Short communication

Pseudo-capacitance of composite electrode of ruthenium oxide with porous carbon in non-aqueous electrolyte containing imidazolium salt

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ABSTRACT

Pseudo-capacitance of composite materials where ruthenium oxide particles are loaded on activated carbon has been evaluated in the electrolyte of 1-ethyl-3-methyl imidazolium tetrafluoroborate dissolved in acetonitrile. The composite materials prepared by conventional a sol–gel method have dispersed structure of ruthenium oxide particle of tens nanometer diameter on the surface of activated carbon. The extent of the pseudo-capacitance of the composite electrodes in the imidazolium salt electrolyte, estimated by the comparison of the capacitance per surface area of electrode in different non-aqueous electrolyte, is ca. 3–5 $\mu F\,cm^{-2}$ in addition to the double-layer capacitance of ca. 6 $\mu F\,cm^{-2}$, depending on the loading status of ruthenium oxide. The symmetric cell consisting of the composite electrode containing 18 wt% of ruthenium oxide and the imidazolium salt electrolyte provides cell capacitance based on the pseudo-capacitance by a constant-current test.

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1. Introduction

Electrochemical capacitors have been attracted as advanced power sources or power assistants with high power density and cycle stability. Many kinds of electrochemical capacitor systems applying with various reactions have been proposed in order to improve the low energy density of double-layer capacitors. Among them, electrochemical capacitors based on ruthenium oxide (RuO_2) electrode has been widely investigated mainly after Zheng et al. reported that hydrated ruthenium oxide ($RuO_2 \cdot xH_2O$) exhibits as a high capacitance as 720 $F\,g^{-1}$ in aqueous solution [1–5]. The adsorption process of proton on $RuO_2 \cdot xH_2O$ has been proposed as the origin of the pseudo-capacitance of RuO_2 [1]. The reason for the high capacitance of $RuO_2 \cdot xH_2O$ has been explained as crystalline water in the material also provides active proton and the effective surface of RuO_2 is enlarged [1,6,7].

In most cases the electrolytes used in capacitors based on RuO_2 are aqueous ones, because the above reaction for the pseudo-capacitance of RuO_2 requires proton in electrolyte. Aqueous electrolyte determines the working voltage of a capacitor cell up to ca. 1.2 V and thus limits the energy density of capacitor cell. Therefore some attempts to apply non-aqueous electrolyte to the capacitor based on RuO_2 have been made. Rochefort et al. revealed that ionic liquid containing proton provides pseudo-capacitance of RuO_2 [8]. The authors have proposed non-aqueous polymeric gel electrolyte, containing CF_3SO_3H dissolved in dimethylformamide and poly(vinyledene difluoride-hexafluoropropylene) matrix, for all-solid-state capacitors based on $RuO_2 \cdot xH_2O$ [9].

Proton itself determines cathodic limit of electrolyte, even if non-aqueous solvent is used. Therefore it is meaningful to find other candidates of cations promoting above adsorption process on RuO_2. The authors previously reported that 1-ethyl-3-methyl imidazolium tetrafluoroborate ($EMIBF_4$) can also promote the pseudo-capacitance of crystalline RuO_2 by selecting adequate solvent such as acetonitrile, by the comparative study with tetraethylammonium tetrafluoroborate ($TEABF_4$) electrolyte [10]. In this sequence EMI cation having hydrogen atoms having tendency to form hydrogen bonding may promote the pseudo-capacitance of RuO_2. In the previous trial, the obtained specific capacitance was still low insufficient to the practical use, because crystalline RuO_2 with low surface area was used as test electrode. Therefore it should be assessed whether such pseudo-capacitance of RuO_2 provided by $EMIBF_4$ electrolyte can be utilized in a practical capacitor system. In the present study, the authors have focused on RuO_2/porous carbon composite electrode, where fine particles of RuO_2 are dispersed on the surface of porous carbon. There have been many attempts to prepare and utilize RuO_2/carbon composite electrode for capacitors for the purpose of obtaining both high capacitance from RuO_2 and rate capability from carbon substrate with high surface area [11–21]. In addition, the authors would emphasize the necessity of high surface area of RuO_2 fine particles to be applied in non-aqueous capacitor system. The present preliminary study includes the preparation of composite electrodes of RuO_2 with conventional activated carbon (AC) with a conventional

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sol–gel method [1,13], and the evaluation of capacitance of the RuO_2/AC composite electrode in non-aqueous electrolyte containing $EMIBF_4$.

2. Experimental

2.1. RuO_2/AC electrode preparation

RuO_2/AC composite materials having prescribed RuO_2/AC gravimetric ratios have been prepared by sol–gel method. Activated carbon (AC; capacitor grade) was dispersed into water together with prescribed amount of hydrated ruthenium chloride ($RuCl_3·3H_2O$) (Kanto Chemical, Japan). An alkali solution was titrated into this suspension and thus ruthenium hydroxide was precipitated. In the present study, two kinds of $1.0\,mol\,dm^{-1}$ alkali solutions, sodium hydroxide NaOH and sodium hydrocarbonate $NaHCO_3$, were applied in order to vary the size of precipitated ruthenium hydroxide. Ruthenium hydroxide/AC composite was collected by the filtration from the resulted suspension. After calcined at 200 °C and dried in a vacuum, resulted RuO_2/AC composites were obtained. The morphology of loaded RuO_2 particles in the composites was observed by transmitted electron microscope (TEM; JEM-2010F, JEOL Co., Japan). The pore structure of the composites was estimated from N_2 adsorption–desorption isotherm (NOVA2000, Quantach Instruments Co., Italy). The content of ruthenium in a RuO_2/AC composite was estimated by comparing the mass of a composite before and after the burning-out of AC at 600 °C for 5 h. For electrochemical measurements, RuO_2/AC composites were molded in sheets with the thickness of ca. 1 mm by the aid of poly(tetrafluoroethylene) (PTFE; Mitsui Fluorochem Co., Japan) binder (10 wt%). Hereafter each composite is denoted with used alkali (OH or HCO) and its RuO_2 content: for example, the composite prepared by using $NaHCO_3$ and containing 18 wt% of RuO_2 is denoted as $RuO_2/AC(HCO, 18)$.

2.2. Electrolyte preparation

$TEABF_4$ used in the present study is a commercial material (Tomiyama Pure Chemical Co., Japan). $EMIBF_4$ was prepared by the procedure reported previously [10,22]. Each salt was dissolved into acetonitrile (AN; Synthesis grade, Wako Chemicals, Co., Japan) to $1.0\,mol\,dm^{-3}$ solution. The dissolving procedure was conducted in a glove box filled with argon. The water content of the electrolytes was checked by a Karl-Fischer titrator (Hiranuma Co., AQ-7) to be in a range from 100 to 200 ppm.

2.3. Measurement of electrochemical properties

For determining the electrochemical properties of RuO_2/AC composites, $RuO_2/AC/PTFE$ composite sheet was cut into a disk, and then fixed with platinum current collector by a PE holder with a screw cap having a hole of 7 mm diameter. A 3-electrode sealed glass cell was assembled with a $RuO_2/AC/PTFE$ composite as working electrode, a silver wire as quasi-reference electrode, and a Pt plate as counter electrode in a glove box filled with argon. Cyclic voltammetry (CV) measurement was conducted by using a potentiostat (HA-151, Hokuto Denko Co., Japan), equipped with a function generator (HB-104, Hokuto Denko Co., Japan) and a digital recorder (8835, Hioki Electrc Co., Japan), under the scan rate of $2\,mV\,s^{-1}$ between $-1.0\,V$ and $0.5\,V$ vs. Ag. The specific capacitances of RuO_2/AC electrodes are estimated from the estimated charge by the voltammograms. The capacitor cell behavior using the RuO_2/AC composites was evaluated by using a 2-electrode symmetric cell. The $RuO_2/AC/PTFE$ composite disks with 7 mm diameter (containing ca. 0.27 g of the composite) were enclosed with a glass fiber cloth separator (Whatman) and small amount of electrolyte

Table 1
Compositions and specific surface areas of RuO_2/AC composites.

	RuO_2 content expected from starting material/wt%	Estimated RuO_2 content/wt%	Specific surface area/m^2 g^{-1}
AC	0	0	1173
$RuO_2/AC(OH, 3)$	10	3	1094
$RuO_2/AC(OH, 18)$	20	18	874
$RuO_2/AC(OH, 34)$	40	34	745
$RuO_2/AC(OH, 42)$	50	42	544
$RuO_2/AC(HCO, 8)$	10	8	986
$RuO_2/AC(HCO, 18)$	20	18	957
$RuO_2/AC(HCO, 32)$	40	32	870
$RuO_2/AC(HCO, 62)$	80	62	541

into a sealed cell with platinum current collectors and PTFE body. Constant-current charge–discharge measurement was conducted by using a cycler (BTS-2004, Nagano Co., Japan) under the current of 30 or 150 mA per weight of active material, between 2.0 V and 0 V cut-off voltages.

3. Results and discussion

3.1. Characterization of RuO_2/AC electrodes

The RuO_2 contents and specific surface areas of the RuO_2/AC composites prepared using NaOH and $NaHCO_3$ solutions are summarized in Table 1. The RuO_2 contents are compared with their expected values from the ratio of starting materials. The estimate RuO_2 content in a composite is always slightly lower than an expected content due to the incompleteness of the precipitation in the sol–gel process; i.e., the ruthenium deposition the wall of glassware, or remain in the solution phase. In both cases, the RuO_2 contents in the composites are more or less assumed to be similar to those expected values except for $RuO_2/AC(OH, 42)$. In the case of some higher loading amount of RuO_2, the incompleteness of the precipitation is not ignorable. The specific surface area of the composite decreases when the RuO_2 content increases, likely due to the covering of pores of AC by RuO_2. For comparable RuO_2 contents, the RuO_2/AC composites prepared by the $NaHCO_3$ titration have higher specific surface area than those by the NaOH titration. This indicates that RuO_2 particle in the former composites are smaller than the latter.

Fig. 1 shows the TEM images of some RuO_2/AC composites. In all the TEM images, RuO_2 particles are shown as black spots in the AC matrices. The size of RuO_2 particles appears to be varied by the RuO_2 content of composites and the alkali used in the preparation procedure. In the image of $RuO_2/AC(OH, 18)$, RuO_2 particles of ca. 2 nm forming aggregate of ca. tens nanometer are observable. RuO_2 particles in the composite prepared with $NaHCO_3$ are similar ($\sim$2 nm) to those with NaOH but appear to be more dispersed. Such effects are as expected from the previous reports [13]. The smaller particles of RuO_2, and the dispersion of the particles, provide larger specific surface area of RuO_2/AC (HCO) compared with $RuO_2/AC(OH)$.

3.2. Capacitance of RuO_2/AC in imidazolium salt electrolyte

Fig. 2 shows the voltammograms at 3rd cycle of the $RuO_2/AC(OH, 18)$ composite electrode in $EMIBF_4/AN$ and $TEABF_4/AN$ electrolytes. $TEABF_4/AN$ electrolyte provides a typical rectangular voltammogram for a porous polarized electrode. In contrast, the voltammogram in $EMIBF_4/AN$ is somewhat distorted and some feature like broad peaks are found around 0 V and $-0.5\,V$. The apparent charging current of the double-layer in the voltammogram is higher in $EMIBF_4/AN$ than in $TEABF_4/AN$. Specific
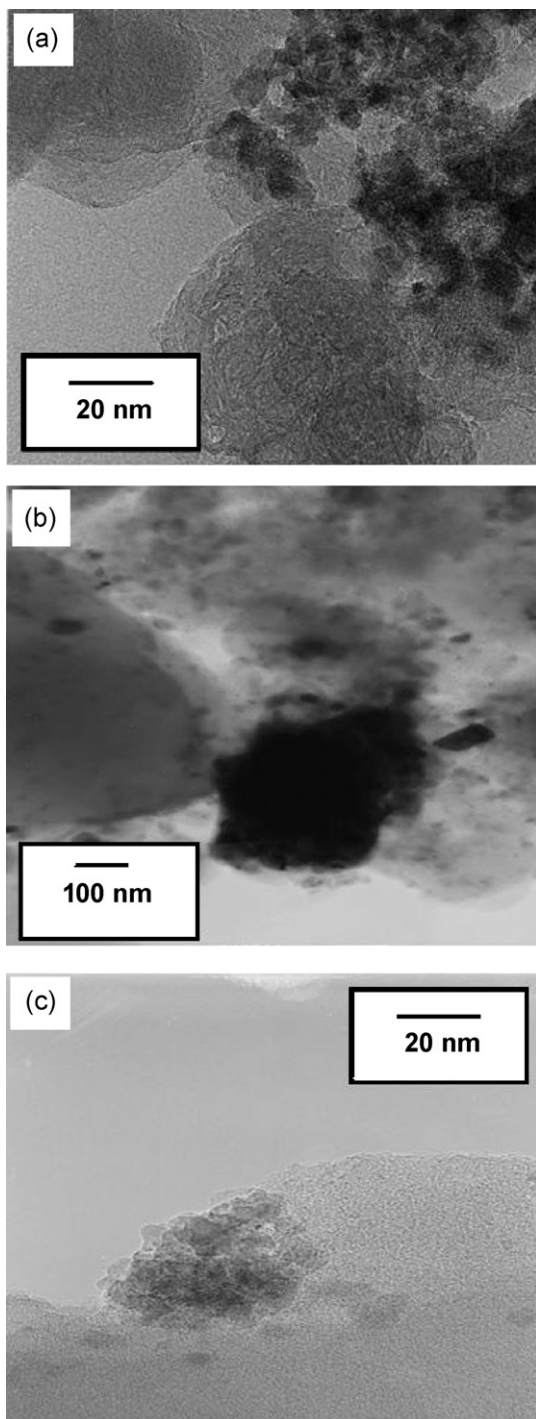
Fig. 1. TEM images of the RuO_2/AC composites. (a) $RuO_2/AC(OH, 18)$; (b) $RuO_2/AC(OH, 42)$; (c) $RuO_2/AC(HCO, 18)$.

Fig. 2. Cyclic voltammograms of $RuO_2/AC(OH, 18)$ electrode in (a) $EMIBF_4/AN$ and (b) $TEABF_4/AN$ electrolytes.

increase of the RuO_2 content. As shown in Table 1, the surface area of the RuO_2/AC composites decreases by the increase of the RuO_2 content. The decrease of capacitance of the RuO_2/AC electrodes in the $TEABF_4/AN$ electrolyte indicates that the double-layer capacitance mainly contributes in this case. In contrast, the capacitance in $EMIBF_4/AN$ shows a maximum when the RuO_2 content is around 20 wt%, and is higher than that in $TEABF_4/AN$ at the same composite electrode. The higher capacitance of the RuO_2/AC electrodes in $EMIBF_4/AN$ than in $TEABF_4/AN$, and the existence of the maximum RuO_2 content for the capacitance indicate the existence of an additional capacitance, i.e., pseudo-capacitance, in this electrolyte, similar to crystalline RuO_2 electrode reported previously [10]. The $RuO_2/AC(HCO)$ composites at a loading amount of RuO_2 to 20 wt% exhibit slightly higher capacitances than the $RuO_2/AC(OH)$ composites in the $EMIBF_4$ electrolyte, probably due to their distributions of smaller RuO_2 particles.

In order to clarify the contribution of pseudo-capacitance, the capacitances by unit surface areas are calculated from the specific capacitance and the specific surface area values. Fig. 3 is rearranged and the dependence of the capacitances per surface area of RuO_2/AC on the RuO_2 content is exhibited in Fig. 4. The capacitance of the

capacitances of various RuO_2/AC composites in both electrolytes are estimated from the voltammograms and plotted in Fig. 3 in function of RuO_2 content in the composites. In this figure, specific capacitance values are calculated based on the mass of RuO_2/AC composites except for the case of pristine AC electrode. Pristine AC shows ca. $70 \, F \, g^{-1}$ of specific capacitance regardless of electrolyte regardless of the kind of electrolyte salt. This capacitance can be assumed to be a double-layer capacitance formed on the carbon surface. For the RuO_2/AC composite electrodes, the capacitance shows different dependence on the RuO_2 content. In $TEABF_4/AN$, the capacitance monotonously decreases by the
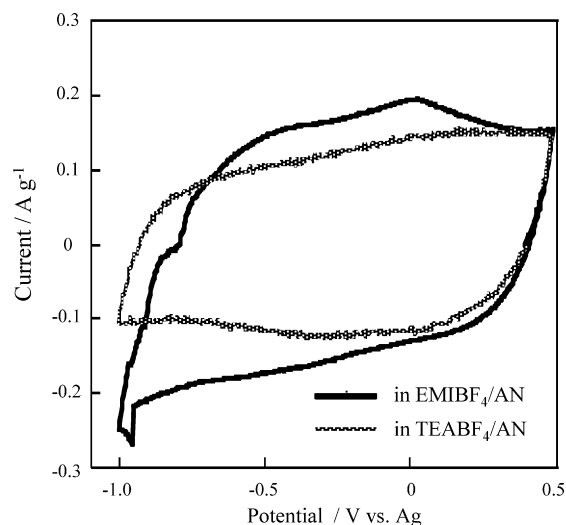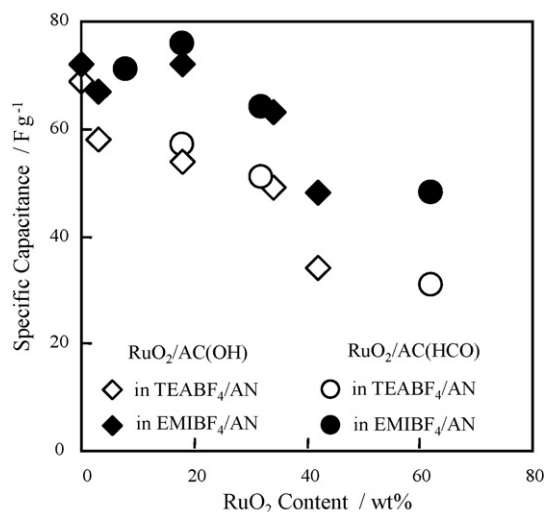

Fig. 3. RuO_2 content dependence of specific capacitance of RuO_2/AC electrodes in $EMIBF_4/AN$ and $TEABF_4/AN$ electrolytes.
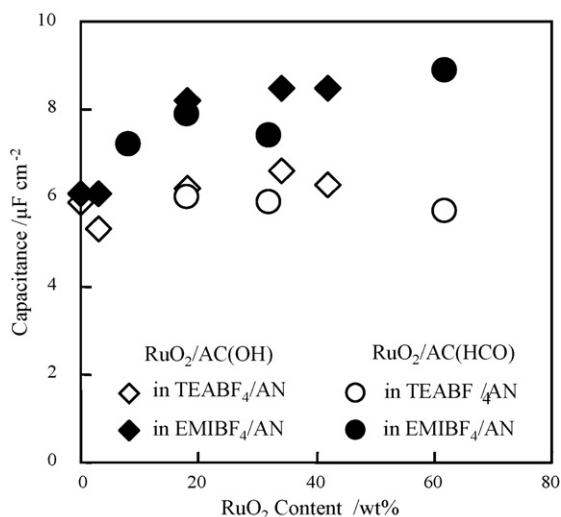
Fig. 4. RuO$_2$ content dependence of capacitance of RuO$_2$/AC electrode per surface area in EMIBF$_4$/AN and TEABF$_4$/AN.

Fig. 5. Constant-current charge–discharge profiles of RuO$_2$/AC(OH, 18) electrode at 2nd and 300th cycles in EMIBF$_4$/AN electrolyte. Current density: 30 mA g^{-1}, cut-off voltage: 2.0–0.1 V.

neat AC electrode is around 6 μF cm^{-2} regardless of the electrolyte. In this case only double-layer capacitance on the AC surface exhibits for both the electrolytes. The capacitance values per surface area of RuO$_2$/AC electrodes are different by the electrolyte. The TEABF$_4$/AN electrolyte provides the capacitance as high as 6 μF cm^{-2}, similar to the double-layer capacitance shown on the AC electrode, regardless of the loading amount of RuO$_2$. In contrast, the capacitances per unit surface area of the RuO$_2$/AC composite electrodes are above 6 μF cm^{-2} and are dependent on the RuO$_2$ content in the EMIBF$_4$/AN electrolyte. Such an additional capacitance in this electrolyte is considered to be pseudo-capacitance of RuO$_2$, as reported previously for crystalline RuO$_2$ electrode. The dependence of the additional capacitance on the RuO$_2$ content appears to depend on the preparation method of the RuO$_2$/AC composite. When the RuO$_2$/AC is prepared by the titration of NaOH solution, the additional capacitance saturates at the RuO$_2$ content of ca. 20% and then is stable at ca. 8 μF cm^{-2}. On the other hand, when the preparation procedure including NaHCO$_3$ titration is applied, the additional capacitance increases as the increase of the RuO$_2$ content to 60 wt%. Such a difference in the capacitance behavior for the preparation method of RuO$_2$/AC electrode may be related with the difference in the morphology of RuO$_2$ in the composite. The smaller size of RuO$_2$ particle in the composite may offer the higher reaction interface and then provide rather unsaturated capacitance behavior toward the increase of the RuO$_2$ content. The calcination temperature of the RuO$_2$/AC, 200 °C, is expected to provide partially hydrated ruthenium oxide according to the previous study of Zheng and Jow [1]. Nevertheless, the pseudo-capacitance in EMIBF$_4$/AN electrolyte is dependent on the surface area of ruthenium oxide particle on the composite. The result suggests that the influence of crystalline water is minor and that the adsorption process of EMI cation on ruthenium oxide contribute mainly to the pseudo-capacitance.

A symmetric cell by RuO$_2$/AC(OH, 18) electrodes with EMIBF$_4$/AN electrolyte was assembled and evaluated for the cell performance. Fig. 5 shows the voltage profiles of the cell at different cycles in a constant-current test. The cell exhibits typical triangular charge–discharge profiles for capacitor without significant IR drop. The cycle performances, even only at initial stage, of the cell capacitance from such discharge profiles for symmetric cells by AC or RuO$_2$/AC(OH, 18) electrodes are plotted in Fig. 6. The capacitance for the AC symmetric cell under 30 mA g^{-1} of current decreases from 22 F g^{-1} at initial cycle to 20 F g^{-1} at 30th cycle, probably due to the existence of negligible amount of impurity water in the pores of AC.
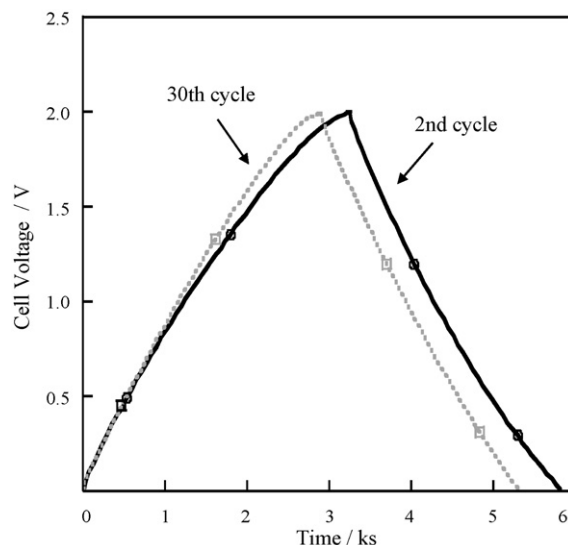
Such impurity water is considered to affect significantly the electrode behavior only after cycles. The RuO$_2$/AC cell exhibits rather stable cycle behavior. Such impurity water would be removed after calcination process when preparing the RuO$_2$/AC composite. Here the authors insist that the pseudo-capacitance based on the interaction between EMIBF$_4$ and RuO$_2$ is available under a practical constant-current condition during several tens cycles. Fig. 6 shows the capacitances at two cases of different current densities, 30 mA and 150 mA per weight of active material in either electrode. The capacitance decrease at higher current is more significant at the RuO$_2$/AC cell compared with the AC cell. This behavior suggests that the slower pseudo-capacitive surface process may be dominant in the capacitance in the RuO$_2$/AC cell under such a constant-current situation.

From the above results, the RuO$_2$/AC electrode for this purpose should be designed as nanoparticles of RuO$_2$ dispersed highly onto porous carbon having adequate pore structure. Future efforts are made for preparing optimum RuO$_2$/porous carbon composite, and the investigation of cell performances including long-term cycle
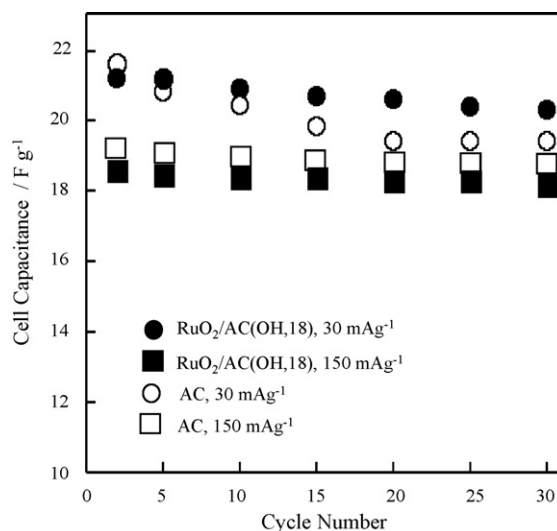

Fig. 6. Cycle performances of specific capacitances of AC and RuO$_2$/AC(OH, 18) electrodes.

stability. Here it is intended that the pseudo-capacitance of ruthenium oxide electrode by the existence of substituted imidazolium cation has possibility to be extended to electrochemical capacitor system with applicable capacitance.

4. Conclusion

RuO_2/AC composite electrodes exhibit pseudo-capacitance in the EMIBF$_4$/AN electrolyte. The existence of such pseudo-capacitance is obvious from the dependence of the capacitance per surface area on the RuO_2 content in the composite electrodes. The extent of the pseudo-capacitance is strongly influenced by the loaded content and status, e.g. particle size, of RuO_2. The pseudo-capacitance of the RuO_2/AC electrode is obtained by constant-current test of a symmetric cell as well as by voltammetric test. At the present stage, the increase of the specific capacitance of the RuO_2/AC composite electrode in the EMIBF$_4$ electrolyte is still small. Further optimization on porous carbon substance and preparation process is inevitable to realize the potential energy density of such RuO_2/carbon composite electrode in the non-aqueous media.

Acknowledgements

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