

INDIGO CARMINE AS ELECTROLYTIC ADDITIVE FOR ELECTROCHEMICAL DOUBLE LAYER CAPACITORS

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Introduction

Multiwalled carbon nanotubes (MWCNT) are carbonaceous material with interesting properties such as high electronic conductivity, accessible surface area due to their marked mesoporous character, high stability and low mass density. These properties make them suitable materials for electrodes in supercapacitors [1, 2]. However, due to their low specific capacitance values, a variety of treatments have been proposed to increase them [3, 4].

In this work, the effect of incorporating an electrochemically active compound to the electrolyte of a MWCNT-based electrical double layer capacitor (MWCNT-EDLC) was evaluated. The aim of this work is to increase the specific capacitance values of the MWCNT-EDLC through the pseudocapacitive contribution of the redox reaction of this compound within the potential window of the cell.

Experimental

MWCNT were used as electrode material. The total surface area of the nanotubes, determined from the N_2 -adsorption isotherm using the BET equation, was $210 \text{ m}^2/\text{g}$ and the average pore size was 2 nm. Electrochemical tests were carried out using 0.05 M indigo carmine dissolved in 1 M H_2SO_4 (IC- H_2SO_4) as redox-active electrolyte, and 1 M H_2SO_4 for comparison. The electrochemical behavior of these two systems were tested in a Swagelok[®]-type cell using a glassy fibrous separator and a gold current collector. Disk types electrodes of 12 mm of diameter were prepared using 25 wt.% of polyvinylidene fluoride (PVDF) as binder and 75 wt.% of active electrode material. The electrodes were dried overnight before the cell assembly. The electrochemical measurements were conducted in a *Biologic* multichannel potentiostat. Galvanostatic charge/discharge ($1-88 \text{ mA}\cdot\text{cm}^{-2}$), cyclic voltammetry ($1-50 \text{ mV}\cdot\text{s}^{-1}$) and impedance spectroscopy ($1-100 \text{ kHz}$) experiments were used for the electrochemical characterization in a two-electrode configuration. The specific capacitance values of the electrode were obtained applying the following expression: $C = (2 I dt)/(m dV)$ to the galvanostatic cycles performed at constant current, I ; m is the mass of active material in the lightest electrode. Measurements were performed in an operating voltage window of 0-1 V. Also, synchronous experiments in a T-type Swagelok[®] cell and voltammetry experiments in a three-electrode cell, using Pt and Hg/Hg_2SO_4 as counter and reference electrode, respectively, were done to study the redox behavior of the

electrode/electrolyte pair. The effect of the long-term cycling on the cell constructed with IC- H_2SO_4 was studied by galvanostatic cycling at a current density of $8.8 \text{ mA}\cdot\text{cm}^{-2}$.

Results and Discussion

Fig. 1 shows the influence of the current density on the specific capacitance values determined from the galvanostatic experiments for the two electrolytes studied. The addition of IC to the supporting electrolyte caused a great improvement in the specific capacitance values. An increase by three (from 17 to 50 Fg^{-1}) was obtained at the lowest current densities, being the C_e values multiplied by two at greatest regimens.

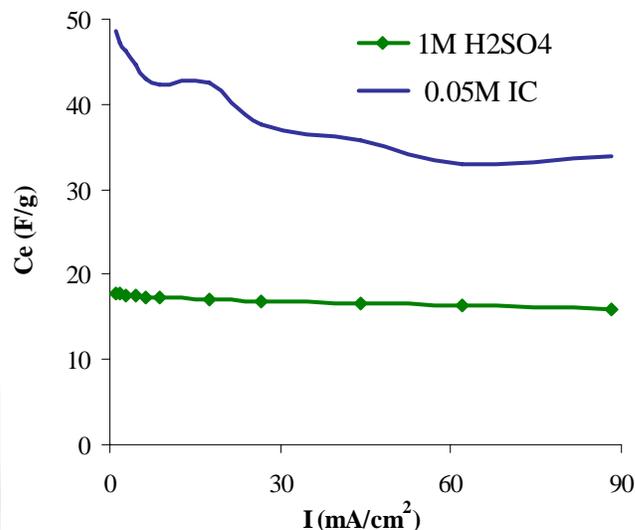


Fig. 1 Variation of the specific capacitance with the current density (two-electrode system).

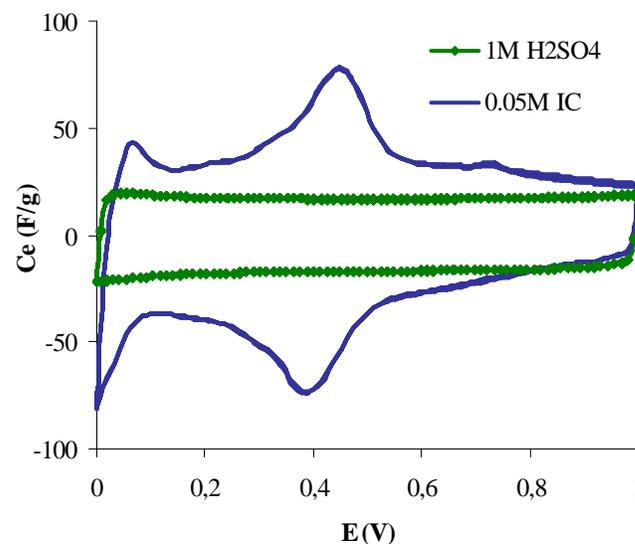


Fig. 2 Cyclic voltammetry performed at a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$ (two-electrode system).

The resistance of the electrochemical cell was not modified with the use of this novel redox-active electrolyte, as is reflected in the similar ESR values obtained for the two samples: $0.4 \Omega \cdot \text{cm}^{-2}$. The behavior observed in IC- H_2SO_4 can be ascribed to the redox reactions associated to the IC, as can be expected from the shape of the voltammetry cycles (Fig. 2) which show well-defined humps characteristic of a faradaic process.

For a deeper understanding of the role of IC in this system, cyclic voltammetry study was done in a three-electrode configuration in the operating voltage of the cell (from -0.73 to $+0.25$ V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$) (Fig. 3). A perfect rectangular voltammogram can be observed in the supporting electrolyte, characteristic of an ideal electric double layer capacitor. However, in the IC- H_2SO_4 media, the CV response exhibited a set of anodic and cathodic peaks, with high reversibility, associated to the oxidation/reduction of the IC (Scheme 1) [5]. It is interesting to note that the redox reactions occur both in the anodic and cathodic directions, which means that this pseudocapacitance is readily used in a symmetric cell.

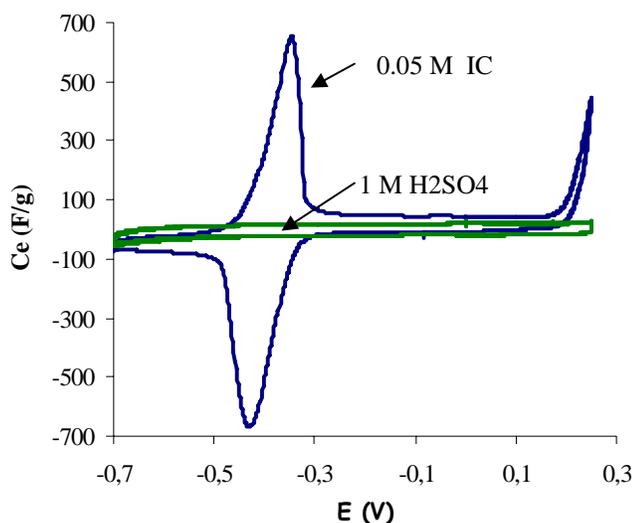
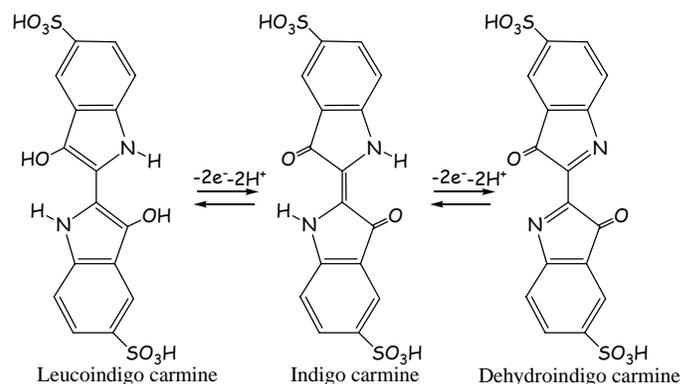


Fig. 3 Cyclic voltammograms in a three-electrode configuration at a scan rate of 1 mVs^{-1} .

A long-term cycling study was carried out in order to evaluate the suitability of the redox-active electrolyte over long periods of time. A moderate reduction in the initial specific capacitance values ($\sim 30\%$) after 10,000 galvanostatic cycles was observed. The main reduction occurring during the first 5,000 cycles. Then the capacitance values remain practically constant during the rest of the test. The initial loss of capacitance can be attributed to the reduction of the redox activity of the process situated at 0 V. The efficiency of the cell was close to 100 % during the study. It is important point out the high reversibility achieved with this innovative electrolyte.

Scheme. 1 Schematic electrodic processes of IC.



Conclusions

A new promising route to increase the specific capacitance of the carbon-based EDCL has been shown through the pseudocapacitive contribution of an electrochemically active compound dissolved in the supporting electrolyte.

A novel redox-active electrolyte obtained by dissolving IC in H_2SO_4 was tested. The faradaic reactions associated to the IC allowed increase at least by two the specific capacitance values of the cell. The resistance of the electrochemical cell was not significantly modified ($\text{ESR} \sim 0.4 \Omega \cdot \text{cm}^{-2}$ for the two electrolytes tested).

Long-term cycling experiments showed a rather good behavior, with a total loss of the initial capacitance values of 30% after 10,000 galvanostatic charge-discharge cycles. The efficiency of the cell was close to 100% during all the experiment.

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