Self-limiting Lithiation of Vanadium Diboride Nanosheet as Ultra-stable Mediator Towards High-sulfur Loading and Long-cycle Lithium Sulfur Batteries

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Table S1. Electrochemical performance of the VB_2-based Li_2S_6 cell and other similar cathode materials reported in literature.

Polysulfide host	Sulfur loading ($mg\ cm^{-2}$)	Specific capacities ($mAh\ g^{-1}$)	Cycling stability ($mAh\ g^{-1}$)	Reference
Li_2S_6-VB_2	2.0 mg cm^{-2}	1280 at 0.5 C	590 after 1000 cycles	**This work**
	2.0 mg cm^{-2}	1210 at 1 C	470 after 1000 cycles	
	2.0 mg cm^{-2}	980 at 2 C	340 after 1000 cycles	
	4.0 mg cm^{-2}	624 at 1 C	452 after 500 cycles	
V_2O_5-CNF	2.0 mg cm^{-2}	816 at 3 C	576 after 1000 cycles	*Small.* 2017, 1602539
VN-NBs	1.2 mg cm^{-2}	1100 at 1 C	837 after 1000 cycles	*Nano Lett.* 2017, 17, 7839-7846
	1.2 mg cm^{-2}	960 at 2 C	704 after 1000 cycles	
	3.3 mg cm^{-2}	1143 at 0.5 C	951 after 200 cycles	
	5.4 mg cm^{-2}	1075 at 0.5 C	799 after 200 cycles	
	6.8 mg cm^{-2}	797 at 0.5 C	563 after 200 cycles	
MoN-VN	Not given	766 at 1 C	555 after 500 cycles	*Angew. Chem. Int. Ed.* 2018, 57, 16703-16707.
	3.0 mg cm^{-2}	708 at 2 C	467 after 500 cycles	
PCF/VN	8.1 mg cm^{-2}	1310.8 at 0.1 C	1052.5 after 250 cycles	*Adv. Funct. Mater.* 2018, 1706391
$VO_{2@}$rGO	1.5 mg cm^{-2}	1358 at 0.2 C	1049 after 370 cycles	*J. Mater. Chem. A,* 2019,7, 1658-1668
	1.5 mg cm^{-2}	1071 at 1 C	751 after 200 cycles	
	4.0 mg cm^{-2}	711 at 0.5 C	685 after 20 cycles	
VO_2 HSs	0.942 mg	930 at 0.1 C	789 after 80 cycles	*J. Mater. Chem. A,* 2019,7, 3618-3623
	0.942 mg	576 at 1 C	440 after 200 cycles	
rGO-VS_2(/S-64)	1.15 mg cm^{-2}	1194 at 0.2 C	929 after 200 cycles	*Adv. Energy Mater.* 2017, 1702337
	1.15 mg cm^{-2}	1027 at 1 C	879 after 1200 cycles	
	1.15 mg cm^{-2}	832 at 2 C	662 after 1200 cycles	
G-VS_2	1.0 mg cm^{-2}	1270 at 1 C	923 after 150 cycles	*Adv. Energy Mater.* 2018, 1800201
	1.0 mg cm^{-2}	1185 at 2 C	990 after 100 cycles	
	2.0 mg cm^{-2}	786 at 1 C	559 after 150 cycles	
	3.5 mg cm^{-2}	701 at 1 C	520 after 150 cycles	
$VS_{4@}$RGO	3.0 mg cm^{-2}	937 at 1 C	601 after 500 cycles	*ACS Energy Lett.* 2020, 5, 4, 1177-1185
	5.0 mg cm^{-2}	1116 at 0.2 C	996 after100 cycles	
	7.0 mg cm^{-2}	1030 at 0.2 C	853 after100 cycles	
	10.0 mg cm^{-2}	834 at 0.2 C	705 after100 cycles	

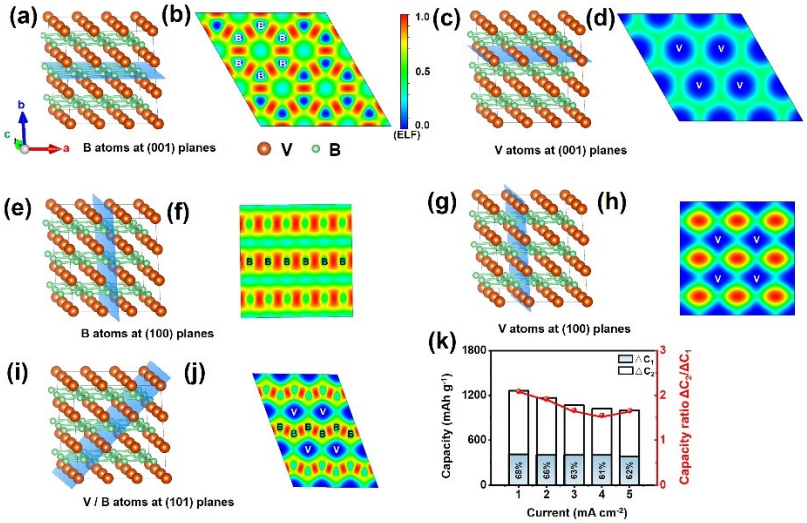

Fig. S1. Crystal structure and electron location function of VB_2 with B atoms at (001) planes (a-b), V atoms at (001) planes (c-d), B atoms at (100) planes (e-f), V atoms at (100) planes (g-h), and V and B atoms at (101) planes (i-j), respectively. The corresponding ratios (k) of $\Delta C_2/\Delta C_1$ from 1 to 5 mA cm^{-2}

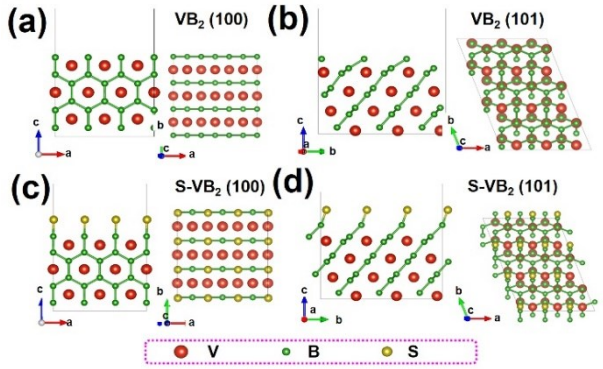

Fig. S2. Top and side views of the VB_2 (100) facets (a), and (101) facets (b), respectively. Top and side views of the passivated VB_2 (100) facets with sulfur atoms (c), and (101) facets with sulfur atoms (d), respectively.

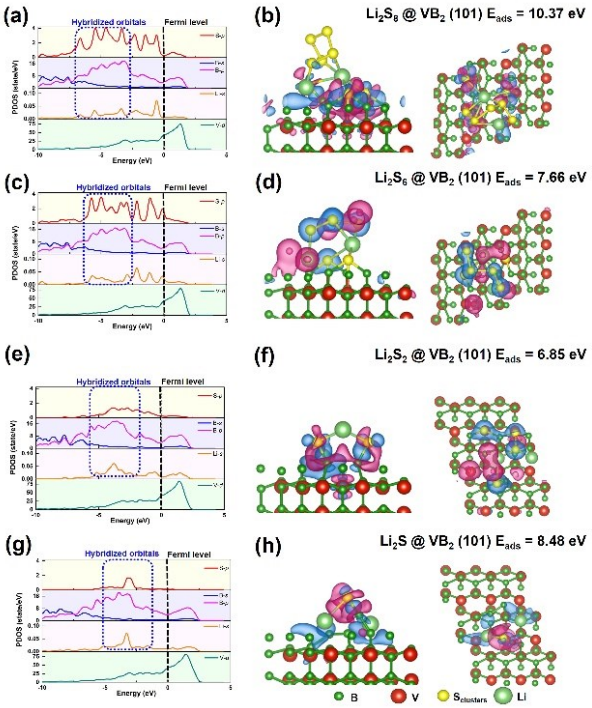

Fig. S3. Density functional theory calculations of the PDOS, side and top views of charge density difference of Li_2S_8 (a, b), Li_2S_6 (c, d), Li_2S_2 (e, f) and Li_2S (g, h) molecules adsorbed on the pure VB_2 (101) facets. The blue and pink areas are the regions of trapped and lost charge.

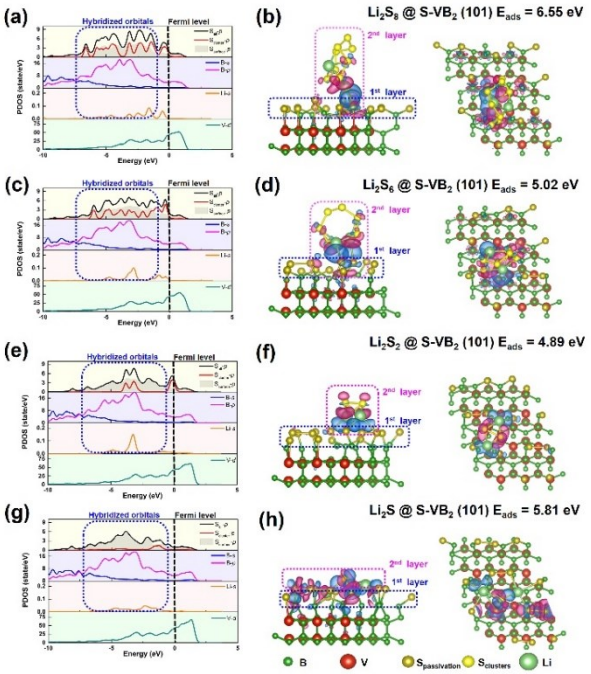

Fig. S4. Density functional theory calculations of the PDOS, side and top views of charge density difference of Li_2S_8 (a, b), Li_2S_6 (c, d), Li_2S_2 (e, f) and Li_2S (g, h) molecules adsorbed on the passivated VB_2 (101) facets. The blue and pink areas are the regions of trapped and lost charge.

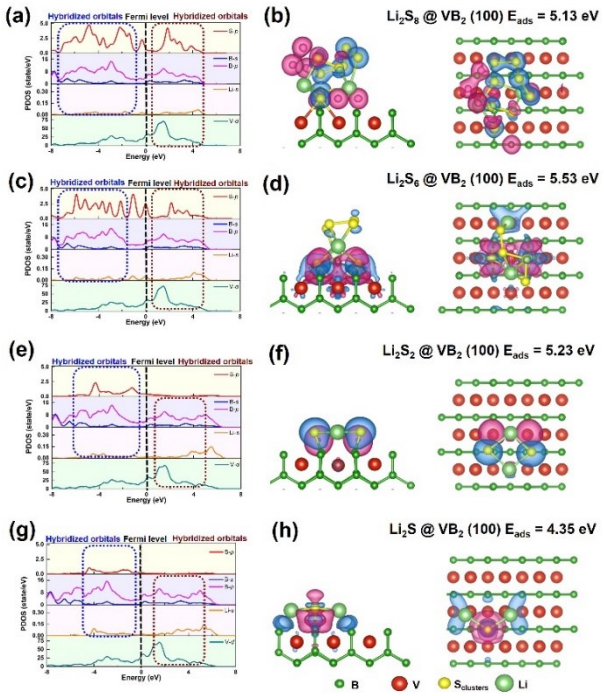

Fig. S5. Density functional theory calculations of the PDOS, side and top views of charge density difference of Li_2S_8 (a, b), Li_2S_6 (c, d), Li_2S_2 (e, f) and Li_2S (g, h) molecules adsorbed on the pure VB_2 (100) facets. The blue and pink areas are the regions of trapped and lost charge.

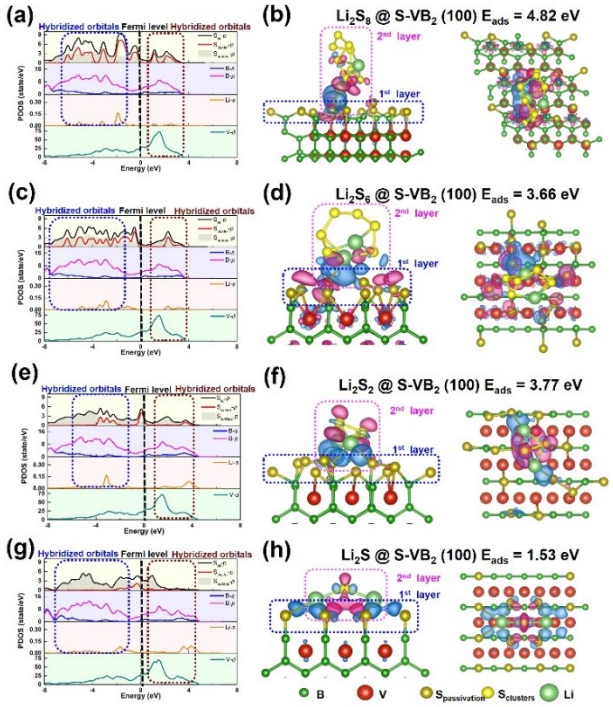

Fig. S6. Density functional theory calculations of the PDOS, side and top views of charge density difference of Li_2S_8 (a, b), Li_2S_6 (c, d), Li_2S_2 (e, f) and Li_2S (g, h) molecules adsorbed on the passivated VB_2 (100) facets. The blue and pink areas are the regions of trapped and lost charge.