Inhibition of Aluminum Corrosion by $LiN(SO_2CF_3)_2$ /Methyl Difluoroacetate Electrolyte for Use in Li-Ion Cells

J. Yamaki, T. Tanaka, I. Watanabe, M. Egashira, and S. Okada
Institute for Materials Chemistry and Engineering, Kyushu University
Kasuga Koen 6-1, Kasuga 816-8580, Japan

Introduction

An aluminum cathode current collector for Li-ion cells was corroded by pitting in $LiN(SO_2CF_3)_2$ /PC and $LiN(SO_2CF_3)_2$ /EC+DME electrolytes [1, 2]. It was also reported that $LiN(SO_2CF_3)_2$ /THF and $LiN(SO_2CF_3)_2$ /DME electrolytes were effective in preventing aluminum corrosion due to their low dielectric constants [2]. We have been studying methyl difluoroacetate (MFA) to improve the thermal stability of Li-ion cells [3]. $LiPF_6$ / MFA and $LiN(SO_2CF_3)_2$ /MFA both showed better thermal stability than EC+DMC electrolytes [4].

In the present study, we investigated an inhibitory effect on aluminum corrosion by the use of $LiN(SO_2CF_3)_2$ /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 $LiN(SO_2CF_3)_2$ /MFA electrolyte was used. This experiment showed that the $LiN(SO_2CF_3)_2$ /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+DMC 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+DMC (Fig. 2). However, the corrosion current measured after 3 hr was 2 $\mu A/cm^2$ for $LiN(SO_2CF_3)_2$ /MFA (Fig. 2). SEM observation of the aluminum electrode surface after this experiment showed many pits for the sample using EC-DMC but none for that using MFA. For EC+DMC, the XPS spectra obtained from the aluminum electrode, kept at 4.2 V (vs Li) for 3 hr, showed two strong peaks of AlF_3 or Al_2O_3, and Al metal. However, the two peaks were very weak for MFA. The C (1s) peaks were stronger for MFA than EC-DMC. 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_2O_3 with $N(SO_2CF_3)_2^-$) 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 $LiN(SO_2CF_3)_2$ /MFA electrolyte was used (Fig. 3).

Acknowledgement

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

References

[1] L. J. Krause, W. Lamanna, J. Summerfield, M. Engle, G. Korba, and R. Loch, J. Power Sources, 68, 320 (1997).
[2] X. Wang, E. Yasukawa, and S. Mori, *Electrochimica Acta*, 45, 2677 (2000).
[3] M. Ihara, B. T. Hang, K. Sato, M. Egashira, S. Okada and J. Yamaki, *J.Electrochem. Soc.*, 150, A1476 (2003).
[4] J. Yamaki, T. Tanaka, I. Watanabe, M. Egashira, and S. Okada, ECS 204th Meeting Abstract, #290, Orlando, FL, USA, Oct. 12-16 (2003).

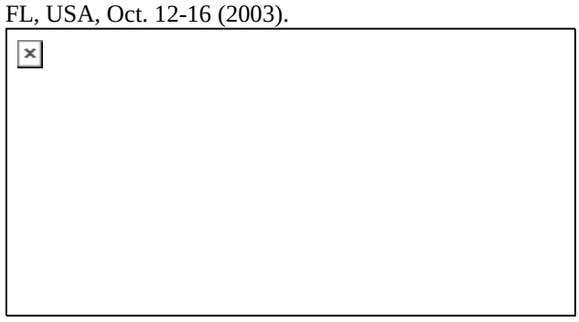

Fig. 1 Cyclic voltammograms of Al plate electrode. (Vertical line: current density/ $mAcm^2$) (Left: $LiN(SO_2CF_3)_2$ /EC-DMC, Right: $LiN(SO_2CF_3)_2$ /MFA)

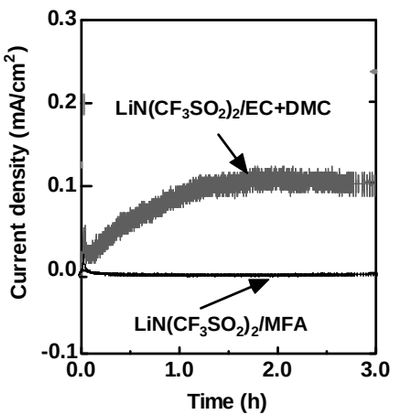

Fig. 2 Aluminum corrosion current density at 4.2 V.

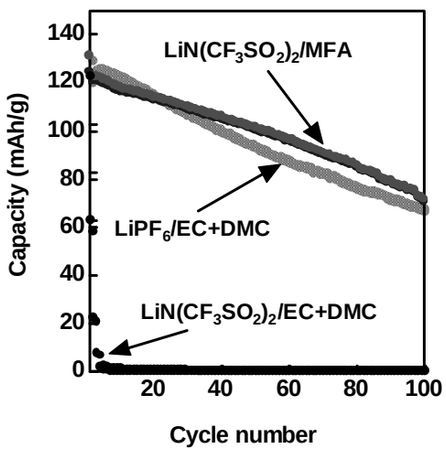

Fig. 3 Cycling performance of Li/LiCoO2 cell with aluminum cathode current collector; the electrolytes are $LiN(SO_2CF_3)_2$ /MFA, $LiN(SO_2CF_3)_2$ /EC+DMC, and $LiPF_6$ /EC+DMC.