

P(VDF-co-HFP)/tetramethylurea sodium salt polymer gel electrolytes. Electrical and electrochemical characterization

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Introduction

Rechargeable batteries had become indispensable, as they supply the energy needed for our cars, phones, cameras or even our books. Lithium-ion batteries (LIBs) completely surpassed previous secondary batteries in terms of power density (maximum energy-to-weight ratios). However, problems have arisen related to the low abundance of lithium and its localization in conflictive areas of the planet [1,2], limiting the use of these batteries in long-size stationary electric energy storage systems. Since sodium is the sixth most abundant element in Earth and worldwide distributed, sodium-ion batteries (SIBs) have emerged as a promising alternative to LIBs. Our group is working on the three main components of batteries, both electrodes and the electrolyte. In this communication, we will focus on this last component. The electrolyte plays a crucial role regarding the safety of the system. Carbonate solvents, commonly used in electrolytes, are associated with high flammability. [3]. In order to circumvent this risk, alternative electrolyte components have been proposed. In particular, DESs (deep eutectic solvents) are a good alternative for common organic solvents as the manipulation of the melting temperature, ionic conductivity and the reduction stability of the system can be carried out by selecting a suitable HBD and HBA and their ratios.

On the other hand, the use of solid electrolytes, such as gel polymer electrolytes (GPEs), formed by incorporating liquid electrolytes to a polymer matrix, offers many advantages regarding liquid electrolytes, such as immunity from leakage, good ionic conductivity ($>10^{-3}$ S cm⁻¹ at room temperature), wide electrochemical stability window, high specific capacity, long cycle life, rapid charge and discharge, small size and mechanical flexibility [4].

In this work sodium ion P(VDF-co-HFP)/tetramethylurea-Na salt gel polymer electrolytes have been synthesized by solvent casting technique with varying sodium salt (NaTFSI, NaFSI) and tetramethylurea/Na salt ratio.

Experimental

Tetramethylurea and Na-salt (i.e. NaTFSI or NaFSI) in the corresponding ratio (10:1, 5:1, 4:1, 3:1, 2:1 TMU:Na-salt) were placed in a glass vial in an Ar-filled glovebox. After sealing the vial with a cap, the mixtures were heated at 100°C for 5h to obtain the electrolytes.

Polymer gel electrolytes, having 30 wt% of the P(VdF-co-HFP) copolymer and 70 wt% of the 10:1 TMU:Na-salt electrolyte, were obtained by dissolving in acetone, stirring for 1 h, casting on PTFE moulds and drying under controlled conditions. All operations and handling were made inside an argon-filled dry box with a humidity level below 1 ppm.

The phase transition and thermal stability of the samples were studied using differential scanning calorimetry and thermogravimetric analysis. The temperature dependence of the ionic conductivity was measured using a Novocontrol Alpha analyser in combination with a Novocontrol Quatro temperature controller, in the frequency range between 10⁷ and 0.1 Hz. The electrochemical stability window of the electrolytes was determined by cyclic voltammetry using a VMP3 multichannel potentiostat/galvanostat (Bio-Logic). The measurements were performed at room temperature in the potential range from -1 to 5V vs. Na/Na⁺ and 1 mV s⁻¹ scan rate.

Results and Discussion

Polymer gel electrolytes, having 30 wt% of the P(VdF-co-HFP) copolymer and 70 wt% of the 10:1 TMU:Na-salt electrolytes have been synthesized.

The mass ratio 10:1 was selected because these mixtures outperformed the more concentrated ones in terms of ionic conductivity and reduction stability. The corresponding characterization of the gel electrolytes is being carried out at the moment and the results will be discussed in the AMAPOLA workshop.

Fig. 1 (a) and (b) show the variation of ionic conductivity (σ) with the temperature obtained for the liquid electrolytes with NaTFSI and NaFSI respectively. Room temperature ionic conductivity of the liquid electrolytes reach values in the 10^{-3} S cm^{-1} range, in every ratio, the value of σ increasing when lowering the sodium salt concentration. This result suggests that high salt concentrations lead to high viscosity solutions decreasing ion mobility, which imply lower conductivity. It can be concluded that the viscosity of the electrolyte plays a crucial role, being the concentration of charge carriers of less importance.

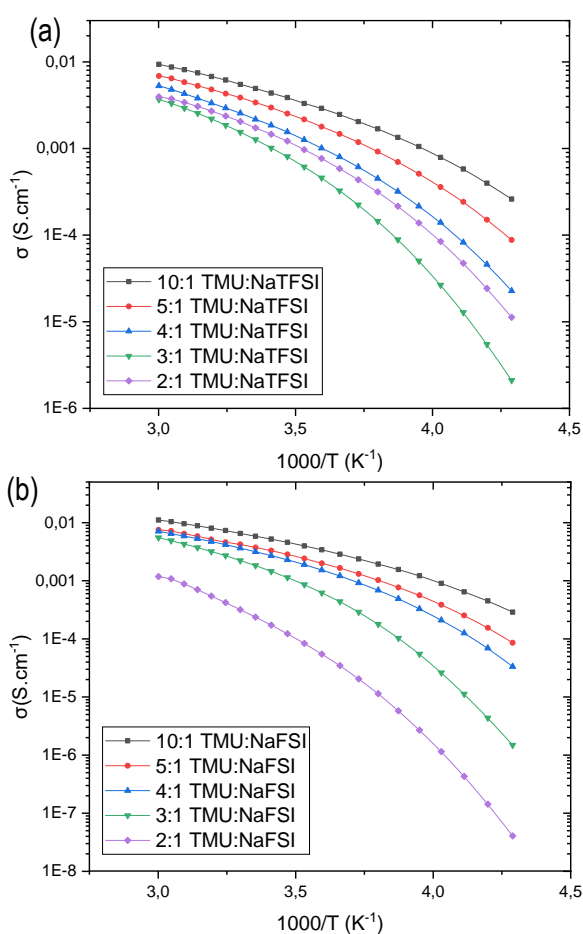


Fig. 1 Ionic conductivities obtained for liquid electrolytes (a) TMU:NaTFSI (b) TMU:NaFSI.

Cyclic voltammetry test between -1 and 5V of the liquid electrolytes with the higher ionic conductivity (Fig. 2) shows no significant peaks suggesting that no secondary chemical or decomposition reactions against sodium take place. On cycling, there are no drastic changes in the redox peaks and the similarity of the sweeps indicates that the charge transfer reaction at the interface between the electrolyte and sodium is reversible and the liquid electrolyte is stable in the 0 to 3.7V voltage window.

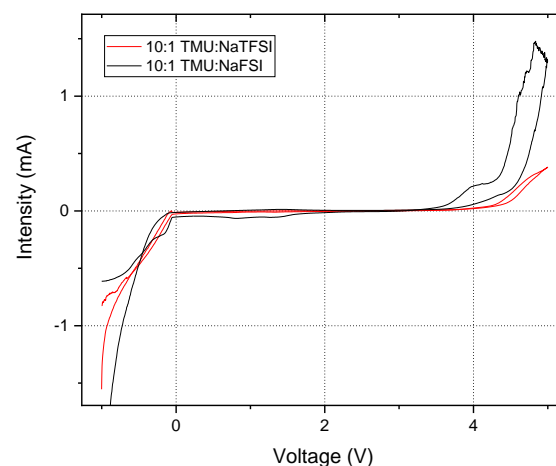


Fig. 2. Room temperature cyclic voltammograms at 1 mV s⁻¹ scan rate of TMU/NaTFSI and TMU/NaFSI with an TMU/sodium salt ratio 10:1.

Acknowledgements

This study was supported by the Spanish Ministry of Science, Innovation and Universities; project “Environmentally-guided electricity storage devices: from materials to the Na-ion battery prototypes”, Ref: RTI2018-095425-B-I00.

References

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