High-Tap-Density Fe-Doped Nickel Hydroxide with Enhanced Lithium Storage Performance

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ABSTRACT: Nickel hydroxide has attracted much attention as an anode material for lithium-ion batteries (LIBs) due to its high specific capacity, low cost, and easy preparation. However, the poor cycling stability greatly hampers its application. Herein, Fe-doped nickel hydroxide powders with a high tap density (2.16 g cm$^{-3}$) are synthesized by a simple chemical co-precipitation method. Compared to undoped nickel hydroxide, this Fe-doped nickel hydroxide exhibits better lithium storage activity, enhanced cycling stability and rate capability, and improved electrochemical reaction kinetics. As an anode material for LIBs, the Fe-doped nickel hydroxide delivers a specific discharge capacity of 1080 mA h g$^{-1}$ at 200 mA g$^{-1}$ after 30 cycles, which is almost twice that (519 mA h g$^{-1}$) of undoped nickel hydroxide; at a high current density of 2000 mA g$^{-1}$, Fe-doped nickel hydroxide shows a specific capacity of 661 mA h g$^{-1}$, significantly higher than that (182 mA h g$^{-1}$) of undoped nickel hydroxide. Kinetic analysis reveals that Fe doping decreases the electrochemical reaction resistance and improves the lithium ion diffusivity in a nickel hydroxide electrode.

1. INTRODUCTION

Development of lithium-ion batteries (LIBs) with high energy density, high rate capability, good safety, and long cycle life is urgently needed for future portable electronics, electric vehicles, and energy storage stations. To meet the ever-increasing demand of next-generation LIBs, it is very crucial to explore high-performance electrode active materials. The conventional carbon-based anode materials suffer from low theoretical capacity (≈372 mA h g$^{-1}$) and safety issues due to the problem of lithium deposition. In recent years, transition-metal oxides (such as Fe$_2$O$_3$, Co$_3$O$_4$, NiO, and ZnO) as anode materials for LIBs have attracted great attention because of their large theoretical capacity, low cost, environmental friendliness, good safety, and high natural abundance. Other than these transition-metal oxides, some transition-metal hydroxides, such as Ni(OH)$_2$ and Co(OH)$_2$, are also reported as novel anode materials for LIBs. Compared with transition-metal oxides, transition-metal hydroxides have the advantages of low preparation cost (without the need of high-temperature metal oxides, transition-metal hydroxides have the advantages of low preparation cost (without the need of high-temperature metal oxides), low-temperature synthesis, and low safety issues due to the problem of lithium deposition. In recent years, transition-metal oxides (such as Fe$_2$O$_3$, Co$_3$O$_4$, NiO, and ZnO) as anode materials for LIBs have attracted great attention because of their large theoretical capacity, low cost, environmental friendliness, good safety, and high natural abundance. Other than these transition-metal oxides, some transition-metal hydroxides, such as Ni(OH)$_2$ and Co(OH)$_2$, are also reported as novel anode materials for LIBs. As compared with transition-metal oxides, transition-metal hydroxides have the advantages of low preparation cost and low-temperature synthesis. However, the poor cycling stability greatly hampers its application. Herein, Fe-doped nickel hydroxide powders with a high tap density (2.16 g cm$^{-3}$) are synthesized by a simple chemical co-precipitation method. Compared to undoped nickel hydroxide, this Fe-doped nickel hydroxide exhibits better lithium storage activity, enhanced cycling stability and rate capability, and improved electrochemical reaction kinetics. As an anode material for LIBs, the Fe-doped nickel hydroxide delivers a specific discharge capacity of 1080 mA h g$^{-1}$ at 200 mA g$^{-1}$ after 30 cycles, which is almost twice that (519 mA h g$^{-1}$) of undoped nickel hydroxide; at a high current density of 2000 mA g$^{-1}$, Fe-doped nickel hydroxide shows a specific capacity of 661 mA h g$^{-1}$, significantly higher than that (182 mA h g$^{-1}$) of undoped nickel hydroxide. Kinetic analysis reveals that Fe doping decreases the electrochemical reaction resistance and improves the lithium ion diffusivity in a nickel hydroxide electrode.

2. RESULTS AND DISCUSSION

Figure 1a gives the XRD patterns of the Fe-doped nickel hydroxide and pure nickel hydroxide samples. For comparison, the standard XRD patterns of β-Ni(OH)$_2$ (JCPDS 14-117)
and α-Ni(OH)$_2$·0.75H$_2$O (JCPDS 38-715) are also shown at the bottom of Figure 1a. All the diffraction peaks of pure nickel hydroxide can be indexed to the standard spectrum of β-Ni(OH)$_2$ (JCPDS 14-117), suggesting the sample has a β-phase structure. The interlayer distance of this pure nickel hydroxide is calculated to be 4.62 Å. In contrast, the Fe-doped nickel hydroxide sample shows additional diffraction peaks from α-phase nickel hydroxide (JCPDS 38-715), revealing it has mixed α-/β-phase structures. The interlayer distance of the α-motifs in the Fe-doped nickel hydroxide sample is calculated to be 7.84 Å, much larger than that (4.56 Å) of the β-motifs. The larger interlayer space of α-motifs in the Fe-doped nickel hydroxide sample could facilitate the fast diffusion of the lithium ion and alleviate the volume changes of an electroactive material during lithiation/delithiation cycles, which are very important for improving the rate performance and cycling stability of an electrode.

Figure 1. (a) XRD patterns and (b) TGA plots of the as-prepared pure nickel hydroxide and Fe-doped nickel hydroxide samples.

Figure 2. SEM images of the as-prepared (a−c) pure nickel hydroxide and (d−f) Fe-doped nickel hydroxide samples.

respectively; the larger weight loss for Fe-doped nickel hydroxide can be ascribed to the existence of structural water in the α-motifs. These structural water molecules in the α-motifs could act as pillars to maintain the larger interlayer distance and on the other hand, contribute to shielding Li$^+$ from the lattice host, which is favorable to the fast diffusion of Li$^+$ in the electrode and accordingly enhances the rate capability. The second weight loss in the range of 200−310 °C is caused by the decomposition of nickel hydroxide to nickel oxide; the weight loss values in this interval for pure nickel hydroxide and Fe-doped nickel hydroxide are 16.3 and 16.2%, respectively. The third weight loss in the range of 310−450 °C results from the decomposition of adsorbed and/or intercalated anions (such as NO$_3^-$ and CO$_3^{2-}$). For the Fe-doped nickel hydroxide sample, the molar ratio of [Fe/Ni] coming from the EDS result is 15.8%, which is in accordance with the initial molar ratio of [Fe$^{3+}$/Ni$^{2+}$] in the reaction solution.

Figure 2 presents the SEM images of the pure nickel hydroxide and Fe-doped nickel hydroxide samples. Both samples show irregular-shaped microparticles (Figure 2a,d) with a rough surface (Figure 2b,e). By a detailed observation, one can find that microparticles are actually composed of the conglomeration of nanoplates (Figure 2c,f). By comparison,
Fe-doped nickel hydroxide has a much denser microstructure than pure nickel hydroxide. The tap density of Fe-doped nickel hydroxide is measured to be approximately 2.16 g cm$^{-3}$, much higher than that (1.25 g cm$^{-3}$) of pure nickel hydroxide, meaning that Fe-doped nickel hydroxide could provide higher volumetric energy density. Because the $K_{sp}$ value of Fe(OH)$_3$ ($2.8 \times 10^{-39}$) is far lower than that of Ni(OH)$_2$ ($5.5 \times 10^{-16}$), the deposition of Fe$^{3+}$ in the nickel hydroxide lattice will be more rapid than Ni$^{2+}$; thus, these initially formed Fe(OH)$_3$ colloidal particles would provide a net structure and help the agglomeration of colloidal nickel hydroxide particles. On the basis of this agglomeration, the Fe-doped nickel hydroxide has a much denser microstructure than pure nickel hydroxide. The tap density of Fe-doped nickel hydroxide is measured to be approximately 2.16 g cm$^{-3}$, much higher than that (1.25 g cm$^{-3}$) of pure nickel hydroxide, meaning that Fe-doped nickel hydroxide could provide higher volumetric energy density. Because the $K_{sp}$ value of Fe(OH)$_3$ ($2.8 \times 10^{-39}$) is far lower than that of Ni(OH)$_2$ ($5.5 \times 10^{-16}$), the deposition of Fe$^{3+}$ in the nickel hydroxide lattice will be more rapid than Ni$^{2+}$; thus, these initially formed Fe(OH)$_3$ colloidal particles would provide a net structure and help the agglomeration of colloidal nickel hydroxide particles. On the basis of this agglomeration, the Fe-doped nickel hydroxide

Figure 3. (a) Nitrogen adsorption/desorption isotherms and (b) the corresponding BJH pore size distribution curve for the pure nickel hydroxide and Fe-doped nickel hydroxide samples.

Figure 4. (a) First and (b) fourth CV curves at a scan rate of 0.08 mV s$^{-1}$ for the pure nickel hydroxide and Fe-doped nickel hydroxide samples.

Figure 5. (a) Cycling performance and (b, c) selected discharge/charge curves for the pure nickel hydroxide and Fe-doped nickel hydroxide electrodes at a current density of 200 mA g$^{-1}$. (d) Rate performance of the pure nickel hydroxide and Fe-doped nickel hydroxide electrodes.
nanoparticles are prone to grow and crystallize during the co-precipitation reaction process, which leads to a much denser structure and higher tap density.

Figure 3a shows the adsorption−desorption isotherms of the as-prepared Fe-doped nickel hydroxide and pure nickel hydroxide samples, which exhibit a mesoporous material type IV curve with an obvious hysteresis loop.27 The Fe-doped nickel hydroxide and pure nickel hydroxide samples show high BET surface areas of 98.8 and 98.0 m² g⁻¹, respectively. Figure 3b shows the pore size distributions calculated from adsorption data using the Barrett−Joyner−Halenda (BJH) model. For the pure nickel hydroxide sample, the pore size distribution mainly centers at ∼2.8 nm; in addition, there is a very wide pore size distribution between 5 and 100 nm. For Fe-doped nickel hydroxide, the pore size distribution mainly centers at ∼2.3 nm; in addition, there is an obvious pore size distribution between 5 and 30 nm. The high BET surface area and mesoporous structure of the Fe-doped nickel hydroxide nanostructures offer the possibility of efficient transport of electrons and ions in the electrode, which are expected to enhance lithium storage performance. The BJH pore volumes for Fe-doped nickel hydroxide and pure nickel hydroxide are 0.35 and 0.62 cm³ g⁻¹, respectively. These results are consistent with the SEM images (Figure 2) and tap density measurement results.

Figure 4a provides the first cycle CV curves of the Fe-doped nickel hydroxide and pure nickel hydroxide electrodes measured at the scan rate of 0.08 mV s⁻¹ in a potential range from 0.02 to 3.0 V. For the initial cathodic process, both electrodes show two obvious reduction peaks at the potential from 1.3 to 0.3 V, which can be due to the initial reduction of nickel hydroxide to metallic Ni (and Fe for the Fe-doped sample), the generation of LiOH and a solid electrolyte interface (SEI) film, and the further reduction of H in the electrochemical active materials.10,12 At the initial anodic process, the complex oxidation peaks at 0.9−1.9 V can be ascribed to the partial decomposition of the SEI film and the oxidation of LiH to LiOH; the broad oxidation peak at ∼2.24 V can be attributed to the oxidation of metallic Ni and the formation of Ni(OH)₂.²⁸ In the fourth CV curves (Figure 4b), there appears only one obvious reduction peak, and its intensity decreases greatly as compared with the first cycle CV curve, which can be attributed to the structural rearrangement of an electrode active material and the formation of the SEI film in the initial cathodic process. Compared with the pure nickel hydroxide electrode, the Fe-doped nickel hydroxide electrode shows larger redox peak areas, implying it has a better reversible lithium storage activity.

Figure 5a compares the cycling performances of the Fe-doped nickel hydroxide electrode and pure nickel hydroxide electrode at a current density of 200 mA g⁻¹. Clearly, the Fe-doped nickel hydroxide electrode exhibits higher specific discharge capacity and better cycling stability than the pure nickel hydroxide electrode. After 30 cycles, the Fe-doped nickel hydroxide electrode delivers a specific discharge capacity of 1080 mA h g⁻¹, which is two times as high as that (519 mA h g⁻¹) of pure nickel hydroxide. Figure 5b,c shows the discharge/charge plots at various cycles for the pure nickel hydroxide electrode and Fe-doped nickel hydroxide electrode, respectively. In the first discharge process, both electrodes show two long plateaus for the multistep electrochemical reaction processes; in the first charge process, both electrodes display two sloping plateaus at the potential ranges of 1.25−1.75 and 2.0−2.5 V, corresponding to the reversible electrochemical delithiation reactions. The first cycle discharge/charge capacities for the pure nickel hydroxide electrode and Fe-doped nickel hydroxide electrode are 1702/1116 and 2446/1510 mA h g⁻¹, respectively. The corresponding Coulombic efficiencies are 66 and 62%. The huge irreversible capacity loss in the first cycle is mainly due to the formation of the SEI layer.
on the surface of an electrode active material.\textsuperscript{29} In the subsequent discharge/charge cycles, the discharge curves show one sloping potential plateau (1.25–0.75 V), and the capacities decrease gradually. The change of the discharge/charge curves is in accordance with the CV results (Figure 4). The Fe-doped nickel hydroxide electrode also shows better rate capability than the pure nickel hydroxide electrode (Figure 5d). At a current density of 100 mA g\textsuperscript{-1}, the stable discharge capacities of the Fe-doped nickel hydroxide electrode and pure nickel hydroxide electrode are 1435 and 1309 mA h g\textsuperscript{-1}, respectively. As the current density increases, the difference of specific discharge capacity between the two electrodes becomes more and more obvious. Even at a high current density of 2000 mA g\textsuperscript{-1}, the specific discharge capacity of Fe-doped nickel hydroxide still maintains at 661 mA h g\textsuperscript{-1}, which is far higher than that (182 mA h g\textsuperscript{-1}) of the pure nickel hydroxide electrode.

Figure 6a gives the Nyquist plots of the Fe-doped nickel hydroxide electrode and pure nickel hydroxide electrode in their fully charged state. Prior to the EIS measurement, the cells were activated by five discharge/charge cycles at a current density of 200 mA g\textsuperscript{-1}. Both Nyquist plots consist of one depressed semicircle at high frequencies and an inclined line at the low frequencies, which are assigned to the charge-transfer resistance ($R_c$) on the active material/electrolyte interface and lithium ion diffusion impedance in the active material (Warburg impedance).\textsuperscript{30} The Nyquist plots were fitted with the equivalent circuit (the inset of Figure 6a) in which the symbols $R_w$, CPE, $R_c$, and $W$ are the electrolyte resistance, constant phase element, charge-transfer resistance, and Warburg impedance, respectively. The fitted $R_w$ values of pure nickel hydroxide and Fe-doped nickel hydroxide are 165.1 and 108.9 $\Omega$, respectively. The above result means that the electrochemical reaction at the Fe-doped nickel hydroxide/electrolyte interface occurs more easily than that at the pure nickel hydroxide/electrolyte interface, which account for the enhanced rate capability of Fe-doped nickel hydroxide (Figure 5d). To further elucidate the difference of lithium storage performance between pure nickel hydroxide and Fe-doped nickel hydroxide, CV measurements were conducted with various scan rates from 0.02 to 1.0 mV s\textsuperscript{-1} (Figure 6b,c). For the pure nickel hydroxide electrode (Figure 6b), with the increase of scan rate, the redox peaks disappear gradually; at a scan rate of 0.08 mV s\textsuperscript{-1}, the oxidation and reduction peaks cannot be discerned, implying the electrochemical reversibility of pure nickel hydroxide is very poor, especially under the high scan rate. In contrast, the Fe-doped nickel hydroxide electrode shows distinct redox peaks under all the scan rates (Figure 6c), suggesting its superior electrochemical reversibility during lithiation/delithiation cycles. It is noted that the reduction peak is significantly higher than the oxidation peaks, indicating an obvious kinetic difference between lithiation and delithiation processes. Under the same scan rate, the redox peak areas of Fe-doped nickel hydroxide are larger than those of pure nickel hydroxide. This is in good agreement with the rate performance result (Figure 5d). For the Fe-doped nickel hydroxide electrode, the peak current ($i_p$) and square root of scan rate ($v^{1/2}$) show a linear relationship (Figure 6d). This is a typical diffusion-controlled process. In this case, the chemical diffusion coefficient of Li\textsuperscript+ ($D_{li}$) in active materials can be evaluated based on the Randles–Sevcik equation:\textsuperscript{31,32}

$$i_p = (2.06 \times 10^5)n^{3/2}AD_{Li}^{1/2}C_{Li}^{1/2}$$

(1)

where $i_p$ is the peak current (A), $n$ is the charge transfer number in the redox process, $A$ is the electrode area (cm\textsuperscript{2}), $C_{Li}$ is the concentration of Li\textsuperscript+ in the electrode (mol cm\textsuperscript{-3}), and $v$ is the scan rate (V s\textsuperscript{-1}). The calculated chemical diffusion coefficients of $D_{Li}$ (O1), $D_{Li}$ (O2), and $D_{Li}$ (R) are 3.78 $\times$ 10\textsuperscript{-13}, 1.05 $\times$ 10\textsuperscript{-13}, and 3.42 $\times$ 10\textsuperscript{-12} cm\textsuperscript{2} s\textsuperscript{-1}, respectively.

The superior lithium storage performance of Fe-doped nickel hydroxide can be attributed to the unique mixed $\alpha$-$\beta$-phase composition, mesoporous structure, and synergistic effect between Ni and Fe dopants. The larger interlayer space of $\alpha$-motifs in Fe-doped nickel hydroxide provides fast diffusion paths for Li\textsuperscript+; moreover, the structural water molecules in the $\alpha$-motifs may also contribute to shielding Li\textsuperscript+ from the lattice host and facilitate the fast diffusion of Li\textsuperscript+ in the electrode; because the valence state of Fe\textsuperscript{3+} is higher than that of Ni\textsuperscript{2+}, Fe\textsuperscript{3+} doping would introduce a large amount of local structural defects in a nickel hydroxide lattice, such as vacancies, dislocations, and additional dopant energy levels, which can increase the electrochemical activity and electronic conductivity. Therefore, the rate capability of Fe-doped nickel hydroxide is significantly improved. On the other hand, the larger interlayer space of $\alpha$-motifs in Fe-doped nickel hydroxide and the microporous structure could effectively alleviate the volume changes of the electroactive material during repeated lithiation/delithiation cycles. Thus, the cycling stability of Fe-doped nickel hydroxide is remarkably strengthened.

3. CONCLUSIONS

In summary, Fe-doped nickel hydroxide was synthesized by a very simple chemical co-precipitation method. Because of the unique $\alpha$-$\beta$-phase composition, mesoporous structure, and synergistic effect between Ni and Fe dopants, this Fe-doped nickel hydroxide demonstrated much improved cycling stability, rate capability, and electrochemical reaction kinetics as compared to the undoped nickel hydroxide counterpart. The Fe-doped nickel hydroxide delivered a high specific capacity of 1080 mA h g\textsuperscript{-1} after 30 cycles at a current density of 200 mA g\textsuperscript{-1}, which is almost twice that (519 mA h g\textsuperscript{-1}) of undoped nickel hydroxide. Even at a high current density of 2000 mA g\textsuperscript{-1}, Fe-doped nickel hydroxide can still maintain a specific capacity of 661 mA h g\textsuperscript{-1}, far higher than that (182 mA h g\textsuperscript{-1}) of undoped nickel hydroxide. This work provides an effective strategy for enhancing the lithium storage performance of nickel hydroxide by metal cation doping. Fe-doped nickel hydroxide has a promising potential for applications as a novel anode material for next-generation lithium-ion batteries.

4. EXPERIMENTAL SECTION

4.1. Preparation of the Fe-Doped Nickel Hydroxide.

Fe-doped nickel hydroxide was prepared via a very facile chemical co-precipitation method. In a typical process, 100 mL of NaOH solution (1 M) was added dropwise into 100 mL of mixed metal nitrate solution (0.4 M total concentration) containing Ni\textsuperscript{2+} and Fe\textsuperscript{3+} (the molar ratio of [Fe\textsuperscript{3+}]/[Ni\textsuperscript{2+}] is 15\%) under continual stirring at 50 °C. After reaction for 3 h, the resulting suspension was kept in a mother solution for 20 h. After filtration, washed to neutral pH with distilled water, and freeze-dried to a constant weight. For comparison, pure nickel hydroxide was also prepared by the same procedure described above but without adding Fe\textsuperscript{3+} ions.
4.2. Physical Characterizations. The phase structure of the prepared samples was studied using multifunction X-ray diffraction (XRD, Dutch PANalytical X'Pert³ powder) at a scanning speed of 4° min⁻¹. The surface morphology and element composition of the prepared samples were characterized by a field emission scanning electron microscope (FESEM, Japan Hitachi S-4800) coupled with an energy-dispersive X-ray (EDX, Oxford Instrument) spectrometer. Fourier transform infrared spectra (FT-IR) were recorded using a FT-IR spectrometer (Thermo Nicolet NEXUS 470). Thermal gravity analysis (TGA) was conducted with a thermal analyzer (American TA SDTQ 600) in a nitrogen atmosphere at a heating rate of 10 °C min⁻¹ from 25 to 500 °C. Brunauer–Emmett–Teller (BET) surface areas of the samples were evaluated by nitrogen adsorption and desorption using a Micrometrics ASAP 2020 analyzer. The tap density of the as-prepared nickel hydroxide samples was measured as follow: a certain amount of the nickel hydroxide powder was added into a measuring cylinder; then, the measuring cylinder was repeatedly tamped until the volume of the powder does not decrease; the ratio between the mass and the volume determines the tap density of the sample.

4.3. Electrochemical Characterization. The electrochemical performance of the prepared samples was evaluated in coin-type cells (CR2032), which were assembled in an argon-filled glove box (Etelux, Lab 2000) with water and oxygen contents below 1 ppm. The working electrodes were fabricated by coating a slurry, containing prepared nickel hydroxide, acetylene black (Super-P), and poly(vinylidene fluoride) (PVDF) (with a mass ratio of 6:3:1) dispersed in N-methyl-2-pyrrolidinone (NMP), onto a copper foil substrate. The mass loading of an active material on each working electrode was ~0.5 mg cm⁻². A Celgard 2400 membrane was used as a separator. Lithium metal foil was used as a counter electrode. The electrolyte was 1 M LiPF₆ solution, consisting of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) with a volume ratio of 1:1:1. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out using an electrochemical workstation (CHI760E) at ambient temperature. For the EIS measurement, the frequency range was set from 100 kHz to 0.01 Hz, with an AC amplitude of 5 mV. The galvanostatic discharge/charge measurement was performed on an LAND 0.01 Hz, with an AC amplitude of 5 mV. The galvanostatic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a FT-IR spectrometer (Thermo Nicolet NEXUS 470). Thermal gravity analysis (TGA) was conducted with a thermal analyzer (American TA SDTQ 600) in a nitrogen atmosphere at a heating rate of 10 °C min⁻¹ from 25 to 500 °C. Brunauer–Emmett–Teller (BET) surface areas of the samples were evaluated by nitrogen adsorption and desorption using a Micrometrics ASAP 2020 analyzer. The tap density of the as-prepared nickel hydroxide samples was measured as follow: a certain amount of the nickel hydroxide powder was added into a measuring cylinder; then, the measuring cylinder was repeatedly tamped until the volume of the powder does not decrease; the ratio between the mass and the volume determines the tap density of the sample.

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Notes
The authors declare no competing financial interest.

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