Texture Tailorable Hierarchical Porous Carbon Monolith with Large Mass Loading for High Performance Supercapacitor

Hedong Jiang, Xingke Ye, Yucan Zhu, Jianliang Xie and Chunyang Jia*

School of Electronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu, China

*Corresponding author e-mail: cyjia@uestc.edu.cn

Abstract. In this research, texture tailorable 3-dimension (3D) interconnected hierarchical porous carbon (HPC) monoliths were prepared by a simple method. By regulation of the polymerization rate of furfural alcohol in solvent, 3D HPC monoliths with various textures are obtained. The optimum HPC monolith shows high specific surface area of ~580 m² g⁻¹ and desired morphology, texture and pore structure. The HPC monolith with ~15 mg cm⁻² mass loading delivers a high capacitance of 129.1 F g⁻¹ at 0.1 A g⁻¹ and shows high rate capability of 76.9% capacitance retention when the current density increased 50-fold to 5 A g⁻¹. The assembled supercapacitor can drive a toy fan for more than 30 min.

1. Introduction
Supercapacitor as an emerging energy storage device attracts enormous attention in wide range owing to its ultrafast charging/discharging rate, excellent power density, super stable cycle ability and safety [1]. Based on the capacitance storage mechanism, supercapacitor is split into two types: electrical double layer capacitance (EDLC) and pseudocapacitance type. The EDLC utilized the electrostatic effect to store charges and the pseudocapacitance stores energy through redox reaction on surface [2]. Owing to the low-cost, high stability, eco-friendly and superior electric conductivity, and carbon materials are widely used in the commercial supercapacitor and under extensively study [3].

Hierarchical porous carbon (HPC) is a promising carbon material for supercapacitor attributed to its multi-scale pores which can simultaneously meet the requirement of charge storage, fast ion diffusion and offering ion accommodation. Although there already have many researches on HPC, most of them are in need of binder to build electrode, leading to existence of dead weight, which is a disadvantage for achieving high performance [4]. Besides, it is also a challenge to prepare 3-dimension (3D) interconnected HPC monolith with high mass loading that can be used for practical utilization directly. In addition to the above difficulties, a favorable morphology and texture of HPC is also extreme important to achieve high performance supercapacitor. However, in current state, the preparation of morphology and texture tailorable HPC is usually complicated. Thus, it is urgent to prepare binder free, high mass loading, texture and morphology tailorable 3D HPC monolith through a simple way.

In this paper, a simple polymerization of furfural alcohol (FA) method was proposed to prepare texture and morphology tailorable 3D HPC monolith with high mass loading. By the regulation of the polymerization rate of FA, 3D HPC monoliths with various morphologies and textures were obtained.
The optimum monolith is composed of interconnected $\sim 10 \ \mu m$ particles which is constructed by $\sim 20 \ \text{nm}$ carbon spheres and shows a high specific surface area (SSA) of $\sim 580 \ \text{m}^2\text{g}^{-1}$. The HPC monolith with $\sim 15 \ \text{mg cm}^2$ mass loading delivers a high capacitance of $129.1 \ \text{F g}^{-1}$ and high rate capability of 76.9% capacitance retention when the current density increased 50-fold. This research proposes a simple method to tailor the morphology and texture of 3D HPC monolith and achieves a high performance electrode with high mass loading.

2. Experimental

2.1. Fabrication of HPC monolith electrode

Furfuryl alcohol (FA, 2 g), dipropylene glycol (DPG, 2 g) and para-to-luene sulfonylic acid (PTSA, 0.16 g) were mixed and drastically stirred to a transparent liquid. Then different dosages of hydroiodic acid (HI, 0.3 g, 0.5 g and 0.7 g) were added into the above solution and stirred for 10 min to change the polymerization rate of FA. Afterward, the solution was spread onto 5 cm×12 cm glass and cured at room temperature and 60 °C for 24 h and 1h, respectively. Finally, the cured poly-FA monoliths were carbonized at 800 °C for 2h with 2 °C min$^{-1}$ in N$_2$ atmosphere to obtain HPC monoliths. The prepared HPC monolith electrodes were named as HPC-x (x represents the amount of HI).

2.2. Characterization

The morphologies of the monoliths were obtained on JEOL JSM-7600F scanning electron microscopy (SEM) and ZEISS Libra 200 FE high resolution transmission electron microscopy (HRTEM). Raman spectra and X-ray diffraction (XRD) patterns were characterized on Princeton Instruments and Bruker D8 ADVANCE A25X, respectively. Brunauer-Emmett-Teller (BET) and density functional theory (DFT) methods were used to obtain SSA and pore size distribution (PSD) of HPC-0.3, respectively.

2.3. Electrochemical measurements

Before electrochemical test, the HPC monoliths ($\sim 15 \ \text{mg cm}^2$) were immersed in 6M KOH aqueous solution overnight in vacuum condition. Symmetrical supercapacitors were assembled by using monoliths, polypropylene and 6M KOH as electrodes, separator and electrolyte, respectively. The cyclic voltammetry (CV) curves, galvanostatic charge/discharge (GCD), electrochemical impedance spectroscopy (EIS) and cycling life test were measured on CHI660E electrochemical working station (Shanghai, China). The potential range for CV and GCD were both from 0~1 V. The frequency range for EIS was from $10^{-2}$~$10^5$ Hz. The cycling life was tested at 5 A g$^{-1}$ for 5000 cycles.

The specific capacitance ($C_s, \text{F g}^{-1}$), energy density ($E, \text{Wh kg}^{-1}$) and power density ($P, \text{W kg}^{-1}$) of the HPC can be obtained by the GCD plots through the following equations:

$$C_s = \frac{4It}{m\Delta V}$$

$$E = \frac{c_s}{28.8}V_{\text{max}}^2$$

$$P = \frac{3600E}{\Delta t}$$

Where $m$ (g) is the total mass of monolith electrodes, $\Delta V$ (V) is the potential window after ohmic drop, $I$ (A) is the discharging electrical current, $t$ (s) is the discharging time, $V_{\text{max}}$ (V) is the operation potential during discharging period after ohmic drop.

3. Results and discussion

Fig. 1a shows the preparation process of HPC monoliths. In the precursor solution, DPG worked as both solvent and pore forming agent for forming HPC monolith. After the strong catalyst HI mixed with the
precursor, the solution was casted onto a certain area glass to form a solid poly-FA monolith. HPC monolith was obtained after curing and carbonized at 800 °C. Owing to HI has a significant influence the polymerization degree of FA, the final morphology of HPC monoliths can be tailored by the amount of HI. As depicted in Fig. 1b-d, HPC-0.3, HPC-0.5 and HPC-0.7 monoliths are composed of interconnected nanoparticles and possess large amount of pores inside it. Besides, with the increasing adding amount of HI, the particles become smaller, decreasing from ~20 μm to several micrometers. Furthermore, from Fig. 1e-g, it can be found the micrometer scaled interconnected particles are constructed by nanometer scaled spheres. Besides, with the increasing dosage of HI, the nanospheres size become smaller, displaying a similar trend as that of interconnected carbon particles. The reason for these phenomena is that the concentration of H+ ion can catalyze FA polymerize into poly-FA, which would improve the viscosity of the solution. However, the higher viscosity would decrease the FA molecule migration rate, leading to smaller size poly-FA particles [5]. In addition, in Fig. 1e-g, it can be seen that for HPC-0.3, the carbon spheres size is larger than those of HPC-0.5 and HPC-0.7. There also can be found no pores for HPC-0.3 and HPC-0.7. As for HPC-0.5, the carbon spheres (~20 nm) are much smaller and there are abundant pores, which is favorable for supercapacitor properties.

Fig. 2a shows the HRTEM images of HPC-0.5. The relative dark area and bright dots are the carbon and pores, respectively. It can be seen that the dark areas are interconnected and there is large amount of bright dots among the dark areas, which verified HPC-0.5 is interconnected and with large amounts of micro- and meso-pores inside it. N2 adsorption-desorption measurement is carried out to further prove the hierarchical structure of HPC-0.5. As it displayed in Fig. 2b, the PSD plot shows peaks in the range from 0.5 to 0.6 nm and around 1nm, demonstrating there is plenty of micropores. Besides, in the inset of Fig. 2b, the N2 adsorption-desorption curve. The curve shows a significant increase in relative pressure range below than 0.01, which indicates there exists large amount of micropores. Besides, in the relative pressure range of 0.4-1.0, a hysteresis loop is found, reflecting there is large amount of mesopores. Thus, according to the results of SEM, TEM and BET measurement, the monolith possesses hierarchical structure, which is advantageous for achieving high performance supercapacitors. XRD patterns (Fig. 2c) and Raman spectra (Fig. 2d) are used to characterize the crystallographic structure.
Fig. 2c, HPC-0.3, HPC-0.5 and HPC-0.7 all show two broad peaks at ~22.2° and ~43.7°, which corresponding to (002) and (100), a typical character of carbon materials. Moreover, in Raman spectra, two distinct peaks at 1323 cm⁻¹ (D band) and 1592 cm⁻¹ (G band), are found for all three monoliths. For all the three monoliths, the intensity ratio between D-band and G-band are 1.02. Both XRD and Raman results demonstrate the three monoliths are carbonized and possess similar graphitized degree.

Figure 2. (a) TEM image of HPC-0.5; (b) PSD plot of HPC-0.5 (inset shows the N₂ adsorption-desorption curve); (c) XRD patterns and (d) Raman spectra of HPC samples;

To investigate the electrochemical properties of the three HPC monolith electrodes, symmetrical supercapacitors are assembled and tested in 6M KOH aqueous electrolyte. Fig. 3a shows the CV curves at 1 mV s⁻¹ for the three monolith electrodes, all displaying rectangle shape, demonstrating the EDLC is the main energy storage mechanism. Besides, HPC-0.5 shows the largest profile area, implying a higher capacity storage capability. As shown in Fig. 3b, HPC-0.5 monolith electrode also exhibits much better performance at 50 mV s⁻¹. Compared with other two samples, the CV of HPC-0.5 remains rectangular shape without obvious distortion. The reason for these phenomena can be attributed to its better morphology and texture. Fig. 3c exhibited the GCD curves of HPC-0.3, HPC-0.5 and HPC-0.7 at 0.1 A g⁻¹. The linear charging and discharging curves demonstrate the fast surface charge storage, which is consistent with CV results. Additional, HPC-0.5 monolith electrodes exhibit the longest discharging time, verifying its high performance. To evaluate the rate capability, Fig. 3d exhibits the relationship between current density and Cₛ for the three monolith electrodes. At 0.1 A g⁻¹, HPC-0.3, HPC-0.5 and HPC-0.7 deliver 47.5, 129.1 and 103.8 F g⁻¹, respectively. When enlarges the current density by 10-fold to 1 A g⁻¹, HPC-0.5 can still deliver 116.2 F g⁻¹, remaining ~90%. While for HPC-0.3 and HPC-0.7, the values are 5.1 F g⁻¹ (remaining 10.7%) and 73.6 F g⁻¹ (remaining 70.9%), respectively. Even when the current density increases 50-fold to 5 A g⁻¹, the Cₛ for HPC-0.5 still remains 99.3 F g⁻¹ (remaining 76.9%), which is a high value for electrode with mass loading of ~15 mg cm⁻². The corresponding E and P for HPC-0.5 at 0.1 A g⁻¹ are 4.48 Wh kg⁻¹ and 50 W kg⁻¹, respectively. Fig. 3e shows the Nyquist plots of monolith electrodes. At low frequency area, both HPC-0.5 and HPC-0.7 displayed a nearly vertical line indicating a better capacitive performance [6]. Meanwhile, for HPC-0.3, the slope is inclined, indicating a slower charge storage layer formation rate. Besides, there is almost no Warburg line, which located in the medium frequency, demonstrating fast ion transportation speed. The radius of semi-circle in the high
frequency range for the three monolith electrodes decrease firstly and then increase with the increasing amount of HI dosage. It demonstrates that the HPC-0.5 shows a fast charge transfer rate, which is also consistent with the high rate capability for HPC-0.5 electrode. Cycling stability is an important index in practical use for supercapacitor. As it shown in Fig. 3f, the HPC-0.5 monolith based supercapacitor displayed an increasing capacitance retention (112%) after 5000 cycles at 5 A g\(^{-1}\). The reason for the increasing capacitance is that the electrode is activated under cycling and the ions get access into the inner part of the monolith. Furthermore, a toy fan can be driven by the supercapacitor (active electrode area: 3 cm × 2 cm) for more than 30 min.

Figure 3. CV curves of HPC-0.3, HPC-0.5 and HPC-0.7 at (a) 1 mV s\(^{-1}\) and (b) 50 mV s\(^{-1}\); (c) GCD curves at 0.1 A g\(^{-1}\); (d) The relationship between \(C_s\) and current density; (e) Nyquist plots for HPC monoliths; (f) cycling life test for HPC-0.5 (inset is a toy fan driven by supercapacitor)

4. Conclusion

In summary, a facile method is proposed to synthesize texture tailorable 3D HPC monoliths. By adjusting the dosage of HI, various monoliths with different morphologies and textures are obtained. The optimum monolith shows high SSA of ~580 m\(^2\) g\(^{-1}\) and desired pore structure. The monolith with 15 mg cm\(^{-2}\) mass loading delivers high capacitance of 129.1 F g\(^{-1}\) and 99.3 F g\(^{-1}\) at 0.1 A g\(^{-1}\) and 5 A g\(^{-1}\), respectively. After 5000 cycling test, the assembled supercapacitor show an extremely high capacitance retention of 112%. Besides, the supercapacitor can drive a toy fan for more than 30 min. This work puts forward a simple method to prepare texture tailorable 3D HPC monolith with large mass loading for fabricating high performance supercapacitor.

Acknowledgments

This work was financially supported by National Natural Science Foundation of China (Grant nos. 51773027, 21572030) and National Key R&D Program of China (No. 2017YFB0702800).

References

[1] D. Zhang, J. Wang, C. He, Y. Wang, T. Guan, J. Zhao, J. Qiao, K. Li, Rational Surface Tailoring Oxygen Functional Groups on Carbon Spheres for Capacitive Mechanistic Study, ACS Appl. Mater. Interfaces 11 (2019) 13214-13224.

[2] H. Jiang, X. Ye, Y. Zhu, L. Wang, P. Zhao, Z. Yue, J. Xie, Z. Wan, C. Jia, Toward high-rate supercapacitor: Preparation of hierarchical porous carbon binder-free electrode with controllable texture, Appl. Surf. Sci. 470 (2019) 573-580.
[3] X. Lu, C. Shen, Z. Zhang, E. Barrios, L. Zhai, Core-shell composite fibers for high-performance flexible supercapacitor electrodes, ACS Appl. Mater. Interfaces 10 (2018) 4041-4049.

[4] C. Zhou, Y. Zhang, Y. Li, J. Liu, Construction of high-capacitance 3D CoO@poly-pyrrole nanowire array electrode for aqueous asymmetric supercapacitor, Nano Lett. 13 (2013) 2078-2085.

[5] Y. Wang, S. Tan, D. Jiang, X. Zhang, Preparation of porous carbon derived from mixtures of furfuryl resin and glycol with controlled pore size distribution, Carbon 41(2003) 2065-2072.

[6] J. Zhao, Y. Jiang, H. Fan, M. Liu, O. Zhuo, X. Wang, Q. Wu, L. Yang, Y. Ma, Z. Hu, Porous 3D few-layer graphene-like carbon for ultrahigh-power supercapacitors with well-defined structure-performance relationship, Adv. Mater. 29 (2017) 1604569.