Supporting Information

Comparative Study of Ni-rich Layered Cathodes for Rechargeable Lithium Batteries: Li[Ni$_{0.85}$Co$_{0.11}$Al$_{0.04}$]O$_2$ and Li[Ni$_{0.84}$Co$_{0.06}$Mn$_{0.09}$Al$_{0.01}$]O$_2$ with Two-Step, Full Concentration Gradients

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Experimental

Material synthesis: To synthesize the TSFCG-Al Li[$Ni_{0.84}Co_{0.06}Mn_{0.09}Al_{0.01}$]$O_2$ layered oxide cathode material, an $NiSO_4 \cdot 6H_2O$ solution in tank 1 was used as the starting material for the co-precipitation process. Then, an Ni-less aqueous solution consisting of $NiSO_4 \cdot 6H_2O$ and $CoSO_4 \cdot 7H_2O$ (molar ratio of Ni:Co= 90:10) in tank 2 was slowly pumped into tank 1. Simultaneously, the homogeneously mixed solution in tank 1 was fed into a batch reactor (40 L) that was filled with certain amounts of deionized water, an NH_4OH solution (aq.), and an NaOH solution (aq.) in a replenished N_2 atmosphere. At the same time, a 4.0 mol L^{-1} NaOH solution (aq.) (molar ratio of sodium hydroxide to transition metal = 2.0) and an NH_4OH chelating agent solution (aq.) (molar ratio of ammonium hydroxide to transition metal = 1.0) were pumped separately into the reactor. During the early stages of the process, $Ni(OH)_2$ (the center composition) was co-precipitated first. Nickel-cobalt-manganese hydroxides with different compositions were then gradually coated onto the formed $Ni(OH)_2$ particles, resulting in a designed composition of Ni, Co, and Mn toward the outer surface of the particles. In order to synthesize the TSFCG hydroxide precursor with the second concentration gradient layer, an aqueous solution in tank 3 with an Ni-poor concentration consisting of $NiSO_4 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, and $MnSO_4 \cdot 5H_2O$ (molar ratio of Ni:Co:Mn = 67:6:27) was slowly pumped into the mixed solution in tank 1. The precursor powders were obtained by filtering, washing, and drying in a vacuum oven at 110 ^{o}C overnight. The obtained TSFCG [$Ni_{0.85}Co_{0.05}Mn_{0.10}$]$(OH)_2$ was mixed with $LiOH \cdot H_2O$ and $Al(OH)_3 \cdot xH_2O$ (Li/(Ni + Co + Mn + Al) = 1.01 and Al/(Ni + Co + Mn + Al) = 0.01 in a molar ratio), and the mixture was calcined at 750 ^{o}C for 15 h in oxygen.

To synthesize Li[$Ni_{0.85}Co_{0.11}Al_{0.04}$]$O_2$, an aqueous solution consisting of $NiSO_4 \cdot 6H_2O$ and $CoSO_4 \cdot 7H_2O$ (molar ratio of Ni:Co = 88:12) with a concentration of 2.0 mol L^{-1} was fed into

a batch reactor (40 L) that was filled with certain amounts of deionized water, a NH_4OH solution (aq.), and an NaOH solution (aq.) in a replenished N_2 atmosphere. At the same time, a 4.0 mol L^{-1} NaOH solution (aq.) (molar ratio of sodium hydroxide to transition metal = 2.0) and an NH_4OH chelating agent solution (aq.) (molar ratio of ammonium hydroxide to transition metal = 1.0) were pumped separately into the reactor. The pH, temperature, and stirring speed of the mixture in the reactor were carefully controlled. The precursor powders were obtained by washing, filtering, and drying. The synthesized $[Ni_{0.88}Co_{0.12}](OH)_2$ hydroxide precursor, obtained via the co-precipitation process, was mixed with $LiOH \cdot H_2O.Al(OH)_3 \cdot xH_2O$ (Li/(Ni + Co + Al) = 1.01 and Al/(Ni + Co + Al) = 0.04 in a molar ratio) and calcined at 750 ^{o}C for 10 h in oxygen.

Material characterization: The chemical compositions of the powders were analyzed via inductively coupled plasma spectrometry (ICP-MS, NexION 300). The chemical composition of the prepared powders was determined using inductively coupled plasma (ICP, OPIMA 8300, Perklin Elmer). Powder X-ray diffraction (XRD) (Rigaku, Rint-2000) using Cu Kα radiation was employed to identify the crystalline phases of the prepared powders. XRD data were obtained between 10 and 80° 2θ with a step size of 0.03^o, and the collected XRD data were analyzed by the Rietveld refinement program Fullprof.[1] To obtain the localized composition, cross-sections of the TSFCG-Al particles were prepared by focused-ion beam (FIB) and examined with a JEOL, Model JEM 2100F instrument. Line scans of the polished surfaces were analyzed with an electron probe micro-analyzer (EPMA, JXA-8500f, JEOL); beam size: 1μm, accelerating voltage: 15 kV, current: 10 nA, standard used: pure metal (100%). The morphologies of the prepared powders were observed using scanning electron microscopy (SEM, JSM-6340F, JEOL).

Electrochemical evaluation: To fabricate the cathode material, the working electrode consists of 85 wt. % of the prepared powders, 7.5 wt. % of carbon, and 7.5 wt. % of poly(vinylidene fluoride) (PVDF) binder. The obtained slurry was coated onto Al foil and roll-pressed. The coated electrodes were dried overnight at 120 ^{o}C in a vacuum prior to use. The electrolyte solution was 1.2 M $LiPF_6$ in ethylene carbonate-ethyl methyl carbonate (EC:EMC = 3:7 by volume with 2 wt. % of a vinylene carbonate (VC), which decreases the surface impedance of cathode materials[2] PANAX ETEC Co.). Electrochemical testing was performed in a 2032 coin-type cell adopting Li metal as the anode. The cells were typically cycled in the constant current mode at a rate of 0.5 C within the voltage range of 2.7 – 4.3 V versus Li+/Li (where 1 C = 200 mA g^{-1}). AC impedance measurements were performed with an impedance analyzer (Bio-Logic, VMP3) over the frequency range of 1 MHz to 10 mHz with an amplitude of 10 mV$_{rms}$.

Thermal properties of delithiated state: For the differential scanning calorimetry (DSC) analysis, 2032 coin-type cells were charged to 4.3 V and opened in an Ar-filled dry room. After the remaining electrolyte was carefully removed from the surface of the electrode, the cathode materials were recovered from the current collector. A stainless steel sealed pan with a gold-plated copper seal was used to collect 3 – 5 mg samples. Measurements were performed using a DSC 200 PC (Netzsch, Germany) at a temperature scan rate of 1 °C min^{-1}.
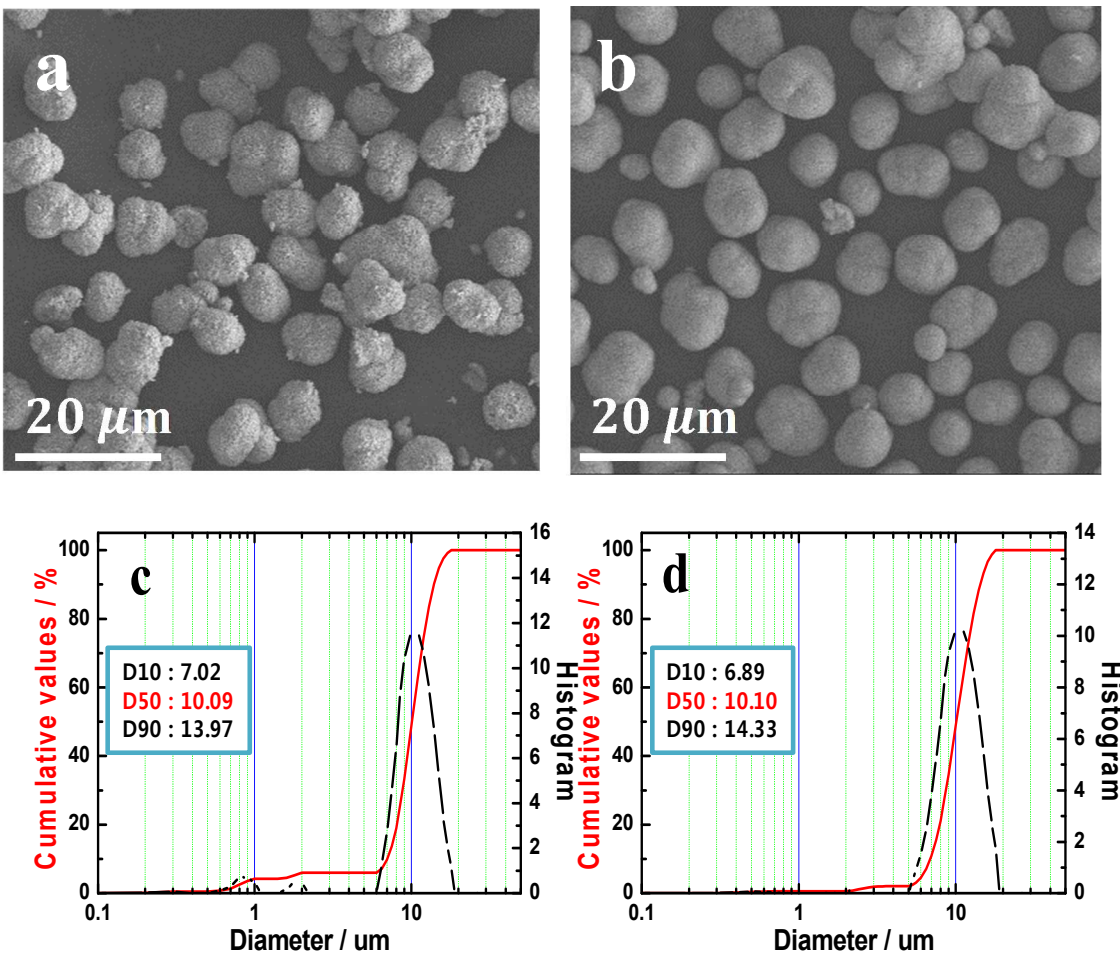
Figure SI 1. Low magnification SEM images of (a) Li[Ni$_{0.85}$Co$_{0.11}$Al$_{0.04}$]O$_2$ NCA and (b) Li[Ni$_{0.84}$Co$_{0.06}$Mn$_{0.09}$Al$_{0.01}$]O$_2$ TSFCG-Al and the resulting particle size distribution of (c) NCA and (d) TSFCG-Al.
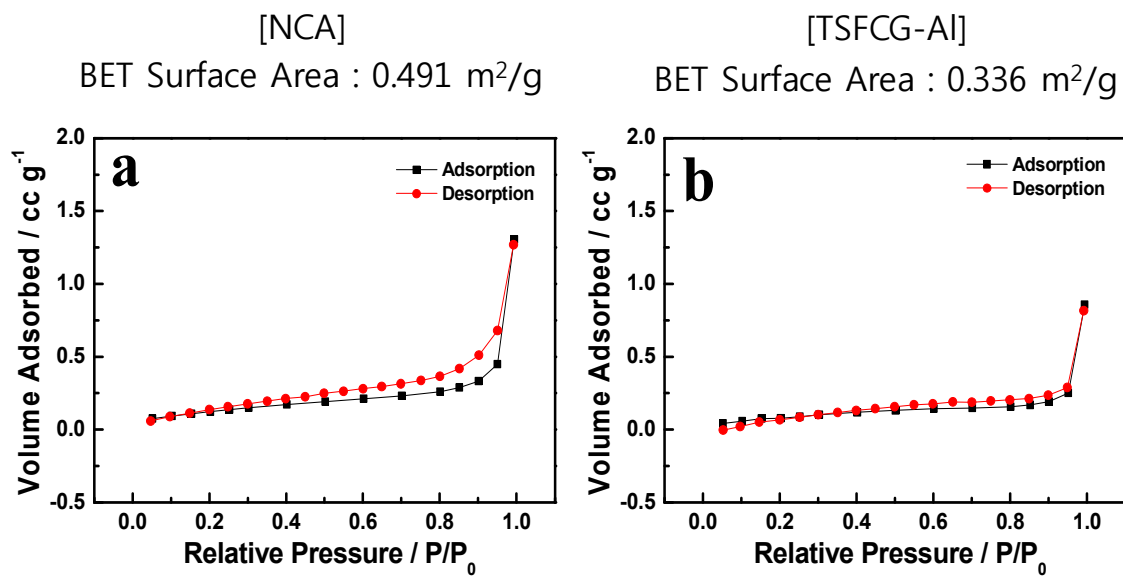
Figure SI 2. BET surface area measurement plots for (a) Li[Ni$_{0.85}$Co$_{0.11}$Al$_{0.04}$]O$_2$ NCA and (b) Li[Ni$_{0.84}$Co$_{0.06}$Mn$_{0.09}$Al$_{0.01}$]O$_2$ TSFCG-Al.
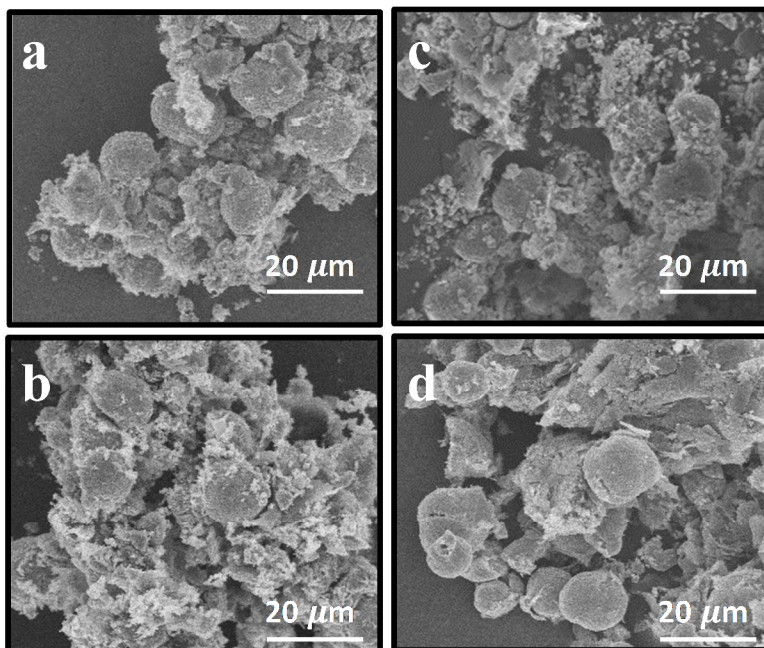
Figure SI3. SEM images of as prepared electrode of (a) Li[Ni$_{0.85}$Co$_{0.11}$Al$_{0.04}$]O$_2$ NCA and (b) Li[Ni$_{0.84}$Co$_{0.06}$Mn$_{0.09}$Al$_{0.01}$]O$_2$ TSFCG-Al, and cycled electrode after 100 cycles at 4.5 V of (c) Li[Ni$_{0.85}$Co$_{0.11}$Al$_{0.04}$]O$_2$ NCA and (d) Li[Ni$_{0.84}$Co$_{0.06}$Mn$_{0.09}$Al$_{0.01}$]O$_2$ TSFCG-Al.
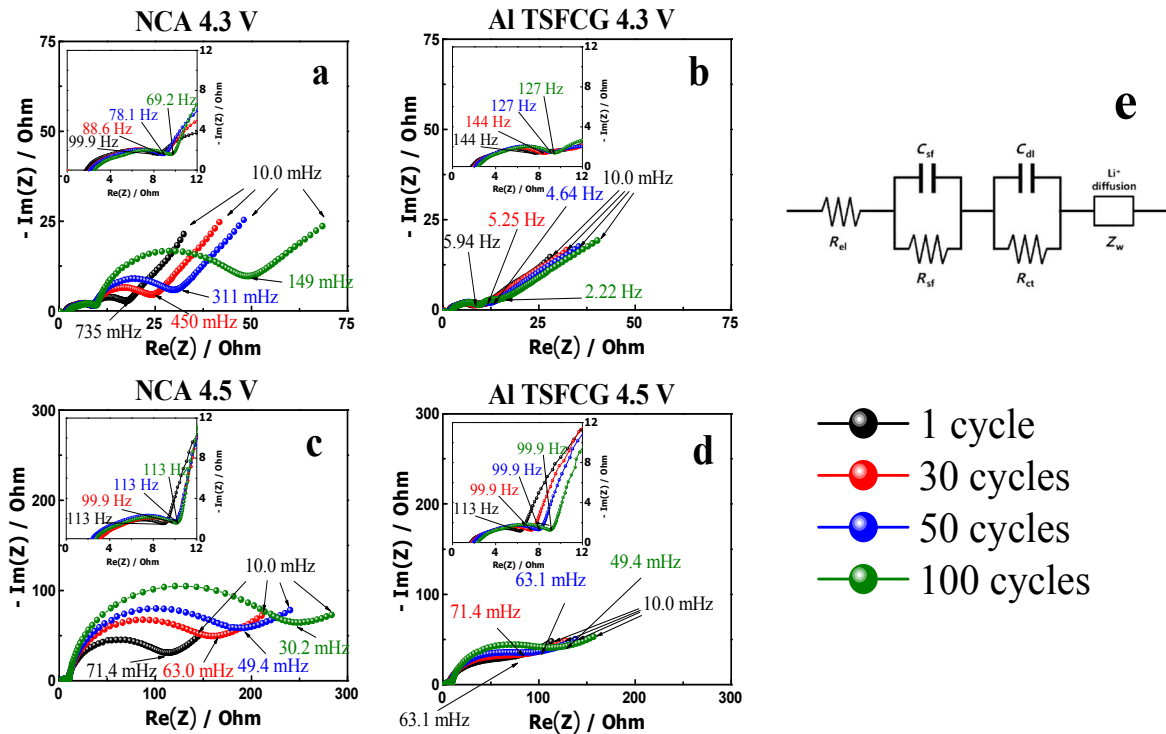
Figure SI4. Electrochemical impedance spectra (Nyquist plots) of (a) $Li[Ni_{0.85}Co_{0.11}Al_{0.04}]O_2$ NCA and (b) $Li[Ni_{0.84}Co_{0.06}Mn_{0.09}Al_{0.01}]O_2$ TSFCG-Al in the voltage ranges of 2.7-4.3 V and (c) $Li[Ni_{0.85}Co_{0.11}Al_{0.04}]O_2$ NCA and (d) $Li[Ni_{0.84}Co_{0.06}Mn_{0.09}Al_{0.01}]O_2$ TSFCG-Al in the voltage ranges of 2.7-4.5V as function of the number of cycles at a current of 100 mA g^{-1} (0.5 C rate); (e) Equivalent circuit used for fitting.

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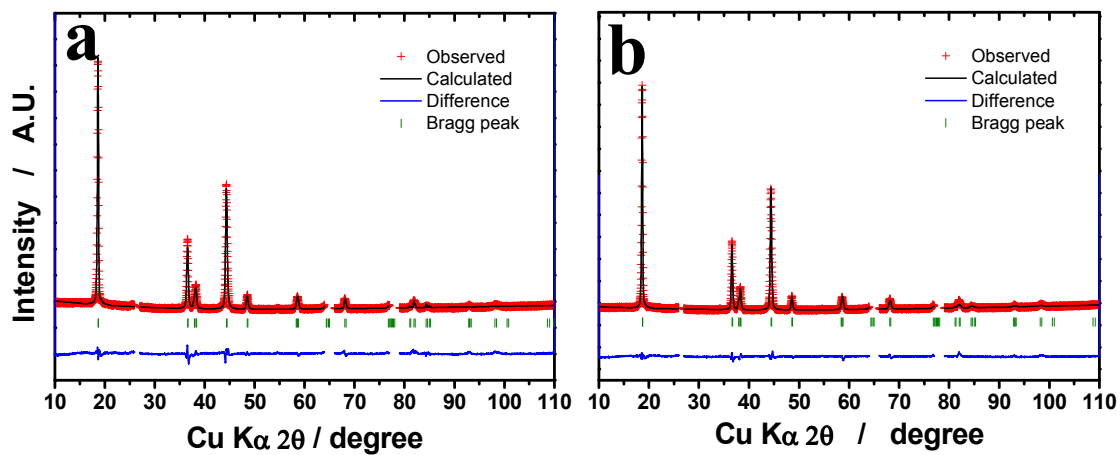
Figure SI5. Rietveld refinement results of XRD patterns of (a) Li[Ni$_{0.85}$Co$_{0.11}$Al$_{0.04}$]O$_2$ NCA and (b) Li[Ni$_{0.84}$Co$_{0.06}$Mn$_{0.09}$Al$_{0.01}$]O$_2$ TSFCG-Al electrodes after 100 cycles with an upper cutoff voltage of 4.5 V.
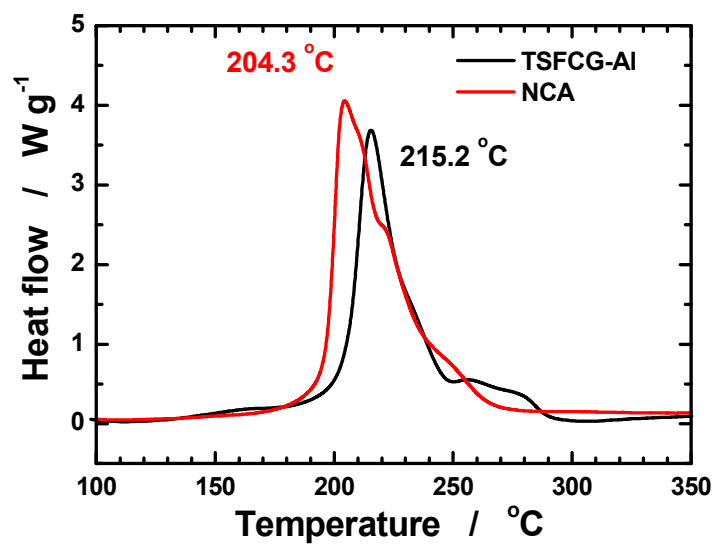
Figure SI6. Differential scanning calorimetry (DSC) results of Li[Ni$_{0.85}$Co$_{0.11}$Al$_{0.04}$]O$_2$ NCA and Li[Ni$_{0.84}$Co$_{0.06}$Mn$_{0.09}$Al$_{0.01}$]O$_2$ TSFCG-Al charged to 4.3 V.

Table S1. Fitted R_{sf} and R_{ct} of $Li[Ni_{0.85}Co_{0.11}Al_{0.04}]O_2$ NCA and $Li[Ni_{0.84}Co_{0.06}Mn_{0.09}Al_{0.01}]O_2$ TSFCG-Al electrodes upon charging after various cycles.

Cycle number	TSFCG-Al				NCA			
	4.3 V		4.5 V		4.3 V		4.5 V	
	R_{sf}/Ω	R_{ct}/Ω	R_{sf}/Ω	R_{ct}/Ω	R_{sf}/Ω	R_{ct}/Ω	R_{sf}/Ω	R_{ct}/Ω
1 cycle	5.6	2.9	4.6	69.0	5.5	9.2	6.1	101.8
30 cycles	6.2	3.1	5.5	75.8	5.8	15.2	6.8	144.4
50 cycles	6.9	3.5	6.1	85.9	6.7	20.8	7.5	175.0
100 cycles	7.0	5.8	6.7	105.7	7.2	39.1	7.4	233.4

Table S2. Rietveld refinement results of XRD data for extensively-cycled Li[$Ni_{0.85}Co_{0.11}Al_{0.04}$]$O_2$ NCA and Li[$Ni_{0.84}Co_{0.06}Mn_{0.09}Al_{0.01}$]$O_2$ TSFCG-Al (after 100 cycles).

	Ni^{2+} in Li site / %	a / Å	c / Å	R_{wp} / %
NCA to 4.3 V	5.5	2.8650(1)	14.2231(4)	10.4
NCA to 4.5 V	6.8	2.8646(1)	14.2459(1)	12.9
TSFCG-Al to 4.3 V	3.4	2.8749(2)	14.2185(2)	14.1
TSFCG-Al to 4.5 V	4.1	2.8754(2)	14.2246(2)	14.2

REFERENCE

(1)   T Roisnel, J. Rodriguez-Carjaval, *Fullprof Manual*, Institut Laue- Langevin, Grenoble, France, 2002.

(2) Aurbach, D.; Gamolsky, K.; Markovksy, B.; Gofer, Y.; Schmidt, M.; Heider, U. On the use of vinylene carbonate (VC) as an additive to electrolyte solutions for Li-ion batteries *Electrochim. Acta* **2002**, *47*, 1423-1439