

Lithium Air Battery with a Lithiated Al/Carbon Anode

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19 March 2021

Note added after first publication: This supplementary information file replaces that originally published on 14 November 2014, in which incorrect data were included in Fig. S2 in error. This has now been corrected and this does not affect the conclusions in the article.

Experimental Section

Preparation of Al/carbon composite electrode and O₂ catalytic electrode: Carbon Black (CB) and poly (tetrafluoroethylene) (PTFE) binder was dispersed in isopropanol to form slurry with a weight ration of 9:1 (CB: PTFE). Next, the slurry (CB + PTFE) was rolled into a membrane, and then pressed on an Al mesh to form an Al-carbon composite anode. In the preparation of carbon-based O₂ catalytic electrode, carbon black Super P (80 wt %) and a polyvinylidene fluoride binder (PVDF, 20 wt %) were intimately mixed in an N-methyl-2-pyrrolidone (NMP) solution, and the resulting slurry was coated on a carbon paper (TGP-H-060 carbon paper, Torray). The total mass loading of Super P is around 0.8 mg/cm². The coated electrode was dried for 12 h at 100 °C under vacuum to remove residual solvent.

Preparation of Li-O₂ (or air) battery with a Li_xAl/C anode: Lithiated Al/carbon (Li_xAl/C) composite electrode was first prepared by electrochemical method. Typically, an Al/carbon composite electrode was coupled with a metallic Li-foil to form a half-cell using LiPF₆-EC/DMC/EMC electrolyte [i.e. LB303 electrolyte produced by Zhangjiagang Guotai-huarong New Chemical Materials Co., LTO. (China) for conventional Li-ion batteries], and then was discharged for 25 hours with a current 0.4 mA/cm² to form a Li_xAl/C composite electrode with a uniform solid electrolyte interface (SEI) film that arises from the decomposition of EC/DMC/EMC-based electrolyte. Then, the cell was disassembled in a glove box filled with Ar to obtain Li_xAl/C electrode. Next, resulting Li_xAl/carbon electrode was coupled with a carbon-based O₂ catalytic electrode in a tetra(ethylene) glycol

dimethyl ether–LiN(CF₃SO₂)₂ (TEGDME–LiTFSI) electrolyte to form a Li-O₂ (or air) battery with a Li_xAl/C anode. The “Li_xAl/C-electrode/ separator containing electrolyte / O₂-electrode” was sealed into a Swagelok cell with an air hole 0.8 cm² placed on the positive electrode side to allow the O₂ (or air) to flow in. Li-O₂ (air) battery was assembled with the same method. LAND cycler (Wuhan Land Electronic Co. Ltd.) was used for electrochemical investigation.

Detection of Li₂O₂ via XRD: Firstly, a Li-O₂ battery with a Li_xAl/C anode was discharged at a current density of 100 mA g⁻¹ with a fixed capacity of 1000 mAh g⁻¹. After that, the cell was disassembled in a glove box filled with Ar to obtain the discharged electrode. Then, the discharged O₂ catalytic electrode was washed with DMC and was dried under vacuum at room temperature for 3 hours. Next, the resulting electrode was detected by XRD. The O₂ catalytic electrode before discharge (or after recharge) was detected with the same method.

Characterization: XRD patterns were recorded on Bruker D8 Advance Diffractometer using Cu K α radiation. The morphologies of the sample were characterized with SEM (FE-SEM S-4800) and TEM (Joel JEM2010).

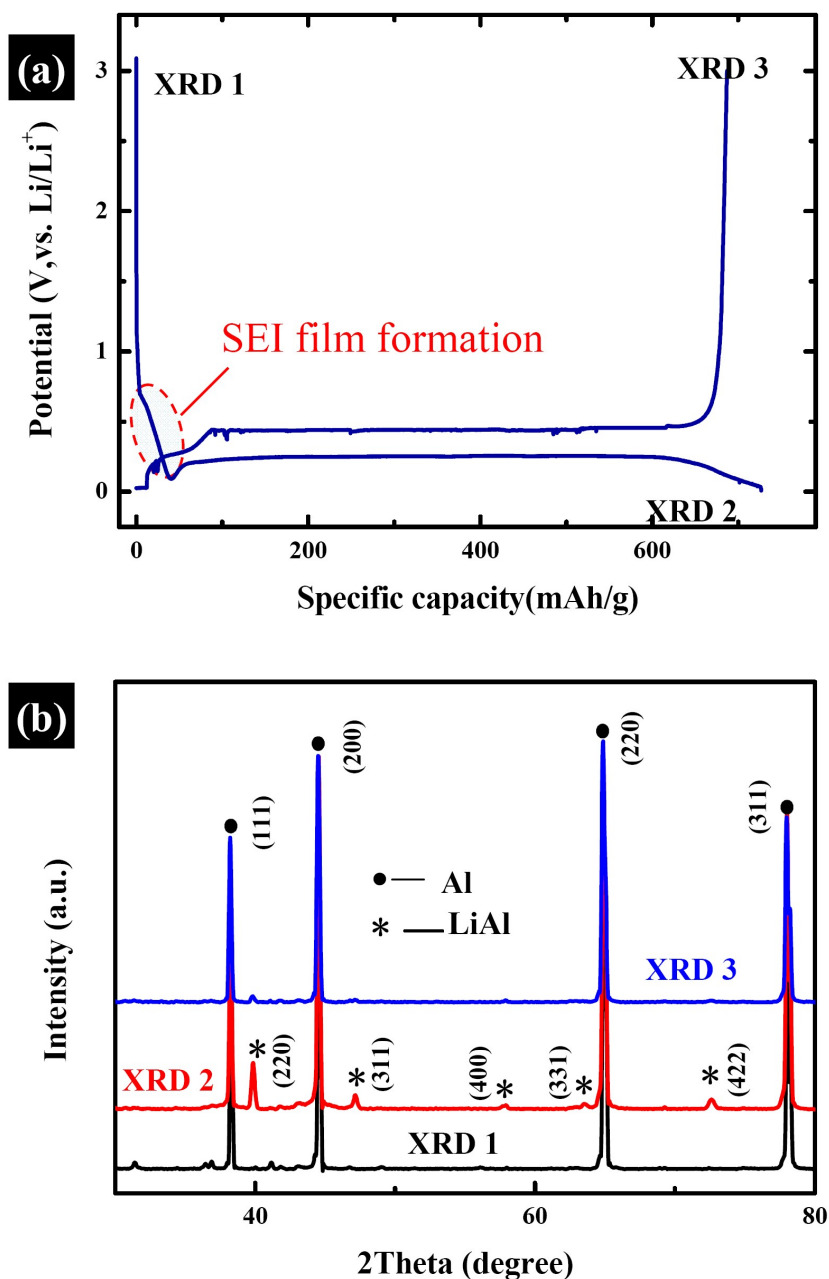


Fig. S1 (a) charge/discharge curves of Al/Carbon (Al/C) composite electrode investigated in $\text{LiPF}_6\text{-EC/DMC/EMC}$ electrolyte within the potential window from 3.0 V \sim 0.02 V (vs. Li/Li^+) at a current density of 25 mA g^{-1} (or 0.4 mA/cm^2) and (b) ex situ XRD analysis carried out on the carbon-coated Al anode in its pristine state (XRD 1), after full discharge (XRD 2), and after full charge (XRD 3).

Fig. S1a gives the discharge/charge curves of Al/C composite electrode within the potential window from 3.0 V \sim 0.02 V (vs. Li/Li^+) at a current density of 25 mA g^{-1} . As shown in **Fig. S1a**, lithiation of the Al electrode exhibits a discharge capacity of

720 mAh g⁻¹ with a cutoff potential of 0.02 V (vs. Li/Li⁺). The main lithiation potential of the Al/carbon composite electrode can be observed at around 0.26 V which is consistent with previous reports.^{RS1} The initial plateau between 0.7 V and 0.2 V arises from the reduction of EC/DMC/EMC-based electrolyte on the surface of carbon layer to form solid electrolyte interface (SEI) film, which has been widely reported in previous investigations about conventional Li-ion batteries.^{RS2, 3} On charge (or de-lithiation) process, the Al/C composite electrode displays a capacity of 680 mAh g⁻¹ with an average potential of 0.45 V (Fig. 1a). The lithiation/delithiation mechanism of Al anode can be summarized as equation (1):



In theory, the formation of LiAl (x =1) from Al should provide a theoretical capacity of 993mAh g⁻¹. In order to clarify this operating mechanism, *ex situ* XRD analysis (see **Fig. S1b**) was conducted, in sequence, on the Al/C composite electrode in its pristine state (XRD1), after full lithiation for formation of Li_xAl (XRD2) and after complete recharge for the reconversion of Al (XRD3).^{RS1} It can be detected in the XRD2 discharge pattern (**Fig. S1b**) that formation of a LiAl alloy is apparent from the presence of characteristic peaks corresponding to the (220), (311), (400), (331), (422) and (511) planes (JCPDS 03-1215). The aluminium peaks were also present (JCPDS04-078), but no peaks for Li (JCPDS 15-401), Li₃Al₂ (JCPDS 26-1008) or Li₉Al₄ (JCPDS 24-0008) were detected. These results indicated that Al reacted only partially, consistent with the fact that the calculated capacity was lower than theoretical capacity. One can also observe that these characteristic peaks related to LiAl vanish again in the XRD3 charge pattern. These results well support the interpretation about the operating mechanism of Al anode, and also quite agree with Morales *et al.*' recent report.^{RS1}

RS1. J. Morales, R. Trocoli, S. Franger, J. Santos-Pena, *Electrochim. Acta*, 2010, **55**, 3075.

RS2. K. Xu, *Chem. Rev.*, 2004, **104**, 4303; S. H. Zhang, M. S. Ding, K. Xu, J. Allen, T. R. Jow, *Electrochem. Solid-State Lett.*, 2001, **4**, A206; P. Verma, P. Maire, P. Novak, *Electrochim. Acta*, 2010, **55**, 6332.

RS3. H. Buqa, A. Wursig, J. Vetter, M. E. Spahr, F. Krumeich, P. Novak, *J. Power Sources*, 2006, **153**, 385; F. Kong, R. Kostecki, G. Nadeau, X. Song, K. Zaghib, K. Kinoshita, F. McLarnon, *J. Power Sources*, 2001, **97**, 58.

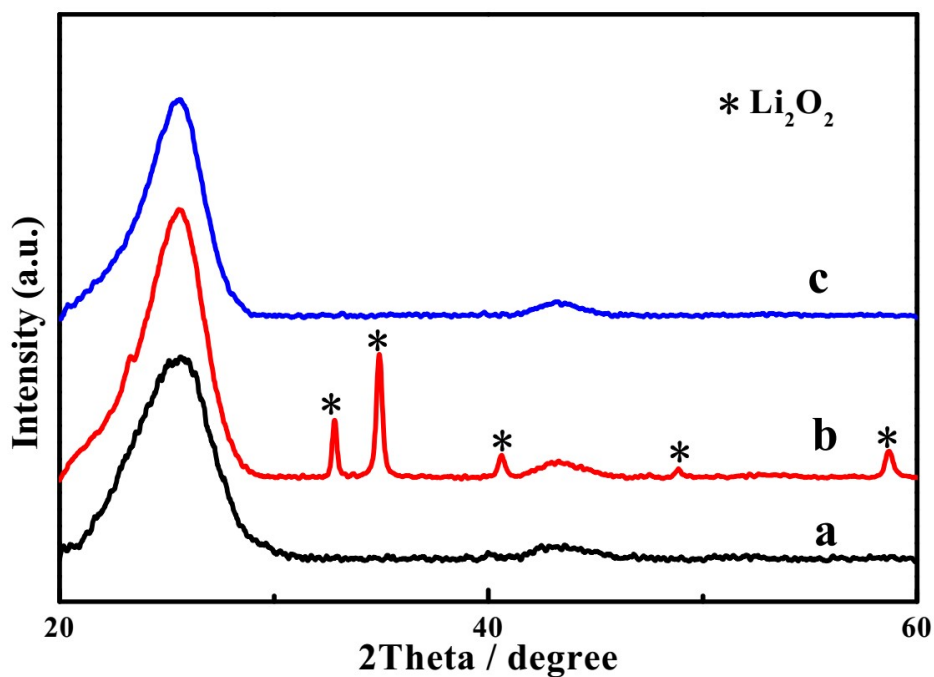


Fig. S2 XRD patterns of O_2 catalytic electrode of Li- O_2 battery with a $\text{Li}_x\text{Al/C}$ anode. (a) before discharge, (b) after discharge and (c) after recharge.

It can be detected from **Fig. S2** that the characteristic peaks related to Li_2O_2 exist in the XRD pattern after discharge and vanish again in the XRD pattern after recharge, indicating the reversible conversion between O_2 and Li_2O_2 over discharge/charge process.

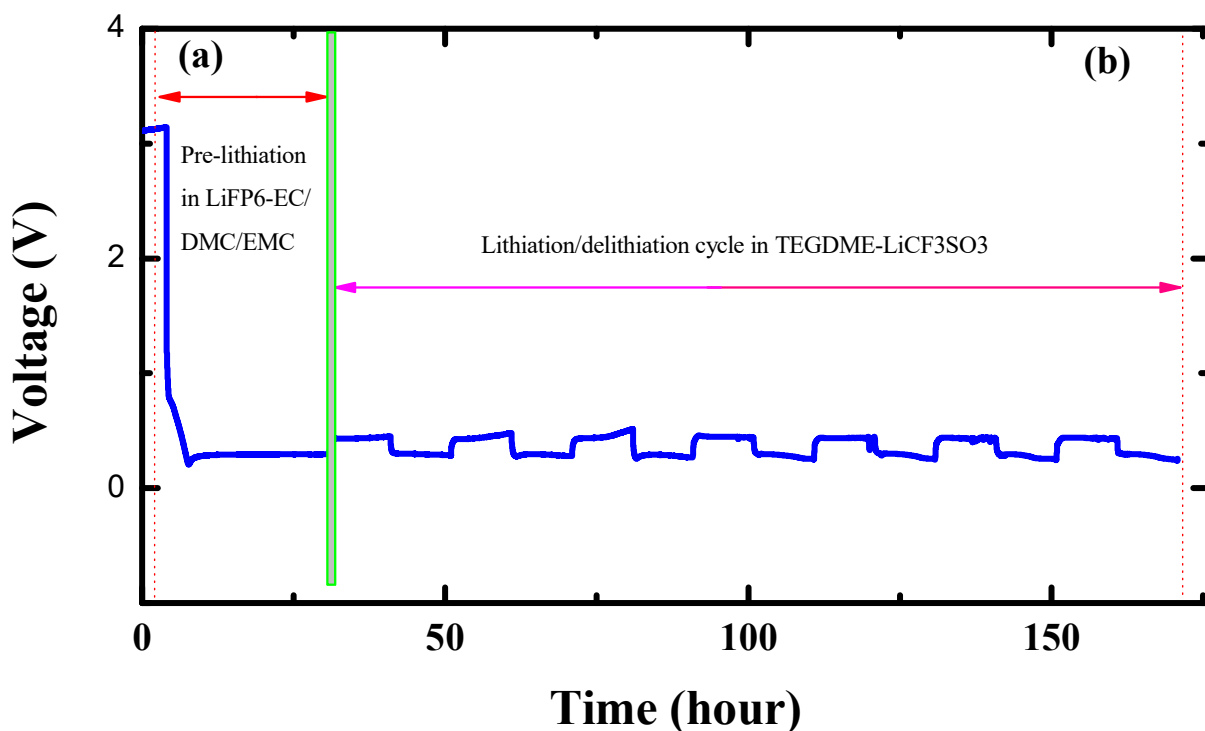


Fig. S3 (a) Pre-lithiation of Al/C electrode in LiFP₆-EC/DMC/EMC electrolyte and (b) Lithiation/delithiation cycle of Li_xAl/C electrode in TEGDME-LiCF₃SO₃ electrolyte at a current of 25mA/g (0.4mA/cm²).

An Al/C electrode was coupled with metallic Li-foil to form a half-cell using LiPF₆-EC/DMC/EMC electrolyte, and then was discharged for 25 hours with a current 0.4 mA/cm² to realize pre-lithiation. Then, the cell was disassembled in a glove box filled with Ar to obtain Li_xAl/C electrode. Next, the resulting Li_xAl/C was coupled with a fresh Li-foil anode to form a half-cell using TEGDME-LiCF₃SO₃ electrolyte. The performance of the Li_xAl/C electrode in TEGDME-LiCF₃SO₃ electrolyte was investigated with a fixed charge/discharge time of 10 hours.

As shown in **Fig. S3**, lithiation/delithiation polarization of Li_xAl/C anode is about 0.19V in TEGDME-LiCF₃SO₃ electrolyte.

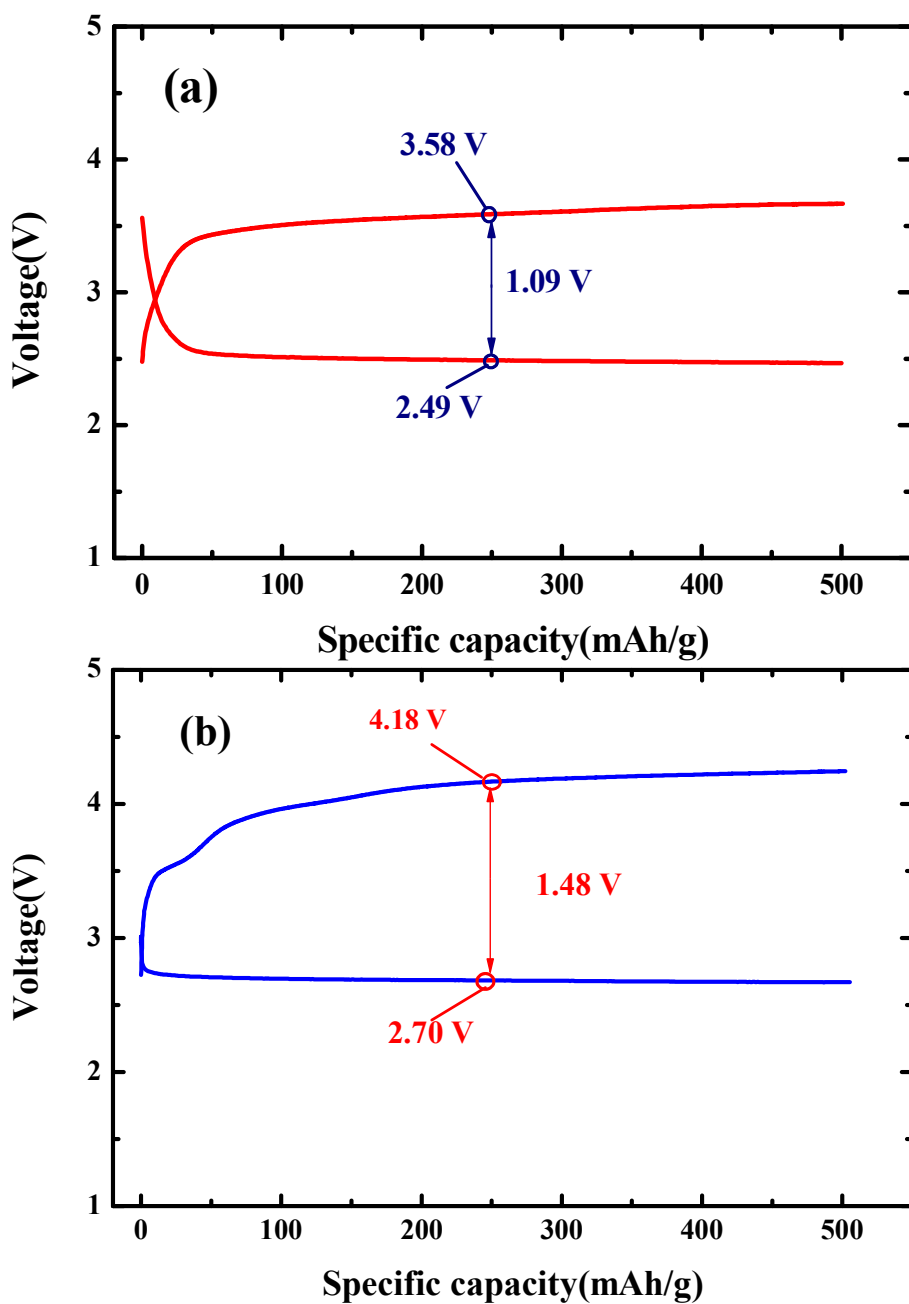


Fig. S4 Discharge/charge voltage profiles of Li-O₂ battery with a Li_xAl/C anode (a) and Li-O₂ battery with a Li-anode (b) investigated at low current density of 50 mA/g.

It can be detected from **Fig. S4a** that Li-O₂ battery with a Li_xAl/C anode displays a total polarization (i.e. the voltage gap between discharge and charge) of 1.09V at the current density of 50mA/g. However, a total polarization between discharge and charge of 1.48V can be detected in the voltage profiles of Li-O₂ battery with a Li-anode (**Fig. S4b**).

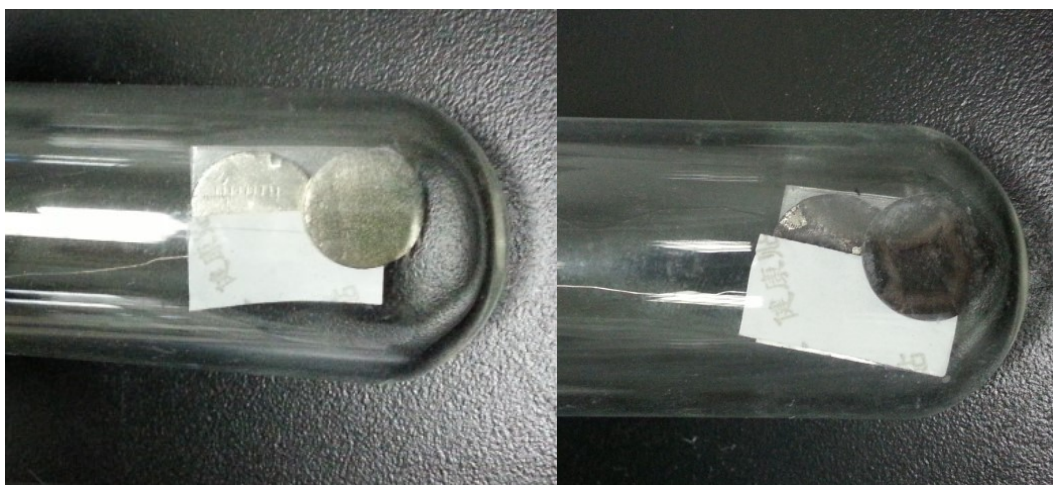


Fig. S5 photos of fresh metallic Li (a) and metallic Li that was exposed in ambient air for several minutes (b). As shown in **Fig. S5**, only after been exposed in ambient air for several minutes, the silvery white Li-metal have been converted into brown/black Li-metal.

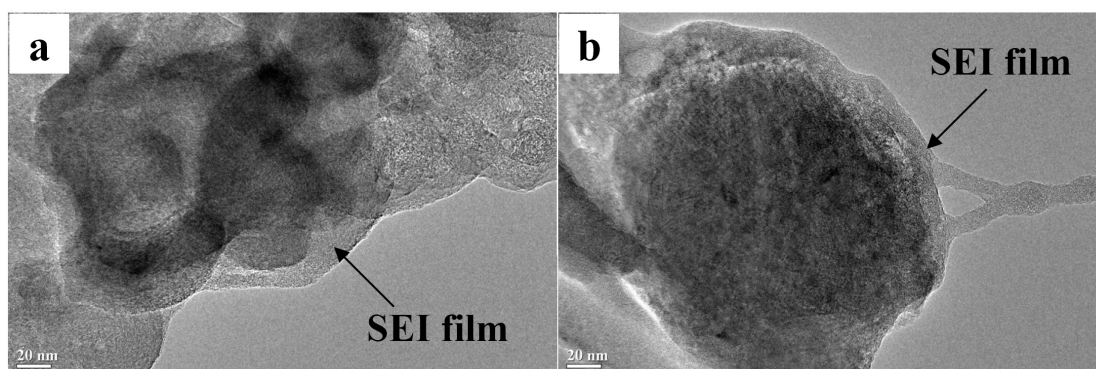


Fig. S6 TEM images (a, b) with different magnifications of carbon layer in lithiated Al/carbon composite electrode. As shown in **Fig. S6**, the carbon material (i.e. carbon black) is full coated by SEI film.

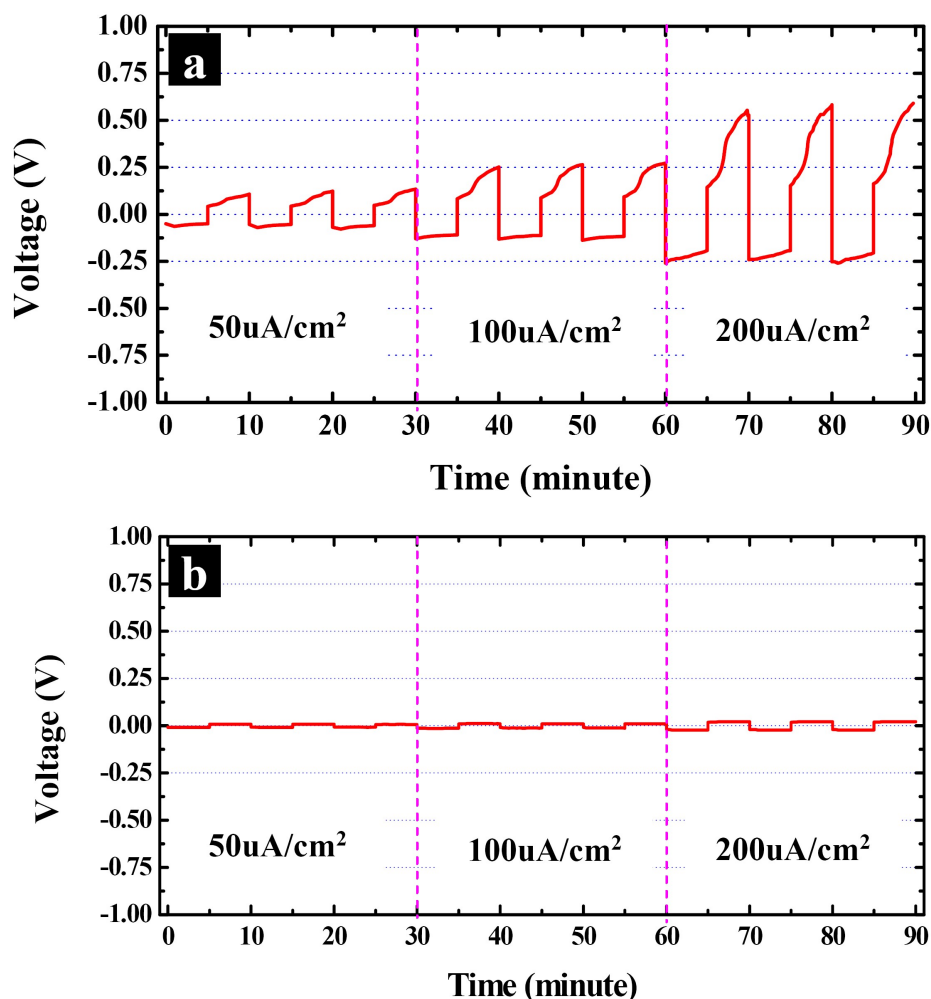


Fig. S7 charge/discharge curves of “air-attacked-Li (+)/fresh-Li (-)” half-cell (a) and “fresh-Li (+)/fresh-Li (-)” half-cell (b) with different applied current densities.

In this investigation, a fresh Li electrode was exposed in ambient air with a relative humidity (R.H.) of 40% for 10 minutes. Next, the air-attacked Li electrode was coupled with a fresh metallic Li electrode to form an “air-attacked-Li(+)/fresh-Li (-)” half cell using TEGDME–LiCF₃SO₃ electrolyte. After sealed in the glove box filled with argon gas, the cell was used for electrochemical investigation. **Fig. S7a** gives the discharge/charge curves of air-attacked Li electrode at different applied current densities. The electrochemical performance of a “fresh-Li (+)/fresh-Li (-)” half cell

was also investigated for comparison (**Fig. S7b**). As shown in **Fig. S7a**, the air-attacked Li electrode displays an obvious polarization of about 150 mV between dissolution/deposition reactions (i.e. charge/discharge reactions) even at the low current density of 50 uA cm^{-2} . When the applied current density is enhanced to 200 uA cm^{-2} , this polarization is even as high as 500 mV (**Fig. S7a**). However, such obvious polarization can not be observed in the investigation of fresh-Li electrode at various current densities (**Fig. S7b**).

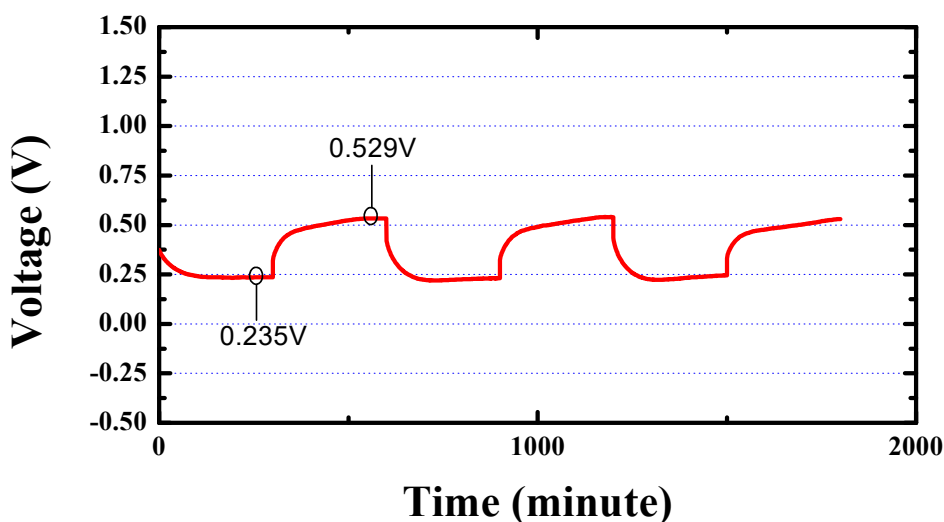


Fig. S8 discharge/charge curves of the air-attacked Li_xAl /carbon electrode at a current density of 0.4 mA/cm^2 .

Herein, electrochemical performance of air-attacked “ Li_xAl /carbon electrode” is also investigated by discharge/charge test (See **Fig. S8**) for comparison with that of air-attacked Li-electrode (**Fig. S7**). Specifically, a carbon-coated Al electrode was coupled with metallic Li-foil to form a half-cell using $\text{LiPF}_6\text{-EC/DMC/EMC}$ electrolyte, and then was discharged for 25 hours with a current 0.4 mA/cm^2 to realize pre-lithiation. Then, the cell was disassembled in a glove box filled with Ar to obtain lithiated carbon-coated Al electrode (i.e. Li_xAl /carbon electrode). Next, the lithiated carbon-coated Al electrode was exposed in ambient air with a relative humidity (R.H.)

of ~ 40% for 10 minutes, which is as same as the air-attacking condition for metallic Li-electrode (see explanation for **Fig. S7**). After that, air-attacked Li_xAl /carbon electrode was coupled with a fresh metallic Li electrode to form an “air-attacked Li_xAl /carbon (+)/fresh-Li (-)” half cell. After sealed in the glove box filled with argon gas, the cell was used for electrochemical investigation. As shown in **Fig. S8**, the air-attacked $\text{Li}_x\text{Al}/\text{C}$ electrode displays a polarization of about 0.294 V (= 0.529 V-0.235 V) which is slightly higher than the polarization of the fresh $\text{Li}_x\text{Al}/\text{C}$ electrode (0.19 V=0.45-0.26 V; see **Fig. S3**). However, the air-attacked metallic Li-anode exhibits very high polarization (see **Fig. S7**). Therefore, it can be assumed that the carbon layer with a uniform SEI film plays the role of buffer layer that can alleviate the air-attacking on Li_xAl anode. In addition, the hydrophobic character of carbon black and polytetrafluoroethylene also potentially reduces the H_2O -attacking.