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Solid Electrolytes

Rapid I^-/I_3^- Diffusion in a Molecular-Plastic-Crystal Electrolyte for Potential Application in Solid-State Photoelectrochemical Cells**

Qing Dai, Douglas R. MacFarlane, Patrick C. Howlett, and Maria Forsyth*

A molecular plastic crystal based electrolyte is described which has almost liquidlike diffusion properties for I^-/I_3^-, a redox couple of interest in photoelectrochemical cells. These cells, which are typically composed of TiO_2 photoanodes covered with dye molecules or a conducting polymer and a liquid-based electrolyte, are currently under intense investigation because of their relatively low-cost materials and extremely simple fabrication techniques.[1] Although dye-sensitized nanocrystalline solar cells (DSSCs) offer high efficiency, comparable to that of amorphous silicon solar cells, a major disadvantage of such devices is the necessity of using a liquid-based electrolyte which includes the dissolved I^-/I_3^- redox couple.[2] A number of difficulties in encapsulation of this liquid electrolyte considerably hinder the long-term stability of these devices. Thus hole-transporting organic materials,[3,4] *p*-type semiconductors,[5] and polymers incorporating the redox couple have been investigated to replace the organic solvent-based liquid electrolytes for solid-state DSSCs.[6–8] Wang et al. have succeeded in employing quasi-solid-state electrolytes based on room-temperature ionic liquids, which yielded up to 7% efficiency in AM 1.5 sunlight.[9,10] However, so far, true solid-state DSSCs have still shown much lower efficiency because of the mass transport limitation of current electrolytes.

In the past we have investigated a family of ionic plastic crystals[11–13] and molecular plastic crystals[14,15] for potential application in Li batteries and fuel cells. In the present study,

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[*] Dr. Q. Dai, Prof. D. R. MacFarlane, Dr. P. C. Howlett
School of Chemistry, Monash University
Clayton, Victoria 3800 (Australia)
Fax: (+61) 3-9905-4597
E-mail: qing.dai@sci.monash.edu.au

Prof. M. Forsyth
School of Physics & Material Engineering
Monash University
Clayton, Victoria 3800 (Australia)

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succinonitrile, a molecular plastic crystal, was chosen for investigation as a solvent with potential application in solid-state photoelectrochemical cells. This material was chosen because of its similarity to acetonitrile and glutaronitrile, which are commonly used as solvents for DSSCs. Succinonitrile displays the typical behavior of a molecular plastic crystal and has potentially good solvent properties.[16–19] The plastic phase is stable between 233 and 331 K in a body-centered cubic (bcc) structure.[15–20] In this phase the molecules exist in three isomeric conformations: two (identical) *gauche* and one *trans* isomer,[15–19] which are interrelated by a 120° rotation around the central C–C bond.[15–20,22] The bcc unit cell contains two molecules with the C–C bonds oriented along the diagonals of the cube.[16,19,21,23] Below 233 K the molecules exist exclusively in the *gauche* conformation.[16,20] At 233 K the material undergoes a phase change to a plastic phase. The disorder in this phase is related to *trans–gauche* isomerization (involving rotation about the central C–C bond) of the molecules and molecular jumps from one diagonal position of the cubic structure to another.[19,23] Hawthorne and Sherwood suggested that the availability of three possible conformers in succinonitrile has a major effect on the diffusion capability of the molecules, whereby the *trans* isomers act as "impurities" that create monovacancies in the lattice[16,23] and hence lead to high molecular diffusivity. These properties triggered our interest in the concept of fast I^-/I_3^- diffusion in a molecular plastic crystal. Here we communicate our preliminary results which support this concept. The materials described are the first examples of electrolytes based on molecular plastic crystals and exhibit mass transport rates high enough to be of relevance to applications such as DSSC.

The plastic crystal based electrolyte is composed of 0.375 M tetrabutylammonium iodide and 0.225 M iodine in succinonitrile. The redox couple showed good miscibility with succinonitrile, and the electrolyte was a waxy solid at ambient temperature. Typical thermal traces are presented in Figure 1 (left axis). Apparently, the solid–solid transition temperature does not change significantly on addition of the redox couple, as would be expected if the transition is an equilibrium thermodynamic phase change related to structural changes of the matrix phase. The melting behavior is complex, but it is apparent that the material is in a completely solid state below 45 °C. This is still low enough to allow fabrication of a DSSC with the electrolyte in the liquid state, which ensures good penetration into the pores of the nanocrystalline TiO_2. Comparing the enthalpy of the solid–solid transition of succinonitrile in the mixture (65.3 J g^{-1}) with the expected value (66.5 J g^{-1}) indicates that the physical properties of succinonitrile itself are not changed after addition of the solutes. Figure 1 (right axis) shows the ionic conductivity. There is a significant step in the conductivity at the melting point, as compared with the pure material, which is consistent with the presence of a significantly greater number of mobile ionic species. The NMR diffusivities and the apparent transport numbers of the cation and the anions are also listed in Table 1. The NMR data suggest that mobile succinonitrile molecules diffusing in the matrix do so at a faster rate (1.3×10^{-6} cm^2 s^{-1}) than the cation. The calculated transport numbers further indicate that the mobilities of both I^- and I_3^- are much higher than that of the cation in the succinonitrile electrolyte system.

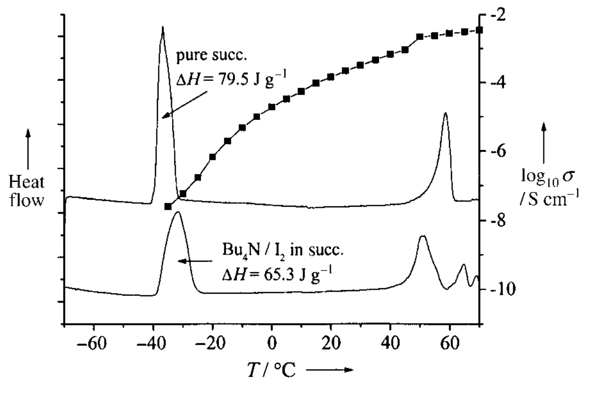

Figure 1. Conductivity (■, right axis) versus temperature for succinonitrile doped by 0.375 M Bu_4NI/0.225 M I_2 and its DSC thermogram (left axis). The thermogram of pure succinonitrile is shown for comparison.

Table 1: Diffusion properties of a molecular plastic crystal based electrolyte at 25 °C (error: ±5 %).

	D_{app} [10^{-6} cm^2 s^{-1}]		D_{PFG} [10^{-6} cm^2 s^{-1}]		Transport number[a]		
	I_3^-	I^-	succ.	Bu_4N^+	I_3^-	I^-	Bu_4N
Bu_4NI/I_2	1.6	6.5	1.3	0.53	0.23	0.64	0.13

[a] The transport number t was calculated from the formula: $t(I_3^-) = [I_3^-]\,D_{app}(I_3^-)/\{[I_3^-]\,D_{app}(I_3^-) + [I^-]\,D_{app}(I^-) + [Bu_4N]\,D_{PFG}(Bu_4N)\}$.

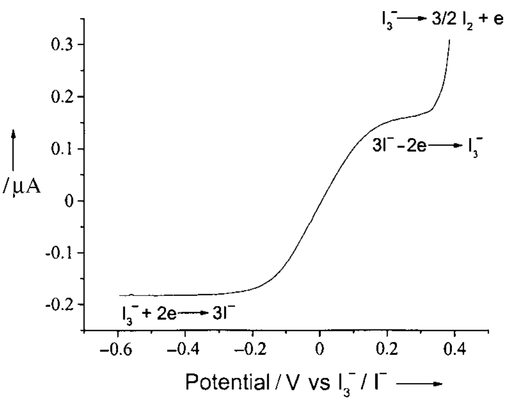

Figure 2. Linear sweep of molecular plastic crystal based electrolyte with Pt ultramicroelectrode at 25 °C. Scan rate: 50 mV s^{-1}.

Figure 2 shows the linear sweep of the molecular plastic crystal based electrolyte. The apparent diffusion coefficients D_{app} of iodide and triiodide (Table 1) were calculated from the anodic and cathodic limiting current I_{lim} by using Equation (1)[24] where n is the number of electrons per molecule, F

$$I_{lim} = 4\,n\,F\,D\,C\,r \qquad (1)$$

the Faraday constant, C the concentration, and r the radius of the electrode. Comparable data for a commonly used liquid solvent (acetonitrile) were reported by Matsumoto et al.[25] and recently for a gelled ionic liquid by Wang et al.[10] The results indicate that the diffusivity of I_3^- in the plastic solid is higher than in the gelled ionic liquid. Diffusivities that are higher in the solid state than in the corresponding liquid state have been observed previously[26] and are related to defect motion in the ordered crystalline lattice. Moreover, $D_{app}(I^-)$ in the plastic crystal based electrolyte is 4.7 times larger than in the gel electrolytes.[9,10] The high diffusivity of the iodide ion may reflect the formation of polyiodide species, so that iodide transport is facilitated in a Grotthus-type mechanism. A spectroscopic investigation of these species is underway.

Figure 3 presents short-circuit current densities J_{sc} as a function of light intensity for the plastic crystal electrolyte. For comparison, J_{sc} of the conventional organic liquid electrolyte system under 1 Sun illumination is also shown.

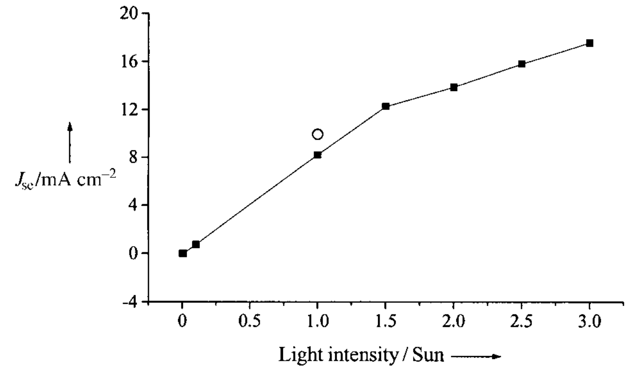

Figure 3. Short-circuit current J_{sc} as a function of light intensity for plastic crystal (■) and organic liquid (○) electrolytes. Photoelectrode size: 5×5 mm.

As described in the Experimental Section, these cells did not contain optimized photoanodes, and the standard thin electrolyte layer (25-μm thick Surlyn) was unavailable; therefore, J_{sc} for the conventional organic liquid electrolyte system is not as high as some published data at 1 Sun illumination. Nevertheless, the data in the figure also show that the electrolyte is capable of carrying currents as high as 18 mA cm^{-2} in the solid state, which corresponds to some of the highest published 1 Sun currents. Furthermore, under 1 Sun conditions, J_{sc} of the plastic crystal electrolyte system reachs 82.8 % of that of the conventional liquid electrolyte system. All these values are of sufficient magnitude to be of interest for photoelectrochemical cells. Further increases in short-circuit current for both electrolyte systems are possible by optimizing the electrolyte systems, the TiO_2 working electrode, and the thickness of the electrolyte layer.

This is the first example of a DSSC based on a plastic crystalline electrolyte with high current-carrying capacity. Although the melting point of about 45 °C of the succinonitrile electrolyte system is somewhat low for practical devices for outdoor applications, it is high enough for devices for indoor application. More important, the new concept established here will be very helpful in developing other types of plastic crystal systems with rapid I^-/I_3^- mobility and higher melting points for potential application in photoelectrochemical cells. Further work to optimize the electrolyte composition and cell construction, to characterize the device performance of the succinonitrile electrolyte in photoelectrochemical cells, and to explore better plastic crystal electrolyte systems for application in photoelectrochemical devices are underway.

Experimental Section

Analytical grades of succinonitrile, tetrabutylammonium iodide, and iodine were used. Tetrabutylammonium iodide was recrystallized and iodine was sublimed prior to use. The sample was prepared in an N_2-filled glove box and dried under vacuum at 65 °C for at least 48 h before the measurements. The thermal properties were measured on a Perkin Elmer DSC7 at a scanning rate of 20 °C min^{-1}. Solid–solid phase transition temperatures T_{s-s} and melting/liquid points T_m were determined as a function of composition. Conductivity measurements were carried out in a locally designed conductance cell. During the measurements, the temperature was raised at a steady rate of 0.3 °C min^{-1}. An electrochemical cell equipped with a Pt ultramicroelectrode of 6.4 μm radius as the working electrode, a Pt wire as the counterelectrode, and a Pt wire pseudoreference electrode were used to study mass transport in the electrolyte at 25 °C. ^{1}H NMR pulsed field gradient (PFG) diffusion experiments were used to determine the diffusion coefficients of the doped species in the sample on a Bruker Advance 300 spectrometer at 25 °C.

DSSCs were constructed from TiO_2-coated transparent conducting oxide (TCO) plates (purchased from STA Ltd, Australia), $[Ru(dcbpy)_2(SCN)_2]$ (dcbpy = 2,2′-bipyridyl-4,4′-dicarboxylate), and a Pt-catalyzed TCO counterelectrode. Prior to dye adsorption, electrodes were heated at 450 °C for 15 min to remove any adsorbed water. The electrodes underwent chemical adsorption in the dye solution at 80 °C for 12 h. A 200-μm thick Surlyn gasket was then cut to fit around the TiO_2 film on the electrodes and seal the cells during heating. The plastic electrolyte was sandwiched between the electrodes by filling the cell with the molten electrolyte under vacuum. For comparison, the conventional volatile electrolyte (0.5 M LiI and 0.04 M I_2 in acetonitrile) was then administered by capillary force into the open sandwich cell. The TiO_2 electrodes were soaked in a solution of 0.1 M 4-*tert*-butylpyridine (Aldrich) in acetonitrile (BDH) just before constructing the cells. The current–voltage curves were determined under illumination with an 80-W halogen lamp (Phillips). Labview 6.1 (National Instruments) drove a Keithley 2400 source meter to record the current across a linear voltage sweep from −0.2 to 0.8 V. Light intensity corresponding to 1 Sun was determined by a luxmeter (RS Components, 180–7133). The cells were tested by using an externally calibrated photodiode. Cells were mounted on a heat sink and measurements were limited to less than 1 min to minimize temperature rises.

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