



High power density aqueous hybrid supercapacitor combining activated carbon and highly conductive spinel cobalt oxide



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HIGHLIGHTS

- Original conductive nano cobalt oxide is used in hybrid C/Co supercap.
- The positive/negative ratio was optimized.
- Best performances for a positive/negative weight ratio of 1.25.
- This system is among the best ones of its category (61.6 F g⁻¹).
- The system exhibits excellent electrochemical ageing over 3000 cycles.

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ABSTRACT

The remarkable electrochemical behavior of complete activated carbon/cobalt oxide cells is reported in the present work. Among the various weight ratios between the positive and negative electrodes evaluated, the best features are obtained with an overcapacitive cobalt oxide electrode. The energy densities obtained by this system (20 Wh kg⁻¹ for a power density of 209 W kg⁻¹) are twice higher than those measured for a activated carbon/activated carbon symmetric cell, in the same operating conditions. With discharge capacities around 62 F g⁻¹, this system is among the best ones reported in the literature for this category.

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1. Introduction

Numerous investigations on supercapacitors are focusing on increasing energy densities, in particular with the development of hybrid “metal oxide/activated carbon” supercapacitors [1]. We recently reported the potentialities of original nanometric conductive cobalt oxides, with spinel structure, as positive electrode of supercapacitor in alkaline medium [2,3]. These phases, which were synthesized by oxidizing precipitation of cobalt nitrate in a basic medium (T < 90 °C), exhibit a modified spinel - Co₃O₄

type structure, with protons, lithium and cobalt vacancies, as well as Co⁴⁺ ions in the octahedral trivalent cobalt network [4–6]. Such octahedral tetravalent cobalt ions entail electronic delocalization and very good electronic conductivity properties (5 × 10⁻⁴ S cm⁻¹, against 10⁻⁶ S cm⁻¹ for ideal Co₃O₄), which can still be improved by a controlled thermal treatment at a moderate temperature (200 °C), while keeping particle size and specific surface area (200 m² g⁻¹) suitable for electrochemical cycling [5,6].

These materials, mixed with additional organic binder and carbon black, were then conditioned as autosupported thin films, which were pasted on current collector, and then characterized by various electrochemical techniques (chronoamperometry, potentiometry, impedance spectrometry, cyclic voltametry), in a classical three-electrode cell configuration, filled with a 5M-KOH electrolyte [3]. The electrochemical properties of the materials were also

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evaluated in a cavity microelectrode. The overall results, based on combined electrochemical, X ray diffraction and microscopy studies of the electrodes, tend to prove that redox reactions take place during cycling at the very surface of the materials (on a depth in the range of 10 Å). With capacity values reaching 70 mAh g⁻¹ at 5 mV s⁻¹, our cobalt oxides compete favorably with other metal oxides reported in the literature as electrode materials for supercapacitors. Only a very small amount of added carbon black is necessary to get optimized capacities in the case of our materials (5% carbon added only against often more than 20% for the major part of studies reported in the literature for this kind of materials).

The work reported in this paper aims at evaluating the performances of complete hybrid cells assembling an optimized positive electrode based on our conductive spinel cobalt oxide, with a negative microporous active carbon electrode, in alkaline medium (5M-KOH). The combination of a positive electrode based on our cobalt oxides (electrochemically active between 0.1 and 0.7 V vs SHE) and of an activated carbon electrode, electrochemically active in the whole stability domain of water, should lead to a system exhibiting an electrochemical activity window higher than that reached for the cobalt material alone. Moreover, the activated carbon (AC)/nano-cobalt oxide hybrid system is expected to benefit from the different natures and advantages of its two electrodes: EDLC-type for the former one, which leads to a good behavior at high power and to an excellent cycle ability, and redox-type electrode for the latter one, which leads to a high capacity.

After a preliminary electrochemical evaluation of the two electrode materials in KOH electrolyte, the two electrodes will be balanced in order to determine the optimized configuration. Special attention will be paid to the electrochemical ageing.

2. Experimental

2.1. Material preparation

As described in detail in a previous paper [4], nano-spinel type cobalt oxide was prepared by precipitation at 90 °C of a cobalt salt in a 8M-KOH + 0.5M-NaOH + 0.5M-LiOH alkaline solution. Cobalt nitrate hexahydrate (Fluka) was dissolved into distilled water, mixed with hydrogen peroxide (Fluka) (with a Co(NO₃)₂:H₂O₂ molar ratio of 3:2), and then added drop-wise to the ternary alkaline solution to induce precipitation of the nanometric cobalt oxide. The suspension obtained was allowed to ripen for 4 h at 90 °C. Afterward, the precipitate was centrifuged and washed with distilled water until neutrality, and then dried at 60 °C for 24 h. As previously reported, X ray diffraction confirms the spinel structure of this material, with the presence of structural defects which are responsible for the good electronic conductivity observed (5 × 10⁻⁴ S cm⁻¹). The specific area of this material is close to 200 m² g⁻¹. The nanostructure of the material is illustrated in [Supplementary Fig. 1](#). The material is constituted of polydisperse agglomerates of nano-crystallites, with size of 5–10 Å.

Since cobalt oxide (positive electrode) was the main object of the present study, activated carbon (AC) for the negative electrode of the supercapacitor was not really optimized. Commercial activated carbon YP-17, provided by Kuraray (Japan), was selected for its good electronic properties and its high specific area (1600 m²/g).

2.2. Electrode preparation

As far as spinel nano cobalt oxide is concerned, a proper amount of powdered material, 5% in mass PTFE (Dupont de Nemours), and 5% of carbon black (conductive additive made of acetylene, 100% compressed, Alfa Aesar) were mixed with ethanol. The mixture was set as an autosupported film, in which a 11 mm-diameter disc was

cut and then pressed on nickel foam (current collector) at 100 MPa. The electrode was finally dried at 60 °C for 12 h. Electrodes based on activated carbon are prepared according to the same procedure, but without carbon black added.

2.3. Electrochemical characterization

The preliminary study reported in section 3.1 was performed with a three-electrode cell (classical corrosion cell from Radiometer Analytical, France), filled with a 5M-KOH electrolyte. The preparation of the working electrodes (cobalt oxide or activated carbon) is detailed just above. Platinum was used as counter electrode and HgO/Hg as reference electrode. Cyclic voltammetry was completed using a VMP3 potentiostat (Biologic).

The other electrochemical measurements were performed in a three-electrode Swagelok cell, because of its more optimized geometry. AgO/Ag was used as reference electrode. It should be noticed that the cells were not sealed, to avoid any overpressure hazard due to electrolyte oxidation.

3. Results and discussion

3.1. Preliminary study of the potential windows for activated carbon (negative electrode) and spinel cobalt oxide (positive electrode) in 5 M – KOH electrolyte

The potential window for the cobalt oxide was already discussed in details in a previous paper [3]. Voltammograms registered at 5 mV s⁻¹ between a minimum potential of –0.2 V and increasing maximum potentials (E_{max}) up to 0.80 V are shown in [Fig. 1a](#). As can be deduced from the integration of the cathodic branches, the cathodic capacity increases with E_{max} value. The coulombic efficiency, which maintains above 97% for E_{max} < 0.70 V, strongly decreases for higher potential values, due to the oxidation of water based electrolyte. Between –0.2 V and 0.72 V, which is the limit value beyond which the coulombic efficiency drops, the capacity obtained for the material is 73 mAh g⁻¹. Note that the open circuit potentials of both cobalt and carbon electrodes are close to 0 V vs NHE.

In the case of the activated carbon, the voltammograms were collected between a maximum potential of 0.3 V and minimum potentials (E_{min}) decreasing from –0.3 V down to –1.1 V, as shown in [Fig. 1b](#). The oxidation current observed above 0.3 V (vs NHE) for AC is known to be mainly due to carbon oxidation [7–9] leading to CO evolution. At the lowest potentials, below –1.0 V, the potential window of AC is limited by water reduction. Between –1.0 V and 0.3 V, the voltammogram exhibits a near-rectangular shape, with close absolute values of anodic and cathodic currents, which is characteristic of a pure capacitive behavior (double layer capacity), reversible in this potential range [10]. The anodic capacity is around 54 mAh g⁻¹. This is the interesting parameter, from the application point of view, since activated carbon is intended to be used at the negative electrode of the target hybrid supercapacitor i.e. it will work in oxidation during the discharge of the supercapacitor. It should be noticed that the voltammetry curves exhibit an increase of the anodic current when the electrochemical window is enlarged towards the lowest potentials (for E_{min} ≤ –0.9 V), while the cathodic current remains quite stable. As shown by Jurewicz et al., polarizing the activated carbon electrode below the thermodynamic stability potential (–0.87 V in 5M-KOH) leads to produce hydrogen, which is not directly released, but adsorbed in the carbon micropores [11], and then reversibly oxidized during the anodic step. Such a process causes the observed increase of the anodic current. In addition, the lower the polarizing potential, the higher the produced hydrogen amount, and the higher the anodic

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