Inhibition of Aluminum Corrosion by LiN(SO$_2$CF$_3$)$_2$
/Methyl Difluoracetate Electrolyte for Use in Li-Ion Cells

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Introduction

An aluminum cathode current collector for Li-ion cells was corroded by pitting in LiN(SO$_2$CF$_3$)$_2$/PC and LiN(SO$_2$CF$_3$)$_2$/EC+DME electrolytes [1, 2]. It was also reported that LiN(SO$_2$CF$_3$)$_2$/THF and LiN(SO$_2$CF$_3$)$_2$
/DME electrolytes were effective in preventing aluminum corrosion due to their low dielectric constants [2]. We have been studying methyl difluoracetate (MFA) to improve the thermal stability of Li-ion cells [3]. LiPF$_6$/MFA and LiN(SO$_2$CF$_3$)$_2$/MFA both showed better thermal stability than EC+DME electrolytes [4].

In the present study, we investigated an inhibitory effect on aluminum corrosion by the use of LiN(SO$_2$CF$_3$)$_2$/MFA, arising from MFA’s very low dielectric constant.

Experimental and Results

Figure 1 shows cyclic voltammograms of an Al plate electrode. Faradic current increased with cycling. However, the current was very small when the LiN(SO$_2$CF$_3$)$_2$/MFA electrolyte was used. This experiment showed that the LiN(SO$_2$CF$_3$)$_2$/MFA electrolyte inhibits aluminum corrosion. The potentials at 0.15 mA/cm$^2$ after 5 cycles were 3.77 V and 4.46 V for EC+DME and MFA, respectively. Under a potentiostatic condition of 4.2 V (vs Li), aluminum can develop a dissolution current of 0.1 mA/cm$^2$ for EC+DME (Fig. 2). However, the corrosion current measured after 3 hr was 2 μA/cm$^2$ for LiN(SO$_2$CF$_3$)$_2$/MFA (Fig. 2). SEM observation of the aluminum electrode surface after this experiment showed many pits for the sample using EC-DME but none for that using MFA. For EC+DME, the XPS spectra obtained from the aluminum electrode, kept at 4.2 V (vs Li) for 3 hr, showed two strong peaks of AlF$_6$ or Al$_2$O$_3$, and Al metal. However, the two peaks were very weak for MFA. The C (1s) peaks were stronger for MFA than EC-DME. From those results, we think that the aluminum surface in the MFA electrolyte was covered by an organic compound, probably the complex ion (a reaction product of Al$_2$O$_3$ with N(SO$_2$CF$_3$)$_2$) reported by X. Wang et al. [2].

The cycling performance of the Li/LiCoO$_2$ cell with an aluminum cathode current collector was very good when the LiN(SO$_2$CF$_3$)$_2$/MFA electrolyte was used (Fig. 3).

Acknowledgement

This work has been supported by CREST of JST (Japan Science and Technology Corporation).

References