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# Stabilized Lithium Anode via a Uniform Li-Ions Distribution Enabled by a Robust LLZTO/Polysulfone Electrospun Membrane

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**Abstract:** Lithium metal batteries (LMBs) using lithium metal as the anode is a promising technical route for the next battery. lithium metal anode delivers the highest energy density. Therefore, it has been extensively studied by scientists. Unfortunately, Li-metal anode is incapable to practical applications due to the dendritic propagation during the repeated charging/discharging process leading to short-circuit and severe safety issues. we loaded the fast Li-ions conductor LLZTO ceramic particles on the polysulfone (PSU) fiber. The LLZTO/PSU composite fiber membrane networks inherited both lithiophilic properties and strong rigidity from LLZTO particles, which could suppress the local electric field and exert influence of adjusting the distribution and deposition behavior of Li-ions while the improved mechanical properties against lithium dendrites. Therefore, the lithium metal anode with modified surface of composite fiber can effectively inhibit the formation of lithium dendrites with a prolong life-span.

#### 1. Introduction

As the first choice for the next generation of electrochemical power sources, lithium metal batteries (LMBs) have been extensively researched by virtue of extremely high specific energy. However, they cannot be practically applied because of potential safety hazards arising out of the lithium dendrites-induced interfacial instability problem. Here, the fast ion conducting material— $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$  (LLZTO)—is loaded into polysulfone (PSU) fibrous membrane to form a LLZTO/PSU composite fibrous membrane, which is then used to stabilize the negative electrode of lithium metal. As shown in Figure 1, LLZTO is loaded into the PSU fibrous network as a lithiophilic site to form a lithiophilic fibrous network on the surface of lithium metal electrode. The fiber structure occupies the cutting-edge bulge on the electrode surface and guides Li-ions to form uniform distribution and deposition behaviors, expecting to overcome local electric field and repress the lithium dendrites. In addition, LLZTO has strong mechanical properties. By means of theoretical calculation and nanoindentation, etc., its shear modulus was once determined as 56-61GPa<sup>[2]</sup>, being much higher than the strength of lithium dendrites. Therefore, the composite process of LLZTO and PSU is hopeful to improve mechanical strength of the material and suppress lithium dendrites, so as to improve the battery performance.



Figure 1. Schematic diagram of negative electrode stabil-ization for lithium metal via LLZTO/PSU composite fiber

# 2. Physicochemical characterization of LLZTO/PSU composite fibrous membrane

- 2.1. Morphological characterization of LLZTO/PSU composite fibrous membrane

Figure 2. SEM graphs (a) (b) LLZTO particles after ball milling; (c) (d) LLZTO/PSU composite fiber

Figure 2 (a) and (b) show the scanning electron microscope (SEM) graphs of the sintered and synthesized LLZTO inorganic electrolyte particles. Through ball milling, their particle sizes are distributed within 200-800 nm. The SEM-assisted morphological characterization of electrospinning fiber synthesized by LLZTO/PSU composite with LLZTO mass fraction being 10% is presented in Figure 2 (c) and (d). Although the mass fraction of LLZTO in the composite fibrous membrane also reaches 10%, the LLZTO particles are not agglomerated, so they will not influence the fibrous network structure. High porosity and typical 3D fibrous network structure are observed, and fiber diameter is about 700 nm. As lithiophilic sites of LLZTO are densely distributed on the fiber, the synthesized composite fibrous network can play the role of "Li-ion redistributor" very well so that Li-ions can be uniformly distributed and migrated along such fibrous structure, and in the end, dendrites-free Li deposition is formed on the electrode surface.



#### 2.2. X-ray diffraction (XRD) analysis of LLZTO/PSU composite fiber

Figure 3. XRD analysis chart of LLZTO/PSU composite fibrous membrane

Typical characteristic peaks of LLZTO are displayed in the XRD analysis of both LLZTO powder samples and composite fibrous membrane, where the characteristic peaks of both powders and composite fibrous membrane appear at angles of 16.81°, 19.459°, 25.807°, 27.621°, 30.966°, 32.621°, 34.05°, etc. It is verified through the analysis results that the LLZTO garnet ceramic particles used in this study are cubic phases with high ion conductivity, and their sharp diffraction peaks indicate their considerable crystallinity. The existence of LLZTO in the LLZTO/PSU composite fibrous network can provide Li-ions with a continuous fast transport path. <sup>[3,4]</sup>

#### 2.3. Conductivity test of LLZTO electrolyte particles

The impedance spectrogram of LLZTO is shown in Figure 4. Within the medium and high frequency range in the spectrogram, there is only one semicircle, which corresponds to the impedance contributions of ceramic electrolyte grain ( $R_b$ ) and the whole grain boundary ( $R_{gb}$ ). The fitted circuit is shown in the illustration. The total Li-ion conductivity is calculated according to  $R = R_b + R_{gb}$ . The ionic conductivity of LLZTO can be obtained as  $4.808 \times 10^{-4}$  S cm<sup>-1</sup>. The superior conductivity verifies the ability of LLZTO to guide and transport Li-ions as a lithiophilic site in the fibrous membrane.



Figure 4. Impedance spectrogram of LLZTO ceramic electrolyte particles

#### 2.4. Mechanical properties of LLZTO/PSU composite fibrous membrane



Figure 5. Load force-displacement curve; (a) PSU fibrous membrane; (b) LLZTO/PSU composite fibrous membrane

Figure 5. shows the nanoindentation test results of the fibrous membrane material. During the whole loading-unloading process, both load force-displacement curves keep linear deformation, and the curves return to the initial positions during the unloading process, which fully verifies that the fibrous membrane undergoes reversible elastic deformation during the whole process. Through the Derjaguin–Muller–Toporov (DMT)<sup>[5]</sup> method, the Young's modulus in compression of PSU fibrous membrane and LLZTO/PSU composite fibrous membrane is calculated as 0.717 GPa and 1.48 GPa, respectively, indicating that the adulterated rigid LLZTO ceramic electrolyte particles can not only exert the conducting effect of Li-ions but also can significantly enhance the rigidity of the composite fibrous membrane. The previous theoretical study manifests that the solid membrane with modulus of 1 GPa is enough to inhibit the growth of lithium dendrites on the negative electrode surface of lithium metal. The LLZTO/PSU composite fibrous membrane synthesized in this study is of strong rigidity, and its mechanical modulus reaches as high as 1.48GPa, which is sufficient to repress the lithium dendrites <sup>[6-8]</sup>.

# **3.** Electrochemical properties characterization of LLZTO/PSU composite fiber for negative electrode protection of lithium metal

## 3.1. Lithium depositional morphology



Figure 6. Lithium depositional morphology on electrode surface of copper foil; (a-c) Control group of PSU fiber; (d-f) Blank group; (g-i) Experimental groupof LLZTO/PSU composite fiber; (c), (e) and (f) are sectional morphologies after lithium deposition

Cu-Li half-cells, which experienced a certain number of cycles, were taken apart to observe the lithium deposition and sectional morphology on the copper foil surface and investigate the influence of surface modification of the LLZTO/PSU composite fiber on Li-ion decomposition on electrode surface as shown in Figure 6. On the copper foil in the unmodified blank group and that in the control group treated only with PSU fibrous membrane, the lithium deposition means that a macroscopic dendritic structure with much loose and porous "dead lithium" is observed. This loose and porous structure will lead to unstable solid electrolyte interface (SEI) film, which is then continuously thickened in the repeated crushing process and forms a thick passivation layer together with "dead lithium", and as a result, the interfacial impedance is increased and the battery performance is degraded. With continuous growth, these "tree-shaped" lithium dendrites will pierce the membrane, thus giving rise to short circuit of the battery and triggering safety problems. Comparatively speaking, the lithium deposition on the electrode surface of the copper foil modified using LLZTO/PSU composite fiber is compact and flat, no lithium dendrites or "dead lithium" are observed, and the section of lithium deposition is quite compact and complete, presenting a dendrite-free electrolytic depositional morphology as a whole.



3.2. Cyclic test of coulombic efficiency in Cu|Li half-cells

Figure 7. Charge-discharge cycle performance comparison of Cu|Li half-cells

In order to verify the improving effect of composite fiber modification on the electrode performance, Cu-Li half-cells were assembled to do a cyclic test of Coulombic efficiency, and the electrolyte used in the test was DOL/DME electrolyte solution, where the mass fraction of LiNO<sub>3</sub> was 2%. As shown in Figure 7, the battery with composite fiber-coated copper foil electrode was used at current density of 1.0 mA cm<sup>-2</sup>, its average Coulombic efficiency was kept above 96.5% within 300 circles, while the Coulombic efficiency of the blank group with bare copper electrode and that of the PSU control group started declining obviously after 120 circles. As the current density was elevated to 2 mA cm<sup>-2</sup>, over 91% Coulombic efficiency was kept within 100 circles on the composite fiber-coated copper electrode surface in the experimental group. Both blank group and PSU control group underwent drastic fluctuation just within 30 circles, and their Coulombic efficiencies declined to below 80%. The Coulombic efficiencies of the blank group could not be kept stable during the long cycling time.

## 3.3. Performance test of Li|Li symmetric cells



Figure 8. Cycling time-voltage comparison chart of Li | Li symmetric cells

Li | Li cells were assembled to study the stability of electrode interface and comparatively analyze the impact of lithium dendrites on short circuit of the cells. All symmetric cells were cycled at current densities of 2.0 mA cm<sup>-2</sup> and 1.0 mAh cm<sup>-2</sup>. As shown in Figure 8, the voltages of the symmetric cells in the unprotected blank group could be maintained stable in early stage, but as time went on, the voltages experienced fluctuation after a certain number of cycles with a sign of short-circuit, manifesting that the unstable interface between Li-metal anode and electrolytes leading by dendrites. For the LLZTO/PSU composite fiber-coated lithium metal electrode, after their voltage experienced the early

stable phase, the polarization voltage of 35 mV was maintained for the sake of stable cycling for 600 h, a stable interface was then acquired, and no short circuit fault occurred.

3.4. Performance test of LiFePO<sub>4</sub> full-cells



Figure 9. Long-cycling performance comparison of LiFePO<sub>4</sub> full cells

As shown in Figure 9, all cells were tested with ester-based electrolyte solution at rate of 2C. The blank group and PSU control group had excellent performance in the first 200 cycles, over 90% of the capacity was held, and the Coulombic efficiency was kept at 99% or so. However, in the follow-up cycles, the capacity dropped more obviously until decreasing sharply. At the 400<sup>th</sup> cycle, the capacity holding rates in the two groups were only 51% and 58.6%, respectively, and their Coulombic efficiencies were fluctuating. By comparison, the full cell with composite fiber-coated lithium metal electrode showed remarkable improving performance. After 550 cycles, its capacity holding rate still reached 82% and the Coulombic efficiency was kept over 99%.

#### 3.5. Full-cell rate performance test



Figure 10. Rate performance comparison of LiFePO<sub>4</sub> full-cells

The rate performance test was namely charge-discharge cyclic test of cells from low to high rates and then back to low rate. As shown in Figure 10, different LiFePO<sub>4</sub> cells were continuously tested at rates of 0.5, 1, 2, 5, 10 and 1C (10 cycles at each rate). The average discharge capacities of the cells with modified negative electrode in the experimental group were 159.8, 154.5, 147.7, 134.4 and 120.1 mAh g<sup>-1</sup>, respectively. When the rate was elevated back to 1C, the cells in the experimental group could still bear long cycling at high specific capacity of 153.5 mAh g<sup>-1</sup>, being superior to both control groups.

3.6. Electrochemical impedance analysis



Figure 11. Electrochemical impedance spectrograms; (a) LLZTO/PSU fiber coated electrode; (b) Blank group

Figure 11 shows the corresponding impedance spectrograms and data fitting graphs. For the blank group, two significant semicircles were observed in the test area (100 KHz-50 mHz), where the semicircle in the high-frequency area represented impedance  $R_{SEI}$  of interfacial SEI film and that in the low-frequency area denotes charge transfer impedance  $R_{ct}$ . As seen in Table 1, continuously thickening SEI film and mass "dead lithium" were caused by nonuniform lithium deposition on the surface of blank electrode, and the interfacial impedance value  $R_{SEI}$  rapidly rose from 173  $\Omega$  at the 17<sup>th</sup> cycle to 515  $\Omega$  at the 100<sup>th</sup> cycle. After 200 cycles, both  $R_{SEI}$  and  $R_{ct}$  dropped sharply, and this conformed to the result that the development of lithium dendrites led to short circuit fault in the cells.

		Bare				•	MCFM		
	$10^{\text{th}}$	$100^{\text{th}}$	$200^{\text{th}}$	$300^{\text{th}}$		$10^{\text{th}}$	$100^{\text{th}}$	$150^{\text{th}}$	$200^{\text{th}}$
R <sub>b</sub>	5.470	5.249	6.701	4.212	R <sub>b</sub>	11.26	14.21	12.02	11.71
$R_{\text{SEI}}$	173.0	515.0	7.546	7.156	$R_{\rm SEI}$	124.7	129.4	91.02	78.97
$R_{ct}$	21.76	31.18	25.75	3.611	$R_{\rm fi}$	390.3	484.8	320.7	354.9
					R <sub>ct</sub>	47.38	29.21	14.25	19.82

Table 1. Fitting results of impedance data

Li-ions could arrive at the electrode surface only after passing the composite fibrous network structure in modified anode, the corresponding equivalent circuit was in series connection with a resistance  $R_{\rm fi}$  parallel to a capacitive-type resistance-constant element, and  $R_{\rm fi}$  represented the resistance when Li-ions passed through the fibrous membrane. The fitting results are listed in Table 1.  $R_{\rm SEI}$  remained stable in the whole cycling process, manifesting that the electrode/electrolyte interface was kept stable, in other words, relatively stable SEI film and uniform lithium deposition were acquired, and this should be ascribed to the uniform Li-ions flux and inhibiting effect of high strength on lithium dendrites. The results of EIS analysis confirmed the positive effect of surface modification on stabilizing the interface of lithium metal anode. And the uniform Li-ions flux and mechanical strength synergistically inhibit Li-dendrites and improve electrochemical performance.

# 4. Conclusion

Based on the formation mechanism of lithium dendrites on the Li-metal anode, the lithiophilic LLZTO inorganic ceramic electrolyte particles were loaded onto the PSU fibrous network structure to prepare and acquire a LLZTO/PSU composite fibrous membrane with lithiophilicity and favorable mechanical modulus. As a stable interfacial layer on the negative electrode surface, this membrane was used to guide uniform Li-ions flux and deposition on the electrode surface, inhibit the impact brought by local electric

fields and resist against lithium dendrites. The positive effect of rigid LLZTO/PSU lithiophilic composite fibrous membrane on the LMBs performance is verified in this paper from the angles of characterization and performance.

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