Corrosion inhibition of aluminum in lithium imide electrolyte by lithium borate addition

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DGIST

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A thesis submitted to the faculty of DGIST in partial fulfillment of the requirements for the degree of Master of Science in the Department of Energy System Engineering. The study was conducted in accordance with Code of Research Ethics¹

11. 15. 2013

Approved by

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¹ Declaration of Ethical Conduct in Research: I, as a graduate student of DGIST, hereby declare that I have not committed any acts that may damage the credibility of my research. These include, but are not limited to: falsification, thesis written by someone else, distortion of research findings or plagiarism. I affirm that my thesis contains honest conclusions based on my own careful research under the guidance of my thesis advisor.
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Accepted in partial fulfillment of the requirements for the degree of Master of Science.

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ABSTRACT

Lithium bis(fluorosulfonyl)imide (LiFSI) is a promising imide group salt due to its comparable ionic conductivity and superior thermal stability to common Lithium hexafluorophosphate (LiPF₆), but aluminum (Al) corrosion issue is a bottleneck for its wide use. The Al corrosion becomes much severe in higher ionic conductive imide-based electrolytes while no trends are observed in non-corrosive electrolytes. This study demonstrates that Al corrosion in LiFSI electrolyte is clearly suppressed by the addition of Li borates salts. For anodic corrosion of Al in LiFSI ethylene carbonate (EC)/diethyl carbonate (DEC), inhibition ability of borate additives is remarkable while fluoride and phosphate additives do not help inhibit the corrosion. The corrosion resistance of Al in 0.8 M LiFSI + 0.2 M lithium difluoro(oxalato)borate (LiDFOB) is comparable to that in 1 M LiPF₆. Moreover, borates also suppress the corrosion of Al in LiTFSI solutions. Suppression of corrosion by borates is ascribed to the passive organic layer. Unfortunately, LiDFOB-added electrolytes suffer from severe Mn dissolution.

This study provides a way to improve energy density of LIBs without compromising reliability. The discovery of this study enables the use of LiFSI electrolyte for various cathode materials in addition to LiFePO₄, and provides huge implication in developing highly reliable LIBs without compromising energy and power densities.

Keywords: Al corrosion, Li-imide salts, LiFSI, Li-borate salts, LiDFOB
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I. Introduction

Nowadays, Li ion batteries are forced to achieve larger capacity and higher operating potential for the smooth operation of devices. Most Li ion batteries on these days contain LiPF$_6$ salts since LiPF$_6$ has high ionic conductivity which contributes to get larger capacity. Moreover, LiPF$_6$ prevents the corrosion of aluminum current collectors by forming stable aluminum fluoride (AlF$_3$) layer on the surface of Al [1]. Thus, it has been beneficial to make full use of LiPF$_6$ salts judging by its high ionic conductivity as well as non-corrosive behaviors.

Nevertheless, LiPF$_6$ cannot satisfying our demands on Li battery market due to its poor thermal stability [2]. It may result in the formation of hydrogen fluoride (HF) from PF$_6$ anion in LiPF$_6$, and it also can be a flash point of metal dissolution from cathode materials [3].

Many other Li salts such as LiBF$_4$, LiBOB, LiClO$_4$, LiBETI, LiNFSI and LiTFSI are found to be much resistive to thermal decomposition[4, 5, 6], but all of them are found to have relatively poor ionic conductivities only except for LiFSI [7]. LiFSI which is the one of imide group salts can be a good candidate for them due to its higher ionic conductivity and better thermal stability which may contribute to achieving larger
capacity and better stability for commercial batteries [7, 8]. However, the electrolytes containing LiFSI salts suffer from severe corrosion of Al current collectors [9].

With respect to Al corrosion inhibition, there have been lots of studies with an attempt to fully utilize imide group salts. Solvents are the one of possible affecting factors. M. Morita et al. [10] have reported that 1 M LiTFSI in EC/DEC (1/1, v/v) has less corrosion of Al wire while the Al corrosion is much severe in 1 M LiTFSI EC/dimethyl carbonate (DMC) (1/1, v/v) solutions. After the potential cycling tests, the surface analysis by scanning electron microscope (SEM) revealed that the Al surface in 1 M LiTFSI EC/DEC solutions is less rough as compared with EC/DMC electrolytes, which is in good agreement with repect to the results that the extent of Al corrosion in EC/DEC is not as large as that in EC/DMC. E. Kramer et al. [11] also have reported that Adiponitrile (ADN) as solvents does not cause the corrosion of Al with lithium bis(trifluoromethan- sulfonyl)imide (LiTFSI) salts.

The concentration of Li salts also has an effect on the Al corrosion in imide-based solutions. K. Matsumoto et al. [12] have reported that 1.8 M LiTFSI in EC/DEC (3/7, v/v) solvents shows much less current density even after 4.5 V while 1.0 M LiTFSI EC/DEC (3/7, v/v) solutions begin to be corroded rapidly at around 4.0 V.

In fact, those two affecting factors cannot be the decisive solutions for the corrosion
inhibition. Solvents for commercial batteries are usually limited to very few kinds, especially organic carbonate group solvents such as EC, DEC, DMC and EMC. Thus, many solvents which are less conductive than carbonate solvents are abandoned even if they do not cause Al corrosion.

Adding much amount of Li salts also results in high viscosity of electrolytes which can degrade the performance of Li ion batteries although the high concentration of imide salts can suppress the Al corrosion.

Addition of additives is plausible for inhibition of corrosion rather than others above. Indeed, many additives have been examined to suppress the Al corrosion in imide-based electrolytes. S.-W. Song et al. [13] have reported that Al corrosion has clearly been suppressed by adding more than 20% of lithium tetrafluoroborate (LiBF₄) in 1 M mixture of LiTFSI and LiBF₄ EC/DMC (1/1, v/v) solutions.

The addition of lithium bis(oxalate)borate (LiBOB) and LiPF₆ in imide-based electrolytes also have been discussed. X. Zhang et al. [14] have studied the effects of LiBOB additives. LiTFSI/LiBOB (9/1, mol/mol) in EC/DMC (1/1, v/v) shows less corrosive behaviors, and SEM images of Al surface after cyclic voltammetry (CV) tests also show that the number of corrosion pits clearly decreases after LiBOB is added.

Results presented by M. Morita et al. [1] revealed that the addition of LiPF₆ in
LiTFSI EC/DMC (1/1, v/v) solutions distinctly curbs the Al corrosion. Utilizing LiPF$_6$ as additives is not confined to organic solvents. E. Cho et al. [15] used LiPF$_6$ in FSI imide-based ionic liquid (N-methyl-N-propyl-pyrrolidinium bis(fluorosulfonfyl)imide) solvent to suppress the Al corrosion problem. Without additives, the Al begins to be corroded at around 4 V, but the corrosion greatly reduces by adding 0.1 M of LiPF$_6$ since HF from the decomposition of LiPF$_6$ attacks the Al to produce a strong passivation film containing AlF$_3$. However, adding LiPF$_6$ seems to be unpromising due to HF formation which may cause the metal dissolution problems just as pure LiPF$_6$ containing electrolytes case.

Unfortunately, none of those studies has accomplished to make non-corrosive imide-based electrolytes, but only has achieved less corrosive behaviors even though hundreds of researches on Al corrosion inhibition have been conducted. In this work, we investigated the suppressed Al corrosion in LiFSI-based electrolytes, which can provide the foundation on further researches about imide group salts.
II. Experimental

2.1 Chemicals

Lithium salts and additives - LiFSI and LiDFOB were prepared from LG Chem, and LiPF₆ was prepared from FOOSUNG. LiTFSI, lithium perchlorate (LiClO₄) and LiBF₄ were purchased from Sigma-Aldrich. LiBOB and LiDFPB were made in POSCO ESM and Kumoh Institute of Technology, respectively. Sodium phosphate dibasic (Na₂HPO₄), Tris(trimethylsilyl) borate (TMSB), Tris(trimethylsilyl) phosphate (TMSPa), Tris(trimethylsilyl) phosphite (TMSPi) and lithium fluoride (LiF) from Sigma-Aldrich were used, and lithium tungstate (Li₂WO₄) and lithium molybdate (Li₂MoO₄) are purchased from Alfa-Aesar.

Solvents - We use EC, DEC and DMC from LG Chem, and fluoroethylene carbonate (FEC) from FOOSUNG.

All chemicals were stored, and all electrolytes were made in an Argon-filled glove box with a moisture level below 10 ppm.
2.2 Methodologies

CV experiment - Three-electrode system was employed in the Ar-filled globe box, and the corrosion behaviors were studied by CV using potentiostat. The potential for CV tests ranged from 3 to 6 V, and their scan rate was 10 mVs\(^{-1}\). Temperature in the globe box was kept at 27±3 °C.

In case of TMSB, TMSPa and TMSPi additives, the composition of solution is 1 M LiFSI + 2 wt% of these additives in EC/DEC or EC/DMC (3/7, v/v). For studying the effects of borates additives, the solutions were 0.8 M LiFSI in EC/DEC (3/7, v/v) and EC/DMC (3/7, v/v), and various kinds of additives were added by the concentration of 0.2 M. Comparing the behaviors of LiFSI-based electrolytes, CVs using 1 M LiPF\(_6\) in EC/DEC (3/7, v/v) and EC/DMC (3/7, v/v) were also examined.

We used an Al working electrode which has a diameter of 3mm, and was insulated by epoxy bond to restrict the surface area rigorously. Li foil and Pt wire were used as a reference electrode and counter electrode, respectively.

After the CV experiments, all electrodes and vials were removed from globe box and washed by ethanol and pure H\(_2\)O. They were then dried in oven at 60 °C for about 5 minutes except the aluminum working electrode.
Al rod was polished by emery paper of #1200 (15 μm), #3000 (7 μm) and alumina (0.3 μm) for about 5 minutes, treated by sonicator, and then washed by pure H₂O. Note that #1200 was used for Al surface treatment if there is no elucidation. Al rod has not been dried at elevated temperature since we regarded that the extent of formation of aluminum oxide (Al₂O₃) layer on the surface of Al might be affected by the temperature conditions. Thus, it was dried enough using nitrogen spray gun at room temperature.

CV conditions only for borates additives are summarized by table 2.1.

<table>
<thead>
<tr>
<th>Wk</th>
<th>Ref</th>
<th>Ctr</th>
<th>E range</th>
<th>Salt</th>
<th>Electrolyte</th>
<th>Additives</th>
<th>Comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al rod   (d=3.0mm)</td>
<td>Li metal</td>
<td>Pt  wire</td>
<td>3 – 6 V</td>
<td>10 mVs⁻¹</td>
<td>0.8 M LiFSI</td>
<td>0.2 M LiBF₄, LiBOB, LiDFOB, LiDFPB, LiPF₆</td>
<td>1 M LiPF₆</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>EC/DEC EC/DME (3:7 v%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1

Chronoamperometry (CA) experiment – The effects of additives on corrosion inhibition were also examined by CA experiments. Three-electrode system was employed, and its configuration was same as CV experiment. All other conditions were exactly equal to those for CV tests only except for potential applied. The
potentials for each CA experiment were different, they vary from 4.5 V to 4.8 V, and those potentials held for 10 minutes.

The electrolytes used to examine the corrosion behaviors of Al were 1.0 M LiFSI and LiTFSI salts in EC/DEC (3/7, v/v). 1 wt% of Na₂HPO₄, LiF, Li₂WO₄ and Li₂MoO₄ were utilized as additives in 1 M LiFSI and LiTFSI solutions. The CA conditions for the solutions containing Li borates additives except for LiDFPB are especially shown in table 2.2.

<table>
<thead>
<tr>
<th>Wk</th>
<th>Ref</th>
<th>Ctr</th>
<th>Potential</th>
<th>Salt</th>
<th>Electrolyte</th>
<th>Additives</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al rod</td>
<td>Li metal</td>
<td>Pt wire</td>
<td>4.5 V</td>
<td>4.8 V</td>
<td>LiFSI</td>
<td>0.2 M LiBF₄, LiBOB, LiDFOB, LiPF₆</td>
<td>10 minutes</td>
</tr>
</tbody>
</table>

Table 2.2

Ionic conductivity measurement - Ionic conductivity was measured for various temperature between -10 and 60 °C with ionic conductivity meter (THERMO SCIENTIFIC). The electrolytes were prepared in Ar-filled globe box. After the solutions were taken away from the globe box, they were sealed with Teflon tape in order to fix the position of conductivity meter and sample since the ionic conductivity
measurement might be affected by a stir or a shake of electrolytes. The sealed conductivity meter and sample were then inserted into the chamber which can control and maintain the temperature. Temperature of electrolytes was kept for 30 minutes in the temperature-maintained chamber, and at last ionic conductivity was measured.

Manganese (Mn) dissolution measurement – the amount of dissolved Mn$^{2+}$ is measured by atomic absorption spectrophotometer (AA-7000 from SHIMADZU). Lithium manganese oxide (LMO) and lithium nickel manganese oxide (LNMO) are dried for one day, and they are immersed in 1 mL of electrolytes at 60 °C for three days and nine days, respectively. The electrolytes for Mn dissolution experiments are shown in table 2.3.

<table>
<thead>
<tr>
<th>No.</th>
<th>Electrolytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 M LiPF$_6$ EC/DEC (3/7, v/v)</td>
</tr>
<tr>
<td>2</td>
<td>1 M LiPF$_6$ EC/DMC (3/7, v/v)</td>
</tr>
<tr>
<td>3</td>
<td>1 M LiFSI EC/DEC (3/7, v/v)</td>
</tr>
<tr>
<td>4</td>
<td>1 M LiFSI EC/DMC (3/7, v/v)</td>
</tr>
<tr>
<td>5</td>
<td>0.8 M LiFSI + 0.2 M LiDFOB EC/DEC (3/7, v/v)</td>
</tr>
<tr>
<td>6</td>
<td>0.8 M LiFSI + 0.2 M LiDFOB EC/DMC (3/7, v/v)</td>
</tr>
</tbody>
</table>

Table 2.3
III. Results and Discussion

3.1. Corrosion Behaviors in LiFSI-based electrolytes

3.1.1. Polishing effects

Surface treatment of electrode is one of affecting factors for the Al corrosion behaviors. M. Morita et al. [10] has reported that the corrosion peak current for electro-polished Al wire is much lower than that for mechanical polished Al wire.

Thus, before finding other affecting factors, the corrosion behaviors are examined with regard to polishing methods. Emery paper #1200, #3000 and alumina A were used for mechanical treatment of Al surface, and the CV results are shown in figure 3.1.

The corrosion behaviors for all treatments are same, but the extent of corrosion is different. For the 1 M LiFSI EC/DMC (3/7, v/v) electrolytes with the mechanical treatment using emery paper #1200, Al begins to be corroded at 4.8 V, and the current becomes pretty much large during the forward scan up to 6 V. During the reverse scan from 6 V, the corrosion proceeds until the potential reaches at 3.5 V where the maximum current value is observed, and the current then goes to zero rapidly. The current becomes almost zero at 3.4 V where the re-passivation occurs. The onset of Al
corrosion is a little delayed for emery paper #3000 treatment, and the re-passivation point is almost equal to that for #1200. Also, much delayed onset point of Al corrosion is observed for the treatment by alumina A.

The extent of Al corrosion is by following order: #1200 > #3000 > Alumina A, which reveals that the Al corrosion becomes severe as the surface of Al gets rough.

![Figure 3.1](image-url)
3.1.2. Corrosion behaviors without additives

Figure 3.2 shows that the severe Al corrosion occurred at 1 M LiFSI and LiTFSI salts in EC/DEC and EC/DMC (3/7, v/v). For LiFSI salts, the onset of corrosion is at around 4.9 V for EC/DEC and 4.8 V for EC/DMC. The current gets larger until the potential is scanned forward from near 5 V to 6 V and back from 6 to 4.5 V approximately. After the largest peak is observed at around 4.5 V, the current goes down, and becomes almost zero at 3.5 V for EC/DEC and 3.4 V for EC/DMC. The peak current value of 1 M LiFSI in EC/DEC is larger than 1.5 mA, and that of 1 M LiFSI in EC/DMC is approximately equal to 4.5 mA.

For LiTFSI salts, the maximum current peak for EC/DEC is larger than 1.5 mA, and that for EC/DMC is less than 4.5 mA. From the results of current peaks, Al corrosion behaviors of LiTFSI-based solutions appear to be same as that of LiFSI-based electrolytes. However, the current rapidly increases at 5.4 V, and the repassivation occurs at around 3.7 V, which indicates that the corrosion resistance of LiTFSI-based solutions is higher than that of LiFSI-based one. Namely, the extent of Al corrosion of LiTFSI-based electrolytes is still severe, but a little less than that of LiFSI-based solutions.
The trends of nearly non-corrosive LiClO$_4$ salts in organic solvents are shown in figure 3.3. Unlike other imide group salts, the current of LiClO$_4$-based solutions increases by degrees at the beginning and falls down rapidly to zero during reverse scan. Note that the scale of current value is much smaller than that of imide group salts.
Figure 3.3
3.1.3. Composition ratio effects

We tried to characterize the Al corrosion by specific factors. During the research, we found the specific corrosion behaviors by changing the composition ratio of solvents in Li imide salts.

Figure 3.4 shows the relation between the extent of Al corrosion and the composition ratio of solvents. For Li imide salts, the corrosion becomes less severe in EC/DEC or EC/DMC (1/9, v/v) solutions whose ionic conductivities are relatively low. In case of DMC-based solutions, EC/DMC whose volume ratio is 3/7 shows the highest ionic conductivity and the most severe corrosion. Likewise, EC/DEC (5/5, v/v) which is found to be highly ionic conductive solution has severe corrosion behavior.
Meanwhile, we tried to utilize FEC as solvents in LiFSI salts instead of EC. We presume that F elements from FEC may form AlF$_3$ passivation layer, so the Al corrosion might be suppressed.

The CVs for FEC-based solutions are shown in figure 3.5. Note that the current scale of 1 M LiFSI in FEC/DEC is lower as compared with other CVs. Unlike our presumption, the Al corrosion is not thoroughly suppressed just as LiPF$_6$ case. The Al corrosion is much less, and the relation for imide salts based solutions is still valid.
even in FEC/DEC solvents. Interestingly, the trends for FEC/DMC solutions are clearly different from other imide salts based electrolytes. In case of FEC/DMC solvents, the extent of Al corrosion is by the following order: 5:5 < 3:7 < 1:9, which seems to be irrelevant to ionic conductivity of solutions. Thus, we assume that these results come from the competition between suppressive FEC effects and ionic conductivities.

Next, the solutions including non-corrosive salts were also investigated by CV method. Figure 3.6 is the CV results of those solutions. Unlike Li imide salts, the relation between the corrosion behaviors and the composition ratio of solutions is not valid for LiClO₄-based electrolytes, and they do not show any further relation.
Figure 3.6

1 M LiClO₄ EC/DEC

5:5 v%, 6.7 mS/cm
3:7 v%, 4.8 mS/cm
1:9 v%, 2.1 mS/cm

1 M LiClO₄ EC/DMC

5:5 v%, 9.4 mS/cm
3:7 v%, 8.2 mS/cm
1:9 v%, 4.4 mS/cm

Current / mA

Potential / V (vs. Li/Li⁺)
3.1.4. Additives effects

Since PF₆ anions from LiPF₆ salts are known to have the Al corrosion inhibiting ability by forming stable layer on the surface of Al, phosphate (Na₂HPO₄) and lithium fluoride which have P and F elements respectively were introduced in Li imide-based electrolytes. With phosphate and fluoride group additives, Li₂WO₄ and Li₂MoO₄ were also used as additives. They have been reported as the Al corrosion inhibitors in acid solutions [16].

Figure 3.7 shows the effects of Na₂HPO₄, LiF, Li₂WO₄, Li₂MoO₄ additives in Li imide salts-based solutions. The potential for CA experiment was held at 4.6 V for 10 minutes. Unfortunately, none of those additives suppresses the corrosion of Al. Thus, it is found that the passivation of Al does not occur by the only addition of P or F, which indicates different types of reactions may exist in case of PF₆ anions.
Further studies focusing on the corrosion inhibiting effects of fluoride and phosphate were also conducted. Figure 3.8 shows CV results of 2 wt% TMSB, TMSPa and TMSPi additives in 1 M LiFSI EC/DEC (3/7, v/v) and EC/DMC (3/7, v/v). Since we wanted to know the effects of phosphite on the Al corrosion, TMSPi was also introduced.

Unfortunately, none of those additives suppress Al corrosion, and TMSB even causes worse Al corrosion problem.

![Figure 3.8](image)

The corrosion behaviors for 0.8 M LiFSI EC/DEC (3/7, v/v) and EC/DMC (3/7, v/v) solutions with the addition of 0.2 M of Li borates additives (LiBF₄, LiBOB,
LiDFOB, LiDFPB) are shown in figure 3.9, and figure 3.10 shows their expanded views. For most borates salts added electrolytes, the onset point of Al corrosion is a little delayed and the re-passivation is earlier than the pristine one. It is obvious that the peak current is much reduced, which is the evidence of suppressed corrosion of Al. Among the borates additives, LiDFPB discriminatively has a negative effect on Al corrosion even if the current values are relatively low as compared with pure 1 M LiFSI salts containing electrolytes. Especially, the onset of Al corrosion is even much earlier than that of pure 1 M LiFSI salts-added solutions. (4.1 V and 4.3 V, respectively.)

![Graph showing corrosion behaviors](image)

**Figure 3.9**

In case of 0.2 M LiBF₄, LiBOB, and LiPF₆ additives, the corrosion behaviors are
similar, but the extent of corrosion is pretty much less than the pristine case (1 M LiFSI) without reference to kinds of linear carbonates.

Moreover, adding 0.2 M of LiDFOB perfectly prevents the Al corrosion problem in 0.8 M LiFSI EC/DEC electrolyte system. The CV result of LiDFOB additives in EC/DEC is pretty similar to that of 1 M LiPF$_6$ case which is known to non-corrosive salts. The current for LiDFOB-added and pure LiPF$_6$-based electrolytes gradually increases during forward scan up to 6 V, and then rapidly decrease to zero value.

LiDFOB has a powerful effect on the corrosion inhibition of Al even in EC/DMC electrolyte system. Although it is not as good as pure LiPF$_6$-based electrolyte, the huge amount of current is reduced as compared with pristine (1 M LiFSI, EC/DMC) case. During the forward scan, the current behavior for LiDFOB-added electrolyte is similar to that for pure LiPF$_6$ solution, but the current suddenly increases at around 5.6 V.
Figure 3.11 convinces the effects of LiDFOB additives on corrosion inhibition of Al. The electrolyte which consists of 0.8 M LiFSI + 0.2 M LiDFOB in EC/DEC shows the current behaviors just as the non-corrosive electrolyte (1 M LiPF₆ in EC/DEC and EC/DMC) case. At first cycle, a little amount of current is observed, but the current becomes much reduced at the second cycle. This indicates the surface of Al is well protected. The Al corrosion becomes much milder in 0.8 M LiFSI + 0.2 M LiDFOB EC/DMC though it does not show exactly non-corrosive behaviors.
We also examined the corrosion behaviors of imides-based solutions with the addition of Li borates except for LiDFPB at a certain potential. The applied potential values of the following CA results which are shown in figure 3.12 were 4.5 and 4.8 V. Note that each graph has different scale in y axis (current value). For 4.5 V-class CA results, EC/DEC (3/7, v/v) solutions with Li borates do not suffer from the Al corrosion. LiBF₄-added EC/DEC experiences corrosion problem, yet the corrosion is weak. Al in EC/DMC electrolytes suffers from the corrosion much more than EC/DEC case. All Li borates prevent Al from being corroded well rather than 0.2 M
LiPF$_6$. It is clearly observed that the addition of LiDFOB into both 0.8 M LiFSI EC/DEC and 0.8 M LiFSI EC/DMC solutions remarkably inhibits the Al corrosion, which is already confirmed from CV results.

Considering 4.8 V-class CA results, the extent of corrosion gets severe for all additives except for LiDFOB as compared with the results at 4.5 V. Again, LiDFOB exhibits extraordinary corrosion inhibiting ability which is analogous to that of pure LiPF$_6$ even in much severe condition (4.8 V). Although the other borates cannot inhibit the Al corrosion perfectly, they contribute to much reduced Al corrosion behaviors.
3.2. Ionic conductivity measurement

Figure 3.13 shows the ionic conductivities of 1 M LiPF$_6$, 1 M LiFSI and 0.8 M LiFSI + 0.2 M LiDFOB solutions. It is found that 1 M LiFSI solutions have the highest ionic conductivities over all temperature. For 0.8 M LiFSI + 0.2 M LiDFOB electrolytes, EC/DMC shows slightly lower ionic conductivities at elevated temperature as compared with 1 M LiPF$_6$ EC/DEC electrolyte. However, the ionic conductivities of 0.8 M LiFSI + 0.2 M LiDFOB in EC/DEC solvents are better than those of 1 M LiPF$_6$ in EC/DEC solvents, which are promising results for higher capacitive batteries.

![Figure 3.13](image-url)
3.3. Mn dissolution measurement

Figure 3.14 and table 3.1 show Mn dissolution results for LMO and LNMO electrodes in various electrolytes. Note that those electrodes are immersed for three days. Unfortunately, 0.8 M LiFSI + 0.2 M LiDFOB EC/DEC (3/7, v/v) which shows outstanding inhibiting ability of Al corrosion is found to have serious Mn dissolution problems. In particular, Mn$^{2+}$ ions are severely dissolved in LMO electrode. However, Mn is almost not dissolved in 0.8 M LiFSI + 0.2 M LiDFOB EC/DMC (3/7, v/v) which also shows great suppression of Al corrosion. 1 M LiFSI salts-based electrolytes do not suffer from Mn dissolution problems at all. Meanwhile, 1 M LiPF$_6$-based solutions are not resistive to Mn dissolution.

![Figure 3.14](image_url)
However, 0.8 M LiFSI + 0.2 M LiDFOB EC/DMC (3/7, v/v) also suffers from severe Mn dissolution problems when it is stored in high temperature condition for a long time. Figure 3.15 and table 3.2 show Mn dissolution results on the 9th days of high temperature storage for LMO and LNMO electrodes. Unlike figure 3.14, 0.8 M LiFSI + 0.2 M LiDFOB EC/DMC (3/7, v/v) dissolve the huge amount of Mn$^{2+}$ ions.

Therefore, we conclude that LiDFOB addives are not suitable for high temperature conditions even though LiDFOB suppresses the Al corrosion very effectively.
Figure 3.15

Table 3.2

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Mn$^{2+}$ conc. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M LiPF$_6$ EC/DEC (3/7 v%)</td>
<td>16.19</td>
</tr>
<tr>
<td>0.8 M LiFSI + 0.2 M LiDFOB EC/DEC (3/7 v%)</td>
<td>941.79</td>
</tr>
<tr>
<td>0.8 M LiFSI + 0.2 M LiDFOB EC/DMC (3/7 v%)</td>
<td>906.65</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Mn$^{2+}$ conc. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M LiPF$_6$ EC/DEC (3/7 v%)</td>
<td>15.08</td>
</tr>
<tr>
<td>0.8 M LiFSI + 0.2 M LiDFOB EC/DEC (3/7 v%)</td>
<td>235.51</td>
</tr>
<tr>
<td>0.8 M LiFSI + 0.2 M LiDFOB EC/DMC (3/7 v%)</td>
<td>152.07</td>
</tr>
</tbody>
</table>
IV. Conclusions

We investigated the corrosion behaviors of Al in imide-based electrolytes. Without additives, LiFSI-based electrolytes have the most severe Al corrosion out of LiTFSI, LiFSI, and LiClO$_4$-based solutions. LiTFSI solutions also suffer from corrosion problems, but the extent of corrosion is less severe than LiFSI solutions. LiClO$_4$-based electrolytes show nearly non-corrosive behaviors. Imide salts containing solutions have the specific characteristics which can be explained by the relation between the extent of Al corrosion and the composition ratio of solvents: The higher ionic conductivity solution has, the severer Al corrosion occurs.

By changing cyclic carbonates of solvents from EC to FEC, FEC/DEC shows reduced Al corrosion. FEC/DMC, however, shows the most severe Al corrosion in the solutions with 1/9 volume ratio whose ionic conductivity is lowest among three volume ratios (5/5, 3/7, 1/9). We assume that these results come from the competition between suppressive FEC effects and ionic conductivities. This relation does not work for the electrolytes including non-corrosive salts.

Electrochemical analysis for electrolytes with all additives shows various characteristics. When Na$_2$HPO$_4$, LiF, Li$_2$WO$_4$, Li$_2$MoO$_4$, TMSB, TMSPa, and TMSPi
are added into imide salts based electrolytes, they are not effective at all for preventing corrosion problems. However, Li borates additives in Li imides salts containing solutions show remarkable corrosion inhibition abilities only except for LiDFPB. LiDFPB is found to accelerate the corrosion behaviors, especially the onset of corrosion. Among the other borates, LiDFOB shows exceptionally suppressed corrosion behaviors of Al. Moreover, the corrosion behavior of 0.8 M LiFSI + 0.2 M LiDFOB EC/DEC (3/7, v/v) is comparable to that of the LiPF$_6$-based electrolytes which is known as non-corrosive salts by forming passive layer on Al current collectors.

Ionic conductivity of LiDFOB-added solutions is comparable to that of LiPF$_6$-based electrolytes for EC/DMC (3/7, v/v) solvents, and that of LiDFOB containing electrolytes is even higher than that of LiPF$_6$ containing electrolytes in EC/DEC (3/7, v/v) solvents.

The problem is that LiDFOB-added electrolytes suffer from Mn dissolution. Mn$^{2+}$ ions are seriously dissolved in 0.8 M LiFSI + 0.2 M LiDFOB EC/DEC (3/7, v/v) regardless of high temperature storage period. Even though 0.8 M LiFSI + 0.2 M LiDFOB EC/DMC (3/7, v/v) shows almost no Mn dissolution in case of high temperature storage only for three days, it eventually dissolves Mn$^{2+}$ ions seriously as the high temperature storage period gets longer.
We conclude that LiDFOB additives are not suitable for high temperature conditions even though LiDFOB suppresses the Al corrosion very effectively.
References


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요 약 문

Li borate 첨가를 통한 Li imide염 전해액에서의 알루미늄 부식 억제

본 논문은 imide염 중 하나인 LiFSI를 알루미늄 부식 없이 활용할 수 있는 방안에 대해 다룬다. LiFSI는 가장 많이 쓰이는 염인 LiPF6에 비해 열적 안정성이 매우 우수하다. 그러나, 다른 염 역시 우수한 Li 염들의 경우 LiPF6보다 이온 전도도가 낮기 때문에 다양화로 활용되지 못한 반면, LiFSI 염은 LiPF6보다도 더 높은 이온 전도도를 보여주고 있다. 이러한 장점을 모두 갖춘 LiFSI를 사용한 전해액에서의 부식 특성이 어떠한지 조사하였다. LiFSI의 부식 억제를 위해 전해액에 다양한 종류의 Li 염들을 첨가하였다. 그중, Na2HPO4, LiF, Li2WO4, Li2MoO4, TMSB, TMSPa, TMSPi 첨가제를 넣은 경우에는 알루미늄 부식 억제 효과를 보지 못하였다. 다음으로 borate 계열 염들을 첨가제로 사용하여 실험을 진행하였고, 그 결과 LiBF4, LiBOB, LiDFOB는 우수한 알루미늄 부식 억제 효과를 보였다. 특이하게도 LiDFPB를 첨가한 경우에는 알루미늄 부식이 더 가속화 되는 것을 발견했다. 상기한 borate염들 중 LiDFOB가 첨가된 0.8 M LiFSI + 0.2 M LiDFOB EC/DEC (3/7, v/v) 전해액에서는 부식 문제가 없다고 알려진 LiPF6염에서의 부식 특성과 견줄 만한 성능을 보였으며, 0.8 M LiFSI + 0.2 M LiDFOB EC/DMC (3/7, v/v) 전해액에서도 또한 부식이 상당히 억제되는 것을 확인하였다. 부식 문제에서 더 나아가, LiDFOB를 0.2 M 첨가한 0.8 M LiFSI염 전해액의 이온전도도 역시 조사한 결과, 0.8 M LiFSI + 0.2 M LiDFOB EC/DEC (3/7, v/v) 전해액의 경우 LiPF6의 이온 전도도 값을 상회하는 것을 확인하였고, 같은 염 조성비에 EC/DMC (3/7, v/v) 용매에서는 LiPF6와 거의 동등한 이온 전도도 값을 보였다. 한편, 알루미늄 부식이 나타나지 않는 0.8 M LiFSI + 0.2 M LiDFOB EC/DEC (3/7, v/v) 전해액의 경우 LMO 및 LNMO에 망간 용출이 발생하였다. 0.8 M LiFSI + 0.2 M LiDFOB EC/DMC (3/7, v/v)에서는 망간 용출 문제가 없는 것으로 보였으나, 고온 보존 기간이 길어지게 되면 망간 용출이 발생하는 것을 확인하였다.

핵심어: 알루미늄 부식, imide 염, LiFSI, borate 염, LiDFOB