

Thermal stability of methyl difluoroacetate electrolyte as a novel candidate for lithium 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

Many of the fluorine-containing organic compounds are nonflammable themselves and have quite unique properties. Therefore, many partly fluorinated organic solvents have been studied as co-solvents of electrolytes to improve the flammability and low temperature performance of graphite anode and lithium ion cells [1-3].

In order to improve the thermal stability of lithium metal anode cells, we have been studying partially fluorinated carboxylic acid esters, which were used as the electrolyte solvent. In our study, we found that 1 M methyl difluoroacetate (MFA)/LiPF₆ electrolyte was very stable in the presence of Li metal or lithiated carbon[4, 5].

In the present study, we investigated the thermal stability of MFA / Li imide salt electrolytes with/without Li metal or charged Li_{0.48}CoO₂.

Experimental and Results

LiN(CF₃SO₂)₂ and LiN(C₂F₅SO₂)₂ were selected as the Li imide salts. The thermal stability of 1 M Li imide salts /MFA with/without Li metal or charged Li_{0.48}CoO₂ was monitored by a TG-DSC apparatus (Rigaku Thermo plus TG8110, Rigaku, Japan) (scan rate: 5 °C / min.). 1M LiPF₆ /MFA and 1M LiPF₆ /EC:DMC(1:1) were also investigated for comparison. Each sample for TG-DSC measurement was packed in a stainless steel case, which was then crimp-sealed in a glove box filled with argon gas. The chemical delithiation of LiCoO₂ was carried out to obtain the charged Li_{0.48}CoO₂ by stirring a suspension of 5 g of LiCoO₂ in 250 ml of 0.5 M H₂SO₄ [6].

The DSC curves of electrolyte (3 μl) are shown in Fig. 1. The electrolytes with the Li-imide salt were not stable compared with LiPF₆ /MFA. However, the Li-imide electrolytes showed better stability than LiPF₆ /EC:DMC(1:1). There was no exothermic peak at 300 °C for LiPF₆ /MFA, although solid LiPF₆ decomposes to LiF and PF₅ at around 300 °C.

The DSC curves of electrolyte (3 μl) with 0.56 mg of Li metal are shown in Fig. 2. The Li imide salt electrolytes were stable; however their SEI was found to be slightly different from that of LiPF₆ /MFA by FT-IR measurement. A main component of SEI formed between LiPF₆ /MFA and Li metal is CHF₂COOLi [5], which is a reaction product of Li and MFA. However, there was another component formed by a reaction with Li salts.

The DSC curves of electrolyte (3 μl) with 3 mg of Li_{0.48}CoO₂ are shown in Fig. 3. There was not so much difference between the Li imide salt electrolytes and LiPF₆ /MFA. This result suggests that the exothermic reaction was an oxidation of MFA by oxygen created by the decomposition of Li_{0.48}CoO₂.

Acknowledgement

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

References

- [1] T. Nakajima, K. Dan, and M. Koh, *J. Fluorine Chem.*, **87** (1998) 221.
- [2] J. O. Besenhard, W. K. Appel, L. H. Lie, G. H. Wroldnigg, K-C. Moeller, and M. Winter, Abstracts of the second Hawaii battery conference, Big island of Hawaii, Jan. 4-7, p. 181 (1999).
- [3] R. McMillan, H. Slegel, Z. X. Shu, and W. Wang, *J. Power Sources*, **81-82** (1999) 20.
- [4] J. Yamaki, I. Yamazaki, M. Egashira, and S. Okada, *J. Power Sources*, **102** (2001) 288.
- [5] J. Yamaki, M. Ihara, and S. Okada, ECS 203rd Meeting Abstract, #1071, Paris France, April 27-May 2 (2003).
- [6] Y. Baba, S. Okada, and J. Yamaki, *Solid State Ionics*, **148** (2002) 311.

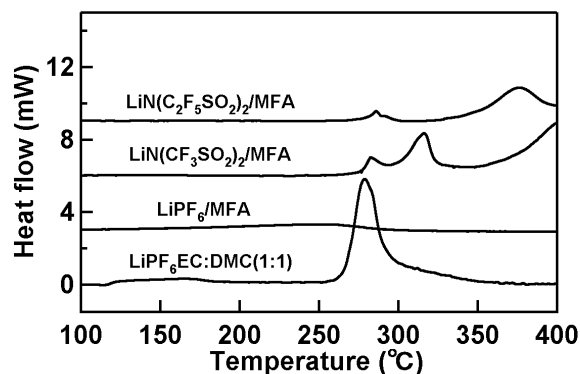


Fig. 1 DSC curves of electrolyte (3 μl).

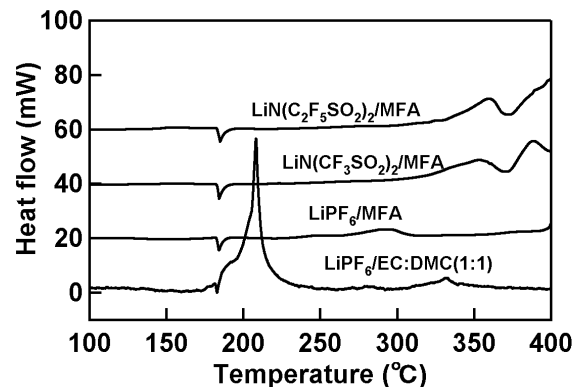


Fig. 2 DSC curves of electrolyte (3 μl) with 0.56 mg of Li metal.

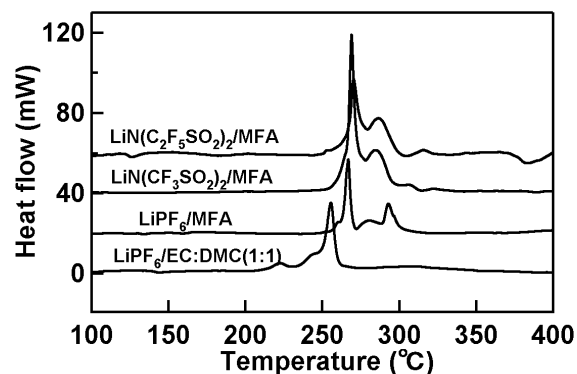


Fig. 3 DSC curves of electrolyte (3 μl) with 3 mg of Li_{0.48}CoO₂.