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A Flexible and Wearable Lithium–Oxygen Battery with Record Energy Density achieved by the Interlaced Architecture inspired by Bamboo Slips

*Qing-Chao Liu, Tong Liu, Da-Peng Liu, Zhong-Jun Li, Xin-Bo Zhang, and Yu Zhang**

Flexible electronics, being bendable, portable, foldable, and potentially wearable, are emerging and promising technologies for next-generation electronic devices that will revolutionize our daily lives.[1–6] However, well-matched flexible energy-storage/conversion devices are a key prerequisite to the widespread use of flexible electronics. On the other hand, due to their low theoretical energy density, currently available flexible power devices, including rechargeable lithium-ion batteries,[7–9] flexible solar cells,[10–13] and supercapacitors,[14–20] intrinsically fail to meet the requirements of next-generation flexible electronics. Fortunately, the emerging rechargeable lithium–oxygen (Li–O$_2$) battery may be an ideal candidate for flexible electronics applications due to its remarkable theoretical energy density, 3600 W h kg^{-1} ($2Li^+ + O_2 + 2e^- \leftrightharpoons Li_2O_2$, 2.96 V vs Li/Li$^+$), approximately 5–10 times higher than that of the state-of-the-art lithium-ion batteries.[21–32]

However, because Li–O$_2$ batteries are still in their infancy, while exciting progress has been made to improve their electrochemical performances, almost all studies are still based on and limited to a rigid bulk structure: a coin cell or the Swagelok design, where heavy and electrochemically inactive packing materials, such as stainless-steel shells or engineering plastic, are required to ensure tight contact among the anode, cathode, and separator inside the Li–O$_2$ battery, as well as to avoid leakage of the liquid electrolyte; these components account for the majority of the battery weight, and, thus, not only seriously decrease the energy density of a practical Li–O$_2$ battery, but also fail to satisfy the requirements of next-generation electronic devices, which are expected to be flexible and even wearable.

In response to these needs, in 2015, a Li–O$_2$ battery with a pouch-type structure using a flexible, free-standing, and recoverable cathode was proposed to achieve flexibility; however, this battery was neither stretchable nor wearable.[33,34] More importantly, fiber-shaped Li–O$_2$ batteries have been realized by designing a gel polymer electrolyte, an aligned carbon-nanotube-sheet air electrode, and a heat-shrinkable tube.[35] Although these attempts significantly improved the flexibility of the Li–O$_2$ battery, good wearability, especially together with high energy density, remains challenging due to many daunting obstacles: i) the assembly of a flexible Li–O$_2$ battery at present still requires an air-diffusion layer (nickel foam, steel mesh, etc.) and soft packaging fixation (aluminum soft packaging, shrinkable tube, etc.), greatly decreasing the energy density of the entire practical battery (currently, most reported Li–O$_2$-battery energy densities are based only on the weight of the cathode or even only on the weight of the catalyst); and ii) soft-package and cable-type batteries are still “stack-type” Li–O$_2$ batteries, limiting their application in practical wearable electronic devices. Therefore, development of novel battery components and a sophisticated battery structure design that avoids using packing materials while ensuring good flexibility and even wearability is highly desirable yet extremely challenging for achieving high-energy-density wearable Li–O$_2$ batteries.

Bamboo slips were invented thousands of years before the introduction of paper and were used by Chinese artists to express people’s feelings and emotions to convey knowledge and information from one generation to another. Interestingly, bamboo slips were fabricated using bamboo chips and hide ropes that can be rolled up easily. Inspired by the unique structure of Chinese bamboo slips, herein, as a proof-of-concept demonstration, we present for the first time a solution for fabricating flexible and wearable Li–O$_2$ batteries in a novel interlaced manner.

Figure 1 shows a sketch of the fabrication process for the flexible and wearable Li–O$_2$ battery, where fabricated anodes (Figure S1, Supporting Information) and air cathodes (Figure S2, Supporting Information) were woven togther, similar to the “bamboo chips” and “hide ropes” in bamboo slips. This assembly structure presents many advantages for flexible and wearable Li–O$_2$ batteries: i) the fabricated battery is similar to but surpasses bamboo slips in terms of rollability, as it can be rolled from any arbitrary direction, endowing this fabricated battery with excellent flexibility; ii) the woven structure also has a unique property of allowing gas access to the cathodes via both sides of the weave, endowing the fabricated battery with good gas breathability; iii) the anodes were protected by a polypropylene membrane and hydrophobic gel polymer electrolyte (GPE), avoiding the sudden hazards posed by moisture or even water, so that the assembled flexible and wearable Li–O$_2$ battery can operate even when immersed in water; iv) the tightly

Dr. Q.-C. Liu, T. Liu, Prof. X.-B. Zhang
State Key Laboratory of Rare Earth Resource Utilization
Changchun Institute of Applied Chemistry
Chinese Academy of Sciences
Changchun 130022, P. R. China
Dr. D.-P. Liu, Prof. Y. Zhang
Key Laboratory of Bio-Inspired Smart Interfacial Science
and Technology of Ministry of Education
School of Chemistry and Environment
Beihang University
Beijing 100191, P. R. China
E-mail: jade@buaa.edu.cn
Dr. Q.-C. Liu, Prof. Z.-J. Li
The College of Chemistry and Molecular Engineering
Zhengzhou 450001, P. R. China

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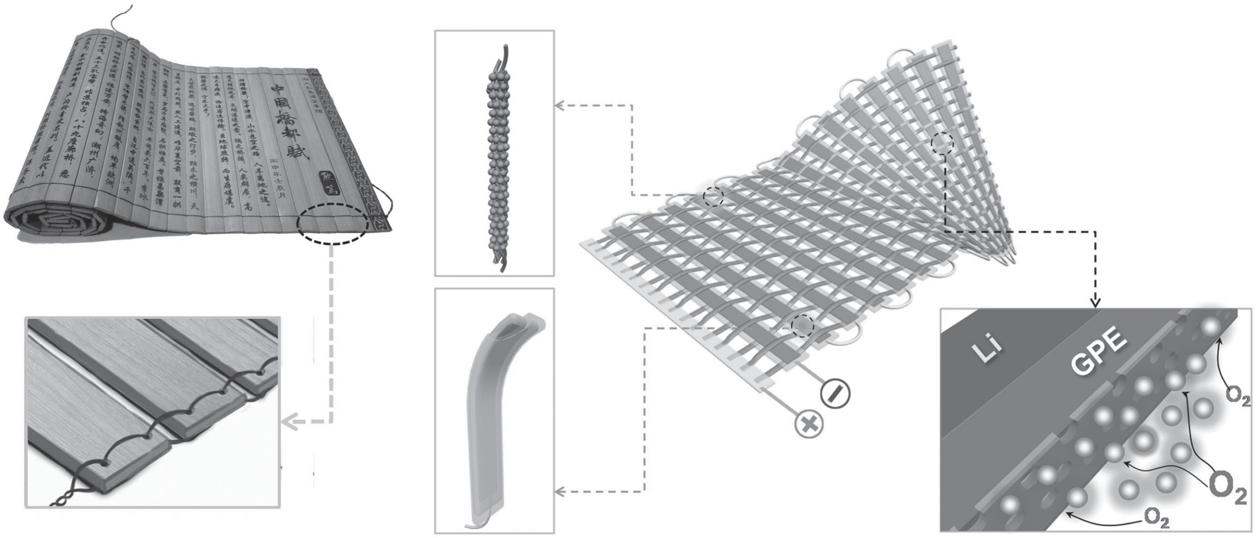

Figure 1. Inspired by the ancient bamboo slips, a flexible and wearable Li–O_2 battery was fabricated.

interwoven anodes and cathodes obviate the need for an air-diffusion layer and packaging fixation materials (these account for a major proportion of the conventional battery weight) so that the entire battery is free of packing materials and is composed only of an anode, a GPE, and an air cathode; thus, this approach can significantly improve the energy density of the entire practical Li–O_2 battery.

Figure 2a shows scanning electronic microscopy (SEM) (left) and optical (right) images of pristine carbon wire consisting of carbon fiber with a diameter of approximately 5 µm and forming macroporous structures that can promote mass transfer in the electrochemical-reaction process. Super P (SP) was coated on the carbon wire, forming a flexible air cathode,[34] and carbon nanoparticles (SP) with a size of approximately 50 nm were uniformly coated on the carbon fiber without affecting the flexibility of the carbon wire (Figure 2b). Prior to the fabrication of the anode, we characterized the synthesized GPE, which exhibits excellent bendability and mechanical stability, as shown in Figure 2c. The SEM image shows that the GPE is porous and that the interconnected pores provide sufficient channels to transfer lithium ions freely between the cathode and the anode, ensuring the uniform reactant distributions required for

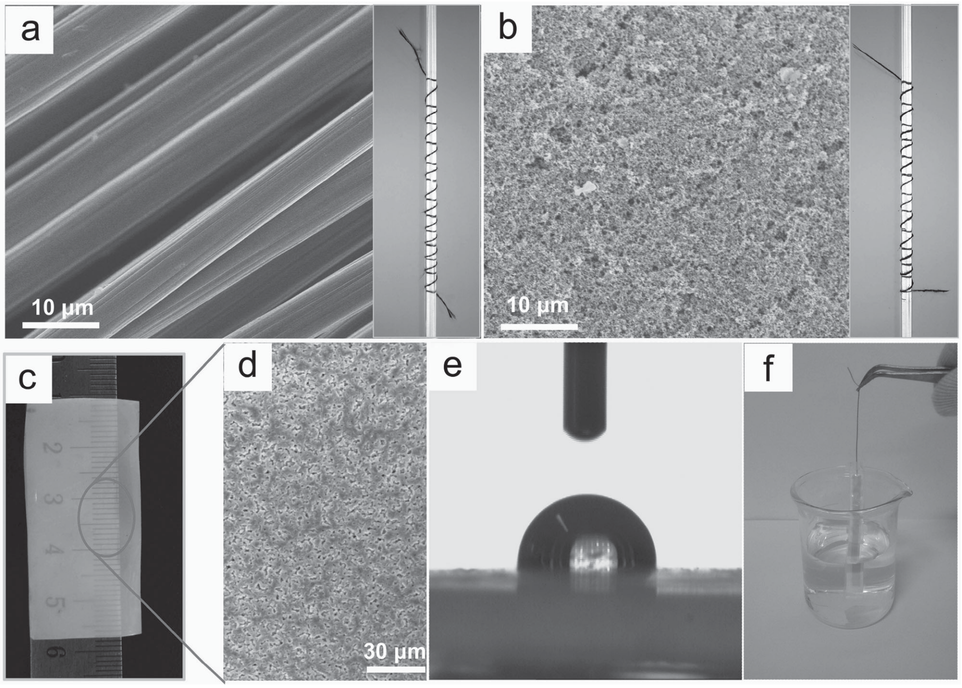

Figure 2. SEM and optial images of pristine carbon wire (a) coated with carbon nanoparticles (b). c,d) Optical photograph (c) the fabricated membrane and its corresponding SEM image (d); e) the water contact angle; and f) photograph of a Li anode immersed in water.

the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) during the discharge and charge processes of the Li–O_2 battery, respectively (Figure 2d). To test the hydrophobicity of the obtained GPE, the contact angles of water droplets were measured and were found to be 97.7° (Figure 2e), effectively preventing the penetration of moisture and thus protecting the lithium anode from corrosion. Additionally, the fabricated GPE also delivers a good ionic conductivity that guarantees the transport of lithium ions between the cathode and anode (Figure S3, Supporting Information). For the fabrication of the anode, a lithium belt with a width of 4 mm and a length of 100 mm was encapsulated into a polypropylene membrane and was then injected into a polymer electrolyte precursor solution. We then exposed to UV-irradiation for several minutes and obtained the integrated and protected anode (Figure S2, Supporting Information). The assembled anode showed very steady behavior in air (Figure S4, Supporting Information) and (Figure 2f). These properties endow the fabricated Li–O_2 battery with durability against moisture.

Figure 3a schematically shows the cross section of the fabricated battery and the mechanism of electrochemical growth of Li_2O_2 that has been reported in many other studies.[36,37] Furthermore, due to the crisscross weave, the cathodes and anodes can tightly press each other and do not need extra components to provide pressure for the battery, thus improving the energy density (vide infra). Although the fabricated flexible and wearable Li–O_2 battery exhibits numerous advantages, as discussed above, the electrochemical performance of this battery must be evaluated. To exclude possible electrochemical contributions from intercalation or/and conversion reactions with the cathode, the cell is discharged in pure argon atmosphere, and a negligible capacity is found (12.8 mA h g^{-1}) (Figure S5, Supporting Information), demonstrating that the electrochemical capacity is derived from the Li–O_2 battery catalytic reaction.[38] The rate performance is also tested, as shown in Figure 3b, and it was found that the discharge capacity of the cell could achieve as high as 8200 mA h g^{-1} with a current density of 100 mA g^{-1}; even when the current density was increased to 800 mA g^{-1}, a discharge capacity over 1000 mA h g^{-1} could still be obtained. Figure 3c presents the typical discharge–charge curves for the flexible and wearable Li–O_2 battery cycled at a current density of 200 mA g^{-1}, with the capacity limited to 500 mA h g^{-1}. The terminal voltage obtained at the discharged Li–O_2 battery was above 2.0 V for more than 100 cycles (Figure 3d). The morphology variation of the cathode was then tracked and compared with the pristine cathode (Figure 3e); toroidal products with a size of approximately 500 nm are found on the cathode after the initial discharge (Figure 3f); this morphology has been reported in many other studies.[39–44] The X-ray diffraction (XRD) technique was then employed to identify the discharge products of the Li–O_2 battery. Compared to the XRD pattern of the pristine cathode, new diffraction peaks at 32.9°, 35°, and 58.7° emerged (Figure 3g) that could be assigned to the (100), (101), and (110) signals of Li_2O_2, respectively, showing that Li_2O_2 dominates the discharge product.

To demonstrate its potential application in flexible electronics, the as-fabricated flexible and wearable Li–O_2 battery was used to power a commercial red-light-emitting diode in various bending and twisting conditions (**Figure** 4a–f); it was found that the fabricated Li–O_2 battery can not only be rolled up as easily as bamboo slips (Figure 4a–d) but it can also be folded along other directions (Figure 4e,f), meaning that the fabricated battery realizes flexible and wearable functions. Furthermore, we tracked the discharge curves of the Li–O_2 battery with different shapes, as shown in Figure 4g, and found that the discharge capacity was hardly influenced; additionally, the mean discharge voltage of the devices after bending and twisting was also only slightly influenced (Figure 4h). Unprecedentedly, the obtained flexible and wearable Li–O_2 battery can still work even when it was partially immersed in

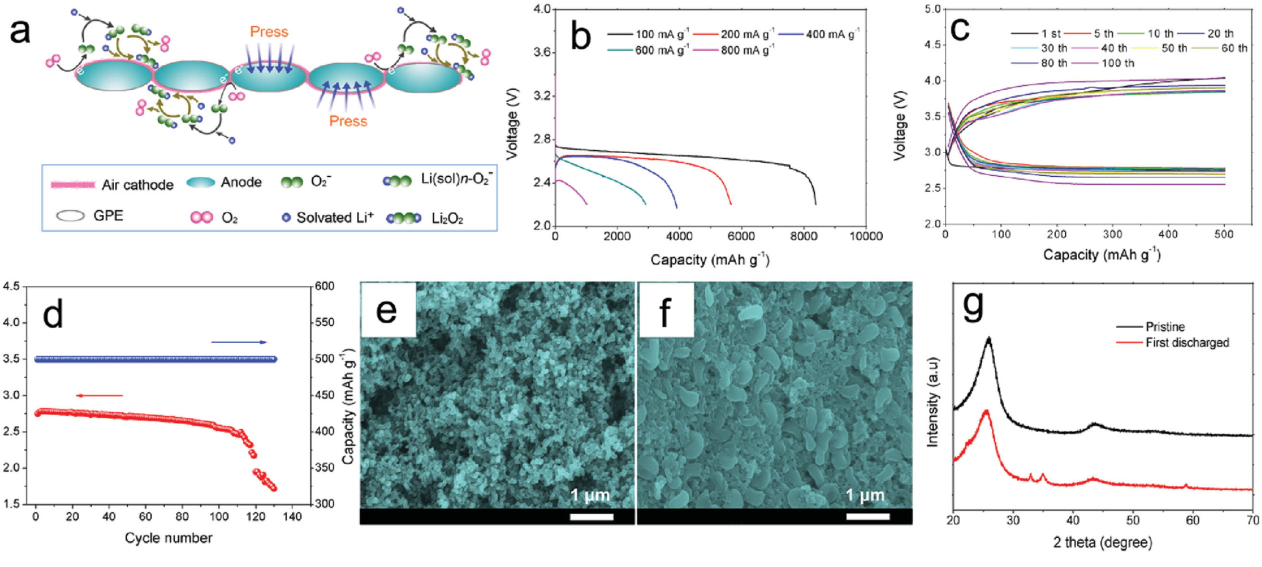

Figure 3. a) Schematic diagram of the discharge/charge process mechanism; b) rate performance of the flexible and wearable Li–O_2 battery; c,d) discharge–charge curves (c) and cycling performance (d) of the flexible and wearable lithium–oxygen battery; e–g) SEM images (e,f) and XRD patterns (g) of the carbon wire cathode with pristine and initially discharged conditions.

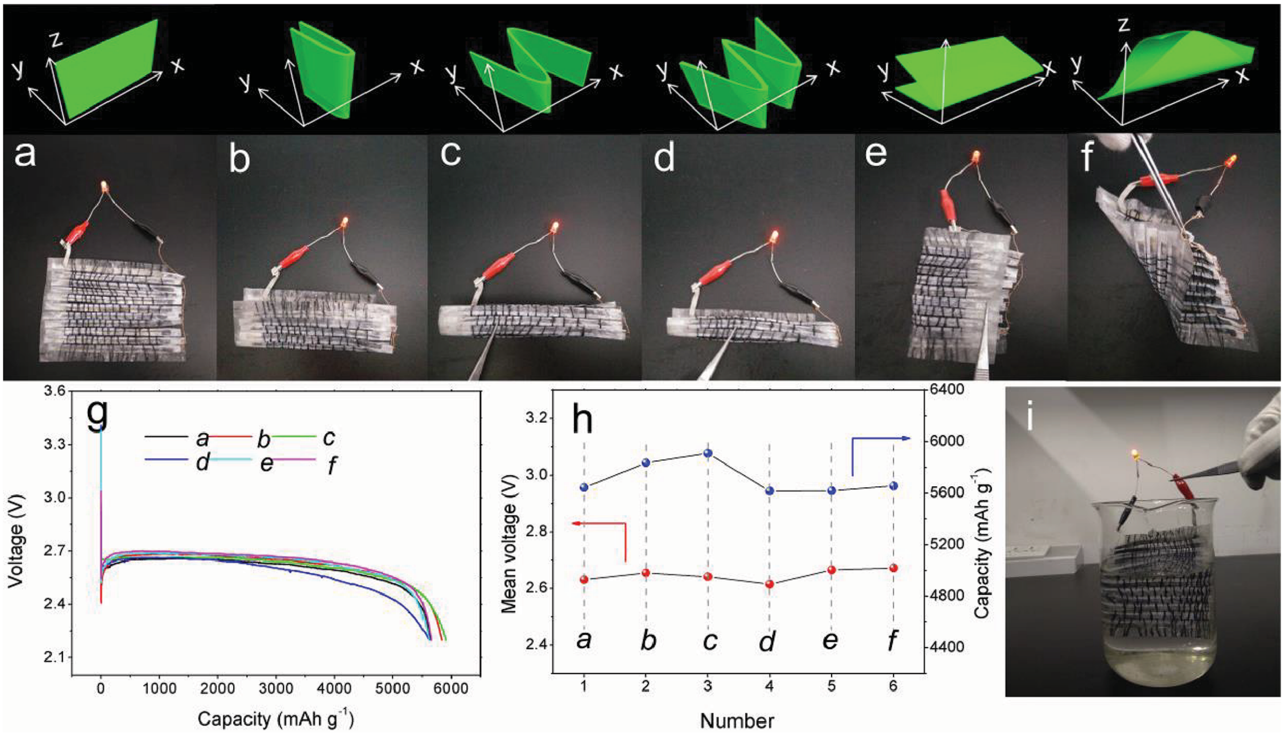

Figure 4. a–f) Optical images of the fabricated flexible and wearable Li–O_2 battery powering a commercial red-light-emitting diode under various bending and twisting conditions. g) First discharge curves of the flexible and wearable Li–O_2 battery under various bending and twisting conditions. h) The contradistinction of mean discharge voltage and discharge capacity of the flexible and wearable Li–O_2 battery under various bending and twisting conditions. i) The flexible and wearable Li–O_2 battery powered a commercial red-light-emitting diode immersed in water.

water (Figure 4i), demonstrating the water survivability of our obtained battery, further confirming that the use of the GPE is an effective strategy to protect the anode even of the fabricated battery in water from serious hazard; this increases the safety of the Li–O_2 battery.

As described above, the assembled Li–O_2 battery possesses many advantages: a novel battery structure, good security features, and excellent electrochemical performance. For its application in the future, the energy density of this type of Li–O_2 battery must be evaluated. In this work, the total mass of the fabricated Li–O_2 battery is 3.091 g, meaning that the energy density of this battery can be as high as 523.1 W h kg^{-1}, as displayed in **Figure 5**a, which is far beyond the values of commonly commercial Li-ion batteries;[45] however, there is still a very long way to go to reach this theoretical value. This high energy density mainly derives from its assembly structure by avoiding bulky and rigid air-diffusion layers and packaging fixation materials. To further highlight the energy-density advantage of the flexible and wearable Li–O_2 battery, another three Li–O_2 battery types, coin-type, cable-type, and soft packages, were

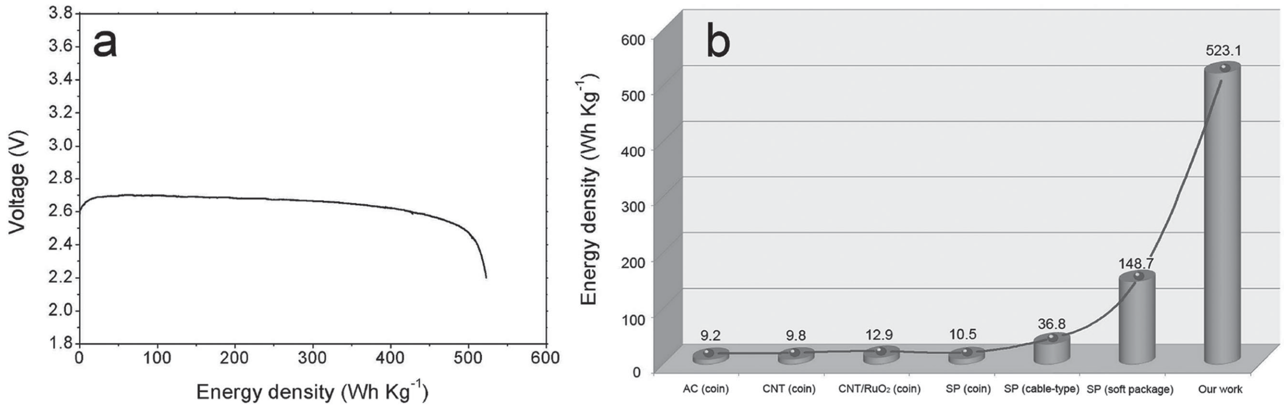

Figure 5. a) Discharge voltage versus energy density and b) a rough comparison of energy densities with various types of Li–O_2 battery based on the discharge curve.

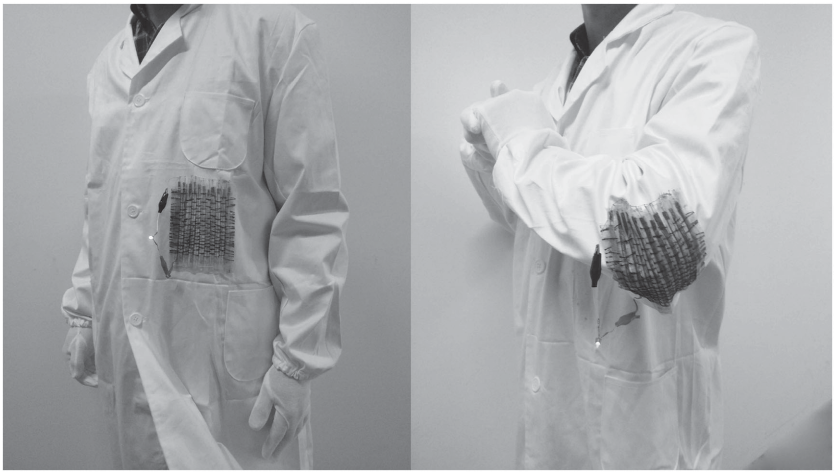

Figure 6. Photographs of the fabricated flexible and wearable Li–O_2 battery integrated with clothes.

also fabricated, and their corresponding energy-density values are listed in Figure 5b. The active materials used in this work are acetylene carbon (AC), carbon nanotubes (CNT), carbon nanotube/RuO_2 (CNT/RuO_2), and Super P (SP). It was found that the energy density of the coin type with AC, CNT, CNT/RuO_2, and SP as active materials is very low, despite the very high specific capacity based on the active material (Figure S6, Supporting Information). Additionally, flexible Li–O_2 batteries with cable-type and soft package were also assembled following a fabrication procedure similar to those reported in the current literature;[33–35] while the energy densities of both batteries were improved; however, even the improved energy density value is still far from satisfactory. The most fundamental reason for the low energy density of these batteries, including the coin-type, cable-type, and soft package batteries, is that an air-diffusion layer and packaging fixation materials are required due to the limitation of the battery structure, accounting for the majority of the battery weight; in contrast, our newly designed flexible and wearable Li–O_2 battery developed in this work is free of packing materials and an air-diffusion layer.

To demonstrate the practicability of this fabricated flexible and wearable Li–O_2 battery, here, we integrated this battery on clothes, as shown in **Figure 6**, with the battery running normally, regardless of whether it was placed under the chest or elbow joint. Furthermore, when the elbow joint was moved, the performance of the battery was not affected. The combination of the features described above may enable practical wearable flexible electronics.

In conclusion, for the first time, inspired by bamboo slips, a flexible and wearable Li–O_2 battery was assembled; in contrast to the traditional assembly manner (stack-type), the cathodes and anodes were crisscross-woven, enabling them to press against each other and eliminate the need for other components to provide pressure to ensure the normal operation of the battery, inevitably improving the energy density and, thus, the possibility of powering next-generation versatile flexible electronics. Due to its assembly method, this fabricated Li–O_2 battery is more suitable for "wearable" applications than other flexible Li–O_2 batteries in previous reports and brings us closer to the realization of wearable electronics. Although the woven assembly method was first introduced in the Li–O_2 battery field, the electrochemical performance characteristics, including specific capacity, rate capability, and cycling performance, were not influenced even when the battery was in various bending and twisting conditions. Furthermore, the GPE used in this work also endows this flexible and wearable Li–O_2 battery with water-survival properties, ensuring safety when the battery is operated under a moist atmosphere. Unexpectedly, a record energy density of over 523 W h kg^{-1} is achieved for the flexible and wearable Li–O_2 battery, which is 2–3 times higher of that of state-of-the-art lithium-ion batteries. It should be noted that the active material used in this work is commercial SP; therefore, if the proposed concept of a flexible and wearable of Li–O_2 battery presented in this work is coupled with a more efficient cathode, the electrochemical performance characteristics of this battery may be significantly improved, and the high energy and density wearable storage devices will be closer to use in our daily lives.

Supporting Information

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

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[1] J. A. Rogers, T. Someya, Y. G. Huang, *Science* **2010**, *327*, 1603.
[2] L. Hu, Y. Cui, *Energy Environ. Sci.* **2012**, *5*, 6423.
[3] M. F. L. De Volder, S. H. Tawfick, R. H. Baughman, A. J. Hart, *Science* **2013**, *339*, 535.
[4] L. Li, L. Z. Wu, S. Yuan, X. Zhang, *Energy Environ. Sci.* **2014**, *7*, 2101.
[5] G. Zhou, F. Li, H. H. Cheng, *Energy Environ. Sci.* **2014**, *7*, 1307.
[6] X. Wang, X. Lu, B. Liu, D. Chen, Y. Tong, G. Shen, *Adv. Mater.* **2014**, *26*, 4763.
[7] B. Liu, J. Zhang, X. F. Wang, G. Chen, D. Chen, C. W. Zhou, G. Z. Shen, *Nano Lett.* **2012**, *12*, 3005.
[8] S. Xu, Y. Zhang, J. Cho, J. Lee, X. Huang, L. Jia, J. A. Fan, Y. Su, J. Su, H. Zhang, H. Cheng, B. Lu, C. Yu, C. Chuang, T.-I. Kim, T. Song, K. Shigeta, S. Kang, C. Dagdeviren, I. Petrov, P. V. Braun, Y. Huang, U. Paik, J. A. Rogers, *Nat. Commun.* **2013**, *4*, 1543.
[9] K.-H. Choi, S.-J. Cho, S.-H. Kim, Y. H. Kwon, J. Y. Kim, S.-Y. Lee, *Adv. Funct. Mater.* **2014**, *24*, 44.

[10] Z. K. Liu, J. H. Li, F. Yan, *Adv. Mater.* **2013**, *25*, 4296.
[11] D. J. Lipomi, B. C.-K. Tee, M. Vosgueritchian, Z. N. Bao, *Adv. Mater.* **2011**, *23*, 1771.
[12] M. Kaltenbrunner, M. S. White, E. D. Głowacki, T. Sekitani, T. Someya, N. S. Sariciftci, S. Bauer, *Nat. Commun.* **2012**, *3*, 770.
[13] Y. H. Lee, J. S. Kim, J. Noh, I. Lee, H. J. Kim, S. Choi, J. Seo, S. Jeon, T. S. Kim, J. Y. Lee, J. W. Choi, *Nano Lett.* **2013**, *13*, 5753.
[14] Y. N. Meng, Y. Zhao, C. G. Hu, H. H. Cheng, Y. Hu, Z. P. Zhang, G. Q. Shi, L. T. Qu, *Adv. Mater.* **2013**, *25*, 2326.
[15] L.-F. Chen, Z.-H. Huang, H.-W. Liang, Q.-F. Guan, S.-H. Yu, *Adv. Mater.* **2013**, *25*, 4746.
[16] N. S. Liu, W. Z. Ma, J. Y. Tao, X. H. Zhang, J. Su, L. Y. Li, C. X. Yang, Y. H. Gao, D. Golberg, Y. Bando, *Adv. Mater.* **2013**, *25*, 4925.
[17] W. Gao, N. Singh, L. Song, Z. Liu, A. L. M. Reddy, L. Ci, R. Vajtai, Q. Zhang, B. Q. Wei, P. M. Ajayan, *Nat. Nanotechnol.* **2011**, *6*, 496.
[18] Y. N. Meng, K. Wang, Y. J. Zhang, Z. X. Wei, *Adv. Mater.* **2013**, *25*, 6985.
[19] X. H. Lu, M. H. Yu, G. M. Wang, T. Zhai, S. L. Xie, Y. C. Ling, Y. X. Tong, Y. Li, *Adv. Mater.* **2013**, *25*, 267.
[20] X. H. Lu, T. Zhai, X. H. Zhang, Y. Q. Shen, L. Y. Yuan, B. Hu, L. Gong, J. Chen, Y. H. Gao, J. Zhou, Y. X. Tong, Z. L. Wang, *Adv. Mater.* **2012**, *24*, 938.
[21] G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson, W. Wilcke, *J. Phys. Chem. Lett.* **2010**, *1*, 2193.
[22] F. J. Li, T. Zhang, H. S. Zhou, *Energy Environ. Sci.* **2013**, *6*, 1125.
[23] P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J. M. Tarascon, *Nat. Mater.* **2012**, *11*, 29.
[24] Y. C. Lu, B. M. Gallant, D. G. Kwabi, J. R. Harding, R. R. Mitchell, M. S. Whittingham, Y. Shao-Horn, *Energy Environ. Sci.* **2013**, *6*, 750.
[25] S. H. Oh, L. F. Nazar, *Adv. Energy Mater.* **2012**, *2*, 903.
[26] Z. L. Wang, D. Xu, J. J. Xu, X. B. Zhang, *Chem. Soc. Rev.* **2014**, *43*, 7746.
[27] B. Sun, X. Huang, S. Chen, P. Munroe, G. Wang, *Nano Lett.* **2014**, *14*, 3145.
[28] J. Liu, M. N. Banis, Q. Sun, A. Lushington, R. Li, T. K. Sham, X. Sun, *Adv. Mater.* **2014**, *26*, 6358.
[29] L. Zhao, X. Yu, J. Yu, Y. Zhou, S. N. Ehrlich, Y.-S. Hu, D. Su, H. Li, X.-Q. Yang, L. Chen, *Adv. Funct. Mater.* **2014**, *24*, 5557.
[30] L. Shen, E. Uchaker, X. Zhang, G. Cao, *Adv. Mater.* **2012**, *24*, 6502.
[31] W. Ai, Z. M. Luo, J. Jiang, J. H. Zhu, Z. Z. Du, Z. X. Fan, L. H. Xie, H. Zhang, W. Huang, T. Yu, *Adv. Mater.* **2014**, *26*, 6186.
[32] F. X. Ma, H. Hu, H. B. Wu, C. Y. Xu, Z. C. Xu, L. Zhen, X. W. Lou, *Adv. Mater.* **2015**, *27*, 4097.
[33] Q. C. Liu, Z. J. J. Xu, D. Xu, X.-B. Zhang, *Nat. Commun.* **2015**, *6*, 7892.
[34] Q. C. Liu, L. Li, J. J. Xu, Z. W. Chang, D. Xu, Y. B. Yin, X. Y. Yang, T. Liu, Y. S. Jiang, J. M. Yan, X. B. Zhang, *Adv. Mater.* **2015**, *27*, 8095.
[35] Y. Zhang, L. Wang, Z. Y. Guo, Y. F. Xu, Y. G. Wang, H. S. Peng, *Angew. Chem., Int. Ed.* **2016**, *55*, 4487.
[36] S. H. Oh, R. Black, E. Pomerantseva, J. H. Lee, L. F. Nazar, *Nat. Chem.* **2012**, *4*, 1004.
[37] J.-J. Xu, Z.-L. Wang, D. Xu, L.-L. Zhang, X.-B. Zhang, *Nat. Commun.* **2013**, *4*, 2438.
[38] Z.-L. Wang, D. Xu, J.-J. Xu, L.-L. Zhang, X.-B. Zhang, *Adv. Funct. Mater.* **2012**, *22*, 3699.
[39] Y.-C. Lu, D. G. Kwabi, K. P. C. Yao, J. R. Harding, J. Zhou, L. Zuin, Y. Shao-Horn, *Energy Environ. Sci.* **2011**, *4*, 2999.
[40] R. Black, S. H. Oh, J. H. Lee, T. Yim, B. Adams, L. F. Nazar, *J. Am. Chem. Soc.* **2012**, *134*, 2902.
[41] B. D. Adams, C. Radtke, R. Black, M. L. Trudeau, K. Zaghib, L. F. Nazar, *Energy Environ. Sci.* **2013**, *6*, 1772.
[42] R. R. Mitchell, B. M. Gallant, Y. Shao-Horn, C. V. Thompson, *J. Phys. Chem. Lett.* **2013**, *4*, 1060.
[43] E. Yilmaz, C. Yogi, K. Yamanaka, T. Ohta, H. R. Byon, *Nano Lett.* **2013**, *13*, 4679.
[44] R. Black, J. H. Lee, B. Adams, C. A. Mims, L. F. Nazar, *Angew. Chem., Int. Ed.* **2013**, *52*, 392.
[45] N. Mahmood, T. Y. Tang, Y. L. Hou, *Adv. Energy Mater.* DOI: 10.1002/aenm.201600374.