**Electronic supplementary information**

# Fluoroalkyl Ether-diluted Dimethyl Carbonate-based Electrolyte Solutions for High-voltage Operation of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ Electrodes in Lithium Ion Batteries

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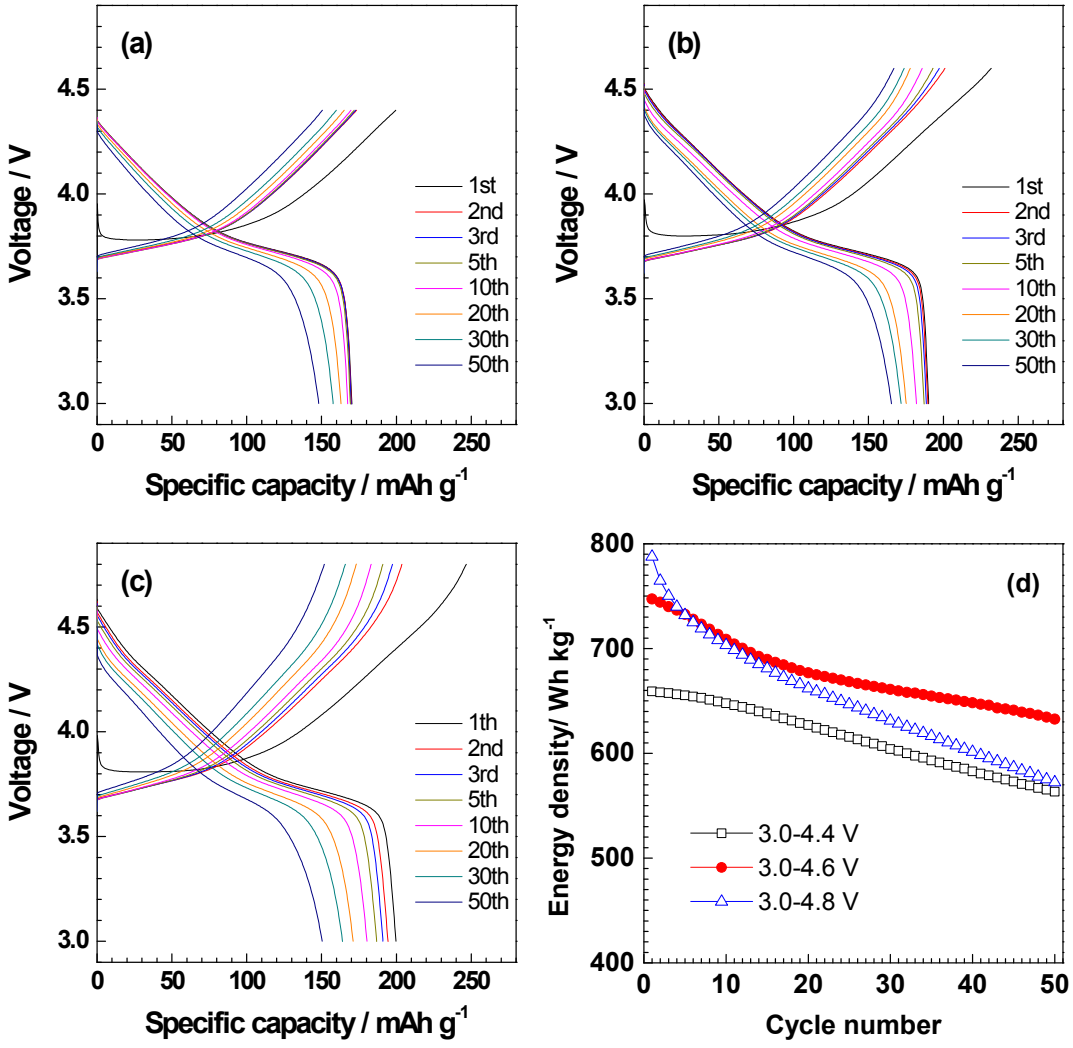


**Figure S1.** (a-c) Charge and discharge curves of Li|$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cells using 1 M $LiPF_6$/EC+DEC (1:1 by volume). Charge/discharge tests were carried out at 30 °C at a C/10 rate (ca. 120 μA $cm^{-2}$) between 3.0 and (a) 4.4, (b) 4.6, and (c) 4.8 V. (d) Variation of discharge capacities of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ with cycle number in 1 M $LiPF_6$/EC+DEC. The charging cut off voltages were 4.4, 4.6, and 4.8 V.

**Table S1.** Charge, discharge, and irreversible capacities and Coulombic efficiency in the 1st cycle, and capacity retention and energy density at the 50th cycle of Li|$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cells using 1 M $LiPF_6$/EC+DEC (1:1 by volume).

| | 1st cycle | | | | 50th cycle | |
|---|---|---|---|---|---|---|
| Charging cut-off voltage | Charge capacity | Discharge capacity | Irreversible capacity | Coulombic efficiency | Capacity retention [a)] | Energy density |
| | (mAh $g^{-1}$) | (mAh $g^{-1}$) | (mAh $g^{-1}$) | (%) | (%) | (Wh $kg^{-1}$) |
| 4.4 | 200 | 170 | 30 | 85.3 | 87.1 | 563 |
| 4.6 | 232 | 190 | 42 | 82.0 | 86.9 | 632 |
| 4.8 | 247 | 200 | 47 | 81.0 | 75.3 | 572 |

[a)]defined as percent ratios of discharge capacity in the 50th cycle to that in the 1st cycle.

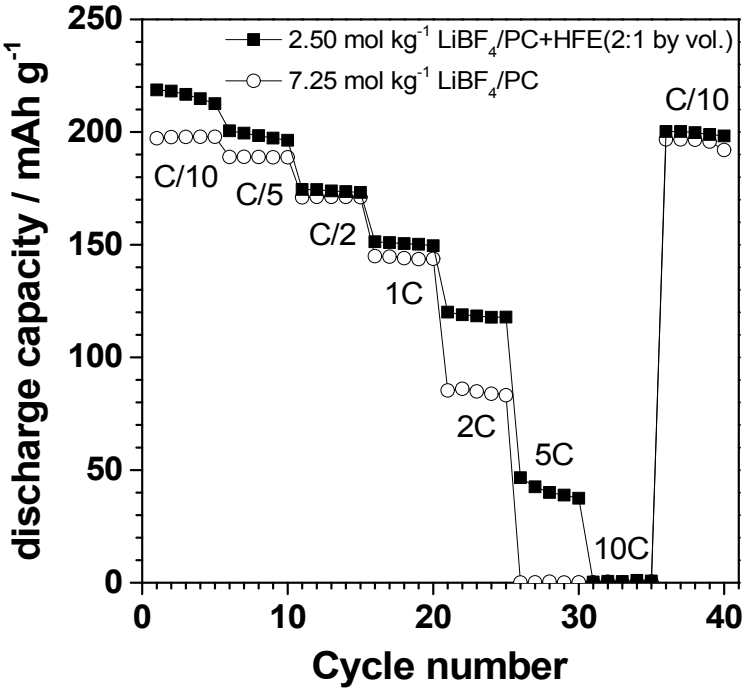


**Figure S2.** Rate performance of Li|$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cells with 2.50 mol $kg^{-1}$ $LiBF_4$/PC+HFE (2:1, PC/$Li^+$ molar ratio=2.39) and nearly saturated 7.25 mol $kg^{-1}$ $LiBF_4$/PC (PC/$Li^+$=1.35). The discharge capacities decreased with an increase in discharge rate in both solutions, but 2.50 mol $kg^{-1}$ $LiBF_4$/PC+HFE (2:1) provided a higher capacity at any rate than 7.25 mol $kg^{-1}$ $LiBF_4$/PC.

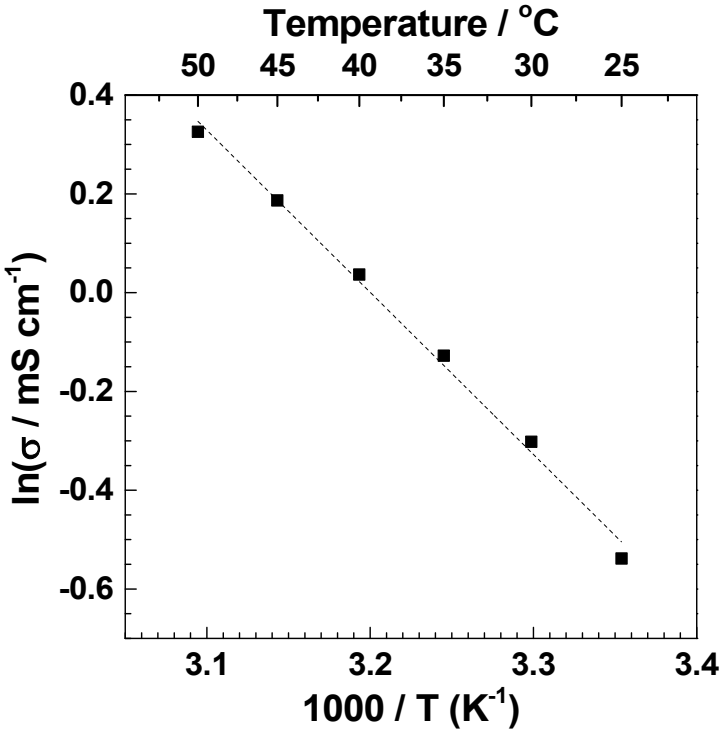


**Figure S3.** Ionic conductivity of 2.50 mol $kg^{-1}$ $LiBF_4$/PC+HFE (2:1, PC/Li molar ratio=2.39). A line was drawn using the least-squares method, and the activation energy was evaluated to be 27 kJ $mol^{-1}$.

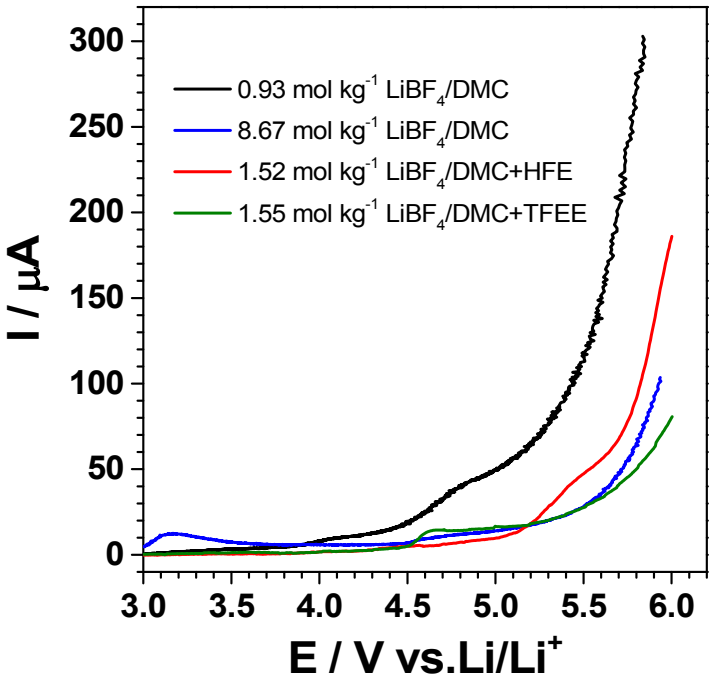


**Figure S4.** Linear sweep voltammograms of Pt in a potential range from 3.0 to ca. 6 V. The reference and counter electrodes were Li foil. The scan rate was 1 mV $s^{-1}$.

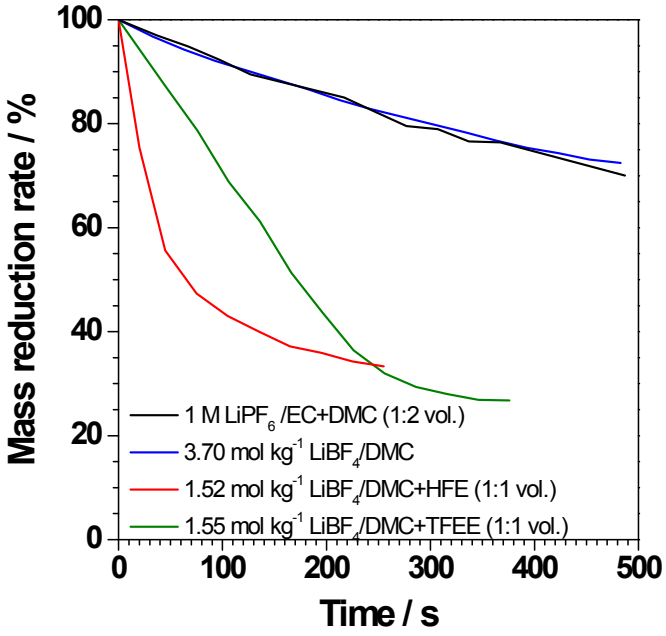


**Figure S5.** Mass reduction rate of electrolyte solutions in a glovebox with a dew point of -92 $^{o}$C and ambient temperature of 27 $^{o}$C. About 100 mg of each electrolyte solution was put on an electric balance, and then the variation of the mass with time was measured. HFE- and TFEE-diluted electrolyte solutions were more volatile than the conventional 1 M $LiPF_6$/EC+DMC.