Application of Electrochemical Impedance Spectroscopy to Manganese-Modified Polypyrrole Thin Films for Electrochemical Capacitors

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Electrodeposition of Mn-modified polypyrrole (PPy) thin films has been successfully carried out using a potenstiotatic method. An appropriate step potential was chosen to deposit the thin film on a platinum substrate from electrolytes with different concentrations of pyrrole monomer and Mn^{2+} for electrochemical capacitor applications using an aqueous environment. The specific capacitance of the thin films (determined using cyclic voltammetry) prepared from 0.1 M Py+0.1 M Mn^{2+}; 0.01 M Py+0.01 M Mn^{2+}; 0.001 M Py+0.001 M Mn^{2+} were 63±6 F/g, 169±24 F/g and 2117±50 F/g, respectively. The thin films have been examined physically by atomic force microscopy (AFM), transmission electron microscopy (TEM), and profilometry analysis. However, to more fully complete electrochemical characterization of the thin film electrochemical impedance spectroscopy (EIS) has been employed.

The Mn-modified PPy thin films prepared in this work were examined using a combination of step potential electrochemical spectroscopy (SPECS) and EIS. Initially after preparation the thin film electrodes were rinsed thoroughly with water, and without being dried the electrode was then immersed into a 0.1 M K_2SO_4 solution, together with SCE reference and graphite counter electrodes. The experiment was controlled using the combination of a Solartron 1254 Frequency Response Analyzer and a Solartron 1287 Electrochemical Interface controlled by ZPlot software. From the open circuit potential of the thin films electrode (0.300 V) the potential was stepped in the anodic direction 25 mV, after which it was allowed to equilibrate for 10 minutes. After this, an impedance spectrum on the thin film electrode was measured using the frequency range 20 kHz to 0.1 Hz and a 10 mV excitation signal. This sequence was repeated to the upper potential limit (1.0 V versus SCE), down to the lower potential limit (0.0 V versus SCE), and then once more back up to the upper potential limit.

A discussion on this work will be presented. However, we present the EIS data of each the Mn-modified PPy thin films prepared in different concentration of pyrrole and Mn^{2+} in 0.1 M H_2SO_4. Figure 1 presents the impedance spectra data of the thin films. An appropriate equivalent circuit model was used to analyze the EIS data. By fitting the data we are able more fully understand the electrochemical mechanism on the thin films. This circuit should be able to model the electrified interface, which in reality is not ideal. As consequence, a constant phase element (CPE) was used to simulate a non-ideal double layer capacitance, instead of an ideal capacitance (C). Therefore, the equivalent circuit for this study consists of a series resistance (R1) in series with the parallel combination of a charge transfer resistance (R2) and a constant phase element (CPE1), as illustrated in Figure 2.

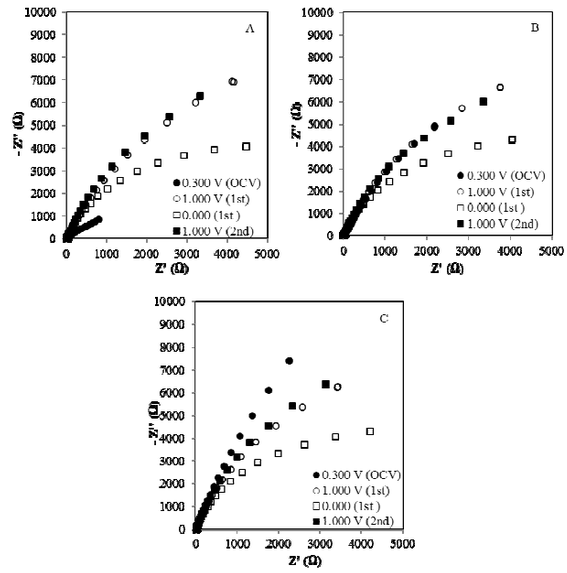

Figure 1. Electrochemical impedance spectra of the Mn modified PPy thin films prepared from [A] 0.1 M pyrrole+0.1 M Mn^{2+} [B] 0.01 M pyrrole+0.01 M Mn^{2+} [C] 0.001 M pyrrole+0.001 M Mn^{2+} in 0.1 M H_2SO_4

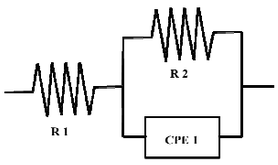

Figure 2. Equivalent circuit used for electrochemical impedance modelling.

References

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