Supporting Information

Modelling Oxygen Vacancy Defect Migration in Titanate (001) Surfaces: Effects of the Hubbard Correction and A-site Cation

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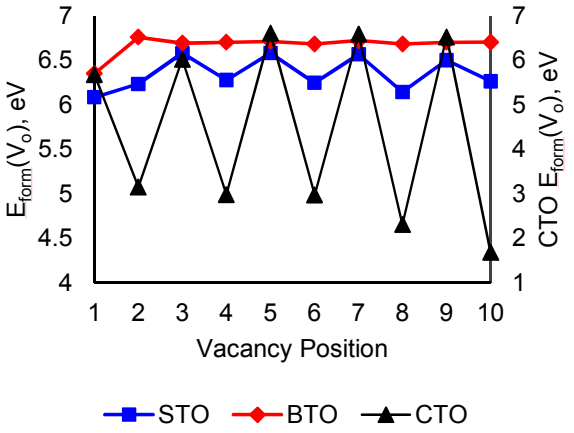

Figure S1. PBEsol+U Oxygen vacancy formation energies for AO-surface terminated $ATiO_3$ ($A = Sr^{2+}$, Ba^{2+} & Ca^{2+}) slabs.

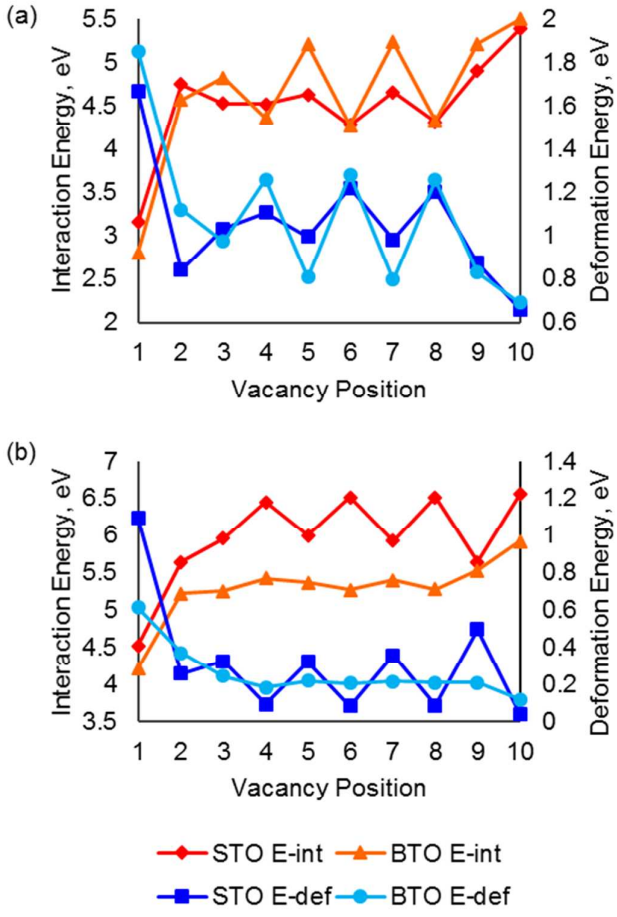

Figure S2. EDA deformation and interaction energy results for 2x2x6 slabs for STO and BTO with (a) PBEsol and (b) PBEsol+U

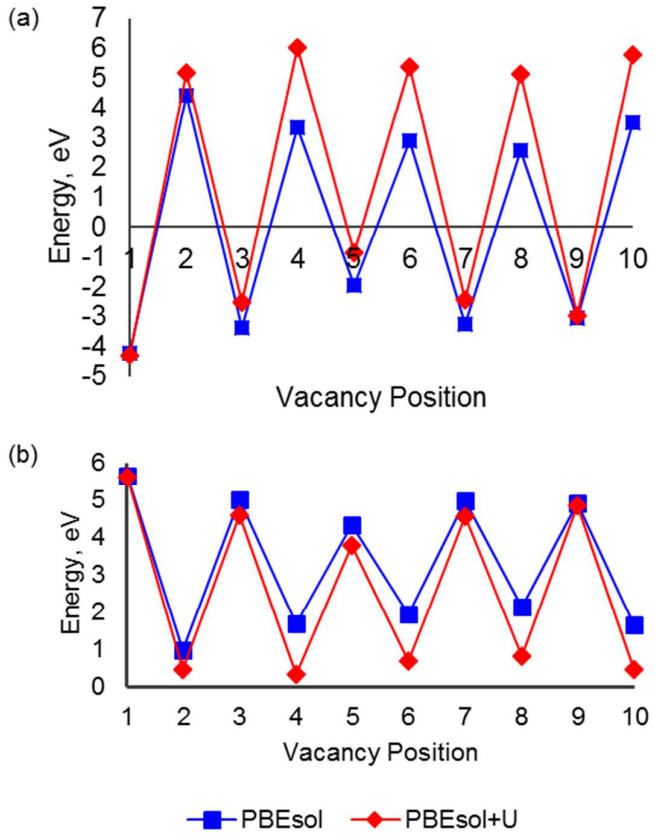

Figure S3. EDA results for 2x2x6 slab of CTO are sorted by (a) Deformation Energy and (b) Interaction Energy

Energy Decomposition Analysis

Geometrical energy decomposition analysis (EDA) was undertaken to decouple the contributions of the structural deformation and interaction contributions to the saw-tooth E_{form} profiles esatblished in the preceding section. The EDA scheme employed here is illustrated in Figure 5. In this scheme, A is a defective slab and B is the removed O atom, thereby making the E(A+B) complex the pristine slab. The difference between the energy of a relaxed defect slab and the energy of a pristine slab with a single oxygen atom taken out gives the E_{def} contribution. Then, accordingly the difference between the E_{form} and E_{def}

energies at position $V_{o,I}$, where i is the vacancy position provied the interaction energy contribution, E_{int}.

Figure 5.(a-d) shows E_{def} and E_{int} for STO, BTO calculated with PBEsol and PBEsol+U. It is evident from this figure that, for STO and BTO, the major contribution giving rise to the saw-tooth energy profile comes from E_{int}, with a less distinct but still observable opposing contribution from structural deformation to the saw-tooth pattern can be seen in E_{def}. This means that, while the +U implementation lowers E_{int} of V_o in the TiO_2-layers relative to those for the V_o AO-layers, the reverse is the case for E_{def}. A distinct rise in deformation energy can be seen at the immediate surface layer (Vo-1). However, the proportion of E_{int} to E_{def} at position V_o-2 appears to be more consistent with the rest of the slab bulk rather than position Vo-1.

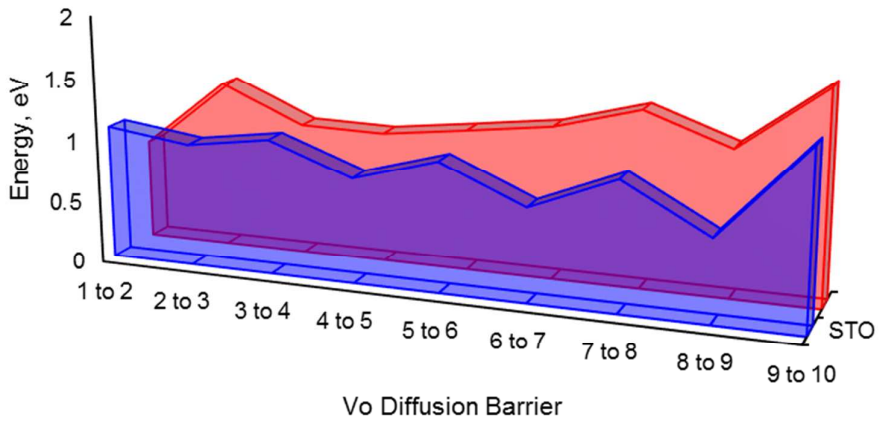

Figure S4. Summarized surface to subsurface Vo diffusion barrier heights for STO and BTO with PBEsol+U (2x2x6 cell)