Room-temperature molten salt system based on 1-methyl-3-propylimidazolium iodide (MPII) has been used to investigate the performance characteristics of dye-sensitized solar cells. The ionic liquids attract a great deal of attention as possible replacement for conventional organic solvents. They showed good photo energy conversion efficiencies even at high illumination intensity up to full AM 1.5 sunlight. The efficiency of solar cell was found to depend strongly on the thickness and nature of the TiO₂ film. Applying a scattering layer over the transparent anatase film improved the red response of the photocurrent. Using a 1-methyl-3-propylimidazolium iodide based ionic liquid a conversion efficiency of 5.4% was obtained at 1 sun with a double layer structured film. The self-diffusion of tri-iodide species in the molten salt electrolyte was determined. An investigation was carried out on the physical-electrochemical properties of MPII and its mixtures with water and the lower viscosity molten salt, 1-methyl-3-propylimidazolium nitrate (MPINO₃). The advantage of using molten salt electrolyte is to use them in flexible solar cells in the near future as solvent free electrolytes.

INTRODUCTION

The continuous search for renewable, cheap, efficient and long-term energy sources has increased and new demands were added for the fabrication of photovoltaic devices. In recent years, dye sensitized solar cells based on nanocrystalline TiO₂ films (1) have received significant attention because of their high efficiency and low cost compared to those of silicon solar cells. An added advantage of the dye-sensitized solar cell with respect to competing technologies is that its performance is remarkably insensitive to temperature change. The characteristic of this type of cells is the utilization of nanostructured TiO₂ electrodes coated with dye to absorb the light energy, which greatly enhance the light harvesting and thus the energy conversion efficiency of the cell. The dye-coated electrode is sandwiched with another conducting glass electrode that is
coated with a small amount of Pt and works as a counter electrode. The intervening space is filled with an organic electrolyte containing a redox couple (I\textsubscript{3}^-/I\textsubscript{3}^-). The presence of organic solvent in the electrolyte is one of the concerns for the long-term stability of solar cells. Many groups have been focusing their attention on fundamental aspects of dye-sensitized solar cell components (2). Several attempts were made to replace the organic liquid electrolyte with inorganic p-type semiconductors (3), ionic conducting polymers (4), and organic hole conducting materials (5). Very recent efforts have focused on the application of molten salts with gelators in photovoltaic applications (6). Polymerization of molten salts has also been tried in order to prepare solid polymer electrolytes (7). But the polymerization of charged monomers induces a considerable decrease in the ionic conductivity.

In our search for highly stable solvents for the dye-sensitized nanocrystalline solar cell developed in our group we screened a series of molten salts for use as electrolytes because they are benign alternatives to conventional organic solvents (8). Since the first molten salt composed of N-ethylpyridinium bromide-aluminum chloride was reported in 1951 (9), various molten salts have been investigated. Considerable attention has been paid to non-chloroaluminiate room-temperature molten salts containing 1,3-dialkylimidazolium cations (8). Room-temperature ionic liquids have attractive features like low vapor pressure, good thermal stability (10), high ionic conductivity (11), large electrochemical window (12) and miscibility with other solvents or salts. Molten salts have a wider spectrum of physical and chemical properties than that of organic solvents. They are attracting attention as novel solvent systems for chemical reactions and separations (13). The main advantage of these solvents is the possibility to tune their physical and chemical properties by varying the nature of cations and anions. Because of these characteristics, the neat 1,3-dialkylimidazolium iodides are promising candidates as an electrolyte for dye sensitized solar cells. Earlier we demonstrated the use of the molten salt, 1-methyl-3-hexylimidazolium iodide (MHII), as an electrolyte for low power applications (14). The lowest viscosity for imidazolium based ionic liquids reported to date is of 4.9 cP for EMIF.2.3HF (15).

We present here the applicability and enhanced performance of the ionic liquid, 1-methyl-3-propyl-imidazolium iodide (MPII), as an efficient and stable electrolyte for the dye-sensitized solar cell by utilizing the iodide/tri-iodide couple as redox mediator. In the family of 1,3-dialkylimidazolium iodide molten salts MPII has the smallest cation and lowest viscosity. As dialkyl imidazolium iodides are hygroscopic in nature it was considered important to investigate the influence of water on the viscosity and diffusion coefficient. We also studied the effect of the nitrate based co-solvent MPINO\textsubscript{3}, which has a lower viscosity than the corresponding iodide salt.

During the final stage of our work a paper by Kubo et al. appeared (6) reporting different 1-methyl-3-alkyl imidazolium iodides as electrolytes for use in dye-sensitized solar cells. They observed that the solar cell efficiency increased from 2.11 to 3.26 by increasing the chain length from propyl to hexyl group. The cell efficiency improved to 5.0% by increasing the concentration of I\textsubscript{3}^- in the MHII. We report here 5.4 % light-to-electricity power conversion efficiency under AM 1.5 irradiation by using MPII based electrolyte in conjunction with a double layer structured film.

Electrochemical Society Proceedings Volume 2002-19
EXPERIMENTAL

The most widely used methodology in the synthesis of 1,3-dialkylimidazolium iodides is a straightforward reaction between the 1-alkyl-imidazole and alkyl iodides. By using a similar procedure (8), 1-methyl-3-propyl-imidazolium iodide (MPII) was prepared. 1-methyl-3-propyl-imidazolium nitrate (MPI(NO3)) was obtained by mixing two aqueous solutions of equal concentrations of AgNO3 and MPII. The resulted AgI precipitate filtered and the filtrate solvent evaporated under vacuum to get the MPI (NO3) molten salt. These molten salts were dried under vacuum. The purity of these ionic liquids was checked with 1H NMR spectrum. The synthesis and characterization of the hydrophobic dye called as Z-907, (Ru(H2dcbpy)(dnbpy)(NCS)2) (where the ligands H2dcbpy = 4,4'-dicarboxy 2,2'-bipyridine, dnbpy= 4,4*-dinonyl 2,2' bipyridine), which is used in all these experiments, will be reported elsewhere (16). N-methylbenzimidazolone (NMBI) was purchased from Aldrich and recrystalised from diethyl ether.

Photoelectrodes used in dye-sensitized solar cells consisted of a TiO2 film of single and double-layer structure. The acidic TiO2 colloid particles prepared by using published procedure (17) were screen-printed onto a conducting glass substrate (Nippon sheet glass, F-doped SnO2 (FTO), sheet resistance of 10 Ω/sq). The conducting glass sheet had been cleaned well, treated with 50 mM TiCl4 aqueous solution at 70°C for 30 min to get a good adhesion between the TiO2 layer and the glass. The screen-printed layer was dried at 150°C and gradually heated up to 500°C under oxygen then left for 10 min for sintering. The resulting transparent layer was treated with TiCl4 and annealed again. Finally, the layer was rinsed with ethanol and dried. The layer thickness was determined by a TENCOR Instruments alpha-step 200. The particle diameter and the porosity were determined to be 18 nm and 68% respectively by a Micromeritics ASAP 2000 nitrogen adsorption-desorption apparatus. The double layer structure was made with TiO2 scattering particles specially offered by CCI, Japan. For the second layer, in the screen-printing paste 10 g of TiO2 scattering particles were mixed with 2 g of basic TiO2 fine particles (15 nm) to fabricate mechanically tough layer. In double layer fabrication the second layer was made on the first screen-printed layer that had been dried and the two were heated together for sintering.

To remove organic impurities the layer was treated with UV/O3 and heated at 450°C under oxygen and then transferred into ethanol dye solution (3 x 10^-4 M) immediately after a final annealing under argon. The electrode was left overnight for dye adsorption, rinsed, dried and then assembled with thermally platinitized conducting glass (18). The electrodes were spaced with 25 μm thick surlyn sheet and sealed up by heating. The internal space of the cell was filled with molten salt electrolyte consisting of 0.25 M I2 dissolved in MPII molten salt with 0.45 M N-methylbenzimidazolone (NMBI) and 2% water by using a vacuum pump. The electrolyte-injecting hole made by a drill on the counter glass substrate was sealed with bynel a hot melt and a glass cover shell.

Photovoltaic performance data were obtained using a 450 W xenon light source that was focused to give 1000 W/m², the equivalent of standard full airmass 1.5 sunlight at the surface of the test cell. The spectral output of the lamp was matched in the region of 350-750 nm with the aid of a Schott KG-5 sunlight filter so as to reduce the mismatch between the simulated and the true solar spectrum to less than 2%. The light intensity was...
modulated with neutral wire mesh attenuators. The applied potential and measured cell current was performed using a Keithley model 2400 digital source meter. The fully automated experiment was run using Wave metrics software (19). The spectral response of the cell was determined by measuring the incident photon-to-current conversion efficiency (IPCE). Light from a 300 W Xe lamp was focused through a high throughput monochromator onto the photovoltaic cell under test. The monochromator was incremented through the visible spectrum to generate the IPCE ($\lambda$) curve as defined below,

$$\text{IPCE} (\lambda) = 1240(I_{SC}/\lambda \phi)$$  \[1\]

Where $\lambda$ is the wavelength, $I_{SC}$ is the current at short circuit (mA/cm$^2$), and $\phi$ is the incident radiative flux (W/m$^2$). The surface of the cell was masked to have 0.152 cm$^2$ photoactive area.

The Autolab P20 potentiostat of Ecochemie was used for cyclic voltammetry. The diffusion coefficient measurements were carried out as reported earlier (14). 50µm thick Mylar (polyester) sheet from Dupont was employed as spacer between two electrodes. The measurements were done under argon or air carefully checking moisture influence. All dynamic viscosity's measurements were carried out on a Haake microviscosimeter VT 500 viscositester, thermally controlled by Haake D8 thermostat-cryostat.

**RESULTS AND DISCUSSION**

**Viscosity and Conductivity Studies.**

MPII was found to be a good liquid electrolyte for solar cell application due to the relatively low viscosity among the family of ambient temperature ionic liquid iodides. For the series of 1-methyl-3-alkyl imidazolium iodides, when alkyl is methyl or ethyl they are solids at room temperature, whereas 1-methyl-3-propylimidazolium iodide is a liquid. This decrease in the melting point is likely to cause by producing disorder and reduced coulombic interaction. Changing the alkyl chain length from propyl (MPII) to hexyl (MHI) doubles the viscosity is almost from 865 cP to 1800 cP, respectively due to increased Vander Waals interactions. It is advantageous to use a low viscosity ionic liquid as electrolyte for solar cell applications in order to avoid mass transport limitations of the current at the counter electrode.

The diffusion coefficient of tri-iodide in molten salt electrolyte was determined by measuring the limiting current in a thin layer cell. Presence of excess of iodide in the composition of electrolyte tested ensures that tri-iodide is the current limiting species. The tri iodide diffusion coefficient obtained with water free MPII is 1 X 10$^{-7}$ cm$^2$/s whereas with 1% water present it increases to 4 X 10$^{-7}$ cm$^2$/s and in acetonitrile it is 2 X 10$^{-6}$ cm$^2$/s. The temperature dependence of tri-iodide diffusion coefficient is shown in Figure 1. It deviates from the Arrhenius behaviors and obeying to the Vogel-Tammann-Fulcher (VTF) equation (equation 2) as reported for other molten salts in the literature (14, 20):

$$D = AT^{-1/2} \exp (-B/T-T_0)$$  \[2\]

Electrochemical Society Proceedings Volume 2002-19
The theoretical glass transition temperature of 220 K derived from the VTF equation agrees well with the experimental value.

Two MPII containing systems were investigated for the tri-iodide diffusion coefficient, the one diluted with water and the other by a low viscosity molten salt MPI (NO₃) as a co-solvent. The viscosity of the MPII/water mixture as a function of mole fraction of water with the empirical formulation curves (21) of mixed solvent system is calculated by the equation

\[ \eta_{\text{mix}} = \Pi_i \eta_i^x \text{ where (}\Sigma x_i = 1\) \]  

[3]

As shown in Figure 2 the accuracy of formula depends on the assumption whether the molten salts are completely ionized or stay as ion pair. The diffusion coefficient and viscosity of MPII was plotted against the mole fraction of added water in Figure 3. The diffusion coefficient increased significantly by adding water. When the water content was small, the measured values fit with the solid line that is derived from the assumption that MPII is not dissociated. On the other hand when the water content was dominant in the mixture, it came in between the solid line and the broken line that is derived from the assumption that MPII is completely dissociated into methylpropyl imidazolium cations and iodide anions. This suggests that the MPII ion pairs became partially dissociated by adding water. It seems that even 4 equimolar amounts of water (25% by weight) was not sufficient to dissociate the MPIII completely. The decrease in viscosity with the addition of water is more than the increase in tri-iodide diffusion. This means a discrepancy in the Stokes-Einstein relation, as the Walden product is not constant at constant temperature. In MPIII/water mixture the Walden product dropped 10 times.

\[ D\eta = k_BT/6\pi r_{\text{eff}} \]  

[4]

From this equation \( D\eta \) (Walden product) should be constant at same temperature for a given solute in any solvent system (22).

In Figure 4 the viscosity of the MPII/MPI (NO₃) mixture was plotted as a function of mole fraction of MPI (NO₃). It shows that by diluting with low viscosity melt has less influence when compared with water in breaking the ion pair effect of MPII. The diffusion coefficient and Walden's product of MPII with MPI (NO₃) mole fraction is presented in Figure 5. The increase in the diffusion coefficient of MPII by diluting with water is 4 times more than that of MPI (NO₃). It clearly shows that water is more efficient than MPI (NO₃) in making the charge separation of MPII, could be due to the formation of hydrogen bonding between water molecule and iodide anion. It is known that the presence of water molecule in room temperature ionic liquids lead to the charge separation by forming H-bonding depending on the strength of the anion of ionic liquid (23).

**Solar Cell Fabrication and Photovoltaic Performance.**

Photo electrodes used in dye-sensitized solar cells consisted of a double layer structure. The FTO surface was coated with 18 nm diameter TiO₂ nanoparticles.
producing a transparent film which in turn was covered by a second layer of 400 nm diameter TiO$_2$ anatase particles. The latter act as scattering centers to enhance the optical path length (24). The electrolyte used for the photovoltaic measurements consisted of MPII containing 0.25 M iodine, 0.45 M N-methylbenzimidazole (NMBI) and 2 % water by weight. Because MPII is a hygroscopic liquid; it attracts water into the electrolyte, which may lead to desorption of the sensitizers. Therefore we specially designed the hydrophobic dye Z-907 to avoid the water interference. This was employed throughout the studies. This is much less prone to desorption from the surface of the semiconductor film in the presence of water in the electrolyte than the standard N3 dye. The iodine concentration was optimized to minimize the losses through light absorption by I$_3^-$, recombination and diffusion overvoltage. The presence of NMBI in the electrolyte has a stabilizing effect on the cell performance under high temperature and UV light stress. Also, NMBI increases the V$_{oc}$ potential of the cell without effecting on the photocurrent.

Figure 6 shows the photocurrent action spectrum of such a cell containing molten salt electrolyte, where the incident photon to current conversion efficiency (IPCE) is plotted as a function of wavelength. The IPCE value in the plateau region where the absorbance of dye has a maximum is around 75%. The drop at around 400 nm is due to the absorption by tri-iodide in the electrolyte that absorbs strongly in this wavelength range. By applying the scattering layer significantly improved the efficiency in the range of 600-800 nm and enhanced the overall short circuit currents greatly. The photocurrent - voltage characteristics (Figure 7) of the cell gives a short circuit photo current density of 11.1 mA/cm$^2$, an open circuit potential of 671 mV, and a fill factor of 0.73, yielding for the overall solar to chemical conversion efficiency a value of 5.4%. The latter does not depend significantly on the light intensity. Even though MPII is a highly viscous liquid, the fill factor is excellent and indeed superior to low viscosity organic solvent based electrolytes. This striking behavior is probably due to the very effective screening of photo generated charge carriers by the ionic liquid avoiding space charge induced performance losses. Short circuit current density was plotted as a function of light intensity in Figure 8. The observed linearity suggests absence of any mass transport limitations up to full AM 1.5 sun light. It is likely that the transport of tri-iodide is assisted by a Grothus-type exchange mechanism.

From the overlap integral of the IPCE spectra with the standard AM 1.5 solar emission values of the short circuit current can be calculated;

$$J_{sc} = \int_{o}^{c} \text{IPCE}(\lambda) \ I_{sun}(\lambda) \ d\lambda \ [5]$$

The latter one compared to the experimental values in Table 1. The good agreement in measured and calculated values indicates that the simulator matched well with the solar emission with different kinds of films at full sun and 1/10 of sun, respectively.

Figure 9 compares the solar cell characteristics of a single layer transparent film with that of a double-layer film cell at AM 1.5 solar irradiance 1000 W m$^{-2}$. Increasing the thickness of the scattering layer did not affect the open-circuit voltage and fill factor but the photo current density was significantly enhanced. This is due to the increase in the average optical path optical length of light within the film. This length can be larger than the thickness of the film if light is largely scattered or if it is reflected at the back of the film.
cell. This demonstrates the importance of light harvesting ability of the photo anode with and without external reflector that is in contact with the molten salt electrolyte. UV irradiation treatment of electrode has found to enhance the photo current probably due to removal of organic impurity from the surface of anatase.

CONCLUSIONS

The ionic liquid 1-methyl-3-propylimidazolium iodide (MPII) is an attractive electrolyte for use in nanocrystalline dye-sensitized solar cells. The red region of the action spectrum improved by using a double layer structure electrode; where a light scattering layer was placed over the transparent TiO₂ film. The ionic liquid based solar cell gave an efficiency of 5.4% at full AM 1.5 solar irradiance 1000 W m⁻². Even though MPII is a viscous liquid no mass transfer limitation was detected even at under full AM 1.5 sun light. A Grotthus exchange mechanism for tri-iodide is evoked to rationalize this striking observation. Equally surprising is the that the fill factors of solar cells exceed 0.7 under full sun light underlining the effectiveness of the molten salt to reduce space charge related performance losses.

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### Table 1. Short circuit current density, J<sub>sc</sub> of dye sensitized solar cells with molten salt electrolyte.

| Film Thickness | Measured mA x cm<sup>2</sup> at AM 1.5 | Calculated<sup>a</sup> mA x cm<sup>2</sup> at 0.1 of AM 1.5 | Measured μA x cm<sup>2</sup> at 0.1 of AM 1.5 | Calculated<sup>a</sup> μA x cm<sup>2</sup> at 0.1 of AM 1.5 |
|----------------|----------------------------------------|----------------------------------------------------------|------------------------------------------|----------------------------------------------------------|
| 5.3            | 7.67                                   | 8.9                                                      | 794                                      | 890                                                      |
| 6.1            | 8.92                                   | 10.1                                                     | 920                                      | 1010                                                     |
| 7.2            | 9.07                                   | 10.4                                                     | 952                                      | 1040                                                     |
| 6.1+1.3        | 10.98                                  | 11.3                                                     | 1120                                     | 1130                                                     |

<sup>a</sup> Calculated from overlap of IPCE spectra and the Solar AM 1.5 standard emission.
Figure 1. (A) Plot of tri-iodide diffusion coefficient of the molten salt electrolyte used in solar cells as a function of temperature (°C). The electrolyte contains MPII, 0.25 M of iodine, 0.45 M of NMBI with 2% of water by weight. (B) The Arrhenius plot of (A). (C) VTF plot of (A) fitted with Least square line.
Figure 2. Variation of MPII viscosity with mole fraction content of co-solvent water.

Figure 3. Plot of tri-iodide diffusion coefficient, electrolyte dynamic viscosity and Walden product as a function of MPII mole fraction in its mixture with H$_2$O.
Figure 4. Variation of MPII viscosity with mole fraction content of co-solvent MPI(NO₃) ionic liquid.

Figure 5. Plot of tri-iodide diffusion coefficient, electrolyte dynamic viscosity and Walden product as a function of MPII mole fraction in its mixture with MPI (NO₃).

Electrochemical Society Proceedings Volume 2002-19
Figure 6. Photocurrent action spectrum of the cell obtained with hydrophobic dye and molten salt electrolyte A) without external Al diffuse reflector B) with external Al diffuse reflector. The incident photon to current conversion efficiency is plotted as a function of the wavelength of the exciting light.
Figure 7. Photocurrent - voltage characteristics of a nanocrystalline photoelectrochemical cell by using molten salt electrolyte. The electrolyte contains MPII, 0.25 M of iodine, 0.45 M of NMBI with 2% of water by weight. Electrode projection active surface area is 0.152 cm$^2$.

Figure 8. Comparison of the short-circuit photocurrent $J_{sc}$ of cells with different films as a function of light intensity. Cube = 5.3 μm; diamond = 6.2μm; circle = 7.2μm; triangle = 6.1μm + 1.3μm double layer.
Figure 9. Comparison of photovoltaic characteristics of solar cells made with different films, with and without Al reflector. 5.3, 6.1, and 7.2 represents a cell with 5.3, 6.1 and 7.2 μm single transparent layers respectively. 6.1 + 1.3 represents a cell with double layer structure that has 1.3μm light scattering layer on top of 6.1μm transparent layer. 6.1 + 1.3 + UV represents the double layered structured film treated with 3 hours UV illumination.