



Short communication

# A lithium-air battery with a potential to continuously reduce O<sub>2</sub> from air for delivering energy

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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## ABSTRACT

A lithium-air battery, in which the catalytic reduction of O<sub>2</sub> in an alkaline aqueous electrolyte and the metallic lithium in a non-aqueous electrolyte were subtly united together by a super-ionic conductor glass film (LISICON), was established in the present work. For this system, Mn<sub>3</sub>O<sub>4</sub> based air diffusion electrode and metallic lithium were used as positive electrode and negative electrode, respectively. 500 h continuous discharge performance indicates that this kind of lithium-air battery has a potential to realize continuous reduction of O<sub>2</sub> from air to deliver energy like a fuel cell. During the long-time discharge process, the air electrode has delivered a special capacity of 50,000 mAh g<sup>-1</sup> based on total mass of catalytic electrode (carbon + binder + catalyst). This result is much higher than that of previous studies about Lithium-air batteries.

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## 1. Introduction

Although large capacity lithium-ion battery for electric vehicle (EV) has attracted much attention [1–7], its energy density is still limited by the positive electrode. Different from conventional lithium-ion batteries, the air electrode of lithium-air batteries can reduce O<sub>2</sub> from air to deliver capacity. If the inexhaustible O<sub>2</sub> 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 [8]. The first lithium-air battery with a structure of Li |organic electrolyte| air was reported in 1996 by Agraham and Jiang [8]. Then, several research groups followed this work [9–15]. However, for this kind of lithium-air battery, the discharge product Li<sub>2</sub>O<sub>2</sub> is not soluble in organic electrolyte, and clogs porous air electrode step by step.

The O<sub>2</sub> reduction in aqueous solution is quite different from that in organic solution. For example, in Zn-air battery (or Mg-air battery [16]), the O<sub>2</sub> reduction product is OH<sup>-</sup> that is soluble in aqueous electrolyte. Thereby, uniting the reduction of O<sub>2</sub> in aqueous electrolyte and metallic Li-anode through a lithium super-ionic conductor glass film (LISICON) should be a promising method to overcome these drawbacks of lithium-air batteries using organic electrolyte. This idea has been patented by PolyPlus Battery Company in 2007 [17]. Simultaneously, a conference review article (2007) also mentioned this idea based on unpublished data [18].

However, both the reports did not give the academic research results. Recently, Imanishi et al. reported the stability of LISICON in aqueous solution, and established a lithium-air battery with a structure of Li |LISICON| 1 M LiCl| Pt [19,20]. However, for system performance, they just gave a very primary result. For example, their system only achieved 1 h discharge at a current density of 0.25 mA cm<sup>-2</sup> [20]. As mentioned above, this idea is a current hot topic in battery community. The more interesting questions are: could this idea really realize the continuous reduction of O<sub>2</sub> from air to deliver energy? Which is its future study direction?

Herein we developed a lithium-air battery with a structure of Li|organic electrolyte|LISICON| 10 ml 1 M KOH| Mn<sub>3</sub>O<sub>4</sub> catalytic electrode, and studied its electrochemical performance in detail.

## 2. Experiment

The preparation of Mn<sub>3</sub>O<sub>4</sub>/activated carbon composite is given in Wang et al. [21] previous report. The air catalytic electrode includes a catalyst layer and a gas diffusion layer. The prepared Mn<sub>3</sub>O<sub>4</sub>/carbon composite (85 wt.%) and polytetrafluoroethylene (PTFE) (15%) were well mixed, and then was roller-pressed into a sheet to form catalytic layer. The gas diffusion layer was prepared by mixing acetylene black (60 wt.%) and PTFE emulsion (40 wt.%) with isopropanol into paste and then rolling the paste into a film. The air catalytic electrode was finished by pressing the catalyst layer and gas diffusion layer onto a nickel mesh. The area of the air electrode was 1 cm<sup>2</sup>, and the mass load of catalyst layer was 5 mg cm<sup>-2</sup>.

The structure of developed lithium-air battery shown in Fig. 1 can be summarized as: (I) the organic electrolyte (1 M LiClO<sub>4</sub> in

\* Corresponding author. Tel.: +81 29 861 5795; fax: +81 29 861 5799.  
E-mail address: [hs.zhou@aist.go.jp](mailto:hs.zhou@aist.go.jp) (H. Zhou).

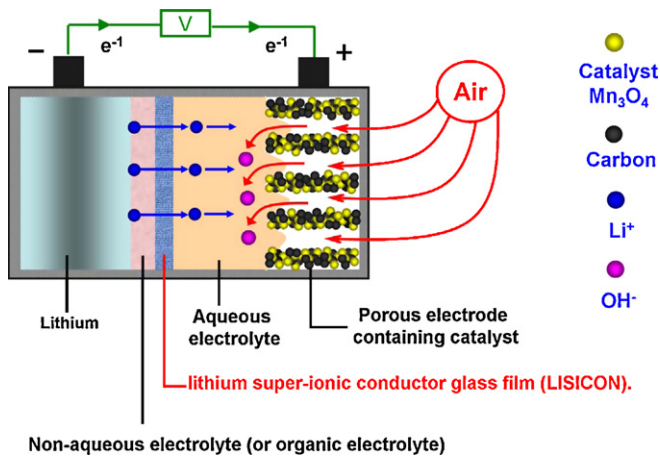


Fig. 1. A schematic representation of the developed lithium-air battery.

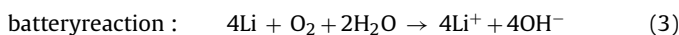
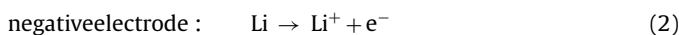
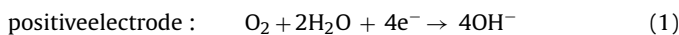
ethylene carbonate/dimethyl carbonate) and 10 ml 1 M KOH are separated by a LISICON film. (II) The organic electrolyte is just a thin liquid layer (or electrolyte adsorbed by porous membrane) that is used to separate and wet Li-anode and LISICON film. (III) The air catalytic electrode is between aqueous electrolyte solution and air atmosphere. The used LISICON is provided by Ohara Inc., Japan [22].

Electrochemical tests were performed using a Solartron Instrument Model 1287 controlled by a computer.

### 3. Results and discussion

As shown in Fig. 1, the organic electrolyte used for Li-anode and the alkaline aqueous electrolyte used for air catalytic electrode are separated by a LISICON film. The  $Mn_3O_4$  based air catalytic electrode including catalytic layer and gas diffusion layer is between aqueous electrolyte solution and air atmosphere, forming continuous liquid–solid–gas three-phase interface. Accordingly, it has the potential to achieve long-time discharge. In Refs. [19,20], Pt immersed in LiCl solution was used as  $O_2$  catalytic electrode, where only the  $O_2$  dissolved in water can be reduced to deliver capacity. However, both low solubility of  $O_2$  in water and slow dissolving speed of  $O_2$  cannot support long-time continuous discharge, especially at high discharge current density. Furthermore, Li-anode and LISICON were contacted together through solid–solid interface in Refs. [19,20]. With the continuous consumption of metallic Li-anode during the long-time discharge process, the contact at solid–solid interface would be broken gradually. In our system, the Li-anode and LISICON were contacted together through solid–liquid–solid interface (Li-organic electrolyte-LISICON), which could alleviate this fading phenomenon mentioned above.

The electrodes reactions within this lithium-air battery can be summarized as follows:



In the discharge process,  $O_2$  from air continuously diffuses into porous catalytic electrode, where electrocatalytic reduction reaction takes place according to Eq. (1). Simultaneously, metal lithium transforms into  $Li^+$ , and then  $Li^+$  diffuses from non-aqueous solution to aqueous solution through LISICON film.

Fig. 2a gives the discharge curve of developed lithium-air battery at a current density of  $0.5 \text{ mA cm}^{-2}$ . During 500 h continuous discharge, the operating voltage of developed lithium-air battery keeps at about 2.8 V. This result demonstrates that the porous

catalytic electrode of new developed lithium-air battery can continuously reduce  $O_2$  from air to provide capacity. In order to clearly distinguish this new type lithium-air battery from these ever reported lithium-air batteries using organic electrolyte, we also calculated the delivered capacity of porous catalytic electrode. During the discharge process, the air electrode has delivered a special capacity of  $50,000 \text{ mAh g}^{-1}$  based on total mass of catalytic electrode (carbon + binder + catalyst). This result is much higher than that of any previous studies about lithium-air batteries using organic electrolyte [8–15]. Herein, it should also be noted that all previous studies about lithium-air batteries use the capacity calculated from carbon mass (or air electrode mass: carbon + binder + catalyst) to evaluate battery performance [8–15]. Fig. 2b displays the discharge curves at different current densities. The operating voltage of developed lithium-air battery keeps at 3.3 V at a current density of  $0.01 \text{ mA cm}^{-2}$ , whereas it still keeps 2.3 V even at the current density of  $5 \text{ mA cm}^{-2}$ . With the growth of applied current densities, linear decrease of operating voltage is clearly observed in Fig. 2c, which is mainly owing to the resistance of LISICON. During the same process, its power density sharp increases (Fig. 2c). At the current density of  $11 \text{ mA cm}^{-2}$ , the developed lithium-air battery reaches its maximal power density ( $3200 \text{ W kg}^{-1}$ ). This calculation is just based on the total mass of catalytic electrode. Fig. 2d gives the typical impedance spectra of the developed lithium-air battery at a discharge state of 3 V. As shown in Fig. 2d, three semicircles were observed at high, medium, and low frequency range. The semicircles are the characters of interface resistance (high frequency), charge transfer resistance (medium frequency) and  $O_2$  diffusion resistance (low frequency). According to the point intersecting with the real axis at high frequency range, the internal resistance of developed lithium-air battery is about  $120 \Omega$ .

On the other hand, as shown in Fig. 1, during the discharge process, the concentration of LiOH in aqueous electrolyte solution increases gradually. However, the inherent solubility of LiOH is low ( $12.8 \text{ g}/100 \text{ g H}_2\text{O}$  at room temperature), which is the drawback of this kind of lithium-air battery including LISICON. Namely this idea can be developed as rechargeable battery [20], whereas the added water used for LiOH dissolution would limit its energy density. According, this idea could be further developed with a cycle operating model like fuel cell, in which generated LiOH should be separated from system during discharge process (see Fig. 3a). In fact, this established cycle operating model is close to one of possible operating models of  $H_2$ – $O_2$  fuel cell, where generated  $H_2O$  during discharge process is used to prepare  $H_2$  (see Fig. 3b). According to the chemical reaction  $4Li + O_2 + 2H_2O \rightarrow 4Li^+ + 4OH^-$  and its theoretical operating voltage (3.4 V), the theoretical energy density of the developed lithium-air battery is  $5695 \text{ Wh kg}^{-1}$  excluding the weight of  $O_2$ . This value is higher than that of  $H_2$ – $O_2$  fuel cell ( $3660 \text{ Wh kg}^{-1}$  including the weight of  $O_2$ ), and even comparable with that of methanol/air fuel cell ( $6226 \text{ Wh kg}^{-1}$  excluding the weight of  $O_2$ ) [23]. The theoretical energy conversion efficiency ( $E_{th}$ ) of new type lithium-air system can be calculated by

$$E_{th} = \frac{\Delta G}{\Delta H} \times 100\% \quad (4)$$

According to the battery reaction and Eq. (4), the theoretical energy conversion efficiency ( $E_{th}$ ) of developed lithium-air battery is 90.84%, which is even higher than that of  $H_2$ – $O_2$  fuel cell (83%). Thereby, it is possible to develop lithium-air fuel cell, in which gas  $H_2$  is replaced by metal lithium. Surely, the long-time discharge curve shown in Fig. 2a can be regarded as a primary fuel cell performance. Furthermore, immature  $H_2$  (gas) storage technology and expensive catalyst (Pt) hold back the wide application of  $H_2$ – $O_2$  fuel cell greatly, whereas these problems do not exist in “lithium-air fuel cell”. However, the operating model given in Fig. 3a is just

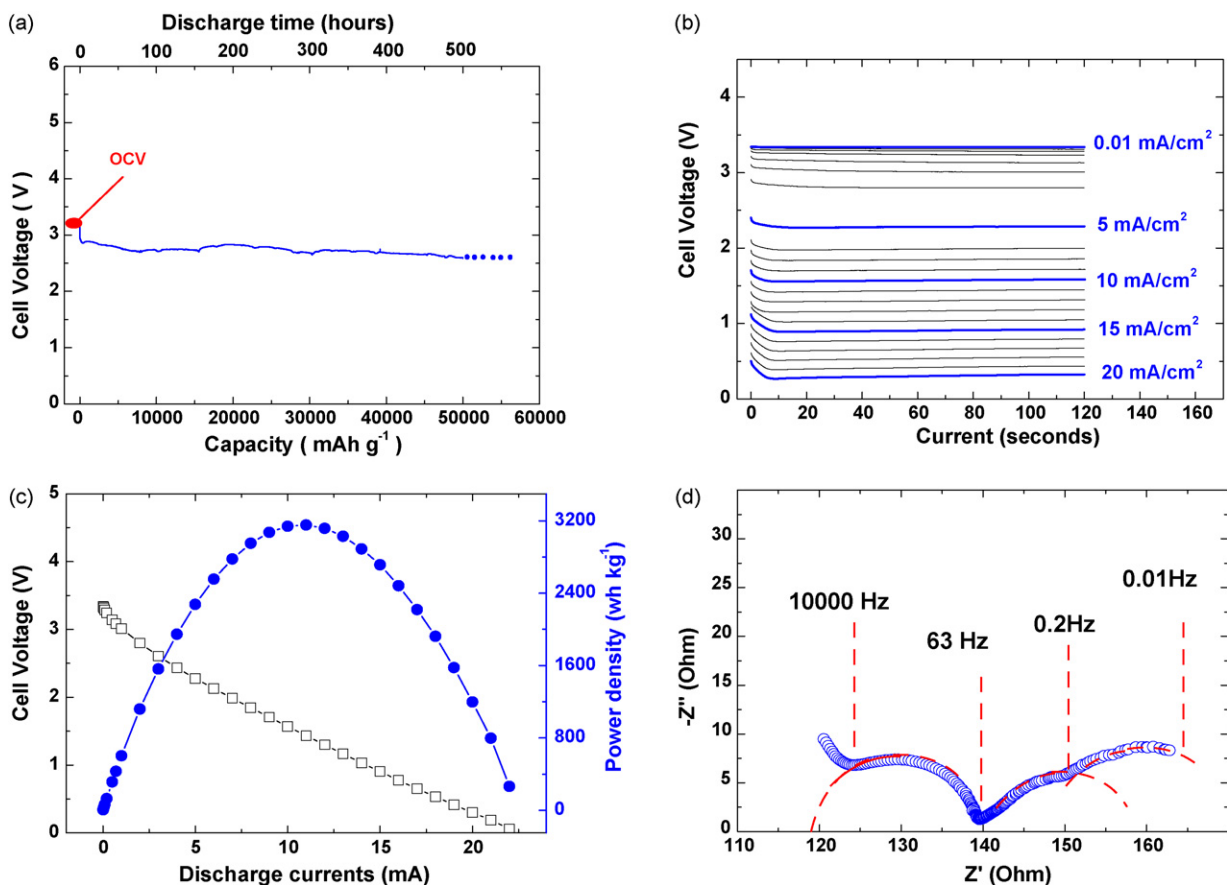


Fig. 2. Electrochemical characterization of the developed lithium-air battery: (a) long-time continuous discharge curve; (b) discharge curves at different current densities; (c) power performance; (d) impedance spectra tested at a discharge state of 3 V.

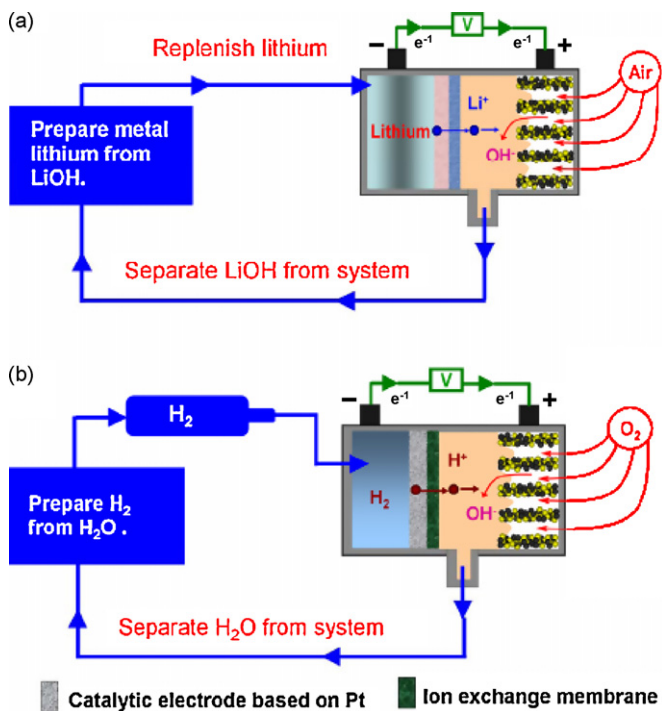


Fig. 3. Cycle operating model established for developed lithium-air battery and one of possible operating models of  $H_2$ – $O_2$  fuel cell. (a) Model for developed lithium-air battery. (b) One of possible operating models for  $H_2$ – $O_2$  fuel cell.

a possible future development direction. The further technology investigation of “lithium-air fuel cell” really requires co-operation between research groups in battery field and fuel cell field.

By the way, the LISICON film is not stable in alkaline solution for long-time use. Acid aqueous solution, instead of alkaline electrolyte, can alleviate this unstable problem. However, after long-time discharge, the acid (or neuter) aqueous electrolyte solution would be converted into an alkaline solution, inevitably (see Fig. 1). Furthermore, for the solution (acid or neuter), expensive catalyst (such as Pt) is necessary [19,20]. Thereby, increasing stability of LISICON in alkaline solution is necessary in the future study about this system.

#### 4. Conclusion

Summarily, the performance of lithium-air battery based on uniting the reduction of  $O_2$  in aqueous electrolyte and metallic lithium through LISICON was investigated in detail. In view of its high theoretical energy density and energy conversion efficiency, the developed system with cycle operating model may provide a new solution for serious energy situation, and would attract wide attention. However, the study about this kind of lithium-air battery is really at the primary state.

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