

Supporting Information

Hierarchical Porous LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ Nano-/Micro Spherical Cathode Material: Minimized Cation Mixing and Improved Li⁺ Mobility for Enhanced Electrochemical Performance

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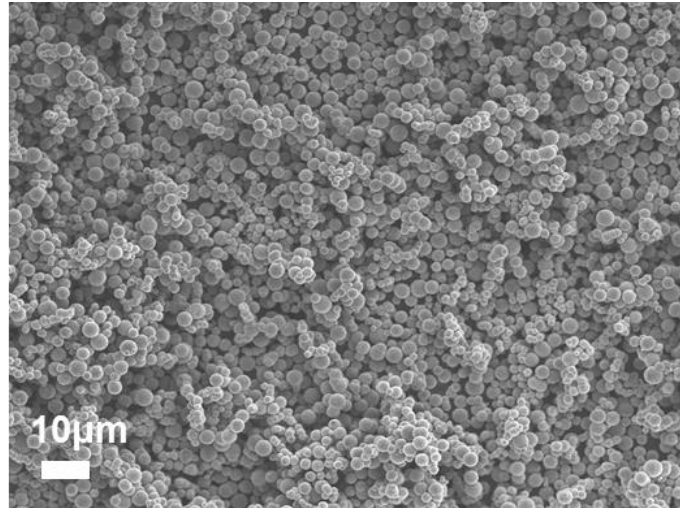


Figure S1. FESEM image of porous fluffy MnO₂.

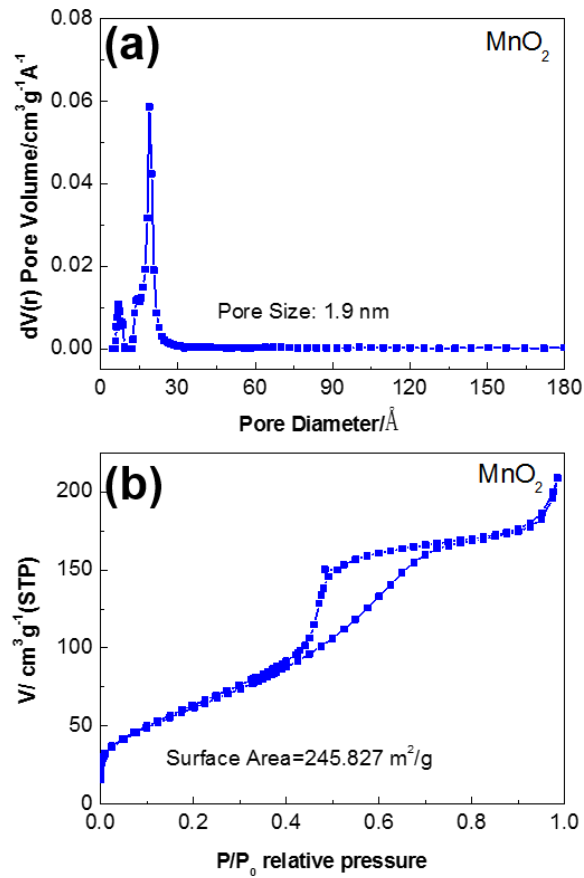


Figure S2. (a) The pore size distribution, and (b) N₂ adsorption/desorption isotherms of fluffy MnO₂.

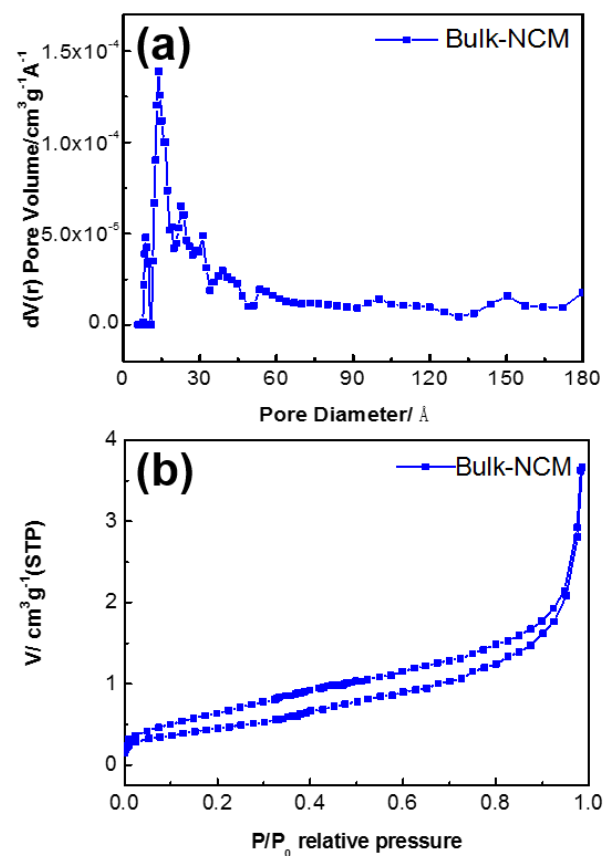


Figure S3. (a) The pore size distribution, and (b) N₂ adsorption/desorption isotherms of Bulk-NCM.

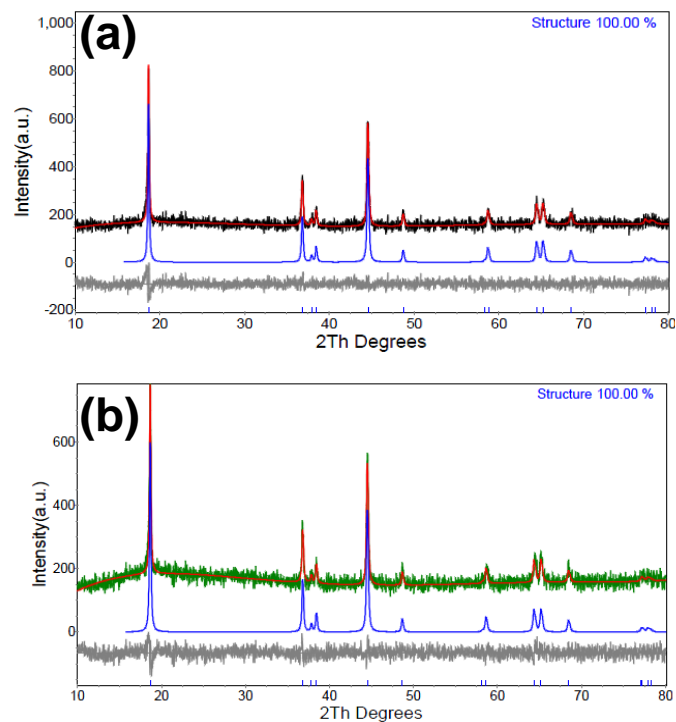


Figure S4. Rietveld refinement of the XRD data for (a) PNM-NCM; (b) Bulk NCM.

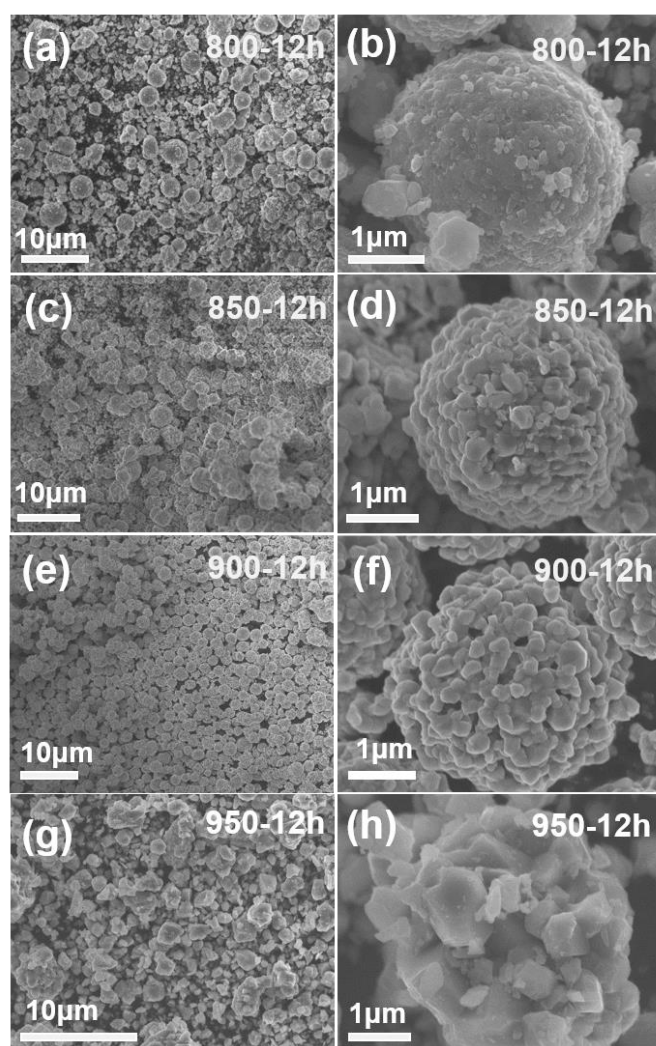


Figure S5. FESEM images of NCM microspheres calcined at different temperature: (a) and (b) 800 °C; (c) and (d) 850 °C; (e) and (f) 900 °C; (g) and (h) 950 °C.

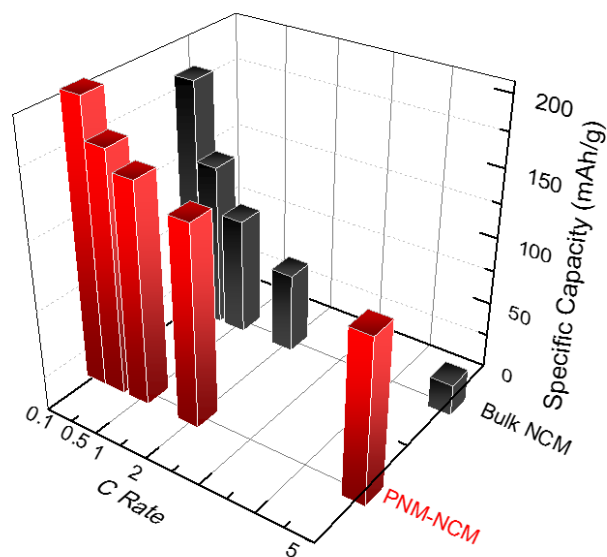


Figure S6. The comparisons of rate capability of electrodes made by PNM-NCM (red columns) and Bulk-NCM (black columns).

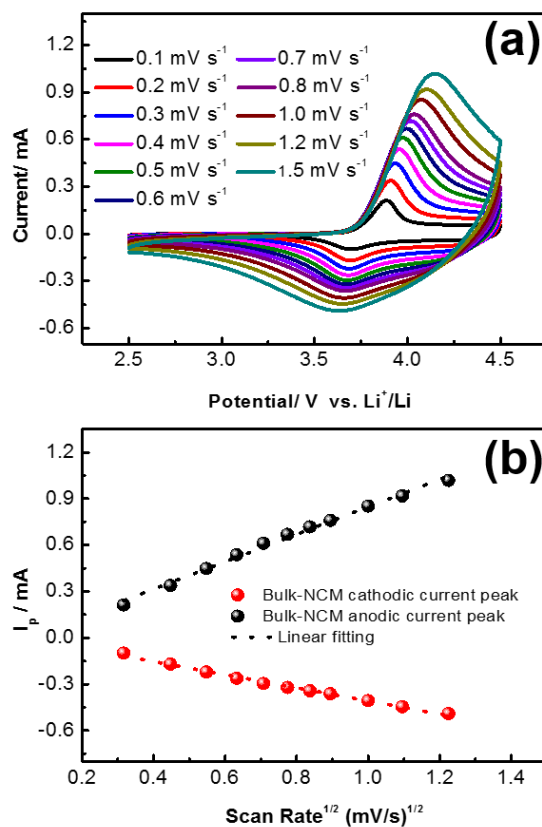


Figure S7. (a) Cyclic voltammetric profiles at various scan rates of 0.1-1.5 mV s^{-1} , (b) Linear response of the peak current density as a function of the square root of scan rate of Bulk-NCM.

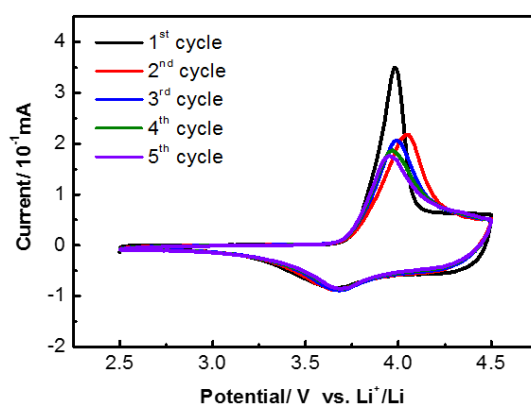


Figure S8. The first five consecutive cyclic voltammograms curves at a scan rate of 0.1 mV s^{-1} over the voltage range 2.5-4.5 V versus Li^+/Li of Bulk-NCM.

Table 1. Summary of PNM-NCM Refinement

Cell Parameters					
Space Group	R3m				
a=2.860(2)Å; c=14.216(8) Å; V=100.50 Å ³ ; Z=3					
I(003)/I(103)=1.399; R=0.875; crystal size=56.6nm, R-factor=0.52					
Atomic Positions					
site	x	y	z	atom	fract
3a	0.00000	0.00000	0.00000	Li^{1+}	0.981
3a	0.00000	0.00000	0.00000	Ni^{2+}	0.019
3b	0.00000	0.00000	0.50000	Li^{1+}	0.019
3b	0.00000	0.00000	0.50000	Ni^{2+}	0.314
3b	0.00000	0.00000	0.50000	Co^{3+}	0.333
3b	0.00000	0.00000	0.50000	Mn^{4+}	0.333
6c	0.00000	0.00000	0.26030	O^{2-}	1

Table 1. XRD pattern refinement parameters of PNM-NCM microspheres.

Table 2. Summary of bulk NCM Refinement

Cell Parameters					
Space Group	R3m				
a=2.865(2)Å; c=14.281(8) Å; V=101.50 Å ³ ; Z=3					
I(003)/I(103)=1.484; R=1.583; crystal size=97.0nm, R-factor=0.58					
Atomic Positions					
site	x	y	z	atom	fract
3a	0.00000	0.00000	0.00000	Li^{1+}	0.957
3a	0.00000	0.00000	0.00000	Ni^{2+}	0.043
3b	0.00000	0.00000	0.50000	Li^{1+}	0.057
3b	0.00000	0.00000	0.50000	Ni^{2+}	0.276
3b	0.00000	0.00000	0.50000	Co^{3+}	0.333
3b	0.00000	0.00000	0.50000	Mn^{4+}	0.333
6c	0.00000	0.00000	0.26030	O^{2-}	1

Table 2. XRD pattern refinement parameters of Bulk NCM.

Reference	Delithiation/ $\text{cm}^2 \text{s}^{-1}$	Lithiation/ $\text{cm}^2 \text{s}^{-1}$
S1 ¹	1.39×10^{-10}	1.51×10^{-10}
S2 ²	4.4×10^{-10}	2.6×10^{-10}
S3 ³	6.6×10^{-10}	3.9×10^{-10}
S4 ⁴	2.04×10^{-8}	6.12×10^{-9}
S5 ⁵	7.8×10^{-10}	4.3×10^{-10}
This work	3.126×10^{-9}	6.921×10^{-10}

Table 3. Comparison of apparent diffusion coefficient of lithium ions among the references.

PNM-NCM	1 st cycle	2 nd cycle	3 rd cycle	4 th cycle	5 th cycle
Oxidation Peak	3.950	3.798	3.792	3.788	3.792
Reduction Peak	3.732	3.727	3.730	3.724	3.720
Bulk NCM	1 st cycle	2 nd cycle	3 rd cycle	4 th cycle	5 th cycle
Oxidation Peak	3.980	4.045	3.992	3.966	3.953
Reduction Peak	3.668	3.668	3.682	3.690	3.690

Table 4. Peak positions of the initial five consecutive cyclic voltammetric curves of PNM-NCM and bulk-NCM microspheres at a scan rate of 0.1 mV s^{-1} in the voltage range 2.5-4.5 V versus Li^+/Li .

Reference	Year	Journal	Redox Peak Separation Value
S1 ⁶	Sept, 2010	Scripta Materialia	~0.2V
S2 ³	May, 2011	J. Mater. Chem.	~0.3V
S3 ⁴	Jun, 2013	Nano Energy	~0.2V
S4 ⁷	Jul, 2013	J. Mater. Chem.A	~0.23V
S5 ⁸	Feb, 2014	Journal of Power Sources	~0.1V
S6 ⁹	Mar, 2014	ACS Appl. Mater. Interfaces	~0.18V
S7 ¹⁰	Aug, 2014	Journal of Power Sources	~0.23V
S8 ¹¹	Jul, 2015	J. Mater. Chem.A	~0.27V
S9 ⁵	Jul, 2015	Nano Energy	~0.2V
S10 ¹²	Sept, 2015	ACS Appl. Mater. Interfaces	~0.3V

Table 5. Comparison of redox peak separation values among the references.

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