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Electrical Properties of Porous Nano Modified Lithium-ion Battery Negative Electrode Materials

Abstract: The negative electrode material of lithium-ion batteries is one of the key factors affecting the overall performance of the battery. Traditional carbon/graphite materials are prone to safety issues such as capacity loss and metal precipitation during application. Due to its high conductivity and flexibility, as well as its excellent properties in battery energy density, cycle life, and other aspects, Ti3C2 nanomaterials have brought new opportunities for the lithium-ion batteries development. The development of convenient electronic products and power equipment has put forward higher requirements for the performance of lithium-ion batteries. On the basis of introducing modification technologies for lithium-ion battery electrode materials (such as carbon coating, nanocomposition, etc.), this study further reviews and analyzes the electrochemical performance characteristics of batteries under porous nanomaterials. The purpose is to provide reference value for the selection and design synthesis of battery negative electrode materials.

Keywords: Lithium-ion batteries; Ti3C2; Nanodot materials; Electrochemical performance; Cyclic stability

Introduction

Lithium-ion batteries (LIBs), as an important means of storing and supplying renewable energy, are widely used in various devices and systems, such as mobile phones, electric vehicles, and renewable energy storage systems. LIBs themselves have advantages like High Specific Capacity (HSC) and high operating voltage, and can be well applied to various portable devices. With the continuous deepening of research on LIBs, Negative Electrode Materials (NEMs) related to the charging and discharging rate, cycle life, and safety of batteries have also attracted the attention of most scholars. The application effect of NEMs is directly related to the Electrochemical Performance (ECP) and structural stability of batteries. However, traditional NEMs often suffer from capacity decay, volume expansion, and other issues during the cycling process due to the differences in material selection. Therefore, using modified materials to overcome these problems has become an urgent task [1]. Currently, the main types of LIBs NEMs used include graphite, silicon-based materials, etc., which commonly suffer from capacity loss and structural damage caused by expansion during cycling. Currently, the negative electrodes for LIBs mainly include two types: carbon-based materials (graphite, carbon nanotubes, graphene, etc.) and Non-Carbon-based Materials (NCMs) (silicon-based, transition metal nitrdes, sulfides, etc.). As a layered material, graphite itself has good conductivity, but its adaptability to electrolytes inevitably leads to graphite volume expansion during the reaction process. The reason is that the interplanar spacing of the composite material after lithium atom insertion is greater than the interlayer spacing of graphite, which leads to significant material peeling and pulverization phenomena, affecting the survival life of the battery [2]. Although Carbon Nano Tubes (CNTs) and graphene can also exhibit good conductivity and mechanical properties, they inevitably face issues such as capacity degradation and high preparation costs. NCMs, such as MXene materials, have low operating voltage and good conductivity. Among them, two-dimensional titanium carbide (Ti3C2) has a fast diffusion rate and charge discharge rate when used as LIBs NEMs, and the material has low requirements for experimental preparation conditions, making it scalable. Ti3C2 is a layered structure material composed of titanium and carbon elements, which has excellent conductivity, electrocatalytic and photocatalytic properties, mechanical properties, etc. [3]. This study utilizes Porous Nano Materials (PNMs) to modify LIBs NEMs Ti3C2 to better enhance the battery performance of NEMs and provide more reliable and efficient solutions for the application of LIBs.

1. The construction and working principle of LIBs

The development of social economy has led to an increasing demand for fossil fuels, resulting in prominent and severe environmental pollution and resource depletion issues. By utilizing energy storage devices, the

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storage of emerging energy can effectively avoid intermittent drawbacks that can lead to demand fluctuations. LIBs have advantages such as high energy density and long cycle life, and are widely utilized in the field of electronic devices. Since the development of LIBs, various positive electrode materials have been developed, including positive and negative electrodes, separators, electrolytes, current collectors, and battery shells. The main choices for positive electrodes and negative electrode materials are lithium containing transition metal oxides and lithium embedded materials with lower potentials. Figure 1 shows the working principle of the battery.

![Electron Flow During Discharge](image)

**Figure 1 Working principle diagram of LIBs**

During the charging period, the forward lithium ions (Li) are detached from the lithium containing lithium cobalt oxide compound and cross the separator to reach the negative electrode. While in discharge, the lithium electrons released from the negative electrode will cross the separator and return to the positive electrode. The migration and flow changes between the two materials can also demonstrate the conversion relationship between electrical and chemical energy. As the main electrode of a battery, the properties of the negative electrode are closely connected to the ECP of the battery. For the conditions of material selection, it is required to provide a stable lithium insertion potential, with characteristics such as structural stability and good conductivity. Among them, Ti$_3$C$_2$ has a faster diffusion rate and higher charge discharge rate in lithium electrons. When used as a battery NEMs, this material can effectively alleviate the volume expansion of the material, and due to the ease of preparation, it has lower requirements for experimental conditions and equipment.

Ti$_3$C$_2$ material itself has a high specific capacitance. The active sites of the rich functional group sieve evolution reduction reaction on its surface lead to continuous changes in the valence state of Ti element, which enables the rapid migration of positive lithium atoms on the material surface, leading good conductivity and specific capacitance. This material film has good mechanical strength when combined with other materials. Most studies have shown that the material nanosheets exhibit good performance when loaded with LIBs and NEMs. However, it is prone to stacking during the electrochemical reaction process, resulting in the loss of ion adsorption sites and a decrease in the performance of the device. Therefore, many scholars have carried out surface modification treatment on the nanosheets of this material to improve its ECP. Scholar Bitew Z has provided numerous discussions on the preparation, design, and performance of silicon nanostructures and related composite materials. Hao H proposed using thermal expansion materials to modify nickel rich ternary cathode materials in response to the impact of heat and deformation factors on battery performance. Negative thermal materials could effectively improve the current retention rate of nickel rich materials in batteries, and effectively reduce the side effects during their reaction process, thereby improving the performance and safety of batteries. Carbon materials were widely used in battery NEMs due to their abundant resources, low prices, and obvious ECP advantages. Among them, the modification of nanomaterials is an effective way to lift the quality of electrode materials. Intermetallic antimony tin alloy could effectively solve the problem of capacity decay when used as anode material for LIBs and sodium-ion batteries, and the addition of CNTs could significantly improve the capacity performance and Cycling Stability (CS) of composite materials.

2. Modification of LIBs electrode materials

In LIBs cathode materials, nickel rich layered oxides are widely used due to their good performance, but their CS is poor. Therefore, Si Z studied titanium and fluorine doped lithium through solid-state reactions. The results indicated that the modified nickel rich layered oxide could effectively stabilize the crystal structure of lithium, improve its LIBs nickel rich cathode ECP, and improve its discharge capacity. Ji X et al. doped lithium manganese coatings with molybdenum to ensure the structural stability by increasing lattice parameters.
The initial coulombic efficiency and capacity of the modified lithium manganese oxide have been improved, with an increase of over 66%, and the coating performance of the energy storage device has been significantly improved [12]. Jiang M cross-linked CNTs onto silicon carbide titanium to improve the fracture toughness of silicon carbide ceramics, and modified CNTs with polydopamine. The prepared composite material exhibited good micro-structure and mechanical properties [13].

Zhang L treated lithium iron phosphate (LiFePO4, LFP) with porous layered carbon coating. The prepared composite material exhibited high rate performance and CS in Ti3C2 material, and its capacitance retention efficiency in the initial discharge capacity was good (over 99%) [14]. Jia Z et al. utilized titanium to prepare high-performance composite material C2-MXene, which exhibited excellent conductivity when combined with modified carbon black and waterborne polyurethane. The network construction of conductive nanomaterials could greatly improve the sensitivity of composite materials, and they had broad prospects in sensing areas such as wearable devices and intelligent robots [15]. Transition metal sulfides were prone to volume expansion and structural collapse during the application of LIBs NEMs. Therefore, Tian S et al. utilized the concept of nano engineering materials to nano treat sulfides on the Ti3C2-MXene conductive network structure. Experiments have shown that composite materials could effectively improve material utilization and electronic conductivity, while improving the reaction kinetics and high CS of devices under HSC and load conditions [16]. To reduce the impact of electromagnetic interference and extreme cold weather on electronic instruments, Zhou Z prepared composite materials by assembling cellulose nanoparticles. This material had good mechanical properties and adhesion in thin film coatings, and its dense layered structure also gave it excellent photochromic performance and electromagnetic shielding effectiveness. Titanium metal films prepared by bacterial cellulose exhibited good mechanical properties [17]. Alsafari I A et al. prepared nanohybrids using ultrasound, and the composite material had better photocatalytic performance and antibacterial activity. The characterization results also indicated that the composite material had a good internal structure [18].

Ti3C2, a 2D MXene material, is prone to oxidation and deterioration in conventional storage environments. Chen S used polydopamine to modify titanium to achieve uniform loading of metal nanoparticles. The catalytic reaction rate between gold and titanium has been improved under the modification of polydopamine, and the degradation rate under repeated catalysis could still be maintained above 89% [19]. Wang Y et al. synthesized Ti3C2 composite materials using microwave and etching methods. The α-Fe2O3 porous nanoparticles in this composite material were attached to Ti3C2 two-dimensional materials, effectively exposing more gas adsorption sites, enhancing the reaction transmission ability of gas sensors to electrical signals, and exhibiting good selectivity and stability [20]. Zhu B et al. found that the interaction between MXene and the surface of organic molecules was related to the type of functional group of the molecule. The type of surface functional groups and the number of hydrogen bonds could lead to differences in the strength of interactions, while the more hydrogen bonds there were, the stronger the adsorption energy between molecules. The rich surface functional groups of MXene enabled molecules to exhibit special electro-optical properties [21].

3. Electrical properties of porous nano modified LIBs NEMs
3.1 ECP study on porous Ti3C2 materials
When analyzing the ECP of LIBs NEMs, it is necessary to control the electrode load at around 1mg.cm-2. Excessive load can increase the diffusion impedance between ions, leading to a decrease in device performance. The preparation of porous Ti3C2 nanosheets often improves their lithium storage performance under loading conditions by changing their morphology and structure. The addition time for material preparation by etching method should be at least fifteen minutes, because during the addition reaction process, the material will release a large amount of heat. Excessive addition speed can cause local overheating and cause material oxidation. Excessive reaction time between the material and etching solution can lead to the pulverization of nanosheets, transforming their original layered structure into a layered structure. After mixing lithium fluoride and hydrochloric acid, they can react with atoms in the nanomaterials, leading to the insertion of Li+ into the material in the etching solution, expanding their spacing. This can be achieved by using ultrasound to peel off the nanosheets. Figure 2 shows the electron microscopy results of different materials [22].
There is no significant change in the electron microscopy morphology of porous Ti$_3$C$_2$ material and Ti$_3$C$_2$ material, only a decrease in layer size. After treatment, the surface of porous Ti$_3$C$_2$ material shows wrinkles and an increase in porosity between layers. There is a right shift in the diffraction peak of the crystal plane of Ti$_3$C$_2$ material before and after modification, which may be related to the interaction of functional groups on the surface of porous materials. The increase of internal structural pores in porous materials can facilitate the migration and storage of ions. The rate (the charging and discharging rate of a battery) can reflect the battery’s ability to charge and discharge quickly, and a higher rate means that the battery’s reaction performance is better.

Figure 3 shows the magnification of different materials under different loads.

After the first round of Constant current Voltage (CV) testing, some of the reduction peaks of the porous modified Ti$_3$C$_2$ material disappeared. The reason is that it has formed a stable Solid Electrolyte Interphase (SEI) film on the surface. There are also differences in the magnification of the two materials under different load conditions. The discharge specific capacity of porous materials remains above 98% under different current density settings, indicating good electrochemical reversibility. The original material may lose active sites due to its stacking situation, resulting in a lower capacity retention rate than porous materials. The impedance results also indicate that the semi-circular diameter of the curve of the porous material is small, and its slope is approximately 90°, indicating that the diffusion assistance of Li ions in the material is relatively small. The pore structure of porous materials increases their wettability with the electrolyte, shortens the ion transport path, and thus improves their charge transfer ability.

The mismatch of electrochemical reaction dynamics between the anode and cathode of lithium-ion capacitors has to some extent limited their application prospects. Adding carbon nanofibers to Ti$_3$C$_2$ MXene, the nanocomposites under the carbon framework exhibit good capacitance...
and power density. Moreover, 2D nanosheets enrich the active sites of LIs, enabling rapid electron transfer and particle diffusion, thereby improving the material’s ECP and energy storage performance. Different load conditions can also have an impact on the magnification of materials. Figure 4 is the magnification of materials under two different load conditions.

The discharge specific capacity loss of porous materials under two loading conditions is smaller than that of simple 2D materials. Under low load conditions, when the current densities are 50mAg\(^{-1}\) and 100mAg\(^{-1}\), their corresponding discharge specific capacities exceed 115mAhg\(^{-1}\) and 70mAhg\(^{-1}\), far higher than the specific capacities of 2D materials approaching 80mAhg\(^{-1}\) and 40mAhg\(^{-1}\). Porous materials have good lithium storage performance and CS. During multiple charging and discharging processes, their porous materials do not exhibit significant capacity degradation.

3.2 ECP study on porous nanodots modified Ti\(_3\)C\(_2\) materials

LIBs are prone to material crushing and detachment during ion insertion and extraction, which in turn affects battery performance. The addition of PNMs can to some extent buffer the volume expansion of the material and improve its electrode conductivity. Porous nanodot materials are a type of material with a highly porous structure and nanoparticle size. It is commonly utilized in catalysis, electrochemical sensors, energy storage, etc. cause its benefits like regular arrangement, large specific surface area, and adsorption capacity. This material has a large surface area and its porous structure can provide more active sites for electrochemical reactions, shorten the transport path between ions, and greatly improve its diffusion rate. When hydrofluoric acid is used to etch Ti\(_3\)C\(_2\) materials, its weak ionization characteristics result in a shift in the peak value of Ti\(_3\)C\(_2\) prepared at different temperatures. When the etching temperature reaches its optimum, the structure of porous nanodot materials can be more clearly exposed. Figure 5 shows the XRD pattern of nanomaterials.

![Figure 4 Multiplication of materials under two load conditions](image-url)

![Figure 5 XRD patterns of Ti\(_3\)C\(_2\) materials under different temperature reactions](image-url)

![Figure 6 XRD patterns of different materials](image-url)
Figure 5 XRD pattern of nanomaterials
Compared with Ti$_3$C$_2$ material, the diffraction peak of nanodot Ti$_3$C$_2$ material shows a significant left shift, for the interlayer spacing expansion between its crystal planes. Its peak near 39° has disappeared. The reason is that the etching process reacts with metal atoms, causing the substitution of hydroxide ions with the functional groups indicated by the 2D material, resulting in an increase in the oxygen content of the nanodot material. The surface atoms in Ti$_3$C$_2$ material will react with Tetramethylammonium Hydroxide (TMAOH), leading to the formation of voids on the surface of Ti$_3$C$_2$ material. The detached Ti$_3$C$_2$ material will adhere to the surface of the porous material in the form of nanodots through electrostatic adsorption. During this process, the specific surface area and pore volume of the nanomaterial will increase, as shown in Figure 6 [26].

Figure 6 Nitrogen adsorption and desorption curves and pore size distribution before and after modification of nanomaterials
When conducting electrochemical tests on PNMs, there is a reduction peak in the voltage range of less than 1.5V that occurs when the material stores Li$^+$ and forms thin films. In the second and third tests, there are some side effects on the material surface that resulted in the generated curves not completely overlapping, as shown in Figure 7 [27]. As the reaction process continues, the nano modified materials have high similarity and overlap, and their performance is relatively stable.

Figure 7 CV curve results of PNMs
PNMs and graphene (GO) are mixed and ground in a ratio of 1:0, 1:1, 1:3, 3:1, 0:1. It is found that there are ECP differences in the electrode plates under copper foil current collecting medium, as shown in Figure 8 [28].
Figure 8 Multiplication of materials under different composite proportions

The rate changes of various materials under different composite ratio conditions also vary. Specifically, in low current densities, the mixed material with the highest specific capacity is a 1:3 ratio, while the nanomaterials without GO addition have the lowest specific capacity. Adding GO to nanomaterials can enhance their lithium storage performance. When the current density increases to 100, 200, 500 Ag\(^{-1}\) or even higher, composite materials mixed in a 3:1 ratio can still exhibit higher lithium storage performance. Its specific capacity has reached 235.90mAh.g\(^{-1}\), 180.91mAh.g\(^{-1}\), and 123.08mAh.g\(^{-1}\). A composite material with a ratio of 3:1 can still maintain a good discharge specific capacity when the current density decays. Its retention rate exceeds 95% and it has high electrochemical reversibility, with PNMs having a capacity retention rate of over 90%. In the cyclic performance results, five materials experience capacity degradation during initial testing due to the lack of a complete SEI film on their surface. After 500 electrochemical cycles, the composite material with a 3:1 ratio can still maintain a HSC and has good CS. The more reactive sites there are in composite materials, the more their specific capacity will gradually increase. PNMs provide structural voids for NEMs, making the flow and activity of ions more convenient and rapid, which promotes the overall electrical performance of the material.

Figure 9 Charge discharge curve under 3:1 nanomaterials

In Figure 9, the nanomaterial has a lower Coulombic efficiency due to the consumption of material functional groups in the first cycle, which to some extent leads to irreversible capacity loss. As the electrochemical reaction process continues, the Coulombic efficiency of porous nanodot materials has been improved, with a maximum value of over 90%, and the reaction loss has been effectively reduced, resulting in improved CS. This material exhibits good charging capacity at different current densities and exhibits good cycling characteristics [29].

4. Conclusion

With the adjustment and upgrading of China's energy and industrial structure, the demand and application prospects of high energy density LIBs are relatively broad. On the basis of understanding the structural principles of LIBs, this study analyzed the modification technology and electrochemical research progress of Ti\(_2\)C\(_2\) nanomaterials. The loading and current density of nanomaterials under porous modification treatment were discussed. It has been found that porous nano modified materials could greatly improve the ECP of lithium ion NEMs, shorten the ion transport path, and improve their cycling characteristics and structural stability while ensuring their HSC. When the ratio of nanomaterials to GO was 3:1, NEMs still exhibited good discharge specific capacity retention (greater than 90%) despite current density attenuation. As the electrochemical reaction process continued, the Coulombic efficiency of porous nanodot materials has been improved, with a maximum value of over 90%, and the reaction loss has been effectively reduced, resulting in improved CS. In the future, the surface pore size of Ti\(_2\)C\(_2\) materials under different processing times and more safe and effective new etchants are meaningful for the research of LIBs NEMs. This research direction can better improve the efficiency and sustainability of nanomaterials in energy storage and conversion.

Reference


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