Full paper

Operando liquid cell electron microscopy of discharge and charge kinetics in lithium-oxygen batteries

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ABSTRACT

Despite the promising future of lithium-oxygen (Li-O$_2$) battery in replacing conventional lithium ion battery for high-energy applications, the complicated reaction mechanisms determining the sluggish discharge-charge kinetics have not been fully understood. Here, utilizing *in situ* liquid transmission electron microscopy, the (electro)chemical fundamentals in a working Li-O$_2$ battery is explored. During discharge, the nucleation of Li$_2$O$_2$ is observed at the carbon electrode/electrolyte interface, and the following growth process exhibits Li$^+$ diffusion-limited kinetics. Nucleation and growth of Li$_2$O$_2$ are also observed within the electrolyte, where there is no direct contact with the carbon electrode indicating the existence of non-Faradaic disproportionation reaction of intermediate LiO$_2$ into Li$_2$O$_2$. The growth of Li$_2$O$_2$ isolated in the electrolyte exhibits O$_2^-$ diffusion-limited kinetics. Li$_2$O$_2$ at the carbon electrode surface and isolated in the electrolyte are both active upon charging and gradually decomposed. For Li$_2$O$_2$ particles rooted at the carbon electrode surface, the decomposition starts at the electrode/Li$_2$O$_2$ interface indicating electron-conduction limited charge kinetics. For Li$_2$O$_2$ isolated within the electrolyte, surprisingly, a side-to-side decomposition mode is identified indicating the non-Faradaic formation of dissolvable O$_2^-$, whose diffusion in the electrolyte controls the overall charge kinetics. This work reveals further details of underlying mechanisms in a working Li-O$_2$ battery and identifies various limiting factors controlling the discharge and charge processes.

1. Introduction

The fast development of electric vehicle market has cast an urgently growing demand on the improvement of energy density of the built-in battery system, which cannot be fully met by current lithium ion battery (LIB) technology [1]. Alternatively, new battery systems with high energy and power density, such as lithium-oxygen (Li-O$_2$) batteries, are being investigated as promising energy sources [2,3]. A typical Li-O$_2$ battery is composed of an anode (Li metal), organic liquid electrolyte (O$_2$-rich) and a porous and conductive cathode (carbon). During discharge, solid Li$_2$O$_2$ particles form on the cathode side *via* the so called oxygen reduction reaction (ORR, $2Li^+ + 2e^- + O_2 = Li_2O_2$), while the charge process is the decomposition of Li$_2$O$_2$ *via* oxygen evolution reaction (OER, $Li_2O_2 = 2Li^+ + 2e^- + O_2$) [4]. Such reactions provide a theoretical energy density over 3500 W h kg^{-1}, which is ten times higher than that of current LIB system [5–7].

However, Li-O$_2$ battery is far from commercialization due to several hurdles that originate from the inherent complicated (electro)chemistry [8,9]. The ORR and OER proceed at the three-phase (solid-liquid-gas) interfaces with sluggish reaction kinetics, which finally leads to the huge overall charge and discharge overpotentials that largely decreases the energy efficiency of the battery system [10]. Therefore, an in-depth understanding of the ORR and OER mechanisms is necessary to boost further development of Li-O$_2$ battery. In spite of the many reports on the study of Li-O$_2$ electrochemistry, the working mechanisms regarding the Li$_2$O$_2$-associated reactions are still in debate [11,12]. Thus far, various reaction pathways concerning the evolution of Li$_2$O$_2$ have been proposed, such as the two one-electron transfer reactions with formation of intermediate LiO$_2$ and then Li$_2$O$_2$, one direct two-electron transfer reaction with formation of Li$_2$O$_2$, and even the non-Faradaic (chemical) disproportionation reaction of two LiO$_2$ to Li$_2$O$_2$ and O$_2$ [2,11]. Unfortunately, these proposed mechanisms are so far hard to be

testified due to the highly dynamic nature of the battery reactions that disqualifies most of the conventional *ex situ* battery characterization methods [13].

Recently, *in situ* liquid cell scanning transmission electron microscopy (STEM) has been rapidly developed in the study of solution-based reactions such as particle nucleation and growth, bioreactions and metal corrosion [14,15]. Coupled with built-in circuits, it has also enabled the study of battery reactions in organic electrolyte environments. Its capability in revealing the real working mechanisms has been demonstrated in many lithium ion battery materials, such as LiFePO$_4$ and Li metal [16–18]. Yet, there are few reports on its application in Li-O$_2$ battery study and because of the various electrolytes (either solid or liquid states) and electrode materials (carbon or gold) utilized in these studies, the detailed ORR and OER kinetics remain debating [19–21]. Here, using *in situ* liquid cell STEM capable of biasing control, the charge and discharge processes of a Li-O$_2$ battery are systematically studied with the reaction details revealed at nanoscale resolution. The nucleation and growth of Li$_2$O$_2$ during discharge are observed not only at the carbon-electrolyte interfaces, but also in the electrolyte environment isolated from the carbon current collector. Both cases are limited by ion-diffusion in the electrolyte, with the former kinetics limited by Li$^+$ diffusion and the latter limited by O$_2^-$ diffusion resulted from the formation of dissolvable LiO$_2$ and their subsequent non-Faradaic disproportionation reaction. During charge, the decomposition of Li$_2$O$_2$ rooted at the electrode surface initiates at the Li$_2$O$_2$/carbon interfaces instead of the Li$_2$O$_2$/electrolyte interfaces, suggesting electron conduction-limited OER kinetics. Li$_2$O$_2$ isolated in the electrolyte are decomposed *via* a side-to-side mode starting from the location closer to carbon electrode, indicating the existence of comproportionation reaction (Li$_2$O$_2$ + O$_2$ = 2 LiO$_2$) limited by the subsequent O$_2^-$ diffusion through the electrolyte. The limiting factors revealed in this work account for the origins of high ORR and OER overpotentials, and rational structural engineering and compositional design are thus needed to effectively address these issues before Li-O$_2$ batteries can be commercialized.

2. Materials and methods

2.1. Preparation of LiCoO$_2$-coated liquid cell chips

In our liquid electrochemical cell, we utilized the glassy carbon transparent electrode as the anode/working electrode (WE) and RF-sputtered LiCoO$_2$ as cathode/counter electrode (CE). 1 M LiCF$_3$SO$_2$ in TEGDME (Tetraethylene glycol dimethyl ether) is used as the electrolyte. In order to load the LiCoO$_2$ film precisely onto the counter electrode, combined photolithography and lift-off technique was used. First, AZ1518 photoresist was spin coated all over the chip surface at 4000 rpm for 40 s followed by baking at 110 °C for 1 min. Employing MA6 mask aligner and a properly designed chrome (Cr) mask, a 0.25 mm^2 circle was accurately patterned onto the counter electrode. Then the exposed photoresist was removed using AZ 340 (1:3) developer. A cryo-pumped vacuum chamber (CVC) radio frequency (RF) magnetron sputtering was used to deposit 100 nm LiCoO$_2$ film onto the chip surface. Then the LiCoO$_2$/photoresist was removed by lift-off technique leaving the LiCoO$_2$ only at the desired area on the counter electrode. Considering the counter electrode is only used as Li$^+$ reservoir, we believe that the use of LiCoO$_2$ in our work does not affect significantly the observations made on the carbon electrode. However, for future studies, it would be interesting to replace the LiCoO$_2$ cathode with Li metal in order to mimic the real Li-O$_2$ batteries.

2.2. Assembly of the liquid cell for in situ operation

The top and bottom silicon chips are aligned together with the liquid-flowing area sealed using O-rings. For the entire experiment, the thickness of liquid (sandwiched by the two chips) along the electron pathway is controlled using a 500 nm spacer, which guarantees enough space for the nucleation and growth of Li$_2$O$_2$ as well as the electron transparency through the liquid mass. The liquid electrolyte is composed of 1 M LiCF$_3$SO$_2$ in O$_2$-rich TEGDME (Tetraethylene glycol dimethyl ether). After flowing the electrolyte into the cell, the discharge and charge processes are controlled by applying $+2.5$ V and -2.5 V bias at the CE against WE, respectively. All the *in situ* liquid TEM observations are carried out under an electron dose rate of ~ 0.04 electron/Å^2/s. To calculate the dose rate, we took into account several aspects. The microscope was operated at STEM mode at the emission
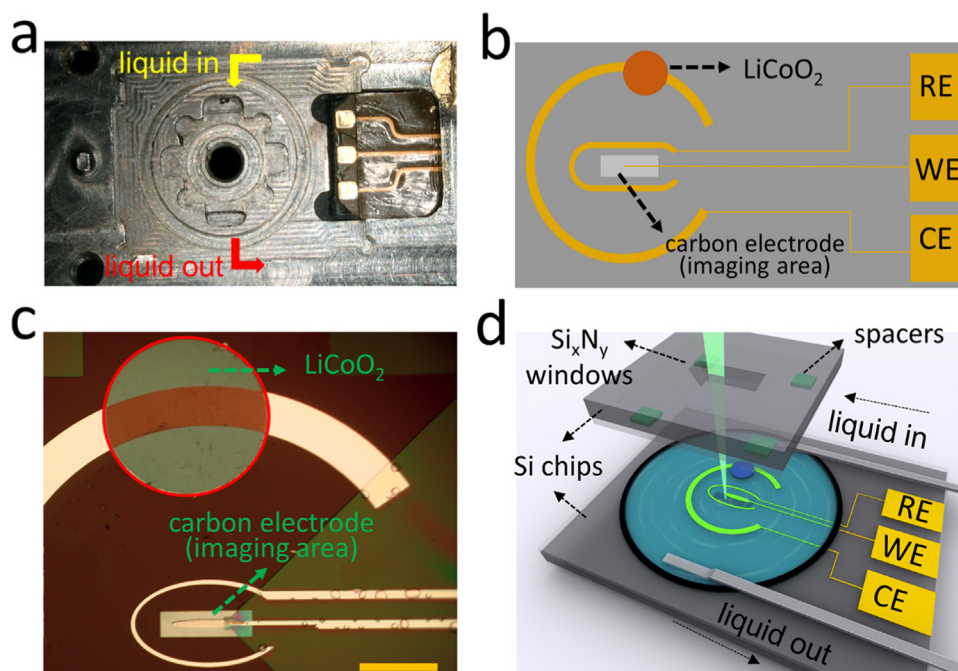

Fig. 1. (a) Optical image of the hardware design of the specimen area of the *in situ* liquid TEM holder before the insertion of Si chips. The yellow and red arrows indicate the liquid inlet and outlet of the reacting area, respectively. The three shining pads are the electrical connections of the reacting area to the outside potentiostat. (b) The schematic showing the realization of a nominal Li-O$_2$ battery rooted on silicon chips, where LiCoO$_2$ is deposited at the CE and glassy carbon is used as the WE in the observing area. (c) Optical image showing the liquid cell chip after deposition of LiCoO$_2$ onto the counter electrode as highlighted in red circle. Scale bar is 250 µm. (d) The schematic showing the side view of the *in situ* liquid cell design.