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Pseudocapacitive behavior of Ti/$RhO_x + Co_3O_4$ electrodes in acidic medium: application to supercapacitor development

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Abstract

Mixtures of $RhO_x + Co_3O_4$ have been electrochemically studied by cyclic voltammetry in acid solution as a function of composition. The electrodes were prepared by thermal decomposition at 400 °C of mixtures of nitrate precursors. Their electrochemical behavior shows substantial dependence on the electrode's composition. The Co site controls the electrochemical behavior of the system in the 5–10 mol.% Rh composition range. A significant increase in the electrodes' active area is observed for compositions corresponding to more than 10 mol.% RhO_x in admixture with Co_3O_4. Above 10 mol.% Rh, the voltammetric curves become more similar to that for RhO_x and then RhO_x becomes able to stabilize the Co_3O_4 in the mixture. Electrodes of this kind have been found to perform as good materials in electrochemical capacitor applications, exhibiting specific capacitances of 500–800 F g^{-1} over to 20–60 mol.% RhO_x composition range. The large specific capacitance exhibited by this system arises from a combination of the double-layer capacitance and the pseudocapacitance associated with Rh surface redox-type reactions.

Keywords: Supercapacitors; Cobalt oxide; Rhodium oxide; Pseudocapacitance

1. Introduction

Electrochemical capacitors (EC) or supercapacitors are being developed as an alternative to pulse batteries, and they have been considered as a promising high power energy source for digital communication devices and electric vehicles. The EC technology has been reviewed for a number of electrode materials, including carbon, conducting polymers and transition metal oxides [1–4]. Thus, the EC electrode materials should have a large surface area for charge accumulation, and an appropriate pore structure for electrolyte wetting and rapid ionic motion.

Amorphous $RuO_2{\cdot}xH_2O$ has been found to possess significant energy storage capabilities due to its ability to act as a "proton condenser", and it represents the best material for application in electrochemical capacitors [5]. RuO_2 systems prepared by the sol–gel process possess very high specific capacitance (720 F g^{-1}) [5], which is associated with surface redox reactions including the participation of proton exchange between the surface groups and the electrolytic solution.

Noble metal oxides such as IrO_2 and RhO_x also appear as alternatives for applications as electrode materials in electrochemical capacitors. These oxides show characteristics similar to those as observed for the RuO_2. They are conducting materials with high surface area when prepared as films deposited on a metallic substrate [6]. These oxides possess high double-layer capacitance, and the reversible redox surface processes can enhance the energy density of a device.

However, up to the present, not many researches are found applied to the study of these materials as a basis in the construction of electrochemical capacitors [3,7,8]. This is related to the fact that these oxides, as expensive as RuO_2 are costly for commercial use. A considerable reduction in the cost of the electrode material is needed to make such supercapacitor technology commercially viable. Alternative strategies have been pursued in this regard. The dispersion of a noble transition oxide in other less expensive oxide matrices has been examined with this objective [9,10]. In this context, $Ti/RhO_x + Co_3O_4$ mixed electrodes were prepared as candidates for a supercapacitor device. The effect adding of Co_3O_4 to the electrochemical performance of RhO_x-based electrode in 0.5 mol dm^{-3} H_2SO_4

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was analyzed as a function of composition of the electrode. The potential range of the redox processes, the degree of their reversibility, and the specific capacitance values were established by means of cyclic voltammetry (CV). In addition, the structure and morphology of the $Ti/RhO_x + Co_3O_4$ electrodes were also systematically examined.

2. Experimental

2.1. Electrode preparation

Oxide layers of nominal composition $Ti/RhO_x\,(1-y) + Co_3O_4\,(y)$ $(0 \leq y \leq 1)$ were deposited on a Ti support by thermal decomposition at 400 °C of ca. 0.1 mol dm^{-3} from solutions of $Rh(NO_3)_3$, and $Co(NO_3)_2{\cdot}xH_2O$ in a HNO_3, 6.0 mol dm^{-3}. The Rh precursor solution was prepared by precipitating $Rh(OH)_3$ from a $RhCl_3{\cdot}xH_2O$ solution by addition of NaOH. The $Rh(OH)_3$ obtained was filtered off, washed several times with Milli-Q quality water and dissolved in 6.0 mol dm^{-3} HNO_3, thus resulting in the rhodium nitrate precursor solution. This procedure is the same employed by De Campos et al. in their preparation of the $Rh(NO_3)$ precursor solution [11].

Brushing on both sides of 10 mm × 10 mm × 0.15 mm Ti support, which was pre-treated by sandblasting and etched in boiling 10% oxalic acid, the mixtures of appropriate volumes of precursors were spread at the desired mole ratio. After each application, the solvent was evaporated at about 90 °C and the dried layer fired for 5 min, under a 5 l min^{-1} O_2 stream, in a preheated oven. The procedure was repeated until the desired catalyst loading was achieved (2.43–2.88 mg cm^{-2}). The total deposited mass on the Ti support was calculated based on the sum of the specific density of the RhO_2 (7,195 g cm^{-3}) and Co_3O_4 (6,07 g cm^{-3}) [12] considering the desired mole ratio and a nominal coating thickness value constant (2 μm). The electrodes were then annealed for 1 h at 400 °C. The mounting of the electrodes in a Teflon holder has been described elsewhere [13].

2.2. Electrochemical measurement

The surface features of the mixed oxides were characterized in situ by cyclic voltammetry at 20 mV s^{-1} in the potential range of 0.4–1.4 V RHE^{-1} in 0.5 mol dm^{-3} H_2SO_4 solutions. The electrodes were submitted to continuous cyclization of the potential by 100 cycles to evaluate their chemical stability and to reach a stationary surface condition. The double-layer changing region was determined by changing the positive and negative potential limits. The differential capacity (C_d) of the oxide–solution interface was obtained from CV measurements from 2 to 150 mV s^{-1}. The C_d-values were obtained from the slope of the j (mA cm^{-2}) versus ν (mV s^{-1}) graphics (when j is the current-density at the potential $E = 0.6$ V or 1.4 V RHE^{-1} and ν the voltage sweep-rate (dV/dt) s^{-1}).

The specific capacitance, C_s, was obtained by dividing the differential capacity values by the Rh mass content (m_{Rh}) of the oxide layer (g cm^{-2}). The Rh mass was calculated from its mol.% present in the total mass deposited on titanium. This was done with the objective of evaluating the effect of the reduction of the amount in the precious component on the total charge capacity.

2.3. Potential, solution and equipment

Electrochemical measurements were performed using a four-compartment cell with two counter electrodes (platinized platinum wires) facing the working electrode from opposite sides, and a Luggin capillary approaching the electrode from below in order to minimize uncompensated Ohmic drop. Electrode potentials were measured and reported against that of an hydrogen electrode (RHE) in the same supporting electrolyte. The electrochemical experiments were carried out with an ECO CHEMIE Autolab Potentiostat–galvanostat (PGSTAT30) interfaced to a computer. All experiments were carried out in 0.5 mol dm^{-3} H_2SO_4 (Merck) solutions volumetrically prepared using Milli-Q quality distilled water. The air in these solutions was expelled and stirring achieved by bubbling nitrogen. All the experiments were carried out at room temperature, ca. 298 K.

The coating morphology was examined by scanning electron microscopy (SEM). The compositions of samples were analyzed by the energy-dispersive X-ray (EDX) measurements. Both analyses used a Zeiss Model DSM 960 electron microscope coupled to a microanalyzer, Link Analytical Model QX 2000. Quantitative analysis of the coating was performed by EDX. The atomic percentages of the elements were obtained by corrections for matrix interference, atomic number, absorbance and fluorescence (ZAF correction). Metallic cobalt (99.998% pure) was used for equipment calibration. Iridium and cobalt reference standards (Micro-Analysis Consultants, Cambridge shire) were used for internal calibration. The experimental errors, based on the ZAF correction algorithm, were always below 1% (wt.%).

The microstructural investigation was carried out by X-ray diffraction analysis (XRD) of the Ti-supported film. These analyses were performed on a D5005 SIEMENS diffractometer using Cu Kα radiation (30 kV, 30 mA).

3. Results and discussion

3.1. Morphology, microstructure and composition characterization

Fig. 1 shows typical SE micrographs for freshly prepared $Ti/RhO_x\,(1-y) + Co_3O_4\,(y)$ electrodes as a function of the composition. The film morphology is influenced by the nominal composition of oxide layer.