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+Electronic Supplementary Information

Elucidating the Surface Characteristics and Electrochemistry of High-performance $LiNiO_2$

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TableS1. Refinement results based on Synchrotron XRD of $LiNiO_2$.

Sample	Lattice Parameter (Å)	Ni on 3a site (%)	R value (%)
Solid_10exLi	a = 2.875(7) c = 14.197(2)	1.44(3)	3.02(5)
Solution_10exLi	a = 2.874(0) c = 14.190(1)	1.03(6)	3.09(1)
Solution_2exLi	a = 2.874(1) c = 14.188(5)	1.08(4)	3.12(9)

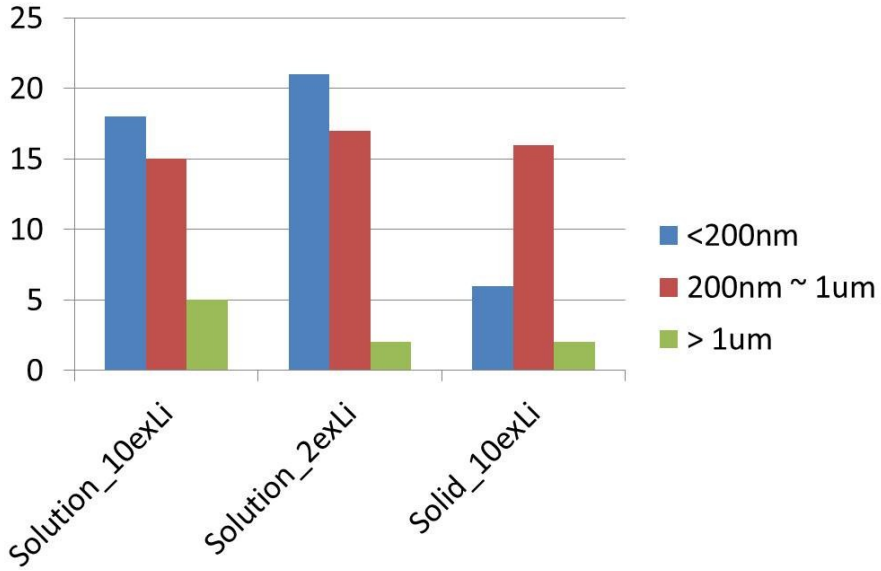

Figure S1. Histogram shows the particle size distribution on the surface (based on the SEM image in Figure 1).

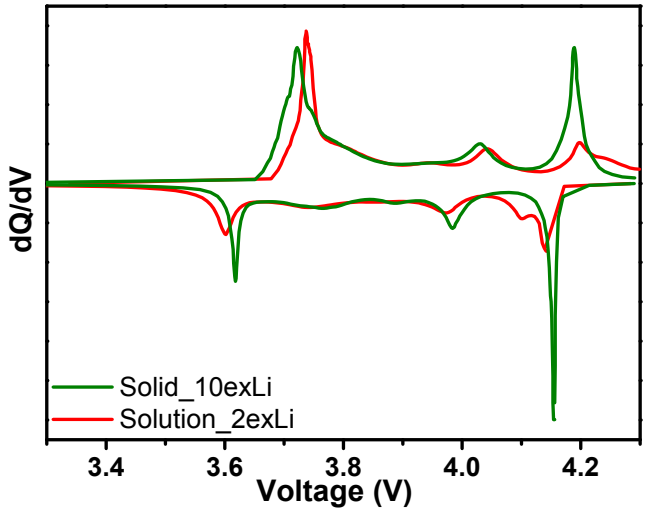

Figure S2. dq / dV for the 1st cycle voltage profiles suggesting the smaller polarization of Solution_10exLi sample.

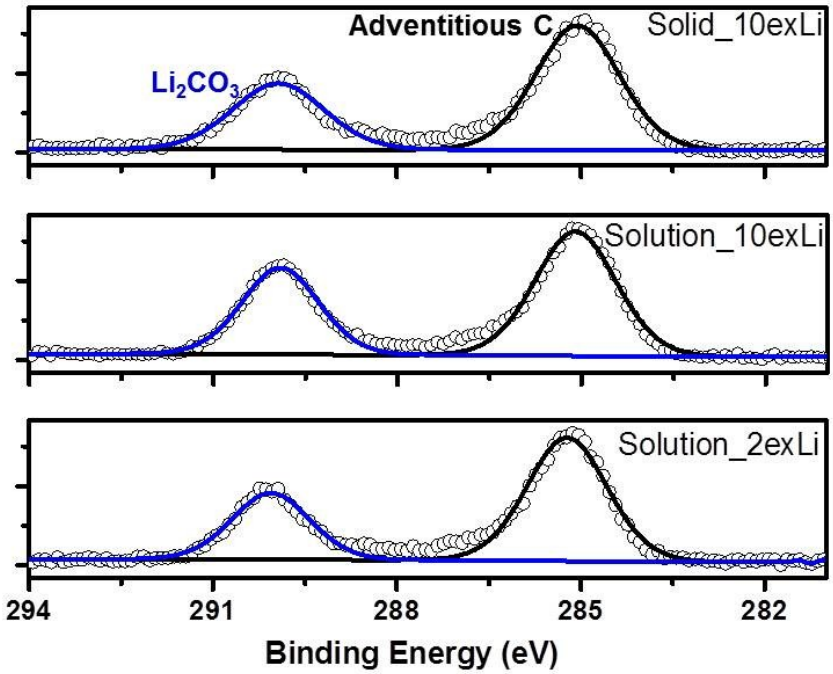

Figure S3. XPS C1s regions of (a) Solution_2exLi, (b) Solution_10exLi, and (c) Solid_10exLi, respectively.Open circles and lines indicate observed and fitted profiles. The peak at 285.0 eV (black curve) is the photoemission of adventitious hydrocarbons, and the peak at ~ 290 eV (blue curve) results from surface carbonate groups.

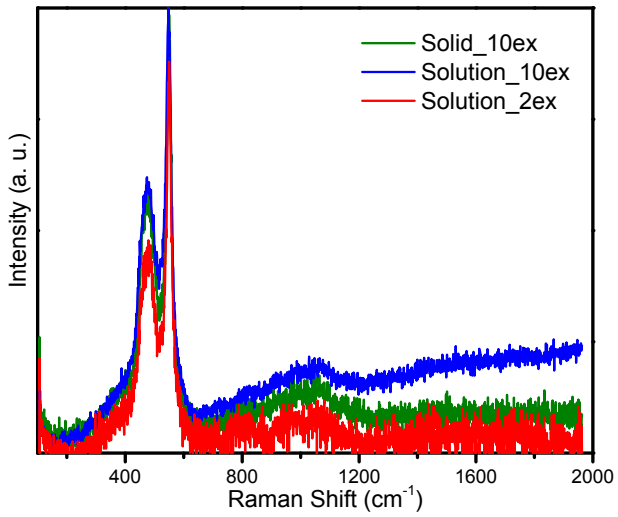

Figure S4. Raman spectra of the as-synthesized powders. Two vibration peaks at the wavenumber 480 cm^{-1} and 550 cm^{-1} that are associated to E_g and A_{1g} active modes in $LiNiO_2$.[1] Meanwhile, a convoluted Raman peak is located around 1010 cm^{-1}. This peak can be assigned to both longitudinal optical mode of NiO and the stretching mode of Li_2CO_3.[2]

Experimental

$Ni(OH)_2$ precursors used for the Solution_10ex and Solution_2ex samples were prepared by a precipitation method. $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich) was dissolved in de-ionized (DI) water (0.4 M) and then slowly dripped into aLiOH (Sigma Aldrich, 0.8 M) solution using a masterflex C/L peristaltic pump and stirred continuously. The precipitate was collected, filtered and washed with deionized water, and then dried overnight at 100 ^{0}C in the oven. The dried precipitate was high energy milled (500rpm, 1h) with LiOH, where 10% excess Li and 2% excess Li was added for the samplesSolution_10ex and Solution_2ex, respectively. The ball-milled mixture was then annealed in O_2 (5 cft) at 750 ^{0}C for 12h. Solid_10exLi sample was prepared by ball milling Li_2CO_3 (Sigma Aldrich) and $Ni(OH)_2$ (Sigma Aldrich) at 500 rpm for 12h (Retsch, PM100) and then annealing at 750 ^{0}C for 12h under O_2 flow.

Scanning electron microscopy (SEM) was performed on a JEOL JSM-7000F equipped with a Thermo Scientific EDS (energy dispersive X-ray spectroscopy) detector. The XAS measurements were carried out on beamline 8-2 at the Stanford Synchrotron Radiation Laboratory and were conducted on powder samples, which were pressed on Au foil to avoid contamination from the adhesive of the carbon tape. Data were acquired under ultrahigh vacuum (10^{-9}Torr) in a single load at room temperature using total electron yield (TEY) via the drain current, Auger electron yield (AEY) via a Cylindrical Mirror Analyzer, and fluorescence yield (FY) modes via a Silicon Photodiodes. The XPS experiments were performed with an incident phonon energy of 670 eV at beamline 9.3.2 at the Advanced Light Source in Lawrence Berkeley National Laboratory using a Scienta 4000R analyzer operated with Pass Energy of 100 eV (total energy resolution of 0.1 eV). The spectra were calibrated to the C1s photoemission peak of adventitious hydrocarbons at 285.0eV. Raman spectra were recorded on a “Labram” Raman confocal microscope system (ISA Groupe Horiba) in the confocal backscattering configuration with a 488 nm Argon ion laser (Coherent Inc. Innova 70), a plan olympus 80× magnification. The beam intensity was adjusted to 0.1 mW for a beam diameter of 1 μm.

Electrodes were prepared from slurries containing 80 wt% of active material, 10 wt% of polyvinylidene fluoride (PVdF) as a binder, and 10 wt% acetylene carbon black (Denka, 50% compressed)in N-methylpyrrolidone (NMP). The slurries were then casted on carbon-coated aluminum current collectors (Exopack Advanced Coatings) using a doctor blade set to 75 μm

height and then dried under vacuum at 120 ^{0}C to form electrodes. Typical loadings of the active materials were around 2.5 mg/cm^2. 2032-type coin cells were assembled in anAr-filled glove box (H_2O < 0.1ppm) with Li metal as the negative electrode. A Celgard 2400 separator and 1M $LiPF_6$ electrolyte solution in 1:2 w/w ethylene carbonate - diethyl carbonate (Ferro Corporation) were used to fabricate the cells. Galvanostatic discharge and charge at various current densities between 4.3 V and 2.7 V were performed on a Maccor 4200 battery cycler. 1C was defined as 180 mA g^{-1} for this work.

Reference

1. Rougier, A.; Nazri, G. A.; Julien, C., Vibrational Spectroscopy and Electrochemical Properties of LiNi(0.7)Co(0.3)O(2) Cathode Material for Rechargeable Lithium Batteries. Ionics 1997,3 (3-4), 170-176.

2. Wang, R.; Yu, X. Q.; Bai, J. M.; Li, H.; Huang, X. J.; Chen, L. Q.; Yang, X. Q., Electrochemical decomposition of Li2CO3 in NiO-Li2CO3 nanocomposite thin film and powder electrodes. Journal of Power Sources 2012,218, 113-118.