Lithium titanate modified separator for long cycling life lithium metal anode

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Abstract

Lithium dendrites produced during the process of lithium metal cycling lead to poor cycle stability and safety problems, seriously hindering the practical application and commercialization of lithium metal. In this work, a facile method is used to coat lithium titanate (LTO) onto polypropylene (PP), resulting in the formation of a lithium titanate separator (LTO@PP). The characteristic properties such as morphology, EIS, and electrochemical performance of the LTO@PP separator are systematically investigated. The results prove that the transformation from $\text{Li}_4\text{Ti}_5\text{O}_{12}$ into $\text{Li}_7\text{Ti}_5\text{O}_{12}$ during the first cycle of discharge promotes the transfer of $\text{Li}^+$, thus accelerating the migration dynamics of lithium ions in the LTO@PP separator. The LTO@PP-based cell can stably cycle for more than 4800 hours in a Li symmetrical battery at a high current density of 3 mA cm$^{-2}$, with an overvoltage as low as 6 mV. The Li | Cu battery can stably cycle for more than 380 cycles under a deposition rate of 1 mAh/cm$^2$. Additionally, the LTO@PP separator-based LFP cell displays a high capacity retention rate and excellent rate performance. Compared with current separator modification methods, this work provides a promising prospect for the simple and rapid preparation of modified separators.

1. Introduction

With the increasing popularity of new energy vehicles, lithium-ion batteries are gradually unable to meet people's demands, making it necessary to develop batteries with higher energy density [1–5]. Lithium metal is an ideal candidate for the negative electrode of high-energy-density batteries due to its high specific capacity (3860 mAh g$^{-1}$) and extremely low potential (-3.04 V vs. standard hydrogen electrode). However, during the electrochemical deposition/stripping process, lithium metal undergoes chemical and free state transformations, resulting in significant volume changes. Additionally, uneven surface morphology and charge distribution of lithium metal lead to irregular lithium deposition. The formation of lithium dendrites, which continuously break and regenerate the solid electrolyte interface (SEI) layer, consumes lithium metal and electrolytes, resulting in low Coulombic efficiency. Moreover, the continuous growth of lithium dendrites can penetrate the separator, causing internal short circuits and safety hazards [9]. Therefore, the elimination of lithium dendrites has become a crucial task in the development of high-energy-density batteries.

In summary, strategies to address the issue of lithium dendrites can be categorized into four main approaches: . Optimizing the electrolyte formulation [10–13]. . Introducing an artificial solid electrolyte interface layer [14], [15]. . Designing the electrode interface and electrode structure [16], [17]. . Modifying the separator [18], [19], [20]. Separator modification is one of the most effective tactics due to its high efficiency, ease of implementation, and potential for large-scale industrial production. For instance, defects present in TiO$_2$ separators can enhance the diffusion kinetics of lithium ions [18]. The Al-doped Li$_{6.75}$La$_3$Zr$_{1.75}$Ta$_{0.25}$O$_{12}$ separator redistributes Li$^+$ ions to create a uniform Li$^+$ flow [19]. The W$_2$N$_3$-doped graphene (WNG) separator is lipophilic and can adjust and redistribute ion flux at the interface[20]. The redistribution of lithium ion flow promotes the uniform deposition of lithium ions, preventing the
growth of lithium dendrites. By improving the migration kinetics of lithium ions, high-rate performance and long-term stability of lithium metal can be achieved. The synergistic effect of these factors effectively enhances the longevity of lithium metal. Therefore, it is crucial to develop strategies that accelerate the kinetics of lithium ion migration.

Spinels $\text{Li}_4\text{Ti}_5\text{O}_{12}$ have gained significant attention in the field of electrochemistry due to its excellent thermal stability, high safety, good rate performance, capacity retention, cycle stability, and remarkable cycle life. Additionally, spinel demonstrates the potential to regulate lithium deposition, leading to a longer cycle life for lithium metal.

In this study, commercial lithium titanate was coated onto a commercial polypropylene separator (LTO@PP) to enhance the diffusion kinetics of lithium ions. During the initial discharge cycle, the conversion of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to $\text{Li}_7\text{Ti}_5\text{O}_{12}$ facilitates the rapid transfer of $\text{Li}^+$, thereby accelerating the migration kinetics of lithium ions on the LTO@PP separator. Ultimately, the LTO@PP separator provides the lithium metal negative electrode with exceptional cycle stability, maintaining its structural integrity even after long-term cycling.

2. Experimental section

2.1 Synthesis of LTO@PP separator

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) powder and polyvinylidene fluoride (PVDF) were mixed at a weight ratio of 9:1 and grinded in a mortar for 30 minutes. N-methylpyrrolidone (NMP) was then added to the mixture, followed by magnetic stirred for 8 hours to gain fully mixing and uniform slurry. Then the slurry was coated on the PP separator. After vacuum drying at 50 °C for 24 hours, the LTO@PP separator was cut into circular discs with the diameter of 18 mm.

2.2 Synthesis of $\text{LiFePO}_4$ cathode material

$\text{LiFePO}_4$ (LFP) powder, Super-P carbon black and poly (vinylidene fluoride) (PVDF) was added into N-methylpyrrolidone (NMP) solvent with a mass ratio of 8:1:1. The obtained mixture was grinded in a mortar for 30 min, followed by magnetic stir for 8 h to gain uniform slurry and then coated on the aluminum foil. After vacuum drying at 120 °C for 8 h, the required positive electrode sheet was obtained. The polar piece was punched into discs with diameter of 13 mm.

2.3 Material characterization and electrochemical measurement

The structure of LTO@PP was characterized by X-ray diffractometer (XRD) on Rigaku mini Flex600X, where the scanning speed was 5 degrees per minute and the scanning range was 10°-90°. The morphology of the diaphragm was observed by scanning electron microscope (SEM) on Nova Nano SEM 450. The element distribution on the surface of the diaphragm was investigated by X-ray energy
dispersive spectroscopy (EDS) attached to SEM. The valence of lithium titanate on the surface of the diaphragm was understood by X-ray photoelectron spectroscopy (XPS) on Thermo Scientific Escalab 250 system. Thermogravimetric analysis (TGA) curves were obtained with a thermal analyzer (STA 449F3). The functional groups on the diaphragm were characterized by Raman (LabRAM HR).

The electrochemical performance of LTO@PP and PP separators was tested in CR 2025 and CR 2032 cells, assembled in an argon atmosphere glove box (Universal 2440 Uniq 750). The electrode is composed of 1M lithiumbis (trifluoromethanesulfonyl) imide (LiTFSI) and dioxolane / dimethoxyethane (DOL/DME, v/v 1:1) with 2 wt% LiNO_{3}. Celgard 2400 was employed as separators. The electrochemical performance of Cu | Li and Li | Li battery was tested on LANDdt (LAND CT-2001A battery test system, LANHE, China) and Neware battery test system (BTS9000 battery test system, NEWARE, China). The charge-discharge cycle performance of Cu | Li battery was tested under different current density and capacity, where the charging cut-off voltage is 0.5 V. While, the charge-discharge cycle performance of Li | Li was tested under different current density and capacity, where the charging cut-off condition is 1 h. Electrochemical impedance spectroscopy (EIS) was measured by electrochemical workstation (PGSTAT302N), in which the frequency ranges from 100 kHz to 0.01 Hz.

The relationship between ionic conductivity and the thickness of the separator follows:

$$\sigma = \frac{d}{R_b S}$$

where \(\sigma\) represents the ionic conductivity, \(d\) (25 microns) is the thickness of the separator, \(R_b\) represents the volume resistance, and \(S\) (1.76 cm\(^2\)) is the area of the stainless steel plate.

Li-Cu electrode was obtained by pre-plated on Cu electrode with lithium (2 mAh). Consequently, the pre-plated negative Cu electrode and the positive LFP electrode were assembled into full cell. The LFP full battery was pre-cycled for 5 times at 0.1 C, and then a long cycle was carried out at 1 C, the voltage range was 2.5 V-4.0 V, with the electrolyte made of 1m lithiumbis (trifluoromethanesulfonyl) imide (LiTFSI) and dioxolane / dimethoxyethane (DOL/DME, V/V 1:1) with 2 wt% LiNO_{3}.

### 3. Result and discussion

Figure 1 presents the XRD pattern, Raman spectra, thermogravimetric profile, EIS image, and electron microscopic images of LTO@PP and PP separators. The XRD pattern and Raman spectra are depicted in Fig. 1(a) and Fig. 1(b), respectively. The diffraction peaks correspond to the standard card of Li\(_4\)Ti\(_5\)O\(_{12}\) (PDF\#49–0207). LTO@PP exhibits peaks at 233.0 cm\(^{-1}\), 426.3 cm\(^{-1}\), and 674.2 cm\(^{-1}\), which correspond to the bending vibration of the O-Ti-O bond, the tensile bending vibration of the Li-O bond in LiO\(_4\) and LiO\(_6\) polyhedra, and the tensile vibration of the Ti-O bond in TiO\(_6\) octahedra, respectively. These results indicate the successful coverage of LTO on the surface of the PP separator.
The stability of LTO@PP and PP separators was compared using TGA measurement and heat treatment. As shown in Fig. 1(c), the decomposition temperature of the LTO-modified separator increased from 350°C to 415°C, indicating an improvement in battery safety. This further confirms the presence of LTO on the surface of the PP separator. Generally, the ionic conductivity of the separator decreases with increasing thickness. EIS test (Fig. 1(d)) and calculation were performed on the PP separator and the modified separator. The results show that the ionic conductivity of the LTO@PP separator (0.96437 ms/cm) is higher than that of the PP separator (0.7201 ms/cm), indicating a positive effect.

SEM test was carried out on the surface and cross-section of LTO@PP and PP separator to observe the microstructure. As present in Fig. 1(e), (f), it can be observed that the thickness of LTO is only 6.36 µm. The element analysis of the modified LTO@PP diaphragm shows that the Ti element is uniformly distributed on the whole cross section of the separator, proving that LTO covered uniformly on the separator by facile coating method.

To study the long cycle performance of LTO@PP and PP separator, the LTO@PP, PP based battery was tested under the condition where the current density of Li symmetrical cell was 3mA cm\(^{-2}\) and the discharge capacity was 3mAh cm\(^{-2}\). As illustrated in Fig. 2(a), it can be observed that in the battery based on the PP separator, there is significant voltage fluctuation, and it fails to operate after 300 hours, possibly due to the occurrence of lithium dendrites. However, the LTO@PP-based battery can cycle stably for 4800 hours, which is due to the fact that the LTO@PP separator can induce the uniform lithium deposition in the electrochemical cycle, which can be reflected in Fig. 3. Consequently, the charge-discharge test was carried out under the condition of current density of 0.5mA cm\(^{-2}\) and discharge capacity of 1mAh cm\(^{-2}\) in Li-Cu cell with LTO@PP, PP separators. The initial cycle of charge-discharge curve of LTO@PP and PP separator was illustrated in Fig. 2(b). It can be drawn that the polarization potential of LTO@PP (57 mv) is much lower than that of PP separators (98 mv). Meanwhile, on the second cycle, the overpotential of PP separator decreased to 34 mv, while that of LTO@PP diaphragm decreased to 18 mv, which is mainly attributed by the fact that LTO@PP has higher ionic conductivity than PP separator, further, high ionic conductivity can accelerate the transport of lithium ions. It can be seen from the Fig. 2(c) that the charge-discharge curve of the LTO@PP based cell at 10th, 50th, 100th, 150th, 200th and 250th cycle coincides well with each other, but the polarization potential of PP increases after 200th cycle, and the battery has failed to work, proving that LTO@PP separator can improve the ionic conductivity to induce the deposition of lithium metal, thus improving its long cycle performance.

The large interface impedance and slow lithium-ion transport will result in the uneven growth of lithium metal on the electrode surface, In other hand, the complete morphology of the separator before and after the cycle is fatal to the operation of cell. Therefore, SEM test was carried out to observe the surface morphology of LTO@PP and PP separators after deposition / stripping and the morphology of Li metal in Li symmetrical battery. As displayed in Fig. 3(a, d). The morphology of LTO@PP separator before and after cycle keeps consistent, attributed by the fact that LTO is a "zero strain" material and is inert to the electrolyte. The morphology of lithium metal surface in the LTO@PP based cell is shown in Fig. 3(b, e). It
can be observed that the deposition of lithium metal is very uniform, which is composed of pieces of lithium metal, attributed by the high ionic conductivity of LTO@PP separator. The high ionic conductivity can make lithium ion uniformly pass through, so that lithium ion can be deposited evenly. The lithium metal surface in the PP separator based cell is shown in Fig. 3 (c, f). It can be seen that the lithium metal deposition is highly uneven and there are many pits and bumps on the surface, which is due to the fact that the dendrite will become "dead lithium" without electrical contact after accumulation of Li deposition and cannot be stripped. Excellent lithium deposition inhibits the growth of lithium dendrite and improves the long cycle performance of the battery.

In order to further explore the reasons for the improved cycle performance, we carried out EIS tests on the LTO@PP, PP separators under the condition of current density 0.5 mA cm$^{-2}$ and discharge capacity 0.5 mAh cm$^{-2}$, and the results are displayed in Fig. 4 (a, b). The impedance of LTO@PP diaphragm keeps stable and smaller than that of PP diaphragm. The small variation range of impedance value proves that LTO@PP diaphragm has more stable circulation ability. The small impedance value indicates that the lithium ion has a small interfacial resistance when it passes through the LTO@PP separator, which is beneficial to reduce the lithium metal deposition overpotential and induce the uniformly deposition of lithium metal on the surface of the electrode. We also performed the XPS on the LTO@PP separator before and after the cycle. As shown in Fig. 4 (c, d), the cyclic LTO@PP separator showed Ti$^{3+}$ diffraction peaks at 457.3 ev and 460.4ev, and the following reactions took place during the electrochemical cycle.

$$\text{Li}_4\text{Ti}_5\text{O}_{12} + 3 \text{Li} \rightarrow \text{Li}_7\text{Ti}_5\text{O}_{12}$$

Compared with Li$_4$Ti$_5$O$_{12}$, Li$_7$Ti$_5$O$_{12}$ can achieve faster lithium ions translation to possess low impedance and high ionic conductivity.

We evaluated the LTO@PP, PP separators based cell at the discharge capacity of 0.5 mAh cm$^{-2}$ and 1 mAh cm$^{-2}$, in order to further analyze the rate performance of LTO@PP and PP separator. Compared with PP separator based cell, the LTO@PP separator based cell exhibits more outstanding long cycle performance, the Coulomb efficiency can be kept above 95% even after 140 cycles. In order to explore the application prospect of LTO@PP separator, we assembled LTO@PP based LFP | Li-Cu full battery. The discharge curves at different cycles of the two separators at 1C are illustrated in Fig. 5 (d-e). It can be observed that the capacity of full cell containing PP separator decays rapidly from 50 laps, while the capacity of LTO@PP based full cell keeps a stable cycling performance. It can be observed from Fig. 5f that LTO@PP based cell provides higher discharge capacity, even after 300 cycles, the capacity can maintain 91.53 mAh g$^{-1}$, which is much higher than that of PP (29.74 mAhg$^{-1}$). The discharge capacity retention rates of cell with LTO@PP and PP after 100 cycles are 75.99% and 24.34%, respectively. It can be drawn from Fig. 5g that full cell with two types of separators show stable Coulomb efficiency. Figure 5h evacuates the rate performance of LTO@PP and PP separator based full cell. It can be seen that even at high rate, the LTO@PP based cell displays higher capacity. When the current density is restored to 0.1 C, the capacity of LTO@PP and PP separator based cell is 154.82 mAh g$^{-1}$, 136.95mAh g$^{-1}$
The improved performance of LTO@PP based cell demonstrated that the uniform lithium deposition with high ionic conductivity makes the LTO@PP separator show more excellent long cycle performance and rate performance.

4. Conclusions

In conclusion, we employed facile coating method to modify the surface of PP separator. The results show that LTO@PP separator based cell display higher thermal safety. The excellent ionic conductivity makes LTO@PP have provide faster lithium-ion transport and uniform lithium-ion deposition to inhibiting the formation of lithium dendrites. The electrochemical performance tests show that LTO@PP cell displays more outstanding cycle performance and rate performance. With the modification of LTO@PP separator, the lithium metal deposition polarization potential of Cu can be reduced by 41 mv in the first cycle and reach half of initial polarization potential in the second cycle. The LTO@PP separator based Li-Li symmetrical battery can cycle stably for more than 4800 h under the current density at 3 mAcm$^{-2}$. In Li-Cu battery, LTO@PP based cell can cycle stably for more than 1400 h at the current density of 0.5 mA cm$^{-2}$. It can still cycle for more than 720 hours even at the discharge capacity of 1.5 mAh cm$^{-2}$. In addition, the full battery matched with LFP also proves that LTO@PP cell display higher capacity retention and more stable rate performance. The modification of separator with high ionic conductivity will be a promising guidance in the field of lithium metal negative electrode protection. The lithium titanate modified separator proposed in this paper is a promising strategy to solve settle the problem of lithium dendrite formation, and the LTO@PP based cell an excellent candidate for safer and long-cycle-life Lithium-ion application.

Declarations


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Availability of data and materials The data that support the findings of this study are available from the corresponding authors.

Ethical approval Not applicable.

Competing interests The authors declare no competing interests.

References


Figures
Figure 1

XRD pattern (a); Raman spectra (b); TGA (c); EIS images of LTO@PP, PP separator (d); SEM image of LTO@PP (e) and Elemental mapping of LTO@PP (f)
Figure 2

The long cycle performance of LTO@PP, PP based cell (a); The charge-discharge curves of the first circle (b) and the second circle (d) of LTO@PP, PP based cell; The charge-discharge curves of LTO@PP, PP based cell in different cycles (c). The illustration in Fig.2 (c) (d) is an enlarged view of selected curves.
Figure 3

SEM image of LTO@PP separator before cycling (a), after cycling (d); (b) SEM image of stripped LTO@PP separator after 100<sup>th</sup> cycle; (c) SEM image of stripped PP separator; (e) high-magnification SEM image of LTO@PP separator; (f) high-magnification SEM image of PP separator.
Figure 4

EIS spectra of LTO@PP (a) and PP (b) based cell after the cycle; XPS diagram of LTO@PP separator based cell before (c) and after (d) the cycle. The cell was tested at the situation of 0.5 mA cm\(^{-2}\) and 1 mAh cm\(^{-2}\).
Figure 5

Coulombic efficiency of LTO@PP, PP based cell at 0.5 mA cm$^{-2}$, 0.5 mAh cm$^{-2}$ (a); 0.5 mA cm$^{-2}$, 1.5 mAh cm$^{-2}$ (b); 0.5 mA cm$^{-2}$, 1 mAh cm$^{-2}$ (c); Voltage profiles of LTO@PP (e), PP (f) based cell at 10th, 30th, 50th, 100th cycle; the long term cycling performance of LTO@PP, PP separator based LFP | Li-Cu (f); Coulombic efficiency of LTO@PP, PP separator based LFP | Li-Cu (g); rate performance of LTO@PP, PP separator based LFP | Li-Cu (h)