Supporting Information

Formation of Small Electron Polaron in Tantalum Oxynitride: Origin of Low Mobility

Manoj Dey[†], Akash Singh[†], and Abhishek K. Singh[*†]

[†]Materials Research Centre, Indian Institute of Science, Bangalore-560012, India

[*]abhishek@iisc.ac.in

Table S1: Geometrical and Electronic Structures

	a (Å)	b (Å)	c (Å)	Band Gap (eV)
U = 4.5 eV	5.062	5.097	5.239	2.55
Expt.[1]	4.97	5.04	5.18	2.4[2], 2.5[3]

Delocalized and Localized electron

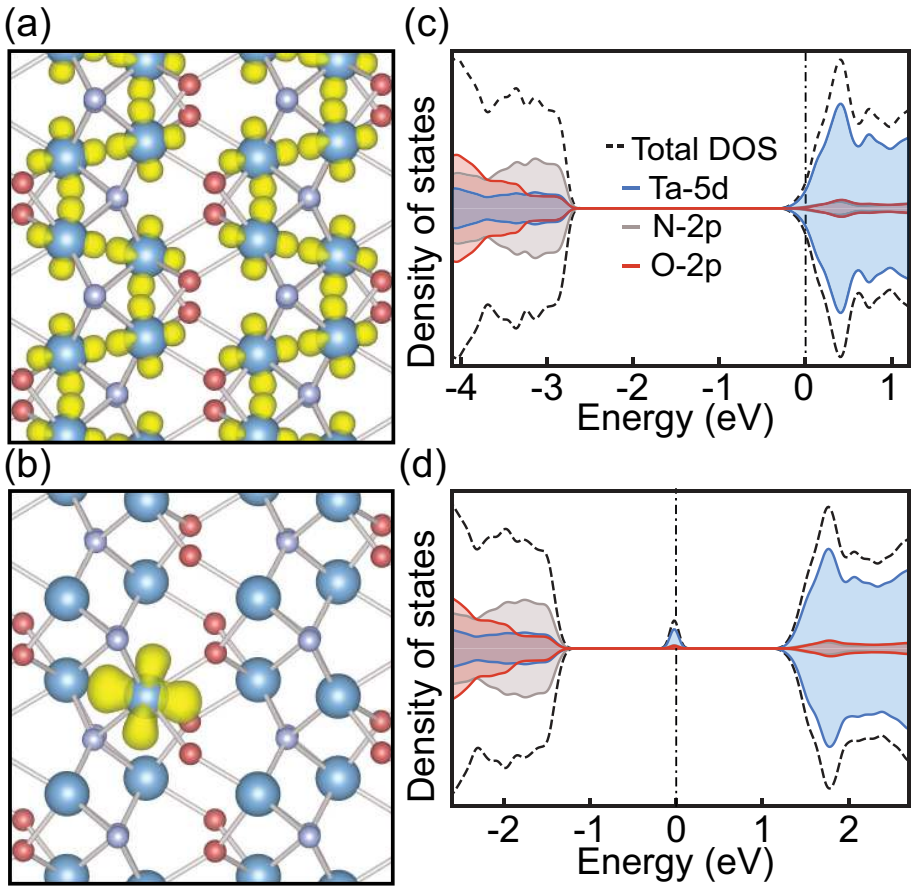

Figure S1: (a) Spin density plot of delocalized state. The isosurface value set to 10% of maximum. The extra electron is distributed over all the lattice, and (b) localized electron polaron at a specific Ta site accompanied by local lattice distortion. Density of states for (c) delocalized state confirms that the added electron remains in CBM (Fermi level moves to the CBM), whereas it forms (d) localized polaronic state in the middle of the bandgap. The localized state is mainly composed of Ta-5d orbital.

Bonding Behavior of Electron Polaron

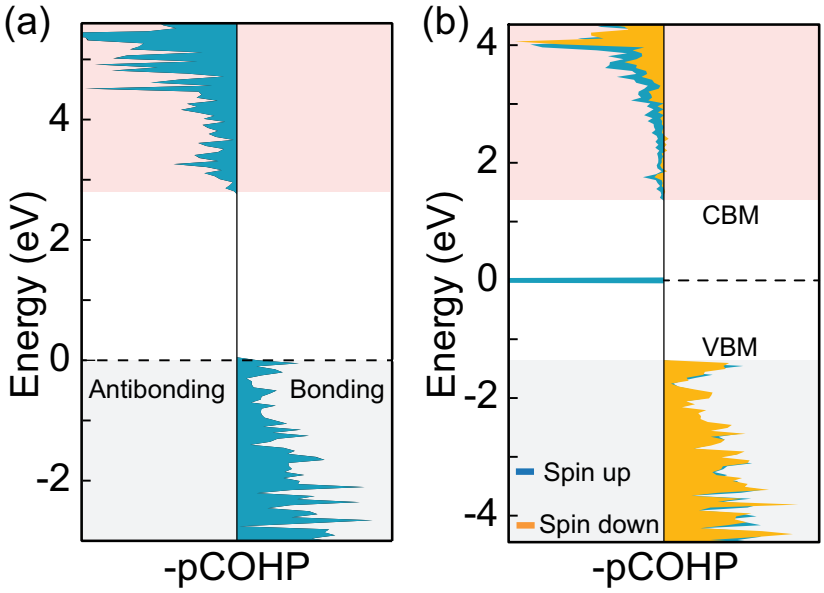

Figure S2: Crystal orbital Hamilton population for (a) pristine, and (b) polaron formation in TaO_3N_4 polyhedra. Low energy localized antibonding state confirms the stabilization of electron polaron.

In order to investigate the bonding behavior around polaron localization, we calculated the partial crystal-orbital Hamilton population (pCOHP) for both pristine and polaronic structure. The negative value of -pCOHP suggests the antibonding, and positive indicates bonding nature. The Figure S2 (a) shows that the CBM is composed of antibonding state comprising Ta-5d orbital whereas, VBM is bonding in nature. The lowest energy antibonding state in CBM, captures an electron and move down in spin-majority channel to form a localized state within the bandgap (shown in Figure S2 (b)). The localization is accompanied by breathing local lattice distortion around the polaronic site (Ta^{+4}). The Ta-O and Ta-N bond lengths are increased to accommodate the electron polaron. The low energy antibonding state below the CBM also confirms the stabilization of polaron from the delocalized state.

Bond Length Distortion

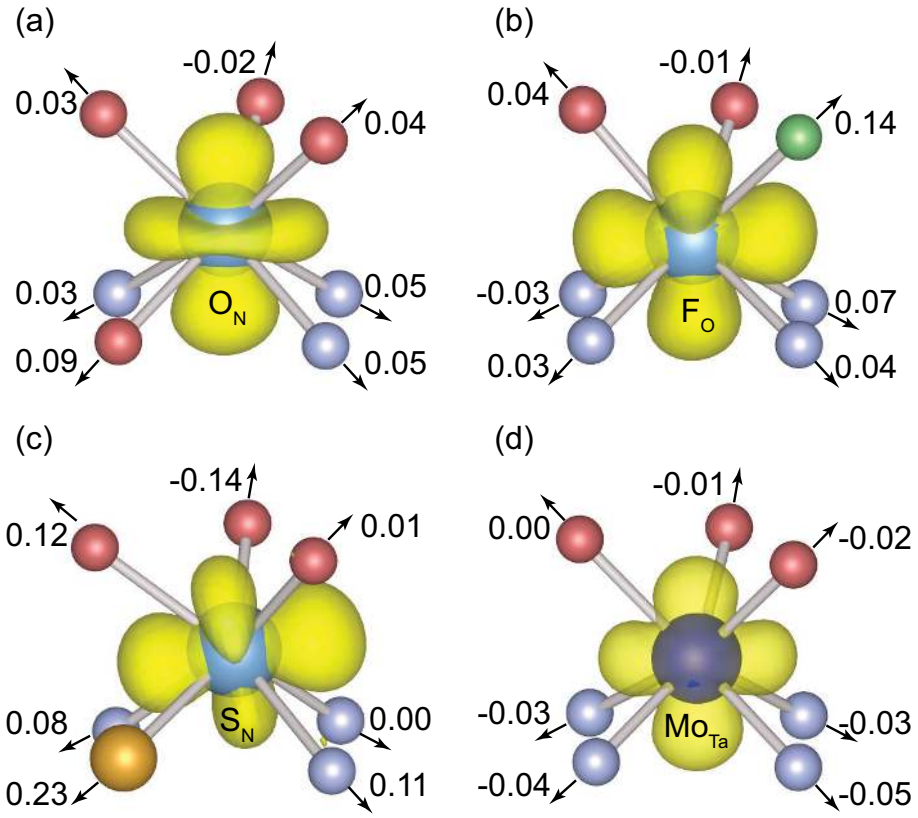

Figure S3: Bond length distortion for localized electronic charge bound to (a) O_N, (b) F_O, (c) S_N, (d) Mo_{Ta} defects, respectively. Bond-length distortions are in angstrom (Å). The positive and negative values signify the breathing and contraction distortions, respectively. The isosurface value set to 10% of maximum.

Interaction of polaron with several defects

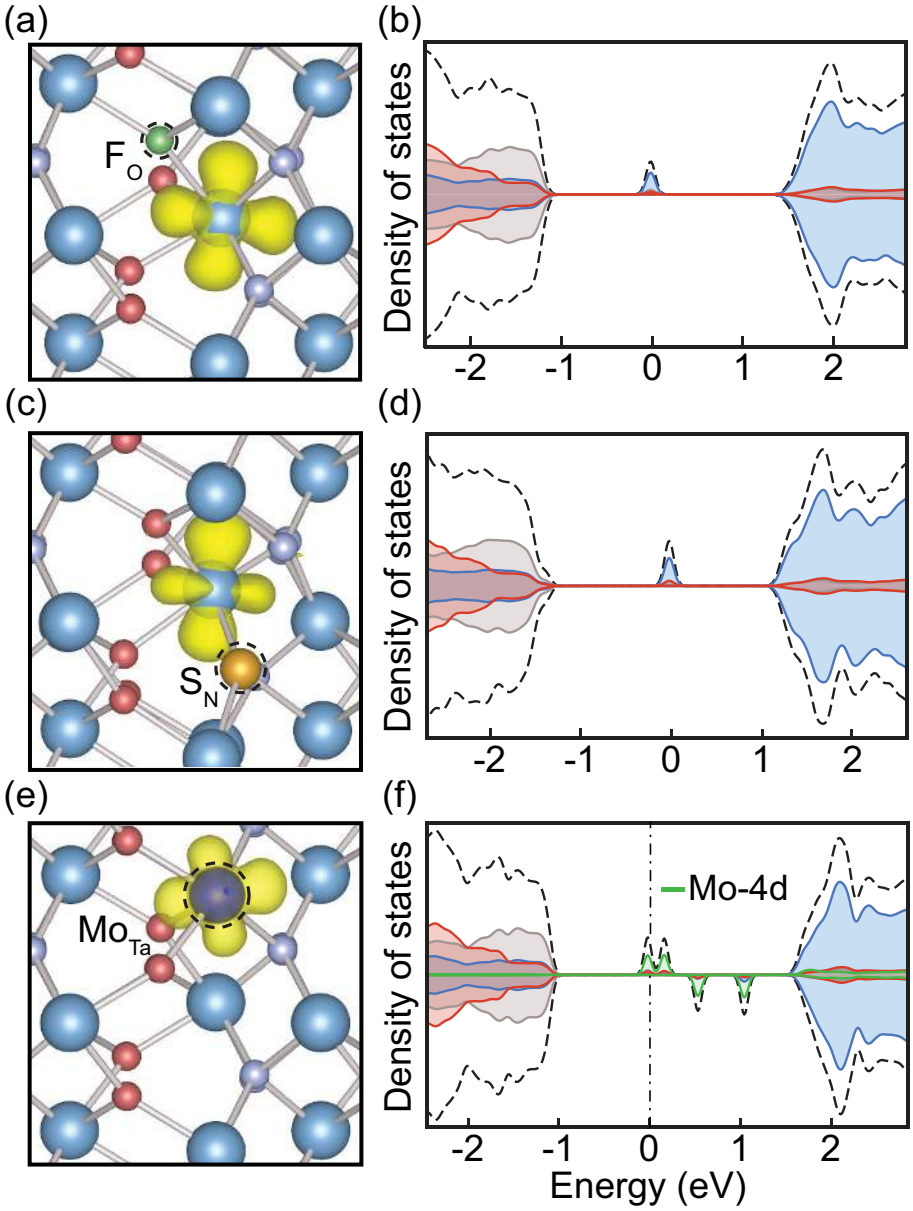

Figure S4: Spin density and density of states of localized electron polaron in presence of (a), (b) F_O; (c), (d) S_N and (e), (f) Mo_{Ta} defects, respectively. Isosurface value set to 10% of maximum.

Hopping Distance and Diffusion Barrier in Different Paths

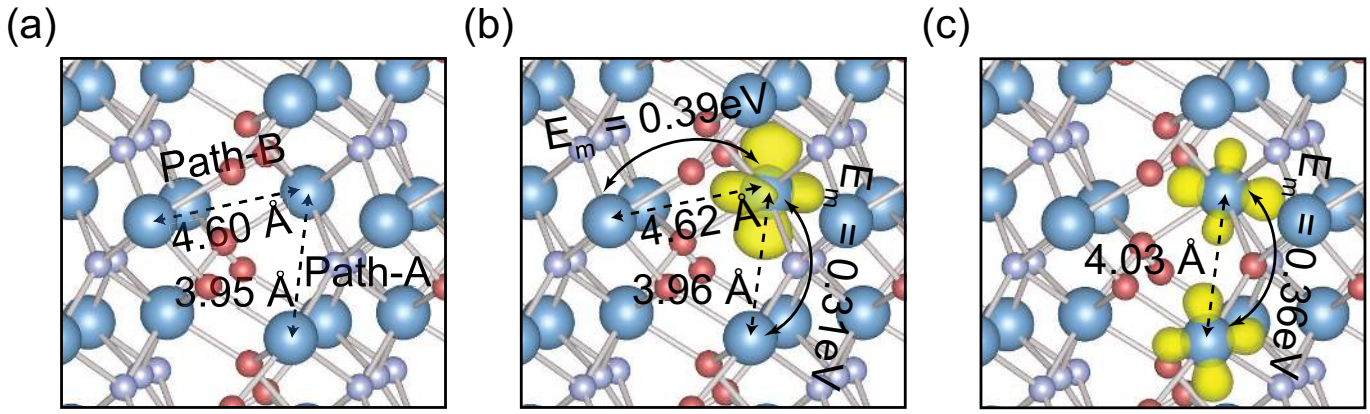

Figure S5: (a) Two different polaron hopping paths A and B. The Ta-Ta distances are shown for pristine structure. (b) The Ta-Ta hopping distance and migration barriers for polaron hopping in pristine β-TaON. (c) The increased hopping distance and hopping barrier because of O_N defects.

Electronic Coupling Parameter

In order to explain the adiabaticity of polaron hopping, we computed the electronic coupling parameter (V_{AB}) using the Mulliken-Hush formalism within Marcus theory as described by Adelstein et al.[4] The electronic coupling parameter is defined as;

$$V_{AB} = \frac{1}{2}\Delta E_{12} \tag{S1}$$

The ΔE_{12} can be estimated from the energy difference of two gap states within the band gap, which are above (highest occupied bonding state) and below (lowest unoccupied antibonding state) the Fermi level in the density of states of the TS. The density of states of the TS for polaron hopping in pristine and with O_N defect is shown in Figure S6. There is only one sharp peak in the DOS for polaron hopping in pristine (Figure S6 (a)). In other word, the bonding and antibonding states are superimposed, which indicates very low electronic coupling between the initial and final states. However, polaron hopping in the presence of O_N defect corresponds to two gap states separated by 0.152 eV for the TS (Figure S6 (b)). The estimated coupling constant is 0.076 eV, which is significant in the presence of O_N defect. Hence, the polaron hopping process in the presence of O_N defect is adiabatic in nature.

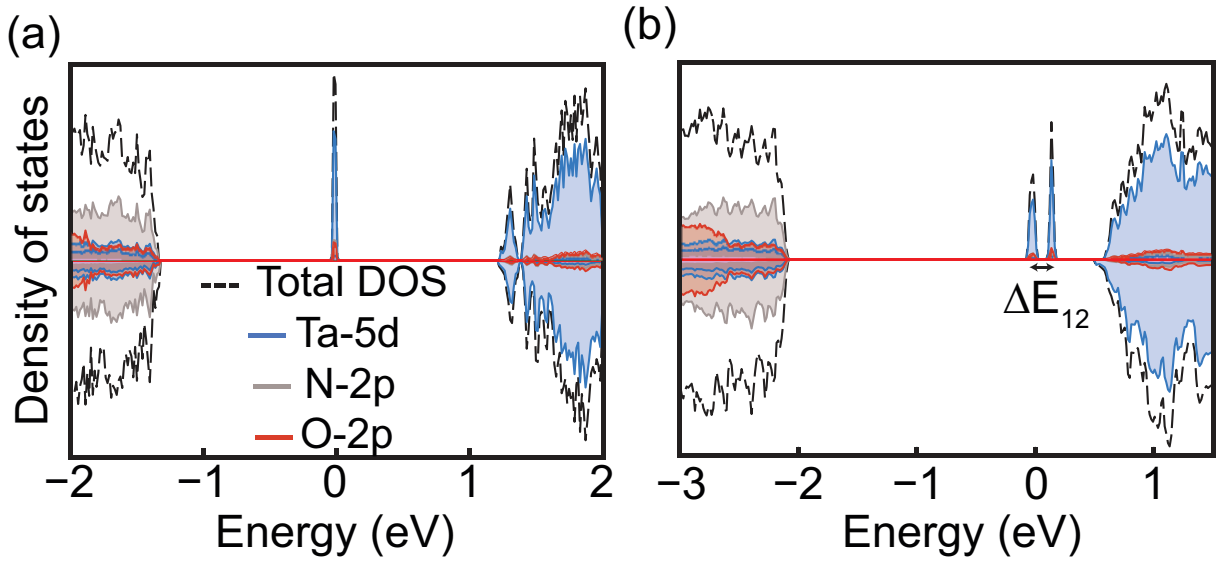

Figure S6: The partial density of states of the transition state (TS) corresponding to small polaron hopping in (a) pristine β-TaON along path A, (b) with O_N defect along the same path.

Polaron Formation in Different U value

The conventional density functional theory with local or semi-local exchange-correlation functional fails to describe localization accurately, owing to well-known self-interaction error. Instead, DFT with an on-site Hubbard U correction on specific orbital, is an efficient approach to deal with materials containing highly correlated electrons[5]. However, charge localization due to lattice distortion, is strongly influenced by the specific choice of on-site U parameter. We computed the polaron formation energy (E_{POL}) by varying U in the range from 4.2 eV to 4.8 eV. The negative polaron formation energies are indicating that the small polaron is more stable than the delocalized state. Moreover, we found stronger charge localization and more negative E_{POL} when the value of U is increased.

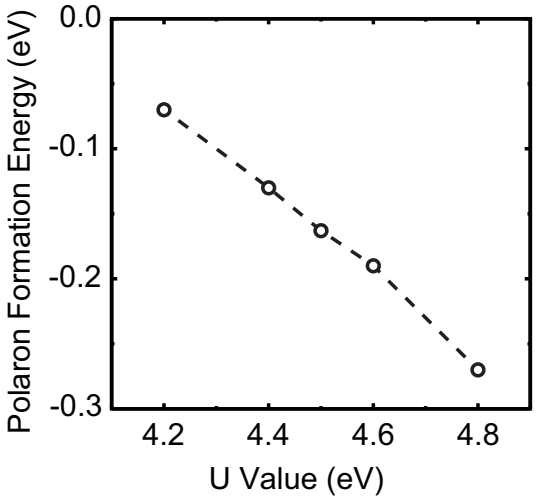

Figure S7: Variation of polaron formation energy (E_{POL}) as a function of on-site U parameter.

Convergence of Total Energies

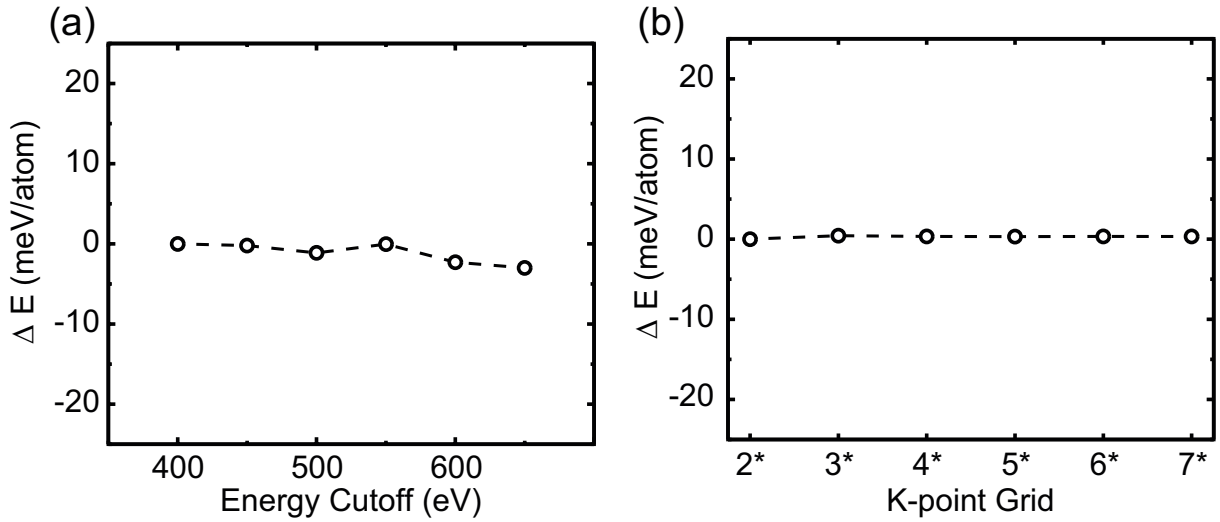

Figure S8: Convergence of total energy difference (ΔE) with respect to the variation of (a) energy cut-off and (b) k-point sampling. Here, 2* denotes the 2x2x2 k-points sampling.

References

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