**Zn substitution NiFe₂O₄ nanoparticles with enhanced conductivity as high-performances electrodes for
lithium ion batteries**

Junwei Mao^{a,b}, Xianhua Hou^{a,b*}, Fengsi Huang^{a,b}, Kaixiang Shen^{a,b}, Kwok-ho Lam^c, Qiang Ru^{a,b}, Shejun Hu^{a,b*}

^a*Guang dong Engineering Technology Research Center of Efficient Green Energy and Environmental Protection
Materials, Guangzhou 510006, China;*

^b*Guang dong Provincial Key Laboratory of Quantum Engineering and Quantum Materials, School of Physics
and Telecommunication Engineering, South China Normal University, Guangzhou 510006, China*

^c*Department of Electrical Engineering, The Hong Kong Polytechnic University, Hunghom, Kowloon, 999077,
Hong Kong;*

Abstract

Zn²⁺ ion substituted nickel ferrite nanomaterials with the chemical formula Ni_{1-x}Zn_xFe₂O₄ for x = 0, 0.3, 0.5, 0.7 and 1 have been synthesized by a facile green-chemical hydrothermal method as anode materials in lithium ion battery. The morphology and structure of the samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The physical and electrochemical properties were tested by electrochemical system. Furthermore, the energetic and electronic properties of the samples were investigated by density functional calculations. The results suggest that Zn substitution can affect the conduction performance of the zinc - nickel ferrite. Meanwhile, electrochemical results show that an enhancement in the capacity with increasing Zn concentration is observed especially for x = 0.3 which exhibit high discharge capacity of 1416 mAh g⁻¹ at the end of 100th cycle. Moreover, the theoretical research method with high yield synthesis strategy described in the present work holds promise for the general fabrication of other metallic elements substitution in complex transition metal oxides for high power LIBs.

*Corresponding author, Tel: +862039318011, e-mail addresses: houxh@scnu.edu.cn (X. H.Hou), hsj@scnu.edu.cn (S. J.Hu)

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1. Introduction

Rechargeable Lithium ion batteries (LIBs) as one of the most attractive electrochemical energy storage devices have been extensively used as portable electronic devices, electric vehicles (EVs) and hybrid electric vehicles (HEVs) due to their high energy density, low self-discharge rate, long cycling lifetime, environmental friendliness and excellent safety [1-5]. Carbon materials like graphite, which popularly used as commercial anode materials for lithium-ion batteries over the past decades. However, the low reversible capacity of 372 mA h g^{-1} has reached its theoretical limit which cannot meet the high energy density and safety requirements for high-end applications including electric vehicles (EVs) [6-8]. In order to meet the increasing demand for Li ion batteries with higher energy densities, further research is vital to develop novel anode materials with high charge-discharge capacity and good cycling stability.

Recently, oxides with spinel structure (AB_2O_4 , A = Fe, Mn, Co, Cu or Ni; B = Co, Fe, Mn, Ni or Cu; A $\neq$ B) [9] have been extensively investigated as promising alternative anode materials for LIBs. Reddy et al. [10] synthesized nano/submicron size CuCo_2O_4 composite using MSM at 510°C showing a high and stable capacity of ~ 680 (quenched) and 740 (slow cooling) mAh g^{-1} at the end of the 40th cycle. Spinel MCo_2O_4 (M = Mg, Mn) materials were synthesized by Reddy et al. [11] demonstrated the feasibility and versatility of producing MnCo_2O_4 for use as an anodic material for lithium-ion batteries at a low cost via the MSM method. Cherian et al. [12] reported NiFe_2O_4 Nanofibers as high capacity anode material by by an electrospinning approach a facile solvothermal method shown excellent electrochemical performance. Teh et al. [13] investigated the electrochemical impact of systematic replacement of Zn by Mn resulting in $\text{Zn}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ nanofibers and the $\text{Zn}_{0.3}\text{Mn}_{0.7}\text{Fe}_2\text{O}_4$ demonstrates the highest capacity of 612 mA h g^{-1} at 50th cycle among the solid solution series. AB_2O_4 can overcome some of the drawbacks of graphite due to owing to their relatively high conductivity and

high reversible capacities [14-18].

Although the numerous varieties of oxides with spinel structure previously prepared by sol-gel and molten methods [10, 16, 19-20] but Fe-based oxides have some advantages over like lower voltage hysteresis when compared to other conversion oxides [9, 20]. Among the numerous varieties of Fe-based oxides, NiFe_2O_4 with an inverse spinel structure where the Ni^{2+} cations occupy octahedral site and Fe^{3+} ions distributed equally among octahedral and tetrahedral site, has become one of the most promising candidates as they displayed a much higher capacity (914 mA h g^{-1}) [21-24]. However, the vital limiting NiFe_2O_4 practical application is that they suffer from many problems, for instance, low conductivity and the large volume change during cycling process. To address these problems, many strategies including synthesis of NiFe_2O_4 - carbon hybrid composites [25-27], fabrication of NiFe_2O_4 with novel architectures [24, 28-29] and combined NiFe_2O_4 with metal oxides [30-32] have been developed. Recently, Cherian et al. [33] reported the Li-cycling properties of nano-crystalline $(\text{Ni}_{1-x}\text{Zn}_x)\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1$). It suggests that the Zn substitution can affect the electrochemical performance of zinc - nickel ferrite. However, few combined theoretical investigations and experimental have been implement to study the effect of Zn substitution on the physical and electrochemical properties of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$.

In this study, we further investigate the electrochemical impact of systematic replacement of Ni by Zn resulting in $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.3, 0.5, 0.7$ and 1) nanoparticles synthesized one-step hydrothermal method. In addition, first principle calculations are used to investigate the effect of Zn substitution on the structural and electronic properties of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, and gave a mechanism interpretation about how Zn substitution would enhance the electrochemical properties of zinc - nickel ferrite materials. It is proved theoretically that with Zn substitution, the electronic and ionic conductivity of zinc - nickel ferrite can be enhanced which will improve its electrochemical performance. Electrochemical results show that electrochemical performance will be enhanced with Zn substitution. Meanwhile, the as-synthesized $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.3$) nanoparticles show a high capacity

of 1430 mA h g⁻¹ at a current density of 100 mA g⁻¹ after 100 cycles.

2. EXPERIMENTAL SLECTION

2.1 Preparation of Materials

Nanocrystalline $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0, 0.3, 0.5, 0.7, 1$) ferrites were synthesized by a facile hydrothermal method followed by sintering. All chemicals (Sigma Aldrich) in this experiment were of commercially available analytical grade and were used without further purification, namely Nickelous sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), ethylene glycol, carbamide, Ammonium bicarbonate and deionized water. In a typical synthesis process, appropriate amount of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was replaced by $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ to mix with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in a mixture solution containing ethylene glycol (EG, 50 mL) and deionized water (10 mL) to form homogeneous suspension. Then carbamide (0.6 g) and Ammonium bicarbonate (2.7 g) were added to the homogeneous slurry with continuous stirring for 1 h and then were sealed in the teflon lined stainlesssteel autoclaves, respectively. The autoclaves were heated to 180°C and maintained at this temperature for 24 h, then cooled to room temperature to form precursor solution. To remove the impurity, firstly the precursor solution collected by centrifugation and washed with ethanol and deionized water for several times, then was dried at 60 °C in an oven for 6 hours. On the basis of the stoichiometric ratio, the samples were labeled as NFO ($x = 0$), $\text{N}_7\text{Z}_3\text{FO}$ ($x = 0.3$), $\text{N}_5\text{Z}_5\text{FO}$ ($x = 0.5$), $\text{N}_3\text{Z}_7\text{FO}$ ($x = 0.7$), and ZFO ($x = 1$) accordingly. In order to obtain the NFO, $\text{N}_7\text{Z}_3\text{FO}$, $\text{N}_5\text{Z}_5\text{FO}$, $\text{N}_3\text{Z}_7\text{FO}$ and ZFO nanostructures microspheres and promote the oxide crystallization, the as-synthesized powders were then annealed at 450 °C for 6 h in air with a heating rate of 2 °C min⁻¹.

2.2 Structure characterization and Computational methods

The crystallographic structures of the materials were determined by a powder X-ray diffraction system (XRD, PANalytical X'pert PRO, Cu/K α radiation, $\lambda=1.5406$ nm) with Cu/K radiation ($\lambda=1.5406$ nm). The

morphologies and microstructure of samples were investigated by scanning electron microscope (SEM, ZEISSULTRA55) **transmission** electron microscope (TEM, JEM-2100) and **Micro-Raman spectroscopy (Jobin Yvon LabRam HR800)**. All calculations on $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0, 0.3, 0.5, 0.7, 1$) were carried out using the density functional theory (DFT) and pseudopotential methods, which were implemented in the first principles calculation program Cambridge Serial Total Energy Package (CASTEP) code. The generalized gradient approximation (GGA) within the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional is employed to describe the exchange and correlation potentials. Convergence testing was performed by the $5 \times 5 \times 5$ k-point mesh and 1×10^{-5} eV/atom for total energy tolerance. An energy cutoff of 340 eV was used with Monkhorst k-points sampling scheme. The atomic positions and cell parameters are fully relaxed to obtain the total energy and optimized cell structure [34-36].

2.4 Electrode Fabrication

The electrochemical experiments of the as-prepared materials were performed with coin cell (CR2530) using lithium foil as counter and reference electrode. The working electrodes were fabricated using slurry of the synthesized compounds $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.3, 0.5, 0.7$ and 1), and super-P and PVDF at a weight ratio of 8: 1: 1. The slurry was then coated onto a Cu foil. After drying in an oven at 80°C for 12 h, **the electrode was punched into a disk with a diameter of 18 mm and the active material per electrode is about 0.2 mg cm^{-2}** . The cell was assembled in an argon glovebox, using 1 mol L^{-1} LiPF_6 (EC: DEC=1:1 in volume, provide by Chei Industries Inc., South Korea) as electrolyte, and a Celgard-2400 membrane as a separator. The lithium storage properties of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoparticles were examined by galvanostatic cycling and cyclic voltammetry measurements. Galvanostatic charge–discharge tests were carried out on a LANDCT2001A battery testing system between 0.01 and 3.00 V at 25°C . Electrochemical impedance spectroscopy (EIS) measurements were studied on an electrochemical workstation (CHI660B) with amplitude of 5 mV in a frequency range between 1 MHz and 0.01

Hz. Fitting of the impedance spectra to the equivalent circuit was carried out by the code Zview.

3. RESULTS AND DISCUSSION

3.1 Structural and morphological characterization

The structural information of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ obtained after the sintering process were first examined by XRD analysis shown in Fig. 1. During the hydrothermal process, the main metal glycolates or alkoxide

molecular resulting from acid–base equilibrium reactions are believed to form as follows: [37-39]

XRD patterns of the precursors further demonstrate the above reaction equation. As shown in Fig. 1(a), the crystalline of the precursors of the as-prepared hydrothermal samples which are similar to the XRD patterns of Zn-EG, Zn–Fe-EG, Ni-EG, Ni–Fe-EG and Fe-EG [39-42].

As shown in Fig. 1(b), the diffraction peak of ZFO consistent with cubic ZnFe_2O_4 with good agreement with JCPDS: 22-1012 without obvious impurity. The peaks centered at $2\theta = 29.9^\circ, 35.26^\circ, 42.84^\circ, 53.11^\circ, 56.63^\circ$ and 62.1° correspond to (220), (311), (222), (400), (422), (511) and (440) planes, respectively, resembling XRD patterns are also observed in $\text{N}_7\text{Z}_3\text{FO}$, $\text{N}_5\text{Z}_5\text{FO}$, $\text{N}_3\text{Z}_7\text{FO}$ and NFO. With the increasing content of Zn in the $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ sample, the diffraction peaks at (311) plane gradually moving to the low angle within a narrow range. This difference may be attributing to the cations distributing in nickel–zinc (Ni–Zn) ferrite [43]. Cation distribution is the cations distributing at tetrahedral [A] and octahedral [B] sites. As shown in Fig.1 (c), Ni^{2+} ions

occupy octahedral sites and Fe^{3+} ions equally distribute between octahedral and tetrahedral sites in NiFe_2O_4 primitive cell while in ZnFe_2O_4 primitive cell, Zn^{2+} ions occupy tetrahedral sites and Fe^{3+} occupy octahedral sites. It can be seen, with the Zn substitute with Ni, the Zn^{2+} ions preferentially occupies A site and force the Fe^{3+} ions to transfer to B site in the model. The cations distributing in nickel–zinc (Ni–Zn) ferrite can be represented by $\text{Zn}_x^{2+} \text{Fe}_{1-x}^{3+} [\text{Ni}_{1-x}^{2+} \text{Fe}_{1+x}^{3+}] \text{O}_4^{2-}$ [44-46].

The lattice parameter (a) values was computed using the spacing between two lattice plane ' $d_{(hkl)}$ ' and with their respective (h k l) parameters. The X-ray density ($d_{(hkl)}$) of the material can be calculated as

$$d_{(hkl)} = \frac{8M}{Na^3}$$

where, 'M' is the atomic weight of the sample, 'N' is Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$) and a is the lattice parameter values [47]. The values of lattice parameter 'a' determined from the XRD data listed in Table 1. The lattice parameter, $a = 8.4432 \text{ \AA}$, calculated for ZnFe_2O_4 is close to the reported values (JCPDS: 22-1012). Table 1 indicates that the lattice constant increases with the increasing substitution of Zn^{2+} ions because of the slightly smaller size of Ni^{2+} ions compared with Zn^{2+} ions.

Raman spectra of all the compositions recorded at room temperature are shown in Fig.1(d). Normal spinel structure ZnFe_2O_4 permits five active Raman modes ($A_{1g} + E_g + 3T_{2g}$) [48, 49]. Usually, wave numbers above 600 cm^{-1} mostly corresponds to the motion of oxygen in tetrahedral AO_4 groups that are of the A_{1g} type, while the low frequency phonon modes are related to metal ion involved in octahedral sites (BO_6) [50, 51]. The band at $\sim 650 \text{ cm}^{-1}$ for ZnFe_2O_4 corresponds to motion of oxygen in the ZnO_4 tetrahedral. Previous papers also offer the same explanation [48- 53]. Upon with Ni^{2+} substitution the high frequency band ranges from ~ 630 to ~ 670 due to the change in the environment of the tetrahedral. Similarly, the low frequency ranges from ~ 338 to ~ 364 due to the change in the environment of the octahedral [48].

To further investigate the effect of replacement of Ni by Zn on electro-chemical performance of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, we used the density functional theory to calculate and analyze the electronic properties and structure of $\text{Zn}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$. In order to analyze the electronic properties and structure of the $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, the calculated energy band structures, lattice parameter and free energy of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ are shown in Fig.2. It can be seen from Fig.2 (a)-(e) that Zn^{2+} substitution can affect band gap of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$. The bands near the Fermi level shifts to the high energy (relative to the Fermi level) by increasing Zn content. With increasing of the Zn content, the electronic conductivity of could be enhanced especially for $x=0.3$. Meanwhile, as shown in Fig.2 (f), the proper cell volume and free energy of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoparticles suggests that it has good structure stability for the charge/discharge reaction, and consequently has better cycle performance which is proved in the following experiment. Consequently, the narrower band gap with proper cell volume and free energy for $x=0.3$ indicates that the electronic conductivity of nickel–zinc (Ni–Zn) ferrite could be enhanced by Zn substitution thereby possibly impacting its electrochemical performance. Following electrochemical results also indicates that the electrode ($x=0.3$) delivers higher discharge capacity of approximately 808 mAh g^{-1} even at a high rate of 3.2 A g^{-1} .

It is generally known that the electrochemical performance and mechanism of lithium storage strongly relate to the morphology and microstructure of the anode materials as it must be able to allow Li-ions insertion/extraction easily so as to have a more efficient charge/discharge process, thus reducing capacity fading. The morphologies and microstructures of the as-prepared materials were characterized by SEM shown in Fig.3. All the Ni–Zn ferrite compounds have fairly similar microspheres with an average diameter range of 2–4 μm except for NFO sample which is agglomerated with small particles. In addition, the particle size, particles agglomeration and particle distribution are relatively changed after Zn substitution. It suggests that the Zn substitution can affect particles morphology. This may be dependent on their site preference energy and the

different ionic radius and valence states of the metal ions [54]. Compared with all the anode materials, the N_3Z_3FO sample (shown in Fig. 3(b)) consists of more uniform and regular spheres range of 2-3 μ m and these uniform spheres are accumulation of a large number of nanoparticles which could contribute to enhance its electrochemical performance. On account of aggregated primary nanoparticles, with as pherical or flaky morphology, may generate secondary particles with a macroporous structure [54]. These structures are found to exhibit high and stable reversible capacities over a long period of cycling. Overall, all samples except for NFO anodes consist of small particles which gathered into a sphere with plenty of voids and no agglomeration that may be favorable for lithium-ion kinetics.

The TEM images, HRTEM images, EDS spectrum of N_3Z_7FO nanoparticles are shown in Fig. 4. Fig. 4(a) further confirm N_3Z_7FO (Fig. 4a) consists of microspheres with an average diameter range of 2–3 μ m. And the result is similar to the above SEM observation. From the HRTEM images (Fig. 4(b)), the N_3Z_7FO nanoparticles are single crystalline, as indicated by the well-resolved lattice fringes. And the lattice spacing is 0.255 nm, which is corresponded to the interplanar distance of the (311) plan of the $ZnFe_2O_4$ cubic structure. The crystal structural of N_3Z_7FO products was further determined according to the selected area electron diffraction (SAED) pattern shown in the insert pictures of Fig. 4(b), indicating a polycrystalline nature for the N_3Z_7FO sample, and all the diffraction rings can be indexed as (111), (220), (311), (400), (511) and (440) from the inside out, respectively. Additionally, in order to quantify the atomic ratio of Ni and Zn, the as-prepared N_3Z_7FO sample was further analyzed by EDS. As shown in Fig. 4(d), the elements of Zn, Ni, Fe, O can be seen clearly and the atomic ratios of Zn, Ni exhibited in the EDS patterns are close to the presumed stoichiometric ratios indicating the N_3Z_7FO sample was successfully synthesized.

The specific surface area of the various compositions samples are also given in Table 1. The specific surface area was determined according to the BrunauereEmmetteTeller (BET) method in the relative pressure range of 0.05-0.2. The specific surface areas of the samples are in the range

$\sim 16\text{--}18\text{ m}^2\text{ g}^{-1}$, which suggests with the increasing substitution of Zn^{2+} ions does not have much influence on the surface area because the samples are prepared at identical temperatures [48].

3.2 Electrochemical analysis

To understand the influence of Zn substitution in spinel structure on battery performance, galvanostatic cycling of all materials at a current density of 100 mA g^{-1} in the voltage window of $0.01\text{--}3.00\text{ V}$ were recorded. Fig.5 (a) shows the first charge and discharge cycles of these electrodes. For the $\text{N}_7\text{Z}_3\text{FO}$ composite, the initial discharge and charge capacities are 1579.6 and 1940.8 mAh g^{-1} , respectively, with an initial columbic efficiency of 81.4% . The first cycle irreversible capacity loss of 28.6% could be contributed from the solid electrolyte interphase (SEI) formation on the surface of the electrode due to electrolyte decomposition and the reduction of metal oxide to metal with Li_2O formation. Compared with the $\text{N}_7\text{Z}_3\text{FO}$ composite, the first discharge and charge capacities reach 1225.8 and $1591.5\text{ mA h g}^{-1}$ for ZFO, 1114.2 and $1523.1\text{ mA h g}^{-1}$ for NFO, 1279.8 and $1611.8\text{ mA h g}^{-1}$ for $\text{N}_5\text{Z}_5\text{FO}$ and 1157.4 and $1537.2\text{ mA h g}^{-1}$ for $\text{N}_3\text{Z}_7\text{FO}$ respectively. In conclusion, the initial specific capacity of the as-prepared $\text{N}_7\text{Z}_3\text{FO}$ electrodes present a higher value compared with other electrodes owing to the complementarities and synergies among different metallic elements in the Li discharge-charge process, which means that $\text{N}_7\text{Z}_3\text{FO}$ electrodes possess a much better electronic conductivity and higher electrochemical activity, which also consist with the result of the above theoretical calculations. The first charge cycle has a slope between 1.5 and 2.0 V spanning capacity of about 600mAh g^{-1} shown in Fig.5 (a). During these charging cycles, the reverse electrochemical reaction takes place. On the basis of pervious literatures [55-57], the proposed reaction mechanism of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ can be listed as follows:

By using formula $C = \frac{x \times F}{\varepsilon \times M}$ (where the C is theoretical capacity, x is the number of the lithium ions, F is the Faraday constant, ε is the geometry structural coefficient of materials, and M is the relative molecular weight of the anode material) [58], the theoretical capacity of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ materials can be list as:

$$C = \frac{x \times F}{\varepsilon \times M} \approx \frac{(8+x) \times 96485}{3.6 \times [59(1-x) + 65x + 176]} = \frac{(8+x) \times 16801}{6x + 235}$$

So the theoretical capacity will increase as the value of x increased. Actually, lithium ions diffusion in anode materials influenced by many aspects which will led to the difference of the experimental values and theoretical values. Following electrochemical results confirm this point.

Cycling performance is shown in Fig.5 (b) after 100 cycle lithiation/dislithiation at a current density of 100 mA g^{-1} . It can be observed that the capacities of all the materials decreased slowly for the first few cycles and eventually reached a stable capacity up to 100 cycles. Reversible capacity is one of the key factors for electing anode material in LIBs, so increasing composition of Zn in $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanofibers has shown success in effectively enhancing the reversible capacity in the anodes. After 100 cycles, $\text{N}_7\text{Z}_3\text{FO}$ demonstrates the highest reversible capacity of $\sim 1416.4 \text{ mA h g}^{-1}$ as compared to $\text{N}_5\text{Z}_5\text{FO}$ with capacity of $\sim 854.4 \text{ mA h g}^{-1}$, $\text{N}_3\text{Z}_7\text{FO}$ with capacity of $\sim 1294.8 \text{ mA h g}^{-1}$, ZFO with capacity of $\sim 1011.5 \text{ mA h g}^{-1}$ and NFO with capacity of $\sim 826.3 \text{ mA h g}^{-1}$. These results prove that the appropriate doping of element Zn in the NFO electrodes substantially enhance the capacity and cycling properties of the electrodes.

Besides the good specific capacity and excellent cyclability, the rate capability is also crucial for Lithium ion batteries. Different charge rates from 0.1 to 3.2 A g^{-1} current densities are applied to investigate the high-rate capability of the Ni–Zn ferrite samples. As shown in Fig.5 (c) that substituting the Ni with Zn in the inverse spinel anodes enhances the rate capability of NFO. Especially in high rate of 3.2 A g^{-1} , the $\text{N}_7\text{Z}_3\text{FO}$ electrode reveals the best rate capability with a charge capacity of 808 mA h g^{-1} among all the samples which is much

higher than the theoretical capacity of graphite electrode (372 mAh g⁻¹), suggesting the better rate capacity of the electrode. What is more, a stable high specific capacity of 1206 mA h g⁻¹ of N₇Z₃FO electrode can be obtained when the current density returns to the 0.1 A g⁻¹. This shows that the as prepared N₇Z₃FO material is of good retention capability and good rate performance. Therefore, it can be concluded that the controllable doping of Zn content can conduce to a better rate performance.

In order to validate the influence of Zn substitution on the electronic conductivity of zinc - nickel ferrite anodes, an electrochemical impedance spectroscopy (EIS) was utilized. Typical Nyquist plots of (Ni_{1-x}Zn_x)Fe₂O₄ (x = 0, 0.3, 0.5, 0.7, 1) at select discharge-charge voltage (1.5 V vs. Li) at the current rate of 100mA/g during the 20th discharge-charge cycle are shown in Figure 6 (a-c). Each plot consists of a semicircle in the high medium frequency range and an inclined line in the low frequency region. The semicircles in high and middle frequency are relative to the SEI resistance (R_f), charge transfer resistance (R_{ct}) [59, 60]. The inclined line is assigned to the Warburg impedance data are fitted to the equivalent circuit shown in Fig. 6 inset. The diffusion coefficient values of the Li⁺ ion diffusion into the bulk electrode and the exchange current density I₀ could be calculated by the following equation [60]:

$$D_{Li} = 0.5 \left(\frac{RT}{AF^2 \sigma_w C} \right)^2$$

$$I_0 = \frac{RT}{nFR_{ct}}$$

Herein, R is the gas constant, A is the surface area of the electrode, T is the absolute temperature, C is the concentration of lithium ions, F is the Faraday constant, σ_w is the Warburg impedance coefficient and n is the number of transferred electrons, respectively. The fitting results are given in Table 2. During cycling, all compounds showed a surface film and charge transfer resistance values which are on the order of 50–320 ohm. The observed D_{Li} value was found to be in the range of 1.96 E-15 – 6.23 E-15 cm² s⁻¹ and these values are close to

previous reported [20]. The R_f and R_{ct} values were found to increase with the discharge voltage during discharge cycle. However, R_c decreased during discharge cycle. Contrary phenomenon has taken place in the charge voltage. EIS studies shows that impedance values are dependent on the cell voltage [61-63].

4. Conclusions

In summary, nanocrystalline $Ni_{1-x}Zn_xFe_2O_4$ ($x = 0, 0.1, 0.3, 0.5, 0.7, 1$) have been successfully synthesized by a facile hydrothermal method. Theoretical studies reveal that with Zn^{+} substitution in zinc - nickel ferrite, the electronic and ionic conductivity of the materials can be changed thus influencing the electrochemical performance of zinc - nickel ferrite. Meanwhile, theoretical analysis shows N_7Z_3FO nanoparticles owning proper cell volume and free energy which will contribute its lithium intercalation capacity. Further electrochemical evaluation also suggests that the N_7Z_3FO electrode compared with the other samples showed the high irreversible specific capacity of $1612.7 \text{ mA h g}^{-1}$ after 50 cycles at a current density of 100 mA g^{-1} . What is more, a stable high specific capacity of 808 mA h g^{-1} of N_7Z_3FO electrode can be obtained in high rate of 3.2 A g^{-1} . This article not only demonstrates the metallic elements substitution methods could change the morphologies, conductivity and electrochemical performance of complex transition metal oxides with spinel cubic structure, but also reveals the appropriate substitution content of metallic element is very critical of the performance for lithium-ion battery.

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Figure captions and table captions

Fig. 1 (a) XRD patterns of the precursors of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ (a) $x = 1$, (b) $x = 0.7$, (c) $x = 0.5$, (d) $x = 0.3$, (e) $x = 0$, (b) XRD patterns of the $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples, (c) Cations distributing in nickel–zinc (Ni–Zn) ferrite, (d) Raman spectra of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ (a) $x = 0.3$, (b) $x = 0.7$, (c) $x = 1$, (d) $x = 0.5$, (e) $x = 0$.

Fig. 2 Band structures of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ (a) $x = 0$, (b) $x = 0.3$, (c) $x = 0.5$, (d) $x = 0.7$, (e) $x = 1$; (f) Free energy and cell volume of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.3, 0.5, 0.7$ and 1)

Fig.3 SEM images of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanocomposites (a) $x = 0$, (b) $x = 0.3$, (c) $x = 0.5$, (d) $x = 0.7$, (e) $x = 1$

Fig. 4 (a) TEM images, (b) HRTEM images and (c) EDS spectrum of the $\text{N}_3\text{Z}_7\text{FO}$ nanoparticles

Fig.5 (a) First galvanostatic cycle plots of the $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ electrode at the specific current of 100 mA g^{-1} , (b) Cycle performance of the $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ electrode at the specific current of 100 mA g^{-1} , (d) Rate capability of the $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ electrodes at current of 0.1 A g^{-1} to 3.2 A g^{-1} .

Fig.6 Electrochemical impedance spectra of the $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ electrodes (a) at open circuit voltage, (b) discharged state (1.5 V vs. Li) at 20th discharge–charge cycles, (c) charged state (1.5 V vs. Li) at 20th discharge–charge cycles; The insert shows Equivalent circuit for fitting experimental EIS data.

Table 1 Lattice Parameter and Surface Area of Various Compositions.

Table 2 Electrode kinetic parameters obtained from equivalent circuit fitting of experimental data for $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0, 0.3, 0.5, 0.7, 1$).

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Table 1

Zn content	lattice parameter a (Å)	specific surface area (m ² g ⁻¹)
0	8.4191	16.5
0.3	8.4178	17.2
0.5	8.4266	16.8
0.7	8.4381	18.1
1	8.4432	17.4

Table 2

Zn content	Cell voltage, V	$R_e (\Omega)$	$R_f (\Omega)$	$R_{ct} (\Omega)$	$i_0 (\text{mA cm}^{-2})$	$D_{Li} (\text{cm}^2 \text{s}^{-1})$
0	2.5 (OCV)	9.24	37.72	58.95	1.65	1.96E-15
	1.5(discharge)	8.15	38.21	59.23	2.14	3.21 E-15
	1.5(charge)	9.75	34.28	45.23	1.75	2.18 E-15
0.3	3.0 (OCV)	10.24	20.53	77.05	3.84	2.55E-15
	1.5(discharge)	9.84	25.36	84.05	2.97	3.17 E-15
	1.5(charge)	11.57	20.17	69.26	3.41	2.24 E-15
0.5	2.8 (OCV)	9.12	27.63	65.75	2.37	1.21E-15
	1.5(discharge)	6.05	30.62	72.41	2.11	3.24 E-15
	1.5(charge)	8.10	21.54	55.32	3.24	1.18 E-15
0.7	3.0 (OCV)	8.36	35.81	49.59	4.62	6.23E-15
	1.5(discharge)	7.14	40.35	54.13	5.32	3.15 E-15
	1.5(charge)	9.26	32.6	48.91	1.21	2.72 E-15
1	2.6 (OCV)	9.81	38.42	62.19	2.19	3.41E-15
	1.5(discharge)	6.21	38.71	78.93	4.28	3.86 E-15
	1.5(charge)	10.24	30.17	50.12	2.28	4.75 E-15