

Application of Fluorinated Phosphate and Carbonate to LiBF₄-based Electrolyte Solutions for High-voltage-operating Lithium-ion Cells

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1. Introduction

Enhancement of electrolyte solutions durability against oxidation is essential for practical application of high-voltage-operating lithium-ion cells with enlarging energy density. In concentrated electrolyte solutions, HOMO level of solvent molecules were lowered by solvation to lithium-ion^[1]. Previously, LiBF₄-concentrated electrolyte solutions showed good oxidation durability compared to conventional electrolytes^[2]. However, the charge/discharge cycle life performances of the cells with these electrolyte solutions were not sufficient because of high-viscosity of the concentrated electrolyte solutions (viscosity > 1000 mPa s). In this report, LiBF₄-based electrolyte solutions diluted by fluorinated phosphate and carbonate to reduce viscosity were applied to both high-voltage-operating LiNi_{0.5}Mn_{1.5}O₄ (LNMO)/graphite (Gr)-system and LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ (NCM523)/Gr-system cells for enlarging energy density.

2. Experimental

We selected TFEP (: tris(2,2,2-trifluoroethyl) phosphate) and MFEC (: methyl 2,2,2-trifluoroethyl carbonate) as the diluent fluorinated-solvents for the LiBF₄-based electrolyte solutions. LiPF₆-based conventional electrolyte as 1.0 mol dm⁻³ LiPF₆/EC:EMC (3:7 by vol.), electrolyte (a) (viscosity = 3.2 mPa s), and 1.0 mol kg⁻¹ LiBF₄/propylene carbonate (PC):TFEP:MFEC (1:2:3 by vol.)+5 mass% FEC, electrolyte (b) (viscosity = 7.1 mPa s), were injected into both LNMO/Gr-system and NCM523/Gr-system cells. Operating cell voltage of the LNMO/Gr-system cells was between 4.80-3.50 V and that of the NCM523/Gr-system cells was between 4.55-2.80 V. Charge/discharge cycle life performances of the cells were carried on under 0.1 C-rate constant current-constant voltage charge and constant current discharge at 30°C.

3. Results and Discussion

As shown in Figure 1, both the LNMO/Gr-system and the NCM523/Gr-system cells with electrolyte (b) showed higher energy density and energy retention than those of cells with electrolyte (a). On the other hand, HOMO level of TFEP and MFEC are lower than triethyl phosphate and EMC, respectively. These facts indicated that electrolyte (b), which was achieved suppression of oxidative decomposition and reduction of viscosity, improved the electrochemical performance of high-voltage-operating lithium-ion cells.

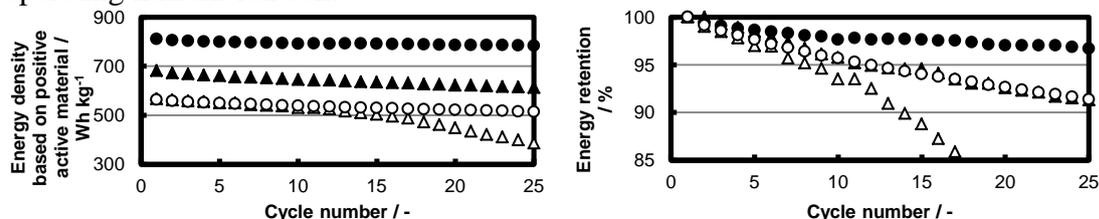


Figure 1 Charge/discharge cycle life performance of LNMO/Gr-system cells with electrolyte a(Δ), and b(\circ), and NCM523/Gr-system cells with electrolyte a(\blacktriangle), and b(\bullet).

References:

[1] Y. Yamada, *Electrochemistry* 85 (9) (2017) 559-565.

[2] T. Doi, Y Shimizu, M. Hashinokuchi, M. Inaba, *J. Electrochem. Soc.* 163 (2016) A2211-2215.