Effects of moist air on the cycling performance of non-aqueous lithium-air batteries


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HIGHLIGHTS

- The effect of moist air on the cycling performance of Li-air batteries is studied.
- The energy efficiency increases with relative humidity.
- The improved performance is due to the increased fraction of LiOH in the products.
- A cathode with activities for the decomposition of both Li$_2$O$_2$ and LiOH is required.

GRAPHICAL ABSTRACT

As the fraction of LiOH among the discharge products increases with relative humidity, designing a cathode with electrocatalytic activities for the decomposition of both Li$_2$O$_2$ and LiOH is essential to enable a non-aqueous lithium-air battery to operate in moist air.

ABSTRACT

Most non-aqueous lithium-air batteries reported in the literature are limited to operating with pure oxygen. To practically operate the battery in ambient air, understanding how the battery’s performance varies with humidity of moist air is essential. Here we study the effects of moist air on the cycling performance through operating a non-aqueous lithium-air battery with a stable anode and a nanostructured RuO$_2$/NiO cathode at various relative humidities. Results show that in the dry air, the discharge and charge terminal voltages are around 2.51 and 4.12 V, respectively, but change to 2.79 and 3.87 V when the relative humidity reaches 84%. The energy efficiencies corresponding to the dry air and the relative humidity of 84% are 66.2% and 73.8%, respectively. The improved performance is found to be mainly due to the increased fraction of LiOH among the discharge products at high relative humidities. The discharge voltage for the formation of LiOH is higher than that for the formation of Li$_2$O$_2$, while the charge voltage for the decomposition of LiOH is lower than that for the decomposition of Li$_2$O$_2$. The results suggest that to enable a non-aqueous lithium-air battery to operate in moist air, in addition to protecting the lithium anode from water, designing a cathode with electrocatalytic activities for the decomposition of both Li$_2$O$_2$ and LiOH is required.

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1. Introduction

Non-aqueous lithium-air batteries have received much attention in recent years, since they can theoretically store several times more energy than that of Li-ion batteries [1–4]. The super-high energy density comes from two factors: first, lithium is the lightest metal and has the highest specific capacity (3.86 × 10^3 mAh g^-1) and energy density (1.14 × 10^4 Wh kg^-1) [5–7]; and second, the cathode active material, oxygen, can be obtained from ambient air without occupying the battery volume. The main electrochemical reactions in non-aqueous lithium-air batteries during discharge and charge are the reversible formation and decomposition of lithium peroxide (Li₂O₂) as

\[
2\text{Li}^+ + 2e^- + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2 \quad (E^0 = 2.96 \text{ V vs. Li/Li}^+) \quad (1)
\]

To make this technology commercially viable, however, a number of technical barriers must be overcome, including the low practical discharge capacity, low energy efficiency, and short cycling life [8–13]. During the past decade, tremendous efforts have been made to address these issues to improve the battery's performance [14,15]. However, most non-aqueous lithium-air batteries reported in the literature are limited to operating in a pure oxygen environment with an oxygen pressure equal to or greater than 1.0 atm [16], while the common ambient air is mainly composed of N₂ (78%), O₂ (21%), CO₂ (0.03%), and H₂O (0.01%). To realize the high theoretical energy density, the non-aqueous lithium-air battery should be really operated in ambient air rather than in pure oxygen [16].

The barriers for the operation in ambient air are the contaminations of gases (e.g., H₂O, CO₂) to the lithium anode [18] and the cathode [19]. Even though a lithium-protected anode is applied [20,21], the side reactions occur in the cathode:

\[
\begin{align*}
2\text{Li}_2\text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 4\text{LiOH} + \text{O}_2 \\
4\text{Li}^+ + 4e^- + \text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 4\text{LiOH} \quad (E^0 = 3.39 \text{ V vs. Li/Li}^+) \\
2\text{LiOH} + \text{CO}_2 & \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O} \\
4\text{Li}^+ + 4e^- + \text{O}_2 + 2\text{CO}_2 & \rightarrow 2\text{Li}_2\text{CO}_3 \quad (E^0 = 3.82 \text{ V vs. Li/Li}^+).
\end{align*}
\]

As the concentration of CO₂ in ambient air is low while the moisture is varied [22], to operate a non-aqueous lithium-air battery in ambient air, it is therefore important to understand the effects of moist air on the battery's performance. Meini et al. reported a very strong capacity enhancing effect of water in lithium-air batteries due to the formation of soluble products on the carbon surface [23]. Guo et al. investigated the performance of a battery with a carbon cathode in pure oxygen, pure oxygen with a relative humidity (RH) of 15% and ambient air with a RH of 50%. They found that although the discharge capacities increased with the growth of RH value, the cycling and rate performance were influenced in an opposite way due to the composition and morphology changes of the discharge product [24]. Zhao et al. investigated the effects of H₂O and CO₂ on the performance of lithium-air batteries with a cathode made of Au/δ-MnO₂, and found that H₂O has a more detrimental influence on the battery's performance due to the cathode passivation [25]. Although the poor chargeability of LiOH has been experimentally [19] and theoretically [26] demonstrated, Zhou et al. found that the decompositions of LiOH is strongly related to the applied catalysts, and Ru nanoparticles supported on Super P can help its decomposition at a low charge overpotential [27]. Hence, applying a trace amount of water in electrolytes to convert Li₂O₂ to LiOH can catalyze the cathode reactions during discharge and charge. They further integrated a hydrophobic ionic liquid-based electrolyte and a cathode composed of MnO₂ and RuO₂ supported on Super P to construct a lithium-oxygen battery that can work in dry O₂ and various humid atmospheres [28]. Their results showed that a high discharge potential of 2.94 V and a low charge potential of 3.34 V for 218 cycles were achieved at a RH of 51%. Guo et al. investigated the influence of ambient air with a RH of 40% on the battery's performance [29]. They found that the Li₂O₂ forms during the initial discharge process and turns Li₂CO₃ and LiOHz owing to its reaction with CO₂ and H₂O, while the lithium anode becomes expanded and pulverized after cycles. Consequently, the lithium anode should be well protected and the formed side products should be timely cleaned up during cycles.

Most of the above-mentioned works focused on the effects of moist air or O₂ with a fixed RH on the discharge capacity and the charge performance. To practically operate the battery in ambient air, understanding how the battery's cycling performance varies with humidity of moist air is essential. Recently, we developed a cathode composed of RuO₂ nanoparticle-decorated NiO nanosheets, which enabled a non-aqueous lithium-air to be operated in ambient air with a RH of 60 ± 5% [30]. However, as the moisture in ambient air is varied, the robustness of the battery's cycling performance was still unknown. In line with this issue, we investigated the effects of moist air on the battery's cycling performance based on the cathode in this work. We first tested the cycling stability of a battery with a stable anode and a nanostructured RuO₂/NiO cathode at various relative humidities. Then, the energy efficiencies were summarized, and the product compositions and morphologies were characterized. Moreover, the reaction mechanisms in the discharge and charge processes at different humidities were proposed. The results from present work facilitate the further development of non-aqueous lithium-air batteries operated in ambient air.

2. Experimental

2.1. Cathode fabrication and characterization

The nano-structured RuO₂/NiO electrode was fabricated as previously reported [30]. Briefly, after immersing in a 0.5 M oxalic acid ethanol solution with 5 wt% water, the nickel foam was heat treated at 400 °C for 45 min in air to obtain the NiO nanosheet-anchored nickel foam [31]. Then, the Ru(OH)₃ precursor dispersed in ethanol was dropped directly onto the prepared NiO nanosheet-anchored nickel foam. After drying for 30 min, the sample was heated at 300 °C for 4 h in air and cooled to room temperature [32]. The loading of RuO₂ was measured to be around 0.06 mg cm⁻².

The morphology of the RuO₂/NiO electrode was observed by a scanning electron microscope (SEM, JEOL-JSM-6700F) under an accelerating voltage of 5.0 kV, and the elements were studied with energy dispersive X-ray spectrometry (EDS) operating at 15 kV. Transmission electron microscopy (TEM) images were obtained by operating a high-resolution JEOL 2100F TEM system with a LaB₆ filament at 200 kV. The compositions were analyzed by a Micro-Raman spectrophotometer (Renishaw RM 3000) at 514 nm exciting wavelength. The results are presented in Fig. S1.

2.2. Electrochemical characterization

A non-aqueous lithium-air battery was constructed consisting of an anode, a glass-fiber separator (Whatman GF/C), and the RuO₂/NiO electrode with a diameter of 14 mm. The electrolyte was 180 µL 1.0 M lithium Bis(Trifluoromethanesulfonyl)Imide (LiTFSI, Sigma-Aldrich, 99.95%) in tetraethylene glycol dimethyl ether (TEGDME, Sigma-Aldrich, 99%), which was dried with molecular sieves before use, and the water concentration was less than 5 ppm. To eliminate the water contamination on the anode
(Fig. S2), for present study we employed LiFePO4 anode instead of lithium metal [33–35], which was made of LiFePO4, carbon powder, and polytetrafluoroethylene (PTFE) with the weight ratio of 7:2:1. Before use, the anode electrode was dried at 120 °C under vacuum for 12 h and activated. The LiFePO4 electrode against a Li-metal showed flat discharge/charge plateaus at around 3.44 V, and thus all potentials in this work were reported against Li/Li+ (Fig. S3). The battery was assembled in an argon-filled glove box (Etelux, Lab 2000) at water and oxygen contents below 1 ppm. After assembly, the battery was put out in a closed container filled with air. The different humidities were controlled through different supersaturated solutions in the container (Table 1) [36] and monitored by a hygrometer. The cycling tests were conducted on a battery cycling system (Neware, CT-3008W) at a current density of 250 mA g\textsuperscript{-1} with a fixed capacity of 500 mAh g\textsuperscript{-1} based on the loading of RuO\textsubscript{2}. All tests were performed at the temperature of 23 ± 2 °C.

The discharge product compositions were analyzed by a Fourier transform-infrared spectrometer (FT-IR, Vertex 70, Bruker) in the frequency range of 400–2000 cm\textsuperscript{-1}. The X-ray photoelectron spectroscopy (XPS) characterization was determined by a Physical Electronics PHI 5600 multi-technique system using Al monochromatic X-ray at a power of 350 W. The peak position correction was corrected by referencing the C 1s peak position of carbon. The product morphologies were observed by a SEM. The cathode was rinsed by pure dimethoxyethane (DME, Sigma-Aldrich, anhydrous, 99.5%) to remove the residual lithium salt over the cathode surface, and then dried at room temperature in a vacuum chamber. For all measurements, a home-made gas container filled with argon was used to transfer the cathodes.

### 3. Results and discussion

The battery was cycled under the current density of 250 mA g\textsuperscript{-1} with a fixed capacity of 500 mAh g\textsuperscript{-1}, and the results are shown in Fig. 1. Fig. 1a shows the discharge–charge voltage profiles with cycling at different humidities, and some selected cycling profiles are shown in Fig. 1b and c. It is seen that after 80 cycles (320 h), the capacity does not vary with humidity, indicating an excellent stability of the battery. Such stable performance is attributed to the facts that: (i) the LiFePO4 electrode is used instead of lithium metal, avoiding the failure of the anode [29]; and (ii) the nanostructured RuO\textsubscript{2}/NiO cathode not only catalyzes the oxygen reduction and evolution reactions, but also promotes the decomposition of the side products from water and carbon dioxide in the air, retaining the active surfaces [30]. Although the capacity is maintained, the battery presents different discharge and charge voltages at different humidities, as indicated in Fig. 1a. In the dry air (RH = 0), the discharge voltage decreases with a terminal value of 2.35 V at the first cycle. This is because that the dry air is composed of oxygen with a partial pressure of only 0.21 atm, much lower than that of a conventional test environment with an oxygen pressure equal to or greater than 1.0 atm [16]. The low oxygen pressure affects the reaction kinetics and thus leads to a large discharge overpotential. In the charge process, the voltage gradually increases, and reaches 4.29 V at the end. After the first cycle, the discharge voltage gradually increases, and the charge voltage decreases, which may be caused by the increased oxygen concentration in the electrolyte, leading to the stable discharge and charge terminal voltages at around 2.51 and 4.12 V, respectively and an average energy efficiency of 66.2%. When operated at a RH of 22%, it is interesting to find that at the first cycle the discharge voltage presents a plateau of 2.44 V, higher than that in the dry air. When charged, a lower charge voltage is also pre-

### Table 1

<table>
<thead>
<tr>
<th>Salt</th>
<th>RH at 25 °C (%)</th>
<th>Salt weight (g)</th>
<th>Water (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{3}COOK</td>
<td>22.5</td>
<td>200</td>
<td>65</td>
</tr>
<tr>
<td>K\textsubscript{2}CO\textsubscript{3}</td>
<td>43.2</td>
<td>200</td>
<td>90</td>
</tr>
<tr>
<td>NaBr</td>
<td>57.6</td>
<td>200</td>
<td>80</td>
</tr>
<tr>
<td>KCl</td>
<td>84.3</td>
<td>200</td>
<td>80</td>
</tr>
</tbody>
</table>

Fig. 1. Cycling stability of the battery with the RuO\textsubscript{2}/NiO cathode at 250 mA g\textsuperscript{-1} with a fixed capacity of 500 mAh g\textsuperscript{-1}: (a) Discharge-charge profiles at different humidities; (b, c) Discharge-charge profiles of the (b) 1st and (c) 80th cycle.
sented as shown in Fig. 1b. The discharge and charge voltages keep at around 2.53 and 4.06 V, respectively, resulting in an improved energy efficiency of 67.4%. When further increasing the humidity, the discharge voltage increases; on the contrary, the charge voltage decreases. At a RH of 43%, the discharge and charge terminal voltages are 2.61 and 4.04 V, respectively; but change to 2.79 and 3.87 V when the RH increases to 84%. Consequently, the energy efficiency increases with an increase in the relative humidity, as shown in Fig. 2, from 70.4% (RH = 43%) to 73.8% (RH = 84%). It is worth noting that even at the high humidity of 84%, the discharge voltage shows only one plateau rather than two plateaus [37], as shown in Fig. 1c, indicating one dominant electrochemical reaction during the discharge process.

To look inside the cycling performance at different humidities, the discharge product compositions were examined by FT-IR and XPS, and the product morphologies were characterized by SEM, as shown in Figs. 3 and 4, respectively. In the dry air, the FT-IR and XPS results indicate that the main product is Li$_2$O$_2$ (54.5 eV) [38], with a small amount of Li$_2$CO$_3$ (1440 cm$^{-1}$ and 55.3 eV) which comes from the participation of CO$_2$ in the discharge process (Eq. (5)). The SEM result shows that the cathode surface is covered by
toroid-shaped nanoparticles with the size around 400 nm (Fig. 4b), which is consistent with the previous reported morphology of Li$_2$O$_2$ [30]. At the humidity of 22%, the FT-IR and XPS results indicate that the products are mainly the combination of Li$_2$O$_2$ and LiOH, and from SEM image we find that the product morphology keeps toroid-like but with a larger particle size (Fig. 4c). This may be due to the introduction of H$_2$O, which changes the electrolyte properties and leads to an increased particle size [39,40]. The existence of Li$_2$CO$_3$ can also be detected, which is attributed to the chemical (Eq. (4)) or electrochemical reaction (Eq. (5)) of CO$_2$ in the discharge process. At the humidity of 43%, the main product composition becomes LiOH, and the SEM image shown in Fig. 4d presents a plate-like morphology with a diameter of 1.5 μm and a thickness of 50 nm, similar to the reported LiOH morphology [41]. Consequently, the charge process is mainly the decomposition of LiOH through RuO$_2$. When further increasing the humidity, the product composition becomes LiOH, and the SEM image shown in Fig. 4d presents a plate-like morphology with a diameter of 1.5 μm and a thickness of 50 nm, similar to the reported LiOH morphology [41].

Based on the above results, we proposed the reaction mechanisms at different humidities in Fig. 5. At a very low humidity, the formation and decomposition of Li$_2$O$_2$ dominate the cycling process (Eq. (1)). Even with trace amounts of water (e.g., 4000 ppm) in the electrolyte, H$_2$O can help the formation of crystalline Li$_2$O$_2$ rather than form LiOH [40]. With an increase of humidity in the moist air, the water concentration in the electrolyte also increases. During discharge, H$_2$O reacts with the discharge product Li$_2$O$_2$ to form LiOH (Eq. (2)). As a result, the products become a combination of Li$_2$O$_2$ and LiOH, and the fraction of LiOH among the discharge products increases with an increase in the relative humidity. During charge, two possible routines occur: (i) the direct electrochemical decomposition of Li$_2$O$_2$ and LiOH; (ii) H$_2$O continuously transforms Li$_2$O$_2$ to LiOH, and the decomposition of LiOH follows [27]. When the relative humidity further reaches a high level, a large amount of water exists in the electrolyte and participates in the electrochemical process to form LiOH (Eq. (3)). Similar results have been reported by Zhou et al. [28], in which water was supposed to change the electrochemical route and resulted in a high discharge voltage at high humidities. The formed LiOH may even dissolve in the excessive H$_2$O, as evi-
denced by the SEM image of the product at the RH of 84% (Fig. 4f). Thus, the charge process is the electrochemical decomposition of the solid and/or soluble LiOH. Hence, to enable a lithium-air battery to operate in moist air, a protected lithium anode in which the lithium metal is isolated from the non-aqueous electrolyte by a lithium ion conducting but electronically insulating membrane (e.g., Li1+xAl1-xTi2-x(PO4)3 − LATP) should be used [44]. In addition to protecting the lithium anode from water, designing a cathode with electrocatalytic activities for the decomposition of both Li2O2 and LiOH is required.

4. Conclusions

In this work, we investigated the effects of moist air on the battery’s cycling performance through operating a non-aqueous lithium-air battery with a stable anode and a nano-structured RuO2/NiO cathode at various relative humidities. It is seen that after 80 cycles (320 h), the capacity does not vary with humidity, indicating an excellent stability of the battery. Although the capacity is maintained, the battery presents different discharge and charge voltages at different humidities. In the dry air, the discharge and charge terminal voltages are around 2.51 and 4.12 V, respectively, but change to 2.79 and 3.87 V when the relative humidity reaches 84%. The energy efficiencies corresponding to the dry air and the relative humidity of 84% are 66.2% and 73.8%, respectively. FT-IR and SEM results indicate that in the dry air, the discharge product is Li2O2 with the toroid-like morphology, but changes to a combination of Li2O2 and LiOH with the plate-like morphology when the humidity increases, and further changes to LiOH with film-like morphology at a high humidity. Hence, the improved performance is found to be mainly due to the increased fraction of LiOH among the discharge products at high relative humidities. The discharge voltage for the formation of LiOH is higher than that for the formation of Li2O2, while the charge voltage for the decomposition of LiOH is lower than that for the decomposition of Li2O2. The results suggest that to enable a non-aqueous lithium-air battery to operate in moist air, in addition to protecting the lithium anode from water, designing a cathode with electrocatalytic activities for the decomposition of both Li2O2 and LiOH is required.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apenergy.2016.08.113.

References


