Molten Salt Synthesis of Different Ionic Radii Metallic Compounds Doped Lithium Titanate Used in Li-Ion Battery Anodes

Qingjun Guo¹, Qiang Wang¹, Gang Chen¹, Miao Shen² and Bing Li^{1,*}

¹East China University of Science and Technology, 130Meilong Road, Shanghai 200237, P.R. China

²Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, P.R. China

In order to systematically characterize the effects of ion doping on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) through the molten salt method, different metallic compounds with varying ionic radii doped into LTO were investigated. The results show that doped ions (Al^{3+} , Ni^{2+} , Fe^{2+} , Fe^{3+} and F^-) with similar ionic radius as Li^+ , Ti^{4+} or O^{2-} ions can enter into LTO, which leads to smaller particle size than pure LTO, therefore, increasing the specific surface area and shortening Li^+ transfer path of LTO. However, La^{3+} with a much larger ionic radius cannot enter into LTO. Ion doping can enhance the intrinsic conductivity of LTO, thus improving the electrochemical performance of LTO. As the ionic radii of Fe^{2+} and Fe^{3+} are the closest to those of Li^+ and Ti^{4+} , Fe_3O_4 doped LTO exhibits the best electrochemical performance, an excellent first discharge capacity of $269.3 \text{ mAh}\cdot\text{g}^{-1}$ at the 0.15 C, good high-rate capability ($123.4 \text{ mAh}\cdot\text{g}^{-1}$ at 10 C); even after 300 discharge/charge cycles, the discharge capacity is $141.1 \text{ mAh}\cdot\text{g}^{-1}$, gives an excellent cycle performance with 12.4% loss of capacity at 1 C rate. Due to these factors, Fe_3O_4 is the most suitable metallic compound doped in LTO via molten salt method. [doi:10.2320/matertrans.MK201607]

(Received August 30, 2016; Accepted December 5, 2016; Published February 25, 2017)

Keywords: molten salt, metallic compound, lithium titanate, lithium-ion battery

1. Introduction

Spinel-type lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO) with zero variation and high redox potential (ca. 1.55 V vs Li^+/Li) have garnered extensive attention owing to excellent reversibility in lithium insertion/extraction reactions and high safety^{1,2}. Its intrinsic advantages also include fast electrode kinetics enhanced and its high thermodynamic stability³. However, the low intrinsic electrical conductivity ($\sim 10^{-13} \text{ S cm}^{-1}$) and the inherently sluggish lithium-ion diffusion coefficient of bulk LTO greatly limit its rate capability, as well as its practical implementation⁴⁻⁹.

The improvement for the rate performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode have been widely studied over the past decade, which can be roughly divided into two strategies. One strategy is to improve electron transfer by ion doping, surface modification, and/or incorporation of carbon¹⁰⁻²⁶. The other approach is to reduce the electron and Li-ion diffusion lengths by producing nanostructured analogues of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ itself²⁷⁻³¹. Among these methods, ions doping can efficiently improve the intrinsic conductivity of LTO, smaller particle size can shorten the Li-ion transfer route, thereby improving the rate performance.

Commercially, LTO is synthesized by a conventional solid-state method. The process is usually assisted by long-time ball-milling and high-temperature sintering. The synthesized LTO materials are composed of bulk particles, inhomogeneous and hard to be removed from the reaction vessel. The molten salt synthesis method has shown more advantages in controlling composition, morphology, homogeneity and high crystallinity¹¹. In addition, the molten salt method is one of the most effective paths to one-step synthesis of multiple compounds, so it will be easier to introduce hetero-elements through molten salt method. For instance, Mn^{4+} doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was synthesized by molten salt method via calcination of the mixture of MnO_2 , $\text{LiOH}\cdot\text{H}_2\text{O}$, TiO_2 and LiCl-KCl at 800°C for 10 h, has shown a relatively lower particle size

(around $1.125 \mu\text{m}$) than the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, giving better first discharge capacity (305 mA h g^{-1}) between 0–3 V and a corresponding to coulombic efficiency of 89% at 0.1 C rate¹³. In our previous work, Fe_2O_3 and Co_3O_4 were used to optimize modified LTO through the molten salt method to improve LTO's electrical conductivity. Also the modification exhibited other good effects: the obtained $\text{Li}_4\text{Ti}_{4.8}\text{Fe}_{0.2}\text{O}_{12}$ gave a capacity of $103.4 \text{ mA h g}^{-1}$ at 10 C, $137.4 \text{ mA h g}^{-1}$ at the 0.2 C rate after 50 cycles¹¹. The $\text{Li}_4\text{Ti}_{4.9}\text{Co}_{0.1}\text{O}_{12}$ exhibited a better high-rate capacity $106 \text{ mAh}\cdot\text{g}^{-1}$ at 10 C, and $144.8 \text{ mAh}\cdot\text{g}^{-1}$ at 1 C rate with the capacity loss of 8.8% after 100 charge/discharge cycles¹².

In order to systematically characterize the effects of ion doping on the particle size, conductivity and electrochemical performances of LTO as Li-ion battery anodes via the molten salt method, the different metallic compounds (Al_2O_3 , NiO , Fe_3O_4 , La_2O_3 , LaF_3 , CeF_3) with varying ionic radii doped in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were investigated. The results show that doped cations (Al^{3+} , Ni^{2+} , Fe^{2+} , Fe^{3+}) or anion (F^-) with similar ionic radii to Li^+ , Ti^{4+} or O^{2-} ions can enter into LTO, which leads to smaller particle size compared to pure LTO. However, La^{3+} with a larger ionic radius cannot enter into LTO. Because the ionic radii of Fe^{2+} and Fe^{3+} are the closest to that of Li^+ and Ti^{4+} and variable valency ions co-doping, Fe_3O_4 doped LTO exhibits the best rate and cycle performance: an excellent first discharge capacity of $269.3 \text{ mA h g}^{-1}$ at the 0.15 C; excellent high-rate capability ($123.4 \text{ mA h g}^{-1}$ at 10 C); even after 300 discharge/charge cycles, it gives an excellent cycle performance with 12.4% loss of capacity at 1 C rate. It seems Fe_3O_4 is the most suitable metallic compound doped in LTO via molten salt method.

2. Experimental Procedure

2.1 Materials synthesis

Anatase TiO_2 (100 nm in average particle diameter, 99.5% AR, XiyaReagent, Ltd.), $\text{LiOH}\cdot\text{H}_2\text{O}$ (99.9% RG, Adamas Reagent, Ltd.), LiCl , KCl , Al_2O_3 , NiO , Fe_3O_4 (99.0% AR, Sino-

*Corresponding author, E-mail: bingli@ecust.edu.cn, drlibing@163.com

pharm Chemical Reagent Co., Ltd.), La_2O_3 , LaF_3 , CeF_3 were used as raw materials.

Pure LTO, as well as Al_2O_3 , NiO , Fe_3O_4 , La_2O_3 , LaF_3 , CeF_3 doped LTO were prepared by $\text{LiOH}\cdot\text{H}_2\text{O}$ (0.85 g), TiO_2 (2 g), LiCl (10.2 g), KCl (12.46 g) without or with Al_2O_3 (0.106 g), NiO (0.078 g), Fe_3O_4 (0.04 g), La_2O_3 (0.194 g or 0.388 g), LaF_3 (0.049 g, 0.098 g, 0.147 g or 0.196 g) or CeF_3 (0.05 g or 0.1 g), after the same treatment processes as described in our previous work¹¹). The obtained products were labeled as pure LTO, LTAO, LTNO, LTFO, LTLa_xO ($x = 0.1, 0.2$), $\text{LTLa}_x\text{OF}_{3x}$ ($x = 0.05, 0.1, 0.15, 0.2$), $\text{LTCe}_x\text{OF}_{3x}$ ($x = 0.05, 0.1, 0.15$), respectively.

2.2 Characterization

X-ray diffraction (XRD) patterns of the products were recorded on a D/max 2550 V using $\text{Cu K}\alpha$ radiation. Scanning electron microscopy (SEM) images were obtained on a S-3400N scanning electron microscope.

Electrochemical characterization of the products was carried out in half cells (CR2016 coin cells), using Li metal ($\Phi 16\text{ mm} \times 1.5\text{ mm}$, China Energy Lithium Co., Ltd.) as the counter electrode, PP-PE-PP three layer composite separators (25 μm , UBE, Japan) saturated with 1 M LiPF_6 in EC, DMC and EMC (1:1:1 in volume) as the electrolyte (Shenzhen Capchem Polytron Technologies Inc, China). The working electrode consisted of 80 mass% active products, 10 mass% polyvinylidene fluoride (PVDF) as a binder, 10 mass% carbon black (Super-P) as conductive additive, and copper foil as current collector. Typically, about 1.5 mg of the active materials was used per cell. Discharge/charge tests were conducted at room temperature using a New Ware CT-3008 battery tester at various rates C between 2.5 and 1.0 V (1 C = 175 $\text{mAh}\cdot\text{g}^{-1}$).

3. Results and Discussion

3.1 Effect on structure and morphology by Al_2O_3 , NiO and Fe_3O_4 doping

Figure 1(a) gives the XRD patterns of the pure LTO, LTAO, LTNO, LTFO samples. All the samples are in good agreement with the standard pattern of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$, with all the diffraction peaks indexed to the cubic spinel structure from the Fd3m space group (JCPDS No. 49-0207, the blue peaks at the bottom). Neither the new lithium titanium oxide phase nor doped compound (Al_2O_3 , NiO or Fe_3O_4) was detected, which indicates that there is no structural change in $\text{Li}_4\text{Ti}_5\text{O}_{12}$. However, from the enlarged XRD patterns of Fig. 1(b), the peaks of the LTAO, LTNO, LTFO shift to higher diffraction angles to various degrees, indicating the lattice parameters decrease. It can be concluded that the Al^{3+} , Ni^{2+} , Fe^{2+} and Fe^{3+} ions enter the crystal lattice. The decreased lattice parameter of LTAO may be explained that the ionic radius of Al^{3+} ion (0.050 nm, in Table 1, the same below) is smaller than that of Li^+ ion (0.060 nm) and Ti^{4+} ion (0.068 nm), so that they can

enter into the crystal lattice and substitute Li^+ or Ti^{4+} ion. As for LTFO samples, the ionic radius of Ti^{4+} ion is between that of Fe^{2+} ion (0.076 nm) and Fe^{3+} ion (0.064 nm), and the ionic radii of the three ions and Li^+ ion are extremely close, so Li^+ and Ti^{4+} ions are easily substituted by Fe^{2+} or Fe^{3+} ^{11,32}. However, the radius of Ni^{2+} ion (0.072 nm) is a little larger than that of Li^+ ion and Ti^{4+} ion, so the influence of Ni^{2+} is not so obvious. Ion doping can improve the intrinsic conductivity of LTO as the substitution atoms could cause vacant sites of LTO. The co-doping of variable valence Fe^{2+} and Fe^{3+} ions has relatively large effect on the redox reaction as the two-phase reaction of $\text{Li}_7\text{Ti}_5\text{O}_{12}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ base on the redox couple of $\text{Ti}^{3+}/\text{Ti}^{4+}$ during the Li^+ intercalation/deintercalation processes¹⁶). So the effect of Fe_3O_4 doping is supposed to be the best, which could be verified in the subsequent electrochemical performance.

The SEM images of pure LTO, LTAO, LTNO and LTFO samples with the inserted histograms of particle size distribution are given in Fig. 2(a)–(d), respectively. After Al_2O_3 , NiO , Fe_3O_4 doping, the particle size of LTAO, LTNO and LTFO samples are smaller than that of pure LTO. The average particle size of pure LTO, LTAO, LTNO and LTFO samples are

Fig. 1 XRD patterns of pure LTO, LTAO, LTNO, LTFO samples with PDF card of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (No. 49-0207).

Table 1 Ionic radius of the relevant ions.

Ions	Li^+	Ti^{4+}	Al^{3+}	Ni^{2+}	Fe^{2+}	Fe^{3+}	La^{3+}	Ce^{3+}	O^{2-}	F^-
Ionic Radius (nm)	0.060	0.068	0.05	0.072	0.076	0.064	0.1061	0.1034	0.140	0.136

Fig. 2 SEM images of (a) pure LTO, (b) LTAO, (c) LTNO, (d) LTFO inserted with the histograms of particle size distribution calculated from the SEM images.

1.3 μm , 0.31 μm , 0.51 μm and 0.45 μm , respectively. The additive compound can participate in the synthesis reaction and enter into the crystal structure of LTO, resulting in smaller particle size of doped LTO, which coincided with the previous XRD results.

3.2 Effect on structure and morphology by La_2O_3 , LaF_3 and CeF_3 doping

Figure 3(a) compares the XRD patterns of pure LTO, $\text{LTLa}_{0.1}\text{O}$, $\text{LTLa}_{0.2}\text{O}$ samples. A impurity peak ($2\theta = 32.5^\circ$) corresponding to $\text{Li}_{0.485}\text{La}_{0.505}\text{TiO}_3$ phase was detected and it becomes stronger as the amount of added La_2O_3 increases. In Fig. 3(b), the peaks of the (111) plane have little shift after La doping, indicating that La^{3+} ions hardly substitute Ti^{4+} or Li^+ ions in LTO, in agreement with the previous report³³). The possible reason is that the ionic radius of La^{3+} ion (0.106 nm) is much larger than that of Ti^{4+} ion or Li^+ ion. Figure 3(c) shows the XRD patterns of pure LTO, LaF_3 modified LTO samples, no impurities were found in the samples of LTO or $\text{LTLa}_{0.05}\text{OF}_{0.15}$. Nevertheless, the impurity peaks in the XRD patterns of $\text{LTLa}_{0.1}\text{OF}_{0.3}$, $\text{LTLa}_{0.15}\text{OF}_{0.45}$, $\text{LTLa}_{0.2}\text{OF}_{0.6}$ samples were observed. The peak of the (111) plane in Fig. 3(d) shows the peak shift to lower diffraction angles, implying that the lattice parameter of LTO increases after LaF_3 modification. The purity structure in $\text{LTLa}_{0.05}\text{OF}_{0.15}$ samples may be caused by the substitution of O^{2-} ions (0.140 nm) by the slightly smaller F^- ions (0.136 nm) and a small amount of La^{3+} ions as charge compensation enter into the crystal lattice of LTO³⁴).

Figure 4(a)–(h) display the SEM images of $\text{LTLa}_{0.1}\text{O}$, $\text{LTLa}_{0.2}\text{O}$, $\text{LTLa}_{0.05}\text{OF}_{0.15}$, $\text{LTLa}_{0.1}\text{OF}_{0.3}$, $\text{LTLa}_{0.15}\text{OF}_{0.45}$, $\text{LTLa}_{0.2}\text{OF}_{0.6}$, $\text{LTCE}_{0.05}\text{OF}_{0.15}$ and $\text{LTCE}_{0.1}\text{OF}_{0.3}$ samples, respectively. In Fig. 4(a)–(b), $\text{LTLa}_{0.1}\text{O}$ and $\text{LTLa}_{0.2}\text{O}$ samples have exhibited similar morphology, octahedron particles with a size around 1.5 μm and some nanorod impurities. However, SEM results of the $\text{LTLa}_{0.05}\text{OF}_{0.15}$, $\text{LTLa}_{0.1}\text{OF}_{0.3}$ samples in

Fig. 4(c)–(d) clearly displays pure, well-crystallized with particle sizes that are slightly smaller than that of pure LTO (in Fig. 2(a)). Furthermore, SEM images of $\text{LTLa}_{0.15}\text{OF}_{0.45}$ and $\text{LTLa}_{0.2}\text{OF}_{0.6}$ in Fig. 4(e)–(f), some nanorod impurities appear, which are similar to the morphology of $\text{LTLa}_{0.1}\text{O}$ and $\text{LTLa}_{0.2}\text{O}$ samples. The results indicate that some La^{3+} ions can enter into the crystal lattice of LTO after F^- ion doping. However, with the amount of LaF_3 increasing, the impurities, like $\text{Li}_{0.485}\text{La}_{0.505}\text{TiO}_3$, generate. The SEM images of $\text{LTCE}_{0.1}\text{OF}_{0.3}$ and $\text{LTCE}_{0.2}\text{OF}_{0.6}$ samples in Fig. 4(g)–(h) show similar results compared with the $\text{LTLa}_{0.05}\text{OF}_{0.15}$ and $\text{LTLa}_{0.1}\text{OF}_{0.3}$ samples after CeF_3 modifying. A small amount of La^{3+} or Ce^{3+} , with a large ionic radius, can enter into the vacant space of the crystal lattice of LTO that is caused by F^- ions substitution of O^{2-} ions in the structure of LTO. As a result, well-crystallized samples ($\text{LTLa}_{0.05}\text{OF}_{0.15}$ and $\text{LTLa}_{0.1}\text{OF}_{0.3}$) with smaller particles and no impurities were obtained.

3.3 Effect on rate performance after metallic oxide doping

The pure LTO, LTAO, LTNO, LTFO and LTLa_xO ($x = 0.1, 0.2$) samples were used as coin battery anodes to examine the effects of different ionic radii on the electrochemical performances of LTO.

Figure 5(a) shows the rate performances of pure LTO, LTAO, LTNO and LTFO electrodes at different discharge/charge rates in the 1.0–2.5 V voltage range. LTFO electrode exhibits the best discharge/charge capacity among the four electrodes, after the first discharge capacity of 269.3 $\text{mAh}\cdot\text{g}^{-1}$, substantially stable at 240 $\text{mAh}\cdot\text{g}^{-1}$ at 0.15 C, then the rate is gradually increased to 0.2 C, 0.5 C, 0.75 C, 1 C, 2 C, 5 C and 10 C in sequence, the corresponding capacities of LTFO electrode are 230.4, 215.8, 207.3, 201.3, 186.3, 155.1 and 123.4 $\text{mAh}\cdot\text{g}^{-1}$, respectively, while the pure LTO electrode delivers 134.2, 119.3, 108.5, 90.1, 82.9, 69.4 and

Fig. 3 (a) XRD patterns and (b) the (111) plane XRD peaks of pure LTO, $\text{LTLa}_{0.1}\text{O}$, $\text{LTLa}_{0.2}\text{O}$ samples. (c) XRD patterns and (d) the (111) plane XRD peaks of pure LTO, $\text{LTLa}_{0.05}\text{OF}_{0.15}$, $\text{LTLa}_{0.1}\text{OF}_{0.3}$, $\text{LTLa}_{0.15}\text{OF}_{0.45}$, $\text{LTLa}_{0.2}\text{OF}_{0.6}$ samples.

Fig. 4 SEM images of (a) $\text{LTLa}_{0.1}\text{O}$, (b) $\text{LTLa}_{0.2}\text{O}$, (c) $\text{LTLa}_{0.05}\text{OF}_{0.15}$, (d) $\text{LTLa}_{0.1}\text{OF}_{0.3}$, (e) $\text{LTLa}_{0.15}\text{OF}_{0.45}$, (f) $\text{LTLa}_{0.2}\text{OF}_{0.6}$, (g) $\text{LTCE}_{0.05}\text{OF}_{0.15}$ and (h) $\text{LTCE}_{0.1}\text{OF}_{0.3}$ samples, respectively.

$44.4 \text{ mAh}\cdot\text{g}^{-1}$, respectively. LTAO electrode delivers a better discharge/charge capacity at high-rate than that of pure LTO electrode, substantially stable at $91 \text{ mAh}\cdot\text{g}^{-1}$ at 10 C. However, LTNO electrode has a worse capacity than that of pure LTO. At 10 C rate, the capacity of LTNO electrode just receives $33 \text{ mAh}\cdot\text{g}^{-1}$. Figure 5(b) displays the first cycle discharge/charge curves of LTAO and LTFO electrodes at different C rates. All the curves show a flat voltage plateau around 1.55 V (vs. Li/Li^+), corresponding to the reduction/oxidation reaction between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_7\text{Ti}_5\text{O}_{12}$ during the Li^+ intercalation/deintercalation process^{35,36}.

The rate performances of $\text{LTLa}_{0.1}\text{O}$ and $\text{LTLa}_{0.2}\text{O}$ electrodes are also shown in Fig. 5(c). The $\text{LTLa}_{0.2}\text{O}$ electrode gives better capacities (160.7, 116.4, 98.3, 75.5 and $55 \text{ mAh}\cdot\text{g}^{-1}$ at 0.2 C, 0.5 C, 0.75 C, 1 C, 2 C and 5 C, respectively) than that of $\text{LTLa}_{0.1}\text{O}$ electrode. However, the rate performance of $\text{LTLa}_{0.2}\text{O}$ electrode is worse than that of pure LTO. Figure 5(d) compares the specific discharge capacity at different rates for pure LTO and all the doped samples synthesized by molten salt method in our lab. The capacity for the samples decreases with increasing rate, while the capacity drops slowly when the rate is higher than 1 C. Obviously, the capacity and rate capability improves as the Al_2O_3 , Fe_3O_4 , Fe_2O_3 and Co_3O_4 doped into LTO. In particular, the Fe_3O_4

Fig. 5 (a) The rate performances of pure LTO, LTAO, LTNO and LTFO electrodes at different C rates. The first discharge/charge curves of (b) LTAO and LTFO, (c) LTLA_{0.1}O and LTLA_{0.2}O electrodes at different C rates. (d) Dependence of specific capacity for the metallic oxide doped LTO samples by molten salt method on current density.

doped LTO (LTFO) shows the best capacity and rate performance.

3.4 Effect on cycle performance after metallic oxide doping

Figure 6(a)–(d) display the discharge/charge cycle performance and coulombic efficiency of pure LTO, LTAO, LTNO and LTFO, respectively. In Fig. 6(a), the pure LTO electrode, with obvious fluctuation, delivers the first discharge capacity of 179.3 mAh·g⁻¹ at 0.2 C rate, after 5 cycles, it decreases to 96 mAh·g⁻¹, and then 106.5 mAh·g⁻¹ after the following 205 cycles at 1 C rate. Fig. 6(b) shows that the LTAO electrode exhibits a first discharge capacity of 150.9 mAh·g⁻¹ (93.6% coulombic efficiency of the first cycle), then capacity fades to 136.8 mAh·g⁻¹ after 100 cycles at 0.2 C rate. However, the LTNO electrode in Fig. 6(c), with the slight fluctuation, delivers the first discharge capacity of 116.9 mAh·g⁻¹ at 0.2 C rate, then 110.8 mAh·g⁻¹ after 100 cycles at 0.2 C rate. From Fig. 6(d), the LTFO electrode exhibits a first discharge capacity of 161.1 mAh·g⁻¹ at 1 C rate, stable at 147 mAh·g⁻¹ for 100 cycles, then fading to 141.1 mAh·g⁻¹ at the 300th cycle, which gives 12.4% loss of capacity. From Fig. 6(a)–(d), the coulombic efficiency of the first cycle of pure LTO is 80.4%, which are 93.6% for LTAO, 90.4% for LTNO and 90.1% for LTFO, respectively. Then the four electrodes receive high recharge coulombic efficiency close to 100%. The 1st, 50th, 100th, 200th, 300th discharge/charge curves of LTFO electrode in Fig. 6(e) clearly illustrate that the LTFO electrode has good cycling stability after 300 discharge/charge cycles and the reduction/oxidation reaction of LTFO electrode occurs at about 1.55 V, corresponding to the two-phase transition between Li₄Ti₅O₁₂ and Li₇Ti₅O₁₂. Figure 6(f) exhibits the similar cycle performance of the LTLA_{0.1}O and LTLA_{0.2}O electrodes at 0.2 C rate for 50 cycles. The first discharge capacity of the LTLA_{0.1}O electrode is 166 mAh·g⁻¹, then stable at 135 mAh·g⁻¹ in the following 49 cycles.

In conclusion, the LTFO electrode shows the best electrochemical performance in all the electrodes. This may be caused by the smaller particle size, uniform particle distribution, the similar ionic radii with Li⁺ and Ti⁴⁺, and the co-doping of variable valence Fe²⁺ and Fe³⁺ ions largely affect the redox reaction as the two-phase reaction of Li₇Ti₅O₁₂/Li₄Ti₅O₁₂ based on the redox couple of Ti³⁺/Ti⁴⁺ during Li⁺ intercalation/deintercalation process^{16,37}.

4. Conclusions

In this paper, different metallic compounds (Al₂O₃, NiO, Fe₃O₄, La₂O₃, LaF₃, CeF₃) with different ionic radii doped into LTO were synthesized via the molten salt method. Al₂O₃, Fe₃O₄, NiO or LaF₃ doping can generate smaller particle size of LTO. However, the addition of La₂O₃ cannot decrease the particle size of LTO. Thereafter, the addition of LaF₃ or CeF₃ can lead to slightly smaller particle sizes. Hence, doped cations (Al³⁺, Ni²⁺, Fe²⁺, Fe³⁺) or anion (F⁻) with similar ionic radius as Li⁺, Ti⁴⁺ or O²⁻ ions can enter into LTO. La³⁺ with a much larger ionic radius cannot enter into LTO.

With the most closest ionic radius to that of the Li⁺, Ti⁴⁺ ions, the co-doping of Fe²⁺ and Fe³⁺ ions in LTO exhibits the best rates and cycle performance among all the doped sam-

Fig. 6 The cyclability and coulombic efficiency of (a) pure LTO, (b) LTAO, (c) LTNO and (d) LTFO electrodes. (e) The first, 50th, 100th, 200th, and 300th discharge/charge curves in the 1–2.5 V voltage of LTFO electrode at 1 C rate. (f) The discharge cyclability of LTLA_{0.1}O and LTLA_{0.2}O electrode under 0.2 C rate for 50 cycles.

ples: an excellent first discharge capacity of 269.3 mAh·g⁻¹ at the 0.15 C, 201.3 mAh·g⁻¹ at 1 C, good high-rate capability (123.4 mAh·g⁻¹ at 10 C); even after 300 discharge/charge cycles at 1 C rate, the discharge capacity is 141.1 mAh·g⁻¹, gives an excellent cycle performance with 12.4% loss of capacity. These result indicate that ions doping can improve the intrinsic conductivity of LTO and also can reduce the particle size of LTO, leading to the improved specific surface area and shortened Li⁺ transfer path, which could efficiently enhance the electrochemical performance of LTO. As such, the molten salt method with ion doping promises to be the next generation industrial production method of LTO.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (no. 51474107).

REFERENCES

- J. Guo, W. Zuo, Y. Cai, S. Chen, S. Zhang and J. Liu: *J. Mater. Chem. A* **3** (2015) 4938–4944.
- L. Wen, Z. Wu, H. Luo, R. Song and F. Li: *J. Electrochem. Soc.* **162** (2015) A3038–A3044.
- L. Wang, Y. Zhang, M.E. Scofield, S. Yue, C. McBean, A.C. Marschillok, K.J. Takeuchi, E.S. Takeuchi and S.S. Wong: *ChemSusChem* **8** (2015) 3304–3313.
- W. Li, X. Li, M. Chen, Z. Xie, J. Zhang, S. Dong and M. Qu: *Electrochim. Acta* **139** (2014) 104–110.
- L. Zhao, Y.S. Hu, H. Li, Z. Wang and L. Chen: *Adv. Mater.* **23** (2011) 1385–1388.
- Y.B. He, B. Li, M. Liu, C. Zhang, W. Lv, C. Yang, J. Li, H. Du, B. Zhang, Q.H. Yang, J.K. Kim and F. Kang: *Sci. Rep.* **2** (2012) 913.
- K. Wu, J. Yang, Y. Liu, Y. Zhang, C. Wang, J. Xu, F. Ning and D. Wang: *J. Power Sources* **237** (2013) 285–290.
- B. Zhao, R. Ran, M.L. Liu and Z.P. Shao: *Mater. Sci. Eng. Rep.* **98** (2015) 1–71.
- L. Wang, X. He, J. Li, W. Sun, J. Gao, J. Guo and C. Jiang: *Angew. Chem. Int. Ed. Engl.* **51** (2012) 9034–9037.
- M. Lao, X. Lin, P. Li, L. Shao, K. Wu, M. Shui, N. Long, Y. Ren and J. Shu: *Ceram. Int.* **41** (2015) 2900–2907.
- Q. Guo, S. Li, H. Wang, Y. Gao and B. Li: *RSC Adv.* **4** (2014) 60327–60333.
- Q. Guo, Q. Wang, G. Chen, H. Xu, J. Wu and B. Li: *ECS Trans.* **72** (2016) 11–23.
- V.D. Nithya, R. Kalai Selvan, K. Vediappan, S. Sharmila and C.W. Lee: *Appl. Surf. Sci.* **261** (2012) 515–519.
- T.-F. Yi, S.-Y. Yang, X.-Y. Li, J.-H. Yao, Y.-R. Zhu and R.-S. Zhu: *J. Power Sources* **246** (2014) 505–511.
- D. Wang, C. Zhang, Y. Zhang, J. Wang and D. He: *Ceram. Int.* **39** (2013) 5145–5149.

- 16) M. Ji, Y. Xu, Z. Zhao, H. Zhang, D. Liu, C. Zhao, X. Qian and C. Zhao: *J. Power Sources* **263** (2014) 296–303.
- 17) Z. Wang, Z. Wang, W. Peng, H. Guo and X. Li: *Ceram. Int.* **40** (2014) 10053–10059.
- 18) Y.Q. Wang, L. Gu, Y.G. Guo, H. Li, X.Q. He, S. Tsukimoto, Y. Ikuhara and L.J. Wan: *J. Am. Chem. Soc.* **134** (2012) 7874–7879.
- 19) S. Zheng, Y. Xu, C. Zhao, H. Liu, X. Qian and J. Wang: *Mater. Lett.* **68** (2012) 32–35.
- 20) J. Liu, W. Liu, S. Ji, Y. Wan, H. Yin and Y. Zhou: *Eur. J. Inorg. Chem.* **2014** (2014) 2073–2079.
- 21) M. Hu, Y. Jiang and M. Yan: *J. Alloy. Compd.* **603** (2014) 202–206.
- 22) J. Wang, Z. Yang, W. Li, X. Zhong, L. Gu and Y. Yu: *J. Power Sources* **266** (2014) 323–331.
- 23) M. Krajewski, M. Michalska, B. Hamankiewicz, D. Ziolkowska, K.P. Korona, J.B. Jasinski, M. Kaminska, L. Lipinska and A. Czerwinski: *J. Power Sources* **245** (2014) 764–771.
- 24) Q. Zhang, Y. Liu, H. Lu, D. Tang, C. Ouyang and L. Zhang: *Electrochim. Acta* **189** (2016) 147–157.
- 25) W. Li, H. Wang, M. Chen, J. Gao, X. Li, W. Ge, M. Qu, A. Wei, L. Zhang and Z. Liu: *Electrochim. Acta* **188** (2016) 499–511.
- 26) Z. Ding, L. Zhao, L. Suo, Y. Jiao, S. Meng, Y.S. Hu, Z. Wang and L. Chen: *Phys. Chem. Chem. Phys.* **13** (2011) 15127–33.
- 27) J. Chen, L. Yang, S. Fang and Y. Tang: *Electrochim. Acta* **55** (2010) 6596–6600.
- 28) T. Kimijima, K. Kanie, Y. Tsujikawa, M. Nakaya, N. Zettsu, K. Teshima and A. Muramatsu: *Ceram. Int.* **41** (2015) 10988–10994.
- 29) X. Li, H. Hu, S. Huang, G. Yu, L. Gao, H. Liu and Y. Yu: *Electrochim. Acta* **112** (2013) 356–363.
- 30) W. Yao, W. Zhuang, X. Ji, J. Chen, X. Lu and C. Wang: *Mater. Res. Bull.* **75** (2016) 204–210.
- 31) T. Ogihara, M. Yamada, A. Fujita, S. Akao and K. Myoujin: *Mater. Res. Bull.* **46** (2011) 796–800.
- 32) T.-F. Yi, S.-Y. Yang, M. Tao, Y. Xie, Y.-R. Zhu and R.-S. Zhu: *Electrochim. Acta* **134** (2014) 377–383.
- 33) T.-F. Yi, Y. Xie, Q. Wu, H. Liu, L. Jiang, M. Ye and R. Zhu: *J. Power Sources* **214** (2012) 220–226.
- 34) S. Huang, Z. Wen, Z. Gu and X. Zhu: *Electrochim. Acta* **50** (2005) 4057–4062.
- 35) J. Haetge, P. Hartmann, K. Brezesinski, J. Janek and T. Brezesinski: *Chem. Mater.* **23** (2011) 4384–4393.
- 36) M.R. Jo, G.H. Lee and Y.M. Kang: *ACS Appl. Mater. Interfaces* **7** (2015) 27934–27939.
- 37) M.R. Jo, J. Jung, G.-H. Lee, Y. Kim, K. Song, J. Yang, J.S. Chae, K.C. Roh, Y.-I. Kim, W.-S. Yoon and Y.-M. Kang: *Nano Energy* **19** (2016) 246–256.