Carbon Aerogels With Kaolin Addition For Supercapacitors Application

Yuelong Xu a,b*, Bin Ren a,b, Shasha Wang a,b, Zhenfa Liu a,b

a Institute of Energy Resources, Hebei Academy of Sciences, Shijiazhuang 050081, China
b Hebei Engineering Research Center for Water Saving in Industry, Shijiazhuang, China
*Corresponding author’s e-mail: xudalong.cool@163.com

Abstract. Carbon aerogels with excellent electrochemical properties and 3D porous structure are prepared from the reaction of phloroglucinol (P), resorcinol (R) and formaldehyde (F) under ascorbic acid (VC) catalyzing with kaolin (KL) addition. Because of the double-layer capacitance behavior, CAs have been used as supercapacitors for energy storage. The reaction mechanism of the wet aerogels formation is analyzed. Meanwhile, the chemical environments of CAs surface is systematically investigated using X-ray photoelectron spectroscopy (XPS). The cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) measurements and electrochemical impedance spectroscopy (EIS) are adopted to studied the excellent electrochemical properties of different samples. The specific capacitance (SC) is up to 162 F g⁻¹, and 97% of initial capacitance is retained over 1000 cycles at a current density of 1.0 A g⁻¹.

1. Introduction
CAs are traditional porous carbon materials with low density, excellent chemical properties and abundant interconnected porous structure. The first report for CAs came from Pekala in the 1990s, which shown the preparation method and the application fields [1-3]. The formation of CAs is the carbonization of wet aerogels which was obtained from the polymerization of resorcinol anions and hydroxymethyl derivatives. R-F CAs are the traditional CAs, however which owned some shortcomings: low specific surface area (SSA), poor double-layer capacitance behavior and long preparation period. Recently, different methods (such as metal ions doping, heteroatom addition and acidic catalysts) have emerged to improve the properties of CAs [4,5].

The porous structure of CAs contributes a double-layer capacitance (DLC) behavior for energy storage. The traditional preparation method can not effectively improve the electrochemical properties. Therefore, nonmetal heteroatom and metal ions doping have been reported to improve the electrochemical properties [6,7]. The metal ions can afford the pseudocapacitance to facilitate the capacitance of CAs; the nonmetal heteroatom can accept the redundant electron to improve the double-layer capacitance behavior. In recent years, some methods to increase the SSA and the ratio of mesopore surface area / micropore surface area have been widely adopted to prepare high-performance CAs. As known, the high mesopore surface area can accelerate the transit of electron to higher the capacitance of CAs.

The addition of KL can facilitate electrochemical properties of CAs. The heteroatom of KL plays a vital role to increase the specific capacitance of CAs. Different acidic catalysts have been reported to...
shorten the preparation period of wet aerogels in recent decades. The main element of KL is Si, which can be beneficial for electrochemical properties. In this paper, CAs with different addition amount of KL are prepared with VC as the catalysts. The catalytic mechanism of acid is systematically analyzed. XPS is adopted to study the chemical environments of CAs surface. CV, GCD and EIS are all used to investigate the electrochemical performance.

2. Experimental

2.1. Materials
All the reagents are all analytical grade in this work. GAMRY Interface 1000 electrochemical workstation (GAMRY, USA) and X-ray photoelectron spectroscopy (XPS, PHI5600 Physical Electronics).

2.2. Preparation of CAs
The relevant preparation route are presented in Scheme 1.

2.3. Measurements of electrochemical properties
The work electrodes of CAs are obtained as follows. The partical size of CAs powders is less than 75 um. The mixture of CAs powders and polytetrafluoroethylene (PTFE) (mass ratio: 95 / 5) is put into a 100 ml beaker with 50 ml DI water. Then stirred for 6 hours at 25℃, kept in a drying oven for 12 h at 105℃and then obtaining work electrodes of CAs with nickel foam coated.

The DLC behavior were studied by CV, GCD and EIS analysis methods. A GAMRY Interface 1000 electrochemical workstation (GAMRY, USA) is used in this work. The work electrodes of CAs are kept in 6 M KOH for 24 h. The voltage range of CV measurement is from −0.8 to 0.0 V at a scan rate of 10 mV·s⁻¹. The GCD measurements were adopted at a current density of 1.0 A·g⁻¹, over the voltage range from −0.8 to 0.0 V. The investigated frequency range for the Nyquist plots was 100 kHz to 0.1 Hz.

The DLC behavior is investigated through a three-electrode system. The prepared CA electrode was used as the working electrode. A Hg/Hg₂Cl₂ electrode was the reference electrode, and Pt was the counter electrode. The SC were obtained from GCD.

3. Results and discussion
(1) addition reaction

(2) polycondensation reaction
The reaction mechanism of acid catalyst is shown in Figure 1. The reaction route exhibited two main steps: 1) the formation of phloroglucinol / resorcinol anions and hydroxymethyl derivatives; and 2) the polymerization of different resorcinol anions and hydroxymethyl derivatives. The acidic catalyst (VC) can induce the formation of phloroglucinol / resorcinol anions and bind with formaldehyde to form the hydroxymethyl. Meanwhile, the addition of KL plays a vital role to facilitate the reaction speed.

Figure 1 The reaction mechanism

The xps spectra of CAs surface is presented in Figure 2. As shown in Fig. 2 (a), the elements of C, O and Si can be observed. The peaks of sp² C (284.6 eV), sp³ C (285.3 eV), C–O (285.9 eV), C=O

Figure 2 XPS spectra: (a) full-scan spectrum (b) C 1s, (c) O 1s and (d) Si 2p
(287.4 eV) and O–C=O (289.1 eV) can be obtained in Figure 2 (b). The 531.0 eV (C=O bonds), 532.0 eV (O–C=O bonds) and 535.0 eV (C–O–C bonds) peaks were visible in the O 1s spectrum. Si peak is 102 eV, which comes from the addition of KL.

Figure 3 CV curves of Cas

CV curves of different addition amount (0 wt %, 2.5 wt %, 5 wt %, 7.5 wt % and 10 wt %) are shown in Figure 3. Clearly, all the curves exhibit a nearly rectangular shape, which indicates all the samples possess an excellent DLC behavior for supercapacitors application.

Figure 4 GCD curves of Cas

The SC values are obtained from GCD curves and the results are listed in table 1, the GCD curves are presented in Figure 4. A nearly linear shape and triangular distribution outline can be observed in Figure 4. As listed in table 1, when the addition amount is 5 wt %, the SC is high to 162 F / g at a current density of 1.0 A.g⁻¹. Compared with blank sample (CA-1), the addition of KL can markedly improve the electrochemical properties.

The cycling performance at a current density of 1.0 A g⁻¹ is shown in Figure 5. A slow loss of specific capacitance was clearly visible and CA–3 retained a stable performance, up to 99.9% of the initial discharge capacity after 1200 cycles.

Table 1 SC values of different samples

| Entry | C (F / g)_{1.0 A.g⁻¹} |
|-------|------------------------|
| CA-1  | 92                     |
| CA-2  | 105                    |
| CA-3  | 162                    |
| CA-4  | 105                    |
| CA-5  | 97                     |
The cycling performance at a current density of 1.0 A g\(^{-1}\) is shown in Figure 5. A slow loss of specific capacitance was clearly visible and CA–3 retained a stable performance, up to 99.9% of the initial discharge capacity after 1200 cycles.

The Nyquist plots of CAs are obtained from 100 kHz to 0.1 Hz and the result is shown in Figure 6. Obviously, a semi-circle loop can be seen, which indicates the presence of the charge transfer resistance; a 45° line can be also observed, which is the presence of the bulk solution resistance. Compared with each other, CA–3 has the smaller resistance.

4. Conclusion
CAs have been successfully prepared with the addition of KL. The acidic catalytic mechanism have been investigated. The chemical environments of CAs surface is obtained through XPS dates. When the addition amount is up to 5 wt\%, the sample has the highest SC values and an excellent stable performance.

Acknowledgments
This work was financially supported by the Science and Technology Program of Hebei Academy of Sciences (20705, 20706 and 201503).

Reference
[1] Zhao H.Y., Chen Y., Peng Q.S., Wang Q.N., Zhao G.H., (2017) Catalytic activity of MOF(2Fe/Co)/carbon aerogel for improving \(\text{H}_2\text{O}_2\) and \(\text{•OH}\) generation in solar photo–electro–Fenton process, App. Cata. B: Environmental 203: 127–137.
[2] Moreno-Castilla C., Maldonado-Hódar F.J., (2005) Carbon aerogels for catalysis applications: An overview, Carbon, 43: 455–465.
[3] Zubizarreta L., Arenillas A., Pis J.J., (2009) Carbon materials for \(\text{H}_2\) storage. Int. J. Hydrog. Energy., 34:4575–4581.
[4] Ruben G.C., Pekala R.W. (1995) High-resolution transmission electron microscopy of the nanostructure of melamine–fomaldehyde aerogels. J Non-Cryst Solids 186:219–231.

[5] Alhwaige A.A., Ishida H., Qutubuddin S., (2016) Synthesis of ultralight phosphorylated carbon aerogel for efficient removal of U(VI): Batch and fixed-bed column studies J. ACS Sustain. Chem. Eng. 4: 1286-1295.

[6] Ubeyitogullari A., Ciftci O.N., (2016) Phytosterol nanoparticles with reduced crystallinity generated using nanoporous starch aerogels, RSC Adv., 6: 108319–108327.

[7] Wu D.M., (2012) Kinetic performance of Li$_4$Ti$_5$O$_{12}$ anode material synthesized by the solid-state method, Ionics, 18: 559–564.