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Insight into high areal capacitances of low apparent surface area carbons derived from nitrogen-rich polymers

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ABSTRACT

The energy storage mechanism of N-doped carbons with low apparent specific surface areas (Brunauer–Emmett–Teller specific surface area determined by N_2 adsorption) has puzzled the researchers in the supercapacitor field in recent years. In order to explore this scientific problem, such carbon materials were prepared through pyrolysis of N-rich polymers such as melamine formaldehyde resin and polyaniline. Although these carbons possess low apparent specific surface areas of no more than 60 $m^2 g^{-1}$, their areal capacitance could reach up to an abnormally high value of 252 μF cm^{-2}. The results of systematical materials characterizations and electrochemical measurements show that these carbons contain numerous ultramicropores which could not be detected by the adsorbate of N_2 but are accessible to CO_2 and electrolyte ions. These ultramicropores play dominant roles in the charge storage process for these low apparent surface area carbons, leading to an energy storage mechanism of electric double layer capacitance. The contribution of pseudocapacitance to the total capacitance is calculated to be less than 15%. This finding challenges the widely accepted viewpoint that the high capacitance of N-doped carbon is mainly attributed to the pseudocapacitance generated from the faradic reactions between nitrogen functionalities and electrolyte.

1. Introduction

Carbon materials are the most promising electrode materials for supercapacitors, which are known as a new type of energy storage device bridging the gap between batteries and traditional capacitors [1]. There are plenty of merits for carbon electrode materials such as high specific surface area, long cycle life and tunable pore structure. Studies dealing with carbon materials for supercapacitor applications have thus far focused mainly on the following three aspects: (1) The texture/morphology of the carbon materials is regulated in order to obtain a three-dimensional (3D) architecture through adjustment of the pore structure, thus providing a large pore surface accessible to electrolytes for the formation of the electric double layer. On this basis, Ruoff group prepared microporous graphene through chemical activation of graphite oxide [2,3]. Also, Shen and coworkers synthesized a hierarchical 3D porous graphene-based material exhibiting interconnected micropores, mesopores and macropores, by using a one-step ion-exchange/activation method. This carbon material showed a high rate capability and highly stable cycling performance as a supercapacitor electrode [4]. Other researchers have developed 3D carbon materials for supercapacitor applications using low-dimensional materials, such as graphene, carbon nanotubes, and other carbon nanostructures [5,6]. (2) Carbon materials are utilized as supports for other pseudo-capacitive electrode materials to prepare hybrid materials owing to their large specific surface areas and good electrical conductivities. Such properties could significantly enhance ion/charge transport in the electrode and promote the rate capability of the electrode materials [7]. For example, nickel cobaltite was deposited on carbon aerogel using a sol–gel method to obtain a composite material, which showed an ultrahigh capacitance (~1700 F g^{-1}) [8]. A one-pot method was also used to synthesize an ordered mesoporous tungsten-oxide/carbon nanocomposite with high surface area and hexagonally ordered pores. The composite exhibited a high rate performance owing to its low internal resistance [9]. (3) Preparation of carbon materials with doped heteroatoms, e.g., N, O, B and P, which could interact with electrolytes to bring about

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pseudocapacitance during energy storage. Such elements are usually introduced from heteroatom-containing carbon precursors [10,11] or by post-doping of mesoporous carbon, graphene and carbon nanofibers [12–14]. Similarly, highly wrinkled N-doped graphene nanosheets with high pore volume (3.42 $cm^3 g^{-1}$) were prepared, which exhibited a good supercapacitive performance, owing to their particular structure, high pore volume and N-doping [15].

As for introducing heteroatoms to generate pseudocapacitance, nitrogen has been investigated more extensively than other elements in the literature due to its remarkable pseudocapacitance contribution. Many researchers prepared N-doped carbon materials using nitrogen-rich precursors such as biomass [16] or polymers [17–20], and the latter ones are more widely studied in recent years. For example, polypyrrole-derived carbon material was prepared by a simple pyrolysis method, and this sample has an high areal capacitance of 157 $\mu F cm^{-2}$, although its apparent specific surface area (Brunauer–Emmett–Teller (BET) specific surface area determined by N_2 adsorption) is only 36 $m^2 g^{-1}$ [21]. Liu group synthesized a series of polymer-derived carbons using polyaniline or phenol–melamine-formaldehyde resin as carbon precursors. The carbon materials obtained by direct pyrolysis of these precursors possess an apparent specific surface area of lower than 50 $m^2 g^{-1}$, however, their areal capacitances were within the range of 87–833 $\mu F cm^{-2}$ [22–26]. Park group prepared N-doped carbons using the precursors of polyaniline/melamine or polyvinylidene fluoride/melamine composite. Although their apparent specific surface area is no more than 100 $m^2 g^{-1}$, their areal capacitance could reach up to 221 $\mu F cm^{-2}$ [27,28]. In summary, the areal capacitances of these low apparent surface area carbons are larger than 80 $\mu F cm^{-2}$, which is beyond the widely accepted capacitance of <25 $\mu F cm^{-2}$ that could be formed on carbon surface [1]. The above authors just simply attribute these abnormal high areal capacitances to the pseudocapacitance afforded by nitrogen functionalities on carbon surface. However, such high areal capacitances could not be achieved even if all the surface nitrogen functionalities on carbon materials participate in redox reactions. Therefore, the energy storage mechanism for low apparent surface area carbons derived from nitrogen-rich polymers is still unclear so far. To the best of our knowledge, there are few reports on the energy storage mechanism of N-doped low apparent surface area carbons [29,30].

In this paper, we prepared two commonly studied polymer-derived carbons (PDCs) using the precursor of nitrogen-rich polymers such as melamine formaldehyde resin and polyaniline. Although these PDCs possess apparent surface areas of no more than 60 $m^2 g^{-1}$, their areal capacitance based on apparent surface area could reach up to 252 $\mu F cm^{-2}$. In order to explore the link between nitrogen contents and capacitive performance, hydrogen reduction at different temperatures (700 and 900 °C) was adopted to tune their nitrogen contents. Systematical pore structure analysis using different adsorbates (N_2 and CO_2) and electrochemical measurements were adopted to investigate their energy storage mechanism. The results show that PDCs contains abundant ultramicropores which could not be probed by N_2 but are accessible to CO_2 and electrolyte ions. These ultramicropores play more dominant roles in the energy storage process for PDCs compared with the contribution of nitrogen functionality-induced pseudocapacitance. Therefore, the energy storage mechanism of these PDCs is mainly electric double layer (EDL) capacitance and the contribution from pseudocapacitance is largely overestimated. We also suggest that, whenever carbon materials are used as supercapacitor electrodes, CO_2 adsorption should be a mandatory tool to verify the effective carbon surface available for the formation of EDL capacitance.

2. Experimental section

2.1. Preparation of PDCs

N-rich carbon precursors such as melamine formaldehyde resin and polyaniline were synthesized according to the literatures [31,32]. The polymers were transferred into a tube furnace and heated at 700 °C for 1 h with a heating ramp of 5 °C min^{-1} under Ar atmosphere at a flow rate of 50 ml min^{-1}. The obtained carbons were labeled as CX, where X could be M or A, corresponding to the precursor of melamine formaldehyde resin or polyaniline, respectively. For tuning the nitrogen content of the carbons, CX samples were reduced under pure H_2 atmosphere at a flow rate of 50 ml min^{-1} for 1 h at the high temperatures of 700 or 900 °C with a heating ramp of 5 °C min^{-1}. The reduced samples are labeled according to the reducing temperature, for example, CXH7 and CXH9, corresponding to the reducing temperature of 700 and 900 °C, respectively.

2.2. Characterization of PDCs

The crystal structure of the PDCs was determined by X-ray diffraction (XRD, X'Pert PRO MPD, PANalytical, Holland) using Cu Kα radiation (λ = 0.15418 nm). The chemical compositions of PDCs were determined by an elemental analyzer (EA, ElementarVario EI III, Elementar, Germany). The surface properties of PDCs were characterized by X-ray photoelectron spectroscopy (XPS, PHI5000VersaProbe, ULVAC-PHI, Japan). Nitrogen adsorption–desorption isotherms were measured at liquid nitrogen temperature (77 K) and CO_2 adsorption was performed at 273 K using a surface area and porosity analyzer (ASAP2020M, Micromeritics, USA). The carbon samples were degassed under turbomolecular vacuum at 300 °C for 4 h before sorption measurements. N_2 and CO_2 gases with super high purity (99.999%) were used for the physisorption measurements. The BET equation was used to calculate the apparent surface area from N_2 adsorption data obtained at P/P_0 between 0.05 and 0.2. For advanced porosity analysis, pore size distributions and cumulative pore volumes were determined by using quenched solid state density functional theory (QSDFT) method considering sorption of nitrogen at 77 K in carbon as a model adsorbant and slit-like pores as a pore model, or in the case of CO_2 (273 K), non-local density functional theory (NLDFT) methods for carbon with slit-like pores as a pore model. The implemented QSDFT and NLDFT models were supplied by the Quantachrome Autosorb ASiQwin 2.0 software. Note that, microscopic methods based on statistical mechanics, such as NLDFT and QSDFT, which allow describing the configuration of the adsorbed phase on a molecular level, are currently considered as the more accurate methods [33–38].

2.3. Fabrication of electrodes and electrochemical measurements

Working electrodes were made by pressing the electrode materials onto nickel foam, in which the electrode materials contained 5 wt% polytetrafluoroethylene (PTFE) as a binder. The mass of active materials in each working electrode is about 2 mg. In order to ensure that the active materials are thoroughly wetted with the electrolytes of 6 M potassium hydroxide and 1 M sulfuric acid solution, the working electrode was vacuum-impregnated with the electrolyte before electrochemical tests. The electrochemical capacitive performances of samples were studied on a CHI660D electrochemical workstation. All electrochemical measurements including cyclic voltammetry (CV), galvanostatic potential (GP) and electrochemical impedance spectroscopy (EIS) were performed in a three-electrode system using a platinum film as a