

Low-viscosity concentrated LiBF₄-based electrolyte solutions for LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ positive electrodes in lithium-ion batteries

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A LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ positive-electrode exhibits a high initial discharge capacity of ca. 200 mAh g⁻¹ by charging up to 4.3 V vs. Li/Li⁺ [1]. However, the cycle performance is poor in conventional electrolyte solutions due to the oxidative decomposition of the electrolyte at such a noble potential. In our previous work, the charge/discharge cycle performance of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ was greatly improved in the nearly saturated 8.67 mol kg⁻¹ LiBF₄/dimethyl carbonate (DMC) electrolyte solution, which has low DMC/Li⁺ molar ratio of 1.28 [2]. However, the viscosity (310 mPa s) was critically high, compared to a conventional electrolyte solution containing 1 mol dm⁻³ Li salt. To reduce the viscosity, we used fluorinated linear ether, 1,1,2,2-tetrafluoroethyl - 2,2,3,3-tetrafluoropropyl ether (HFE), as a diluting solvent. The dilution with HFE resulted in a decrease of the viscosity and concentration of LiBF₄, while the DMC/Li⁺ molar ratio slightly increased due to the low miscibility between HFE and LiBF₄/DMC.

To improve the cycle performance of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂, we replaced a part of DMC in LiBF₄/DMC+HFE with propylene carbonate (PC) which should be more stable against oxidation than DMC. The electrolyte solutions used in this study were 4.15 mol kg⁻¹ LiBF₄/DMC+HFE (2:1 in volume, DMC/Li⁺=1.56, 38 mPa s) and 4.00 mol kg⁻¹ LiBF₄/PC+DMC+HFE (1:3:2 in volume, PC+DMC/Li⁺=1.58, 55 mPa s). LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂/Li half-cells were prepared using these electrolyte solutions and cycled galvanostatically at 27.5 mA g⁻¹ between 3.0 and 4.3 V at 30°C.

In 4.15 mol kg⁻¹ LiBF₄/DMC+HFE, the discharge capacity decreased to 89.1 % of the initial one in 50 charge/discharge cycles. On the other hand, 95.5% of the initial discharge capacity (193 mAh g⁻¹) was maintained even at the 50th cycle in 4.00 mol kg⁻¹ LiBF₄/PC+DMC+HFE. The average coulombic efficiency (99.7 %) in the 50 cycles was higher than that obtained for 4.15 mol kg⁻¹ LiBF₄/DMC+HFE (99.5%). In addition, charge/discharge profiles of both cells indicated almost no change between before and after cycled. Thus, the introduction of PC into the DMC+HFE system suppressed the oxidative decomposition of electrolyte solution, and improved the charge/discharge cycle performance of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂.

References:

[1] Y. Bi *et al.*, J. Power Sources, 283 (2015) 211-218.

[2] Z. -Y. Cao *et al.*, the 58th Battery Symposium in Japan, (2017) 1E02.