Supporting Information

General Preparation of Three-dimensional Porous Metal Oxide Foams Coated with Nitrogen-doped Carbon for Enhanced Lithium Storage

Ke Lu¹, Jiantie Xu², Jintao Zhang^{1,*}, Bin Song³, and Houyi Ma^{1,*}

¹Key Laboratory for Colloid and Interface Chemistry of State Education Ministry, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China.

²Department of Macromolecular Science and Engineering, School of Engineering, Case Western Reserve University, Cleveland, Ohio 44106, USA.

³Jiangsu Key Laboratory for Carbon-Based Functional Materials and Devices, Institute of Functional Nano and Soft Materials (FUNSOM), Soochow University, Suzhou 215123, China.

*To whom correspondence should be addressed

E-mail: jtzhang@sdu.edu.cn; hyma@sdu.edu.cn.

KEYWORDS. Porous structure \cdot metal oxide foam \cdot nitrogen-doped carbon \cdot lithium storage \cdot surfactant

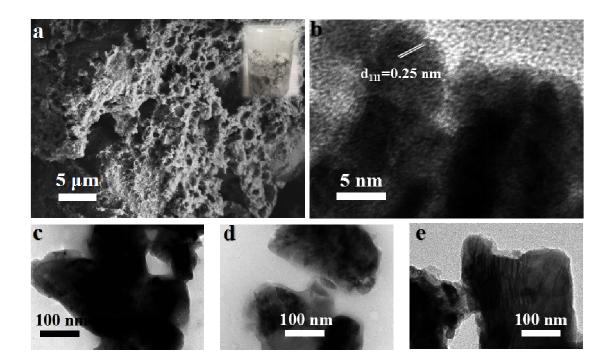


Figure S1. SEM images (a) and HRTEM images (b) of the MnO@N-C foam. Inset is the digital photo image of MnO₂ foam. The exposed lattice fringes (b) exhibit a spacing of 0.25 nm, corresponding to the (111) plane of MnO. TEM images of MoO₂@N-C (c), $VO_2@N-C$ (d), and MnO@N-C (e).

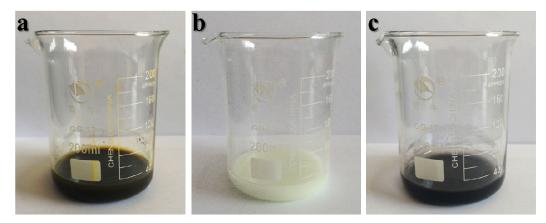


Figure S2. Digital photo images of (a) V_2O_5 , (b) MoO_3 , and (c) MnO_2 synthesized without the addition of HDA. It can be seen that metal oxide foams cannot be formed in the absence of surfactant.

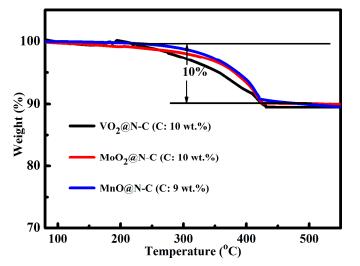


Figure S3. Thermal gravimetric analysis for VO₂@N-C, MoO₂@N-C and MnO@N-C.

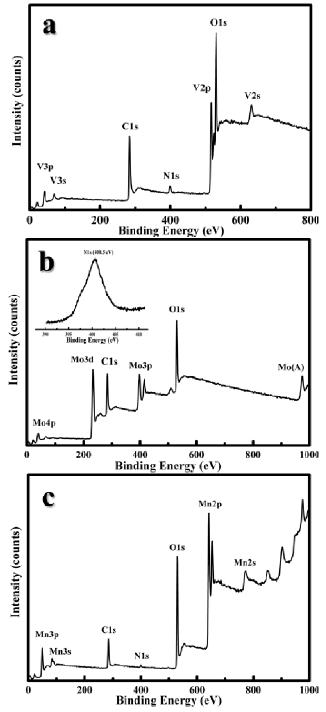


Figure S4. XPS survey spectra of $VO_2@N-C$ (a), $MoO_2@N-C$ (b) and MnO@N-C (c).

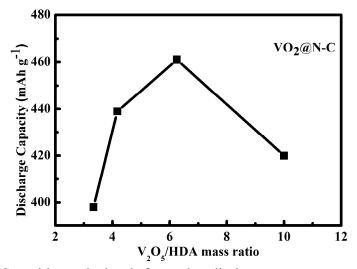


Figure S5. Capacities calculated from the discharge curves as a function of V_2O_5 /HDA mass ratio at 30 mA g⁻¹.

To optimize the capacity performance, the $VO_2@N-C$ samples were prepared by changing the mass ratio of vanadium oxide to HDA. It can be seen that the maximal capacity is achieved at the ratio of 6.25.

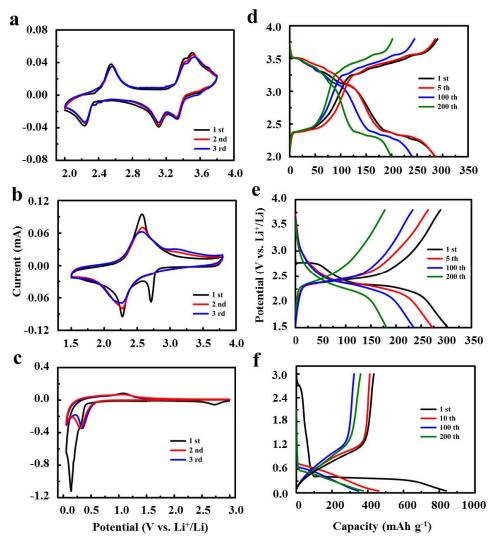


Figure S6. Cyclic voltammogram curves of (a) V_2O_5 , (b) MoO_3 , and (c) MnO_2 at a scan rate of 0.1 mV s⁻¹. Galvanostatic charge/discharge curves (d) V_2O_5 , (e) MoO_3 , and (f) MnO_2 foam materials (for V_2O_5 and MoO_3 , the current density: 30 mA g⁻¹, for MnO_2 current density: 100 mA g⁻¹).

The CV curves of the as-prepared MoO₃ foam show the substantial variation of redox peaks in comparison with the initial cycle. Typically, the absence of the peak at around 2.75 V due to the irreversible lithium insertion suggests the phase transformation to a favorable one with the highly reversible redox peaks at 2.26/2.57 V in the subsequent cycles. In good agreement with the CV curves, the initial discharge curve with two plateau regions gives a capacity of as high as 302 mA h g⁻¹.

It can be seen that the discharge and charge plateaus generally remain stable over the repeated cycles, indicating the good structural reversibility.

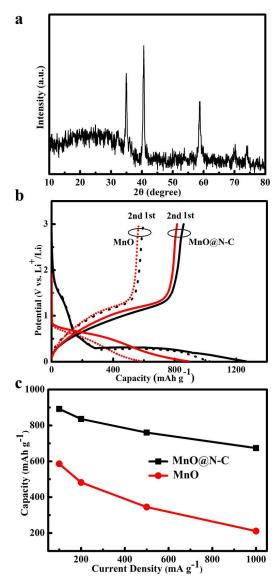


Figure S7. XRD pattern of MnO (a). Galvanostatic discharge/charge curves of MnO@N-C and MnO (b). Capacity calculated from the charge/discharge curves at various current densities (c).

To demonstrate of the crucial role of carbon networks for Li storage, pure MnO foam was prepared by reduction of MnO_2 foam in the presence of hydrogen (7 vol%). The XRD pattern (Figure S7a) can be indexed to the face-centered cubic MnO (JCPDS no. 07-0230). It can be seen that the performance of MnO can be enhanced in the presence of carbon coating.

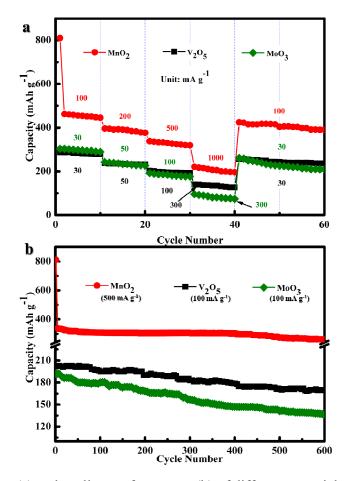


Figure S8. Rate (a) and cycling performances (b) of different materials.

The rate performance of the electrode materials was tested by varying the current density. When the current was restored to the initial current density after 40 cycles, around 89, 86, and 91% of the initial specific capacity for V_2O_5 , MoO_3 , and MnO_2 can be recovered. When the current density was increased by 10 times (30 to 300 mA g⁻¹ or 100 to 1000 mA g⁻¹), the capacity retention of V_2O_5 , MoO_3 , and MnO_2 were about 71, 63, and 72%, exhibiting a good high-rate performance. The reversible capacity of V_2O_5 , MoO_3 , and MnO_2 foams are 166.6, 135.9, and 257.5 mAh g⁻¹ after 600 cycles, with the capacity retention of around 82.5, 70.8, and 76.1% (for the second cycle), respectively.

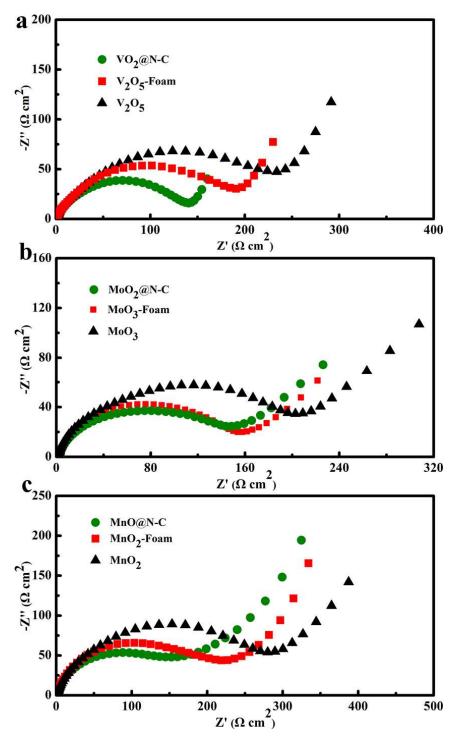


Figure S9. Nyquist plots of different electrode materials. (a) V-based metal oxide, (b) Mo-based metal oxide, and (c) Mn-based metal oxide materials.

| Sample | Current density (mA g ⁻¹) | Capacity (mAh g ⁻¹) | |
|-----------------------|---------------------------------------|---|--|
| VO ₂ @N-C | 30 | 461 | |
| | 50 | 437 | |
| | 100 | 402 | |
| | 200 | 369 | |
| | 500 | 332.8 | |
| | 1000 | 269 | |
| MoO ₂ @N-C | 100 | 856 ^{1st} /613 ^{2nd} | |
| | 200 | 565 | |
| | 500 | 520.5 | |
| | 1000 | 465 | |
| MnO@N-C | 100 | 1265 ^{1st} /892 ^{2nd} | |
| | 200 | 836 | |
| | 500 | 760 | |
| | 1000 | 674 | |

Table S1. The capacities of metal oxides@N-C at various current densities.

| Materials | Potential range (V vs. Li ⁺ /Li) | Capacity (mAh g ⁻¹)/ current density (mA g ⁻¹) | Cycling stability/cycles | Citation |
|------------------------------------|---|---|-------------------------------------|------------|
| VO_2/C | 2-3 | 219/50 | 85%/100 (100 mA g ⁻¹) | S 1 |
| V_2O_5 | 2-4 | 275/294 | 88.4%/200 (294 mA g ⁻¹) | S2 |
| Microspheres | | | | |
| N-G-VO ₂ | 1.5-4 | 418/50 | 60%/50 (50 mA g ⁻¹) | S 3 |
| V_2O_5 | 2-4 | 256/100 | 89%/50 (100 mA g ⁻¹) | S4 |
| V_2O_5/C | 2-4 | 297/1000 | 97.3%/50 (1 A g ⁻¹) | S 5 |
| V_2O_5 | 2.75-4 | 427/7.5 | 30%/20 (7.5 mA g ⁻¹) | S 6 |
| VO ₂ -Graphene | 1.5-3.5 | 415/196 | 93%/1000 (37.2 A g ⁻¹) | S7 |
| VO ₂ Hollow | 2-3 | 203/100 | 90%/100 (100 mA g ⁻¹) | S 8 |
| Microspheres | | | | |
| V ₂ O ₅ Foam | | 237/50 | 82.5%/600(100 mA g ⁻¹) | This |
| VO ₂ @C Foam | 2-3.8 | 438/50 | 87.5%/600 (100 mA g ⁻¹) | work |

Table S2. The comparison of vanadium oxides as active materials for Li storage.

REFERENCES

S1 Mai, L. Q.; Wei, Q. L.; An, Q. Y.; Tian, X. C.; Zhao, Y. L.; Xu, X.; Xu, L.; Chang, L.; Zhang, Q. J. Noscroll Buffered Hybrid Nanostructural VO₂(B) Cathodes for High-Rate and Long-Life Lithium Storage. *Adv. Mater.* **2013**, *25*, 2969-2973.

S2 Dong, Y.; Wei, H.; Liu, W.; Liu, Q.; Zhang, W.; Yang, Y. Template-Free Synthesis of V₂O₅ Hierarchical Nanosheet-Assembled Microspheres with Excellent Cycling Stability. *J. Power Sources* **2015**, *285*, 538-542.

S3 Nethravathi, C.; Rajamathi, C. R.; Rajamathi, M.; Gautam, U. K.; Wang, X.; Golberg, D.; Bando, Y. N-Doped Graphene-VO₂(B) Nanosheet-Built 3D Flower Hybrid for Lithium Ion Battery. *ACS Appl. Mater. Interfaces* **2013**, *5*, 2708-2714.

S4 Pan, A. Q.; Wu, H. B.; Yu, L.; Lou, X. W. Template-Free Synthesis of VO₂ Hollow Microspheres with Various Interiors and Their Conversion into V₂O₅ for Lithium-Ion Batteries. *Angew. Chem., Int. Ed.* **2013**, *125*, 2282-2230.

S5 Zhang, X. F.; Wang, K. X.; Wei, X.; Chen, J. S. Carbon-Coated V₂O₅ Nanocrystals as High Performance Cathode Material for Lithium Ion Batteries. *Chem. Mater.* **2011**, *23*, 5290-5292.

S6 Ragupathy, P.; Shivakumara, S.; Vasan, H. N.; Munichandraiah, N. Preparation of Nanostrip V₂O₅ by the Polyol Method and Its Electrochemical Characterization as Cathode Material for Rechargeable Lithium Batteries. *J. Phys. Chem. C* **2008**, *112*, 16700-16707.

S7 Yang, S.; Gong, Y.; Liu, Z.; Zhan, L.; Hashim, D. P.;Ma, L.; Vajtai, R.; Ajayan,
P. M. Bottom-up Approach toward Single-Crystalline VO₂-Graphene Ribbons as
Cathodes for Ultrafast Lithium Storage. *Nano Lett.* 2013, *13*, 1596-1601.

S8 Niu, C. J.; Meng, J. S.; Han, C. H.; Zhao, K. N.; Yan, M. Y.; Mai, L. Q. VO₂ Nanowires Assembled into Hollow Microspheres for High-Rate and Long-Life Lithium Batteries. *Nano Lett.* **2014**, *14*, 2873-2878.