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POLYPYRROLE ELECTRODES. CHARGE TRANSFER TO AQUEOUS AND SOLID POLYMER ELECTROLYTES

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Résumé - Nous avons étudié l'interface entre le polypyrrole conducteur et des polymères électrolytes solides ou aqueux. Le polypyrrole est poreux pour le solvant et les ions de l'électrolyte mais pas pour des polymères électrolytes solides. Les deux types d'interfaces montrent sans ambiguité que la porosité, et donc la surface spécifique réelle, est responsable du rapide taux de transfert de charge vers les ions en solution qui est observé.

Abstract - We have studied interfaces between conducting polypyrrole and aqueous and solid polymer electrolytes. Polypyrrole is porous to solvent and electrolyte ions but not to solid polymer electrolytes. Contrasting the two interfaces shows unambiguously that the porosity, and consequently large actual surface area, is responsible for the observed rapid rate of charge transfer to ionic species in solution.

INTRODUCTION

One of the more promising areas of applications of conducting polymers is as electrode materials. Polyacetylene has been extensively studied both as anode and cathode material for rechargable storage batteries (1) and as photoanode in electrochemical photovoltaic cells (EPC) (2), and polypyrrole (PP), coated onto semiconductor electrodes, has been shown to efficiently mediate transfer of photogenerated holes between semiconductors and aqueous electrolytes(3).

There have been several studies of the solid state properties and redox chemistry of PP which have shown that it can act as a quasi-reversible electrode. We will show that PP is porous to electrolyte penetration and has a large actual surface area in contact with the electrolyte. Furthermore, we will show that the large contact area is responsible for the rapid rate of charge transfer observed with many redox species by contrasting the charge transfer characteristics of PP-aqueous electrolyte interfaces with those of PP-solid polymer electrolyte interfaces where the solid polymer electrolyte does not penetrate the PP phase. This will be illustrated by using solid state EPC devices with PP coated single crystal n-Si photoanodes.

EXPERIMENTAL

The Si and Pt electrodes were prepared and coated with electrochemically polymerized PP from TEABF4/Acetonitrile solution according to the manner reported previously (3b,4). The PP films were consequently doped conductive with BF_4 ions. For the electrochemical characterization care was taken to purify and dehydrate all salts and solvents. All the solid polymer electrolyte

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studies were performed in high vacuum after heating and pumping for at least 24 hours to remove traces of oxygen and water.

RESULTS.

Cyclic Voltammetry (CV) in Supporting Electrolyte.

Fig. 1 shows CV scans for a PP film on a Pt substrate in 0.2M acetonitrile-tetraethylammoniumtetrafluoroborate (ACN-TEABE₄) for different scanning velocities. The scans exhibit large background currents in the anodic region which ressemble charging currents due to the electrochemical double layer. These currents indicate the presence of a large surface area in contact with the electrolyte. If we plot the magnitude of the charging current as a function of the thickess of the polymer film as measured with a surface profilometer we obtain a linear relationship as shown in Fig. 2. The surface area is proportional to the thickness up to at least 0.2 um.Similar results have been obtained by measuring the small signal capacitance across the polymer film (5).

Additional evidence for the porosity of the PP film comes from the fact that electrochemical reactions occur at the substrate as for example oxidation of Si electrodes, although the reaction is considerably slower than for uncoated electrodes (3b, d, e). The electronic coupling, and consequently the charge transfer characteristics, between the Si and PP can be greatly improved by coating the Si surface with thin (5-20 Å) of Pt or Au, resulting in long term stability of the photoanode in aqueous electrolytes (3b, d).

The question still remains as to whether additional oxidation of the polymer is also taking place concurrently with the double layer charging, i.e. whether additional valence band states are being emptied as the potential is being increased. Since the double layer charging appears to be the dominant effect, the density of states being oxidized in the anodic region must be low. This has indeed been observed to be the case (6).

The additional charging implies that the fermi level of PP moves down in the valence band with the anodic voltage. This can be observed by checking the rest potential of the PP electrode along the oxidation curve. The rest potential stays fixed at any point in the anodic region when the cell is left in open circuit. This has also been observed with PP membranes (7). This implies that the fermi level of PP can be varied over more than 0.5V and should be determined by the potential at which the circuit is opened. This behavior is very different from that of an ordinary metal but is consistent with the model of a degenerate semiconductor with a low density of valence band states (6).

When PP is synthesized on semiconductor substrates and the work function is measured indirectly by measuring the barrier height the measured work function is invariably large (8). This can be explained by the highly anodic reduction potential of the valence band holes oxidizing pyrrole to form PP leaving the PP fermi level in the far anodic regime.

Electrochemistry of Solution Species

The value of PP as an electrode material is determined by how efficiently it can oxidize and reduce species in solution. The electrochemical reversibility, or absence of an overvoltage to electron transfer, can be measured by the peak to peak separation of the cyclic voltammogram of the species in question. A peak to peak separation of 59mV implies complete electrochemical reversibility (9). A larger peak to peak separation can be indicative of either the presence of an overvoltage to electron transfer and/or a resistance to the movement of the ions.

Iodide oxidation is of particular interest in this case since the singly charged iodide and triiodide species transport easily in solid polymer electrolytes as well. Fig. 3 shows the redox chemistry of iodide at a PP film on an indium-tin oxide substrate (ITO) which by itself is an inert electrode towards iodide oxidation in the potential region considered. The peak to peak separation was 240 mV for the PP electrode which compares with 170 mV at a Pt electrode. The i values varied linearly with v up to 200 mV/sec. PP is therefore a quasireversible electrode for iodide oxidation, almost as good as Pt. Other species, e.g. ferrocene, exhibit essentially complete electrochemical reversibility at PP electrodes. (4c,5) . We attribute the reversibility, and consequently rapid charge transfer characteristics, of the PP electrodes to the large actual surface area in contact with the electrolyte. This will become clear from the discussion of the solid polymer electrolytes below.

Electrode Stability

An important criterion for judging the usefulness of an electrode material is the range of stability of the electrode material itself against irreversible reduction or oxidation. When PP electrodes are cycled in aqueous solutions to potentials more anodic than about 0.7V vs the Standard Calomel Electrode (SCE) irreversible oxidation of the polymer film takes place. This is shown by a decrease in current and a permanent loss of electroactivity. This has also been observed to be the region of stability of EPC devices based on PP coated n-Si and a-Si photoanodes (3b,c). When ion couples with redox potential less anodic than about 0.7V (SCE) are used (Fe(CN) $\frac{3}{74}(0.12V)$, $I^{-}/I_{3}(0.3V)$, Fe2+/3+(0.53V)) the cells exhibit good stability. With redox couples more anodic than 0.7V (Br-/Br₃(0.83V), Ce^{3+/4+}(1.35V)) a precipitous decline in the photocurrent is observed leading to irreversible decay of the PP coated electrode. Large open circuit voltages are also observed in this region. In organic electrolytes, e.g. TEABF4/ACN, PP electrodes are stable to at least 1.0V. If PP electrodes are left in air for extended periods of time (weeks) it results in loss of film oxidation/reduction.

Solid Polymer Electrolyte

Independent evidence for the importance of electrolyte penetration for rapid charge transfer from PP to ionic species in solution comes from comparing PP/liquid electrolyte interfaces with PP/solid polymer electrolyte interfaces where the contact area is limited to the incident geometric area due to the fact that the solid polymer electrolyte does not penetrate the PP phase. The solid polymer electrolytes are based on solvent free high

The solid polymer electrolytes are based on solvent free high molecular weight poly(ethylene oxide) (PEO) complexed with alkali metal salts (KI,NaI).Molecular weights from 3400 to 600 000 have been used. The solvating properties of PEO derive from the unpaired electrons on the oxygen atoms in the polymer backbone. Anions move by diffusing interstitially between the chains whereas the cation moves by hopping inside the polymer helix (10a). Iodide transference numbers of 0.2-0.3 have been reported (10b). Although the resistivity of PEO electrolytes are rather high at room temperature (about 10^6 ohm-cm) they drop to the $10^3 - 10^4$ ohm-cm in the 80-100 deg. celcius range. By spin coating techniques continuous, pinhole free films of less than 1.0 ohm/cm or less.

PEO based solid polymer electrolytes are of interest both for EPC devices and all solid state batteries (11,10a). The potentially large voltage stability window of PEO makes it an interesting candidate for batteries with electode materials corresponding to widely different chemical potentials (e.g.Li,TiS) The main concern is the possible

irreversible chemical oxidation of the nonbonding orbitals formed by the ether oxygen atoms. Fig. 4 shows the CV of PEO of molecular weight 3400 in methylene dichloride/tetrabutylammonium perchlorate supporting electrolyte. The oxidation of PEO starts at 1.6V vs SCE. However, PEO complexed with potassium (PEO.K+), which is accomplished by adding excess KCl, shows no oxidation wave in that region indicatng that the oxygen-potassium complexation inhibits the oxidation. The voltage stability window of PEO may therefore approach the \mathbf{G}, \mathbf{G}^* transition value (valence to conduction band) which for insulating polymers is typically 8-10 eV. (12). Chloride oxidation is not observed either, which implies that the PEO.K+.Cl- forms a complex and is not dissociated. This is confirmed by ac conductivity measurments of the solution which shows the electrolyte to be essentially an insulator. This is in contrast to complexation with KI which yields a conductive solution implying dissociation.

If complexed PEO is not oxidized in solution it is even less likely to be oxidized in the solid state since the polymer matrix is an insulator and the electrons will consequently not be transported easily.

We have adapted the technique of three electrode CV to the solid state and Fig. 5 shows the results for PEO complexed with NaI. The working electrode and the reference electrode were both 2 mm² Pt electrodes and the counter electrode was ITO on glass. The reference electrode was connected to a high impedance electrometer (10E14 ohms). Consequently no current passed through its interface with the electrolyte and its potential relative to the electrolyte remained constant. The thickness of the PEO film was 0.1 mm and the experiments were performed under high vacuum at 80 deg.C. In the cathodic domain no peak is visible before the sodium reduction starting at -1.7V (vs. the Pt reference electrode). In the anodic regime there is a peak at about 2V corresponding to an iodide oxidation starting at 1.7V. The stability regime for the PEO.NaI electrolyte is thus 3.4V. With more anodically stable anions a stability window as high as 4.9V has been observed (13a,b).

PP-PEO electrolyte interfaces

The efficiency of charge transfer between PP and PEO electrolytes can be studied using a solid state EPC device as schematically illustrated in Fig. 6 (11). A rectifying junction is formed between the n-Si and the PEO electrolyte in which is dissolved KI and I $\,$ in order to form an iodide/triiodide redox couple. The the transparent ITO counter electrode has a thin (10 A) Pt layer in order to make it reversible to iodide oxidation/reduction. The n-Si becomes a current source when illuminated with light of energy larger than the band gap. The current collected by the external circuit will then be directly proportional to the efficiency of charge transfer of the semiconductor-electrolyte interface. In Table I we compare the photocurrent collected with constant illumination as a function of the semiconductor-electrolyte interface. As can be seen the bare n-Si electrode is a highly irreversible electrode for iodide oxidation. A $40\,$ fold increase in the photocurrent collection efficiency is observed when the Si electrode is coated with PP after first preparing the surface with 10A of vacuum evaporated Pt for better electronic coupling between the Si and the PP. The photocurrent is still about an order of magnitude smaller than that of a similar device using an aqueous electolyte(3b). This we attribute to a lack of electrolyte penetration into the PP phase. When the PP film is photoelectrochemically deposited onto the n-Si from a solution containing 0.8M PEO repeat units complexed with KI the interface produced is still more efficient by almost a factor of four. This may be attributed to a possible interpenetration of the polymer phases in which the PEO is entrapped in the PP phase as it grows. As the

interpenetation is still very small, the FTIR spectra are inconclusive. However, ESCA studies on PP synthesized in the pesence of PEO.NaClO does show a small Na signal in the polymer indicating that a certain amount of PEO has been entrapped in he PP phase. This clearly demonstrates the effect of interpenetration of the PP and the electrolyte for rapid charge transfer. Despite the increased efficiency of the composite interface the mixing is still insufficient to produce the desired rate of charge transfer for efficient solid state EPC devices.

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TABLE I. Short circuit photocurrent as a function of surface preparation of the n-Si photoanode. The cell configuration was that of Fig. 6 with 0.5 um thick PEO.KI/I electrolyte. The illumination was 100 mW/cm tungsten-halogen light.

ANODE

PHOTOCURRENT (mA/cm)

bare n-Si	0.02							
n-Si/Pt/PP	0.96							
n-Si/Pt/PP.PEO.KI	3.1	(PP	synthesized	in	the	presence	of	PEO.KI)

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Fig.3. Cyclic voltammogram of 10^{-2} M KI (0.2M KCl) at a 750 Å thick PP electrode on ITO.



Fig.5. Solid state CV of PEO.NaI(MW= 600,000). Na concentration relative to PEO oxygen atoms: O/Na = 8



Fig.2. Double layer capacitance calculated from charging current as function of PP film thickness in TEABF $_{\rm A}/\rm{ACN}$.



Fig.4. Cyclic voltammogram of 0.5 M PEO repeat units (MW 3400) in CH₂Cl₂/TBAP (solid line) and PEO.KCl (dotted line). Background sweep follows dotted line.



Fig.6. Schematic solid state EPC configuration.