Proceedings of the 4th International Conference on Materials Chemistry and Environmental Engineering
DOI: 10.54254/2755-2721/60/20240892

Advanced carbon nanomaterials and nanotechnology applied in anode for lithium metal/ion batteries

Wang Wang

College of Chemistry, Chemical Engineering and Resource Utilization, Northeast Forestry University, Harbin 150000, China

ww20021215@nefu.edu.cn

Abstract. Lithium batteries have a significant impact on the automotive industry and play an indispensable role in modern life. The demand for lithium batteries has increased with the advent of carbon nanomaterials. These materials provide higher energy storage and have the potential to replace graphite as the negative battery material. Although graphite is the most frequently used material on the market, it has an amorphous structure and limited capacity. To enhance the capacity of lithium batteries and increase their ability to store more lithium ions within a smaller volume, researchers have developed many advanced carbon nanomaterials with great specific properties. These materials not only increase the battery's capacity but also offer viable solutions to the challenges encountered by lithium batteries. The focus of this article is on how these advanced carbon nanomaterials from 3 dimensions to 1 dimension can realize material performance improvements and changes in battery lifespan, energy density, resistance in dendritic lithium-deposition, and other aspects.

Keywords: Carbon nanomaterials; Anode; Lithium metal battery; Lithium ion battery; Nanotechnology

1. Introduction

To fulfill the requirements of the electric vehicle industry, lithium batteries are currently undergoing a revolution. Lithium batteries can be grouped into lithium ion batteries and lithium metal batteries, such as lithium-ion batteries (LIBs), lithium–sulfur batteries (Li–S batteries), and lithium–oxygen batteries ($Li–O_2$ batteries) are significantly transforming people's daily lives [1]. However, during the early stages of development, organic electrolyte was accidentally found forming a protective layer on the surface of electrodes. Sadly, it exhibited noticeable shortcomings: i) the expansion and deformation of the volume of lithium battery electrodes during operation, which lack proper morphology [2]; ii) dendritic lithium deposition on the lithium anode causes irreversible reduction of current density, energy density, and lifetime of the lithium battery [3]. However, Lithium metal batteries and lithium ion batteries are two completely distinct types of batteries. Lithium-ion batteries are very ubiquitous in daily life, such as cell phones, tablets, laptops, and other portable devices. In addition, lithium-ion batteries are also one of the most commonly used batteries in electric and hybrid vehicles. In comparison, lithium metal ions can only be used once, belonging to primary batteries, which limits their wide applications. However, in recent years, lithium metal anode has re-entered the public's view again due to its advantages such as high energy density, lightweight, and low potential. As a matter of fact, a number of researchers have

DOI: 10.54254/2755-2721/60/20240892

already realized the multi-cycle use of lithium metal batteries in their research. In order to realize the multi-cycling of lithium metal batteries, the application of carbon nanomaterials in the anode is of great significance and to address these challenges, scientists have implemented carbon nanomaterials to improve the anode. These nanomaterials not only effectively inhibit lithium dendrite formation, but also improve the energy density, current density, and rapid electron transport.

Carbon nanomaterials are widely utilized in lithium ion/metal batteries. This paper classifies carbon nanomaterials based on their dimensional structure. One-dimensional carbon nanotubes possess superior electrical conductivity, chemical stability, and mechanical properties. Two-dimensional graphene exhibits remarkable electrical conductivity, notable flexibility, and abundant specific surface area, ideal for diverse morphologies of batteries. Three-dimensional graphite nanomaterials and porous materials display intriguing electrical conductivity and physicochemical properties. However, batteries containing graphite nanomaterials slightly trail behind in all measured properties when compared to the previously mentioned nanomaterials. Moreover, their remarkable mechanical properties and chemical stability make them highly desirable as lithium battery electrodes. In recent years, there has been a focus on blending carbon nanomaterials with other materials to ameliorate the electrochemical characteristics of the initial carbon nanomaterials. The outcomes of these researches have been the enhancement of electrical conductivity, energy density, electrode lifetime, and cycle time of anodes in lithium batteries. This paper will provide an in-depth analysis and comparison of the advanced applications of each type of carbon nanomaterial in lithium batteries as anodes.

2. Three-dimensional (3D) materials

The complex structure and flexibility of 3D carbon nanomaterials allow for high ion capacity and efficient transport. Their unique hierarchical structure and micro/mesoporous pores effectively prevent electrode expansion during charging and discharging. Additionally, their high energy density and consistent performance make them excellent choices for electricity storage.

2.1. Graphite-based nanomaterials

The stable electrochemical properties and high specific capacity of graphite render it a prime candidate for a lithium battery anode. Graphite is not considered a type of nanomaterial. Moreover, the drawbacks of utilizing graphite as a negative electrode in batteries are quite evident: i) the layered structure of graphite is unstable and increasingly susceptible to collapse over time, which ultimately culminates in a reduction of the battery's energy storage capacity and specific capacity; ii) The battery has insufficient capacity; iii) Its performance is poor during multiplication, with the potential for serious damage with higher currents. To address these issues, Jiang et al. utilized a simple ball milling approach to create a lithium metal carbon composite called GKBLi, using stabilized lithium metal powder (SLMP) and graphitized Ketjen black (GKB) [4]. The anode material obtained through this method has a theoretical specific capacity of 3420 mA h g^{-1}. Additionally, the Li3N that is formed in situ displays high ionic conductivity and selectivity. This not only speeds up the kinetic transfer of lithium ions but also efficiently curbs the occurrence of dendritic lithium ion deposition. As a result, uniform Li plating/stripping at high current densities has been achieved. GKBLi and commercial $LiFePO_4$ (LFP) cathode exhibit remarkable cycling stability with cell capacity maintained at 90.9% even after 1000 cycles at 2 C. The production of graphite nanomaterials is challenging due to their relatively weak electrical conductivity compared to other carbon nanomaterials. Furthermore, fabricating graphite-based nanomaterials is an expensive and complex process. Heng et al. have presented a novel method involving the application of nano 2,2-dimethylvinylboronic acid (DEBA) to establish steady covalent bonds with -COOH and -OH functional groups on the graphite surface [5]. As a result, a nano DEBA film was created on the graphite surface, which proves to be a reliable solid electrolyte interphase (SEI) layer. Even after 200 cycles, full cells with 20 nm DEBA-decorated nature graphite (NG) anodes successfully maintain over 90% capacity. The first discharge capacity of the NG@DEBA-20 nm anode is 7.4 mAh g^{-1} higher at 155.7 mAh g^{-1}, and the first Coulombic efficiency improves by 5.43% at 85.77%, as compared with the NG anode lacking a DEBA film. The SEI precursor enables cost-effective lithium batteries by detaching them from pricey electrolyte solutions. Moreover, it offers a novel and dependable prospect for the application of graphite in lithium batteries, in contrast to traditional modifications made to graphite.

Additionally, its unstable layer structure seriously impacts the lifespan of the battery. Furthermore, graphite also has voltage hysteresis. While recent research has resolved the issue of lithium dendrite deposition and made commendable strides in fast charging, there is still a considerable way to address these challenges.

2.2. Porous carbon nanomaterials

Zhao et al. synthesized a three-dimensional porous material named OSPC-1 through Eglinton homocoupling, exhibiting a sp-sp^3 hybridization and possessing high porosity and electron transport capacity [6]. The conductance of OSPC-1 is higher than that of diamond (1×10^{-15} S cm^{-1}) at 1.2×10^{-4} S cm^{-1}, but lower than the conductance of graphene (2×10^{3} S cm^{-1}) and graphite ($2\text{-}3 \times 10^{4.6}$ S cm^{-1}). OSPC-1's reversible lithium capacity can reach up to 748 mAh g^{-1}. In comparison to graphene and graphite, OSPC-1 does not display dendrite lithium deposition even after 100 charge/discharge cycles. The typical organic material utilized for the reaction electrode exhibits low conductivity and poor long-term cycling stability, leading to a larger battery that is prone to leakage issues. However, this research breakthrough addresses these concerns and offers a new direction for implementing organic porous materials in battery electrodes. Melamine sponge (MS) can be carbonized directly to obtain porous carbon nanomaterials because of its high nitrogen content. MS has low bulk density, good elasticity, high porosity, flame retardancy, and heat insulation [7]. Most importantly, it is inexpensive. However, compared with OSPC-1, its direct carbonization leads to uneven pore size distribution and unstable voltage during operation. Moreover, MS might not do as great as OSPC-1 in resistance to dendrite lithium deposition. OSPC-1 demonstrates significant resistance to the formation of hazardous dendritic lithium crystals. Furthermore, after undergoing 100 cycles at a current density of 200 mAg^{-1}, the XRD analysis of the cell exhibited no evidence of lithium crystalline dendrite formation. In contrast, when OSPC-1 underwent 10 cycles at various current densities ranging from 100 to 3000 mAg^{-1}, its cell capacity soared back up to 944 mAhg^{-1} once the current density reverted to 100 mAg^{-1}.

3. Two-dimensional (2D) materials

Two-dimensional carbon nanomaterials are composed of thick planar sheets of single atoms of sp- and sp^2-bonded carbon arranged in a lattice structure. Two-dimensional carbon nanomaterials, such as graphene, demonstrate exceptional electrical conductivity. Their flexible network, better homotopy, and high specific area, compared to 3D carbon nanomaterials, enable efficient ionic and charge conductivity. They adapt well to various battery geometries.

3.1. Graphene

3.1.1. Composition. Composition of graphene with other materials can enhance its stabilizing and conductive properties. Yang et al. prepared a graphene/carbon nanotube composite (GCNT) aerogel host using a facile one-pot hydrothermal reaction method to stabilize the anode of a lithium metal battery [8]. While lithium deposition occurs on the surface of the GCNT, it does so in a non-dendric manner surprisingly. This is due to the electrode's large surface area which averagely reduced current density, which causes the deposited lithium to form spherical shapes. The GCNT aerogel electrode achieved up to 97.7% Coulombic efficiency (CE) for 430 cycles at 1 mA/cm² and demonstrated high current density performance up to 8 mA/cm² in the symmetric cell. When paired with LFP or $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) cathode, the respective composite anodes exhibited remarkably high capacities of 97.6% and 83.2%, and average CE values of 99.1% and 99.8% in 570 4C cycles and 470 2C cycles, respectively. Currently, it is typical for anode materials to cycle 1000-2000 times. However, those data indicate that while graphene/carbon nanotube composite host lithium anodes have a high CE value, their cycling stability must improve. A study conducted by Zhao et al. demonstrated the fabrication technique of a

Li_xM/graphene anode by employing a lithium-containing alloy with graphene [9]. The resulting anode showed a notable capacity to operate in fast charging, enabling a considerable increase in the charging rate and energy density. Compared to GCNT, the anode displayed over two times higher energy density and better adaptability in fast charging conditions. However, the alloy anode demonstrated poor resistance to dendrite lithium deposition. These two studies propose an innovative approach for designing three-dimensional conductive carbon hosts, projected to further enhance the development of high-energy-density lithium-metal batteries.

3.1.2. Surface engineering. The addition of particular organic functional groups onto graphene provides a possible approach for altering its electronic energy band structure by utilizing the quantum confinement effect that arises due to molecular scale. Currently, a high-density carboxylated graphene material with a surface layer, identified as graphene acid (GA), has been produced by means of selective acid hydrolysis of cyanographene (G-CN) [10]. This material is capable of overcoming the limitations associated with traditional organic anodes, specifically low conductivity, electrolyte solution leakage, and solubility. The GA anode exhibited capacity and rate of 800 mAh g^{-1} and 174 mAh g^{-1} at 0.05 A g^{-1}, and 2.0 A g^{-1}, respectively. The enhanced conductivity rate could be traced back to the -COOH groups on the graphene surface that facilitated accelerated electron transport along the carbon skeleton. The resistance values experienced by GA during lithiation and delithiation at 0.1~2.7 V stayed mostly within 5 Ω. This suffices to demonstrate the improvement of graphene conductivity by -COOH groups. This study offers a viable solution for utilizing organic anodes. However, the issue of leakage remains a significant challenge in organic anode development. Although the method utilized in this study effectively produced organic anode materials with exceptional performance and successfully addressed the leakage issue, the preparation process is not universally applicable. The advancement of organic anodes still requires substantial progress.

3.1.3. Doping. Pristine graphene (PG) exhibits a property of lithium-rejection. Doping can enhance electrical conductivity and mitigate issues pertaining to uncontrolled dendrite lithium growth and volume expansion of the lithium anode during charge and discharge cycles. Wang et al. demonstrated the introduction of lithium-friendly sites by adding a minimal amount of S atoms, which orderly guides homogeneous lithium deposition [11]. Huang et al. employed the addition of nitrogen atoms. N-doping graphene lithium grades have limited capacity to accommodate lithium ions due to their small porosity, leading to the expansion of electrode volume during battery charging and discharging [12]. In addition to non-metal atoms, monoatomic metals such as Ni, Pt, and Cu can be introduced to deposit non-dendrite lithium metal on the carbon surface [13]. The incorporation of Ni atoms results in graphene-based lithium deposition with the lowest formation energy, making it the optimal selection for uniform lithium deposition. These studies demonstrate high CE values and enhance battery longevity while introducing novel design concepts for high-energy lithium battery production.

4. One-dimensional (1D) materials

One-dimensional carbon nanomaterials are a clear preference as lithium battery anodes, due to their superior electrical conductivity, extensive surface area, and flexible networks. These properties provide ample space for lithium ion transmission and transfer of charge. The exceptional mechanical and electrochemical features render them ideal anode materials for lithium batteries.

4.1. Carbon nanotubes (CNTs)

Carbon nanotubes offer several advantages, such as high electrical conductivity, stable structure, good mechanical properties, and adjustable surface functionality. The structure of carbon nanotubes comprises carbon atoms arranged in a hexagonal pattern forming a concentric hollow lumen comprising several to dozens of layers. There exists a fixed gap between layers and various defects in the tube, allowing adequate space for lithium ion displacement. Nevertheless, the primary hindrance of carbon nanotubes is the unstable voltage. Secondly, there is an apparent potential hysteresis phenomenon, which was addressed by Wang and his colleagues [14]. It was suggested to cover the carbon nanotubes with molten lithium while ensuring favorable thermodynamic and kinetic conditions to ensure a uniform metal film formation. The resulting LiCSMF electrode demonstrated remarkable stability even after 2000 cycles of recharging and discharging, ranging from 10 to 40 mA cm^{-2}. The electrode exhibits an exceptionally low resistivity of 11.9 Ω. The absence of dendrite lithium and dead lithium deposition can be attributed to LiCSMF's effective current density averaging at various locations in the cell, as well as its ability to replenish the electrolyte promptly via a network of CNTs. The electrode demonstrates greater stability than the previously described GCNT as a host for a lithium metal anode, and it operates more effectively under challenging conditions. Not only does it serve as a benchmark for non-dendrite deposition, but it also offers a solution for enhancing lithium batteries.

4.2. Carbon nanofibers (CNFs)

Carbon nanofibers are cylindrical nanostructures that possess excellent electron conductivity and ion transport abilities, making them the optimal candidate for anode materials in lithium-ion batteries. However, it is difficult to achieve nanoscale dispersion of carbon nanofibers in polymers, which hinders the utilization of cellulose nanofibers' impressive thermal and mechanical characteristics. Moreover, the deficiency of chemical bonds between the two substances makes it difficult to enhance performance through the compositing process with other materials. Producing carbon nanofibers on an industrial scale presents significant challenges due to the expensive and complex technology required. Various factors contribute to the difficulties of manufacturing high-quality carbon nanofibers. However, Huang et alhave successfully produced composite carbon nanofibers with Mo_2C as an anode in a SEI, referred to as Mo_2C@CNF. The resulting battery, composed of this anode and LFP, achieved an energy density of 378 Wh kg^{-1} and a high energy density at 1 C [15]. The material can be recharged up to 300 cycles under 1 C conditions. Lithium dendrite formation was effectively prevented by utilizing lithophilic Mo_2C clusters. This research presents a promising approach to the regeneration of carbon nanofibers.

5. Conclusion

In conclusion, this study provides an overview of the latest advancements in applying carbon nanomaterials and nanotechnology in lithium batteries with the support of illustrative examples. The carbon nanomaterials presently utilized in lithium batteries include graphite-based nanomaterials, porous carbon nanomaterials, graphene, carbon nanotubes, and carbon nanofibers. These materials exhibit remarkable benefits regarding specific surface area, mechanical characteristics, and electrical conductivity. Additionally, their composites exhibit persistent resistance to lithium dendrite formation.

However, electrodes composed of materials such as graphene typically exhibit a low number of cycles and a relatively short lifespan. Nonetheless, their large specific surface area, multiple active sites, good geometric properties, surface engineering, and composites have been used for improved electrochemical performance. Carbon nanotubes possess a flexible structure and good homotopy, rendering them an excellent choice for flexible lithium batteries. However, the substantial quantity of dust produced during the manufacturing process of carbon nanomaterials like carbon nanotubes and graphene can pose a potential risk to human health. Compared to graphene and carbon nanotubes, 3D carbon nanomaterials exhibit higher rigidity but poorer homotopy, but their composite electrode performance and resistance to lithium deposition are comparable to the former two. Therefore, the composition of multiple nanomaterials is a feasible solution to the above challenges. These advanced applications offer numerous valuable starting points and milestones for the innovative development of battery electrodes.

References

[1] Xu Z, Kim J and Kang K. 2018 *Nano. Today* **19** 84-107
[2] Zhang Z, et al. 2022 *Science* **375** 66-70
[3] Li W, et al. 2023 *Sci. Adv.* **9** eadh4626

[4] Jing Z, Liu H, Liu T, Meng C, Jing Z, Tabish M, Yu X, Li A, Chen X and Song H. 2023 *J. Mater. Chem. A* in press
[5] Heng S, Shan X, Wang W, Wang Y, Zhu G, Qu Q and Zhen H. 2020 *Carbon* **159** 390–400
[6] Zhao Z, Das S, Xing G, Fayon P, Heasman P, Jay M, Bailey S, Lambert C, Yamada H, Wakihara T, Trewin A, Ben T, Qiu S and Valtchev V. 2018 *Angew. Chem. Int. Ed.* **57** 11952–56
[7] Shi Y, Liu G, Jin R, Xu H, Wang Q and Gao S. 2019 *Carbon Energy* **1** 253–75
[8] Yang T, Li L, Zhao T, Ye Y, Ye Z, Xu S, Wu F and Chen R. 2021 *Adv. Energy. Mater.* **11** 202102454
[9] Zhao J, Zhou G, Yan K, Xie J, Li Y, Liao L, Jin Y, Liu K, Hsu P, Wang J, Chen H and Cui Y. 2017 *Nat. Nanotechnol.* **12** 993–999
[10] Obraztsov I, Bakandritsos A, Šedajová R, Langer R, Jakubec P, Zoppellaro G, Pykal M, Presser V, Otyepka and MZbořil R. 2021 *Adv. Energy. Mater.* **12** 202103010
[11] Wang T, Zhai P, Legut D, Wang L, Liu X, Li B, Dong C, Fan Y, Gong Y and Zhang Q. 2019 *Adv. Energy. Mater.* **9** 1804000
[12] Huang G, Han J, Zhang F, Wang Z, Kashani H, Watanabe K and Chen M. 2019 *Adv. Mater.* **31** 1805334
[13] Zhai P, Wang T, Yang W, Cui S, Zhang P, Nie A, Zhang Q and Gong Y. 2019 *Adv. Energy. Mater.* **9** 1804019
[14] Wang Z, Lu Z, Guo W, Luo Q, Yin Y, Liu X, Li Y, Xia Bao Y and Wu Zi Ping. 2020 *Adv. Mater.* **33** 2006702
[15] Huang A, Wu Y, Huang H, Li C, Sun Y, Li L and Peng S. 2023 *Adv. Funct. Mater.* **33** 2303111