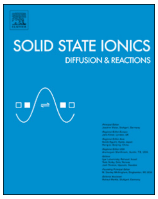
Solid State Ionics 324 (2018) 13–19

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi



Preparation and electrochemical performance of F-doped $Li_4Ti_5O_{12}$ for use in the lithium-ion batteries

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ARTICLE INFO

Keywords:
$Li_4Ti_5O_{12}$
F-doped
Electrochemical performance
Lithium-ion batteries

ABSTRACT

Spinel $Li_4Ti_5O_{12}$ doped with F was synthesized via the solid-state reaction of anatase TiO_2, Li_2CO_3, and NH_4F. The structural characterization and electrochemical performance evaluation of the prepared materials were carried out utilizing X-ray diffraction, scanning electron microscopy, galvanostatic charge-discharge, electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV) tests. The lattice parameters of all samples were calculated using an internal standard and Rietveld refinement method. The results indicate that the F was successfully doped into the lattice structure of $Li_4Ti_5O_{12}$, and this process did not influence the crystal structure and superficial morphology. Moreover, the best-performing material, $Li_4Ti_5O_{11.9}F_{0.1}$ delivers superior rate capacities of 165, 162.1, 160.0, 142.3, 125.1, and 99.2 mAh g^{-1}, at 0.2 C, 0.5 C, 1 C, 3 C, 5 C, and 10 C, respectively, which is higher than those of $Li_4Ti_5O_{12}$ (150.0, 135.0, 123.5, 93.7, 76.4, and 56.8 mAh g^{-1} at the same C-rates), and the cycling retention is 82.7% after 150 cycles at 5 C. Meanwhile, the charge-transfer resistance (R_{ct}) of $Li_4Ti_5O_{11.9}F_{0.1}$ (56.4 Ω) is lower than that of pure $Li_4Ti_5O_{12}$ (80.6 Ω), and the lithium-ion diffusion coefficients (D_{Li^+}) of $Li_4Ti_5O_{11.9}F_{0.1}$ (2.505×10^{-10} cm^2 s^{-1}) is higher than that of pure $Li_4Ti_5O_{12}$ (1.694×10^{-10} cm^2 s^{-1}).

1. Introduction

Spinel $Li_4Ti_5O_{12}$ is a promising anode material for use in lithium-ion batteries because of its zero-strain on the transformation of $Li_4Ti_5O_{12}$ to $Li_7Ti_5O_{12}$, excellent cycling stability and safer battery operation with a high voltage plateau around 1.55 V versus Li^+/Li, avoiding the formation of lithium dendrite during the over-charge process [1, 2]. Therefore, spinel $Li_4Ti_5O_{12}$ seems to be a promising alternative to carbon anode material for electric vehicles, hybrid electric vehicles and energy storage [3].

However, $Li_4Ti_5O_{12}$ in the unlithiated state is nearly electronically insulating (10^{-9} S cm^{-1}) because of the empty 3d orbitals of Ti^{4+} and the large band gap of about 2 eV [4]. Being such a strong insulator is a major disadvantage of pure $Li_4Ti_5O_{12}$ and has limited its use in practical applications. As a result, many research efforts in recent years have been focused on improving the electronic conductivity of $Li_4Ti_5O_{12}$ in order to utilize many of its promising properties.

Isovalent and aliovalent metal ions doping (e.g., Na^+, Mg^{2+}, Ca^{2+}, Al^{3+}; Fe^{3+}, Mo^{4+}, Mn^{4+}, Ta^{5+}, V^{5+}, and Nb^{5+}) or non-metal ions (e.g., F^- and Br^-) at Li^+, Ti^{4+} and O^{2-} sites have been used in enhancing the electronic conductivity of $Li_4Ti_5O_{12}$ [5–16]. The ions doping process can induce the reduction of Ti^{4+} to charge compensating Ti^{3+}, and the unstable trivalent titanium ions can serve as electron donors to increase the conductivity and decrease the electrode polarization of $Li_4Ti_5O_{12}$ materials [17]. In our previous work, we synthesized a Mg^{2+} and F^- co-doped $Li_4Ti_5O_{12}$ anode material, which exhibited a superior rate performance compared to one composed of pure $Li_4Ti_5O_{12}$ [18]. We found that Mg^{2+} and F^- had co-doped into the bulk phase $Li_4Ti_5O_{12}$ particles, resulting in an enhancement of the conductivity and electrochemical properties. Meanwhile, F-doping also enhanced the integrity of the $Li_4Ti_5O_{12}$ structure, which could increase the cycling performance of the $Li_4Ti_5O_{12}$ material. However, the systematic F-doped $Li_4Ti_5O_{12}$ anode materials were not synthesized. Hence, in this paper, the nano-sized F-doped $Li_4Ti_5O_{12}$ was prepared via a conventional solid-state reaction, and the structural and electrochemical performance of the F-doped $Li_4Ti_5O_{12}$ are reported herein.

2. Experimental

2.1. Synthesis and characterization

$Li_4Ti_5O_{12-x}F_x$ (x = 0, 0.1, 0.2, 0.3) samples were prepared via the

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https://doi.org/10.1016/j.ssi.2018.06.005
Received 27 April 2018; Received in revised form 14 May 2018; Accepted 3 June 2018
0167-2738/

solid-state method. The precursor mixture was composed of Li_2CO_3 (99.99%, Aladdin), anatase TiO_2 (99.8%, Aladdin) and NH_4F (98%, Aladdin), in a 4:5 M ratio of Li:Ti, mixed via ball milling for 4 h at a grind speed of 350 rpm, dispersed in deionized water, and then dried. The well-crystallized $Li_4Ti_5O_{12-x}F_x$ (x = 0, 0.1, 0.2, 0.3) was synthesized after that the precursor was calcined at 800 °C for 12 h in an air atmosphere and annealed at room temperature.

The crystal structures and phase composition of all samples were characterized by X-ray diffraction (XRD, Ultima IV, Rigaku) with Cu-Ka radiation utilizing silicon as the internal standard. The particle size and surface morphology of the samples were observed by scanning electron microscopy (SEM, MAIA3, Tescan).

2.2. Electrochemical measurements

The electrochemical performances of electrode materials were carried out with CR2032 coin cells, which were assembled in an argon-filled glove box. From here, the working electrode was obtained by following process that the slurry-coated copper foil was cut into circular electrodes with diameters of 14 mm and then dried at 105 °C for 12 h under vacuum. These electrodes contain the active material $Li_4Ti_5O_{12-x}F_x$ (x = 0, 0.1, 0.2, 0.3) with a super-P and polyvinylidene fluoride (PVDF) binder at an 85:10:5 weight ratio. The microporous polypropylene membrane (Celgard 2400, Celgard Inc., USA) and 1 mol L^{-1} $LiPF_6$ in ethylene carbonate, dimethyl carbonate, and diethyl carbonate (1:1:1 v/v/v) (Capchem Technology (Shenzhen) Co., Ltd., Shenzhen, China) were used as the separator and electrolyte, respectively.

Galvanostatic charge-discharge tests were carried out under different C-rates of 0.2 C, 0.5 C, 1 C, 3 C, 5 C, and 10 C (the current density is 160 mA g^{-1} at the 1 C rate) over a voltage range of 1–3 V using an automatic galvanostatic charge-discharge unit (Land 2001A, Wuhan, China). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on an electrochemical workstation (Interface 1000, Gamry, USA) with scan rates ranging from 0.1 to 5 mV s^{-1} between 1 and 3 V potential and a frequency range of 10 MHz to 100 kHz, respectively.

3. Results and discussion

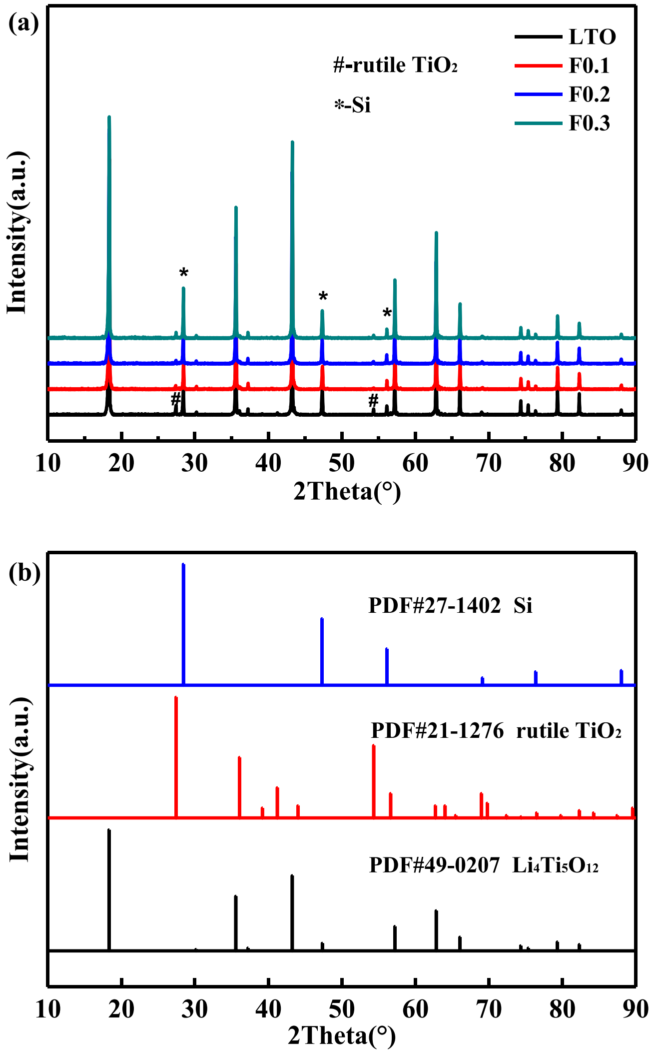

Fig. 1. (a) XRD patterns of all samples and (b) the standard XRD patterns of $Li_4Ti_5O_{12}$, rutile TiO_2, and Si.

Table 1
Lattice parameters of all samples.

Samples	Lattice parameters		Interplanar spacing
	α/Å	V/Å^3	d/Å
LTO	8.35653	583.54981	4.82479
F0.1	8.35562	583.35919	4.82426
F0.2	8.35535	583.30264	4.82411
F0.3	8.35529	583.29007	4.82407

As shown in Fig. 1(a), the powder XRD patterns of $Li_4Ti_5O_{12-x}F_x$ (x = 0, 0.1, 0.2, 0.3) exhibit sharp and well-defined diffraction peaks, and the standard XRD patterns of $Li_4Ti_5O_{12}$, rutile TiO_2, and Si are also shown in Fig. 1(b). An internal standard method and Rietveld refinement were used for lattice parameters analysis. Fig. 1(a) reveals that all diffraction peaks of $Li_4Ti_5O_{12-x}F_x$ (x = 0, 0.1, 0.2, 0.3) correspond to a cubic spinel structure from the Fd3m space group (ICSD No. 49-0207), and there are no obvious diffraction peaks, signifying a lack of other impurities in the XRD patterns of $Li_4Ti_5O_{12-x}F_x$ (x = 0, 0.1, 0.2, 0.3). This diffraction pattern also indicates that fluorine was doped into the lattice structure of $Li_4Ti_5O_{12}$ and did not influence its structure. In addition, the XRD patterns of $Li_4Ti_5O_{12-x}F_x$ (x = 0, 0.1, 0.2, 0.3) contain rutile TiO_2 peaks, marked with hash tags (#). These peaks result from a small amount of rutile TiO_2 existing within the lattice that was converted from unreacted anatase because of lithium evaporation during the calcination process [19]. The refined XRD results of $Li_4Ti_5O_{12-x}F_x$ (x = 0, 0.1, 0.2, 0.3) are shown in Table 1, which indicates that the lattice parameters decrease slightly after the F was doped into the $Li_4Ti_5O_{12}$. Notably, there were no apparent differences in lattice constant between these samples. These results are consistent with Vegard's rule for substitution, where the larger O^{2-} ion (0.140 nm) is replaced with the smaller F^- ion (0.133 nm) [20]. Fig. 2 shows the molecular structure of $Li_{21}Ti_{27}O_{64}$ and F-doped $Li_{21}Ti_{27}O_{63}F_1$ (x = 0.2), which have a composition similar to $Li_4Ti_5O_{12}$ and $Li_4Ti_5O_{11.8}F_{0.2}$, respectively. The ordered compound $Li_{21}Ti_{27}O_{64}$ with a 2 × 1 × 1 super cell was chosen to indicate the molecular structure of lithium titanate [6]. As shown in Fig. 2(a), the 3/4 Li atoms locate at tetrahedral 8a sites, the other Li atoms and all Ti atoms occupy the octahedral 16d sites, and O atoms are distributed at 32e sites in the Fd3m space group [15]. Moreover, the molecular structure of F-doped $Li_{21}Ti_{27}O_{63}F_1$ (x = 0.2) is shown in Fig. 2(b). By comparison of Fig. 2(a) and (b), the molecular structure of $Li_4Ti_5O_{12}$ has not changed after F doping and also belongs to the Fd3m space group, except that the unit-cell contains one F atom at 32e sites replacing one O atom [15].

The SEM images, as shown in Fig. 3, reveal the particle size and morphology of the $Li_4Ti_5O_{12-x}F_x$ (x = 0, 0.1, 0.2, 0.3) materials. As can be seen in Fig. 3(a–c), the first three samples of $Li_4Ti_5O_{12-x}F_x$ (x = 0, 0.1, 0.2) have homogeneous particle dimensions and no apparent differences in particle size of approximately with an average radius of