

Preparation and optimization of RuO₂-impregnated SnO₂ xerogel supercapacitor

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Abstract

A Sb (6 mol%)-doped SnO₂ xerogel impregnated with RuO₂ nanocrystallites is prepared via an incipient-wetness method and is optimized for its electrochemical capacitance in aqueous 1 M KOH electrolyte by adjusting the calcination temperature and the RuO₂ loading. The electrode capacitance does not increase monotonically with increasing RuO₂ loading. A maximum electrode capacitance of 15 F g⁻¹, which represents a three-fold increase compared with the blank xerogel and a specific RuO₂ capacitance of 710 F g⁻¹ RuO₂, is obtained with a RuO₂ loading of 1.4 wt.% and by calcination at 200 °C. Higher loadings presumably result in a homogeneous nucleation upon drying, which causes severe reduction in the total surface area of the RuO₂ crystallites. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

A supercapacitor (SC) is a unique electrochemical device which is designed to possess high specific energy and power [1–3]. Ruthenium oxide (RuO₂) is known to be a very promising electrode material that is capable of achieving both goals, due to its large capacitance and high conductivity [2–7]. Extraordinary capacitances for RuO₂ are known to result from under-potential hydrogenation and oxygenation in acidic and alkaline electrolytes, respectively. For instance, a specific capacitance of 720 F g⁻¹ has previously been reported [7] for amorphous hydrous ruthenium oxide, RuO_y·xH₂O, in sulfuric acid. Nevertheless, because of its high cost, efficient utilization of ruthenium oxide is essential for making the devices more cost-effective.

There have been several studies [8–11] of combining ruthenium oxide with other materials to form composite electrodes with the intention to increase the dispersion of the oxide. Sato et al. [8] dispersed ruthenium oxide on to activated carbon and achieved a specific capacitance of about 650 F g⁻¹ RuO₂, while Lin et al. [9] prepared a carbon–ruthenium xerogel that gave a capacitance of ~720 F g⁻¹ RuO₂. Combinations of RuO₂ with other oxides, including VO_x, TiO₂, MoO₃, SnO₂ and CaO, have resulted

in a maximum capacitance of 290 F g⁻¹ observed for a Ru–V–O composite [10,11]. All of these studies used aqueous H₂SO₄ electrolyte.

Among all of the ‘second-component’ materials mentioned above, SnO₂, particularly with proper doping, has the advantage of high conductivity [12–14], viz. as high as 10² to 10³ S cm⁻¹. While crystalline RuO₂ is also highly conductive, RuO_y·xH₂O is not. RuO₂–SnO₂ composite electrodes are now widely used in the chlor-alkali industry as dimensionally stabilized anodes [15–17]. These electrodes, which contain the oxides in comparable percentages, have low surface areas and are not suitable for SC applications. We report here the preparation and characterization of RuO₂-impregnated SnO₂ composite electrodes that contain only a few percent (≤3.3 wt.%) of RuO₂ in nano-particles form on porous Sb-doped SnO₂. The aim is to maximize RuO₂-effected capacitance enhancement.

2. Experimental

The SnO₂ xerogel was prepared as follows [18]. Ammonia was introduced into an aqueous solution containing 0.1 M SnCl₄ to cause condensation. The gelatinous precipitate thus produced was collected by filtration, washed with de-ionized water, and finally peptized at pH ~10.0. An alcoholic solution of SbCl₃ that gives a final Sb:Sn molar ratio of 0.06:1 was then added. This resulted in a second

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condensation. Once the precipitate sedimented, the supernatant liquid was decanted and fresh water was added. The cycle of solution-decating and water-replenishing steps was repeated, in order to remove chloride ions, until the solution pH reached ~ 4.0 . The hydrous powder was prepared by drying the precipitate at $30\text{ }^\circ\text{C}$ at 75% humidity. The xerogel was finally calcined at $500\text{ }^\circ\text{C}$ for 1 h.

Ruthenium oxide was loaded by an incipient-wetness method, in which an aqueous solution of RuCl_3 was added to the calcined SnO_2 xerogel powder in an amount that was just sufficient to wet completely the powder. Finally, the wetted powders were calcined in air for 5 h at selected temperatures between 150 and $250\text{ }^\circ\text{C}$, with a $25\text{ }^\circ\text{C}$ increment. The loading ranged from 0 to 3.3 wt.% RuO_2 .

For powder characterization, nitrogen adsorption (ASAP2000, Micromeritics) was conducted to determine the BET surface area, pore volume (the “single-point” method) and pore-size distribution (BJH). X-ray diffraction (XRD) was carried out by means of a Mac-Science/MXP diffractometer with $\text{Cu K}\alpha$ radiation.

Cyclic voltammetric (CV) analysis was performed using an electrochemical analyzer (Eco Chemie PGSTAT30) and a plane-type capacitor cell which comprised two planar electrodes each of a $1\text{ cm} \times 1\text{ cm}$ active area, a glass-fiber separator, and an aqueous electrolyte. The electrodes have a thickness of $\sim 55\text{ }\mu\text{m}$ and comprise calcined powders and 3 wt.% PVDF binder, which were spread on to a Ti foil. The capacitance quoted in this work for each of the electrode pairs, C_e , was determined by the equation: $C_e = 2[(i_c + i_a)/2]/s$, where i_c and i_a are the currents at 0.0 V during the cathodic and anodic sweeps, respectively and s is the sweep rate. The multiplication of two accounts for the fact that each of the electrodes forms one capacitor at the interface, and hence, there are totally two serial capacitors in one cell.

3. Results

The SnO_2 substrate has a porous structure with pore-size distribution peaks at 8 nm (Fig. 1a), a pore volume of $0.10\text{ cm}^3\text{ g}^{-1}$, and a surface area of $66\text{ m}^2\text{ g}^{-1}$. XRD analysis show a diffraction pattern which is characteristic of cassiterite SnO_2 (Fig. 1b) and an average crystallite size of 5.8 nm, as calculated by the Debye–Scherrer equation. The microstructures remain unchanged after the entire impregnation process, which includes the follow-up drying and calcination steps. No XRD reflection due to RuO_2 has been detected even in the samples with the highest loading (3.3 wt.%).

It has previously been established [18] that the calcination procedure has two effects on the capacitive properties of SnO_2 xerogel. The improved crystallinity upon calcination helps to increase the capacitance, while the surface loss due to sintering results in a reduction in capacitance. The capacitance of the blank xerogel reaches a maximum by calcination at $500\text{ }^\circ\text{C}$, which has a value of $\sim 5.0\text{ F g}^{-1}$ or

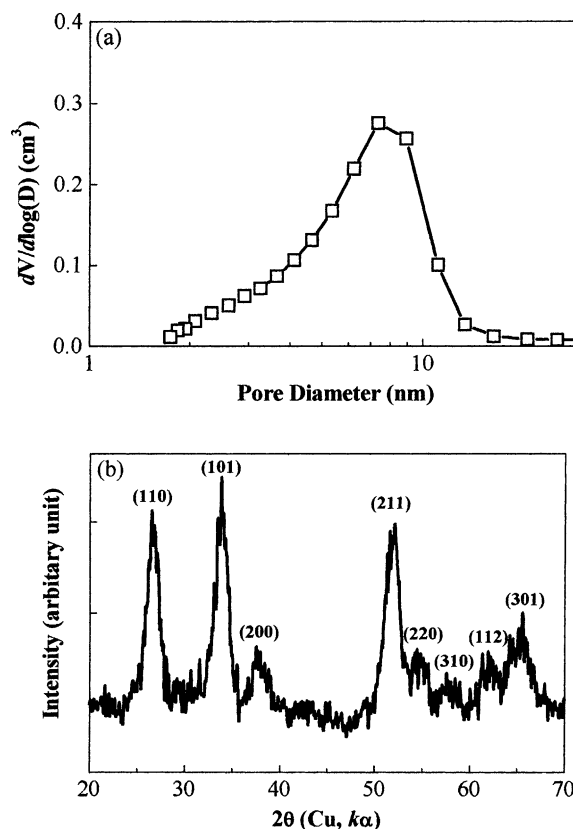


Fig. 1. Microstructure of Sb-doped SnO_2 xerogel substrate: (a) adsorption pore-size distribution; (b) XRD pattern, showing cassiterite SnO_2 crystallites with an average size of 5.8 nm. XRD reflections are indexed according to cassiterite SnO_2 .

$8\text{ }\mu\text{F cm}^{-2}$ of real surface at a sweep rate of 4 mV s^{-1} (Fig. 2). The capacitance, nonetheless, decreases with increasing sweep rate (Figs. 2 and 3).

A systematic study on the effect of calcination temperature on the capacitive properties of the composite electrodes between 150 and $250\text{ }^\circ\text{C}$ with a $25\text{ }^\circ\text{C}$ increment established that heat treatment at $200\text{ }^\circ\text{C}$ resulted in the largest capacitance. Voltammograms for a cell consisting of electrodes

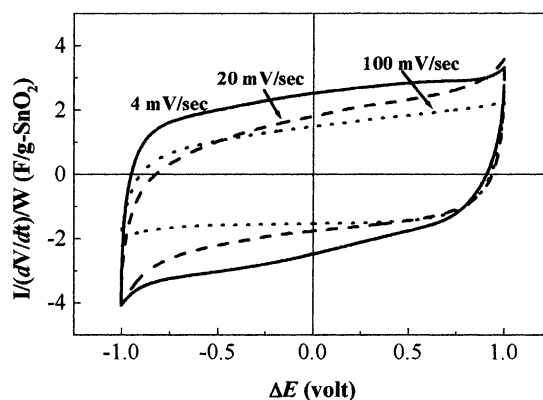


Fig. 2. Voltammograms for blank SnO_2 xerogel electrodes calcined at $500\text{ }^\circ\text{C}$ for 1 h (electrolyte: 1 M KOH).

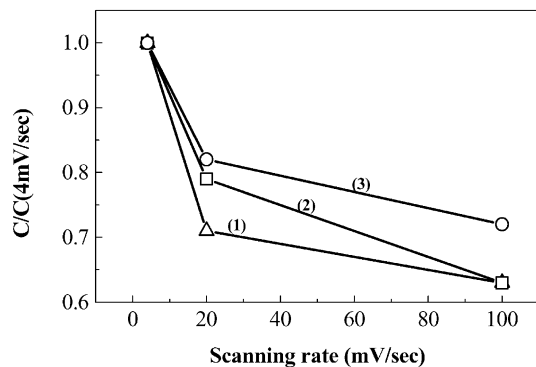


Fig. 3. Effect of sweep rate on specific electrode capacitance: (1) blank SnO_2 xerogel electrode; (2) electrode with 1.4 wt.% loading of RuO_2 ; and (3) electrode with 3.3 wt.% loading.

containing 1.4 wt.% RuO_2 , which have the largest capacitance among the composite electrodes are presented in Fig. 4. The following characteristic capacitive properties were identified. First, the electrodes have an operating voltage range of 1.0 V, i.e. the same as that of the blank SnO_2 xerogel. Second, the electrodes have a capacitance which is approximately three times greater than that of the xerogel (Figs. 2 and 4). At a sweep rate of 4 mV s^{-1} , for instance, the composite electrodes exhibit a specific capacitance of $\sim 15 \text{ F g}^{-1}$, in comparison with $\sim 5 \text{ F g}^{-1}$ for the xerogel. Finally, the capacitance of the composite electrodes also decreases with increasing sweep rate. For the 1.4 wt.%-composite electrodes, the capacitance decreases at about the same rate as that of the blank xerogel (curves 1 and 2, Fig. 3). Reduction in capacitance is, however, slower for the electrodes with higher RuO_2 loadings (curve 3, Fig. 3).

The decreasing trend of the capacitance suggests that parts of the surfaces of both SnO_2 and RuO_2 are inaccessible at high charging–discharging rates. Hence, the specific capacitance based on the data obtained at the slowest sweep rate, i.e. at 4 mV s^{-1} , is believed to be closest to that of full utilization of the electrode materials. Fig. 5 (curve 1) plots the specific electrode capacitance, which is based on unit

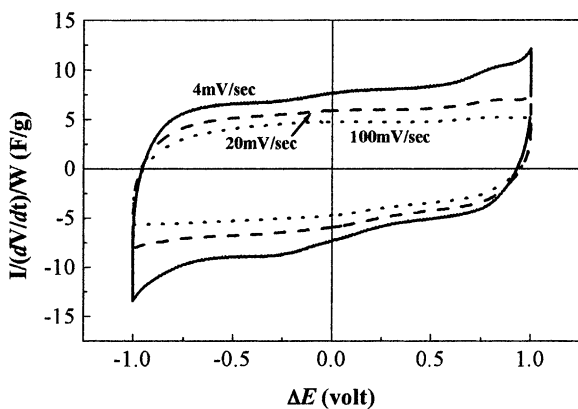


Fig. 4. Voltammograms of the composite electrodes containing 1.4 wt.% RuO_2 and calcined at 200°C (electrolyte: 1 M KOH).

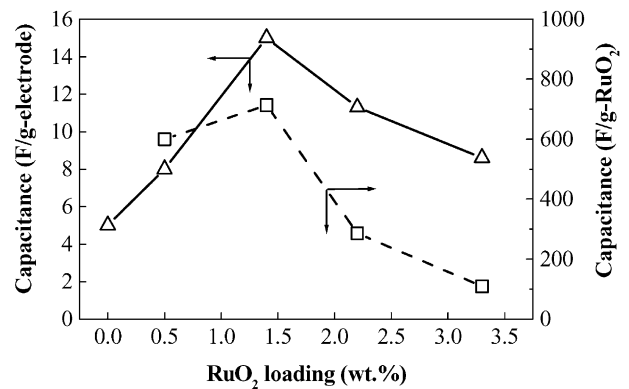


Fig. 5. Effects of RuO_2 loading on (curve 1) specific electrode capacitance and (curve 2) specific RuO_2 capacitance.

weight of the entire electrode, obtained at 4 mV s^{-1} as a function of RuO_2 loading. The capacitance exhibits a maximum of $\sim 15 \text{ F g}^{-1}$ at 1.4 wt.%. If we attribute the capacitance enhancement relative to the blank xerogel electrode completely to the loaded RuO_2 , we determine the specific RuO_2 capacitances, which are also shown in Fig. 5 (curve 2). A maximum of $\sim 710 \text{ F g}^{-1} \text{ RuO}_2$ was found at 1.4 wt.% loading.

In studying the effect of calcination on $\text{RuO}_y \cdot x(\text{H}_2\text{O})$ in sulfuric acid electrolyte, Zheng and Jow [7] demonstrated that the material exhibited a maximum capacitance of 720 F g^{-1} upon calcination at 150°C , where the oxide remained amorphous, and that the capacitance decreased rapidly to $\sim 150 \text{ F g}^{-1}$ upon crystallization at 200°C . In contrast, the maximum capacitance in KOH was obtained in this work by calcination at 200°C , where the oxide is supposed to be crystalline. The difference possibly resides in the fact that the pseudo-capacitive behaviors under acidic and alkaline environments involve different reaction mechanisms which, in turn, show different sensitivity toward crystallinity. For instance, while the pseudo-capacitance of RuO_2 in acid can be explained by protonation–deprotonation of surface hydroxyls, it has been suggested to involve redox reaction(s) of surface ruthenium peroxide or some other anionic oxy-hydroxide complexes in alkaline solution [5].

The specific capacitance of $\sim 350 \text{ F g}^{-1}$ is the highest reported for a crystalline RuO_2 electrode, which had a specific surface area of $120 \text{ m}^2 \text{ g}^{-1}$ RuO_2 , in sulfuric acid electrolyte [6]. On the other hand, the maximum specific capacitance of RuO_2 achieved in this work is $\sim 710 \text{ F g}^{-1}$. The difference cannot be attributed to the pH effect, since crystalline RuO_2 has been shown [5] to have approximately the same capacitance in sulfuric acid and NaOH solutions (both are 1 M). Rather, it is believed to be due to the difference in particle dispersion. Burke et al. [5] once determined a storage capacity of ~ 13 units of electronic charge per nm^2 for the surface processes. By applying this value, we estimate a specific surface area of $\sim 340 \text{ m}^2 \text{ g}^{-1}$ RuO_2 in the 1.4 wt.%-composite. This, in turn, is translated

into a crystallite size of no greater than 3.0 nm, assuming non-agglomerate crystallites. The small crystallite size also explains why no XRD reflection of RuO₂ was detected for the composite powders.

At RuO₂ loadings ≤ 1.4 wt.%, as shown in Fig. 5, the specific electrode capacitance increases with increasing loading. This may be attributed to the fact that a higher loading can increase both the total number and size of the RuO₂ crystallites. Both result in a greater total surface area of RuO₂, and hence, a larger electrode capacitance. On the other hand, the decreasing trend at higher loadings is less expected. This can occur only when there is significant reduction in the total number of the crystallites accompanied by large crystallite sizes. An explanation based on the particle nucleation aspect is suggested. It is possible that the particle nucleation mechanism during the drying step of the impregnation process changes as the Ru salt concentration increases. It is logical to expect that, under the same drying rate, heterogeneous nucleation predominates at lower salt concentrations, while homogeneous nucleation prevails at higher concentrations.

The proposed shift in nucleation mechanism may also have left a clue in the observations that, as shown in Fig. 3, the capacitances of the blank xerogel and 1.4 wt.%-composite electrodes fall at about the same rate with increasing sweep rate, while the composite electrodes with higher loadings show a much slower rate of decline in capacitance. Extensive homogeneous nucleation arising from rapid drying could have occurred to cause preferential deposition of Ru salt near the peripheries of the xerogel particles. This will lead to reduced sensitivity of electrode capacitance toward sweep rate, as the RuO₂ crystallites are accessible at both high and low sweep rates.

In summary, RuO₂-impregnated SnO₂ xerogel electrode has been prepared and optimized for its capacitance in KOH by adjusting the calcination temperature and the RuO₂ loading. A maximum specific electrode capacitance of 15 F g⁻¹ and a maximum specific RuO₂ capacitance of 710 F g⁻¹ were simultaneously achieved by adopting a RuO₂ loading of 1.4 wt.% and a calcination of 200 °C. Higher loadings presumably cause extensive homogeneous

nucleation which, in turn, result in a reduction in the total surface area of RuO₂.

Acknowledgements

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