Capacitive Behaviours of Phosphorus-Rich Carbons Derived from Lignocelluloses

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ABSTRACT

A series of phosphorus and oxygen enriched carbons prepared by phosphoric acid activation of the ligno-cellulosic waste, fruit stones, are studied as the electrodes of supercapacitor in 1 M H_2SO_4 electrolyte. The microstructure and surface properties of the carbons are characterized by N_2 and CO_2 sorptions and X-ray photoelectron spectroscopy (XPS), respectively. Cyclic voltammetry, galvanostatic charge/discharge and wide potential window test are carried out to evaluate the electrochemical performances of the carbon electrodes. Statistical analysis is employed to confirm the limitation of the operation potential of the supercapacitors. The results show that the sample with balanced porous structure and higher phosphorus content exhibits a specific capacitance of 165 F g^{-1}, delivers an energy density of 13 Wh kg^{-1} at an operation window of 1.5 V, and shows stable cycling performance with a retention ratio of 99% even after 20000 cycles. This work suggests that the adjusted pore structure and surface functional groups which influenced the capacitive performance of the carbon electrode can be finely adjusted by the activation temperature.

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1. Introduction

Supercapacitors have been used as energy storage devices in hybrid electric vehicles, smart grids, aircraft emergency systems and portable consumer electronics where pulse power supply, excellent stability and long cycle life are critically important [1,2]. Moreover, in some instances the supercapacitors with high energy density are anticipated to replace the traditional batteries in the future [3]. Undoubtedly, the successful commercial applications of supercapacitor depend on developing affordable, suitable and superior electrode materials. From the industry point of view, porous carbons based on biomass are believed to be the most promising electrode materials for supercapacitor because of their abundant porosity, controllable surface functionalities, good electron conductivity and relatively low cost.

It is well known that the energy storage capacity of carbon-based supercapacitor predominantly depends on the i) porosity and ii) the surface chemistry of the carbons with two different energy storage mechanisms [4–7]. The former energy storage mechanism involves accumulation of ionic charges on the double-layer between the electrode and the electrolyte, which can be finely controlled by the accessible surface area and pore size distribution of carbon electrode [8]. On the other hand the latter mechanism involves Faradic redox reactions between the surface functional groups and electrolyte ions. The extend of such mechanism is determined by the type and content of heteroatoms on the carbon surface[6,9] and the tolerability of the carbon electrode towards operational voltage [10].

Recently, various biomass based carbons serving as the electrodes for supercapacitor have been reported. For example, coconut shell [11], animal bone [12], celtuce leaves [13], sugarcane bagasse [14], sunflower seed shell [15], have been used as the carbon precursors. However, most of the above works are focused on how to design appropriate pore structure to increase the double-layer capacitance neglecting the role of some surface functionalities that can facilitate the cycling stability and charge efficiency of the biomass based materials. It is generally accepted that the organic electrolyte based supercapacitors need to eliminate the surface functional groups of the carbon to keep their steady performance

[16,17]. In contrary, by using the aqueous electrolyte, porous carbons with heteroatoms, such as nitrogen and oxygen, can not only enhance the surface wettability [18], but also introduce Faradaic pseudocapacitive reactions [1,4,19].

The relatively low energy density of supercapacitor is the biggest obstacle for their wide-spread application. Hence, lots of effort has been paid towards improving their energy density. Taking into account the equation $E = 1/2CV^2$, the energy density is proportional to the square of the highest attainable voltage [20,21], and accordingly increasing the voltage of the cell can promote the energy density greatly. Even though the ionic liquids and organic electrolytes remain stable up to 4.0 V, they generally exhibit poor conductivity, lower specific capacitance and unstable cycling performance [22]. On the other hand aqueous electrolytes have better electrical conductivity, lower cost, cycling stability and environmental friendliness which are important characteristics for practical applications of supercapacitors, particularly for large-scale applications including energy storage for renewable sources. A definite disadvantage of aqueous electrolytes over organic/ionic electrolytes is their limited working voltage being 1 V vs. 3-4 V for organic/ionic electrolytes. Accordingly, the energy density of aqueous supercapacitors is significantly lower than that of organic/ionic supercapacitor.

The possible ways to achieve higher energy density of an aqueous supercapacitor is to (i) utilise electrode material with high specific capacitance values and/or (ii) select electrode material capable of operating at voltages above 1 V. While the specific capacitance has a significant influence on the energy density, widening of the potential window impede energy density much more remarkably.

In our previous work [23] we have discovered that the porous phosphorus-enriched carbon electrodes can be operated stably even at the potential window of 1.3 V in aqueous electrolyte. In the present work, we attempt to understand further the mechanism of the combined effect of porous structure and the surface functionalities on the electrochemical behaviours, which may shed some light in tailoring more suitable carbon materials for low cost high-performance supercapacitors. The supercapacitive performance of porous phosphorus-rich carbons prepared from apricot stones and peach stones by phosphoric acid activation are investigated in 1 M H_2SO_4 electrolyte.

2. Experimental

2.1. Preparation of carbon samples.

The preparation of phosphorus-rich carbons was described in previous studies [24–27]. Briefly, crushed and sieved fruit stones (a mixture of apricot and peach stones) were impregnated with phosphoric acid in a phosphoric acid/fruit stones weight ratio of 0.89. The mixtures were dried in air for 1 h and then activated at different temperatures (400–1000 °C) in argon flow. The activated samples were extensively washed with hot water until a neutral pH followed by drying at 110 °C. Phosphorus-containing carbons are referred as APPXXX where XXX represents the activation temperature. For example, APP800 corresponds to carbon activated at 800 °C.

2.2. Characterization of carbons

2.2.1. Determination of pore structure and surface morphology

Porosity parameters of APP carbons (APPs) were analysed by N_2 adsorption/desorption at −196 °C (ASAP 2010, Micromeritics, USA) and CO_2 adsorption at 0 °C (NOVA 1200, Quantachrome, USA). Prior to measurements, samples were degassed at 250 °C overnight under vacuum. Surface area was calculated by Brunauer-Emmett-Teller (BET) method from N_2 sorption, micropore volume from N_2 sorption and CO_2 sorption was calculated using Dubinin-Radushkevich (DR) method. Pore size distributions (PSD) were estimated from both N_2 and CO_2 adsorption isotherms using the DFT Plus Software (Micromeritics Instrument Corporation), using the non-local density functional theory method (NLDFT)[28].

2.2.2. Surface chemistry characterization

The X-ray photoelectron spectroscopy (XPS) measurements were performed on ESCALAB220i-XL (VG Scientific, UK) using monochromated Al Kα excitation source. The spectra were calibrated for a carbon C1s excitation at binding energy of 284.6 eV and taken as an internal standard. The quantitative analysis was performed with CasaXPS software after Shirley background subtraction. The best peak fits were obtained using mixed 30% Gaussian–Lorentzian line shapes at the same FWHM for all fitted peaks.

2.3. Electrochemical measurements

The capacitive performance of carbon samples was carried out in 1 M H_2SO_4 electrolyte using both 2-electrode (2E) and 3-electrode (3E) testing cells. In electrode preparation, 90 wt% of active material (APPs), 5 wt% of carbon black (Mitsubishi #32), and 5 wt% of polyvinylidene-fluoride were mixed in N-methyl pyrrolidone to form homogeneous slurry. The resulting slurry was coated on a Ti foil (current collector) with total area of 1 cm², and typically 2-4 mg carbon applied to each electrode. A sandwich type cell was constructed using two electrodes with similar weights, facing each other and separated by glassy fibre paper. 1 M H_2SO_4 electrolyte was added to the cell under vacuum to reduce air contamination and improve wettability of the electrodes.

Both 2E and 3E system were used to evaluate the electrochemical performance of APPs. In 2E system, two carbon electrodes with similar weight were assembled symmetrically. The 2E setup was simply converted into the 3E setup by choosing one carbon electrode as working electrode and other one as the counter electrode, respectively and by adding the Ag/AgCl (NaCl) reference electrode. Cyclic voltammetry (CV) measurements at the scan rates of 5 and 100 mV s⁻¹ were obtained between0.1-0.9 V (3E), 0-1.0 V (2E). Galvanostatic charge/discharge (GC) with the current loads of 0.05 and 20 A g⁻¹ within the potential range of 0-1.0 V were used for assessment of specific capacitances. Wide potential tests were used to evaluate how large the potential window the electrode material can sustain. CV and GC were recorded using 2E under stepwise increasing the potential from 0-1.0 V to 0-1.6 V.

The specific capacitance was calculated from the discharge branch of the galvanostatic cycle curves and is listed as specific cell capacitance (C_{cell-g}) measured in 2-electrode setup, and the material capacitance (C_{3E-g}) measured in a 3-electrode setup.

First, the cell capacitance C_{cell} in Farads was obtained according to Equation (1):

$$C_{cell}(F) = \frac{I(A) \times \Delta t(s)}{\Delta U(V)} \tag{1}$$

where I in Amperes is the current load, Δt in seconds is discharge time and ΔU in Volts is the potential difference between the start and the finish of the discharge process after omitting any iR drop.

Next the specific gravimetric cell capacitance C_{cell-g} in Farads per gram was calculated using Equation (2):

$$C_{cell-g}(F/g) = \frac{C_{cell}(F)}{\sum m(g)} \tag{2}$$