



Short communication

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 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.

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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 vs. 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 (LiB(C₂O₄)₂) has been introduced as a possible candidate to replace the LiPF₆ 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 1 M LiBOB-containing EC:EMC solution. Zhang and Devine [10] demonstrated

that a passive film formed on the Al in EC:DMC with 1 M LiBOB was protective against corrosion and suggested that the protective film is AlBO₃. Very recently, Markovsky et al. [11] suggested that LiBOB may decompose at anodic potentials, thus forming passive films comprising B₂O₃ 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 0–5 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 0.8 M 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

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electrodes, cathodic polarizations were first applied to 0V 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 1 s 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

Fig. 1a depicts cyclic voltammograms of the Al foil polarized in LiBOB and LiPF_6 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 LiPF_6 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 LiPF_6 salt-containing electrolyte [12,13]. Under potential deposition (UPD) of Li is commonly seen for these metal surfaces in the LiPF_6 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 $20 \mu\text{A cm}^{-2}$. 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.

Fig. 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 formation of Li–Al alloy

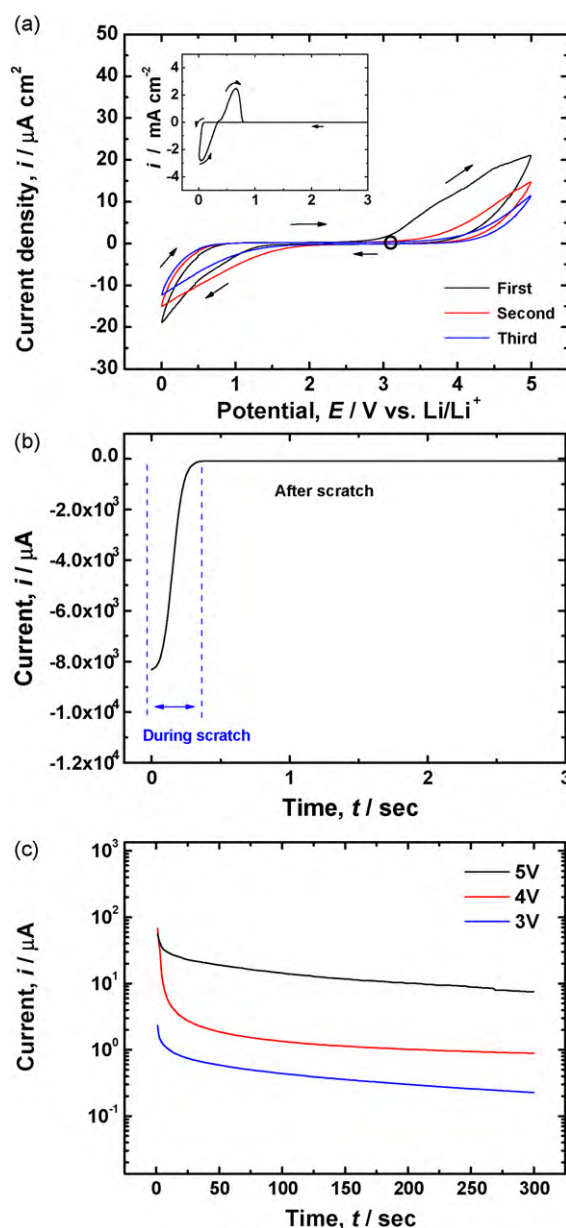


Fig. 1. (a) Three consecutive cyclic voltammograms of Al foil polarized in 0.8 M LiBOB in EC-DMC (1:1 in volume). Scanning started from OCP in the cathodic direction with a sweeping rate of 10 mV s^{-1} at 40°C . The inset is the first cyclic voltammogram of Al foil polarized in 1 M LiPF_6 in EC-DMC (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 0.8 M 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 .

(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 0 V 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 fluctu-

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