Platinum-loaded Carbon Electrochemical Capacitors Prepared by Plasma CVD Method

Keiichi Okajima, Takashi Toya, Naotake Sakumoto, and Masao Sudoh
Department of Materials Science and Chemical Engineering, Shizuoka University
3-5-1 Johoku, Hamamatsu, Shizuoka 432-8561, Japan

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. Aiming to increase the electric capacity 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, and 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 plasma CVD system is a conventional planar capacitive type consisting of a reaction chamber, a gas feeding system, a pumping system and a RF-power supply (Fig .1).[1] Platinum was used as the loaded material, and an ACF cloth was used as the support and its specific surface area was 1500 m^2/g (Toyobo, KF-1500F). H_2PtCl_6 was used as the reactant and introduced with H_2 gas as the reducing agent into the reaction chamber. The H_2PtCl_6 flow rate was controlled by changing the concentration of the H_2PtCl_6 aqueous solution. The standard H_2 flow rate was 10 cm^3min^{-1} and the H_2/Ar flow ratio was 20 %. The substrate was heated with a conventional coil heater in the reaction chamber and its temperature was controlled in the range to 450 °C. For the electrochemical measurements using cyclic voltammetry, a two-electrode coin type shaped cell was used. As the electrolyte solution, 0.5 mol/l H_2SO_4 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. And, AC impedance measurements were carried out using a Solartron FRA 1260 controlled by a personal computer.

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 H_2PtCl_6 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. Besides, particles were also formed in the macroscopic hole and the grain size was about 50 nm. The effect of substrate temperature during RF-CVD treatment on the capacitance is shown in Fig. 3. For the case of the H_2PtCl_6 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. 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. 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 agglomerated grain plugged the pores of the ACF. Figure 4 shows the result of the AC impedance measurement with a 0.32 mol/l concentration of H_2PtCl_6 solution. The charge-transfer resistance (R_{ct}) decreased with increasing the capacitance. For the electrode prepared at 250 °C that capacity was the highest, R_{ct} decreased by 32 % in comparison with the untreated electrode.

1) K. Okajima, N. Sakumoto, T. Toya and M. Sudoh, *Electrochemistry*, (in printing).

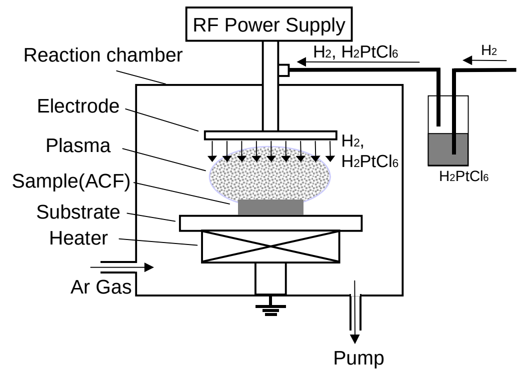

Fig.1 Schematic diagram of apparatus for plasma treatment

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

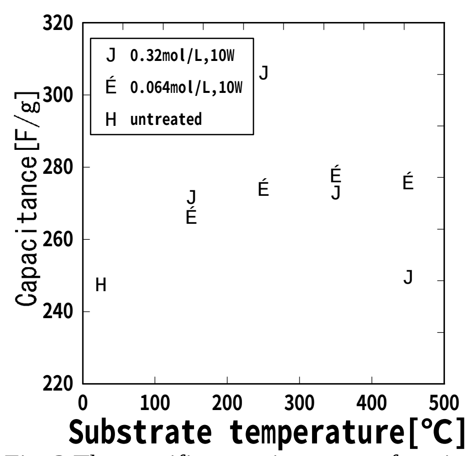

Fig. 3 The specific capacitance as a function of the substrate temperature during CVD treatment for Pt-loaded ACF electrodes.

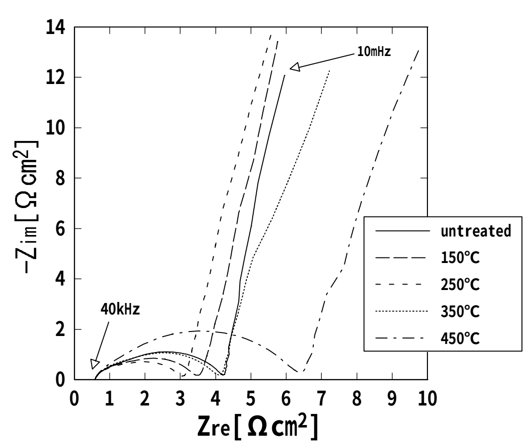

Fig. 4 Cole-Cole plot of Pt-loaded ACF electrode with H_2PtCl_6 concentration of 0.32 mol/L.