Evaluation of Metal-loaded Activated Carbon Electrode for Electrochemical Capacitor Prepared by Plasma CVD Method

Keiichi OKAJIMA,* Naotake SAKUMOTO, Takashi TOYA, and Masao SUDOH

Department of Materials Science and Chemical Engineering, Faculty of Engineering, Shizuoka University (3-5-1 Johoku, Hamamatsu 432-8561, Japan)

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Aiming to increase the capacitance with double-layer capacitance and pseudocapacitance, metal-loaded active carbon fiber (ACF) electrodes for use in electrochemical capacitors were prepared by the plasma enhanced chemical vapor deposition method. Platinum was used as the loaded material, and the preparation conditions such as substrate temperature, concentration of the aqueous Pt solution and plasma output were investigated. For the Pt-loaded ACF samples with a specific surface area of 1,500 m²/g, the capacitance increased by 24% compared to the untreated sample, and the highest electric capacity value of 306 F/g was achieved at a substrate temperature of the 250°C.

Key Words : Electrochemical Capacitor, Active Carbon Fiber, Plasma CVD, Metal-loaded Electrode

1 Introduction

Electrochemical capacitors have recently become of major interest as energy storage systems because of their higher power density than those of dielectric capacitors, and have a longer cycle life than batteries.^{1, 2)} The electric double layer capacitor using the activated carbon electrode is one of the main developmental research areas in this field. An activated carbon fiber³⁻⁵⁾ and an activated carbon powder^{6, 7)} are popular materials for the electrode of the electric double layer capacitor because of their high specific surface area and high conductivity. However, there seems to be a limit to the double layer capacity only by increasing the specific surface area of the activated carbon. On the other hand, the capacitors based on a faradic process due to redox reactions are called pseudocapacitors. These electrodes are formed with a noble metal or transition metal oxide such as Pt, RuO₂, IrO₂, NiO_x, and have the advantages of high specific capacitance and high conductivity.⁸⁻¹⁰⁾ However, proton diffusion is a relatively slower process so that the power of such faradic devices is limited. It would be advantageous to disperse nano-size particles of a metal or metal oxide on a double layer support with a high surface area such as an activated carbon. The composite electrode fabricated by the Sol-Gel method has been reported.^{11, 12)}

In this study, aiming to increase the capacitance with double-layer capacitance and pseudocapacitance, metal-loaded active carbon fiber (ACF) electrodes for the electrochemical capacitor were prepared by the plasma enhanced chemical vapor deposition (plasma CVD) method. The formation of nano-size fine particles can be expected using the plasma CVD process. In this study, platinum was used as the loaded material, and the preparation conditions such as substrate temperature, concentration of the aqueous Pt solution and plasma output were investigated.

2 Experimental

An ACF cloth was used as the support and its specific surface area was 1,500 m²/g (Toyobo, KF-1500F). Figure 1 shows a schematic diagram of the apparatus used for the RF-plasma enhanced chemical vapor deposition treatment (Samco BP-1). The plasma CVD system is the conventional planar capacitive type consisting of a reaction chamber, a gas feeding system, a pumping system and a RF-power supply. H₂PtCl₆ was used as the reactant and introduced with H₂ gas as the reducing agent into the reaction chamber. H₂PtCl₆ and H₂ passed through the inside of the RF-electrode, and then these reactive species were uniformly sprayed from the RF-electrode located above the ACF cloth. The H₂PtCl₆ container was kept at room temperature and the H₂PtCl₆ flow rate was controlled by changing the concentration of the H₂PtCl₆ aqueous solution. The standard H₂ flow rate was 10 cm³ min⁻¹ and the H₂/Ar flow ratio was 20%. The pressure in the reactor was set at 67 Pa and an RF Power of 5 W to 10 W was supplied to generate the plasma. The substrate was heated with a conventional coil heater in the reaction chamber and its temperature was controlled in

Fig. 1 Schematic diagram of the plasma CVD apparatus.

the range to 450°C. Each electrode was exposed to the plasma for 1 min. Pt contents were estimated from the measured dry weight of RF-CVD treated samples. The crystallinity of the Pt particles was investigated using an X-ray diffractometer (Rigaku, RINT-2000) with CuK α radiation. The morphology of loaded Pt particles was observed using scanning electron microscopy (JEOL JSM-5600, JSM-6401F).

For the electrochemical measurements using cyclic voltammetry, a two-electrode coin-type shaped cell was used. The ACF and Pt-loaded ACF electrodes were all 16 mm in diameter. The measurements were carried out at room temperature using a potentiostat (Hokuto Denko HZ-3000). A glass filter was used as the separator. As the electrolyte solution, 0.5 mol/l H₂SO₄ was used for all of the measurements and the electrochemical treatments. The typical sweep rate was 5 mVs⁻¹ and the number of cycles was 5 for the cyclic voltammetry in order to determine the capacitance.

3 Results and Discussion

Figure 2 shows a SEM image of a Pt-loaded ACF electrode prepared at a substrate temperature of 150°C, with a 0.064 mol/l concentration of H₂PtCl₆ solution and a 10 W of RF-power. From this result, the formation of particles 20 nm or less was confirmed, though the particle size was about 150 nm for the sample prepared by impregnation.¹³⁾ Besides, particles were also formed in the macroscopic hole and the grain size was about 50 nm. Based on the SEM observation of the cross sectional direction, the Pt particles were uniformly formed on the carbon fibers. This indicated that CVD deposition was taken place even inside the ACF felt. In the XRD measurement, the peak corresponding to Pt was confirmed, while the peaks of Pt-oxide or Pt-chloride were not observed.

Figure 3 shows the result of the cyclic voltammetry for the electrode formed at 350°C. Each curve had almost an ideal rectangular shape. The CV curve for the Pt-loaded electrodes is similar to those for the RuO₂ electrode¹⁴⁾ and the RuO₂-carbon composite electrode,¹⁵⁾ and was mainly featureless between the hydrogen and oxygen evolutions. This result indicates that the charge exchanged between the Pt and the electrolyte at a constant rate.¹⁴⁾

The effect of substrate temperature during RF-CVD treatment on the capacitance is shown in Fig. 4. For the case of the H₂PtCl₆ solution concentration of 0.064 mol/l, the capacitance increased with increasing substrate temperature, and the capacitance became a maximum at 350°C. Pt contents also increased with rising substrate temperature. Maximum values of the Pt content were 7.3% and 10.3% by weight with plasma outputs of 5 W and 10 W, respectively. Both values were obtained at the same substrate temperature of 350°C. This suggested that the capacitance improved by increasing the quantity of Pt particles. However, the Pt particles were agglomerated at the substrate temperature of 450°C from the SEM results. Therefore, it was considered that the specific surface area of the Pt particle decreased and the agglomer-

Fig. 2 SEM image of the Pt-loaded ACF surface.

Fig. 3 Cyclic voltammogram of the Pt-loaded ACF electrode with a substrate temperature of 350°C during CVD treatment. Sweep rate: 1)1, 2)5, 3)10, 4)15, 5)20 mV s⁻¹.

Fig. 4 The specific capacitance as a function of the substrate temperature during CVD treatment for Pt-loaded ACF electrodes.

ated grain plugged the pores of the ACF. For the solution concentration of 0.32 mol/l and plasma output of 10 W, the highest electric capacity value of 306 F/g was achieved for the substrate temperature of 250°C. This result corresponded to an increase of 24% over that of the untreated electrode. This was different from the result at the low concentration (0.064 mol/l), where the electrode capacitance drastically decreased at the substrate temperature above 350°C. It seemed that the capacity de-

Fig. 5 Dependence of the deposition temperature on the Pt content ratio.

Fig. 6 SEM images of Pt-loaded ACF electrodes prepared at 250°C (a), 450°C (b), with a H_2PtCl_6 concentration of 0.32 mol/l.

creased with a relatively high concentration of H_2PtCl_6 solution because the agglomeration of the Pt particle was promoted at the lower temperature.

The Arrhenius-type plot of the relation between the substrate temperature and the Pt content is shown in Fig. 5. In the low solution concentration of H_2PtCl_6 (0.064 mol/l), the Pt content increased for plasma outputs of 5 W and 10 W with an increase in the substrate temperature, and a linear relation was found. For the plasma outputs of 5 W and 10 W, the apparent activation energies for the Pt deposition assuming an Arrhenius-type equation were 194 J/mol and 52 J/mol, respectively. The effect of a thermal assist was higher with the plasma output of 5 W as was expected, and the increment of the electrode capacitance increased with rising substrate temperature compared to the plasma output of 10 W (Fig. 4). On the other hand, there was no correlation with the substrate temperature and the Pt content for the high solution concentration of H_2PtCl_6 (0.32 mol/l), and the Pt content did not agree with the change in the electrode capacitance (Fig. 4). Especially, there was quite a difference for the electrode capacitance between the electrode prepared at 250°C and that at 450°C substrate temperatures during CVD treatment in spite of the Pt content of about 10% for both electrodes. SEM images of these electrodes are shown in Fig. 6a and Fig. 6b, respectively. It was confirmed that large Pt particles agglomerated and formed grains of about 1 μm or larger at the substrate temperature of 450°C (Fig. 6b). In addition, no Pt particle of 20

nm or less was observed on the ACF surface and it was considered that large grains were formed with small particles by surface diffusion. This agglomeration decreased the specific surface area of the Pt particle, therefore the capacitance became lower than that of prepared at the substrate temperature of 250°C (Fig. 6a).

4 Conclusion

Pt-loaded ACF electrodes for use in electrochemical capacitors were prepared by the plasma enhanced chemical vapor deposition method, and the electrode capacitance was improved by the contribution of the Pt pseudo-capacitance. Pt particles of 20 nm or less were formed by using the plasma CVD technique. In addition, Pt particle formation in the macroscopic holes was confirmed. For the Pt-loaded ACF electrodes with a specific surface area of 1,500 m^2/g , the capacitance increased by 24% compared with the untreated sample, and the highest value of the electric capacity of 306 F/g was achieved with the sample prepared at the 250°C substrate temperature. At a low concentration of reactive species, an Arrhenius-type plot for the relationship between the substrate temperature and the Pt content became linear, and the electrode capacitance increased with the increase in the Pt content. However, the electrode capacitance decreased even with the equivalent Pt content by agglomeration of the Pt particles for the sample having high content of reactive species.

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