

Short communication

Effects of dopant on the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as electrode material for lithium ion batteries

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Abstract

The effects of dopant on the electrochemical properties of spinel-type $\text{Li}_{3.95}\text{M}_{0.15}\text{Ti}_{4.9}\text{O}_{12}$ ($\text{M} = \text{Al}, \text{Ga}, \text{Co}$) and $\text{Li}_{3.9}\text{Mg}_{0.1}\text{Al}_{0.15}\text{Ti}_{4.85}\text{O}_{12}$ were systematically investigated. Charge–discharge cycling were performed at a constant current density of 0.15 mA cm^{-2} between the cut-off voltages of 2.3 and 0.5 V, the experimental results showed that Al^{3+} dopant greatly improved the reversible capacity and cycling stability over the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The substitution of the Ga^{3+} slightly increased the capacity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$, but did not essentially alleviate the degradation of cycling stability. Dopants such as Co^{3+} and Mg^{2+} to some extent worsened the electrochemical performance of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

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Keywords: Lithium ion battery; Anode materials; Spinel-type; $\text{Li}_4\text{Ti}_5\text{O}_{12}$

1. Introduction

Recently, the lithium titanium spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are gaining more and more attention as anode materials applied in solid-state lithium ion batteries [1–4]. As extensively reported [3,5,6], the main feature of the compounds is their unique insertion–deinsertion mechanism that involves a two-phase process between two compounds having the same symmetry. The lattice parameter variation associated with this process is confined to less than 0.1%, and the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode material was therefore classified as a “zero-strain” intercalation compound.

Following this trend, there have been a few reports dealing with the substituted spinels with various original stoichiometry $\text{Li}_{4/3-y/3}\text{M}_y\text{Ti}_{5/3-2y/3}\text{O}_4$ (e.g., Fe^{3+} , Ni^{3+} and Cr^{3+}) [7–10], $\text{Li}_4\text{M}_y\text{Ti}_{5-y}\text{O}_{12}$ (Al^{3+} , Mn^{4+} , V^{4+} and Fe^{3+}) [11,12], $\text{Li}_{4-y}\text{M}_y\text{Ti}_5\text{O}_{12}$ (Mg^{2+}) [13] and $\text{Li}_4\text{Al}_x\text{Ti}_{5-x}\text{O}_{12-y}\text{F}_y$ [14] on their crystal and electrochemical properties. It was found that the small amount of Mg^{2+} improved the electronic conductivity of the material by many orders of magnitude [13] and the Al^{3+} greatly increased the reversible capacity and cycling stability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [12].

In this work, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -type materials with various dopants were prepared by a solid-state reaction method and the effects of dopant on cycling performance and electronic prosperity were systematically investigated.

2. Experimental

$\text{Li}_{3.95}\text{M}_{0.15}\text{Ti}_{4.9}\text{O}_{12}$ materials ($\text{M} = \text{Al}, \text{Ga}, \text{Co}$) and $\text{Li}_{3.9}\text{Mg}_{0.1}\text{Al}_{0.15}\text{Ti}_{4.85}\text{O}_{12}$ were prepared using appropriate amounts of Li_2CO_3 , rutile-type TiO_2 , Al_2O_3 , Ga_2O_3 , Co_2O_3 or MgO as precursors which were mixed by planetary ball milling with alcohol medium. The dried samples were heated in a muffle furnace at 850°C for 12 h in air. Phase purity of the synthesized materials was identified by powder X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation as diffraction source ($\lambda = 1.5405 \text{ \AA}$) and Si as an internal standard. The lattice parameters ‘ a ’ of all the samples were calculated by a least square method using eight diffraction lines. The final stoichiometry of the substituted spinel compounds was performed on a VISTA AX simultaneous ICP-OES spectrometer with axial view configuration (Varian, Australia).

The charge and discharge capacities were measured with coin cells in which lithium metal foil was used as the counter electrode. The electrolyte employed was 1 M solution of LiPF_6 in ethylene carbonate and dimethyl carbonate (EC + DMC) (1:1 in

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Table 1

The final chemical composition of spinel-type $\text{Li}_{3.95}\text{M}_{0.15}\text{Ti}_{4.9}\text{O}_{12}$ ($\text{M} = \text{Al}, \text{Ga}, \text{Co}$) and $\text{Li}_{3.9}\text{Mg}_{0.1}\text{Al}_{0.15}\text{Ti}_{4.85}\text{O}_{12}$ materials

Nominal formula	Composition (wt%)							The final chemical composition
	Li	Al	Mg	Ga	Co	Ti	O	
$\text{Li}_4\text{Ti}_5\text{O}_{12}$	5.92	/	/	/	/	52.09	41.79	$\text{Li}_{3.92}\text{Ti}_5\text{O}_{11.96}$
$\text{Li}_{3.95}\text{Al}_{0.15}\text{Ti}_{4.9}\text{O}_{12}$	5.50	0.77	/	/	/	51.54	41.78	$\text{Li}_{3.61}\text{Al}_{0.13}\text{Ti}_{4.9}\text{O}_{11.8}$
$\text{Li}_{3.95}\text{Ga}_{0.15}\text{Ti}_{4.9}\text{O}_{12}$	5.78	/	/	2.34	/	51.08	41.30	$\text{Li}_{3.82}\text{Ga}_{0.15}\text{Ti}_{4.9}\text{O}_{11.94}$
$\text{Li}_{3.95}\text{Co}_{0.15}\text{Ti}_{4.9}\text{O}_{12}$	5.80	/	/	/	1.92	50.86	41.45	$\text{Li}_{3.85}\text{Co}_{0.15}\text{Ti}_{4.9}\text{O}_{11.95}$
$\text{Li}_{3.9}\text{Mg}_{0.1}\text{Al}_{0.15}\text{Ti}_{4.85}\text{O}_{12}$	5.94	0.82	0.45	/	/	51.98	41.87	$\text{Li}_{3.82}\text{Mg}_{0.08}\text{Al}_{0.14}\text{Ti}_{4.85}\text{O}_{11.9}$

volume). The composite electrodes were made of the titanate powder (85 wt%), acetylene black (8 wt%) and polyvinylidene fluoride (PVDF) binder (7 wt%) homogeneously mixed in *N*-methyl pyrrolidinone (NMP) solvent by planetary ball milling and then coated uniformly on an aluminum foil. Finally, the electrode was dried under vacuum at 100 °C for 10 h. Cell assembly was carried out in an argon-filled glove box (VAC AM-2). The coin cells were cycled between cutoff voltages of 2.3 and 0.5 V with a CT2001A cell test instrument (LAND Electronic Co.) at room temperature. The sample powders were pressed into pellets and sintered at 900 °C in the air for 12 h. Polished pellets with symmetric blocking silver electrodes on both sides were served for complex impedance and electronic conductivity measurements. The complex impedance measurements were carried out on a Solartron 1260 impedance analyzer in the fre-

quency range of 10^{-1} to 10^6 Hz and the electronic conductivity was determined by the high resistance meter (HP4329A).

3. Results and discussion

Slight loss of the lithium content owing to its evaporation during the sintering process was found on the basis of ICP analysis. The final chemical formula of the nominal

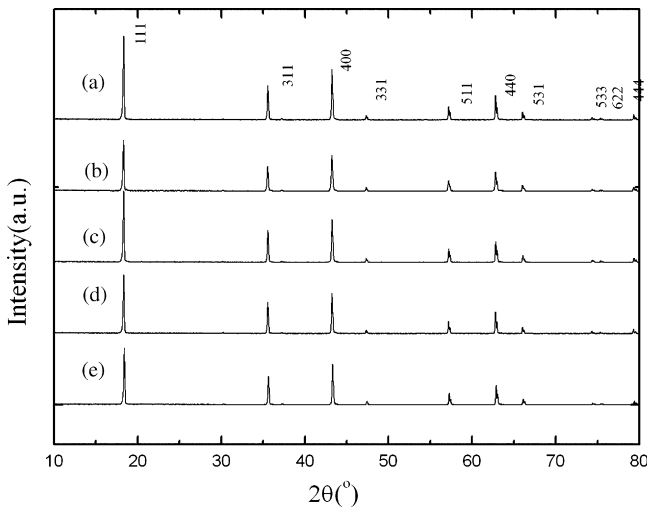


Fig. 1. XRD patterns of (a) $\text{Li}_{3.92}\text{Ti}_5\text{O}_{11.96}$, (b) $\text{Li}_{3.61}\text{Al}_{0.13}\text{Ti}_{4.9}\text{O}_{11.8}$, (c) $\text{Li}_{3.82}\text{Ga}_{0.15}\text{Ti}_{4.9}\text{O}_{11.94}$, (d) $\text{Li}_{3.85}\text{Co}_{0.15}\text{Ti}_{4.9}\text{O}_{11.9}$ and (e) $\text{Li}_{3.82}\text{Mg}_{0.08}\text{Al}_{0.14}\text{Ti}_{4.85}\text{O}_{11.9}$.

Table 2

Lattice parameter 'a' for spinel-type $\text{Li}_{3.95}\text{M}_{0.15}\text{Ti}_{4.9}\text{O}_{12}$ ($\text{M} = \text{Al}, \text{Ga}, \text{Co}$) and $\text{Li}_{3.9}\text{Mg}_{0.1}\text{Al}_{0.15}\text{Ti}_{4.85}\text{O}_{12}$ materials

Sample	Lattice parameter 'a' (Å)
$\text{Li}_{3.92}\text{Ti}_5\text{O}_{11.96}$	8.3716
$\text{Li}_{3.61}\text{Al}_{0.13}\text{Ti}_{4.9}\text{O}_{11.8}$	8.3693
$\text{Li}_{3.82}\text{Ga}_{0.15}\text{Ti}_{4.9}\text{O}_{11.94}$	8.3697
$\text{Li}_{3.85}\text{Co}_{0.15}\text{Ti}_{4.9}\text{O}_{11.95}$	8.3696
$\text{Li}_{3.82}\text{Mg}_{0.08}\text{Al}_{0.14}\text{Ti}_{4.85}\text{O}_{11.9}$	8.3682

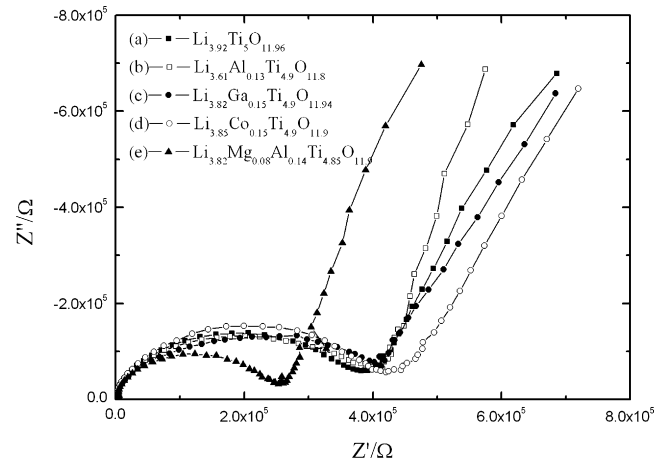


Fig. 2. Complex impedance plots at room temperature for (a) $\text{Li}_{3.92}\text{Ti}_5\text{O}_{11.96}$, (b) $\text{Li}_{3.61}\text{Al}_{0.13}\text{Ti}_{4.9}\text{O}_{11.8}$, (c) $\text{Li}_{3.82}\text{Ga}_{0.15}\text{Ti}_{4.9}\text{O}_{11.94}$, (d) $\text{Li}_{3.85}\text{Co}_{0.15}\text{Ti}_{4.9}\text{O}_{11.9}$ and (e) $\text{Li}_{3.82}\text{Mg}_{0.08}\text{Al}_{0.14}\text{Ti}_{4.85}\text{O}_{11.9}$.

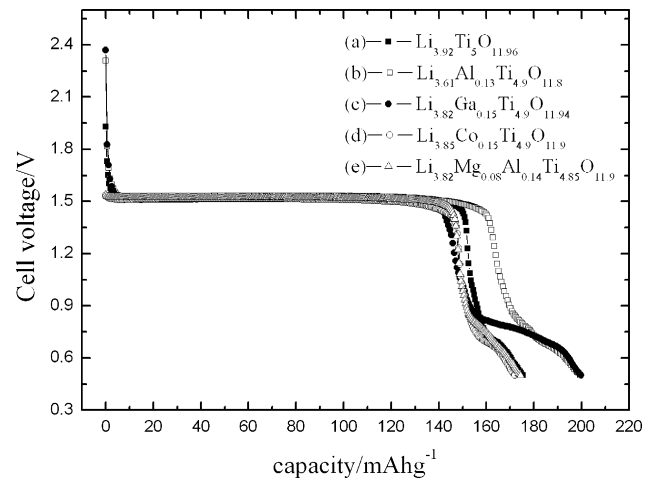


Fig. 3. First discharge curves for (a) $\text{Li}_{3.92}\text{Ti}_5\text{O}_{11.96}$, (b) $\text{Li}_{3.61}\text{Al}_{0.13}\text{Ti}_{4.9}\text{O}_{11.8}$, (c) $\text{Li}_{3.82}\text{Ga}_{0.15}\text{Ti}_{4.9}\text{O}_{11.94}$, (d) $\text{Li}_{3.85}\text{Co}_{0.15}\text{Ti}_{4.9}\text{O}_{11.9}$ and (e) $\text{Li}_{3.82}\text{Mg}_{0.08}\text{Al}_{0.14}\text{Ti}_{4.85}\text{O}_{11.9}$ at current density of 0.15 mA cm^{-2} .

composition $\text{Li}_{3.95}\text{M}_{0.15}\text{Ti}_{4.9}\text{O}_{12}$ materials ($\text{M} = \text{Al}, \text{Ga}, \text{Co}$) and $\text{Li}_{3.9}\text{Mg}_{0.1}\text{Al}_{0.15}\text{Ti}_{4.85}\text{O}_{12}$ were determined as $\text{Li}_{3.92}\text{Ti}_5\text{O}_{11.96}$, $\text{Li}_{3.61}\text{Al}_{0.13}\text{Ti}_{4.9}\text{O}_{11.8}$, $\text{Li}_{3.82}\text{Ga}_{0.15}\text{Ti}_{4.9}\text{O}_{11.94}$, $\text{Li}_{3.85}\text{Co}_{0.15}\text{Ti}_{4.9}\text{O}_{11.95}$ and $\text{Li}_{3.82}\text{Mg}_{0.08}\text{Al}_{0.14}\text{Ti}_{4.85}\text{O}_{11.9}$, respectively, as listed in Table 1.

The XRD patterns of all the final powders were shown in Fig. 1. It was found that the diffraction patterns of all the specimens were similar, with all the peaks indexable in the $Fd\bar{3}m$ space group with cubic lattice. The variation of the lattice parameter 'a' was shown in Table 2. As seen, the overall evolution of the 'a' was consistent with the modification of the ionic radii induced by the respective substitution. Since the ionic radii of Ga^{3+} (0.062 nm), Co^{3+} (0.063 nm), Mg^{2+} (0.066 nm) and Al^{3+} (0.051 nm) were smaller than Ti^{4+} , Li^+ (0.068 nm), the lat-

tice parameters of all the substitutions were smaller than the undoped $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

The conductivity of the specimen was determined from the AC impedance spectroscopy and the high resistance meter at ambient temperature. The electronic conductivities for $\text{Li}_{3.92}\text{Ti}_5\text{O}_{11.96}$, $\text{Li}_{3.61}\text{Al}_{0.13}\text{Ti}_{4.9}\text{O}_{11.8}$, $\text{Li}_{3.82}\text{Ga}_{0.15}\text{Ti}_{4.9}\text{O}_{11.94}$, $\text{Li}_{3.85}\text{Co}_{0.15}\text{Ti}_{4.9}\text{O}_{11.95}$ and $\text{Li}_{3.82}\text{Mg}_{0.08}\text{Al}_{0.14}\text{Ti}_{4.85}\text{O}_{11.9}$ were 3.7×10^{-9} , 1.1×10^{-8} , 2.0×10^{-9} , 1.3×10^{-9} and $7.9 \times 10^{-9} \text{ S cm}^{-1}$, respectively. It was indicated that Al^{3+} and Mg^{2+} dopants increased the electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ while the Co^{3+} , Ga^{3+} behaved contrarily. It was also found that except Mg^{2+} , all the other dopants did not change the total conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ obviously, as was shown in Fig. 2. It was probable that the conductivity of the

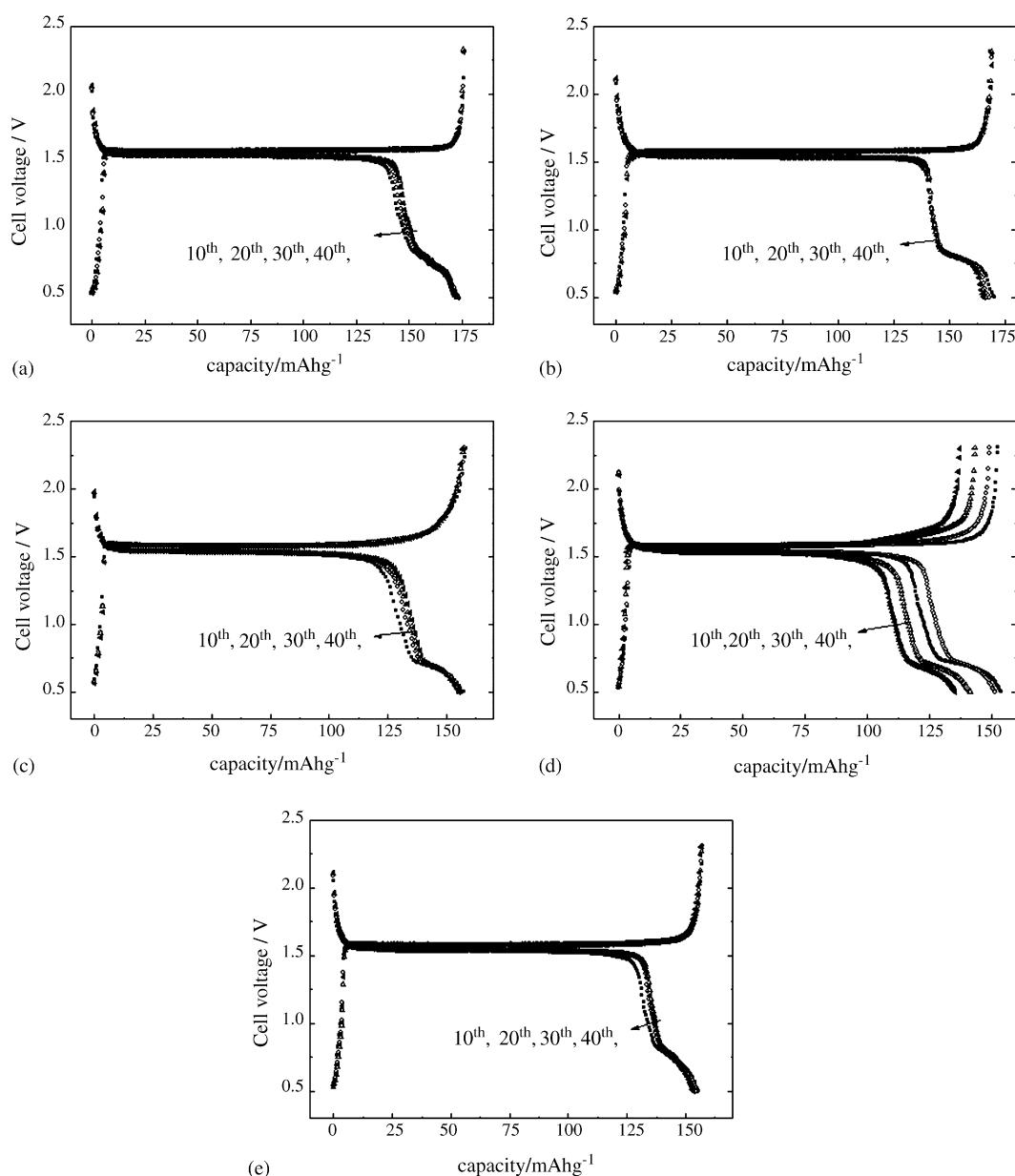


Fig. 4. The charge and discharge curves of (a) $\text{Li}_{3.92}\text{Ti}_5\text{O}_{11.96}$, (b) $\text{Li}_{3.61}\text{Al}_{0.13}\text{Ti}_{4.9}\text{O}_{11.8}$, (c) $\text{Li}_{3.82}\text{Ga}_{0.15}\text{Ti}_{4.9}\text{O}_{11.94}$, (d) $\text{Li}_{3.85}\text{Co}_{0.15}\text{Ti}_{4.9}\text{O}_{11.95}$ and (e) $\text{Li}_{3.82}\text{Mg}_{0.08}\text{Al}_{0.14}\text{Ti}_{4.85}\text{O}_{11.9}$ in every 10 times.

lithium-titanium-oxide spinel electrode was connected with the valence of titanium which was immediately influenced by the valence of the dopants: the substitution of Li^+ by Mg^{2+} led to mixed $\text{Ti}^{4+}/\text{Ti}^{3+}$ valences and enhanced the conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, while the substitution of the other ions, i.e., Al^{3+} , Ga^{3+} and Co^{3+} did not change the valence of titanium, which was therefore not beneficial to the improvement of the conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Chen et al. [13] ever reported that doping the structure with small amounts of Mg^{2+} under reduced atmosphere could improve the electronic conductivity of the titanate by many orders of magnitude. In this work, we found that the Mg^{2+} doped material prepared in air atmosphere could slightly improve the total conductivity of $\text{Li}_{3.95}\text{Al}_{0.15}\text{Ti}_{4.9}\text{O}_{12}$, but it decreased the electronic conductivity. It would be suggested that the reduction of part of the Ti^{4+} to Ti^{3+} under reduced atmosphere was beneficial to the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [4,15].

Fig. 3 showed the first discharge curves of the specimens at a constant current density of 0.15 mA cm^{-2} between the cut-off voltages of 2.3 and 0.5 V. The first discharge capacities were 175.3, 199.7, 199.8, 171.9 and 174.4 mAh g^{-1} for $\text{Li}_{3.92}\text{Ti}_5\text{O}_{11.96}$, $\text{Li}_{3.61}\text{Al}_{0.13}\text{Ti}_{4.9}\text{O}_{11.8}$, $\text{Li}_{3.82}\text{Ga}_{0.15}\text{Ti}_{4.9}\text{O}_{11.94}$, $\text{Li}_{3.85}\text{Co}_{0.15}\text{Ti}_{4.9}\text{O}_{11.95}$ and $\text{Li}_{3.82}\text{Mg}_{0.08}\text{Al}_{0.14}\text{Ti}_{4.85}\text{O}_{11.9}$, respectively. It was found that the Al^{3+} , Ga^{3+} dopants increased the capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ while the Co^{3+} and Mg^{2+} decreased the capacity of the first cycle. Furthermore, it was also seen that the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was associated with the doping level of Al^{3+} or the atomic ratio of Li:Al:Ti. As tested, the capacity of $\text{Li}_{3.61}\text{Al}_{0.13}\text{Ti}_{4.9}\text{O}_{11.8}$, 199.7 mAh g^{-1} , was higher than that of $\text{Li}_{3.595}\text{Al}_{0.127}\text{Ti}_{4.85}\text{O}_{11.688}$, 195.6 mAh g^{-1} [12,14].

The charge and discharge curves of all the specimens in every 10 cycles were shown in Fig. 4. It was found that all samples displayed two platforms at about 1.53 and 0.65 V, respectively. As seen, the kind of doping ions would influence the relative ratio of the two platforms. For example, Ga^{3+} dopant increased the capacity at 0.65 V, but it reduced the discharge capacity of the 1.53 V platform at the same time. Moreover, all the substitutes with different dopants (Al^{3+} , Ga^{3+} , Co^{3+} , Mg^{2+}) displayed little degradation in capacity. In addition, the capacity distribution for both discharge voltages was also associated with the doping level. As we reported previously, the relative capacity ratio for the two platforms of $\text{Li}_{3.61}\text{Al}_{0.13}\text{Ti}_{4.9}\text{O}_{11.8}$ was slightly different from that of $\text{Li}_{3.595}\text{Al}_{0.127}\text{Ti}_{4.85}\text{O}_{11.688}$ [12].

The cycling stability of various doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was shown in Fig. 5. The reversible capacities after 40 cycles for $\text{Li}_{3.92}\text{Ti}_5\text{O}_{11.96}$, $\text{Li}_{3.61}\text{Al}_{0.13}\text{Ti}_{4.9}\text{O}_{11.8}$, $\text{Li}_{3.82}\text{Ga}_{0.15}\text{Ti}_{4.9}\text{O}_{11.94}$, $\text{Li}_{3.85}\text{Co}_{0.15}\text{Ti}_{4.9}\text{O}_{11.95}$ and $\text{Li}_{3.82}\text{Mg}_{0.08}\text{Al}_{0.14}\text{Ti}_{4.85}\text{O}_{11.9}$ were 161.7, 172.8, 165.5, 155.2 and 153.4 mAh g^{-1} with capacity losses of 4.32, 1.31, 4.39, 4.79 and 5.6%, respectively. It was indicated that different dopants acted differently, Al^{3+} substitution greatly increased both the reversible capacity and cycling stability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Although the Ga^{3+} dopant increase the discharge capacity effectively, its substitution did not alleviate the capacity degradation remarkably. The other doping ions, i.e., Co^{3+} and Mg^{2+} decreased the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

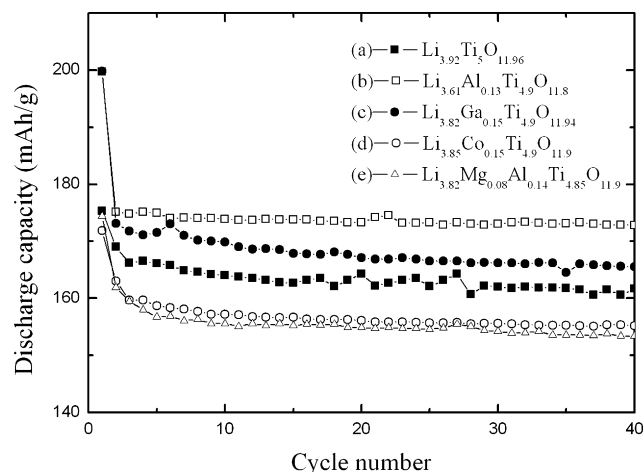


Fig. 5. Variation of the discharge capacities for (a) $\text{Li}_4\text{Ti}_5\text{O}_{12}$, (b) $\text{Li}_{3.95}\text{Al}_{0.15}\text{Ti}_{4.9}\text{O}_{12}$, (c) $\text{Li}_{3.95}\text{Ga}_{0.15}\text{Ti}_{4.9}\text{O}_{12}$, (d) $\text{Li}_{3.95}\text{Co}_{0.15}\text{Ti}_{4.9}\text{O}_{12}$ and (e) $\text{Li}_{3.9}\text{Mg}_{0.1}\text{Al}_{0.15}\text{Ti}_{4.85}\text{O}_{12}$ with the number of cycles between 0.5 and 2.3 V at a current density of 0.15 mA cm^{-2} .

The different behaviors of various doping ions could be explained as follows: the electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was increased by Al^{3+} dopant and in addition, the stability of the Al–O bond is higher than the Ti–O one in the octahedral coordination polyhedron in the spinel structure [16], it was reasonable that Al^{3+} substitution increased both the reversible capacity and cycling stability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. On the contrary, Co^{3+} dopant decreased the electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, while the stability of the Co–O bond is lower than the Ti–O one, so the electrochemical performance of the Co^{3+} substitution was decreased. The lower capacity delivered by $\text{Li}_{3.82}\text{Mg}_{0.08}\text{Al}_{0.14}\text{Ti}_{4.85}\text{O}_{11.9}$ electrodes suggested that some of the Mg^{2+} ions were located at the tetrahedral 8a sites of the spinel structure and inhibited the movement of Li^+ ions in the interstitial space of the spinel framework, therefore decreased the capacity of the material [13].

4. Conclusion

Spinel-type materials $\text{Li}_{3.95}\text{M}_{0.15}\text{Ti}_{4.9}\text{O}_{12}$ ($\text{M} = \text{Al}, \text{Ga}, \text{Co}$) and $\text{Li}_{3.9}\text{Mg}_{0.1}\text{Al}_{0.15}\text{Ti}_{4.85}\text{O}_{12}$ were prepared by solid-state reaction method. Al^{3+} substitution greatly improved the reversible capacity and cycling stability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ while Mg^{2+} substitution improved its total conductivity. The substitution of Ga^{3+} to some extent increased the capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. However, the doping ions such as Co^{3+} and Mg^{2+} decreased the electrochemical performance of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

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