

Electrochemical properties of PEO-based solid polymer electrolytes blended with different room temperature ionic liquids

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Introduction

Room temperature ionic liquids (ILs) that consist of organic cations and inorganic anions find increasing interest in lithium electrochemistry since they possess many desirable properties like good thermal and chemical stability, low flammability, negligible vapor pressure, high ionic conductivity and wide electrochemical window [1,2]. Poly(ethyleneoxide) (PEO) based solid polymer electrolytes are one of the most promising materials for application in rechargeable lithium metal/ion polymer batteries due to their good thermal properties and interfacial stability with the Li electrode. However, their wide range application is hindered by the low room temperature ionic conductivity. In order to overcome this limitation, a promising approach being studied intensively in recent years is to incorporate an IL in such polymer matrices so as to transfer the benefits of ILs to polymer electrolytes [3].

Experimental

PEO (Aldrich, $M_w=2 \times 10^6$) and Lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) (Aldrich) were vacuum dried prior to use. The ILs were 1-butyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide (BMIMTFSI), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIMCF₃SO₃) were synthesized by reported procedure. The PEO₂₀-LiTFSI electrolyte was made by blending PEO corresponding to 20 EO units and 1 mole of Li salt. For preparing the electrolytes containing ILs, 100 wt% of PEO-LiTFSI was blended with 80 wt% of the IL. The ingredients were blended in a ball mill at 100rpm for 1h and then hot pressed at 100°C for 30 min to get a homogenous thin electrolyte film.

The ionic conductivities of the polymer electrolytes were measured by the AC impedance method using SS Swagelok cells with an IM6 frequency analyzer in the range 25-80°C. The measurements were carried out over the frequency range of 100mHz to 2MHz. The interfacial resistance of the electrolytes on Li metal was measured with the electrolyte sandwiched between Li electrodes over the frequency range 10mHz to 2MHz. Electrochemical stability window of the electrolyte was determined by linear sweep voltammetry (LSV) in Li/electrolyte/SS cells at the scan rate of 1mV/s. Cyclic voltammetry (CV) of the electrolyte sandwiched between Li electrodes was measured at a scan rate of 1mV/s between -1 and +1 V.

Results and discussion

The incorporation of 80 wt% of BMIMBF₄ and BMIMCF₃SO₃ in 100 wt% of PEO₂₀-LiTFSI resulted in free standing films with handling strength, whereas the film containing the same quantity of BMIMTFSI was more tacky and difficult to handle. The variation of ionic conductivity with temperature for the PEO₂₀-LiTFSI electrolyte as such and after blending with the three ILs is presented in Fig. 1. The incorporation of all the ILs resulted in enhancing the ionic conductivity and the effect was more pronounced at lower temperatures. At 25°C, the enhancement in ionic conductivity was by about 2 orders of magnitude compared to the system without IL. The effectiveness of the three ILs in enhancing the room temperature ionic conductivity of PEO electrolyte was in the order BMIMTFSI > BMIMBF₄ > BMIMCF₃SO₃. The highest value of ionic conductivity at 25°C was 3.2×10^{-4} S/cm, obtained with the incorporation of BMIMTFSI in the electrolyte.

Cyclic voltammogram of all the three IL-incorporated PEO₂₀-LiTFSI systems showed the presence of anodic and cathodic peaks at ~0.5V and -0.5V, respectively. The peaks were seen to be well-defined with good reversibility in repeated cycles, compared to the redox peaks observed for the system without IL. The interfacial resistance comparison showed that the system with BMIMTFSI had a much low interfacial resistance, less than half of that shown by the electrolyte without IL. The BMIMBF₄ system exhibited the highest interfacial resistance, probably due to the less permeable solid interface formed on the electrode because of the highly reactive HF that is invariably present along with (BF₄)⁻ anion. The performance of BMIMCF₃SO₃ system was intermediate compared to that of the other two ILs. The electrochemical window of the electrolytes was studied by LSV and the results are shown in Fig. 2. Compared to PEO₂₀-LiTFSI, all the electrolytes containing the IL had lower dissociation voltage. Among the three systems with IL, the order of electrochemical stability being BMIMTFSI > BMIMCF₃SO₃ > BMIMBF₄. Still, all the systems had stability >4.5V versus Li, thus demonstrating their suitability in lithium batteries.

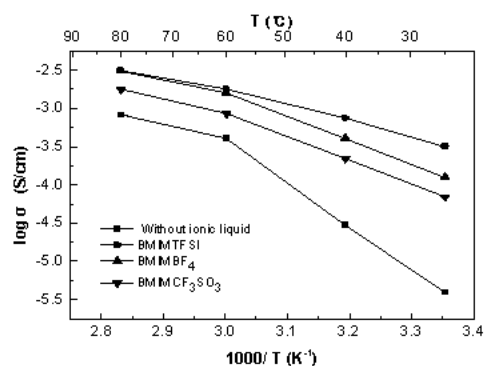


Fig.1. Variation of ionic conductivity with temperature for the polymer electrolytes with and without ionic liquids

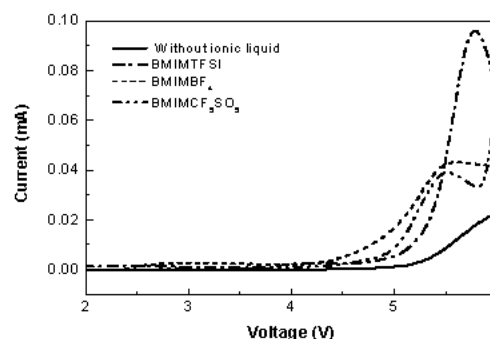


Fig.2. Electrochemical stability comparison of the polymer electrolytes with and without ionic liquids

Conclusions

The effect of incorporating three room temperature ionic liquids namely BMIMTFSI, BMIMBF₄ and BMIMCF₃SO₃ in the solid polymer electrolyte PEO₂₀-LiTFSI was studied for ionic conductivity and electrochemical properties. All the ILs enhanced ionic conductivity, and the effect was more at lower temperatures. The electrolytes had good electrochemical stability. BMIMTFSI was found to give the optimum results with a reduced interfacial resistance.

References

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