Morphology and electrochemical behaviour of ruthenium oxide thin film deposited on carbon paper

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Abstract

In order to improve the efficiency of ruthenium dioxide, RuO_2, as an electrochemical capacitor electrode, a RuO_2 thin film is deposited on carbon paper and its structure and properties are evaluated. This new composite material is prepared via solution dip-coating of a Ru-ethoxide precursor and heat conversion. The coating thickness is easily controlled by varying the number of repetitions of the preparation process. The resulting structure consists of a by homogeneously coated RuO_2 film on carbon paper which has a porous graphite matrix. Extensive electrochemical studies have been performed in 1 M H_2SO_4 electrolyte in order to evaluate the properties of the composite as an electrode in an electrochemical capacitor. The composite material shows not only high specific capacitance ($620 \, F \, g^{-1}$) but also good power characteristics. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

It was first recognised by Trasatti and Buzzanca [1] and later by Galizzoli et al. [2] that the current responses of ruthenium dioxide (hereafter RuO_2) films are similar to those of an EDLC (electric double-layer capacitor) which has almost constant capacitance. Thus, hydrous RuO_2 has been recognised as a promising candidate for replacing carbon-based EDLCs. The superior performance of this material in sulfonic acids has been attributed to a surface-driven reversible redox process which includes proton intercalation and de-intercalation. Hydrous RuO_2 has a microporous structure and shows a reversible faradic capacitive reaction in acidic electrolyte solutions, as indicated by the following reaction:

$$RuO_X(OH)_Y + \delta e^- + \delta H^+ \rightarrow RuO_{X-\delta}(OH)_{Y+\delta} \qquad (1)$$
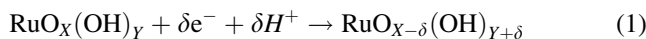
Generally, $RuCl_3$ has been used as a precursor in preparing RuO_2 by heat treatment above 300 °C. When the processing temperature of the precursor exceeds 175 °C, however, the resulting material can crystallise and exhibit a sharp decrease in capacitance [3]. Recently, Jow and co-workers [4–6] obtained amorphous RuO_2 by processing at a relatively low temperature. In this case, high specific capacitance values

above $720 \, F \, g^{-1}$ could be obtained depending on the heat treatment conditions.

Another approach for obtaining an electrode material with high specific capacitance is to prepare a composite material by depositing ruthenium nanoparticles on carbon aerogel [7], or activated-carbon [8,9] with a very high specific surface-area. It was found that the capacitance of activated-carbon increased with the loading of RuO_2, despite a decrease in surface area. The reason is that the pseudo-capacitance of RuO_2 can be combined with the double-layer capacitance of the activated-carbon. A host material loaded with about 7–10 wt.% of RuO_2 can exhibit much higher specific capacitance compared with that of the host material. On the other hand, further loading of RuO_2 to the host material decreases the contribution of pseudocapacitance to the total specific capacitance per loaded RuO_2.

Even though RuO_2 has a great advantage in terms of via a wide potential range of highly reversible redox reactions with high specific capacitance [10], it is somewhat expensive for commercial electrodes in bulk-type electrochemical capacitors. Therefore, it is desirable to develop a thin film process for the fabrication of electrochemical capacitors in order to reduce the cost of the materials.

In the present paper, an attempt has been made to synthesise amorphous RuO_2 film deposited on the surface of a graphite fibre substrate by a dip-coating method [11]. Carbon paper composed of a three-dimensional network graphite fibre

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substrate, which acts as a current-collector, has a porous structure. The resultant composite structure can increase the contact area between the ruthenium oxide film and the electrolyte. Consequently, the contribution of loaded ruthenium oxide to the capacitance is maximised.

2. Experimental

$RuCl_3 \cdot nH_2O$ and sodium ethoxide were purchased from Aldrich Chemistry and carbon paper was obtained from Toray. The amorphous RuO_2 film was prepared by the following reaction:

$$RuCl_3 + 3Na(OC_2H_5) \rightarrow Ru(OC_2H_5)_3 + 3NaCl \qquad (2)$$
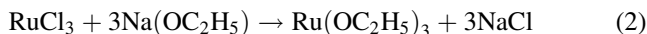
This reaction can occur in ethanol solvent at a temperature of 78 °C under a dried nitrogen atmosphere. After 3 h, the precipitated NaCl was filtered out and the resulting solution of ruthenium ethoxide was cooled to room temperature.

Carbon paper with a three-dimensional network structure of graphite fibres was dipped in the precursor solution for 3 s and then moved to a heat chamber under an oxygen atmosphere in order to convert the precursor into amorphous RuO_2. After annealing at 120 °C for 3 h, RuO_2-coated carbon paper was washed with distilled water. The amount of deposited RuO_2 was allotted by the number of repeats of the dip-coating process. X-ray diffraction (XRD) patterns of the composite samples were obtained by means of a Rigaku X-ray generator. The morphology of the ruthenium oxide-coated on the graphite fibre was investigated with a high resolution scanning electron microscope (Philips SEM 535 M). The electrode capacitances were determined by measurements from cyclic voltammograms (hereafter CVs). The CVs of the electrodes were performed in 1 M H_2SO_4 with a computer-controlled potensiostat/galvanostat (EG&G 273A). The impedance characteristics of the electrode were carried out at various states of charge by superimposing 5 mV ac on the electrode with a constant dc potential at frequencies which ranged from 0.1 Hz to 100 MHz. This was achieved with a Solatron HF response analyser model 1255.

3. Results and discussion

Electron micrographs of the carbon paper and RuO_2-coated carbon paper one shown in Fig. 1a–d, respectively. The surface of the pure carbon paper is very smooth compared with that of RuO_2-coated graphite fibres. The latter has flows which include grooves and voids. The structure of RuO_2 deposited on graphite fibre is somewhat different from RuO_2 nanoparticles impregnated on carbon aerosol [12], and it is also different from the RuO_2 film prepared by the reactive sputtering method [13]. From Fig. 1d, it can be seen that the surfaces of the graphite fibres are well covered with RuO_2 films. This can be easily

understood considering the adsorbance of ethanol by the carbon paper. The carbon paper can suck ethanol-containing Ru-ethoxide so powerfully that the RuO_2 precursor can be adsorbed on graphite fibres homogeneously, which results in well covered RuO_2 films.

The XRD patterns of carbon paper and RuO_2-coated carbon paper are presented in Fig. 2. There are peaks from the graphite substrate but no indication of a crystalline phase in the RuO_2. The latter is due to the low heat conversion temperature, which is far below the crystallisation temperature of RuO_2 (300 °C) [3]. These results confirm that RuO_2-coated on the graphite fibre is amorphous. Generally, the capability of electrochemical capacitors using RuO_2 is strongly dependent on the electrode microstructure because of the difference in the proton intercalation/de-intercalation characteristics [11]. In order to increase the capacitance per unit loaded RuO_2, it is desirable to use amorphorous RuO_2.

Cyclic voltammograms for of RuO_2-coated carbon paper as a function of the deposited RuO_2 mass (sample 1: 0.15 mg/4 cm^2; sample 2: 1.7 mg/4 cm^2; sample 3: 3.4 mg/4 cm^2) are given in Fig. 3. As more RuO_2 is loaded into the carbon paper, the response current reaches much higher values. This indicates that the specific capacitance is related directly to the deposited RuO_2 mass. The CV curves in Fig. 3 deviate from a rectangular shape with equal current density, in the positive and negative directions as reported in a previous study [4]. A very thin RuO_2 film coated on graphite fibres displays oxidation and reduction peaks between 400 and 500 mV (versus Ag/AgCl), as shown in Fig. 3a. As the weight of deposited RuO_2 is increased, shifts in the oxidation and reduction peaks are observed. In the case of a pseudocapacitor, it is usually necessary to have some time interval to show the opposite discharging current after a reversed potential sweep because a chemical reaction is involved. In this study, a very short time interval is required at low and high potential sweep rates. This indicates a good power property, similar to that of carbon-based EDLCs.

From CV sweep data for various RuO_2-coated carbon papers, the specific capacitance can be estimated by $C = i/s$, where i is the average current density and s is the potential sweep rate. A specific capacitance of about 620 F g^{-1} is obtained at a CV sweep rate of 5 mV s^{-1}, irrespective of deposited RuO_2. This value is similar to that reported [14] for a composite electrode of 80 wt.% RuO_2 and 20 wt.% carbon, viz. 620 F g^{-1}, but is a little low compared with the specific capacitance of 768 F g^{-1} obtained by optimising not only the potential range but also the heat-treatment temperature [4,5]. Though the weight of deposited RuO_2 on the carbon paper was increased, the specific capacitance was not seriously sensitive to the voltage sweep rate and showed good power characteristics.

The CVs of both hydrous RuO_2 and carbon/hydrous RuO_2 composite showed nearly rectangular structures at low voltage sweep rates (1–5 mV s^{-1}), as is found for carbon-based EDLCs. But as the voltage sweep rate is increased, the
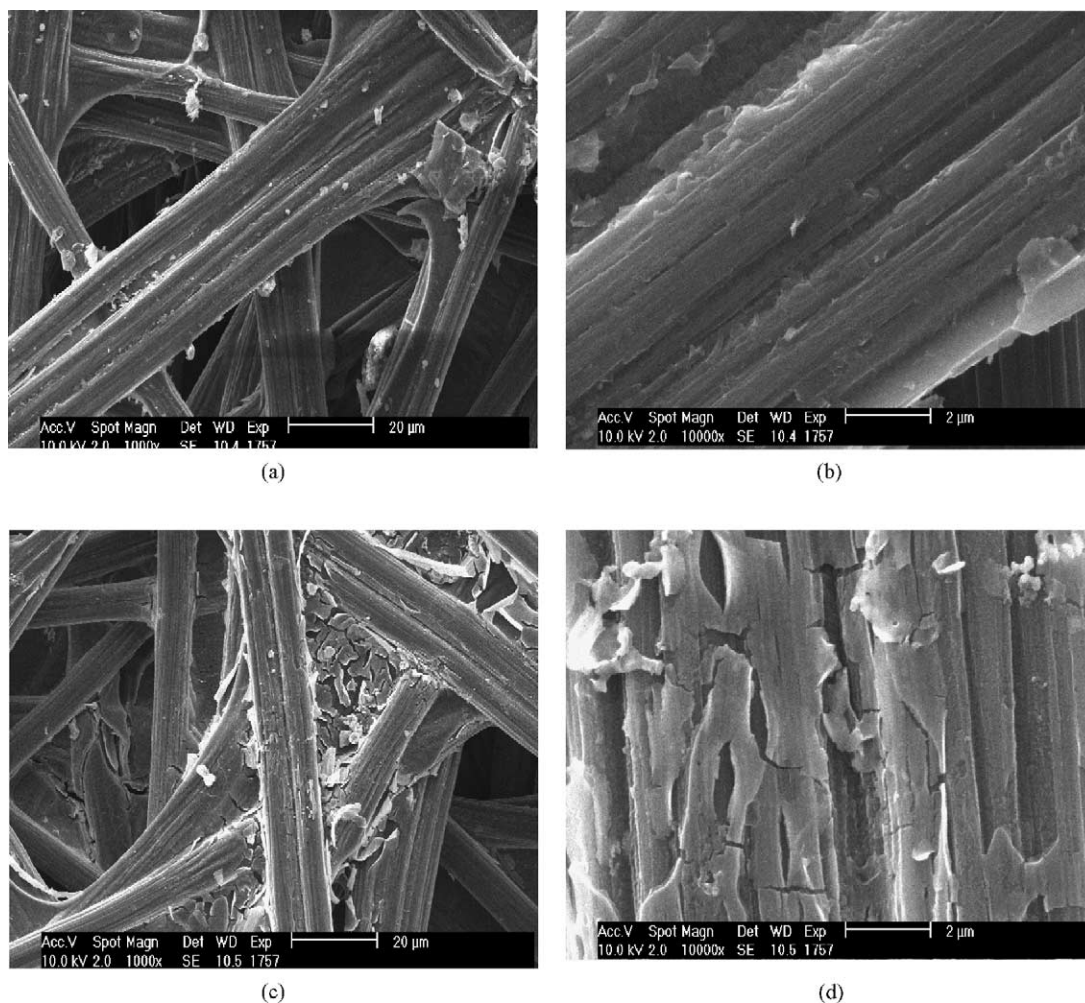
Fig. 1. Electron micrographs images of graphite interwoven carbon paper ((a) ×1000; (b) ×10,000) and corresponding RuO$_2$-coated carbon paper ((c) ×1000; (d) ×10,000).
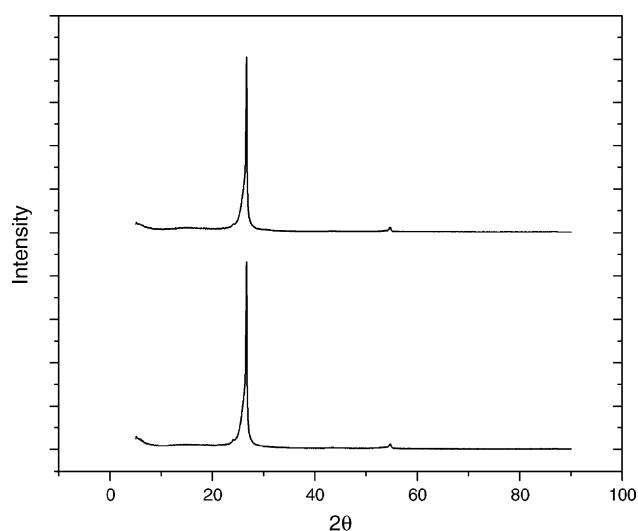

Fig. 2. XRD patterns for carbon paper and ruthenium oxide-coated carbon paper treated at 120 °C (top: pure carbon paper, bottom: RuO$_2$-coated carbon).

CV diagram becames more inclined (45° to the voltage-axis) with a lower current density. As a result, the specific capacitance is determined to be sensitive to the voltage sweep rate due to the capacitive (*RC*) time constant of the sample [12]. In Fig. 4, it can seen that the CV shapes of all samples are not affected by the voltage sweep rate, and this results in just slightly decreased slopes of specific capacitance. The reduction in the capacitance calculated at the 50 mV s^{-1} sweep rate is less than 20% of the value the at 5 mV s^{-1} sweep rate. Two explanations are possible. The interwoven structure of a host material which has a higher specific surface-area (2.89 m^2 g^{-1}) than a two-dimensional, foil-type, current-collector can act as a very effective substrate, and increase the contact area between RuO$_2$ and the electrolyte. The other explanation is that the composite structure of coated RuO$_2$ with a very thin film thickness creates a shorter ionic diffusion distance.
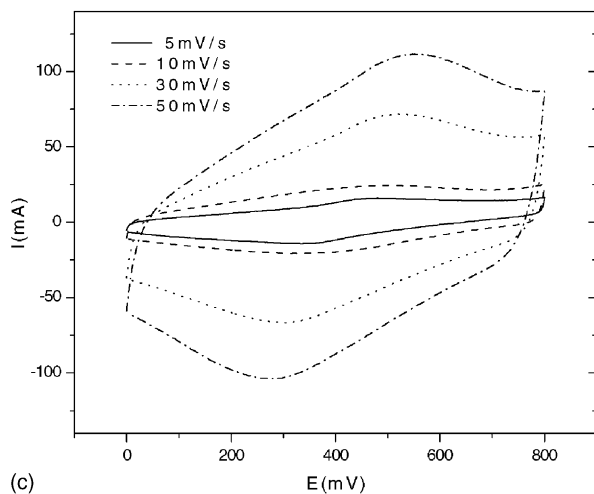
Voltammetry measurements can also be used to characterise cycle life behaviour. Samples have been examined for up to 100 cycles. A typical cycling response for sample 2 is
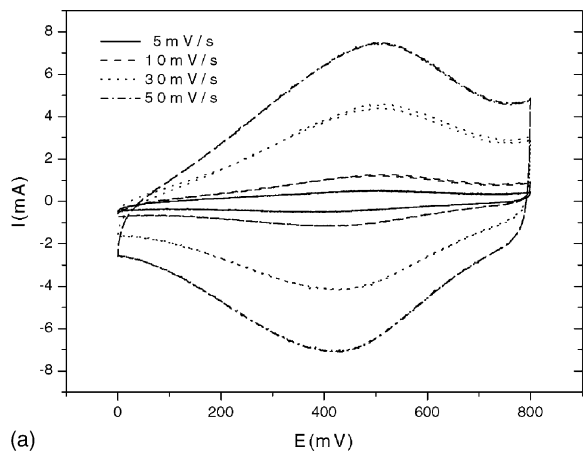
(a)
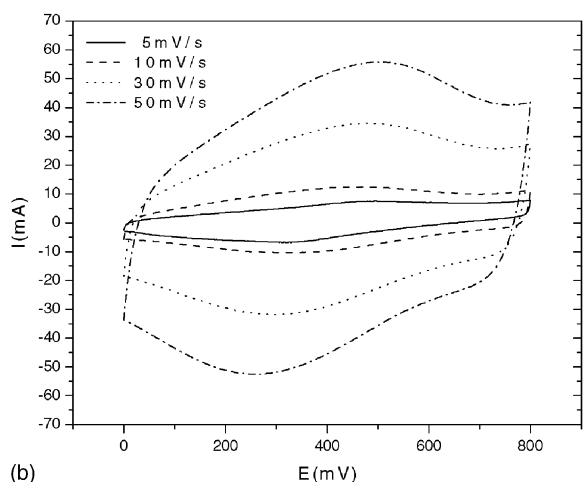
(b)

(c)

Fig. 3. CVs of RuO$_2$-coated carbon paper in 1 M H$_2$SO$_4$ at room temperature ((a) sample 1; (b) sample 2; (c) sample 3).
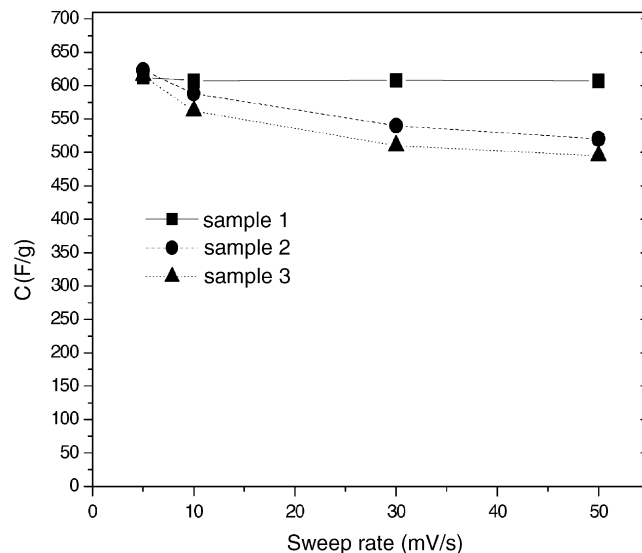

Fig. 4. Capacitance behaviour of RuO$_2$-coated carbon paper as function of sweep rate.

any chemical interaction between RuO$_2$ and the graphite substrate, the portion of RuO$_2$ that can contribute to the reaction will reduce with increasing cycle number.

A complete kinetic characterisation of the intercalation/de-intercalation of proton ions is provided by impedance measurements. The impedance spectrum of a RuO$_2$-coated carbon paper electrodes (sample 2) is shown in Fig. 6. The electrode has been potentiostatically charged at several potentials until equilibrium was reached. The spectrum consists of three distinct regions which are dependent of the frequency range, i.e. a semicircle in the high frequency region, a 45° line in the middle frequency region, and a quasi-vertical line in the low frequency region. The region at

shown in Fig. 5. The capacitance can be maintained at 82% after 80 cycles, which is a little lower than that of pure RuO$_2$-based ECs (95%) [4], but is similar to that of RuO$_2$ impregnated carbon aerosol. Because of the loosely bound surface group of RuO$_2$ on graphite fibres caused by the absence of
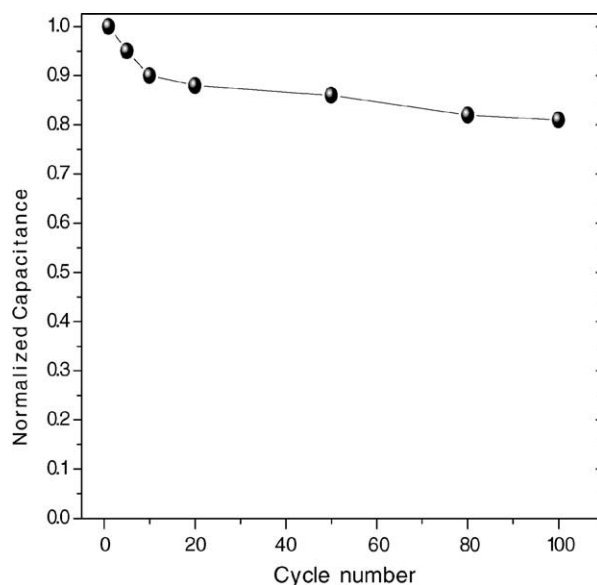

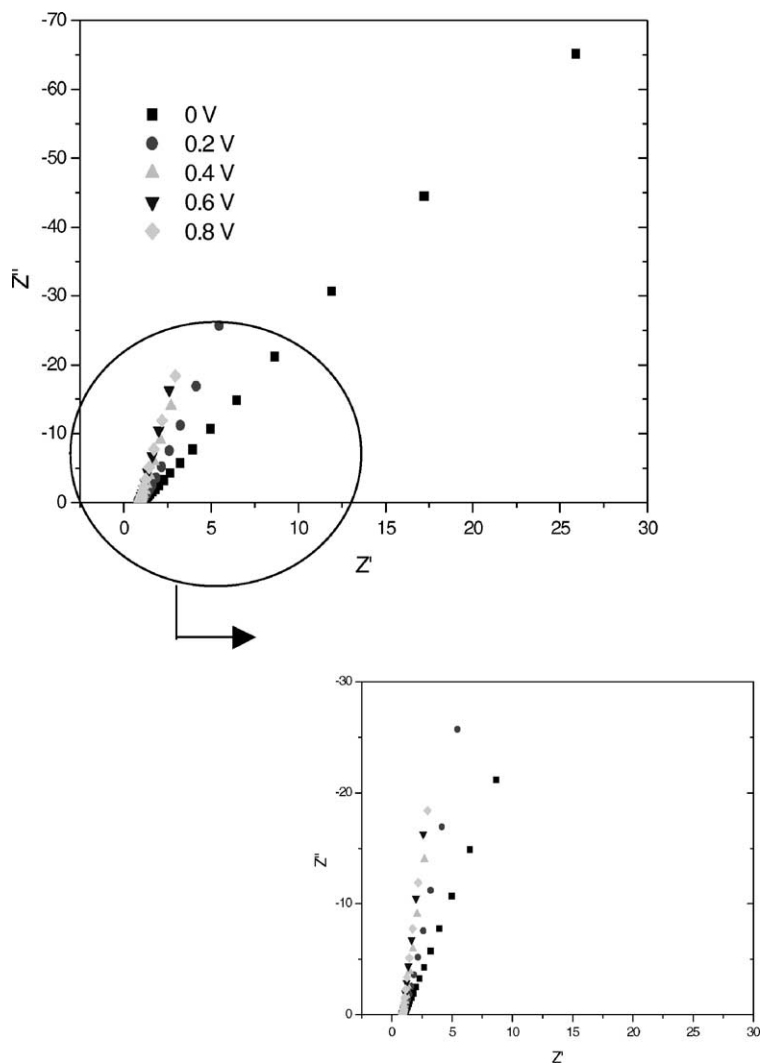Fig. 5. Normalised variation in capacitance as function of cycle number.

Fig. 6. Impedance diagram obtained with RuO$_2$-coated carbon paper in 1 M H$_2$SO$_4$ at potentials between 0 and +0.8 V.

high frequency identifies the electrolyte properties, while the impedance response in the mid-frequency region is associated with the electrode/electrolyte interface process [15]. The corresponding relaxation effect is represented by a semicircle whose intersections at high and mid-frequency with the real axis are the electrolyte and the charge transfer resistances, respectively. At low frequency, the response of a 90° straight line in the ideal case resembles that of a pure capacitance [16]. Due to the difference of oxidation levels of RuO$_2$ film, as shown in the CV voltammograms, nonidentical spectra are obtained over various potential ranges. A very similar spectrum shape was also obtained in the case of samples 1 and 3. The capacitance can be predicted by the following equation and showed a similar value to that obtained from CVs:

$$Z'' = \frac{-j}{wC} \tag{3}$$

From Fig. 6, it can be seen that the capacitances at 0 and 0.2 V versus Ag/AgCl are lower than those at higher voltages.

These results are compared with the behaviour of the CVs. In the latter, the current response increases in proportion to the imposing potential by 0.5 V and then decreases with increased potential level. The bulk resistance is of the order of a few ohms and the middle frequency semicircle remains confined within low amplitude in both charged and discharged states. The total charge-transfer resistance is represented by the difference in the real part of the impedance between the low and high frequencies, and can be seen from Fig. 6 to be about 6 Ω cm^2 for a half-oxidised state.

An expected advantage of an amorphorous RuO$_2$-based electrochemical capacitor is a high specific capacitance with a wide working voltage range, which is caused by including the chemical reactions of the whole mass of the electrode material. The major doubts regarding its application are economic constraints imposed by the high cost of RuO$_2$, and inadequate cycleability due to the irreversible reaction that is caused by the electrode thickness of the device. Our results have focused on solving two challenges related to thin films, namely, developing preparing a very simple preparation

method, and depositing the film on a porous carbon paper substrate. Once the preparation conditions are optimised, the performance of the films is expected to be applicable to electrochemical capacitors and other energy storage devices.

4. Conclusions

RuO_2 thin film electrodes have been prepared by heat treatment of metal alkoxide adsorbed on to carbon paper. Although the samples have been prepared in a non-optimised state, RuO_2-coated carbon paper had a relatively high specific capacitance of 620 F g^{-1}. This is due to the porous graphite fibre substrate that acts to increase the contact area and allows complete reaction between the RuO_2 and the electrolyte. In CVs, the capacitance of the composite electrode shows non-sensitive behaviour to voltage sweep rates between 5 and 50 mV s^{-1} with low ionic diffusion resistance.

For a further improvement of the present electrode, it is necessary to optimise the heat treatment temperature and Ru-ethoxide precursor concentration. The heat-treatment temperature influences the internal structure and the conversion of RuO_2 that, in turn, affect electrochemical properties such as specific capacitance and energy and power densities. The precursor concentration directly determines the adhesive property of the RuO_2 film on the carbon paper and the evolution of the electrode structure. Therefore, RuO_2-coated carbon paper prepared at an optimised heat-treatment temperature as well as with an optimised precursor concentration will provide maximum electrode performance for practical application in electrochemical capacitors.

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