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High capacity and excellent rate capability of Ti-doped Li$_2$MnSiO$_4$ as cathode materials for Li-ion batteries

Min Wang $^{a,b}$, Meng Yang $^{a,*}$, Liqun Ma $^{a,*}$ Xiaodong Shen $^{a}$

Ti-doped Li$_2$Mn$_{0.94}$Ti$_{0.06}$SiO$_4$ as cathode materials for Li-ion batteries was successfully synthesized by a facile sol-gel method. The addition of Ti to the precursors changed particle sizes and specific surface areas of Li$_2$MnSiO$_4$. The galvanostatic charge-discharge measurements showed that Ti-doped Li$_2$Mn$_{0.94}$Ti$_{0.06}$SiO$_4$ electrodes delivered high charge capacity of 298, 286, 248 mAh g$^{-1}$ and discharge capacity of 203, 211, 171 mAh g$^{-1}$ in the first cycle, much higher than that of undoped Li$_2$MnSiO$_4$ (52 mAh g$^{-1}$ for charging and 26 mAh g$^{-1}$ for discharging). Moreover, Ti-doped samples exhibited good cycling stability and superior rate capability, as compared to that of pristine sample. Even at high rate (2C), the Ti-doped Li$_2$Mn$_{0.94}$Ti$_{0.06}$SiO$_4$ still kept high discharge capacities. The remarkable enhancement of battery performance in terms of capacity and rate capability for doped Li$_2$Mn$_{0.94}$Ti$_{0.06}$SiO$_4$ was primarily attributed to the decrease of charge transfer resistance and the improvement of Li$^+$ diffusion coefficient.

Introduction

Recently, Li$_3$MnSiO$_4$ as cathode materials for Li-ion batteries has attracted remarkable attention since first reported by R. Dominko et al. $^{1}$ in 2007. This material is expected to be the candidate cathode materials for next-generation rechargeable Li-ion batteries due to its high energy density, power density, high thermal stability, abundant resources, and environmentally friendly et al. $^{2-5}$ Most importantly, the transition metal manganese ion can easily achieve the transformation of Mn$^{2+}$/Mn$^{3+}$ and Mn$^{3+}$/Mn$^{4+}$ to carry out extraction of two Li$^+$, resulting high theoretical capacity of 330 mAh g$^{-1}$. $^{1,3}$ However, low intrinsic electronic conductivity and slow Li$^+$ mobility which cause excessive polarization during charge-discharge process, lead to low capacity and inferior electrochemical performance of this material. $^{6,7}$ Although carbon coating can improve electronic conductivity and reduce particle size which can shorten the pathway of Li$^+$ migration, Li$_2$MnSiO$_4$ still has large irreversible capacity loss and unsatisfactory cycling stability so that not sufficient for practical battery applications. $^{5,9}$ Thus, other feasible methods to enhance its battery performance should be found in urgent. Recently, few studies on ion doping of Li$_3$MnSiO$_4$ material have been reported. Zhang et al. $^{10}$ prepared Cr-doped Li$_2$MnSiO$_4$ with a citric acid-assisted sol-gel method. The obtained Li$_2$Mn$_{0.94}$Cr$_{0.06}$SiO$_4$ showed the best cycling performance and could deliver the discharge capacity of 306 mAh g$^{-1}$ in the fifth cycle. Choi et al. $^{11}$ synthesized various ions (Al$^{3+}$, Ga$^{3+}$, Mg$^{2+}$) doped Li$_2$MnSiO$_4$ via the conventional sol-gel method. The sample doped with Ga$^{3+}$ showed high charge/discharge capacity and initial efficiency with well-dispersed nanoparticle formation. Hence, doping with metal ions might be a new strategy to improve the electrochemical performance of Li$_2$MnSiO$_4$ material.

Herein, we chose Ti element as doping cation for following reasons: 1) according to defect chemistry, aliovalent ion doping can induce defects (vacancies or interstitials) in the lattice by charge compensation so as to enhance the materials’ conductivity. $^{11-14}$ 2) this element is inactive in the potential range of 1.5-4.8V, so the lattice shrinking of Li$_2$MnSiO$_4$ during charging is minimized by the support of unchanged radius of Ti$^{4+}$. $^{10,15}$

In this paper, we successfully synthesized pristine Li$_2$MnSiO$_4$ and Ti-doped Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$ (x=0.06, 0.1 and 0.2) materials by a facile sol-gel method. The effects of Ti-doped Li$_2$MnSiO$_4$ materials in terms of structure, morphology and electrochemical properties have been investigated by X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), inductively coupled plasma-atomic emission spectrometer (ICP-AES), Brunauer-Emmett-Teller (BET), galvanostatic charge-discharge and electrochemical impedance spectra (EIS) in details.

Experimental

Ti-doped Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$ (x=0.06, 0.1 and 0.2) powders were prepared by a facile sol-gel method. Analytical grade lithium acetate dihydrate, manganese acetate tetrahydrate, ethyl silicate and tetrabuty titanate were employed as raw materials. First, stoichiometric amounts of lithium acetate dihydrate and manganese

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acetate tetrahydrate were dissolved in ethanol stirring for half an hour. Then, ethyl silicate in ethanol solution and tetrabuty titanate in ethanol solution was slowly added to above mixed solutions in order. The solutions were maintained at 80 °C for 24 hours under vigorously stirring and then dried in oven at 80 °C overnight. Subsequently, the obtained xerogel were fine ground by ball-milling and then calcined at 650 °C for 10 hours with a flow of argon. For comparison, undoped Li$_2$MnSiO$_4$ powder was prepared by identical process without adding tetrabuty titanate as the doping agent.

X-ray powder diffraction (XRD) was collected by diffractometer (SmartLab, Japan) with Cu Kα (λ=1.5406 Å) radiation. The scanning angle 2θ was ranging from 10 to 80° at a step of 0.02°. The morphology and particle size distribution were observed by field emission scanning electron microscopy (FESEM, HITACHI-S94800, Japan). N$_2$ adsorption-desorption isotherms were measured by F-Sorb 2400 analyzer. The specific surface areas were calculated by using Brunauer-Emmett-Teller (BET) method. Chemical composition of all the samples were determined by inductively coupled plasma–atomic emission spectrometer (ICP-AES).

The electrochemical characterization of the materials was measured using a typical CR2032 coin cell. The working electrodes were prepared by mixing 80 wt. % active materials, 10 wt. % carbon black with 10 wt. % polyvinylidene fluoride (PVDF) via using 1-methyl-2-pyrrolidone as a solvent. Then, the resulting slurries were uniformly pasted on Al foils and dried in vacuum at 100 °C overnight. Circular electrodes were cut-off from the sheets with a diameter of 12 mm and the active materials (Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$) weights were maintained in the range of 1.9-2.1 mg cm$^{-2}$. The coin cells were assembled in a glove box filled with high pure argon (less than 1 ppm of water and oxygen) using Li metal as the anodes, celgard2400 film as the separator and 1 M LiPF$_6$ dissolved in EC and DMC (1:1 w/w) as the electrolyte. Meanwhile, galvanostatic charge-discharge measurements on (Land, China) were performed in the voltage range of 1.5-4.8 V (vs. Li$^+$/Li) under the current density of 10 mA g$^{-1}$ at 30 °C. Rate capability of electrodes was examined at various current densities: 0.03C, 0.1C, 0.5C, 1C, 2C (1C=330 mA g$^{-1}$). Electrochemical impedance spectra (EIS) were recorded by electrochemical workstation (CHI660D, China) in a frequency range from 10 mHz to 100 kHz with amplitude of 5 mV.

**Results and Discussion**

The typical powder X-ray diffraction (XRD) patterns of as-prepared pristine Li$_2$MnSiO$_4$ and Ti-doped Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$ (x=0.06, 0.1 and 0.2) powders are shown in Fig.1. It can be seen that all the samples are well indexed to orthorhombic structure with Pmn$_2$1 space group, which is in accord with previous reports. However, with the increasing of Ti content, some diffraction peaks identified as Mn$_3$TiO$_4$ and Li$_3$SiO$_3$ impurities are observed in the case of x=0.2, which are also reported by other researchers. But neither of these impurities is considered for quantitative analysis, since they are electrochemically inactive in the voltage window of 1.5-4.8 V. In order to clarify the actual sites of dopants, Rietveld refinement is adopted. The refinements results are presented in Table 1. Noting, doping Ti element induces the slight volume shrinkage of Li$_2$MnSiO$_4$, which might be ascribed to the smaller ionic radius of Ti$^{4+}$ (0.68 Å) than that of Mn$^{2+}$ (0.80 Å), but the values of b-axis are a little enlargement. According to previous reports, layers of SiO$_2$ and MnO$_4$ tetrahedral lying on the ab-plane link along the b-axis by LiO$_4$ tetrahedra, so enlargement of b value can expand the Li$^+$ diffusion channel to facilitate Li$^+$ mobility so as to enhance the electrochemical activity. The results of ICP-AES element analysis are demonstrated in Table 2, where the amount of element Mn is normalized to stoichiometry. As is seen, the actual compositions of all as-prepared powders are generally in line with nominal compositions.

FE-SEM images display the morphology of pristine and Ti-doped samples, as shown in Fig.2. We can see that pristine Li$_2$MnSiO$_4$ powders exhibit severe agglomeration by nanosized...
Fig. 2 Refinement results of as-prepared Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$ (x = 0, 0.06, 0.1 and 0.2) powders.

Table 1 Lattice parameters and unit cell volumes of as-prepared Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$ (x = 0, 0.06, 0.1 and 0.2) samples

<table>
<thead>
<tr>
<th>samples</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>V/Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$MnSiO$_4$</td>
<td>6.3077</td>
<td>5.3884</td>
<td>4.9753</td>
<td>169.1025</td>
</tr>
<tr>
<td>Li$<em>2$Mn$</em>{0.94}$Ti$_{0.06}$SiO$_4$</td>
<td>6.3185</td>
<td>5.3908</td>
<td>4.9708</td>
<td>169.3142</td>
</tr>
<tr>
<td>Li$<em>2$Mn$</em>{0.9}$Ti$_{0.1}$SiO$_4$</td>
<td>6.3128</td>
<td>5.3913</td>
<td>4.9676</td>
<td>169.0683</td>
</tr>
<tr>
<td>Li$<em>2$Mn$</em>{0.8}$Ti$_{0.2}$SiO$_4$</td>
<td>6.2943</td>
<td>5.4117</td>
<td>4.9457</td>
<td>168.4647</td>
</tr>
</tbody>
</table>

Table 2 Chemical compositions of as-prepared Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$ (x = 0, 0.06, 0.1 and 0.2) samples obtained from ICP-AES, where the amounts of Mn are normalized

<table>
<thead>
<tr>
<th>samples</th>
<th>Li</th>
<th>Mn</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$MnSiO$_4$</td>
<td>1.91</td>
<td>1.0</td>
<td>—</td>
</tr>
<tr>
<td>Li$<em>2$Mn$</em>{0.94}$Ti$_{0.06}$SiO$_4$</td>
<td>1.93</td>
<td>0.94</td>
<td>0.064</td>
</tr>
<tr>
<td>Li$<em>2$Mn$</em>{0.9}$Ti$_{0.1}$SiO$_4$</td>
<td>2.03</td>
<td>0.9</td>
<td>0.101</td>
</tr>
<tr>
<td>Li$<em>2$Mn$</em>{0.8}$Ti$_{0.2}$SiO$_4$</td>
<td>2.06</td>
<td>0.8</td>
<td>0.198</td>
</tr>
</tbody>
</table>
primary particles (~50 nm), while Ti-doped samples represent alleviative agglomeration between particles and the mean particle sizes are approximately 30 nm, much less than that of pristine sample. Moreover, the BET specific surface areas of primary particles (~50 nm), while Ti-doped samples represent alleviative agglomeration between particles and the mean particle sizes are approximately 30 nm, much less than that of pristine sample. Moreover, the BET specific surface areas of particle sizes are approximately 30 nm, much less than that of pristine Li$_2$MnSiO$_4$ electrodes are ascribed to i) according to the XRD results, for Ti-doped samples, the enlargement of Li$^+$ diffusion channel is beneficial to facilitate Li$^+$ mobility; ii) decreased particle size and increased specific surface area can shorten the Li$^+$ migration pathway and enable good contact between particles and the electrolyte so as to benefit the electrochemical reaction; iii) Li$_2$MnSiO$_4$ is a typical n-type semiconductor, its electronic conduction takes place by electron hopping between high-valence (Mn$^{4+}$ or Mn$^{3+}$) and low-valence (Mn$^{2+}$ or Mn$^{3+}$) cations, Ti doping can increase the amount of Mn$^{3+}$ and probably Mn$^{4+}$, thus increase its electric conductivity; iv) the lattice shrinking of Li$_2$MnSiO$_4$ during charging is minimized by the support of unchangeable radius of Ti$^{4+}$ to stabilize the structure.

Fig.4 demonstrates the rate capabilities of pristine Li$_2$MnSiO$_4$ and Ti-doped Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$ ($x=0.06$, 0.1 and 0.2) samples. The charge-discharge current densities are various from 0.03C to 2C (1C=330 mA g$^{-1}$). It is surprising to note that Ti-doped Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$ samples exhibit superior rate capability, as shown in the Fig.6. At 1C-rate, the discharge capacities of Ti-doped samples in the second cycle are 114, 120, 76 mAh g$^{-1}$ for 0.06Ti, 0.1Ti, 0.2Ti, respectively. Even at higher rate (2C), the Ti-doped samples still keep the discharge capacity of around 70 mAh g$^{-1}$, whereas the undoped sample almost loses the ability to discharge. The excellent rate capabilities of Ti-doped samples should be ascribed to the enhancement of electronic conductivity and migration rate of Li ions, which can be further confirmed by the results of electrochemical impedence spectra in the following section.

![Fig.4 Charge-discharge curves of Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$($x=0$, 0.06, 0.1 and 0.2) electrodes in different cycles](image)

![Fig.5 Cycling performance of Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$($x=0$, 0.06, 0.1 and 0.2) electrodes in the voltage range of 1.5-4.8V under the current density of 10 mA g$^{-1}$ at 30°C](image)
Fig. 6 Charge-discharge curves of Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$ (x=0, 0.06, 0.1 and 0.2) electrodes with various current densities at 30 °C (1C=330mA g$^{-1}$).

Electrochemical impedance spectra (EIS) are employed to characterize the kinetic properties of pristine Li$_2$MnSiO$_4$ and Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$ (x=0.06, 0.1 and 0.2) samples. Fig. 7a demonstrates the Nyquist plots of the impedance spectra for all samples, and the equivalent circuit mode in the inset of Fig. 7a is used for fitting the impedance data. All spectrums are consisted of a depressed small semicircle in the high-frequency region, a large semicircle in the middle-frequency and a slightly inclined line in the low-frequency region. The semicircles represent the solution resistances ($R_s$), film...

![Electrochemical impedance spectra](image)

Table 3 The fitting impedance parameters of as-prepared Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$ (x=0, 0.06, 0.1 and 0.2) samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_s$/ohm</th>
<th>$R_1$/ohm</th>
<th>$R_2$/ohm</th>
<th>$D_{Li}^{+}$/cm$^2$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$MnSiO$_4$</td>
<td>1.923</td>
<td>100.2</td>
<td>433.6</td>
<td>2.3×10$^{-15}$</td>
</tr>
<tr>
<td>Li$<em>2$Mn$</em>{0.94}$Ti$_{0.06}$SiO$_4$</td>
<td>1.727</td>
<td>55.6</td>
<td>81.14</td>
<td>3.2×10$^{-15}$</td>
</tr>
<tr>
<td>Li$<em>2$Mn$</em>{0.9}$Ti$_{0.1}$SiO$_4$</td>
<td>3.82</td>
<td>57.69</td>
<td>68.3</td>
<td>3.3×10$^{-15}$</td>
</tr>
<tr>
<td>Li$<em>2$Mn$</em>{0.8}$Ti$_{0.2}$SiO$_4$</td>
<td>1.733</td>
<td>81.14</td>
<td>88.65</td>
<td>1.9×10$^{-15}$</td>
</tr>
</tbody>
</table>
Resistances ($R_1$) and charge transfer resistance ($R_2$), respectively. The inclined lines are attributed to the Li ions diffusion in the electrode bulks, which are called Warburg diffusion ($Z_w$). The obtained fitting parameters are displayed in Table 3. It is seen that almost all of the resistances of Ti-doped Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$ are smaller than that of undoped Li$_2$MnSiO$_4$, especially charge transfer resistance ($R_2$). The values of charge transfer resistance are 81.14, 68.3, 88.65 $\Omega$ for 0.06Ti, 0.1Ti, 0.2Ti samples, respectively, much smaller than that of undoped sample (433.6 $\Omega$). The lower $R_2$ of Ti-doped samples indicates that Ti doping facilitates the charge transfer at the interface, leading to high capacity and superior rate capability as observed. Besides, the diffusion coefficients of Li$^+$ in the electrodes can be calculated based on the following equation:

$$D_{Li^+} = \frac{(R^2T^2)}{(2A^nF^4C^2\omega^2)} \tag{1}$$

Where, $R$ is gas constant, $T$ is the absolute temperature, $A$ is the electrode area, $n$ is the transfer electron, $F$ is the Faraday’s constant, $C$ is the molar concentration of Li$^+$ and $\omega$ is the Warburg coefficient which can be obtained by following equation:

$$Z_{re} \propto \omega \omega^{-1/2} \tag{2}$$

Where, $\omega$ is the angular frequency in the low frequency region. As shown in Table 3, the calculated values of Li$^+$ diffusion coefficients are $2.3 \times 10^{-15}$, $3.2 \times 10^{-15}$, $3.3 \times 10^{-15}$, $1.9 \times 10^{-15}$ cm$^2$·s$^{-1}$ for undoped, 0.06Ti, 0.1Ti, 0.2Ti samples, respectively. We observe from the results that the Li$^+$ diffusion coefficients do not present an obvious increasing tendency with the increasing of Ti content. For 0.06Ti and 0.1Ti samples, the Li$^+$ diffusion coefficients have a little improvement, indicating that Li$^+$ can easily migrate to the active materials so as to enhance ionic conductivity. However, for 0.2Ti sample, the value has a slight decline. This might be ascribed to impurities existed in the powder which block the lithium ion mobility. Therefore, we can conclude that the content of doping elements is not the much, the better. Moderate substitution of Mn with supervalent cation Ti is beneficial to improve the electronic and ionic conductivity of Li$_2$MnSiO$_4$ material to enhance the electrochemical performance.

Conclusions

In summary, we successfully prepared pristine Li$_2$MnSiO$_4$ and Ti-doped Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$ ($x=0.06, 0.1$ and $0.2$) powders by a facile sol-gel method. XRD measurements confirm the structures of all the as-prepared powders are in agreement with orthorhombic Pmn2$_1$ space group. FE-SEM images and BET specific surface areas demonstrate that Ti-doped Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$ ($x=0.06, 0.1$ and $0.2$) samples possess smaller particle sizes, better monodispersion and larger specific surface areas, as compared to those of pristine Li$_2$MnSiO$_4$. Ti-doped Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$ electrodes exhibit dramatically increased capacity of 298, 286, 248 mAh g$^{-1}$ for first charging and 203, 211, 171 mAh g$^{-1}$ for first discharging, respectively, much higher than that of pristine sample. Among these Ti-doped materials, Li$_2$Mn$_{0.8}$Ti$_{0.2}$SiO$_4$ shows the best cycling performance, maintaining the capacity around 100 mAh g$^{-1}$ after 50 cycles. Moreover, Ti-doped samples also present superior rate capability. At 1C rate, they have the discharge capacities of 114, 120, 76 mAh g$^{-1}$ for 0.06Ti, 0.1Ti, 0.2Ti samples, respectively. Even at higher rate (2C), the Ti-doped samples still keep the discharge capacity of around 70 mAh g$^{-1}$. The remarkable enhancement of battery performance in terms of capacity and rate capability for Ti-doped Li$_2$Mn$_{1-x}$Ti$_x$SiO$_4$ is primarily attributed to the decrease of charge transfer resistance and the improvement of Li$^+$ mobility coefficient. Nevertheless, we don’t clearly understand the mechanism of defects formation about aliovalent doping at present, the results indeed demonstrate a new strategy for conductivity enhancement and the possible structural stabilization which may lead to excellent electrochemical properties of Li$_2$MnSiO$_4$ cathode materials.

Acknowledgements

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