Electrochemical Capacitor Behavior of RuO$_2$ Nanosheets in Buffered Solution and Its Application to Hybrid Capacitor

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ABSTRACT

The electrochemical property of RuO$_2$ nanosheets in acetic acid-lithium acetate buffered electrolytes was studied in an attempt to understand the charge storage mechanism in neutral solutions and to improve the charge storage capability of aqueous hybrid capacitors. High specific capacitance and good rate capability were obtained for RuO$_2$ nanosheets in acetic acid buffered solution containing Li$^+$ (pH $\sim$ 5.3). Maximum capacitance of 1038 F g$^{-1}$ was achieved, which is higher than the values in acidic electrolyte. Using RuO$_2$ nanosheet electrodes as positive electrode in acetic acid-lithium acetate buffered electrolyte with a multi-layered Li negative electrode, high specific energy of 724 Wh kg$^{-1}$ based on the positive electrode mass was attained.

Keywords: Hybrid Capacitor, Ruthenium Oxide, Nanosheets, Buffer Solution

1. Introduction

Electrochemical capacitors utilize the electrical-double layer formed at the electrode/electrolyte interface as well as fast surface redox reactions to store electrical charge. Since charge storage is confined to the surface of porous electrodes, higher power density and longer cycle life is attainable when compared with rechargeable batteries which make use of bulk intercalation or conversion reactions.$^{1,2}$ However, the energy density of a typical electrochemical capacitor is much lower than conventional rechargeable batteries, limiting its use to power-accentuated applications. In order to increase the energy density of electrochemical capacitors, the capacitance of the electrode material and operating voltage must be increased. In terms of capacitance, RuO$_2$-based nanomaterials can provide capacitance close to 700 F g$^{-1}$ in acidic electrolyte, which is at least a few times higher than carbonateous materials.$^{3,7}$ The operating voltage of a typical aqueous system will be limited to the potential within water electrolysis.

We have reported that 4-V operation in neutral electrolytes can be realized by using a multi-layered, protected Li negative electrode in combination with pseudo-capacitive positive electrodes.$^8$ Specific energy of 544 Wh (kg-RuO$_2$)$^{-1}$ was obtained by combining high specific capacitance of RuO$_2$ nanosheets in 1.0 M Li$_2$SO$_4$ and high cell voltage of 3.8 V. The specific capacitance of RuO$_2$ nanosheets in 1.0 M Li$_2$SO$_4$ was lower than that in 0.5 M H$_2$SO$_4$. So far, most electrochemical studies concerning RuO$_2$-based materials have been conducted in acidic electrolytes,$^{9}$ and the electrochemical behavior of such electrodes in neutral electrolyte has not been investigated in detail. In this study, the electrochemical properties of RuO$_2$ nanosheets in various neutral electrolytes were studied in an attempt to understand the charge storage mechanism and to improve the specific energy of this hybrid capacitor.

2. Experimental

RuO$_2$ nanosheets were derived from $\alpha$-NaFe$_2$O$_4$ type NaRuO$_2$ according to literature.$^7$ The acetic acid (AcOH)-lithium acetate (AcOLi) buffered solution was prepared by mixing solutions of AcOH and AcOLi with a predefined concentration (0.5, 2.0, 5.0 M) in a volume ratio of 31.3:238.8 giving buffered solutions with pH of 5.3. 1.0 M Li$_2$SO$_4$ (pH 7.64) and 0.5 M H$_2$SO$_4$ were also used as typical electrolytes for comparison. All electrochemical measurements were carried out at 60°C.

The positive electrodes were prepared by depositing a colloidal solution of RuO$_2$ nanosheets onto a mirror-polished glassy carbon electrode (5 mm in diameter). The deposited amount was 20.4 µg cm$^{-2}$. Single electrode characterization was carried out using a beaker-type electrochemical cell composed of a Pt mesh counter electrode and a Ag/AgCl/KCl (sat.) reference electrode connected with a salt bridge. A Luggin capillary faced the working electrode at a distance of 2 mm. Electrode potentials will be referred to the reversible hydrogen electrode (RHE) potential scale. Cyclic voltammetry was conducted between 0.2 and 1.2 V vs. RHE at scan rates of 500 to 2 mV s$^{-1}$. Constant current charge/discharge measurements in two-electrode system were conducted to characterize the properties of hybrid capacitor composed of RuO$_2$ nanosheet positive electrode and multi-layered Li negative electrode. The multi-layered Li negative electrode was prepared following previous reports.$^{5,19,20}$

3. Results and Discussion

The cyclic voltammograms of RuO$_2$ nanosheets in 0.5 M H$_2$SO$_4$, 1.0 M Li$_2$SO$_4$, and 0.5 M AcOH-AcOLi are shown in Fig. 1. In 0.5 M H$_2$SO$_4$ [Fig. 1(a)], redox peaks attributed to fast, reversible surface reaction are observed near 0.7 V vs. RHE.$^7$ In the case of 1.0 M Li$_2$SO$_4$ [Fig. 1(b)], no redox peaks are evident at fast scan rates, while contribution from pseudocapacitance can be seen at low scan rates. The specific capacitance was 425 F g$^{-1}$ at 200 mV s$^{-1}$, which is 58% of the value in 0.5 M H$_2$SO$_4$ (735 F g$^{-1}$) at the same scan rate. The redox-related charge in Li$_2$SO$_4$ is much more dependent on the scan rate compared to 0.5 M H$_2$SO$_4$, and seems like a slow, irreversible electrochemical reaction. For 0.5 M AcOH-AcOLi buffered solution [Fig. 1(c)], broad peaks in the range of 0.2–0.7 V vs. RHE were observed. The specific capacitance in AcOH-AcOLi buffered solution at 2 mV s$^{-1}$ was 891 F g$^{-1}$ which is comparable to the value in 0.5 M H$_2$SO$_4$ (831 F g$^{-1}$).

Cyclic voltammograms of RuO$_2$ nanosheets in 0.5, 2.0, 5.0 M AcOH-AcOLi buffered solution are shown in Fig. 2. The broad redox peaks observed in 0.5 M AcOH-AcOLi buffered solution
becomes clearly evident with increasing concentration of buffered solution and is separated into two redox couples at approximately 0.4 and 0.6 V vs. RHE. The potential difference of the redox couples are narrow, indicative of a reversible surface reaction somewhat similar to the case for H2SO4. Between 0.7 and 1.2 V vs. RHE, excellent current response is obtained with rectangular voltammograms up to high scan rate. This region should represent the electrical double layer charging and is 700–750 F g⁻¹. The specific capacitance at 2 mV s⁻¹ in 2.0 and 5.0 M AcOH-AcOLi buffered solutions were 941 and 1038 F g⁻¹, respectively. Remarkably, the specific capacitance in 5.0 M AcOH-AcOLi buffered solution is higher than that in 0.5 M H2SO4. The specific capacitance at 500 mV s⁻¹ in 5.0 M AcOH-AcOLi buffered solution is an astonishing 745 F g⁻¹, which is comparable to in H2SO4. So far, acidic electrolyte has been considered to offer the best electrochemical capacitor performance for RuO2-based materials. To the best of our knowledge, this is the first time that capacitance values exceeding that of 0.5 M H2SO4 have been achieved.

The hybrid capacitor performance using RuO2 nanosheets as the positive electrode in AcOH-AcOLi buffered electrolyte in combination with a multi-layered Li negative electrode was investigated by constant current charge/discharge measurements in two-electrode system. The charge/discharge curve at 0.255 mA cm⁻² showed a capacitor-like behavior (Fig. 3). The obtained specific charge and energy based on the mass of the positive electrode were 223 mAh g⁻¹ and 724 Wh kg⁻¹, respectively. These values are roughly 30% higher than the performance in 1.0 M Li2SO4.

4. Conclusion

The electrochemical properties of RuO2 nanosheet electrodes derived from NaRuO2 was evaluated in acetic acid-lithium acetate buffered electrolytes. The RuO2 nanosheet electrodes exhibited high specific capacitance of 1038 F g⁻¹ at 2 mV s⁻¹ and good rate capability in 5.0 M AcOH-AcOLi buffered solution (pH ~ 5.3). The capacitive performance in buffered electrolyte was better than H2SO4 and Li2SO4. The contribution from electrical-double layer capacitance is about 70% of the overall capacitance, and exceeds 700 F g⁻¹ even at high scan rate. A hybrid capacitor using RuO2 nanosheets in 5.0 M AcOH-AcOLi buffered electrolyte as the positive electrode with a multi-layered Li electrode exhibited specific energy of 724 Wh (kg-RuO2)⁻¹.
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References


**Figure 3.** (a) Charge/discharge curve at 0.255 mA cm$^{-2}$ and (b) discharge curves with various current densities of the hybrid capacitor using RuO$_2$ nanosheets positive electrode and multilayered Li negative electrode in 5.0 M AcOH-AcOLi buffered electrolyte.