



Electrochemical storage mechanisms in non-stoichiometric cerium oxide/multiwalled carbon nanotube composites



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ARTICLE INFO

Article history:

Received 5 February 2016

Received in revised form 4 May 2016

Accepted 6 May 2016

Available online 10 May 2016

Keywords:

Cerium oxide/carbon nanotube composites

Electric Double Layer Capacitors

Charge storage mechanisms

Square wave voltammetry

Deconvolution analysis

ABSTRACT

Cerium oxide/multiwalled carbon nanotube composites with different oxide loadings (5–60 wt. %) were prepared by sol-gel deposition of the oxide onto the carbon support. The morphology, texture and surface properties of the prepared materials were studied and correlated with their electrochemical behavior. The different charge storage mechanisms occurring on the surface of the composites were successfully identified by a newly developed electrochemical method, namely the combination of sweep wave voltammetry with deconvolution analysis in 1 M H₂SO₄. The deposition of moderate oxide loadings (up to 10 wt. %) leads to small and well distributed oxide particles on the nanotubes surface. Therefore, the appearance of defects on the oxide structure is favored, promoting both electronic conduction and faradaic activity. Curiously, cerium oxide loadings above 10 wt. % induce a higher dispersion of the carbon support. This convenient synergism enhances the electroactive area of the composites by increasing molecular diffusion.

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1. Introduction

The use of transition metal oxides as active components for electric double layer capacitor (EDLC) electrodes has been actively explored due to their high reactivity and stability [1]. Cerium, an environmentally friendly and relative low cost metal, is one of the most reactive elements in the lanthanide series. Cerium oxide crystallizes preferentially as CeO₂ (ceria) since Ce⁺⁴ is the most favorable oxidation state for this element. Due to the low ionization potential of the Ce 4f electrons, a continuous range of partially reduced phases CeO_{2-x} (0 < x < 0.5) can co-exist within the oxide structure, lending a high faradaic activity to ceria [2]. The reduction of Ce⁺⁴ to Ce⁺³ is accompanied by the loss of negatively charged oxygen atoms from the oxide lattice [3,4]. The vacancies thus generated play an important role in the oxide properties since they are associated with oxygen mobility (catalysis applications [5–7]) and electronic conduction (n-type semiconductor [4,8]) throughout the solid structure. Despite all these advantages, transition metal oxides frequently suffer from conductivity problems, agglomeration and degradation during cell operation

[9]. Thus, both the rational design of EDLC electrodes and the exploration of novel materials are key points for further progress in energy storage technologies. Previous works have studied the benefits of coupling the outstanding redox properties of cerium oxide with the stability/conductivity of carbon materials [10–14]. Nevertheless, due to the limitations of conventional electrochemical analysis, the different charge storage mechanisms occurring on a given electrode have not been studied in detail. The development of novel methods in order to determine the specific contribution of each storage mechanism is a big challenge. The energy storage in hybrid EDLCs takes place through two different mechanisms; capacitive and pseudocapacitive charge storage. The former consists in electrostatic adsorption of electrolyte ions on the electrode surface (Helmholtz double layer formation) whereas the latter arises from effective charge transfer at the electrode interface. The formation of the double layer is a surface limited and fast process, while pseudocapacitance presents diffusional control and slow kinetics. On that basis, Conway et al. [15] developed a voltammetric analysis to quantitatively separate both currents by fitting the dependence of the current versus the scan rate to a diffusion model. Dupont et al. [16] presented a more sophisticated quantitative method, considering both the kinetic and diffusional limitations of the pseudocapacitive current. They demonstrated that step potential electrochemical spectroscopy

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(SPECS) can be used to separate the different phenomena occurring during the electrodes cycling. To this end, the electrode is charged in a series of small potential steps and is allowed to equilibrate during a certain period of time. The current after each charging step decays quickly for capacitive processes but slowly for redox reactions. Thus, the residual current at the end of the pulse will correspond to effective charge transfer phenomena. Bearing this in mind, they succeeded in separating those storage mechanisms by performing SPECS and modeling the current response. To the best of our knowledge, an electrochemical method enabling both a qualitative and quantitative study of the different storage contributions has never been reported. Here, we have used square wave voltammetry (SWV) to separate the electric double layer capacitance from the pseudocapacitance. Subsequently, a deconvolution analysis was performed in order to identify the different faradaic phenomena on the electrode surface. Although it is true that SWV has been widely used for electrochemical analysis [17,18], it is not usually used for energy storage applications. This technique has the same fundamentals as SPECS but the electrode is charged-discharged subsequently in the same potential step [19,20]. Therefore, the pore/surface blockage that could eventually occur during SPECS is eliminated. Thus, if any species is formed during oxidation/reduction it will be readily dissolved in the reverse pulse. On the other hand, SWV counts with fast acquisition times allowing higher sweep rates (1 V/s) than SPECS. The aim of the present work is to provide an in depth understanding of the different electrochemical storage mechanisms in CeO₂/carbon nanotube composites by using this novel analysis methodology.

2. Experimental

2.1. Samples preparation

CeO₂/carbon nanotube composites with different ceria loadings were prepared by using commercial Nanocyl 3100 MWCNTs as support (CNT sample) and cerium (III) nitrate [Ce(NO₃)₃·6H₂O] as ceria precursor. The CNT were dispersed in different aqueous solutions with adequate cerium nitrate concentrations in order to achieve nominal ceria loadings of 5, 10, 20, 40 and 60 wt. %. The mixtures were stirred at room temperature until solvent evaporation (3 days) to promote the hydrolysis/condensation of Ce(NO₃)₃ [6]. The thus obtained composites were designated as CeCNT_x series where x is the theoretical amount of deposited ceria. Pure cerium oxide was prepared by dissolving 15 g of Ce(NO₃)₃·6H₂O in 100 mL of H₂O, followed by the dropwise addition of a sodium hydroxide solution (200 mL, 3 M) under continuous stirring [7]. The suspension was shaken for 5 h at room temperature, filtered and thoroughly washed with distilled water. The pure cerium oxide was denoted as CeO. All the materials were dried at 100 °C during 24 h and annealed at 400 °C during 4 h under N₂ flow (100 cm³/min). Prior to characterization and electrochemical measurements, the samples were ball-milled at 15 vibrations/s during 240 min in a Retsch MM200 equipment and sieved to a particle size below 100 μm.

2.2. Characterization

The textural properties of the prepared materials were determined by N₂ adsorption-desorption isotherms at -196 °C on an IQ2 volumetric adsorption analyzer (Quanta chrome). Before measurements, the samples were degassed at 150 °C during 12 h under vacuum. The BET surface area (S_{BET}) was calculated according to the BET model from the adsorption isotherms in the relative pressure range of 0.05–0.25. The α_t method was used to obtain the micropore volume [21] in the relative pressure range of 0.1–0.25. The relative amount of metal oxide in the composite

was determined by thermogravimetric analysis under air in a STA 409 PC/4/H Luxx Netzsch thermal analyser. XPS analysis was performed using a Kratos AXIS Ultra HSA, with VISION software for data acquisition. The analysis was carried out with a monochromatic Al Kα X-ray source (1486.7 eV), operating at 15 kV (90 W), in Fixed Analyser Transmission (FAT) mode, with a pass energy of 40 eV for regions of interest and 80 eV for survey. Data acquisition was performed with a pressure lower than 10⁻⁶ Pa and with a charge neutralization system. The binding energies were calibrated by reference the C1s peak (284.6 eV). Deconvolution of spectra was performed using the XPS Peak program and peaks were fitted to a Gaussian-Lorentzian function (80/20) and using a Shirley type background subtraction. The compositions (expressed as wt.%) were determined from the survey spectra by considering the integrated areas of the main XPS peaks assigned to the different elements (C_{1s}, O_{1s} and Ce_{3d}) and their respective sensitivity factors. The proportion of Ce⁺³ on the composites surface was determined by Eq. (1):

$$Ce(III)\% = \frac{100 \times [A(v_o) + A(v') + A(u_o) + A(u')]}{\sum [u + v]} \quad (1)$$

where $\sum [A(X)]$ is the sum of the areas of the peaks corresponding to Ce⁺³ and $\sum [u + v]$ is the sum of all the peaks in the Ce_{3d} spectra. X-ray diffraction (XRD) analysis was performed in a PANalytical X'Pert MPD equipped with an X'Celerator detector and secondary monochromator (Cu Kα λ = 0.154 nm, 50 kV, 40 mA). Rietveld refinement with PowderCell software was applied for identification of the crystallographic phases. The crystallite size was calculated by the Williamson-Hall model [22]. SEM-EDS analysis was performed using a high resolution Environmental Scanning Electron Microscope (Schottky) with X-Ray Microanalysis and Electron Backscattered Diffraction analysis (Quanta 400 FEG ESEM/EDAX Genesis X4 M).

2.3. Electrochemical measurements

A paste was prepared by mixing 80 wt.% of the prepared samples and 20 wt.% of PTFE in absolute ethanol. The electrodes were obtained by pressing 17 mg of the paste in a mould with 1 t during 15 s. The as-obtained circular pellets (1 cm²) were sandwiched in a stainless steel mesh (w/w %: 67.77% Fe, 0.08% C; 0.04% P; 1.95% Mn; 0.50% Si; 0.03% S; 10.30% Ni; 17.65% Cr; 1.68% Mo) by pressing with 5 t during 15 s. The counter electrode was prepared in the same manner but using 30 mg of paste prepared with Norit DLC Supra 50® as active component. All the prepared electrodes were vacuum-degassed for 4 h at 120 °C, soaked into the electrolyte and kept immersed into the solution during 1 day. The electrochemical behaviour of the prepared carbons was studied in a beaker-type cell in 1 M H₂SO₄ with an Ag/AgCl (KCl 1 M) reference electrode. Both the working and counter electrodes were arranged in a stack, separated by filter paper and connected to two Pt wires as current collectors. Nitrogen gas was bubbled into the electrolyte for 15 min prior to the measurements to remove any O₂ present into the electrolyte solution. The electrochemical characterization was performed on an Autolab (PGSTAT302N) potentiostat controlled by Nova 1.10 software. Cyclic voltammetry (CV) measurements were performed at 10 mV/s and in a voltage window from -0.3 to 0.7 V. The Square Wave Voltammetry (SWV) measurements were performed using a step potential of 0.001 V and fixing the amplitude and the frequency to 0.01 V and 1 Hz, respectively. The potentials for each proposed pseudocapacitive phenomena were calculated according to the Nernst equation:

$$E = E_0 + \frac{RT}{nF} \log \frac{[Ox]}{[Red]} \quad (2)$$

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