Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

First principles calculations on oxygen vacant hydrated α-MnO_2 for activating water oxidation and self-healing mechanism

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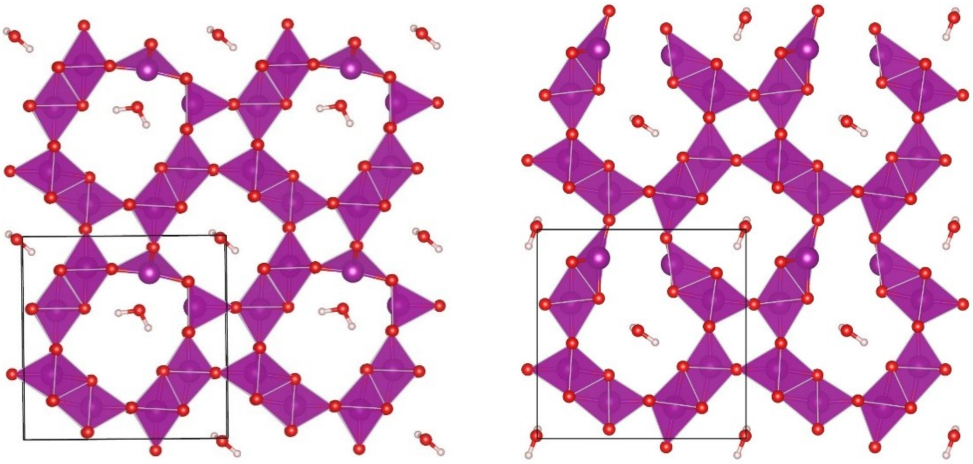

Figure S1: The polyhedral model of optimized structures (z-axis view) of α-MnO_2 compound with oxygen vacancy at pyramidal (left side) and planar sites (right side). Red, magenta, and pale white coloured balls represent O, Mn, and H atoms, respectively. Boundary of unit cell is also marked by black line.

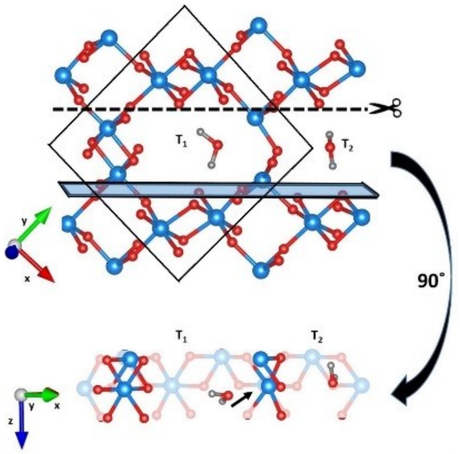

Figure S2: Optimized crystal structure of 1SC (top panel) and cross sectional view (bottom panel), in which water molecule occupied at oxygen vacant site. Red, blue, and pale white coloured ball corresponds to O, Mn, and H atoms, respectively. Boundary of unit cell is also marked by black line.

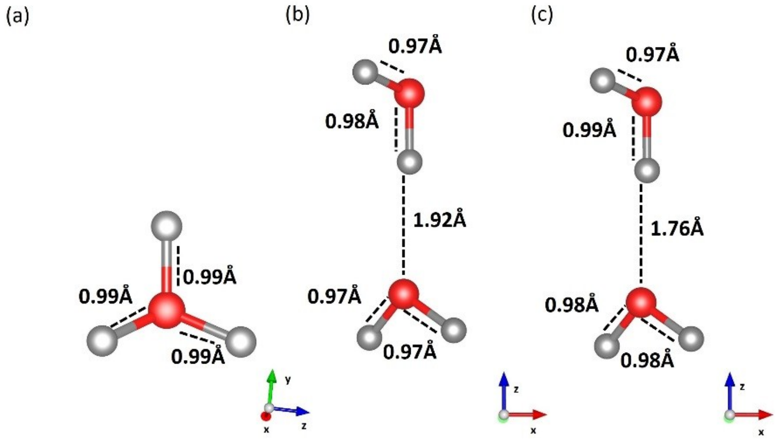

Figure S3: Optimized geometry of various protonic moieties are given along with bond distances, (a) hydronium ion, (b) water dimer in isolated case, and (c) water dimer presented in T_2 of α-$MnO_{2-\delta}$. Red and light grey balls represent O and H atoms, respectively.

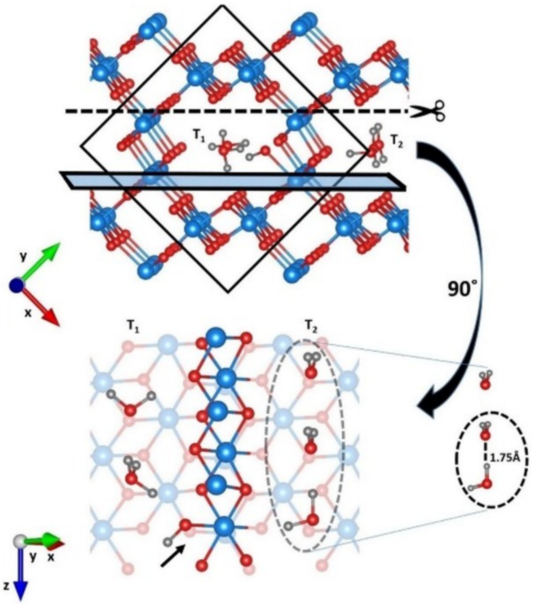

Figure S4: Optimized crystal structure of 3SC (top panel) and its cross sectional view (bottom panel), in which, hydroxide ion (indicated by arrow), Zundel cation at T_1 and water dimer at T_2 are shown. Red, blue, and pale white coloured ball corresponds to O, Mn, and H atoms, respectively. Boundary of unit cell is also marked by black line.

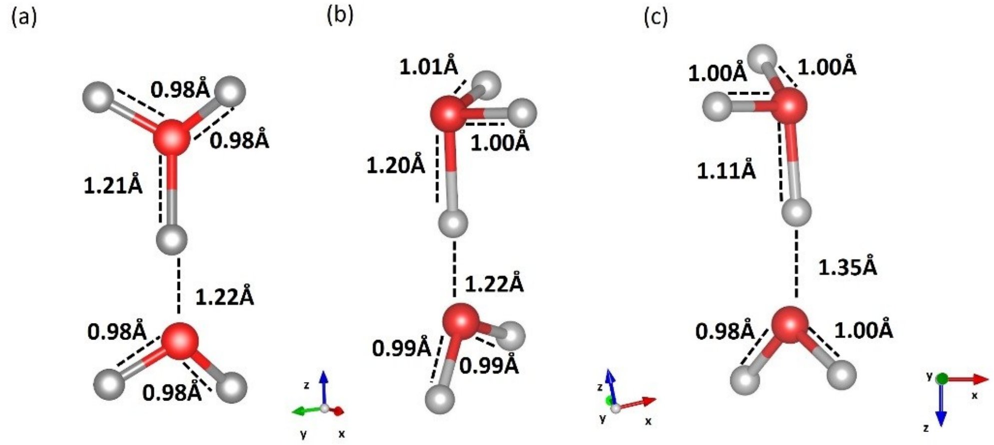

Figure S5: Optimized geometry of (a) Zundel cation presented in isolated case, (b) inside of T_1 in 3SC, and (c) 4SC, are shown along with various bond distances. Red and light grey balls represent O and H atoms, respectively.

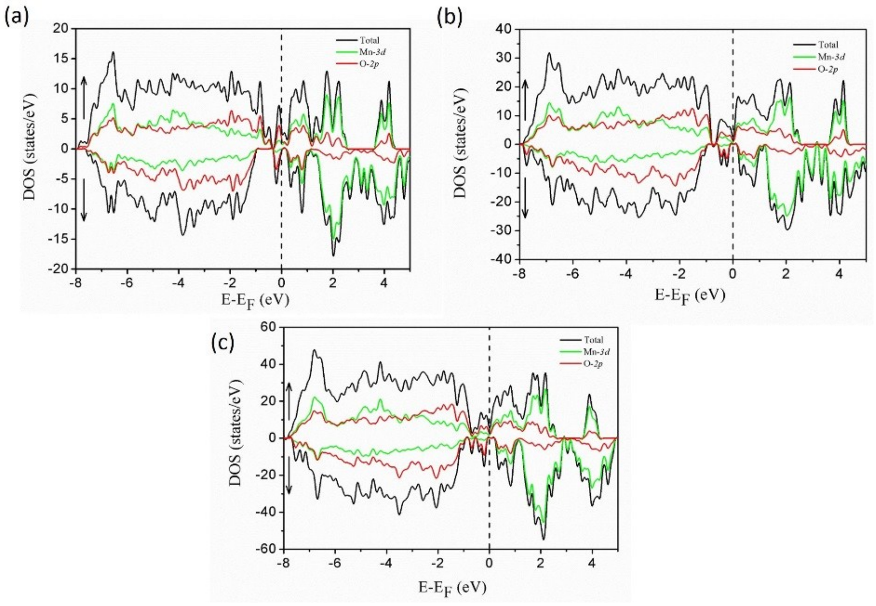

Figure.S6. Total and partial DOS of ferromagnetically aligned (a) 1SC, (b) 2SC, and (c) 3SC system. In 1SC, the states near the Fermi level (E_F) are quite sharper, as compared to other two systems, because the proton moieties are presented in latter two cases.

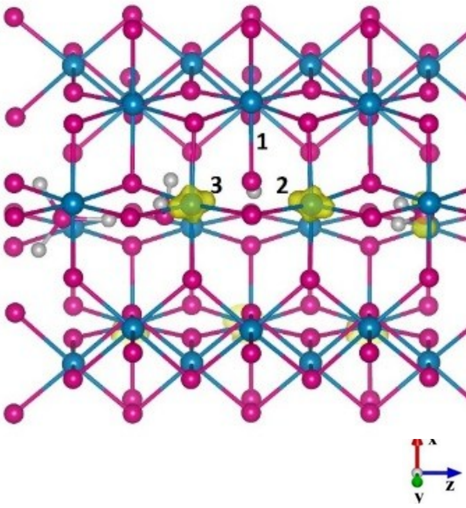

Figure S7: Partial charge density distribution of the states that lie in the energy range of -0.7 to 0.0 eV are shown for 4SC with water molecules in the tunnel. Three Mn atoms, nearer to vacancy are marked as 1, 2, and 3.

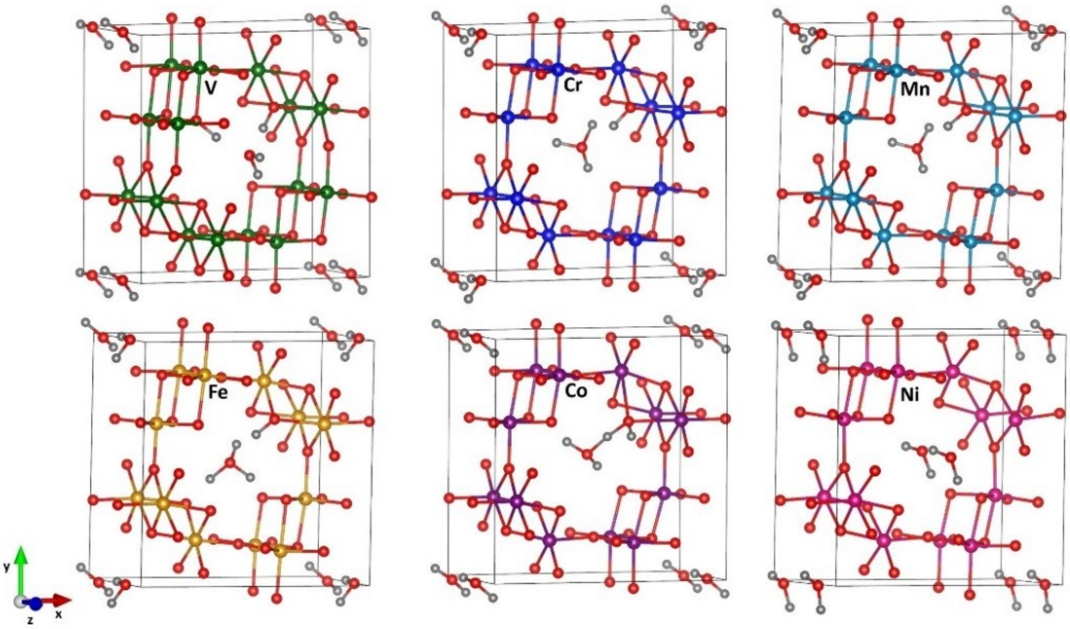

Figure S8: The reactivity towards water molecule for hypothetical compounds formed by the replacement of transition metal atoms (M= V, Cr, Fe, Co, Ni) instead of Mn atoms in α-$MnO_{2-\delta}$ 0.25 H_2O.

Our calculations show that the VO_2 is observed to behave as an amphoteric oxide, which act as an acid by adsorbing hydroxide ion near the oxygen vacancy as well as base by protonation of lattice oxygen. The compounds, such as CrO_2 and FeO_2, adsorb the hydroxide ion with its moderate bond strength and the hydronium ion is formed in T_1, as similar to hydrated MnO_2 compound. On the other hand, the CoO_2 compound just attracts the water molecule, but it cannot able to dissociate it. While NiO_2 cannot afford the lattice energy nor to dissociate or absorb the water molecule. Water dimer is also observed in the adjacent tunnel T_2 of all compounds except Ni case.

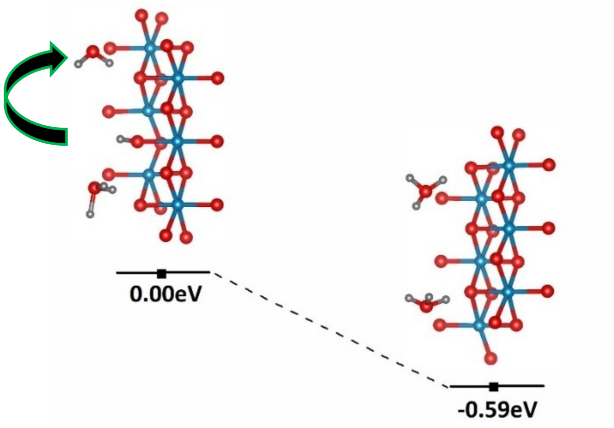

Figure S9: Self-healing nature is demonstrated in 3SC. In which, self-healed system is more stable by 0.59 eV, with respect to another. These two hydronium ions can be exchanged with Li$^+$ ions. The arrow indicates the destination of proton in the next conformation.

Table S1: The bond lengths of hydrogen bonded network inside the tunnel structure responsible for proton diffusion.

Parameters	Step 1 (Å)	Parameters	Step 2 (Å)	Parameters	Step 3 (Å)	Parameters	Step 4 (Å)
O-H in hydroxide	0.98	O-H in hydronium1	1.00, 1.00, 1.09	O-H in water	0.98, 0.99	O-H in hydronium1	1.00, 1.01, 1.11
O-H in water1	1.00, 0.98	O-H in water	0.98, 0.98	O-H in hydronium1	1.00, 1.13, 0.98	O-H in hydronium2	0.99, 0.98, 1.14
O-H in hydronium	1.00, 1.11, 1.00	O-H in hydronium2	1.15, 0.99, 0.99	O-H in hydronium2	1.04, 1.05, 0.99	O-H in water	0.98, 0.98
O(hydroxide)-O(water1)	2.49	O(hydronium1)-O(water)	3.75	O(water)-H(hydronium2)	1.32	O(hydronium1)-O(hydronium2)	3.61
O(water1)-H(hydronium)	1.35	O(water)-H(hydronium)	1.31	O(hydronium1)-O(hydronium2)	3.98	H(hydronium2) -O(water)	1.32
O(hydronium) -O(water2)	2.69	-	-	-	-	-	-
O-H in water2	0.98, 0.98	-	-	-	-	-	-

a) nSC (without H_2O) + 2n H_2O $\rightarrow$ nSC (with H_2O)

where $n = 1, 2, 3,$ and 4.

ΔE (product – reactant) = -1.15 eV ($n = 1$), -2.13 eV ($n = 2$), -2.18 eV ($n = 3$), -2.25 eV ($n = 4$)

b) $2H_2O \rightarrow H_3O^+ + OH^-$ (isolated case)

ΔE (product – reactant) = 7.47eV

c) $H_2O + H_2O \rightarrow H_4O_2$ (isolated case)

ΔE (product – reactant) = -0.23 eV

d) 2SC(without H_2O in T_1) + OH $\rightarrow$ 2SC(with OH)

ΔE (product – reactant) = -3.71 eV

e) 2SC(without H_2O in T_1) + H_3O $\rightarrow$ 2SC(with H_3O)

ΔE (product – reactant) = -4.90 eV

Scheme: The chemical reactions with corresponding reaction energies are shown. (a) Energy gain due to adsorption of water molecules (b) dissociation of water molecules in isolated case (c) water dimer formation in isolated case (d) adsorption of hydroxide in the MnO_2 network (e) intercalation of hydronium in the MnO_2 network.

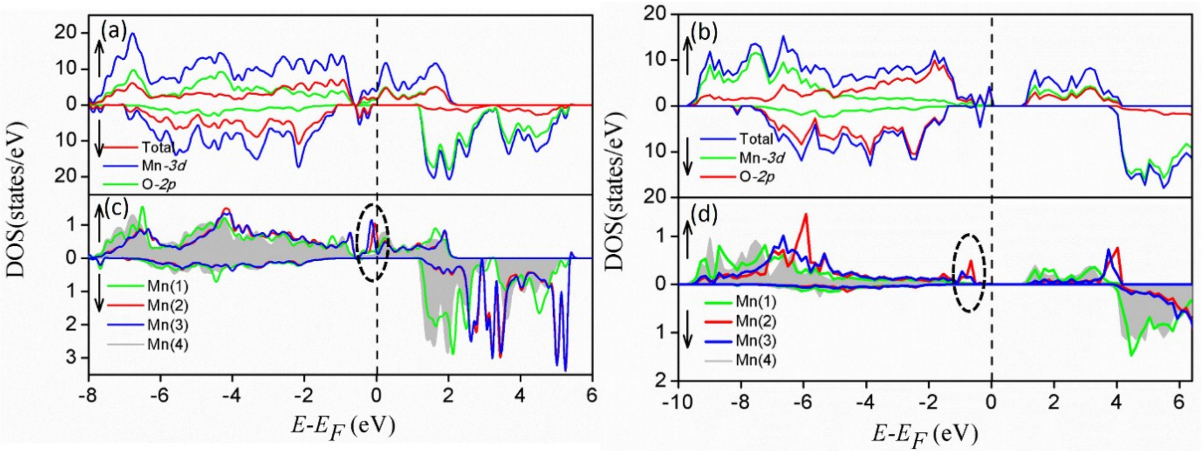

Figure S10 : Total and Partial DOS of FM aligned 2SC of hydrated oxygen vacant α-MnO_2 (a) GGA+U (b) HSE06+U functionals, Site decomposed DOS of 3d states of three Mn atoms (green, red, blue) nearby oxygen vacant site are shown along with bulk Mn atom (grey shade) (c) GGA+U (d) HSE06+U functionals. Up and down arrows refer atoms with up and down spins respectively.

From the above figure, the features of the DOS calculated using both GGA+U and HSE06+U functionals are found to be almost similar except the energy position of valence and conduction band. As generally expected, the HSE06 hybrid functional significantly overestimated the band gap and it is 0.95 eV. In the site decomposed DOS calculated using both functionals, the dotted circle below Fermi level indicates the occupied e_g states of two among three Mn atoms nearby the oxygen vacant site. The above result again confirms the presence of mixed charge state of Mn atoms in the compound.