

Electronic Supplementary Material

Fe₂Mo₃O₈ nanoparticles self-assembling 3D mesoporous hollow spheres toward superior lithium storage properties

Lifeng Zhang (✉)^{1,2}, Yifei Song¹, Weiping Wu (✉)², Robert Bradley^{3,4,5}, Yue Hu¹, Yi Liu¹, Shouwu Guo (✉)^{1,6}

1 School of Materials Science and Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China

2 Department of Electrical and Electronic Engineering, School of Mathematics, Computer Science and Engineering, City, University of London, London, EC1V 0HB, UK

3 Department of Materials, University of Oxford, Oxford, OX1 3PH, UK

4 MatSurf Technology Ltd., The Old Stables Marion Lodge, Cumbria, CA10 1NW, UK

5 School of Energy Resources, University of Wyoming, Laramie, WY 82071, USA

6 School of Electronic Information and Electrical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

E-mails: zhanglifeng@sust.edu.cn (Zhang L F); Weiping.Wu@city.ac.uk (Wu W P); guoshouwu@outlook.com (Guo S W)

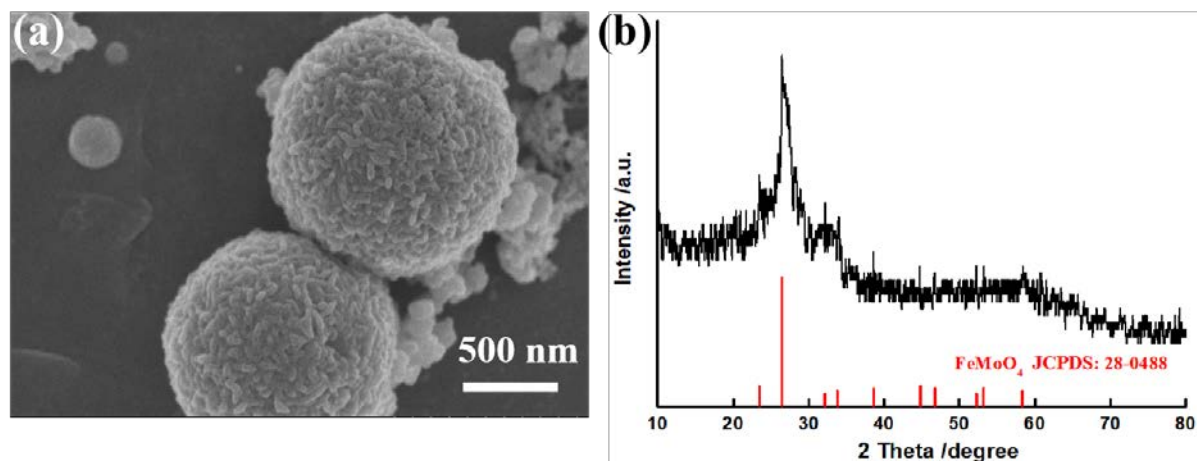


Figure S1. (a) Scanning electron microscopy (SEM) image; (b) X-ray diffraction (XRD) pattern of the Iron(II) molybdate FeMoO₄.

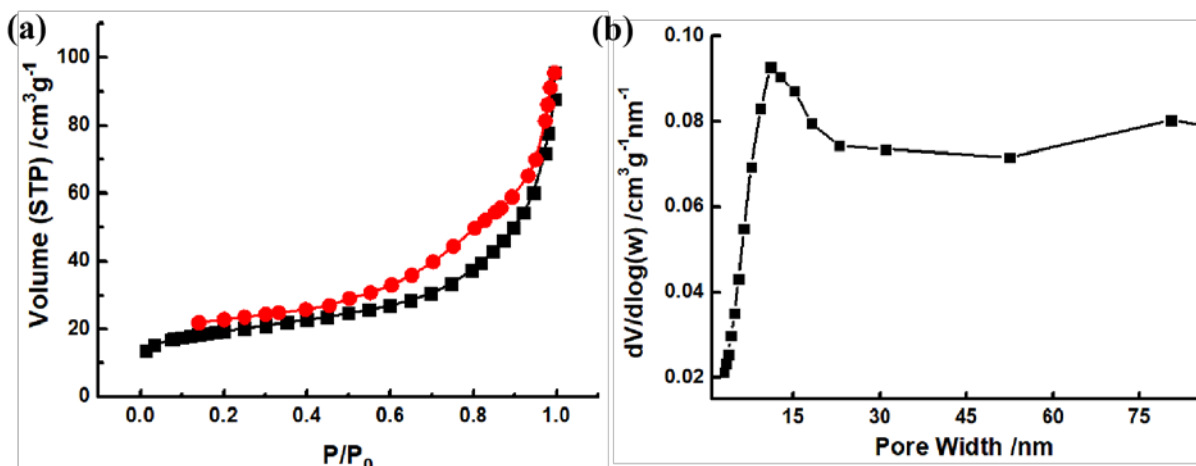


Figure S2. (a) Nitrogen (N_2) adsorption and desorption isotherms; (b) pore size distribution of the Iron (II) molybdenum (IV) oxide $Fe_2Mo_3O_8$ hollow spheres.

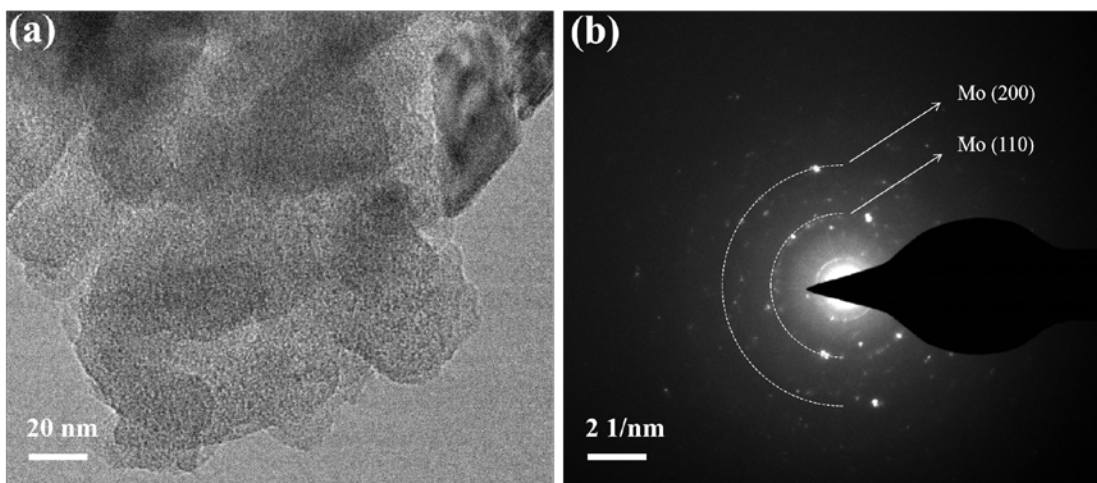


Figure S3. Ex-situ TEM of the $Fe_2Mo_3O_8$ electrode during 1st discharge to 0.01 V. (a) TEM image and (b) selective area electron diffraction (SAED) pattern.

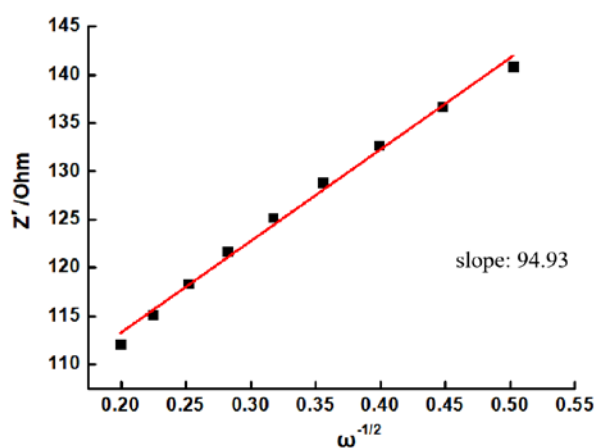
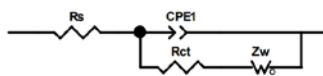


Figure S4. Linear fitting of Z' versus $\omega^{-1/2}$ of $Fe_2Mo_3O_8$ electrode, calculated from the EIS data. The Li^+ diffusion coefficient (D_{Li^+}) is calculated according to the following equation: $D_{Li^+} = R^2 T^2 / 2 A^2 n^4 F^4 c^2 \sigma^2$, where R is the gas constant, T is the absolute temperature, A is the area of electrode, n is the number of electron transfers, F is the Faraday constant, C is the concentration of Li^+ , and σ is the slope of the line of $Z' \sim \omega^{-1/2}$.

Table S1. The impedance parameters derived from the equivalent circuit model of Fe₂Mo₃O₈

	Rs	Rct
Before cycle	2.947	279.4
After 1 st cycle	3.703	76.06

**Table S2.** Comparison of electrochemical performance of M₂Mo₃O₈ molybdates anode materials

Molybdates	Initial D/C capacity (mAh g ⁻¹)	Capacity (mAh g ⁻¹)	Number of cycles and current density	Reference
Fe ₂ Mo ₃ O ₈ hollow spheres	1189/997	866	70 cycles at 0.1 A g ⁻¹	This work
Fe ₂ Mo ₃ O ₈ block	899/- ^{a)}	420	100 cycles at 0.05 A g ⁻¹	[1]
LiYMo ₃ O ₈	305/180	385	120 cycles at 0.03 A g ⁻¹	[2]
Mn ₂ Mo ₃ O ₈	710/565	205	50 cycles at 0.03 A g ⁻¹	[3]
Co ₂ Mo ₃ O ₈	1185/850	790	60 cycles at 0.06 A g ⁻¹	[3]
Cu ₃ Mo ₂ O ₉ micropompons	1224/432	153	100 cycles at 0.1 A g ⁻¹	[4]
Fe ₂ Mo ₃ O ₈ -RGO	1275.2/923.5	835	40 cycles at 0.2 A g ⁻¹	[5]
Fe ₂ Mo ₃ O ₈ -EG	1224/945	490	50 cycles at 0.05 A g ⁻¹	[6]
FLG-Co ₂ Mo ₃ O ₈	1229/827	762	50 cycles at 0.09 A g ⁻¹	
FLG-Mn ₂ Mo ₃ O ₈	1349/942	523	50 cycles at 0.09 A g ⁻¹	[7]
FLG-Zn ₂ Mo ₃ O ₈	787/403	554	50 cycles at 0.09 A g ⁻¹	

D/C: Discharge/Charge

RGO: Reduced Graphene Oxide

EG: Exfoliated Graphene Oxide

FLG: Few Layered Graphene

a) -: not available

References

1. Chu Y Y, Shi X Y, Wang Y, Fang Z Q, Deng Y J, Liu Z X, Dong Q S, Hao Z M. High temperature solid-state synthesis of dopant-free Fe₂Mo₃O₈ for lithium ion batteries. *Inorganic Chemistry Communications*, 2019, 107: 107477–107481
2. Das B, Reddy M V, Krishnamoorthi C, Tripathy S, Mahendiran R, Subba Rao G V, Chowdari B V R. Carbothermal synthesis, spectral and magnetic characterization and Li-cyclability of the Mo-cluster compounds, LiYMo₃O₈ and Mn₂Mo₃O₈. *Electrochimica Acta*, 2009, 54(12): 3360–3373

3. Das B, Reddy M V, Tripathy S, Chowdari B V R. A disc-like Mo-metal cluster compound, $\text{Co}_2\text{Mo}_3\text{O}_8$, as a high capacity anode for lithium ion batteries. *RSC Advances*, 2014, 4(64): 33883–33889
4. Xia J, Song L, Liu W, Teng Y, Wang Q, Zhao L, Ruan M. Highly monodisperse $\text{Cu}_3\text{Mo}_2\text{O}_9$ micropompons with excellent performance in photocatalysis, photocurrent response and lithium storage. *RSC Advances*, 2015, 5(16): 12015–12024
5. Sun Y M, Hu X L, Luo W, Shu J, Huang Y H. Self-assembly of hybrid $\text{Fe}_2\text{Mo}_3\text{O}_8$ -reduced graphene oxide nanosheets with enhanced lithium storage properties. *Journal of Materials Chemistry A*, 2013, 1(14): 4468–4474
6. Maseed H, Petnikota P, Srikanth V V S S, Srinivasan M, Chowdari B V R, Reddy M V, Adams S. $\text{Fe}_2\text{Mo}_3\text{O}_8$ /exfoliated graphene oxide: solid-state synthesis, characterization and anodic application in Li-ion batteries. *New Journal of Chemistry*, 2018, 42(15): 12817–12823
7. Petnikot S, Marka S K, Srikanth V V S S, Reddy M V, Chowdari B V R. Elucidation of few layered graphene-complex metal oxide ($\text{A}_2\text{Mo}_3\text{O}_8$, A = Co, Mn and Zn) composites as robust anode materials in Li ion batteries. *Electrochimica Acta*, 2015, 178: 699–708