

The influence of the electrolyte concentration in the current density of the fuel cell is showed on the figure 2. The stationary current density is greater when the electrolyte concentration increases.

[KOH]	T ^a /°C	E ⁰ _{an} /mV	E ⁰ _{cat} /mV	E _{an (st.)} /mV	E _{cat (st.)} /mV
5M	20	-878	50	-45	-11
5M	50	-904	103	-70	-20
5M	70	-921	57	-427	-95
3M	70	-874	70	-365	-77

Table 1: Anode and cathode potentials for different temperature and electrolyte concentration. E⁰ is the equilibrium potential

Table 1 shows the potentials of the electrodes at open circuit (E⁰) and at the stationary state (st.), with the different work conditions

The effect of the temperature is greater in the anode than in the cathode.

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"IN-SITU" SPECTROELECTROCHEMICAL STUDIES OF A POLYPYRROLE/POLYVINYLSULPHONATE COMPOSITE.

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SUMMARY

In this work an UV-vis spectrophotometer technique adapted to "in-situ" absorption-reflection experiments is presented. Visible spectra at different oxidation potentials for Polypyrrole/Polyvinylsulphonate composite controlled in 0.1 M LiClO₄ water solution were performed. The evolution of the visible-absorption spectra in the oxidized and reduced states as a function of the number of cycles of the coloration/decoloration was followed.

Keywords: "in-situ" absorption-reflection, polypyrrole/polyvinylsulphonate, stability.

1. INTRODUCTION

The simultaneous oxidation-polymerization processes during the electrogeneration of conducting polymers in presence of polyelectrolytes, promote the participation of the polyanion in the polymer film required to compensate the positive charges generated along the chains of the growing conducting molecules. A conducting polymer/polyelectrolyte composite has an open structure due to the great free volume of the polyanion. This great

free volume, joint to the fact that those composites interchange cations [1-4] with the electrolyte along redox processes, point to those materials like candidates for electrochromic devices having a very short switching time between different colors (< 0.2 s).

In this way, the optical properties of polypyrrole/polyvinylsulphonate composite were studied. Chemical and electrochemical parameters of synthesis were optimized in our laboratory [5].

2. EXPERIMENTAL

The optical measurements were performed using a monobeam 8700 Philips UV-Vis spectrophotometer. The potentiostat, electrodes and cell were similar to those described in a previous work [6].

Pyrrole (Janssen) was distilled under vacuum at 65 °C before use. Poly-vinylsulphonate(PVS) sodium salt (Aldrich), and LiClO₄ (Janssen) were used without further purification. Water was obtained from a Milli Q. Reagent Water System, fed by a Milli RO4 Water Purification System.

The PPY/PVS film was synthesized by consecutive potential sweeps between -700 mV and 800 mV at 0.1 V.s⁻¹ from 0.4 M pyrrole and 0.1 M PVS in aqueous solution. The concentration of PVS is related to sulphonate groups.

3. RESULTS AND DISCUSSION.

The electrochromic properties of thin PPY-PVS composite were studied in 0.1 M LiClO₄ aqueous solution under different potentials of

polarization. Experimental spectra are depicted by figure 1. Under polarization at -800 mV (solid curve) a broad absorption region is present between 370 and 500 nm related to transitions from the valence band to the conduction band. Moreover, a new absorption maximum appears centered on 835 nm. As this absorption increases at increasing oxidation level (higher potentials), their presence under polarization at -800 mV points to a partially oxidized PVS-composite.

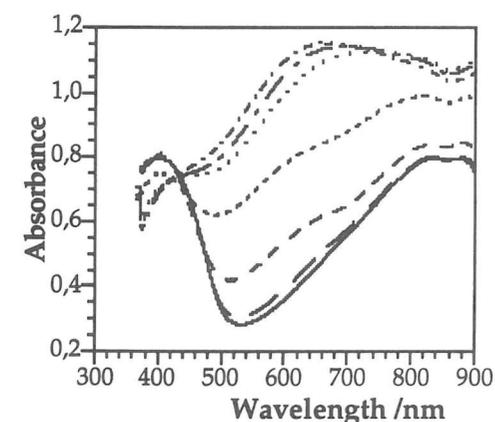


Fig 1.- Reflectance-absorption spectra of PPY/PVS film polarized at different potentials: -800 (—), -650 (— —), -500 (— — —), -350 (- - - -), -200 (.), -100 (- - - -) and 0 mV (- . . . -) in 0.1 M LiClO₄ aqueous solution.

When the polymer oxidation level increases, a continuous decrease on the absorption band present at lower wavelengths than 500 nm is observed. When the composite is submitted to - 650 mV a similar spectrum to -800 mV is obtained. Under polarization at -500 mV a shoulder between 550 and 700 nm is observed and the absorbance at 830 nm increases. While at -350 mV the absorption of the two shoulders rise, at -200 mV an unique maximum which includes both is observed. The absorbance of this

maximum increases progressively at -100 and 0 mV. These two bands are related to polaron and bipolaron states formed upon oxidation.

The PPY/PVS composite was submitted to consecutive potential steps between -800 mV and 0 mV in 0.1 M LiClO₄ aqueous solution. Both potentials were kept for 1 second. After a certain number of cycles of bleaching/coloration, spectra between 350 and 900 nm were recorded under polarization at -800 mV and 0 mV. In figure 2 the absorbances for PPY/PVS obtained at 660 and 820 nm are depicted versus the number of cycles of coloration/bleaching. At these wavelengths, while the relative variation on absorbance rises in oxidized state, a decrease of absorbances under polarization at -800 mV at the beginning of treatment (1000 cycles) is observed. After these first cycles an increase on the absorbance is obtained.

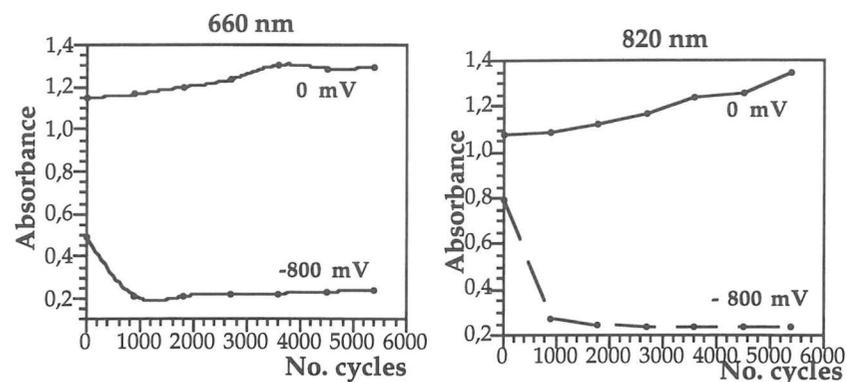


Fig 2.- Evolution of the absorbance in reduced and oxidized states as a function of the number of consecutive potential steps between -800 (1s) and 0 mV (1s) for a PPY/CMC in 0.1 M LiClO₄ aqueous solution at 660 and 820 nm.

The polypyrrole/PVS composite presents a progressive recovering on electrochromic properties with cycling, pointing to the presence of a fraction of the composite inaccessible to ions during redox processes at the beginning of the treatment. This fact can be due to the rigidity of the chains of PVS.

4. CONCLUSIONS

As a general conclusion electrogenerated composites between PVS polypyrrole present a good stability after 5500 cycles. During the oxidation of the polymer composite two new absorptions appear, related to polaronic and bipolaronic structures.

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