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A Review on Graphene Composite Nanomaterials in Anode of Lithium-Ion Battery

Shuangshuang Chen *

College of Energy, Xiamen University, Xiamen, Fujian, 361000, China
*** Corresponding author Email:** 32420222202001@stu.xmu.edu.cn

Abstract: The article discusses the current research status and development trend of graphene composite anode materials which is made for lithium-ion batteries. With the rapid growth of the electric vehicle industry, batteries have become an increasingly significant component, and graphene composites have attracted extensive interest from researchers as a promising material. Graphene has a high surface area and excellent electrical conductivity, but there is still room for improvement in its application in anode materials for lithium-ion batteries. Compounding graphene with other materials can further improve the battery performance. Here the research results of several graphene composites are listed, and these composites show excellent performance in terms of cycling performance and capacity, which provide an important reference direction for further research on graphene composites.

Keywords: Graphene; Lithium-ion Battery; Nanomaterials.

1. Introduction

Under the vigorous expansion of the electric vehicle industry, the importance of batteries is gradually coming to the fore. At present, lithium batteries are mainly used for power storage, and batteries of lithium-ion have many benefits, such as high operating voltage, great energy density, safety, and environmentally friendly, etc. These make them the most promising chemical power source. How to further enhance the power and energy density of lithium-based energy storage battery has become a hotspot of new energy science and technology.

And because graphite is not that expensive while the production scale is large, the existing anode materials for batteries of lithium-ion are mainly based on carbon materials. However, the low theoretical capacity of graphite (about 372mAh/g) greatly limits the capacity improvement and large-scale application of lithium-ion batteries. Therefore, the improvement of new and high-capacity anode materials is currently the focus of electrode materials research. [1]

Graphene is layers of flaky carbon atoms that are assembled in a way to obtain higher storage capacity and cycle life than that of lithium batteries assembled with conventional graphite electrodes. However, if pure graphene is applied as the anode material of lithium batteries, there is still much room for improvement in cycles and battery capacity. If graphene with high electrical and thermal conductivity is doped into nanomaterials, high-capacity and cycle performance lithium-ion batteries can be obtained. At present, the main materials compounded with graphene are metal, metal oxide and lithium metal.

2. Research Purposes

Graphene composite nanomaterials still have great development potential in the future because of their properties of high capacity and excellent cycling performance. There are several existing mainstream graphene composite nanomaterials, and the article hopes to provide a reference direction for future research by summarising the performance of the existing materials. The analyses of performance include current density, charging capacity, rate performance and cycling performance. Different materials have different advantages in different aspects.

3. Progress on the Current Status of Graphene Doping Research

The current research results of graphene doping of different materials are mainly focused on the following directions, and their general performance data are as follows:

3.1. Graphene Composite with CoSe

Liu et al. successfully prepared a series of C@CoSe/rGO composites with porous structure by an effortless process of hydrothermal energy utilizing glucose and graphene for carbon. Results from the electrochemical capability tests show that C@CoSe/rGO-2 composites can achieve a capacity of 751 mAh/g following 150 cycles at a current density of 200 mA/g. Despite undergoing 150 cycles at elevated current densities of 1000 mA/g and 2000 mA/g, C@CoSe/rGO-2 composites maintain their ability to achieve capacities of 525mAh/g and 285mAh/g, indicating superior electrochemical efficiency. The composite of graphene and CoSe can efficaciously alleviate the volume expansion and pulverisation of CoSe particles, and effectively prevent the agglomeration of its molecules. At the same time, it provides a convenient transmission channel for the transmission of electrons and improves the overall electrochemical performance of the material. [2]

Wang et al. from Northwest Normal University used the Hermes method to prepare CoSe/rGO, and the electrochemical performance test results exhibited that the capacity of the composite could be as good as 730 mAh/g. Despite a substantial current density of 1000 mAh/g, the capacity might still attain 570 mAh/g following 1000 cycles. During the composite preparation, the shape of CoSe shifted from a larger petal to a smaller rod form, diminishing the volume change's impact in the lithium-ion intercalation phase and reducing the diffusion distance between lithium and ions,

thereby enhancing the composite's capacity.[3]

3.2. Silicon Composite with Redox Graphene

The preparation method used by Lee et al. was roughly as follows: Which graphite was first treated with are conc. H_2SO_4, P_2O_5 and $K_2S_2O_8$. after filtration, washing and drying, then re-suspended the solid in conc. H_2SO_4 was further oxidised with $KMnO_4$ and H_2O_2 for achieving a delay in the brownish-yellow postponement. The GO postponement was washed with 10% hydrochloric acid, then with DDI (distilled, deionised) water repeatedly then washed and stored as a suspension (∼7 mg ml-1) in the dark until put in use.

In an aerial environment, Si-graphene (SG) paper composites were meticulously prepared. Nanoparticles of silicon (H-terminated, preserved in Ar, <30 nm, using Meliorum nanotechnology) were moved from storage to containers and then left in the air overnight to guarantee the creation of a silicon oxide coating on the surface, facilitating their distribution in water.

Characterisation showed that the reversible cycling capacity of the cells was higher than 2200 mAh/g after 50 cycling test and remained higher than 1500 mAh/g after 200 cycling test.[4]

Domestic Zhang introduced water (H_2O) and boric acid (H_3BO_3) into Hummers' method of synthesising GO to add to the content of hydroxy and epoxy functional groups in GO, which enhanced the coating effect of GO on Si particles, and better enhanced the electrochemical outcoming of silicon/reduced graphene oxide composites (Si/rGO). Characterisation shows that the composites mainly exhibit a lamellar honeycomb structure, while the curved folds of the rGO (reduced graphene oxide) lamellae form a large number of microporous channels, which improves the lithium ion transport efficiency. The capacity of initial discharge reaches up to 2230.2 mAh/g (0.1 A/g), and the initial discharge capacity reaches up to 1002.8 mAh/g (0.1 A/g) after several cycles. In the form of an electrode substance at 1 A/g current density under stable cycling for 800 cycles, the capacity remained 82.4% and reached 511mAh/g.[5]

3.3. Fe3O4 Composite with rGO

Wu et al. composited Fe_3O_4 particles with graphene oxide (GO) by a simple and effective solvothermal method to obtain Fe_3O_4/GO composites. The Fe_3O_4/rGO was milled with glucose. A conductive carbon layer with a mesh structure was prepared on the surface of Fe_3O_4/rGO while reducing GO to reduced graphene oxide (rGO) at elevated temperature to obtain a three-dimensional network transport structure C/Fe_3O_4/rGO composite. The XRD characterisation shows that the dual carbon layers consisting of carbon network and made the graphene oxide decreased not only inhibit the volume enlargement of Fe_3O_4 while in the battery cycling process, but also the three-dimensional electron transport structure improves the electron transport rate of the composites. The composites showed good cycling capability, with a capacity of 363 mAh/g after 300 cycles at a current density of 4A/g.[6]

Ershadi et al. from abroad innovatively used an allosteric approach for the creation of amino-functionalized mesoporous nanocomposites based on Fe_3O_4 and graphene. Mesoporous Fe_3O_4 nanoparticles (Fe_3O_4-E) were filled by synthesising Fe_3O_4 nanoparticles by adding ethylenediamine (EDA). Leveraging electrostatic forces, the Fe_3O_4-E/rGO nanocomposites achieved a well-prepared state. These nanocomposites showed effective cycling performance, with notable reversibility (∼465 mAh g-1), and maintained an average Coulombic efficiency of approximately 98% at a current density of 1000 mA g-1 over 250 cycles. The researchers ascribe these findings to the emergence of EDA during the formation of mesoporous nanoparticles and within the three-dimensional configuration of the resultant composites. This mechanism inhibits the disintegration of Fe_3O_4 particles resulting from mesoporous structure creation and also stops the rearrangement of rGO sheets by altering the spacing between layers.[7]

3.4. SnO2 Composite with Graphene

Wang et al. prepared composites by mechanically combining SnO_2 nanoparticles with graphene nanosheets based on the redox reaction between graphene oxide and $SnCl_2$-$2H_2O$. Sn^{2+} ions were hydrolysed in order to produce SnO_2 nanoparticles at room temperature in the reaction system, graphene oxide nanosheets were synchronously reduced to graphene nanosheets.

The SnO_2/graphene hybrid electrode material was shown to have a discharge capacity of 1700 mAh/g in the initial time, a charging capacity of 978 mAh/g, and a Coulombic efficiency of 58% by means of characterisation such as TEM, SEM, etc., demonstrating excellent lithium storage capacity. Data showed a SnO_2/graphene molar ratio of 3.2:1. Current density is 400 mA/g, which corresponds to a rate of ~0.5C, the composite can maintain a charge capacity of ~590 mAh/g for up to 50 cycles. When the current density is increased to 1000 mA/g (equivalent to ~1.3C rate), the composite is still able to provide a capacity of 270mAh/g for up to 50 cycles. This shows the superior rate performance and cycling performance. [8]

Abroad, Birrozzi synthesized composite nanomaterials by Microwave-reduced poly (acrylic acid)-functionalized graphene oxide dispersed in ethylene glycol and tin oxide organic precursor. This composite material was synthesized by microwave reduction process for polyacrylic acid-functionalized graphene oxide and its tin oxide organic precursor, mixed in ethylene glycol. As shown by battery charge/discharge assessment, after more than 140 cycles (most of Executed at a rate of 500 mAg-1, the electrodes exhibited an impressive stable capacity of approximately 430 mAh g-1 and nearly complete Coulombic efficiency. The researchers deduced that the functionalization of graphene oxide with polyacrylic acid somewhat hinders the rearrangement of graphene strata., and that polyacrylic acid, as a surfactant, facilitates optimal dispersion of the metal and contributes to the formation of a carbon layer upon thermal decomposition, thus improving the electrical conductivity. [9]

3.5. Nanoparticles (NPs) Composite with Nitrogen-doped Graphene

Hou et al. devised a facile strategy to fabricate mixtures of the interaction of Co_3Sn_2@Co nanoparticles (NPs) with nitrogen-infused graphene (NG) sheets via hydrothermal synthesis and annealing techniques. The core-shell configuration of Co_3Sn_2@Co needles, crafted on NGs, facilitates the dual encapsulation of Co_3Sn_2 using both Co and NGs, aiming to enhance the anode's structural and interfacial steadiness. The distinct design of the Co_3Sn_2@CoNG hybrid features a sealed cobalt layer that blocks tin from directly interacting with the electrolyte, thanks to its encapsulation framework, while preserving the structural and surface

integrity of Co3Sn2. And the resilient, flexible and conductive NG outer coating can adapt to volume changes, resulting in more stable structural and electrical properties of Co_3Sn_2@CoNPs. Electrochemical performance tests showed that the Co_3Sn_2@Co-NG hybrid battery displayed a superior reversible capacity of 1615 mAh/g with a capacity retention rate of 102% after 100 cycles at 250 mA/g. The reversible capacity at 2500 mA/g was 793.9 mAh/g with a Coulombic efficiency close to 100%. [10]

Based on the above results the table Fig. 1 is plotted so that the difference in the properties of different composites can be seen more clearly for comparison.

Composite Material	China/Other country	Current density	Capacity	Initial discharge capacity
C@CoSe/rGO	China	200mA/g	751mAh/g (150cycles)	/
		1000mA/g	525mAh/g (150cycles)	
		2000mA/g	285mAh/g (150cycles)	
Si	Other	/	>2200mAh/g (50cycles)	/
			>1500mAh/g (200cycles)	
	China	/	/	2230.2mAh/g(0.1A/g)
		1 000mA/g	511 mAh/g (800cycles)	1002.8mAh/g(0.1A/g)
Fe3O4	China	4000mA/g	363mAh/g (300cycles)	/
	Other	1000 mA/g	/	/
SnO2	China	400 mA/g	590mAh/g (cycles)	1700mAh/g
		1000 mA/g	270mAh/g (50cycles)	
	Other	/	430 mAh/g (140cycles)	/
Co3Sn2@Co	China	250mA/g	1615mAh/g (100cycles)	/
		2500mA/g	793.9mAh/g (100cycles)	

Fig 1. The difference in the properties of different composites can be seen more clearly for comparison

Through comparison, we can see that the composite of graphene with nanomaterials such as cobalt selenide showed superb electrochemical efficiency coupled with substantial capacity and consistent cycling results in the study. On the other hand, the composites of silicon and reduced graphene oxide showed excellent performance in terms of reversible cycle capacity and cycling performance of the battery. By comparing the results of the domestic and international teams, the battery performance derived by different teams has their own advantages and disadvantages, which may be related to the synthesis method and experimental conditions.

Meanwhile, Fe_3O_4 and rGO composites demonstrated excellent cycling performance, maintaining high capacity at high current density. In addition, the composite of SnO_2 with graphene also exhibits excellent lithium storage capacity and great rate performance. The Co_3Sn_2@Co-NG hybrid material, on the other hand, solves stability at the structural and interface level problems of the anode by designing the core-shell structure of the Co_3Sn_2@Co nanoparticles and taking advantage of the excellent performance of nitrogen-doped graphene, showing superior electrochemical performance and stability. The innovation is that the structural design can effectively improve the cycling stability of the material, ensuring that the battery performance will not significantly deteriorate during long-term use.

4. Challenges and Outlook

4.1. Possible Challenges of Graphene Composite Nanomaterials

Long Cycle Stability. Although experimental data show that the materials basically have good cycling performance, if they are put into long-term use, they have to face problems such as structural fatigue caused by long-term use.

Secondly, the complexity of the preparation process may limit the large-scale production of composite materials. Currently, to put efficient graphene composites into use, a more delicate and costly preparation process is required. The development of simple preparation methods and production equipment is also a key issue in bringing graphene composites to scale.

Finally, the challenges of cost and large-scale production are also key constraints to the application of graphene composite nanomaterials. More competitive production techniques and technological innovations are sought to reduce costs and increase production efficiency. Continuous research and innovation must be conducted to address the application and development of graphene composites in electrochemical energy storage.

4.2. Prospects for the Future of Graphene Composites

Graphene composites in the field of lithium-ion battery anode may achieve enhanced energy density, quicker charging and is charging speeds, extended cycle duration, and reduced future expenses, promoting the innovation and progress of battery technology. At the same time, the composite of graphene and other materials will also become a hotspot for future development, and customized design of lithium-ion battery systems that are more suitable for different scenarios. Overall, graphene composite anode materials have good application prospects and potential due to their good electrochemical properties.

5. Summary

Graphene composite materials have great application potential and development prospects as anode for batteries of lithium-ion. Due to its wide surface area, excellent electrical conductivity, excellent mechanical strength and flexibility, and sustainability advantages, graphene composites have a huge range of applications in the professional area of lithium-ion batteries. In the future, graphene composites are expected to realise the prospects of higher energy density, faster charging and discharging speeds, and longer cycle life, thus promoting the progress and innovation of lithium-ion battery technology. Comprehensive use of graphene composite with other materials is also a hotspot for future development, and the customised design of composite materials is more suitable for different scenarios of lithium-ion battery systems. Overall, graphene composites show broad application prospects and

development opportunities in the area of lithium-ion battery anode.

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