Ionic Liquids and Solid-state Lithium Metal Batteries

J.-H. Shin, W.A. Henderson, S. Scaccia, P.P. Prosini and S. Passerini*

ENEA (Italian National Agency for New Technology, Energy and the Environment), IDROCOMB Via Anguillarese 301, 00060 Rome, Italy e-mail: passerini@casaccia.enea.it, tel. (+) 39 06 3048 4985, fax (+)39 06 3048 6357.

Lithium-ion batteries are currently the battery of choice for high-energy applications such as portable electronics, telecommunications and hybrid electric vehicles. The next generation lithium metal batteries require different, preferably solid-state, electrolytes. Polymer electrolytes appear to be the most promising, but their ionic conductivity at ambient-moderate temperatures is much too low. New methodologies are required to improve the performance of such electrolytes [1].

Ionic liquids (ILs) - salts which are liquids at or near temperature – are revolutionizing room manv technologies resulting in more environmentally friendly chemistry. Here it is shown that the 'greener' incorporation of room-temperature ILs into conventional PEO-lithium salt electrolytes dramatically improves the performance (i.e., specific energy and power) of solidstate lithium metal batteries at low temperatures. These are true 'dry' polymer electrolyte consisting only of commercial PEO and two salts (with $\mathrm{Li}^{\scriptscriptstyle +}$ and organic cations and common anion). The resulting membranes have high ionic conductivities and both excellent mechanical properties and electrochemical stabilities [2].

The polymer electrolytes and the cathodes containing the ionic liquid have been subjected to an extensive electrochemical characterization that will be presented at the meeting. Figures 1 and 2 illustrate the cycling behavior of a Li/LiFePO₄ battery operating at 40°C. In spite of the relatively low temperature for a dry polymer electrolyte, the battery was able to deliver more than 90% of the cathode nominal capacity in C/20 rate discharges. The battery showed a full cycle efficiency with no fading on cycling. To our knowledge this is the best performance obtained for 'dry' polymer electrolytelithium metal batteries at such a moderate temperature. A further optimization of the ionic liquid is expected to allow room temperature operation.

It is often found that varying the materials of a polymer electrolyte (polymer, salt, inorganic fillers, molecular solvents) may improve the ionic conductivity. Very often, however, such an improvement is associated with detrimental effects on other properties such as electrochemical or mechanical stabilities, or is too limited to enable the practical use of the polymer electrolyte. Many of these 'improved conductivity' materials reported did never find utility in commercial-like devices. It is important to emphasize that, as opposed to materials reported previously [3-6], the solid polymer electrolyte membranes proposed here were actually utilized and tested in flexible, thin solid-state Li metal batteries (with no volatile components) at low temperatures.

Much of the research on solid polymer electrolytes has stagnated over the past decade due to a lack of original ideas for further improvements. The IL methodology demonstrated in this work is likely to dominate future electrolyte research in lithium metal battery technology.

Acknowledgement

Financial contribution from MIUR is kindly acknowledged. W.A.H. gratefully acknowledges the postdoctoral fellowship from the NSF International Research Fellowship Program (IRFP 0202620).

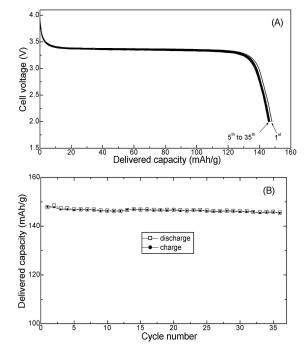


Figure 1. Voltage profiles (A) and delivered capacity (B) of a solid-state Li/polymer electrolyte/LiFePO₄ cell with $P(EO)_{20}LiTFSI + 80$ wt% PYR₁₃TFSI electrolyte discharged with C/20 rate at 40 °C.

References

- 1. J.-M. Tarascon, M. Armand, Nature 414 (2001), p.359.
- J.-H. Shin, W.A. Henderson, S. Passerini, Electrochem. Comm. 5 (2003) p.1016.
- 3. Z. Gadjourova, Y.G. Andreev, D.P. Tunstall, P.G. Bruce, *Nature* **412** (2001), p.520.
- 4. D.R. MacFarlane, J. Huang, M. Forsyth, *Nature* **402** (1999), p.792.
- C. Tiyapiboonchaiya, J.M. Pringle, J. Sun, N. Birne, P.C. Howlett, D.R. MacFarlane, M. Forsyth, *Nature Materials* 3 (2004), p.29.
- F. Croce, G.B. Appetecchi, L. Persi, B. Scrosati, *Nature* **394** (1998), p.456.