Pyrrole modified biomass derived hierarchical porous carbon as high performance symmetrical supercapacitor electrodes

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Abstract:

Nitrogen-doped hierarchical porous carbon has been prepared *via* a direct carbonization of pyrrole modified biomass for using as electrochemical double layers capacitance electrodes materials. The hierarchical porous carbon features high specific area ($2959 \text{ m}^2 \text{ g}^{-1}$) and porosity, which originated from the etching, gasification and intercalation effect during heat treatment. Based on this unique porous structure, specific capacitance of 270 F g^{-1} at low current density of 0.1 A g^{-1} and 232 F g^{-1} at high current density of 10 A g^{-1} was obtained in 6 M KOH electrolyte. Excellent cycles durability was obtained after initial charge/discharge, the high specific capacitance remained nearly unchanged for total 4,000 cycles tested over a broad current density ranging from 0.1 A g^{-1} to 10 A . This study indicates that hierarchical porous carbon derived from pyrrole modified biomass is a promising electrode material for symmetric supercapacitors.

Keywords: biomass, N-doped, hierarchical porous carbon, symmetric supercapacitor

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1. Introduction

Supercapacitors are promising energy storage devices due to their long life cycle, high power and energy density, and excellent stability. Based on their working principles, supercapacitors can be divided into two major types: pseudocapacitors and electrochemical double layer capacitors (EDLCs). Pseudocapacitors store energy storage *via* faradic redox reactions where occurs on the surface of electrode materials immersed into an electrolyte [1]. The EDLCs, also referred as symmetric supercapacitors, store energy via electric charge accumulation at the electrode/electrolyte interface [2]. Pseudocapacitors use metal oxides as electrode materials. Among the available metals oxides, RuO_2 displayed excellent capacitance performance but are expensive [3]. To overcome this drawback, alternative metal oxides (such as NiO , MnO_2 , Co_3O_4 and WO_3 [4-7]) have been developed. However, the capacitance is still limited by poor conductivity, low power density and poor rate capability [8]. On the other hand, carbon has been used as electrode material for EDLCs due to its stable physicochemical properties, good conductivity, low cost, and abundant source. A well accepted opinion is that carbon material with high specific surface area (SSA) and porosity is particularly suitable for EDLC electrodes. The high SSA can provide enough accessible contact area between the electrolyte and electrode surface, and the porous structure can serve as reservoir and facilitate the electrolyte diffusion from exterior into interior of the electrode material. Porous carbon electrodes have been demonstrated with very high specific capacitance in carbon EDLCs [9, 10]. As a result, considerable effort has been made to create ideal porous carbon for EDLCs. Among those reported approaches, KOH activation under pyrolysis is considered an efficient way because the chemical activation produces a porous network by etching the physical activation further develops the pores through gasification, and the metallic K expands the carbon lattice by

intercalation effect [11, 12]. Based on these synergistic effects, various activated carbon materials with large SSA and high porosity have been developed for EDLCs.

However, the specific capacitance achieved using porous carbon was still not high enough. The relatively low conductivity of porous carbon appeared to be one limiting factor. It was found recently that introducing heteroatom, such as N, B, and S [13-15], was a promising way to improve the EDLCs performance. Among these dopants, N exhibited more advantages than others because it not only improved conductivity, but also enhanced surface wettability and induced pseudo-capacitance [16-18]. In addition, the cost of activated carbon is also a big concern for mass production. Compared with conventional carbon nanomaterials (carbon nanotubes, carbon fibers, and graphene), biomass-derived activated carbon is very attractive because of its availability, low cost and sustainability [19-22]. As a consequence, using N-modified biomass as carbon precursor is expected to be a good strategy to prepare high performance EDLCs.

Herein, the authors report a kind of hierarchical activated carbon derived from pyrrole modified fungus *via* efficient KOH activation. The KOH induced physical and chemical activation, created hierarchical porous structure with high SSA. Meanwhile, N composite was converted into beneficial N species during the pyrolysis process. The activated carbon was then used to prepare electrodes for EDLCs, which exhibited high specific capacitance, excellent stability, and long life time.

2. Experimental

2.1 Preparation of activated carbon

Dried fungus (3 g), prepared from pullulans, was mixed with pyrrole (1.5 ml) and 30 ml ethanol in a beaker, followed by stirring at 80 °C until the ethanol was evaporated. Then the mixture was

heated at 400 °C for one hour with a heating rate of 10 °C min⁻¹ in a muffle furnace (1100 box furnace, Lindberg/Blue M, Thermo Scientific Inc.) under the protection of nitrogen (flow rate was 96 ml min⁻¹). After the precarbonized material was cooled to room temperature, it was mixed with potassium hydroxide (KOH, Fisher Scientific Inc.) in a mass ratio of 1:3 in a steel crucible that contained 30 mL deionized water. The crucible was placed in an oven and dried at 110 °C for 24 h. Then, the crucible was transferred into a muffle and activated at 800 °C for 1 h with a heating rate of 10 °C min⁻¹ under N₂ protection (flow rate was 96 ml min⁻¹). Afterwards, the carbonized solids were washed with 30 mL 0.1 mol L⁻¹ HCl (Fisher Scientific Inc.) at 110 °C for 1 h in a 60 mL polytetrafluoroethylene (PTFE) autoclave to remove the residual KOH and impurities. Finally, the carbon solids was washed several times with deionized water until the pH stabilized at 7. The material was then dried at 105 °C overnight in an oven. The carbonized samples were denoted as KPF.

For comparison, samples prepared using the same procedure but without KOH were denoted as PF, and raw fungus directly carbonized with the same procedure as PF but without adding pyrrole was denoted as F.

2.2 Preparation of electrodes

Electrodes were prepared by mixing the F, PF or KPF (80 wt%) with acetylene black (10 wt%) and PTFE (10 wt%), and then pressing onto a nickel foam (EQ-bcnf-16m, MTI Corp.) of 1 cm² surface area. The electrodes were dried at 60 °C for 12 h in an oven. Afterwards, a sandwich structure was formed by placing two pieces of microporous Polypropylene (PP) separator celgard-3501 between two electrodes in a coin cell 2032 type system. Finally, the cell was pressed under a pressure of 1,000 kg cm⁻² to finish the assembly.

2.3 Physical characterization

The surface analysis was performed on a Kratos Axis Ultra high performance X-ray photoelectron spectroscopy (XPS) (Kratos Analytical Ltd.). For high resolution data, the lowest binding-energy C 1s peak was set at 285.0 eV and used as the reference for other elements. Raman spectra were obtained on a Horiba LABRam confocal Raman microscopy system with excitation wavelength of 532 nm from a diode pumped solid state laser. Isothermal adsorption analysis with dry N₂ was carried out at 77 K (liquid nitrogen bath), using ASAP2020 (Micromeritics Inc.) micropore analyzer. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was calculated according to the density functional theory (DFT) method using non-local density functional theory (NLDFT) analysis for carbon with slit pore model. A transmission electron microscope (TEM) (JEM-2100 LaB6, JEOL) equipped with energy-dispersive X-ray spectroscopy (EDX) was used to study the morphology and microstructure at an acceleration voltage of 200 kV.

2.4 Electrochemical characterization:

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy tests were measured on an electrochemical work station (SP-150, BioLogical, France) in 6 mol L⁻¹ KOH electrolyte. The galvanostatic charge/discharge curves were obtained from a battery test system (BTS series, NEWARE, China).

3. Results and discussion

To observe the morphology of F, PF and KPF, TEM and SEM were conducted (Fig. 1). As can be seen (Fig. 1a and b), samples F and PF were strongly aggregated chunks. On contrast, hierarchical and porous structure clearly appeared in the KPF (Fig. 1c and d). In addition, the pore structures was examined by high resolution TEM (Fig. 1e and f), revealing large amount of

pores with different sizes. Such a porous network was believed to be originated from KOH activation during the pyrolysis process. As mentioned above, synergistic effects, including etching, gasification and intercalation effect were responsible for pore network formation, porosity enhancement, and lattice expansion, respectively [11]. Such hierarchical morphology could provide large SSA. Moreover, from electrochemical perspective, a smaller resistance and shorter diffusion pathways were created by channels connected with pores of different sizes to facilitate the ion transport [9, 10], and were expected to lead to an improvement in capacitance performance as EDLCs electrodes.

To verify the speculation on high SSA and pore structure observed in TEM images, N₂ adsorption/desorption isotherm measurement was performed (Fig. 2a). The plot showed a typical type I isotherm according to IUPAC classification and high SSA up to 2959 m² g⁻¹. The inset in Fig. 2a depicted pore size distribution of KPF. A strong peak located at 15 nm was showed, indicating the pore network mainly consisted of mesopores, while micropore and macropore took a small percentage. Among these three kinds of pores, mesopores were believed to offer lower ion-transport resistance *via* mesoporous channels [10, 23-26]. Micropores would impose a long diffusion distance (> 5 nm) and a high ion-transport resistance led to a large electrode-potential drop (IR_{drop}) and a low ion-accessible surface area at high current values [27]. Macropores played a role as ion-buffering reservoirs, which would lead to a decreased diffusion distance[10]. Raman spectrum was used to characterize the carbon structures of KPF. As shown in Fig. 2b, two characteristic peaks located at around 1340 cm⁻¹ and 1580 cm⁻¹ were presented, which were assigned to *D*-band and *G*-band, respectively [28]. The *D*-band was related with the vibration of the carbon atoms with dangling bonds in plane terminations of the disordered structure, while *G*-band reflected the vibration of *sp*²-bonded carbon atoms [28, 29].

XPS was employed to characterize the carbon, oxygen and nitrogen chemical states in the KPF sample (Fig. 3). As shown in Fig. 3a, the high resolution C 1s spectrum was deconvoluted into five peaks at binding energy of *ca.* 285.2, 286.3, 287.5, 289.1 and 291.0 eV, corresponding to C-C, C-O/C-OH, C=O/C-N, COOH, and CO₂/CO₃²⁻ bonds and functional groups, respectively[30, 31]. In addition, high resolution spectrum of O1s was deconvoluted into three peaks (Fig. 3b), which were assigned to O-I, O-II and O-III at *ca.* 531 eV, 532 eV, and 535 eV, respectively. The three species O represented C=bond quinone type groups for O-I, C-OH phenol groups and/or C-O-C ether groups for O-II, and chemisorbed oxygen for COOH carboxylic groups and/or water for O-III, respectively. However, it was believed that only O-I represented the pseudo-capacitance effect[32]. Besides, two peaks were detected at binding energy *ca.* 398.9 and 401.2 eV for N species, and were attributed to pyridinic-N, and quaternary-N, respectively (Fig. 3c). As reported previously[16, 17], N introduction would improve the conductivity and pyridinic-N could lead to great pseudocapacitance effect, both of which would enhance the capacitance performance.

To verify the performance of prepared electrode materials, electrochemical measurements were employed. As presented in Fig. 4a c and e, the CV tests were conducted at various scanning rates ranging from 5 to 300 mV s⁻¹ for F, PF and KPF, respectively. The F and PF electrodes exhibited distorted rectangular shapes even at low scanning rate, while typical rectangular shape was observed for KPF electrode. In addition, the KPF electrodes retained rectangular shape CV curves when the scanning rate increased from 5 mV s⁻¹ to high 300 mV s⁻¹. These results indicated the high capacitive performance with rapid charging-discharging characteristics due to efficient charge transfer and electrolyte diffusion within the porous KPF[22].

The capacitive performance was further evaluated using the following equation[33] in the two-electrode system:

$$C = \frac{2I\Delta t}{m\Delta v} \quad (1)$$

where C is the specific capacitance, I is the charge/discharge current, Δt is the corresponding charge or discharge time, m is the mass of active materials on single electrode, and Δv is the total corresponding potential change. As can be observed in Fig. 4a and c, the specific capacitance was only around 60 F g⁻¹ for both F and PF electrodes. On contrast, high specific capacitance of 245, 243, 238, 234, 233, 223 and 204 F g⁻¹ was obtained at scanning rate of 5, 10, 20, 50, 100, 200 and 300 mV s⁻¹ for KPF, respectively. Combining the physical measurements results, it was deduced that the high specific capacitance could be attributed to large specific surface area, hierarchical porous structure, and high degree of graphitization of KPF.

Galvanostatic charge/discharge measurements were performed at different current densities ranging from 0.1 to 10 A g⁻¹ for F, PF and KPF (Fig. 4b, d and f). Differing from the comparable symmetric triangle shape and an obvious IR_{drop} for F and PF electrodes, KPF displayed a symmetric triangle shape, suggesting a very small internal resistance and less energy being wasted during charge/discharge process[27].

Fig. 5a shows Nyquist plots that was obtained from KPF electrodes in 6 mol L⁻¹ KOH electrolyte. In general, the total resistance (~2.5 Ω) consisted of bulk electrolyte resistance (R_1), interfacial impedance between electrode and bulk solution (R_2), and the impedance associated with intra-particle pores (R_3), corresponding to x -intercept at the highest frequency region, semicircle at the middle frequency region and spike at the low frequency region, respectively [34]. R_1 and R_2 , related to the electrolyte solution, while R_3 depended on both electrode materials and electrolytes.

This result was in consistent with the expected low resistance, hierarchical structure and high SSA confirmed above.

As another significant parameter of EDLCs performance, cycling life of KPF electrodes was recorded in 6 mol L⁻¹ KOH electrolyte at different current density ranging from 0.1 to 10 A g⁻¹. As shown in Fig. 5b, large specific capacitance of 270, 243, 235, 233 and 232 F g⁻¹ were obtained at current density of 0.1, 0.5, 1.0, 5.0 and 10.0 A g⁻¹ for each individual 1,000 cycles, respectively. Apart from a little bit degradation in the first 1,000 cycles at current density of 0.1 A g⁻¹, excellent cycle stability (almost 100% retention) was displayed, which demonstrated the excellent stability of KPF as electrode materials for EDLCs.

3. Conclusion

N-doped hierarchical porous carbon has been successfully prepared from pyrrole modified abundant fungus as high-performance electrodes for EDLCs. The prepared KPF carbon exhibited extraordinarily large SSA (2959 m² g⁻¹) and porosity, which served as ion diffusion channels and electrolyte reservoir contributed to capacitance enhancement. Large specific capacitance of 270 F g⁻¹ at low current density of 0.1 A g⁻¹ and 232 F g⁻¹ at high current density of 10 A g⁻¹ was obtained in 6 M KOH solution. In addition, excellent cycle stability for continuous 1,000 cycles at different current densities was achieved for assembled EDLCs. This work demonstrated the pyrrole modified biomass derived porous carbon was a promising electrode material for electric energy storage.

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Fig. 1 TEM images of F (a), PF (b) and KPF (c, e and f); SEM image of KPF (d).

Fig. 2 (a) N₂ sorption-desorption isotherms of KPF. The insert in (a) shows pore size distribution; (b) Raman spectra of KPF.

Fig. 3 High resolution C 1s (a), O 1s (b) and N 1s (c) XPS spectra of KPF.

Fig. 4 CV curves of F (a), PF (c) and KPF (e) electrodes at various scanning rates ranging from 5 to 300 mV s⁻¹; and galvanostatic charge/discharge curves of F (b), PF (d) and KPF (f) electrodes at different current densities ranging from 0.1 to 10 A g⁻¹.

Fig. 5 (a) Nyquist plots of KPF electrodes; (b) Cycle life of KPF electrodes in 6 mol L⁻¹ KOH electrolyte at different current density ranging from 0.1 to 10 A g⁻¹.

Fig. 1

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GRAPHICAL ABSTRACT