Review and Prospect of NiFe₂O₄-Based Materials for Li-Ion Battery

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Abstract. NiFe₂O₄ with high theoretical capacity, natural abundance as well as low cost exhibits tremendous potential as the electrode for lithium ion battery. Nevertheless, the great volume change upon the charge-discharge cycling gives rise to pulverization of NiFe₂O₄ electrode. The electron transport pathways are broken down, and ultimately, the cycling stability and reversible capacity fade rapidly, which restricts its commercial applications. Consequently, it is necessary to consider nano-size effect, interface property, defects and hybridization to satisfy the requirement of practical application. In this review, we comprehensively overview and analyze the latest progress in NiFe₂O₄-based anode, covering the representative synthesis method and advanced structure to realize improved Li⁺ storage performance. Furthermore, we objectively evaluate the Li⁺ storage performance of NiFe₂O₄-based anode materials and dissect the existing problems. Finally, an outlook for the development of advanced NiFe₂O₄-based anode materials is provided.

1. Introduction

Global energy consumption is increasing at an amazing speed, and the traditional fossil fuel is exhausted [1]. Therefore, it is of great significance to construct the new energy system. Compared with the developed countries, China is undergoing a more serious energy situation. To achieve the transformation of energy resources structure, it is urgently needed to accelerate the application of solar energy, wind energy and tidal energy, promote low-carbon development. As an intermediate process between energy production and utilization, the energy storage technology has attracted increasing attention. Electrochemical storage technology is the most promising because of its high efficiency, long life, no pollution, low maintenance cost and controllability.

Among the electrochemical storage technologies, lithium ion batteries (LIBs) having high energy density, high voltage and low self-discharge exhibit unique advantages. Consequently, they are widely applied in cellphone, tablet, electric vehicles and satellite [2]. The research for LIBs focuses on how to achieve higher capacity, energy density/power density, safety, as well as longer cycling life. Electrode materials are a key part of LIBs, and strongly affects its electrochemical performance [3]. Plenty of cathode materials have been successfully commercialized, while the commercialization of anode is restricted in graphite with low specific capacity and Li₄Ti₅O₁₂ with low energy density. The alternative anode with superior lithium storage performance is desperately needed.

In recent years, NiFe₂O₄ has drawn a lot of concern because the material possess high theoretical capacity, has no disadvantage effects on environment and its cost is low. This paper summarizes the key progress and foreground of NiFe₂O₄-based anode material, covering state-of-the-art fabrication
and characterization methods, lithium storage mechanisms, and future research for new application and promoting industrial application.

2. Fabrication of NiFe$_2$O$_4$-Based Materials

2.1. Hydrothermal Method
Gao [4] synthesized NiFe$_2$O$_4$ with nanoparticle and layer structure via a facile hydrothermal method with different precipitants of CH$_3$COONa and urea, respectively. Results show that the NiFe$_2$O$_4$ nanosheet has a larger specific surface area. Zhang [5] adopted the two-step hydrothermal process to design a unique three-dimensional structure on Ni foam with ultrathin MnO$_2$ nanoflakes as the shell and NiFe$_2$O$_4$ nanosheets as core.

2.2. Electrospinning
Cherian [6] prepared NiFe$_2$O$_4$ nanofibers by electrospinning. Their average diameter are ~200 nm and length are several millimeters. The magnified image indicates the nanofibers is intact and continuous, meanwhile, it is composed of interconnected nanoparticles of 10-20 nm. Moreover, Lee [7] and Luo [8] also prepared NiFe$_2$O$_4$ Nanofibers and investigated its lithium storage performance. Wang [9] synthesized diverse one-dimensional NiFe$_2$O$_4$, containing nanotube, solid nanofiber and yolk/shell nanofiber. The special surface area of nanotube, solid nanofiber and yolk/shell nanofiber are 72.02, 39.06 and 51.12 m$^2$·g$^{-1}$, respectively. Electrospinning-calcination process is adopted by Dong [10] to realize the encapsulation of NiFe$_2$O$_4$ nanoparticles (18 nm) into the porous carbon fibers. The average diameter of the nanofibers with smooth surface morphology is 400 nm and specific surface area is as high as 248.8 m$^2$·g$^{-1}$.

2.3. Template Method
Zhang [11] synthesized 3D ordered macroporous NiFe$_2$O$_4$ using close-packed PMMA spheres as template. The 3D NiFe$_2$O$_4$ exhibits uniform spherical macropores with a walls thickness of 20 nm and a diameter of ~140 nm. Gao [12] employed the Fe$_2$Ni MIL-88 as template and precursor to design amorphous carbon nanorod anchored with NiFe$_2$O$_4$ nanoball. The novel strategy integrated the hollow structure with hybridization and obtained a new composite consisting of metal oxide and carbon materials without adding carbon source.

2.4. Sol-gel Method
Li [13] synthesized NiFe$_2$O$_4$ with a flake structure by polyacrylamide sol-gel method. Islam [14] also employed sol-gel method to prepare single-phase spinel NiFe$_2$O$_4$ nanoparticles with diameter of ~20 nm.

3. Recent Development of NiFe$_2$O$_4$-based Anode Materials

3.1. NiFe$_2$O$_4$
In 2003, Alcantara [15] adopted NiFe$_2$O$_4$ as anode of LIBs for the first time, meanwhile, the reversible capacity reached ~900 mAh·g$^{-1}$. Abarca [16] prepared two kinds of NiFe$_2$O$_4$ samples at different temperatures and explored the origin of capacity fading via $^{57}$Fe Mössbauer spectroscopy. They reveal the annealing temperature affects the contributions of internal and surface atoms. The decreased particle size facilitate decreased blocking temperature in ferromagnetic-superparamagnetic transition of the discharged electrodes. Cherian [6] compared the lithium storage performance of NiFe$_2$O$_4$ nanofibers and NiFe$_2$O$_4$ particles. The nanofibers display the better lithium storage performance. After 100 cycles, the charge-storage capacity maintains 1000 mAh·g$^{-1}$. Moreover, the coulomb efficiency is as high as 100% from 10th to 100th cycle. Kumar [17] synthesized NiFe$_2$O$_4$ nanocrystalline via a sol-gel combustion strategy. The maximum discharge capacity of NiFe$_2$O$_4$ can reach 880 mAh·g$^{-1}$ when experimental condition is controlled at 0.1 C, achieving 96% of the theoretical capacity. The specific
capacity remains 740 mAh·g⁻¹ when experimental condition is 1 C. Furthermore, the material also possesses a superior capacity retention ability.

Liu [18] systematically investigated the effect of hydrogenation on the morphology, structure and electrochemical characteristics of NiFe₂O₄. The octahedron morphology is altered, and Ni as well as oxygen vacancies appear after hydrogenation. Meanwhile, the capacity retention increases by 60% after 50 cycles, and rate capability increases by three times of not hydrogenated samples.

It is an important strategy to boost the lithium storage property by adjusting morphology of materials. Wang [9] developed NiFe₂O₄ with one-dimensional structure, including solid nanofibers, core/shell nanofibers as well as nanotubes using the “electrospinning-hydraulic agitation” method. Among them, nanotube demonstrates the best lithium storage capacity (1349 mAh·g⁻¹ after 220 cycles at a current density of 100 mA·g⁻¹). Its superior electrochemical property is associated to the distinct advantage in high specific surface area and continuous one-dimensional tubular nanostructure. More importantly, this strategy is universal, and can be widened to the other ferrite materials.

Zhou [19] explored the electronic as well as local structural change of NiFe₂O₄ in the process of lithiation and de-lithiation. In the initial lithiation stage, Fe³⁺ at tetrahedral site changes into Fe²⁺ and moves to the unoccupied octahedral sites, however, the Ni²⁺ does not change. Therefore, the spinel structure turns into an intermediate rock-salt monoxide phase. As the lithiation proceeding, the monoxide is reduced to a highly disordered metallic Fe/Ni nanoparticle. During the de-lithiation, Fe/Ni is reoxidized to Fe₂O₃ and NiO. Islam [14] believes that Fe²⁺ is completely reversible; however, Ni²⁺ may exist in the form of metallic Ni or NiO, which gives rise to a partial reversible capacity.

3.2. NiFe₂O₄-Metal Oxide
Balaji [20] synthesized SnO₂/NiFe₂O₄ with 10 wt.% SnO₂ and the discharge capacities was about 980 mAh·g⁻¹. Huang [21] constructed NiFe₂O₄/Fe₂O₃ nanotubes through annealing of Fe₂Ni MIL-88/Fe MIL-88 MOFs. Their diameters are 78 nm as well as length are ~1 nm. After 100 cycles at 100 mA·g⁻¹, the reversible specific capacity can reach 936.9 mAh·g⁻¹. More importantly, the discharge capacity at can still reach 423.6 mAh·g⁻¹ when the current density is 2000 mA·g⁻¹. Meanwhile, Huang [22] prepared NiFe₂O₄@TiO₂ nanorods with core-shell structure. After 100 cycles at the current density of 100 mA·g⁻¹, the nanorods owning the length of 300-600 nm and an average diameter of 48 nm maintain a reversible specific capacity of 1034 mAh·g⁻¹. The discharge capacity can still reach 358 mAh·g⁻¹ even at 2000 mA·g⁻¹. Xu [23] prepared Fe₂O₃/NiFe₂O₄, and the initial capacity is about 1437 mAh·g⁻¹ when the current density is 200 mA·g⁻¹. And after 750 cycles, the reversible capacity can also maintain 500 mAh·g⁻¹. The electrochemical test demonstrates the shortened lithium ion diffusion path and the synergistic effect of Fe₂O₃ and NiFe₂O₄ contribute to the improved initial capacity and cyclic stability. Wang [24] investigated the influence of particle size, porosity as well as shell/interior structure on the performance of NiO/NiFe₂O₄ as anode of LIBs. Results show that the hetero-structure, small particle size as well as high porosity facilitate enhanced lithium storage property. The capacity can reach 1052 mAh·g⁻¹ after 300 cycles at a current density of 5.0 A·g⁻¹. Moreover, the capacity can maintain 344 mAh·g⁻¹ at 20 A·g⁻¹ after 2000 cycles.

3.3. NiFe₂O₄-Carbon
Fu [25] prepared NiFe₂O₄-graphene heteroarchitecture to take full advantage of the active material, enhance charge transport as well as improve structural stability. The reversible capacity of NiFe₂O₄-graphene reaches a 960 mAh·g⁻¹. Xiao [26] adopted the polydopamine functionalized graphene to increase the interactions between graphene and NiFe₂O₄. The nanocomposite has a reversible capacity of 947 mAh·g⁻¹, and its rate capability increases by 7 times. Chen [27] modified graphene nanosheets with lower-shaped and spherical NiFe₂O₄, respectively. The flower-shaped NiFe₂O₄/graphene exhibits better electrochemical properties and cycling stability.

Ding [28] prepared hierarchically NiFe₂O₄/C using polymer pyrolysis. The specific capacity of the material is 780 mAh·g⁻¹ at 1/8 C after 40 cycles. And its coulombic efficiency is up to ~99%. Furthermore, the reversible specific capacity of 200 mAh·g⁻¹ are achieved at a high rate of 4 C. Han
Liu [31] employed the modified arc-discharge and annealing to prepare NiFe$_2$O$_4$/onion-like carbon nanocapsules with a specific capacity of 914 mAh·g$^{-1}$ at 0.1 C after 500 cycles. Moreover, the specific capacity can still be constant as the current density increases to 4 C. The onion-like C shell and the void spaces can increase the contact areas between the electrolyte and electrode, boost the electronic conductivity and enhance ionic mobility. Qu [30] prepared ultrathin flake graphite decorated with floral NiFe$_2$O$_4$ microspheres. The composite demonstrates remarkable initial coulombic efficiency (83.4%) and high specific capacity of 963.4 mAh·g$^{-1}$ (200 mA·g$^{-1}$) after 300 cycles. Liu [31] systematically studied the influence of dopamine content on the electrochemical properties of NiFe$_2$O$_4$/C. The reversible capacity of the NiFe$_2$O$_4$/C with 20% dopamine is as high as 1297 mAh·g$^{-1}$ after 50 cycles at the current density of 100 mA·g$^{-1}$. Furthermore, the capacity can also retain 1204 mAh·g$^{-1}$ after 300 cycles when the current density increases to 500 mA·g$^{-1}$. The excellent electrochemical properties can be associated to the outstanding structural stability and electrical conductivity.

Dong [10] adopted electrospinning-calcination process to encapsulate NiFe$_2$O$_4$ in carbon fibers with porous structure. The diameter of the material is 400 nm, and the specific capacity is 497 mAh·g$^{-1}$ at a current density of 100 mA·g$^{-1}$ after 100 cycles.

Heidari [32] assembled sandwich-structured graphene-NiFe$_2$O$_4$-carbon, and the specific capacity of 1195 mAh·g$^{-1}$ was obtained at 500 mA·g$^{-1}$ after 200 cycles. The superior electrochemical performance is related to the ultrathin NiFe$_2$O$_4$, conductive graphene substrate and the protective carbon layer.

Chen [33] demonstrated electrochemical-grinding effect induced by high current could give rise to more active sites and fast pulverization of C@NiFe$_2$O$_4$ hierarchical fibrous bundle at the initial cycles. Moreover, the thin and dense SEI appears, and electron as well as Li$^+$ transport kinetics are enhanced in latter cycles. Thus, the rate capability and cycling stability are enhanced. Their findings lay the foundation for construction of conversion-type anode materials with high performance. Permien [34] investigated the reaction mechanisms, structural and electronic variations of NiFe$_2$O$_4$/CNT through XRD, XAS. In the initial stage, Fe$^{3+}$ is reduced to Fe$^{2+}$, accompanied by the moving of Fe$^{2+}$ from tetrahedral 8a sites to empty octahedral 16c sites. As the uptake is 0.8Li, a new phase is formed. The uptake continues to 2.5Li, Fe$^{3+}$ is reduced completely and the tetrahedral 8a sites are empty. While the Li content exceeds 2.5 Li/NiFe$_2$O$_4$, the cations are reduced to metal particles existing in Li$_2$OMatrix. In time of Li release, metal particles are reoxidized to Ni$^{2+}$ and Fe$^{3+}$.

4. Conclusions and Outlook
The key progress of NiFe$_2$O$_4$-based materials for application in Li-ion battery is summarized in the paper. The advantages of NiFe$_2$O$_4$ as anode of LIBs are emphasized. Moreover, the hybridization, modification as well as charge/discharge mechanisms is discussed in this paper. Despite many achievements in NiFe$_2$O$_4$-based anode material, challenges are still here. The current manufacture technology is hard to meet commercial production, especially direct integration of large area NiFe$_2$O$_4$-based materials. Besides, electrolyte plays a vital role, and electrolyte degradation as well as SEI film formation can never be neglected. Finally, detailed phase conversion and morphology change should be further detected.

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