Anodic behavior of aluminum current collector in LiTFSI solutions with different solvent compositions

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Abstract

The anodic behavior of aluminum (Al) current collector of Li-ion batteries has been investigated in organic electrolyte solutions containing lithium bis[trifluoromethylsulfonyl]imide ($Li(CF_3SO_2)_2N$: LiTFSI) with different compositions of solvents. The Al anode was subjected to anodic corrosion in the LiTFSI solution, but the degree of the corrosion depended on the solvent composition. The surface of Al pre-treated by mechanical polishing has suffered serious corrosion in the mixed solvent solution of ethylene carbonate (EC) and dimethyl carbonate (DMC), whereas the Al surface pre-treated by electro-polishing was relatively stable in the mixed solvent of γ-butyrolactone (GBL) and DMC. The results of electrochemical quartz crystal microbalance (EQCM) experiments showed that the mass change of the Al surface during the potential cycling in GBL + DMC was much different from that in the EC + DMC solution. Scanning electron microscope (SEM) observation proved that the corrosion pits evolved on the electro-polished Al surface after potential cycling, but GBL resulted in a smaller amount of the corrosion product on the Al surface.
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1. Introduction

Rechargeable lithium (Li) ion batteries have widely been used in such portable electronics as VCRs, cellular phones and laptop PCs. Advanced battery systems with higher performance are now required for power sources of energy storage and electric vehicle (EV) applications. For those purposes, the batteries should have higher energy and power densities, higher cell voltage, wider working temperature range, more rapid rechargeability, and longer cycle life. Many attempts have been made examined to achieve the improved battery performances [1]. With respect to the current collector of the positive electrode, for example, aluminum (Al) foil or screen is used in the commercial Li-ion batteries. Thinner but mechanically tough Al foil is preferable to improve the energy density of the battery. Metallic Al is generally stable in air and in neutral water environments due to its protective surface film composed of oxide and hydroxide of Al. This character is also expected in organic electrolyte solutions containing small amounts of oxidants.

On the other hand, the electrolytic solutions commonly used are mixed alkyl carbonates that dissolve inorganic Li salts ($LiPF_6$, $LiBF_4$, etc.). However, alternative salts for $LiPF_6$ have widely been examined because of its chemical and thermal instability in organic media containing trace levels of water [2]. Recently, some research groups reported basic electrochemical behavior of Al in organic electrolyte solutions with different compositions [2–7]. We have also investigated the anodic behavior of Al in the organic electrolyte solutions that are practically used in Li-ion batteries [8]. The anodic characteristics of Al depended much on the composition of the electrolyte solution as well as the metallurgy of the electrode sample [6,8]. The Al current collector is stable in $LiPF_6$ and $LiBF_4$ solutions but is susceptible to corrode anodically in solutions containing $LiCF_3SO_3$ and lithium bis[trifluoromethylsulfonyl]imide ($Li(CF_3SO_2)_2N$: LiTFSI) [3,6,8].

As the LiTFSI solutions are much superior to $LiPF_6$ solutions with respect to their thermal stability, the inhibition of the Al corrosion in the LiTFSI solutions becomes an important issue in the Li-ion battery technology. Wang et al. [9,10] have reported that the addition of $LiPF_6$ to the LiTFSI solution inhibited the anodic corrosion of Al. The present authors have also observed the effects of the electrolyte (anion) blending on the anodic corrosion behavior of the Al

current collector in an organic solvent system [11]. The electrochemical and spectroscopic experiments showed that the formation of fluoride-containing surface film takes an important role to inhibit the anodic corrosion of Al in organic electrolyte solutions [7,11]. It is also expected that the solvent components will affect the electrochemistry of Al, but little has so far been published on this issue. Thus, in this paper, we report the anodic polarization behavior of Al in LiTFSI solutions with different solvent composition. We have adopted an electrochemical quartz crystal microbalance (EQCM) technique combined with scanning electron microscopy (SEM) to investigate the influence of the solvent component on the anodic behavior of Al.

2. Experimental

The test electrode for cyclic voltammetry (CV) was a high-purity Al wire (Nilaco, >99.999% purity, 0.8 mm of diameter, 0.26 cm^2 of geometric surface area). The Al wire was pre-treated either by mechanical polishing using emery paper (#1500) or by electro-polishing at a constant voltage of 10 V for 30 min in a mixed aqueous acid solution (CH$_3$COOH/HClO$_4$ = 4/1 by volume). An Al film electrode for EQCM experiments was prepared by RF-sputtering on a Ti-coated AT-cut quartz crystal piece (6 MHz) in an inert Ar atmosphere [11]. The thickness of the Al film was about 150 nm.

The solvents of the electrolytic solution, ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC) and γ-butyrolactone (GBL) were extra pure grade (Kishida Chemical, Battery Grade, water content <20 ppm) and used as received. The electrolytic salt, Li(CF$_3$SO$_2$)$_2$N (LiTFSI) received from 3M Co., was dried under a vacuum at 120 °C for 24 h or longer before use. For comparison, LiPF$_6$ and Li(C$_2$F$_5$SO$_2$)$_2$N (LiBETI) were also used as the electrolytic salts. These Li salts were dissolved in mixed solvents, EC + DMC, EC + DEC, and GBL + DMC (50:50 by volume), to make 1 mol dm^{-3} (M) solutions. The water contents in the resulting electrolytic solutions were less than 40 ppm.

A glass beaker three-electrode cell (inner volume: ca. 50 cm^3) was used for CV experiments, where the counter and the reference electrodes were a Li sheet with large surface area and a Li chip in the same solution (Li/Li$^+$), respectively. The voltammograms were recorded in a potential range between 1.0 and 6.0 V versus Li/Li$^+$ with a potential scan rate of 10 mV s^{-1}. The experiment was conducted under a dry Ar atmosphere at room temperature (18–25 °C).

The surface morphology of the Al electrode before and after the potential cycling was observed by SEM (Hitachi, S2300). The sample was well rinsed with the organic solvent examined, and dried under a mild condition before attaching it on a sample holder in the SEM chamber.

A cylindrical Teflon$^®$ cell (inner volume: ca. 25 cm^3) equipped with an oscillator unit (Hokuto Denko, HQ-304A)

was used for EQCM experiments. The Al-coated quartz crystal piece as the test electrode was mounted at the bottom of the cell. A Li chip reference and a Li sheet counter electrodes were set above the test electrode. The resonance frequency (*f*) of the quartz crystal was monitored by a frequency controller unit (Hokuto Denko, HQ-101B) during the potential cycling. The mass change on the quartz crystal piece was calculated by Sauerbrey's equation [12]. The mass sensitivity of the present EQCM system was calibrated by the electrodeposition of copper from an aqueous solution, and found to be consistent with that derived from the theoretical equation [13].

3. Results and discussion

In the previous reports [8,11], the anodic behavior of Al in solutions containing different Li salts has been discussed using the results of cyclic voltammetry for Al wire electrodes in a mixed solvent system of EC + DMC (50:50 by volume). In the LiPF$_6$ solution, no significant anodic current was observed up to 6 V (versus Li/Li$^+$) or above, which suggests the Al electrode being anodically stable in the LiPF$_6$ solution. On the other hand, rather high anodic currents were detected in the LiBETI solution. Higher anodic current during the reverse potential scan (cathodic direction) than the current observed during the forward scan (anodic scan) showed that the process involves a pitting corrosion step, or formation of a less protective surface film [11]. The LiBETI salt had once been reported to be suitable for Li battery system [3], but practically it showed some corrosive characteristics, especially under highly anodizing conditions. The magnitude of the anodic current in the LiBETI solution was also dependent on the surface pre-treatment of the Al wire electrode. The mechanically polished rough surface gave higher anodic current than the electro-polished smooth surface [6,11].

The voltammetric responses of the Al wire in LiTFSI solutions are shown in Fig. 1. Much higher anodic currents were observed in the LiTFSI solutions, compared with those in the LiPF$_6$ and LiBETI solutions [11]. The anodic current increased at about 4.0 V or higher for the mechanically polished Al wire, while the current increase started at 5.5 V or higher for the electro-polished electrode. The intensity of the current was different among the electrolyte solvents, especially for the electro-polished electrode. The anodic current in EC + DEC (Fig. 1B) was lower than in EC + DMC (Fig. 1A), but the shape of the voltammograms looks like each other. This suggests that the anodic processes on the Al electrode are essentially the same in both solutions using different solvent compositions. The anodic behavior of the mechanically polished Al in GBL + DMC (Fig. 1C) was also similar to that observed in EC + DMC. However, the electro-polished Al gave much lower current in GBL + DMC than those in the solutions with the EC-based mixed solvents.
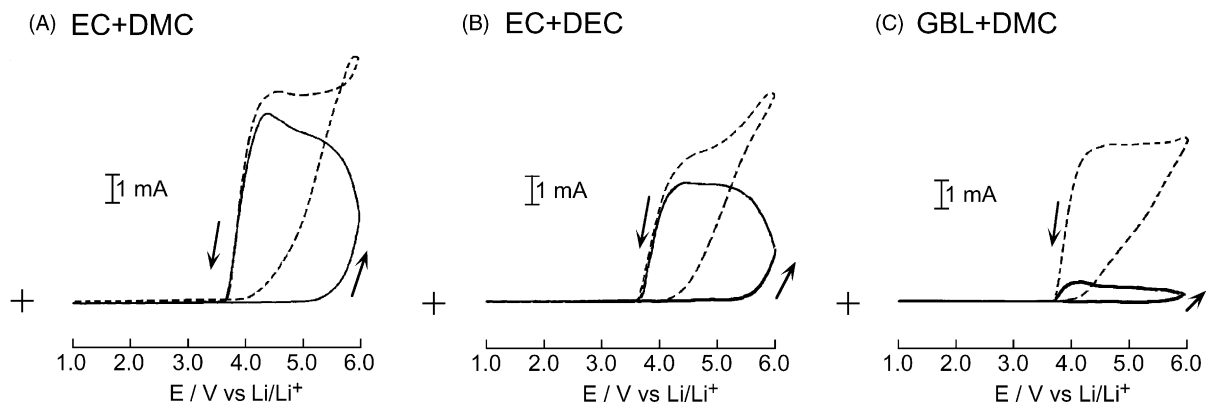
(A) EC+DMC

E / V vs Li/Li$^+$

(B) EC+DEC

E / V vs Li/Li$^+$

(C) GBL+DMC

E / V vs Li/Li$^+$

Fig. 1. Cyclic voltammograms for Al wire electrodes at the first scan in the mixed solvent (1:1 by volume) containing 1 mol dm^{-3} Li(CF$_3$SO$_2$)$_2$N, with scan rate of 10 mV s^{-1}. Solid lines: electro-polished, dashed lines: mechanically polished.

Fig. 2 shows the comparison of the SEM images for the Al surface after the potential cycling (five cycles) in the LiTFSI solutions with different solvents. The potential cycling in the LiTFSI/EC + DMC solution lead to significant change in the surface image from the original one. That is, some corrosion products were deposited on the Al surface after the potential cycling in EC + DMC. The surface morphology after the potential cycling in EC + DEC and GBL + DMC also showed the anodic corrosion, but the features of the surface products looked quite different from that observed in EC + DMC. Corrosion pits are clearly observed on the Al surface, especially for the electro-polished samples, after the potential cycling in GBL + DMC. The SEM images also proved that the susceptibility of the anodic corrosion depends much on the surface pre-treatment. That is, the rough surface of Al tends to suffer overall corrosion, whereas pitting corrosion mainly proceeds on the smooth Al surface.

EQCM experiments were carried out to monitor the mass changes at the Al surface during the anodic polarization in the LiTFSI solutions with different solvent compositions. Fig. 3 shows the voltammetric responses (i) and the frequency change (Δf) of the sputtered Al film electrode at the first potential scan. In LiTFSI/EC + DMC (Fig. 3A), the frequency response lead to a reaction scheme consisting of the anodic formation of a surface film followed by the dissolution of the resulting products. That is, the first frequency decrease during the polarization in the anodic direction (forward scan) corresponds to the low anodic current, which is probably accompanied by the accumulation of the oxidized compounds on the Al anode. The subsequent high anodic current during the polarization in the cathodic direction (reverse scan) is due to the anodic dissolution of Al in this solution [6,8,13]. In EC + DEC (Fig. 3B), although the anodic current and hence the frequency response were smaller than those in the EC + DMC solution, their variations with the potential in EC + DEC showed similar profiles to those in EC + DMC. This suggests that the anodic process on Al is intrinsically common in both solutions.
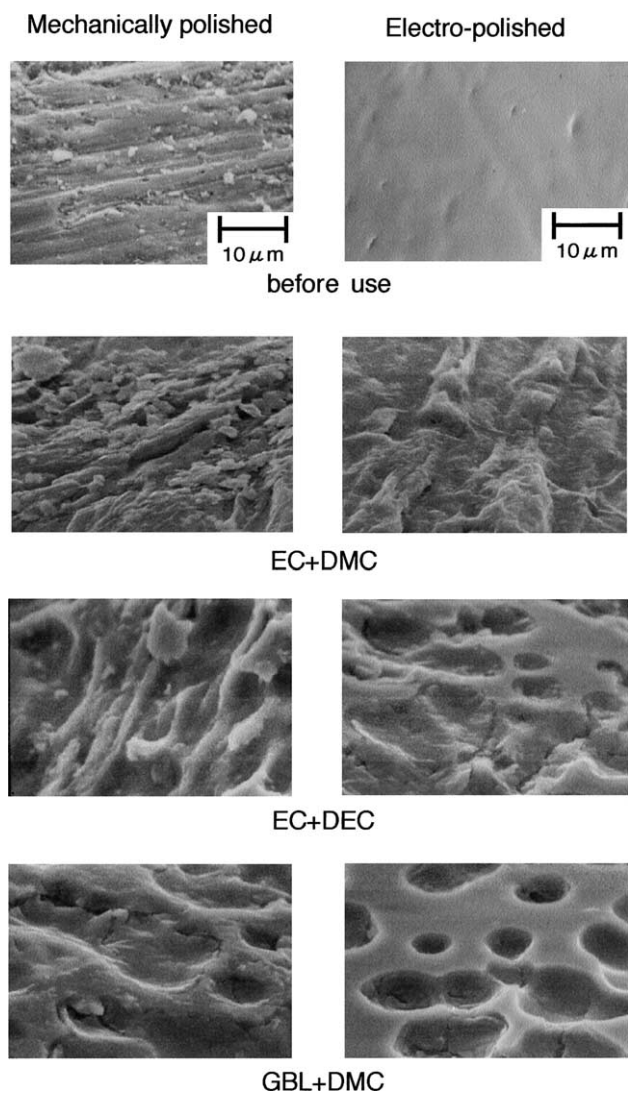
Mechanically polished   Electro-polished

before use

EC+DMC

EC+DEC

GBL+DMC

Fig. 2. SEM images of Al surface after the potential cycling in the mixed solvent (1:1 by volume) containing 1 mol dm^{-3} Li(CF$_3$SO$_2$)$_2$N.
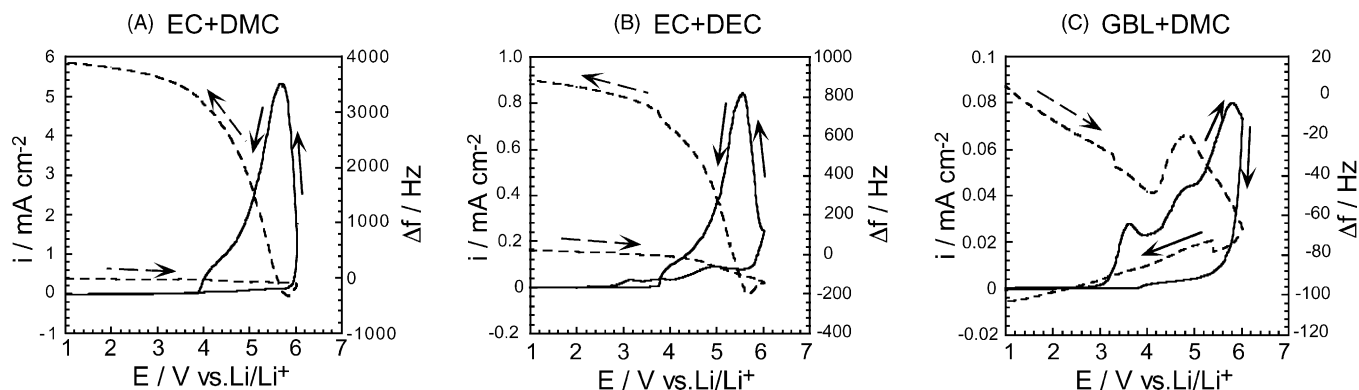
Fig. 3. Current responses (*i*) and frequency changes (Δ*f*) for Al film electrodes at the first potential scan in the mixed solvent (1:1 by volume) containing 1 mol dm^{-3} Li(CF$_3$SO$_2$)$_2$N, with scan rate of 10 mV s^{-1}. Solid lines: current response (*i*), dashed lines: frequency change (Δ*f*).

The mass change per amount of charge passed (Δ*m*/*Q*) was calculated from the frequency change per anodic charge [12,13], and the results are summarized in Table 1. The average value of Δ*m*/*Q* was about 15 g F^{-1} (1 F denotes 96,500 C) during the anodic potential scan from 3 to 6 V in LiTFSI/EC + DMC, which suggests the formation of oxide and/or fluoride of Al on the electrode surface [11]. The frequency decrease during the anodic potential scan from 3 to 6 V in LiTFSI/EC + DEC gave about 35 g F^{-1}, which is much higher than in LiTFSI/EC + DMC but rather similar to the value obtained in the LiPF$_6$ solution [8,11]. The frequency increase during the reverse potential scan (cathodic direction) from 6 to 5 V yielded the mass decrease of about −30 g F^{-1} in both EC + DMC and EC + DEC. These mass decreases correspond to the dissolution of the substrate Al accompanied by sloughing of surface deposits that were formed during the preceding anodic (forward) potential scans [8,11].

On the other hand, the frequency response in the GBL + DMC solution (Fig. 3C) was different from those in EC + DMC and EC + DEC. The gradual decrease in the resonance frequency during the anodic polarization to about 4 V is probably due to the formation of the oxidation products on the Al surface. The steep increase in the frequency in the potential region from 4 to 5 V corresponds to the anodic dissolution of Al and/or the stripping of the surface film. The subsequent decrease in the frequency during the polarization in the cathodic direction (reverse scan) means continuous

formation of the surface film, which would be rather stable in a solution containing GBL. The mass change per charge passed (Δ*m*/*Q*) was around 30 g F^{-1} throughout whole potential region, except for the region with the steep increase in the frequency. The value of about 30 g F^{-1} has commonly been observed in the organic electrolyte solutions that show good electrochemical stability of Al [8,11]. Thus, the solvent GBL can act as a stabilizing component for Al anode even in the solution containing highly corrosive salt LiTFSI.

The cause of the differences in the anodic behavior of Al with the solvent composition is not clear in the present stage. It is proved that the composition of the surface film takes an important role in the stability of the Al anode in organic media [5–7,11]. Thus, differences in the solvent composition would affect the surface chemistry of the Al anode in the LiTFSI solutions, details of which are now under investigation.

Acknowledgements

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Table 1

Mass change per quantity of electricity passed (Δ*m*/*Q*) in LiTFSI solutions

Potential range/V vs. Li/Li$^+$ (polarization direction)	Δ*m*/*Q* (g F^{-1})[a]		
	EC + DMC	EC + DEC	GBL + DMC
3.0–4.0 (forward)	15	[b]	[b]
4.0–5.0 (forward)	17	35	35
5.0–6.0 (forward)	9	35	30
6.0–5.0 (reverse)	−30	−30	35

[a] 1 F denotes 96,500 C.
[b] The electricity passed was too low to calculate.

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