

Supporting Information

Access to high-performance Li-rich layered oxide cathodes via ammonium phosphate surface treatment

Xiaobao Huang,^a Ding Zhang,^{*ab} Shoudong Xu,^a Liang Chen,^a and Xiaochuan Duan^{*a}

^a College of Chemical Engineering and Technology, Taiyuan University of Technology, No.79 Yingze West Street, Taiyuan, 030024, P. R. China. Email: duanxiaochuan@tyut.edu.cn

^b School of Chemical Engineering and Pharmacy, Wuhan Institute of Technology, Wuhan, 430205, P. R. China. E-mail: zhangding@tyut.edu.cn

Experimental Section

Pristine materials synthesis. The cobalt-free lithium-rich layered oxide material $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (LNMO) was synthesized by the sol-gel method. Firstly, 2.5954 g $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$, 0.9954 g $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ and 2.9411 g $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ (lithium salt in excess of 6%) were weighed and dissolved in 30 mL of deionized water and stirred for 30 min to obtain a homogeneous solution labeled as solution A. Meanwhile, a certain amount of $\text{C}_6\text{H}_8\text{O}_7\cdot \text{H}_2\text{O}$ was dissolved in 60 mL of deionized water according to the ratio of n (citric acid): n (metal ion) = 1:1, and stirred to form solution B. Slowly add solution B to solution A and adjust the pH of the mixed solution to 8 with ammonia. Then transfer the mixed solution to a constant temperature water bath at 80 °C and continue to stir until a green sol and dry at 105 °C for 12 h to form a gel. Finally, the dried material is removed from the oven, ground and placed in a muffle furnace, calcined at 450 °C for 5 h, continued grinding, and then sintered again at 900 °C for 10 h to obtain LNMO.

Surface treatment process. 0.5 g of LNMO and different amounts of $(\text{NH}_4)_3\text{PO}_4$ were added to 50 mL of deionized water. The amounts of $(\text{NH}_4)_3\text{PO}_4$ were 0.0263 g, 0.0439 g and 0.0615 g, respectively. The obtained solutions were stirred continuously at 80 °C until the solvent evaporated. They were placed in a blast dryer for 12 h, followed by vacuum drying for 12 h. Finally, the modified material was obtained by sintering at 400 °C for 4 h. The obtained samples were labeled as NP-3, NP-5 and NP-7, depending on the amount of $(\text{NH}_4)_3\text{PO}_4$ treated.

Materials Characterizations. X-ray powder diffraction (XRD) (Rigaku Ultima IV, Japan) measured the materials' phases using a Cu $K\alpha$ radiation source. The phase change was investigated by the Raman spectrum (LabRAM HR Evolution, Japan). The samples' unpaired electrons were qualitatively and quantitatively evaluated by EPR spectroscopy (Bruker EMXplus-6/1, Germany). The morphology of the materials is observed using a scanning electron microscope (SEM, JEOL JSM-7001F) in combination of an energy dispersive spectrometer (EDS) and a high-resolution transmission electron microscope (HRTEM, JEOL JEM-2100F). X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI) were used to understand the surface atomic valence and surface energy states.

Electrochemical Measurements. To prepare the electrode, the cathode sample, Super P and poly (vinylidene fluoride) (PVDF) were homogeneously mixed in an appropriate amount of anhydrous N-methyl-2-pyrrolidone (NMP) in a weight ratio of 8:1:1. The resulting slurry was poured onto Al foil after 3 h of stirring. After drying on a hot plate at 60°C, the NMP is evaporated and transferred to a vacuum oven at 100°C for 12 h. After pressing the foil, it were cut into circular slices with a diameter of 12 mm. To evaluate the electrochemical capacity, coin-type (CR2025) cells were assembled in an argon-filled glove box (MBraun, Germany). A lithium metal sheet was used as the anode, the above slices as cathode sheets, Celgard 2400 as the separator, and 1.0 M LiPF_6 in ethylene carbonate (EC)-diethyl carbonate (DEC) (volume ratio 1:1) as the electrolyte. The full cell was assembled with a commercial graphite anode. The graphite anode was made of commercial graphite, PVDF, and acetylene black in a ratio of 8:1:1, which was evenly coated on the Cu foil. After being dried at 100°C for 12 hours, the anode was obtained. Then, the graphite negative electrode and lithium metal were assembled into a half-cell, discharged and charged three

times at a specific current. Finally, the anode as the half-cell was taken out in a glove box, and then assembled with the positive electrode to form a full battery. The electrochemical performance of the half-cell and full-cell is based on a LAND 2001A battery-testing instrument in a voltage range of 2.0-4.8 V (the half-cell) and 2.0-4.7 V (the full-cell) at room temperature. The cyclic voltammetry (CV) measurement was executed on an electrochemical workstation (CHI660E, Chenhua in China) between 2.0V and 4.8 V at a scan rate of 0.1 mV s⁻¹. Meanwhile, electrochemical impedance spectroscopy (EIS) was acquired in the frequency range from 0.01~10⁵ Hz.

Collection and characterization of cycled samples. Specifically, EIS test after cycling were obtained by direct electrochemical impedance testing of half-cells after 100 cycles at 1C in the frequency range of 0.01~10⁵ Hz. The cycled half-cells was disassembled in an argon-filled glove box, and the obtained positive electrode sheet was placed in a bottle containing dimethyl carbonate (DMC) solvent to wash away the electrolyte remaining on the surface of the electrode sheet. Then the electrode sheet is removed, the Celgard 2400 separator is placed on the electrode sheet, the residual DMC solvent is wiped off, and the obtained positive electrode sheet is vacuum encapsulated. Finally, SEM, XPS and Raman tests of the samples after cycling were carried out.

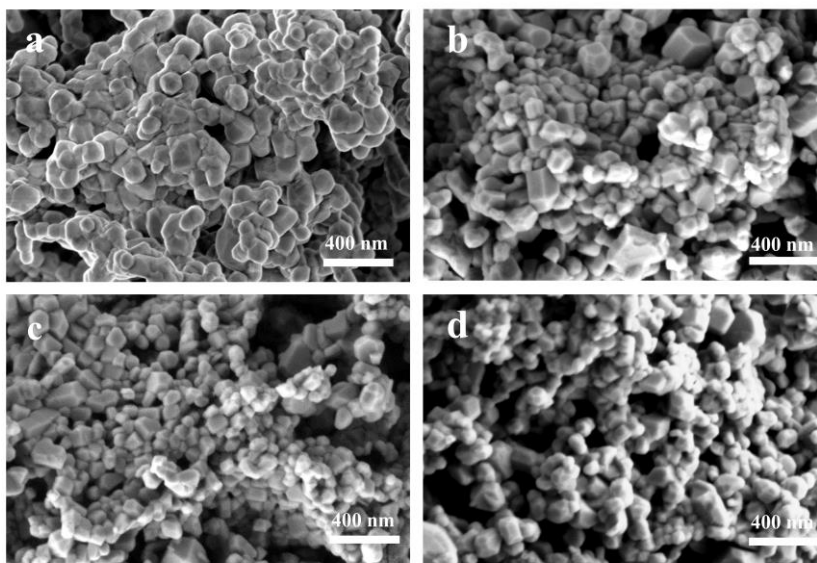


Fig. S1 SEM images of (a) LNMO, (b) NP-3, (c) NP-5, (d) NP-7.

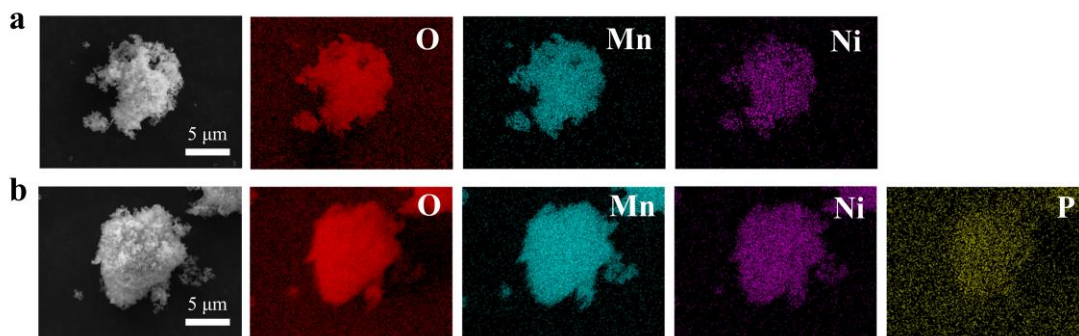


Fig.S2 EDS mapping of (a) LNMO, (b) NP-5.

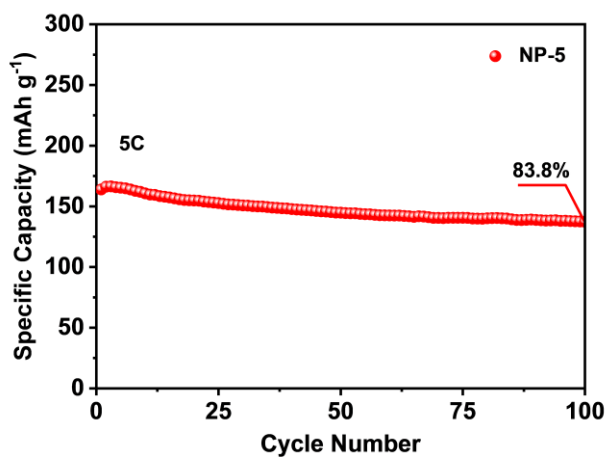


Fig.S3 Half-cell cycling performance of NP-5 at 5C.

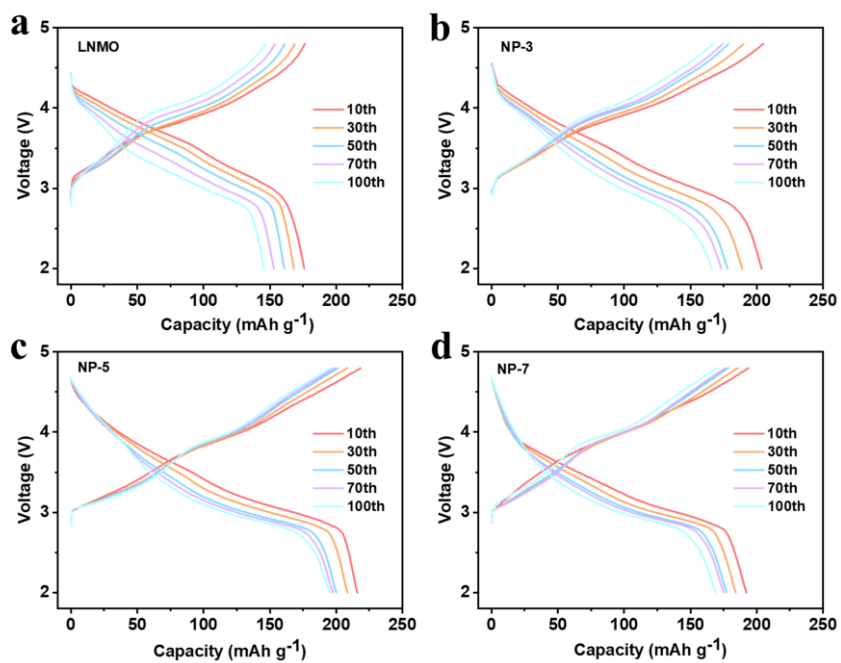


Fig. S4 (a) LNMO, (b) NP-3, (c) NP-5, (d) NP-7 charge/discharge curves for the 10th, 30th, 50th, 70th, and 100th in the voltage range 2.0-4.8 V at rate of 1 C.

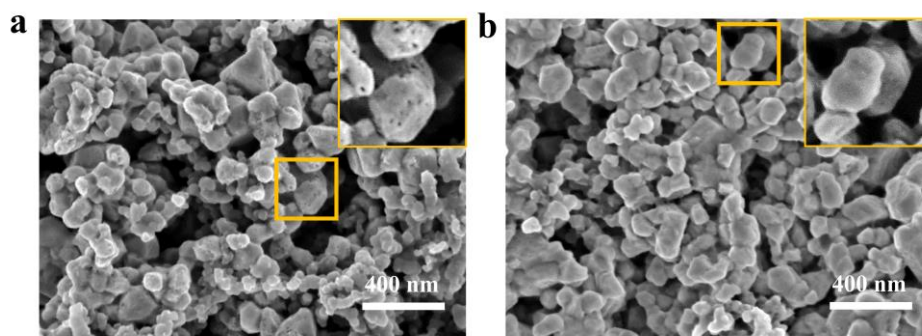


Fig. S5 SEM images of (a) LNMO and (b) NP-5 after 100 cycles at 1 C.

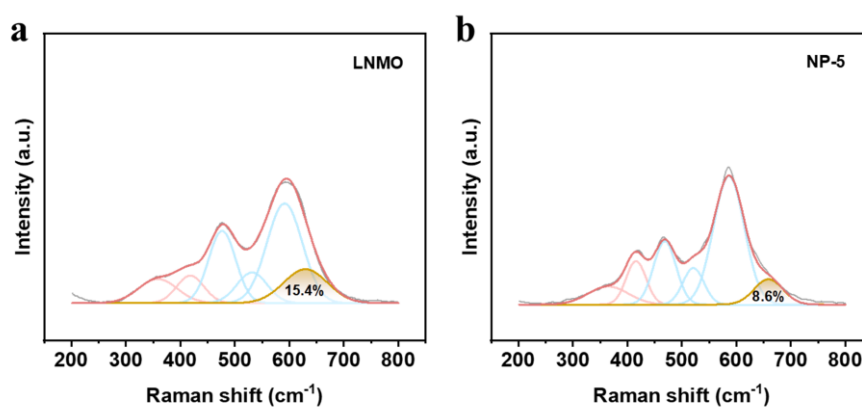


Fig. S6 Peak-differentiating Raman spectra of (a) LNMO, (b) NP-5 after 100 charge/discharge cycles at 1 C.

Table S1. Detailed Parameters of the EIS Test of LNMO and NP-5 before cycling and after 100 cycles at 1C.

Fresh	$R_s(\Omega)$	$R_{ct}(\Omega)$
LNMO	1.8	209.6
NP-5	1.3	160.6
After 100 cycles	$R_s(\Omega)$	$R_{ct}(\Omega)$
LNMO	3.4	253.4
NP-5	3.3	67.7