



# Iron-nickel spinel oxide as an electrocatalyst for non-aqueous rechargeable lithium-oxygen batteries



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## ABSTRACT

A lithium-oxygen (Li–O<sub>2</sub>) battery requires effective catalyst to enable oxygen reduction and evolution. Herein, we report the synthesis of novel macroporous NiFe<sub>2</sub>O<sub>4</sub> nanoparticles by a facile and cost-effective urea assisted co-precipitation process. Characterization of the catalysts by X-ray diffraction and transmission electron microscopy confirms the formation of a single phase NiFe<sub>2</sub>O<sub>4</sub> structure. The use of macroporous NiFe<sub>2</sub>O<sub>4</sub> particles as oxygen electrode catalyst in rechargeable Li–O<sub>2</sub> batteries, exhibits a superior catalytic activity with high reversible capacity of 5940 mA h g<sup>−1</sup>. Additionally, catalytic activity results in low charge over potential and comparable discharge capacity and cycling stability, indicating its potential as a promising catalyst for Li–O<sub>2</sub> batteries. The simple and cost effective chemical co-precipitation method can be explored for synthesis of another oxides based catalyst materials.

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## 1. Introduction

Increasing standards of living and rising population are leading to inevitable increase in global energy consumption [1–3]. Meeting to our energy needs in an environmentally and geopolitically sustainable fashion is likely the most important technological challenge facing society today. The ever-increasing demand for powering portable devices has generated a worldwide effort for development of high-energy-density power sources. Although advancements in lithium-ion battery technology in recent years have provided higher-power devices, this progress has not kept pace with the portable technologies, leaving a so-called power gap that is widely expected to grow in coming years. There is no expectation that current or even future lithium-ion batteries will ever reach this target because of the intercalation reaction mechanism limit in lithium-ion battery system. A novel energy system must be considered.

Metal–air batteries (e.g. Al, Mg, Si, Li) have attracted much attention as a possible alternative due to their relatively high

energy densities because the oxygen electrode of a metal–air battery utilizes oxygen from ambient air as reactant in the electrochemical reaction rather than storing heavy active materials as in other battery systems [4,5]. Among them, lithium–air batteries have received more attention recently due to their high theoretical specific energies, almost 10 times that of the state-of-the-art Li-ion battery technology. However, the oxygen reduction reaction (ORR) at the oxygen electrodes in an aprotic organic lithium electrolyte is well-known to limit the discharge rate and capacity of the lithium–O<sub>2</sub> batteries [6]. The use of an active oxygen electrode catalyst with porous architecture would increase energy storage capacity by facilitating the oxygen reduction reaction (ORR) during discharge and the oxygen evolution reaction (OER) during charge [7–10]. The commonly used catalyst includes transition metal oxides such as MnO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, NiCo<sub>2</sub>O<sub>4</sub>, and CoMn<sub>2</sub>O<sub>4</sub> [11–16]. A previous study shows that, Cobalt and manganese spinels are also highly potential candidates as electrocatalysts for bifunctional air electrodes because of high catalytic activity and good corrosion stability in alkaline solutions [17–19].

NiFe<sub>2</sub>O<sub>4</sub>, is a well-known iron-nickel spinel oxide (commonly named as ferrite), has an inverse spinel structure with Ni<sup>2+</sup> and half of the Fe<sup>3+</sup> cation occupying the octahedral site and the remaining Fe<sup>3+</sup> on the tetrahedral site, Fe<sup>3+</sup>[Ni<sup>2+</sup>, Fe<sup>3+</sup>]<sub>2</sub>O<sub>4</sub> [20]. In recent

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times,  $\text{NiFe}_2\text{O}_4$  has gained much research interest owing to its electrochemical application such as supercapacitors and LIBs [21–25]. But upto our best knowledge, there are only few reports on the  $\text{NiFe}_2\text{O}_4$  as oxygen electrode catalyst for Li– $\text{O}_2$  batteries. In the present work macroporous  $\text{NiFe}_2\text{O}_4$  particles synthesized by simple and cost-effective chemical co-precipitation method were investigated as oxygen electrode catalyst in Li– $\text{O}_2$  batteries.

## 2. Experimental

The macroporous spinel  $\text{NiFe}_2\text{O}_4$  was synthesized by urea assisted co-precipitation method.  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$  (2 mM, 99% Junsei, Japan),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (1 mM, 99% Junsei, Japan), and  $\text{NH}_2\text{CONH}_2$  (1M, 99% Aldrich) were dissolved in distilled water under vigorous stirring with maintained pH. Then, the obtained homogeneous solution was kept at 90 °C for 10 h to yield a precipitate. Furthermore, the obtained precipitate was washed several times with deionized water and ethanol to remove the organic impurities and dried in vacuum oven for overnight at 100 °C. Then, the as prepared hydrated precursor powder was annealed at 500 °C for 2 h with heating rate of 3 °C per min in air atmosphere.

### 2.1. Material characterization

Thermo-gravimetric analysis (TGA) measurement was carried out using Perkin Elmer (USA) TGA7 Thermogravimetric analyzer at a rate of 3 °C  $\text{min}^{-1}$  in air atmosphere. The microstructure and morphology of the annealed sample was characterized by X-ray diffraction (XRD, Rigaku DIII Ultima with  $\text{Cu K}\alpha$  radiation) with  $2\theta$  range from 5 to 80° and field-emission scanning electron microscopy (FE-SEM, S-4700 Hitachi) equipped with energy dispersive spectroscopy (EDS) and high-resolution transmission electron microscopy (HR-TEM, Philips Tecnai F20 at 200 kV). The FE-SEM mapping technique used to analyse the distribution of Co, Ni and O elements. X-ray photoelectron spectrum (XPS) was measured by using an ESCALAB-MKII spectrometer (UK) with Al  $\text{K}\alpha$  radiation (1486.6 eV) as the X-ray source for excitation, and the binding energies (BEs) were evaluated using  $\text{C}_{1s}$  spectrum (BE = 284.6 eV) as reference with the accuracy of  $\pm 0.1$  eV. The surface area and pore size distribution of the sample can be determined based on the nitrogen adsorption and desorption isotherms using Brunauer–Emmett–Teller (BET, Micromeritics ASAP2010 Instrument Co., Norcross, GA, USA).

### 2.2. Electrochemical measurements

The electrochemical measurements were performed using CR-2032 coin cells. The coin cells assembled in high purity argon filled glove box. The oxygen electrodes were prepared by roll pressing the mixture of 70 wt% Ketjen black (carbon source), 20 wt% spinel  $\text{NiFe}_2\text{O}_4$  (catalyst), 10 wt% polyvinylidene difluoride in N-methyl pyrrolidinone (binder) on current collector and dried at 80 °C overnight in a vacuum oven. The lithium metal is used as anode electrode and electrolyte was tetra-ethylene glycol dimethyl ether containing 1M lithium bis(trifluoromethane) sulfonamide (LiTFSI-TEGDME). Between the anode and oxygen electrodes there was separator (glass microfiber, Whatman, GF/F, 150) soaked with electrolyte. Galvanostatic discharge-charge measurements were carried out on WON-A-TECH potentiostat/Galvanostat at a current density of 0.2 mA  $\text{cm}^{-2}$  between 2.0–4.1 V (Vs. Li/Li<sup>+</sup>) in a pure  $\text{O}_2$  atmosphere. The AC impedance measurements of spinel Li– $\text{O}_2$  cell were carried out before and after cycling using the ZIVE SP2 instrument in the 1 Hz–1 MHz frequency range at voltage amplitude of 10 mV.

## 3. Results and discussion

Macroporous  $\text{NiFe}_2\text{O}_4$  nanoparticles were synthesized by chemical co-precipitation method. In the particular process, Ni and Fe chloride precursors and urea were mixed in aqueous solutions and kept in preheated bath to yield precipitate. (See experimental section for details, Electronic Supplementary Information, ESI). Fig. 1 shows the thermal gravimetric analysis (TGA) of the as synthesized precursor. The net weight loss of 14.5% was occurred in the temperature range R.T to 490 °C. The initial weight loss is owing to the removal of water of crystallization and weight loss at higher temperature corresponding to conversion of hydroxyl-carbonate to oxide. Fig. 2a shows the X-ray diffraction (XRD) pattern of calcined precipitate powder at 500 °C for 2 h. All detected diffraction peaks are assigned as  $\text{NiFe}_2\text{O}_4$  with face centred cubic and Fd3m space group (JCPDS file No: 10-0325) and are indexed with the lattice parameter of  $a = 8.3367$  Å. The morphology and structure of the spinel  $\text{NiFe}_2\text{O}_4$  catalyst are investigated by FE-TEM as demonstrated in Fig. 2b–c. The FE-TEM image reveals the spinel  $\text{NiFe}_2\text{O}_4$ , composed of nanoparticle ranging from 50 to 200 nm, as shown in Fig. 2c. The large particles may be formed by aggregation of nanoparticles.

The HR-TEM image for  $\text{NiFe}_2\text{O}_4$  particle is shown in Fig. 2d confirms the unidirectional fringe pattern and thereby indicates the high crystalline nature of sample. The measured interlayer spacing is 0.48 nm, which corresponds to the (111) plane. The corresponding selected area electron diffraction (SAED) pattern in this region is shown in inset of Fig. 2d. All the diffraction rings in this pattern can be indexed to the spinel  $\text{NiFe}_2\text{O}_4$  crystal structure. The individual composition of Ni, Fe and O in spinel  $\text{NiFe}_2\text{O}_4$  was analysed by FE-SEM EDS analysis as shown in Fig. S1. The EDS analysis reveals that the Fe/Ni ratio was ~2.2 in the spinel  $\text{NiFe}_2\text{O}_4$ , which is close to designed ratio. Additionally, Fig. 3 shows the XPS survey spectra of macroporous  $\text{NiFe}_2\text{O}_4$  and individual spectral features of Ni, Fe and O. The Fe/Ni ratio obtained from XPS analysis was ~2.15, which is in good agreement with FE-SEM EDS analysis result.

Apart from catalytic activity, it also important for  $\text{O}_2$  electrode to possess high surface area and high electrical conductivity to achieve large specific capacities of Li– $\text{O}_2$  batteries [15]. Fig. 4 shows  $\text{N}_2$  adsorption–desorption isotherm recorded for spinel  $\text{NiFe}_2\text{O}_4$ . The obtained isotherm could be classified as type-III isotherm and were

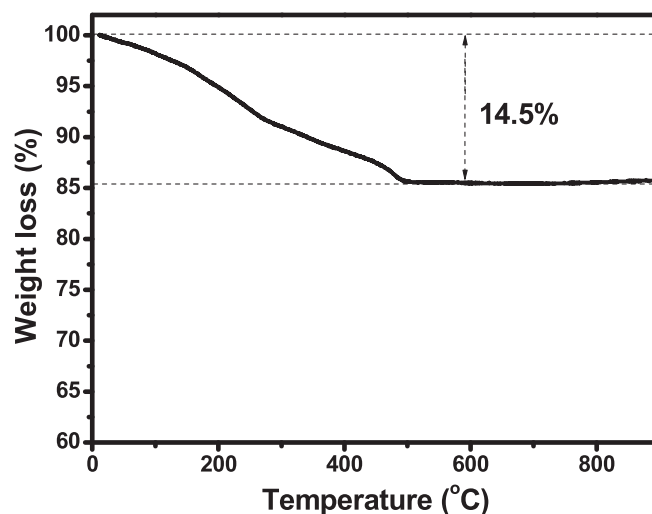


Fig. 1. TGA profiles of the  $\text{NiFe}_2\text{O}_4$  under air flow with a temperature ramp of 3 °C  $\text{min}^{-1}$ .

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