POLYOL-BASED DEEP EUTECTIC SOLVENTS AS SUSTAINABLE ELECTROLYTES IN ELECTROCHEMICAL ENERGY STORAGE DEVICES

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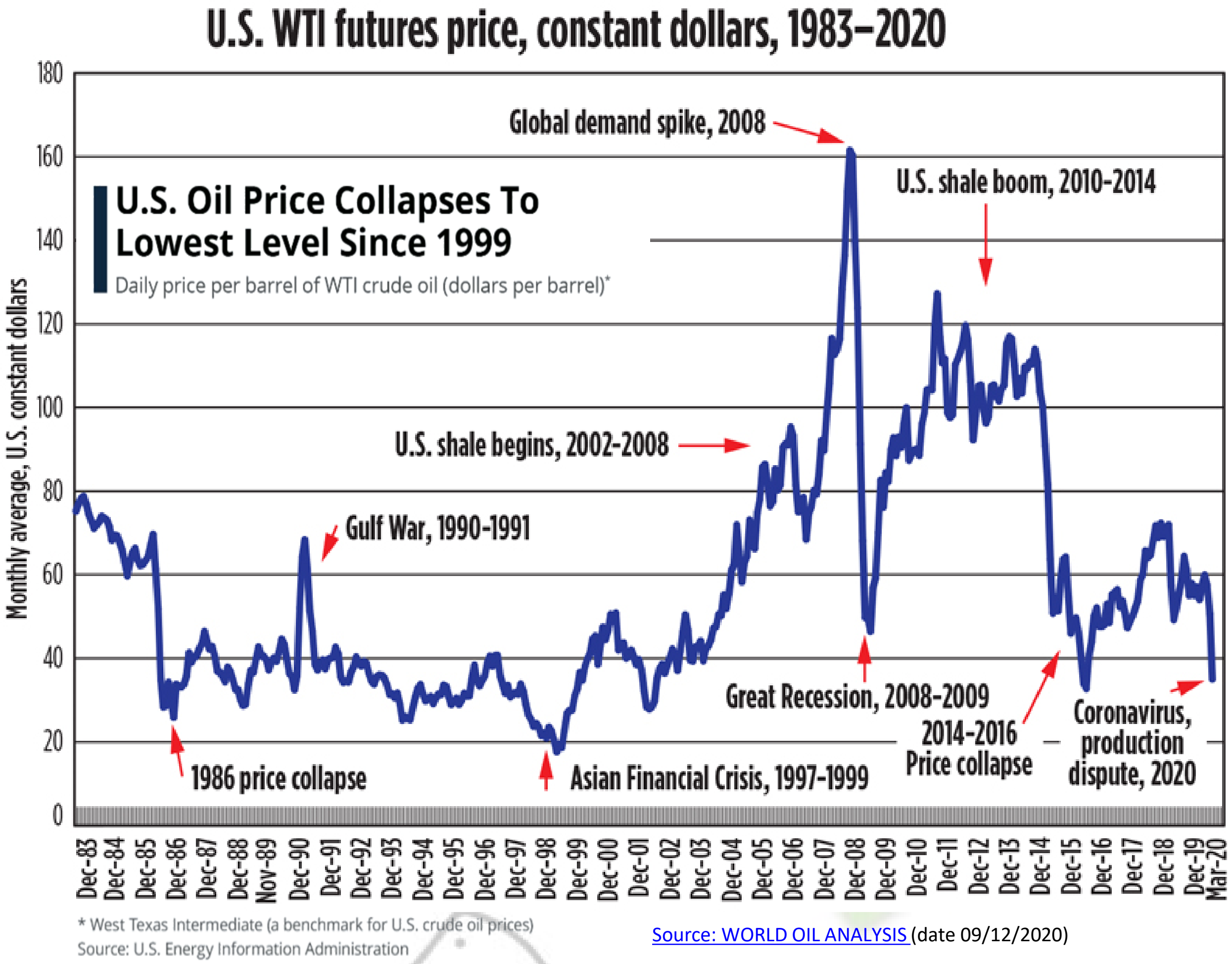


Source: WORLD OIL ANALYSIS (date 09/12/2020)

→ Global warming: suppression of CO_2

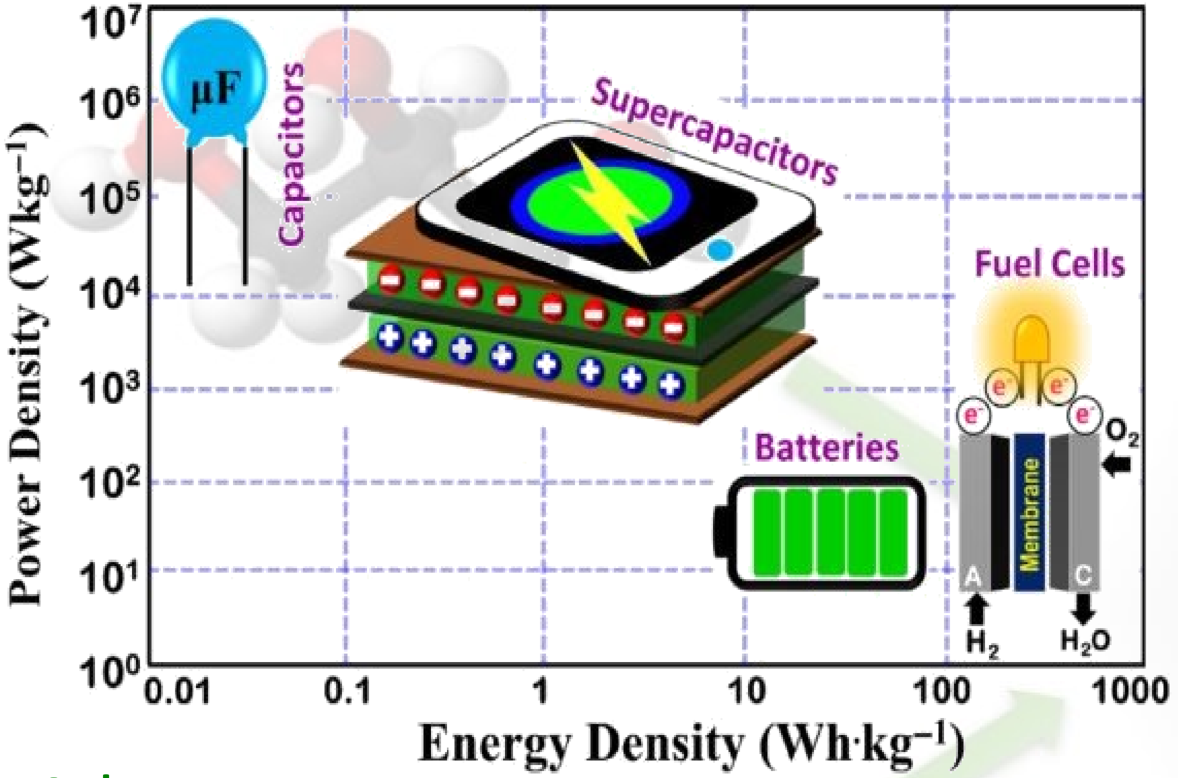
→ Demand of oil in the world (particularly in BRICs)

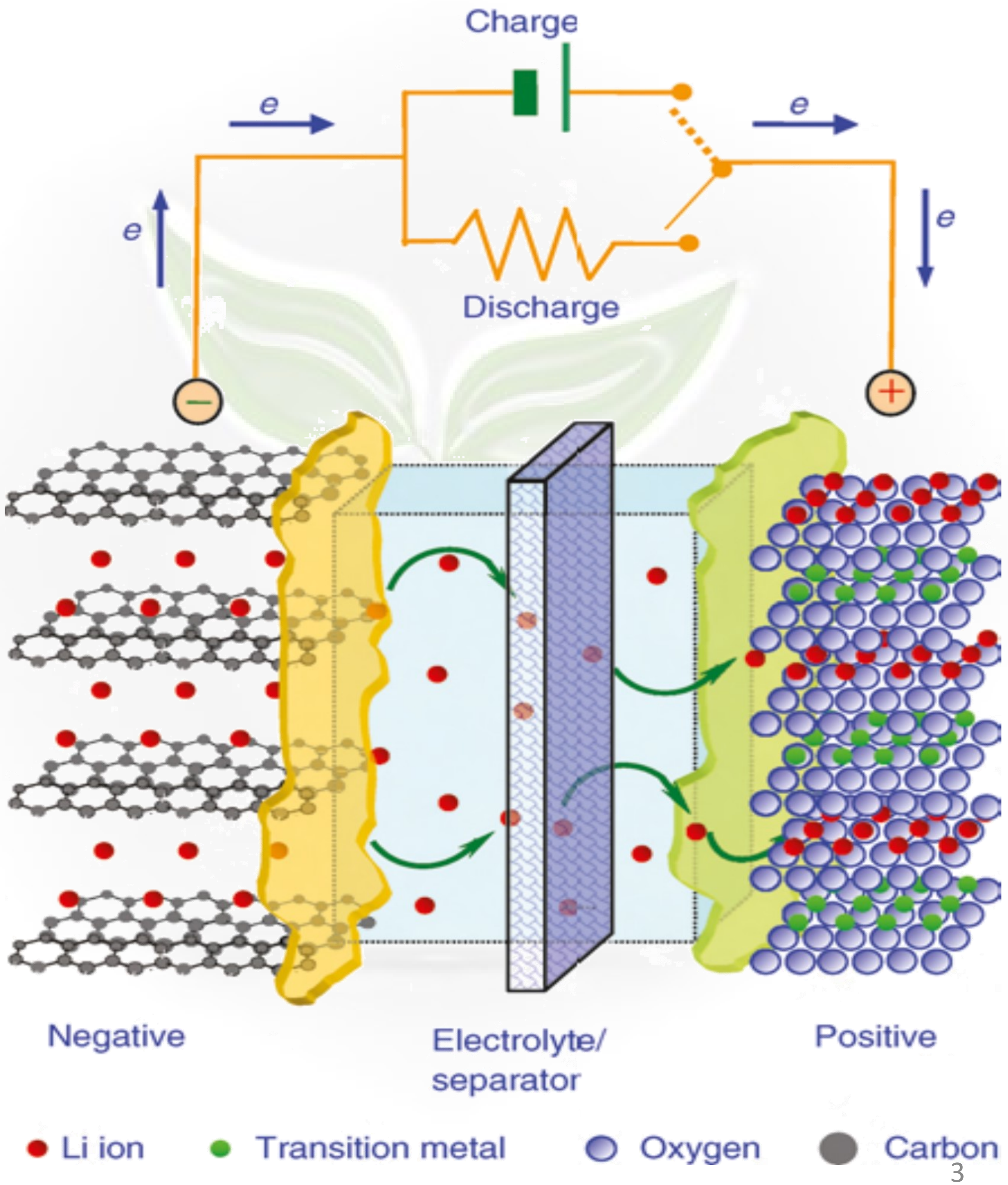
→ Energy Storage, Vehicle

Protocol Kyoto
Paris Agreement COP21

Intermittent alternative energy sources (REPs), as well as electric transportation, require convenient energy storage systems, e.g., batteries

ELECTROCHEMICAL ENERGY STORAGE SYSTEMS





Advantages:

- High Voltage
- High Efficiency (close to 100%)
- Compact, Light
- Fast Charge
- Long Life

Drawbacks:

- fragile
- Costly

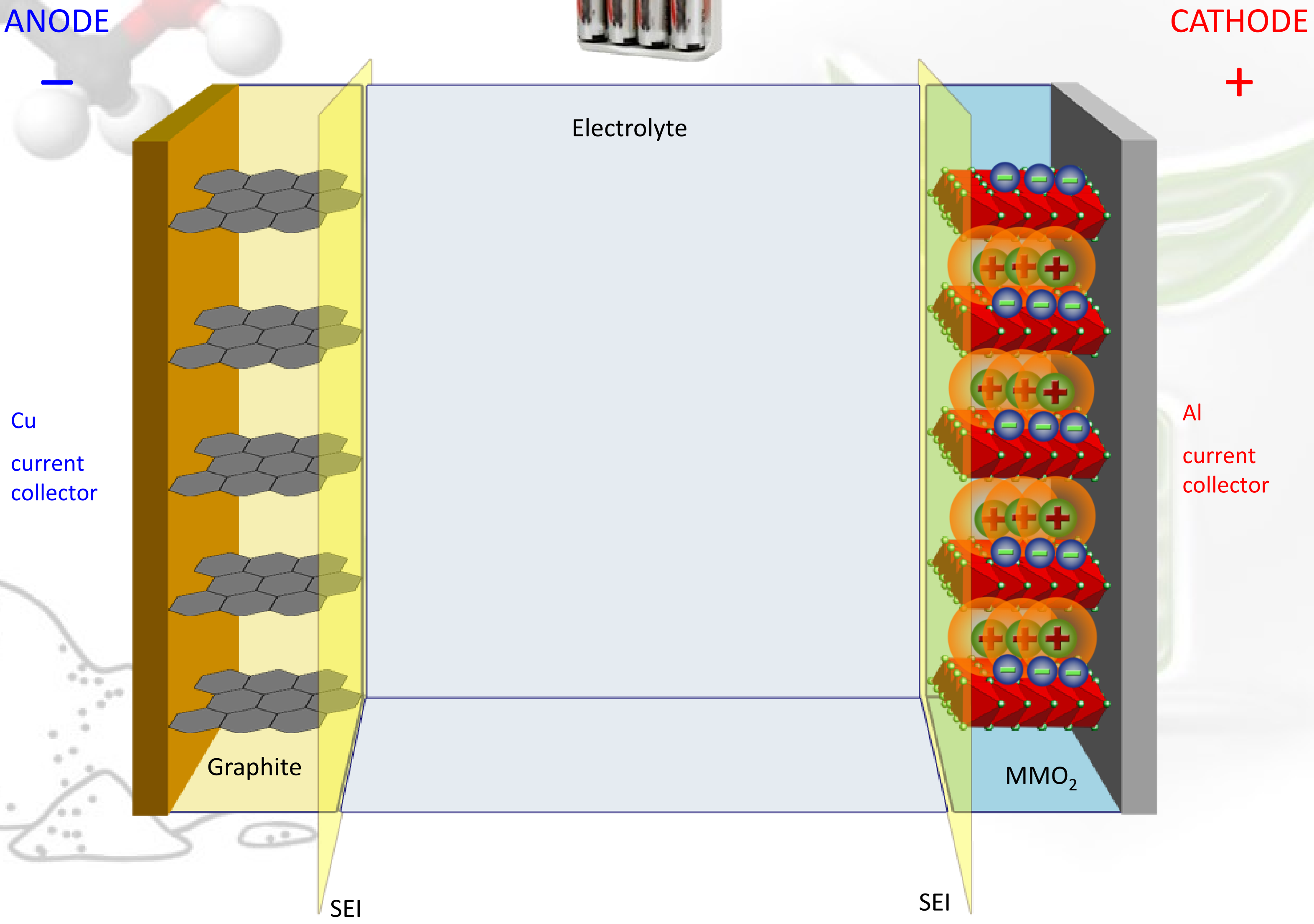
Open questions:

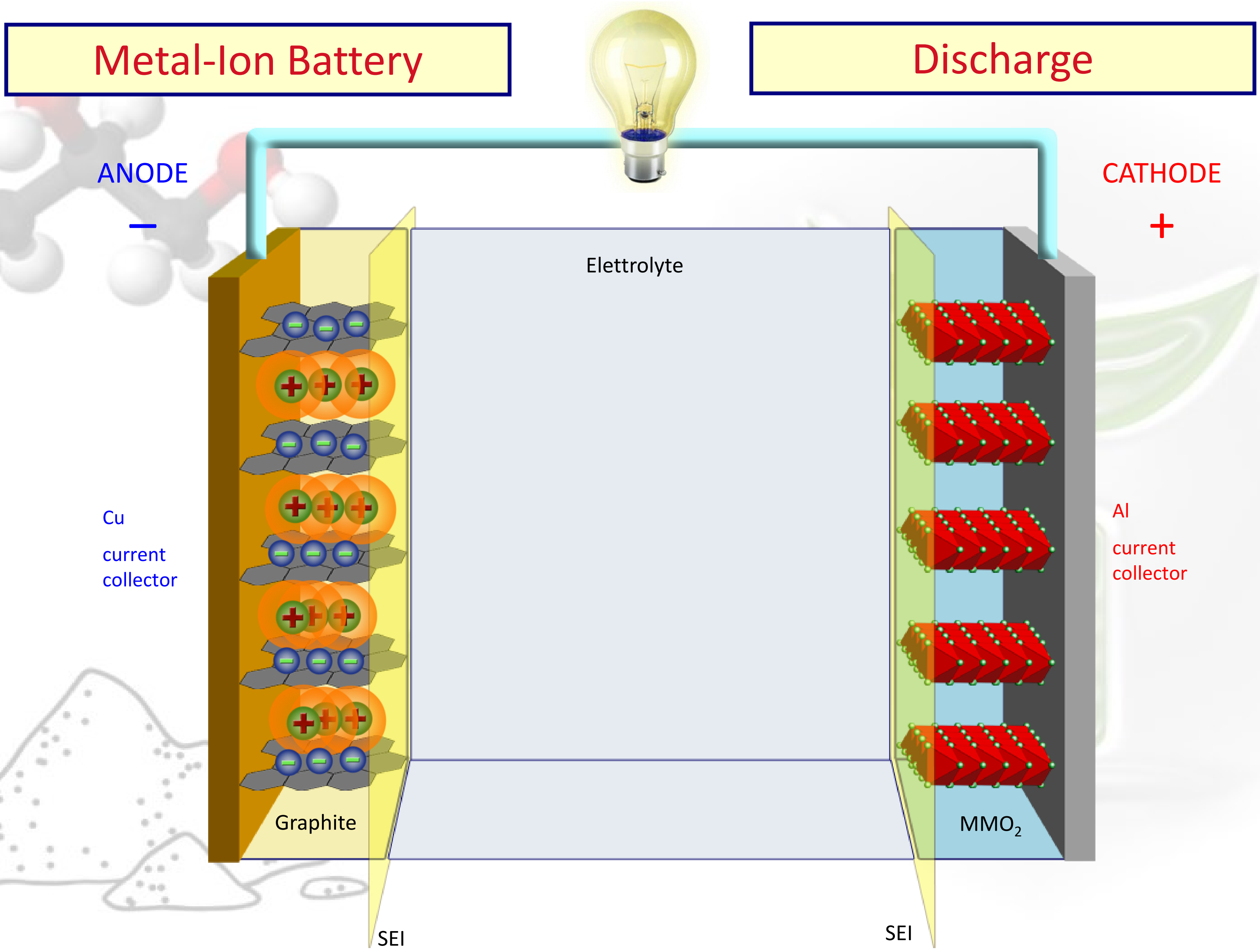
- Safety
- Sustainability (CRM)

Christen, T., & Carlen, M. W. *Journal of Power Sources*, **2000**, 91, 210–216

Metal-Ion Batteries

Charge




Metal-Ion Battery
Discharge
ANODE
–
CATHODE
+
Elettrolyte
Cu
current
collector
Al
current
collector
Graphite
MMO2
SEI
SEI

ELECTROLYTE AS A KEY COMPONENT

(+)(e-P)Mat / El. / (e-N)Mat (-)

Electrolyte: medium for the movement of ions

- e^{-}-insulating
- easily transport M-ions
- electrochemically inert at both electrodes

Liquid solution (M^{+} salt and solvent)	Gel electrolyte (M^{+} salt, solvent and polymer)	Polymer electrolyte (M^{+} salt and polymer)	Solid electrolyte (crystalline M^{+} ionic conductor)

ELECTROLYTES

References:

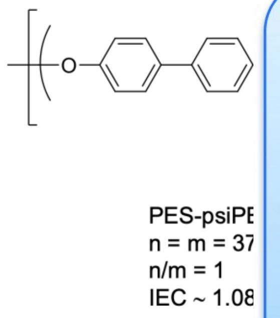
H. Kim, et al. Chemical reviews 2014

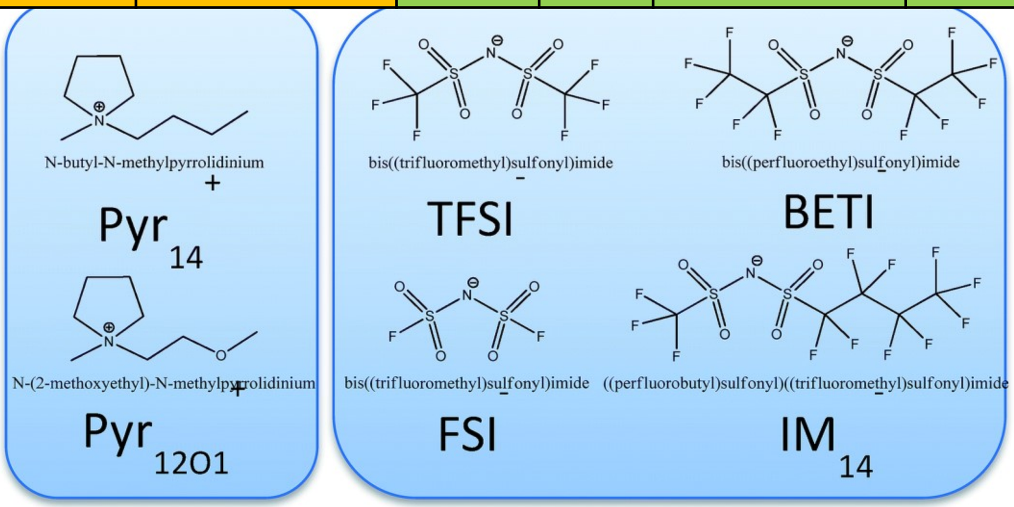
A. Mayer et al. ACS Macro Lett. 2022, 11, 982–990

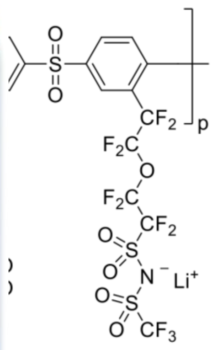
S.S. Zhang et al. Journal of Power Sources 2004, 125, 114–118

Di Pietro et al. Journal of Molecular Liquids, 2021, 338, 116597

	Stability	Performances	Safety	Cost	Sustainable	Health	Green	TRL
Polymers					*If not fluorinated*			
Gels								
Organic Solvents					*Depends on the source of the starting materials*			*Affected by VOC Politics*
Ionic Liquids								
Aqueous solutions								
Deep Eutectic Solvents								



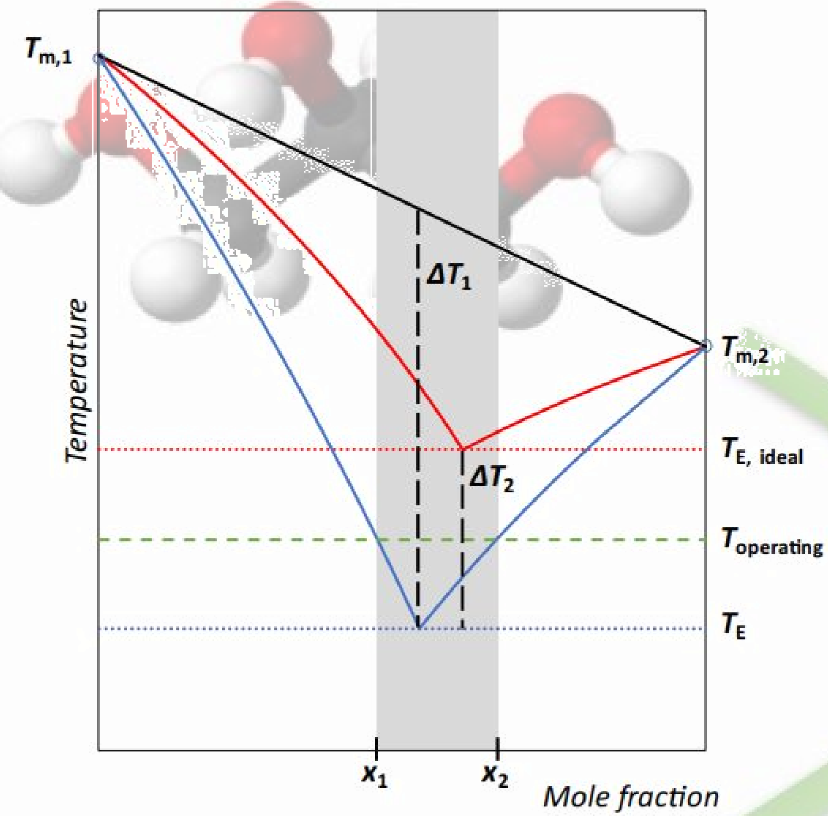




Huang, Y., et al., *Advanced Materials*, ***2019***, *1808393*

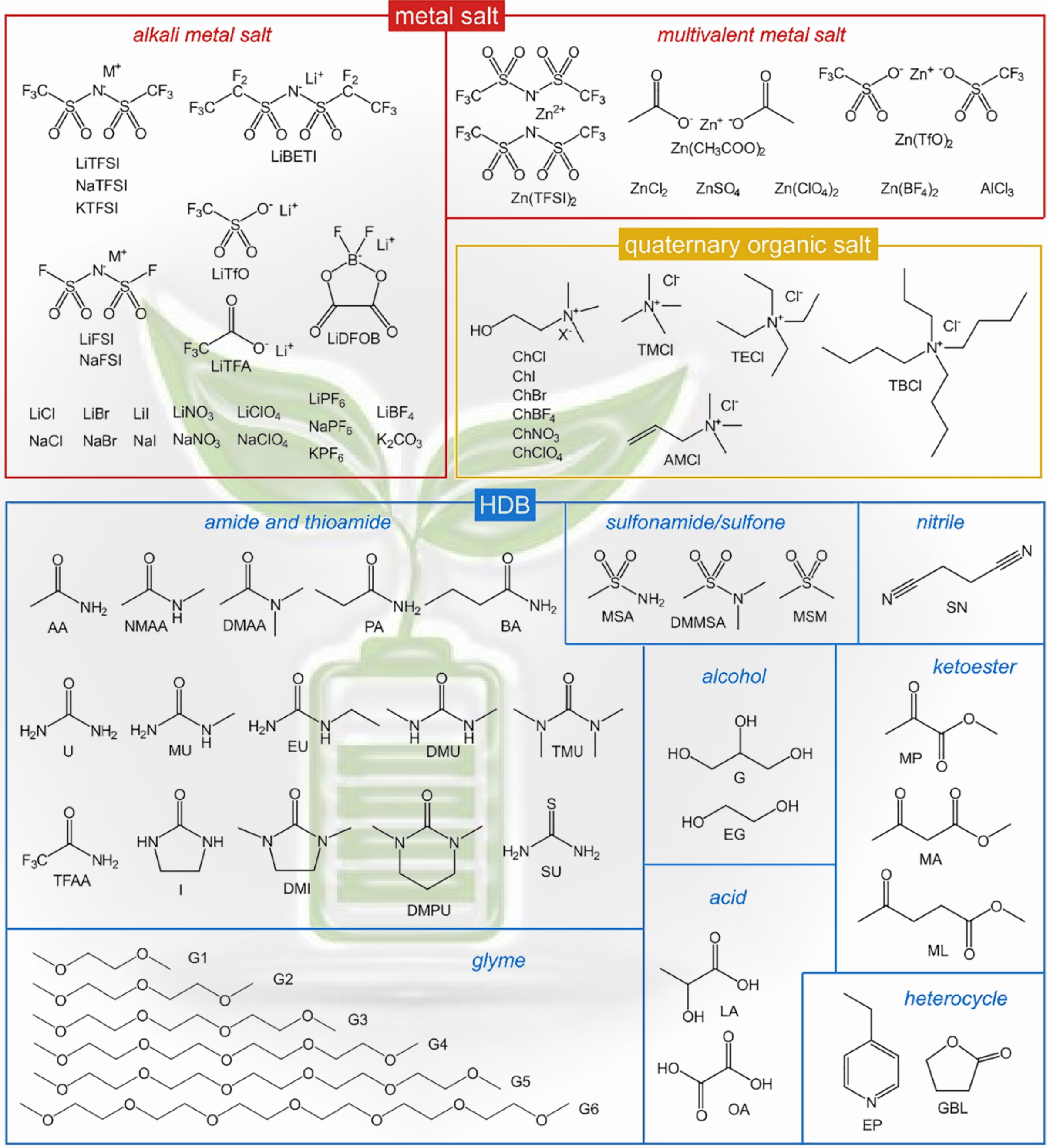
Courtesy of Dr. Alessandro Mariani, Elettra Synchrotron of Trieste

DEEP EUTECTIC SOLVENTS



Type	General composition
I	Metal salt + organic salt
II	Metal salt hydrate + organic salt
III	Organic salt + HDB
IV	Metal salt (hydrate) + HBD

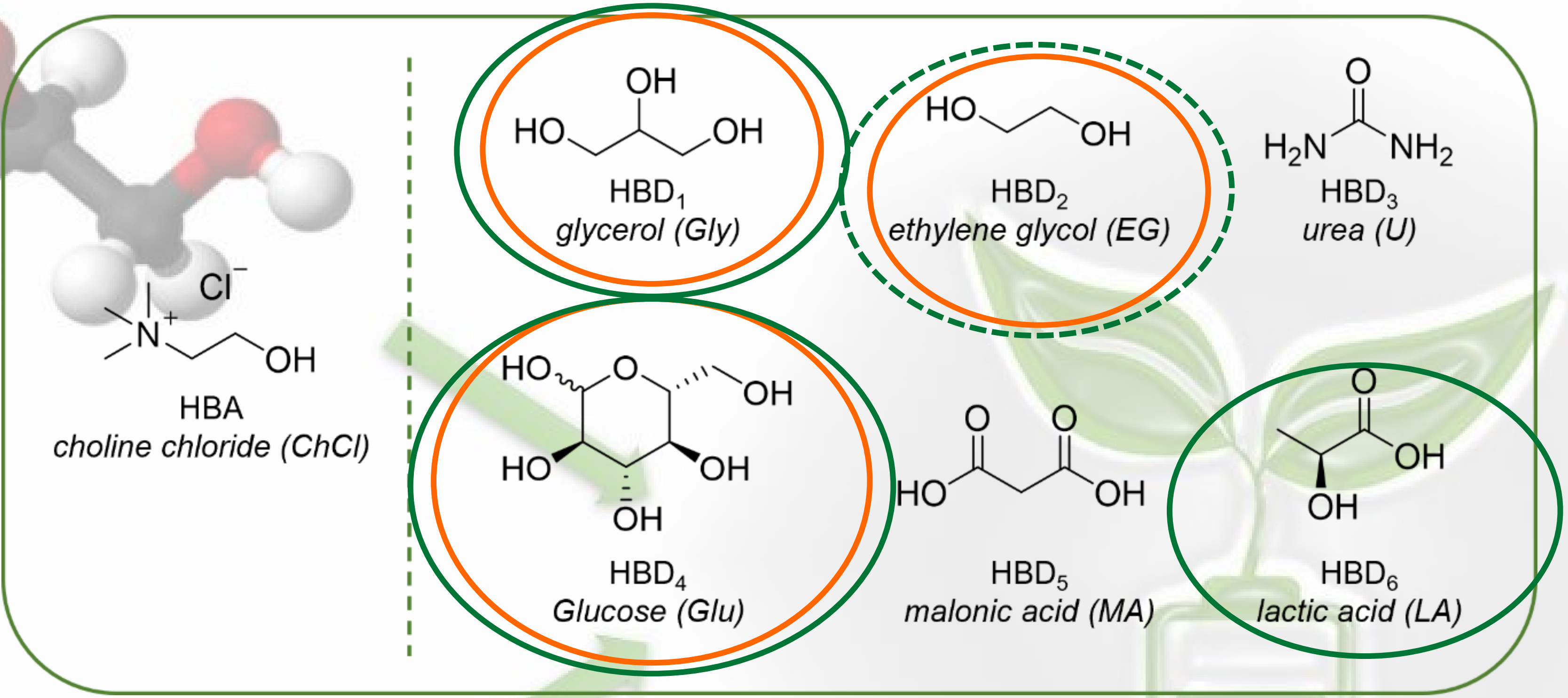
Cat^+ = any ammonium, phosphonium, or sulfonium cation
X^- = Lewis base, generally a halide anion



metal salt + HDB = type IV DES

quaternary organic salt + HDB = type III DES

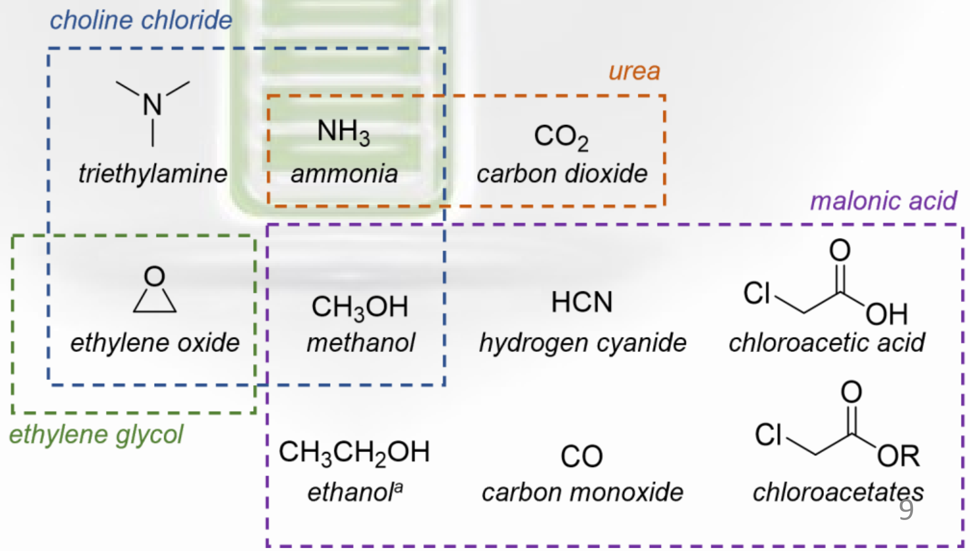
ARE DESs REALLY SUSTAINABLE?



High Biodegrability (% ThOD* > 60%in 14 days) – 100 mg/L

Green feed-stocks (no fossil fuel-based supply chain)

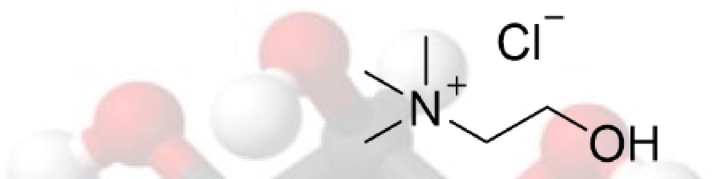
Production phase (cheap and environmentally-friendly)



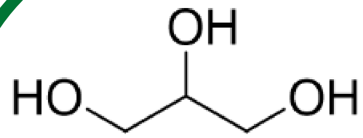
* %ThOD = Biochemical OD / Theoretical OD

Nejrotti et al. *ACS Omega*, **2022**, 7, 47449–47461, **10.1021/acsomega.2c06140**

APPROACH 1 – Li-ION

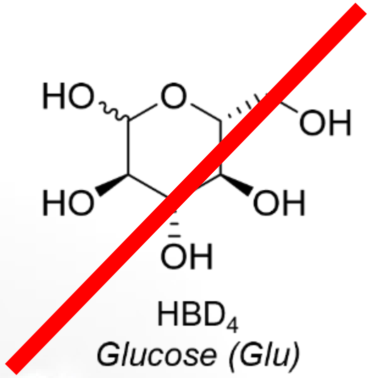


HBA
choline chloride (ChCl)



HBD_1
glycerol (Gly)

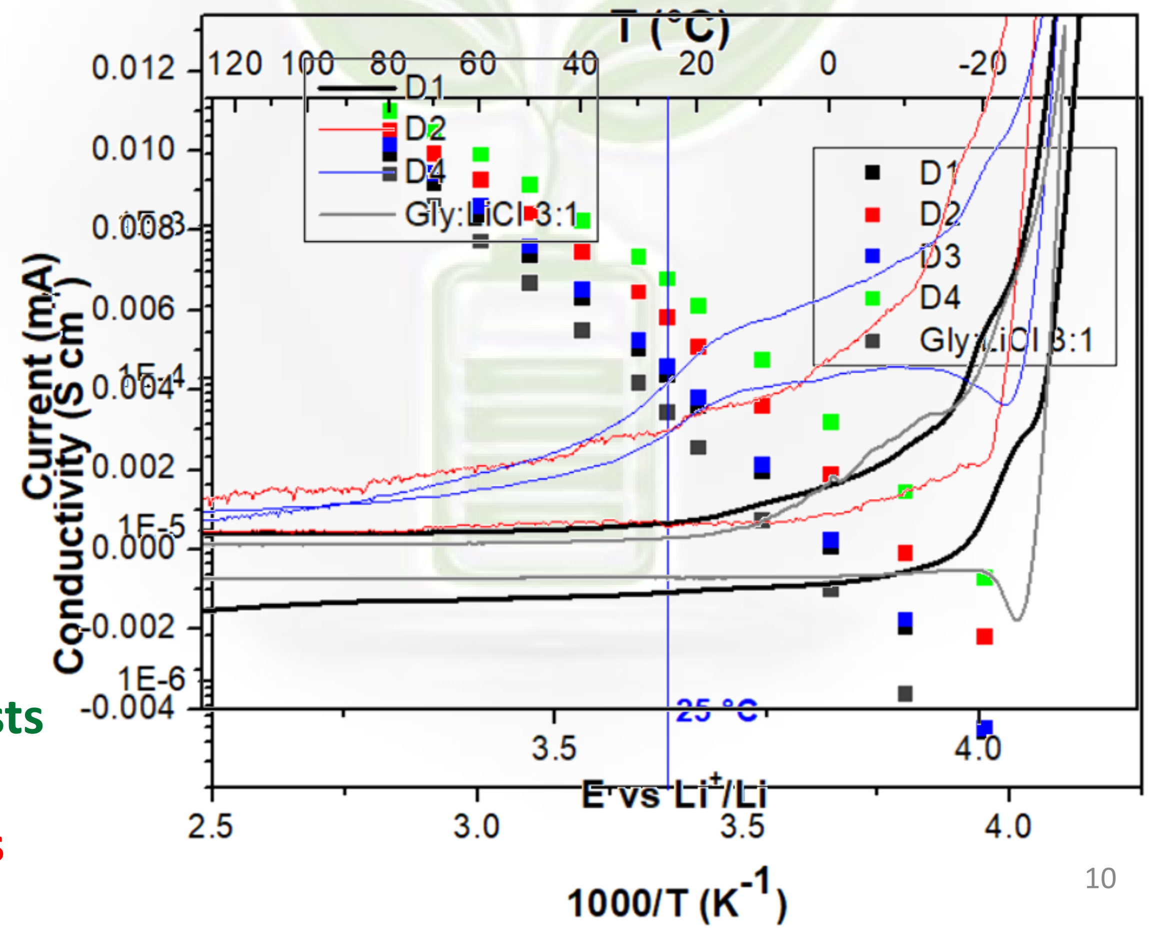
HBD_2
ethylene glycol (EG)



HBD_4
Glucose (Glu)

A Metal Ion should be added

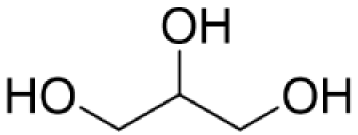
sample	Ch-Cl	Gly	LiCl
D1	1	3	1
D2	0.5	3	0.5
D3	0.25	3	0.75
D4	0.75	3	0.25
Gly:LiCl 3:1	-	3	1



✅ **Deep Eutectic Electrolytes pass the preliminary tests**

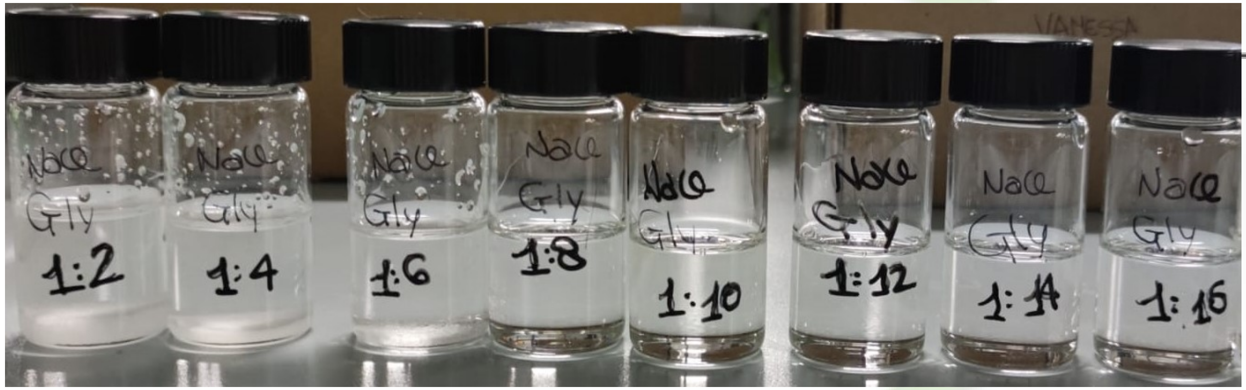
❌ **Need to be improved to approach SoA Electrolytes**

APPROACH 2 – Na-ION

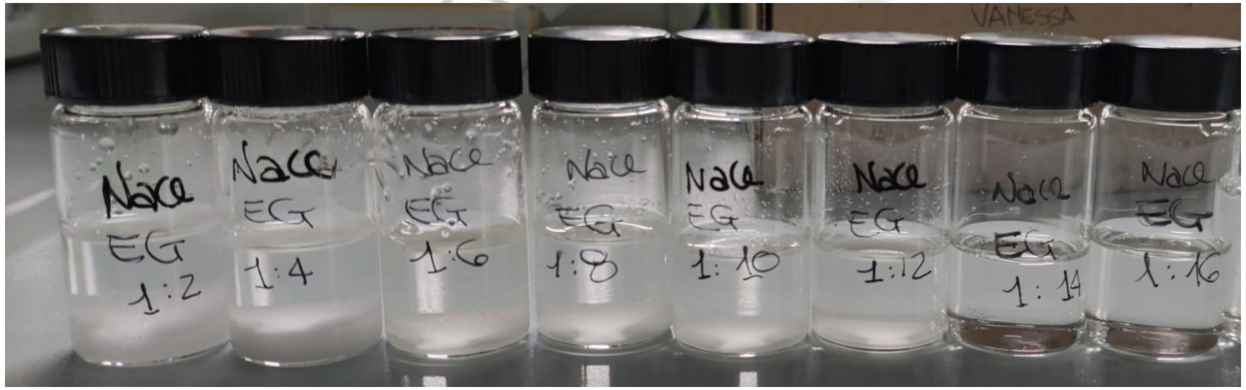


HBD_1
glycerol (Gly)

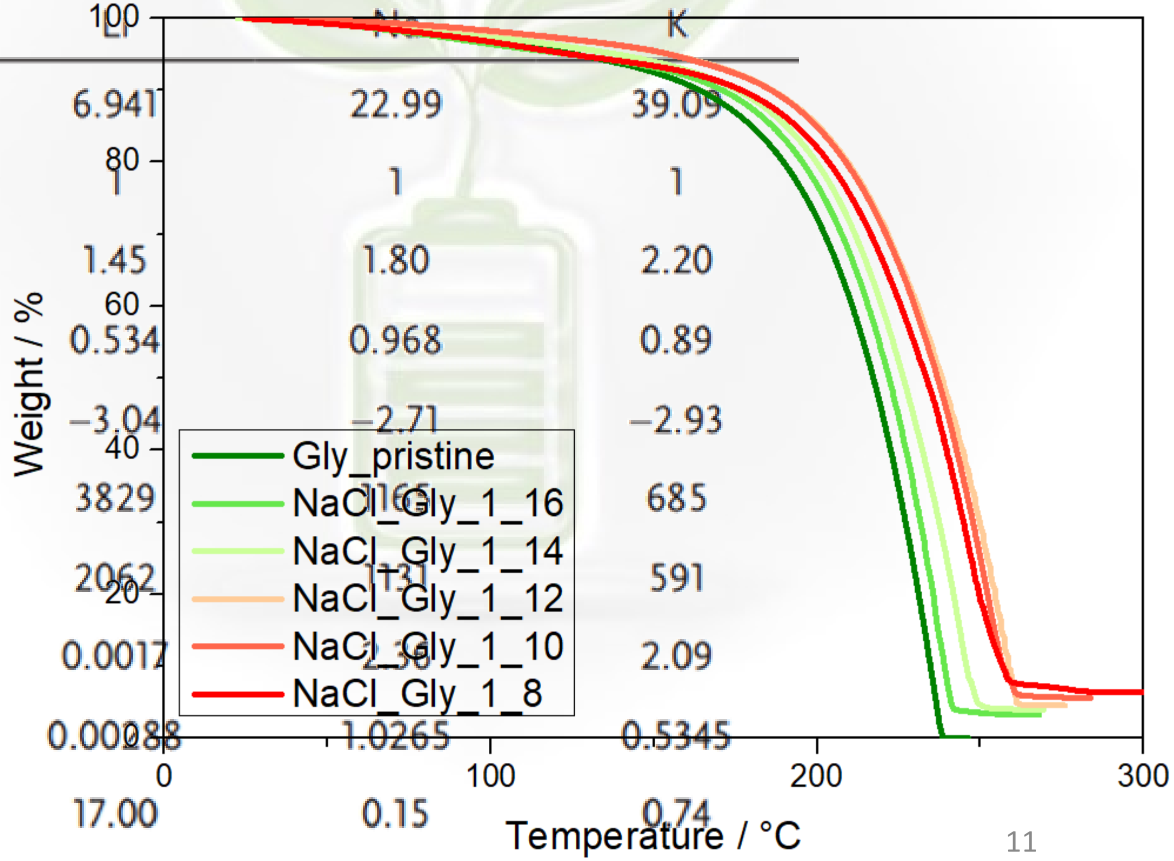
HBD_2
ethylene glycol (EG)



Std reduction potential (V) versus SHE



Li	Na	K
6.941	22.99	39.09
1	1	1
1.45	1.80	2.20
0.534	0.968	0.89
−3.04	−2.71	−2.93
3829	1165	685
2062	1131	591
0.0017	2.36	2.09
0.00288	1.0265	0.5345
17.00	0.15	0.74



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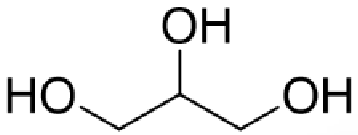
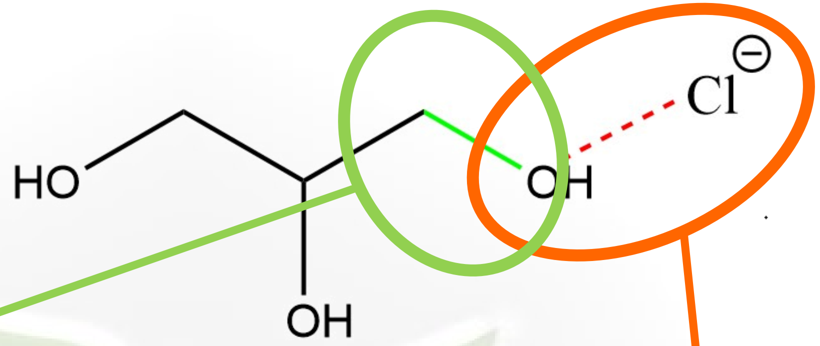
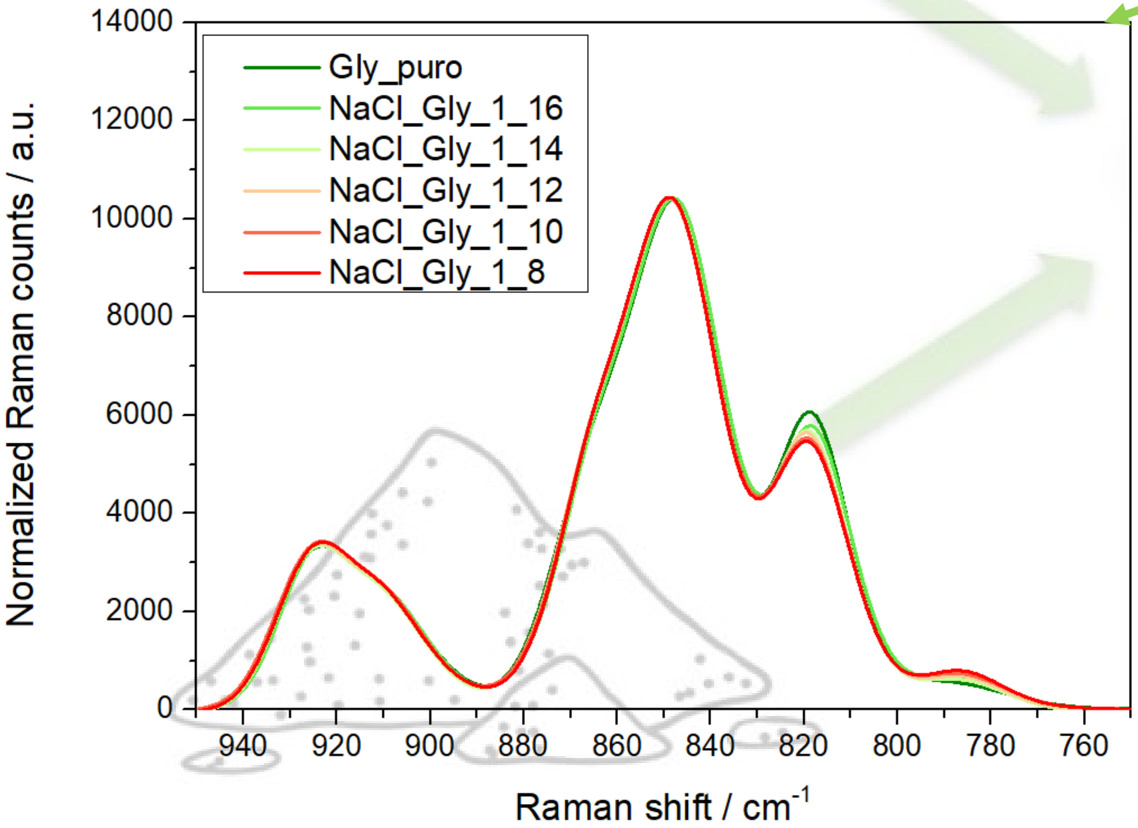
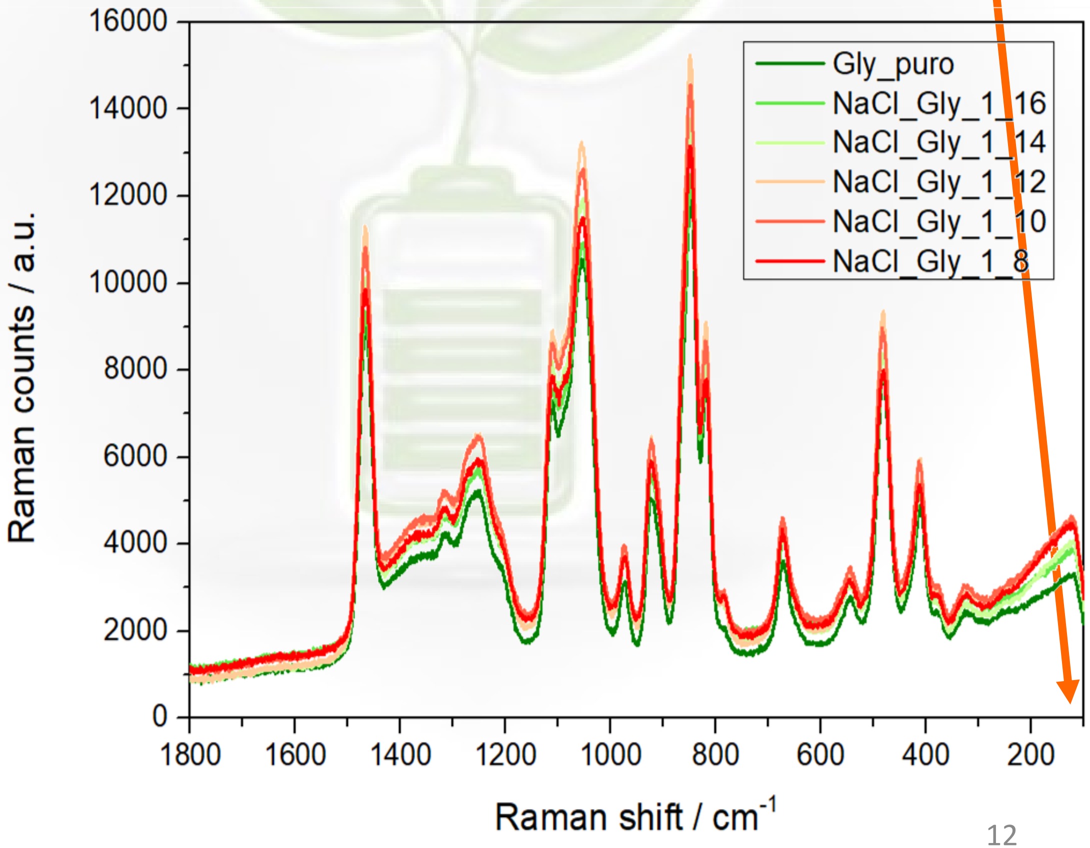


HBD$_1$
glycerol (Gly)







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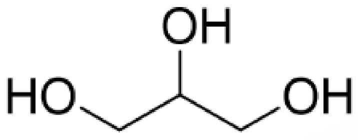
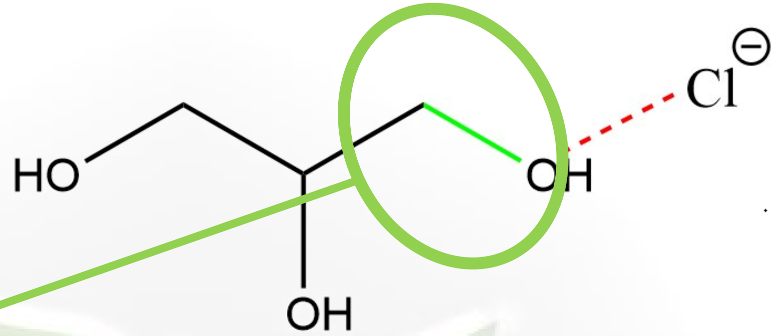
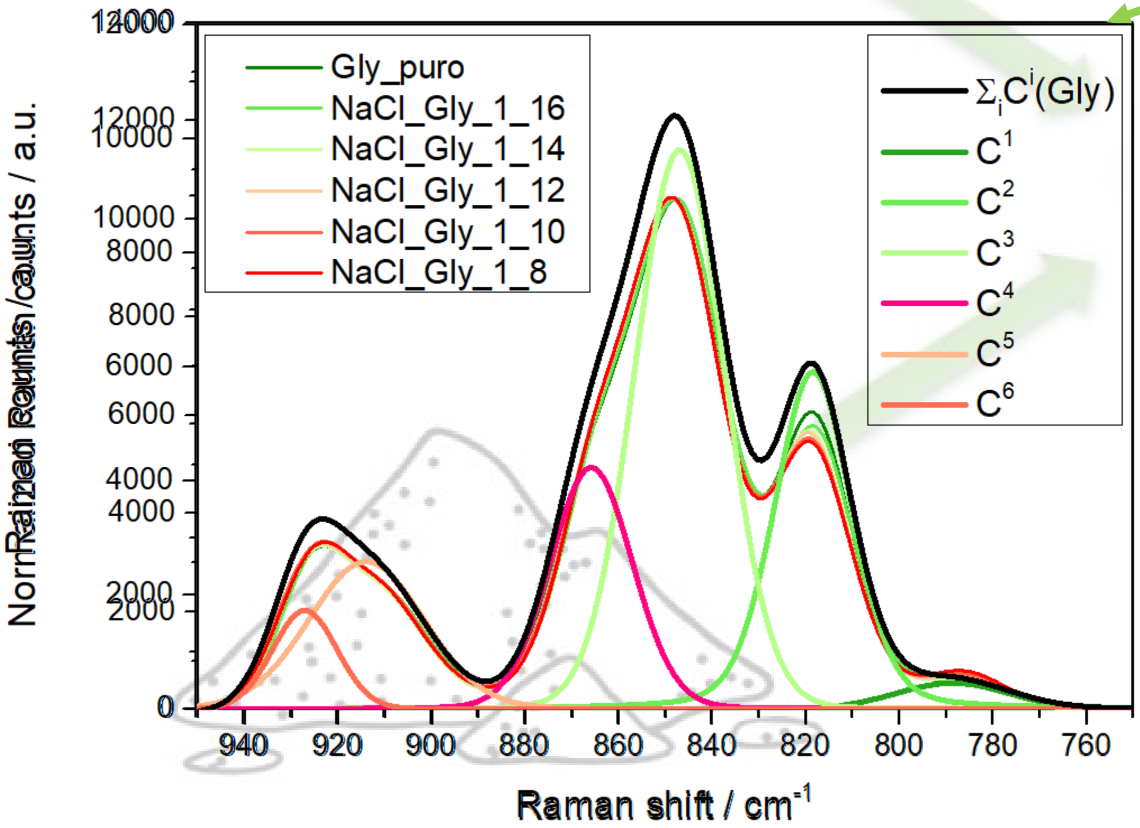
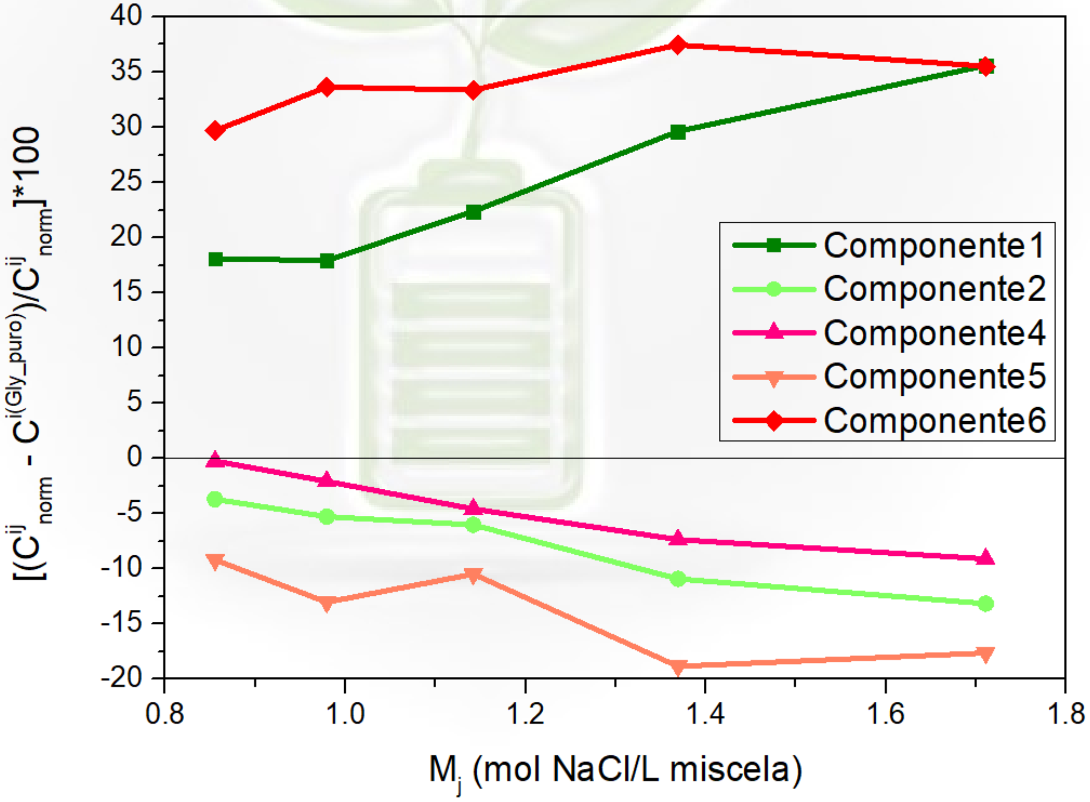


HBD_1
glycerol (Gly)







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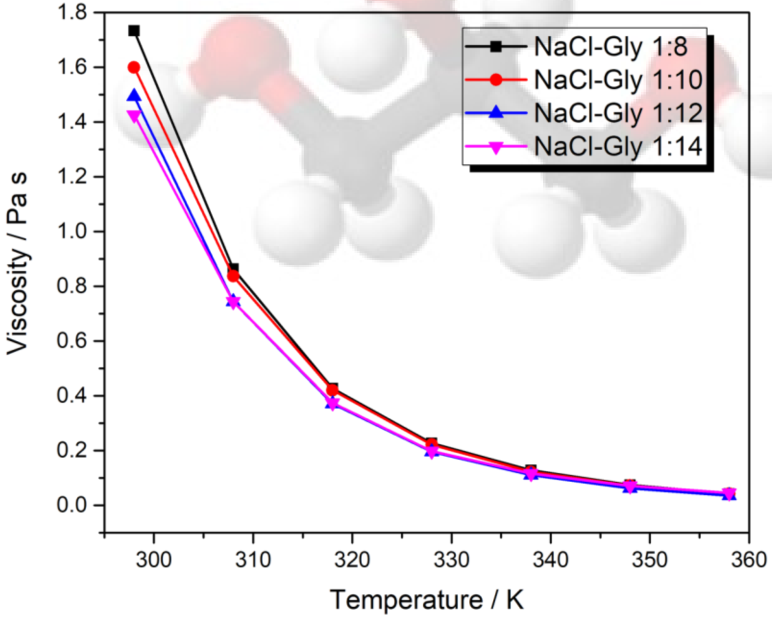
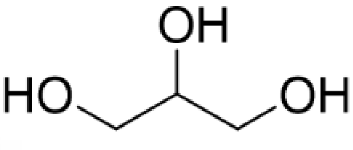
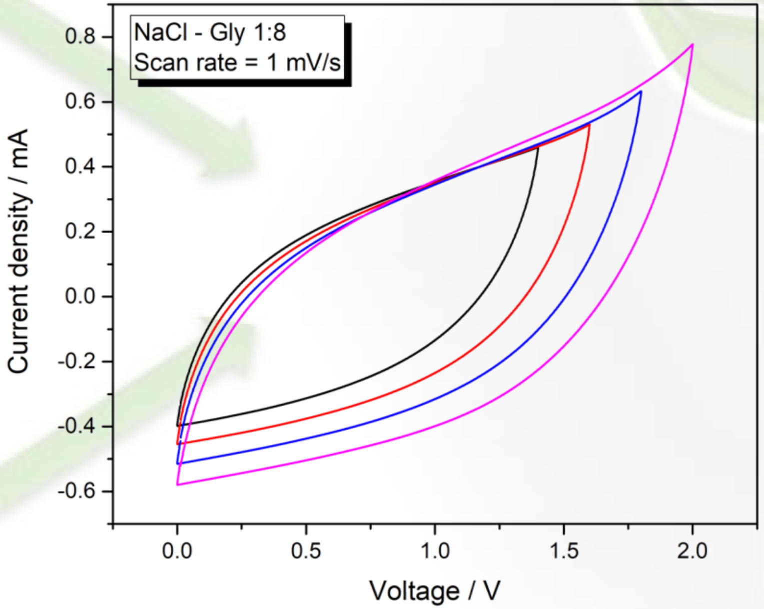
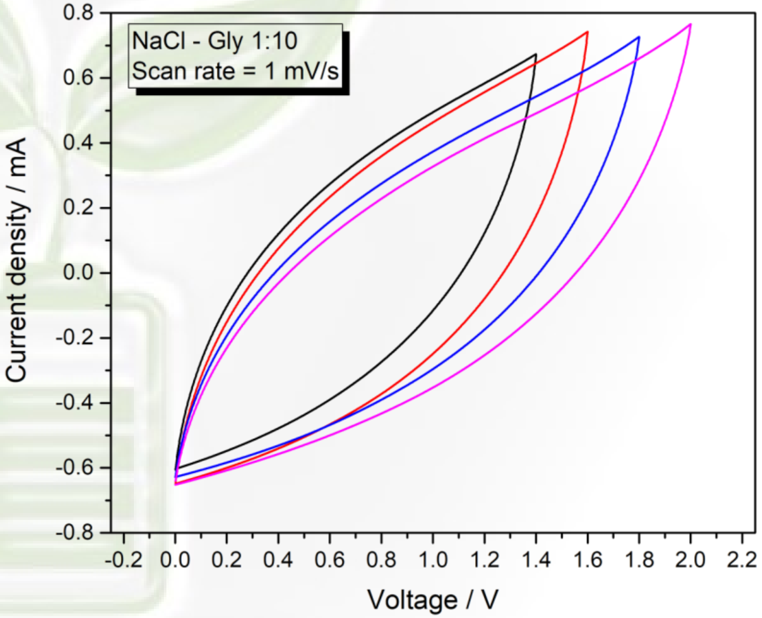




HBD_1
glycerol (Gly)



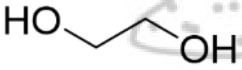


Relatively High Viscosity

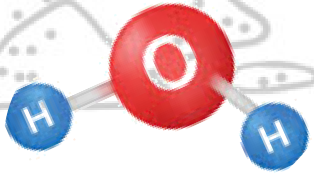
Reduced Conductivity

Ion Transport Issues

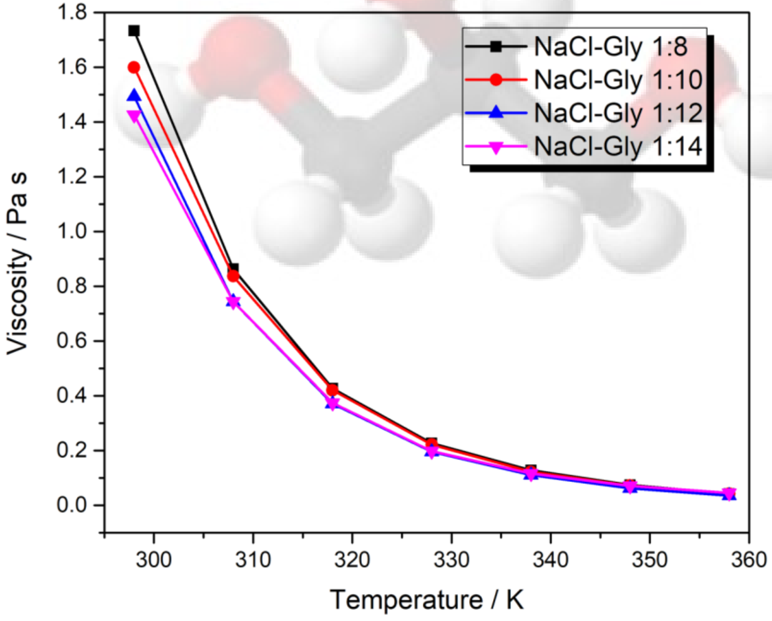
Unexpectly large ESW (up to 2 V and counting)

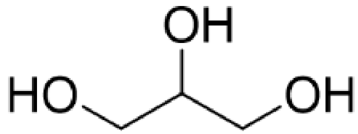


HBD_2
ethylene glycol (EG)



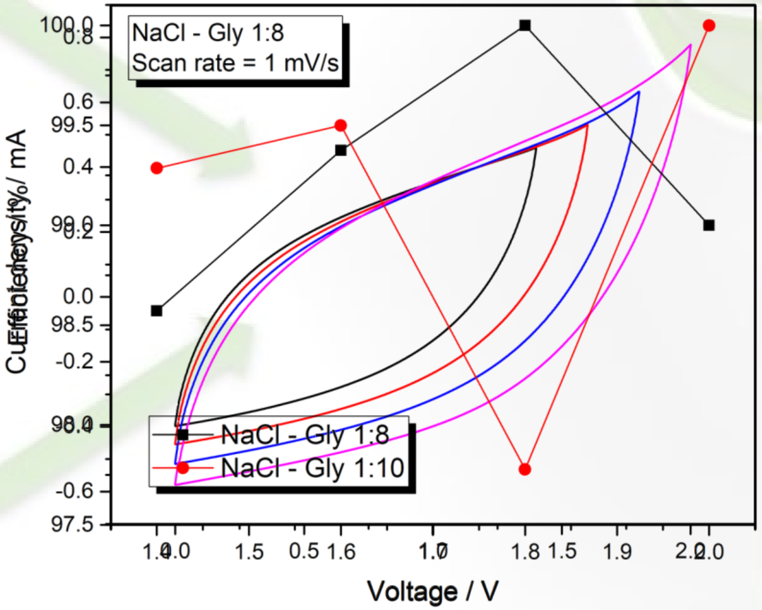
APPROACH 2 – Na-ION

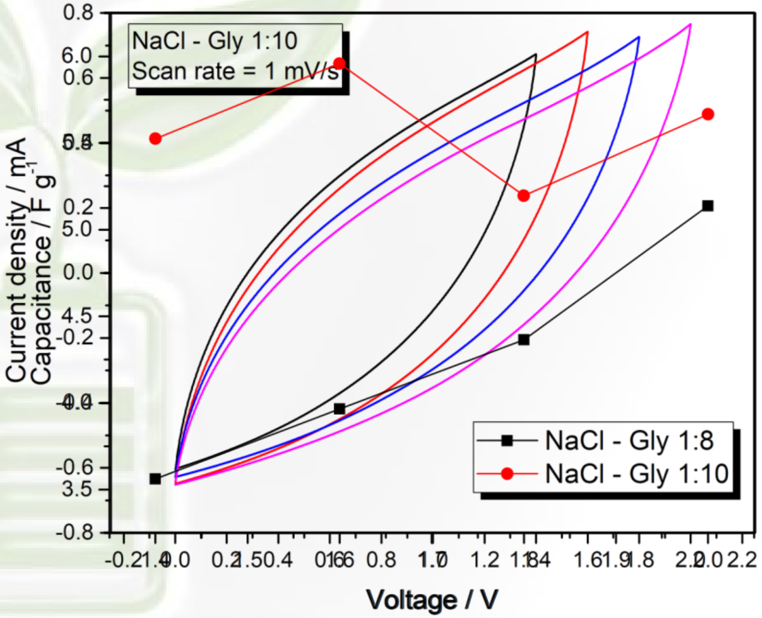




HBD_1

glycerol (Gly)



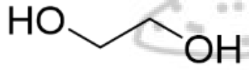


Relatively High Viscosity

Reduced Conductivity

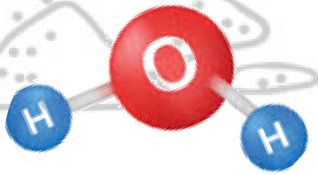
Ion Transport Issues

Unexpectly large ESW (up to 2 V and counting)



HBD_2

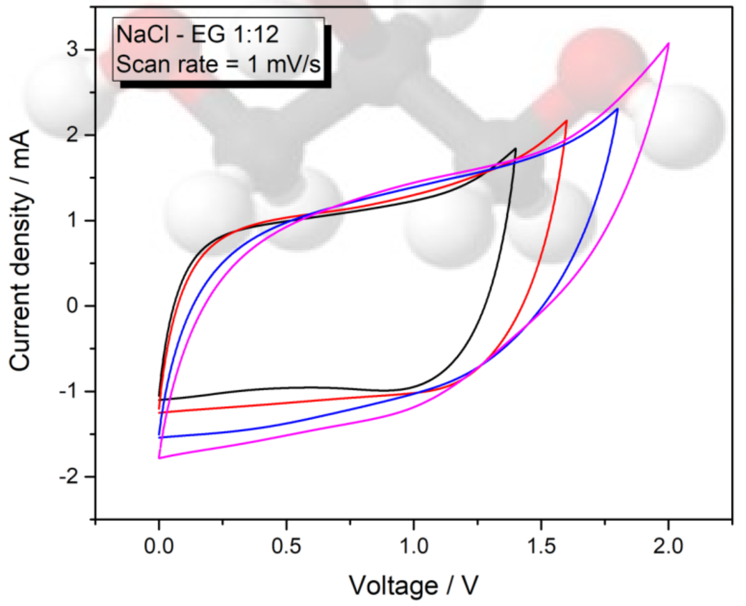
ethylene glycol (EG)

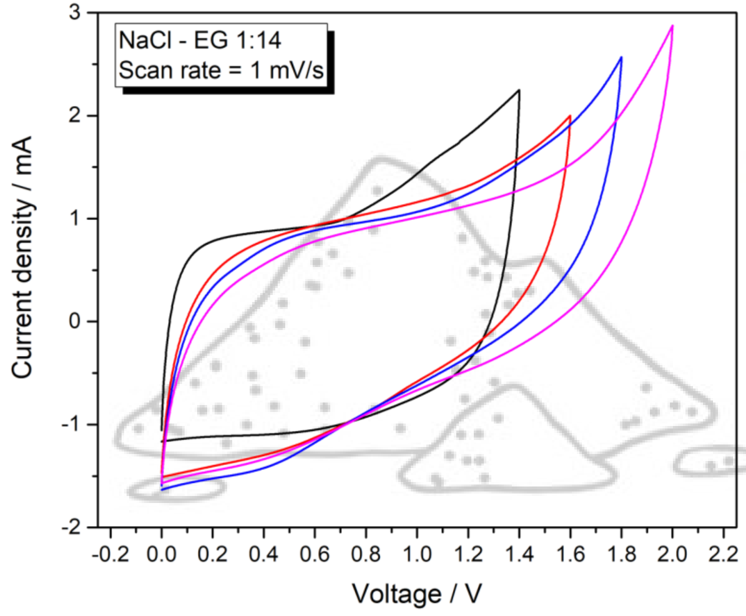


Faradic Efficiency appraoching 100%

Relatively High Capacitance

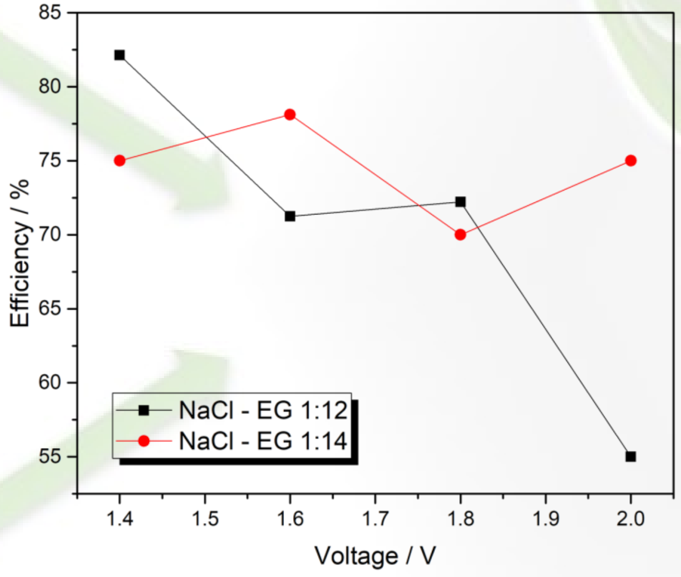
APPROACH 2 – Na-ION

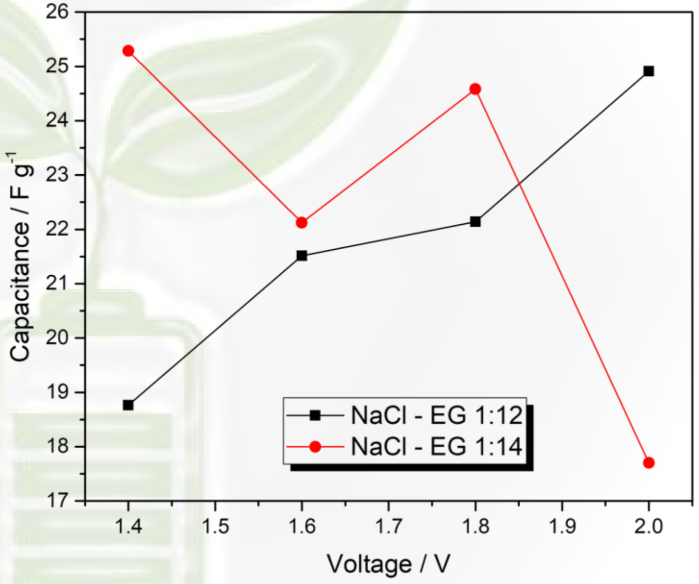




HBD_2

ethylene glycol (EG)





QUASI-REVERSIBLE Redox-Processes

Promising ESW

Lower Faradic Efficiency (75%)

Much Higher Capacitance (4x)

CONCLUSIONS AND…FUTURE OUTLOOKS

- Promising assessment on the sustainability of Deep Eutectic Solvents to be used as electrolytes in Electrochemical Energy Storage Devices
- Glycerol and Ethylene Glycol-based DESs showed the best trade-off between sustainability and electrochemical properties
- Replacement of Choline Chloride with NaCl toward ready-to-apply electrolytes
- Very promising preliminary results using NaCl-Gly(EG) eutectic mixture for Supercapacitor applications

- Testing of ternary system NaCl-Gly-H20 to improve the electrochemical properties (reduce viscosity and increasing conductivity)
- Testing in complete super-capacitors (running @PoliTo)
- Testing of selected electrolytes in Na-Ion batteries (ongoing)

ACKOWLEDGEMENTS

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2023 - 2027 DIPARTIMENTO DI ECCELLENZA
Ministero dell'Università e della Ricerca

PRIN MIUR
PROGETTI DI RICERCA DI RILEVANTE INTERESSE NAZIONALE

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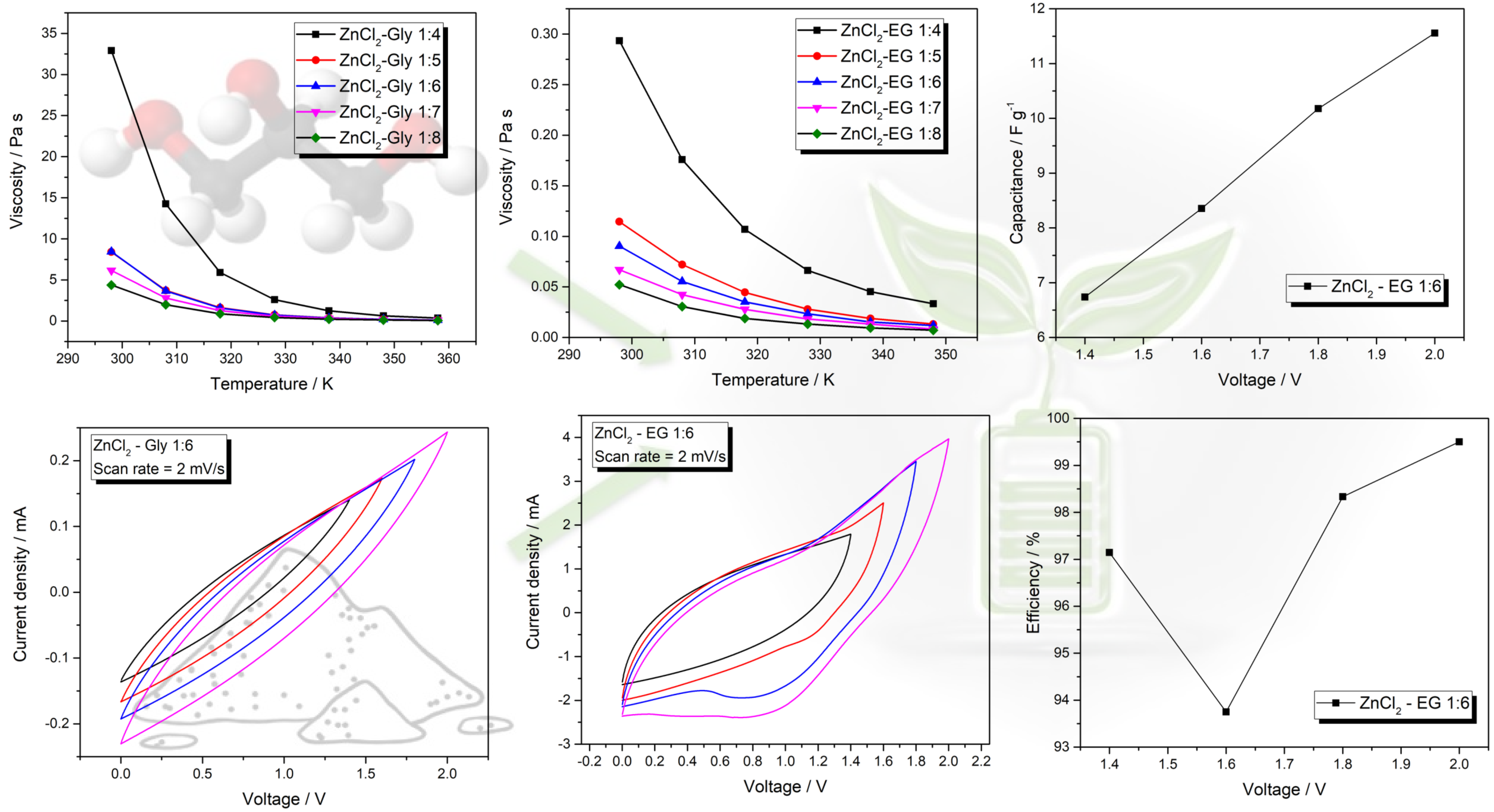
GFI – Grant For Internationalization

BACKUP SLIDES

Animal model	DES components	DES ratio	Results	
Brine shrimp **(Artemia salina)**	ChCl/Gly ChCl/EG ChCl/U	1/3 1/3 1/3	• All DESs were toxic • Higher toxicity for DESs than for components alone or their mixture	
Hydra **(Hydra sinensis)**	ChCl/Gly ChCl/EG ChCl/U	various[b] various[b] various[b]	• All DESs were toxic • Lower toxicity for DESs than for components alone (particularly ChCl) or their mixture	
Crustacean **(Daphnia magna)**	ChCl/Gly ChCl/EG ChCl/U	1/2 1/2 1/2	EC_{50} (mg/L) 2’530 1’870 1’100	• All DESs were “relatively harmless” • The DES components alone were not tested
Fish **(Cyprinius carpio)**	ChCl/Gly ChCl/EG ChCl/U ChCl/Glu ChCl/MA	1/2, 1/3 1/2, 1/3 1/2 2/1 1/1	LC_{50} (mg/L) >100 >100 >100 >100 >100	• All DESs were “practically harmless”, as well as their components alone or their mixture • Among DES components, slight toxicity for MA solution (LC_{50}=50±15 mg/L) and ChCl+MA solution (LC_{50}=55±13 mg/L)
Mice	ChCl/Gly ChCl/EG ChCl/U	1/3 1/2 1/3 1/3 1/2	LD_{50} (g/kg) 6.39±0.53 7.73[c] 5.33±0.49 toxic 5.46±0.36	• All DESs were relatively toxic • Higher toxicity for DESs than for components alone • Liver and kidney injury detected (oxidative stress) • Ammonia stress detected with ChCl/U 1/2

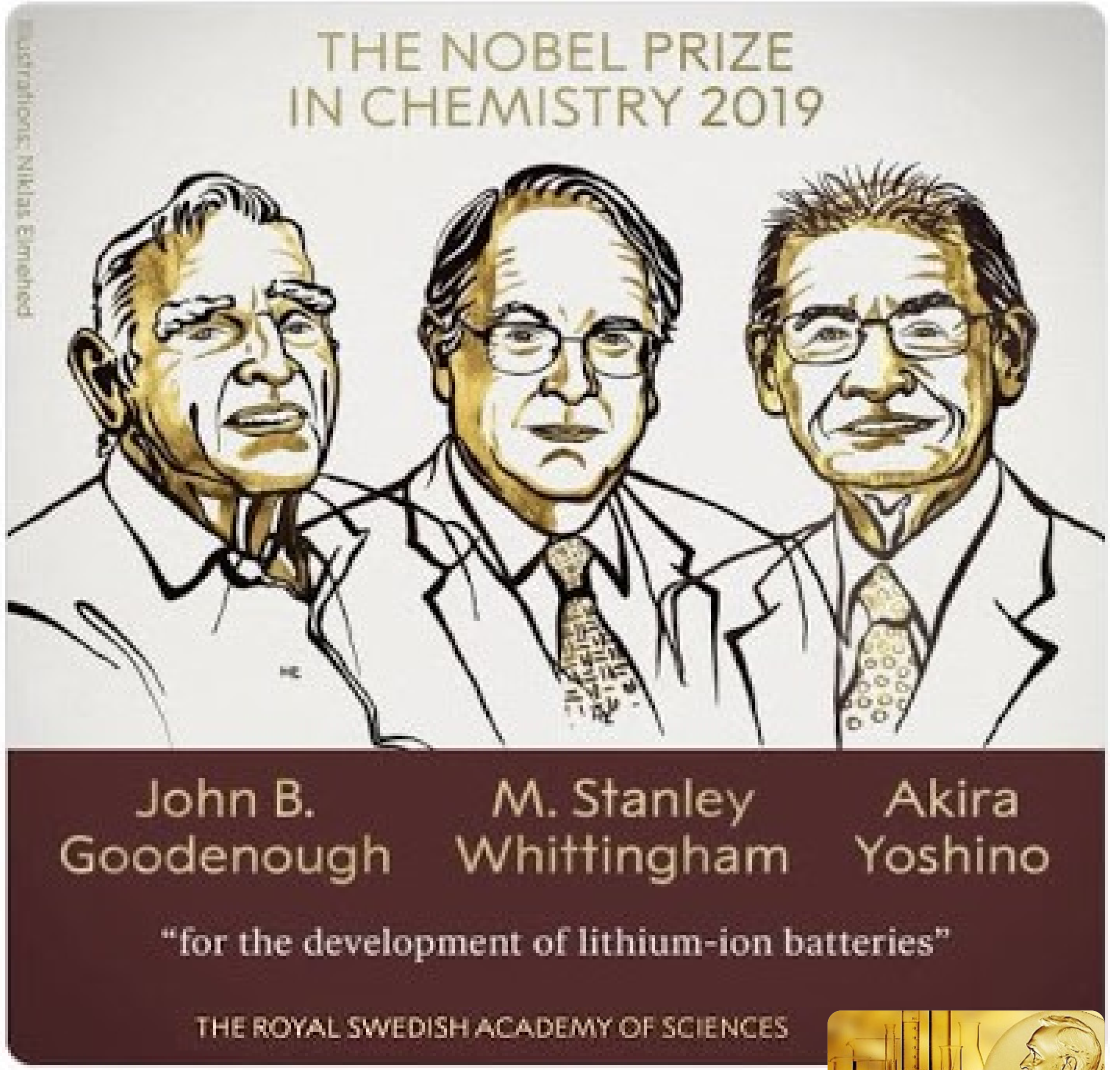
Plant	DES components	DES ratio	Results
Garlic **(Allium sativum)**	ChCl/Gly ChCl/EG ChCl/U	1/1 1/1 1/1	• Root growth inhibition by DESs as well as their components • High toxicity of ChCl, mitigated in ChCl/U, but not in ChCl/EG • ChCl/Gly significantly less toxic than both its components
Wheat **(Triticum aestivum)**	ChCl/Gly ChCl/Glu	1/2 2/1	• Practically harmless towards seed germination • Relatively higher toxicity for shoot and root growth inhibition

Nejrotti et al. *ACS Omega*, **2022**, 7, 47449–47461, **10.1021/acsomega.2c06140**



ZnCl2-Gly 1:4
ZnCl2-Gly 1:5
ZnCl2-Gly 1:6
ZnCl2-Gly 1:7
ZnCl2-Gly 1:8
Viscosity / Pa s
Temperature / K
ZnCl2-EG 1:4
ZnCl2-EG 1:5
ZnCl2-EG 1:6
ZnCl2-EG 1:7
ZnCl2-EG 1:8
Viscosity / Pa s
Temperature / K
Capacitance / F g-1
Voltage / V
ZnCl2 - EG 1:6
ZnCl2 - Gly 1:6
Scan rate = 2 mV/s
Current density / mA
Voltage / V
ZnCl2 - EG 1:6
Scan rate = 2 mV/s
Current density / mA
Voltage / V
Efficiency / %
Voltage / V
ZnCl2 - EG 1:6

The Li-ion Battery (LIB): Nobel prize in Chemistry

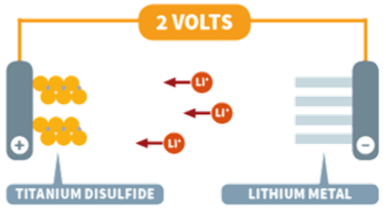


Nature Research Collection on Li-ion batteries and beyond:
https://www.nature.com/collections/faagahedhh/

The foundation of the Li-ion battery was laid during the oil crisis in the 1970s

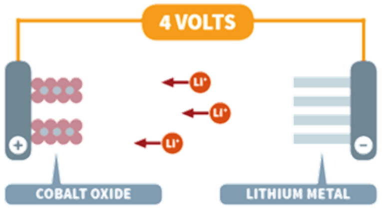
WHITTINGHAM → *GOODENOUGH* → *YOSHINO*

WHITTINGHAM
First functional Li-based battery with sulfide cathode



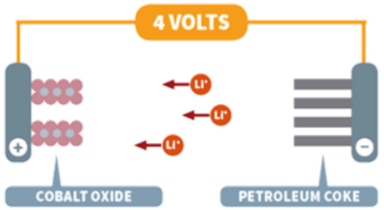
In the 1970s, **Whittingham** created the first functional lithium battery with a titanium disulfide cathode and lithium metal anode. The lithium metal made it explosive and unsafe.

GOODENOUGH
Metal oxide intercalation cathodes with Li metal



In the 1980s, **Goodenough** used a cobalt oxide cathode instead of a metal sulfide. This doubled the battery's voltage, but it still contained lithium metal in the anode.

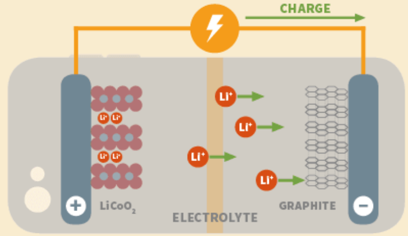
YOSHINO
First commercially viable Li-ion battery with C anode



Yoshino replaced the lithium metal anode with petroleum coke, a carbon-based by-product from the oil industry. This lead to commercial lithium-ion batteries in 1991.

Nobel Prize in Chemistry press release: https://www.nobelprize.org/uploads/2019/10/press-chemistry-2019-2.pdf

They created a rechargeable world!



Lithium-ion batteries power many of our electronic devices. When lithium-ion batteries charge, lithium ions and electrons move from the positive electrode to the negative electrode. When the battery is discharging, the opposite happens and the flow of electrons powers the device.