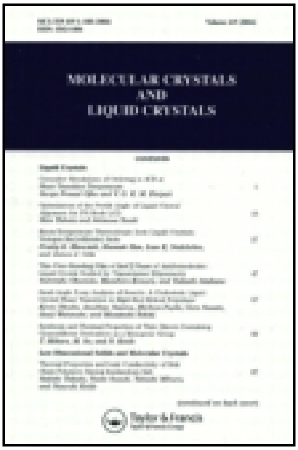

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Charge Transfer Between Polypyrrole Coated n-Si Electrodes And Solid Polymer Electrolytes

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CHARGE TRANSFER BETWEEN POLYPYRROLE COATED n-Si ELECTRODES AND SOLID POLYMER ELECTROLYTES

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Abstract

We have developed photoelectrochemical cells based on rectifying junctions between n-Si and thin film polymer solid electrolytes. We describe various surface modifications applied to the n-Si electrodes which overcome a high activation energy barrier for efficient charge transfer to redox ions in the polymer solid electrolytes.

Solvent free solid polymer electrolytes represent an important new class of ionically conducting materials (1). Their compatibility with thin film technology makes them potential candidates for a wide variety of technological applications.

We have developed a new type of photoelectrochemical cell (PEC) based on rectifying junctions between semiconductor electrodes and thin film polymer solid electrolytes. This holds out the hope of being able to manufacture all thin film solid state PEC's without the semiconductor surface corrosion problems associated with liquid electrolyte PEC's. In addition, it allows easy construction of multispectral thin film cells based on more than one semiconductor material in optical and electrical series (2).

Our present study has focussed on surface modification techniques for improving the rates of charge transfer between semiconductor electrodes and redox ion couples in polymer electrolytes (3). Specifically, we have shown that surface modifications of n-Si electrodes with thin films of polypyrrole can dramatically reduce the large activation energy barrier against efficient charge transfer between bare semiconductor electrodes and solid polymer electrolytes.

Solid Polymer Electrolytes

Linear polyethers like poly(ethylene oxide), $(CH_2-CH_2-O)_n$, (PEO) give conducting complexes with alkali metal salts (1). Such adducts are either crystalline materials or amorphous elastomers. The cations are solvated by a fraction of the ether oxygens and a limited stoichiometry of four oxygen atoms per cation has been observed. Both the cations and the anions move in the polymer matrix. The transference number of iodide has been measured to be in the range of 0.2 to 0.4.

The conductivity of these electrolytes is relatively low at room temperature, typically in the 10^{-6} $(\text{ohm-cm})^{-1}$ range and increases to 10^{-4} $(\text{ohm-cm})^{-1}$ at 50 - 80 degrees C. Devices therefore require thin films. The electrolyte films used in the PEC's are solution cast from MeOH by spin coating and have thicknesses of 0.5 - 1.0 um. The ion concentration, as given by the ratio of oxygen atoms in the polymer backbone to cations, was 8.

Photoelectrochemical Cells

Thin films of PEO complexed with KI and I_2 to generate the iodide/triiodide redox couple are produced by spin coating from MeOH solutions onto a transparent conducting substrate, indium-tin oxide (ITO) on glass, and subsequently dried by heating under vacuum. The ITO is coated with 5-10 Å electron beam evaporated Pt. Without the Pt, which is invisible at this thickness, the ITO is a highly irreversible electrode for iodide oxidation-reduction (4). The PEO film is subsequently contacted with a 1 cm^2 n-Si chip by heating with light pressure under vacuum. Fig. 1 shows a schematic energy level diagram of the cell including polypyrrole surface modification of the n-Si electrode (vide infra).

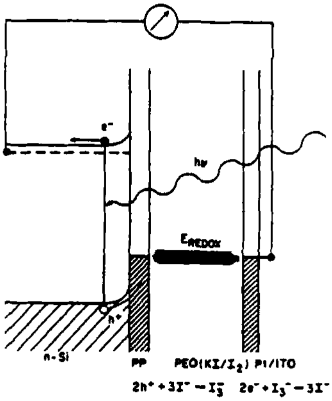

Fig.1 Schematic energy level diagram of solid state photoelectrochemical cell

Silicon Surface Modification

The effect of various types of surface modification of the n-Si electrode on the efficiency of charge transfer across the interface with the PEO electrolyte can be studied by monitoring the photocurrent as a function of the surface modification under constant illumination.

The n-Si surface modifications we have studied include the following: (i) bare n-Si (etched in HF only); (ii) n-Si coated with 200-400 Å polypyrrole.BF_4; (iii) n-Si coated with 10-20 Å electron beam evaporated Pt; (iv) n-Si coated with 10-20 Å Pt followed by deposition of polypyrrole.BF_4;

(v) n-Si with 10-20 Å Pt followed by deposition of polypyrrole.iodide. The n-Si was always etched in HF before the surface modifications.

The polypyrrole films were grown on the n-Si surface with the technique of photoassisted electrochemical oxidation (5). With light of energy larger than the band gap minority carriers are generated which diffuse to the interface with the application of a posiive bias.

As shown in fig. 2, bare n-Si is a highly irreversible electrode for iodide oxidation in this medium. A high degree of electrochemical irreversibility has also been observed with bare semiconductor surfaces of II-VI compounds and polysulfide electrolytes (2).

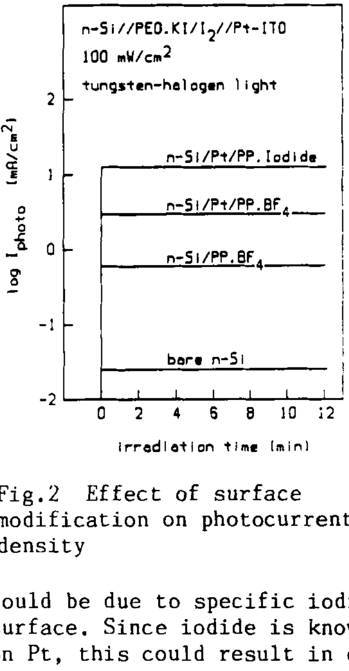

Fig.2 Effect of surface modification on photocurrent density

A thin coating of polypyrrole.BF_4 greatly improves the charge transfer characteristics of the interface. 10-20 Å of Pt improves the electronic coupling between the polypyrrole and the Si (6) leading to more efficient hole scavenging. A Pt coating alone without the polypyrrole produced slightly less efficient charge transfer.

The most efficient interfaces incorporate iodide as the anion dopant in the polypyrrole, synthesized from MeCN solution containing tetraethylammonium iodide. With the Pt-polypyrrole.iodide coating the charge transfer characteristics relative to bare n-Si are improved by about three orders of magnitude. The enhanced efficiency with iodide doped polypyrrole could be due to specific iodide adsorption on the platinized Si surface. Since iodide is known to have a strong specific adsorption on Pt, this could result in efficient oxidation, or hole scavenging.

We believe these surface modification techniques represent an important advance in the control of charge transfer between semiconductor electrodes and solid polymer electrolytes.

Current-Voltage Characteristics

The illuminated I-V characteristics of PEC's with n-Si/Pt/polypyrrole.iodide photoanodes show different behavior when different size areas are illuminated. Fig. 3 shows the response with the illumination of 0.2 cm^2 and 0.02 cm^2 areas. The size of the Si chip was 1 cm^2. The illumination was 100 mW/cm^2

tungsten-halogen white light and the transmission of the PEO/ITO was 55%. With the 0.02 cm^2 area illuminated the fill factor (the fraction of the theoretical maximum efficiency with a given short circuit current and open circuit voltage) was 0.5 and the energy conversion efficiency about 2%, or 3.6% corrected for absorption in the PEO/ITO. The fill factor is strongly dependent on the series resistance of the cell.

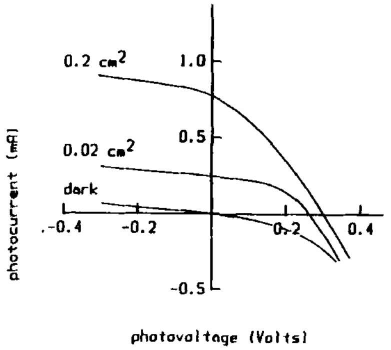

Fig.3 Illuminated I-V characteristics of solid state photoelectrochemical cells

Large reverse bias dark currents are associated with low shunting resistance due to edge effects. The degraded response for larger illuminated areas are due to inhomogeneities of the contact area between the Si and the PEO. Smaller illuminated areas (less than 1mm^2) result in even higher photocurrent densities indicating that technological optimization will lead to more efficient cells.

Spectral Response

The wavelength dependent transmission characteristics of the PEO/ITO and the spectral response of the short circuit photocurrent has been determined with cutoff filters. The photocurrent exhibits a sharp drop for wavelengths below 500 nm, or photon energies above 2.5 eV. The drop is much sharper than that of the transmission characteristics of the PEO/ITO which is due to the iodide absorption. We attribute the sharp drop in the photocurrent to high surface recombination velocities associated with a high density of surface states. Since the absorption constant increases with increasing photon energy, the higher energy photons are absorbed closer to the surface where the high recombination velocities decrease the carrier lifetimes.

Summary

In summary, we have demonstrated techniques for derivatizing semiconductor surfaces which overcome the large activation energy barriers to efficient charge transfer between semiconductors and redox ions in PEO electrolytes.

The particular coupling of electronically and ionically conducting polymers to achieve efficient charge transfer which these techniques demonstrate are compatible with thin film technology and could therefore have important technological implications.

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References

1. M. Armand, Solid State Ionics 9/10, 745 (1983)
2. T. Skotheim, Appl. Phys. Lett. 38, 712 (1981)
3. T. Skotheim and I. Lundstrom, J. Electrochem. Soc. 129, 824 (1982)
4. T. Skotheim, S. W. Feldberg, and M. Armand, J. de Physique C3, 615 (1983)
5. T. Skotheim, L.G.Petersson, O.Inganas, and I. Lundstrom, J. Electrochem. Soc. 129, 1737 (1982)
6. O. Inganas, T. Skotheim, and I. Lundstrom, J. Appl. Phys. 54, 3636 (1983)