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Supporting Information

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Revealing the Origin of Highly Efficient Polysulfide Anchoring and Transformation on Anion-Substituted Vanadium Nitride Host

Shuangshuang Tan, Yuhang Dai, Yalong Jiang, Qiulong Wei, Guobin Zhang, Fangyu Xiong, Xingqi Zhu, Zhi-Yi Hu, Liang Zhou, Yongcheng Jin, Kiyoshi Kanamura,* Qinyou An,* and Liqiang Mai*

Supporting Information

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Shuangshuang Tan[1], Yuhang Dai[1], Yalong Jiang[1], Qiulong Wei[5], Guobin Zhang[1], Fangyu Xiong[1], Xingqi Zhu[7], Zhi-Yi Hu[1,6], Liang Zhou[1], Yongcheng Jin[3,], Kiyoshi Kanamura[2,*], Qinyou An[1,4,*], Liqiang Mai[1,4]*

Mr. S. S. Tan, Mr. Y. H. Dai, Dr. Y. L. Jiang, Dr G. B. Zhang, Mr. F. Y. Xiong, Prof Z. Y. Hu, Prof L. Zhou, Prof. Q. Y. An, Prof. L. Q. Mai
State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, Hubei, China, E-mail: mlq518@whut.edu.cn, anqinyou86@whut.edu.cn
Prof. K. Kanamura
Department of Applied Chemistry for Environment Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Tokyo 192-0397, Japan, E-mail: kanamura@tmu.ac.jp
Prof. Y. C. Jin
School of Materials Science and Engineering, Ocean University of China, Qingdao 266100, Shandong, China, E-mail: jinyc@qibebt.ac.cn
Prof. Q. Y. An, Prof. L. Q. Mai
Foshan Xianhu Laboratory of the Advanced Energy Science and Technology Guangdong Laboratory, Xianhu hydrogen Valley, Foshan 528200, China
Prof. Q. L. Wei
Department of Materials Science and Engineering, Fujian Key Laboratory of Materials Genome, College of Materials, Xiamen University, Xiamen 361005, Fujian, China
Prof. Z. Y. Hu
Nanostructure Research Centre (NRC), Wuhan University of Technology, Wuhan 430070, Hubei, China
Dr. X. Q. Zhu
Bruker China Application Lab, Beijing 100871, China

Experimental Section

Material synthesis. *Preparation of VN/rGO xerogels*: The VN/rGO xerogels were prepared using hydrothermal method, according to the previously reported procedure.[1] 80 mg NH_4VO_3 powders were dissolved in graphene oxide aqueous (8 mL, 2 mg mL^{-1}), and then 2 mL of $NH_3 \cdot H_2O$ was added to adjust pH value. After 30 min ultrasonication, the mixtures were transferred to a 25 mL Telfon-lined autoclave and hydrothermally treated at 180 ^{o}C for 12 h. Finally, the obtained samples were freezedried and calcinated at different temperatures (450, 550, 650 and 900 °C) for 2 h under a flowing ammonia atmosphere. The rGO xerogel was prepared following the same procedure without the adding of NH_4VO_3. VN-550 and VN-900 bulks were prepared by NH_3 annealing with commercial NH_4VO_3 powders.

Preparation of the Li_2S_6 solution. Sulfur and Li_2S at a molar ratio of 5:1 were added to an appropriate amount of 1,2-dimethoxyethane (DME) and 1,3-dioxolane by vigorous magnetic stirring at 60 ^{o}C until the sulfur was fully dissolved.

Polysulfide adsorption test. 12 mg of VN-550 xerogel, VN-900 xerogel, rGO, and VN-550 bulk, VN-900 bulk powder were separately added to 2.0 mL of 0.05 M Li_2S_6 in DME solution. After 2h's standing, the thorough adsorptions were obtained. The same Li_2S_6 solution is as a comparison.

Preparation of sulfur electrodes. VN/rGO xerogels were cut and compressed into 1.5 mg VN/rGO electrode. Next, 24.5 µL Li_2S_6 catholyte equal to 1.96 mg of sulfur was dropped into VN/rGO xerogels to obtain the sulfur electrode in an Argon-filled glovebox. The final areal sulfur loading of the electrode was determined about 2.5 mg cm^{-2}.

Materials characterization. XRD data of the samples were collected with a D8 Advance X-ray diffractometer with an area detector using Cu Kα radiation ($\lambda = 1.5418$ Å) and Mo Kα radiation ($\lambda = 0.7093$ Å). The PDFs were calculated from Mo Kα diffraction patterns. The microstructures were observed by FESEM (JEOL-7100F). TEM and HRTEM were performed on a Thermo Fisher Talos microscope, operated at 200kV. STEM-EELS were performed on a double corrected Thermo Fisher Titan Themis microscope, fitted with Gatan Quantum 965 GIF system, operated at 300 kV. For XPS, the samples were sealed in a vial before being quickly transferred to the chamber of an ultra-high vacuum Imaging XPS Microprobe system for analysis (VG MultiLab 2000 instrument). All spectra were fitted with Gaussian–Lorentzian functions and a Shirley-type background using XPSPEAK software. S2p peaks were fit using two equal full-width half maximum S2p doublets with 2:1 area ratios and splittings of 1.1 eV. X-ray absorption fine spectroscopy (XAFS) experiments were performed at the beamline 1W1B of Beijing Synchrotron Radiation Facility (BSRF) at Institute of High Energy Physics, Chinese Academy of Sciences. The first inflection point of the spectrum of V foil was used to carry out energy calibration. The X-ray absorption near edge structure (XANES) and the Fourier transforms and Wavelet transforms of extended X-ray absorption fine structure (FT-EXAFS and WT-EXAFS) spectra were processed employing the software packages Athena 0.9.

Electrochemical measurements. The electrochemical properties were characterized in 2016-type coin cells with Li metal foil as the anode and Celgard 2400 as the separator. The electrolyte was 1M lithium bis-trifluoromethaesulphonylimide dissolved in 1, 3-dioxolane and 1, 2-dimethoxyethane (1:1 ratio by volume) with 0.2 M lithium nitrate as the additive. The cells were assembled in an argon-filled glove box. The actual amount of electrolyte in single coin cell is ~7 μL Ah^{-1} (~10 μL mg_s^{-1}). Galvanostatic charge/discharge measurements were performed with a multichannel battery testing system. Cyclic voltammetry was conducted with a CHI 1000C electrochemical workstation. All measurements were carried out at room temperature.

DFT calculations. The present calculations were carried out by using the projector augmented wave (PAW)[2] method within the DFT as implemented in the Vienna ab initio simulation package (VASP)[3]. The generalized gradient approximation (GGA) in the forms of Perdew-Burke-Ernzerhof (PBE) is used to treat the exchange-correlation energy.[4] The cutoff energy of 400 eV was chosen for wave functions expanded in plane wave basis. In order to calculate the binding energy between Li_2S_6 and substrates (VN and $VN_{0.8}O_{0.64}$), a slab model of a 3×3×2 supercell with four atomic layers was constructed to simulate the (200) facet of VN and $VN_{0.8}O_{0.64}$ substrate based on XRD results (Figure 1a) and HRTEM observations (Figure S2). As for the (200) facet of $VN_{0.8}O_{0.64}$, three type of V vacancies were introduced, including single vacancy (V_s), diagonal divacancy (V_{d1}) and meta-divacancy (V_{d2}) (Figure 5d). A vacuum slab of about 10 Å was inserted between the surface slabs for all the models. For the Brillouin-zone sampling, 1×2×2 of k-point was set for the structure relaxation and increased to 3×6×6 for the electronic structure calculations. Except for the bottom three atomic layers of the VN and $VN_{0.8}O_{0.64}$ slabs, all atoms were allowed to be fully relaxed while keeping the supercell boxes unchanged until the residual force per atom are less than 0.05 eV $Å^{-1}$. Ultrasoft pseudopotentials were used to describe the interaction of ionic core and valence electrons. The binding energies (E_b) between Li_2S_6 and substrates (VN and $VN_{0.8}O_{0.64}$) are defined by equation:

$$E_b = E_T - E_S - E_{\mathrm{Li}_2 s_6}$$

Where E_T, E_S and $E_{\mathrm{Li}_2 s_6}$ are the total energies of a composite system of the substrate with Li_2S_6, substrate and an isolated Li_2S_6 cluster, respectively.

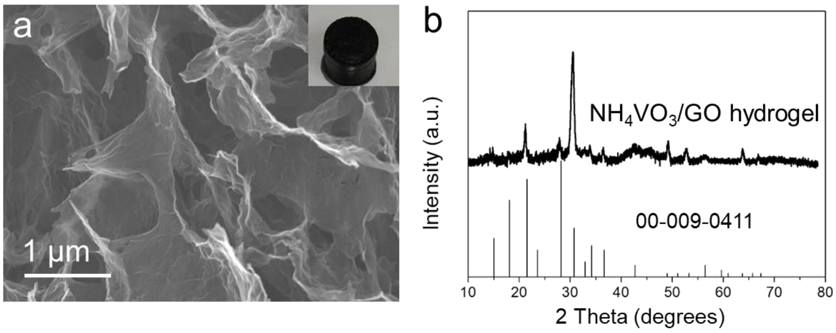

Figure S1. SEM image (a) and XRD pattern (b) of NH_4VO_3/GO hydrogel precursor.

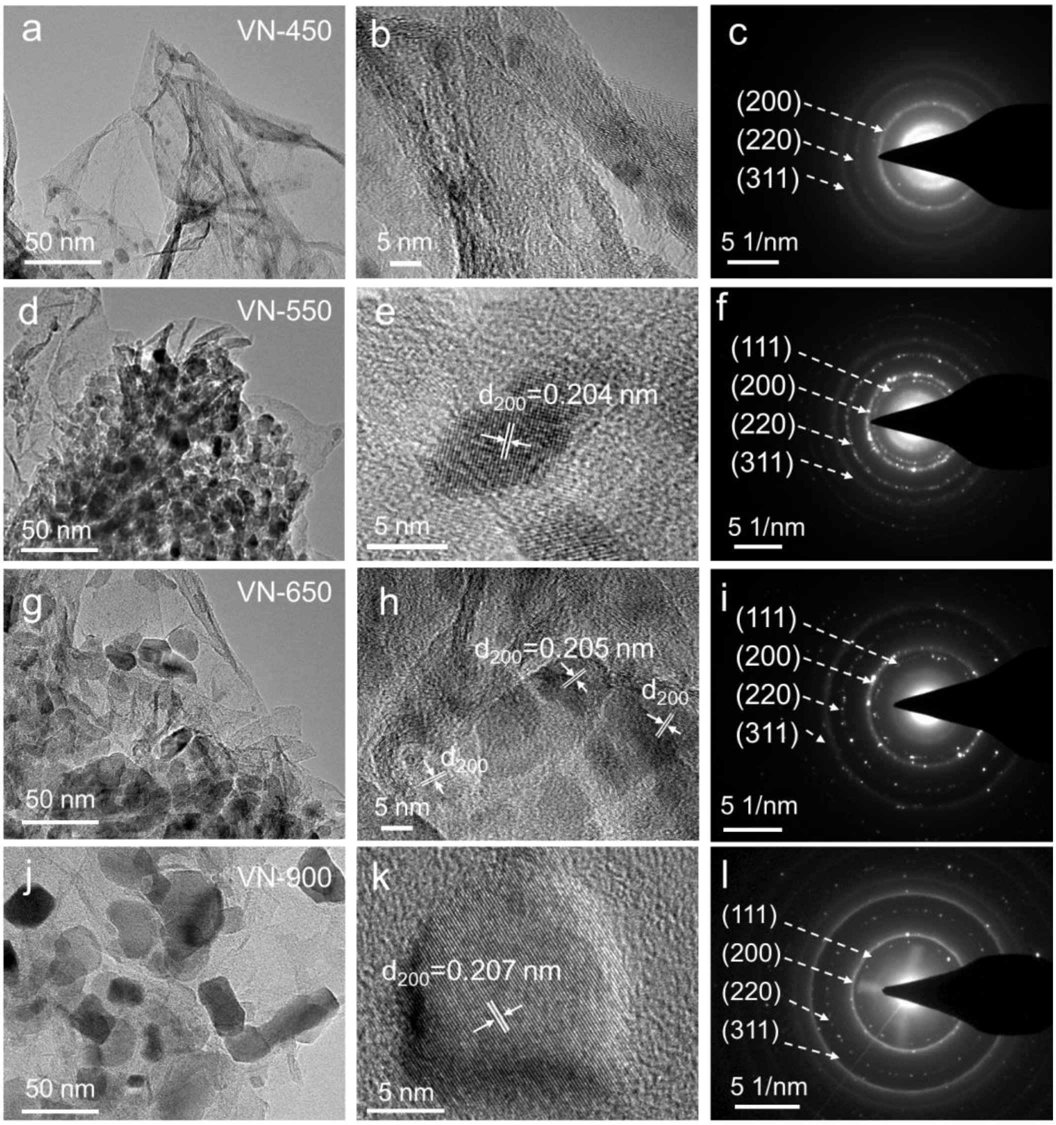

Figure S2. TEM, HRTEM and SAED images of VN/rGO xerogels obtained by calcining in NH_3 at different temperatures: (a-c) 450 ^{o}C (VN-450); (d-f) 550 ^{o}C (VN-550); (g-i) 650 ^{o}C (VN-650); (j-l) 900 ^{o}C (VN-900).

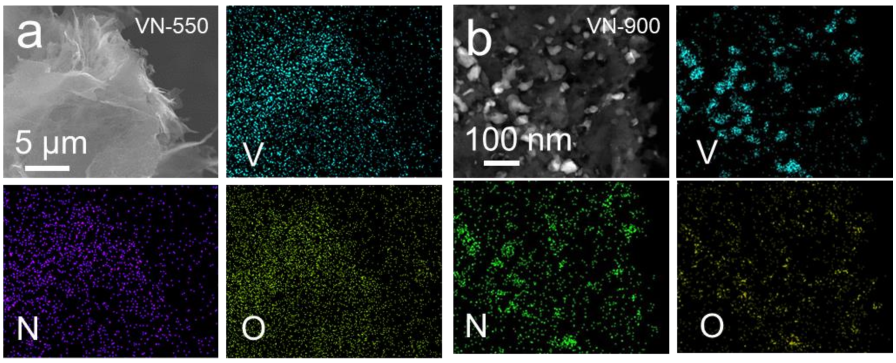

Figure S3. EDS mapping images of VN-550 (a) and VN-900 (b).

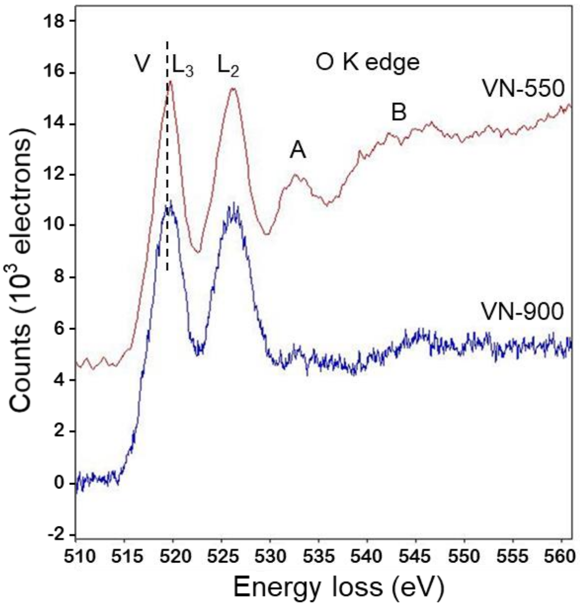

Figure S4. STEM EELS spectra of VN-550 and VN-900.

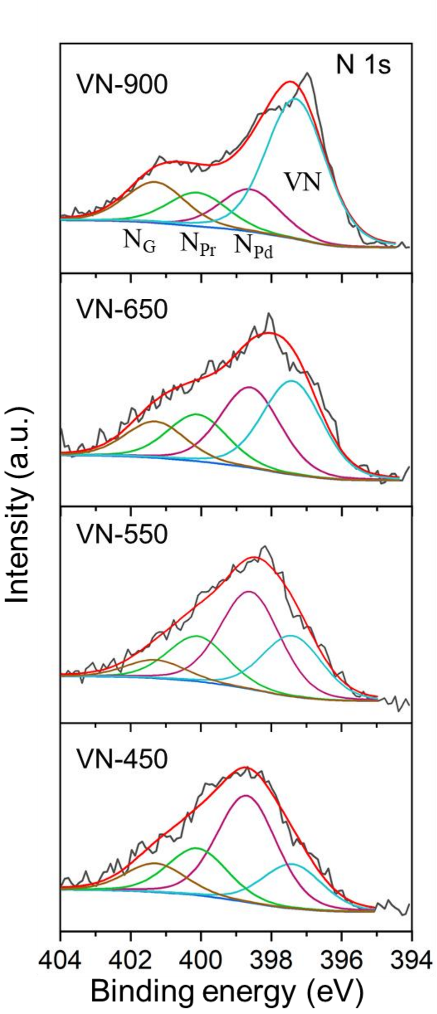

Figure S5. N1s XPS spectra of VN-900, VN-650, VN-550 and VN-450. N_{Pd}: pyridinic N; N_{Pr}: pyrrolic N, N_G: graphitic N; VN: metallic nitride.

Table S1. The proportions of V^{5+}-O, V^{4+}-O-N and V^{3+}-N based on XPS results.

Samples	V^{5+}	V^{4+}	V^{3+}
VN-450	46.3%	45.3%	8.4%
VN-550	45.0%	29.2%	25.8%
VN-650	43.6%	20.1%	36.3%
VN-900	39.7%	14.8%	45.5%

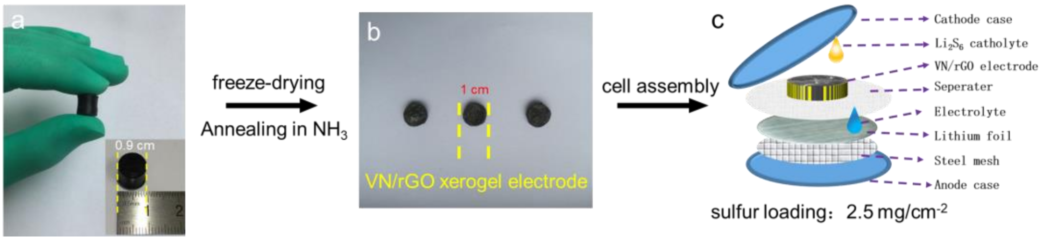

Figure S6. The preparation of VN/rGO xerogel and the assembly of coin Li-S cell.

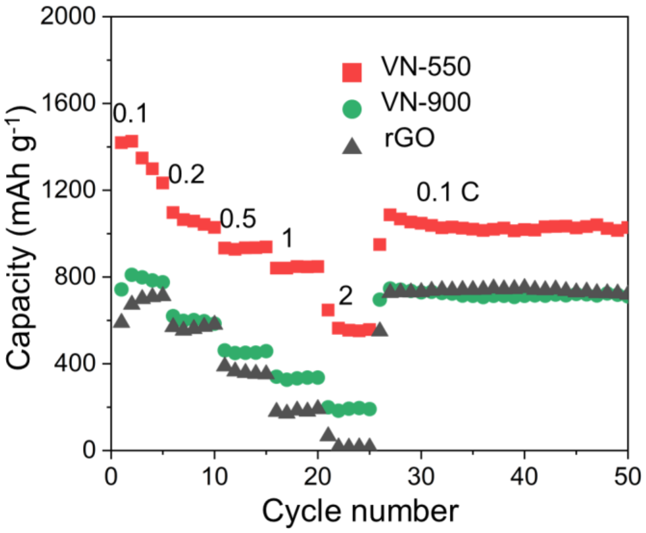

Figure S7. Rate performance of VN-550/Li_2S_6, VN-900/Li_2S_6 and rGO/Li_2S_6 cathodes at different current densities.

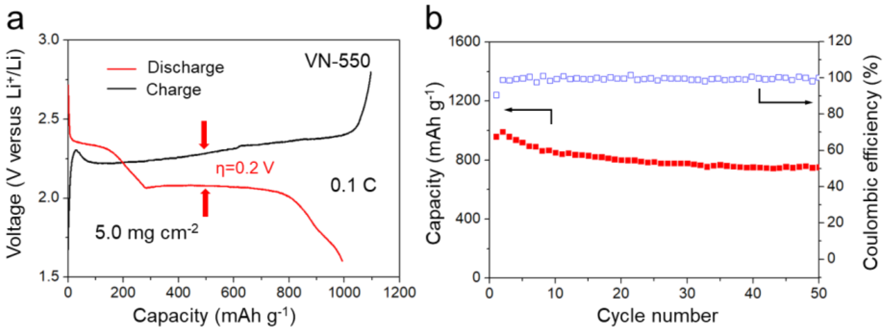

Figure S8. The discharge-charge profile (a) and cycling performance (b) of VN-500/Li_2S_6 at a high sulfur loading of 5 mg cm^{-2} and 0.1 C.

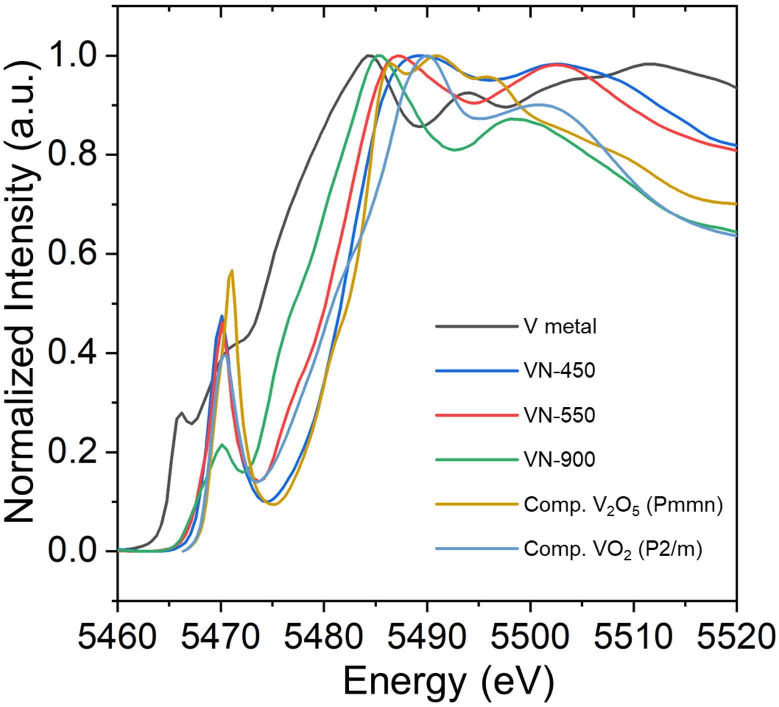

Figure S9. V K-edge XANES spectra of VN-450, VN-550, VN-900, computational V_2O_5 (Pmmn), computational VO_2 (P2/m) and V metal. The spectra of the computational V_2O_5 (Pmmn), computational VO_2 (P2/m) are cited from Materials Projects.

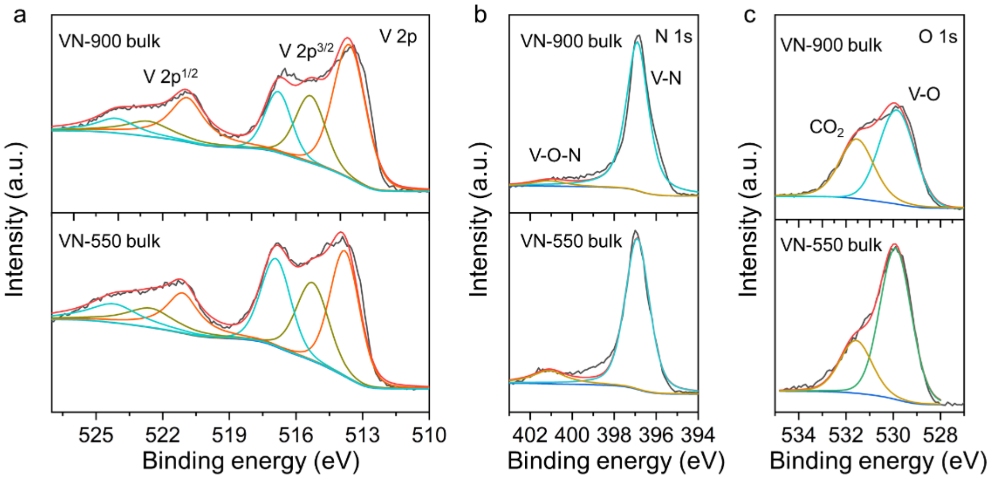

Figure S10. XPS spectra of VN-550 and VN-900 bulks: V2p (a); N1s (b); O1s (c).

Table S2. The proportions of V^{5+}-O, V^{4+}-O-N and V^{3+}-N in VN-550 and VN-900 bulks, respectively.

Samples	V^{5+}	V^{4+}	V^{3+}	Average valence
VN-550 bulks	30.5%	25.2%	44.3%	+3.9
VN-900 bulks	20.2%	24.2%	55.6%	+3.6

Table S3. The contents of N and O elements in VN-550 and VN-900 bulks based on EDS spectra.

Samples	N	O	O/N
VN-550 bulks	4.99	3.94	0.79
VN-900 bulks	4.54	2.38	0.52

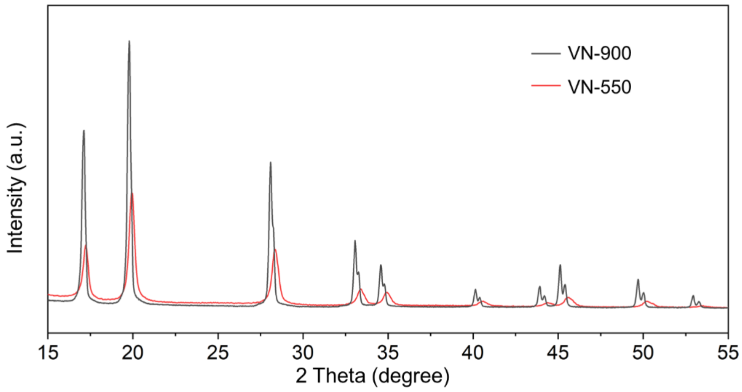

Figure S11. XRD patterns of VN-550 and VN-900 bulks by using Mo Ka radiation (λ= 0.071 nm).

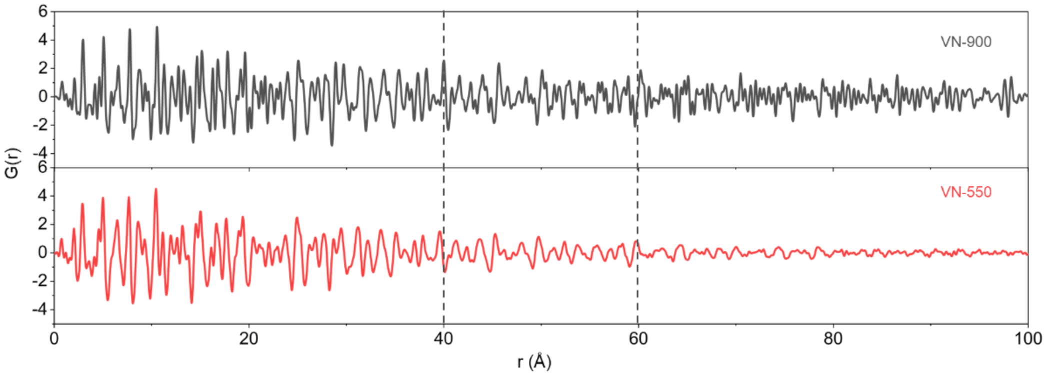

Figure S12. PDFs of VN-550 and VN-900 bulks from 0 to 100 Å.

Table S4. The proportions of V^{5+}-O, V^{4+}-O-N and V^{3+}-N in VN-550, VN-900, VN-550+Li_2S_6 and VN-900+Li_2S_6.

Samples	V^{5+}	V^{4+}	V^{3+}
VN-550	45.0%	29.2%	25.8%
VN-550+Li_2S_6	44.6%	21.2%	34.2%
VN-900	39.7%	14.8%	45.5%
VN-900+Li_2S_6	40.0%	12.1%	47.9%

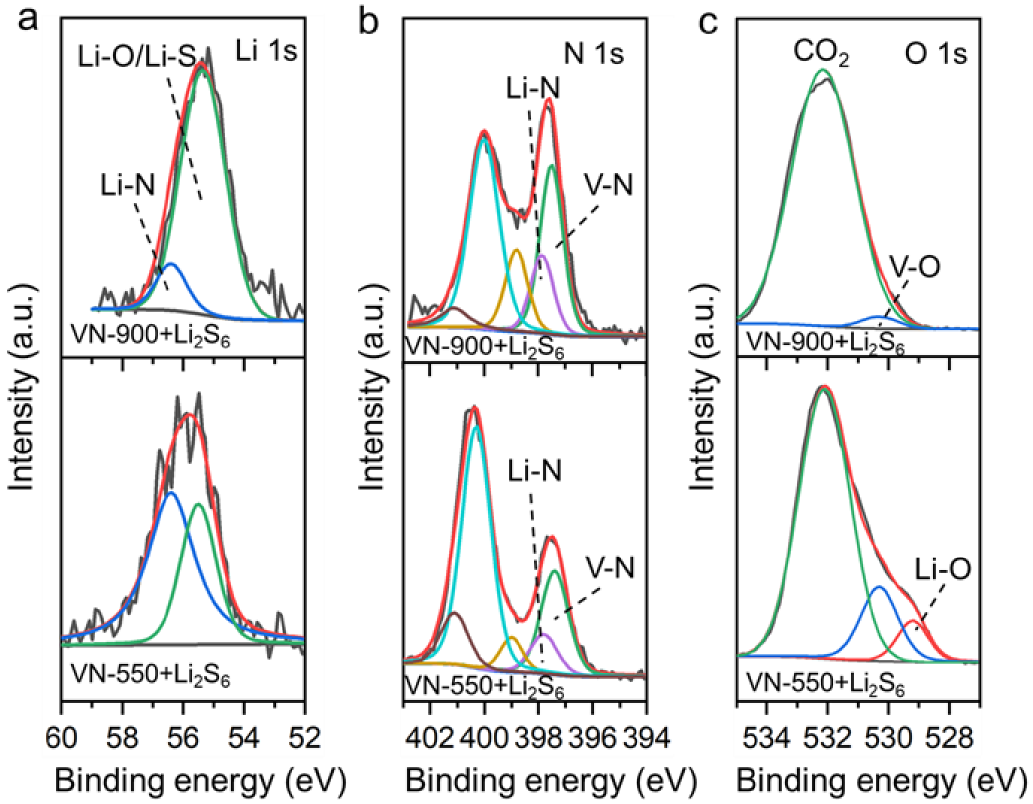

Figure S13. XPS spectra of VN-550/Li_2S_6 and VN-900/Li_2S_6 electrodes: Li 1s (a), N 1s (b) and O 1s (c).

Table S5. The proportions of Li_2S, Li_2S_2/S_t^{-1}, LiPSs/S_b^0, sulfite, thiosulfate, polythionate complex and sulfate in VN-550/Li_2S_6 and VN-900/Li_2S_6 at the initial state, 2.1 V and 1.6 V.

Samples	Li_2S	Li_2S_2/S_t^{-1}	LiPSs/S_b^0	Sulfite	Thiosulfate	Polythionate complex	Sulfate
original VN-550+Li_2S_6	-	-	13.7%	-	12.8%	7.0%	66.5%
original VN-900+Li_2S_6	-	-	9.7%	-	8.7%	7.4%	74.2%
VN-550+Li_2S_6 at 2.1 V	9.5%	41.8%	6.8%	18.2%	5.6%	3.5%	14.6%
VN-900+Li_2S_6 at 2.1 V	1.6%	29.5%	9.5%	13.2%	11.9%	5.3%	29.0%
VN-550+Li_2S_6 at 1.6 V	46.9%	21.3%	-	3.2%	3.0%	25.6%	-
VN-900+Li_2S_6 at 1.6 V	3.5%	23.7%	7.6%	9.4%	21.5%	11.8%	22.5%

Table S6. The normalized contents of Li_2S, Li_2S_2, and LiPSs in VN-550/Li_2S_6 and VN-900/Li_2S_6 cathodes at the initial state, 2.1 V and 1.6 V. In normalized calculations, the LiPSs is considered as Li_2S_3.

Samples	Li_2S	Li_2S_2	LiPSs
original VN-550+Li_2S_6	0	0	100%
VN-550+Li_2S_6 at 2.1 V	21.3%	63.4%	15.3%
VN-550+Li_2S_6 at 1.6 V	68.7%	31.3%	0
original VN-900+Li_2S_6	0	0	100%
VN-900+Li_2S_6 at 2.1 V	7.4%	48.6%	44.0%
VN-900+Li_2S_6 at 1.6 V	17.9%	43.4%	38.7%

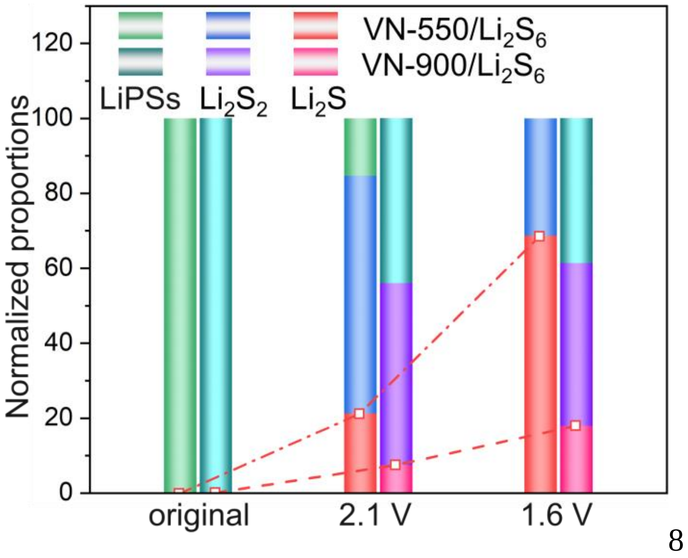

Figure S14. The normalized contents of Li_2S, Li_2S_2, and LiPSs in VN-550/Li_2S_6 and VN-900/Li_2S_6 cathodes at the original state, 2.1 V and 1.6 V.

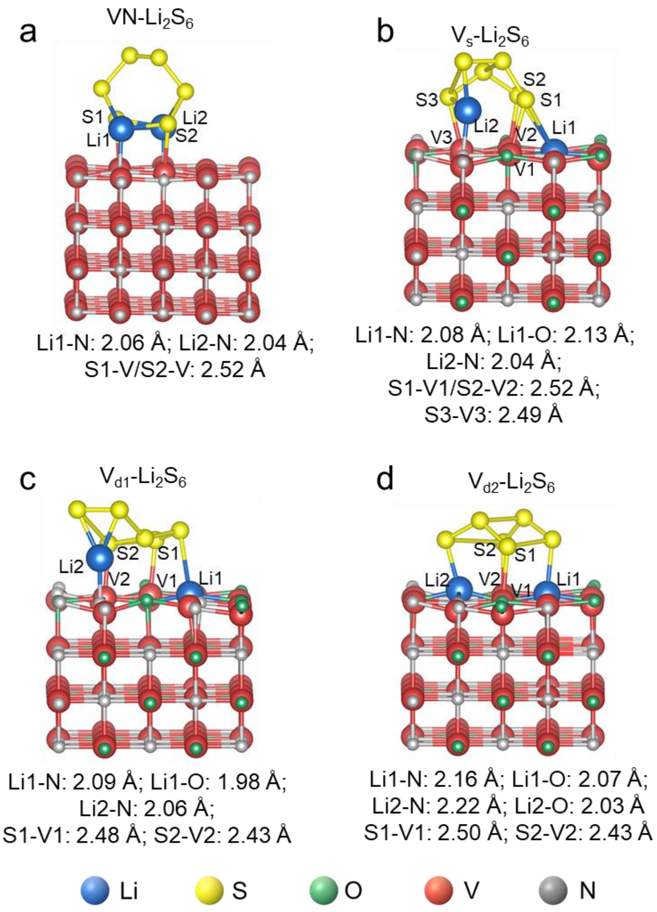

Figure S15. The relaxed adsorption configurations between Li_2S_6 species and VN (a), $VN_{0.8}O_{0.64}$: V_s (b), V_{d1} (c), V_{d2} (d).

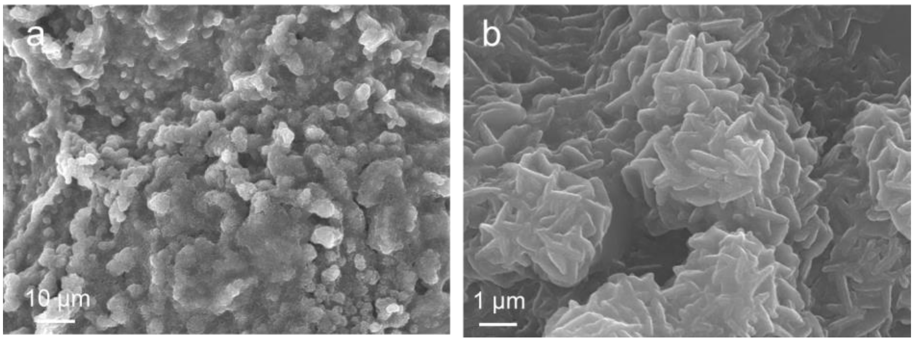

Figure 16. SEM images of the fully discharged products on VN-550 after 400 cycles at 2C.

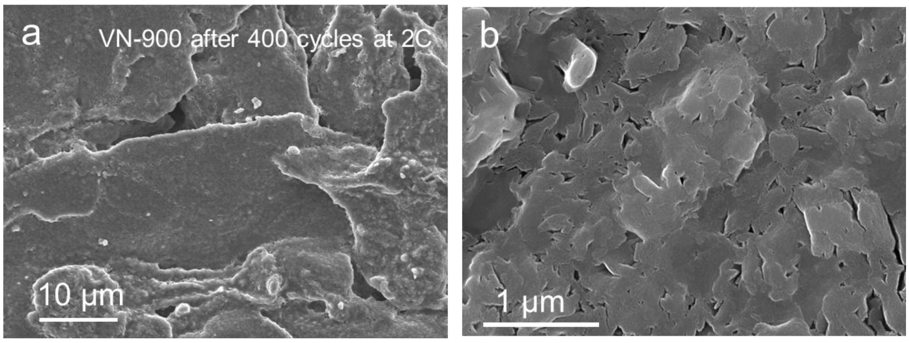

Figure S17. SEM images of the fully discharged products on VN-900 after 400 cycles at 2C.

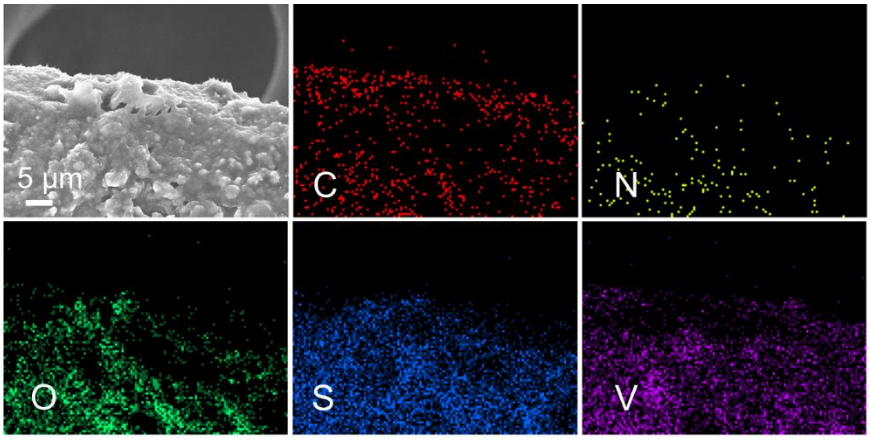

Figure 18. EDS mapping of VN/S electrode after 400 cycles at 2C.

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