Italian National Agency for New Technologies,
Energy and Sustainable Economic Development

Ionic liquid electrolytes for safer and more reliable sodium battery systems

NanoInnovation2020 (New Materials for Storage and Conversion)

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Outlines

- Energy worldwide demand
- Safety limitation of lithium/sodium batteries
- Ionic liquid electrolytes for sodium batteries
- Closing remarks

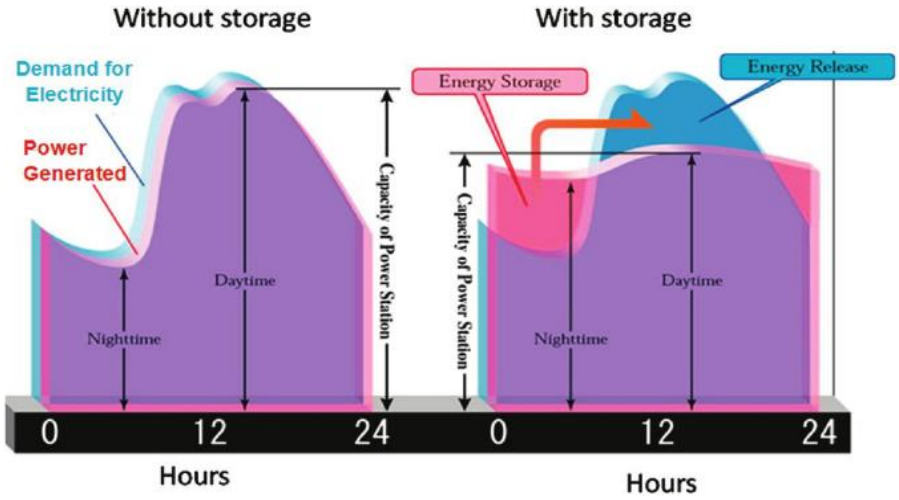
Energy worldwide demand

1) Why do we need to store energy?

- Demand of energy not corresponding to its availability
- Storage from renewable power sources



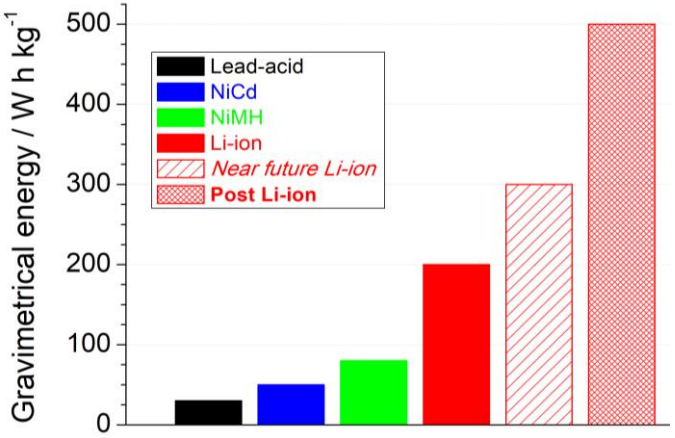
- Electric/hybrid vehicles

Z. Yang *et al*., , *Chemical Reviews* 111 (2011) 3577

Energy worldwide demand

2) Lithium *vs*. Sodium



G.B. Appetecchi, Safer electrolyte components for rechargeable lithium batteries, in *Electrochemical Storage Materials: From Crystallography to Manufacturing Technology*, D.C. Meyer, T. Leisegang, M. Zschornak, H. Stöcker, eds., De Gruyter Publishing, 2019, ISBN 978-3-11-049137-1.

- Sodium much more delocalized and available than lithium (> 1,000 times more)
- Na cheaper than Li
- $Na^+/Na°$ (2.7 V vs H^+/H_2) vs. $Li^+/Li°$ (3.0 V vs H^+/H_2)
- Al° as cathodic current collector instead Cu° (cheaper and lighter)

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Safety limitations of lithium/sodium batteries

1) The electrolyte drawback

- Volatile & flammable organic compounds (EC, DEC, EMC, DMC) as solvents for lithium/sodium batteries
- Overheating (!) and/or Overcharging (!)

↓

Temperature increase!
Internal pressure increase!

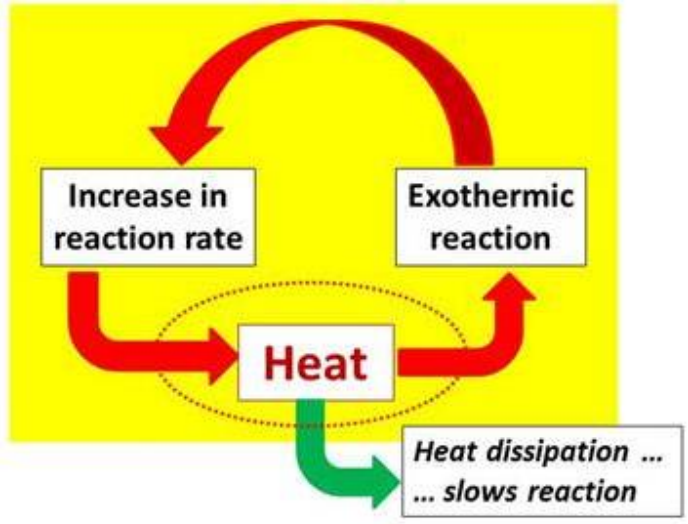
↓

Safety problems (*thermal runaway → venting, fire, explosion*)

✝ death of lithium battery …

☠ development of toxic HF gas …

G.B. Appetecchi, Safer electrolyte components for rechargeable lithium batteries, in *Electrochemical Storage Materials: From Crystallography to Manufacturing Technology*, D.C. Meyer, T. Leisegang, M. Zschornak, H. Stöcker, eds., De Gruyter Publishing, 2019, ISBN 978-3-11-049137-1.



Battery failure at ENEA (May 2015)

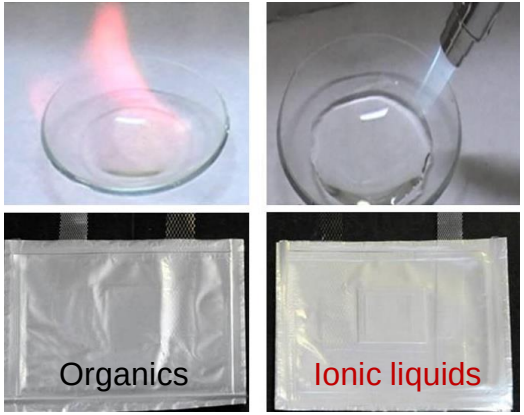
Towards safer and more reliable electrolyte components:
Ionic liquids

Safety limitations of lithium/sodium batteries
2) Ionic liquids

- Salts molten at room T or below (down to -60 °C)
- Organic cations & organic/inorganic anions

- **Favorable properties of this new class of materials**

- no measurable vapor pressure
- no flammability
- high specific heat
- high thermal/chemical/electrochemical stability
- high ionic conductivity
- able to dissolve lithium salts
- recyclability
- possibility of finely tuning the properties by modulating the chemical structure



Very wide application range …

Solvents for synthesis & catalysis processes

Separation/extraction/purification processes
Lubricants

Fluids for heat exchangers

Food industry

Artistic heritage maintenance

Electrochemical devices

G.B. Appetecchi, M. Montanino, S. Passerini, Ionic Liquid-based Electrolytes for High-Energy Lithium Batteries, in *Ionic Liquids Science and Applications*, ACS Symposium Series1117, A.E. Visser, N.J. Bridges and R.D. Rogers editors, Oxford University Press, Inc., American Chemical Society, Washington, DC, USA, 2013.

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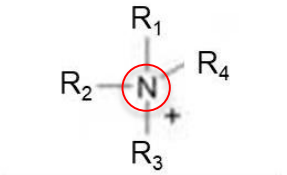
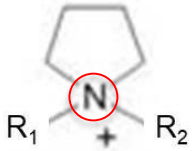
Ionic liquids electrolytes for sodium batteries

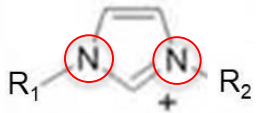
1) Viable ions



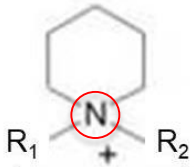
Tetraalkylammonium



Pyrrolidinium



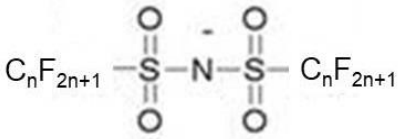
Imidazolium



Piperidinium

R_1, R_2, R_3, R_4 = methyl, ethyl, propyl … dodecyl

Cations



Per(fluoroalkylsulfonyl)imide

n = 0, 1, 2, 3, 4

Anions

Selected ions

Relatively small, asymmetrical ammonium, imidazolium and piperidinium ***cations***

- lower viscosity → faster transport properties
- low melting temperature
- good thermal/electrochemical stability

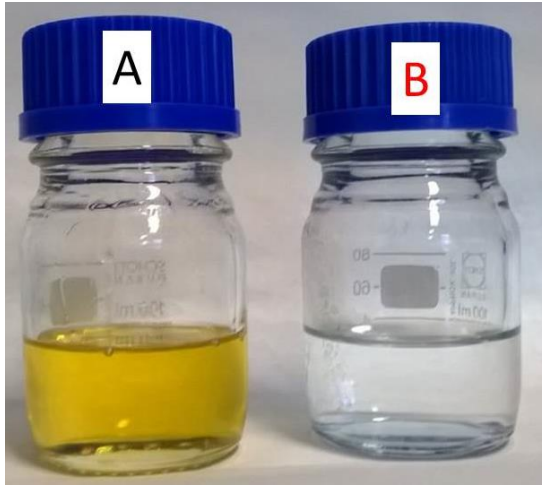
Symmetric (FSI and TFSI) and asymmetric (IM_{14}) per(fluoroalkylsulfonyl)imide ***anions***

- high anodic stability
- SEI forming ability (FSI)
- very low melting temperature (IM_{14})

Ionic liquids electrolytes for sodium batteries

2) Synthesis route

- Synthesis route designed and developed at ENEA
- Water as the only processing solvent
- Feasibility of full chemical recycling



A = before purification

B = upon purification

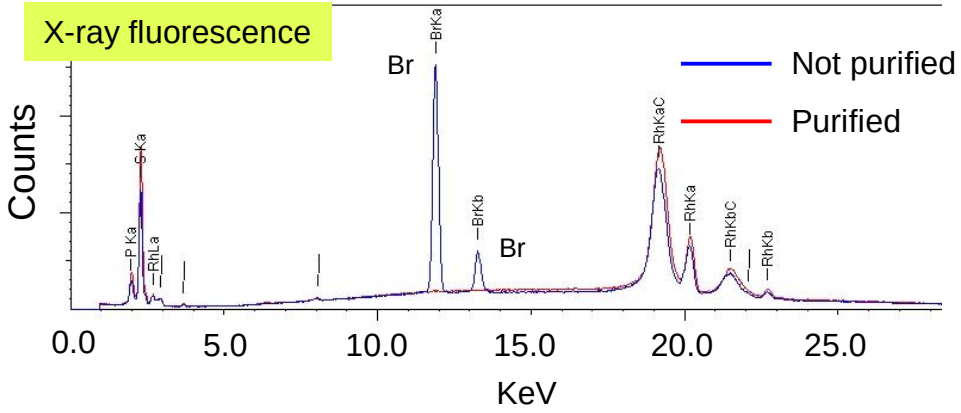
Summary of the investigated IL families

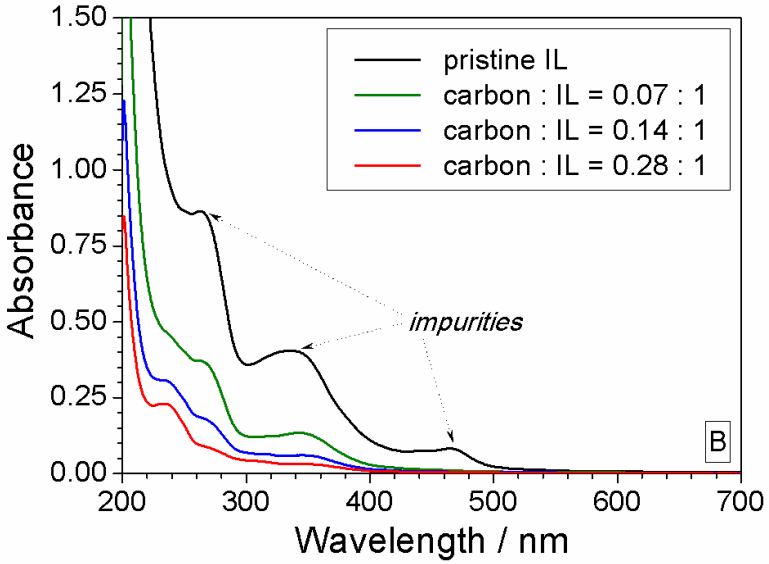
Acronym	IL sample
EMI-FSI	1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide
EMI-TFSI	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
$N_{1114}FSI$	bis(fluorosulfonyl)imide
$N_{1114}TFSI$	bis(trifluoromethylsulfonyl)imide
$N_{1114}IM_{14}$	(nonafluorobutylsulfonyl)(trifluoromethylsulfonyl)imide
$PIP_{13}TFSI$	*N*-methyl-*N*-propylpiperidinium bis(trifluoromethylsulfonyl)imide
$PIP_{14}TFSI$	*N*-butyl-*N*-methylpiperidinium bis(trifluoromethylsulfonyl)imide

Ionic liquids electrolytes for sodium batteries

3) Quality control

X-ray fluorescence



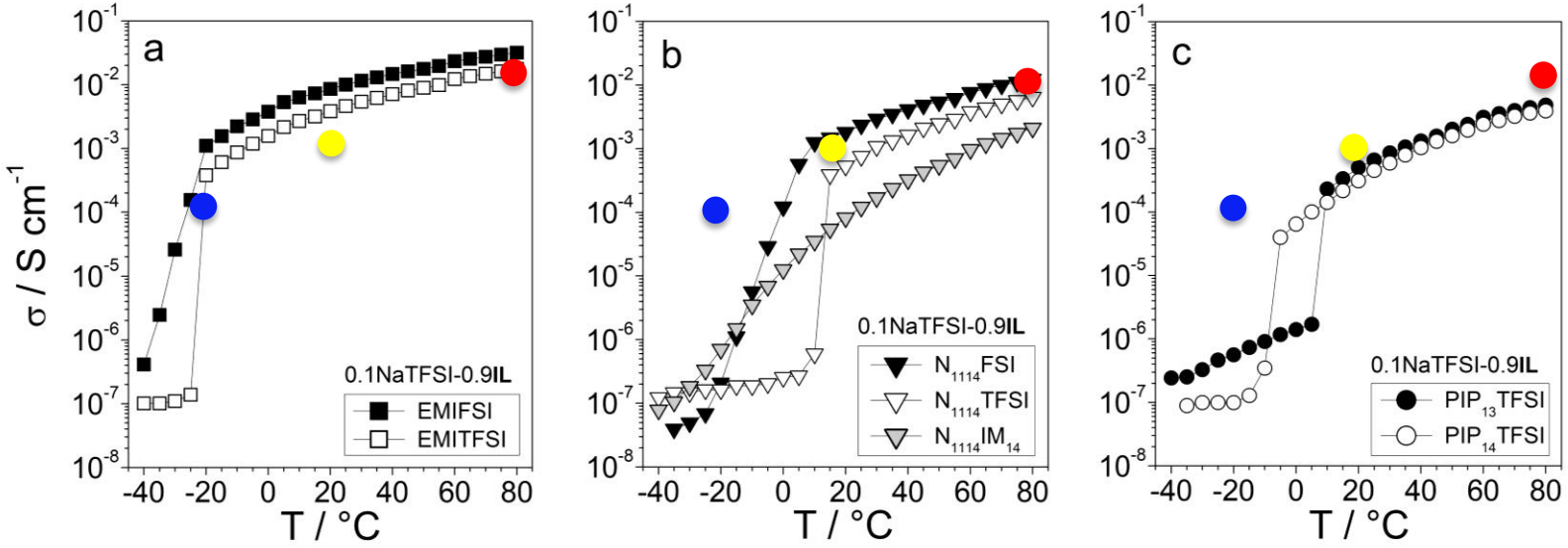


UV-Vis spectrophotometry

- Purification route through sorbents and water
- < 2 ppm halide, alkaline metals, water
- Overall purity level > 99.9 %

Ionic liquids electrolytes for sodium batteries

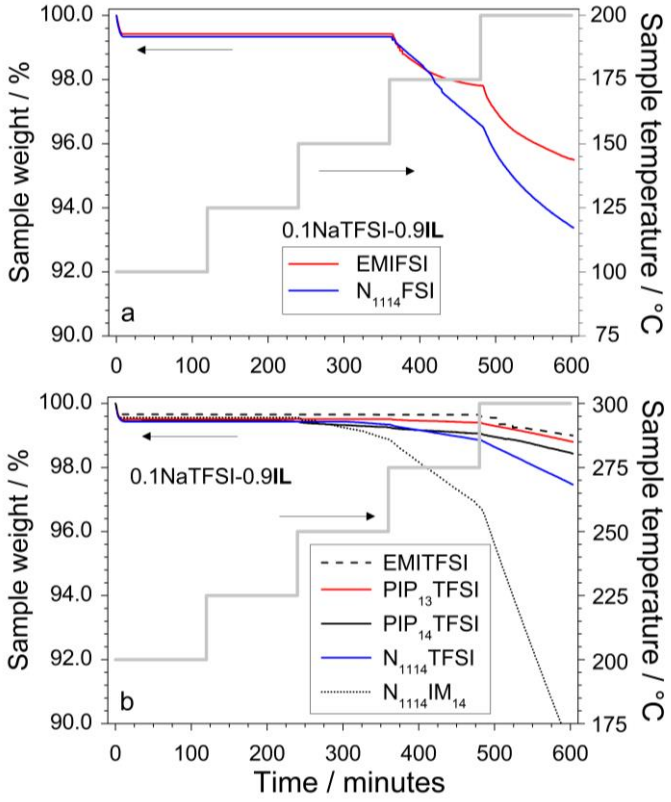
4) Ion transport properties



- *Ionic conductivity vs. temperature of 0.1NaTFSI-0.9IL sodium electrolytes*
- EMI-based electrolytes appealing even at low temperature (around 10^{-3} S cm^{-1} at -20 °C)
- The FSI electrolytes display faster transport properties than the TFSI and IM_{14} ones
- Conductivity > 10^{-2} S cm^{-1} is approached at 80 °C

Ionic liquids electrolytes for sodium batteries

5) Thermal stability



- *Thermal stability of 0.1NaTFSI-0.9IL sodium electrolytes*
- Isothermal TGA more reliable than the T-ramp one
- Thermal stability generally ranging from 225 to 250 °C
- Lower stability for the FSI electrolytes (150 °C)
- EMITFSI-based electrolyte thermally robust up to 275 °C

Possibility to be used in devices operating at temperatures (i.e., > 100 °C) not allowed to the standard organic solutions

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Closing remarks

- Ionic liquids, based on tetraalkylammonium, imidazolium, piperidinium cations combined with per(fluoroalkylsulfonyl)imide anions, are viable electrolyte components for safer sodium batteries
- Ionic liquids synthesized/purified according to an eco-friendly procedure
- Good ion transport properties
- Very wide operative temperature range (from -20 to 150 °C)
- The thermal stability, in conjunction with the flame retarding properties and the very low volatility, strongly increases the reliability and the safety of the device, particularly in the case of prolonged overheating

Acknowledgements

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Thanks a lot for your attention !