TOF-SIMS Analysis of Lithium Reaction Products on Electrodes of Lithium Air Batteries*

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For TOF-SIMS characterization of lithium reaction products on electrodes of lithium air batteries (LAB), characteristic secondary ion species were found for identification and differentiation of their chemical states utilizing gas cluster ion beam (GCIB) sputtering for surface stabilization. Lithium peroxide and related products such as carbonate and formate were identified and confirmed under coexistence of electrolyte components to be produced on the real LAB carbon cathode by conducting discharge experiments using \(^{18}O_2\) reaction gas, which would be suitable method for further investigation on mechanisms of related electrode reactions.

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I. INTRODUCTION

The lithium air battery (LAB) has been intensively studied recently as one of the most promising candidates for future energy storage system because of its large theoretical capacity. The principle of LAB and chemical reactions on electrodes during discharge process are described in Fig. 1. In the most advanced research in LAB, detailed analysis of reaction products on electrodes is of great importance for the elucidation of various reaction processes and their mechanisms. Especially for the characterization of lithium compounds at the surface and interface regions, an analytical technique capable at differentiating their chemical states with high sensitivity and also with high spatial resolution is strongly required. Surface analysis by XPS, SIMS, and AES can be used for the characterization of reaction products on electrodes [1–3], but the evaluation of the composition of lithium compounds, remains difficult due to not only spectral similarity among their chemical states, but also instability of samples in the atmosphere as well as damage due to electron or ion beam irradiation during measurements [4].

Recently we have found that utilization of argon gas cluster ion beam (Ar-GCIB) sputtering can be effective for stabilizing surface conditions of electrodes, i.e., removing contamination without losing chemical information, and enables identification of lithium reaction products on the LAB carbon cathode by TOF-SIMS. In this study, further experiments using \(^{18}O_2\) as a reaction gas for discharge process have been carried out for tracing various products at revealing mechanisms of related electrode reactions.

II. EXPERIMENTAL

TOF-SIMS measurements were performed with TOF.SIMS5 (ION-TOF GmbH) equipped with commercially available GCIB source for this instrument. TOF-SIMS spectra and ion images were acquired using pulsed \(\text{Bi}_3^{3+}\) cluster ion beam accelerated at 30 kV. \(\text{Ar}^{2+}_{1000}\) GCIB accelerated at 10 kV was also used for the purpose of surface stabilization. Raster areas of pulsed \(\text{Bi}_3^{3+}\) for measurements of lithium reference materials and LAB electrodes were typically 200 \(\mu\)m by 200 \(\mu\)m and 400 \(\mu\)m by 400 \(\mu\)m, and those of GCIB for sputtering was 500 \(\mu\)m by 500 \(\mu\)m and 700 \(\mu\)m by 700 \(\mu\)m, respectively. In both cases, dose densities of GCIB were around
FIG. 3: Negative TOF-SIMS spectra of reference materials of Li$_2$CO$_3$ (top) and Li$_2$O$_2$ (bottom). They were acquired after surface stabilization by GCIB sputtering.

FIG. 4: Negative TOF-SIMS spectra of LAB carbon cathodes after discharging process under normal condition (top) and with $^{18}$O$_2$ gas (bottom). They were acquired after surface stabilization by GCIB sputtering.

$1.3 \times 10^{15}$ ions/cm$^2$ which was optimized to remove the altered layer of sample surface based on the dose dependence of TOF-SIMS spectra of lithium reference materials.

Lithium reference materials (Li$_2$O$_2$, Li$_2$CO$_3$, LiOH, and Li$_2$O) were purchased as powder reagents, and used without further purification. A schematic of cell structure is shown in Fig. 2. In sequence we see cell top-cover with holes that permit oxygen diffusion into the cell, the gas diffusion layer (GDL) coated by Ketjen black supporting the oxygen diffusion and its electrochemical redox process, the separator (Cellgard) soaked by TEGDME-LiCF$_3$SO$_3$ electrolyte, the lithium electrode on a stainless steel support, and the cell bottom-cover. After discharged under normal condition or with $^{18}$O$_2$ gas, the cell was disassembled. Carbon cathodes were taken out, and rinsed with solvent of TEGDME, then followed by drying in vacuum. Samples of lithium reference materials and LAB carbon cathodes were prepared in the glove box, and then transferred to the TOF-SIMS instrument without exposure to air using a dedicated vessel filled with argon gas.

III. RESULTS AND DISCUSSION

A. TOF-SIMS spectra of reference materials

In the negative TOF-SIMS spectra of as prepared samples of four reference materials (Li$_2$O$_2$, Li$_2$CO$_3$, LiOH, and Li$_2$O), fragment ions of CN$^-$, C$_2$H$_7$O$^-$ as well as SO$_3^-$ were commonly observed as surface contaminants together with CO$_3^-$ and LiCO$_3^-$ due to lithium carbon-
ate that might be produced as an altered layer on the surface of each reference material by ambient conditions. After surface stabilization by GCIB sputtering, however, their spectra were changed to simple ones with much reduced intensities of contaminants but without losing essential information on chemical states of respective compounds. Figure 3 shows negative TOF-SIMS spectra of Li$_2$CO$_3$ and Li$_2$O$_2$, acquired after GCIB sputtering. Consequently, 60CO$_2^-$ and 67LiCO$_2^-$ are seen as characteristic negative species for identification of Li$_2$CO$_3$, whereas 32O$_2^-$ and 71LiO$_2^-$ seem to be more specific for Li$_2$O$_2$. A similar behavior with GCIB sputtering was also observed in the positive TOF-SIMS spectra, and $^{81}$Li$_3$CO$_3^+$ was found as a characteristic peak for Li$_2$CO$_3$.

**B. TOF-SIMS spectra of real LAB cathodes after discharging process using $^{18}$O$_2$ reaction gas**

Based on the results of reference materials, TOF-SIMS measurements have been performed on real samples of LAB carbon cathodes, in order to see how we can identify reaction products under coexistence of various electrolyte components, and to verify the validity of characteristic peaks selected from reference materials including confirmation of Li$_2$O$_2$ production by O$_2^-$ detection. So, we have conducted to do experiments using $^{18}$O$_2$ gas in discharge reaction where Li$_2$O$_2$ should be produced on carbon cathode, then to compare TOF-SIMS spectra of the discharged cathode with $^{18}$O$_2$ and those obtained under normal condition. Figure 4 shows negative TOF-SIMS spectra of carbon cathodes after discharging process. These spectra were taken after GCIB sputtering, where the contribution of 149CF$_3$SO$_4^-$ due to electrolyte was still very strong, showing this component penetrated deep enough into the carbon substrate. In the spectrum of cathode discharged with $^{18}$O$_2$ reaction gas, strong peak of $^{18}$O$^-$ and a number of $^{18}$O containing species can be recognized. $^{47}$(HCO$^{18}$O)$^-$ and $^{49}$(HC$^{18}$O$_2$)$^-$ were identified as formate, and confirmed as a related product of HCO$_2$Li in discharging process by $^{18}$O substitution for the first time. O$^-$ and O$_2^-$ images obtained under same experimental condition are shown in Fig. 5. A bright $^{18}$O$^-$ signal is seen from the cathode discharged with $^{18}$O$_2$, and O$_2^-$ species were unambiguously confirmed as coming from Li$_2$O$_2$, because O$_2^-$ images of m/z 34 or 36 from the cathode under normal discharge show only background. In the positive spectrum which is not shown here, 16O containing Li$_3$O$_y$ fragments as well as 18O substituted Li$_3$CO$_y^+$ were identified similarly, from the cathode sample discharged with $^{18}$O$_2$.

Figure 6 compares intensities of $^{16}$O and/or $^{18}$O containing negative species to estimate rough ratios of concentration of both isotopes in various compounds. It is obvious that $^{18}$O is concentrated in O$_2^-$ and LiO$_2$H$^-$ due to reaction product of Li$_2$O$_2$, but also in HCO$_2$ due to the related product of LiCO$_2$H. In addition, $^{18}$O is observable even in unrelated reaction product such as SO$_2^-$, therefore in this case there might be possibility of $^{18}$O diff-

FIG. 5: TOF-SIMS images of O$^-$ and O$_2^-$ of LAB carbon cathodes after discharging process under normal condition (top) and with $^{18}$O$_2$ gas (bottom). They were acquired after surface stabilization by GCIB sputtering. The field of view was 400×400 μm$^2$.

FIG. 6: Comparison of intensities of $^{16}$O and/or $^{18}$O containing species of selected negative secondary ions between discharged LAB carbon cathodes under normal condition (blue) and with $^{18}$O$_2$ reaction gas (red). Intensities of respective negative ion species were normalized by that of $^7$Li$^-$. 

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FIG. 7: Comparison of intensities of $^{16}\text{O}$ and/or $^{18}\text{O}$ containing species of selected positive secondary ions between discharged LAB carbon cathodes under normal condition (blue) and with $^{18}\text{O}_2$ reaction gas (red). Intensities of respective positive ion species were normalized by that of $^6\text{Li}^+$. Fusion from $\text{Li}_2^{18}\text{O}_2$ and exchange with $^{16}\text{O}$ of $\text{SO}_2$ after cathode reaction. Comparisons of concentration of oxygen isotopes in positive detection were exhibited in Fig. 7 in the same manner. $^{18}\text{O}$ is contained in $\text{Li}_2\text{O}_y^+$ fragments which can be commonly observed from all of lithium compounds. It should be noted that the concentration of $^{18}\text{O}$ in $\text{Li}_2\text{CO}_3$ estimated from data in Fig. 7 might be lower than $^{18}\text{O}$ in $\text{Li}_2\text{O}_2$ from data in Fig. 6, suggesting one of the pathway of $\text{Li}_2\text{CO}_3$ would include side-reaction of $\text{Li}_2^{18}\text{O}_2$ with solvent or its depleted materials, but further study would be needed to elucidate the mechanisms.

IV. CONCLUSIONS

In conjunction with GCIB sputtering, characteristic secondary ion species have been found for identification and differentiation of lithium compounds. Based on this information, discharging products on real LAB carbon cathodes were analyzed to validate this method for detection of $\text{Li}_2\text{O}_2$ and other related products by doing experiments with $^{18}\text{O}_2$ for discharging reaction. As a result, $^{18}\text{O}$ substituted $\text{O}_2$ species were confirmed as coming from $\text{Li}_2\text{O}_2$ of the reaction product by discharge. $\text{HCO}_2$ and $\text{Li}_3\text{CO}_3^+$ due to $\text{HCO}_2\text{Li}$ and $\text{Li}_2\text{CO}_3$ respectively, were identified and confirmed as related products by $^{18}\text{O}$ substitution. Several production pathways for those compounds would be possible as side reactions during or after the discharging process. Further study using $^{18}\text{O}$ will help to explore these mechanisms. Electrolyte components of $\text{LiCF}_3\text{SO}_3$ and TEGDME, which were not removable by GCIB sputtering, should penetrate into the carbon cathode.

Acknowledgments

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