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Ionic Conductivity in Crystalline $PEO_6:Li(AsF_6)_{1-x}(SbF_6)_x$

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Lithium-ion conducting polymer electrolytes, composed of a lithium salt, such as $LiPF_6$, dissolved in a solid coordinating polymer, such as poly(ethylene oxide) (PEO), hold the key to realizing the major goal of an all-solid-state rechargeable lithium battery.[1] Recent research has shown that ordered or crystalline polymer electrolytes can conduct, in contrast to the established view for 25 years that considered conduction to be confined to the amorphous phase above the glass transition temperature, T_g.[2] The α polymorphs of the crystalline polymer electrolytes $PEO_6:LiXF_6$, where X = P, As, or Sb, conduct, but the levels of conductivity are low, approximately 10^{-7} Scm^{-1}.[3] Recently, we have shown that modifying these stoichiometric crystalline complexes by replacing a few mol % of the XF_6^- ions by monovalent ions of very different shape and size (e.g., $N(SO_2CF_3)_2^-$) or anions of different charge (e.g., SiF_6^{2-}) can raise the ionic conductivity by 1.5−2 orders of magnitude compared with the stoichiometric complexes.[4] Here we report the remarkable result that when replacing one XF_6^- anion by another of the same shape and charge and similar size, that is, by forming the solid solution $PEO_6:Li(AsF_6)_{1-x}(SbF_6)_x$, the ionic conductivity also increases by more than 1 order of magnitude compared with either of the end members, $x = 0, 1$.

Experimental details are given in the Supporting Information. Briefly, methoxy end-capped PEO of average molecular weight, 1000 Da $[CH_3O(CH_2CH_2O)_{22}CH_3]$, was dissolved in acetonitrile along with $LiAsF_6$ and $LiSbF_6$. Samples consisting of various ratios of the salts were prepared, but in all cases, the ratio of ether oxygens to Li was maintained at 6:1. Following complete dissolution and then solvent removal, the resulting powders, which were shown by IR spectroscopy to contain no residual acetonitrile, were subjected to powder X-ray diffraction measurements (Figure 1). For all compositions examined in the range of $0 < x < 1$, the powder diffraction patterns exhibited peaks corresponding to the structure of the previously reported α polymorph of the 6:1 complex.[5] Note that a β polymorph with a significantly lower conductivity has recently been reported.[6] A continuous shift in the peak positions on varying the composition between $PEO_6:LiAsF_6$ and $PEO_6:LiSbF_6$ indicated a continuous solid solution exists across the entire composition range. There was no evidence of residual salts, PEO, or two phase mixtures between the end members.

How then does the solid solution formation influence the ionic conductivity? Pellets were pressed from powders forming self-supporting disks, which were placed between stainless steel electrodes and subjected to AC impedance measurements as a function of temperature. A single semi-circle was observed in all cases, associated with a capacitance of ∼2 $pFcm^{-1}$. This indicated that there were no grain boundary resistances impeding ion transport in these soft solids, consistent with previous observations for the stoichiometric 6:1 complexes, and that the conductivity is dominated by transport in the bulk of the materials. The variation of conductivity with composition at two different temperatures is shown in Figure 2a. The plots are symmetrical, showing a similar and dramatic rise in conductivity, starting from either of the end members.

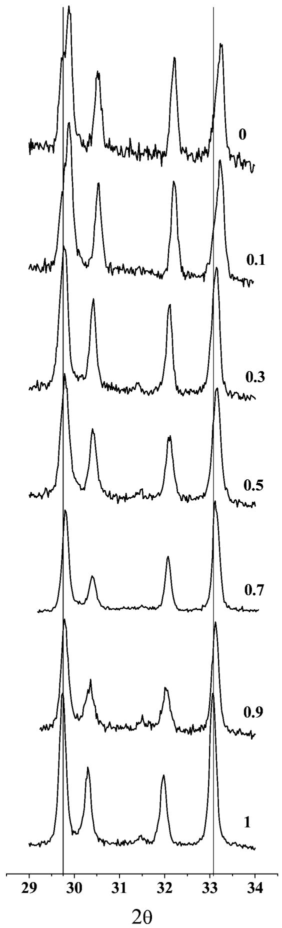

Figure 1. X-ray diffraction patterns of $PEO_6:Li(AsF_6)_{1-x}(SbF_6)_x$. Numbers indicate the values of x. Vertical lines mark the position of the strongest peaks of $PEO_6:LiSbF_6$ ($x = 1$).

Between the conductivity maxima at $PEO_6:(LiAF_6)_{1-x}(SbF_6)_x$, $x = 0.1$ and 0.9, the conductivities remain higher than the end members but do show a broad and shallow minimum centered around $x = 0.5$ (Figure 2a). The temperature-dependent conductivities are presented in Figure 2b. As noted previously for the crystalline 6:1 polymer electrolytes, the linearity of the log σ versus $1/T$ plots is consistent with ion hopping in a crystalline polymer electrolyte as opposed to conduction in an amorphous phase.[3] The temperature range is limited by melting at higher temperatures and difficulties of measuring low conductivities at low temperatures. There is a general trend indicating that the activation energies decrease on departing from stoichiometry, for either end member, and then increase again for compositions between 0.3 and 0.7, in keeping with the variation in conductivity with composition (Figure 2a).

In our previous studies of doped 6:1 complexes, the increase in conductivity could be understood in terms of substitution of the monovalent anion by another much larger and differently shaped monovalent anion, such as $N(SO_2CF_3)_2^-$, or by the introduction of

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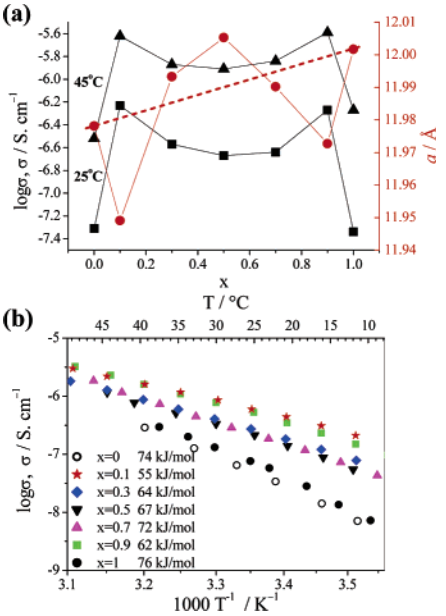

Figure 2. Conductivity of PEO_6:Li$(AsF_6)_{1-x}(SbF_6)_x$. (a) Conductivity isotherms, black, and variation of *a* lattice parameter, red, as a function of *x*. Dotted line represents a linear variation of *a* with composition. (b) Ionic conductivity as a function of temperature. Activation energies are given on plot.

interstitial lithium ions to maintain electroneutrality due to the substitution of the monovalent anions XF_6^- by divalent anions such as SiF_6^{2-}. However, in this case, the anions are of the same shape and charge and similar size. How might this conductivity enhancement be explained and why does the conductivity increase substantially on initial doping but exhibits a shallow minimum centered at $x = 0.5$?

AsF_6^- (ionic radius = 1.67 Å) and SbF_6^- (ionic radius = 1.81 Å) do exhibit a small difference in size, and it has been shown previously, in ceramic ionic conductors, that size difference alone is sufficient to induce an increase in conductivity. The ionic conductivity of AgI is increased by almost 3 orders of magnitude by replacing ~20 mol % of I^- with Br^-.[7] The increase was attributed to strain in the $AgI_{1-x}Br_x$ crystal structure due to the size difference between Br^- and I^-. Similarly, we propose that replacement of one XF_6^- anion by another, of smaller or larger size, will lead to strain and hence local disruption of the potential around the Li^+ ions in the 6:1 crystal structure, resulting in the observed higher conductivities. Although in the case of the polymer electrolyte a PEO chain lies between the Li^+ ions and anions, resulting in a greater distance between the charges than in AgI, the conductivity rises rapidly on replacing 10% of one XF_6^- ion by another, $x = 0.1$ and 0.9 in Figure 2a, consistent with the greatest disruption occurring on initial departure from stoichiometry. Once more than 1 out of 10 of the anions have been substituted, further doping does not lead to an increase in conductivity.

The variations of the monoclinic lattice parameters with composition are shown in Figures 2a and 3. It is striking to note how the variation in the *a* parameter, in particular, appears to correlate with the trends in conductivity (Figure 2a). The *a* lattice direction is coincident with the axis of the tunnels formed by PEO chains along which the Li^+ ions migrate. The data imply a contraction along the PEO tunnels up to $x = 0.1$, followed by an expansion to $x = 0.5$ and contraction again to $x = 0.9$. These trends are not reflected in the variation of *b* and *c* with composition; however, this is an anisotropic material. Vegard's law states that on replacement of an ion, A, by one of a different size, B, in a solid solution, if random, leads to a linear variation of the lattice parameters with composition.[8] Originally developed in the context of ceramic solid solutions and metal alloys, Vegard's law has been extended to molecular solids.[9] However, substitution is generally not random, and if ion A is more frequently surrounded by B and vice versa, then negative departures from Vegard's law may be observed, whereas positive deviations are associated with segregation, such that A and B are more likely to be surrounded by ions of their own type.[10] The negative deviations observed here for the *a* lattice parameter over the composition ranges $0 < x \leq 0.1$ and $0.9 \leq x < 1$ may indicate favorable mixing of the two XF_6^- anions on the atomic scale, consistent with local disruption of the potential around Li^+ and increasing conductivity (Figure 2a). The positive deviation around $x = 0.5$ is consistent with segregation of the two types of anions, which although insufficient to promote separation into two phases may be responsible for the shallow minimum around $x = 0.5$.

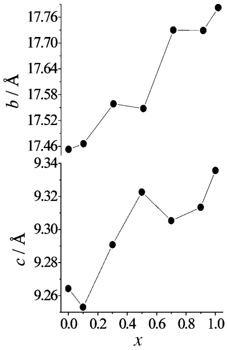

Figure 3. Variation of *b* and *c* lattice parameters in PEO_6:Li$(AsF_6)_{1-x}$-$(SbF_6)_x$ as a function of *x*.

Whatever the detailed interpretation of conductivity variation with composition, the results reported here represent the first example, outside the field of ceramic ionic conductors, of conductivity enhancement due to doping with ions differing only in size.

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Supporting Information Available: Experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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