Supplementary Materials

Mo-Doped Inducing Amorphous and Sulfur Vacancy Healing in VS_4 for Enhancing the Storage of Lithium Ions

Lü-qiang Yu [a,b], Shi-Xi Zhao [a*], Ye Yuan [a,b], Guo-dan Wei [c], Jian-Wei Zhao [d]

[a] Shenzhen International Graduate School, Tsinghua University, Shenzhen, 518055, China

[b] School of Materials Science and Engineering, Tsinghua University, Beijing, 100084, China

[c] Tsinghua- Berkeley Shenzhen Institute, Tsinghua University, Shenzhen, 518055, China

[d] Shenzhen HUASUAN Technology Co. Ltd. Shenzhen, 518055, China

[*] Corresponding author: E-mail: zhaosx@sz.tsinghua.edu.cn (S.X. Zhao).

Table S1. The atomic content of various elements of four materials through EDX.

Element / Sample	Atomic content (%)		
	Mo	**V**	**S**
VS_4	0	24.02	75.98
$Mo_{0.01}V_{1.56}S_4$	0.18	27.97	71.86
$Mo_{0.03}V_{2.13}S_4$	0.45	34.59	64.96
$Mo_{0.04}V_{2.10}S_4$	0.66	34.16	65.17

Table S2. The pore parameters of the as-prepared samples.

Material	S_{BET} ($m^2 \cdot g^{-1}$)	Total pore volume （$cm^3 \cdot g^{-1}$）	Pore size (nm)
VS_4	10.91	0.025	2.10
$Mo_{0.01}V_{1.56}S_4$	21.17	0.052	1.64
$Mo_{0.03}V_{2.13}S_4$	29.62	0.17	1.21
$Mo_{0.04}V_{2.10}S_4$	25.70	0.14	1.21

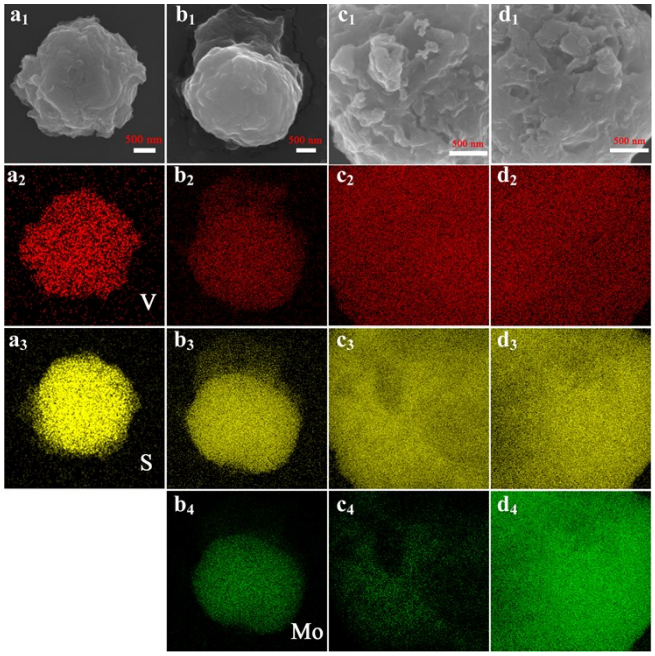

Fig. S1. EDX mapping (V: red, S: yellow, and Mo: green) of VS_4 (a_1-a_3), $Mo_{0.08}V_{0.92}S_4$ (b_1-b_4), $Mo_{0.15}V_{0.85}S_4$ (c_1-c_4), and $Mo_{0.33}V_{0.67}S_4$ (d_1-d_4).

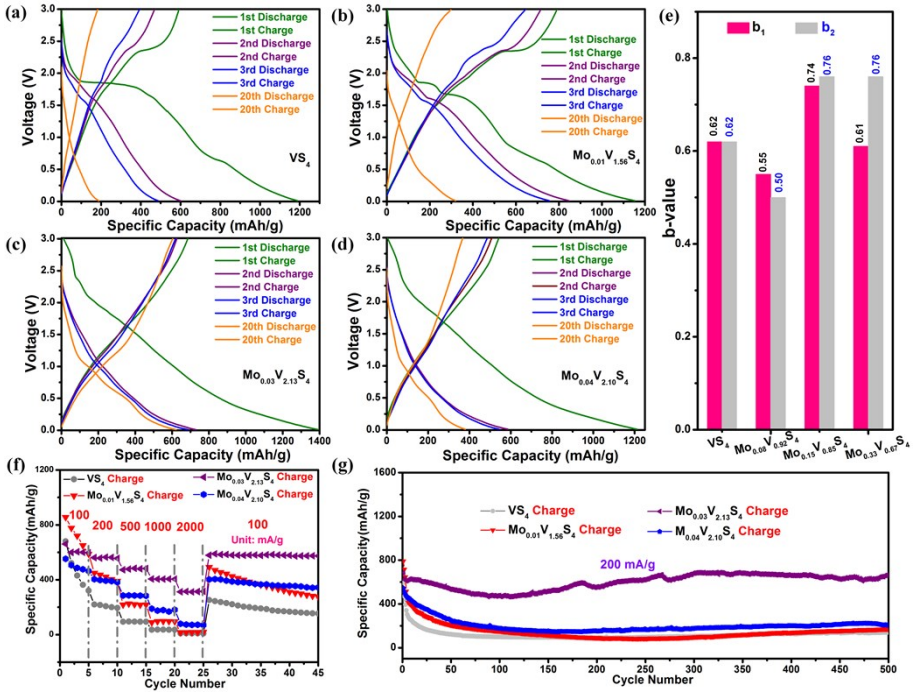

Fig. S2. The selected galvanostatic discharge-charge curves of VS_4 (a), $Mo_{0.08}V_{0.92}S_4$ (b), $Mo_{0.15}V_{0.85}S_4$ (c), and $Mo_{0.33}V_{0.67}S_4$ (d) at 200 mA·g^{-1}; The *b*-values (e) of four samples calculated from the CV curves; The charge specific capacity of four materials at different current densities (f) and 200 mA·g^{-1} (g).

Table S3. The first coulombic efficiency of four samples.

Material	First discharge capacity ($mAh \cdot g^{-1}$)	First discharge capacity ($mAh \cdot g^{-1}$)	Coulombic efficiency (%)
VS_4	1189.5	592.4	49.80
$Mo_{0.01}V_{1.56}S_4$	1152.8	791.5	68.66
$Mo_{0.03}V_{2.13}S_4$	1392.3	684.8	49.18
$Mo_{0.04}V_{2.10}S_4$	1211.9	542.9	44.79

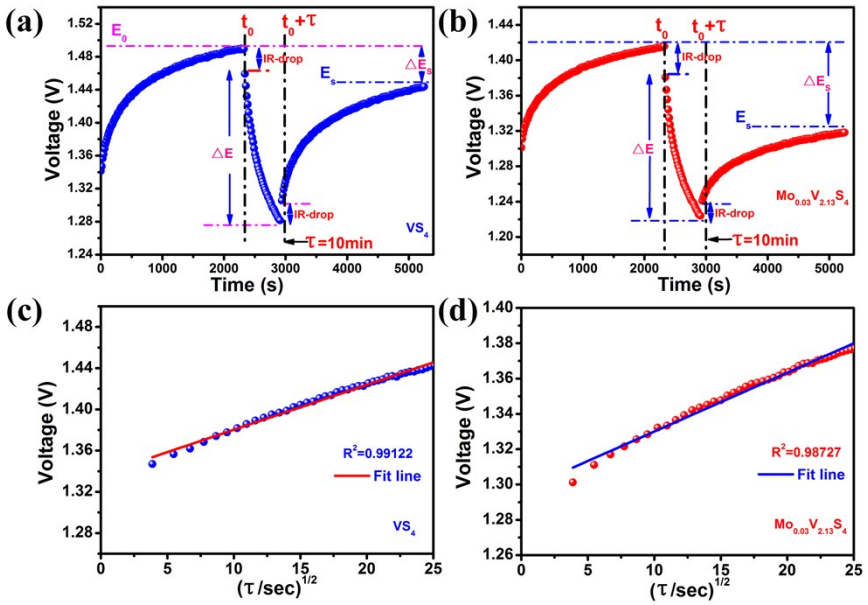

Fig. S3. The single step of GITT curves and voltage changes as a function of $\tau^{1/2}$ of VS_4 (a, c) and $Mo_{0.03}V_{2.13}S_4$ (b, d).

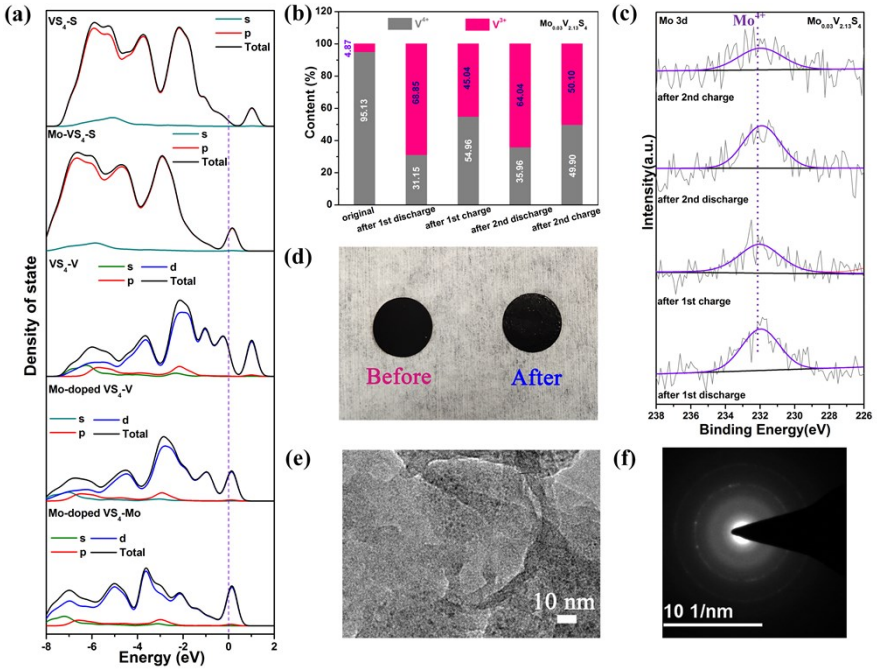

Fig. S4. Density of states (a) of each element of VS_4 and Mo-doped VS_4; The content (b) of V at different states after various cycles and XPS spectra of Mo 3d (c) at different state; Digital photos (d), HRTEM (e), and SAED images (f) of $Mo_{0.03}V_{2.13}S_4$ after 500 cycles.

Table S4. The structure and capacity of the VS_4 and its composites as anode materials for LIBs.

Material	Morphology	Structure	Capacity	Ref.
VS_4-PANI	Sphere	Crystalline	A reversible capacity of 755 mAh·g^{-1} after 50 cycles at 0.1 A·g^{-1}	1
VS_4-RGO	Nanoparticle	Crystalline	A reversible capacity of 954 mAh·g^{-1} after 100 cycles at 0.1 A·g^{-1}	2
VS_4-RGO	Nanoparticle	Crystalline	A reversible capacity of 890.8 mAh·g^{-1} after 80 cycles at 0.2 A·g^{-1}	3
VS_4-CNTs	Nanoparticle	Crystalline	A reversible capacity of 447 mAh·g^{-1} after 400 cycles at 1 A·g^{-1}	4
VS_4-porous carbon	Flower	Crystalline	A reversible capacity of 562.4 mAh·g^{-1} after 150 cycles at 0.1 A·g^{-1}	5
VS_4	Urchin	Crystalline	A reversible capacity of 500 mAh·g^{-1} after 100 cycles at 0.1 A·g^{-1}	6
VS_4	Nanoparticle	Crystalline	A reversible capacity of 452 mAh·g^{-1} after 150 cycles at 0.5 A·g^{-1}	7
$Mo_{0.03}V_{2.13}S_4$	**Flower**	**Amorphous**	**A reversible capacity of 671.4 mAh·g^{-1} after 500 cycles at 0.2 A·g^{-1}**	**This work**

Table S5. Parameters of the impedance and diffusion of lithium ion calculated from the EIS of as-obtained materials.

Material	**R_e (Ω)**	**R_{ct} (Ω)**	**D_{Li^+} (cm^2·s^{-1})**
VS_4	2.44	121	1.19*10^{-11}
$Mo_{0.01}V_{1.56}S_4$	1.92	95	2.10*10^{-11}
$Mo_{0.03}V_{2.13}S_4$	3.61	82.5	7.62*10^{-11}
$Mo_{0.04}V_{2.10}S_4$	2.32	50	1.30*10^{-10}

References:

1 Y. Zhou, Y. Li, J. Yang, J. Tian, H. Xu, J. Yang and W. Fan, *ACS Appl. Mater. Inter.*, 2016, **8**, 18797-18805.

2 C. S. Rout, B. Kim, X. Xu, J. Yang, H. Y. Jeong, D. Odkhuu, N. Park, J. Cho and H. S. Shin, *J. Am. Chem. Soc.*, 2013, **135**, 8720-8725.

3 Q. Li, Y. Chen, J. He, F. Fu, J. Lin and W. Zhang, *J. Alloy. Compd.*, 2016, **685**, 294-299.

4 S. Wang, W. Ma, X. Zang, L. Ma, L. Tang, J. Guo and B. A. X. Z. Qingyun Liu, *ChemSusChem*, 2019, **12**, 1-9.

5 L. Q. Yu, S. X. Zhao, Q. L. Wu, J. W. Zhao and G. D. Wei, *Adv. Funct. Mater.*, 2020, **30**, 2000427.

6 G. Yang, B. Zhang, J. Feng, H. Wang, M. Ma, K. Huang, J. Liu, S. Madhavi, Z. Shen and Y. Huang, *ACS Appl. Mater. Inter.*, 2018, **10**, 14727-14734.

7 L. Wang, L. Xue, J. Wang, L. Miao, W. Chen, M. Wan, W. Gong, Q. Liu, N. Zhang and W. Zhang, *J. Alloy. Compd.*, 2018, **768**, 938-943.