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In-situ designing a gradient Li⁺ capture and quasi-spontaneous diffusion anode protection layer towards long-life Li-O₂ batteries

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Abstract: Lithium metal is the only anode material that can enable Li-O₂ battery to realize its high theoretical energy density (~3500 Wh/kg). However, the inherent uncontrolled dendrite growth and serious corrosion limitations of lithium metal anode make it experience fast degradation and thus impede the practical application of Li-O₂ batteries. To solve these challenges, herein, we have developed a multifunctional complementary LiF/F-doped carbon gradient protection layer (F-doped carbon rich in the top side and LiF rich in the bottom side) on lithium metal anode by one-step in-situ reaction of molten Li with polytetrafluoroethylene (PTFE). The abundant strong polar C-F bonds in the upper carbon can not only act as Li⁺ capture site to pre-uniform Li⁺ flux but also regulate the electron configuration of LiF to make Li⁺ quasi-spontaneously diffuse from carbon to LiF surface, avoiding the strong Li⁺ adhesion induced Li aggregation. For the LiF, it can behave as fast Li⁺ conductor, homogenize the nucleation sites on lithium as well as ensure firm connection with lithium. As a result, this well-designed protection layer restricts Li deposition under the protection layer/Li interface and endows Li metal anode with dendrite-free plating/stripping and anticorrosion behavior both in ether-based and carbonate ester-based electrolytes without the requirement of any additives. Even applied the protected Li anodes in Li-O₂ batteries, its superiority can still maintain, making the cell achieve stable cycling performance (180 cycles). This cheap and scalable method illustrates fresh insight towards protection of other metal anodes for a wide range of metal based batteries.

The energy densities of current commercial Li-ion batteries (LIBs) are approaching their achievable limit and restrict the rapid development of electric vehicles and smart grid storage.¹⁻⁶ To this end, Li-O₂ battery with ultrahigh theoretical energy density (~3500 Wh kg⁻¹) increasingly draws the scientists' attention and has been regarded as a promising next-generation energy storage system to substitute LIBs.⁷⁻⁹ However, the Li-O₂ battery confronts with plenty of challenges, such as electrolyte decomposition, cathode failure and anode degradation.¹⁰⁻¹² In the past decade, most of the efforts have been devoted to improve the stability and effectiveness of the electrolyte and cathode, while the importance of the lithium anode protection has long been ignored, making the long-term operation of Li-O₂ battery become impossible. Since lithium possesses the highest theoretical specific capacity (3860 mAh g⁻¹) and lowest redox potential (-3.04 V versus standard hydrogen electrode), it is irreplaceable and also the only candidate anode in enabling Li-O₂ battery to deliver the maximum energy density.¹³⁻¹⁵ Nevertheless, the highly active nature of lithium and the uncontrollable lithium dendrite growth during cycling will constantly expose new lithium and continuously react with the electrolyte and "contaminants" (H₂O, O₂, strong oxidizing reaction intermediates) in Li-O₂ batteries, causing lithium experiences serious corrosion and quick exhaustion, thus severely deteriorating the cycling stability of Li-O₂ batteries and limiting their practical applications.¹⁶⁻¹⁹ Therefore, except optimization of the electrolyte and cathode, it is urgent and crucial to resolve the Li anode associated issues so as to further improve the electrochemical performance of Li-O₂ batteries.

It has been demonstrated that designing 3D porous lithium host is an effective method to prevent lithium dendrite growth in LIBs.²⁰⁻²¹ However, unlike the close and non-gas involving system of LIBs, the high specific surface area of the 3D host will make lithium expose more corrosion reaction sites in the semi-open Li-O₂ batteries, consequently accelerating the consumption of active lithium and battery failure. To avoid this high surface area induced adverse effects, surface modification of the bare lithium sheet is a powerful solution. Among the various strategies used to modify the lithium surface, electrolyte regulation has been widely adopted to build stable SEI film on lithium for inhibiting dendrite growth. For example, the electrolyte regulation can facilitate the formation of LiF-riched SEI layer, which is effective to restrict dendrite growth and parasitic side reactions.²² Despite efficient, the formation of the SEI film is usually accompanied with the decomposition of the electrolyte solvent, which makes the SEI compose of multiple components with diverse Li⁺ conductivities, consequently, inducing different lithium plating/stripping behaviors at different areas and eventually SEI rupture, that is, this method will become invalid in the long run. In contrast, directly constructing artificial protection layer on lithium can avert this disadvantage, because the layer composition can be accurately designed and controlled.^{11, 16} An ideal artificial protection layer should simultaneously possesses the functions of homogenizing the Li⁺ flux at the electrode/electrolyte interface and enabling fast Li⁺ diffusion. Previous results revealed that LiF could act as a main effective component in the protection layer for inhibiting lithium dendrite growth because of the multifunctional protection effects it brought. The high interfacial

energy and low Li^+ surface diffusion barrier of LiF can guide uniform lithium deposition and reduce uncontrollable dendrite growth,²² while its large bandgap (13.6 eV) can assist to block electron tunneling through the protection layer, which is beneficial for minimizing the occurrence of corrosion reactions.²³ Besides, LiF also has a wide electrochemical stability window and a high shear modulus (55.1 GPa),²⁴⁻²⁵ avoiding the high voltage induced decomposition and lithium dendrite caused protection layer breakage. At present, the only limitation of LiF to be a prospective artificial protection layer is its weak adsorption ability to Li^+ , which can not homogenize surface Li^+ flux, as a result, there is a possibility leading to non-uniform Li deposition. For homogenizing the surface Li^+ flux, carbon based materials have unique advantages due to their adjustable electronic structure by heteroatom doping.²⁶⁻²⁸ For example, the introduction of N-containing function groups into the graphene can increase its binding energy to Li^+ , so that pre-uniforming the Li^+ flux before deposition.²¹ Moreover, carbon materials can also work as physical barrier to retard corrosion reactions between lithium, electrolyte and “contaminants”.²⁹⁻³¹ However, it should be noted that the Li^+ binder energies of the polar functional groups in the carbon materials are usually too strong that renders the Li^+ directly get an e^- and deposit on the carbon surface rather than diffuse through the carbon layer to reach the lithium surface. This newly deposited lithium will expose to the electrolyte and “contaminants” again and experience serious corrosion. To date, there is no artificial protection layer that can homogenize the Li^+ flux while allowing fast Li^+ diffusion. If we can combine the homogenizing Li^+ flux function of carbon

materials with the fast Li^+ diffusion ability of LiF together to make an integrated protection layer, the lithium associated issues in Li-O₂ batteries will be undoubtedly resolved.

With this in mind, herein, we designed an in-situ one-step reaction between molten Li and polytetrafluoroethylene (PTFE) for constructing a multifunctional complementary LiF/F-doped carbon gradient protection layer that firmly coated on lithium anode surface. The upper rich F-doped carbon can act as Li^+ capturing sites to pre-uniform Li^+ distribution and regulate the electron configuration of LiF to increase its binding energy to Li^+ and assist Li^+ almost spontaneously migrate from the carbon to the Li^+ conductive LiF with lithium only deposited on the protection layer/Li interface (**Scheme 1**). This protection layer integrates the high Li^+ adsorption surface and fast Li^+ diffusion bulk together, as a consequence, it enables dendrite-free lithium plating/stripping with a lower nucleation overpotential, guarantees a stable electrode/electrolyte interface, and facilitates faster electrochemical and mass transport kinetics in both ether-based and carbonate ester-based electrolytes. With these benefits as well as the corrosion-resistant ability, the protected lithium anode prolongs the lifetime of Li-O₂ battery to 180 cycles, more than two times that of the cell using bare lithium anode (78 cycles).

As schematically illustrated in **Figure 1a**, a dual-phase LiF/F-doped carbon protection layer with abundant strong polar C-F bonds in the upper side can be quickly and easily obtained via in-situ one-step reaction between

polytetrafluoroethylene (PTFE) micro powders and lithium sheet. For convenience, hereinafter, the abbreviation “BL” stands for bare lithium, “PTL” refers to the lithium metal anode after protection and “PT layer” stands for the as-prepared protection layer. Under argon atmosphere at 300 °C, the molten lithium sheet reacts with PTFE micro powders to generate two phases as equation 1 indicated — Li atom bonds with F atom to produce LiF and the rest C atom will form carbon (Figure 1b). To demonstrate the morphology and chemistry composition of the PT layer, scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Raman spectra were employed. It can be seen from Figure 1c and 1d that the as-prepared black color PT layer is seamlessly connected to the lithium sheets and displays a uniform surface morphology with a thickness about 20 μm . As expected, the Raman spectrum (Figure 1e) verifies the existence of carbon and the LiF phase in the XRD curves (Figure 1f and Figure S1) confirms the formation of LiF in the PT layer. These are in accord with the proposed reaction equation. In addition, the F 1s XPS spectra reveals that the carbon is functionalized with F element and the content of F-doped C decreases as the increase of depth, while the LiF exhibits opposite trend, indicating the richness of the F-doped carbon in the top side and the LiF in the bottom side of the PT layer (Figure 1g). It is worth mentioning that the strong polar electron-rich C-F bonds in the F-doped carbon can perform as effective Lewis base sites to adsorb Lewis acidic Li^+ and homogenize the Li^+ flux (Figure 1h).³²

With the successful synthesis of PT layer, we then evaluated the nucleation energy barrier of lithium on the PTL by checking the Li nucleation overpotential during lithium deposition process. For comparison, the same lithium source was used to deposit lithium onto the BL and PTL in carbonate ester-based electrolyte. Generally, the nucleation overpotential (μ_n) and the plateau overpotential (μ_p) are related to the energy barrier of heterogeneous nucleation process and mass-transfer process,³³ respectively. As indicated in **Figure 2a**, for BL, the voltage drops to -0.227 V at the initial stage of nucleation and then reaches a plateau at -0.1046 V under a current density of 3 mA cm⁻². By contrast, the voltage dip on PTL is only -0.1562 V and stabilizes at -0.0794 V during subsequent lithium growth process (Figure 2b). Even under a higher current density of 5 mA cm⁻², the μ_n (0.1302 V) and μ_p (0.1276 V) on PTL are still much lower than the μ_n (0.1801 V) and μ_p (0.1406 V) on BL (Figure S2). Besides, lower μ_n (0.0057 V) and μ_p (0.0321 V) are also achieved on PTL with ether-based electrolyte (Figure S3). These obvious reductions of μ_n and μ_p in both the carbonate ester-based and ether-based electrolytes can be explained by the reduced energy barrier of lithium nucleation and growth steps with the assistance of PT layer.

Besides the nucleation and growth overpotentials, the morphology of the plated lithium is also of vital importance. Here, SEM and in-situ optical microscopy were combined to investigate the lithium plating behavior on the BL and PTL. As shown in Figure 2c, after depositing 2 mAh cm⁻² of lithium in carbonate ester-based electrolyte,

the surface of BL exhibits obvious dendrite growth with a chaotic structure. For PTL, it is clear that the PT layer well maintains its original morphology without lithium plating induced change (Figure S4), indicating that the Li^+ passes through the PT layer and deposits on the PT layer/lithium interface. To obtain an intuitive observation for this, we then checked the morphology of the PTL after peeling off the PT layer. Different from the lithium dendrite growth on BL, the deposited lithium on PTL demonstrates a dendrite-free morphology with a much more uniform and smooth surface (Figure 2d), revealing that the PT layer can indeed effectively prevent lithium dendrite growth. This can be further confirmed by using in-situ optical microscope to monitor the morphology evolution of the BL and PTL during lithium plating process (Figure 2e-j). Just after 30 min of deposition, the dendrite begins to appear at the cross section of BL and then serious inhomogeneous lithium depositions aggregate on the BL surface as the deposition time prolongs (Figure 2e-g). In contrast, the PTL displays pretty smooth morphology with no observable dendrite growth and inconspicuous volume expansion during the whole plating process, indicating the lithium deposited under the PT layer and its guided uniform plating on the whole electrode (Figure 2h-j). As for the plating behavior in ether-based electrolyte, similar phenomenon of homogeneous lithium deposition and less volume expansion can be observed for the PTL (Figure S5-S7), demonstrating the satisfying dendrite suppression effect of PT layer in both ether-based and carbonate ester-based electrolytes.

Considering that the charge transfer and Li^+ diffusion kinetics of the protection layer play a key role in obtaining a satisfying performance, time-dependence electrochemical impedance spectra (EIS) were employed to compare the impedance of BL and PTL based Li/Li symmetrical batteries with carbonate ester-based electrolyte. In the EIS plot, the high frequency semi-circle, mid-frequency semi-circle and low frequency region are associated with interfacial resistance (R_{int}), charge transfer resistance (R_{ct}) and Li^+ diffusion process,³⁴ respectively. The values of the R_{int} and R_{ct} for BL or PTL based symmetrical batteries can be obtained by fitting the EIS curves to the equivalent circuit (**Figure 3a-c**). It is clear that the PTL based battery exhibits low R_{int} (4.203 Ω) and R_{ct} (3.108 Ω) values, while the R_{int} and R_{ct} for BL based battery are very large, about 6.8 and 7.7 times of those of PTL based battery (Figure 3c), indicating that the PT layer can enable high ion transport and fast charge transfer kinetics. Even after resting for 7 days, different from the significant increase of the R_{int} (57.15 Ω) and R_{ct} (46 Ω) for BL based battery, the R_{int} (5.659 Ω) and R_{ct} (9.024 Ω) for PTL based battery only experience a small increase and still maintain a low value, revealing that the PT layer can facilitate a stable electrode/electrolyte interface with much reduced parasitic reactions.³⁵⁻³⁶ The other thing to note is that the low frequency range slope of the PTL based battery is also much higher than that of BL based battery, demonstrating an improved Li^+ diffusion characteristics.¹⁶ Moreover, in ether-based electrolyte, the PTL based battery still exhibits much lower impedance with high ion transport and fast charge transfer kinetics both before and after storing for 9 days (Figure S8).

The long-term stability of the BL and PTL were then evaluated by conducting galvanostatic plating/stripping cycling tests on BL and PTL based Li/Li symmetrical batteries. In carbonate ester-based electrolyte, the symmetrical batteries with PTL exhibit lower overpotentials and longer cycling stabilities of about 1400 and 800 hours than those of the batteries with BL under the current densities of 0.5 and 1 mA cm⁻² (Figure S9, S10). Even at a high current density of 3 mA cm⁻², the battery with PTL can still run for 350 cycles with less polarization compared with the battery with BL (Figure S11). The excellent cycling stability of the PTL based batteries can be attributed to the PT layer enabled dendrite-free lithium plating/stripping and stable electrode/electrolyte interface, which make the PTL based battery exhibit a much lower impedance than the BL based battery after cycling for 70 cycles under 3 mA cm⁻² (Figure S12). Importantly, the protection effects of the PT layer on lithium anode are more obvious in ether-based electrolyte, which prolong the cycling stability from 235 hours to 1000 hours at a lower current density of 0.1 mA cm⁻² (Figure 3d). Increased the current density to 0.4 mA cm⁻², the battery with PTL still shows nearly three times longer cycle life than that of BL based battery (Figure 3e). The short lifetime of the BL based battery is due to the continuous dendrite growth induced repeated damage and reestablishment of the SEI film, which produces a thick SEI film, and thus a high R_{int} up to 10375 Ω after cycling for 235 hours (Figure 3f, g). Such a high R_{int} makes the ion transport become very difficult and causes the sudden death of the battery. Whereas, the PT layer endowed stable electrode/electrolyte interface makes the PTL based battery exhibit a 61 fold lower R_{int} than that of the BL based

battery, as a result, significantly boosting the cycling stability of the PTL based battery.

In order to further verify the advantage of the PTL, exchange current density (j^0), another important electrochemical kinetics parameter, was checked. Since j^0 is proportional to the gradient of the cyclic voltammetry (CV) curves, the larger gradient of the CV curves of the PTL based battery indicates it has a higher j^0 in both ether-based and carbonate ester-based electrolytes (Figure 3h and S13), meaning that the lithium plating/stripping process can be proceeded at a higher speed and a lower polarization, which is consistent with the above mentioned small impedance and lithium plating/stripping overpotential of the PTL based battery.³⁴⁻³⁶ The higher j^0 confirms that the introduction of PT layer can accelerate the charge transfer and ion diffusion processes thus an enhanced Li plating/stripping kinetic.

To reveal the mechanism of the PT layer on regularizing the lithium deposition process, first-principle density functional theory-based (DFT) calculations were conducted to analyze the interactions between Li^+ and LiF, LiF/C or PT layer. The Li^+ adsorption energy and charge density distribution of PT layer, LiF/C and LiF are summarized in **Figure 4a**, 4b and S14, S15. Compared with LiF and carbon layer, the C-F bonds in the F doped carbon make it has the highest adsorption energy to Li^+ (-3.87 eV) and form negative charge centers, which can pre-uniform Lewis acid Li^+ and effectively assist to form homogeneous Li^+ flux for further deposition. Surprisingly, with the presence of F doped carbon, the Li^+ adsorption energy of LiF

is fifteen-fold higher than that of pure LiF (-4.99 vs. -0.33 eV), indicating that the F-doped carbon can change the electron configuration of LiF, so increase the affinity between Li^+ and LiF. Besides the Li^+ adsorption energy, the diffusion energy barrier of Li^+ should be also considered. If it is too high, it may introduce lithium accumulation. As shown in Figure 4c, the PT layer exhibits a greatly reduced Li^+ diffusion energy barrier, which is 3 eV lower than that of pure carbon, suggesting that Li^+ can almost self-diffusion in the PT layer by just overcoming a small energy barrier. The entire functional mechanism of the PT layer is schemed in Figure 4d and 4e. The Li^+ in the electrolyte is first homogeneously captured by the C-F bonds in the upper F-doped carbon layer, then nearly spontaneously diffuses to the surface of LiF, and finally overcomes 0.29 eV diffusion energy barrier to plate on lithium metal anode. This is in well agreement with the above experimental results, the stronger adsorption and lower diffusion barrier of Li^+ on PT layer effectively promote uniform Li^+ flux and smooth lithium deposition. The calculation results also demonstrate that the PT layer integrates the homogenizing Li^+ flux function of F-doped carbon and the fast Li^+ diffusion ability of LiF together as well as endows F-doped carbon and LiF with Li^+ quasi self-diffusion and strong Li adsorption capability.

In light of the ultrahigh energy density of Li-O₂ battery and its lack of stable lithium metal anode, we employed PTL to assemble Li-O₂ batteries to demonstrate its practical application ability. Figure S18 shows the CV curve of Li-O₂ battery with PTL. The cathodic and anodic peaks represent the typical O₂ reduction and evolution

reactions in Li-O₂ batteries, consisting with the reported literature.^{38, 39} Galvanostatic charge-discharge cycling test of Li-O₂ batteries with BL and PTL were then evaluated. As shown in **Figure 5a,b**, the Li-O₂ battery with PTL can achieve a long cycling stability of 180 cycles, much than two times of the battery with BL, which can only run 78 cycles under the same condition. This difference can be ascribed to the improved stability of the PT layer protected lithium metal anode.¹⁸⁻¹⁹ To confirm this, the morphology evolution of BL and PTL after multiple cycles has been compared. From Figure S19 we can see that, the PTL maintains the surface morphology just like the pristine condition after 50 cycles, revealing the good stability of the PT layer. For getting the morphology information of the lithium under PT layer, we peeled off the PT layer and exposed the lithium surface. As expected, the lithium under PT layer has a relative smooth surface without obvious dendrite growth and corrosion reaction induced morphology change (Figure 5c, d), indicating that the PT layer can inhibit lithium dendrite growth and isolating lithium from attacking by the rigorous environment in Li-O₂ batteries. Whereas, the BL exhibits serious corrosion morphology with a lot of sags and crests (Figure 5f, g), which can be regarded as the culprit of battery failure. To further reveal the protection effect of PT layer, XRD was used to characterize the composition of the cycled lithium anodes.³⁷ Figure 5e and 5h shows that there is almost no observable LiOH peaks on the PTL after 50 cycles (Figure S20), while the LiOH peaks on the cycled BL are quite strong, implying that the PT layer can endow a satisfying anticorrosion effect on the lithium anode. We even use the cycled BL and PTL to assemble symmetrical batteries and find that the

PTL based battery displays a much lower impedance than that of the BL based battery (Figure S22), again verifying the much improved stability of the lithium anode with the assistance of PT layer. Moreover, the discharged cathode in the PTL based Li-O₂ battery is also evaluated and it shows typical toroid-like crystalline Li₂O₂ (Figure S23), which is consistence with previously literatures.³⁸⁻³⁹ All these results demonstrate that the PTL can effectively improve the cycling stability of Li-O₂ batteries without affecting the reaction mechanism.

In summary, a one-step in-situ reaction between lithium sheet and PTFE micro powders has been designed to generate a multifunctional complementary LiF/F-doped carbon gradient protection layer that seamlessly coated on lithium metal anode, thus resolving the long-lasting dendrite growth and corrosion challenges of lithium anodes in Li-O₂ batteries and enhancing the electrochemical performance. Revealed by first-principle calculations, this gradient protection layer integrates the homogenizing Li⁺ flux function of F-doped carbon and the fast Li⁺ diffusion ability of LiF together, meanwhile, the two phases can complementary each other by decreasing the Li⁺ diffusion barrier of F-doped carbon and increasing the Li⁺ adsorption energy of LiF. As a result, this protection layer enables faster charge/mass transfer kinetics and dendrite free lithium plating/stripping at lower nucleation/growth energy barriers in symmetrical batteries with both ether-based and carbonate ester-based electrolytes. Furthermore, a successful practical application of the PTL has been realized in Li-O₂ batteries, in which the fatal dendrite growth and parasitic reactions on lithium metal

anode are greatly remitted and the cycling stability is significantly improved (180 cycles). This unique anode protection design strategy opens a new avenue for practical study of alkali metal anodes in metal based batteries.

Supporting Information

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

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Scheme 1. Schematic illustration of the design guideline of PTL. (Here we use 15_7 helix configuration of PTFE to stand for the PTFE molecule)⁴⁰

Figure 1. Schematic illustrations of the (a) film formation reaction and (b) preparation process of PTL. (c) Surface SEM image of PTL. Inset is the optical image of PTL. (d) Cross-section SEM image of PTL. (e) Raman spectrum and (f) XRD curves of PTL. (g) F 1s XPS spectra of PTL at different depth. (h) Dipole moment of C-C, C-N, C-O and C-F.

Figure 2. Voltage-capacity curves of Li plating on (a) BL and (b) PTL at a current density of 3 mA cm^{-2} . SEM images and corresponding schematic illustrations of (c) BL and (d) PTL after plating with 2 mAh cm^{-2} of Li. In-situ optical microscopy observation of Li plating behavior on (e-g) BL and (h-j) PTL after (e, h) 0, (f, i) 30 and (g, j) 60 minutes of deposition.

Figure 3. EIS curves of Li/Li symmetrical batteries with (a) BL and (b) PTL as electrodes before and after staying for 7 days and (c) corresponding comparison of R_{int} and R_{ct} impedance values. Long-term cycling performance of BL and PTL based Li/Li symmetrical batteries with 1 M LiCF₃SO₃ in TEGDME electrolyte at current densities of (d) 0.1 mA cm⁻² and (e) 0.4 mA cm⁻². (f) EIS curves of Li/Li symmetrical batteries with BL and PTL after cycling for 235 hours at a current density of 0.1 mA cm⁻², and (g) corresponding R_{int} value comparison. (h) CV curves of Li/Li symmetrical batteries with BL and PTL electrodes scanned at a fixed rate of 1 mV s⁻¹.

Figure 4. (a) Adsorption energies of Li^+ on different species. (b) Charge density difference plot of a Li^+ on the F doped carbon layer in the PT layer. (c) Li^+ diffusion energy barriers of different species. Li^+ diffusion path through (d) F doped carbon layer and (e) LiF (100) facet in the PT layer. Li, F and C elements are represented by green, light purple and brown spheres, respectively. The migrating Li^+ is represented by a cyan sphere.

Figure 5. Long-term cycling performance of Li-O₂ batteries with (a) BL and (b) PTL as anodes. SEM images of PTL after cycling in Li-O₂ batteries for (c) 20 cycles and (d) 50 cycles, (e) XRD patterns of PTL after cycling in Li-O₂ batteries for 50 cycles. SEM images of BL after cycling in Li-O₂ batteries for (f) 20 cycles and (g) 50 cycles. (h) XRD patterns of BL after cycling in Li-O₂ batteries for 50 cycles.