Electronic Supplementary Information (ESI)

Alternate Heterogeneous Superlattices Control of Lattice Strain to Stabilize Li-rich Cathode

Ying Zhang,^{ad} Xiaoyu Shi,^{ac} Shuanghao Zheng,^{ac} Yuguo Ouyang,^{ae} Mingrun Li,^{ac} Caixia Meng,^{acf} Yan Yu,*^b Zhong-Shuai Wu*^{ac}

^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

^b Hefei National Research Center for Physical Sciences at the Microscale, Department of

Materials Science and Engineering, CAS Key Laboratory of Materials for Energy

Conversion, University of Science and Technology of China, Hefei 230026, Anhui, China

^c Dalian National Laboratory for Clean Energy, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

^d University of Chinese Academy of Sciences, 19 A Yuquan Road, Beijing 100049, China

^e School of Materials Science and Engineering, China University of Petroleum, Qingdao, Shandong 266580, China

^fDivision of Energy Research Resources, Dalian 116023, China

Experimental Section

Preparation of lithium-rich cathode materials

The pristine cathodes of $Li_{1.2-\sigma}Mn_{0.6}Ni_{0.2}O_2$ (P-LROs) were prepared by a coprecipitation method as reported in our previous work.¹ The lithium-rich cathode with layered-spinel alternate heterostructure combined with coating layer (S-LROs) is prepared by further etching and coating. Typically, 0.05 g/mL P-LROs aqueous dispersion was treated successively by sulfuric acid and aluminum nitrate (1:25, wt%), stirred, centrifuged, washed, and freezing-dried for 48 h. Finally, S-LROs was obtained by calcination at 300 °C with a rate of 5 °C/min for 12 h.

Materials characterization

The transmission electron microscope (TEM) and high resolution-transmission electron microscope (HRTEM) images were observed on a JEM-2100. The time-of-flight secondary ion mass spectrometry (TOF-SIMS) was captured on TOF.SIMS5-100. The electron energy-loss spectroscopy (EELS) spectra, annular bright-field scanning transmission electron microscopy (ABF-STEM) images and high-angle annular dark-field scanning transmission electron microscope with spherical aberration corrector. The sample for STEM and EELS observation were prepared via focused ion beam milling (FIB, FEI Scios). The X-ray photoelectron spectroscopy (XPS) was conducted by a Thermofisher Escalab 250 Xi+, and the binding energy scale was calibrated by the C 1s peak at 284.8 eV. Raman spectra were collected on a bench Raman dispersive microspectrometer (LabRAM HR 800) with a laser source of 532 nm. The electron paramagnetic resonance (EPR) spectra were performed using a Bruker A200 spectrometer. The X-ray diffraction (XRD) was collected in a SmartLab. Rietveld refinements of the XRD patterns were fitted based on the GSAS+EXPGUI software by

using a layered monoclinic phase (C2/m), hexagonal phase, ($R^{3}m$) and spinel phase (Fd³m) as a model. In-situ XRD studies were conducted by coupling an in situ XRD cell and an X-ray diffractometer to simultaneously observe the charge-discharge behavior. Electrode pellets for the in situ XRD measurements contained 5 wt% ketjen black, 5 wt% PVDF binder, and 90 wt% cathode materials.

Electrochemical testing

Electrochemical performances of P-LROs and S-LROs were evaluated with CR2016type coin cells between 2.0 and 4.8 V using a LAND battery tester (Wuhan, LAND Electronics Co., Ltd.) in a programmable constant temperature test chamber (Nanjing, MJS energy technology Co., Ltd.). Cathode slurry was prepared by mixing cathode materials (80 wt%), ketjen black (10 wt%), and PVDF binder (10 wt%) in N-methyl-2pyrrolidone solvent. Coin cells were assembled by using prepared cathodes, lithium foil, and the ceramic membrane in an argon-filled glovebox (< 0.1 ppm of H₂O and O₂), and the electrolyte was 1 M LiPF₆ in a 2:2:6 (mass ratio) mixture of fluoroethylene carbonate-hydrofloroether–fluoroethylene carbonate. The amount of electrolyte used in each cell is about 50 μ L for all tested cells.



Fig. S1 ABF-STEM images of S-LROs. And the inset structure is the layered and spinel phases. Green, Li; red, O; blue, Mn; yellow, Ni.



Fig. S2 (a) The TEM image and (b) HRTEM image of P-LROs.



Fig. S3 (a) HAADF-STEM image and (b) ABF-STEM image of P-LROs.



Fig. S4 (a) TOF-SIMS investigation and (b) 3D overlay distribution of secondary ion AlO⁻ for surface coating layer of S-LROs and P-LROs.



Fig. S5 (a) STEM image of S-LROs for EELS line scan. (b) 2D line scan map imagesand (c) the corresponding EELS spectra of O K, Mn L, and Ni L edge for S-LROs fromthesurfacetothebulk.



Fig. S6 (a) STEM image of P-LROs for EELS line scan. (b) 2D line scan map images and (c) the corresponding EELS spectra of O K, Mn L, and Ni L edge for P-LROs from the surface to the bulk. (d) The enlarged O K edge contour images of P-LROs.



Fig. S7 The fitted Raman spectrum of P-LROs.



Fig. S8 Discharge curves of (a) P-LROs and (b) S-LROs from 0.1, 0.2, 0.5, 1, 2 to 5 C.



Fig. S9 The comparison of specific energy and discharge medium voltage for P-LROs and S-LROs at a current density of 1 C.



Fig. S10 (a, b) The corresponding voltage profiles of Fig. 5b and Fig. 5c. The dQ/dV curves of (c) P-LROs and (e) S-LROs tested from 4.8 V to gradually declined discharge window until 2.0 V and the corresponding voltage profiles of (d) and (f).



Fig. S11 TOF-SIMS investigation on the surface of (a) MnF_3^- and (b) NiF_3^- after cyclingforP-LROsandS-LROs.



Fig. S12 (a) TOF-SIMS investigation to LiF_2 - near the surface, and the corresponding 2D overlay mapping of (b) cycled P-LROs and (c) cycled S-LROs.



Fig. S13 HAADF-STEM images of (a) P-LROs and (b) S-LROs after cycling.



Fig. S14 (a) STEM image of cycled P-LROs for EELS line scan. (b) 2D line scan map image and (c) the corresponding EELS spectra of O K, Mn L, and Ni L edge for cycled P-LROs from the surface to the bulk. (d) The enlarged O K edge contour images of cycled P-LROs.



Fig. S15 (a) STEM image of cycled S-LROs for EELS line scan. (b) 2D line scan mapimage and (c) the corresponding EELS spectra of O K, Mn L, and Ni L edge for cycledS-LROsfromthesurfacetothebulk.

| Phase | Sample | a (Å) | b (Å) | c (Å) | α (°) | β (°) | γ (°) | V (Å ³) |
|-----------------------------|--------|----------|----------|-----------|--------|---------|---------|---------------------|
| C2/m | P-LROs | 4.966755 | 8.551456 | 5.030934 | 90.000 | 109.185 | 90.000 | 201.811 |
| | S-LROs | 4.959684 | 8.575058 | 5.046184 | 90.000 | 109.191 | 90.000 | 202.686 |
| _R 3 _m | P-LROs | 2.854836 | 2.854836 | 14.207832 | 90.000 | 90.000 | 120.000 | 100.282 |
| | S-LROs | 2.858108 | 2.858108 | 14.277330 | 90.000 | 90.000 | 120.000 | 101.003 |
| $Fd^{3}m$ | P-LROs | 8.221109 | 8.221109 | 8.221109 | 90.000 | 90.000 | 90.000 | 555.637 |
| | S-LROs | 8.325827 | 8.325827 | 8.325827 | 90.000 | 90.000 | 90.000 | 577.141 |

Table S1 Structural constants of P-LROs and S-LROs in terms of space group C2/m, R^3m and Fd^3m .

| Materials | Voltage (V) | Capacity (mAh/g) | Initial Efficiency (%) | Cycle capability | Rate capability | Refs. |
|--|-------------|---------------------|------------------------------|--|----------------------|--------------|
| S-LROs | 2.0-4.8 | 307 (25 mA/g) | 103.6 | 84%, 198.5 mAh/g (200 cycles, 250 mA/g) 92.6%, 218.7 mAh/g (100 cycles, 250 mA/g) | 180 (1250 mA/g) | This work |
| LiTaO ₃ coated Li _{1.13} Mn _{0.517} Ni _{0.256} Co _{0.097} O ₂ | 2.0-4.8 | 272.8 (20 mA/g) | 83.72 | 85%, 187 mAh/g (200 cycles, 200 mA/g) | 153.2 (1000 mA/g) | 2 |
| $Li_{1.2}Mn_{0.2}Ti_{0.4}Cr_{0.2}O_2$ | 1.5-4.8 | 257 (20 mA/g) | ~77 | | 155 (1000 mA/g) | 3 |
| $Li_{1.2}Ni_{0.1}Ti_{0.5}Cr_{0.2}O_2$ | 1.5-4.6 | 271 (20 mA/g) | ~76 | | 160 (1000 mA/g) | 3 |
| $Li_{1.2}Mn_{0.6}Ni_{0.2}O_{2\delta}$ | 2.0-4.8 | 260 (25 mA/g) | ~79 | 90%, ~184 mAh/g (200 cycles, 250 mA/g) | ~130 (1250 mA/g) | 4 |
| $\begin{array}{c} Li_{2}MnO_{3}\ modified \\ 0.5Li_{2}MnO_{3}- \\ 0.5LiNi_{0.44}Mn_{0.32}Co_{0.24}O_{2} \end{array}$ | 2.0-4.8 | 292.7 (25 mA/g) | 88.86 | 90.1%, ~205 mAh/g (100 cycles, 250 mA/g) | ~151 (1250 mA/g) | 5 |
| Li _{1.2} Mn _{0.56} Ni _{0.24} O ₂) with gas- solid interface reaction | 2.0-4.8 | 254 (25 mA/g) | ~80 | 86.4%, 171.9 mAh/g (300 cycles, 250 mA/g) | 155.1 (1250 mA/g) | 6 |

 Table S2 Comparison of S-LROs with the previously reported Li-rich metal oxides.

| Sample | Energy loss (eV) | L ₃ /L ₂ ratio |
|---------------|------------------|--------------------------------------|
| P-LROs | 641.75 | 1.48616 |
| S-LROs | 640.5 | 2.221 |
| Cycled P-LROs | 640.5 | 1.54329 |
| Cycled S-LROs | 639.75 | 1.67089 |

Table S3 L_3/L_2 ratio value for the spectra of P-LROs, S-LROs, cycled P-LROs and cycled S-LROs on the surface.

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