Electronic Supporting Information

 $Co_3O_4@MnO_2/Ni$ nanocomposite as a carbon- and binder-free cathode for rechargeable Li-O₂ batteries

Xiaopeng Han,^{a,b} Fangyi Cheng,^a Chengcheng Chen,^a Fujun Li*^a and Jun Chen^{a,c}

^aKey Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China.

^bKey Laboratory of Advanced Ceramics and Machining Technology (Ministry of Education), School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China.

^cCollaborative Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin, 300071, China.

E-mail: fujunli@nankai.edu.cn



Fig. S1 (a-c) SEM images of Co_3O_4 nanohorns at various magnifications, (d) SEM image of the cross section of Co_3O_4 nanohorns, and (e) TEM and (f) HRTEM images of Co_3O_4 nanohorns.



Fig. S2 SEM images of Co_3O_4 obtained at different hydrothermal reaction temperatures and durations.



Fig. S3 EDS spectrum of the as-synthesized $Co_3O_4@MnO_2/Ni$. The signal of element potassium is ascribed to the K cations in the birnessite-type MnO_2 , which stabilize the lattice structure of manganese oxide and originate from the precursor KMnO₄.



Fig. S4 SEM image of MnO_2 nanosheets supported on a Ni foam.



Fig. S5 XRD patterns and SEM images of Co_3O_4 (a, c and d) and MnO_2 (b, e and f) nanomaterials for the mechanically mixed $Co_3O_4/MnO_2/C$ electrode. Without the support of Ni foam, the Co_3O_4 nanohorns tend to aggregate as porous microspheres. From the enlarged image in (d), it can be seen that the Co_3O_4 nanohorns are several micrometers in length and nanometers in diameter, which are in the same order of magnitude with those of the $Co_3O_4@MnO_2$ nanocomposite in Fig. 2. MnO_2 nanosheets were also obtained with similar thickness to those of the $Co_3O_4@MnO_2$ nanocomposite.



Fig. S6 Cycle performance of Li-O_2 batteries based on the *in-situ* formed nanocomposite of Co_3O_4 @MnO₂/Ni and the mechanical mixture Co_3O_4 /MnO₂/C cathode with the EMITFSI and TEGDME-based electrolyte.

Catalysts	Loading (mg cm ⁻²)	Overpotential /current density	Cycling	
			performance/	Ref.
			cutoff capacity	
			190	
Mesoporous Li _{0.5} MnO ₂	1.0	0.87 V/100 mA g ⁻¹	cycles/1000 mA	1
			h g ⁻¹ carbon	
Co ₃ O ₄ /graphene	1±0.1	~ 1.3 V/200 mA g-1	80 cycles/1000	2
nanoflakes			mA h g ⁻¹	
MnCo₂O₄/graphene hybrid	0.5	0.8 V/100 mA g ⁻¹	40 cycles/1000	3
			mA h g ⁻¹	
Co ₃ O ₄ /3D graphene	1.06	\sim 1.0 V/100 mA g ⁻¹	62 cycles/583	4
			mA h g ⁻¹	
			124	
Porous La _{0.75} Sr _{0.25} MnO ₃	0.9±0.1	~ 1.1 V/27.7 mA g $^{-1}$	cycles/1000 mA	5
nanotubes			h g⁻¹	
lpha-MnO2/graphene		1.0 V/200 mA g ⁻¹	30 cycles/3000	6
composite	N/A		mA h g ⁻¹ carbon	
Porous CaMnO ₃	N/A	0.98 V/50 mA g ⁻¹	80 cycles/500	7
nanostructure			mA h g ⁻¹ carbon	
Meso-LaSrMnO	N/A	1.03 V/100 mA g ⁻¹	50 cycles/500	8
/graphene			mA h g ⁻¹	
			132	
δ -MnO ₂ /3D graphene	1.72±0.1	1.5 V/194 mA g ⁻¹	cycles/1000 mA	9
			$h g^{-1}_{carbon}$	
NiCo ₂ O ₄	0.9	\sim 1.2 V/200 mA g ⁻¹	38 cycles/1000	10
nanosheets			mA h g⁻¹	

Table S1 Comparison of Li- O_2 battery performance based on $Co_3O_4@MnO_2/Ni$ to theother reported cobalt or manganese-based cathode catalysts.

Co ₃ O ₄ @MnO ₂ /Ni		0.76 V/100 mA g ⁻¹	170	This	
	0.8		cycles/1000 mA	wor	
NAs			h g⁻¹	k	

References

- 1. Y. Hu, T. Zhang, F. Cheng, Q. Zhao, X. Han and J. Chen, *Angew. Chem. Int. Ed.*, 2015, **54**, 4338.
- W.-H. Ryu, T.-H. Yoon, S. Song, S. Jeon, Y.-J. Park and I.-D. Kim, *Nano Lett.*, 2013, 13, 4190.
- 3. H. Wang, Y. Yang, Y. Liang, G. Zheng, Y. Li, Y. Cui and H. Dai, *Energy Environ. Sci.*, 2012, **5**, 7931.
- 4. J. Zhang, P. Li, Z. Wang, J. Qiao, D. Rooney, W. Sun and K. Sun, *J. Mater. Chem. A*, 2015, **3**, 1504.
- J. Xu, D. Xu, Z. Wang, H. Wang, L. Zhang and X. Zhang, *Angew. Chem. Int. Ed.*, 2013, 52, 3887.
- Y. Cao, Z. Wei, J. He, J. Zang, Q. Zhang, M. Zheng and Q. Dong, *Energy Environ. Sci.*, 2012, 5, 9765.
- 7. X. Han, Y. Hu, J. Yang, F. Cheng and J. Chen, Chem. Commun., 2014, 50, 1497.
- Y. Yang, W. Yin, S. Wu, X. Yang, W. Xia, Y. Shen, Y. Huang, A. Cao and Q. Yuan, ACS Nano, 2016, 10, 1240.
- 9. S. Liu, Y. Zhu, J. Xie, Y. Huo, H. Yang, T. Zhu, G. Cao, X. Zhao and S. Zhang, *Adv. Energy Mater.*, 2014, **4**, 1301960.
- 10. B. Sun, X. Huang, S. Chen, Y. Zhao, J. Zhang, P. Munroe and G. Wang, *J. Mater. Chem. A*, 2014, **2**, 12053.