***Supporting Information***

# To draw an air electrode of Li-air battery by pencil

*Yonggang Wang, Haoshen Zhou**

Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Umezono, 1-1-1, Tsukuba, 305-8568 Japan

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* Corresponding author: (E-mail) hs.zhou@aist.go.jp

## *Experimental Section*

The preparation of thin-film electrode— a HB type pencil was used to draw the thin-film electrode on LISICON film. The used LISICON film was provided by Ohara Inc., Japan. The prepared pencil-trace was characterized by Scanning electronic microscopy (SEM), transmission electron microscopy (TEM) and Raman spectra tests. The total mass of the pencil-trace (0.20mg) is weighted by an electronic balance with readability of 0.01 mg.

The fabrication of the developed lithium-air battery— as shown in figure 1, the lithium-air battery can be summarized as: "Li | organic electrolyte | LISICON | pencil-trace thin-film electrode." Its structure can be explained as following: 1) Metallic lithium was used as anode (or negative electrode). 2) A small quantity of liquid organic electrolyte solution ($LiClO_4$ in ethylene carbonate/dimethyl carbonate), absorbed by a porous membrane, was just used to separate and wet lithium electrode and LISICON film. 3) LISICON film was used as a solid-state electrolyte film, across which only Li-ions can pass. 4) The pencil-trace on the surface of LISICON film was used as a catalytic electrode (cathode or positive electrode).

Electrochemical test—charge-discharge tests were performed using a Solartron Instrument Model 1287 controlled by a computer

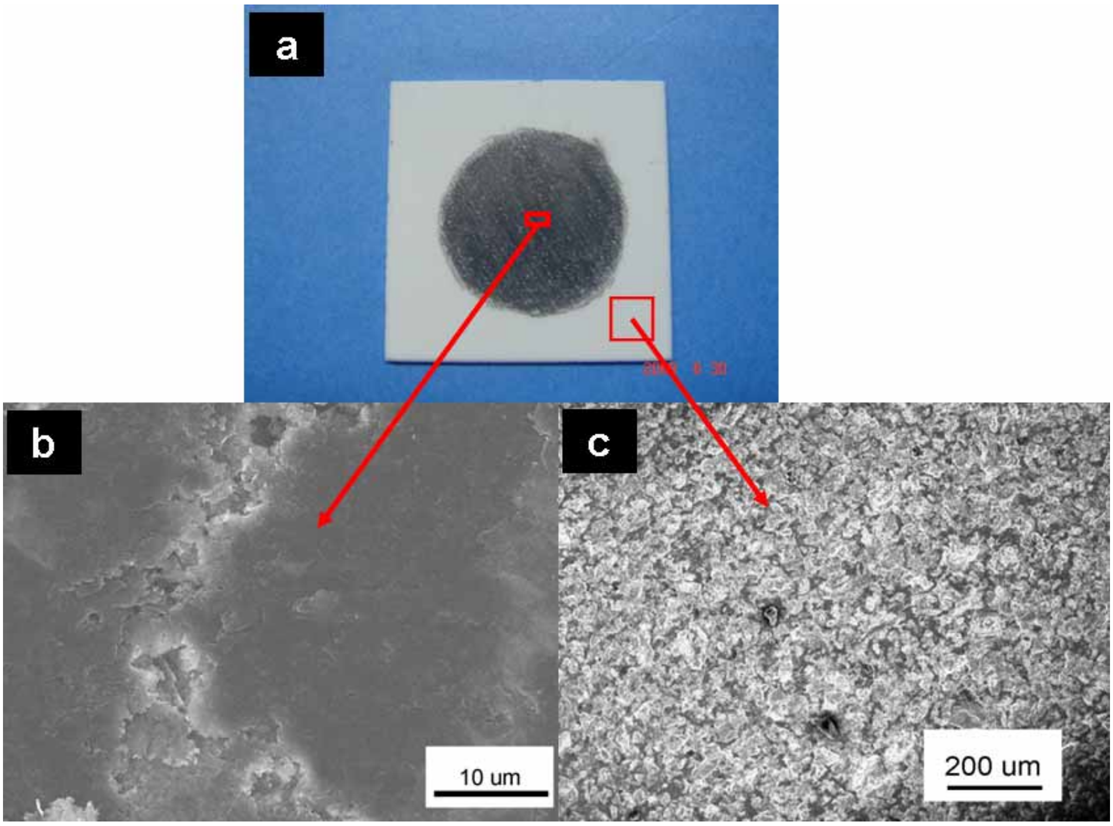

**Figure S1** The photo and SEM images of LISICON film including the pencil trace. (a) Photo image. (b) SEM image of pencil trace. (c) SEM image of LISICON surface.

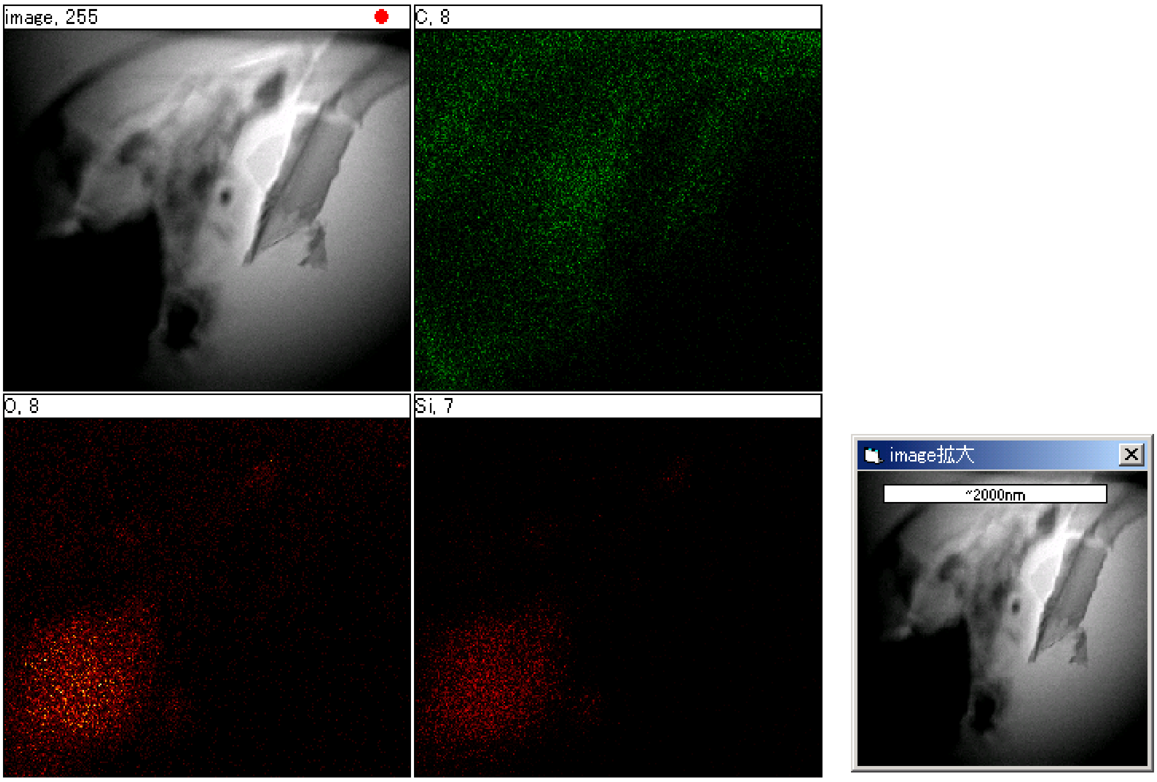

**Figure S2** TEM image of the pencil trace and its EDX mapping. As shown in figure S2, some $SiO_2$ exists in the pencil trace. It is well known that pencil-lead is made up of graphite and clay ($SiO_2$+$Al_2O_3$).

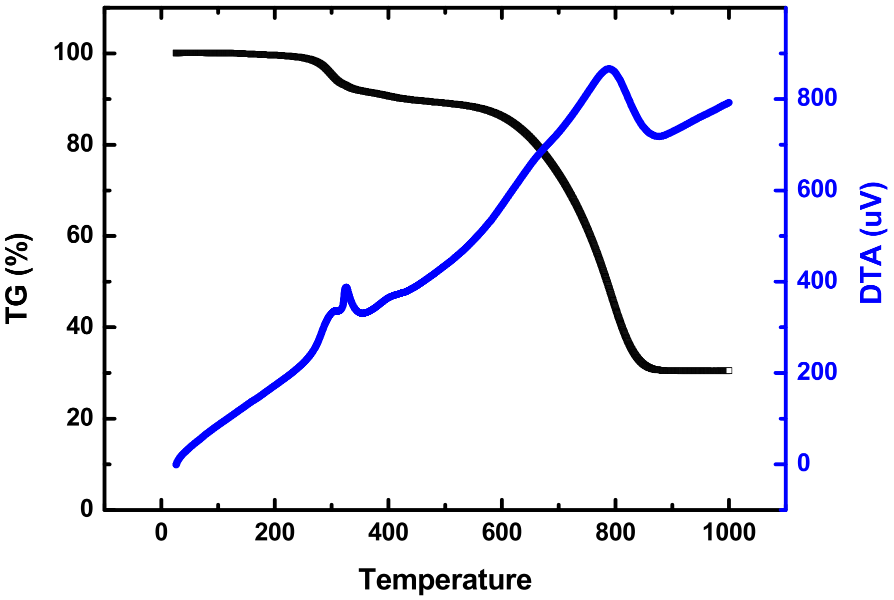

**Figure S3** TG-DTA curves of pencil-lead

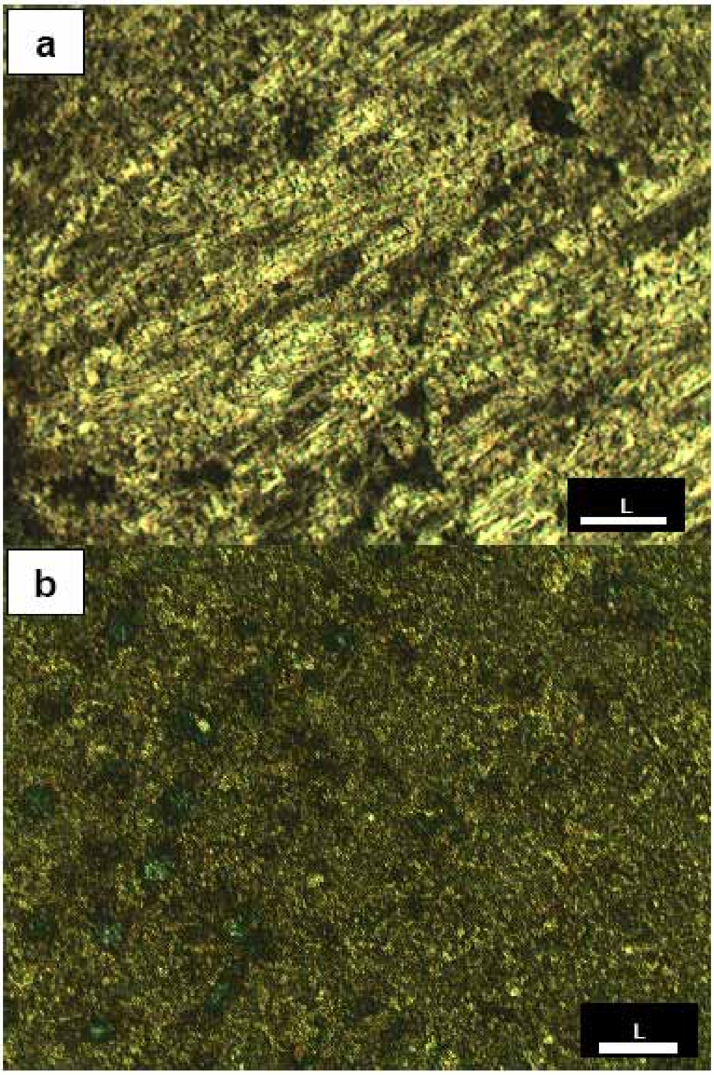

**Figure S4** Microscope image of the pencil trace thin-film electrode. (a) Before charge-discharge cycle. (b) After charge-discharge cycle. *L= 20 um*.

As shown figure S4, the surface morphology of pencil trace thin-film electrode changed obviously after continuous charge-discharge cycle. This is due to the character of $O_2$ catalytic reaction within lithium-air battery. It has been demonstrated that Li-ions from the electrolyte and $e^{-1}$ from the external circuit combine reversibly with $O_2$ from the air within catalytic electrode of lithium-air battery [5a]. Accordingly, the solid/gas ($Li_2O_2/O_2$) conversion on discharge-charge process inevitably changes the surface morphology of pencil trace thin-film electrode.

[5a] Ogasawara, T., Débart, A., Holzapfel, Novák, P. & Bruce, P.G. Rechargeable $Li_2O_2$ electrode for lithium batteries. *J. Am. Chem. Soc.***128**, 1390-1933(2006).

# Extension Discussion

The improved cycling stability comes from that the new structure of current lithium-air battery gets rid of the some undesired reactions which exist in previous lithium-air (or $O_2$) batteries. This can be explained as following:

(1) With the ceramic electrolyte (LISICON, see figure 1 of our manuscript), $O_2$ can not directly contact the metallic lithium. This ceramic protect layer effectively gets rid of the undesired reaction between $O_2$ and metallic lithium. For previous lithium-air batteries, the $O_2$ dissolved in organic electrolyte can directly oxide the lithium by chemical reaction.

(2) The ceramic electrolyte (LISICON, see figure 1 of our manuscript) can prevent the contact between organic electrolyte and air electrolyte, and thus gets rid of the undesired reactions arising from the decompounding of organic solvent in electrolyte during discharge or charge process. Although the recharge ability of lithium-air battery has been demonstrated in 2006, good cycling performance was rarely reported in the following years. In our opinion, the decompounding of organic solvent in electrolyte is one of main reasons. Very recently, Mizuno et al. (Toyota Motor Corporation) investigated the rechargeable Li-$O_2$ battery using carbonate-based liquid electrolyte (LiTFSI/PC), and demonstrated that the discharge product of Li-$O_2$ battery is $Li_2CO_3$ and RO-(C=O)-OLi (R= alkyl group ), where the RO-(C=O)-OLi comes from the decompounding of the carbonate-based organic solvent PC (**See ref. 8 of our manuscript**). This is because that organic carbonates are unstable in the presence of catalyst and $O_2$. In current lithium-air battery, the $O_2$ or catalyst can not contact the liquid organic electrolyte. On the other hand, Mizuno et al. also demonstrate the main charge product of their battery is $CO_2$, but not $O_2$ (**See ref. 8 of our manuscript**). It can be assumed that the $CO_2$ generation mainly arises from the oxidation of organic electrolyte at high charge voltage. In current lithium-air battery, the stable ceramic electrolyte would not be oxidized on charge process.

As mentioned above, the proposed lithium-air battery in present manuscript can prevent the undesired reactions arising from the lithium oxidation and organic electrolyte decompounding, and thus displays improved cycle performance.

Besides these undesired reactions, the large volume variety of air electrode resulting from the solid/gas ($Li_2O_2/O_2$) conversion on discharge-charge process also much limits the cycling performance of lithium-air battery. Although the proposed lithium-air battery can effectively prevent these undesired reactions, it still can not alleviate the volume variety resulting from the solid/gas conversion. **As shown in Figure S4 (see supporting information)**, the smooth pencil trace (or air electrode) has been broken after 15th cycle. Accordingly, the capacity of the proposed lithium-air began reducing after 15th cycle. In current manuscript, we only directly drew an air electrode on ceramic electrolyte film (LISICON), which may provide a snapshot for future lithium-air battery. For future practical application, it is necessary to further improve the air electrode structure, especially the contact between the air electrode and ceramic electrolyte.