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Supplementary Information

Approaching the Maximum Capacity of Nickel-Rich $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ Cathode by Charging to High-Voltage in Non-Flammable Electrolyte of Propylene Carbonate and Fluorinated Linear Carbonates

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Experimental Methods

Preparation, characterization and fire-test of non-flammable electrolyte: Conventional electrolyte of 1M $LiPF_6$/ethylene carbonate (EC): ethyl methyl carbonate (EMC) (3:7 volume ratio) was used as purchased (Panax E-Tec), and lithium hexafluorophosphate ($LiPF_6$) and propylene carbonate (PC) as purchased (Sigma-Aldrich). Methyl (2,2,2-trifluoroethyl) carbonate (FEMC) and di-(2,2,2 trifluoroethyl) carbonate (DFDEC) were supplied by Lichem Co., Ltd. Our non-flammable electrolyte was prepared by dissolving 1M $LiPF_6$ salt in the mixture of PC:FEMC:DFDEC at a 3:2:5 volume ratio. Room temperature ionic conductivity of conventional electrolyte and non-flammable electrolyte are 9.19 and 3.08 mS cm^{-1}, respectively, which was measured using ionic conductivity meter (Mettler Toledo S230).

Electrochemistry: Linear sweep voltammetry (LSV) of electrolytes was conducted to evaluate the anodic stability of electrolytes at a scan rate of 1 mV s^{-1} from open-circuit potential (OCP) of ~3.0 to 7.0 V versus Li/Li^+. A three-electrodes cell was used with platinum disk (Ø = 14 mm) as a working electrode, and lithium metal as a counter electrode and a reference electrode, and conventional electrolyte or our non-flammable electrolyte.

The cathode was prepared by coating the slurry, which was composed of 80 wt% $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NCM811; received from a cathode active material manufacturer in Korea (confidential)) active material, 10 wt% carbon black (super-P, Timcal) and 10 wt% polyvinylidenefluoride binder (PVdF, Aldrich) in *N*-methyl-2-pyrrolidone (NMP, Aldrich) solvent, onto an aluminum foil, followed by vacuum drying at 60 °C for 2 h and at 110 °C overnight. The average active material mass loading was ~3.0 $mgcm^{-2}$. Lithium 2032 coin half-cells, consisting of NCM811 cathode as a working electrode, Li metal foil as a counter electrode, separator (Celgard C210), and conventional electrolyte of 1M $LiPF_6$/EC:EMC or non-flammable electrolyte of 1M $LiPF_6$/PC:FEMC:DFDEC, were assembled in an argon-filled glove box (MOTek) with water and oxygen contents less than 1 ppm. Their cycling

performance was tested in the voltage ranges of 2.7−4.2, 4.3, 4.4, 4.5 and 4.6 V, respectively at 0.2C (40 mAg^{-1}) at room temperature, using a multichannel battery cycler (WBCS3000, Won-A Tech). Cycling performance displayed in Figures 2b,c and 3 includes two formation cycles at 0.1C. Rate capability of half-cell was tested at 0.1C, 0.2C, 0.5C, 1C, 2C, 5C and 10C. The AC impedance spectra were collected during cycling in the frequency range of 10 mHz–100 kHz with an amplitude of 10 mV, using an impedance spectroscopic analyzer (Bio Logic SAS), after the cells were fully discharged to 2.7 V at the given cycle number followed by letting them at open circuit voltage (OCV) till reaching the equilibrium. For full-cell fabrication, graphite anode was prepared by coating the slurry, which was composed of 85 wt% artificial graphite active material (SDK, Japan), 5 wt% carbon black (super-P, Timcal) and 10 wt% binder of sodium carboxymethyl cellulose (CMC; MW 250,000, Aldrich) mixed with styrene butadiene rubber (SBR) in water, on a copper foil. The N/P ratio was 1.1. Lithium 2032 coin full-cells, consisting of NCM811 cathode, graphite anode, separator (Celgard C210) and non-flammable electrolyte of 1M $LiPF_6$/PC:FEMC:DFDEC without and with 1 wt% vinylene carbonate (VC; Aldrich) additive, were assembled in an argon-filled glove box (MOTek). Their first and second charge-discharge cycles were tested between 2.7 and 4.45 V (corresponding to 4.5 V versus Li/Li^+) at 0.1C (20 mAg^{-1}) at room temperature, using a multichannel battery cycler (WBCS3000, Won-A Tech).

Rate capability of Li||NCM811 half-cells

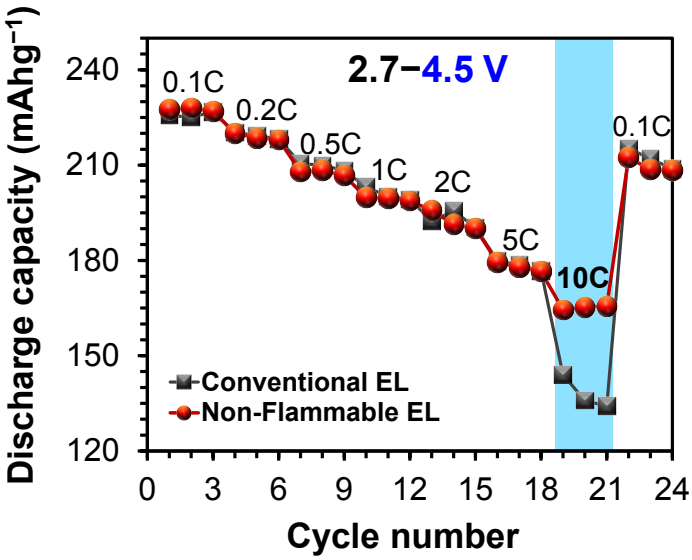

Fig. S1. Rate capability of Li NCM811 half-cells with conventional electrolyte of 1M $LiPF_6$/EC:EMC and non-flammable electrolyte of 1M $LiPF_6$/PC:FEM:DFDEC.