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Specific capacitance of electrochemical capacitor using RuO_2 loading arc-soot/activated carbon composite electrode

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ABSTRACT

An AS-containing CNH and graphite ball was synthesized using a twin-torch-arc apparatus to make an electrode for an electrochemical capacitor with RuO_2 of metallic catalyst. The electrode was composed of activated material, graphite, and binder. RuO_2-AS was prepared by oxidization of Ru-AS. The capacitance current of RuO_2-AS electrode increases with an increase in the catalyst loading amount. RuO_2-AS electrode in case of 4 wt.% RuO_2 has a capacitance current comparable to an AC electrode. The increase of specific capacitance for a composite electrode loading of 2 wt.% RuO_2 was 360% (16.6–60 F/g), while that for a loading of 4 wt.% was 640% (16.6–106 F/g). RuO_2-AS electrodes have a smaller internal resistance than not only AC but also AS. Capacitance current of RuO_2-AS/AC electrode is about twice that of AC electrode and RuO_2-AS electrode. The RuO_2-AS/AC electrode has a high specific capacitance and smaller internal resistance than AC electrode and RuO_2-AS electrode.

1. Introduction

Electrochemical capacitors attract great interest as electricity storage devices due to their high power capability and long cycle life. These electrochemical capacitors may be classified into two groups, namely electric double-layer capacitors (EDLCs) and pseudo-capacitors (PCs) [1,2]. EDLCs are mainly for carbon materials [3,4], which utilize the capacitance arising from charge separation at an electrode/electrolyte interface. PCs are mainly for catalytic metal [5–7], which utilize the charge-transfer pseudo-capacitance arising from reversible Faradaic reactions [8].

In terms of long cycle-life and high specific capacitance, carbon and catalytic metal have been recognized as promising electrode materials for supercapacitors. Activated carbons (AC) [9–14], carbon nano-tubes (CNTs) [15], carbon fibers [16–18] and carbon aerogels [19,20] are some of the materials that have been investigated for their charge-storage behavior. Among them, activated carbon is the cheapest material and hence much research has been devoted to its development as a supercapacitor electrode. Despite the high specific capacitance (up to 250 F/g) of carbonaceous materials, they suffer from poor specific energy density. Metal oxides such as RuO_2 [21–29], MnO_2 [30,31], NiO_x [32,33], IrO_2 [34], etc. are also under evaluation for their charge-storage behavior. Among all of these metal oxides, RuO_2 in its amorphous hydrous form ($RuO_2 \cdot xH_2O$) has been found to be the best material for supercapacitor applications due to its high specific capacitance, high specific energy density, high electrochemical reversibility, and long cycle-life [35].

Carbon nano-horn (CNH), which is a kind of nano-carbon, has attracted attention as an electrode material of DMFC [36]. It was found able to be synthesized as an arc-soot nano-carbon (AS) by the arc discharge method under specific conditions [37,38]. In addition, it was indicated that AS contained the non-dahlia-like CNH loaded the finer Pt/Ru particles with high dispersion [39]. AS contained the dahlia-like CNH, however, has low electrical conductivity and this adversely affects cell performance.

In the present paper, some electrodes which contained AS, AC, RuO_2 loading AS, and there mixture were prepared, and specific capacitance of electrochemical capacitor using these electrodes was evaluated.

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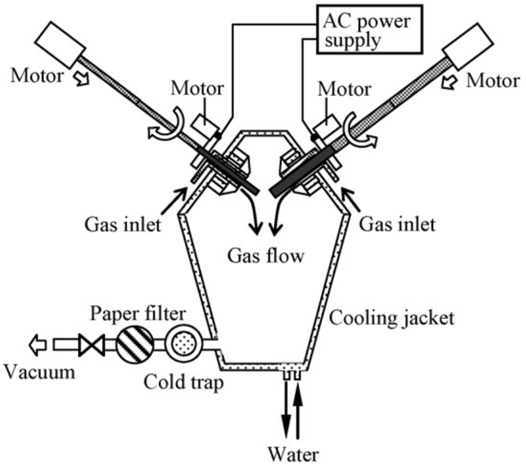

Fig. 1. Schematic diagram of the twin-torch-arc apparatus to synthesize carbon nano-materials by arc discharge.

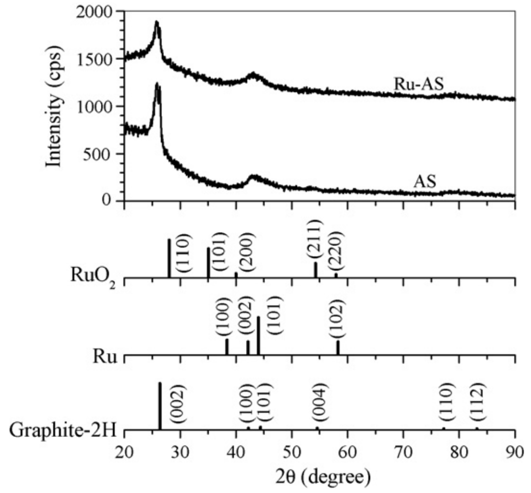

Fig. 2. XRD patterns of AS and RuO_2-AS.

2. Experimental

The AS was prepared by arc discharge plasma with a graphite-rod electrode in nitrogen (N_2) ambient. The experimental apparatuses for arc discharge are depicted in Fig. 1. A twin-torch-arc apparatus with two arc torch electrodes is positioned with an angle of 80° in order to prevent materials from depositing on the cathode. An AC arc discharge was then generated between the electrodes. Both electrodes of the arc torches were continuously supplied for long-term operation. In the apparatus, a constant amount of gas flows in from the torches and is evacuated by the pump. Pressure in the chamber was constantly controlled by a conductance valve, balancing the gas supply and exhaust. Synthesized materials were deposited on chamber walls, a cold trap chilled by liquid nitrogen, and a paper filter. Synthesis conditions were as follows: ambient N_2 gas pressure, 80 kPa; cathode diameter, 10 mm; anode diameter, 6 mm; anode current density, 7.1 A/mm^2; electrode gap, less than 1 mm; discharge time, 5 min; arc voltage, 28 V; and gas flow rate, 20 L/min.

AS was modified to add a functional group as the hydroxy group (–OH) and carboxy group (–COOH) in 3 mol/l H_2O_2 solution at 120 °C for 2 h, and was filtered and washed with de-ionized water and then dried at 120 °C for 2 h. Metallic catalyst (Ru) particles were loaded on AS by the colloidic process [28]. The modified AS was activated to support catalyst at 250 °C for 2 h in air. 300 mg of the activated AS was homogenized with 38 ml ethylene glycol (EG) solution so that the pH of the solution was adjusted to above 13.5 by KOH at 80 °C. Ru·EG was dissolved into AS·EG·nOH over a period of 30 min. Ru·EG solution was made by dissolving 280 mg of the $RuCl_3 \cdot nH_2O$ in EG, then heated at a dispersion temperature 150 °C, which was a parameter of the performance of dispersion in our research for 2 h. After filtration, washing by de-ionized water, and vacuum drying at 120 °C for 2 h. As a result of the above process, Ru was loaded on AS. This material was named Ru-AS. Ru also was loaded on AC by the same process as Ru-AS. This material was named Ru-AC.

Raw materials of the electrode were activated materials, conductive material (ketjen black), and binder. Three kinds of activated materials such as AS, AC, and Ru-AS were prepared. The mass ratio of these materials was changed. The mass ratio of activated materials/ketjen black was 8:1, the powder mixture was mixed with 10 wt.% polytetrafluoroethylene (PTFE) as a binder, then mixed well to obtain a paste. The 400 mg paste was pressed to form a tablet electrode 20 mm in diameter. Ru, which contained the Ru-AS electrode, was electrochemically oxidized in 1 mol/l H_2SO_4 solution at 0.75 V. We prepared and evaluated some capacitors in which AS, AC, RuO_2 loading AS that was named RuO_2-AS, and a new type of electrode composed of RuO_2-AS and AC that was called the RuO_2-AS/AC, were employed for the electrode. The mass ratio of RuO_2-AS/AC electrode (RuO_2-AS:AC:ketjen black:PTFE) was 4:4:1:1.

The morphologies and structures of RuO_2 were analyzed with a field emission type scanning electron microscope (FE-SEM; Hitachi, S-4500), a transmission electron microscope (TEM; JOEL, JEM-2010), X-ray diffraction analyzer (XRD; Rigaku, RINT-2500), and energy-dispersive X-ray spectroscope (EDX; IXRF Systems, EDS2004). The cyclic voltammetric behavior and charge–discharge curve of the electrodes were measured by means of electrochemical analyzer systems (Hokuto Denko, HZ-5000).

3. Results and discussion

EDX confirmed that prepared compositions of Ru-AS were carbon and Ru. Ru-AS contained 4 wt.% Ru. However, the XRD pattern of Ru-AS did not have the Ru and RuO_2 peaks, since Ru was in the amorphous state in Ru-AS (Fig. 2).

SEM and TEM micrographs in Fig. 3 show the AS and Ru-AS. The Ru particle is not found using FE-SEM, since the particle size of the loaded Ru is very small. The TEM micrograph of Ru loading AS shows that the size of a Ru particle is 3 nm or less. The Ru nanocomposite provides excellent high-rate performance and high capacitance retention, because the effective reaction area increased [40].

Cyclic voltammograms recorded for all five types of electrode in 1.0 mol/l H_2SO_4 solution at a scan rate of 10 mV/s are presented in Fig. 4. In case of AS electrodes, the capacitance current is small compared to the AC electrode and RuO_2-AS electrode. The capacitance current of RuO_2-AS electrode increases with the increase in the catalyst loading amount. RuO_2-AS electrode in case of 4 wt.% RuO_2 has a capacitance current comparable to that of an AC electrode. The capacitance current of the RuO_2-AS/AC electrode is about twice as high as that of an AC electrode or RuO_2-AS electrode. The capacitance current of RuO_2-AS/AC electrode has a peak at around 0.2 V, because of the Faradaic current due to oxidation–reduction reaction of RuO_2.

Fig. 5 shows the charge–discharge curves for capacitors with five types of electrode at a charge–discharge current of 100 mA. The IR drop as indicated in the Fig. 5 is a direct measure of equivalent series resistance which influences the overall power performance of a supercapacitor [41]. RuO_2-AS electrode has a smaller IR drop

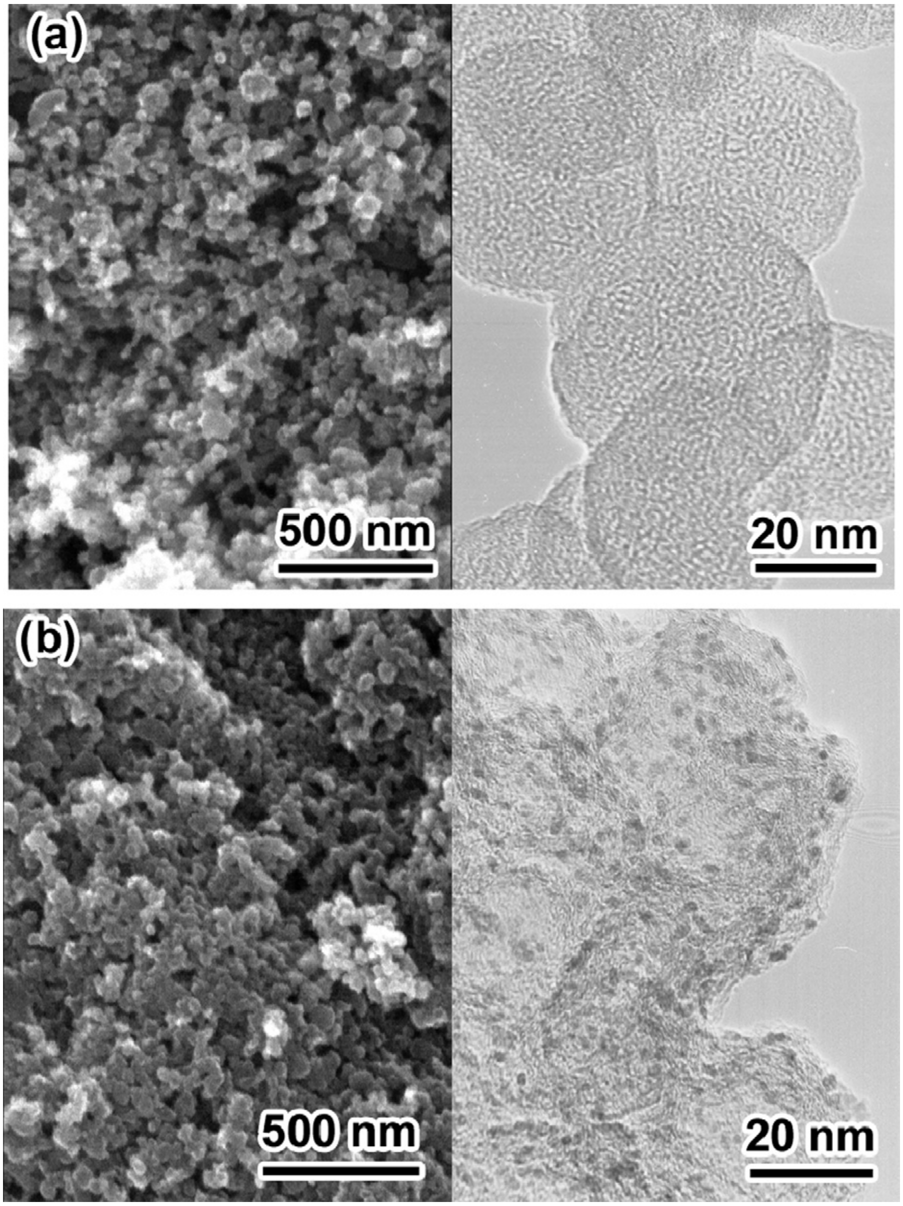

Fig. 3. SEM and TEM photographs of (a) AS and (b) RuO_2-AS.

than an AC electrode. RuO_2-AS/AC electrode has a smaller IR drop than the AC electrode. The discharge capacitance can be calculated from the discharge curve observed after IR drop as

$$C = \frac{I_c}{dV/dt} \tag{1}$$

where C is the capacitance (F), I_c is the charge–discharge current (A), and dV/dt is the voltage scan rate (V/s). The specific capacitance C_s (F/g) is given as

$$C_s = \frac{C}{m} \tag{2}$$

where m is the electrode mass (g).

Table 1 tabulates the specific capacitance and internal resistance of composite materials with different activated materials such as AS, AC, RuO_2-AS, and RuO_2-AS/AC. The specific capacitance of AC electrode is five times or more as high as that of AS electrode. However, AC electrode has a higher internal resistance than AS electrode. The increase of specific capacitance for a composite electrode loading of 2 wt.% RuO_2 was 360% (16.6–60 F/g), and that of 4 wt.% was 640% (16.6–106 F/g). RuO_2-AS electrodes have a smaller internal resistance than not only AC but also AS. These measurements show that AS is able to disperse RuO_2 particle enough to work actively as catalyst. The RuO_2-AS/AC electrode has a higher specific capacitance than the AC electrode and RuO_2-AS electrode. This is because RuO_2-AS enters the mesopores of the AC, and hence, the reaction area of RuO_2 surface increases. The internal resistance of the RuO_2-AS/AC electrode containing AC, which has high resistance, was as low as that of the RuO_2-AS electrode.

Table 1
Specific capacitance and internal resistance of AS, AC, RuO_2-AS, and RuO_2-AS/AC electrodes with different RuO_2 contents.

Electrode	AS	AC	RuO_2-AS (2 wt.%)	RuO_2-AS (4 wt.%)	RuO_2-AS/AC
Specific capacitance (F/g)	16.6	96	60	106	244
Internal resistance (mΩ)	590	817	500	425	400

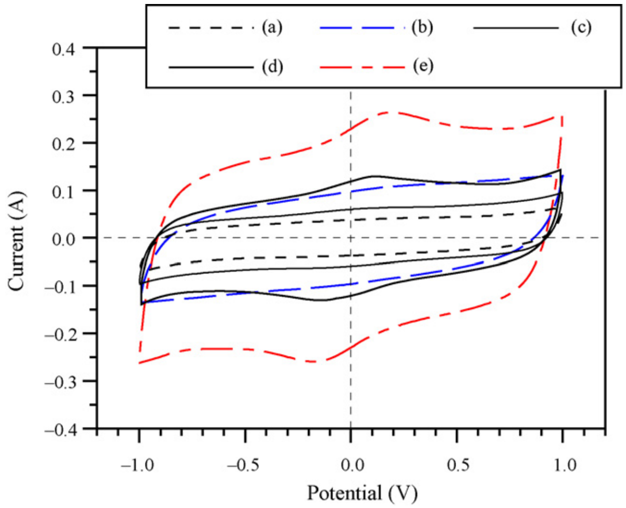

Fig. 4. Cyclic voltammograms of (a) AS, (b) AC, (c) RuO_2-AS (2 wt.%), (d) RuO_2-AS (4 wt.%), and (e) RuO_2-AS/AC electrodes at a scan rate of 10 mV/s.

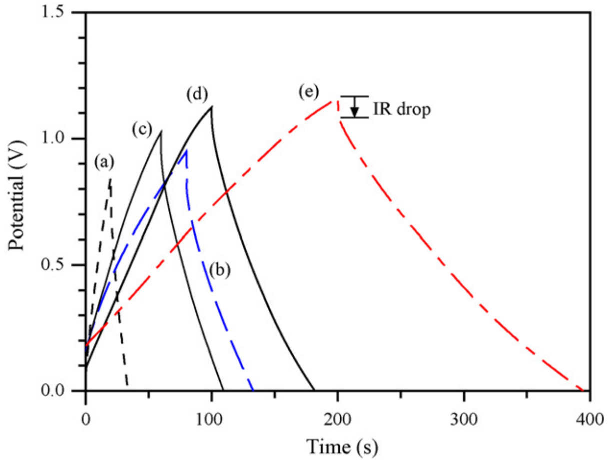

Fig. 5. Charge–discharge curves of (a) AS, (b) AC, (c) RuO_2-AS (2 wt.%), (d) RuO_2-AS (4 wt.%), and (e) RuO_2-AS/AC electrodes at a charge–discharge current of 100 mA.

4. Conclusions

The AS-containing CNH and graphite ball was synthesized using the twin-torch-arc apparatus. The AS was modified to add a functional group as a hydroxy group and a carboxy group, and Ru particles of metallic catalyst were loaded on the AS by the colloidic process. The carbon electrode was composed of activated material, graphite, and binder. Three kinds of activated materials, AS, activated carbon, and Ru-AS, were prepared. RuO_2-AS was prepared by oxidization of Ru-AS. The capacitance current of RuO_2-AS electrode increases by increasing the catalyst loading amount. RuO_2-AS electrode in case of 4 wt.% RuO_2 has a capacitance current comparable to that of the AC electrode. RuO_2-AS electrode has a smaller IR drop than the AC electrode. The specific capacitance of the AC electrode is five times or more as high as that of the AS electrode. However, the AC electrode has a higher internal resistance than the AS electrode. The increase of specific capacitance for a composite electrode loading of 2 wt.% RuO_2 was 360% (16.6–60 F/g), and 640% (16.6–106 F/g) for a loading of 4 wt.%. RuO_2-AS electrodes have a smaller internal resistance than not only AC but also AS. The capacitance current of RuO_2-AS/AC electrode is about two times as high as that of the AC electrode and RuO_2-AS electrode. RuO_2-AS/AC electrode has a smaller IR drop than the AC electrode. The RuO_2-AS/AC electrode has a high specific capacitance and smaller internal resistance than the AC electrode and RuO_2-AS electrode, because RuO_2-AS enters the mesopores of the AC, thereby increasing the reaction area of Ru surface.

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