# Supporting Information

## Suppressing voltage fading and improving cycling stability for Li-rich Mn-based materials by introducing $MgSO_4$

Jiaxi Xue,† Yajing Wang,† Cui Sun, Pan Xu, Xiaoxiang Fan, Jingmin Fan*, Mingsen Zheng and Quanfeng Dong*

State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, iChem (Collaborative Innovation Center of Chemistry for Energy Materials), Engineering Research Centre of Electrochemical Technologies of Ministry of Education, Xiamen University, Xiamen, Fujian 361005, China.

† These authors contributed equally to this work

*Correspondence: qfdong@xmu.edu.cn; jmfan@xmu.edu.cn

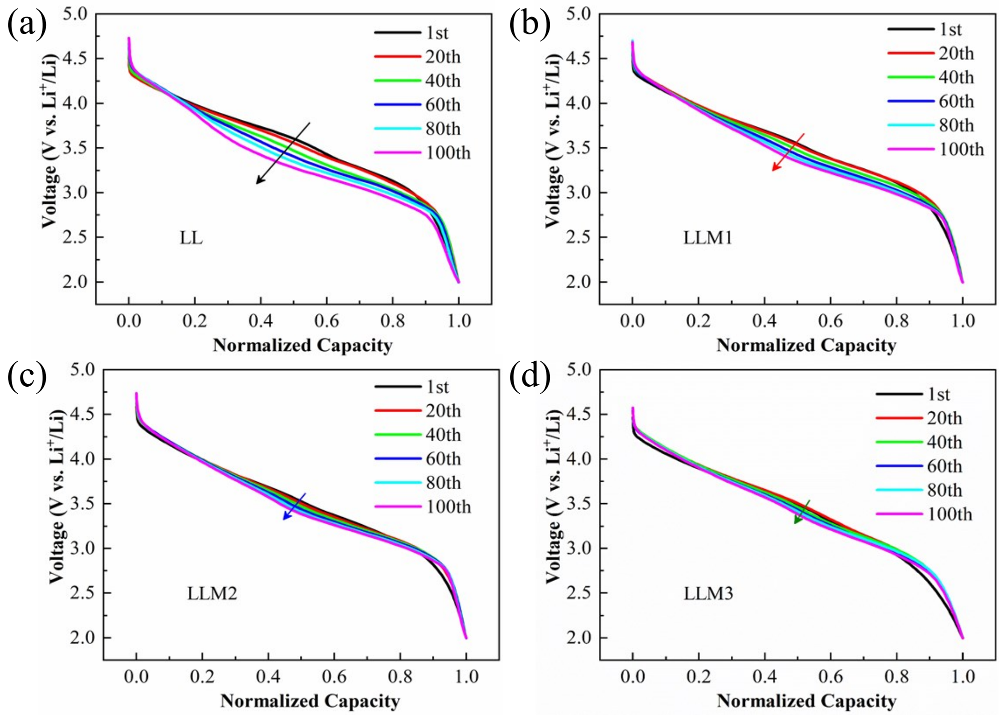


**Fig. S1** The discharge curves of cycling at 1C normalized by discharging capacities of LL, LLM1, LLM2, and LLM3 respectively.

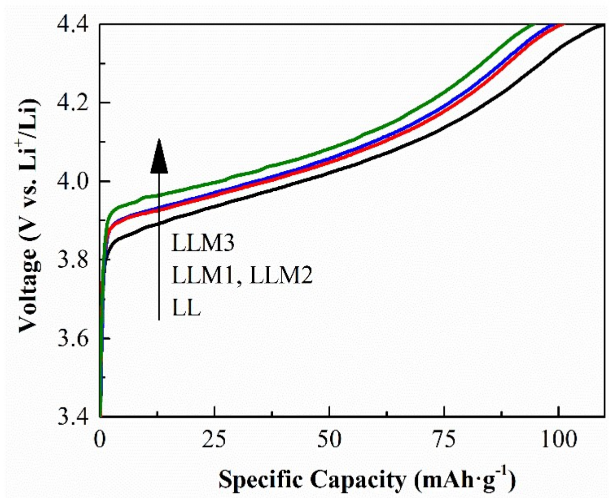


**Fig. S2** Initial charge curves at 3.4-4.4 V of LL,LLM1,LLM2 and LLM3 cathodes.

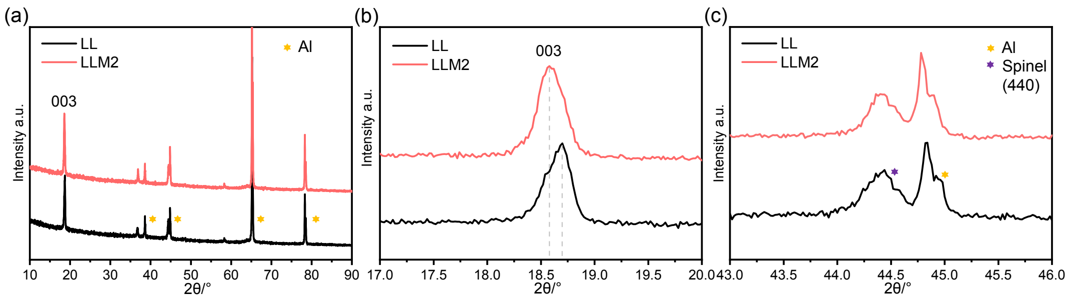


**Fig. S3** (a) XRD patterns of the electrodes after 100 cycles at 1C, (b) the enlarge XRD pattern between 17.0 and 20.0 degree, (c) the enlarge XRD pattern between 43.0 and 46.0 degree.

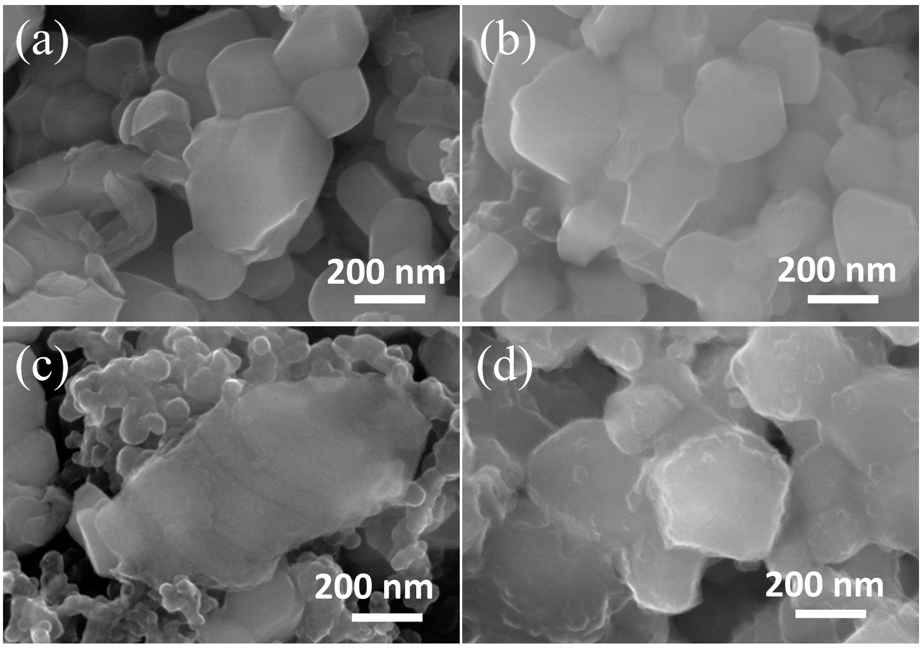


**Fig. S4** The FE-SEM images of (a)LL, (b)LLM2 before cycling and (c)LL, (d)LLM2 after cycling at 1C for 100 cycles.

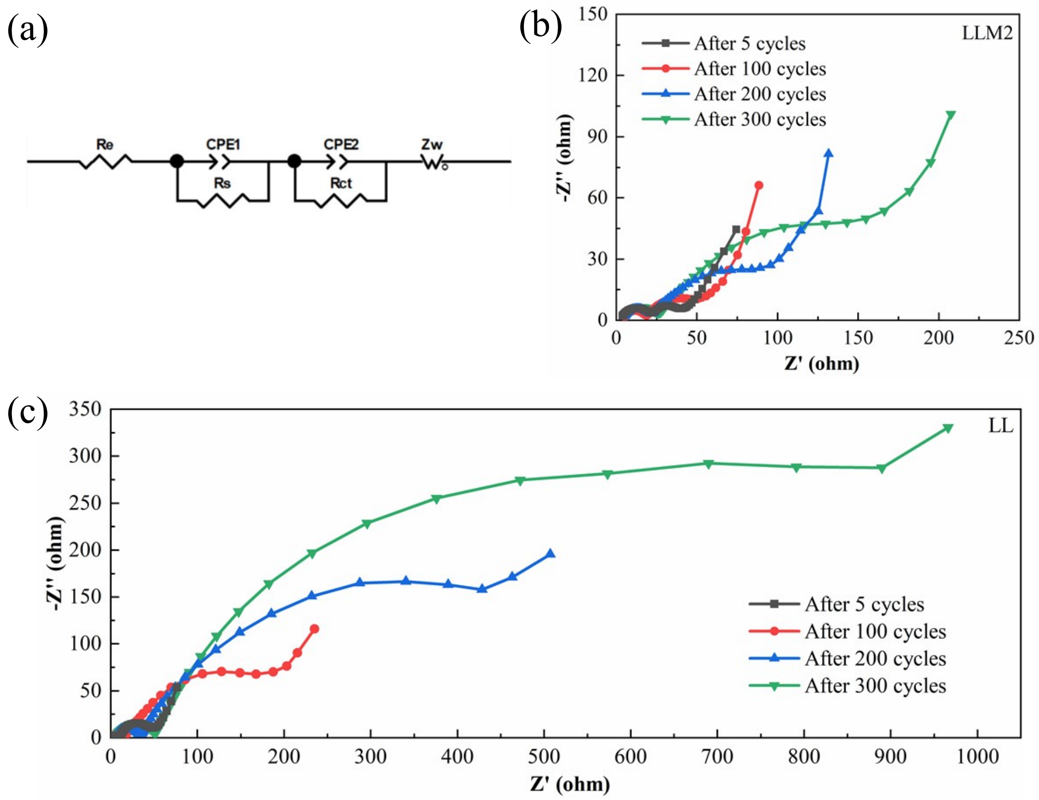


**Fig. S5** (a) the equivalent circuit model, and the EIS Nyquist plots of (b)LLM2, (c)LL.

The electrochemical impedance spectra (EIS) of LL and LLM2 were recorded at 4.0 V charged state after cycling for 5, 100, 200 and 300 cycles at 1C. All recorded Nyquist plots have similar two semicircles at high and medium frequency regions and one slant line at low frequency region. The intercept of Nyquist plot with real axis (Z') represents the electrolyte resistance (Re). The first semicircle at high frequency region represents the surface resistance (Rs) including the interface between the electrode and electrolyte which the $Li^+$ needs to across and the second semicircle at medium frequency region is related to charge transfer resistance (Rct). The slant line can be attributed to Warburg resistance (Rw) indicating the solid diffusion of $Li^+$ in the bulk of the particles.[1] Rct indicates the difficulty of electrochemical reaction during the cycling, and the value of Rct raises after cycling due to the cracking of particles,[2] irreversible phase transition[3]and the increasement of surface layer from the side reaction with electrolyte.[1]

**Table S1.** The specific capacity and coulombic efficiency of the initial cycle

| ($mAh \cdot g^{-1}$) | Charging | Charging (<4.4 V) | Charging (>4.4 V) | Discharging | Coulombic Efficiency (%) |
|---|---|---|---|---|---|
| LL | 321 | 111. | 210 | 253 | 78.8 |
| LLM1 | 300 | 99 | 201 | 250 | 83.2 |
| LLM2 | 291 | 100 | 191 | 250 | 85.8 |
| LLM3 | 273 | 94 | 178 | 238 | 87.6 |

**Table S2.** The rate performance of LL, LLM1, LLM2 and LLM3

| $(mAh \cdot g^{-1})$ | 0.2C | 0.5C | 1C | 2C | 5C | 10C |
|---|---|---|---|---|---|---|
| LL | 238 | 210 | 182 | 160 | 133 | 114 |
| LLM1 | 238 | 213 | 193 | 170 | 142 | 119 |
| LLM2 | 237 | 209 | 190 | 166 | 136 | 108 |
| LLM3 | 222 | 196 | 175 | 151 | 113 | 72 |

**Table S3.** Fitted results of EIS using the equivalent circuit in Fig.S4 (a)

| | LL | | | LLM2 | | |
|---|---|---|---|---|---|---|
| | $R_e(\Omega)$ | $R_s(\Omega)$ | $R_{ct}(\Omega)$ | $R_e(\Omega)$ | $R_s(\Omega)$ | $R_{ct}(\Omega)$ |
| after 5 cycles | 2.48 | 7.08 | 27.28 | 2.09 | 19.07 | 11.42 |
| after 100 cycles | 4.35 | 9.60 | 113.0 | 4.33 | 13.08 | 22.48 |
| after 200 cycles | 5.42 | 27.80 | 580.5 | 3.98 | 16.14 | 76.35 |
| after 300 cycles | 5.99 | 45.61 | 992.8 | 4.46 | 19.89 | 135.6 |

## References:


1 B. Xu, C. R. Fell, M. Chi, Y. S. Meng, Energy Environ. Sci. 2011, **4**, 2223-2233.

2 J. Zheng, M. Gu, J. Xiao, P. Zuo, C. Wang, J. G. Zhang, Nano Lett. 2013, **13**, 3824-3830.

3 S. Sallis, N. Pereira, P. Mukherjee, N. F. Quackenbush, N. Faenza, C. Schlueter, T. L. Lee, W. L. Yang, F. Cosandey, G. G. Amatucci, L. F. J. Piper, Appl. Phys. Lett. 2016, **108**, 263902.