

**Supplementary information**

**Insight into microscopic morphology and electrochemical performance  
correlation mechanism upon calcination temperature of novel spherical cobalt-  
free  $0.6\text{Li}_2\text{MnO}_3 \cdot 0.4\text{Li}[\text{Fe}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$  cathode**

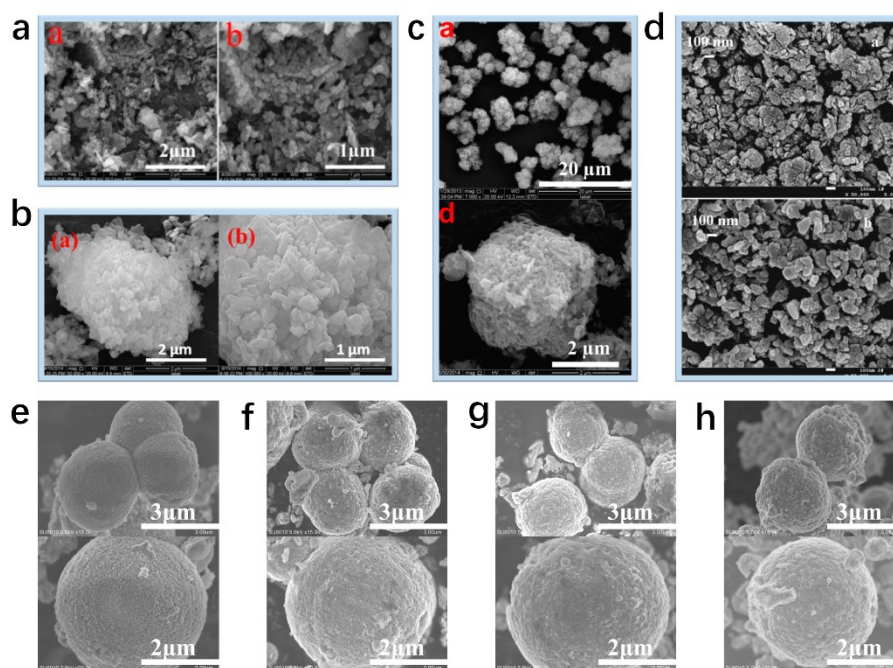
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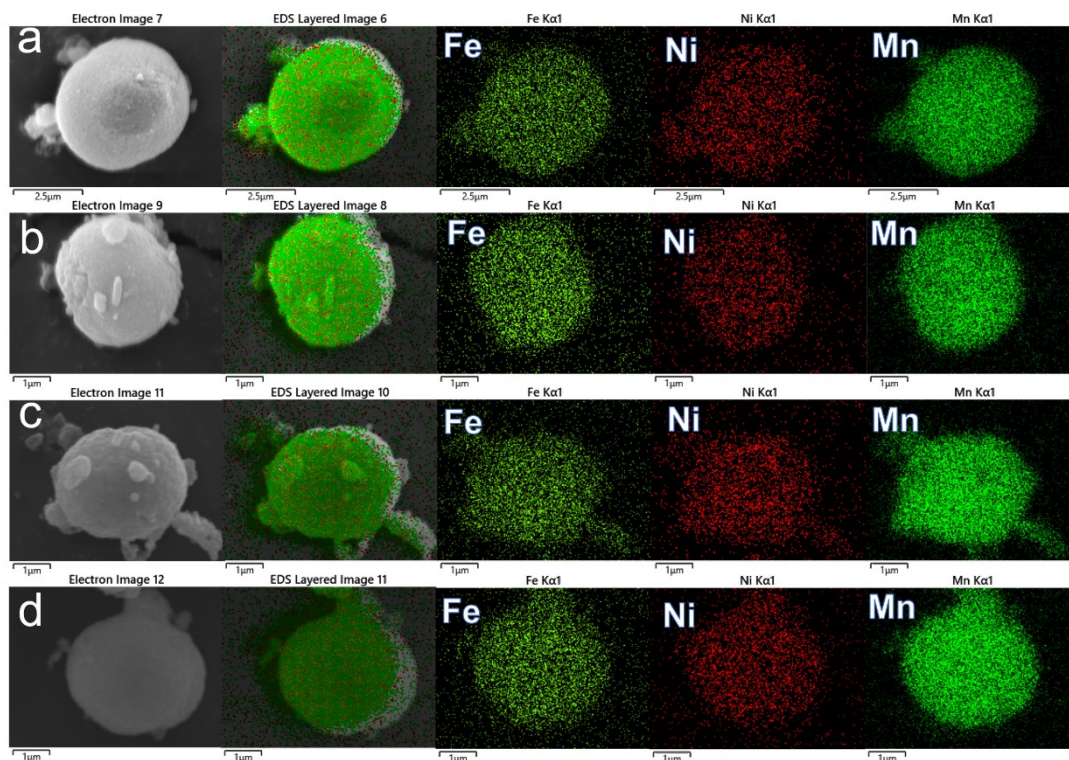
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**Fig. S1** SEM images of (a)  $0.4\text{Li}_2\text{MnO}_3 \cdot 0.6\text{Li}[\text{Fe}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$  <sup>[1]</sup>, Reprinted (adapted) with permission from (ACS Applied Materials & Interfaces, 2014, 6, 22305-22315.). Copyright (2014) American Chemical Society; (b)  $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{Li}[\text{Fe}_{0.25}\text{Ni}_{0.375}\text{Mn}_{0.375}]\text{O}_2$  <sup>[2]</sup>, Reprinted (adapted) with permission from (ACS Applied Materials & Interfaces, 2015, 25, 51-53.). Copyright (2015) American Chemical Society; (c)  $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{Li}[\text{Fe}_{0.25}\text{Ni}_{0.375}\text{Mn}_{0.375}]\text{O}_2$  <sup>[3]</sup>, Reprinted (adapted) with permission from (ACS Applied Materials & Interfaces, 2014, 6, 21711-21720.). Copyright (2014) American Chemical Society; (d)  $0.6\text{Li}_2\text{MnO}_3 \cdot 0.4\text{Mn}_{1/3}\text{Ni}_{1/3}\text{Fe}_{1/3}\text{O}_2$  <sup>[4]</sup>, Reproduced with permission-Copyright 2013, Elsevier (Electrochimica Acta, 2013, 88, 112-116.). SEM images of the  $[\text{Fe}_{2/15}\text{Ni}_{2/15}\text{Mn}_{11/15}]\text{CO}_3$  precursor (e), LFNMO cathodes prepared at different calcination temperatures: (f)800 °C, (g) 850 °C, (h) 900 °C in this work.



**Fig. S2** EDX mapping of the (a)  $[\text{Fe}_{2/15}\text{Ni}_{2/15}\text{Mn}_{11/15}]\text{CO}_3$  precursor, LFNMO cathodes prepared at different calcination temperatures: (b) 800 °C, (c) 850 °C, (d) 900 °C.

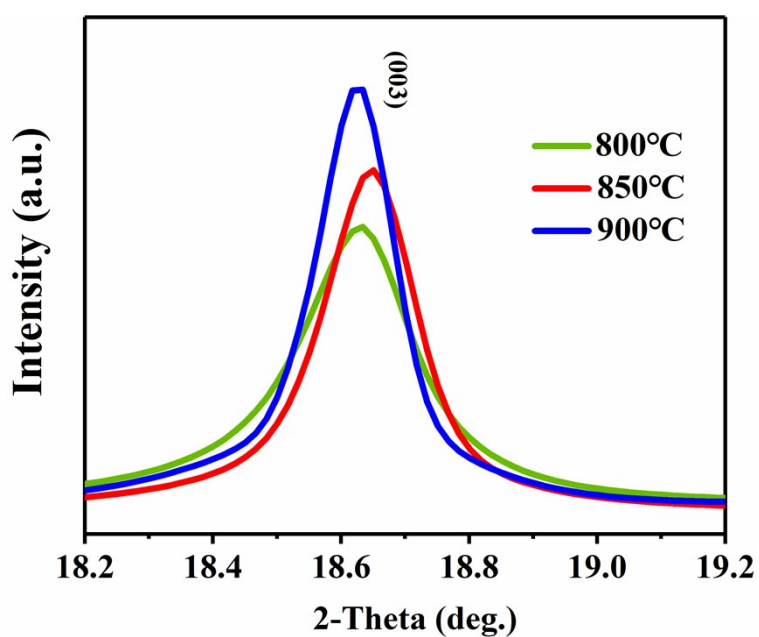
**Table S1** Transition metal element ratios in the precursor and LFNMO cathodes prepared at different calcination temperatures via ICP-OES analysis.

Sample	Element	wt.%	Theoretical value (wt.%)
precursor	Mn	72.51	72.51
	Fe	13.58	13.40
	Ni	13.91	14.09
	total	100	100
800 °C	Mn	72.60	72.51
	Fe	13.24	13.40

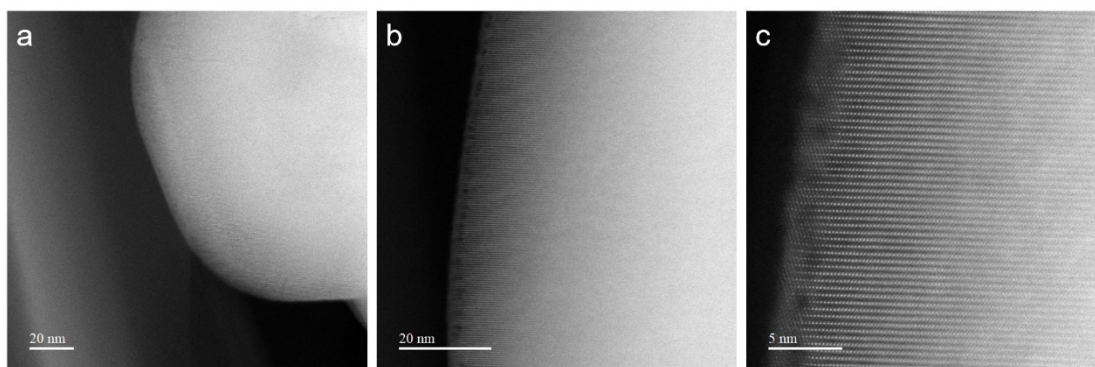
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	Ni	14.16	14.09
	total	100	100
850 °C	Mn	72.49	72.51
	Fe	13.40	13.40
	Ni	14.11	14.09
	total	100	100
900 °C	Mn	72.60	72.51
	Fe	13.01	13.40
	Ni	14.39	14.09
	total	100	100

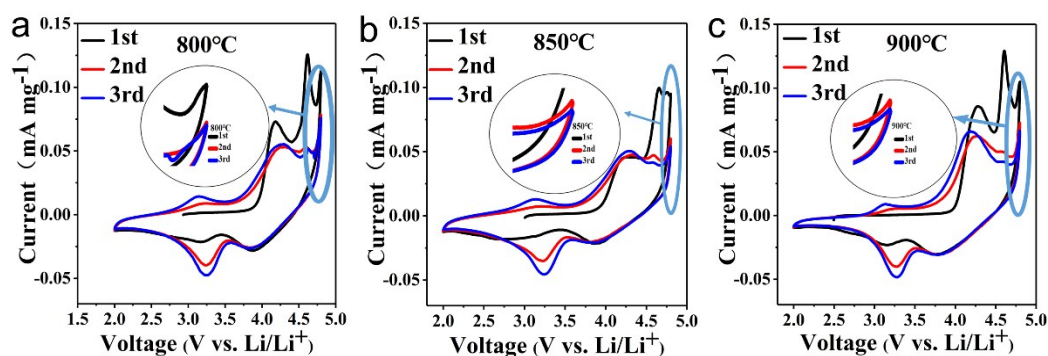
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**Fig. S3** (003) diffraction peaks of the LFNMO cathodes prepared at different calcination temperatures.



**Fig. S4** HAADF-STEM images of the LFNMO sample calcinated at 900 °C.



**Fig. S5** The first three cyclic voltammetry curves of LFNMO cathodes calcinated at (a) 800 °C, (b) 850 °C and (c) 900 °C.

**Table S2** Comparison of the electrochemical performance and tap density of the as-prepared material with the other reported cobalt-free cathodes.

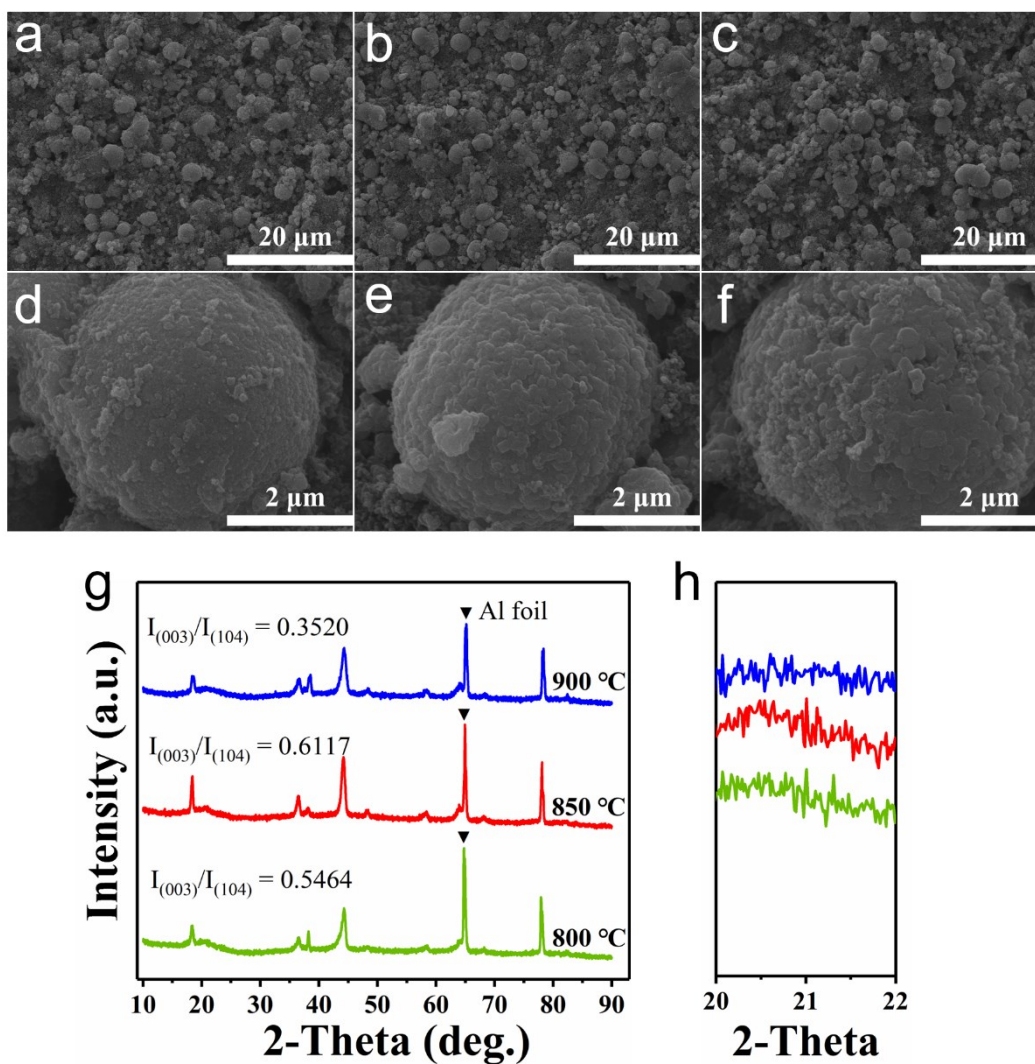
Cathodes	Cycle number	Discharge capacity in voltage range of 2-4.8 V (mAh g <sup>-1</sup> )	Current Densities (mA g <sup>-1</sup> )	Tap Density (g cm <sup>-3</sup> )
In this work. 0.4Li <sub>2</sub> MnO <sub>3</sub> ·	100 <sup>th</sup>	800 °C	163.8	1.91
0.6Li[Fe <sub>1/3</sub> Ni <sub>1/3</sub> Mn <sub>1/3</sub> ]O <sub>2</sub>		850 °C	208.1	25
		900 °C	201.9	
	200 <sup>th</sup>	800 °C	136.7	

		850 °C	189.7		
		900 °C	183.6		
0.4Li <sub>2</sub> MnO <sub>3</sub> ·	50 <sup>th</sup>		151.2	20	n/a
0.6Li[Fe <sub>1/3</sub> Ni <sub>1/3</sub> Mn <sub>1/3</sub> ]O <sub>2</sub> [1]					
0.5Li <sub>2</sub> MnO <sub>3</sub> ·	50 <sup>th</sup>		165.8	20	n/a
0.5Li[Fe <sub>0.25</sub> Ni <sub>0.375</sub> Mn <sub>0.375</sub> ]O <sub>2</sub> [2]					
0.5Li <sub>2</sub> MnO <sub>3</sub> ·	50 <sup>th</sup>		164.8	20	n/a
0.5Li[Fe <sub>0.25</sub> Ni <sub>0.375</sub> Mn <sub>0.375</sub> ]O <sub>2</sub> [3]					
0.6Li <sub>2</sub> MnO <sub>3</sub> ·	20 <sup>th</sup>		192.4	30	n/a
0.4Mn <sub>1/3</sub> Ni <sub>1/3</sub> Fe <sub>1/3</sub> O <sub>2</sub> [4]					

**Table S3** Specific discharge capacity at different rates.

Sample		800 °C	850 °C	900 °C
		Specific capacity (mAh g <sup>-1</sup> )		
	C/10	165	213	200
	C/5	139	168	166
Rate	C/3	119	144	140
(1C=250 mA g <sup>-1</sup> )	C/2	106	130	122
	1C	96	106	97
	2C	60	82	72
	3C	46	67	54





**Fig. S6** SEM images of cycled LFNMO cathodes prepared at (a, d) 800 °C, (b, e) 850 °C and (c, f) 900 °C. (g, h) XRD patterns of cycled LFNMO cathodes prepared at different calcination temperatures.

References:

- [1]. T. Zhao, S. Chen, L. Li, X. Zhang, H. Wu, T. Wu, C. Sun, R. Chen, F. Wu, J. Lu and K. Amine, *ACS Applied Materials & Interfaces*, 2014, **6**, 22305-22315.

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[2]. F. Wu, X. Zhang, T. Zhao, L. Li, M. Xie and R. Chen, ACS Applied Materials & Interfaces, 2015, 25, 51-53.

[3]. T. Zhao, S. Chen, R. Chen, L. Li, X. Zhang, X. Man and W. Feng, ACS Applied Materials & Interfaces, 2014, 6, 21711-21720.

[4]. G. B. Liu, H. Liu and Y. F. Shi, Electrochimica Acta, 2013, **88**, 112-116.