Ionic liquids to the rescue? Overcoming the ionic conductivity limitations of polymer electrolytes

Dr. S. Passcrini

(ENEA-IDROCOMB)

Ionic liquids to the rescue? Overcoming the ionic conductivity limitations of polymer electrolytes

W. A. Henderson, J. H. Shin, F. Alessandrini and S. Passerini

ENEA - IDROCOMB
Via Anguillarese 301, Rome, Italy

ENEA

Abstract

Polymer electrolytes - solid polymeric membranes with dissolved salts - are being intensively studied for use in all-solid-state lithium-metal-polymer (LMP) batteries to power consumer electronic devices. The low ionic conductivity at room temperature of existing polymer electrolytes, however, has seriously hindered the development of such batteries for many applications. The incorporation of salts molten at room temperature (room temperature ionic liquids or RTILs) into polymer electrolytes may be the necessary solution to overcoming the inherent ionic conductivity limitations of 'dry' polymer electrolytes.

ENEA

ENEA

Italian Agency for New Technologies, Energy and the Environment

ENEA is a **governmental organisation** working in the fields of research and innovation for sustainable growth, with the aim of promoting development, competitiveness and new jobs together with environmental protection.

ENEA acts as a **technology agency**, providing scientific and technological consulting and support to national and local bodies for the solution of problems, the preparation of regulations and participation in international initiatives and projects.

3000 employees with a large share (45%) of graduated people

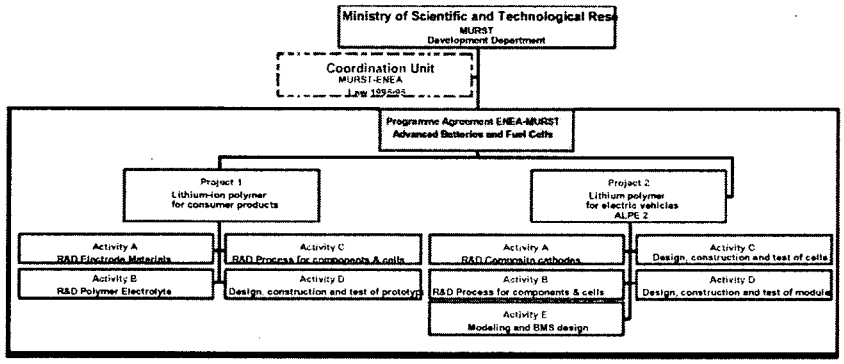
Expertise and Activities:
Engineering, Materials Science, Chemistry, Physics, Geology, Mathematics, Agriculture, Oceanography, Biology, Information Science & Technology, ...

ENEA

ELECTROCHEMICAL ENERGY STORAGE

Lithium Battery Projects

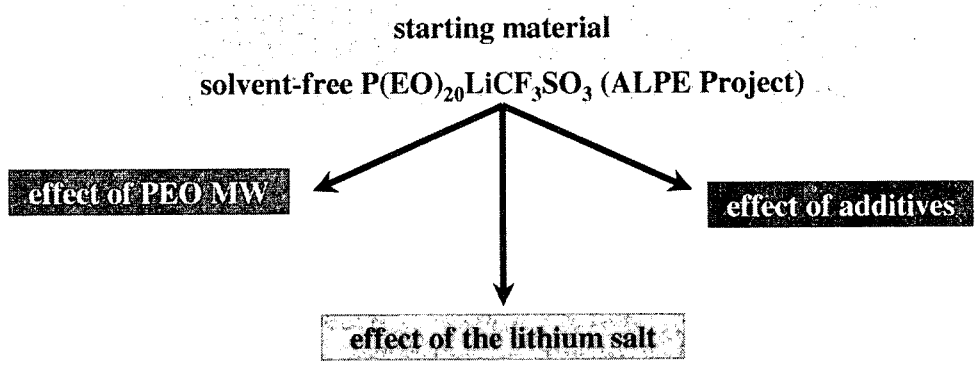
ENEA- Ministry of Research



4-year projects with a total budget of EUR 4 M

ENEA

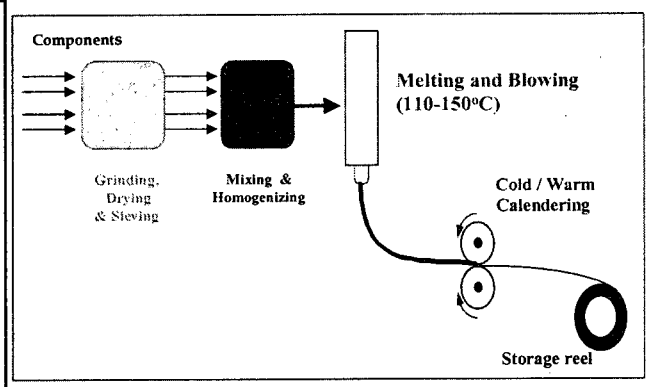
Development of Polymer Electrolytes for Lithium Metal Batteries at ENEA



ENEA

Solvent-free Processing of Polymer Electrolytes

- preparation in <u>water-free controlled environment (dry-room)</u>
- drying and sieving of high purity materials
- homogenizing of components
- melting and blowing of mixed powders
- calendering of extruded tapes (50 - 100 μm)

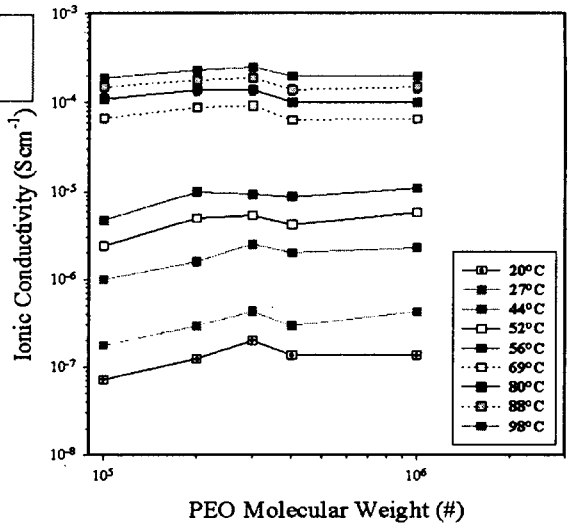


ENEA

Effect of PEO Molecular Weight

$P(EO)_{20}LiCF_3SO_3$
MW = 10^5 - 10^6

The PEO molecular weight plays a minimal role on the ionic conductivity of the $P(EO)_nLiCF_3SO_3$ complexes.

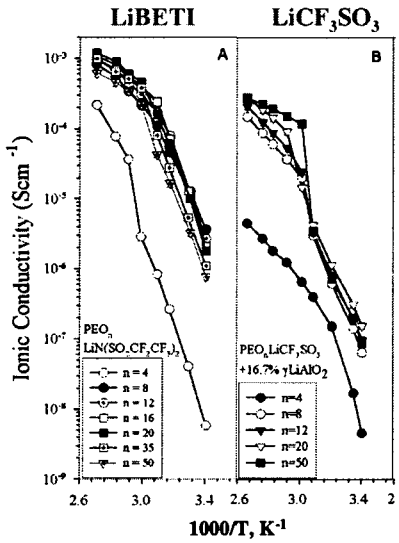


G.B. Appetecchi et al. , J. Power Sources, **97-98**, 790-794 (2001)

Effect of Salt: Nature

The ionic conductivity is strongly affected by the nature of the lithium salt.

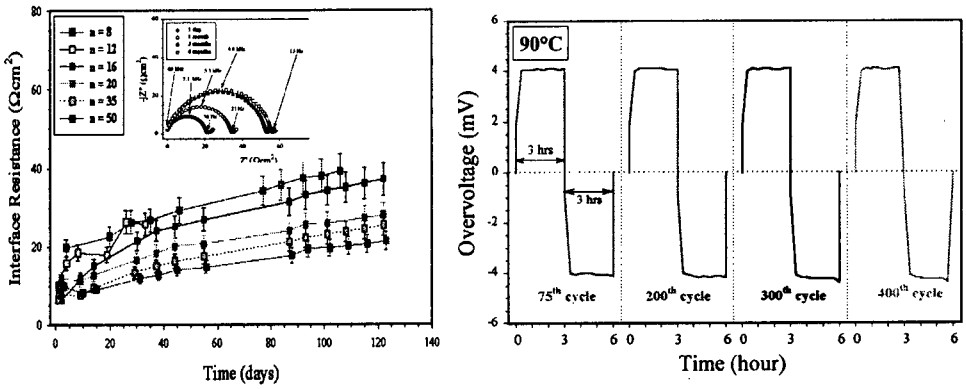
At least one order of magnitude increase in conductivity is obtained by using lithium salts able to plasticize the polymer matrix (i.e., LiBETI).



G.B. Appetecchi et al. , J. Power Sources, **97-98**, 790-794 (2001)

Effect of Salt: Lithium Interface

Li / $P(EO)_n$LiBETI / Li PEO M.W. = 4*10⁶ T = 90°C

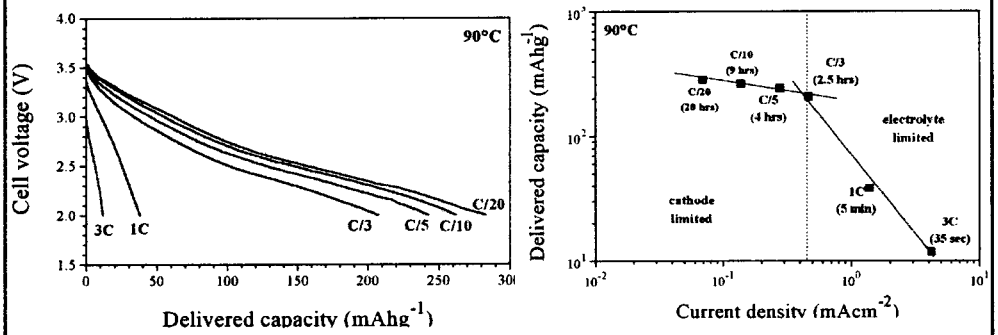


- **High stability of the Li/SPE interface upon very long storage times**
- **High reversibility of the lithium plating-stripping process.**

G.B. Appetecchi and S. Passerini , J. Electrochem. Soc, **149**, A891 (2002)

Effect of Salt:Performance in Batteries

Li / $P(EO)_{20}$LiBETI / V_2O_5-C-PEG-PEO

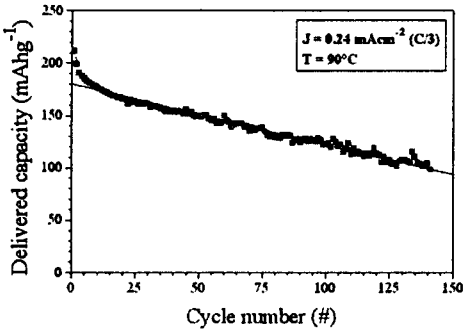


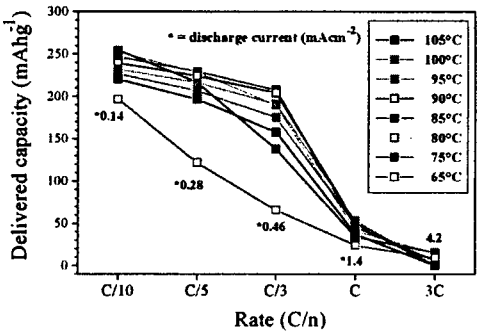
- **Similar voltage profiles are detected from C/20 (285 mAh g^{-1}) to C/3 rate.**
- **A capacity larger than 200 mAh g^{-1} is still delivered at C/3 rate.**

P. Villano, M. Carewska, G.B. Appetecchi and S. Passerini , J. Electrochem. Soc. **149**, A1282 (2002)

Effect of Salt: Performance in Batteries

Li / P(EO)$_{20}$LiBETI / V_2O_5-C-PEG-PEO



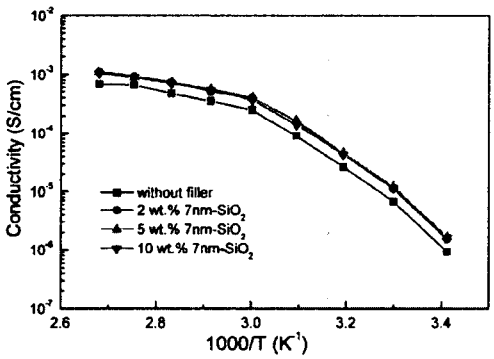


- The capacity fading (0.28) is lower than reported in the literature
- Delivered capacity is almost constant in the 80°C-105°C interval

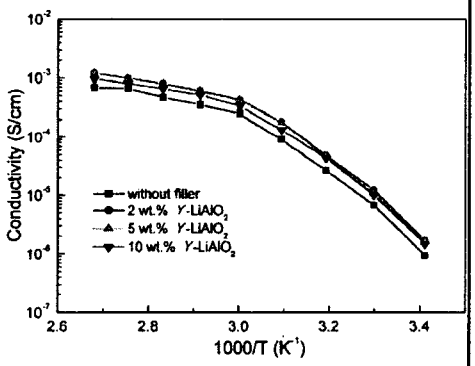
P. Villano, M. Carewska, G.B. Appetecchi and S. Passerini, J. Electrochem. Soc. 149, A1282 (2002)

Effect of Additives

Nano-sized fumed silica



Micro-sized lithium aluminate



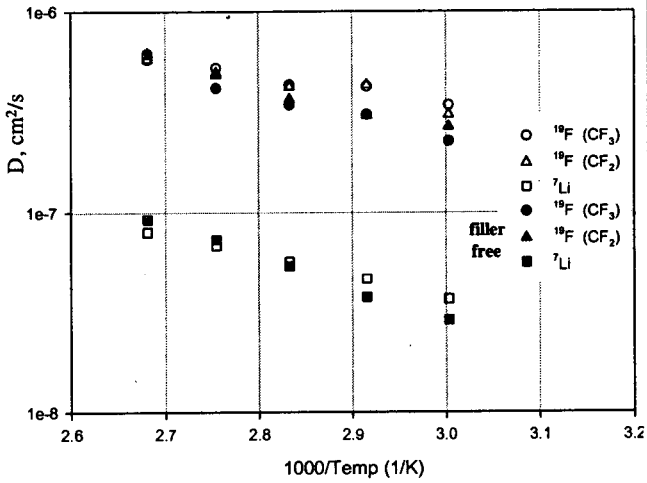
- Only a slight increase of the ionic conductivity is observed
- Independent on the nature and size of the filler

J.H. Shin and S. Passerini, J. Electrochem. Soc, accepted 2003

Effect of Additives: Diffusion Coefficients by Pfg-NMR

$P(EO)_{20}LiBETI$- 10% SiO_2 (7 nm)
PEO M.W. = 4*10⁶

- Only a slight increase of the Li diffusion coefficient is observed at 60-70°C.
- Most of the conductivity enhancement is associated with the anion

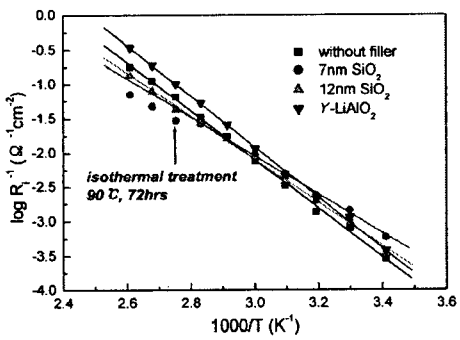


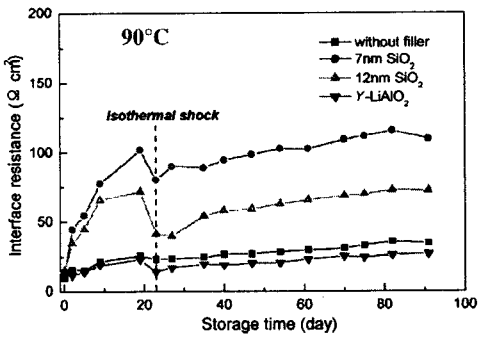
ENEA

S. Suarez, S. Abbrent, S.G. Greenbaum, J.H. Shin and S. Passerini, Solid State Ionics, submitted (2003)

Effect of Additives: Lithium Interface

Li / $P(EO)_{20}LiBETI$- 10% SiO_2 (7nm) / Li





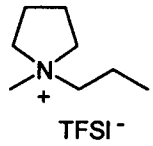
- No substantial improvement of the lithium interface by the addition of fillers

ENEA

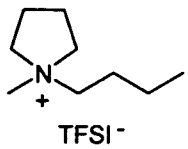
J.H. Shin F. Alessandrini and S. Passerini, Electrochim. Acta, submitted 2003

New Additives: Ionic Liquids

Typically consist of organic cations and anions such as $TFSI^-$ or $BETI^-$. The low melting temperature results from unfavourable crystal packing and ion flexibility.



T_m= 12°C



T_m= -18°C

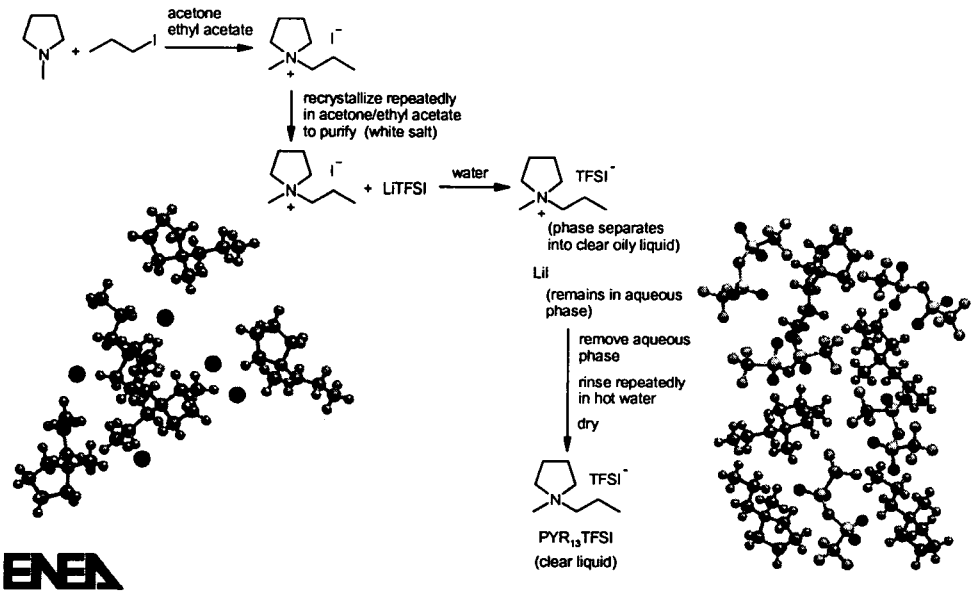
N-methyl N-alkyl pyrrolidinium TFSI

Properties

negligible vapor pressures
high ionic conductivities
electrochemically/thermally stable
easily dissolve lithium salts (doping)

ENEA

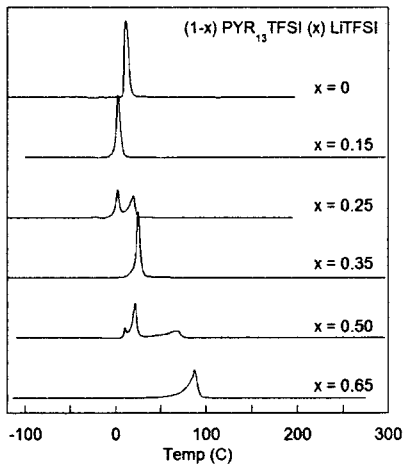
Synthesis of Ionic Liquids



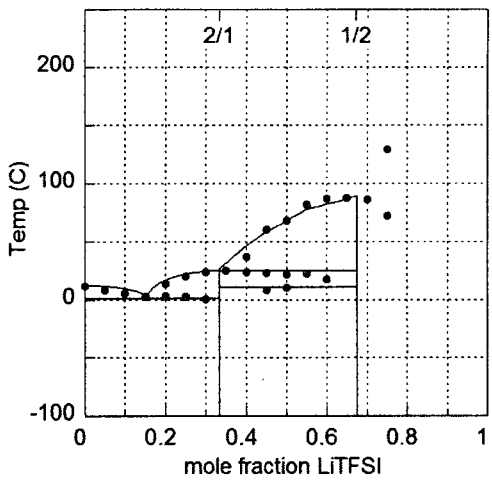
ENEA

LiTFSI-IL Thermal Properties

DSC

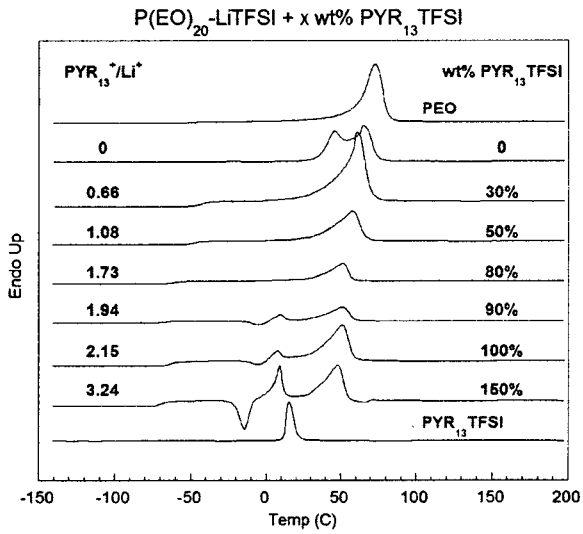


Phase Diagram



- **Liquid at room temperature down to IL/LiTFSI ratio of 2**

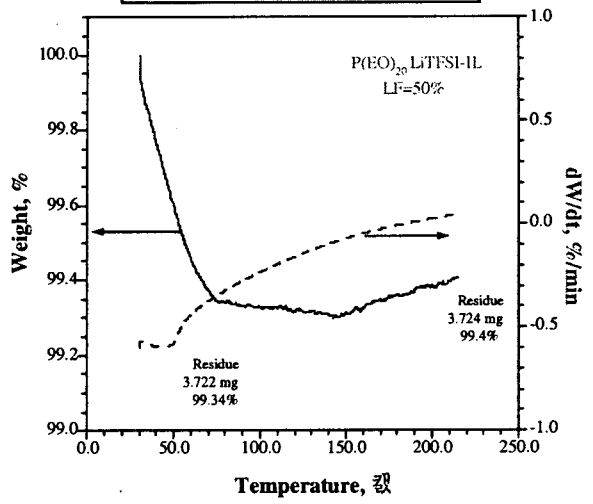
$P(EO)_{20}$LiTFSI-IL Thermal Properties



- **Lowers the crystallinity of the pure polymer and the polymer-salt (conducting) phases**

$P(EO)_{20}LiTFSI$-IL Thermal Properties

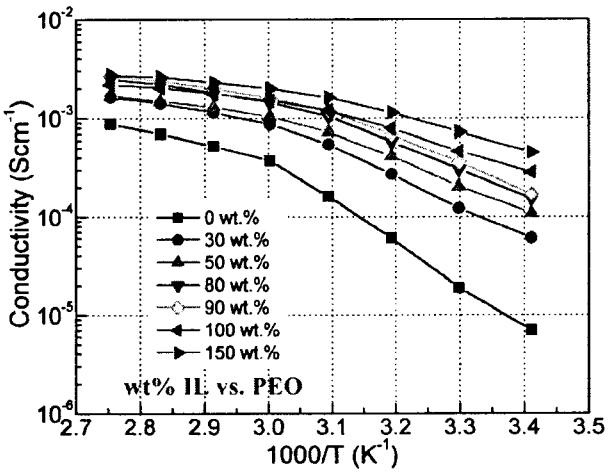
Thermal Stability



• Virtually no weight loss up to 220°C

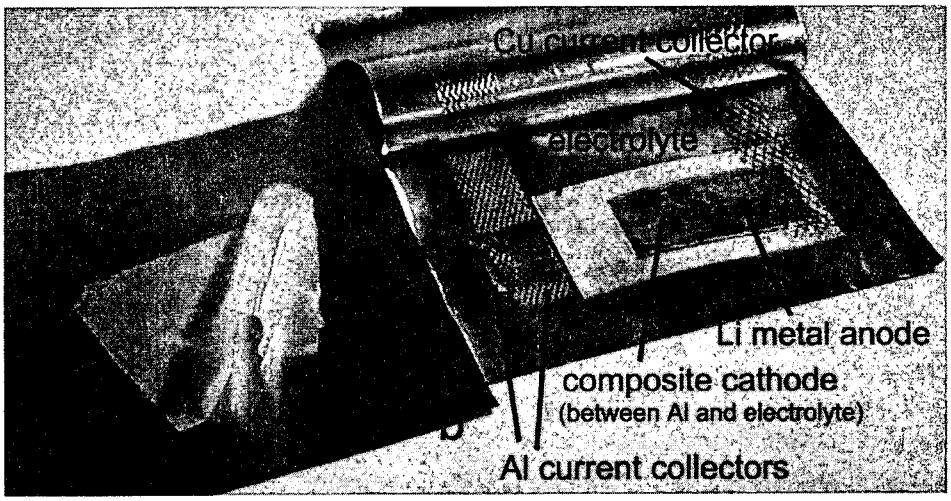
$P(EO)_{20}LiTFSI$-IL

Ionic Conductivity



• Very good ionic conductivity (> 10^{-4} S/cm @ RT for IL 50 wt.%)

$P(EO)_{20}LiTFSI$-IL

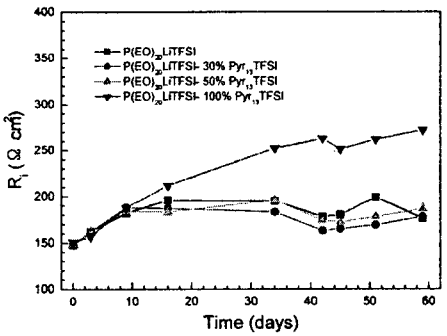


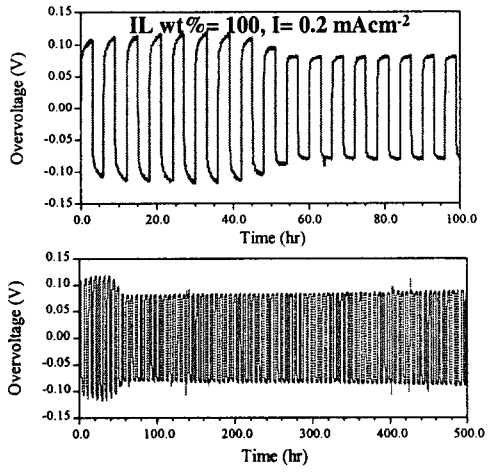
- Good mechanical properties of the polymer electrolyte (IL wt% = 150)
- Vacuum-sealed, laminated solid-state cells

ENEA

$P(EO)_{20}LiTFSI$-IL Lithium Interface

Li / $P(EO)_{20}LiTFSI$-IL / Li @ 60°C



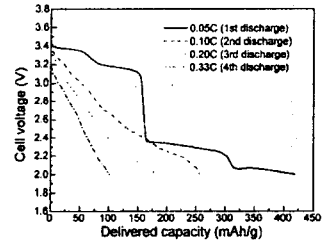


- Good interfacial properties with lithium for IL wt% 100
- Very good lithium plating/stripping (IL wt% = 100)

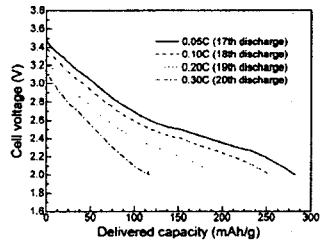
ENEA

$P(EO)_{20}LiTFSI$-IL Battery Tests

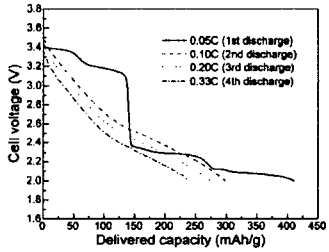
$Li/P(EO)_{20}LiTFSI$-80wt.%IL/V_2O_5 @ 60°C

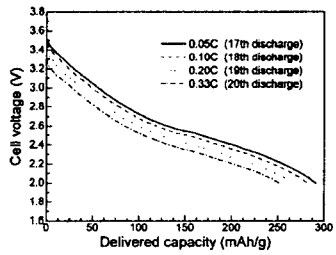


Charge: C/20
Discharge: C/20
C/10
C/5
C/3



$Li/P(EO)_{20}LiTFSI/V_2O_5$ @ 90°C





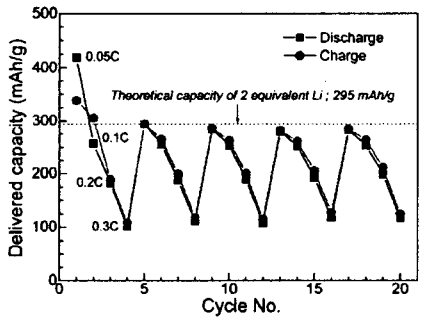
Operating temperature is lowered of almost 30°C by the addition of the ionic liquid

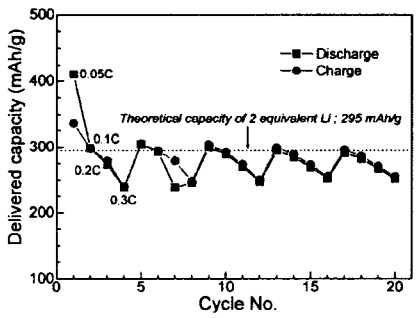
$P(EO)_{20}LiTFSI$-IL Battery Tests

$Li/P(EO)_{20}LiTFSI$-80wt.%IL/V_2O_5 @ 60°C

$Li/P(EO)_{20}LiTFSI/V_2O_5$ @ 90°C

Charge: C/20
Discharge: C/20
C/10
C/5
C/3

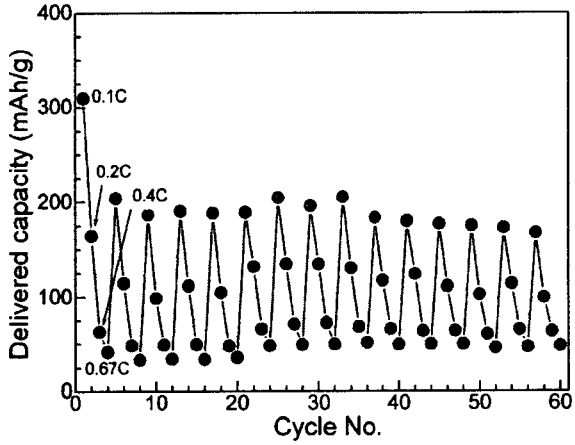




Operating temperature is lowered of almost 30°C by the addition of the ionic liquid

$P(EO)_{20}LiTFSI$-IL Battery Tests

$Li/P(EO)_{20}LiTFSI$-80wt.%IL/V_2O_5 @ 60°C



Charge: C/20
Discharge: C/10
C/5
C/2.5
C/1.5

- High battery capacity at C/10 rate
- Promising cyclability

ENEA

Conclusions

Amorphous polymer electrolytes show much higher ionic conductivity than crystalline ones:

Salt (anion)...concentration...additives (ionic liquids)...temperature

Ceramic additives (SiO_2 and lithium aluminate) do not significantly affect the ionic transport properties of PEO-LiBETI electrolytes).

Ionic liquids reduce the operating temperature of PEO-based polymer electrolytes without worsening the material properties such as thermal and mechanical stability, lithium interface and cathode interface.

ENEA

Acknowledgements

Financial support by MIUR-Italian Ministry of Education, University and Research

Dr. Steve Boyd (3M) for kindly providing LiTFSI and LiBETI