3.3-V-Rated EDLC Performance with an Alternative Conducting Agent
(nc-RuO2·nH2O/KB)

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Abstract
Nano-crystalline hydrous RuO2 particles that are hyper-dispersed within Ketjen Black (KB) matrix have been added as an alternative-conducting agent. In the present study, the authors succeeded in enhancing the EDLC’s withstanding voltage from 2.7 to 3.3 V by addition of small amount of MOx/KB (MOx = RuO2) composite. Addition of 4 wt% RuO2/KB only in the positive activated carbon electrode dramatically increased the voltage limitation up to 3.3 V. To date 3.3-V-rated EDLC (activated carbon based electrochemical capacitor) has never been attained. The test EDLC cell demonstrated a high energy density (18 Wh kg⁻¹) with prolonged charge-discharge cycling up to 9000 times in the voltage range of 0–3.3 V. In this study, the critical factors enabling such a high voltage operation have been investigated in relation to the mechanism that efficiently prevents consecutive water-induced chained failure mode reactions.

Keywords : Electric Double Layer Capacitor, Hydrous RuO2, Conducting Agent, High Voltage Operation

1. Introduction

Electric double-layer capacitors (EDLCs), which are high-power energy storage devices capable of effectively utilizing energy, have been studied and are practically used in trucks, buses, elevators, and in heavy-duty construction and railway usage such as forklifts, yard cranes, and bullet trains. However, since the electrodes generally have low energy densities, their uses are limited and they cannot fully meet various performance demands required by the target markets. Particularly in the field of automobiles, new energy devices are strongly desired to have hybrid characteristics between lithium ion batteries and EDLCs and thereby which can be suitably employed in idle reduction systems. Accordingly, it is expected for them to form a large market. In order to satisfy the performance demands, it is said to be necessary for the EDLCs to enhance their energy density to 20–30 Wh L⁻¹, which is approximately twice or triple compared to the present EDLCs, namely, 5 to 10 Wh L⁻¹. For realizing the above high energy density, hybrid capacitor systems comprising non-aqueous redox materials are being dynamically researched and developed in recent years. As it is described above, increasing the energy density is one of the most crucial matters. For conventional EDLC systems, designed with two symmetrical activated carbon (AC) electrodes, increasing voltage is more effective to increase energy density because of the quadratic dependence of voltage. Thus, it is essential to develop higher electrochemical durability at the electrode/electrolyte interface. Currently, the maximum voltage of a conventional EDLC consisting of activated carbon for both their electrodes is however limited to 2.5–2.7 V. Exceeding this voltage limitation will normally cause serious damage of an EDLC cell and considerable side reactions such as gas evolution and the surface film formation on electrode surfaces. Applying voltage over 2.7 V causes a significant decrease in capacitance and an increase in damages of activated carbon electrodes. The undesired faradic process (failure modes) that leads to a capacitance fade is the most critical metrics that determines the energy density limitation of the current EDLCs. In the present paper, we report a remarkable enhancement of this withstand voltage limitation to 3.3–3.5 V simply by adding a new and alternative conducting agent nanomaterial (RuO2/Ketjen Black) in the conventional EDLC configuration.

2. Experimental

2.1 Preparation of nc-RuO2·nH2O/KB composite
1.982 g of RuCl3·3H2O was dissolved into 40 mL of distilled water under ultrasonication (solution A). Ultra-centrifugation (UC) has been impaired under 75,000 G to the (solution A) with 1.0 g KB (KB-EC600JD; Ketjen Black International) and 25 mL of 1.0 M NaOHaq. for 5 min to let the hydrolysis reaction of RuCl3 proceed in air atmosphere (Fig. 1). The obtained slurry was then filtered, washed with deionized water several times. After drying the filtrate at 150°C, the final product of nc-RuO2·nH2O/KB (50/50 wt%) composite powder was obtained.

2.2 Preparation of AC + nc-RuO2·nH2O/KB electrode
Activated carbon (RP-20; Kuraray Chemical), KB, the obtained nc-RuO2·nH2O/KB composite, and PTFE (POLYFLON; Daikin Industries) were mixed at a weight ratio of 84:4:4:8. The powder mixture was rolled into a film of ca. 150 μm in thickness and then dried at 150°C for 24 h. The film was attached on an etched Al current collector using Hitasol EC1 (Hitachi Powdered Metals) as conductive adhesive. The electrode was again dried at 150°C under vacuum for 24 h to give a test EDLC electrode. The same electrode prepared without nc-RuO2·nH2O/KB was used as a reference (AC:KB:PTFE = 84:8:8).
2.3 Electrochemical characterizations

The prepared electrode (electrode area: 2.0 cm², electrode weight: ca. 0.02 g) with and without addition of nc-RuO₂/nH₂O/KB was characterized for its supercapacitor performances on two kinds of 2032 coin cells configured with (cell A): AC/(1.0 M TEMABF₄/PC)/AC and (cell B): AC/(1.0 M TEMABF₄/PC)/(AC + 4 wt% RuO₂/nH₂O/KB). The withstand voltage was evaluated by cycling these cells (cell A and cell B) at applied voltages raised in stepwise (10 cycles each) with a CC-CV mode, viz., constant current (2 mA cm⁻²), constant voltage (varied from 2.5 to 2.7, 3.0, 3.3, 3.7, and 4.0 V) at 25°C. The impedance spectroscopy was measured on a frequency response analyzer/potentiostat (Solartron, model 1260/1286) to evaluate the interfacial electronic and ionic transport phenomena with and without adding-RuO₂/nH₂O/KB. The frequency range was from 5 mHz to 1 MHz, and the perturbation amplitude was 10 mV. To confirm a detailed mechanism, we attempted to analyze the obtained electrochemical impedance spectra by fitting them to a suggested appropriate equivalent circuit (Fig. 2). The circuit has two RC elements of \( R_L \) and \( C_L \) in parallel and \( R_{bd} \) and \( C_{bd} \) in the parallel with Warburg component (W) composed of several components as shown in the caption of Fig. 2. These components were estimated as their summations, viz., \( \sum R_f = R_{f/5} \), \( \sum R_j = R_{j/5} \), and \( \sum C_j = C_{j/5} \).

2.4 Physicochemical characterizations

The nanostructures and particle size of as-prepared nc-RuO₂/nH₂O were confirmed by high-resolution transmission electron microscopy (HRTEM) on a Hitachi H-7500 model. After cycling for 100 times, the cell was disassembled and the positive and negative electrodes were extracted for SEM (Hitachi, S-4300 model) observation after washing with dehydrated acetone for several times.

3. Results and Discussion

3.1 Nanostructure of RuO₂/nH₂O/KB composite

Figure 3 shows the HRTEM image of the obtained RuO₂/nH₂O/KB composite.¹² Nanosized (ca. 2 nm) RuO₂ particles are accommodated by the edge sites of continuous graphene layers of KB. It is found that all of the observed RuO₂/nH₂O particles are attached on the KB. The supported nanoparticles speculated to be strongly adsorbed by interactions between the graphene edge surface and ruthenium hydroxides. The result suggests that the RuO₂ particles were built up on the edge sites of graphene fragments with outer hydrous layer strongly sandwiched by the graphenes. The network of the graphene layers should play a role for the electron pathways in this composite. This could bring about an establishment of good electronic paths between the two species, RuO₂/nH₂O and KB. The highly dispersed nanosized-RuO₂/nH₂O in the KB not only provides facile ionic transportation but also electrochemical activity.¹² By adding RuO₂/nH₂O/KB to AC electrode will play important role to improve EDLCs performance.

3.2 Withstand voltage of EDLCs with and without addition of RuO₂/nH₂O/KB

Figure 4 (Bottom) show the raw data for the discharge capacity vs. cycle number (each 10 cycle) for cell A and cell B, respectively. Figure 4 (Top) summarizes the average discharge voltage (at each
is shown in the inset Fig. 5(b), there observed a slight decay in the capacity in the voltage range of 0.0–3.3 V at a current density of 20 mA cm⁻² (ca. 2.4 A g⁻¹). The cells were cycled up to 9,000 times and showed a stable with almost unchanged discharge capability (ca. 23 mAh g⁻¹) even at a high voltage end of 3.3 V. (b) The cycling performance at even higher voltage end of 3.5 V, confirming that the discharge capacity of ca. 27 mAh g⁻¹ was maintained up to 100 times at the same current density.

Figure 5. (Color online) Cycling performance on an EDLC test cells configured (cell B) AC/(1.0 M TEMABF₄/PC)/(AC + 4 wt% RuO₂·nH₂O/KB). (a) The cycling performance in the voltage range of 0.0–3.3 V at a current density of 20 mA cm⁻² (ca. 2.4 A g⁻¹). The cells were cycled up to 9,000 times and showed a stable with almost unchanged discharge capability (ca. 23 mAh g⁻¹) even at a high voltage end of 3.3 V. (b) The cycling performance at even higher voltage end of 3.5 V, confirming that the discharge capacity of ca. 27 mAh g⁻¹ was maintained up to 100 times at the same current density.

10th cycle) against the operation voltage for with (cell B) and without (cell A) addition of RuO₂·nH₂O/KB, respectively. Up to 2.7 V, both cells showed the identical discharge capacity meaning that the degradation reaction has not yet occurred. The cell A started to decrease its capacity over 3.0 V as is often seen for normal EDLCs. Interestingly, the cell B with addition of RuO₂·nH₂O/KB shows completely different behavior. The discharge capacity linearly increases up to 3.3 V, indicative of no degradation keeping the same capacitance value with the cell B. In the voltage range of 3.3–3.7 V, the cell B maintained a constant discharge capacity (25 mAh g⁻¹) and there observed less significant degradation as is observed at 4.0 V. These results clearly indicate that the cell B is superior to the cell A in regard to the withstand voltage.

Figure 5 shows the long-term cycling tests for the cell B in the range of (a) 0–3.3 V and (b) 0–3.5 V. In the voltage range of 0–3.3 V, the cell B maintained its initial discharge capacity (ca. 23 mAh g⁻¹) even after 9,000 cycles. The result indicates that the cell B is electrochemically stable up to 3.3 V. We confirmed the cycleability of the cell B under the condition of (b) 0–3.5 V up to 100 cycles. As is shown in the inset Fig. 5(b), there observed a slight decay in the capacity in the voltage range of 0–3.5 V.

It should be noted here that we can instantly obtain an increased withstand voltage by just adding the RuO₂·nH₂O/KB composite in place of KB by half weight ratio in the same PC-based media. One does not need to sacrifice the power capability by using higher-withstand-voltage media such as sulfolane, linear sulfones, and ionic liquids most of them have high viscosity leading to less power than carbonate counterparts.

3.3 Electrode surface conditions with and without RuO₂·nH₂O/KB composite

Figure 6 shows the SEM images for the positive electrode for cell A and cell B after cycling 50 times in the voltage range of 0–3.0 V. For the cell A (without addition), several graphene layers are found exfoliated from the AC particles due to swelling by the gas generation. For cell B (with RuO₂·nH₂O), there observed no such exfoliation, no cracks. In the case of the cell A tested after 0–4.0 V (see Fig. 7), the positive electrode surface is completely different from that of Fig. 6 (cell A). The film-like deposition products covered the electrode surface and became invisible. While, the cell B tested at 4.0 V (Fig. 7 cell B) did not have any film deposition but with serious damages for most of the AC particles of
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**Figure 7.** SEM images of the positive AC electrode surfaces for the same EDLC cells after cycling at 0–4.0 V. (cell A) No addition. (cell B) With addition.

**Figure 8.** (Color online) The pore resistance ($R_{sw}$) characterized by fitting the respective Nyquist plots (cell A) and (cell B) obtained at 2.5, 3.3, 4.0 V. (cell A) Without addition. (cell B) With addition.

the lost capacity (15 mAh g⁻¹). The results suggest that RuO₂·nH₂O may suppress gas evolution and other failure mode reactions.

**3.4 Impedance behavior featuring ionic transport**

The electrochemical impedance spectra (EIS) were analyzed as a function of potential (2.5–4.0 V) to determine the pore resistance with and without addition of RuO₂·nH₂O/KB composite (Fig. 8). The pore resistance ($R_{sw}$) has been characterized by fitting the respective Nyquist plots for (cell A) and (cell B). The Nyquist plots are typical of EDLCs cell, which involve the slopes changing from 45 to 90° in the lower frequency range. The $R_{sw}$ of the cell A dramatically increases by 85% from 2.5 to 3.3 V and reaches 15 Ω cm⁻². An electrochemical side reaction such as SEI formation causes an increase in the $R_{sw}$ leading to a slowed ionic diffusion. While, the $R_{sw}$ for the cell B does not show such a large increases compare to the cell A but shows a slight linear increase (by 21%) against the potential from 2.5 to 4.0 V. The large increase in $R_{sw}$ for cell A indicates that undesired faradic reaction occur in the pore above 3.3 V. On the other hand, cell B maintains non faradic process with gradual degradation up to 4.0 V.

**3.5 SEI formation in inner pores and its effects**

According to our previous paper, we attempt to characterize the average inner pore size by the variation of the $R_{sw}$ at increasing cell voltages. The $R_{sw}$ is more rigorously expressed by the radius ($r$) and the length of the pores ($L$) as in the following equation [Eq. (1)]:

$$R_{sw} = \frac{L}{\kappa \pi r^2}$$  

where $\kappa$ is the electrolyte conductivity in the pores. Accordingly the decreased ratio ($r_p$) of the pore radius due to the SEI formation can be calculated from the following equation [Eq. (2)]:

$$r_p = \frac{r}{r_{2.5V}} = \frac{R_{sw}^{2.5V}}{R_{sw}^{2.5V}}$$

Where $R_{sw}^{2.5V}$ and $r_{2.5V}$ represent the $R_{sw}$ and the pore radius ($r$) at 2.5 V, respectively. In Fig. 9 the $r_p$ was plotted as function of voltage. The $r_p$ for the cell A decreases from 1.0 (@2.5V) to 0.73 (@3.3 V) corresponding to the shrinkage in the pore volume (by ca. 47%) due to the SEI accumulations on the inner surface walls of pores. On the other hand, the cell B showed much lesser change in the $r_p$ for from 1.0 to 0.91 at 2.5–4.0 V, meaning that 83% of the initial pore volume is preserved. It is reported that RuO₂·nH₂O shows redox behavior against proton in the voltage range of 3.3–4.3 V (vs. Li/Li⁺). The suppression of SEI formation in high voltage operation (3.3–4.0 V) for cell B is considered to be due to the prevention of the failure mode by RuO₂·nH₂O that has something to do with the residual water released from the AC.

**4. Conclusions**

In this study, we successfully designed EDLCs with 3.3 V withstand voltage by replacing KB in the electrode to RuO₂·nH₂O/KB. The EDLCs designed by this method shows stable cycleability in the high voltage of 3.3 V, and could achieve high energy density (18 Wh kg⁻¹). This new technology brings high energy density to
EDLCs without losing power density. We revealed that the reason for this high stability in the high voltage operation may be that RuO$_2$·$n$H$_2$O/KB suppressed undesired faradic process such as SEI formation. In the future, the EDLCs with 3.3 V withstand voltage may have the potential to expand the field of practical EDLCs.

References