

Matteo Bonomo,^{i,j} Daniele Motta,ⁱ Giuseppe Antonio Elia,^{j,z} Alessandro Damin,ⁱ Gabriele Lingua,^{j,z} Stefano Nejrotti,ⁱ Simone Galliano,ⁱ Claudia Barolo,^{i,j} Claudio Gerbaldi,^{j,z}

ⁱ Department of Chemistry and NIS Interdepartmental Centre, University of Turin, Via Pietro Giuria 7, Torino, 10125, Italy

^j National Reference Center for Electrochemical Energy Storage (GISEL) - INSTM, Firenze 50121, Italy

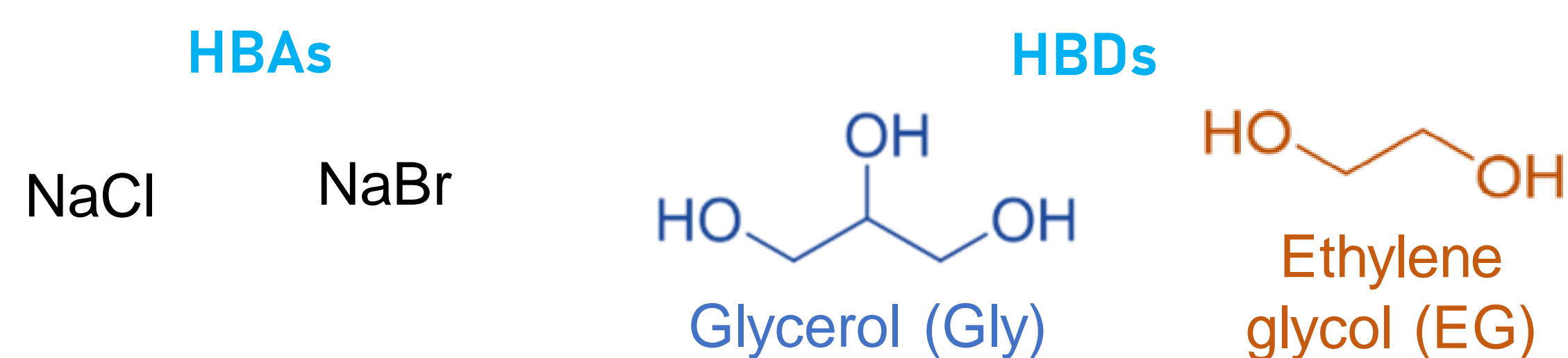
^z GAME Lab, Department of Applied Science and Technology (DISAT), Politecnico di Torino, Torino 10129, Italy

Introduction

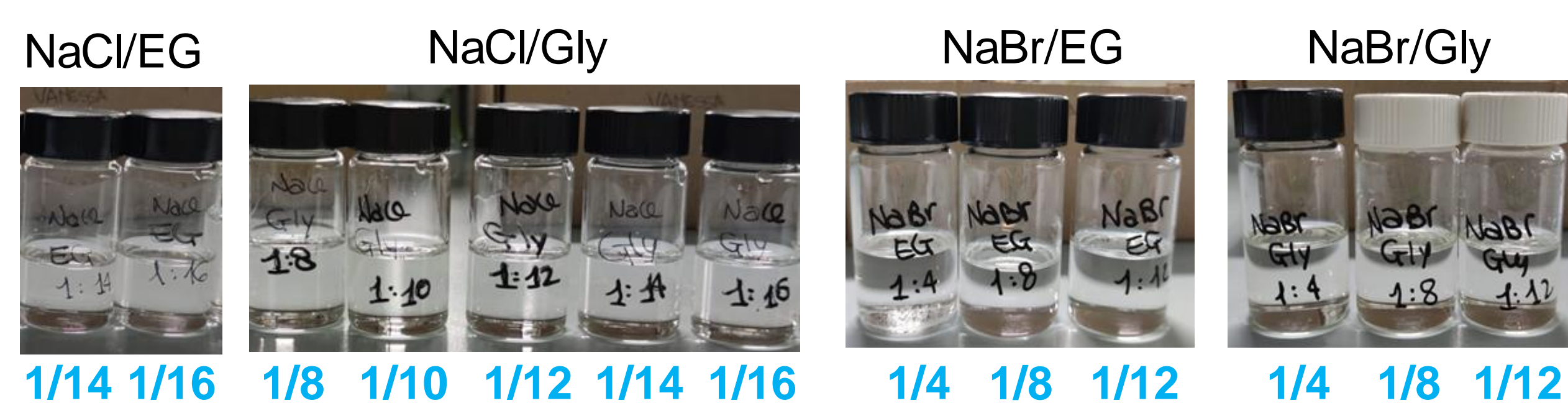
The substantial growth of renewable energy production in the coming years requires efficient massive storage to improve large-scale grid integration of intermittent electricity sources (e.g. solar, tides, wind). Nowadays, a more in-depth penetration of renewable electricity production is limited by our ability to store energy efficiently. Lithium-ion batteries (LIBs) are the state-of-the-art in the field. However, the expected demand for LIBs driven by the automotive sector may raise issues regarding materials supply for lithium (viz. Li_2CO_3) and electrode raw materials (e.g. Co/Ni precursors, natural graphite). Developing low-cost Na-ion batteries (NIBs) based on abundant and sustainable elements/materials can relieve the market constraints, guaranteeing a substantial growth of the renewable energy sector by supplying more flexibility/balance to the grid. Developing new NIB-based technologies mainly requires: i) discovery/investigation of new materials/components widely accessible in large amounts and without strategic contingencies; ii) utilization of green and sustainable materials through all their life cycle (production, use, end-of-life).

In this context, green, cost-effective and sustainable electrolytes are of pivotal importance. Deep Eutectic Solvents (DES) are an emerging class of materials showing promising properties to be exploited as electrolytes. Indeed, they are obtained by a straightforward and sustainable syntheses [1] without any specific equipment (i.e. glove box); moreover, they couple tunable conductivity and viscosity with high sustainability. In their most common fashion, they are made by a halide salt behaving as a hydrogen bond acceptor (HBA) and an alcohol/carboxylic acid playing the role of hydrogen bond donor (HBD). Just few records report on the use of DESs as electrolytes and even less in the battery field [2]. Albeit promising results were already described, a correlation between DES structure and their properties is lacking [3]. In addition, as far as we know, there are no reports on the use of DES in NIBs, whereas some attempts have been made in Li-, Zn- and Al-based technologies [3,4].

Preparation of new eutectic mixtures



Clear and homogeneous liquids are obtained for specific HBA/HBD molar ratios. Yet this is not enough to rule out the Eutectic Nature of the mixtures



Characterization of the eutectic mixtures

Melting point

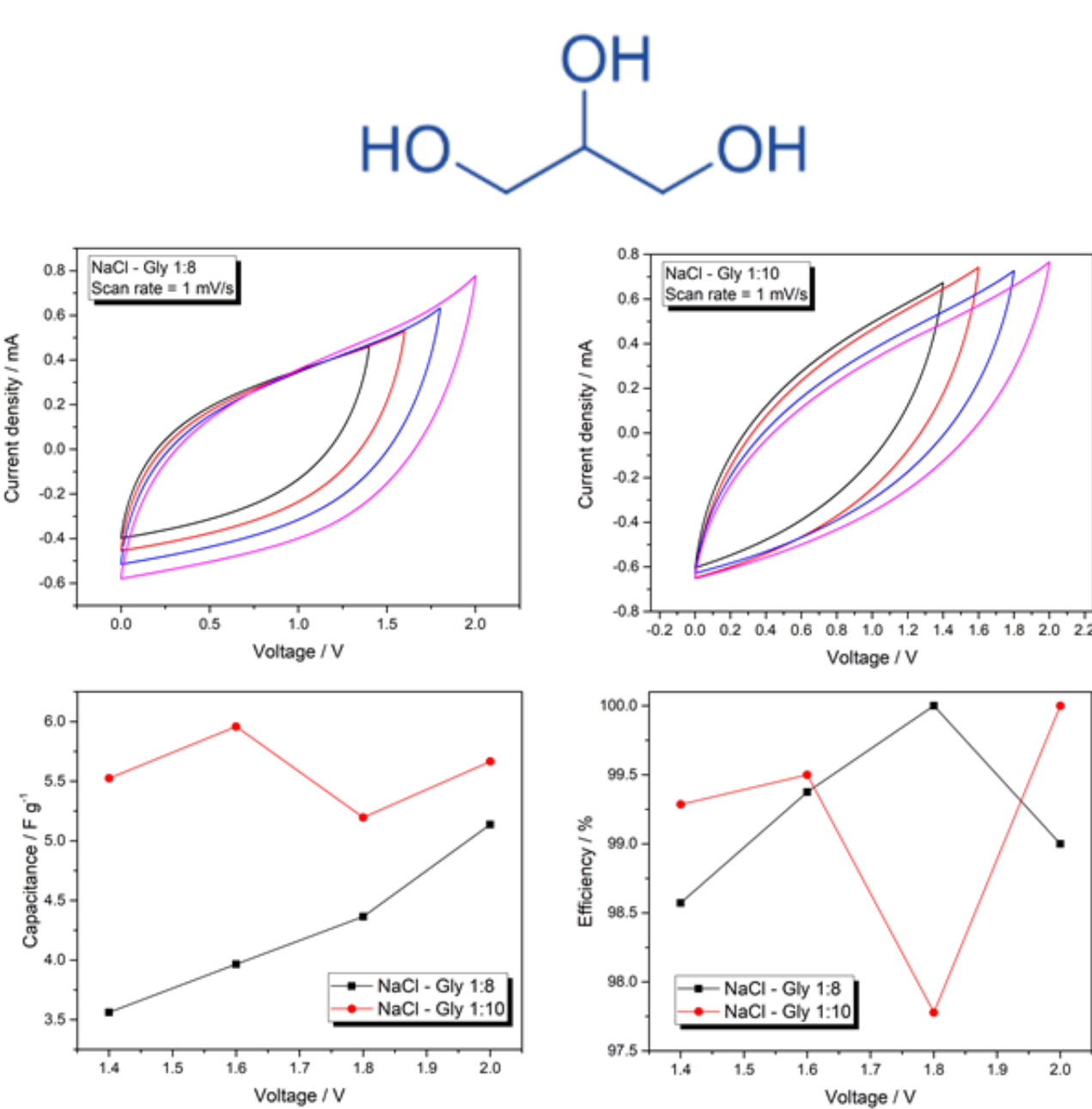
molar ratio NaCl/Gly	T_m (°C) experimental	ΔT_{cr} (°C) ^a theoretical
pure Gly	4	0
1/16	-8	9.64
1/14	-15	11.01
1/12	-18	12.85
1/10	-19	15.41
1/8	-16	19.28

^a calculated accordingly to the equation $\Delta T_{cr} = i \cdot K_{cr} \cdot m$ ($i = 2$, $K_{cr} = 7.1$ °C Kg mol⁻¹)

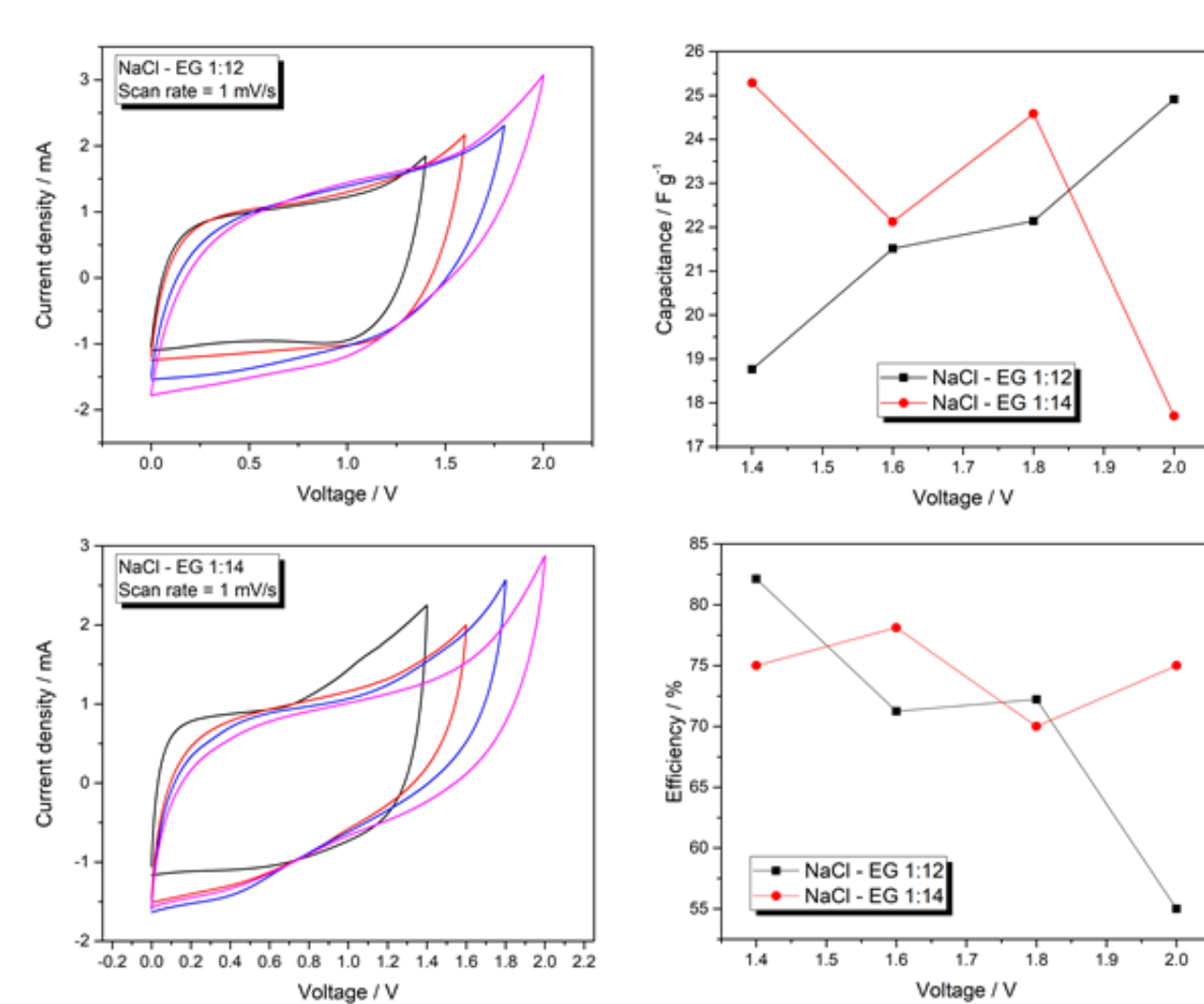
The glass-like behavior of both HBDs does not allow to obtain reliable data by means of DSC; thus we checked the melting point using a custom-made set-up consisting of a thermometer frozen inside the eutectic mixture. In the case of NaCl/Gly, the 1/10 mixture showed the deeper depression of the T_m , pointing toward the formation of a DES.

Electrochemical properties

After the preliminary spectroscopic and thermal characterization, the mixture showing an unconventional (DES-like) behavior have been further analyzed by means of electrochemical techniques.



Ionic conductivity of the mixture ranges between 0.2 and 5 mS cm⁻¹, with EG-based systems showing a higher values due to the lower viscosity. A good capacitive behavior (5–25 F g⁻¹) was proven for all the selected systems, that showed remarkable electrochemical stability up to 1 V for EG-based electrolytes, further extended at V > 2V for Gly-based ones.



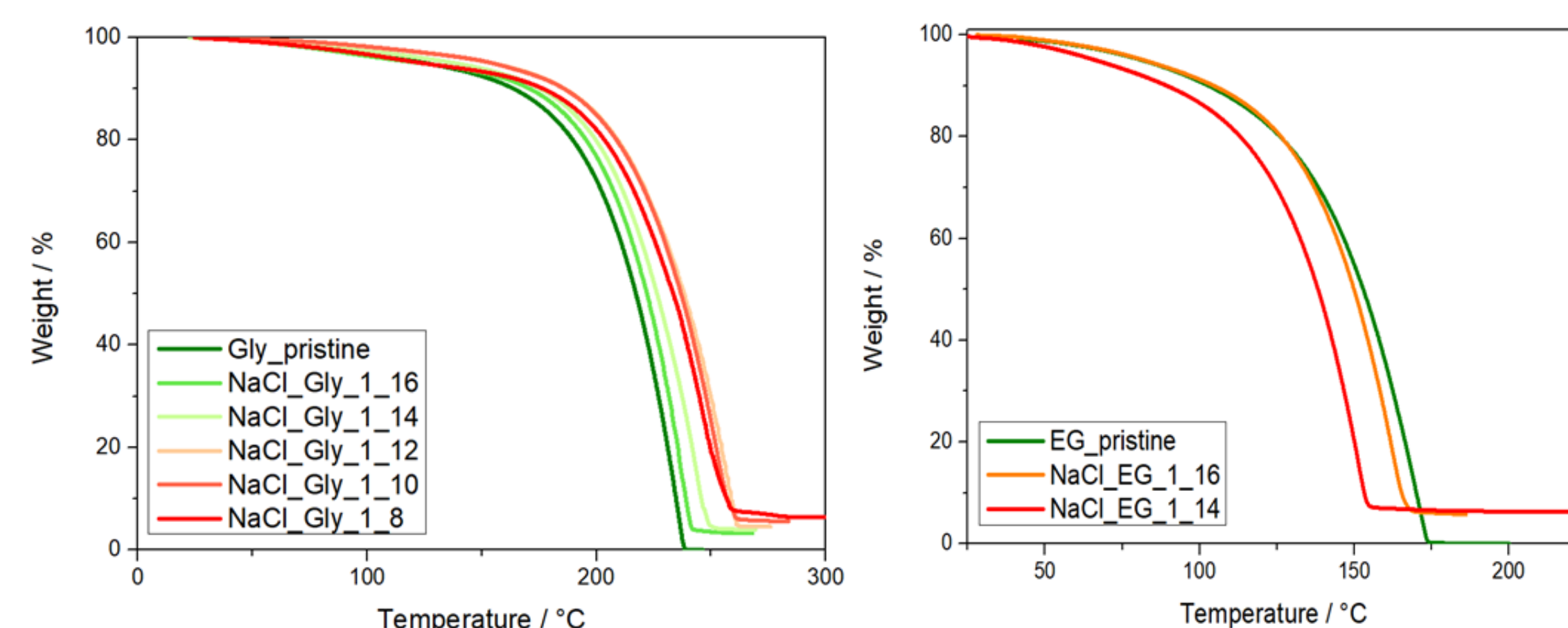
On going measurements

- **Karl-Fisher:** water is expected to play a dramatic role
- **Charge-Discharge** cycles in T-cell: suitability as real-life electrolytes for supercapacitors
- Evaluation of the precursors' whole life-cycle: are our electrolytes really **sustainable**?

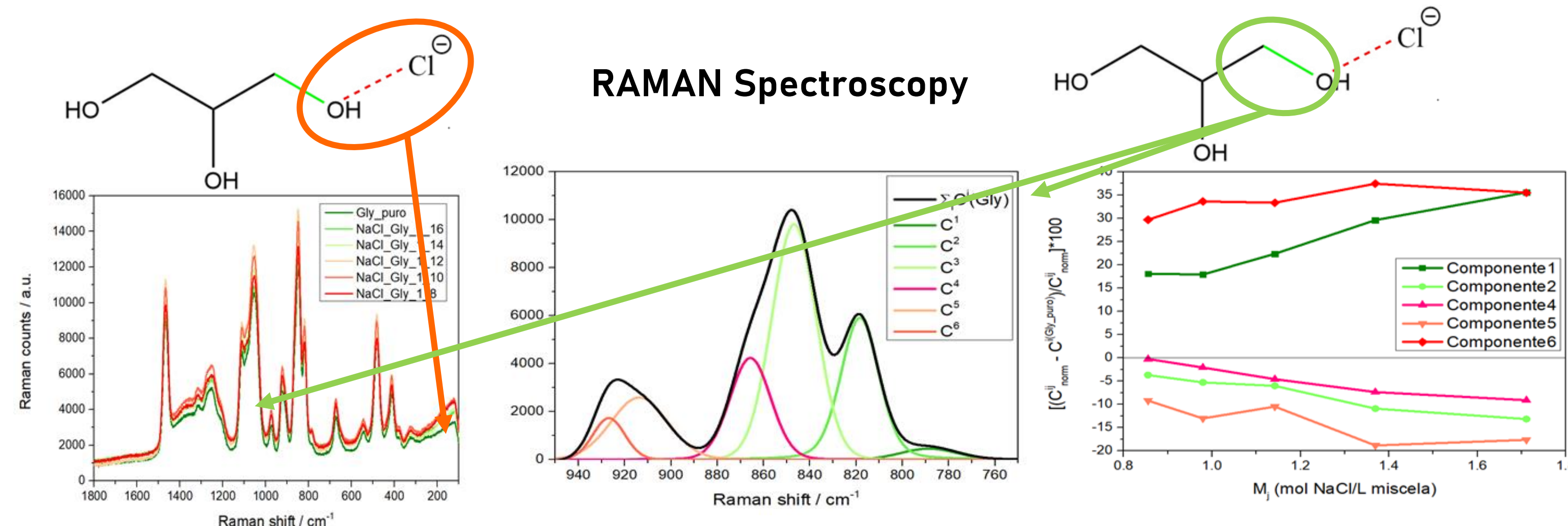


Thermogravimetric analysis

TGA gives some useful information on the thermal stability of our mixture, as well as insights on the possible interaction taking place into the mixtures. Indeed, in the present case, NaCl/Gly 1/8 or 1/10 have a non-monotonic behavior pointing toward unconventional interactions between the HBD and the HBA.



RAMAN Spectroscopy



Raman Spectroscopy measurements provide more specific insight into the nature of the HBD bonds directly involved in the interaction with the salt. From the comparison of the different spectra, the bands in the range of 780–940 cm⁻¹ (ascribable to C-C stretching) seem to be the most influenced by the presence of the salt. A clear change from the monotonic behavior could be seen for higher salt concentration (i.e. HBA/HBD ratio as high as 1:8), further confirming preliminary data from thermal analyses.

Conclusions

The characterization of different DES and DES-like mixtures, based on poly-alcohols as HBD and alkaline halides as HBA, has been performed. Spectroscopic and thermal analyses were proven to be essential to discriminate between DES and common salt-insolvent systems. Raman spectroscopy also gave useful insight to clarify the functional groups directly involved in the eutectic formation. Once selected, the DES(-like) systems were preliminary tested as electrolytes for supercapacitors, showing promising results.

Acknowledgements

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