New Approach to Structure Determination of Crystalline Polymer Electrolytes

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Polymer electrolytes consist of salts, e.g. NaI, $LiN(SO_2CF_3)_2$, dissolved in high molecular weight polymers, e.g. poly(ethylene oxide) (PEO). The recent discovery of ionic conductivity in crystalline polymer electrolytes [1] was prompted by the elucidation of the crystal structure of PEO_6:$LiAsF_6$ [2] from powder diffraction data using a simulated annealing technique [3]. This challenged the established view that conduction occurs exclusively in amorphous polymer electrolytes above their glass transition temperature and opened a new avenue in polymer electrolyte research.

Recently we have established even more complex crystal structures of polymer electrolytes, such as PEO_8:$NaBPh_4$ and PEO_4:$ZnCl_2$, using a combination of single crystal diffraction data from a material prepared with a low-molecular weight polymer and powder data from a material with the same chemical composition but synthesized using a high molecular weight PEO. The combination proved to be successful when the individual methods failed to produce a reliable structural model.

We have also discovered polymorphism in PEO_6:$LiAsF_6$ and determined the crystal structure of the new phase. The differences in the crystal structure of the two polymorphs account for the difference in their ionic conductivity.

[1] Gadjourova Z., Andreev Y.G., Tunstall D.P., Bruce P.G., *Nature*, 2001, **412**, 520. [2] MacGlashan G., Andreev Y.G., Bruce P.G., *Nature*, 1999, **398**, 792. [3] Andreev Y. G., Lightfoot P, Bruce P.G., *Chem.Comm.*, **1996**, 2169.

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