Conducting Materials

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Crystalline Small-Molecule Electrolytes**

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Solids that conduct by the transport of ions rather than electrons were discovered by Faraday in the mid-1800s.[1] Today, interest in such solid ionic conductors (solid electrolytes) has reached unprecedented heights, because they hold the key to developing a new generation of batteries and fuel cells, which is important in addressing global warming.[2] For many years, the investigation of ionic conductivity in the solid state concentrated on crystalline or amorphous ionic solids, such as α-AgI (Ag^+ ions), Na-β-Al_2O_3 (Na^+ ions), Li_2S–P_2S_5 glasses, and ZrO_2 (O^{2-} ions), until the pioneering discovery in the 1970s, by Wright, Armand, and co-workers, that solid polymers could support ionic conductivity.[3,4] Herein we report a new class of ionic conductors that are different from ceramic or polymer electrolytes. They are soft (malleable and flexible) solids, unlike ceramic electrolytes, yet, unlike polymer electrolytes, they are highly crystalline, of low molecular weight, and have no polydispersity (distribution in chain length) or chain entanglement. They are solid coordination compounds in which the cations of a salt are coordinated by small molecules. They do not exhibit plasticity and are therefore distinct from the fascinating plastic crystalline ionic conductors.[5]

Ion transport in polymer electrolytes, which are distinguished by high molecular weight (greater than 100000 Da), polydispersity, and chain entanglement, has been dominated by the amorphous phase above the glass-transition temperature (T_g), with the local segmental motion of the polymer chains playing a key enabling role in transporting the ions.[4,6] Only recently has the ubiquitous view that crystalline polymer electrolytes are insulators been challenged by several groups.[7]

Crystalline polymer electrolytes form the same crystal structures over a very wide range of molecular weights, from greater than 500 to several million daltons, and their ionic conductivity depends profoundly on the structural arrangement.[8] On reducing the molecular weight below 500 Da, a rich variety of crystal structures is observed.[9,10] The difference in the crystal structures between polymeric and small-molecule materials, even with the same ethylene oxide coordinating groups, sets these two classes of compounds apart. For example, the crystal structure of PEO_6:$LiAsF_6$ (PEO = poly(ethylene oxide)) is composed of continuous polymer tunnels, in which the Li^+ ions are located.[11] Below a molecular weight of 500 Da, the structures, and hence conductivities, are completely different, owing to the discreteness of the molecules and the absence of polydispersity in the case of small-molecule materials. When the chain lengths become short, the interaction between the chain ends becomes a significant factor in determining the molecular packing in the crystal structure. The absence of polydispersity is also an important factor in determining the crystal structure, because the chain ends will no longer be randomly distributed and hence can exhibit order.[12] The difference in the crystal structures, as well as the absence of polydispersity and chain entanglement, sharply distinguish low-molecular-weight electrolytes, in which the salts are solvated by discrete molecules of identical chain length, from polymer electrolytes.

In examining small-molecule electrolytes, we have chosen to focus on molecules containing discrete ligands based on the C–C–O repeat because of its excellent coordinating properties. Low-molecular-weight complexes can be formed between a variety of discrete dimethyl ethers (glymes), $CH_3O(CH_2CH_2O)_nCH_3$ (hereafter denoted Gn, where $1 \leq n \leq 12$), and salts such as $LiBF_4$, $LiCF_3SO_3$, and $LiSbF_6$.[9,10] Herein the small-molecule electrolyte $(G4)_{0.5}$:$LiBF_4$ ($(CH_3O(CH_2CH_2O)_4CH_3)_{0.5}$:$LiBF_4$) is considered, and is shown to exhibit a conductivity (σ) approaching 10^{-5} S cm^{-1} at 30 °C and a lithium transport number (t_+) of 0.65. Conductivity data are also presented for several other ethylene oxide based small-molecule electrolytes, demonstrating that these coordination compounds represent a large class of ionic conductors.

$(G4)_{0.5}$:$LiBF_4$ was prepared as a powder by dissolving the salt and the glyme in a cosolvent, which was then slowly evaporated, as described in the Experimental Section. The powder X-ray diffraction pattern (XRD) of the resulting material is shown in Figure 1a. The peaks are narrow and well-defined, indicating a highly crystalline material. The single-phase nature of the material was confirmed by differential scanning calorimetry (DSC) measurements (see the Supporting Information). The structure refined from the powder XRD pattern (Figure 1b) is very similar to that determined previously from single-crystal XRD data.[10]

The $(G4)_{0.5}$:$LiBF_4$ powder was pressed into a disk of 13-mm diameter and approximately 1-mm thickness, and the disk was placed between a pair of stainless-steel electrodes in a cell that was then subjected to ac impedance measurements (see the Experimental Section). The ac impedance data consist of a well-defined semicircle and a low-frequency spike (see the Supporting Information). The single, well-defined semicircle is associated with a capacitance of 1.3 pF cm^{-1}, typical for the bulk response of an electrolyte. These data show no evidence of grain-boundary resistances; thus, the resistance obtained

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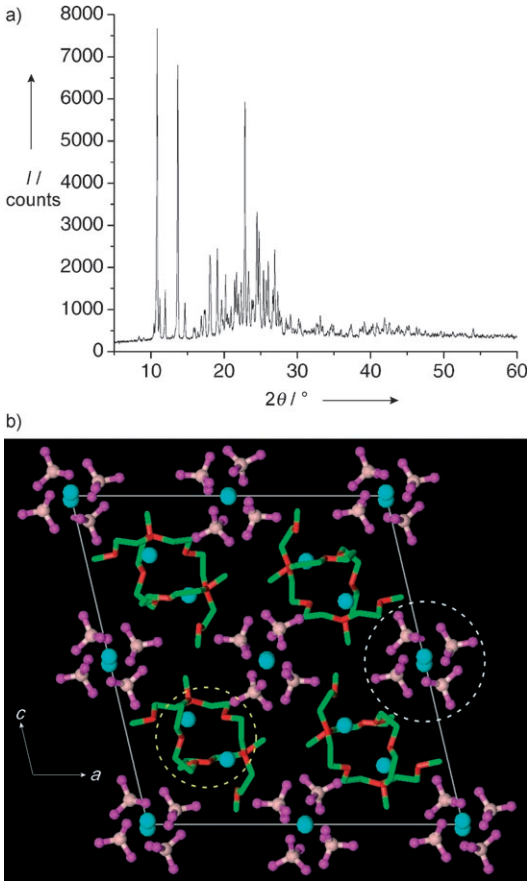

Figure 1. a) The powder XRD pattern of $(G4)_{0.5}$:$LiBF_4$, and b) the structure refined from the pattern (space group $P2_1/c$), viewed along the *b* axis. The yellow dashed circle highlights a tunnel lined by tetraglyme molecules and filled by Li^+ ions; the white dashed circle a tunnel lined by BF_4^- ions and filled by Li^+ ions. Li blue, B pink, C green, O red, F purple; H omitted.

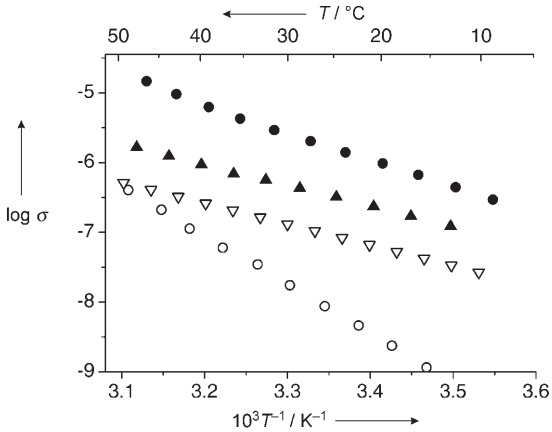

Figure 2. Ionic conductivity (σ) [$S\,cm^{-1}$] as a function of temperature for $(G4)_{0.5}$:$LiBF_4$ (●), $(G12)_{0.5}$:$LiAsF_6$ (▲), $(G9)_2$:$(LiAsF_6)_3$ (▽), $(G4)_2$:$(LiBF_4)_3$ (○).

from the semicircle is that of the bulk material. The conductivity of the electrolyte was extracted from the ac impedance data at a series of temperatures and plotted in Figure 2. The linearity of the Arrhenius plot is consistent with a mechanism of ion hopping in a crystalline material. This behavior contrasts with the curved Vogel–Tammann–Fulcher (VTF) behavior of an amorphous electrolyte above its glass transition temperature, where transport is controlled by the local chain dynamics. An activation energy of 76 kJ mol^{-1} was obtained from Figure 2 for the $(G4)_{0.5}$:$LiBF_4$ complex.

Considering the structure in more detail, it may be described as an intergrowth of two structural moieties, which are highlighted by the yellow and white circles in Figure 1b. One consists of a pair of Li^+ ions complexed by two tetraglyme chains; the chains form a short tunnel within which each Li^+ ion is coordinated by five ether oxygen atoms, three from one chain and two from the other. The short tunnels are arranged end to end, such that the Li^+ ions form a row along the *b* axis of the monoclinic unit cell (Figure 1b). Each ether oxygen atom is coordinated to only one Li^+ ion. Between these moieties, another set of channels runs in the same direction. These channels are formed by rows of Li^+ ions, each of which is coordinated by four BF_4^- ions (Figure 1b). Only two of the four fluorine atoms of the BF_4^- ion are involved in coordinating the Li^+ ions, the remaining two being free. Each coordinating fluorine atom is associated with only one Li^+ ion, and the BF_4^- ions bridge neighboring Li^+ ions along the chains. Considering these structural features, Li^+ ions could migrate along the channels lined with tetraglyme molecules, those lined with BF_4^- ions, or both. In this regard, it is interesting to note that the five-coordinate nature of the Li^+ ions in the tetraglyme tunnels (with three ether oxygen atoms from one molecule and two from the other coordinating each Li^+ ion) is highly reminiscent of the conducting channels in crystalline PEO_6:$LiXF_6$ (X = P, As, Sb). Such a structural feature may be important in promoting conductivity in crystalline lithium–ether complexes in general.

To explore whether the Li^+ ions are entirely responsible for ion transport in $(G4)_{0.5}$:$LiBF_4$ or whether the BF_4^- ions are also mobile, transport-number measurements were carried out. The method used was that of Bruce, Evans, and Vincent.[13] A transport number of 0.65 was obtained, which indicates that the majority of the current is carried by the Li^+ ions, but that the BF_4^- ions are also mobile.

Although the transport-number measurements demonstrate that both type of ions are mobile, they cannot distinguish the degree of ion transport due to the Li^+–BF_4^- and Li^+–tetraglyme channels. To address such a question concerning this particular small-molecule electrolyte will require detailed investigation using solid-state NMR spectroscopy. Such an investigation is beyond the scope of the present paper, but measurements are underway and will be reported when completed.

To demonstrate that the tetraglyme complex is but one member of a class of small-molecule electrolytes, the temperature-dependent conductivities of several other complexes composed of discrete low-molecular-weight dimethyl ethers complexing lithium salts are shown in Figure 2. These include $(G9)_2$:$(LiAsF_6)_3$, $(G12)_{0.5}$:$LiAsF_6$, and $(G4)_2$:$(LiBF_4)_3$, a complex formed between tetraglyme and $LiBF_4$, but with a different composition. For all the complexes, the Arrhenius plots are linear, and the activation energies also vary from one complex to another. Powder XRD data (see the Supporting

Information) indicate that they all are highly crystalline. It is evident from the differences in the powder XRD patterns that their crystal structures differ. That such differences are important in determining the conductivity is highlighted by comparing the data for the two G4–$LiBF_4$ complexes. In the case of $(G4)_{0.5}$:$LiBF_4$, the conductivity is high, whereas $(G4)_2$:$(LiBF_4)_3$, which has a different composition and crystal structure, has a much lower conductivity. Whether there are common structural moieties in the more highly conducting materials (such as the similarity in the Li^+–glyme tunnels within $(G4)_{0.5}$:$LiBF_4$ and PEO_6:$LiXF_6$) will be determined once we have obtained complete crystal structures for a range of the small-molecule electrolytes and correlated these with the detailed variations in conductivity.

In conclusion, we have reported the existence of ionic conductivity in small-molecule complexes composed of salts in which the cations are coordinated by low-molecular-weight ligands. The small-molecule electrolytes are distinct from ceramic and polymer electrolytes. They are soft solids but, unlike polymers, they are based on short-chain molecules that do not entangle, and they are monodispersed. The crystal structures of the small-molecule electrolytes are also distinct from those of long-chain polymers. Several small-molecule electrolytes based on glyme ligands coordinating lithium salts have been shown to conduct. The conductivities and activation energies differ between the different complexes; the origin of this difference is likely to lie in their different crystal structures. There may also be common structural moieties that are responsible for the ionic conductivity. The small-molecule electrolyte $(G4)_{0.5}$:$LiBF_4$ has been discussed in some detail. It has the highest conductivity of the small-molecule electrolytes studied to date, with a lithium transport number of 0.65.

Experimental Section

$(G4)_{0.5}$:$LiBF_4$ was prepared by dissolving appropriate quantities of $LiBF_4$ (Aldrich, 99.998%) and G4 (tetra(ethylene glycol) dimethyl ether; Aldrich, $\geq$99%) in dry acetonitrile (Aldrich, 99.8%). $LiBF_4$ was purchased as anhydrous and used as received, while G4 was dried over 4-Å molecular sieves and used without further purification. All manipulations were carried out in a high-integrity argon-filled MBraun glove box. After dissolution, the solution was transferred into glass vials, and the solvent was allowed to evaporate slowly. The resulting complex was dried at room temperature under dynamic vacuum for at least 24 h. DSC was carried out using a Netzch DSC 204 Phoenix at a heating rate of 10° min^{-1}.

Powder XRD data were collected at room temperature in transmission mode using a STOE STADI/P diffractometer with $Cu_{K\alpha1}$ radiation and a position-sensitive detector. The polymer electrolyte sample was sealed inside a glass capillary.

For conductivity measurements, the self-supporting disk of $(G4)_{0.5}$:$LiBF_4$ (with a density in excess of 85% of the theoretical density) was placed into a two-electrode cell and sealed inside an argon-filled can for removal from the glove box. The can was then placed into an oil bath equipped with a Haake EK30 cooler and a Haake DL30 temperature controller connected to a personal computer. All internal cell temperatures were monitored using K-type thermocouples also connected to the computer. Conductivity data were obtained using ac impedance measurements carried out with a Solartron 1255 frequency-response analyzer coupled with a Solartron 1286 electrochemical interface. A perturbation voltage of 15 mV was applied over the frequency range 500 000–1 Hz. Before the measurement was made at each temperature, a 2-h equilibration period was employed after the internal cell temperature had reached a steady state. For the transport-number measurements, a dc potential of 25 mV was applied. The cell was equilibrated in an oil bath at 25 °C for at least 48 h.

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