

Preparation and performance of cobalt-doped carbon aerogel for supercapacitor

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Abstract—Carbon aerogels were prepared by polycondensation of resorcinol with formaldehyde in ambient conditions. The effect of resorcinol-to-catalyst ratio (R/C ratio) on volume shrinkage, BET surface area, and electrochemical property was investigated by changing R/C ratio from 50 to 2000. Carbon aerogel prepared at R/C ratio of 500 showed less than 2% of volume shrinkage and the highest BET surface area (706 m²/g). Specific capacitance of carbon aerogel prepared at R/C ratio of 500 was found to be 81 F/g in 1 M H₂SO₄ electrolyte. Cobalt-doped carbon aerogels were then prepared by an impregnation method with a variation of cobalt content, and their performance was investigated. Among the samples prepared, 7 wt% cobalt-doped carbon aerogel showed the highest capacitance (100 F/g) and the most stable cyclability. The enhanced capacitance of cobalt-doped carbon aerogel was attributed to the faradaic redox reactions of cobalt oxide.

Key words: Carbon, Aerogel, Doping, Electrochemical Properties

INTRODUCTION

Carbon aerogels have been widely employed as electrode materials of electrochemical capacitors because of their versatile properties, such as high surface area, fine pore size, outstanding electrical conductivity, and high porosity [1-9]. Resorcinol-formaldehyde (RF) method has been generally used for the preparation of carbon aerogels, because physical properties of carbon aerogels can be easily controlled by changing preparation conditions, such as concentration, pH, reaction time, and temperature [10]. In the conventional RF method, however, severe conditions (high pressure up to 1,000 psi) are required to prepare authentic aerogel, which are disadvantageous in term of cost and safety. To overcome these disadvantages and to minimize volume shrinkage, alternative drying processes for producing carbon aerogel at ambient pressure have been proposed [11-17].

Electrochemical capacitors can be classified into two types according to the mechanism of energy storage: electrical double-layer capacitors (EDLCs) and pseudocapacitors. Energy is charged on the surface of electrode by an electrostatic attraction between ions in EDLCs, while energy is stored by faradaic reactions on the electroactive species such as Ru, Mg, W, Mn, and Co in pseudocapacitors [18-22]. These metals in pseudocapacitors formed metal oxides on the electrode surface, accelerating the faradaic reactions. Many researches have been performed to incorporate these metals into porous carbon, with an aim of improving electrochemical properties of carbon [3,4].

In this work, cobalt-doped carbon aerogels were prepared by an

impregnation method to combine pseudocapacitive property of cobalt oxide with excellent electrochemical performance of carbon aerogels. Carbon aerogels were prepared by an RF method using sodium carbonate as a catalyst and by a subsequent acetone exchange process in ambient conditions for use as an electrode of supercapacitor. Cobalt was then impregnated onto carbon aerogels with a variation of cobalt content (1, 3, 5, 7, 10, and 15 wt%). The effect of resorcinol/catalyst ratio (R/C ratio) on volume shrinkage, BET surface area, and electrochemical property of carbon aerogels was investigated to find optimum preparation conditions. Based on this result, the effect of cobalt doping on the electrochemical properties for supercapacitor was investigated.

EXPERIMENTAL

1. Preparation of Carbon Aerogel Electrode

Fig. 1 shows the overall preparation route for carbon aerogel in ambient conditions. In short, sodium carbonate (a base catalyst) was mixed with resorcinol and deionized water to accelerate dehydrogenation of resorcinol. After the solution was stirred for a few minutes, formaldehyde was added into the solution to form a sol. Molar ratio of resorcinol (C₆H₆O₂, Sigma-Aldrich) with respect to formaldehyde (H₂CO, Sigma-Aldrich) was fixed at 1 : 2 (R/F=1/2), and weight percentage of reactants in solution was about 40%. R/C (resorcinol/catalyst) ratio was varied from 50 to 2000. After the resulting sol was stirred, it was cured in a vial to form cylindrical shape at 80 °C for two days. Solvent exchange was performed with acetone at 50 °C for one day. Residual solvent was replaced with fresh acetone every 3 h to remove water thoroughly from the pore of RF wet gel. Ambient drying was then done at room temperature and 50 °C for one day. Before and after drying, dimensions of each cylin-

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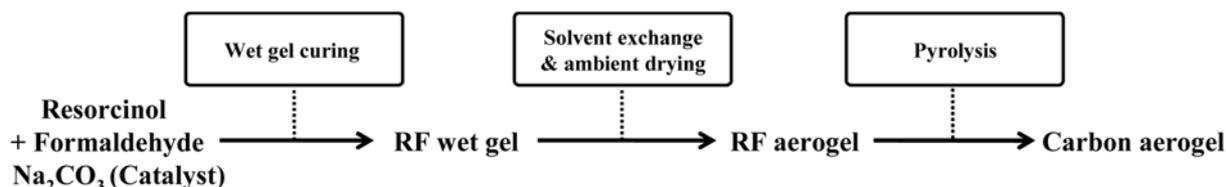


Fig. 1. Overall preparation route for carbon aerogel.

der were measured to evaluate volume and density changes. Carbon aerogel was prepared by pyrolysis of RF aerogel at 800 °C for 2 h under nitrogen flow. The prepared carbon aerogel was cast into an electrode using ketjen black and polytetrafluoroethylene (PTFE) as a conductive additive and a binder, respectively. A mixture of carbon aerogel, conductive additive, and binder with weight ratio of 75 : 15 : 10 was dispersed in 2-propanol. The resultant was mixed with mortar and pestle, and then it was rolled to be 8-10 μm thickness. The electrode material was cut into 1 cm×1 cm and pressed onto stainless steel mesh, which was used as a working electrode. The weight of the electrode was ca. 5 mg.

2. Preparation of Cobalt-doped Carbon Aerogel Electrode

After cylindrical carbon aerogel was ground into powder, cobalt was impregnated onto carbon aerogel by an incipient wetness impregnation method using aqueous solution of cobalt (II) nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich) as a cobalt precursor. Cobalt content was fixed at 1, 3, 5, 7, 10, and 15 wt%. A known amount of cobalt nitrate was dissolved in deionized water. An appropriate amount of solution was then added dropwise onto the carbon aerogel powder for impregnation. The resulting mixture was dried at 80 °C for 12 h, and finally, it was calcined at 200 °C for 4 h to obtain a cobalt-doped carbon aerogel. The prepared cobalt-doped carbon aerogel was fabricated as an electrode according to the same procedures described above.

3. Characterization and Measurement of Electrochemical Property

To investigate the degree of solvent exchange, UV-visible spectra of residual water/acetone mixture in solution were obtained at room temperature with a Lambda-35 spectrometer (Perkin-Elmer). Surface area and average pore diameter were measured with an ASAP 2010 instrument (Micromeritics). Crystallinity of cobalt-doped carbon aerogel was examined by XRD measurement (Rigaku, D/MAX-2000). Dispersion of cobalt oxide particles on the surface of carbon aerogel was investigated by high resolution-transmission electron microscopy (HR-TEM) (Jeol, JEM-3010). Electrochemical property of carbon aerogel electrodes was measured with a conventional three-electrode cell system in 1 M H_2SO_4 electrolyte. A platinum plate and Ag/AgCl were used as a counter electrode and a reference electrode, respectively. Cyclic voltammetry measurements were conducted to evaluate the electrochemical performance of carbon aerogel and cobalt-doped carbon aerogel electrodes. Galvanostatic charge/discharge measurements were carried out at constant current within the voltage range of 0-0.7 V.

RESULTS AND DISCUSSION

1. Physical Properties of Carbon Aerogels

Solvent exchange was performed with acetone every 3 h to replace

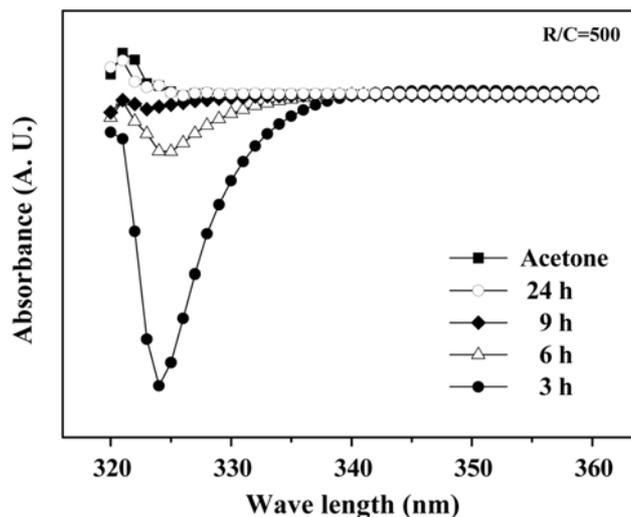


Fig. 2. UV-visible spectra of residual water/acetone mixture in RF wet gel ($R/C=500$) obtained after solvent exchange.

residual water with fresh acetone. UV-visible spectra of residual water/acetone mixture in RF wet gel ($R/C=500$) obtained after solvent exchange are shown in Fig. 2. Pure acetone showed no characteristic absorbance peak at around 324 nm. However, a strong peak at around 324 nm was observed after 3 h-exchange, indicating that water was partly exchanged with acetone. The peak intensity of the mixture decreased with increasing exchange time, and it became almost identical to that of pure acetone after one day-exchange. This indicates that one day-exchange is sufficient for complete exchange of water with acetone.

Physical properties of carbon aerogel prepared at different R/C ratio are listed in Table 1. It is noticeable that shrinkage parameters (volume shrinkage and density) rapidly decreased at low R/C ratio ($R/C < 500$), and became almost constant at high R/C ratio ($R/C > 500$). Such a behavior can be explained by the particle size change of polymer with regard to R/C ratio. When R/C ratio is low ($R/C < 500$), small polymer particles interconnected with large necks are produced. When R/C ratio is high ($R/C > 500$), however, large polymer particles interconnected with narrow necks are produced [23]. Thus, particle size difference with respect to R/C ratio affects the shrinkage behavior. Judging from the fact that low shrinkage is favorable for promising physical properties of carbon aerogel [24,25], it is concluded that R/C ratio of 500 is appropriate for ambient drying in the preparation of carbon aerogel.

It is noteworthy that BET surface area showed a volcano-shaped trend with respect to R/C ratio. Among the samples, the carbon aerogel prepared at R/C ratio of 500 showed the highest BET surface area (706 m^2/g). BET surface area is considered to consist of mi-

Table 1. Physical properties of carbon aerogels

R/C Ratio	Volume shrinkage (%)	Density (g/cm ³)	BET surface area (m ² /g)	Micropore surface area (m ² /g)	Mesopore surface area (m ² /g)	Average pore diameter (nm)
50	56.7	0.98	161	130	31	1.1
100	52.5	0.86	407	285	122	2.2
250	33.5	0.62	683	168	515	4.1
500	1.2	0.42	706	344	360	10.9
1000	0.2	0.45	689	409	280	12.5
1500	2.0	0.42	624	406	218	14.8
2000	6.6	0.48	635	431	204	15.7

cropore and mesopore surface area, and both surface areas are also listed in Table 1. Micropore surface area roughly increased with increasing R/C ratio, while mesopore surface area showed a volcano-shaped trend with respect to R/C ratio. This result can be explained by the variation of polymer particle size with respect to R/C ratio. The size of RF polymer particle increases with increasing R/C ratio through condensation reaction. At high R/C ratio (above 1000), however, RF clusters tend to aggregate, resulting in the formation of larger clusters [26,27]. It has also been reported that mesoporous structure prevents the RF aerogel matrix from collapse during ambient drying by reducing capillary pressure [25]. Therefore, the low shrinkage of carbon aerogel prepared at R/C ratio of 500 can be explained by the existence of well-developed mesoporous structure.

2. Electrochemical Properties of Carbon Aerogel Electrodes

To examine the electrochemical properties of carbon aerogel electrodes, cyclic voltammetry measurements were performed. Specific capacitances of carbon aerogel electrodes prepared at different R/C ratio were measured at a scan rate of 10 mV/sec in an aqueous solution of 1 M H₂SO₄. Specific capacitances and BET surface areas of carbon aerogels are plotted with respect to R/C ratio in Fig. 3. Interestingly, specific capacitance was well correlated with BET surface area. The capacitance of carbon aerogel is known to strongly depend on surface area [28]. The maximum specific capacitance (81 F/g) was obtained with the carbon aerogel prepared at R/C ratio of 500, which showed the highest BET surface area. One again, this result supports that the optimum R/C ratio for the preparation of carbon aerogel is 500. In this work, therefore, carbon aerogel

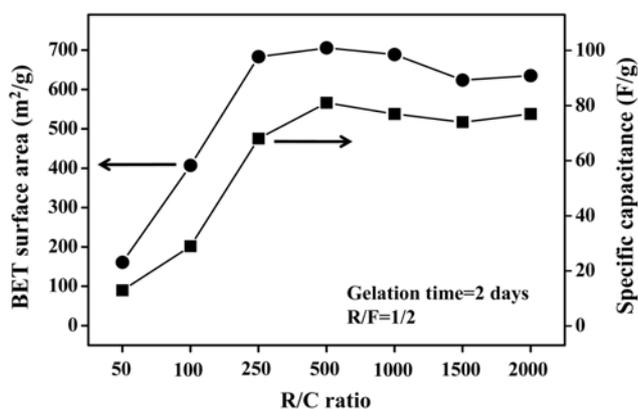


Fig. 3. Variation of BET surface area and specific capacitance of carbon aerogel with respect to R/C ratio.

prepared at R/C ratio of 500 was used for cobalt doping.

3. Physical Properties of Cobalt-doped Carbon Aerogel

Successful impregnation of cobalt oxide on carbon aerogel was confirmed by XRD measurement, as shown in Fig. 4. Carbon aerogel shows two broad peaks at 23.5° and 43.8°, which are attributed to (0 0 2) and (1 0 1) reflections of graphite carbon, respectively. The formation of cobalt oxide was confirmed by observing several peaks indicative of Co₃O₄ [22]. After calcination of cobalt-doped carbon aerogel, cobalt precursor was converted into cobalt oxides on the surface of carbon aerogel. Considering that metal oxides are closely related to the faradaic redox reactions, it is expected that cobalt-doped carbon aerogel would show an enhanced capacitance than carbon aerogel [3,4].

HR-TEM image of cobalt-doped carbon aerogel is shown in Fig. 5. In the TEM image, carbon particles are observed to form an interconnecting network structure with non-uniform textural porosity. TEM image also shows that cobalt oxide particles were finely and uniformly dispersed on the surface of carbon aerogel.

4. Electrochemical Properties of Cobalt-doped Carbon Aerogel Electrodes

Fig. 6 shows the cyclic voltammograms of cobalt-doped carbon

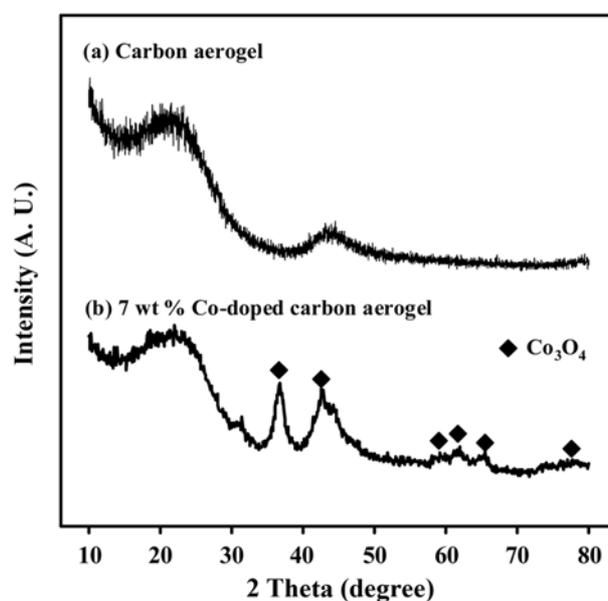


Fig. 4. XRD patterns of (a) carbon aerogel and (b) 7 wt% cobalt-doped carbon aerogel.

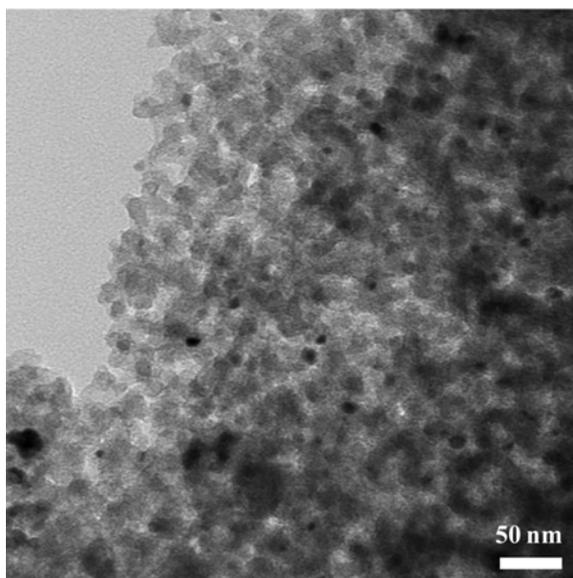


Fig. 5. HR-TEM image of 7 wt% cobalt-doped carbon aerogel.

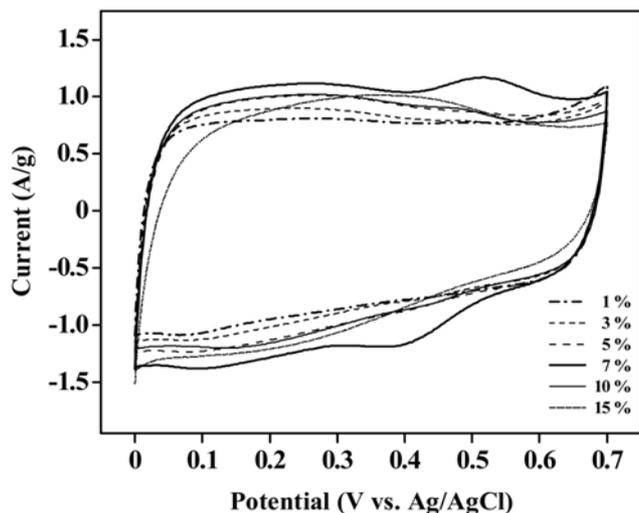


Fig. 6. Cyclic voltammograms of cobalt-doped carbon aerogels with different cobalt content (scan rate=10 mV/sec).

Table 2. Specific capacitance of cobalt-doped carbon aerogel electrodes with different cobalt content in an aqueous solution of 1 M H_2SO_4 (scan rate=10 mV/sec)

Cobalt content (wt%)	1	3	5	7	10	15
Specific capacitance (F/g)	77	80	87	100	86	72

aerogels (scan rate=10 mV/sec) with different cobalt content (1, 3, 5, 7, 10, and 15 wt%), and the calculated specific capacitances are listed in Table 2. The specific capacitance shows a volcano-shaped trend with respect to cobalt content. Among the samples tested, 7 wt% cobalt-doped carbon aerogel exhibited the highest capacitance (100 F/g). At low cobalt content below 7 wt%, specific capacitance increased with increasing cobalt content. At high cobalt content above 7 wt%, however, carbon surface is probably covered with excess amount of cobalt, resulting in the decrease of specific capacitance.

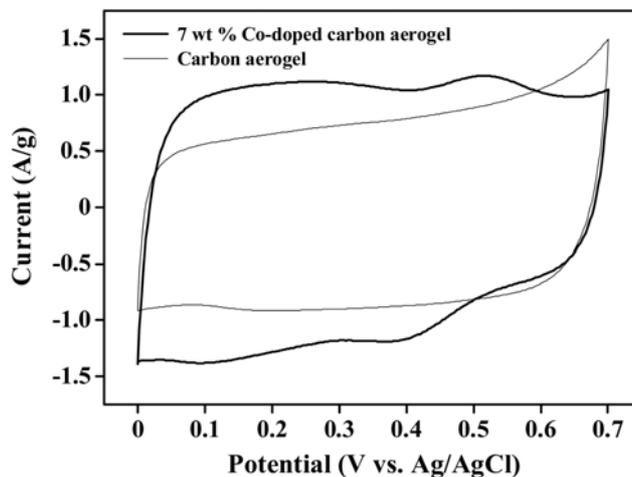


Fig. 7. Cyclic voltammograms of carbon aerogel (R/C=500) and 7 wt% cobalt-doped carbon aerogel (scan rate=10 mV/sec).

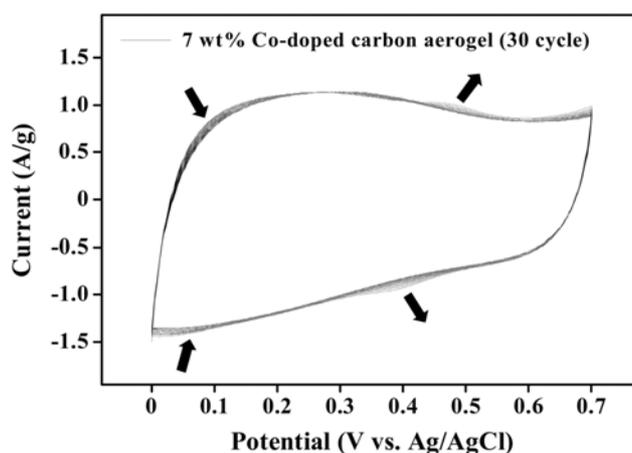


Fig. 8. Cyclic voltammograms of 7 wt% cobalt-doped carbon aerogel electrode with cycling number (scan rate=10 mV/sec).

Fig. 7 compares the cyclic voltammetric curves between carbon aerogel (R/C=500) and 7 wt% cobalt-doped carbon aerogel within the voltage range of 0-0.7 V at a scan rate of 10 mV/sec. 7 wt% cobalt-doped carbon aerogel shows much higher specific capacitance than carbon aerogel. Carbon aerogel (thin line) shows a quasi-rectangular, symmetric, and reversible behavior, indicating the excellent electrochemical properties. It is noticeable that two anodic peaks and two cathodic peaks are observed for 7 wt% cobalt-doped carbon aerogel (thick line), which might be attributed to the redox reactions of cobalt oxide. Co_3O_4 is first oxidized to $CoOOH$, and then $CoOOH$ is oxidized to CoO_2 . $CoOOH$ and CoO_2 are reported to be reversibly reduced to Co_3O_4 and $CoOOH$, respectively [29]. As shown in Fig. 6 and Table 2, impregnation of certain amount of cobalt significantly improved the capacitance of carbon aerogel, probably due to the faradaic reactions of cobalt oxide.

Cyclic voltammograms of 7 wt% cobalt-doped carbon aerogel electrodes with cycle number are plotted in Fig. 8. Symmetric peaks originating from the faradaic redox reactions are observed. Furthermore, 7 wt% cobalt-doped carbon aerogel exhibits relatively stable cyclability, although these peaks degrade slightly with increas-

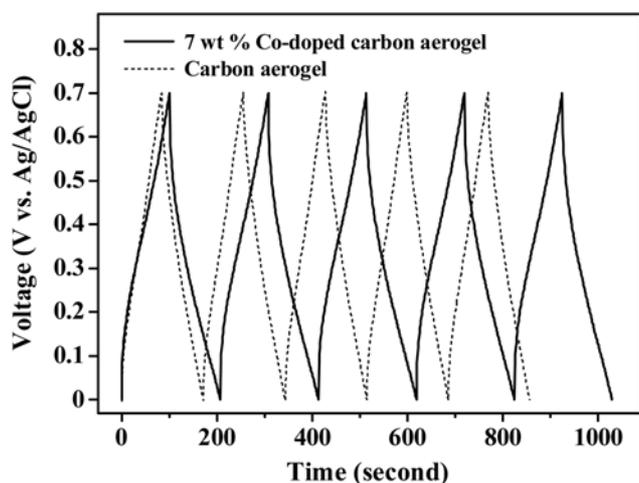


Fig. 9. Charge/discharge profiles of carbon aerogel ($R/C=500$) (dotted line) and 7 wt% cobalt-doped carbon aerogel (solid line) at constant current (0.7 A/g).

Table 3. Specific capacitance of carbon aerogel electrode ($R/C=500$) and 7 wt% cobalt-doped carbon aerogel electrode calculated from charge/discharge measurements

Number of cycle	Specific capacitance of carbon aerogel (F/g)	Specific capacitance of 7 wt% Co-doped carbon aerogel (F/g)
1	87	107
2	87	105
3	89	105
4	88	106
5	87	105

ing cycle number.

Fig. 9 shows the charge/discharge behaviors of carbon aerogel ($R/C=500$) and 7 wt% cobalt-doped carbon aerogel at constant current (0.7 A/g). The calculated specific capacitances are summarized in Table 3. Cobalt-doped carbon aerogel exhibits a higher specific capacitance than carbon aerogel (approximately 105 F/g vs. 87 F/g), although both electrodes show stable cycling behaviors (Table 3). The enhanced electrochemical property of cobalt-doped carbon aerogel was attributed to the faradaic redox reactions of cobalt oxide.

CONCLUSIONS

Carbon aerogels were prepared under ambient drying process with a variation of R/C ratio. Shrinkage behavior of carbon aerogels strongly depended on R/C ratio. BET surface area was also dependent on R/C ratio. From the results of volume shrinkage and BET surface area, the optimum R/C ratio was found to be 500. Cobalt-doped carbon aerogels were then prepared by an impregnation method with a variation of cobalt content, and their performance for supercapacitor electrode was investigated. Cobalt-doped carbon aerogel was prepared by impregnating cobalt nitrate onto carbon aerogel ($R/C=500$). Among the samples prepared, 7 wt% cobalt-doped carbon aerogel showed the highest capacitance and excellent cyclability. Compared to carbon aerogel, 7 wt% cobalt-doped carbon aerogel

exhibited a higher specific capacitance. The enhanced electrochemical property of cobalt-doped carbon aerogel was due to the faradaic redox reactions of cobalt oxide.

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REFERENCES

1. A. Burke, *J. Power Sources*, **91**, 37 (2000).
2. C. Moreno-Castilla and F. J. Maldonado-Hódar, *Carbon*, **43**, 455 (2005).
3. A. G. Pandolfo and A. F. Hollenkamp, *J. Power Sources*, **157**, 11 (2006).
4. M. Jayalaxmi and K. Balasubramanian, *Int. J. Electrochem. Sci.*, **3**, 1196 (2008).
5. Y. Zhang, H. Feng, X. Wu, L. Wang, A. Zhang, T. Xia, H. Dong, X. Li and L. Zhang, *Int. J. Hydrogen Energy*, **34**, 4889 (2009).
6. R. W. Pekala, *J. Mater. Sci.*, **24**, 3221 (1989).
7. H.-J. Kim, J.-H. Kim, W.-I. Kim and D. J. Suh, *Korean J. Chem. Eng.*, **22**, 740 (2005).
8. S. T. Mayer, R. W. Pekala and J. L. Kaschmitter, *J. Electrochem. Soc.*, **140**, 446 (1993).
9. J. Fricke, X. Lu, R. Caps, C. T. Alviso and R. W. Pekala, *J. Non-Cryst. Solids*, **8**, 226 (1995).
10. R. W. Pekala, US Patent, 4,873,218 (1989).
11. H. Probstle, M. Wiener and J. Fricke, *J. Porous Mat.*, **10**, 213 (2003).
12. E. Frackowiak and F. Béguin, *Carbon*, **39**, 937 (2001).
13. D. Wu, R. Fu, S. Zhang, M. S. Dresselhaus and G. Dresselhaus, *Carbon*, **42**, 22033 (2004).
14. S. J. Kim, S. W. Hwang and S. H. Hyun, *J. Mater. Sci.*, **40**, 725 (2005).
15. R. Saliger, V. Bock, R. Petricevic, T. Tillotson, S. Geis and J. Fricke, *J. Non-Cryst. Solids*, **221**, 144 (1997).
16. E. J. Zanto, S. A. Al-Muhtaseb and J. A. Ritter, *Ind. Eng. Chem. Res.*, **41**, 3151 (2002).
17. Y. Z. Wei, B. Fang, S. Iwasa and M. Kumagai, *J. Power Sources*, **141**, 386 (2005).
18. J. P. Zheng, *Electrochem Solid State Lett.*, **2**, 359 (1999).
19. C.-C. Hu, Y.-H. Huang and K.-H. Chang, *J. Power Sources*, **108**, 117 (2002).
20. S. Yoon, C. Lee, S. M. Oh, Y.-K. Park and W. C. Choi, *J. Non-Cryst. Solids*, **355**, 252 (2009).
21. T.-Y. Wei, C.-H. Chen, K.-H. Chang, S.-Y. Lu and C.-C. Hu, *Chem. Mater.*, **21**, 3228 (2009).
22. I.-H. Kim and K.-B. Kim, *J. Electrochem. Soc.*, **153**, 383 (2006).
23. S. A. Al-Muhtaseb and J. A. Ritter, *Adv. Mater.*, **15**, 101 (2003).
24. S.-W. Hwang and S.-H. Hyun, *J. Non-Cryst. Solids*, **347**, 238 (2004).
25. J. Li, X. Wang, Q. Huang, S. Gamboa and P. J. Sebastian, *J. Power Sources*, **158**, 784 (2006).
26. C. Lin and J. A. Ritter, *Carbon*, **35**, 1271 (1997).
27. L. Zhang, H. Liu, M. Wang and L. Chen, *Carbon*, **45**, 1439 (2007).
28. G. Reichenauer, J. Fricke and W. Li, *Carbon*, **40**, 2955 (2002).
29. X. M. Liu, Y. H. Zhang, X. G. Zhang and S. H. Fu, *Electrochim. Acta*, **49**, 3137 (2004).