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Morphological Effects on the Electrical and Electrochemical Properties of Carbon Aerogels

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Carbon aerogels are prepared by a sol-gel process. By controlling the mass ratio of reactants and the molar ratio of resorcinol to catalyst (R/C), carbon aerogels with different microstructures can be developed. The electrical conductivity is measured by the van der Pauw method. The results show that the electrical conductivity increases with increase of both temperature and density of carbon aerogel. Cyclic voltammetry is a useful technique to investigate the electrochemical properties of carbon aerogel electrodes. The maximum specific capacitance of carbon aerogel electrode in H_2SO_4 electrolyte is ~86 F/g.
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Carbon aerogel, derived from resorcinol-formaldehyde (RF) aerogel, can be prepared by the sol-gel process and supercritical drying. The molar ratio of resorcinol to catalyst (R/C) controls the particle size, while the mass ratio of reactants determines the density of the material.[1] Because of its monolithic structure, high specific surface area (400-1100 m^2/g), and high electrical conductivity, carbon aerogel can be used as an electrode for electrochemical double-layer capacitors (EDLCs).[2] The basic principle of EDLCs is that energy can be stored via separation of charges across a polarized electrode/electrolyte interface. The stability of charge of the electrode/electrolyte interface will influence the characteristics of EDLCs, such as self-discharge property. It is required that electrodes should be good conducting materials, and that there is no participation in faradaic reactions with the electrolyte at the applied voltage.

In this paper, carbon aerogels are developed under different conditions. The relation between the electrical conductivity and the microstructure of carbon aerogels is investigated in the temperature range from 20 to 300 K, while the electrochemical properties of carbon aerogel are investigated by cyclic voltammetry.

Experimental

Two sets of carbon aerogel samples were prepared; the first set had the same R/C ratio of 200 with different mass ratios, 30, 40, and 50%, respectively; while the second set had the same mass ratio of 30% with different R/C ratios of 50, 100, and 200, respectively. The preparation of RF aerogels and carbon aerogels have been described in Ref. 3 in detail. Briefly, resorcinol and formaldehyde were mixed in a 1:2 molar ratio. Deionized water was used as a solvent to control the final gel concentration. Sodium carbonate was added as a base catalyst. Each mixture was poured into individual glass containers and kept at $\sim 85 \pm 5°C$. Next, the cross-linked gels were exchanged with acetone and subsequently dried supercritically using liquid carbon dioxide ($T_c = 31°C$, $P_c = 7.4$ MPa). RF aerogels were pyrolyzed in a flow of N_2 for 4 h at 1050°C in a tube furnace.

Carbon aerogel was cut into 1.0 mm thick wafers. The electrical conductivity was measured using van der Pauw method, and four contacts were made. The measurement was carried out in the temperature range 20-300 K.

Cyclic voltammetry was used for the investigation of the electrochemical properties of carbon aerogel electrode/H_2SO_4 electrolyte system. A Pb wafer was used as the counter electrode, and a saturated calomel electrode (SCE) was used as a reference electrode. The voltage sweep of the cyclic voltammetry was from −600 to 600 mV. The measurement was carried out by using a potentiostat (ZF-3) and a voltage scanner (ZF-4), and the sweep rates were 1.67, 5, and 10 mv/s, respectively.

Results and Discussion

Electrical conductivity.—The temperature dependence of the electrical conductivity (σ) for all prepared samples is shown in Fig. 1. Figure 1a shows the behavior of the electrical conductivity for samples having R/C ratio of 200 and mass ratios of reactants 30, 40, and 50%, while Fig. 1b shows the behavior of the electrical conductivity for samples having the mass ratio of reactants 30% but different R/C ratios of 50, 100, and 200. It is shown that the electrical conductivity increases with increase of both temperature and density of the samples.

Figure 2 shows the scanning electron micrographs (SEMs) of carbon aerogels. The microstructure of carbon aerogels consists primarily of interconnected carbon grains. Raman scattering and X-ray diffraction (XRD) experiments[4] showed that there are graphitic carbon ribbons present within the single particles of carbon aerogels. These ribbons are cross-linked with each other within the particles, so the particle can be viewed as conducting, while the structural links between neighboring grains are not necessarily electrically conducting.

By changing the mass ratio of reactants during the sol-gel process, carbon aerogels with various densities can be developed. With increasing mass density, the particle size remains constant, but the packing ratio of these particles increases, and the space due to the mesopores that span the distance between chains of interconnected particles decreases. Therefore, the more closely packed the conducting grains, the higher the electrical conductivity of carbon aerogels.

As the mass ratio of reactants determines the packing ratio, the R/C ratio determines grains size. Under high catalyst concentration (*e.g.*, R/C = 50), many clusters are generated during the sol-gel process but they cannot grow very large in diameter. The resultant carbon aerogel has a polymeric microstructure, in which no distinct single grains present, if some, with sizes 7-9 nm. Under low catalyst concentration (R/C = 200, 300), fewer clusters are generated and they can grow larger in diameter than their high catalyst counterparts. The resultant carbon aerogel has a colloidal microstructure, in which some distinct grains are present, with sizes 11-14 nm. Therefore, it is expected that more nonconducting regions (defects) are present in polymeric carbon aerogels, leading to lower electrical conductivity at a given density as compared to colloidal carbon aerogels.

From Fig. 1b, we cannot confirm the role played by the particle size on the electrical conductivity of carbon aerogels. The R/C = 50 carbon aerogel is more microscopically disordered (more defects) than R/C = 200, 100 samples, which depresses the increment of the electrical conductivity of R/C = 50 carbon aerogels. This is effecting the favorable effect due to the high packing ratios of grains for R/C = 50 sample which can counteract the negative effect of defects.

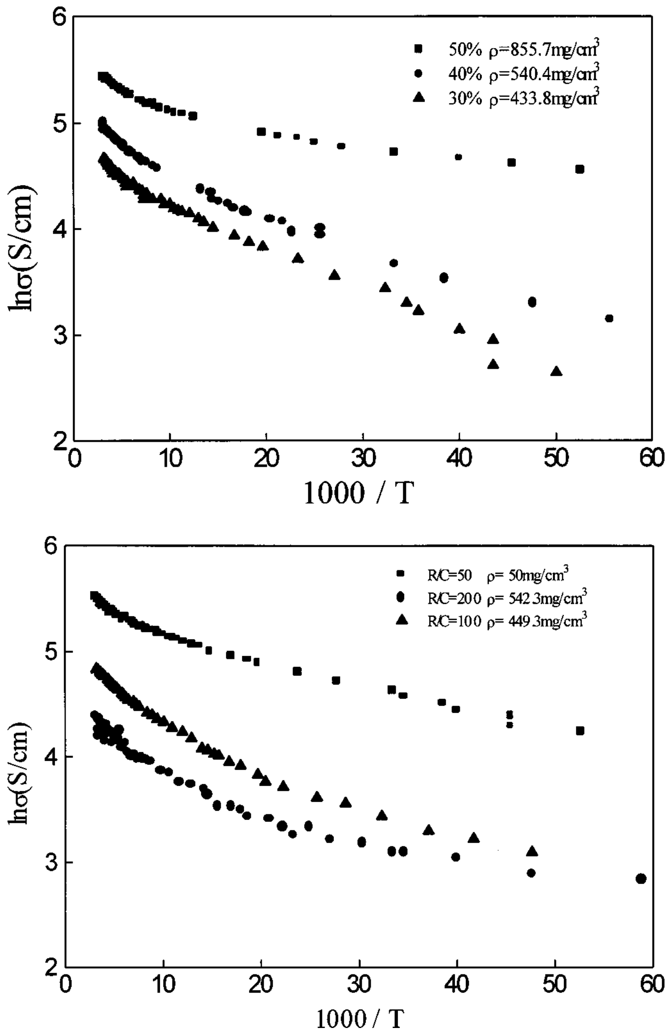

Figure 1. Effect of temperature on electrical conductivity of carbon aerogels.

Cyclic voltammetry.—The electrochemical behavior of carbon aerogels is characterized by cyclic voltammetry (CV) shown in Fig. 3. The measurement is carried out over potential ranges from −600 to 600 mV *vs.* saturated calomel electrode (SCE). The measurements are carried out with different sweep rates and we get three

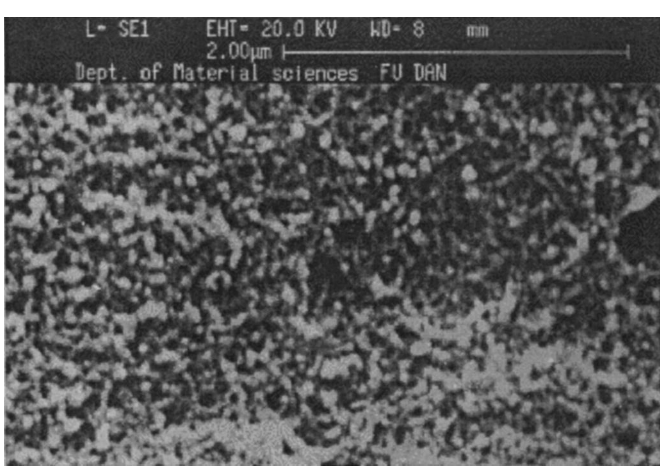

Figure 2. SEM of the carbon aerogel.

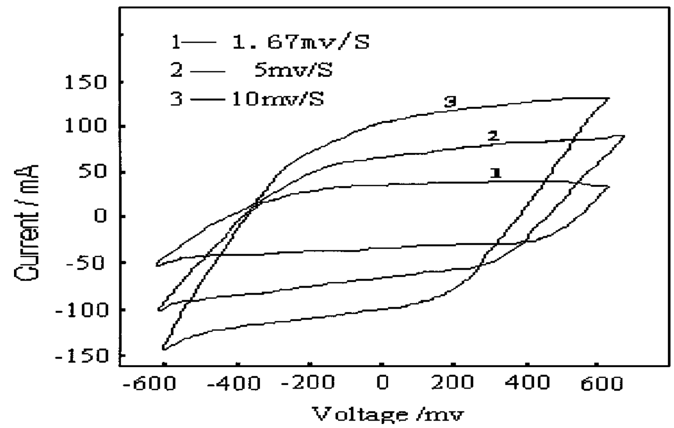

Figure 3. Cyclic voltammetry of carbon aerogel electrode/H_2SO_4 electrolyte.

loops. It is shown that, for the first loop, where the sweep rate is 1.67 mV/S, the current is constant for a wider range (from −200 to +400 mV) than those currents for other loops with higher sweep rates. We have to mention that in order to get any one of the loops, we had to repeat the measurements at the same condition 20 times to get stable results. The relation between the current (at 100 mV *vs.* SCE, the midpoint of the current plateau) and the sweep rate is linear as shown in Fig. 4. As the sweep rate increases, the electric current increases. The specific capacitance of carbon aerogel electrode in H_2SO_4 electrolyte is calculated using the relation[5]

$$C_s = I/(V_s M)$$

Here I is the current (mA) at 100 mV *vs.* SCE, V_s is the sweep rate (mV/S), and M is the weight of the electrode (g). The maximum value of C_s is found to be ~86 F/g for the carbon aerogels with the R/C ratio of 200 and the mass ratio of 40%. Previous work has shown that the capacitance density appears to peak or plateau near aerogel density of ~0.8 and ~1.0 g/cm^3 for the organic electrolyte and 5 M KOH. The specific capacitance values of carbon aerogels in 5 M KOH is 45 F/g, while in 1 M H_2SO_4 is 95 F/g.[6]

It is found that every cyclic loop begins to overlap at a constant sweep rate after the measurement is repeated 20 times. When the voltage signal begins to scan for the first time (*e.g.*, from 0 to 600 mV), ions can occupy some pores within the electrode to participate the formation of the electrochemical double-layer. While the voltage signal begins to scan reversely (*e.g.*, from 600 mV to 0), the voltage imposed on the electrode is decreased gradually, and the ions collected on the electrode begin to leave the electrode, but some ions

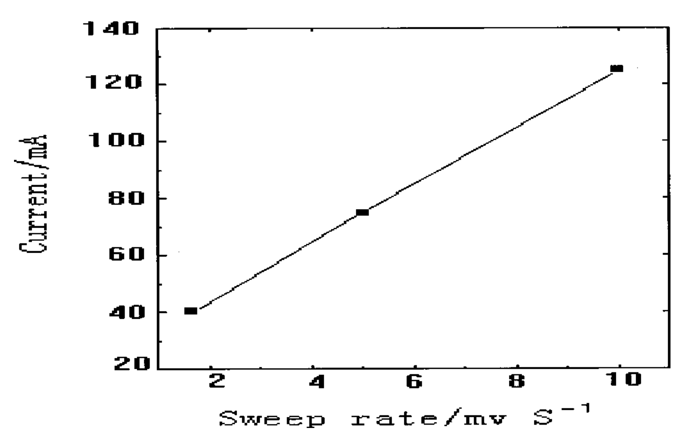

Figure 4. The relation between the current and sweep rate.

plunged into the pores cannot come out immediately, resulting in the next loop not overlapping with the former one. With increasing scan cycles, some pores become larger because of the effect of the ''plunging'' and ''squeezing'' of the ions, so such pores become unblocked for ions, which results in the overlapping of the later loops at a constant sweep rate. To increase the capacitance, some international study groups usually take the method of activating the electrode.[7,8] The purpose is to improve pore structure, which is useful to the formation of the electrochemical double layer.

Conclusion

The electrical conductivity of carbon aerogel increases with increasing both the temperature and density of the sample. Cyclic voltammetry is a useful technique for investigating the electrochemical properties of carbon aerogel electrodes. The maximum special capacitance of carbon aerogel electrode in H_2SO_4 electrolyte is ~86 F/g.

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