Batteries & Supercaps

Supporting Information

Enhanced High Voltage Stability of Spinel-Type Structured $LiNi_{0.5}Mn_{1.5}O_4$ Electrodes: Targeted Octahedral Crystal Site Modification

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Experimental Methods

Material synthesis

Spinel-type structured LNMO and Zn-LNMO ($LiNi_{0.5}Mn_{1.45}Zn_{0.05}O_4$) materials were synthesized *via* a solid-state reaction method. Typically, stoichiometric amounts of Li_2CO_3, NiO, MnO_2, and ZnO (for Zn-LNMO) were mixed by ball milling at 400 rpm for 20 h, followed by calcination at 5 °C per min to 850 °C for 10 h in a muffle furnace. All chemicals used in this work were purchased from Sigma-Aldrich® without further purification.

Material characterization

The morphology of battery materials was characterized using scanning electron microscopy (SEM) on a JEOL JSM 7500 instrument at the University of Wollongong. The samples were applied onto a conductive and adhesive carbon tape on the SEM stub for subsequent measurement. The accelerating voltage and emission current during measurement were set at 5 kV and 10 μA, respectively. Aberration-corrected transmission electron microscopy (TEM) was performed on a JEOL ARM-200F in high-angle annular dark-field (HAADF) mode at the University of Wollongong. Samples of interest were first ultrasonicated in ethanol for 30 min to achieve homogeneous suspension and then pipetted onto lacey carbon support films. The accelerating voltage was set to 120 kV during measurements. The obtained data were analyzed by the software of Gatan DigitalMicrograph. The concentration of Zn in the materials was determined using inductively coupled plasma mass spectrometetry (ICP-MS) on an Agilent 7900 ICP-MS at the University of Adelaide. Neutron powder diffraction (NPD) data of both LNMO and Zn-LNMO were acquired on the high-resolution neutron powder diffractometer Echidna[1] at the Open Pool Australian Light water (OPAL) research reactor at the Australian Nuclear Science and Technology Organisation (ANSTO). NPD data were collected in the angular (2θ) range 4 - 164° with step size of 0.05°. The neutron beam wavelength (1.618946(3)Å) and instrumental contributions to peak shape were determined using data for the $La^{11}B_6$ National Institute of Standards and Technology (NIST) standard reference material 660b and fixed during the refinement of the sample structure. Rietveld refinements were carried out using GSAS-II,[2] and refinements of the sample structure against NPD data included sample shift, background coefficients, lattice parameters, site occupancy factors, scale factors, oxygen positional parameters, as well as isotropic atomic displacement parameters.

Electrochemical testing

Cathode materials were mixed with 10 wt.% carbon black (super-P, SPCNPs, > 99.9%), 10 wt.% polyvinylidene difluoride (PVDF, Sigma-Aldrich, molecular weight = 534.000), and N-methyl pyrrolidone (Sigma-Aldrich, 99.5%) to form a homogenous slurry, which was subsequently coated onto aluminum foil using coating blade, dried in vacuum oven at 60 °C overnight, and pressed using stainless steel plates to form an electrode. The electrode was cut into disks and assembled into CR2032-type coin cells with Li foil (Goodfellow, 200 µm thickness) as the counter electrode, Celgard® membrane (Celgard, LLC) as separator, and an electrolyte (1 M $LiPF_6$ dissolved in ethylene carbonate/diethyl carbonate (EC: DEC=1:1 by volume), Sigma-Aldrich, battery grade) in an Ar-filled glovebox. Assembled batteries were rested for 12 h and then tested using a Land 2001A cell test system between 3.5 and 4.9 V (versus Li) at room temperature.

In operando and *ex situ* structure characterization

In operando synchrotron-based X-ray powder diffraction (SXRPD) measurements were conducted at the Powder Diffraction beamline of the Australian Synchrotron, ANSTO. The preparation method for the customized batteries used in this work can be found in our previous work.[3] The wavelength of synchrotron beam during testing was determined to be 0.688762(1) Å using data for the $La^{11}B_6$ NIST standard reference material 660b, with refinements performed using GSAS-II[2]. During SXRPD data collection, the batteries were mounted on the sample holder that was developed by Powder Diffraction beamline without rotation and oscillation. Electrochemical measurement of the batteries was carried out on the NEWARE battery testing system within the voltage range of 3.5-4.9V vs. Li at current density of 0.1 C, which corresponds to 10 h for a complete charge/discharge process. Data were recorded using a MYTHEN microstrip detector in two positions with an acquisition time of 60 s and interval time of 299 s.

Ex situ near-edge X-ray absorption fine structure spectroscopy (NEXAFS) studies were carried out at the soft X-ray beamline of the Australian Synchrotron, ANSTO. Active cathode material obtained from batteries at various states of charge, then extracted in a glovebox, and washed with diethyl carbonate (DEC, Sigma-Aldrich, 99.5%). The *ex situ* battery electrodes were adhered to a specialized stainless-steel ruler developed for the soft X-ray beamline using carbon tape. An X-ray incident angle of 55° was used for all measurements. The data collection was conducted in total electron yield (TEY) mode, with concurrently collected reference spectra that were appropriately energy-calibrated. This was achieved by inserting reference samples into the beam, thereby cutting approximately 5% of the beam flux. NEXAFS data were processed using the Igor Pro 8 program, with the aid of the QANT program.[4] The recorded signals were normalized by dividing the sample signal with an Izero signal and by setting the pre-edge to zero and the post-edge to one.

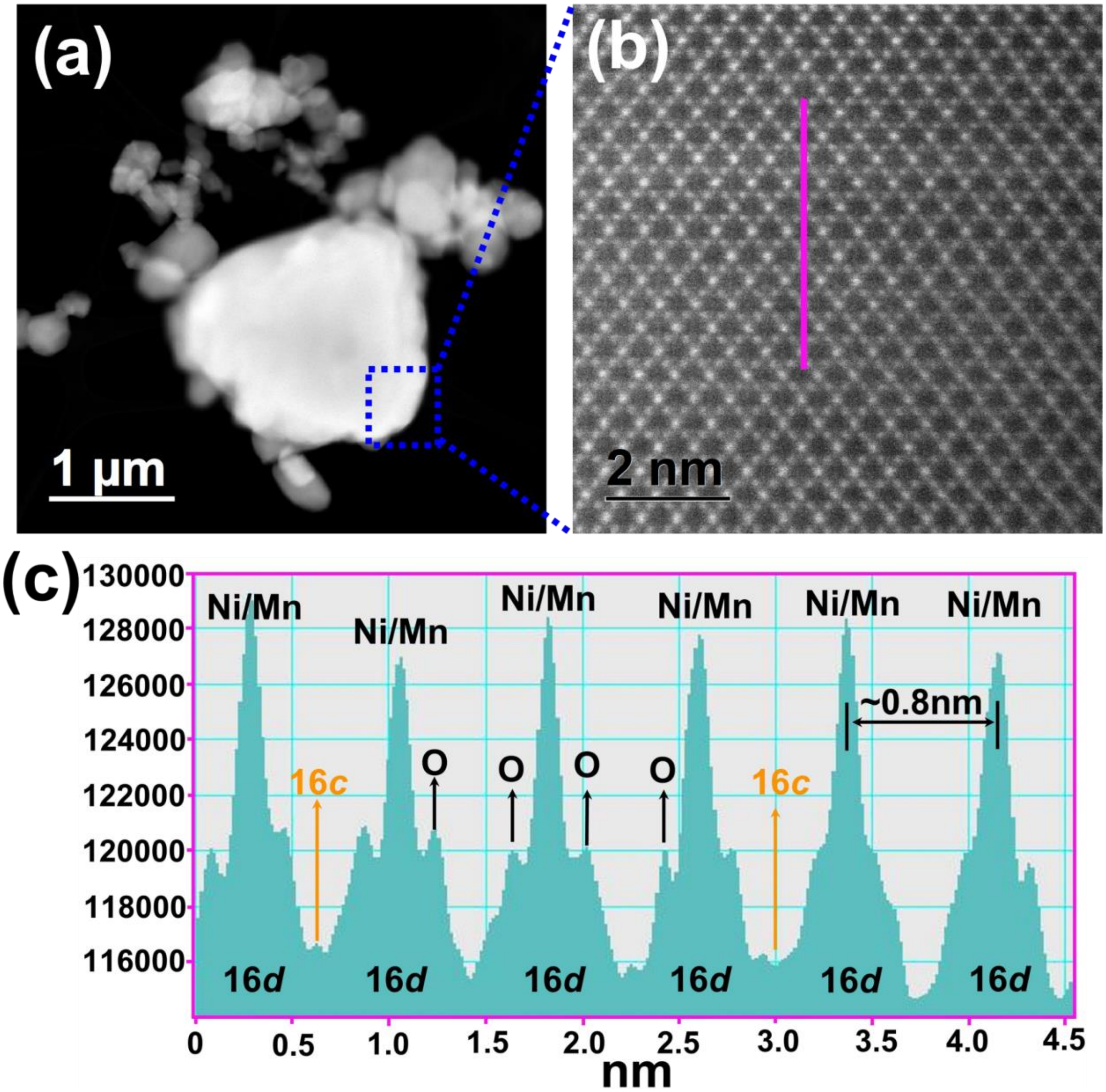

Figure S1. (a) HAADF STEM image of the near-surface region of unmodified LNMO; (b) magnification of the selected region in (a) with corresponding (c) line profile intensity along the light purple line in (b).

Table S1. Phase composition and crystallographic details of unmodified LNMO and Zn-LNMO obtained from Rietveld refinement using NPD data.

	Spinel-type structured phase	Rock-salt type structured phase
Unmodified LNMO	98.3(1) wt.%	1.7(1) wt.%
Zn-LNMO	98.4(1) wt.%	1.6(1) wt.%

Unmodified LNMO
Space group $Fd\bar{3}m$

a = 8.1761(2) Å; V = 546.56(5) Å^3

Atom	Wyckoff site	*x*	*y*	*z*	Uiso (Å^2)	Site occupancy factor
Li	8*a*	0.125	0.125	0.125	0.011(1)	1
Ni	16*d*	0.5	0.5	0.5	0.026(2)	0.203(2)[a]
Mn						0.797(2)[a]
O	32*e*	0.26291(5)	0.26291(5)	0.26291(5)	0.0076(2)	1

Zn-LNMO
Space group $Fd\bar{3}m$

a = 8.1847(3) Å; V = 548.29(6) Å^3

Atom	Wyckoff site	*x*	*y*	*z*	Uiso (Å^2)	Site occupancy factor
Li	8*a*	0.125	0.125	0.125	0.037(2)	1
Ni	16*d*	0.5	0.5	0.5	0.038(3)[c]	0.194(3)[b]
Mn						0.806(3)[b]
O	32*e*	0.26295(6)	0.26295(6)	0.26295(6)	0.010(1)	1
Zn	16*c*	0	0	0	0.038(3)[c]	0.05

[a, b] constrained to be 1; [c] constrained to be the same.

Reference:

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[4] E. Gann, C. R. McNeill, A. Tadich, B. C. Cowie, L. Thomsen, *J. Synchrotron Rad.* **2016**, *23*, 374-380.