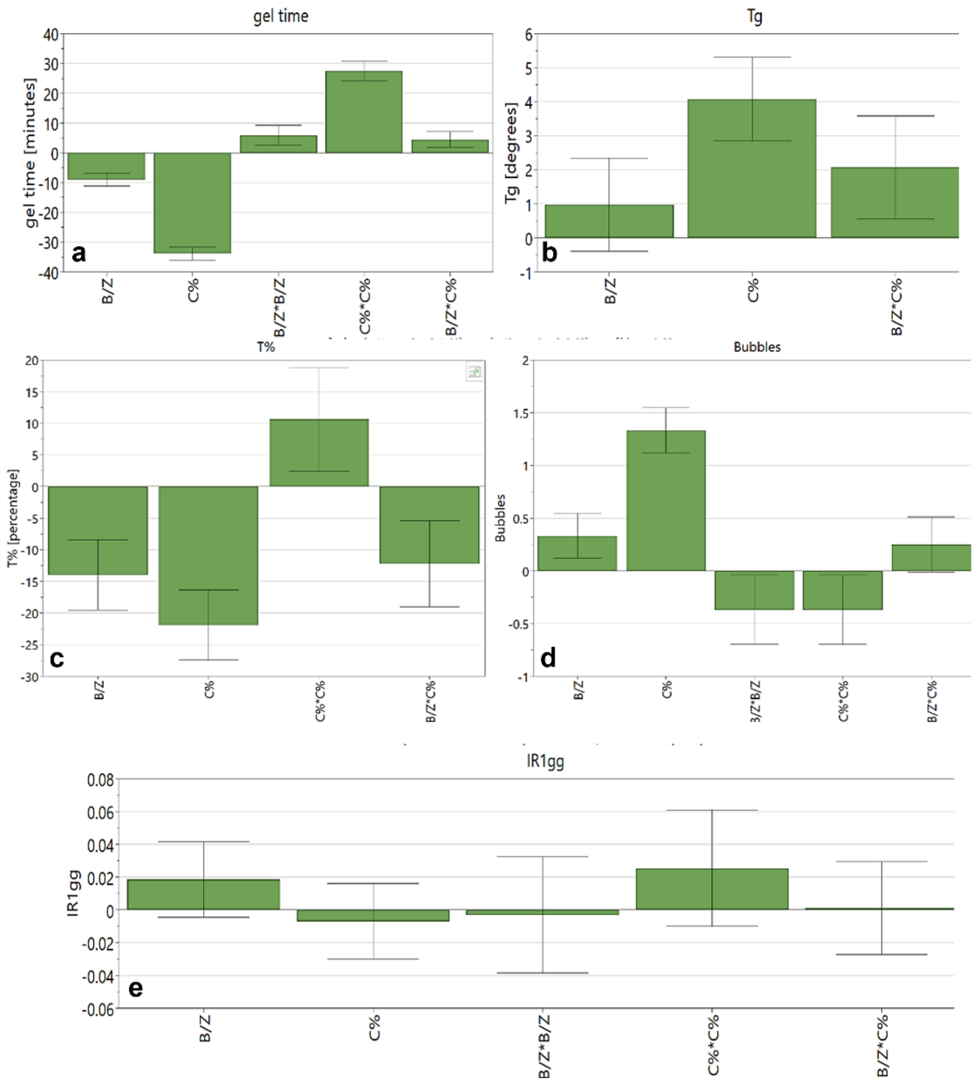


Figure 32 DoE 3 coefficient plots. Evaluation of the most influential catalysts related factors.
a) Gel time; b)T_g; c) %T_{555nm}; d) bubbles; e) IR ratio after 1 day.
Non-relevant factors are omitted for clarity.

The relevant difference between the two studies is that no factor affected the IR$_{1gg}$ since the uncertainty was greater than the influence of the factors themselves. This can be explained by the fact that after 1 day, the new formulations show an almost complete curing (**Figure 31**) for all the 11 experiments leading to a high uncertainty in the identification of relevant factors.

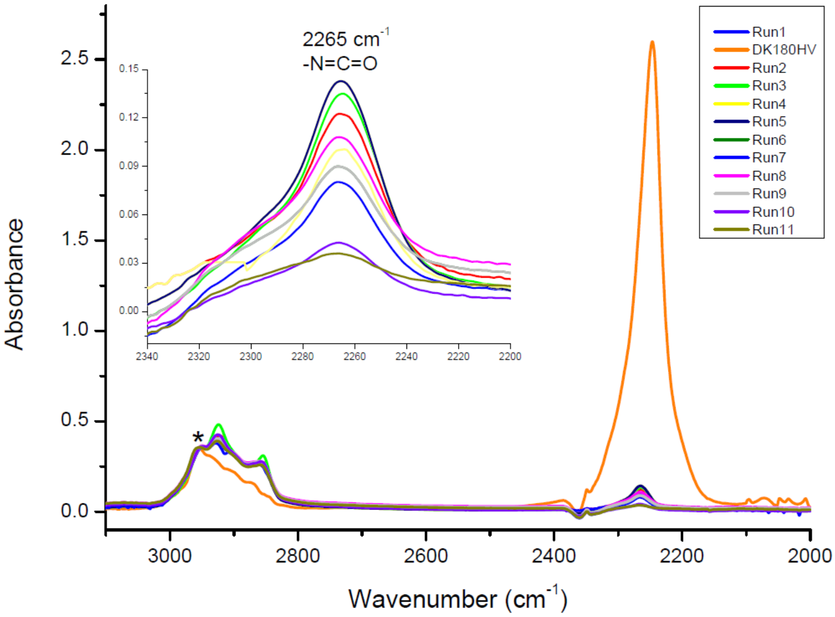


Figure 33 ATR-IR spectra of the 11 PUs formulated according DoE3 plan. Data were collected 1 day after the formulation.
Peaks are normalized at 2950 cm^{-1} (*) with the pure isocyanate (DK180HV) peak

6.4.4 Optimal catalytic system determination for DK180HV

The promising results for gel time, curing rate and transparency obtained from the second plans offer the opportunity to explore the Sweet Spot Plots both for DoE 2 and DoE 3 (**Figure 34 and 36**) for the optimal formulation parameters. The process factors choice has been made taking into account transparency and gel time requirements along with a low bubble amount value.

The same transparency target of the first Sweet Spot Plot has been set as the desired one, that is $\%T_{555nm} \geq 88\%$. Gel time values between 60 and 80 minutes have been selected to achieve values as close as possible to the commercial one (70 minutes). Bubbles amount value < 2 has been chosen although it does not guarantee a bubble-free PU. However, it is worth highlighting that a continuous under vacuum process might furtherly reduce or even remove bubbles from the final PU.

The generated Sweet Spot Plot for the second DoE (**Figure 34**) presents 3 different areas which define catalytic system combinations to achieve the required criteria. In particular, the blue area describes the combination of conditions to reach a bubble amount lower than 2. The turquoise area represents the conditions to achieve a PU with a $\%T_{555nm} \geq 88\%$. The green area is the sweet spot where all the criteria are met.

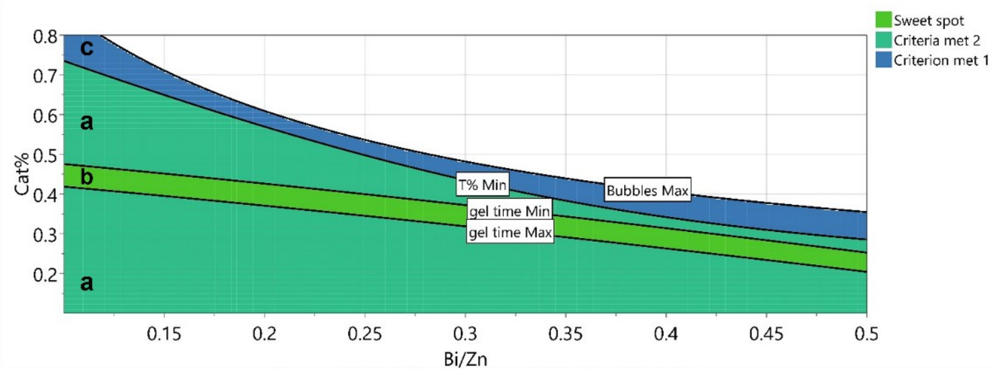


Figure 34 DoE 2 Sweet Spot Plot. Turquoise area (a) $\%T_{555nm}$ and bubbles <2 criteria are met. Green area (b): sweet spot. Blue area (c): only bubble amount criterion is met.

The model was validated for two formulations from the Sweet Spot Plot. The glass transition temperature was not included as a response for model validation due to the high uncertainty. The IR ratio of the measurements after 10 days was not considered as the curing resulted complete for all the 11 samples. The IR ratio after 1 day was calculated after 3 replicas on two samples; the model is validated.

After model validation, the formulations from the sweet spot can be considered suitable to obtain optimized PUs. It is interesting to highlight that high $r_{Bi/Zn}$ allow to exploit lower catalyst amount; on the other hand, low $r_{Bi/Zn}$ requires higher % catalyst amounts.

The sweet spot area has its own limits within the following ranges:

$0.1 \leq r_{Bi/Zn} \leq 0.5$ and $0.21 \leq \%cat \leq 0.47$.

The complete elimination of Hg was successfully achieved from the second DoE. Furthermore, the replacement of organomercuric catalyst with different Bi-Zn catalytic systems in the PU_{opt1} did not threat the final target requirements.

6.4.5 Optimal catalytic system determination for Desmodur® N 7300

The Sweet Spot Plot for the third DoE was generated following the same criteria of the second one. **Figure 35** presents 3 different areas which define catalytic system combinations to achieve the required criteria. In particular, the blue area describes the combination of conditions to reach a bubble amount lower than 2. The turquoise area represents the conditions to achieve a PU with a $\%T_{555nm} \geq 88\%$. The green area is the sweet spot where all the criteria are met.

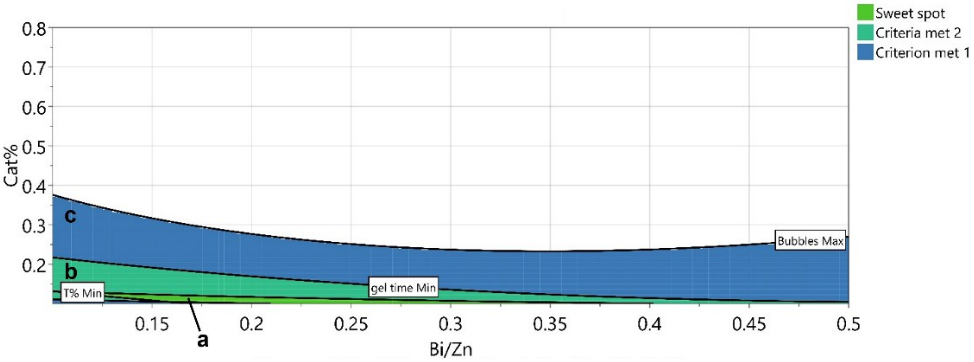


Figure 35 DoE 2 Sweet Spot Plot. Green area (a): sweet spot. Turquoise area (b) $\%T_{555nm}$ and bubbles <2 criteria are met. Blue area (c): only bubble amount criterion is met.

Also in this case, the model was validated.

The sweet spot area has its own limits within the following ranges:

$r_{Bi/Zn} \leq 0.12\%$ and $0.15 \leq \%cat \leq 0.35$.

It is worth highlighting that glass transition temperatures (**Figure 28**) resulted decreased using Desmodur® eco N 7300. However, the obtained T_g values are either equal or higher than the commercial one, hence in compliance with the market requirements.

6.5 Aging tests on optimized PUs

Encapsulants for optoelectronics must provide electrical insulation, good resistance to UV irradiation and thermal degradation,[504] prevent leakages and ensure both mechanical and weathering protection.[425] To test the stability of the obtained PUs, thermal and QUV accelerated weathering tests have been performed. In a first attempt, we mainly focused our attention on the modification of the optical response of the film. Influences on the optical properties from thermo- and photo-oxidative aging were characterized via UV-Vis spectroscopy.[505] In this perspective, the difference between $\%T_{555nm}$ before and after aging ($\Delta\%T_{555nm}$) was calculated.

Three polyurethanes, formulated from the Sweet Spot conditions of each DoE, have been subjected to the stress tests.

After 50 days at 80° C, the PU_{opt1} exhibited the lowest loss in transmittance value, while PU_{opt2} the highest. All the samples, however, show a loss in $\%T_{555nm}$ almost equal or lower compared to the standard (**Table 23**).

Table 23 Transmittance losses after thermal aging. $\%T_0$ is the transmittance before aging.

Sample	$\%T_0$	$\Delta\%T_{555nm}$*
PU_{opt1}	87	11.7
PU_{opt2}	90	23.4
PU_{opt3}	89	12.4
Standard	88	21.7

*$\Delta\%T_{555nm}$ calculated as a difference between $\%T_{555nm}$ after and before thermal aging

The samples have been also subjected to the QUV accelerated weathering. This test aims at simulating the action of sun and humidity condensation on the material. This test accelerates the normal exposure conditions allowing to check the resistance of the material extended in time. It can even simulate a 10-year-exposure period.[506] After 480 h under stress cycles, the transmittance was measured.

Table 24 Transmittance losses after QUV accelerated weathering test.

Sample	% BHET	$\%T_0$	$\Delta\%T_{555nm}$*
PU_{opt1}	4.36	88	4.1
PU_{opt2}	4.36	90	26.1
PU_{opt3}	3.82	89	0.8
Standard	0	88	Measurements in progress

*$\Delta\%T_{555nm}$ calculated as a difference between $\%T_{555nm}$ after and before thermal aging

As in the thermal aging test, the PUs from DoE 1 and DoE 3 show the lowest $\Delta\%T_{555nm}$, hence the best resistance.

The best thermal stability for the polyurethanes formulated with Desmodur® eco N7300 (PU_{opt3}) can be explained by the presence of polyisocyanurates moieties deriving from the bio-based hardener (**Figure 21**). In fact, polyisocyanurates are reported as thermal stability enhancer of PUs.[507,508] This effect is confirmed by the thermograms presented in **Figure 36**.

On the other hand, UV stability (**Table 24**) depends on the presence of non-aliphatic components. In particular, the presence of aromatic structures threats the PU stability when exposed to light and enhance degradation during UV exposure.[508,509] In this context, it is important to consider two factors: the presence of UV stabilizers into LCR540RT and the aromatic structure of BHET. According to the n° OH and n° NCO, the formulations from DoE 3 contains a higher amounts of isocyanate components than polyols; hence, the aromatic BHET concentration is lower for PUs obtained using Desmodur® eco N7300. The combination of polyisocyanurates components and low BHET amounts explain the superior stability of these PUs. The lowest stability for PU_{opt2} could be due to a not complete polymerization not detected from the ATR-IR measurement for its superficial nature.

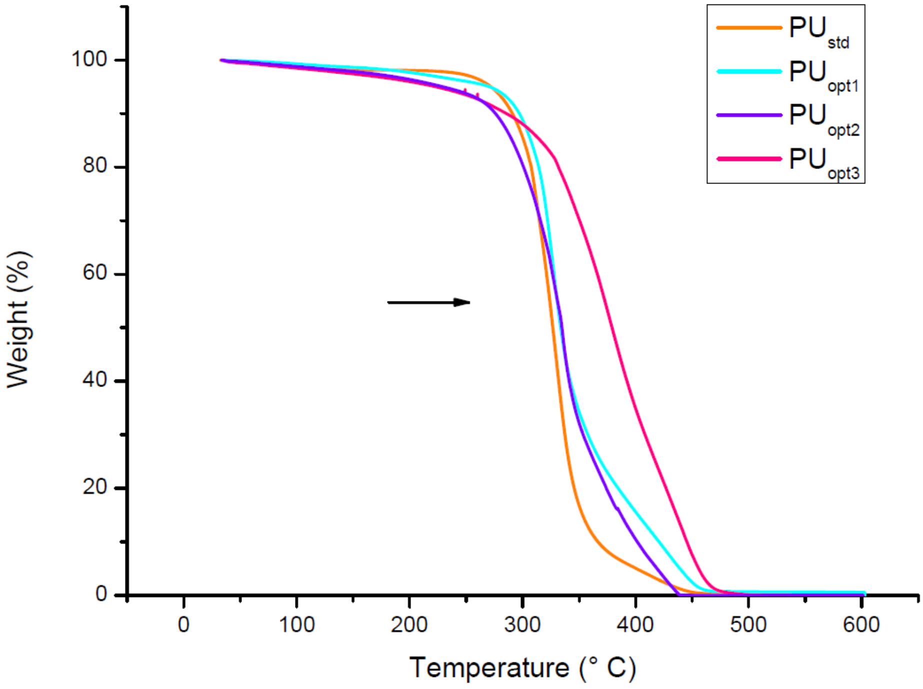


Figure 36 TGA of the standard PU (orange) and those from DoE 1 (light blue), DoE 2 (violet) and DoE 3 (pink). N_2 atmosphere, Ramp 5° C/min from 30° C to 600° C.

The thermograms presented in **Figure 36** show that the thermal degradation of the PU obtained from the third DoE is delayed, probably for the presence of polyisocyanurates from Desmodur® eco N7300.

6.6 Circular PUs and sustainability

The progressive substitution of the fossil-based polyol and polyisocyanate, along with the elimination of Hg-based catalyst was the followed pathway towards more sustainable PUs. But this is only a mere articulation of sustainability.

Actually, facts, data and externalities must be presented to clearly understand the achieved improvements, the unintended negative consequences and the lacking information necessary to determine the sustainability profile of a new material. Again, the sustainability matrix is a powerful tool to collect relevant information for a critical final reflection. **Table 25** shows the main sustainability aspects related to the commercial PU synthesis, while **Table 26** is the sustainability matrix for the obtained circular PU.

Table 25 Sustainability matrix for commercial PUs

Commercial PU	**RELIABLE AND SECURE**	**CLEAN**	**AFFORDABLE**
RAW MATERIALS	**(-)** Mainly fossil-based raw materials	**(0) No data**	**(0) Not relevant info**
MATERIALS PRODUCTION	**(-)** Toxic metal complexes as catalysts **(-)** Phosgene is a lethal gas **(-)** Diisocyanates are toxic	**(-)** Diisocyanates are environmentally harmful **(+)** Room temperature	**(+)** € 5.5/Kg
DEVICE ASSEMBLING	**(0) Not relevant info**	**(+)** It may lower CED value wrt glass	**(+)** Low cost wrt device with glass substrates m^2 should be considered
DEVICE DISTRIBUTION	**(+)** Flexibility	**(+)** Low weight	**(+)** Low weight, less fuels, low distribution costs wrt glass
USE and MAINTAINANCE	**(-)** shorter encapsulation time wrt glass **(-)** Worse thermal resistance wrt circular PU ($\Delta\%T = 21.7$)	**(0) No data**	**(0) No relevant info**
END of LIFE	**(-)** Leakages	**(-)** Leakages **(-)** It can require less energy wrt glass **(+)** Glycolysis is a quite mature recycling process	**(0) No data**

Table 26 Sustainability matrix for circular PUs

Circular Polyurethane	**RELIABLE AND SECURE**	**CLEAN**	**AFFORDABLE**
RAW MATERIALS	**(+)** Mainly circular	**(0) No data**	**(-)** Desmodur is expensive (€ 12/Kg)
MATERIALS PRODUCTION	**(+)** No phased out metal complexes as catalysts **(-)** Phosgene is a lethal gas **(-)** Diisocyanates are toxic	**(-)** Diisocyanates are environmentally harmful **(-)** Heating is required 0.09 kWh	**(-)** higher cost wrt standard PU (€ 9.18/ Kg_only materials)
DEVICE ASSEMBLING	**(0)**	**(+)** It may lower CED value wrt glass	**(+)** Low cost wrt device with glass substrates m^2 should be considered
DEVICE DISTRIBUTION	**(+)** Flexibility	**(+)** Low weight	**(+)** Low weight, less fuels, low distribution costs wrt glass
USE and MAINTAINANCE	**(-)** shorter encapsulation time wrt glass **(+)** Better thermal resistance wrt commercial PU ($\Delta\%T = 12.4$)	**(0) No data**	**(0) Not relevant info**
END of LIFE	**(-)** Leakages	**(-)** Leakages **(-)** It can require less energy wrt glass **(+)** Glycolysis is a quite mature recycling process	**(0)**

Considering the percentage of bio-based and secondary raw materials as an indicator of circularity, the obtained PU has a 61.15% of circular inputs. In fact, Sovermol® 780 and Desmodur® ECO N 7300 have 65% and 68% of bio-based content, respectively.

The high circular content represents a positive achievement towards fossil-based sources decoupling but does not ensure lower environmental impacts. The lack of data is one of the most faced issues when dealing with sustainability. However, normatives and non-financial reporting are pushing industries to supply data on emissions.

Another important aspect to highlight is the importance of the progressive substitution approach. Each substitution step allows to explore if the alternative reagent leads to the PU with the desired properties. Moreover, if the desired properties are met, other parameters, for instance the final cost, can be used to select one of the obtained formulations. Considering the final costs (**Table 27**), PU_{opt1} and PU_{opt2} are cheaper than PU_{opt3} because of the cost of Desmodur® ECO N 7300.

Table 27 Polyurethanes' costs

PU_{comm}	PU_{opt1}	PU_{opt2}	PU_{opt3}
€ 5.5	€ 6.0	€ 6.0	€ 9.2

7 Conclusion

This thesis aims at providing a novel and pragmatic approach for sustainability assessment for innovative materials for energy. The focus is on the early-stage of lab-scale product development. The presented strategy is a useful tool to drive well-researched responses and aware decisions in the sustainable materials field. Two new matrices to guide the sustainability assessment have been developed starting from the theory of Pope and the methodologies suggested by Patel and Othman along with those presented by Hallstedt and Ashby. In this way, the approaches used for the applied research sphere and the market dimension have been merged. As matter of fact, the former does not really consider the final use in the sustainability assessment, and it is mainly focused on the production process; on the other hand, the assessment for market products is related to data and stakeholder analyses difficult to reliably consider at lab-scale. The approach designed and developed throughout this thesis wants to build a bridge for sustainability between the applied research and the market by looking at the system on different conceptual scales. Hence, not only the material production is considered but also its involvement in the final device without neglecting its possible real use (for instance consider weight for distribution).

The developed sustainability matrices involve both sustainability principles and life-cycle phases. They are thought to overcome the mere process analysis of the applied research and they can be used both for comparison and benchmarking iteratively. Moreover, they want to be a versatile tool in the energy field from the energy harvesting systems to the storage (*i.e.*, batteries)

The two presented matrices are the sustainability criteria matrix (**Table 2**) and the sustainability tool matrix (**Table 4**).

The sustainability criteria matrix is a guideline on what to consider during the sustainability assessment of materials for energy. Its development required a framework analysis (**Section 2**) to define which are the sustainability principles in the renewable energy context (*i.e.*, reliable and secure, clean and affordable). Moreover, forecasting solar energy as one of the largest sources of electricity by 2030, a brief introduction to emerging photovoltaics was provided for a better comprehension of the potential technologies and materials of the future. The sustainability tool matrix offers an indication of which indicators and information are necessary to collect to assess each life phase according to each principle.

The sustainability matrices have been used as guidelines for a thorough analysis of Dye-Sensitized Solar Cells, searching for data and information useful for the sustainability assessment (**Section 4**). This part can be identified as the fact-finding phase of Ashby's layered approach. From this analysis, 8 sustainability matrices (**Section 5**) have been extrapolated for 4 different components (i.e., dye, counter electrode, electrolyte, and substrate); the matrices are used comparatively for traditional and alternative materials to highlight unintended consequences of each articulation. In this way, each material has been assessed systematically.

From these matrices, the Dye-Sensitized Solar Cells' glass replacement with polyurethanes has been selected as a case-study (**Section 6**) because of the high energy consumption from glass production. The case-study reveals the iterative nature of the approach due to the unintended consequences resulting from the alternatives. The glass replacement is not straightforward because, in turn, PUs exhibit their own criticisms from raw materials selection to end-of-life which requires a further assessment step. Hence, starting from a commercial PU for encapsulation and assessing the traditional PU criticisms, a new PU (PU_{opt3}) has been formulated through a progressive substitution approach, following sustainability guidelines to overcome the hotspots. Time and waste minimization for experiments have been achieved by planning the formulation through the Design of Experiment. The formulation of PU_{opt3} required 3 steps for polyol, catalyst, and isocyanate substitution planned through 3 different DoEs. In particular, the fossil-based polyol has been substituted with the bio-based Sovermol® 780 adding the bis(2-hydroxyethyl) terephthalate as chain extender (PU_{opt1}). The Hg-based catalyst and the fossil-based polyisocyanate have been replaced with a Bi-Zn-based catalyst (PU_{opt2}) and Desmodur ECO N 7300, respectively (PU_{opt3}). The selection of bis(2-hydroxyethyl) terephthalate offers an interesting and attractive opportunity. It can be obtained from PET chemical recycling allowing the creation of an industrial symbiosis process where it is supplied as secondary raw material.

Each substitution led to a different PU with the desired transparency and glass transition temperature for encapsulation. The Hg-based PU_{opt1} from the first DoE contains 24.2% of circular inputs and good thermal and weathering resistance. Its final cost is € 6.0 kg^{-1}. The Hg-free PU_{opt2} does not show good resistance hence it requires a further investigation on the polymerization degree. Finally, from a 100% fossil-based PU, a Hg-free PU_{opt3} with 61.2% of circular inputs has been formulated. It presents the best thermal and weathering resistance, but also the highest cost (€ 9.2 kg^{-1}). Here, the progressive substitution approach can be well appreciated for the opportunity to monitor the desired properties aiming at a ready-to-market PU. For instance, PU_{opt3} should be selected for applications demanding high thermal and weathering resistance, despite its cost. However, a firm might decide to select the less expensive formulations, PU_{opt1} and PU_{opt2}. However, the presence of mercury in PU_{opt1} pushes towards the re-optimization of PU_{opt2} to have a Hg-free, low-cost, and good resistance PU.

One of the most critical aspects faced during this thesis work is the lack of data. For instance, data on emissions and impacts are not available neither for the commercial PU nor for commercial reagents (i.e., Sovermol® 780 and Desmodur® ECO N 7300). The lack of data is one of the main reasons behind the failure of sustainability-driven decisions, especially at early-stage. Most of the suppliers do not declare CO_2 emissions or provide a complete LCA eliminating the opportunity to compare the final products. Moreover, in academia, the researchers seldom provide useful data, claiming sustainability without any consistent information. In this context, the presented matrices, especially the tool matrix, are two roadmaps pointing out which data are necessary for a complete assessment.

It is fundamental to highlight that some data are not defined in static ranges and values, *e.g.,* prices, supply risk, and criticality. The use of future scenarios and previsions can be an implementation of the assessment for better *hotspot* identification.

The matrices indicate criteria, guidelines, and indicators selected for the early-stage, where there is a restrained availability of data and time; however, the selection should be critically made from interdisciplinary groups to better incorporate and collect solid and reliable data and information.

The presented sustainability assessment can be implemented in different ways: for instance, data and information might be transformed into indicators to create a scale for sustainability compliance. Furthermore, criteria for priority identification in the decisional process should be defined.

Sustainability is a broad and complex topic; this thesis offers an innovative approach to deal with it in the materials field coupling traditional presented data (*e.g.,* efficiency) with emerging constraints on materials and broadening the vision from the lab-scale to the market one. Furthermore, the use of sustainability principles in the presented matrices involves the time scale; in fact, sustainable development is possible only if long-term thinking is involved in any decisional process.

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Appendix A

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CRITICAL BARRIERS FOR PLASTIC RECYCLING. A CC CASE-STUDY IN TURIN*

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Abstract

Waste accumulation is one of the most discussed environmental issues which is jeopardizing our planet from an environmental, economic and social point of view. In this context, plastic plays a pivotal role, because its accumulation and persistence is becoming a matter of great concern. In 2017, 43% of plastic packaging is recycled.. In order to understand the barriers and the criticisms which hamper the development of a more efficient recycling pathway for plastics, one of the most important material recovery plants of Turin has been selected as case of study. The plants belongs to Amiat, the multi-utility working in waste collection on the behalf of Turin Municipality. This plant can treat up to 66 ktons/year of plastic packaging. Its function is to pre-select the materials coming from the separate collection, in order to guarantee the necessary level of quality to allow the recycling process. In fact, pre-selection is required for different reasons: a non-efficient separation performed by the citizen, as well as administrative and legal constraints on plastics treatment, such as recycling plastic packaging only. Hence, this work is willing to identify the key-actors involved in the plastic recycling process as well as to analyse the role of the selected plant using a case study methodology, assessing the key barriers and suggesting possible solutions for future scenarios of plastics recycling.

Keywords: circular economy, plastic market, plastic recycling

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1. Introduction

From 1950 onwards, it is estimated that about 6’300 Mtons of primary and secondary plastic waste have been produced on the planet. Furthermore, it is estimated that 79% of plastic waste has been accumulated in landfill or discarded in the environment, whereas only 9% has been recycled (Geyer et al., 2017). Although public opinion has recently been affected by impactful media exposition, such as the dissemination of news and data about the island of plastics in the Pacific Ocean (Lebreton et al., 2018) called *Pacific Trash Vortex (Great Pacific garbage patch)*, environmental policies in developed countries are struggling to reach effective results. In the developed areas supposed to be keen on environmental awareness, such as Europe, policies to optimize and improve plastic recovery are unable to take off the ground (DESA, 2013). Thus, the awareness of the issue is not consistent with data about plastic recycling. For instance, European citizens declared themselves aware about the environmental impact of plastics, and concerned about the management of this kind of waste (Syberg et al., 2018). On the other hand, according to Eurostat Report (2018), each European citizen produces 31 kg of plastic packaging waste every year, which leads to a total of 15.8 Mtons in the European Union (EU). Nevertheless, in European countries, only 40% of plastic packaging is currently recycled (EC, 2015). In Italy, the amount of plastic packaging actually recycled is around 43% (PlasticsEurope, 2018). This dynamic is consistent with the continuous growth in the rate of separate collection, by now close to 55%, which led to the progressive increase of the plastic percentage transported to recovering and recycling centers (ISPRA, 2017).

In the City of Turin, the rate of separate collection is only around 45% and the quantity of plastic addressed to material recovery plants is constantly growing (Commune di Torino, 2018). The plant selected for this case-study stores and sorts the plastic waste coming from the separate collection of the City of Turin. It represents a preliminary step for plastics before going into the recycling process to guarantee suitable plastic waste for the recycling process.

The main objective of this work is to investigate the barriers for plastic recycling starting from the case-study of the selected plastics recovery plant in Turin. The analysis of the material and money flows, the study of plastic materials and the examination of the normative led to the identification of relevant key barriers which might hamper the already "complex" recycling process of plastics. In this research, we aim to identify whether the selected plant is necessary to guarantee an efficient recycling process or why it might not be in the next future.

The authors rebuilt the whole plastic recycling framework through the definition of plastics as polymeric materials (3.1) with their specific characteristics and the main categories for the recycling (3.2). The Italian situation (3.3), the stakeholder analysis and the plastic ecosystem are explained afterwards (3.4). Finally, the plant is analyzed (3.5) as well as an exploration of the relevant regulations including the birth of CONAI is done, providing the starting point for potential future scenarios (3.6).

2. Methodology

The methodology chosen is the case-study analysis. The choice of the plant is relevant because dynamics of CCs (*Centro Comprensoriale*-Plants of recovering materials) are not explored at all, because their value is often underestimated due to their small dimension. In fact, this research wants to analyze their role, considering their work of pre-selection is fundamental for the whole plastic recycling value chain. It is acknowledged that CCs are complex systems and it is worth investigating why they are necessary and whether they might not be in the next future. In order to reach this purpose, official documents of COREPLA are used, as well as information provided on COREPLA website.

3. Results and discussion

In this section, the definition of plastic is presented, in order to give clarity to the concepts involved. Then a quick excursus about different kinds of plastic recycling is proposed. Afterwards, the Italian packaging ecosystem is analyzed, identifying the most relevant actors involved, as well as the case study of the selected CC is taken into careful consideration, in terms of money and materials flow, highlighting pros and cons of the actual existing Italian plastic recycling network. Finally, the enactment of Ronchi Decree is discussed, explaining the reasons and the perspectives after the birth of CONAI.

3.1. Plastic: one definition for a plethora of materials

The International Union of Pure and Applied Chemistry defines plastic as a "*polymeric material that may contain other substances to improve performance and/or reduce costs*" (Vert et al., 2012). Actually, there are a plethora of different plastics whose our products are made of and there are codes (Table 1) to help the identification of the type of plastic in order to facilitate the recycling process according to international standards.

Table 1. Classification of plastics according to the International Standards (adapted from Wong, 2010)

Symbol	***Type of Plastics***	***Main Use***
1 PETE	Polyethylene Terephthalate (PET)	PET is used for containers for foods and liquid, soft drink bottles, fibers for clothing.
2 HDPE	High Density Polyethylene (HDPE)	HDPE is used for bottles, piping for water and sewer, milk jugs, detergent bottles, nursery pots, oil containers, snowboards, boats and chairs
3 V	Polyvinyl Chloride (PVC)	PVC (or vinyl) is common for products such as plumbing products, medical tubing, pressure pipes, electrical cable insulation, outdoor furniture, liquid detergent containers, etc.
4 LDPE	Low Density Polyethylene	This polyethylene is ductile and, thus, used for shopping bags, food containers, films or bags and stretch wrap
5 PP	Polypropylene (PP)	PP is a thermoplastic polymer and one of the worldwide most common used plastic. It is used for laboratory equipment, automotive parts, medical devices, etc.
6 PS	Polystyrene (PS)	PS is commonly used for yoghurt pots, foodservice containers, CD cases, envelope windows, video cassettes, appliance housings as televisions.
7 OTHER	Other types of plastics	Various usages.

3.2. Plastics recycling

Plastic recycling process can be mechanical or chemical: the former consists of the re-melting and the re-extrusion of the polymer. The latter one is the chemical break of the polymer in smaller molecules which can be re-used either to produce a new polymer or another material. In any case, each process requires resources, such as water, and energy: thus, the golden rule, i.e. the most efficient solution to the waste accumulation issue, it must always be the minimization of waste. It is relevant to know that plastics are divided in two main classes. Each class of plastics exhibits different properties and different behaviors towards the recycling processes. Plastics that are solid materials obtained through the melting and subsequent cooling of the polymer are called *thermoplastics.* The recycling of these plastics is easy enough: it is sufficient to heat and reshape these materials. It is important to highlight that repeated processing may alter the properties of the polymers. Plastics having their set properties and shapes obtained through the so-called crosslinking reactions are called *thermosetting plastics*. These plastics are more difficult to recycle because the heating process leads to their chemical degradation. There are four different classes of plastic recovering processes (Elias, 2003):

1. *Primary mechanical recycling*: uncontaminated plastic is directly recycled (usually for industrial waste);
2. *Secondary mechanical recycling*: post-consumer plastics are sorted and purified and then recycled;
3. *Chemical recycling*: plastics are broken into smaller molecules. In this way, it is possible to obtain the starting material, a new plastic or another different product;
4. *Incineration*: plastic is burnt. The released heat is used to produce energy.

Another kind of plastic disposal is composting: the material is broken through a biodegradation process into smaller molecules, carbon dioxide and water without the formation of toxic substances, within the time and with the conditions described by the regulation. In Italy, the characteristics for compostability are defined in the UNI EN 13432 (2002). Not all plastics can be recycled and the first step to correctly recycle in an efficient way is the proper separation of plastic waste from other materials. Each recycling process exhibits its own criticisms due to different reasons: citizens' awareness, technology readiness, economic feasibility, lack of policies. In Table 2 the criticisms, from a chemical point of view, for the different kind of disposal are listed (presented). From Table 2, it is possible to observe that there are some issues which need to be overcome yet. From a chemical point of view, it is important to consider the strategies adopted to have a good quality final material (conditions of the process), as well as the energy and the resources exploited in the recycling process.

It is relevant to notice that, when discussing about chemical recycling, materials, and not products, are taken into account. On the contrary, the Italian law, with the establishment of CONAI (2015), regulates the recycling of packaging; thus, it is based on products and not on materials. Indeed, in Italy, certain products made of recyclable materials are not collected only because they don't act as packaging. The in-use Italian normative is discussed in details in next sections. A sound idea to simplify the entire process might be to regulate the collection of all plastics based on material types instead of product types.

In this way, the rate of recyclable plastics could be improved as well as the separation between plastic and non-plastic materials could be easier both for citizens and for a plant as the case-study considered. In addition, chemistry must innovate materials at the first stage of production, i.e. when they are synthesized, to make them more recyclable and it must continue to study new processes to recycle the plastics that are not yet recycled and to make the already existent ones more efficient.

The re-design of materials with the purpose to make them easier to recycle and following a production process closer to the Green Chemistry Principles (Anastas and Warner, 1998) is, nowadays, one of the main challenges for a chemist. To sum up, it is worth highlighting that materials must satisfy a certain function, comply with the legislation and be economically viable at the same time.

Table 2. Plastic recycling processes: criticism and solutions

Plastic recycling process	***Criticisms***
MECHANICAL RECYCLING	Loss of qualities. Use of energy and resources. The presence of additives or mixed materials can jeopardize the recycling.
CHEMICAL RECYCLING	Difficult for some plastics to recover *selectively* the starting materials. Use of energy and resources. The presence of additives or mixed materials can jeopardize the recycling.
INCINERATION	The material cannot be re-used in the production cycle but energy is recovered. Life Cycle Assessments are necessary to evaluate which way is the most sustainable.
COMPOSTING	Misunderstanding of right collection rules by citizens. Lack of effective campaigns of information on key-terms as "biodegradable" and "compostable".

3.3. The Italian situation

In the last decade, every year around 2'200 ktons of plastic packaging are introduced by the Italian market (PlasticsEurope, 2018). The recycling system allows to recover 87.5% of post-consumer plastic packaging: 44.5 % was used to produce new raw material, while 43% was destined to energy recovery. According to PlasticsEurope (2018), from 2006 to 2016 the volumes for recycling increased by 46%, while energy recovery increased by 53% and landfill decreased by 49%.

The Italian plastic packaging supply chain is regulated, at national level, by a unique actor, COREPLA. COREPLA is the national consortium intended for collecting, recycling and recovering plastic packaging and it contributed to collect the 51% of plastic packaging in 2018. It collected 1'219'571 tons, whose 110'823 tons consisted of outer fraction, allowing to avoid the production of around 900 ktons of CO_2. The outer fraction, according to the Italian laws, is the part of waste coming from the separated collection, not homogeneous with the type of material collected (e.g.: glass in the paper bin). Generally, the outer fraction reduces the purity of the collected material, decreases its value and must be disposed of separately (ETRA, 2011). The Italian plastic packaging ecosystem is composed by several private and public stakeholders. The simplified material flow is depicted in Fig. 1.

The plastic packaging value chain starts along with production, distribution and utilization. On the left side, indeed, there is the Plastic Packaging Recovering Chain, i.e. the packaging producers, the product companies and the retailers, who produce the packaging, the products and sell them to the consumers. On the right side, instead, the Plastic Waste Recovering Chain is represented. The recycling process takes place in different phases: (i) the separate collection of waste (citizen); (ii) the collection of separated waste from a company (public or private) and the pre-sorting and cleaning of plastics; (iii) the sorting of different plastics and, (iv) the recycling, i.e. the sorted plastics are processed in order to have materials suitable for a new use.

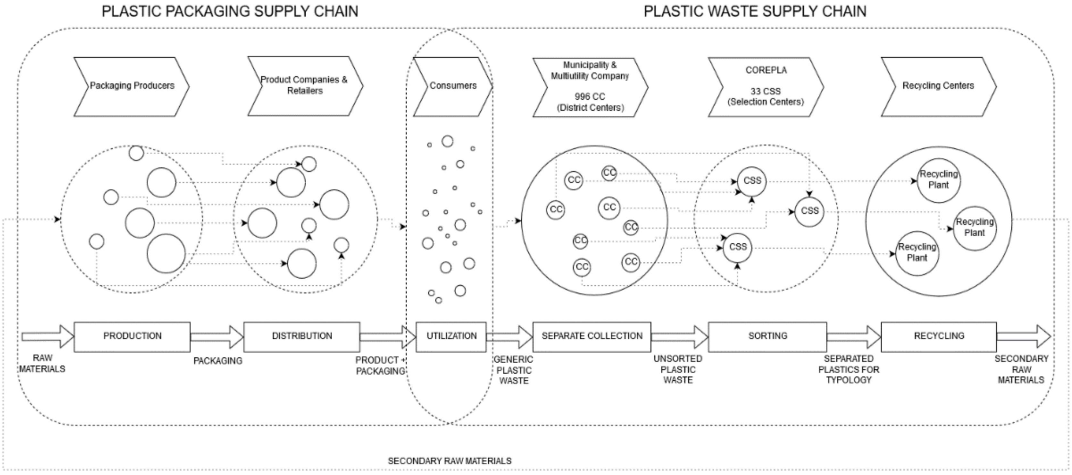

Fig. 1. Simplified plastic packaging value chain in Italy

3.4. The plastics ecosystem

Figure 2 represents the national Money and Material Flow (MMF) for the plastics recycling supply chain. The dashed lines represents the money flows, where the direction of the arrows means who pays who, while the filled lines represent the materials flows. The plastic packaging ecosystem, in terms of materials flows, starts from the producers, i.e. packaging and product producers, who use raw (primary or secondary) materials to produce the plastic packaging. Consequently, they sell the products, and the packaging, to the consumers.

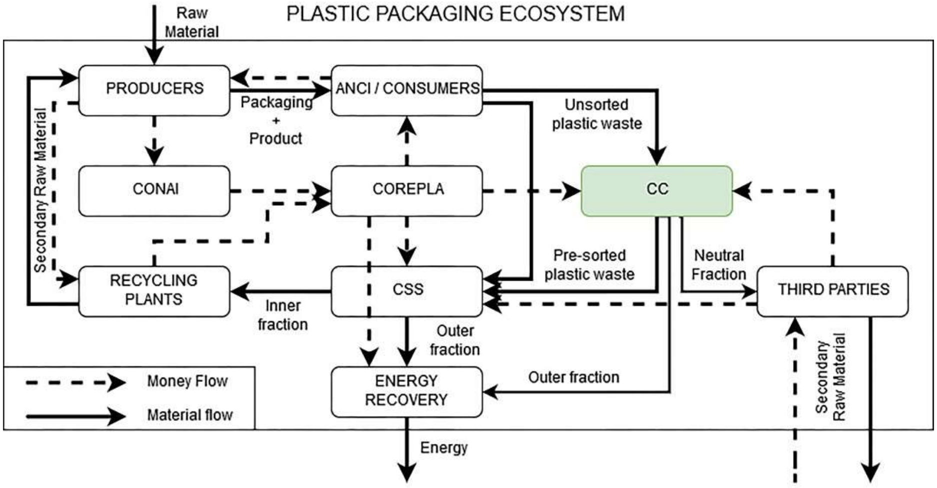

Fig. 2. Money and Material Flow for the plastic packaging supply chain in Italy

In the graph it is represented by ANCI ("Associazione Nazionale dei Comuni Italiani / National Association of Italian Municipalities") and consumers' box. Then the municipalities (i.e.

ANCI) collect the plastic waste with separate collection, generally through a private or public multi-utility service company, and bring the waste to the CC (the District Center), owned by a third party company or by the municipality/multiutility itself, for the pre-sorting and cleaning process, or directly to the CSSs (the Sorting Centers) owned by COREPLA's subcontractors. The CCs, and the CSSs, sort the plastic waste dividing them into 1) an inner fraction, i.e. the recyclable plastics; 2) an outer fraction, the waste part composed by other materials (glass, paper and not-packaging plastics) and 3) a neutral fraction, products not recognized by CONAI-COREPLA (Consorzio Nazionale Imballaggi, National Packaging Consortium). In Italy there are 996 CCs held by municipalities and local multiutilities while COREPLA holds 33 Sorting Centers (CSSs), scattered throughout the national territory (MISE, 2018): the choice of center happens according to a territorial proximity principle, in order to reduce both costs and transportation environmental impact. At this point, the material is ready to be recycled.

The outer fraction, generally, ends to District Heating (DH) plants, in order to recover the energy of the plastics by incineration, or to landfill. The neutral fraction is sold to third parties who recycle the materials and resell it on the materials' market. Finally, the inner fraction, the most valuable fraction of the plastic waste is brought to recycling plants which transform the waste into secondary raw materials, ready to be sold either again to packaging producers or for the production of other products. Although the Material Flow seems to be decentralized, involving several private and public stakeholders, from the municipalities to the citizens, include private companies, the Money Flow is completely centralized and guided by a unique actor, COREPLA, as member of the CONAI system of consortia which manages the whole post-consumer packaging material in Italy. COREPLA signs contracts directly with municipalities or operators, as District Centers or Sorting Centers, who receive the approval for the treatment by local public administrations. Indeed, the packaging ecosystem Money Flow can be read again starting from the packaging producers who pay a fee for each packaging sold on the market to CONAI, the general packaging Italian consortium. CONAI pays directly COREPLA for each plastic packaging. COREPLA, with the fees received by the private companies, pays 1) the municipalities, or the local multiutilities who collect plastic waste and 2) the owners of the District Centers who pre-sort and clean the unsorted plastic waste, 3) the subcontractors who own the Sorting Centers and the owners of the District Heating systems for Energy Recovery. Finally, the Recycling Plants, who receive the final sorted and split plastic materials, pay again COREPLA to receive the inner fraction of the plastic wastes and sell the secondary raw materials, after the recycling process, to the producers.

3.5. A case-study in Turin: a starting point to understand the complexity of plastics recycling chain

The selected plant is classified as a CC; it is a district center from which the selected plastics will be moved to the CSS, the Sorting Center. It deals with plastic packaging and other kinds of bulky waste, in fact in this case-study the authors choose to focus only on plastic waste. The plant holds ISO9001 (2015), ISO14001 (2015) and OSHAS 18001 (1999), certifications and it has the main goal of storing and selecting non-dangerous waste to facilitate the selection process to generate secondary raw materials to reintegrate in products' life-cycle.

The plant is authorized to treat up to 66.5 ktons per year of waste. In 2018 it treated 23 ktons of waste, fulfilling around 34.6% of its potential. This is an encouraging figure, as in the previous years the amount of generic plastic waste collected was lower. Piedmont increased from 2017 its amount of generic plastic collected by 14%. On the other hand, only around 19 ktons consisted of plastic packaging, while around 4 ktons made up the outer and the neutral fraction. According to the quantity of plastic packaging given to the CSS, COREPLA gives to the CC an economic reward. The price per ton varies according to the kind of packaging given to the CSS as described by Table 3.

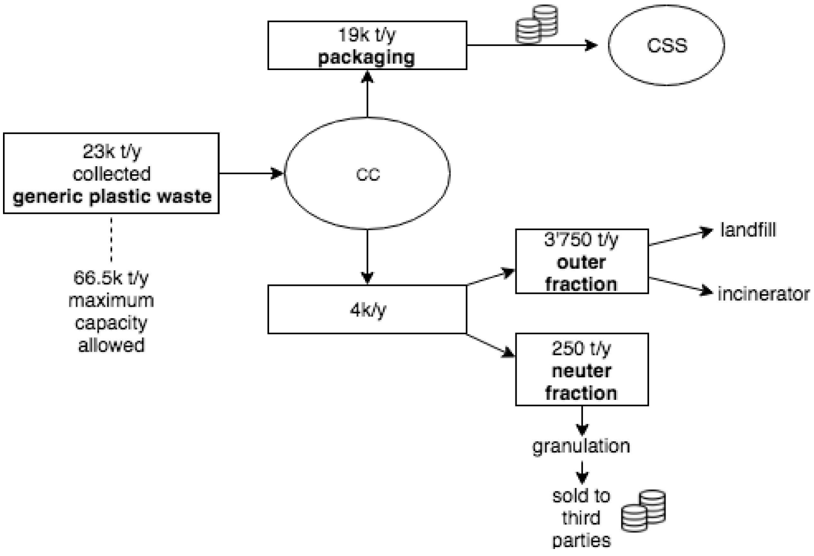

Fig. 3. Plant's Material Flow

Table 3. Flow of plastic materials and reward per tons on material (ANCI-COREPLA, 2014)

Flow	*Euro per ton*	*Description*
A	303	mono-material of urban origin
B	80	mono-material of non-domestic origin with a relevant quota of tracers
C	394	mono-material of urban origin, mainly CPL ("Contenitori Per Liquidi / Beverage Container")
D	295	multi-material of urban origin

Each flow has a maximum percentage of allowed outer fraction (FE - "Frazione Estranea"), in order to be accepted by the CSSs and COREPLA according to the national ANCI-CONAI agreement for the period 2014-2019: A) FE < 20%, B) FE < 20%, C) FE < 10% and D) $\%FE_{Plastic} < 22\%$. For the Flow D, $FE_{Plastic}$ is quantified according to Eqs. (1, 2):

$$\%FE_{Plastic} = \frac{PlasticPackaging * \%FE_{tot}}{PlasticPackaging + OtherPackaging} \tag{1}$$

where:

$$\%FE_{Tot} = \frac{FE * 100}{PlasticPackging + OtherPackaging + FE} \tag{2}$$

PlasticPackaging and *OtherPackaging* represent the amount of plastic and of other materials in tons. When only mono-material is given to the CSS the formula to calculate the economic reward is while, when the flow is multi-material, the economic reward is given by the formula where CN is the net fee, Cu the unitary fee per ton, IC the quantity of packaging in tons, FE the outer fraction in tons and Cfes and Cfer the unitary cost for selection and recovery of outer fraction, respectively. The COREPLA reward constitutes the main source of income for the plant.

On the other hand, the plant deals with different stakeholders, who influence the flows of incoming materials, as well as the end market of recycled plastics. The first actor which influences the plastic cycle is composed by the citizens who decide whether or not to respect the separate collection. Secondly, Amiat, the local multi-utility of the City of Turin, plays a key-role as the company which steers waste management, in which the plant plays an active role. Amiat collects waste, including plastics, which reaches the plant on a daily basis, taking it from selected areas of the city. Once treated by the plant, specific plastics are sent to specific CSSs. Specifically, the consortium buys plastic bales from the selected plant. Afterwards, in the CSS the bales of plastic material would be treated and separated in diverse types such as: colourless PET bottles (mineral water, soft drinks, etc.), blued PET bottles, PET bottles of other colours, high-density polyethylene bottles-HDPE; polyethylene film (bags, bottle packs, appliance packs, etc.) and mixed packaging (mainly rigid and flexible polyethylene or polypropylene). The complex network of stakeholders created by the plastic packaging ecosystem is depicted in Figs. 1 and 2.

3.6. Establishment of CONAI: an important actor for the recycling system of plastic packaging.

The regulation relating to the management and recycling of plastic packaging dates back to Legislative D.Lgs 22/97, the so-called "Ronchi Decree". This decree gave rise to CONAI, which manages exclusively the packaging waste. It clarified the current collaboration between public and private sectors: Ministries, Authorities and Public Administration, on one side, and Material Consortia like COREPLA (for plastics) on the other (CONAI, 2017). On the other hand, it led to the creation of a private market for the recycling of packaging (Pierobon, 2012). After that legal framework, several laws disposed by national and European institutions determined the conditions of work of COREPLA and CCs as the case-study.

As mentioned before, COREPLA only accepts plastics from packaging as it is under CONAI regulation (CONAI Environmental Declaration) which obliges packaging producers to pay a fee to guarantee the collection and the recovery of the packaging sold in the Italian market (extended producer responsibility). Thus, the recycling potentiality in Italy is not fully disclosed, as many plastic products are not accepted by CONAI (2018) and, consequently, they are discarded during the sorting and the selection processes within the CC and, afterwards, within the CSS plants. In the case of the selected plant, pre-sorting is useful to separate the plastic packaging from the non-packaging. These conditions and constraints depend on the legal and administrative barriers which regulate the whole process.

Currently, CCs as plants of plastic treatment receive compensation linked with the amount and the quality of separate collection. It decreases as the "outer fraction" increases with respect to the plastic packaging, i.e. the inner fraction, on the basis of the provisions of the ANCI-Conai Framework Agreement (Ciotti and Paravidino, 2018). As declared in the Agreement, the plant works on sorting only plastics from packaging into material to recycle and to use other potentially recyclable plastics for energy recovery. Although the amount of packaging flows is considerable, as COREPLA offers a financial compensation for 14 types of flows, the packaging constraint prevents a larger proportion of plastics from being sent for recycling. The Agreement defines as outer fractions, objects of daily use that are very common: plastic cutlery, toys, construction products and, more generally, any object that is not intended to be used as a packaging. For this reason, the 16% of the total amount of plastics received by the plant is considered by the Agreement as outer fraction, and it is actually sent to incinerator or to landfill.

At European level, the legislation seems to have taken a step forward, with the entry into force of Directive 2018/852, which provides for an extension of the responsibility of the packaging producer to ensure high quality and recyclability. This action could influence the future quality of input flows received by the plant; however it does not boost the recyclability of other plastic products.

To sum up, at legislative level there is a clear need to improve another aspect: the reusability and durability of plastic products. To reach these goals, four main administrative challenge are identified to improve the legislation about plastic reuse and recycling. They involve different policy fields: 1) taxes on the use of virgin plastics or differentiated value added taxes for recycled plastics; 2) reform of support for fossil fuel production and consumption; 3) introduction of recycled content standards, targeted public procurement requirements, or recycled content labelling; and 4) education and awareness campaigns in order to stimulate demand for products containing recycled plastics (OECD, 2018). The first step for plastic reusability is actually represented by Deposit Return System (DRS): 10 European countries have allowed more than 130 million citizens to return and reuse empty beverage containers (CM Consulting, 2016). However, this plan should be shared by all EU Member States, including Italy, to guarantee significant outputs. These aspects explain not only the quality of the work of the selected plant, but also its purpose in the current Italian plastics management ecosystem.

4. Conclusion

The plant considered in this case-study plays a relevant role in the plastic value chain. After an analysis of the flows (materials and money) from the plant and a careful regulations' evaluation, some interesting conclusions can be drawn. From an administrative and legal point of view, the renewal of the current legislation on management might be able to improve the whole recovery system; at the same time, it could open new scenarios for the plant. If this legal update took place, the plant would work with a wider amount of plastics which would be sold to recycling public and private companies. In particular, the D.lgs 22/97 should be updated, in order to include products different from plastic packaging, thus enlarging the range of recyclable products; the ANCI-CONAI agreement should be revised as well, in order to allow municipalities to bring to the CCs not only plastic packaging but other kinds of plastic as well. A relevant aspect which comes up from this research is that plastic recycling system is based on a material and product selection instead of only on a material one, indeed. Hence, from a recycling point of view, the material is the subject and not the product. Opening the access to the recycling process to all the products made of plastics could simplify the separation operations both from the citizen and the CCs, or more in general, the separation plant perspective. The regulation on products should be applied more to the recycle field, such as the Deposit-Return System for beverage containers, e.g. for glass bottles or plastic cups, while for the recycling field we should focus the attention on materials.

On the one hand, Chemistry and more in general the technological field, should continue its effort towards the innovation of materials that are easier to recycle. The challenging work in the research addressing an increasing sustainability for a pivotal material like plastic is jeopardized by the high performances required for this material. These requirements lead to a change in our behavior as consumers and this is an interesting challenge.

On the other hand, this "material" approach might be difficult for economic reasons because the payment for the recycling system should be made by the companies which produce plastic and not by the packaging producers. This could further hamper the cost-effectiveness of recycled plastic because, considering the cost of virgin plastic is influenced by the cost of oil, any additional cost bore by companies might be reflected in the final price of recycled plastic. A possible solution might consist in the introduction of tax relieves for the companies but the complex cost structure of plastic production should be further deepened to provide more insightful suggestions. Furthermore, the case study points out how plants as the CC considered continue to play an important role in the plastic waste treatment.

In conclusion, this research shows the future challenges which are going to be faced by every actor who want to change the process with a circular perspective. A circular approach might deeply change the function and the work of CCs in the plastic value chain and opens new scenarios of study.

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FULL PAPER

Urban Living Labs, Circular Economy and Nature-Based Solutions: Ideation and Testing of a *New Soil* in the City of Turin Using a Multi-stakeholder Perspective

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Abstract

In the attempt to foster circular economy (CE), cities are increasingly adopting urban living labs (ULLs) as sites of co-production aimed at testing alternative solutions based on the reuse of products, reduction of consumption and recycling of materials. Taking this perspective, our study adopts an exploratory research design to discover the pragmatic implications emerging from a case study. The City of Turin joined proGIreg, a European project that entails the regeneration of former industrial districts by means of nature-based solutions (NBS). Ranging from aquaponics to green roofs, seven NBS have been experimented in Turin, which rely on the use of natural systems to tackle social, economic and environmental challenges efficiently and sustainably. Among them, the most promising is related to the production and test of the '*new soil*', a blend obtained by mixing earth materials coming from construction sites with compost, zeolites and mycorrhizae. The case herein presented is interesting to analyse for the multi-stakeholder management setting used, where public institutions, private companies, research institutions, citizens and associations collaborated in the co-creation and testing phase of the NBS. Consequently, the data collected through participant observation and direct interviews allow researchers to describe multi-stakeholders' dynamics and how they work. Thus, this paper narrates a micro-contextual experience while providing a critique. Results include an analysis of the unique combination of different stakeholders, which strongly impacted on the management and the effectiveness of the entire project. By consequence, the paper offers both theoretical contributions to the relational branch of stakeholder theory and practical evidence in demonstrating the importance of the relational branch of the theory over a more traditional transactional view.

Keywords Circular economy · Urban living lab · Nature-based solutions · *New soil* · Sustainable transition · Turin

Introduction

Urban living labs (ULLs) are deemed to be innovative policy processes developed around the concept of multi-stakeholder engagement, where co-producers explore, examine, experiment, test and evaluate innovative ideas and alternative solutions in a real urban setting. ULLs can be, in fact, unusual sites where stakeholders can cooperate and collaborate to test innovations designed to tackle the grand challenges that affect cities and megalopolis worldwide, such as soil consumption and erosion, food access, social policies and assistance to vulnerable populations [1]. Adopting a similar viewpoint, nature-based solutions (NBS) are technologies, actions and business settings developed to preserve sustainability through a recovering process of resources based on natural production systems [2]. Acting on a larger scale, the circular economy (CE) paradigm proposes to revise the traditional model of development and consumption, promoting the reuse of products, the recovery of materials and the recycling of waste [3].

CE policies and business ideas have in common with NBS the need for spaces to test their reliability, scalability and future sustainability [4]. The literature recognises in the ULLs potential arenas of experimentation [5]. For instance, according to Doherty [6], ULLs are good examples of ways through which local farmers can collaborate with scientific institutions to develop a resilient urban food system. Despite the fact that the research on CE and NBS is proliferating in a wide range of disciplines, the matches between ULLs to test CE and NBS solutions are somehow limited. At the same time, due to the specific features of each urban environment, the stakeholders populating a ULL can be different, and arriving at a shared consensus into a ULL is not always a linear process.

ULLs, NBS and CE might be complementary in promoting policies and actions to regenerate and redesign the urban environment, but to be effective, they should be designed and tested to reach a shared consensus among the actors involved. Prioritisation and salience are usually two fundamental principles applied by scholars of stakeholder theory [6]. Unfortunately, when stakeholders are deeply bonded in a territory and among themselves, like in the case of a dynamic and critical urban environment, such principles lose their applicability, as they are thought to work when relationships are transactional [7]. Transactional perspectives of the stakeholder theory are usually designed for the normativism branch of the theory itself, entailing that a particular stake is owned by a well-identified party [8]. As recently supported by Casalegno et al. [8], in analysing the dynamics of actors towards a CE problem, the transactional approach fails, because CE requires to extend the analysis including the relationships among stakeholders and the reallocation of stakeholder roles. The presence of multi-stakeholder dynamics, in a context related to CE in urban spaces, is recognised by scholars as one of the most intriguing research problems of modern stakeholder theory [9].

In our paper, we present a case study of a systemic experience where a *'new soil'* (artificial ground or technogenic soil) is tested as one of the most promising NBS for the urban requalification projects of the City of Turin (Italy), where the ULL is placed. The new soil presented in our paper is a blend obtained by mixing earth materials coming from construction sites with compost, zeolites and mycorrhizae and developed in the context of the proGIreg European project (productive Green Infrastructures for urban regeneration). ProGIreg is an initiative planned and funded by the European Commission (EC), which proposes the experimentation of NBS in suburbs with a relevant industrial past. The 5-year project (2018–2023) is part of the wider Horizon 2020 funding programme, and it is based on the collaboration between four front-runner cities, which lead directly to the NBS experimentation: Dortmund (Germany), Turin (Italy), Zagreb (Croatia) and Ningbo (China). The City of Turin focused its efforts on building a ULL composed by seven different NBS in the neighbourhood: new regenerated soil (NBS 2), community-based urban farms and gardens (NBS 3), aquaponics (NBS 4), green wall and roofs (NBS 5), accessible greenway and cycling corridors bordered by autochthonous tree species (NBS 6), local environmental compensation of big events processes (NBS 7); activities of pollinator biodiversity defence aimed at monitoring the life conditions of bees and butterflies to assess the pollinator friendliness of the urban area (NBS 8).

In this framework, the new soil case study could represent a starting point for future investigation about the potential overlapping of ULLs, CE and NBS. Thus, we aim to shed light on how to examine the interplay between ULLs, CE and NBS, identifying in a multi-stakeholder approach a key driver of success and, lastly, providing a critique of the case tested. The paper is divided into four main sections. In ‘Theoretical Framework’, we briefly introduce how urban living labs, nature-based solutions and circular economy concepts are reciprocally interconnected. ‘Methods’ presents a methodological focus and the background of the case with technical insights, while ‘Results and Discussion’ provides the multi-stakeholder analysis and the critique. ‘Conclusion’ offers final remarks and future research avenues.

Theoretical Framework

As pointed out by the Sustainable Development Goals (SDGs) of the United Nations [10], the creation of partnerships (represented by the SDG 17) is one of the most critical suggestions, as it gives the key operating guidelines. As SDGs are by nature interconnected, the involvement of different stakeholders can be helpful in providing different perspectives about the same issue. In this paper, ULLs, CE and NBS are concepts reciprocally interlinked, representing an example of *where* partnerships can take place (the local innovation ecosystem), *how* in the sense of what adopted principles should support and, lastly, the content of such experiments (*what*).

ULLs: Where

ULLs, inspired by the traditional living lab definition of MIT of a ‘living laboratory’ [11], transpose its logic to an urban scale with a specific multi-stakeholder and participatory nature [12]. Co-creating innovations and testing them in a real-life context is one of the main aims of this study [13]. A recent study on ULL sees the existence of similarities between ULL and forms of open innovations, like the ones of n-tuples helix, where a wide range of actors, including public institutions and citizens, are simultaneously engaged in a collaborative practice of co-production [14, 15].

ULLs are characterised by a strong presence of municipalities and public actors who act like principal leaders and coordinators, handling social challenges that are peculiar to that specific area [16]. At a city scale, ULL initiatives are engines for urban regeneration and requalification, especially in those areas that are polluted and where the social fabric might be compromised by the industrial downturn [17]. In such vulnerable areas, ULLs can generate social and sustainable transformations that can also be developed in line with CE principles [18]. Consequently, multi-stakeholder partnerships should be created to engage actors in the process of designing, developing, implementing, testing and evaluating an innovation [19].

Circular Economy: How

Circular economy has proven to be an innovative yet multidisciplinary paradigm, despite raising many questions about the feasibility of technological innovations, changes in regulations and the need of starting new alliances [20, 21]. To boost European economies towards a more circular one, the European Commission has recently published its Circular Economy Action Plan, where it calls all the actors of the economic system to work together under its guidance [22]. The transition from the 'take-make-dispose' linear principle to 'reuse-reduce-recycle' of resources requires investments to test and prototype innovations and business models [23]. ULLs could be used as a fertile ground for circular economy innovations and experiments [23]. Today, and more in the near future, cities and megalopolis will be called to solve pressing social issues, such as supporting vulnerable and poor populations, guaranteeing food access and food security to everyone [24]. For this reason, ULLs can be identified as the right physical places where citizens and end-users actively look for solutions, closing the loops in terms of resources and energy, enacting virtuous partnerships between public and private actors [25, 26].

Moreover, the European Union set its goal to zeroing the soil consumption by 2050. Looking forward to this ambitious goal, recovering abandoned areas might be a step in the right direction [27]. Notwithstanding the costs and high risks involved in regeneration processes, implementing circular economy processes could help in reducing costs in terms of virgin soil use, generating at the same time positive externalities regarding social and environmental impacts [28, 29]. The circular approach allows the creation of a 'community of relationship', which, along with reactivating and recovering resources already in the system, might help in exploiting unexpressed potential [30]. Indeed, circularity might be identified as a feasible option to increase efficiency and achieve synergies among different stakeholders in the cities, thus being a key driver for urban regeneration processes [31]. The ultimate goal would be the rise of a circular city, where the consumption of virgin natural resources would be reduced.

Several studies acknowledge the importance of the relationship between urban regeneration, stakeholders' consideration and circular processes [31–33]; however, to our knowledge, no research links the idea of soil recovery with circular practices in the context of an urban regeneration process. To this end, this research presents the case study of the City of Turin. We discuss the results of new soil experimentation as an example of circular practice, aimed at the urban regeneration of the dismissed area of Mirafiori Sud.

NBS: What

NBS can be defined as 'any transition to using ecosystem services with decreased input of non-renewable natural capital and increased investment in renewable natural processes' [34]. Several NBS applications have been developed during the last years in a wide range of fields, from agriculture to urban management [35, 36]. Recent literature in environmental studies looks at NBS as key leverages to underpin sustainable and circular activities in modern cities [37]. In that sense, green infrastructure can increase the green coverage in the urban environment and create new synergies within city ecosystems, coupling humans and the environment.

Financially supported by the European Union, NBS can play a pivotal role in assisting cities during the sustainable transition, and this journey can start from ULLs [38]. Hence, ULLs' strength lies in the integrated perspective in tackling social challenges [39]. In this effort, NBS are deemed to be open innovation systems based on the engagement of multiple actors, capable of proposing unconventional solutions to stimulate new green economies and green jobs in urban areas [40]. When looking at soil management, NBS usage is not mainstream. However, NBS can be critical factors in reaching sustainability in soil management, considering they use the natural flow of matter and energy often exploiting local solutions at the same time. Therefore, NBS could help in restoring ecosystems, with an eye on both sustainability and cost-effectiveness [41]. This is possible because using NBS would entail less need for maintenance, while usually traditional infrastructures require high-maintenance strategies, relying on external sources of inputs and capital [42].

The process of urban deindustrialisation took place in thousands of cities around the world, leaving many brownfield sites abandoned due to the high recovery costs [43]. According to Song et al. [43], in such situations, NBS might represent a feasible solution, providing at the same time social, economic and environmental benefits as, for instance, improving living conditions for people living in these areas while increasing real estate value through the recreation of the ecological habitat lacking in brownfields. In the case study presented in this research, new soil represents a NBS aimed at directly improving the condition of a post-industrialised brownfield area of Turin, named Mirafiori.

The Potentialities of Multi-stakeholder Management Perspective in ULLs

Scholars of stakeholder management theory are stressing the importance of a multi-stakeholder management perspective by public institutions [9]. According to the recent work of Wicks et al. [9], the involvement of different actors is a prerogative to create a democratic and collaborative process in creating public policies. According to this view, the relational perspective of stakeholder management is opposed to the transactional one, widely used by private institutions. Freeman et al. [44] clarify that the relationships among stakeholders play a vital role in aligning all the stakeholders' interests around a purpose, and its importance increases in the case of public values and public policies. The result is to move away from the pure analysis of the nature of the transaction and to devote more attention to the narrative on the relationships. The quality of the relationships, the interactions and the values that ground such relationships are fundamental.

Unfortunately, studies involving multi-stakeholder value creation in implementing a public policy around a CE issue are scarce [8, 9]. Studies involving public institutions are usually narrowed towards a stakeholder analysis to orient processes of communications, while less frequently the analysis has the strategic intent of interpreting relationships between actors to better frame future policies for co-management or co-design public initiatives. Nevertheless, cases of effective participation for the so-called new public governance are emerging [45]. According to the new public governance paradigm, scholars emphasise the role of public institutions as leader of open innovation and collaboration, with the attempt of eliminating the command-and-control approaches to policy [46].

Wicks et al. [9] link this shift to the participatory democracy literature, especially for the need of involving multi-stakeholder partnerships in the formation of a policy process, with collaborative solutions and with an increase of civic engagement. According to the authors, the study of multi-stakeholders' dynamics in localised systems deserves more attention, especially regarding policies that affect the sustainability of the natural environment. Citizens, public managers, practitioners, academics, companies and investors are among the stakeholders that can be involved in the design of a ULL, where the ULL is a localised system [6]. In a ULL, the knowledge-generating process takes place through several rounds of co-design sessions, and it outputs a business model that aims to guarantee the long-term sustainability of the project itself while simultaneously guaranteeing proper levels of environmental preservation of resources.

The novelty of the application of CE principles is that the entire business model can be concretely co-designed with the intent of reducing costs, hence improving the economic sustainability of the whole ULL by retrieving returned and recycled material [7]. Orchestrating an effective multi-stakeholder management model for CE in public policies is of paramount importance also for the growing interest of stakeholder management researchers. As clarified by the team of Freeman in one of his recent papers, 'when stakeholders stop being treated and seen as abstract entities and they become individuals with common and integrated goals, the value created has higher chances of being recaptured in a CE system' (p. 160). With this study, we want to contribute to narrowing the gap presented in stakeholder theory, offering a valid example of multi-stakeholder management of an NBS. In the following section, the NBS will be in-depth presented within the research design.

Methods

Case research enriches the understanding of emerging phenomena through a multifaceted perspective [47]. Specifically, the research design applied in our study privileges a mixed method where data collection is based on interviews conducted during field observations and document analysis. According to Bergvall [48], case studies based on mixed methods apply content analysis on primary and secondary data sources. Moreover, case studies should be privileged in the context of living lab analysis, as through them, the researchers can offer a comprehensive analysis of fieldwork data.

As argued by Smith [49], a mixed method research applied in urban studies offers flexibility that best suits the research object and provides the advantages of a predefined structure without excessive rigidity. For instance, the narrative required to account for the process of testing a new soil can be different from the research methodology required to demonstrate the feasibility of other NBS solutions. Specifically, the research design applied in our case is an exploratory mixed method, a technique that is suitable in pragmatic cases where sustainability real-world practices are explored [50]. In addition, case studies serve the purpose of offering a pragmatic view of the multi-stakeholder management problem in a pluralistic context of the ULL where the new soil is tested.

Formulation of the Artificial Ground New Soil

This paper shows the micro-context of a ULL where the development and testing of a new soil composite have been experienced. Specifically, the testing of such new soil has been selected among the other experiments for being in an advanced level of development and execution. In the proGIreg framework, the artificial ground new soil has been formulated according to the following general composition:

- Building earth materials resulting from construction sites (particles with a diameter lower than 2 cm);
- Compost obtained from organic waste, in particular, plant waste;
- Natural zeolites, mainly chabazite;
- Natural mycorrhizae.

Mycorrhizae are composed of *Glomus* sp. GB67, *Glomus mosseae* GP11 and *Glomus viscosum* GC11. Mycorrhizae are inoculated in plants after planting as a microbial inoculation associated with a diversity of organisms, among which there are rhizosphere bacteria such as

Bacillus amyloliquefaciens BA41 and *Agrobacterium radiobacter* AR3; actinomycetes such as *Streptomyces* sp. SB14; saprophyte fungi such as *Trichoderma harzianum* TH01 and *Pochonia chlamydosporia* PC50 and ascomycetes such as *Pichia pastoris* PP59.

This new soil fits with the definition of NBS reported in the literature [34] as this mixture has been generated decreasing input of non-renewable natural capital, the virgin soil, as well as being consistent with the CE paradigm of reusing (soil already used in construction sites), reducing (the exploitation of virgin soil) and recycling (processing soil from excavation sites adding elements to create soil that can be redeployed).

It is important to notice that the composition of the inert soil recovered from the excavations depends on its origin. The mixture of excavated earth, compost and zeolites, impacts specifically on the top 15 cm of the land, while the mycorrhizae can highly vary in terms of quality and quantity, depending on the type of vegetation present in the area. Moreover, the final application affects the final formulation of the technogenic soil new soil. Hence, it is not possible to have a fixed mix respecting perfectly the same percentage of the component. On the contrary, the final composition must be tuned to meet all the necessary chemical and physical properties, to allow both a proper plant growth and compliance with regulations (presented in 'The Context of New Soil'). While tunability can be considered a constraint for the patentability of new soil, the customisation represents a solid market opportunity in providing the proper formulation for the final applications (i.e. geographical areas, biodiversity rate and climate variables shape the profile of the final application).

The Context of New Soil

The ULL of Turin has taken place in Mirafiori Sud, one of the most important post-industrial districts of the city, characterised both by large disused spaces and a meaningful cultural and environmental heritage. The site of the experimentation of the new soil has been an industrial area for years, placed along the southern border of the city, where buildings and plants of the automotive industries were established. In the last 30 years, Mirafiori Sud has been highly impacted by the deep economic downturn, which has forced one of the primary automotive manufacturers (former FIAT, now Fiat Chrysler Automobile Group) to dismiss most of the industrial sites located in the area. Therefore, most of the citizens of Mirafiori Sud employed in the automotive poles have gradually been laid off from the company, leading to a vacuum in employment and social terms. Nowadays, the historical and essential link between the Mirafiori Sud dwellers and the automotive sector has been radically weakened, leaving the district looking for a new economic and environmental identity.

Since the turbulent phase of industrial sites dismissal, the City of Turin has planned to regenerate and transform that area, getting inspired and following principles of the circular economy for cities [3]. Specifically, during proGIreg, the area has been identified by the public managers to be the best available space to test innovative solutions within a ULL. By means of the 7 NBS foreseen by proGIreg, the ULL has been trying to transform discarded buildings and brownfields into attractive spaces open to co-production and sustainable development processes (Fig. 1). The idea to carry out the experimentation on soil arose from the interest of the City to solve a significant environmental problem that affects most of Europe, namely, soil and land erosion [51] because soil is considered the 'most complex biomaterial on the planet' [25].

To build or restore urban green areas, one of the most implemented techniques is to use brownfield or excavating soil from the greenfield. This technique is, of course, unsustainable as tons of virgin terrain are removed from one place to recover those areas where the soil is

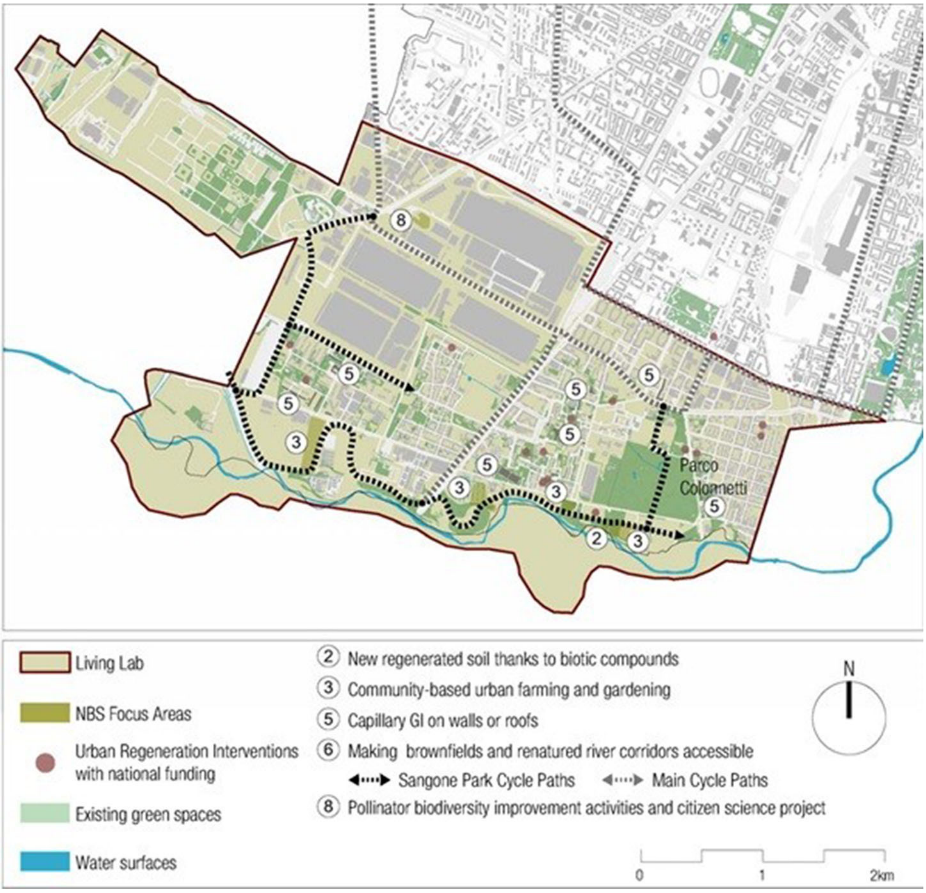

Fig. 1 The proGIreg Living Lab in Turin (source: RWTH Aachen University, Institute of Landscape Architecture). This image shows the proGIreg NBS collocation in one district of the City of Turin

inert because it has been for long years cemented. On the other side, such inert soil can become a resource mainly because it represents a vast area of the city grounds. However, according to the Italian regulation on earth materials (mainly regulated by the no. 161/2012 Decree of the Italian Ministry of the Environment and the no.120/2017 Decree of the President of the Republic), every new public green area, as well as every restorative initiative, must be carried out using high-quality soil in full compliance with certain parameters concerning the content of heavy metals.

Due to those regulatory constraints, the City of Turin has always struggled to implement and enable initiatives concerning the reuse of soil for the construction or renovation of urban green areas. Because the high relevancy of the topic about the use of excavated earth and rocks is crucial, starting from July 2019 onwards, all the regional environmental agencies have edited precise guidelines to identify excavated earth as a by-product excluded from the waste regulation, which has been formally introduced by the Law 128 of 2 November 2019 [43].

These guidelines help organisations define processes for the verification of environmental requirements, determine the percentages of anthropic material and determine the background values that are needed to reuse excavated earth and rocks [52]. Therefore, inside the proGIreg project, the innovative new soil has been tested in the ULL where an area of 2000 m^2, near the course of the Sangone River, has been dedicated to such an experiment. For the first time, researchers and public managers have started mixing up inert soil coming from construction sites with compost, zeolites and mycorrhizae, able to abide by the regulations and creating a new mixture that can be used to create new urban green areas.

Data Collection

In our case, field observations have been fundamental. Three phases compose the data collection. First, we conducted an extended content analysis of the scientific literature and material focused on ULLs, NBS, circular economy and proGIreg project. Moreover, to better frame the existent dynamics between the stakeholders involved in the project, we have analysed 24 official documents (proposals, reports and deliverables) provided by the City of Turin regarding the experiments and their strategic intent. Second, we did an in-depth participatory observation of 15 meetings organised by the City of Turin and proGIreg stakeholders, which allowed the researchers to observe and assist in the governance and stakeholder relationships from a privileged viewpoint [53, 54]. Third, we collected primary data through 12 semi-structured interviews that have enabled us to further explore the difficulties and barriers of the operational process. The total number of the interviews carried out conforms with the criteria of theoretical saturation laid out by Guest [55], and it allows us to start identifying meta-themes related to multi-stakeholder management, as theorised by Grafton et al. [56].

Interviews have been conducted from June 2019 to March 2020 and have involved a wide range of stakeholders and representatives (five civil servants, two representatives of the company and six technical experts). A summary of the interviews is reported in Table 1. Data resulting from the interviews have been used in interpreting those collected during the participant observation, where researchers were passively involved. Interviews have been conducted by means of non-directive questions, in order to unravel underlying multi-stakeholder dynamics. Meta-themes have been subsequently identified triangulating the different data sources. Examples of meta-themes that emerged during the interviews have been reported in Table 1.

Stakeholder Identification and Dynamics

Several actors have been involved in the ULL ecosystem where the new soil has been tested. First, the City of Turin with its personnel, public managers and civil servants has played the role of the orchestrator managing most of the legal concerns and bureaucratic implications. The city was also in charge of a study aimed at testing the possibility of effectively commercialising the new soil, given the legal requirements in terms of proprietorship. Only through the collaboration with ARPA Piemonte, the regional agency in charge of preventing damages and protecting the environment, the city had the opportunity to point out how the regulations and laws about the reuse of soil in urban areas should be changed to allow an extensive application of the new soil after the experiment.

In terms of public value and democratic participation, the geographical area identified for the ULL and its proximity to the Sangone river has been strategic to involve citizens in repopulating and living the park with its new urban gardens. During the public meeting organised with a representative of the citizens and local associations, it emerged that the area

Table 1 Summary of the interviews run during the period of observation

Interviewee	Gender	Organisation	Mode of interview	Date and length	Focus of the interview
Civil servant 1	F	City of Turin—Innovation and Smart Area	Face-to-face	04/02/2020 35 min	ULL framework Administrative barriers Stakeholders' dynamics
Civil servant 2	F	City of Turin—Innovation and Smart Area	Face-to-face	07/03/2020 60 min	ULL framework Administrative barriers Stakeholders' dynamics
Civil servant 3	M	City of Turin—Green and Public Space Area	Face-to-face	07/03/2020 40 min	Characteristics and aims of proGIreg Administrative barriers Stakeholders' dynamics
Geologist consultant	M	DUAL srl	Face-to-face	20/04/2020 60 min	Composition of the new soil Potentials and weaknesses of the new soil
Company administrator	M	DUAL srl	Face-to-face	16/05/2020 30 min	Scope of the experimentation Market opportunities of the new soil
Company administrator	M	DUAL srl	Virtual	10/06/2020 50 min	Scope of the experimentation Market opportunities
Citizen of Mirafiori 1	F	Resident of the area of Mirafiori Sud	Face-to-face	30/06/2020 35 min	History and social change of the neighbourhood Environmental issues
Citizen of Mirafiori 2	M	Resident of the area of Mirafiori Sud	Face-to-face	30/06/2020 35 min	History and social change of the neighbourhood Environmental issues
Citizen of Mirafiori 3	M	Resident of the area of Mirafiori Sud	Virtual	24/07/2020 40 min	History and social change of the neighbourhood Environmental issues
Associate professor of systemic design	M	Polytechnic of Turin	Virtual	14/08/2019 60 min	Value of the reuse of materials in the building sector Local issues in the regeneration of green areas
PhD student of systemic design	F	Polytechnic of Turin	Face-to-face	02/10/2020 30 min	Value of the reuse of materials in the building sector Local issues in the regeneration of green areas
Area manager	F	Environment Park	Face-to-face	05/10/2020 45 min	Market opportunities

was identified as one of the most proper locations to test the potential benefit of such regenerative intervention and also that the district is highly populated by elders and families with babies, which will would take advantage of the new gardens created with the new soil.

Three private companies have been involved to provide technical support. DUAL was the company responsible for the provision of the inert soil coming from its construction sites, which is usually discarded and not reused for any economic purpose. DUAL is already producing a technogenic soil similar to one created during the project. However, disregarding the environmental regulations hampers its placement on the market [57], and the convenience in the project lays in the possibility to correct the formula with the support of scientific stakeholders (i.e. universities). With the support of the laboratories, the development of a product that can comply with the environmental regulations is guaranteed.

Another company, ACEA, a local multi-utility company, has specific expertise in waste processing, and its role has been crucial in providing the mix of its compost with the earth materials, upgrading the quality of the inert one and turning it into a fertile mixture. Besides, ACEA has previous experience in commercialising composite and compost through specific distribution channels. One of the aims of the testing has been to evaluate the commercial power of such a mixture in terms of financial flows. Moreover, the conversion of the organic fraction of municipal solid waste in certified compost, to be applied as fertiliser in the new soil application, contributes to lowering the greenhouse gas emissions as it replaces fossil-based chemical fertilisers with compost.

Lastly, the company CCS Aosta has been involved as a provider of the mycorrhizae, a symbiotic association between a fungus and a plant [58] capable of increasing nutrient absorption and plant resistance. CCS studied a specific mixture to foster the growth of mycorrhizae on the plant roots for the new soil. In particular, CCS Aosta supplied a microbial inoculation composed of fungi, bacteria and yeasts listed in the ‘Formulation of the Artificial Ground New Soil’ section. The market of natural additives and the knowledge exchange about the use of mycorrhizae are opening new market segments, mostly linked to CE services. In addition, Bal-co Spa provided the natural zeolites, mainly chabasite, used as a fertiliser.

The scientific stakeholders were mainly the University of Turin, with its Department of Chemistry, which has been involved in the quality control of the soil, and it has played a role in managing specific tasks in business model evaluation, as well as collecting data to test the reliability and replicability of the experiment (with the Department of Economics). The Polytechnic of Turin played the role in supervising the coherence of the new soil experiment with the overall research project with many NBS and developing knowledge exchange dynamics between actors involved. Environment Park (EnviPark), a sort of local business incubator for green technologies, had a role in identifying, analysing and overcoming the technical barriers during the development of the new soil. Among its duties, EnviPark has been deeply involved in creating new knowledge and training materials linked to the development of the new soil, through training events and the creation of Massive Open Online Courses (MOOCs).

Figure 2 shows the stakeholders involved grouped by their specific area of intervention in the project: economic, social and environmental and innovation. Inside the red circle, there are the actors with a specific economic interest; in blue, there are public actors along with the civil society who hold a social and environmental interest in restoring and preserving the local area. At the same time, in orange, there are those institutions responsible for generating knowledge and innovation during the project.

Results and Discussion

The Development of the New Soil Business Model: Multi-stakeholder Implications

During the interviews, researchers collected data about the future opportunities or constraints of new soil with the intent of developing a business model. As suggested by Nesti [59],

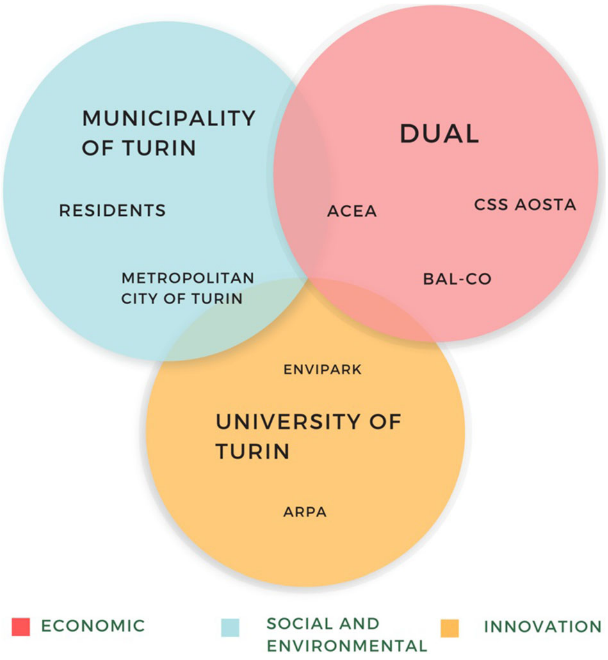

Fig. 2 Stakeholder divided by the area of interest (source: authors' elaboration)

experiencing a ULL could be a driver to help public administration and governments to innovate existent regulations and overcome bureaucratic barriers that can be a constraint for the scalability of sustainable solutions. In the case study of new soil, one of the most significant barriers in the development of a scalable business model has been the presence of strict environmental regulations that fix some limits in the presence of earth compounds when someone develops an earth composite.

The involvement of an actor responsible for revising and adopting the new regulations, ARPA Piemonte, has been of paramount importance in guaranteeing effective results of the NBS. Its involvement has been essential in letting the new soil be included as a regional best practice that, in turn, can represent a valid base to the development of less restrictive new regulations. In addition, the companies involved during the market validation phase have been advantaged by the presence of ARPA Piemonte because a change in the existent regulation can positively alter how the entire market works towards new products like new soil [52].

To guarantee that the outcome of the ULL for the NBS is effective, the business model of the new soil must be resilient, scalable and profitable. Scalability and profitability are usually seen as a prerogative of private and profit-oriented stakeholders and less in the case of environmental and social innovations [59]. Thanks to the multi-stakeholder perspective, indeed, scalability and profitability have been matched with the shared purpose of decreasing land consumption, reusing damaged soils and giving back to the community a post-industrial site. As such, the ULL of Mirafiori has been the place where actors have envisioned the future development of an innovation, understanding that scalability and profitability had to be matched with the interests of the citizens, communities and the public value [17, 60]. As stressed by DUAL interviewees, new soil turned out to be an 'up-cycled' product economically feasible as it offers the opportunity of reintroducing into the market earth and rock materials from construction sites usually used as filler materials or discarded in landfills.

As an example, in establishing its market price, private companies suggested that the new soil could be priced less than a virgin soil when sold to public institutions. This decision is justified by budget constraints that usually a public institution must stick to in renovating public and urban gardens. On the other side, the new soil is designed to be a highly customisable product, and as such, its market price for private companies and users could be increased. In the future, the new soil could become a versatile product, as the mixture of additives could be patented, and tailored consulting services can be developed around the concept of product-as-a-service logic. Besides, the collaboration with research centres could be vital in obtaining a sort of certification that could guarantee the high quality of the product. A niche market of low-impact buildings and green architectures could be targeted by new soil.

It is worthy to note that all the economic convenience calculus has been made by the public managers of the city, in collaboration with the University of Turin. Specifically, the power of the ULL here narrated is the match of different stakes with a specific purpose, that is, to let the experiment of new soil become/be beneficial to all the parties involved. In the next section, a critical perspective in terms of theoretical implications for stakeholder theory is provided.

Critical perspective on Multi-stakeholder Management During the New Soil Experiment

The collaborative design applied to the case of the new soil has been realised inside the boundaries of a ULL. As clarified by Jonas [45], new public governance implies that public institutions are deeply involved in an intricate net of relationships with a wide range of stakeholders, sharing a precise intent. In the project herein described, the ULL has incentivised the collaboration between different public and private actors, facilitating dialogue and the exchange of knowledge about the creation of a practical innovation for the CE.

With the help of universities and research centres, the city, through its public managers, has developed a pivotal role in connecting different actors with different needs and different inter-organisational dynamics [59]. As confirmed by Annessi-Pessina [46], the co-creation of public policy and the co-management of resources, among which there are natural resources, push the public institution to overcome the traditional command-and-control model to play a more active role. In our case, we find exactly a strong evidence of what Casalegno et al. [8] describe as real actors, and not abstract entities, with a specific purpose of collaborating into a CE system. With its multi-stakeholder model, the ULL has increased the level of trust and cooperation between the actors, and this could be an advantage for the future development of a concrete business plan, because it is possible to include different stakeholders' perspectives, ranging from suppliers to customers and final users.

In our case, the relational approach recently supported by the scholars of stakeholder theory aims to be more appropriate than Mitchell's model of salience [6]. For instance, in our case, there is not a prioritisation of the stakeholders' interest but instead a democratic and collaborative process that puts at the core of the project a common good (the soil protection). Moreover, instead of having fixed categories and fixed stakes, in our example, stakeholders' relationships have been built and will be strengthened in the future to guarantee that an experiment will be turned into an effective business model. With a pragmatic intent, the relational stakeholders' view of the theory does not discriminate stakeholders as fixed categories, but it focuses more on the nature of the relationships that could be fluid over time and on a specific geographical space.

Finally, our study shows how multi-stakeholders' dynamics happened into a localised system (the ULL) that, according to Wicks et al. [9], represent the unique settings through which a public institution can innovate its policies on the sustainability of the natural environment. This inclusive and democratic approach here discussed contributes directly to stakeholder theory, by providing an example of establishing relationships of value, even when a subject does not have any institutional power or interest in affirming its authority [7]. To sum up, in the case herein presented, we give evidence to the fact that the relational view of stakeholder theory is playing and will play a pivotal role for the CE, and sooner or later, whoever wants to operate in developing sustainability innovation will not be exempted from adopting a multi-stakeholder management model.

Conclusion

This paper presented the development of new soil, a new type of circular product that uses recycled terrain (a portion of brownfield already exhausted and excavated) to convert it into fertile ground that can be used for public green areas. The pilot project presented here is an example of a NBS developed within the European project proGIreg, aimed at supporting the experimentations of circular economy solutions in urban areas. Specifically, our study provides pragmatic insights of the experience tested in the ULL coordinated by the City of Turin (Italy).

While the literature on the practical experience of NBS tested in ULL is currently not vast, our paper has been designed to narrate a micro-contextual experience while providing a critique. The experience here described shows that a unique combination of different stakeholders has strongly impacted on the management and the effectiveness of the entire project. By consequence, our study adds value to stakeholder theory and especially in demonstrating the importance of the relational branch of the theory over a more traditional transactional view.

In our case, for instance, actors representing different stakes are not described as abstract entities but as dynamic protagonists collaborating together. In the respect of the new public governance role, the City of Turin has been pivotal in reconciling diverse interests, from private ones (like in the case of making pressure to change regulations) to public and common goods as well. Specifically, in our case, the recycled terrain of the post-industrial sites is turned into high-quality soil, which could represent a potential solution for the growing concern about the issue of soil scarcity. While matching the interest of opening new market opportunities for the private sectors, the city guarantees the stewardship of the citizens' rights to live in a more sustainable urban area. Nevertheless, more tests and interviews are needed to determine the exact economic convenience of the new soil, in relation to the need of complying with the national and local regulation while being competitive on the market.

The new soil illustrated here might represent an example of the co-creation of a CE innovation, but there is more. The city, through a multi-stakeholder management setting, has guaranteed a public and democratic participation of a wide range of interests. Moreover, with the ULL, the city has reinvigorated the public interest towards the purpose of limiting the depletion of scarce resources, and it has played an active role in promoting a factual change in the regulation not only for the benefit of the project but also for all the private actors operating in the backfilling soil market. Nonetheless, new soil is characterised by a varying composition, according to the building earth materials combined for its creation. This entails that the new soil's composition is flexible so that it can be modulated according to specific needs; on the other hand, the possibility of exact replication is hampered by both chemical features of the earth materials and the requirements of diverse contexts of urban experimentation.

While our study suffers from the classical limitations of a single case study, it offers a pragmatic perspective on stakeholders' dynamics in ULL. With the hype of CE projects and ULL, experts of stakeholder theory and sustainability experts need to engage in studies that narrate how multi-stakeholder's arrangement happens in practice. Future work is needed to explore the presence of critical issues, controversies, mission's drifts and organisational orchestrations of multi-stakeholders' partnership at a different developmental stage of ULL and in a different geographical context and apply to a wide range of NBS.

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Availability of Data and Material The interview track is available by sending an email to the authors.

Code Availability Not applicable

Declarations

Conflict of Interest The authors declare no competing interests.

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