A novel material Li$_2$NiFe$_2$O$_4$: Preparation and performance as anode of lithium ion battery

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HIGHLIGHTS

- A novel anode material Li$_2$NiFe$_2$O$_4$ was prepared under the air conditions.
- Li$_2$NiFe$_2$O$_4$ showed well-defined octahedron crystal morphology.
- 9 h-annealed Li$_2$NiFe$_2$O$_4$ delivered a capacity of 203 mAh g$^{-1}$.

ABSTRACT

For the first time, the preparation and characterization of a novel anode material Li$_2$NiFe$_2$O$_4$ are reported in this work. The preparation of Li$_2$NiFe$_2$O$_4$ is conducted under the air conditions by using a subsection calcination method. The influence of annealing periods on the properties of the resultant materials is thoroughly explored. The characteristics of the materials are mainly examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), cyclic voltammetry (CV), galvanostatic charge-discharge tests and electrochemical impedance spectroscopy (EIS). The results of the XRD patterns effectively demonstrate the formation of crystalline Li$_2$NiFe$_2$O$_4$, and the SEM images indicate that particles with octahedron crystal morphology are prepared and the 9 h-annealed sample has the smallest particle size among all the prepared samples. The results of electrochemical measurements reveal that 9 h-calced sample delivers a high specific capacity of 203 mAh g$^{-1}$ after 20 cycles at a current density of 100 mA g$^{-1}$. The successful preparation of Li$_2$NiFe$_2$O$_4$ is believed to be able to trigger the research work concerning the novel group of Li$_2$MFe$_2$O$_4$ materials.

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1. Introduction

Although Lithium-ion batteries (LIBs), due to their high operating voltage, high energy density and low self-discharge rate, have been commercialized as power sources for some portable electronics and electric vehicles, the cycling life, power density and safety issue still greatly impede their further applications [1]. Thus, improving the properties of the components that were employed to construct a lithium ion battery is still the main task for electrochemistry researchers.

Except cathode and electrolyte, the property of an anode material in LIBs is also a key factor influencing the electrochemical performances of LIBs. Graphite is the most commonly used anode material in commercial LIBs, however, some drawbacks of it were urgently claimed recently [2]. Firstly, the theoretical capacity (372 mAh g$^{-1}$) of graphite is relatively lower, which can not meet the demand for LIBs with high power and high energy density. Secondly, the potential for lithium intercalation in graphite is very close to the equilibrium potential of the Li$^+/Li$ redox couple, thus, during the lithium intercalation process, especially in the case of overcharging, lithium plating may come into being which could
lead to the formation of Li dendrites, and the produced Li dendrites may generate short circuit and fire accidents [3]. Thirdly, it was reported that the electrolyte reduction reaction can happen at the interface between electrode and electrolyte due to the higher Fermi level of graphite anode, which would result in the formation of SEI (solid electrolyte interphase) layer during the first charge-discharge process. The formed SEI layer may lower the coulombic efficiency, which is detrimental to the capacity and power density as well as the cycle-life [4,5]. Additionally, it is found that during the full lithium insertion and extraction process graphite anode undergoes a 9 vol% variation, which may cause the undesirable safety and stability. However, recent research works indicated that the poor electronic and ionic conductivities of LTO heavily limited its practical applications [7]. Thus, the hunt for anode materials of LIBs still remains the main research objectives.

Recently, numerous kinds of anode materials alternative to graphite, such as Si [8], Sn [9] and metal oxides like SnO2 [10], Co3O4 [11] and NiO [12], etc., have been developed with an intention to generate novel anode materials with highly electrochemical performance. Fe-based anode materials, such as FeO4/ carbon nanocomposites [13], Fe3O4 [14], FeOOH/SWNT composite [15], and so on [16], were also prepared as anode materials for LIBs due to their nontoxicity, low cost, natural abundance and higher theoretical specific capacity. Very recently, ferrites-based anode materials were demonstrated to have higher specific capacities and could be used as anode materials in LIBs. For instance, Yang et al. [17] reported a simple polymer pyrolysis method for the synthesis of hierarchically nanostructured NiFe2O4/C composites, in which the obtained composite retained a high specific capacity of 780 mAh g⁻¹ even after 40 cycles at a current density of 1/8 C. Dong et al. [18] prepared self-assembled three-dimensional mesoporous ZnFe2O4 submicron-sized spheres wrapped in graphene sheets using a one-pot hydrothermal strategy, and the resultant ZnFe2O4-graphene composites exhibited a high specific capacity of 1182 mAh g⁻¹ cycling at a specific current of 100 mA g⁻¹. CuFe2O4 [19] and MnFe2O4 [20] were also fabricated as anode materials for LIBs. Other reports relevant to the FeO4-based materials were also found in the previous literature [21–23]. However, to the best of our knowledge, the preparation of Li2NiFe2O4 as anode materials for LIBs has not been reported so far.

In the present work, Li2NiFe2O4 was prepared for the first time by using a subsection calcination method under the air conditions. The discharge capacity of Li2NiFe2O4 was able to achieve 203 mAh g⁻¹ after 20 cycles at the current density of 100 mA g⁻¹, which was higher than the theoretical capacity value of Li4Ti5O12. The impact of annealing periods on the properties of resultant samples was thoroughly studied, revealing that as the sintering time was 9 h, the best electrochemical performance was displayed by the as-prepared material. Although the electrochemical performance of this novel anode material is not superior to the currently studied anode material of NiFe2O4, a novel class of anode material like Li2MFe2O4 was really presented in this preliminary work. As far as we know, this is the first report on the preparation of Li2NiFe2O4 and its electrochemical performance for LIBs so far.

2. Experimental

2.1. Materials

α-Fe2O3, LiOH·H2O, H3PO4, Ni(NO3)2·6H2O, glucose and oxalic acid were all purchased from Tianjin Chemical Reagent Co. Ltd. All materials used in the electrochemical measurement, such as polytetrafluoroethylene (PTFE) binder, acetylene black, electrolyte of 1 M LiClO4 and the cell were all supported by the Tianjin Lianghuo S&T Developing Co. Ltd. All the chemicals were used as received without any further treatment.

2.2. Preparation of Li2NiFe2O4

Briefly, α-Fe2O3 (0.60 g), H3PO4 (0.86 g), Ni(NO3)2·6H2O (1.45 g), LiOH·H2O (0.59 g), glucose (0.30 g) and oxalic acid (3.75 g) were dissolved in 80 mL of distilled water to form a brownish red suspension solution. And then the suspension solution was evaporated in a drier at 150 °C until brownish red powders were obtained. After cooling down to the room temperature, the resultant powders were placed in a crucible, and then the crucible was transferred into an electronic furnace with temperature controlled at 800 °C for various hours under air conditions. It should be mentioned that the temperature of the electronic furnace was increased from room temperature to 800 °C at the rate of 14 °C min⁻¹, and when the calcinations periods were achieved, the temperature decreased to room temperature at a rate of 10 °C min⁻¹. The resultant black powders annealed for 5, 7, 9 and 11 h were denoted as sample a, b, c and d, respectively.

2.3. Characterization

X-ray diffraction (Bruker AXS, D8 ADVANCE (Database version PDF-2004), Germany) was used to examine the phase homogeneity. The particle morphology was observed by scanning electron microscopy (HITACHI, SEM-S570) and transmission electron microscopy (HITACHI, TEM H-7650). Energy dispersive spectrometer (EDS, INCA Energy 350, England) was employed to analyze the components of the as-prepared samples. Fourier transform infrared spectrometry (FT-IR) measurements were carried out on a Hitachi FT-IR-8900 spectrometer (Japan).

Electrochemical measurements including Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) were carried out on a CHI 660B electrochemical workstation (Shanghai Chenhua Apparatus, China) connected to a personal computer. The oscillation voltage applied to the cells and the frequency ranges were 5 mV and 100 kHz~0.1 Hz in the EIS measurements, respectively. All the experiments were carried out at room temperature.

The working electrodes were fabricated by pasting slurries onto a Cu foil, in which the slurry was prepared by blending prepared active material powders with acetylene black and PTFE binder at a weight ratio of 80:10:10. The loading of all electrodes was around 1.6 mg cm⁻². Namely, prior to the assembly of half battery Li2NiFe2O4/Li, the obtained slurry was pasted onto Cu foil current collector and dried at 120 °C for 6 h in a vacuum oven. Two-electrode electrochemical cells consisting of lithium metal foil as the negative electrode, Celgard 2400 separator, and an electrolyte of 1 M LiClO4 in ethylene carbonate (EC):diethyl carbonate (DEC):dimethyl carbonate (DMC) (2:5:11, vol.) were assembled in a high pure nitrogen-filled glove box. Metallic lithium foils were used as both the reference and counter electrodes. The electrochemical cycle tests were performed using a battery testing system (CT-3008W-5V20 mA–54, Shenzhen Neware Electronics Co., Ltd. China) at various current densities between 0 and 3 V at room temperature. The theoretical capacity value of Li2NiFe2O4 is close to 215 mAh g⁻¹ when assuming that two Li ions can be inserted into or extracted from per molecule.
3. Results and Discussion

3.1. XRD analysis

XRD patterns of the as-prepared samples including the standard XRD patterns of Li$_3$PO$_4$, Li$_2$NiFe$_2$O$_4$ and NiFe$_2$O$_4$ are illustrated in Fig. 1. For all the prepared samples, five characteristic diffraction peaks located at 30.5°, 35.9°, 43.6°, 57.6° and 63.3° can be respectively, matched well with the (220), (311), (400), (511) and (440) crystal planes of Li$_2$NiFe$_2$O$_4$ (JCPDS no. 00-039-1277), indicating a cubic spinel structure.

The presence of intense peaks in the XRD pattern effectively demonstrated the higher crystallinity of the products. Meanwhile, three small diffraction peaks that appeared in the 2θ range of 22.2°–24.6° can be well indexed as the phase of Li$_3$PO$_4$, strongly indicating the existence of Li$_3$PO$_4$ as impurities in the synthesized samples. The lattice parameters ($a = b = c$) estimated from the standard XRD pattern using a TOPAS software for sample a, b, c and d are estimated to be 8.3509, 8.3456, 8.3450 and 8.3385 Å. Apparently, the lattice parameters for sample c and d are very close to the theoretical lattice parameter (8.337 Å) evaluated from the standard XRD pattern of Li$_2$NiFe$_2$O$_4$. It indicated that sample c and d have better crystallinity compared with other samples. The average crystallite sizes calculated using Scherrer’s equation from (220), (311), (400), (511) and (440) facet, for sample a, b, c and d were about 94, 200,113 and 210 nm, respectively. These crystallite sizes calculated from XRD patterns were smaller than those particle sizes estimated from the SEM images. Also, at least two conclusions can be obtained after a close observation of Fig. 1. (1) When the sintering time was up to 7 h, the diffraction peaks corresponding to the phase of Li$_3$PO$_4$ became apparent as shown by the green-circled part; (2) As the annealing timed reached 11 h, as shown by the red-circled part, a novel diffraction peak centered at 74.9° appeared which indicated the formation of Li$_2$NiFe$_2$O$_4$.

The composition of the sample was examined by EDS analysis. The typical results are presented in Fig. 2. Except element of lithium, the peaks belonging to O, P, Fe and Ni elements were all displayed clearly. The atomic ratios of Fe to Ni were 1.82, 1.55, 2.05 and 2.28, respectively, for sample a, b, c and d. Therefore, the atomic ratio of Fe to Ni in sample c was very close to the theoretical value in Li$_2$NiFe$_2$O$_4$. That indicated that the annealing time of 9 h was the optimal period for fabricating well-defined crystalline Li$_2$NiFe$_2$O$_4$. The presence of element P in the resultant products further indicated that the main impurities existing in the resultant products were Li$_3$PO$_4$ rather than other substances. The results obtained from XRD and EDS measurements strongly demonstrated that the developed method, namely, a subsection calcination method under the air condition, was a feasible way to synthesize crystalline Li$_2$NiFe$_2$O$_4$.

FTIR spectra for the as-prepared products are given in Fig. 3. Compared to the spectrum of the precursor (the dry starting materials prior to calcination), some novel absorption peaks emerged after the calcination process, indicating that some new substances were produced via the developed method. Generally, the bands at 460 cm$^{-1}$, 512 cm$^{-1}$ and 602 cm$^{-1}$ are ascribed to the stretching vibration modes associated to the metal-oxygen absorption Fe–O bands in the crystalline lattice of NiFe$_2$O$_4$ [21,23]. And the wide sluggish absorption bands appearing at 1038 cm$^{-1}$ in all the curves may correspond to the C–O stretching mode which was resulted from the carbon intercalation compound [23]. It seemed that the intensity of the absorption band for sample c was slightly higher than other samples. It indicated that more amounts of well-defined Fe–O bonds were generated in sample c relative to other samples [24]. That is to say, the characteristic absorption bands for ferrites having a spinel structure were well exhibited in the FTIR spectra, further indicating the formation of Li$_2$NiFe$_2$O$_4$.
3.2. Morphology characterization

SEM images of the as-prepared Li$_2$NiFe$_2$O$_4$ samples are displayed in Fig. 4. It is evident that for sample a, b and c, most particles have a regular octahedron crystal morphology and the surface of each particle is very smooth. While for sample d, octahedron-shaped particles are rarely observed. Obviously, the largest particles were found in sample a, and sample c presented a more uniform particle size distribution as compared to other samples. Approximately, the particle size ranges for sample a, b, c and d were 100–800 nm, 80–500 nm, 80–380 nm and 80–700 nm, respectively. The average particle sizes for sample a, b, c and d were 431 nm, 324 nm, 270 nm and 347 nm, respectively. Thus, sample c showed the smallest particle size among all the samples.

When the annealing time reached 11 h, some crushed small particles were found anchoring on the surface of some huge particles, indicating that some new substances were formed which can be testified by the presence of a small diffraction peak at 74.9° in XRD patterns (as shown by the red (in the web version) circled part in pattern d of Fig. 1).

It is well known that the research work concerning NiFe$_2$O$_4$ has been widely carried out recently. For example, NiFe$_2$O$_4$ particles with irregular shape and a mean grain size of 1.7 μm were prepared by Balaji’s group [25], Nanocrystalline particles of NiFe$_2$O$_4$ with a particle size from 50 nm to 100 nm were prepared by Yang’s group [17], in which no explicit morphology was observed. In Feng’s work [26], NiFe$_2$O$_4$ particles with an average particle size of 1–2 μm were demonstrated to have an agglomerate porous structure. The reports on the nanorods [27] and hollow microspheres [28] of NiFe$_2$O$_4$, etc. [29] were also published recently. Although the research works of Fe$_2$O$_4$-based anode materials have been published, the preparation of Li$_2$NiFe$_2$O$_4$ particles with well-defined octahedron crystal morphology, to the best of our knowledge, has not been published yet.

Fig. 5 shows the TEM microstructures of the obtained samples. For all the samples, cubic rather than spherical particles are exhibited. The average particle sizes of sample a, b, c and d were, respectively, estimated to be 208 nm, 204 nm, 144 nm and 256 nm. Thus, sample c showed the smallest particle size among all the samples, which agreed with the results obtained from SEM observation. On the base of the previous works [18,30], the property of smaller size may bring about at least two superior properties: (1) The contacting areas of the electrode/electrolyte interface will be markedly increased as the particle size became smaller, which will offer better contacting between the electrode and electrolyte and benefit the lithium storage during the lithiation/delithiation processes; (2) Lowering the particle size may shorten the diffusion paths of lithium ions in the bulk electrode material. Close observation also indicated that some silk-shaped carbon materials were formed in the resultant particles. Apparently, the silk-shaped carbon was generated by the incomplete combustion of glucose and oxalic acid. Many authors have claimed that the residual carbon in the final products may behave as an elastic layer for buffering the volumetric changes and as a conductive additive for enhancing the electric conductivity [14,31].

3.3. Electrochemical properties

Fig. 6A presents the initial charge-discharge profiles obtained in the potential range of 0–3 V at a current density of 100 mA g$^{-1}$ for the Li$_2$NiFe$_2$O$_4$ samples which were prepared at various annealing periods. Evidently, as marked by the red (in the web version) arrows, two voltage plateaus are observed during the discharge process. The discharge plateaus at 0.76–0.63 V and 0.63–0.44 V probably correspond to the reduction of Fe$^{3+}$ to Fe$^{2+}$ and the formation Li$_2$NiFe$_2$O$_4$. The presence of one sloping plateau at
1.60–1.84 V in the charge processes should be ascribed to the oxidation reaction of Fe$^{2+}$ to Fe$^{3+}$ accompanying with the formation of NiFe$_2$O$_4$. Also, it can be seen that all the charge-discharge curves showed similar shape, indicating a similar charge-discharge mechanism for all the prepared electrodes. Evidently, the initial discharge capacities were approximately 276, 543, 572 and 226 mAh g$^{-1}$, respectively, for sample a, b, c and d. It indicated that sample c delivered the largest specific capacity among all the materials, which was mainly attributed to its smaller particle size and uniform particle size distribution when compared with other samples. Meanwhile, it should be noted that although the discharge capacities exhibited above were rather lower than that of the NiFe$_2$O$_4$ nanofibers [32], the values of discharge capacity were significantly higher than the theoretical value of LTO (Li$_4$Ti$_5$O$_12$). Commonly, the voltage plateaus in charge/discharge curves corresponded to the extraction/insertion process of lithium ions in an electrode, and the flat voltage plateau corresponds to a pure phase transformation [30]. Actually, sloping rather than flat voltage plateaus were displayed in Fig. 6A. According to the published work [33], the generation of oblique voltage plateau was usually due to the fact that the charge compensation was unable to keep pace with the ionic transfer at a certain current rate, as a result, a higher polarization was produced which led to a quicker capacity fading. Yoon et al. [34] stated that the sloping voltage plateau should be noted as “an intermediate region” which covered from the latter part of the sloping region in between two voltage plateaus to the beginning of the second voltage plateau in the charge or discharge curves. And he also pointed out that in the intermediate region, many redox reactions may occur simultaneously. In our case, as verified by the XRD pattern, some impurities like Li$_3$PO$_4$ were contained in the resulting products which may affect the charge-discharge process to some extent. For the charge-discharge profiles of the second cycle, as shown in Fig. 6B, no evident difference in shape was found in charging curves. However, as for the discharge curves, a sloping plateau at 1.56–1.05 V followed by a flat voltage plateau at 0.98 V was presented. Generally, the promotion of the discharging potential plateaus was due to the formation of SEI layer and the rearrangement of electrode material structure. It is apparent that the discharge voltage plateau for the second cycle was lower than that of LTO (Li$_4$Ti$_5$O$_12$) [35,36]. According to the previous researches of NiFe$_2$O$_4$ and our works presented in this paper, the discharge and charge processes are believed to mainly proceed as follows:

**Charging process:** Li$_2$NiFe$_2$O$_4$ $\rightarrow$ NiFe$_2$O$_4$ + 2Li$^+$ + 2e

**Discharging process:** NiFe$_2$O$_4$ + 2Li$^+$ + 2e $\rightarrow$ Li$_2$NiFe$_2$O$_4$

Although the capacity values presented in this work were markedly lower than those of NiFe$_2$O$_4$ [17], this capacity value was comparable to that of LTO. The cycling performance profiles of these materials are shown in Fig. 7A. As can be seen, the discharge capacities for sample b and c in the first and second cycles are 544 and 232 mAh g$^{-1}$, 574 and 317 mA h g$^{-1}$, respectively. The large initial capacity loss is, generally, attributable to the irreversible formation of SEI layer and
the reduction of metal oxide to metal and the decomposition of electrolyte [25]. The discharge capacities of the second cycle for sample a, b, c, and d were 231, 232, 317 and 304 mAh g\(^{-1}\), respectively. And at the 20th cycle, the discharge capacities for the sample a, b, c, and d remained 136, 128, 203 and 162 mAh g\(^{-1}\), which were equal to 58.9, 53.7, 63.6, and 53.3% of their discharge capacities at the second cycle, respectively. The fact that LIB capacity fades with cycles is normally caused by the deactivation of electrode materials or the disability of lithium insertion/extraction during long time cycling. Evidently, sample c exhibited the largest discharge capacity as well as the highest capacity retention among all the samples. Although the discharge capacity of sample c was largely lower than the theoretical value of commercial graphite anode (372 mAh g\(^{-1}\)), the discharge capacity of sample c was still higher than the theoretical value of LTO (Li\(_4\)Ti\(_5\)O\(_{12}\)) (175 mAh g\(^{-1}\)). More importantly, the discharge voltage plateau of sample c (about 1.0 V vs. Li/Li\(^+\)) was remarkably lower than that of LTO (around 1.5 V vs. Li/Li\(^+\)), which means that the output voltages of the cell assembled by sample c are higher than that constructed by LTO when employing both identical cathode materials and electrolyte. Apparently, the small particle size may generate a larger surface area when the loading amounts of electrode materials are identical, which, in turn, can significantly augment the contacting surface area between the electrode and electrolyte solution, and the resulting large surface area can effectively reduce the current density per unit surface area, leading to an lowered polarization potential based on the Tafel’s equation [37]. As a result, the electronic conductivity of the electrode materials was promoted significantly. Meanwhile, the smaller particle size may shorten pathways for lithium-ion diffusion, which may promote the ionic conductivity of an electrode.

Fig. 7. A. Cycling performance of the as-prepared samples at the current density of 100 mAh g\(^{-1}\) for 20 cycles. B. Coulombic efficiency vs. cycle number for Li\(_2\)NiFe\(_2\)O\(_4\) obtained at 800 °C for 5, 7, 9, and 11 h at a current density of 100 mAh g\(^{-1}\). C. The rate performance of (a) Li\(_2\)NiFe\(_2\)O\(_4\) prepared at 800 °C for 9 h and (b) 11 h. The sample was cycled 10 times at each rate and forwarded to the next step.
materials. And the discharging process is an electrochemical reaction occurring between the electrons supplied by the electrochemical instrument and the electrochemical active materials. Or in other words, the charging and discharging process, respectively, corresponded to an oxidation and reduction electrochemical reaction. Therefore, the much larger discharge specific capacities delivered by sample c were definitely resulted from the electrochemical reduction of excess active materials. Other possible reduction reactions such as the reduction of lithium ions to metallic lithium, the reduction of electrolyte and the reduction of some metal oxides formed in the charging process, can also bring about the higher discharge capacity [37]. For sample c, the values of CE dropped quickly at the first several cycles and then increased and stabilized at about 95.5% in the subsequent cycles. For other samples, the values of CE were all larger than 93% even after 20 cycles. Above results substantially demonstrated that the degree of reversibility for the lithium ion insertion/extraction process in the as-synthesized materials was comparable to that of NiFe$_2$O$_4$ [17] and ZnFe$_2$O$_4$ [27], though the capacity value was not satisfied as compared to the currently reported anode materials.

To study the rate capability of the as-prepared Li$_2$NiFe$_2$O$_4$ electrodes, the current rate was increased stepwise from 100 mA g$^{-1}$ to 600 mA g$^{-1}$ and 10 cycles were measured at each current rate as shown in Fig. 7C. Although the discharge capacity values decreased with increasing the current rate, the 9 h-annealed Li$_2$NiFe$_2$O$_4$ electrode delivered much higher capacity value as compared with the 11 h-annealed sample in the whole testing period. This indicated that 9 h-annealed sample had better rate capability than other samples.

To better understand the mechanism of redox reactions occurring during charge-discharge processes, cyclic voltammetry (CV) technique was employed to explore the electrochemical behaviors of the electrodes. Cyclic voltammograms (CVs) of the electrode assembled by 9 h-annealed Li$_2$NiFe$_2$O$_4$ for first three cycles were given in Fig. 8A. In the anodic process, one broad peak in the first cycle centered at about 1.74 V was exhibited which can be attributed to the extraction of Li ions from Li$_2$NiFe$_2$O$_4$ accompanied with the oxidation of Fe$^{2+}$ to Fe$^{3+}$. And in the first cathodic scan two broader peaks at 0.81 V and 1.20 V corresponded to the two voltage plateaus appearing in the discharging curves of Fig. 6A, which is commonly related to the insertion process of Li ions into the electrode materials. It is clear that both the cathodic and anodic peak currents decreased with increasing the cycling number and the peak potentials had a slight shift. Commonly, the slight shift in the peak potentials was originated from the minor structural rearrangement of active material, which could lead to a suitable electrical contact between the electrode materials and the liquid electrolyte. It was evident that the potential separation ($\Delta E_p$) of the oxidation and reduction peak ($\Delta E_p = E_{pa} - E_{pc}$), was slightly enlarged with increasing the cycle number. For instance, the values of $\Delta E_p$ for the first, second and third cycle were 0.94 V, 1.05 V and 1.15 V, respectively. It suggested that the lithium insertion/extraction kinetics in the electrode became slower as the cycle number increased [30], which may lead to an evident capacity fading as shown in Fig. 7A. Meanwhile, at each cycle, the cathodic peak current was largely bigger than the anodic peak current. For example, in the third cycle, the absolute value of the ratio of cathodic peak current to anodic peak current was 1.60 rather than unit. This indicated that the insertion/extraction process of Li ions in the as-prepared Li$_2$NiFe$_2$O$_4$ was not a reversible process [30], which can be well employed to explain the obvious capacity fading occurring in the cycling performance (Fig. 7A). Yang’ group [17] have studied the CVs of NiFe$_2$O$_4$ electrode systematically, and they reported that a peak at 0.59 V, which was originated from the reduction of Ni$^{2+}$ and Fe$^{3+}$ and an irreversible reaction concerning the decomposition of the electrolyte, was observed in the first cathodic process, and correspondingly, an anodic peak at 1.8 V attributed to the oxidation of the metallic iron and nickel was observed in the first cycle and no obvious shift in the subsequent cycles was found. After probing CVs of MFe$_2$O$_4$ electrodes, Xu [27] revealed that during the anodic process two peaks in the first cycle assigned to the oxidation of Zn$^0$ and Fe$^0$ were observed clearly. Obviously, above results presented were different from the results shown in this work. Besides, the discharge specific capacities of NiFe$_2$O$_4$ reported in previous refs [17,27] were much larger than that of the present Li$_2$NiFe$_2$O$_4$, further confirming that the substance prepared in this work was a novel electrode material rather than NiFe$_2$O$_4$.

To compare the CV behaviors of as-prepared samples, the CVs of the prepared samples, which were recorded at the third cycle, are displayed in Fig. 8B. Although the currents for 7-annealed sample were the largest among all the samples, the 9 h-annealed sample exhibited the smallest value of $\Delta E_p$. Generally, a smaller value of $\Delta E_p$ corresponds to a better reversibility [39]. Therefore, sample c possessed better reversibility of Li ion insertion/extraction process as compared to other samples.

Electrochemical impedance spectroscopy (EIS), a conventional method that can reflect the total electrochemical behavior of an electrode reaction or a cell, has been widely used in the investigation of lithium ion batteries mainly owing to its simplicity in analysis [30]. Nyquist plot as one typical kind of curves in EIS has been introduced to analyze the electrochemical performance of a Li half cell though the exact mechanism occurring in the cells can not
be revealed. Fig. 9 shows Nyquist plots obtained from the as-prepared various Li2NiFe2O4 electrodes after 20th cycle tests. It should be noted that all the curves were recorded at their open circuit potentials. Generally, for a typical Li half cell, the intercept at the Zreal axis in highest frequency region corresponded to the ohmic resistance (R0) representing the total resistance of the electrolyte, separator, and electrical contacts. The depressed semicircle in the high frequency range was attributed to the Li-ion migration resistance (Rct) through the SEI film formed on the electrode or another coating layer. Second semicircle in the high-middle frequency range was originated from the charge transfer resistance (Rct). The inclined line in the low frequency stood for the Warburg impedance, which was associated with lithium-ion diffusion in the electrode materials [40]. Among above parameters, Rct was the most widely used parameter that can compare the kinetics of an electrode reaction directly. And the values of Rct could be estimated from the diameter of semicircle approximately. Apparently, the 38

bance, which was associated with lithium-ion diffusion in the elec-

preparation of Li2NiFe2O4 was accomplished under air conditions, 

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material will degrade with the increasing annealing time has been 

reported in the former papers. For example, Dimesso et al. [41]

interpreted that the degradation of the electrochemical perform-

ance with the annealing time was originated from the growth of 

the secondary phases on the grain boundaries, and he explained 

that the newly formed phases could behave like resistors allowing 

the electron transfer but adding an additional potential at the 

surface that would inhibit the Li-ions transfer. In this work, the 

preparation of Li2NiFe2O4 was accomplished under air conditions, 

thus, some metal elements in the samples would be converted into 

metal oxides owing to the presence of excess amount of oxygen. 

Additionally, the amount of lithium ions in the products will 

decrease with increase in annealing time due to the volatilization 

of lithium ions, as could be verified by the fact that the diffraction 

peak centered at 74.9° for sample d (pattern d of Fig. 1) became 

more evident when compared to other samples. Due to above 

possible reasons, poor electrochemical performance was exhibited 

by the 11 h-annealed sample. Although some results presented 

here were not well explained in this work, the preparation of 

Li2NiFe2O4 was successfully exhibited in this preliminary work. It is 

believed that Li2NiFe2O4 as a pioneering material in the family of 

Li2MFe2O4 (M = Zn, Co, Cu, etc.), will trigger the research work 

concerning Li2MFe2O4 widely, which is the main contribution of 

this preliminary work.  

4. Conclusions  

For the first time, well-defined crystal octahedral particles of 

Li2NiFe2O4 were prepared by a subsection calcination method un-

der the air conditions. The influence of annealing time on the 

properties of the resultant samples was systematically investigated. 

Results obtained from XRD analysis demonstrated that although 

some impurities like Li3PO4 were contained in the final products, 

all the samples prepared showed better crystallinity. Both SEM 

and TEM observations indicated that 9 h-annealed Li2NiFe2O4 particles 

presented the smallest particle size among all the prepared samples. 

Also, results of electrochemical measurements indicated that 

among the produced electrodes, 9 h-annealed Li2NiFe2O4 electrode 

showed the best electrochemical performance in terms of 

discharge capacity and cycling stability. Showing the preparation of 

a pioneering material Li2NiFe2O4 is the main contribution of this 

work, which will not only enrich the research work of anode ma-

terials but also will trigger the research on the Li2MFe2O4 materials.  

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