

True location of insulating byproducts in discharge deposits in Li–O₂ batteries

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KEYWORDS

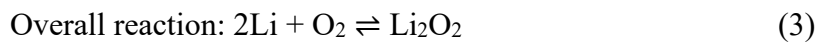
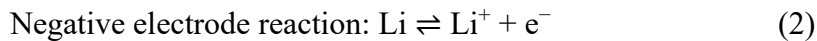
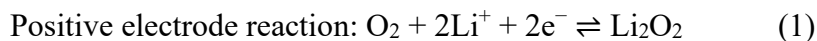
lithium-air battery • lithium-oxygen battery • SIMS • byproducts • lithium peroxide

ABSTRACT

Lithium–oxygen batteries (LOBs) are next-generation rechargeable energy storage devices with a high theoretical gravimetric energy density. However, the expected energy density has not been fully achieved, mainly because of high charging overvoltages. The inclusion of insulating byproducts in the discharge products has been suggested to be a critical factor for the high overvoltages. However, these previous studies did not consider the growing/ retreating fronts of the discharge deposits (i.e., the deposits/electrode interface or the deposits/electrolyte interface), potentially misleading conclusions. The aim of the present study is set to precisely determine the locations of insulating byproducts in individual discharge products in a LOB system, where the growing/ retreating fronts have already been identified, thereby indicating the right direction for effectively reducing charging voltage. The analysis revealed the consistent presence of Li_2CO_3 , a byproduct of decomposition of the electrolyte and/or positive electrode, inside the individual discharge products composed mainly of Li_2O_2 , as expected from the growing/ retreating fronts. The successful identification of the true locations of insulating byproducts in discharge deposits is pivotal because it can enhance our understandings on battery reactions, which can, in turn, pave the way for the development of design guidelines for advanced battery systems.

INTRODUCTION

Lithium–oxygen batteries (LOBs) have attracted considerable attention as next-generation rechargeable batteries because of their substantial theoretical gravimetric energy density^{1–5}. Ideally, O₂ undergoes electrochemical reduction during discharge of a LOB, resulting in the deposition of solid lithium peroxide (Li₂O₂) within the porous carbon electrode (Equation 1):



During charge, the reverse reactions proceed, where Li₂O₂ undergoes electrochemical oxidation to evolve O₂. However, in contrast to the overvoltage during discharge, that during charge is high even at the initial stage and increases with increasing charge capacity⁶. As a consequence, LOBs have failed to achieve their anticipated high gravimetric energy density and cycle life. Effectively addressing this fundamental challenge requires understanding the underlying origins of the high charging overvoltages.

Coverage of the discharge product by insulating byproducts derived from the decomposition of the electrolyte and/or electrode has been considered one of the potential causes of the high charge overvoltage^{7–13} (Figure 1a). McCloskey et al. used X-ray photoelectron spectroscopy (XPS) and isotope labeling combined with differential electrochemical spectroscopy (DEMS) in an experimental system equipped with an ether-based electrolyte and a vertically aligned carbon nanotube (VACNT) electrode¹⁴. They proposed that the increase in the overvoltage during charge is attributable to the coverage of Li₂O₂ by insulating byproducts. Gallant et al. also demonstrated

through X-ray absorption near edge structure (XANES) experiments that a Li_2CO_3 -like species is generated at the interface connecting a VACNT and Li_2O_2 in a cell containing a 1,2-dimethoxyethane (DME)-based electrolyte¹⁵. Black et al. reported that a small amount of water, generated through reactions involving the superoxide radical, undergoes a reaction with Li_2O_2 , leading to the formation of a LiOH film on the positive electrode¹⁶. This film hinders the catalytic reaction at the positive electrode¹⁶.

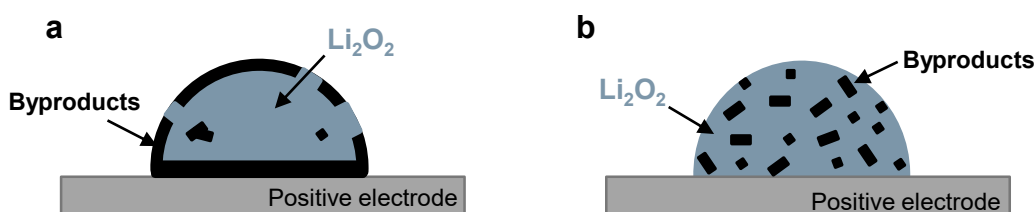


Figure 1 Schematic illustrations showing the possible location of byproducts in a discharge deposit. (a) The individual discharge products are covered by insulating byproducts, and (b) insulating byproducts are distributed in the discharge deposits uniformly.

In principle, the location of such insulating byproducts should be determined by the growing or retreating front of Li_2O_2 during discharge and charge. For example, if the growing front during the discharge reaction is the Li_2O_2 /electrode interface, the discharge products should be covered by insulating byproducts generated via the reaction between the electrolyte and Li_2O_2 (Figure 1a). However, if the growing front is the Li_2O_2 /electrolyte interface, the insulating byproducts generated via the reaction between the electrolyte and Li_2O_2 should be continuously incorporated into the Li_2O_2 particles as the discharge deposits grow and the byproducts could be distributed in

the deposits uniformly, as schematically shown in Figure 1b. Moreover, if the system exhibits different growth interfaces from retreat interfaces¹⁷, there is a possibility that the states depicted in Figure 1a and 1b coexist simultaneously. Notably, whether the growing/retreating front is the Li_2O_2 /electrode interface or the Li_2O_2 /electrolyte interface could depend on the combination of the electrolyte and the electrode^{17–24}. Therefore, the growing/retreating front must be identified when discussing the exact location of byproducts in the discharge products. The discharge products can be deposited with diverse sizes, morphologies, and crystallinity, depending on the local environment on the positive electrode^{25,26}. In addition, the particle size of the discharge products typically ranges from several tens of nanometers to $1\text{ }\mu\text{m}$ ^{27–31}. Nevertheless, previous studies have drawn conclusions based on analyses of electrode surface areas spanning at least $10\text{ }\mu\text{m}^2$, which only allowed the average properties of the discharge products to be obtained. Drawing conclusions based solely on the outcomes of such analyses could potentially mislead interpretations.

In light of the above issues, the aim of this study is set to determine the true locations of insulating byproducts in individual discharge products in the LOB system, where both the growing and retreating front during discharging and charging have already been clarified as the Li_2O_2 /electrolyte interface through various analytical techniques³².

EXPERIMENTAL SECTION

Cell configuration

The electrochemical cell used in this study has been described elsewhere¹². Li foil (25 mm diameter, 100 or 400 μm thick, Honjo Metal) was used as a negative electrode. Carbon paper (CP,

20 mm diameter, TGP-H-060, Toray) was used as a positive electrode. The CP was prepared by immersing pristine CP in hot acid ($\text{H}_2\text{SO}_4\text{:HNO}_3 = 3\text{:}1$) for 2 h, as described in the literature³³. A glass-fiber filter (GF/A, 22 mm diameter, Whatman) was used as the separator after it was dried under vacuum at 110 °C overnight. Dehydrated DMA (Wako) was used as the solvent for the electrolyte. LiNO_3 (Kishida, Japan) was used as the salt. The electrolytes were prepared by stirring the salt and solvent overnight. The water content of the electrolyte was confirmed to be 100 ppm or less by Karl Fischer titration. The volume of the electrolyte was fixed at 300 μL . The cells were assembled in an Ar-filled glovebox. O_2 (>99.99% purity) was supplied by attaching a small cylinder (50 mL, 0.25 MPa).

Electrochemical measurements

Electrochemical measurements were performed using a VMP3 electrochemical test unit (Bio-Logic, France) or a battery measuring apparatus (HJ1020mSD8, HOKUTO DENKO) in a thermostatic chamber maintained at 25 °C. All electrochemical tests were conducted after the cells were maintained at their open-circuit voltage for 12 h or more.

SEM-EDX and XRD

SEM-EDX measurements were conducted using a field-emission scanning electron microscope (JSM 7800F, JEOL). Prior to these measurements, the samples were treated with anhydrous acetonitrile and handled in an environment devoid of air. The electron acceleration voltage of the electron microscope was set at 5 kV for SEM image acquisition. The electron acceleration voltage

of the EDX was varied between 1 and 5 kV, whereas the probing current was maintained at ~100 nA. The software AZtec 4.3 (Oxford Instruments) was used for automatic quantification of the elements Li, C, N and O in all the spectra. The samples were attached to the sample holder using nonconductive double-sided tape.

XRD measurements were conducted with an X-ray diffractometer (SmartLab, Rigaku). The patterns were collected within the range $30^\circ \leq 2\theta \leq 60^\circ$ with a step size of 0.1° without the sample being exposed to the atmosphere.

ToF-SIMS

All samples were transferred under Ar atmosphere using a LEICA EM VCT500 (Leica Microsystems, Wetzlar, Germany) transfer system. ToF-SIMS analysis was carried out with an M6 Hybrid secondary ion mass spectrometer (IONTOF, Münster, Germany). All samples were analyzed in negative polarity with delayed extraction mode for high lateral resolution. Depth profiles were collected using 30 kV Bi_3^+ primary ions with noninterlaced gas cluster ion beam 20 kV Ar_{2890}^+ cluster sputtering between analysis steps with a 100 μs cycle time. The analysis area was set to $50 \times 50 \mu\text{m}^2$ with 512×512 pixels, whereas the sputter area was set to $400 \times 400 \mu\text{m}^2$. The mass resolution was in the range $m/\Delta m$ 2000–4000 because of the challenging topography of the samples. Data evaluation was conducted with the SurfaceLab 7.3 software (IONTOF, Münster, Germany).

XPS

XPS measurements were carried out with a VersaProbe II instrument (ULVAC-PHI). All samples were transferred to the instrument in an Ar-filled transfer vessel. Monochromatic Al K α radiation (1486.6 eV) was used; the power of the X-ray source was 50 or 100 W, and the beam voltage was 15 or 20 kV. The examined areas were 0.03 mm² or 1 mm². For depth profiling, Ar⁺ ions with accelerating voltages between 1 and 2 kV were applied using the following sputter steps: (1) pristine, (2) 1 min 1 kV, (3) 3 min 1 kV, and (4) 5 min 2 kV. All data were calibrated in relation to the signal of adventitious carbon at 284.8 eV. A Shirley background was used, and all spectra were fitted with a GL line shape.

RESULTS AND DISCUSSION

The cell was discharged at 0.1 mA cm⁻² for a capacity of 1.5 mAh cm⁻² in 1 M LiNO₃/DMA using carbon paper (CP) as the positive electrode; it was then recharged for the same capacity (Figure S1). The X-ray diffraction (XRD) pattern of the positive electrode after discharge shows clear peaks attributed to Li₂O₂ (Figure 2a). These peaks disappeared after the recharge, indicating that the main discharge product is Li₂O₂. In addition, scanning electron microscopy (SEM) images of the positive electrode after discharge indicate the formation of Li₂O₂ particles with diameters of ~2 μ m (Figures 2b–d). After the cell was charged, the XRD peaks assigned to Li₂O₂ disappeared but the presence of solid residual products was confirmed in the SEM images (Figure 2e). As will be explained in detail later, these products were identified also as Li₂O₂.

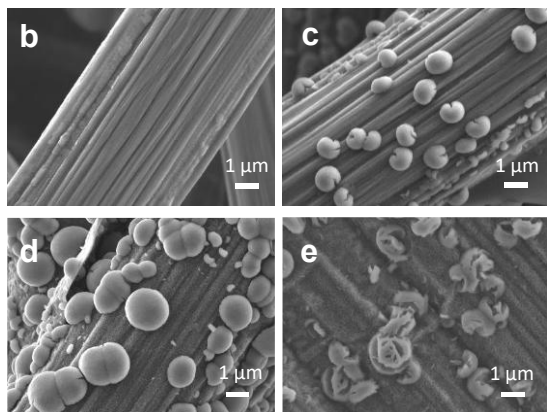
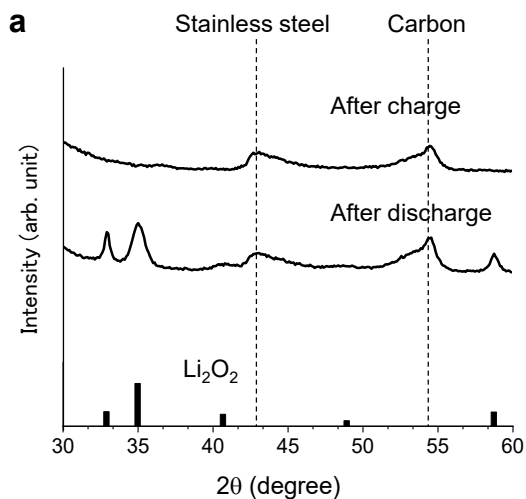


Figure 2 (a) XRD patterns of the CP electrode discharged (lower) and recharged (upper) at 0.1 mA cm^{-2} for 1.5 mAh cm^{-2} in $1 \text{ M LiNO}_3/\text{DMA}$. SEM images of CP electrodes (b) in the pristine state, (c–d) after discharge at 0.1 mA cm^{-2} for 0.5 mAh cm^{-2} (c) and 1.5 mAh cm^{-2} (d), and (e) after recharge at 0.1 mA cm^{-2} for 1.5 mAh cm^{-2} in $1 \text{ M LiNO}_3/\text{DMA}$.

Analyses of the positive electrode after discharge

Energy dispersive X-ray spectroscopy

To determine the average elemental composition of the particles formed on the positive electrode, we used energy-dispersive X-ray spectroscopy (EDX). Oxygen element (O) derived from Li_2O_2 was prominently detected in the region labeled "X," which is located on the particle, whereas carbon element (C) was detected in the region labeled "Y," where the presence of particles could not be clearly confirmed (Figure 3a). As the acceleration voltage was systematically varied, we conducted point measurements, focusing either on region X or region Y. Increasing the electron acceleration voltage led to greater penetration of the electron beam into the sample, leading to the emission of X-rays from deeper sample regions. Notably, the relationship between the accelerating voltage and the analysis depth is not proportional^{34,35} because of various factors such as the spatial dispersion of the electron beam, sample damage induced by the electron beam, subsequent emission of characteristic X-rays from the sample, etc.; however, this analysis provides meaningful qualitative insights regarding the depth profiles of elements.

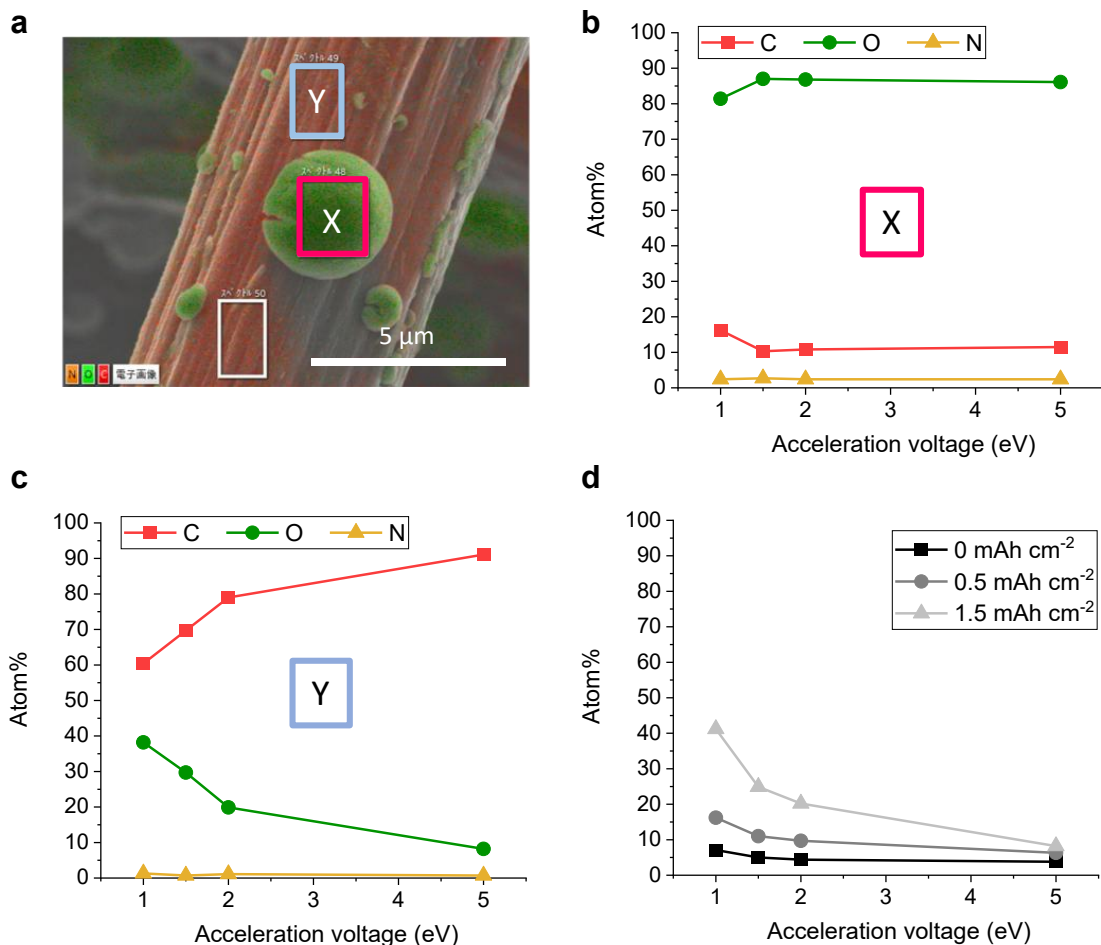


Figure 3 (a) EDX mapping image of the CP discharged at 0.1 mA cm^{-2} for 1.5 mAh cm^{-2} in 1 M LiNO_3 . (b,c) EDX static depth profiles determined atomic fractions of C, O, and N as a function of the electron acceleration voltage for (b) region X corresponding to particles and (c) region Y where the presence of particles cannot be clearly seen in Figure 3a. (d) EDX static depth profiles determined atomic fractions of O for region Y in Figure 3a.

Figures 3b and c show EDX static depth profiles with the atomic fractions of C, O, and N plotted as a function of the electron acceleration voltage for regions X and Y in Figure 3a, respectively.

In region X, which corresponds to particles, the O ratio exceeded 85% and the C ratio was ~10% in the acceleration voltage range 1.5–5 eV, whereas the C ratio was relatively high at 1 eV (16.2%). By contrast, in region Y, which does not correspond to particles, the O ratio decreased and the C ratio increased as the acceleration voltage was increased. In addition, we observed that a larger discharge capacity led to a higher atomic ratio of O at low acceleration voltages (Figures 3d and S2), implying that O-containing compounds are also deposited during discharge even in region Y. The presence of nitrogen (N) within the particles became evident when the analysis depth was extended by increasing the acceleration voltage to 5 eV (Figure S3). This result means that an N-containing component is incorporated into the particles, consistent with the observation of a peak in the N 1s region of the XPS spectrum after Ar⁺ sputtering (Figure S4).

Time-of-flight secondary ion mass spectrometry

We subsequently conducted analyses of the three-dimensional composition within discharge products by time-of-flight secondary ion mass spectrometry (ToF-SIMS), a technique with its exceptional high detection sensitivity and resolution in both the lateral and depth dimensions³⁶. A $50 \times 50 \mu\text{m}^2$ area on the electrode surface was first investigated (see Figure 4a). Within this area, regions corresponding to particles were selected for further analyses. The CP electrode used in the present work consisted of a carbon-fiber structure woven in three dimensions. The three-dimensional topography of the sample influences the mass resolution, peak intensity, and peak shape in delayed extraction mode^{37,38}. Hence, we focused on a specific carbon fiber in the analyzed area (step 1) and extracted the depth profiles of Li₂O₂ particles formed on it (step 2). Multiple

particulate deposits in close proximity were targeted in this analysis because a single deposit alone cannot provide sufficient intensities.

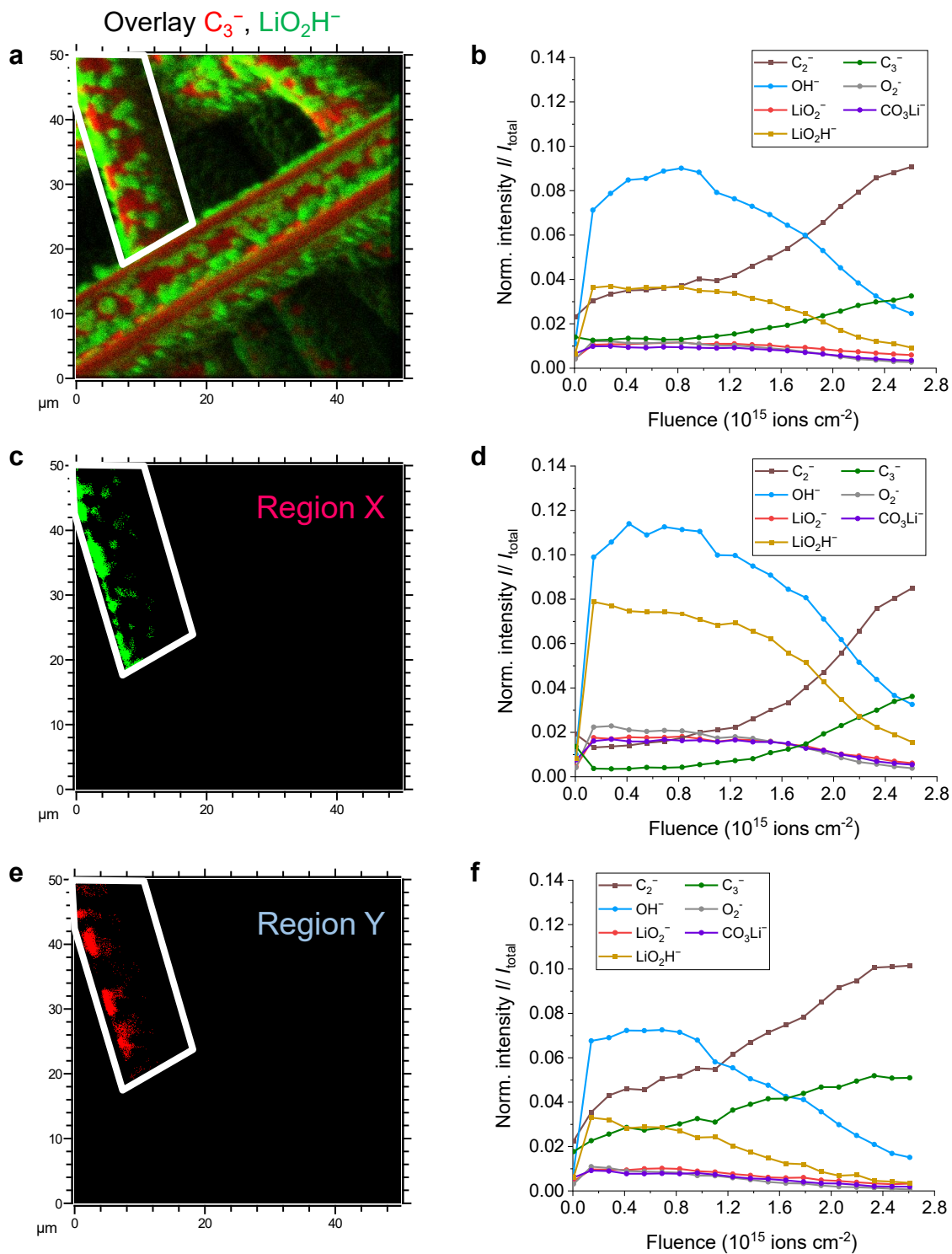


Figure 4 (a) ToF-SIMS overlay image of a $50 \times 50 \mu\text{m}^2$ area on the CP electrode surface. The green and red areas mainly can be assigned to discharge deposits and the CP substrate, respectively. (b) The ToF-SIMS depth profile for the selected region focused on a specific fiber marked in Figure 4a. (c) ToF-SIMS image and (d) corresponding depth profiles for region X which is on particles. (e) ToF-SIMS image and (f) corresponding depth profiles for region Y where the presence of particles cannot be clearly confirmed.

Figure 4a shows the ToF-SIMS overlay image of a $50 \times 50 \mu\text{m}^2$ area on the CP electrode surface with C_3^- and LiO_2H^- signals. The lithium- and oxygen-containing fragments observed in a region corresponding to Figure 4a could be attributed to Li_2O_2 particles, while C_2^- and C_3^- signals could originate from the carbon fiber of the CP substrate. Thus, the green and red areas can be considered to show regions X and Y, respectively. As step 1, we extracted the depth profile while focusing on a single carbon fiber, without distinguishing between regions X and Y. Figure 4b shows the ToF-SIMS depth profile for the selected region marked in Figure 4a. In the depth profiles, LiO_2^- , CO_3Li^- , O_2^- , OH^- , and LiO_2H^- exhibit similar profiles. Notably, the intense OH^- signal is due to its ease of ionization in the negative-ion mode and does not represent the absolute quantity of OH^- . These secondary ions and C_3^- ions were confirmed to be detected at different locations from each other in the ToF-SIMS overlay images (Figure S5). In addition, as the intensity of these peaks began to decrease with increasing sputter time, the intensity of the C_2^- and C_3^- signals increased synchronously. These results suggest that LiO_2^- , CO_3Li^- , O_2^- , OH^- , and LiO_2H^- indeed originate from the discharge deposits and that C_2^- and C_3^- originate mainly from the substrate.

As step 2, we analyzed region X, which corresponds to particles (Figure 4c), separately. The corresponding depth profiles are plotted in Figure 4d. Similar to the case where regions X and Y were not distinguished (Figure 4b), LiO_2^- , CO_3Li^- , O_2^- , OH^- , and LiO_2H^- exhibited similar profile behaviors. The intensities of peaks that originated from the particulate deposits remain constant across the range from 0.2×10^{15} to 1.0×10^{15} ions cm^{-2} , where the C_2^- and C_3^- peak intensities are weak. This result indicates a spatially uniform chemical composition within the discharge product, as schematically shown in Figure 1b. We observed no significant compositional change in the range from 1.6×10^{15} to 2.8×10^{15} ions cm^{-2} corresponding to the analysis of the $\text{Li}_2\text{O}_2/\text{electrode}$ interface. This result clearly indicates that byproducts are not localized at this interface as shown in Figure 1a.

We also analyzed the depth profile observed in region Y (Figures 4e and f). The analytical data show a trend that differs from that observed for the CP substrate that was simply immersed in the electrolyte without being discharged (Figure S6). Comparison of the profiles from X and Y also showed similar trends in the signals, albeit with a higher intensity of carbon signals for the region Y. Notably, a marginal increase in intensity of the LiO_2^- and LiO_2H^- peaks (red and yellow lines, respectively) was also observed near the surface after sputtering. These results suggest that a small amount of discharge deposits formed even in region Y, where the presence of such deposits is not apparent in the corresponding SEM images. This interpretation is consistent with the EDX analysis results in Figure 3d.

X-ray photoelectron spectroscopy (XPS)

The EDX and ToF-SIMS measurements enabled us to elucidate the spatial compositional distribution in individual particles. However, Li compounds have been reported to decompose upon Ar^+ sputtering or electron beam irradiation because of their high reactivity^{39–41}. In addition, in ToF-SIMS analyses, easily ionizable secondary ions are detected more strongly, which might lead to misinterpretation of the absolute amount of the compound to be analyzed. Hence, samples prepared using the same protocol were characterized by XPS. Although XPS lacks sufficient lateral resolution to distinguish between regions X and Y, the insights gained from this technique are beneficial for supporting conclusions derived from the ToF-SIMS analysis. For depth analysis, the following Ar^+ sputtering conditions were applied sequentially: (1) pristine, (2) 1 min at 1 kV, (3) 3 min at 1 kV, and (4) 5 min at 2 kV. As control samples, pristine CP and CP that was simply soaked with electrolyte but not discharged were also prepared.

In the C 1s region, clear peaks corresponding to carbonate, C–H, C–C, and C–O bonds are observed (Figure 5a). The XPS spectra of the control samples are shown in Figures S7 and S8. Notably, the intensity of the peak assignable to carbonate at ~290 eV in the spectrum of the examined sample was constant even with increasing sputtering time. This result is reasonable given that the discharge reaction occurs at the Li_2O_2 /electrolyte interface in this system³². Concretely, because Li_2CO_3 , a side-reaction product, is constantly generated at the growing interface, it is uniformly distributed inside the discharge products, as schematically shown in Figure 6a. This conclusion is consistent with that deduced from the previously discussed ToF-SIMS analysis results.

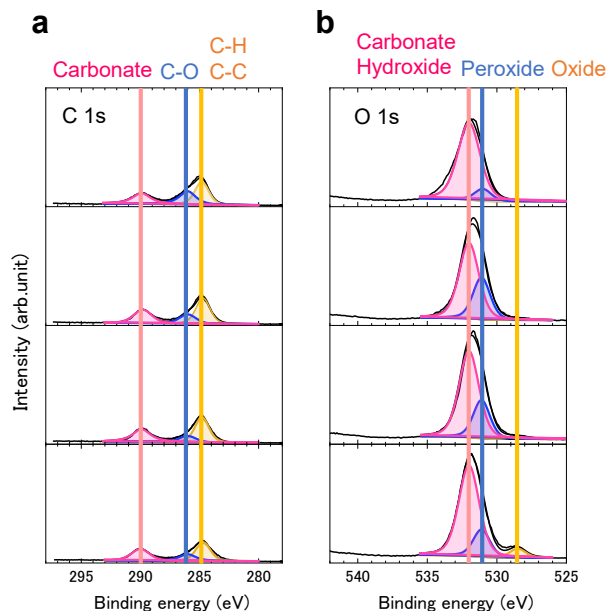


Figure 5 (a) C 1s and (b) O 1s regions of the XPS spectra of the CPs discharged for 1.5 mAh cm^{-2} in 1 M LiNO_3/DMA . The XPS spectra after each Ar^+ sputter step are arranged in the following order from top to bottom: (1) pristine; (2) 1 min, 1 kV; (3) 3 min, 1 kV; and (4) 5 min, 2 kV

In the O 1s region of the XPS spectrum of the discharged sample, noticeable peaks corresponding to peroxide, carbonate, and hydroxide were observed after Ar^+ sputtering (Figure 5b). The depth profiles of the carbonate and hydroxide species are similar to those of the carbonate species in the C 1s region and can be assumed to originate mainly from Li_2CO_3 formed at the $\text{Li}_2\text{O}_2/\text{electrolyte}$ interface during discharge. Notably, a peak attributed to oxide was observed only after step (4). This peak could have appeared because of partial decomposition of LiOH , Li_2CO_3 , and Li_2O_2 into Li_2O by Ar^+ sputtering⁴². This interpretation is consistent with the experimental fact that the atomic ratio of Li 1s increases when the Ar^+ sputtering progressed (Table S1).

Short summary for the chemical composition of discharge deposits

As previously mentioned, we have clarified that both growing front at discharge and retreating front at charge reactions locate at the Li_2O_2 /electrolyte interface in the LiNO_3/DMA systems used in the present work³². Thus, the insulating byproducts formed by the reaction between the electrolyte and Li_2O_2 during discharge should, in principle, be incorporated into the discharge deposits as the Li_2O_2 growth progresses, as schematically shown in Figure 6a. We confirmed this behavior experimentally by analyzing the depth profiles using XPS and ToF-SIMS, which confirmed that no significant difference existed in chemical composition.

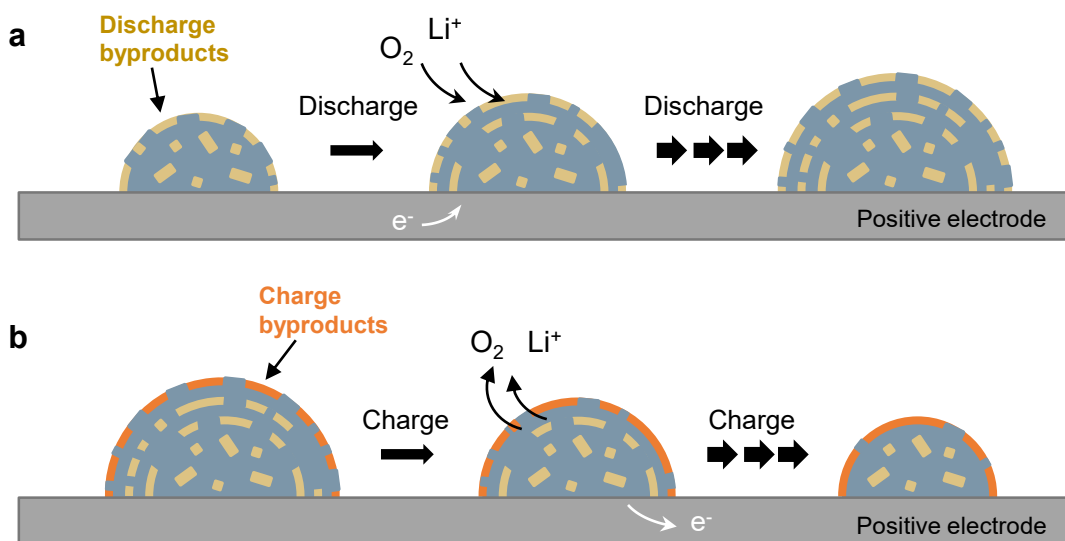


Figure 6 Schematic summarizing the possible spatial distribution of byproducts during (a) discharge and (b) charge when both discharge and charge proceed at the Li_2O_2 /electrolyte interface.

We here comment on the signals assignable to carbonate. Although the CO_3Li^- signal was detected through ToF-SIMS analysis, this is known to be detected even in the analysis of commercial Li_2O_2 ⁴³. Carbonate peaks that appear to be derived from carbonate are also confirmed by the XPS analysis of the CP substrate not subjected to discharge (Figure S7a). However, the carbonate peak observed in the XPS spectrum of the sample not subjected to discharge is substantially smaller than the same peak observed in the spectrum of the sample after discharge. Thus, the carbonate peak observed for the samples with the discharge test likely originates from the substrate itself and byproducts formed by the reaction between the Li_2O_2 and the electrolyte (Figure 6a). This interpretation is consistent with the observation that a C-element fraction of ~10% was always identified in region X (corresponding to Li_2O_2 particles) by EDX analysis (Figure 3b). Collectively, these results lead to the conclusion that the chemical composition within individual discharge products is spatially uniform (Figure 1b) and that the formation of passivation products at the Li_2O_2 /electrode interface (Figure 1a), which was reported in other electrolyte systems¹⁴, was not observed.

Analyses of the positive electrode after charge

We here discuss the case of the positive electrode after charge. The retreating front during charging process has been shown to also locate at the Li_2O_2 /electrolyte interface³². Therefore, because of the reaction between the Li_2O_2 and the electrolyte, new byproducts should be localized at the Li_2O_2 /electrolyte interface, which is continuously exposed during charging (Figure 6b). To verify this speculation, we conducted ToF-SIMS measurements on the sample surface after one discharge–charge cycle. Figures S9a and b show ToF-SIMS images of the carbon fiber on which

observations were carried out and the depth profile in this region, respectively. In the spectrum corresponding to the region near the surface, intense peaks of C_3^- and C_2H^- are observed, whereas LiO_2^- , CO_3Li^- , O_2^- , OH^- , and LiO_2H^- exhibit similar profile in their behaviors, remaining nearly constant, similar to the results for the discharged sample. The ToF-SIMS image shows the deposition of the carbon components that may have been formed by electrolyte decomposition on Li_2O_2 particles, and this deposition was gradually removed as the analysis progressed. The boundary between the particles and the carbon matrix became more distinct (Figures S9a and b). No indication of an increase in CO_3Li^- near the surface was observed. That is, some carbon species other than Li_2CO_3 accumulated on the Li_2O_2 surface after charging. Similar trends were observed for region X corresponding to particles (Figure S10).

Next, to further confirm the reliability of the ToF-SIMS results, we conducted XPS analysis of the positive electrode surface subjected to one discharge–charge cycle (Figure S11). Notably, the results include information from both regions X and Y. Peaks attributable to oxides induced by Ar^+ sputtering and peroxides were detected in the O 1s region. This result supports that the remaining solid after charging shown in the SEM image is Li_2O_2 (Figure 2e). However, the C 1s and O 1s regions of the XPS spectrum of the sample after charging are similar to those of the sample after discharging. This result could be attributable to the relatively poor surface sensitivity of XPS compared with that of ToF-SIMS. The aforementioned ToF-SIMS and XPS results indicate that byproducts resulting from electrolyte decomposition are formed at the interface between the residual Li_2O_2 and the electrolyte during charging, in good agreement with the result that the charging reaction proceeds at the Li_2O_2 /electrolyte interface.

Implications for the battery system improvements

Previous studies have suggested that the accumulation of insulating byproducts at the Li_2O_2 /electrolyte and/or Li_2O_2 /electrode interfaces can be a cause of high charging voltages^{14–16}. However, we revealed through comprehensive analyses using ToF-SIMS and XPS that the discharge products formed in the DMA-based electrolyte were not covered with any insulative byproducts. Rather, the insulative byproducts were distributed almost uniformly within the discharge products (Figure 6a). We speculate that the primary byproducts are carbonate species. On the other hand, electrolyte-derived byproducts formed during charging were localized near the Li_2O_2 /electrolyte interface, forming a film (Figure 6b). These locations of insulating byproducts are consistent with their distribution expected from the positions of the growing/retreating fronts of the discharge product in the present experimental system. Based on our observations, it is inferred that, as a result of repeated charge-discharge cycles, these insulating byproducts gradually accumulate in density within the discharge deposits, leading to further deterioration in subsequent charging behavior.

Should insulating byproducts localize at the Li_2O_2 /electrode interface, as reported in previous studies^{15,16}, then the development of a chemically stable positive electrode to suppress their formation becomes crucial. Furthermore, if insulating byproducts are indeed present at the Li_2O_2 /electrode interface, employing redox mediators^{44,45} to oxidize Li_2O_2 from the Li_2O_2 /electrolyte interface side becomes necessary. However, as mentioned above, we did not observe any localization of insulating byproducts at the Li_2O_2 /electrode interface in this study. This suggests that strategies aimed at oxidizing Li_2O_2 from the Li_2O_2 /electrode interface side through physical and chemical modifications of the positive electrode, such as promoting the formation of highly-decomposable Li_2O_2 and accelerating electrode reactions^{46–48}, can be effective.

Given that byproducts are typically insulating, an effective strategy to decrease overvoltages can be devised by identifying their location alone, without the need to distinguish their specific species.

Note that the location of the byproduct is considered to depend on the components of the battery system because the growing/retreating fronts of the discharge deposits vary with the type of electrolyte, type of electrode, and their combination^{17–24}. That is, the necessary improvement measures and critical considerations vary according to the location of the growing/retreating fronts of the discharge products. For instance, the approach to addressing its enhancement will differ depending on whether the insulating byproduct is solely covering the surface of the discharge product or dispersed within its interior. We would like to emphasize here that the determination of the true location of byproducts using the approach presented in this study contributes to the rational consideration of appropriate improvement measures for each specific case.

CONCLUSIONS

In this study, ToF-SIMS and XPS were employed to clarify the true location of insulating byproducts formed during the discharge and charge processes. The determination of the exact locations of byproducts is crucial for accurately guiding the direction of future improvements. For instance, because it was clarified that the Li_2O_2 /electrode interface remained uncovered by insulating products in the battery system examined in this study, various strategies based on the modifications of the positive electrode surface can be effective. On the other hand, the necessity for ongoing development of chemically stable electrolytes has been emphatically reaffirmed. Given that the growing/retreating front of discharge products can differ based on the electrolyte, the positive electrode, and their respective combinations, the corresponding countermeasures

should also vary accordingly. Considering the current stage of LOB research, continuous efforts in the development of novel positive electrodes, electrolytes, and additives are necessary. When researchers use such new materials, the location of the growing/retreating fronts of discharge products and, consequently, the localization of byproducts are not inherently obvious. In other words, the accurate determination of the actual location of byproducts is crucial for both exploring potential materials and devising strategies for their improvement. The approach introduced in this study is expected to play a significant role in addressing these challenges, thereby contributing to the development of practical and innovative battery materials.

ASSOCIATED CONTENT

The Supporting Information is available free of charge at <http://pubs.acs.org>.

Additional EDX, XPS, and ToF-SIMS data

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Funding Sources

This work was financially supported by JSPS KAKENHI (grant no. 20J20091). Additionally, partial funding was provided by JST ALCA-SPRING (grant no. JPMJAL1301) and JST (grant no. JPMJPF2016).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was performed with support from the National Institute for Materials Science (NIMS) Battery Research Platform.

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