A novel material $\text{Li}_2\text{NiFe}_2\text{O}_4$: preparation and performance as anode of lithium ion battery

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Abstract

For the first time, the preparation and characterization of a novel anode material $\text{Li}_2\text{NiFe}_2\text{O}_4$ are reported in this work. The preparation of $\text{Li}_2\text{NiFe}_2\text{O}_4$ 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 voltammometry (CV), galvanostatic charge-discharge tests and electrochemical impedance spectroscopy (EIS). The results of the XRD patterns effectively demonstrate the formation of crystalline $\text{Li}_2\text{NiFe}_2\text{O}_4$, 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-calcined 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 $\text{Li}_2\text{NiFe}_2\text{O}_4$ is believed to be able to trigger the research work concerning the novel group of $\text{Li}_2\text{MFe}_2\text{O}_4$ materials.

Keywords: Nanostructures; oxides; annealing; electrochemical techniques

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 the graphite anode undergoes a 9 vol.% variation, which may cause the undesirable thickness change and mechanical degradation as well [6]. In recent years, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) has been thought as a very promising candidate for the next generation of anode materials in LIBs mainly due to its 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 SnO_2 [10], Co_3O_4 [11] and NiO [12], and etc., have been developed with an intention to generate novel anode materials with highly electrochemical performance. Fe-based anode materials, such as Fe_3O_4 /carbon nanocomposites [13], Fe_2O_3 [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 $\text{NiFe}_2\text{O}_4/\text{C}$ 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 $1/8 \text{ C}$. Dong, et al. [18] prepared self-assembled three-dimensional mesoporous ZnFe_2O_4 submicron-sized spheres wrapped in graphene sheets using a one-pot hydrothermal strategy, and the resultant ZnFe_2O_4 -graphene composites exhibited a high specific capacity of 1182 mAh g^{-1} cycling at a specific current of 100 mA g^{-1} . CuFe_2O_4 [19] and

MnFe₂O₄ [20] were also fabricated as anode materials for LIBs. Other reports relevant to the Fe₂O₄-based materials were also found in the previous literatures [21, 22, 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 100mA 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 $\text{Li}_2\text{NiFe}_2\text{O}_4$

Briefly, $\alpha\text{-Fe}_2\text{O}_3$ (0.60g), H_3PO_4 (0.86g), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.45g), $\text{LiOH} \cdot \text{H}_2\text{O}$ (0.59g), glucose (0.30g) and oxalic acid (3.75g) 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 S-570) 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-5V20mA-S4, 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_3PO_4 , $\text{Li}_2\text{NiFe}_2\text{O}_4$ and NiFe_2O_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 $\text{Li}_2\text{NiFe}_2\text{O}_4$ (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 rang of $22.2\text{--}24.6^\circ$ can be well indexed as the phase of Li_3PO_4 , strongly indicating the existence of Li_3PO_4 as impurities in the synthesized samples. The lattice parameters ($a=b=c$) estimated from XRD pattern using a TOPAS software for sample **a**, **b**, **c** and **d** are estimated to be 8.3509, 8.3456, 8.3450 and $8.3385 \text{ \AA}$. Apparently, the lattice parameters for sample **c** and **d** are very close to the theoretical lattice parameter ($8.337 \text{ \AA}$) evaluated from the standard XRD pattern of $\text{Li}_2\text{NiFe}_2\text{O}_4$. 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_3PO_4 became apparent as shown by the green-circled part; (2) As the annealing time reached 11 h, as shown by the red-circled part, a novel diffraction peak centered at 74.9° appeared which indicated the formation of a new substance in the resultant

sample. Thus, it is confirmed that the as-prepared products were mainly composed of $\text{Li}_2\text{NiFe}_2\text{O}_4$ even if a negligible amount NiFe_2O_4 could be present.

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 $\text{Li}_2\text{NiFe}_2\text{O}_4$. That indicated that the annealing time of 9 h was the optimal period for fabricating well-defined crystalline $\text{Li}_2\text{NiFe}_2\text{O}_4$. The presence of element P in the resultant products further indicated that the main impurities existing in the resultant products were Li_3PO_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 $\text{Li}_2\text{NiFe}_2\text{O}_4$.

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_2O_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 $\text{Li}_2\text{NiFe}_2\text{O}_4$.

3.2 Morphology characterization

SEM images of the as-prepared $\text{Li}_2\text{NiFe}_2\text{O}_4$ 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 average 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 circled part in pattern d of Fig.1).

It is well known that the research work concerning NiFe_2O_4 has been widely carried out recently. For example, NiFe_2O_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_2O_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_2O_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_2O_4 , etc. [29] were also published recently. Although the research works of Fe_2O_4 -based anode materials have been published, the preparation of $\text{Li}_2\text{NiFe}_2\text{O}_4$ 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 Li₂NiFe₂O₄ samples which were prepared at various annealing periods. Evidently, as marked by the red arrows, two voltage plateaus are observed during the discharge process. The discharge plateaus at 0.76-0.63V and 0.63-0.44V probably correspond to the reduction of Fe³⁺ to Fe²⁺ and the formation Li₂NiFe₂O₄. The presence of one sloping plateau at 1.60-1.84V in the charge processes should be ascribed to the oxidation reaction of Fe²⁺ to Fe³⁺ accompanying with the formation of NiFe₂O₄. 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 NiFe₂O₄ nanofibers [32], the values of discharge capacity were significantly higher than the theoretical value of LTO (Li₄Ti₅O₁₂).

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_3PO_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 1.56-1.05V 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 ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) [35, 36]. According to the previous researches of NiFe_2O_4 and our works presented in this paper, the discharge and charge processes are believed to mainly proceed as follows:

Charging process: $\text{Li}_2\text{NiFe}_2\text{O}_4 \longrightarrow \text{NiFe}_2\text{O}_4 + 2\text{Li}^+ + 2\text{e}^-$

Discharging process: $\text{NiFe}_2\text{O}_4 + 2\text{Li}^+ + 2\text{e}^- \longrightarrow \text{Li}_2\text{NiFe}_2\text{O}_4$

Although the capacity values presented in this work were markedly lower than those of NiFe_2O_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 (Li₄Ti₅O₁₂) (175 mAh g⁻¹). More importantly, the discharge voltage plateau of sample **c** (about 1.0V vs. Li/Li⁺) was remarkably lower than that of LTO (around 1.5V 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.

The plots of coulombic efficiency (CE) (the ratio of charging capacity to discharging capacity at the same cycle) vs. cycle number for all as-synthesized samples were also drawn in Fig.7B. The values of CE in each cycle for all samples were always lower than unit. Some possible reasons have been proposed in the previous work [38]. Theoretically, the charging process is an electrochemical reaction between the positive electrical charges, which were provided by the electrochemical equipment, and the electroactive 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

NiFe₂O₄ [17] and ZnFe₂O₄ [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 Li₂NiFe₂O₄ 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 Li₂NiFe₂O₄ 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 discharge-charge 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 Li₂NiFe₂O₄ 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 Li₂NiFe₂O₄ accompanied with the oxidation of Fe²⁺ to Fe³⁺. 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 (ΔE_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 ΔE_p for the first, second and third cycle were 0.94V, 1.05V and 1.15V, 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 $\text{Li}_2\text{NiFe}_2\text{O}_4$ 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_2O_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_2O_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_2O_4 reported in previous refs [17, 27] were much larger than that of the present $\text{Li}_2\text{NiFe}_2\text{O}_4$, further confirming that the substance prepared in this work was a novel electrode material rather than NiFe_2O_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 ΔE_p . Generally, a smaller value of ΔE_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 ions 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 $\text{Li}_2\text{NiFe}_2\text{O}_4$ 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 Z_{real} axis in highest frequency region corresponded to the ohmic resistance (R_Ω) 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 (R_f) 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 (R_{ct}). 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, R_{ct} was the most widely used parameter that can

compare the kinetics of an electrode reaction directly. And the values of R_{ct} could be estimated from the diameter of semicircle approximately. Apparently, the semicircle corresponding to the 9 h-annealed sample showed the smallest value of R_{ct} among all the samples, which suggested that 9h-annealed sample had faster lithium insertion/extraction kinetics as compared to other samples.

Why did the annealing period have such a significant impact on the electrochemical properties of the resultant sample? The fact that the electrochemical performance of a cathode or an anode 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 performance 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 $\text{Li}_2\text{NiFe}_2\text{O}_4$ 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 $\text{Li}_2\text{NiFe}_2\text{O}_4$ was successfully exhibited in this preliminary work. It is believed that $\text{Li}_2\text{NiFe}_2\text{O}_4$, as a pioneering material in the family of $\text{Li}_2\text{MFe}_2\text{O}_4$ (M= Zn, Co, Cu, etc.), will

trigger the research work concerning $\text{Li}_2\text{MFe}_2\text{O}_4$ widely, which is the main contribution of this preliminary work.

4. Conclusions

For the first time, well-defined crystal octahedral particles of $\text{Li}_2\text{NiFe}_2\text{O}_4$ were prepared by a subsection calcination method under 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 Li_3PO_4 were contained in the final products, all the samples prepared showed better crystallinity. Both SEM and TEM observations indicated that 9 h-annealed $\text{Li}_2\text{NiFe}_2\text{O}_4$ 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 $\text{Li}_2\text{NiFe}_2\text{O}_4$ electrode showed the best electrochemical performance in terms of discharge capacity and cycling stability. Showing the preparation of a pioneering material $\text{Li}_2\text{NiFe}_2\text{O}_4$ is the main contribution of this work, which will not only enrich the research work of anode materials but also will trigger the research on the $\text{Li}_2\text{MFe}_2\text{O}_4$ materials.

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Figure captions and figures

Fig. 1 XRD patterns for all the prepared samples. Pattern **a**, **b**, **c** and **d** correspond to sample **a**, **b**, **c**, and **d**. The annealing periods for sample **a**, **b**, **c** and **d** were 5, 7, 9 and 11h. The standard XRD patterns for Li_3PO_4 , $\text{Li}_2\text{NiFe}_2\text{O}_4$ and NiFe_2O_4 were also plotted.

Fig. 2 EDS spectra for all the resultant samples that were sintered at 800 °C for various periods in air. Pattern **a**, **b**, **c** and **d** correspond to sample **a**, **b**, **c** and **d**.

Fig.3. FTIR spectra for the as-synthesized samples. Spectrum **a**, **b**, **c** and **d** correspond to sample **a**, **b**, **c** and **d**.

Fig.4. SEM images of the resultant samples. Image **A**, **B**, **C** and **D** correspond to sample **a**, **b**, **c** and **d**. The direct magnification was 50.0K.

Fig.5. TEM images for the resultant samples. Image **A**, **B**, **C** and **D** correspond to sample **a**, **b**, **c** and **d**. The direct magnification was 150K.

Fig.6A. The first galvanostatic charge-discharge curves of the as-synthesized samples obtained at a current density 100 mA g⁻¹ rate. The curves of **a**, **b**, **c** and **d** correspond to sample **a**, **b**, **c** and **d**.

Fig.6B. The galvanostatic charge-discharge curves of the second cycle for all the as-synthesized samples obtained at a current density 100 mA g⁻¹ rate. The curves of **a**, **b**, **c** and **d** correspond to sample **a**, **b**, **c** and **d**.

Fig.7A. Cycling performance of the as-prepared samples at the current density of 100mA g⁻¹ for 20 cycles.

Fig.7B. Coulombic efficiency vs. cycle number for $\text{Li}_2\text{NiFe}_2\text{O}_4$ obtained at 800°C for 5, 7, 9, and

11h at a current density of 100 mA g⁻¹.

Fig.7C. The rate performance of (a) Li₂NiFe₂O₄ prepared at 800 °C for 9h and (b) 11h. The sample was cycled 10 times at each rate and forwarded to the next step.

Fig.8A. Cyclic voltammograms of the 9h-annealed Li₂NiFe₂O₄ electrode for the 1st, 2nd, 3rd cycle at a scan rate of 0.5mV s⁻¹ between 0 and 3.00 V(vs. Li/Li⁺) at room temperature.

Fig.8B. Cyclic voltammograms of the as-prepared electrodes for the 3rd cycle at a scan rate of 0.5 mV s⁻¹.

Fig.9. Nyquist plots of electrochemical impedance of the cells including the as-prepared samples.

Plots **a**, **b**, **c** and **d** correspond to the resultant anode materials **a**, **b**, **c** and **d**.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6A

Figure 6B

Figure 7A

Figure 7B

Figure 7C

Figure 8A

Figure 8B

Figure 9