

In Situ Construction of Stable Tissue-Directed/Reinforced Bifunctional Separator/Protection Film on Lithium Anode for Lithium–Oxygen Batteries

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To achieve a high reversibility and long cycle life for Li–O₂ battery system, the stable tissue-directed/reinforced bifunctional separator/protection film (TBF) is in situ fabricated on the surface of metallic lithium anode. It is shown that a Li–O₂ cell composed of the TBF-modified lithium anodes exhibits an excellent anodic reversibility (300 cycles) and effectively improved cathodic long lifetime (106 cycles). The improvement is attributed to the ability of the TBF, which has chemical, electrochemical, and mechanical stability, to effectively prevent direct contact between the surface of the lithium anode and the highly reactive reduced oxygen species (Li₂O₂ or its intermediate LiO₂) in cell. It is believed that the protection strategy describes here can be easily extended to other next-generation high energy density batteries using metal as anode including Li–S and Na–O₂ batteries.

Rechargeable nonaqueous lithium–oxygen (Li–O₂) batteries with metallic lithium anode, based on the electrochemical reaction of $2\text{Li}^+ + 2\text{e}^- + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2$ ($E^0 = 2.96 \text{ V vs Li/Li}^+$), have attracted intensive attentions thanks to their extremely high theoretical specific energy (3505 Wh kg⁻¹), which is nearly ten times higher than that of the state-of-art lithium-ion batteries (LIBs).^[1,2] In a typical Li–O₂ cell, the cathode active material is oxygen, while metallic lithium is employed as anode to obtain the high energy density because of its high specific capacity (3860 mAh g⁻¹) and low potential (–3.04 V vs standard hydrogen electrode).^[3,4]

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As Li–O₂ batteries are still in infant stage, to improve the discharge capacity and energy efficiency, many works have been devoted to the cathode structure, catalyst activity, and so on.^[5] However, in practice, we should pay more attentions to the daunting corrosion problem of metallic lithium as anode in Li–O₂ battery: on the one hand, even without discharge/charge process, the active metallic lithium can react with the dissolved O₂ in electrolyte due to its semi-open nature of Li–O₂ batteries; on the other hand, during cycling, besides the dissolved O₂, discharge intermediates (especially superoxide radical anion O₂⁻ and peroxide radical anion O₂²⁻) and H₂O (derived from

the electrolyte decomposition) would lead to serious corrosion of metallic lithium anode, which inevitably cause the formation of by-products, low reversibility of lithium, and especially, premature death of Li–O₂ batteries.^[3b,6] Unfortunately, in conventional Li–O₂ battery with commonly used porous separator (e.g., glass fiber, GF), the crossing of O₂, discharge intermediates, H₂O and electrolyte cannot be blocked.^[7] Although progress has been made to protect lithium anodes by coating protective layers,^[8] the currently available very few strategy is still from satisfying due to the inferior chemical stability of the protection film, complicated preparation procedures, dependence on special equipment, and, especially, limited improvement in performance of Li–O₂ battery. Therefore, besides restrain the side reaction between electrolyte/solvent and high reactive intermediate species (such as superoxide radical) at the cathode side, development of an effective and facile strategy to protect metallic Li and thus enhance the stability of Li–O₂ batteries is urgently required while still very challenging.

Herein, for the first time, we propose and demonstrate a novel and facile strategy to protect the Li anode in Li–O₂ battery by in situ fabricating a stable tissue-directed/reinforced bifunctional separator/protection film (TBF) on the surface of the Li anode. Unexpectedly, the TBF composite film made of lithium-exchanged Nafion (LN) ionomer and the commercial low-cost tissue exhibits excellent performances, including superior chemical, electrochemical, and mechanical stability, and good ionic conductivity. More importantly, the TBF composite film is found to be able to effectively protect lithium from the corrosion of O₂, discharge intermediates, H₂O and electrolyte, and reduce morphology change of the surface of lithium anode. As a proof-of-concept experiment, the as-prepared TBF not only

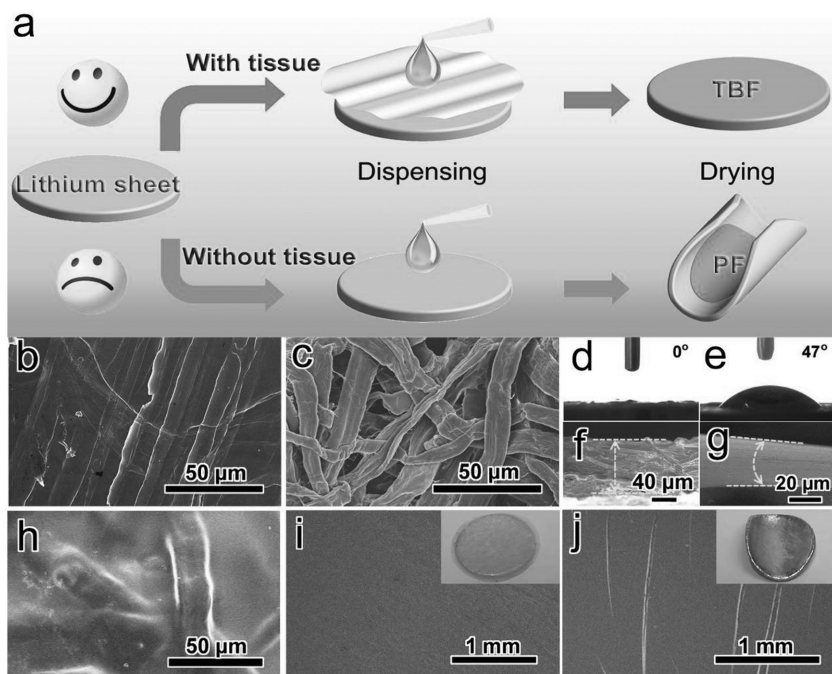


Figure 1. a) A schematic representation of the design and preparation of TBF and PF; the scanning electron microscopy (SEM) images of the surface of b) pristine metallic lithium, c) tissue fibers; the TEGDME contact angles for d) the lithium covered by tissue and e) the pristine lithium; the SEM images of the cross-section of f) TBF and g) PF on the surface of lithium; the SEM images of h) TBF and the low magnified images and photographs (inset of i) TBF and j) PF.

significantly increases the anodic reversibility but also effectively improves the cycle stability of Li–O₂ battery.

Figure 1a shows the process of in situ fabricating TBF on the surface of Li anode. First, the lithium sheet (Figure 1b), without any treatment, was covered with commercial tissue composed of plant fibers (Figure 1c; Figures S1 and S2, Supporting Information). Then, the LN solution was dropped to the surface of the tissue, forming TBF adhering to metallic lithium after drying in argon atmosphere. Interestingly, it can be seen that the LN solution quickly and evenly spread to the entire surface after the very simple preparation process. To analyze the reason, the contact angle (CA) measurement was carried out. As shown in Figure 1d, when the droplet of LN solution contacted the surface of the tissue, it was instantaneously adsorbed, and the tissue was lipophilic with a CA of 0°. This characteristic of tissue can ensure the even distribution of LN on the upper surface of metallic lithium. In contrast, the CA of pristine lithium metal was 47° (Figure 1e), which may cause uneven dispersion of LN on the surface of pristine lithium sheet. To further examine it, three types of lithium sheets without and with treatment were exposed to air to observe the change in color. We can find that the lithium sheet with TBF kept the homogeneous color, but the lithium sheet without the assistant of tissue, the only polymer-containing film (PF) on its surface, was partial black (Figure S3, Supporting Information), which strongly supports the homogeneous distribution of LN in TBF. To further confirm the advantage of TBF, the scanning electron microscopy (SEM) was used to observe the morphology of TBF. The conclusion above is also supported by the morphology

of the cross-section of TBF and PF on the surface of lithium, which demonstrated that the thickness of TBF was more uniform than that of PF (Figure 1f,g). In addition, benefiting from the inherent characteristics of LN and the excellent lipophilicity of tissue, there were no holes in the TBF (Figure 1h), which may be an efficient barrier to above-mentioned corrosive substances compared with the GF separator. Moreover, the lithium sheet covered by TBF could still keep relatively flat (inset of Figure 1i) and its surface was smooth (Figure 1i) as a result of the LN uniform distribution. In sharp contrast, the lithium sheet bent seriously after drying (inset of Figure 1j). Unfortunately, when the lithium sheet was flattened for assembling Li–O₂ battery, there were many fissures on its surface (Figure 1j), which is detrimental not only to the lithium uniformly stripping/plating process upon cycling but also to the prevention metallic lithium from the corrosion from O₂, discharge intermediates, H₂O and electrolyte. Furthermore, to demonstrate the function of the tissue, bending/stretching experiment was carried out (Figure S4a,b, Supporting Information). There were many big fissures on the surface of PF after 200 cycles of bending/stretching (Figure S5a, Supporting Information). Interestingly,

the TBF on the surface of lithium anode still kept unchanged (Figure S3b, Supporting Information), showing enhanced mechanical stability of the TBF with the help of tissue, which is beneficial to the storage, transportation, and battery assembly of metallic lithium sheets.

Due to the specific characteristics of semi-open nature for Li–O₂ battery, even without discharging/changing process, the lithium anode has to endure the attack of oxidizing gases, which would lead to serious self-discharge and poor anodic reversibility. The capability of anticorrosion toward air is a key indicator for the anode of Li–O₂ battery. To verify the protective effect of TBF, both metallic lithium sheets with and without TBF were placed in atmospheric condition, respectively. As shown in **Figure 2a,b**, the pristine lithium was corroded quickly to dull silvery gray and then black tarnish, which can be attributed to the reaction products formed on the surface of lithium. In sharp contrast, the Li sheet with the TBF still maintained its fresh state even after 20 min. These results suggest that TBF effectively prevented the lithium from the corrosion in the atmospheric condition. To further investigate this phenomenon, Fourier transform infrared spectroscopy (FTIR) was used to identify the black products. Note that the FTIR spectra in Figure 2c are indicative of the presence of the lithium carbonate (Li₂CO₃) and a small quantity of the lithium hydroxide (LiOH) on the pristine lithium sheet. Interestingly, besides the peaks belonging to the tissue and LN, there are no other peaks on the curve of 20 min TBF (Figure 2b). The results indicate that TBF can effectively protect the lithium sheet from the corrosion of air, which inspired us to further investigate its properties.

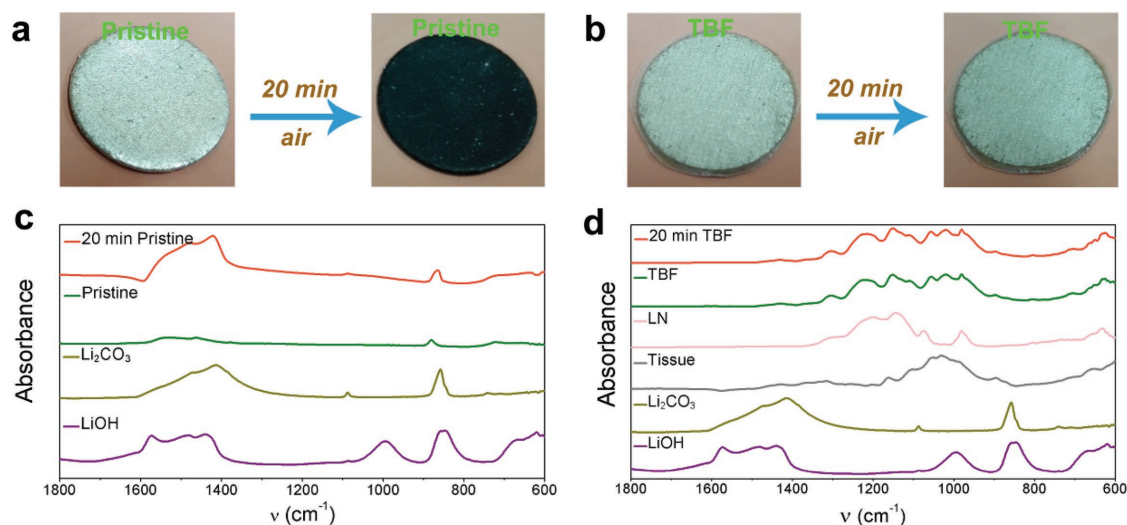


Figure 2. Photographic images showing the corrosion of metallic lithium a) without and b) with TBF; FTIR curves of lithium sheet c) without and d) with TBF exposed to the atmosphere after 20 min.

During the discharging and charging cycle in Li–O₂ battery, the high reactive discharge intermediates (O₂^{•−} and O₂^{2−}) will be produced, which would cause the decomposition of electrolyte and cathode leading to short cycle life. Therefore, the stability of the selected polymer toward the reduced oxygen species in Li–O₂ battery system is prerequisite. A variety of polymer are generally used as the electrolyte or binder in the LIBs, such as poly(acrylonitrile), poly(ethylene oxide), poly(vinyl chloride), poly(vinylpyrrolidone), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and PVDF. Unfortunately, they are unstable or may undergo cross-linking in the presence of Li₂O₂ (the main discharge product in Li–O₂ batteries).^[9] Nafion, widely used as membranes in fuel cells, has a polytetrafluoroethylene backbone, featuring a 3D structure. The side chains of

perfluorinated vinyl ethers terminated by sulfonic groups provide high cation (proton) conductivity. In consideration of stability, the high content of Nafion protons were removed by ion exchange in LiOH solution, forming LN (Figure S6, Supporting Information), which would avoid the reaction with the metallic Li and increase Li ion conductivity.^[10] The chemical stability of LN has been reported in the presence of commercial Li₂O₂.^[9] To further examine the stability against O₂^{•−}, the chemical reaction between LN and KO₂ was investigated by FTIR spectroscopy. As shown in Figure 3a, there were five peaks on the curves of Nafion and LN, stemming from the vibration of C–F₂, C–F₂, S–O, C–F, and C–O–C, respectively, which is consistent with the notation given in ref. [9a]. Interestingly, after 150 h reaction between LN and KO₂, the peaks on FTIR spectra of 150 h-LN

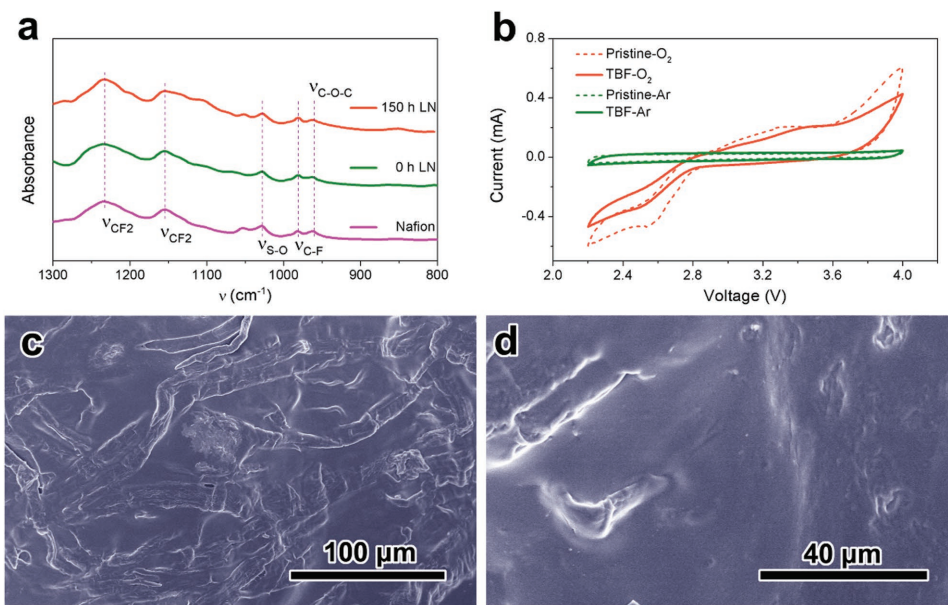


Figure 3. a) FTIR spectra of the LN:KO₂ reaction after 150 h; b) CV curves of the Li–O₂ cells using the pristine lithium and the lithium with TBF in argon and oxygen atmosphere, respectively; c,d) the SEM images of the TBF after 40 discharge–charge cycles.

was the same as that of Nafion, which suggests that there are no decomposition products and fracture of chemical bonds, and LN possesses excellent chemical stability. Further, the electrochemical stability of the TBF in Li–O₂ cell was investigated using cyclic voltammetry (CV). Figure 3b presents the CV response of the cells in the atmosphere of oxygen and argon, respectively. It can be seen that, except the peaks related to the formation and deposition of discharge product,^[28,11] the extra peaks did not appear whether in argon or oxygen, confirming the superior electrochemical stability of TBF in the Li–O₂ battery system. Similarly, the superior electrochemical stability of the tissue and LN was also verified by CV curves (Figure S7, Supporting Information). In addition, compared with the curve of the pristine anode in oxygen atmosphere, the Li anode with TBF exhibited a lower peak current, and the reduced and oxidized peaks moved left and right, respectively, which are derived from the passivation of lithium anode coated by TBF, and might be beneficial to decrease the side reactions involving metallic lithium with O₂, discharge intermediates, H₂O and electrolyte. Moreover, the morphology of discharge product of the Li–O₂ cells with the TBF and pristine anode was investigated after the first discharge. The similar toroid-like discharge product appeared on the cathodes disassembled from Li–O₂ batteries with and without TBF, indicating that the same reaction occurred during the discharge process, and there is no interference toward the formation of discharge product (Figure S8, Supporting Information), which also illustrates the stability of TBF, and was consistent with the results of the CV.^[12] In addition, to further investigate the electrochemical stability, the morphology evolution of TBF and the tissue was observed via SEM. Remarkably, compared with that of the pristine TBF (Figure 1h) and the pristine tissue (Figure 1c), the morphology and structure of the TBF and the tissue after the 40 discharge–charge cycles (Figure 3c,d; Figure S9, Supporting Information) were still well maintained in the harsh electrochemical redox environment, which further indicated the good stability of TBF and the tissue. Thanks to the excellent properties mentioned above, the film can be used as the separator in Li–O₂ battery.

The electrochemical properties of Li–O₂ cells with TBF-modified lithium anodes were investigated. For comparison, the tests related to the cells with the pristine lithium anodes were also carried out. The electrochemical impedance spectrums of Li–O₂

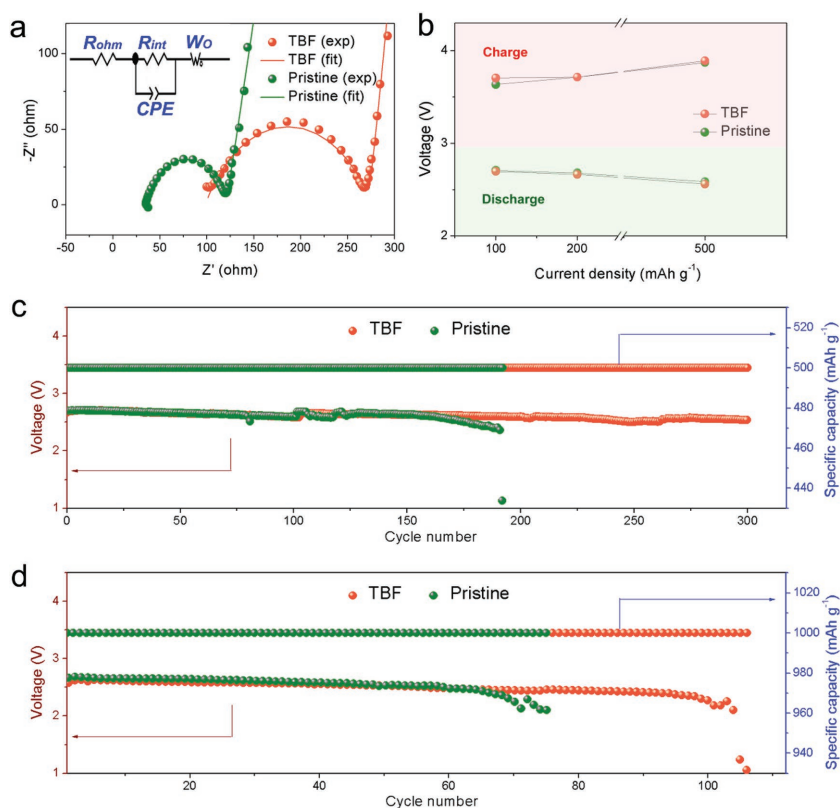


Figure 4. a) Impedance spectra, b) the first discharge and charge medium voltage at specific capacity limit of 1000 mAh g⁻¹ and the specific capacity limit of 500 mAh g⁻¹ and c) the ultimate life of anodes at the current density of 200 mA g⁻¹ and d) the cycle life at the current density of 300 mA g⁻¹ and the specific capacity limit of 1000 mAh g⁻¹ of Li–O₂ cells with and without TBF.

cells with the two types of anode were displayed in Figure 4a. The equivalent-circuit parameters were acquired by curve fitting with the equivalent circuit shown in the inset of Figure 4a. Data points are the experimental values and the solid lines

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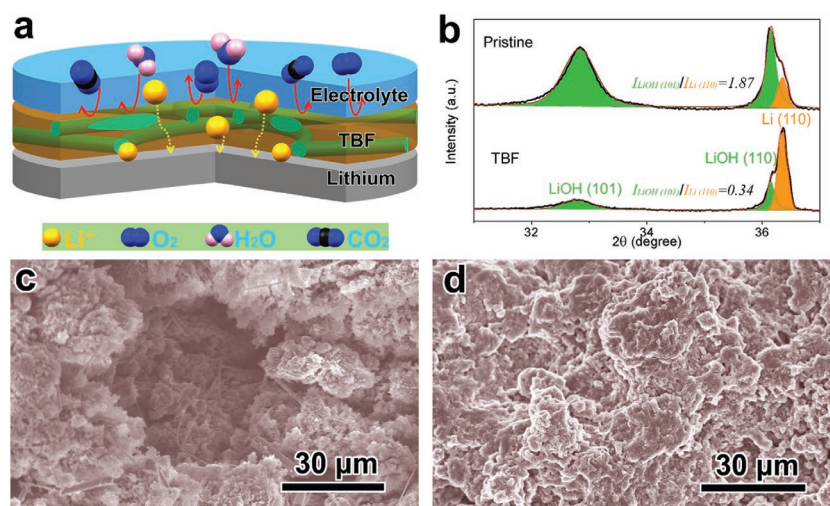


Figure 5. a) A schematic representation of protection mechanism of TBF; b) XRD curves of the by-product on the lithium anodes; SEM images of morphology evolution of lithium anodes c) without and d) with the TBF after 40 discharge–charge cycles.

are the calculated curves using the equivalent circuit. R_{ohm} is Ohmic resistance of the Li–O₂ cell. R_{int} is the interfacial resistance and W_o is Warburg impedance from the Li⁺ concentration gradients. Based on the calculation of the fitted value, the ionic conductivity of TBF is 3.1×10^{-5} S cm⁻¹. It can be found that the R_{int} of Li–O₂ cells with TBF increased from 85.7 (pristine) to 174.7 Ω, suggesting that the composite layers can effectively passivate the metallic lithium. Interestingly, compared with that of the pristine, the first discharge and charge potentials of TBF did not change notably at the current densities of 100, 200, and 500 mA g⁻¹ (Figure 4b). It should be noted that impedance of TBF increased due to the protective film (Figure 1f,h), but the cells with TBF could guarantee the normal reaction kinetics of Li–O₂ battery system, which is benefited from the good ionic conductivity of TBF.^[10] In addition, as mentioned above, the metallic lithium has to endure the strong oxidation environment both in the static state and the discharging/charging cycle, which seriously decreases the reversibility of lithium anode. The consumption of metallic lithium will greatly limit the practical application of Li–O₂ battery. To investigate the reversibility of lithium anodes, the Li–O₂ batteries with and without TBF modified anode were cycled in the condition of replaced cathodes every one hundred cycles to eliminate the interference of cathodes. As shown in Figure 4c, the Li–O₂ battery with TBF could be discharged and charged up to 300 times at a current density of 200 mA g⁻¹ with the specific capacity limited to 500 mAh g⁻¹. In sharp contrast, the Li–O₂ battery with pristine anode only ran 192 cycles. These results indicate that TBF can efficiently avoid corrosion and improve the reversibility of metallic lithium. Figure 4d further illustrates the cycling performance of the Li–O₂ battery with TBF anode without replacing the cathode. The Li–O₂ battery with pristine anode and GF separator can operate 75 cycles at a current density of 300 mA g⁻¹ with the specific capacity limited to 1000 mAh g⁻¹. Unexpectedly, the 106 discharge–charge cycles of the Li–O₂ batteries with TBF can be obtained. This considerable improvement of cycle performance suggests that the TBF can be well used as separator. The above obtained excellent reversibility and cycle stability should be attributed to the combined advantages of TBF, as illustrated in Figure 5a: (1) the novel and facile strategy to protect the Li anode in Li–O₂ battery via in situ fabrication of the stable TBF can form even film on the surface of the Li anode, ensuring the durable and full range protection; (2) the excellent chemical/electrochemical stability of the LN and tissue ensures that the electrochemical reaction of Li–O₂ battery is in a relatively stable condition; (3) the good mechanical stability of TBF may avoid damage from the battery assembly and cyclic process and improve the durability of the battery; (4) the TBF made up of LN and tissue not only permitting the transmission of lithium ion, but also effectively resists the corrosion of O₂, discharge intermediates, H₂O and electrolyte, which would reduce the anodic side reaction and improve the reversibility of lithium anode. Therefore, we believe that TBF using simple method of solution-casting is a viable strategy for high reversible and long-life Li–O₂ batteries.

To further understand the mechanism of the obtained enhanced cell performances, the X-ray diffraction (XRD) analysis demonstrated that the discharge by-products on the two types of anodes were LiOH (Figure 5b), which is

consistent with the previous reports.^[3b,8d] The degree of corrosion of anode is generally judged by the amount of LiOH on the metallic lithium surface.^[3b] The $I_{LiOH(101)}/I_{Li(110)}$ ratios of pristine lithium and coated lithium are found to be 1.87 and 0.34, respectively, indicating that more LiOH generated by side reaction in the pristine lithium. That is to say, our coated lithium anode with TBF significantly restrains the side reaction and lithium consumption during the cycling of Li–O₂ battery. In addition, the morphology evolution of the discharge lithium anodes with and without TBF was investigated. After 40 discharge–charge cycles, the surface of the anode without TBF became much rougher than that of the anode with the TBF (Figure 5c,d), suggesting that the TBF on the lithium surface effectively protected the metallic lithium from corrosion.

In summary, to achieve a high reversibility and long cycle life for Li–O₂ battery system, the stable TBF was designed and in situ fabricated on the surface of metallic lithium. The fabrication process is very facile by solution-casting, forming a composite layer of the stable LN and a very cheap tissue. The obtained TBF possessed effective protection capability thanks to chemical, electrochemical, and mechanical stability. As a proof-of-concept application, the Li–O₂ batteries with the TBF-modified lithium anodes exhibited an excellent anodic reversibility (300 cycles), and effectively improved cathodic long lifetime (106 cycles). We believe that the protection strategy described here could be easily extended to other next generation high energy density batteries using metal as anode including Li–S and Na–O₂ batteries.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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