Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Unveiling the benefits of potassium doping on the structural integrity of Li-Mn-rich layered oxides during prolonged cycling by dual-mode EPR spectroscopy

Jianyin Wang,[†] Mengchu Yang,[†] Chong Zhao,[†] Bei Hu,[†] Xiaobing Lou,[†] Fushan Geng,[†] Wei Tong,[‡] Bingwen Hu,[†] and Chao Li[†,]*

[†]Shanghai Key Laboratory of Magnetic Resonance, State Key Laboratory of Precision Spectroscopy, School of Physics and Electronic Science, East China Normal University, Shanghai 200062, P. R. China

[‡]Anhui Key Laboratory of Condensed Matter Physics at Extreme Conditions, High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, P. R. China

Corresponding Author:

*(C. L.) E-mail: lchao@phy.ecnu.edu.cn

Experimental section

Material Synthesis

Potassium-Doped $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ (KLNMO). In brief, 6 mmol of $KMnO_4$ and 10 mmol of $MnSO_4 \cdot H_2O$ were mixed into sulfuric acid solution (prepared by 2 mL of H_2SO_4 and 30 mL of H_2O) under vigorous stirring. After 15 min, the solution was then sealed in a 50 mL Teflon-lined stainless autoclave and held for 20 min at 160 °C. Subsequently, the K^+-doped α-MnO_2 was acquired by washing and drying at 60 °C overnight. Then, stoichiometric amounts of K^+-doped α-MnO_2, $Ni(NO_3)_2 \cdot 6H_2O$, and $LiOH \cdot H_2O$ were mixed together. Excess $LiOH \cdot H_2O$ (5 wt%) was used to compensate for the evaporation of Li during high-temperature sintering. The compound was firstly calcinated at 500 °C for 5 h and then at 900 °C for 12 h. After quenching to room temperature, the as-fabricated sample was named as KLNMO.

Potassium-Free $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ (LNMO). By contrast, 20 mmol $(NH_4)_2S_2O_8$, 13.6 mmol $MnSO_4 \cdot H_2O$ and 100 mmol $(NH_4)_2SO_4$ were firstly dissolved into 50 mL deionized water under continuous magnetic stirring. After being ultrasonicated for 15 min, the solution was then sealed in a 50 mL Teflon-lined stainless autoclave and held at 180 °C for 12h. Similarly, the potassium-free sample (denoted as LNMO) was obtained by calcining the mixture of K^+-free α-MnO_2, $Ni(NO_3)_2 \cdot 6H_2O$, and $LiOH \cdot H_2O$ (5 wt% excess) at 900 °C for 12 h.

Materials characterization

The X-ray diffraction (XRD) measurements of as-synthesized samples were conducted in synchrotron beam line BL14B at Shanghai Synchrotron Radiation Facility (SSRF). The wave length of the incident monochromatic X-ray is 0.6889 Å. Structural refinement was performed using the Rietveld method and FullProf software. The morphological features and element distribution were explored by the combination of scanning electron microscopy (SEM, S-4800 HITACHI) and transmission electron microscopy (TEM, JEOL J2M-2100). The

chemical composition ratio was acquired by inductively coupled plasma atomic emission spectrometry (ICP-AES).

EPR Tests

Ex-situ electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EMX plus 10/12 X-band spectrometer with a dual-mode microwave cavity and an Oxford ESR910 liquid helium cryostat. The parameters for perpendicular polarization EPR experiments are as follow: microwave frequency, 9.647 GHz; microwave power, 2 mW; modulation amplitude, 2 G; temperature, 90 K. The parameters for parallel polarization EPR experiments are as follow: microwave frequency, 9.403 GHz; microwave power, 2 mW; modulation amplitude, 2 G; temperature, 2 K.

In-situ perpendicular-mode EPR spectra were recorded at room temperature on a Bruker Elexsys 580 X-band spectrometer equipped with HS (high sensitivity) cavity. The in-situ electrochemical cell is fabricated by a similar procedure reported in our previous work.[1] All EPR spectra during battery cycling were recorded under kinetics mode. The total scanning time for each spectrum was 15 minutes, including the stabilization time (10 minutes) and spectrum acquisition period (average of 5 scans). The microwave power and modulation amplitude were set to 0.2 mW and 5 G, respectively.

Electrochemical testing

The electrochemical performance was explored with CR2032 coin cells composed of Li-rich layered oxide cathode, Li metal anode and a separator with1 M $LiPF_6$ in EC: EMC: DMC (1:1:1 in volume) as electrolyte. The cathodes were made up by the as-prepared Li-rich cathode materials, carbon black and PVDF binder (with a weight ratio of 80:10:10) mixing in N-methyl-2-pyrrolidone (NMP). The acquired loading of the active materials is 3.5-4.5

mg/cm^2. The assembled cells were cycled at 0.1C within the voltage window of 2.0-4.8 V (*vs.* Li^+/Li) on a Land 2001A battery testing system at room temperature (1 C = 200 mA g^{-1}). The cyclic voltammetry (CV) tests were carried out by an electrochemical workstation (CHI660e) with a scanning rate of 0.1 mV s^{-1} between the potential range of 2.0-4.8 V (*vs.* Li^+/Li). For the ex-situ characterizations, the cycled electrodes were collected by disassembling the electrochemical cells inside an Ar-filled glovebox and then washed several times with DMC. The wet electrodes were dried overnight at room temperature in Ar-filled glovebox before performing ex situ HRTEM and EPR characterizations.

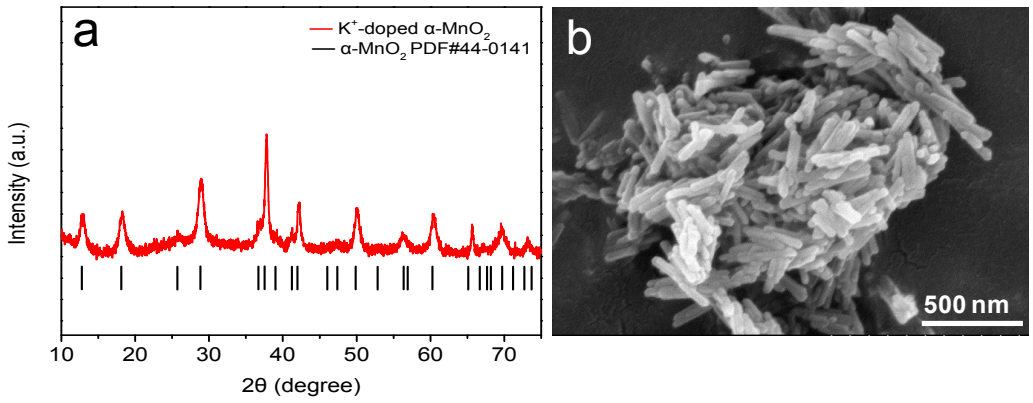

Fig. S1 (a) XRD patterns and (b) SEM images of the K^+-doped α-MnO_2 precusor.

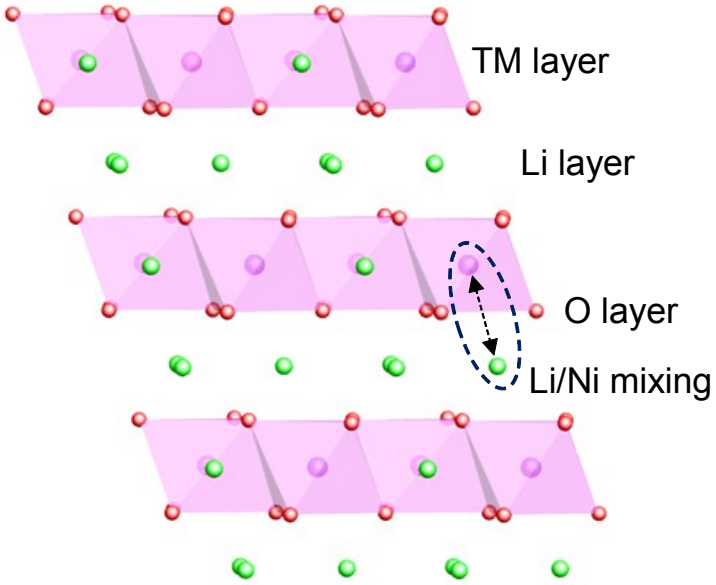

Fig. S2 The corresponding structure model for the KLNMO and LNMO samples.

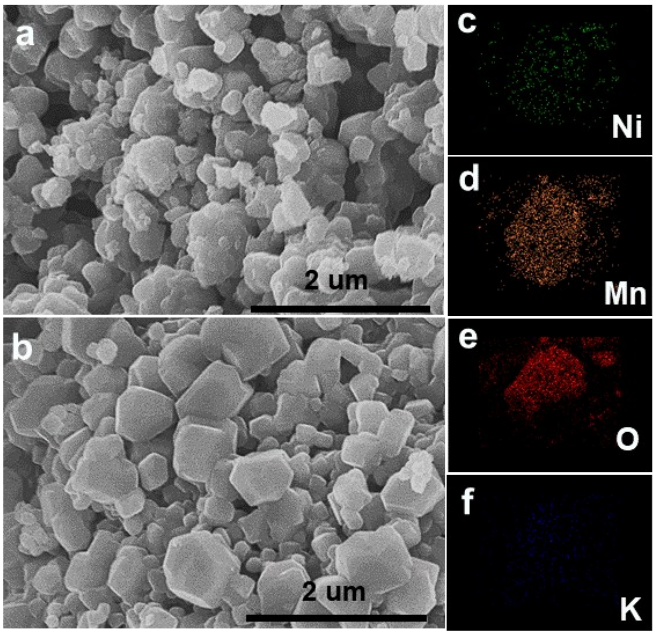

Fig. S3 (a) SEM image and (c-f) the corresponding EDS mapping images of bare KLNMO. (b) SEM image of bare LNMO.

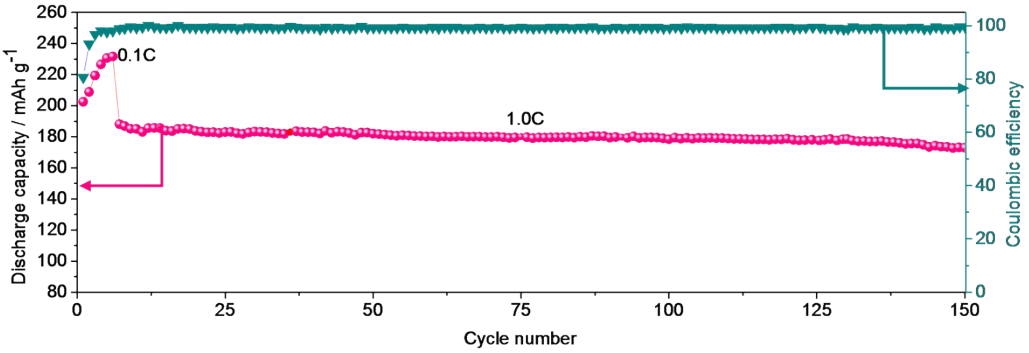

Fig. S4 Cyclic performance of KLNMO under a high current rate of 1C. To activate the electrode, 0.1C was applied in the first 5 cycles.

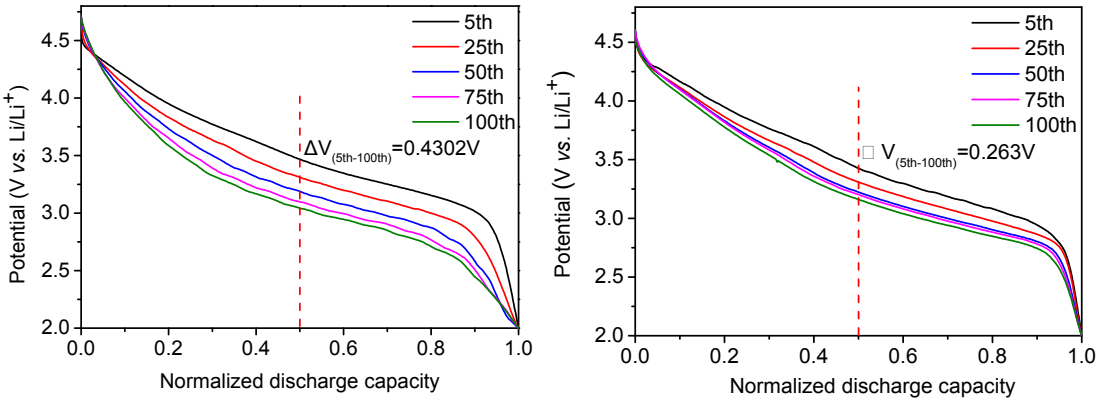

Fig. S5 The discharge voltage *versus* normalized discharge capacity plots of (a) LNMO and (b) KLNMO.

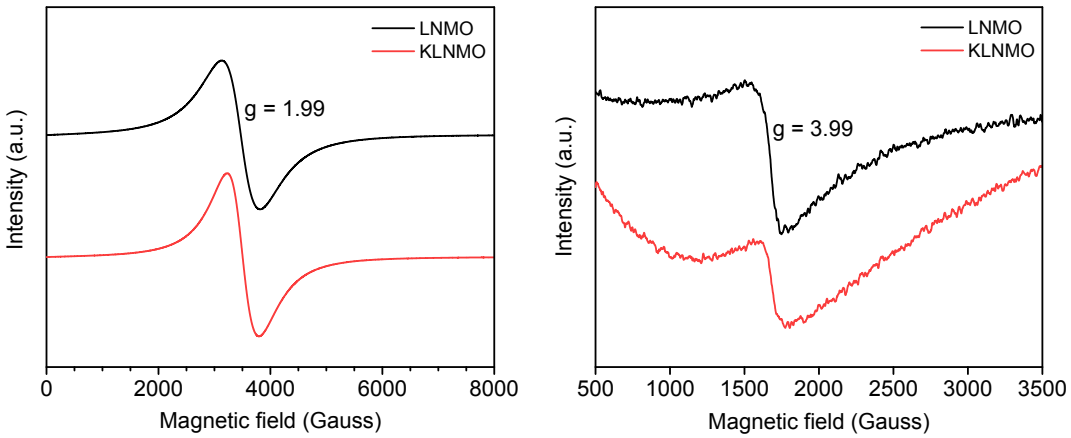

Fig. S6 (a) ⊥-mode EPR spectra at 90 K and (b) ∥-mode EPR spectra at 2 K of pristine LNMO and KLNMO.

Table S1. Rietveld refinement results on the sXRD patterns of pristine LNMO.

Space group *R*-3*m*, R_p(%)=5.92, R_{wp}(%)=7.58, χ^2=2.43.					
Atom	Site	x	y	z	Occ.
O	6c	0	0	0.2424	2.000
Ni1	3a	0	0	0	0.041
Ni2	3b	0	0	0.5	0.159
Mn	3b	0	0	0.5	0.600
Li1	3a	0	0	0	0.959
Li2	3b	0	0	0.5	0.241

Table S2. Rietveld refinement results on the sXRD patterns of pristine KLNMO.

Space group *R*-3*m*, R_p(%)=5.43, R_{wp}(%)=6.95, χ^2=1.69.					
Atom	Site	x	y	z	Occ.
O	6c	0	0	0.2432	2.000
Ni1	3a	0	0	0	0.060
Ni2	3b	0	0	0.5	0.140
Mn	3b	0	0	0.5	0.596
Li1	3a	0	0	0	0.940
Li2	3b	0	0	0.5	0.246
K	3a	0	0	0	0.012

Supplementary references

1. C. Li, M. Shen, X. Lou and B. Hu, *J. Phy. Chem. C*, 2018, **122**, 27224-27232.