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Functional Carbon Materials for Electrochemical Energy Storage

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Author
Zhou, Huihui

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Functional Carbon Materials for Electrochemical Energy Storage

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Chemical Engineering

By

Huihui Zhou

2015
ABSTRACT OF DISSERTATION

Functional Carbon Materials for Electrochemical Energy Storage

By

Huihui Zhou

Doctor of Philosophy in Chemical Engineering

University of California, Los Angeles, 2015

Professor Yunfeng Lu, Chair

The ability to harvest and convert solar energy has been associated with the evolution of human civilization. The increasing consumption of fossil fuels since the industrial revolution, however, has brought to concerns in ecological deterioration and depletion of the fossil fuels. Facing these challenges, humankind is forced to seek for clean, sustainable and renewable energy resources, such as biofuels, hydraulic power, wind power, geothermal energy and other kinds of alternative energies. However, most alternative energy sources, generally in the form of electrical energy, could not be made available on a continuous basis. It is, therefore, essential to store such energy into chemical energy, which are portable and various applications. In this context, electrochemical energy-storage devices hold great promises towards this goal.

The most common electrochemical energy-storage devices are electrochemical capacitors (ECs, also called supercapacitors) and batteries. In comparison to batteries, ECs posses high power density, high efficiency, long cycling life and low cost. ECs commonly utilize carbon as both (symmetric) or one of the electrodes (asymmetric), of which their performance is generally limited by the capacitance of the carbon electrodes. Therefore,
developing better carbon materials with high energy density has been emerging as one the most essential challenges in the field.

The primary objective of this dissertation is to design and synthesize functional carbon materials with high energy density at both aqueous and organic electrolyte systems. The energy density (E) of ECs are governed by $E = CV^2/2$, where C is the total capacitance and V is the voltage of the devices. Carbon electrodes with high capacitance and high working voltage should lead to high energy density. In the first part of this thesis, a new class of nanoporous carbons were synthesized for symmetric supercapacitors using aqueous Li$_2$SO$_4$ as the electrolyte. A unique precursor was adopted to create uniformly distributed nanopores with large surface area, leading to high-performance electrodes with high capacitance, excellent rate performance and stable cycling, even under a high working voltage of 1.6V. The second part of this dissertation work further improved the capacitance of the carbon electrodes by fluorine doping. This doping process enhances the affinity of the carbon surface with organic electrolytes, leading to further improved capacitance and energy density. In the third part, carbon materials were synthesized with high surface area, capacitance and working voltage of 4V in organic electrolyte, leading to the construction of prototyped devices with energy density comparable to those of the current lead-acid batteries. Besides the abovementioned research, hierarchical graphitic carbons were also explored for lithium ion batteries and supercapacitors. Overall, through rational design of carbons with optimized pore configuration and surface chemistry, carbon electrodes with improved energy density and rate performance were improved significantly.

Collectively, this thesis work systematically unveils simple yet effective strategies to achieve high performance carbon-based supercapacitors with high power density and high energy density, including the following aspects:
1) Constructed electrodes with high capacitance through building favorable ion/electron transportation pathways, tuning pore structure and pore size.

2) Improved the capacitance through enhancing the affinity between the carbon electrodes and electrolytes by doping the carbons with heteroatoms.

3) Explored and understand the roles of heteroatom doping in the capacitive behavior by both experimental measurement and computational modeling.

4) Improved energy density of carbon electrodes by enlarging their working voltage in aqueous and organic electrolyte.

5) Scalable and effective production of hierarchically porous graphite particles through aerosol process for use as the anode materials of lithium ion batteries.

These strategies can be extended as a general design platform for other high-performance energy storage materials such as fuel cells and lithium-ion batteries.
The dissertation of Huihui Zhou is approved.

SENKAN, SELIM M
DUAN, XIANGFENG
LU, YUNFENG Committee Chair

University of California, Los Angeles
2015
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ACKNOWLEDGEMENT

I still clearly recall that time when I was a junior student at Sichuan University, my class adviser encouraged me to participate in an information session called “Cross-disciplinary Scholars in Science and Technology (CSST) Program”. Before that moment, the biggest dream I could imagine is to pass the postgraduate entrance exams of Chinese Academy of Sciences in Beijing, go back to somewhere near my hometown, and flee from the frigid and humid weather in Sichuan forever.

That must be a watershed of my life. I decided to have a try to step further, even further than the “biggest dream” I had before, to apply for the research program hold by University of California in Los Angeles. That sudden decision stirred up my passion so deeply that I quickly wrapped up my bag, went to a computer and finished the online-application by that day. I think I was lucky, especially considering my zero preparation in applying for graduate school abroad, a professor in UCLA unexpectedly offered me an olive branch to volunteer in his lab for a whole summer. Moreover, this professor finally turned out to be my Ph. D supervisor, thesis advisor, guider and philosophier in the past four years. Thank you, dear Dr. Lu, you really lighted my life and opened an unanticipated window that I therefore saw a brand new world.

And this world in not only new, but full of fun! The four years in Dr. Lu’s lab was the most rewarding time in my life. I could not say enough to thank Dr. Lu, who has just been a great mentor in every meaning of the word. In lab, he set me on the right track and let go, giving timely guidance while granting me full freedom to explore new frontiers. In life, he is a kind and generous man, with a truly free and fun-loving spirit. I still remember the Brand Lu’s Thanksgiving Parties hosted in his family every year, the yummy turkeys with glutinous rice, the home-made lobster plate, the countless drinking time in faculty center, and all those interesting stories he shared with us. I couldn’t count how many good advices he has given
me on my professional as well as personal growth, even if sometimes the guidance sounds like very strict. While, this rigorous and logical thinking training was approved to be the most valuable treasure that I couldn’t estimate how much I benefited and will continue to benefit from them.

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I would like to say special thanks to my dear friends. Wenke, the girl always standing by my side, we have known each other since we were 13 years old! This impregnable friendship has lasted for another 13 years already and will be forever! Ying and Beijia, you two are my best friends in UCLA. I just can’t tell how many times you two raised me up and helped me with your full-hearted love and trust. Thanks to my close sisters, Lisa Yuxi Wang, Julie Jue Liao, Eve Yuanxiu Luo, Anna Juan Wu, Wanru Liu, Fangting Xia, Dan Duan, and et al, your Christ-like love, help and support made my life fulfilled with happiness and joy. Especially thanks to Hang Yu, you gave me full support and encouragement during the past
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Finally, I thank my parents, especially my mother, who has always supported my choices and decisions, and offered me unconditional love and hope. You teach me to be an honest and righteous person, to be always optimistic and friendly to life. I wish you two will be the happiest and most blessed parents in the world, since as your daughter, I am already the most happiest and blessed girl.
VITA

2007-2011  B. S., Biomedical Engineering
           Sichuan University
           Chengdu, P. R. China

2011-2015  Teaching Assistant, Research Assistant
           Department of Chemical and Biomolecular Engineering
           University of California, Los Angeles, USA
Chapter 1: Introduction

1.1 Background

In the beginning God created the heavens and the earth, God said, “Let there be light”, and there was light.[1] Solar energy then transfers into various energy types such as chemical energy, electrical energy, geothermal energy and so on. Energy drives the evolution of nature and human beings since the beginning of creation. However, modern civilization along with industrial revolution rapidly accelerates the consumption of non-renewable fossil fuel energy and lead to serious greenhouse gas emission and environmental pollution, as shown in Figure 1.1 A.[2] Facing these challenges, humankind is forced to move towards sustainable and renewable resources.[3]

![Figure 1.1](image)

*Figure 1.1 (A)*, the forecasting fossil fuel consumption in the next 20 years based on the statistical result in past 50 years, unit for y-axis is billion toe. [2] (B) renewable electricity generation from 2000-2040, unit of y-axis is billion kilowatthours. [4]

In terms of alternative energy, there emerge lots of options in the recent years, such as biofuel, hydraulic power, wind power, geothermal energy and so on.[5] Geothermal energy comes from the heat of the earth, which is clean and “free”. However, it is not practical to set up a geothermal power station anywhere, and the potential danger of running out of steam cannot be ignored.[6] Wind and hydraulic power play a critically important role in world
commercial energy use. As expected in Annual Energy Outlook 2015 published by U.S. Energy information administration, wind energy will account for the largest absolute increase in renewable generation and for 40.0% of the growth in renewable generation from 2013 to 2038, displacing hydropower and becoming the largest source of renewable generation by 2040.[4] Nevertheless, the construction of dams and wind farms are extremely expensive and the locations with special geological conditions are required. Biomass and biofuel is a potential way to produce high-quality energy (e.g. alcohol, biodiesel) from renewable sources, such as crops, plants and other organic compounds.[7] However, the biomass processing is expensive and inefficient. It requires large land and lots labors to grow and burn the biomass. Moreover, due to the low conversion efficiency, the biofuel usually needs to be mixed with other gasoline to power the machines properly, which not only does it take a lot more fuel to do the same job as using conventional fuels, but it also creates environmental problems of its own.[8]

Despite all the energy resources mentioned above, the variability of these sources has led to concerns regarding the reliability of an energy supply network. Because the sun does not shine during the night and wind does not blow at any given location, there has been an increased call for the deployment of energy storage as an essential component of future energy systems. However, this often-characterized “need” for energy storage to enable renewable integration is actually a complicated question not only consisting technical breakthrough, industrial chain revolution, but also economic and political adjustment. The amount of storage or any other “enabling” technology used will depend on the costs and benefits of each technology relative to the other available options.

1.2 Energy Storage Techniques

Energy storage is accomplished by devices or physical media that store energy to perform useful processes at a later time. It is aimed to convert energy from forms that are
difficult to store to more conveniently or economically storable forms.[9] Diverse technologies have been developed such as electrical energy storage devices (including capacitors, lead-acid batteries, lithium batteries, et al), mechanical energy storage devices (flywheel, compressed-air, et al), chemical storage devices (hydrogen, methane, biofuel, et al) and so on. [10]

Mechanical energy storage devices have a great potential in commercialization as they are large scale and durable. Compressed air energy storage (CAES) store energy in the form of a compressed air in underground caverns, and the energy is later supplied to electrical networks through a conversion process. The air is compressed into an underground reservoir, which facilitates the storage of energy in a “pressure gradient”, the energy is discharged through a combustion process to operate an expansion turbine which spins and electrical generator. CAES systems have round trip efficiency (RTE) of ~85%, and an expected life time of 20-40 years, making it a suitable option for large-scale storage applications. Similarly, the RTE and lifetime for other mechanical energy storage devices like flywheel energy storage and gravitational potential energy storage are also very high, namely 75%, 40-60 years and 95%, 15 years.[10] However, as shown in Table 1.1, the mechanical energy storage technologies usually have large physical dimensions, long construction time (8-12 years), high investment cost (1000-2000 $/kW), which is expensive and time consuming. [11]
Table 1.1: Energy Storage plants: Capital Cost Data [11]

<table>
<thead>
<tr>
<th>Energy Storage Technology</th>
<th>$/kW+</th>
<th>$/kWh x</th>
<th>H=</th>
<th>Total Capital $/kW</th>
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<tbody>
<tr>
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<tr>
<td>-Large (110 MW)</td>
<td>390</td>
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<td>400</td>
</tr>
<tr>
<td>-Small (50 MW)</td>
<td>530</td>
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<tr>
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<td>1200</td>
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<tr>
<td>-Underground (2000MW)</td>
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<td>50</td>
<td>10</td>
<td>1700</td>
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<tr>
<td>Battery (target) (100 MW)</td>
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<td>-Lead Acid</td>
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<td>-Advanced</td>
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<td>720</td>
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</tbody>
</table>

Chemical energy storage technologies such as hydrogen storage are increasing studied as a promising replacement energy storage form due to its high energy density. At 143.0MJ/kg, hydrogen storage has the highest energy density of common fuels by weight (three times larger than gasoline). Unfortunately, at 0.0108 MJ/L, gaseous hydrogen also has the lowest energy density by volume (over 3000 times smaller than gasoline) and it can explode violently when brought into contact with air. There is limited space to store fuel on a vehicle and the fuel tank must be reinforced enough to prevent explosion during a crash. Therefore, a compact, safe, reliable, inexpensive and energy efficient method of storing hydrogen is needed if a hydrogen energy-driven vehicle is to become commonly used.[12] Methods of hydrogen storage span many approaches, including high pressures, cryogenics, and chemical compounds that reversibly release hydrogen upon heating. High pressure gas and cryogenic liquid is a possible option, however, they have technical and practical challenges, especially when considering emerging commercial markets. When considering
the hydrogen storage materials, as shown in Figure 1.2, the suitable materials with a reasonable release/sorption temperature and observed hydrogen capacity is quite limited. [13]

**Figure 1.2** Plot of hydrogen storage materials as a function of observed temperature release or sorption. Dashed lines denotes DOE 2017 and Ultimate targets.[13]

### 1.3 Electrochemical Energy Storage

As compared in Table 1.1 and Table 1.2, a desired energy storage system should have high energy density, high conversion efficiency, facial and fast construction, and low cost as much as possible. Based on these criteria, electrochemical energy storage (EES) is an established, valuable approach for improving the reliability and overall use of the entire power system (generation, transmission, and distribution). EES usually contains of batteries and electrochemical capacitors (EC), which are highly portable and environmental friendly, enabling their broad use in portable electronics, electric vehicles, and other applications.
<table>
<thead>
<tr>
<th>Energy Storage</th>
<th>Efficiency (1), (2), (3)</th>
<th>Size</th>
<th>Construction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technology</td>
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<td>Delivery</td>
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<tr>
<td>Pumped Hydro</td>
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<tr>
<td>Battery/Capacitors</td>
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</tr>
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<td>Flywheel</td>
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<tr>
<td>Superconducting magnetic energy</td>
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<td>31</td>
<td>91</td>
</tr>
</tbody>
</table>

Footnotes: (1) Conversion efficiency: for energy storage technology only, and is not to be used if the storage device uses anything other than electricity as input; (2) Delivery efficiency: from primary fuel through base load power generator and energy storage technology, including any supplemental fuel used in the storage facility; (3) Effective efficiency: useful for comparing all types of storage plants, represents the ability of the storage plant to efficiently store electrical energy.
Figure 1.3. Specific power against specific energy, also called a Ragon plot, for various electrical energy storage devices. If a supercapacitor is used in an electric vehicle, the specific power shows how fast one can go, and the specific energy shows how far one can go on a single charge. Times shown are the time constants of the devices, obtained by dividing the energy density by the power.

Performance requirements of EES for stationary use is a combined consideration of energy density and power density, as shown in the typical Ragon plot in Figure 1.3.[14] Energy density represents the total amount of energy that could be stored in the material per mass/volume, while power density displays how fast you can charge/discharge your device. Batteries, which operate based on redox reactions between their cathodes and anodes, offer high energy density but low power density. Capacitors, on the other hand, which are operated based on charge accumulation on parallel electrodes separated by dielectrics, usually offer much higher power density but much lower energy density. In the aspect of lifetime, capacitors exhibit dramatically longer lifetimes (e.g., >1,000,000 cycles) than batteries (e.g., 1000 cycles). Electrochemical capacitors, also called supercapacitors, exhibit storage performance intermediate that of capacitors and batteries. They are generally operated based
on electrical double layer capacitance or pseudocapacitance, and are referred to electrical
double-layer capacitor (EDLC) and pseudocapacitor, respectively. As shown in Table 1.3,
Supercapacitors can deliver at least 1,000 times more energy than dielectric capacitors and 10
times more power than batteries. In addition, they often exhibit long cycling lives of over
500,000 cycles.[15] Such superior performance is essential for various applications where
fast charging, high power and long cycling life are required. Typical applications include
energy recovery, energy harvesting from intermittent power sources, back-up power supply,
heavy-duty loading and uninterruptible power supplies.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>State of the Art Lithium Ion Battery</th>
<th>Supercapacitors</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Charge Time</td>
<td>~ 3-5 minutes</td>
<td>~ 1 second</td>
</tr>
<tr>
<td>*Discharge Time</td>
<td>~ 3-5 minutes</td>
<td>~ 1 second</td>
</tr>
<tr>
<td>Cycle life</td>
<td>&lt; 5,000 @ 1C rate</td>
<td>&gt; 500,000</td>
</tr>
<tr>
<td>Specific Energy (Wh/kg)</td>
<td>70-100</td>
<td>5</td>
</tr>
<tr>
<td>Specific Power (kW/kg)</td>
<td>** 0.5-1</td>
<td>5-10</td>
</tr>
<tr>
<td>Cycle Efficiency (%)</td>
<td>&lt; 50% to &gt;90%</td>
<td>&lt; 75 to &gt;95%</td>
</tr>
<tr>
<td>Cost/Wh</td>
<td>$ 1-2/Wh</td>
<td>$ 10-20/Wh</td>
</tr>
<tr>
<td>Cost/kW</td>
<td>$ 75-150/kW</td>
<td>$ 25-50/kW</td>
</tr>
</tbody>
</table>

Table 1.3 Comparison of some important characteristics of state of the art of electrochemical
capacitors and lithium-ion batteries. * Time for discharge and charge of the useable total energy
stored in the devices. ** Power capability of the battery for short duration partial discharge at 90%
efficiency.[15]

Cost is probably the most important and fundamental issue of EES for a broad market
penetration. Capital cost and life-cycle cost are the typical concerned important factors. As
shown in Table 1.1, the capital cost is typically expressed in terms of the unit cost of power ($/kW) for power applications (e.g., frequency regulation) or the unit cost of energy capacity ($/kWh) for energy applications (e.g. load leveling). Compared with other currently established energy storage devices, electrochemical storage system shows a lowest capital price of only 320-460 $/kW, whereas the cost for compressed air, pumped hydro energy storage, flywheel energy storage and superconducting magnetic storage is 400-550 $/kW, 1200-1700 $/kW, 750 $/kW and 720$/kW, respectively.

Considering the aforementioned technical and economic factors, it is more clear and rational to offer a guide in the R&D of electrochemical storage devices. As the detailed requirements for different electrochemical devices also distinguish a lot with each other, we will discuss the main-stream electrochemical storage systems as follows.

1.3.1 Batteries

A battery is one or more electrically connected electrochemical cells having terminals/contacts to supply electrical energy. A secondary battery is a cell or group of cells for the generation of electrical energy in which the cell, after being discharged, may be restored to its original charged condition by an electric current flowing in the direction opposite to the flow of current when the cell was discharged. Other terms for this type of battery are rechargeable battery or accumulator. As secondary batteries are usually assembled in the discharged state, they have to be charged first before they can undergo discharge in a secondary process.[16]
A Common Cell structure and components which usually consist of anode, cathode, electrolyte and a separator, which are electrically connected in an appropriate series or parallel arrangement to provide the required operating voltage and current levels.[17]

As shown in Figure 1.4, from the chemistry point of view, electrode process in a battery is an electrochemical redox reaction process. During procedure of converting chemical energy into electric energy, anode is oxidized to release electrons into the external circuit. When the electrons are transported to the cathode, reductive reaction takes place and electrons from the external circuit are consumed. At the same time, in internal circuit, anions move to the anode and cations diffuse to the cathode. In this way, the energy produced from chemical reaction can be converted to electricity, the so-called discharge process. During the process of storing electric energy in chemical energy, the redox reaction and current charge process take place in the reverse direction, which restores the cell from discharged status to its original charged condition, the so-called charge process. Herein we take a typical reversible battery for example to illustrate a more detailed process.[17] The battery is based on graphite (C) as anode and lithium cobalt oxide (LiCoO₂) as cathode. The discharge reaction can be written as follows:
Negative electrode: anodic reaction (oxidation, generation of electrons)

\[
\text{Li}_x\text{C}_6 \rightarrow x\text{Li}^+ + C + e^-
\]

Positive electrode: cathodic reaction (reduction, gain of electrons)

\[
\text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \rightarrow \text{LiCoO}_2
\]

The overall reaction of discharge process can be expressed as

\[
\text{Li}_x\text{C}_6 + \text{Li}_{1-x}\text{CoO}_2 \rightarrow C + \text{LiCoO}_2
\]

During the course of charge, the cell is connected to direct current power source and the current and ions flow is opposite to direction of the discharge process, as well as the electrochemical reactions. Keeping in mind that the anode is the electrode where oxidation occurs and cathode is the one where reduction takes place, the positive electrode becomes anode and the negative is cathode. Similarly, the charge reaction can be written as follows:

Negative electrode: cathodic reaction (reduction, gain of electrons):

\[
x\text{Li}^+ + C + e^- \rightarrow \text{Li}_x\text{C}_6
\]

Positive electrode: anodic reaction (oxidation, generation of electrons):

\[
\text{LiCoO}_2 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-
\]

The overall reaction of discharge process can be expressed as:

\[
C + \text{LiCoO}_2 \rightarrow \text{Li}_x\text{C}_6 + \text{Li}_{1-x}\text{CoO}_2
\]

The storage electricity or capacity of a cell is determined by the amount of active materials in the electrode. It is expressed as the total quantity of electricity produced in the electrochemical reaction and is defined in terms of coulombs or ampere-hours. The theoretical capacity of a battery, based only on the active materials participating in the electrochemical reaction, is calculated from the equivalent weight of the reactants, where one gram-equivalent weight is the atomic or molecular weight of the active material in grams divided by the number of electrons involved in the reaction. Similarly, the
specific capacity based on volume can be calculated using the appropriate data for ampere-hours per cubic centimeter. The specific energy (E) of a cell can be calculated by taking both the voltage and the quantity of electricity into consideration, using the following equation (1.1):

\[ E \text{ (Wh/g)} = U \text{ (V)} \times C \text{ (Ah)} \] (1.1)

Where, the cell voltage is determined by the difference of potentials between the two half-cells in the battery. If the discharge current density is expressed as I, then the specific power (P) of the battery can be evaluated by equation (1.2):

\[ P \text{ (W/g)} = U \text{ (V)} \times I \text{ (A/g)} \] (1.2)

Rechargeable batteries can be divided into different categories according to their electrode materials, and mainly include lead-acid, nickel-cadmium, nickel-metal hydride and lithium-ion batteries. Currently, lithium-ion batteries are the most widely used rechargeable batteries due to their high energy density, high cell voltage, low self-discharge, long cycling life and absence of memory effect. Typically, a lithium battery mainly contains four parts, namely cathode materials, anode materials, electrolyte and separator. Figure 1.5 shows the schematic of the relative electron energies in the electrodes and the electrolyte of a

Figure 1.5 Schematic open-circuit energy diagram of an aqueous electrolyte.[18]
thermodynamically stable battery cell in electrolyte.[18] The anode is reductant, the cathode is oxidant, and the energy separation $E_g$ of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the electrolyte is the “window” of the electrolyte. The electrochemical potentials of cathode and anode are $\mu_A$ and $\mu_B$ respectively. Thermodynamically, $\mu_A$ should below LUMO and $\mu_B$ should above HOMO, otherwise, the electrolyte will be either reduced or oxidized and form a passivating solid/electrolyte-interface (SEI) layer at the electrode/electrolyte boundary. Therefore, once the window of electrolyte is fixed, it is necessary to select and design electrodes of high capacity that have their $\mu_A$ and $\mu_B$ matched to the LUMO and HOMO of the electrolyte.

Based on the design criteria, to date, numerous kinds of materials have been developed towards the application of cathode and anode for lithium ion batteries. Among them, carbon-based materials have attracted more and more attention due to their super conductivity, cheap price, good intercalation/de-intercalation reversibility and excellent electrochemical stability, leading carbon to a promising candidate both for lithium anode materials and also super conductive agents for cathode materials. Especially for anode materials, graphite takes over 85% of the whole anode materials market in 2014 in China.[19] Due to the huge marketing potential, various types of carbons have been designed and studied, such as graphite, hard carbon, CNT, graphene, et al.

1.3.2 Electrochemical Double Layer Capacitor (EDLC)

When an electrode (electronic conductor) comes into contact with an electrolyte (ionic conductor), it shows some potential and attracts ions with the opposite sign, forming an “electrical double-layer” at the electrode/electrolyte interface, as shown in Figure 1.6.[20][21] From Figure 1.6 (A) to (C), the model to explain EDL evolves from the Helmholtz Model to Couy-Chapman Model, and finally to Stern Model. As shown in Figure 1.6 (C), there are two regions called compact layer and diffuse layer. In the compact layer, ions (very often
hydrated) are strongly adsorbed by the electrode. In addition, the compact layer consists of specifically adsorbed ions (in most cases they are anions irrespective of the charge nature of the electrode) and non-specifically adsorbed counterions. The inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP) are used to distinguish the two types of adsorbed ions. The capacitance in the EDL ($C_{dl}$) is the sum of capacitances from two regions, the Stern type of compact double layer capacitance ($C_{H}$) and the diffusion region capacitance ($C_{diff}$). Thus, $C_{dl}$ can be expressed by the following equation (1.3):

$$\frac{1}{C_{dl}} = \frac{1}{C_{H}} + \frac{1}{C_{diff}}$$

The capacitance is dependent on the specific surface area of the electrode, the type of electrolyte and the effective thickness of the double layer (the Debye length), according to the formula of a parallel-plate capacitor (1.4):

$$C = \varepsilon_r \varepsilon_0 A/d \quad (1.4)$$

Where $C$ is the capacitance of the EDLC, $\varepsilon_r$ is the electrolyte dielectric constant, $\varepsilon_0$ is the dielectric constant of the vacuum, $d$ is the effective thickness of the double layer which is also approximated as the Debye length, and $A$ is the electrode surface area. Based on this model, for a long time, it was believed that the micropores (typical pore size smaller than 2nm) have no contribution to the SC of electrode due to their inaccessibility to electrolyte. However, as shown in Figure 1.7 (A) to (D), reports of Simon and Gogotsi showed an anomalous capacitance increase in carbon electrodes with pore size less than 1nm, in which the solved electrolyte ions will experience a desolvation process and fit into the micropores.[22] Based on this abnormal
Figure 1.6 Models of the electrical double layer at a positively charged surface: (a) the Helmholtz model, (b) the Gouy–Chapman model, and (c) the Stern model, showing the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP). The IHP refers to the distance of closest approach of specifically adsorbed ions (generally anions) and OHP refers to that of the non-specifically adsorbed ions. The OHP is also the plane where the diffuse layer begins. \( d \) is the double layer distance described by the Helmholtz model. \( \Psi_0 \) and \( \Psi \) are the potentials at the electrode surface and the electrode/electrolyte interface, respectively.\[20\][21]

phenomenon, Huang et al proposed a heuristic approach to illustrate the capacitance storage more precisely by considering different pore curvatures.\[23\] As shown in Figure 1.7 (E), for the mesoporous materials, it is generally assumed that the mesopores are cylindrical and solvated counterions enter pores and approach the pore walls to form EDLC, the double cylinder capacitance is given in Equation (1.5):

\[
C = \frac{2\varepsilon_r\varepsilon_0L}{\ln(b/a)}
\]

in which \( L \) is the pore length and \( b \) and \( a \) are the radii of the outer and inner cylinders, respectively.
Figure 1.7, (A) Plot of specific capacitance normalized by BET SSA for the carbons varying with average pore sizes. (B) to (D) drawings of the behavior of solvated ions residing in pores with distance between adjacent pore walls (B) greater than 2nm, (C) between 1 and 2 nm, and (D) less than 1nm. (E) schematic diagrams (top view) of a negatively charged mesopore with solvated cations approaching the pore wall to form an electric double-cylinder capacitor (EDCC) with radii \( b \) and \( a \) for the outer and inner cylinders, respectively, separated by a distance \( d \), and (F) a negatively charged micropore of radius \( b \) with solvated cations of radius \( a_0 \) lining up to form an electric wire-in-cylinder capacitor (EWCC). [23]

For micropores, however, the small pores do not allow the formation of a double cylinder. Assuming cylindrical micropores, solvated (desolvated) counterions enter the pores and line up to form electric wire-in-cylinder capacitors (EWCC). Although the molecular geometries of the counterions might be anisotropic, the pore walls experience the average effect owing to the translation or room temperature rotation of the counterions along or with respect to the pore axes, leading to an inner cylinder. Conversely, the counterions experience the average effect if the micropore shape is slightly distorted from a cylinder, leading to an outer cylinder, as shown in Figure 1.7 (F). In a way, EWCCs can also be viewed as EDCCs, but the key quantity for EWCCs is no longer \( d \), but rather the radius of the inner cylinder \( a_0 \).
which is the effective size of the counterions (that is, the extent of electron density around the ions). By using $a_0$, Equation (1.5) then becomes Equation (1.6):

$$C/A = \frac{\varepsilon_r \varepsilon_0}{b \ln(b/a_0)}$$

Equation (1.5) and (1.6) are used to fit the available experimental data for supercapacitors of nanoporous carbon materials with diverse pore sizes and electrolytes.

Energy and power densities are two crucial parameters for evaluating the electrochemical performance of supercapacitors. The maximum energy ($E$ in Wh kg$^{-1}$) and power densities ($P$ in W kg$^{-1}$) of a supercapacitor can be obtained using the equations (1.5) (1.6), respectively.

$$E = CV^2/2 \quad (1.5)$$
$$P = V^2/4R \quad (1.6)$$

Since the first discovery of the carbon-based electrochemical capacitor by Becker in 1957, numerous kinds of supercapacitor have been developed and commercialized as shown in Table 4.[25] Among the multitudinous choices, carbon-based material is attracting more and more interest due to their high electrical conductivity, low cost, versatile forms, broad chemical stability in different electrolytes (from strongly acidic to basic), and highly durability in a wide range of temperatures. Consequently, diverse forms of carbon have been synthesized and developed towards the application in supercapacitors, such as carbon nanotube (CNT), graphene, template microporous carbon, activated carbon, carbon nanocages, carbon onions, carbon fibers, heteroatom-doped carbons and so on.[26][27]

Table 1.4 Summary of the performance characteristics of commercialized supercapacitors [25]

<table>
<thead>
<tr>
<th>Material</th>
<th>Energy density at 400 W kg$^{-1}$ constant power ($V_{\text{rated}}^{-1/2}V_{\text{rated}}$)</th>
</tr>
</thead>
</table>

a Energy density at 400 W kg$^{-1}$ constant power, $V_{\text{rated}}^{-1/2}V_{\text{rated}}$
1.4 Development of Carbon Materials for Energy Storage

Carbon, as one of the most abundant elements on the Earth, has been a source of energy which is closely associated with the development of human history. The technologies that move forward our modern society such as automobiles, airplanes, lasers and portable electronics et al, rely on the carbon-based materials which could supply energy continuously.

Thereafter, carbons have been studied in a wide range of fields. For example, fullerene-containing P-type semiconducting polymers are one of the key foundations in rapidly advancing organic photovoltaics.[28][29] CNT and graphenes are emerging as next generation of typically transparent electronically conductive films for solar cells.[30][31]

Other carbon-based materials such as active carbons and porous carbons also show great promise in the applications such as batteries, supercapacitors, and fuel cells.[32][33][34][35]

### 1.4.1 Carbon Materials for Lithium-Ion Batteries
Since the elements of electrochemical intercalation into carbons and graphites was established by Besenhard[36] and used in a rechargeable cell by Basu[37], and later combined with the cathode materials developed by Goodenough et al[38], for the first time, the energy storage capability of a rechargeable system approached that of the primary battery system.[39] Carbon, thereafter, becomes the preferred anode materials for LIB due to its relatively high capacity, good cyclability and low redox potential versus lithium metal. Intercalation/deintercalation of Li$^+$ in and out of the carbon upon charge/discharge forms the basis of carbon as the anode of the battery. To date, graphite is the most commonly used form of carbon towards the application of LIB anode materials. Thermodynamically, the equilibrium saturation concentration of graphite is LiC$_6$, corresponding to a theoretical capacity of 372 mAh g$^{-1}$.[40] Assuming the cathode capacity to be 140-200 mAh g$^{-1}$, the total cell capacity is saturated when the anode capacity reaches 1000-1200 mAh g$^{-1}$, and such value can be a target capacity for the anodes from a practical point of view. Therefore, more and more types of carbon have been developed towards a higher capacitance and better stability.

**Lithium-Ion Batteries with Graphite Electrodes** Graphite has been long attractive as LIB anode materials because of its high in-plane electron conductivity owing to the π-bond and weak interaction with Li ions, giving rise to high Li ion storage capacity and fast Li ion diffusion. There are also other models to explain the energy storage mechanism, like storage in cavities or nanopores, or the house-of-cards model, et al.[41][42][43] However, the intercalation capacity of Li ions is still limited at 372 mAh g$^{-1}$, leading to great efforts to increase this capacity by adjusting carbon structures, expanding lattice spaces, making hierarchical pores and developing more functional surface areas.[41][44][45]

**Lithium-Ion Batteries with Carbon Nanotube Electrodes** Since the discovery of carbon nanotube[46][47], this material draws much attention due to its novel properties of
high electrical conductivity ($10^5 \text{ Sm}^{-1}$ to $10^6 \text{ Sm}^{-1}$), high tensile strength up to 60GPa, high charge transport capability, relatively high specific surface area and high electrolyte accessibility.[40][48][49][50] For anode material, it is usually assumed that Li$^+$ can be stored in the central core, the interlayer space for multi-wall CNT (MWCNT), or the empty space between the nanotubes when assembled into bundles. Reversible Li$^+$ intercalation capacities of as high as 400 mAh g$^{-1}$ for MWCNTs and 520 mAh g$^{-1}$ for single-wall carbon nanotube (SWCNT) have been reported.[51][52] However, the improved capacitance of CNT is still quite limited compared with traditional graphite. Consequently, much effort has been dedicated to design and modify the chemical or physical properties of CNT, like introducing sidewall defects, chemical etching, ball-milling, changing CNT diameters, varying CNT lengths and so on.[52] Although the varieties introduced to CNT could usually lead to a higher capacitance, more serious side reaction and unwanted solid-electrolyte interface (SEI) formation till limits the practical application of CNT. To overcome this natural shortcoming, fabricating composite materials of CNT with other materials shows as a promising resolution, but how to combine hybrid materials together to obtain safe, stable, and high-capacity electrodes has always been the radical problem that many researchers are trying to solve.

1.4.2 Carbon Materials for Supercapacitors

Supercapacitors are electrochemical energy storage devices that combine the high energy-storage capability of conventional batteries with the high power-delivery capability of conventional capacitors. Supercapacitors have been utilized in a wide range of applications, such as power assists for hybrid electric vehicles, peak power during acceleration and hill-climbing, and catapults for airplane.[53] To date, for supercapacitors, there are mainly three types of electrode materials which consist of carbons[54], transition metal oxides,[55] and electro-active polymers.[56] The latter two cases rely on the redox reaction and are usually called “pesudocapacitors”, whereas the carbon-based capacitors are based on electro-double
layer capacitance. Generally, pseudo-capacitors has a higher capacitance than EDLC, for example, V$_2$O$_5$ has a high theoretical capacity as high as 590 mAh g$^{-1}$,[57] and recent work shows that the capacity of composite V$_2$O$_5$/CNT thin film could reach as high as 680 mAh g$^{-1}$.[58] Other candidates like Nb$_2$O$_5$, MnO$_2$, polypyrrole, polyaniline et al, also show good performance both in aqueous and organic electrolyte system.[40] However, the pseudo-capacitance rising from chemical reaction always suffers from capacitance decay, poor conductivity and structure instability. Therefore, carbon materials, with super conductivity, thermal stability in large temperature ranges, chemical stability in acid/basic electrolytes, excellent rate and cycling performance, holds great promise in this field. Diverse kinds of carbon materials have been developed and the exploration is still going on. Up to now, the most widely studied carbon forms include graphene, CNT, active carbons, template porous carbons, biomass-derived carbons, carbon onions, graphene ribbons, heteroatom-doped carbons and so on.

**Supercapacitors with Graphene Electrodes** Since the mechanism of EDLC rely on the electrolyte ion accumulation on material surface, a high accessible surface area and facilitated pore penetrability is desired. From this point of view, graphene has the natural two dimensional structures (see Figure 1.8),[59] large surface area (theoretical surface area of 2630 m$^2$ g$^{-1}$), high theoretical gravimetric capacitance of about 550 F g$^{-1}$, superior conductivity, and well exposed surface to electrolyte, which makes it to become quite popular in the field of supercapacitors. However, due to the strong π-π interaction between graphene sheets, the graphene flakes tend to restack to form graphite-like powders or films, which can severely decrease the accessible surface area and reduce the ion diffusion rate, resulting in unsatisfactory gravimetric capacitances (typically <180 F g$^{-1}$ in organic electrolytes) and relatively low charge/discharge rates.[60][61] Recent report on holey graphene gels showed a breakthrough towards this long-held problem, in which the free-standing frameworks
structure was maintained and kept moist by electrolyte. The capacitance of this kind of structure in aqueous system reaches 310 F g\(^{-1}\) and 298 F g\(^{-1}\) in organic system, which is by far the highest capacitance obtained of EDLC in organic system.

**Figure 1.8.** Scheme of chemical route to the synthesis of chemically derived graphene [59]

*Supercapacitors with Carbon Nanotube Electrodes* Owing to their high electrical conductivity, high charge transport capability, high mesoporosity, and high electrolyte accessibility, CNTs are attractive electrode materials for developing high-performance supercapacitors.[62][63] Since the surface area of most CNT (both MWCNT and SWCNT) is not high, and EDLC relies on the accessible surface area that could store the electrolyte ions, researchers have developed CNTs with different diameters, lengths, synthesis routes, and also with various chemical modifications and functional groups.[64][65] It is reported that the CNT electrodes after ammonia plasma treatment could reach a capacitance to 207.3 F g\(^{-1}\) from 38.7 F g\(^{-1}\) of the pristine ones.[64]
Figure 1.9, SWNT forest grown with water-assisted CVD. (A) Picture of a 2.5-mm-tall SWNT forest on a 7-mm by 7-mm silicon wafer. A matchstick on the left and ruler with millimeter markings on the right is for size reference. (B) Scanning electron microscopy (SEM) image of the same SWNT forest. Scale bar, 1 mm. (C) SEM image of the SWNT forest ledge. Scale bar, 1 mm. (D) Low-resolution TEM image of the nanotubes. Scale bar, 100 nm. (E) High-resolution TEM image of the SWNTs. Scale bar, 5 nm. [66]

Recent work also demonstrated the advantageous performance of Vertically-aligned CNT (VACNT) compared with their randomly entangled counterparts. The unique structure of VACNT is as shown in Figure 1.8.[66] It is assumed that the VACNT not only provide a more electrolyte-accessible surface, but also improve the charge storage/delivery properties as each of the constituent aligned tubes can be connected directly onto a common electrode to allow them to effectively participate. Moreover, the top end-caps of VACNT can be properly opened under appropriate conditions (e.g., by plasma etching). The end-cap-opening then allows the electrolyte access to the inner cavity of the VACNTs, resulting in an enhanced overall surface area (both internal and external walls of tubes) for charge storage on VACNTs.[40] Recent research has demonstrated the superior performance of VACNT, in
which a high capacitance of 365 F g\(^{-1}\) was obtained in 1M H\(_2\)SO\(_4\) via a template-assisted CVD method. [67]

*Supercapacitors with High-surface-area Activated Carbon Electrodes* Different from the well-ordered graphitic carbon mentioned above, the structure of activated carbon (AC) is usually less ordered due to their poor-crystallized carbonaceous precursors (e.g. biomass, polymers et al) and hash synthesis routes by physical/chemical activation. Physical activation refers to the treatment of carbon precursor at elevated temperatures (up to 1200 °C) in the presence of an oxidizing gas, such as steam, air and CO\(_2\). Chemical activation is usually carried out at relatively low temperatures (from 400 °C to 900 °C) with an activating agent like potassium hydroxide, sodium hydroxide and zinc chloride. Although the activation process lead to corrosion to carbon structure, the internal compact carbon matrix will be opened up and the surface area will increase dramatically. Therefore, the overall capacitance of activated carbon is usually comparable or even better compared with those of graphene and CNTs. Diverse forms of activated carbons have been developed by researchers, such as biomass-derived carbons, carbide-derived carbons (CDC), heteroatom-doped carbons, templated carbons and so on. The capacitive behavior was also studied both in aqueous (acid and basic) and organic system. It is reported that a 3D interconnected microporous carbon network synthesized by a single step pyrolysis of poly(acrylamide-co-acrylicacid) potassium salt ([CHCO\(_2\)RCH\(_{\text{m}}\)]\(_{\text{n}}\)[CHCONH\(_2\)]\(_{\text{n}}\)) where R=K or H, has a high capacitance of 254 F g\(^{-1}\) in 1M H\(_2\)O\(_4\) and 138 F g\(^{-1}\) in 1M LiPF\(_6\) in EC-DMC.[68] Reports on heteroatom-doped carbon also show great potential in the functionalization and modification of carbon materials for supercapacitors. Nitrogen, sulfur, phosphate, boron and their functional groups are successively introduced to the carbon surface, leading to a series of changes of carbon properties, such as enhanced conductivity, improved electrochemical stability, better wettability with electrolyte, extra pesudocapitance and so on.[69]
1.5 Design Criteria of Carbon for Electrochemical Energy Storage

In summary, no matter for batteries or supercapacitors, to realize high energy density and power density, sufficient number of ions and electrons need to be effectively stored and rapidly shuttled between cathode and anode. To obtain long cycling life, the electrodes and device structure must keep stable during charge/discharge cycling. These principles imply that high-performance electrodes and devices should meet the following criteria:

1) Effective electrochemical-active interface between electrode and electrolyte.
2) Efficient ion-electron transportation pathway.
3) Mechanically robust and chemically stable electrode architecture.

To achieve the criteria mentioned above, the design of high-performance carbons is supposed to follow these directions:

1) Well-defined carbon structure and pore configuration.

To achieve a high energy density, LIB requires the carbon to efficiently intercalate Li\(^+\) and EDLC requests the carbon surface to accumulate as much electrolyte ions as possible, thus a large surface area and approachable surface/bulk interiors is desired when designing and synthesizing carbons. From another aspect, to obtain a high power density, the carbons are demanded to transport ions (both Li\(^+\) and other electrolyte ions used in EDLC) and electrons efficiently. Therefore, a good conductive framework including interconnected pores and appropriate pore size are desired.

2) Electrochemically active and stable interface chemistry.

All the chemical reactions take place at the interface, and electrochemical reaction is not excluded. Hence, foremost, the carbons should be well approached and infiltrative by electrolyte. The hydrophobic/hydrophilic properties are influenced by the carbon materials
nature, carbon surface functionalities, and carbon surface charge properties. Moreover, during the electrochemical charging/discharging process, carbon should be chemically/mechanically stable in electrolyte in the given electronic conditions. The carbon with less/no side reactions, tolerant voltage/current ranges, and robust frameworks are desired to achieve this goal.

1.6 Thesis Objective and Research Scope

The objective of my dissertation is to address the limitation of current carbon materials for energy storage (especially for EDLC) by rational structure design according to the above principles and criteria. The ultimate goal of this research is to develop high energy, high power, low cost and long life electrochemical devices for various applications, including portable electronics, EVs and grid-scale energy storage. To achieve this goal, my research strategy is to fundamentally understand the operational mechanism of carbon as energy storage materials and address its limitations by creating a new family of high-performance carbon structures with desired properties. Generally, my dissertation is dedicated to the following aspects:

1) Fundamentally understand and explore the mechanism/behavior of materials under electrochemical energy storage process.

2) Fundamentally and technically find the bottlenecks of current carbon materials for energy storage.

3) Design and implement of novel synthetic method to obtain new class of carbon materials aiming at its current limitations.

4) Fabrication and integration of carbon materials into electrochemical devices and examine their performance to further guide the materials design.
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Chapter 2: High-voltage Symmetric Carbon

Supercapacitors in Aqueous Electrolyte

2.1 Introduction

Supercapacitors, served as intermediates between conventional dielectric capacitors and batteries, offer a promising alternative approach to meet the increasing demands of energy storage systems such as portable electronic devices and automotive vehicles.[1][2][3] Among the various materials adopted in supercapacitor, carbon shows a particularly promising prospect due to its low cost, high conductivity, robust mechanical behavior, and excellent stability in different temperatures and electrolytes. Carbon based supercapacitors have demonstrated higher power density and super long cycling life (over 10,000 W kg\(^{-1}\) for over 10,000 cycles) than most batteries (below 1000 W kg\(^{-1}\) under 1000 cycles).[4] However, their lower energy density (5 W h kg\(^{-1}\) for commercial supercapacitors) remains far not satisfied than Lithium-ion batteries (70-100 W h kg\(^{-1}\)).[5] Therefore, intensive efforts have been dedicated to increase the energy density of carbon based supercapacitors without sacrificing its high power density and stable long cycling life.[6][7][8]

According to the formula estimating the energy density of supercapacitor \(E = C_s V^2/2\), it is apparent that two directions can be considered to enhance the energy density, namely increasing the specific capacitance \(C_s\) and enlarging the cell working voltage \((V)\). Due to the square term of \(V\), it is more efficient to extend working voltage to achieve a higher energy density. Consequently, extensive research aims at enlarging the operating voltage of supercapacitors.[9][10][11][12] Basically, \(V\) is limited by the matching between electrochemical potentials of electrodes and the stable voltage window of electrolytes.[13] From this point of view, the organic electrolytes usually yield a wider operating potential
window (2.5V-2.7V) than aqueous electrolyte (less than 1.0V).[9] However, nonaqueous electrolytes generally give rise to a series of shortcomings, such as low conductivity, environmental unfriendliness, unsatisfied security issue, high cost in materials and production, and complicated manufacturing condition like moisture isolated building atmosphere.[9][10] Accordingly, from the practically industrial vision, aqueous electrolyte system is assumed to be more acceptable and applicable.

Currently used aqueous electrolytes mainly include acid (H₂SO₄, H₃PO₄, et al), basic (KOH, NaOH, et al) and neutral solutions (Li₂SO₄, Na₂SO₄, et al). According to the Nernst equation, the thermodynamic limits for di-oxygen and di-hydrogen evolution at the positive and negative electrodes are pH dependent and given simplified by the equations $E_{\text{ox}}=1.23-0.059\text{pH}$ and $E_{\text{red}}=-0.059 \ \text{pH}$ vs SHE, respectively.[14] In other words, either over-low or over-high pH values will lead to a more narrow working voltage window, which explains why the working voltages of acid and basic electrolyte are usually less than 1V.[15][16] By contrast, recent reports find that salt aqueous electrolyte exhibits excellent stability under high galvanostatic charging/discharging voltage up to 1.6V-1.9V, which demonstrate the potential of carbon materials for developing a high-voltage, long-cyclability system with neutral aqueous electrolyte. Thereafter, different kinds of carbon have been studied towards the application in high-voltage symmetric capacitors, such as commercial activated carbon and carbon nanotube (CNT).[10][11][17] Whereas, the capacitance of neither commercial activated carbon nor CNT is not satisfied due to their low surface, ununiformed pore size distribution and non-stable carbon structures. Therefore, how to develop a carbon with well-defined structure, controllable pore structure, remains a challenging issue.

2.2 Results and Discussion

Here, we develop a new class of nanoporous carbons towards the application of high-voltage symmetric supercapacitors used in aqueous Li₂SO₄ electrolyte. As shown in Figure
2.1 A unique precursor called diphenylsilanediol (DPSD) was adopted to prepare the porous carbon. One DPSD molecule consists of two benzene rings and two hydroxyl groups, centered with a silicon atom. After polymerization with assistance of HCl and carbonization under high temperature, DPSD will polymerize into a consistent interlinked benzene rings with embedded ultrafine silica nanoparticles, leading to a high char yielding and robust carbon framework. Due to the atomically integrated organic and inorganic components distributed in the carbon-silica matrix, uniformly sized nanopores can be generated after removing the silica moiety by hydrofluoric acid (HF). Finally, the as-prepared nanoporous carbon (devoted as NC) were activated by potassium hydroxide (KOH) and followed by HNO₃ washing, with a synchronous introduction of oxygen-enriched functionalities onto carbon surface. The porosity and oxygen content of the resulting oxygen-enriched nanoporous carbon (ANC) are controlled by the mass of KOH to NC during activation (see details in the experimental section). ANC prepared with different KOH/carbon ratios (1:1 and 3:1) are denoted as ANC-1 and ANC-2, respectively. The obtained ANC effectively increases the capacitance of the nanoporous carbon and shows a stable electrochemical performance in aqueous Li₂SO₄ electrolyte up to 1.6V.
The nitrogen-sorption isotherms and pore size distributions of NC and ANC are illustrated in Figure 2.1 B and C. Before activation, the Brunauer-Emmett-Teller (BET) surface area of NC is only 440 m$^2$ g$^{-1}$ and the pore size is less than 1nm. During reaction with KOH, it is suggested that the activation of carbon with KOH proceeds as $6\text{KOH} + \text{C} \rightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3$,

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.jpg}
\caption{(A) Schematic illustration of the synthesis procedure of oxygen-enriched nanoporous carbon. TEM images of (B) NC and (C) ANC-2. Insets are the corresponding HRTEM images.}
\end{figure}

followed by decomposition of $\text{K}_2\text{CO}_3$ and/or reaction of $\text{K}/\text{K}_2\text{CO}_3/\text{CO}_2$ with carbon.[18] The process will generate nanoscale pores in the product carbon. As shown in Figure 2.1B, the
The surface areas of ANC-1 and ANC-2 are enlarged to 1076 m$^2$ g$^{-1}$ and 2634 m$^2$ g$^{-1}$, respectively, and the pore size distributions of ANC-1 and ANC-2 are also extended to around 2 to 3 nm. The inner structures of NC and ANC are further revealed by transmission electron microscope (TEM) images, as shown in Figure 2.1D and E. In Figure 2.1D, the NC shows an amorphous and compact network of tiny pores less than 1 nm with low visibility (see the inset High-resolution TEM images, (HRTEM)). By contrast, for product ANC-2, the worm-like carbon framework is apparently loosened and opened up. The pore size is enlarged to around 2.5 nm, as shown in Figure 2.1E and its inset.

![Figure 2.2](image)

**Figure 2.2** (A) XRD patterns of NC, ANC-1 and ANC-2. (B) Raman images of NC and ANC-2 respectively.

**Figure 2.2 A** shows the powder X-ray diffraction (XRD) images of the as-obtained carbon samples. For product NC, two slight peaks positioned near 2$\Theta$ values of 26.3° and 44.1° refer to the (002) and (100) plane of graphite, reflecting an incomplete and weak graphitization in the amorphous carbon.[19] Considering the high content of sp$^2$ carbon in DPSD polymer, it is suspected that the weak graphitization in NC comes from the long-range orderly benzene rings rising from the DPSD-derived carbon. After activation, compared with
NC, the (002) peak of ANC-2 has a markedly reduced intensity and is dramatically broadened. A large increase in the low-angle scatter from ANC-2 is also noted, which is consistent with the presence of a high density of pores. All of these results are consistent with the observations from HR-TEM, which indicate that the higher porosity induced by chemical activation interrupted the originally weak graphitization but contribute to a more loose and open amorphous carbon structure.

The surface chemistry of the samples before and after the activation is characterized using X-ray photoelectron spectroscopy (XPS), as shown in Figure 2.3. The carbon peak of the non-activated NC (Figure 2.3A) is deconvoluted into 4 constituents located at 284.6, 286.2, 287.9, and 289.0 eV, which are assigned to carbon sp2/sp3, C-O, C=O, and -COO- bonds, respectively. The atom percent of carbon bonding state is listed in Table 1, which shows that the C-C occupies a high content of the total material. In contrast to the control,
C1s spectra of the ANC-1 and ANC-2 (Figure 2.3B and Figure 2.3C) can be deconvolved into the same peaks; however the percent of C-C bonds decreases to 71.6% and 65.5% respectively. The decrease in the carbon content illustrates that the activation process corrodes the carbon and introduces oxygen-containing groups instead. Similarly, the O1s spectrum of the NC sample in Figure 2.3E is deconvolved into two constituent peaks located at 531.0 and 532.4 eV, which are assigned to the carbonyl/carboxyl groups and hydroxyl groups, respectively.\textsuperscript{[22],[23]} In line with the carbon bonding state distribution mentioned above, the oxygen bonding shows a similar tendency. For ANC-1 and ANC-2 shown in Figure 2.3F and Figure 2.3G, the proportion of C-OH peak gradually decrease whereas the content of C=O peak increase instead, indicating that the activation process will lead to a higher degree of oxidation and more carbon oxygen double bonds are formed. As shown in Table 1, for NC before activation, the oxygen atom displayed by hydroxyl groups takes account for 86.1%. By comparison, the C=O bonding percent increase from 3.2% to 30.7% and 34.4% for ANC-1 and ANC-2.

\textbf{Table 2.1} Composition and pore properties of F-rich nanoporous carbons.

| Sample | MC:KOH w:w | $S_{BET}$ m$^2$ g$^{-1}$ | at.% of carbon bonding state | at.% of oxygen bonding state |
|--------|-------------|-------------------|-----------------|-----------------|-----------------|
|        |             |                   | C-C | C-O | C=O | O-C=O | C=O | OH | ads |
| NC     | 0           | 440               | 77.9 | 15.1 | 7.0  | 3.2   | 86.1 | 10.7 |
| ANC-1  | 1           | 1076              | 71.6 | 18.4 | 5.0  | 4.9   | 30.7 | 47.7 | 21.6 |
| ANC-2  | 3           | 2634              | 65.5 | 18.9 | 5.5  | 10.1  | 34.4 | 42.1 | 23.5 |
Under working voltage of 1V, cyclic voltammograms of (A) ANC and (B) ANC-2 at various scan rates. Galvanostatic charge/discharge curves of (C) NC and (D) ANC-2 at different current densities.

The electrochemical performance of the ANCs was evaluated in Li$_2$SO$_4$ electrolyte at both regular voltage and high-voltage window (see the SI for experimental details). Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) curves were used to characterize the capacitive properties of our carbon materials. Figure 2. 4A shows that the non-activated sample NC exhibits a distorted and narrow shape at various scan rates ranging from 5 to 200 mV s$^{-1}$ at the working voltage window to 1V, which corresponds to a low capacitance due to its low surface area (440 m$^2$ g$^{-1}$) and very small pore size (less than 1nm). To the contrary, the CV curves of activated sample ANC-2 is distinctly expanded and
enlarged under the same testing conditions, as shown in Figure 2. 4B. ANC-2 presents a typical capacitive behavior with a rectangular-like shape of the voltammetry characteristics, suggesting an improved capacitance and better ion transportation capability. The GCD test also shows a clear difference of the charge/discharge behavior for the carbon before and after activation (Figure 2. 4C and 4D), which is consistent with the CV curves. ANC-2 in Figure 2. 4D exhibits inclining straight lines at different current densities while the curves for NC (see Figure 2. 4C) is asymmetric and bent. Both the results of CV and GCD analysis reveal nearly ideal double layer capacitive behavior and excellent rate capability of the ANCs. Based on the GCD analysis, the specific capacitances of ANCs at different current densities are summarized and compared in Figure 2. 6A. There is a strong correlation between the degree of activation and the specific capacitance of the ANCs; namely, ANCs prepared with higher degree of activation deliver higher electrochemical capacitance. In particular, ANC-1 and NC only show specific capacitances of 53, and 181 F g\(^{-1}\) at a current density of 0.5 A g\(^{-1}\), respectively. In contrast, ANC-2 delivers a highest specific capacitance of 241 F g\(^{-1}\) at a current density of 0.5 A g\(^{-1}\), and retains a high value of 147 F g\(^{-1}\) when the current density even increases to 80 A g\(^{-1}\). Note that for most currently studied oxygen-doped carbons, the current densities applied during test are usually quite narrowed and limited due to the severe self-discharge causing by the surface functionalities, which limits the power density of carbon materials. Here in our work, ANC-2 could remain 61\% of the maximum capacitance even under a quite high current density of 80 A g\(^{-1}\), which is comparable to the best results reported until now.

Besides the regular working voltage window of 1V, capacitive performance of ANC-1 and ANC-2 were also evaluated under high voltage of 1.6V in Li\(_2\)SO\(_4\) electrolyte assessed with the best-practice symmetric two electrode system. As illustrated in Figure 2. 5A and 5B, both ANC-1 and ANC-2 show a near-rectangular shape in CV test, which represent favorable
ion transportation and good conductivity of the carbon materials. The GC curves for ANC-1 and ANC-2 at different current densities are shown in Figure 2. 5C and 5D. The specific capacitance of ANC-1 and ANC-2 at a current density 0.5A g\(^{-1}\) was calculated to be 357 F g\(^{-1}\) and 253 F g\(^{-1}\) from the discharge curve respectively (see Figure 2. 6B), both of which are higher than its counterparts tested in 1V. This capacitance improvement at higher voltage is assumed to reveal an improved access of ions to hardly accessible pores of the carbon electrodes under the effect of the electric field.[22] Even at high current densities of 10 A g\(^{-1}\), the capacitance of ANC-1 and ANC-2 still remain 253 F g\(^{-1}\) and 145 F g\(^{-1}\), showing an excellent rate performance of the carbon materials at high voltage.

Figure 2. 5. Under high working voltage of 1.6V, cyclic voltammograms of (A) ANC-1 and (B) ANC-2 at various scan rates. Galvanostatic charge/discharge curves of (C) ANC-1 and (D) ANC-2 at different current densities
Figure 2.6 Relationships of the specific capacitance and current densities of different carbons under different working voltages of (A) 1V and (B) 1.6V. (C) Nyquist plots of different carbon-based electrodes; inset shows the plots in high frequency region. (D) Long-term cycling performance of symmetric supercapacitors based on ANC-2 at 1.6V.

To further study the facilitated ion-transport kinetics of the carbons, electrochemical impedance spectroscopy (EIS) was tested. The Nyquist plots were obtained in the frequency range 10MHz to 10 kHz with a two electrode test system, as shown in Figure 2.6C. The vertical nature of the Nyquist plots clearly indicates the capacitive behavior of the carbon materials. The Nyquist plot expanded in the high frequency region is given in the inset. The x-intercept of the Nyquist plot in Figure 2.6C gives the Ohmic resistance of the circuit which is a combination of the resistance of the electrolyte, internal resistance of the active materials and the substrate, and the contact resistance at the active material-current collector.
interface. The intercept values of NC, ANC-1 and ANC-2 are close to zero, illustrating a superior conductivity of the devices we set up. The small semicircles in the high frequency region are due to the electrical double layer formation at the electrode electrolyte interface. The equivalent series resistance is the sum of the Ohmic resistance and the charge transfer resistance, which is observed to be 15 Ω, 2.6 Ω, and 1.73 Ω for NC, ANC-1 and ANC-2 respectively. Since the Ohmic resistance of these three carbon materials is near zero and almost can be negligible, the decrease of charge transfer resistance is thought to attribute to the better wettability induced by the oxygen-functional groups from activation process.

![Figure 2.7](image)

**Figure 2.7** Ragone plots comparing the energy density and power density of the supercapacitor based on ANC-2 in this work and representative literature reports: (■) Polymer derived carbon, (●) Activated graphene, (▲) 3D hexaporous carbon, (▼) Nitrogen enriched carbon, (☆) this work tested under 1V, and (★) this work tested under 1.6V.

Additionally, symmetric supercapacitors based on ANCs demonstrate excellent stability for long-term operation. As shown in **Figure 2.6D**, at a large working voltage window of 1.6 V, only minor capacitance decay is observed after GCD measurement at a high current density of 5 A g⁻¹ for 10000 cycles. In virtue of the high specific capacitance,
excellent rate capability and large operation voltage window, the symmetric supercapacitor assembled based on the representative sample, namely ANC-2, shows high energy and power density. As shown in the Ragone plots (Figure 2.7), when the working voltage is 1V, the ANC-2 supercapacitor delivers a moderate gravimetric energy density of 9.31 Wh kg\(^{-1}\) at a power output of 127.3 W kg\(^{-1}\), and the energy density could remain up to 61% (5.64 Wh kg\(^{-1}\)) when the power density increases to 40090 W kg\(^{-1}\). Moreover, when the working voltage is up to 1.6V, the energy density is boosted to almost double than before. The energy density of ANC-2 reaches as high as 31.7 Wh kg\(^{-1}\) at a power of 100 W kg\(^{-1}\), and it still remains 12.9 Wh kg\(^{-1}\) at a high power density of 10108 W kg\(^{-1}\). The electrochemical performance of the ANC-2 supercapacitor is much better to the reports of carbon-based materials due to its enlarged working voltage, such as polymer derived carbon, activated graphene, 3D hexaporous carbon, and nitrogen enriched carbon.

### 2.3 Conclusion

In summary, we have developed a novel and facile approach to synthesize oxygen-enriched nanoporous carbons with tunable porosity and oxygen content. The key synthesis procedure involves a precursor with unique structure to maintain its uniformly-distributed pores and subsequent KOH activation. The KOH activation process effectively enlarges the pore size, increases the surface area, and facilitates the oxygen doping in the nanoporous carbons, all of which significantly improve the electrochemical capacitive performance of activated nanoporous carbons. The optimized ANC-2 nanoporous carbon manifests a high specific capacitance of up to 241 F g\(^{-1}\) in a symmetric cell with excellent retention at high rates and upon prolonged cycling. In particular, this kind of nanoporous carbon also shows high capacitance, excellent rate performance as well as stable cycling under a high voltage of 1.6V in Li\(_2\)SO\(_4\) electrolyte. The enlarged working voltage window significantly boosted the energy
density. The symmetric cell exhibits a high energy density of 31.7 Wh kg\(^{-1}\) at a power density of 100 W kg\(^{-1}\), and retains a high value of 12.9 Wh kg\(^{-1}\) at an ultrahigh power output of 10108 W kg\(^{-1}\), which outperforms most of the representative carbon-based supercapacitors. The present study demonstrates a simple and effective strategy to increase the double layer capacitance in carbon-based materials, and provides some important insights regarding the high voltage carbon electrodes in supercapacitors. The as-developed nanoporous carbon would also find its applications in many other fields, such as fuel cells and lithium-ion batteries.

### 2.4 Experimental Section

*Synthesis of nanoporous carbon (NC):* Diphenylsilanediol (3g) was dissolved in 20 ml of anhydrous ethanol. Concentrated hydrochloride acid (0.7 ml) was drop wise added in the solution in 5 min. The solution was continuously stirred and heated at 200 °C until the solvent evaporated thoroughly and turned into a transparent and viscous oily liquid. The oily liquid was cooled down under room temperature and then carbonized at 900 °C for 3 h in nitrogen gas with a heating rate of 3 °C min\(^{-1}\). The as-obtained product was successively washed with 5 % hydrofluoric acid and distilled water until the solution is neutral. The nanoporous carbon was finally treated at 900 °C under the atmosphere of nitrogen to be purified.

*Synthesis of Oxygen-enriched nanoporous carbon (ANC):* The NC was mixed with potassium hydroxide under different mass ratios of 1:1 (ANC-1) and 3:1 (ANC-2), respectively. The samples were then heated to 800 °C for 1 h in nitrogen gas with a heating rate of 5 °C min\(^{-1}\). The activated samples were washed with a 10 % nitric acid for 5 times. Then the samples were washed with distilled water and dried at 110°C under vacuum.
**Characterizations:** Nitrogen-sorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 analyzer (Micromeritics Instrument Corporation, Norcross, GA). Specific surface areas (SSA) were calculated by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was determined from the adsorption branch of the isotherm based on the Barrett-Joyner-Halenda (BJH) method. TEM analysis was conducted on a FEI Tecnai™ transmission electron microscope (200kV). Powder X-ray diffraction was operated on the Rigaku MiniFlex II (Rigaku, Japan) using Cu Kα radiation (λ=0.15406 nm). XPS was conducted with a PHI 3057 spectrometer using Mg Kα X-rays source at 1253.6 eV. Raman spectra were obtained using a Renishaw 1000, with a 50 objective lens at an excitation wavelength of 514 nm.

**Electrode Fabrication and Electrochemical Measurements:** A two-electrode cell configuration was used to measure the electrochemical performance of the ANCs. Briefly, 10 % of polytetrafluoroethylene (PTFE; 5 wt% dispersion in water), 10 % of carbon black and 80 % of the electrochemical active material was dispersed in ethanol. The slurry was mixed into a paste using a mortar and pestle, rolled into electrode sheets with size of 0.5 cm * 0.5 cm (size variation < 5 %). A pair of electrodes typically had a weight of 6 mg (mass variation < 5 %) after drying overnight at 110 °C under vacuum. The two identical electrodes were coated onto nickel-foam substrates and pressed at a pressure of 2MPa for 5 minutes. The electrochemical impedance measurements were carried out on a Solartron 1860/1287 Electrochemical Interface (Solartron Analytical, Oak Ridge, TN). The EIS tests were operated in the frequency range of 10 mHz to 100 kHz with 10 mV AC amplitude. The cyclic voltammetry test and galvanostatic charge and discharge test were conducted using EC-LAB on a Bio Logic VMP-3 (Bio Logic Science Instruments, Claix, France). Symmetric cells were charged and discharged between 1V to 0 V for the normal voltage range, and 1.6V to 0V for
the high voltage range. The specific gravimetric capacitance of the supercapacitor cell was calculated according to the following Equation (2.1):

\[
C_{cell} = \frac{I\Delta t}{m\Delta V}
\]

where I (A), \(\Delta t\) (s), \(\Delta V\) (V), and m (g) are the discharge current, discharge time, potential window during the discharge process, and the mass of a single electrode, respectively. The specific capacitance of the single electrode was calculated by the following equation of \(C_s = 2C_{cell}\). The energy density and power density were calculated using the formula in Equation (2.2) and Equation (2.3):

\[
E_s = C_sV_{max}/8\times 3.6
\]

\[
P_s = E_s/t
\]

where \(E_s\) is the specific energy density, \(V_{max}\) is the maximum voltage window, \(P_s\) is the power density and \(t\) is the discharge time.

Reference


Chapter 3: Fluorine-rich Nanoporous Carbon with Enhanced Surface Affinity in Organic Electrolyte for High-Performance Supercapacitors

3.1 Introduction

Supercapacitors are desirable energy-storage devices due to their high power density and long cycling life, yet their low energy density still limit their broad applications. Supercapacitors commonly utilize carbon as both (symmetric supercapacitors) or one of the electrodes (asymmetric supercapacitors), of which the device capacitances are generally limited by the capacitance of the carbon electrodes. Developing better carbon materials with higher capacitance and working voltage has been emerging as one the most essential challenges in the field.

Generally, carbon electrodes store electrochemical energy in the form of electrical double layer capacitance, which requires high surface area and highly effective electron-conducting pathways. Towards this goal, a large variety of carbons have been studied, such as biomass-derived carbons, polymer-templated carbons, carbide-derived microporous carbons, and carbon onions. While most of the research has been focused on engineering the pore structure, recent studies have shown that doping the carbons with heteroatoms could improve the capacitance, possibly owning to the improved charge mobility and wettability with electrolytes. Such doping processes are generally achieved by reacting carbons with heteroatom-containing agents or by carbonizing heteroatom-containing precursors. Nitrogen is by far the most intensely studied n-type dopant, which is generally doped into carbons by treating the carbons with ammonia gas or urea, or by carbonizing nitrogen-containing precursors such as melamine, poly(acrylonitrile), poly(vinylpyridine), and
quinolone-polymerized pitch.\textsuperscript{[5][12]} Doping with other heteroatoms such as boron, phosphorous and sulfur, was also explored, which was realized by carbonizing boron-containing precursors\textsuperscript{[13]} by carbonizing sulfurated polymers\textsuperscript{[14]} or by activating carbon precursors using phosphoric acid, respectively\textsuperscript{[15]} However, despite of the improved capacitance, most dopant moieties (e.g., quinoid, quinhydrone, phenolic, carbonxyl, carbonyl and lactone) are electrochemically unstable, often resulting in increased leakage current and poor cycling performance\textsuperscript{[16][17]}

Fluorine (F), the element with the highest electronegativity, is capable of forming the fluorine-carbon bond with high polarity and stability\textsuperscript{[18][19]} F-doped carbons have enabled widespread applications such as semiconductor-based devices, primary lithium-ion batteries, and supercapacitors\textsuperscript{[20][21][22]} Most of the existing F-doped carbons are prepared using gaseous phase or plasma dissociation of F-containing agents (e.g., F\textsubscript{2}, XeF\textsubscript{2}, CF\textsubscript{4} et. al.), which are hazardous and expensive\textsuperscript{[23][24][25][26]} Especially for supercapacitors, both gaseous and isoionic fluorine could corrode the pristine carbon and lead to an unexpected structural distortion, resulting in decrease of surface area and drop in capacitance\textsuperscript{[27][28]} Therefore, it remains a critical challenge to achieve F-doping carbons with high F content, intact carbon structure and superior electrochemical performance using a facile synthesis approach.

3.2 **Results and Discussion**

In this work, we report a simple method to synthesize F-rich nanoporous carbons for high-performance supercapacitors. As shown in Figure 3. 1A, a diphenylsilanediol (DPSD)-derived polymer is chosen as a unique carbon precursor that atomically integrates both the organic and inorganic components. Carbonization process leads to the formation of carbon/silica nanocomposites embedding ultrafine silica moieties. Subsequent removal of the silica moieties by hydrofluoric acid (HF) etching creates nanoporous carbons with uniform
pore structure. Finally, the as-prepared nanoporous carbon (denoted as NC) is activated using KOH, and followed by a simple F doping approach via washing with a mixture of HF and nitric acid. The porosity and F content of resulting F-rich nanoporous carbons (denoted as FNCs) are controlled by the mass ratios of KOH to NC used during the activation (see experimental details in the Supporting Information (SI)). F-rich nanoporous carbons prepared with different KOH/carbon ratios (1:1, 3:1, 6:1 and 9:1) are denoted as FNC-1, FNC-2, FNC-3, and FNC-4, respectively. The F doping effectively increases the stability and capacitance of the nanoporous carbons, offering a new class of electrode materials for high-performance supercapacitors.
**Figure 3.** (A) Schematic illustration of the synthesis procedure of fluorine-rich nanoporous carbon. (B) Nitrogen sorption isotherms and (C) pore size distribution of NC and FNCs. TEM images of (D) NC and (E) FNC-4. Insets are the corresponding HRTEM images.

**Figure 3.** 1B and C show the nitrogen-sorption isotherms and pore size distributions of the nanoporous carbons before and after the activation and F doping. Before the activation, the NC exhibits a microporous structure (pore size around 1nm) with a moderate Brunauer-Emmett-Teller (BET) surface area of \( \sim 455 \text{ m}^2 \text{ g}^{-1} \). After the activation and doping process, the pore size and surface area of FNCs are substantially increased with increasing mass ratios of KOH to carbon. For example, FNC-4 prepared with a high KOH/carbon ratio (9:1) exhibits an exceptionally high BET surface area of 3231 m\(^2\) g\(^{-1}\). Meanwhile abundant mesopores with size centered at around 3.4 nm are also generated.

The pore structure of the NC and FNCs is also investigated by transmission electron microscopy (TEM). The pristine NC exhibits a less porous texture (**Figure 3.** 1D), which is consistent with the results of nitrogen-sorption analysis. The insufficient porosity and small pore size make the inner region of the NC hardly accessible to electrolyte, which is unfavorable for electrical double layer charge storage. On the other hand, higher porosity and larger pores can be easily observed in FNCs with increasing KOH/carbon ratio during the activation (**Figure 3.** S1, see the SI, and **Figure 3.** 1E). Specifically, in line with the previous discussion, the high resolution (HR) TEM image (inset of **Figure 3.** 1E) reveals that the pores in FNC-4 are enlarged to around 3 nm with high uniformity and well interconnected, offering a highly porous and open framework. NC and FNCs all exhibit an amorphous feature with low graphitic degree as confirmed by both the powder X-ray diffraction (XRD) patterns and Raman spectra (**Figure 3.** S2, see the SI).
Figure 3. 2. (A) XPS wide scan spectra of NC, FNC-1, FNC-2, FNC3, and FNC-4. (B) F1s XPS spectrum of FNC-4. C1s XPS spectra of (C) NC and (D) FNC-4. O1s XPS spectra of (E) NC and (F) FNC-4.

The surface chemistry of the samples before and after the activation and F doping is characterized using x-ray photoelectron spectroscopy (XPS), as shown in Figure 3. 2. The wide scan spectrum shown in Figure 3. 2A illustrates sharp C1s and O1s peaks in NC. After activation and F doping, the C1s and O1s peaks are weakened, whereas distinct F1s and F KLL peaks are observed. No other elemental peaks can be observed in the FNCs, indicating
the absence of impurities in the samples. The F1s spectrum of FNC-4 (Figure 3. 2 B) is further deconvolved into four peaks located at 687.7, 688.6, 689.6 and 690.9 eV, which are assigned to covalent CF₃, covalent CF₃ with charge effect (CE), perfluorinated CF bonding, and perfluorinated CF bonding with CE, respectively. The covalent bonding state and high content of F reveal stable and efficient F doping on the carbon surface, which is further confirmed by the C1s and O1s spectra as shown in Figure 3. 2C to F. The carbon peak of the non-activated NC (Figure 3. 2C) is deconvolved into 5 constituents located at 284.6, 286.2, 287.9, and 289.0 eV, which are assigned to carbon sp²/sp³, C-O, C=O, and -COO- bonds, respectively. In contrast to the control, C1s spectra of the FNC-4 (Figure 3. 2D) are deconvolved into additional peaks, including CF₃ (x = 1, 2), CF₄ (x = 2, 3), CF₃, and CF₃ with CE that are located at 288.8, 290.6, 292.0, and 294.0 eV, respectively. Similarly, the O1s spectrum of the NC sample in Figure 3. 2E is deconvolved into two constituent peaks located at 531.0 and 532.4 eV, which are assigned to the carbonyl/carboxyl groups and hydroxyl groups, respectively. An extra peak at 535.2 eV appears in the deconvolved O1s spectrum of FNC-4 as shown in Figure 3. 2F, which is contributed to oxygen bonded to perfluorinated (CF₃O). FNC-1 to FNC-3 also exhibit similar XPS spectra with F-containing species as shown in Figure 3. S3 (see SI).

Table 1 summarizes the information of the porous structure and chemical composition of FNCs obtained from nitrogen-sorption and XPS analysis, respectively. It is obvious that the degree of activation (i.e., the KOH/carbon ratio) primarily plays dual roles to the FNCs. First, a higher degree of activation results in larger pores and higher surface area, as discussed earlier. Second, the F content in the FNCs also strongly depends on the degree of activation. Specifically, from FNC-1 to FNC-4, the F content increases remarkably from 7.8 to 17.5 atom-%, accompanied by the reduction of carbon content. This phenomenon suggests that KOH activation plays a critical role in the subsequent F doping. Note that most
of reported F doping methods rely on the gaseous phase reactions between F and carbon at high temperature, which is highly toxic, operationally inconvenient and casing unwanted changes of carbon texture.\textsuperscript{[18][19]} In a sharp contrary, the F doping in this work is achieved under ambient conditions without altering the carbon structure, which easily introduces a rather high and controllable F content on the carbon surface. Comparison of the synthesis methods and carbon structure between our work and previous studies is summarized in Table S1 (see the SI), which highlighted the advantages of our F doping method.

Table 1 Composition and pore properties of F-rich nanoporous carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MC:KOH w:w</th>
<th>S\textsubscript{BET} m\textsuperscript{2} g\textsuperscript{-1}</th>
<th>PMD\textsuperscript{[a]} nm</th>
<th>C at.%</th>
<th>O at.%</th>
<th>F at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>FNC-1</td>
<td>1:1</td>
<td>1400</td>
<td>&lt; 2</td>
<td>84.7</td>
<td>7.5</td>
<td>7.8</td>
</tr>
<tr>
<td>FNC-2</td>
<td>3:1</td>
<td>2526</td>
<td>&lt; 2</td>
<td>84.3</td>
<td>7.6</td>
<td>8.1</td>
</tr>
<tr>
<td>FNC-3</td>
<td>6:1</td>
<td>3035</td>
<td>2.66</td>
<td>78.1</td>
<td>9.0</td>
<td>12.9</td>
</tr>
<tr>
<td>FNC-4</td>
<td>9:1</td>
<td>3231</td>
<td>3.04</td>
<td>73.8</td>
<td>8.7</td>
<td>17.5</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} (Peak maximum diameter)

A possible mechanism for such KOH-activation-assisted F doping method is proposed here. During the KOH activation, carbon reacts with metal alkalis and generates abundant defects, edge carbon atoms and dangling bonds. When the mixture of reaction products (including carbon, K, K\textsubscript{2}CO\textsubscript{3}, K\textsubscript{2}O, KOH) is washed with hydrofluoric acid, the potassium compounds are removed and the fresh unsaturated carbon surface is exposed.\textsuperscript{[33]} To reduce surface energy, the carbon dangling bonds tend to be terminated by forming covalent bond with foreign groups. In general cases, the dangling bonds are either stabilized by H or by oxygen compounds, such as phenolic, carbonxyl, carbonyl and so on.\textsuperscript{[34]} However in this work, fluorine possesses stronger electronegativity than oxygen, and thus has the
priority to bond with the carbon. Consequently, with increasing activation intensity, higher fluorine content is obtained as a result of more unsaturated carbon bonds generated during activation.

Figure 3. 3. (A) Cyclic voltammogram and (B) galvanostatic charge/discharge curves of FNC-4 at various scan rates and current densities. (C) Relationship of the specific capacitance and current densities of different FNCs. (D) Nyquist plots of different FNC-based electrodes; inset shows the plots in high frequency region. (E) Long-term cycling performance of symmetric supercapacitors based on FNCs. (F) Ragone plots comparing the energy density and power density of the supercapacitor based on FNC-4 in this work and representative literature reports: (■) active carbon,[36] (●) graphic carbon sphere,[37] (▲) sandwich-type carbon nanosheet,[38] (▼) 3D microporous carbon,[39] (♦) interconnected carbon sheet,[40] and (★) FNC-4 in this work.
The electrochemical performance of the FNCs was evaluated using symmetric two-electrode cells with non-aqueous electrolyte (see the SI for experimental details). Figure 3. 3A shows the typical cyclic voltammetry (CV) curves of FNC-4, which exhibit near rectangular shape at various scan rates ranging from 5 to 100 mV s$^{-1}$. Galvanostatic charge/discharge (GCD) curves also exhibit inclining straight lines at different current densities (Figure 3. 3B), which is consistent with the CV curves. Other FNC samples demonstrate similar electrochemical characteristics during CV and GCD measurements (Figure 3. S4 and S5, see the SI). Nevertheless, the ability of the FNCs to preserve the shapes of CV and GCD curves and the delivered specific capacitance increases with the degree of activation, as discussed shortly. Both the results of CV and GCD analysis reveal nearly ideal double layer capacitive behavior and excellent rate capability of the FNCs. Based on the GCD analysis, the specific capacitances of FNCs at different current densities are summarized and compared in Figure 3. 3C. There is a strong correlation between the degree of activation and the specific capacitance of the FNCs; namely, FNCs prepared with higher degree of activation deliver higher electrochemical capacitance. In particular, FNC-4 delivers a high specific capacitance of 168 F g$^{-1}$ at a current density of 0.5 A g$^{-1}$, and retains a high value of 153 F g$^{-1}$ when the current density increases to 10 A g$^{-1}$. In contrast, FNC-3, FNC-2, and FNC-1 only show specific capacitances of 138, 128, and 56 F g$^{-1}$ at a current density of 0.5 A g$^{-1}$, respectively.

To get further insight into the different supercapacitive activity of FNCs, electrochemical impedance spectroscopy measurements were performed. As shown in Figure 3. 3D, the Nyquist plots consist of a straight line in low frequency region and a semicircle in the high frequency region, which are typical for electrochemical capacitors. The semicircles in the high frequency region are illustrated in the inset of Figure 3. 3D. The first intercept of
the plots with x-axis reflects the Ohmic resistance of the cells,\textsuperscript{[35]} whereas the diameter of the semicircle corresponds to the charge transfer resistance. It is found that FNCs with more intense activation exhibit smaller Ohmic resistance and charge transfer resistance, which might be due to the improved wettability of electrolyte on carbon surface as discussed shortly. Meanwhile, the slope of the straight lines in low frequency regions increases along with the activation intensity, indicating promoted ion/electron transportation.

Additionally, symmetric supercapacitors based on FNCs demonstrate excellent stability for long-term operation. As shown in Figure 3. 3E, with a large voltage window of 2.7 V, only minor capacitance decay is observed after GCD measurement at a high current density of 5 A g\textsuperscript{-1} for 10000 cycles. Particularly, FNC-4 exhibits the highest capacitance retention of about 92% after 10000 cycles. In virtue of the high specific capacitance, excellent rate capability and large operation voltage window, the symmetric supercapacitor assembled based on the representative sample, namely FNC-4, shows high energy and power density. As shown in the Ragone plots (Figure 3. 3F), the FNC-4 supercapacitor delivers a high gravimetric energy density of 42.2 Wh kg\textsuperscript{-1} at a power output of 134.9 W kg\textsuperscript{-1}, and the energy density could remain up to 91.8% (38.7 Wh kg\textsuperscript{-1}) when the power density increases to 6750 W kg\textsuperscript{-1}. Even at a very high power density of 40500 W kg\textsuperscript{-1}, the energy density of the supercapacitor is still preserved at 26.5 Wh kg\textsuperscript{-1}. The electrochemical performance of the FNC-4 supercapacitor is superior to that of previous reported F-doped carbon (Table S2, see the SI), and also among the best reports of carbon-based materials, such as activated carbon,\textsuperscript{[36]} hierarchical graphic carbon spheres,\textsuperscript{[37]} interconnected carbon nanosheets,\textsuperscript{[38]} 3D micro-porous carbon from polymer carbonization,\textsuperscript{[39]} and sandwich-type microporous carbon nanosheets.\textsuperscript{[40']} Particularly, the FNC-4 supercapacitor shows excellent energy density retention at ultra-high power output over 10000 W kg\textsuperscript{-1} and obviously outperforms
conventional carbon-based supercapacitors, manifesting its promising high-power applications.

**Figure 3.4.** The simulated electrostatic potential surface for (A) pristine graphene and (B) fluorine doped graphene. The inset is electrostatic potential scale bar; the most negative value is red while the most positive value is blue. Optimized configuration of TEA$^+$ adsorbed on (C) pristine graphene and (D) fluorine doped graphene.

The improved electrochemical capacitive properties of FNCs could be attributed to a synergistic effect of both the pore configuration and carbon surface chemistry. Specifically, a higher surface area could provide more electrolyte accumulation and lead to a higher capacitance. Meanwhile, a suitable pore size would effectively facilitate the electrolyte infusion and ion transport without sacrificing the surface area and the robustness of the porous structure. In particular, the pore size of FNC-4 is marginally larger than twice diameter of the solvated ions, which is proved to be an optimized size distribution to form double layer capacitor.$^{[41]}$ However, high surface area alone does not necessarily result in
high specific capacitance.\textsuperscript{[42][43][44][45]} Incomplete utilization of carbon surface to form electrical double layer in electrolyte due to limited accessibility might be the major reason accounted for the non-linear relationship between surface area and specific capacitance.\textsuperscript{[46]} In this work, we found that F doping is another critical factor that contributes to the high capacitance of FNCs. **Figure 3. S6** (see the SI) compares the capacitances of NCs with and without F doping. All of the FNCs exhibit higher specific capacitances at various current densities compared with their F-free counterparts with the same porous structure. The beneficial effect of F doping is especially significant in FNC-1 with low surface area, which shows capacitance as high as eight times that of F-free counterpart.

To better understand the role of carbon surface chemistry in the capacitive performance, theoretical models of pure carbon surface (CS) and F-containing carbon surface (FCS) with one typical F-containing group were developed to study the interactions between F-doped carbon and electrolyte ions. **Figure 3. 4A and B** shows the simulated electrostatic potential surface for CS and FCS models, respectively. After introducing a F atom into the carbon cluster, the surrounding area becomes more electro-negative, which would alter the interaction with ions in the electrolyte. The most stable geometric configuration between a single tetraethylammonium ion (TEA\textsuperscript{+}) and the CS/FCS models is simulated and illustrated in **Figure 3. 4C and D**, respectively. The calculated adsorption energy changes from -48.97 kJ mol\textsuperscript{-1} for CS model to -67.52 kJ mol\textsuperscript{-1} for FCS model, indicating a stronger affinity between the electrolyte ions and the F-containing surface. Meanwhile the dipole moment of reduces from 4.30 Å in CS model to 3.60 Å in FCS model, which suggests a stronger polarity. Such enhanced interactions between electrolyte ions and F-rich carbon surface might help to build up the electric double layer on the electrode surface. Meanwhile, it is found that F doping also improves the wettability of electrolyte on carbon surface as verified by contact angle measurement in **Figure 3. S7** (see the SI). The contact angle between electrolyte and
electrode decreases from 88.9° for NC to 55.1° for FNC-4, which indicates that F-doping improves the affinity of electrolyte to carbon surface, facilitating transport of electrolyte within the porous frameworks.

3.3 Conclusion

In summary, we have developed a novel and facile approach to synthesize fluorine-rich nanoporous carbons with tunable porosity and F content. The key synthesis procedure involves KOH activation and subsequent hydrofluoric acid washing of a polymer-derived nanoporous carbon. The KOH activation process effectively enlarges the pore size, increases the surface area, and facilitates the F doping in the nanoporous carbons, all of which significantly improve the electrochemical capacitive performance of the F-rich nanoporous carbons. In particular, with the assistance of both experimental and computational methods, we successfully demonstrate that the F-rich carbon surface with higher polarity provides stronger affinity and wettability for the organic electrolyte, which is accounted for the enhanced electrochemical performance. The optimized F-rich nanoporous carbon manifests a very high specific capacitance of up to 168 F g⁻¹ in a symmetric cell with excellent retention at high rates and upon prolonged cycling. The present study demonstrates a simple and effective strategy to increase the double layer capacitance in carbon-based materials, and provides some important insights regarding the origin of enhanced performance in heteroatom-rich carbons. The as-developed F-rich nanoporous carbon would also find its applications in many other fields, such as fuel cells and lithium-ion batteries.

3.4 Experimental Section

Synthesis of nanoporous carbon (NC): Diphenylsilanediol (3g) was dissolved in 20 ml of anhydrous ethanol. Concentrated hydrochloride acid (0.7 ml) was drop wise added in the
solution in 5 min. The solution was continuously stirred and heated at 200 °C until the solvent evaporated thoroughly and turned into a transparent and viscous oily liquid. The oily liquid was cooled down under room temperature and then carbonized at 900 °C for 3 h in nitrogen gas with a heating rate of 3 °C min⁻¹. The as-obtained product was successively washed with 5 % hydrofluoric acid and distilled water until the solution is neutral. The nanoporous carbon was finally dried at 110 °C under vacuum.

**Synthesis of fluorine-rich nanoporous carbon (FNC):** The NC was mixed with potassium hydroxide under different mass ratios of 1:1 (FNC-1), 3:1 (FNC-2), 6:1 (FNC-3) and 9:1 (FNC-4), respectively. The samples were then heated to 800 °C for 1 h in nitrogen gas with a heating rate of 5 °C min⁻¹. The activated samples were washed with a mixing solution of 20 % hydrofluoric acid and 10 % nitric acid for 5 times. Then the samples were washed with distilled water and dried at 110°C under vacuum.

**Characterizations:** Nitrogen-sorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 analyzer (Micromeritics Instrument Corporation, Norcross, GA). Specific surface areas (SSA) were calculated by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was determined from the adsorption branch of the isotherm based on the Barrett-Joyner-Halenda (BJH) method. TEM analysis was conducted on a FEI Tecnai™ transmission electron microscope (200kV). Powder X-ray diffraction was operated on the Rigaku MiniFlex II (Rigaku, Japan) using Cu Kα radiation (λ=0.15406 nm). XPS was conducted with a PHI 3057 spectrometer using Mg Kα X-rays source at 1253.6 eV. Raman spectra were obtained using a Renishaw 1000, with a 50 objective lens at an excitation wavelength of 514 nm.

**Electrode Fabrication and Electrochemical Measurements:** A two-electrode cell configuration was used to measure the electrochemical performance of the FNCs. Briefly, 10 % of polytetrafluoroethylene (PTFE; 5 wt% dispersion in water), 10 % of carbon black and 80 %
of the electrochemical active material was dispersed in ethanol. The slurry was mixed into a paste using a mortar and pestle, rolled into electrode sheets with size of 0.5 cm * 0.5 cm (size variation < 5 %). A pair of electrodes typically had a weight of 3 mg (mass variation < 5 %) after drying overnight at 110 °C under vacuum. The two identical electrodes were assembled into a symmetric cell, which consisted of two current collectors, two electrodes, and an ion-porous separator (glass fiber, GF/C from Whatman). Conductive carbon coated aluminum foils were used as current collectors. The electrolyte was 1 M of tetralkylammoniumtetrafluoroborate (TEA BF4, Sigma Aldrich) in polypropylene carbonate (PC). The assembly of the test cell was done in a glove box filled with Ar. The electrochemical impedance measurements were carried out on a Solartron 1860/1287 Electrochemical Interface (Solartron Analytical, Oak Ridge, TN). The EIS tests were operated in the frequency range of 10 mHz to 100 kHz with 10 mV AC amplitude. The cyclic voltammetry test was conducted using EC-LAB on a Bio Logic VMP-3 (Bio Logic Science Instruments, Claix, France). Galvanostatic charge and discharge test was carried out by LAND CT2000 (Wuhan Jinnuo Electronics, Ltd., Wuhan, China). Symmetric cells were charged and discharged between 2.7 and 0 V. The specific gravimetric capacitance of the supercapacitor cell was calculated according to the following Equation (3.1):

\[ C_{\text{cell}} = \frac{I \Delta t}{m \Delta V} \]  

(3.1)

where I (A), \( \Delta t \) (s), \( \Delta V \) (V), and m (g) are the discharge current, discharge time, potential window during the discharge process, and the mass of a single electrode, respectively. The specific capacitance of the single electrode was calculated by the following equation of \( C_s = 2 C_{\text{cell}} \). The energy density and power density were calculated using the formula in Equation (2.2) and Equation (2.3):

\[ E_s = \frac{C_s V_{\text{max}}}{2} \times 3.6 \]  

(3.2)

\[ P_s = \frac{E_s}{t} \]  

(3.3)
where $E_s$ is the specific energy density, $V_{\text{max}}$ is the maximum voltage window, $P_s$ is the power density and $t$ is the discharge time.

**Method of Computational Modeling:** The fluorine-containing carbon surface (FCS) model was constructed based on a previous work established by Wu et al.[38] Pure carbon surface (CS) model was derived based on C42H16 clusters adopted from investigation of both lithium adsorption and ORR on doped graphene.[39] Density functional theory (DFT) at the B3LYP/6-31G* level was employed for geometry optimization and vibrational frequency analysis, which ensured no imaginary frequencies.[40] The combination of function and basis sets were proved to be reliable and computationally expedient. All the calculations were carried out on Gaussian 09 suite package.[41]

### 3.5 Supporting Information

![Figure S 3.1](image)  
**Figure S 3.1.** TEM images of (A) FNC-1, (B) FNC-2, (C) FNC-3. Insets are the HRTEM images of the corresponding samples.
Figure S 3.2. (A) XRD patterns and (B) Raman spectra of NC and FNC-4.

Figure S 3.3. F1s XPS peaks of (A) FNC-1, (B) FNC-2, and (C) FNC-3, respectively. C1s XPS peaks of (D) FNC-1, (E) FNC-2, (F) FNC-3, respectively. O1s XPS peaks of (G) FNC-1, (H) FNC-2, (I) FNC-3, respectively.
Figure S 3.4. CVs of (A) FNC-1, (B) FNC-2, (C) FNC-3 at different scanning rates ranging from 5 to 100 mV s\(^{-1}\).

Figure S 3.5. Galvanostatic charge/discharge curves of (A) FNC-1, (B) FNC-2, (C) FNC-3 at different current rates ranging from 0.5 to 10 A g\(^{-1}\).

Figure S 3.6. Capacitance of FNCs and corresponding activated samples without HF wash measured at different current densities. The dashed columns numbered 1 to 4 represents FNC-1 to FNC-4, while the blank columns are corresponding counterparts without fluorination.
Figure S 3.7. Contact angle of TEABF$_4$ on (A) NC and (B) FNC-4.
Table S 3.1 Brief summary of current fluorinated carbon on their synthesis method, fluorination content and structure configuration.

<table>
<thead>
<tr>
<th>F-carbon</th>
<th>Fluorination agent</th>
<th>Synthesis Temperature (°C)</th>
<th>Maximum F-doped content [atom%]</th>
<th>SSA_{rc}^{[a]} (m²/g)</th>
<th>SSA_{fc}^{[b]} (m²/g)</th>
<th>SSA_{V}^{[c]} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorinated carbon fibers(^{(1)})</td>
<td>F₂ gas</td>
<td>380–480</td>
<td>45</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Fluorinated mesoporous carbon(^{(2)})</td>
<td>5 vol % diluted fluorine gas (F₂/He)</td>
<td>RT~250</td>
<td>44</td>
<td>437</td>
<td>332</td>
<td>-24</td>
</tr>
<tr>
<td>Fluorinated single wall carbon nanotube(^{(3)})</td>
<td>9 vol % diluted fluorine gas (F₂/He)</td>
<td>150–600</td>
<td>50</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Fluorinated active carbon(^{(4)})</td>
<td>Mixture gas F₂/O₂ (7:3)</td>
<td>RT</td>
<td>7.51</td>
<td>1924</td>
<td>1556</td>
<td>-19</td>
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<tr>
<td>Fluorinated graphene(^{(5)})</td>
<td>XeF₂ gas</td>
<td>30</td>
<td>25</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Fluorinated graphite(^{(6)})</td>
<td>Gaseous mixture of HF, F₂, and IF₅</td>
<td>100–600</td>
<td>49</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Fluorinated multi wall carbon nanotube(^{(7)})</td>
<td>CF₄ plasma</td>
<td>N/A</td>
<td>66</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Fluorinated diamond-like carbons(^{(8)})</td>
<td>CF₄ plasma-assisted CVD</td>
<td>N/A</td>
<td>60</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Fluorinated nanoporous carbon in this work</td>
<td>HF solution (5 wt%)</td>
<td>RT</td>
<td>17.5</td>
<td>3320</td>
<td>3231</td>
<td>-2.7</td>
</tr>
</tbody>
</table>

[a] (Specific surface area of raw carbon) [b] (Specific surface area of fluorinated carbon) [c] (Specific surface area variation before and after fluorination)
<table>
<thead>
<tr>
<th>F-carbon</th>
<th>Fluorination agent</th>
<th>Synthesis Temp (°C)</th>
<th>F-doped content (atom%)</th>
<th>SSA_{NC}^{[a]} (m²/g)</th>
<th>SSA_{NC}^{[a]} (m²/g)</th>
<th>APS_{NC}^{[c]} (nm)</th>
<th>APS_{NC}^{[d]} (nm)</th>
<th>SC_{NC}^{[e]} (F/g)</th>
<th>SC_{NC}^{[f]} (F/g)</th>
<th>SSA_{NC}^{[g]} (%)</th>
<th>SSA_{NC}^{[h]} (%)</th>
<th>SC_{NC}^{[i]} (F/g)</th>
<th>SC_{NC}^{[j]} (F/g)</th>
<th>SC_{NC}^{[k]} (%)</th>
<th>SC_{NC}^{[l]} (%)</th>
<th>F-carbon energy density (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorinated SWCNT^{[9]}</td>
<td>F₂ gas (0.2bar)</td>
<td>200</td>
<td>N/A</td>
<td>133</td>
<td>134</td>
<td>0.12</td>
<td>0.11</td>
<td>72.5 (KOH)</td>
<td>63 (KOH)</td>
<td>0.8</td>
<td>-11.7</td>
<td>-15.1</td>
<td>1.77</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Fluorinated commercial active carbon MSP20^{[10]}</td>
<td>1M HF solution</td>
<td>RT</td>
<td>0.7</td>
<td>2379</td>
<td>2312</td>
<td>0.6</td>
<td>0.6</td>
<td>18.4 F/cm³ (TEATBF₄)</td>
<td>19.8 F/cm³ (TEABF₄)</td>
<td>-2.8</td>
<td>0</td>
<td>7.5</td>
<td>8.4 Wh/L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorinated phenol-based active carbon^{[11]}</td>
<td>F₂O₃ gas (3:7)</td>
<td>RT</td>
<td>4.17</td>
<td>1924</td>
<td>1894</td>
<td>0.6</td>
<td>0.75</td>
<td>325 (H₂SO₄)</td>
<td>371 (H₂SO₄)</td>
<td>-1.6</td>
<td>25.0</td>
<td>14.1</td>
<td>12.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorinated phenol-based active carbon^{[11]}</td>
<td>F₂O₃ gas (5:5)</td>
<td>RT</td>
<td>4.23</td>
<td>1924</td>
<td>1876</td>
<td>0.6</td>
<td>0.75</td>
<td>325 (H₂SO₄)</td>
<td>397 (H₂SO₄)</td>
<td>-2.5</td>
<td>25.0</td>
<td>22.2</td>
<td>13.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorinated phenol-based active carbon^{[11]}</td>
<td>F₂O₃ gas (7:3)</td>
<td>RT</td>
<td>7.51</td>
<td>1924</td>
<td>1556</td>
<td>0.6</td>
<td>0.78</td>
<td>325 (H₂SO₄)</td>
<td>269 (H₂SO₄)</td>
<td>-19.1</td>
<td>30.0</td>
<td>-17.2</td>
<td>9.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorinated phenol-based active carbon^{[11]}</td>
<td>F₂N₂ gas (1:9)</td>
<td>RT</td>
<td>0.04</td>
<td>1875</td>
<td>2036</td>
<td>0.6-2.0</td>
<td>0.6-2.0</td>
<td>375 (H₂SO₄)</td>
<td>422 (H₂SO₄)</td>
<td>8.6</td>
<td>-</td>
<td>12.5</td>
<td>14.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorinated phenol-based active carbon^{[11]}</td>
<td>F₂N₂ gas (2:8)</td>
<td>RT</td>
<td>0.77</td>
<td>1875</td>
<td>2338</td>
<td>0.6-2.0</td>
<td>0.6-2.0</td>
<td>375 (H₂SO₄)</td>
<td>491 (H₂SO₄)</td>
<td>24.7</td>
<td>-</td>
<td>30.9</td>
<td>17.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorinated phenol-based active carbon^{[11]}</td>
<td>F₂N₂ gas (3:7)</td>
<td>RT</td>
<td>1.13</td>
<td>1875</td>
<td>2286</td>
<td>0.6-2.0</td>
<td>0.6-2.0</td>
<td>375 (H₂SO₄)</td>
<td>255 (H₂SO₄)</td>
<td>21.9</td>
<td>-</td>
<td>-32.0</td>
<td>8.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorinated activated carbon nanofibers^{[12]}</td>
<td>1M KOH activation</td>
<td>RT</td>
<td>7.0</td>
<td>777</td>
<td>590</td>
<td>0.6</td>
<td>1.2</td>
<td>106 (H₂SO₄)</td>
<td>117 (H₂SO₄)</td>
<td>-24.1</td>
<td>100</td>
<td>10.4</td>
<td>4.1</td>
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<tr>
<td>Fluorinated activated carbon nanofibers^{[12]}</td>
<td>4M KOH activation</td>
<td>RT</td>
<td>12.4</td>
<td>1694</td>
<td>1102</td>
<td>0.6</td>
<td>1.2</td>
<td>181 (H₂SO₄)</td>
<td>221 (H₂SO₄)</td>
<td>-34.9</td>
<td>100</td>
<td>22.1</td>
<td>7.7</td>
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<td></td>
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<tr>
<td>Fluorinated activated carbon nanofibers^{[12]}</td>
<td>6M KOH activation</td>
<td>RT</td>
<td>21.7</td>
<td>2369</td>
<td>1209</td>
<td>1.2</td>
<td>1.5</td>
<td>199 (H₂SO₄)</td>
<td>230 (H₂SO₄)</td>
<td>-95.9</td>
<td>25</td>
<td>15.6</td>
<td>8.0</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Fluorinated carbon cloth ACC50^{[13]}</td>
<td>Reflux with pitch fluoride</td>
<td>100</td>
<td>0.20</td>
<td>1291</td>
<td>1256</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>2.8</td>
<td>N/A</td>
<td>N/A</td>
<td>3.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorinated DPSD-derived carbon in this work</td>
<td>FNC-1</td>
<td>RT</td>
<td>7.8</td>
<td>1432</td>
<td>1400</td>
<td>0.94</td>
<td>0.96</td>
<td>12 (TEABF₄)</td>
<td>63 (TEABF₄)</td>
<td>-2.2</td>
<td>2.1</td>
<td>425</td>
<td>15.9</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Fluorinated DPSD-derived carbon in this work</td>
<td>FNC-4</td>
<td>RT</td>
<td>17.5</td>
<td>3320</td>
<td>3231</td>
<td>3.29</td>
<td>3.04</td>
<td>137 (TEABF₄)</td>
<td>168 (TEABF₄)</td>
<td>-2.7</td>
<td>7.6</td>
<td>22.6</td>
<td>42.5</td>
<td></td>
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</table>

[a] (Specific surface area of raw carbon) [b] (Specific surface area of fluorinated carbon) [c] (Average pore size of raw carbon) [d] (Average pore size of fluorinated carbon) [e] (Specific capacitance of raw carbon) [f] (Specific capacitance of fluorinated carbon) [g] (Specific surface area variation before and after fluorination) [h] (Average pore size variation before and after fluorination) [i] (Specific capacitance variation before and after fluorination)
Reference


**Supporting Information Reference**


Chapter 4: Fluorinated Nanoporous Carbon for High Voltage Supercapacitors

4.1 Introduction

The increasing consumption of non-renewable fossil fuels and subsequent climate change pose the challenge for human society to develop clean and sustainable energy resources.[1][2][3] Supercapacitors, usually considered to bridge the advantages of traditional dielectric capacitor and batteries, have attracted more and more attention because of their high power density, stable and long cycling life (>10,000 cycles), no memory effect, low cost, as well as simple charging circuit installation.[4][5] However, the energy density of commercial supercapacitors ranges from 5 to 10 Wh kg\(^{-1}\), which is too low compared with other electrochemical energy storage systems such as 25-35 Wh kg\(^{-1}\) of lead-acid, 40-100 Wh kg\(^{-1}\) of Ni metal hydride, and 120-170 Wh kg\(^{-1}\) of lithium-ion-batteries.[6] Therefore, a supercapacitor that is capable of delivering high energy density is attracting more and more attention in energy technology.

Depending on the charge storage mechanism as well as the active materials used, two main types of supercapacitors can be distinguished. Electric double layer capacitor (EDLC), the most common devices at present, uses carbon-based active materials with high surface area. The second group of supercapacitors, known as pseudo-capacitors or redox supercapacitors, uses fast and reversible surface or near-surface reactions for charge storage. Since supercapacitors commonly utilize carbon as both (symmetric supercapacitors) or one of the electrodes (asymmetric supercapacitors), of which the device capacitances are generally limited by the capacitance of the carbon electrodes, developing better carbon materials with prompted energy density has been emerging as one the most essential challenges in the field.[7][8]
Energy density is dependent on both the capacitance of electrode materials as well as its working voltage, in which the cell voltage plays a more crucial role since it increases two orders of magnitude than capacitance. Hence, enlarging the cell working voltage becomes a more important issue to be addressed.[9][10] Basically for carbon-based EDLCs, the thermodynamic stability requires locating the differential electrode electrochemical potentials within the LUMO and HOMO window of the electrolyte.[1] Exceeding the safe voltage window will lead to severe consequences. First, operation at high voltage approaching the upper limit of the voltage window of the electrolyte produces a large amount of Joule heat in the supercapacitor cell with large internal resistance and results in the decomposition of the electrolyte gradually. Second, the presence of impurities, such as metal and oxygen on the carbon surface, accelerates the decomposition of the electrolyte at high voltage. As a result, the operation voltage of the carbon-based supercapacitor cell in practical use is often between 2.5-3V, quite lower than the voltage window of electrolyte with a theoretical value of over 4V. Consequently, how to fully utilize the full range of voltage window of the electrolyte and therefore increase the energy density of the supercapacitors remains an unsolved problem in the energy storage field.

Up to now, there have been only a few reports on the development of carbon materials towards the high-voltage application in supercapacitors. Ali et al extracted the full potential of single-walled carbon nanotubes (SWCNT) as durable supercapacitor electrodes operable at 4V, in which shows that the highly conductive SWCNT with high purity (>99.98%) would perform as a promising candidate in the high-voltage application.[11] Cui et al reported the fabrication of one-dimensional highly electroconductive mesoporous graphene nanofibers (GNFs) by a chemical vapor deposition method using MgCO₃ · 3H₂O fibers as the template, and was used for a 4V supercapacitor.[12] However, all the reported carbons for high voltage supercapacitors are
purely graphitic structure, which mostly rely on the metal-catalysis method through CVD deposition. Specifically customized equipment is required to ensure the high purity of carbon nanotube/fibers, making the synthesis method complicated and expensive. Activated carbon, which is cheap and easy handling, has been widely used as electrode materials for EDLCs. The specific application for high voltage supercapacitors, however, is really rare since the oxygen-rich functional groups on activated carbon surface are assumed to decompose at high voltage and cause a series of problems like increasing resistance, severe self-discharging and poor cycling performance.[5] Consequently, it is of considerable importance to develop a facial kind of activated carbon for high voltage supercapacitors and diminish the adverse impact from surface oxygen-related functional groups.[13]

Fluorine (F), the element with the highest electronegativity, is capable of forming the fluorine-carbon bond with high polarity and stability.[14][15] F-doped carbons have enabled widespread applications such as semiconductor-based devices, primary lithium-ion batteries, and supercapacitors.[16][17][18] Most of the existing F-doped carbons are prepared using gaseous phase or plasma dissociation of F-containing agents (e.g., F₂, XeF₂, CF₄ et. al.), which are extremely hazardous and expensive.[19][20][21][22] Especially for supercapacitors, both gaseous and isoionic fluorine could corrode the pristine carbon and lead to an unexpected structural distortion, resulting in decrease of surface area and drop in capacitance.[23][24] Therefore, it remains a critical challenge to achieve F-doping carbons with high F content, intact carbon structure and superior electrochemical performance using a facile synthesis approach.

Here, we develop a new kind of fluorinated nanoporous carbon (FNC) which can be operated under 4V for supercapacitors. This carbon possesses a high surface area up to 3474 m² g⁻¹, and high capacity up to 141 F g⁻¹ in TEA BF₄ electrolyte in propylene carbonate (PC). After
enlarging the working voltage to 4V, the power density of this FNC supercapacitor is increased to 78.3 Wh/kg, even comparable to the energy density of nickel-hydrogen battery (75 Wh/kg). The improved supercapacitive performance is speculated to arise from the much stronger fluorine-carbon bond at high voltage and better wettability of FNC surface with electrolyte.

### 4.2 Results and Discussion

![Figure 4.1 TEM images of (A) NC and (B) FNC. Insets are the corresponding HRTEM images.](image)

The synthesis method is similar with that discussed in Chapter 3. Briefly, diphenylsilanediol (DPSD) and resorcinol were used as the starting precursors. The two precursors were polymerized into silane oil under the catalysis of hydrochloric acid. After carbonization at high temperature, carbon matrix with embedded ultrafine silica nanoparticles is obtained due to the atomically integrated organic and inorganic components in the polymer precursor. Instead of only using DPSD as precursors as discussed in Chapter 3, we also introduced resorcinol to polymerize with DPSD in this work, and the silica moiety will be more concentrated in the carbon-surrounded framework. Such hybrid material can ensure the generation of uniformly distributed and sized nanopores throughout the entire carbon material.
after removing the silica moiety by hydrofluoric acid (HF) etching. Finally, the as-prepared nanoporous carbon (denoted as NC) is activated using KOH, and followed by a simple F doping approach via washing with a mixture of HF and nitric acid. The resulting F-rich nanoporous carbons (denoted as FNCs) is doped by fluorine from a simple solution based washing, which effectively increases the stability and capacitance of the nanoporous carbons, offering a new class of electrode materials for high-voltage supercapacitors.

Figure 4.2 (A) Nitrogen sorption isotherms and (B) pore size distribution of NC and FNC.

Figure 4.1 (A) shows the transmission electron microscope (TEM) of the NC. It can be seen that the NC derived directly from carbonized DPSD/resorcinol composite is dense and compact with an average pore size below 1nm. The insufficient porosity and small pore size make the inner region of the NC hardly accessible to electrolyte, which is unfavorable for electrical double layer charge storage. After activation, as shown in Figure 4.1 (B), the structure is significantly loosen and opened up. This pore-enlarging effect is better revealed by the high-resolution TEM (HRTEM) in the insets of Figure 4.1 (A) and (B). After KOH activation, the average pore size of carbon significantly enlarges to over 3nm.
The pore structures of NC and FNC are also illustrated by nitrogen-sorption isotherms and the pore size distributions of the nanoporous carbons before and after the activation and F doping are shown in Figure 4. 2 (A) and (B). Before the activation, the NC exhibits a microporous structure (pore size less than 1 nm) with a moderate Brunauer-Emmett-Teller (BET) surface area of ~ 474 m$^2$ g$^{-1}$. After the activation and doping process, the surface area of FNC could be substantially increased to an exceptionally high value of 3474 m$^2$ g$^{-1}$, which is around seven times that of the NC. Meanwhile abundant mesopores with size centered at around 3nm are generated. Generally, chemical activation like KOH treatment will lead to a diverse pore size distribution of carbon structure. However in this work, the pore size distribution of FNC is uniformly distributed around 3nm to 4nm, which is supposed to come from the uniform nanopores originated from removing the silicon-atom in the carbon-silica composite.
Figure 4. 3 shows the powder X-ray diffraction (XRD) pattern of the carbons before and after activation. In the spectrum of NC, flat peaks located near 2θ values of 21.9° and 43.9° reflect an amorphous structure of the carbon. Comparing the spectrum of NC to that of FNC reveals that the intensity of (002) and (100) peaks reduces after activation while its full width half maximum broadens significantly. A large increase in the low-angle scattering after activation is also noted, which is regarded as the presence of a high density of pores. [25]

![Figure 4. 4 XPS C1s of (A) NC and (B) FNC](image)

The surface chemistry of the samples before and after the activation and F doping is characterized using X-ray photoelectron spectroscopy (XPS), as shown in Figure 4. 4. The carbon peak of the non-activated NC (Figure 4. 4A) is deconvolved into four constituents located at 284.6, 286.2, 287.9, and 289.0 eV, which are assigned to carbon sp2/sp3, C-O, C=O, and -COO- bonds, respectively. [28][29] In contrast to the control, C1s spectra of the FNC (Figure 4. 4B) are deconvolved into additional peaks, including CFx (x = 1, 2), CFx (x = 2, 3) that are located at 288.8 and 290.6 eV, respectively. [26] A possible mechanism for such KOH-
activation-assisted F doping method has been proposed in **Chapter 3**. Briefly, during the KOH activation, carbon reacts with metal alkalis and generates abundant defects, edge carbon atoms and dangling bonds. When the mixture of reaction products (including carbon, K, K₂CO₃, K₂O, KOH) is washed with hydrofluoric acid, the potassium compounds are removed and the fresh unsaturated carbon surface is exposed.[30] To reduce surface energy, the carbon dangling bonds tend to be terminated by forming covalent bond with foreign groups. In general cases, the dangling bonds are either stabilized by H or by oxygen compounds, such as phenolic, carbonyl, carbonyl and so on.[31] However in this work, fluorine possesses stronger electronegativity than oxygen, and thus has the priority to bond with the carbon. Consequently, with increasing activation intensity, higher fluorine content is obtained as a result of more unsaturated carbon bonds generated during activation.

![Figure 4.5](image)

**Figure 4.5** (A) Cyclic voltammogram of FNC at different working voltage windows under scanning rate of 50 mV/s, (B) Cyclic voltammogram of FNC at various scan rates under the working voltage window of 4V.

The electrochemical performance of the FNC was evaluated using symmetric two-electrode cells with non-aqueous electrolyte. **Figure 4.5 (A)** shows the typical cyclic
voltammetry (CV) curves of FNC at constant scanning rate of 50 mV/s and at different working voltage windows. The voltage window varies from 2.7V, 3.5V, 3.7V until to 4V, and the CV curves at all voltage windows exhibit near rectangular shape, which illustrates an efficient ion transportation and excellent resistance to high voltage of the FNC electrodes. The rate performance under different scanning rates at 4V was also tested and the corresponding CV curves are shown in Figure 4.5 (B). With increasing the scanning rate from 5 mV/s to 100 mV/s, the CV curves show a robust rectangular shape, which reveals an efficient ion transportation and electrode stability at high voltage under different scanning rates.

![Figure 4.6](image)

Figure 4.6 (A) Cyclic voltammogram of FNC under scanning rate of 50 mV/s at different working voltage of 2.7V, 3V, 3.3V, 3.7V and 4V. (B) Cyclic voltammogram of FNC under scanning rate of 50 mV/s at different working voltage window of 4.2V and 4.4V.

Except from the performance evaluation of a two electrode device, the absolute electrochemical potentials that a single FNC electrode could achieve was also tested using three-electrode system, which is consisted of a platinum counter electrode, Ag/Ag⁺ reference electrode and FNC-based working electrode. As shown in Figure 4.6 (A) and (B), the FNC electrode was tested under different working voltage window of 2.7V, 3V, 3.3V, 3.7V, 4V, 4.2V and 4.4V.
respectively. The detailed voltage range for each test is -1.5 to 1.2V, -1.7 to 1.3V, -2 to 1.3V, -2.3 to 1.4V and -2.3 to 1.7V respectively. Compared with the initially operation voltage of 2.7V (-1.5V to 1.2V), the FNC-electrode reaches an extended working window of 4V (-2.3 to 1.7V) finally. Specifically, this improvement is seen more clearly in the negative scanning region (1.2 V difference from -1.5 to -2.7V). In comparison, the positive scanning region only improved by 0.5V from 1.2V to 1.7V. The near-rectangular shapes of the CV curves at different voltage windows indicate a well-conserved electrode structure and stable electrochemical properties of fluorine doped nanocarbons. Additionally, if we extend the voltage to an even higher point of 4.2V and 4.4V (see Figure 4. 6 (B)), the CV curves begin to become distorted and polarized, which illustrates that the stable testing voltage region may be controlled under 4V and a higher applied voltage will lead the structure change of the electrode materials.
Figure 4.7 (A) galvanostatic charge/discharge curves of FNC at various current densities, (B) IR drop of FNC under the current density of 10 A g⁻¹. (C) Relationship of the specific capacitance and current densities of FNC, (D) Nyquist plots of NC and FCN electrodes; inset shows the plots in high frequency region.

Galvanostatic charge/discharge (GCD) curves also exhibit inclining straight lines at different current densities (Figure 4.7 (A)), which is consistent with the CV curves. Especially at high voltage region, the FNC electrode displays a very small IR drop at various current densities. Further details can be found in Figure 4.7 (B), under a high current density of 10 A/g, the IR drop of FNC is only 0.07V. Note that under high working voltage window, the main drawback of current carbon materials is the inevitable side reaction between electrode material and electrolyte, which will lead to the decomposition of electrolyte and increase of internal
resistance. Here, the IR drop of FNC electrode at 4V is hardly detected, reflecting the stable electrochemical performance at high voltage. Based on the GCD analysis, the specific capacitances of FNCs at different current densities are summarized and compared in Figure 4. 7 (C). In particular, FNC-4 delivers a high specific capacitance of 141 F g$^{-1}$ at a current density of 0.3 A g$^{-1}$, and retains a high value of 123 F g$^{-1}$ when the current density increases to 10 A g$^{-1}$.

To get further insight into the different supercapacitive activity of FNCs, electrochemical impedance spectroscopy measurements were performed. As shown in Figure 4. 7 (D), the Nyquist plots consist of a straight line in low frequency region and a semicircle in the high frequency region, which are typical for electrochemical capacitors. The semicircles in the high frequency region are illustrated in the inset of Figure 4. 7D. The first intercept of the plots with x-axis reflects the Ohmic resistance of the cells,[32] whereas the diameter of the semicircle corresponds to the charge transfer resistance. Compared with NC, it is found that FNC exhibits smaller Ohmic resistance and charge transfer resistance, which might be due to improved wettability of electrolyte on carbon surface. Meanwhile, the slope of the straight lines in low frequency regions of FNC is also sharper than NC, indicating promoted ion/electron transportation.
Figure 4. 8 Ragone plots comparing the energy density and power density of the supercapacitor based on FNC in this work and representative literature reports: (■) active carbon,[31] (●) graphic carbon sphere,[5] (▲) sandwich-type carbon nanosheet,[32] (▼) 3D microporous carbon,[33] (♦) interconnected carbon sheet,[34] (○) DPSD-derived nanoporous carbon in Chapter 3, and (★) FNC in this work.

In virtue of the high specific capacitance, excellent rate capability and large operation voltage window, the symmetric supercapacitor assembled based on the representative sample, namely FNC, shows high energy and power density. As shown in the Ragone plots (Figure 4. 8), the FNC supercapacitor delivers a high gravimetric energy density of 78.3 Wh kg⁻¹ at a power output of 307.6 W kg⁻¹, and the energy density could remain up to 88.1% (69 Wh kg⁻¹) when the power density increases to 10041 W kg⁻¹. Even at a very high power density of 40090 W kg⁻¹, the energy density of the supercapacitor is still preserved at 47 Wh kg⁻¹, almost twice of the number than the current state of arts, such as activated carbon,[33] hierarchical graphic carbon
spheres,[34] interconnected carbon nanosheets,[35] 3D micro-porous carbon from polymer carbonization,[36] and sandwich-type microporous carbon nanosheets.[37] Particularly, the FNC supercapacitor shows unparalleled energy density retention at ultra high power output over 10000 W kg\(^{-1}\) and obviously outperforms conventional carbon-based supercapacitors, manifesting its promising high-power applications.

4.3 Conclusion

In summary, we have developed a novel and facile approach to synthesize fluorine-rich nanoporous carbons with tunable porosity and F content. The key synthesis procedure involves KOH activation and subsequent hydrofluoric acid washing of a polymer-derived nanoporous carbon. The KOH activation process effectively enlarges the pore size, increases the surface area, and facilitates the F doping in the nanoporous carbons, all of which significantly improve the electrochemical capacitive performance of the F-rich nanoporous carbons. In particular, this kind of optimized F-doped carbon shows excellent electrochemical performance even at high voltage up to 4V. The symmetric cell exhibits a high energy density of 78.3 Wh kg\(^{-1}\) at a power density of 307.6 W kg\(^{-1}\), and retains a high value of 47 Wh kg\(^{-1}\) at an ultrahigh power output of 40090 W kg\(^{-1}\), which outperforms all of the representative carbon-based supercapacitors. The high working voltage and high capacitance is speculated to arise from the much stronger fluorine-carbon bond at high voltage and better wettability of FNC surface with electrolyte. Collectively, the present study demonstrates a simple and effective strategy to increase the working voltage and capacitance in carbon-based materials, which would find its broad applications in many fields such as fuel cells and lithium-ion batteries.

4.4 Experimental Section
Synthesis of nanoporous carbon (NC): Diphenylsilanediol (2.16g) and resorcinol (1.1g) were dissolved in 20 ml of anhydrous ethanol. Concentrated hydrochloride acid (0.7 ml) was drop wise added in the solution in 5 min. The solution was continuously stirred and heated at 200 °C until the solvent evaporated thoroughly and turned into a transparent and viscous oily liquid. The oily liquid was cooled down under room temperature and then carbonized at 900 °C for 3 h in nitrogen gas with a heating rate of 3 °C min-1. The as-obtained product was successively washed with 5 % hydrofluoric acid and distilled water until the solution is neutral. The nanoporous carbon was finally dried at 110 °C under vacuum.

Synthesis of fluorine-rich nanoporous carbon (FNC): The NC was mixed with potassium hydroxide under mass ratios of 9:1 (FNC). The samples were then heated to 800 °C for 1 h in nitrogen gas with a heating rate of 5 °C min-1. The activated samples were washed with a mixing solution of 20 % hydrofluoric acid and 10 % nitric acid for 5 times. Then the samples were washed with distilled water and dried at 110°C under vacuum.

Characterizations: Nitrogen-sorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 analyzer (Micromeritics Instrument Corporation, Norcross, GA). Specific surface areas (SSA) were calculated by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was determined from the adsorption branch of the isotherm based on the Barrett-Joyner-Halenda (BJH) method. TEM analysis was conducted on a FEI Tecnai™ transmission electron microscope (200kV). Powder X-ray diffraction was operated on the Rigaku MiniFlex II (Rigaku, Japan) using Cu Kα radiation (λ=0.15406 nm). XPS was conducted with a PHI 3057 spectrometer using Mg Kα X-rays source at 1253.6 eV. Raman spectra were obtained using a Renishaw 1000, with a 50 objective lens at an excitation wavelength of 514 nm.
Electrode Fabrication and Electrochemical Measurements: A two-electrode cell configuration was used to measure the electrochemical performance of the FNCs. Briefly, 10% of polytetrafluoroethylene (PTFE; 5 wt% dispersion in water), 10% of carbon black and 80% of the electrochemical active material was dispersed in ethanol. The slurry was mixed into a paste using a mortar and pestle, rolled into electrode sheets with size of 0.5 cm * 0.5 cm (size variation < 5%). A pair of electrodes typically had a weight of 3 mg (mass variation < 5%) after drying overnight at 110 °C under vacuum. The two identical electrodes were assembled into a symmetric cell, which consisted of two current collectors, two electrodes, and an ion-porous separator (glass fiber, GF/C from Whatman). Conductive carbon coated aluminum foils were used as current collectors. The electrolyte was 1 M of tetraethylammoniumtetrafluoroborate (TEA BF4, Sigma Aldrich) in polypropylene carbonate (PC). The assembly of the test cell was done in a glove box filled with Ar. The electrochemical impedance measurements were carried out on a Solartron 1860/1287 Electrochemical Interface (Solartron Analytical, Oak Ridge, TN). The EIS tests were operated in the frequency range of 10 mHz to 100 kHz with 10 mV AC amplitude. The cyclic voltammetry test was conducted using EC-LAB on a Bio Logic VMP-3 (Bio Logic Science Instruments, Claix, France). Galvanostatic charge and discharge test was carried out by LAND CT2000 (Wuhan Jinnuo Electronics, Ltd., Wuhan, China). Symmetric cells were charged and discharged between 4 and 0 V. The specific gravimetric capacitance of the supercapacitor cell was calculated according to the following Equation (4.1):

$$C_{cell} = \frac{I \Delta t}{m \Delta V}$$ (4.1)

where I (A), \(\Delta t\) (s), \(\Delta V\) (V), and m (g) are the discharge current, discharge time, potential window during the discharge process, and the mass of a single electrode, respectively. The specific capacitance of the single electrode was calculated by the following equation of \(C_s = 2\)
C_{cell}. The energy density and power density were calculated using the formula in Equation (4.2) and Equation (4.3):

\[
E_s = C_s V_{\text{max}}^2 / 8 \times 3.6 \tag{4.2}
\]

\[
P_s = E_s / t \tag{4.3}
\]

where \( E_s \) is the specific energy density, \( V_{\text{max}} \) is the maximum voltage window, \( P_s \) is the power density and \( t \) is the discharge time.

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Chapter 5: Facial Aerosol-assisted Synthesis of Hierarchical Porous Carbon for Li-Ion Battery

5.1 Introduction

Modern civilization has become dependent on fossil fuels of finite supply and uneven global distribution, which leads to severe problematic consequences like vulnerability of nation states to fossil-fuel imports, exceeding CO$_2$ emissions and environmental pollutions such as global warming. Clear and distributed energy supply is significantly required to secure a sustainable and environmental friendly energy resource. Among the multi-optional alternative choices, lithium ion batteries (LIB) have been extensively used in portable electronic devices due to their high energy density and long cycle life.[1][2][3] The ever-increasing and urgent demand for the widespread application in electric or hybrid electric vehicles has largely promoted the global research interests to develop LIBs with high reversible capacity, excellent rate capability and cycling stability.[4]

Graphite, the most commonly used commercial anode material, outperforms than many other anode alternatives (Si, Sn, P, et al) due to its excellent features such as flat and low working potential vs. lithium, low cost and good cycling life.[5] However, graphite allows the intercalation of only one Li-ion with six carbon atoms, with a resulting stoichiometry of LiC$_6$ and thus an equivalent reversible capacity of only 372 mA h g$^{-1}$.[6] Additionally, the diffusion rate of lithium ion into graphite is between $10^{-9}$ and $10^{-7}$ cm$^2$ s$^{-1}$, which results in batteries in low power density limited rate capability.[7][8] Therefore, there is an urgency to develop a kind of carbon materials that could allow efficient lithium ion mobility and improved capacity.
Many carbonaceous anode materials with various microstructures have been investigated consequently, such as carbon nanotubes,[9] nanofibers,[10] nanobeads,[11] hollow nanospheres,[12] graphene, porous carbon,[13] and their hybrids.[14][15][16]. Chen et al develops a kind of two-dimensional (2D) porous graphitic carbon nanosheets as a high-rate anode material for lithium storage. The reversible capacity of up to 722 mA h/g at current density of 100 mA/g after 100 cycles was achieved.[5] Sun et al obtained the 1D nanocarbons by surfactant–template assembly for use of lithium anode, and the carbon nanofibers demonstrated good rate performance (reversible capacity of 160 mA h/g at current density of 1500 mA/g, which is much higher than the commercial artificial graphite. Among these materials, nanostructured porous carbon attracts much more attention in providing high lithiation capability and excellent cycling stability because the porous nanostructure can not only shorten the transport length for Li⁺ ions but also offer large electrode/electrolyte interface for the charge-transfer reaction. Generally, template-assisted methods involving hard and soft templates could be the most frequently used technique to prepare porous carbons, which is either based on coating carbon precursor onto existed solid template structures or decomposing soft template agent during the carbonization process. [17] This strategy allows for fine control of hollow cores by selection of different template sizes. However, the conductivity of porous carbon may be infected compared with the solid carbon structure, since the hollow pore space is insulated and therefore increase the internal resistance. Furthermore, it is very difficult to control the diameter of hollow pores below 100 nm, a size that is critical to the nanoscale effects. This is due to the preferential aggregation of small template particles, which leads to ill-defined hollow structures. Consequently, a nanoporous structure with high conductivity and well-controlled pore size
distribution is emerging as a big challenge in the field of carbon materials as anodes for lithium ion batteries.

5.2 Results and Discussion

Scheme 5.1, (A) DPSD-nickel composite particles after aerosol process, (B) hierarchical porous carbon after template removal, (C) the aerosol process used to synthesize the carbon particles.

Here, we report the design and fabrication of high-performance anode material for lithium ion batteries based on hierarchically porous graphite particles. As illustrated in Scheme 1 (A) and (B), our carbon electrodes are constructed from such particles containing hierarchical porous structure including micro-, meso and macropores. In comparison to the graphite with low capacitance, and activated carbon with low conductivity and poor rate performance, this unique
structure provides the critical features required for high-performance carbon anode electrodes: i) the multi-scale pores provide the electrode with high surface areas and active sites to facilitate the interaction between electrolyte ions and carbon surface, ii) uniform particle size distribution and hierarchically interconnected micropores, mesopores and macropores facilitate ion transport, which ensure high rate capability; iii) graphitic carbon structure catalyzed by nickel could provide excellent electronic conductivity towards for high rate capability.

The synthesis of such particles is based on a simple aerosol process. First, diphenylsilanediol was chosen as the starting precursor for polymerization under the catalyst of hydrochloric acid. The polymerized silane oil was then dispersed in an approximate amount of anhydrous ethanol. Nickel nitrate was dissolved and dispersed in deionized water. After mixing the DPSD-containing ethanol solution and aqueous nickel nitrate solution, a homogeneous emulsion solution was prepared for the further use. The aerosol processing was as reported before,[18] as shown in Scheme 1, the mixing solution underwent an atomization process using nitrogen as the carrier gas to form continuously generated aerosol droplets, which were passed through a heating zone and converted into nanocomposite particles. Subsequent carbonization in the presence of the nickel moieties converted the polymerized DPSD into graphitized carbon. Further removal of the templates as well as the silica in DPSD resulted in graphitized, porous carbon particles with high surface area and hierarchical pores. It is important to point out that such a continuous synthesis approach can be scaled up.

Figure 5.1 shows the representative scanning electron microscope (SEM) and transmission electron microscope (TEM) images of the aerosol-carbon particles. It is shown in Figure 5.1 (A) that most of the carbons are sphere-like particles with a size ranging from 300nm to 1um, which are much smaller than that of the activated carbon normally used in commercial
devices (5-20 μm). The generally uniform particle size distribution is attributed to the facile fabrication process of aerosol, in which the atomizer produces meso-sized droplets automatically.

![Figure 5.1](image)

**Figure 5.1** (A) SEM image of the obtained aerosol-assisted hierarchical porous carbon. (B) and (C) are the TEM images of the aerosol-assisted hierarchical porous carbon. (D) the graphitic lattice under TEM view of the products.

The in-depth structure information is further revealed by TEM images as shown in **Figure 5.1 (B)**. It is observed that the carbon particles are intrinsically hollow and the thickness of carbon shell is only 5 to 10nm. Furthermore, except from the macro-sized hollow space inside the carbon particles, there are also abundant ring-like mesopores embedded on the carbon wall,
which can be seen from Figure 5.1 (C). The size of the mesopores ranges from 3 to 10 nm, providing effective surface area to interact with electrolyte and improve the ion transportation efficiently. Figure 5.1 (D) shows that the high-resolution image of the outer edge of the ring-like mesopores. A graphitic structure with lattice distance around 3.1 Å can be observed, indicating the mesopores are originated from the nickel clusters and the graphitic ring-like outer edge is due to the nickel catalyzed graphitization. There are about ten graphitized layers in the graphitic zone, and the rest of the carbon shells are still composed of amorphous carbon, as shown in Figure 5.1 (D). The micropores in the amorphous carbon region have an average size below 1nm and it mainly comes from the removal of silica atoms from DPSD. The micropores provide a high surface area and active sites for the lithium ion storage. This unique hierarchical porous structure consisting of macropores, mesopores as well as micropores establish an interconnected and consistent carbon network, which is beneficial for electrolyte penetration and ion transportation. Moreover, the rich pores also perform as a lithium ion reservoir and improve the capacitance accordingly.
Figure 5. 2. (A) X-ray diffraction pattern of the aerosol-assisted hierarchical graphitic carbon. (B) the isothermal nitrogen-sorption isotherms and inset is pore-size distributions of the aerosol-assisted hierarchical graphitic carbon.

The phase structure of the as-prepared aerosol-assisted hierarchical graphitic carbons (AHGC) was detected by the wide-angle X-ray diffraction test, and it is shown in Figure 5. 2 (A). The diffraction of the AHGC exhibits a strong peak located at $2\Theta = 26.32^\circ$ and $44.36^\circ$, which is associated with the graphite (002) and (100) plane. Pore structure of the AHGC was investigated using nitrogen-sorption experiments. Figure 5. 2 (B) and its inset show the nitrogen-sorption isotherms and pore-size distributions of the particles, which clearly suggest the coexistence of the micropores and mesopores. The nitrogen adsorption-desorption isotherms of the AHGC are typical of type IV according to the International Union of Pure and Applied Chemistry nomenclature, and they exhibit a prominent hysteresis loop at a relative pressure in the range of 0.45~0.97. A sharp increase of nitrogen uptake above 0.97 and a slow increase of nitrogen uptake below 0.45 can also be observed, indicating that the AHGC should also have macropores and micropores as well in their pore structure. On the basis of the above results, it can be concluded that pore structure of AHGC is hierarchical because of the simultaneous presence of macropores, mesopores, and micropores, which can be further verified by the pore size distribution plot of inset Figure 5. in Figure 5. 2 (B). From the pore size distribution, the pore size was estimated to be concentrated distributed below 1nm and 4.01nm, and the AHGC show a BET specific surface area of 736 m$^2$/g and a pore volume of 0.32 cm$^3$/g. The pore size below 1nm is speculated to come from the removed atomic silica from polymerized DPSD. It is specifically noticed that the pore size distribution in the mesopore region is quite concentrated at around 4.01nm, indicating that the nickel-based catalyst is embedded uniformly among the
carbon matrix. Since it remains a long-existed challenge to prevent the aggregation and overgrowth of nickel clusters in traditional synthesis of nickel-catalyzed graphitic carbon. Here in our approach, the aerosol process ensures a short standing time of reaction due to the gas flow passing by tube furnace consistently and rapidly. The high temperature at 900°C immediately evaporates the precursor solution and pre-carbonized the nickel-DPSD composites, leaving no time for further aggregation of nickel clusters. In line with the SEM and TEM images, it is revealed that after the metal-catalyst-assisted pyrolysis and carbonization, highly porous graphitic carbon was synthesized. The pores in the AHGC were probably induced by the catalyzed effect and the elimination of the Ni-based nanoparticles from the carbon. The co-existed micropores are originated from the removal of silica in the polymerized DPSD clusters.
The lithium-ion insertion/extraction reactions of the AHGC electrode were first investigated by cyclic voltammetry (CV) tests. **Figure 5. (3)** shows representative CV curves of the AHGC electrode conducted over voltages between 0.01V and 3V at a scanning rate of 5 mV/s. In the first scanning cycle, we can clearly see one obvious cathodic current peaks located at around 0.375V, although it disappeared during the second cycle. This result may be attributed to some irreversible reactions associated with the decomposition of electrolyte, the formation of a SEI film, and/or loss of some irreversible lithium storage sites during the initial cathodic scan.[19][20][21][22][23][24] In addition, it should be noted that after the initial scanning cycle, the CV profiles of the following cycles are almost overlapped, which indicates that the structural integrity of the AHGC electrode is well preserved during subsequent charge-discharge cycles. Moreover, the typical CV characteristics of AHGC are completely different from those of
reduction/oxidation reactions of NiO/Ni(OH)$_2$, further indicating that the nickel related metal oxides have been completely removed from the AHGC.

**Figure 5.3** (A) The cyclic voltammetry test of AHGC carbon, (B) the 1$^{st}$, 2$^{nd}$ and 3$^{rd}$ galvanostatic charging and discharging profile, (C) rate performance of commercial graphite 325 and AHGC, (D) cycling performance of AHGC after rate performance test.

**Figure 5.3** (B) depicts the galvanostatic charge-discharge profiles of the AHGC electrode at 85 mA/g within a cutoff voltage window of 0.01 to 3V versus Li$^+$/Li. As can be seen, the charge and discharge curves exhibit a common shape that is similar to other carbonaceous nanostructures. In the initial discharge curves, the voltage drops fast, with one plateau appearing at around 0.9V and most of the discharge capacity decreasing between 0.01V to 0.9V. As for the
charge curves, it behaves nearly steep lines at the applied voltage window. In addition, it is worth noted that the first discharge process disappeared after the first cycle, which may be due to the irreversible insertion of lithium into the deep-seated superfine micropores.[25][26][27][28]

Figure 5. 3 (D) shows the rate performance of the AHGC electrode at different current rates (from 0.5C to 10 C, 1C=372 mA/g). At a charge-discharge rate of 1C, a reversible capacity of over 1376 mA h/g was obtained, indicating a high reversible capacity of the AHGC electrodes. When the current rate is increased to high rates of 3C, the electrode still can deliver 997 mA h/g, which is larger than the theoretical capacity of a commercial graphite anode (~372 mA h/g).[29] Even at ultrahigh current rates of 5C and 10C, large reversible capacities of 732 and 599 mA h/g are still obtained, respectively. Remarkably, when the current rate was restored to 0.5 C after 50 cycles at different rates, a reversible capacity was still retained at 1539 mA h/g after 50 cycles. These results suggest that the AHGC possess an easy charge-transport process and that the structure of the AHGC remains extraordinarily stable even under high rate cycling.

To understand the reasons for the excellent rate performance of the AGHC electrode material, EIS measurements were performed, and the results are displayed in Figure 5. 4 (A). As can be seen, the impedance spectra obtained of AGHC electrode and commercial graphite electrode are composed of a depressed semicircle arc in the high-to-medium frequency region and a linear tail in the low-frequency region. The semicircle at high frequency is an indication of SEI resistance (R_{SEI}) and contact resistance (R_d), the semicircle across the medium-frequency region represents the charge-transfer impedance (R_{ct}) between the electrode and the electrolyte, and the linear tail is the Warburg impedance (Z_w) associated with the diffusion of lithium ions in the carbon electrodes (R_e). [14][31][32] According to Figure 5. 4 (A), we find that the diameters of the semicircles at both the high and medium frequencies of AHGC-based electrode are larger
than that of commercial graphite electrode. This result implies that the aerosol-assisted hierarchical graphitic carbon possesses a high electronic conductivity and a low contact and charge-transfer resistances, which are very beneficial for the fast insertion/extraction of lithium ions and thus results in a remarkable improvement of the rate performance of the AHGC electrode.[14][32][30][31]

![Figure 5. 4](image)

Figure 5. 4 (A) Impedance spectra of AHGC and commercial graphite 325 electrode, (B) After rate test, the cycling performance of the commercial graphite 325 and AHGC at a charging/discharging rate of 10C.

A comparison of commercial graphite 325 with our AHGC electrodes demonstrates a much larger reversible capacity and superior cycling performance after rate test at high charge-discharge rate of 10C (Figure 5. 4 (B)).[23][20][33][14][34][27][28][26][12][35][36][5] The outstanding electrochemical performance of the AHGC material is due to its well graphitized and hierarchical porous structure as well as the large specific surface area and the porous structures. First, the integrative feature and porous nature of carbon can ensure a large contact area between the electrode and electrolyte, which is very beneficial for the access of liquid electrolyte into the interior of the lithium ions into the deep locations of the stacked graphene layers. Furthermore, the micropores derived from DPSD matrix are also very favorable for the adsorption of lithium ions storage. Second, the well-graphitized micrometer-sized carbon can form a continuous
conductive network, which gives rise to the very high electronic conductivity of the overall electrode and is thus very beneficial for improving the rate performance of the electrode. Third, the carbon with outstanding mechanical flexibility and stability can accommodates the volume changes upon lithium insertion and thus can preserve the structural integrity of the whole electrode. Finally, the abundant macropores and mesopores can alleviate the local volume expansions of the nanosheet electrode during the charge-discharge processes, which can endow the electrode with structural integrity and stability and thus lead to superior lithium storage capacity and cycling stability at high rates. [28]

5.3 Conclusion

In this chapter, we developed a simple process to produce the hierarchical porous graphitic carbon through a facial aerosol-assisted method. The porous carbon shows an ultra-high and stable lithium ion capacitance up to 1539 mA h/g at 1C and still remains 599 mA h/g even under the charging/discharging rate of 10C. The superior electrochemical performance is speculated to arise from the hierarchical porous and high conductive graphitic structure, which will lead the carbon to perform as a promising candidate in many other fields, such as supercapacitors and fuel cells.

5.4 Experimental Section

*Material Synthesis* Diphenylsilanediol (3g) was dissolved in 20 ml of anhydrous ethanol. Concentrated hydrochloride acid (0.7 ml) was drop wise added in the solution in 5 min. The solution was continuously stirred and refluxed at 100 °C for 2 hours. 2.3g nickel nitrate was dissolved in water first, and then mix with the DPSD-containing ethanol to form a stable emulsion dispersion. The final solution was sent through an atomizer using nitrogen as a carrier gas. The atomizer dispersed the solution into aerosol droplets, which was then passed through a
ceramic tube that was heated to 900°C. The particles were then collected on a membrane filter in apress, and subsequent carbonization to 900°C of the composite nanoparticles under nitrogen atmosphere resulted in the formation of nickel/DPSD-derived carbon composite. 1M HF solution and 1M HNO₃ were used in sequence to remove the nickel and silica to produce the porous carbon particles with hierarchically porous graphite carbon.

**Material Characterization** Nitrogen-sorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 analyzer (Micromeritics Instrument Corporation, Norcross, GA). Specific surface areas (SSA) were calculated by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was determined from the adsorption branch of the isotherm based on the Barrett-Joyner-Halenda (BJH) method. TEM analysis was conducted on a FEI Tecnai™ transmission electron microscope (200kV). Powder X-ray diffraction was operated on the Rigaku MiniFlex II (Rigaku, Japan) using Cu Ka radiation (λ=0.15406 nm).

**Electrochemical measurement.** A coin-type test cell (CR2032) was utilized to evaluate the electrochemical performance of the aerosol-assisted hierarchical porous carbon electrode. The working electrode was produced by coating the mixture of hierarchical porous carbon (80 wt%), carbonaceous additive (acetylene black, 10 wt%), and poly(vinylidene difluoride) (PVDF, 10 wt%) binder on copper foil, which was first dried in a vacuum furnace at 80°C for 4h and then at 120 °C for 12h. The lithium metal was used as counter electrode, and the separator was Whatman® glass microfiber filters, Grade GF/C. The electrolyte used in this work is a 1M LiPF₆ solution in a mixture (1:1:1, in vol%) of dimethyl carbonate (DMC), ethylene carbonate (EC), and ethylmethyl carbonate (EMC). The cells were assembled in an argon-filled glovebox in which both the moisture and oxygen contents were controlled to be less than 0.1ppm. The electrochemical impedance measurements were carried out on a Solartron 1860/1287
Electrochemical Interface (Solartron Analytical, Oak Ridge, TN). The EIS tests were operated in the frequency range of 10 mHz to 100 kHz with 10 mV AC amplitude. The cyclic voltammetry test was conducted using EC-LAB on a Bio Logic VMP-3 (Bio Logic Science Instruments, Claix, France). Galvanostatic charge and discharge test was carried out by LAND CT2000 (Wuhan Jinnuo Electronics, Ltd., Wuhan, China).

Reference


Chapter 6: Conclusion

Energy storage performance of current carbon-based electrochemical double layer capacitors and lithium ion batteries are constrained by poor carbon properties. The work in this dissertation is to address the limitation of current carbon materials with low energy density by rational structure designs according to well-recognized principles and criteria. The overall research strategy is to design and synthesis functional carbon materials with high energy density at both aqueous and organic electrolyte systems. From the definition of energy density \( E = CV^2/2 \), the design methodology is to have carbon electrodes with high capacitance and high working voltage.

Different types of carbon architectures were investigated and compared with conventional structures to demonstrate such design concepts. In the first part of this thesis, a new class of nanoporous carbon was represented towards the application of symmetric supercapacitors in aqueous \( \text{Li}_2\text{SO}_4 \) electrolyte. A unique precursor was adopted to ensure the generation of uniformly distributed nanopores and large surface area. Specifically, this kind of carbon also showed outperformed high capacitance, excellent rate performance and stable cycling even under a high working voltage of 1.6V. The second part of work further improved the carbon electrode capacitance by enhancing the carbon surface affinity in organic electrolyte through a simple fluorine doping. Higher capacitance and enlarged energy density was obtained consequently. In the third part of the thesis, an optimized carbon framework was created with an impressive large surface area, high capacitance and high working voltage of 4V in organic electrolyte, showing outstanding energy density which is comparable to current commercial lead-acid battery. Other parts of work also explore the fabrication of hierarchical graphitic carbon used for lithium ion batteries and supercapacitors. In a word, by a rational design of carbon
materials through optimized pore configuration and more comparable surface chemistry, the carbon electrode energy density in different parts of this thesis were improved incrementally.

Collectively, this thesis systematically unveils simple and effective strategies to achieve high performance carbon-based supercapacitors with high power density and high energy density. The contributions of this thesis are dedicated to the following aspects:

1) High electrode capacitance and favorable ion/electron transportation pathway by well-designed carbon framework with uniform pore size distribution, interconnected pore configuration and high surface area.

2) High electrode capacitance and fully utilization of surface area through enhanced affinity between carbon and electrolyte by doping heteroatoms.

3) Fundamentally explore and understand the roles of heteroatom doping chemistry in the influence of carbon capacitor behavior by both experimental measurement and computational modeling.

4) Extensively improve the energy density of carbon electrode by enlarging the working voltage of capacitors both in aqueous and organic electrolyte.

5) Scalable and effective production of hierarchically porous graphite particles through aerosol process to act as better anode materials for lithium ion batteries.

The strategies above can be extended as a general design platform for many other high performance energy storage materials towards broad applications, such as supercapacitors, fuel cells, lithium-ion batteries and so on.