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# A Li-air fuel cell with recycle aqueous electrolyte for improved stability

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ABSTRACT

A lithium-air fuel cell with a new designed cell structure for improved stability is proposed. The cell consists of two subunits: an energy conversion unit that employs a cation exchange membrane and a reaction-product recycling unit that collects/removes LiOH and thus protects the LISICON plate from corrosion under strong alkaline conditions. The aqueous electrolyte recycling system allows the newly structured Li-air fuel cell to attain higher theoretical energy density, and hence potential application as an alternative energy source for transportation.

## 1. Introduction

Global warming and dwindling resources of fossil fuels have accelerated research efforts to find alternative energy sources. Serious consideration is given to clean electrochemical energy production as a sustainable and environmentally friendly system. The lithium-ion battery with the highest energy density among available rechargeable batteries already dominates the portable consumer electronic market [1–4]. However, even this energy density cannot satisfy industrial needs, such as power sources for the transportation and residential sectors [2,4]. The first Li-air battery with an organic electrolyte was introduced in 1996 and attracted much interest due to its higher energy density [5]. The essential advantage of this system is the use of inexhaustible oxygen in the air as the reagent, rather than carrying the necessary chemicals inside the battery. At a nominal potential of 3 V, the theoretical specific energy of the Li-air battery is about 3500 Wh $kg^{-1}$. The problem is that the battery's discharge product, $Li_2O_2$, is not soluble in the organic electrolyte and gradually clogs the porous air electrode, which deteriorates the battery performance [5–10].

To overcome this problem, a new system employing a hybrid electrolyte was recently proposed. In this system, a metallic lithium anode in an organic electrolyte and an $O_2$-reduction cathode in an aqueous electrolyte are united and separated by a LISICON (lithium super ionic conductor) plate [10,11]. Instead of being an obstacle in the porous air electrode in the organic electrolyte, the $O_2$-reduction product, $OH^-$, is soluble in the aqueous solution. However, the rechargeable Li-air battery with the LISICON plate in the hybrid electrolyte still suffers from the following intrinsic drawbacks: i) Dendritic growth of lithium during the charge process leads to reaction with LISICON; ii) The extra water for LiOH dissolution limits the energy density; and iii) The LISICON plate is unstable in the strong alkaline aqueous solution [12]. Practical application of the Li-air system depends on the resolution of these three issues. Considering the first drawback, the preferred direction of the Li-air battery should be as a fuel cell rather than a rechargeable battery, which was indicated in our previous work [10]. However, the second and particularly third drawbacks are major problems even for the fuel cell type. In this work, in order to protect the LISICON plate, we designed a new type of a Li-air fuel cell with a high theoretical energy density based on an aqueous electrolyte recycling system. The structure and electrochemical performance of the developed Li-air battery were investigated.

## 2. Experimental

The design of the cell structure of our improved Li-air fuel cell is shown in Fig. 1. The cell contains two subunits: an energy conversion unit and a product recycling unit. In the energy conversion unit, a lithium anode is used as the fuel in the organic electrolyte while the porous catalytic air cathode is arranged with its catalytic layer contacting the aqueous electrolyte and its gas diffusion layer facing the air. The two electrolytes, organic and aqueous, are separated by a LISICON plate ($[Li_{1+x+y}(Al,Y)_x(Ti,Ge)_{2-x}Si_yP_{3-y}O_{12}]$ from Ohara Inc., Japan) with a thickness of 0.15 mm. The porous air electrode has an area of 1 $cm^2$, a thickness of 0.3 mm and a catalyst layer mass load of 4.5 mg $cm^{-2}$. Preparation of the $Mn_3O_4$/activated carbon composite used as the catalytic layer and the gas diffusion layer was described in our previous report [13].

The container for the aqueous electrolyte is further divided into two rooms, A (30 mL) and B (15 mL), by a cation exchange membrane (CEM) with a thickness of 0.05 mm. This is a semipermeable membrane made from ionomers and designed to conduct only cations. Electrochemical

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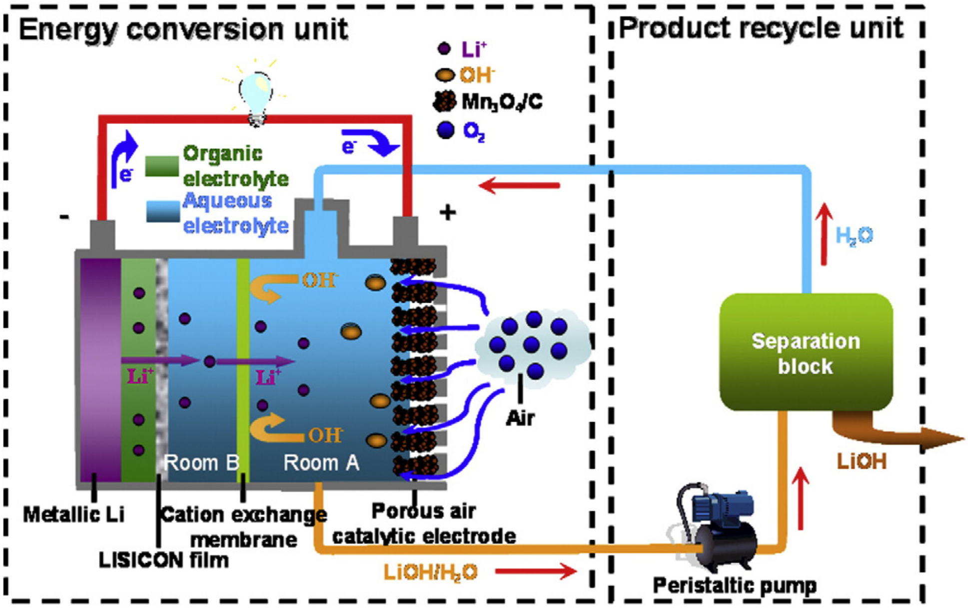

**Fig. 1.** A schematic representation of the developed Li-air fuel cell system with energy conversion unit and product recycle unit.

tests were performed using a Solartron 1287 electrochemical interface analyzer. The morphology of the LISICON plate was characterized via field-emission scanning electron microscopy (FESEM, LEO Gemini Supra 35).

## 3. Results and discussion

As seen in Fig. 1, the aqueous solution in rooms A and B is 1 M LiOH and $LiNO_3$, respectively. It is well known that the LISICON plate is unstable in the strong alkaline solution [12]. In order to maintain the $OH^-$ concentration value in room A, the LiOH reaction product yielded in room A is conducted into the product recycling unit employing a peristaltic pump for precise control of the solution flow. For large-scale industrial applications, distillation or ion-exchange of the LiOH solution could be adopted in a separation block to produce solid-state LiOH and distilled water. Subsequently, the distilled water would flow back to room A. In our experiment, pure water was directly injected into room A by a mini injector accurately instead of conducting distilled water back into room A. The LiOH recycled product can be used to fabricate metallic Li for fuel in plants. Based on this recycling system, the pH in room A can be maintained at the initial value since the LiOH product can be completely removed from the energy conversion unit. Moreover, the aqueous electrolyte in room B can be maintained at weak alkalinity because the anion $OH^-$ cannot easily pass through the CEM. Further discussion is presented later.

The battery reactions in the energy conversion unit are summarized as follows:

$$\text{Cathode}: O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{R1}$$

$$\text{Anode}: Li \rightarrow Li^+ + e^- \tag{R2}$$

$$\text{Battery reaction}: 4Li + O_2 + 2H_2O \rightarrow 4Li^+ + 4OH^- \tag{R3}$$

The $Mn_3O_4$/C-based catalytic air cathode including a catalytic layer and gas diffusion layer is located between the alkaline aqueous electrolyte and air atmosphere, forming a continuous liquid–solid–gas three-phase interface. During discharge, $O_2$ from the air continuously diffuses into the porous catalytic air electrode where electrocatalytic reduction takes place. Simultaneously, $Li^+$, the oxidation product of lithium metal in the organic electrolyte diffuses to room A across the LISICON plate and CEM in turn. Fig. 2(a) gives the galvanostatic discharge curve of the improved cell at 0.5 mA $cm^{-2}$ for one week. This clearly shows that the lithium metal serving as the fuel realizes continuous reduction of inexhaustible $O_2$ from the air with a voltage plateau near 2.8 V to deliver a high electrode capacity of about 19,000 mAh $g^{-1}$. It is worth mentioning that this calculation of the electrode capacity based on the mass of the catalytic layer (including carbon, catalyst and binder) in order to facilitate comparison was adopted in all previous reports [5–10]. The discharge curves at different currents and power performance are also presented in Fig. 2(b) and (c). The operating voltage is maintained at 3.2 V at a current density of 0.01 mA $cm^{-2}$, and is even maintained at 2.6 V at 1 mA $cm^{-2}$. Fig. 2(c) clearly shows a linear decrease in the operating voltage with the increase in the applied current density, which is mainly due to the resistance of the LISICON plate and polymer CEM [10]. Furthermore, this developed Li-air fuel cell can deliver a maximum power density of 1127 W $kg^{-1}$. For comparison, this calculation is also based on the total mass of the catalytic electrode, which was adopted in our previous work [10]. The power density can be improved by enhancing the Li-ion conductivity through the membrane and LISICON plate.

The chemical instability of LISICON plate in strong alkaline electrolyte is a core issue which influences the stability of the whole system with the hybrid electrolyte. To protect the LISICON plate, the CEM was employed to block the $OH^-$ from room A. In addition, the LiOH solution yielded was pumped out from the energy conversion unit and the distilled water flowed back into room A, which helped maintain a low-pH solution in room B. It is worth noting that the solution flow should be precisely controlled to match the discharge current. In our case, at 0.5 mA, the flow of the LiOH solution pumped from room A was about 0.43 mL for 24 h. The pH values in rooms A and B during the discharge process are presented in Fig. 3(a). Room A had a steady pH value of 12.6, while that in room B remained at pH 10.8 after the second day. This indicates that the LiOH concentration in room A is constant and the aqueous solution in room B maintained weak alkalinity. In fact, a very small amount of $OH^-$ diffused into room B to form the concentration balance of LiOH on both sides of the CEM, which caused a slight increase in pH in room B at the beginning of discharge. However, the weak alkalinity in room B is still approximately one hundredth of that in room A. When the initial LiOH concentration in room A was decreased to 0.01 M, the corresponding pH value in room B stayed at 9.9 during the discharge. These results suggest that the alkalinity in room B weakens with decreasing initial pH in room A. Fig. 3(b) shows the XRD patterns of the LISICON plate