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Graphene-based quasi-solid-state lithium–oxygen batteries with high energy efficiency and a long cycling lifetime

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Abstract

An aprotic lithium–oxygen battery with an ultrahigh theoretical energy density has attracted significant attention as the next-generation electrochemical energy device demanded by all-electric vehicles and other high-energy devices. Extensive effort has recently been devoted to improving the performances of cathodes, anodes, and electrolytes. However, as an integrated system, the overall battery properties are not determined by the individual components but by the synergy of all components. Despite important progress in the development of cathodes, anodes, and electrolytes, the system-level design and assembly of lithium–oxygen batteries have not benefited from these recent advances. Here, we report a graphene-based quasi-solid-state lithium–oxygen battery consisting of a rationally designed 3D porous graphene cathode, redox mediator-modified gel polymer electrolyte, and porous graphene/Li anode. This integrated prototype battery simultaneously addresses the major challenges of lithium–oxygen batteries and achieves stable cycling at a large capacity, low charge overpotential and high rate in both coin-type and large-scale pouch-type batteries. For the first time, these lithium–oxygen batteries as a whole device deliver gravimetric and volumetric energy densities higher than those of a commercial Li-ion polymer battery. This study represents important progress toward the practical implementation of full-performance lithium–oxygen batteries.

Introduction

A nonaqueous rechargeable Li–O₂ battery with a high theoretical specific energy of 3500 Wh/kg based on the reversible redox reaction $2\text{Li} + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2$ is the only electrochemical energy storage system that can potentially rival the energy level of internal combustion engines^{1–6}. A typical aprotic Li–O₂ battery consists of three key components: a porous cathode, a metal Li anode, and a nonaqueous liquid electrolyte. In the last several years, extensive efforts have been devoted to the improvement of the three major components of the Li–O₂ battery^{7–13}. On the basis of the working principle of the aprotic Li–O₂ battery, an ideal Li–O₂ cathode is expected to have open

porosity, high conductivity, good electrochemical stability, and high catalytic activity toward Li–O₂ reactions^{14,15}. However, a porous cathode that can concurrently deliver large discharge capacities, high energy efficiency, and a long cycling lifetime needs to be compatible with electrolytes to retain high performance. To overcome the large voltage polarization upon charging, redox mediators (RMs), such as tetrathiafulvalene (TTF), have been successfully employed as charge transfer carriers to enhance oxidation kinetics during charging^{16–19}. Nevertheless, the issue that RM molecules shuttle to anodes and oxidize metal Li must be addressed if RMs are to be used in practical Li–O₂ batteries. In addition, the requirements for large amounts of open space and pore channels for fast mass transport of RMs and accommodation of solid Li₂O₂ usually render a large-porosity cathode highly desirable. However, a high-porosity cathode has a low density, which makes large specific capacities of the cathode difficult to translate to an entire device. Unstable solid

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electrolyte interfaces (SEI) and Li dendrite growth have been long-standing problems with using metal Li anodes^{10,11}. If the Li dendrite issue is not addressed, then the use of metal Li in a Li-O₂ battery will present serious safety issues. Moreover, in an open Li-O₂ cell system, the exposure of metal Li to oxygen and RMs will cause passivation. Aside from the cathode and anode, the electrochemical stability of electrolytes towards reduced oxygen species is also a problem^{9,10}. In addition, the volatile organic liquid-state electrolyte is also problematic in terms of safety. Bearing the above mentioned challenges in mind, the realization of practically promising Li-O₂ batteries requires both the development of high-performance electrode and electrolyte materials and a smart design of entire cells. Graphene is an ideal option for a cathode material owing to its high conductivity, mechanical and chemical stabilities, and large surface area^{20,21}. In particular, the recently developed 3D nanoporous graphene possesses a bicontinuous porous structure with retained high conductivity and large specific surface area of graphene and has been demonstrated to be appealing for Li-O₂ battery cathodes^{16,21-23}. However, due to the low mass density (~5-80 mg/cm³) of nanoporous graphene, it accounts for only a very small portion of the weight of the entire cell, and as a result, the high capacity advantage of the porous graphene cathode degrades when the total weight of the battery is considered¹⁶. For the metal Li electrode, it has been proven that Li dendrite growth can be efficiently suppressed by increasing the effective surface areas of the Li electrodes to dissipate the current density for a uniform Li-ion flux^{11,24}. This could be realized by embedding Li inside a porous matrix that has high chemical and mechanical stabilities^{25,26}. For the electrolytes, a solid-state electrolyte has been gradually recognized as a required option in practical Li-O₂ batteries simply due to safety considerations. For instance, a gel polymer electrolyte (GPE) would be able to protect metal Li anodes from oxygen and inhibit the self-discharge of RMs²⁷⁻²⁹. Although there has been considerable progress in the development of graphene-based cathodes, dendrite-free Li anodes, and solid-state electrolytes, the successful integration of these recent advances in one Li-O₂ system for full-performance, practically promising Li-O₂ batteries has not yet been realized. Herein, we report a graphene-based quasi-solid-state rechargeable Li-O₂ battery consisting of a 3D nanoporous graphene cathode, a TTF-modified quasi-solid-state GPE (GPE-TTF), and a Li-meal-loaded 3D nanoporous graphene anode. This graphene-based Li-O₂ battery has outstanding performance with stable cycling at large capacities and low charge potentials. In particular, the overall cell gravimetric and volumetric energy densities are appealing for practical applications.

Materials and Methods

Synthesis of nanoporous graphene

The nanoporous graphene was synthesized by a porous, Ni-based chemical vapor deposition (CVD) method²¹⁻²³. Porous Ni dealloyed from NiMn alloy sheets with a thickness of 10 μm was employed as the template. To grow nanoporous graphene, the CVD process was conducted at 900 °C using pyridine as the precursor. Next, the graphene-coated nanoporous Ni substrate was immersed in 2.0 M HCl solution to etch away the Ni, and free-standing nanoporous graphene film was obtained after supercritical CO₂ drying. Thick nanoporous graphene sheets for synthesizing nanoporous graphene/Li anodes and increasing the gravimetric energy density of quasi-solid-state rechargeable Li-O₂ pouch batteries were fabricated by a similar method by using porous Ni dealloyed from NiMn alloy sheets with thicknesses of 200 and 100 μm.

Synthesis of the porous graphene/Li anode

The free-standing nanoporous graphene sheets with a thickness of ~100 μm were first transferred to an argon-filled glove box with O₂ and H₂O levels below 0.1 ppm and then placed into Li melt in a stainless steel boat for 20 s, which was heated by a hot plate at 300 °C. The molten Li was absorbed into the porous graphene sheets through the pores with the color changing from black to silver. The Li loading amount can be tuned by controlling the contact time between the graphene sheet and the molten Li. For example, the 40-s-treated anode has a much higher Li loading than that of the 20-s-treated anode. The proportions of Li in the porous graphene/Li composites were determined by measuring the maximum Li stripping capacity of the composites and comparing it with the theoretical specific capacity of Li metal (3860 mAh/g). Before being loaded into cells, the surfaces of the porous graphene/Li films were smoothed for better electrical contact by slightly pressing the films between two stainless steel plates.

Synthesis of the gel polymer electrolyte

In total, 0.16 g fumed silica was uniformly dispersed into 30 ml acetone with the assistance of ultrasonication for 0.5 h. The resultant solution was mixed with 3.84 g PVDF-HFP copolymer and kept still for 12 h for complete dissolution. Subsequently, this solution was vigorously stirred at 50 °C for 2 h and then kept at 50 °C for one additional hour. The obtained viscous solution was uniformly coated on an aluminum foil sheet with a controlled thickness and cured at 70 °C in a vacuum overnight. The solidified polymer film was transferred to an argon-filled glove box and soaked in 1 M LiClO₄-DMSO electrolyte with and without 50 mM TTF for 24 h. Finally, filter paper was used to wipe away excess liquid electrolyte from the polymer film.

Materials characterization

X-ray diffraction (XRD) patterns were collected on a RIGAKU SmartLab 9MTP diffractometer. Raman measurements were carried out by using a Renishaw InVia RM 1000 micro-Raman spectrometer. Scanning electron microscopy (SEM) was performed on a JEOL JIB-4600F field-emission scanning electron microscope. Thermogravimetric (TG) analysis was conducted by using a Thermo plus EVO2 TG-DTA thermogravimetry analyzer from room temperature to 600 °C. X-ray photoelectron spectroscopy (XPS) was collected on an AXIS ultra DLD Shimadzu XPS system with an Al K α (mono) source in a vacuum of 10⁻⁷ Pa.

To investigate the discharge products on the nanoporous graphene cathodes at different states, discharged and recharged Li-O₂ coin batteries were disassembled in a glove box. The graphene cathodes were rinsed several times with dimethyl carbonate (DMC). Before XRD measurements, the samples were placed on a glass substrate and sealed by a Kapton polyimide film. The morphological changes in the pure Li foil in a symmetric cell and porous graphene/Li in symmetric and Li-O₂ batteries upon cycling were examined by SEM. The cells were disassembled in a glove box, and the electrodes were washed with DMC and dried in a vacuum.

Electrochemical measurements

R2032-type symmetric cells were employed to check the cycling stability of the pure Li and porous graphene/Li anodes. The electrolyte consisted of 1 M LiPF₆ dissolved in an ethyl carbonate and diethyl carbonate (1:1, w/w) solution. The stripping/plating capacity was 1 mAh/cm² at a current density of 0.5 mA/cm². To measure the Coulombic efficiency, Li/porous graphene or Li/copper foil cells were assembled, followed by the cycling procedures of depositing 1 mAh/cm² of Li onto the porous graphene or copper foil at a current density of 0.5 mA/cm² and stripping Li until the charge potential reached 0.5 V at the same current density. The electrochemical impedance spectra were collected by a BioLogic VMP3 electrochemical workstation at frequencies ranging from 10 mHz to 100 kHz. Linear sweep voltammetry measurements were conducted on a BioLogic VMP3 electrochemical workstation to evaluate the electrochemical window of electrolytes.

R2032-type coin batteries assembled in an argon-filled glove box were used to study the electrochemical performance of Li-O₂ batteries. The free-standing nanoporous graphene cathode and porous graphene/Li anode were separated by GPE or GPE-TTF. Ti mesh was used as the cathode current collector. The quasi-solid-state rechargeable Li-O₂ pouch cell was assembled layer by layer with a porous graphene/Li anode, two pieces of GPE-TTF and two pieces of nanoporous graphene

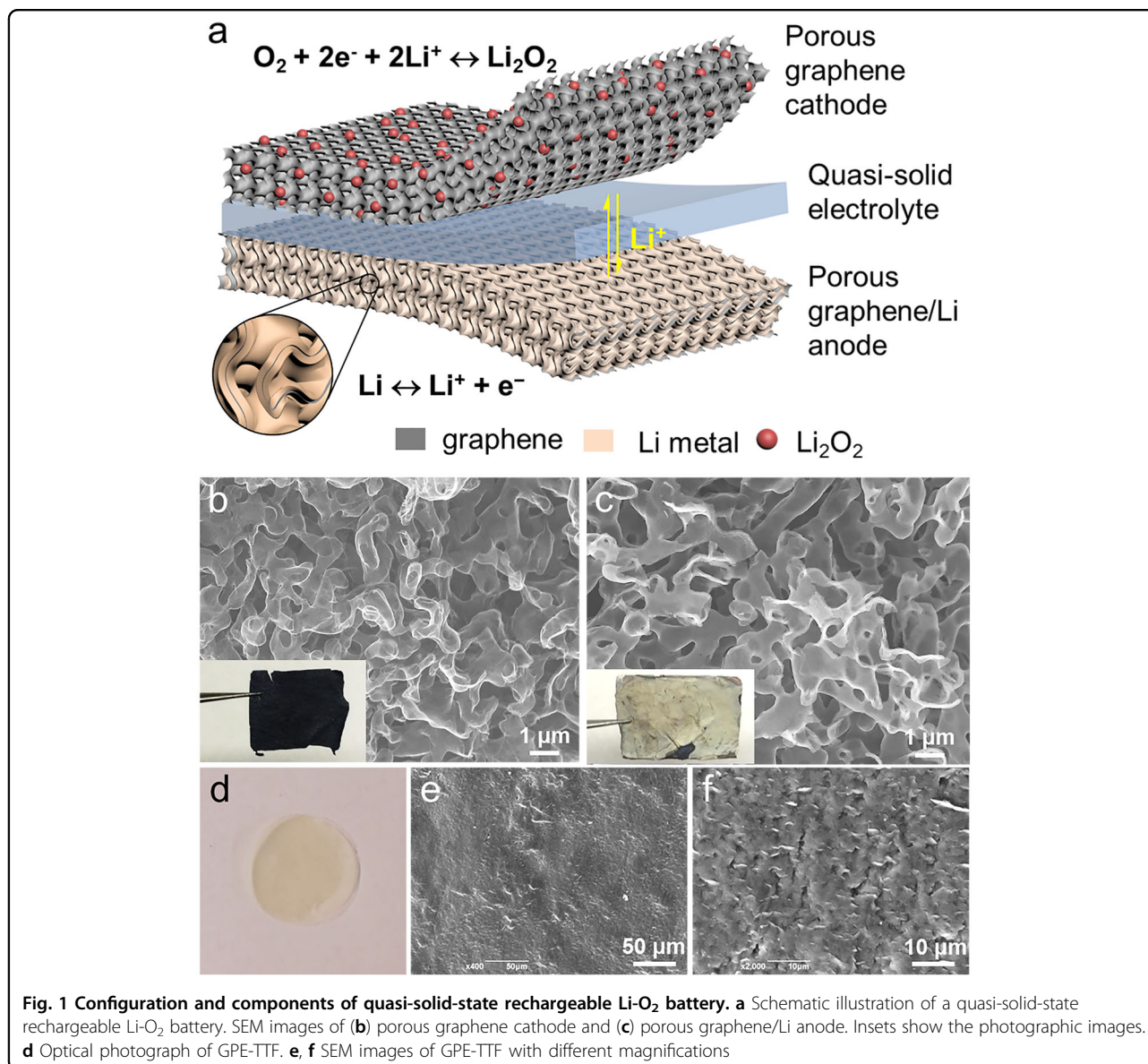
cathodes backed by porous Al foils and were finally sealed inside an aluminum-laminated film case (Fig. 4a, b). The assembled batteries were then transferred into an Ar-filled chamber and purged with high-purity O₂ gas before electrochemical testing. Galvanostatic discharge/charge tests were performed on a Hokuto discharging/charging system at room temperature. All the current densities and specific capacities were calculated on the basis of the mass of graphene cathodes unless otherwise noted.

Results

Synthesis and properties of the graphene cathode, GPE-TTF, and graphene/Li anode

Figure 1a schematically presents the structure of the graphene-based quasi-solid-state rechargeable Li-O₂ battery composed of a porous graphene cathode, a GPE containing 0.05 M TTF (GPE-TTF) and a porous graphene/Li metal composite anode. As shown in Fig. 1b, the flexible and free-standing 3D porous graphene cathode has a distinct bicontinuous porous architecture built by seamfree multilayer graphene sheets and interconnected open pore channels (Supplementary Figure 1a). The high electrical conductivity ($\sim 1.2 \times 10^4$ S/m), large specific surface area (700–1000 m²/g), and ultrahigh porosity (> 95%), verified by our previous studies^{16,21,22,30}, make this 3D nanoporous graphene a highly promising cathode material for Li-O₂ batteries.

The porous graphene/Li anode is prepared by placing a porous graphene sheet into Li melt. As a result of the lithophilic nature of graphene and the capillary forces generated by porosity, the molten Li penetrates into the entire bicontinuous scaffold in several seconds and uniformly coats the internal surfaces of the tubular graphene sheets (Fig. 1c). The graphene/Li composite inherits the 3D porous structure of the nanoporous graphene matrix. XRD confirms the successful loading of metallic Li in the composite (Supplementary Figure 1b). To assess the Li stripping/plating behaviors of the porous graphene/Li electrode, symmetrical cells are assembled and tested with a fixed capacity of 1 mAh/cm² at a current density of 0.5 mA/cm² (Supplementary Figure 2a). Significantly, the cell manifests stable voltage profiles with very slow increase in voltage hysteresis over 150 cycles, which obviously contrasts with the pure metal Li electrode that has almost 10 times the increase in the voltage hysteresis after 50 cycles. Furthermore, the Coulombic efficiency (CE) (capacity ratio of Li stripping/plating) of the porous graphene-based cell can be stabilized quickly from 60.2% in the initial several cycles to a value higher than 95% after 10 cycles and remains stable for 100 cycles. In contrast, the CE of the Cu foil-based cell is rather scattered and declines quickly (Supplementary Figure 2b). These results reveal the excellent reversibility of the porous graphene/Li electrode. The superb property of the 3D porous graphene/Li electrode can be attributed to its



large effective surface area, which enlarges the Li/electrolyte contact interface, decreases the effective current density and reduces the charge transfer resistance (Supplementary Figure 2c). Remarkably, the porous graphene/Li composite can also suppress the formation of Li dendrites. As shown in Supplementary Figure 2d, e, the planar Li metal is fully covered by fibrous Li dendrites after cycling, whereas the graphene/Li composite retains the original porous architecture with a smooth and dendrite-free surface.

An ultrathin quasi-solid-state GPE-TTF electrolyte is fabricated by integrating hemi-crystalline poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), nanosized fumed SiO₂, and 1 M LiClO₄/DMSO solution with 50 mM TTF additive (see Experimental section). As shown in Fig. 1d–f, the transparent GPE-TTF film is compact and has a thickness of ~10 μm. The GPE-TTF

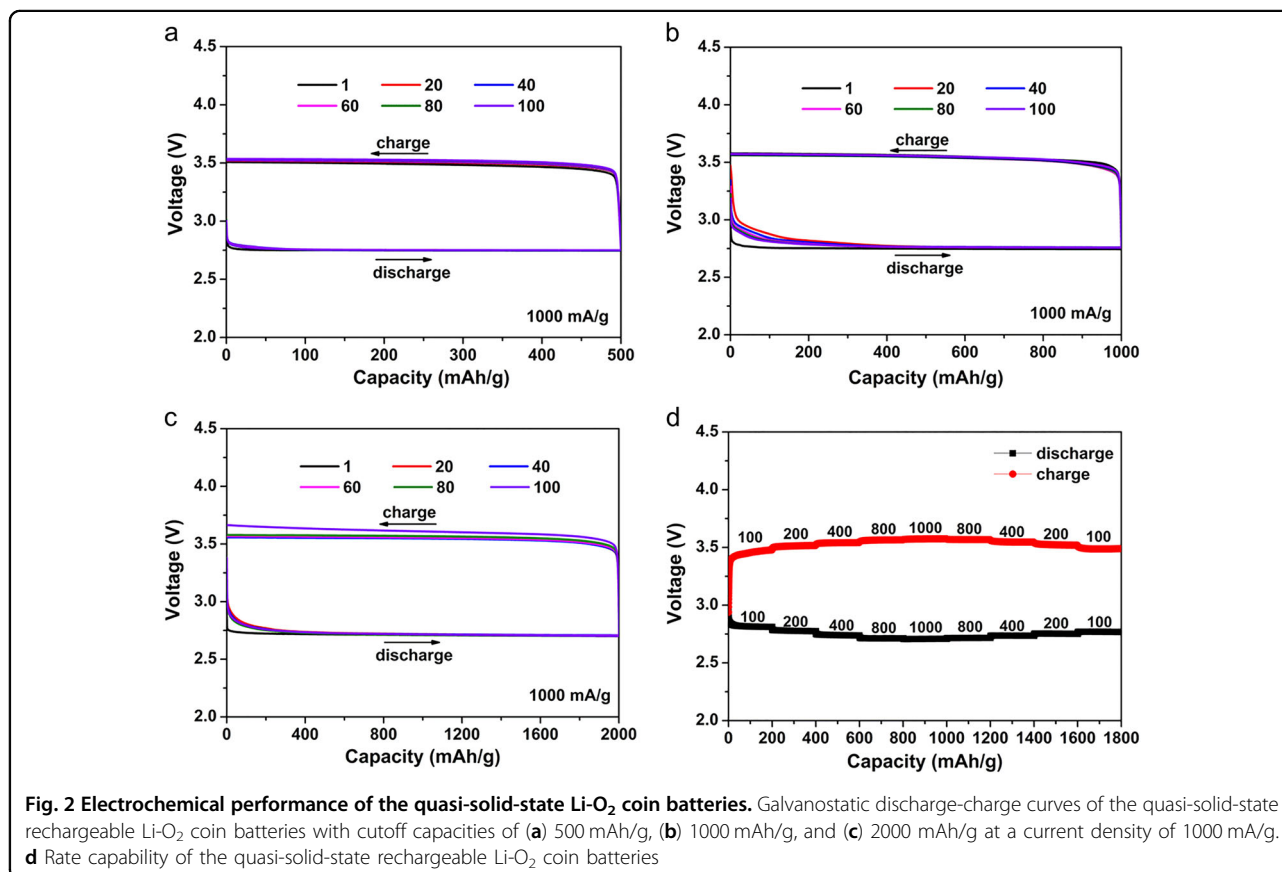
surface is smooth without the obvious presence of large pores. Although TTF was added initially as a redox mediator to assist the charging reaction of the Li-O₂ battery, it was found that it also enhances the amorphization of GPE as revealed by XRD (Supplementary Figure 3 and Figure 4a), which is expected to boost the ionic conductivity of the solid-state electrolyte³¹. Indeed, electrochemical impedance spectroscopy (EIS) measurements suggest a Li⁺ ion diffusion resistance of 5.1 Ω for GPE-TTF, lower than the 8.4 Ω for GPE and the 75.4 Ω for a conventional glass fiber separator wetted by liquid electrolyte (glass fiber-LE) (Supplementary Figure 4b). Thermal gravity analysis indicates that GPE-TTF exhibits an elevated DMSO solvent volatilization temperature (Supplementary Figure 4c), demonstrating that GPE-TTF can restrain electrolyte volatilization and has higher thermal

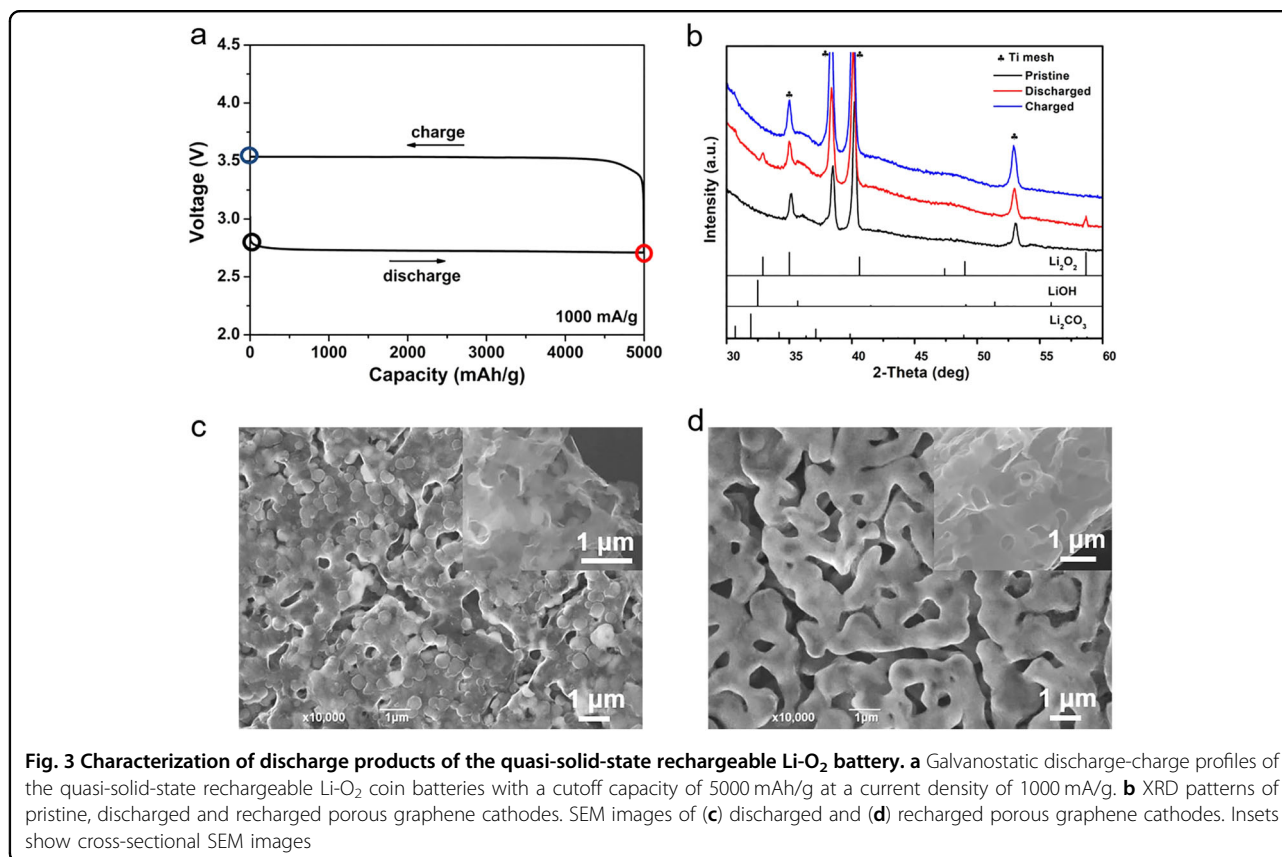
stability than the glass fiber-LE. The GPE-TTF also exhibits enhanced electrochemical stability, remaining substantially stable at potentials below 4.75 V (Supplementary Figure 4d and Fig. 5). Moreover, the compact GPE-TTF can serve as a protective layer for the metal Li anode to mitigate air-induced Li passivation (Supplementary Figure 6a, b). Even after 50 cycles, the lithium foil of the GPE-TTF-based Li-O₂ battery remains stable with a metallic luster, while the cycled lithium foil in the Li-O₂ battery using glass fiber-LE loses its metallic luster and becomes partially pulverized (Supplementary Figure 6c). The inhibition of the self-discharge behavior of TTF by GPE-TTF can be demonstrated by permeation tests (Supplementary Figure 7a, c) and electrochemical demonstration (Supplementary Figure 7b, d), revealing the outstanding performance of GPE-TTF in restraining the shuttling of TTF to the anode sides in Li-O₂ batteries. All the advantages mentioned above indicate the highly practical value of GPE-TTF.

Assessment of electrochemical performance in coin cells

By taking the advantages of a porous graphene cathode, a graphene/Li anode and GPE-TTF, a quasi-solid-state Li-O₂ coin cell is constructed with the configuration shown in Fig. 1a. As shown in Fig. 2a–c, galvanostatic discharge-

charge tests are conducted at cutoff capacities of 500, 1000, and 2000 mAh/g and a current density of 1000 mA/g, demonstrating the high stability of the quasi-solid-state Li-O₂ battery up to 100 cycles (Supplementary Figure 8a). The discharge potential is \sim 2.75 V and the charge potential is as low as \sim 3.60 V, corresponding to a high energy efficiency of 76%. Moreover, with the increase in cutoff capacities from 500 to 2000 mAh/g, the terminal voltages of both discharge and charge remain nearly unchanged (Supplementary Figure 8a). For comparison, the cycling performance of a pure GPE-based Li-O₂ battery is also tested. As indicated in Supplementary Figure 8b, c, the cell with GPE exhibits a consistently higher charge overpotential (\sim 1.65 V) than that of the GPE-TTF-based cell at each discharging/charging cycle, indicating the effectiveness of the introduction of TTF in reducing the charge overpotential. The rate performance shows that the quasi-solid-state Li-O₂ battery manifests stable discharge-charge voltage plateaus and mild polarization for current densities ranging from 100 to 1000 mA/g (Fig. 2d). The exceptional rate capability of the cell can be attributed to the high conductivity and large surface areas of the porous graphene cathode and graphene/Li anode as well as the high ionic conductivity of the ultrathin GPE-TTF. As a control experiment, quasi-solid-state Li-O₂





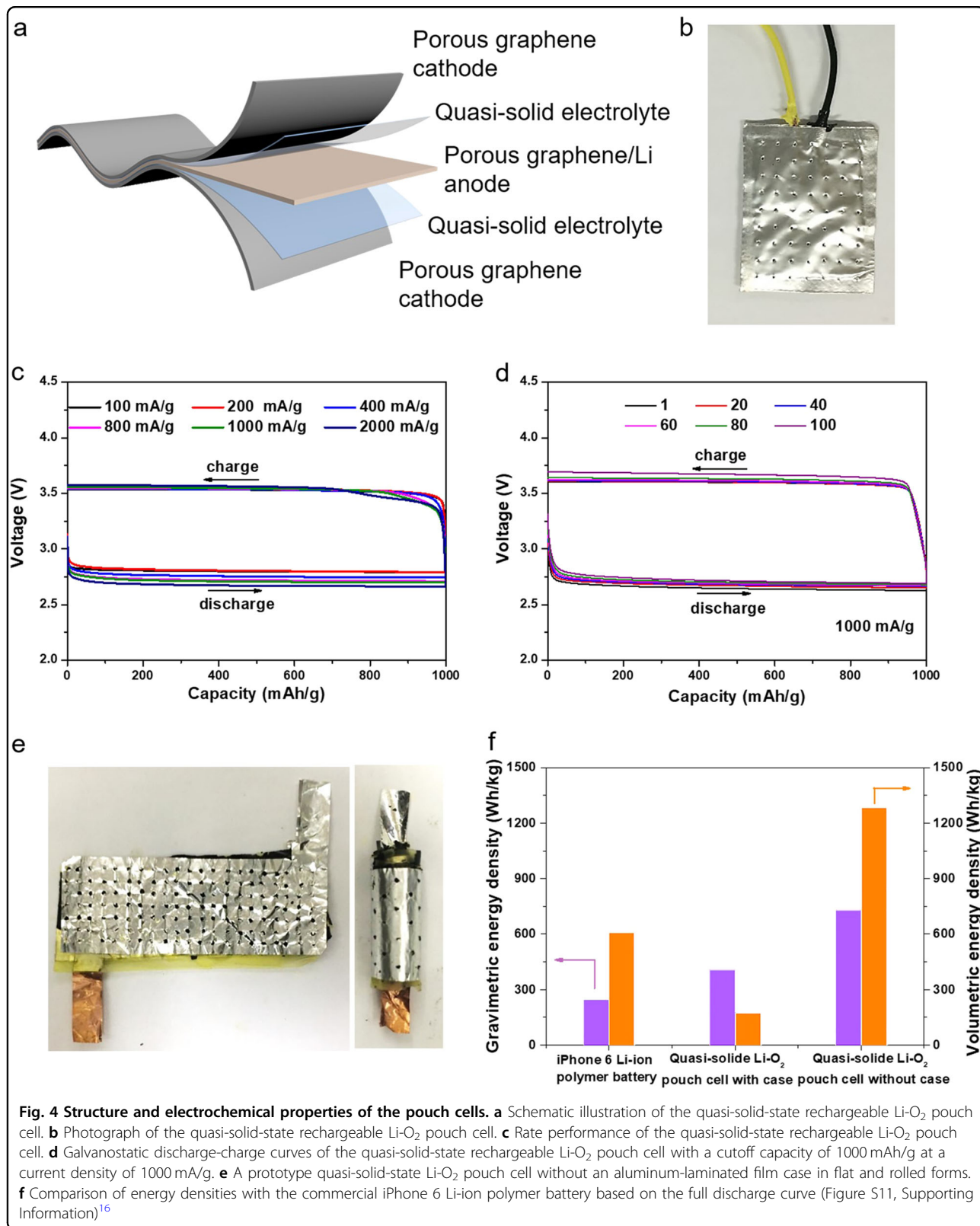
batteries with a 115 μm thick GPE-TTF tested under identical conditions exhibit obvious decline in discharge-charge voltage plateau (Supplementary Figure 8d), demonstrating the critical role of the GPE-TTF film thickness in rate performance. To investigate the impact of the Li loading amount on the cycling performance of Li-O₂ batteries, we prepared a graphene/Li anode with a higher loading amount of Li (82.5 wt.%, Supplementary Figure 9b, c) by prolonging the contact time between the graphene sheet and the molten Li from 20 s to 40 s. Even though a higher loading amount of Li would enable a higher packing density for the graphene/Li electrode, electrochemical testing shows that increasing the Li proportion from 44.4 wt.% to 82.5 wt.% does not significantly affect the cycling performance of the quasi-solid-state Li-O₂ batteries (Supplementary Figure 9d), suggesting that the graphene/Li anode in this quasi-solid-state Li-O₂ battery is not the determining factor for the cyclic performance.

The discharge products on the porous graphene cathode of the quasi-solid-state Li-O₂ batteries were characterized by XRD and SEM. As shown in Fig. 3a, b, characteristic diffraction peaks corresponding to crystalline hexagonal Li₂O₂ are detected from a discharged cathode with a cutoff capacity of 5000 mAh/g; these peaks disappear after subsequent recharge, implying the

formation and complete decomposition of Li₂O₂. SEM reveals the formation of particulate Li₂O₂ with diameters of 300–500 nm uniformly distributed on the surfaces and inner pores of the porous graphene cathode (Fig. 3c). With the assistance of TTF, the Li₂O₂ particles can be completely decomposed at the low charging overpotential, as evidenced by the clean surface of the recharged porous graphene cathode (Fig. 3d). All these results verify that the reactions in the quasi-solid-state Li-O₂ battery follow the typical Li-O₂ electrochemistry of $2\text{Li} + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2$ and permit the highly reversible Li₂O₂ formation and decomposition. For the graphene/Li anodes, the 3D porous structure and the uniform Li coating are well maintained except that the surface becomes slightly rough (Supplementary Figure 10a). No Li dendrites are observed, suggesting the formation of robust and uniform solid electrolyte interphase (SEI) films on the Li surfaces. XPS reveals that the SEI layer is mainly composed of the decomposition products of DMSO and PVDF-HFP, including Li₂SO₄, Li₂S, Li₂O, LiF, and some organic Li species (Supplementary Figure 10b–f).

Graphene-based quasi-solid-state Li-O₂ pouch batteries

To explore the capability of the graphene-based quasi-solid-state Li-O₂ batteries for practical applications, we scaled up the coin battery to a large pouch-



type cell with a size of 26 mm × 38 mm × 1.2 mm. As schematically illustrated in Fig. 4a, the quasi-solid-state Li-O₂ pouch cell is assembled by laminating one piece of porous graphene/Li sheet as the anode, two pieces of GPE-TTF as the electrolyte and separators, and two pieces of porous graphene sheets as the cathodes, which are then sealed inside an aluminum-laminated film case with pinholes on both sides. Fig. 4b is a photograph of a prototype pouch-type cell. The cell is mechanically flexible and can be scrolled without degeneration in battery performance (Supplementary Figure 11a). Excellent rate performance has been achieved for the quasi-solid-state Li-O₂ pouch cell. As shown in Fig. 4c, with the increase in current density from 100 to 2000 mA/g, the charge voltage plateau exhibits good reproducibility, and the discharge voltage plateau experiences a gentle and insignificant decrease. Cycling tests of the Li-O₂ pouch cell demonstrate a high durability with stable cycling up to 100 cycles at a cutoff capacity of 1000 mAh/g and a current density of 1000 mA/g (Fig. 4d). Apparently, the excellent performance that was achieved with coin cells can be completely reproduced by large-sized pouch batteries. Importantly, a full discharge capacity up to 33230 mAh/g_{cathode} can be delivered when 70 μm thick porous graphene is used as the pouch cell cathode (Supplementary Figure 11b, Tables 1 and 2). The gravimetric energy density and volumetric energy density of the pouch cell reach 408.48 Wh/kg_{cell} and 174.83 Wh/L_{cell}, respectively, which are calculated based on the total mass and volume of the device (Supplementary Table 2). These values far exceed those of our recently reported liquid electrolyte-based Li-O₂ batteries (260.30 Wh/kg_{cell}, 110.81 Wh/L_{cell})¹⁶. If the pouch-type cell obviates the use of an aluminum-laminated film case (which accounts for a major proportion of the weight and volume in the cell), then the energy densities can reach 727.84 Wh/kg_{cell without case} and 1285.05 Wh/L_{cell without case} (Supplementary Table 2). These metrics that do not consider the packages are of practical significance since the case would not require the same lateral size as the main cell components for the large-scale integration of flexible quasi-solid-state Li-O₂ cells. A preliminary prototype for such a cell is shown in Fig. 4e. The cell laminates were rolled into a rod shape, saving a large volume of package materials. Figure 4f compares the energy densities of the graphene-based quasi-solid-state Li-O₂ pouch cell with those of a commercial Li-ion polymer battery, highlighting the gravimetric energy-density advantage of our quasi-solid-state Li-O₂ pouch batteries. Furthermore, the volumetric energy density calculated without packaging fixation materials far exceeds the value for commercial Li-ion polymer

batteries, demonstrating an appealing design for boosting the volumetric energy density of Li-O₂ batteries.

Discussion

The outstanding battery performance achieved in both the coin-type and pouch-type quasi-solid-state Li-O₂ batteries originates from the unique structural features of the porous graphene cathode, the GPE-TTF, and the graphene/Li anode as well as their synergistic effects in the integrated cells. First, the nanoporous graphene cathode, with its high surface area and large porosity, offers a high density of active sites for O₂ reduction and TTF oxidation and plentiful channels facilitating O₂, Li⁺, and TTF transport. Second, GPE-TTF affords low Li⁺ ion diffusion resistance, relieves shuttle reactions between the TTF and the graphene/Li anode, and suppresses electrolyte volatilization and Li dendrite formation. In addition, TTF can mediate Li₂O₂ oxidation at a low overpotential, alleviate the decomposition of GPE, and suppress side reactions. Third, the porous graphene/Li anode simultaneously solves the dendrite growth and infinite volume change issues of the metal Li anode. Therefore, all three components are indispensable and vitally important to guarantee the excellent electrochemical performance of quasi-solid-state Li-O₂ batteries.

In summary, we have developed a full-performance quasi-solid-state Li-O₂ battery consisting of a rationally designed porous graphene cathode, TTF-modified GPE, and porous graphene/Li anode. The issues of high charge overpotential, instability of liquid electrolytes, and dendrite growth and pulverization of metal Li anodes can be efficiently resolved in the integrated battery. As a result, outstanding battery performance in terms of round-trip efficiency, cycling stability, and rate capability have been realized in both coin-type and large-scale pouch-type batteries. In particular, the pouch batteries deliver high gravimetric energy density and volumetric energy density that exceed those of the commercial Li-ion polymer battery. This study paves a new avenue for designing and fabricating safe and stable Li-O₂ batteries with full performance and represents important progress for the practical implementation of high-energy Li-O₂ batteries.

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Author contributions

M.C. conceived and supervised the research project. G.H. and J.H. prepared the samples and conducted the electrochemical measurements. C.Y. and Z.W. contributed to the SEM data analysis. G.H., J.H., and M.C. wrote the paper. All the authors discussed the results and reviewed the paper.

Conflict of interest

The authors declare that they have no conflict of interest.

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