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Supporting Information

High-voltage spinel cathodes for lithium-ion batteries: controlling the growth of preferred crystallographic planes through cation doping

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Table S1: ICP compositional data and lattice parameters of $LiMn_{1.5}Ni_{0.42}M_{0.08}O_4$

	Compositional Data				Lattice
M	Li	Mn	Ni	M	Parameter (Å)
Ni	0.99	1.50	0.50	0	8.1744(1)
Fe	1.03	1.48	0.40	0.09	8.1812(2)
Ga	1.02	1.49	1.40	0.09	8.1907(1)
Zn	1.03	1.48	0.40	0.09	8.1849(1)
Al	1.04	1.47	0.40	0.09	8.1792(2)
Cr	1.03	1.47	0.40	0.10	8.1900(2)
Co	1.01	1.49	0.41	0.09	8.1760(2)
Cu	1.01	1.48	0.40	0.09	8.1734(1)

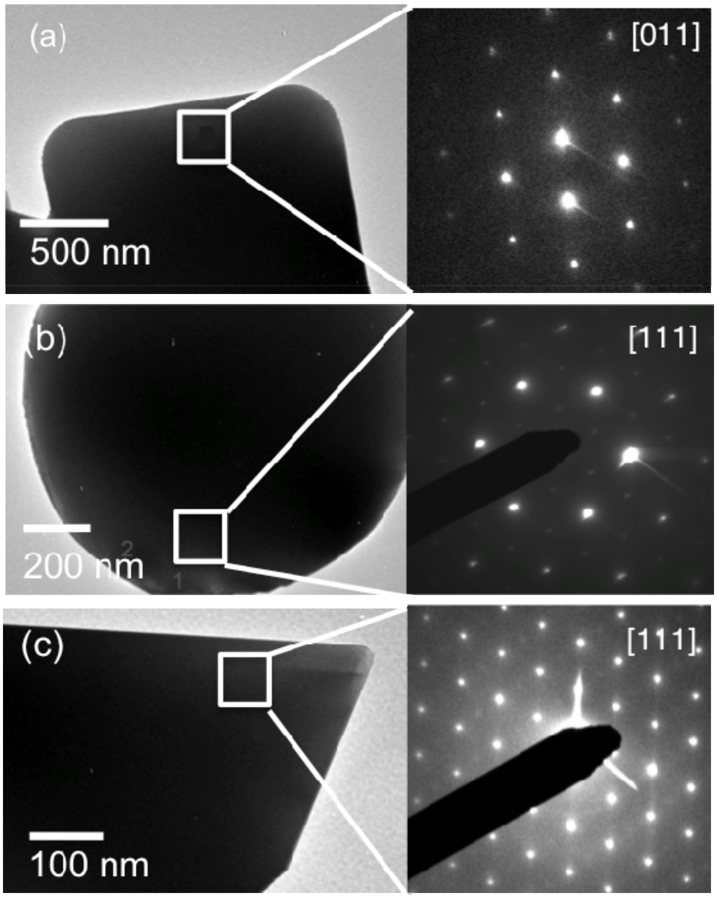

Figure S1. Supplemental TEM overview and electron diffraction patterns of (a) Al-doped, (b) Co-doped, and (c) Cu-doped spinel samples.

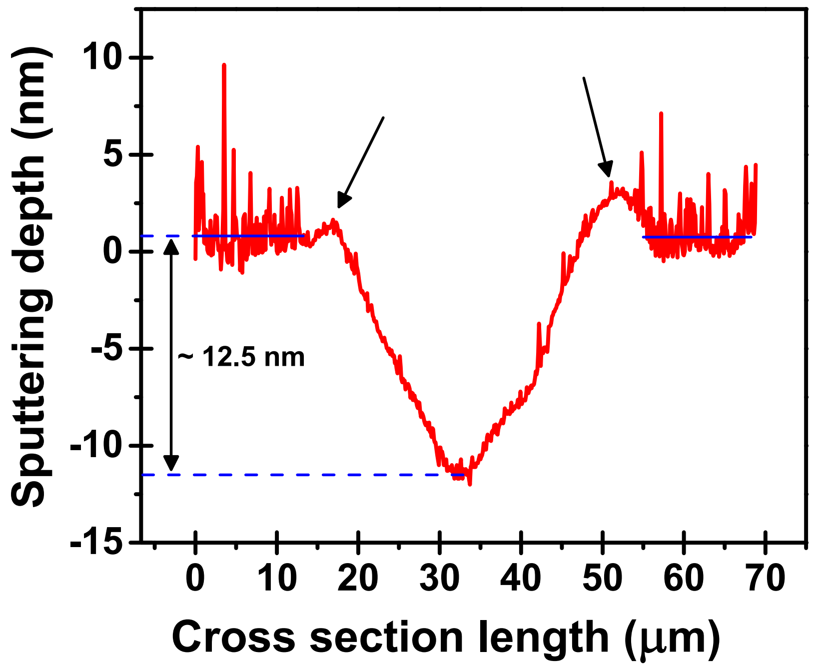

Figure S2. Sputtering depth of Si measured with atomic force microscopy.

A silicon wafer was sputtered with the TOF-SIMS instrument with the same conditions used for the spinel cathode materials (described in detail in the Characterization portion of the manuscript). In 3000 seconds, the sputtering depth on the silicon wafer was measured to be ~ 12.5 nm by the atomic force microscope as seen in Figure S2 (provided through a private communication with Dr. Andrei Dolocan, Texas Materials Institute, The University of Texas at Austin). A general equation used for the sputtering rate of elements is

$$\nu = \frac{\mathbf{JYA}}{\rho \mathbf{eNn}} \qquad \text{Eqn. 1}$$

where

J – ion current density (A/m^2) – same for both

Y – sputter yield (secondary ions/primary ion) – the total secondary ion yield can be used for the spinel and Si samples for the same sputtering time (3000 sec) and primary ion dose; spinel: ~ 146,000,000 ions ; silicon: ~ 35,000,000 ions

A – molecular weight (kg/mol) – spinel: 0.183 kg/mol (using $LiMn_{1.5}Ni_{0.5}O_4$); silicon: 0.0281 kg/mol

ρ – mass density (kg/m^3) – spinel: 1600 kg/m^3; silicon: 2329 kg/m^3

e – electron charge – same for both

N – Avogadro's constant (6.023×10^{23}/mol) – same for both n – number of atoms in a molecule (*i.e.* 7 in Ta_2O_5) – spinel: 7 (using the general AB_2O_4); silicon: 1

The ratio of the sputtering rates provides an estimate for the sputtering depth for the spinel samples in comparison to silicon.

$$\frac{\nu_{spinel}}{\nu_{Si}} = 9.04$$

According to this ratio, the sputtering rate for the spinel material is ~ 9 times greater than for silicon. Although other factors may contribute to lowering the ratio between the sputtering rates (*i.e.* powder sample vs. thin film, etc.), we provide a conservative sputtering depth for our samples to be ≥ 12.5 nm in the doped spinel oxide materials studied by TOF-SIMS in this investigation.