Synthesis of Hollow Ni0.75Zn0.25Fe2O4 Nanospheres and Their Sodium Storage Performance Post-print

Authors: Wei Hechun, Pang Hao, Li Huanjian, Dongliang Yan, Yan Dongliang

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Abstract

To investigate the electrochemical performance of ternary transition metal oxides as anode materials for sodium-ion batteries, hollow Ni0.75Zn0.25Fe2O4 nanospheres with a diameter of approximately 230 nm were successfully prepared via a hydrothermal method. The as-prepared hollow Ni0.75Zn0.25Fe2O4 nanospheres exhibit a high specific surface area of 32.6 m^2/g and good dispersibility. When used as an anode material for sodium-ion batteries, the hollow Ni0.75Zn0.25Fe2O4 nanospheres demonstrate excellent cycle life and rate capability: after 800 cycles at a current density of 200 mA/g, a specific discharge capacity of 178.5 mA · h/g is retained, with a high capacity retention of 91.6%; after 800 cycles at a current density of 500 mA/g, the capacity retention is 89.3%. Furthermore, at current densities of 100, 200, 500, 1,000, and 2,000 mA/g, the average specific discharge capacities are 212.7, 191.4, 148, 121.8, and 100 mA · h/g, respectively. The excellent electrochemical performance of the hollow Ni0.75Zn0.25Fe2O4 nanosphere electrode can be attributed to its unique nanohollow structure, high specific surface area, and shortened electron and ion transport pathways, which improves its electrochemical performance during the Na+ insertion/extraction process.

Full Text

Synthesis and Sodium Storage Performance of Ni0.75Zn0.25Fe2O4 Hollow Nanospheres

Hechun Wei[1], Huanjian Li[1], Dongliang [Last Name Missing][1]
[1]School of Materials Science and Engineering, Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin 541004, China

Abstract

To investigate the electrochemical performance of ternary transition metal oxides as anode materials for sodium-ion batteries, hollow Ni0.75Zn0.25Fe2O4 nanospheres were successfully synthesized via a hydrothermal method. The prepared hollow nanospheres exhibit high specific surface area and good dispersibility. When employed as a sodium-ion battery anode, the material demonstrates excellent cycling stability and rate capability. At a current density of [value] mA/g, the electrode maintains a discharge specific capacity of [value] mA · h/g after [number] cycles, with a capacity retention of 91.6%. The average discharge specific capacities at current densities of 100, 200, 500, and 1000 mA/g are 212.7, 191.4, 148, and 121.8 mA · h/g, respectively. The superior electrochemical performance can be attributed to the unique hollow nanostructure, which shortens electron and ion transport pathways and enhances electrochemical kinetics during sodium insertion/extraction processes.

Keywords: Ni0.75Zn0.25Fe2O4; sodium-ion battery; anode material; hollow nanospheres

Introduction

Sodium-ion batteries (SIBs) have emerged as the most promising alternative to lithium-ion batteries (LIBs) due to the natural abundance and low cost of sodium resources, coupled with the similar physicochemical properties of sodium and lithium. However, the larger ionic radius of Na^+ (0.102 nm) compared to Li^+ (0.076 nm) poses significant challenges for electrode materials, as it impedes ion diffusion and causes substantial volume expansion during cycling. Among various anode materials under investigation, transition metal oxides have attracted considerable attention because of their high theoretical capacities. Within this family, iron-based oxides are particularly promising for SIBs due to their low toxicity, environmental benignity, and theoretical specific capacities ranging from 720 to 900 mA · h/g.

Zinc-nickel ferrite (Ni0.75Zn0.25Fe2O4) has garnered increased interest because the complementary and synergistic effects of nickel and zinc enhance electronic and ionic conductivity, thereby improving electrochemical performance. Nevertheless, like many transition metal oxide anodes, it suffers from rapid capacity fading and poor rate performance. To address these issues, rational design of nanostructured materials with special morphologies has proven effective. Hollow nanosphere architectures are especially advantageous as they provide abundant electrochemical reaction active sites, shorten ion diffusion distances, accommodate volume expansion, and facilitate electrolyte penetration, ultimately delivering superior rate capability and cycling stability.

This work presents a facile hydrothermal synthesis of hollow Ni0.75Zn0.25Fe2O4 nanospheres and evaluates their performance as SIB anode materials. The

unique structural features and their correlation with electrochemical properties are systematically investigated.

Experimental Methods

Materials Synthesis

Hollow Ni0.75Zn0.25Fe2O4 nanospheres were prepared via a simple hydrothermal method followed by thermal annealing. Stoichiometric amounts of $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in ethylene glycol containing polyvinylpyrrolidone (PVP) as a surfactant. The mixture was magnetically stirred to obtain a homogeneous solution, which was then transferred to a stainless steel autoclave and subjected to hydrothermal treatment at [temperature] for [duration]. After cooling, the precursor was collected by centrifugation, thoroughly washed with deionized water and ethanol, and dried. Finally, the precursor powder was calcined in a muffle furnace at [temperature] to obtain the hollow Ni0.75Zn0.25Fe2O4 nanospheres.

Characterization

The crystal structure of the product was characterized by X-ray diffraction (XRD, D8-Advance, Bruker). Morphology and microstructure were examined using field emission scanning electron microscopy (FESEM, Tecnai-450) and transmission electron microscopy (TEM, Talos F200X). The specific surface area and pore size distribution were determined by nitrogen adsorption-desorption measurements (ASAP 2020, Micromeritics) using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. The elemental composition and chemical states were analyzed by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher).

Electrochemical Measurements

The working electrode was prepared by mixing the active material, conductive carbon, and sodium carboxymethyl cellulose (CMC) binder in a mass ratio of 7:2:1 with an appropriate amount of deionized water. The slurry was ground in a mortar and uniformly coated onto copper foil, followed by vacuum drying at [temperature]. CR2032 coin cells were assembled in an argon-filled glove box using metallic sodium as the counter electrode, Whatman glass fiber as the separator, and 1 mol/L $NaClO_4$ in EC/DEC as the electrolyte. Galvanostatic charge-discharge tests were conducted on a Land battery testing system within a voltage window of 0.01–3.0 V (vs. Na^+/Na). Cyclic voltammetry (CV) was performed on a CHI660E electrochemical workstation at a scan rate of 0.1 mV/s.

Results and Discussion

Structural and Morphological Characterization

The XRD pattern of the prepared Ni0.75Zn0.25Fe2O4 hollow nanospheres is shown in [FIGURE:N]. All diffraction peaks at 18.4°, 30.1°, 35.5°, 37.2°, 43.2°, 53.3°, 57.2°, and 62.8° can be indexed to the (111), (220), (311), (222), (400), (422), (511), and (440) crystal planes of spinel Ni0.75Zn0.25Fe2O4 (JCPDS No. 52-0277), respectively. The absence of any impurity peaks confirms the high phase purity of the product.

Scanning electron microscopy images reveal that the Ni0.75Zn0.25Fe2O4 sample consists of uniform spherical particles with an average diameter of approximately [value] nm [FIGURE:N]. The nanospheres exhibit excellent dispersibility without apparent aggregation, which is crucial for maintaining stable electrochemical performance. Transmission electron microscopy analysis further confirms the hollow interior structure of the nanospheres [FIGURE:N]. This hollow architecture increases the electrode-electrolyte contact area and provides ample space to accommodate volume changes during sodiation/desodiation, thereby enhancing cycling stability.

Nitrogen adsorption-desorption isotherms display typical type-IV characteristics with a distinct hysteresis loop, confirming the presence of mesopores [FIGURE:N]. The BET specific surface area is calculated to be [value] m^2/g, and the average pore size is [value] nm according to the BJH method. The high specific surface area provides more active sites for electrochemical reactions and facilitates ion transport, contributing to the superior performance.

X-ray photoelectron spectroscopy was employed to determine the surface elemental composition and oxidation states. The Fe 2p spectrum exhibits two prominent peaks at 710.8 eV and 724.9 eV, corresponding to Fe $2p_3/_2$ and Fe $2p_1/_2$, respectively, which are characteristic of Fe^{3+}. Satellite peaks appear at 719.5 eV. The Ni 2p spectrum shows binding energies at 856.2 eV and 872.8 eV for Ni $2p_3/_2$ and Ni $2p_1/_2$, with satellite peaks at 862.3 eV and 876.7 eV, consistent with Ni^{2+}. The Zn 2p spectrum displays peaks at 1021.4 eV and 1044.7 eV, confirming Zn^{2+}. The O 1s spectrum reveals two components: a peak at 529.8 eV attributed to metal-oxygen bonds and another at 531.5 eV corresponding to lattice oxygen.

Electrochemical Performance

The cyclic voltammetry curves of the Ni0.75Zn0.25Fe2O4 hollow nanosphere electrode at a scan rate of 0.1 mV/s in the voltage range of 0.01–3.0 V are presented in [FIGURE:N]. In the first cathodic scan, a pronounced reduction peak appears at approximately [voltage] V, corresponding to the reduction of Ni^{2+}, Zn^{2+}, and Fe^{3+} to metallic Ni, Zn, and Fe, respectively, along with the formation of a solid electrolyte interphase (SEI) layer. This peak shifts to a higher potential in subsequent cycles, indicating an irreversible phase transformation

during the initial sodiation process. In the anodic scan, strong oxidation peaks observed at [voltage] V are attributed to the oxidation of Zn, Ni, and Fe to ZnO, NiO, and Fe_2O_3, respectively. The nearly overlapping CV curves from the second cycle onward demonstrate excellent reversibility and structural stability of the electrode.

The overall sodiation/desodiation mechanism can be expressed by the following equations:

$$Ni_{0.75}Zn_{0.25}Fe_2O_4 + 8Na^+ + 8e^- \rightarrow 0.75Ni + 0.25Zn + 2Fe + 4Na_2O \quad (1)$$

$$0.25Zn + Na_2O \leftrightarrow 0.25ZnO + 2Na^+ + 2e^- \quad (2)$$

$$2Fe + 3Na_2O \leftrightarrow Fe_2O_3 + 6Na^+ + 6e^- \quad (3)$$

Galvanostatic charge-discharge curves at a current density of [value] mA/g are shown in [FIGURE:N]. The initial discharge and charge capacities are 341.1 and 176.2 mA·h/g, respectively, yielding a Coulombic efficiency of 51.7%. The irreversible capacity loss in the first cycle is primarily attributed to electrolyte decomposition and SEI film formation. In the second cycle, the discharge and charge capacities are 194.8 and 173.2 mA·h/g, respectively, with the Coulombic efficiency increasing to 88.9%. From the third cycle onward, the Coulombic efficiency remains near 100%, indicating excellent reversibility.

The cycling performance of the Ni0.75Zn0.25Fe2O4 hollow nanosphere electrode is presented in [FIGURE:N]. At a current density of [value] mA/g, the electrode delivers a discharge capacity of [value] mA·h/g after [number] cycles, corresponding to a capacity retention of 91.6% relative to the second cycle. Even at a higher current density of [value] mA/g, the electrode maintains [value] mA·h/g after [number] cycles with 89.3% capacity retention. These results surpass previously reported values for similar materials, demonstrating the superior cycling stability of the hollow nanosphere architecture.

Rate capability tests further highlight the advantages of the hollow structure. As shown in [FIGURE:N], the electrode achieves average discharge capacities of 212.7, 191.4, 148, and 121.8 mA·h/g at current densities of 100, 200, 500, and 1000 mA/g, respectively. When the current density is reduced back to [value] mA/g, the discharge capacity recovers to [value] mA·h/g, confirming the robustness of the electrode structure under varying operating conditions. This rate performance compares favorably with literature reports [9-10,14].

Conclusion

In summary, hollow Ni0.75Zn0.25Fe2O4 nanospheres with good dispersibility have been successfully synthesized via a facile hydrothermal method. When evaluated as an anode material for sodium-ion batteries, the material exhibits excel-

lent electrochemical performance, including high specific capacity, outstanding cycling stability (91.6% and 89.3% retention under different conditions), and superior rate capability. The enhanced performance is primarily attributed to the unique hollow nanostructure, which provides a high specific surface area, shortens electron and ion diffusion pathways, accommodates volume expansion during cycling, and improves electrode-electrolyte contact. This simple synthesis strategy offers a promising approach for designing other unary or multinary transition metal oxide nanostructures for advanced energy storage applications beyond batteries, including supercapacitors and other electrochemical devices.

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