

Supporting Information

Facet Dependent SEI Formation on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode Identified by in-situ Single Particle Atomic Force Microscopy

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Experimental Section

The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles were synthesized by a sol-gel method. Firstly, stoichiometric amounts of $\text{Li}(\text{CH}_3\text{COO})\cdot 2\text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$, with a cationic ratio of Li: Ni: Mn = 1.03: 0.5: 1.5 were dissolved in ultrapure water and stirred at the room temperature. Eathylene diamine tetraacetic acid (EDTA) and citric acid monohydrate were added into the solution above, then $\text{NH}_3\cdot\text{H}_2\text{O}$ was poured slowly into the mixture until the aqueous solution was formed. Secondly, the resulting solution was stirred at 90 °C for 12 h to form a sol, then the sol was heated at 120 °C to form a dry gel. Thirdly, the resulting gel was fired at about 400 °C to produce an ash-like powder by the decomposition of the organic material. Finally, the decomposed powder was heated at 900 °C for 10 h.

The schematic diagram for SEP electrode is shown in Scheme 1. The sample for AFM was prepared by (a) spin-coating a PMMA layer (40 mg/ml) onto the silicon wafer; (b) casting the particles dispersed in NMP on the PMMA coated silicon and vacuum drying; (c) spin-coating a PMMA layer (10mg/ml) onto the sample above once again; (d) magnetron sputtering (PVD75, Kurt J. Lesker) Al onto the sample to form about 500 nm thick Al films and affixing Celgard 2400 separator to the sample; (e) tearing off to separate the particles embedded in Al film from silicon wafer; (f) rinsing the sample with acetone twice to remove the PMMA layer and drying the sample in air dry oven.

The morphologies and surface chemical analysis of the samples were observed using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS, JEOL-6701F). X-ray photoelectron spectroscopic (XPS) measurements were performed on a ESCALab220i-XL electron spectrometer (VG Scientific) using 300W Al $K\alpha$ radiation. The base pressure was about 3×10^{-9} mbar, and the binding energies were referenced to C1s line at 284.8 eV from adventitious carbon. The crystal structure of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powder was investigated by X-ray diffraction (XRD) using a Regaku D/Max-2500 diffractometer equipped with a Cu $K\alpha 1$ radiation ($\lambda = 1.54056 \text{ \AA}$). The cyclic voltammetry experiments were carried out on an Autolab PG302N at room temperature. In situ and ex situ electrochemical AFM (EC-AFM) measurements were carried out with an AFM system (Bruker Multimode 8 with a Nanoscope V controller) and a custom-designed electrochemical cell. Electrochemical holder with an O-ring was put on the top of sample to form an airtight space where only the basal plane of the sample was in contact with the electrolyte. The electrolyte solution was 1 mol dm^{-3} LiPF_6 dissolved in ethylene carbonate/diethyl carbonate (EC/DEC/DMC, volume ratio of 1:1:1) (BASF, LP-71). Both the reference and the counter electrodes were lithium metal. Samples for ex situ EC-AFM measurements were washed by dimethyl carbonate (DMC). All electrochemical and AFM measurements were carried out in a homemade argon flowed glove box where the oxygen and water content was well below 1 ppm at room temperature. In order to minimize the noise signal, the AFM apparatus was mounted on top of a suspended marble. Cyclic voltammetry was measured at a sweep rate of 0.1 mV/s between 3.8 V and 4.85 V. Peak force tapping mode was used for recording the morphology when the electrode was set to the desired potential. The contact mode was applied to scratch the surface.

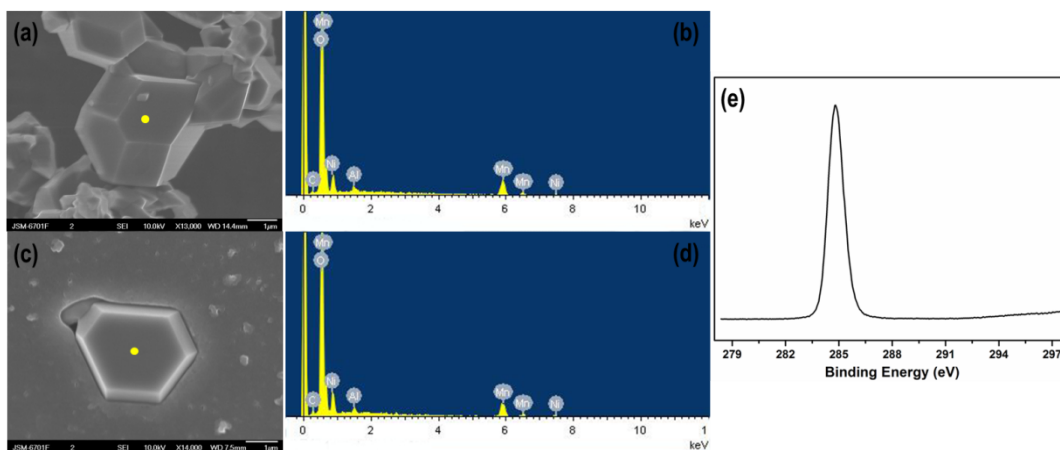


Figure S1. (a) SEM image of particles directly dispersed on the Al foil; (b) EDS of the particle which is marked by yellow point on (a); (c) SEM image of a particle on the SEP electrode; (d) EDS of the particle which is marked by yellow point on (b); (e) Carbon 1s spectra of the SEP electrode.

Surface chemical analysis of particles directly dispersed on Al foil and SEP electrode was investigated by SEM–EDS. The EDS results show that elemental composition of particles on Al foil and SEP electrode are almost the same. Particles mainly contain Mn, Ni and O. Trace amounts of C and Al result from the inevitable contamination and substrate.

We measured the surface chemical compositions of the SEP electrode by XPS. From the carbon 1s (C 1s) spectra, there is no signals indicative of the PMMA being present.

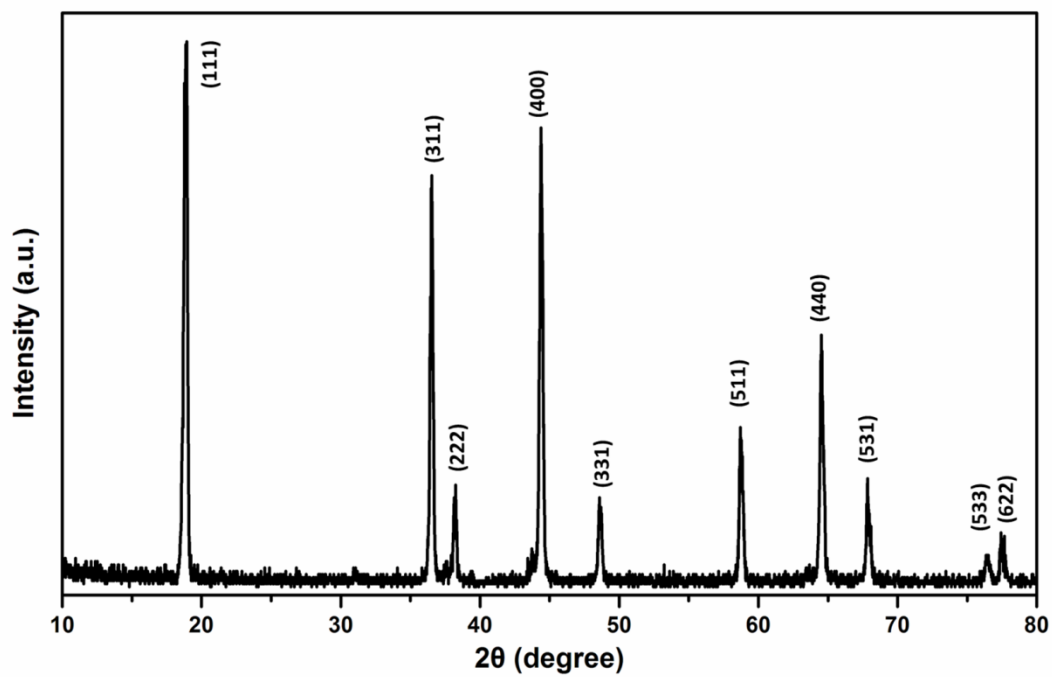


Figure S2. X-ray diffraction pattern of LiNi_{0.5}Mn_{1.5}O₄ powder.

All the fundamental diffraction peaks can be assigned to a nonstoichiometric cubic spinel structure ($Fd3m$)

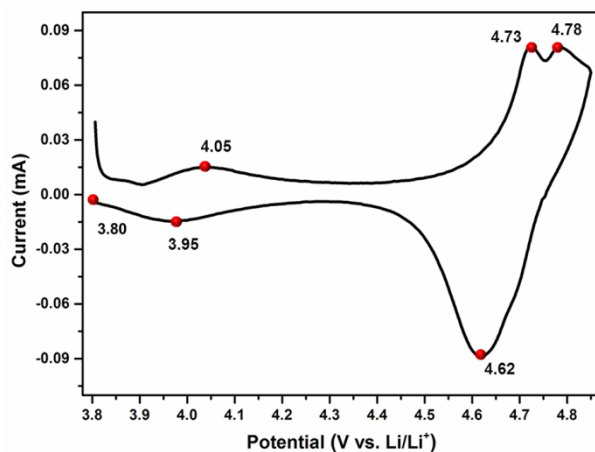


Figure S3. The first cyclic voltammetry curve of LiNi_{0.5}Mn_{1.5}O₄ cathode at a scan rate of 0.1 mV s⁻¹.

Two pairs of redox peaks were clearly seen at around 4.0 and 4.7 V. A small current around 4 V corresponds to a Mn³⁺/Mn⁴⁺ redox reaction, which suggests that Mn ions are present in mainly Mn⁴⁺ and a small amount of Mn³⁺ remained in this material. The doublet oxidation current peak at around 4.75 V and the reduction peak at 4.6 V correspond to the Ni²⁺/Ni⁴⁺ redox reaction.

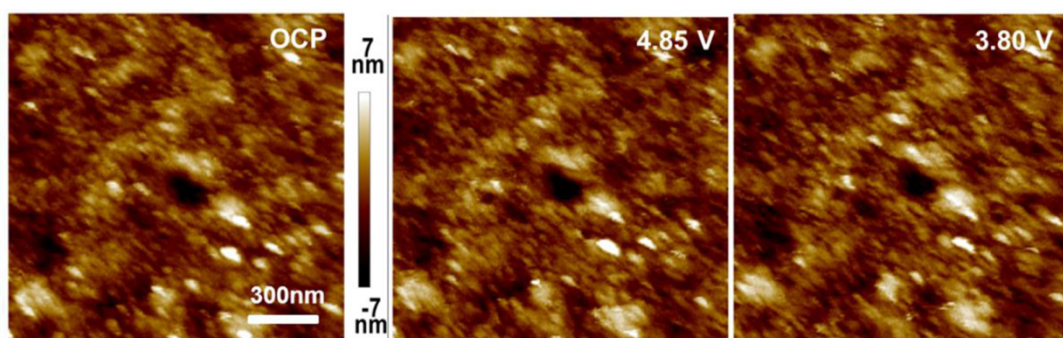


Figure S4. In situ AFM topography images of Al substrate surface at the given potential during the first charge-discharge cycle. The area is $1.5 \times 1.5 \text{ } \mu\text{m}^2$.

The $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple is beyond the potential window of the conventional electrolyte (1.0 M LiPF_6 in EC/DEC). We found LP-71 electrolyte (BASF) can bear high voltage. The surface morphology of Al substrate is checked by in situ AFM during the first cycle. The results show that there are no morphology changes before and after battery operation, which demonstrates that using this electrolyte can avoid morphology changes caused by degradation of electrolyte on Al substrate at the high voltage.

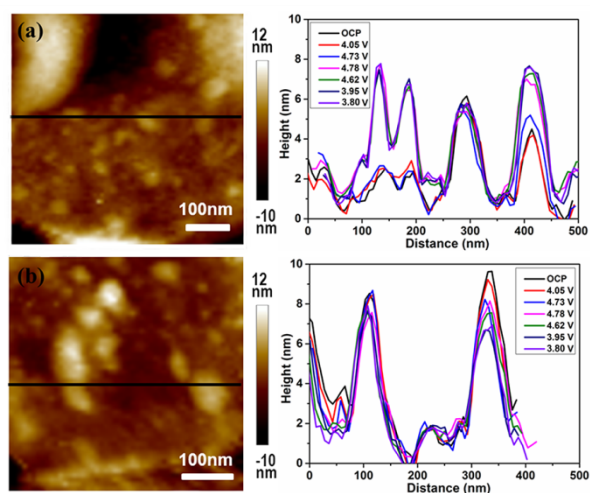


Figure S5. In situ AFM topography images and corresponding height profiles of the line which are marked by black lines on (a) (111) surface and (b) (100) surface. Voltage of the AFM scan lines is given.

The height on (111) surface stayed nearly the same in the initial potential. When potential increased to 4.78 V, the height raised about 4 nm. And then it stayed almost unchanged during the following charging-discharging process. The height on (100) surface stayed almost unchanged throughout the first charging-discharging process.