

Electrochemical Behavior of Al in a Non-Aqueous Alkyl Carbonate Solution Containing LiBOB Salt

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Abstract

Aluminum was studied as a current collector for rechargeable lithium batteries to understand electrochemical and passivation behavior. Electrochemical polarization tests, *in situ* scratch polarization tests and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) analysis in lithium bis-oxalato borate (LiBOB)-containing alkyl carbonate solution were conducted. The Al foil did not follow the alloy and de-alloy process with the LiBOB salt in electrolyte at 0 V vs. Li/Li⁺ in the cathodic sweep. During the anodic

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scan to the noble direction, the absence of an oxidation peak up to 3 V vs. Li/Li⁺ indicated that the air-formed oxide layer of Al was not reduced to metal. Oxide-free Al surfaces made by the *in situ* scratch test during the electrochemical polarization resulted in abrupt alloy formation with Li at 0 V vs. Li/Li⁺, but the newly formed surface formed passive films at higher potential with oxygen, namely, Al-O compound, as confirmed by ToF-SIMS.

Keywords; Al; Current Collector; Passivation; LiBOB; Lithium; Battery

1. Introduction

The lithium-ion cell is composed of a cathode, anode, separator, and electrolyte. The cathode and anode active materials are applied the form of a thin film on Al and Cu foils, respectively. LiPF₆ is used in commercial lithium-ion batteries as an electrolytic salt. In particular, the thermal decomposition and its hydrolysis under the presence of water in the electrolyte generate toxic and corrosive product like HF. Although the air-formed oxide layer, Al₂O₃, on the Al current collector forms a stable passive layer (AlF₃) by reacting with HF at higher potential (> 4 V vs. Li/Li⁺, hereafter V indicates potential versus Li) [1-4], alloy formation with Li close to 0 V is inevitable. In addition, the HF

can dissolve the cathode active material and Al current collector during usage over 10 years, which threatens the safety of lithium-ion batteries.

Recently, LiBOB ($\text{LiB}(\text{C}_2\text{O}_4)_2$) has been introduced as a possible candidate to replace the LiPF_6 salt [5-8]. Since LiBOB is composed of Li, B, C, and O elements, the formation of toxic and corrosive products is not expected although the salt decomposes at higher potential. Xu et al. [9] reported that Al passivates in 1M LiBOB containing EC:EMC solution. Zhang et al. [10] demonstrated that a passive film formed on the Al in EC:DMC with 1M LiBOB was protective against corrosion and suggested that the protective film is AlBO_3 . Very recently, Markovsky et al. [11] suggested that LiBOB may decompose at anodic potentials, thus forming passive films comprising B_2O_3 and metal-oxalate species on the aluminum electrodes polarized to 4.50–5.30 V.

In the present study, we report electrochemical behavior of Al foil in LiBOB containing an anhydrous alkyl carbonate solution in potential range of 0 to 5 V vs. Li/Li^+ . To understand the details of passivation at higher potential, the Al surface was investigated by ToF-SIMS.

2. Experimental

Pure Al foil (lithium battery grade, 20 μm) was purchased from Niraco. The Al foil

was cut into a square (10 mm × 10 mm) for polarization tests. Then, the Al foil was washed with pure ethanol. Al pouch cells were fabricated in an Ar-filled glove box. The electrochemical cells consisted of the Al foil (0.283 cm²) as a working electrode and lithium metal as counter and reference electrodes separated by a porous polypropylene separator. The used electrolyte was 0.8M LiBOB in ethylene carbonate – dimethyl carbonate mixture (1:1 ratio by volume).

A cathodic polarization was first applied to 0 V from an open circuit potential (OCP, 3.101 V), and then the polarization was progressed in the anodic direction up to 5 V with a sweeping rate of 10 mV s⁻¹ at 40 °C. To make the oxide layer-free surfaces of the Al electrodes, cathodic polarizations were first applied to 0 V from an open circuit potential (OCP) with a sweeping rate of 10 mV s⁻¹ at 40 °C. After reaching the desired potential (0, 3, 4, and 5 V), surfaces of the Al electrodes were scratched using a diamond polishing tip at 100 rpm for one second in the H-type cell [12,13]. After scratching the electrode surface, current variation vs. time was monitored for 300 s in a transient mode.

To analyze the scratched surfaces of the metals after the transient polarization, the polarized electrodes were examined by ToF-SIMS (ULVAC-PHI TRIFT2000) at 10⁻⁹ Torr. During the analysis, the targets were bombarded by pulsed 15 keV Ga⁺ beams (0.5

pA target current). The total collection time was 1000 s over a $12 \times 12 \mu\text{m}^2$ area located on the scratched surface.

3. Results and discussion

Figure 1a depicts cyclic voltammograms of the Al foil polarized in LiBOB and LiPF₆ salts (inset) contained an alkyl carbonate solution in range of 0 – 5 V at 40 °C. It is well known that Al exhibits the formation of the alloy and de-alloy process (see inset) with a high current density in the LiPF₆ contained alkyl carbonate solution [13]. However, the Al foil does not show the alloy and de-alloy process when it is polarized in the LiBOB-containing electrolyte in the range of 0 to 2 V. A broad cathodic peak appears in the $\mu\text{A cm}^{-2}$ scale in the potential range, which is a result of the reduction processes of the air-formed Al-oxide, electrolytic solvents, and formation of solid electrolytic interface. There are some metals (e.g. Cu, Ti, Cr, Fe, type 304 stainless steel) which do not undergo the alloy formation process even in the LiPF₆ salt containing electrolyte [12,13]. Under potential deposition (UPD) of Li is commonly seen for these metal surfaces in the LiPF₆ salt-containing electrolyte [12,13]. However, this process is difficult to observe for the LiBOB-containing electrolyte, and the reverse reaction, as well (Fig. 1a), providing evidence for the absence of the UPD process

because the reaction always occurs reversibly. For both cases, the only difference is the electrolytic salt, which prohibits the formation of the Li-Al alloy even at 0 V. It is likely that, although the air-formed film Al_2O_3 is somehow reduced, the Al_2O_3 layer might not be completely reduced to Al metal in the presence of LiBOB salt. Assuming the air-formed layer of Al_2O_3 to be 10 nm, the necessary charge density to reduce the air-formed Al_2O_3 layer to metal is 0.0106 C cm^{-2} . On the other hand, the measured charge density from the OCP to 0 V was $0.00325 \text{ C cm}^{-2}$, which is quite lower than the calculated value. This result supports the above hypothesis that the air-formed oxide layer was partially reduced in the presence of LiBOB salt. However, a corrosive fluorine element contained in the LiPF_6 salt seemed to facilitate the elimination of the air-formed layer at lower potential so that the alloy formation of Al with Li readily occurred.

For the anodic scan, no oxidation peak was seen up to 3 V. This finding indicated that no Li layer was formed as a result of the UPD process and that Al did remain passivated, which supports the hypothesis that the air-formed Al_2O_3 layer was not reduced to Al metal under the LiBOB presenting environment. Raising the potential resulted in a gradual increase in the anodic current to 5 V, at which the resulting peak current was retained at a lower level, approximately $20 \mu\text{m cm}^{-2}$. The reaction would be related to oxidation of the electrolyte. We speculate that the absence of the fluorine

element in the LiBOB salt keeps the surface of Al passivated even at 0 V, and this consequently prevents Li-Al alloy formation.

Figure 1b shows the results of a polarization test at 0 V after the scratch. As soon as the oxide layer of the Al was removed, the newly formed oxide-free Al very immediately reacted with Li, and a great surge of cathodic current was observed. This results primarily from the formation of the Li-Al alloy. The reaction takes place within a second. This result clearly indicates that no of formation of Li-Al alloy (Fig. 1a) could be due to the presence of the air-formed oxide layer on the Al through the cathodic polarization to 0 V. Namely, the air-formed film has been kept even at 0V under the LiBOB environment.

For the *in situ* scratch at 3, 4, and 5 V (Fig. 1c), of which the resulting optical microscopic images are shown in insets of Fig. 2a-c, the resulting currents abruptly decreased, meaning that a new passive film was immediately formed on the scratched surface. After the fast decay of the transient current, the current was retained at a low level. Namely, as soon as the whole surface was covered by the passive film, the current to maintain the passivation became very low. Retention of the current at a lower level indicated the growth of a passive film without critical defect that can be caused by corrosion on the scratched film. Provided that the passive film is not stabilized, the

resulting current should fluctuate due to the breakdown of the passive film. This result suggested that the Al metal readily forms a stable passive film under the LiBOB environment.

Since the scratched grooves were very narrow below 20 μm (see insets of Fig. 2a-c), we used ToF-SIMS that is able to produce a small Ga^+ ion beam less than $12 \times 12 \mu\text{m}^2$. The images exhibit clear vestiges after the *in situ* scratch (insets), and the resulting secondary ion mapping images were obtained without bunching the primary Ga^+ ions so that the clear image of secondary ions could be collected for the area. Irrespective of the potentials, we detected Li_2B^+ , LiO^+ , B_2O^+ , and LiC^+ fragments which compose LiBOB salt. What we concentrated on was not the salt components but complexes which constitute the passive film related to Al. Thus, we observed the Al_2O^+ fragment as present in Fig. 2a-c. At 3 V, there was an obvious advent of the Al_2O^+ fragment on the scratched new surface (Fig. 2a). This indicated that the scratched new surface readily passivates with oxygen after the polarization in the transient mode at 3 V. For the unscratched part (see inset of Fig. 2a), the same fragment of Al_2O^+ as the scratched part was found. We mentioned that there was no detectable anodic curve to 3 V in Fig. 1a, indicating that no reaction occurred. If the air-formed oxide surface layer of Al was reduced to metal, then the metallic state should be preserved to 3 V, because there was

no observable anodic peak to the potential from 0 V. However, the appearance of the Al_2O^+ fragment strongly supports that the air-formed oxide surface layer of Al was not reduced to Al metal at 0V. From a thermodynamic standpoint, Al metal can be completely oxidized to a trivalent Al-oxide around 1.4 V vs. Li/Li^+ (-1.66 V vs. SHE [14]). For this reason, when the oxide layer was scratched at 3 V, the scratched new surface was immediately passivated by the Al-O passive film, which, in turn, leads to an abrupt decrease in the current (Fig. 1c).

Similarly, the Al_2O^+ fragment was observed at 4 V (Fig. 2b) and became much stronger at 5 V (Fig. 2c), indicating that the newly formed Al metal surface was covered with a passive layer in this potential range. The passive layer was composed of Al and O ingredients. Other evidence of passivation was that the resulting anodic currents were gradually greater, as the potential raised to 5 V from 3 V in Fig. 1. However, the Al_2B^+ fragment was not observed at 3 V and even at 5 V in Fig. 2d and e. Recently, Zhang et al. [10] suggested that a possible passive film of Al polarized in LiBOB electrolyte is aluminum borate, AlBO_3 , by means of an electrochemical quartz crystal microbalance. From our ToF-SIMS results, we found that the passive film of the Al was not composed of the AlBO_3 compound under the LiBOB environment because the chemical bond of Al and B was not detected by the ToF-SIMS (Fig. 2e). On the other hand, that of an

Al-O complex was found in the passivation region, as shown in Fig. 2a-c. The chemical composition of LiBOB is $\text{LiB}(\text{C}_2\text{O}_4)_2$. Although a detailed decomposition process is unknown, several byproducts, such as Li_2O , B_2O_3 , Li_2CO_3 , CO or CO_2 , and O_2 , are likely formed. The clear ToF-SIMS signal of the AlO^+ fragment supports that the generated oxygen would adhere to the surface of the newly formed Al metal such that the surface is oxidized to $\text{Al}^{\text{III}}\text{-O}$ compound, forming a passive film on the most outer surface of the scratched surface, as illustrated in Fig. 3. Therefore, we believe that the $\text{Al}^{\text{III}}\text{-O}$ layer, probably Al_2O_3 , is the most plausible passive layer for the Al metal in the LiBOB-containing alkyl carbonate solution.

Figure 4 shows charge and discharge curves of Li/nano SnO_2 (< 30 nm, Wako Chemicals) cell using Al current collector operated in 0.8M LiBOB in EC-DMC. For the fabrication of the electrode we used poly(acrylic acid) as the binder to avoid fluorine element contained in the PVDF binder. Though we did not present here, PVDF binder containing nano SnO_2 electrode showed alloy process between Li and Al below 0.35 V. However, the Li/nano SnO_2 cell exhibits a typical charge and discharge behavior of SnO_2 in Fig. 3. The delivered capacity is approximately $300 \text{ mAh (g-oxide)}^{-1}$ in the voltage range of 0.25 – 2 V, whose capacity is comparable to that of graphite, and the capacity is maintained during 10 cycles without showing the Li-Al alloy formation.

Conclusion

The electrochemical behavior and passivation process of an Al foil in LiBOB-containing alkyl carbonate solutions were investigated with combination of cyclic and *in situ* scratch polarization tests and ToF-SIMS analysis. The electrochemical behavior of the Al foil varied strikingly depending on the electrolytic salts. Under the LiPF₆ environment, the Al foil experienced the alloy and de-alloy process with Li, Li-Al alloy, around 0 V. However, the alloy formation process did not appear in the presence of LiBOB salt. From the *in situ* scratch polarization in a transient mode and the resulting ToF-SIMS analysis, we found that the newly scratched surface of the Al metal passivated with an oxide layer was primarily the Al^{III}-O compound. Smaller anodic current at 5 V was indicative that the formed passive layer is very protective and is stable in the whole potential window.

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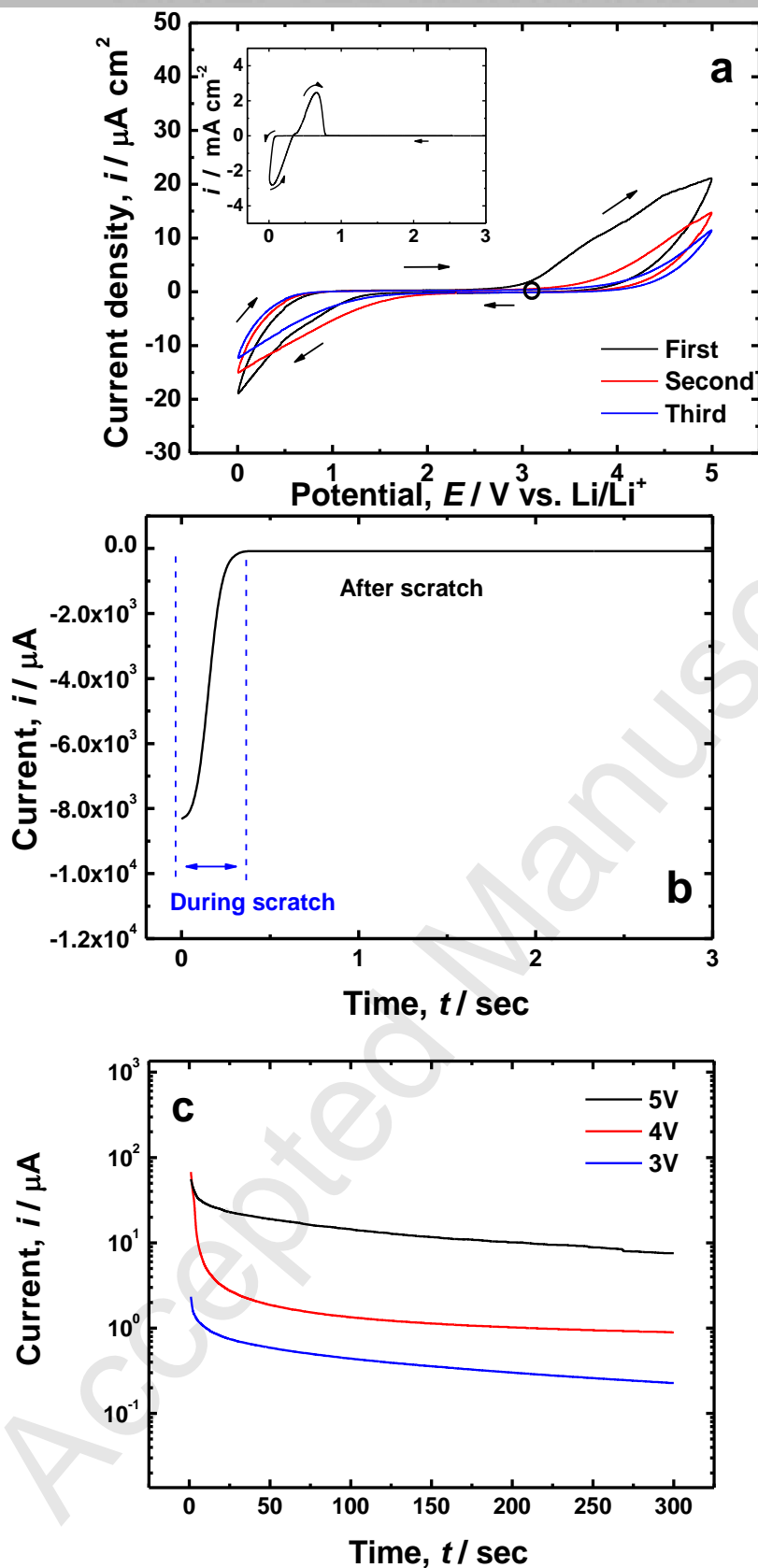


Figure 1. (a) Three consecutive cyclic voltammograms of Al foil polarized in 0.8M LiBOB in EC-DMC (1:1 in volume). Scanning started from OCP in the cathodic direction with a sweeping rate of 10 mV s^{-1} at 40°C . The inset is the first cyclic voltammogram of Al foil polarized in 1M LiPF_6 in EC-DMC (1:1 in volume). Time and current (i - t) curves of the Al foil after the scratching test at (b) 0 V and (c) 3, 4, and 5 V vs. Li/Li^+ polarized in 0.8M LiBOB in EC-DMC (1:1 in volume). Scanning started from OCP in the cathodic direction with a sweeping rate of 10 mV s^{-1} at 40°C .

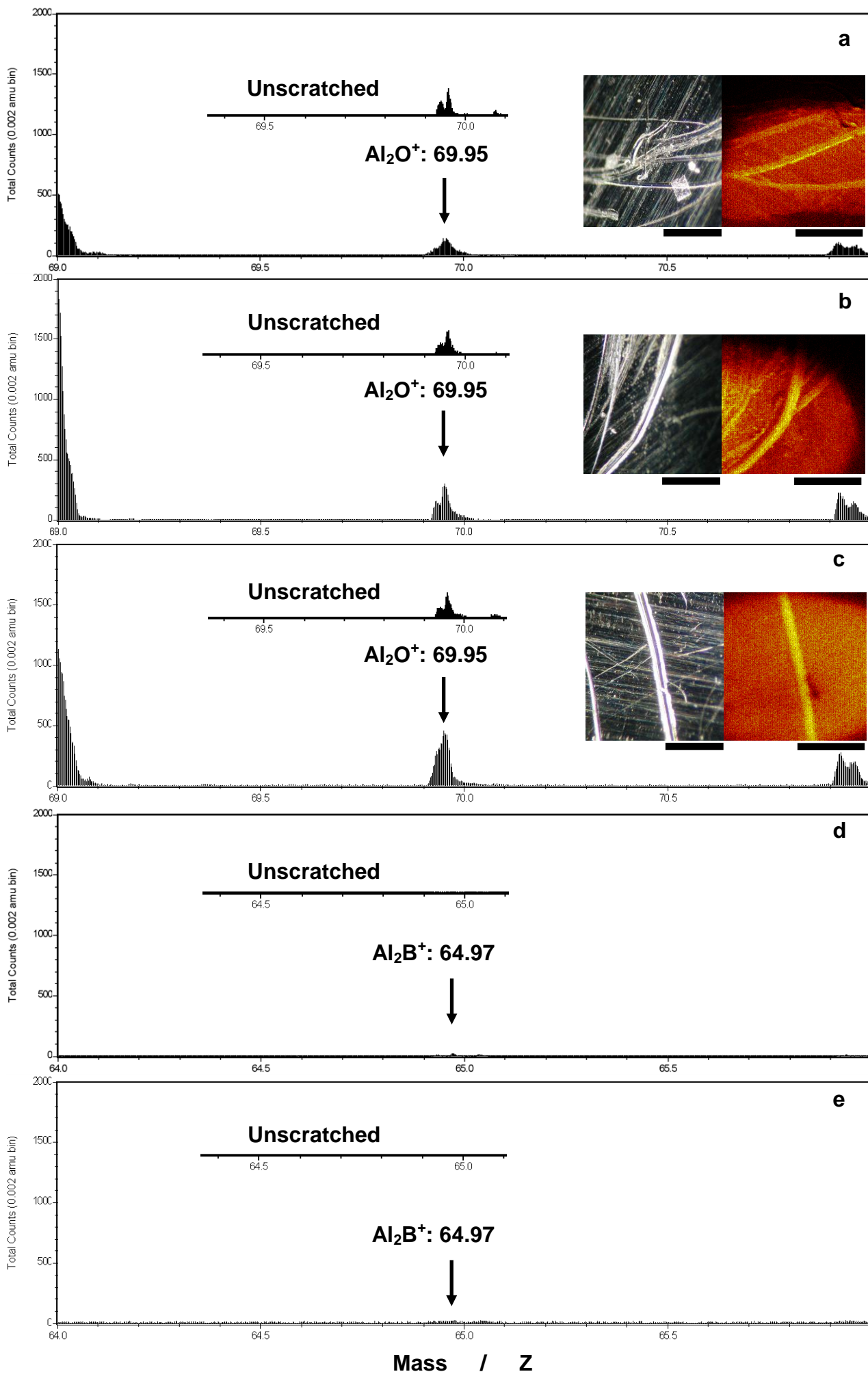


Figure 2. ToF-SIMS fragments of Al_2O^+ after the scratch test at (a) 3 V, (b) 4 V, (c) 5 V vs. Li/Li^+ and Al_2B^+ after the scratch test at (d) 3 V and (e) 5 V vs. Li/Li^+ . Insets in (a) to (c) present optical microscopic images (left) and total secondary-ion mapping images (right). ToF-SIMS spectra shown as insets are for the unscratched parts. The scale bar denotes 100 μm .

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Under LiBOB environment

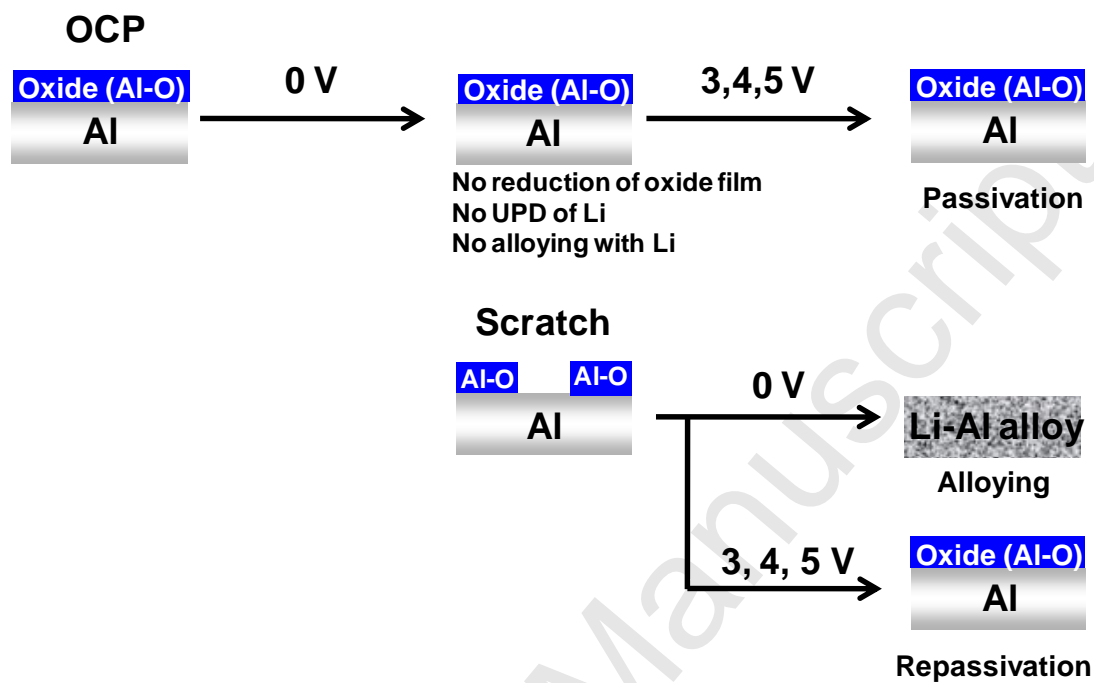


Figure 3. Schematic drawing of the passivation process for Al foil in a non-aqueous alkyl carbonate solution containing LiBOB salt.

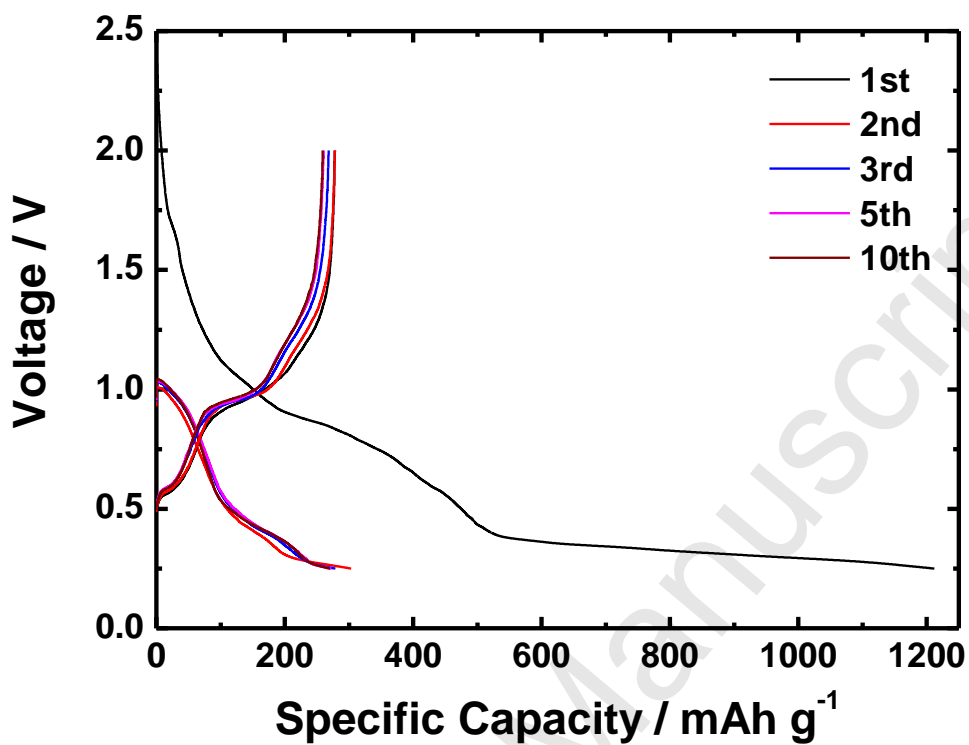


Figure 4. Continuous charge and discharge curves of nano SnO₂ coated on Al foil. The cell was operated in voltage range of 0.25 – 2 V by applying a constant current of 30 mA g⁻¹ at 30 °C.