

## Supporting Information

### **A high-rate and long cycle life solid-state lithium-air battery**

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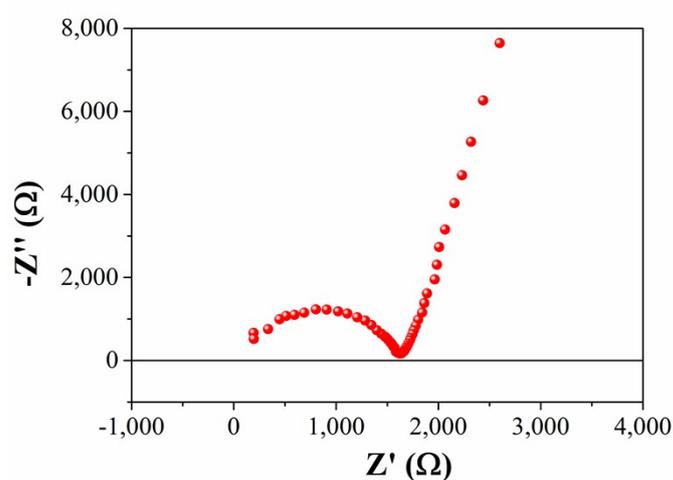
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## **Integrated LATP structure preparation**

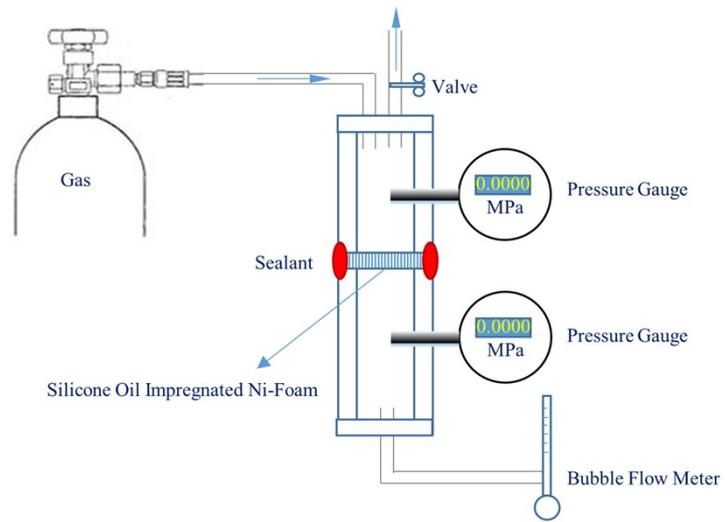
$\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  (LATP) raw powders were prepared via two different methods, namely solid-phase reaction and sol-gel. For the solid-phase reaction,  $\text{Li}_2\text{CO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $(\text{NH}_4)\text{H}_2\text{PO}_4$  were ball-milled in ethanol for 30 h, dried at room temperature, and heated at 900 °C for 5 h. 20% excess lithium was included in the mixture to avoid the deficiency of lithium in the final specimens. For the sol-gel procedure, a precursor sol was prepared from  $\text{LiNO}_3$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ti}\{\text{OCH}(\text{CH}_3)_2\}_4$ ,  $(\text{NH}_4)\text{H}_2\text{PO}_4$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$ , which was heated at 800 °C for 5 h after pre-heating at 100 °C for 24 h. 10% excess lithium was also included in the sol to avoid lithium deficiency.

To prepare the porous cathode support, sol-gel derived LATP powders were thoroughly mixed with a pore former (starch) at a weight ratio of 6:5 and uniaxially pressed into pellets under 200 MPa prior to sintering at 850 °C for 15 h. The ultra-thin LATP membrane was then coated onto one surface of pre-sintered LATP pellets by a slurry spin-coating technique (3,000 rpm) and finally sintered at 1,000 °C for 5 h to form an integrated structure with an ultra-porous cathode support (75% porous), and an ultra-thin (19  $\mu\text{m}$  thick) and ultra-dense (96% dense) electrolyte membrane. There is no interface between the electrolyte and cathode support since only LATP is used, eliminating the potential barrier at the conventional interface between the electrolyte and the electrode, allowing faster transport of Li ions. The slurry for spin coating was prepared from two kinds of LATP raw powders (sol-gel and solid-phase reaction) mixed with terpenol, ethyl cellulose and polyvinyl pyrrolidone (PVP) at a weight ratio of 8:10:15:1:0.08, which was ball-milled in ethanol for 24 h before use. The weight ratio of the two kinds of powders was calculated by the *Alfred Equation* based on the results of particle size distribution. Since LATP based materials suffer from two critical weaknesses: (i) extreme sensitivity to sintering temperature and duration, and (ii) prone to micro-crack formation due to high thermal expansion anisotropy of the crystal lattice, the use

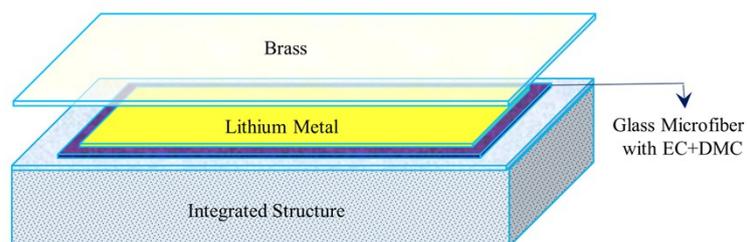
of mixed powders in this study aims to increase the apparent density and then to improve the sintering property, while the introduction of buffer agents (ethyl cellulose and PVP) is intended to modify the sedimentation speed of the suspension.



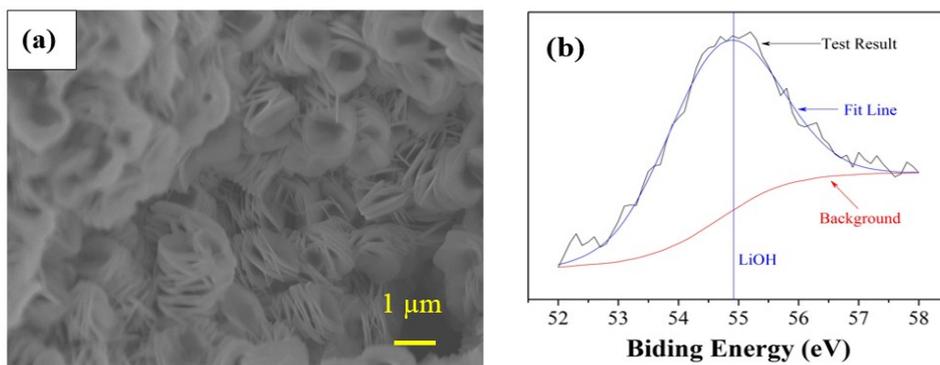
**Figure S1** Impedance spectra for the 75% porous LATP cathode-support. Au was deposited as symmetrical electrodes, *i.e.*, working electrode (WE) and counter electrode (CE). Pt paste was fired at 800 °C for 1 h as reference electrode (RE) by positioning it as close to WE as possible.



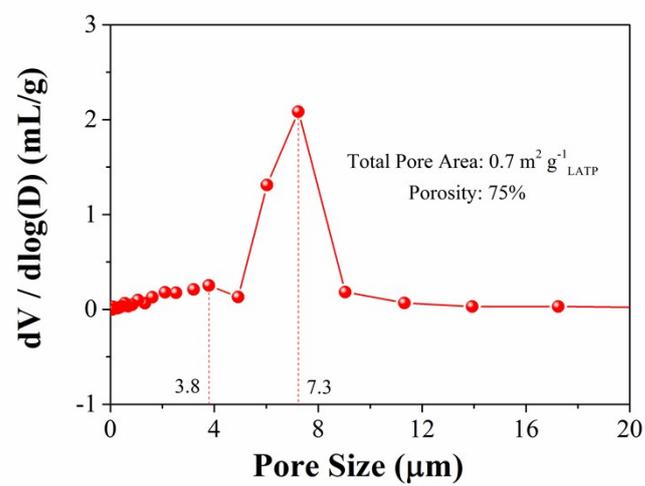
**Figure S2** Experimental setup for gas permeability measurements.



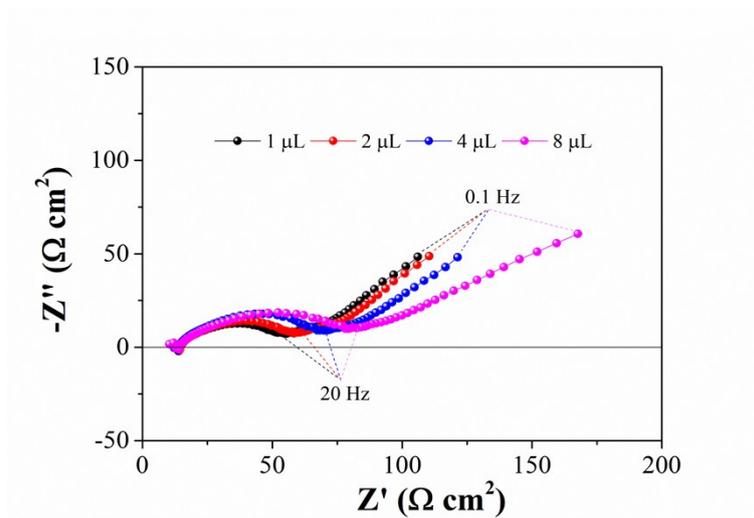
**Figure S3** Schematic illustration of the proposed lithium-air battery. At the anode, Li metal was sandwiched between a brass lid and a dense LATP electrolyte layer, and was sealed with glue (Shanghai Kangda New Materials Company, WD1001, China). Brass was closely connected with Li metal and hence used as the current collector of the anode. A glass microfiber filter (Whatman, Cat. No. 1822-047) immersed with commercial electrolyte (EC/DMC=1:3, Guangzhou Tianci Technology LTD. Co., China) was used to prevent the reaction between Li metal and LATP electrolyte and connected the  $\text{Li}^+$  transport pathway.



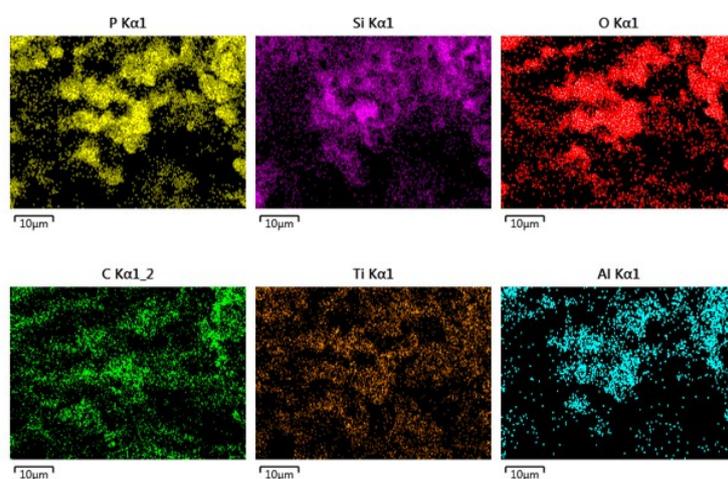
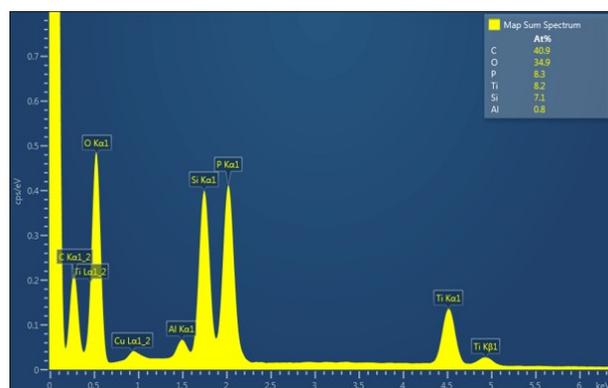
**Figure S4** (a) The SEM image and (b) XPS spectra for discharge product of LiOH inside the porous carbon-coated LATP cathode without a silicone-oil film after discharging in pure oxygen (100% RH) at a current density of  $0.3 \text{ mA cm}^{-2}$  with a discharge capacity of  $81,984 \text{ mA h g}^{-1}_{\text{carbon}}$ .



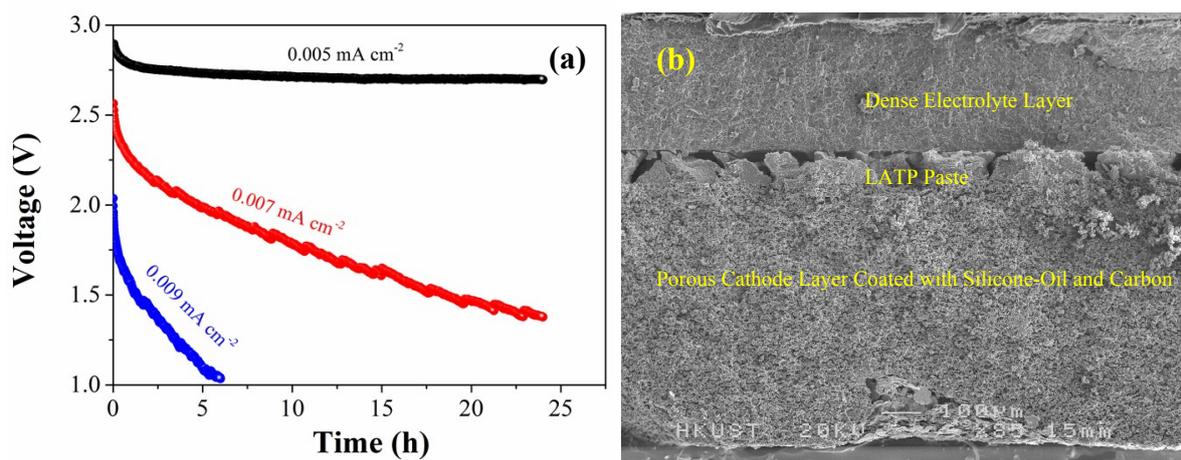
**Figure S5** Pore size distribution of the proposed porous cathode prior to infiltration.



**Figure S6** Change of impedance spectra of four lithium-air batteries with its cathodes infiltrated with 1  $\mu\text{L}$ , 2  $\mu\text{L}$ , 4  $\mu\text{L}$ , or 8  $\mu\text{L}$  silicon oil prior to discharge. It was performed at open circuit voltage (OCV) in ambient air with  $\sim 50\%$  RH.



**Figure S7** EDS analysis for the 2 µL silicon-oil infiltrated LATP cathode in order to confirm the existence of the silicon-oil film and to detect the distribution of the silicon-oil film inside the porous cathode.



**Figure S8** (a) Galvanostatic discharge/charge curves ( $U$  vs capacity) for a lithium-air battery with a thick LATP electrolyte physically connected to a porous LATP cathode (coated with silicone-oil and carbon) operated in ambient air at different current densities. In order to increase the contact points, a LATP paste (70 wt% LATP powder + 30 wt% terpinol) was filled into the gap between solid-state electrolyte and cathode followed by sintering at 800 °C for 3 h. (b) The SEM image for the whole lithium-air battery after discharging in ambient air at different current densities.