Mini Review

Recent Research and Advances of Gradient Graphene and 3D Collectors for Lithium Metal Anode

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Lithium metal anode is one of the most important potential materials in lithium-ion battery system because of its high energy density. In this paper, the problems of lithium metal anode are reviewed. Then, the application of 3D collector on lithium metal anode is summarized. 3D conductive collector is an effective way to solve this problem. The uniform deposition of lithium metal is realized by using high specific surface and low current density. The lipophilic performance of three-dimensional conducting collector was optimized by doping and lithium melting techniques. Finally, the research progress of gradient 3D graphene is investigated. Based on the literature survey, we believe that gradient 3D graphene is expected to be applied to lithium metal anode.

Keywords: Lithium metal anode; Gradient 3D graphene; 3D collector; Lithium dendrite

1. INTRODUCTION

As a representative of new energy, lithium-ion battery has the advantages of high energy density, low self-discharge, no memory effect and green environmental protection, and has replaced the traditional lead-acid battery and cadmium-nickel battery. With the increasing demand for high energy density batteries, lithium metal is considered as one of the potential application materials for the negative electrode of batteries in the future, and is also an important part of new high energy density energy storage systems such as lithium-sulfur batteries and lithium-air batteries. Lithium metal has a theoretical specific capacity of 3860 mAh/g and an electrode potential of -3.04 V (vs. Standard hydrogen electrode) and high electrical conductivity, is an ideal anode material. However, some key problems, such as dendrite growth of lithium, low coulomb efficiency of lithium metal batteries and
volume expansion caused by lithium free deposition, have long restricted the application of lithium anode [1-3]. Therefore, in recent years, it has aroused increasing research enthusiasm and large amount of investment in the world.

2. LITHIUM DENDRITE

Serious volume expansion and dendrite growth occur in lithium anode during charging and discharging cycle. With the continuous growth of lithium dendrite, "dead lithium" forms due to root fracture, resulting in the loss of battery active components. Dendrites may also pierce the diaphragm bringing serious safety problems such as causing internal short circuit or even explosion of the battery. In addition, the growth of lithium dendrites destroys the solid electrolyte interface (SEI), causes the negative electrode to constantly expose new surface in the battery cycle, and leads to the production of new SEI film by the reaction between lithium metal and electrolyte, resulting in the consumption of battery active components and reducing the coulombic efficiency of the battery. Therefore, inhibition of dendrite growth of lithium is a key technical issue in the application of rechargeable lithium metal batteries [1].

To date, a variety of lithium dendrite nucleation and growth models have been proposed to explain the formation process of lithium dendrite. They mainly include diffusion model [4], SEI model [5], space charge model [6], heterogeneous nucleation model [7], Sand's Time model [8], etc. Although none of these models can fully explain the reason of lithium dendrite formation, all the dendrite growth models believe that the effective current density during lithium deposition/dissolution has an important effect on the dendrite formation and growth. Lithium is deposited smoothly under the condition of uniform low current density, while high current density accelerates the growth of lithium dendrite [8-10]. Three-dimensional (3D) structure can effectively reduce the current density of electrode surface, so in recent years, the construction of 3D lithium anode has become a hot research direction of lithium anode optimization.

3. 3D COLLECTOR

3D lithium anode effectively controls the deposition behavior of lithium metal and inhibits the growth of lithium dendrite by building a stable 3D structure base and substrate material [11]. The 3D structure forms a 3D conductive network in the electrode, so that the internal electric field is evenly distributed and lithium-ion deposition is induced uniformly. According to Sand's Time model, the generation of lithium dendrites is closely related to the current density [12]. Therefore, the extremely high specific surface area and internal cavity structure of 3D lithium metal efficiently reduces the current density on the negative electrode surface, thus inhibiting the growth of lithium dendrites. In addition, the cavity structure of 3D metal lithium anode competently alleviate the volume effect generated during the circulation process. At present, 3D lithium metal anode is mainly divided into
metal base and carbon base 3D lithium metal anode according to different substrates or substrate materials.

The metal-based 3D materials used as the fluid collector of lithium metal anode have the characteristics of high conductivity and good stability. The commonly used materials include nickel foam [13-15] and copper foam [16-19]. However, the metal matrix materials have some problems such as poor structural plasticity, inflexible composite modification method and difficult mechanical properties for battery processing.

Due to its light weight, large specific surface area, high electrical conductivity, physical and chemical stability and excellent mechanical strength, carbon-based bodies have attracted extensive research attention. Carbon-based materials in various 3D structures have been synthesized. For example, Cui Yi's research group of Stanford University coated a single layer of amorphous hollow carbon nanospheres with interconnect structure on the surface of lithium metal [20]. Xie et al. sprayed a reduced graphene oxide (GO) layer on the negative surface of Li and made graphene coating by directly reducing GO with alkali metals [21]. Choi et al. fabricates 3D carbon-based porous anode (3D-CPA) with a pore-size gradient using PMMA as the pore-forming template [22]. Compared with metal-based materials, carbon-based materials are simple and flexible.

Both experiments and theoretical calculations [23, 24] show carbon material with plane ideal structure has poor hydrophilicity with lithium metal, and is not suitable for lithium metal anode bracket or fluid collector. Defects of carbon material will reduce the deposition overpotential of lithium, so that lithium will preferentially adsorb at the defect of carbon. Therefore, in order to increase the hydrophilicity of matrix and lithium metal and reduce the nucleation overpotential of lithium metal, the method of doping or compound active site is generally adopted to realize uniform deposition of lithium and avoid dendrite formation.

Common doping elements are N, P, F, metal, etc. For example, nitrogen-doped graphene is used as a 3D conductive skeleton for battery electrode [25, 26], self-supported 3D fluorine-doped graphene/porous carbon network is used as a multifunctional substrate for lithium [27], metal mono-atom doped graphene material [28], etc. Common lipophilic compounds mainly include lithium compounds, oxides, metals, etc. For example, the functionalized solid electrolysis interface membrane structure constructed by LiF modification of layered graphene [29], multilevel Co₃O₄ nanofiber-carbon sheet skeleton as stable substrate of alkali metal electrode [30], porous honeycomb structure of go loaded with lithium metal as negative electrode [31], and modified with a layer of uniformly distributed Sn/Ni alloy nanoparticles particle carbonized resin based biomimetic artificial wood [32], Ag nanoparticles uniformly loaded on 3D carbon fiber [33], LiF/F-doped carbon gradient protection layer [34], 3D double-gradient lithiophilic Si@carbon nano-fibers (CNFs) @ZnO skeleton coated ZnO-Cu foil as a current collector [35] etc. According to experiments and theoretical calculations, the introduction of doping or composite materials reduces lithium metal deposition resistance, increases nucleation sites, induces uniform lithium metal nucleation deposition, effectively inhibits the growth of lithium dendrite, and improves the cyclic stability of lithium metal battery. Moreover, the electrochemical performance can be further optimized by gradient control of structure or composition, as shown in Table 1.
Table 1. Electrochemical performances of Li-metal anodes under Different 3D Current Collectors

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Coulombic efficiency</th>
<th>Full cell</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>The porous Cu metal frameworks with gradient pore size distribution</td>
<td>~98.8% for more than 350 cycles, at 2 mA/cm² for 1 mAh/cm²</td>
<td>LiFePO₄</td>
<td>1.0 M LiFSI in DME</td>
</tr>
<tr>
<td>The porous Cu metal frameworks with a monodisperse large pore size distribution</td>
<td>~70% for more than 300 cycles, at 2 mA/cm² for 1 mAh/cm²</td>
<td>LiFePO₄</td>
<td>1.0 M LiFSI in DME</td>
</tr>
<tr>
<td>3D-carbon-based porous anode with a pore-size gradient</td>
<td>~98.8% for more than 250 cycles, at 2 mA/cm² for 1.2 mAh/cm²</td>
<td>LFP/3D-CPAs, ~131 mAh/g at 0.1 C, no significant capacity loss and an average CE of ~99.86% after 250 cycles at 0.5 C</td>
<td>22</td>
</tr>
<tr>
<td>3D-carbon-based porous anode contains pores with an average diameter of 15 μm</td>
<td>~98% for more than 250 cycles, at 2 mA/cm² for 1.2 mAh/cm²</td>
<td>LFP/3D-CPAs, ~131 mAh/g at 0.1 C, 117 mAh/g at the end of the 187th cycle</td>
<td>22</td>
</tr>
<tr>
<td>3D-carbon-based porous anode contains pores with an average diameter of 50 μm</td>
<td>~97.6% for more than 250 cycles, at 2 mA/cm² for 1.2 mAh/cm²</td>
<td>-</td>
<td>22</td>
</tr>
</tbody>
</table>

Many of these scaffolds are half-battery tested as lithium-free aggregates, not prefabricated with lithium metal. Such lithium-free fluid collection is difficult to apply directly to a full battery, so researchers have developed a melt injection method as a new technology to combine lithium metal with carbon bodies. For example, a high-performance composite lithium metal anode (CF/Ag-Li) was prepared by inhaling liquid molten lithium metal into a carbon fiber skeleton with silver coating [36]. CO₃O₄-embedded and nitrogen-doped porous carbon nanosheets derived from MOF were used as the main body to fuse lithium [37]. Molten Li or Na is injected into 3D carbon fiber skeleton with high alkali wettability to produce metal anode [38], et al. The 3D carbon base of molten lithium metal not only avoids the introduction of unwanted SEI or electrolyte impurities in the lithium pre-storage process, but also lays a foundation for the application of all-battery.

4. GRADIENT 3D GRAPHENE

Two-dimensional material represented by graphene has grown into a large family of new materials. Graphene block material, is the third after powder, film graphene material form. It can solve
many problems such as the loss of surface area, higher contact thermal resistance and contact electrical resistance due to the weak connection between layer stack, and unfavourable mass transfer owing to the twisted and disordered channels of the stack. It has broad application prospects [39]. 3D graphene bulk materials can transfer such excellent properties of nanoscale to macroscopic scale as high surface area, high conductivity, through-channel and excellent mechanical properties. It is expected to reduce the technical difficulty of application and explore new properties and applications of graphene materials. At present, 3D graphene materials have achieved a series of research achievements in mechanics, thermal, adsorption, electrochemistry, electricity and other aspects [40, 41]. Various preparation methods of 3D graphene have been reported, such as bulk gelation, ice template method, chemical vapor deposition based on nickel foam, biomass pyrolysis, foaming, 3D printing and so on [42].

Gradient 3D materials can further endue materials with brand-new interface characteristics, versatility and gradual response characteristics, and is expected to solve the interface and structural stress problems in the current material application process [43], and have a wide application prospect in artificial intelligence materials, bionic materials and wearable applications [44]. With the improvement of 3D design capability of 2D materials, how to realize the gradient change of performance in a certain direction after 3D assembly of 2D materials has become a new research direction.

Gradient structure 3D graphene materials have found wide applications in concentration generation, supercapacitors, material mechanics, seawater desalination, electromagnetic shielding and other fields. He et al. [43] reviewed the progress of realizing excellent mechanical and physical properties of carbon nanophase reinforced bulk composites through configuration design, and proposed: "Carbon nanomaterials such as carbon nanotubes and graphene, traditionally used more evenly distributed configuration does not guarantee and improve the physical properties of the composite material mechanics, a new special configurations such as hierarchical configuration and gradient design and mechanism research, can break through the performance bottlenecks, and achieve a boost of integrated performance of composite materials". Qu et al. [45, 46] reported a humidity generator made of graphene oxide (GO) thin film with a gradient change of oxygen functional groups along the upper and lower surface of the film. Li et al. [47] reported a porous gradient 3D graphene with excellent conductivity (18.2 S/cm) as an electrode for supercapacitors, showing super stability (capacitance retention rate up to 95.9% after 10,000 cycles). Cheng et al. [48] constructed a 3D skeleton of GO and sodium alginate with gradient change of layer spacing, which can effectively sense the change of external temperature and realize the organic combination of mechanical properties and functions of materials. Hu et al. [49] reported a 3D carbon material with channel gradient, which can be used for seawater desalination. Dai et al. [50] prepared a GO nanoribbon network structure membrane (g-GOR-nm) with concentration gradients of oxygen-containing functional groups, and realized potential-driven g-GOR-nm ion channel switching by capturing ion concentration gradients of different contents of water. Shen et al. [45] prepared polymer/graphene composites with different gradient structures and found that the gradient structure could significantly improve the wave impedance between the composite and air, thus enhancing the absorption of electromagnetic waves.
In terms of the construction methods of 3D graphene gradient materials, there are electrochemical reduction method, directional thermal reduction method, gas-phase induced carbonization method, ice template method, etc. For example, electrochemical reduction [45] and directional thermal reduction [46] are used to realize the reduction degree and the gradient change of oxygen-containing functional groups. Carbonization was induced by alkali vapor to achieve gradient change of pore structure [47]. The ice template method was used to control the ice crystal growth rate to realize the gradient change of layer spacing [48]. 3D materials were obtained by superposition combination of film materials with different ratios to achieve gradient changes in properties and composition [51]. Cheng et al. [44] prepared an I-rGO/rGO film material with Janus asymmetric structure through the steam gradient reduction strategy of hydroiodic acid.

The preparation methods of other gradient materials also provide reference for the preparation and application of 3D graphene gradient materials. For example, the gradient electrodeposition method proposed by Pan et al. [52] is used to construct graphene/metal composite gradient materials. Tetsu et al. [53] proposed the concept of "single material electrode" AlLi compound combining active material and collector fluid, and constructed a composition gradient in AlLi compound to drive the diffusion of aluminum to the surface, thus avoiding the fatal pole-sheet powder problem. Zhu et al. [54] developed a Janus intelligent textile that can automatically respond to temperature by functionalizing the difference between two surfaces of membrane materials. Broekmann et al. [55] used dynamic hydrogen bubble template to prepare bimetallic AgCu foam material with pore gradient along the surface normal direction by electrodeposition method, which has superior ethanol selectivity and stability for catalysis.

5. CONCLUSION

In summary, the current density plays a crucial role in the formation and growth of lithium dendrite and the collector and the interface membrane of solid electrolyte have a significant impact on the current density. These two materials have opposite conductivity properties: the collector is an excellent electronic conductor, while the solid electrolyte interface film is an insulator conducting lithium ions. Consequently, is it possible to construct a similar two-dimensional two-sided Janus structure to solve the dendrite problem faced by lithium metal anode and related problems caused by solid electrolyte interface films? We propose to prepare a 3D metal lithium anode system using GO and graphene with electronic conductivity on one side and ionic conductivity on the other side and gradient change of the electronic conductivity and ionic conductivity in the vertical direction. In this material, the electronic conductive surface is fused with lithium metal and the high conductivity of graphene is utilized to achieve low current density. The porous structure buffers the volume changes caused by lithium deposition. Lithium fused in the 3D conductive network can reduce the contact with the electrolyte and reduce the reaction consumption with the electrolyte. Ionic conductive surface, i.e., the artificial solid electrolyte interface film is constructed by GO composite lithium ion conductor material realizes lithium ion conduction and electron insulation, as well as stabilizing the interface. The buffer region of lithium dendrite is formed by the inside gradient change of electrical conductivity,
which improves the overall safety and stability of the anode material. This material in developing is expected to restrain the growth of lithium dendrite, providing experimental reference for the application of lithium metal anode, and for the nucleation growth of lithium metal.

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