

Research Review of Hard Carbon Anode Materials for Sodium-ion Batteries

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Abstract. In recent years, sodium-ion batteries (SIBs) have been regarded as the most promising energy storage batteries to replace lithium batteries for their abundant resources and excellent energy storage capabilities. There are many kinds of anode materials for SIBs, and hard carbon (HC) is considered the most promising anode material for SIBs for its lower cost and high reversible specific capacity. However, the research on HC anode materials is still immature with some problems such as poor cycle performance, low initial Coulombic efficiency and difficult commercialization. In order for HC anode materials to meet the needs of SIBs, the principles of HC for optimization should be understood. This paper reviews recent research on the sodium storage mechanism of HC anode materials and design methods to optimize their electrochemical performance, and introduces four storage mechanisms of sodium ions and optimized modification methods of HC anode materials, which provide references for the research of advanced SIBs.

Keywords: Sodium-ion Battery; Hard Carbon Anode; Material Modification.

1. Introduction

Environmental problems are increasingly serious nowadays. The massive exploitation and utilization of traditional energy causes an energy crisis and further aggravates environmental damage. Thus, it is urgent to develop new energy channels. In recent years, the research of various new energy sources such as wind energy, solar energy, nuclear energy, tidal energy, etc. has been developing. However, the better use of these intermittent energy sources requires stable energy storage equipment.

Lithium-ion batteries (LIBs), as the most popular clean energy storage batteries, have formed a complete commercial chain, accounting for 63% of the world energy storage market [1]. With the advantages of good cycle performance, low density, and low negative potential [2], LIBs are favored in new energy vehicles and electronic products. Given the limited, scarce and expensive distribution of lithium resources on the earth, so people need a new energy storage battery that can replace lithium batteries. The most promising substitute for lithium is sodium belonging to the same main group as lithium. Its chemical characteristics that are similar to lithium provide a good foundation for subsequent battery development. The reserve of sodium on the earth is 2.09%, about 320 times that of lithium [1]. It is widely distributed, abundant in resources, low in price with unique structural stability. However, sodium ions will not react with the aluminum of the negative electrode during battery operation, which allows aluminum to be used as the negative current collector of SIBs. It reduces the cost of SIBs and the total weight of SIBs. The main components of SIBs are positive electrode, negative electrode, separator, electrolyte and outer packaging, with Figure 1 as a schematic diagram of SIBs. As an indispensable part of SIBs, the selection and preparation of anode materials determine the performance of SIBs. Hence, the current research on SIBs anode materials is trending.

There are four main types of anode materials, including carbon-based materials, metal oxides [3], alloys, and organics. Besides, HC is the most promising anode material for SIBs for its extended graphene interlayer, suitable operating voltage, relatively low cost, and high reversible specific capacity. There are also many studies related to HC anode materials. In 2011, Komaba et al. [4] studied the structural changes of commercial HC during sodium insertion and confirmed that the storage mechanism of sodium ions is consistent with the insertion-fill model. Liu et al. [5] developed a thermal conductive agent and controlled oxidation method to prepare potato starch-based carbon

microspheres with natural potatoes as precursors. Guo et al. [6] used biomass waste-pine nut shell as a precursor to prepare HC materials, and obtained a pine nutshell HC (PNSHC-1400) sample with a reversible capacity of about $300 \text{ mAh} \cdot \text{g}^{-1}$, an initial Coulombic efficiency of up to 84% and good cycling performance. Although people have made progress in the research of HC materials, there are many problems to be solved in HC materials, such as low initial Coulombic efficiency (ICE), large volume expansion, moderate cycle/rate performance, insufficient exploration of sodium storage mechanism, etc. At present, people cannot find a perfect material for the commercial application of SIBs, so the optimization of HC materials is urgent for the research of HC anode materials.

This paper mainly introduces the research review of HC anode materials in recent years, and summarizes some representative research results. Firstly, HC anode materials and their sodium storage mechanism are briefly introduced, and then some modification methods of HC anode materials are emphatically demonstrated. Finally, the research direction and prospect of high-performance HC anode are prospected.



Figure 1 Illustration of a Na-ion Battery System [7]

2. Principle of HC Anode Material

2.1 Storage Mechanism of SIBs

The main working principle of SIBs is the intercalation and extraction of Na^+ in the electrode. Therefore, studying the storage mechanism of Na^+ is beneficial to design a high-performance and easy-to-commercialize HC anode. The research on the storage mechanism of sodium ions has always been indispensable for the research of SIBs, and remarkable progress has been made in the past few decades. Although the microstructures of various HCs are disordered, complex and diverse [8], it is still in the exploratory stage to clarify the universal sodium storage mechanism. However, many sodium storage models have been developed. This section mainly analyzes four typical HC sodium storage models, including “insertion-filling”, “adsorption-filling”, “adsorption-insertion” and “three-stage” (adsorption-insertion-filling), with each sodium storage model shown in Figure 2a.

Stevens et al. [9, 10] studied the storage characteristics of glucose source HC in batteries and proposed an “insertion-filling” model. They suggest that the structural changes in the sodium process of HC materials are similar to playing card stacking, but the stacked form of carbon layers is not ordered. Some of the carbon layers are parallel to each other, and the electrochemical curve is ramp-like when Na^+ is inserted. However, most of the carbon layers are disorderly distributed, and micropores are formed between each carbon layer for Na^+ to shuttle. When Na^+ is inserted into these nanopores, the electrochemical curve is a plateau region. However, this early model ignored the influence of defects in HC on Na^+ storage. Zhang et al. [11] proposed an “adsorption-filling” model, which considers the influence of HC defects on sodium ions, but it is not perfect. Alptekin et al. [12]

synthesized a series of HC materials and understood the storage process of Na^+ through in-situ expansion measurements. They also obtained the storage mode of sodium ions in three stages as follows. Na^+ entered the anode material by adsorption at the defect site, stored by insertion in the high-pressure inclined region, and entered the anode material by void filling in the low-pressure plateau region. At present, most of the research is in “adsorption-filling”.

Cao et al. [13] studied hollow carbon nanowires and proposed an “adsorption -insertion” model, which proposes that in the inclined region, sodium ions are adsorbed at the defect site, while the inserted nanopores exist in the plateau region. Qiu et al. [14] also further verified this storage model. Bommier et al. [15] tested sodium ion storage by varying the size of nanodomains in the disordered layer and proposed a “three-stage” (adsorption-insertion-fill) model, which proposes that sodium ions are adsorbed by defects in the slope region, but stored in the plateau region by inserting carbon layer, and finally filled into nanopores.

2.2 HC Anode Material

The sources of HC anode materials are diverse, and each material has unique electrochemical properties. Generally, HC precursors cannot be used directly, and they need to be selected, prepared and improved. Selecting a suitable precursor is the prerequisite for the preparation of HC materials, which is related to the complexity of subsequent operations, the performance of the prepared HC anode materials and the cost of battery commercialization. The selection of HC materials needs to consider the acquisition cost, carbon content, required microstructure and target performance characteristics of the materials. At present, the more studied HC anode materials are biomass-derived HC [1], polymer-based HC and soft carbon (SC)-based HC, as shown in Figure 2b.

Biomass HC includes a wide range, such as potatoes, pine nuts, rice, seafood waste and glucose. It is currently the most studied material source because biomass HC materials are not only widely available and cheap, but also environmentally friendly to achieve sustainable development. Moreover, HCs derived by thermochemical treatment have relatively good performance, and the LHA samples prepared by Zhu et al. [16] have high reversible capacity ($345 \text{ mAh} \cdot \text{g}^{-1}$ at 0.1 C), moderate ICE (73%) and excellent cycle stability (95% capacity retention after 250 cycles). In addition, biomass materials contain abundant heteroatoms (such as N, S, O, and P), which can be self-doped into the carbon layer during pyrolysis, providing additional active sites for improving electrochemical performance [17]. Figure 2c and Figure 2d are schematic diagrams of starch-based HCs synthesis by a fermentation process and schematic diagrams of NPDCs synthesis process, respectively. However, the shortcomings of biomass-derived HC are obvious. For example, it has a large ash content and extremely low carbonization yield, seriously affecting the electrochemical performance and cost of HC anode [18].

Preparing HC anode material from polymer has the advantages of a controllable synthesis process, easy microstructure design, and good electrochemical performance of polymer HC, but the cost is relatively high. There are many studies on this method. At present, the most popular precursor is epoxy resin. Wang et al. [19] prepared the resin precursor by a simple hydrothermal method using phenol and formaldehyde. The specific capacity of the obtained resin-based carbon sphere is as high as $311 \text{ mAh} \cdot \text{g}^{-1}$. However, the source of this HC material is relatively expensive, which is unfavorable to its commercialization. To avoid the shortcomings of the low carbonization rate of the first two materials, people turn their attention to SC-based HC anode materials derived from petrochemical and coal chemical products with high carbon content and low cost. The primary problem solved by this method is how to make SC into HC. There are many ways to deal with this problem, such as forming more C-O-C bonds in SC through oxidative cross-linking, oxidizing bituminous coal through gas phase and liquid phase oxidation [21], pre-oxidation process [22], etc.

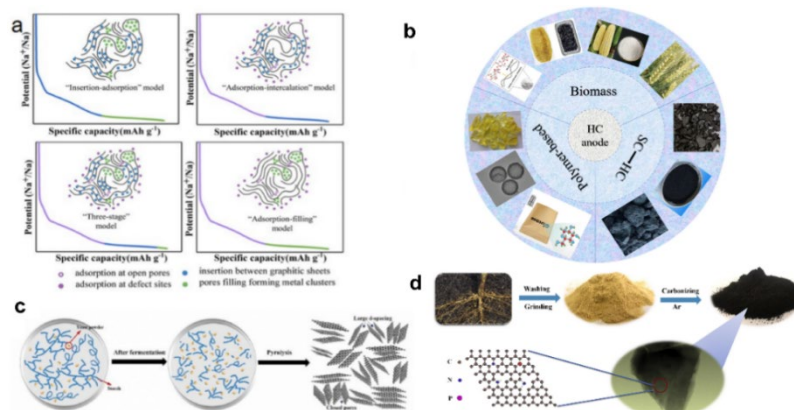


Figure 2.a. The mechanism of sodium storage in HC [23]; b. Schematic diagram of various HC that have been reported for the sodium-based energy storage [18]. c. Schematic illustration for the synthesis of starch-based HCs by a fermentation process [24]. d. Schematics of the synthesis process of NPDCs [25].

3. Optimization of HC Anode Materials

The formation of SEI film and the capture of sodium ions by defects in the carbon layer during the charging and discharging process of HC material as the battery anode will affect the battery performance. Nowadays, HC is not widely used in industry because of a lack of HC anode materials with high specific capacity and ICE and excellent cycle stability and rate performance. To synthesize high-performance HC anode materials that can be applied to industry, it is necessary to optimize HC materials. Although the storage mechanism of sodium in HC materials is unclear, we still have many methods to optimize HC materials. This chapter mainly introduces modification methods such as heteroatom doping, activation treatment, and polymer to optimize the properties of HC materials from various angles.

3.1 Heteroatom Doping

Heteroatom doping refers to replacing carbon atoms in the voids of uniform carbon structure with other atoms or inserting other foreign atoms. Most of the atoms used for doping are non-metal atoms, such as N, P, S, etc. In addition to increasing the interlayer spacing of HC, changing the electron/ion state of active materials, and expanding the interlayer spacing of HC materials, this method can accelerate the diffusion rate of sodium ions, change the number of active sites between graphite layers, and improve the electrochemical performance of HC anode materials. Thus, it is widely used in optimization experiments of HC anode materials. Moreover, heteroatom doping can bring different functions to HC according to its properties. For example, the strong electronegativity of F will weaken the repulsive force of sodium ion insertion, thus reducing the energy barrier of sodium ion insertion [26].

There are many methods of N-doping in carbon, which can be achieved by carbonizing N-containing precursors in an environment of NH_3 , or by incorporating nitrogen organic compounds into the precursors before carbonization. Zhao et al. [27] used sodium carboxymethyl cellulose as the precursor to prepare HC with N-doped nanosheet structure by $\text{CN} \cdot$ or $\text{C-C} \cdot$ free radicals generated by conversing nitrile intermediates during pyrolysis, as shown in Figure 3a, a schematic diagram of the formation of N-doped carbon nanosheets. This work further investigated the sodium storage mechanism of N-doped carbon, which contains different types of nitrogen defects, as shown in Figure 3b to explain the source of capacity. It increases the sodium storage capacity of the negative electrode and is beneficial to capture sodium ions through coordination. The abundant pore structure and high specific surface area of this material greatly enhance the rate capability ($192.8 \text{ mAh} \cdot \text{g}^{-1}$ at $5.0 \text{ A} \cdot \text{g}^{-1}$) and ultra-long cycle stability ($233.3 \text{ mAh} \cdot \text{g}^{-1}$ after 2000 cycles at $0.5 \text{ A} \cdot \text{g}^{-1}$).

Notably, the use of N doping may thicken the SEI film, resulting in low ICE, so some experiments prefer to use P and S as doping elements. Yuan et al. [28] prepared sulfur-doped interconnected carbon microspheres (S-CSs) by hydrothermal method and vulcanization treatment. This material showed an ultra-high reversible capacity of $520 \text{ mAh} \cdot \text{g}^{-1}$ after 50 cycles at $100 \text{ mA} \cdot \text{g}^{-1}$, which can maintain a reversible capacity of $257 \text{ mAh} \cdot \text{g}^{-1}$ at a high current density of $2 \text{ A} \cdot \text{g}^{-1}$. Regarding the electrochemical enhancement mechanism of NIBs by S-CSs after sulfur doping, they considered three possible adsorption sites of Na atoms on carbon based on DFT calculations, as shown in Figure 3c. In addition to the doping of single elements mentioned above, there are many studies of doping by two or more elements together [29].

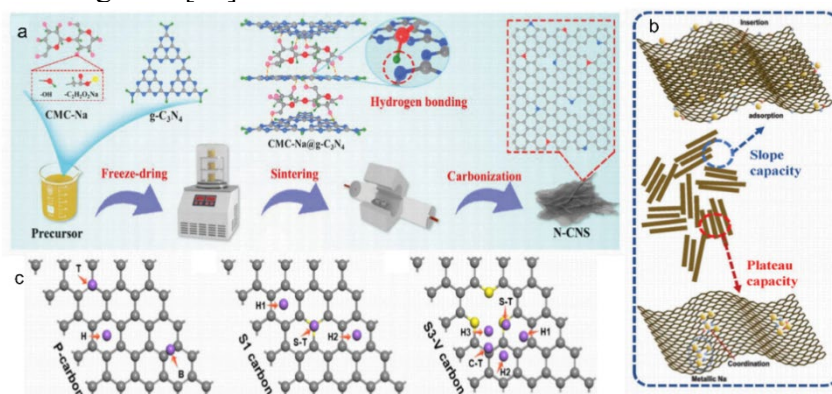


Figure 3. a. Schematic illustration of the formation of N-doped carbon nanosheets [27]. b. Schematic diagram of the source of sodium storage capacities [27]. c. The possible adsorption sites of Na atom on P-carbon layer, S1 carbon, and S3-V carbon [28].

3.2 Activation Treatment

There are three kinds of activation treatments for HC materials, namely physical activation, chemical activation and template activation. Activation treatment optimizes battery performance by adjusting HC pore structure, so activated HC materials often have high specific surface area, abundant pores, large contact area with electrolyte, high sodium storage capacity, and fast ion diffusion rate.

Physical activation refers to obtaining anode materials with better battery electrochemical performance by adjusting the carbonization temperature when preparing anode materials. This method can change the volume of HC pores, thereby affecting the speed of sodium ion insertion and extraction and the number of storage active sites. HC materials tend to show different characteristics in various carbonization temperature ranges. Generally, the higher the temperature, the higher the graphitization of HC and the smaller the interlayer spacing. Dahbi et al. [30], by comparing the HC prepared at various carbonization temperatures, found that Argan-1300 showed a small shell-like structure with a large number of curved graphene-like, illustrating the high defects of graphene sheets of argan material even at the high temperature of 1300°C . Moreover, the electrode can maintain a reversible capacity of $300 \text{ mAh} \cdot \text{g}^{-1}$ at a current density of $25 \text{ mA} \cdot \text{g}^{-1}$ with a capacity retention rate of 94.1% after 70 cycles.

Chemical activation refers to the treatment of HC materials with chemical reagents. These chemical reagents can remove impurities from HC materials and enrich their internal pore structure, thereby increasing the specific surface area and active sites of HC. Compared with physical activation, this method is more energy-saving and environmentally friendly, which is a commonly used material processing method in laboratories. The chemical reagents used to adjust the structure of HC are often various acids and bases. Some experiments also use ethanol, which is less dangerous and has more environmentally friendly materials as an activator. Wang et al. [31] used hydrochloric acid to treat hazelnut shells to obtain high-quality HC materials with higher layer spacing and active sites (as shown in Figure 4a, the material synthesis process), and the surface area of HCl-1000 is much higher than that of 0M-1000 (307.1 and $22.9 \text{ m}^2 \cdot \text{g}^{-1}$, respectively). This makes the electrochemical

performance of HCl-1000 superior. Its electrode also has a high reversible specific capacity of $342 \text{ mAh} \cdot \text{g}^{-1}$ as well as a high ICE of 91%.

Template activation refers to the use of inorganic materials (MgO , KCl , SiO_2 , etc.) as templates to adjust the internal pore size and distribution of HC. Generally, the inorganic molten salt with adjusted size enters the HC material, undergoes a series of operations such as pyrolysis and will be removed by acid or water washing. This modification is clean and effective with a good modification effect, which has been used in many experiments. In addition, template activation can be used in combination with other modification methods. For example, through liquid salt template-assisted and KOH dual activation with rosin as the precursor, Guo et al. [32] prepared an “egg bubble”-shaped HC containing a small amount of N doping. Figure 4b shows the synergistic engineering of the defect formation mechanism in carbon and the “pores in the graphene domain”. This structure facilitates the rapid transfer of electrons in the graphite domain. The fabricated SIBs exhibited an ICE of 92.9% at $0.05 \text{ A} \cdot \text{g}^{-1}$ and a high specific capacity of $367 \text{ mAh} \cdot \text{g}^{-1}$. Although the reversible specific capacity was not high at high current density, their average Coulombic efficiency was about 99%.

3.3 Material Compounding

HC materials derived from a single monomer often have a single structure, making it difficult to produce high-performance anode materials. We can change the internal pore structure of carbon materials, and increase the specific surface area and carbon layer spacing by combining carbon materials with other materials. The anode materials prepared in this way often have higher reversible specific capacity and Coulombic efficiency. In addition, the composite polymer will have the characteristics of each material. The electrochemical performance of HC materials can be improved by compounding to make HC materials have the characteristics of other materials (such as strong conductivity and sodium storage capacity, high capacity density, etc.).

Xu et al. [33] prepared hollow porous three-dimensional $\text{Co}(\text{Ni})\text{Se}_2/\text{N}$ doped carbon composite particles with metal-organic frameworks (MOFs) as templates. Figure 4c demonstrates the fabrication of the $\text{Co}(\text{Ni})\text{Se}_2/\text{NCC}$ schematic diagram. This particle presents good chemical properties as an anode material and a specific capacity as high as $735.2 \text{ mAh} \cdot \text{g}^{-1}$ after 100 cycles at a current density of $0.1 \text{ A} \cdot \text{g}^{-1}$. The composite of alloy materials and HC is also the focus, which can significantly improve the efficiency and energy storage capacity of SIBs. At the same time, it can alleviate the material crushing caused by the drastic volume change of alloy materials during charge and discharge. Ying et al. [34] prepared ultrafine Sn nanodots embedded doped carbon microcages (NMCs) by spray drying and annealing process, with Figure 4d shown as a schematic diagram of the material preparation. This material provides an initial reversible capacity of $439 \text{ mAh} \cdot \text{g}^{-1}$ at $50 \text{ mAh} \cdot \text{g}^{-1}$ and maintains $332 \text{ mAh} \cdot \text{g}^{-1}$ after 300 cycles.

There are various types of composite materials, such as MOF and carbon composites, carbon-based alloys, etc. Most of them have excellent properties, high specific capacity and cycle performance, but their synthesis methods are mostly complicated, costly and low in yield. At present, composite materials with excellent performance and simple and low cost are still being explored. In conclusion, material compositing is an effective strategy to optimize the anode of SIBs, which is not only remarkable but also environmentally friendly.

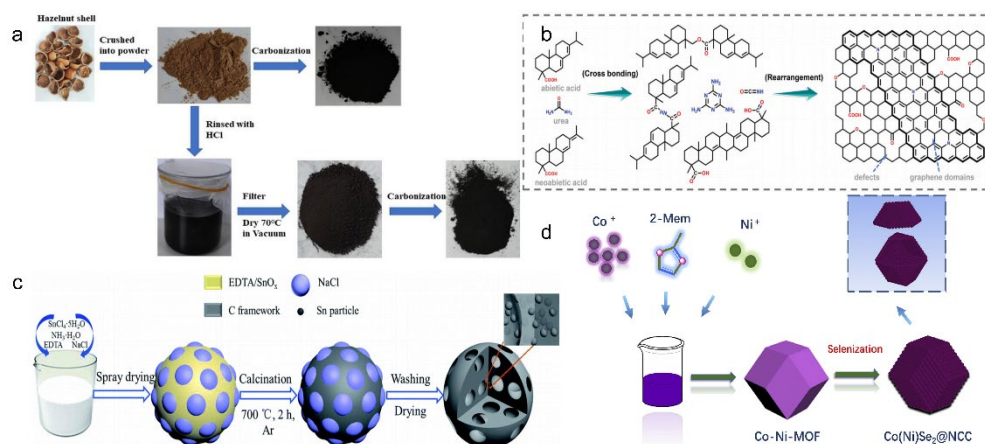


Figure 4. a. Two processes for the synthesis of hard carbon using hazelnut shells as a precursor [31]. b. Schematic illustration of the structure transformation [32]. c. Schematic diagram of Co(Ni)Se₂@NCC fabrication process [33]. d. Schematic diagram of the preparation process of Sn/N-doped carbon microcage composites [34].

4. Conclusion and Outlook

From the perspective of the principle and application of HC, this paper introduces in detail the storage mechanism of sodium ions, the classification of HC anode materials, the modification strategies of three HC anode materials and advanced research cases, so as to provide references for the research of HC anode and accelerate the industrialization of sodium batteries. Nowadays, the research of SIBs has made remarkable progress. However, due to the low specific capacity and ICE of HC anode materials and large-scale production, large-scale industrialization still cannot be achieved. In summary, HC anode materials face many challenges, and the future development of HC can be further studied in the following aspects:

(1) Explore new precursors. HC anodes made of different precursors will have various characteristics. Suitable precursors can not only improve electrochemical performance, but also achieve the effect of protecting the environment while reducing costs. Therefore, exploring new precursors is the key to the development of HC.

(2) Further investigate the sodium storage principle of SIBs. The sodium storage principle of HC guides the improvement of anode materials. However, the existing models are not universal now. The construction of new sodium storage models may be constructed by mixing the existing models.

(3) Improve the design method and synthesis strategy. Finding lower-cost, efficient and green synthesis methods and developing scalable new instruments and equipment are helpful for commercialization. The establishment of a mature testing and evaluation system can also guide the development of HC more efficiently.

References

- [1] B. Lu, C. Lin, H. Xiong, C. Zhang, L. Fang, J. Sun, Z. Hu, Y. Wu, X. Fan, G. Li, J. Fu, D. Deng, Q. Wu, Hard-Carbon Negative Electrodes from Biomasses for Sodium-Ion Batteries, *Molecules* 28 (2023) 4027. Retrieved from <https://doi.org/10.3390/molecules28104027>.
- [2] S. Roberts, E. Kendrick, The re-emergence of sodium ion batteries: testing, processing, and manufacturability, *NSA Volume 11* (2018) 23-33. Retrieved from <https://doi.org/10.2147/NSA.S146365>.
- [3] S. Qiu, L. Xiao, X. Ai, H. Yang, Y. Cao, Yolk-Shell TiO₂@C Nanocomposite as High-Performance Anode Material for Sodium-Ion Batteries, *ACS Appl. Mater. Interfaces* 9 (2017) 345–353. Retrieved from <https://doi.org/10.1021/acsami.6b12001>.

- [4] S. Komaba, et al. Electrochemical Na Insertion and Solid Electrolyte Interphase for Hard-Carbon Electrodes and Application to Na-Ion Batteries, *Adv Funct Materials* 21 (2011) 3859-3867. Retrieved from <https://doi.org/10.1002/adfm.201100854>.
- [5] X. Liu, Potato-starch-based hard carbon microspheres: Preparation and application as an anode material for sodium-ion batteries, *Solid State Ionics* (2024).
- [6] H. Guo, K. Sun, Y. Lu, H. Wang, X. Ma, Z. Li, Y.-S. Hu, D. Chen, Hard carbons derived from pine nut shells as anode materials for Na-ion batteries*, *Chinese Phys. B* 28 (2019) 068203. <https://doi.org/10.1088/1674-1056/28/6/068203>.
- [7] J.-Y. Hwang, S.-T. Myung, Y.-K. Sun, Sodium-ion batteries: present and future, *Chem. Soc. Rev.* 46 (2017) 3529–3614. <https://doi.org/10.1039/C6CS00776G>.
- [8] S. Tan, H. Yang, Z. Zhang, X. Xu, Y. Xu, J. Zhou, X. Zhou, Z. Pan, X. Rao, Y. Gu, Z. Wang, Y. Wu, X. Liu, Y. Zhang, The Progress of Hard Carbon as an Anode Material in Sodium-Ion Batteries, *Molecules* 28 (2023) 3134. Retrieved from <https://doi.org/10.3390/molecules28073134>.
- [9] D.A. Stevens, J.R. Dahn, An In Situ Small-Angle X-Ray Scattering Study of Sodium Insertion into a Nanoporous Carbon Anode Material within an Operating Electrochemical Cell, *J. Electrochem. Soc.* 147 (2000) 4428. Retrieved from <https://doi.org/10/bp73w6>.
- [10] D.A. Stevens, J.R. Dahn, High Capacity Anode Materials for Rechargeable Sodium-Ion Batteries, *J. Electrochem. Soc.* 147 (2000) 1271. Retrieved from <https://doi.org/10/b85tn9>.
- [11] B. Zhang, F. Kang, J.M. Tarascon, J.K. Kim, Recent advances in electrospun carbon nanofibers and their application in electrochemical energy storage, *Progress in Materials Science* 76 (2016) 319-380. Retrieved from <https://doi.org/10/gmv98f>.
- [12] H. Alptekin, H. Au, A.C. Jensen, E. Olsson, M. Goktas, T.F. Headen, P. Adelhelm, Q. Cai, A.J. Drew, M.-M. Titirici, Sodium Storage Mechanism Investigations through Structural Changes in Hard Carbons, *ACS Appl. Energy Mater.* 3 (2020) 9918-9927. Retrieved from <https://doi.org/10/gmq99f>.
- [13] Y. Cao, L. Xiao, et al. Sodium Ion Insertion in Hollow Carbon Nanowires for Battery Applications, *Nano Lett.* 12(2012)3783-3787. Retrieved from <https://doi.org/10/f334p4>.
- [14] S. Qiu, L. Xiao, et al. Manipulating Adsorption–Insertion Mechanisms in Nanostructured Carbon Materials for High-Efficiency Sodium Ion Storage, *Advanced Energy Materials* 7 (2017) 1700403. Retrieved from <https://doi.org/10/gbwtp>.
- [15] C. Bommier, T.W. Surta, M. Dolgos, X. Ji, New Mechanistic Insights on Na-Ion Storage in Nongraphitizable Carbon, *Nano Lett.* 15 (2015) 5888-5892. Retrieved from <https://doi.org/10/f7rmd>.
- [16] High-yield humic acid-based hard carbons as promising anode materials for sodium-ion batteries, *Carbon* 123 (2017) 727-734. Retrieved from <https://doi.org/10.1016/j.carbon.2017.08.030>.
- [17] R. Liu, B. Zhang, L. Fu, Z. Fu, H. Xie, Y. Tang, H. Wang, D. Sun, Classification, fabrication, and modification of carbon spheres for sodium-ion batteries, *Materials Today Chemistry* 35 (2024) 101903. <https://doi.org/10.1016/j.mtchem.2024.101903>.
- [18] L. Liu, Q. Xu, S. Yin, Z. Liu, Y. Li, W. Pang, Recent progress on hard carbon-based anode for sodium-ion battery, *Journal of Power Sources* 615 (2024) 235116. Retrieved from <https://doi.org/10.1016/j.jpowsour.2024.235116>.
- [19] H. Wang, Z. Shi, J. Jin, C. Chong, C. Wang, Properties and sodium insertion behavior of Phenolic Resin-based hard carbon microspheres obtained by a hydrothermal method, *Journal of Electroanalytical Chemistry* 755 (2015) 87-91. Retrieved from <https://doi.org/10.1016/j.jelechem.2015.07.032>.
- [20] C. Fan, R. Zhang, X. Luo, Z. Hu, W. Zhou, W. Zhang, J. Liu, J. Liu, Epoxy phenol novolac resin: A novel precursor to construct high performance hard carbon anode toward enhanced sodium-ion batteries, *Carbon* 205 (2023) 353-364. Retrieved from <https://doi.org/10/gt678f>.
- [21] Z. Lou, H. Wang, D. Wu, F. Sun, J. Gao, X. Lai, G. Zhao, Microcrystalline regulation of bituminous coal derived hard carbon by pre-oxidation strategy for improved sodium-ion storage, *Fuel* 310 (2022) 122072. <https://doi.org/10/gtkjsc>.
- [22] Y. Lu, C. Zhao, X. Qi, Y. Qi, H. Li, X. Huang, L. Chen, Y. Hu, Pre-Oxidation-Tuned Microstructures of Carbon Anodes Derived from Pitch for Enhancing Na Storage Performance, *Advanced Energy Materials* 8 (2018) 1800108. Retrieved from <https://doi.org/10.1002/aenm.201800108>.

- [23] S. Wu, X. Lu, K. Zhang, J. Xu, Z. Sun, Nitrogen/Phosphorus Dual-Doped Hard Carbon Anode with High Initial Coulombic Efficiency for Superior Sodium Storage, *Batteries & Supercaps* 6 (2023) e202200427. <https://doi.org/10.1002/batt.202200427>.
- [24] Y. Chen, Sustainable and scalable fabrication of high-performance hard carbon anode for Na-ion battery, *Journal of Power Sources* (2023).
- [25] Soybean roots-derived N, P Co-doped mesoporous hard carbon for boosting sodium and potassium-ion batteries, *Carbon* 178 (2021) 233-242. Retrieved from <https://doi.org/10.1016/j.carbon.2021.03.022>.
- [26] P. Wang, B. Qiao, Y. Du, Y. Li, X. Zhou, Z. Dai, J. Bao, Fluorine-Doped Carbon Particles Derived from Lotus Petioles as High-Performance Anode Materials for Sodium-Ion Batteries, *J. Phys. Chem. C* 119 (2015) 21336-21344. Retrieved from <https://doi.org/10.1021/acs.jpcc.5b05443>.
- [27] Y. Zhao, Z. Hu, C. Fan, P. Gao, R. Zhang, Z. Liu, J. Liu, J. Liu, Novel Structural Design and Adsorption/Insertion Coordinating Quasi-Metallic Na Storage Mechanism toward High-performance Hard Carbon Anode Derived from Carboxymethyl Cellulose, (2023). Retrieved from <https://doi.org/10.1002/sml.202303296>.
- [28] X. Yuan, S. Chen, J. Li, J. Xie, G. Yan, B. Liu, X. Li, R. Li, L. Pan, W. Mai, Understanding the improved performance of sulfur-doped interconnected carbon microspheres for Na-ion storage, *Carbon Energy* 3 (2021) 615-626. Retrieved from <https://doi.org/10.1002/cey2.98>.
- [29] H. Wang, S. Liu, C. Lei, H. Qiu, W. Jiang, X. Sun, Y. Zhang, W. He, Ammonium polyphosphate assisted thermal polymerization of pre-oxidized asphalt to prepare N/P double-doped hard carbon for improved sodium ion storage, *Journal of Energy Storage* 85 (2024) 111045. Retrieved from <https://doi.org/10.1016/j.est.2024.111045>.
- [30] M. Dahbi, M. Kiso, K. Kubota, T. Horiba, T. Chafik, K. Hida, T. Matsuyama, S. Komaba, Synthesis of hard carbon from argan shells for Na-ion batteries, *J. Mater. Chem. A* 5 (2017) 9917-9928. Retrieved from <https://doi.org/10.1039/C7TA01394A>.
- [31] J. Wang, Hard carbon derived from hazelnut shell with facile HCl treatment as high-initial-coulombic-efficiency anode for sodium ion batteries, *Sustainable Materials and Technologies* (2022). <https://doi.org/10.1016/j.susmat.2022.e00446>.
- [32] M. Guo, H. Zhang, Z. Huang, W. Li, D. Zhang, C. Gao, F. Gao, P. He, J. Wang, W. Chen, X. Chen, M. Terrones, Y. Wang, Liquid Template Assisted Activation for “Egg Puff”-Like Hard Carbon toward High Sodium Storage Performance, *Small* 19 (2023) 2302583. Retrieved from <https://doi.org/10.1002/sml.202302583>.
- [33] MOF-derived hollow Co(Ni)Se₂/N-doped carbon composite material for preparation of sodium ion battery anode, *Ceramics International* 46 (2020) 4532-4542. Retrieved from <https://doi.org/10.1016/j.ceramint.2019.10.181>.
- [34] H. Ying, S. Zhang, Z. Meng, Z. Sun, W.-Q. Han, Ultrasmall Sn nanodots embedded inside N-doped carbon microcages as high-performance lithium and sodium ion battery anodes, *J. Mater. Chem. A* 5 (2017) 8334-8342. Retrieved from <https://doi.org/10.1039/C7TA01480E>.