Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Experimental Considerations to Study Li-Excess Disordered Rock Salt Cathode Materials

Hyeseung Chung,[a] Zachary Lebens-Higgins,[b] Baharak Sayahpour,[a] Carlos Mejia,[a] Antonin Grenier,[c] Gabrielle E. Kamm,[c] Yixuan Li,[a] Ricky Huang,[a] Louis F.J. Piper,[b] Karena W. Chapman,[c] Jean-Marie Doux,*[a] and Ying Shirley Meng*[a]

[a] Department of Nanoengineering, University of California San Diego, La Jolla, California 92093, USA

[b] Department of Physics, Applied Physics and Astronomy, Binghamton University, Binghamton, New York 13902, USA

[c] Department of Chemistry, Stony Brook University, Stony Brook, New York 11794, USA

* Correspondence to: shirleymeng@ucsd.edu, jdoux@ucsd.edu

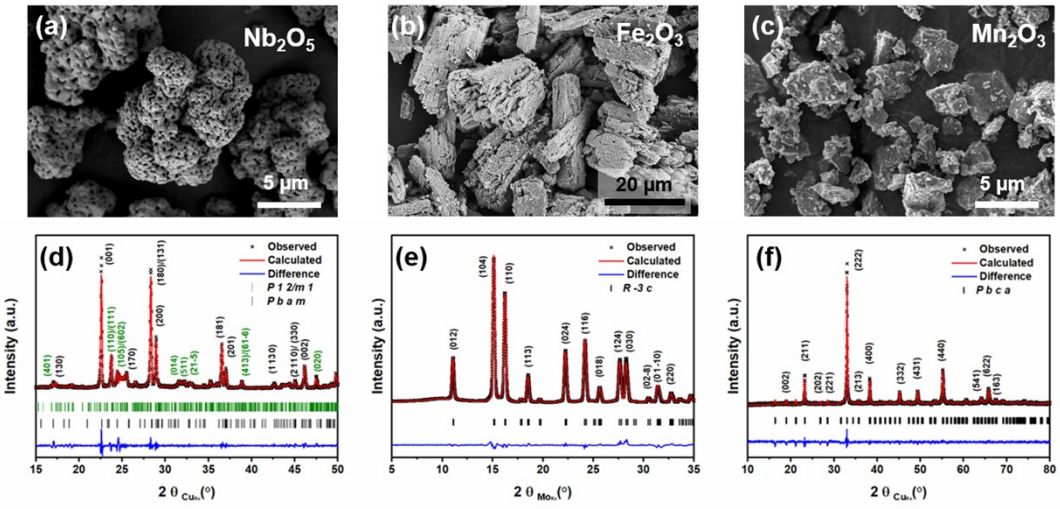

Figure S1. SEM images and XRD patterns of commercial micron-sized a, d) Nb_2O_5, b, e) Fe_2O_3, and c, f) Mn_2O_3 precursors used for the solid-state synthesis.

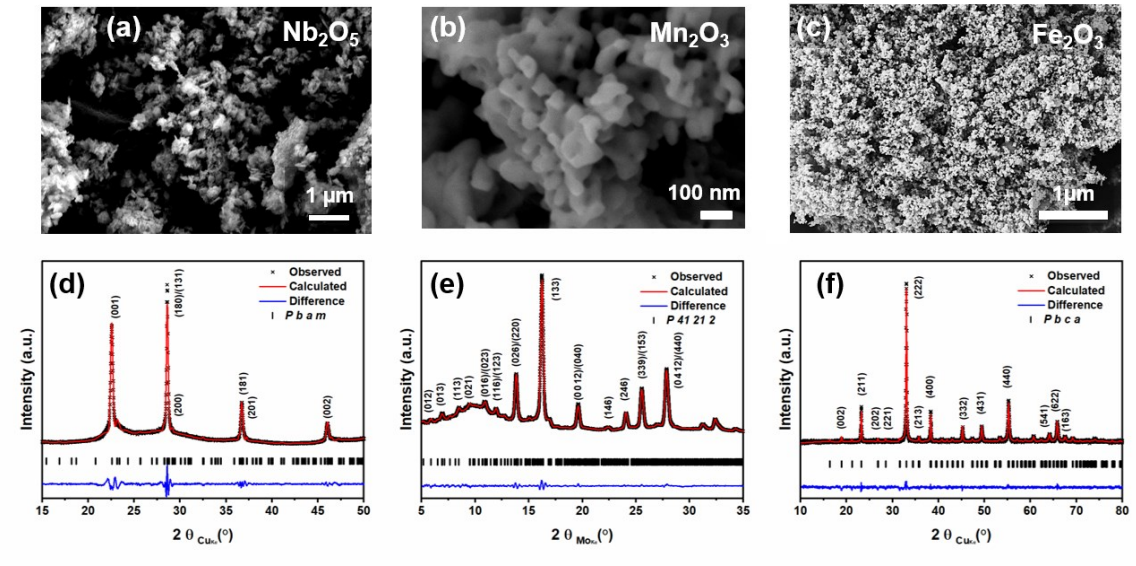

Figure S2. SEM images and XRD patterns of nano-sized a, d) Nb_2O_5, b, e) Mn_2O_3, and c, f) Fe_2O_3 precursors used for the solid-state synthesis.

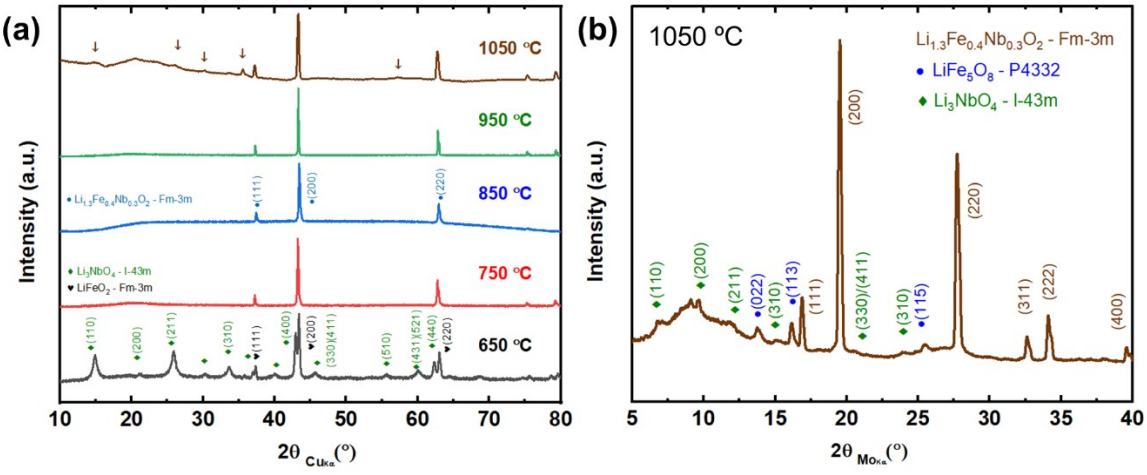

Figure S3. a) XRD pattern of $Li_{1.3}Fe_{0.4}Nb_{0.3}O_2$ nano-sized precursor heated treated at different temperatures. Arrows mark decomposition species present in the 1050 °C heat-treated sample. b) Higher-resolution XRD of the same sample identifies the impurities to be $LiFe_5O_8$ and Li_3NbO_4.

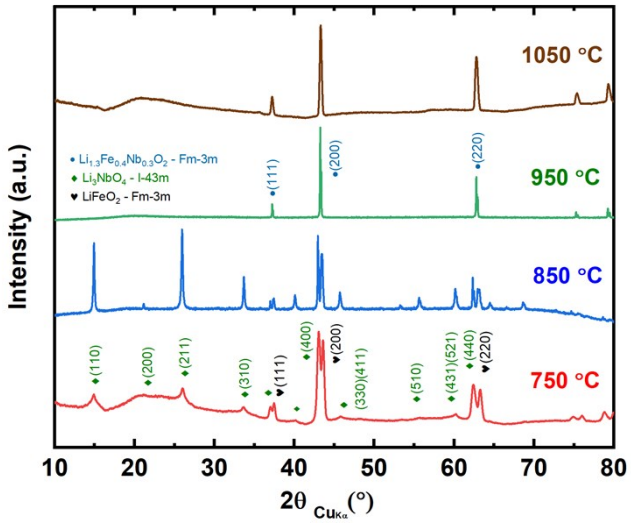

Figure S4. XRD pattern of $Li_{1.3}Fe_{0.4}Nb_{0.3}O_2$ micro-sized precursor heated treated at different temperatures.

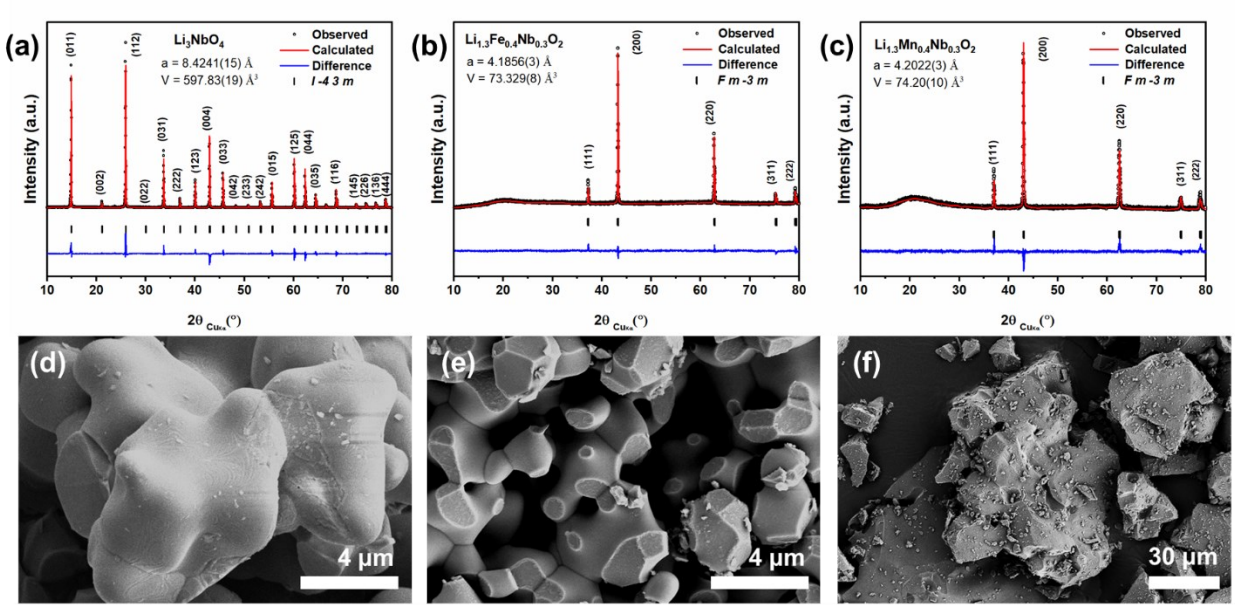

Figure S5. Rietveld refinements of the XRD patterns and SEM images of a, d) Li_3NbO_4, b, e) $Li_{1.3}Fe_{0.4}Nb_{0.3}O_2$, and c, f) $Li_{1.3}Mn_{0.4}Nb_{0.3}O_2$ obtained by solid-state synthesis with commercial micron-sized precursors.

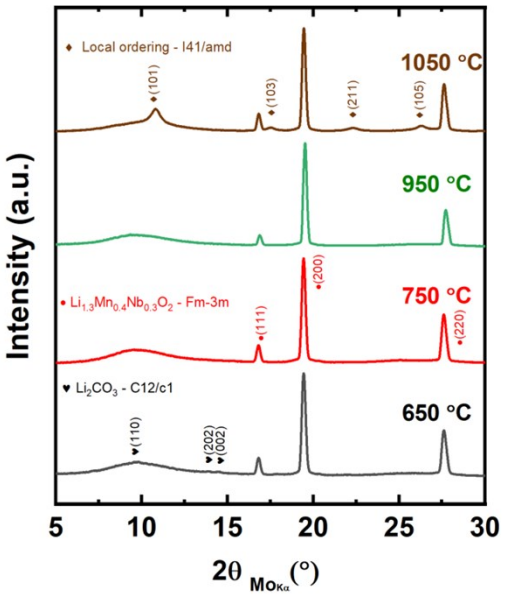

Figure S6. XRD pattern of $Li_{1.3}Mn_{0.4}Nb_{0.3}O_2$ nano-sized precursor heated treated at different temperatures.

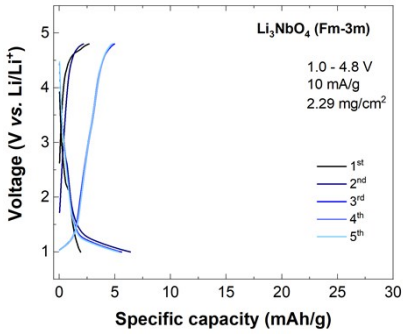

Figure S7. Voltage profile of disordered Li_3NbO_4 nanoparticles.

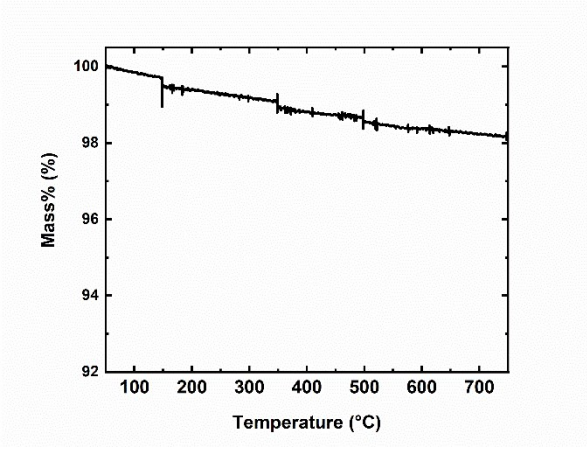

Figure S8. Thermogravimetric analysis of Al_2O_3 reference.

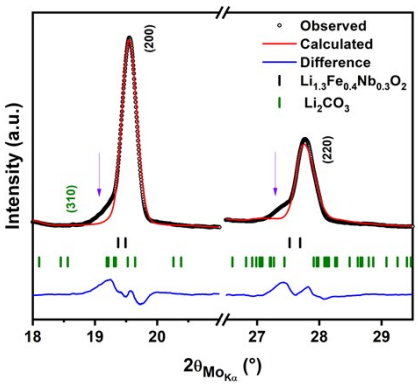

Figure S9. Selective theta range of profile matched XRD patterns of air-exposed nanosized $Li_{1.3}Fe_{0.4}Nb_{0.3}O_2$ that highlights the widening at lower angle (marked by purple arrows)

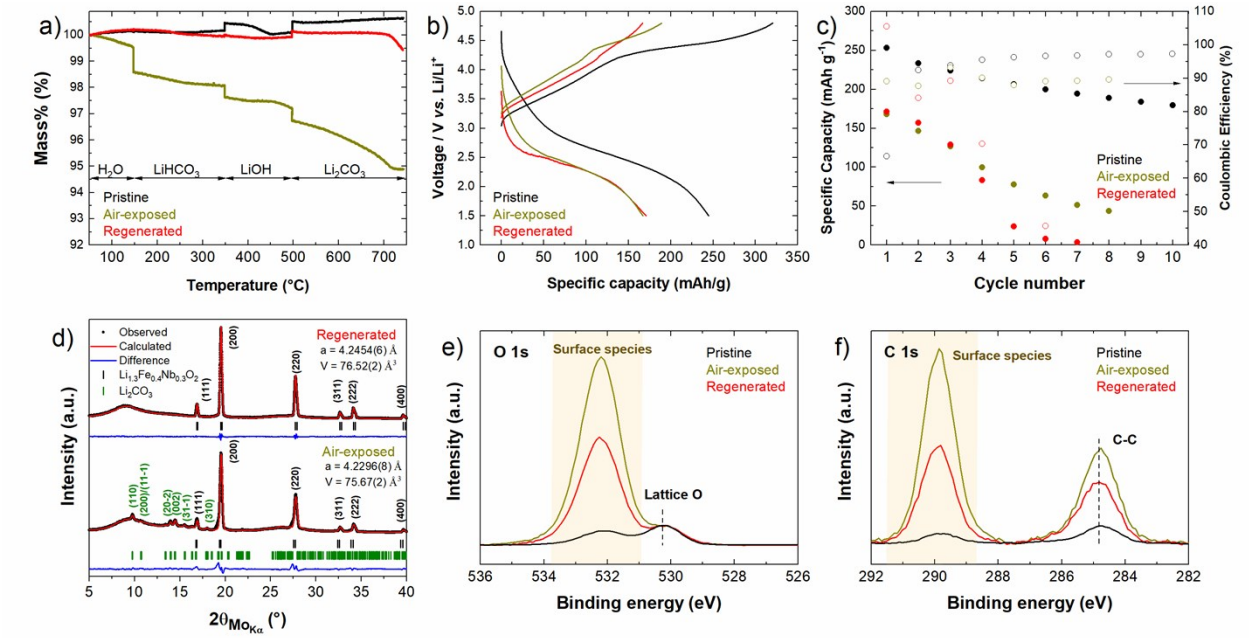

Figure S10. Study of the effect of surface contamination on the morphology-controlled sample of $Li_{1.3}Mn_{0.4}Nb_{0.3}O_2$ in pristine state, after 4 weeks of air exposure, and after regeneration by heat treatment: a) Thermogravimetric analysis, b) First voltage profiles, c) Cycling stability, d) Profile matching refinement of the XRD patterns, and XPS measurements of the e) O 1s and f) C 1s core regions.

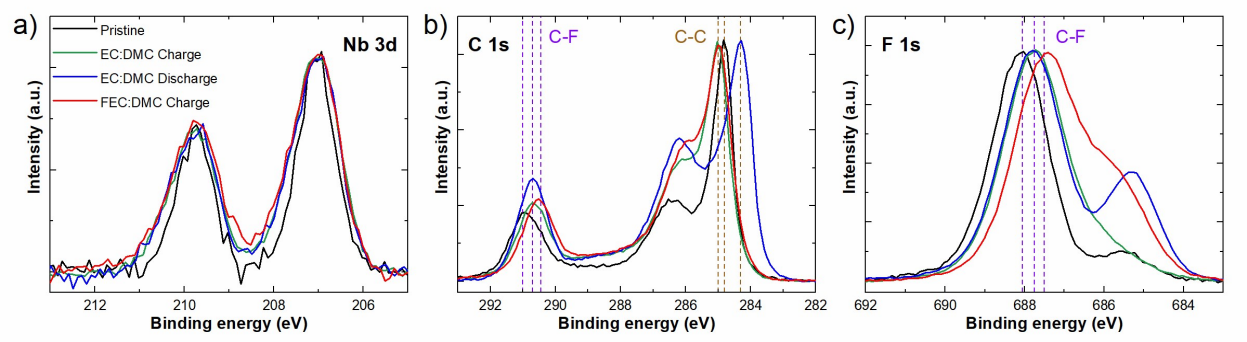

Figure S11. XPS spectra of the a) Nb 3d, b) C 1s, and c) F 1s regions of $Li_{1.3}Mn_{0.4}Nb_{0.3}O_2$ in the pristine state, after first charge and discharge for EC:DMC (3:7) with 1M $LiPF_6$ and after the first charge for FEC:DMC (1:4) with 1M $LiPF_6$.

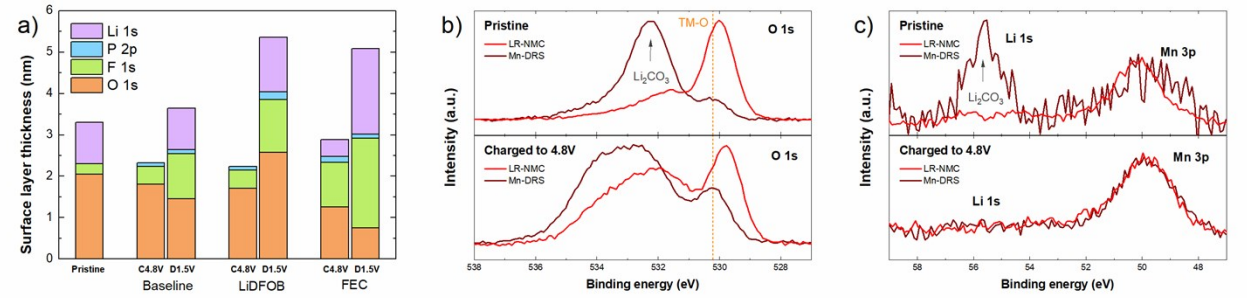

Figure S12. a) Surface layer thickness of Mn-DRS electrode in pristine, 4.8 V charged (C4.8V), and 1.5 V discharged (D1.5V) states with three electrolytes. Baseline corresponds to EC:DMC (3:7) with 1M $LiPF_6$, LiDFOB represents EC:DMC (3:7) with 1M $LiPF_6$ + 2 % LiDFOB, and FEC represents FEC:DMC (1:4) with 1M $LiPF_6$ electrolyte systems. Comparison of XPS spectra of the b) O 1s region and c) Li 1s and Mn 3p region of Mn-DRS and Li-rich NMC in the pristine state and after the first charge with EC:DMC (3:7) with 1M $LiPF_6$.

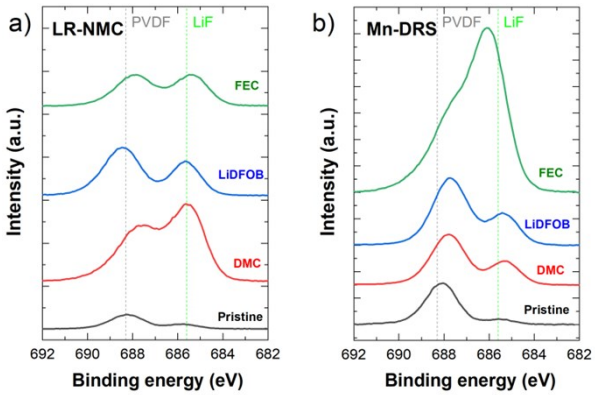

Figure S13. F 1s XPS spectra of a) $Li[Li_{0.144}Ni_{0.136}Co_{0.136}Mn_{0.544}]O_2$ and b) $Li_{1.3}Mn_{0.4}Nb_{0.3}O_2$ in the pristine state and after first discharge for the 3 electrolyte tested: EC:DMC (3:7) with 1M $LiPF_6$, EC:DMC (3:7) with 1M $LiPF_6$ + 2 % LiDFOB, and FEC:DMC (1:4) with 1M $LiPF_6$.

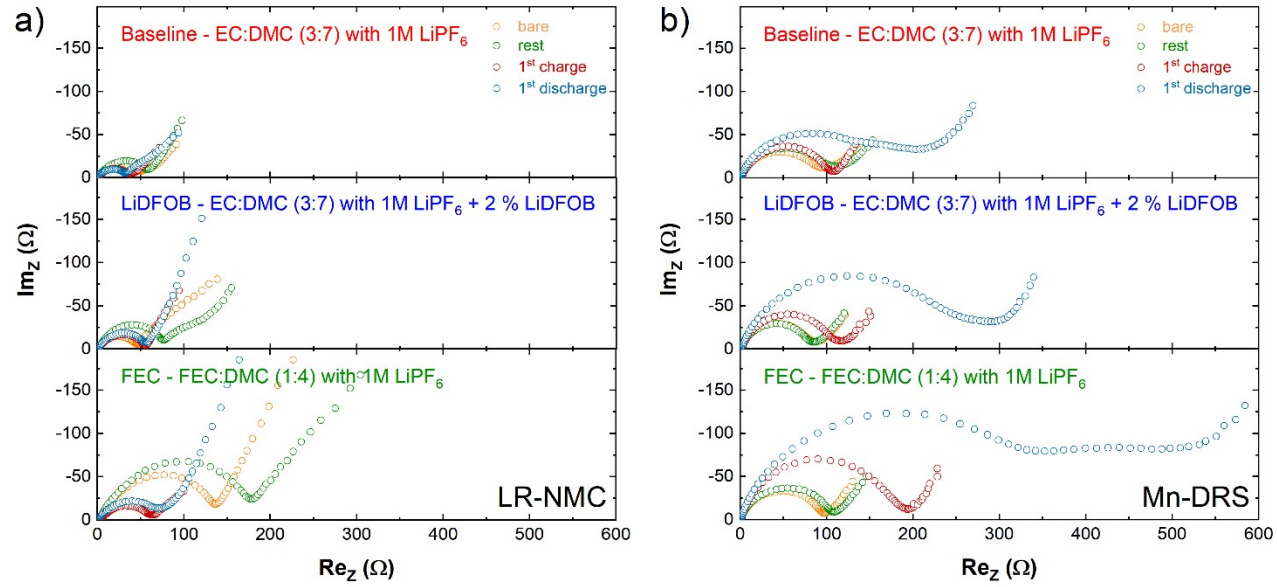

Figure S14. Nyquist plots of a) $Li[Li_{0.144}Ni_{0.136}Co_{0.136}Mn_{0.544}]O_2$ and b) $Li_{1.3}Mn_{0.4}Nb_{0.3}O_2$ cycled at room temperature with 3 different electrolytes. For each sample, the EIS spectra were acquired at 4 different steps: as assembled (bare), after 6 hours resting time (rest), after the 1st charge, and after the 1st discharge.

Table S1. Summary of XPS peak assignments.[1–4]

Peak	Binding energy (eV)	Assignment
Li 1s	≈ 55.6	Li_2CO_3
	≈ 56.1	LiF
	≈ 56.3	Lattice Li
	≈ 57.53	Li-P-F
P 2p	≈ 134.2	P-O/P-O-F
	≈ 136.2	Li-P-O-F
	≈ 137.3	Li-P-F
O 1s	≈ 530.2	Lattice O
	≈ 531.2	-O-H
	≈ 532.3	C=O/CO_3
	≈ 533.5	C-O
	≈ 534.5	P-O-F
F 1s	≈ 685.6	LiF
	≈ 688.3	PVDF

Table S2. Coin cell testing specifications used for nanosized $Li_{1.3}TM_{0.4}Nb_{0.3}O_2$(*TM* = Fe, Mn).

Fe-/Mn-DRS Specification	
Active material	$Li_{1.3}Fe_{0.4}Nb_{0.3}O_2$ or $Li_{1.3}Mn_{0.4}Nb_{0.3}O_2$ – 72 %
Conductive agent	SPC65 – 18 %
Binder	HSV900 – 10 %
Counter electrode	Li metal chip (Thickness: 1 mm, diameter: 15.4 mm)
Separators	Celgard 2325
Electrolyte type	1M $LiPF_6$ in EC:DMC = 3:7 vol. %
Electrolyte amount	55 µl
Cell type	CR2032
Coin cell setup	0.5 mm thick spacer and one spring at the anode side
Voltage range	1.5 -4.8 V
Test protocols	Rest for 6 h after assembling, then 20 mA g^{-1} (equivalent to 0.75 - 0.89 mA cm^{-2}) for all cycles at room temperature
Active material loading	3.7 - 4.4 mg cm^{-2}

Table S3. Coin cell testing specifications used in electrolyte compatibility study.

LR-NMC Specification	
Active material	$Li[Li_{0.144}Ni_{0.136}Co_{0.136}Mn_{0.544}]O_2$ – 80 %
Conductive agent	SPC65 – 10 %
Binder	HSV900 – 10 %
Counter electrode	Li metal chip (Thickness: 1 mm, diameter: 15.4 mm)
Separators	Celgard 2325
Electrolyte type	1) Baseline: 1M $LiPF_6$ in EC:DMC = 3:7 vol. % 2) LiDFOB: 1M $LiPF_6$ in EC:DMC = 3:7 vol. % with 2 wt. % LiDFOB additive 3) FEC: 1M $LiPF_6$ in FEC:DMC = 1:4 vol. %
Electrolyte amount	55 µl
Cell type	CR2032
Coin cell setup	0.5 mm thick spacer and one spring at the anode side
Voltage range	2.0 - 4.8 V
Test protocols	Rest for 6 h after assembling, then 12.5 mA g^{-1} (equivalent to 0.044 - 0.050 mA cm^{-2}) for first cycle, the rest at 25 mA g^{-1} (equivalent to 0.088 - 0.100 mA cm^{-2}) at room temperature
Active material loading	3.5 - 4.0 mg cm^{-2}
Mn-DRS Specification	
Active material	$Li_{1.3}Mn_{0.4}Nb_{0.3}O_2$ – 72 %
Conductive agent	SPC65 – 18 %
Binder	HSV900 – 10 %
Counter electrode	Li metal chip (Thickness: 1 mm, diameter: 15.4 mm)
Separators	Celgard 2325
Electrolyte type	1) Baseline: 1M $LiPF_6$ in EC:DMC = 3:7 vol. % 2) LiDFOB: 1M $LiPF_6$ in EC:DMC = 3:7 vol. % with 2 wt. % LiDFOB additive 3) FEC: 1M $LiPF_6$ in FEC:DMC = 1:4 vol. %
Electrolyte amount	55 µl
Cell type	CR2032
Coin cell setup	0.5 mm thick spacer and one spring at the anode side
Voltage range	1.5 - 4.8 V
Test protocols	Rest for 6 h after assembling, then 10 mA g^{-1} (equivalent to 0.034 - 0.036 mA cm^{-2}) for all cycles at room temperature
Active material loading	3.4 - 3.6 mg cm^{-2}

Reference

1 Y. Lu, A. N. Mansour, N. Yabuuchi and Y. Shao-horn, *Chem. Mater.*, 2009, **21**, 4408–4424.

2 L. Baggetto, N. J. Dudney and G. M. Veith, *Electrochim. Acta*, 2013, **90**, 135–147.

3 Z. W. Lebens-Higgins, N. V. Faenza, M. D. Radin, H. Liu, S. Sallis, J. Rana, J. Vinckeviciute, P. J. Reeves, M. J. Zuba, F. Badway, N. Pereira, K. W. Chapman, T. L. Lee, T. Wu, C. P. Grey, B. C. Melot, A. Van Der Ven, G. G. Amatucci, W. Yang and L. F. J. Piper, *Mater. Horizons*, 2019, **6**, 2112–2123.

4 Q. Li, Y. Wang, X. Wang, X. Sun, J. N. Zhang, X. Yu and H. Li, *ACS Appl. Mater. Interfaces*, 2020, **12**, 2319–2326.