

Supplementary Information for:

Vanadium oxynitrides as stable catalysts for
electrochemical reduction of nitrogen to ammonia: the role
of oxygen

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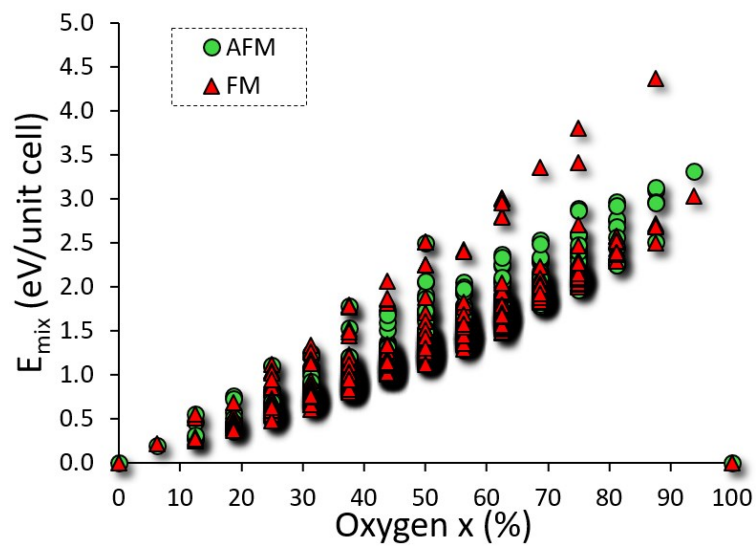


Figure S1. The mixing enthalpy of VN and VO with respect to V_2O_5 .

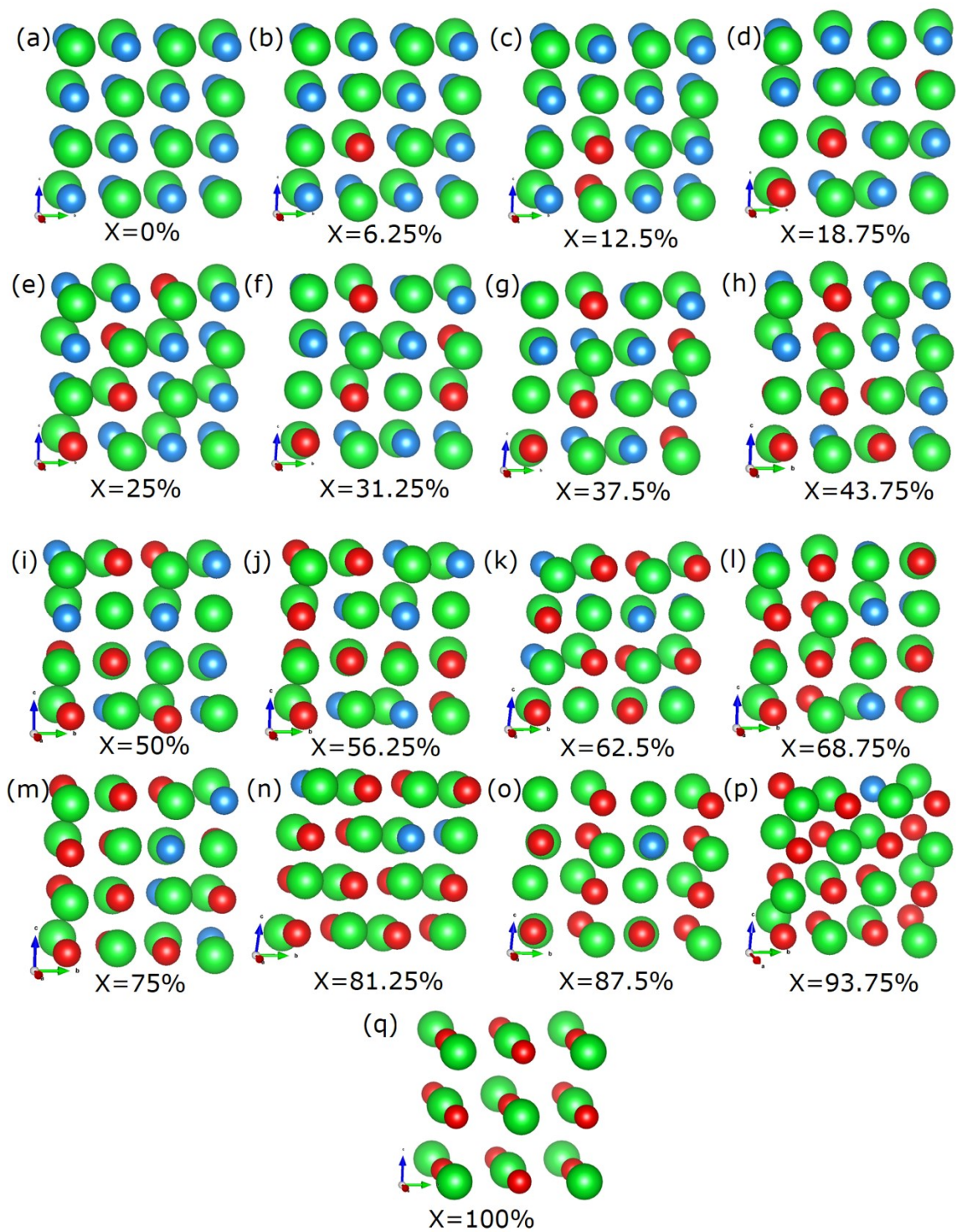


Figure S2. Crystal structures of minimum energy configuration with different N/O compositions along the convex hull of the mixing enthalpy calculated for rock-salt VN and VO phases (V: green, O: red and N: blue).

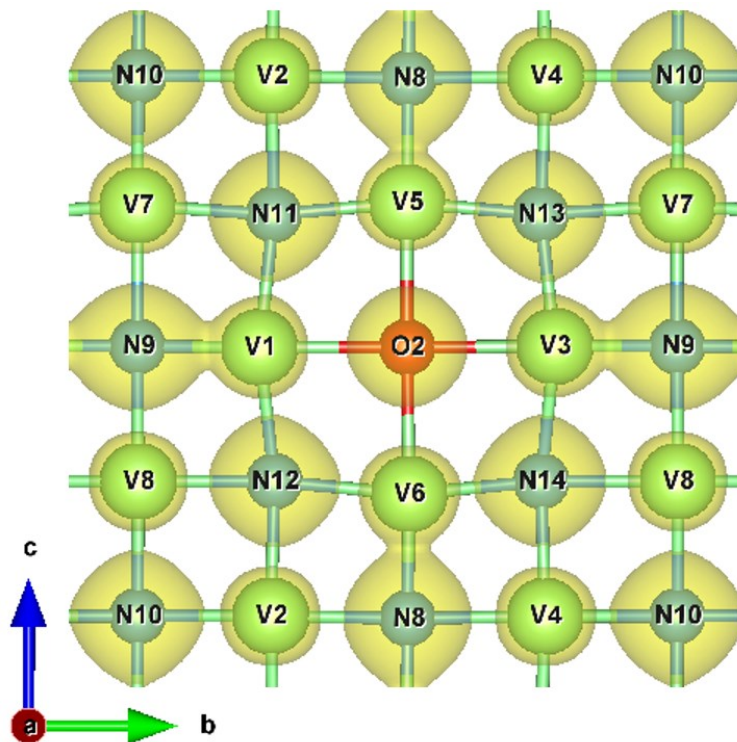


Figure S3. Charge density plot of (001) cross-section of VON ($x=12.75\%$) showing the disparity in the chemical bonding between V-N and V-O (V: green, O: red and N: blue).

Table-S1. Cell parameters of the lowest energy configurations of VON with different N/O ratio.

X (%)	a (Å)	b (Å)	c (Å)	α ($^{\circ}$)	β ($^{\circ}$)	γ ($^{\circ}$)	Volume (Å ³)
00.00	4.10	8.20	8.20	90.00	90.00	90.00	276.12
06.25	4.15	8.33	8.33	90.00	90.00	90.00	287.61
12.50	4.21	8.29	8.31	89.93	91.22	90.22	289.84
18.75	4.14	8.43	8.43	89.93	90.00	90.00	294.28
25.00	4.22	8.27	8.29	90.91	87.84	91.66	289.55
31.25	4.16	8.33	8.38	88.18	87.35	88.10	289.77
37.50	4.15	8.34	8.42	86.96	86.45	87.51	290.38
43.75	4.15	8.37	8.71	90.00	90.00	90.00	302.59
50.00	4.16	8.37	8.43	90.87	94.64	89.26	292.19
56.25	4.15	8.56	8.49	89.70	90.00	90.00	302.40
62.50	4.18	8.47	8.31	85.05	90.51	90.85	293.71
68.75	4.20	8.45	8.43	90.65	86.60	90.87	298.45
75.00	4.21	8.62	8.59	90.00	90.00	90.00	311.51
81.25	4.17	8.54	8.54	84.07	85.34	85.52	300.79
87.50	4.04	9.63	8.23	86.28	84.64	81.26	314.81
93.75	4.18	8.48	8.47	90.35	89.73	86.76	299.60
100.0	4.14	8.28	8.28	90.00	90.00	90.00	284.31

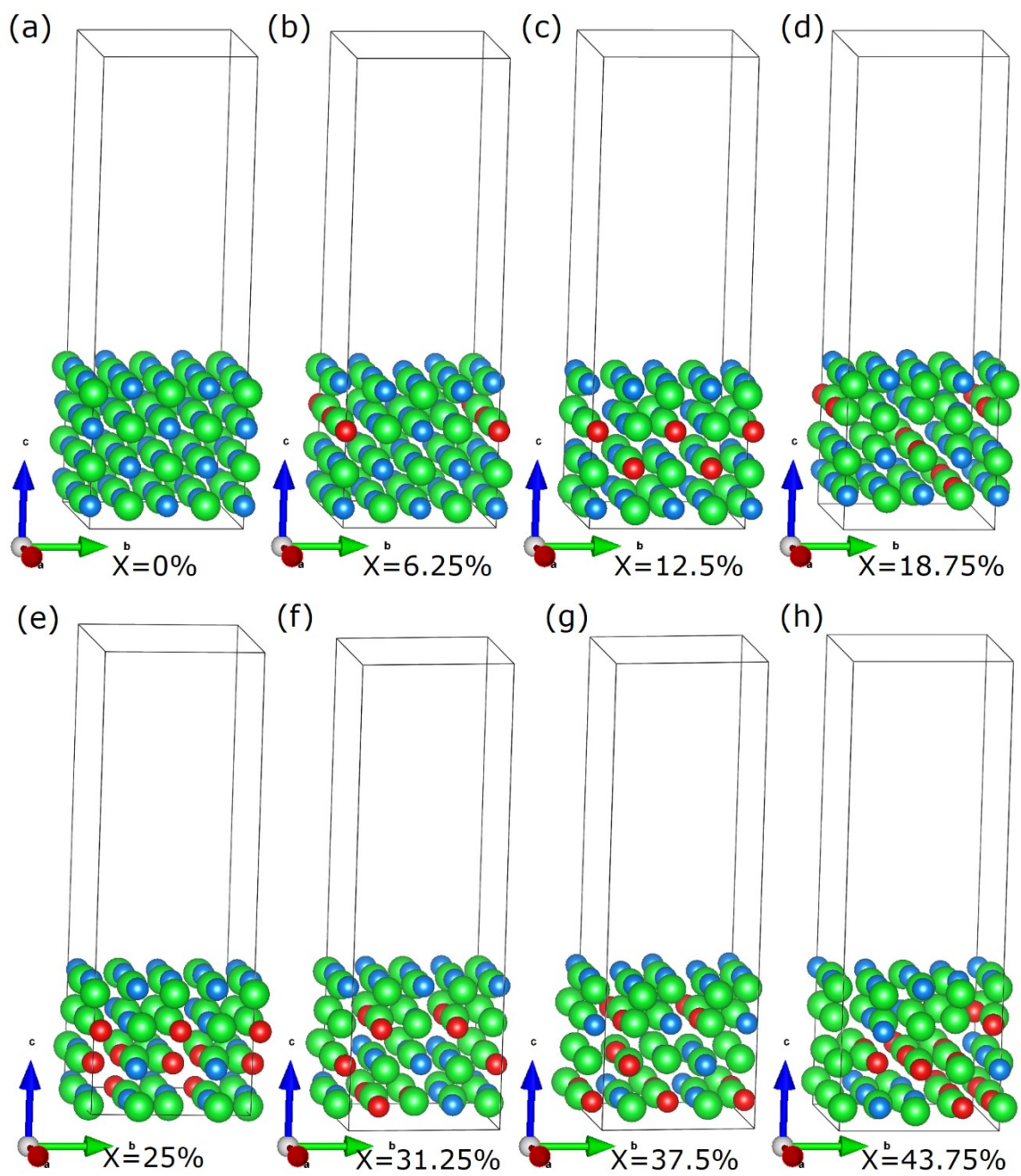


Figure S4. (100) slab cleaved from VON crystal with oxygen concentration $x=0\%$ to $x=43.75\%$, (b) (V: green, O: red and N: blue).

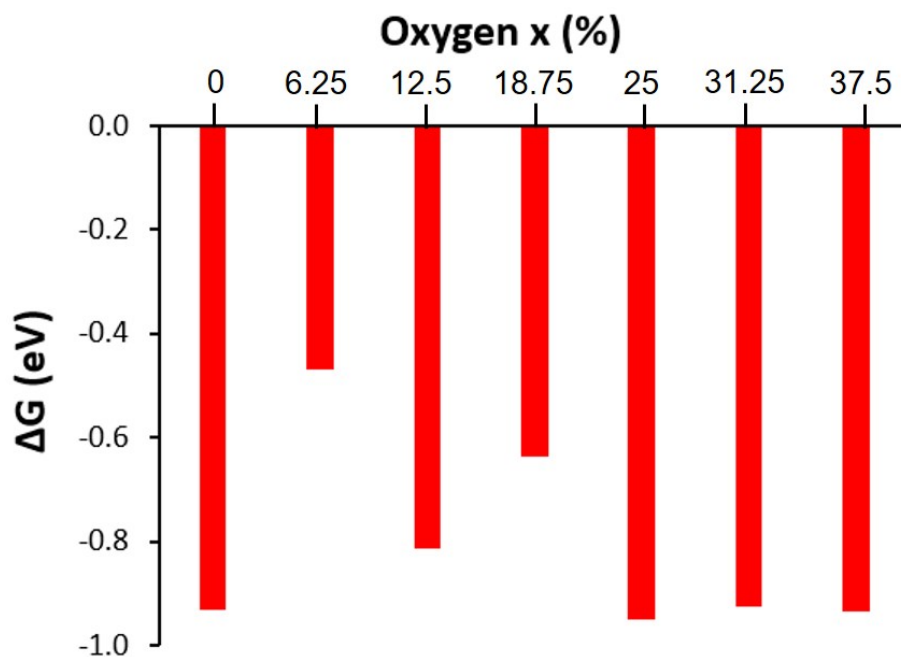


Figure S5. Free energy of H₂ formation from hydride ion and proton located at the neighboring V and N on the VON surface.

Table-S2. Bader charges on different H ions

Type of H ions	Bader charge
* ^N H	+1.00
* ^V H	-0.46
* ^{N-vac} H	-0.77

Table-S3. Zero point energy and entropy correction for the gaseous molecules and adsorbates used in the free energy calculations of VON surface at ambient condition (300K and 1atm pressure).

System	ZPE (eV)	TS (eV)
H_2O	0.56	0.584
NH_3	0.89	0.74
H_2	0.27	0.41
N_2	0.15	0.6
* N	0.17	0.09
* VH	0.14	0.03
* NH	0.25	0.04
* N_2H	0.69	0.07
* N_3H	1	0.17
* VN	0.08	0.04
* VNH	0.34	0.06
* VNH_2	0.69	0.07
* VNH_3	0.99	0.18
* $N-vacOH$	0.328	0.103
* $N-vacO$	0.055	0.056

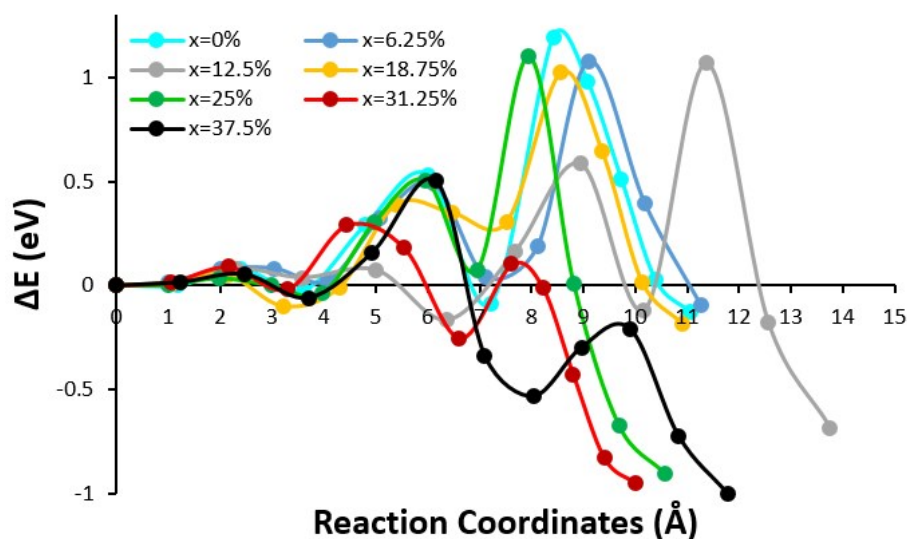


Figure S6. N-N adsorption and dissociation path on VON ($x=0-37.5\%$).

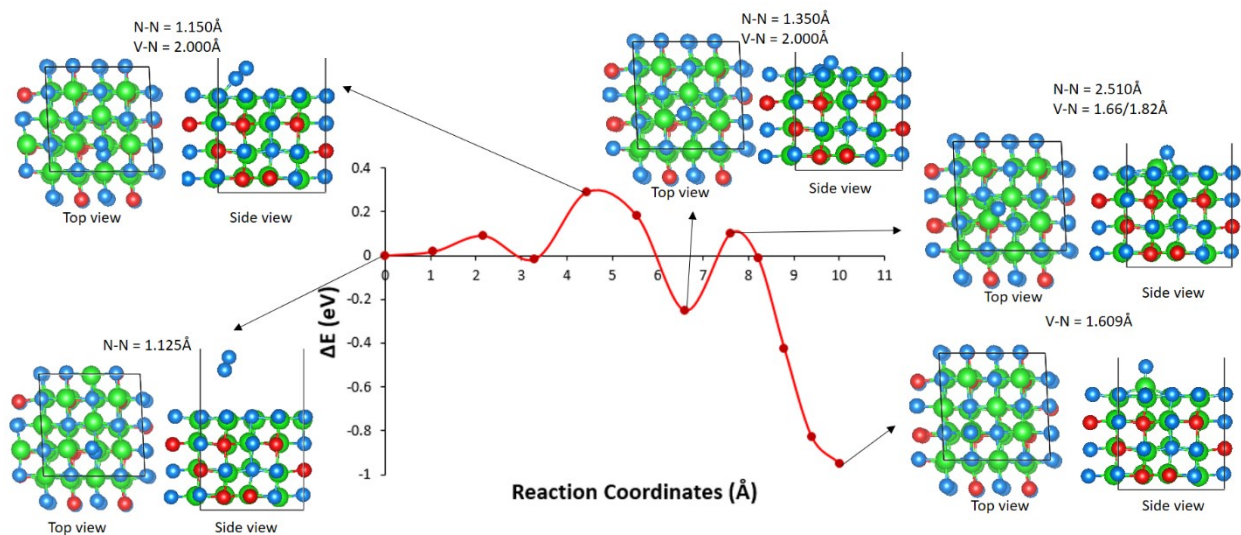


Figure S7. N-N adsorption and dissociation path on VON ($x=31.25\%$). Color scheme: green-V, blue-N, and red-O.

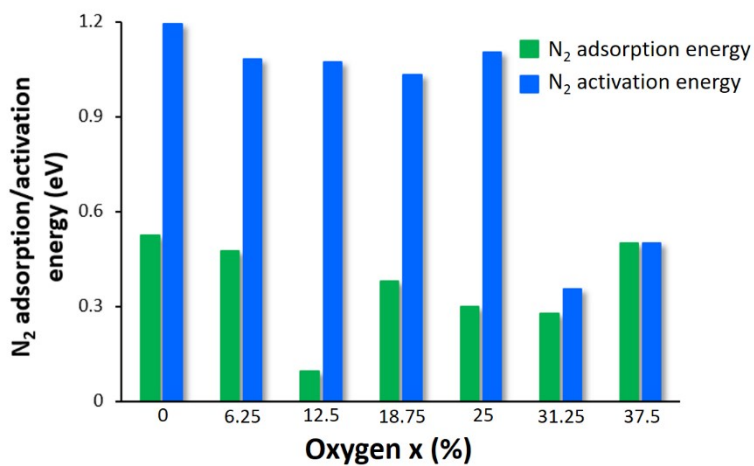


Figure S8. The non-dissociative N₂-adsorption energy (green bars) and the N-N dissociation barrier (blue bars) on VON surface ($x=0-37.5\%$).

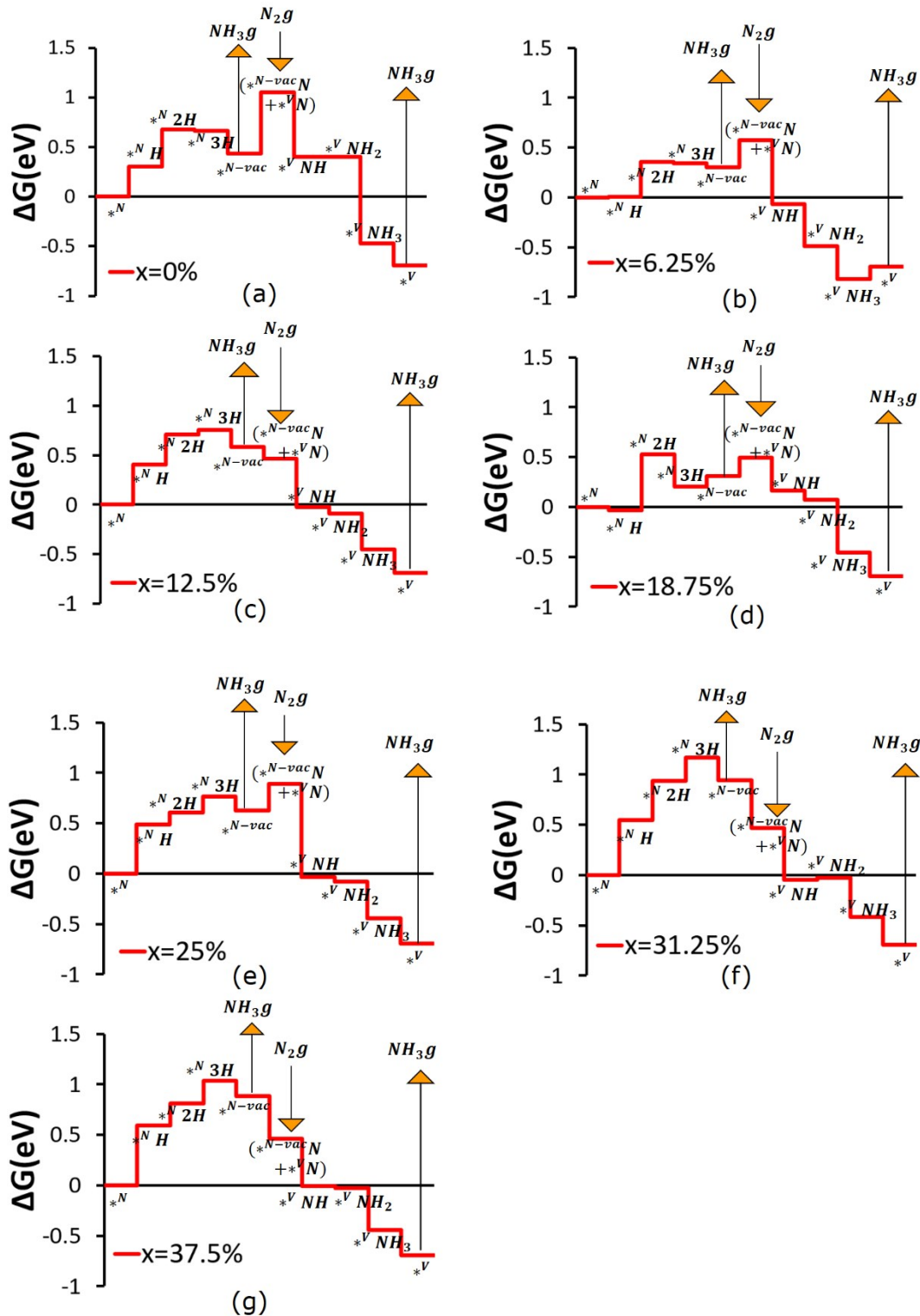


Figure S9. Free energy path of dissociative MvK NRR on VON with $x=0\%$ to $x=37.25\%$

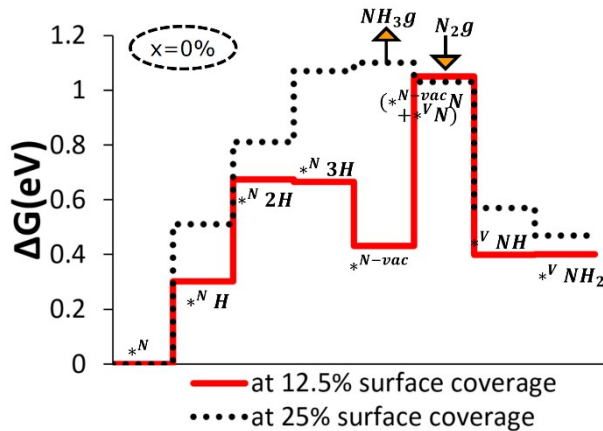


Figure S10. The effect of surface coverage of N-vacancy on N-adsorption energy.

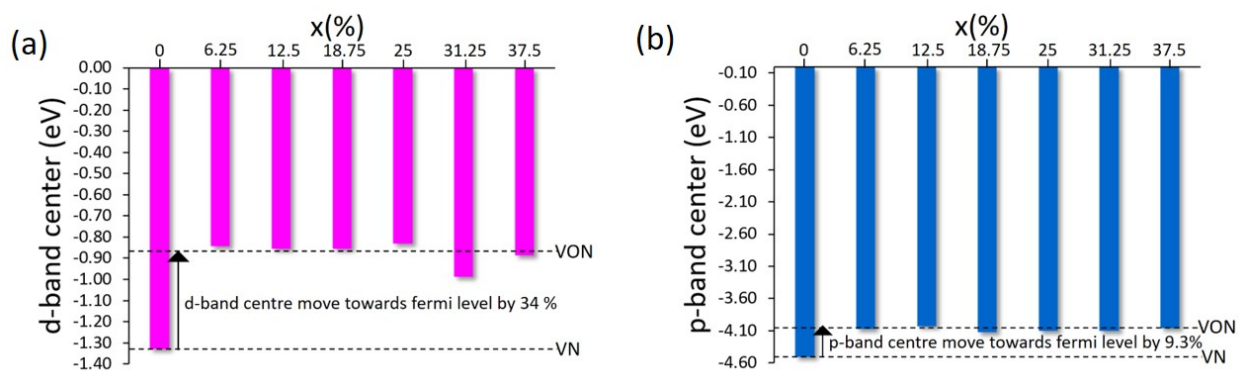


Figure S11. **a** d-band center of the surface V ions and **b** p-band center of the anions moved energetically up towards fermi level in presence of O in the system compare to the pure VN.