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Lithium–doped plastic crystal electrolytes exhibiting fast ion conduction for secondary batteries

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Rechargeable lithium batteries have long been considered an attractive alternative power source for a wide variety of applications. Safety and stability[1] concerns associated with solvent-based electrolytes has necessitated the use of lithium intercalation materials (rather than lithium metal) as anodes, which decreases the energy storage capacity per unit mass. The use of solid lithium ion conductors—based on glasses, ceramics or polymers—as the electrolyte would potentially improve the stability of a lithium-metal anode while alleviating the safety concerns. Glasses and ceramics conduct via a fast ion mechanism, in which the lithium ions move within an essentially static framework. In contrast, the motion of ions in polymer systems is similar to that in solvent-based electrolytes—motion is mediated by the dynamics of the host polymer, thereby restricting the conductivity to relatively low values. Moreover, in the polymer systems, the motion of the lithium ions provides only a small fraction of the overall conductivity[2], which results in severe concentration gradients during cell operation, causing premature failure[3]. Here we describe a class of materials, prepared by doping lithium ions into a plastic crystalline matrix, that exhibit fast lithium ion motion due to rotational disorder and the existence of vacancies in the lattice. The combination of possible structural variations of the plastic crystal matrix and conductivities as high as $2 \times 10^{-4} \, \text{S cm}^{-1}$ at 60 °C make these materials very attractive for secondary battery applications.

A fast ion conductor is a substance in which one of the ionic species is able to conduct much more rapidly—often by a factor of many orders of magnitude—than any other species present. A typical example is the ceramic material Li$_{1-x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ (refs 4, 5); at room temperature the ions involved in the structure of this material are essentially immobile, in the sense of long-range diffusive and conductive motions. In contrast, the Li$^+$ ions exhibit conductivity as high as $10^{-3} \, \text{S cm}^{-1}$ at room temperature. The occurrence of this decoupling of the motion of one ion from the motions of others has been of fundamental interest for many years. Models of fast ion conduction in ceramics consider the motion to be along interconnected tunnels in the solid lattice and/or involve ion hopping between empty sites in the lattice. Although the single-crystal conductivity of these materials can be high, the polycrystalline nature of the bulk material creates grain boundaries which lower the overall conductivity.

Plastic crystalline substances have also been known for many years[6] and those based on ionic species can exhibit ion conduction[7–15]. The crystalline state of these substances is typically fully ordered at low temperatures, but as the temperature is increased one or more first-order solid–solid phase transitions are observed. In these higher-temperature phases, there exists some degree of rotational disorder; for example, in Li$_2$SO$_4$ (refs 13–15) the SO$_4^{2-}$ anion is free to rotate in the face-centred cubic (f.c.c.) phase of this compound above 575 °C, but is nonetheless fixed on its lattice site. Also, organic ion plastic crystals have been studied[8–12], and most exhibit some level of intrinsic conductivity. This is understood to be associated with the rotational motions of one or more of the ions; motion of the lattice defects is also involved. "Double salt" compounds have been prepared[12] that showed plastic crystal behaviour, and had conductivities as high as $4 \times 10^{-6} \, \text{S cm}^{-1}$ at 25 °C, the bulk of which was attributed to Li$^+$ ion motion. A new family of plastic crystal ionic compounds, involving the alkylmethyl-pyrrolidinium cation (I in Fig. 1) and the bis(trifluoromethane-sulphonyl)imide anion (II in Fig. 1, referred to here as the 'imide' ion) was recently reported[16,17]. The salts are referred to via an acronym, P$_{1x}$, the subscripts indicating the number of carbons in each alkyl chain. They show a characteristic series of solid–solid phase transitions below their melting points, and have ambient-temperature conductivity between 10^{-7} and $10^{-9} \, \text{S cm}^{-1}$.

Here we obtained phases with fast lithium ion conduction by doping a lithium compound into these P$_{1x}$ phases. The organic salt acts as a solid-state solvent or 'matrix' for the Li ions. The lithium salt contains the same anion as the matrix phase, hence the doping can be considered as a cation substitution. Doping is achieved by
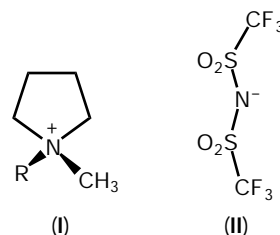

Figure 1 Structure of the alkylmethylpyrrolidinium imide matrix compounds. In the text, II is referred to as 'imide'.
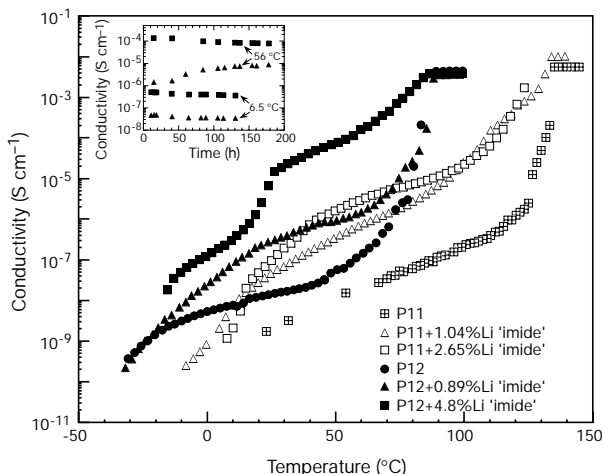
Figure 2 Ionic conductivity as a function of temperature for P_{11} and P_{12} solid phases doped with Li^+. Inset, conductivity versus time, at temperatures shown, indicating that all samples approach a conductivity limit. In the case of P_{12} doped with 0.89 mol% Li 'imide', the conductivity at 56 °C in fact increases. This may represent a homogenizing of the dopant in the sample. The fact that little change is seen in conductivity over a period of more than 1 week indicates that the phases are stable at least over this time period. The rate of diffusion-controlled events can be expected to be slower at the lower temperature.

mixing the lithium salt (3M) into the molten state of the P_{1x} compound, and then cooling the material into its plastic crystalline state. The result is a material that is a waxy solid at room temperature in the cases of the P_{11} and P_{12} members of the family. Electrochemical studies show that Li(s) can be reduced from the doped materials, and that they are stable over a potential 'window' of ~5 V.

The conductivity behaviour of these doped P_{1x} phases over a wide range of temperatures—measured by standard impedance spectroscopy methods[16,17] and after thorough drying of the material—is unexpectedly complex (Fig. 2). As noted above, the pure matrix phase compounds (P_{11} and P_{12}) are slightly conductive, their conductivity rising sharply at their final melting points. Doping with less than 1 cation% Li^+ produces a 20-fold increase in conductivity at 25 °C in both cases. Figure 3 presents the effect of composition on conductivity up to 50 mol% Li 'imide'. Beyond this point the conductivity continues to fall; pure Li 'imide' is practically non-conductive. Whereas at low compositions only one phase is
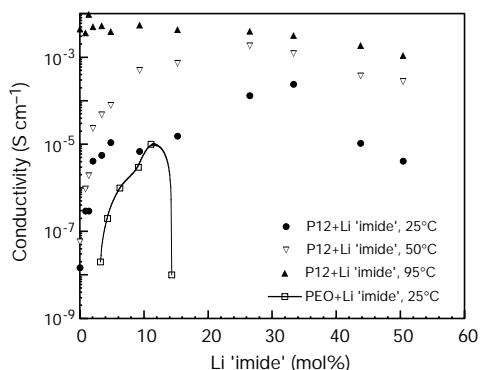
observed and Li^+ can be considered to be a dopant in the matrix phase, at concentrations between 5 and 45 mol% Li 'imide' we observed a eutectic transition in the thermal data at 30 °C indicating the presence of two phases in the samples. Thus the 25 °C isotherm in Fig. 3 represents solid-state conductivity in all cases (as discussed further below). The 95 °C isotherm corresponds to liquid-state samples in all cases; in contrast to the doped solid-state materials, the addition of small amounts of Li ions to this molten state produces a gradual decrease in conductivity. The comparison in Fig. 3 with the Li 'imide' containing polymer electrolyte[18] indicates that the plastic crystal materials are as conductive as analogous solid polymer electrolytes, but at substantially lower lithium ion concentrations. On a gravimetric basis the highest conductivity in the polymer electrolyte case is reached beyond 1 mol kg^{-1} at 25 °C (ref. 18), whereas equivalent conductivity is reached in the plastic crystal materials at less than 0.1 mol kg^{-1}.

Some light is shed on the complexity of the conductivity behaviour by the thermograms shown in Fig. 4, which were obtained by thermal analysis of the samples at a heating rate of 10 °C min^{-1}. The thermograms show a number of solid–solid phase transitions that are present in both the pure host (P_{12}) and in the doped materials (P_{12} + 0.89% Li). Some of these phase transitions, the first of which takes place at −90 °C, correspond to the onset of rotational motion of one or more parts of the molecules involved[7–11,16]. Whether it is the cation or the anion in the matrix phase that is responsible for the rotational disorder is not yet known. The melting transition of the doped compound is broadened and slightly shifted compared to the pure compound. In addition, no new thermal transitions—for example, eutectic melting—are observed, indicating that the material probably represents a solid solution of the dopant in the parent structure. (The thermal behaviour of P_{11}-based systems is similar, showing solid–solid transitions at −90 and 81 °C before melting at 132 °C.) At much higher Li 'imide' concentrations the P_{12}-based material exhibits a clear eutectic transition as well as the final melting (data not shown). It is therefore likely that the behaviour of the 4.8 cation% sample in Fig. 2 is a result of it being a multiphase mixture; nonetheless, the material retains its waxy solid properties close to its final melting point. At 50 mol% Li 'imide' the thermal data (not shown) suggest that a new, possibly metastable, mixed salt compounds forms, as observed in a study of double salts[13].

That there are diffusive motions of the ions present in these materials at temperatures well below the melting point has been confirmed by NMR experiments (Fig. 5) in which the width of the ^7Li resonance is probed as a function of temperature. The ^7Li linewidth tends towards a low-temperature limit, often referred to as the rigid lattice linewidth, characteristic of lithium ions trapped
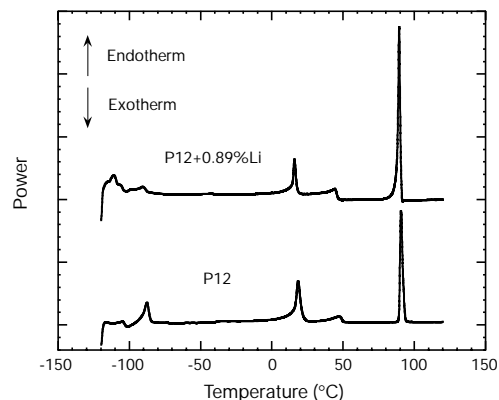

Figure 3 Dependence of conductivity on Li content in the P_{12}-Li 'imide' binary system. The PEO-Li 'imide' data from ref. 18 refers to a polyethylene oxide based polymer electrolyte material.

Figure 4 Thermal analysis traces obtained by differential scanning calorimetry of pure and Li^+-doped P_{12}.

Figure 5 ^{7}Li NMR linewidth data as a function of temperature for P_{12} doped with 9.3 mol% Li^+.

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in a non-diffusing state in a static matrix. With increasing temperature, the onset of diffusive motions causes the linewidth to fall towards values characteristic of a fluid liquid. In a simple lithium compound, this line narrowing would take place just below the melting point. In contrast, two distinct steps as a function of increasing temperature are observed in Fig. 5. The higher-temperature step corresponds to the melting transition in P_{12}. The much larger line-narrowing event takes place around −20 °C and is complete by 0 °C, well below the melting point of the compound. The diffusive motions causing line narrowing could involve the lithium ion itself or its immediate neighbours. Line narrowing therefore does not offer conclusive proof of lithium ion motion below the melting point. However, in combination with the observation that the addition of the lithium ion dopant, along with an anion which is common to the matrix, produces a 50-fold increase in conductivity without altering the phase behaviour of the material, it appears likely that it is lithium ion motion which is responsible for both the NMR line narrowing and the increased conductivity. Conduction thus being substantially due to the Li^+ ion alone is in stark contrast to polymer electrolyte materials in which lithium ion motion makes up only a small ($<20\%$) fraction of the ion conductivity[2].

The doped P_{1x} materials we report here can be classified as fast ion conductors on the basis of the high conductivities observed in a crystalline lattice. These crystalline materials have plastic mechanical properties at room temperature; that is, at some value of applied stress the materials will yield and exhibit plastic flow. Both the flow and the fast ion conduction properties are a result of rotational disorder and the existence of vacancies in the lattice. The materials therefore express an important decoupling of various molecular motions from one another such that an unusual combination of properties is exhibited. NMR relaxation measurements in progress should determine the various motional timescales that are present in these materials. □

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Patterning liquid flow on the microscopic scale

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Microscopic fluidic devices, ranging from surgical endoscopes[1] and microelectromechanical systems[2] to the commercial 'lab-on-a-chip' (ref. 29), allow chemical analysis and synthesis on scales unimaginable a decade ago. These devices transport miniscule quantities of liquid along networked channels. Several techniques have been developed to control small-scale flow, including micromechanical[3] and electrohydrodynamic[4] pumping, electro-osmotic flow[5], electrowetting[6,7] and thermocapillary pumping[8–10]. Most of these schemes require micro-machining of interior channels and kilovolt sources to drive electrokinetic flow. Recent work[8–10] has suggested the use of temperature instead of electric fields to derive droplet movement. Here we demonstrate a simple, alternative technique utilizing temperature gradients to direct microscopic flow on a selectively patterned surface (consisting of alternating stripes of bare and coated SiO_2). The liquid is manipulated by simultaneously applying a shear stress at the air–liquid interface and a variable surface energy pattern at the liquid–solid interface. To further this technology, we provide a theoretical estimate of the smallest feature size attainable with this technique.

A thin, wetting film in contact with a solid substrate bearing a temperature gradient will flow from warmer to cooler regions because of the development of a thermocapillary shear stress at the air–liquid interface[11]. For sufficiently thin films in which the thermal conductive resistance is much smaller than the convective resistance (that is, at small Biot number), the applied thermal gradient at the solid surface is directly transferred to the air–liquid interface. Because most liquids maintain a negative and constant value of $d\gamma/dT$, where γ is the surface tension and T is the temperature, the application of a constant thermal gradient in