



# Mesoporous spinel ferrite composite derived from a ternary MgZnFe-layered double hydroxide precursor for lithium storage



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## ABSTRACT

Layered double hydroxides (LDHs), also known as hydrotalcite-like anionic clays, are very convenient precursors with a tunable flexibility toward multifunctional nanomaterials, especially in energy storage. Typical methods to improve lithium storage are to introduce additional or self-generating carbonaceous supports to LDH-derived transition metal oxides as anode nanomaterials which can host lithium mainly through a conversion mechanism. Here, we describe a preparation of mesoporous spinel ferrite composite (MgFe<sub>2</sub>O<sub>4</sub>/ZnFe<sub>2</sub>O<sub>4</sub>) for lithium storage, which is assisted by a combined conversion and alloying mechanism. The composite is derived by a thermal decomposition of a scalably produced single-resource precursor of ternary Mg<sup>2+</sup>Zn<sup>2+</sup>Fe<sup>3+</sup>-layered double hydroxide (Mg<sup>2+</sup>Zn<sup>2+</sup>Fe<sup>3+</sup>-LDH), and subsequent selective etching. Electrochemical test shows that the electrode delivers an exceptional electrochemical performance, i.e., a reversible capacity of 1190 mA h g<sup>-1</sup> after 100 cycles at 100 mA g<sup>-1</sup>, and, in particular, a reversible capacity of 981 mA h g<sup>-1</sup> at 500 mA g<sup>-1</sup> after 330 cycles, as well as a reversible capacity of 541 mA h g<sup>-1</sup> at 2000 mA g<sup>-1</sup> after 1000 cycles. The high electrochemical performance could be attributed to the following features: the combined alloying and conversion mechanisms of ZnFe<sub>2</sub>O<sub>4</sub>, synergistic MgFe<sub>2</sub>O<sub>4</sub>, and slight-content MgO as a non-active matrix, as well as an appropriate specific area and mesoporous size distribution. Our results show that the cation-tunable LDH precursor-derived synthesis route might be an alternative to prepare multiple-component composites of spinel ferrites and transition metal oxides.

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## 1. Introduction

Layered double hydroxides (LDHs), also known as hydrotalcite-like anionic clays, have attracted increasing interest in various potential applications, especially including electrochemical energy storage and conversion [1–7]. LDHs with structure based on Mg(OH)<sub>2</sub>-like layers, possess the general formula of [M<sup>2+</sup><sub>1-x</sub>M<sup>3+</sup><sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup>(A<sup>n-</sup>)<sub>x/n</sub>·yH<sub>2</sub>O, in which cationic M<sup>2+</sup> (such as Mg<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, and Co<sup>2+</sup>) and M<sup>3+</sup> (such as Al<sup>3+</sup>, Fe<sup>3+</sup>, and Co<sup>3+</sup>) are well-orderedly occupied within a LDH layer, A<sup>n-</sup> anions (such as CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and surfactant anion) are well-intercalated between the LDH interlayer galleries, and the value (x) of M<sup>3+</sup>/(M<sup>2+</sup> + M<sup>3+</sup>) molar ratio ranges typically between 0.2 and 0.33. Despite the huge

family, the LDHs could be basically recognized as convenient precursors with a unique feature to easily tune the types of metal cations and intercalated anions, as well as M<sup>2+</sup>/M<sup>3+</sup> molar ratios over a wide range, which have enabled the LDHs as tunable precursors to prepare electrode nanomaterials for lithium ion batteries (LIBs).

Two main approaches have hitherto been applied to prepare LDH precursor-derived products as anode nanomaterials for LIBs. On one hand, transition metal oxide/spinel/carbon composites were prepared typically by calcining tunable LDH precursors supported on the *additionally introduced* carbon (such as carbon nanotube (CNT) and graphene (G)). The TMOs/carbon composites included CoFe<sub>2</sub>O<sub>4</sub>/CNT [8], CoO/CoFe<sub>2</sub>O<sub>4</sub>/G [9], and NiO/NiFe<sub>2</sub>O<sub>4</sub>/G [10] derived from Co<sup>2+</sup>Fe<sup>2+</sup>Fe<sup>3+</sup>-LDH/CNT, Co<sup>2+</sup>Fe<sup>3+</sup>-LDH/G, and Ni<sup>2+</sup>Fe<sup>3+</sup>-LDH/G precursors, respectively, which were able to exhibit highly cycling stability and rate capability compared with the spinels without carbonaceous support. On the other hand, diverse spinel/carbon composites were also synthesized via the

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utilization of the *self-generating* carbon during the carbothermal process of different LDH/organic molecule precursors. Such spinel/carbon composites included Ni@NiO/Al<sub>2</sub>O<sub>3</sub>/C from a NiAl-LDH/glucose mixture [11], and C-NiO/NiFe<sub>2</sub>O<sub>4</sub> derived by a rapid catalyzing C<sub>2</sub>H<sub>2</sub> flow on NiFe-LDH surface at 300 °C via chemical vapor deposition (CVD) [12]. The self-generating carbon is able to greatly promote the cycling stability and rate capability of the resulting spinel/carbon composites, with the aid of the high conductivity of the self-generating carbonaceous nanomaterials. Indeed, both types of spinel-containing composites delivered the high electrochemical performances, which were based mainly on the conversion mechanism of the nanosized active transition metal oxide/spinel and also benefit from the additionally introduced or self-generating conductive carbonaceous supports.

In this present study, we describe a preparation of MgFe<sub>2</sub>O<sub>4</sub>/ZnFe<sub>2</sub>O<sub>4</sub> composite as a conversion/alloying nanomaterials for lithium storage. The carbon-free composite was prepared via a thermal decomposition of a scalably prepared Mg<sup>2+</sup>Zn<sup>2+</sup>Fe<sup>3+</sup>-LDH single-source precursor and subsequent selective etching (Scheme 1), and thus endowed with the features of boosting the electrochemical performances: conversion/alloying ZnFe<sub>2</sub>O<sub>4</sub>, synergistic active MgFe<sub>2</sub>O<sub>4</sub>, and low-content non-active MgO, as well as an appropriate specific area and mesoporous size distribution. Electrochemical test shows that the composite is indeed able to deliver the expected electrochemical performances.

## 2. Experimental

### 2.1. Preparation of Mg<sup>2+</sup>Zn<sup>2+</sup>Fe<sup>3+</sup>-LDH precursor

The Mg<sup>2+</sup>Zn<sup>2+</sup>Fe<sup>3+</sup>-LDH precursor was prepared via a scalable procedure of separate nucleation and aging steps (SNAS) [13]. In brief, a salt solution, which contained Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O with a (Mg+Zn)/Fe molar ratio of 2: 1, was obtained via dissolution of the salts into a freshly deionized water to yield a resulting solution with a total cationic concentration of 1.2 M. An aqueous base solution was also acquired, with a fixed concentration of NaOH ([OH<sup>-</sup>] = 1.6([Mg<sup>2+</sup>] + [Zn<sup>2+</sup>] + [Fe<sup>3+</sup>]) and Na<sub>2</sub>CO<sub>3</sub> ([CO<sub>3</sub><sup>2-</sup>] = 2[Fe<sup>3+</sup>]). The as-prepared solutions were introduced automatically and simultaneously into a commercial chemical reactor operated at a rotor speed of 3000 rpm. The resulting slurry was mixed continuously for 2 min, then collected, and aged at 70 °C for 48 h. The Mg<sup>2+</sup>Zn<sup>2+</sup>Fe<sup>3+</sup>-LDH precursor was obtained by centrifugation, then rinsing thoroughly the slurry several times with alternate deionized water and ethanol, and finally by drying in vacuum at 60 °C overnight.

### 2.2. Preparation of MgFe<sub>2</sub>O<sub>4</sub>/ZnFe<sub>2</sub>O<sub>4</sub>/MgO composite

The composite was prepared by calcining the as-prepared Mg<sup>2+</sup>Zn<sup>2+</sup>Fe<sup>3+</sup>-LDH precursor. The calcination was carried out in

a muffle furnace at 900 °C for 3 h with a ramping rate of 5 °C/min. The calcined product was then rinsed by carefully stirring in an aqueous solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (10 wt %) at 70 °C for 48 h to remove the partial MgO, and then in aqueous solution of NaOH (1 M) at 40 °C for 5 h to remove ZnO completely.

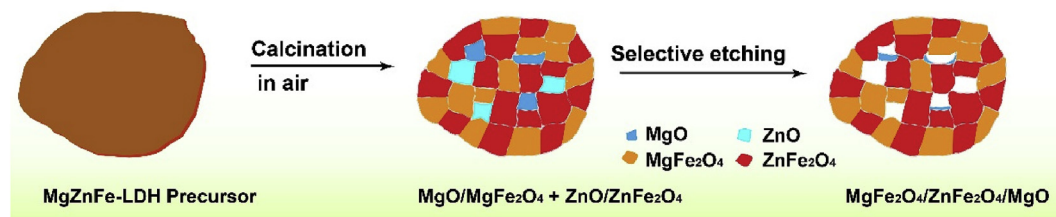
For comparison of XRD patterns, the mixture of MgFe<sub>2</sub>O<sub>4</sub> and ZnFe<sub>2</sub>O<sub>4</sub> was prepared by physically mixing the individual MgFe<sub>2</sub>O<sub>4</sub> and ZnFe<sub>2</sub>O<sub>4</sub>. The individual MgFe<sub>2</sub>O<sub>4</sub> and ZnFe<sub>2</sub>O<sub>4</sub> were derived from MgFe-LDH and ZnFe-LDH precursors obtained under the same experimental conditions, respectively. Effective removals of MgO and ZnO were performed by using HCl aqueous solution (1 M) at 80 °C for 3 h and NaOH aqueous solution (1 M) at 40 °C for 5 h, respectively.

### 2.3. Characterization

Powder X-ray diffraction (XRD) was used on a powder diffractometer (Rigaku XRD-6000, Cu-Kα radiation, λ = 1.542 Å) operated at a scanning speed of 10°/min. To acquire sample morphology, scanning electron microscopy (SEM) images were recorded on a Zeiss Supra 55 instrument. Transmission electron microscopy (TEM) observation was carried out on an electron microscope (JEOL JEM-2100) with an equipped EDX, which was operated at an accelerating voltage of 200 kV. The samples for SEM and TEM visualizations were dispersed in ethanol via sonication and then deposited manually onto silicon wafer or copper microgrid. Elemental analysis was conducted for metal ions by using an inductively coupled plasma emission spectrometer (ICP-ES, Shimadzu). Specific surface area and pore size distribution were determined quantitatively from nitrogen adsorption/desorption isotherms collected at 77 K on a Nova 1200, Quantachrome apparatus. For the pre-treatments before the measurement, the sample was kept for drying in vacuum at 393 K for 8 h. The surface area was computed via the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was calculated through the Barrett–Joyner–Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) measurement was applied on an X-ray Photoelectron Spectrometer (Kratos Axis ULTRA) assembled with a 165 mm hemispherical electron energy analyser.

### 2.4. Electrochemical measurement

The assembly of all Swagelok-type cells was conducted in a commercial argon-filled glove box. To prepare the working electrodes, a mixer was prepared by using active material/poly(vinyl difluoride) (PVDF)/super-P acetylene black at 70/10/20 (wt %), and then carefully pasted on a clean surface of Cu foil. The loading mass of the composite was ca. 10 mg cm<sup>-2</sup>. Lithium foil and glass fiber (GF/D, both from Whatman) were utilized as the counter electrode and the separator, respectively. The electrolyte consisted of a solution of 1 M LiPF<sub>6</sub> salt, which was dissolved into a solvent mixture of ethylene carbonate (EC): dimethyl carbonate (DMC): diethyl



**Scheme 1.** Schematic illustration of preparing mesoporous MgFe<sub>2</sub>O<sub>4</sub>/ZnFe<sub>2</sub>O<sub>4</sub>/MgO composite derived from a ternary MgZnFe-LDH precursor: initial calcination at 900 °C in air, subsequent partial removal of MgO by (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution and removal of ZnO by NaOH solution.

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