Communication

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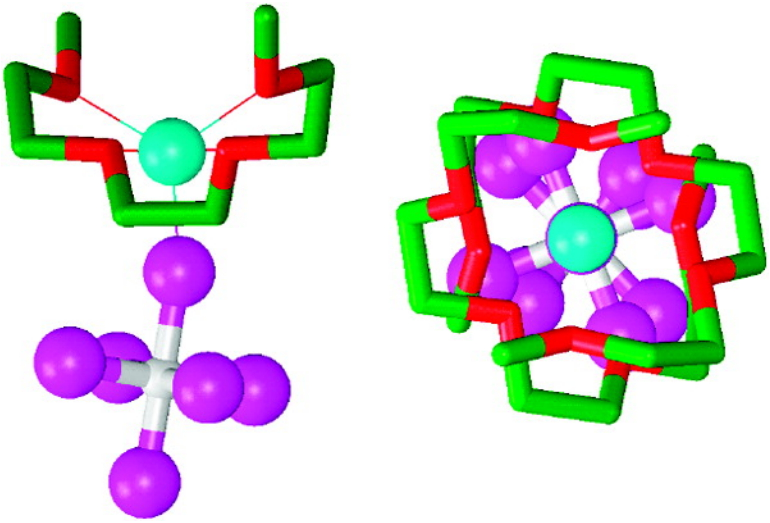

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Ionic Conductivity in the Solid Glyme Complexes $[CH_3O(CH_2CH_2O)_nCH_3]$:$LiAsF_6$ ($n = 3,4$)

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Ionic conductivity in the solid state has traditionally been dominated by ceramic materials (e.g., the O^{2-} ion conductor $[Zr_{1-2x}Y_{2x}]O_{2-x}$ or the Na^+ conductor $Na\beta Al_2O_3$) and polymeric materials (e.g., PEO_x:$LiN(SO_2CF_3)_2$ or PEO_6:$LiAsF_6$).[1,2] Several years ago ionic conductivity was also recognized in plastic crystalline solids.[3] Very recently, we presented the first report of ionic conductivity in a new class of solid electrolytes.[4] Such solids consist of cations coordinated by discrete, low molecular weight, ligands, such as the glyme $[CH_3O(CH_2CH_2O)_3CH_3]$. They are distinct from ceramic electrolytes, being soft solids, and from polymer electrolytes, which consist of molecules of higher (greater than 1000 Da) and distributed molecular weight. Whereas the crystal structure of a polymer electrolyte remains the same over a wide range of molecular weights (10^3-10^6 Da), low molecular weight complexes exhibit a rich variety of structures on varying the molecular weight of their ligands.[5] Here we present results on two low molecular weight complexes, $[CH_3O(CH_2CH_2O)_3CH_3]$:$LiAsF_6$ and $[CH_3O(CH_2CH_2O)_4CH_3]$:$LiAsF_6$, hereafter designated as G3:$LiAsF_6$ and G4:$LiAsF_6$. Despite differing by only one ethylene oxide (EO) unit, their crystal structures are very different (in contrast to polymer electrolytes). We show that this difference leads to markedly varying cation transport numbers ($t_+ = 0.8$ for G3:$LiAsF_6$ and 0.1 for G4:$LiAsF_6$), yet their conductivities are remarkably similar. Learning how to construct solid electrolytes that exhibit high Li^+ transport numbers is important in minimizing polarization when such electrolytes are used in all-solid-state cells, such as lithium batteries.

Powder X-ray diffraction patterns for G3:$LiAsF_6$ and G4:$LiAsF_6$ complexes are in good agreement with those calculated from previous single-crystal data, as illustrated for the G3:$LiAsF_6$ complex in Figure 1.[6]

Conductivity measurements were carried out using ac impedance spectroscopy on pressed pellets between blocking (stainless steel) electrodes. A representative complex impedance plot is available in the Supporting Information. In all cases, a single semicircle with a lower frequency spike was observed. The semicircle was associated with a capacitance of 1−2 $pFcm^{-1}$, indicating that the impedance is dominated by bulk (intracrystalline) response, with no significant contribution from grain boundary resistances.

Conductivities at different temperatures were extracted from the ac impedance plots and are presented in Figure 2a (for G3:$LiAsF_6$ and G4:$LiAsF_6$).

The linear variation of log σ versus $1/T$ for both complexes is consistent with ion hopping between fixed sites, rather than the curved plots normally associated with conduction in amorphous polymer electrolytes. The conductivities of the two glymes reported in Figure 2a are similar, something that, at first sight, might be thought consistent with the difference of only one EO unit between the G3 and G4 complexes. However, the crystal structures of the two complexes are very different, and this is reflected in the difference in the activation energies for G3:$LiAsF_6$ (55 kJ mol^{-1}) and G4:$LiAsF_6$(68 kJ mol^{-1}). These results encouraged a deeper analysis of ion transport in the two glyme complexes, involving determination of their transport numbers. The method of combined ac and dc measurements, described previously by Bruce and

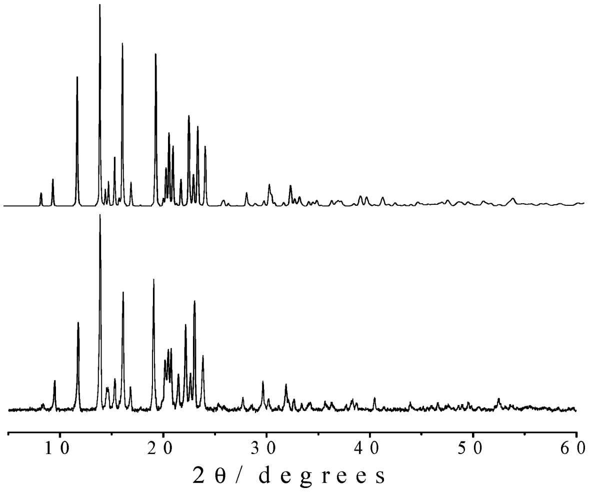

Figure 1. Experimental (bottom) and calculated (top) powder X-ray diffraction patterns for G3:$LiAsF_6$.

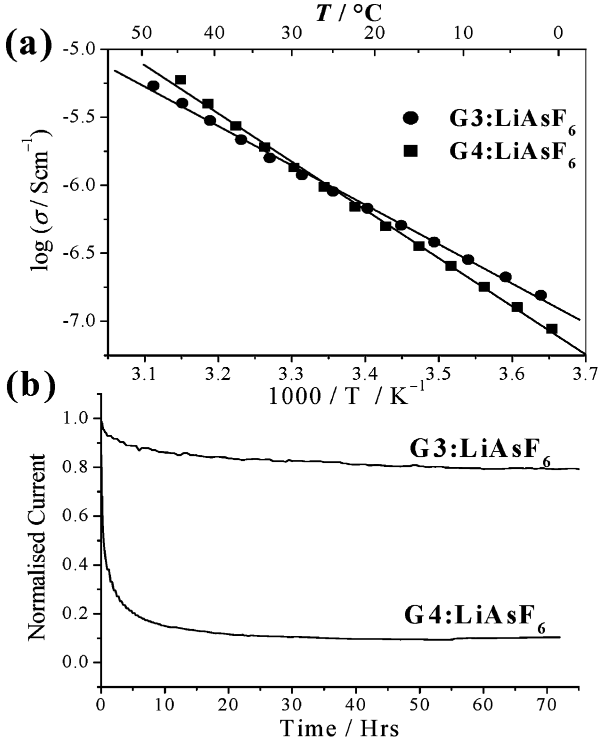

Figure 2. (a) Ionic conductivity, σ, as a function of temperature. (b) The dc current as a function of time during t_+ measurements.

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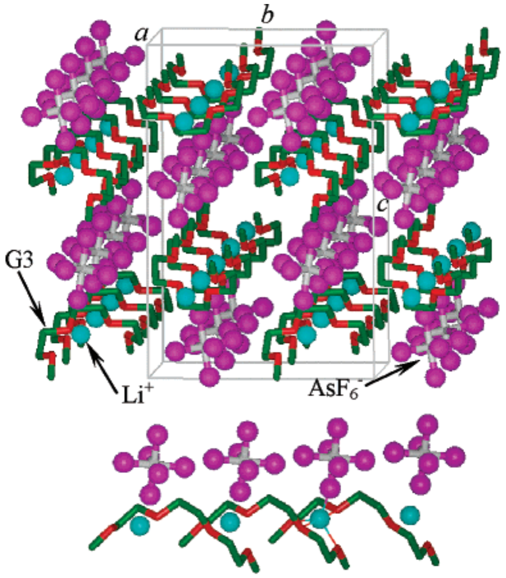

Figure 3. The structure of G3:LiAsF$_6$. Blue, lithium; white, arsenic; purple, fluorine; green, carbon; red, oxygen. Top: view of complete structure. Bottom: fragment of the structure showing one tunnel.

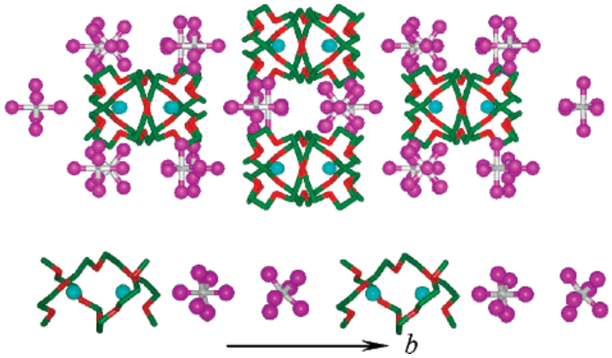

Figure 4. The structure of G4:LiAsF$_6$. Top: the complete structure viewed along the [101] direction. Bottom: one segment of the structure with the *b* direction running from left to right.

Vincent, was employed to determine the transport numbers of the two solid complexes.[7] The variation of the dc currents as a function of time for the G3 and G4 complexes is presented in Figure 2b. The cation transport numbers, t_+, are 0.8 (G3:LiAsF$_6$) and 0.1 (G4:LiAsF$_6$). The transport number measurements were made at 50 °C because the lower conductivities at lower temperatures precluded accurate measurements. Unlike the conductivities, which at 50 °C differ by only a factor of 1.3, the t_+ values differ by a factor of 8.

A rationale for the very different transport numbers between these two glymes, differing by only 1 EO unit, may be found by comparing their crystal structures (Figures 3 and 4).

In the case of the G3:LiAsF$_6$ complex, the G3 molecules are arranged in rows parallel to the *a*-axis. In each row, the molecules form a tunnel within which the Li$^+$ ions reside. A G3 molecule contains four ether oxygens. Each Li$^+$ ion is coordinated by two ether oxygens from each of two neighboring glyme molecules (Figure 3, bottom). The Li$^+$ ion is five coordinated, the fifth position being occupied by a fluorine from an AsF$_6^-$ anion. Each glyme molecule bridges between two neighboring Li$^+$ ions. The anions are also arranged in rows, with each anion coordinating to only one Li$^+$ ion, its remaining interactions being with the surrounding glyme molecules. Although this structure is different from that of the PEO$_6$:LiXF$_6$ (X = P, As, or Sb), there are similarities in that the 6:1 polymer electrolyte consists of PEO tunnels lined by ether oxygens and within which the Li$^+$ ions reside. The presence of tunnels for Li$^+$ ion transport in both G3 and PEO crystalline structures promotes a high t_+ in both cases.[2] Comparing the G3 with the G4 structure (Figure 4), the G4 complex lacks continuous pathways for Li$^+$ ion transport. Pairs of Li$^+$ ions and pairs of G4 molecules form discrete binuclear complexes, where each Li$^+$ ion is coordinated by three ether oxygens from one glyme and by two from the other. Each ether oxygen coordinates to only one Li ion, that is, there are two Li$^+$ ions and 10 ether oxygens in each binuclear complex. There are no continuous pathways from one complex to the next in any direction since these are interrupted by the presence of AsF$_6^-$ anions and are too far apart (Figure 4).

Considering the anion transport in G3 and G4 complexes, in the latter case, the anions only interact with the glyme molecules, such interactions are of a weak van der Waals nature. In contrast, the anions in G3, although also interacting with the glyme molecules, exhibit one strong ion−ion interaction with a neighboring Li$^+$ ion. These differences are consistent with the much higher anion transport number for G4, where the anions are only weakly bound to their surroundings, and where one may expect the activation energy for transport from one position to the next to be smaller than in the case of G3, where the anion has to break away from the stronger interaction with its neighboring Li$^+$. The anions in G4 do possess continuous pathways for transport along the [101] direction.

In conclusion, we have shown that two small molecule solid electrolytes, [CH$_3$O(CH$_2$CH$_2$O)$_3$CH$_3$]:LiAsF$_6$ and [CH$_3$O(CH$_2$CH$_2$O)$_4$CH$_3$]:LiAsF$_6$, differing by only one ethylene oxide unit exhibit markedly different transport numbers, $t_+ = 0.8$ and 0.1, respectively. Such differences are related, on the one hand, to the presence of tunnels for Li$^+$ migration in the crystal structure of the G3 complex, but not G4, and, on the other hand, to the weaker binding of AsF$_6^-$ in the structure of G4 than in G3. Such differences are also consistent with the observed difference in the activation energies for ion transport between the two complexes.

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

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