Electrodeposited reduced-graphene oxide/cobalt oxide electrodes for charge storage applications

A. García-Gómez [a], S. Eugénio [a,*], R.G. Duarte [a,b], T.M. Silva [a,c], M.J. Carmezim [a,d], M.F. Montemor [a]

[a] CQE, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal
[b] ESTBarreiro, Instituto Politécnico de Setúbal, Setúbal, Portugal
[c] ADEM, GI-MOSM, ISEL-Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, Lisboa, Portugal
[d] ESTSetúbal, Instituto Politécnico de Setúbal, Setúbal, Portugal

ARTICLE INFO

ABSTRACT

In the present work, electrochemically reduced-graphene oxide/cobalt oxide composites for charge storage electrodes were prepared by a one-step pulsed electrodeposition route on stainless steel current collectors and after that submitted to a thermal treatment at 200 °C. A detailed physico-chemical characterization was performed by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and Raman spectroscopy. The electrochemical response of the composite electrodes was studied by cyclic voltammetry and charge-discharge curves and related to the morphological and phase composition changes induced by the thermal treatment. The results revealed that the composites were promising materials for charge storage electrodes for application in redox supercapacitors, attaining specific capacitances around 430 F g^{-1} at 1 A g^{-1} and presenting long-term cycling stability.

1. Introduction

Redox supercapacitors are considered very attractive devices for electrochemical energy storage, namely for applications requiring good cycling stability and increased power density. Charge storage electrodes in redox-based supercapacitors require specific characteristics, such as high conductivity, increased surface area, suitable porosity, chemical/thermal stability and corrosion resistance. Presently, charge storage materials for supercapacitors are based on carbon materials or metallic oxides (or their composites), each one presenting advantages and drawbacks that have been widely discussed [1–3].

Carbon-based materials have been widely used due to their nearly ideal capacitive behavior and good cycling stability. The charge storage process is essentially based on the electrochemical double layer mechanism where charge is stored via reversible ion adsorption onto the carbon surface. The process is therefore strongly limited by the accessible surface area and these materials are characterized by modest energy density. On the other hand, transition metal oxides, such as cobalt oxides or manganese oxides [4], display pseudocapacitance which is associated with fast faradaic processes occurring at electrode surface and can display

increased capacitance but lack long-term stability due to increased resistivity. It has been demonstrated that appropriate combinations of metallic oxides, with tailored composition, stoichiometry, morphologies and structure create synergies that overcome drawbacks [5–7], allowing the development of high performance electroactive materials. These effects can also be enhanced by thermal treatment due to the formation of oxides with multiple valences, with an improved pseudocapacitive response [8,9].

Another interesting possibility resides on the combination of carbon-based materials with transition metal oxides/hydroxides [10–12]. These electrodes may display increased cycling stability and specific capacitance due to the additional contribution of the redox response of the metallic species [12]. In this frame, carbon structures, such as nanotubes or nanopowders, have been used as support for deposition of metal oxides [3,13] allowing a wide range of porosity structures and superior mechanical and electrical properties [10,14] ensuring this way increased specific capacitances and larger potential windows. In the recent years, graphene has been considered an interesting material for supercapacitor electrodes due to its good electronic conductivity, high theoretical capacitance and increased surface area [15]. However, it has been reported that electrodes made of graphene may display decreased surface area due to formation of agglomerates or restacking of the graphene sheets [16]. This drawback can be overcome by the addition of transition metal oxides, such as Ni(OH)$_2$, MnO$_2$ or CoO$_x$ to graphene which leads to a considerable decrease of restacking

* Corresponding author.
E-mail address: s.eugenio@tecnico.ulisboa.pt (S. Eugénio).

of the graphene sheets, increasing the interlayer distance (pore size) between them and consequently the surface area exposed to the electrolyte [11,16,17]. For example, pseudocapacitive cobalt oxides/hydroxides when combined with reduced graphene oxide create a synergetic effect resulting in improved electrochemical performance [18,19].

Graphene and transition metallic oxides composites have been prepared by various routes such as chemical and hydrothermal precipitation or chemical vapor deposition [1,20]. However, the electrode assembly requires the use of organic binders and other foreign additives that increase the electrode resistance. These films are in most cases coated on the current collector and, loss of adhesion and corrosion induced by the presence of halogenates, is likely to occur [9]. To overcome these drawbacks, electrodeposition directly on current collectors allows preparing binder-free composite electrodes displaying increased energy density and decreased equivalent series resistance. Also, by optimizing the electrodeposition parameters, it is possible to tailor the morphology and composition of the films [6,7,21]. For example, using pulsed electrodeposition it is possible to control the size and composition of the deposits by varying peak current densities, peak potentials and on/off time. Moreover, pulsed electrodeposition promotes higher nucleation rates, increasing the number of grains per unit area which results in finer grained deposits [22].

In the present paper, electrochemical reduced graphene oxide (Er-GO) and cobalt oxide (CoOx) composite electrodes were prepared by pulsed electrodeposition. The composite material was further oxidized by thermal treatment to produce oxides with different stoichiometry. The electrochemical performance of the Er-GO/CoOx composite electrodes was assessed by cyclic voltammetry and charge-discharge testing. The physico-chemical characterization was studied by X-Ray photoelectron spectroscopy, Raman spectroscopy and scanning electron microscopy. The effect of the thermal treatment step on the electrochemical response of the electrodes revealed improved specific capacitances and increased cycling stability, attributed to the formation of a cobalt oxide with multiple valence states.

2. Experimental section

2.1. Electrodeposition of the composite electrode

A commercial graphene oxide (GO) aqueous solution ($4 \, mg \, ml^{-1}$) obtained from Graphenea Tech and $Co(NO_3)_2 \cdot 7H_2O$ (pro-analysis grade) from Sigma Aldrich were used to prepare the electrolytes. The GO aqueous solution was diluted to $0.5 \, mg \, ml^{-1}$ in an electrolyte containing $0.5 \, mg \, ml^{-1}$ of $Co(NO_3)_2 \cdot 7H_2O$. Prior to electrodeposition, an ultrasonic treatment was performed for 30 min, in order to create a stable exfoliated $GO/Co(NO_3)_2$ dispersion.

The electrodeposition was performed in a 3-electrode cell connected to a PGZ 100 Voltalab galvanostat/potentiostat. The working electrode was a stainless steel plate (AISI 304, Goodfellow), the counter electrode a platinum foil and the saturated calomel electrode (SCE) was used as reference. The Er-GO/CoOx composites were electrodeposited by pulsed electrodeposition applying pulse potentials between −0.9 to −1.2 V (SCE) for 0.5 s and for 1800 cycles. After electrodeposition, the electrode was washed with distilled water and dried in air overnight.

The electrodeposited films were then submitted to a thermal-treatment at 200 °C for 2 h in air (Er-GO/CoOx-TT) in order to promote further oxidation of the material.

2.2. Physico-chemical characterization

Scanning electron microscopy (FEG-SEM, JEOL 7001F) was used to characterize the surface morphology of the electrodes. Raman spectroscopy was performed using a LabRAM HR Evolution Raman spectrometer (HORIBA, Jobin Yvon, Edison, NJ) with an integrated BX41 microscope (Olympus, Tokyo, Japan). A solid-state laser operating at 532 nm was focused on the samples surface, using a 100X objective lens. The spectra were obtained with an acquisition time of 10 s and 6 accumulations. In all cases, the system was calibrated to better than $1 \, cm^{-1}$ before the measurements, using a silicon sample. A spectrograph with a 600 lines/mm grating was used to provide a spectral resolution of $2 \, cm^{-1}$, and the confocal hole size was set at 100 mm. The Raman spectra of each sample was truncated (100 and $3500 \, cm^{-1}$).

Surface analysis was performed by XPS, using a Kratos Axis Ultra HSA. XPS spectra were acquired in constant analyzer energy (CAE) mode at 30 eV with a monochromated aluminum anode and an acceleration voltage of 15 kV. For peak fitting Gaussian–Lorentzian product function was used was and the algorithm was based on Simplex optimization (Avantage software).

2.3. Electrochemical testing of the composite electrodes

The electrochemical performance of the composites electrodes was studied in 1 M KOH, using the apparatus described above. Cyclic voltammetry and galvanostatic charge/discharge curves were carried out at $50 \, mV \, s^{-1}$ and $1 \, A \, g^{-1}$, respectively for each electrode. The potential window tested was in the range of −0.2 to +0.4 V versus SCE.

3. Results and discussion

3.1. Characterization of Er-GO/CoOx

The morphology of the Er-GO/CoOx and Er-GO/CoOx-TT electrodes was observed by SEM. As shown in Fig. 1a, the Er-GO/CoOx film is continuous, covering all the electrode surface, and exhibits a rough structure. The film is formed of wrinkled/folded flexible 2D sheets with embedded nanosized particles, attributed to cobalt oxide. Similar structures have been reported for electrochemically reduced GO [23,24]. Hasan et al. [24] observed this type of morphology in electrochemically reduced GO in acidic media and described it as a "brick microstructure" where the Er-GO sheets adhered to each other forming multilayers (bricks). According to these authors, these multilayers are formed in the electrolyte, prior to deposition.

Thermal treatment at 200 °C resulted in significant changes on the morphology of the films. As it can be seen in Fig. 1b, Er-GO/CoOx-TT presents a smoother morphology, with fewer wrinkles, formed of nearly flat sheets that lie parallel to the electrode, where similar type of randomly distributed sub-micrometric size particles of cobalt oxide are embedded. This type of morphology has been described in the literature as a rug-type microstructure [24]. The change in morphology can be associated with de-oxidation of GO promoted by the thermal treatment which leads to the release of intercalated oxygenated functional groups. In fact, it is well known that heating Er-GO at 100 °C promotes evaporation of water molecules and a decreases of the oxygen-containing functional groups [25,26]. At higher temperatures, a significant de-oxidation of GO may also occur with the evolution of carbon monoxide/carbon dioxide [25–27]. This can create a very large pressure between the stacked layers, higher than that necessary to separate two stacked GO platelets [28]. As consequence, mechanical disaggregation of the previously observed Er-GO bricks is expected resulting in the observed smother surface.