Supplementary Material for *Ab initio* study of vacancy formation in cubic $LaMnO_3$ and $SmCoO_3$ as cathode materials in Solid Oxide Fuel Cells

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The Electronic Supporting Information contains a graph showing the band gap dependence on U_{eff}-parameter (Figure S1), a comparison of Co PBE functionals and U_{eff} in relation to lattice parameter and band gap (Table SI), calculated and experimental metal oxide formation energies and enthalpies (Table SII), and cation vacancy formation energies (Table SIII).

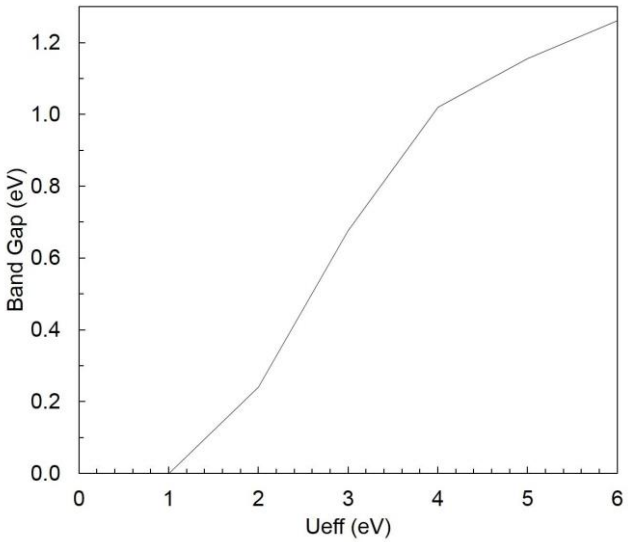

Figure S1. Band gap of $SmCoO_3$ as a function of U_{eff}.

Table SI. Comparison of functionals and U_{eff} values for $SmCoO_3$. Co pseudopotentials have their semi core states frozen, whereas Co_pv pseudopotentials have *p*-electrons treated as valence electrons.[1] Experimental lattice parameter is 3.751 Å.

		U_{eff}	Lattice parameter (Å)	Band gap (eV)
Co	PBE	N/A	3.757	0
	PBE+U	2	3.754	0.240
		3	3.754	0.675
		4	3.752	1.020
		5	3.751	1.155
		6	3.750	1.261
Co_pv	PBE	N/A	3.759	0
	PBE+U	2	3.757	0.270
		3	3.756	0.690
		4	3.757	1.035
		5	3.755	1.185
		6	3.756	1.291

Table SII. Calculated and experimental formation energies for the oxides

Oxide	**Calculated E (eV)**	**Experimental ΔH^f (eV)**	**Polymorph**
$LaMnO_3$	-14.90	-14.77	Pm-3m
$SmCoO_3$	-13.07	-12.95	Pm-3m
La_2O_3	-18.41	-18.54	P-3m1
MnO	-3.85	-3.99	Fm-3m
Mn_3O_4	-14.14	-14.38	I41/amd
Mn_2O_3	-9.76	-9.94	Ia-3
MnO_2	-5.27	-5.39	P42/mnm
Sm_2O_3	-18.68	-18.86	I213
CoO_2	-1.35	-1.47	C2/m
CoO	-2.40	-2.46	F43-m
Co_3O_4	-9.00	-9.23	Fd-3m
La	-4.89	-	P63/mmc
Mn	-4.76	-	I43-m
Sm	-4.66	-	P63/mmc
Co	-4.75	-	Fm-3m

Table SIII. Vacancy formation energies at the valence band maximum (VBM) and conduction band minimum (CBM) respectively, E_f^{VBM} and E_f^{CBM}, (eV), for the cation vacancies at different charge states (q) of the defective bulk 2x2x2 supercell in the oxygen-poor regime. For the La and Mn vacancies, VBM, $\Delta E_F = 0$ eV and CBM, $\Delta E_F = 1.7$ eV, whereas for Sm and Co vacancies, VBM, $\Delta E_F = 0$ eV and CBM, $\Delta E_F = 0.68$ eV.

A-site				**B-site**			
Vacancy	q	$\boldsymbol{E_f^{VBM}}$ (eV)	$\boldsymbol{E_f^{CBM}}$ (eV)	Vacancy	q	$\boldsymbol{E_f^{VBM}}$ (eV)	$\boldsymbol{E_f^{CBM}}$ (eV)
La	3+	10.18	14.08	Mn	3+	7.30	7.49
	2+	8.80	11.40		2+	6.30	8.90
	1+	7.73	9.03		1+	5.76	7.06
	0	6.95	6.95		0	5.74	5.74
	1-	6.30	4.99		1-	5.78	4.48
	2-	6.01	3.41		2-	6.13	3.53
	3-	6.22	2.32		3-	11.20	3.59
Sm	3+	10.17	12.20	Co	3+	4.86	6.88
	2+	10.0	11.35		2+	4.65	6.00
	1+	8.35	9.02		1+	4.79	5.46
	0	7.98	7.98		0	5.17	5.17
	1-	6.89	6.21		1-	3.56	2.89
	2-	6.39	5.04		2-	3.48	2.13
	3-	4.97	2.95		3-	1.93	-0.09

References

[1] G. Kresse, J. Furthmüller, and M. Marsman, Comput. Physics, Faculaty Physics, Vienna Univ. Technol. Austria (2012).