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Polypyrrole composite films prepared by Square Wave Cyclic Voltammetry

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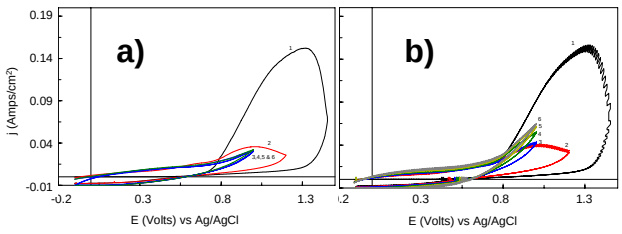
Abstract – Square wave cyclic voltammetry (SWCV) was used for the first time to grow polypyrrole films in the presence of the following electrolytes / doping anions: $LiClO_4$, $NaCF_3CO_2$, p-toluenesulfonic sodium salt, p-octylbenzesulfonate sodium salt and dodecylbenzenesulfonate sodium salt. PPy films grown by SWCV method have enhanced properties such as lower charge transfer resistance and lower Warburg impedance with respect to films prepared by cyclic voltammetry (Fig. 2).

This work reports for the first time the use of square wave cyclic voltammetry (SWCV) method to grow polypyrrole (PPy) films. In the SWCV method a square wave is added to the CV wave during the potential scan. CV has been mainly used to obtain qualitative information about the redox processes involved in the polymerization reaction, and to characterize the polymer films after electrodeposition. With SWCV and by tuning the amplitude and period of square wave form, we expect to overcome the problems related to the diffusion and entrapment of large anions, and at the same time to be able to follow the polymerization and entrapment processes.

PPy films were grown on a polished Pt disk from a N_2 saturated 0.1 M Py monomer aqueous solution. To evaluate the effect of the anion size, anion type, and solution conductivity the following 0.1M electrolyte solutions were used: $LiClO_4$, $NaCF_3CO_2$, p-toluenesulfonic sodium salt, p-octylbenzesulfonate sodium salt and dodecylbenzenesulfonate sodium salt. FT-IR was used on PPy films deposited on ITO substrates to confirm the formation of PPy polymer and anion incorporation. A three-electrode cell equipped with a Ag/AgCl reference electrode and a Pt wire counter electrode was used in all electrochemical experiments.

Figure 1 reports the voltammograms of PPy films grown in $LiClO_4$ solution by CV and SWCV methods. The films were grown for a total of 6 cycles, and the upper potential was 1.45V, 1.2V and 1.0V for the 1st, 2nd and four last cycles, respectively. The sweep rate was 50 mV/s for CV and the step size and time were -10mV and 0.02s for SWCV. The 1st cycle is characterized by an irreversible oxidation peak at 1.32V due to the oxidation of Py monomer and the 2nd cycle is characterised by one peak at 1.0V due to the oxidation of a mixture of oligomer and Py monomer [1]. The main differences are seen on the third to sixth cycles where films prepared by SWCV keep growing, and on the higher deposition rate (measured as the variation of the deposition charge with time during the first deposition cycle) for films prepared by the SWCV method regardless the nature of the electrolyte solution.

After the deposition process the PPy films were cycled in 0.1M electrolyte solution of their corresponding doping anion until a stable CV was obtained. The films were also characterised by AC impedance spectroscopy and Figure 2 compares the impedance spectra (Nyquist diagram) recorded for PPy-p-octylbenzesulfonate (OBS) films prepared by the two methods. Values of charge transfer resistance (Rct) and Warburg impedance (Zw) were extracted from the spectra using a Randles circuit including the Warburg diffusion element in series with Rct. The Rct and Zw values for PPy films prepared by SWCV are significantly smaller than those prepared by CV regardless the electrolyte. This means that the electron transfer and the ion diffusion are easier in the films prepared by SWCV. It is proposed that PPy-SWCV films are more porous than the films prepared by CV. SEM analysis will be done to confirm this hypothesis and chemical analysis will be done to quantify the anions content. These results clearly show the benefits of the SWCV method on the preparation of PPy porous films.



LiClO4 and 0.1 M Py by, **a)** CV and **b)** SWCV.

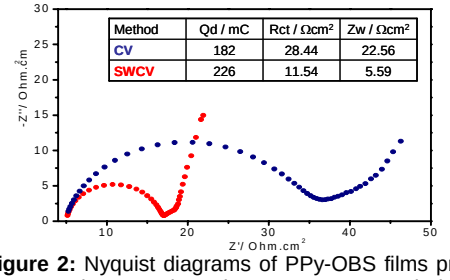


Figure 2: Nyquist diagrams of PPy-OBS films prepared by CV and SWCV; impedance spectra recorded in 0.1M OBS solution and at -0.3 V vs Ag/AgCl.

References

[1] R. John and G.G. Wallance, J. Electroanal. Chem 306 (1991) 157-167