



## Short communication

Preparation and characterization of  $\text{Ti}^{4+}$ -doped  $\text{LiFePO}_4$  cathode materials for lithium-ion batteriesShe-huang Wu<sup>a,\*</sup>, Mao-Sung Chen<sup>a</sup>, Chao-Jung Chien<sup>b</sup>, Yen-Pei Fu<sup>b</sup><sup>a</sup> Department of Materials Engineering, Tatung University 40, Changshan N. Rd., Sec. 3, Taipei 104, Taiwan<sup>b</sup> Department of Materials Engineering, National Dong Hwa University 1, Da Hsueh Rd., Sec. 2, Shoufeng, Hualien 974, Taiwan

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## ABSTRACT

Olivine structured  $\text{LiFePO}_4$  (lithium iron phosphate) and  $\text{Ti}^{4+}$ -doped  $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$  ( $0.01 \leq x \leq 0.09$ ) powders were synthesized via a solution route followed by heat-treatment at  $700^\circ\text{C}$  for 8 h under  $\text{N}_2$  flowing atmosphere. The compositions, crystalline structure, morphology, carbon content, and specific surface area of the prepared powders were investigated with ICP-OES, XRD, TEM, SEM, EA, and BET. Capacity retention study was used to investigate the effects of  $\text{Ti}^{4+}$  partial substitution on the intercalation/de-intercalation of  $\text{Li}^+$  ions in the olivine structured cathode materials. Among the prepared powders,  $\text{LiFe}_{0.97}\text{Ti}_{0.03}\text{PO}_4$  manifests the most promising cycling performance as it was cycled with C/10, C/5, C/2, 1C, 2C, and 3C rate. It showed initial discharge capacity of  $135 \text{ mAh g}^{-1}$  at  $30^\circ\text{C}$  with C/10 rate. From the results of GSAS refinement for the prepared samples, the doped- $\text{Ti}^{4+}$  ions did not occupy the  $\text{Fe}^{2+}$  sites as expected. However, the occupancy of the doped  $\text{Ti}^{4+}$  ions are still not clear, and theoretical calculations are needed for further studies. From the variation of lattice parameters calculated by the least square method without refinement, it suggested that  $\text{Ti}^{4+}$ -doped  $\text{LiFePO}_4$  samples formed solid solutions at low doping levels while  $\text{TiO}_2$  was also observed with TEM in samples prepared with doping level higher than 5 mol%.

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## 1. Introduction

Since Sony Energy Tech Inc. published the first rechargeable lithium-ion batteries system in 1991, lithium-ion batteries have been extensively used for electronic products, such as digital cameras, laptop computers, and mobile phones. Because their high specific capacity, high energy density, low weight, excellent cycling performance, and low impact to environment, lithium-ion batteries have attracted a lot of attentions [1]. They had become the principal power sources for portable electronic devices. Several types of cathode materials have been introduced for lithium-ion batteries, such as  $\text{LiCoO}_2$  [2],  $\text{LiNiO}_2$  [3],  $\text{LiMn}_2\text{O}_4$  [4],  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  [5], and  $\text{LiFePO}_4$  [6,7]. Among the cathode materials,  $\text{LiFePO}_4$  has been recognized as one of the most promising cathode materials for large format lithium batteries because of its high theoretical capacity of  $170 \text{ mAh g}^{-1}$ , environmental benign, and high thermal stability since the report done by Padhi et al. was published in 1997 [8]. The three-dimensional framework structure of  $\text{LiFePO}_4$  is not built on close packing of oxygen anions, but built on  $\text{PO}_4^{3-}$  polyanions and octahedral  $\text{MO}_6$  groups ( $M = \text{Fe, Li}$ ) that make the cells comprised with this material manifest higher thermal sta-

bility than others. However, this material is suffered from its low electronic conductivity and low  $\text{Li}^+$  ions diffusivity in the  $\text{LiFePO}_4$  host structure. There are many possible ways to improve the rate capability of  $\text{LiFePO}_4$  materials, such as coating with conductive carbon [9,10], reducing the particle size [11], and doping with various cations [12–14]. In this study,  $\text{Ti}^{4+}$ -doped  $\text{LiFePO}_4$  ( $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$ ,  $0 \leq x \leq 0.09$ ) powders were prepared via a solution route. The physical and electrochemical properties of the prepared powders were investigated.

## 2. Experimental

$\text{Ti}^{4+}$ -doped  $\text{LiFePO}_4$  ( $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$ ,  $0 \leq x \leq 0.09$ ) powders were synthesized via a solution route. Iron powder (NC100.24, 99%, Hogan, Sweden) was dissolved in aqueous solution of citric acid (99.5%, Wako Pure Chem. Ind., Ltd., Japan) and  $\text{H}_3\text{PO}_4$  (85%, Wako Pure Chem. Ind., Ltd., Japan).  $\text{LiOH}$  (95%, Wako Pure Chem. Ind., Ltd., Japan),  $\text{TiO}_2$  (99.9%, Wako Pure Chem. Ind., Ltd.), and 10 wt% of sucrose were added into the iron-dissolved citric solution. Then the mixtures were heated and stirred at  $50^\circ\text{C}$  to become dry. The precursors were heated at temperatures ranging between 650 and  $750^\circ\text{C}$  for 8 h in flowing  $\text{N}_2$  atmosphere. The compositions, crystalline structures, morphologies, carbon content, and specific surface areas of the prepared powder were investigated by ICP-OES (Optima 2100, Perkin Elmer), XRD (beam line 01C2, NSRRC, Tai-

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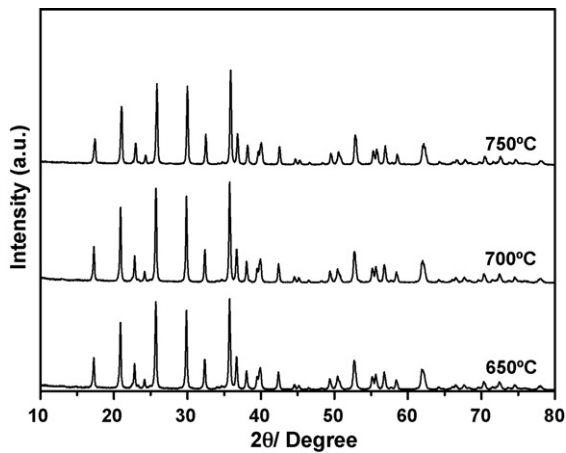


Fig. 1. XRD patterns of the  $\text{LiFePO}_4$  powders finally prepared at 650, 700, and 750 °C for 8 h, respectively.

wan), FEG-TEM (JEM-2100, JEOL), element analyzer (EA, Vario EL III, Heraeus Elementar), and BET (SA 3100, Beckman Coulter TM).

The composite cathodes were prepared by mixing with the prepared powders, acetylene black (99.99%, Strem Chemicals Inc., USA), and polyvinylidene fluoride (PVDF, Kynar 740, ELF, Germany) in the weight ratio of 83:10:7 with adequate amount of N-methyl-2-pyrrolidone (NMP, ultra, ISP Technologies Inc., U.S.A.) to become slurries. After coating on Al foil, cathode disks with diameter of 10 mm were prepared by drying, punching, and pressing. The prepared cathodes were assembled into CR2032 coin-type cells with Li anode and 1 M  $\text{LiPF}_6$  in EC-PC-DEC (volume ratio of 1:1:1) electrolyte (Tomiyama, Japan) in an argon-filled glove box. The capacity retention studies of the prepared powders were performed by cycling the coin-type cells with various C rates within cutoff voltages of 2.5 and 4.3 V at 30 °C.

### 3. Results and discussion

No significant composition difference among the powders prepared at temperatures between 650 and 750 °C was determined by ICP-OES. From the XRD patterns shown in Fig. 1, olivine structure (orthorhombic  $Pnma$ ) is observed exclusively in the pure  $\text{LiFePO}_4$  powders prepared by calcinations at 300 °C for 8 h and then heat-treatment at temperatures ranging between 650 and 750 °C for 8 h. The sample prepared at 700 °C exhibits larger values in calculated lattice parameters than others. It was also found the carbon content determined by EA decreased from 4.5 wt% in 650 °C prepared powder to 4 wt% in 750 °C sample, while the specific surface area determined by BET decreased linearly from 55 to 48  $\text{m}^2 \text{g}^{-1}$  as the heat-treatment temperature was increased from 650 to 750 °C.

The initial charge/discharge curves of the powders prepared at various temperatures are shown in Fig. 2. They show voltage plateaus at 3.41–3.45 V versus  $\text{Li/Li}^+$  as the cells were charged which corresponding to the phase transition from triphylite  $\text{LiFePO}_4$  to heterosite  $\text{FePO}_4$ , and voltage plateaus at 3.37–3.38 V as the cells were discharged. The initial specific discharge capacity of pure  $\text{LiFePO}_4$  samples heat-treated at 650, 700, and 750 °C are 120, 131, and 121  $\text{mAh g}^{-1}$  at C/10 rate, respectively. It is found that the sample prepared at 700 °C for 8 h does not only show the highest charge/discharge capacities, but also demonstrates the smallest voltage difference between charge and discharge plateaus among the samples prepared at various temperatures. Therefore,  $\text{Ti}^{4+}$ -doped  $\text{LiFePO}_4$  powders were heat-treated at 700 °C for 8 h thereafter.

From the results of the composition determination, it was found that the 700 °C prepared  $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$  powders show molar ratios

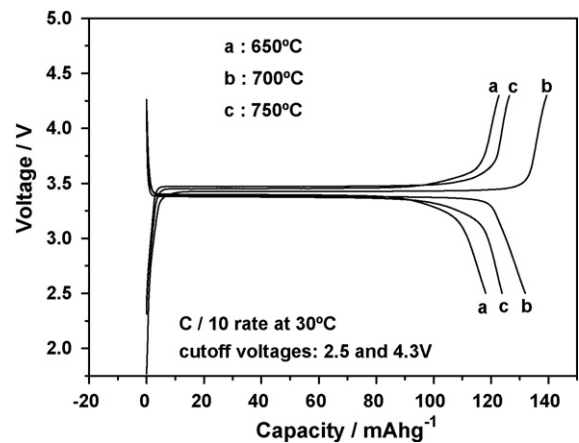


Fig. 2. Initial charge/discharge curves of the cells comprised with  $\text{LiFePO}_4$  powders prepared at 650, 700, and 750 °C for 8 h.

among Li, Fe, Ti, and P close to those of expected values, respectively. In addition to the olivine phase,  $\text{Li}_3\text{PO}_4$  phase is also detected in the  $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$  powders prepared by calcinations at 300 °C for 8 h and then heat treating at 700 °C for 8 h, as shown in Fig. 3. That may be attributed to the powders having been prepared without considering the valence effect [15].  $\text{Li}_3\text{PO}_4$  phase had been usually reported as impurity in aliovalent-doped  $\text{LiFePO}_4$  samples [16]. The patterns were refined with GSAS (General Structure Analysis Sys-

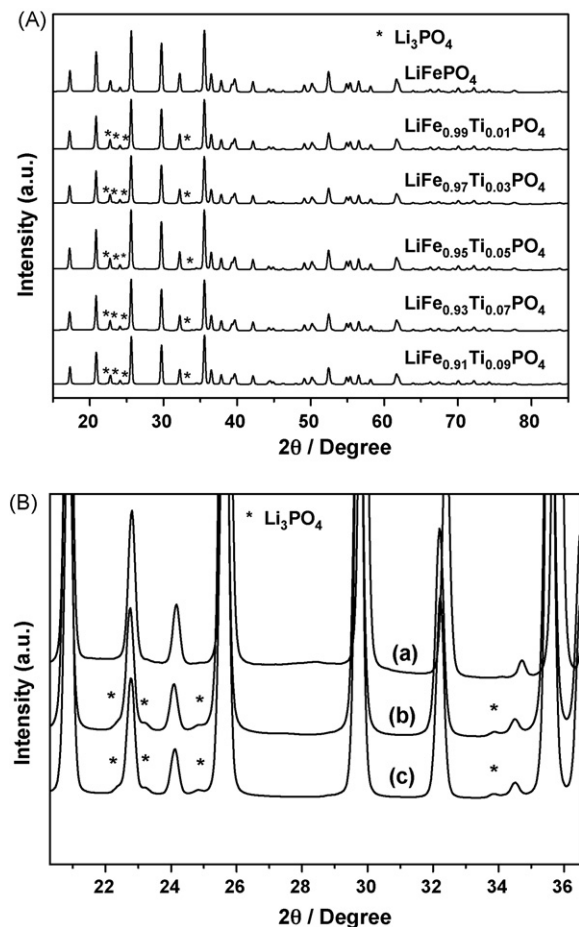
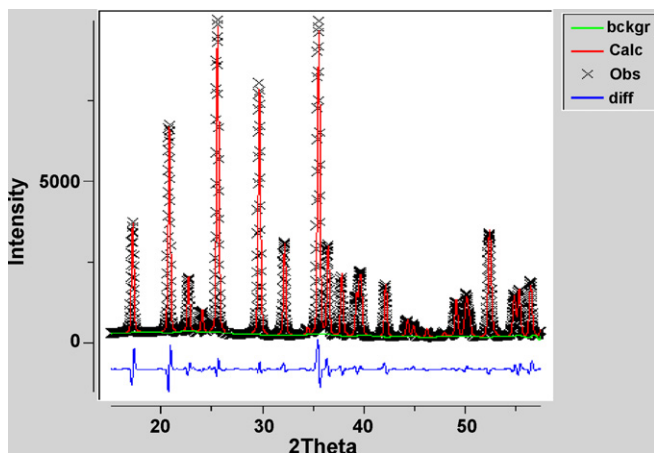


Fig. 3. (A) XRD patterns of  $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$  ( $0 \leq x \leq 0.09$ ) powders prepared at 700 °C for 8 h and (B) enlargements of the XRD patterns of (a)  $\text{LiFePO}_4$ , (b)  $\text{LiFe}_{0.99}\text{Ti}_{0.01}\text{PO}_4$ , and (c)  $\text{LiFe}_{0.91}\text{Ti}_{0.09}\text{PO}_4$  powders.

**Table 1**  
Lattice parameters of the 700 °C prepared  $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$  powders obtained from GSAS refinement by assuming  $\text{Ti}^{4+}$  ions occupy  $\text{Fe}^{2+}$  sites. The values in brackets were calculated by the least square method without refinement.

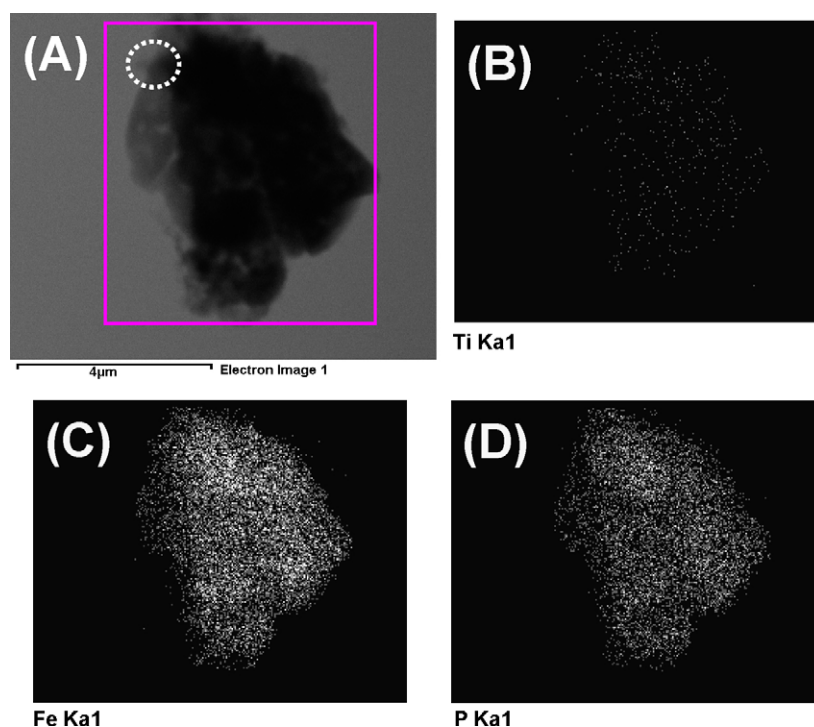
Sample	Lattice parameter		
	$a$ (Å)	$b$ (Å)	$c$ (Å)
$\text{LiFePO}_4$	10.2722(1) [10.30(4)]	5.9752(2) [5.99(0)]	4.6688(4) [4.696(6)]
$\text{LiFe}_{0.99}\text{Ti}_{0.01}\text{PO}_4$	10.3748(5) [10.31(7)]	6.0329(0) [6.00(9)]	4.7149(1) [4.699(6)]
$\text{LiFe}_{0.97}\text{Ti}_{0.03}\text{PO}_4$	10.3781(7) [10.30(2)]	6.0361(7) [6.03(8)]	4.7157(9) [4.706(8)]
$\text{LiFe}_{0.95}\text{Ti}_{0.05}\text{PO}_4$	10.3772(4) [10.29(6)]	6.0349(8) [5.99(2)]	4.7153(1) [4.694(6)]
$\text{LiFe}_{0.93}\text{Ti}_{0.07}\text{PO}_4$	10.3757(2) [10.29(4)]	6.0343(5) [5.98(6)]	4.7150(9) [4.697(2)]
$\text{LiFe}_{0.91}\text{Ti}_{0.09}\text{PO}_4$	10.3739(4) [10.29(2)]	6.0302(8) [5.99(0)]	4.7090(3) [4.702(8)]



**Fig. 4.** Typical results of Rietveld refinements with GSAS for  $\text{LiFe}_{0.97}\text{Ti}_{0.03}\text{PO}_4$  powder heat-treated at 700 °C for 8 h ( $R_{\text{wp}} = 4.48\%$  and  $R_p = 3.23$ ).

tem) until  $R_{\text{wp}} < 10\%$  and  $R_{\text{wp}}/R_p < 1.5$  by assuming  $\text{Ti}^{4+}$  ions occupy the  $\text{Fe}^{2+}$  sites. The typical results are shown in Fig. 4. The calculated lattice parameters of the 700 °C prepared  $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$  are shown in Table 1. Significant increases in parameters  $a$ ,  $b$ , and  $c$  are found when 1 mol% of  $\text{Fe}^{2+}$  ions were substituted by  $\text{Ti}^{4+}$  ions,

while the differences in  $a$ ,  $b$ , and  $c$  between those of  $\text{LiFe}_{0.99}\text{Ti}_{0.01}\text{PO}_4$  and  $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$  ( $0.03 \leq x \leq 0.09$ ) are small. The  $\text{LiFe}_{0.97}\text{Ti}_{0.03}\text{PO}_4$  sample exhibits the largest values in  $a$ ,  $b$ , and  $c$  among the prepared powders. Similar results were also obtained by simply combining the Bragg's law and the plane-spacing equation, shown in brackets in Table 1. These results seem not to be consistent with the expected results that the lattice parameters decrease with increasing amount of  $\text{Ti}^{4+}$  substitution for  $\text{Fe}^{2+}$  ions, since the ionic radius of  $\text{Ti}^{4+}$  is smaller than that of  $\text{Fe}^{2+}$ . That may support the suggestion of Islam et al. that  $\text{LiFePO}_4$  is not tolerant to aliovalent doping on energetic grounds [17]. However, titanium compounds were not detected in the  $\text{Ti}^{4+}$ -doped samples till doping level higher than 5 mol%. It can be supported by the uniform distribution of Ti ions in the  $\text{LiFe}_{0.97}\text{Ti}_{0.03}\text{PO}_4$  powders revealed by the EDX mapping performed with FEG-TEM, shown in Fig. 5. From the SAD pattern of the circled area, shown in Fig. 6, value of 2.562 Å for  $d_{311}$  of olivine was obtained by Gatan Digital-Micrograph. This value is higher than that of the un-substituted  $\text{LiFePO}_4$  (2.520 Å). These results manifest that the  $\text{Ti}^{4+}$ -doped samples may form solid solutions at low  $\text{Ti}^{4+}$ -doping levels while  $\text{TiO}_2$  particles form in samples with doping level higher than 5 mol%. Though these results suggest  $\text{Ti}^{4+}$  ions do not occupy  $\text{Fe}^{2+}$  sites, the occupancy of  $\text{Ti}^{4+}$  ions are still not clear and theoretical calculations are needed for further studies. Nevertheless, the enlargement in lattice parameters may enhance the diffusivity of  $\text{Li}^+$  ions in olivine structure as suggested by previous reports [18].



**Fig. 5.** (A) FEG-TEM photographs of the prepared  $\text{LiFe}_{0.97}\text{Ti}_{0.03}\text{PO}_4$  sample and the corresponding EDX of (B) Ti, (C) Fe, (D) P.

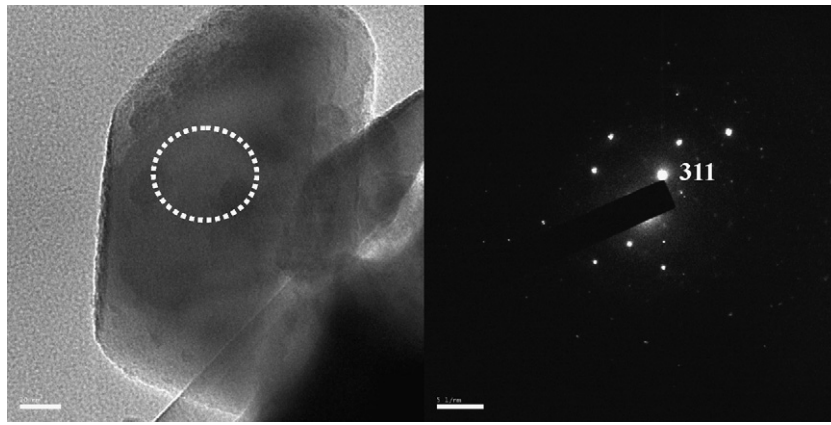


Fig. 6. SAD pattern of the circled area is shown in Fig. 5.

For comparison, the initial charge/discharge curves of the coin-type cells comprised with  $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$  ( $0 \leq x \leq 0.09$ ) samples are shown in Fig. 7. Voltage plateaus at 3.43–3.45 V versus  $\text{Li}/\text{Li}^+$  are observed during charge, whereas voltage plateaus at 3.35–3.38 V are found from the discharge curves of the prepared samples.  $\text{LiFe}_{0.97}\text{Ti}_{0.03}\text{PO}_4$  sample heat-treated at  $700^\circ\text{C}$  for 8 h shows the smallest voltage difference between the initial charge/discharge plateaus and the highest initial discharge capacity of  $135 \text{ mAh g}^{-1}$  among the prepared  $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$  ( $0 \leq x \leq 0.09$ ) samples as cells were cycled with C/10 rate.

The results of capacity retention study of the  $700^\circ\text{C}$  heat-treated  $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$  samples performed at  $30^\circ\text{C}$  with C/10 rate between cutoff voltages of 2.5 and 4.3 V are shown in Fig. 8. Negligible capacity fade and reversible capacities of 131, 126, 135, 123, 126, and  $109 \text{ mAh g}^{-1}$  are measured for cells comprised with various  $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$  samples with  $x=0, 0.01, 0.03, 0.05, 0.07,$  and  $0.09$ , respectively.  $\text{LiFe}_{0.97}\text{Ti}_{0.03}\text{PO}_4$  sample exhibits the highest reversible capacity among the prepared  $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$  ( $0 \leq x \leq 0.09$ ) powders. That may be attributed to the sample has the largest parameters in  $b$  and  $c$ , thus it shows higher  $\text{Li}^+$  ions diffusivity than others [19,20]. For comparison, the results of capacity retention study for cells comprised with  $\text{LiFePO}_4$  and  $\text{LiFe}_{0.97}\text{Ti}_{0.03}\text{PO}_4$  cathode materials cycled with C/10, 1C, and 3C rates are plotted in Fig. 9. Improvement in rate capability is also observed by  $\text{Ti}^{4+}$ -doping. It may also be attributed to the enlargement of the lattice parameters that make the diffusion of  $\text{Li}^+$  ions become easier than in  $\text{LiFePO}_4$ .

Comparing with the results reported by Wang et al. [21], a  $\text{Ti}^{4+}$ -doped sample,  $\text{LiFe}_{0.99}\text{Ti}_{0.01}\text{PO}_4$  prepared sol-gel route, exhibited specific discharge capacities of 165 and  $120 \text{ mAh g}^{-1}$  with C/8

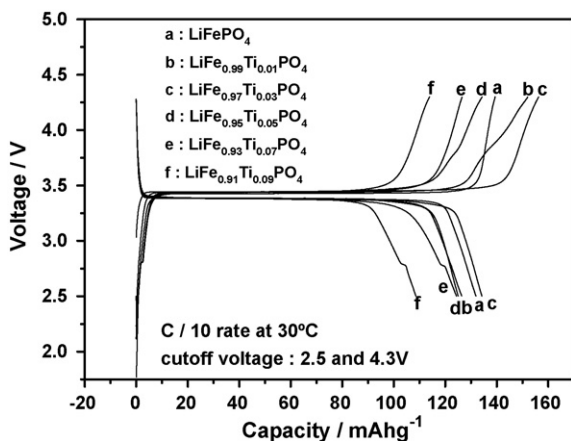


Fig. 7. Initial charge/discharge curves of the coin-type cells comprised with  $700^\circ\text{C}$  prepared  $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$  ( $0 \leq x \leq 0.09$ ) cathodes.

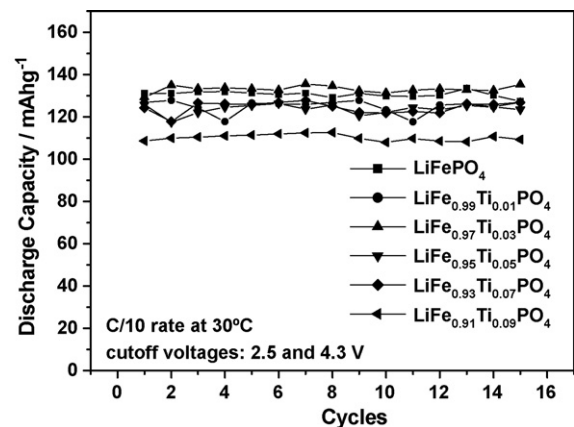


Fig. 8. Cycling performance of the coin-type cells comprised with  $700^\circ\text{C}$  prepared  $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$  ( $0 \leq x \leq 0.09$ ) powders with C/10 rate.

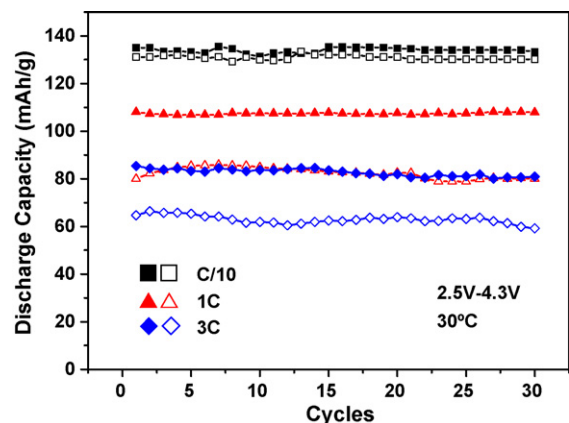


Fig. 9. Cycling performance of the cells comprised with  $\text{LiFe}_{0.97}\text{Ti}_{0.03}\text{PO}_4$  (filled) and  $\text{LiFePO}_4$  (open) electrodes prepared at  $700^\circ\text{C}$  with various C rates.

and C/2 rates, respectively. The specific reversible capacities of the  $\text{LiFe}_{0.97}\text{Ti}_{0.03}\text{PO}_4$  sample prepared in this study are lower than those reported previously. That may be caused by the differences in primary particle size of the prepared powders, composition and thickness of the prepared cathodes for testing.

#### 4. Conclusions

Olivine structured  $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$  ( $0 \leq x \leq 0.09$ ) powders were prepared via a solution route by dissolving iron powder in mixed

solution of citric acid and phosphoric acid. In addition to the olivine phase,  $\text{Li}_3\text{PO}_4$  phase was also observed in the  $700^\circ\text{C}$  heat-treated  $\text{LiFe}_{1-x}\text{Ti}_x\text{PO}_4$  samples. From the variation of lattice parameters with amount of  $\text{Ti}^{4+}$  doping,  $\text{Ti}^{4+}$ -doped samples became solid solutions at low  $\text{Ti}^{4+}$ -doping levels while  $\text{TiO}_2$  also formed as the doping level higher than 5 mol%.  $\text{Ti}^{4+}$  ions did not occupy the  $\text{Fe}^{2+}$  sites, though the details are still not clear.  $\text{LiFe}_{0.97}\text{Ti}_{0.03}\text{PO}_4$  sample showed the highest reversible capacity among the prepared powders and manifested improved rate capability. That may be attributed to it has larger lattice parameters in  $b$  and  $c$  than those of other samples prepared in this study. The  $\text{LiFe}_{0.97}\text{Ti}_{0.03}\text{PO}_4$  sample exhibited specific discharge capacity of 135, 127, 116, 107, and  $81 \text{ mAh g}^{-1}$  as it was cycled with  $C/10$ ,  $C/5$ ,  $C/2$ ,  $1C$ , and  $3C$  rates.

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