

Supplementary Materials

Bifunctional Au-Pd Decorated MnO_x Nanomembranes as Cathode Materials for Li-O₂ batteries

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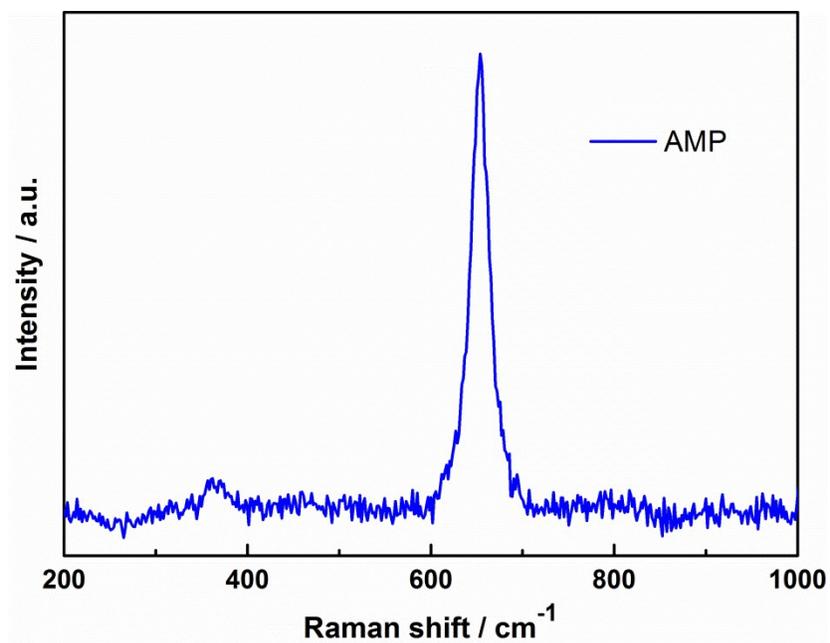


Figure S1. Raman spectrum of Au and Pd decorated MnO_x nanomembranes. The intense peak located at ~654 and ~362 cm⁻¹ are the characteristics of manganese oxides, including possible MnO and MnO₂.¹⁻³

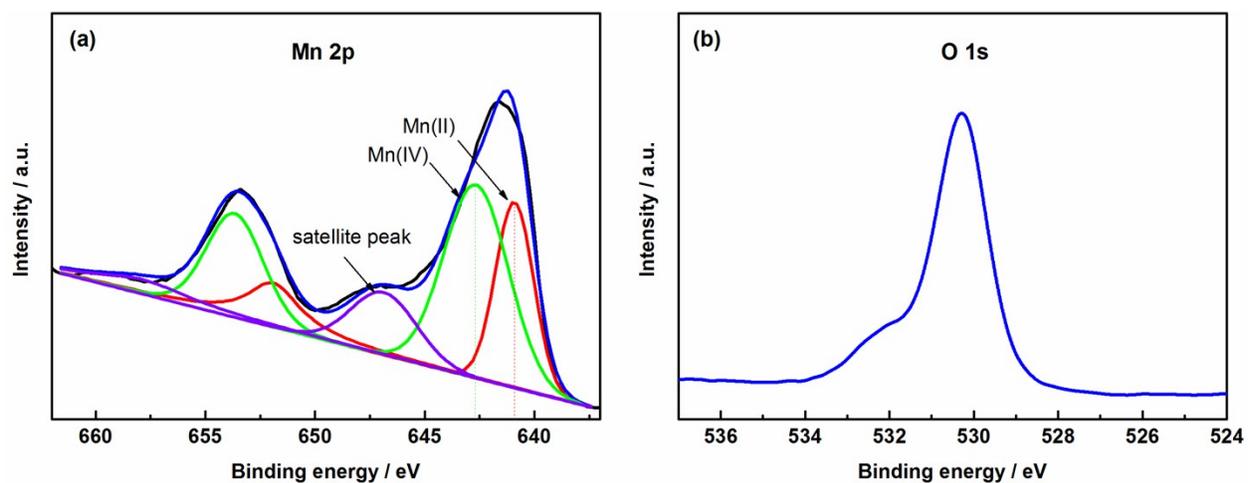


Figure S2. Detailed XPS spectra of Mn 2p and O 1s of pure MnO_x nanomembranes. The Mn 2p spectra of MnO_x is similar to AMP while the binding energies of Mn (II) and Mn (IV) are ~ 1.0 eV lower than that of AMP, which indicates that there exists synergy between metals and MnO_x in the AMP.

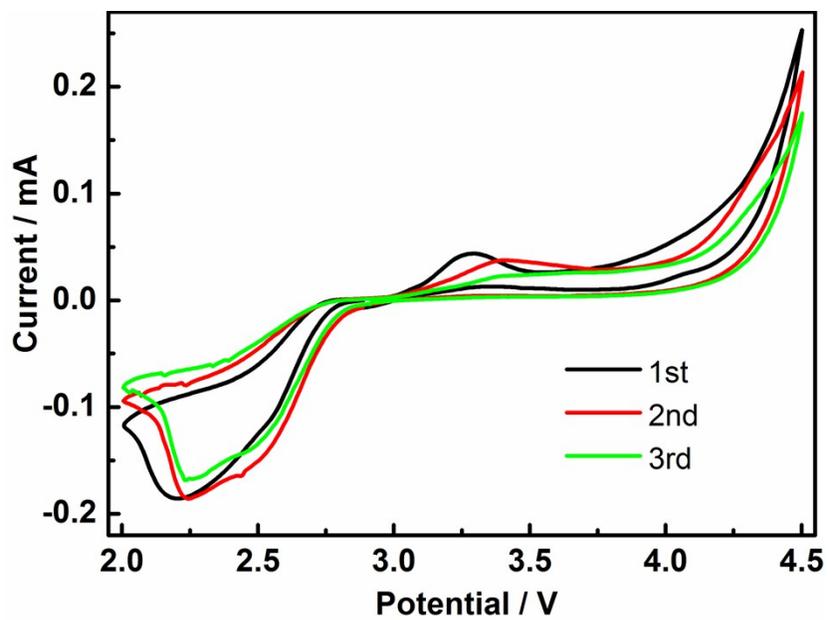


Figure S3. Cyclic voltammetry of Li-O₂ battery with AMP electrode at a scan rate of 0.1 mV s⁻¹.

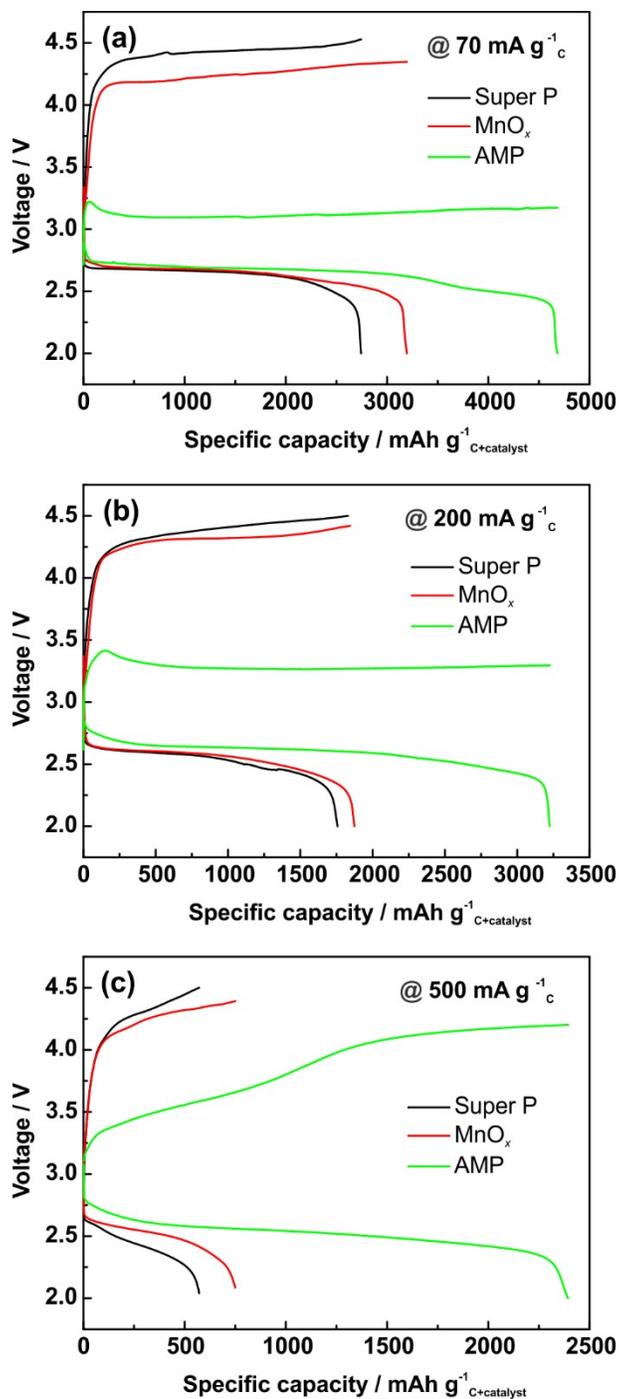


Figure S4. Discharge-charge curves of Li-O₂ batteries with Super P, MnO_x and AMP electrodes at current densities of 70 mA g⁻¹, 200 mA g⁻¹ and 500 mA g⁻¹. The capacity was calculated based on the weight of carbon and catalyst.

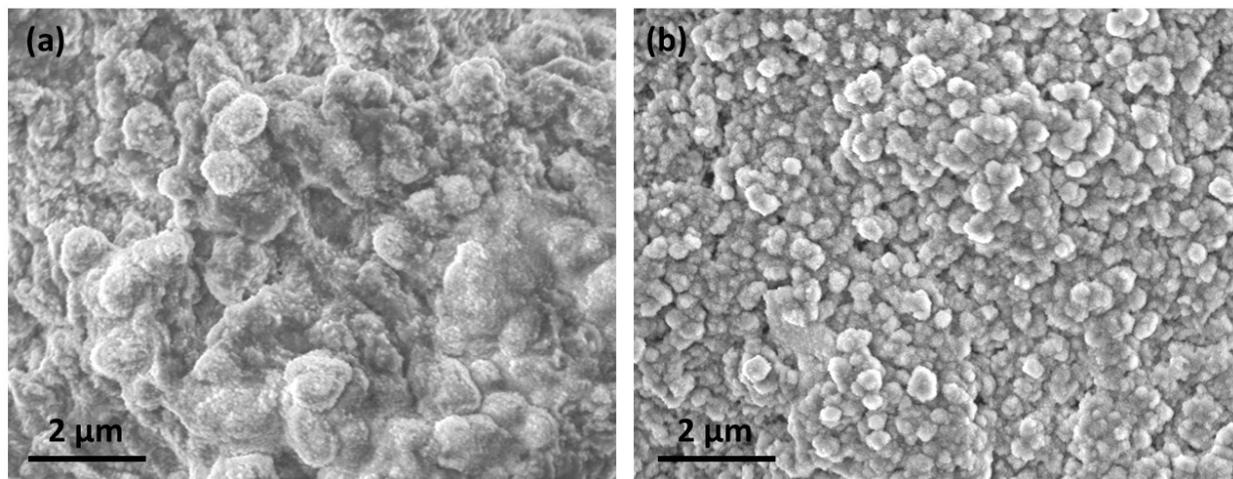


Figure S5. SEM images of Super P and MnO_x electrodes after the 1st discharge process. Large spheres are formed on the Super P electrode. Compared with Super P electrode, more and smaller spheres are generated on the MnO_x electrode after discharging.

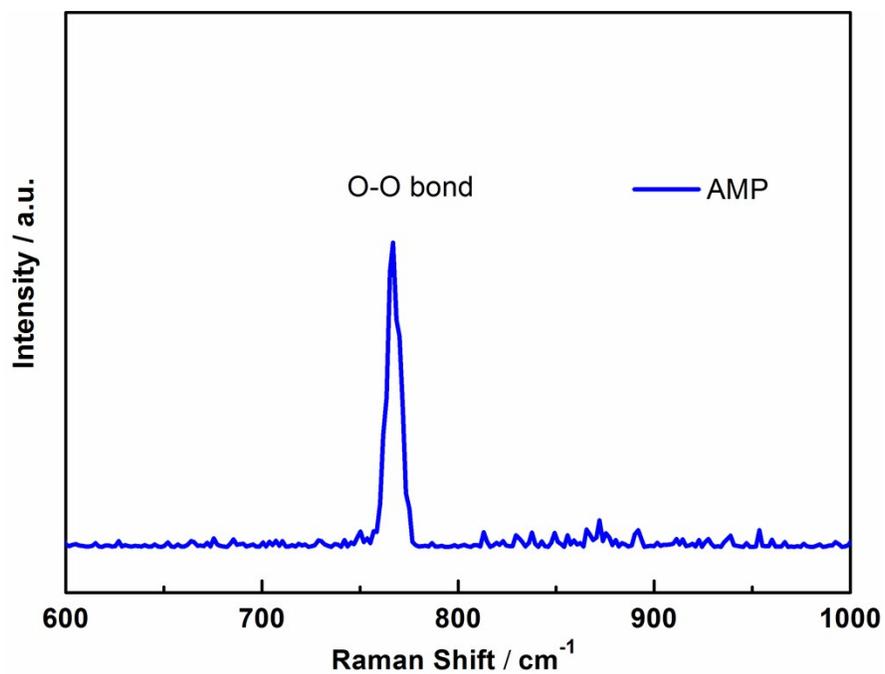


Figure S6. Raman spectra of the discharge product on AMP electrode after the 1st discharge process. The intense peak located at 770 cm⁻¹ corresponds to O-O bond,⁴⁻⁶ indicating that the discharge product consists of Li₂O₂.

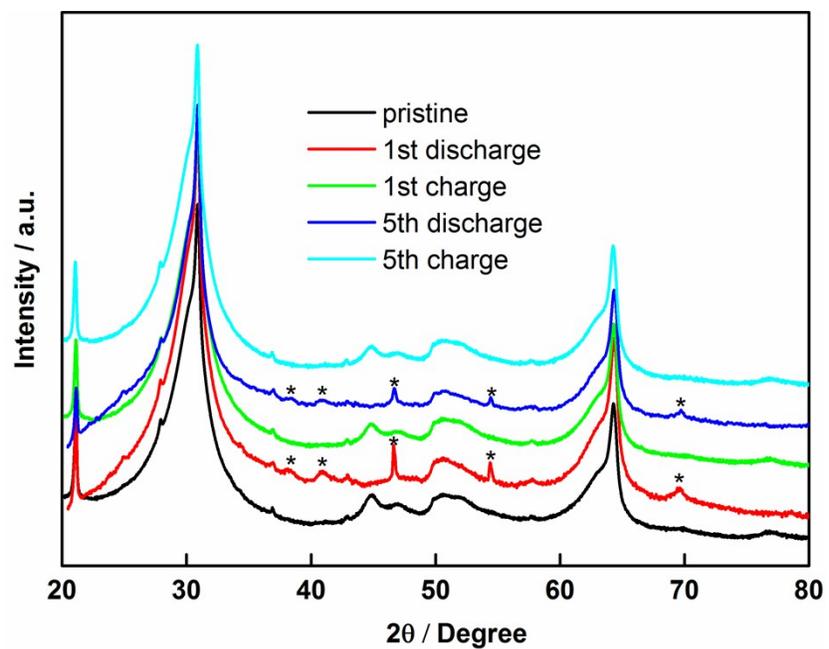


Figure S7. XRD spectra of the pristine AMP electrode and the electrode after discharge/charge processes.

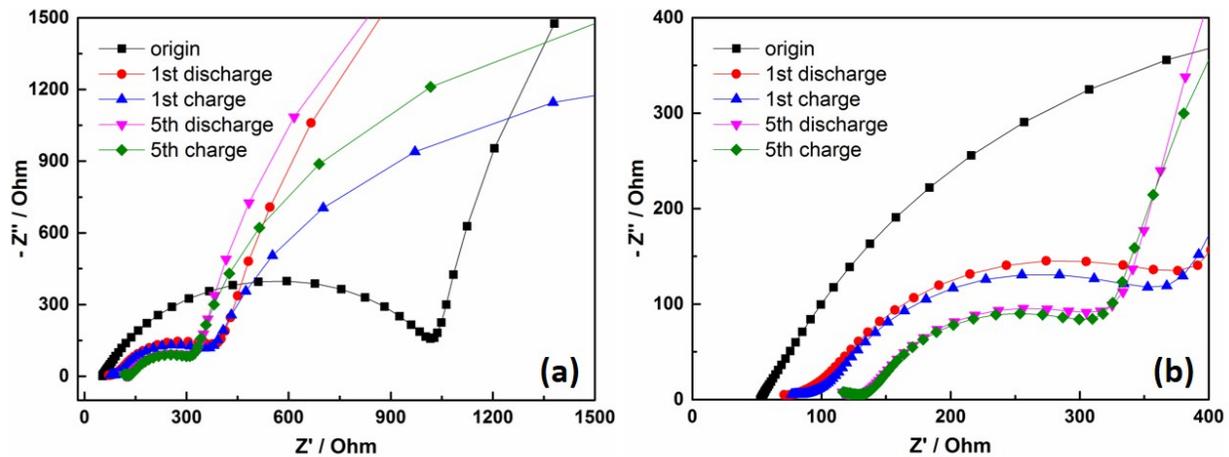


Figure S8. (a) EIS spectrum of Li-O₂ battery with AMP. (b) Magnification of the graph at high frequencies.

Table S1. Electrochemical properties of Li-O₂ batteries with manganese based materials.

Materials	Current density	Capacity /mAh g ⁻¹ _C	Charge voltage /V	Cycle number	References
Au/MnO _x /Pd	70 mA g ⁻¹ _C	6250 mAh g ⁻¹ _C	3.12	120	Our work
MnO ₂ nanowires	70 mA g ⁻¹ _C	3000 mAh g ⁻¹ _C	4.10	-	6
MnO ₂ nanorods	100 mA g ⁻¹ _C	1400 mAh g ⁻¹ _C	4.05	60	7
MnO ₂ nanotubes	0.04 mA cm ⁻²	-	4.31	30	8
MnO ₂ /Graphene	0.083 mA cm ⁻²	7469 mAh g ⁻¹ _C	4.20	132	9
Freestanding MnO ₂	0.1 mA cm ⁻²	1250 mAh g ⁻¹	4.10	90	10
δ-MnO ₂ nanoboxes	0.08 mA cm ⁻²	7862 mAh g ⁻¹ _C	4.10	113	11
Au/MnO ₂	0.2 mA cm ⁻²	10600 mAh g ⁻¹ _C	3.78	100	12
Pt/MnO ₂	70 mA g ⁻¹ _C	10 981 mAh g ⁻¹ _C	3.75	14	13
Pd/MnO _x	100 mA g ⁻¹ _{total}	10620 mAh g ⁻¹ _C	3.60	50	14
La _{0.75} Sr _{0.25} MnO ₃	0.025 mA cm ⁻²	7333 mAh g ⁻¹ _C	4.10	124	15
MnCo ₂ O ₄	0.4 A g ⁻¹ _C	3780 mAh g ⁻¹ _C	3.80	40	16

References

- 1 T. Gao, H. Fjellvag and P. Norby, *Anal Chim Acta*, 2009, **648**, 235-239.
- 2 C. Julien, M. Massot, S. Rangan, M. Lemal and D. Guyomard, *J. Raman Spectrosc.*, 2002, **33**, 223-228.
- 3 Q. Javed, F. P. Wang, M. Y. Rafique, A. M. Toufiq, Q. S. Li, H. Mahmood and W. Khan, *Nanotechnology*, 2012, **23**, 415603-415610.
- 4 K. M. Abraham and Z. Jiang, *J. Electrochem. Soc.*, 1996, **143**, 1-5.
- 5 F. Gittleson, K. P. C. Yao, D. G. Kwabi, S. Y. Sayed, W.-H. Ryu, Y. Shao-Horn and A. Taylor, *ChemElectroChem*, 2015, DOI: 10.1002/celec.201500218.
- 6 A. Debart, A. J. Paterson, J. Bao and P. G. Bruce, *Angew. Chem. Int. Ed.*, 2008, **47**, 4521-4524.
- 7 Y. Qin, J. Lu, P. Du, Z. Chen, Y. Ren, T. Wu, J. T. Miller, J. Wen, D. J. Miller, Z. Zhang and K. Amine, *Energy Environ. Sci.*, 2013, **6**, 519-531.
- 8 T. T. Truong, Y. Liu, Y. Ren, L. Trahey and Y. Sun, *ACS Nano*, 2012, **6**, 8067-8077.
- 9 S. Liu, Y. Zhu, J. Xie, Y. Huo, H. Y. Yang, T. Zhu, G. Cao, X. Zhao and S. Zhang, *Adv. Energy Mat.*, 2014, **4**, 1301960.
- 10 L. Zhang, F. Zhang, G. Huang, J. Wang, X. Du, Y. Qin and L. Wang, *J. Power Sources*, 2014, **261**, 311-316.
- 11 J. Zhang, Y. Luan, Z. Lyu, L. Wang, L. Xu, K. Yuan, F. Pan, M. Lai, Z. Liu and W. Chen, *Nanoscale*, 2015, **7**, 14881-14888.
- 12 S. Liu, G. Wang, F. Tu, J. Xie, H. Y. Yang, S. Zhang, T. Zhu, G. Cao and X. Zhao, *Nanoscale*, 2015, **7**, 9589-9596.
- 13 J. Liu, R. Younesi, T. Gustafsson, K. Edström and J. Zhu, *Nano Energy*, 2014, **10**, 19-27.
- 14 D. Oh, J. Qi, Y. C. Lu, Y. Zhang, S. H. Yang and A. M. Belcher, *Nat. Commun.*, 2013, **4**, 2756-2763.
- 15 J. J. Xu, D. Xu, Z. L. Wang, H. G. Wang, L. L. Zhang and X. B. Zhang, *Angew. Chem. Int. Ed.*, 2013, **52**, 3887-3890.
- 16 H. Wang, Y. Yang, Y. Liang, G. Zheng, Y. Li, Y. Cui and H. Dai, *Energy Environ. Sci.*, 2012, **5**, 7931-7935.

