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Inverse spinel transition metal oxides for lithium-ion storage with different discharge/charge conversion mechanisms

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A B S T R A C T

Inverse spinel transition metal oxides (Fe_3O_4, $MnFe_2O_4$, Fe_3O_4/reduced graphene oxide and $MnFe_2O_4$/reduced graphene oxide) are prepared by a facile ethylene-glycol-assisted hydrothermal method. The stability of inverse spinel structure and the high specific surface area of nanoscale provide transition metal oxides with high specific capacity. And the surface modification with reduced graphene oxide improves the poor conductivity of pristine transition metal oxides. Pristine Fe_3O_4 and $MnFe_2O_4$ deliver the high initial discharge capacity of 1137.1 and 1088.9 mAh g^{-1}, respectively. Fe_3O_4/reduced graphene oxide and $MnFe_2O_4$/reduced graphene oxide get the reversible capacity of 645.8 and 720 mAh g^{-1}, respectively, even after 55 cycles. The different discharge/charge conversion mechanisms make them different capacity stability. The great electrochemical performances of composites offer electrodes with suitable characteristics for high-performance energy storage application.

1. Introduction

Anodes with stable structure have great significance to the application of energy storage devices. The common commercial anode, graphite with layer structure, undergoes the serious structure collapses during cycling, along with the layer deformation. And the anodes, $Li_4Ti_5O_{12}$-based materials with spinel structure have great structural stability due to the zero-strain effect [1,2]. However, the low specific capacity limits their application to the large-scale power devices [3]. Because of the high theoretical specific capacity [4], transition metal oxides with inverse spinel structure become the suitable candidates as anodes for lithium-ion storage. It is octahedral interstices and tetrahedral interstices of inverse spinel structure that provide lithium-ion with more shorter and unblocked channels to insert and move without serious volumetric changes. Liu [5] prepared inverse spinel Fe_3O_4 spheres with the reversible capacity of 956.2 mAh g^{-1} after 50 cycles at the current density of 100 mA g^{-1}; Wang [6] fabricated inverse spinel $MnFe_2O_4$ sphere with the reversible capacity of 710 mAh g^{-1} after 100 cycles at the current density of 100 mA g^{-1}; Zhu [7] prepared inverse spinel Fe_3O_4 by solvothermal method with the second discharge capacity of 800 mAh g^{-1} and the 35th discharge capacity of 661 mAh g^{-1} at the current density of 100 mA g^{-1}; Lin [8] prepared inverse spinel $MnFe_2O_4$ by solvothermal method with the second discharge capacity of 1000 mAh g^{-1} and the 35th discharge capacity of 400 mAh g^{-1} at the current density of 0.1C (about 93.3 mA g^{-1}). It is interesting to find that there is big difference in the capacity performances between Fe_3O_4 and $MnFe_2O_4$ [9–13], despite the similar theoretical specific capacity. The reversible capacity of $MnFe_2O_4$ is always lower than that of Fe_3O_4. It is because of different discharge/charge conversion mechanism. To thoroughly analyze the electrochemical behavior of inverse spinel transition metal oxides, Fe_3O_4 (FO) and $MnFe_2O_4$ (MFO) are taken as examples with the same manufacture process. Meanwhile, the high theoretical specific capacity determinates their potential values for lithium-ion storage. To further improve the electrochemical performances of inverse spinel structure, reduced graphene oxide (rGO) is introduced, due to its large

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specific surface area and high conductivity. The supporting of rGO sheets also further strengthens the structural stability of pristine transition metal oxides.

2. Experimental

2.1. Chemicals

All the chemicals are manufactured by Sinopharm Chemical Reagent Co., Ltd, except for polyvinylpyrrolidone (PVP, Aladdin Industrial Corporation).

2.2. Sample preparation

Graphite oxide (GO) is prepared by a modified Hummers method mentioned in literature [14]. $MnFe_2O_4$/reduced graphene oxide (MFG) is fabricated as follows: GO (20 mg) is dispersed in deionized water (20 mL) with ultrasonic treatment for 3 h; ethylene glycol (20 mL) and polyvinylpyrrolidone (0.2 g, 58000 (avg.) k29-32) are added with ultrasonic treatment for 10 min; $FeCl_3{\cdot}6H_2O$ (10 mL, 2 mol L^{-1}) and of $MnCl_2{\cdot}4H_2O$ (10 mL, 1 mol L^{-1}) is injected with stirring for 30 min; ammonia (1.5 mL, 25%) is injected with stirring for 1 h; $NaBH_4$ (0.02 g) is added with stirring for 10 min; the resulting dispersion is aged in an autoclave (100 mL) at 180 °C for 10 h; After cooled to room temperature, the samples are filtered and washed with distilled water repeatedly; MFG are precipitated by vacuum drying at 80 °C for 4 h; Finally, the dried products are calcined in a quartz tube at 500 °C for 3 h under a nitrogen atmosphere. MFO, FO, Fe_3O_4/reduced graphene oxide (FOG) and reduced graphene oxide (rGO) are synthesized by the similar method.

2.3. Characterization of the samples

The equipment models of X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectrophotometer (FT-IR), Raman Spectrometer and thermogravimetric analysis (TGA) are all same as mentioned in literature [42], and the equipment model of X-ray photoelectron spectroscopy (XPS) is mentioned in literature [43].

2.4. Electrochemical test

The preparation of cell and the equipment models of electrochemical measurements are all same as mentioned in literature [42]. The loading material of each electrode has the thickness of 130 ± 10 μm. And the loading mass on the electrode is

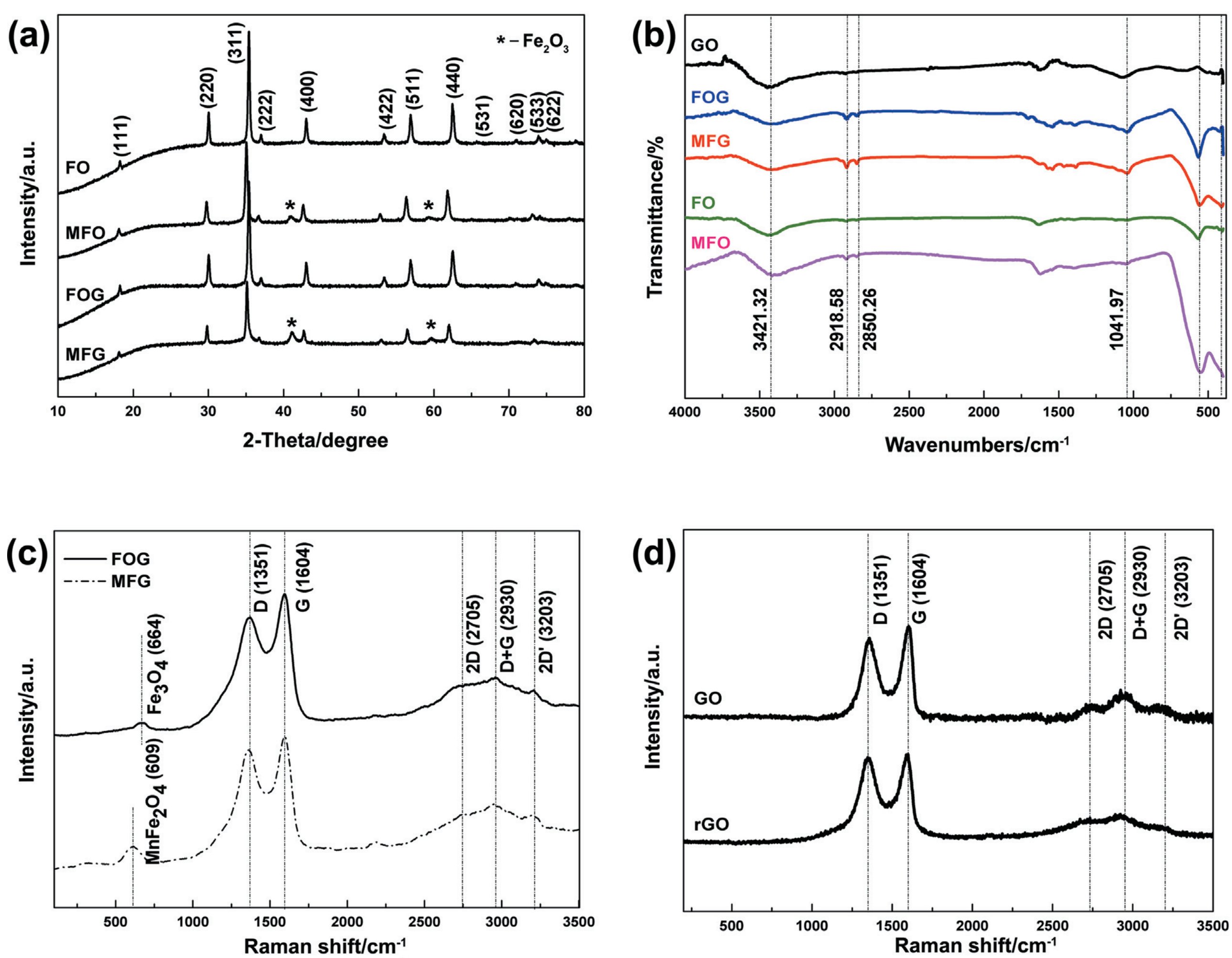

Fig. 1. (a) XRD pattern, (b) FT-IR and (c, d) Raman spectra of samples.