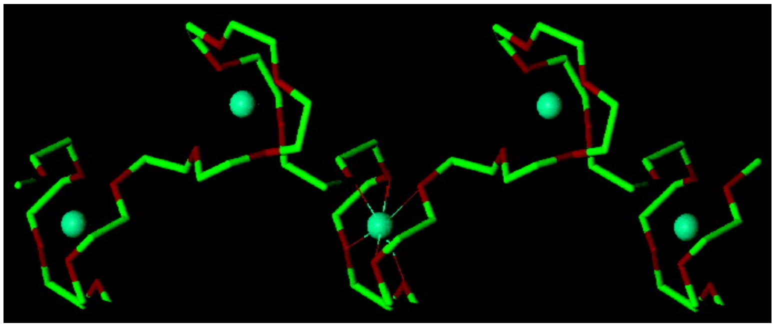
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Structure and Conductivity of the Crystalline Polymer Electrolyte β-PEO:LiAsF

Edward Staunton, Yuri G. Andreev, and Peter G. Bruce

J. Am. Chem. Soc., **2005**, 127 (35), 12176-12177• DOI: 10.1021/ja053249v • Publication Date (Web): 12 August 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Structure and Conductivity of the Crystalline Polymer Electrolyte β-PEO$_6$:LiAsF$_6$

Edward Staunton, Yuri G. Andreev, and Peter G. Bruce*

School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, Scotland

Received May 18, 2005; E-mail: p.g.bruce@st-and.ac.uk

Polymer electrolytes consist of salts dissolved in solid polymers; they hold the key to realizing the major goal of an all-solid-state rechargeable lithium battery.[1] For 25 years, it was believed that ion transport occurred only in amorphous polymer electrolytes above T_g, and that crystalline polymer electrolytes were insulators.[2] Recently, this view has been overturned by the first reports of ionic conductivity in the crystalline polymer electrolytes, poly(ethylene oxide)$_6$:LiXF$_6$, where X = P, As, or Sb, and in stretched fibrous polymers.[3] Here, we report the structure and conductivity of a second polymorph of the 6:1 complex, β-poly(ethylene oxide)$_6$:LiAsF$_6$. The conductivity is 1 order of magnitude lower than the previously reported α polymorph, thus demonstrating the important role that the crystal structure plays in determining the conductivity of crystalline polymer electrolytes.

Polymer electrolytes based on lithium salts, such as PEO:LiN(SO$_2$CF$_3$)$_2$, have the potential to be excellent electrolytes for all-solid-state rechargeable lithium batteries. Amorphous polymer electrolytes have been studied intensively for 25 years, and although the conductivities have increased substantially over that period, they remain too low ($<10^{-4}$ Scm^{-1}) for many applications. The recently discovered crystalline polymer electrolytes represent a new class of solid ionic conductors and offer a different approach to ionic conductivity in the solid state. Recent work has demonstrated that by doping PEO$_6$:LiXF$_6$, where X = P, As, or Sb, the conductivity may be increased by 1.5−2 orders of magnitude.[3,4]

Although ion transport is present in the crystalline state, the question remains to what extent the structures of crystalline polymer electrolytes are important in determining their conductivity. To address this issue, it is necessary to compare polymer:salt complexes that are identical except for their crystal structures. For this, we require a polymorph of the conducting PEO$_6$:LiXF$_6$ compounds. Such compounds do exist. We shall refer to the original 6:1 crystal structure as α-PEO$_6$:LiXF$_6$ and the new polymorph as β-PEO$_6$:LiXF$_6$. The β polymorph forms only with AsF$_6^-$ and SbF$_6^-$ anions; the existence of the β polymorph with the latter anion has been reported previously, although no structure or conductivity data were presented.[5]

The DSC data for PEO$_6$:LiAsF$_6$ (PEO M_w = 1000, methoxy end capped) are shown in Figure 1.

The first endotherm at 89 °C corresponds to the transformation of the α structure to the new β polymorph. Further heating results in the β phase melting at 110 °C. The formation of a new polymorph was confirmed by cooling the material from a temperature between the two endotherms. A powder X-ray diffraction pattern for this phase, cooled to room temperature, confirmed the presence of a new structure that is quite different from that of the α phase (Figure 2). On subsequent heating of the β phase, only one endotherm, corresponding to β phase melting, was observed.

The initial structural model for β-PEO$_6$:LiXF$_6$ was obtained ab initio from X-ray powder diffraction data using the program FOX.[6] The location of Li$^+$ ions and the conformation of the PEO chain were verified using Rietveld refinement based on neutron diffraction data. The sample for neutron diffraction was prepared with deuterated PEO (Polymer Source). Data were collected on the GEM diffractometer at ISIS, Rutherford Appleton Laboratory. The final structural model (51 atoms in the asymmetric unit) obtained after refinement by means of the GSAS program package[7] produced an excellent fit to the diffraction pattern (Figure 3), with R_{wp} = 2.2% (3559 data points, 375 reflections, 159 variables, 106 soft constraints). The crystal structure of β-PEO$_6$:LiAsF$_6$ is quite different from that of the α polymorph.[8]

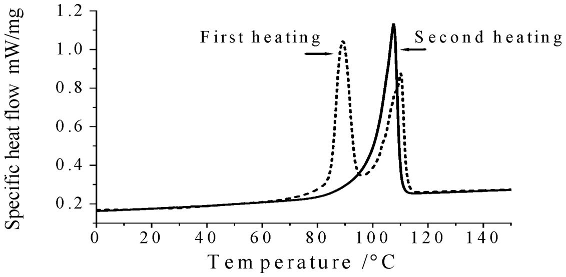


Figure 1. DSC data for PEO$_6$:LiAsF$_6$.

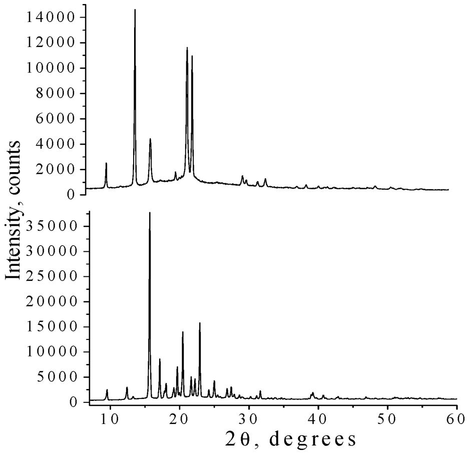


Figure 2. X-ray diffraction patterns of α (top) and β phases (bottom) of PEO$_6$:LiAsF$_6$.

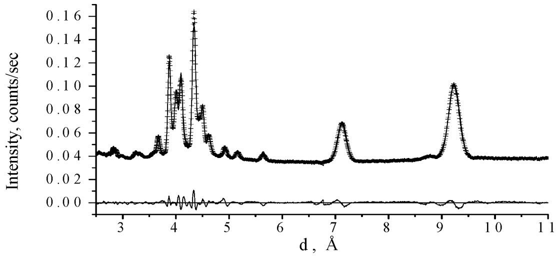


Figure 3. Rietveld fit to the neutron diffraction pattern of β-PEO$_6$:LiAsF$_6$.

The latter consists of pairs of PEO chains, each folding to form a half-cylinder; the half-cylinders interlock to form tunnels within

10.1021/ja053249v CCC: $30.25

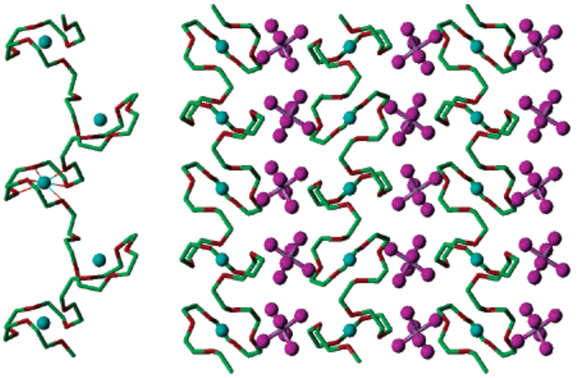


Figure 4. The structure of β-PEO$_6$:LiAsF$_6$. Blue, lithium; white, arsenic; purple, fluorine; green, carbon; red, oxygen. (Left) Single PEO chain with associated Li$^+$ ions (thin lines indicate coordination of Li$^+$ by ether oxygens). (Right) Packing of chains and ions. Hydrogen atoms are not shown.

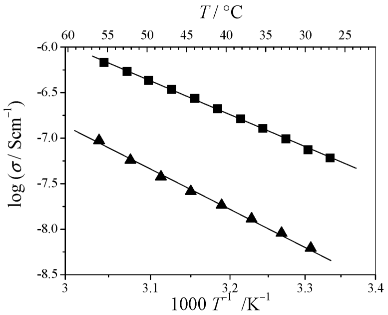


Figure 5. Conductivity of α- (squares) and β-PEO$_6$:LiAsF$_6$ (triangles).

which the Li$^+$ ions reside coordinated by three ether oxygens from one chain and two from the other. The anions are located between the tunnels. In the case of the β polymorph, a single PEO chain folds to form a ring, presenting six ether oxygens to the Li$^+$ ion located within the ring (Figure 4), with Li−O distances equal to 2.2 Å.

Each ether oxygen coordinates to just one Li$^+$ ion. The PEO chain does not, however, form a continuous tunnel. The Li$^+$ ions are arranged in a zigzag fashion along the PEO chain. The Li$^+$−Li$^+$ distances are 7.5 Å. The chain is not a helix. Given the arrangement of Li$^+$ ions, the distance between the sites, and the lack of continuous pathways, it is difficult to see how this structure could support significant Li$^+$ ion transport. The PEO chains are arranged in layers lying in the *bc* plane, with the AsF$_6^-$ anions located between these layers. The anions are arranged in rows, and they do not coordinate to the cations (Figure 4). The structural differences between the α and β polymorphs are so significant that it is difficult to see, by inspection, how one transforms into the other.

The variation of conductivity with temperature for the α and β phases is shown in Figure 5. The results indicate that the β phase does conduct but with a conductivity 1 order of magnitude lower than that of the α phase, despite both being formed from the same polymer and salt as well as possessing the same composition. This demonstrates that differences in crystal structure have a profound effect on the conductivity of the materials. Both α and β phases exhibit linear Arrhenius plots with activation energies of 70(1) and 77(1) kJ mol^{-1}, respectively. Such linearity is consistent with ion hopping in a crystalline material for both α and β phases. The conductivity of the α phase is believed to be dominated by Li$^+$ transport, whereas the crystal structure of the β phase (Figure 4) implies that, in this case, such transport will be more difficult, consistent with its lower conductivity. However, this is not sufficient to explain why the activation energies, although not identical, are similar. We are currently investigating this issue; however, we offer here a possible rationale. The static picture of a crystal structure does not reveal all of the features that are important for ion transport. In these soft solids, one might anticipate significant local motion of the polymer chains. We propose that such local motion facilitates ion transport by opening up bottlenecks between sites, thus lowering the activation energy for conduction. In short, we must consider both the crystal structure and the polymer dynamics when interpreting ion transport. The polymer chains lie between the cations and anions, and the polymer chain motion will facilitate both cation and anion transport; however, in the α phase, the presence of channels in the crystal structure favors Li$^+$ ion transport. Thus, the crystal structure and dynamics in the α phase act together to ensure that the conductivity is dominated by Li$^+$ motion, whereas in the β phase, where the crystal structure makes Li$^+$ ion transport difficult, the dynamics aids only anion transport. Because cation and anion transport are controlled by similar polymer chain relaxations, the activation energies are not too dissimilar between the two phases. Of course, at present, these ideas only constitute a hypothesis. Much detailed work is required using, for example, NMR or computer modeling to investigate polymer chain relaxations and their correlation to cation and anion transport. We are endeavoring to probe, in greater detail, the differences between the conductivity in the α and β phases.

Acknowledgment. P.G.B. is indebted to The Royal Society, the EPSRC, and the EU for financial support.

Supporting Information Available: Experimental procedures and crystallographic data for β-PEO$_6$:LiAsF$_6$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Fenton, D. E.; Parker, J. M.; Wright, P. V. *Polymer* **1973**, *14*, 589. (b) *Solid State Electrochemistry*; Bruce, P. G., Ed.; Cambridge University Press: Cambridge, 1995. (c) *Applications of Electroactive Polymers*; Scrosati, B., Ed.; Chapman & Hall: London, 1993.
(2) (a) Berthier, C.; Gorecki, W.; Minier, M.; Armand, M. B.; Chabagno, J. M.; Rigaud, P. *Solid State Ionics* **1983**, *11*, 91. (b) Gorecki, W.; Donoso, P.; Berthier, C.; Mali, M.; Roos, J.; Brinkmann, D.; Armand, M. B. *Solid State Ionics* **1988**, *28−30*, 1018. (c) Wintersgill, M. C.; Fontanella, J. J.; Pak, Y. S.; Greenbaum, S. G.; Almudaris, A.; Chadwick, A. V. *Polymer* **1989**, *30*, 1123.
(3) (a) Gadjourova, Z.; Andreev, Y. G.; Tunstall, D. P.; Bruce, P. G. *Nature* **2001**, *412*, 520. (b) Stoeva, Z.; Martin-Litas, I.; Staunton, E.; Andreev, Y. G.; Bruce, P. G. *J. Am. Chem. Soc.* **2003**, *125*, 4619. (c) Chung, S. H.; Wang, Y.; Greenbaum, S. G.; Golodnitsky, D.; Peled, E. *Electrochem. Solid State* **1999**, *2*, 553.
(4) Christie, A. M.; Lilley, S. J.; Staunton, E.; Andreev, Y. G.; Bruce, P. G. *Nature* **2005**, *433*, 50.
(5) (a) Stoeva, Z. Ph.D. Thesis, University of St Andrews, St. Andrews, Scotland, 2001. (b) Seneviratne, V.; Frech, R.; Furneaux, J. E. *Electrochim. Acta* **2003**, *48*, 2221.
(6) Favre-Nicolin, V.; Cerny, R. *J. Appl. Crystallogr.* **2002**, *35*, 734.
(7) Larson, A. C.; Von Dreele, R. B. Los Alamos National Laboratory Report Number LA-UR-86-748; Los Alamos National Laboratory, Los Alamos, NM, 1987.
(8) MacGlashan, G. S.; Andreev, Y. G.; Bruce, P. G. *Nature* **1999**, *398*, 792.

JA053249V