

Suppression of Aluminum Corrosion in Lithium Bis(trifluoromethanesulfonyl)imide-based Electrolytes by the Addition of Fumed Silica

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The corrosion property of aluminum by lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt is investigated in liquid and gel electrolytes consisting of ethylene carbonate/propylene carbonate/ethylmethyl carbonate/diethyl carbonate (20:5:55:20, vol %) with vinylene carbonate (2 wt %) and fluoroethylene carbonate (5 wt %) using conductivity measurement, cyclic voltammetry, scanning electron microscopy, and energy dispersive X-ray spectroscopy. All corrosion behaviors are attenuated remarkably by using three gel electrolytes containing 3 wt % of hydrophilic and hydrophobic fumed silica. The addition of silica particles contributes to the increase in the ionic conductivity of the electrolyte, indicating temporarily formed physical crosslinking among the silica particles to produce a gel state. Cyclic voltammetry also gives lower anodic current responses at higher potentials for repeating cycles, confirming further corrosion attenuation or electrochemical stability. In addition, the degree of corrosion attenuation can be affected mainly by the electrolytic constituents, not by the hydrophilicity or hydrophobicity of silica particles.

Key Words : Aluminum corrosion, LiTFSI-based electrolytes, Fumed silica, Gel electrolytes

Introduction

Lithium-ion batteries have been used as a key component of various portable electronic devices such as cellular phones, laptop computers, and even hybrid electric vehicles. The success of the lithium-ion battery has made their usage in applications, such as electric vehicle power stations and electric storage systems, also possible.^{1,2} For these systems, lithium-ion batteries with higher energy and power densities, higher operating voltage, and wider working range of temperature as well as longer cycle life are needed.³ This requires that intensive research should be directed into the development of lithium-ion batteries with these properties.

Lithium hexafluorophosphate (LiPF₆) in a mixture of ethylene carbonate and dimethyl carbonate is a standard electrolyte solution used in commercial lithium-ion batteries.³ Many studies have been done on this electrolyte, which revealed that the LiPF₆ could decompose under high voltage and at high temperatures.¹ Also, the LiPF₆ might deteriorate in the presence of water³⁻⁶ to liberate HF.⁶ This could lead to the characteristic poor cycle performance of LiPF₆ in the ethylene carbonate/dimethyl carbonate mixture.^{4,7} Another electrolyte salt proposed for use in lithium-ion batteries is lithium bis(trifluoromethanesulfonyl) imide (LiTFSI). In addition to the properties possessed by LiPF₆, the LiTFSI is thermally stable and highly tolerant to water.^{3,7} However, its corrosion property has made its application a matter of concern in lithium-ion batteries.^{4,5,8,9} The degree of aluminum corrosion by LiTFSI depended on the composition of the

solvent used.^{3,7,10,11} In ethylene carbonate/dimethyl carbonate solvent, for instance, the aluminum corrosion increased with cycling due to the decrease in potential.⁷ Recently, electrolytes with ionic liquids^{7,9,12-15} containing TFSI⁻ anion have been found out to suppress the aluminum corrosion effectively by the stable passivation of compounds formed between cationic species of the ionic liquid and the TFSI on the aluminum surface.

More precisely, the aluminum corrosion by LiTFSI is due to the lack of fluorine-containing films formed on the aluminum surface,³ which plays a role by inhibiting the corrosion. The TFSI⁻ anion dissociated in the solvent medium attacks the native aluminum oxide (Al₂O₃) film on the aluminum surface to form Al-TFSI salt that is soluble in the solvents.^{11,16} This exposes aluminum to the electrolyte and then allows the oxidation of aluminum metal at higher potentials.¹¹ It was also proved that the addition of small amounts of LiPF₆ at this stage surely inhibits the corrosion in LiTFSI-based electrolytes, due to the formation of fluorine-containing films on the aluminum surface.^{3,17,18}

Gel-type electrolytes can be a candidate to inhibit the aluminum corrosion. Gel electrolyte containing fumed silica particles has the ability to stabilize aluminum surfaces in contact with the electrolyte as it absorbs moisture impurities which would promote the aluminum corrosion.^{19,20} The silica particles also play a role by filling defect sites of aluminum to inhibit the corrosion. At this stage, the size effect of the silica particle may become significant: there is an example that smaller sized particles involve better *anti*-corrosion effect.²¹

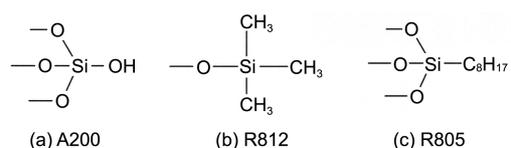


Figure 1. Structural representation of fumed silicas (Aerosil[®] Series, Degussa) used in this study.

In this study, the effect of adding three commercial fumed silica particles on the corrosion properties of aluminum is investigated in LiTFSI-based electrolyte over the potential range of 3.3–5.1 V (*vs.* Li/Li⁺). In contrast to the previous report^{19,20} which used the electrolyte solution consisting of LiTFSI in poly(ethylene glycol)dimethylether, a carbonate-based mixture with some additives is used in this study as a solvent component. Ionic conductivity is measured for the electrolytes (in liquid and gel) by impedance spectroscopy. The aluminum corrosion phenomena are observed through cyclic voltammetry using an aluminum||electrolyte||lithium cell. The readers should focus on the attenuation behavior of aluminum corrosion by the addition of fumed silica.

Experimental

Aluminum foil (40 mm thick, purity > 99%) and lithium foil (purity > 99.9%) were supplied from Aldrich Chemicals. As a base electrolyte solution, 1 M LiTFSI dissolved in ethylene carbonate/propylene carbonate/ethylmethyl carbonate/diethyl carbonate (20:5:55:20, vol %) was used with additives of vinylene carbonate (2 wt %) and fluoroethylene carbonate (5 wt %). Three species of fumed silica with the average surface area of $100\text{--}260 \pm 30 \text{ m}^2 \text{ g}^{-1}$, designated as A200, R812, and R805 (Aerosil[®], Degussa), were used. The chemical structures of the silica particles are shown in Figure 1. The A200 is hydrophilic while the R812 and R805 are hydrophobic. According to the data of Aerosil[®],²² the R812 and R805 are fumed silica powders after-treated from the A200 with a trimethylsiloxane and an octylsilane, respectively, to allow the carbon content of about 2.0–6.5 wt %. Preparation of electrolytes and cell assembly were done in a glove box under an argon gas condition.

Prior to use, the aluminum foil was washed with acetone to give a clean surface, cut into a square (1 cm × 1 cm), and dried in a vacuum oven at 80 °C for 10 h. The fumed silica powders were dried in a vacuum oven at 100 °C for 24 h. All materials were transferred into the glove box quickly after vacuum drying. To form the gel-type electrolytes, 3 wt % of the fumed silica was dispersed in the base electrolyte solution and then stirred for 18 h. Ionic conductivities of base and gel electrolytes were obtained from impedance spectroscopy measurement using an Autolab instrument (Eco Chemie, PGstat 100). The room-temperature ionic conductivity value for the base electrolyte solution was determined to be 10.2 mS cm^{-1} , whereas those for the gel electrolytes containing A200, R812, and R805 were 13.4, 13.5, and 12.8 mS cm^{-1} , respectively.

Lithium metal foil was also cut into a square (1 cm × 1

cm) in the glove box. A coin-type cell of Li||electrolyte||Al was fabricated by sandwiching a separator (Celgard S20) between lithium and aluminum foils. The coin cell was aged for 2 h at ambient temperature before measurement. Cyclic voltammetry for the coin cell was performed 5 times using an Autolab instrument (Eco Chemie, PGstat 100) at 10 mV s^{-1} in the potential range of 3.3–5.1 V (*vs.* Li/Li⁺). Surface morphology observation and elemental analysis for the aluminum foil were carried out after cycling five times of the cyclic voltammetry measurement using a scanning electron microscope (Hitachi S-4800) equipped with an energy dispersive X-ray spectroscopy, respectively.

Results and Discussion

As noted above, the addition of silica particles into the base electrolyte solution contributes to an increase in room-temperature ionic conductivity (*i.e.*, 10.2 mS cm^{-1} for the base electrolyte solution → $12.8\text{--}13.5 \text{ mS cm}^{-1}$ for the gel electrolytes). Such an increase is probably due to easier ionic transport through the temporarily crosslinked networks of silica particles on the aluminum surface. In addition, it is notable that the electrochemical performance of LiTFSI as an electrolyte salt for lithium-ion batteries would be still maintained because the formation of gel electrolytes by silica addition does not involve chemical change, but a physical transformation.

In general, aluminum corrosion by LiTFSI salt can be explained by a simple equation set as follows:



Eq. (3) may be closely related to the solubility of $\text{Al}(\text{TFSI})_3$ in the electrolyte solvents, which is already soluble in the base electrolyte solution. The solubility of $\text{Al}(\text{TFSI})_3$ drives Eq. (3) to allow the repetition of the whole process, *i.e.*, Eqs. (1)–(3). If a pit is once generated on the aluminum surface, further attack by TFSI^- is much easier, yielding an enlargement of the pit. On the other hand, a gel electrolyte formed by the addition of silica particles is so viscous that the solubility of $\text{Al}(\text{TFSI})_3$ is sufficiently suppressed to induce the reduction of aluminum corrosion. That is, silica particles coat the aluminum surface by temporarily crosslinking with each other to create the uniform surface, which inhibits the attack of the TFSI^- anion. Though the LiTFSI has a higher moisture-tolerance than LiPF_6 , some amounts of moisture present in the electrolyte can impact on its pitting corrosion ability. Hydrophilic silica particles absorb the moisture to reduce the corrosion. In the case of hydrophobic silica particles, however, it is the temporarily crosslinked networks formed on the aluminum surface that repel the water component to reduce the corrosion. These roles of silica particles help produce a drastic reduction of aluminum corrosion in the LiTFSI-based electrolyte.

Many studies^{3,5,7,17–20} employ the cyclic voltammetry techni-

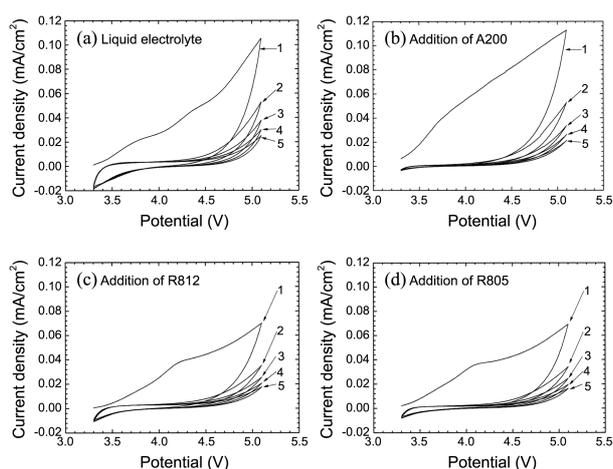


Figure 2. Cyclic voltammograms of aluminum, recorded at a scan rate of 10 mV s^{-1} , (a) in the base electrolyte solution and in the gel electrolytes containing 3 wt % of (b) A200, (c) R812, and (d) R805 fumed silica particles.

que to examine the aluminum corrosion in LiTFSI-based electrolytes. As shown in Figure 2, the hysteresis of cyclic voltammograms²³ and sharp rises in current density during anodic scans appear as the proof of aluminum corrosion. Figure 2 shows large anodic current densities during the first cycle and also the decrease in anodic current densities with cycling for all electrolytes. Fortunately, gel electrolytes containing silica particles show greater reduction in their anodic current densities with cycling, compared to the base electrolyte solution. That is, the aluminum corrosion of gel electrolyte can be relaxed to an almost negligible state in the fifth cycle. Table 1 obviously shows the decay of current density response at the highest potential of 5.1 V after cycling. In particular, gel electrolytes adopting hydrophobic R812 and R805 respond with lower current densities after cycling than that adopting hydrophilic A200. For example, the current density of the gel electrolyte containing the hydrophobic R805 retains $16.34 \mu\text{A cm}^{-2}$ after the fifth cycle, while the gel electrolyte containing the hydrophilic A200 exhibits $21.23 \mu\text{A cm}^{-2}$. Such a result is quite contrary to the fact²⁰ that hydrophobic silica results in a better attenuation of aluminum corrosion than hydrophobic silica, thereby leading to the enhanced inhibition of lithium dendrite.^{24,25}

Except for the silica used, the main difference between the previous report²⁰ and the present study lies on the electro-

Table 1. Current density response [$\mu\text{A cm}^{-2}$] evolution during cycling, recorded at the highest potential of 5.1 V in the cyclic voltammogram (Figure 2)

Cycle no.	Base electrolyte	Adding A200	Adding R812	Adding R805
1	105.29	112.70	70.04	69.27
2	52.89	52.80	35.36	34.24
3	37.90	33.74	25.62	24.67
4	30.26	26.25	20.72	19.55
5	25.35	21.23	17.66	16.34

lytic constituents: LiTFSI with poly(ethylene glycol)dimethylether versus 1 M LiTFSI dissolved in ethylene carbonate/propylene carbonate/ethylmethyl carbonate/diethyl carbonate (20:5:55:20, vol %) with additives of vinylene carbonate (2 wt %) and fluoroethylene carbonate (5 wt %). It is well known²⁰ that the gel electrolyte containing silica particles attenuates aluminum corrosion due to less fluidic behavior and the immobilization of the corrosion reaction product. In the gel electrolyte containing many carbonate species that have more moisture content than polymeric ether, the hydrophilic A200 absorbs the moisture fully and can permit the excess water on the aluminum surface to lead the corrosion. Meanwhile, the hydrophobic R812 and R805 in this situation can repel the moisture more efficiently to form a protective layer on the surface, thus prohibiting the aluminum corrosion. Thus, in the electrolyte system with comparatively higher moisture content, the current density responses for the gel electrolytes containing hydrophobic R812 and R805 are lower than the case of hydrophilic A200. It can also be said that the degree of corrosion attenuation can be affected mainly by the electrolytic constituents, not by the hydrophilicity or hydrophobicity of silica particles.

To determine the surface property of the aluminum metal foil before and after five rounds of cyclic voltammetry, morphology observation with an elemental analysis by energy dispersive X-ray spectroscopy is performed. As shown in Figure 3, large dark patches can be observed on the surface of the aluminum foil cycled in the base electrolyte solution. The patches may be recognized as the pitting corrosion of aluminum by the LiTFSI. In contrast, the aluminum foil cycled in the gel electrolytes containing fumed silica shows comparatively clean surfaces with a very small number of patches. This indicates that pitting corrosion of aluminum in the gel electrolytes is almost attenuated. By more precise observation for the aluminum surfaces, however, the corrosion patterns are slightly deviated by the gel electrolytes: for instance, the aluminum surface in the gel electrolyte containing hydrophobic R812 shows that tiny dark patches are locally distributed. That is, the surface in the gel electrolyte containing the R812 is more corroded than those electrolytes containing hydrophilic A200 and hydrophobic R805. This

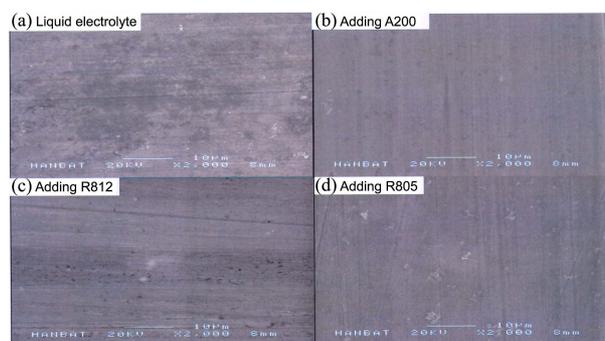


Figure 3. Surface images of aluminum after cycling five times (a) in the base electrolyte solution and in the gel electrolytes containing 3 wt % of (b) A200, (c) R812, and (d) R805 fumed silica particles.

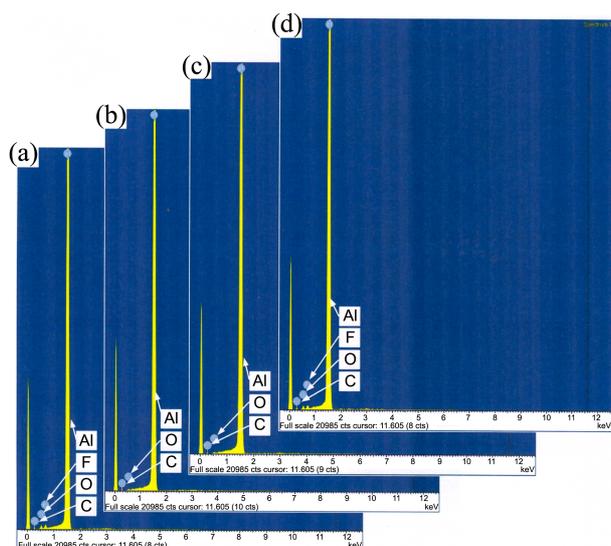


Figure 4. Energy dispersive X-ray spectroscopic graphs of aluminum surface after cycling five times (a) in the base electrolyte solution and in the gel electrolytes containing 3 wt % of (b) A200, (c) R812, and (d) R805 fumed silica particles.

indicates that surface group of fumed silica particles can play an important role of determining minuscular corrosion level.

The energy dispersive X-ray spectroscopic results (see Figure 4 and Table 2) reveal that the gel electrolyte containing fumed silica particles forms a passive protective film on the aluminum surface, which contributes to the relaxation of aluminum corrosion. Carbon and oxygen species, obtained from the decomposition of vinylene carbonate and fluoroethylene carbonate in the base electrolyte solution, become the main constituents of the protective layer on the aluminum surface. Fluorine components obtained in the base electrolyte and the gel electrolyte containing R805 (see Figures 4(a) and 4(d)) originate from the decomposition of LiTFSI salt. That is, the end group ($-\text{CF}_3$) of dissociated TFSI⁻ may be attacked by oxygen-rich species of the carbonate group (in the base electrolyte) and octylsilane group (in the gel electrolyte containing R805 particles) to decompose into fluorine components. Compared to the other electrolyte system, the oxygen-rich species can be found in the base electrolyte and

Table 2. The energy dispersive X-ray results for the surface of aluminum in the base electrolyte and the gel electrolytes containing 3 wt % of fumed silica

	Al	C	O	F
(Weight%)				
Base electrolyte	84.93	8.47	4.01	2.59
Adding A200	89.84	8.77	1.39	
Adding R812	91.43	6.54	2.03	
Adding R805	83.76	9.78	3.77	2.69
(Atomic%)				
Base electrolyte	74.24	16.63	5.91	3.22
Adding A200	80.30	17.60	2.10	
Adding R812	83.47	13.40	3.13	
Adding R805	72.27	18.95	5.49	3.29

the gel electrolyte containing R805 (see Table 2). Moreover, the long aliphatic chain unit ($-\text{C}_8\text{H}_{17}$) of hydrophobic R805 may be associated with the promotion of $-\text{CF}_3$ decomposition. Further analytical studies with high-precision equipments should be carried out to understand the possible interactions between the electrolytic constituents and the surface groups of silica particles. In addition, it is rather surprising that the energy dispersive X-ray spectroscopic results after cycling do not reveal silicon component as a constituent of the film formed on the aluminum surface. This effect can only be understood by the fact that the stability of the silica layer, which is generated as a temporarily crosslinked network, may be broken during the cathodic reduction in the cyclic voltammetry or the discharge process in galvanostatic cycling.

Conclusion

The aluminum corrosion by LiTFSI salt is studied in the carbonate-based solvent as an electrolyte solution base. The aluminum corrosion appears obviously in the base electrolyte solution by forming large dark patches on the aluminum surface. The addition of fumed silica particles sufficiently relaxes the corrosion by forming a gel-type electrolyte. Such effect can be evidenced by small anodic currents in the cyclic voltammograms. The impedance measurement also proves that the silica addition to the base electrolyte increases the ionic conductivity. Thus, the gel electrolytes containing fumed silica particles can be used in lithium-ion batteries for better performance without further promoting aluminum corrosion. In addition, rather than the surface behavior (hydrophilic or hydrophobic) of the silica particles, the degree of aluminum corrosion can be affected mainly by the electrolytic constituents.

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