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## ELECTROSYNTHESIS AT DIFFERENT POTENTIALS AND PROPERTIES OF POLYPYRROLE DOPED WITH HETEROPOLYTUNGSTATE

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### Abstract

The influence of the synthesis potential on the kinetics of electropolymerization and the properties of a hybrid material polypyrrole doped with heteropolytungstate was studied in organic solutions by potential steps and cyclic voltammetry techniques. It was found the presence of side reactions at low potentials when thin films were electrogenerated. The productivity of the hybrid material kept always a high constant value whatever the studied potentials.

**Key words:** polypyrrole, heteropolyanions, hybrid material, productivity, electrosynthesis, specific charge.

### Introduction

Other works about thin polypyrrole film doped with polyoxometalate anions to be used as catalyst have been reported, due to the good catalytic properties of polyoxometalate anions, to the easy immobilization of Polyoxometalate anions in the film and the easy separation of the catalyst from the reaction mixture [1-5]. However, polyoxometalate anions in films can provide a secondary charge storage mechanism, since that they are capable of reversible redox reactions and to interchange a great number of electrons without any modification in the original structure[4,6]. So, from these points, polymers doped with polyoxometalate anions should have an higher specific storage charge for the secondary batteries. Though some electrochemical properties of polypyrrole doped with heteropolyanion have been investigated [7-8], no works were carried out from the point of view of the specific charge.

Generally, the synthesis conditions have great influence on the electrogeneration and on the polymeric properties. From results on the electrosynthesis of basic polypyrroles (using small anion) or polymeric blends (polypyrrole-polyelectrolytes) in our Lab [9-12], the electropolymerization potential is one of the most important variables of synthesis, affecting both the composition and the properties of the material. The aim of this paper is to determine if a similar influence exists during the synthesis of hybrid materials polypyrrole-macroanions. The influence of

the synthesis potential on kinetics of electropolymerization was also studied by using microgravimetric monitoring of the polymer film.

**Experimental**

The heteropolyacid  $H_3PW_{12}O_{40}$  was supplied by Fluka and used as received. Pyrrole (Jansen) was distilled At 59 °C under vacuum (50 torr) and stored at low temperature in dark before use. All other chemicals were reagent grade and used as received. The hybrid films were prepared by electrochemical oxidation from fresh acetonitrile + 2 %  $H_2O$  (v/v) solutions containing 0.1 M monomer and 0.005 M heteropolyanion in three-electrode cell (Metrohm), by polarizing at 500 mV for 60s and following a step up to different potentials for 60 s. A platinum sheet with a surface area of 1 cm<sup>2</sup> was used as working electrode, and a stainless steel having 3 cm<sup>2</sup> of surface area was the counter electrode. All electrode potentials quoted in this paper are referred to the Ag/AgCl electrode. All experiments were performed under nitrogen atmosphere and at room temperature. After generation, the coated electrode was rinsed with acetone and weighted after dried in hot air. The film weight was evaluated by the difference between the uncoated working electrode and the coated electrode, using a 4504 MP8 Sartorius ultramicrobalance (10<sup>-7</sup> g precision).

A M273 PAR potentiostat-galvanostat connected to a PS-5 IBM microcomputer and driven by means of M273 software from EG&G was used for both electrogeneration and checking of the film.

**Results and discussion**

In order to identify the potential window for electropolymerization processes, a cyclic voltammogram was carried out in either the background or the monomeric solution using the platinum sheet as working electrode. The cyclic voltammogram performed in 0.005 M  $H_3PW_{12}O_{40}$  acetonitrile solution containing a 2 %  $H_2O$  (v/v) carried out between -1000 mV to 2800 mV at a scan rate of 20 mV s<sup>-1</sup> starting from 0.0 mV is shown in Fig.1a. A strong reduction process started at potentials lower than 0.0 mV and the oxidation process of background solution occurs at an anodic potential higher than 1750 mV.

An analogous voltammogram performed in the same background solution after addition of pyrrole attaining a concentration of 0.1 M, is depicted in Fig.1b. The monomer oxidation-polymerization is initiated at 750 mV vs Ag/AgCl. The preliminary results allow us to determine that the potential window to study of the hybrid material ranges between 700 and 1600 mV.

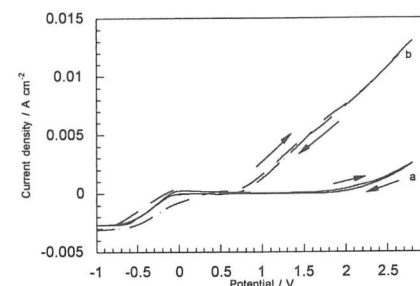


Fig.1. Cyclic voltammograms obtained using a clean platinum electrode in: (a) 0.005 M  $H_3PW_{12}O_{40}$  acetonitrile solution with 2%  $H_2O$  (v/v) and (b) 0.005 M  $H_3PW_{12}O_{40}$  and 0.1 M pyrrole acetonitrile solution with 2%  $H_2O$  (v/v) , scan rate: 20 mV s<sup>-1</sup>.

No film was formed on the electrode by polarization at 700 mV. A thin yellow film and a thick dark blue film were formed at 800 mV and 1600 mV, respectively. Whatever the synthesis potential, the obtained films were extremely adherent and quite smooth and shine.

The weight of the rinsed and dried films increases linearly with the potential of synthesis (Table 1). By integrating of each chronoamperogram recorded during every synthesis, the electric charge consumed during each electropolymerization was obtained. The ratio between the polymer weight and the consumed polymerization charge gives the productivity of the charge consumed during synthesis, productivity of the polymerization charge =  $\frac{W}{Q_{pol}}$ . A constant productivity ( around 1.91 x 10<sup>-3</sup> mg mC<sup>-1</sup> ) independent of the studied potential was obtained (Fig.2). The constant productivity seems to point to the presence of a polymerization mechanism independent of the potential inside the studied potential range.

Table 1 Formed film weight and specific energy stored by film variation with synthesis potential

Potential of synthesis (V)	Film weight (mg)	Specific energy (mAh g <sup>-1</sup> )
0.8	0.0162	10.94
0.9	0.0297	14.22
1.0	0.0755	15.11
1.1	0.1226	16.02
1.2	0.161	16.86
1.3	0.2146	16.85
1.4	0.253	16.56
1.5	0.2943	16.76
1.6	0.3422	16.88

If the electrogeneration mechanism of the hybrid material is independent of the potential of generation, films generated at different potentials will have the same properties. In order to check this hypothesis we chose the specific charge (electrical charge stored per mg of electrogenerated material) as a property of reference.

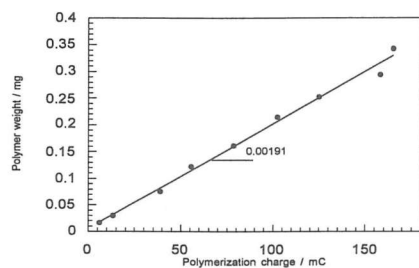


Fig.2 Evolution of film weight with polymerization film variation with polymerization charge.

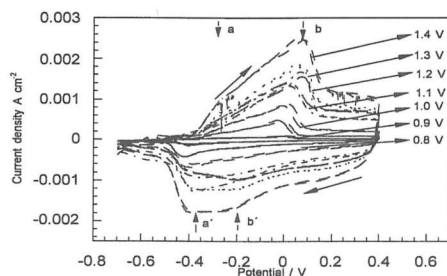


Fig.3 First two cyclic voltammograms performed for the films electrogenerated at different potentials in the range from 800 mV to 1400 mV in 0.005 M  $H_3PW_{12}O_{40}$  and 0.1 M pyrrole acetonitrile solution with 2% (v/v)  $H_2O$ , and checked by cyclic voltammetry from -700 mV to 400 mV at a scan rate of  $20 \text{ mV s}^{-1}$  in 0.1 M  $LiClO_4$  acetonitrile solution.

As the polymer weight ( $W$ ) was already obtained we need to determine the stored charge  $Q_{ox}$  by voltammetric control. Every film was controlled by cyclic voltammetry from -700 mV to 400 mV at a scan rate of  $20 \text{ mV s}^{-1}$  in 0.1 M  $LiClO_4$  acetonitrile solution. Fig.3 shows the first two cyclic voltammograms of the polymers electrogenerated in the potential range from 800 mV to 1400 mV. There are two main anodic (marked a and b) and cathodic (marked a' and b') peaks which can be related to the polymer redox couples in addition to the electrochemical response of the macroanion inside the polymer matrix. The stored charge was obtained by integrating of each anodic area from the second cycle. The specific energies (Table 1) initially increase as the anodic potential rises and

then keep an almost constant value when the material was generated at more anodic potential than 1200 mV.

These results should indicate the presence of side reactions at low potentials when thin films were electrogenerated, consuming a very low fraction of charge (mind that the productivity remains constant) promoting a partial degradation of the film.

### Conclusions

Polypyrroles doped with heteropolytungstate anion  $[PW_{12}O_{40}]^{3-}$  can be electrogenerated from acetonitrile solutions at an anodic potentials higher than 750 mV. The film weight increases linearly when the synthesis potential increases between 800 and 1600 mV. The specific energies stored by the hybrid materials increase initially as the anodic synthesis potential rises and then keep an almost constant value when the material is generated at an anodic potential higher than 1200 mV. The productivity of the hybrid material always remains at high constant value of about  $1.91 \times 10^{-3} \text{ mg mC}^{-1}$ , whatever the potential of synthesis inside the studied range.

### ACKNOWLEDGEMENTS

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