Supporting information

Structural transformation during Li/Na insertion and theoretical cyclic voltametry of δ-$NH_4V_4O_{10}$ electrode: A first-principles study

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Methodology:

DFT based first principles calculations, which is implemented in the plane wave code VASP, were used for total energy calculation of $Li_x/Na_xNH_4V_4O_{10}$ systems. Furthermore, Generalized Gradient Approximations (GGA)[1] was used to approximate the correlation energy. Also, to incorporate the onsite correlation of V d-orbital, we used U=3 eV in all the structures and Perdew-Burke-Ernzerhof (PBE)[1] potential was used for all the atoms. The plane energy cutoff was set to 500eV and the Brillouin Zone integrations in k-mesh grids of 3x9x9 were used for sampling. All the lattice parameters and atoms coordinates were fully relaxed until the magnitude of forces on each atom were less than 0.02 eV / Å and pressure of the system was less than 0.01 kbar. Initial structural information of δ-$NH_4V_4O_{10}$ are taken as '$(NH_4)_{0.5}(V_2O_5)(H_2O)_{0.5}$[2], where Na^+ or Li^+ ions are inserted in the inter and intra layer spacing of the δ-$NH_4V_4O_{10}$ structure.[3] Crystallographic information of $(NH_4)_{0.5}(V_2O_5)(H_2O)_{0.5}$ (JCPDS File No. 31-0075) was used for the indexing of XRD pattern of δ-$NH_4V_4O_{10}$.[3]

Electrochemical potential was calculated from the Nernst equation as mentioned earlier.[4,5] The average electrochemical potential:

$$V = \frac{E_{M_aNH_4V_4O_{10}} - E_{M_bNH_4V_4O_{10}} + (b-a)E_M}{(b-a)e}$$

Where, (b-a) is the number of moles of electrons transferred. $E_{MbNH4V4O10}$, $E_{MaNH4V4O10}$ and EM are the total energies per formula unit of intercalated and deintercalated structures of cathode material and inserted metal atom (M=Li/Na), respectively.

Structural details:

In the structure of δ-$NH_4V_4O_{10}$, the NH_4^+ ion lies into a gallery space of V_4O_{10}. To select the lowest energy structure of δ-$NH_4V_4O_{10}$, we calculated formation energy of the different configurations. The configurations of δ-$NH_4V_4O_{10}$ with the same site for nitrogen have different orientational arrangement of the NH_4 molecules. To choose the sites for Li^+/Na^+ in

δ-$NH_4V_4O_{10}$, we have used the 4i Wyckoff position of N in $(NH_4)_{0.5}(V_2O_5)(H_2O)_{0.5}$ (i.e. 4i) for gallery space. Similarly, 2b sites of $Li_3V_6O_{13}$ were chosen for Li^+ incorporation within V_4O_{10} layer. Both $(NH_4)_{0.5}(V_2O_5)(H_2O)_{0.5}$ and $Li_3V_6O_{13}$ exhibit the same space group C1 2/m 1. Theoretical work by Kim et. al.[6] also used a similar methodology to study intercalation mechanism in vanadium layered compound. Based on our analysis of possible configurations, we found gallery space and the above-mentioned sites within V_4O_{10} layers as a most favourable ion insertion site. For optimising the $NaNH_4V_4O_{10}$ structure, we arrived lower energy configuration (one type of configuration is where Na^+ ions are in different sites within the VO layer, another type of configuration is Na^+ stays only in gallery space) with insertion of two Na ions in the gallery space of δ-$NH_4V_4O_{10}$ compare to the other configurations. It suggests that Na ions first diffuse in the gallery space followed by interlayer position.

Table S1: Calculated lattice parameters of $Li_xNH_4V_4O_{10}$ and $Na_xNH_4V_4O_{10}$ at different concentration of intercalated ions in the host material.

Lattice parameter	$Li_xNH_4V_4O_{10}$					
	x=0	x=0.5	x=1	x=2	x=2.5	x=3
a(Å)	11.77(11.71)*	11.73	11.7	11.48	11.55	11.59
b(Å)	3.74 (3.66)*	3.75	3.78	3.89	3.92	3.96
c(Å)	9.75 (9.72)*	9.68	9.6	9.76	9.76	9.77
α	90°	90°	90°	90°	90°	90°
β	86.97°	87.74°	89.96°	89.21°	89.08°	88.97°
γ	90°	90°	90°	90°	90°	90°
Volume ($Å^3$)	428.91	425.49	424.29	436.15	442.53	448.04

Lattice parameter	$Na_xNH_4V_4O_{10}$					
	x=0	x=0.5	x=1	x=2	x=2.5	x=3
a(Å)	11.77	11.79	12.07	12.26	12.35	12.51
b(Å)	3.74	3.74	3.77	3.88	3.92	3.94
c(Å)	9.75	9.71	9.08	9.3	9.72	9.86
α	90°	90°	90°	90°	90°	90°
β	86.97°	84.32°	89.45°	87.9°	86.89°	85.27°
γ	90°	90°	90°	90°	90°	90°
Volume ($Å^3$)	428.91	426.55	413.49	442.54	469.93	484.4

* JCPDS File No. 31-0075

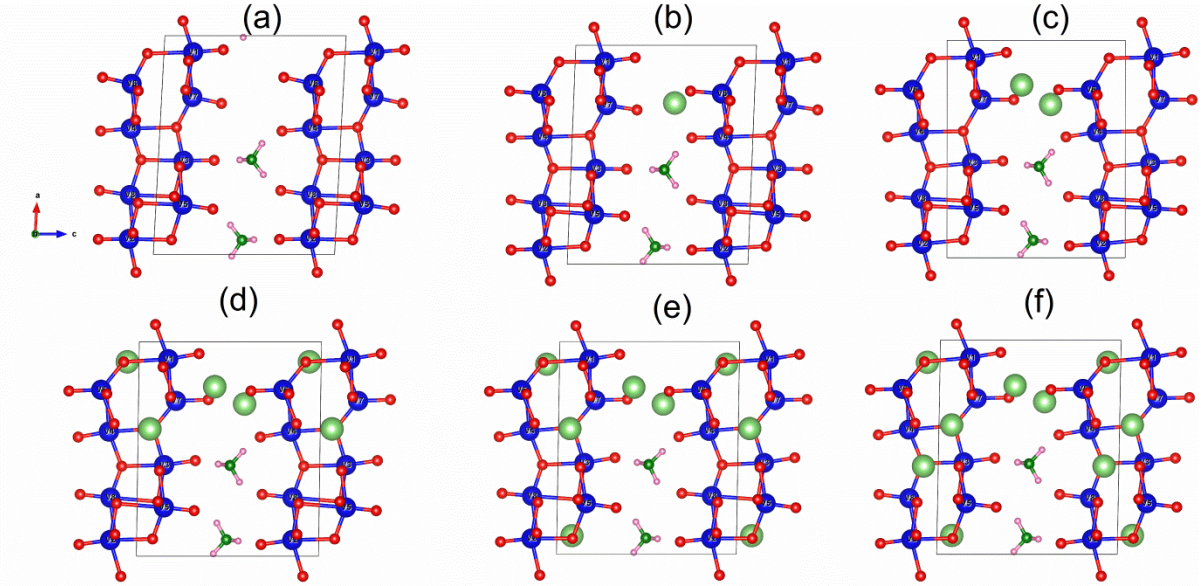

Figure S1: Changes in the structure upon intercalation of Li^+ ions in (a) δ-$NH_4V_4O_{10}$ (b) $Li_{0.5}NH_4V_4O_{10}$ (c) $LiNH_4V_4O_{10}$ (d) $Li_2NH_4V_4O_{10}$ (e) $Li_{2.5}NH_4V_4O_{10}$ (f) $Li_3NH_4V_4O_{10}$.

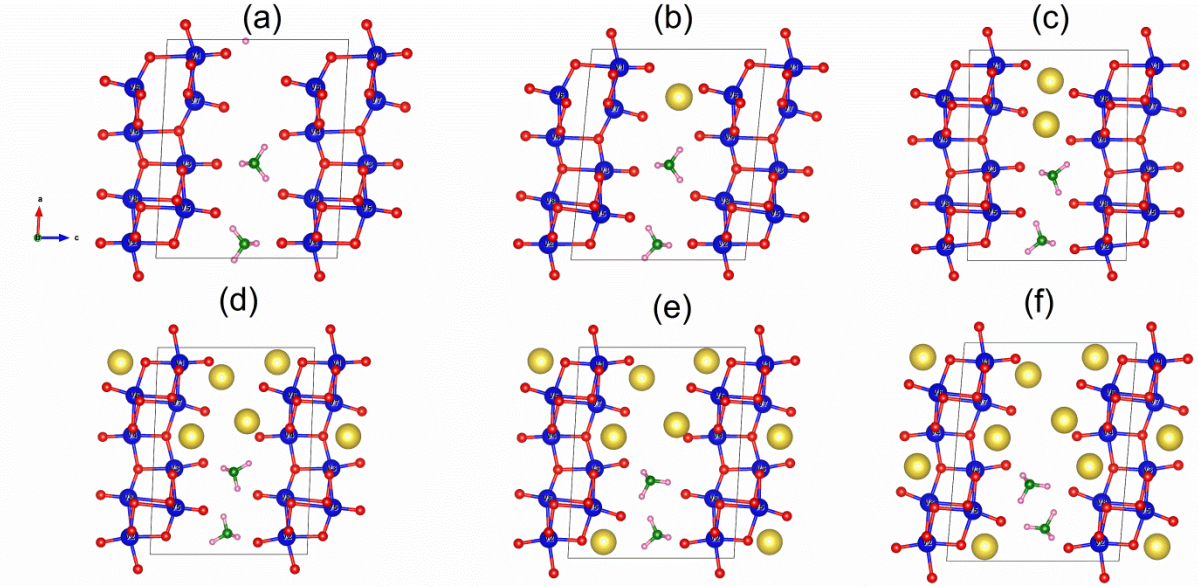

Figure S2: Changes in the structure upon intercalation of Na^+ ions in (a) δ-$NH_4V_4O_{10}$ (b) $Na_{0.5}NH_4V_4O_{10}$ (c) $NaNH_4V_4O_{10}$ (d) $Na_2NH_4V_4O_{10}$ (e) $Na_{2.5}NH_4V_4O_{10}$ (f) $Na_3NH_4V_4O_{10}$.

Table S2: Calculated magnetic moment of vanadium atoms in δ-$NH_4V_4O_{10}$ as function of ion concentration. Magnetic moment(μ_B) approximately equal to the number of unpaired electron(e). For changing oxidation state of V in between +5 to +4, number of unpaired electron is always approximately ≤1. μ_B=1 indicates number of unpaired electron is equal to 1, which is d^1 orbital configuration of V^{+4}. Whereas μ_B=0 indicates d^0 configuration of V^{+5} which is highest oxidation state of V. For further reduction from V^{+5} state, upcoming electrons occupy unfilled d^0 orbital. So, we can write oxidation state (O.S) ≈ +5- e ≈ +5 - μ_B (when e ≤1 approximately)

$Na_xNH_4V_4O_{10}$	Magnetic moment of vanadium							
(x)	V1	V2	V3	V4	V5	V6	V7	V8
0	0.2	0	0	0.2	1	0	0	1
0.5	1	0.2	0.2	0.2	0.2	1	0.3	0.7
1	1	0.2	0.2	1	0.3	1.1	1.1	0.3
2	1.1	1.1	1.1	1.1	0.2	1.1	1.1	0.2
2.5	1.1	1.1	1.1	1.1	1.1	1.1	1.1	0.3
3	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1

$Li_xNH_4V_4O_{10}$	Magnetic moment of vanadium							
(x)	V1	V2	V3	V4	V5	V6	V7	V8
0	0.2	0	0	0.2	1	0	0	1
0.5	1	0.2	0	0.2	0.3	1	0	1
1	1	0.1	0.1	1	0.2	1.1	1.1	0.2
2	1.1	1.1	1.1	1.1	0.2	1.1	1.1	0.2
2.5	1.1	1.1	1.1	1.1	1.1	1.1	1.1	0.2
3	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1

Table S3: Calculated oxidation state of vanadium atoms in δ-$NH_4V_4O_{10}$ as function of ion concentration. With increasing concentration of Li^+ or Na^+ ion in δ-$NH_4V_4O_{10}$, the change in oxidation state of V is not uniform suggesting different local environment for the V at different concentration of ions. Further, the change in magnetic moment of V from μ_B=0 to μ_B=1 with increasing concentration of ion suggests the change in oxidation state of V from +5 to +4.

$Li_xNH_4V_4O_{10}$	Oxidation state of vanadium (+e)								
X	V1	V2	V3	V4	V5	V6	V7	V8	Average
0	4.8	5.0	5.0	4.8	4.0	5.0	5.0	4.0	4.7
0.5	4.0	4.8	5.0	4.8	4.7	4.0	5.0	4.0	4.5
1	4.0	4.9	4.9	4.0	4.8	3.9	3.9	4.8	4.4
2	3.9	3.9	3.9	3.9	4.8	3.9	3.9	4.8	4.1
2.5	3.9	3.9	3.9	3.9	3.9	3.9	3.9	4.8	4.0
3	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9

$Na_xNH_4V_4O_{10}$	Oxidation state of vanadium (+e)								
X	V1	V2	V3	V4	V5	V6	V7	V8	Average
0	4.8	5.0	5.0	4.8	4.0	5.0	5.0	4.0	4.69
0.5	4.0	4.8	4.8	4.8	4.8	4.0	4.7	4.3	4.50
1	4.0	4.8	4.8	4.0	4.7	3.9	3.9	4.7	4.37
2	3.9	3.9	3.9	3.9	4.8	3.9	3.9	4.8	4.13
2.5	3.9	3.9	3.9	3.9	3.9	3.9	3.9	4.7	4.01
3	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.89

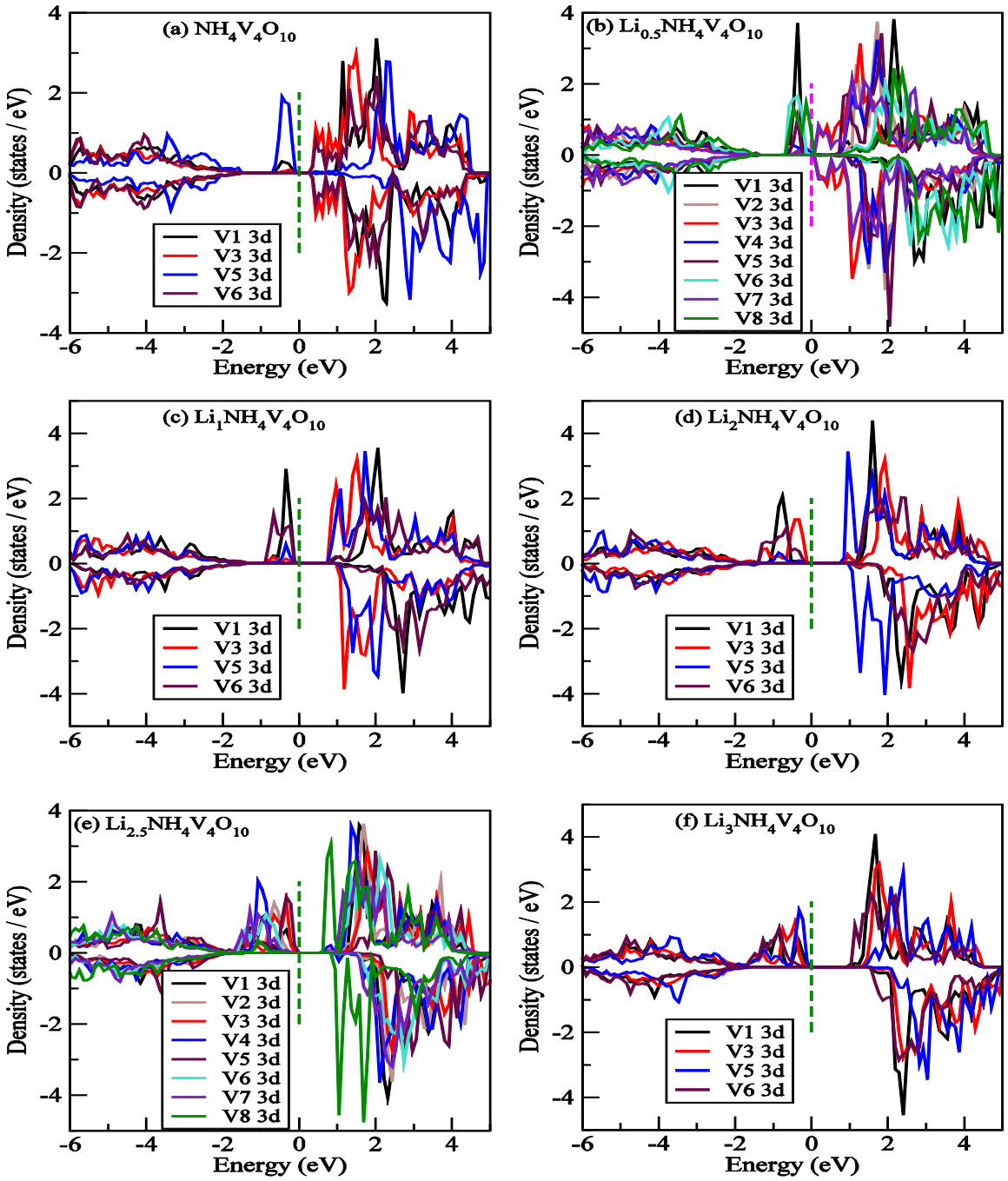

Figure S3: Partial density of state of 3d orbitals of all the vanadium atoms at different concentration of Li in $Li_xNH_4V_4O_{10}$.

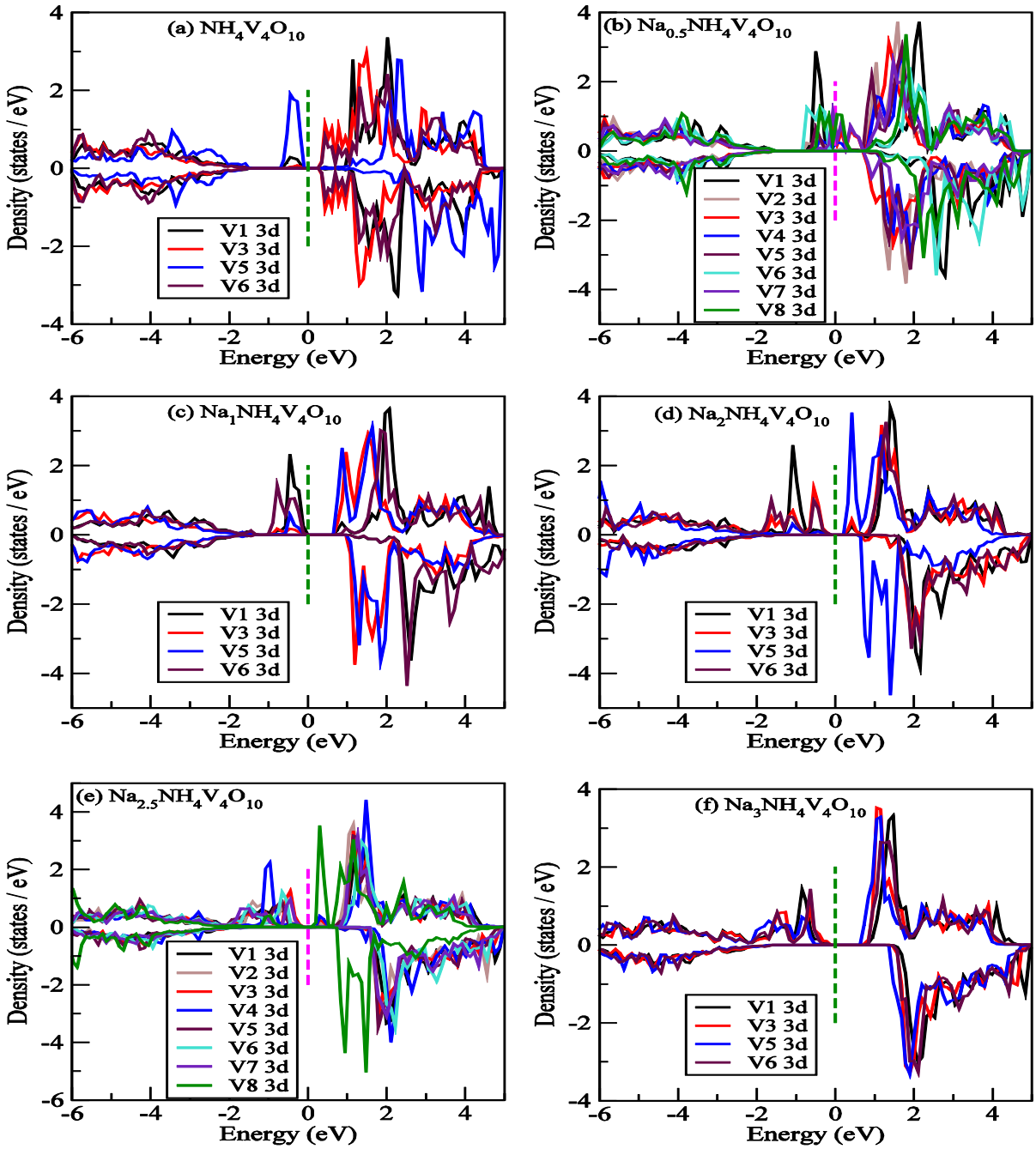

Figure S4: Partial density of state of 3d orbitals of all the vanadium atoms at different concentration of Na in $Na_xNH_4V_4O_{10}$.

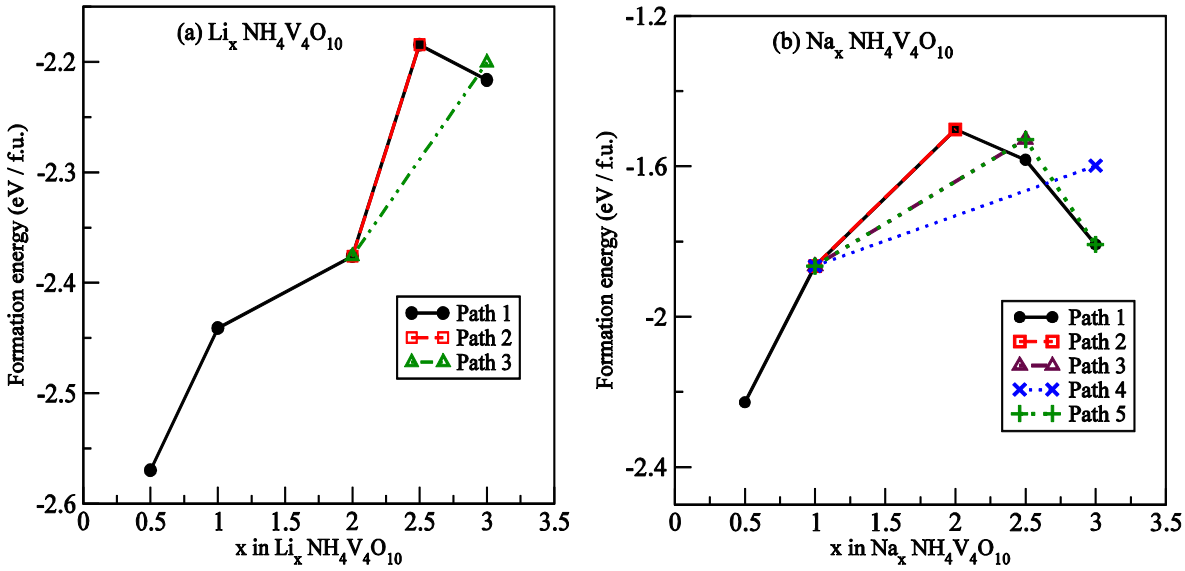

Figure S5: Calculated formation energy as a function of ion concentration for (a) $Li_xNH_4V_4O_{10}$ and (b) $Na_xNH_4V_4O_{10}$.

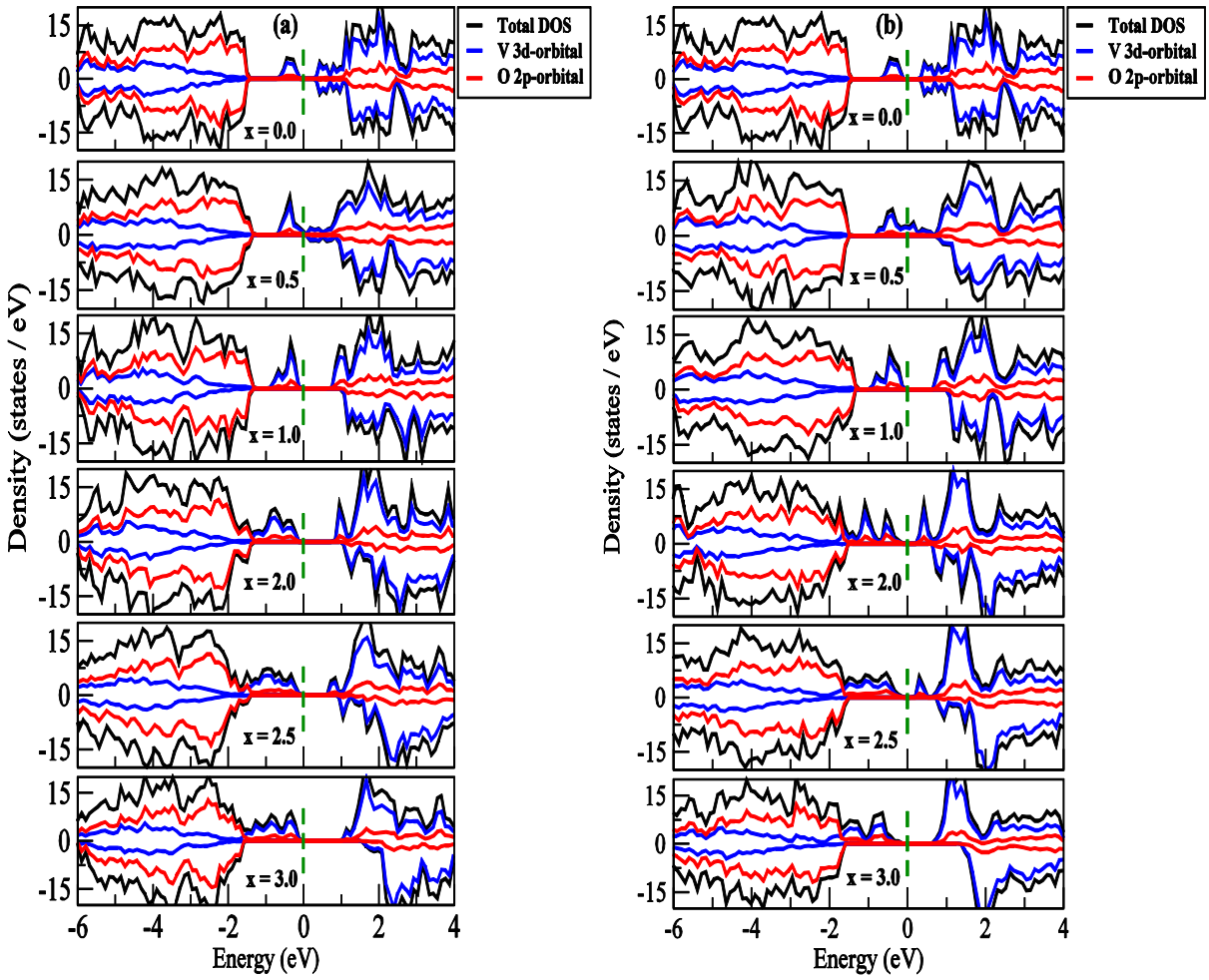

Figure S6: Partial density of state of V-d and O-p along with total density of states of a. $Li_xNH_4V_4O_{10}$ and (b) $Na_xNH_4V_4O_{10}$.

References:

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