



Comparative study on lithium borates as corrosion inhibitors of aluminum current collector in lithium bis(fluorosulfonyl)imide electrolytes



Kisung Park ^a, Sunghun Yu ^b, Chulhaeng Lee ^b, Hochun Lee ^{a,*}

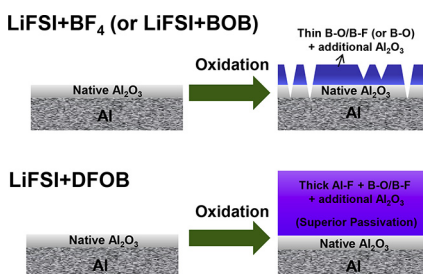
^a Department of Energy Systems Engineering, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu 711–873, South Korea

^b Batteries R&D, LG Chem Ltd., Daejeon 305–380, South Korea

HIGHLIGHTS

- Lithium borates are compared as Al corrosion inhibitors in LiFSI electrolytes.
- LiDFOB as an additive is a superior inhibitor compared to LiBF₄, LiBOB, and LiPF₆.
- 0.8 M LiFSI + 0.2 M LiDFOB shows comparable Al corrosion to 1 M LiPF₆ solution.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium bis(fluorosulfonyl)imide (LiFSI) is a promising salt that can possibly overcome the limitations of lithium hexafluorophosphate (LiPF₆) in current Li-ion batteries (LIBs). Aluminum (Al) corrosion issue, however, is a major bottleneck for the wide use of LiFSI. This study investigates lithium borate salts as Al corrosion inhibitors in LiFSI electrolytes. Through a systematic comparison among lithium tetrafluoroborate (LiBF₄), lithium bis(oxalato)borate (LiBOB), and lithium difluoro(oxalato)borate (LiDFOB), and LiPF₆, the inhibition ability of the additives is revealed to be in the following order: LiDFOB > LiBF₄ ≈ LiPF₆ > LiBOB. In particular, the inhibition effect of LiDFOB is outstanding; the anodic behavior of Al in 0.8 M LiFSI + 0.2 M LiDFOB ethylene carbonate (EC)-based electrolyte is comparable to that of corrosion-free 1 M LiPF₆ solution. The superior inhibition ability of LiDFOB is attributed to the formation of a passive layer composed of Al–F, Al₂O₃, and B–O species, as evidenced by X-ray photoelectron spectroscopy (XPS) measurements. A LiCoO₂/graphite cell with 0.8 M LiFSI + 0.2 M LiDFOB electrolyte exhibits a rate capability comparable to a cell with 1 M LiPF₆ solution, whereas a cell with 0.8 M LiFSI solution without LiDFOB suffers from poor power performance resulting from severe Al corrosion.

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1. Introduction

Nowadays, Li-ion batteries (LIBs) are forced to achieve both higher energy density and extreme long-term stability for the reliable operation of IT devices and electric vehicles [1–4]. Most of the current LIBs are employing lithium hexafluorophosphate

* Corresponding author.

E-mail address: dukelee@dgist.ac.kr (H. Lee).

(LiPF₆)-based electrolytes due to high ionic conductivity, decent safety, and innate immunity to aluminum (Al) current collectors [5]. Nevertheless, LiPF₆ electrolytes are inevitably contaminated by hydrogen fluoride (HF), a byproduct of LiPF₆ hydrolysis, which facilitates metal dissolution from cathode materials [6,7] and exacerbates unwanted side reactions at the anode side [8].

As an alternative candidate to LiPF₆, various Li salts that are inherently free from HF contamination (e.g., lithium bis(oxalato)borate (LiBOB), lithium difluoro(oxalato)borate (LiDFOB), lithium bis(pentafluoroethanesulfonyl)imide (LiBETI), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)) have been extensively investigated [9–16]. None of the Li salts, however, have been successful to replace LiPF₆, mainly due to their low ionic conductivity. Recently, lithium bis(fluorosulfonyl)imide (LiFSI) has been reported to exhibit comparable or higher ionic conductivity to LiPF₆ while maintaining HF-free nature, which suggests that LiFSI can offer both the superior energy density and long-term stability of LIBs [17,18]. LiFSI, however, is subjected to severe corrosion of Al current collector [18,19], a common chronic issue of lithium imide salts [1,20].

So far, a vast amount of effort has been directed toward the prevention of Al corrosion in imide-based electrolytes [20–29]. Some recent studies have tried to inhibit the Al corrosion by employing new types of solvents other than carbonates. It was reported that Al corrosion in LiTFSI solutions is significantly suppressed in solvents, such as adiponitrile, tetrahydrofuran, dimethoxyethane, methyl difluoroacetate, and γ -butyrolactone, compared to conventional ethylene carbonate (EC)-based electrolytes [20–23]. These solvents commonly show low dielectric constants compared to EC, which suggests a possibility that low solubilities of corrosion products (Al(TFSI)_nⁿ⁻³, n = 1–3) are beneficial in Al corrosion suppression [24–26]. It was also claimed that fluorinated solvents such as methyl difluoroacetate, fluoroethylene carbonate (FEC), and fluorodiethyl carbonate (FDEC) exhibit suppressed Al corrosion by forming a protective fluoride surface layer [23,27]. In addition, the concentration of Li salts has been found to have substantial influence on Al corrosion behavior. It was reported that Al corrosion is alleviated in highly concentrated (>1.8 M) LiTFSI solutions [28,29]. Even though these studies are quite informative, altering the solvent nature and salt concentration are bound to affect not only Al corrosion behavior, but also the other physicochemical properties of the electrolyte (e.g., ionic conductivity, wettability, compatibility with active materials), which significantly depreciates their practical potential.

In this regard, employing electrolyte additive is a promising strategy because it hardly affects the bulk properties of original electrolyte systems. In particular, it has widely been known that the addition of LiPF₆ to LiTFSI electrolytes can notably suppress Al corrosion [5]. LiPF₆ was also used as an Al corrosion inhibitor in FSI-based ionic liquids [30]. The presence of LiPF₆, however, even if the amount is limited (ca. 0.1–0.2 M), can cause unwanted HF generation, which again raises all of the drawbacks of LiPF₆-based electrolytes. The addition of Li-borate salts like LiBF₄ and LiBOB were also claimed to mitigate Al corrosion [31–33], but the inhibition abilities of the borates seem to be inferior to that of LiPF₆ additive. Moreover, quantitative comparison among the borate additives has been deterred because prior studies employed different experimental conditions (e.g., solvent composition, additive content, Al pretreatment method, electrochemical measurement conditions). Also, the study on the corrosion inhibition of Al in LiFSI solutions is scarce in contrast to that in LiTFSI ones [30,34].

In this work, we performed a systematic comparison on the inhibition effects of Li-borate (LiBF₄, LiDFOB, and LiBOB) and LiPF₆ additives on Al corrosion in LiFSI EC/DEC (3/7, v/v) solutions. Among the additives, LiDFOB was revealed to be the most efficient

inhibitor of Al corrosion in LiFSI-based electrolytes. The Al corrosion behavior in 0.8 M LiFSI + 0.2 M LiDFOB was determined to be comparable to that of 1 M LiPF₆ solution, an Al corrosion-immune medium. The excellent inhibition ability of LiDFOB additive was further examined using the X-ray photoelectron spectroscopy (XPS) analysis of the Al surface layer and was also confirmed through the rate capability/electrochemical impedance spectroscopy (EIS) measurements of LiCoO₂ cells.

2. Experimental

2.1. Chemicals

Battery grade LiFSI, LiDFOB, LiBOB, EC, dimethyl carbonate (DMC), and diethyl carbonate (DEC) were provided by LG Chem. Reagent grade LiBF₄ and Al rod (99.999%, 3 mm diameter) were purchased from Aldrich. The studied electrolytes are 0.8 M LiFSI (hereafter called LiFSI), 0.8 M LiFSI + 0.2 M LiBF₄ (LiFSI + BF₄), 0.8 M LiFSI + 0.2 M LiBOB (LiFSI + BOB), 0.8 M LiFSI + 0.2 M LiDFOB (LiFSI + DFOB), 0.8 M LiFSI + 0.2 M LiPF₆ (LiFSI + PF₆), and 1 M LiPF₆ (LiPF₆) in EC/DEC (3/7, v/v). All the electrolytes were prepared in an Ar-filled glove box (H₂O and O₂ levels < 5 ppm and 25 ± 1 °C). The water content of the electrolytes was in the range of 18–45 ppm.

2.2. Electrochemical experiments

All the electrochemical experiments were carried out using a three-electrode system with a flooded cell (polyethylene round bottle) with 2.5 ± 0.1 ml of electrolyte in an Ar-filled glove box. An Al rod (0.07 cm²) was used as a working electrode. Li foil and Pt wire were used as a reference electrode and counter electrode, respectively. It was found that Al corrosion becomes severer with increasing surface roughness of the Al electrode (see [appendix A](#) and [Fig. S1](#) for details). In this study, the Al working electrode was polished on emery paper (#1200, 15 μm grit size) to examine the Al corrosion/inhibition behaviors under relatively harsh conditions. After polishing, the Al electrode was sonicated in double-distilled water for 5 min to remove any residuals. Finally, Al electrode was dried using dry nitrogen flow at room temperature. Cyclic voltammetry (CV) was performed over 3–6 V (vs. Li/Li⁺) with a scan rate of 10 mV s⁻¹. Chronoamperometry (CA) was carried out by applying a potential step from the open circuit voltage to 4.8 V (vs. Li/Li⁺) for 2 h at 45 °C. The ionic conductivities of electrolytes were measured over 10–60 °C with an ionic conductometer (Thermo Scientific). The deviations in the temperature and the ionic conductivity were ±0.2 °C and ±0.04 mS cm⁻¹, respectively. Before each measurement, the electrolyte sample was kept for 30 min at a given temperature. Although molality (mol kg⁻¹) is the more appropriate unit than molarity (mol L⁻¹) in determining the ionic conductivity over the temperature range, this study adopted molarity because it is more popular in the LIB society. In addition, the difference between molarity and molality was not significant (less than 5% over 10–60 °C).

2.3. X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed to examine the composition of the Al surface layer using ESCALAB 250Xi (Thermo Scientific). For the preparation of samples, Al foils (battery grade, 45 μm thickness) were subjected to two cycles over 3–6 V (vs. Li/Li⁺) in four different electrolytes: LiFSI, LiFSI + BF₄, LiFSI + BOB, and LiFSI + DFOB. After the cycling, the Al foils were rinsed in DMC to eliminate residual electrolyte and then dried for 24 h inside a glove box. For depth profiles measurements, the Al foils were sputtered for 100 s with an etching rate of 7 nm min⁻¹ calibrated for SiO₂. In

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