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ENHANCEMENT OF THE PERFORMANCE OF LIGNIN-DERIVED HARD CARBONS FOR BATTERY APPLICATIONS BY CHEMICAL PRETREATMENT

by

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Bachelor of Engineering, University of Jinan, 2020

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This thesis, submitted by Ruiqing Zhang in partial fulfillment of the requirements for the Degree of Master of Chemical Engineering from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

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2023

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ABSTRACT

Because of lignin's renewable and low-cost characteristics, lignin-derived hard carbons have been extensively studied as electrode materials for energy storage applications. However, the formation of solid electrolyte interface (SEI) during the first cycle in electrode materials and the loss of lithium/sodium ions during long-term cycling has a fatal impact on the performance of batteries. Recent technology is needed to improve lignin-based electrode materials' initial Coulombic efficiency (ICE).

In this study, pre-lithiation/pre-sodiation through the spontaneous chemical reaction between the aryl etherification reagent was used to improve the low ICE of the lignin-based anode material. Our results show that the ICE of the lignin-based anode material can be significantly improved with only a few minutes of treatment. It indicates that the treated is a promising renewable electrode material for battery applications. It can be used in electrochemical energy storage and conversion devices, such as supercapacitors, fuel cells, etc.

Keywords: Lignin, lithium-ion batteries, sodium-ion batteries, hard carbon, pre-lithiation, pre-sodiation.

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CHEMICAL PRE-LITHIATION OF LIGNIN-DERIVED HARD CARBON

1. Introduction

1.1 Lithium-ion Batteries

More than thirty years ago, ever since Sony successfully produced the world's first commercial lithium battery through Goodenough's theory[1], lithium-ion batteries have never left people's attention. Lithium-ion batteries are widely used in energy storage power systems such as hydraulic, thermal, wind, and solar power stations, uninterruptible power supplies for postal and telecommunications, as well as in electric vehicles, military equipment, aerospace, and other fields. Lithium-ion batteries can be found with lithium-based battery technology making significant progress time and time again, whether it’s the popular Tesla electric cars or the electric pumping engines for Rocket Lab’s Electron rocket[2].

As a critical component of lithium batteries, the evolution of anode materials has extensively promoted the development of lithium batteries. However, since traditional graphite anode lithium batteries cannot meet the growing demand for high energy/power density in different application scenarios (such as electric vehicles and large power supplies), various improvement strategies and alternative anode materials have been developed for better electrochemical performance[3].

At this stage, commercial lithium-ion battery anode materials are mainly carbon materials with high specific capacity, low electrodes, and good cycle performance. The physical and chemical properties are stable. Carbon materials can be divided into graphite materials and amorphous carbon materials according to the degree of crystallization. Graphite has become an ideal lithium battery anode material because of its good conductivity, high crystallinity, stable layered structure, and suitability for the intercalation and deintercalation of lithium. Artificial graphite and natural graphite are the two primary graphite materials. Amorphous carbon materials are carbon materials with no fixed crystalline shape, mainly including soft carbon and hard carbon.

In the following introduction, we detail the advantages and disadvantages of four representative rechargeable lithium battery anode materials and the necessity of introducing biomass-derived lithium-ion battery anode materials. The strategies and significance of perfecting the electrolyte interface of biomass materials are summarized.

1.2 Carbon-based Anode Material

1.2.1 Graphite Anode Material

Graphite has a layered structure. Carbon atoms are connected through sp2 hybridization to form C=C bonds, forming a hexagonal structure and extending in the two-dimensional direction (a-axis) into a plane (graphene plane). These planes are stacked in layers to form Graphite crystals. The carbon atoms in the graphene plane are connected through covalent bonds with a large bond energy (342kJ/mol). The graphene planes are connected through van der Waals forces, with a small bond energy (16.7kJ/mol), which supplies conditions for lithium's stable deintercalation and intercalation.

There are three main ways to store lithium in carbon anodes:

(1) Lithium is embedded between graphite layers to form graphite insert compounds. The wider the graphene surface extends, the better the lithium storage performance.

(2) Lithium is stored on the end face of the graphene layer. The end face includes the zigzag end perpendicular to the C-C bond on the graphene surface and the chair-shaped end parallel to the C-C bond on the graphene surface. The more defects there are on the graphene surface, the more edge-end surfaces there are, and the more lithium is stored. The better the performance.

(3) Lithium is stored on the crystal surface, and the lithium storage method is related to the surface area of the material. The lithium storage methods of graphite and soft carbon materials are mainly interlayer intercalation, while hard carbon materials have underdeveloped microcrystals, many end faces, and large surface areas. Their lithium storage methods are mainly end-face storage and surface storage.

Natural graphite

Natural graphite can be divided into flake graphite and earthy graphite. The negative electrode material usually uses flake graphite, which has enormous reserves, low cost, low potential, and stable curve. In a suitable electrolyte, the Coulombic efficiency of the first week is 90%~93%, and the reversible capacity can reach 340~370 mAh·g-1 and is one of the most mainstream anode materials for lithium-ion batteries. However, the regular layered structure of natural graphite leads to its high anisotropy, slow intercalation of lithium ions, and insufficient contact between graphite particles and current collectors. This is also the main reason for the low-rate performance of natural graphite. The mechanical grinding method is often used to increase the isotropy of natural graphite. Incompatibility with propylene carbonate (PC) - -based electrolytes with good low-temperature performance is also a significant shortcoming of natural graphite. It is usually modified by adding additives to the electrolyte and coating the graphite surface.

Artificial graphite

Artificial graphite is produced by calcining easily graphitizable carbon (petroleum coke, needle coke, pitch, etc.) at a specific temperature, then grinding, shaping, classifying, and high-temperature graphitization[4]. Its high crystallinity is achieved through high-temperature graphitization. Petroleum coke is a combustible solid product obtained by coking petroleum residue and asphalt. It is the primary raw material of artificial graphite. It is divided into raw coke and calcined coke according to its heat treatment temperature. Needle Coke is a high-quality Coke with an apparent fibrous structure. It has the advantages of good electrical and thermal conductivity in the direction parallel to the long axis of the particles, a small thermal expansion coefficient, and is easy to graphitize. Pitch is one of the leading products of coal tar deep processing and is used as a binder and impregnating agent in the graphite production process. After continuous research, artificial graphite has surpassed natural graphite in capacity, first-cycle efficiency, cycle life, etc. However, high-temperature graphitization also brings the disadvantage of high cost.

1.2.2 Amorphous Carbon Anode Material

Graphitized carbon generally requires high-temperature treatment. Due to the low heat treatment temperature (500~1200°C), the graphitization process is incomplete. The resulting carbon material mainly comprises graphite microcrystals and amorphous regions called amorphous carbon. From a microscopic perspective, the structure of the amorphous region is a turbulent layer-disordered structure. Because the van der Waals force between graphite layers is weak, the graphene surface's random translation and rotation leads to varying degrees of stacking dislocations. Most carbon atoms deviate from their regular positions, and the periodic stacking is no longer continuous. This is a turbulent layer disordered structure, and turbulent layer disordered carbon forms two forms:

(1) Soft carbon, when heated to above 2500°C, quickly eliminates the disordered structure.

(2) Hard carbon's disordered structure is complex to eliminate at any temperature.

Soft carbon

Soft carbon is easily graphitized when treated at high temperatures (above 2500°C). Compared with graphite, soft carbon has a large specific surface area, stable crystal structure, and strong electrolyte adaptability. Since graphitization treatment is avoided, soft carbon materials cost less. Soft carbon is often considered an anode material for power batteries, mainly because it is difficult to deposit metallic lithium under high currents, improving the battery's safety performance. As the specific surface area involved in lithium reactions increases, its rate performance is also enhanced; the charging depth of the soft carbon negative electrode can be adjusted so voltage changes can be controlled. The specific capacity of soft carbon materials is generally 200~250mAh·g-1, and the cycle performance can be improved to more than 1,500 times.

Hard carbon

Hard carbon refers to carbon that is difficult to graphitize even under high-temperature treatment (above 2500°C). Its structure is disordered; there are few stacks of graphite sheets and many defects. Compared with graphite, hard carbon does not suffer from solvent co-intercalation and significant lattice expansion and contraction and has good cycle performance. Without the lithium insertion potential limitation, hard carbon's specific capacity can be 400~600 mAh·g-1. However, hard carbon materials have problems, such as low initial Columbic efficiency.

1.3 Problem Statement

Among the four common carbon anode materials are artificial graphite, natural graphite, soft carbon, and hard carbon. Hard carbon has been widely studied as an anode material for lithium-ion batteries due to its excellent cycle performance and high stability[5]. Lignin-derived hierarchical porous carbons have been widely studied as promising electrode materials for energy storage applications because lignin is renewable and abundantly available. Chemical activation agents cause lignin to release some carbon, hydrogen, and oxygen atoms, forming porous structures in lignin macromolecules, thus enhancing the lithium storage and adsorption capacity. However, these pore structures significantly reduce the initial Coulombic efficiency (ICE). This large initial capacity loss results in high lithium ions consumption in the electrolyte and needs to be compensated by an excess amount of cathode material, posing severe challenges for practical battery applications. New technology is required to solve the problem of low ICE of lignin-based electrode materials.

2 Literature Review

With the in-depth research on anode materials for human lithium-ion batteries (LIB), the impact of the initial Coulombic efficiency (ICE) of the anode material on the battery energy density cannot be ignored. Generally, additional loading of cathode material in LIBs is chosen to compensate for the anode material's low ICE. However, since the specific capacity of the ordinary lithium metal oxide cathode is lower than that of the anode, an excess of cathode material (10%~15% for graphite anode material) must be added to overcome the problem of insufficient ICE of the anode material, but this will result in a significant reduction in energy density[6].

The review section first discusses the relationship between ICE and energy density. The reasons for the initial capacity loss (low ICE) of hard carbon anode materials are then explained in detail. The growing number of methods used to enhance ICE and the associated basic mechanisms are then summarized. And elicit the academic gaps we hope to fill. These additions could facilitate further improvements in ICE and the fabrication of higher energy-density cells.

2.1 Initial Coulombic Efficiency

The ICE of anode materials in half cells can be calculated from the ratio of initial charge capacity to initial discharge capacity, which defines the ability of anode materials to prevent the occurrence of irreversible reactions and the loss of irreversible capacity. This ability will significantly affect the electrochemical performance of the anode material in the battery; specifically, it is closely related to its energy density. Typically, many reasons lead to a decrease in the ICE of the anode material. The first and most important reason is the formation of the SEI layer. Second, the irreversible absorption of alkali-ions. Third, the coarsening of active materials. Fourth, some adverse side reactions. Last, the irreversible decomposition of oxides ultimately results in a relatively low battery energy density.

For example, the low ICE of anode materials is compensated for in current commercial LIBs by additional loading of cathode materials[7]. Nevertheless, as common lithium-metal oxide cathodes have lower specific capacity (<200 mAhg 1) than that of anodes, an excessive amount of cathode materials (10%–15% for a graphite anode material) must be added to overcome the insufficient ICE of anode materials, which leads to an appreciable reduction of energy density[8]. Specifically, the reduction is about 5%–20% of the total available capacity in commercial graphite electrodes, and it can even reach as high as 15–50% for next-generation high-capacity anode materials (such as Si)[9-11]. Therefore, improving the ICE of carbon anode materials will play an essential role in promoting the further development of lithium-ion batteries.

2.2 Causes of Low ICE

According to the different reaction mechanisms of lithium, lithium-ion battery anode materials are mainly divided into conversion-type anode materials, alloy-type anode materials, and intercalation-type anode materials[6]. Among them, hard carbon materials are intercalation-type anode materials. Their reaction mechanism is the reversible insertion and deintercalation of lithium ions in the lattice of the primary anode material with a layered structure.

For intercalated anode materials, the main cause of irreversible capacity loss during the initial cycle is the forming of the solid electrolyte interface (SEI) layer and the irreversible absorption of lithium ions or other ions within the material. Zhang et al. Attribute the initial capacity loss to the formation of the SEI layer[12]. When graphite is used as the anode material for lithium-ion batteries, the irreversible capacity reaches 23%. Nearly half of the irreversible capacity is lost when the voltage exceeds 0.25V, and the other half is lost during the remaining charging cycles. Kalisvaart et al.'s study of applying pseudo-graphitic carbon in lithium-ion batteries found that many irreversible ions were adsorbed into the amorphous regions between pseudo-graphitic domains[13]. The material's properties determine the irreversible absorption of lithium ions, thereby affecting the initial capacity. When a material cannot provide enough space and energy for lithium ions to leave, the lithium ions will be trapped in the material, ultimately leading to a loss of initial capacity.

2.3 Methods to Improve ICE

Through the previous summary of the research on the Initial Coulombic Efficiency (ICE), it is not difficult to find that the level of the ICE is crucial to the research of batteries. In the next part, we will summarize various ways to improve the ICE and compare the advantages and disadvantages of different methods to choose the one that best matches our research.

2.3.1. Control Irreversible Oxides

Many attempts have been made to reduce the irreversible oxides produced during electrochemical reactions, such as Li_2O, and reduce their negative impact on ICE.

Kang et al. attempted to coat the Co_3O_4 surface with Ni by ball milling to exploit the observation that Ni has the highest catalytic activity for the decomposition of Li_2O among transition metals. FTIR spectroscopy confirmed that Ni successfully catalytically decomposed the irreversible oxides produced during the electrochemical process, increasing the ICE to nearly 80%[14]. Similarly, to improve the reversibility of irreversible oxides, lithium sulfide, and lithium oxide, Li et al. enhanced the mobility of charges by introducing $Sn-SnO_2$ heterostructure, and the ICE of the prepared composite material was increased by 16%[15]. Furthermore, Zhang et al. prepared a new $Sn_2Fe@SiOx$ composite. By firmly attaching nano-Sn_2Fe particles to the SiO_x surface to form a layer of the metal interface, the lithium transfer speed can be increased, and its ICE value is greatly increased from 48.9% to 78%[6].

2.3.2 Control Side Reactions

Generally, side reactions are associated with (i) inert additives and (ii) surface defect sites/harmful functional groups of active materials. Hence, avoiding adverse additives and obtaining a “cleaner” surface of active materials can be effective solutions for suppressing side reactions[6]. The Ge microcubic electrode prepared by Zhang et al. showed an ICE of more than 90%[16]. The designed hierarchical structure of Ge microcubes has good crystallinity, preventing the growth of irreversible oxide layers, and the absence of inert additives also reduces irreversible reactions. In addition, Zhang et al. tightly combined amorphous carbon with MoS_2 by adding a protective layer to cover the harmful functional groups of the material itself[17]. This operation changes the material in contact with the electrolyte to a more stable carbon material, hindering the generation of side reactions. The resulting nanomaterial exhibited an initial Coulombic efficiency of 92%.

2.3.3 Control the Formation of the SEI Layer

The formation of the SEI layer occurs during the electrochemical reaction on the surface of the anode material. To reduce its impact on battery performance, the formation of the SEI layer is limited by reducing the contact area between the electrolyte and anode material. For example, Ryu et al., by modifying the microstructure and the degree of hierarchical porosity, the ICE of hyper porous silicon flakes (HPSFs) can be as high as 92.7%. This exceptionally high ICE of the HPSFs anode is attributed to the reduced contact area between HPSFs and electrolyte, which is realized by retaining its macrosize structure with dominant macropores (Vmacro ¼ 83.1%). Even though HPSFs show a relatively high surface area (127 m2g-1), they can still avoid large initial irreversible capacity loss by minimizing the fraction of mesopores (Vmeso ¼ 16.7%) and micropores (Vmicro ¼ 0.2%)[18]. Hu et al. reported that Saqima-like Co_3O_4/CNTs secondary microstructures with more stable SEI films were synthesized, increasing the ICE of nanomaterials applied to lithium batteries to 85%[19].

Feng et al. developed a process for coating the anode material with Al_2O_3[20]. Their research shows that to reduce the amount of SEI film generated by consuming lithium ions during the electrochemical reaction, a more stable Al_2O_3 film can be added to the anode material in advance to serve as the SEI layer. It can be seen that artificially adding a SEI-like layer or a SEI layer generated in advance can effectively reduce the SEI layer spontaneously generated during the electrochemical reaction. Thereby reducing lithium ions, or the purpose of initial capacity loss, and ultimately improving Initial Coulomb Efficiency.

2.3.4. Pre-lithiation Material

Pre-lithiation is one of the most effective techniques for improving ICE. Generally speaking, pre-lithiation is mainly targeted at anode materials. Common pre-lithiation reagents include stable lithium metal powder, lithium silicon nanoparticles, lithium alloys, lithium oxide composite materials, etc.

For example, Jarvis et al. suggested that lithium metal powder can be added to the anode[21, 22]. Provides a lithium source for the formation of the SEI layer and pre-lithiation of carbon. The high ICE of the pre-lithiated carbon anode material increased to 95.4%, while the ICE of the untreated anode material was less than 80%. Liu et al. presented a facile method for pre-lithiating a Si nanowire anode by a self-discharge mechanism[23]. In the pre-lithiation process, the anode material was directly attached to a piece of Li metal foil in the presence of an electrolyte. Pressure was applied to induce electrical shorting between the anode and the Li foil, resulting in electrochemical pre-lithiation.

Because the liquid pre-lithiation reagent can better control the pre-lithiation process by controlling the treatment time, the interface of the anode material after treatment is more uniform, and it has also become a supplement to the pre-lithiation of lithium-ion batteries. For instance, Ai et al. developed a facile pre-lithiation strategy using lithium naphthalenide to partially pre-lithiate Si into a Li-Si anode, which was realized by immersing the Si electrode into lithium naphthalenide in the glovebox[24]. After pre-lithiation, the ICE of the treated silicon anode is as high as 96.1%. Liquid pre-lithiation can adjust the degree of lithiation by adding different amounts of lithium and organic reagents. Guo et al. developed a liquid chemical pre-lithiation strategy[25]. Improved surface uniformity of SiO_x anode material, increasing ICE to 90%.

2.3.5 Gaps in Literature

Among the many pre-lithiation methods, the research on chemical pre-lithiation, which is the most efficient, is very limited. Chemical pre-lithiation refers to using lithium-containing reagents with strong reduction strength to transfer active lithium to the negative electrode material through a redox reaction. For example, using metal lithium and naphthalene (Li-Naph) in 1,2-dimethoxyethane (DME) or tetrahydrofuran (THF) solvent for chemical pre-lithiation of the negative electrode. This experiment focuses on the performance improvement of lignin-derived hard carbon and attempts to use chemical pre-lithiation to treat hard carbon. Try to improve the chemical performance of biomass materials such as ICE and cycle stability and fill the academic gaps in pre-lithiation technology and biomass lithium-ion battery anode materials in this area.

3 Research Methodology

3.1 Materials Synthesis

The dried lignin powder was put into a tube furnace (TFM2 2-Zone, China) and carbonized at 800 °C for two hours at a heating rate of 5 °C min^{-1} under nitrogen flow. Then, the powder was ground for 30 min and sieved, and the final sample was named CL. The pre-lithiation process was performed by simply immersing the HC electrode in 1 mL of 1 mol L^{-1} naphthalene lithium solution in a vacuum oven (LABstar, MBraun, Germany) before assembling the battery. Afterward, the pre-lithiated hard carbon anode was washed two times with DME and dried in a vacuum chamber for 10 min. DME was used as a solvent because it is compatible with Li naphthalenide reagent.

3.2 Materials Characterization

For the characterization of the materials, the sample's morphology was observed by scanning electron microscopy (SEM, FEG-650, U.S.), and the carbon contents of the samples were measured by Total Organic Carbon Analyzer (TOC-V_{SN}, Japan). Finally, the electrochemical performance of the assembled battery is characterized through the battery testing system and potentiostat. The detailed appearance of the equipment used during the experiment is in Appendix 1.

3.3 Electrochemical Measurements

The electrochemical electrode was prepared as explained below. 80 wt% active materials (CL), 10 wt% acetylene black, and 10 wt% carboxymethyl cellulose (CMC) were mixed in aqueous solution to form a uniform slurry and then cast on 10 microns of Cu foil using a doctor blade. The electrode was dried at 80 °C in a vacuum oven for 12 h and punched into a circular electrode before use. The loading mass of the CL is controlled around 3.0 mg cm^{-2}. An electrolyte of 1.0M $LiPF_6$ in Ethyl Methyl Carbonate (EMC)/dimethyl carbonate (DMC)/ethylene carbonate (EC) (1/1/1 by volume) with 2% fluoroethylene carbonate (FEC) was used therein. Cells were assembled in an argon-filled glove box and evaluated over a voltage range of 0–3.0 V at 25 °C using the Neware battery test system (China). Cyclic voltammetry was measured on the Interface 1010E General-purpose electrochemical workstation (U.S.) at a scan rate of 0.1mV/s in the voltage range from 3.0 to 0.01V (vs. Li+/Li and hereafter). Alternating current electrochemical impedance spectroscopy (EIS) was measured in the frequency range from 100 kHz to 100 MHz with an alternating current voltage amplitude of 10 mV at the open-circuit voltage. All electrochemical measurements were performed using CR-2032-type coin cells.

4 Results

The synthesis and redox behavior of L-N was selected as an efficient and widely applicable pre-lithiation agent. As shown in Fig. 1, when the circular electrode piece is soaked in the pre-lithiation solution, the HC undergoes a chemical reduction reaction, and electrons are transferred from naphthalene anion to Li^+ and simultaneously inserted into the graphite layer of HC to form a lithiated host (PHC). Once the PHC is formed, its low potential initiates the reductive decomposition of dimethyl ether (DME) solvent to form a porous and immature SEI layer that consists of organic composition (ROLi). This immature SEI layer would be further strengthened when contacted with the Li-ion battery electrolyte, where FEC and PF_6^- anions decompose to produce a LiF-rich SEI layer, finally leading to a dense and robust SEI film. [6]

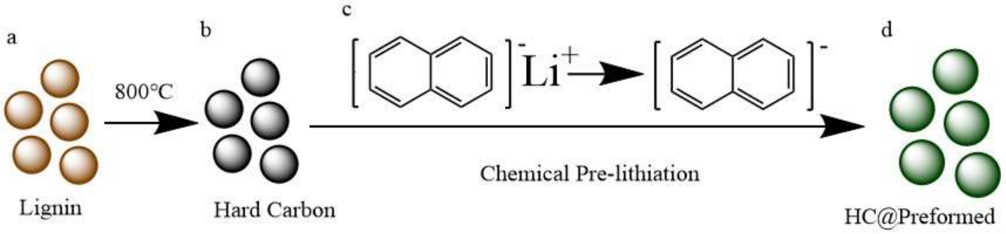
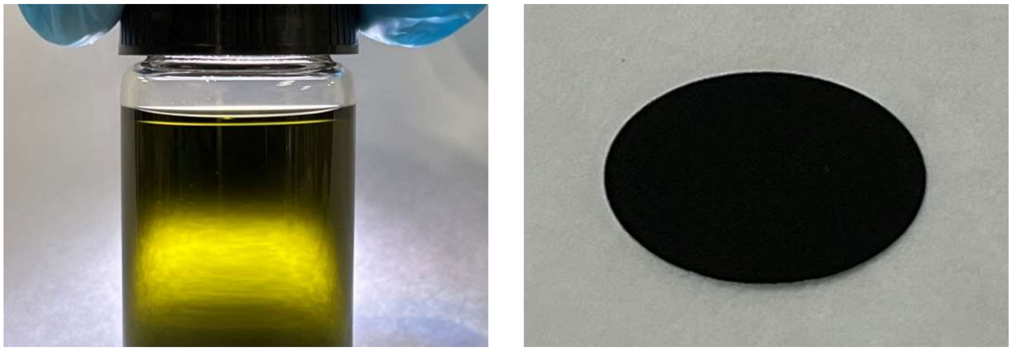


Figure. 1 Schematic illustration of the chemical pre-llithiation reaction of HC in Li-Naphthalenide/DME solution and SEI formation on the PHC anode

a. Alkali Lignin

b. Hard Carbon



c. Chemical Pre-lithiation with $LiC_{10}H_8$

d. Treated anode disk

Figure. 2 Schematic illustrations of the chemical pre-lithiation reaction of HC in Li-Naphthalenide/DME solution and SEI formation on the PHC anode

Figures 3(a) and 3(b) show the SEM images of the treated and untreated electrode materials after cycling. We can find that the SEI film on the surface of the pre-lithiated anode disk is denser and more uniform. In contrast, the SEI distribution on the surface of the anode disk without pre-lithiation, which only spontaneously generates an SEI film through battery cycling, is very uneven, and a part of the hard carbon material is not covered by the SEI film and is directly exposed to the electrolyte. The uneven distribution of SEI may have an adverse effect on the electrochemical performance of the battery.

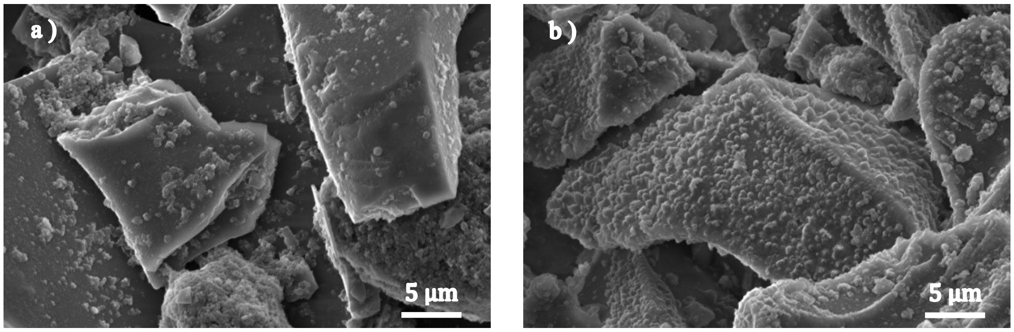
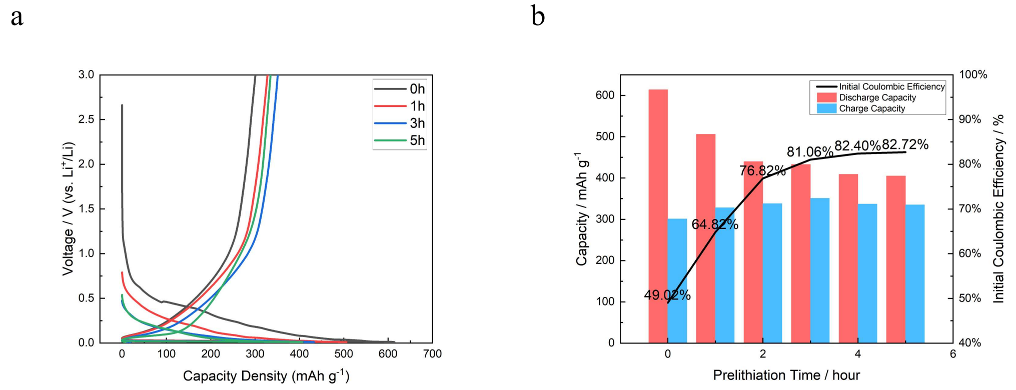


Figure 3. SEM image at a magnification of 500X for lignin-derived hard carbon anode electrode (a) Electrode without pre-lithiation (b) Electrode with pre-lithiation.

We compared the charge/discharge behaviors and the ICE values of the PHC anodes obtained at different pre-lithiation times to optimize the pre-lithiation degree. Figures 3(a) and 3(b), the PHC anode exhibited significantly lowered discharge (lithiation) plateaus and decreased initial irreversible capacities with increased pre-lithiation time. After 3 hours of pre-lithiation, the PHC anode exhibited a sufficiently high ICE value above 81%, which means that the initial irreversible capacity has been improved by a full 32% from the original 49%, which shows that pre-lithiation can significantly improve the Initial Coulombic Efficiency of lignin-derived hard carbon.

The rate capabilities of both the HC and PHC anodes were comparatively evaluated by galvanostatic charge/discharge at varying current rates from 100 to 2000 mA g^{-1}. As shown in Figure 3c, the PHC anode demonstrates an improved rate performance with reversible capacities of 178, 130, and 61 mAh g^{-1} at high rates of 500, 1000, and 2000 mA g^{-1}, respectively. In comparison, pristine HC anode delivers much lower capacities of 130, 75, and 27 mAh g^{-1} at the current rates of 5000, 1000, and 2000 mA g^{-1}, respectively. This significant difference in the rate capability suggests that the chemical pre-lithiation may produce a better SEI film than conventional electrochemical cycling pre-lithiation on HC anodes, thus leading to improved high-rate performance.

The better SEI film produced by chemical pre-lithiation can also be evidenced by the cycling performances of the HC and PHC electrodes. As displayed in Figure 3d, the HC anode delivers a specific capacity of 293.0 mAh g^{-1} at a current of 200 mA g^{-1} over 700 cycles. Nevertheless, the PHC anode can not only realize a high reversible capacity of 296 mAh g^{-1}over 500 cycles at 200 mA g−1 but also display a high capacity retention of close to 100% over 700 cycles, mainly due to the higher stability of the SEI layer on the PHC anode.



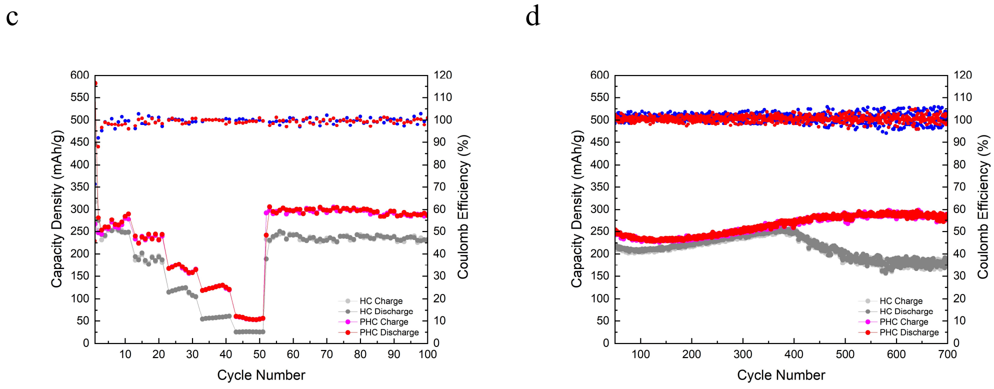


Figure 3. Compare (a) first cycle charge/discharge profiles and open circuit voltages. (b) initial charge/discharge capacities and initial Coulombic efficiencies of the PHC anodes obtained at different pre-lithiation times. (c) rate capability at various current rates from 100, 200, 500, 1000, and 2000 mA $g^{-1,}$ respectively (d) Long-term cycling performance at a current rate of 200 mA g^{-1}.

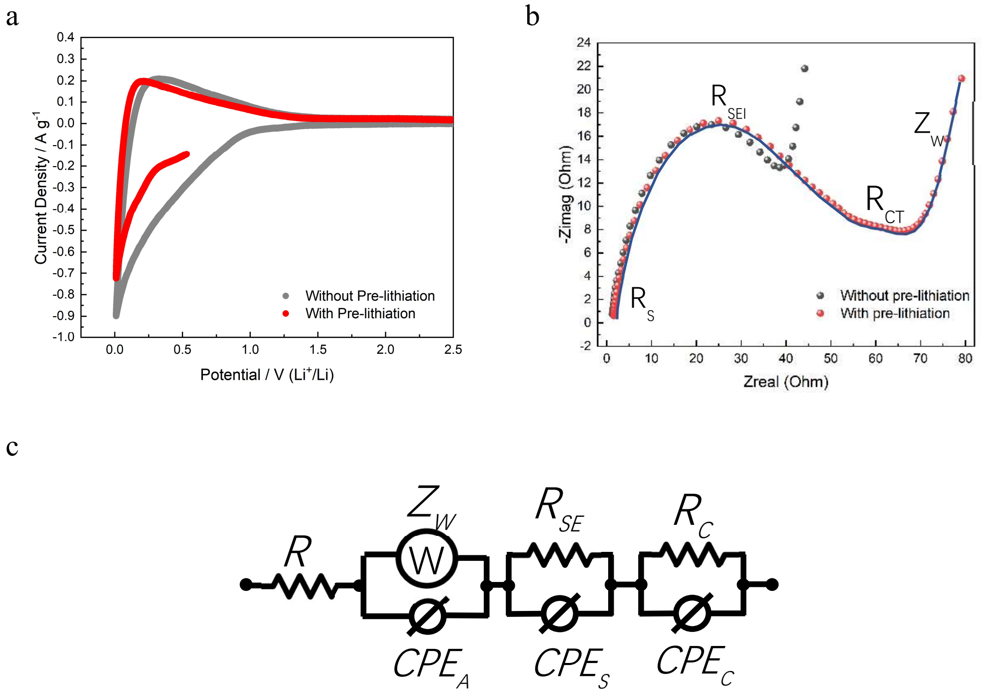


Figure 4. (a) CV curves (b) Nyquist plot of HC and PHC measured at the open circuit of HC/Li and PHC/Li half-cell. (c) Equivalent circuit diagram corresponding to the EIS curves.

Figure 4(a) shows the cyclic voltammetric (CV) curves of the HC anode and PHC anode at the first cycles. We can see that the initial voltage of the pre-lithiated battery drops to 0.5 watts, suggesting that there has been an SEI film already existing on the surface of the anode, and the preformed SEI functions well for Li+ insertion reaction. We also conducted a kinetic analysis for fresh anodes. Electrochemical impedance spectroscopy (EIS) is a tool used for mechanistic and kinetic analysis inside the lithium-ion battery. Figure 4(b) illustrates the Nyquist plots of EIS spectra and the equivalent circuit model. According to the EIS, we can build an equivalent circuit for analyzing the resistance of every part of the lithium-ion battery. R-S, the part of the impedance curve close to zero ohms, is the ohmic series resistance associated with the cell components. R-SEI, a large semicircle, represents the Li-ion transfer resistance through the SEI layer. R-CT, a small semicircle, is the charge transfer resistance. Z-W, like a straight line, is the Lithium-ion diffusion impedance associated with the Li-ion diffusion into the active electrode. From here, we can see that the pre-lithiated anode shows an SEI semi-cycle. This means a SEI layer was generated in a fresh pre-lithiated anode.

5 Discussion

In summary, we demonstrated a facile and effective approach to obtain a PHC by a chemical reaction of HC with lithium naphthalenide. This pre-lithiation process generates a preformed SEI layer on the PHC electrode, which then transforms into a dense and robust SEI film upon infiltration into the electrolyte after initial discharge. This SEI film can effectively compensate for the irreversible capacity loss and greatly enhance the initial and cycle Coulombic efficiencies, leading to high rate performance and cycle stability of PHC anodes. Based on the PHC anode, we assembled PHC/Li half cells and evaluated their electrochemical performances. The PHC/Li cells demonstrated very high ICE values of >81.0% and very high stability with little capacity fading after 700 cycles. The practical application of pre-lithiated lignin-derived hard carbon materials in next-generation high-capacity and high-rate performance LIBs is demonstrated.

CHEMICAL PRE-SODIATION OF LIGNIN-DERIVED HARD CARBON

1 Introduction

1.1 Sodium-ion Batteries

Today, lithium-ion batteries (LIB) are considered one of the most advanced energy storage technologies. However, lithium resources are limited and unevenly distributed globally, so alternatives are needed. A sodium-ion battery is a secondary battery (rechargeable battery) that mainly relies on the movement of sodium ions between the positive and negative electrodes to work, similar to the working principle of lithium-ion batteries[26]. The concept of sodium-ion batteries was first proposed by the Armand team in the 1980s and was applied technologically through industrialization in the 1990s[27]. As the sixth most abundant element in the earth's crust, sodium is far more abundant than lithium. At the same time, aluminum foil will be used to replace expensive copper foil as the current collector for sodium-ion batteries. The cost of sodium-ion batteries will be significantly reduced compared to lithium-ion batteries. Like oil, lithium resources have gradually become an important strategic resource for the country. As an alternative to lithium-ion batteries, sodium-ion batteries have begun to receive attention from various countries. The U.S. Department of Energy has designated sodium-ion batteries as a development system for energy storage batteries; the EU Energy Storage Plan "Battery 2030" project has ranked sodium-ion batteries first among non-lithium-ion battery systems.

1.2 Carbon-based Anode Material

Graphite is the most used anode material for lithium-ion batteries (LIB). However, since the diameter of sodium ions is larger than that of lithium ions, the ionic radius of sodium ions (1.02Å) is approximately 1.34 times that of lithium ions (0.76Å). It cannot be embedded into the graphite structure, and the sodium carbon compound formed during the reaction is extremely unstable. This is coupled with other difficulties such as low energy density due to high operating potential, volume expansion and pulverization of the material during cycling, and low Coulombic efficiency[28]. Therefore, the more advantageous soft and hard carbon materials with large interlayer spacing have become the best partners for sodium-ion batteries. Carbonaceous materials are considered the most promising anodes in commercial SIBs due to their diverse structures and properties as well as wide availability and low cost[29-31]. Among carbon-based materials, hard carbon materials have the advantages of diverse structures, low price, good conductivity, high sodium storage capacity, small volume deformation after sodium embedding, environmental friendliness, and low redox potential. The distance between soft carbon layers is smaller than that of hard carbon. The specific capacity of soft carbon for sodium storage is only 220mAh/g. Its volumetric capacity is difficult to increase, and its low-temperature performance and fast charging performance are not as good as those of hard carbon.

1.2.1. Soft Carbon Anode Materials

Soft carbon is mainly derived from tar, hydrocarbon-based materials, etc. Through heat treatment under different conditions, soft carbon with different degrees of carbonization is obtained. Unlike hard carbon, soft carbon is a special carbon material with ordered layers but disordered structure that can be converted into graphite when annealed above 2500 °C[32, 33]. As early as 27 years ago, people discovered that soft carbon materials can be used as negative electrodes for sodium-ion batteries, but their storage mechanism has been ignored. It was not until today, more than 20 years later, with the rise of the energy storage battery industry, that people began to pay new attention to the storage mechanism of sodium ions in soft carbon. It was found that the insertion of Na^+ into the graphite layer resulted in an irreversible 0.5 V quasi-plateau and irreversible expansion[34]. Although soft carbon is one of the competitive anode material options for sodium-ion batteries, it is a highly graphitized soft carbon material. The large sodium ion radius will cause large changes in the interlayer spacing of soft carbon during the sodium ion intercalation/deintercalation process. In order to improve the problem of structural collapse, it is important to develop soft carbon with good structural stability[35].

1.2.2. Hard Carbon Anode Material

Graphite, as an anode material for lithium-ion batteries, has achieved success in both scientific research and business. So naturally, people's expectations for the best anode material for sodium-ion batteries have been placed on carbon-based materials that have low voltage to sodium and are chemically and thermally stable. However, it has been confirmed that graphite is not suitable as an anode material for sodium-ion batteries because the interlayer spacing is too small. The existence of interaction forces between graphite and sodium ions was also demonstrated by theoretical calculations reported by Di Vincenzo et al. [36]. In the electrochemical reaction of sodium-ion batteries; sodium ions will accumulate on the surface of graphite materials in large quantities, Thomas et al. The reversible capacity of graphite dissolved in NaClO4 in ethylene carbonate was studied, and the result was only 14 $mAhg^{-1}$ [37].

Hard carbon (HC) structure is defined by a falling card model possessing random stacking of graphene sheets, resulting in nano-porosity. It is non-graphitic, non-graphitizable carbon formed by the solid-phase pyrolysis of cellulose, charcoal, coal sugar, etc[38].

It is generally believed that changing solvent from ester to ether increases initial columbic efficiency, capacity retention, and rate capability of carbon-based anode materials because thin and stable SEI layer formation is promoted[39]. Hu et al. synthesized nitrogen-doped expanded graphite and utilized it as anode material both in ether and ester-based electrolytes. In ester solvent, the first discharge capacity of 170.2 mAh g^{-1} was observed, while in ether-based solvent, the capacity delivered was only one-third of it, with initial columbic efficiencies of 24.73% and 72.08%, respectively. They showed excellent rate capability, delivering capacities of 125 and 110 $mAhg^{-1}$ at a high rate of 30 $Ag^{-1,}$ respectively. The better results were attributed to stable and thin SEI layer formation, which causes low irreversible capacity losses, leading to better columbic efficiency[40].

Alcantra et al. also studied the reversible intercalation of Na ions into carbon black and observed a reversible capacity of 121 $mAhg^{-1}$ with 100% capacity retention after 3rd cycle. The high capacity was attributed to the disordered structure and low density of carbon black[41]. Capacity for carbon materials can be improved by changing solvents. Therefore, Xiao et al. employed an ether-based solvent for carbon black and observed an initial reversible capacity of 234 $mAhg^{-1}$ at 50 mAg^{-1} with 61.45% columbic efficiency. When cycled at 3200 mAg^{-1} over 2000 cycles, it still retained 72 $mAhg^{-1}$ of its initial capacity and also showed a superior rate capability of 105 $mAhg^{-1}$ at 3200 mAg^{-1}. This high performance was attributed to the robust and thin SEI layer formation due to the ether solvent[42].

1.3 Non-carbon-based Anode Material

At present, research on non-carbon-based anode materials for sodium-ion batteries mainly focuses on alloy materials, transition metal oxides, and organic compounds.

1.3.1 Alloy Materials

Alloy materials commonly have problems such as serious volume expansion, material pulverization, poor cycle stability, and prohibitive cost during sodium storage. Common metal anode materials are silicon-based, lithium titanate, and tin-based materials. The advantage of silicon-based negative electrode materials is that they have a high theoretical capacity ($Li_{4.4}Si$, 4200mAh/g), Natural abundance (silicon is an abundant element on earth), and suitable electrochemical potential (0.4V vs. Li/Li+) - it is less likely to form "lithium dendrites" than hard carbon. Nevertheless, its shortcomings are also obvious: the inevitable volume change of the silicon material will cause the structure of the silicon-based electrode to crack or pulverize, which will lead to the uncontrollable growth of the SEI film; the conductivity itself is also poor.

Lithium titanate anode material is also a battery anode material. Its advantages include a simple preparation method, high charge and discharge platform, stable cycle, and high Coulombic efficiency; in "zero strain" material, the volume of the crystal during the reaction cycle remains within a stable range (Effectively solves the problem of electrode material falling off due to volume changes); the electrode voltage platform is stable. Disadvantages also exist: low conductivity and lithium-ion diffusion coefficient, severe polarization of the electrode at high current density, which sharply reduces the capacitance of the electrode, and the formation of SEI film, which causes adverse reactions in long-term contact between the electrode and the electrolyte.

Tin-based anode materials have also attracted widespread attention due to abundant resources high theoretical capacity ($Li_{22}Sn_5$ produces a total theoretical capacity of approximately 994mAh/g, $Na_{15}Sn_4$ produces a theoretical capacity of 847mAh/g); the lithium insertion potential is higher than the lithium precipitation potential, and lithium deposition can be avoided at high rates; The packing density is high (75.46mol/L, close to the packing density of lithium 73.36mol/L). The disadvantage is that the volume expansion rate of Sn during cycling reaches 259% (lithium-ion battery) and 423% (sodium-ion battery), respectively, seriously affecting the cycle performance.

1.3.2 Organic Materials

Organic materials are particularly of great interest for developing sustainable, flexible, and low-cost green batteries with abundant natural sources, diverse structures, and high electrochemical performance due to multielectron reversible redox reactions[43]. The applications of organic anode materials for lithium-ion batteries are roughly divided into two categories: organic small molecules and polymers. Among them, polymers can be subdivided into Schiff base polymers, polyamides, and conductive polymers[39].

Recently, the first-ever novel organic compound used as an anode for SIBs is disodium terephthalate ($Na_2C_8H_4O_4$), similar to di-lithium terephthalate ($Li_2C_8H_4O_4$)[44], which showed a reversible capacity of 250 $mAhg^{-1}$ at a voltage of 0.45 V with a low initial columbic efficiency of 60%. The rate capability and cycling stability of the material are low due to its tendency to dissolve in organic solvents, which can be overcome by applying a thin layer of Al_2O_3 coating[45].

Other organic electrodes are derived from natural biomolecules such as Wang et al. prepared juglone/RGO composite showing the reversible capacity of 305 $mAhg^{-1}$, which is exceptionally higher than pure juglone with 40 $mAhg^{-1}$ and pure RGO with 123 $mAhg^{-1}$ after ten cycles[46].

Organic negative electrode materials are low-cost and pollution-free but are easily soluble in organic electrolytes and have poor cycle stability. Compared with inorganic anode materials, organic anode materials are characterized by low cost and diverse structures. However, this material still needs to be optimized and improved.

1.4 Problem Statement

The consumption of traditional fossil fuels has caused the global average temperature to continue to rise, making it urgent to find a more environmentally friendly way to produce, distribute, and consume energy. Therefore, the development and utilization of renewable biomass-derived materials for renewable energy applications have received great attention.

Although soft carbon materials have higher capacity values, their fast decay speed poses obstacles to practical applications; hard carbon materials are easier to prepare, have higher cycle life, and have already gained some practical applications. Compared with soft carbon, hard carbon has a more disordered structure, higher defect concentration, higher heteroatom content, and larger distance between graphite layers, as well as a more closed pore structure. This helps provide more storage sites and diffusion pathways for sodium ions. However, the economic efficiency of hard carbon is slightly worse than that of soft carbon. Among sodium-ion batteries, hard carbon is the mainstream of current applications due to its advantages. In addition, low cost, sustainability, and simpler preparation also provide more possibilities for the commercialization of hard carbon materials.

A unique feature of lignin is the presence of abundant aromatic carbon ring skeletons. Coupled with its renewable and low-cost properties, lignin-derived hard carbon has been widely studied as electrode materials for energy storage applications. Combining the low cost brought by the high abundance and uniform distribution of sodium resources and the successful application of hard carbon materials in sodium batteries, lignin-derived hard carbons have broad prospects in the research of sodium batteries. However, the formation of a solid electrolyte interface (SEI) during the first cycle in electrode materials and the loss of sodium ions during long-term cycling has a fatal impact on the performance of sodium batteries. New technology is needed to improve the initial Coulombic efficiency (ICE) of lignin-based electrode materials.

2 Literature Review

2.1 Initial Coulombic Efficiency

Compared with lithium-ion batteries, sodium-ion batteries have the advantages of abundant sodium resources, wide distribution, and low cost and are expected to be used in large-scale energy storage fields of smart grids and renewable energy power generation. Hard carbon is considered to be the most promising anode material for sodium-ion batteries, but its low first Coulombic efficiency severely reduces the energy density of the full battery, thus limiting its industrialization process.

2.2 Causes of Low ICE

The large number of defects and disordered structure contained in hard carbon causes the irreversible deintercalation of sodium ions during the first charge and discharge process, which is the main reason for the first irreversible capacity loss. This will lead to a lack of sodium source, the formation of the solid electrolyte interface (SEI) during the first cycle, and the loss of sodium ions during long-term cycling, ultimately having a fatal impact on the electrochemical performance of sodium-ion batteries.

2.3 Methods to Improve ICE

2.3.1 Control Material Structural

The microstructure of hard carbon is composed of curved graphene-like sheets stacked to form short-range ordered micro-domains. At the same time, the random and disordered stacking of each micro-domain leaves many nanopores. Sodium ions can be absorbed through defects, interlayer embedding, and nanopore filling. The method is stored in hard carbon, so the microstructure of hard carbon will directly affect the sodium storage capacity. There are two main ideas for regulating the microstructure of hard carbon. One is to regulate the carbonization process, including carbonization temperature, temperature change rate, carbonization method, etc. It is generally believed that increasing the carbonization temperature and reducing the heating ramp can provide enough energy and time for the rearrangement of the carbon layer, which is beneficial to increasing the orderliness of the hard carbon structure and reducing pores and defects, which is beneficial to improving the ICE and cycling stability.

2.3.2 Introduction of Anions

The introduction of one or more heteroatoms (N, O, P, etc.) will also cause changes in the microstructure of hard carbon. Usually, the introduction of anions can effectively change the interlayer spacing, surface wettability, and electronic conductivity of hard carbon materials, thereby improving their sodium storage performance. Among them, N doping has been widely studied because it can introduce defects, increase electronic conductivity, and thereby improve specific capacity and rate performance. In addition to single anion doping, researchers have found that the doping of two or more heteroatoms can often produce synergistic effects and help further optimize performance. In recent years, cation doping has also been studied and found to have the effect of improving the sodium storage performance of hard carbon. Doping Li/Na, also known as pre-lithiation/pre-sodium technology, can effectively reduce the irreversible capacity and significantly improve the first-cycle Coulombic efficiency.

2.3.3 Control Material Interface

Since sodium ions have a larger atomic radius, the researchers used morphological design to increase diffusion channels and shorten diffusion distances to optimize rate performance. For example, 0D carbon quantum dots, 1D carbon fiber, 2D carbon nanosheets, 3D carbon balls, carbon frames, etc., as well as hollow structures, porous structures, hierarchical structures, etc.[47]. Some researchers use the special morphological characteristics of some biomass carbon sources for morphology design. In addition, people have also widely tried to artificially synthesize some hard carbon anodes with special morphologies, such as using template methods to prepare porous or hollow structures, designing hierarchical structures, etc. The interface between the electrode and the electrolyte often has a significant impact on the decomposition process of the electrolyte, thereby affecting the thickness and stability of the SEI film and the interface impedance, etc., thereby affecting the first cycle Coulombic efficiency, sodium ion diffusion kinetics and cycle stability. The impact is larger, which motivates researchers to optimize performance through interface construction. Commonly used methods include surface coating, oxide covering defects, etc. For example, some researchers used sucrose hydrothermal method to prepare carbon spheres. During the high-temperature carbonization process, toluene is introduced. Toluene cracks on the hard carbon surface to form a soft carbon coating. The Coulombic efficiency increases from 54% to 83% in the first cycle while achieving a capacity retention rate of 93%[48].

2.3.4 Optimize Electrolyte

In addition to the above methods, the electrochemical performance of hard carbon anode materials can also be improved through electrolyte control. As the reaction medium that transports ions and connects current channels in the battery system, the physical properties of the electrolyte system greatly affect the electrochemical performance of the battery material. Therefore, choosing a suitable electrolyte system is crucial to achieving high energy density, long cycle life, and high battery safety.

Because ester solvents have good oxidation resistance, the electrolyte solution widely used in lithium-ion batteries is mainly ethylene carbonate (EC), combined with other linear carbonate electrolyte systems. Continuing the experience of using lithium-ion batteries, the current mainstream electrolyte system in sodium-ion batteries is basically based on esters (ethylene carbonate-diethyl carbonate (EC-DEC), ethylene carbonate-dimethyl carbonate (EC-DMC)). Studies have shown that using EC as the electrolyte in pure solvents can achieve the highest ICE. However, a single EC is solid at room temperature, so it is not suitable to be used alone as a solvent for the electrolyte. Among binary mixed solvents, EC-DEC shows the best cycle performance and ICE, and the mixed solvent electrolyte has higher conductivity than a single solvent. The introduction of EC can greatly improve the ion concentration of the electrolyte-conductivity. In addition, when researchers studied the difference in SEI film and electrochemical performance of TiO2 anode in ether-based and ester-based electrolytes, they found that the surface of the SEI layer in the ether-based system is mainly composed of organic compounds, while more inorganic compounds exist in inside SEI. They detected more organic compounds in the SEI film of the ester, which made the SEI film thicker and resulted in higher charge transfer resistance and energy barrier[49]. Therefore, batteries generally exhibit better rate performance in ether electrolytes. Their results have a certain guiding significance for clarifying the differences between hard carbon electrodes in ether and ester electrolytes. Other researchers have proven through experiments and theoretical calculations that the fast sodium ion diffusion coefficient and thin and low internal resistance SEI film in ether systems can promote the improvement of the rate performance of hard carbon materials.

2.3.5 Control Side Reactions

Hard carbon is considered one of the most promising anode material candidates in Na-ion batteries. However, its low ICE severely hinders its further development. Zhu et al. synthesized high-performance hard carbon[43] from waste apricots from the perspective of improving the Initial Coulombic efficiency. In this work, various characterization methods have been utilized to reveal the role of H2 reduction treatment (HRT) in reducing the oxygen-containing covalent bond and dangling. The elemental analyses directly confirm the impact of H2 reduction on oxygen content with the use of HRT. FTIR spectra were also applied to investigate the functional group variation. Combined with the elemental analysis, it can be concluded that the decreased oxygen content is mainly ascribed to the removal of the C–O (peaks located at around 1715 cm^{-1}) and C-

O (peaks located at around 1250 cm^{-1}) by HRT. Furthermore, the Raman spectroscopy result shows that the IG/ID values of samples with HRT are larger than those of the samples without HRT, further confirming the reduction of defects. Thus, they concluded that the high ICE of 79% for hard carbon is the result of a fewer oxygen functional groups and defect concentrations after HRT, which greatly reduces the occurrence of unwanted side reactions[39].

2.3.6 Pre-sodiation Material

The sodium ions migrated from the positive electrode of sodium-ion batteries participate in the irreversible reaction of the solid interface film (SEI) on the surface of the negative electrode, which greatly consumes the active material, resulting in lower initial Coulombic efficiency, energy density, and cycle stability. To improve the reversible cycle capacity and first Coulombic efficiency, pre-sodiation technology for sodium-ion battery electrode materials has been developed. This technology can replenish the active materials consumed by the solid interface film generated by the negative electrode reaction and improve the reversible cycle capacity of the battery. Pre-sodiation technology can alleviate the dilemma caused by low ICE and is a key step in expanding the sodium-ion battery market in the future.

3 Research Methodology

3.1 Materials Characterization

For the morphology observation of the samples, we used scanning electron microscopy (SEM, FEG-650, U.S.) to monitor their morphology changes and measured the carbon content of the samples with a total organic carbon analyzer (TOG, ASI-V, Japan). The electrochemical electrode was prepared as explained below. 80 wt% active materials

(CL), 10 wt% acetylene black, and 10 wt% carboxymethyl cellulose (CMC) were mixed in an aqueous solution to form a uniform slurry and then cast on Cu foil. The electrode was dried at 80 °C in a vacuum oven for 12 h and punched into a circular electrode before use. The loading mass of the CL is controlled around 3.0 mg cm^{-2}. An electrolyte of 1.0M $NaPF_6$ in dimethyl carbonate (DMC)/ethylene carbonate (EC) (1/1 by volume) was used therein.

3.2 Electrochemical Measurements

Cells were assembled in an argon-filled glove box and evaluated over a voltage range of 0.01-3.0 V at 25 °C using the Neware battery test system (China). Cyclic voltammetry was measured on the Interface 1010E General-purpose electrochemical workstation (U.S.) at a scan rate of 0.1mV/s in the voltage range from 3.0 to 0.01V (vs. Li+/Li and hereafter). Alternating current electrochemical impedance spectroscopy (EIS) was measured in the frequency range from 100 kHz to 100 MHz with an alternating current voltage amplitude of 10 mV at the open-circuit voltage. All electrochemical measurements were performed using CR-2032 type coin cells.

4 Results

The synthesis and redox behavior of L-N was selected as an efficient and widely applicable pre-sodiation agent. As shown in Fig. 1, when the circular electrode piece is soaked in the pre-sodiation solution, the hardon carbon undergoes a chemical reduction reaction, and electrons are transferred from naphthalene anion to Na^+ and simultaneously inserted into the graphite layer of HC to form sodiated host (PHC). Once the PHC is formed, its low potential initiates the reductive decomposition of dimethyl ether (DME) solvent to form a porous and immature SEI layer that consists of organic composition (ROLi). This immature SEI layer would be further strengthened when contacted with the Na-ion battery electrolyte, where FEC and PF_6^- anions decompose to produce NaF^- rich SEI layer, finally leading to a dense and robust SEI film. [6]

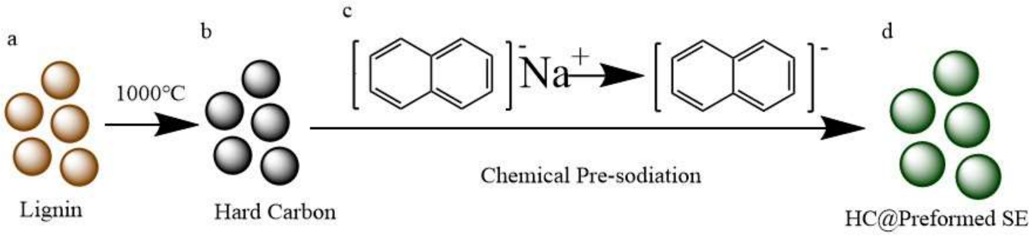
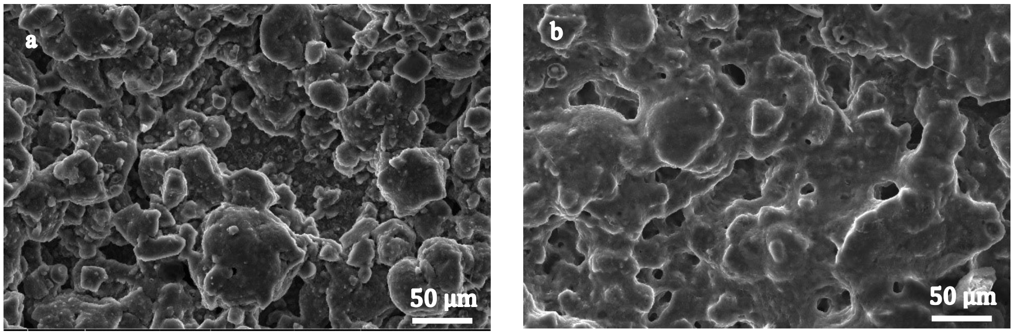


Figure. 5 Schematic illustration of the chemical pre-sodiation reaction of HC in Na-Naphthalenide/DME solution and SEI formation on the PHC anode

As shown in figure 6(b). Through the SEM, we can see that compared with the untreated anode disk, the surface of the treated anode disk has been covered with a layer of material. We preliminarily judge that this layer of material is the SEI film generated during the pre-sodiation process.



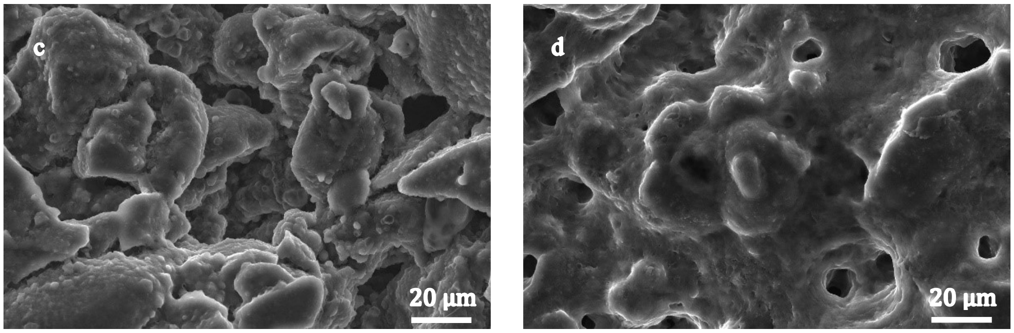
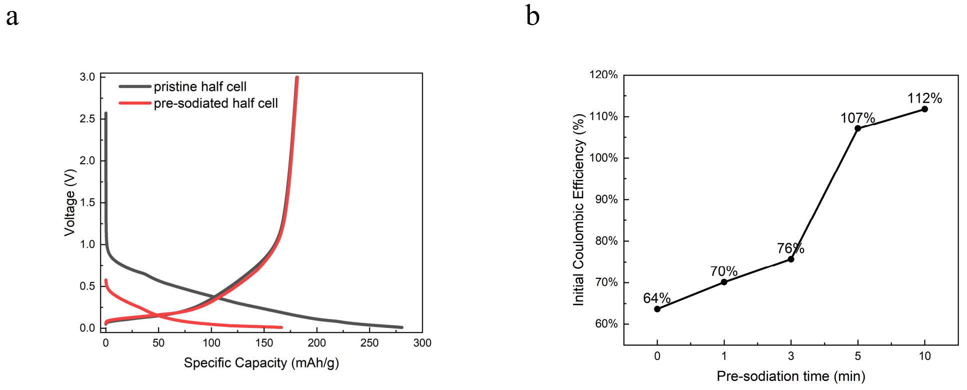


Figure 6. SEM image at a magnification of 500X for lignin-derived hard carbon anode electrode (a) Electrode without pre-lithiation (b) Electrode with pre-lithiation.

As shown in Figure 6(d), it can be found that the SEI film on the surface of the pre-sodiated anode disk is more denser and more uniform. The SEI film completely covers the original hard carbon material. In contrast, the surface of the non-treated anode disk is shown in Figure 6(c). The self-generated SEI film distribution is very uneven, and these uneven surfaces will keep consuming sodium ions in subsequent battery cycles, resulting in a continuous decline in battery capacity.



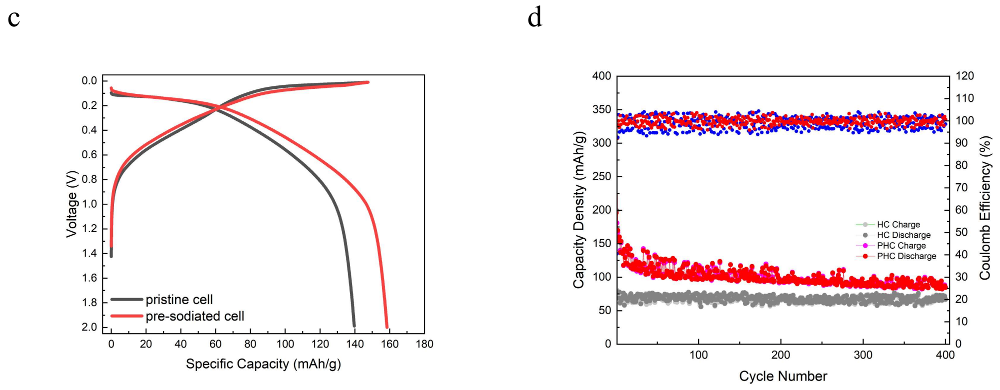


Figure 7. A comparison of (a) first cycle charge/discharge profiles and open circuit voltages. (b) initial Coulombic efficiencies of the PHC anodes obtained at different pre-sodiation times. (c) HC and PHC electrodes at a constant current of 50mA g^{-1}. (d) Long-term cycling performance at a current rate of 200 mA g^{-1}.

We treated our anode disk in pre-sodiation reagents for different lengths of time. After several sets of experiments, it was found that the improvement of the Initial Coulombic Efficiency was positively correlated with the pre-sodiation time. From Figure 7(b), it can be said that the optimal solution of initial Coulombic efficiency can be obtained after the anode disk is treated in the pre-sodiation reagent for 5 minutes, from 64% to 107%. As shown in Figure 7(a). At a current of 50 mA/g， 5 mins of pre-sodiation compensates for an irreversible capacity of more than 100 mAh/g.

Similarly, as shown in Figure 7(c), the 5-minute pre-sodiation enables the hard carbon anode to store and release more sodium ions when the discharge capacity is equal. After 400 charge and discharge cycles, the battery-specific capacity stabilized and increased by approximately 33%. This shows that the sodium ions added by pre-sodiation successfully compensated for the ion loss caused by the formation of the SEI film. This agrees with the stable SEI layer we just saw in the SEM images.

5 Discussion

In summary, we demonstrated a facile and effective approach to obtain a PHC by a chemical reaction of HC with sodium naphthalenide. This pre-sodiation process generates a preformed SEI layer on the PHC electrode, which then transforms into a dense and robust SEI film upon infiltration into the electrolyte after initial discharge. This SEI film can effectively compensate for the irreversible capacity loss and greatly enhance the initial and cycle Coulombic efficiencies, leading to high rate performance and cycle stability of PHC anodes. Based on the PHC anode, we assembled PHC/Na half cells and evaluated their electrochemical performances. The PHC/Na cells demonstrated very high ICE values of >100%. The practical application of pre-sodiated lignin-derived hard carbon materials in next-generation high-capacity and high-rate performance SIBs is demonstrated.

CONCLUSION

Lignin-derived hard carbon (HC) materials are ideal anode materials for lithium-ion/sodium-ion batteries due to their abundant reserves, low cost, non-toxicity, and environmental protection. In order to solve the problem of low Initial Coulombic Efficiency (ICE) in the practical application of derived hard carbon anode materials, the research started with chemical pre-lithiation/pre-sodiation and demonstrated a simple way to obtain pre-treated hard carbon (PHC) through the chemical reaction of hard carbon and lithium naphthide/sodium naphthide. Effective method. This chemical reagent treatment process creates a preformed SEI layer on the HC electrode, which then penetrates the electrolyte after the initial discharge and transforms into a dense and strong SEI film. This SEI film can effectively compensate for the irreversible capacity loss and greatly improve the ICE, thereby enabling the hard carbon anode to have high-rate performance and cycle stability. This experiment demonstrates the practical application of pretreated lignin-derived hard carbon materials in next-generation high-capacity and high-rate performance lithium-ion/sodium-ion batteries, filling the academic gap in chemical pre-sodiation in biomass-derived carbon materials. With the gradual advancement of sodium-ion battery industrialization and the demand for energy conservation and environmental protection, the demand for renewable hard carbon materials will also increase. It is believed that more hard carbon materials will participate in the development and application of lithium-ion and sodium-ion batteries in the future.

APPENDICES

Appendix 1. The instruments involved in the experimental process.

a. Tube Furnace, TFM2 2-Zone (China)

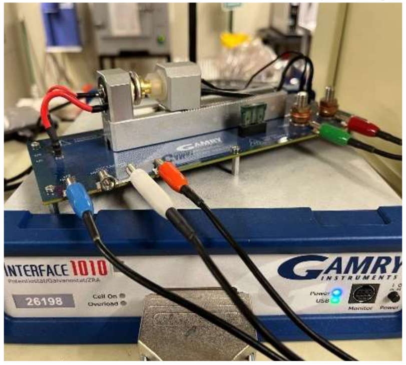
b. SEM, FEG-650 (FEI, U.S.)

c. Total Organic Carbon Analyzer, ASI-V (Shimadzu, Japan)

d. Glove Box, LABstar (MBraun, Germany)

e. Battery Testing System, Neware (China)

f. Interface 1010E Potentiostat (Gamry, U.S.)



REFERENCES

1. Li, M.; Lu, J.; Chen, Z.; Amine, K., 30 Years of Lithium-Ion Batteries. *Adv Mater* **2018**, e1800561.
2. Bai, X.; Xu, M.; Li, Q.; Yu, L., Trajectory-battery integrated design and its application to orbital maneuvers with electric pump-fed engines. *Advances in Space Research* **2022,** *70* (3), 825-841.
3. Zhang, L.; Zhu, C.; Yu, S.; Ge, D.; Zhou, H., Status and challenges facing representative anode materials for rechargeable lithium batteries. *Journal of Energy Chemistry* **2022,** *66*, 260-294.
4. Wang, C.; Zhao, H.; Wang, J.; Wang, J.; Lv, P., Electrochemical performance of modified artificial graphite as anode material for lithium ion batteries. *Ionics* **2012,** *19* (2), 221-226.
5. Wang, K.; Xu, Y.; Wu, H.; Yuan, R.; Zong, M.; Li, Y.; Dravid, V.; Ai, W.; Wu, J., A hybrid lithium storage mechanism of hard carbon enhances its performance as anodes for lithium-ion batteries. *Carbon* **2021,** *178*, 443-450.
6. Li, X.; Sun, X.; Hu, X.; Fan, F.; Cai, S.; Zheng, C.; Stucky, G. D., Review on comprehending and enhancing the initial Coulombic efficiency of anode materials in lithium-ion/sodium-ion batteries. *Nano Energy* **2020,** *77*.
7. Hu, R.; Ouyang, Y.; Liang, T.; Wang, H.; Liu, J.; Chen, J.; Yang, C.; Yang, L.; Zhu, M., Stabilizing the Nanostructure of SnO(2) Anodes by Transition Metals: A Route to Achieve High Initial Coulombic Efficiency and Stable Capacities for Lithium Storage. *Adv Mater* **2017,** *29* (13).
8. Zhao, J.; Lu, Z.; Liu, N.; Lee, H. W.; McDowell, M. T.; Cui, Y., Dry-air-stable lithium silicide-lithium oxide core-shell nanoparticles as high-capacity prelithiation reagents. *Nat Commun* **2014,** *5*, 5088.
9. Cao, Z.; Xu, P.; Zhai, H.; Du, S.; Mandal, J.; Dontigny, M.; Zaghib, K.; Yang, Y., Ambient-Air Stable Lithiated Anode for Rechargeable Li-Ion Batteries with High Energy Density. *Nano Lett* **2016,** *16* (11), 7235-7240.
10. Crum, R. S.; Homel, M. A.; Pagan, D. C.; Herbold, E. B.; Miller, D.; Lind, J.; Jensen, B. J.; Iverson, A. J.; Akin, M. C., In situ X-ray imaging of heterogeneity in dynamic compaction of granular media. *Journal of Applied Physics* **2019,** *125* (2).
11. Wang, F.; Sun, L.; Zi, W.; Zhao, B.; Du, H., Solution Synthesis of Porous Silicon Particles as an Anode Material for Lithium Ion Batteries. *Chemistry* **2019,** *25* (38), 9071-9077.
12. S. Zhang, M. S. D., K. Xu, J. Allen, T.R. Jow, Understanding Solid Electrolyte Interface Film Formation on Graphite Electrodes. *SSL* **2001**.
13. Memarzadeh Lotfabad, E.; Kalisvaart, P.; Kohandehghan, A.; Karpuzov, D.; Mitlin, D., Origin of non-SEI related coulombic efficiency loss in carbons tested against Na and Li. *J. Mater. Chem. A* **2014,** *2* (46), 19685-19695.
14. Yong-Mook Kang, K.-T. K., Ki-Young Lee, Seo-Jae Lee, Jae-Han Jung, and Jai-Young Leea,, Improvement of Initial Coulombic Efficiency of Co3 O 4 by Ballmilling Using Ni as an Additive. *Journal of The Electrochemical Society* **2003**.
15. Li, M.; Deng, Q.; Wang, J.; Jiang, K.; Shang, L.; Hu, Z.; Chu, J., In-situ gas reduction in reversible SnS-SnO2@N-doped graphene anodes for high-rate and lasting lithium storage. *Journal of Alloys and Compounds* **2018,** *769*, 1007-1018.

16. Zhang, C.; Lin, Z.; Yang, Z.; Xiao, D.; Hu, P.; Xu, H.; Duan, Y.; Pang, S.; Gu, L.; Cui, G., Hierarchically Designed Germanium Microcubes with High Initial Coulombic Efficiency toward Highly Reversible Lithium Storage. *Chemistry of Materials* **2015,** *27* (6), 2189-2194.
17. Zhang, X.; Li, X.; Liang, J.; Zhu, Y.; Qian, Y., Synthesis of MoS2 @C Nanotubes Via the Kirkendall Effect with Enhanced Electrochemical Performance for Lithium Ion and Sodium Ion Batteries. *Small* **2016,** *12* (18), 2484-91.
18. Ryu, J.; Hong, D.; Shin, M.; Park, S., Multiscale Hyperporous Silicon Flake Anodes for High Initial Coulombic Efficiency and Cycle Stability. *ACS Nano* **2016,** *10* (11), 10589-10597.
19. Hu, A.; Cao, W.; Liu, D.; Tang, Q.; Deng, W.; Chen, X., Saqima-like Co3O4/CNTs secondary microstructures with ultrahigh initial Coulombic efficiency as an anode for lithium ion batteries. *Journal of Solid State Electrochemistry* **2017,** *22* (2), 417-427.
20. Feng, T.; Xu, Y.; Zhang, Z.; Du, X.; Sun, X.; Xiong, L.; Rodriguez, R.; Holze, R., Low-Cost Al2O3 Coating Layer As a Preformed SEI on Natural Graphite Powder To Improve Coulombic Efficiency and High-Rate Cycling Stability of Lithium-Ion Batteries. *ACS Appl Mater Interfaces* **2016,** *8* (10), 6512-9.
21. Jarvis, C. R.; Lain, M. J.; Yakovleva, M. V.; Gao, Y., A prelithiated carbon anode for lithium-ion battery applications. *Journal of Power Sources* **2006,** *162* (2), 800-802.
22. Jarvis, C. R.; Lain, M. J.; Gao, Y.; Yakovleva, M., A lithium ion cell containing a non-lithiated cathode. *Journal of Power Sources* **2005,** *146* (1-2), 331-334.
23. <Prelithiated Silicon Nanowires as an Anode for Lithium Ion Batteries.pdf>.
24. Shen, Y.; Zhang, J.; Pu, Y.; Wang, H.; Wang, B.; Qian, J.; Cao, Y.; Zhong, F.; Ai, X.; Yang, H., Effective Chemical Prelithiation Strategy for Building a Silicon/Sulfur Li-Ion Battery. *ACS Energy Letters* **2019,** *4* (7), 1717-1724.
25. Yan, M. Y.; Li, G.; Zhang, J.; Tian, Y. F.; Yin, Y. X.; Zhang, C. J.; Jiang, K. C.; Xu, Q.; Li, H. L.; Guo, Y. G., Enabling SiO(x)/C Anode with High Initial Coulombic Efficiency through a Chemical Pre-Lithiation Strategy for High-Energy-Density Lithium-Ion Batteries. *ACS Appl Mater Interfaces* **2020,** *12* (24), 27202-27209.
26. Hwang, J. Y.; Myung, S. T.; Sun, Y. K., Sodium-ion batteries: present and future. *Chem Soc Rev* **2017,** *46* (12), 3529-3614.
27. Armand, M.; Touzain, P., Graphite intercalation compounds as cathode materials.pdf. *Materials Science and Engineering* **1977,** *31*, 319-329.
28. Palomares, V.; Serras, P.; Villaluenga, I.; Hueso, K. B.; Carretero-González, J.; Rojo, T., Na-ion batteries, recent advances and present challenges to become low cost energy storage systems. *Energy & Environmental Science* **2012,** *5* (3).
29. Tarascon, J.-M., Na-ion versus Li-ion Batteries: Complementarity Rather than Competitiveness. *Joule* **2020,** *4* (8), 1616-1620.
30. Ni, D.; Sun, W.; Wang, Z.; Bai, Y.; Lei, H.; Lai, X.; Sun, K., Heteroatom-Doped Mesoporous Hollow Carbon Spheres for Fast Sodium Storage with an Ultralong Cycle Life. *Advanced Energy Materials* **2019,** *9* (19).
31. Xu, X.; Si, L.; Zhou, X.; Tu, F.; Zhu, X.; Bao, J., Chemical bonding between antimony and ionic liquid-derived nitrogen-doped carbon for sodium-ion battery anode. *Journal of Power Sources* **2017,** *349*, 37-44.
32. Li, Y.; Mu, L.; Hu, Y.-S.; Li, H.; Chen, L.; Huang, X., Pitch-derived amorphous

carbon as high performance anode for sodium-ion batteries. *Energy Storage Materials* **2016,** *2*, 139-145.

33. Guo, Y.; Shi, Z.-q.; Chen, M.-m.; Wang, C.-y., Hierarchical porous carbon derived from sulfonated pitch for electrical double layer capacitors. *Journal of Power Sources* **2014,** *252*, 235-243.

34. Jian, Z.; Bommier, C.; Luo, L.; Li, Z.; Wang, W.; Wang, C.; Greaney, P. A.; Ji, X., Insights on the Mechanism of Na-Ion Storage in Soft Carbon Anode. *Chemistry of Materials* **2017,** *29* (5), 2314-2320.

35. Zhang, L.; Wang, W.; Lu, S.; Xiang, Y., Carbon Anode Materials: A Detailed Comparison between Na-ion and K-ion Batteries. *Advanced Energy Materials* **2021,** *11* (11).

36. DiVincenzo, D. P.; Mele, E. J., Cohesion and structure in stage-1 graphite intercalation compounds. *Phys Rev B Condens Matter* **1985,** *32* (4), 2538-2553.

37. P. Thomas; J. Ghanbaja; Billaud, D., Electrochemical insertion of sodium in pitch-based carbon fibres in comparison with graphite in NaClO4–ethylene carbonate electrolyte. *Electrochimica Acta* **1999,** *45*, 423–430.

38. Irisarri, E.; Ponrouch, A.; Palacin, M. R., Review—Hard Carbon Negative Electrode Materials for Sodium-Ion Batteries. *Journal of The Electrochemical Society* **2015,** *162* (14), A2476-A2482.

39. Perveen, T.; Siddiq, M.; Shahzad, N.; Ihsan, R.; Ahmad, A.; Shahzad, M. I., Prospects in anode materials for sodium ion batteries - A review. *Renewable and Sustainable Energy Reviews* **2020,** *119*.

40. Hu, M.; Zhou, H.; Gan, X.; Yang, L.; Huang, Z.-H.; Wang, D.-W.; Kang, F.; Lv, R., Ultrahigh rate sodium ion storage with nitrogen-doped expanded graphite oxide in ether-based electrolyte. *Journal of Materials Chemistry A* **2018,** *6* (4), 1582-1589.

41. Ricardo Alcántara, J. M. J.-M., Pedro Lavela, José L. Tirado, Carbon black-a promising electrode material for sodium-ion batteries. *Electrochemistry Communications* **2001**.

42. Xiao, W.; Sun, Q.; Liu, J.; Xiao, B.; Glans, P.-A.; Li, J.; Li, R.; Guo, J.; Yang, W.; Sham, T.-K.; Sun, X., Utilizing the full capacity of carbon black as anode for Na-ion batteries via solvent co-intercalation. *Nano Research* **2017,** *10* (12), 4378-4387.

43. Zhu, Y.; Chen, M.; Li, Q.; Yuan, C.; Wang, C., A porous biomass-derived anode for high-performance sodium-ion batteries. *Carbon* **2018,** *129*, 695-701.

44. Armand, M.; Grugeon, S.; Vezin, H.; Laruelle, S.; Ribiere, P.; Poizot, P.; Tarascon, J. M., Conjugated dicarboxylate anodes for Li-ion batteries. *Nat Mater* **2009,** *8* (2), 120-5.

45. Zhao, L.; Zhao, J.; Hu, Y. S.; Li, H.; Zhou, Z.; Armand, M.; Chen, L., Disodium Terephthalate (Na2C8H4O4) as High Performance Anode Material for Low-Cost Room-Temperature Sodium-Ion Battery. *Advanced Energy Materials* **2012,** *2* (8), 962-965.

46. Wang, H.; Hu, P.; Yang, J.; Gong, G.; Guo, L.; Chen, X., Renewable-juglone-based high-performance sodium-ion batteries. *Adv Mater* **2015,** *27* (14), 2348-54.

47. Tiwari, J. N.; Tiwari, R. N.; Kim, K. S., Zero-dimensional, one-dimensional, two-dimensional and three-dimensional nanostructured materials for advanced electrochemical energy devices. *Progress in Materials Science* **2012,** *57* (4), 724-803.

48. Li, Y.; Xu, S.; Wu, X.; Yu, J.; Wang, Y.; Hu, Y.-S.; Li, H.; Chen, L.; Huan, X., Amorphous monodispersed hard carbon micro-spherules derived from biomass.

Journal of Materials Chemistry A **2015**.

49. Zhang, J.; Gai, J.; Song, K.; Chen, W., Advances in electrode/electrolyte interphase for sodium-ion batteries from half cells to full cells. *Cell Reports Physical Science* **2022,** *3* (5).