Symmetric supercapacitors using urea-modified lignin derived N-doped porous carbon as electrode materials in liquid and solid electrolytes

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Abstract:

N-doped porous carbon materials derived from urea-modified lignin were prepared *via* efficient KOH activation under carbonization. The synthesized N-doped carbon materials, which displayed a well-developed porous morphology with high specific surface area of 3130 m² g⁻¹, was used as electrode materials in symmetric supercapacitors with aqueous and solid electrolytes. In consistent with the observed physical structures and properties, the supercapacitors exhibited specific capacitances of 273 and 306 F g⁻¹, small resistances of 2.6 and 7.7 Ω, stable charge/discharge at different current densities for over 5000 cycles and comparable energy and power density in 6 mol L⁻¹ KOH liquid and KOH-PVA solid electrolytes, respectively.

Keywords: N-doped porous carbon, supercapacitors, solid electrolyte

1. Introduction

With increasing consumption of energy, considerable attention was paid to new sustainable energy technologies, such as Li-ion batteries, fuel cells, solar cells and supercapacitors. Of these devices,

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supercapacitors have attracted extensive attention due to their fast charge/discharge rate, long lifetime, and high power density [1-4]. Depending on the working principles, supercapacitors can be divided into two major types: asymmetric supercapacitors and symmetric capacitors. Asymmetric supercapacitors are also referred as pseudocapacitors, which achieve energy storage through a reversible redox Faradic reaction between the electrolyte and electroactive species on the electrode surface. While the accumulation and release of electrostatic charge in the electrical double layer formed at the electrode-electrolyte interface lead to symmetric capacitors, which are also called electrical double layer capacitors (EDLCs). Differing from pseudocapacitors, in which metal oxides (such as NiO, MnO₂, Co₃O₄ and WO₃) [5-8] are widely used as electrode materials, carbonaceous materials are served as electrode materials of EDLCs. As a result, EDLCs have the potential to overcome the common drawbacks of pseudocapacitors, such as unstable cyclicality, poor electrical conductivity and high-cost materials [9].

Achieving high performance EDLCs requires the electrode materials to possess high specific surface area (SSA), porous structure and sustainability. These requirements ensure large accessible contact area between the electrolyte and electrode, suitable reservoirs to facilitate electrolyte diffusion and channels to smoothly transport ions, and low cost devices, respectively [10, 11]. Traditional carbon materials, such as carbon nanotubes, graphite, carbon fiber, etc., cannot satisfy current demands for specific capacity. Thus, developing new porous carbon materials is a pressing issue to achieve high capacitance EDLCs. To obtain high SSA and porous structures, a variety of methods have been studied, including chemical and physical activation. In comparison with physical activation, chemical activation has more advantages. Generally, chemicals such as KOH, ZnCl₂, K₂CO₃ and KCl, etc., are mixed with biochar or carbon materials and pyrolyzed at high temperatures under inert atmosphere [12-14]. At high temperatures, multiple chemical and

physical reactions occur, which produce porous structures through etching and gasification effect [15]. Among the reported chemical activation methods, KOH activation is considered the most efficient way.

In addition to the electrode material, electrolyte is another important factor that affects the performance of EDLCs. Conventional supercapacitors use liquid electrolyte, which results in two major issues [16]: 1) high standard safety encapsulation materials are required, leading to large volume and low package energy; and 2) liquid electrolyte supercapacitors suffer from leakage risk; the harsh electrolyte (acid, base and organic [17-19]) is harmful to the environment and even rises fire. These issues restrict the applications of EDLCs. Recently, all-solid supercapacitors using ion gel electrolyte, such as polyvinyl alcohol (PVA)-H₂SO₄, PVA-H₃PO₄, and PVA-KOH, are reported [20-22]. For all-solid supercapacitors, the ion gel not only serve as separator, but also as electrolyte. Wide electrochemical window (0-3.5 V), excellent thermal stability, non-volatility, nonflammability, and non-toxicity are offered by ion gel electrolyte. Consequently, ion gel electrolyte provides a good solution to the common short-circuit problem in liquid electrolyte EDLCs.

A few recent studies indicated that introducing heteroatoms, such as N and B [23-27] can boost the specific capacitance of EDLCs. Inspired by this idea, the authors speculated that using N-rich chemicals to modify biomass *via* pyrolytic chemical activation would lead to N-contained carbon materials. Consequently, using the N-doped porous carbon as EDLCs' electrode materials would produce high-performance supercapacitors due to the bi-contribution of porous network and N introduction. Although biomass-derived carbon materials are abundant and cheap, N-containing biomass is limited. Therefore, combining N-containing chemicals with biomass can be a promising way to produce carbon materials suitable for supercapacitor electrodes. An attractive example is

urea modified lignin. Lignin is a biopolymer representing nearly 30% of the organic carbon on Earth. Over 50 million tons of lignin are produced every year [28, 29], which eventually becomes industrial solid waste and is burned. While urea is widely used as fertilizer because it contains up to 46.67wt% N. Both urea and lignin are cheap, abundant and accessible. Hence, urea-modified lignin can be an ideal raw material to prepare N-doped porous carbon for using as electrode materials in EDLCs.

In this work, N-doped porous carbon was derived from urea modified lignin *via* efficient KOH activation under pyrolysis. The prepared porous activated carbon was subsequently used as EDLCs electrodes in liquid and solid electrolytes, respectively. A variety of physical characterization techniques were employed to confirm the N-rich porous material, which was essentially important to achieving high capacitance. Electrochemical measurement was used to analysis the performance of EDLCs made of the N-rich porous carbon, which yielded high specific capacitance, excellent stability, low resistance and long life cycle in both electrolytes.

2. Experimental

2.1 Preparation of activated carbon

Solvent lignin was mixed with urea (Fisher Scientific Inc. USA) in a mass ratio of 1 to 2 first. Proper amount of deionized water was added, while keeping stirring till the urea was dissolved. Then the mixture was placed into an oven at 110 °C to dry. The dried powder was transferred into a steel crucible and heated for one hour at 400 °C 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 pre-carbonized 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. USA) at 110 °C for 1 h in a 60 mL polytetrafluoroethylene (PTFE) autoclave to remove the residual KOH and impurities. Finally, the carbon solid was washed with deionized water until the pH stabilized at 7. The material was then dried at 105 °C for 12 hours in an oven. The carbonized samples were denoted as L-U.

2.2 Preparation of solid electrolyte

PVA (Fisher Scientific Inc. USA) (6 g) with molecular weight of 86000 was added into 100 ml beaker with 60 ml deionized water. The mixture was heated to 100 °C and stirred for 2 h till the PVA was completely dissolved and the mixture became transparent liquid. After that, the temperature was reduced to 85 °C, while keeping stirring. Then, 6 g KOH was dissolved into 20 ml deionized water and added into the above mixture. Keeping stirring at 85 °C till the subsequent mixture became transparent and homogeneous liquid. The prepared homogeneous liquid was poured into a petri dish immediately and the thickness was around 0.5 mm. The petri dish was horizontally placed in atmosphere with a porous cover for 3 days to evaporate the extra water. The prepared thin solid electrolyte was donated as KOH-PVA.

2.3 Preparation of electrodes

Electrodes were prepared by mixing the L-U (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 loading mass on each nickel foam was ~4 mg). 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 1000 kg cm^{-2} to finish the assembly. In terms of the all-solid supercapacitors, the same procedure and parameters described above was followed but the separators were substituted by one piece of KOH-PVA with a diameter of 1 cm and thickness $\sim 0.5 \text{ mm}$,

2.4 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 N_2 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 (NLDF) 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.

2.5 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

The morphology and microstructure of L-U were examined by TEM. Figure 1a showed the images of L-U with different magnification. Plenty of pores with different sizes were observed in low magnification images (Fig. 1a and b), which were dispersed on the carbon chunk randomly. In high resolution images (Fig. 1c and d), hierarchical pore structures were displayed. The macro pores went through the whole carbon chunk, while meso and micro pores were shown around the holes walls. These penetrated pores with different sizes were believed to be originated from KOH activation contribution. As reported by *Kaskel* [15], raw carbon materials were etched due to redox reactions to form the pores, the produced gas further boosted the formation of porosity and intercalated metallic K in carbon lattice resulted in the expansion of carbon lattices. All these synergistic effects contributed to form porous carbon materials. In addition, the elemental mapping was conducted to confirm the distribution of elements (Fig. 2). It was found that C, O and N elements were dispersed uniformly in L-U, which would keep the L-U working as superior EDLCs electrodes considering the contribution of N.

Fig. 1 Different magnifications TEM images of L-U.

Fig. 2 Elemental mapping of L-U.

The porous structure observed in TEM images implied that the prepared L-U would possess a high surface area. To verify the specific surface area (SSA) and pore size distribution, N₂ sorption-desorption isotherms were employed (Fig. 3a). According to the classification of the International Union of Pure and Applied Chemistry [30], the isotherm belongs to the type I curve. The BET SSA and pore volume reached $\sim 3130 \text{ m}^2 \text{ g}^{-1}$ and $1.67 \text{ cm}^3 \text{ g}^{-1}$, respectively, which was expected to provide large contact area and space between the electrodes and electrolyte. The pore size distribution analysis showed that most of the pores had sizes around 27 nm and there were fewer micropores and macropores. Such a pore size distribution was reflected by a very weak hysteresis

loop at a relative pressure of $P/P_0 > 0.9$ and a steep increase in the adsorbed volume at a very low relative pressure ($P/P_0 < 0.05$), respectively [31, 32]. It is worth to note that all these pores would serve as channels for electrolyte ion transport and result in low resistance. Meanwhile, the pores acted as electrolyte reservoirs to shorten the distance of electrolyte ion transmission [10]. All these features were supposed to improve the capacitance performance of the L-U based EDLCs electrodes.

Raman spectroscopy was carried out to analyze the carbon structure (Fig. 3b). Two characteristic peaks located at ~ 1348 and 1590 cm^{-1} were observed, which corresponded to *D-band* and *G-band*, respectively. The *D-band* was associated with A_{1g} symmetry assigned to local defects and disorder carbon with sp^3 bonding, while the *G-band* was related to the bond stretching of sp^2 -hybridized carbon atoms in rings and chains according to the zone center E_{2g} mode. In addition, the ratio of the intensity of the *D* peak to the *G* peak (I_D/I_G) was used to evaluate the degree of graphitization in carbon materials [33, 34]. The intensity ratio of the signals I_D/I_G for L-U was 0.91, which was smaller than 1, indicating high graphitization degree was obtained.

Fig. 3 N_2 sorption-desorption isotherms (a) and Raman spectra (b) of L-U.

The elemental composition and chemical states were investigated by XPS (Fig. 4). In XPS survey analysis (Fig. 4a), signals of C, O and N were detected with atomic contents of 90.4%, 8.4% and 1.3%, respectively. This result was consistent with the TEM elemental mapping and confirmed

that N was successfully incorporated *via* thermal annealing. The chemical states of N were studied due to their significant effect on EDLCs performance (Fig. 4b). N 1s spectrum was deconvoluted into two peaks located at binding energy *ca.* 398.9 and 401.2 eV, which were attributed to pyridinic-N and quaternary-N, respectively [35]. It was reported that N introduction would improve the conductivity and pyridinic-N could lead to great pseudocapacitance effect, both would improve the capacitance performance[35, 36].

Fig. 4 XPS survey (a) and high resolution N 1s (b) XPS spectra of L-U.

The capacitive performance was further evaluated using the following equation[37] 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.

Fig. 5a showed the CV curves at different scanning rate ranging from 5 to 200 mV s^{-1} of L-U electrodes in 6 mol L^{-1} KOH electrolyte. At different scanning rates, all the CV curves appeared rectangular shape, indicating the excellent capacitance behaviors of L-U. The calculated specific capacitances were 258, 255, 251, 249, 245, and 232 F g^{-1} , respectively, which kept 90%

retainability with the increasing scanning rates, demonstrating the high specific capacitance of L-U electrodes, as well as potential stability.

The galvanostatic charge/discharge curves of activated electrodes at current densities from 0.1 to 10 A g⁻¹ of L-U electrodes in 6 mol L⁻¹ KOH electrolyte are shown in Fig. 5b. A symmetric triangle curve with no obvious Ohmic drop (IR_{drop}) was observed under all different current densities, implying less energy loss or heat produced during the charge/discharge process [38].

Impedance was considered another important factor of EDLCs electrodes. The EIS measurement was performed and shown by Nyquist plot scanned from 100 kHz to 10 mHz in Fig. 5c. The impedance curve consisted of an x -intercept at high frequency range (0.6 Ω), a semi-circle at medium frequency range (1.2 Ω) and vertically linear spike at low frequency range (0.8 Ω), which could be assigned to bulk electrolyte resistance, interfacial impedance between electrode and bulk solution, and the impedance that is associated with intra-particle pores, respectively [39-41]. The lower resistance implied the higher conductivity, which was necessary as EDLCs electrode materials.

To access the stability of assembled EDLCs, cycle life at current density from 0.1 to 10 A g⁻¹ of L-U electrodes in 6 mol L⁻¹ KOH electrolyte was performed (Fig. 5d). At each current density ranging from 0.1 to 10 A g⁻¹, the specific capacitance of 1000 charge/discharge cycles was recorded. The specific capacitances were 273, 253, 250, 245 and 245 F g⁻¹ under current densities of 0.1, 0.5, 1.0, 5.0 and 10.0 A g⁻¹, respectively. An exception of a little degradation (93%) at initial 1000 cycles at 0.1 A g⁻¹ appeared, almost 100% capacitance retention was obtained after each individual 1000 cycles at other current densities. Moreover, the specific capacitance restored to 267 F g⁻¹ after 5000 cycles at current density of 0.1 A g⁻¹, which was close to the specific capacitance of 273 F g⁻¹ obtained at initial 1000 cycles at the same current density. These results

suggested the prepared L-U electrode materials possessed superior stability in KOH aqueous electrolyte.

Fig. 5 CV curves (a) at different scanning rate ranging from 5 to 200 mV s⁻¹, galvanostatic charge/discharge (b) nyquist plots (c) and cycle life (d) at current density from 0.1 to 10 A g⁻¹ of L-U electrodes in 6 mol L⁻¹ KOH electrolyte.

To evaluate the electrochemical performance of L-U electrodes in KOH-PVA solid electrolyte, CV test (Fig. 6a), galvanostatic charge/discharge (Fig. 6b) nyquist plots (Fig. 6c) and cycle life (Fig. 6d) were conducted at the identical testing conditions employed in aqueous electrolyte. In the CV measurements, the specific capacitances were 296, 282, 273, 268, 263, and 226 F g⁻¹ at scanning rates of 5, 10, 20, 50, 100 and 200 mV s⁻¹, respectively, which was larger than that of L-U in 6 mol L⁻¹ KOH in general but with slightly faster degradation.

Symmetric triangle curves with no IR_{drop} were shown as that of L-U in 6 mol L⁻¹ KOH, indicating the good capacitive performance in KOH-PVA solid electrolyte.

In impedance analysis, a little larger resistance of bulk electrolyte resistance ($1.2\ \Omega$), interfacial impedance between electrode and bulk solution ($1.2\ \Omega$), and the impedance that is associated with intra-particle pores ($1.2\ \Omega$) were obtained, which might arise from the increase in the interface resistance between the electrodes and electrolytes since the solid electrolyte was difficult to diffuse into the inner layer of the electrodes [42].

In addition, specific capacitances of 306, 284, 276, 260 and 251 F g^{-1} were obtained under current densities of 0.1, 0.5, 1.0, 5.0 and 10.0 A g^{-1} , which were much higher than that of using 6 mol L^{-1} KOH electrolyte. In addition, excellent retention (almost 100%) at each individual 1000 cycles was displayed for each current density. After 5000 cycles, a comparable specific capacitance of 294 F g^{-1} was restored, revealing the excellent stability in KOH-PVA solid electrolyte.

Fig. 6 CV curves (a) at different scanning rate ranging from 5 to $200\ \text{mV s}^{-1}$, galvanostatic charge/discharge (b) nyquist plots (c) and cycle life (d) at current density from 0.1 to $10\ \text{A g}^{-1}$ of L-U electrodes in PVA-KOH solid electrolyte.

To demonstrate the operational characteristics, the energy and power densities in both the electrolytes were calculated according to the following equations [38]:

$$E = \frac{1}{2} C (\Delta V)^2 \quad (2)$$

$$P = \frac{E}{t} \quad (3)$$

where E is the average energy density (Wh kg^{-1}), C is the specific capacitance of the symmetric supercapacitor, ΔV is the voltage range, P is the average power density (W kg^{-1}) and t is the discharge time, respectively. As shown in Fig. 7, Ragone plots of L-U electrodes displayed slightly higher energy density of $\sim 17 \text{ Wh kg}^{-1}$ in PVA-KOH solid electrolyte than that of $\sim 15 \text{ Wh kg}^{-1}$ in 6 mol L^{-1} KOH electrolyte,. In addition, comparable higher power density at different current density was exhibited for L-U electrodes in PVA-KOH solid electrolyte than in 6 mol L^{-1} KOH electrolyte.

Fig. 7 Ragone plots of L-U electrodes in 6 L^{-1} KOH electrolyte and PVA-KOH solid electrolyte, respectively.

4. Conclusions

A supercapacitor electrode material with excellent performance has been prepared by the carbonization of urea-modified lignin under the activation of KOH. The resulting N-doped carbon materials exhibited porous structure with extraordinarily large SSA ($3130 \text{ m}^2 \text{ g}^{-1}$), which greatly enhanced the electrochemical performance. High specific capacitances of 273 and 306 F g^{-1} were obtained at a charge/discharge current density of 0.1 A g^{-1} for L-U electrode in 6 mol L^{-1} KOH aqueous and KOH-PVA solid electrolytes, respectively. With increasing in the current density and cycle number, good retention was kept for prepared porous N-doped materials in both electrolytes, demonstrating the excellent stability and reliable lifetime. Comparable energy and power density were obtained in both electrolytes. The excellent electrochemical performance of L-U indicated that it was a promising electrode material for EDLCs.

Acknowledgement

This research was funded by: 1) China Scholarship Council; 2) NSF MRI award #1427888; 3) NSF EPSCoR Track II Dakota BioCon Center #1330840; 4) NSF award #1462389; 5) NSF award #1536209; 6) NSF CHE-0840507. 7) North Central Regional Sun Grant Center at South Dakota State University through a grant provided by the US Department of Energy Bioenergy Technologies Office under award number DE-FG36-08GO88073.

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