

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



P. Tan, W. Shyy, T.S. Zhao*, R.H. Zhang, X.B. Zhu

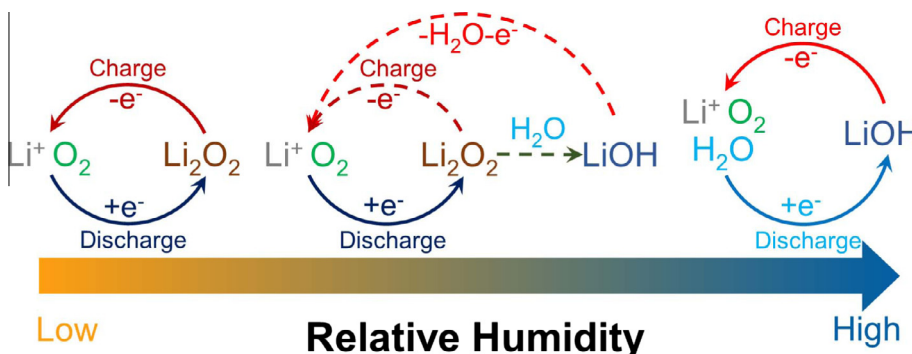
Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

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_2O_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_2O_2 and LiOH is essential to enable a non-aqueous lithium-air battery to operate in moist air.



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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 nano-structured 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_2O_2 , while the charge voltage for the decomposition of LiOH is lower than that for the decomposition of Li_2O_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_2O_2 and LiOH is required.

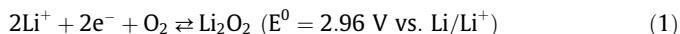
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* Corresponding author.

E-mail address: metzhao@ust.hk (T.S. Zhao).

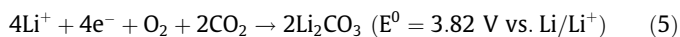
1. Introduction

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 ($3.86 \times 10^3 \text{ mAh g}^{-1}$) and energy density ($1.14 \times 10^4 \text{ Wh kg}^{-1}$) [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 (Li_2O_2) as



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 addressing 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 N_2 (78%), O_2 (21%), CO_2 ($\approx 0.03\%$), and H_2O [17]. 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. H_2O , CO_2) 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:



As the concentration of CO_2 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 H_2O and CO_2 on the performance of lithium-air batteries with a cathode made of $\text{Au}/\delta\text{-MnO}_2$, and found that H_2O 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 decomposition 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 Li_2O_2 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 MnO_2 and RuO_2 supported on Super P to construct a lithium-oxygen battery that can work in dry O_2 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 Li_2O_2 forms during the initial discharge process and turns Li_2CO_3 and LiOH owing to its reaction with CO_2 and H_2O , 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 O_2 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 RuO_2 nanoparticle-decorated NiO nanosheets, which enabled a non-aqueous lithium-air to be operated in ambient air with a RH of $60 \pm 5\%$ [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 nano-structured RuO_2/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 RuO_2/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 $\text{Ru}(\text{OH})_3$ 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 RuO_2 was measured to be around 0.06 mg cm^{-2} .

The morphology of the RuO_2/NiO electrode was observed by a scanning electron microscope (SEM, JEOL-6700F) under an acceleration 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 2010F TEM system with a LaB_6 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 RuO_2/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

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