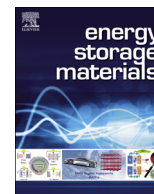




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# High-capacity pseudocapacitive Li storage on functional nanoporous carbons with parallel mesopores

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## ABSTRACT

Pseudocapacitive storage of monovalent alkali cations, such as Li<sup>+</sup> and Na<sup>+</sup>, is critically important for the development of metal-ion capacitors. Functional carbon materials decorated with ketone-containing groups are excellent candidates for this purpose. An epoxidation approach was deployed in this work to decorate electroactive oxygen groups on a high surface area nanoporous carbon with aligned mesopores. Because of the turbostratic structure, the intermediate epoxides dissipated into double-bonded oxygen groups in the functionalized carbon. The synergy of large porosity, good conductivity and enhanced surface redox activity endows the functionalized carbon cathode with high capacity (313 mA h/g@50 mA/g), good stability (> 200 cycles) and high rate capability (148 mA h/g@400 mA/g).

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## 1. Introduction

Deployment of alternative renewable energy resources, including solar, wind, or tide, is becoming global consensus for secure sustainability of modern society. Nevertheless the typical non-fossil renewable energy is intermittent and non-dispatchable. Full spectrum utilization of renewable energy for either stationary, portable or remote conditions will thus rely on the dispatchable energy storage devices.

At present the most popular energy storage devices are batteries and supercapacitors because of the high efficiency and reliability. Batteries have high energy density while supercapacitors provide large power output. For instance commercial lithium ion batteries possess a specific energy upwards to 200 W h/kg but with a maximum specific power of 300–400 W/kg. On the contrary, supercapacitors can deliver a very high specific power of 10 kW/kg but with a specific energy of only about 5–20 W h/kg. It would be ideal to realize a hybrid energy storage device that stores both high power and high energy.

Metal-ion capacitors, including Li-ion capacitors and Na-ion capacitors, are a family of hybrid energy storage system [1,2]. The normal Li/Na-ion capacitors use an intercalation-type negative electrode (anode) and an electric double layer-type positive electrode (cathode). Various materials have been paired for this

purpose, for instance V<sub>2</sub>O<sub>5</sub>/carbon nanotubes(–)//activated carbon(+)[1], Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>(–)//graphene(+)[2], nanotubular TiO<sub>2</sub>(–)//mesoporous carbon(+)[3], TiO<sub>2</sub>(B)(–)//activated carbon(+)[4]. All-carbon Li/Na-ion capacitors are a relatively new concept, where the graphitic materials, including graphene and biomass carbons, are used for the anode intercalation storage [5,6]. However, the energy density of metal-ion capacitors is limited by the low cathode capacity due to the absence of Faradaic reactions.

The electroactive oxygen groups on conjugated network can reversibly react with monovalent cations (H<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, etc.) via fast surface redox reactions [7–13]. Carbon materials are conjugated and contain a variety of oxygen groups on the surfaces, edges and defects. This physicochemical nature obviously endows carbon materials with intrinsic electrochemical redox activities. This understanding inspired the use of functional carbons as a new generation cathode in Li/Na-ion capacitors as long as the reaction potentials are reasonably higher than the counter anode reactions. Recently a range of carbon materials (graphene, carbon nanotubes, etc.) rich in oxygen functional groups have been tested as cathodes with high capacity, long-term stability and good rate performance for Li/Na-ion storage [14–23]. Alternatively Li-storage cathodes can be achieved via surface decorations of carbons with quinone-containing electroactive polymers [24,25]. Most of these studies are on graphitic nanocarbons, like graphene or carbon nanotubes. Graphitic nanocarbons are extremely popular in regards of macroscopic assembly and flexible device. Nevertheless nanoporous carbons with high surface area, good conductivity and tunable texture are important traditional carbon materials in energy

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storage. The functionalization of nanoporous carbons with periodic textures for pseudocapacitive Li-storage may bring more interest back to this 'old' branch of carbon materials towards emerging technologies.

Herein, we report the use of epoxidation to functionalize nanoporous carbons (NPC) with aligned mesopores to improve the lithium storage capacity. Our previous study showed the reversible lithium storage by epoxides on the basal plane of graphene oxide [20]. It was reported that epoxidation of graphite produced graphite epoxide [26]. As the conductivity of graphene oxide is low, the original aim of this work was hence to functionalize conducting porous carbons through epoxidation with the purpose of comprehensively utilizing the electroactive epoxide groups on a relatively conducting matrix. Compared with the pristine NPC, the oxidized NPC (oNPC) contains more oxygen due to epoxidation. However ketone-containing groups represent the majority oxygen in oNPC. This result was surprising but reasonable as the carbon structure of NPC is turbostratic rather than graphitic. Nevertheless our electrochemical tests showed the enhanced lithium storage capacity in the oNPC cathodes. The cathodes made of oNPC showed a maximum capacity up to 313 mA h/g at 50 mA/g in comparison with 195 mA h/g for NPC. A stable capacity around 225 mA h/g is achievable for 160 cycles at 100 mA/g. Despite the partially collapsed nanoporous texture caused by epoxidation, the oNPC exhibited a capacity of 148 mA h/g at 400 mA/g, whereas the capacity of NPC was only 95 mA h/g at the same current density.

## 2. Experimental

### 2.1. Synthesis and epoxidation of nanoporous carbons

The pristine nanoporous carbon sample was synthesized by a templating approach for which an ordered mesoporous silica (SBA-15) was used as a template [27]. The NPC sample was synthesized by filling the nanochannels with sucrose as the carbon precursor. The sucrose-filled silica was carbonized in argon atmosphere. The resultant silica/carbon composites were washed with NaOH dissolved in a deionized water/ethanol (volume ratio 1:1) (0.1 M) solution at 90 °C for 3 h to remove the silica template. The remaining carbon was then filtered and rinsed until the pH was 7. Thereafter, the wet powder was dried under vacuum at 100 °C for 12 h and denoted as NPC.

The epoxidation of NPC was conducted by dispersing NPC in a dichloromethane solution of 3-chloroperbenzoic acid and stirred for 5 days at room temperature. The solid product was collected by filtration and washed by using dichloromethane. The final product was dried in vacuum at 100 °C for 12 h and denoted as oNPC.

### 2.2. Materials characterization

Transmission electron microscopy (TEM) was collected by using JEOL 1010 at an accelerating voltage of 100 kV. X-ray photoelectron spectroscopy (XPS) was measured on a Kratos Axis Ultra spectrometer using Al K $\alpha$  radiation (15 kV, 150 W). The survey spectra were recorded from 0 to 1000 eV at an energy interval of 1 eV/step. Thermal gravimetric analysis (TGA) was carried out on a TGA Mettler Toledo analyzer under nitrogen protection at a heating rate of 5 °C min<sup>-1</sup> from 25 to 800 °C. Porosity measurement was conducted on a Micromeritics Tristar II at 77 K. The Raman spectra were collected with a Renishaw Raman microscope by using 514 nm Ar laser. Fourier transform infrared (FTIR) spectroscopy was performed on the PerkinElmer Spectrum 400 Spectrometer with a sensitive liquid nitrogen-cooled MCT detector.

### 2.3. Electrode preparation and characterization

Both of the NPC and oNPC samples (80 wt%) were ground and homogeneously mixed with conductive carbon black (10 wt%) and polyvinylidene fluoride (PVDF) (10 wt%) in N-methyl-2-pyrrolidone to form a slurry. The slurry was stirred for 6 h and coated onto Al foil. After vacuum-drying at 120 °C overnight, the foil was punched into circular pieces with a diameter of 15 mm, which was used as the cathodes. The electrolyte was 1 M LiTFSI salt in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 vol). The cathodes were assembled into 2032 coin cells in an argon-filled glove box (MBraun UniLab) with a lithium chip as an anode and a polypropylene film as a separator.

The galvanostatic charge–discharge tests were conducted on a LAND battery test system. The voltage window is 1.0–4.0 V vs. Li<sup>+</sup>/Li<sup>0</sup>. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were measured on a Biologic VMP-3 electrochemical workstation. EIS measurements were conducted at the frequency range from 100 kHz to 10 mHz.

## 3. Results and discussion

The XPS survey spectra of the oNPC and NPC are shown in Fig. 1a. The pristine NPC sample contains mainly carbon and oxygen with a trivial signal from nitrogen. The atomic percentages of oxygen and carbon in the pristine NPC are 7.5 at% and 92.5 at%, respectively. The NPC was synthesized through carbonizing dehydrated sucrose loaded in mesoporous silica template. The dehydrated sucrose contains considerable amount of hydroxyl groups, part of which would remain in the final sample after thermal treatment. This is the origin of the oxygen in NPC. The epoxidation of NPC was carried out in a dichloromethane solution by using 3-chloroperbenzoic acid as the oxidizing chemical. After epoxidation, the oxygen content increased to 19.1 at%, which led to the reduction in carbon content to 79.3 at%. Around 1.8 at% chlorine was detected on the surfaces of oNPC which is from the residues of either dichloromethane or 3-chloroperbenzoic acid. Given the rather low concentration of chlorine, the effect of epoxidation on the physicochemical and electrochemical properties of oNPC is believed to originate from the newly born oxygen groups.

On account of the different sources for the oxygen in NPC and oNPC, it is interesting to differentiate their respective chemical components. The deconvoluted profiles of C1s spectra of NPC and oNPC are displayed in Fig. 1b. The spectra were fitted by taking into account various possible chemical structures of carbon in our samples. The peak C-I at 284.8 ± 0.2 eV is assigned to the sp<sup>2</sup> type carbon, while the C-II peak at 285.8 ± 0.2 eV is allocated to the sp<sup>3</sup> type carbon considering the fairly turbostratic structure of sucrose-derived carbons. The peaks of C-III (286.8 ± 0.2 eV), C-IV (288.2 ± 0.2 eV) and C-V (289.1 ± 0.2 eV) are respectively correlated with singly bonded oxygen, carbonyl and carboxyl groups. The peak C-VI (291.1 ± 0.2 eV) reflects carbon atoms forming the pi–pi\* bond. The variation of percentage for individual chemical component of C1s is compared in Fig. 1c. With the similar content of sp<sup>2</sup> carbon in both samples, the population of sp<sup>3</sup> carbon drops from 12.88% of NPC to 6.52% of oNPC. This change may indicate that the epoxidation occurred on those less stable or more reactive sp<sup>3</sup> carbon instead of the sp<sup>2</sup> carbon. Surprisingly, the epoxidation did not give rise to a higher portion of singly bonded oxygen (either epoxide or phenol/hydroxyl) in the oNPC sample, in comparison with the pristine NPC sample. It has been known that stable graphite epoxide was synthesized from epoxidation of graphite by using a similar approach [26]. However, since the C–C bonds are more reactive sites relative to C=C in sucrose-derived

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