Phase behaviour and conductivity in phosphonium-based organic ionic plastic crystals mixed with sodium salts

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Organic ionic plastic crystals are highly promising solid state conductors for battery applications which have attracted much attention recently. Their unique properties include various solid-solid phase transitions before melting which causes a disordered phase after each transition, combined with negligible volatility, electrochemical and thermal stability have prompted many researchers to investigate different kinds of OIPCs, especially for the Li device applications. Nevertheless, due to some advantages of Na batteries versus Li devices and given that just two studies[1,2] have been conducted on mixtures of OIPCs with Na salts, this work focuses on a study of the physicochemical behaviour of the phosphonium cation organic ionic plastic crystal (OIPC) trimethyisobutylphosphonium bis(trifluoromethanesulfonyl)imide $P_{111i4}NTf_2$ (figure 1) upon addition of $NaNTf_2$ to determine the phase behaviour and derive fundamental understanding of the structure and dynamics in these mixtures.

The properties of these electrolytes, including phase behaviour and ion conductivity, have been studied using differential scanning calorimetry (DSC), electrochemical impedance spectroscopy (EIS), electrochemical techniques and nuclear magnetic resonance (NMR) spectroscopy.

The phase diagram for the $P_{111i4}NTf_2/NaNTf_2$ binary systems is determined (figure 2) and shows: (1) a eutectic transition at 35℃ with the composition of 5 mol% (2) a mixed salt crystalline phase at 20 mol% of $NaNTf_2$ with a stoichiometry of 4/1($P_{111i4}NTf_2$/ $NaNTf_2$) (3) an incongruous melting of this new crystalline phase at 45℃ which is probabaly a result of a peritectic reaction. Synchrotron XRD, solid-state NMR and SEM all consistent with the proposed phase diagram. Conductivity measurements indicate that ionic conductivity of two compositions (25 mol% and 50 mol%) high even in the solid state. This work suggests that these materials could be used as solid state electrolytes for all-solid state sodium batteries and will be the topic of future work.

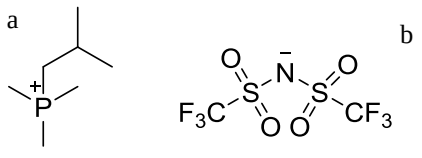

Figure 1. Structure of (a) TFSI$^-$ or NTf_2^- (b) P_{111i4}^+

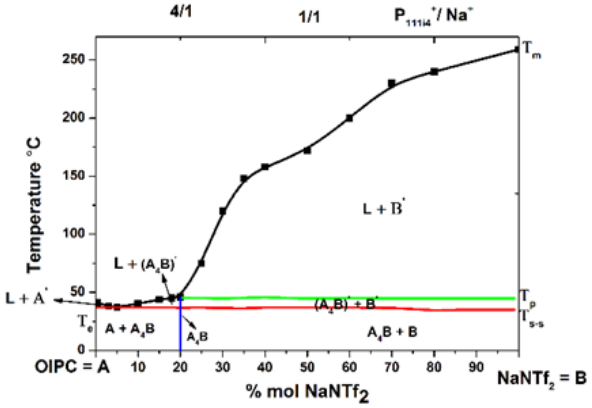

Figure 2. Phase diagram of mixed $P_{111i4}NTf_2/NaNTf_2$

[1] M. Forsyth, T. Chimdi, A. Seeber, D. Gunzelmann, P.C. Howlett, J. Mater. Chem.A, 2 (2014) 3993–4003.

[2] T. Chimdi, D. Gunzelmann, J. Vongsvivut, M. Forsyth, J. Solid State Ionics 272 (2015) 74–83.