Supplementary Information

Resolving the degradation pathways on O3-type layered oxides cathode surface through the nano-scale aluminum oxide coating for high-energy density sodium-ion batteries

Jang-Yeon Hwang,[a] Seung-Taek Myung,[b] Ji Ung Choi,[b] Chong Seung Yoon,[c] Hitoshi Yashiro,[d] Yang-Kook Sun[a,*]

[a]Department of Energy Engineering, Hanyang University, Seoul, 04763, Republic of Korea

[b]Department of Nanotechnology and Advanced Materials Engineering & Sejong Battery Institute, Sejong University, Seoul, 05006, South Korea

[c]Department of Materials Science and Engineering, Hanyang University, Seoul, 04763, Republic of Korea

[d]Department of Chemistry and Bioengineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551, Japan

* To whom correspondence should be addressed.

Phone: (82) 2220-1749. Fax: (82) 2298-5416. E-mail: yksun@hangyang.ac.kr

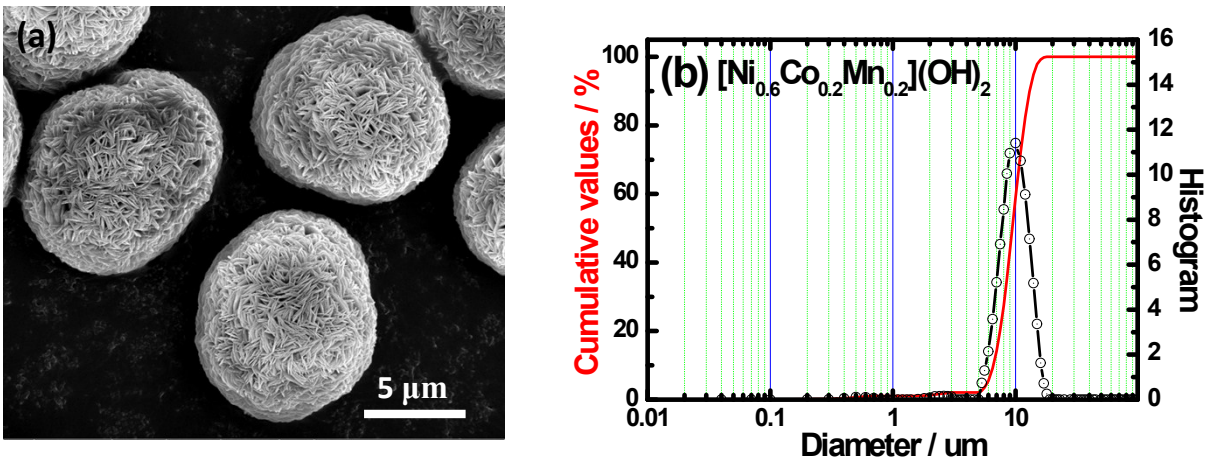

Fig. S1 (a) Scanning electron microscopy (SEM) image and (b) particle size analysis (PSA) of the $[Ni_{0.6}Co_{0.2}Mn_{0.2}](OH)_2$ precursor.

Table S1. ICP-AES results for the $[Ni_{0.6}Co_{0.2}Mn_{0.2}](OH)_2$ precursor.

Metal stoichiometry determined by ICP-AES			
Sample	Ni	Co	Mn
$[Ni_{0.6}Co_{0.2}Mn_{0.2}](OH)_2$	0.61	0.21	0.19

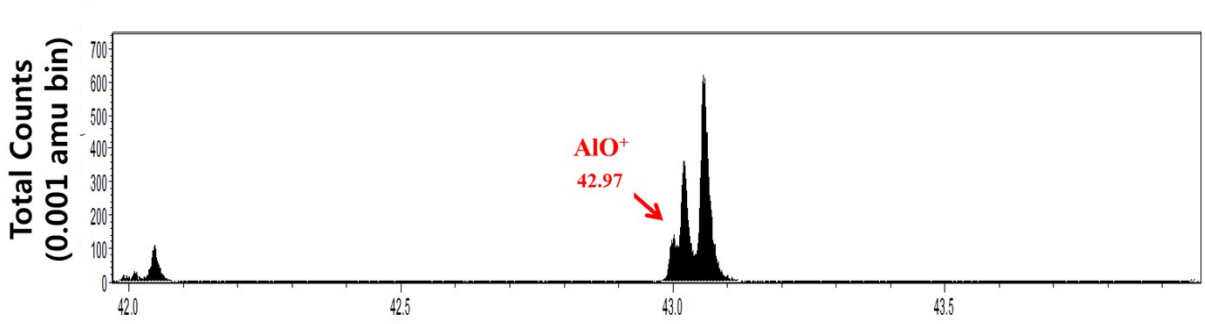

Fig. S2 ToF-SIMS spectra of the outmost surface of the Al_2O_3 coated $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ cathode.

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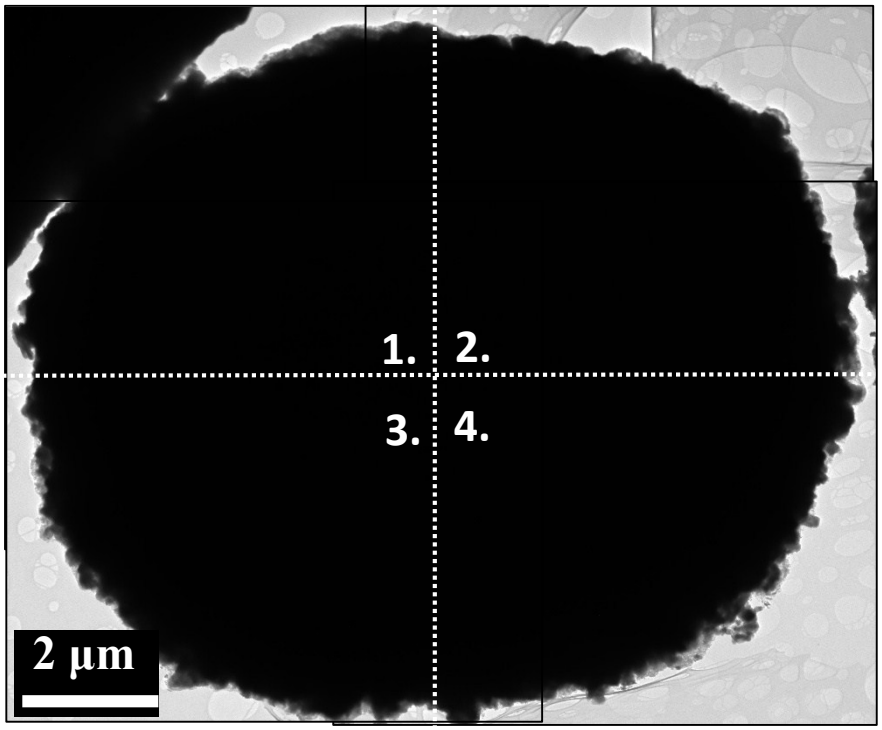

Fig. S3 Mosaic TEM image of Al_2O_3 coated $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ particle.

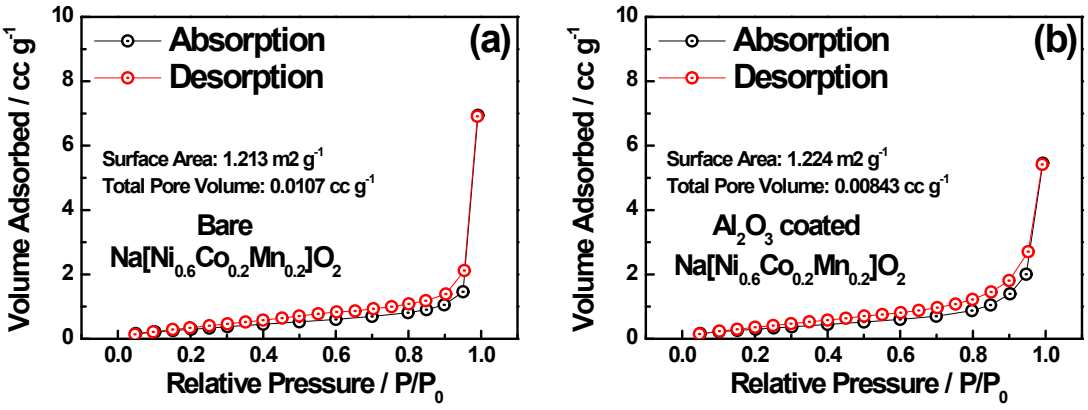

Fig. S4 Isotherm profiles with surface area and total pore volume of bare $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ and Al_2O_3 coated $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ cathodes.

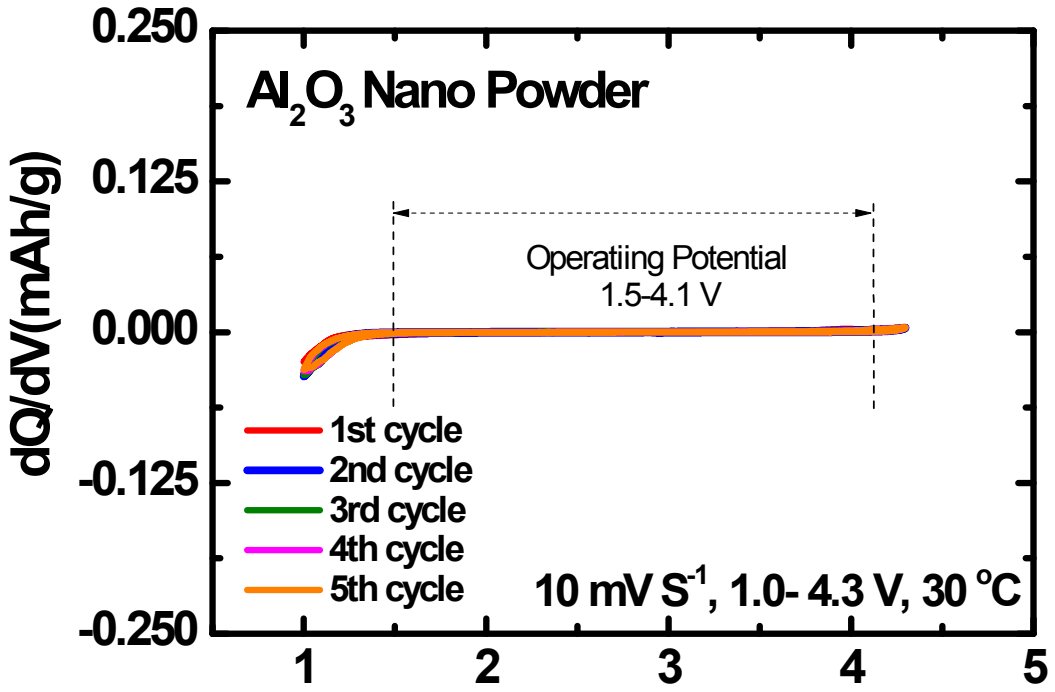

Fig. S5 Cyclic voltammetry (CV) curves of Al_2O_3 nano powder.

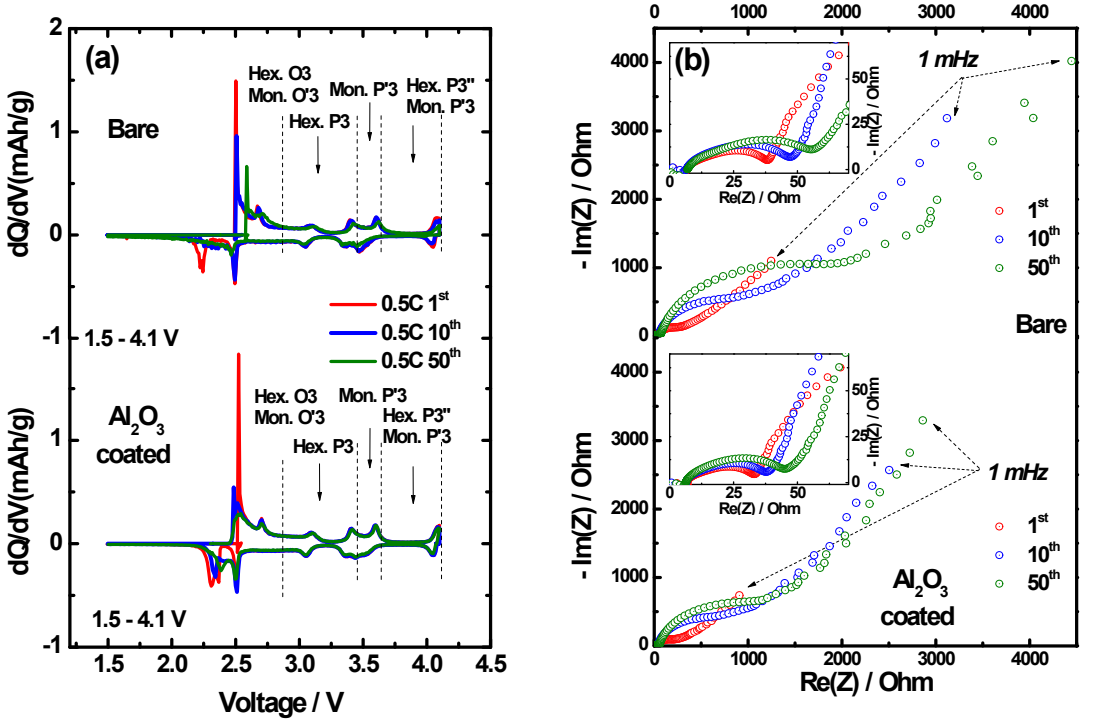

Fig. S6 (a) dQ dV^{-1} (mAh g^{-1}) curves and (b) electrochemical impedance spectroscopy (EIS) results for bare $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ and Al_2O_3 coated $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ cathodes during cycling at a 0.5 C rate (75 mA g^{-1}) in a half cell.

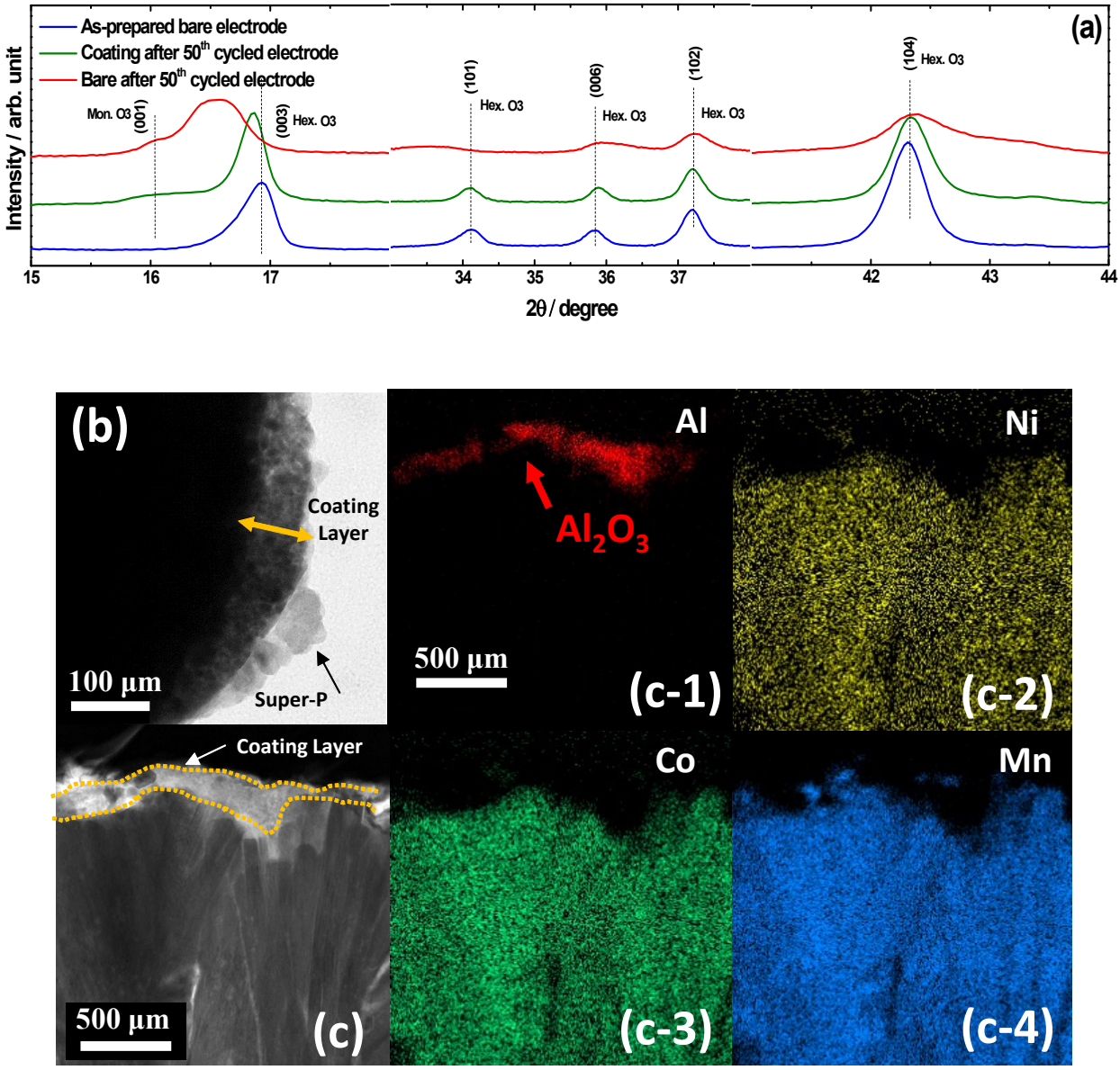

Fig. S7 Post-cycling study: (a) ex-situ XRD results before and after cycling for bare $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ and Al_2O_3 coated $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ electrodes. (b) Bright field TEM image and (c) cross sectional TEM image with (c-1 to c-4) corresponding EDX mapping results for cycled Al_2O_3 coated $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ cathode in a half cell.

Table S2. Electrochemical impedance spectroscopy (EIS) results for pouch-type bare $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$/hard carbon full cell and Al_2O_3 coated $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$/hard carbon full cell at the 1^{st} and 300^{th} cycles at a 0.5 C rate (75 mA g^{-1}).

Cathode materials	Cycles	R_{sf} (Ω)	R_{ct} (Ω)
Bare	**1^{st}**	3.7	12.8
$Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$	**300^{th}**	11.7	220.2
Al_2O_3 coated	**1^{st}**	3.2	10.7
$Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$	**300^{th}**	3.1	77.5

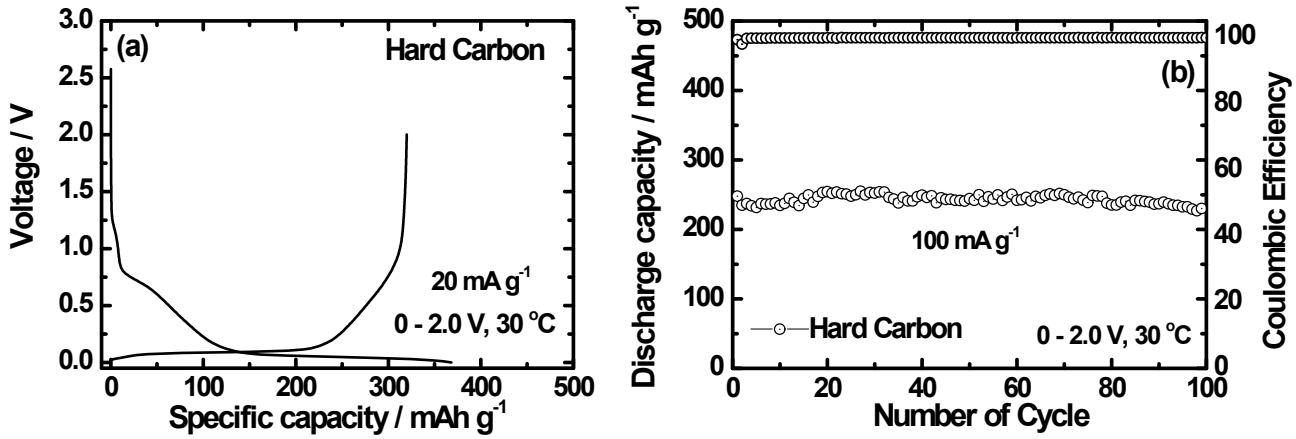

Fig. S8 Electrochemical performance of hard carbon electrode: (a) 1st discharge-charge curves at 20 mA g^{-1} and (b) cycle life test at 100 mA g^{-1} in the voltage range of 0–2.0 V.

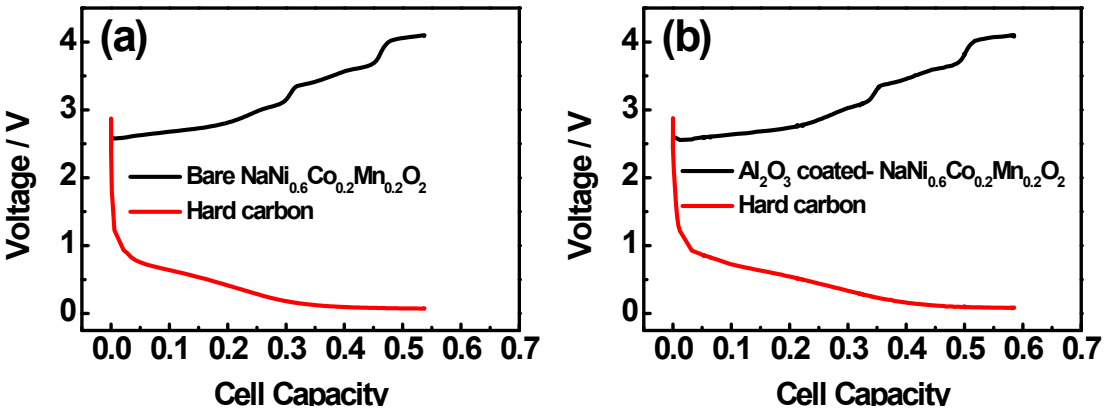

Fig. S9 Galvanostatic voltage profiles of (a) bare $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$/hard carbon and (b) Al_2O_3 coated $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$/hard carbon cells upon charge process.

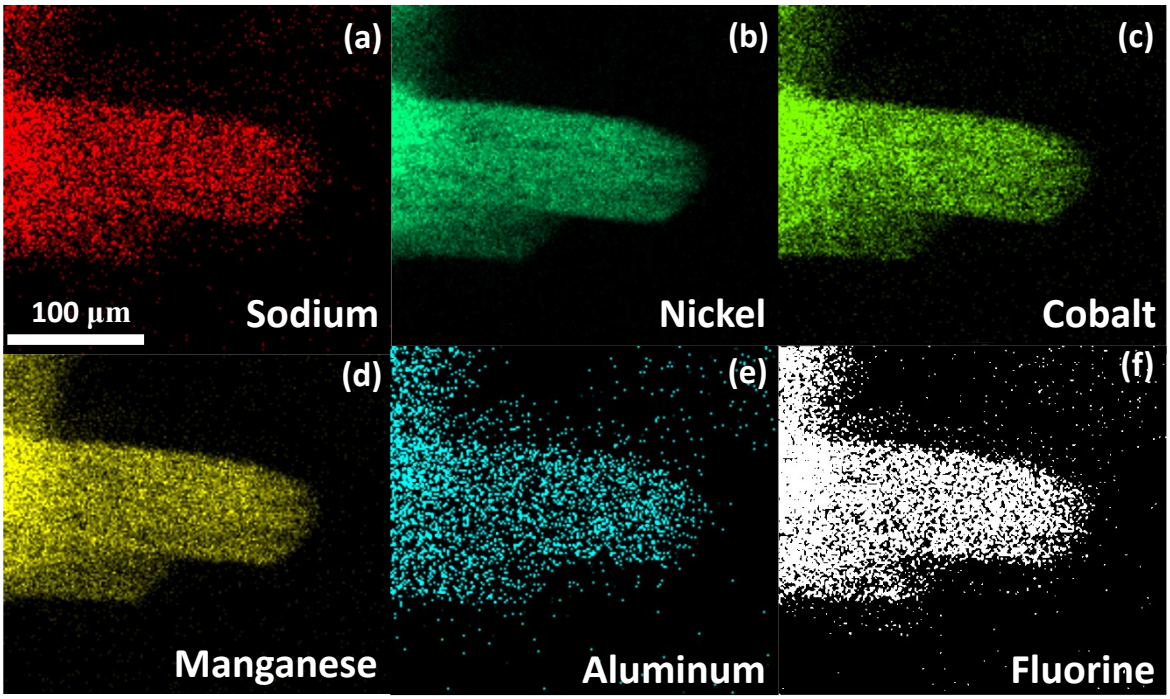

Fig. S10 TEM EDX mapping data of cycled Al_2O_3 electrode collected from pouch-type full cell: (a) sodium, (b) nickel, (c) cobalt, (d) manganese, (e) aluminum and (f) fluorine.

Table S3. HF amounts in bare $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ and Al_2O_3 coated $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ cathodes collected from pouch-type full cells after 300 cycles.

Sample	HF Amount (ppm)
Blank	50.02526
Bare $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ cathode	349. 6795
Al_2O_3 coated $Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ cathode	83.33222

Table S4. Estimated energy density calculation and individual mass fraction based on pouch cell parameters of traditional LIB cells.

Energy Density Calculation (Wh/kg)						
		Energy Density Calculation (Wh/kg)		Value	Quantity	weight
N/P ratio	1.15					
Cathode	Cathode	Capacity (mAh/g)		151		
		Working potential (vs Na+)		3		
		Composition of Active material		0.95		
		Mass Loading of active materials (mg/cm^2)		25	7.5	7.894737
		Length (mm)		50		
		Width (mm)		30		
		Area capacity (mAh/cm^2)		3.75		
	Al foil	Thickness (mm)		0.012	10	0.48
	Cathode tab				1	0.04
	Anode	Capacity (mAh/g)		300		
		Working potential (vs Na$^+$)		0		
		Composition of Active material		0.95		
		Mass Loading of active materials (mg/cm^2)		14.375	4.543	4.784

		Length (mm)				51		
		Width (mm)				31		
		Area capacity (mAh/cm^2)				4.3125		
	Cu foil	Thickness (mm)				0.008	11	1.265
	Anode tab						1	0.13
	Packing foil	Thickness (mm)				0.086	1	0.6
	Electrolyte							4
	Separator	Thickness (mm)				0.011		0.33
	Sealant						1	0.01
					Cell weight (g)			19.534

Cell Size (mm x mn)		Layers	Cell weight (g)	Cell capacity (mAh)	Voltage (V)	Energy density (Wh/kg)
35	57.5	20	19.53	843.75	3	130.23