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Original Conductive Nano-Co₃O₄ Investigated as Electrode Material for Hybrid Supercapacitors

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Cobalt oxides have been extensively used as conductive additives for Ni-MH batteries. We report in this paper the performances of an original nanometric cobalt oxide, close to Co₃O₄, as electrode material for hybrid supercapacitors. This spinel type phase contains hydrogen, lithium, cobalt vacancies, and especially Co⁴⁺ ions within the structure, leading to a high electronic conductivity. Cyclic voltammetry and impedance spectroscopy measurements show interesting capacitance (320 F/g in 8M-KOH), as well as good electrochemical cycling with a small amount of carbon black (5%).

Among the various systems allowing to store electrical energy, supercapacitors are energy storage devices that fill the gap between batteries (lithium-ion or nickel-metal hydride for instance), which are able to supply high energy but intermediate power, and conventional capacitors, which are characterized by low energy density but high power. Between the two, supercapacitors, also called as electrochemical capacitors, can supply high discharge currents (higher than batteries) over several seconds (longer than capacitors).¹ Supercapacitors were first developed in the late 1950s, but they have been booming only in the early 1990s with the development of large-size applications in the military, aerospace, aviation and transport fields (especially hybrid vehicle and trolley). Nevertheless, although supercapacitors could respond to the power required for such applications, they suffer for now from too low energy density (about 5 Wh/kg).

Beside the work on electrochemical double layer capacitors (composed of two carbon-based electrodes), another way to improve the energy density is to develop hybrid supercapacitors. These systems combine a classical capacitive electrode with a battery electrode, leading to a faradic energy storage through a redox reaction. This approach was initiated by Amatucci et al. in 2001 with a Li₄Ti₅O₁₂/activated carbon device.² Such asymmetric cells are very encouraging since the specific pseudo-capacitance exceeds that of carbon materials using double layer charge storage. Nevertheless, because of the redox reaction, hybrid supercapacitors often suffer from a lack of stability during cycling.

Among these systems, RuO₂-based electrochemical capacitors exhibit the highest capacitance,³ more than 700 F/g, but their cost limits the applications to small electronic devices. Less expensive oxides such as cobalt oxides,⁴ MnO₂,⁵⁻⁷ V₂O₅,⁸ Fe₃O₄,⁹ NiO,¹⁰ as well as electrically conducting polymers,¹¹ have been extensively studied in the past decades. But no system has been investigated as much as the C/MnO₂ one, which is particularly interesting because (i) it can work in aqueous media at potentials up to 2 V, and (ii) high stability in ageing has been demonstrated; capacitances from 100 to 300 F/g are usually obtained.⁵⁻⁷

Many surveys have been carried out on cobalt oxides as materials for energy storage; in particular they were shown to be effective as conductive additives for the positive electrode of Ni-MH batteries.^{12,13} In this context, conductive cobalt oxides, prepared by electrochemical oxidation of CoO, and exhibiting a spinel structure close to Co₃O₄, were developed several years ago in ICMCB.¹⁴ Co₃O₄ exhibits generally the normal cubic spinel structure (space group Fd3m) and is insulating. Its structure can be described as a three-dimensional network of Co³⁺ ions in octahedral sites (16d), with empty channels in the 3 space directions; Co²⁺ ions being located in tetrahedral sites (8a), at the intersection of the channels. The conductive cobalt oxides prepared in ICMCB contain hydrogen

and lithium within the structure and exhibit a high electronic conductivity (up to 10⁻¹ S.cm⁻¹ at room temperature). This property is mainly explained by the presence of Co⁴⁺ ions, which ensure a charge balance when lithium or hydrogen is substituted for Co²⁺ or Co³⁺, and allow an electronic delocalization in the octahedral network, improving therefore the conductivity.

Recently, phases with compositions close to the latter ones (exhibiting typical formula such as H_{0.60}Li_{0.19}Co_{2.62}O₄),¹³ but with a nanometric texture, were prepared in ICMCB.¹⁵ These materials, named nano-Co₃O₄ in the following, are synthesized by precipitation at low temperature in various alkaline media. They also show a high electronic conductivity due to the presence of lithium, hydrogen and cobalt vacancies. Thanks to a high conductivity and a high specific surface induced by the nanometric dimensions, these nano-Co₃O₄ phases are promising candidates as electrodes materials for hybrid supercapacitors. This paper will focus on the synthesis, the characterization and the electrochemical properties of a nano-Co₃O₄ phase prepared in a ternary medium composed of KOH, NaOH and LiOH.

Experimental

Nano-Co₃O₄ powder was prepared at 90°C by precipitation of a cobalt salt in the following alkaline solution: 8M-KOH + 0.5M-NaOH + 0.5M-LiOH. Cobalt nitrate hexahydrate (Fluka) was dissolved into distilled water, mixed with hydrogen peroxide (Fluka) with a ratio 3:2, and then added dropwise to the ternary solution to induce precipitation of the nanometric cobalt oxide. The obtained solution was ripened for 4 h, washed with distilled water, and finally dried at 60°C for 24 h. Reference high temperature Co₃O₄ (HT-Co₃O₄) was obtained from thermal treatment of cobalt carbonate (Alfa Aesar), at 450°C under an oxygen flow for 15 h.

X-Ray Powder Diffraction patterns were recorded on a Philips Panalytical X'Pert Pro diffractometer using cobalt K_α radiation in the 10–110° 2θ range. TEM pictures were recorded on a JEOL JEM-2200 FS microscope at an accelerating voltage of 200 kV. Chemical analysis was performed by Inductive Coupled Plasma (ICP) for Co, Li, Na, K titration, and by elementary analysis for H and C titration. The average oxidation state of cobalt was determined by the iodometric titration method. Electronic conductivity was measured with the four-probe technique,¹⁶ using a direct current at room temperature, on 8 mm-diameter pellets, which were obtained by compacting around 200 mg of powder at 8 t/cm². Because of their low-temperature synthesis, the materials could not be sintered.

Electrochemical performances were evaluated in a three-electrode cell (classical corrosion cell from Radiometer Analytical, France), filled with an 8M-KOH electrolyte. Platinum was used as counter electrode and HgO/Hg as reference electrode. The working electrode was prepared by mixing nano-Co₃O₄ powder, 5% PTFE (Dupont de Nemours), and from 0 up to 20% of carbon black (conductive additive made of acetylene, 100% compressed, Alfa Aesar) with ethanol. The mixture was set as an autosupported film, in which

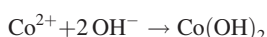
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a 11 mm-diameter disc was cut and then pressed on nickel foam (current collector) at 100 MPa; the electrode was finally dried at 60°C for 12 h. A typical electrode is around 200 μm thick, has porosity close to 10%, and density close to 4.9 g.cm⁻³. Electrochemical impedance spectroscopy and cyclic voltammetry were completed using a VMP3 potentiostat (Biologic). Impedance tests have been carried out at 0 V between 10 mHz and 200 kHz. Cyclic voltammetry was performed at 5 mV/s between -0.5 and 0.65 V.

Results and Discussion

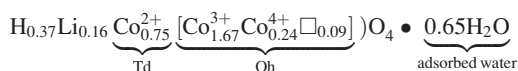
As it has been shown by Pourbaix et al.,¹⁷ the existence domain of Co₃O₄ in a potential-pH equilibrium is very limited, which explains that its formation requires very specific conditions. Indeed, the process includes both hydroxylation and oxidation of the initial Co²⁺, involving the following reactions



The number of steps occurring in the formation of nano-Co₃O₄ is not clearly demonstrated, but cobalt hydroxide β(II)-Co(OH)₂ and oxyhydroxide β(III)-CoOOH appear as intermediate species. However, the presence of these two phases as impurities in the final material can be avoided by adjusting the precipitation conditions, especially using a fast addition of cobalt nitrate, which suggests that the formation of Co₃O₄ is kinetically promoted.

The XRD patterns of such a nano-Co₃O₄ phase (Fig. 1a) is compared to that of reference HT-Co₃O₄ (Fig. 1b), which has a structure close to ideal Co₃O₄. Both patterns can be indexed on the basis of a normal cubic spinel structure (Fd-3m space group) and confirm the presence of a pure nano-Co₃O₄ phase, without any β(II)-Co(OH)₂ or β(III)-CoOOH impurity. The pattern of nano-Co₃O₄ exhibits very broad diffraction peaks, in accordance with the presence of nanometric coherent domains. By applying Scherrer's formula on the four most intense peaks ((220), (311), (511) and (440)), the size of these domains can be estimated to be between 10 and 13 nm. This matches perfectly with the TEM measurements (Fig. 1c), which reveals crystallites from 5 to 15 nm. Furthermore, an inversion of the line intensity ratio (220)/(111) can be noticed on Fig. 1 between nano-Co₃O₄ and the reference phase. It could be explained by the presence of cobalt vacancies in the structure of the nano-material, as discussed elsewhere.^{13,18}

Chemical analysis (ICP and elementary analysis), cobalt oxidation state titration and crystal refinement (using the FullProf program¹⁹ with the Rietveld method²⁰) were used to establish the chemical formula of the material. ICP reveals that carbon, nitrogen, sodium and potassium amounts are negligible. It shows the presence of lithium in the compound (0.47 mass %) and reveals that the cobalt amount is lower than that in ideal Co₃O₄ (64.9 instead of 73.4 mass %), which can be correlated with the presence of water and/or cobalt vacancies in the structure. The Rietveld refinement of the structure highlights indeed the presence of cobalt vacancies in both tetrahedral and octahedral sites. In addition, the average oxidation state of cobalt is higher in this nano-material (2.81) than in the ideal spinel (2.67), which was correlated to the presence of Co⁴⁺ ions.^{15,21} On the basis of these results, and if it is assumed that H and Li are in tetrahedral sites, according to similar results obtained on micrometric cobalt oxides,²¹ and that Co⁴⁺ ions are more stable in octahedral sites, such a typical formula can be written for nano-Co₃O₄



According to this formula, proton and lithium ions are too numerous to be only located in the vacant tetrahedral sites of the spinel struc-

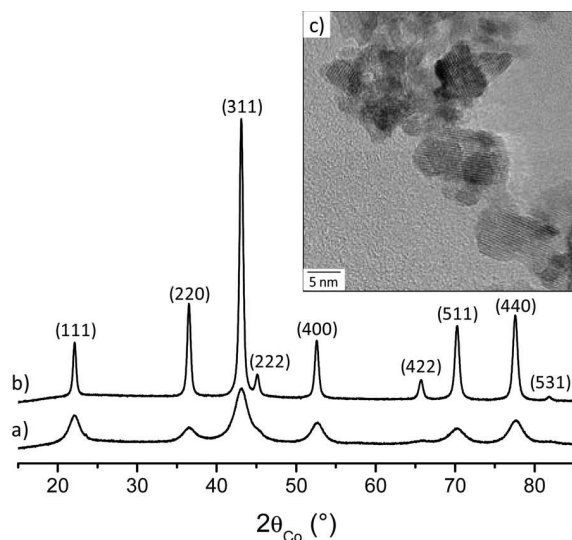


Figure 1. X-ray diffraction patterns of nano-Co₃O₄ (a) and reference HT-Co₃O₄ (b), with indexations in the Fd-3m space group. (c) TEM picture of a nano-Co₃O₄ suspension in water (magnification: X 400 000).

ture (0.25/molecule), and might also occupy the other tetrahedral sites of the cubic structure (8b or 48f). Anyway, it should be noticed that this material exhibits nanometric dimensions, with a large amount of atoms at the surface of particles, so that the formula can only be considered as an average over the whole powder.

A comparison of the electronic properties of nano-Co₃O₄ ($\sigma = 3.2 \cdot 10^{-4} \text{ S.cm}^{-1}$ at room temperature) and HT-Co₃O₄ ($\sigma = 7.3 \cdot 10^{-7} \text{ S.cm}^{-1}$) confirms that the conductivity of the nanometric cobalt oxides is much higher (more than three orders of magnitude at room temperature) than that of bulk material. As discussed in previous papers,^{13,18} substitution of H and Li for Co in the tetrahedral sites is compensated by the presence of some Co⁴⁺ (d⁵) ions in the octahedral network of the Co³⁺ (d⁶) ions, which induces holes in the t_{2g} band, resulting in an overlapping of the t_{2g} orbitals of cobalt ions within the octahedral network. Electronic delocalization, restricted to domains surrounding the Li and H defects, occurs, entailing high electronic conductivity.

Electrochemical performances of nano-Co₃O₄ were evaluated by means of cyclic voltammetry and electrochemical impedance spectroscopy. The amount of carbon black was optimized by testing electrodes containing from 0 up to 20% of additive. The resulting voltammograms (Fig. 2a) show a reversible redox behavior. They also reveal that the oxidation peaks are hidden by the oxygen evolution (which appears from 0.6 V vs. HgO/Hg)²² and that the addition of carbon black tends to widen the curve shape. This trend is confirmed by the evolution of the discharge capacity, determined by integrating the cathodic peaks, and presented in Fig. 2b. First, it can be noticed that the addition of only 5% of carbon black enables to increase the initial capacity by more than 70% (from 35 to 60 mA.h/g). Then, this discharge capacity keeps rising up to 15% of carbon black. These results are in accordance with the Bode diagram in Fig. 3, which shows the frequency dependence of the impedance of electrodes made with different amounts of conductive additive. Indeed, a constant decrease of the low frequency impedance can be noticed while increasing carbon black amount, which can be explained by an improvement of the ionic conductivity. The addition of carbon black enhances the electrochemically active surface accessibility by inducing percolation network, so that the capacity is increased. This effect is more significant at middle and low frequencies (< 100 Hz), where the influence of mass transport is predominant, whereas high frequency impedance is mostly driven by the electrolyte bulk resistance, which is highly cell geometry dependent. For 20% of carbon black, the capacity is lower than for 15%; this

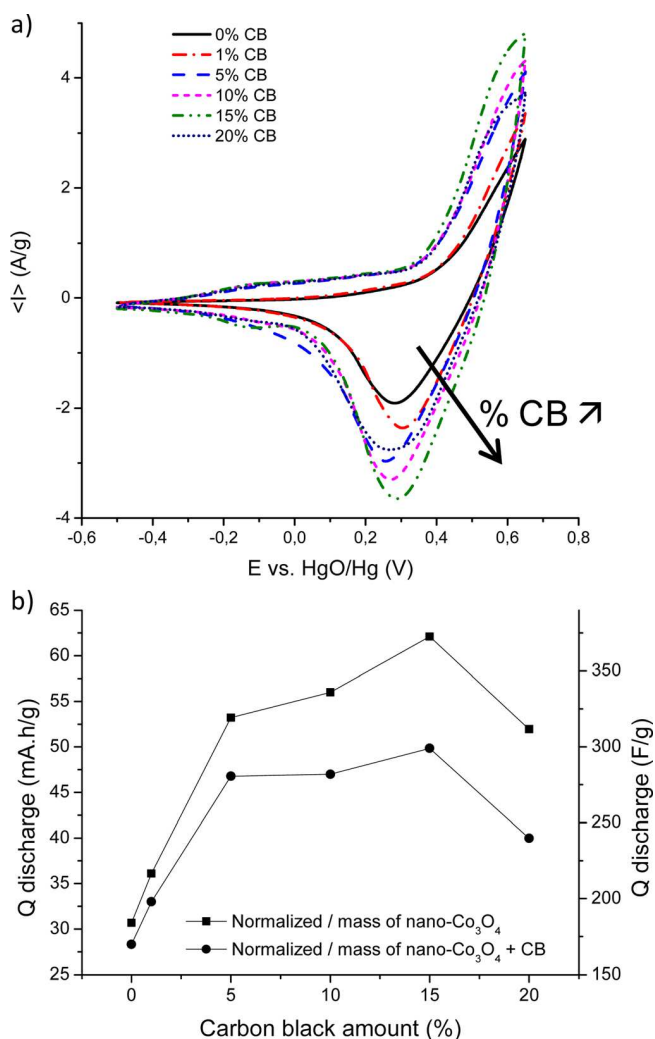


Figure 2. (Color online) (a) Cyclic voltammograms (5th cycle) at 5 mV/s in 8M-KOH of nano-Co₃O₄ electrodes containing from 0 up to 20% of carbon black (CB). Potential is relative to the HgO/Hg reference electrode and current is normalized to the weight of nano-Co₃O₄ alone. (b) Discharge capacities of the latter electrodes, normalized to the active material weight (nano-Co₃O₄ alone) and to the total material weight (nano-Co₃O₄ + carbon black).

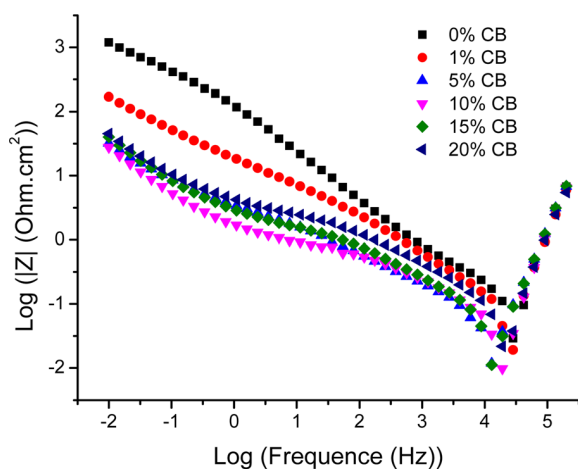


Figure 3. (Color online) Electrochemical impedance spectroscopy performed at a bias voltage of 0 V, after 5 cycles (cyclic voltammetry) at 5 mV/s in 8M-KOH, on electrodes made of nano-Co₃O₄ and containing from 0 up to 20% of carbon black (CB).

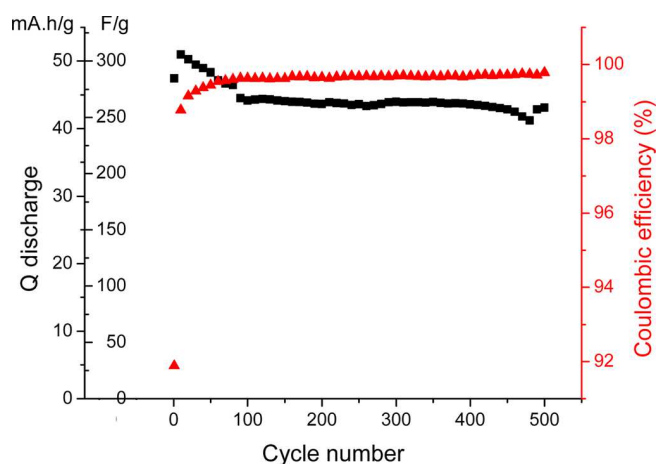


Figure 4. (Color online) Evolution of the discharge capacity ■ and of the coulombic efficiency ▲ over 500 cycles, between -0.5 and 0.65 V, for an electrode made of nano-Co₃O₄ and containing 5% of carbon black. Values were extracted from a cyclic voltammetry measurement performed at 5 mV/s in a 8M-KOH + 0.5M-NaOH + 0.5M-LiOH electrolyte.

behavior is probably due to the hydrophobicity of carbon black, which is not compensated by the grain percolation any more. Finally, the best performances are reached for 15% of additive. However, as presented in Fig. 2b, if the capacity is normalized to the total active material weight (cobalt oxide + carbon black), and not only to the mass of cobalt oxide, the compositions between 5 and 15% give almost the same results in terms of specific capacity.

The studied nanometric cobalt oxides exhibit also satisfying electrochemical ageing properties, as compared with literature which reveals that from 75 to 95% of the initial capacity is usually retained after 500 cycles on cobalt oxides materials.^{23–25} As shown in Fig. 4, an electrode made of nano-Co₃O₄ with 5% of carbon black was evaluated in 8M-KOH + 0.5M-NaOH + 0.5M-LiOH at 5 mV.s⁻¹; it revealed that more than 85% of the initial capacity was retained after 500 cycles. Furthermore, Fig. 4 reveals a coulombic efficiency very close to 100%.

A capacity Q (mA.h/g) can be converted to a capacitance C (F/g) over a voltage U (V), thanks to the following formula: $C = \frac{3.6Q}{U}$. Thus, the obtained capacity of 60 mA.h/g is equivalent to 320 F/g over 0.6 V. This capacitance is much greater than those obtained for many oxide-based electrode materials, such as MnO₂ (100–300 F/g),^{5–7} Fe₃O₄ (75 F/g) (Ref. 9) or NiO (138 F/g).¹⁰ It is also in the same magnitude as the capacitance of other reported cobalt oxides, which is ranging from 110 F/g for powders prepared by hydrothermal synthesis,²⁵ to 570 F/g for nanorods synthesized by chemical deposition.²⁶

Conclusion

Conductive spinel-type cobalt oxides were prepared in a low temperature precipitation process. Nano-Co₃O₄ obtained exhibits quite high electronic conductivity and interesting electrochemical properties, which enable the use of such active material as electrodes for supercapacitors. Specific capacities close to 60 mA.h/g (or 320 F/g over 0.6 V) were reached with only 5% of carbon black, making them promising among other electrode materials for hybrid supercapacitors.²⁷ Nevertheless, ongoing studies are carried out to go further toward a better understanding of charge transport mechanisms. Enhanced active materials in terms of capacity and capacitance will be got.

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