Unravelling Catalytic Trends of Ceria Surfaces for the Oxygen Reduction and Water Oxidation Reactions

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Table S1: Adsorption free energies (eV) of oxygen reduction reaction intermediates on CeO_2 surfaces for $U = 0$.

Surface-site	$\Delta G(*OOH)$	$\Delta G(*O)$	$\Delta G(*OH)$
(100)	4.40	3.31	0.96
(111)	5.48	2.85	2.77
(110)	5.05	4.54	1.94
(221)-Ce1	5.09	2.77	2.20
(221)-Ce2	5.57	2.91	2.75
(221)-Ce3	5.46	3.05	2.94
(331)-Ce1	5.22	2.77	0.12
(331)-Ce2	5.60	0.86	0.78

Table S2: Calculated free energies (eV) for the associative mechanism reaction steps for $U = 0$.

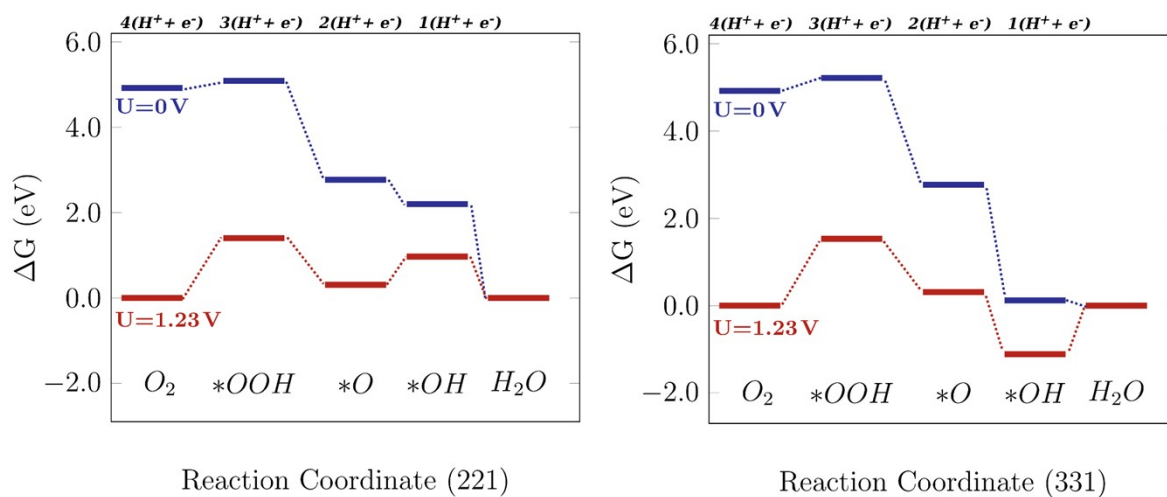| Surface-site	ΔG_1	ΔG_2	ΔG_3	ΔG_4
(100)	-0.52	-1.10	-2.35	-0.96
(111)	0.56	-2.63	-0.08	-2.77
(110)	0.13	-0.50	-2.60	-1.94
(221)-Ce1	0.17	-2.37	-0.52	-2.20
(221)-Ce2	0.65	-2.66	-0.16	-2.75
(221)-Ce3	0.54	-2.41	-0.11	-2.94
(331)-Ce1	0.30	-2.45	-2.65	-0.12
(331)-Ce2	0.68	-4.74	-0.08	-0.78

Figure S1: Free energy diagrams for the associative mechanism of the oxygen reduction reaction on stepped CeO$_2$ surfaces.
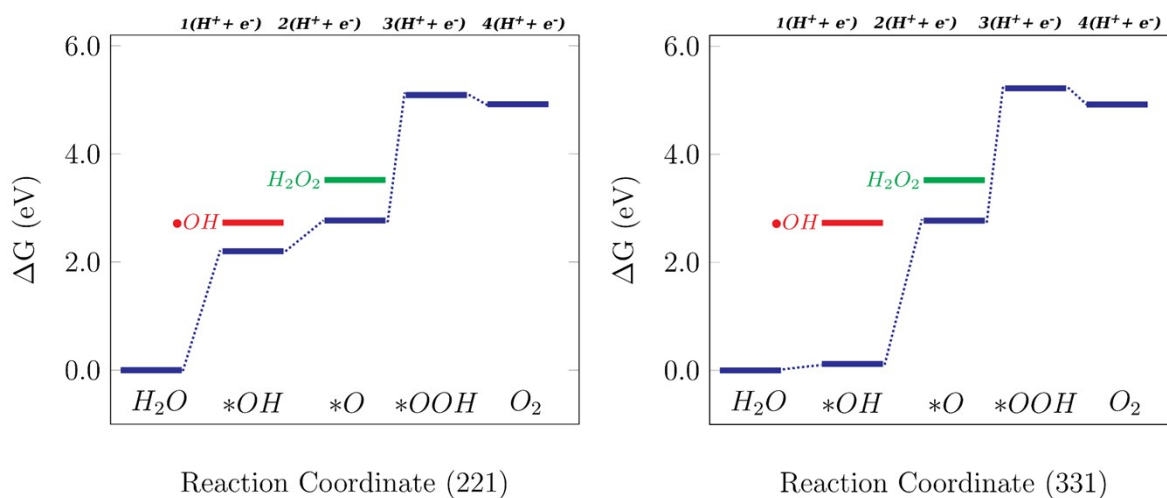

Figure S2: Free energy diagrams for the water oxidation reaction on stepped CeO$_2$ surfaces.

Table S3: Calculated formation energies for oxygen vacancy defects on surfaces (110) and (111), 1 and 2 indexes refer to the uppermost or second surface layer; oxygen reduction reaction free energies for $U = 0$.

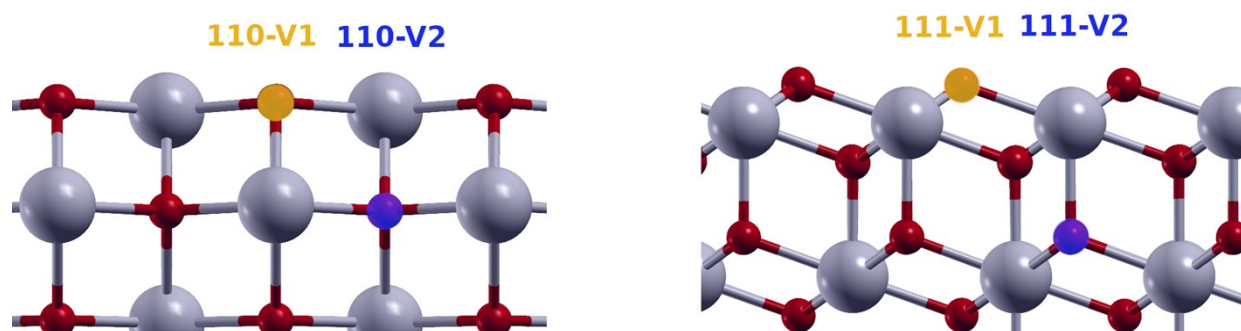| Surface	Formation Energy (eV)	$\Delta G(*OOH)$	$\Delta G(*O)$	$\Delta G(*OH)$
(110)-V1	0.49	4.52	2.30	1.11
(110)-V2	1.54	3.65	2.04	0.11
(111)-V1	1.83	2.91	0.94	0.06
(111)-V2	1.72	4.35	3.50	1.79

Figure S3: Schematic illustration of oxygen vacancies (V1 and V2) created in (110) and (111) CeO$_2$ surfaces.