

Ruthenium Oxide-Loaded Activated Carbons as High Energy Density Capacitor

Materials

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Activated carbon has high power density, but has limited specific capacity. To increase the capacity of activated carbon, ruthenium oxide was loaded into various types of activated carbon by suspending the activated carbon in an aqueous RuCl_3 solution followed by neutralization. Although the BET surface area of the activated carbon decreased upon ruthenium oxide loading compared to that of the starting material, its capacitance increased. The maximum capacity obtained in this study was 308 F/g for activated carbon loaded with 7.1 wt% ruthenium, an increase of about 20 %.

Key words: ruthenium oxide, activated carbon, capacitor

Introduction

Electrochemical capacitors are unique energy storage devices that exhibit high power density and long cycle life. In conjunction with batteries, they have been considered for use in high-power applications not only for electric vehicle technology, but also for internal combustion engines. Energy storage mechanisms for electrochemical capacitors include the separation of charges at the interface between a solid electrode and an electrolyte, and/or fast faradaic reactions occurring near a solid electrode surface at an appropriate potential. The capacitance corresponding to the first mechanism is generally called double-layer capacitance, and activated carbon is generally used as the electrode. The capacitance resulting from the second mechanism is often called pseudo-capacitance. Both crystalline ruthenium oxide, $\text{RuO}_2^{1, 2)}$, and hydrous ruthenium oxide, $\text{RuO}_2 \cdot x\text{H}_2\text{O}^{3, 4)}$ are among the best candidates for use as a pseudo-capacitance material, but ruthenium is a very expensive material compared to activated carbon. Miller et al.⁵⁾ reported on the preparation and electrochemical characterization of a composite electrode using carbon aerogels as high-surface-area substrates for pseudo-capacitive RuO_2 nanoparticles. Recently, Zheng reported a ruthenium oxide-carbon composite electrode⁶⁾. This composite electrode shows a high capacitance of 620 F/g and was less sensitive to a high voltage scan rate. The electrode contained, however, 80% ruthenium oxide. In the present study, we examined the electrochemical behavior of activated carbon loaded with a small quantity of ruthenium oxide to increase its capacitance. This paper represents the first example of the increasing capacitance of the activated carbon

loaded with a small quantity of ruthenium oxide.

Experimental

In this study, we used 6 types of activated carbon (see Table 1), including coal-based activated carbons (C-1, 2, 3), phenolic resin-based activated carbons (Ph-1, and 2) and a coconut-shell based activated carbon (Y-1). All are products of Osaka Gas Co. Ltd. The nitrogen BET surface areas range from about 1300 to 3000 m^2/g . Ruthenium oxide was loaded into the carbon as follows. Three g of activated carbon was suspended in 100 ml of various concentration of $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ solution and stirred for 4 h using ultrasonic waves. After filtration and washing with water, this activated carbon was placed in a 1 M NaOH solution and stirred for 30 min using ultrasonic waves to produce the hydroxide from the chloride. After filtration and washing with water, the activated carbon was dried at 150°C for 24 hrs. The amount of the ruthenium loaded was analyzed by ICP. The electrode used for measurement was fabricated from a blend of 85 wt% activated carbon and 15% conductive binder (66% acetylene black, 33% PTFE, 1% surface active agent). The mixture of activated carbon and conductive binder was pressed onto a Ti net collector at 3.76 t/cm^2 to form a tablet 13 mm in diameter. The capacity of the electrode was determined through measurement of cyclic voltammograms (CVs). CVs for this electrode were measured in 0.5 M H_2SO_4 at 30°C using a potentiostat/galvanostat (Hokuto Denko Co., HAB-151) and an X-Y recorder (Rikendenshi Co., F-3F). The reference and counter electrodes were $\text{Hg}/\text{Hg}_2\text{SO}_4$ and a gold plate respectively. As the capacitance decreased with increasing scan rate, we determined the optimum scan rate as 2 mV/s.

When the switching potential was less than or equal to -0.7 V, evolution of hydrogen was observed. For the anodic switching potential, oxygen evolution occurred above than 0.3 V. Therefore, the potential scan range was determined from -0.6 V to 0.3 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$. As the soaking time of electrodes in electrolytic solution increased, the capacitance increased, in addition a higher value was always obtained with vacuum treatment. Therefore, we adopted 3 h vacuum soaking as a standard. X-ray diffraction analysis of the ruthenium oxide-loaded carbon was conducted using a Geigerflex RAD- γ A Diffractometer (Rigaku Co., $\text{Cu K}\alpha$, 40 kV, 100 mA).

Results and Discussion

Figure 1 shows the SEM images of the coke-based activated carbons (left) and the respective ruthenium oxide-loaded carbons (right). The ruthenium oxide loaded activated carbons are identified as C-1-Ru, for example. No obvious changes in appearance after ruthenium oxide loading can be seen in these images. It was suspected that the activated carbons were not broken by the exposure of ultrasonic waves. XRD analysis was conducted, in order to confirm that ruthenium oxide was loaded to the activated carbons. Figure 2 shows the XRD patterns of coal-based ruthenium oxide-loaded activated carbon treated to various temperatures. When the carbon was dried at 150 °C, no diffraction peak appeared, showing that even though loaded, the ruthenium oxide was in an amorphous state³. As the heat-treatment temperature was increased, diffraction peaks due to ruthenium oxide began to appear at about 300 °C and became clearer. These results confirm that ruthenium oxide was loaded into the activated carbons.

Figure 3 shows the CV-curves of coal based activated carbon and their ruthenium oxide-loaded derivatives. It can be seen that the charging current is higher for the loaded carbon, i.e., there is a good effect of RuO_2 loading. The CV curve is mostly featureless between hydrogen and oxygen evolution over the limited potential range between -0.6 V and 0.3 V vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$. For phenolic resin-based and coconut-shell-based activated carbons and their ruthenium oxide-loaded derivatives, the charging current for the ruthenium oxide-loaded carbon was also larger than that for the starting material. The capacitance can be obtained from these CV curves with the equation $c = i/v$, where i and v are the current and voltage scan rate, respectively. The values obtained for capacitance and the specific surface area for various activated carbons are summarized in Table 1. Arrows indicate changes due to ruthenium oxide loading. The capacitance increased with increasing specific surface area for each carbon system. When ruthenium oxide was loaded into the activated carbon,

the capacitance increased, although the specific surface area decreased. The capacitance increased by about 34% in comparison to the unloaded carbon in the case of Ph-1 and 2, though the capacitance itself is smaller than that of ruthenium oxide-loaded C-3. According to the above results, we changed the amount of loaded ruthenium oxide loaded into the carbon using coal-based activated carbon (C-3), which has the largest BET surface area as 3000 m^2/g in this study. It can be seen that increasing the level of ruthenium oxide loading increased the capacitance and decreased the surface area (Fig. 4). The significant increase in electrode capacitance while the effective surface area decreased is consistent with the hypothesis that ruthenium oxide introduces a pseudocapacitance responsible for a significant increase in total capacitance. The highest capacitance obtained in this study was 308 F/g when the ruthenium content was 7.1 wt%. Though this value is much smaller than that of Zheng's (620 F/g)⁶, his composite electrode consisted of 80 wt% ruthenium oxide and 20 wt% carbon. Because the hydration number attached to the oxide is unknown, the ruthenium content can not be calculated, but the content is much higher than that of our case (7.1 wt% of ruthenium). Assuming the chemical formula of ruthenium oxide as $\text{RuO}_2 \cdot 2 \text{H}_2\text{O}$, the ruthenium content should correspond to 47.8 wt% when the ruthenium oxide content is 80 wt%. When the ruthenium content in the electrode is extrapolated to 47.8 wt% in Fig.4, the expected capacitance should be about 606 F/g, which is nearly equal to Zheng's value. Therefore our results appear to be consistent with his.

For some of electrode made with activated carbon loaded with RuO_2 , for example, for phenolic resin-based activated carbon system in Table 1, the specific capacitance is greater than the sum of the double-layer capacitance and the pseudocapacitance. When coal-based activated carbon with and without RuO_2 was heated at 150 °C, carbon dioxide was evolved from the former carbon as shown in Fig. 5, which shows the RuO_2 is a good catalyst for converting carbon into CO_2 even at low temperatures such as 150 °C. It is possible that mesopores are created in carbon. Some of increase in capacitance may attribute to the mesopores.

Conclusion

It was found that the capacitance of activated carbon increased by loading it with ruthenium oxide in spite of a decrease of the surface area, because the pseudo-capacitance of ruthenium oxide was combined with the double-layer capacitance of the activated carbon. The maximum capacity of ruthenium oxide-loaded activated carbon obtained in this study was 308 F/g for the 7 wt% ruthenium loaded activated carbon. Some of increase in capacitance may attribute to the

mesopores created in ruthenium oxide-loaded activated carbon by heating at 150 °C.

References

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Table 1 Activated Carbon Characteristics and Capacitance

Activated* carbons	Loaded Ru (wt%)	BET surface area(m ² /g) before and after Ru loading	Capacitance(F/g) before and after Ru loading	Increase of capacitance(%)
C-1	6.6	1353 → 953	177 → 214	20.9
C-2	6.2	1844 → 1717	190 → 235	23.7
C-3	3.6	2951 → 2415	260 → 288	10.8
Ph-1	2.1	1533 → 1424	151 → 202	33.8
Ph-2	2.1	2341 → 2011	180 → 242	34.4
Y-1	2.7	1269 → 1139	149 → 181	21.5

* C-1, 2, 3 : coal based activated carbon, Ph-1, 2 : phenolic resin based activated carbon, and Y-1 : coconut-shell based activated carbon. Ruthenium oxide-loaded carbons were heated at 150°C for 24 hrs. Arrows indicate changes due to ruthenium oxide loading.

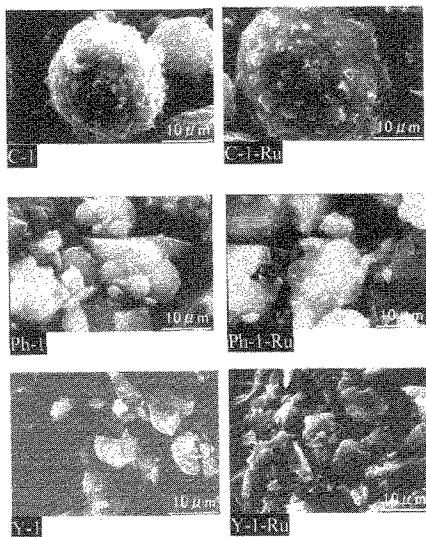


Fig. 1 SEM images of coal-based activated carbon (C-1), phenolic resin-based activated carbon (Ph-1) and coconut-shell-based activated carbon (Y-1) (left) and their ruthenium oxide-loaded activated carbons (right).

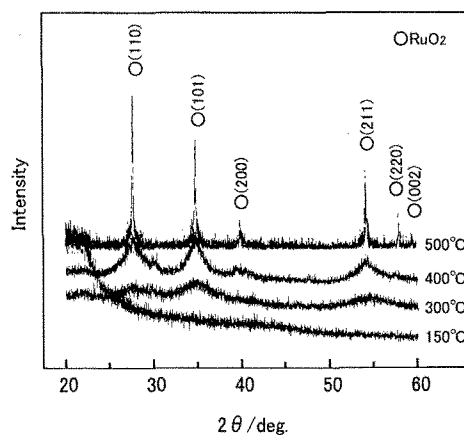


Fig. 2 XRD patterns for ruthenium oxide-loaded coal-based activated carbon (C-3-Ru) treated to various temperatures.

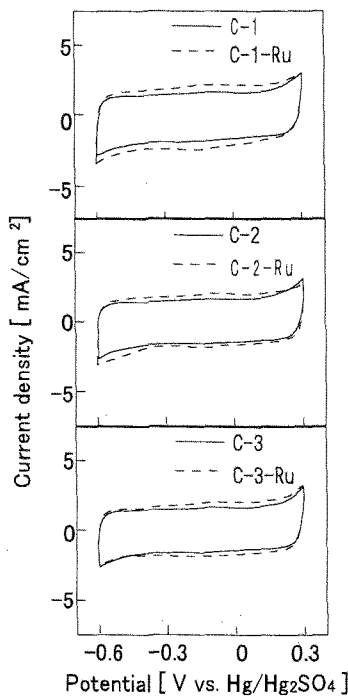


Fig. 3 Cyclic voltammograms of coal-based activated carbons (solid lines) and ruthenium oxide-loaded activated carbons treated at 150°C (dotted lines) in 0.5M H₂SO₄ at 30°C. Sweep rate is 2mV/s.

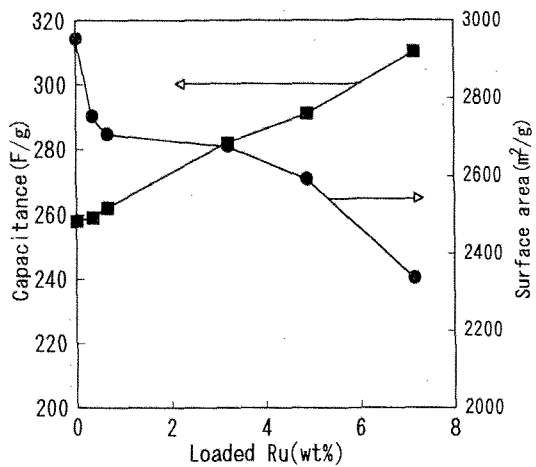


Fig. 4 Effect of amount of loaded ruthenium on the capacitance of coal-based activated carbon treated at 150°C (C-3) in 0.5M H₂SO₄ at 30°C.

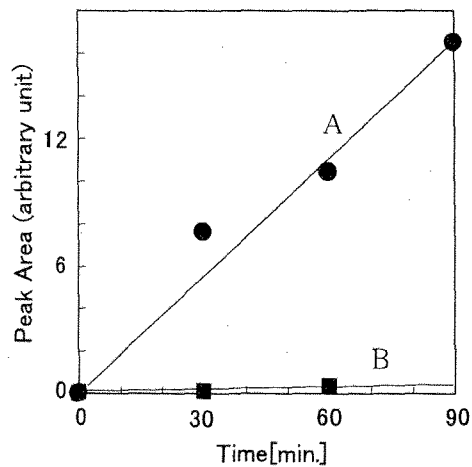


Fig. 5 Relation between carbon dioxide concentration measured using gas chromatography and heating time of coal-based activated carbon (C-3) loaded with 7wt% Ru (A) and without Ru (B) at 150°C.

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