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Supporting Information

First-principles study of initial oxygen reduction reaction on stoichiometric and reduced CeO_2 (111) surfaces as cathode catalyst for lithium-oxygen batteries

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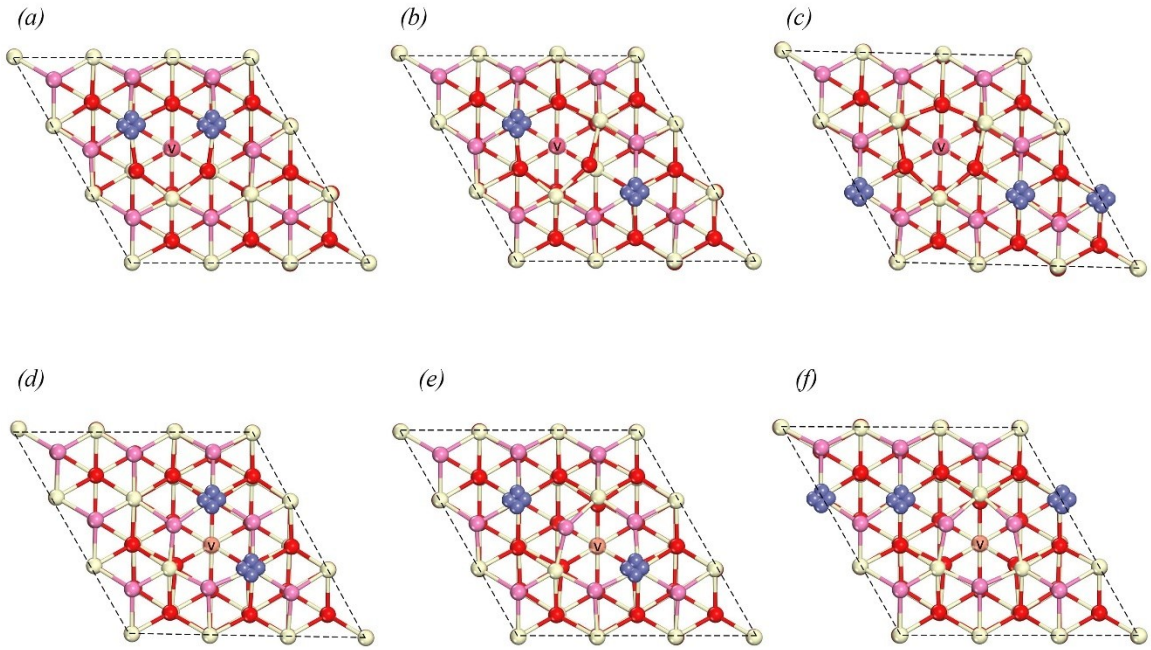


Figure S1 Optimized configurations of reduced $CeO_2(111)$ with one surface oxygne vacancy (a-c) or subsurface oxygen vacancy (d-f). Ce^{3+} are in blue.

Table S1 Calculated formation energies (eV) of one oxygen vacancies with different Ce^{3+} at $CeO_2(111)$. Corresponding structures in Figure S1.

	a	b	c	d	e	f
E_f(eV)	2.34	2.19	2.13	2.16	1.96	1.84

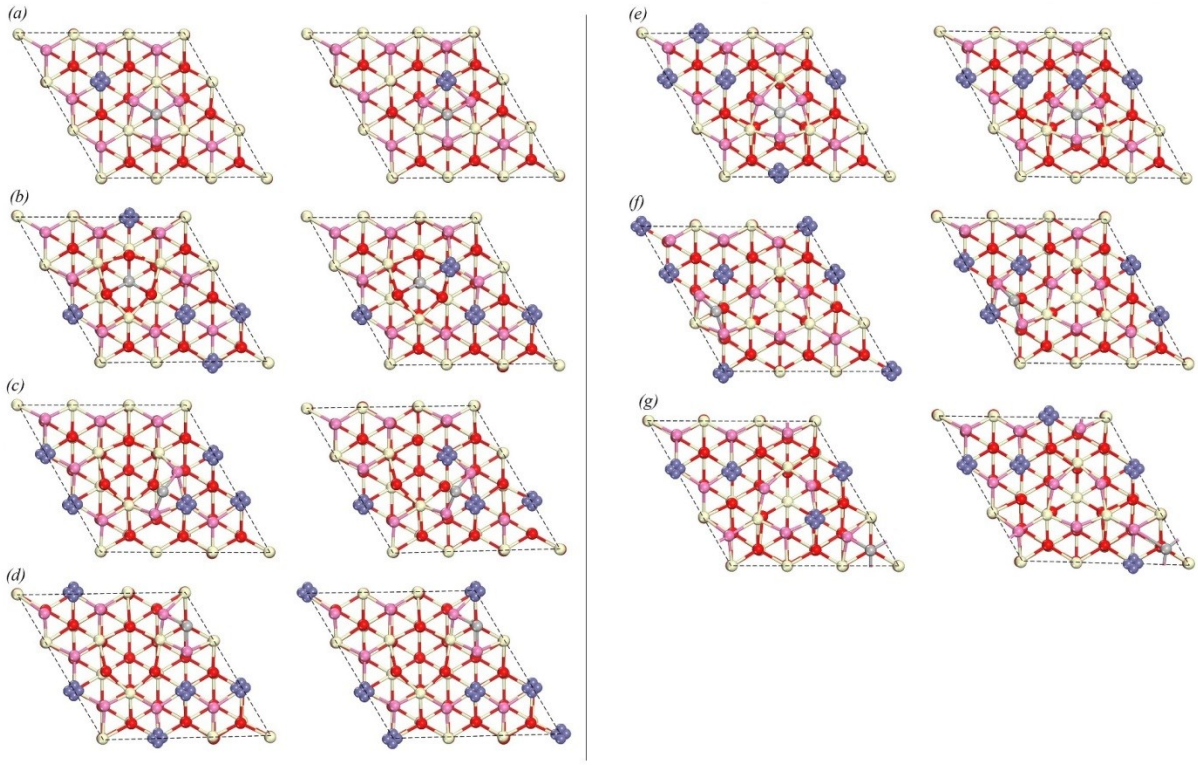
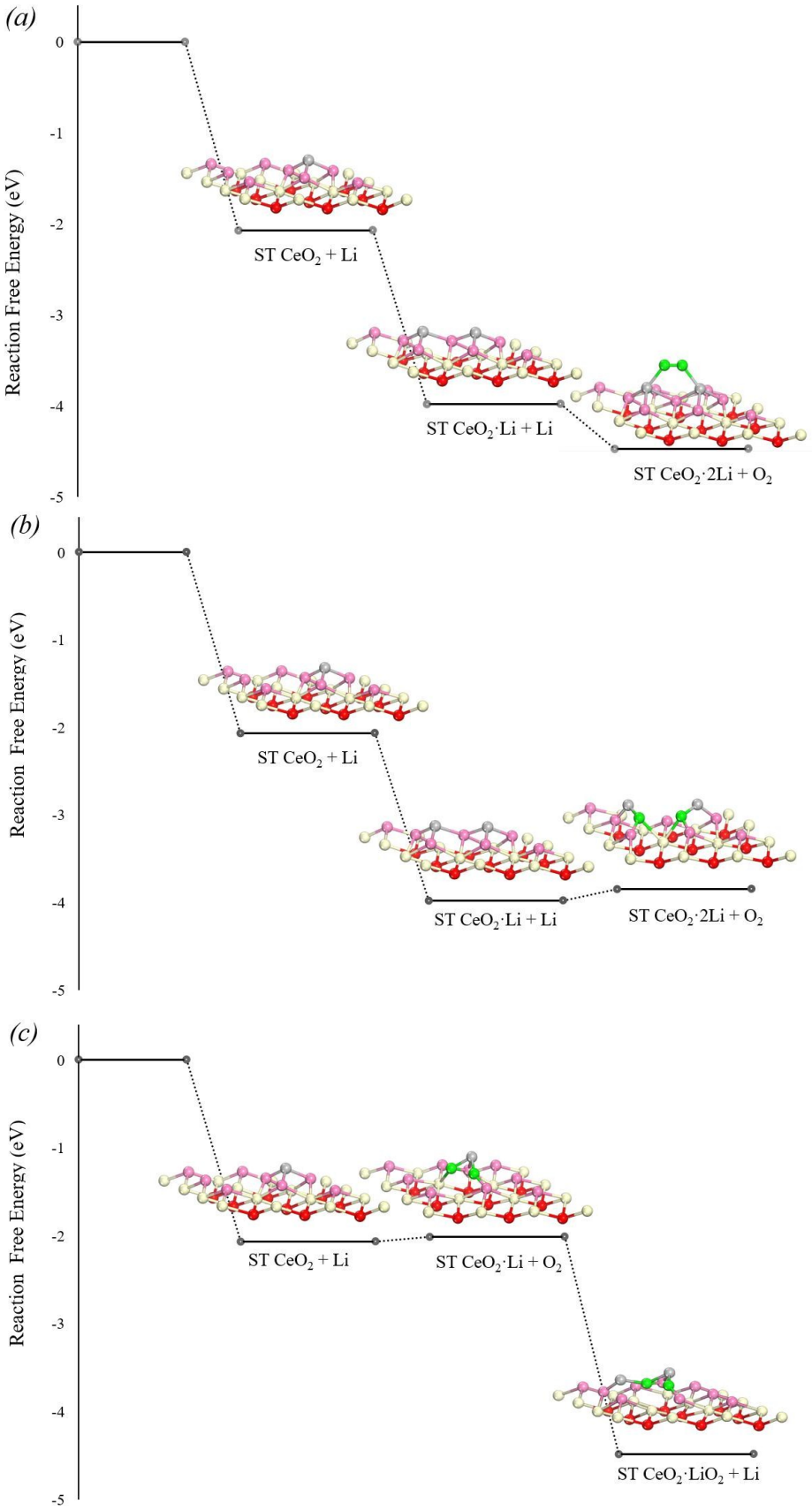
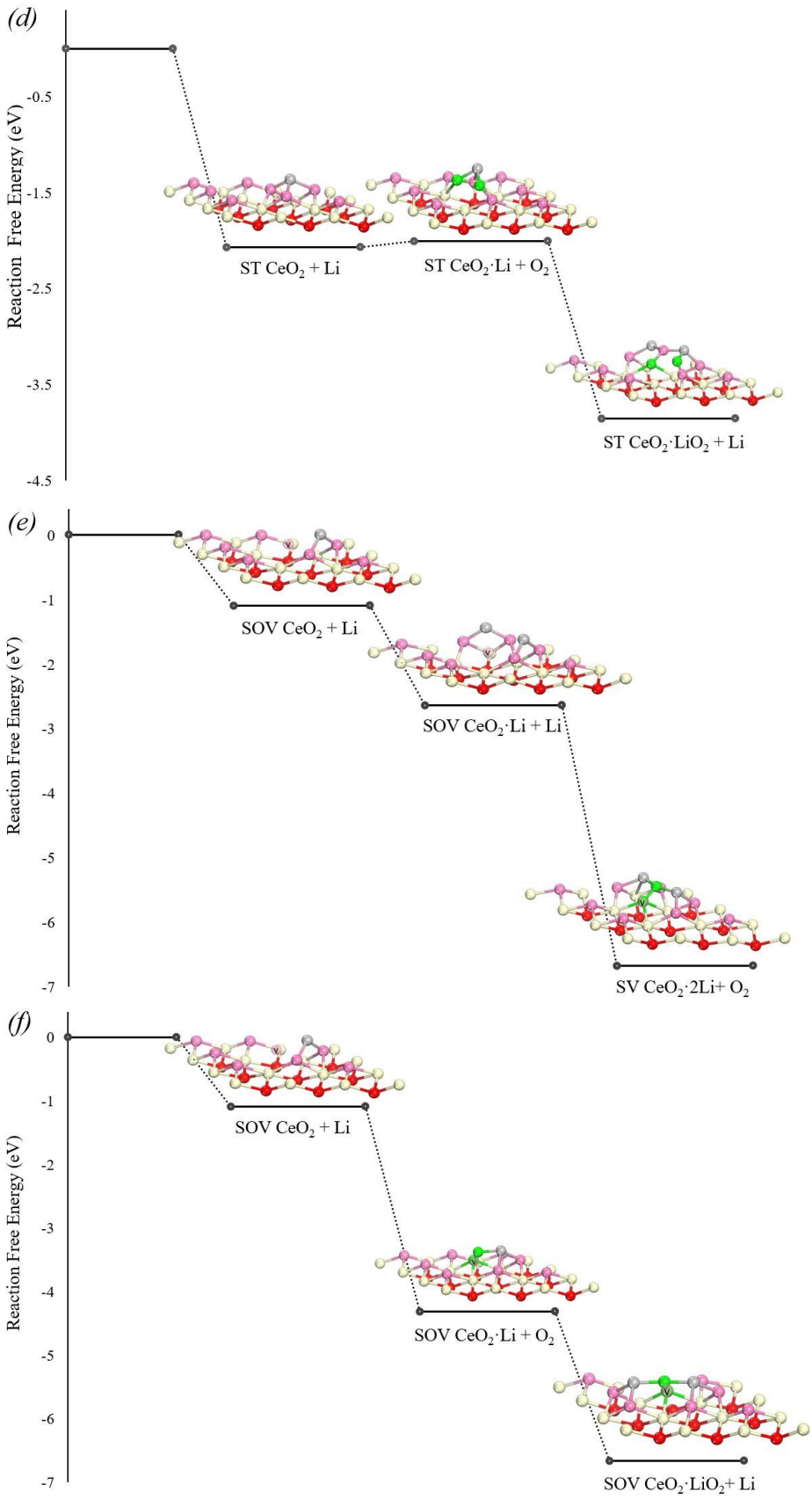


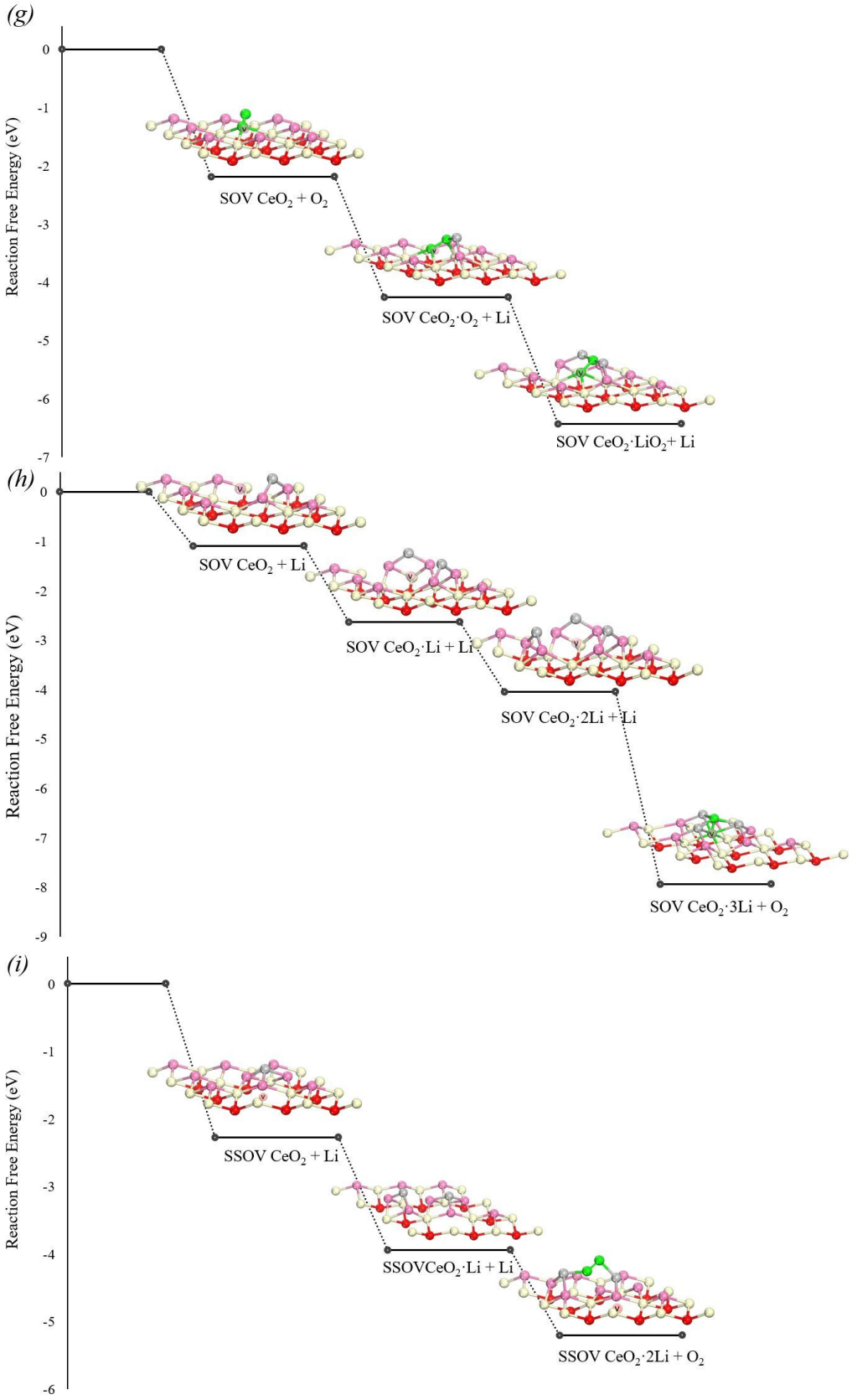
Figure S2 Optimized configurations of Li adsorption on stoichiometric and reduced CeO_2(111) with next nearest(NN) Ce^{3+} and nearest(N) Ce^{3+}. Ce^{3+} are in blue.

Table S2 The adsorption energies (eV) of Li at the stoichiometric and reduced CeO_2 (111) surfaces with next nearest (NN) Ce $^{3+}$ and nearest (N) Ce^{3+}. Corresponding structures in Figure S2.

	a	b	c	d	e	f	g
Left (NN Ce^{3+})	-2.06	-0.78	-1.12	-1.78	-2.25	-1.61	-1.74
Right(N Ce^{3+})	-1.78	-0.99	-0.95	-1.64	-2.01	-1.25	-1.41


(a)
Reaction Free Energy (eV)
0
-1
-2
-3
-4
-5
ST CeO2 + Li
ST CeO2·Li + Li
ST CeO2·2Li + O2
(b)
Reaction Free Energy (eV)
0
-1
-2
-3
-4
-5
ST CeO2 + Li
ST CeO2·Li + Li
ST CeO2·2Li + O2
(c)
Reaction Free Energy (eV)
0
-1
-2
-3
-4
-5
ST CeO2 + Li
ST CeO2·Li + O2
ST CeO2·LiO2 + Li


(d)
Reaction Free Energy (eV)
-0.5
-1.5
-2.5
-3.5
-4.5
ST CeO_2 + Li
ST CeO_2·Li + O_2
ST CeO_2·LiO_2 + Li
(e)
Reaction Free Energy (eV)
0
-1
-2
-3
-4
-5
-6
-7
SOV CeO_2 + Li
SOV CeO_2·Li + Li
SV CeO_2·2Li+ O_2
(f)
Reaction Free Energy (eV)
0
-1
-2
-3
-4
-5
-6
-7
SOV CeO_2 + Li
SOV CeO_2·Li + O_2
SOV CeO_2·LiO_2+ Li


(g)
Reaction Free Energy (eV)
0
-1
-2
-3
-4
-5
-6
-7
SOV CeO2 + O2
SOV CeO2·O2 + Li
SOV CeO2·LiO2+ Li
(h)
Reaction Free Energy (eV)
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
SOV CeO2 + Li
SOV CeO2·Li + Li
SOV CeO2·2Li + Li
SOV CeO2·3Li + O2
(i)
Reaction Free Energy (eV)
0
-1
-2
-3
-4
-5
-6
SSOV CeO2 + Li
SSOVCeO2·Li + Li
SSOV CeO2·2Li + O2

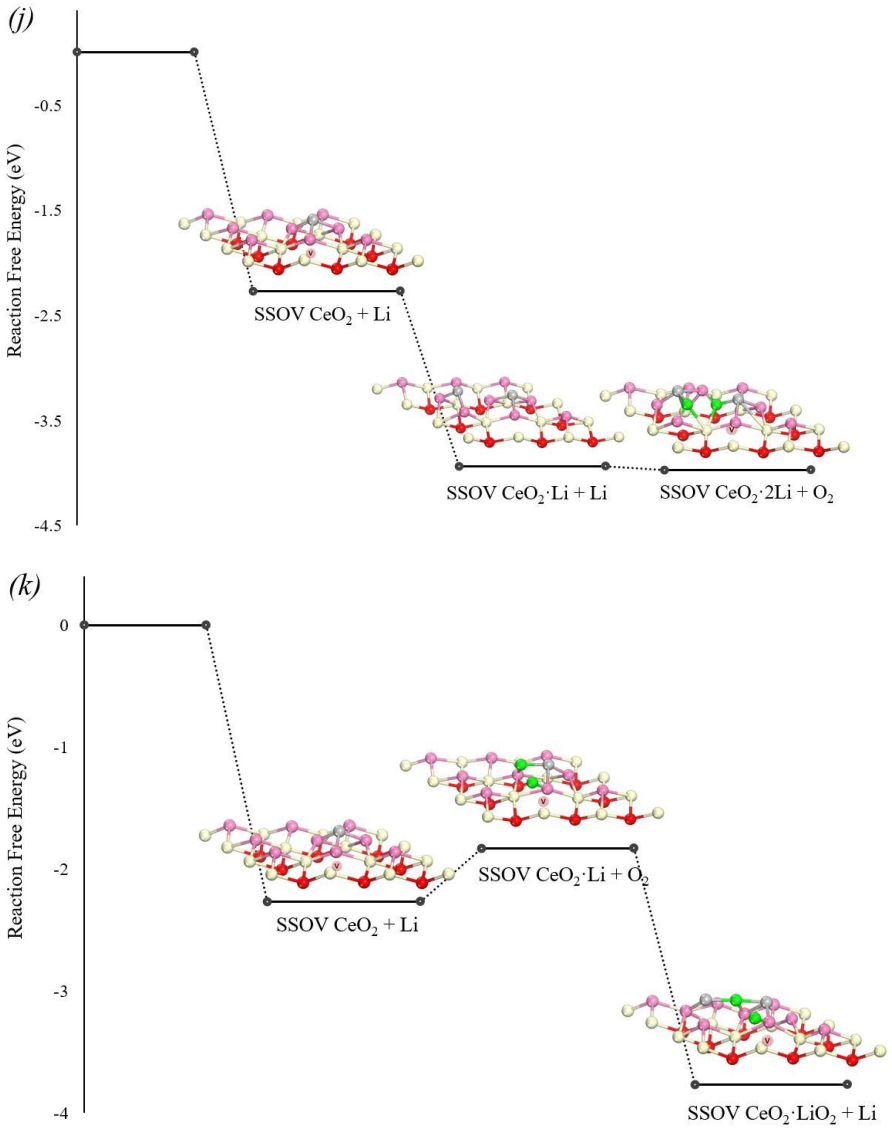


Figure S3 Detailed energy diagram and the schematics for the initial ORR process through different pathway, a, b, c, d at the ST CeO_2 surface, e, f, g, h at the SOV CeO_2 surface and i, j, k at the SSOV CeO_2 surface.

Table S3 Detailed reaction steps and corresponding ΔG_n (eV) for the initial ORR on the ST, SOV, and SSOV CeO_2 surfaces.

	Surface Type	Reaction step	ΔG_n (eV)
a	ST CeO_2 (111)	ST + Li → ST_Li	-2.07
		ST_Li + Li → ST_2Li	-1.91
		ST_2Li + O_2 → ST_Li_2O_2	-0.49
b	ST CeO_2 (111)	ST + Li → ST_Li	-2.07
		ST_Li + Li → ST_2Li	-1.91
		ST_2Li + O_2 → ST_Li_2O_2	+0.13
c	ST CeO_2 (111)	ST + Li → ST_Li	-2.07
		ST_Li + O_2→ ST_LiO_2	+0.07
		ST_LiO_2 + Li → ST_Li_2O_2	-2.48
d	ST CeO_2 (111)	ST + Li →ST_Li	-2.07
		ST_Li + O_2→ ST_LiO_2	+0.07
		ST_LiO_2 + Li → ST_Li_2O_2	-1.85
e	SOV CeO_2 (111)	SOV + Li → SOV_Li	-1.09
		SOV_Li + Li→ SOV_2Li	-1.55
		SOV_ 2Li + O_2 → SOV_Li_2O_2	-4.03
f	SOV CeO_2 (111)	SOV + Li → SOV_Li	-1.09
		SOV_Li + O_2→ SOV_LiO_2	-3.22
		SOV_ LiO_2 → SOV_Li_2O_2	-2.35
g	SOV CeO_2 (111)	SOV + O_2 → SOV_ O_2	-2.19
		SOV_ O_2 + Li → SOV_ LiO_2	-2.06
		SOV_ LiO_2 + Li → SOV_Li_2O_2	-2.17
h	SOV CeO_2 (111)	SOV + Li → SOV_Li	-1.09
		SOV_Li + Li→ SOV_2 Li	-1.55
		SOV_ 2 Li+ Li → SOV_3 Li	-1.41
		SOV_3 Li+ O_2 →SOV_Li_3O_2	-3.90
i	SSOV CeO_2 (111)	SSOV + Li → SSOV_Li	-2.27
		SSOV_Li + Li→ SSOV_2Li	-1.67
		SSOV_ 2Li + O_2 → SSOV_Li_2O_2	-1.27
j	SSOV CeO_2 (111)	SSOV + Li → SSOV_Li	-2.27
		SSOV_Li + Li→ SSOV_2Li	-1.67
		SSOV_ 2Li + O_2 → SSOV_Li_2O_2	-0.03
k	SSOV CeO_2 (111)	SSOV + Li → SSOV_Li	-2.27
		SSOV_Li + O_2→ SSOV_LiO_2	+0.45
		SSOV_ LiO_2 → SSOV_Li_2O_2	-1.94