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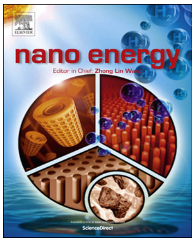

COMMUNICATION

Understanding the combined effects of microcrystal growth and band gap reduction for $Fe_{(1-x)}Ti_xF_3$ nanocomposites as cathode materials for lithium-ion batteries

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Microcrystal growth;
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Antagonistic effect

Abstract
Whether FeF_3 can take active part in electrochemical reaction is largely determined by its conductivity, which can be affected by the band gap and crystallite dimension. In this communication, the density of states (DOS) of FeF_3 and Ti-doped FeF_3 were calculated using a first principle density functional theory (DFT). Moreover, crystalline size was calculated according to Debye-Scherrer Equation. The results indicate that Ti-doping can reduce the band gap and impact the microcrystal growth of FeF_3 at the same time. Both effects work synergistically on capacity loss and cycling stability; while impact antagonistically on charge transfer resistance (R_{ct}), Li^+ diffusion coefficient (D_{Li}^+) and specific capacity, leading to the excellent electrochemical performances of $Fe_{(1-x)}Ti_xF_3$/C. The $Fe_{0.99}Ti_{0.01}F_3$/C nanocomposite achieves an initial capacity of 219.8 mA h/g and retains a discharge capacity of 173.6 mA h/g after 30 cycles at room temperature in the voltage range of 2.0–4.5 V. The hysteresis of discharge voltage plateau is significantly mitigated as well. In addition, the three-electron reaction of $Fe_{0.99}Ti_{0.01}F_3$/C during 1.0–4.5 V exhibits a high initial specific discharge capacity of 764.6 mA h/g. This study suggests that not only the band gap, but also the microcrystalline

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structure can be changed by Ti-doping, both of which have remarkable effects on the electrochemical properties, providing a new perspective on the effect of cation dopant.

Introduction

Lithium-ion batteries (LIBs) have been considered as the most promising energy storage devices for portable electronics, electric vehicles and large-scale energy storage [1-5]. Although the great progress has been made in the last decades, the commercial cathode materials (e.g., $LiCoO_2$, $LiFeO_4$) still have limited capacity, because of the fact that the intercalation mechanism allows only one electron transfer per transition metal [6]. In order to improve LIBs with satisfactory power and energy density, masses of new cathode materials have been explored [7]. Among them, multi-electron material, especially transition metal fluoride, has attracted substantial interest because all oxidation states of the active material can be utilized and high specific capacities are supplied, which is quite different from cathode materials based on intercalation mechanism [8-10]. For instance, BiF_3 [11,12], CuF_2 [13,14], NiF_2 [15], FeF_3 [16,17], FeF_2 [18], have been preferred as cathode materials of lithium-ion batteries and FeF_3 stands out due to its high potential, high specific capacity, low cost, and being environmental friendly.

Despite its remarkable features as a promising candidate for LIBs, poor electronic conductivity of FeF_3 limits its electrochemical activity, and prevents the use of high voltage metal fluorides in the macrocrystalline state [19]. FeF_3 as high voltage cathode material for LIBs was first studied by Arai et al. [20]. Due to the insulative characteristic of FeF_3, a low rechargeable capacity of only 80 mA h/g was detected, in the voltage range from 2.0 to 4.5 V. In recent years, high energy ball-milling with carbon to form carbon–metal-fluoride nanocomposites (CMFNCs) has been proved to be an effective way to improve the reversible capacity of FeF_3 [16,17,21-24], which can be attributed to increasing electronic conductivity and reducing the small grain size. In our previous work [25], FeF_3/C nanocomposite was synthesized through a one-step hydrothermal method followed by ball milling. However, the capacity and cycleability of FeF_3/C nanocomposite are still required to be improved.

TiF_3 has the same structure as FeF_3 and shows similar electrochemical activity [20,26]. In addition, Ti has been widely applied as doping element to improve cathode material performance due to its polyvalence and strong bond with nonmetalloid [27-30], but it has never been used in FeF_3. It is expected to understand if there is a synergistic effect of Ti-doping on the structure and the electrochemical performances of FeF_3. In this communication, the first principles calculations are employed to elucidate the reducing of band gap for FeF_3 after Ti-doping, which is similar to the phenomenon after Co-doping [31,32]. What is more interesting, we also find that microcrystal growth is induced by Ti-doping, which is confirmed by calculation according to Debye-Scherrer equation. A synergic-antergic mechanism is put forward to expound the combined effects of band gap reduction and microcrystal growth, providing an indepth understanding of how to design desired cathode material for LIBs.

Experimental

Preparation of $Fe_{(1-x)}Ti_xF_3/C$ nanocomposites

The preparation of $Fe_{(1-x)}Ti_xF_3/C$ nanocomposites is shown in Scheme 1. Firstly, $Fe_{(1-x)}Ti_xF_3 \cdot 3H_2O$ precursors were prepared by a facile hydrothermal method. In a typical experiment, 10.69 g $Fe(OH)_3$, TiO_2 (0 g, 0.08 g and 0.16 g) and 40 ml deionized water were added in a Teflon-lined stainless steel autoclave. After 1 h's stirring, 30 ml HF aqueous solution (40 wt%) was added. The autoclave was sealed and hydrothermally treated at 70 °C for 12 h. Then the lid of capsule was removed and the mixture was heated at 70 °C for another 12 h in order to remove the remaining HF and water. Subsequently the residue in bottle was dried at 80 °C in vacuum to obtain the $Fe_{(1-x)}Ti_xF_3 \cdot 3H_2O$ precursor, and the as-prepared precursor was heated at tube furnace (200 °C for 3 h and 300 °C for 3 h) in high-purity argon to remove the crystal water. Finally, carbon black (Super P, Timcal) was added ($Fe_{(1-x)}Ti_xF_3$: SP=85:15 by weight), and after high energy ball-milling at 300 rpm for 3 h, the mixture was converted into $Fe_{(1-x)}Ti_xF_3/C$ nanocomposites.

Structural characterizations

The crystal structures of the samples were characterized by X-ray diffraction (XRD, Rigaku DMA2400 X-ray diffractometer) with Cu Kα radiation. The diffraction patterns were recorded at room temperature in the 2θ range from 10° to 80°, and the scanning rate was 8°/min. The apparent morphologies of the as-prepared samples were characterized by scanning electron microscopy (SEM, JEOL JSM-6301 F). The successful Ti-doping in precursor was verified by energy dispersive X-ray spectroscopy (EDX).

First principal calculations

The density of states (DOS) and partial density of states (PDOS) of FeF_3 and Ti-doped FeF_3 were calculated using the first-principles density functional theory (DFT) through CASTEP software. The exchange-correlation functional energy was dealt with by means of the Perdew-Burke-Ernzonhof (PBE) function within the generalized gradient approximation (GGA) [33-35]. Besides, the on-site Coulomb interactions in the localized *d* electrons of the transition metal ions in the Ti-doped FeF_3 were taken into account