

Electronic Supporting Information

3D Porous Li-rich cathode material with *in situ* modified surface for high performance lithium ion batteries with reduced voltage decay

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Experimental

Preparation of the monodispersed polystyrene (PS) template:

The PS sphere is synthesized by emulsion polymerization method. Potassium peroxy sulfate (0.12 g) used as an initiator and sodium dodecyl sulfate (SDS 0.4 g) used as a surfactant. Both are first dissolved in aqueous alcohol in a 250 ml three-neck flask. Then the styrene (40 ml) monomer is gradually added under Ar atmosphere with continuous rapid stirring.^{1, 2} After heated to 70 °C for 8 hours, the polymerization process come to complete, the PS sphere powder was then collected by evaporating the water solvent in freeze dryer. The SEM image of obtained PS particles can be viewed in Figure S1, and the size is between 50 – 80 nm.

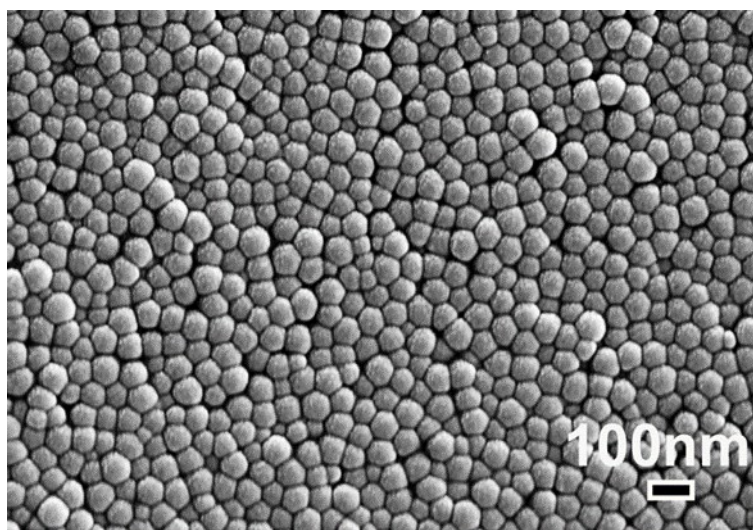


Figure S1. The SEM image of obtained PS particles

Table S1. Lattice parameters of CP-LMNC and PS-LMNC materials obtained by Rietveld refinement

		CP-LMNC	PS-LMNC
MNC (<i>R-3m</i>)	<i>a</i> (Å)	2.8561(1)	2.8563(1)
	<i>c</i> (Å)	14.246(1)	14.259(1)
	<i>c/a</i>	4.988	4.992
	<i>V</i> (Å ³)	100.64(1)	100.75(2)
	Phase content %	61.0(4)	60.8(4)
LMO (<i>C2/m</i>)	<i>a</i> (Å)	4.975(1)	4.959(1)
	<i>b</i> (Å)	8.559(2)	8.561(3)
	<i>c</i> (Å)	5.009(1)	5.021(1)
	<i>V</i> (Å ³)	201.60(9)	201.28(9)
	Phase content %	39.0(4)	39.2(4)
<i>R</i> _{wp}	3.69	4.28	

Table S2. CHN-Analysis results for PS-LMNC and CP-LMNC materials

	C	H	N
PS-LMNC	0.2	0.25	-
CP-LMNC	-	-	-

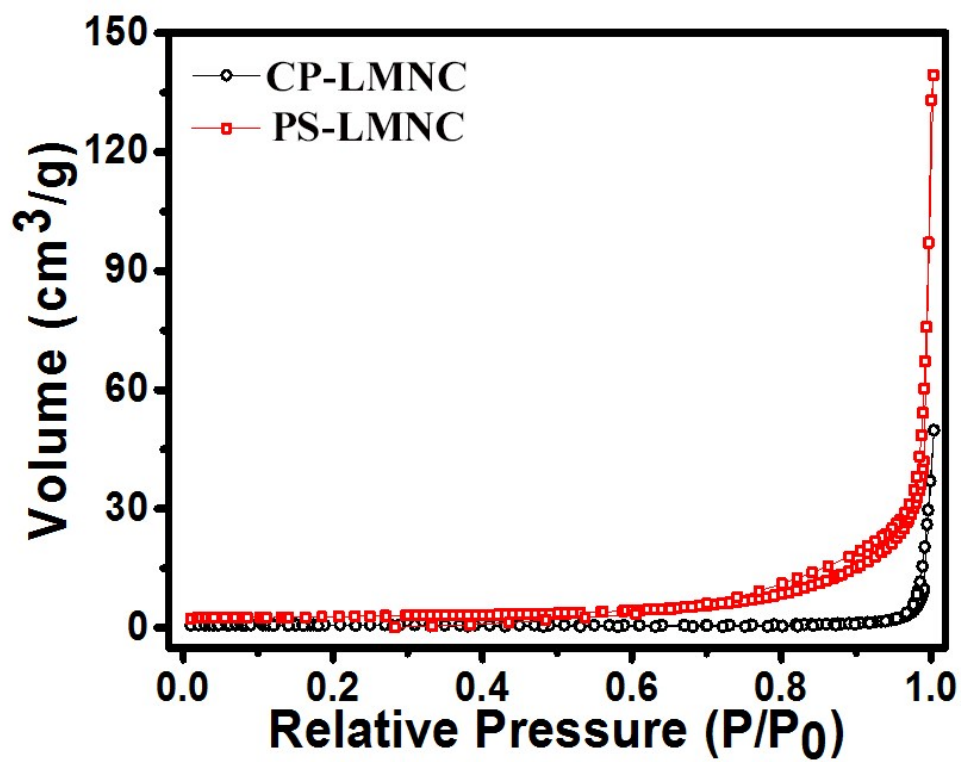


Figure S2. Nitrogen adsorption-desorption isotherms of CP-LMNC and PS-LMNC materials.

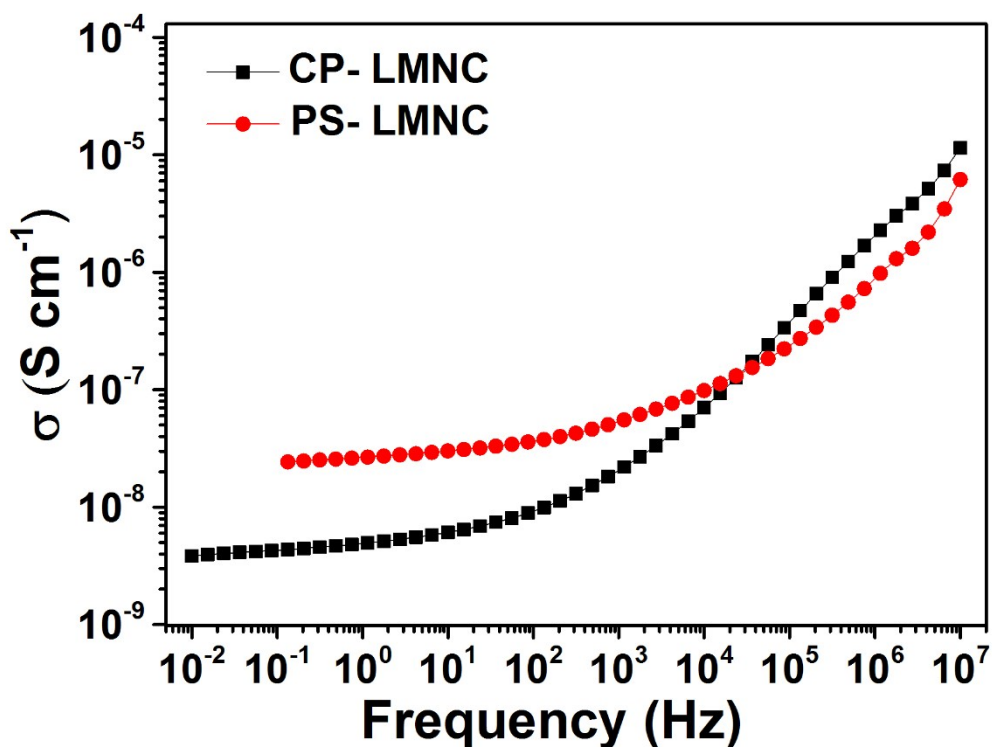


Figure S3. Plots of the conductivity vs. frequency for CP-LMNC and PS-LMNC materials.

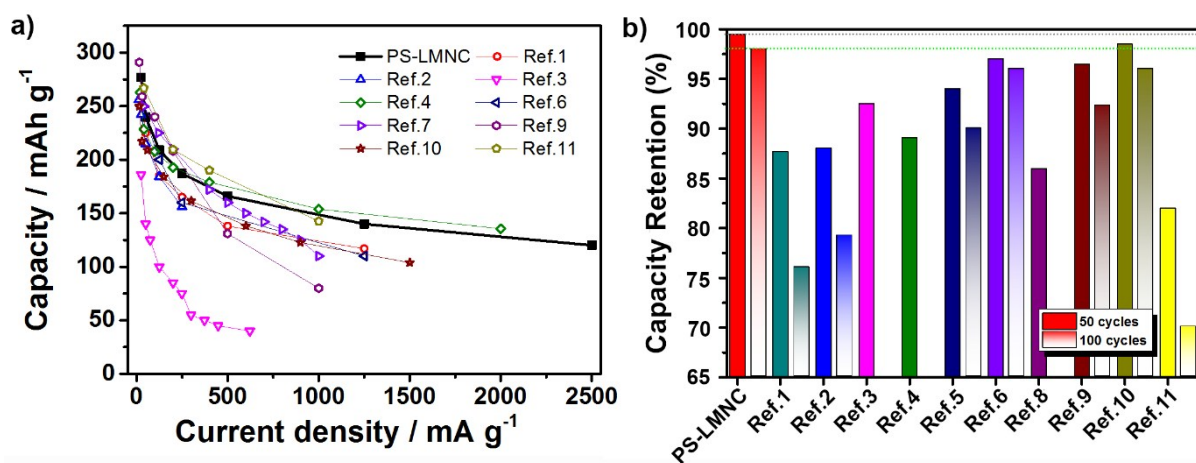


Figure S4. Comparison in the rate performance (a) and cycling stability (b) of the porous Li-rich materials prepared in this work with the literature reports. The detail information of literature materials are given in the table S3.

Table S3. The list of the literatures and the properties of corresponding Li-rich materials which are compared in the Figure S4.

Sample name	Composition	Morphology	Rate for cycling test (mA g ⁻¹)	Mass loading (mg cm ⁻³)
Ref.1 ³	Li _{1.2} Mn _{0.54} Ni _{0.13} Co _{0.13} O ₂	Hierarchically porous	50	
Ref.2 ⁴	Li _{1.2} Mn _{0.54} Ni _{0.13} Co _{0.13} O ₂	Porous hollow structure	250	
Ref.3 ⁵	Li _{1.2} Mn _{0.54} Ni _{0.22} Fe _{0.04} O ₂	Porous	28	3-5
Ref.4 ⁶	Li _{1.2} Mn _{0.54} Ni _{0.13} Co _{0.13} O ₂	Macroporous	200	
Ref.5 ⁷	Li _{1.1} Mn _{0.55} Ni _{0.35} O ₂	Porous nanorods	50	
Ref.6 ⁸	Li _{1.2} Mn _{0.54} Ni _{0.13} Co _{0.13} O ₂	Porous fiber	1250	~10
Ref.7 ⁹	Li _{1.2} Mn _{0.53} Ni _{0.13} Co _{0.13} O ₂	Porous	40	1.5-2.5
Ref.8 ¹⁰	Li _{1.2} Mn _{0.54} Ni _{0.13} Co _{0.13} O ₂	Porous micro-rod	50	
Ref.9 ¹¹	Li _{1.17} Mn _{0.50} Ni _{0.33} O ₂	Mesoporous foams	15	
Ref.10 ¹²	Li _{1.2} Mn _{0.534} Ni _{0.133} Co _{0.133} O ₂	Porous	300	~ 1.5
Ref.11 ¹³	Li _{1.19} Mn _{0.32} Co _{0.49} O ₂	Porous nanorods	40	
PS-LNCM (in this work)	Li _{1.2} Mn _{0.56} Ni _{0.16} Co _{0.08} O ₂	Porous	125	2-2.5

1. D.-l. Ma, Z.-y. Cao, H.-g. Wang, X.-l. Huang, L.-m. Wang and X.-b. Zhang, *Energy & Environmental Science*, 2012, **5**, 8538-8542.
2. J. Zhang, Z. Chen, Z. Wang, W. Zhang and N. Ming, *Materials Letters*, 2003, **57**, 4466-4470.
3. M. Chen, X. Xiang, D. Chen, Y. Liao, Q. Huang and W. Li, *Journal of Power Sources*, 2015, **279**, 197-204.
4. Z. He, Z. Wang, H. Chen, Z. Huang, X. Li, H. Guo and R. Wang, *Journal of Power Sources*, 2015, **299**, 334-341.
5. T. R. Penki, D. Shanmughasundaram and N. Munichandraiah, *Electrochimica Acta*, 2014, **143**, 152-160.
6. S. J. Shi, J. P. Tu, Y. Y. Tang, Y. Q. Zhang, X. L. Wang and C. D. Gu, *Journal of Power Sources*, 2013, **240**, 140-148.
7. J. Yang, F. Cheng, X. Zhang, H. Gao, Z. Tao and J. Chen, *Journal of Materials Chemistry A*, 2014, **2**, 1636-1640.
8. C. Yang, S. Han, J. Huang and M. Qian, *Materials Chemistry and Physics*, 2015, **149-150**, 695-700.
9. T. Rao Penki, D. Shanmughasundaram, A. V. Jeyaseelan, A. K. Subramani and N. Munichandraiah, *Journal of The Electrochemical Society*, 2014, **161**, A33-A39.
10. L. Zhang, W. Borong, L. Ning and W. Feng, *Electrochimica Acta*, 2014, **118**, 67-74.
11. Y. Jiang, Z. Yang, W. Luo, X.-L. Hu, W.-X. Zhang and Y.-H. Huang, *Journal of Materials Chemistry*, 2012, **22**, 14964-14969.
12. C. Cao, L. Xi, K. L. Leung, M. Wang, Y. Liu, R. Ma, S. Yang, Z. Lu and C. Y. Chung, *RSC Advances*, 2015, **5**, 30507-30513.
13. D. Chen, Q. Yu, X. Xiang, M. Chen, Z. Chen, S. Song, L. Xiong, Y. Liao, L. Xing and W. Li, *Electrochimica Acta*, 2015, **154**, 83-93.