Supporting Information

## Interfacial Framework for Breaking through Li-Ion Transport Barrier of Li-Rich Layered Cathode Materials

Yu Zheng,<sup>1</sup> Lai Chen,<sup>1,\*</sup> Yuefeng Su,<sup>1,2,3,\*</sup> Jing Tan,<sup>4</sup> Liying Bao,<sup>1,3</sup> Yun Lu,<sup>1</sup> Jing Wang,<sup>1,2,3</sup> Renjie Chen, <sup>1,2,3</sup> Shi Chen <sup>1,2,3</sup> and Feng Wu<sup>1,2,3\*</sup>

 <sup>1</sup> School of Material Science and Engineering, Beijing Institute of Technology, Beijing, 100081, P. R. China.
<sup>2</sup> Collaborative Innovation Center for Electric Vehicles in Beijing, Beijing, 100081, P. R. China.
<sup>3</sup> Development Center of High Technology Green Materials, Beijing, 100081, P. R. China.
<sup>4</sup> School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing, 100081, China.

*E-mail:* chenlai144@sina.com; suyuefeng@bit.edu.cn; wufeng863@vip.sina.com

## **Experimental Section**

*Synthesis* of *Pristine Li-rich Material (PLR):* The pristine Li-rich material,  $Li_{1,35}Ni_{0,167}Co_{0,167}Mn_{0,667}O_x$  (or  $0.4Li_2MnO_3 \cdot 0.5LiNi_{0,333}Co_{0,333}Mn_{0,333}O_2 \cdot 0.05LiMn_2O_4$ ) was prepared by a carbonate co-precipitation method, involving two steps: step one for synthesis of precursor NiCoMn<sub>4</sub>( $CO_3$ )<sub>6</sub> by a carbonate co-precipitation reaction, and step two for lithiation through a solid-state reaction. The minor spinel structure integrated with layered structure is beneficial for rate performance of Li-rich material<sup>1, 2</sup>. To synthesize the precursor, stoichiometric NiSO<sub>4</sub>·6H<sub>2</sub>O, CoSO<sub>4</sub>·7H<sub>2</sub>O and MnSO<sub>4</sub>·H<sub>2</sub>O (molar ratio 1:1:4) were dissolved together in distilled water with a cationic concentration of 2 M. The aqueous solution was pumped simultaneously with a 2 M Na<sub>2</sub>CO<sub>3</sub> solution and 0.2 M NH<sub>3</sub>·H<sub>2</sub>O solution into a continuously stirred tank reactor (CSTR, volume of 1 L). The co-precipitation temperature was set at 50°C, and the pH was kept at 8.0. The precipitate was separated from the aqueous medium after 6 h. Then it was washed several times, and was dried in a vacuum oven at 120°C for 12 hours. Thereafter, the precursor was mixed with stoichiometric amounts of Li<sub>2</sub>CO<sub>3</sub> by a pestle and mortar. The resulted mixture was calcined in air in two steps: calcination at 500°C for 5 h to decompose the carbonate precursors, then calcination at 900°C for 12 h to obtain PLR.

Synthesis of spinel-skinned Li-rich material (SSLR): The reconstruction of surface structure also involves two steps: step one for partly extracting Li ions from the surface of PLR by ion exchange in an acidic solution, and step two for converting Li-deficient structure into spinel structure through heat treatment. To avoid impairing the bulk structure, a suitable acidic medium is critical. Thackeray<sup>3</sup> has reported that acid treatment (0.1 M HNO<sub>3</sub>) could eliminate the first-cycle capacity loss of the electrodes but damaged their cycling stability and rate capability. Here, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> was selected as our acid medium because of its moderate acidity, low cost and environmental benignity. We could tailor the depth of the treatment layer by

varying the mass ratio of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> to pristine electrode materials. The experiment details are as follows:

Firstly, 100 mL of  $NH_4H_2PO_4$  aqueous solution was prepared. Then, 5 g PLR powders were added into the aqueous solution. The solution was continuously stirred until the variation ratio of pH fell less than 0.01/10min (see the variation in Fig. S1). Thereafter, the solution was filtered, and the obtained powders were washed serval times before drying them in vacuum oven at 80 °C for 12 h. Finally, the powders were calcined at 450°C for 5h to obtain the sample with spinel surface. We described this material as spinel-skinned Li-rich material (SSLR).

To tailor the content of extracted Li ions from the surface of PLR, we prepared a series concentration of  $NH_4H_2PO_4$  solutions. The concentrations were 0.01 M, 0.05 M, 0.25 M, and the corresponding products were labeled as SSLR1, SSLR2, SSLR3, respectively.

## Synthesis and Modification of Li<sub>1.2</sub>Ni<sub>0.2</sub>Mn<sub>0.6</sub>O<sub>2</sub>

To further demonstrate the effectiveness of our modification strategy, we also synthesized another component ( $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ ) of Li-rich material by a sol-gel method, and then applied the same strategy as SSLR3 to it. The detailed synthesis of  $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$  are as follows.

Stoichiometric amounts of  $Mn(CH_3COO)_2 \cdot 4H_2O$ ,  $Ni(CH_3COO)_2 \cdot 4H_2O$  and  $CH_3COOLi \cdot 2H_2O$  were dissolved together in distilled water. A 5 % excess of lithium salt was used to offset lithium evaporative loss in the process of calcination. As chelating agent, citric acid was added dropwise into the salt solution after dissolution. Later,  $NH_3 \cdot H_2O$  was added to adjust the pH value to 7. A gel was obtained after the solution was evaporated at 75 °C with continuous stirring. Then, the obtained gel was dried in vacuum oven at 120 °C for 12 h. The dried precursors were preliminary calcined at 450 °C for 5 h in air. At last, the obtained

powders were pressed into pellets and calcined at 900 °C for 12h in air. After cooling, another component of Li-rich material was obtained.

The modified sample was gained after above pristine Li-rich material was treated as the same way as SSLR3.

## **Characterization Methods**

Structure and Morphology Characterization: The elemental compositions were obtained using inductively coupled plasma-atomic emission spectroscopy (Agilent 7500ce, USA). Power X-ray diffraction (XRD) was performed on Rigaku UITIMA IV-185 with Cu K<sub>a</sub> radiation from  $2\theta = 10^{\circ} \sim 70^{\circ}$  at a scan rate of 1° per minute. High-resolution transmission electron microscope (HRTEM) was conducted on a JEM-1200EX instrument. Raman spectroscopies were performed on the Renishaw RM2000 with RL 633 nm laser. The X-ray photoelectron spectroscopy (XPS) was carried out on PHI Quantera II then was analyzed by the software of XPSpeak. The energy of the spectra was calibrated by the binding energy of the hydrocarbon (C-H) at 284.6 eV. The thermal stability of the electrode was analyzed by differentia scanning calorimetry (DSC, Mettler Toledo) using a sealed high-pressure DSC pan. In the thermal test, the electrodes were firstly charged and discharged in the voltage range of 2-4.6V for one cycle before recharging to 4.6V.

*Electrochemical Properties Tests*: The positive electrode was made of 85 wt% as-synthesized cathode materials, 10 wt% acetylene black and 5 wt% polyvinylidene difluoride. Circular lithium metal was used as negative electrode and Celgard 2400 membrane was used as the separator.1 M LiPF<sub>6</sub> dissolved in mixed solvents of ethylene carbonate (EC) and dimethyl carbonate (DMC) with volume ratio 1:1 was used as electrolyte.

Electrochemical properties of all samples were characterized with coin-type half cell (2025) at 30 °C by Land battery test system (Wuhan, China) in the voltage range of 2.0~4.6V. The current density of 250 mA·g<sup>-1</sup> was defined as 1 C rate during test. Cyclic voltammetry (CV)

measurement was conducted on CHI660 electrochemical workstation. The potential window was 2-4.8V and the scan rates was  $0.1 \text{ mV} \cdot \text{s}^{-1}$  in CV test.



**Fig. S1.** The pH values vs time in a 0.25 M  $NH_4H_2PO_4$  solution. The initial pH of the 0.25 M  $NH_4H_2PO_4$  solution was 4.32, and it rose to 5.48 right after PLR powders were added in. In the first 10 minutes, pH increased rapidly, indicating that the ion exchange reaction occurred extensively. Thereafter, pH rising rate slowed down, which was mostly due to the fact that the majority of Li ions in the surface have been exchanged out. After 80 minutes in this case, the rising rate of pH fell to 0.01/10 min, which was set to be the end signal of ion exchange. Obviously, our surface treatment strategy is facile and efficient. Moreover, the bulk structure is avoided to be damaged owing to the moderate acidity of  $NH_4H_2PO_4$  solution.



**Fig. S2.** (a-c) HRTEM images of PLR; (d,e) corresponding FFT patterns of the regions in (b) and (c). The FFT patterns reveal the (-110) plane of pristine Li-rich cathode material. As we desired, there is minor spinel structure integrated with the layered structure, which is established by the spots that are indicated by the white arrows in (d). The small amount of spinel structure is beneficial for enhancing the rate performance of traditional Li-rich cathode materials. However, their distribution is random and not be controllable.



**Fig. S3.** (a-c) HRTEM images of SSLR attained from different surface areas. All the surfaces are covered by cubic spinel structure, validating the interfacial framework of spinel structure as a skin for the bulk layered structure.



Fig. S4. The first two cycles of the CV profiles of PLR (a) and SSLR (b).



**Fig. S5.** Plots of the peak current density versus the square root of potential scan rate derived from the CVs of PLR (a, c) and SSLR (b, d). (a, b) and (c, d) correspond to the oxidation peak at 3.9V and reduction peak at 3V, respectively.



Fig. S6. Rate capability of the samples treated with various  $NH_4H_2PO_4$  concentrations. The concentrations of  $NH_4H_2PO_4$  are 0, 0.01, 0.05 and 0.25 M, respectively. The measurements

were carried out at 1C, 2C, 5C and 10C charge/discharge rate. Constant voltage at 4.6 V to 0.1C current density was applied during charging.



**Fig. S7.** The voltage-fade issue: (a) charge/discharge curves of the 10<sup>th</sup> and 100<sup>th</sup> cycles for both samples at 1 C rate, (b) the average voltage vs. cycle number. Both samples show clear voltage drop, signifying the phase transformation of Li-rich cathode materials<sup>4-8</sup>. Nevertheless, SSLR shows a more suppressed voltage drop than PLR, and its average voltage in the 150<sup>th</sup> cycle retains more than 3.1 V. The less structure transformation for SSLR should be attributed to the supporting atoms in Li layer that could suppress the migration of TM ions.



Fig. S8. DSC profiles of PLR and SSLR after charging to 4.6V in the second cycle.



**Fig. S9.** Electrochemical properties of pristine  $Li_{1,2}Ni_{0,2}Mn_{0,6}O_2$  and the modified sample: (a) initial charge/discharge curves at 0.1 C rate, and (b) the corresponding dQ/dV plots; (c) rate capability at various charge/discharge rates; (d) cycling performance at 1 C charge/discharge rate; constant voltage at 4.6 V to 0.1C current density was applied during charging in c-d. The initial coulombic efficiency of pristine  $Li_{1,2}Ni_{0,2}Mn_{0,6}O_2$  is improved from 77.2% to 84.9% after applying the same modification strategy. The dQ/dV plot of the modified sample clearly shows the redox peaks corresponding to spinel phase. More importantly, the rate performance of the modified sample exhibits significant improvements in contrast to pristine material due to its surface spinel structure.

Performance -	2-4.6V 1C=250 mAg <sup>-1</sup>		Ref. S9 Li <sub>1.19</sub> Ni <sub>0.16</sub> Co <sub>0.08</sub> Mn <sub>0.57</sub> O <sub>2</sub> 1C=200 mAg <sup>-1</sup>		Ref. S10 Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub> 2-4.8V		Ref. S11 Li <sub>1.17</sub> Mn <sub>0.5</sub> Ni <sub>0.17</sub> Co <sub>0.17</sub> O <sub>2</sub> 1C=200 mAg <sup>-1</sup>		Ref. S12 Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub> 2-4.8V	
	PLR	SSLR	Pristine	AlF <sub>3</sub> coated	Pristine	Carbon coated	Pristine	rGO coated	Pristine	LiVO <sub>3</sub> coated
Initial capacity (mAhg <sup>-1</sup> )	259.1	277.5	227.6	245.6	253	264	250	247	249.8	272
Initial coulombic efficiency (%)	85.2	93.3	82.8	90.8	84.3	96.4	91	99.5	79.4	92.6
1C (mAhg <sup>-1</sup> )	210.8	249.2	ca. 190	ca. 210	200	225	225	228	ca. 180	215
Retention (%, 100 cycles)	75.8 (1C)	83.9 (1C)	73.4 (0.5C)	79.6 (0.5C)	44 (0.2C)	ca. 66.7 (0.2C)	ca. 77.8 (1C)	ca. 84.4 (1C)	ca. 78.9 (1C)	ca. 82.7 (1C)
2C (mAhg <sup>-1</sup> )	165.1	224.8	ca. 165	ca. 190	ca. 160	ca. 185	/	/	136.2	181
5C (mAhg <sup>-1</sup> )	135.4	190.6	ca. 115	ca. 135	ca. 120	ca. 140	ca. 150	ca. 180	65	135
10C (mAhg <sup>-1</sup> )	109	148.6	/	/	ca. 50	ca. 105	ca. 80	ca. 155	31	111
Loading (mg/cm <sup>2</sup> )	3.5-4		/		2-3		4-4.2		4-5	

Table S1. Comparison of the electrochemical performances of SSLR with reported results

References

- S1 J. R. Croy, J. S. Park, Y. Shin, B. T. Yonemoto, M. Balasubramanian, B. R. Long, Y. Ren and M. M. Thackeray, *J. Power Sources*, 2016, **334**, 213.
- S2 B. R. Long, J. R. Croy, J. S. Park, J. Wen, D. J. Miller and M. M. Thackeray, J. *Electrochem. Soc.*, 2014, **161**, A2160.
- S3 S. H. Kang, C. S. Johnson, J. T. Vaughey, K. Amine and M. M. Thackeray, J. *Electrochem. Soc.*, 2006, **153**, A1186.
- S4 J. R. Croy, M. Balasubramanian, K. G. Gallagher and A. K. Burrell, Acc. Chem. Res., 2015, 48, 2813.
- S5 D. Mohanty, J. Li, D. P. Abraham, A. Huq, E. A. Payzant, D. L. Wood, III and C. Daniel, *Chem. Mater.*, 2014, **26**, 6272.
- S6 J. Zheng, P. Xu, M. Gu, J. Xiao, N. D. Browning, P. Yan, C. Wang and J.-G. Zhang, *Chem. Mater.*, 2015, 27, 1381.
- S7 P. Yan, A. Nie, J. Zheng, Y. Zhou, D. Lu, X. Zhang, R. Xu, I. Belharouak, X. Zu, J. Xiao, K. Amine, J. Liu, F. Gao, R. Shahbazian-Yassar, J. G. Zhang and C. M. Wang, *Nano Lett.*, 2015, 15, 514.
- S8 D. Mohanty, A. S. Sefat, J. Li, R. A. Meisner, A. J. Rondinone, E. A. Payzant, D. P. Abraham, D. L. Wood, 3rd and C. Daniel, *Phys. Chem. Chem. Phys.*, 2013, **15**, 19496.
- S9 Y. K. Sun, M. J. Lee, C. S. Yoon, J. Hassoun, K. Amine and B. Scrosati, *Adv. Mater.*, 2012, 24, 1192.
- S10 B. Song, C. Zhou, Y. Chen, Z. Liu, M. O. Lai, J. Xue and L. Lu, RSC Adv., 2014, 4, 44244.
- S11 P. Oh, M. Ko, S. Myeong, Y. Kim and J. Cho, Adv. Energy Mater., 2014, 4, 1400631.
- S12 X. Liu, Q. Su, C. Zhang, T. Huang and A. Yu, ACS Sustainable Chemistry & Engineering, 2016, 4, 255.