Supporting Information

Probing the Reaction Kinetics of the Charge Reactions of Nonaqueous Li-O_2 Batteries

_Yi-Chun Lu*†,‡,§ and Yang Shao-Horn*†,‡,§_

†Department of Mechanical Engineering, ‡Department of Materials Science and Engineering, and §Electrochemical Energy Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

*E-mail: shaohorn@mit.edu

*E-mail: yichunlu@mit.edu

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Supporting Experimental Details.

**Li-O₂ Cell Assembling.** Li-O₂ cells were assembled in the following order: 1) placing a lithium foil onto the stainless steel current collector of the cell, 2) adding 50 µl electrolyte, 3) placing two pieces of the separator (Celgard C480, vacuum-dried at 75 °C for at least 12 hours, transferred without exposing to the ambient) onto the lithium foil, 4) adding 50 µl electrolyte, 5) placing the air electrode onto the separator, 6) adding 50 µl electrolyte, 7) placing a current collector (316 stainless steel mesh and spring) on top, and, 8) purging the cell with dry O₂ for 10 minutes in a water-free glovebox (H₂O < 0.1 ppm).

**X-Ray Powder Diffraction Measurements.** X-ray powder diffraction (XRD) patterns of pristine and discharged VC electrodes were collected using a Panalytical X’Pert Pro Multipurpose Diffractometer (Cu Kα) with a continuous scan of 0.09 °/min between 30 ° and 70 ° 2θ. Samples for XRD analysis were prepared in the glovebox and sealed with Kapton film to minimize ambient exposure during XRD scans.

**Scanning Electron Microscopy Measurements.** The surface morphologies of pristine and discharged Vulcan VC and Au/C electrodes were examined by a JEOL 6320 high resolution scanning electron microscope (SEM) at 5 kV accelerating voltage. All samples were cut into semi-circles to expose the cross section of the electrode for SEM analysis. SEM samples of discharged electrodes were prepared in a glovebox (MBRAUN, USA, H₂O < 0.1 ppm, O₂ < 0.1 ppm). Each SEM sample was then mounted with carbon tape on a tilted sample holder with a 70-degree tilt from horizontal to increase signal yield.
Supporting Figures.

**Figure S1:** SEM images of (a) a pristine VC electrode at low magnification (25000x), (b) a VC electrode discharged at 10 mA/g\textsubscript{c} to 200 mAh/g\textsubscript{c} at low magnification (22000x) (c) a pristine VC electrode at high magnification (40000x), and (d) a VC electrode discharged at 10 mA/g\textsubscript{c} to 200 mAh/g\textsubscript{c} at high magnification (40000x). Li\textsubscript{2}O\textsubscript{2} formed in the VC electrode are not discrete particles but exhibit coating-like morphologies.
Figure S2: Li$_2$O$_2$ formation is observed on carbon surfaces in O$_2$-saturated 1M LiClO$_4$ TEGDME at 10, 100 and 1000 mA/g. This is consistent with a number of studies reporting Li$_2$O$_2$ formation on carbon in TEGDME.$^{3,4}$
Figure S3: (a) Charge potential as a function of capacity obtained by GITT with current pulse of 2 mA/g_c for 4 hours followed by an OCV relaxation of 5 hours of an electrode that was discharged to 200 mAh/g_c at 100 mA/g_c in O_2-saturated 1.0 M LiClO_4 in TEGDME. (b) The zoom-in of (a) in the stage I. (c) The zoom-in of (a) in the stage II. (d) The zoom-in of (a) in the stage III. For the stage I (b), most of the relaxed OCVs were below the thermodynamic equilibrium potential of Li_2O_2 (2.96 V_{Li}), suggesting that the major reaction phase here can be a nonstoichiometric Li_{2-x}O_2-phase that exhibits lower thermodynamic equilibrium potentials compared to the stoichiometric Li_2O_2-phase. The stage II shown in (c) shows typical nucleation and growth-type galvanostatic response where the potential first increases to support the initial nucleation events then decrease as a result of increased total surface area of supercritical nuclei (i.e., lower overpotential needed for sustaining the same current). This result agrees nicely with the current responses observed via PITT for the stage II indicating nucleation and growth type reaction processes (Figure 3c). Considering the flat plateau observed via galvanostatic charging shown in Figure 2a at 2 mA/g_c, stage II, the increase in the OCVs observed here is likely due to the insufficient relaxation time. For the stage III (d), the charge capacity again exceeds the discharge capacity, which supports the existence of side reactions (e.g., decomposition of by-products and electrolytes), as also suggested by the PITT results (Figure S7). In addition, the GITT responses of the stage III are quite different from that of stage I and II where the charge potentials were stable at ~3.6 V_{Li} (consistent with Fig. 2a, stage III, ~3.65 V_{Li} at 2 mA/g_c) and the OCVs were stable at all times with overcharge, which supports the existence of parasitic reactions of the electrolyte.
Figure S4: Net mass-normalized current vs. time for potentiostatic charging of Pt/C+ Li₂O₂ electrode at 3.6 V$_{\text{Li}}$, and VC + Li₂O₂ electrode at 4.1 V$_{\text{Li}}$. Ref. #7
Figure S5 shows the oxygen K edge (O K) X-ray absorption near edge structure (XANES) spectra of the Li$_2$O$_2$ particles formed in a discharged VC electrode. Interestingly, small differences were noted between the TEY and FY spectra of the Li$_2$O$_2$. The ratio of the peak intensity between the components at 532.0 eV and 534.9 eV increases from the TEY spectrum (probing the outer part of the Li$_2$O$_2$) to the FY spectrum (probing the bulk part of the Li$_2$O$_2$). This suggests that the stoichiometry and/or oxygen local environments are different between the outer part and the bulk part of the Li$_2$O$_2$ formed, which can give rise to different charging behaviors at stage I (outer part) and stage II (bulk part). Further investigation including simulating XANES spectra with different “Li$_2$O$_2$” stoichiometry and/or defect structures is ongoing to reveal the physical origins responsible for these differences.
Figure S6: (a) Charge profiles of VC electrodes in Li-O\textsubscript{2} cells (that were discharged to 200, 500, 1000 mAh/g\textsubscript{c}) at an equivalent of C/100 (2, 5, and 10 mA/g\textsubscript{c}, respectively) in O\textsubscript{2}-saturated 1M LiClO\textsubscript{4} TEGDME. (b) The charge profiles shown in (a) with normalized capacity.

The charge potential at the stage II increases as the discharge capacity increases. We hypothesize that the increase in the charge potential is due to the decrease in the electrical conductance with increasing Li\textsubscript{2}O\textsubscript{2} thicknesses.\textsuperscript{8,9} Assuming the voltage gap between the charge profiles with different discharge capacities is only related to the differences in the electrical conductance of the Li\textsubscript{2}O\textsubscript{2} deposit, the electronic conductivity of Li\textsubscript{2}O\textsubscript{2} can be estimated to be \(\sim 2\times10^{-13}\) S/cm using a formula of \(\sigma_{\text{Li}_2\text{O}_2} = \left(\left|i_2-d_2-i_1-d_1\right| / \Delta V*A\right)\), where \(i\) is the total current applied, \(d\) is the estimated Li\textsubscript{2}O\textsubscript{2} thickness assuming uniform distribution of Li\textsubscript{2}O\textsubscript{2} on carbon surfaces based on the total discharge TSAC, \(A\) is the estimated true carbon surface area, \(\Delta V\) is the voltage gap observed in stage II. Interestingly, the electrical conductivity estimated here is in reasonable agreement with that estimated from a recent study (\(1\times10^{-12}\ - 10^{-13}\) S/cm) reporting an increase of 0.1 V of overpotential associated with an increase in Li\textsubscript{2}O\textsubscript{2} thickness of 1 nm \(\left(\sigma_{\Delta d} = \left(\Delta d/i\right) / \Delta V*A\right)\), where \(\Delta d\) = 1 nm, \(i = 1\) \(\mu\)A/cm\textsuperscript{2}, \(\Delta V = 0.1\) V, \(A = 1.1\) cm\textsuperscript{2}.\textsuperscript{8} The low Li\textsubscript{2}O\textsubscript{2} conductivity estimated (\(10^{-12}\ - 10^{-13}\) S/cm) suggests that the electrical transport losses will be significant in Li-O\textsubscript{2} cells with increasing Li\textsubscript{2}O\textsubscript{2} thickness and/or at high rates, which is in agreement with our recent observations from in situ transmission electron microscopy revealing significant electronic conductivity limitations at very high rates / overpotentials upon charging of Li\textsubscript{2}O\textsubscript{2}. Figure S6b shows the capacity-normalized charge profiles of electrodes that were pre-discharged to 200, 500 and 1000 mAh/g\textsubscript{c} at 100 mA/g\textsubscript{c} (shown in Figure S6a). The increasing normalized capacity (or capacity percentage) at state I with decreasing total discharge capacity supports the hypothesis that the reaction at stage I is associated with oxidizing the outer part of the Li\textsubscript{2}O\textsubscript{2}. This is because the percentage of the outer part of the Li\textsubscript{2}O\textsubscript{2} is expected to increase as the particle size decreases (lower total discharge capacity).
Figure S7: The extension of Figure 3a to over charge region.

Supporting Information References.


