

Thermal studies of methyl difluoroacetate as a novel candidate for electrolyte solvent of lithium ion cells

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Introduction

The nonaqueous electrolytes used in lithium-ion cells consist of certain lithium salts and flammable organic solvents, and this makeup has been considered one of the reasons for the failure of these batteries in terms of safety.

Many fluorine-containing organic compounds are nonflammable and have quite unique properties. Therefore, many partly fluorinated organic solvents have been studied as co-solvents of electrolytes in order to reduce the flammability and improve the 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. Our study revealed that 1 M methyl difluoroacetate (MFA)/ LiPF₆ electrolyte is very stable and does not react with lithium metal up to 250 °C [4].

In the present study, we investigated the thermal stability of MFA / LiPF₆ electrolyte with lithiated carbon with the goal of applying the electrolyte for use in lithium-ion cells. Cell performance was also studied.

Experimental and Results

The anodes used in this study were prepared by mixing 95 wt% of natural graphite (LF-18D from Chuestu Graphite) or non-graphitized MCMB (MCMB-6-10 from Osaka Gas) with 5 wt% of poly(vinylidene fluoride) (PVdF) -binder (KF#9100 from Kureha Chemical) dissolved in 1-methyl-2-pyrrolidinone (NMP). The slurry was coated onto a copper current collector, and then dried. A coin cell with the carbon anode, a counter electrode composed of a Li metal sheet, and 1 M LiPF₆ /MFA were used to prepare lithiated carbon. The thermal stability of 1 M LiPF₆ /MFA with the lithiated carbon was monitored using a DSC apparatus (Thermo plus TG8230L, Rigaku, Japan) (scan rate: 5 °C / min.). 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. A large exothermic peak is observed at 400 °C for both natural graphite (C₆Li_{0.8}) and non-graphitized MCMB (C₆Li_{0.44}) as shown in Figures 1 and 2, respectively. Compared with a practical 1 M LiPF₆ /EC-DMC, the thermal stability is improved for about 100 °C, though there is a small exothermic reaction from 110 °C to the main peak temperature.

The carbon/Li coin cell was cycled at 25 °C between 0.01V and 1V at 0.2 mA/cm² with a constant voltage charge at 0.01V for 3 h. (Fig. 3). 1 M LiPF₆ /MFA indicates very good cycling performance. The cell impedance is higher when 1 M LiPF₆ /MFA was used compared with the cell with 1 M LiPF₆ /EC-DMC. Because the electrolyte conductivity of both electrolytes is the same, the SEI of the carbon in 1 M LiPF₆ /MFA probably shows a higher impedance compared with that in 1 M LiPF₆ /EC-DMC.

LiCoO₂/1 M LiPF₆ /MFA /carbon cells were cycled between 3.0 V and 4.2 V. for 50 cycles. The lithium-ion cell shows a high level of capacity retention.

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. Wrodnigg, 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.

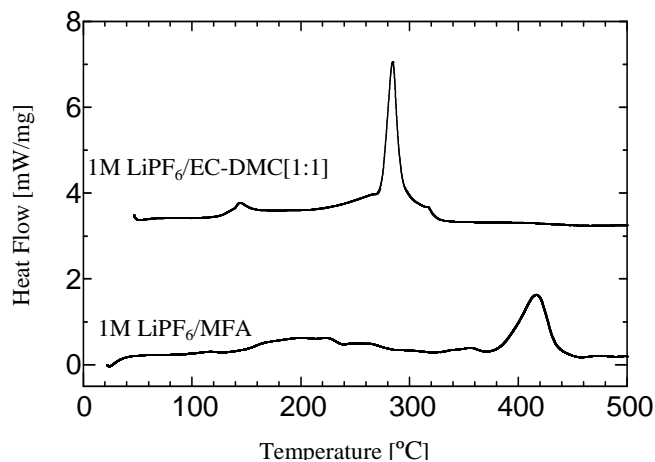


Fig.1. DSC profiles of electrolytes with natural graphite.

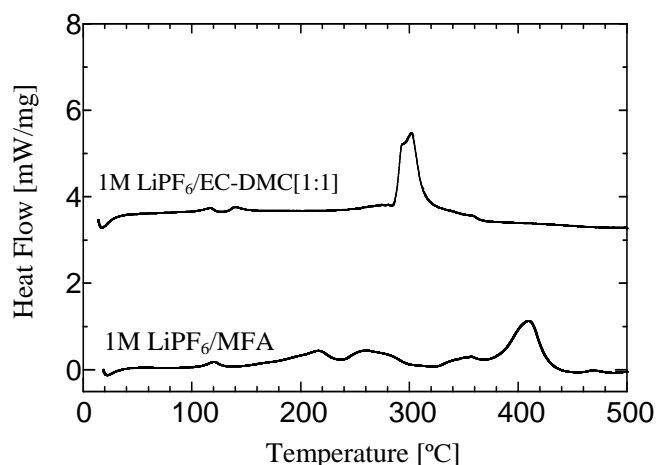


Fig.2. DSC profiles of electrolytes non-graphitized MCMB-6-10.

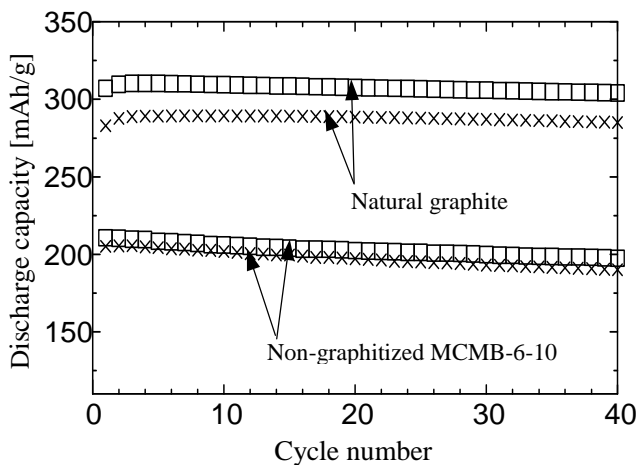


Fig.3. Cycling performance of carbon anode.

□ : 1M LiPF₆/EC-DMC [1:1]
× : 1M LiPF₆/MFA