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A Solid State, Dye Sensitized Photoelectrochemical Cell

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A quasi-solid-state photoelectrochemical cell employing a dye-sensitized, nanocrystalline TiO_2 electrode and a polymer gel electrolyte has been fabricated. The cells show open-circuit voltages close to 0.6 V and short-circuit currents larger than 3 mA cm^{-2} under 30 mW cm^{-2} white light illumination. Fill factors and open circuit voltages of the cell are comparable to those of similar cells with liquid electrolytes. Overall energy conversion efficiencies of 3–5% have been achieved. Photocurrent transients have relatively long rise time constants, indicating that electron transport in the TiO_2 electrodes is controlled by a trapping process. At high light intensity the photocurrent rise is followed by a decay process due to the limitation of ion transport in the electrolyte.

Introduction

Recent studies on porous nanocrystalline semiconductor electrodes have revealed a wide range of novel electrical and photoelectrochemical properties.[1] Grätzel and co-workers first reported remarkably high photon-to-current conversion efficiencies from dye-sensitized porous nanocrystalline TiO_2 electrodes.[2] A characteristic feature of the porous TiO_2 electrodes used in these systems is the high surface area that allows a long optical path length for the dye molecules attached to the film while maintaining contact with the electrolyte. The electrolyte used in these cells is usually a redox couple such as I^-/I_2 in an organic solvent such as propylene carbonate. To take advantage of the high surface area of these films, the electrolyte must fully penetrate the porous structure. The presence of a liquid electrolyte in a practical device, however, can result in stability and performance limitations not present in solid state cells. Although solid polymer electrolyte films have been used in the fabrication of solid state silicon photoelectrochemical cells,[3] electrolyte membranes cannot be used with porous photoelectrodes due to the small contact area. An alternative strategy for high surface area electrodes is to use a polymer gel electrolyte that can be solution cast into the porous structure. In this letter, we report on the fabrication and performance of a quasi-solid-state solar cell using dye-sensitized porous TiO_2 films with a polymer gel electrolyte.

Experimental Section

The TiO_2 films were fabricated as follows. A colloidal solution was prepared by adding TiO_2 powder (Degussa P-25) to a small amount of water and surfactant (Triton X-100). The colloidal solution was then applied to a conducting indium–tin–oxide (ITO) glass substrate (Libby Owens Ford, 8 $\Omega/\square$), and the film was sintered for about 30 min at 450 °C after air-drying.

The dye 4,4′-(dcb)$_2$Ru(SCN)$_2$ was attached to the TiO_2 electrodes by immersion for 24 h or more in an ethanoic solution with a dye concentration of about 0.1 mM.[4] The polymer electrolyte was prepared by refluxing a mixture of polyacrylonitrile, ethylene carbonate, propylene carbonate, acetonitrile, and a desired concentration of NaI at about 90 °C under N_2 atmosphere for a few hours. All the components were distilled
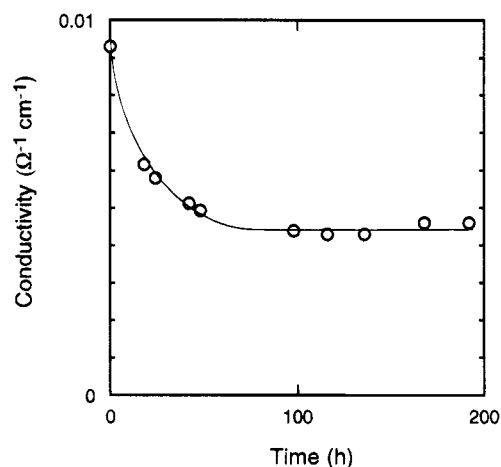
Figure 1. Conductivity of the polymer gel electrolyte versus gelation time.

and dried prior to electrolyte preparation. Due to its high vapor pressure, the iodine was added to the solution in the final stage of the refluxing process. A typical example of an electrolyte composition was 1.4 g of polyacrylonitrile, 10 g of ethylene carbonate, 5 mL of propylene carbonate, 5 mL of acetonitrile, 1.5 g of NaI, and 0.1 g of I_2. The electrolyte was solution cast onto the dye-coated TiO_2 film and pressed together with a platinum-coated ITO counter electrode under N_2 atmosphere in a glovebox. After 3 days of gelation, the edges of the device were sealed with epoxy to avoid intrusion of moisture.

Photocurrent–voltage curves were recorded using a 150 W quartz-halogen white-light source (Cole-Parmer). Transient measurements were performed using the 524 nm line of an argon ion laser (Spectra Physics 164-5); the light intensity was varied by using neutral density filters. In all experiments, the sample was illuminated through the conducting glass substrate and no corrections were made for the 30% reflection and transmission losses in the ITO glass.[5]

Results and Discussions

Figure 1 shows the conductivity of the electrolyte as a function of gelation time measured by casting the electrolyte between two titanium foil electrodes separated by a 0.4 mm thick spacer. The conductivity decreases and reaches a stable value of 4.5 × 10^{-3} Ω^{-1} cm^{-1} after about 3 days of gelation. In comparison, the conductivity of a propylene carbonate

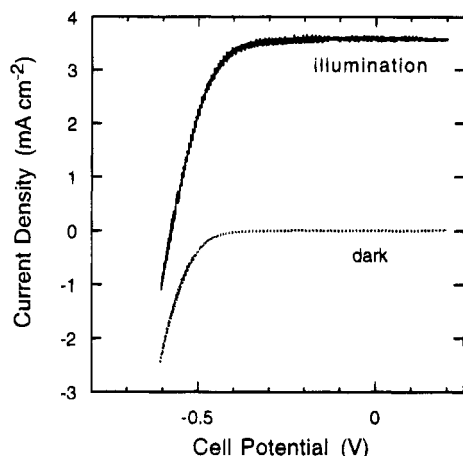**17072** *J. Phys. Chem., Vol. 99, No. 47, 1995*

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Figure 2. Current—voltage curves for a polymer gel electrolyte cell in the dark and under 30 mW cm^{-2} white-light illumination. The curves were obtained in a two electrode arrangement at a scan rate of 5 mV s^{-1}.
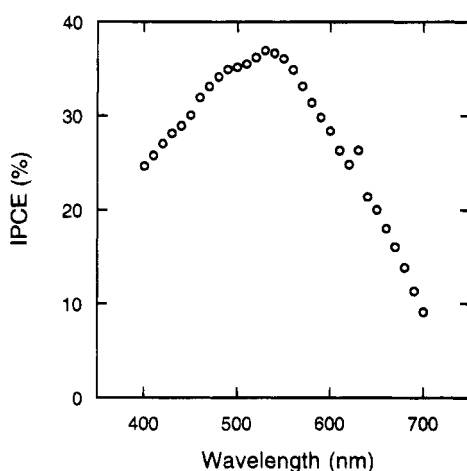

Figure 3. Incident photon-to-current conversion Efficiency (IPCE) of a polymer gel electrolyte cell versus wavelength.

solution with 0.5 M NaI and 0.1 M I$_2$ was 6.7 × 10^{-3} Ω^{-1} cm^{-1}. The relatively high conductivity of the polymer gel electrolyte indicates that it will not substantially increase the internal resistance of the cell. The gel electrolyte is flexible, retains its shape, and does not exhibit any significant loss in conductivity after extended exposure to air.

Figure 2 shows current—voltage curves for a cell with the polymer gel electrolyte in the dark and under white light illumination at an intensity of 30 mW cm^{-2}. The current—voltage curves were obtained at a scan rate of 5 mV s^{-1} in a two-electrode arrangement. The short circuit current for the cell, shown in Figure 2, is 3.4 mA cm^{-2} and the open-circuit voltage is 0.58 V, comparable to cells with a liquid electrolyte. The fill factor is 0.67, giving an overall energy conversion efficiency of 4.4%. Identical results were obtained from current—voltage curves recorded by varying an external load resistor. The dark current—voltage curve shows a very small anodic current in the potential range of the photocurrent plateau and the onset of a cathodic current at about −0.4 V, presumably due to iodine reduction.

Figure 3 shows the incident photon-to-current conversion efficiency (IPCE) versus wavelength for the polymer gel electrolyte cell. The photocurrent spectrum is relatively broad, characteristic of the 4,4′-(dcb)$_2$Ru(SCN)$_2$ dye absorption spectrum.[4] The IPCE exhibits a peak at 540 nm with a maximum of 37%, about a factor of 2 lower than the values usually obtained for cells with a liquid electrolyte.
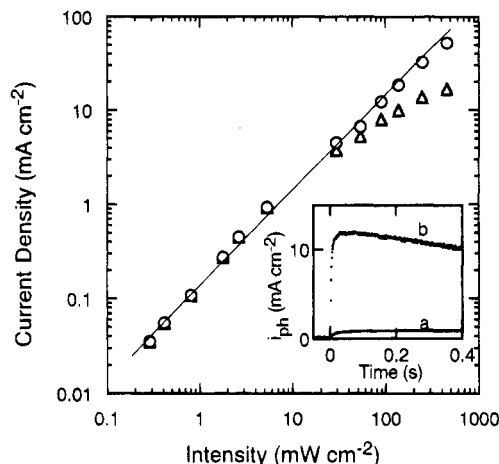

Figure 4. Photocurrent maximum and steady state photocurrent obtained from photocurrent transients versus monochromatic (524 nm) light intensity; (O) photocurrent maximum, (△) steady-state photocurrent. The inset shows the photocurrent transients at light intensities of (a) 5.4 mW cm^{-2} where i_{ss} = 0.93 mA cm^{-2}, and (b) 90 mW cm^{-2} where i_{max} = 12.3 mA cm^{-2} and i_{ss} = 8.0 mA cm^{-2}.

Figure 4 shows the dependence of the photocurrent on the light intensity for a polymer gel electrolyte cell. Examples of photocurrent transients at high and low light intensity are shown in the inset. At light intensities below 20 mW cm^{-2} the photocurrent increases approximately exponentially with time up to a steady-state value. At high light intensity, a photocurrent decay is observed following the rise and, as a result, the steady-state photocurrent is smaller than the photocurrent maximum. As can be seen from Figure 4, the photocurrent maximum is proportional to the light intensity over more than 3 orders of magnitude, similar to results obtained from cells with liquid electrolyte. The dependence of the photocurrent maxima on light intensity corresponds to an IPCE value of about 37% through the whole light intensity range. The magnitude of the light intensity where the onset of the decay process was observed varied from cell to cell.

A unique feature of the dye sensitized TiO$_2$ photoelectrochemical cell is the relatively slow photocurrent response to illumination. The time constant associated with the photocurrent rise was inversely proportional to the light intensity and was larger than 1 s at very low light intensity. The slow photocurrent rise is also observed in similar cells with a liquid electrolyte and is a characteristic of the TiO$_2$ film, not the electrolyte. The slow photocurrent transients are thought to be related to slow electron transport in the porous TiO$_2$ film.[6] A theoretical model of steady-state electron diffusion limited transport in these films has been proposed by Sodergren et al.[7]

The decay part of the photocurrent transients at high light intensity has a power law dependence with a characteristic slope of −0.5, which suggests that it is due to a diffusion-controlled transport process. The iodine concentration in the electrolyte is usually lower than the iodide concentration, and it is likely that the transport of iodine to the counter electrode in the electrolyte is the rate-limiting step of the redox process.

The relatively low IPCE values for the quasi-solid state cells compared to similar cells with a liquid electrolyte are not due to ion-transport limitations, as described above. The probable explanation for the lower IPCE is incomplete wetting of the porous film by the polymer gel electrolyte. In these cells photon absorption by the dye results in electron injection into the TiO$_2$ film; the oxidized dye is then reduced by the redox couple in solution. Dye molecules not in contact with the electrolyte cannot be reduced by the redox couple resulting in a decrease in the absorption efficiency.

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In summary, we have fabricated a dye-sensitized porous TiO_2 photoelectrochemical cell with a polymer gel electrolyte. These cells exhibit open-circuit voltages and fill factors comparable with liquid electrolyte cells and have an energy conversion efficiency of 3−5% under white light illumination. The quasi-solid-state cells exhibit transient behavior similar to cells with liquid electrolyte, suggesting that ion transport in the polymer gel electrolyte does not inherently influence the performance of these cells. Preliminary results under extended illumination suggest that the long-term stability of the gel electrolyte cells is similar to that of liquid electrolyte cells. Optimization of the TiO_2/polymer gel interface should help to further increase the efficiency and stability of the cells.

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