



Structural and electrochemical characteristics of SiO₂ modified Li₄Ti₅O₁₂ as anode for lithium-ion batteries



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ABSTRACT

The commercial Li₄Ti₅O₁₂ is modified with SiO₂ directly via a simple sol–gel method. The SiO₂ modified Li₄Ti₅O₁₂ samples are characterized by a variety of means such as powder X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX) mapping, transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), galvanostatic charge–discharge test, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Compared with pure Li₄Ti₅O₁₂, the structure of SiO₂ modified Li₄Ti₅O₁₂ has no change, and there is a SiO₂ coating layer over the Li₄Ti₅O₁₂ particles. Appropriate amount of SiO₂ could effectively reduce the electrochemical polarization of Li₄Ti₅O₁₂ and enhance electrochemical reaction kinetics of Li⁺ insertion/deinsertion. As a result, the Li₄Ti₅O₁₂ modified with 2.5 mol% SiO₂ exhibits higher specific capacity and better rate capability. Moreover, the SiO₂ coating layer is likely to cover the catalytic sites on the Li₄Ti₅O₁₂ surface for the decomposition of electrolyte, thereby restraining the formation of solid electrolyte interphase (SEI), which is very favorable for improving the cycle performance of Li₄Ti₅O₁₂. The SiO₂ modification process is easy to control and carry out for industrialization, which could improve the electrochemical performance of Li₄Ti₅O₁₂.

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1. Introduction

Lithium ion battery (LIB) as an energy storage device is attracting more and more attentions due to its high energy and power density. Currently, Li₄Ti₅O₁₂ (LTO) has been demonstrated as a promising alternative of graphite anode materials for high power applications [1–4]. This is mainly because LTO exhibits excellent Li⁺ insertion/extraction reversibility with zero structural change and a relatively higher operating voltage (1.55 V vs Li/Li⁺) to ensure better safety of the battery by avoiding the trouble of LIBs [5–8]. Despite these advantages, LTO presents a poor rate capability due to the poor electrical conductivity (<10^{−13} S cm^{−1}) and sluggish Li⁺ diffusion [9–11]. Thus, some strategies have been proposed to overcome the significant drawbacks, by reducing the particle size [12–15], doping [16–25] and surface modification [26–31].

In previous works, AlF₃ has been successfully used to modify commercial LTO via a low-temperature reaction approach [32]. For the AlF₃ modified LTO, a part of Al³⁺ and F[−] can be doped into

the bulk phase of LTO particles, and the rest remains on the surface of LTO particles to form a coating layer. The ions doping could enhance the electrical conductivity, while the coating layer over the LTO could prevent the decomposition of electrolyte. Therefore, the AlF₃ modification process is regarded as a simple yet very effective strategy, which cannot only improve the high-rate charge/discharge performance of LTO, but also suppress the gassing behavior of LTO anode battery. Unfortunately, the AlF₃ modification method is not suitable for industrial production because fluoride is not environmentally friendly. Moreover, if the addition of this reagent could not be well controlled during the co-precipitation process, the electrochemical performance of the resulting AlF₃ modified LTO will be less satisfactory. Therefore, it is very necessary to develop a simple method, which is environmentally friendly and easily controllable.

To the best of our knowledge, SiO₂ has been widely used to modify the surface of cathode materials, such as LiFePO₄, LiNi_{0.5}Mn_{1.5}O₄, LiNi_{0.8}Co_{0.2}O₂ and Li_{1.03}Mn_{1.97}O₄ particles, to enhance their electrochemical performance [33–35]. This enhancing effect is attributed to the presence of SiO₂ on the particle surface, which effectively prevents the anode material particles from

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direct contact with the electrolyte solution, improves the structural stability, reduces the interfacial resistance and increases Li^+ conductivity. Recently, SiO_2 -incorporated LTO has been synthesized directly using a facile cellulose-assisted combustion technique [36]. The incorporation of SiO_2 was found to improve the cycling stability under hurdle conditions.

In this paper, we innovatively use SiO_2 to modify the commercial LTO directly via a sol-gel method, which is not only environmentally friendly, but also simple to carry out. The SiO_2 modified LTO samples were calcined at low temperature (500 °C), which is likely to avoid the crystal structure damage of LTO. The structural and electrochemical characteristics of the SiO_2 modified LTO samples will be intensively studied.

2. Experimental

The LTO powders (Chengdu Xingneng New Materials Co., LTD) was mixed with tetraethyl orthosilicate (TEOS, 99%) in ethanol and the molar ratio of TEOS/LTO is 2.5 mol%, 5.0 mol% and 10 mol% for three different samples, respectively. Then the slurry was stirred for 5 h and dried at 70 °C. Finally, the dried materials were fired at 500 °C for 1 h in air and the SiO_2 modified LTO samples were obtained.

Powder X-ray diffraction (XRD, Xpert MPD DY1219) with $\text{Cu K}\alpha$ radiation was used to identify the phase composition and crystal lattice parameters of all the LTO samples. The diffraction patterns were collected at room temperature by step scanning in the range of 10–90° at a scanning rate of 0.02° per 10 s. The particulate morphology was examined by scanning electron microscope (SEM, Sirion 200 FEI Netherlands) and transmission electron microscope (TEM, JEOL, JEM-2010F). The chemical composition of the LTO sample was determined by X-ray photoelectron spectroscopy (XPS, PHI5600 Physical Electronics). The specific surface area of all samples was derived using the multipoint Brunauer–Emmett–Teller (BET) method.

The working electrode was prepared by mixing 85 wt.% active material (pure LTO or SiO_2 modified LTO), 10 wt.% conductive Super-P and 5 wt.% LA-132 binder into a slurry, and coating the slurry on an alumina foil by painting. Afterward, the working electrode was dried in a vacuum oven at 105 °C for 12 h to remove any residual solvent and possible adsorbed moisture. Electrochemical measurements were performed using coin-type half cells assembled in an argon-filled glove box. The cell consisted of the as-prepared working electrode, microporous polypropylene membrane (Celgard 2400, Celgard Inc., USA) as a separator and lithium foil as a counter electrode. The electrolyte was 1M LiPF_6 solution in ethylene carbonate (EC):diethyl carbonate (DEC):ethyl methyl carbonate (EMC) with a volume ratio of 1:1:1.

Galvanostatic charge and discharge experiments were carried out on an automatic galvanostatic charge/discharge unit (Land CT 2001A, Wuhan, China) between 1.0 and 3.0 V at different charge/discharge rates at 25 °C. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were conducted on an electrochemical workstation (PARSTAT 2273). In the case of CVs, the potential range was set from 1.0 to 3.0 V while the scan rate was set at 0.1 mV s^{-1} . EIS tests were operated with an alternating current voltage in the frequency range of 10 mHz–100 kHz at the first cycle charged state.

3. Results and discussion

Fig. 1 shows the XRD patterns of pure LTO and SiO_2 modified LTO. For all samples, the main diffraction patterns can be well indexed based on a cubic spinel-type LTO with a space group of $Fd3m$, indicating that the SiO_2 modifying process does not change the structure of LTO. However, the SiO_2 peaks of SiO_2 modified LTO are not detected, which might be due to the low content and amorphous state of SiO_2 [33].

Fig. 2 displays the SEM images of pure LTO and the LTO modified with 2.5 mol% SiO_2 . One can see that both LTO samples show a well-crystallized structure, suggesting the SiO_2 modification process does not change the morphology of LTO particles. The LTO modified with 2.5 mol% SiO_2 was further analyzed using EDX mapping (shown in Fig. 3), indicating that all of the Ti, O and Si were distributed homogeneously within the particles. This result indicates that the SiO_2 is likely to form a coating layer over the LTO particles instead of separated phase.

The pure LTO and the LTO modified with 2.5 mol% SiO_2 were subsequently subjected to TEM observation to prove directly the presence of SiO_2 coating layer over the LTO particles modified with

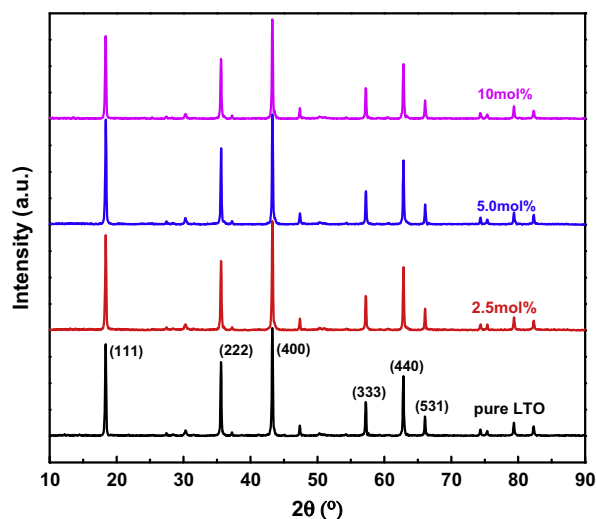


Fig. 1. XRD patterns of all samples.

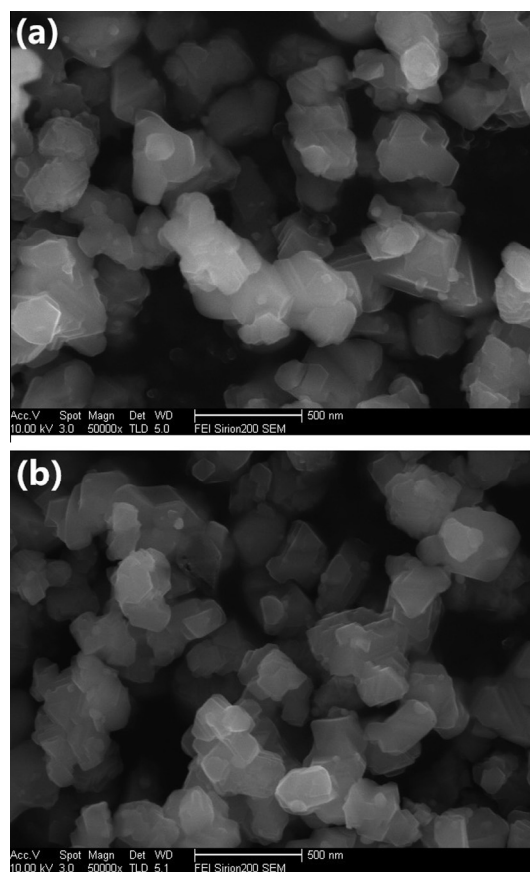


Fig. 2. SEM images of (a) pure LTO and (b) the LTO modified with 2.5 mol% SiO_2 .

2.5 mol% SiO_2 . In Fig. 4, one can see that the pure LTO particles show very smooth edge lines, whereas the particles LTO modified with 2.5 mol% SiO_2 are rough and covered with a thin and amorphous layer. HR-TEM was carried out to further study the outer layer on the LTO particle modified with 2.5 mol% SiO_2 and the result was shown in Fig. 5. It is evident that the surface of the LTO particle modified with 2.5 mol% SiO_2 is covered by a dense and thin coating layer with thickness of about 6 nm, which is likely to be SiO_2 .

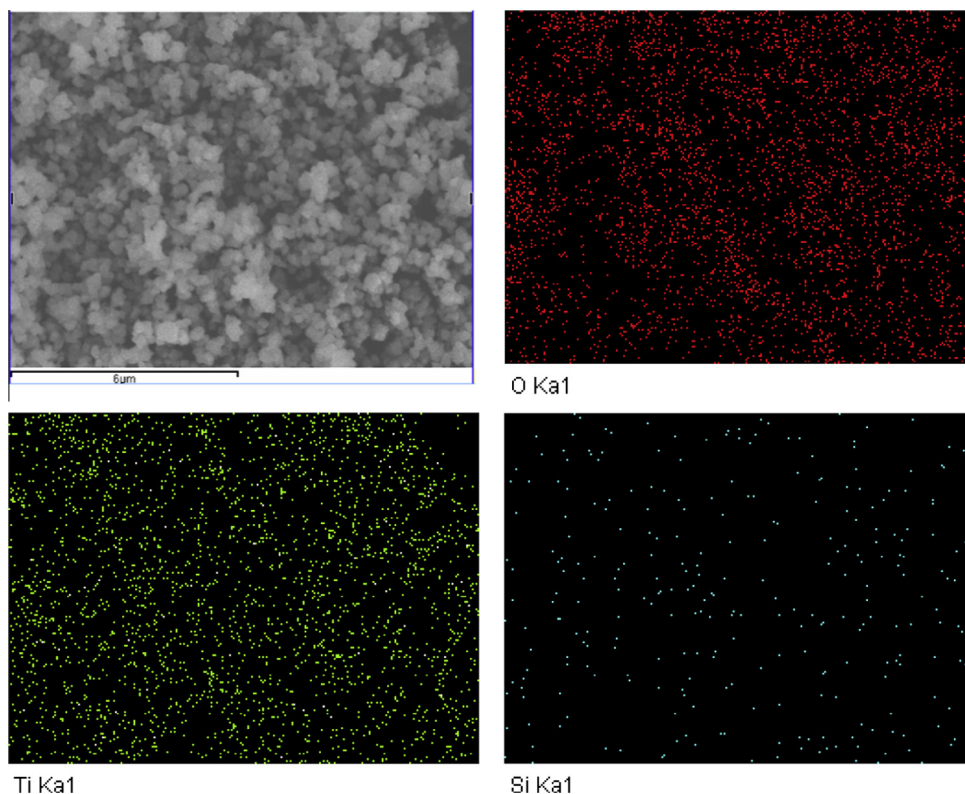


Fig. 3. SEM images of the LTO modified with 2.5 mol% SiO₂ and the corresponding EDX mapping of Ti, O and Si.

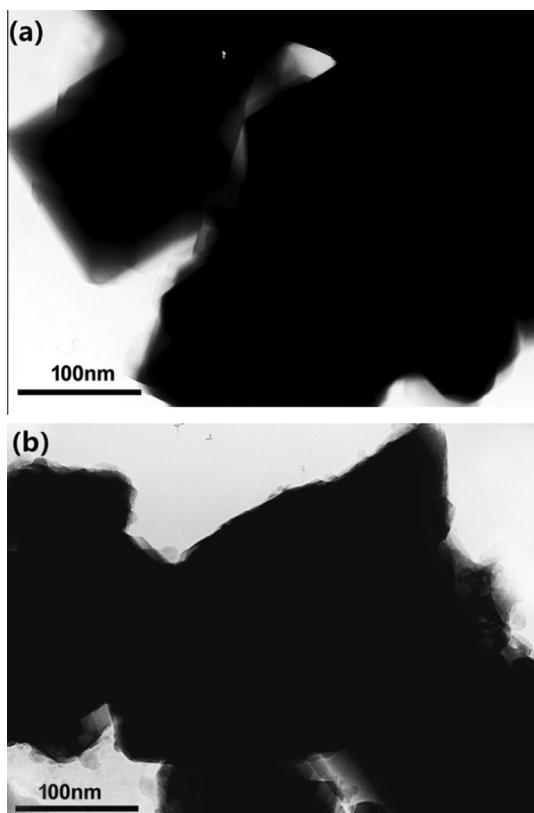


Fig. 4. TEM images of (a) pure LTO and (b) the LTO modified with 2.5 mol% SiO₂.

XPS measurement was conducted to determine the surface composition of the LTO modified with 2.5 mol% SiO₂ and the results are shown in Fig. 6. In Fig. 6a, the O 1s peak at 530 eV and 531.75 eV observed are both related to TiO₂, while the peak at 532.6 eV observed is associated with SiO₂. The Si 2p peak at 102.5 eV observed in Fig. 6b is also associated with SiO₂. The results above further verify the presence of SiO₂ coating layer on the surface of SiO₂ modified LTO.

The electrochemical performance of pure LTO and SiO₂ modified LTO was evaluated in order to study the effects of SiO₂ modification process systematically. Fig. 7a shows the rate capacity of all samples at various C-rates, and the second-cycle discharge capacity at each rate is compared in Fig. 7b (1 C = 160 mA h g⁻¹). In Fig. 7a, it can be seen that the capacity of the LTO modified with 2.5 mol% and 5.0 mol% SiO₂ are obviously better than that of pure LTO, especially at a high rate of 5 C and 10 C, while the LTO modified with 10 mol% SiO₂ displays worse capacity than pure LTO. With the increase of rate, the discharge capacity gradually decreases for all the samples, as seen in Fig. 7b. At a high rate of 10 C, the discharge capacity is 131.1, 144.8, 136.5 and 120.4 mA h g⁻¹ for pure LTO, LTO modified with 2.5 mol%, 5.0 mol%, and 10 mol% SiO₂, respectively. Therefore, the LTO modified with 2.5 mol% SiO₂ exhibits the best rate capability and the LTO modified with 10 mol% SiO₂ displays the worst rate capability.

In order to study the mechanism for the improved performance of SiO₂ modified LTO, CVs of all samples were conducted in the range of 1.0–3.0 V at different scan rates. In Fig. 8a and b, one can see that one pair of redox peaks appear at 1.6–2.2 V (anodic) and 1.1–1.4 V (cathodic) for all samples, which are correlated to the spinel/rock-salt phase transition (Li₄Ti₅O₁₂/Li₇Ti₅O₁₂) [31,37]. All samples show similar redox peaks, suggesting that the SiO₂ modification process does not change the electrochemical reaction process of LTO. The CV curves of all samples are broadened with

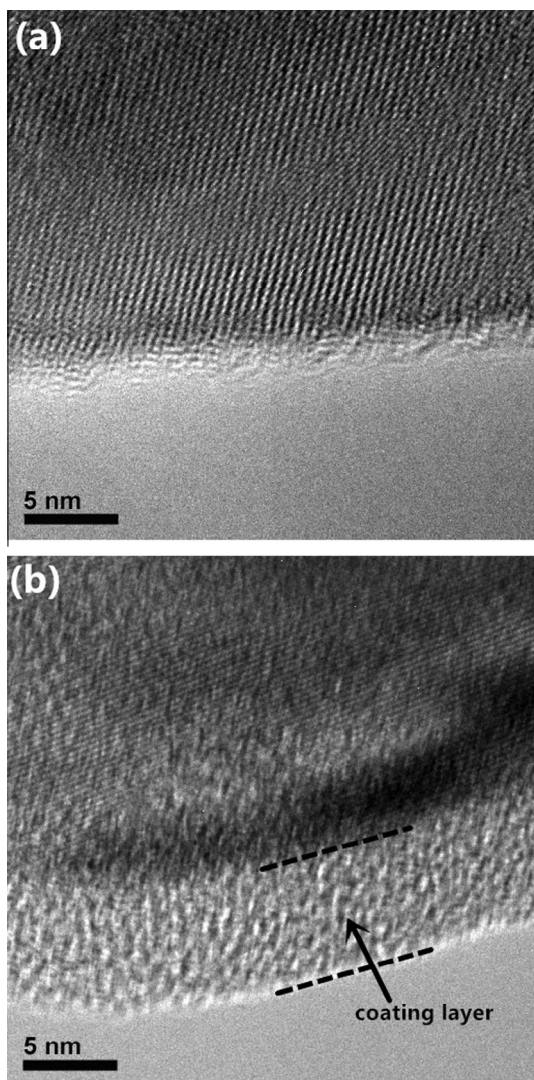


Fig. 5. HR-TEM images of (a) pure LTO and (b) the LTO modified with 2.5 mol% SiO₂.

the increase of scan rate and the degree of electrochemical polarization is different. Table 1 shows the potential differences between the anodic and cathodic peaks for all samples at different C-rates. Compared with pure LTO, the LTO modified with 2.5 mol% SiO₂ exhibits an obviously decrease in potential difference between anodic and cathodic peaks, while the LTO modified with 10 mol% SiO₂ presents an obvious increase. The results indicate that using 2.5 mol% amount of SiO₂ to modify LTO is favorable for reducing the electrode polarization, but high adding amount such as 10 mol% SiO₂ generates opposite effect. Fig. 8c compares the first cycle voltage profiles of Li⁺ insertion (i.e. discharge process) and de-insertion (i.e. charge process) of all samples in half cells in the voltage range between 1.0 and 3.0 V at 5 C. All samples demonstrate a long range of flat voltage at around 1.50 V during discharge process and around 1.58 V during charge process, which are assigned to the Li⁺ insertion and de-insertion of two-phase reaction and are also corresponding to the one pair of strong redox peaks in the CV curves shown in Fig. 8a and b. It also can be seen that the LTO modified with 2.5 mol% SiO₂ presents the lowest potential differences in all samples, which is also in accord with the result of CV curves. In addition, all the peak currents of the pure LTO are lower than those of the LTO modified with 2.5 mol% SiO₂, but higher than those modified with 10 mol% SiO₂. The relation of peak currents to scan rates can indicate the electrochemical reaction characteristics

[38–41]. For the diffusion-limited process, the peak current is proportional to the square root of the scan rate ($v^{1/2}$), as is shown in the following Randles–Sevcik equation [41]:

$$i_p = 2.69 \times 10^5 n^{3/2} D^{1/2} C v^{1/2}$$

where D is the diffusion coefficient, C is concentration of the reactant and n represents the number of transfer electrons. The linear correlation between peak currents and the square roots of the scan rate in the anodic process can be observed, as shown in Fig. 8d, which signifies diffusion controlled electrode process obviously. Furthermore, the slope of the fitted line is dependent on the diffusion coefficient in this equation. Therefore, it can be deduced that the LTO modified with 2.5 mol% SiO₂ has the highest diffusion coefficient and the LTO modified with 10 mol% SiO₂ possesses the smallest diffusion coefficient. These results demonstrate that the addition of 2.5 mol% SiO₂ can effectively improve the electrochemical reaction kinetics of Li⁺ insertion/deinsertion. However, the addition of more SiO₂ such as 10 mol% is unfavorable for the electrochemical reaction kinetics of Li⁺ insertion/deinsertion.

Electrochemical impedance spectroscopy (EIS) measurement of the LTO electrodes was carried out at the first cycle and half charged state (1.5 V), and typical Nyquist plots were fitted by a simple modified Randles–Ershler equivalent circuit [19], shown in Fig. 9. Here, R_s is the resistance of electrolyte, R_{ct} is the charge transfer resistance at the particle/electrolyte interface, and Z_W is the Warburg impedance. The values of R_s , R_{ct} and Z_W are obtained from the simulated data of EIS by the equivalent circuit, listed in Table 2. The R_s , R_{ct} and Z_W of the LTO modified with 2.5 mol%

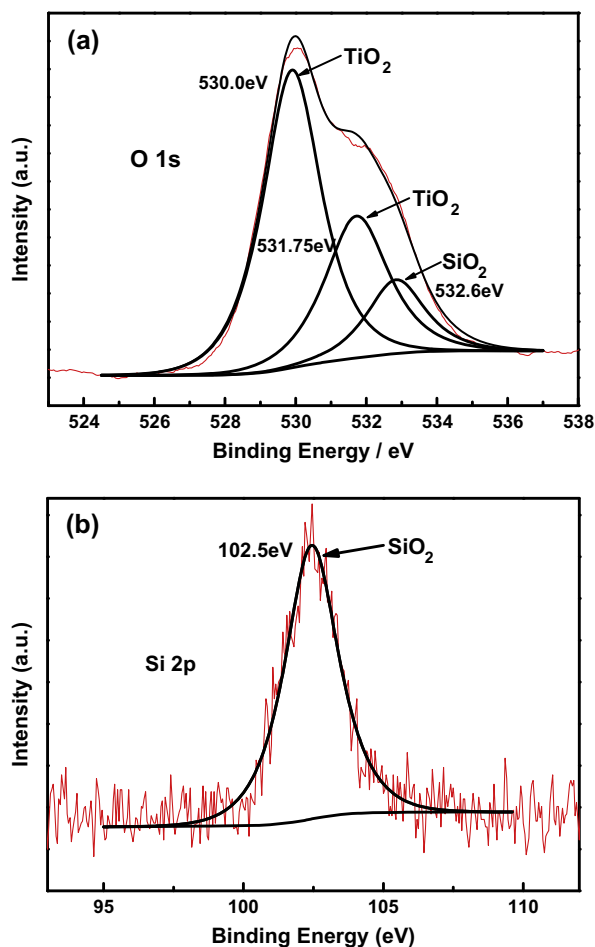


Fig. 6. (a) O 1s and (b) Si 2p spectra of the LTO modified with 2.5 mol% SiO₂.

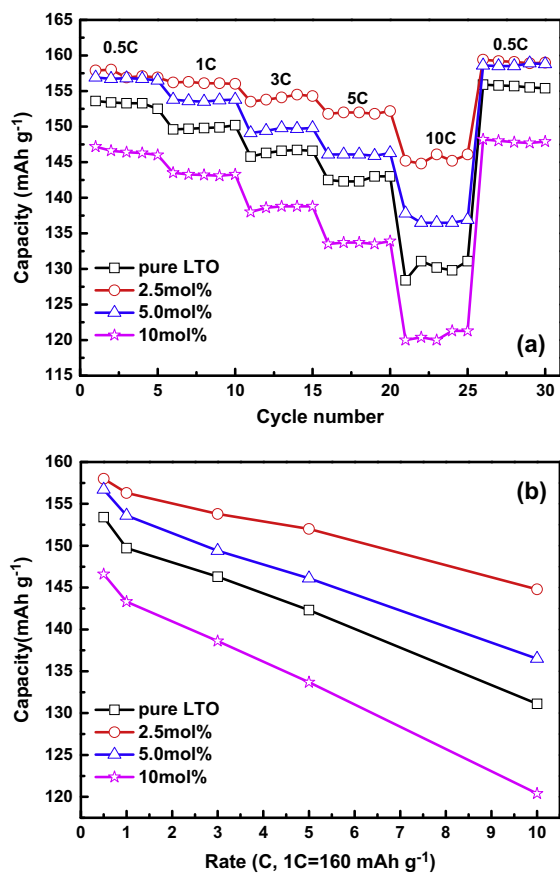


Fig. 7. (a) Discharge capacity retention at different C-rates and (b) discharge charge capacity as a function of the C-rates (1 C = 160 mA h g⁻¹).

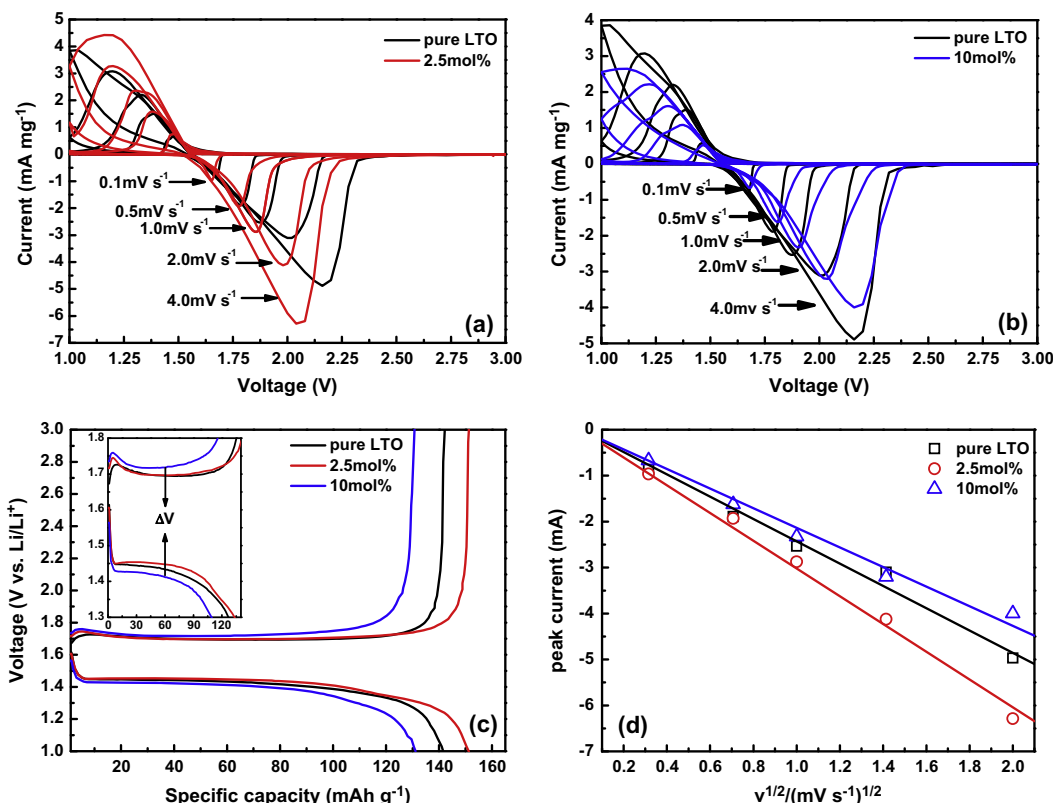


Fig. 8. (a) and (b) CV curves during different scan rates, (c) the discharge/charge profiles at 5 C rate and (d) anodic peak currents against square roots of scan rate.

SiO₂ are 2.3 Ω, 21.1 Ω and 12.5 Ω, respectively, which are smaller than those of pure LTO. The exchange current density ($i_0 = RT/nFR_{ct}$) of the LTO modified with 2.5 mol% SiO₂ is 1.21 mA cm⁻², which is higher than that of pure LTO. These results also imply the SiO₂ coating modification has effectively enhanced the Li⁺ diffusion and restrained the interfacial resistance among particles during the cycles. For the interpretation of the enhanced Li⁺ diffusion for SiO₂ modification, Li et al. has reported that the electrolyte seeps into these amorphous nano-SiO_x to form solid electrolyte, which could enhance the ionic conductivity [33]. In this study, we found that the amorphous SiO₂ coating layer is likely to provide larger contact area between electrode and electrolyte, thereby accelerating the diffusion of Li⁺. The specific surface area of all samples was calculated using the multipoint BET method and shown in Table 3. One can see that the SiO₂ modified LTO samples present larger surface area than pure LTO.

Fig. 10 shows the cycle performance of all samples at 25 °C. It can be observed that LTO modified with 2.5 mol% and 5.0 mol% SiO₂ present better cycling stability than pure LTO at both 1 C and 10 C rate. In particular, after 100 cycles, the LTO modified with 2.5 mol% SiO₂ can maintain a specific capacity of 155.4 mA h g⁻¹ with a capacity loss of 0.4% at 1 C/1 C rate and 141.7 mA h g⁻¹ with a capacity loss of 3.6% at 10 C/10 C rate, respectively. This result demonstrates that the SiO₂ modification can improve the cycling stability of LTO anode materials. As we know, it has been reported that atomic layer deposition was used to deposit ZrO₂ and Al₂O₃ on LTO to improve its electrochemical performance. Mechanism for the enhanced electrochemical performance of LTO was attributed to that the ZrO₂ and Al₂O₃ coating layer on LTO could act a barrier to prevent the direct contact between LTO particles and electrolyte, and cover the catalytic sites on the LTO surface for the decomposition of electrolyte [31,42]; thus, the coating layer could restrain the formation of solid electrolyte interphase (SEI), thereby accelerating effectively the diffusion of Li⁺, which could improve

Table 1
Potential differences (ΔV , V) between anodic peaks (φ_{pa} , V) and cathodic peaks (φ_{pc} , V).

	Pure LTO			2.5 mol%			10 mol%		
	φ_{pa}	φ_{pc}	ΔV	φ_{pa}	φ_{pc}	ΔV	φ_{pa}	φ_{pc}	ΔV
0.1 mV s ⁻¹	1.672	1.479	0.193	1.663	1.481	0.188	1.683	1.468	0.215
0.5 mV s ⁻¹	1.785	1.390	0.395	1.770	1.380	0.390	1.810	1.375	0.435
1 mV s ⁻¹	1.880	1.330	0.550	1.850	1.320	0.530	1.900	1.310	0.590
2 mV s ⁻¹	2.000	1.200	0.800	1.980	1.200	0.780	2.040	1.220	0.820
4 mV s ⁻¹	2.160	1.040	1.120	2.040	1.160	0.880	2.180	1.080	1.100

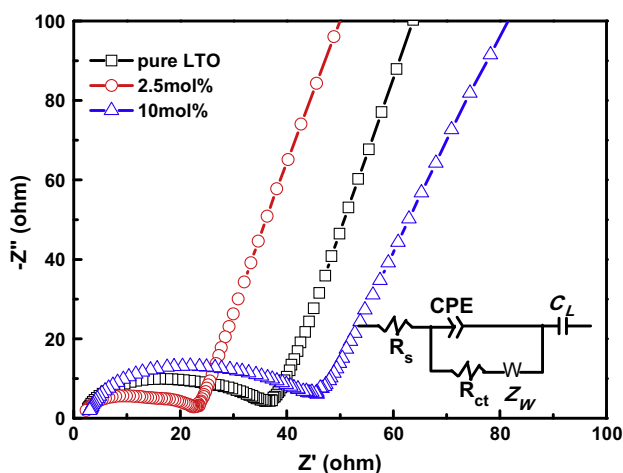


Fig. 9. Nyquist plots of pure LTO and SiO₂ modified LTO.

Table 2
Fitted parameters of equivalent circuit of Fig. 9.

Samples	R_s (Ω)	R_{ct} (Ω)	Z_W (Ω)	i_0 (mA cm ⁻²)
Pure LTO	2.7	33.5	21.8	0.77
2.5 mol%	2.3	21.2	12.6	1.21
10 mol%	3.0	41.3	26.1	0.62

Table 3
Specific surface area (S_{BET}) of samples.

Samples	S_{BET} (m ² g ⁻¹)
Pure LTO	6.72
2.5 mol%	7.81
5.0 mol%	8.35
10 mol%	11.9

the electrochemical performance of LTO. Therefore, as the same mechanism, the improvement in cycle performance of SiO₂ modified LTO over pure LTO is largely due to the fact that the SiO₂ coating layer also can restrain the formation of SEI, which could accelerate the diffusion of Li⁺.

Based on the above results, it can be concluded small adding amounts (e.g. 2.5 or 5.0 mol% SiO₂) could improve the electrochemical performance of LTO. Moreover, the electrochemical performance of SiO₂ modified LTO deteriorates with further increasing amount of SiO₂. Thus an appropriate amount of SiO₂ should be adopted to enhance the electrochemical performance of LTO. In the present work, we found that 2.5 mol% SiO₂ is the most appropriate adding amount, which makes the LTO present the best electrochemical performance.

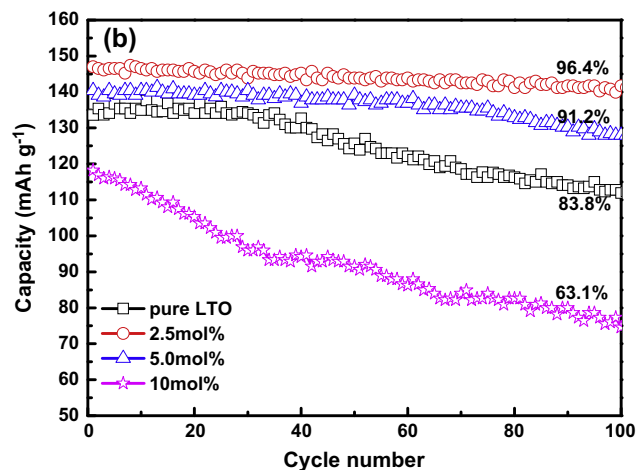
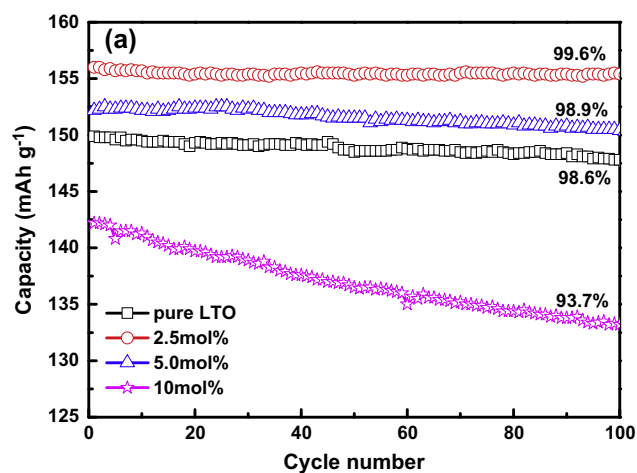


Fig. 10. (a) Cycling stability at 1 C/1 C rate and (b) cycling stability at 10 C/10 C rate (1 C = 160 mA h g⁻¹) for all samples.

4. Conclusion

The commercial LTO was modified with SiO₂ via a simple sol-gel method. The structural characterization results show that the SiO₂ modification process does not change the structure of LTO and there is a SiO₂ layer over the LTO particles. The SiO₂ modified LTO samples show greatly improved capacity and rate capability. This is attributed to that the SiO₂ coating layer could effectively reduce electrochemical polarization of electrode and enhance the electrochemical reaction kinetics of Li⁺ insertion/deinsertion. Moreover, the SiO₂ coating layer over the LTO could cover the catalytic sites on the LTO surface for the decomposition of electrolyte, thereby restraining the formation of SEI. Hence, the SiO₂ modified LTO samples present better cycle performance than pure LTO. It is worthy to mention that an appropriate amount of SiO₂ should be

adopted to enhance the electrochemical performance of LTO. In this study, the LTO modified with 2.5 mol% SiO₂ exhibits best electrochemical performance. The SiO₂ modification process is easy to control and carry out for industrialization, which will have an encouraging prospect for commercial applications.

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