A Combined Conductivity and XAS Study of Plastically Crystalline Electrolytes

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Abstract. We report a study of the conductivity of LiBr and copper salt doped succinonitrile along with X-ray absorption measurements for the bromide and copper ions. The work shows that the ions are in well-ordered sites for most of the plastic phase and relatively high conductivity is due to a small fraction of the ions which are mobile.

1. Introduction

Plastic crystals are a class of molecular materials [1, 2] that consist of roughly spherical or globular molecules; thus the simplest examples are methane (CH\textsubscript{4}) and carbon tetrachloride (CCl\textsubscript{4}) and more complex systems are the bridged cyclic terpenoids, such as camphor and camphene. The materials are characterized by a solid state phase transition or transitions. In the lowest temperature non-plastic phase the materials are typical organic solids with low crystallographic symmetries and are mechanical brittle and friable. In the solid phase prior to melting the solids are soft, hence the name plastic crystals, and show relatively rapid translational diffusion [2]. In the plastic phase the molecules are undergoing rapid endospherical reorientation and are often referred to as rotator phase solids. In addition, the plastic phases tend to be high symmetry, either fcc, hcp or bcc. On melting there are relatively small increases in the entropy as the only gain is translational freedom.

Two types of plastically crystalline electrolyte are possible. One type is when the ion or ions of the salt are exhibiting plastic behaviour, i.e. one or both ions are undergoing rapid rotation, the conductivity being improved by doping with a salt [3, 4]. The second is when a plastic solid with a high dielectric constant dissolves a salt [5, 6]. Both types can have solid state conductivities at room temperature in excess of 10\textsuperscript{3} S cm\textsuperscript{-1}, and coupled with appropriate mechanical properties, have potential applications as the electrolytes in solid-state batteries. They offer an alternative to solid polymer electrolytes as the conductivities are higher and the cation transport numbers appear higher.

We have just initiated a programme of XAS studies on plastically crystalline electrolytes and the results presented here are for succinonitrile electrolytes. In the pure material the plastic phase extends from 238 to 335K and the dielectric constant is 55, i.e. higher than that for many organic solvents (e.g. acetonitrile has a dielectric constant of 36.6). Succinonitrile will dissolve a wide range of salts and in the non-plastic phase the ionic conductivity is low, typically ~ 10\textsuperscript{-5} S cm\textsuperscript{-1}. On heating the conductivity of the solutions rapidly rises to 10\textsuperscript{-4} to 10\textsuperscript{-3} S cm\textsuperscript{-1} at 300K and then there is a further less pronounced increase up to the melting point. This indicates a link between the molecular motion of the organic molecule, rotation and possibly translational diffusion, with the migration of the ions. We will report
ionic conductivity and X-ray absorption spectroscopy (XAS) results for lithium and copper salt doped succinonitrile.

2. Experimental

2.1. Materials
All preparation work was carried out in a glove box under inert nitrogen atmosphere (water ≤ 1ppm). The basic components for the plastic crystalline electrolytes were mixed in the appropriate compositions. The composite electrolytes were loaded into 2 × 4 in poly bags (Aldrich Z183377-1PAK) cut into 20 × 20mm squares and heat-sealed before removal from the glove box for XAS measurements.

Impure succinonitrile (Aldrich, 99%) was purified by zone-refing and dried with molecular sieve. The salts used were all purchased from Aldrich, except for the copper(I) trifluoromethanesulfonimide and the copper(II) trifluoromethanesulfonimid (Cu(I) TFSI and Cu(II) TFSI, respectively), and are listed below:
- Lithium bromide, LiBr (99.995%, Aldrich).
- Copper(I) trifluoromethanesulfonate, available as a 1:1 complex with toluene, copper(I) triflate (99.99%, Aldrich).
- Copper(II) trifluoromethanesulfonate, copper(II) triflate (≥97%, Aldrich).

The preparation of Cu(I) TFSI and Cu(II) TFSI followed the procedures used to synthesise these materials for conductivity studies [3]. Detailed reaction conditions were supplied by Professor Armand [7]. The Cu(II) TFSI was synthesised by boiling copper(II) oxide, CuO (99.99%, Aldrich) under reflux with bis(trifluoromethane)sulfonimide (≥95.0%, Aldrich) in distilled water. The water was then carefully distilled off and the Cu(II) TFSI dried under vacuum. The Cu(I) TFSI was synthesised by boiling Cu(II) TFSI under reflux with copper metal-60-100 mesh.

The samples discussed here contained 1 mole per cent dopant in succinonitrile.

2.2. Conductivity measurements
The conductivity cell was constructed from brass and PTFE. The sample was sandwiched between two carbon discs separated by a small PTFE ring producing a sample disc of a consistent geometric dimensions (thickness = 0.88 mm, diameter = 12.75 mm). The cell was contained within a Pyrex tube with electrical feeds. Temperature was measured with a chrome-alumel thermocouple. Conductivity measurements were carried out at 50 kHz using a 4192ALF Impedance Analyzer 5Hz-13MHz, Hewlett-Packard. Tests showed that there was no appreciable frequency dependence of the conductivity up to 1MHz.

The samples were melted and loaded between the two carbon discs in a glove box to avoid moisture. This was then loaded into the cell, which was in turn loaded into the Pyrex tube and all openings sealed. The entire setup was then removed from the glove box and connected to a nitrogen supply. The sample was then heated to above the melting point of the pure plastic crystal under investigation and then left to cool for a day. Conductivity measurements were then made at approximately every 10K from room temperature (in the case of NPG) to above the melting point of the pure crystal and then back again. For succinonitrile, which has its plastic phase transition at 238K, measurements were made from approximately 210K. The sample was left to equilibrate for 1 hour before a measurement was made at each temperature. The sample temperature was then recycled to check reproducibility.

2.3. XAS measurements
Measurements were made on station 9.3 at the CLRC Daresbury Synchrotron Radiation Source. The synchrotron has electron energy of 2 GeV and the average current during the measurements was 150 mA. Station 9.3 is equipped with a double Si (220) or Si (111) crystal monochromator that can be
offset from the Bragg angle to reject harmonic contaminants from the monochromatic beam. The Si (111) was used for the softer edges (3d metals) and the Si (220) for the harder edges (Rb and Br). In the present work the harmonic rejection was set at 50%. The detectors were standard ion chambers for transmission experiments and a 13 element solid state detector for fluorescence experiments. The poly bag sample containers were mounted in an Oxford cryostat specially designed for XAS experiments. There are Mylar windows on four sides of the sample; an entry and exit for the X-ray beam and windows to detect the fluorescence X-rays. Spectra were collected at various temperatures, depending on the system. The cryostat was capable of maintaining samples to ±0.1°C over the temperature range -193 to 100°C.

The data were processed in the conventional manner using the Daresbury suite of EXAFS programmes: EXCALIB, EXBACK (or EXBROOK) and EXCURV98 [8,9]. Phase shifts were derived from *ab initio* calculations within EXCURV98. This code also includes routines to treat multiple scattering effects in highly symmetric structures. For each spectrum a theoretical fit was obtained by adding shells of atoms around the central excited atom and least-squares iterating the Fermi energy ($E_F$), the radial distances ($R_D$), and the Debye-Waller type factors, $A (=2\sigma^2)$. This latter factor will contain contributions from both thermal disorder and static variations in $R_D$. The programme also allowed iteration of the co-ordination number ($CN$). The quality of the fit is measured by an $R$-factor and the errors in $R_D$ are $\sim\pm$ 0.02 Å and $\sim\pm$ 20% in $A$ and $CN$.

3. Results and Discussion
As will be seen later the results for the lithium bromide and copper salt doped succinonitrile presented significant differences. We will begin by presenting the results for the lithium bromide doped system.

The conductivity results for 1 mole per cent LiBr doped succinonitrile are shown in Figure 1. The plots show similar features to the data reported by Long et al [5] for a series of lithium salts dissolved

![Figure1](image_url)
in succinonitrile. There is clearly a change in conductivity on changing from the plastic to non-plastic phase, although the transition temperature appears to be considerably reduced in the conductivity measurements. In most of the plastic phase the conductivity plot is roughly linear; i.e. 1000K/T from 4.5 to 3.3. What is striking is the rapid rise in the conductivity in the temperature regime prior to melting. This suggests that there is some onset of disorder prior to melting.

Br K-edge XAS data were collected in transmission mode at four temperatures, namely 200K (non-plastic phase), 273K (plastic phase), 323K (plastic phase) and 343K (melt) for the 1 mole per cent doped sample. The EXAFS and Fourier transform for the sample measured at 200K are shown in Figure 2. The spectrum was fitted to a simple model where the Br ion was coordinated to four succinonitrile molecules through the CN grouping. A comparison of the spectra at different temperatures is shown in Figure 3 which plots the Fourier transforms of the spectra. It can be seen that

![Figure 2](image_url)

Figure 2 The Br K-edge EXAFS of 1 mole percent LiBr in succinonitrile at 200K; (a) normalised EXAFS, (b) the Fourier transform. The solid line is experiment and the dotted line the best-fit.
there is no major change in going from non-plastic to plastic phase. However, the peaks are attenuated at 323K (1000K/T = 3.1) and are lost in the molten sample. We have performed a detailed fitting of the spectra but only a qualitative interpretation is needed here. The attenuation of the peaks is due to a loss of order in the system and is therefore consistent with the conductivity results.

The conductivity results for some of the copper salt doped succinonitrile samples are shown in Figure 4. The results are in reasonable agreement with the published data for these systems [3]. In these systems the plots were roughly linear in the plastic phase, unlike the plots for lithium bromide. The Cu K-edge EXAFS of all the copper salt doped samples showed remarkably similar spectra. The results for 1 mole percent Cu(II)TFSI sample are shown in Figure 5. All the systems showed three dominant peaks in the Fourier transforms which were modeled with four succinonitrile molecules coordinated to the copper ion. In addition there was remarkably little attenuation of the
spectra on heating and even on melting. This indicates that there is a strong complex formed by the copper ion and the host. This is consistent with the linearity of the conductivity plots.

Figure 5 The Fourier transform of the Cu K-edge EXAFS of 1 mole percent Cu(II)TFSI in succinonitrile at a range of temperatures.

The present results for both the LiBr and the copper salt doped succinonitrile suggest that the systems are highly ordered for most of the plastic phase; in the former case to within ~ 50K of the melting point and in the latter case the whole of the plastic phase. Unfortunately, we could not explore the Li⁺ or anion environments with XAS and the differences may reflect the stronger binding between copper ions and the host compared to bromide ions and the host. The overall order in the systems raises interesting questions concerning the mechanism of the ionic transport. The intuitive assumption would be assign the relatively high conductivities to the high levels of rotational disorder and the rapid diffusion of the host molecules; i.e. similar to a molten salt. Indeed the diffusion studies show for lithium salts in succinonitrile that the diffusion of anions, cations and host molecules, albeit at temperature within 40K of the melting point, are similar in magnitude. However, succinonitrile is a complex material showing ‘extrinsic’ rather than intrinsic plastic crystal behaviour [2]. Succinonitrile molecules have trans and gauche forms and can be considered as ‘self-doped’. The current XAS results suggest that in the region of the dopant ions there is a high degree of order, except at temperatures close to the melting point for the case of lithium bromide doping. In this case the thermal disorder is presumably sufficient to ‘break’ the interactions between ion and host. Hence the majority of the ions, as XAS monitors the average structure of the local environment, is in highly ordered sites and is relatively immobile. This suggests that conductivity may be due to a small fraction of ions (<10%) that dissociate from the host molecules and are mobile.

4. Conclusions
We have reported conductivity and XAS results for LiBr and copper salt doped succinonitrile. The conductivity results are in reasonable agreement with previous studies [3,5] of the systems and are sufficiently high at ambient temperatures ($10^{-4}$ to $10^{-3}$ S cm$^{-1}$) to be considered for application as electrolytes in solid state batteries [3,10]. The XAS results show that the ions studied here, Br⁻ in LiBr...
doped succinonitrile and Cu\(^+\) and Cu\(^{2+}\) in copper salt doped succinonitrile, are in highly ordered environments for the bulk of the plastic phase. This suggests that only a small fraction of the ions in the systems are responsible for the relatively high ionic conductivity.

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