



Short communication

Capacitive behavior of amorphous and crystalline RuO₂ composite electrode fabricated by spark plasma sintering techniqueP. Bharali¹, K. Kuratani, T. Takeuchi, T. Kiyobayashi*, N. Kuriyama

Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

ARTICLE INFO

Article history:

Received 13 January 2011

Received in revised form 31 March 2011

Accepted 31 March 2011

Available online 8 April 2011

Keywords:

Pseudocapacitor

Amorphous ruthenium oxide

Crystalline ruthenium oxide

Electronic conductivity

Spark plasma sintering

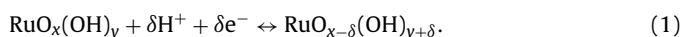
ABSTRACT

This study is intended to determine if the capacitive properties are improved when a specific amount of crystalline ruthenium oxide (c-RuO₂) is added to an amorphous hydrous ruthenium oxide (a-RuO₂) electrode fabricated by the spark plasma sintering technique. For at the cyclic voltammetry scan rates higher than 10 mV s⁻¹, the capacitance of a highly pseudo-capacitive, but less electron-conductive a-RuO₂ electrode is augmented by adding 5–20 wt.% of c-RuO₂ which is less capacitive, but more electron-conductive than a-RuO₂. The capacitance fades when more than 20 wt.% of c-RuO₂ is added because the less capacitive nature of c-RuO₂ prevails. The proximate cause of this phenomenon is the electronic conductivity, σ , of the composite electrode as we observe a maximum in σ at around a 5–20 wt.% c-RuO₂ content. The fact that c-RuO₂ is composed of smaller particles than a-RuO₂ seems to be related to the maximum σ value for a certain c-RuO₂ content of the composite electrode.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Both the amorphous and crystalline forms of ruthenium dioxide (RuO₂) have been receiving significant research interests in various applications of electrochemical devices [1–8]. It is used as an electrode material for oxygen reduction, the treatment of waste effluents, water electrolysis, etc. [2,3]. Crystalline RuO₂ (c-RuO₂) electrodes have been used in gas-evolving reactions, such as hydrogen, oxygen and chlorine evolution [4–6]. On the other hand, amorphous hydrous RuO₂ (RuO₂·nH₂O, a-RuO₂), after the seminal work of Zheng and co-workers, emerged as an excellent electrode material for an electrochemical pseudocapacitor with capacitance of above 700 F g⁻¹ [7,8]. The high capacitance is attributed to a series of reversible redox processes with the simultaneous exchange of protons and electrons according to the following reaction:



It is obvious that both the protonic conductivity and electronic conductivity at the surface and in the bulk of the electrode material through the grain boundaries of the RuO₂·nH₂O particles are of prime importance for high capacitance [9]. The electronic conductivity of a-RuO₂ can be improved by annealing the material at high

temperature. However, the annealing also gives rise to a loss of protonic conductivity which is related to the amount of physically and chemically bound water at the surface of the RuO₂ particles that decreases upon annealing [10]. In recent years, to increase the capacitance of a-RuO₂, various electronic conductive materials, such as acetylene black, graphene, and carbon nanotubes, have been used as an additive, though at the expense of increasing the total mass of the electrode by using these electrochemically inactive additives [11–13]. Barbieri and co-workers made an interesting attempt to improve the capacitance of the RuO₂ electrode by fabricating composite electrodes of a-RuO₂ and c-RuO₂ in which the former has a high capacitance, but low electronic conductivity and the latter *vice versa* [9]. They reported that a small fraction of c-RuO₂ in a-RuO₂ could improve the capacitive behavior without sacrificing the per-mass capacitance. However, in all the above cases, 5–10 wt.% of a polymer binder (e.g., polyvinylidene difluoride (PVDF)) is always added to fix the powder. It is highly desirable that the amount of the electrochemically inert additives be minimized in order to increase the capacitance and to make the electrode viable for commercial use.

In a recent study, we employed the spark plasma sintering (SPS) technique to fabricate a RuO₂ electrode without using any binder [14]. The results enabled us to establish that the SPS technique is effectual for fabricating a-RuO₂ electrodes without negatively affecting the bulk properties of the material using a highly intense, but short pulse of electric current passing through the RuO₂ powder under high pressure. Our subsequent trial to improve the electronic conductivity of the SPS a-RuO₂ electrode by adding a few weight percentage of acetylene black was not successful because the pow-

* Corresponding author. Tel.: +81 72 751 9651; fax: +81 72 751 9629.

E-mail address: kiyobayashi-t@aist.go.jp (T. Kiyobayashi).¹ Present address: Inorganic and Physical Chemistry Department, Indian Institute of Chemical Technology, Hyderabad 500607, India.

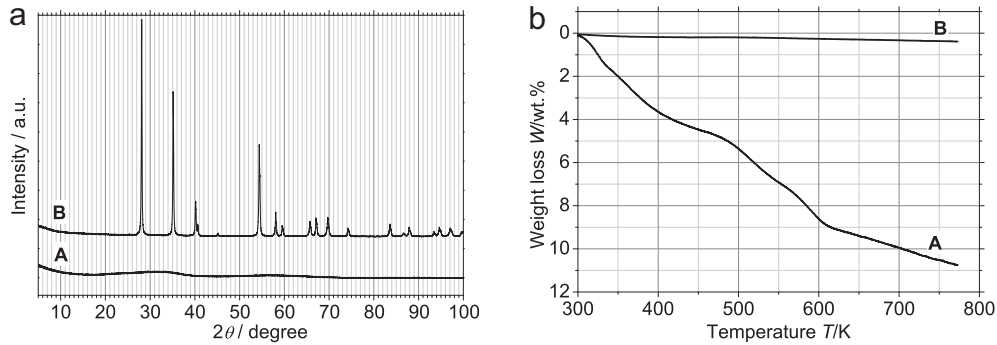


Fig. 1. X-ray diffraction profiles (a) and TG patterns (b) of amorphous hydrous and crystalline RuO₂ compacted by SPS. (A) Amorphous hydrous RuO₂ annealed at 423 K (100% a-RuO₂) and (B) crystalline RuO₂ annealed at 973 K (100% c-RuO₂).

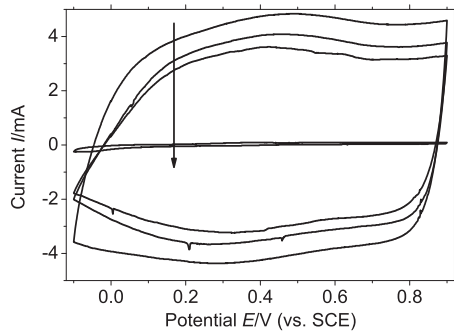


Fig. 2. CV patterns of RuO₂ electrodes compacted by SPS with various amorphous to crystalline ratios at the scan rate of 1 mV s⁻¹. Along the arrow; amorphous:crystalline = 100:0, 95:5, 90:10 and 0:100 in weight.

der mixture of the metal oxide and carbon refused to adhere to each other in order to form a rigid electrode by the SPS technique. In the present study, being encouraged by the work of Barbieri et al. [9], we tried to fabricate a binderless RuO₂ electrode by adding a certain fraction of c-RuO₂ to a-RuO₂ in which we anticipated that the proximity in the chemical and physical nature between the a- and c-RuO₂s should allow a rigid electrode to form using the SPS technique.

2. Experimental

The RuO₂ powder was synthesized by the hydrolysis of RuCl₃·nH₂O (aq., 0.1 mol dm⁻³, 100 ml) with the dropwise addition of NaOH (aq., 0.3 mol dm⁻³, 100 ml) based on a reported procedure [7,8]. The obtained powder was washed with distilled H₂O, dried overnight in the hood, and finally annealed at 423 K for 17 h in air

to obtain a-RuO₂. c-RuO₂ was obtained by heating a-RuO₂ at 973 K for 6 h in air. Both the a- and c-RuO₂ powders were sieved into a <75 μm fraction. The composite amorphous–crystalline RuO₂ (a–c RuO₂) was obtained by thoroughly mixing them in an agate mortar for 0.5 h in different weight ratios, viz., a:c = 100:0, 95:5, 90:10, 80:20, 75:25, 50:50, 25:75 and 0:100.

The crystal structure of the RuO₂ powders was determined by powder X-ray diffraction (XRD, PANalytical, Cu Kα). Thermogravimetry and differential thermal analysis (TG–DTA, Shimadzu, DTG 50) were used to see the differences in the water content of the a- and c-RuO₂s. The specific surface area was measured by nitrogen adsorption and desorption at 77 K using a Micromeritics ASAP 2010. These characterizations were carried out before and after the SPS, for which the once compacted RuO₂ discs were ground into powders again in the agate mortar.

The particle size distribution of the RuO₂ powders was measured by the laser diffraction technique using the dry method (Nikkiso SPR-7340). For each specimen, we ran three measurements, the mean of which is presented as the result.

SPS was performed using an SPS-515S (SPS Syntex) apparatus as described in our previous report [14]. In a typical experiment, the a–c RuO₂ powder was loaded in conductive tungsten carbide punches and an alumina insulator die (Ø 10 mm), so that the electric current (SPS current) flows only through the RuO₂ powder. The air in the SPS chamber was replaced by nitrogen before processing. In the present study, we used the compacting pressure of 50 MPa and the SPS current of 380 A, fixing the mass of the RuO₂ powder to 200–250 mg and the electrifying period as 1 s whereby we obtained a round disc of about 1-mm thickness.

The cyclic voltammogram (CV) was measured in H₂SO₄ (aq., 0.5 mol dm⁻³) using an Iviumstat electrochemical interface analyzer with the three-electrode setup using a platinum plate as the counter electrode and the standard calomel electrode (SCE) as the

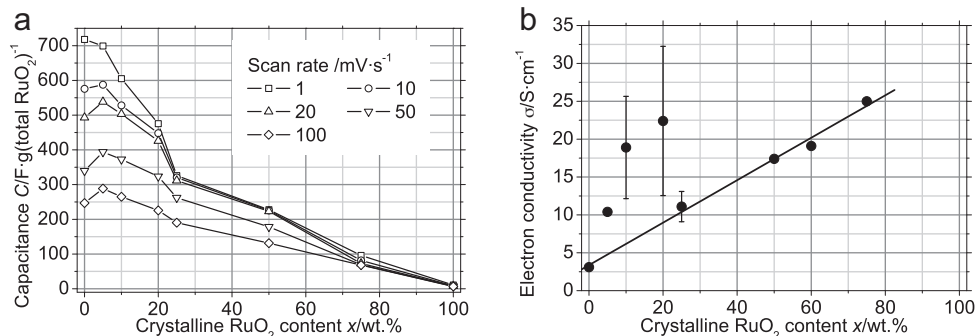


Fig. 3. Capacitance C (a) and electronic conductivity σ (b) of various composite RuO₂ electrodes as a function of crystalline RuO₂ content x in the electrodes compacted by SPS. Points with error bar in (b) indicate (average) \pm (maximum – minimum)/2 of the result of specimens prepared in two or three different batches. Straight line in (b) is the result of the linear optimization of $x = 0, 25, 50, 60$ and 75 wt.%.

reference electrode. The working electrode was prepared by wrapping the compacted RuO₂ disc with a gold mesh as the current collector. CV was performed between -0.1 and 0.9 V vs. SCE at the scan rates of 1, 10, 20, 50 and 100 mV s⁻¹. In order to confirm the reproducibility of the experiment, we prepared three specimens from different batches for each measurement.

To determine the electronic conductivity of the SPS RuO₂ disc, the galvanostatic method was employed by recording the current–voltage values in the current range from 0.1 to 1.0 A with step of 0.1 A. For this measurement, the Pt plates were fixed with silver paste to both sides of the SPS RuO₂ disc. We confirmed that the resistance of the Pt plate and silver paste was negligible compared to that of the RuO₂ disc. The electronic conductivity σ was calculated by dividing the inverse of the nominal resistance by the geometrical area and multiplied by the thickness of the disc.

3. Results and discussion

The representative X-ray powder diffraction profiles and thermogravimetry patterns of the a- and c-RuO₂s compacted by SPS are presented in Fig. 1. The figures show that c-RuO₂ is in a highly crystalline state bearing negligible water content. The amorphous nature of a-RuO₂ can be recognized by its very broad XRD pattern, while the diffraction peaks of c-RuO₂ are assigned to the rutile-type RuO₂ (JCPDS No. 40-1290). The sharp and intense diffraction peaks indicate a high crystallinity. The XRD and TG examination of the samples of various a–c RuO₂ ratios showed a minor result; namely, the higher the crystalline content, the greater the overall crystallinity and the lower water content of the SPS electrode. Also, the BET specific surface area linearly varies from ~ 55 to 8 m² g⁻¹ when the a–c ratio varies from 100% a-RuO₂ to 100% c-RuO₂. These characteristics of the a- and c-RuO₂s did not differ between before and after the SPS process.

As presented in Fig. 2, the electrodes with a high a-RuO₂ content retain the rectangular shape of the CV curves at the scan rate of 1 mV s⁻¹, indicating a capacitive behavior. We need to mention here that the 100% c-RuO₂ electrode prepared by SPS was very fragile and could not be used for the CV measurement. Therefore, only for the 100% c-RuO₂ electrode case, we mixed the c-RuO₂ with polytetrafluoroethylene (PTFE) keeping the weight ratio of RuO₂:PTFE as 90:10 and the total mass to 200 mg in order to form a tablet of \varnothing 10 mm similar to that of the SPS compacted one by pressing it using ca. 40 MPa pressure.

Fig. 3(a) shows the total capacitance C in F g⁻¹, in which the mass in the denominator is the total mass of RuO₂ (i.e., a-RuO₂ + c-RuO₂), as a function of the c-RuO₂ content x in the composite electrodes at various CV scan rates. The capacitance values are calculated on the basis of the method described in our previous study [14].

The 100% a-RuO₂ (i.e., $x=0$) compacted by SPS shows the highest capacitance of ~ 710 F g⁻¹ at the CV scan rate of 1 mV s⁻¹ which reproduces our previous study [14]. On the contrary, the highly crystalline RuO₂ exhibits a negligibly low capacitance of ~ 10 F g⁻¹. A peculiar phenomenon was observed when the CV scan rate was higher than 10 mV s⁻¹: the capacitance values of the composite electrodes do not monotonously decrease with x , giving the highest capacitance for the composite electrode at $x=5$ wt.% as seen in Fig. 3(a). Drawing a straight line between the capacitance values of $x=0$ and $x=75\%$ in Fig. 3(a), one can observe the positive deviation of the capacitance from the linear relation at $5 \leq x \leq 20$ wt.%.

To reveal what lies behind this phenomenon, we measured the electronic conductivity σ of the a–c composite electrodes. The electronic conductivities of the composite electrodes as a func-

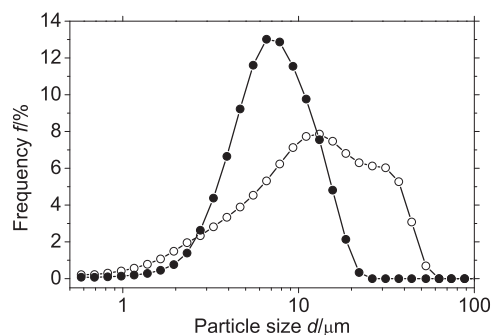


Fig. 4. Particle size distribution. Open circle: amorphous RuO₂ (a-RuO₂) and filled circle: crystalline RuO₂ (c-RuO₂).

tion of x are presented in Fig. 3(b). (As in the CV measurement, the 100% c-RuO₂ electrode was so fragile that we were not able to determine its electronic conductivity.) Even if the experimental errors are taken into account, the electronic conductivities positively deviate from the linear relation in the range $5 \leq x \leq 20$ wt.% as does the capacitance. Notice that the values of σ are scattered by batch only in this composition range, and fall on the line in the other range. As Fig. 3(a) and (b) imply, the proximate cause that enhances the capacitive behavior in the range $5 \leq x \leq 20$ wt.% is the higher electronic conductivity of the composite electrode for these compositions. The electronic conductivity of the bulk RuO₂ crystal is known to be $\sim 3 \times 10^4$ S cm⁻¹ which is far higher than those observed for the a–c composite electrodes. Hence, Fig. 3(b) suggests that the electrical contact between particles and/or between grain boundaries must be dominantly reflected in the electronic conductivity of the a–c composite electrodes. The particle size distribution of the a- and c-RuO₂ powders is shown in Fig. 4 which indicates that the RuO₂ particles shrink in size during the crystallization and dehydration at 973 K. At present, what caused the peculiar behavior in σ in $5 \leq x \leq 20$ wt.% range is unknown. One can speculate that when the c-RuO₂ content is high, the electric resistance between particles becomes significant because of the smaller particle size of the c-RuO₂ than the a-RuO₂. In the composition range of $5 \leq x \leq 20$ wt.%, the powder mixture of the a- and c-RuO₂s probably makes the best composition to provide the best electric contact between particles during the SPS process under the conditions used in the present study. Further work is necessary to verify (or falsify) the above speculation to explain the curious capacitive behavior of the SPS RuO₂ composite electrodes.

The capacitive properties of the SPS RuO₂ electrode have been to some extent improved from the SPS 100% a-RuO₂ electrode by forming a composite of amorphous and crystalline RuO₂ powders. Nonetheless, the performance of the SPS composite electrode at high rates, such as at the CV scan rate of 100 mV s⁻¹, is far below that of the RuO₂ electrode prepared by the conventional way in which the RuO₂ powder was mixed with acetylene black and PVdF (see Fig. 6 in our previous study [14]). The primary reason of the poor rate performance is, we postulate at present, the thickness of the SPS electrode (ca. 1 mm). We need to develop a maneuver to fabricate much thinner electrodes using the SPS technique to improve the rate performance.

References

- [1] S. Trasatti, *Electrochim. Acta* 36 (1991) 225–241.
- [2] C.C. Hu, W.C. Chen, K.H. Chang, *J. Electrochem. Soc.* 151 (2004) A281–A290.
- [3] L.C. Chiang, J.E. Chang, T.C. Wen, *Water Res.* 29 (1995) 671–678.
- [4] T.C. Wen, C.C. Hu, *J. Electrochem. Soc.* 139 (1992) 2158–2163.
- [5] S.M. Lin, T.C. Wen, *J. Electrochem. Soc.* 140 (1993) 2265–2271.
- [6] S.M. Lin, T.C. Wen, *J. Appl. Electrochem.* 23 (1993) 487–494.
- [7] J.P. Zheng, T.R. Jow, *J. Electrochem. Soc.* 142 (1) (1995) L6–L9.

- [8] J.P. Zheng, P.J. Cygan, T.R. Jow, *J. Electrochem. Soc.* 142 (8) (1995) 2699–2703.
- [9] O. Barbieri, M. Hahn, A. Foelske, R. Kötz, *J. Electrochem. Soc.* 153 (2006) A2049–A2054.
- [10] J.P. Zheng, Y. Xin, *J. Power Sources* 110 (2002) 86–90.
- [11] H. Kim, B.N. Popov, *J. Power Sources* 104 (2002) 52–61.
- [12] M. Min, K. Machida, J.H. Jang, K. Naoi, *J. Electrochem. Soc.* 153 (2006) A334–A338.
- [13] I.H. Kim, J.H. Kim, Y.H. Lee, K.B. Kim, *J. Electrochem. Soc.* 152 (2005) A2170–A2178.
- [14] K. Kuratani, H. Tanaka, T. Takeuchi, N. Takeichi, T. Kiyobayashi, N. Kuriyama, *J. Power Sources* 191 (2009) 684–687.