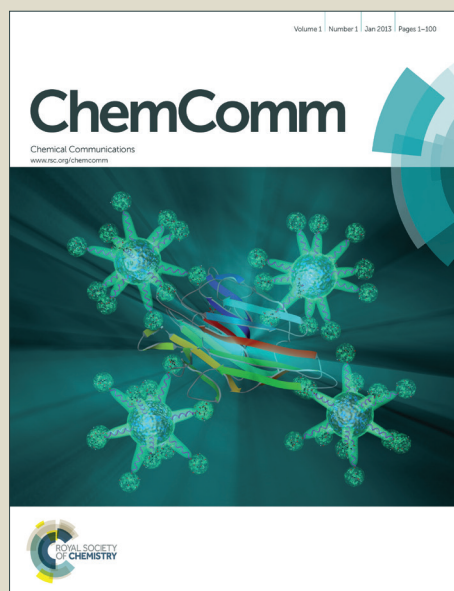


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COMMUNICATION

Lithium Air Battery with a Lithiated Al/Carbon Anode[†]

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A lithiated Al/carbon composite electrode with a uniform SEI film was prepared by electrochemical method, and was then coupled with an O₂ catalytic electrode to form a rechargeable Li-O₂ (or air) battery with a Li_xAl/C anode.

Rechargeable non-aqueous Li-O₂ batteries have recently attracted extensive attention because they can theoretically store 5–10 times more energy than current Li-ion batteries.¹ A typical rechargeable non-aqueous Li-O₂ battery theoretically exhibits a high energy density of 3552 Wh kg⁻¹ that is even compatible with that of gasoline.¹ Therefore, Li-O₂ system is being considered as the most promising choice for future energy storage technology.

Despite such great potential mentioned above, there are still many challenges before practical applications can be contemplated. The terribly sluggish oxygen reduction/evolution reaction (ORR/OER) kinetics not only increases the overpotential, but also causes pitiful rechargeability and low rate capability.¹ Furthermore, conventional Li-ion electrolyte solutions, such as organic carbonates, cannot be used in lithium-O₂ batteries because they decompose, leading to the rapid decay of the battery performance.² Accordingly, extensive efforts have been made to develop highly effective O₂ catalytic cathodes coupled with stable electrolytes for high performance rechargeable Li-O₂ batteries, and thus some promising results have been achieved very recently.^{3–9} However, besides these challenges from cathode, there are also a lot of obstacles in the metallic Li-anode for developing Li-O₂ system. These obstacles from Li-anode can be summarized as: 1) the issue of dendritic Li growth on anode still exists in rechargeable Li-O₂ batteries. 2) In Li-O₂ batteries, the presence of O₂ inevitably results in the passivation of metallic Li-anode,⁸ which may also aggravate the polarization. 3) It is undoubted that the ultimate target for developing Li-O₂ batteries should be Li-air batteries which can breathe O₂ from environment. Only through this way, Li-O₂ couples could realize the high theoretical energy density that is even compatible with that of gasoline. However, almost all these reported “rechargeable Li-O₂ (or air) batteries” employed dry and pure O₂ as active material, because it is a huge challenge to prevent “O₂+N₂+H₂O” from attacking on Li-anode. Owing to these obstacles mentioned above, it should be necessary to develop promising alternative anode materials for

present rechargeable Li-O₂ system. Unfortunately, up to present, this topic is still rarely investigated. Only recently, Scrosati *et al.* developed a Li-ion oxygen battery by using lithiated Si as anode.^{8a}

In present work, we use a lithiated Al/carbon (Li_xAl/C) composite electrode with a uniform SEI film to fabricate Li-O₂ (or air) battery, and investigated its performance in comparison with the Li-O₂ (or air) battery with a metallic Li-anode. It was demonstrated that when dry O₂ was applied as cathodic active material, the Li-O₂ battery with a Li_xAl/C anode exhibits lower voltage gap between charge/discharge than the Li-O₂ battery with a Li-anode. When ambient air with a limited humidity was used as cathodic active material, Li-air battery with a Li_xAl/C anode displays better cycling performance than the Li-air battery with a Li-anode.

Before fabricating the Li-O₂ battery with a Li_xAl/C anode, we investigated the Li-storage performance of the Al/carbon (Al/C) composite electrode (Fig. S1, the preparation of Al/C composite electrode is shown in the ESI[†]). It can be detected from Fig. S1 that the lithiated Al/C electrode can be considered as the anode alternative to metallic Li-anode for Li-O₂ battery system. Herein, we coupled the resulting lithiated Al/carbon (Li_xAl/C) composite electrode and a carbon-based O₂ catalytic electrode in a tetra(ethylene) glycol dimethyl ether–LiN(CF₃SO₂)₂ (TEGDME–LiTFSI) electrolyte to form a Li-O₂ battery (The preparation of Li-O₂ (or air) battery with a Li_xAl/C anode is shown in the ESI[†]). At the same time, we also use metallic Li-anode to prepare a Li-O₂ battery with the same O₂ catalytic electrode using TEGDME–LiTFSI electrolyte. Fig. 1 presents typical voltage profiles for the Li-O₂ battery with a Li_xAl/C anode and the Li-O₂ battery with a Li-anode cycled at a current density of 100 mA g⁻¹ and at a fixed capacity of 1000 mAh g⁻¹. As shown in Fig. 1a, the discharge/charge voltage profiles of the Li-O₂ battery with a Li_xAl/C anode are reproducible, with no sign of deterioration over 20 cycles, indicating a good cycling performance. The Li₂O₂/O₂ conversion in the battery was demonstrated over discharge/charge process (Fig. S2, ESI[†]). Similarly, the Li-O₂ battery with a Li-anode also keeps very stable discharge/charge profiles over 20 cycles (Fig. 1b). The voltage gap (ΔV) of a rechargeable battery between charge voltage (V_{charge}) and discharge voltage ($V_{discharge}$) can be summarized as:

$$\Delta V = V_{\text{Charge}} - V_{\text{discharge}} = (E_{\text{O}}^{\text{C}} - E_{\text{R}}^{\text{A}}) - (E_{\text{R}}^{\text{C}} - E_{\text{O}}^{\text{A}}) = (E_{\text{O}}^{\text{C}} - E_{\text{R}}^{\text{C}}) + (E_{\text{O}}^{\text{A}} - E_{\text{R}}^{\text{A}}) \quad (1)$$

Where, E_{O}^{C} , E_{R}^{C} , E_{O}^{A} and E_{R}^{A} are the oxidation potential (V) of cathode, the reduction potential (V) of cathode, the oxidation potential (V) of anode and the reduction potential (V) of anode, respectively. Obviously, the both batteries should display the same potential polarizations in cathode [i.e. ($E_{\text{O}}^{\text{C}} - E_{\text{R}}^{\text{C}}$)]. In addition, according to conventional knowledge, the Li-O₂ battery with a Li_xA/C anode should display higher voltage gap than Li-O₂ battery, because the inherent lithiation/delithiation polarization [i.e. ($E_{\text{O}}^{\text{A}} - E_{\text{R}}^{\text{A}}$)] of Li_xAl anode (0.19V=0.45V-0.26V; Fig. S3, ESI†) seems to be larger than the reversible dissolution/deposition polarization of metallic Li-anode (~0V). However, the achieved results demonstrate a quite different conclusion. As shown in Fig. 1a, the discharge and charge voltages of the Li-O₂ battery with a Li_xA/C anode are 2.35 V and 3.65 V, respectively, indicating a total polarization of 1.3V. However, a total polarization between discharge and charge of 1.6V (= 4.3V-2.7 V) can be detected in the voltage profiles of Li-O₂ battery with a Li-anode (Fig. 1b). Discharge/charge voltage profiles investigated at low current density of 50mA g⁻¹ display the same phenomenon (Fig. S4, ESI†). This phenomenon indicates that there is obvious polarization between the Li-anode dissolution and deposition in Li-O₂ battery, which may be owing to the O₂-attacking-induced passivation of Li-anode. In previous reports,³⁻⁵ it

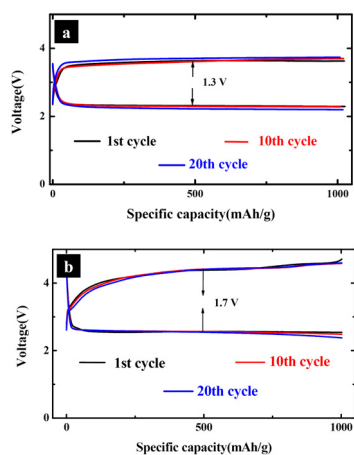


Fig. 1 Voltage profiles of the Li-O₂ battery with a Li_xA/C anode (a) and the Li-O₂ battery with a Li-anode (b) cycled at a current density of 100 mA g⁻¹ and at a fixed capacity of 1000 mAh g⁻¹.

has been widely reported that the huge polarization of Li-O₂ batteries is mainly caused by the anodic reaction of Li₂O₂ decomposition. Kang *et al.*'s work well demonstrated this point.^{9a} However, the result from Fig. 1 indicates that passivation of Li-anode may be another reason for the polarization of Li-O₂ batteries, besides the Li₂O₂ decomposition in cathode. Recent investigations about Li-O₂ battery also demonstrate that the O₂ crossover can result in the passivation of Li-anode.¹⁰ On the other hand, it can be assumed that the carbon layer with a uniform SEI film efficiently alleviates the O₂-attacking on Li_xAl anode. This point will be further discussed later.

As mentioned in the introduction section, most reported Li-O₂ or Li-air batteries employed pure and dry O₂ as cathodic active material. The key reason is that only a small amount of H₂O can result in very serious O₂/N₂-attacking reactions. Herein we employed ambient air

with a limited relative humidity (R.H.) of ~ 40% as cathodic active material, and investigated the electrochemical performance of the Li-air battery with a Li_xAl/C anode and the Li-air battery with a Li-anode. Fig. 2 presents typical voltage profiles for the both batteries cycled at current density of 100 mA g⁻¹ and at a fixed capacity of 1000 mAh g⁻¹. As shown in Fig. 2a, the Li-air battery with a Li_xAl/C anode displays a reproducible discharge/charge voltage profile without sign of deterioration over 20 cycles. On the contrary, the voltage gap between discharge and charge of the Li-air battery with a Li-anode obviously increases over discharge/charge cycles (Fig. 2b). At the 20th cycle, the loss of discharge capacity above 2V is almost 50%, indicating very poor cyclic ability (Fig. 2b). The poor cyclic ability of Li-air battery should be attributed to the air-attacking-induced passivation of Li-anode.

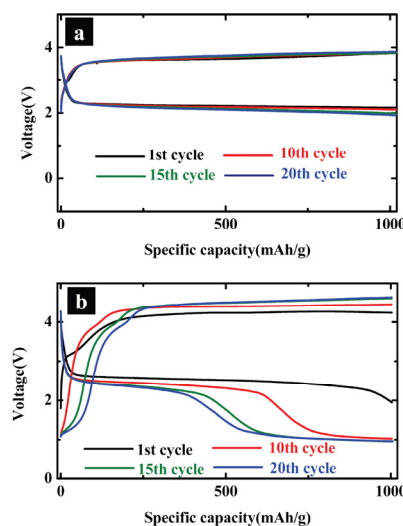
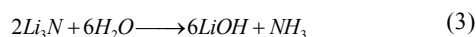


Fig. 2 Voltage profiles of Li-air battery with a Li_xAl/C anode (a) and Li-air battery with a Li-anode (b) cycled at a current density of 100 mA g⁻¹ and at a fixed capacity of 1000 mAh g⁻¹.

It is well known that dry air is composed of 21% O₂, 78 % N₂, and 1 % other gas (e.g., CO₂, O₃, Ar₂, etc.). Only a small amount of H₂O can result in very fast N₂-attacking reaction to form Li₃N and LiOH (see equation 2, 3):



As shown in Fig. S5, only after been exposed in ambient air for several minutes, the silvery white Li-metal have been converted into brown/black Li-metal, indicating the formation of Li₃N/LiOH layer. Furthermore, we also de-assembled the cycled Li-air battery with a Li-anode, and employed scanning electron microscope (SEM) and energy dispersive X-ray (EDX) mapping technology to investigate the surface characteristic of the cycled Li-anode. Prior to SEM/EDX investigation, the cycled Li-anode was washed with C₃H₆O₃ (DMC) solvent, and then dried at vacuum for 2 hours to vaporize DMC solvent. As shown in Fig. 3a-c, a lot of N and O elements have been dispersed on the surface of cycled Li-anode, indicating the formation of Li₃N and LiOH. The SEM image with higher magnification (Fig. 3d) indicates that there are a lot of Li₃N (and/or LiOH) particles formed on the surface of Li-anode. In order to demonstrate the air-attacking-induced polarization, the charge/discharge profiles of an air-attacked

metallic Li-electrode and $\text{Li}_x\text{Al/C}$ electrode were investigated (Fig. S7 and S8, ESI†). However, for the Li-air battery with a $\text{Li}_x\text{Al/C}$ anode, the carbon layer (i.e. 90% carbon black + 10% polytetrafluoroethylene) with a uniform SEI film plays the role of buffer layer that could alleviate the air-attacking on Li_xAl anode (TEM images of the SEI film coating layer is given in Fig. S6, ESI†). Furthermore, the hydrophobic character of carbon black and polytetrafluoroethylene also potentially reduces the H_2O -attacking. Therefore, Li-O_2 battery with a $\text{Li}_x\text{Al/C}$ anode displays much better cyclic performance than Li-air battery. However, it also should be noted that the carbon layer with a SEI film can only alleviate air/ H_2O -attacking on anode, and thus is not an immediate solution. Especially, lithiated Al still can result in safety issue in ambient air with high humidity. In addition, the full cycle performance of Al anode is poor, and use of excess amount of Li_xAl is required. Theoretically, it should be a thorough and immediate solution for protecting anode from air/ H_2O -attacking to use a water-stable ceramic Li-ion exchange film as the protective layer^{3d, 11}. However, the low ionic conductivity of ceramic Li-ion exchange film still limits the performance of batteries.

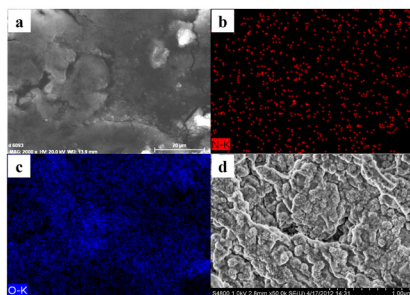


Fig. 3 (a) SEM image of cycled Li-anode in Li-air battery with corresponding EDX mapping image of (b) N element and (c) O element and (d) its SEM image with higher magnification.

Conclusions

Summarily, Li_xAl /carbon composite electrode with a uniform SEI film was coupled with O_2 catalytic electrode with TEGDME-based electrolyte to form a Li-O_2 (or air) battery. Because the carbon layer with SEI film can alleviate O_2 -attacking or air-attacking on anode, the Li-O_2 battery with a $\text{Li}_x\text{Al/C}$ anode displays lower voltage gap between charge and discharge than the Li-O_2 battery which a Li-anode. In addition, when ambient air with a limited humidity was used as active material, Li-air battery with a $\text{Li}_x\text{Al/C}$ anode displays better cycling performance. These results indicate that it should be the next logic step for Li-O_2 (or air) system investigation to develop promising alternative anode with a stable protective layer.

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Notes and references

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- (a) T. Ogasawara, A. Debart, M. Holzapfel, P. Novak, P. G. Bruce, *J. Am. Chem. Soc.*, 2006, **128**, 1390; (b) P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J. M. Tarascon, *Nat. Mater.*, 2012, **11**, 19.
- (a) S. A. Freunberger, Y. H. Chen, Z. Q. Peng, J. M. Griffin, L. J. Hardwick, F. Barde, P. Novak, P. G. Bruce, *J. Am. Chem. Soc.*, 2011, **133**, 8040; (b) Y. Chen, S. A. Freunberger, Z. Peng, F. Barde, P. G. Bruce, *J. Am. Chem. Soc.*, 2012, **134**, 7952.
- (a) H. G. Jung, J. Hassoun, J. B. Park, Y. K. Sun, B. Scrosati, *Nat. Chem.*, 2012, **4**, 579; (b) Z. Peng, S. A. Freunberger, Y. H. Chen, P. G. Bruce, *Science*, 2012, **337**, 563; (c) S. H. Oh, R. Black, E. Pomerantseva, J. H. Lee, L. F. Nazar, *Nat. Chem.*, 2012, **4**, 1004; (d) T. Zhang, H. S. Zhou, *Nat. Commun.*, 2013, **4**, 1817 (DOI: 10.1038/ncomms2855).
- (a) J. J. Xu, Z. L. Wang, D. Xu, L. L. Zhang, X. B. Zhang, *Nat. Commun.*, 2013, **4**, 2438 (DOI: 10.1038/ncomms3438); (b) Z. Y. Guo, D. D. Zhou, X. L. Dong, Z. J. Qiu, Y. G. Wang, Y. Y. Xia, *Adv. Mater.*, 2013, **25**, 5668; (c) X. Wu, J. Xiao, D. Y. Wang, J. Zhang, J. G. Zhang, *J. Power Sources*, 2010, **13**, A48.
- (a) E. Nsybulin, W. Xu, M. H. Englhard, Z. Nie, S. D. Burton, L. Cosimbescu, M. E. Gross, J. G. Zhang, *J. Phys. Chem. C*, 2013, **117**, 2635; (b) H. G. Jung, H. S. Kim, J. B. Park, I. H. Oh, J. Hassoun, C. S. Yoon, B. Scrosati, Y. K. Sun, *Nano Lett.*, 2012, **12**, 4333; (c) C. O. Laoire, S. Mukerjee, E. J. Plichta, M. A. Hendrickson, K. M. Abraham, *J. Electrochem. Soc.*, 2011, **3**, A302.
- (a) J. Lu, Y. Lei, K. C. Lau, X. Y. Luo, P. Du, J. G. Wen, R. S. Assary, U. Das, D. Miller, J. W. Elam, H. M. Albishri, D. Abd El-Hady, Y. K. Sun, L. A. Curtiss, K. Amine, *Nat. Commun.*, 2014, **5**, 3290 (DOI: 10.1038/ncomms4290); (b) J. Xiao, D. H. Mei, X. L. Li, W. Xu, D. Wang, G. L. Graff, W. D. Bennett, Z. Nie, L. V. Saraf, I. A. Aksay, J. Liu, J. G. Zhang, *Nano Lett.*, 2011, **11**, 5071; (c) B. M. Gallant, D. G. Kwabi, R. R. Mitchell, J. G. Zhou, C. V. Thompson, Y. Shao-Horn, *Energy & Environmental Science*, 2013, **6**, 2518.
- (a) Y. Li, J. Wang, X. Li, D. Geng, R. Li, X. Sun, *Chem. Commun.*, 2011, **47**, 9438; (b) Y. C. Lu, D. G. Kwabi, K. P. C. Yao, J. R. Harding, J. G. Zhou, L. Zuin, Y. Shao-horn, *Energy & Environmental Science*, 2011, **4**, 2999; (c) S. Meini, N. Tsiouvaras, K. U. Schwenke, M. Piana, H. Beyer, L. Lange, H. A. Gasteiger, *Phys. Chem. Chem. Phys.*, 2013, **15**, 11478.
- (a) J. Hassoun, H. G. Jung, D. J. Lee, J. B. Park, K. Amine, Y. K. Sun, B. Scrosati, *Nano Lett.*, 2012, **12**, 5775; (b) J. B. Park, J. Hassoun, H. G. Jung, H. S. Kim, C. S. Yoon, I. H. Oh, In-Hwan B. Scrosati, Y. K. Sun, *Nano Lett.*, 2013, **13**, 2971; (c) J. Hassoun, F. Grocer, M. Armand, B. Scrosati, *Angew. Chem. Int. Ed.* 2011, **50**, 2999.
- (a) H. D. Lim, H. Song, J. Kim, H. Gwon, Y. Bae, K. Y. Park, J. Hong, H. Kim, T. Kim, Y. H. Kim, X. Lepro, R. Ovalle-Robles, R. H. Baughman, K. Kang, *Angew. Chem. Int. Ed.*, 2014, **53**, 3926; (b) H. D. Lim, K. Y. Park, H. Song, E. Y. Jang, H. Gwon, J. Kim, Y. H. Kim, M. D. Lima, R. O. Robles, X. Lepro, R. H. Baughman, K. Kang, *Adv. Mater.*, 2013, **25**, 1348.
- (a) R. S. Assary, J. Lu, P. Du, X. Y. Luo, Z. Y. Zhang, Y. Ren, L. A. Curtiss, K. Amine, *ChemSusChem*, 2013, **6**, 51; (b) J. L. Shui, J. S. Okasinski, P. Kenesei, H. A. Dobbs, D. Zhao, J. D. Almer, D. J. Liu, *Nat. Commun.*, 2013, **4**, 2255 (DOI: 10.1038/ncomms3255).
- (a) Y. G. Wang, H. S. Zhou, *J. Power Sources*, 2010, **195**, 358; (b) Y. G. Wang, H. S. Zhou, *Chem. Commun.*, 2010, **46**, 6305.