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In-situ XRD study of the succinonitrile–lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) phase diagram

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ABSTRACT

The salt lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) when dissolved in plastic crystal succinonitrile has been demonstrated to have particularly good conductivity even at room temperature. *In-situ* X-ray diffraction (XRD) measurements have previously proved invaluable in interpreting the differential scanning calorimetry (DSC) behavior, but the practical lower temperature limit of approximately −45 °C was higher than the −100 °C starting temperature of the DSC measurements, and the important crystalline to plastic crystal transition of succinonitrile. An improved cryo-flow system capable of capillary sample temperatures down to −192 °C without icing can now easily match the DSC conditions. The previously puzzling DSC behavior of the succinonitrile–LiTFSI phase diagram at low temperatures has now been explained, with a surprising formation of a TFSI-rich adduct on heating from −100 °C even at concentrations as low as 2 mol%.

1. Introduction

Previous studies [1–3] have shown that plastic crystal succinonitrile can form the basis of a solid electrolyte with high conductivity (10^{-3} S cm^{-1}) at room temperature and desirable mechanical properties when coupled with a suitable lithium salt such as LiTFSI. Previous XRD studies have shown that other salts such as $LiClO_4$ and $LiPF_6$ perform poorly in plastic crystal succinonitrile due to the formation of very stable crystalline LiX(succinonitrile)$_2$ adducts at room temperature [3], even at very low salt concentrations.

The behavior with the organic TFSI anion is very different from the inorganic lithium salts. Substantial fractions of LiTFSI may be dissolved in succinonitrile with no precipitation evident. The lack of adduct formation is supported by the high ionic conductivities observed up to 15 mol% additions [3]. Very large additions of LiTFSI above 20 mol% do lead to the formation of a crystalline phase [3]. The addition of approximately 17 mol% LiTFSI has been observed to lead to unusual behavior in the thermal analysis data, pointing to the existence of a ‘crystallinity gap’ between certain LiTFSI concentrations analogous to that observed in the LiTFSI(PEO) system [4]. This different phase behavior is probably due in part to steric effects with the large, elongated TFSI$^-$ anion versus the more compact and isotropic inorganic ClO_4^-, PF_6^-, BF_4^-, etc.

A systematic, XRD study of the LiTFSI–succinonitrile phase diagram between −100 and +80 °C has been undertaken in an attempt to better understand the properties of these potential electrolyte materials.

2. Experimental

The succinonitrile–LiTFSI samples were produced in an argon-filled glovebox by dissolving the LiTFSI (Aldrich, 99.995%) in molten succinonitrile (Aldrich, 99%) and mixing before injecting the molten mixture into a 1 mm diameter borosilicate capillary or placing into a DSC pan. The capillaries were sealed with wax prior to removal from the glovebox to prevent contact with moisture. DSC measurements were performed using a TA 2920 instrument. Samples were cooled down to −100 °C in approximately 10 min before heating to 85 °C at a rate of 10 °C/min. The XRD measurements were carried out using a Bruker D8 diffractometer (Bruker-AXS Inc, WI, USA) using a primary focusing mirror with CuKα radiation and a Vantec PSD detector. The sample temperature was controlled using a custom built liquid nitrogen cryo-flow system (Cryoindustries of America Inc, NH, USA) that creates a laminar flow of nitrogen gas along the length of the capillary to avoid turbulence and icing (see Fig. 1). The goniometer head was protected from icing by an electrically heated shield (Crystal Positioning Systems, PA, USA). Fig. 2 shows a schematic outline of the control setup of the cryo-flow system. A Lakeshore 331S cryocontroller was used to control the temperature of the gas stream with a Pt100 sensor in the tip. Both the cryocontroller and DC power supply were connected to the PC controlling the D8 diffractometer and could be programmed from the diffractometer control software. The reliability of the sample temperature was checked using the low-temperature phase transitions of ammonium nitrate [5] and literature

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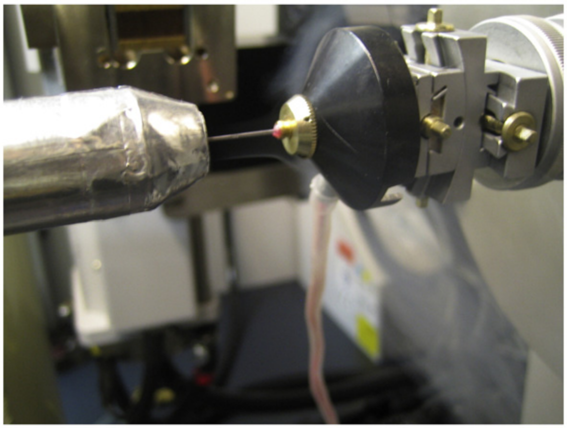

Fig. 1. Orientation of the liquid nitrogen cryo-flow system with respect to the capillary and the goniometer heat shield. The sample in this case is SRM640c silicon.

values for the lattice parameter of aluminium metal at different temperatures [6–8]. Datasets were taken between −100 °C and +80 °C every 5 °C. Diffraction data were obtained with a 10° PSD window between 5 and 80° 2θ with a 0.0214° step and a 0.5 s count time. An air-scatter sink was used to reduce air scatter at low 2θ angles. The cryo-flow nozzle was positioned approximately 4 mm away from the centre of the beam. The temperature profile along the flow direction is constant for approximately 10 mm away from the nozzle tip. The effective width of the Vantec detector is 16 mm, so a 4 mm Debye slit was used to sample the constant temperature portion of the sample whilst avoiding scattering from the cryo-nozzle.

The crystal structure of low-temperature crystalline succinonitrile was only described recently and the LiTFSI(succinonitrile) adduct is still unknown. The low-temperature crystal structure of succinonitrile was solved by the authors using laboratory data [9] and another group using synchrotron data [10]. The space group was described in the monoclinic space group P2$_1$/a, with unit cell parameters at −100 °C of a = 5.8721(6) Å, b = 8.5878(7) Å, c = 9.1132(11) Å, β = 100.428(4)° and Z = 4. The unit cell of the LiTFSI(succinonitrile) adduct at −100 °C and room temperature was indexed using the singular value decomposition method [11] incorporated in TOPAS 4 [12] after single line fitting. The resulting unit cells were reduced using LePage for Windows [13].

3. Results and discussion

The XRD behavior of pure succinonitrile between −100 and +80 °C can be seen in Fig. 3(a). The crystalline to plastic crystal transition occurs at −45 °C and it melted at 55 °C, exactly as it should behave from numerous thermal analyses [14] and spectroscopy studies [15]. The additional plots (b)–(e) show the XRD behavior of 2, 10, 25, and 33 mol% LiTFSI in succinonitrile as well as pure LiTFSI. The XRD pattern of the 15 mol% sample remained amorphous across the temperature range. The data show a significant change in low-temperature crystalline behavior between 10 and 25 mol% once the crystallinity gap has been passed. The similarity with the low-temperature succinonitrile data disappears with the higher LiTFSI contents; more complex patterns emerge dominated by the LiTFSI(succinonitrile) adduct. Although the crystal structure of the LiTFSI(succinonitrile) adduct has not yet been solved, the variable temperature datasets do allow an attempt at indexing what is a complex pattern. In the absence of a phase transition, the different thermal expansion in different lattice directions in low symmetry structures can be used to confirm a tentative indexing. The unit cell of LiTFSI(succinonitrile) at room temperature (25 °C) was found to be triclinic in space group P-1, with a = 12.130(1) Å, b = 12.438(1) Å, c = 13.4045(8) Å, α = 101.544°, β = 105.232(4)° and γ = 115.829(4)°.

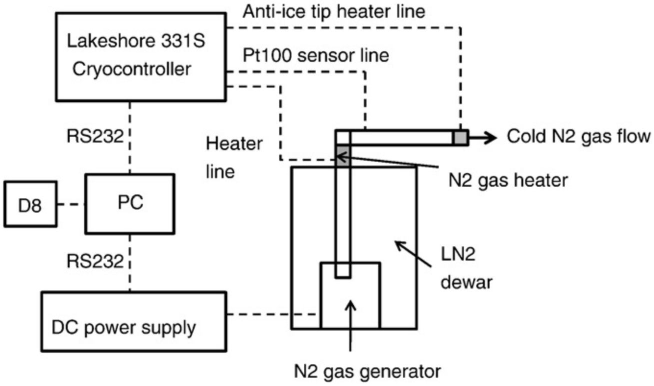

Fig. 2. Schematic diagram showing the setup of the cryo-flow system and control system.

The sample with 25 mol% was very difficult to crystallize. This behavior was expected with a 'crystallization gap' and was demonstrated in the previous XRD study down to −40 °C together with the DSC of the 15 mol% sample shown in Fig. 4. The Brigman method of crystallization with a temperature gradient previously used with pure succinonitrile [16] was used to crystallize the 25 mol% sample by a series of slow cool/rapid heat cycles. Attempts to make a 20 mol% LiTFSI sample crystallize were unsuccessful over a period of 1 day. The XRD and DSC results may be combined to produce a composition-temperature phase diagram for material heated from −100 °C as shown in Fig. 5. This figure also draws on information from a previous publication [3] to make a more complete picture. It is evident that the crystallinity gap separates two areas with very different phase behavior. Below the crystallinity gap the phase behavior is dominated by succinonitrile in its crystalline and plastic crystal forms. The crystalline LiTFSI(succinonitrile) adduct only has a limited temperature stability range before melting and incorporation into the plastic crystal phase. Above the crystallinity gap the crystalline LiTFSI (succinonitrile) adduct dominates and is the final phase to melt. In these samples the succinonitrile melts below −20 °C, so is actually molten at room temperature.

Although the LiTFSI is soluble in plastic crystal succinonitrile, it is not expected to be soluble in crystalline succinonitrile. Consequently, cooling the samples through the plastic crystal to crystalline transition phase separation of the TFSI salt and the succinonitrile is expected to occur. The LiTFSI salt is not visible in the XRD patterns below the phase transition, but the LiTFSI is quite diluted, likely to be in very small domains and is not a very strong X-ray scatterer. The formation of crystalline LiTFSI (succinonitrile) adduct on heating samples with low salt concentrations through the crystalline to plastic crystal transition is very surprising. The 50:50 composition of the adduct would suggest that regions of high concentration of LiTFSI should be required prior to crystallization. Pure LiTFSI was not visible in the diffraction patterns after formation of crystalline succinonitrile, therefore it must have been highly dispersed in domains of insufficient size to be visible by diffraction. To form LiTFSI (succinonitrile) diffracting domains of sufficient size to be easily visible at 2 mol% LiTFSI concentration, suggests that the LiTFSI was concentrated somehow prior to LiTFSI(succinonitrile) crystallization. The mechanism for concentrating the LiTFSI is unknown, but one possibility is the significant density difference between LiTFSI (2.25 g/cm^3) and succinonitrile (0.99 g/cm^3). Transport of the LiTFSI through the rigid matrix of crystalline succinonitrile is very unlikely. This means that any density-based separation must occur during the reformation of the plastic crystal at −55 °C. By this hypothesis the LiTFSI must redissolve in the succinonitrile and then be sufficiently mobile for agglomeration of the LiTFSI within the few minutes whilst the capillary is stationary between datasets. If this is the case then the crystalline adduct should only form if crystalline succinonitrile is produced on cooling. If the sample is only cooled to −40 °C the adduct should not form and the previously puzzling