Voltammetric Behavior of Ruthenium Oxide in Organic Electrolyte Containing Imidazolium Salt

Minato EGASHIRA,* Tomoya UNO, Nobuko YOSHIMOTO, and Masayuki MORITA

Graduate School of Science & Engineering, Yamaguchi University (2-16-1 Tokiwadai, Ube, Yamaguchi 755-8611, Japan)

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The pseudo-capacitance of ruthenium oxide electrode has been compared in organic solvent electrolytes having different solutes, tetrafluoroborate salts with tetraethylammonium and ethylmethyldiazolium cations, and various solvents using cyclic voltammetry. Some kinds of solvents such as acetonitrile promote substantial capacitance of ruthenium oxide in imidazolium-based electrolyte salt over tetraethylammonium-based one, while propylene carbonate exhibited no such difference between these two electrolyte systems. The pseudo-capacitance of ruthenium oxide in imidazolium-based electrolyte is stable over cycles under limited anodic potential range of 0.5 V vs. Ag. The contamination of ca. 1000 ppm of water induces further substantial capacitance only for imidazolium-based electrolyte.

Key Words : Electrochemical Capacitor, Ruthenium Oxide, Organic Solvent Electrolyte, Imidazolium Salt

1 Introduction

Electrochemical capacitor which consists of metal oxide electrodes is promising as a next-generation energy storage device with sufficient energy density, high rate and cycle stabilities. A number of metal oxides have been proposed as electrode active materials of electrochemical capacitor. Since Zheng et al. exhibited the availability of hydrated RuO₂ as a novel electrode material with specific capacitance as large as 720 F g⁻¹, ruthenium oxide appears to be the most promising candidate for electrode active material. While oxides of nickel and manganese have been proposed as alternative candidates for electrode because of the high cost of ruthenium oxide, the limitation such as low conductivity or low chemical stability prevent them to substitute them to ruthenium oxide.

Aqueous electrolyte has been applied in most of these studies because proton is considered to be necessary for the redox process which relates to pseudo-capacitance. However, aqueous electrolyte limits the working voltage of capacitor and available electrode or other materials in cell assembly. The application of non-aqueous electrolyte in electrochemical capacitor based on metal oxide is therefore attractive in the viewpoint of the enlargement of material selection. Rochefort et al. made an attempt to use protic ionic liquid obtained by 2-methylpyridine and CF₃COOH as non-aqueous electrolyte toward RuO₂ electrode. The present authors proposed a gel electrolyte system composed by CF₃SO₂H/dimethylsulfoxide (DMF) and a comonomer of polyvinylidene difluoride (PVdF) with hexafluoropropylene (HFP) matrix compatible for the capacitor cell using RuO₂ electrode.

In the present study the authors highlight imidazolium salt as a solute for non-aqueous electrolyte. Some imidazolium salts have been attracted recently from wide research field as ionic liquid at ambient temperature. The proton at 2-position of 1, 3-substituted imidazolium cation is known to provide easily hydrogen bond with Lewis bases. The authors have expected that this type of cation provide a certain pseudo-capacitance by adsorbing on ruthenium oxide surface. Here the influences of solvent species and contaminated water on pseudo-capacitive behavior of RuO₂ in organic solvent electrolytes have been investigated.

2 Experimental

In the present study two kinds of electrolyte salt was applied: tetraethylammonium tetrafluoroborate (TEABF₄; Tomiyama Pure Chemical Co.) and 1-ethyl-3-methyl imidazolium tetrafluoroborate (EMIBF₄). Battery grade TEABF₄ was used as received. EMIBF₄ was prepared using the method as described previously and dried further in vacuum at 100°C. The solvents used in the present study, propylene carbonate (PC; Kishida Chemical Co., Japan, battery grade), ethylene carbonate (EC; Kishida Chemical Co., battery grade), dimethyl carbonate (DMC; Kishida Chemical Co., battery grade), acetonitrile (AN; Wako Pure Chemical Co., dehydrated) and dimethylformamide (DMF; Kanto Chemical Co., dehydrated) was used without further purification. A salt of 1 mol dm⁻³ was dissolved into selected solvent, or mixed solvent of EC: DMC (1: 1 in volume), to prepare electrolytic solution at a glove box filled with Ar. In some cases a small amount of deionized water in the electrolyte. The water content of electrolytes before adding deionized water is determined by a Karl-Fischer water analyzer (MKC-510, Kyoto Electronics Co., Japan).

Ruthenium oxide used in the present study was prepared by a sol-gel process as described by Zheng et al. The obtained precipitate RuO₂·xH₂O was calcined at 400°C in a muffle furnace. The structure of product RuO₂ was checked by X-ray diffraction analyses (XD-D1,
Composite electrode sheet was prepared by mixing obtained RuO₂ and poly (tetrafluoroethylene) (PTFE) with RuO₂:PTFE gravimetric ratio of 90:10 in a mortar, and cut into a disk with 7 mm in diameter. The weight of RuO₂ in a disk was approximately 20 mg. A disk was pressed on a Pt mesh cut into similar size as a current collector and used as working electrode. A sealed glass cell was assembled with the working electrode, Pt plate as counter, and Ag wire as reference in a glove box filled with Ar. The assembled cell was then placed in a sealed vessel to carry out a measurement outside the glove box. Cyclic voltammetry (CV) was applied for the electrochemical characterization of the cell using a potentiostat (HABF-5001, Hokuto Denko Co.) under the scan rate of 2 mV s⁻¹ at a prescribed potential range.

3 Results and Discussion

Figure 1 shows the cyclic voltammograms of RuO₂ electrode at third cycle in TEABF₄/AN and EMIBF₄/AN electrolytes under the potential range from −1 to 1 V vs. Ag. Typical rectangular-shape CV curve is observed in EMIBF₄/AN electrolyte, while a redox couple around 0 to 1 V is significant and pseudo-capacitive current is small in TEABF₄/AN electrolyte. In EMIBF₄/AN electrolyte the adsorption/desorption process may lead to the pseudo-capacitance, while in TEABF₄/AN electrolyte a redox couple around 0 to 1 V vs. Ag, assigned as Ru(III)/Ru(IV) redox without ‘pseudo-capacitive’ adsorption. Significant extent of perturbation in anodic current is observed around 0.5 to 1 V in the CV curve in TEABF₄/AN. Such perturbation is considered to be assigned from some decomposition mode with gas evolution.

The specific capacitances of RuO₂ in various organic solvent electrolytes from CV are summarized in Table 1. The capacitance values are calculated from the cathodic scan of CV. The RuO₂ calcined at 400°C is known to exhibit low capacitance even in aqueous electrolyte. The authors checked the specific capacitance of this RuO₂ electrode in 0.5 mol dm⁻³ H₂SO₄ aq, to be 42 F g⁻¹. Here the authors intend to note that the heating temperature for RuO₂ preparation is selected due to obtaining a dehydrated, crystalline RuO₂. One can see such a tendency as the electrolytes based on EMIBF₄ provides higher specific capacitance of RuO₂ than TEABF₄, while the behavior is also influenced by solvent species. For example, PC solvent provides capacitance as low as 8 F g⁻¹ regardless of the kind of salt. In contrast, AN solvent with EMIBF₄ solute provides higher capacitance value as 27 F g⁻¹ under the potential range of 1 to −1 V vs. Ag, and 14 F g⁻¹ under −1 to 0.5 V vs. Ag. These capacitances are lower than the case of aqueous electrolyte, however, significantly higher than those in TEABF₄/AN electrolyte via the measurement at the same potential range. DMF and EC: DMC also provide the difference in the capacitance of RuO₂ in the electrolyte with different solutes. EMIBF₄ appears to enhance the capacitance of RuO₂ rather than TEABF₄. The properties of solvent species, such as polarity and viscosity, affect the capacitance enhancement. Rochefort et al. reported that RuO₂ exhibited only small amount of pseudo-capacitance in EMIBF₄ ionic liquid without any solvent. This result is reproduced also by the present authors. Perhaps the neat ionic liquid EMIBF₄ is not adequate to provide pseudo-capacitance of RuO₂ by its high viscosity. The scanning potential range also affect the capacitance value; scanning from 1 V provides the larger capacitance than scanning from 0.5 V.

However, scanning to higher potential lowers the cycle stability. The capacitance calculated from cathodic scan over cycles in TEABF₄/AN and EMIBF₄/AN under the potential range from 1 to −1 V and 0.5 to −1 V is plotted in Fig. 2. In both electrolytes, the capacitance values decrease continuously when the scanning potential range from 1 V. From the X-ray diffraction analyses of RuO₂ electrode after 25 cycles, the structure of RuO₂ do not change during the CV process. Therefore, electrolyte may decompose by scanning such potential range. In contrast, the capacitance values are almost constant during cycles in both electrolytes at scanning potential range from −1 to 0.5 V. These results strongly indicate that the electrolyte decomposition occurs at the potential

Table 1: Capacitances of RuO₂ in various electrolytes.

<table>
<thead>
<tr>
<th>solute</th>
<th>solvent</th>
<th>potential range /V vs. Ag</th>
<th>specific capacitance /F g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEABF₄</td>
<td>PC</td>
<td>1.0 to −1.0</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>AN</td>
<td>1.0 to −1.0</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>AN</td>
<td>0.5 to −1.0</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>0.5 to −1.0</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>EC: DMC</td>
<td>1.0 to −1.0</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>EC: DMC</td>
<td>0.5 to −1.0</td>
<td>11</td>
</tr>
<tr>
<td>EMIBF₄</td>
<td>PC</td>
<td>1.0 to −1.0</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>AN</td>
<td>1.0 to −1.0</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>AN</td>
<td>0.5 to −1.0</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>0.5 to −1.0</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>EC: DMC</td>
<td>1.0 to −1.0</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>EC: DMC</td>
<td>0.5 to −1.0</td>
<td>16</td>
</tr>
</tbody>
</table>
range between 0.5 and 1 V.

The result indicates that EMIBF₄ provides a significant amount of substantial capacitance rather than TEABF₄ for the electrolyte salt of capacitor cell. One possibility for such substantial capacitance is due to the contaminated water because the water content of EMIBF₄/AN and TEABF₄/AN used in the present study was ca. 110 ppm and ca. 360 ppm, respectively. In order to assess the influence of water content in the electrolyte, those with controlled water content around 1000 ppm were prepared by the addition of deionized water and applied for CV test. The plots of capacitances over cycle number for (a)TEABF₄/AN and (b)EMIBF₄/AN with various water content under the potential range from 0.5 to −1 V vs. Ag are also included in Fig. 2. The influence of 1000 ppm of water depends on the electrolyte salt. In TEABF₄/AN, the capacitance is similar regardless of the water content. In contrast, EMIBF₄/AN electrolyte with water content of 1000 ppm provides higher capacitance during initial tens cycles than that without water addition. The substantial capacitance by the water addition in EMIBF₄ electrolyte gradually decreases and much of it disappears after twentieth cycle. Even if the substantial capacitance in EMIBF₄ without the addition of water is due to the contaminated water, it can be emphasized that EMIBF₄ contributes to enhance the activity of proton in small amount of water. Perhaps the hydrogen at 2-position of EMI cation, which is known as having high reactivity, interacts with water to increase the activity of proton by the dissociation of water.

From the results in the present study, it is still unclear whether EMIBF₄ provides any intrinsic increase of capacitance of RuO₂ or not. In the viewpoint of cycle stability of capacitance, such stable one over cycles as in EMIBF₄/AN under the potential range from 0.5 to −1 V is possible to be an intrinsic contribution from the adsorption of EMI cation. The precise mechanism of capacitance enhancing effect by EMIBF₄, as well as the optimization of the structure of RuO₂ electrode to obtain the capacitance sufficient for practical use, will be progressed in future.

References

![Fig. 2](image_url)

Fig. 2 Cycle behavior of specific capacitances of RuO₂ in (a) TEABF₄/AN and (b) EMIBF₄/AN electrolytes with or without 1000 ppm of H₂O.