Fabrication and Structure of Carbon Aerogel Spheres Prepared by Inverse Suspension/Emulsion Polymerization and Ambient Pressure Drying

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ABSTRACT: Carbon aerogel (CA) spheres were fabricated by inverse suspension polymerization of an emulsified resorcinol–formaldehyde aqueous solution with a basic surfactant used as catalyst, and then drying by gradually heating the resultant sol–gel spheres at ambient pressure. The fabrication conditions, nanostructures of the resultant CA spheres, and their electrochemical properties were investigated. By controlling the time at which stirring started, the stirring speed, and the recipe of the emulsion solution, the diameter of the CA spheres can be controlled from 70 to 1000 μm. The internal carbon nanoparticles of the spheres are of a size ranging from 20 to 40 nm, and are interconnected into a three-dimensional network. The highest surface area and mesopore volume of the spherical CAs thus prepared reach 626 m^2/g and 0.69 cm^3/g, respectively. These CAs can be used as an electrode in supercapacitors, and the specific capacitance is as high as 197 F/g. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2849–2855, 2007

Key words: carbon aerogel sphere; inverse suspension polymerization; emulsion polymerization; gelation; structure

INTRODUCTION

The pending shortage of fossil fuels and the deleterious emissions resulting from their use have increased interest in the development of high performance power sources for vehicles. Fuel cells and electrochemical double-layer capacitors (EDLC), which can be equipped for hybrid vehicles and other equipments, are considered to be novel energy storage units. Carbon aerogels (CAs), due to their nanocarbon network, high surface area, abundant mesopores, and electrochemical properties, are promising for use as electrode materials for supercapacitors, catalyst carriers for fuel cells, and so on. So far, most carbon aerogels reported are monolithic (bulk) materials, which are generally synthesized with the CO_2 supercritical drying method developed by Pekala and

Kong.[1] There are some disadvantages in monolithic aerogel fabrication. One is that the polymerization heat during gelation is easily accumulated so that the reaction temperature is hardly controlled. Another is that a large bulk aerogel product is hard to extract directly from the reaction container, and as a result, most of those methods reported for monolithic aerogel fabrications are generally unsuitable for large scale production. However, there are several advantages for CA spheres fabrication with suspension polymerization. For example, the accumulation of polymerization heat during gelation could be decreased because the suspension media transfers the heat very well. The microbeads produced with suspension polymerization are easily poured out from the reaction container. As a result, the fabrication of spherical carbon aerogels is more suitable for large scale production than that of monolithic products. On the other hand, it has been recognized that the formation of CAs in small spheres (microbeads) would greatly expand the use of these materials, as well as reduce the process time and equipment costs in applications where they would be appropriate.[2] Recently, Mayer et al.[2] invented a fabrication method for CA microspheres. Their method involved stirring the aqueous organic phase in mineral oil at elevated temperature, curing formed gel spheres, drying the thus cured gel

spheres with supercritical carbon dioxide, or at low pressure or evaporative conditions. Horikawa et al.[3] prepared RF spherical CA particles by an emulsion polymerization and carbon dioxide supercritical drying method. We have also developed an inverse suspension polymerization method for the fabrication of CA spheres.[4] However, in the process of this fabrication method,[4] the aerogels were dried under alcohol supercritical conditions, which will need complicated equipment, thus causing a high cost of the product and this method may increase environmental pollution by the emission of alcohol vapor during drying process.

Ambient pressure drying, due to its simple equipment, easy operation, and low cost, has been reported instead of the supercritical drying process in the fabrication of monolithic CAs.[5,6] However, there are few reports, if any, in the literature about research on the fabrication of spherical CAs with inverse phase suspension gelation and then drying at ambient pressure conditions. Although Mayer et al.[2] mentioned the fabrication of spherical CAs with ambient pressure drying, no details about the synthesis processes and conditions were reported. In this article, based on our previous work on the fabrication of CA spheres with inverse suspension polymerization and the fabrication of monolithic CAs with ambient pressure drying, a modified method has been developed for the fabrication of spherical CAs with inverse suspension polymerization of an emulsified resorcinol–formaldehyde (RF) aqueous solution (inverse suspension/emulsion polymerization method) and then drying the resultant sol–gel spheres under ambient pressure conditions. The preparation conditions, such as the mole ratio of resorcinol to catalyst (R/C), the monomer concentration, the mole ratio of resorcinol to formaldehyde (R/F), the gelation temperature, etc., were explored in this article. The nanostructures of the products prepared were characterized by scanning electron microscope (SEM) and surface area analysis. Finally, the carbon aerogel spheres prepared were used as the electrodes in supercapacitors, and the electrochemical performance was also measured.

EXPERIMENTAL

Preparation of RF organic and carbon aerogel spheres

Appropriate amounts of resorcinol (R) (Sumitomo Chemical, Japan), formaldehyde (F) (A.R., Guangzhou Chemical Reagent Factory, China), surfactant [cetyltrimethyl ammonium bromide (CTAB)] (A.R., Shanghai Yuanju Biologic Technology, China), and water were mixed and stirred into an emulsion solution at room temperature. The emulsion solution was transferred into a 500-mL flask, which was partially

filled with peanut oil (Qingdao Jiali Vegetable Tallow, China). The volume ratio of the emulsion solution and the peanut oil was 1 : 3. After the system was heated to a predetermined temperature and kept at temperature for a certain time, the immiscible phases of RF solution and oil were then stirred with a mechanical stirrer at 120 revolutions per minute to form an inverse suspension. When the suspension drops of RF solution were then transferred on to the nonsticky sol–gel spheres, the suspension slurry was next transferred into a bottle that was then sealed and aged at 80°C for 7 days. Next, the resultant sol–gel spheres were separated from the peanut oil by filtration and washed with 3% liquid detergent to remove the residual oil. Then, the sol–gel spheres were dried at ambient pressure sequentially for 1 day in the air at room temperature, for 5 h under an infrared lamp at about 80°C, and then for 5 h in an oven at 110°C. Finally, the resultant RF aerogel spheres were carbonized at 900°C for 3 h under N_2 atmosphere. The carbonization yield was calculated by dividing the weight of the CA spheres by the weight of as-prepared aerogel spheres.

Detection of solution pH and viscosity

The emulsion solution pH before stirring was detected by a model pHS-29A pH meter. The viscosity of the emulsion solution was detected by a model NDJ-1 revolving viscosity meter as follows: an appropriate volume of emulsion solution mixed with R, F, CTAB, and water was transferred into a big tube and covered by some peanut oil, which was then heated in a water bath. The viscosity was detected by cutting in the rotor of the viscosity meter to the emulsion solution and revolving it.

Characterization of the organic and related carbon aerogel spheres

The particle diameter distribution of the spherical samples was detected using a model Mastersizer 2000 Laser Particle Size Analyzer. The morphology images of the samples were recorded by scanning electron microscopy (SEM), using a model JSM-6330F instrument. The nitrogen adsorption and desorption isotherms of the samples were taken using an ASAP 2010 Surface and Porosimetry System. The BET surface area (S_{BET}), the micropore volume (V_{mic}), the micropore surface area (S_{mic}), the mesopore volume (V_{BJH}), the mesopore surface area (S_{BJH}), and the average mesopore diameter (APD_{BJH}) of the samples were analyzed by BET (Brunauer–Emmett–Teller) theory, t-plot theory, and BJH (Barrett–Johner–Halendar) theory, as appropriate.

The density of the CA spheres was detected by pycnometric determination. Peanut oil was used as the determination media.
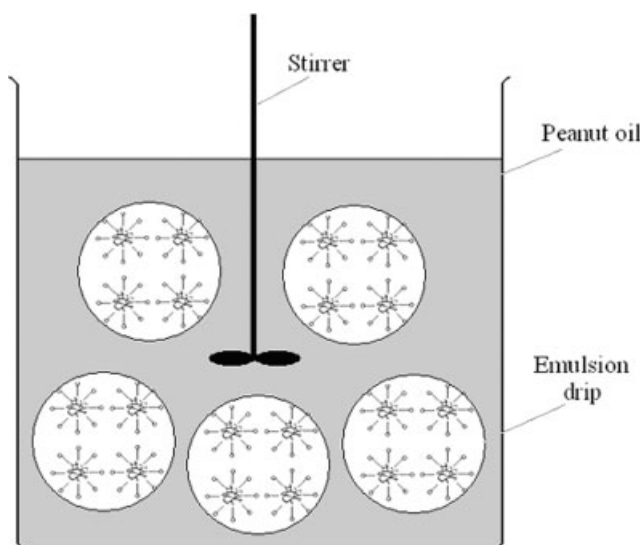
Figure 1 Scheme of inverse suspension/emulsion polymerization.

Figure 3 Diameter distribution of the CA spheres prepared with the indicated conditions.

Electrochemical measurement

The CA samples (ground into powders with diameters less than 125 μm) and polytetrafluorethylene (PTFE) (as a binder) were mixed into a paste in the ratio of 93:7. The paste was coated on a 1×1 cm^2 plain nickel foam (current collector). Then, the electrode was pressed under about 10 MPa. The thickness of the CA layer on the electrode was about 150 μm. Electrochemical measurements [cyclic voltammetry (CV), galvanostatic charge-discharge, and AC impedance] were carried out at room temperature using a 30% KOH aqueous solution as an electrolyte, and using an IM6e Electrochemical Workstation. The CA electrode was used as the working electrode, platinum foil as the counter electrode, and Ag/AgCl as the reference electrode. In cyclic voltammetry measurements, the potential scan rates were
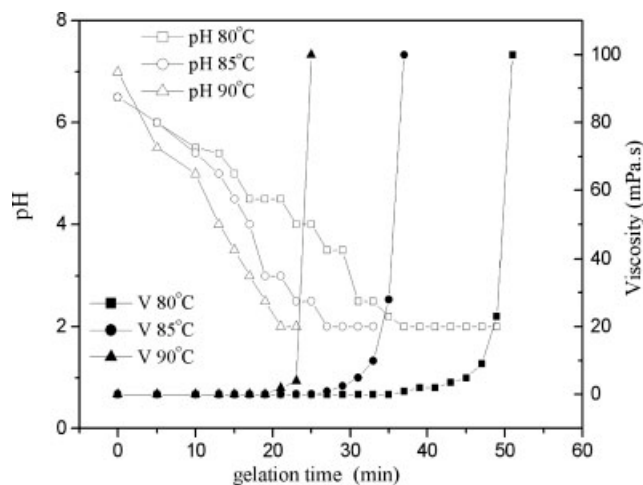
set as 0.5–100 mV/s within a potential range of −0.4 to 0.4 V. In galvanostatic charge-discharge tests, the charge current was set at 2 mA, while the voltage was set at 1 V. In AC impedance measurements, the range of frequency was set at 10 KHz to 20 MHz.

RESULTS AND DISCUSSION

The control of the gelation process

According to our design, carbon aerogel spheres should be synthesized following the reaction system shown in Figure 1. In this reaction system, the RF monomers were inversely suspended in peanut oil in the shape of individual round aqueous solution drops. Inside the microdrops, it was an emulsion system mixed with the RF monomer, surfactant, catalyst, and water. The gelation of the RF was carried out in the emulsion drops to form sol–gel spheres.

Figure 2 Changes of emulsion solution pH and viscosity during the gelation process.

TABLE I
Effect of Different Catalysts on the Shrinkage of Aerogels Under Ambient Pressure Drying Conditions

Catalyst	Gelation time (s)	Volume shrinkage of aerogels (%)	Bulk density of aerogels (g/cm^3)	Theoretical bulk density of aerogels (g/cm^3)
DBSAS	1236	43.6	0.832	0.456
SDS	1460	43.3	0.967	0.456
TAB	1285	44.2	0.912	0.456
CTAB	1180	29.7	0.622	0.456

Predetermined R/C = 100, R/F = 1/2, RF content = 40%, GT = 85°C. Note 1: The drying shrinkage and density of aerogels were detected by simulated experiments on monolithic aerogel samples. Note 2: DBSAS, dodecyl benzene sulfonic acid sodium salt; SDS, sodium dodecyl sulfate; TAB, tetrabutyl ammonium bromide; CTAB, cetyltrimethyl ammonium bromide.

TABLE II
Apparent Densities and Bulk Densities of the Aerogel Spheres Prepared Under Different Conditions

No.	R/F ratio	R/C ratio	RF content (%)	Gelation temperature (°C)	Apparent density (g/mL)	Bulk density (g/cm³)
181	0.5	100	20	85	0.59	0.93
182	0.5	100	30	85	0.48	0.77
214	0.5	100	40	85	0.42	0.79
142	0.5	100	50	85	0.51	0.66
212	0.5	50	40	85	0.43	1.04
197	0.5	150	40	85	0.38	0.96
192	0.5	200	40	85	0.34	0.79
184	0.5	250	40	85	0.42	0.67
196	0.5	100	40	80	0.37	0.88
213	0.5	100	40	90	0.37	0.89
195	0.5	100	40	95	0.47	0.82
183	0.33	100	40	85	0.47	0.82
187	0.67	100	40	85	0.48	0.92
153	0.75	100	40	85	0.47	0.97

Figure 5 SEM image of the internal surface of the CA spheres prepared.

Obviously, the suspension process and conditions affect the shape and spherical size of the aerogel microspheres, while the emulsifying conditions control the internal nanostructures of the aerogel spheres.

It was found that the time at which stirring started is one of the most important factors for controlling the shape of products. In the beginning of our exploration, an inverse suspension process similar to that reported in Refs. 2 and 3 was used. However, if the reaction solution was stirred from the beginning, the inverse suspension system was very unstable or formed a whole oil/water emulsion, so that the oil was usually hard to be separated out from the products or some time obtained a big bulk of gel, but not microspheres. If the reaction solution was stirred too late, the separate RF emulsion phase was polycondensed into a monolithic aerogel. To determine the optimum time to start the stirring, the changes of the
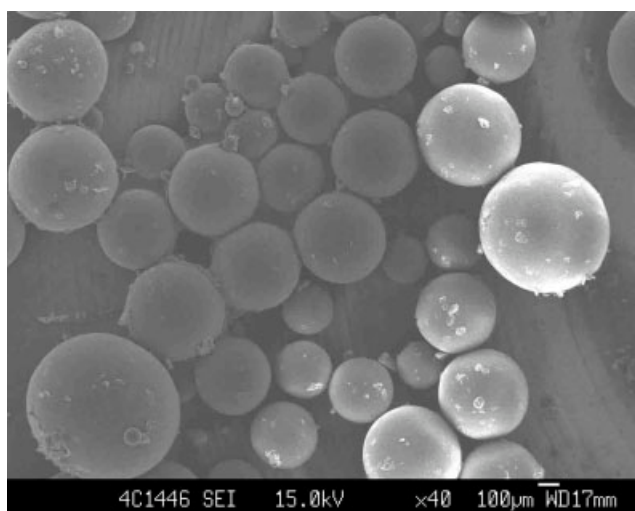
emulsion solution pH and the viscosity during gelation were investigated and the experimental results are shown in Figure 2. It can be seen that acidity of the emulsion solution gradually decreased from about a pH of 6 to about a pH of 2 and then it was kept constant, while, the viscosity of the solution was unchanged during the first stage of the polymerization, but the viscosity quickly increased after a certain time. The decrease of the solution pH showed the degree of polycondensation. The point of greatly increasing solution viscosity showed the gelation point of polycondensation. It can be seen that there is a time gap between the formation of stable solution pH to a greatly increasing viscosity. Experimental results proved that fine round sol–gel microspheres can be obtained when the stirring starts during this time gap. That is, the suitable time at which stirring
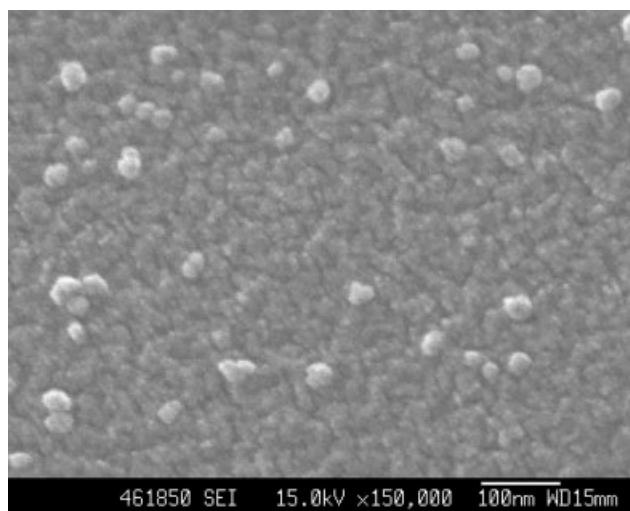

Figure 4 Morphology of typical CA spheres that were prepared.

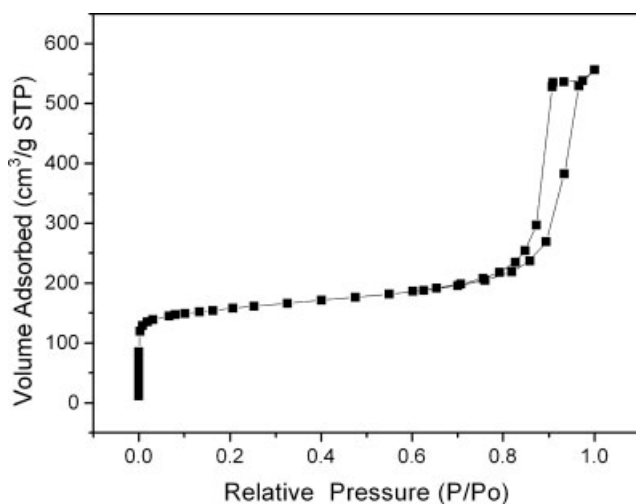**Figure 6** SEM image of the external surface of the CA spheres prepared.

Figure 7 Adsorption–desorption isotherm of CA spheres prepared (Predetermined R/F = 1/2, R/C = 200, gelation temperature 85°C).

started is before the solution viscosity obviously increases and after the solution pH goes down to a balanced low value. The time to start stirring can be determined by detecting the change of solution pH during fabrication. The lower the gelation temperature, the longer is the time gap. A low gelation temperature is advantageous for choosing the starting time of stirring. Therefore, 80–85°C is good choice for the gelation temperature by our method.

The stirring speed greatly affected the spherical size of the sol–gel particles. The faster the stirring, the smaller were the aerogel spheres.[3] To obtain an appropriate size for the microspheres, the stirring speed was controlled at 120 revolutions/min in this work. With this stirring procedure and conditions, the size of the CA spheres could be controlled to be in the range 70–1000 μm. Figure 3 shows the particle size distribution of CA spheres fabricated under different conditions. The particle size of the CA spheres is single peak distribution.

To control the internal nanostructures of the aerogel spheres to meet the requirements of the ambient pressure drying technique, many recipes have been tried with different catalysts, R/F ratios, R/C ratios, RF contents, and so on. By using base surfactants as a catalyst, the drying shrinkage could be controlled to be in an acceptable range and to get good nanostructural aerogel materials under ambient pressure drying conditions. A comparison of the effect of different surfactants on the drying shrinkage of CA spheres (Table I) indicated that CTAB is one of the best catalysts that we tried, with which the sample has the smallest shrinkage during ambient pressure drying.

Table II shows the effects of the R/F ratios, R/C ratios, RF contents, and gelation temperature on the density of the aerogel spheres prepared. The apparent densities of the CA spheres thus produced were in the range of 0.34–0.59 g/mL. Their bulk densities were in the range of 0.66–1.05 g/cm^3, which are higher than the bulk densities of normal monolithic aerogels,[7] but lower than that of the aerogel spheres prepared by alcohol supercritical drying conditions.[4] With increases of the RF content and R/C ratio, the bulk density of the aerogel spheres prepared decreases, while, too high and low R/F ratios would increase the bulk density of the samples.

The structure of the gel spheres

Figure 4 shows the morphology of typical CA spheres prepared. The CA particles thus produced are all fine round spheres with several hundred micrometers in diameter, and they look similar to the spherical CAs prepared by the alcohol or CO_2 supercritical drying technique.[3,4] The external surface of the CA spheres is not so smooth as that of the CA spheres prepared in our previous work.[4] Many small particles are attached to the surface of the microspheres (Fig. 4).

Figure 5 shows an SEM image of the internal nanostructure of the CA spheres prepared. It can be seen that the CA spheres prepared also consisted of interconnected carbon nanoparticles with a size of about 20–40 nm. There are many mesopores among the carbon nanoparticles. Figure 6 shows an SEM image of the external surface of the CA spheres. The nanocarbon particles in the external phase of CA spheres are stacked a little more compactly than those in the in-

TABLE III
Influence of the R/F Ratio and (RF) Concentration on the Pore Structures of CA Spheres

No.	R/F ratio	RF content (%)	S_{BET} (m^2/g)	S_{mic} (m^2/g)	V_{mic} (cm^3/g)	S_{BJH} (m^2/g)	V_{BJH} (cm^3/g)	APD_{BJH} (nm)
183	1/3	40	417	324	0.15	119	0.14	4.59
187	2/3	40	420	301	0.14	128	0.31	9.77
153	3/4	40	602	430	0.20	185	0.55	12.0
181	1/2	20	114	99	0.05	10	0.01	5.17
182	1/2	30	251	200	0.09	59	0.10	6.86
214	1/2	40	530	348	0.16	207	0.46	8.92
142	1/2	50	437	310	0.14	166	0.22	5.41

Predetermined R/C =100, GT= 85°C.

TABLE IV
Influence of the R/C Ratio and Gelation Temperature on the Pore Structures of CA Spheres

No.	GT (°C)	R/C	S_{BET} (m²/g)	S_{mic} (m²/g)	V_{mic} (cm³/g)	S_{BJH} (m²/g)	V_{BJH} (cm³/g)	APD_{BJH} (nm)
196	80	100	454	331	0.15	138	0.29	8.36
214	85	100	530	348	0.16	207	0.46	8.92
213	90	100	545	336	0.16	236	0.60	10.1
195	95	100	475	352	0.16	131	0.25	7.50
212	85	50	626	419	0.20	247	0.42	6.84
197	85	150	514	332	0.15	196	0.60	12.2
192	85	200	534	348	0.16	199	0.69	13.8
184	85	250	405	304	0.14	94	0.41	17.5

Predetermined R/F = 1/2, RF content = 40%.

ternal sites of the CA spheres (Fig. 5), but more loosely than those of the CA spheres prepared by the alcohol supercritical drying technique.[4]

Influence of the preparation conditions on the porous structure

Figure 7 shows the adsorption–desorption isotherms of typical CA spheres prepared under ambient pressure drying conditions. In fact, all the samples prepared in this work have a similar nitrogen Type-IV isotherm and with a H2 hysteresis loop at high relative pressure.[8]

Based on the isotherms, the surface area, pore volume, and pore size of the samples were calculated and the results are shown in Tables III and IV. The BET surface areas of the carbon aerogel spheres are in the range of 114–626 m²/g, the highest mesopore volume reaches 0.69 cm³/g, and the mesopore sizes are in the range from 5 to 18 nm.

Table III shows that with an increase of the R/F ratio, the S_{BET}, S_{mic}, V_{BJH}, and the APD_{BJH} of the CA spheres increase. When the RF content used is changed from 20 to 50%, all pore parameters of the CA spheres, including the S_{BET}, S_{mic}, V_{mic}, S_{BJH}, V_{BJH}, and the APD_{BJH} have a maximum value at 40% RF content. Table IV shows that when the gelation was carried out at a temperature from 85 to 90°C, the CA spheres that were produced have a maximum value for S_{BET}, S_{BJH}, V_{BJH}, and APD_{BJH}. A decrease of the R/C ratio obviously increases the S_{BET}, S_{mic}, V_{mic}, while decreasing the APD_{BJH} of the CA spheres. Therefore, the nanostructures of the CA spheres can be controlled by changing the gelation conditions.

Electrochemical performance

The cyclic voltammetry of the CA spheres prepared by the ambient pressure drying method was shown in Figure 8. These results indicate that the CA spheres prepared are good candidate materials for supercapacitor applications. However, it can be seen that these curves deviate somewhat from an ideal
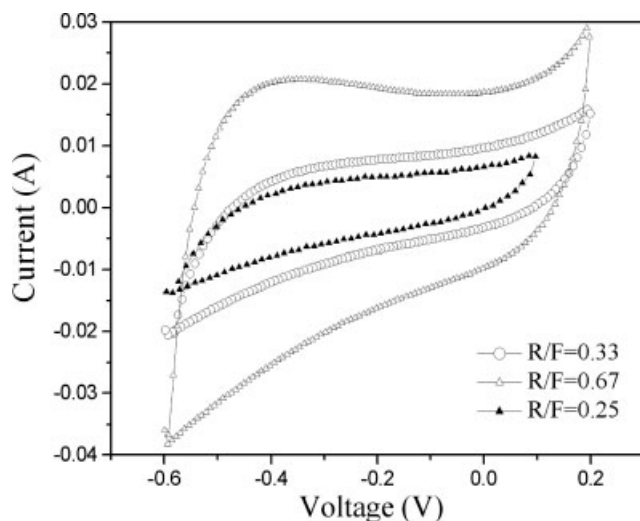

Figure 8 Cyclic voltammograms of CA spheres prepared by the ambient pressure drying method (Predetermined R/C = 100, RF content = 40%, gelation temperature 85°C).
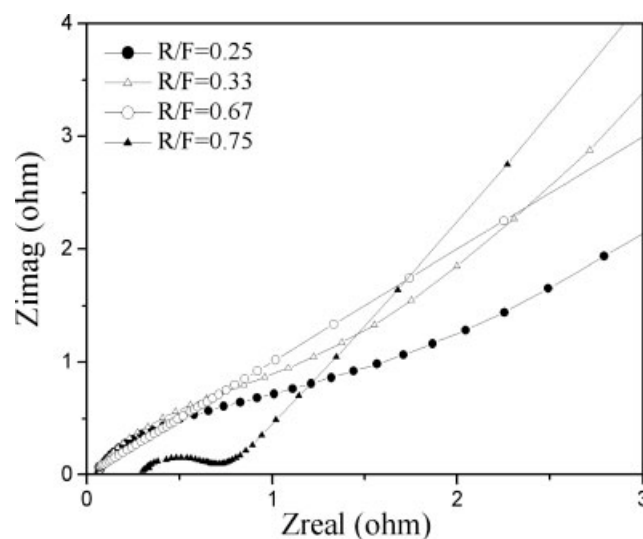

Figure 9 Nyquist diagrams for CA spheres prepared by the ambient pressure drying method (Predetermined R/C = 100, RF content = 40%, gelation temperature 85°C).

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TABLE V
Specific Capacitance and ESR of the CA Spheres Electrodes

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No.	R/F ratio	R/C ratio	RF content (%)	GT (°C)	Capacitance (F/g)	ESR at 57 Hz (Ohm)
181	0.5	100	20	85	152	/
182	0.5	100	30	85	75	/
214	0.5	100	40	85	156	3.7
142	0.5	100	50	85	84	/
212	0.5	50	40	85	197	2.9
197	0.5	150	40	85	135	1.5
192	0.5	200	40	85	81	1.7
184	0.5	250	40	85	147	1.3
196	0.5	100	40	80	135	2.0
213	0.5	100	40	90	115	2.4
195	0.5	100	40	95	177	1.1
194	0.25	100	40	85	95	1.4
183	0.33	100	40	85	106	0.8
187	0.67	100	40	85	138	0.5
153	0.75	100	40	85	178	0.7

rectangular shape compared with cyclic voltammetry curves of the CA spheres prepared by alcohol supercritical drying.[4]

The impedance plots obtained for different aerogel samples are shown in Figure 9. A large semicircle appears in the plots, which may be correlated with contact resistances at the interface of the CAs and the current collector and with internal contact effects inside the electrode.[9]

The capacitance values (C) for the samples investigated here are compiled in Table V. Here, the capacitance was examined by means of galvanostatic charge–discharge tests, and then estimated using the formula $C = It/V$, where I, t, and V are the current, time, and potential, respectively. It can seen that the capacitances of the CA spheres prepared range from tens to about 200 F/g. The highest specific capacitance reaches 197 F/g. The equivalent series resistant (ESR) at 57 Hz was about 0.5–3.7 ohm.

CONCLUSIONS

A modified method has been developed for the fabrication of spherical CAs with inverse suspension polymerization of an emulsified resorcinol–formaldehyde (RF) aqueous solution using CTAB as both the surfactant and catalyst, and then drying the resultant sol–gel spheres under ambient pressure condition. In this method, the starting time of stirring is one of the most important factors for controlling the shape of the reaction products. The optimum starting time for stirring can be judged from the change of the RF emulsion solution pH and the viscosity during gelation. The CA spheres thus prepared are fine round beads with diameters ranging from 70 to 1000 μm. The internal nanostructure of the CA spheres thus prepared is similar to that of monolithic CAs prepared with the CO_2 supercritical drying technique or that of the CA spheres prepared with the alcohol supercritical drying technique. The size of the internal carbon nanoparticles is in the range of 20–40 nm. The sticking density of the carbon nanoparticles in the external surface of the samples prepared by this method is looser than that of the CA spheres prepared by the alcohol supercritical drying technique. The highest surface area and mesopore volume of the spherical CAs prepared reach 626 m²/g and 0.69 cm³/g, respectively. The density, surface area, pore size distribution, and the size of the internal carbon nanoparticles of the spherical CAs can be changed by changing preparation conditions, such as the type of catalyst, the R/C ratio, the monomer concentration, the R/F ratio, and the gelation temperature. The spherical CAs prepared can be used as an electrode in supercapacitors, and the specific capacitance is as high as 197 F/g.

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