“Electrochemical evaluation of a flexible transparent ITO-PET sheet for electrochromic applications”

Santos, João (up201807053@ff.up.pt); Amorim, Célia (camorim@ff.up.pt); Araújo, Alberto (aranujo@ff.up.pt); Montenegro, Maria da Conceição (mcbranco@ff.up.pt)
Faculdade de Farmácia da Universidade do Porto, Portugal

Introduction

Cyclic voltammetry is a scanning technique very useful to assess the redox properties of ions and compounds, for its capability to follow-up the electron transfer process over wide electric potential ranges. Grounded on its use, transparent yet conductive materials can be studied and assembled in increasingly popular portable and wearable devices ranging from novel flexible displays to smart sensors for packed foods. Materials such as indium-tin-oxide (ITO), carbon nanotubes, graphene, sputtered inert metals and conducting polymers were meanwhile described to bring the intended properties, without affecting the transparency of the coated substrate. A lot of investigations on these materials start from prototypes deployed on commercially available ITO-coated soda lime glass slides or ITO-PET substrates. Besides having lower cost this last possess the advantage of being cut with fitted shapes according the envisaged application. However, with this new material the electrical properties seem to vary according the direction in simple cut procedures. This aspect was herein assessed with the redox probe Fe(II)/Fe(III). The electrochemical response of this probe is characterized by an inner-sphere electron transfer pathway mechanism, hence more sensitive to electrode surface properties.

Aims

→ Understand if cutting direction can induce unwanted deterioration in electrochemical performance of ITO films.
→ Understand if electrochemical response to inner-sphere common redox pairs become more or less sluggish according the direction the electrode surface is cut.

Methodology

A rectangular transparent sheet of semiconductive ITO was cut into 1.0x0.5 cm pieces, and the adhesive tape covering the surface was removed in order to expose 0.5x0.3 cm of the conductive surface.

![Figure 1](image1.png)

Figure 1. a) Cut directions adopted and b) closer view of the working electrode; 0.15 cm² of ITO surface at the tip was exposed after removing the covering tape.

![Figure 2](image2.png)

Figure 2. Used electrochemical cell assembly. The working electrode was placed in the vicinity of the reference electrode to minimize the ohmic drop. An equinormal 5 mM Fe⁴⁺/Fe⁵⁺ in 0.1M KCl electrolyte solution was used, purged with N₂ for 16 min to remove dissolved oxygen.

Conclusions

While transparent films such as zinc-doped indium oxide, gallium-doped zinc oxide or aluminum-doped zinc oxide were described as conductive materials, commercial ITO-PET, with a transparent substrate, are still preferred for the high transparency and electrochromic properties needed in the envisaged applications. It is known that buckling, delamination and cracking in ITO films decrease its conductance characteristics. In this work, different cut directions of rectangular electrodes were assessed to evaluate whether they can induce changes unseen at the naked eye, but translated by the less reproducible response. In fact, for a cut direction A, less reproducible responses were obtained as evidenced by oxidation and reduction currents with variations above 30% as well as potential peaks difference values of 10% r.s.d. These observations are congruent with the heterogeneous electron transfer constant obtained, one order of magnitude lower than the observed for the cut direction B. Further observations regarding analysis by microscopy will be needed in order to ascertain if the cracks are preferentially initiated in the polymer substrate or in the ITO outer surface.

Results

![Figure 3a](image3a.png)

Figure 3a) Cyclic voltammograms measured on different ITO-PET electrodes (cut direction A). Scanning rate: 20 mV/s.

![Figure 3b](image3b.png)

Figure 3b) Cyclic voltammograms measured on different ITO-PET electrodes (cut direction B). Scanning rate: 20 mV/s.

![Figure 4](image4.png)

Figure 4 Superimposed voltammograms measured on ITO-PET electrode according the direction selected for cut (A gray vs B blue); Scanning rate: 20 mV/s; starting potential : 0.8 V; vertex potential: -0.7 V; reference electrode: Ag/AgCl(KI 3 M).

Discussion

The charge transfer between the analyte in solution adjacent and the solid electrode surface takes place by inner- or outer-sphere electron-transfer reactions. In outer-sphere electrode reactions, a solvent layer is interposed between the electroactive ion and the surface of the electrode. On contrary, in an inner-sphere electrode reaction, the ligand (Cl⁻ ion) coordinating the probe adsorbs directly to the electrode and mediates the electron transfer. The greater proximity of the electroactive ion to the electrodes surface turns the rate constant for the electrode reaction (kD) more sensitive to the electrode material properties.

The Nicholson’s method allowed the estimation of kD from the peak separation ΔEp value:

$$k_D = \psi \left( \frac{D_{nD,Fe^{3+}}}{R^2} \right)^{1/2} \left( \frac{D_{nD,Fe^{2+}}}{R^2} \right)^{1/2} \text{ and } \psi = f(\Delta E_p)$$

with D_{nD} being the diffusion coefficient for iron³⁺/²⁺ 0.662x10⁻⁹ cm².s⁻¹ and v the selected voltammogram scan rate of 20 mV/sec, n=1 and D_{nD} = D_{nD}.

<table>
<thead>
<tr>
<th>Electrode Direction</th>
<th>ΔEp (mV)</th>
<th>Epc (mV)</th>
<th>Ip (mA)</th>
<th>DnFe³⁺ (cm².s⁻¹)</th>
<th>DnFe²⁺ (cm².s⁻¹)</th>
<th>v (cm/s)</th>
<th>kD (cm/s)</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>4,00E⁻⁴</td>
<td>9,00E⁻⁴</td>
<td>1,00E⁻⁴</td>
<td>2,50E⁻⁴</td>
<td>2,50E⁻⁴</td>
<td>4,00E⁺⁷</td>
<td>1,50E+³</td>
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<tr>
<td>B</td>
<td>7,00E⁻⁴</td>
<td>1,00E⁻⁴</td>
<td>4,00E⁻⁴</td>
<td>2,00E⁻⁴</td>
<td>2,00E⁻⁴</td>
<td>4,00E⁺⁷</td>
<td>1,50E+³</td>
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Table 1. Experimental data obtained from voltammograms

References