A Multiscale Model for the Reactive Mechanisms in Proton / Oxide Ion Conducting Solid Oxide Cells

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Mechanical
SCIENCE AND ENGINEERING

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Outline

- Introduction
- Multiscale Framework
- Model for Oxide Ion Conducting SOCs
  - ✓ Simulation Details
  - ✓ Simulation Results
- Model for Proton Conducting SOCs
  - ✓ Simulation Details
  - ✓ Simulation Results
- Conclusions and Future Work

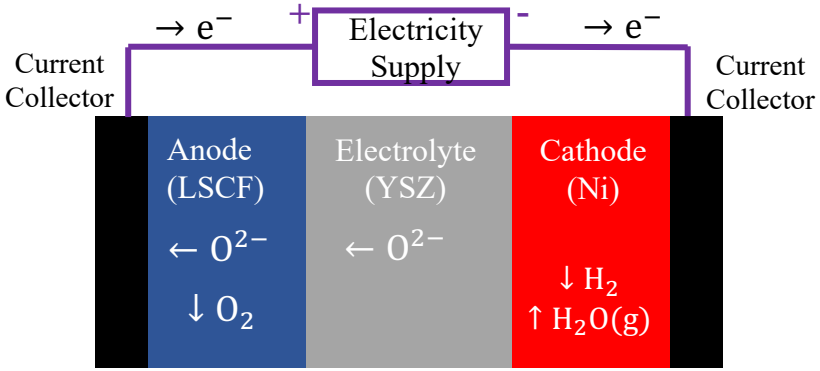
Introduction

Solid oxide electrolysis cell (SOEC)

Oxide ion conducting SOEC

Anode: $O^{2-} \rightarrow 0.5O_2 + 2e^-$

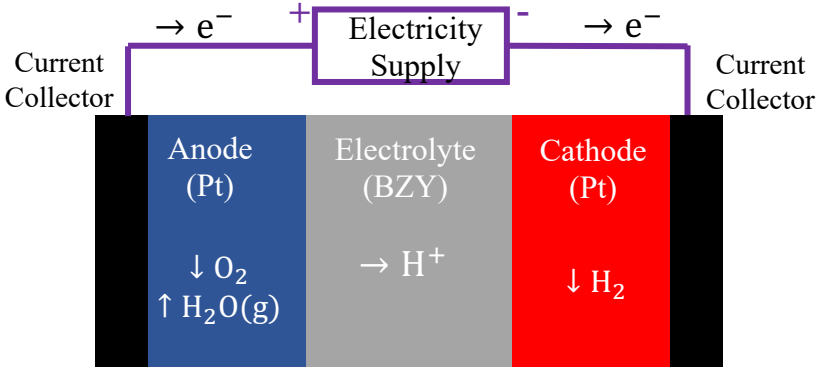
Cathode: $H_2O(g) + 2e^- \rightarrow H_2 + O^{2-}$



Proton conducting SOEC

Anode: $H_2O(g) \rightarrow 0.5O_2 + 2H^+ + 2e^-$

Cathode: $2H^+ + 2e^- \rightarrow H_2$

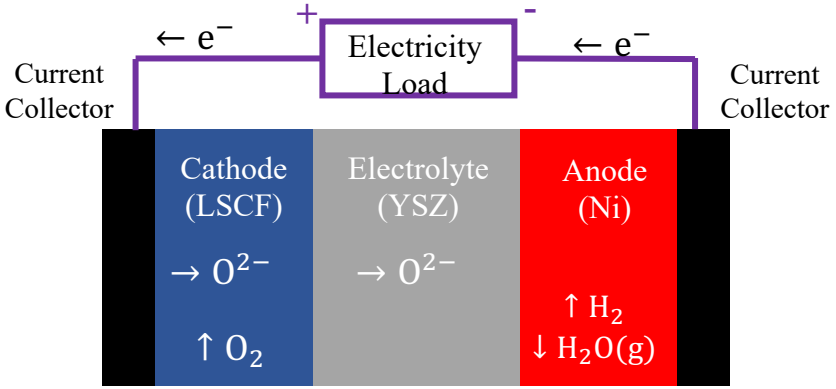


Solid oxide fuel cell (SOFC)

Oxide ion conducting SOFC

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

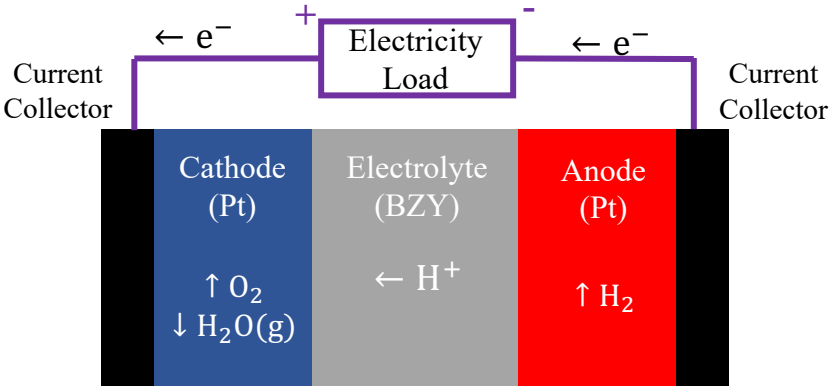
Cathode: $0.5O_2 + 2e^- \rightarrow O^{2-}$



Proton conducting SOFC

Anode: $H_2 \rightarrow 2H^+ + 2e^-$

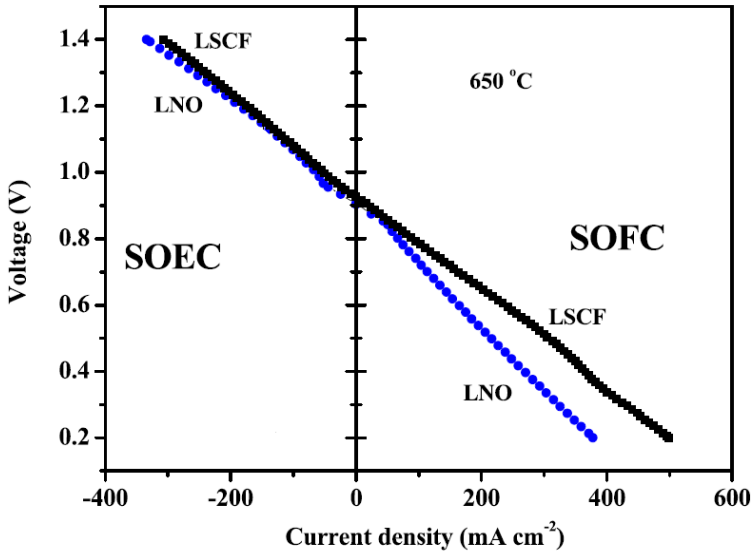
Cathode: $0.5O_2 + 2H^+ + 2e^- \rightarrow H_2O(g)$



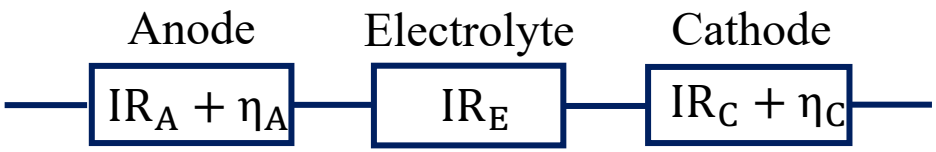
Introduction

Method to evaluate the cell efficiency:

I-V Curve

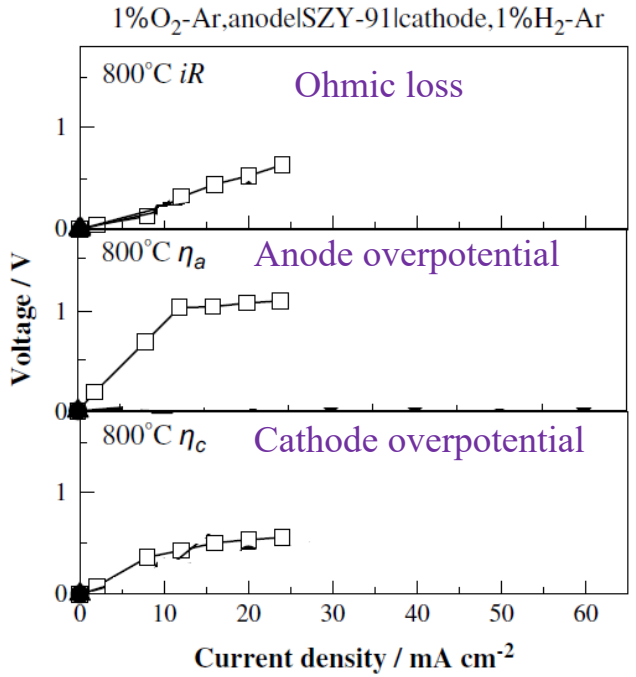


International Journal of Hydrogen Energy 41 (2016) 14497



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.



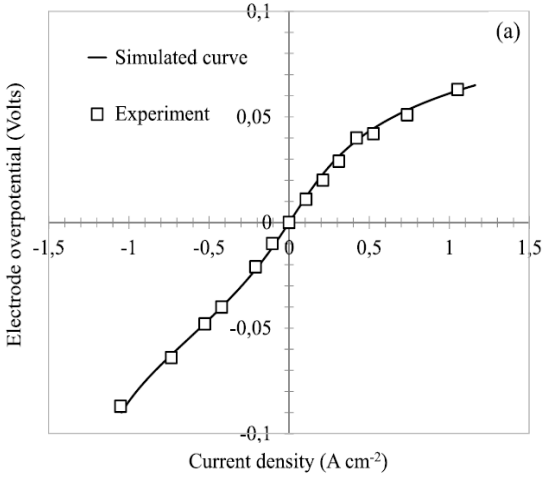
International Journal of Hydrogen Energy 34 (2009) 56–63

Introduction

Why is multiscale model necessary?

- Contradiction between continuum simulation and DFT calculations

- **Continuum simulation**



Parameter:

$D_{O_{suf}^{2-}}^{suf} = 10^{-6} m^2 s^{-1}$

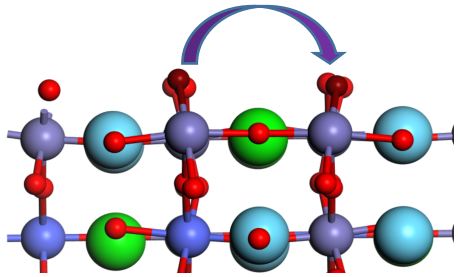
$[\Delta E \approx 0.2 \sim 0.3 ev]$

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

- **DFT calculations**

On Co, Fe terminated LSCF (110) surface

$\Delta E \approx 1.74 \sim 1.9 ev$



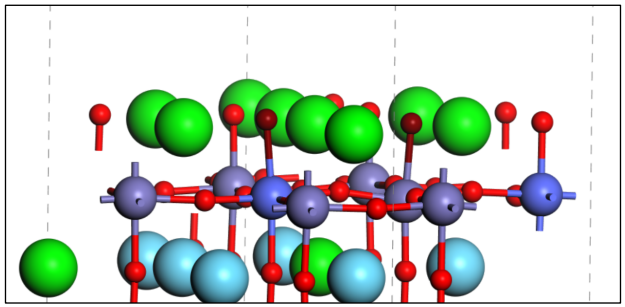
J. Mater. Chem. A, 2013, 1, 12932–12940

Contradiction!!

Reaction steps we are focusing on:

- Oxygen reduction/oxidation reactions in LSCF based oxide ion conducting SOEC/SOFC.
- Overall reactions in Pt/Y-doped BaZrO3/Ag based proton conducting SOFC.

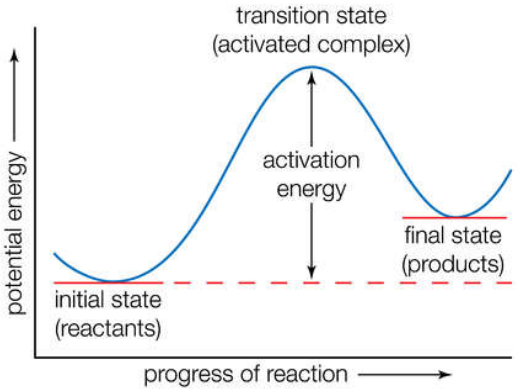
Multiscale Framework



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

↓

Energy barriers ΔE
Vibrational frequencies ν
Transition state positions

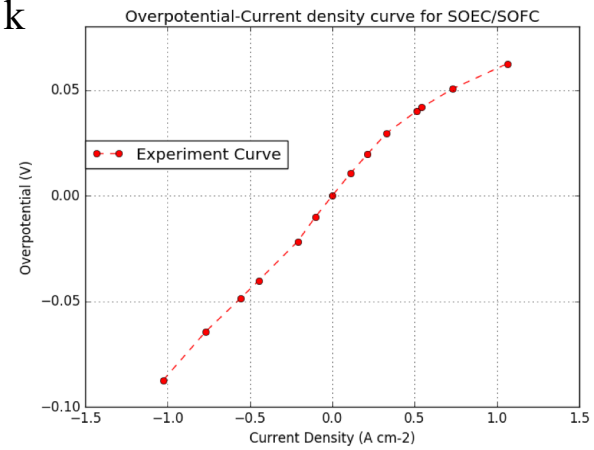


Transition state theory calculations provide the reaction rate constants:

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

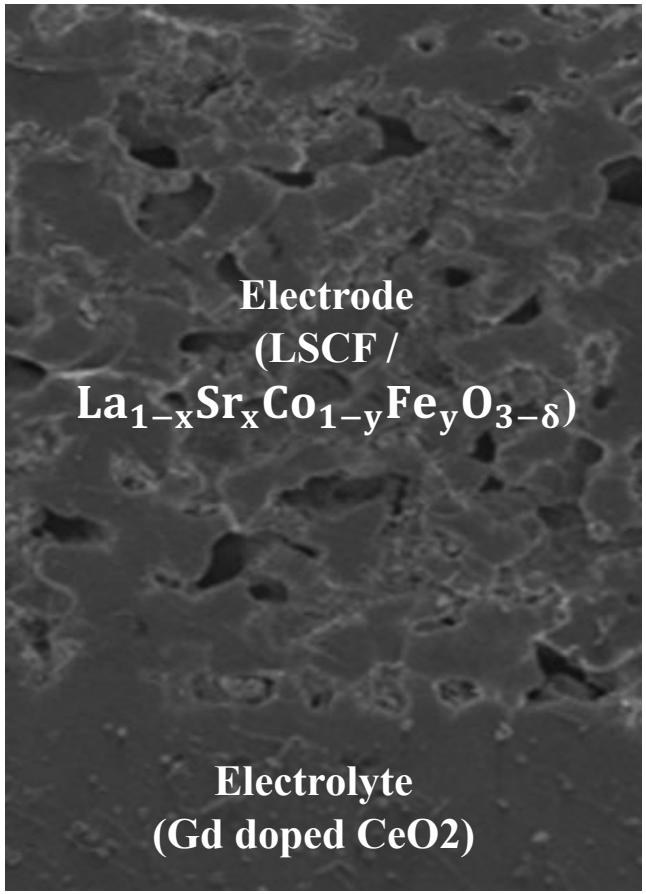
↓

Reaction rate constants k
Diffusivities D

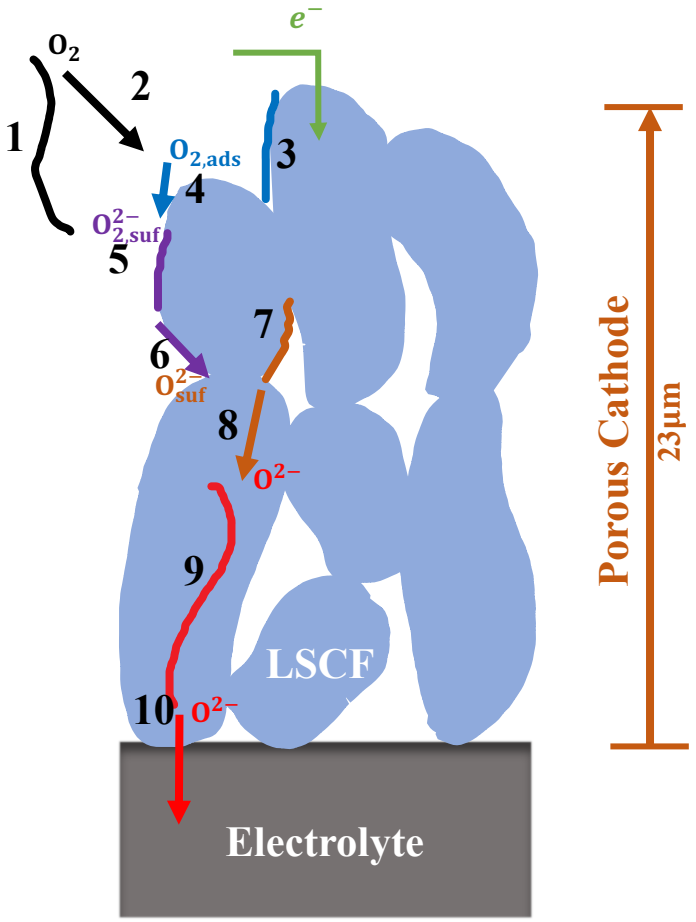


Calculate the Current density-Voltage curve using continuum scale simulation

LSCF based electrode structure



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



$0.5O_2 + 2e^- \rightarrow O^{2-}$
(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 $O_{2,suf}^{2-}$]

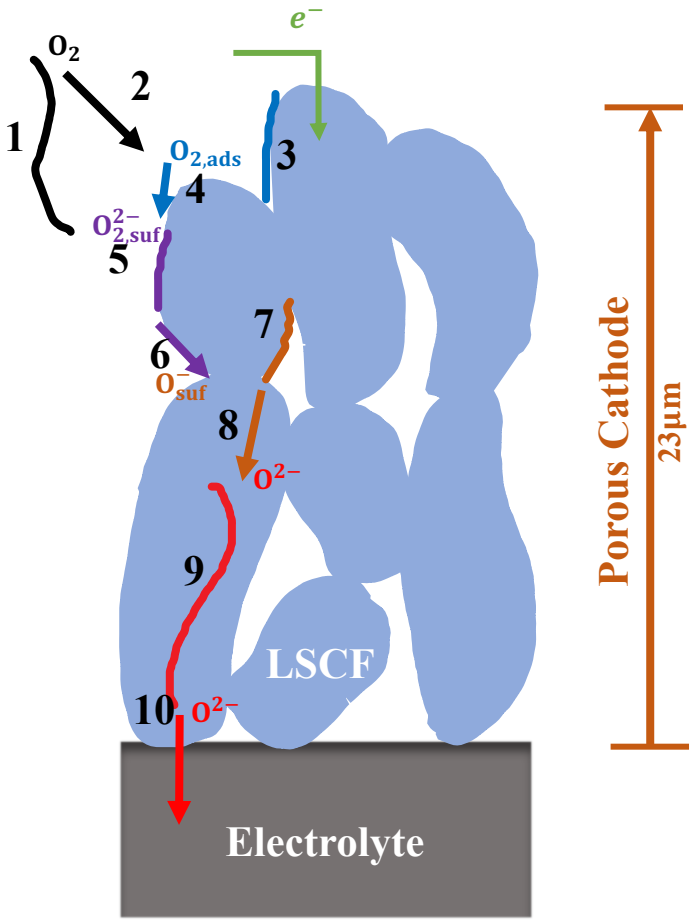
$$O_{2,suf}^{2-} + V_O^{suf,n} \rightarrow 2O_{suf}^{-}$$

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)

Model for Oxide Ion Conducting SOCs

Simulation Details (Continuum Model)

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

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

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

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

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

Expressions for the reaction rates:

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

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

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})

$$r^{int}_{R5}=A_{int}\left\{k^{+}_{5,int}\exp\left(\frac{-0.5F\eta}{RT}\right)C_{V^{int}_{O}}\frac{C_{O^{2-}}}{C^{max}_{O^{2-}}}-k^{-}_{5,int}\exp\left(\frac{0.5F\eta}{RT}\right)C_{O^{2-}_{int}}\frac{C_{V_O}}{C^{max}_{O^{2-}}}\right\}$$

Physical parameters in the model:

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

Model for Oxide Ion Conducting SOCs

Simulation Details (Transition State Theory)

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

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

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

$\Delta G(T)$

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

$\Delta G(C)$

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

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

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

$$F^{electronic} = \mathbf{E_0}$$

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

- The ground state energies $\mathbf{E_0}$ are to be calculated with DFT+U calculations
- The vibrational frequencies $\mathbf{\nu_m}$ are to be calculated with finite displacement method

Model for Oxide Ion Conducting SOCs
Simulation Details (DFT+U Simulation)

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: $E_{V_O} = [0.94,1.03]eV$

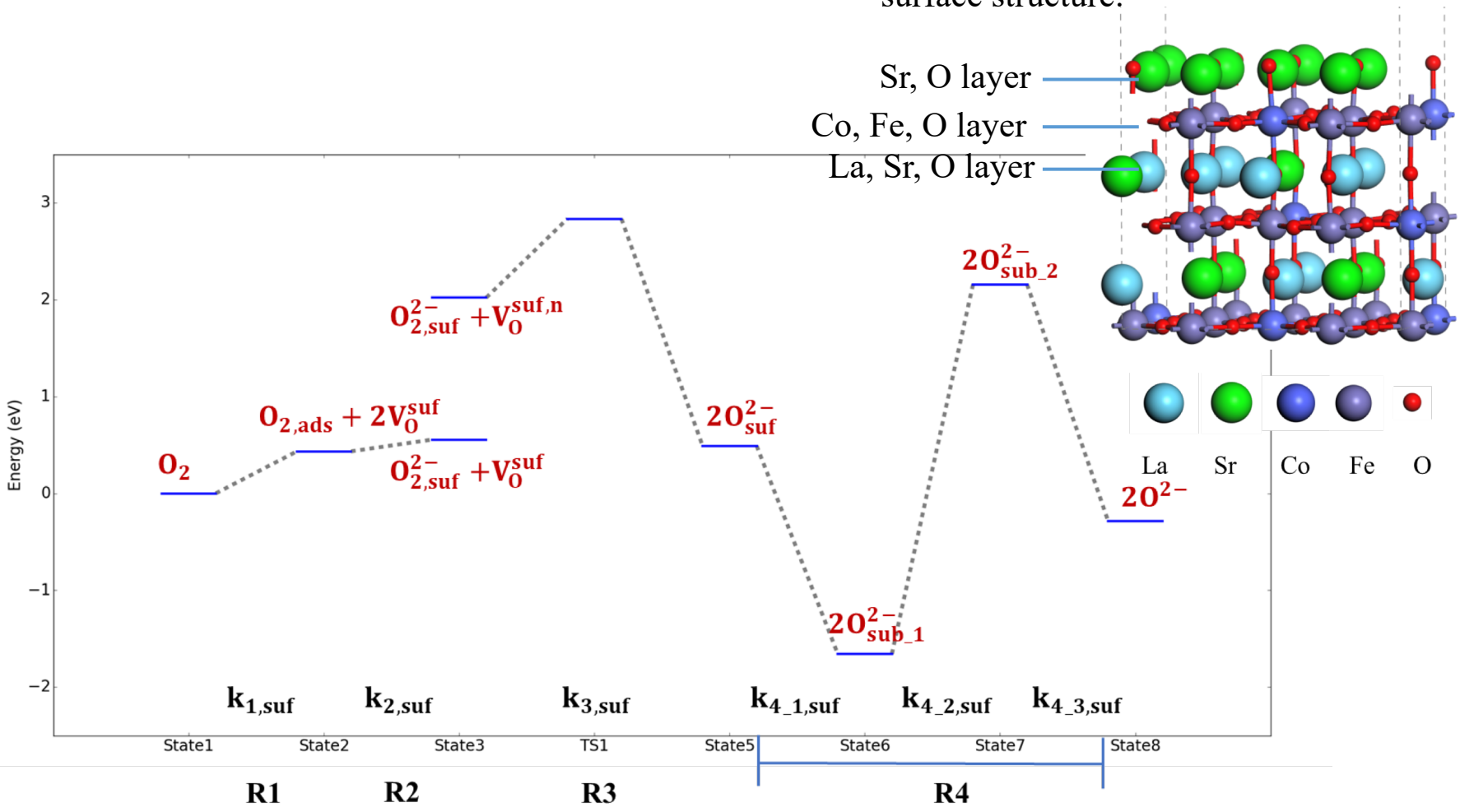
dE	Article
1.036eV	Bucher et al.
0.777eV	Gryaznov et al.
1.14eV	Mizusaki et al.
1.14eV	Wachsman et al.
1.55eV	Jun et al.

Experimental vacancy formation energy results

◆ **DFT+U results are consistent with experimental results**

Free energy profile for reaction $O_2 + 4e^- + 2V_O \rightarrow 2O^{2-}$

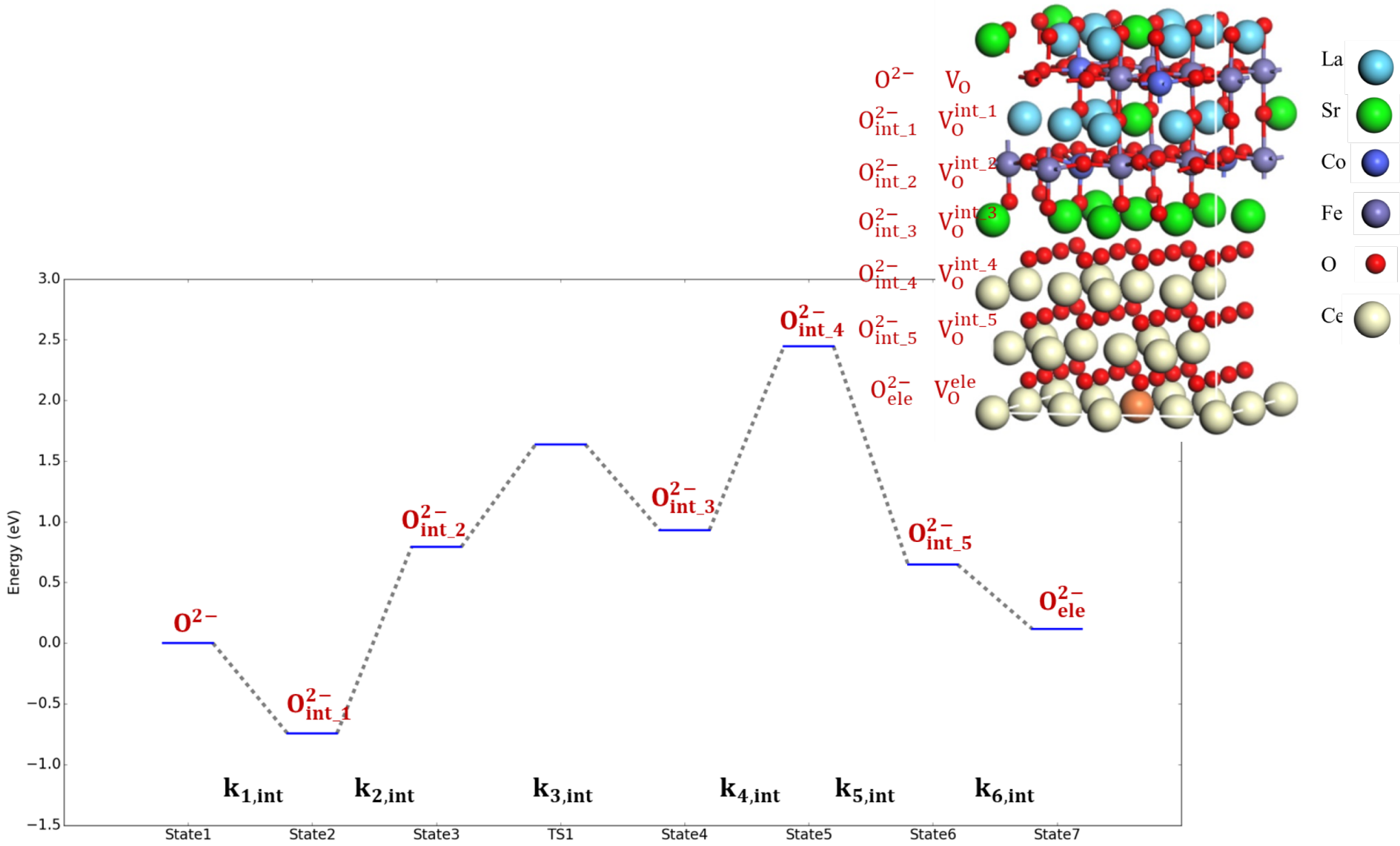
LSCF ($La_{0.6}Sr_{0.4}Co_{0.25}Fe_{0.75}O_{3-\delta}$) 100 surface structure:



Model for Oxide Ion Conducting SOCs

Simulation Details (DFT+U Simulation)

Free energy profile for reaction $O^{2-} + V_O^{ele} \rightarrow O_{ele}^{2-} + V_O$

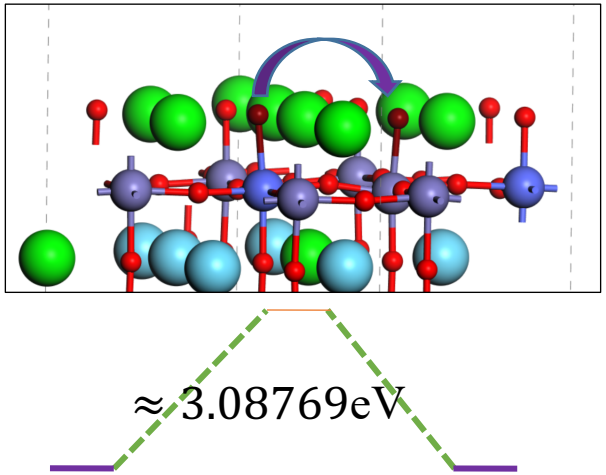


Reaction rate constants in oxide ion conducing cell

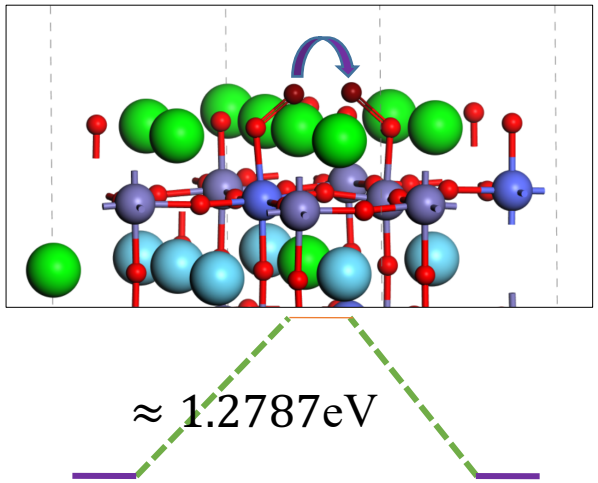
Parameters	$\Delta E(0)(eV)$	$\Delta G(T) - \Delta E(0)(eV)$	$\Delta G(T)(eV)$	Values (s^{-1})
$k^{+}_{1,suf}$	-0.7	1.1337	0.4337	2.06198×10^{11}
$k^{-}_{1,suf}$	0	0	0	2.2347×10^{13}
$k^{+}_{2,suf}$	-0.615	0.7364	0.1214	6.06167×10^{12}
$k^{-}_{2,suf}$	0	0	0	2.2347×10^{13}
$k^{+}_{3,suf}$	0.653	0.16083	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}

Surface diffusivities in oxide ion conducing cell

Diffusion of O^{-}_{suf}



Diffusion of $O^{2-}_{2,suf}$



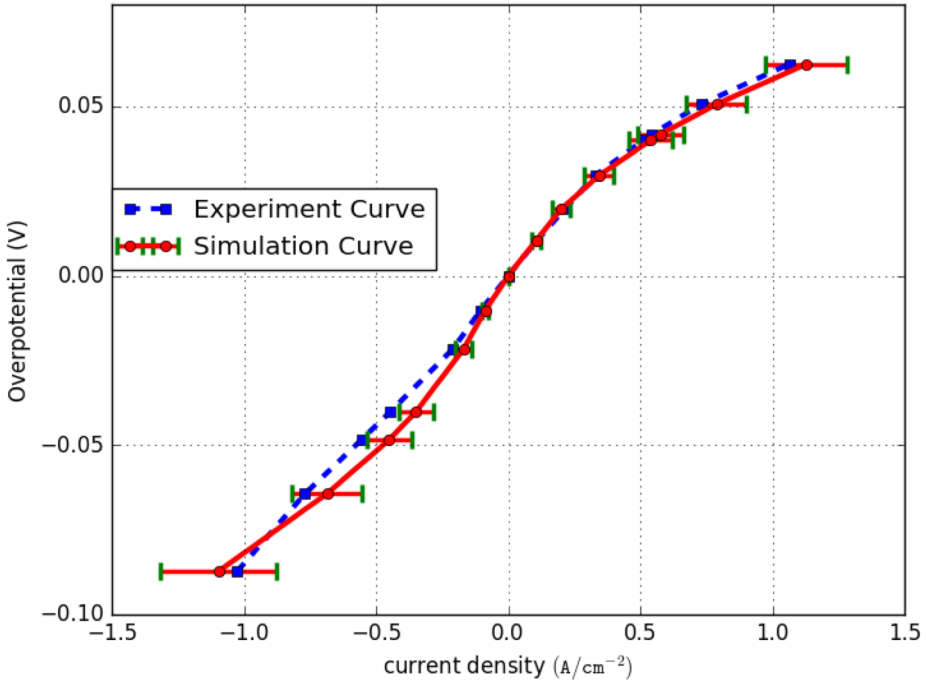
$$D = \frac{\lambda^2}{4}\frac{k_B T}{h}\exp\left(-\frac{\Delta G(T)}{k_B T}\right)$$

◆ **Diffusivity on the LSCF surface is very small**

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

Model for Oxide Ion Conducting SOCs

Simulation Results



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

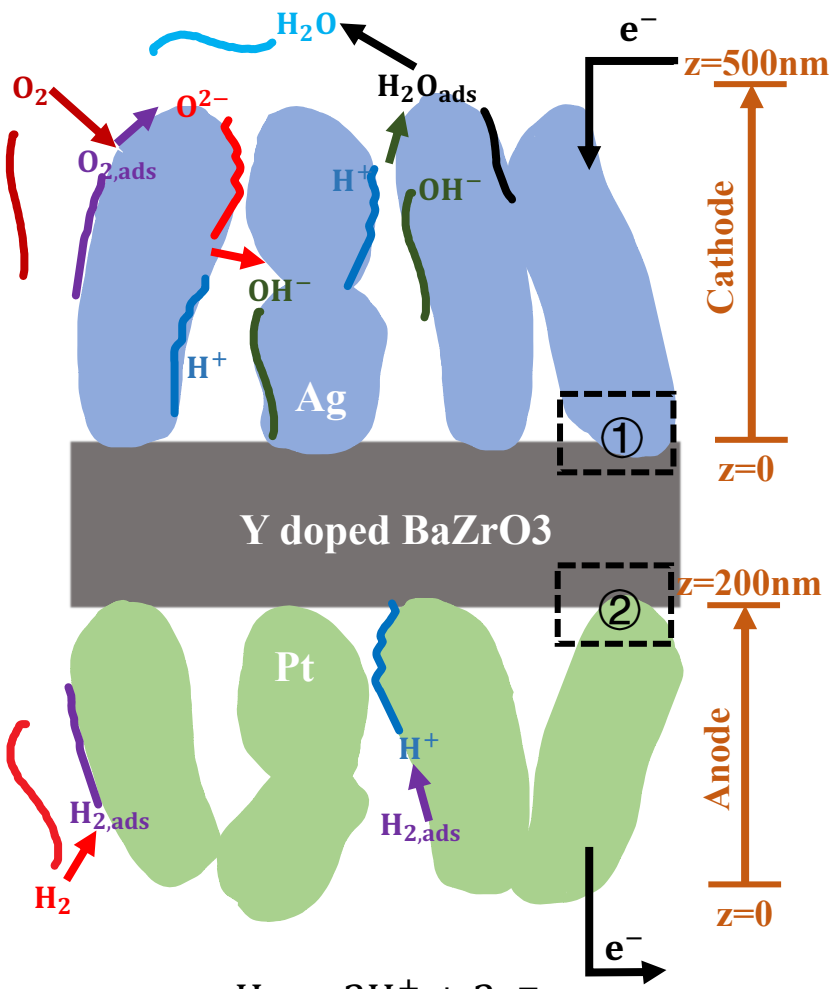
$$S_e = \frac{\partial I/I}{\partial P_a/P_a} \approx \frac{\Delta I/I}{\Delta P_a/P_a}$$

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
$D_{O^{2-}_{2,suf}}$	0.05	≈ 0	≈ 0
$D_{O^{2-}_{suf}}$	0.05	≈ 0	≈ 0

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

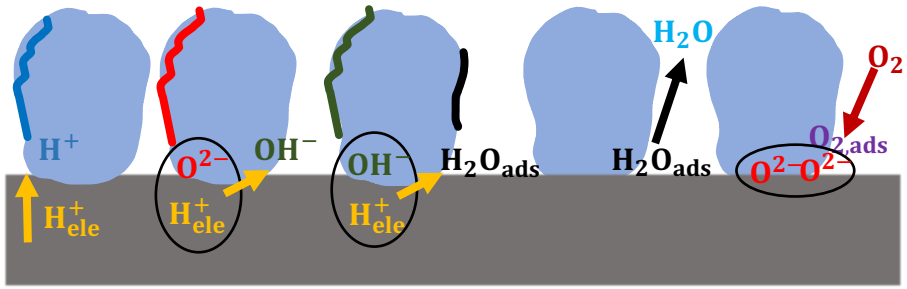
Pt/Y-doped BaZrO3/Ag based proton conducting cell structure

$$0.5O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

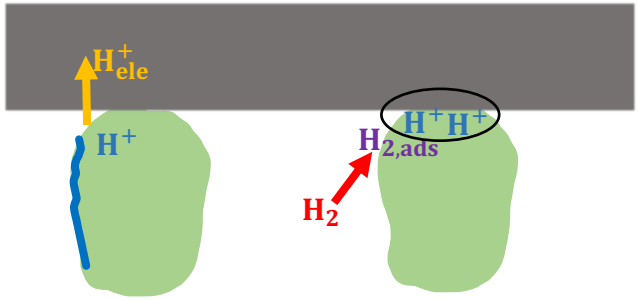


$$H_2 \rightarrow 2H^+ + 2e^-$$

① Reactions at cathode-electrolyte TPB



② Reactions at anode-electrolyte TPB



Model for Proton Conducting SOCs
Simulation Details (Continuum Model)

$$U = \eta_A + IR(\text{electrolyte}) + \eta_C$$

In **Ω0,** $i = H_2, H_{2,ads}, H^+$

$$\frac{d}{dz}\left[-\frac{\phi}{\tau} D_i \frac{dC_i}{dz}\right] = r_i^{\Omega 0}$$

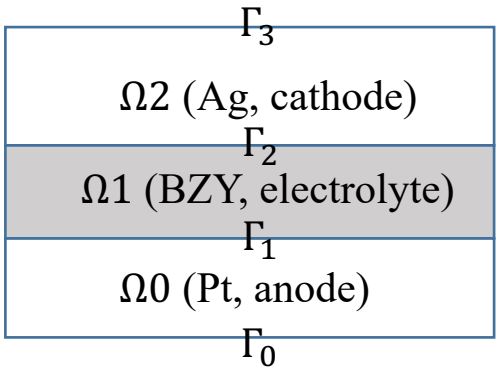
On $\boldsymbol{\Gamma_1}$

$$-D_i \frac{dC_i}{dz} = r_i^{\Gamma_1}$$

(TPB reaction rates, $r_i^{\Gamma_1} = f(\eta_A)$)

On $\boldsymbol{\Gamma_0}$

$$C_{H_2}|_{\Gamma_0} = \text{const}, \frac{dC_i}{dz}|_{\Gamma_0} = 0 \text{ for } i = H_{2,ads}, H^+$$



- For example:

$$r_{H^+}^{\Omega 0} = 2r_{H_{2,ads}\rightarrow 2H^+}^{\Omega 0}$$

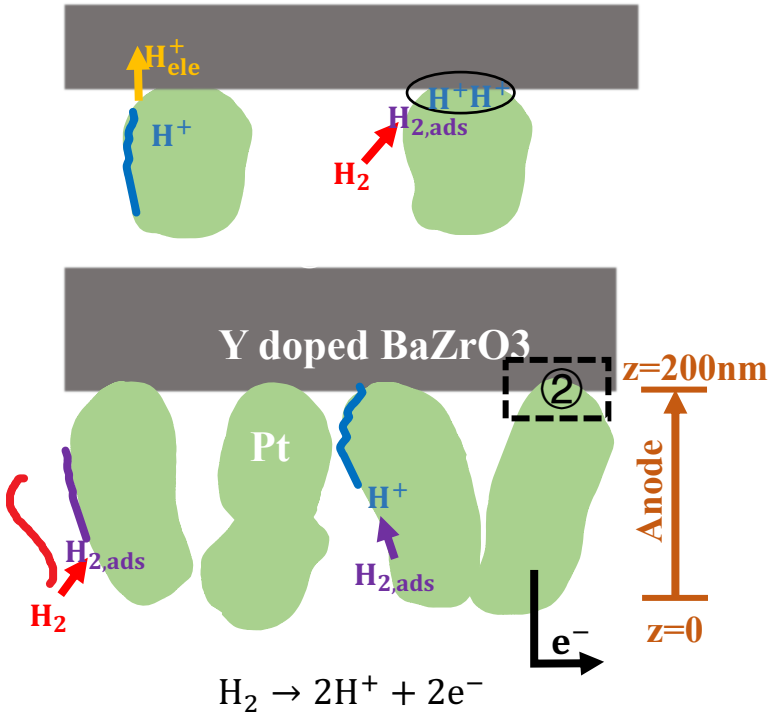
$$= 2A_{suf}\left\{k^+_{H_{2,ads}\rightarrow 2H^+} C_{H_{2,ads}} - k^-_{H_{2,ads}\rightarrow 2H^+}(C_{H^+})^2\right\}$$

$$r_{H^+}^{\Gamma_1} = 2r_{H_{2,ads}\rightarrow 2H^+}^{\Gamma_1} - r_{H^+\rightarrow H^+_{\Gamma_1}}^{\Gamma_1}$$

$$= 2A^a_{TPB}\left\{k^+_{H_{2,ads}\rightarrow 2H^+} C_{H_{2,ads}} - k^-_{H_{2,ads}\rightarrow 2H^+}(C_{H^+})^2\right\}$$

$$-A^a_{TPB}\left\{k^+_{H^+\rightarrow H^+_{\Gamma_1}} \exp\left(\frac{-(1-\alpha)F\eta_A}{RT}\right) C_{H^+} - k^-_{H^+\rightarrow H^+_{\Gamma_1}} \exp\left(\frac{\alpha F\eta_A}{RT}\right) C_{H^+_{ele}}\right\}$$

② Reactions at cathode-electrolyte TPB



$$H_2 \rightarrow 2H^+ + 2e^-$$

Model for Proton Conducting SOCs
Simulation Details (Continuum Model)

$$U = \eta_A + IR(\text{electrolyte}) + \eta_C$$

In **Ω2,** $i = O_2, O_{2,ads}, H_2O, H_2O_{ad}, O^{2-}, H^+, OH^-$

$$\frac{d}{dz}\left[-\frac{\phi}{\tau} D_i \frac{dC_i}{dz}\right] = r_i^{\Omega 2}$$

On $\boldsymbol{\Gamma_2}$

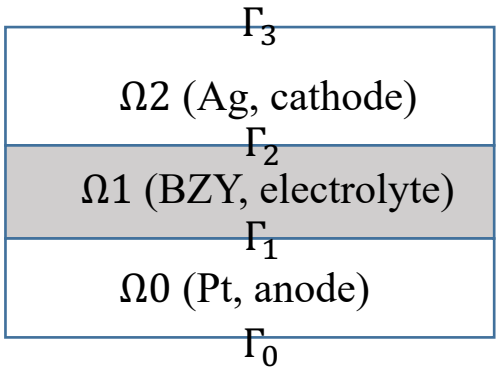
$$-D_i \frac{dC_i}{dz} = r_i^{\Gamma_2}$$

(TPB reaction rates, $r_i^{\Gamma_2} = f(\eta_C)$)

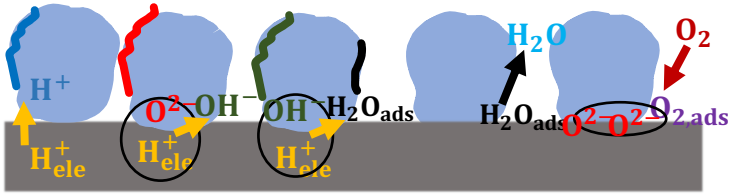
On $\boldsymbol{\Gamma_3}$

$$C_{H_2O}, C_{O_2}|_{\Gamma_3} = \text{const},$$

$$\frac{dC_i}{dz}|_{\Gamma_3} = 0 \text{ for } i = O_{2,ads}, H_2O_{ad}, O^{2-}, H^+, OH^-$$



① Reactions at anode-electrolyte TPB



- For example:

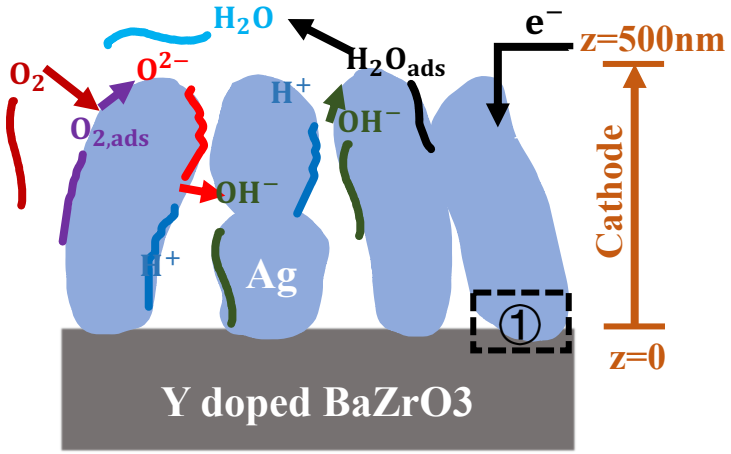
$$r_{O^{2-}}^{\Omega 2} = 2r_{O_{2,ads}\rightarrow 2O^{2-}}^{\Omega 2} - r_{O^{2-}+H^+\rightarrow OH^-}^{\Omega 2}$$

$$r_{O^{2-}}^{\Gamma_2} = 2r_{O_{2,ads}\rightarrow 2O^{2-}}^{\Gamma_2} - r_{O^{2-}+H_{ele}^+\rightarrow OH^-}^{\Gamma_2}$$

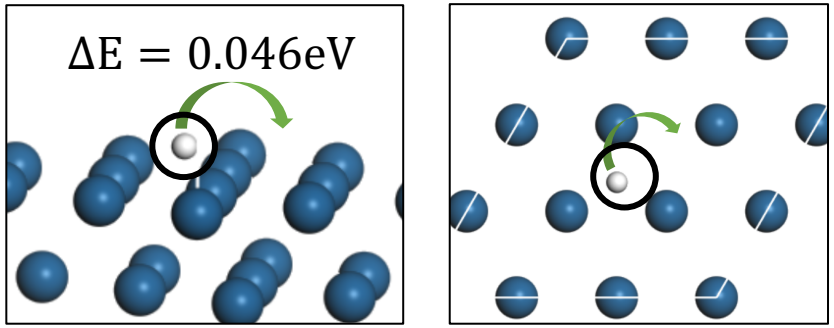
$$= 2A_{TPB}^c \left\{k_{O_{2,ads}\rightarrow 2O^{2-}}^+ C_{O_{2,ads}} - k_{O_{2,ads}\rightarrow 2O^{2-}}^- (C_{O^{2-}})^2\right\}$$

$$-A_{TPB}^c \left\{k_{O^{2-}+H_{ele}^+\rightarrow OH^-}^+ \exp\left(\frac{-(1-\alpha)F\eta_C}{RT}\right) C_{O^{2-}} C_{H_{ele}^+} - k_{O^{2-}+H_{ele}^+\rightarrow OH^-}^- \exp\left(\frac{\alpha F\eta_C}{RT}\right) C_{OH^-}\right\}$$

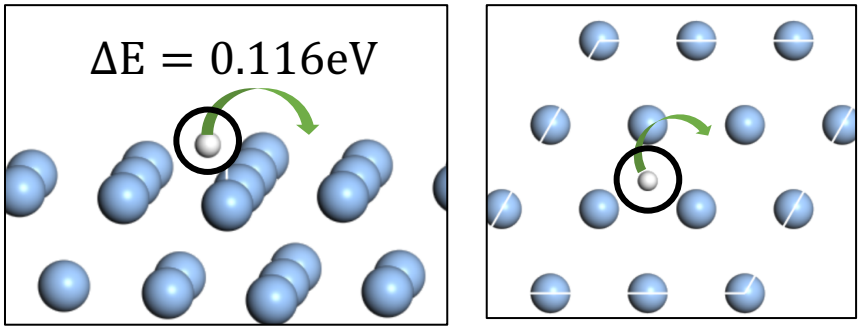
$$0.5O_2 + 2H^+ + 2e^- \rightarrow H_2O$$



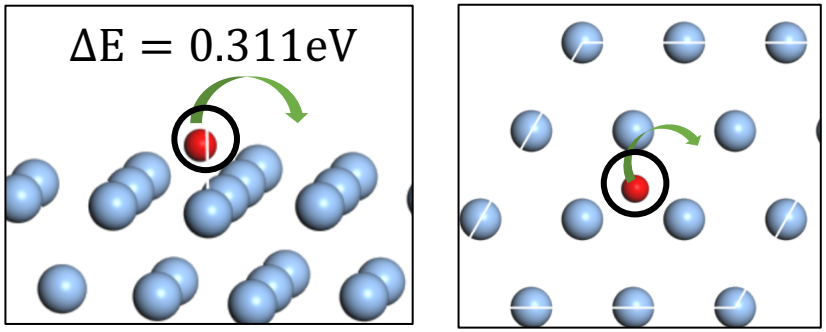
Diffusion energy barriers



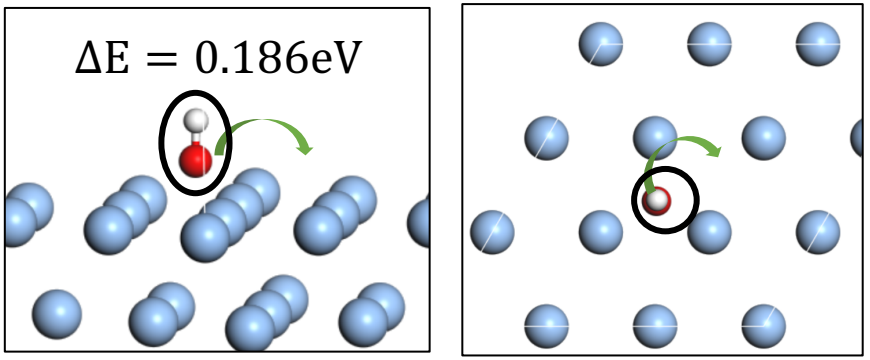
Diffusion of H^+ on Pt surface



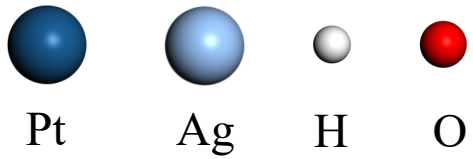
Diffusion of H^+ on Ag surface



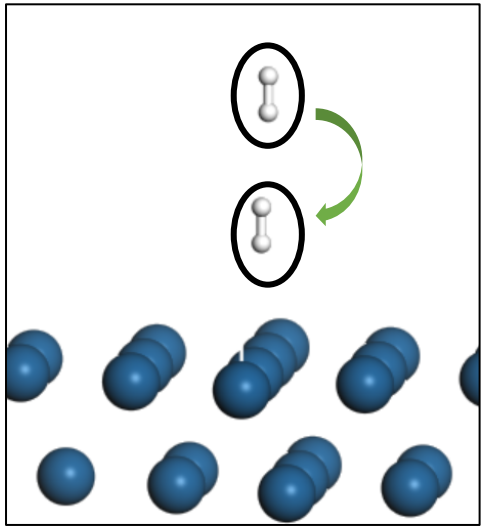
Diffusion of O^{2-} on Ag surface



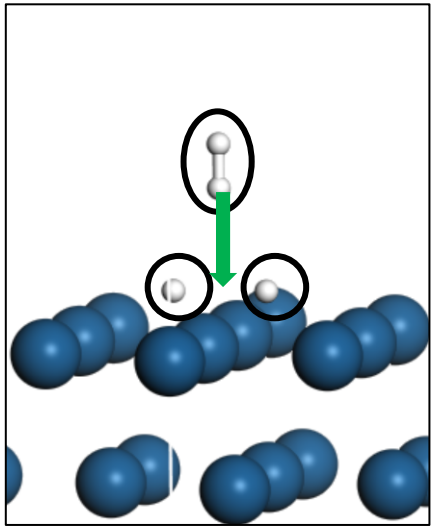
Diffusion of OH^- on Ag surface



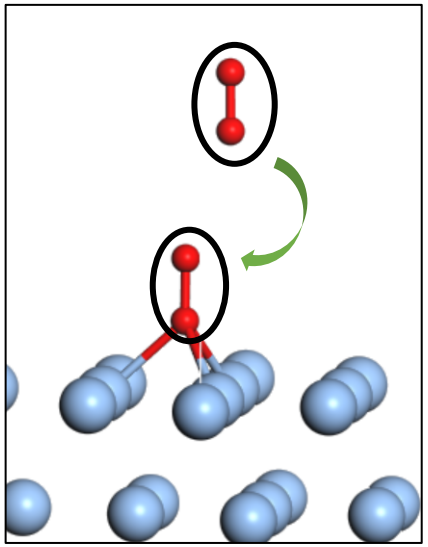
Reaction energy barriers on metal surface



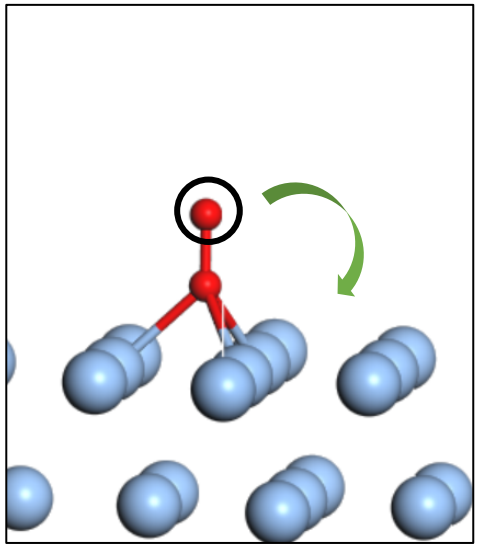
$H_2 \rightarrow H_{2,ads}$



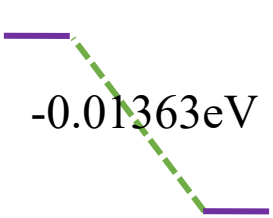
$H_{2,ads} \rightarrow 2H^+ + 2e^-$



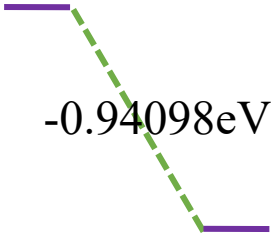
$O_2 \rightarrow O_{2,ads}$



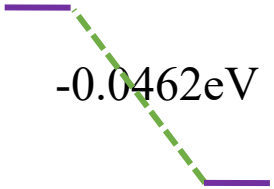
$O_{2,ads} + 4e^- \rightarrow 2O^{2-}$



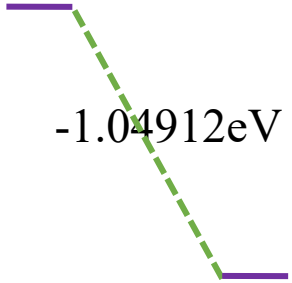
-0.01363eV



-0.94098eV

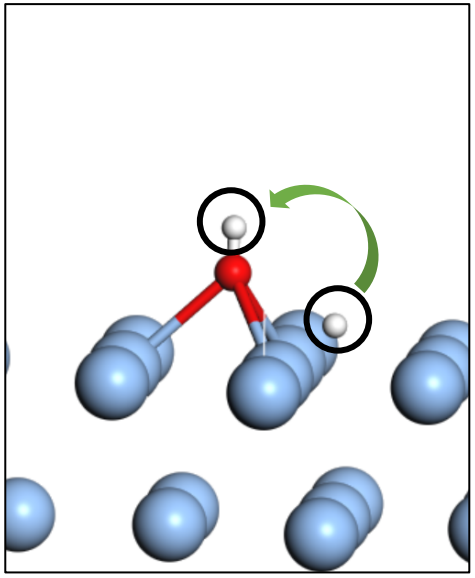


-0.0462eV

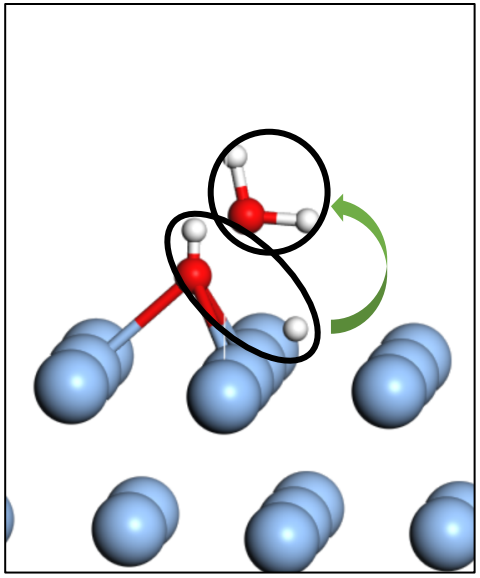


-1.04912eV

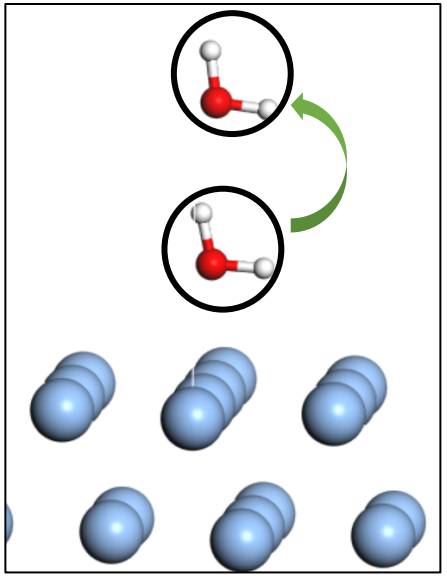
Reaction energy barriers on metal surface



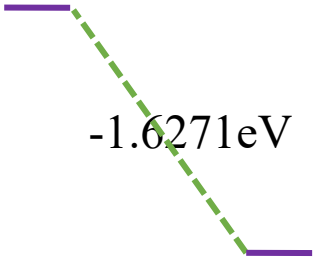
$H^+ + O^{2-} \rightarrow OH^-$

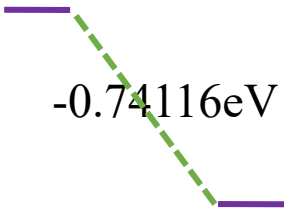


$H^+ + OH^- \rightarrow H_2O_{ad}$

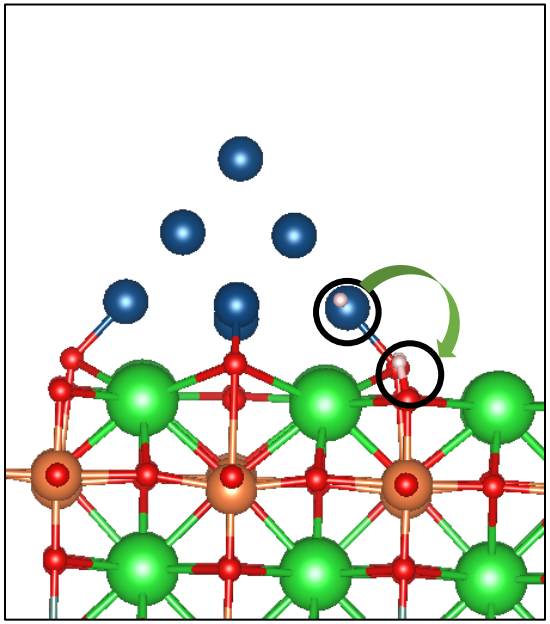


$H_2O_{ad} \rightarrow H_2O$



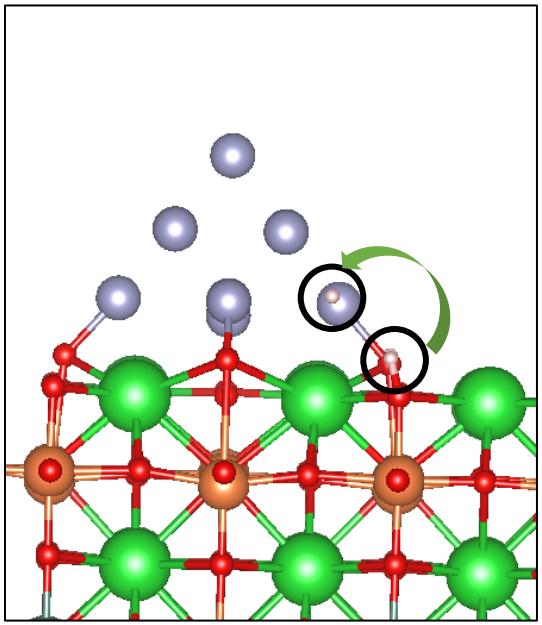


Reaction energy barriers across metal/BZY TPB



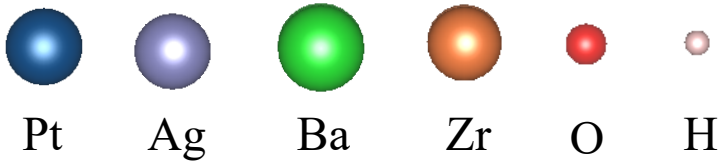
$H^+_{Pt} \rightarrow H^+_{ele}$

-0.3845eV

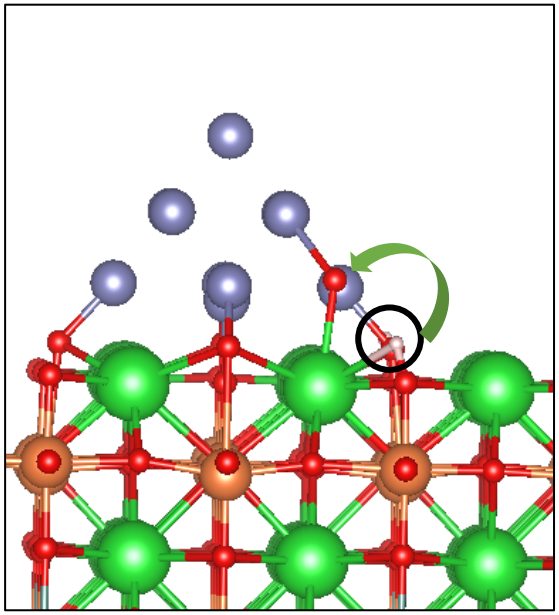


$H^+_{ele} \rightarrow H^+_{Ag}$

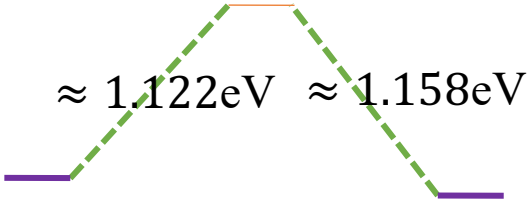
0.983465eV

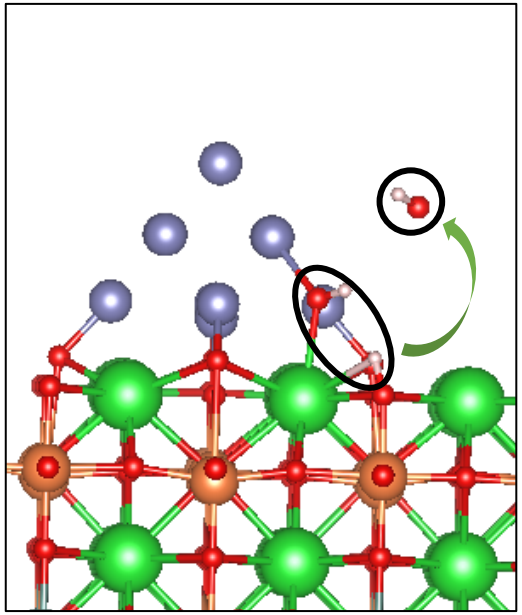


Reaction energy barriers across metal/BZY TPB

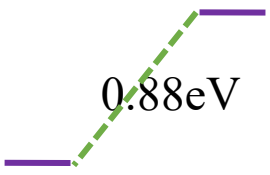


$H^+_{ele} + O^{2-} \rightarrow OH^-$

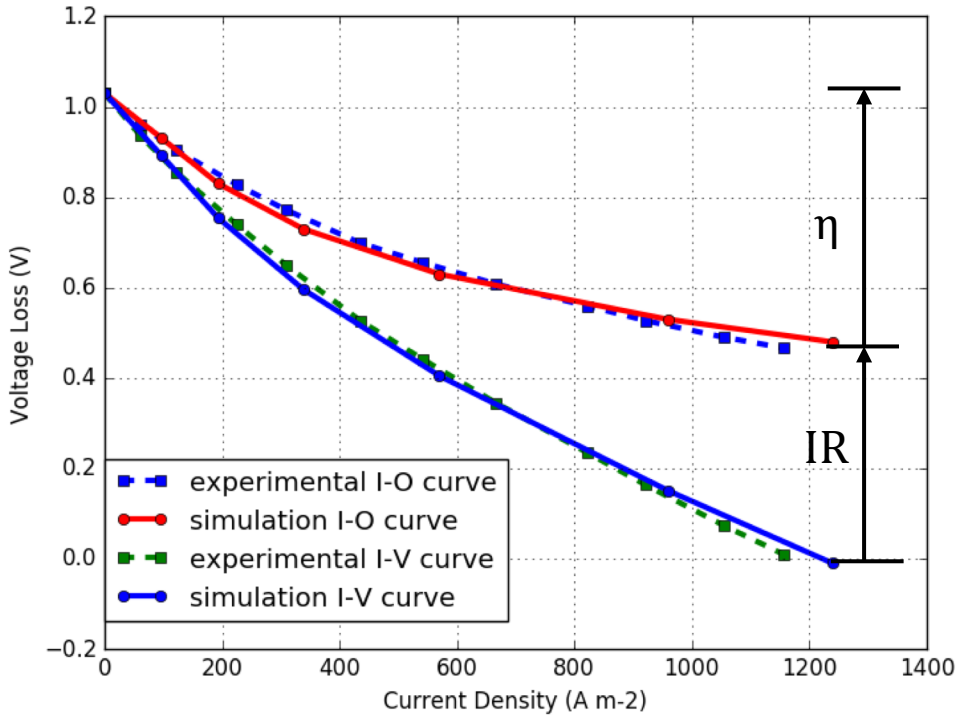




$H^+_{ele} + OH^- \rightarrow H_2O_{ad}$



Model for Proton Conducting SOCs
Simulation Results



Parameters	Experimental Values
A_{suf} (surface area per volume)	$5\mu m^2/\mu m^3$
A^c_{TPB} (cathode/electrolyte TPB area)	2.9 $\mu m/\mu m^2$
A^a_{TPB} (anode/electrolyte TPB area)	3.45 $\mu m/\mu m^2$
ϕ_{gas} (porosity of gas phase)	0.4
ϕ_{metal} (porosity of metal)	0.6
τ (tortuosity)	1.46

- Overpotential and the Ohmic loss have the same order of magnitude.
- Simulation results are consistent with experimental results.

Conclusions and Future Work

Conclusions:

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

2. Multiscale modeling proves to be successful in simulating the Voltage loss-Current density relation for oxide ion / proton conducting SOEC/SOFC.

Future Work:

1. Solve the whole continuum model in a more compact way.

2. Calculate $\Delta G(C)$ term for specific reaction steps from simulation.

Thank you for your attention!

Questions?