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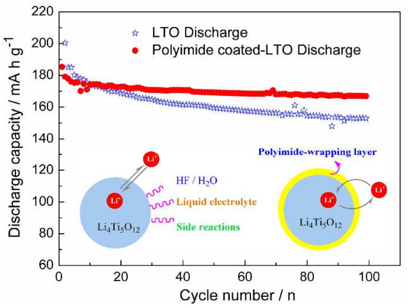
# Graphical Abstract



**The polyimide layer prevents the direct contact of the LTO surface with liquid electrolyte, thus significantly improves the electrochemical performance.**

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**COMMUNICATION**

# A polyimide ion-conductive protection layer to suppress side reactions on $Li_4Ti_5O_{12}$ electrode at elevated temperature

**Qingwen Lu, Jianhua Fang, Jun Yang*, Xuejiao Feng, Jiulin Wang, Yanna Nuli**

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**A novel ion-conductive polyimide nanoscale layer is formed on the $Li_4Ti_5O_{12}$ anode material via a stepwise thermal imidization of polyamic acid to suppress the interfacial side reactions, and leads to a significant improvement in electrochemical performances at elevated temperature.**

Recently, lithium ion batteries have drawn tremendous attention due to the potential application in electric vehicles and smart grid. The spinel lithium titanate ($Li_4Ti_5O_{12}$, LTO) material with a theoretical capacity of 175 mAh $g^{-1}$ has excellent Li-ion intercalation/deintercalation reversibility within the voltage range of 3.0–1.0 V[1-3]. It is regarded as one of the most attractive anode materials for an ultra-long life and high power lithium ion battery owing to its zero volumetric variation[3, 4] and absence of SEI reformation[5, 6].

Unfortunately, lithium ion batteries with LTO anode are still not widely used mainly due to the unexpected interfacial side reactions during charge/discharge cycles and storage, especially at elevated temperatures, which seriously deteriorate the cyclic stability and safety. So far, extensive work has been done to improve the electrochemical performance of LTO material by preparing nanoparticles[7, 8], doping[9, 10] and forming composites with carbon and metal powder[11, 12]. Meanwhile, there are a few reports that specifically refer to the unwanted interfacial side reactions of LTO electrodes, along with gas generation[13-16]. However, less attention has been paid to how to suppress the side reactions between LTO electrode and liquid electrolyte. The research result from K. Wu et al. showed that the side reaction and gas can be partially suppressed by adjusting electrolyte composition[15]. However, this may cause negative effect on the cathode side. Y. B. He et al. used the carbon coated LTO to suppress the reductive decomposition of electrolyte on the LTO electrode at room temperature[17]. They paid more attention on the SEI formation towards 0V. No significant effect was found for the conventional cut-off of 1V. As well known, aromatic polyimide as one kind of high-performance engineering polymers, has been widely used in the proton exchange membrane fuel cells[18], organic cathode material[19], microelectronics[20], displays[21], gas separation[22] and lithium battery separator[23, 24] due to its excellent thermal stability, superior mechanical properties, outstanding film-forming properties and chemical inertness to almost all organic solvents[25]. Therefore, polyimide is expected to be suitable for forming the encapsulating layer of LTO. In this paper, a new attempt based on polyimide gel polymer electrolyte (GPE) layer is proposed as an alternative to conventional carbon coatings. We demonstrate a facile approach to the surface modification of LTO particles and explore the feasibility of suppressing the unwanted interfacial side reactions at 55 °C.

Synthesis of the polyamic acid has been described in details in previous study[26]. The chemical structure and thermal imidization process of 2-component (PMDA/ODA) polyamic acid are shown in Fig. 1a.

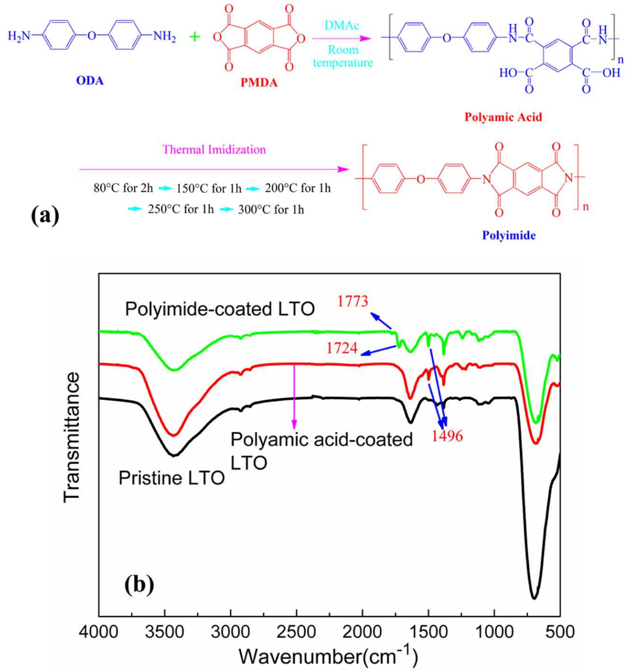

**Fig. 1** **(a)** Schematic synthesis procedure of the polyimide; **(b)** FT-IR spectra of the original LTO, polyamic acid-coated LTO and polyimide-coated LTO.

Fig. 1b presents the FT-IR spectra of original LTO, polyamic acid-coated LTO and polyimide-coated LTO. Before thermal imidization, the FT-IR spectrum of polyamic acid-coated LTO shows benzene ring characteristic peak at 1496 $cm^{-1}$. After thermally cured via a stepwise imidization process, the polyamic acid has been converted into polyimide. The FT-IR spectrum of polyimide-coated LTO shows absorption bands of benzene ring (at 1496 $cm^{-1}$), imide carbonyl (–C=O, at 1773 $cm^{-1}$) and imines group (–CONCO, at 1724 $cm^{-1}$, –C=O symmetrical stretching vibration). It is thus anticipated that the original LTO could be coated with polyimide significantly.

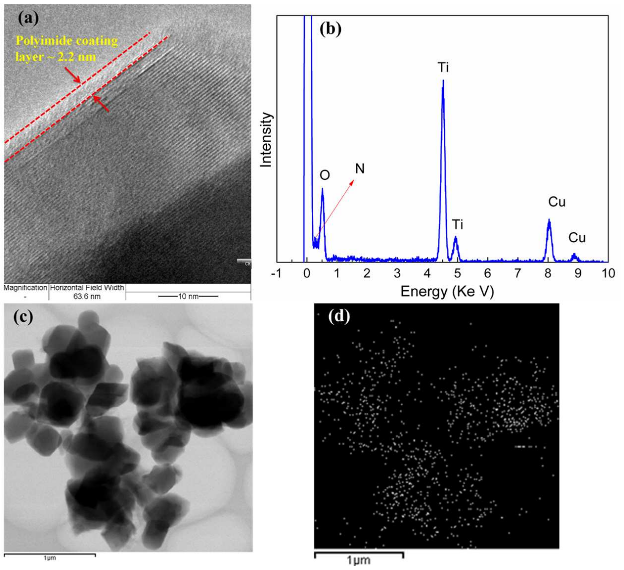

**Fig. 2 (a)** A TEM photograph of polyimide-wrapped LTO; **(b)** EDS spectra of polyimide-wrapped LTO captured for the region shown in **(c)** and **(d)** the bright dots signify nitrogen **(d)** elements of polyimide wrapping layers of LTO.

This unusual structure of the polyimide wrapping layer is further characterized by TEM. As exhibited in Fig. 2a, the surface of LTO is well covered by the polyimide wrapping layer in the thickness of approximately 2.2 nm. It has been reported that the polyamic acid (a precursor polymer of the resulting polyimide) has high polarity[27]. Its carbonyl groups may form strong hydrogen bonding with the hydroxy groups on the surface of the LTO. Thus, the polyimide wrapping layer can be uniformly covered on the surface of LTO after thermal imidization because of the good compatibility of the polyamic acid with LTO. In addition, the presence of the polyimide wrapping layer on the LTO surface is also verified by EDS analysis (Fig. 2b, c, d). The bright dots in Fig. 2d assign to nitrogen element of the polyimide wrapping layer, which is uniformly dispersed on the LTO surface.

For estimating ionic conductivity of the coated polyimide layer, AC impedance spectra was taken for the polyimide film which had been beforehand immersed in the liquid electrolyte (1 M $LiPF_6$ in EC/DMC = 1/1, v/v) for 12h at room temperature. The polyimide-based GPE film provides a high ionic conductivity of 0.23 mS $cm^{-1}$ at room temperature. Therefore, the ultrathin polyimide layer will not lead to significant enhancement of the ionic resistance.

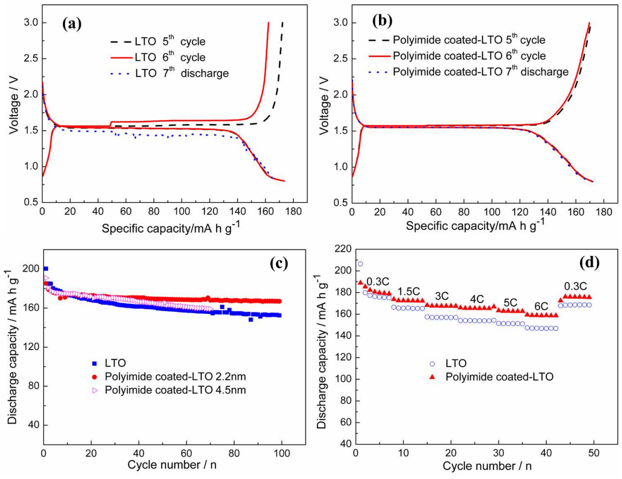

**Fig.3** The discharge and charge profiles of LTO/Li cell **(a)** and polyimide-coated LTO/Li cell **(b)**. The sixth charging process paused for 5 days at 70% lithiation state and 55°C; Cycling performance of LTO/Li and polyimide-coated LTO/Li cells using charge–discharge rate of 0.4C at 55°C **(c)**; Rate performance of the cells of LTO/Li and polyimide-coated LTO/Li cells at 55°C **(d)**.

Our previous investigation found that the undesired side reactions in LTO cells mainly occur in the potential range between 1.55 and 1.75 V vs. $Li/Li^+$ in the charging (delithiation) process[16]. To demonstrate the polyimide-coating effect (all results for 2.2 nm coating layer except indicated elsewhere), LTO/Li and polyimide-coated LTO/Li half-cells were cycled for 5 times in a voltage range of 0.8−3.0 V at 55°C, and then charged until ca. 70% lithiation state at the sixth cycle. Whereafter, the cells were stored in thermal chambers at open circuit voltage and 55°C for five days. Then the cells continued to cycle at 55°C. Fig. 3a and 3b present the 5th and 6th cycle profiles as well as the 7th discharge (lithiation) profiles of LTO/Li and polyimide-coated LTO/Li cells at 55°C, respectively. The LTO/Li cell storage leads to a higher voltage polarization. Moreover, reversible capacity of the sixth cycle is 162.3 mA h $g^{-1}$, which corresponds to a capacity loss of 9.4% compared to the fifth cycle. The main reason could be attributed to the side reactions of partially charged LTO ($Ti^{3+}$) with solvents or water impurity. The dithering curve character in the followed discharging process in Fig. 3a may be related to the gas absorption. By contrast, the whole sixth charge and the followed discharge voltage platforms of polyimide-coated LTO/Li cell are almost overlapped with those at the 5th cycle and the capacity loss is negligible (Fig. 3b). Moreover, Fig. 3c and Fig. 3d show that the cycling and rate performances of polyimide-coated LTO/Li cell are superior to those of LTO/Li cell. It is notable that the discharge capacities of the polyimide-coated LTO are slightly higher than those of the pristine LTO over a wider range of discharge current density at 55°C although the polyimide layer increases the interfacial resistance. Nevertheless, when the coating layer thickness increases from 2.2 nm to ca. 4.5 nm, the cycle performance degrades as shown in Fig. 3c. This could be attributed to the non-uniform polyimide deposition (not shown here) and relatively high electronic resistance. For the polyimide coated-LTO/Li cell, quite stable capacities around 179, 172, 167, 165, 162 and 158 mAh $g^{-1}$ are obtained at current rates of 0.3C, 1.5C, 3C, 4C, 5C and 6C, respectively. As the current rate returns to 0.3C, most of the initial capacity can be retained. These results indicate that polyimide protective layer can effectively suppress the side reactions between the partially charged LTO and the liquid electrolyte, and thereby improve the interfacial stability at elevated temperature.

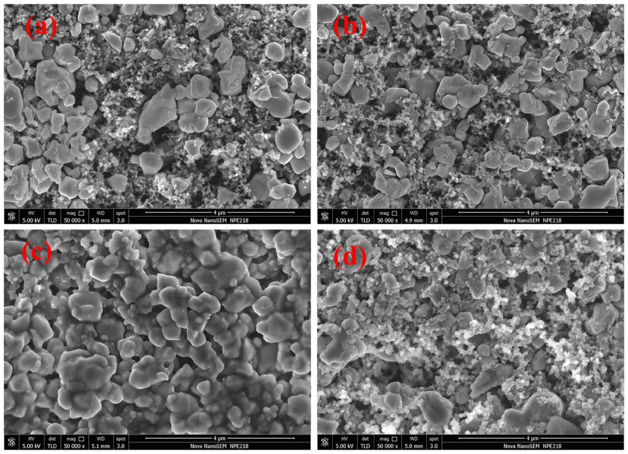

**Fig.4** SEM images of LTO electrodes. **(a)** pristine LTO**, (b)** polyimide coated-LTO**, (c)** after 100 cycles at 55°C for pristine LTO, **(d)** after 100 cycles at 55°C for polyimide coated-LTO.

The surface morphologies of pristine LTO and polyimide coated-LTO electrodes before and after cycling are examined and shown in Fig. 4. The pristine LTO and polyimide coated-LTO electrodes before cycling present similar particle distribution and morphology (Fig. 4a and Fig. 4b). After 100 cycles, the original surface character related to clear LTO and Super-P particles remains for the polyimide coated-LTO electrode (Fig. 4d). However, the Super-P particles can be no longer observed and a lot of agglomerates emerge on the LTO electrode (Fig. 4c). This evolution of the morphology may be related to convergency and coverage of the electrolyte decomposition products. The above comparison indicates that the polyimide protection layer can in deed lessen the side reactions between LTO and liquid electrolyte at 55°C.

In an effort to obtain a better understanding of the advantageous effect of the polyimide layer on the cycle performance at 55°C, the AC impedance spectra of the cells were measured and compared after the 1st and the 50th cycle (Fig. 5a). Both the Nyquist diagrams present two distinct semicircles. It is well known that good SEI film is hardly formed on the pristine LTO electrode above 0.8V. Thus, the 1st semicircle in high frequency range may be associated with electronic resistance of the active material and absorbed decomposition product. For the polyimide coated-LTO electrode, the 1st semicircle may be, at least in part, contributed by the polyimide layer resistance. The semicircles observed at lower frequency range for both the electrodes are ascribed to the charge transfer resistances between the electrodes and liquid electrolyte. Although the initial impedance of the polyimide-coated LTO electrode is slightly higher than that of the pristine LTO due to the presence of a polyimide nanocoating layer, its increase during cycling is not as remarkable as the latter. The obviously larger charge transfer resistance for the LTO after the 50th cycle may be caused by the degradation of the electrolyte and contamination of the decomposition products to the interface.

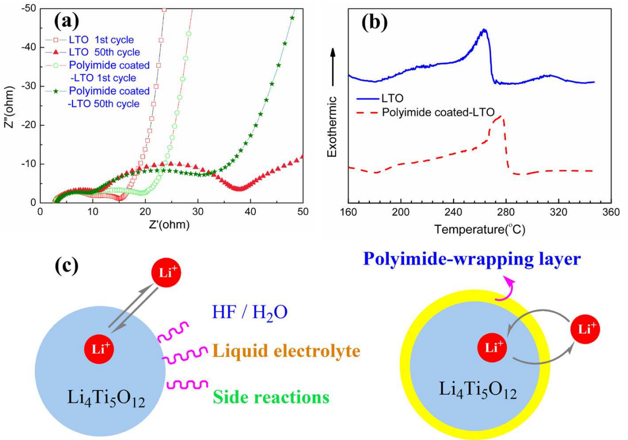

**Fig. 5** **(a)** Variation in AC impedance spectra of cells assembled with pristine LTO and polyimide-coated LTO at 55°C; **(b)** DSC thermograms of the interfacial exothermic reaction between partially charged LTO and polyimide-coated LTO and liquid electrolyte; **(c)** Schematic illustration of ion-conductive polyimide nanocoating layer for suppressing the interfacial side reactions.

The effective protection of polyimide nanolayer on LTO can be further confirmed by DSC result. Fig. 5b shows the DSC thermograms of the pristine and polyimide-coated LTO at 70% lithiation state in contact with the electrolyte. It has been reported that reduction of total amount of heat generated by side reactions or shift of exothermic peak temperatures to higher values in the DSC thermogram indicates more thermally stable interface between electrolyte and electrode[28]. According to exothermic peak area, reaction heat can be calculated[29]. The pristine LTO shows larger exothermic heat ($\Delta H$ = 269.2 J $g^{-1}$) than polyimide-wrapped LTO ($\Delta H$ = 203.3 J $g^{-1}$). In addition, polyimide coating makes exothermic peak temperature shift from 263°C to 276.6 °C. As demonstrated in Fig. 5c, the full surface coverage of the polyimide coating layer is believed to play an important role in preventing the LTO from direct exposure to the reactive liquid electrolyte, thus lessening the side reactions.

In summary, we have demonstrated the positive effect of polyimide coating layer on the electrochemical performance and thermal stability of LTO. The polyimide coating layer shows full surface coverage, nanometer thickness, and facile ion transport. This structural uniqueness of the polyimide coating layer plays a key role in effectively suppressing the side reactions between the partially charged LTO and liquid electrolyte, and improving the cycling and rate performance.

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## Notes and references

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