Polym. Bull. (2012) 68:553–560
DOI 10.1007/s00289-011-0650-5

ORIGINAL PAPER

Supercapacitive properties of polyaniline/hydrous RuO_2 composite electrode

Ho-Seong Nam · Kwang Man Kim · Sang Hern Kim · Byung Chul Kim · Gordon G. Wallace · Jang Myoun Ko

Received: 31 March 2011 / Revised: 4 August 2011 / Accepted: 7 October 2011 /
Published online: 14 October 2011

Abstract A composite electrode based on polyaniline (PANI) and hydrous RuO_2 is prepared by electrochemical deposition of PANI onto hydrous RuO_2 (PANI/RuO_2) and its supercapacitive properties are investigated using cyclic voltammetry. The specific capacitances of PANI/RuO_2 and hydrous RuO_2 electrodes are determined to be 708 and 517 F g^{-1} at 5 mV s^{-1}, respectively. Simple electrodeposition of PANI on the hydrous RuO_2 can achieve comparatively greater capacitance values.

Keywords Polyaniline · Hydrous RuO_2 · Capacitance · Supercapacitor

Introduction

Research on supercapacitors or ultracapacitors remains one of the most important activities in the area of electrochemical energy storage and conversion [1, 2]. The

H.-S. Nam
Department of Chemical & Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, South Korea

K. M. Kim (✉)
Research Team of Power Control Devices, Electronics and Telecommunications Research Institute (ETRI), Daejon 305-700, South Korea
e-mail: kwang@etri.re.kr

S. H. Kim · J. M. Ko (✉)
Department of Applied Chemistry and Biotechnology, Hanbat National University, Daejon 305-719, South Korea
e-mail: jmko@hanbat.ac.kr

B. C. Kim · G. G. Wallace
ARC Centre of Excellence for Electromaterials Science and Intelligent Polymer Research Institute, University of Wollongong, Wollongong, NSW 2522, Australia

importance of these devices has arisen in recent years because of failure of the conventional battery systems in high power conditions for electric vehicles. The predominant electrode materials used in supercapacitors were carbonaceous materials, conducting polymers, and metal oxides. The capacitance of carbon powder was mainly due to charging of the electrical double layer, referred to electrical double-layer capacitors [3]. By contrast, various conducting polymers such as polyaniline (PANI), polypyrrole, and polythiophene [2] or metal oxides such as RuO_2, MnO_2, and NiO_x [4] have been employed as electrode active materials in redox supercapacitors. Among the metal oxides studied, hydrous RuO_2 has been recognized as one of the most promising active materials due to its high specific capacitance, highly reversible redox reactions, wide potential window, and very good cycleability [5, 6]. However, high cost and poor abundance of RuO_2 posed problems for its commercial use. Moreover, only a very thin layer took part in the charge-storage mechanism while the underlying active material remained unreacted [7, 8].

On the other hand, the conducting polymers have received increasing interest as viable alternatives to carbons and metal oxides for supercapacitor application. Conducting polymers are relatively cheap, highly redox active materials that can readily be deposited onto a wide variety of substrates with a low fabrication cost at room temperature [9]. Especially due to its electrical conductivity, redox and environmental stability, PANI has been paid attention for use as an active material in rechargeable batteries and supercapacitors. Recently, different morphological forms of PANI including nanowire, nanotube, nanofiber, and hollow microsphere have been investigated [10]. A recognized limitation of conducting polymers is poor cycleabilty. This is ascribed to the limited mechanical properties and the instability of the radical cations for repeated redox processes [11, 12]. Recently, the supercapacitive properties of composite electrode consisting of PANI/Nafion/hydrous RuO_2 could be improved due to the stabilization of the radical cations by Nafion [10]. In this study, a composite electrode consisting PANI coated on the hydrous RuO_2 is prepared by an electrodeposition and its supercapacitive properties are investigated using a cyclic voltammetry (CV) technique.

Experimental

To prepare hydrous RuO_2, sodium dodecyl sulfate (Fluka) was used as received, and its concentration of 0.2 M was prepared by dissolving in 200 mL of distilled water from Milli-Q quality (Millipore). 0.2 mol of $RuCl_3{\cdot}6H_2O$ (Aldrich) was also dissolved as received. Then, the 40 mL of ethanol was added to the as-prepared solution. After vigorous stirring for 1 h, the 16 mL of 2.0 M KOH aqueous solution was added. After vigorous stirring for 3 h, the resulting black precipitates were separated by decantation, washed repeatedly with distilled water, and then dried. The dried precipitates were heated and incubated at 200 °C for 5 h to remove any residue. The Brunauer–Emmett–Teller surface area was measured using a Smartsorb-92/93 after degassing at 100 °C for 2 h and then resulted in 220 $m^2\ g^{-1}$.

The hydrous RuO_2 electrode was fabricated by mixing an as-prepared RuO_2 powder (80 wt%) as an active material with a vapor-grown carbon fiber (10 wt%) (Showa Denko, specific surface area 13 $m^2\ g^{-1}$, average aspect ratio $L/D = 67$) as a conductive agent, poly(vinylidene fluoride-*co*-hexafluoropropylene) (10 wt%) as a binder, and *N*-methyl-2-pyrrolidone as a solvent. The resulting slurry was cast on a Pt foil (50 μm thick) to obtain electrode film (60 μm thick) using a doctor blade apparatus. The electrodes were dried overnight and then further dried under a vacuum at 60 °C for 24 h. After drying, the coated collector was uniaxially pressed to enhance the contact and adherence to the foil.

Electrochemical deposition was carried out in a one-compartment cell with a three-electrode configuration. An Ag/AgCl was used as a reference electrode, the hydrous RuO_2 electrode (0.05 g, 1 × 1 cm^2) as a working electrode, and Pt foil (2 × 2 cm^2) as a counter electrode. All potentials reported here were measured against Ag/AgCl. Deposition of PANI was carried out potentiodynamically by subjecting the working electrode to potential cycling between −0.05 and 0.85 V at a scan rate of 5 mV s^{-1} in an aqueous electrolyte solution consisting of 0.1 M aniline and 0.2 M H_2SO_4 for 4 cycles under N_2 atmosphere. After deposition, the samples were rinsed with distilled water and dried for 12 h under N_2 atmosphere. The weight of PANI-deposited hydrous RuO_2 electrode was about 0.09 g.

The CV measurements for the hydrous RuO_2 electrode and the PANI-deposited hydrous RuO_2 electrode were carried out using Autolab (Eco Chemie, PGstat 100) instrument. An Ag/AgCl (saturated KCl, 0.222 V vs. SHE) reference electrode equipped with a Luggin capillary was used to control the potentials of the working electrode. The tip of the capillary was kept as close as 1 or 2 mm gap to the surface of the working electrode to minimize the errors due to solution *iR* drop. The CV test was carried out at various scan rates in the potential range of 0–1.0 V (vs. Ag/AgCl) in 1.0 M H_2SO_4 aqueous electrolyte solution. The surface morphologies of the hydrous RuO_2 electrode and the PANI-deposited hydrous RuO_2 electrode were also observed using a field-emission scanning electron microscope (Hitachi S-4800).

Results and discussion

Figure 1 shows the scanning electron microscopic images of the hydrous RuO_2 and PANI-deposited RuO_2 electrodes. In the hydrous RuO_2 electrode, spherical or plate-like particles distributed can be obviously observed to give a porous structure. This is slightly deviated from a previously reported morphology [13] of the hydrous RuO_2 electrode obtained from the thermal treatment of ruthenium ethoxide solution [14], which shows small granular particles coated densely on current collector foil. In contrast, the PANI/RuO_2 electrode clearly shows the deposition of PANI species on the surfaces of porous RuO_2 spherical particles. Such morphology of PANI/RuO_2 electrode can favor the interaction between electroactive material and electrolytic ions, which is an important factor to enhance the oxidation–reduction reactions. That is, the redox reactions can be expected to occur more intensively at the surface of PANI/RuO_2 electrode than that of hydrous RuO_2 electrode.

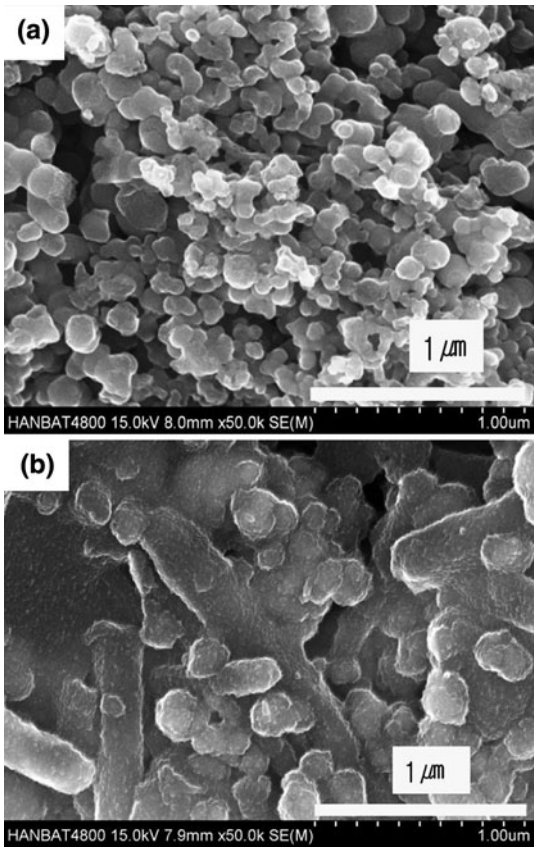

Fig. 1 Scanning electron micrographs of **a** hydrous RuO_2 and **b** PANI-deposited hydrous RuO_2 electrodes

The amounts of active materials (PANI and hydrous RuO_2) in these supercapacitor electrodes can be calculated as follows: the loading of metallic Ru in the hydrous RuO_2 is determined to 55.2 wt% by weighing the hydrous RuO_2 powder. The loadings of metallic Ru in the RuO_2 and PANI/RuO_2 electrodes can also be estimated to 44.2 and 24.6 wt%, respectively. The 24.6 wt% Ru is originated by the amount of PANI (0.04 g) electrodeposited on the surface of hydrous RuO_2 electrode. Such percentage of metallic Ru is lower than the 33 wt%. Ru in a carbon nanofiber/hydrous RuO_2 electrode [13], but much higher than 7 wt% Ru in a PANI/carbon nanotube/RuO_2 electrode [15]. Thus, a sufficient utilization of Ru component can be expected to serve as an active site of supercapacitive property, together with the PANI species.

The cyclic voltammograms for the RuO_2 and PANI/RuO_2 electrodes are shown in Fig. 2a, b, respectively. Both voltammograms include characteristic oxidation–reduction peaks of hydrous RuO_2 around 0.4–0.5 V and the electrical double-layer behavior in the region of 0.9–1.0 V (corresponding to the corner portion of rectangle). The broad current peak pair in the middle of the potential window is attributed to the reversible redox processes by the sorption of proton and water molecules [16]. However, the oxidation–reduction behavior is more intensified in

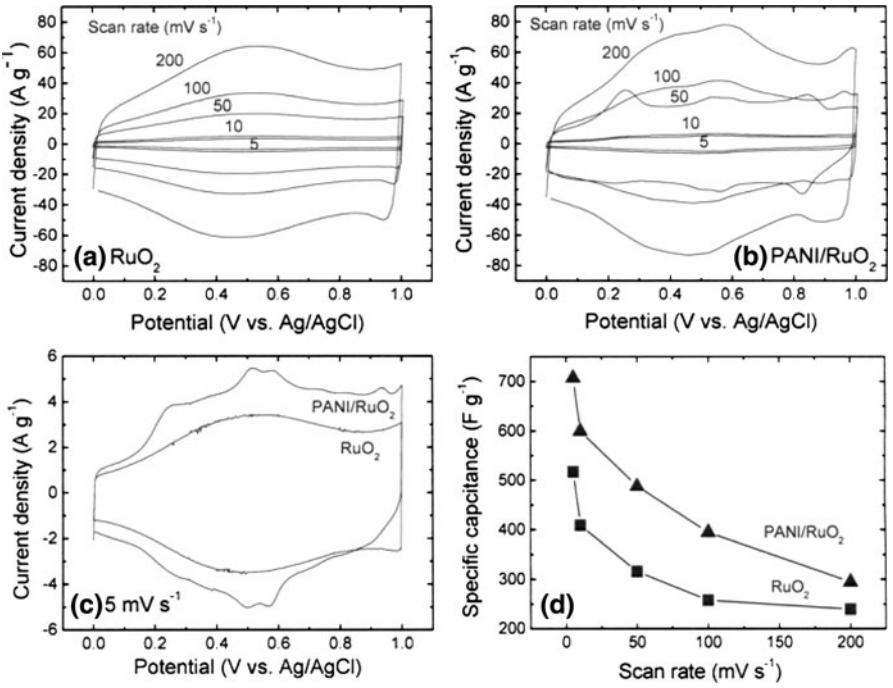

Fig. 2 Cyclic voltammograms of **a** hydrous RuO_2 and **b** PANI/RuO_2 composite electrodes. Enlarged cyclic voltammograms of hydrous RuO_2 and PANI/RuO_2 electrodes at the scan rate of 5 mV s^{-1} are presented in **c** for comparison. Specific capacitances of hydrous RuO_2 and PANI/RuO_2 electrodes are also presented in **d** as function of scan rate

PANI/RuO_2 electrode than the hydrous RuO_2 electrode (see Fig. 2b). For instance, the PANI/RuO_2 electrode shows typical faradaic redox behavior at potentials over 0.2 V. Comparing Fig. 2b and c, the redox peak position (near 0.2 V/0.8 V) shifts slightly with increase in scan rate to yield wider potential range between the cathodic and anodic peaks, indicating a capacitance decrease as the *iR* drop occurs significantly. These indicate that the electrodeposition of PANI component on the hydrous RuO_2 surely provides more opportunity of utilizing the electroactive materials. That is, the more sites of redox reaction, corresponding to the redox peaks of Fig. 2b, can be produced in the bulk of PANI/RuO_2 electrode, as well as the faradaic reactions on the surface of composite electrode. Thus, the increase in the specific capacitance can be expected by the electrodeposition of PANI on the hydrous RuO_2.

For instance, cyclic voltammograms at 5 mV s^{-1} and specific capacitance profiles of hydrous RuO_2 and PANI/RuO_2 electrodes are shown in Fig. 2c, d, respectively. The specific capacitance values are determined from the cyclic voltammograms using the equation $C = (Q_a + Q_c)/(2\ m\Delta V)$, where C, Q_a, Q_c, m, and ΔV denote the specific capacitance, anodic and cathodic charges on each scan, mass of the electroactive material, and the potential window of the CV, respectively. It clearly shows more intensive oxidation–reduction peaks for the PANI/RuO_2

Table 1 Specific capacitances (F g^{-1}) of PANI- and/or hydrous RuO_2-based active electrode materials as function of scan rate

Active material	Scan rate (mV s^{-1})								Ref.
	5	10	50	100	200	300	500	1000	
PANI	–	–	–	330	–	325	310	295	[10][b]
PANI/Nafion	–	–	–	425	–	365	370	367	[10][b]
PANI/Nafion/$RuO_2{\cdot}xH_2O$	–	–	–	475	–	390	380	375	[10][b]
PANI/$RuO_2{\cdot}xH_2O$	708	600	480	400	295	–	–	–	This study
VGCF/$RuO_2{\cdot}xH_2O$	–	1017	–	1000	–	940	920	824	[13]
$RuO_2{\cdot}xH_2O$[a]	–	410	–	400	–	350	305	258	[13]
$RuO_2{\cdot}xH_2O$	517	405	320	260	240	–	–	–	This study

Calculated from CV measurements within the potential range of 0.0–1.0 V (vs. Ag/AgCl) in an aqueous electrolyte of 1.0 M H_2SO_4

VGCF vapor-grown carbon fiber

[a] Prepared by the thermal treatment of ruthenium ethoxide solution [14]

[b] Measured within the potential range of −0.2 to 0.8 V (vs. Ag/AgCl)

electrode than the hydrous RuO_2 electrode. The specific capacitance of the hydrous RuO_2 and PANI/RuO_2 electrodes are evaluated as 708 and 517 F g^{-1}, respectively, recorded at a scan rate of 5 mV s^{-1}. Including this study, the previously reported specific capacitance values of PANI- and/or hydrous RuO_2-based active electrode materials for supercapacitors are summarized in Table 1.

As shown in Table 1, the scan rates measured in this study are moderately shifted to lower range, compared to the previous reports [10, 13], to yield the comparatively greater capacitance values at low scan rates. It is meaningful for supercapacitor application because the simple electrodeposition of PANI on the hydrous RuO_2 can achieve those specific capacitance values at low scan rates. Moreover, the

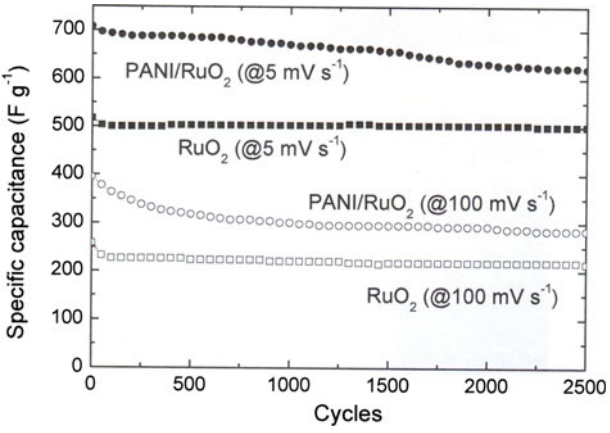

Fig. 3 Specific capacitances of hydrous RuO_2 and PANI/RuO_2 composite electrodes at different scan rates (5 and 100 mV s^{-1}) as a function of cycle number

as-supplied hydrous RuO_2 used in this study can be one of promising active materials to achieve an approximately greater capacitance at low scan rates if compared with a well-purified hydrous RuO_2 from the heat treatment of ruthenium ethoxide [13]. Since, the supercapacitive performance depends on synthetic procedure, loading and hydration number of hydrous RuO_2, specific resistance, specific surface area, electrode thickness, and so on, further studies for the PANI- and/or hydrous RuO_2-based supercapacitor materials should be proceed with controlling such conditions more carefully. In addition, cycle performances of PANI/RuO_2 and hydrous RuO_2 electrodes are shown in Fig. 3, obtained at different scan rates of 5 and 100 mV s^{-1}. The hydrous RuO_2 electrode shows highly stable cycleability after 2500 cycles, similar to other hydrous RuO_2 composite electrode [13]. However, the capacitance retention of PANI/RuO_2 electrode slightly decreases with the cycle number, mainly due to the mechanical degradation occurred during repeated redox process [15].

Conclusions

The electrochemical deposition of PANI on the as-supplied hydrous RuO_2 is carried out and the supercapacitive properties of the composite electrode are characterized using the CV measurement. The surface morphologies clearly show the porous structure of RuO_2 and the deposition of PANI on the hydrous RuO_2. The specific capacitances of PANI/RuO_2 and hydrous RuO_2 electrodes decrease from 708 to 295 F g^{-1} and from 517 to 240 F g^{-1}, respectively, as the scan rate increases from 5 to 200 mV s^{-1}. As a result, it is possible to apply the PANI/RuO_2 composite to the supercapacitor electrode material because such a simple electrodeposition of PANI on the hydrous RuO_2 can achieve comparatively greater capacitance values at low scan rates.

Acknowledgment This study was supported by a grant (M2009010025) from the Fundamental R&D Program for Core Technology of Materials funded by the Korean Ministry of Knowledge Economy.

References

1. Conway BE, Birss V, Wojtowicz J (1997) The role and utilization of pseudocapacitance for energy storage by supercapacitors. J Power Sources 66:1–14
2. Conway BE (1999) Electrochemical supercapacitors. Kluwer, New York
3. Burke A (2000) Ultracapacitors: why, how, and where is the technology. J Power Sources 91:37–50
4. Nam K-W, Kim K-B (2002) A study of the preparation of NiO_x electrode via electrochemical route for supercapacitor applications and their charge storage mechanism. J Electrochem Soc 149:A346–A354
5. Fan L-Z, Maier J (2006) High-performance polypyrrole electrode materials for redox supercapacitors. Electrochem Commun 8:937–940
6. Zheng JP, Jow TR (1995) A new charge storage mechanism for electrochemical capacitors. J Electrochem Soc 142:L6–L8
7. Kim I-H, Kim K-B (2006) Electrochemical characterization of hydrous ruthenium oxide thin-film electrodes for electrochemical capacitor applications. J Electrochem Soc 153:A383–A389

8. Kim I-H, Kim J-H, Kim K-B (2005) Electrochemical characterization of electrochemically prepared ruthenium oxide/carbon nanotube electrode for supercapacitor application. Electrochem Solid State Lett 8:A369–A372
9. Chen L, Sun L-J, Luan F, Liang Y, Li Y, Liu X–X (2010) Synthesis and pseudocapacitive studies of composite films of polyaniline and manganese oxide nanoparticles. J Power Sources 195:3742–3747
10. Song RY, Park JH, Sivakkumar SR, Kim SH, Ko JM, Park D-Y, Jo SM, Kim DY (2007) Supercapacitive properties of polyaniline/Nafion/hydrous RuO_2 composite electrodes. J Power Sources 166:297–301
11. Zhou YK, He B-L, Zhou W-J, Huang J, Li X-H, Wu B, Li H-L (2004) Electrochemical capacitance of well-coated single-walled carbon nanotube with polyaniline composites. Electrochim Acta 49:257–262
12. Park JH, Ko JM, Park OO, Kim D-W (2002) Capacitance properties of graphite/polypyrrole composite electrode prepared by chemical polymerization of pyrrole on graphite fiber. J Power Sources 105:20–25
13. Lee BJ, Sivakkumar SR, Ko JM, Kim JH, Jo SM, Kim DY (2007) Carbon nanofibre/hydrous RuO_2 nanocomposite electrodes for supercapacitors. J Power Sources 168:546–552
14. Park JH, Ko JM, Park OO (2003) Carbon nanotube/RuO_2 nanocomposite electrodes for supercapacitors. J Electrochem Soc 150:A864–A867
15. Ko JM, Ryu KS, Kim S, Kim KM (2009) Supercapacitive properties of composite electrodes consisting of polyaniline, carbon nanotube, and RuO_2. J Appl Electrochem 39:1331–1337
16. Sopčić S, Roković MK, Mandić Z, Inzelt G (2010) Preparation and characterization of RuO_2/polyaniline composite electrodes. J Solid State Electrochem 14:2021–2026