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# **Electronic Supplementary Information**

# Sodium-Ion Battery Cathode Materials: Towards an improved energy-based descriptor for

investigating material stability against moisture

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**Figure S1:** Twelve configurations for bulk Na(Mn<sub>0.5</sub>Ni<sub>0.5</sub>)O<sub>2</sub> material with 12 formula units calculated at PBE+U+D3 level. FE (Formation energy) values are indicated in braces. Yellow, red, silver, and purple represent Na, O, Ni, and Mn-ions, respectively.

Systems	Lattice	PBE+U+D3	<b>Expt.</b> [1,2]	
	Parameters			
O3-NMNO	a (Å)	3.008	2.9997	
	b (Å)	2.987	2.9997	
	c (Å)	15.78	16.172	
	volume (Å <sup>3</sup> )	123.05	126.027	
	α (°)	90.00	90.00	
	β (°)	90.24	90.00	
	γ (°)	119.76	120.00	
O3-NTNO	a (Å)	2.988	2.9623	
	b (Å)	2.996	2.9623	
	c (Å)	15.83	15.955	
	volume (ų)	122.67	121.251	
	α (°)	90.00	90.00	
	β (°)	90.05	90.00	
	γ (°)	120.09	120.00	

**Table S1**. Lattice parameters for O3-NMNO and O3-NTNO systems are computed using PBE+U+D3 (U for  $Mn^{4+}$  =3.9 eV and  $Ni^{2+}$  = 6.2 eV) with experimental data.



**Figure S2.** a) Na-vacancy based O3-NMNO bulk system (a) Water inserted Na-vacancy based O3-NMNO bulk system. c) Na-vacancy based O3-NTNO bulk system (d) water inserted Na-vacancy based O3-NTNO bulk system. Note:  $\Delta E$  (eV) =  $E_{bulk(Na-vacancy)+water} - E_{bulk(Na-vacancy)} - E_{water}$ . Water molecule is oriented perpendicular to Na-layer plane in Na-vacancy in Water inserted configurations. Yellow, red, cyan, sky blue, silver, and purple represent Na, O, H, Ti, Ni, and Mn-ions, respectively. Blue dotted lines show the H-bond formation with oxide layers



**Figure S3.** Various guess configurations of water inside the Na-vacancy based O3-NMNO system (a) water molecule is oriented parallel to Na-layer plane with H-atoms pointing to Naatoms of O3-NMNO, b) water molecule is oriented perpendicular to Na-layer plane, and c) water molecule is oriented parallel to Na-layer plane with H-atoms pointing to O-atoms of oxide layer of O3-NMNO. The corresponding final configurations are shown in panels d-f. Yellow, red, cyan, sky blue, silver, and purple represent Na, O, H, Ti, Ni, and Mn-ions, respectively.



These are labelled as structures 1-3 in Figure 2b-d in the main text.

**Figure S4.** Nine other guess configurations of water inside the Na-vacancy based O3-NMNO system. Yellow, red, cyan, sky blue, silver, and purple represent Na, O, H, Ti, Ni, and Mn-ions, respectively. Blue dotted lines show the H-bond formation with oxide layers.

#### Discussion for various guess and resulted water inserted configurations for Na-vacancy

#### based O3-NMNO system

In first guess configuration, water molecule placed in Na-vacancy and oriented parallel to Nalayer plane with H-atoms are pointing to Na-atoms of O3-NMNO system (see figure S3a). This leads to Na-rearrangement along with water forms an H-bond with with O-atoms of upper and lower oxide layers in resulted configuration obtained after relaxation (see Figure S3d). Water molecule inserted perpendicular to Na-layer plane with H-atoms are pointing to O atoms of top and bottom oxide layers of O3-NMNO systems (see Figure S3b) in second guess configuration. Water insertion is possible via H-bonding even without the Na-arrangement in resulted configuration (as shown in Figure S3e). In third guess configuration, water molecule is inserted perpendicular to Na-layer plane with H-atoms are pointing to O-atoms of top oxide layers of O3-NMNO system (see Figure S3c). Resulted configuration shows that water molecule H-bonding of the with oxide ions of the top layer (see Figure S3f). In all water inserted configurations obtained after relaxation increase in Na-layer distances are observed as compared to Na-vacancy based O3-NMNO slab system.

O3-NMNO slab system		O3-NTNO slab system		
Structure 1	Mn	1.71	Ti	1.91
	Ni	1.21	Ni	1.32
	0	-0.97	0	-1.04
Structure 2	Mn	1.74	Ti	1.91
	Ni	1.22	Ni	1.28

**Table S2.** Oxidation states from the Bader analysis for O3-NMNO and O3-NTNO water inserted slab systems using PBE+U+D3. Effective charges are reported in terms of elementary charge units (e).

	0	-0.98	0	-1.03
Structure 3	Mn	1.74	Ti	1.91
	Ni	1.25	Ni	1.27
	0	-0.98	0	-1.03

Note: Charge on Tm-layer (cation-layer) in NMNO is given by  $2 \times Mn + 2 \times 0$  and charge on

oxide-layer in NMNO is given by  $4 \times 0$ . Similarly, for NTNO Charge on Tm-layer is given by

 $2 \times Ti + 2 \times 0$ .



**Scheme S1.** Flow chart to understand the energy penalties terms. E<sub>1</sub> corresponds to energy difference between Na-vacancy based structure and Na-rearrangement based O3-NMNO slab system and E<sub>2</sub> corresponds to energy difference between Na-vacancy based structure and expanded Na-layer based O3-NMNO slab system. Yellow, red, cyan, sky blue, silver, and purple represent Na, O, H, Ti, Ni, and Mn-ions, respectively. Blue dotted lines show the H-bond formation with oxide layers.



**Electronic Supplementary Information** 

**Figure S5.** a) O3-NM<sub>-1</sub>T<sub>+1</sub>NO system (Na<sub>7</sub>Mn<sub>5</sub>Ti<sub>1</sub>Ni<sub>6</sub>O<sub>24</sub>) with Na-vacancy (black square), b) Structure 1 shows the slab of the O3-NM<sub>-2</sub>T<sub>+2</sub>NO system with water (Na-arrangement and Hbonding of water molecule with oxide layers), c) Structure 2 shows the slab of O3-NM<sub>-1</sub>T<sub>+1</sub>NO system with water (H-bonding of the water molecule with oxide layers). Note: Magnified views shows the regions of interest with H-bond distances. d) Structure 3 shows the slab of the O3-NM<sub>-1</sub>T<sub>+1</sub>NO system with water (H-bonding of water molecule with oxide layers and formation of Ti-O bond). ΔE (eV)=  $E_{slab(Na-vacancy)+water}-E_{slab(Navacancy)}-E_{water}$  (eV). OH bond distances and Nalayer spacing are indicated with black font. Total effective charges are indicated with red font. Effective charges are reported in terms of elementary charge units (e). Yellow, red, cyan, sky blue, silver, and purple represent Na, O, H, Ti, Ni, and Mn-ions, respectively. Blue dotted lines show the H-bond formation with oxide layers.



**Figure S6.** a) O3-NM<sub>-2</sub>T<sub>+2</sub>NO slab system (Na<sub>7</sub>Mn<sub>4</sub>Ti<sub>2</sub>Ni<sub>6</sub>O<sub>24</sub>) with Na-vacancy (black square), b)d) Structure 1, 2 and 3 show the O3-NM<sub>-2</sub>T<sub>+2</sub>NO slab system with water in different orientations (Na-arrangement and H-bonding of water molecule with oxide layers). Note: Magnified views shows the regions of interest with H-bond distances. Here  $\Delta E$  (eV)=  $E_{slab(Na-vacancy)}$  +water- $E_{slab(Navacancy)}$ - $E_{water}$  (eV). OH bond distances and Na-layer spacing are indicated with black font. Total effective charges are indicated with red font. Effective charges are reported in terms of elementary charge units (e). Yellow, red, cyan, sky blue, silver, and purple represent Na, O, H, Ti, Ni, and Mn-ions, respectively. Blue dotted lines show the H-bond formation with oxide layers.



**Figure S7.** a) O3-NM<sub>-3</sub>T<sub>+3</sub>NO slab system (Na<sub>7</sub>Mn<sub>3</sub>Ti<sub>3</sub>Ni<sub>6</sub>O<sub>24</sub>) with Na-vacancy (black square), b)d) Structure 1, 2 and 3 shows the slab of O3-NM<sub>-3</sub>T<sub>+3</sub>NO system with water molecule in different orientations (Na-arrangement and H-bonding of water molecule with oxide layers). Note: Magnified views shows the regions of interest with H-bond distances. Here  $\Delta E$  (eV)=  $E_{slab(Na-vacancy)}$  +water- $E_{slab(Navacancy)}$ - $E_{water}$  (eV). OH bond distances and Na-layer spacing are indicated with black font. Total effective charges are indicated with red font. Effective charges are reported in terms of elementary charge units (e). Yellow, red, cyan, sky blue, silver, and purple represent Na, O, H, Ti, Ni, and Mn-ions, respectively. Blue doted lines show the H-bond formation with oxide layers.



**Figure S8.** O3-NM<sub>-1</sub>T<sub>+1</sub>N<sub>-1</sub>CO slab system with Na-vacancy (black square), b)-d) Structure 1, 2 and 3 show the slab of the O3-NM<sub>-1</sub>T<sub>+1</sub>N<sub>-1</sub>CO system with water molecule in different orientations. Note: Magnified views shows the regions of interest with H-bond distances. Here  $\Delta E$  (eV)=  $E_{slab(Na-vacancy)+water}-E_{slab(Navacancy)}-E_{water}$  (eV). OH bond distances and Na-layer spacing are indicated with black font. Total effective charges are indicated with red font. Effective charges are reported in terms of elementary charge units (e). Yellow, red, cyan, sky blue, silver color, blue and purple represent Na, O, H, Ti, Ni, Cu and Mn-ions, respectively. Blue dotted lines show the H-bond formation with oxide layers.



**Figure S9.** O3-NM<sub>-2</sub>T<sub>+2</sub>N<sub>-1</sub>CO slab system with Na-vacancy (black square), b)-d) Structure 1, 2 and 3 show the slab of the O3-NM<sub>-2</sub>T<sub>+2</sub>N<sub>-1</sub>CO system with water molecule in different orientations. Note: Magnified views shows the regions of interest with H-bond distances. Here  $\Delta E$  (eV)=  $E_{slab(Na-vacancy)+water}-E_{slab(Navacancy)}-E_{water}$  (eV). OH bond distances and Na-layer spacing are indicated with black font. Total effective charges are indicated with red font. Effective charges are reported in terms of elementary charge units (e). Effective charges are reported in terms of elementary charge units (e). Yellow, red, cyan, sky blue, silver color, blue and purple represent Na, O, H, Ti, Ni, Cu and Mn-ions, respectively. Blue dotted lines show the H-bond formation with oxide layers.



**Figure S10.** O3-NM<sub>-3</sub>T<sub>+3</sub>N<sub>-1</sub>CO slab system with Na-vacancy (black square), b)-d) Structure 1, 2 and 3 show the slab of the O3-NM<sub>-3</sub>T<sub>+3</sub>N<sub>-1</sub>CO system with water molecule in different orientations. Note: Magnified views shows the regions of interest with H-bond distances. Here  $\Delta E$  (eV)=  $E_{slab(Na-vacancy)+water}-E_{slab(Navacancy)}-E_{water}$  (eV). OH bond distances and Na-layer spacing are indicated with black font. Total effective charges are indicated with red font. Effective charges are reported in terms of elementary charge units (e). Yellow, red, cyan, sky blue, silver color, blue and purple represent Na, O, H, Ti, Ni, Cu and Mn-ions, respectively. Blue dotted lines show the H-bond formation with oxide layers.

**Table S3:** Oxidation states from the Bader analysis for Na<sub>7</sub>Mn<sub>5</sub>Ti<sub>1</sub>Ni<sub>5</sub>CuO<sub>24</sub> to O3-Na<sub>7</sub>Mn<sub>3</sub>Ti<sub>3</sub>Ni<sub>5</sub>CuO<sub>24</sub> systems water inserted slab systems of type 1 using PBE+U+D3 method. Effective charges are reported in terms of elementary charge units (e).

S. No.	Systems (Type 1)	Mn	Ті	Cu	Ni	0
1	$O3-Na_7Mn_5Ti_1Ni_5CuO_{24}$	1.75	1.93	1.09	1.27	-0.99
2	$O3-Na_7Mn_4Ti_2Ni_5CuO_{24}$	1.75	1.90	1.08	1.23	-0.99
3	$O3-Na_7Mn_3Ti_3Ni_5CuO_{24}$	1.75	1.91	1.10	1.32	-0.99

## References

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- [2] Y.-J. Shin, M.-Y. Yi, Solid State Ion. **2000**, 132, 131–141.