Structural and electrochemical performances of Li$_4$Ti$_{5-x}$Zr$_x$O$_{12}$ as anode material for lithium-ion batteries

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**Abstract**

Zr-doped Li$_4$Ti$_{5}$O$_{12}$ in the form of Li$_4$Ti$_{5-x}$Zr$_x$O$_{12}$ ($x=0, 0.05, 0.1$ and $0.2$) was prepared by solid-state reaction in an air atmosphere. The dopant Zr partly entered the lattice structure of Li$_4$Ti$_{5}$O$_{12}$, and the excessive part existed as the impurity of ZrO$_2$. Zr-doping did not change the electrochemical reaction process of Li$_4$Ti$_{5}$O$_{12}$, but greatly affected its morphology and particle size. The particle size of the Zr-doped Li$_4$Ti$_{5}$O$_{12}$ sample was less than 100 nm and had less agglomeration. Zr-doping obviously improved the rate capability of Li$_4$Ti$_{5}$O$_{12}$ via the generation of small particle size and less agglomeration, however, a high amount of Zr-doping was adverse to the electrochemical performance probably due to much ZrO$_2$ impurity contained in the Li$_4$Ti$_{5}$O$_{12}$. Li$_4$Ti$_{4.9}$Zr$_{0.1}$O$_{12}$ exhibited a relatively good rate capability and cycling stability. At the charge–discharge rate of 5C, 10C and 20C, its discharge capacities were 143 mAh/g, 132 mAh/g and 118 mAh/g, respectively. After 100 cycles at 5C, it remained at 141 mAh/g.

**1. Introduction**

Recently, the spinel Li$_4$Ti$_{5}$O$_{12}$ has been demonstrated as a potential candidate for the anode material of lithium-ion batteries because of some of its unique characteristics [1–6]. It has good structural stability with almost negligible volume change during the Li$^+$ insertion and extraction processes, which suggests virtually unlimited cycle life. It features a flat operating voltage of about 1.5 V vs. lithium, which is higher than the reduction potential of common electrolyte solvents. This voltage makes it safer than the presently available candidate for the anode material of lithium-ion batteries because it is high enough to avoid the dangers of lithium plating that can occur at high-rate and/or low temperature operation [7].

Despite these mentioned advantages, however, Li$_4$Ti$_{5}$O$_{12}$ suffers from the problem of poor rate capability as a result of its low electronic conductivity. In order to improve the electronic conductivity of Li$_4$Ti$_{5}$O$_{12}$, there are two main methods. One is to improve its electronic conductivity by forming a composite of Li$_4$Ti$_{5}$O$_{12}$ and a conductive second phase such as Ag, C and polycanene [8–12]. Another is to synthesise Li$_4$Ti$_{5}$O$_{12}$ with ion doping. For example, doping Li$_4$Ti$_{5}$O$_{12}$ with Mg$^{2+}$ or Al$^{3+}$ on the Li$^+$ sites can increase the amount of mixing Ti$^{3+}$/Ti$^{4+}$ as charge compensation and thus enhance its electronic conductivity [13,14]. In addition, doping Ta$^{5+}$, Br$^{1-}$ into Ti$^{4+}$ or O$^{2-}$ sites can also increase the amount of mixing Ti$^{3+}$/Ti$^{4+}$ as charge compensation [15,16]. Ion-doped Li$_4$Ti$_{5}$O$_{12}$ usually has relatively poor crystallinity according to the literatures, which suggests that the dopant has entered the lattice structure and resulted in lattice distortion. This process might affect the morphology and particle size of the product. However, little research has been attempted to investigate the morphology and particle size of Li$_4$Ti$_{5}$O$_{12}$ with ion doping. It has been reported that the high-rate charge/discharge properties of the Li$_4$Ti$_{5}$O$_{12}$ can be improved by reducing the grain sizes of the particles because small particles can reduce the distance for lithium-ion diffusion while providing a higher electrode/electrolyte contact surface area [17]. Therefore, selecting appropriate ion dopant to produce the Li$_4$Ti$_{5}$O$_{12}$ sample with small particle sizes might be an approach to improve its high-rate charge/discharge properties.

In the present work, we found that Li$_4$Ti$_{5}$O$_{12}$ with Zr$^{4+}$-doping yielded small particle sizes and low particle aggregates by using a solid-state reaction. Here, the effect of Zr-doping on the lattice structure, particle size, morphology and electrochemical characteristics of Li$_4$Ti$_{5}$O$_{12}$ was investigated. By the way of comparison, pristine Li$_4$Ti$_{5}$O$_{12}$ without the Zr-doping was also investigated.

**2. Experimental**

An undoped Li$_4$Ti$_{5}$O$_{12}$ sample was prepared by using a solid-state reaction from CH$_3$COOLi·2H$_2$O and TiO$_2$. Zr-doped Li$_4$Ti$_{5-x}$Zr$_x$O$_{12}$ ($x=0.05, 0.1$ and $0.2$) samples were also prepared by using a solid-state reaction with CH$_3$COOLi·2H$_2$O, TiO$_2$ and Zr(NO$_3$)$_{4}$·5H$_2$O. The undoped and doped Li$_4$Ti$_{5}$O$_{12}$ samples were named as 0Zr, 0.05Zr, 0.1Zr and 0.2Zr, respectively. A 0.2 mol% excessive CH$_3$COOLi·2H$_2$O was provided to compensate for Li volatilization during the high temperature heating.

Firstly, the raw materials were dissolved in distilled water and stirred magnetically provided to compensate for Li volatilization during the high temperature heating. Firstly, the raw materials were dissolved in distilled water and stirred magnetically provided to compensate for Li volatilization during the high temperature heating. Firstly, the raw materials were dissolved in distilled water and stirred magnetically provided to compensate for Li volatilization during the high temperature heating.

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10 h to become dried powder. The dried powder was then calcinated at 800 °C in air atmosphere for 12 h to obtain the final white powder of the samples.

The crystal structures of the samples were characterized by X-ray powder diffraction (XRD) measurement using the Philips X Pert Pro MPD D12191 with a Cu Kα radiation source. Particle morphologies and sizes of the samples were observed by scanning electronic microscopy (SEM FEI INSPECT-F). Specific surface areas of the samples were determined through nitrogen adsorption/desorption at −196 °C using a Build SSA-4200 apparatus.

The electrochemical characterizations were measured by means of two-electrode coin-type half cells. To make the working electrodes, the synthesized samples were mixed with acetylene black (AB) and LA-132 binder with a weight ratio of 85:10:5 and ground into a paste. The prepared paste was spread onto aluminum foil using a doctor blade, with a 150 μm gap. The working electrodes were then dried at 100 °C in vacuum for 6 h before cell assembly. Li metal was used as the counter and reference electrode, and Celgard 2400 was the separator. The electrolyte was 1 M LiPF6/EC:DEC:DMC (1:1:1 in volume). The cells were assembled in a glove box filled with high purity argon gas. Galvanostatic discharge–charge measurements were performed at constant cut-off voltages of 1–3 V at room temperature (25 °C). Cyclic voltammograms were recorded from 1 V to 3 V with a scan rate of 0.2 mV/s using MSTAT4+ Arbin Instruments. The AC impedance spectrum was measured by using a Solatron 1260 Impedance Analyzer in the frequency range 10−2 Hz to 106 Hz.

### 3. Results and discussion

The X-ray diffraction patterns of the synthesized Li4Ti5O12 samples with and without Zr-doping are shown in Fig. 1. In order to correct for 2 theta error due to sample displacement in the XRD pattern measurement, the silicon was used as the internal standard. From Fig. 1, it can be seen that the main phase of all investigated samples is Li4Ti5O12 with a cubic spinel structure, which suggests that the dopant Zr does not obviously change the structural characteristics of Li4Ti5O12 during heat-treatment. However, as shown in Fig. 1, it can be observed that the XRD peak intensities of the samples decrease with the increase of the amount of Zr, which suggests that some dopant Zr has entered the lattice structure and that the Zr-doped Li4Ti5O12 has relatively poor crystallinity.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
</tr>
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<tbody>
<tr>
<td>0Zr</td>
<td>8.354</td>
</tr>
<tr>
<td>0.05Zr</td>
<td>8.356</td>
</tr>
<tr>
<td>0.10Zr</td>
<td>8.360</td>
</tr>
<tr>
<td>0.20Zr</td>
<td>8.361</td>
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</table>

Fig. 1. X-ray diffraction patterns of synthesized Li4Ti5O12 (x=0, 0.05, 0.1, 0.2) samples.

The above results indicate that the Li4Ti5O12 samples with vari-  

died amounts of Zr-doping have smaller particle sizes, less particle agglomerations. The peak positions of (1 1 1) planes of the samples are magnified in Fig. 2. Therefore, as shown in Fig. 2, it can be observed that the lattice parameter increases with the increased amount of Zr-doping, which should be ascribable to the substitution of some Zr for Ti sites and to the fact that the size of the Zr4+ (0.080 nm) ion is larger than that of Ti4+ (0.068 nm) ion.

Further, Fig. 1 shows that ZrO2 impurity peaks were detected in the curves of the 0.1Zr and 0.2Zr, and the peak intensities increase with the increased amount of doping Zr, which indicates that some dopant Zr cannot enter the lattice structure of the Li4Ti5O12 as the dopant amount increases. The ZrO2 impurity peaks in the X-ray diffraction patterns are marked by an asterisk.

Fig. 3 shows the SEM pictures of the Li4Ti5O12 samples with or without Zr-doping. Image A is the Li4Ti5O12 sample without Zr-doping. Images B, C and D are the Zr-doped Li4Ti5O12 (x=0.05, 0.1, 0.2, respectively) samples. Image A reveals that some of the particles of the Li4Ti5O12 sample without Zr-doping form larger agglomerations, whereas images B–D show that the particles of the samples with varied amounts of doping have relatively less agglomerations.

Fig. 4 shows close-up SEM pictures of Li4Ti5O12 samples with or without Zr-doping. It can be observed that the Li4Ti5O12 sample (image A) without Zr-doping has larger particle sizes than the samples (images B–D) with Zr-doping. The particle size as shown in image A is about 100–200 nm, while the sizes shown in images B–D are less than 100 nm. The BET surface areas of the samples with or without Zr-doping were determined by a nitrogen adsorption/desorption method, as shown in Table 1.

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET areas (m²/g)</th>
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<td>0Zr</td>
<td>4.025</td>
</tr>
<tr>
<td>0.05Zr</td>
<td>4.625</td>
</tr>
<tr>
<td>0.10Zr</td>
<td>5.145</td>
</tr>
<tr>
<td>0.20Zr</td>
<td>5.708</td>
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</table>

The above results indicate that the Li4Ti5O12 samples with varied amounts of Zr-doping have smaller particle sizes, less particle agglomerations.

### Table 1

<table>
<thead>
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<tr>
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<td>8.360</td>
</tr>
<tr>
<td>0.20Zr</td>
<td>8.361</td>
</tr>
</tbody>
</table>

Fig. 2. Enlarged (1 1 1) peaks of synthesized Li4Ti5O12 samples doped with different Zr amounts: x=0, 0.05, 0.1, 0.2.

The above results indicate that the Li4Ti5O12 samples with varied amounts of Zr-doping have smaller particle sizes, less particle agglomerations.
agglomerations and larger surface areas than the sample without doping. This could be attributed to two reasons: (1) the dopant Zr that could enter the lattice structure of the Li$_4$Ti$_5$O$_{12}$, resulting in lattice distortion which hindered particle growth and agglomeration during heat-treatment; (2) part of the Zr dopant that could not enter the lattice structure of the Li$_4$Ti$_5$O$_{12}$ and constituted an impurity in the form of ZrO$_2$, which likewise hindered undesirable particle growth and agglomeration.

Fig. 5 shows the AC impedance spectra of the Li$_{4-x}$Ti$_5$Zr$_x$O$_{12}$ ($x = 0, 0.05, 0.1, 0.2$) electrodes, which were measured at the stable voltage of 1.55 V, respectively. AC impedance spectra are fitted using an equivalent circuit. In this equivalent circuit, $R_s$ and $R_{ct}$ are the solution resistance and charge transfer resistance, respectively. CPE is placed to represent the double layer capacitance and passivation film capacitance. $W$ represents the Warburg impedance [18]. The plot of the real axis $Z_{re}$ vs. the reciprocal square root of the lower angular frequencies $\omega^{-0.5}$ is illustrated in Fig. 6. The straight lines are attributed to the diffusion of the lithium ions into the bulk of the electrode materials, the so-called Warburg diffusion. From Fig. 6, we can obtain the value of Warburg impedance coefficient ($\sigma_w$) according to the following equations [19,20]:

$$Z_{re} = R_s + R_{ct} + \sigma_w \omega^{-0.5}$$

$$D = 0.5 \left( \frac{RT}{AF^2 \sigma_w C} \right)^2$$

where $R_{ct}$, charge transfer resistance; $R_s$, solution resistance; $\omega$, angular frequency in the low frequency region; $D$, diffusion coefficient; $R$, the gas constant; $T$, the absolute temperature; $F$, Faraday's constant; $A$, the area of the electrode surface; and $C$, molar concentration of Li$^+$ ions (moles cm$^{-3}$), the Li$^+$ ions diffusion coefficient $D$ can be obtained. The impedance parameters are recorded in Table 3.

From Table 3, it can be seen that the Zr-doped Li$_{4-x}$Ti$_5$Zr$_x$O$_{12}$ ($x = 0.05, 0.1, 0.2$) electrodes have better electronic conductivity and ionic conductivity than the Li$_4$Ti$_5$O$_{12}$ electrode without Zr-doping. This should be ascribed to the fact that the Zr-doped Li$_{4-x}$Ti$_5$Zr$_x$O$_{12}$ ($x = 0.05, 0.1, 0.2$) samples have smaller particle sizes and less particle agglomerations than the Li$_4$Ti$_5$O$_{12}$ sample without Zr-doping. Furthermore, among the Zr-doped electrodes, it can be seen that the 0.1Zr electrode has the best electronic conductivity and ionic conductivity as shown in Table 3, which indicates that the selection of an appropriate amount of Zr dopant is important. This result might be attributed to the impurity of ZrO$_2$. As mentioned above, with the increased amount of the Zr-doping, part of the dopant

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>$\sigma_w$ (Ω cm$^2$/s$^{0.5}$)</th>
<th>$D$ (cm$^2$/s)</th>
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</thead>
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<tr>
<td>0Zr</td>
<td>3.2</td>
<td>165.9</td>
<td>383.5</td>
<td>9.61E-13</td>
</tr>
<tr>
<td>0.05Zr</td>
<td>2.6</td>
<td>124.1</td>
<td>180.3</td>
<td>4.40E-12</td>
</tr>
<tr>
<td>0.10Zr</td>
<td>2.0</td>
<td>99.6</td>
<td>147.2</td>
<td>6.58E-12</td>
</tr>
<tr>
<td>0.20Zr</td>
<td>2.7</td>
<td>135.3</td>
<td>234.0</td>
<td>2.61E-12</td>
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</tbody>
</table>
could not enter the lattice structure of the \( \text{Li}_4\text{Ti}_5\text{O}_{12} \). This part constituted an impurity in the form of \( \text{ZrO}_2 \), as detected by the X-ray diffraction patterns. \( \text{ZrO}_2 \) has high dielectric constant [21], which probably has lower lithium ionic conductivity and electronic conductivity than \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) and thus impedes the transportation of Li-ions and electrons. Therefore, when the amount of Zr-doping is high, there would be much \( \text{ZrO}_2 \) contained in the product, which is adverse to the conductivity of \( \text{Li}_4\text{Ti}_5\text{O}_{12} \).

**Fig. 4.** Close-up SEM pictures of \( \text{Li}_4\text{Ti}_{5-x}\text{Zr}_x\text{O}_{12} \) (\( x = 0, 0.05, 0.1, 0.2 \)) samples.

**Fig. 5.** AC impedance spectra of the \( \text{Li}_4\text{Ti}_{5-x}\text{Zr}_x\text{O}_{12} \) (\( x = 0, 0.05, 0.1, 0.2 \)) electrodes at the voltage of 1.55 V.

**Fig. 6.** Relationship between real impedance with the low frequencies for the \( \text{Li}_4\text{Ti}_{5-x}\text{Zr}_x\text{O}_{12} \) (\( x = 0, 0.05, 0.1, 0.2 \)) electrodes.

**Fig. 7.** shows the cyclic performance of the \( \text{Li}_4\text{Ti}_{5-x}\text{Zr}_x\text{O}_{12} \) (\( x = 0, 0.05, 0.1, 0.2 \)) samples at different rates from 0.5C, 1.0C, 3.0C, 5.0C, 10.0C to 20.0C. The charge–discharge processes of the samples were taken for 10 cycles at 0.5C, 1.0C, 3.0C, 5.0C, 10.0C and 20.0C, respectively. It can be observed that the undoped sample \( 0\text{Zr} \) exhibited a high discharge capacity and good cycling stability at 0.5C and 1.0C. At 0.5C, its initial discharge capacity was 166 mAh/g, and at 1.0C, its
capacity remained at 155 mAh/g. With the rate increase, however, its capacity quickly decreased. At 3.0C, its capacity was 126 mAh/g; at 10.0C, it was 83 mAh/g; and at 20.0C, its capacity remained at only 53 mAh/g. In contrast, the doped samples 0.05Zr, 0.1Zr and 0.2Zr displayed relatively low discharge capacity at 0.5C and 1.0C. At 0.5C, their capacities were 164 mAh/g, 159 mAh/g and 151 mAh/g, respectively; and at 1.0C they were 154 mAh/g, 151 mAh/g and 134 mAh/g. As shown in Fig. 7, however, the discharge capacities of the doped samples manifested less capacity degradation with the rate increase than the undoped sample. For example, at 3.0C, the capacities of the doped samples 0.05Zr, 0.1Zr and 0.2Zr were 141 mAh/g, 146 mAh/g and 126 mAh/g, respectively; at 10.0C, they were 121 mAh/g, 132 mAh/g and 102 mAh/g; and at 20.0C, they still remained at 101 mAh/g, 118 mAh/g and 83 mAh/g. For clear observation, the initial discharge capacities of the samples 0Zr, 0.05Zr, 0.1Zr and 0.2Zr as a function of the charge/discharge rates are shown in Fig. 8. These results indicate that Zr-doping impairs the capacity of the Li4Ti5O12 at low rates, but can obviously enhance its rate capability. This could be ascribed to Zr-doping samples having smaller particle sizes and less particle agglomerations than the undoped Li4Ti5O12. Smaller particles and less particle agglomerations could reduce the distance for lithium-ion diffusion and provide for a higher electrode/electrolyte contact surface area, which improve the electronic conductivity of the electrodes, resulting in good rate capability. It is worth noting that, as shown in Fig. 7, the 0.1Zr sample has the best rate capability of all the doped samples, which indicates that the x = 0.1 dopant amount is appropriate. These results are in good agreement with the AC impedance spectra of the Li4Ti5−xZr2O12 (x = 0, 0.05, 0.1, 0.2) electrodes mentioned above.

For evaluating the cycling stability of the 0.1Zr sample, it was further charge–discharged at a current rate of 5C for another 100 cycles after the 60 cycles electrochemical tests performed at 0.5C, 1.0C, 3.0C, 5.0C, 10.0C and 20.0C. This is shown in Fig. 9. It can be observed that the 0.1Zr sample shows a stable cycle life. The initial discharge capacity of the sample was 143 mAh/g, and even after 100 charge–discharge cycles, its capacity remained at 141 mAh/g. Furthermore, as Fig. 9 shows, the charge and discharge efficiency remained almost at 100%.

### Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anodic peak (V)</th>
<th>Cathodic peak (V)</th>
<th>Difference between anodic and cathodic peak (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0Zr</td>
<td>1.844</td>
<td>1.354</td>
<td>0.490</td>
</tr>
<tr>
<td>0.05Zr</td>
<td>1.769</td>
<td>1.387</td>
<td>0.382</td>
</tr>
<tr>
<td>0.1Zr</td>
<td>1.756</td>
<td>1.404</td>
<td>0.352</td>
</tr>
<tr>
<td>0.2Zr</td>
<td>1.819</td>
<td>1.370</td>
<td>0.449</td>
</tr>
</tbody>
</table>
Cyclic voltammograms of the electrodes 0Zr, 0.05Zr, 0.1Zr and 0.2Zr at a scan rate of 0.2 mV/s between 1 V and 3 V are shown in Fig. 10. It is shown that all the investigated electrodes have similar redox peaks, suggesting that Zr-doping does not change the electrochemical reaction process of Li$_4$Ti$_5$O$_{12}$. The potential differences between anodic and cathodic peaks for the Li$_4$Ti$_{5-x}$Zr$_x$O$_{12}$ ($x=0$, 0.05, 0.1, 0.2) electrodes are shown in Table 4. It can be observed that the Zr-doped Li$_4$Ti$_{5-x}$Zr$_x$O$_{12}$ ($x=0.05$, 0.1, 0.2) electrodes have lower potential differences than the pristine Li$_4$Ti$_5$O$_{12}$ (0Zr) and that the 0.1Zr electrode has the smallest potential difference among the doped samples. These indicate that Zr-doping is favorable for reducing the electrode polarization, but that too high an amount of doping is disadvantageous.

4. Conclusions

The structure and electrochemical characteristics of the Zr-doped Li$_4$Ti$_{5-x}$Zr$_x$O$_{12}$ in the form of Li$_4$Ti$_{5-x}$Zr$_x$O$_{12}$ ($x=0$, 0.05, 0.1, 0.2) were investigated in the present study. The Zr-doped Li$_4$Ti$_5$O$_{12}$ samples had smaller particle sizes and less particle agglomerations than the pristine Li$_4$Ti$_5$O$_{12}$ and Zr-doping did not change the electrochemical reaction process of Li$_4$Ti$_5$O$_{12}$. The dopant Zr partly entered the lattice structure of Li$_4$Ti$_5$O$_{12}$ as the doping amount increased, and thus constituted an impurity in the form of ZrO$_2$. The ZrO$_2$ impurity probably has lower lithium ionic conductivity and electronic conductivity as compared with Li$_4$Ti$_5$O$_{12}$, which was disadvantageous to the electrochemical characteristics. The Zr dopant can yield smaller particle sizes and less particle agglomerations that are favorable to the electrochemical performances of Li$_4$Ti$_5$O$_{12}$, but also it might impair it caused by the impurity of ZrO$_2$. Therefore, there was an optimum amount for Zr-doping. From the overall performance point of view, the 0.1Zr sample exhibited the best rate capability.

Acknowledgements

This work was carried out with financial support from Ministry of Science and Technology of the People’s Republic of China (No. 2006CB932703) and Key Item of knowledge Innovation Project of Chinese Academy of Science (No. KJCX2-YW-M01).

References