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Enhancing energy density of carbon-based supercapacitors using Prussian Blue modified positive electrodes

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ABSTRACT

The modification of *MWCNTs* with Prussian Blue (PB) represents a significant improvement of the energy density values of asymmetric carbon based supercapacitors (CBSCs) in neutral media (KCl). The development of the faradaic processes associated with the presence of PB on the positive electrode increases not only the capacitance but also the operational voltage of these devices (up to 1.4 V) due to the high electrode potentials at which the Prussian Blue/Berlin Green (PB/BG) redox reactions occur. Accordingly, in asymmetric CBSCs assembled using an activated carbon as negative electrode and *MWCNTs* as the positive one, suitable modification of *MWCNTs* with PB increases the energy density of the device fivefold (from 1.46 to 7.68 W h kg^{-1}). The resultant system becomes an asymmetric hybrid device in which the energy is stored due to the double layer formation in the negative electrode and the development of the PB faradaic processes in the positive electrode, which acts as a battery.

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1. INTRODUCTION

Electric double layer capacitors (EDLCs) are considered as to be fast and efficient energy storage devices characterized by high power and good cyclability [1]. Carbon materials have been widely studied as electrodes for this application due to their low cost, good electric conductivity, high capacitance and ready availability [2]. However, the use of carbon-based supercapacitors (CBSCs) has been restricted in several applications by their low energy density values [3]. Consequently, in recent years, different strategies have been followed to improve the energy density of CBSCs by increasing either the capacitance (*C*) or the operational voltage (*V*) of the cell.

The use of high surface area [4–6] or pseudocapacitive electrode materials [7–10] and the incorporation of electrochemically active organic molecules into aqueous electrolytes [11–15] have been powerful tools for enhancing *C*.

On the other hand the use of organic solvents or ionic liquids [16,17] together with new asymmetric configurations [18–20] have proved to be effective methods for increasing *V*.

Recently our research group proposed a very efficient, low-cost and environmentally friendly methodology to increase both the capacitance and the operational cell voltage by using an inorganic redox electrolyte ($Ce_2(SO_4)_3/H_2SO_4$) in CBSCs [21]. In this system the positive electrode (*MWCNTs* or a modified graphite felt, *GF*) acts as a battery-type electrode (in which the redox reactions take place) while the negative electrode (an activated carbon, *AC*) retains its capacitor-like behavior. In short, the device can be considered an asymmetric/hybrid SC, because the active materials and the energy storage mechanisms of both electrodes are different [21,22]. It is for this reason that it is of interest to explore other redox active species as a way to increase the energy density of this type of devices.

Potassium ferrycianide, $K_3[Fe(CN)_6]$, has been widely studied in electrochemical applications due to its good electrochemical behaviour (i.e. its reversibility) associated with the ferry/ferrocianide redox reactions that take place at the electrode/electrolyte interface [23–26]. It is well-known that potassium ferrycianide forms Prussian Blue (PB) deposits in the presence of free iron ions in solution [27–29] or PB films on *MWCNTs*, where the Fe catalyst present in the carbon nanotubes is the source of such free iron ions [30]. Other sources of iron ions to form PB may arise from the slow hydrolysis of potassium ferrycianide. PB is a mixed-valent iron(II/III) hexacyanoferrate compound [31] which has two faradaic processes at 0.35 and 0.9 V *vs* Ag/AgCl/3.5 M KCl corresponding to the redox pairs Prussian White/Prussian Blue (PW/PB) and Prussian Blue/Berlin Green (PB/BG), respectively [32].

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Prussian Blue analogues have been investigated as electrode materials in supercapacitors in combination with other materials such as graphene oxide [33], conducting polymers [34,35] or metal oxides [36]. As the use of Prussian Blue involves the selection of electrolytes containing potassium ions, KCl is an interesting option, as it avoids the need to use the strong acidic or basic media [37]. Nonetheless, the evolution of chlorine needs to be taken into account.

The present study investigates the modification of three different carbon materials (an activated carbon, a modified graphite felt and *MWCNTs*) with Prussian Blue with the aim of increasing the energy density of CBSCs. The growth of the deposits was studied in detail on the *MWCNTs* electrodes. Furthermore the performance of the Prussian Blue modified *MWCNTs* as positive electrodes was evaluated in asymmetric hybrid devices built with an activated carbon as negative electrode and KCl as electrolyte. The cell voltage profile and the potential evolution of each electrode during the galvanostatic cycling of the device were simultaneously monitored by synchronous cyclic chronopotentiometry. The long-term stability of the system was evaluated up to 1,000 cycles by galvanostatic cycling.

2. EXPERIMENTAL

2.1. Reagents and materials

Three different carbon materials were investigated: an activated carbon (*AC*, $S_{BET} \approx 2{,}000\ m^2\ g^{-1}$) obtained in the laboratory by chemical activation of a commercial mesophase (AR24, *Mitshubishi Gas Chemical*) pitch with KOH (ratio KOH/pitch 3:1) at 700 °C for 1 h, under a N_2 flow of 62 mL min^{-1} [38]; commercial multi-walled carbon nanotubes (*MWCNTs*, $S_{BET} \approx 210\ m^2\ g^{-1}$, 1.9 wt % Fe, Sigma-Aldrich); and a modified graphite felt (*GF*), obtained from a commercial felt (RVG-2000, Mersen) after a thermal treatment at 1000 °C under a N_2 flow (150 mL min^{-1}) for 1 hour.

Disk-shaped electrodes (geometric area ≈ 1.13 cm^2) were prepared from *AC* and *MWCNTs* by mixing 90 wt % of the corresponding carbon material and 10 wt % of polytetrafluoroethylene (PTFE) as binder. In the case of *GF*, the electrodes were obtained directly by cutting out disks of similar dimensions with a puncher, without using any binder.

A solution of 0.1 M KCl was used as electrolyte. A solution of 0.1 M $K_3[Fe(CN)_6]$/1.0 M KCl was used to grow the Prussian Blue deposits. Both solutions were prepared daily by solving the suitable quantity of the corresponding salt (potassium chloride or potassium ferrycianide, Sigma-Aldrich) in distilled water.

2.2. Electrochemical experiments

The electrochemical behavior of the active electrode materials (*AC*, *MWCNTs* and *GF)* was initially studied in KCl by cyclic voltammetry (CV) using a three-electrode cell (Fig. S1A, Supporting Information). The cell consisted of an electrode of *AC*, *MWCNTs* or *GF* as the working electrode, Ag/AgCl/3.5 M KCl as reference electrode and a graphite rod as counter electrode. Equivalent experiments were performed in 0.1 M $K_3[Fe(CN)_6]$/1.0 M KCl, in order to evaluate the suitability of each carbon material for the formation of Prussian Blue deposits.

Modification of the *MWCNTs* through the formation of PB deposits was carried out in a "T-type" Swagelok® cell (Fig. S1B, Supporting Information) assembled using *AC* as the negative electrode and *MWCNTs* as the positive one (*AC/MWCNTs*). The mass ratio between both electrodes was (1:1). At the third-end connection an Ag/AgCl/3.5 M KCl reference electrode was incorporated, making it possible to determine the potential at which each of the electrodes was operating when a determined cell voltage was applied. A solution of 0.1 M $K_3[Fe(CN)_6]$/1.0 M KCl was used as electrolyte.

The electrochemical modification process consisted in a sequence of charge/discharge cycles by synchronous cyclic chronopotentiometric tests (GCPL) at 1.00 V and 17.7 mA cm^{-2} (up to 300 cycles). At the same time electrochemical impedance spectroscopy experiments (EIS, at 0.0 V; 1 mHz – 100 kHz; ±10 mV) were performed every 10 charge/discharge cycles to monitor the evolution of the cell resistance. The sample obtained after 300 cycles (*MWCNTs-PB*) was washed with ultrapure water.

The performance of the modified electrode (*MWCNTs-PB*) in CBSCs was evaluated in a similar system to that described above for the formation of the deposits. Two-three electrode asymmetric cells were assembled using *AC* as negative electrode, *MWCNTs-PB* as the positive one and 1.0 M KCl as electrolyte. Additional cells were prepared using *MWCNTs* as positive electrode for purposes of comparison. The mass ratio between the positive and negative electrode was again (1:1).

The cell voltage profile and the potential evolution of each electrode during the galvanostatic cycling of the device were simultaneous monitored by synchronous cyclic chronopotentiometric tests (GCPL, 17.7 mA cm^{-2}) at 1.0 V and at the maximum cell voltage permitted by the cells. Moreover, the long-term stability of the systems (up to 1,000 cycles) was evaluated by galvanostatic cycling between 0 V and the maximum cell voltage at a constant current density of 17.7 mA cm^{-2}.

The energy density (*E*) and power density (*P*) values together with the cell capacitance (*C*) and the efficiency of the charge/discharge processes (**ε**) were calculated by integrating the galvanostatic discharge profiles (avoiding the ohmic drop) [39] by applying equations (1)–(4) respectively to the discharge profiles

$$E = I \int V\, dt / m_t \quad (1)$$

$$P = E / \Delta t_d \quad (2)$$

$$C = 2\, I \int V\, dt / m_t\, (\Delta V_d)^2 \quad (3)$$

$$\varepsilon\ (\%) = (\Delta t_d / \Delta t_c)^{*}100 \quad (4)$$

where *I*/A is the current applied, $\int V\, dt$ /V s is the area under the discharge profile, m_t /g is the total mass of active electrode material in the cell, ΔV_d /V is the discharge voltage (avoiding the ohmic drop), Δt_d /s is the discharge time and Δt_c /s is the charge time.

All the electrochemical measurements were performed on a BioLogic VMP Multichannel Potentiostat at room temperature.

2.3. Characterization of the electrode materials

The quantity of PB deposited on the *MWCNTs* was determined by thermogravimetric analysis performed on a TA Instrument SDT 2960 thermobalance. 15 mg of sample (particle size under 200 μm) was placed on a platinum crucible and heated from 25 °C to 1000 °C using a heating rate of 10 °C min^{-1} and a nitrogen flow of 60 mL min^{-1}.

3. RESULTS AND DISCUSSION

3.1. Electrode materials selection

Hybrid systems are made up of two electrodes which store the energy through two different mechanisms [21,22]. One of the electrodes acts as a double layer capacitor (storing the ions of the

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