High-performance dye-sensitized solar cells based on solvent-free electrolytes produced from eutectic melts

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Low-cost excitonic solar cells based on organic optoelectronic materials are receiving an ever-increasing amount of attention as potential alternatives to traditional inorganic photovoltaic devices. In this rapidly developing field, the dye-sensitized solar cell¹ (DSC) has achieved so far the highest validated efficiency of 11.1% (ref. 2) and remarkable stability³. However, the cells with the best performance use volatile solvents in their electrolytes, which may be prohibitive for outdoor solar panels in view of the need for robust encapsulation. Solvent-free roomtemperature ionic liquids⁴⁻¹¹ have been pursued as an attractive solution to this dilemma, and device efficiencies of over 7% were achieved by using some low-viscosity formulations containing 1-ethyl-3-methylimidazolium thiocyanate⁸, selenocyanate⁹, tricyanomethide¹⁰ or tetracyanoborate¹¹. Unfortunately, apart from tetracyanoborate, all of these low-viscosity melts proved to be unstable under prolonged thermal stress and light soaking. Here, we introduce the concept of using eutectic melts to produce solvent-free liquid redox electrolytes. Using a ternary melt in conjunction with a nanocrystalline titania film and the amphiphilic heteroleptic ruthenium complex Z907Na (ref. 10) as a sensitizer, we reach excellent stability and an unprecedented efficiency of 8.2% under air-mass 1.5 global illumination. Our results are of importance to realize large-scale outdoor applications of mesoscopic DSCs.

The ionic liquid formulations used in the dye-sensitized solar cell (DSC) as solvent-free electrolytes use iodide melts as their major component, because high concentrations of iodide are required to intercept quantitatively the geminate recombination between the electrons injected by the photo-excited sensitizer in the nanocrystalline titania film and its oxidized form¹⁰. The viscosity of the iodide melts should be as low as possible to avoid mass transport limitation of the photocurrent and loss of fill factor under cell operation in full sunlight. Amongst the iodide salts that form room-temperature ionic liquids, 1-propyl-3-methylimidazolium iodide (PMII) has the lowest viscosity. PMII has therefore also been the candidate of choice for binary ionic liquids that have so far achieved the highest efficiency in solar electricity generation by solvent-free DSCs¹⁰.

Figure 1 shows plots of the specific conductivity versus temperature for several imidazolium salts and their mixtures. The conductivity of pure iodide melts increases in the order 1-hexyl-3methylimidazolium iodide < 1-butyl-3-methylimidazolium iodide < PMII, mirroring the behaviour of their fluidity, which follows the same trend. The viscous behaviour of ionic liquids is dictated by the interplay of coulombic and van der Waals interactions as well as hydrogen bond formation¹². Increasing the alkyl chain length decreases the electrostatic attraction between cations and iodide but the van der Waals interaction between the imidazolium cations increases. 1-ethyl-3-methylimidazolium iodide (EMII) and 1,3-dimethylimidazolium iodide (DMII) are solids at ambient temperature on probable account of their high lattice Gibbs energies due to the conformational rigidity of small and symmetric cations. Importantly, Fig. 1 shows that above their melting temperatures, both salts are more conductive than PMII. This surprising observation encouraged us to mix EMII and DMII at a molar ratio of 1:1, resulting in a highly conductive, low-melting binary salt with a eutectic temperature of 47.5 °C (see Fig. 1 and Supplementary Information, Fig. S1). The decrease of melting temperature is due to the increase in entropy¹³ of the components in the eutectic mixture.

We further observed that 1-allyl-3-methylimidazolium iodide (AMII), which has a melting point of 60 °C, also shows a higher conductivity than PMII in the liquid state. We therefore reasoned that a mixture formed from the three solids EMII, DMII and AMII could provide a room-temperature ionic liquid with superior fluidity and ionic conductivity compared with the binary melt. This expectation is borne out by curve h in Fig. 1 referring to the mixture of AMII, DMII and EMII at a molar ratio of 1:1:1. The resulting ternary melt has a melting point below 0 °C and a strikingly high room-temperature conductivity of 1.68 mS cm⁻¹, exceeding that of PMII (0.58 mS cm⁻¹) by almost a factor of three. We attribute this remarkable increase in the conductivity over the pure PMII melt to enhanced fluidity along with higher ion concentrations and the smaller size of the cations in the melt.

In light of this result, we prepared four melts to assess the potential advantages of eutectic-based melts relative



Figure 1 Plots of specific conductivity (σ) of imidazolium melts versus temperature (T). (a) 1-hexyl-3-methylimidazolium iodide. (b) < 1-butyl-3-methylimidazolium iodide. (c) PMII. (d) EMII. (e) DMII. (f) DMII/EMII (1:/1). (g) AMII. (h) DMII/EMII/AMII (1:1:1). (i) EMITCB. Before measurements in a sealed tube, all of the samples were dried at 80 °C under a vacuum of \sim 3 torr for 8 h.

to state-of-the-art systems^{6,11} used in DSCs. The following compositions were tested for comparison (the molar ratio of the components in the melt is given in parenthesis): (24:1); melt II, DMII/EMII/AMII/I₂ melt I, $PMII/I_2$ PMII/1-ethyl-3-methylimidazolium (8:8:8:1);melt III, tetracyanoborate(EMITCB)/I₂ (24:16:1.67);melt IV, DMII/EMII/EMITCB/I₂ (12:12:16:1.67). We measured the effect of temperature (T) on the density (d), viscosity (η) , specific conductivity (σ), molar conductivity (Λ) and apparent triiodide diffusion coefficient (D) of melts I-IV after drying them at 80°C under a vacuum of ~3 torr for 8 h. Even under these severe conditions, we did not detect any volatility of iodine by the simple iodine-starch colourimetric method, suggesting that the complexation of iodine by iodide to form triiodide ions prevents any significant evaporative iodine loss. This removes one major concern for long-term outdoor application of these melts, where loss of iodine would adversely affect the stability of photovoltaic operation.

Compared with the PMII-containing reference melts I and III, formulations II and IV based on the eutectic of DMII and EMII show much improved properties (see Supplementary Information, Figs S3-S6). They exhibit lower viscosities, higher conductivities and faster triiodide transport. These features are highly desirable to enhance the photovoltaic performance in solvent-free DSCs. The electrolyte viscosity can be well fitted by the Vogel-Fulcher-Tammann equation. Recent work by Angell and co-workers14 has shown that the empirical Walden's rule applies rather well to pure ionic liquids. As shown in the Supplementary Information, Fig. S7, $\log(\Lambda)$ of electrolytes I–IV increases linearly with $\log(\eta^{-1})$. The relationship can be expressed as $\Lambda \eta^{\alpha} = \text{constant}$, with α being the slope of the line in the Walden plot and reflecting the degree of ion dissociation. The slopes of the fitted lines corresponding to our four melts and pure EMITCB are all slightly less than unity predicted by the 'ideal' Walden rule, indicating progressive augmentation in the population of less conductive ion-pairs with increasing temperature. However, melts I-IV exhibit anomalous high molar conductivities in view of their high viscosities. This will be further elaborated below



Figure 2 Stokes–Einstein plots of diffusion coefficient (*D***) versus fluidity (** η^{-1} **).** (a)–(e), Melts $\vdash V$. The dashed line is calculated from the Stokes–Einstein relation using a hydrodynamic radius of 2.1 Å for triiodide.

by analysing the triiodide diffusion coefficients measured with ultramicroelectrode voltammetry.

In Fig. 2, the temperature-dependent apparent triiodide diffusion coefficients (*D*) are plotted versus fluidity (η^{-1}) in the Stokes–Einstein coordinate. Whereas $\log(D/T)$ increases linearly with $\log(\eta^{-1})$ for melts I–IV, the fitted slopes (0.74, 0.71, 0.71, and 0.73) are less than unity, departing considerably from the description of the Stokes–Einstein relation, equation (1)

$$\log(D/T) = \log(k_{\rm B}/6\pi r_{\rm H}) + \log(1/\eta).$$
(1)

Moreover, the effective hydrodynamic radii ($r_{\rm H}$) of triiodide derived from the fitted intercepts are unrealistically small, being only several tenths of an ångström as compared with the expected value of 2.1 Å (ref. 15). Previously^{4,6,10,16}, this anomalous transport behaviour has been qualitatively explained by the Grotthus-like exchange mechanism and rationalized by the Dahms–Ruff equation ($D = D_{\rm phys} + D_{\rm ex} = D_{\rm phys} + k_{\rm ex}\delta^2 c/6$, where $D_{\rm phys}$ and $D_{\rm ex}$ are the physical and exchange diffusion coefficients, respectively, $k_{\rm ex}$ is the rate constant of the iodide–triiodide bond exchange, and c and δ are the iodide concentration and average centre-to-centre distances between iodide and triiodide in the encounter complex).

Similar to proton transfer in water, the transport of triiodide by the Grotthus mechanism occurs by bond exchange. The triiodide approaches iodide from one end forming an encounter complex, from which triiodide is released at the other end. In this fashion, the triiodide is displaced by the length of one I–I bond, ~ 2.9 Å (ref. 17), without having to cross that distance. The bond exchange occurs immediately on formation of the encounter complex, rendering the process diffusion-controlled. Thus, the viscosity-dependent transport of triiodide in ionic liquid electrolytes with high iodide concentration can be described by physical diffusion coupled to the Grotthus bond exchange, which augments the diffusional displacement by ~2.9 Å for each diffusional encounter with iodide. This manifests itself by an apparent acceleration of the triiodide diffusion, which however can only be felt at high iodide concentration where the average distance between two adjacent iodide ions is small.

Melt V containing 1-ethyl-3-methylimidazolium bis(trifluoromethanesulphonyl)imide as an inert salt has a low iodide concentration, DMII/EMII/1-ethyl-3-methylimidazolium



Figure 3 Photocurrent density–voltage (J– V) characteristics of devices A and B under AM 1.5G illumination (100 mW cm⁻²). The inset shows the IPCE of device B. Cells were tested using a metal mask with an aperture area of 0.158 cm².

bis(trifluoromethanesulphonyl)imide/I₂ (6:6:800:0.83). Hence, it serves as a reference where the Grotthus contribution to the triiodide transport is negligible. The enhancement of the diffusion coefficient due to the Grotthus contribution can be derived from the ratio of the D/T values for melts I–IV to that for melt V. For example, at a log(η^{-1}) of 1.5, owing to the Grotthus contribution the D/T value for the ternary melt II is about five times larger than that for melt V. The fact that the straight lines for the five melts in Fig. 2 are parallel to each other indicates that the enhancement of the diffusion coefficient due to the Grotthus bond exchange mechanism is similar over the whole investigated viscosity range. Closer inspection of Fig. 2 also shows that the acceleration of the triiodide transport due to the Grotthus mechanism increases with the iodide packing densities in the melts. Melt II has the highest iodide concentration and shows the largest Grotthus effect. As expected, the Grotthus acceleration is significantly smaller in melts III and IV, which both have lower iodide packing densities than melts I and II.

Taking advantage of the properties of eutectic-based melts, we used the routine additives guanidinium thiocyanate (GNCS) and N-butylbenzoimidazole (NBB) to formulate two practical electrolytes for photovoltaic device evaluation. The compositions tested were as follows. Electrolyte A in device A: DMII/EMII/AMII/I₂/NBB/GNCS (8:8:8:1:2:0.4); electrolyte B in device B: DMII/EMII/EMITCB/I2/NBB/GNCS (12:12:16:1.67:3.33:0.67). Detailed fabrication procedures for the mesoporous TiO₂ electrode and sealed cell have been described elsewhere¹⁸. A 7-µm-thick film of 20-nm-sized TiO₂ particles was first printed on the fluorine-doped SnO₂ conducting glass electrode and further coated by a 5-µm-thick second layer of 400-nm-sized light-scattering anatase particles. The sintered TiO2 electrodes were immersed at room temperature for 12h into a solution containing 300 µM Z907Na dye and 300 µM 3-phenylpropionic acid in acetonitrile and *t*-butyl alcohol (1:1, v/v).

Figure 3 shows the photocurrent density–voltage (J-V) characteristics of devices A and B using the above-mentioned molten salts measured under air-mass 1.5 global (AM 1.5G) sunlight. The short-circuit photocurrent density (I_{sc}) , open-circuit voltage (V_{oc}) and fill factor (FF) of device A with the ternary iodides are 12.82 mA cm⁻², 721 mV and 0.768, respectively,



Figure 4 Detailed photovoltaic parameters of a cell measured under the irradiance of AM 1.5G sunlight during successive full-sun visible-light soaking at 60 °C. J_{sc} : short-circuit photocurrent density; V_{sc} : open-circuit voltage; *FF*: fill factor; η : power conversion efficiency.

yielding an overall power conversion efficiency (η) of 7.1%, which is much higher than that of 6.0% previously reported⁶ for the corresponding device with a solvent-free, PMII-based ionic liquid electrolyte. Note that this ternary electrolyte composed of simple imidazolium iodides has shown a comparable efficiency to previously reported solvent-free electrolytes⁸⁻¹¹ containing relatively precious ionic liquids. The photovoltaic parameters $(J_{sc},$ $V_{\rm oc}$, FF and η) of device B with mixed imidazolium iodides and tetracyanoborate are 14.26 mA cm⁻², 741 mV, 0.774 and 8.2%, respectively. For the first time, such a high efficiency under AM 1.5G sunlight is obtained for DSCs with solvent-free electrolytes. It is worth noting that simply replacing the PMII used in our previous work¹¹ by the eutectic melt of DMII and EMII without changing the sensitizer or titania film has resulted in a remarkable 17% photovoltaic performance enhancement. The photocurrent action spectrum of device B is shown in the inset of Fig. 3. The incident photon-to-current conversion efficiencies (IPCEs) exceed 60% in a broad spectral range from 460 to 650 nm, reaching its maximum of about 81% at 540 nm. From the overlap integral of this curve with the standard global AM 1.5 solar emission spectrum, a short-circuit photocurrent density (J_{sc}) of 14.30 mA cm⁻² is calculated, which is in excellent agreement with the measured photocurrent. This confirms that there is no mismatch between the simulator used and AM 1.5 solar emission, showing that the conversion efficiency value of 8.2% truly refers to the standard reporting condition. To test the stability of the eutectic-based electrolyte B for DSCs, photovoltaic cells without 3-phenylpropionic acid as a coadsorbent were subjected for 1,000 h to light soaking with full solar intensity (1,000 W m⁻²) at 60 °C under a Suntest lamp (Hanau corporation). As shown in Fig. 4, the cell retained over 93% of its initial conversion efficiency over this period, confirming the very high stability of the device. With respect to a reference cell using the best previously reported ionic liquid, a DSC based on this new electrolyte B shows a remarkable enhancement in device



Figure 5 Plots of effective electron diffusion coefficient (D_n), lifetime (τ_n) and normalized diffusion length (L_n/d) versus dark current density (J_{dark}).

efficiency while maintaining a similar stability (see Supplementary Information, Fig. S8).

The higher V_{oc} of device B compared with A can be explained by the more positive Nernst potential of its electrolyte due to a lower iodide concentration. In addition, the higher J_{sc} of device B produces an increase in V_{oc} . Photovoltage decay^{19–21} and electrochemical impedance²² measurements were carried out to determine the origin of the difference in the photocurrent. As shown in Supplementary Information, Fig. S9, under the same extracted charge densities, device B always has slower rates of charge recombination than A due to a lower triiodide concentration in the electrolyte. This has been further confirmed by electrochemical impedance measurements of the electron lifetime (τ_n) shown in Fig. 5. Note also that the less viscous electrolyte for device B gives larger effective electron diffusion coefficients (D_n) than A at the same dark current densities. This is in keeping with the notion²³ that the diffusion coefficient is in fact ambipolar, reflecting apart from the electron motion also the mobility of cations that screen the photoinjected electrons in the mesoporous titania film²⁴. The normalized electron diffusion length $(L_n/d,$ where d is the titania film thickness) is significantly larger for device B than for A, indicating that the increase in J_{sc} is caused by a higher charge collection yield. As shown in the Supplementary Information, Fig. S10, the enhanced photovoltaic performance of electrolyte B compared with the previously reported ionic liquid¹¹ can also be rationalized in terms of an increased effective electron diffusion length.

In summary, using mixtures of solid salts has led to the discovery of solvent-free electrolytes for DSCs showing unprecedented efficiency and excellent stability. An efficiency of 8.2% achieved in full sunlight sets a benchmark for solvent-free DSCs. Importantly, their performance now matches that of a low-volatility, 3-methoxypropionitrile-based electrolyte²¹, rendering the use of such solvents obsolete. This is expected to have important practical consequences as the need for using organic-solvent-based electrolytes to achieve high conversion efficiencies has impaired large-scale production and outdoor application of the DSC. Organic solvents not only present challenges for sealing but also permeate across plastics, excluding their use in flexible cells. In contrast, the vapour pressure of molten salts and their permeation rate across plastics are negligible at the typical operating temperature of photovoltaic converters. We believe that our findings on eutectic-based melts will provide useful clues for further improvement of solvent-free electrolytes on the basis of rational design of their constituents, greatly facilitating the large-scale practical application of light-weight, flexible dye-sensitized thin-film cells.

METHODS

The viscosity measurements were carried out using a Brookfield DV-II+Pro viscometer. Densities were determined with an Anton Paar DMA 35N density meter. A Radiometer CDM210 conductivity meter was used to measure conductivities. The Radiometer CDC749 conductivity cell with a nominal cell constant of 1.70 cm⁻¹ was calibrated with 0.1 M KCl aqueous solution before the experiments. A two-electrode electrochemical cell, consisting of a 5.0-µm-radius Pt ultramicroelectrode as the working electrode and a Pt foil as the counter electrode, was used for the measurements of triiodide diffusion coefficients in combination with a CHI 660C electrochemical workstation. A heating-cooling cycle pump was used to control the sample temperatures. I-V and IPCE measurements were carried out as reported previously³. A white-light-emitting diode array powered by varied driving voltages was used to supply different steady-state light intensities in the transient photoelectrical experiments. A red-light-emitting diode array controlled with a fast solid-state switch was used to generate a perturbation pulse with a width of 200 ms. Electrical impedance experiments were carried out with an Echo Chemie Autolab electrochemical workstation, with a frequency range of 0.01-106 Hz and a potential modulation of 5 mV. The obtained impedance spectra were fitted with the Z-view software (v2.8b, Scribner Associates) in terms of appropriate equivalent circuits²².

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