

Article

A High-Performance Li-O₂/Air Battery System with Dual Redox Mediators in the Hydrophobic Ionic Liquid-Based Gel Polymer Electrolyte

Ningning Feng ^{1,*}, Chaoqiang Wang ², Jing Wang ³, Yang Lin ¹ and Gang Yang ^{1,*} 

¹ Suzhou Key Laboratory of Functional Ceramic Materials Department, Changshu Institute of Technology, Changshu 215500, China

² School of Space and Environment, Beijing University of Aeronautics and Astronautics, Beijing 102206, China

³ Engineering Research Center of Advanced Aluminium Matrix Materials of Guangxi Province, Baise University, Baise 533000, China

* Correspondence: nningfeng89@cslg.edu.cn (N.F.); gyang@cslg.edu.cn (G.Y.)

Abstract: Lithium–oxygen (Li–O₂) batteries have captured worldwide attention owing to their highest theoretical specific energy density. However, this promising system still suffers from huge discharge/charge overpotentials and poor cycling stability, which are related to the leakage/volatilization of organic liquid electrolytes and the inefficiency of solid catalysts. A mixing ionic liquid-based gel polymer electrolyte (IL-GPE)-based Li–O₂ battery, consisting of a 20 mM 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) 40 mM N-methylphenothiazine (MPT)-containing IL-GPE and a single-walled carbon nanotube cathode, is designed for the first time here. This unique dual redox mediators-based GPE, which contains a polymer matrix immersed with mixed ionic liquid electrolyte, provides a proper ionic conductivity (0.48 mS cm^{−1}) and effective protection for lithium anode. In addition, DBBQ, as the catalyst for an oxygen reduction reaction, can support the growth of discharge products through the solution–phase pathway. Simultaneously, MPT, as the catalyst for an oxygen evolution reaction, can decompose Li₂O₂ at low charge overpotentials. Hence, the DBBQ-MPT-IL-GPE-based Li–O₂ battery can operate for 100 cycles with lower charge/discharge overpotentials. This investigation may offer a promising method to realize high-efficiency Li–O₂/air batteries.

Keywords: Li–O₂ batteries; dual redox mediator; DBBQ; MPT; ionic liquid; gel polymer electrolyte



Citation: Feng, N.; Wang, C.; Wang, J.; Lin, Y.; Yang, G. A High-Performance Li–O₂/Air Battery System with Dual Redox Mediators in the Hydrophobic Ionic Liquid-Based Gel Polymer Electrolyte. *Batteries* **2023**, *9*, 243. <https://doi.org/10.3390/batteries9050243>

Academic Editors: Xijun Xu, Zhuosen Wang, Ling Kang and David Zitoun

Received: 7 February 2023

Revised: 11 April 2023

Accepted: 23 April 2023

Published: 25 April 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Rechargeable aprotic lithium–oxygen (Li–O₂) batteries have been highlighted as a promising alternative technology for large-scale electric energy storage in recent years due to their highest theoretical specific energy density of 3450 Wh kg^{−1} [1–7]. However, the practical applications of this system are still constrained by substantial issues, such as high charge–discharge overpotentials, serious electrolyte decomposition, and short cell lifespan [8–11]. Moreover, a large number of experimental results have demonstrated that most of these problems are caused by the insulating nature of the discharge product Li₂O₂ and the sluggish kinetics of the oxygen reduction/evolution reactions (ORR/OER) [5,12].

In an aprotic Li–O₂ battery, during the discharging process, O₂ is first reduced to O₂[−] or LiO₂ intermediate [13], according to Equation (1):



Then, LiO₂ is further reduced or disproportionated to the insoluble product lithium peroxide (Li₂O₂), according to Equation (2) or Equation (3):



or



During charge, the discharge product Li_2O_2 can be reversibly decomposed into Li^+ and O_2 . Moreover, the ORR process is strongly related to the electrolyte's properties of the donor/acceptor number [13–15]. In electrolytes with high donor number, for instance, dimethyl sulfoxide (DMSO) [15], the longer lifetime of the $\text{O}_2^-/\text{LiO}_2$ intermediate can promote the growth of Li_2O_2 particles via the solution pathway, resulting in a high discharge capacity. However, this solution mechanism usually aggravates the chemical reactivity of $\text{O}_2^-/\text{LiO}_2$ with the electrolyte [12]. Enhanced stability can be achieved in electrolytes with low donor numbers, such as ethers [15]. However, in these conditions, LiO_2 quickly is disproportionate to Li_2O_2 film on the electrode surface, directly resulting in the passivating of the cathode and premature cell death [13]. Some byproducts, such as carbonates, could be identified on cycling in Li- O_2 batteries with all ether-based electrolytes, owing to the interactions of superoxide radicals or singlet O_2 and the solvents [8,16]. Thus, screening the stable electrolytes against superoxide radicals remains one of the most pressing challenges in high-performance Li- O_2 batteries [17]. Recently, ionic liquids (ILs) have been employed as alternative electrolytes to improve the cycling performance of Li- O_2 batteries because of their advantages over conventional liquid aprotic electrolytes, such as lower volatility, higher hydrophobicity, wider potential window, and more stability against Li anodes and superoxides [5,7,18]. Nevertheless, those Li- O_2 batteries with ILs usually exhibited poor rate capability due to the relatively low conductivity of ILs [19]. Subsequently, some scientists explored a novel type of mixing solvents as the electrolyte for Li- O_2 batteries [18,20–23] and enhanced ORR/OER kinetics were obtained. For instance, Scrosati B. et al. significantly reduced the ORR/OER overpotentials and promoted the reversibility of Li- O_2 batteries by mixing 1-butyl-1-methyl pyrrolidinium bis(trifluoromethanesulfonyl)imide ($\text{PYR}_{14}\text{TFSI}$) and tetraethylene glycol dimethyl ether (TEGDME) as the electrolyte [20]. However, almost all the above IL-based Li- O_2 batteries are operated with an open system, which aggravates the risks of electrolyte leakage and volatility. To mitigate these problems, Lee et al. designed a gel polymer electrolyte (GPE) [24], which contained $\text{PYR}_{14}\text{TFSI}$, PVDF-HFP, and LiTFSI . Additionally, the cell showed enhanced capacity and cycling performance. Hence, developing the mixed ionic liquid-based GPE is supposed to be the most effective strategy for stable electrolytes in Li- O_2 batteries.

Another formidable challenge is the large charge–discharge overpotentials arising from the sluggish kinetics of ORR/OER and the insulating nature of Li_2O_2 . The severe charge–discharge polarizations have deteriorated both the round-trip efficiency and cycling performance of Li- O_2 batteries. Even the higher charging potential usually impairs the electrolyte stability. Therefore, various catalysts have been adopted to reduce the charge/discharge voltage gap in Li- O_2 batteries so far [5–8,10]. Among them, soluble redox mediators (RMs) have been testified as the fascinating candidate for lowering the ORR or OER overpotentials through the liquid–solid interfacial mechanism, such as 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) [13,25–27], tetrathiafulvalene (TTF) [28,29], 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) [30] and so on. These RMs could act as electron carriers either to reduce O_2 forming Li_2O_2 or to oxidize Li_2O_2 releasing oxygen. For example, DBBQ was reported to generate a new complex intermediate during the discharge process, thus facilitating the solution-phase growth of Li_2O_2 and increasing the cell capacity [13]. TEMPO has been demonstrated to promote the decomposition of Li_2O_2 on charging, thus reducing the charging potentials [30]. Therefore, considering the synergistic effects of RMs_{dis} and RMs_{chr} on ORR and OER, Gao et al. have utilized DBBQ and TEMPO simultaneously as dual RMs into the liquid electrolyte-based Li- O_2 battery to form and decompose the discharge product Li_2O_2 in the solution at low charge/discharge overpotentials [25]. However, the redox shuttle problem involved in the liquid electrolyte has impaired the cycling performance of the Li- O_2 cell. As a result, the GPE with dual RMs seems to be the rational choice for high-efficiency Li- O_2 batteries. Unfortunately, this issue has not been reported thus far.

Herein, we synthesized a mixed IL-based GPE containing dual RMs (20 mM DBBQ for a discharge and 40 mM N-methylphenothiazine (MPT) for a charge) by a simple ultraviolet (UV)-crosslinking method, which integrated with single-walled carbon nanotube (SWCNT) cathode to fabricate a Li-O₂ battery. DBBQ, as an ORR mediator, is supposed to accelerate the formation of sLi₂O₂ through the solution-phase mechanism [13]. Additionally, MPT has been demonstrated to be used as an effective RM for the OER on a charge, according to the previous work [31,32]. These dual RMs showed synergistic effects on ORR/OER by increasing capacity and lowering charge overpotentials without any interference with each other. Moreover, this dual RMs-GPE, consisting of a polymer matrix immersed with an ionic liquid electrolyte, possesses a good ion conductivity of 0.48 mS cm⁻¹ at room temperature. The hydrophobic GPE with physical blockage and chemical interaction can effectively mitigate the chemical activity of Li anode and RM⁺ or H₂O. Therefore, the dual RMs-IL-GPE-based Li-O₂/Air batteries with SWCNT cathodes exhibit high capacity, low overpotentials, high energy efficiency, and a long cycle life.

2. Materials and Methods

2.1. Materials

The materials used were lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, Aldrich, St. Louis, MO, USA, 96%), poly vinylidene fluoride-hexafluoro propylene (PVDF-HFP, average Mn of ~130,000, Aldrich), tetraethylene glycol dimethyl ether (TEGDME, Aldrich), N-methyl-2-pyrrolidinone (NMP, Aladdin), Trimethylolpropane ethoxylate triacrylate (TMPET, average Mn of ~428, Aldrich), N-methyl-N-propylpiperidiniumbis(trifluoromethanesulfonyl)imide (PP13TFSI, Lanzhou Greenchem ILs, Lanzhou, China), 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP, 97%, Aldrich), single-walled carbon nanotube (SWCNT, Aladdin), carbon paper (Hesen Corp., Shanghai, China), 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ, Aldrich), and N-methylphenothiazine (MPT, Alfa Aesar, Haverhill, MA, USA).

2.2. Preparation of IL-Based Gel Polymer Electrolyte (IL-GPE)

DBBQ-MPT-IL-GPE Preparation: PVDF-HFP/NMP (mass ratio of 1:4) was denoted as Solution A. A solution of 1 M LiTFSI/PP13TFSI + TEGDME (volume ratio: 3:1) containing 20 mM DBBQ and 40 mM MPT was denoted as Solution B, and the photo-initiator HMPP/TMPET (mass ratio: 0.01:3) was denoted as Solution C. Next, the precursor solution was held by mixing Solution A, B, and C (weight ratio of 5:4:3). Then, it was cast on a polytetrafluoroethylene (PTFE) plate as the support for the polymerization process. At last, the solidified DBBQ-MPT-IL-GPE was formed after UV irradiation (wavelength of 365 nm) for 30 s in an argon-filled glovebox. The thickness of the as-prepared IL-GPE was about 1.5 mm. In addition, the preparation procedure of pure IL-GPE without dual RMs is identical to the above preparation steps. All the IL-GPE films are punched into a disk with an 18 mm diameter.

2.3. Assembling the Li-O₂ Batteries and Electrochemical Measurement

The O₂ cathode was obtained as follows. Cathode active material (SWCNT, 85 wt%) and a polyvinylidene difluoride binder (PVDFs, 15 wt%) were uniformly mixed in an N-methyl-2-pyrrolidone (NMP) solution and then stirred for 12 h. Next, the slurry was coated on carbon paper (12 mm diameter) as the current collector. All the electrodes were dried for 12 h at 120 °C under vacuum to remove residual solvent. The mass loading of the electrode was about 0.1~0.12 mg. Then, the DBBQ-MPT-IL-GPE disk (18 mm in diameter) was covered on the lithium anode. The obtained Li/DBBQ-MPT-IL-GPE/SWCNT electrode was subsequently sealed into a homemade Swagelok cell, which had a 0.8 cm² hole on the cathode top cover to allow the O₂ gas to enter. All the batteries were assembled in an argon-filled glove box (<0.1 ppm H₂O; <0.1 ppm O₂).

Galvanostatic discharge-charge cycling tests were performed on a battery testing system (LAND 2001A Wuhan Jinnuo Corp., Wuhan, China). Cyclic voltammetry (CV) measurements were carried out on an electrochemical workstation (CHI 760E, Chenhua

Corp., Shanghai, China). All the electrochemical tests were performed at 25 °C and in a chamber, which is filled with oxygen gas or simulated air with different humidity.

The in situ differential electrochemical mass spectrometry (DEMS) system (Shanghai LingLu Instrument Corp., Ltd., Shanghai, China) adopts a custom-built Swagelok cell designed to guarantee excellent hermetic integrity. Herein, we have traced the evolution of gaseous O₂ ($m/z = 32$) and CO₂ ($m/z = 44$) during charging. The tested cell was discharged to a fixed capacity of 0.5 mAh under an O₂ atmosphere. Before the charge test, the DEMS system was also purged with an argon gas stream for 4 h to calibrate the background for O₂ content. Online gas analysis was accomplished using a quadrupole mass spectrometer to quantify the O₂ and CO₂ that evolved during the charging process.

2.4. Material Characterization

The morphologies of as-prepared IL-GPE were characterized using field-emission scanning electron microscopy (SEM, FE-SEM S-4800). The thermogravimetric analysis (TGA) was implemented using a Netzsch instrument under the air flow with a heating rate of 10 °C min^{−1}. Fourier transform infrared (FT-IR) spectra were performed on a Nicolet 6700 spectrometer. XPS measurements were carried out on an XSAM800 Ultra spectrometer. X-ray diffraction (XRD) was applied to characterize the pristine, discharged, and recharged electrodes on a Bruker D8 Focus Power X-ray diffractometer with Cu K α radiation. The scanning rate was set as 4° min^{−1} with a step size of 0.02°. In this test, the discharged or recharged electrodes were taken out from the homemade Swagelok cell, then washed with dimethyl ether (DME) solvent and dried for 12 h at 80 °C under vacuum. During analysis, the dried electrodes were covered with a polyethylene film to prevent air exposure.

3. Results and Discussion

3.1. Characterization of Polymer Electrolyte

To alleviate those problems related to the liquid electrolytes, the pure IL-based GPE and IL-based incorporating with 20 mM DBBQ and 40 mM MPT were prepared through the UV-curable method. In our experiment, PVDF-HFP was utilized as the polymer matrix of DBBQ-MPT-IL-GPE because of its superior solubility and higher electrochemical stability toward O₂[−] than that of PVDF [33]. The surface morphology of this dual RMs-IL-based GPE was studied by the SEM image and digital photograph (Figure 1a,b). It can be observed from Figure 1a that the DBBQ-MPT-IL-GPE shows a tight and smooth surface, which facilitates close contact with the lithium anode and SWCNT cathode. Additionally, the Li-ion conductivity of this dual DBBQ-MPT-IL-GPE was also tested by EIS measurement and further compared with pure IL-GPE. The resistance of DBBQ-MPT-IL-GPE can be obtained from the Nyquist plot in Figure 1c. The calculated ion conductivity of DBBQ-MPT-IL-GPE is 0.48 mS cm^{−1}, which is higher than that of pure IL-GPE (0.2 mS cm^{−1}, Figure S1a, Supplementary Materials). Such relatively high ionic conductivity of DBBQ-MPT-IL-GPE provides the rapid transport of Li⁺ during the discharge/charge process. Meanwhile, the linear sweep voltammogram (LSV) was performed to examine the electrochemical stability of this dual RMs-IL-GPE. As illustrated in Figure 1d, the anodic peak at 3.75 V corresponds to the oxidation of MPT to MPT⁺ [32]. Except for this, there is no other oxidative decomposition of DBBQ-MPT-IL-GPE before 4.5 V (vs. Li⁺/Li). It indicates that the DBBQ-MPT-IL-GPE possesses a stable electrochemical window, which makes it the preferred choice for long-life Li-O₂ batteries. Furthermore, the thermal stability and the Li⁺ transference number of DBBQ-MPT-IL-GPE were also investigated (Figures S2 and S3, Supplementary Materials). The DBBQ-MPT-IL-GPE shows relatively high thermal stability below 100 °C without evident weight loss and a Li⁺ transport number of 0.71.

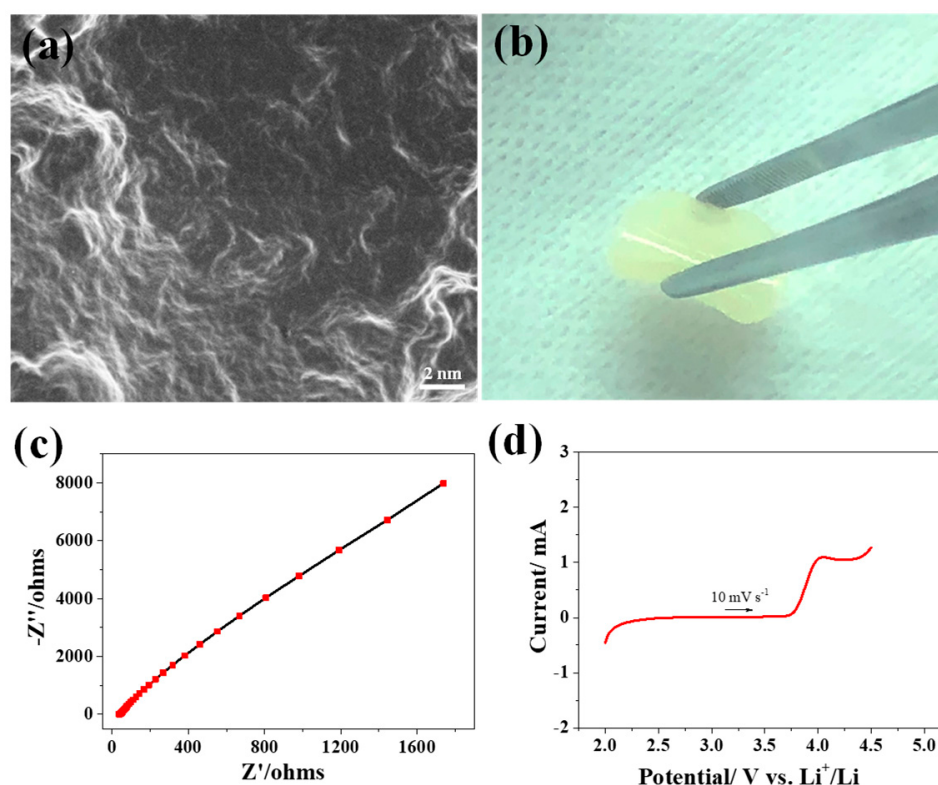


Figure 1. (a) SEM and (b) photographic images of DBBQMPT-IL-GPE. (c) EIS test of DBBQ-MPT-IL-GPE, two stainless steel meshes (SSM) are used with DBBQ-MPT-IL-GPE to form an SSM/IL-GPE/SSM symmetric cell, and the testing frequency range is 0.1 Hz to 100 KHz. (d) Linear sweep voltammetry (LSV) profile of DBBQ-MPT-IL-GPE, and the scan rate is 10 mV s^{−1}.

3.2. Electrochemical Performance of the GPE-Based Li-O₂ Batteries

In view of the above-superior properties, the Li-O₂ cells were assembled with SWCNT cathodes, DBBQ-MPT-IL-GPE or Pure IL-GPE electrolytes, and Li anodes. As shown in Figure 2a,b, the pure IL-GPE-based Li-O₂ battery rapidly decays and just exhibits an initial discharge capacity of 1541 mAh g^{−1}. After four cycles, its discharge capacity reduces to only 321 mAh g^{−1}. In stark contrast, the dual RMs-GPE-based Li-O₂ cell can maintain the capacity of 5000 mAh g^{−1} for 20 cycles with lower charge/discharge overpotentials. Meanwhile, we also investigated the effect of individual ORR or OER mediators on cell performance in Figure 2c,d. The IL-GPE Li-O₂ cell with only DBBQ displays a charge overpotential of about 1.04 V, which is lower than that of the pure IL-GPE-based cell. This result could be ascribed to the solution-grown discharge product Li₂O₂ induced by DBBQ, which has demonstrated that the oxidation of these solution-formed Li₂O₂ is lower than that of surface-grown Li₂O₂. Additionally, with the help of MPT as an OER mediator, the corresponding cells exhibit a much lower charging potential than that of the pure IL-GPE-based cell. While the dual RMs-IL-GPE-based Li-O₂ cell, using both DBBQ and MPT mediators, shows a lowest discharge–charge voltage gap of 1.02 V and a round-trip efficiency of 72%, indicating the synergic effects of DBBQ for ORR and MPT for OER without any interference. This is in accordance with the corresponding CV results (Figure S4, Supplementary Materials). For the IL-GPE-based Li-O₂ cell with dual RMs, DBBQ promotes the O₂ reduction at a cathodic potential of 3.0 V with a reduced polarization on discharging. On charging, MPT oxidizes into MPT⁺ at an anodic onset potential of 3.7 V, then MPT⁺ consumes and decomposes Li₂O₂ by a chemical reaction.

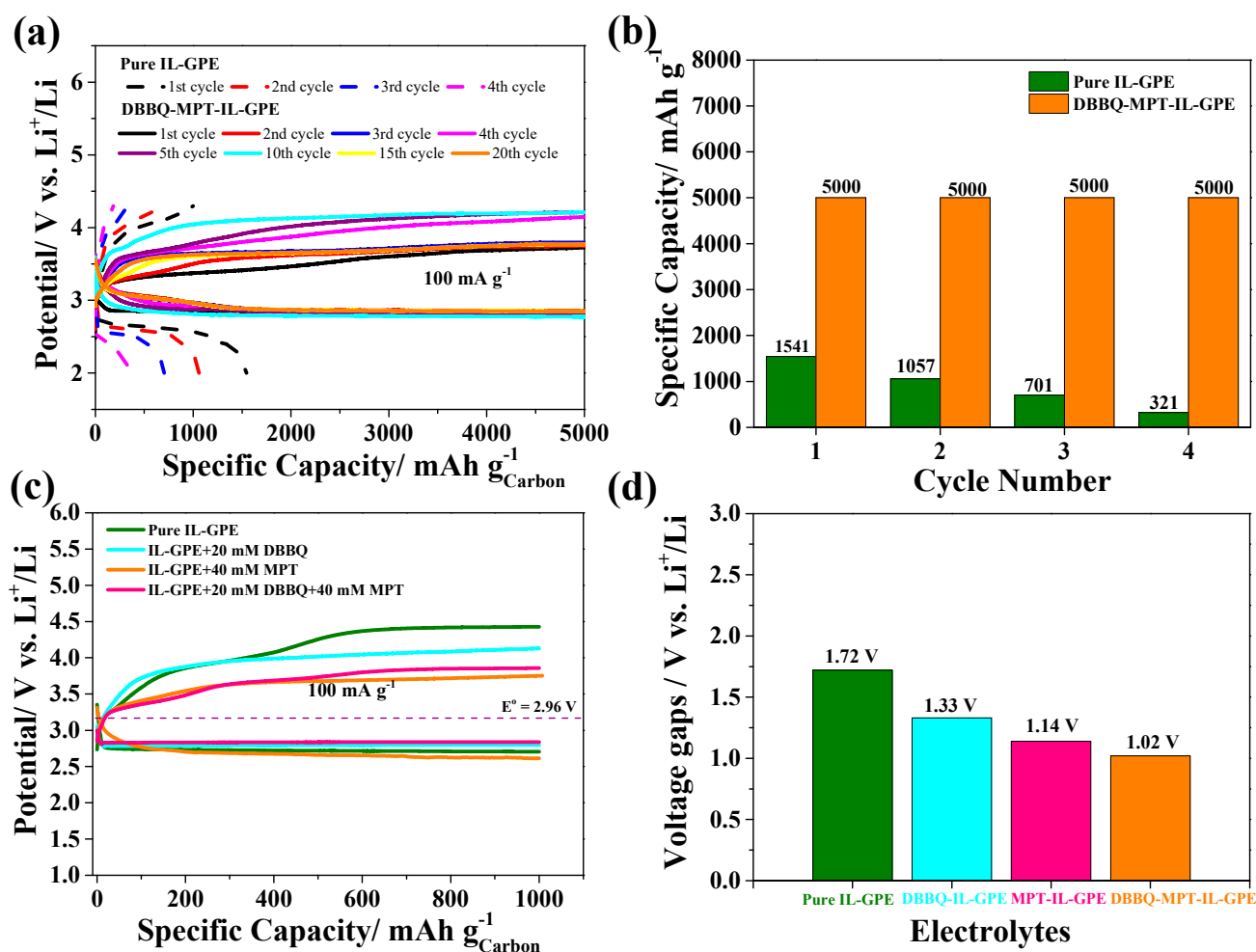


Figure 2. (a) Discharge/charge profiles of the Li-O₂ batteries using pure IL-GPE (dashed lines) and 20 mM DBBQ-40 mM MPT-IL-GPE (solid lines) at an applied current density of 100 mA g⁻¹. (b) The corresponding discharge-specific capacities of the pure IL-GPE and 20 mM DBBQ-40 mM MPT-IL-GPE-based Li-O₂ batteries at different cycle numbers. (c) Initial discharge-charge voltage profiles of the Li-O₂ batteries using different GPE at a fixed capacity of 1000 mAh g⁻¹ with a current density of 100 mA g⁻¹. (d) The corresponding discharge-charge voltage gaps for the Li-O₂ batteries using different GPEs.

The cycling performance of the Li-O₂ batteries with dual RMs-IL-GPE or pure IL-GPE was carried out under a current density of 100 mA g⁻¹ with a limited capacity of 1000 mAh g⁻¹. As depicted in Figure 3a, the discharge/charge voltage curves of the IL-GPE-based Li-O₂ cell with DBBQ and MPT mediators are relatively stable, except for the slightly raised charge overpotentials during 100 cycles. Moreover, the discharge terminal voltages of the dual RMs-IL-GPE-based Li-O₂ battery are almost constant at 2.75 V over 100 cycles, and the corresponding charging end voltages can keep at 4.2 V after 100 cycles (Figure 3b). It is noteworthy that the charging terminal potential increases to 3.75 V after the first five cycles due to the increase in the MPT⁺ concentration. These data of DBBQ-MPT-IL-GPE-based Li-O₂ batteries are much better than most of the previous reports (Table S1, Supplementary Materials), which demonstrate that the utility of dual RMs-IL-GPE improves the round-trip efficiency and cycling stability of corresponding Li-O₂ batteries. However, in the case of pure IL-GPE Li-O₂ battery, the discharge/charge voltage profiles are not reproducible after 35 cycles. Notably, its discharge end voltage of the 35th cycle suddenly decreases to 2.0 V. In addition, the charge terminal voltages are stable above 4.3 V during cycling, which is higher than that of the cells with DBBQ and MPT. Indeed, when these Li-O₂

batteries were discharged/charged at different rates of 200 and 500 mA g⁻¹ under the limited-capacity mode, respectively, it still can be found that the GPE-based Li-O₂ cells with DBBQ and MPT present a superior cycling stability than that of the cells without dual RMs (Figure S5, Supplementary Materials). Based on these above results, we can conclude that the utilization of DBBQ and MPT can reduce the charge/discharge overpotentials and thus prolong the battery lifetime. This may be related to the protective effect of superconcentrated-GPE on the Li anode, alleviating the shuttle reaction between MPT⁺ and Li. Additionally, considering the hydrophobic property of ILs in GPE, we also compared the cycling stability of the DBBQ-MPT-IL-GPE-based Li-air batteries in a simulated-air atmosphere with different humidities in Figure S6, Supplementary Materials. The DBBQ-MPT-IL-GPE-based Li-air battery with dried air can operate relatively at discharge/charge overpotentials for 50 cycles. In contrast, the charge voltage profiles of a similar Li-O₂ battery with 15% humidity can keep at 3.75 V for 26 cycles. Even for the cell with 35% humidity, the lowest charge voltages are constant at 3.5 V for 20 cycles. These phenomena may be attributed to the following two reasons: On the one hand, the higher humidity may favor the formation of Li₂O₂ in the solution phase [34,35], thus accelerating the oxidization of Li₂O₂ and reducing the charge potentials. On the other hand, the higher humidity may be a hazard to the Li anode, resulting in the shortening of the cell lifespan.

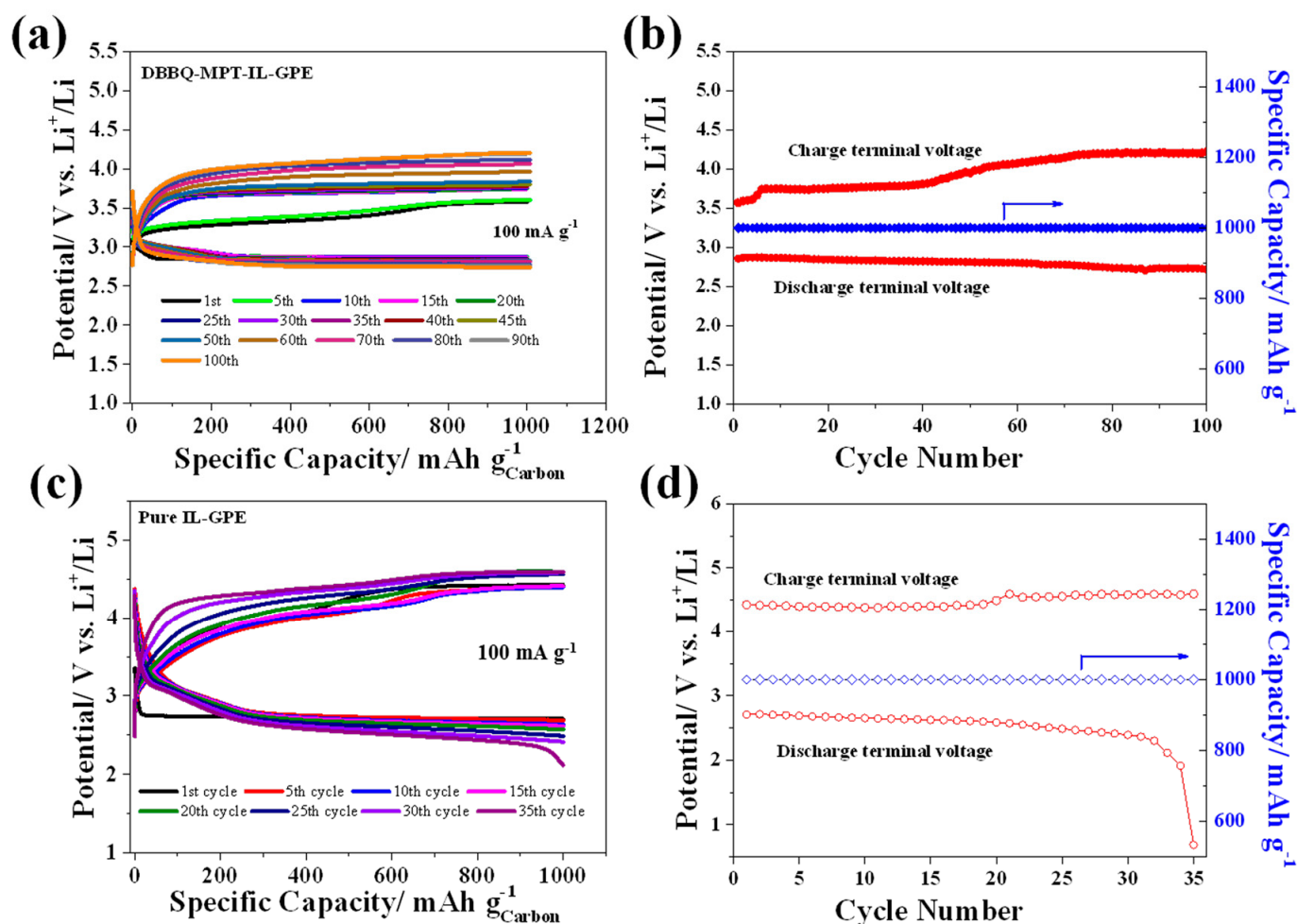


Figure 3. (a) Voltage profiles of the DBBQ-MPT-IL-GPE-based Li-O₂ batteries during cycling and (b) the corresponding discharge/charge terminal voltage vs. cycle number. (c) Discharge/charge profiles of the pure IL-GPE-based Li-O₂ batteries and (d) the corresponding discharge/charge terminal voltage vs. cycle number. Measuring conditions: the current density of 100 mA g⁻¹ and the specifically limited capacity of 1000 mAh g⁻¹.

3.3. Products Characterization of Dual RMs-IL-GPE-Based Li-O₂ Batteries

To further elucidate the relationship between the outstanding electrochemical performance and the reactive products of the IL-GPE-based Li-O₂ batteries with dual DBBQ and MPT mediators, we conducted additional ex situ SEM, XPS, and in situ DEMS analyses. The morphological evolution of the SWCNT electrodes with different states is shown in Figure 4a–c. Compared with the fresh electrode, it can be clearly observed that many disc-assembled spheres are formed on the discharged SWCNT cathode (Figure 4b). After recharging the dual RMs-IL-GPE-based Li-O₂ cell, almost all the sphere-shaped products disappear, except for some trace products (Figure 4c). However, in the case of pure IL-GPE-based Li-O₂ batteries without any RMs, the film-like products are covered on the surface of the discharged SWCNT electrode (Figure S7, Supplementary Materials). These results are different from the surface morphology of the discharged cathode in the DBBQ-MPT-IL-GPE-based Li-O₂ battery. The previous literature has demonstrated that the incorporation of DBBQ can promote the formation of large particle-shaped products rather than film-like products in the solution phase [13], which may be beneficial for lowering the charge/discharge overpotentials and improving cycling stability of the Li-O₂ batteries with dual RMs-IL-GPE. To determine if the discharge product of the dual RMs-IL-GPE-based Li-O₂ battery is Li₂O₂ or not, ex situ XPS spectra of the SWCNT electrodes in different states are obtained in Figure 4d,e and Figure S8, Supplementary Materials. Figure 4d,e compares the Li 1s XPS spectra of the discharged and recharged cathodes, respectively. The Li 1s region for the discharged electrode can be assigned with the underlying Li₂O₂ (Li 1s: 54.4 eV) [36] and surface Li₂CO₃ species (Li 1s: 55.3 eV) [37] generated by the chemical reaction of carbon cathode in contact with Li₂O₂ [38,39]. Upon recharging, the Li 1s peaks related to Li₂O₂ have vanished except for the surface Li₂CO₃ species. This result is also in good agreement with the corresponding O 1s and C 1s XPS spectra. According to the previous study [27,28], the utilization of MPT as the OER catalyst has been demonstrated to effectively decompose Li₂O₂ on the solid–liquid interface, which can dramatically reduce the OER overpotential. To confirm this point, in situ DEMS was performed to study the evolved gases when recharging the DBBQ-MPT-IL-GPE-based Li-O₂ cell. Before the recharge test, the corresponding Li-O₂ cell was discharged to the limited capacity of 0.5 mAh in pure O₂ gas. Then, the DEMS system was purged with an Ar stream for 4 h before recharging. We traced the evolution of gaseous O₂ ($m/z = 32$) and CO₂ ($m/z = 44$) during recharging to the capacity of 0.5 mAh at a current density of 0.3 mA (Figure 4f,g). As depicted in Figure 4g, in situ DEMS result presents that a stronger signal of O₂ evolution can be detected during the overall recharging process. However, a trace of CO₂ is evolved from the decomposition of byproducts Li₂CO₃ when recharged above 4.5 V. Moreover, the IL-GPE-based Li-O₂ cell with DBBQ and MPT could yield $e^-/\text{O}_{2\text{chg}} = 2.11$ through the quantitative analysis, which suggests that some parasitic electrochemical processes occur during charging. Based on these ex and in situ characterizations, we can deduce the electrochemical mechanism in the IL-GPE-based Li-O₂ battery with dual soluble mediators (DBBQ and MPT) in Figure 5: On discharging, DBBQ can facilitate the solution-phase nucleation of Li₂O₂ without passivating the electrode through forming a new intermediate LiDBBQO₂. On charging, MPT can be electrochemically oxidized to MPT⁺ at a lower charge potential, and then MPT⁺ decomposes Li₂O₂ into O₂ through a chemical reaction at the solid/liquid interface. As a result, this unique collaboration between DBBQ and MPT can improve the round-trip efficiency and the cycling stability of the IL-GPE-based Li-O₂ batteries.

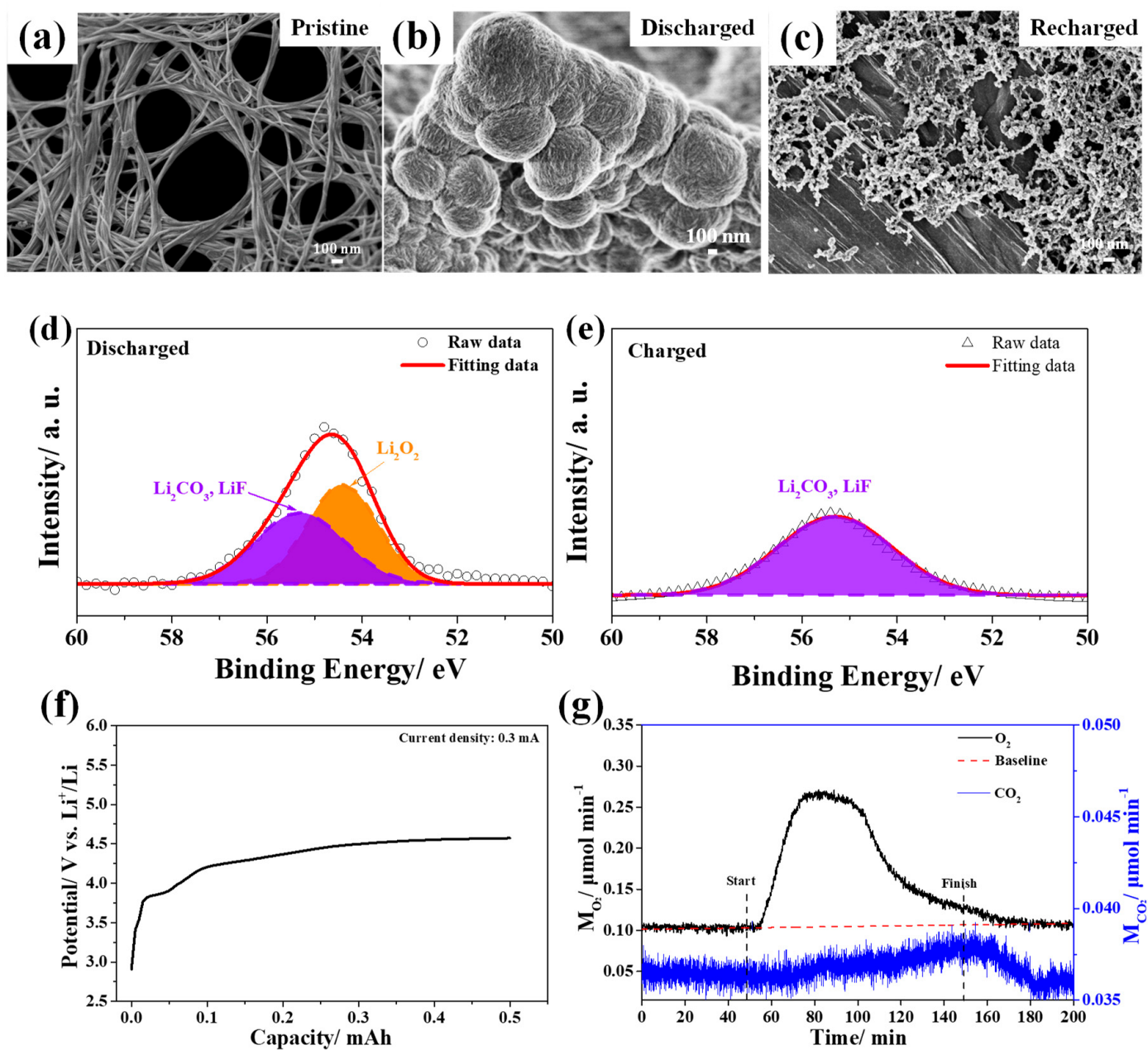


Figure 4. Ex situ SEM images of the SWCNT cathodes at various stages: (a) pristine, (b) discharged, and (c) recharged. Ex situ Li 1s XPS spectra of the SWCNT cathodes at different stages: (d) discharged and (e) recharged. (f) The charge voltage profile of a DBBQ-MPT-IL-GPE-based Li-O₂ battery with a discharged SWCNT cathode and (g) the corresponding gaseous evolution of O₂ and CO₂ detected by in situ DEMS system.

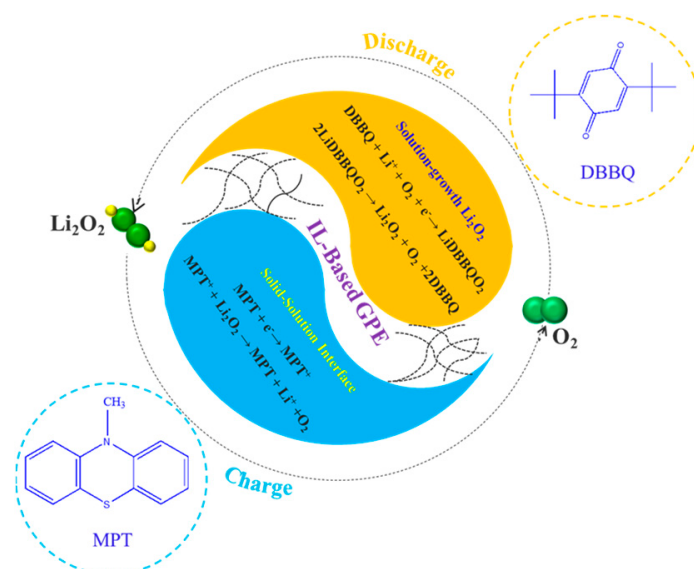


Figure 5. Schematics of cathode electrode reactions on discharging and recharging with DBBQ and MPT. On discharging (orange area), DBBQ is first reduced to the intermediate LiDBBQ₂, then disproportionation into Li₂O₂ and regenerating to DBBQ in solution. On recharging (blue area), MPT is oxidized to MPT⁺, which decomposes Li₂O₂ at the solid–liquid interface, evolving O₂ and regenerating itself to MPT.

4. Conclusions

In summary, a Li-O₂ battery was developed by utilizing a PP₁₃TFSI-TEGDME-mixed GPE with 20 mM DBBQ and 40 mM MPT as electrolyte and SWCNT cathode, respectively. This unique DBBQ-MPT-IL-based GPE possesses a relatively high ion conductivity and wide, stable potential window, considered to be a useful protecting layer for lithium anode in Li-O₂ batteries. Moreover, in this GPE, DBBQ as the ORR catalyst can promote the growth of discharge products without passivating the electrode through the solution-phase pathway, simultaneously MPT/MPT⁺ as an OER mediator can oxidize Li₂O₂ at low charge overpotentials through a solid–liquid chemical reaction. As a result, the DBBQ-MPT-IL-GPE-based Li-O₂ cell can maintain the capacity of 5000 mAh g^{−1} for 20 cycles and 1000 mAh g^{−1} for 100 cycles with lower charge/discharge overpotentials. The conversion between Li₂O₂ and O₂ was confirmed by ex situ SEM, XPS, and in situ DEMS analyses. However, it should be noted that the carbon cathode can still be unstable toward the discharge product Li₂O₂. Hence, optimizing the protected carbon cathodes or designing new porous carbon-free cathodes would be the next step for enhancing the Dual RMs-GPE-based Li-O₂ batteries. This concept proposed here may offer a useful method to realize high-efficiency Li–air batteries.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/batteries9050243/s1>, Figure S1: (a) EIS measurement of pure IL-GPE, two stainless steel meshes (SSM) are used with pure IL-GPE to form an SSM/GPE/SSM symmetric cell, and the measurement frequency ranges from 0.1 Hz to 100 KHz. (d) Linear sweep voltammetry (LSV) profile of pure IL-GPE and the sweep rate is 10 mV s^{−1}; Figure S2: TGA curve of DBBQ-MPT-IL-GPE, the heating rate is 10 °C min^{−1}, and the protected atmosphere is airflow; Figure S3: (a) Chronoamperometry of the Li/DBBQ-MPT-IL-GPE/Li cell at room temperature. (b) Impedance spectra of DBBQ-MPT-IL-GPE recorded before and after the polarization at room temperature; Figure S4: Cyclic voltammogram tested in the Li-O₂ cells using pure IL-GPE (black line) or DBBQ-MPT-IL-GPE (red line) at a scan rate of 10 mV s^{−1}; Figure S5: Discharge–charge voltage profiles of the DBBQ-MPT-IL-GPE-based (a,c) or pure IL-based Li-O₂ batteries (b,d) at different current densities (200 and 500 mA g^{−1}); Figure S6: Discharge–charge voltage profiles of the DBBQ-MPT-IL-GPE-based Li-O₂ batteries with different humidities at the applied current density (100 mA g^{−1} and the fixed specific capacity, 1000 mAh g^{−1}); Figure S7: Ex situ SEM images of the SWCNT

cathodes in the pure IL-GPE-based Li-O₂ batteries at different stages, (a) pristine, (b) discharged, and (c) recharged. (d) Ex situ XRD pattern of the SWCNT cathodes at different stages; Figure S8: Ex situ XPS spectra of O 1s and C 1s of the SWCNT cathodes in the DBBQ-MPT-IL-GPE-based Li-O₂ batteries at different stages; Table S1: Summary of cycle performance and discharge-charge voltage gap in various GPE-based Li-O₂ batteries.

Author Contributions: N.F. conceived the idea, conducted the experiments, directed the research, and accomplished the material synthesis, characterization, and electrochemical measurements. All authors discussed and analyzed the results. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (grant number 22109015), Guangxi Natural Science Funds (grant number 2020GXNSFAA159095), and the Natural Science Foundation of the Higher Education Institutions of Jiangsu Province (grant number 21KJB150025).

Data Availability Statement: Not applicable.

Acknowledgments: In this section, you can acknowledge any support given which is not covered by the author contribution or funding sections. This may include administrative and technical support or donations in kind (e.g., materials used for experiments).

Conflicts of Interest: The authors declare no conflict of interest.

References

- Bruce, P.G.; Freunberger, S.A.; Hardwick, L.J.; Tarascon, J.-M. Li-O₂ and Li-S batteries with high energy storage. *Nat. Mater.* **2012**, *11*, 19–29. [[CrossRef](#)] [[PubMed](#)]
- Kwak, W.J.; Rosy, Sharon, D.; Xia, C.; Kim, H.; Johnson, L.R.; Bruce, P.G.; Nazar, L.F.; Sun, Y.K.; Frimer, A.A.; et al. Lithium-Oxygen Batteries and Related Systems: Potential, Status, and Future. *Chem. Rev.* **2020**, *120*, 6626–6683. [[CrossRef](#)] [[PubMed](#)]
- Chen, Y.H.; Xu, J.J.; He, P.; Qiao, Y.; Guo, S.H.; Yang, H.J.; Zhou, H.S. Metal-air batteries: Progress and perspective. *Sci. Bull.* **2022**, *67*, 2449–2486. [[CrossRef](#)] [[PubMed](#)]
- Zhang, X.H.; Dong, P.P.; Song, M.K. Advances in Lithium-Oxygen Batteries Based on Lithium Hydroxide Formation and Decomposition. *Front. Chem.* **2022**, *10*, 923936. [[CrossRef](#)]
- Feng, N.N.; He, P.; Zhou, H.S. Critical Challenges in Rechargeable Aprotic Li-O₂ Batteries. *Adv. Energy Mater.* **2016**, *6*, 1502303. [[CrossRef](#)]
- Ma, L.; Yu, T.; Tzoganakis, E.; Amine, K.; Wu, T.; Chen, Z.W.; Lu, J. Fundamental Understanding and Material Challenges in Rechargeable Nonaqueous Li-O₂ Batteries: Recent Progress and Perspective. *Adv. Energy Mater.* **2018**, *8*, 1800348. [[CrossRef](#)]
- Zhang, P.; Zhao, Y.; Zhang, X. Functional and stability orientation synthesis of materials and structures in aprotic Li-O₂ batteries. *Chem. Soc. Rev.* **2018**, *47*, 2921–3004. [[CrossRef](#)]
- Guo, H.; Luo, W.; Chen, J.; Chou, S.L.; Liu, H.K.; Wang, J.Z. Review of Electrolytes in Nonaqueous Lithium-Oxygen Batteries. *Adv. Sustain. Syst.* **2018**, *2*, 1700183. [[CrossRef](#)]
- Amici, J.; Marquez, P.; Mangini, A.; Torchio, C.; Dessantis, D.; Versaci, D.; Francia, C.; Aguirre, M.J.; Bodoardo, S. Sustainable, economic, and simple preparation of an efficient catalyst for Li-O₂ batteries. *J. Power Sources* **2022**, *546*, 231942. [[CrossRef](#)]
- Park, J.B.; Lee, S.H.; Jung, H.G.; Aurbach, D.; Sun, Y.K. Redox Mediators for Li-O₂ Batteries: Status and Perspectives. *Adv. Mater.* **2018**, *30*, 1704162. [[CrossRef](#)]
- Khan, Z.; Vagin, M.; Crispin, X. Can Hybrid Na-Air Batteries Outperform Nonaqueous Na-O₂ Batteries? *Adv. Sci.* **2020**, *7*, 1902866. [[CrossRef](#)]
- Shen, X.; Zhang, S.; Wu, Y.; Chen, Y.H. Promoting Li-O₂ Batteries with Redox Mediators. *ChemSusChem* **2019**, *12*, 104–114. [[CrossRef](#)]
- Gao, X.; Chen, Y.; Johnson, L.; Bruce, P.G. Promoting solution phase discharge in Li-O₂ batteries containing weakly solvating electrolyte solutions. *Nat. Mater.* **2016**, *15*, 882–888. [[CrossRef](#)]
- Chang, Z.W.; Xu, J.J.; Zhang, X.B. Recent Progress in Electrocatalyst for Li-O₂ Batteries. *Adv. Energy Mater.* **2017**, *7*, 1700875. [[CrossRef](#)]
- Johnson, L.; Li, C.M.; Liu, Z.; Chen, Y.H.; Freunberger, S.A.; Ashok, P.C.; Praveen, B.B.; Dholakia, K.; Tarascon, J.M.; Bruce, P.G. The role of LiO₂ solubility in O₂ reduction in aprotic solvents and its consequences for Li-O₂ batteries. *Nat. Chem.* **2014**, *6*, 1091–1099. [[CrossRef](#)]
- Freunberger, S.A.; Chen, Y.; Drewett, N.E.; Hardwick, L.J.; Bardé, F.; Bruce, P.G. The lithium-oxygen battery with ether-based electrolytes. *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 8609–8613. [[CrossRef](#)]
- Gu, Z.; Xin, X.; Yang, J.; Guo, D.; Yang, S.; Wu, J.; Sun, Y.; Yao, X. Bilayer NASICON/Polymer Hybrid Electrolyte for Stable Solid-State Li-O₂ Batteries. *ACS Appl. Energy Mater.* **2022**, *5*, 9149–9157. [[CrossRef](#)]

18. Asadi, M.; Sayahpour, B.; Abbasi, P.; Ngo, A.T.; Karis, K.; Jokisaari, J.R.; Liu, C.; Narayanan, B.; Gerard, M.; Yasaei, P.; et al. A lithium-oxygen battery with a long cycle life in an air-like atmosphere. *Nature* **2018**, *555*, 502–506. [\[CrossRef\]](#)
19. Das, S.; Hojberg, J.; Knudsen, K.B.; Younesi, R.; Johansson, P.; Norby, P.; Vegge, T. Instability of Ionic Liquid-Based Electrolytes in Li-O₂ Batteries. *J. Phys. Chem. C* **2015**, *119*, 18084–18090. [\[CrossRef\]](#)
20. Cecchetto, L.; Salomon, M.; Scrosati, B.; Croce, F. Study of a Li-air battery having an electrolyte solution formed by a mixture of an ether-based aprotic solvent and an ionic liquid. *J. Power Sources* **2012**, *213*, 233–238. [\[CrossRef\]](#)
21. Khan, A.; Zhao, C. Enhanced performance in mixture DMSO/ionic liquid electrolytes: Toward rechargeable Li-O₂ batteries. *Electro. Commun.* **2014**, *49*, 1–4. [\[CrossRef\]](#)
22. Garcia-Quintana, L.; Ortiz-Vitoriano, N.; Zhu, H.; Nolis, G.M.; Herrero-Martin, J.; Echeverría, M.; López del Amo, J.M.; Forsyth, M.; Bond, A.M.; Howlett, P.C.; et al. Unveiling the Impact of the Cations and Anions in Ionic Liquid/Glyme Hybrid Electrolytes for Na-O₂ Batteries. *ACS Appl. Mater. Interfaces* **2022**, *14*, 4022–4034. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Ferrari, S.; Quartarone, E.; Tomasi, C.; Bini, M.; Galinetto, P.; Fagnoni, M.; Mustarelli, P. Investigation of Ether-Based Ionic Liquid Electrolytes for Lithium-O₂ Batteries. *J. Electrochem. Soc.* **2015**, *162*, A3001–A3006. [\[CrossRef\]](#)
24. Jung, K.N.; Lee, J.I.; Jung, J.H.; Shin, K.H.; Lee, J.W. A quasi-solid-state rechargeable lithium-oxygen battery based on a gel polymer electrolyte with an ionic liquid. *Chem. Commun.* **2014**, *50*, 5458–5461. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Gao, X.; Chen, Y.; Johnson, L.; Jovanov, Z.P.; Bruce, P.G. A rechargeable lithium-oxygen battery with dual mediators stabilizing the carbon cathode. *Nat. Energy* **2017**, *2*, 17118. [\[CrossRef\]](#)
26. Shen, Z.Z.; Lang, S.Y.; Shi, Y.; Ma, J.M.; Wen, R.; Wan, L.J. Revealing the Surface Effect of the Soluble Catalyst on Oxygen Reduction/Evolution in Li-O₂ Batteries. *J. Am. Chem. Soc.* **2019**, *141*, 6900–6905. [\[CrossRef\]](#)
27. Lee, D.; Park, H.; Ko, Y.; Park, H.; Hyeon, T.; Kang, K.; Park, J. Direct Observation of Redox Mediator-Assisted Solution-Phase Discharging of Li-O₂ Battery by Liquid-Phase Transmission Electron Microscopy. *J. Am. Chem. Soc.* **2019**, *141*, 8047–8052. [\[CrossRef\]](#)
28. Chen, Y.; Freunberger, S.A.; Peng, Z.; Fontaine, O.; Bruce, P.G. Charging a Li-O₂ battery using a redox mediator. *Nat. Chem.* **2013**, *5*, 489–494. [\[CrossRef\]](#)
29. Yang, H.; Wang, Q.; Zhang, R.; Trimm, B.D.; Whittingham, M.S. The electrochemical behaviour of TTF in Li-O₂ batteries using a TEGDME-based electrolyte. *Chem. Commun.* **2016**, *52*, 7580–7583. [\[CrossRef\]](#)
30. Bergner, B.J.; Schurmann, A.; Peppler, K.; Garsuch, A.; Janek, J. TEMPO: A mobile catalyst for rechargeable Li-O₂ batteries. *J. Am. Chem. Soc.* **2014**, *136*, 15054–15064. [\[CrossRef\]](#)
31. Feng, N.; He, P.; Zhou, H. Enabling catalytic oxidation of Li₂O₂ at the liquid-solid interface: The evolution of an aprotic Li-O₂ battery. *ChemSusChem* **2015**, *8*, 600–602. [\[CrossRef\]](#)
32. Feng, N.; Mu, X.; Zhang, X.; He, P.; Zhou, H.S. Intensive Study on the Catalytic Behavior of N-Methylphenothiazine as a Soluble Mediator to Oxidize the Li₂O₂ Cathode of the Li-O₂ Battery. *ACS Appl. Mater. Interfaces* **2017**, *9*, 3733–3739. [\[CrossRef\]](#)
33. Li, J.; Zhao, H.; Qi, H.; Sun, X.; Song, X.; Guo, Z.Y.; Tamirat, A.G.; Liu, J.; Wang, L.; Feng, S. Drawing a Pencil-Trace Cathode for a High-Performance Polymer-Based Li-CO₂ Battery with Redox Mediator. *Adv. Funct. Mater.* **2019**, *29*, 1806863. [\[CrossRef\]](#)
34. Dai, A.; Li, Q.; Liu, T.; Amine, K.; Lu, J. Fundamental Understanding of Water-Induced Mechanisms in Li-O₂ Batteries: Recent Developments and Perspectives. *Adv. Mater.* **2019**, *31*, e1805602. [\[CrossRef\]](#)
35. Aetukuri, N.B.; McCloskey, B.D.; Garcia, J.M.; Krupp, L.E.; Viswanathan, V.; Luntz, A.C. Solvating additives drive solution-mediated electrochemistry and enhance toroid growth in non-aqueous Li-O₂ batteries. *Nat. Chem.* **2015**, *7*, 50–56. [\[CrossRef\]](#)
36. Kim, D.Y.; Kim, M.; Kim, D.W.; Suk, J.; Park, O.O.; Kang, Y. Flexible binder-free graphene paper cathodes for high-performance Li-O₂ batteries. *Carbon* **2015**, *93*, 625–635. [\[CrossRef\]](#)
37. Kundu, D.; Black, R.; Berg, E.J.; Nazar, L.F. A highly active nanostructured metallic oxide cathode for aprotic Li-O₂ batteries. *Energy Environ. Sci.* **2015**, *8*, 1292–1298. [\[CrossRef\]](#)
38. McCloskey, B.D.; Speidel, A.; Scheffler, R.; Miller, D.C.; Viswanathan, V.; Hummelshøj, J.S.; Nørskov, J.K.; Luntz, A.C. Twin Problems of Interfacial Carbonate Formation in Nonaqueous Li-O₂ Batteries. *J. Phys. Chem. Lett.* **2012**, *3*, 997–1001. [\[CrossRef\]](#)
39. McCloskey, B.D.; Scheffler, R.; Speidel, A.; Girishkumar, G.; Luntz, A.C. On the Mechanism of Nonaqueous Li-O₂ Electrochemistry on C and Its Kinetic Overpotentials: Some Implications for Li-Air Batteries. *J. Phys. Chem. C* **2012**, *116*, 23897–23905. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.