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Xiaohua XIE,* Zhongfa YANG, Jian ZHANG, and Baojia XIA

* Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China
* State Key Laboratory of Advanced Chemical Power Sources, Guizhou Meiling Power Sources Co., Ltd., Zunyi, Guizhou 563003, China

Corresponding author: xiexiaohua@mail.sim.ac.cn, Tel: (+86) 021-69976909, Fax: (+86) 021-69976911

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Xiaohua Xie¹ *, Zhongfa Yang², Jian Zhang¹, Baojia Xia¹

1. Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai, 200050, China
2. State Key Laboratory of Advanced Chemical Power Sources, Guizhou Meiling Power Sources Co. Ltd., Zunyi, Guizhou 563003, China

*Corresponding author:
Tel: (+86) 021-69976909
Fax: (+86) 021-69976911
E-mail address: xiexiaohua@mail.sim.ac.cn
Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai, 200050, China

Abstract

Due to its high energy density, lithium-air battery has been one of the research hotspots. However, there are still many issues that need to be addressed, especially when working in an open environment. In this paper, the pouch-type non-rechargeable lithium-air batteries were fabricated by using high loading air electrode and waterproof and breathable PDMS film, and their discharge performance in an open environment was studied. Due to the high waterproof and breathable performance of PDMS, the battery has better discharge and storage performance. The discharge time is more than
900h, and the discharge time can reach more than 370h after the battery is stored in the open environment for 1 month. The results of three electrodes and impedance test show that the electrolyte shortage is the main reason for the increase of polarization of the air electrode and the termination of the discharge of the lithium-air battery.

**Keywords:** lithium air battery, PDMS film, electrochemical performance, three electrodes

**Introduction**

Lithium-air batteries have drawn much attention to researchers because of their huge energy density (more than 11140 wh kg$^{-1}$, based on the reactants’ weight). However, there are still some technology problems that hinder the practical use of the lithium-air battery, such as low energy efficiency, poor cycle life, and Li-metal safety issues, and so on.

In order to solve these problems, many studies have been recently carried out, including catalysts, air electrodes, electrolytes, O$_2$-permeable mebrance, and so on, and many meaningful results are obtained. For example, Shao et al. reported a silica-aerogel-reinforced polydimethylsiloxane (OPSP) as a high performance membrane for Li-air (O$_2$) batteries, which enhanced the stability of lithium air battery in air conditions with a relative humidity. However, most of these studies have only focused on the characteristics of the batteries in the closed environment of pure oxygen or dry air. As we all know, the issues that become more prominent if the operating atmosphere of the batteries is switched from pure oxygen to ambient air.
such as the trace amounts of H\textsubscript{2}O and CO\textsubscript{2} from air on the performance of the batteries, and the side reactions at the lithium metal anode side as environmental contaminants including \textit{O}_2, \textit{CO}_2, \textit{H}_2\text{O} and \textit{N}_2, which are entering the battery through the air cathode may cross over the electrolyte, separator, finally reaching the anode.

On the other hand, most of the research efforts are still conducted only in a small laboratory scale, and the load of air cathode is about 0.5~2 mg cm\textsuperscript{-2}\textsuperscript{21-22} sometimes even lower to \textasciitilde0.5 mg cm\textsuperscript{-2}. We all know that the lower loading is conductive to the improvement of electrochemical performance, such as rate and cycle capability. The lower loading means the more uniform distributions of the carbon (such as super P, carbon black, or KB) and the catalyst, if have. During the process of discharge of lithium-air battery, the pore of the air electrode will provide the space to accommodate the discharge products, so the uniform carbon and catalyst can promote uniform current distribution and accommodate more products, at the same time inhibit the volume expansion of the air cathode.

As the ultimate goal of the lithium-air battery is to operate under real air condition, and the process sees further complications when \textit{O}_2, \textit{H}_2\text{O}, \textit{CO}_2 and \textit{N}_2 are involved in reactions with electrolyte at the anode, especially during the charge process. So in this paper, we mainly focus on the discharge performance of the non-rechargeable lithium-air batteries with high loading air cathode under real air environment.

**Experimental**

**PDMS film preparation**
Polydimethylsiloxane (PDMS) was selected as a waterproof and oxygen-permeable material to prepare a film with a certain thickness.

The preparation method of PDMS film is as follows: firstly, mix PDMS and curing agent at a mass ratio of 10:1; secondly, vacuum at room temperature and keep at 0.7 atm until the bubbles in the colloid are completely eliminated; thirdly, pour the appropriate amount of PDMS on the surface of a glass sheet, gently turn to let the colloid spread on the surface of the glass piece; fourthly, place the glass piece on the glue table and rotate for 45s according to a certain number of rotations; finally, degas under vacuum for 1h and cure at 100 °C for 1h. The thickness of the PDMS film is related to the rotation speed of the turntable on the glue throwing table.

The thickness of PDMS films prepared at 300, 500, and 1000 r/min were 195, 145, and 95 µm, respectively. As shown in Figure S1, the PDMS film was cut into 14mm diameter discs and transferred to the glove box for use. The discharge performance of coin-type batter proved that 145 µm thickness is the best (See S2).

**Air cathode preparation**

Mix 2 g of Ketjen Black (ECP600JD) with 30ml of ultrapure water, after stirring for 30 min, add 0.6 g of polytetrafluoroethylene (PTFE, 60 wt%) emulsion, continue to stir for 1 h. Then the slurry was coated into the foamed nickel, and was rolled into an air electrode with a loading capacity of ~15 mg cm⁻² for coin battery and ~25 mg cm⁻² for pouch battery. The optimized porosity of the air electrode is 78 %, which have the longest discharge time.

**Battery assembly**
A vent hole with a diameter of about 1.5 mm is formed in the center of the positive electrode case of the 2025 button battery. In the glove box (H$_2$O and O$_2$ less than 1 ppm), the lithium metal sheet, glass fiber membrane (GF/C, Whatman), electrolyte (1 M LiPF$_6$ in EC/PC with a volume ratio of 1:1), air electrode, PDMS membrane and sealing ring are assembled into a battery. The purpose of the sealing ring is to prevent the gas entering the battery from spreading around the air electrode into the battery.

Cut the nickel foam into a square of 6*6 cm, leaving a small rectangle of 0.5*0.5 cm at one end for welding the tabs, and press the edge of the nickel foam into a 0.5 mm thick sheet. Wrap the thinned part with adhesive tape to ensure that only 5*5 cm in the middle is applied when coating the air electrode. After applying the air electrode, remove the tape. Immerse the two air electrodes in the electrolyte, take them out after 5 minutes, and dry the surface electrolyte with a non-woven cloth; place lithium foil, PP separator coated with PVdF, air electrode, and PDMS membrane in order, put them in aluminum plastic film with four holes with a diameter of about 1mm, after hot pressing at 110 °C for 1 min, take it out after sealing. The goal of hot pressing is to lower the impedance of the cell, see S3. The photos of coin-type and pouch-type lithium air batteries have been given in S4.

**Three electrode battery assembly**

The stable potential of 50 %SOC lithium titanate (Li$_4$Ti$_5$O$_{12}$, LTO) is 1.55 V vs. Li$^+/\text{Li}$, which is used as the reference electrode in this paper. The manufacturing process of lithium-air battery using LTO reference electrode was as follows: 0.16 g PVDF was dissolved in 3.4 g NMP, 0.06 g SP and 0.08 g KS6 were added, and 1.7 g LTO was
added, magnetically stirred for 2 hours; apply the mixed slurry evenly on the aluminum foil and dry at 80 °C. The LTO electrode was cut into 1*1 cm square and the aluminum electrode ear was welded with ultrasonic waves. The LTO reference electrode was put into the battery, connected with the LTO electrode and lithium metal, and the LTO electrode was activated once at 0.2 C with a cut-off voltage of 1.0~2.5 V. Then the LTO electrode was discharged to 50 % SOC.

Battery characterization

The battery was allowed to stand for 2 h in ambient air, so that oxygen dissolved in the electrolyte, and then discharged to 2.0 V at 0.1mA cm⁻².

Use an electrochemical workstation to test the AC impedance of the battery at different discharge stages. The frequency range is 0.01~10⁵ Hz and the amplitude is 5 mV.

X-ray diffraction (XRD, Rigaku D/max 2200/PC, Japan) was used to characterize the discharge product of the air electrode by using Cu Kα (λ = 0.15406 nm) radiation scanning from 10° to 70° at a rate of 2° min⁻¹.

Results and Discussion

Since the lithium-air battery works in an open air environment, which can afford enough air enters to allow the electrochemical reaction to proceed smoothly, at the same time it also makes the electrolyte volatilize outward, which decreases the electrode/electrolyte interface, increases the impedance of the electrochemical reaction, and causes the polarization of the electrode increases. Besides, impurities such as moisture in the air will enter the battery at the same time, corroding the lithium metal.
In order to overcome the above difficulties, the selection and use of waterproof breathable membrane is very important. Here, we choose PDMS as a waterproof and breathable material to prepare non-porous film (The flow of gas through non-porous membrane is a solution-diffusion mechanism).

PDMS, also known as a silicon rubber, is the earliest used oxygen-rich film material with the highest oxygen permeability coefficient ($P_{O_2}$=600 Barrer, 1Barrer=10$^{10}$ cm$^3$ (STP) cm/cm$^2$·s·cmHg). PDMS solidifies to form elastomers under certain conditions. Due to the Si-O-Si bond angle can vary in a wide range (130~160°), the molecular chain of polysiloxane is highly curled spiral structure, and the intermolecular force is very weak, thus forming a large free volume, which is conducive to the diffusion of oxygen. Furthermore, due to the water vapor permeation coefficient of PDMS is 2.0*10$^{-4}$ cm$^3$ (STP) cm/cm$^2$·s·cmHg, and the corrosion of lithium electrode caused by moisture entering from the air is greatly reduced while the oxygen quantity is ensured.

Unlike the batteries discharged in the oxygen environment in the literature, the opening area was controlled on the shell (button-type & pouch cell), and then controlled the amount of gas that enters the battery. Furthermore, we use the low volatile organic solvent of EC and PC as the main component of the electrolyte to improve the discharge time of the battery. Although, it is a fact that EC/PC are unsuitable as electrolytes for chargeable lithium air battery, because carbonate solvents are known to decompose by discharge reaction, and hardly form lithium peroxide, resulting in lower charge-discharge efficiency. However, here we discussed the discharge process of non-
chargeable lithium air battery. So, owing to their low volatilization, we choose EC/PC as the solvents.

The discharge results of the button-type and pouch-type lithium air battery in an open air environment are shown in Fig. 1a and 1b, respectively.

Fig. 1 Discharge curves of the coin-type (a) and pouch-type (b) lithium air batteries in an open air environment at a current density of 0.1mA/cm$^2$
It can be seen from Fig. 1a and 1b, that the batteries have relatively excellent discharge performances and parallelism. Owing to the use of the PDMS as a waterproof and oxygen permeable membrane, the discharge time of the two coin-type batteries is 1362.0 h and 1311.3 h, respectively, and the two pouch batteries is 918.2 h and 927.3 h, respectively. At the same time, because the discharge curves fluctuate in similar places, we speculated that the fluctuation was caused by the changes in temperature, humidity, etc. in the air environment. To confirm this, we discharged the battery system in a constant temperature and humidity box (25°C, 30%RH), and the result is shown in Fig.S5. At present, the battery discharge time is about 446h, and the discharge curve has no significant fluctuation, which indicates that the large fluctuation of the discharge curve in the open environment should be largely related to temperature and humidity.

According to the result of XRD (See S6), the main discharge product is Li$_2$CO$_3$, with a small amount of LiOH·H$_2$O, and no Li oxides or peroxides were detected. In fact, when the battery is discharged in an open air environment, the PDMS cannot completely inhibit the entry of CO$_2$ and H$_2$O, so electrochemical reaction products will eventually be converted to Li$_2$CO$_3$ and LiOH·H$_2$O.

In order to further illustrate the role of PDMS in inhibiting electrolyte volatilization and waterproofing, we put the prepared pouch battery in the open ambient air for one month, and the discharge result is shown in Fig. 2. The discharge time of the two batteries is 393.1 h and 379.6 h, respectively, which are equivalent to about 42 % of the discharge time of the batteries in Fig.1b. Due to the storage in the open ambient air, the volatilization of the electrolyte and the entry of water vapor are inescapable,
which lead to a larger polarization at the beginning of the battery discharge, but we still believe that this result is relatively good, because of the battery without PDMS membrane has unable to discharge under the same conditions. Of course, the function of PDMS still needs to be improved further.

Fig. 2 Discharge curves of the pouch batteries at a current density of 0.1mA/cm² after stored one month in the ambient air

The thickness and impedance changes of the pouch battery during discharge are shown in Tab. 1 and Fig. 3, and the discharge curve is shown in the inset in Fig. 3. As seen from Tab. 1, when the discharge time is less than 400 h, the thickness of the battery does not change, indicating that the small pores in the air electrode are sufficient to store the discharge products; when the discharge time is longer than 400 h, the thickness increases by about 1mm for every 100 h of discharge time, indicating that the pores of the air electrode cannot continue to store the discharge products, and the products accumulate on the surface of the air electrode, causing the air electrode to expand,
resulting in an increase in the thickness of the battery.

Tab.1 Thickness changes of the pouch battery during the discharge process (discharge curve is the inset in Fig. 3)

| Time (h) | Thickness (mm) |
|---------|----------------|
| Before  | 5.5-5.8        |
| 100h    | 5.5-5.8        |
| 200h    | 5.5-5.8        |
| 300h    | 5.5-5.8        |
| 400h    | 5.5-5.8        |
| 500h    | 5.6-5.9        |
| 600h    | 5.6-6.0        |
| 750h    | 5.8-6.1        |

Fig.3 EIS measurement of the pouch battery at open-circuit voltage (OCV) in open air versus discharge time (inset: Discharge curve of the pouch battery at a current density of 0.1mA/cm$^2$ in an open air)

It can be seen from Fig. 3 that the electrochemical reaction impedance of the battery before discharge, 100, 300, 400, 500, 600 and 750 h are about 10, 15, 16, 19, 25, 35 and 52 ohm, respectively. After the discharge time is longer than 400 h, the impedance of the battery increases significantly, which corresponds to the increase in thickness after 400 h.

According to the impedance results, the increase of electrochemical impedance
(Rct) is the main reason for the failure of the battery. As is known to all, the increase of Rct may be caused by the discharge products blocking the effective reaction sites of the air electrode and reducing the active area of the reaction. It may also be due to the evaporation of the electrolyte resulting in less electrochemical reaction sites. The partial pressure of the organic electrolyte in the open air is almost zero, which may cause the electrolyte in the battery to dry up because of solvent volatilization.

We replenish 1g electrolyte into the battery after discharge, and its impedance and discharge curve are shown in Fig. 4. It can be seen from Fig. 4a that the charge transfer impedance of the battery decreases significantly after the replenishment of electrolyte, after replenishing the electrolyte, the battery could continue discharging for 112 h, as seen from Fig. 4b. These indicates that the air electrode still has some space to hold the discharge products after 750 h of battery discharge. By adding the electrolyte, this part of the space can continue to participate in the electrochemical reaction. Therefore, the increase of charge transfer impedance of lithium-air batteries discharging in air is mainly caused by the relative absence of electrolyte in the air electrode.
Fig. 4 (a) EIS of the pouch battery at open-circuit voltage (OCV) in open air after discharge and replenishing the electrolyte, respectively, and (b) discharge curve of the discharged pouch battery after replenishing the electrolyte.

In order to clarify the failure mode of the lithium-air battery, we added a reference electrode during the production process of the battery, and recorded the potential changes of the air electrode and the lithium electrode during the battery discharge process to clarify the capacity-limiting electrode. The reference electrode uses 50 %...
SOC lithium titanate (LTO) because it is not sensitive to water and oxygen and has a stable potential. The changes of battery voltage and the potential of the air electrode and the lithium electrode during discharge are shown in Fig. 5, where the potential of the air electrode and the lithium electrode has been converted to the potential relative to lithium metal. As can be seen from Fig. 5, during the discharge process of the battery, the potential of the lithium anode is always stable at about 0 V, which imply the PDMS film has a good water vapor resistance, while the potential of the cathode decreases rapidly at the end of the discharge, resulting in the battery voltage reaching the cut-off voltage. So, the air electrode is the limiting electrode of the battery. The results of three electrodes and impedance show that the increase of air electrode polarization due to the volatilization of electrolyte is the main cause of battery discharge termination.

Fig. 5 The changes of pouch battery voltage, anode and cathode potentials during discharge at a current density of 0.1 mA cm\(^{-2}\) in an open air

Conclusions

The discharge performance of lithium air battery with high load air electrode in open air was studied. In order to improve the discharge performance of the battery, low
volatile organic electrolyte and PDMS film were used to suppress the evaporation of electrolyte and the entry of water vapor. The results show that the battery has better discharge performance in open environment (the discharge time of coin-type battery and pouch-type battery can reach more than 1300 h and 900 h, respectively) and storage performance (the battery can still discharge more than 370 h after being stored in open air for 1 month at room temperature). The results of three electrodes and impedance show that the absence of electrolyte is the main reason that leads to the increase of air electrode polarization and the termination of battery discharge. Therefore, it is urgent to develop organic electrolyte system suitable for lithium air battery working in an open air environment.

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References

1 M. Armand and J.-M. Tarascon, Nature, 451, 652 (2008).
2 G. Girishkumar, B. McCloskey, and A. C. Luntz, J. Phys. Chem. Lett., 1, 2193 (2010).
3 K.M. Abraham and Z. Jiang, J. Electrochem. So., 143,1 (1996).
4 F.L. Lu, Y.R. Wang, and C. Jin, J. Power Sources, 293, 726 (2015).
5 Y.J. Xu, A. Tsou, and Y. Fu, Electrochimica Acta, 174, 551 (2015).
6 Q. Xu, X.P. Han, and F. Ding, J. Alloys and Compounds, 664, 750 (2016).
7 Y.L. Ruan, L.M. Yu, and S.D. Song, Int. J. Hydrogen Energy, 44, 31153 (2019).
8 M. Salehia, Z. Shariatiniaa, and A. Sadeghi, J. Electroanalytical Chemistry, 832, 165 (2019).

9 M.L. Wang, Y. Yao, and X.X. Bi, Energy Storage Materials, 28, 73 (2020).

10 A. Chamaani, M. Safa, and N. Chawla, J. Electroanalytical Chemistry, 815, 143 (2018).

11 N. Chawla, A. Chamaani, and M. Safa, J. Electrochem. Soc., 164, A6303 (2017).

12 Y.L. Ruan, J. Sun, and S.D. Song, Electrochemistry Communications, 96, 93 (2018).

13 X.H. Zou, K.M. Liao, and D. Wang, Energy Storage Materials, 27, 297 (2020).

14 T. Liu, X.-L. Feng, and X. Jin, Angew. Chem. Int. Ed., 58, 18240 (2019).

15 T.K. Zakharchenko, M.V. Avdeev, and A.V. Sergeev, Nanoscale, 11, 6838 (2019).

16 C. Li, J.S. Wei, and K.Qiu, ACS Appl. Mater. Interfaces, 12, 23010 (2020).

17 D. Aurbach, Y. Gofer, and M. Ben-Zion, J. Electroanal. Chem., 339, 451 (1992).

18 D. Aurbach, I. Weissman, and A. Zaban, Electrochim. Acta, 39, 51 (1994).

19 K. Takechi, T. Shiga, and T. Asaoka, Chem. Commun., 47, 3463 (2011).

20 D.S. Geng, N. Ding, and T.S. Andy Hor, Adv. Energy Mater., 6, 1502164 (2016).

21 T. Zhang and H.S. Zhou, Nat. Commun., 4, 1817 (2013).

22 A. Minguzzi, G. Longoni, and G. Cappelletti, Nanomaterials, 6, 10 (2016).

23 Y. Yampolskii, Macromolecules, 45, 3298 (2012).

24 S. Yoon, M. Seok, and M. Kim, Scientific Reports, 11, 938 (2021).