

# The plastic-crystalline phase of succinonitrile as a universal matrix for solid-state ionic conductors

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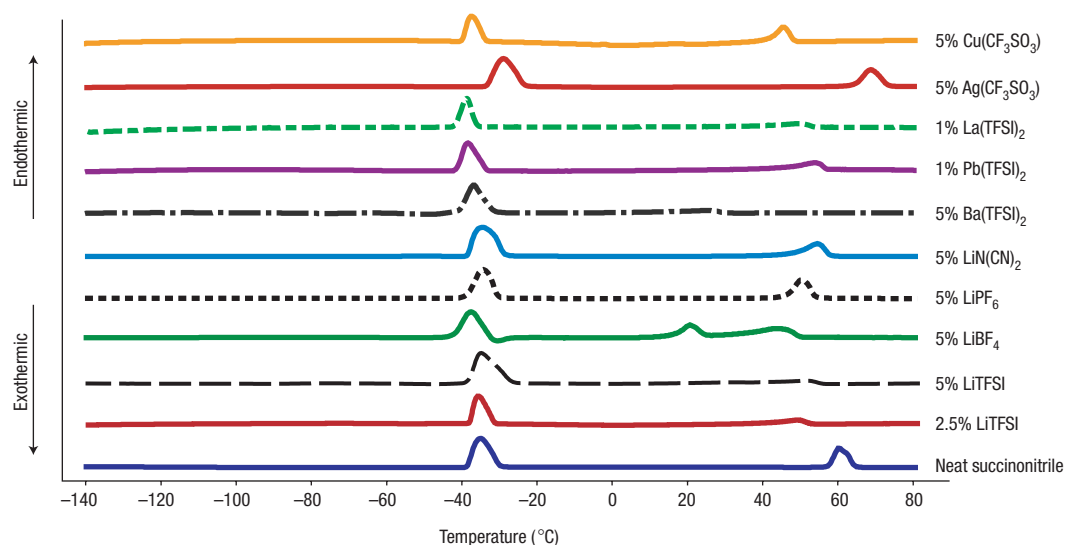
Published online: 13 June 2004; doi:10.1038/nmat1158

Solid ionic conductors are actively sought for their potential application in electrochemical devices, particularly lithium batteries. We have found high ionic conductivity for a large variety of salts dissolved in the highly polar medium based on the plastic-crystal form of succinonitrile ( $\text{N}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{N}$ ). Its high diffusivity, plasticity and solvating power allowed the preparation of a large number of materials with high ionic conductivity, reaching values of  $3 \text{ mS cm}^{-1}$  at  $25^\circ\text{C}$  (two orders of magnitude above polymers). Their ease of preparation and processing allowed us to study the influence of the solute on ionic conduction within this medium. Comparisons revealed a dichotomy between plastic crystals and conventional polymer media. The usefulness of these new, easily processed electrolytes was asserted in electrochemical tests with lithium intercalation electrodes.

Solid-state materials with high ionic conductivities have been the subject of extensive research for applications in power sources and other electrochemical devices, owing to the shortcomings of liquid electrolytes (leakage, flammability, toxicity)<sup>1</sup>. Some of the most interesting solid-state materials are polymer electrolytes (solvating polymer/salt mixtures)<sup>2</sup>. However, their ease of processing into thin films does not compensate the low room-temperature conductivity, limited by chain motion above the glass-transition temperature to values around  $5 \times 10^{-5} \text{ S cm}^{-1}$  at  $25^\circ\text{C}$ ; the main progress came from salt design and polymer architecture<sup>3,4</sup>. Radically new approaches, where some order is induced in the macromolecules, are promising, though at an early stage<sup>5-7</sup>. However, the idea of dissolving a salt in a flexible solid matrix with solvating capability is in itself an attractive approach. For this purpose, we have turned our attention to plastic crystals, as our previous work revealed they could offer a viable alternative owing to their distinct properties.

Plastic crystals display structural disorder that results in greater plasticity and enhanced diffusivities compared with normal rigid crystals<sup>8</sup>. Their potential as a new class of ion-conducting materials became evident from a report of significant ionic conductivities of organic salts based on quaternary ammonium salts<sup>9</sup>. Further reports on ammonium and heterocyclic cations have established their significance<sup>10-12</sup>. This type of plastic electrolyte shows good conductivity in the neat form, which increases when doped with lithium *bis*-trifluoromethanesulphonimide  $\text{Li}[\text{CF}_3\text{SO}_2]_2\text{N}$  (LiTFSI); ambient-temperature conductivities reach  $2 \times 10^{-4} \text{ S cm}^{-1}$  in the case of pyrazolium imides<sup>12</sup>. However, as the matrix is ionic in its own right, the conduction may not be solely attributed to the doping agent.

The approach we have taken involves the use of a non-ionic and highly polar plastic-crystalline organic molecule as a matrix: succinonitrile ( $\text{N}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{N}$ ). The high polarity of succinonitrile ensures its ability to dissolve various types of salts showing ionic conductivity that originates solely from the doping salt in an otherwise non-ionic matrix. In the course of our research, a study by Long *et al.* on the use of succinonitrile as a 'solvent' for LiTFSI at a single composition of 5 wt% and of some protonic acids has been published<sup>13</sup>.



**Figure 1** DSC ( $10\text{ }^{\circ}\text{C min}^{-1}$ ) for succinonitrile /  $M^{n+}(X)_n$  mixtures (in mol%) at the compositions indicated in the legend.

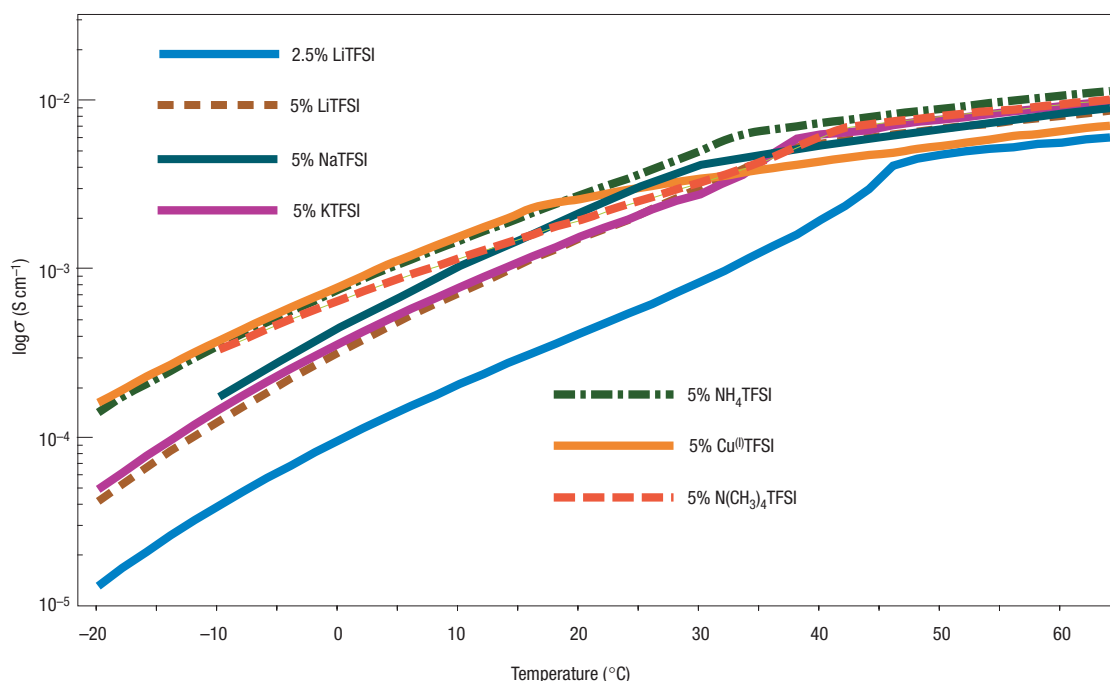
We acknowledge this work as the first introduction of the use of salt in a neutral plastic crystal, but hope to demonstrate here that the concept is of a much wider applicability.

Succinonitrile has a single plastic phase that extends from  $-35\text{ }^{\circ}\text{C}$  to its melting point at  $62\text{ }^{\circ}\text{C}$  (ref. 14). The different conformations possible from *syn* to *anti* result in a dielectric constant ( $\epsilon$ ) of 55 at  $25\text{ }^{\circ}\text{C}$  in the solid state. This gives succinonitrile a greater ability to separate charges than conventional liquid solvents ( $\epsilon_{\text{CH}_3\text{CN}} = 36.6$  at  $25\text{ }^{\circ}\text{C}$ )<sup>15,16</sup>. However, the Gutmann donor number of the nitrile group of succinonitrile is only 15 compared with 22 for the oxygen in polyethylene oxide, PEO) thus indicating the lesser tendency of succinonitrile to ‘solvate’ cations, as discussed below<sup>17</sup>. The plasticity of succinonitrile is similar to that of polymer electrolytes, suggesting that when used as a solid electrolyte in a lithium battery, the electrolyte will accommodate volume changes, that is, mechanical stress, resulting from the intercalation/de-intercalation process during operation<sup>18</sup>.

To assess the versatility of succinonitrile as a matrix, a variety of salts were used as dopants. The solutes were chosen from derivatives of weakly ( $\text{TFSI}^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ) to moderately ( $\text{CF}_3\text{SO}_3^-$ , triflate, abbreviated to Tf) coordinating anions, ending with stronger Lewis bases ( $\text{CF}_3\text{CO}_2^-$ ,  $[\text{N}(\text{CN})_2]^-$ ,  $\text{SCN}^-$ ) and a wealth of monovalent, divalent and trivalent cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{NMe}_4^+$ ,  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$ ). The salts were dissolved in molten succinonitrile under dry atmosphere, at various molar percentages (up to 5 mol%). The mixtures yielded transparent materials, which could be worked into mechanically stable films. As the CN moieties have a low affinity for protons ( $\text{pK}_a$  of  $\text{CN-H}^+ \approx -9.5$ ), we anticipated that adding acids was unlikely to lead to high conductivities, as was found to be the case<sup>13</sup>. Conversely to Long’s restrictions, we did not observe any solubility problem with all the salt s for which conductivity data is reported. The X-ray of the succinonitrile-5-mol%LiTFSI material showed only the succinonitrile lines. Figure 1 displays the differential scanning calorimetry (DSC) traces of the neat and doped compounds. They all display a single endothermic peak (except for  $\text{LiBF}_4$  with two events, and  $\text{LiTf}$ —not shown) corresponding to the rigid-to-plastic crystal transition ( $T_{\text{pc}}$ ) before melting at  $T_{\text{m}}$ . The nature and concentration of the dopant was found to have no effect on  $T_{\text{pc}}$ . All entropies of fusion were less than  $20\text{ J mol}^{-1}\text{ K}^{-1}$ , thus in compliance with Timmermans’ criterion for the

recognition of the plastic-crystal behaviour in non-ionic compounds<sup>19</sup>. The melting points were lowered by the addition of salts. It is tempting to assign, as for classical solids, the decreasing amplitude of the melting event to the existence of a <succinonitrile + salt> solid solution and of a simple liquid eutectic. Indeed, considering the very low residual energy for the plastic-crystal phase to go into a more disordered state, it is likely that the salt-containing domain(s) are disordered and presumably nanodispersed in the plastic-crystalline phase ( $\sim 80\%$  plastic-crystalline volume). But, considering the complexity and limited knowledge of the plastic-crystalline state, some residual order cannot be ruled out. Rapid quenching failed to show a glass transition for a glassy phase, expected in the  $-100$  to  $-30\text{ }^{\circ}\text{C}$  domain. Atomic force microscopy (AFM), used to investigate the mechanical properties of another family of plastic crystals, showed the transition from viscoelastic to viscoplastic behaviour, none of which is characteristic of a liquid<sup>20</sup>. In this respect, the succinonitrile would act both as an electrolyte and a filler, akin to nanoparticle addition to either polymers or liquid electrolytes<sup>21,22</sup>. However, in contrast to conventional ceramic fillers, the different phases are in dynamic equilibrium, as shown by the similar diffusion coefficients for cations, anions and ‘average’ protons in a pulsed-field gradient NMR experiment<sup>13</sup>. The high dielectric constant of the succinonitrile phase may, as for the incorporation of high-permittivity  $\text{BaTiO}_3$  in polymer electrolytes, have a beneficial effect<sup>23</sup>. The conductivity of all the salt–succinonitrile electrolytes was measured as a function of temperature. All the mixtures obey the general behaviour we previously observed for an ionic plastic-crystal matrix: in Arrhenius coordinates, the conductivity below  $T_{\text{pc}}$  increases monotonically, whereas above  $T_{\text{pc}}$ , it obeys a binomial function, returning to a monotonic variation after melting<sup>12</sup>. In cases where two phases were observed, for example,  $\text{LiBF}_4$  and  $\text{LiTf}$ , two consecutive binomials were encountered. The changes in the conductivity profiles with temperature correlate well with those observed from DSC scans. We have already shown that the observed behaviour within the plastic-crystalline phase relates to the existence of high concentration and diffusion of pipe defects<sup>12</sup>.

Many of these new electrolytes display remarkably high conductivity at room temperature and below ( $-20\text{ }^{\circ}\text{C}$ ). Thus at  $25\text{ }^{\circ}\text{C}$ , succinonitrile-5-mol% $\text{NH}_4\text{TFSI}$  ( $\approx 0.55\text{ M}$ ) showed a conductivity



**Figure 2** Conductivity as a function of temperature for succinonitrile  $M^+TFSI^-$  systems (2.5 to 5 mol%) for monovalent cations.

of  $3.16 \text{ mS cm}^{-1}$ , a value that compares well with aqueous solutions of strong electrolytes such as KCl:

$$\sigma_{(10^{-2} \text{ M KCl})} = 1.41 \text{ mS cm}^{-1} < \sigma_{(\text{succ-5-mol\% NH}_4\text{TFSI})} < \sigma_{(10^{-1} \text{ M KCl})} = 12.9 \text{ mS cm}^{-1}.$$

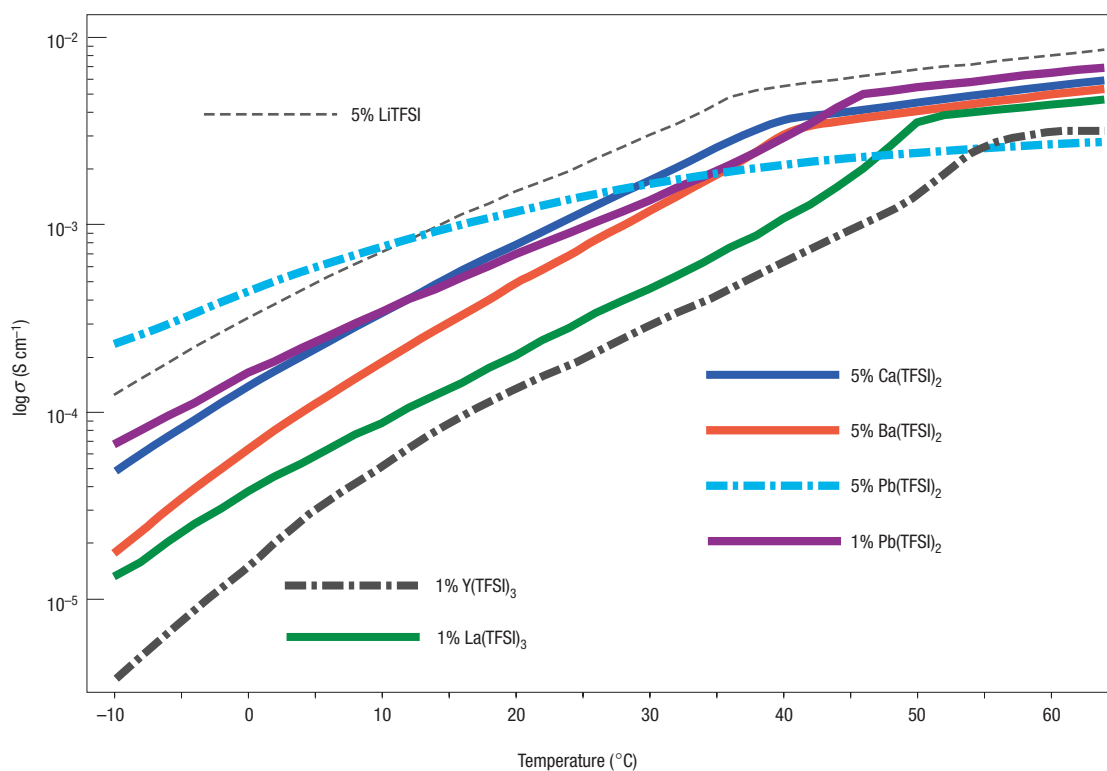
TFSI, an anion designed initially for polymer electrolytes, was considered as a logical choice for a comparison between cations, owing to the very low lattice energy of TFSI salts implying high solubility, and that the anion requires no solvation due to its charge delocalization. Its salts are among the most dissociated (solvent separated)—especially in polymer electrolytes—as measured by Raman spectroscopy, NMR or neutron scattering for the Li salt<sup>24–27</sup>. The conductivity for various TFSI salts curves are presented in Fig. 2 for the monovalent cations and in Fig. 3 for the di- and trivalent cations.

Cations interact with their host according to their charge, Van der Waals radii, and hardness; all these factors play a determining role in their contribution to conductivity. Within the solid state we found that the conductivity follows the order:

$$\sigma_{[Cu^+]} \approx \sigma_{[NH_4^+]} \approx \sigma_{[NMe_4^+]} > \sigma_{[Na^+]} > \sigma_{[Li^+]} \approx \sigma_{[K^+]} > \sigma_{[Pb^{2+}]} > \sigma_{[Ca^{2+}]} \geq \sigma_{[Ba^{2+}]} > \sigma_{[La^{3+}]}$$

The charge has a marked effect: monovalent salts yield better conducting materials than divalent salts, which in turn conduct better than trivalent salts even when considering concentrations (for example,  $Pb^{2+}$  versus  $La^{3+}$ ). Cation size is not a criterion for conductivity: The best conductors,  $Cu^+$  and  $NH_4^+$  have radii of 0.96 and 1.43 Å respectively, yet their conductivity curves are almost superimposed; the known affinity of  $Cu^+$  for the nitrile group would explain strong  $CN \rightarrow Cu$  bonds, promoting charge separation. It is noteworthy that very few  $Cu^+$  conductors are known, despite their interest *per se*, and the desire to find a substitute for silver conductors. The classical alkali ions,  $Li^+$  and  $K^+$  share similar curves, even though the radius of  $K^+$  (1.33 Å) is double that of  $Li^+$  (0.68 Å). As the size of the helical solvation whorl in PEO matches

that of  $Na^+$ , the strongly bound complexes of these ions have poor conductivity, whereas in succinonitrile,  $Na^+$ ,  $Li^+$  and  $K^+$  are all fast ion conductors ( $Na > Li, K$ ). In the previous work on succinonitrile-LiTFSI, the 5 wt% composition corresponds to 2 mol%, and has a conductivity of  $2.9 \times 10^{-4} \text{ S cm}^{-1}$  (ref. 13). In our work, we can see the marked influence of concentration. Almost an order of magnitude in conductivity is gained with 5 mol% ( $1.47 \times 10^{-3} \text{ S cm}^{-1}$ ) and 2.5 mol%; the poorest lithium conductor in Fig. 2 is at  $4 \times 10^{-4} \text{ S cm}^{-1}$ , already a 30% increase compared with 2 mol%. Lastly, for the singly charged cations, the very large  $(Me)_4N^+$  (2.82 Å) is unique as it does not require a solvation shell. For instance, its salts do not form complexes with PEO where the main driving force is oxygen donicity. Here, only the dipolar forces can be responsible for the solubility and dissociation of  $(Me)_4N-TFSI$ , which gives a highly conductive solution in succinonitrile. This is the first example of a solid quaternary ammonium conductor. The other ‘soft’ cation—that is, polarizable in Pearson’s sense—of our study,  $Pb^{2+}$ , does not show the same affinity as  $Cu^+$  for nitrile, but exhibits better conductivity than other reported isocharged species:  $Pb^{2+} > Ca^{2+} > Ba^{2+}$ , which may be explained by  $Pb^{2+}$  having a filled orbital favourable to fast ligand exchange. The 1-mol%  $Pb(TFSI)_2$  compound is already appreciably conductive. The size factor for the divalent element does not translate for the rare earth metals, where the larger  $La^{3+}$  is about two times more conductive than  $Y^{3+}$ ; only 1% concentrations were used as the 5% (40% wt/wt) were amorphous. Though the concepts of ‘full’ solvation in succinonitrile should be treated with caution in such unexplored media, the proof of strong interaction with cations is given, for instance, by the stability of  $Cu^+$  species (only  $Cu^{2+}$  is stable in PEO), suggesting the insertion of CN group(s) between the copper cation and TFSI<sup>-</sup>. Solvation certainly plays a role in competition with the anion, as seen with the rare-earth complexes, where neither  $Y(Tf)_3$  nor  $La(Tf)_3$  are soluble, whereas the corresponding  $Y(TFSI)_3$  and  $La(TFSI)_3$  dissolve easily, in agreement with the Guttmann donor number of the species ( $DN_{Tf^-} = 22 > DN_{succ} \approx 15 > DN_{TFSI^-} = 5.4$ ), prompting an assessment of the role of anions<sup>28,29</sup>.



**Figure 3** Conductivity as a function of temperature for succinonitrile  $M^{n+}$ TFSI $_n$  systems (1 to 5 mol%) for di- and trivalent cations.

The practically important cation  $\text{Li}^+$  was chosen to test the influence of the type of anions on conductivity. The conductivity results for many lithium salts–succinonitrile materials are shown in Fig. 4.

Obviously, the succinonitrile-based electrolytes behave in a very specific fashion compared with other conductive media such as liquids and solvating polymers in amorphous phases (for the latter when prevented from crystallization) and true crystalline solid electrolytes (for example,  $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ ). For this reason, a more legible direct temperature scale could be used in Figs 2 and 3. Neither the classical Arrhenius law for conductivity,  $\sigma = \sigma_0 \exp[-(E_{\text{diss}} + E_{\text{hop}})/KT]$  nor the dissociation-corrected free-volume law apply:  $\sigma = AT^{-1/2} \exp(-E_{\text{diss}}/KT) \cdot \exp[-E_q/\{K(T-T_0)\}]$  where  $T$  is temperature,  $E_{\text{diss}}$  represents the activation energy for dissociation of ion pairs,  $T_0$  the ideal glass transition temperature, and  $K$  the Boltzmann constant; the pre-exponent terms  $\sigma_0$  and  $A$  are proportional to the concentration of dissociable species (here salt). In liquids,  $T_0$  is raised by the added salt, but stays at a low value (below  $-100^\circ\text{C}$ ). Consequently, the conductivity is dominated primarily by dissociation thus the order is related to the basicity of the anions<sup>28,29</sup>:

$$\sigma_{[\text{LiPF}_6]} \approx \sigma_{[\text{LiTFSI}]} > \sigma_{[\text{LiBF}_4]} > \sigma_{[\text{LiCF}_3\text{SO}_3]} \approx \sigma_{[\text{LiN}(\text{CN})_2]} \approx \sigma_{\text{LiSCN}} > \sigma_{[\text{LiCF}_3\text{CO}_2]}$$

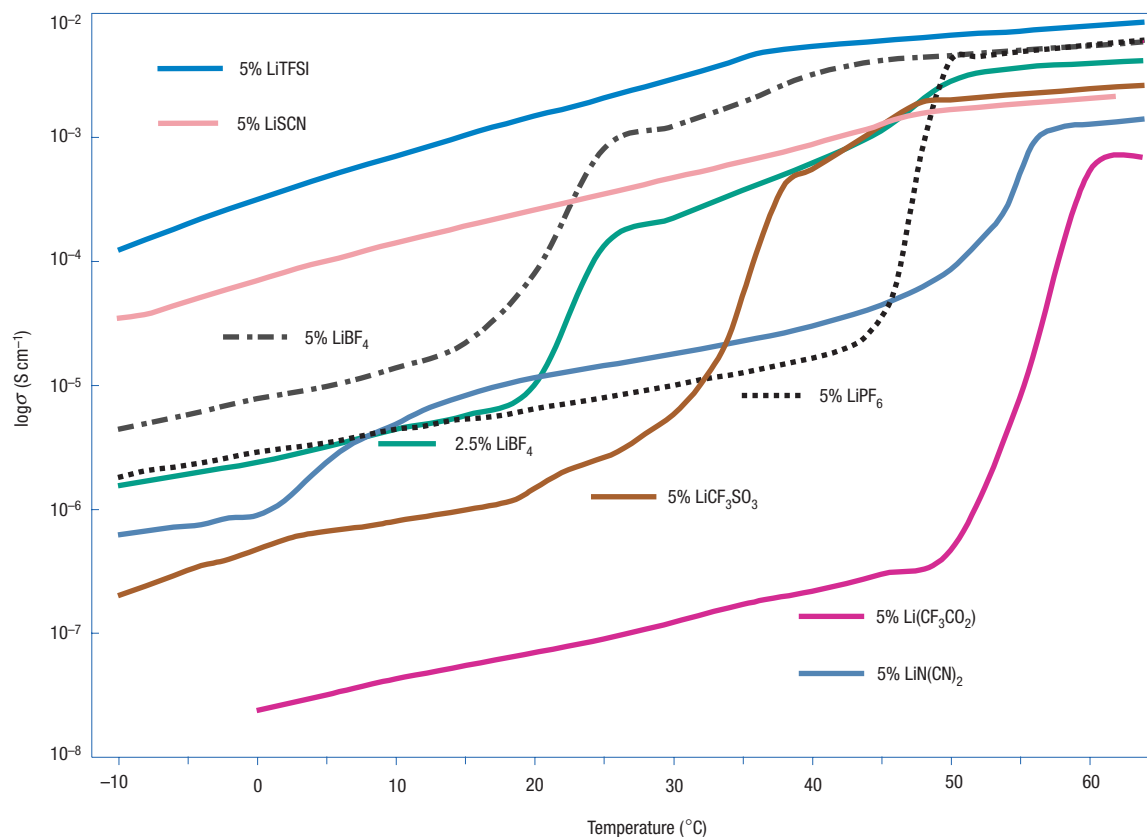
In polymer electrolytes, the  $T_0$  influence is more pronounced, and the order follows:

$$\sigma_{[\text{LiTFSI}]} \gg \sigma_{[\text{LiBF}_4]} \approx \sigma_{[\text{LiPF}_6]} > \sigma_{[\text{LiCF}_3\text{SO}_3]} \approx \sigma_{[\text{LiN}(\text{CN})_2]} \approx \sigma_{\text{LiSCN}} > \sigma_{[\text{LiCF}_3\text{CO}_2]}$$

Flexible and highly delocalized charges, as in TFSI, limit the increase in  $T_0$ . In succinonitrile, the influence of anion delocalization is apparent for  $\text{CF}_3\text{CO}_2^-$  (delocalization between two ‘hard’ oxygen centres), which yields the poorest conductivities. Until the temperature of the second

transition is reached (as observed by DSC, Fig. 1)  $\text{CF}_3\text{SO}_3^-$  (three oxygen centres) remains inferior to dicyanoimide  $[\text{N}=\text{C}-\text{N}-\text{C}=\text{N}]^-$  whose charge is also delocalized on three centres, but on softer nitrogens. This would suggest that the nitrile donor atoms in succinonitrile compete with difficulty with oxygen in anions; the partial charge decreases in the order  $\text{CF}_3\text{CO}_2^- > \text{CF}_3\text{SO}_3^- \gg \text{TFSI}^-$ . The most striking anion effect is seen with  $\text{PF}_6^-$ , which, highly conductive in liquids, is a very poor conductor in succinonitrile until the plastic crystal melts. The basicity cannot be invoked as an explanation, as more associating  $\text{BF}_4^-$  gives better performances; neither can the instability of  $\text{LiPF}_6$ , as the nitrile group is not prone to displace the equilibrium  $\text{LiPF}_6 + \text{succinonitrile} \leftrightarrow \text{PF}_5 \leftarrow \text{succinonitrile} + \text{LiF}$  to the right. Interestingly,  $\text{BF}_4^-$  becomes a good conductor after the second phase transition observed by DSC (Fig. 1). The case of these two fluoro-anions,  $\text{PF}_6^-$  and  $\text{BF}_4^-$ , together with the charge/size effect seen with highly charged cations, is an indication that some selectivity based on structural effects may be present in plastic crystals. Another deviation from conventional wisdom is apparent with the excellent performance of LiSCN, which here comes second to LiTFSI, despite its poor conductivity in both PEO or liquids, and its high Gutmann donor number of 31.9 (ref. 28).  $\text{SCN}^-$  and  $[\text{N}=\text{C}-\text{N}-\text{C}=\text{N}]^-$  are two soft anions, which are usually comparable. Yet, their Li salts show considerable difference in succinonitrile. Also, KSCN (not shown) is as conductive as KTFSI, whereas  $\text{K}[\text{N}(\text{CN})_2]$  is insoluble in the same medium. In addition, the relatively poor conductivity of either CuTf or AgTf ( $\sigma_{20^\circ\text{C}} = 3.4 \times 10^{-6}$  and  $7.6 \times 10^{-6} \text{ S cm}^{-1}$ , respectively), despite the strong nitrile  $\leftrightarrow$  cation interactions, highlight once more the beneficial role of TFSI.

Figure 5 presents cyclic voltammograms of the succinonitrile–5-mol%LiTFSI at  $20^\circ\text{C}$ . The compound shows a wide electrochemical window spanning nearly 6 V. In spite of this exceptional electrochemical stability, metallic lithium was not used as an anode,



**Figure 4** Conductivity as a function of temperature for succinonitrile–Li<sup>+</sup>X<sup>−</sup> systems (5 mol%).

as it is known that Li<sup>0</sup> catalyses the polymerization of nitriles. This suggested the use of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (1.55 V versus Li<sup>+</sup>:Li<sup>0</sup>) as anode material and LiFePO<sub>4</sub> or LiCoO<sub>2</sub> as a cathode material with succinonitrile–5-mol%LiTFSI serving as a solid electrolyte in lithium batteries. The slow-scan voltammograms (SSCV; 50 mV h<sup>−1</sup>) were recorded from 1 to 2.6 V for the LiFePO<sub>4</sub>/Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> system and between 1.7 and 2.8 V for the LiCoO<sub>2</sub>/Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> couple. As can be seen from Fig. 5, very sharply defined peaks are obtained, with no smearing due to ohmic drop; the electrochemical activity of the Fe<sup>3+</sup>/Fe<sup>2+</sup> couple appears around 3.45 V and at 3.85 V for the Co<sup>4+</sup>/Co<sup>3+</sup> couple versus Li<sup>+</sup>:Li<sup>0</sup> (1.9 V and 2.3 V versus the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> anode, which give the actual voltage of the cell). The discharge capacity was 148 mAh g<sup>−1</sup> and 146 mAh g<sup>−1</sup> for LiFePO<sub>4</sub> and LiCoO<sub>2</sub> cathodes, with charge–discharge efficiencies of 95 and 84%, respectively.

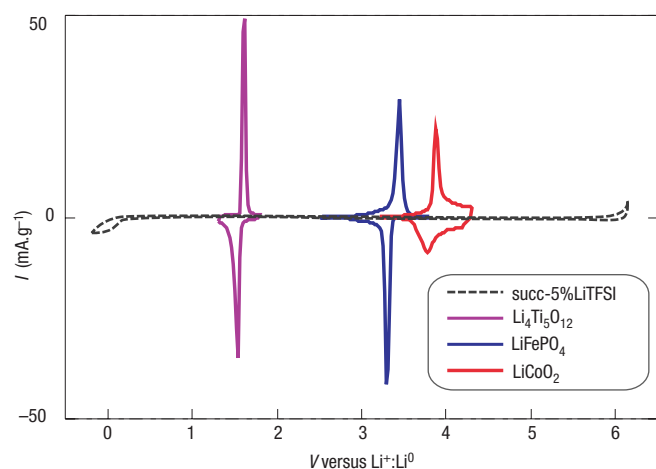
The plastic crystals as hosts for ‘ionogenic’ solutes have resulted, for a first attempt, in the identification of an unprecedented number of new fast-ion conductors, which compare favourably with the best solid electrolytes (such as β-alumina). Although solvating polymers also correspond to a variety of complexes, the transport of cations is limited to those whose exchange kinetics with ether oxygen is fast<sup>30</sup>. In succinonitrile-based complexes, both strongly interacting (for example, Cu<sup>+</sup> but also charge/volume cations such as Li<sup>+</sup>), as well as weakly interacting cations (Me<sub>4</sub>N<sup>+</sup>) give high conductivities. Clearly, the use of low donicity anions such as TFSI is a sure recipe for high conductivities: when the nitrile groups can easily be inserted between the M<sup>+</sup>X<sup>−</sup> pair, further charge separation occurs, being facilitated by the high dielectric constant. One still unsolved question is the role of a disordered fraction coexisting with the succinonitrile, whose remaining degree of order is to be explored; but even in the extreme case of a

liquid-like component, it remains nanodispersed in the succinonitrile matrix with no evidence for phase separation. Vacancies in the plastic crystal may account for several percent of its volume, but obviously a high concentration of solutes, especially of very large molecular size (La(TFSI)<sub>3</sub> ≈ 400 Å<sup>3</sup> compared with 92 Å<sup>3</sup> for succinonitrile) drives towards (partial) loss of plastic-crystal order locally. The intriguing case of LiPF<sub>6</sub> low conductivity, the low and high conductivity subphases in LiBF<sub>4</sub> and the invariance of the *T*<sub>pc</sub> transition, indicate that more complex phenomena than a pure solid solution takes place. Also, the high conductivity of LiSCN was not expected considering the basicity of the anion; interestingly, LiSCN (49 Å<sup>3</sup>) is much smaller than succinonitrile. All these materials possess mechanical strength and plasticity reminiscent of polymers. Initial results, without optimization, confirm that they are effective as electrolytes for lithium batteries. The high fraction of theoretical capacities obtained with the three intercalation materials tested are impressive, and demonstrate an appreciable cation (Li<sup>+</sup>) mobility, corroborated by the NMR results<sup>13</sup>. It appears that the plastic-crystal state, not limited to succinonitrile, should be a source of progress in solid-state science, both in term of practical applications, but also on theoretical ground. Despite the already large number of tests presented here, we share a strong belief that these new electrolytes can be optimized further.

## METHODS

Electrolytes were prepared by dissolving the pre-weighed salt into melted succinonitrile (Aldrich). The following salts were purchased and used without additional purification: LiBF<sub>4</sub> (Tomyama); LiPF<sub>6</sub> (Stella Chemicals); LiTFSI (3M); LiTf and AgTf (Aldrich). LiN(CN)<sub>2</sub> was prepared by reacting LiOH with NH<sub>4</sub>N(CN)<sub>2</sub> in acetonitrile; the ammonium salt was prepared from the commercial sodium salt by adding excess NH<sub>4</sub>F in methanol, drying, extracting with dimethylformamide and precipitating with





**Figure 5** SSCV ( $50 \text{ mV h}^{-1}$ ) of solid-state batteries using  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as the negative electrode and either  $\text{LiFePO}_4$  or  $\text{LiCoO}_2$  as the positive electrode. Electrolyte: 5-mol% LiTFSI in succinonitrile; temperature  $20^\circ\text{C}$ .

$\text{CH}_2\text{Cl}_2$ ; KF give similarly the K salt. This method removes the chloride impurities.  $\text{LiSCN}$  was similarly obtained from  $\text{NH}_4\text{SCN}$ . Other non-commercial salts, still unreported in the literature, were prepared by reacting the acid  $\text{H}[(\text{CF}_3\text{SO}_2)_2\text{N}]$  (Fluka) on excess (hydroxy)carbonate in acetonitrile, filtration and drying ( $80^\circ\text{C}$ , primary vacuum);  $\text{NH}_4$  and  $\text{N}(\text{CH}_3)_3$ -TFSI were prepared from the acid and the hydroxide evaporation, then for the latter by extraction with  $\text{CH}_2\text{Cl}_2$ . Copper TFSI was obtained in the presence of the  $\text{Cu}^{\text{II}}$  carbonate and copper metal. Succinonitrile (Aldrich) was doped by adding the required amount of salt, varied from 1 to 5 mol%. The mixture was then melted and stirred in a He-flushed glove box, (dew point  $-95^\circ\text{C}$ ,  $\text{O}_2 < 1$  volume per million).

DSC tests (Pyris 1, Perkin-Elmer) were done in aluminium pans sealed in the dry box. Starting from ambient, the temperature was brought to  $-150^\circ\text{C}$  and scanned from this temperature to  $+90^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$ .

The conductivity of the compounds was measured with a Hewlett Packard 4192 impedance analyser over a temperature range  $-20$  to  $80^\circ\text{C}$  (Haake DC50-K35 thermostat).

Electrochemical characterization was carried out with coin-type cells. Composite cathodes containing  $\text{LiFePO}_4$  or  $\text{LiCoO}_2$  and anode ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) were prepared by mixing 85:5:10 (w/w) ratio of active material, carbon black (Chevron Phillips) and polyvinylidene fluoride binder (Kynar, Atofina), respectively, in *N*-methyl pyrrolidone (Fluka). The resulting paste was applied to a carbon-coated aluminium film current-collector (Rexam Image Products). The succinonitrile-5-mol%LiTFSI electrolyte was incorporated between the electrodes with the help of a Celgard separator ( $30 \mu\text{m}$  thickness) to avoid short-circuits. The cells were assembled in the dry box. Cell performance was evaluated by SSCV (Mac-Pile, Biologic, Claix, France) at a rate of  $50 \text{ mV h}^{-1}$ .

Received 30 December 2003; accepted 11 May 2004; published 13 June 2004.

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## Acknowledgements

CNRS funding covered full (M.A.) and partial (P.J.A., Y.A.-L., A.A.) salaries and research expenditures. Correspondence and requests for materials should be addressed to M.A.

## Competing financial interests

The authors declare that they have no competing financial interests.