

## SUPPORTING INFORMATION

### Quantum-Mechanics-Based Design Principles for Solid Oxide Fuel Cell Cathode Materials

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#### Computational details

Periodic boundary conditions were employed to model bulk materials. All DFT calculations were carried out spin-polarized with the Vienna Ab initio Simulation Package (VASP) [S1]. Nuclei and (frozen) core electrons were treated with the Projector-Augmented Wave (PAW) method [S2]. The PAW potentials from the VASP repository were used. Plane wave basis sets were used to represent the following electrons for La ( $5s^2, 5p^6, 6s^2, 5d^1$ ), O ( $2s^2, 2p^4$ ), Cr ( $4s^1, 3d^5$ ), Mn ( $4s^2, 3d^5$ ), Fe ( $4s^2, 3d^6$ ), and Co ( $4s^2, 3d^7$ ). Total electronic energies were converged using a plane wave basis kinetic energy cutoff of 800 eV and a  $4 \times 4 \times 4$  Monkhorst-Pack mesh [S3] for  $\mathbf{k}$ -point sampling. These numerical parameters ensured an accuracy in the total energy of  $\sim 5$  meV/formula unit. We used the GGA exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE) [S4]. For DFT+U calculations, we used the *ab-initio*-derived values of 3.2, 4.3 and 4.0 eV for  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$  [S5] and  $\text{Co}^{3+}$  [S6], respectively. In the case of  $\text{Mn}^{3+}(d^5)$  the U-J value should be in between the values of  $\text{Cr}^{3+}(d^3)$  and  $\text{Fe}^{3+}(d^5)$ ; thus we used the effective value of 4.0 eV, that was already tested to provide the best results on modeling the  $\text{LaMnO}_3$  ground state properties [S7]. Using the PBE+U optimized structures, single point total energy calculations were carried out at the HSE06 level of theory, as implemented in the VASP code [J. Paier, M. Marsman, K. Hummer, G. Kresse, I. C. Gerber, and J. G. Angyàn, J. Chem. Phys. 125, 249901 (2006).].

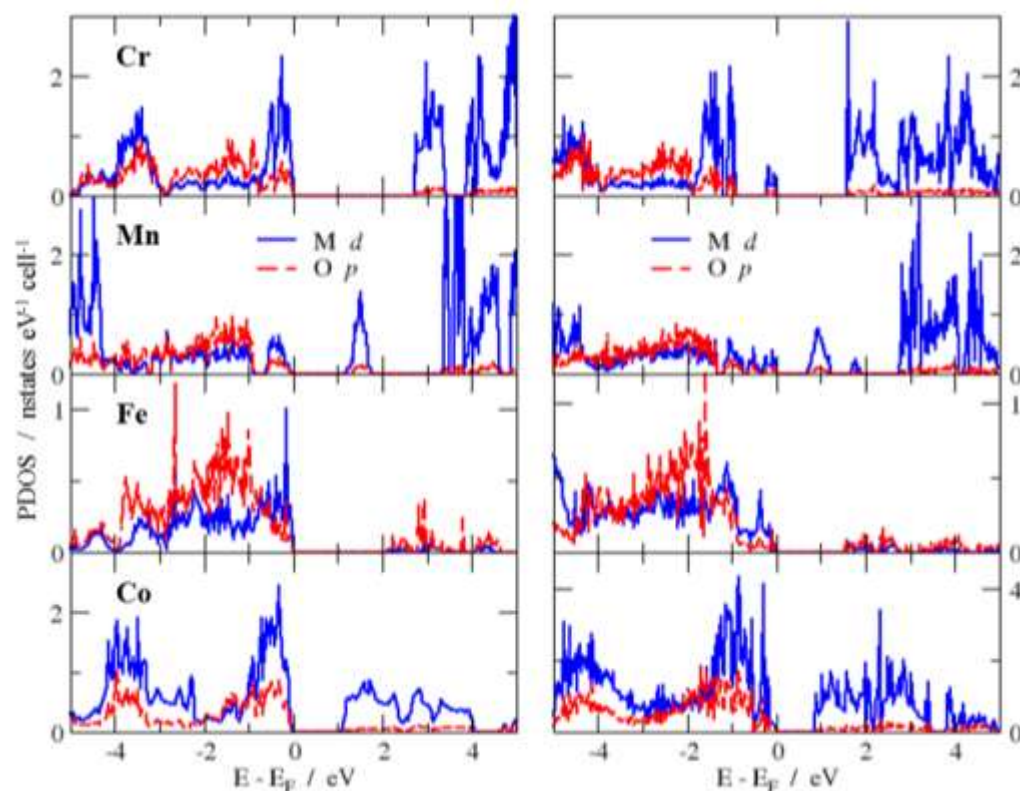
Bader charge analysis was performed on electron densities output from VASP [S8]. The electron density difference isosurface (*Fig. 2* in the main text) was computed from the density of the vacancy defect system plus the spherically symmetrized density of an isolated gaseous triplet oxygen atom placed at the vacancy position, minus the density of the defect-free system.

After some testing, we found that the oxygen vacancy formation energies computed with the 40 atom  $2 \times 2 \times 2$  model cell reported in the main text are converged to within  $\sim 0.3$  eV with respect to cell size. Interaction of the vacancy with its periodic image increases the formation energy. Thus, the reported data can be read as upper bounds to the energy of formation of an isolated oxygen vacancy. Despite potential changes of up to 0.3 eV with concentration, the computed trend in vacancy formation energies – of main concern here – is unaffected by cell size (i.e., is not sensitive to concentration changes).

#### Additional results

*Figure S1* shows the atom- and angular momentum-projected densities of states (PDOS) of the transition metals  $d$ - and oxygen  $p$ -states in all the  $\text{LaMO}_3$  systems before and after formation of the oxygen vacancy. The defect-free materials (left panel) display eigenvalue gaps that are consistent with the corresponding known experimental band gaps. The presence of the vacancy (right panel) induces extra states in the gap, arising from the two electrons given back to the lattice. In all the cases, these new

states at the Fermi level mostly display transition metal *d* band character, thus supporting the analysis of the magnetic moments at the transition metal centers.



**Figure S1.** Atom- and angular momentum-projected density of states (PDOS) before (left) and after (right) oxygen vacancy formation.

### References

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