Supporting Information

A Lithium-air fuel cell using copper to catalyze oxygen-reduction based on copper-corrosion mechanism

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Figure S1

The background about Li-air battery and Li-air fuel cell

Figure S2

Figure S3

Figure S4

Figure S5

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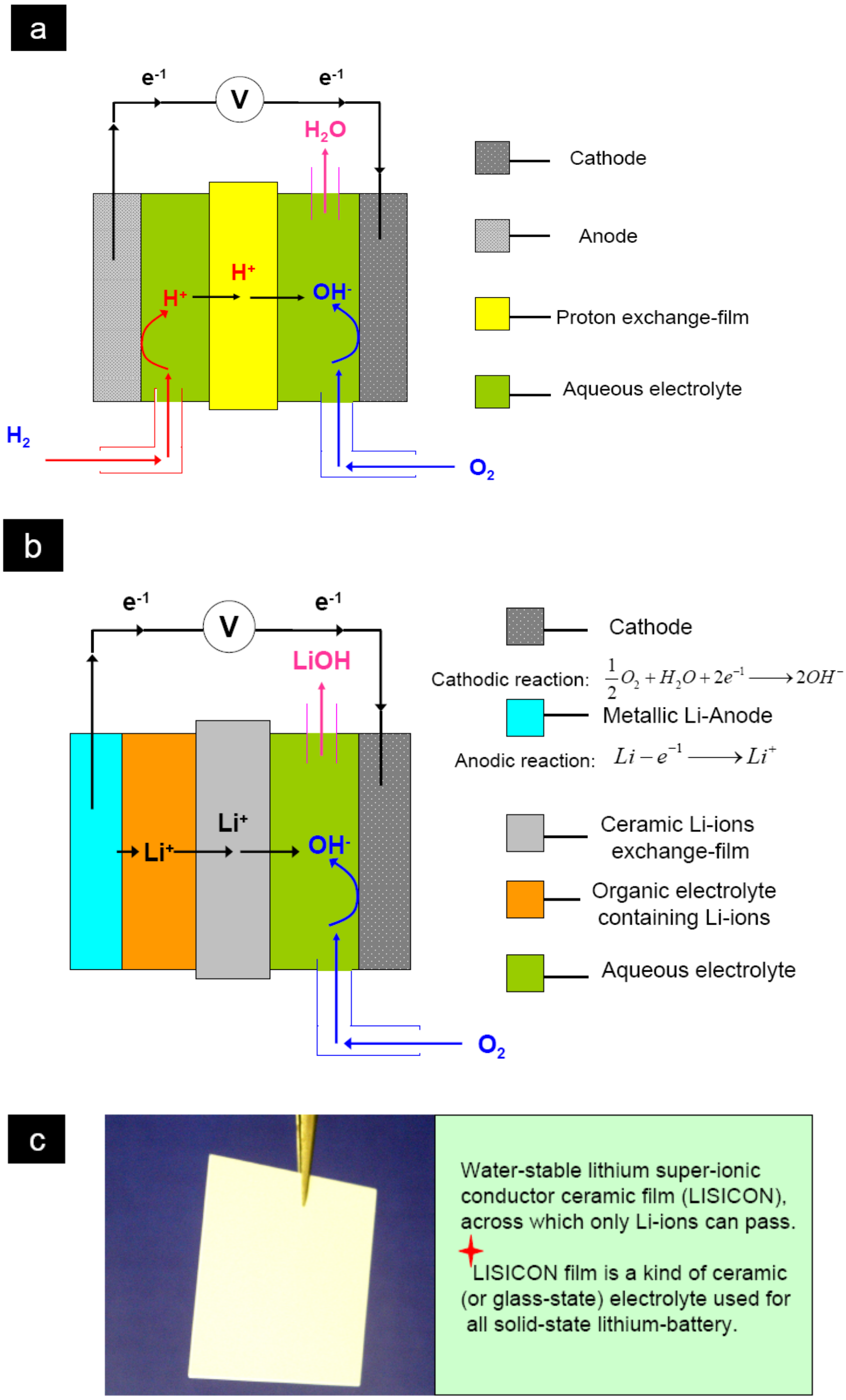

Water-stable lithium super-ionic conductor ceramic film (LISICON), across which only Li-ions can pass.

✦ LISICON film is a kind of ceramic (or glass-state) electrolyte used for all solid-state lithium-battery.

Figure S1 Schematic drawing comparing the structure and operating principle of (a) conventional H_2-O_2 fuel cell and (b) Li-air fuel cell. Figure 1 (c) is the photo of water stable ceramic Li-ions exchange film—"LISICON film", across which only Li-ions can pass. (The LISICON film used in our experiment is provided by Ohara Inc. Japan)

Background about Li-air battery and Li-air fuel cell:

In 1996, Abraham and Jiang first reported the concept of ***rechargeable Li-air battery using organic electrolyte*** with a structure of Li | organic electrolyte | air [S1]. If the inexhaustible O_2 in air can be continuously utilized to provide capacity, theoretical energy density of lithium-air batteries would be much higher than that of other energy storage devices [S1-8]. However, for this kind of lithium-air battery, the discharge product Li_2O_2 is not soluble in organic electrolyte, and clogs porous air electrode step by step.

The O_2 reduction in aqueous solution is quite different from that in organic solution. For example, in fuel cell, the O_2 reduction product is OH^- (or H_2O) that is soluble in aqueous electrolyte. Thereby, uniting the reduction of O_2 in aqueous electrolyte and metallic Li-anode should be a promising method to overcome the drawback of lithium-air batteries using organic electrolyte. Unfortunately, the metallic lithium can react with water directly.

In 2007, ***PolyPlus Battery Company*** first united a metallic lithium-electrode, protected by ceramic electrolyte, with Pt-catalyzed O_2 reduction in aqueous solution [S9]. After protected with water-stable ceramic electrolyte, metallic lithium can work in aqueous solution. *PolyPlus Battery Company* has patented this idea and introduced this idea at some conferences.

In 2008, *N. Imanishi et al.* further investigated these ideas patented by *PolyPlus Battery Company*. In their reported, the metallic lithium-electrode, protected by a water-stable ceramic electrolyte film, was coupled with Pt-catalyzed O_2 reduction in aqueous electrolyte solution to fabricate a ***rechargeable Li-air battery using aqueous electrolyte*** [S10, 11].

In 2009, based on previous study, our group proposed a lithium-air system, which units the O_2 reduction in ***aqueous electrolyte*** and lithium-anode in ***organic electrolyte*** by a ceramic Li-ions exchange film (***its structure is shown in figure S1b***) [S12]. In this work, we also gave a conclusion that the ***lithium-air system including organic /aqueous hybrid electrolyte*** should be further studied as a ***fuel cell*** in future.

As mentioned above, the concept of Li-air fuel cell is a quite new cross-cutting field between lithium battery and fuel cell. It has attracted great attention, although it is still at an infant stage. For example, *national institute of advanced industrial science and technology* (AIST, Japan) has introduced the "concept of lithium-air fuel cell" through internet [S13]. At the 2009 conference about "Scalable Energy Storage: Beyond Lithium Ion" (organized by IBM company, USA), lithium-O_2 battery and lithium-air fuel cell have been widely discussed as a current hot topic [S14].

References

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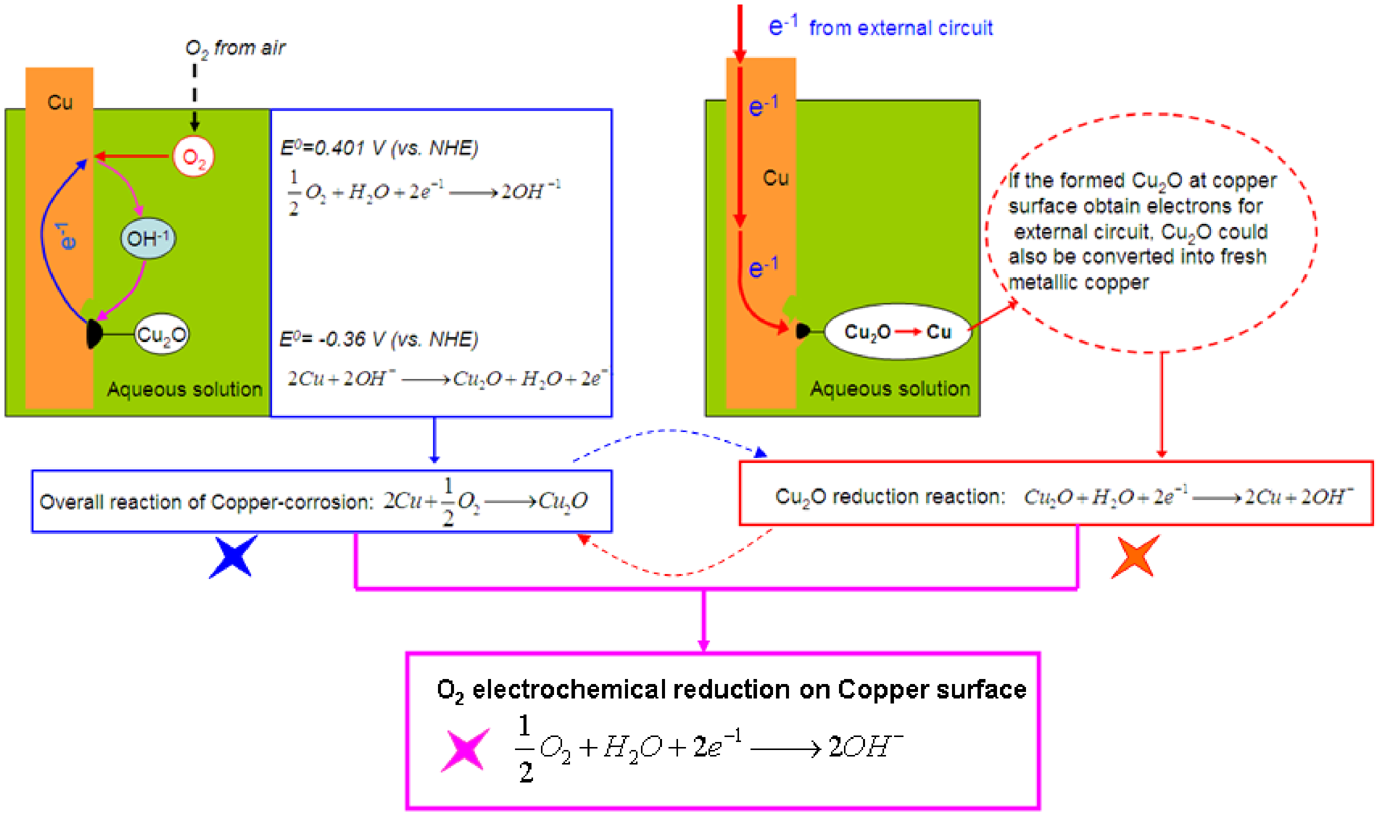

Figure S2 Schematic drawing shows the copper-corrosion phenomenon and Cu_2O electrochemical reduction process. The cycle between copper-corrosion and Cu_2O electrochemical reduction results in the O_2 electrocatalytic reduction at copper surface.

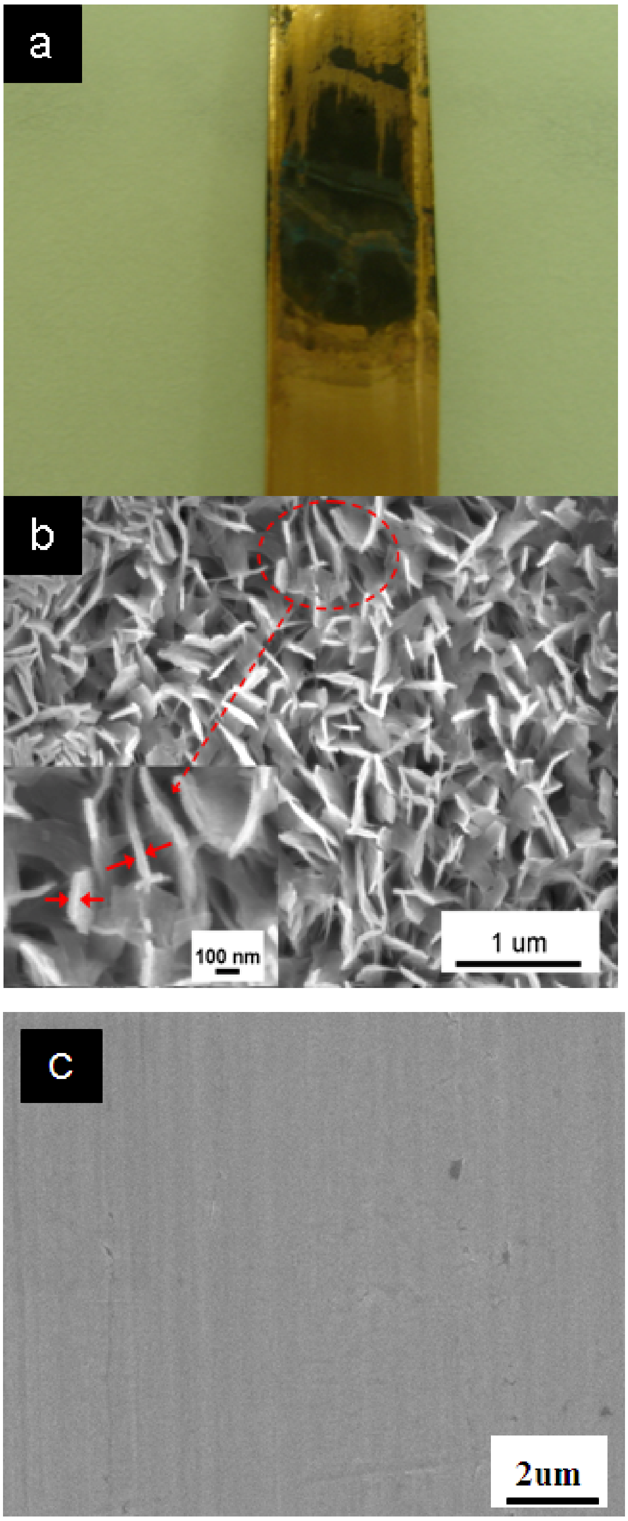

Figure S3 (a) photo of the brown-black deposits grown on the surface of copper electrode during discharge process and (b) its SEM image. As shown in the insert of figure S3b, the thickness of these nano-flakes is about 50 nm. (c) SEM image of the fresh Cu electrode.

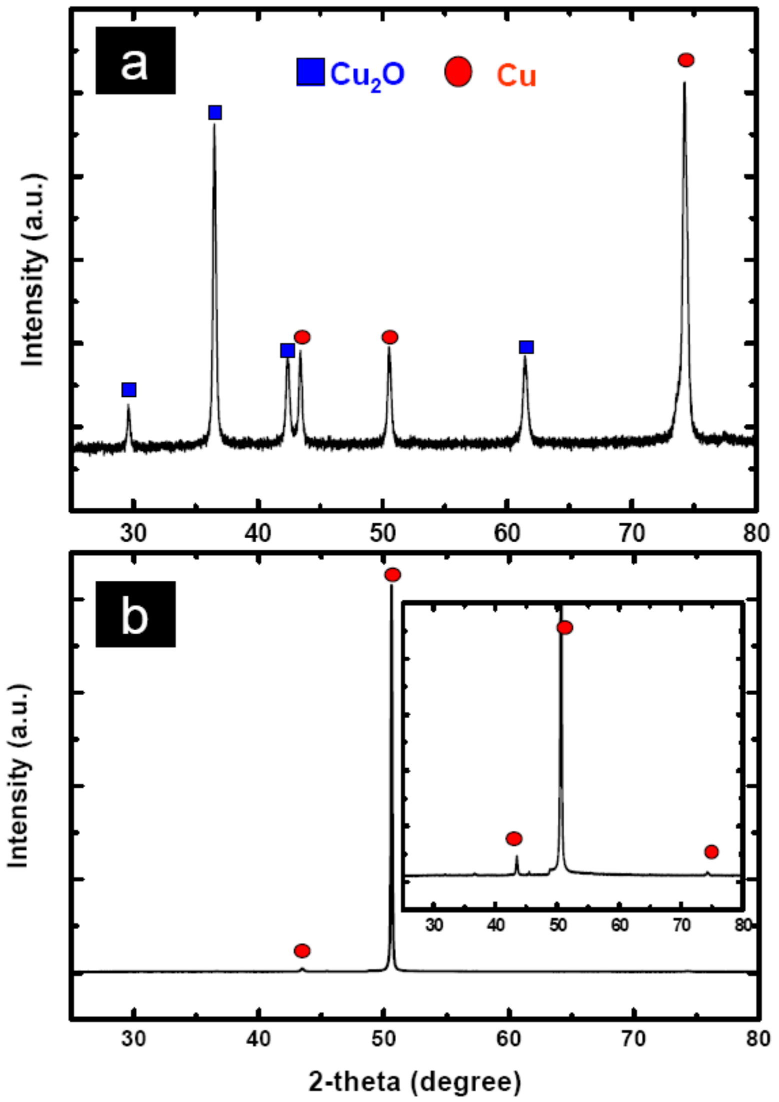

Figure S4 (a) XRD pattern of the brown-black deposits grow on the surface of copper electrode during discharge process and (b) the XRD pattern of fresh copper electrode.

As shown in Figure S4, the XRD pattern of Cu in the Cu/Cu_2O composite is not different from that of the fresh Cu electrode. Comparing the XRD pattern of Cu in the Cu/Cu_2O composite (Figure S4 a) and that of the fresh Cu plate (Figure S4b), we can find that the appearance angles of these diffraction peaks are the same. However, the peak intensity for Cu in the Cu/Cu_2O is quite different from that for fresh Cu plate. This may imply the deposited copper is strongly oriented on the conversion process between Cu and Cu_2O (or the O_2 reduction process on Cu electrode).

As explained in our manuscript, the O_2 electrochemical catalytic reduction on Cu plate $\frac{1}{2}O_2 + H_2O + 2e^{-1} \longrightarrow 2OH^-$ can be divided into two processes:

$$2Cu + \frac{1}{2}O_2 \longrightarrow Cu_2O \qquad (1)$$

$$Cu_2O + H_2O + 2e^{-1} \longrightarrow 2Cu + 2OH^- \qquad (2)$$

In other words, the O_2 electrochemical catalytic reduction on Cu plate is based on the Cu/Cu_2O conversion cycle. According to equation (1) and (2), Cu/Cu_2O composite should be formed on the O_2 electrochemical catalytic reduction process. It also should be noted that the Cu generated from the Cu_2O electrochemical reduction (equation 2) is not the fresh Cu plate.

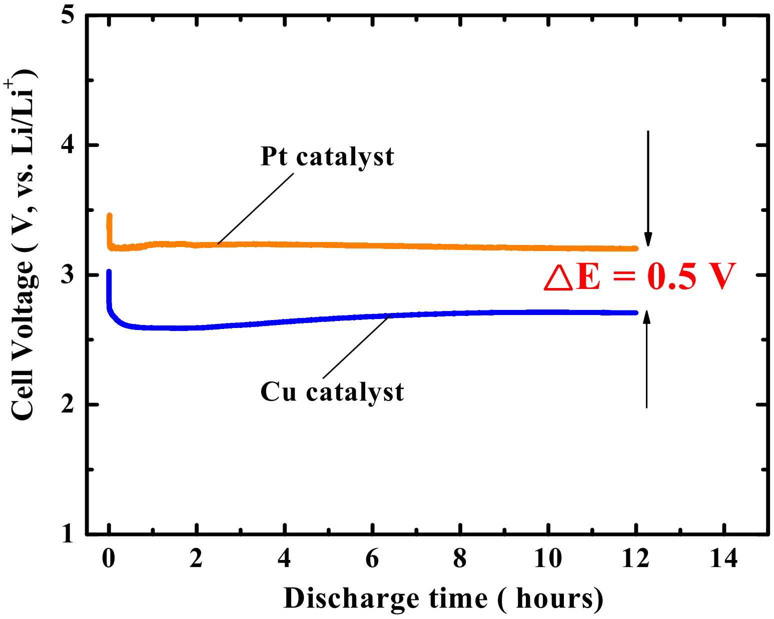

Figure S5: the comparison of catalytic performance between Pt plate and Cu plate. A preliminary lithium-air fuel cell was assembled by using 1 M $LiClO_4$ in ethylene carbonate/dimethyl carbonate as the electrolyte for Li-anode and O_2-saturated aqueous solution contains 1 M $LiNO_3$ as the electrolyte for Pt catalytic cathode. 1cm^2 Pt plate (double sides) was immersed in the aqueous solution, and used as the catalytic electrode for O_2 reduction. Without regard to the thickness, the total area of both sides of Pt palate, which was immersed in the aqueous electrolyte solution, should be 1 ×2 cm^2 (2 cm^2). The applied current density for Pt plate electrode is 0.17 mA/2cm^2 (=0.085 mA/cm^2). In the test for Cu catalytic electrode, 3 cm^2 Cu plate (double sides) was immersed in the aqueous solution, and used as the catalytic electrode for O_2 reduction. The total area of both sides of the Cu plate, which was immersed in the aqueous solution, should be 2 ×3 cm^2 (6 cm^2).The test current density for Cu plate is 0.5 mA/6 cm^2 (about 0.083 mA/cm^2) which is close to that for Pt plate electrode (0.085/cm^2).

As shown in **Figure S5**: the Lithium-air cell using Pt plate as catalytic electrode exhibits an average operating voltage of 3.2 V. However, the average operating voltage of the lithium-air cell based on Cu plate electrode is only 2.7 V. The difference between their operating voltages is about 0.5 V, indicating that the catalytic performance Cu is still much smaller than that of Pt. However, when compared with Pt catalyst, the most important advantage of Cu catalyst is the plenteous storage and low cost. Expensive price and limited storage of Pt is one of the main reasons that limit the wide practical application of H_2-O_2 full cell. Metal corrosion has been investigated for a long time, and has the potential to be employed for O_2 catalytic reduction. Unfortunately, metal corrosion induced O_2 reduction is rarely applied in traditional H_2-O_2 full cell, which is owing to the low theoretical operating voltage of H_2-O_2 fuel cell (about 1.23 V) and the low catalytic performance compared with Pt. However, the theoretical operating voltage of lithium-air fuel cell is more than 3 V. Thereby, low cost metal corrosion induced O_2 catalytic can be applied in lithium-air fuel cell. For example, although the catalytic performance of Cu plate is lower than that of Pt plate, the lithium-air fuel cell using Cu plate as catalyst still exhibits an operating voltage of 2.7 V (see Figure $_{\text{answer}}$ 1). On the other hand, the catalytic activity of metallic copper may be further improved by “nano-sizing” or “nano-structuring”. For instance, during the last decade, a number of strategies have been proposed for improving the performance of catalytic activity of Pt through “nano-sizing” or “nano-structuring”. The fabrication of the proposed preliminary lithium-air fuel cell should also be optimized in future study. For example, nano-sized or nano-structured copper-particles could be used to prepare air (or O_2) diffusion electrode, just like the cathode structure of practical H_2-O_2 fuel cell.

If brief, lithium-air fuel cell is a new concept about energy conversion device, and still at the infant state. We hope the application of metal corrosion induced O_2 catalytic reduction in lithium-air fuel cell could bring a new study direction for both metal corrosion study and energy conversion study.