

A Li-Air Battery with Ultralong Cycle Life in Ambient Air

Lie Wang, Jian Pan, Ye Zhang, Xunliang Cheng, Lianmei Liu, and Huisheng Peng*

The Li–air battery represents a promising power candidate for future electronics due to its extremely high energy density. However, the use of Li–air batteries is largely limited by their poor cyclability in ambient air. Herein, Li–air batteries with ultralong 610 cycles in ambient air are created by combination of low-density polyethylene film that prevents water erosion and gel electrolyte that contains a redox mediator of LiI. The low-density polyethylene film can restrain the side reactions of the discharge product of Li₂O₂ to Li₂CO₃ in ambient air, while the LiI can facilitate the electrochemical decomposition of Li₂O₂ during charging, which improves the reversibility of the Li–air battery. All the components of the Li–air battery are flexible, which is particularly desirable for portable and wearable electronic devices.

Flexible electronics have attracted intensive attention due to their advantages of being bendable, portable, and potentially wearable, which could lead to revolutions in a variety of fields, from consumer products to the automotive and aerospace industries and in medical treatment.^[1–4] To this end, it is urgent to make matching power systems with mechanical flexibility and high energy density. At present, Li-ion batteries have been thus widely studied to realize flexibility for the flexible electronic devices.^[5–7] However, the low theoretical energy densities of Li-ion batteries are unlikely to fully satisfy the rapidly developing flexible electronic devices that need more and more energy.^[8] Consequently, it is critical to develop an alternative to tackle the limitations of Li-ion batteries.

Rechargeable Li–air batteries have recently emerged as one of the most promising candidates owing to their much higher theoretical energy density of about 3500 W h kg⁻¹, which is 5–10 times higher than that of conventional Li-ion batteries.^[9–12] However, numerous problems of the current Li–air batteries have impeded their applications, especially the poor cycle life when the Li–air battery works in ambient air.^[13–15] The main reaction mechanism of Li–air batteries during discharging and charging is the reversible formation and decomposition of Li₂O₂ (2Li⁺ + O₂ + 2e⁻ \Rightarrow Li₂O₂, 2.96 V vs Li/Li⁺).^[16] Due to the solid and nonconductive Li₂O₂ discharge product, the interfacial resistance of the electrolyte, Li₂O₂, and the cathode would be increased during cycling, resulting in a large overcharge potential and low efficiency. The large overcharge potential can

L. Wang, J. Pan, Y. Zhang, Dr. X. Cheng, L. Liu, Prof. H. Peng State Key Laboratory of Molecular Engineering of Polymers Department of Macromolecular Science and Laboratory of Advanced Materials Fudan University Shanghai 200438, China E-mail: penghs@fudan.edu.cn

DOI: 10.1002/adma.201704378

also induce the oxidation decomposition of some components such as electrode and electrolyte. When it comes to the ambient air, water molecules in air can permeate through the air electrode to react with Li_2O_2 and generate LiOH, which then reacts with CO_2 to form Li_2CO_3 . Li_2CO_3 is more chemically stable than Li_2O_2 that gradually accumulates to accelerate the failure of the Li–air battery.^[17] Consequently, most previous studies focused on Li–air batteries that worked in pure oxygen atmosphere,^[18–22] which is supposed to be technically described as "Li– O_2 batteries" (Figure S1, Supporting Information).

Here, through the combination of a low-density polyethylene (LDPE) film to prevent water erosion and a gel electrolyte with LiI as a redox mediator (Figure S2, Supporting Information), we created a new family of Li–air batteries with an aligned carbon nanotube air electrode (Figure S3, Supporting Information). It was found that the LDPE film can restrain the side reactions of discharge product of Li_2O_2 to Li_2CO_3 in ambient air, while LiI can facilitate the electrochemical decomposition of Li_2O_2 during charging (Figure 1a). As a result, the Li–air battery showed a high cyclability up to 610 cycles in ambient air. Furthermore, all components were flexible, which offered the possibility to fabricate flexible fiber-shaped or strap-shaped Li–air batteries that were useful in portable and wearable electronics.

Figure S4 of the Supporting Information showed a photograph of LDPE film, which was ultrathin with a thickness of \approx 20 µm and exhibited a high flexibility (Figure S5, Supporting Information). Due to the nonpolar molecular structure, the LDPE film demonstrated a high selectivity for nonpolar O2 molecules while prevented polar moisture molecules. The O₂ and H₂O permeation experiments indicted that the LDPE film exhibited a high O₂ permeability of 40.3 Barrer and low H₂O permeability of 0.825 g m⁻² d⁻¹. The CO₂ permeability of the LDPE film was also measured, and a slight higher value of 157 Barrer than that of O₂ permeability had been detected. The O₂/H₂O selective permeability of the LDPE film was close to the previous O₂-selective membranes (Figure 1b), which can not only ensure sufficient oxygen supply during the electrochemical reaction in the Li-air battery, but also restrain the side reactions of transforming Li2O2 to Li2CO3 as they depended strongly on H₂O to take place or to be accelerated (Figure S6, Supporting Information).^[23] As shown in Figure S7 of the Supporting Information, two piles of Li2O2 powders with and without the package of LDPE film were placed in ambient air. After 3 d, the Li₂O₂ powder protected under LDPE film remained stable in ambient air, while the Li₂O₂ powder without protection turned into LiOH and Li₂CO₃ quickly (Figure 1c).

www.advancedsciencenews.com





Figure 1. a) Schematic illustration to the working mechanism of the redox mediator (RM) with (i) and without (ii) LDPE film in our Li–air battery operated in ambient air. b) Comparison of O_2 and H_2O permeability for the LDPE film and previous oxygen selective membranes shown at Table S1 of the Supporting Information. c) XRD patterns of pristine Li_2O_2 , Li_2O_2 with protection of LDPE film in ambient air after 3 d, and Li_2O_2 without protection of LDPE film in ambient air after 1 and 3 d.

We first compared the electrochemical performances of the Li–air battery with and without LiI in the presence of LDPE film in ambient air with a relative humidity of 50%. As shown in **Figure 2**a, the battery without LiI exhibited a high overcharge potential of ~1.5 V, while a lower value of ~0.4 V was observed in the presence of LiI. The overcharge potential during charging was nearly identical to the reaction potential of I⁻ to I₃⁻,^[21] demonstrating the smallest polarization to date when the Li–air battery was operated in ambient air. However, when the LDPE film was absent, the overcharge potential of the Li–air battery was slightly increased, which was attributed to the side reactions induced by the air. Therefore, the combination of LDPE film and LiI represent an efficient strategy to reduce the overcharge potential of the Li–air battery in ambient air.

As a consequence of the reduction of the overcharge potential, both the rate capability and cyclability were dramatically improved. As shown in Figure S8 of the Supporting Information, the current density was gradually increased from 500 to 4000 mA g^{-1} and the degree of polarization did not drastically increase, indicating that it can be steadily operated at a wide range of current densities. Figure S9 of the Supporting Information shows typical charge and discharge curves at a high current density of 2000 mA g^{-1} with a cutoff capacity of 1000 mAh g^{-1} , in which the specific capacity presented no decay and the discharge voltage remained almost unchanged over 325 cycles (Figure 2b). When the relative humidity was 5%, the cycle performance could be enhanced to 610 cycles (Figure 2c,d). In a sharp contrast, the Li–air batteries without LDPE film (Figure S10, Supporting Information) or LiI (Figure S11, Supporting Information) were unable to continuously cyclize for over 100 cycles in ambient air.

To compare the performance of our Li-air batteries with previous reports, we summarized the performance of Li-air batteries directly operated in ambient air (Figure 2e).[14,17,23-29] The previous Li-air batteries exhibited poor cycle life within 100 cycles. As one example, for a nonaqueous Li-air battery with dandelion-like NiCo2O4 hollow microspheres as cathode catalyst aiming to enhanced performance, it could only work for 40 cycles due to severe side reactions induced by air. As another example, for an Li-air battery with solid Li-ion conductor and gel cathode to improve the stability of the battery, although an increased cycle life of 100 cycles was observed, the overcharge potential reached as high as 2.0 V and the capacity decayed since the 30th cycle due to the accumulation of Li₂CO₃. In this work, the use of LDPE film can restrain the side reactions of discharge product of Li₂O₂ to Li₂CO₃ in ambient air, while LiI may enhance the decomposition of Li₂O₂ in a low overcharge potential of ≈ 0.4 V, which enabled a stable cycle performance of 610 cycles.

The reaction products of the Li–air battery after discharge and recharge process in ambient air were further investigated. As shown in **Figure 3**a, the cathode surface was homogenously coated with nanosheet-like discharge products, and they were all removed after the subsequent recharge process (Figure 3d).



a

С

www.advancedsciencenews.com





Figure 2. a) Discharge/charge curves and b) cycling performance of the Li-air battery under different conditions with current density of 2000 mA g⁻¹ in ambient air (relative humidity of \approx 50%). c) Discharge/charge curves and d) the corresponding cycling performance at current density of 2000 mA g⁻¹ in ambient air (relative humidity of ~5%). e) Comparison of cycle performance and overcharge potential for the Li-air battery in our study and previous Li-air batteries in ambient air (red five-pointed star: our results; the insert table: the other symbols for the previous reports).

The X-ray diffraction (XRD) characteristic peaks of Li2O2 at 32.9° and 35° were observed after the discharge process, and they all vanished after recharging (Figure 3g). After the 300th cycle, the formation and decomposition of Li₂O₂ discharge products in cathode were also observed (Figures S12 and S13, Supporting Information). These results indicated the main reaction product of Li₂O₂ and a high reversibility during recharging. However, when the Li-air batteries were fabricated without LDPE film, larger sizes of nanosheet-like discharge products were formed (Figure 3b), and they were incompletely removed after the recharge process (Figure 3e). Besides, the XRD results indicated that the discharge products were Li₂CO₃, not

www.advmat.de







Figure 3. a-f) SEM images of the air electrode after discharging (a-c) and recharging (d-f). g-i) XRD patterns of the air electrode after discharging and recharging. a,d,g) With LDPE and LiI; b,e,h) with Li but without LDPE; c,f,i) with LDPE but without LiI.

Li₂O₂, and the characteristic peaks of Li₂CO₃ also existed after recharging (Figure 3h). The X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy further confirmed the formation of Li₂CO₃ in the discharge process (Figures S14 and S15, Supporting Information). The Li₂CO₃ should be produced by the side reaction of Li₂O₂ with moisture and carbon dioxide from the air, which was difficult to be decomposed and considerably deteriorated the cycling life.^[23] On the other hand, when there was no LiI in the electrolyte, toroidal products were found on the cathode (Figure 3c), and the XRD results indicated that the products were only Li₂O₂ (Figure 3i). However, it was different for the Li-air batteries with LDPE film and LiI. The discharge products partly remained on the cathode (Figure 3f), and the characteristic peaks of Li₂CO₃ were detected after recharging (Figure 3i). The large overcharge potential (Figure 2a) can induce the side reaction of oxidation decomposition of electrode and electrolyte during Li₂O₂ oxidation, resulting in the formation of Li₂CO₃.^[30] The accumulation of Li₂CO₃ in the electrode leaded to electrode passivation and capacity fading on cycling.

Different from the previous Li–air batteries that operated in ambient air with solid and fragile electrolyte or cathode, all components in our Li–air batteries were flexible, which paved the way to realize flexible Li–air batteries. A flexible fiber-shaped Li–air battery was successfully demonstrated. **Figure 4**a and Figure S16 (Supporting Information) show the fabrication process and photograph of a flexible fiber-shaped Li–air battery, respectively. As shown in Figure 4b, the fiber-shaped Li–air battery exhibited a high flexibility, and the charge and the discharge curves were perfectly maintained after repeated bending for 1000 cycles. Furthermore, the Li-air battery was also monitored simultaneously when undergoing bending, and the voltage undulation was recorded to be less than 1% (Figure S17, Supporting Information). With the help of the waterproof LDPE film, the water survivability of the flexible fiber-shaped battery was also investigated (Figure 4c). The resulting fiber-shaped Li-air battery stably worked to power a yellow light-emitting diode (LED) even when it was partially immersed in water. Moreover, the charge and discharge curves were perfectly maintained after immersion, while the Li-air batteries without LDPE film were destroyed (Figure 4d). These results demonstrate that the LDPE film can efficiently improve the water survivability of the Li-air battery. These Li-air batteries are particularly promising for wearable applications. As a demonstration, six fibershaped Li-air batteries were integrated into clothes (Figure 4e) to effectively charge a smartphone (Figure 4f). Besides, a flexible strap-shaped Li-air battery (Figure S18a, Supporting Information) was also fabricated and designed as an "energetic strap" to power a watch worn on a human wrist (Figure S18b, Supporting Information).

In summary, we have demonstrated a general and effective strategy to solve the problem of poor cyclability for the Li–air battery in ambient air by combination of LDPE film that prevents water erosion and gel electrolyte that contains a redox mediator of LiI. The resulting Li–air battery showed an ultralong cycle life of 610 cycles in ambient air, which promoted



www.advancedsciencenews.com





Figure 4. a) Schematic illustration to the fabrication of the flexible fiber-shaped Li–air battery. b) Discharge/charge curves of a flexible fiber-shaped Li–air battery before and after bending for 500 and 1000 cycles. c) A flexible fiber-shaped Li–air battery being immersed in water to power a commercial yellow LED. Red arrow indicates the Li–air battery. d) Discharge/charge curves of the flexible fiber-shaped Li–air battery before and after immersion in water with and without LDPE film. e,f) Photographs of flexible fiber-shaped Li–air batteries being woven into clothes to charge a smartphone. Red dashed boxes indicate the Li–air batteries.

SCIENCE NEWS _____ www.advancedsciencenews.com

DVANCED



www.advmat.de

Li–air batteries to a great extent. All the components of the Li–air battery were flexible, which is particularly promising and demonstrated to make flexible fiber-shaped and strap-shaped Li–air batteries with high electrochemical properties. This work may open up a new direction in the development of high-performance batteries.

Supporting Information

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

Acknowledgements

This work was supported by the MOST (2016YFA0203302), the NSFC (21634003, 51573027, 51403038, 51673043, and 21604012), and the STCSM (16JC1400702, 15XD1500400, and 15JC1490200).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

ambient air, carbon nanotubes, fiber, flexible, lithium-air batteries

Received: August 3, 2017

Revised: September 16, 2017

Published online: December 1, 2017

- H. Lee, T. K. Choi, Y. B. Lee, H. R. Cho, R. Ghaffari, L. Wang, H. J. Choi, T. D. Chung, N. Lu, T. Hyeon, S. H. Choi, D. H. Kim, *Nat. Nanotechnol.* **2016**, *11*, 566.
- [2] C. Xie, J. Liu, T. M. Fu, X. Dai, W. Zhou, C. M. Lieber, Nat. Mater. 2015, 14, 1286.
- [3] Y. Zhang, Y. Zhao, J. Ren, H. Peng, Adv. Mater. 2016, 28, 4524.
- [4] Z. Zhang, Y. Zhang, Y. Li, H. Peng, Acta Polym. Sin. 2016, 10, 1284.
- [5] J.-S. Kim, D. Ko, D.-J. Yoo, D. Jung, C. T. Yavuz, N.-I. Kim, I.-S. Choi, J. Song, J. Choi, *Nano Lett.* **2015**, *15*, 2350.

- [6] Y.-H. Lee, J.-S. Kim, J. Noh, I. Lee, H. Kim, S. Choi, J. Seo, S. Jeon, T.-S. Kim, J.-Y. Lee, J. Choi, *Nano Lett.* **2013**, *13*, 5753.
- [7] S. Ahmad, D. Copic, C. George, M. Volder, Adv. Mater. 2016, 28, 6705.
- [8] P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J.-M. Tarascon, *Nat. Mater.* 2012, 11, 19.
- [9] Z. Jian, P. Liu, F. Li, P. He, X. Guo, M. Chen, H. Zhou, Angew. Chem., Int. Ed. 2014, 53, 442.
- [10] J. Xu, Q. Liu, Y. Yu, J. Wang, J. Yan, X. Zhang, Adv. Mater. 2017, 29, 1606552.
- [11] Q. Liu, L. Li, J. Xu, Z. Chang, D. Xu, Y. Yin, X. Yang, T. Liu, Y. Jiang, J. Yan, X. Zhang, Adv. Mater. 2015, 27, 8095.
- [12] Z. Guo, C. Li, J. Liu, Y. Wang, Y. Xia, Angew. Chem., Int. Ed. 2017, 129, 7613.
- [13] D. Geng, N. Ding, T. S. A. Hor, S. Chien, Z. Liu, D. Wuu, X. Sun, Y. Zong, Adv. Energy Mater. 2016, 6, 1502164.
- [14] L. Zou, Y. Jiang, J. Cheng, Y. Gong, B. Chi, J. Pu, L. Jian, *Electrochim. Acta* 2016, 216, 120.
- [15] W. Luo, X. Gao, S. Chou, J. Wang, H. Liu, Adv. Mater. 2015, 27, 6862.
- [16] D. Lee, H. Lee, Y.-J. Kim, J.-K. Park, H.-T. Kim, Adv. Mater. 2016, 28, 857.
- [17] X. B. Zhu, T. S. Zhao, Z. H. Wei, P. Tan, L. An, Energy Environ. Sci. 2015, 8, 3745.
- [18] Q. Liu, J. Xu, D. Xu, X. Zhang, Nat. Commun. 2015, 6, 7892.
- [19] X. Guo, P. Liu, J. Han, Y. Ito, A. Hirata, T. Fujita, M. Chen, Adv. Mater. 2015, 27, 6137.
- [20] B. Zhou, L. Guo, Y. Zhang, J. Wang, L. Ma, W.-H. Zhang, Z. Fu, Z. Peng, Adv. Mater. 2017, 29, 1701568.
- [21] H.-D. Lim, H. Song, J. Kim, H. Gwon, Y. Bae, K.-Y. Park, J. Hong, H. Kim, T. Kim, Y. Kim, X. Lepro, R. Ovalle-Robles, R. H. Baughman, K. Kang, Angew. Chem., Int. Ed. 2014, 53, 3926.
- [22] J. Han, G. Huang, Y. Ito, X. Guo, T. Fujita, P. Liu, A. Hirata, M. Chen, Adv. Energy Mater. 2017, 27, 1601933.
- [23] T. Zhang, H. Zhou, Angew. Chem., Int. Ed. 2012, 51, 11224.
- [24] Y. Shen, D. Sun, L. Yu, W. Zhang, Y. Shang, H. Tang, J. Wu, A. Cao, Y. Huang, *Carbon* 2013, 62, 288.
- [25] T. Zhang, H. Zhou, Nat. Commun. 2013, 4, 1817.
- [26] Y. Zhang, L. Wang, Z. Guo, Y. Xu, Y. Wang, H. Peng, Angew. Chem., Int. Ed. 2016, 55, 4487.
- [27] X. Wang, D. Zhu, M. Song, S. Cai, L. Zhang, Y. Chen, ACS Appl. Mater. Interfaces 2014, 6, 11204.
- [28] L. Cao, F. Lv, Y. Liu, W. Wang, Y. Huo, X. Fu, R. Sun, Z. Lu, Chem. Commun. 2015, 51, 4364.
- [29] J. Amici, C. Francia, J. Zeng, S. Bodoardo, N. Penazzi, J. Appl. Electrochem. 2016, 46, 617.
- [30] M. M. Ottakam Thotiyl, S. A. Freunberger, Z. Peng, P. G. Bruce, J. Am. Chem. Soc. 2013, 135, 494.