Conductive Plastic Crystals

Conductive Organic Plastic Crystals Based on Pyrazolium Imides

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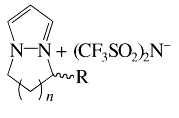
Interest in conductive organic plastic crystals was recently increased when significant conductivity at room temperature was reported and a new type of solid-state ionic conductor was identified.[1,2] Most of the work in the past was focused on salts of either tetraalkylammonium[3] or certain heterocyclic cations.[4] It was suggested that the plastic crystalline phases of *N*-substituted pyrrolidinium[5] or pyrrolinium imides[6] can be doped with a lithium imide salt to be utilized as solid electrolytes for lithium batteries. Although high conductivity is still to be obtained at room temperature, the high plasticity and diffusivities of the plastic phases relative to conventional solid electrolytes[7] enables the use of these materials in lithium batteries and other electrochemical devices.

The disadvantage of the pyrrolidinium-based salts is that they show multiple plastic phases before melting.[8] One may then question the exact nature of the conductivity mechanism; the possibility of the formation of a liquid phase from eutectics at the grain boundaries cannot be totally excluded, especially at high doping levels.

In work presented herein, we synthesized a series of salts based on *N,N'*-cyclized pyrazolium cations (Figure 1). The cations adopt a disklike shape, which is favorable for plastic crystal behavior. Indeed, all the compounds exhibited behavior typical of plastic crystals. Amongst these, 5-methyl-5,6,7,8-tetrahydropyrazolo[1,2-*a*]pyridazin-4-ium trifluoromethanesulfonimide (TFSI, **1**), showed a single plastic crystalline phase with a wide temperature range. Furthermore, the plastic crystal region began at room temperature (precisely at 20 °C), extending up to the melting point at 65 °C. Most interestingly, when we doped this plastic crystalline phase with a lithium trifluoromethanesulfonimide salt (LiTFSI) to increase and possibly add a Li^{+} ion contribution to the total conductivity. To our knowledge, this is the first reported single-phase ion-conducting organic plastic crystal.



$n = 1,2,3$; R = H, CH_3

1 : $n = 2$; R = CH_3

Figure 1. N,N'-cyclized pyrazolium trifluoromethanesulfonimide salts.

DSC curves of the neat and LiTFSI-doped (1 and 2 mol %) salts showed two transitions (Figure 2). The first, at 20 °C (for the neat salt and that doped with 1 mol % LiTFSI), can be assigned to the conventional crystal-to-plastic crystal transition followed by a second peak corresponding to their melting at around 65 °C. In the case of the doped imide (2 mol %), the first transition temperature is shifted upwards to only 25 °C.

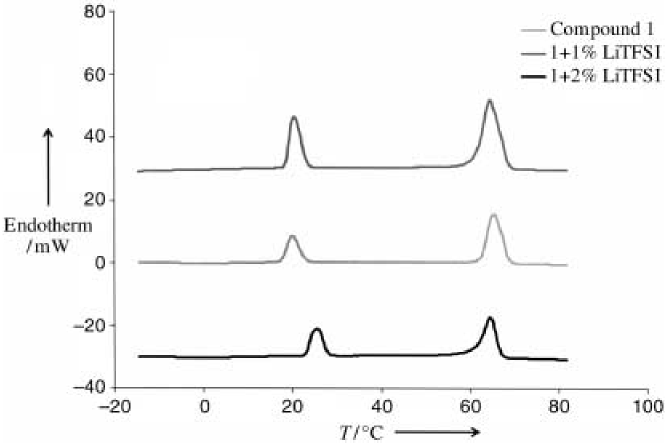


Figure 2. DSC scans of **1** and of **1** doped with 1 and 2 mol % LiTFSI.

The melting entropies (ΔS^{o}_{m}) of the salts are 48.7 (neat), 45.6 (1 mol %), and 38.4 J K^{-1} mol^{-1} (2 mol %). These values are higher than the criterion set by Timmermans:[9] $\Delta S^{o}_{m} \leq 20$ J K^{-1} mol^{-1} for plastic crystals. However, McFarlane et al. have also reported higher ΔS^{o}_{m} values.[10] They attributed this residual entropy of melting to the flexibility of the imide anion, which according to them, contributes largely to the entropy of melting.[11] The nature of this increase is still not clear and remains open to further study. In fact, there is a strong case to consider higher values than the limit of 20 J K^{-1} mol^{-1}, which appears to work only for weakly

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interacting, nonionic, organic compounds. The argument for the use of ΔS^{o}_{m} as a criterion to define ionic organic plastic crystals is beyond the scope of this Communication and can be found elsewhere.[1]

The conductivity of the neat and the doped salts was measured over a temperature range of −10 to 80 °C (Figure 3). From the DSC of **1**, we found that the conventional crystal-to-plastic transition and melting occur at 20 °C and 65 °C, respectively. This observation clearly correlates to the observed conductivity behavior by a small but significant jump in conductivity at 20 °C and the expected change of regime after melting at 65 °C (the lines are provided as a visual guide). Therefore, the temperature dependence of the conductivity behavior can be divided into three distinctive zones:

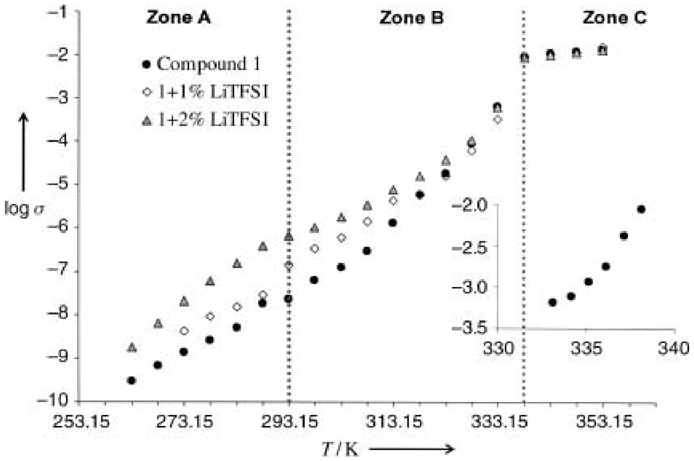

Figure 3. Conductivity of **1** and of **1** doped with 1 and 2 mol % LiTFSI as a function of temperature.

1) Zone A (−10–20 °C): This is the conventional crystal region in which we observe a monotonic increase in conductivity with temperature; such a significant increase in conductivity was observed (up to 30-fold in the presence of 2 mol % Li ions).
2) Zone B (20–65 °C): This is the plastic crystal zone in which the conductivity dependence changes from a linear to a polynomial function. For the 2-mol %-doped material, the conductivity increases from 1.0×10^{-6} S cm^{-1} at the lower limit of the range (25 °C) to 6.2×10^{-4} S cm^{-1} at 60 °C. High conductivities (above 10^{-4} S cm^{-1}) are observed starting at temperatures as low as 55 °C. We believe that the high conductivity is due to the existence of long dislocated defects, which form interconnected channels (or pipes) that provide an efficient pathway for ions and defects to move rapidly. This is perfectly reasonable as it is well-established that, besides lattice diffusion, a pipe-diffusion mechanism is involved in nonionic plastic crystals.[12] When 1 mol % of LiTFSI was added to the neat salt, the conductivity was increased fivefold at the lower limit of the plastic domain. This increased further (to 17-fold) when 2 mol % of the lithium salt was added. Preliminary investigation of the least-squares fit of the temperature–conductivity curves showed a second-order polynomial variation.
3) Zone C (65–80 °C): This is the ionic-liquid zone. The conductivity in this temperature range shows a linear dependence with low activation energy typical of ionic liquids, and values in the order of 10^{-2} S cm^{-1} were obtained. The conductivity decreased with increased doping levels of the lithium imide salt. This could be due to an increase either in the viscosity or in the ionic interactions, thus leading to less-mobile species.

At this stage, the doping-induced increase in conductivity cannot be attributed only to the participation of lithium ions as opposed to the pyrazolium cations. We are presently addressing this aspect by performing measurements of the Li^{+} transport number, $t_{\mathrm{Li+}}$.

The simplicity of having a single-phase plastic-crystal system allowed us to shed light on the temperature–conductivity pattern of such new solid electrolytes. In multiphase systems, the uniqueness of this behavior to plastic crystal electrolytes has either been overlooked or oversimplified to multilinear fittings.[13] This dependence of σ on T cannot be adequately interpreted by the known methods of analysis, such as Arrhenius or VTF (Vogel–Tammann–Fulcher). As we pointed out earlier, it displays a binomial dependence, the details of which will be discussed in the near future.

In conclusion, a single-phase organic plastic crystal based on a cyclic pyrazolium cation was synthesized. Its plastic-crystalline range extends from 20 to 65 °C. Within the plastic-crystal phase, conductivities reached 1.0×10^{-4} S cm^{-1} at 55 °C and 6.2×10^{-3} S cm^{-1} at 60 °C. The conductivity at room temperature increased tenfold (reaching ~10^{-6} S cm^{-1}) by doping with small amounts of LiTFSI.

Experimental Section

All reagents and solvents were commercially available and used without further purification. NMR spectra were run on a 400 MHz Bruker spectrometer.

Doping of **1** was achieved by adding the required amount of lithium imide salt to **1**. The mixture was then melted and stirred in a He-flushed glovebox (dew point −95 °C, $O_2 < 1$ vpm).

Conductivities of the samples were measured on a Radiometer conductivity cell with a cell constant of 0.92 cm^{-1}. All samples and measurements were carried out in the glovebox. Values for the resistance were obtained on an HP frequency analyzer by sweeping the frequency from 10 μ to 13 MHz with an amplitude of 10 mV.

Temperature–conductivity curves were obtained between −10 and 80 °C with 5 °C increments, allowing 30 minutes for thermal equilibration at each temperature.

Differential-scanning-calorimetric analysis (DSC) was performed on a Perkin-Elmer Pyris 1. Samples were sealed in aluminum pans in the dry box and then scanned at 20 °C min^{-1} from −150 to 160 °C.

1: Pyrazole (3.404 g, 50 mmoles) was dissolved in dry dioxane (100 mL) in a 250-mL round-bottomed flask under argon. Dry sodium hydride (95 %; 1.263 g, 50 mmoles) was added, in small portions, to the rapidly stirred solution, at such a rate that the dioxane was barely boiling. The solution was left to cool with stirring, and the reaction flask was fitted with an addition funnel filled with (±)-1,4-dibromopentane (11.498 g, 50 mmoles). The dibromide was added drop wise over a period of 5 min. The reaction mixture was stirred for 20 min at room temperature and then heated at reflux for 16 h. The resulting suspension was allowed to cool, and the precipitate was filtered and rinsed with diethyl ether. The solid was then dissolved in acetone and filtered to remove sodium bromide, and the solvent was removed in vacuo to afford (±)-5-methyl-5*H*,6*H*,7*H*,8*H*-pyrazolo[1,2-*a*]pyridazin-4-ium bromide (9.98 g, 92%). The bromide salt (2.171 g, 10 mmoles) was dissolved in water (50 mL) and the solution was added to a solution of potassium trifluoromethanesulfonimide (3.192 g, 10 mmoles) in water (50 mL). The plastic salt precipitated out of solution as a fine white powder. The solid was collected by filtration and dried under vacuum to yield (±)-5-methyl-5*H*,6*H*,7*H*,8*H*-pyrazolo[1,2-*a*]pyridazin-4-ium trifluoromethanesulfonimide (**1**; 4.055 g, 97%). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25°C): $\delta = 1.61$ (d, $^3J = 6.5$ Hz, 3H, CH_3), 1.85 (m, 1H, CH_2), 1.98–2.28 (m, 2H, CH_2); 3.37 (d, $^3J = 0.7$ Hz, 1H, CH_2), 4.37 (m, 1H, CH), 4.50–4.69 (m, 2H, CH_2), 6.95 (t, $^3J = 2.9$ Hz, 1H, CH), 8.47 (d, $^3J = 2.6$ Hz, 1H, CH), 8.64 ppm (d, $^3J = 2.9$ Hz, 1H, CH); ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25°C): $\delta = 17.58$, 19.66, 26.32, 48.37, 55.89, 106.99, 119.00 (q, $J = 322.3$ Hz, CF_3), 134.84, 136.17 ppm.

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[1] D. MacFarlane, M. Forsyth, *Adv. Mater.* **2001**, *13*, 957–966.
[2] E. Cooper, C. Angell, *Solid State Ionics* **1986**, *18–19*, 570–576.
[3] S. Fukada, H. Yamamoto, R. Ikeda, D. Nakamura, *J. Chem. Soc. Faraday Trans. 1* **1987**, 3207.
[4] D. MacFarlane, P. Meakin, N. Amini, M. Forsyth, *J. Phys. Condens. Matter* **2001**, *13*, 8257–8267.
[5] D. MacFarlane, J. Huang, M. Forsyth, *Nature* **1999**, *402*, 792–794.
[6] J. Sun, D. MacFarlane, M. Forsyth, *Solid State Ionics **2002**, 148, 145–151.*
[7] M. Forsyth, J. Huang, D. MacFarlane, *J. Mater. Chem.* **2000**, *10*, 2259–2265.
[8] D. MacFarlane, J. Sun, J. Golging, P. Meakin, M. Forsyth, *Electrochim. Acta* **2000**, *45*, 1271.
[9] J. Timmermans, *J. Phys. Chem. Solids* **1961**, *18*, 1.
[10] D. MacFarlane, P. Meakin, J. Sun, N. Amini, M. Forsyth, *J. Phys. Chem. B* **1999**, *103*, 4164–4170.
[11] J. Huang, M. Forsyth, D. MacFarlane, *Solid State Ionics* **2000**, *136–137*, 447–452.
[12] J. Sherwood, *The Plastically Crystalline State: Orientationally Disordered Crystals*, Wiley, Chichester, UK, **1979**, p. 51.
[13] A. Hill, J. Huang, J. Efthimiadis, P. Meakin, M. Forsyth, D. MacFarlane, *Solid State Ionics* **2002**, *154–155*, 119–124.