Ferrosilicate Hydroxide/Carbon Nanotube Material for Anode of Lithium Batteries

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Abstract. A ferrosilicate hydroxide/carbon nanotube composite was prepared by a combination of floating chemical vapor deposition and hydrothermal method as a lithium-ion battery anode. The obtained film material has a capacity superior to that of the conventional graphite negative electrode, and has a reversible capacity of 569.5 mAh g\(^{-1}\) at 0.05 A g\(^{-1}\). The material has excellent rate performance and cycle stability. The material can still maintain a capacity of 178.5 mAh g\(^{-1}\) after 500 cycles under a high magnification of 3 A g\(^{-1}\), with a coulomb efficiency is 95-100%.

1. Introduction

With the large-scale commercialization of lithium-ion batteries, graphite has become the most widely used anode material [1]. However, its low theoretical capacity, energy density and power density cannot meet the growing needs of energy storage equipment, electric vehicles, etc. As a potential substitute for graphite, transition metal oxides such as iron oxide [2] and nickel oxide [3] have received increasing attention. Despite the higher theoretical capacity, the poor ionic conductivity, lower Coulomb efficiency, large volume change, and weak cycle stability of these oxides limit their further application in the field of battery anodes.

Recently, researchers have found that ferric silicate has better structural stability than iron oxide [4, 5]. Wei [6] et al. Prepared carbon-coated porous cobalt silicate nanoribbons with excellent performance of 745 mAh g\(^{-1}\) and good cycle stability at 100 mA g\(^{-1}\). Wang [7] et al. Prepared a porous manganese silicate/graphene composite, which has a capacity of 836.4 mAh g\(^{-1}\) after 200 weeks of cycles at 100 mA g\(^{-1}\). In 2014, carbon-coated α-ferroolivine synthesized by the solid-phase method was found to have a good performance of 376.7 mA h g\(^{-1}\) when cycled for 100 weeks at a rate of 1 C. The use of silicates instead of oxides in lithium battery anodes has gradually attracted researchers’ attention [6, 8].

Adding materials with high conductivity for compounding can effectively improve the performance of ferric silicate. Due to the high electrical conductivity of carbon nanotubes [9] in their one-dimensional direction, they are widely used in the construction of conductive networks for electrode materials, which can effectively improve the rate performance of materials. Floating chemical vapor deposition can generate continuous flexible materials in situ, such as carbon nanotube films [10], carbon nanotube fibers [11], silicon oxide carbon nanotube composite films, etc., which has the...
advantages of good uniformity and large-scale production. This method can be used to synthesize materials for electrode films without binders, which has attracted the attention of researchers [12].

In this paper, a floating chemical vapor deposition method combined with a hydrothermal method was used to prepare a ferrosilicate hydroxide/carbon nanotube composite film. By in-situ template synthesis, the obtained material can be used for the negative electrode without a binder and other added conductive agents and has excellent cycle stability and rate performance.

2. Experimental Section

2.1. Materials Synthesis

The preparation of ferrosilicate hydroxide/carbon nanotube composite thin film materials is mainly divided into two steps.

Step 1. Preparation of Silicon Oxide/Carbon Nanotube Composite Films by Floating Chemical Vapor Deposition: (1) Weigh 24 g ethanol, 0.43 g ferrocene, 0.2 g thiophene, in which ethanol as the carbon source for this reaction, ferrocene as the catalyst, and thiophene as the accelerator. Weigh 4% (~1 g) of tetraethyl orthosilicate (TEOS) as the silicon source for the reaction. The above materials were mixed into a solution and ultrasonically dispersed at 50 °C for 60 minutes to obtain a relatively uniform precursor solution. Transfer the precursor to the syringe. (2) In a sealed vertical CVD furnace, in order to eliminate residual air in the furnace, 100 sccm of high-purity argon gas was continuously introduced into the furnace for 30 minutes. The vertical CVD furnace was heated to 1150 °C, and the entire vertical CVD furnace was filled with H2. The precursor solution was injected into the furnace at an injection rate of 8 mL/h, and the silicon oxide/carbon nanotube film was continuously collected at the bottom of the furnace.

Step 2. Preparation of ferrosilicate hydroxide/carbon nanotube composite thin film material by hydrothermal method: (1) Transfer 80 mL of diluted ethanol solution (Et %=25 %), 2 g of urea, and 2.4 mL of ferric nitrate with a concentration of 0.1 M to a 100 mL blue-cap glass bottle, and stir to mix. (2) After soaking 20 mg of the silicon oxide/carbon nanotube film described in step (1) in the above solution, the glass bottle was sealed. The system was reacted at 105 °C for 12 h. (3) Washed with deionized water and dried at 90 °C for 12 hours, the ferric silicate hydroxide/carbon nanotube flexible composite film material was obtained.

2.2. Materials Characterizations

The obtained composite film material was sliced and then placed in a glove box for 24 hours. Finally, a CR2032 button cell was assembled in a glove box in an argon atmosphere. During assembly, a lithium metal sheet is used as a negative electrode, a polypropylene porous separator, and 1 mol/L LiPF6 with a volume ratio of 1: 1 of ethylene carbonate (EC) and dimethyl carbonate (DMC) is used as electrolyte. After assembling the half-cell, electrochemical performance was tested using a Neware battery tester. The structure of the obtained material was analyzed using a Rigaku D/Max 2500 v/pc XRD diffractometer, and the morphology was analyzed using a Hitachi S4800 SEM scanning electron microscope.

3. Results and Discussion

The materials were characterized by SEM. Figures 1b and 1c are low and high resolutions SEM images of ferric silicate hydroxide/carbon nanotubes, respectively. It can be seen from the figure that the iron silicate hydroxide and carbon nanotubes form a mixed three-dimensional network structure. The granular ferric silicate hydroxide is combined into a sponge shape, with pores of about 100 nm, which facilitates the immersion of the electrolyte and the formation of ion channels. The carbon nanotubes pass through the middle of the sponge-like ferric silicate hydroxide, which indicates that the iron silicate hydroxide and the carbon nanotubes are tightly compounded. Some carbon nanotubes remain in a bare state and are intertwined into a network structure, which will facilitate electron transport.
To study the structural characteristics of materials, X-ray diffraction analysis was used. The peak positions appearing at 12.4°, 24.9°, 35.0°, 41.4°, 50.8°, and 59.7° correspond to (001), (002), (201), (202), (310), (061) of Fe₃Si₂O₅(OH)₄ (PDF: 44-0469) respectively, indicating that the experiment has successfully synthesized the ferric silicate hydrate.

Figure 3 of the EDS pattern shows that the main elements of the material are carbon, oxygen, silicon, and iron. The atomic percentage of oxygen, silicon, and iron is about 34:13:12, which is relatively close to that of iron silicate compared to 9:2:3. The element ratio is basically consistent with the expected product.

Figure 4a shows the CV curve of the first three cycles of the material. The voltage ranges from 0.01 to 3.00 V while the scan rate is 0.1 mV s⁻¹. Under the cyclic positive scan, the peaks of 0.6 V and 0.7 V that can be observed and disappeared during the subsequent cycles correspond to the formation of a solid irreversible solid electrolyte interface (SEI) [5] on the electrode. The two peaks at 0.75 V and 1.53 V during charging and the two peaks at 1.52 V and 2.12 V during discharge correspond to the insertion and extraction of lithium ions in the silicate, respectively. From the second cycle, the CV curves can basically overlap, which indicates that the sample showed good reversibility during the process of lithium intercalation and delithiation.

Figure 4b is the voltage curve of the first three cycles of the material at 100 mA g⁻¹. The figure shows that the charge and discharge curves of ferrosilicate/carbon nanotubes have obvious platforms, and their positions correspond to the positions of the peaks in the cyclic voltammetry curve. The first discharge specific capacity reached 977.9 mAh g⁻¹, and the charge specific capacity was relatively small at 630.1 mAh g⁻¹. The first cycle Coulomb efficiency was 64.4%. This capacity loss corresponds to the formation of a SEI film and is significantly better than that of graphite materials. There is no obvious change between the second and third laps, which indicates that the performance of the material is stable from the second lap. The discharge specific capacity and charge specific capacity of the third cycle are 680.5 mAh g⁻¹ and 617.0 mAh g⁻¹, respectively. The Coulomb efficiency is over 90%, which is greatly improved compared to the first cycle.

Figure 4c is the rate curve of ferrosilicate/carbon nanotubes under different current densities. Overall, the material exhibits good rate performance. The capacities at 0.05, 0.1, 0.2, 0.5, 1 and 2 A g⁻¹ are 569.5, 518.2, 405.6, 322.4, 239.2 and 161.8 mAh g⁻¹, respectively. Even at a high current density of 3 A g⁻¹, the reversible capacity can still reach 121.1 mAh g⁻¹. After 70 cycles of charging and discharging at different magnifications, and after changing to 0.05 A g⁻¹, the specific capacity of the material returned to 741.2 mAh g⁻¹, which was close to the initial. The reversible capacity change reflects the material's good rate performance, indicating that the material's internal conductivity is good.
Figure 2. XRD pattern of ferrosilicate hydroxide/carbon nanotube film.

![XRD pattern of ferrosilicate hydroxide/carbon nanotube film](image)

| Element | Wt%  | At%  |
|---------|------|------|
| C       | 23.77| 40.97|
| O       | 26.26| 33.99|
| Si      | 17.77| 13.10|
| Fe      | 32.19| 11.94|

Figure 3. EDS pattern of ferrosilicate hydroxide/carbon nanotube film.

![EDS pattern of ferrosilicate hydroxide/carbon nanotube film](image)

Figure 4. (a) CV curve for the first three cycles at 0.1 mV s⁻¹; (b) Charge/discharge curve at 0.05 A g⁻¹; (c) Rate capability performance at different current densities; cycling stability at current densities of (d) 0.1 A g⁻¹ and (e) 3 A g⁻¹.

![Graphs and diagrams](image)
Figure 4d is a 150-cycle cycle curve of the ferrosilicate hydroxide/carbon nanotube composite film material at 100 mA g\(^{-1}\). With the increase of the number of cycles, the specific capacity of the material is basically stable, maintained at 417.5 mAh g\(^{-1}\), the Coulomb efficiency is 95-100%, and the overall capacity is 100% of the initial value, showing superior cycle stability. This is due to the high structural stability of silicate materials and their stable performance during low rate cycling.

Fast charge is an important field of current battery research, and it requires the stability at high rate charge and discharge. Figure 4e is the cycle curve of the ferrosilicate hydroxide/carbon nanotube composite thin film material at 3 A g\(^{-1}\). The specific capacity of the material has an increase of about 250 cycles before the cycle. The discharge specific capacity in the first cycle is 818.3 mAh g\(^{-1}\). The Coulomb efficiency is 48.5%, and it reaches the highest capacity of 577.1 mAh g\(^{-1}\) when cycling to 266. The material performance gradually decreased after 266th cycle. After 500 cycles of charge and discharge, the capacity was finally stabilized at 178.5 mAh g\(^{-1}\), and the Coulomb efficiency was 95-100%. The possible cause of this phenomenon is that there are some inactive sites inside the membrane material, which are gradually activated during the reaction to gradually increase the capacity, but there is also a capacity loss caused by structural collapse during the reaction.

4. Conclusion
In this paper, a silicon oxide/carbon nanotube composite thin film is synthesised with a floating chemical vapor deposition method, and a ferrosilicate/carbon nanotube composite film material required for hydrothermal synthesis is used for an anode. The obtained material has good rate performance and excellent high rate cycle stability. The material is suitable for use scenarios that require high power, such as large-scale energy storage, electric vehicles, etc. The method uses high abundance of raw material elements such as iron, silicon, and carbon, low cost of producing negative electrode materials, and friendly production process environment, which is suitable for large-scale production and has commercial potential.

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