Cable-Type Water-Survivable Flexible Li-O_2 Battery

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The flexible electronics have attracted intensive attentions because of their advantages including lightweight, bendable, rollable, and foldable, which would revolutionize many industries ranging from consumer products, automotive, and aerospace to medical.[1–7] To realize "flexible electronics" society, well-matched flexible, stretchable, and rechargeable energy storage devices with high energy density should be developed as one of the crucial and urgently required components. In response, recently several inspirational prototypes, including flexible lithium-ion batteries,[8–12] solar batteries,[13–17] and supercapacitors,[18–23] have been successfully developed.[8,24–28] However, their low theoretical energy density intrinsically sets the limit for their application for next-generation flexible devices.

Fortunately, thanks to their ultrahigh energy density,[29–35] rechargeable Li-O_2 batteries have emerged as new generation of energy storage devices holding great promise to be used for flexible electronics. However, up to now, there are only very few reports on the construction of flexible Li-O_2 batteries.[36–38] As a result, there are still many challenges hindering their wide applications in the field of flexible electronics including the easy leakage of liquid electrolyte, unavoidable penetration of moisture into the battery, possible short circuit upon repeated bending due to the frangible property of conventional separator, all of which would cause serious safety problems and/or immature death of the battery.[39–41] Therefore, the development of new prototype of flexible Li-O_2 batteries to significantly improve the moisture resistance, space utilization, mechanical robustness is of critical importance to promote their practical application of this advanced technology.

In response, herein, as a proof-of-concept experiment, we propose and demonstrate a novel strategy to fabricate cable-type water-survivable flexible Li-O_2 battery, wherein a free standing gel polymer electrolyte (GPE) and a flexible cathode composed of commercial carbon material Super P (SP) coated on carbon textiles play key roles. Unexpectedly, the obtained novel cable-type flexible Li-O_2 battery can be fully recovered even bent into various shapes for thousands of times, demonstrating good flexibility and mechanical stability. More importantly, due to the superior hydrophobicity of the GPE, the assembled cable-type flexible Li-O_2 battery can operate normally even immersed in water. Furthermore, the cable-type flexible Li-O_2 battery exhibits superior electrochemical performances including high specific capacity, good rate capability, and cycling stability.

Figure 1 shows the synthesis strategy for assembling the cable-type water-survivable flexible Li-O_2 battery. First, the lithium rod is coated with polymer electrolyte solution by dipping it into a coating bath; second, the coated lithium rod is exposed to UV-irradiation, resulting in the formation of a white, solidified, and non-sticky GPE (Figure S1, Supporting Information); Third, the cathode of SP-loaded carbon textiles wrapped around the GPE, which is then covered by nickel foam to ensure O_2 diffused uniformly inside the cathode; finally, the thus obtained electrode assembly is packed with punched heat-contraction rubber cable and heated to guarantee a close contact of each battery component. Furthermore, the close-up photograph shows the principal components of the novel cable Li-O_2 battery, including the copper wire current collector, lithium rod anode (diameter: 6 mm), GPE on lithium anode (thickness: 60 μm), SP-loaded carbon textiles cathode, nickel foam air diffusion layer, and shrunken packing insulator. Interestingly, the thus fabricated cable-type water-survivable flexible Li-O_2 battery might serve as wristband for next generation smartwatch/iwatch due to its high specific energy density and flexibility (Figure S2, Supporting Information).

To ensure the successful assemble of cable-type flexible Li-O_2 battery, we first characterized the physicochemical property of the GPE. **Figure 2**a exhibits an excellent bendability and mechanical stability of the GPE. Scanning electron microscopic (SEM) images show that the GPE is porous and the interconnected pores provide adequate channels to transfer lithium ion freely between cathode and anode, ensuring uniform reactant distributions required for the ORR and OER during the discharge and charge processes of Li-O_2 battery (Figure 2b). There is no change in the structure of GPE even after bending 1000 cycles, which further demonstrates the mechanical stability of the GPE (Figure S3, Supporting Information). As displayed in Figure 2c, the contact angles of water droplets on the GPE membrane is 98.8°,

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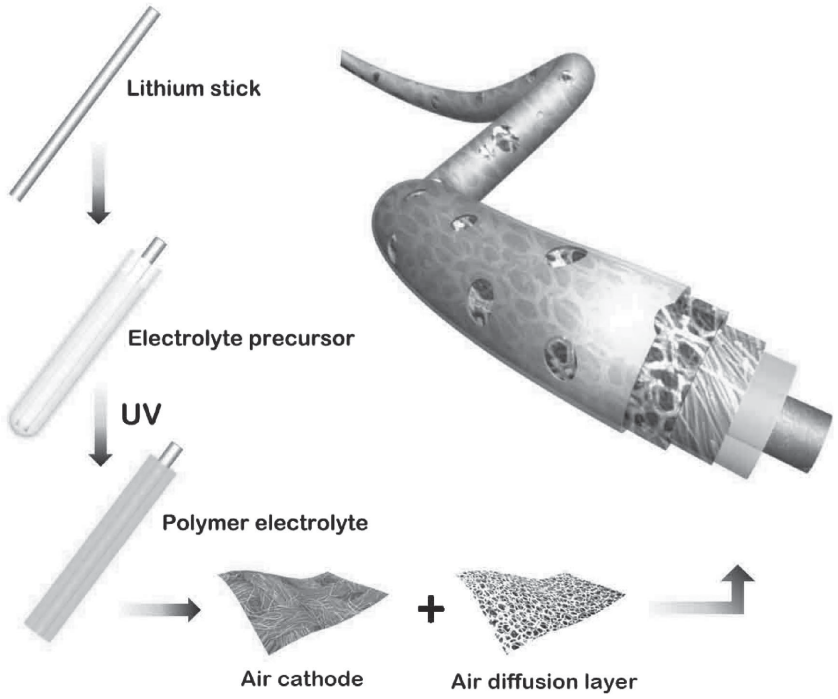

Figure 1. Schematic representation for the design and preparation of the cable-type and water-survivable flexible Li-O_2 battery.

showing the hydrophobicity of this GPE, which might effectively prevent the penetration of moisture into the battery and thus protect the lithium anode from corrosion. To confirm this point, the lithium rods with and without GPE separator are immersed in water. Interestingly, as shown in Figure 2d, the lithium rod with GPE (left) is stable in water. In sharp contrast, without the GPE protection, violent reaction happens immediately, producing a large amount of bubbles (Video S1, Supporting Information). All these results show that the GPE could endow the Li-O_2 battery with survivability toward moisture or even water, which would theoretically improve the safety coefficient and cycling stability of Li-O_2 battery (vide infra).

We then investigate the electrochemical performance of GPE using symmetric batteries composed of Li/GPE/Li assembled in coin-type battery. Figure 2e reveals the battery potential profile at 1 h interval under different applied charge–discharge current density varying from 0.05 to 0.2 mA cm^{-2} (lithium metal disc diameter: 7 mm). The potential profile of the symmetric battery is typical balanced when the current density lower than 0.1 mA cm^{-2} and corresponding to the charge–discharge current 153.9 μA. So the safe limiting current density is 0.1 mA cm^{-2} for the follow-up testing of the flexible Li-O_2 battery with the GPE. Figure 2f shows the discharge curves of Li-O_2 battery with the GPE or the glass fiber (GF) membrane soaked with 1M $LiCF_3SO_3$ in TEGDME (GF-Li/T) at different current densities. The corresponding charge curves were shown in Figure S4 (Supporting Information), and the calculated coulombic efficiency of the Li-O_2 battery with GPE are 90.39%, 99.20%, 96.84%, and 129.46% at current densities of 100, 200, 400, and 1000 mA g^{-1}, respectively. Notably, the specific capacity of the Li-O_2 battery with GPE is almost the same to that with GF-Li/T at the same current density, which indicates no significant compromise in electrochemical performances of Li-O_2 battery when replacing widely used GF-Li/T membrane with the new GPE separator, which is further confirmed by the cyclic voltammetry results of Li-O_2 battery with the GPE and GF-Li/T (Figure S5, Supporting Information). It is found that the GPE delivers good ionic conductivity (0.2843 m S cm^{-1} at 303 K) in contrast to GF-Li/T (1.5925 m S cm^{-1} at 303 K). In addition, the activation energy of GPE and GF-Li/T are calculated to be 11.11 and 9.26 KJ mol^{-1}, respectively (Figure 2g),[42] which further supports the above obtained results. Furthermore, the charging measurement demonstrates that the GPE is electrochemically stable and have no effect on electrochemical performance of Li-O_2 battery before liquid electrolyte decomposition (Figure S6, Supporting Information). All the above results demonstrate the suitability of GPE to be used to fabricate a cable-type flexible Li-O_2 battery.

To investigate their flexibility, the as-fabricated cable-type Li-O_2 batteries are intentionally bended and twisted into different shapes, including linear, arc-shaped, rounded, s-shaped, twisty and spiral. Interestingly, it can be found that red light-emitting diode display screen remain constantly powered under all the testing conditions (**Figure 3**a). Furthermore, the discharge curves of Li-O_2 battery with different shapes are not changed significantly at a current density of 100 mA g^{-1} (Figure 3b). All these results show the superior flexibility and electrochemical stability of the fabricated cable-type flexible Li-O_2 battery. To exclude the possible electrochemical contributions from intercalation reactions of Li^+ with GPE or GF-Li/T, the Li-O_2 battery with GPE and GF-Li/T are tested in pure argon atmosphere. Clearly, the background discharge capacity is negligible within the voltage range, which suggests that the above obtained discharge capacities of the Li-O_2 cells are derived from the oxygen reduction (Figure S7, Supporting Information).

Furthermore, to confirm whether the mechanical stress would degrade the electrochemical performance of cable-type flexible Li-O_2 battery, they are first repeated bended and stretched for thousands times and then are discharged/charged. Surprisingly, even after 4000 cycles of bending/stretching, the discharge–charge curve of the cable-type flexible battery keeps almost unchanged (Figure 3c), showing high mechanical stability of the cable-type Li-O_2 battery. Furthermore, the cable-type flexible Li-O_2 batteries with different lengths were assembled, and we found that the length has little effect on the electrochemical performances (Figure S8, Supporting Information). Unprecedentedly, the obtained cable-type flexible Li-O_2 battery can still works even they are partially immersed in water for more than 5 h (Figure 3d), demonstrating the water survivability of our

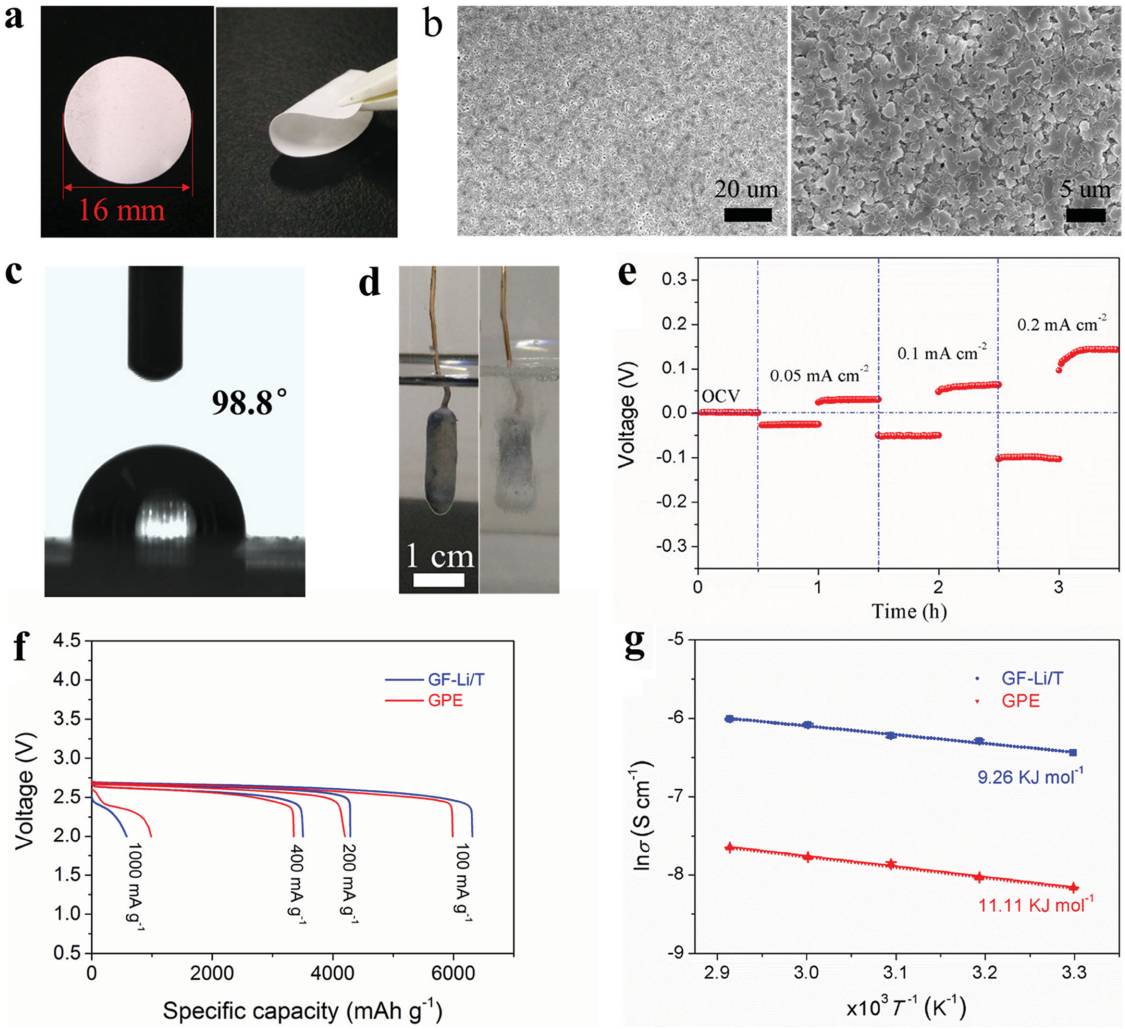

Figure 2. Optical photographs of the fabricated GPE at a) flat and bend conditions, and b) its corresponding SEM images and c) water contact angle. d) The photographs of Li rod immersed in water with (left) and without (right) the protection of the GPE membrane. e) Charge–discharge potential for the symmetric battery of Li/GPE/Li. f) Rate capability and g) ionic conductivity of the Li-O_2 batteries with GPE or glass fiber (GF-Li/T).

obtained flexible Li-O_2 battery, which further confirms that employment of the GPE is an effective strategy to protect the anode in water from serious corrosion and then would increase the safety of Li-O_2 battery.

Figure 4a presents the typical voltage profiles for Li-O_2 batteries with GPE and SP cathode cycled at a current density of 100 mA g^{-1} and a fixed capacity of 500 mAh g^{-1}. The voltage obtained at the discharge terminal of the Li-O_2 battery is above 2.0 V for more than 90 cycles (Figure 4b). In addition, the battery test with capacity limit of 1000 and 2000 mAh g^{-1} (Figure S9, Supporting Information), further corroborating the good cycling performance of the battery and the superior stability of GPE. The superior rechargeability of the flexible Li-O_2 battery with a GPE is examined by the powder X-ray diffraction technique. As shown in Figure 4c, only the characteristic peaks of Li_2O_2 at 32.9°, 35°, and 58.7° are observed after the first discharge, which are all disappeared after the subsequent recharge process, demonstrating the reversible formation/decomposition of Li_2O_2 on the SP cathode during cycling. In addition, we further investigate the compositions of the discharged products after 30 cycles. The characteristic peaks of Li_2O_2 in the obtained FTIR spectra are observed in the SP cathode (Figure S10, Supporting Information), although crystalline Li_2O_2 becomes barely visible and cannot be detected in XRD (Figure S11, Supporting Information), demonstrating the amorphous nature of Li_2O_2 formed in the SP cathode after 30 cycles, which is agree with the previous report.[35] Compared with Figure 4d, after the first galvanostatic discharged to 1 mA h capacity at a current density of 100 mA g^{-1}, toroidal products are found on the cathode with size of about 200 nm (Figure 4e), which is consistent with the reported results.[43–46] The discharge product decomposed during followed recharge process, and the hierarchically SP particles of the whole cathode are almost fully recovered (Figure 4f).

In conclusion, to endow Li-O_2 battery flexibility and thus the possibility to power the next-generation versatile flexible electronics, as a proof-of-concept experiment, we have proposed and fabricated a cable-type water-survivable flexible Li-O_2 battery. Unexpectedly, superior electrochemical performances including a high specific capacity, good rate capability, and cycling stability have been achieved under stringently

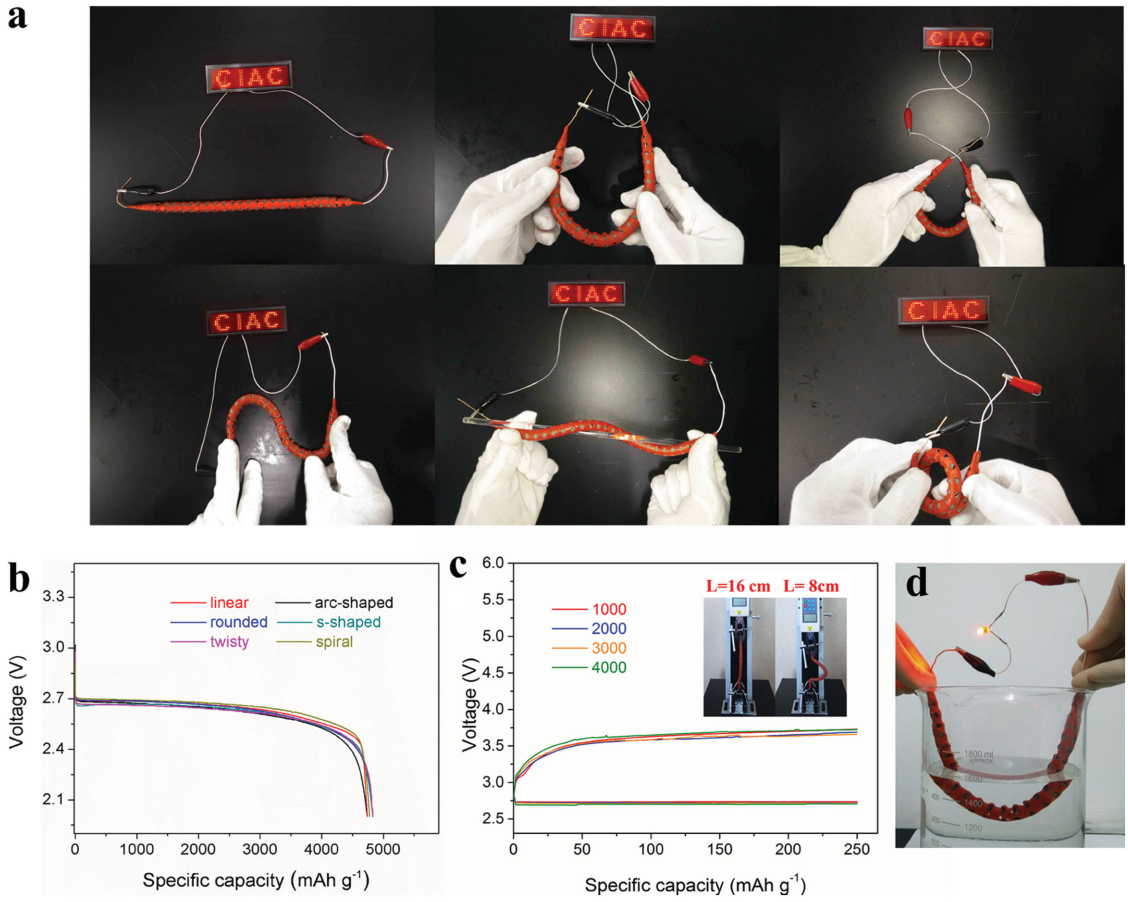

Figure 3. Cable-type flexible Li-O_2 battery powered a commercial red light-emitting diode display screen at a) various bended and twisted conditions, b) the corresponding discharge curves. c) Charge–discharge curves of cable-type flexible Li-O_2 battery after bended thousands of times. d) Cable-type flexible Li-O_2 battery powered a commercial red light-emitting diode immersed in water.

bended, twisted and even immersed in water conditions, which could be attributable to the a flexible cathode and especially the free standing GPE, holding high mechanical flexibility and electrochemical stability as well as high ionic conductivity, which could protect lithium from the corrosion of moisture. Undoubtedly, if the concept of cable-type

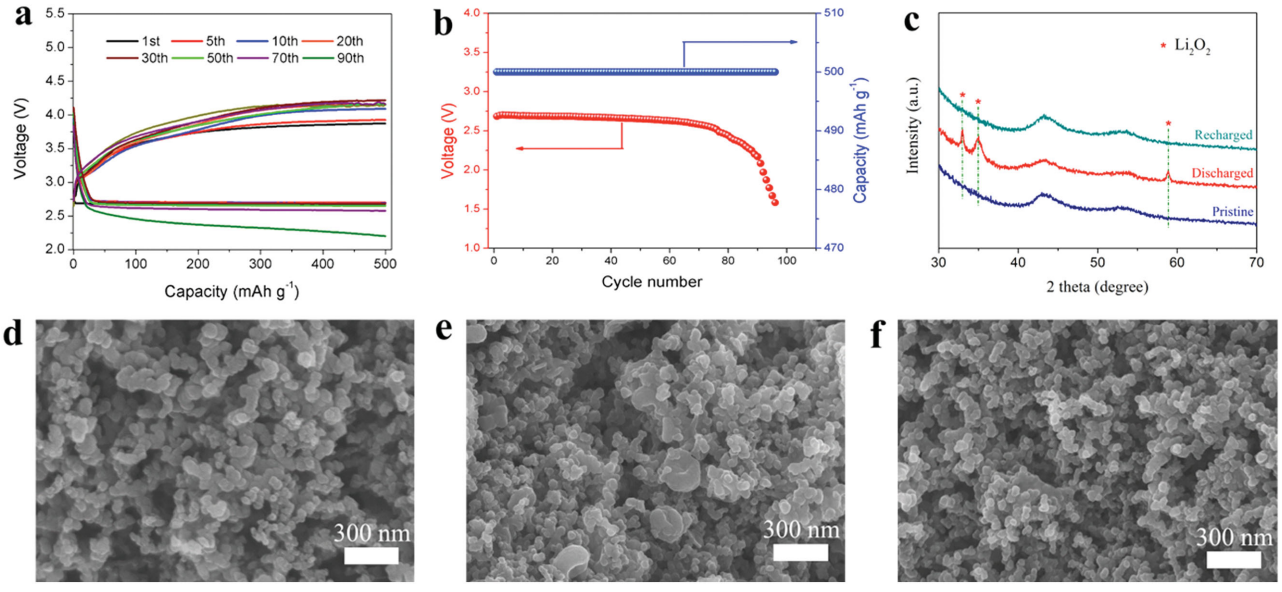

Figure 4. a) Charge–discharge curves of flexible Li-O_2 battery, b) the corresponding cycling performance. c) The XRD patterns of cathodes in different states. SEM images of d) the pristine, e) first discharged and f) first recharged SP cathode.

flexible Li-O_2 battery presented here is coupled with a more highly efficient cathode, the electrochemical performances could be significantly improved, which might assist the efforts to pave the way for the application of Li-O_2 for flexible electronics and inspire more studies on flexible Li-O_2 batteries and other flexible energy storage devices.

Supporting Information

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

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