# A Multiscale Model for the Oxygen Reduction and Oxidation Reactions in LSCF Based Solid Oxide Cell

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Outline
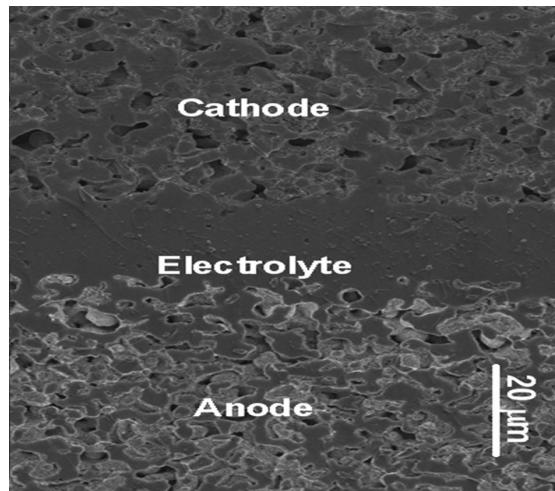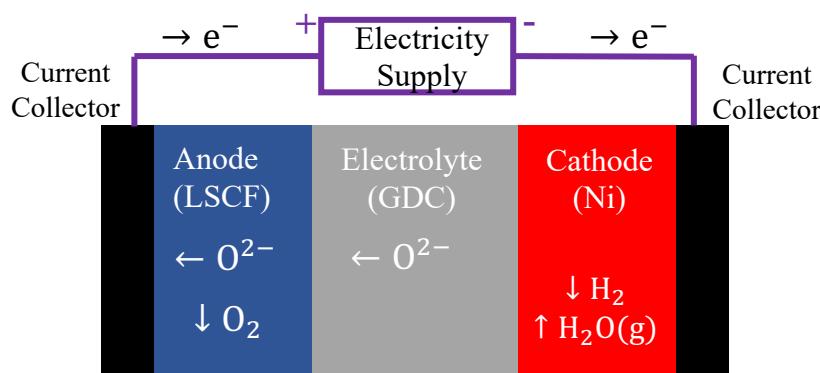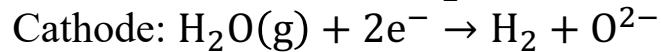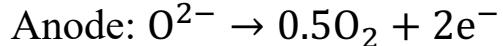
- Introduction

- Multiscale Framework

- Simulation Details

- Multiscale Results

- Discussion

- Conclusions
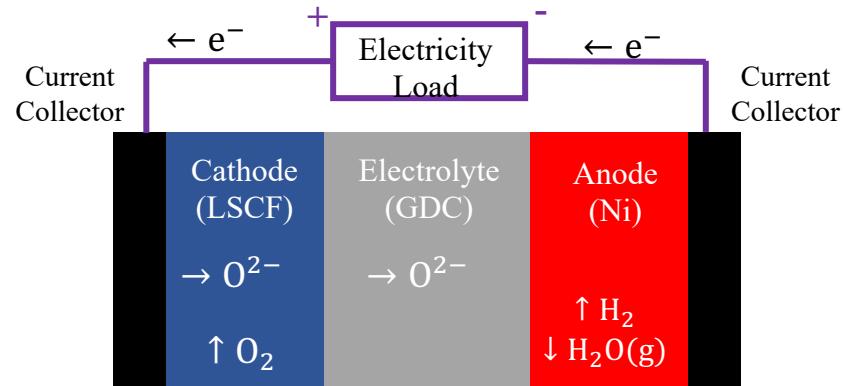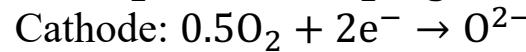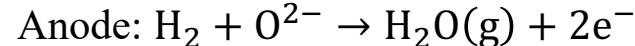
Solid oxide electrolysis cell (SOEC)

Anode: $O^{2-} \rightarrow 0.5O_2 + 2e^-$
Cathode: $H_2O(g) + 2e^- \rightarrow H_2 + O^{2-}$
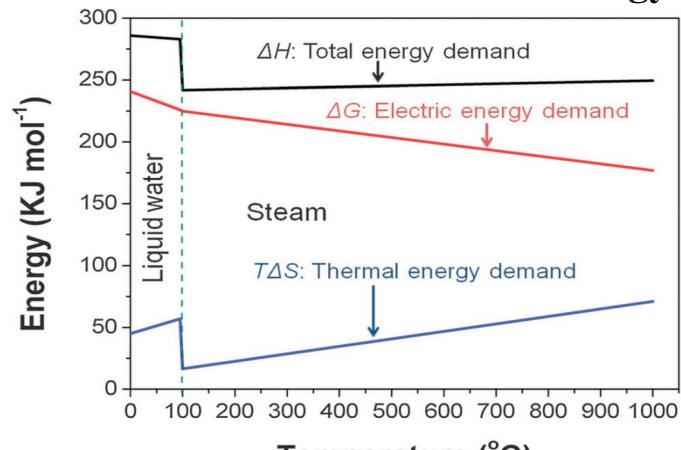
Energy Environ. Sci., 9, 1602, (2016)

Solid oxide fuel cell (SOFC)

Anode: $H_2 + O^{2-} \rightarrow H_2O(g) + 2e^-$
Cathode: $0.5O_2 + 2e^- \rightarrow O^{2-}$

Advantage over other normal electrolyzers: make use of the thermal energy
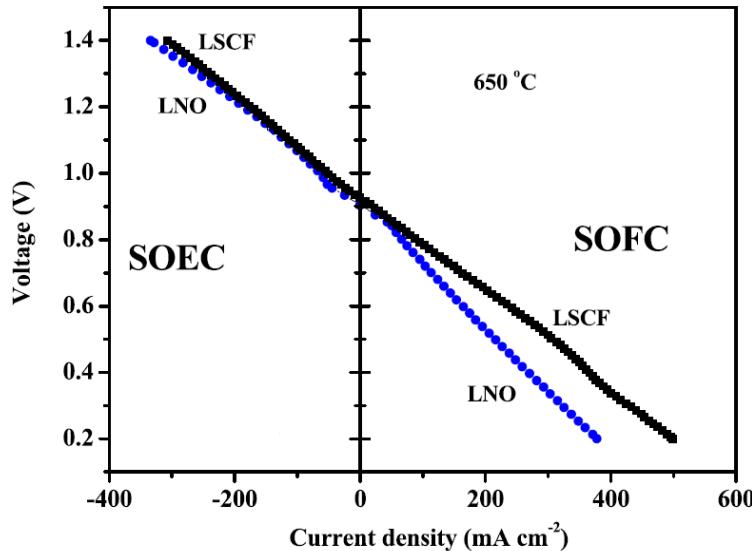
Chem. Soc. Rev. 43, 8254, (2014)

Method to evaluate the cell efficiency:
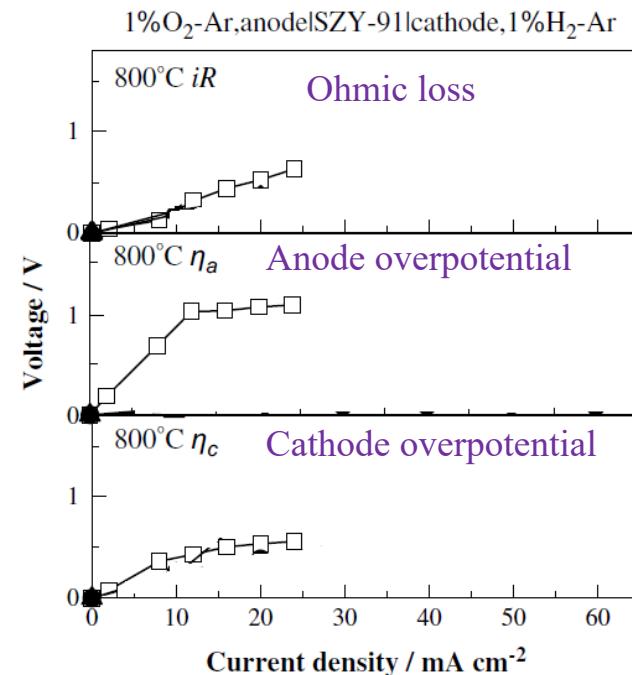
I-V Curve
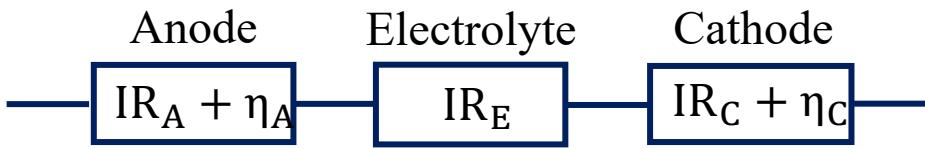
International Journal of Hydrogen Energy 41 (2016) 14497

The whole cell voltage can be split into three parts:
- ✓ Ohmic loss: $IR = I(R_A + R_E + R_C)$,
- ✓ Anode overpotential (polarization resistance): η_A. Nonlinearity comes from the reaction resistance at the interface;
- ✓ Cathode Overpotential (polarization resistance): η_C.

International Journal of Hydrogen Energy 34 (2009) 56–63

Oxygen reduction/oxidation are important steps:

- SOFC cathode part: $0.5O_2 + 2e^- \rightarrow O^{2-}$, SOEC anode part: $O^{2-} \rightarrow 0.5O_2 + 2e^-$

✓ Oxygen reduction/oxidation resistances are high in solid oxide cells
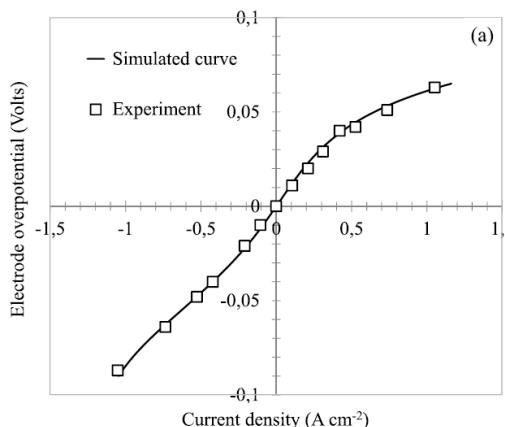
| Resistances Comparison for SOFC at 600 °C [*Energy & Environmental Science* 9.5 (2016): 1602-1644]		
Overpotential of hydrogen electrode	Ohmic loss of YSZ based electrolyte (10μm)	Overpotential of oxygen electrode
$0.1 \sim 1 \ \Omega cm^2$	$\sim 1 \ \Omega cm^2$	$3 \sim 8 \ \Omega cm^2$

Contradiction between continuum simulation and DFT calculations
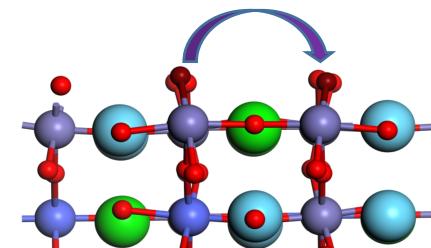
- **Continuum simulation**

Parameter:
$$D_{O_{suf}^{2-}}^{suf} = 10^{-6} m^2 s^{-1}$$
$$[\Delta E \approx 0.2 \sim 0.3 ev]$$

- **DFT calculations**

On Co, Fe terminated LSCF (110) surface
$$\Delta E \approx 1.74 \sim 1.9 ev$$
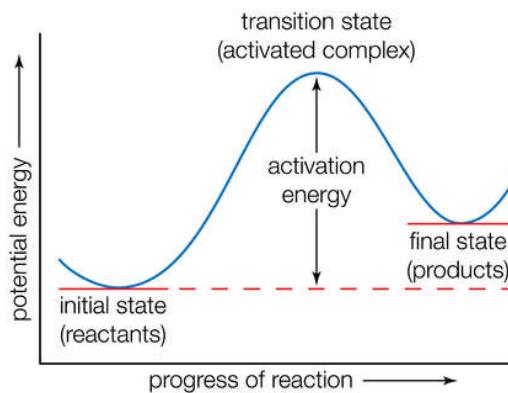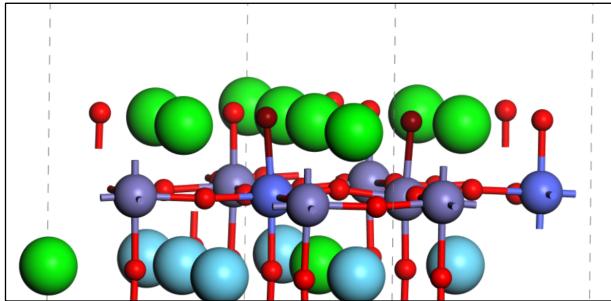
J. Mater. Chem. A, 2013, 1, 12932–12940

J. Laurencin et al. Electrochimica Acta 174 (2015) 1299–1316

Contradiction!!

DFT+U calculations provide the energy barriers and transition state positions

$\downarrow$
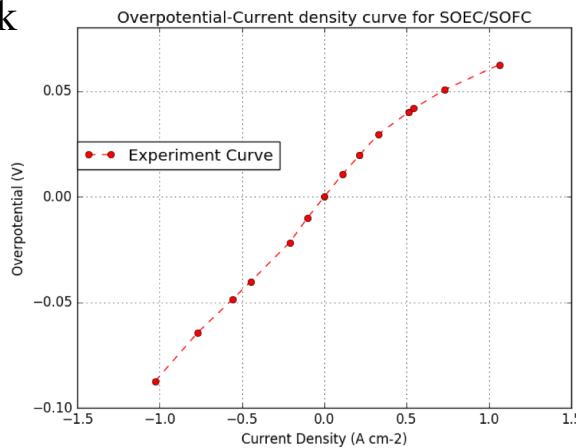
Energy barriers ΔE
Vibrational frequencies ν
Transition state positions

Transition state theory calculations provide the reaction rate constants:

$$k = \frac{k_B T}{h} \exp\left(-\frac{\Delta G}{RT}\right)$$

$\downarrow$

Reaction rate constants k
Diffusivities D
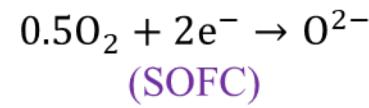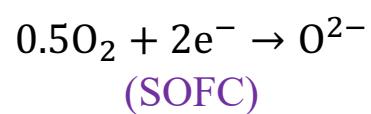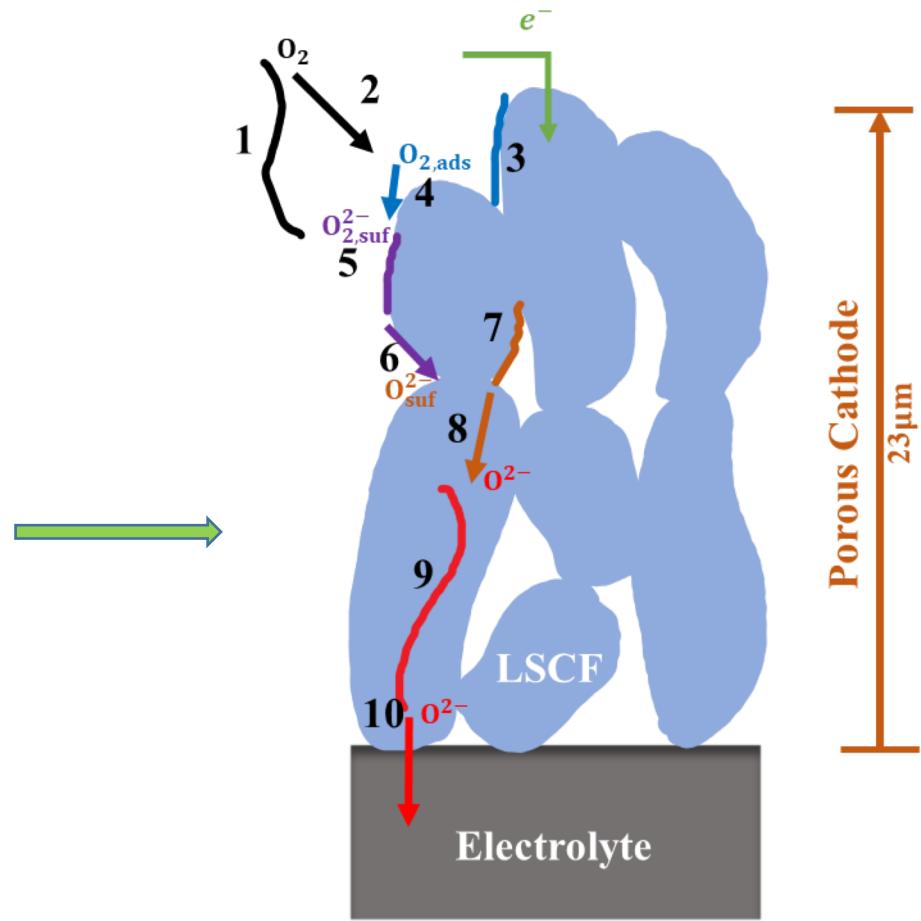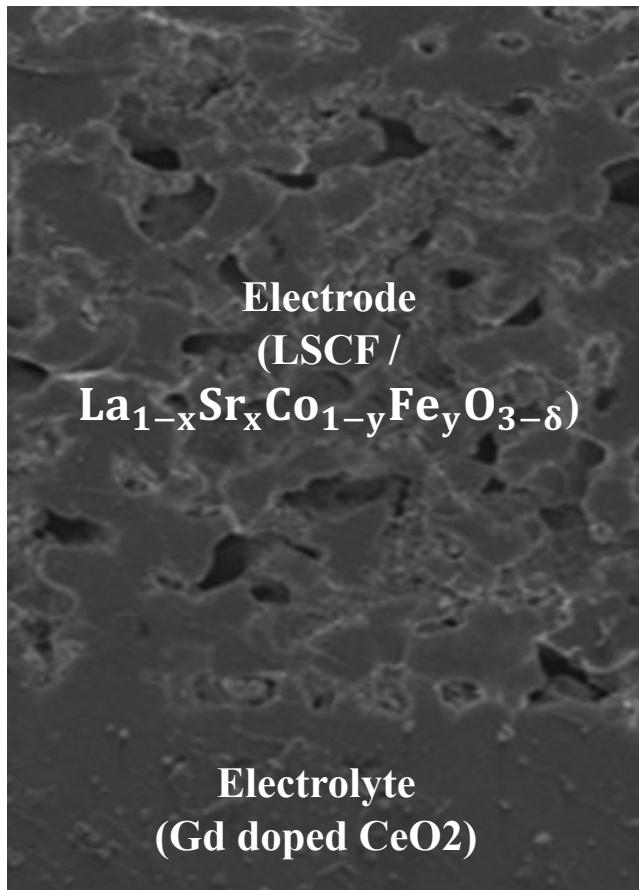
Calculate the Current density-Overpotential curve using continuum scale simulation

Electrode
(LSCF /
$La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$)

Electrolyte
(Gd doped CeO2)

$0.5O_2 + 2e^- \rightarrow O^{2-}$
(SOFC)

e^-

O_2

2

1

$O_{2,ads}$ 3

4

$O_{2,suf}^{2-}$

5

7

6

O_{suf}^{2-}

8

O^{2-}

9

LSCF

10   O^{2-}

Electrolyte

Porous Cathode   23μm

$0.5O_2 + 2e^- \rightarrow O^{2-}$
(SOFC)
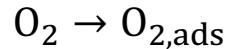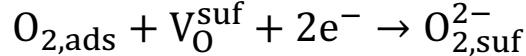
Mechanisms for LSCF based SOFC cathode reactions:

1. Transport of O_2 in gas phase
2. Reaction **R1**: [adsorption of O_2 on LSCF surface]
$$O_2 \rightarrow O_{2,ads}$$
3. Transport of $O_{2,ads}$ on LSCF surface
4. Reaction **R2**: [$O_{2,ads}$ fill in a vacancy on surface]
$$O_{2,ads} + V_O^{suf} + 2e^- \rightarrow O_{2,suf}^{2-}$$
5. Transport of $O_{2,suf}^{2-}$ on LSCF surface
6. Reaction **R3** : [split of $O_{2,suf}^{2-}$]
$$O_{2,suf}^{2-} + V_O^{suf,n} \rightarrow 2O_{suf}^-$$
7. Transport of O_{suf}^- on LSCF surface
8. Reaction **R4** : [O_{suf}^- transports to the bulk]
$$O_{suf}^- + V_O + e^- \rightarrow V_O^{suf} + O^{2-}$$
9. Transport of O^{2-} in bulk LSCF
10. Reaction **R5** : [O^{2-} transports across the interface]
$$O^{2-} + V_O^{ele} \rightarrow O_{ele}^{2-} + V_O$$
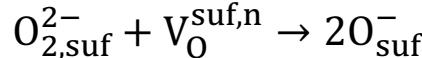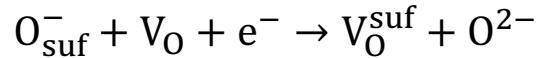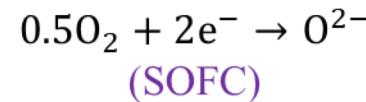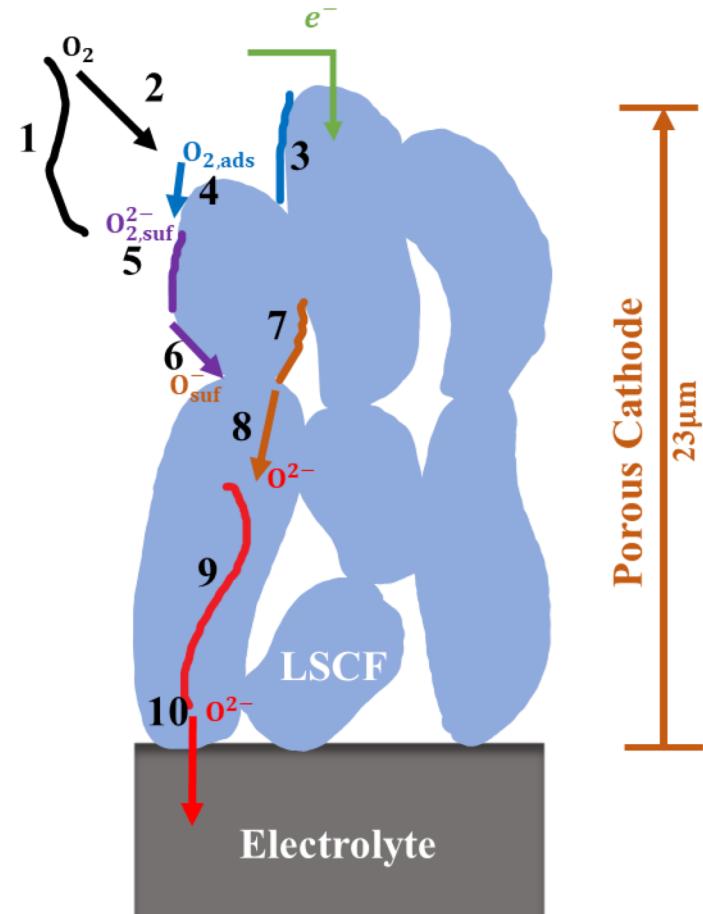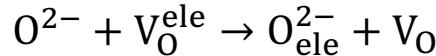
$$0.5O_2 + 2e^- \rightarrow O^{2-}$$
(SOFC)

Transport equations (i= O_2, $O_{2,ads}$, O^{2-}, $O^{2-}_{2,suf}$ and O^-_{suf})

$$\frac{d}{dz}\left[-\frac{\phi}{\tau}D_i\left(\frac{dC_i}{dz}-\frac{n_iFC_i}{RT}\frac{d\phi}{dz}\right)\right]=r_i$$

Expression for $\frac{d\phi}{dz}$

$$I(e^-)+I(O^{2-})=I=I(O^{2-})(\text{bottom})$$

$$-\sigma\frac{d\phi}{dz}+2FD_{O^{2-}}\left(\frac{dC_{O^{2-}}}{dz}-\frac{2FC_{O^{2-}}}{RT}\frac{d\phi}{dz}\right)=2FD_{O^{2-}}\frac{dC_{O^{2-}}}{dz}\ (\text{bottom})$$

Expressions for the reaction rates:

$$O_2\rightarrow O_{2,ads}\ [\text{example}]$$

$$r^{suf}_{R1}=A_{suf}\{k^+_{1,suf}C_{O_2}-k^-_{1,suf}O_{2,ads}\}$$

Boundary conditions:

Top: $C_{O_2}=\frac{p}{RT}$, $\frac{dC_i}{dz}=0$ (i= $O_{2,ads}$, O^{2-}, $O^{2-}_{2,suf}$ and O^-_{suf})

Bottom: $-D_{O^{2-}}\frac{dC_{O^{2-}}}{dz}=-r^{int}_{R5}$, $\frac{dC_i}{dz}=0$ (i= O_2, $O_{2,ads}$, $O^{2-}_{2,suf}$ and O^-_{suf})

Physical parameters in the model:

- Reaction Rate Constants k
- Diffusivities D
- Surface Area Parameters ϕ, τ, A_{suf}…

$$k = \frac{k_B T}{h} \exp(-\frac{\Delta G(T,C)}{k_B T})$$

$$D = \frac{\lambda^2}{z} \frac{k_B T}{h} \exp(-\frac{\Delta G(T,C)}{k_B T})$$

$$\Delta G(T, C)$$

$\Delta G(T)$

- Gibbs free energy G(T) of O_2, $O_{2,ads}$, O^{2-}, $O_{2,suf}^{2-}$ and O_{suf}^{-} need to be calculated.

$\Delta G(C)$

- $\Delta G(C)$ term for specific reaction steps are from experimental observations

Example: $\Delta G_{D_{O^{2-}}}(C_{V_O}) = 2\gamma_{bulk} a \frac{\Delta C_{V_O}}{C_{O^{2-}}^{max}}$

Species	Place	G(T)
O_2, $O_{2,ads}$	Gas phase	$F^{electronic} + F^{translation} + F^{vibration} + F^{rotation} + PV$
O^{2-}, $O_{2,suf}^{2-}$ and O_{suf}^{-}	LSCF	$\approx F = F^{electronic} + F^{vibration}$

$$F^{electronic} = E_0$$

$$F^{vibration} = 0.5 \sum_{m=1}^{3N} h v_m + k_B T \sum_{m=1}^{3N} \ln(1 - \exp(-\frac{h v_m}{k_B T}))$$

- The ground state energies E_0 are to be calculated with DFT+U calculations
- The vibrational frequencies v_m are to be calculated with finite displacement method

Density Functional Theory + U (DFT+U): VASP

- GGA+U - PBE for the exchange and correlation functional is used
- Energy cutoff : 500 eV
- Forces on each ion are less than 0.05 eV/Å
- All the calculations are spin polarized
- Migration energy barriers : the climbing image nudged elastic band (CI-NEB) method
- On-site correlation to the 3d manifolds of Fe^{3+} and Co^{3+}: $U_{eff} = U - J = 4.0eV$ for both ions

DFT+U rather than DFT

- "DFT results predict a strongly metallic system, while DFT+U results predict a half-metallic system, which agrees with the experiment."
- DFT results are not accurate for some parameters like vacancy formation energy.

Vacancy formation energy value for LSCF:

- $E_{V_O} = E_{defective} + 0.5E_{O_2} - E_{host}$
- Calculation results: $E_{V_O} = [0.94, 1.03]eV$

dE	Article
1.036eV	Bucher et al.
0.777eV	Gryaznov et al.
1.14eV	Mizusaki et al.
1.14eV	Wachsman et al.
1.55eV	Jun et al.

Experimental vacancy formation energy results
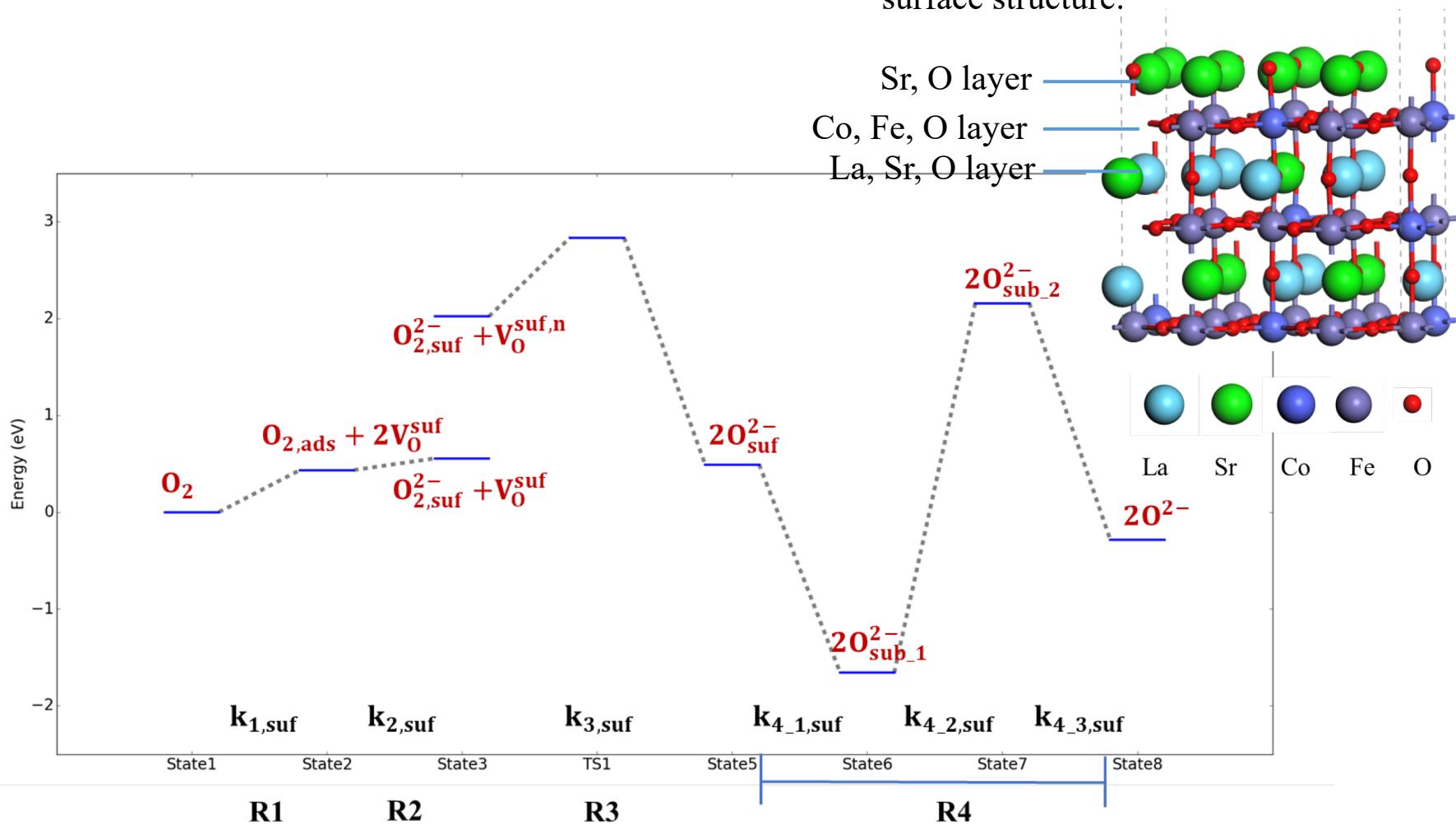
◆ **DFT+U results are consistent with experimental results**

Free energy profile for reaction $O_2 + 4e^- + 2V_O \rightarrow 2O^{2-}$
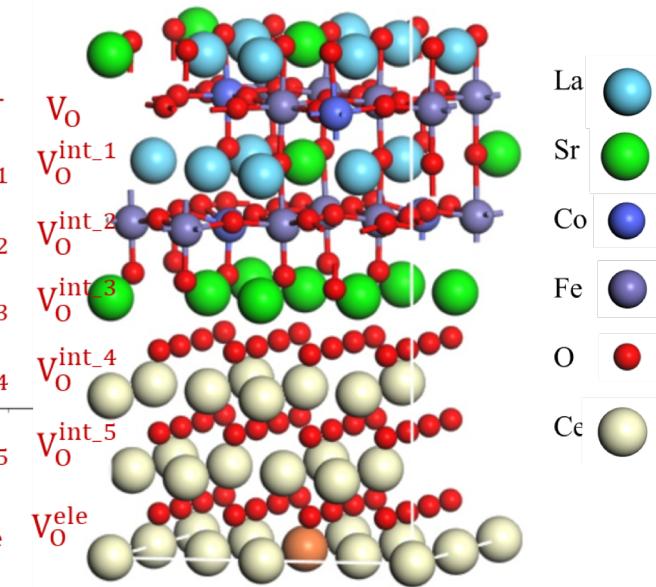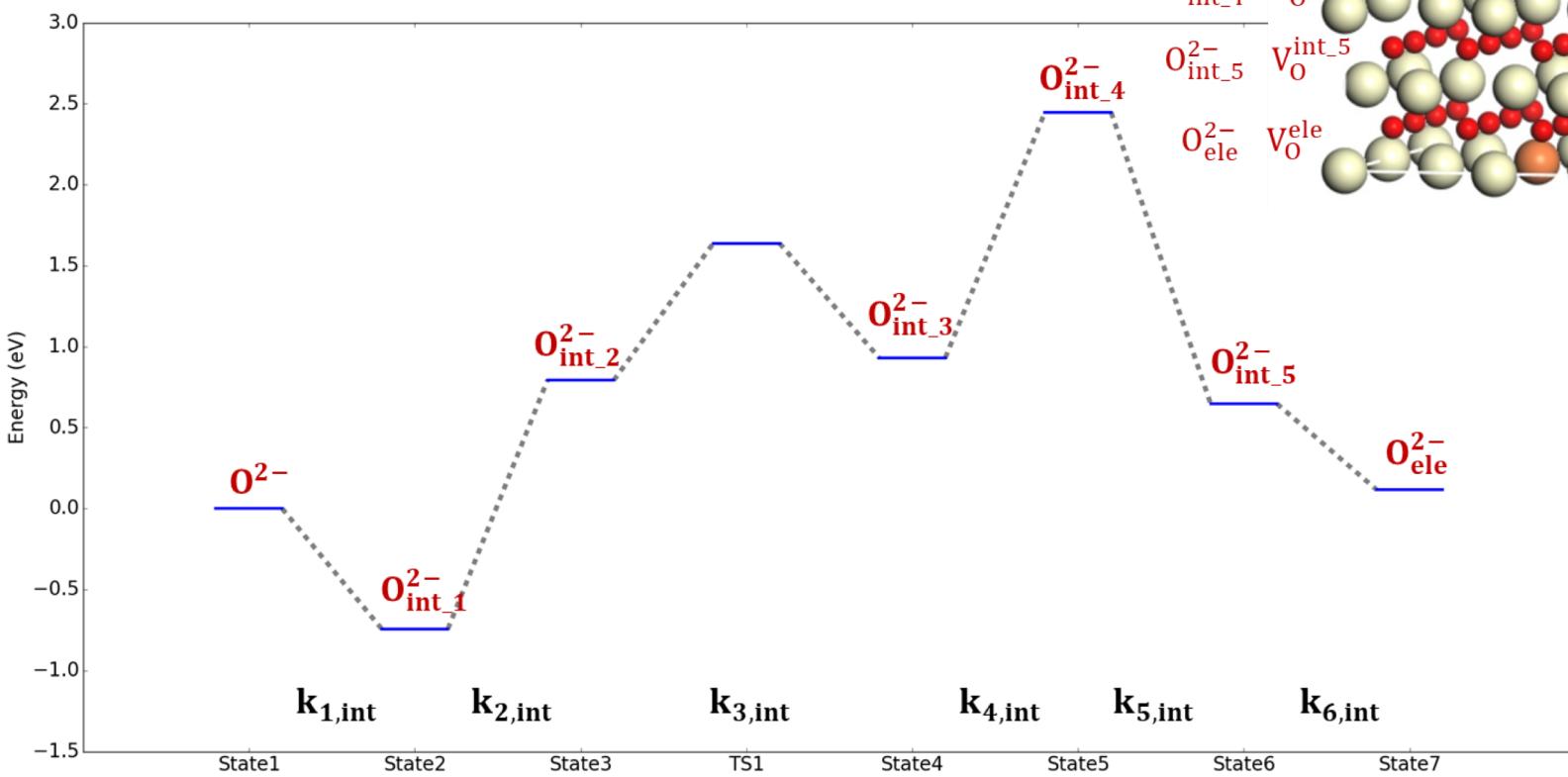
LSCF $(La_{0.6}Sr_{0.4}Co_{0.25}Fe_{0.75}O_{3-\delta})$ 100 surface structure:

Sr, O layer

Co, Fe, O layer

La, Sr, O layer

| La | Sr | Co | Fe | O |

$O_{2,suf}^{2-} + V_O^{suf,n}$

$O_{2,ads} + 2V_O^{suf}$

$O_{2,suf}^{2-} + V_O^{suf}$

$2O_{suf}^{2-}$

$2O_{sub\_2}^{2-}$

O_2

$2O^{2-}$

$2O_{sub\_1}^{2-}$

Energy (eV)

$k_{1,suf}$ $k_{2,suf}$ $k_{3,suf}$ $k_{4\_1,suf}$ $k_{4\_2,suf}$ $k_{4\_3,suf}$

State1   State2   State3   TS1   State5   State6   State7   State8

R1   R2   R3   R4

Free energy profile for reaction $O^{2-} + V_O^{ele} \rightarrow O_{ele}^{2-} + V_O$
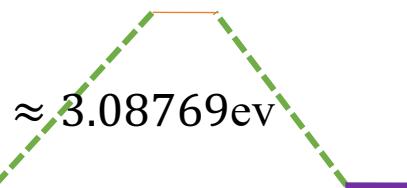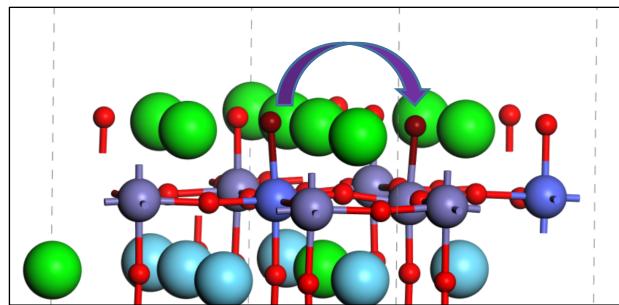
| Parameters	$\Delta E(0)(eV)$	$\Delta G(T) - \Delta E(0)(eV)$	$\Delta G(T)(eV)$	Values (s^{-1})
$k_{1,suf}^+$	-0.7	1.1337	0.4337	2.06198×10^{11}
$k_{1,suf}^-$	0	0	0	2.2347×10^{13}
$k_{2,suf}^+$	-0.615	0.7364	0.1214	6.06167×10^{12}
$k_{2,suf}^-$	0	0	0	2.2347×10^{13}
$k_{3,suf}^+$	0.653	0.16083	0.8138	3.3939×10^{9}
$k_{3,suf}^-$	2.153	0.19023	2.3432	2.2664×10^{2}
$k_{4\_1,suf}^+$	0	0	0	2.2347×10^{13}
$k_{4\_1,suf}^-$	1.17	-0.09572	1.07428	2.03546×10^{8}
$k_{4\_2,suf}^+$	1.94	-0.03236	1.9076	2.5033×10^{4}
$k_{4\_2,suf}^-$	0	0	0	2.2347×10^{13}
$k_{4\_3,suf}^+$	0	0	0	2.2347×10^{13}
$k_{4\_3,suf}^-$	1.3162	-0.03241	1.2838	2.116×10^{7}
$k_{1,int}^+$	0	0	0	2.2347×10^{13}
$k_{1,int}^-$	0.6807	0	0.6807	1.43×10^{10}
$k_{2,int}^+$	1.452	0.08218	1.53418	1.4151×10^{6}
$k_{2,int}^-$	0	0	0	2.2347×10^{13}
$k_{3,int}^+$	0.7	0.1457	0.8457	2.406×10^{9}
$k_{3,int}^-$	0.706	0	0.706	1.088×10^{10}
$k_{4,int}^+$	1.3685	0.1453	1.5138	1.7635×10^{6}
$k_{4,int}^-$	0	0	0	2.2347×10^{13}
$k_{5,int}^+$	0	0	0	2.2347×10^{13}
$k_{5,int}^-$	1.7985	0	1.7985	8.1395×10^{4}
$k_{6,int}^+$	0	0	0	2.2347×10^{13}
$k_{6,int}^-$	0.5297	0	0.5297	7.3046×10^{10}
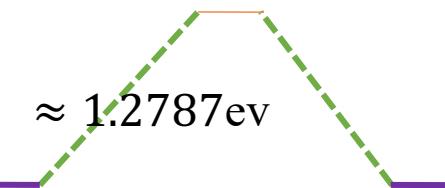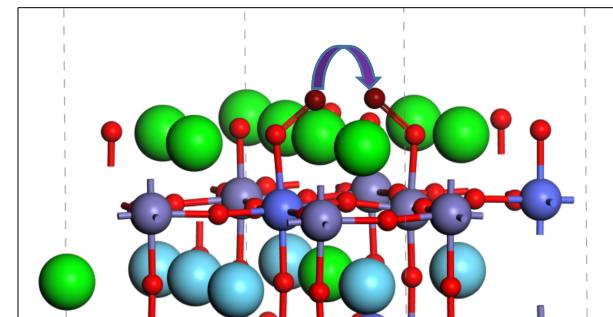
Diffusion of O_{suf}^-

Diffusion of $O_{2,suf}^{2-}$

$\approx 3.08769ev$

$\approx 1.2787ev$

$$D = \frac{\lambda^2}{4}\frac{k_BT}{h}\exp\left(-\frac{\Delta G(T)}{k_BT}\right)$$
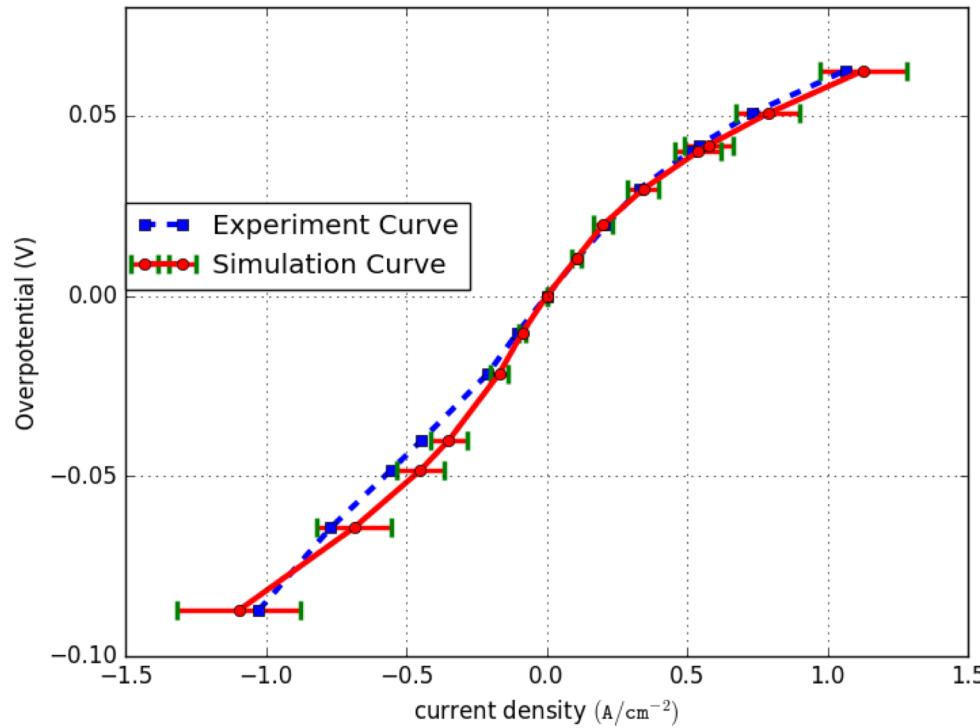
◆ **Diffusivity on the LSCF surface is very small**

Parameters	$\Delta E(0)(eV)$	$\Delta G(T) - \Delta E(0)(eV)$	$\Delta G(T)(eV)$	$\lambda(\text{Å})$	Values (m^2s^{-1})
$D_{O^{2-}}$	/	/	/	/	$(9.73\sim15.85)\times10^{-10}$
D_{O_2}	/	/	/	/	1.2×10^{-5}
$D_{O_{2,ads}}$	0	0	0	3.843	8.25×10^{-7}
$D_{O_{2,suf}^{2-}}$	1.1623	0.1164	1.2787	1.9215	2.0639×10^{-13}
$D_{O_{suf}^{2-}}$	2.99	0.09769	3.08769	3.843	2.6851×10^{-21}

Parameters	Experimental Values
A_{suf} (surface area per volume)	$5\mu m^2/\mu m^3$
A_{int} (interface area)	$0.6\mu m^2/\mu m^2$
ϕ_{gas} (porosity of gas phase)	0.4
ϕ_{LSCF} (porosity of LSCF)	0.6
τ_{gas}, τ_{LSCF} (tortuosity)	1.46

Sensitivity Analysis

$$S_e = \frac{\partial\, I/I}{\partial\, P_a/P_a} \approx \frac{\Delta\, I/I}{\Delta\, P_a/P_a}$$

Parameters	$\Delta P_a/P_a$	S_e ($\eta = -0.08722$)	S_e ($\eta = 0.062555$)
$k_{1,suf}^+, k_{1,suf}^-$	0.05	≈ 0	≈ 0
$k_{2,suf}^+, k_{2,suf}^-$	0.05	≈ 0	≈ 0
$k_{3,suf}^+, k_{3,suf}^-$	0.05	[0.466,0.477]	[0.460,0.476]
$k_{4,suf}^+, k_{4,suf}^-$	0.05	[0.0091,0.0136]	[0.00225,0.0344]
k_{int}^+, k_{int}^-	0.05	[0.0272,0.0334]	[0.00225,0.00939]
$D_{O^{2-}}$	0.05	[0.467,0.482]	[0.477,0.481]
$D_{O_{2,ads}}$	0.05	≈ 0	≈ 0
$D_{O_{2,suf}^{2-}}$	0.05	≈ 0	≈ 0
$D_{O_{suf}^{2-}}$	0.05	≈ 0	≈ 0

✓ Surface reaction is more important than interface reaction
✓ Bulk diffusion of oxide ion is also a key step

1. The multiscale approach eliminate free parameters and increases the reliability of the model.

2. Multiscale modeling proves to be successful in simulating the Overpotential-Current density curve for oxygen reduction/oxidation in SOFC/SOEC.

3. Surface reaction is more important than interface reaction, and reduce the surface reaction barriers can greatly enhance the cell efficiency.

4. Bulk diffusion of oxide ions is a key transport step.

Thank you for your attention!

Questions?