

Potential-dependent Dissolution of Li_2O_2 During Discharge in $\text{Li}-\text{O}_2$ Secondary Batteries with Amide-based Electrolytes

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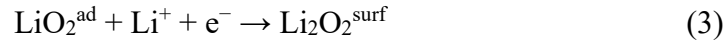
ABSTRACT

The lithium–oxygen battery (LOB) is a promising next-generation secondary battery technology because of its high theoretical gravimetric energy density. During discharge, the formation of lithium peroxide (Li_2O_2) through the solution and surface pathways leads to blockage of the positive electrode, which is considered irreversible. However,

in this paper, we demonstrate that, under certain conditions, Li_2O_2 dissolves into an amide-based electrolyte in a potential-dependent manner, restoring the electrode to an unblocked state. Using a planar glassy carbon positive electrode, we observed that the reduction current, which initially diminishes because of electrode blockage, recovers when the potential is increased, suggesting that Li_2O_2 dissolves at positive potentials. Rotating ring-disk electrode measurements further confirmed that Li_2O_2 , along with lithium superoxide (LiO_2), dissolves in a potential-dependent manner. Electrochemical impedance spectroscopy and linear-sweep voltammetry analyses revealed that this dissolution process occurs over a specific potential range. These findings provide insights into Li_2O_2 behavior and offer a pathway for improving the stability and capacity retention of LOBs.

INTRODUCTION

The development of next-generation secondary batteries with high gravimetric energy density is urgently anticipated because they have the potential to substantially extend the range of electric vehicles, drones, and other mobile platforms. Among various next-generation secondary battery technologies, lithium–oxygen batteries (LOBs) offer a high theoretical gravimetric energy density^{1–4}. Typically, during the discharge process of LOBs, the reaction at the positive electrode follows Equations (1)–(4)^{5,6}:



O_2 is initially reduced to form lithium superoxide (LiO_2) (Equation (1)), which exists either as an adsorbed species on the positive electrode surface (LiO_2^{ad}) or as a dissolved species in the electrolyte ($\text{LiO}_2^{\text{sol}}$) (Equation (2)). LiO_2^{ad} undergoes a second electron reduction, resulting in the formation of lithium peroxide ($\text{Li}_2\text{O}_2^{\text{surf}}$) (Equation (3)). Meanwhile, $\text{LiO}_2^{\text{sol}}$ undergoes a disproportionation reaction to also form lithium peroxide ($\text{Li}_2\text{O}_2^{\text{sol}}$) (Equation (4)). The Li_2O_2 -forming reactions shown in Equations (3) and (4) are referred to as the surface pathway and the solution pathway, respectively. As the discharge

reaction progresses, Li_2O_2 produced via these pathways accumulates on the positive electrode surface.

The surface and solution pathways are known to be favored at more negative and positive potentials, respectively⁷. In addition, although the steric effects of solvent and anion species must be considered, electrolytes with a higher donor number (DN), which reflects their Lewis basicity, tend to promote the solution pathway^{8–10} because solvents with a higher DN more effectively solvate Li^+ ions, increasing the stability of dissolved $\text{LiO}_2^{\text{sol}}$ ¹¹. The acceptor number (AN) of species present in the electrolyte also influences the relative stability of $\text{LiO}_2^{\text{sol}}$. Consequently, some researchers have intentionally enhanced Li_2O_2 formation via the solution pathway by introducing high-AN additives or H_2O into the electrolyte^{12–14}. The morphology of Li_2O_2 depends on the pathway through which it forms. The discharge product $\text{Li}_2\text{O}_2^{\text{surf}}$, which is generated via the surface pathway at more negative potentials, forms as a two-dimensional deposit on the positive electrode surface, leading to rapid blockage of the positive electrode and a limited discharge capacity. By contrast, $\text{Li}_2\text{O}_2^{\text{sol}}$, which is produced through the solution pathway at more positive potentials, is less likely to block the positive electrode, enabling a higher capacity. Because the solution pathway allows for greater capacity at more positive potentials, it is advantageous for achieving the high gravimetric energy density

envisioned for LOBs. However, this pathway also presents challenges for cycle performance. $\text{Li}_2\text{O}_2^{\text{sol}}$, which is formed via disproportionation, can partially disperse into the electrolyte, and its high crystallinity leads to an increase of the charging voltage^{15,16}, which is disadvantageous for stable cycling.

Thus, understanding and controlling Li_2O_2 , the discharge product, is essential for improving the performance of LOBs. Recently, we discovered that, in electrolytes with *N,N*-dimethylacetamide (DMA) solvent, Li_2O_2 with low crystallinity and high decomposability is formed, leading to a reduction of the charging voltage¹⁷. In addition, when a fluorinated amide is mixed with DMA, the crystallinity is further reduced, resulting in an even lower overpotential^{18,19}. Similarly, sulfonamide-based electrolytes have been reported to promote the formation of highly decomposable Li_2O_2 ²⁰. On the other hand, in our previous study on acetonitrile-based electrolytes, we discovered a phenomenon where the positive electrode, once blocked by discharge products, spontaneously recovered from the blocked state without oxidation of the discharge product (i.e., at a potential sufficiently negative potential compared with the oxidation potential of the discharge products)²¹. Although we did not fully elucidate the mechanism in that study, we have now observed the same phenomenon in amide-based electrolytes. Given the advantageous characteristics of Li_2O_2 formed in amide-based electrolytes, as

described above, we here systematically investigate the blocking and reopening behavior of a positive LOB electrode in the electrolyte systems.

RESULTS AND DISCUSSION

For porous positive electrodes commonly used in LOBs, the double-layer potential inevitably varies depending on the location within the porous structure. To clarify the potential dependence of the positive electrode blockage and reopening behavior, we used a planar electrode, which provides a more uniform double-layer potential. Figure 1a presents the cyclic voltammetry (CV) results obtained using a glassy carbon (GC) planar positive electrode in DMA containing 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) at a potential sweep rate of 0.5 mV/s. As the potential was swept negatively from the open-circuit potential (OCP; ~ 3.0 V vs. Li/Li^+), the absolute value of the reduction current, $|j|$, increased, exhibiting a shoulder peak at ~ 2.7 V, followed by a major peak at ~ 2.4 V, before sharply decreasing. When the sweep direction at 2.0 V was reversed, almost no reduction current was observed. Faradaic current was not observed in the potential range 2.0–3.0 V under Ar atmosphere (Figure S1), which indicates that the currents in Figure 1a originated from the oxygen reduction reaction (ORR). The sharp decrease in $|j|$ at potentials less than 2.4 V, as well as the absence of a reduction current

during the subsequent positive sweep, has been attributed to electrode blockage caused by the formation of Li_2O_2 as a reduction product^{22–26}. In addition, oxidative decomposition of Li_2O_2 with O_2 evolution is known to not proceed unless a potential greater than 3.0 V vs. Li/Li^+ is applied²⁶. Importantly, however, the fundamental CV profile remained unchanged beyond the second cycle. A similar phenomenon was observed when different Li salts were used (Figure S2). Similar behavior was also observed when carbon paper electrode was used as the positive electrode in 1 M LiTFSI/DMA (Figure S3).

The recovery of the reduction current in CV measurements beyond the second cycle suggests that, although the electrode initially becomes blocked at low potentials, it reopens at higher potentials. This phenomenon can be more clearly demonstrated by switching the potential between a high potential (2.6 V) and a low potential (2.2 V) while monitoring the corresponding current response. As shown in Figure 1b, when the potential was shifted to 2.2 V and 2.6 V, $|j|$ decreased and increased, respectively, with a reversible response upon repeated potential changes. This potential-dependent current response was further confirmed through impedance measurements. Figure 1c presents potentiostatic electrochemical impedance spectroscopy (PEIS) data obtained over three cycles of potential switching between 2.2 V and 2.6 V. The Cole–Cole plot shows a

larger semicircle at 2.2 V, where the electrode reaction was blocked, and a smaller semicircle at 2.6 V, where the blockage was released. In addition, this behavior was reversible upon repeated potential cycling. The frequency range associated with this reversible behavior was 3–100 mHz.

The results shown in Figure 1 suggest that the conventional understanding—that the positive electrode becomes irreversibly blocked by Li_2O_2 —requires reconsideration. To gain deeper insight into this phenomenon, we conducted experiments using a rotating ring-disk electrode (RRDE) system composed of a GC disk and a Pt ring (Figure 2). Note that the collection efficiency (N) in this experimental system was 0.46, which was confirmed to be in close agreement with the theoretical value (0.424) (Figure S4). The ring potential (E_{Ring}) was held constant within the charging potential range (3.0–4.0 V). Figure 2a presents the results when $E_{\text{Ring}} = 4.0$ V. As E_{Disk} was swept negatively, the ORR current at the disk (J_{Disk}) began to flow at ~ 2.7 V. When E_{Disk} reached 2.4 V, an oxidation current at the ring (J_{Ring}) was observed. When E_{Disk} reached 2.3 V, the absolute value of J_{Disk} ($|J_{\text{Disk}}|$), peaked, followed shortly by a peak in the J_{Ring} absolute value ($|J_{\text{Ring}}|$). Beyond this point, as E_{Disk} continued decreasing toward the lower potential limit, both $|J_{\text{Disk}}|$ and $|J_{\text{Ring}}|$ decreased together. During the subsequent positive potential sweep, almost no reduction current was observed at the disk electrode;

correspondingly, no oxidation current was detected at the ring electrode.

We next conducted similar experiments at various E_{Ring} (Figures 2b and S5). The peak $|J_{\text{Ring}}|$ remained constant at 32 μA when E_{Ring} was between 4.0 V and 3.4 V; however, it decreased to 28 μA at 3.2 V and further decreased to 16 μA at 3.0 V. Notably, as E_{Ring} decreased, the background current also decreased accordingly. This behavior is attributed to the fact that the onset potential for the ORR at the ring electrode is at around 3.2 V (Figure S6). At 3.0 V and 3.2 V, the oxidation of the discharge products generated at the disk electrode occurred simultaneously with a steady-state ORR at the ring electrode. Figure 2c presents a plot of the coulombic charge derived from the oxidation current (Q_{ox}) as a function of E_{Ring} . The Q_{ox} value was calculated on the basis of the difference between J_{Ring} during the positive potential sweep and J_{Ring} during the negative potential sweep of the disk electrode. As evident from Figure 2c, even after correction for background effects, the Q_{ox} values at the ring electrode remained constant at 16.5 nA h for $E_{\text{Ring}} \geq 3.4$ V.

Here, the identity of the chemical species generated on the disk electrode and subsequently oxidized on the ring electrode is considered. Two possible products that are generated at the disk electrode and can be oxidized at the ring electrode are the two-electron O_2 reduction product, Li_2O_2 , and the one-electron reduction product, LiO_2 .

During discharge, Li_2O_2 forms in various sizes, shapes, and crystallinities¹⁶, leading to a broad oxidation potential range from 2.8 V to above 4.4 V²⁷. By contrast, the oxidation potential of LiO_2 (or O_2^-) falls within a relatively narrow range at approximately 2.8 V⁹. Importantly, as shown in Figure 2c, Q_{ox} remained constant for $E_{\text{Ring}} \geq 3.4$ V, suggesting that the species oxidized at the ring electrode is LiO_2 (or O_2^-), consistent with previous interpretations in the literature^{7,28,29}. In Figure 2d, J_{Ring} corrected with the collection efficiency N ($= 0.46$), $J_{\text{Ring,N}}$, is replotted (red line) with a downward orientation for clarity. The difference between $|J_{\text{Disk}}|$ and $|J_{\text{Ring,N}}|$ (gray area) corresponds to the current associated with the two-electron reduction reaction, i.e., the formation of $\text{Li}_2\text{O}_2^{\text{surf}}$. Notably, in practice, $\text{Li}_2\text{O}_2^{\text{sol}}$ generated via the solution pathway also deposits onto the positive electrode. This analysis indicates that $|J_{\text{Ring,N}}|$ is substantially smaller than $|J_{\text{Disk}}|$, clearly demonstrating that Li_2O_2 is the predominant discharge product, in agreement with previous reports. From the results above, we conclude that Li_2O_2 , which leads to positive electrode blockage in the negative potential region, reversibly dissolves in the positive potential region.

This conclusion is further supported by the following experiments. Figure 3 presents the results of linear sweep voltammetry (LSV) conducted at a relatively high potential sweep rate of 100 mV/s in the charging region, using electrodes discharged at 50

$\mu\text{A}/\text{cm}^2$. When LSV was initiated immediately after discharge termination (black line), the oxidation current sharply increased at ~ 3.2 V, with two distinct peaks observed at 3.4 V and 3.8 V. Previous studies with different electrolyte systems identified two oxidation peaks in the forward LSV sweep following discharge; the first peak was attributed to the oxidation of LiO_2 , and the second peak was attributed to the oxidation of Li_2O_2 ⁶. The standard electrode potential for the $\text{O}_2/\text{Li}_2\text{O}_2$ redox couple is 2.96 V, whereas that for the O_2/O_2^- redox couple is 2.65 V, indicating that the oxidation of Li_2O_2 proceeds at a more positive potential from a thermodynamic perspective⁷. It is also well known that the oxidative decomposition of Li_2O_2 , which exists as a poorly conductive solid, requires a higher potential than the oxidation of LiO_2 species. From this perspective as well, the previously mentioned peak assignment is both reasonable and well-justified. These results suggest that both LiO_2 and Li_2O_2 were deposited onto the positive electrode surface immediately after discharge. By contrast, when the electrode was left at the OCP for 30 min after discharge (red line), the subsequent forward potential sweeps revealed no substantial oxidation peaks. Thus, despite the similar discharge capacity in these experiments, the presence or absence of the OCP holding period led to substantial differences in the subsequent LSV behavior. The results suggest that, during the 30-min OCP period, the discharge products LiO_2 and

Li_2O_2 dissolved into the electrolyte, meaning that the positive electrode transitioned from a blocked to an open state.

The above conclusion is further supported by experimental results showing that the second discharge curve, obtained after a 30-min OCP period, almost completely overlaps with the first discharge curve (Figure S7). In addition, the disappearance of Li_2O_2 from the positive electrode at the OCP was recently observed via in situ surface-enhanced Raman spectroscopy (SERS)³⁰ and electrochemical quartz crystal microbalance (EQCM) studies³¹. Furthermore, although the potential dependence of Li_2O_2 dissolution into the electrolyte has not been reported, its presence in solution has been experimentally confirmed through techniques such as Li_2O_2 titration^{32–34}. Notably, in Figure 3, when the potential was maintained at the OCP for 30 min, the oxidation current gradually increased beyond 3.5 V. This behavior is attributed to the oxidation of residual discharge products that remained undissolved on the positive electrode surface, such as Li_2O_2 , or possible side products such as Li_2CO_3 .

Next, to clarify the potential region in which Li_2O_2 dissolves from the positive electrode into the electrolyte, we conducted CV measurements at a low sweep rate (0.5 mV/s) with rotation at 1000 rpm (Figure 4) because the positive electrode reopening is a slow process. Under these conditions, the same behavior—where the reduction current

recovered in each cycle—was observed. However, an anomalous phenomenon appeared at ~ 2.5 V, where $|j|$ decreased at more negative potentials (i.e., at a higher overpotential for the reduction reaction). This trend aligns well with the results in Figures 1b and 1c, and the results above indicate that Li_2O_2 dissolution occurs in a potential-dependent manner in the anomalous region in Figure 4. As the number of cycles increases, the overall $|j|$ value gradually decreases while the fundamental CV profile is maintained. This observation suggests that the reopening of the clogged electrode in a single cycle is incomplete, leading to progressive irreversible clogging of the electrode with increasing number of cycles.

Building on these results, we investigated the cycling characteristics of discharge under various current-density conditions, considering the semi-reversible nature of electrode clogging and reopening. Figure 5a presents the discharge results at a rotation speed of 1000 rpm and a current density of $50 \mu\text{A}/\text{cm}^2$. (The left and right graphs display the same experimental data but with different horizontal axis scales.) The maximum discharge capacity before reaching the cutoff potential (2.0 V) was $220 \mu\text{Ah}/\text{cm}^2$ (black line). However, in the second discharge performed immediately after the first, the discharge capacity decreased by more than 90% (red line). By contrast, in the third discharge, the maximum capacity decreased by only $\sim 30\%$ compared with the

second discharge (blue line).

When the current density was increased to $200\ \mu\text{A}/\text{cm}^2$ (Figure 5b), the first discharge potential slightly decreased and the maximum discharge capacity was reduced to approximately $125\ \mu\text{Ah}/\text{cm}^2$ —approximately one-half of that at $50\ \mu\text{A}/\text{cm}^2$. The second discharge capacity decreased by 80% to $\sim 20\ \mu\text{Ah}/\text{cm}^2$, and the third discharge capacity further decreased by 40%, reaching $12\ \mu\text{Ah}/\text{cm}^2$. At an even higher current density of $600\ \mu\text{A}/\text{cm}^2$ (Figure 5c), the first discharge capacity was limited to $\sim 15\ \mu\text{Ah}/\text{cm}^2$. However, in comparison with the reductions in the second and third discharge capacities at higher current densities, those at lower current densities were minor.

As noted in the Introduction, the discharge reaction of LOBs is now widely accepted to proceed via two distinct pathways: the solution pathway and the surface pathway^{7,9}. Between these, the solution pathway, which enables a higher discharge capacity, occurs preferentially at higher potentials^{7,28}. Given the large discharge capacity indicated by the black lines in Figures 5a and 5b, we speculate that the discharge primarily proceeded via the solution pathway. When discharge terminated via the solution pathway, a large amount of Li_2O_2 accumulated on the positive electrode surface, leaving a limited number of active sites for further O_2 reduction reactions. By contrast, in Figure 5c, where a higher current was applied, the discharge potential was lower, indicating that

the assumption that discharge proceeded via the surface pathway from the first cycle is reasonable.

The second and subsequent discharges in Figures 5a and 5b, as well as the discharges in Figure 5c, were likely dominated by the surface pathway, as indicated by their low potential range and small discharge capacities. A key observation is that, in these cases, the discharge capacity does not substantially decrease in repeated discharge experiments. This finding suggests that the Li_2O_2 product dissolves from the surface as the potential returns to OCP after discharge termination, which aligns well with the results shown in Figures 1, 3, and 4.

The cyclic discharge behavior shown in Figure 5 is closely related to the anomalous behavior observed in the current–potential curves in Figure 4. Figure 6a presents a schematic of the current–potential characteristics. As previously discussed, the current–potential curve contains an anomalous region where its slope reverses. With increasing cycle number, the overall shape of the curve remains unchanged, whereas $|j|$ gradually decreases (transitioning from curve a to e). When $|j|$ is small, as discharge progresses (i.e., as the overall $|j|$ value decreases), the system state shifts from point 1 to 2, then to 3. Once the system enters the anomalous region (point 4), the stable state is lost, causing a sudden shift of the electrode potential in the negative direction, leading to discharge termination.

When $|j|$ is sufficiently small and does not reach the anomalous region, the discharge capacity increases substantially; however, the cathode undergoes irreversible clogging, resulting in a negligible capacity in the second consecutive discharge cycle. A similar sequence of events occurs when $|j|$ is large; however, because the system reaches the anomalous region more quickly (at 2'), the discharge lifetime is shorter. These results suggest that the anomalous region serves as the boundary where the solution and surface discharge pathways switch.

CONCLUSION

This study challenges the conventional understanding that Li_2O_2 accumulation leads to irreversible positive electrode blockage in LOBs. Figure 6b shows a schematic summarizing the understanding discussed above. Through systematic electrochemical measurements, including CV, PEIS, and RRDE analyses, we demonstrated that Li_2O_2 can dissolve into the electrolyte at specific potentials. The observed dissolution behavior correlates with the transition between the solution and surface pathways of Li_2O_2 formation, revealing a potential-dependent dynamic process. These findings suggest that adjusting the electrolyte composition and potential range could facilitate controlled Li_2O_2 dissolution, thereby improving the discharge capacity, energy efficiency, and

cycling performance. Future work will focus on identifying optimal electrolyte additives and operational conditions to further enhance LOB stability. The insights gained from this study provide a new perspective on managing discharge product formation and dissolution, contributing to the development of high-performance LOBs.

Supporting Information.

Experimental details; additional results of CV, RRDE and discharge tests.

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Notes

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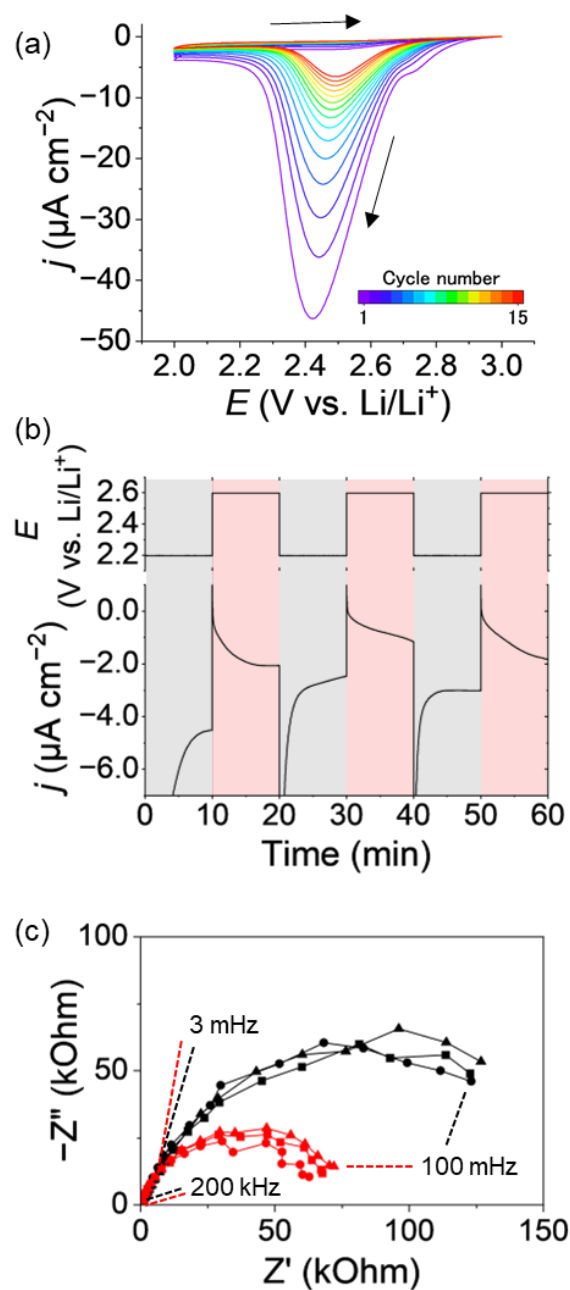


Figure 1. (a) Cyclic voltammograms obtained at a scan rate of 0.5 mV/s using GC as the working electrode in 1 M LiTFSI/DMA. (b) Time course of the current at a constant potential of 2.2 V (black region) and 2.6 V (red region), with the potential switched at 10-min intervals. (c) Cole–Cole plots at 2.2 V (black) and 2.6 V (red), obtained sequentially. Circles (●), squares (■), and triangles (▲) represent the first, second, and third measurements, respectively.

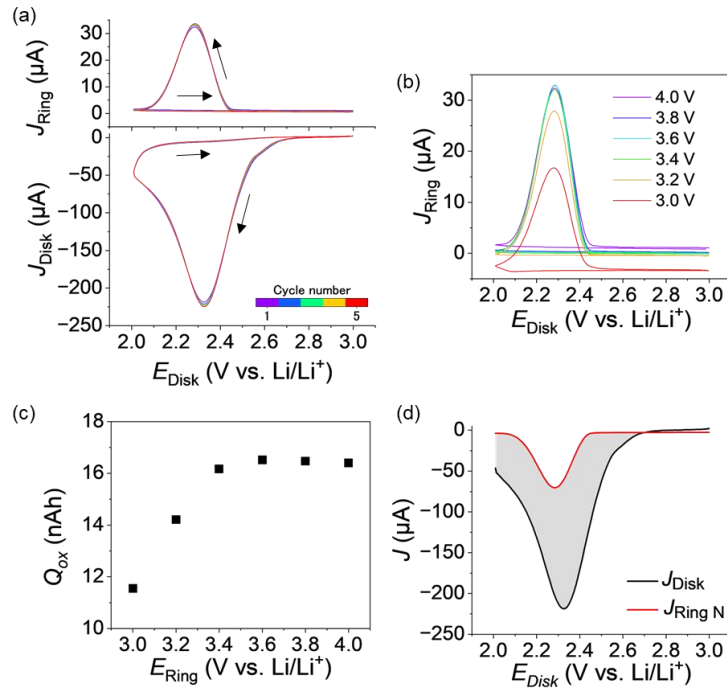


Figure 2. RRDE measurements in 1 M LiTFSI/DMA at a rotation rate of 1000 rpm; a scan rate of 100 mV/s was applied to the disk electrode, and the ring electrode was set at various potentials. (a) J_{Ring} curves at 4.0 V (upper) and cyclic voltammograms for the disk electrode (bottom). (b) J_{Ring} curves at various E_{Ring} . (c) Plot of the coulombic charge obtained by integrating J_{Ring} during the negative sweep relative to J_{Ring} during the positive sweep at the disk electrode (Q_{ox}). (d) Replots of J_{Ring} (red) and J_{Disk} (black) of the first negative scan in Figure 2a. $J_{\text{Ring,N}}$ is J_{Ring} corrected by the collection efficiency of the RRDE ($N = 0.46$).

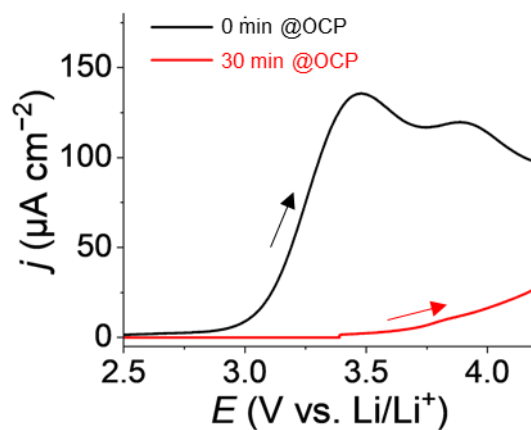


Figure 3. Liner sweep voltammograms obtained in 1 M LiTFSI/DMA using GC after discharging at $50 \mu\text{A/cm}^2$ until the potential reached 2.0 V. The potential was swept at 100 mV/s immediately after discharging (black) and after OCP for 30 min after discharging (red).

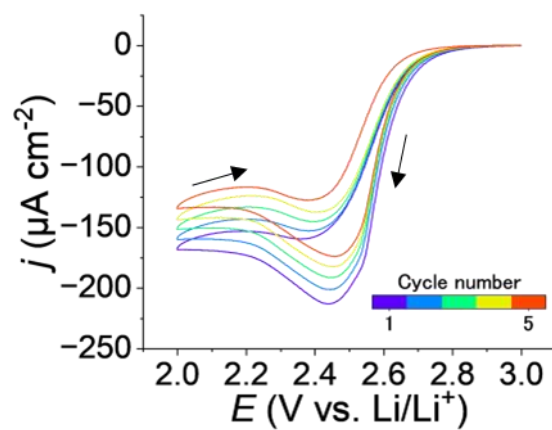


Figure 4. Cyclic voltammograms obtained in 1 M LiTFSI/DMA for the disk electrode at a scan rate of 0.5 mV/s and at a rotation rate of 1000 rpm.

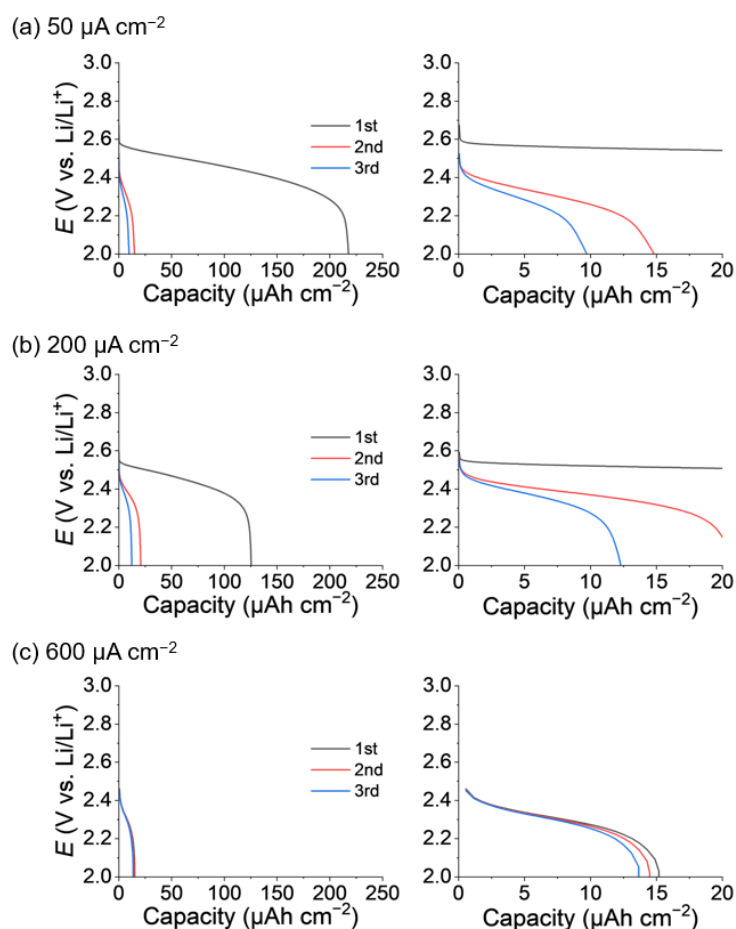


Figure 5. Discharge profiles in 1 M LiTFSI/DMA using RRDE at a rotation rate of 1000 rpm at (a) 50, (b) 200, and (c) 600 $\mu\text{A}/\text{cm}^2$ until the potential reached a cutoff of 2.0 V. The right figures indicate the extended range to 20 $\mu\text{Ah}/\text{cm}^2$ at each current density.

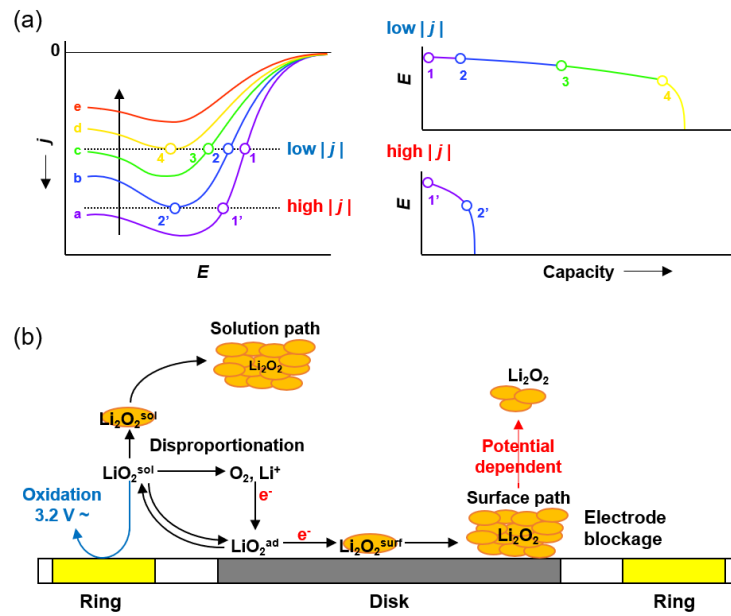


Figure 6. Illustrations (a) explaining the relationship between the anomalous region and the discharge behaviors and (b) summarizing the potential-dependent dissolution of Li_2O_2 during discharge.

Table of content

Li-O₂ secondary battery

