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Understanding $RuO_2{\cdot}xH_2O$/carbon nanofibre composites as supercapacitor electrodes

F. Pico[a], J. Ibañez[b], M.A. Lillo-Rodenas[c], A. Linares-Solano[c],
R.M. Rojas[a], J.M. Amarilla[a], J.M. Rojo[a,*]

[a] *Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Cientificas (CSIC), Cantoblanco, Sor Juana Ines de la Cruz 3, E-28049 Madrid, Spain*
[b] *Centro Nacional de Investigaciones Metalurgicas, CSIC, Avda Gregorio del Amo 8, E-28040 Madrid, Spain*
[c] *MCMA, Departamento de Quimica Inorganica, Universidad de Alicante, P.O. Box 99, E-03080 Alicante, Spain*

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Abstract

Composites made from $RuO_2{\cdot}xH_2O$ particles supported on carbon nanofibres (CNF) have been prepared for supercapacitor electrodes. CNF, produced by Grupo Antolin Ing. SA. using a floating catalyst procedure was treated either in HCl or in HNO_3. Then the composites were obtained by impregnation of CNF with an aqueous $RuCl_3{\cdot}0.5H_2O$ solution followed by filtering and alkali solution treatment. Heat treatment at 150 °C for 2 h was done. Specific capacitance of the composites has been measured and discussed on the basis of their $RuO_2{\cdot}xH_2O$ content and $RuO_2{\cdot}xH_2O$ particle size. The composites having $RuO_2{\cdot}xH_2O$ contents below 11 wt% show $RuO_2{\cdot}xH_2O$ particles, which grow from 2 to 4 nm as the $RuO_2{\cdot}xH_2O$ content increases. The specific capacitance of supported $RuO_2{\cdot}xH_2O$, which can be very high (up to $840\,F\,g^{-1}$), decreases as the $RuO_2{\cdot}xH_2O$ content increases and $RuO_2{\cdot}xH_2O$ particles grow. The composites having $RuO_2{\cdot}xH_2O$ contents above 11 wt% show $RuO_2{\cdot}xH_2O$ particles of nearly constant size (4 nm); the effect of increasing the $RuO_2{\cdot}xH_2O$ content is to increase the amount of particles but not the size of the particles. In these composites the specific capacitance of supported $RuO_2{\cdot}xH_2O$ is nearly constant ($440\,F\,g^{-1}$) and close to bare $RuO_2{\cdot}xH_2O$ ($460\,F\,g^{-1}$).

Keywords: Carbon nanofibres; Hydrous ruthenium oxide; Composites; Supercapacitors

1. Introduction

Since the pioneer work by Miller et al. [1] in which ruthenium oxide nanoparticles were deposited on carbon aerogels, numerous works have dealt with this matter [2–26]. In all of them the objective was to combine the pseudocapacitance (also called redox-type capacitance) of ruthenium oxide with the double-layer capacitance of a carbon in order to take in advantage from the contribution of the two materials and to get high-capacitance ruthenium oxide/carbon composites. Indeed, the composites showed specific capacitances higher than those of the carbons itself. Assuming that the specific capacitance of the composites follows the rule of mixtures, specific capacitances for hydrous ruthenium oxide (usually named $RuO_2{\cdot}xH_2O$) as high as $1000\,F\,g^{-1}$, i.e. even higher than that of bare $RuO_2{\cdot}xH_2O$ ($720\,F\,g^{-1}$) [27], have been reported [7,9,10,15,19,22]. This fact has opened the possibility of achieving very high-capacitance electrode composites.

Despite the great effort done on preparing $RuO_2{\cdot}xH_2O$/carbon composites, e.g. by different procedures, with different carbons (activated carbons, mesoporous carbons, carbon aerogel, carbon black, carbon nanotubes, etc.), with different contents in RuO_2, and by applying different annealing temperatures, several questions remain opened. For instance, how the specific capacitance of the composites and how the specific capacitance of supported $RuO_2{\cdot}xH_2O$ depend on the $RuO_2{\cdot}xH_2O$ content [1,3,4,7,9,10,12,17,22–24], or why the specific capacitance of supported $RuO_2{\cdot}xH_2O$ seems to change with the carbon chosen as support for a given RuO_2 content [10,16]. These questions point out that an understanding of the specific capacitance of the composites and the specific capacitance of the supported $RuO_2{\cdot}xH_2O$ is still lacking.

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* Corresponding author.
E-mail address: jmrojo@icmm.csic.es (J.M. Rojo).

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Regarding carbon nanofibres [28–32], which are the support chosen in this work, only a few ruthenium oxide/carbon nanofibres composites have been prepared by electrospinning. Hence articles dealing with this type of composites are rather scarce [26]. In general carbon nanofibres (CNF) show: (i) moderate specific double-layer capacitance (1–50 $F g^{-1}$ in aqueous electrolyte) because of their small specific surface area (10–200 $m^2 g^{-1}$) [28,29] and (ii) high electric conductivity (1×10^3 $S cm^{-1}$) because of their highly ordered structure [33]. The small surface area would be a drawback limiting the maximum amount of supported ruthenium oxide. The high conductivity, however, is an advantage to get electrodes with high electric conductivity. Compared to other carbons such as activated carbons or mesopore-templated carbons, CNF have been chosen as support because: (i) the specific capacitance of CNF and that of $RuO_2{\cdot}xH_2O$ are very different; it has allowed us to do an accurate study on the variation of the composite specific capacitance as a function of the $RuO_2{\cdot}xH_2O$ content, (ii) $RuO_2{\cdot}xH_2O$/CNF composites are simple composites; because they are easily compacted and show high electric conductivity, neither an inert binder nor an electric conductor are needed to be added to the composites, and (iii) the choice of CNF as support has made easy the study by TEM on the distribution of supported $RuO_2{\cdot}xH_2O$ particles; CNF and $RuO_2{\cdot}xH_2O$ show different shapes and contrasts. Compared to carbon nanotubes (either SWCNT or MWCNT), CNF are cheaper.

In this work $RuO_2{\cdot}xH_2O$ (where x seems to depend on the heating treatment done [27]) has been deposited on CNF following an impregnation method. The composites have been structurally and texturally characterized. Their specific capacitance has been discussed in relation to the $RuO_2{\cdot}xH_2O$ content and $RuO_2{\cdot}xH_2O$ particle size.

2. Experimental

Carbon nanofibres (CNF) were produced by a catalytically vapour-grown procedure in Grupo Antolin Ing. SA., and supplied by the same company. They are highly graphitic cup-stacked fibres showing non-amorphous carbon coating, large hollow core and ca. 100 nm diameter [34]. These CNF, labelled as GANF1 in reference [34], were acid-treated (HCl or HNO_3) and were used in this work as support for the $RuO_2{\cdot}xH_2O$ particles.

Three grams of CNF was dispersed either in 200 ml of 12 M HCl or in 200 ml of 13 M HNO_3, and the dispersions were heated under refluxing at 98 °C for 4 h. The dispersions were filtered and the solids were exhaustively washed with distilled water. The solids were dried at 80 °C overnight. The samples of CNF-treated in HCl or in HNO_3 are hereafter referred as CNF-HCl or CNF-HNO_3, respectively.

0.5 g of either CNF-HCl or CNF-HNO_3 was dispersed in 50 ml of an aqueous 0.034 M $RuCl_3{\cdot}0.5H_2O$ solution under continuous stirring for 24 h. In some particular cases, and in order to get impregnations with very low contents in $RuCl_3{\cdot}0.5H_2O$, lower concentrations (i.e. 0.017 and 0.0015 M) of the $RuCl_3{\cdot}0.5H_2O$ solution were used such as other authors did [8]. In all cases the dispersions were filtered to remove the $RuCl_3{\cdot}0.5H_2O$ solution excess and to get carbon nanofibres impregnated with those solutions. Then the impregnated carbon nanofibres were added to 50 ml of aqueous 10^{-4} M NaOH solution and the pH was measured. Drop wise of another 0.01 M NaOH solution was added to neutralize the dispersion (up to pH 7), then formation of $RuO_2{\cdot}xH_2O$ happened. The dispersions were filtered and the solids were collected. They were washed with distilled water up to negative chloride test. Finally, the composites either $RuO_2{\cdot}xH_2O$/CNF-HCl or $RuO_2{\cdot}xH_2O$/CNF-HNO_3 were dried at 80 °C overnight.

Accumulative treatments consisting of impregnations of both CNF-HCl or CNF-HNO_3 with the 0.034 M $RuCl_3{\cdot}0.5H_2O$ solution followed by filtering and neutralization in 0.01 M NaOH solution were done in order to increase the loading in $RuO_2{\cdot}xH_2O$. The composites are hereafter referred as $n$$RuO_2{\cdot}xH_2O$/CNF-HCl or $n$$RuO_2{\cdot}xH_2O$/CNF-$HNO_3$, where n stands for the number of accumulative treatments done. Using $RuCl_3{\cdot}0.5H_2O$ solutions of lower concentrations (0.017 or 0.0015 M) we got composites having $RuO_2{\cdot}xH_2O$ loadings lower compared to the composites at $n = 1$.

A sample of bare $RuO_2{\cdot}xH_2O$ was also prepared by adding drop wise of 0.01 M NaOH solution on 50 ml of 0.034 M $RuCl_3{\cdot}H_2O$ solution; the added volume of the 0.01 M NaOH solution was that needed to increase the pH solution up to pH 7. The solid obtained, i.e. $RuO_2{\cdot}xH_2O$, was washed with distilled water and then air-dried at room temperature.

All the samples studied in this work, i.e. CNF-HCl, CNF-HNO_3, composites, and bare $RuO_2{\cdot}xH_2O$, were heat-treated at 150 °C for 2 h.

Infrared (IR) spectra were recorded in Bruker IFS 66v/S equipment. KBr-based pellets were prepared by mixing either CNF-HCl or CNF-HNO_3 with dried KBr and then by compacting under a pressure of 2 $tonnes cm^{-2}$. The relative weight content of CNF-HCl or CNF-HNO_3 in the pellets was nearly 2 wt%.

Temperature-programmed desorption (TPD) experiments were carried out on the CNF-HCl and CNF-HNO_3 samples in a DSC-TG equipment (TA Instruments, SDT 2960 Simultaneous) coupled to a mass spectrometer (Thermostar, Balzers, GSD 300 T3), to characterize the surface chemistry of the samples. In these experiments 10 mg were heated up to 900 °C (heating rate 20 $°C min^{-1}$) under helium flow rate of 100 $ml min^{-1}$.

Thermogravimetric (TG) analyses were carried out in air-flow (50 $ml min^{-1}$) at a heating rate of 5 $°C min^{-1}$ with a Seiko Exstar 6300 instrument. In all cases the mass of the composite was of ca. 20 mg.

X-ray powder diffraction (XRD) patterns were recorded at room temperature in a D-8 Bruker diffractometer, with Cu Kα radiation. The XRD patterns were obtained in the step scanning mode of 0.02° (2θ) and 1 s/step counting time, within the range $10 \le 2\theta \le 70°$. The average crystallite size was calculated from the full width at half maximum (FWHM) of several diffraction lines by applying the Scherrer equation:

$$D = \frac{\lambda}{\beta \cos\theta} \quad (1)$$