NOVEL SYNTHETIC CARBON MATERIALS AS SUPERCAPACITORS

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Introduction

Carbon materials are receiving increasing attention as critical materials in energy storage devices, e.g. as electrodes for electrochemical double-layer capacitors (EDLCs) [1-2]. Research on EDLCs has focused on developing new carbon materials that have a large surface area (SA) to improve both the energy and power densities, since the mechanism for energy storage is due to the separation of charges at the electrode/electrolyte interface. It is well known that the double-layer capacitance of pure graphite is around 20 $\mu F/cm^2$ [3]. Scaling this value to a porous activated carbon with a SA of 2000 m^2/g suggests that the capacitance should be around 400 F/g. However, in reality, the capacitance for a typical activated carbon is around 40 F/g ($\approx$ 1/10th of the theoretical value) [4].

Activated carbons contain a significant fraction of micropores (< 2 nm in diameter) [5]. It is now believed [2] that the limited capacitance is associated with the inability of the electrolyte solution to wet the micropores, or the inability of a double layer to form in a region where the pore dimensions are of the same size as the double layer (~ 5 Å). Roughly speaking, it is estimated [6] that pores larger than 2 nm in diameter may be useful in aqueous electrolytes, with organic electrolytes limited to pores larger than 5 nm in diameter. Therefore, it is desirable to develop new carbonaceous materials with a controlled pore structure, i.e., with a controlled SA, PV (PV), pore size distribution, and nanostructure.

Recently, Pekala and co-workers [2, 7] developed a synthetic carbon aerogel for use in energy storage devices, which was derived from a carbonized resorcinol for-maldehyde (RF) resin via a sol-gel route. Other, more recent studies were devoted to understanding how the syn-thesis conditions affect the porous structure of sol-gel derived RF carbon xerogels [8-10]. It was shown [8] that the initial pH of the RF solution had a significant effect on both the SA and PV (PV) of carbon xerogels synthe-sized using a slightly modified procedure compared to that in the literature [2, 7]. It was also determined that the pH window for making high SA carbon xerogels ranged be-tween 5.5 to 6.5 [8]; thus, an initial solution pH of 6 was used to make the RF resin for the carbonization and acti-vation studies [9]. With this material, the effect of differ-ent carbonization temperatures and activation conditions on the pore structure and gas phase adsorbent properties of

carbon xerogel materials was studied [9]. The objective of the present study was to correlate the SA with the double-layer capacitance of carbon xerogels synthesized using different initial solution pHs, carbonization temperatures, and CO_2 activation times.

Experimental

The modified procedure used to synthesize the carbon xerogels was given in detail elsewhere [9]. A typical three-electrode test system in a beaker with 30% H_2SO_4 was used to carry out the electrochemical measurements. The working electrode, containing $\approx$ 5 mg of carbon xerogel, with 5% Teflon used as a binder, was hand-pressed into a 8.5mm diameter and 150 μm thick disk. The disk was placed in the T-cell and hand-pressed between two tantalum rods with a porous glass fiber filter as the separator. A saturated calomel reference electrode was used, along with platinum gauze as the counter electrode.

A Micromeritics Pulse Chemisorb 2700 Analyzer was used to obtain the SAs. The cyclic voltammetry experiments were performed between 0 and 1 V at a sweep rate of 5 mV/s using a potentiostat (EG&G 273A). AC impedance was conducted from 100kHz to 1 mHz with 0 bias using a Lock-In amplifier (EG&G 5210). A solution of 30% H_2SO_4 was used as the electrolyte . A saturated calomel electrode was used as the reference electrode, along with platinum gauze as a counter electrode. All the experiments were conducted at 22 ± 2 °C.

Results and Discussion

All of the results are displayed in Figures 1A to 1C, in terms of the double-layer capacitance as a function of the SA of carbon xerogels synthesized using different ini-tial solution pHs (1A), carbonization temperatures (1B), and CO_2 activation times (1C). The double layer capaci-tance obtained from cyclic voltammetry and AC imped-ance were reasonably close, indicating that both methods were valid. Figure 1A shows a plot of the double layer capacitance as a function of the SA of carbon xerogels synthesized at different pHs and carbonized in nitrogen at 1050 °C. The capacitance increased linearly with the SA (which increased with decreasing pH), with a slope of 19.3 $\mu F/cm^2$. This value was very close to the capacitance of clean graphite (20 $\mu F/cm^2$), indicating that almost all of

the SA of the carbon xerogel was being utilized in the formation of the double-layer.

Figure 1B shows the effect of the carbonization temperature on the SA and double layer capacitance of carbon xerogels synthesized with an initial solution pH of 6. As the temperature increased from 600 to 900 °C, the SA gradually decreased from about 640 to 600 m^2/g, then it sharply decreased as the temperature continued to increase, and finally, a SA of 430 m^2/g was reached at 1200 °C. It was surprising that the double layer capacitance of the carbon xerogel carbonized at 600 °C was almost zero, which implied that there was no active SA available for double layer charging and discharging. This debatable result between the physical and electrochemical SA lead to the speculation that the material remained a non-conductive polymer and was not converted into carbon at this low temperature. But, for the xerogel carbonized at 750 °C, the capacitance peaked at about 180 F/g, a surprisingly high value. At higher temperatures the capacitance continued to decrease to about 100 F/g at 1200 °C.

Figure 1C shows the effect of the CO_2 activation time of the SA and double layer capacitance of carbon xerogels synthesized with an initial solution pH of 6 and carbonized in nitrogen at 1050 °C with 5% CO_2 added for activation. The SA increased linearly with activation time, to about 1800 m^2/g. This corresponded to more than a factor of three increase in the SA compared to that obtained without activation; however, the capacitance only increased by 50 % (175 F/g). It was speculated that the activation process created numerous micropores that were not assessable to the electrolyte; thus, a large fraction of the SA was not available for double layer formation, which was in agreement with that claimed elsewhere [2].

Acknowledgments

References

1. Aoki, M., Sato, K. and Kobayashi, Y., *IEICE Trans. Fundamentals*, 1994, E77-A, 208.
2. Mayer, S. T., Pekala, R. W. and Kaschmitter, J. L., *J. Electrochem. Soc*, 1993, 140, 446.
3. Kimosihta, K., *Carbon: Electrochemical and Physico-chemical Properties*, John Wiley & Sons, 1988.
4. Tanahashi, I., Yoshida, A and Nishino, A., *Bull Chem. Soc. Jpn.*, 1990, 63, 3611.
5. Tanahashi, I., Yoshida, A and Nishino, A., *Bull Chem. Soc. Jpn.*, 1990, 63, 2755.
6. Burke, A., *Proceedings of the Workshop on Carbon for Li-Ion Batteries and Supercapacitors*, U.S. Department of Energy, Reno, Nevada, 1995.
7. Pekala, R. W., Mayer, S. T., Kaschmitter, J. L and Kong, F. M., in *Sol-Gel Processing and Applications*, ed. Attia, Y.A., Plenum Press, NY , 1994, p. 369.
8. C. Lin and J. A. Ritter, *Carbon,* 1997, accepted.
9. C. Lin and J. A. Ritter, in Carbon' 97 (*Ext. Abstr., 23rd Biennial Conf.Carbon*), State College, PA, 1997.
10. V. Srinivansan, C. Lin, J. A. Ritter, and J. W. Weidner, in *Electrochemical Capacitors II, Vol. 96-25*, ed. F. M. Delnick and D. Ingersoll, The Electrochemical Society Proceedings Series, NJ, 1997, p. 153.
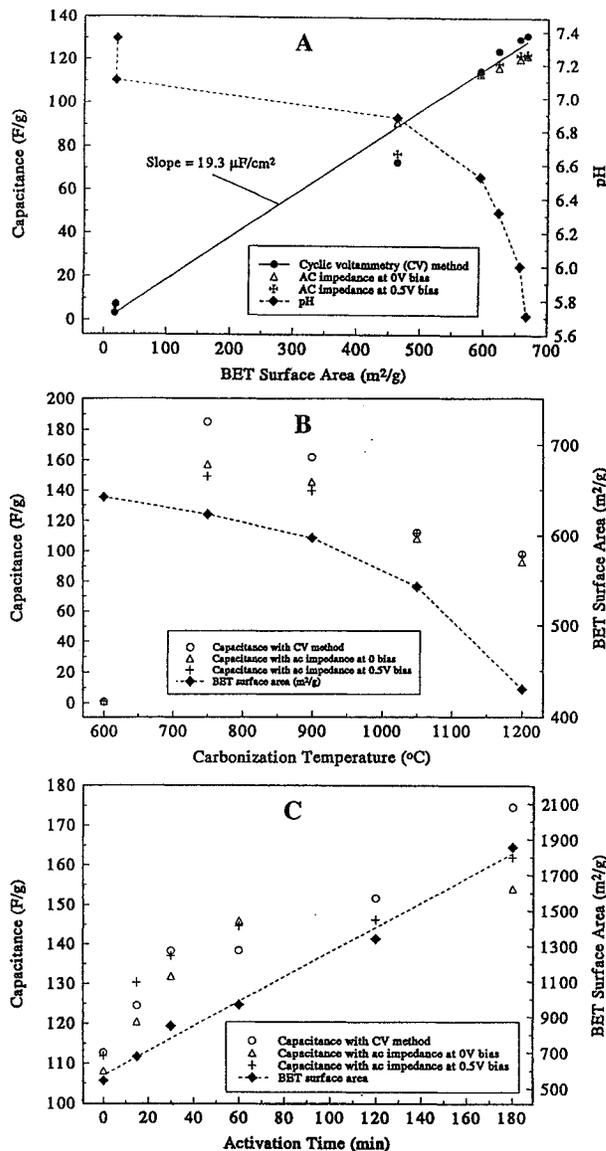
Figure 1. Correlation of double layer capacitance with the surface area of carbon xerogels A) carbonized in nitrogen at 1050 °C: effect of initial solution pH, B) synthesized with an initial solution pH of 6: effect of carbonization temperature, and C) synthesized with an initial solution pH of 6 and carbonized in nitrogen at 1050 °C with 5 % CO_2 added for activation: effect of CO_2 activation time.