Microstructure-Based Modeling of Inner Oxygen Pressure in Solid Oxide Electrolysis Cells

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Delamination of LSM-Based Oxygen Electrode

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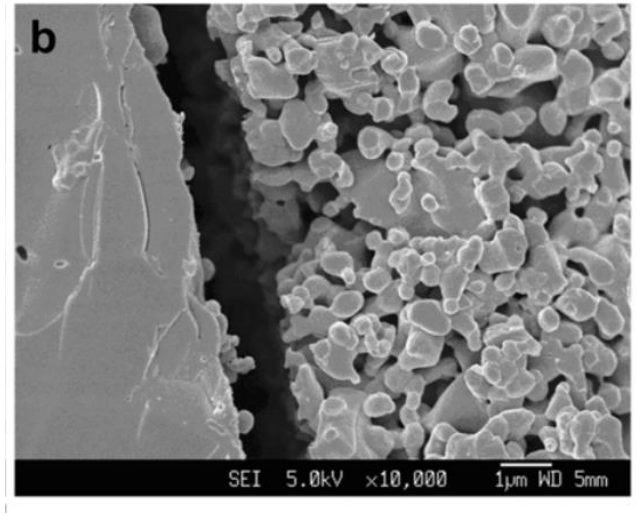
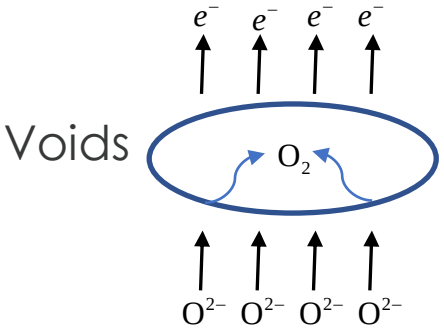
LSM delamination under electrolysis



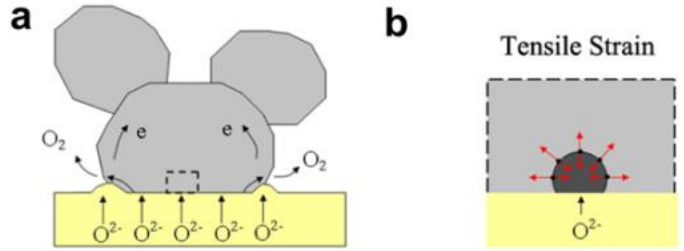
Two popular mechanisms

Inner oxygen pressure

$$\frac{1}{2}O_2 + 2e' \leftrightarrow O^{2-}$$



Lanthanum strontium manganate (LSM) lattice shrinkage due to oxygen vacancy accumulation



The first mechanism becomes dominant in recent years, which explains some experimental results.

The stress from the second mechanism is not large enough to cause delamination even if the oxygen vacancy concentration is extreme high.

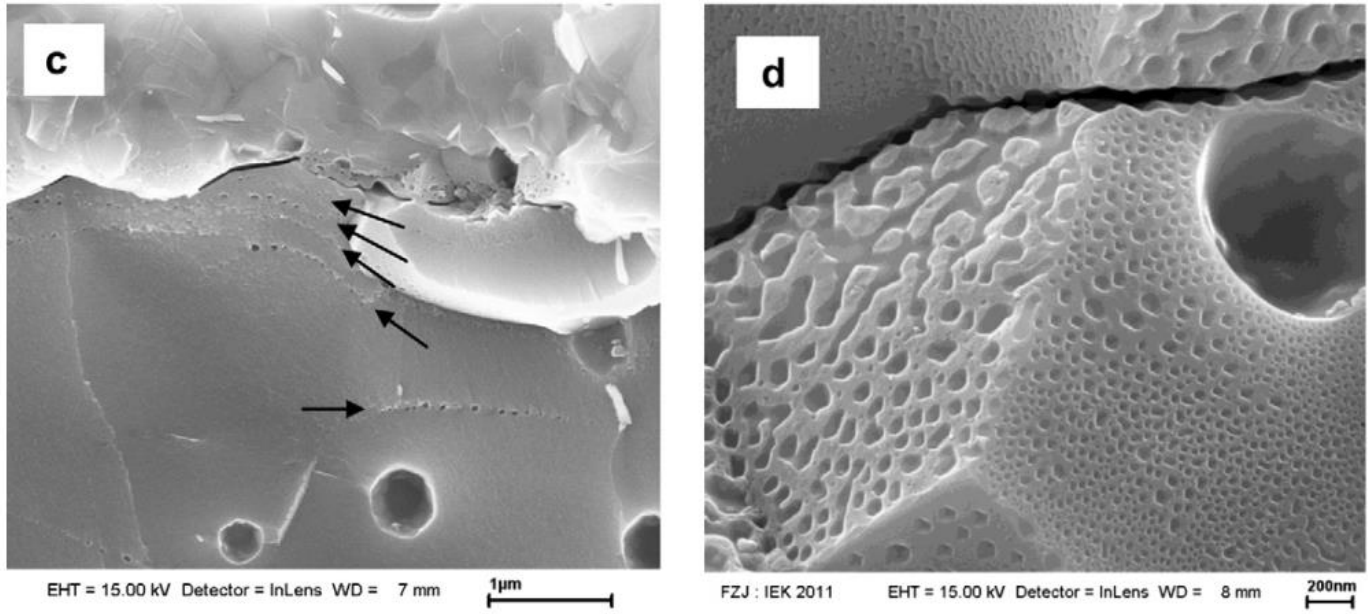
Int. J. Hydrogen Energy 36 (2011) 10541.

Mechanical Degradation in LSCF-Based Cells

NATIONAL ENERGY TECHNOLOGY LABORATORY

Pore formation in YSZ

Intergranular fracture in YSZ

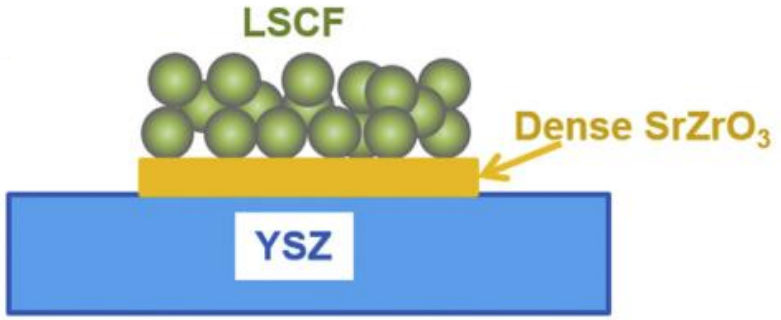


Journal of Power Sources 223 (2013) 129-135.

LSCF: lanthanum strontium cobalt ferrite.
YSZ: yttria stabilized zirconia.

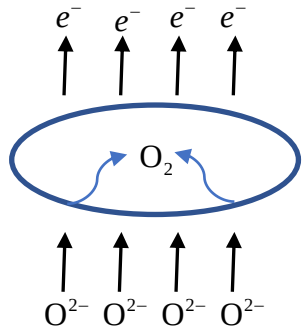
Two popular mechanisms

Formation of secondary phases



Inner oxygen pressure

Voids



Pore formation, intergranular fracture in electrolyte, and electrode delamination are observed.

International Journal of Hydrogen Energy 43, no. 11 (2018): 5437-5450.

Extend Virkar's Model by Incorporating the Microstructures

The key idea of Virkar's model: the electronic current within the electrolyte should be considered.

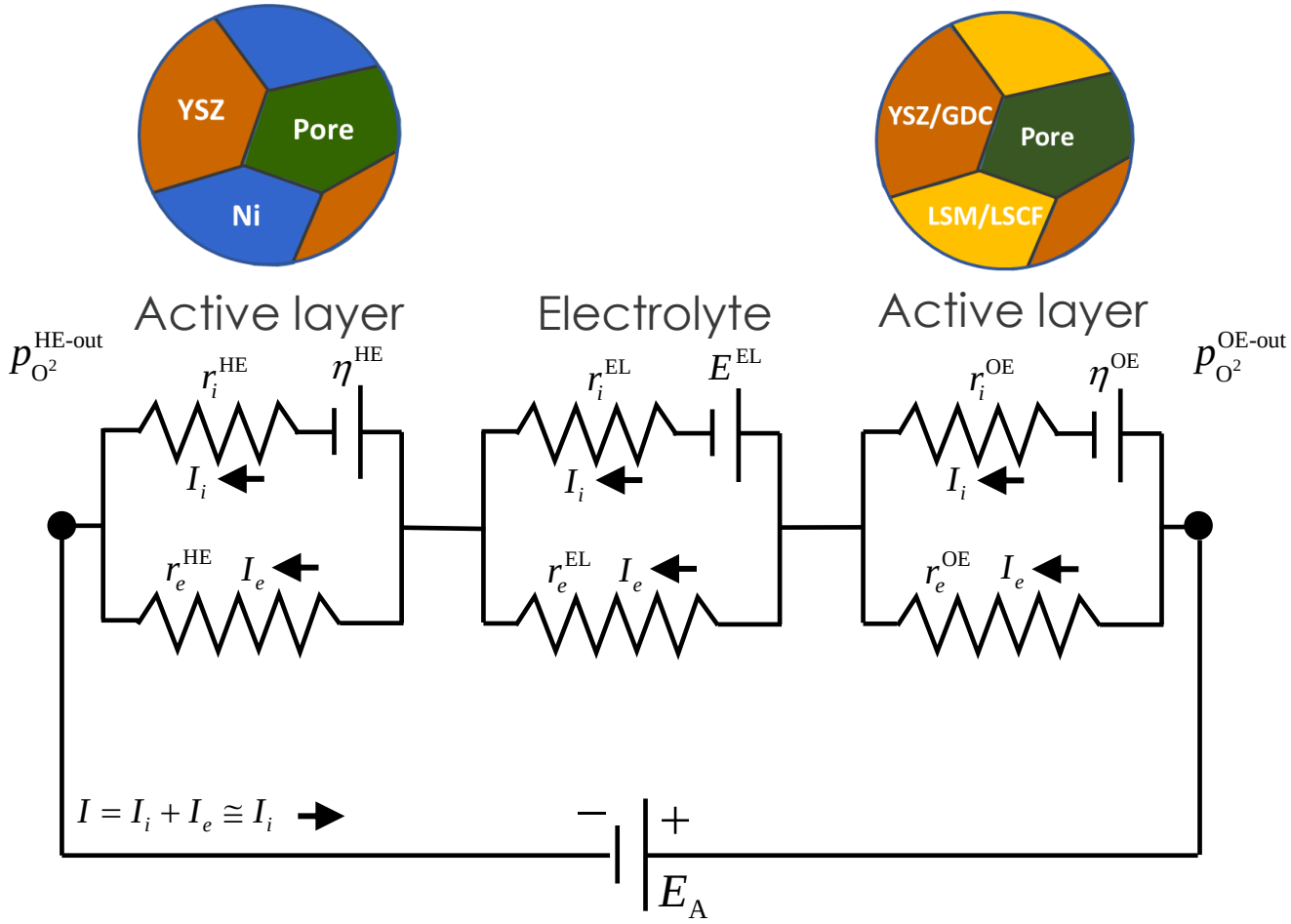
A. V. Virkar, Int. J. Hydrogen Energy, 35, 9527 (2010)

The inner oxygen pressure can be calculated based on the chemical equilibrium of:

$$\frac{1}{2}\mathrm{O}_2 + 2e' \leftrightarrow \mathrm{O}^{2-}$$

Advantages of Yinkai's model:

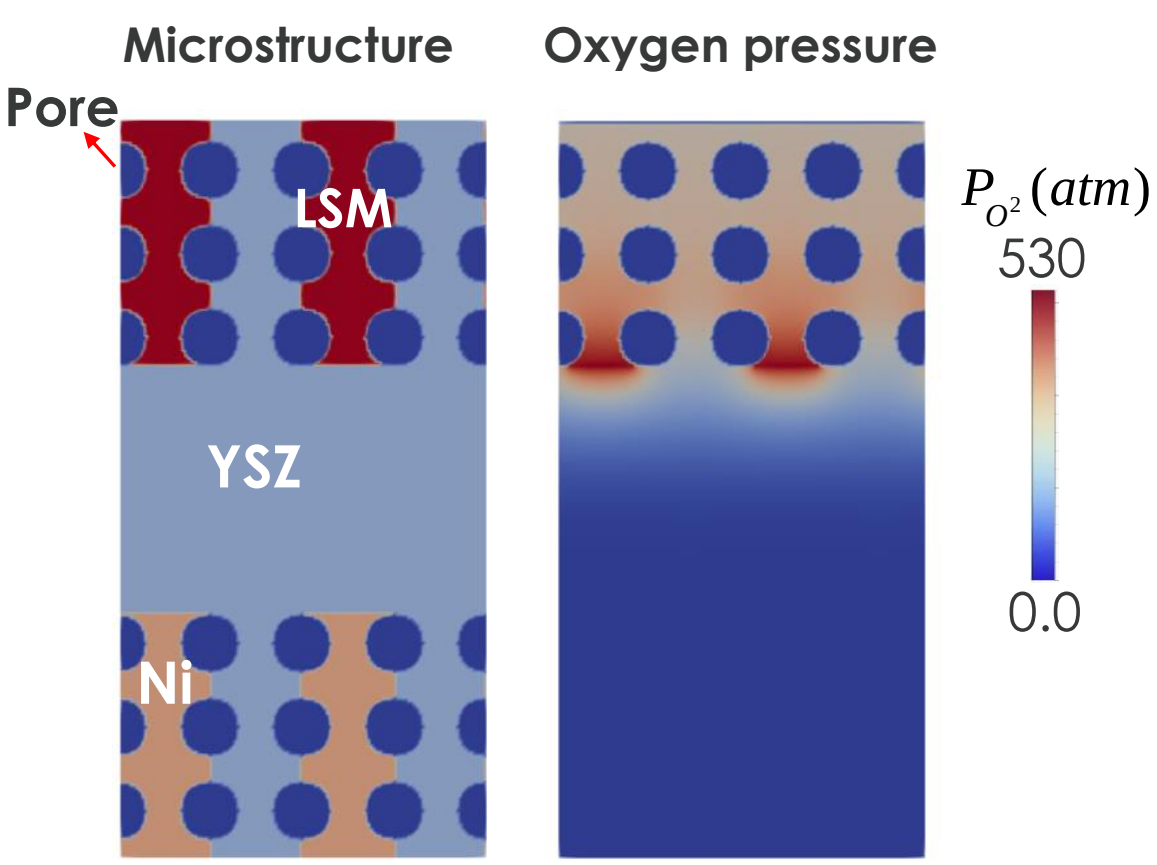
- The microstructures are considered
- Chemical reactions at triple-phase-boundaries (TPBs) and 2-phase-boundaries are described by Butler-Volmer Equations



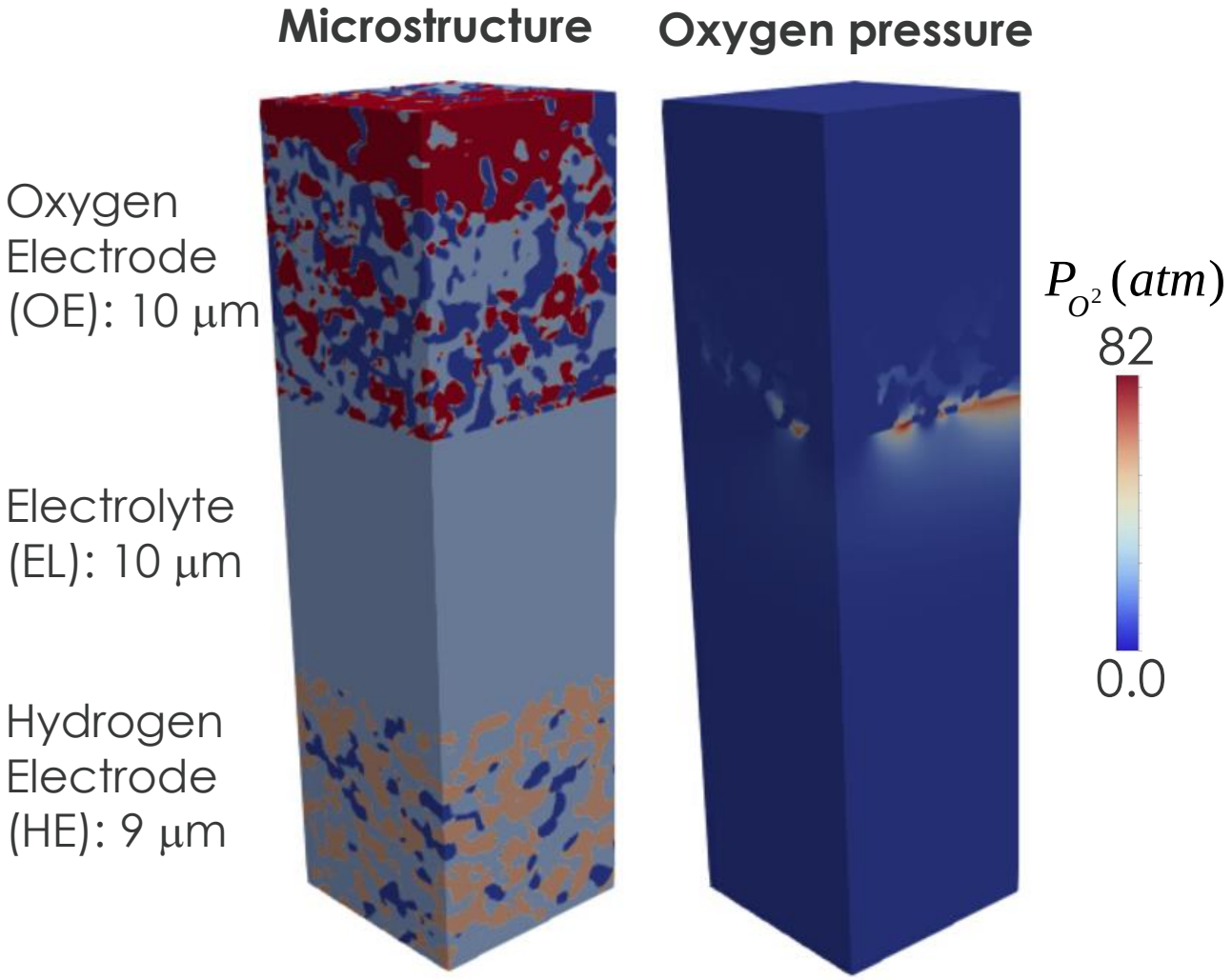
GDC: gadolinia-doped ceria.

Y. Lei et al. ECS Transactions. 2023;111:965.

Two Types of Microstructures: 2D Preset and 3D Reconstructed



The maximum of oxygen pressure is achieved at the OE-EL interface.

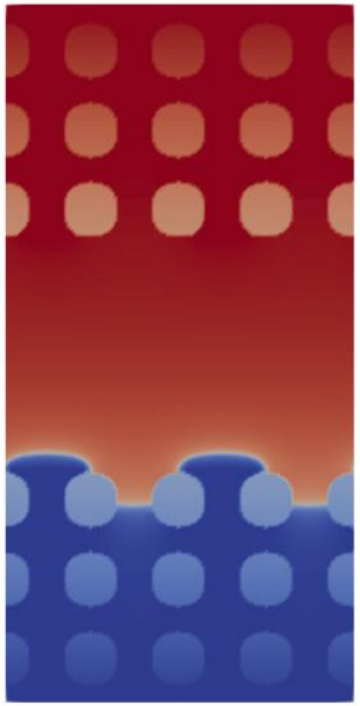


Influence of Tuning Electronic Transport Properties of YSZ

Multiply the e- conductivity of YSZ by 2,000 times, following Lei Zhang et. al JECS, 166 (2019) F1275-F1283.

Before

Electron potential

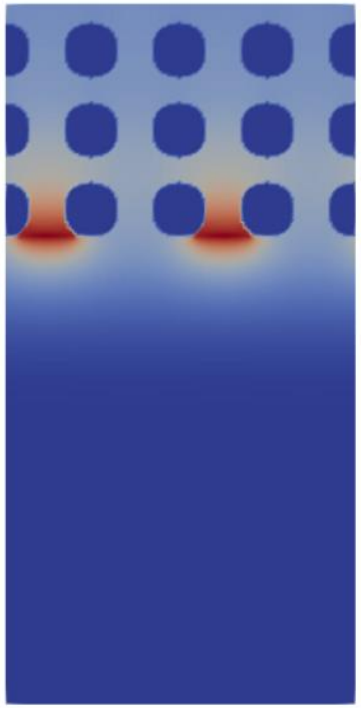


$\mu_{e^-}(V)$

1.3

0.0

Oxygen pressure



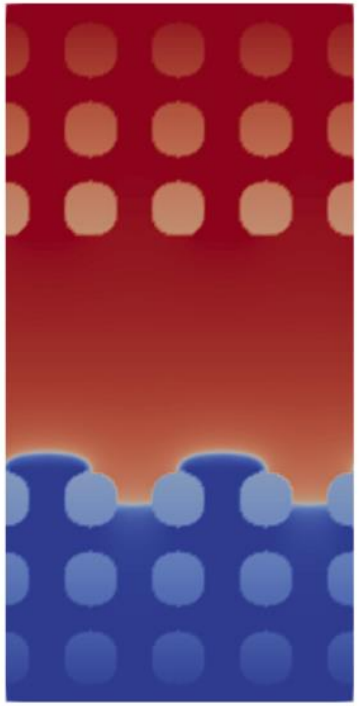
$P_{O^2}(atm)$

917

0.0

After

Electron potential

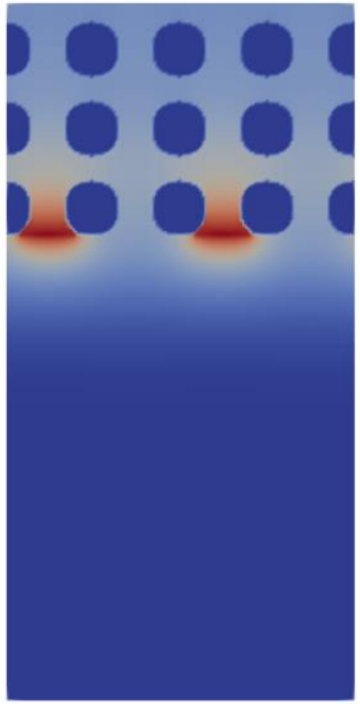


$\mu_{e^-}(V)$

1.3

0.0

Oxygen pressure



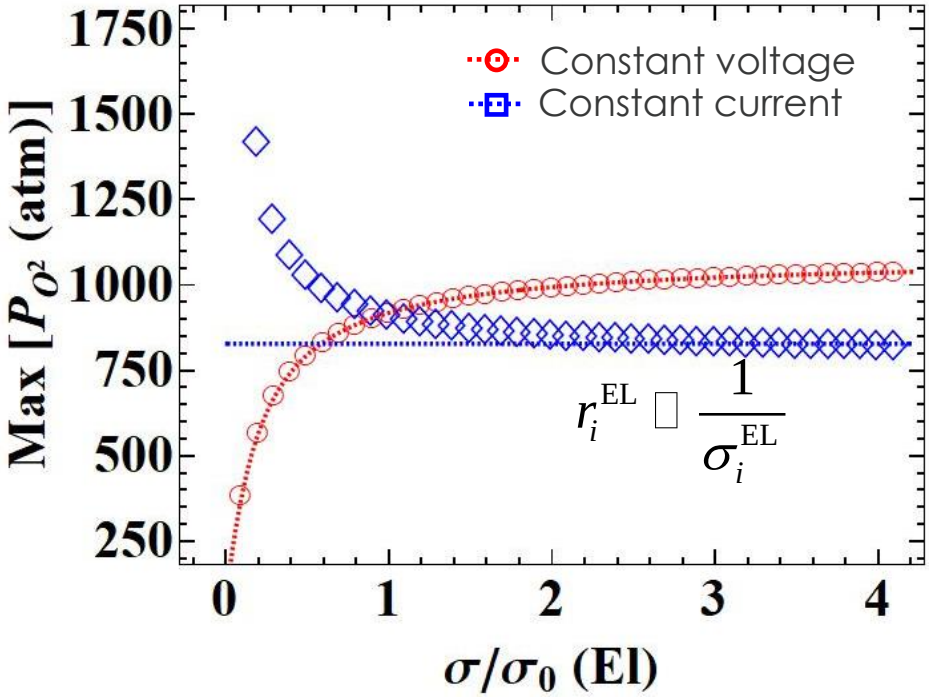
$P_{O^2}(atm)$

917

0.0

$$p_{O_2}^{\text{OE-EL}} = p_{O_2}^{Ox}\exp[\frac{4F}{RT}\{\frac{r_i^{\text{OE}}}{r_i^{\text{OE}}+r_i^{\text{EL}}+r_i^{\text{HE}}}(E_A-E_N)-\frac{r_e^{\text{OE}}}{r_e^{\text{OE}}+r_e^{\text{EL}}+r_e^{\text{OE}}}E_A\}] \xrightarrow{r_e^{\text{OE}}\sim 0} p_{O_2}^{\text{OE-EL}} = p_{O_2}^{Ox}\exp[\frac{4F}{RT}\{\frac{r_i^{\text{OE}}}{r_i^{\text{OE}}+r_i^{\text{EL}}+r_i^{\text{HE}}}(E_A-E_N)\}]$$

Influence of the O^{2-} Conductivity of the YSZ Electrolyte Based on 2D Simulations



The dashed lines are obtained by fitting the analytical solution.

$$p_{O_2}^{\text{OE-EL}} = p_{O_2}^{Ox} \exp\left[\frac{4F}{RT}\left\{\frac{r_i^{\text{OE}}}{r_i^{\text{OE}} + r_i^{\text{EL}} + r_i^{\text{HE}}}(E_A - E_N)\right\}\right]$$

Deviation at small O^{2-} conductivity under galvanostatic operation is due to the change of r_i^{OE}.

r_i^{OE} is effective resistance including the reaction resistance.

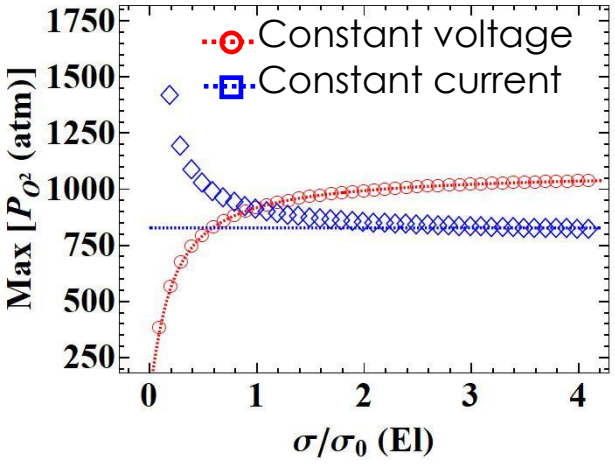
$\sigma(O^{2-})$ of the electrolyte should be small under potentiostatic operation and large under galvanostatic operation.

The analytical solution can be employed to fit to the simulation results, but cannot predict the specific values before fitting, since $p_{O_2}^{Ox}$, r_i^{OE}, and r_i^{HE} are unknown and fitting parameters.

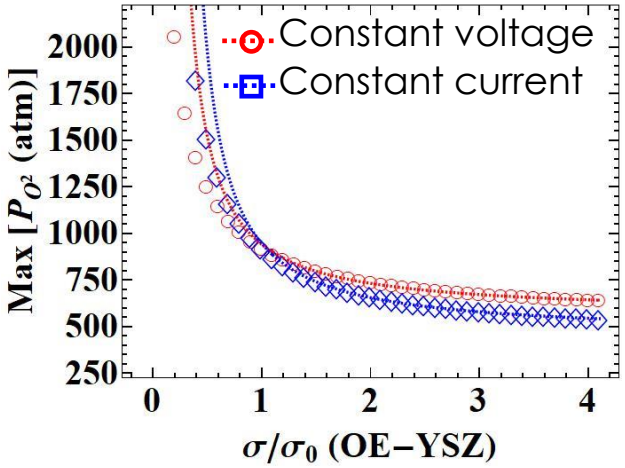
Influence of Tuning the O^{2-} Conductivity of YSZ and LSM

Tuning the O^{2-} conductivity of YSZ and LSM using 2D simulations (constant voltage vs. constant current).

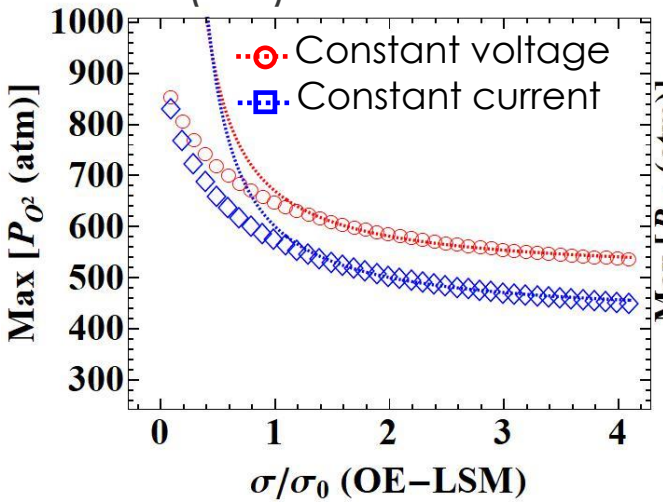
$\sigma(O^{2-})$ of YSZ in El



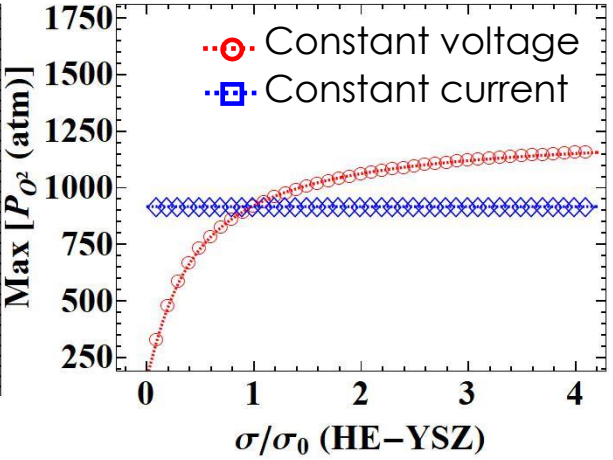
$\sigma(O^{2-})$ of YSZ in OE



$\sigma(O^{2-})$ of LSM in OE



$\sigma(O^{2-})$ of YSZ in HE



$$p_{O_2}^{\text{OE-EL}} = p_{O_2}^{Ox} \exp\left[\frac{4F}{RT}\left\{\frac{r_i^{\text{OE}}}{r_i^{\text{OE}} + r_i^{\text{EL}} + r_i^{\text{HE}}}(E_A - E_N)\right\}\right] \qquad r_i \propto \frac{1}{\sigma_i}$$

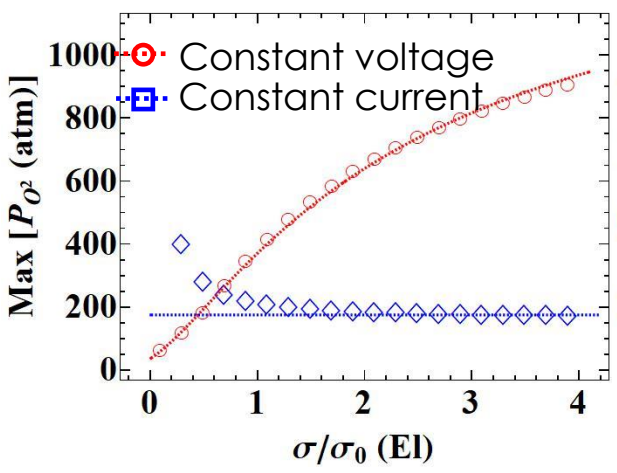
V=1.3 V for constant voltage.

Under potentiostatic operation, $\sigma(O^{2-})$ of YSZ in El and HE: small; $\sigma(O^{2-})$ of YSZ in OE and LSM: large.
Under galvanostatic operation, $\sigma(O^{2-})$ of LSM and YSZ in El and OE should be large.
The simulation results are qualitatively consistent with the analytical solution.

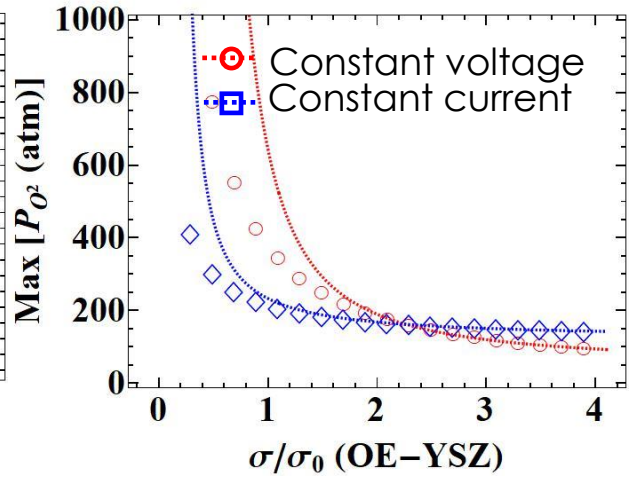
Influence of Tuning the O^{2-} Conductivity of YSZ and LSM from 3D Simulations

Tuning the O^{2-} conductivity of YSZ and LSM using 3D simulations (constant voltage vs. constant current).

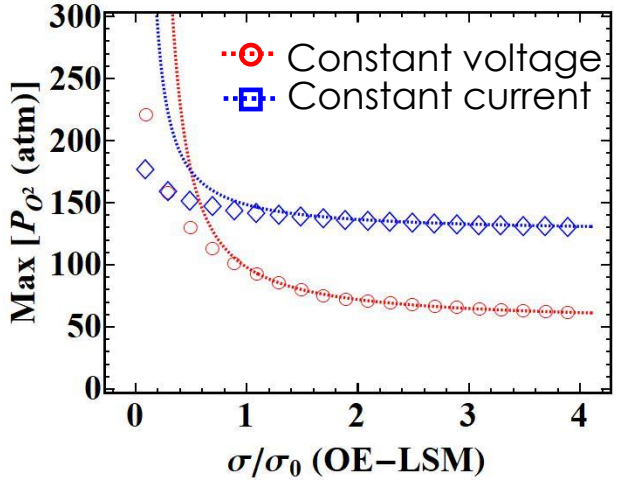
$\sigma(O^{2-})$ of YSZ in El



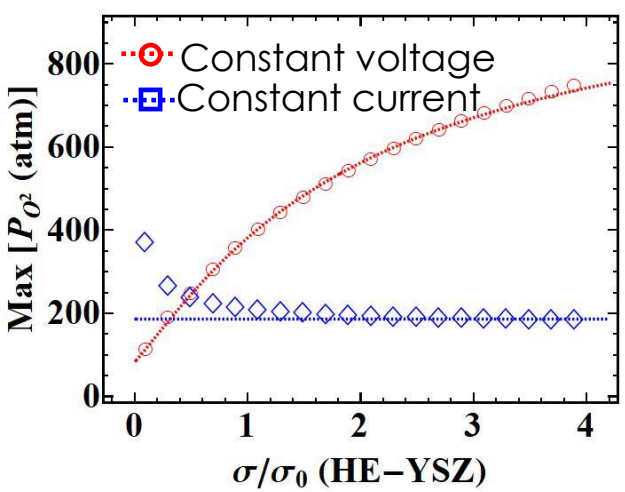
$\sigma(O^{2-})$ of YSZ in OE



$\sigma(O^{2-})$ of LSM in OE



$\sigma(O^{2-})$ of YSZ in HE



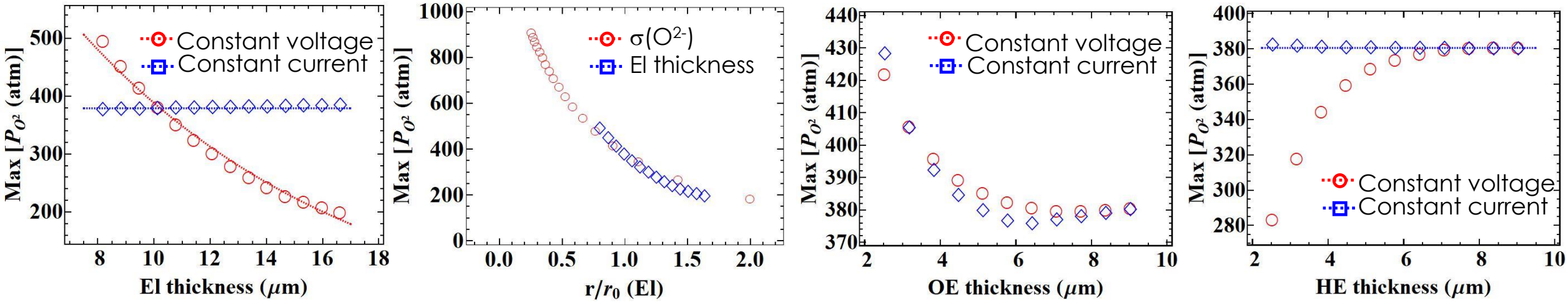
V=1.3 V for constant voltage.

Under potentiostatic operation, $\sigma(O^{2-})$ of YSZ in El and HE: small; $\sigma(O^{2-})$ of YSZ in OE and LSM: large.
Under galvanostatic operation, $\sigma(O^{2-})$ of LSM and YSZ in El and OE should be large.
The results from 3D simulations are consistent with those from 2D simulations.

Influence of Tuning the Electrode/Electrolyte Thickness

Tuning the electrode/electrolyte thickness using 3D reconstructed microstructures.

El thickness | Comparison to tuning YSZ $\sigma(O^{2-})$ | OE thickness | HE thickness

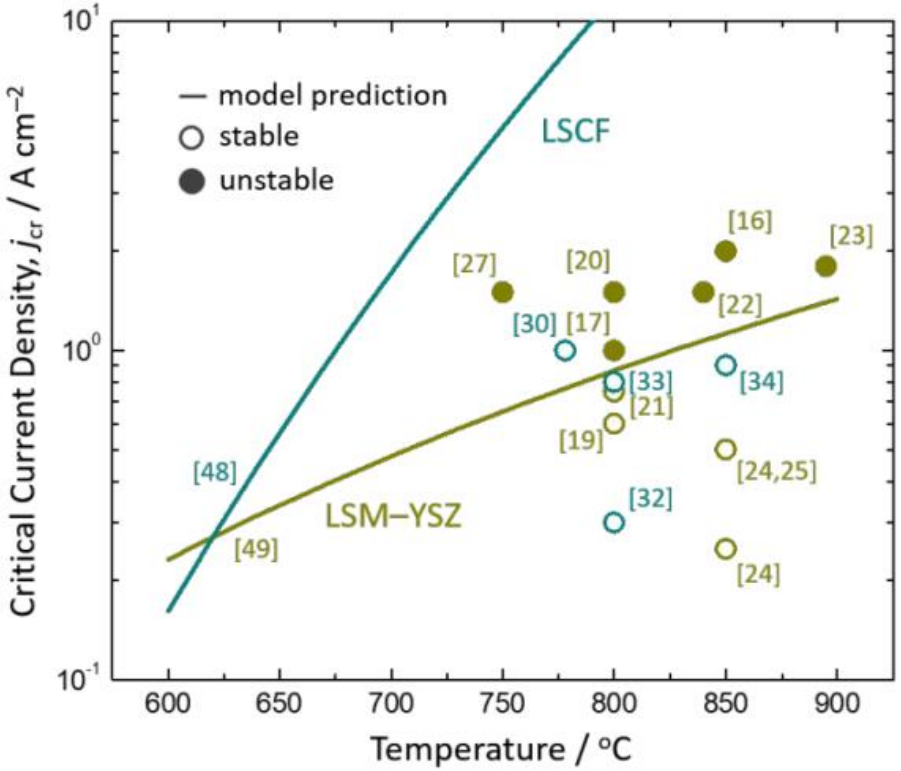


V=1.3 V for constant voltage.

Under constant voltage, thicker electrolyte, thicker OE, and thinner HE are favored.
Under constant current, thinner electrolyte, an intermediate OE thickness, and thicker HE are favored.

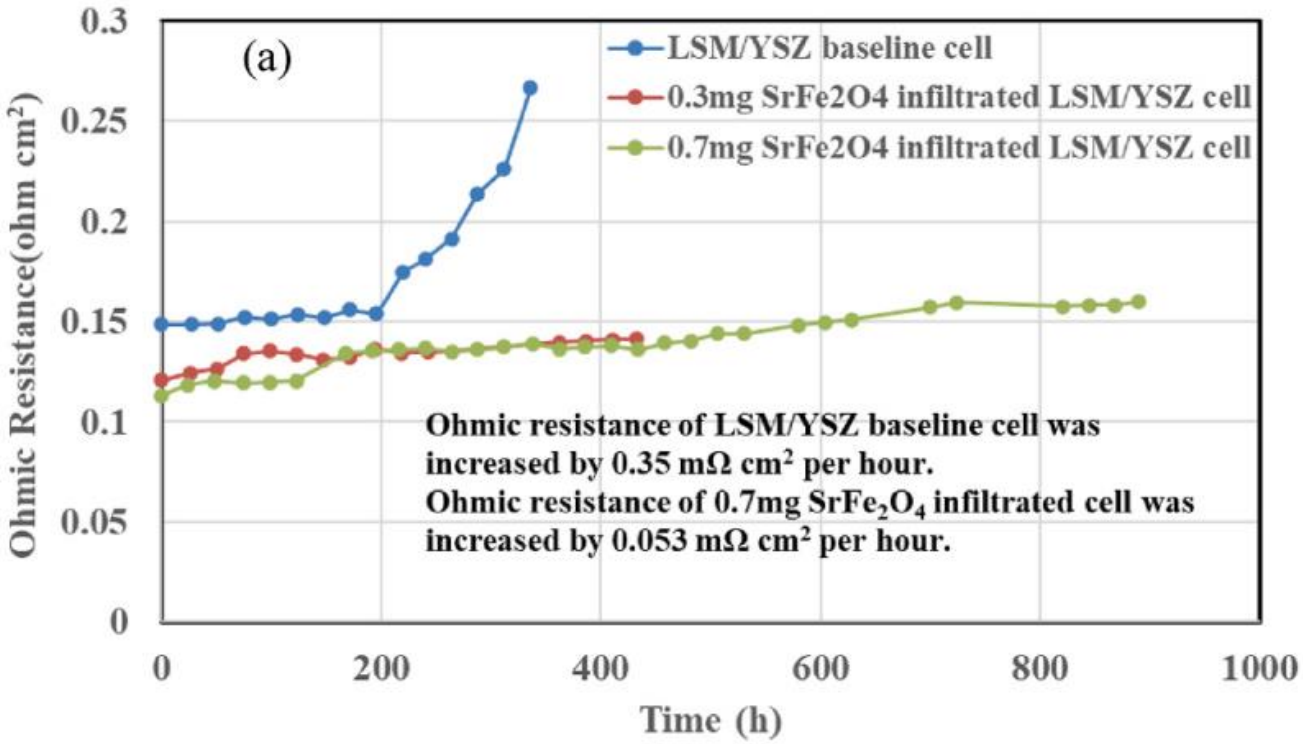
Comparison to Experiments in Literature

Mixed conductor LSCF mitigates delamination



Energy & Environmental Science. 2019;12:3053-62.

Infiltration changes the effective conductivity of LSM



Y. Fan et al. Journal of Power Sources 580 (2023) 233389.

Phase-Field Fracture Model and Coupled Performance-Crack Model

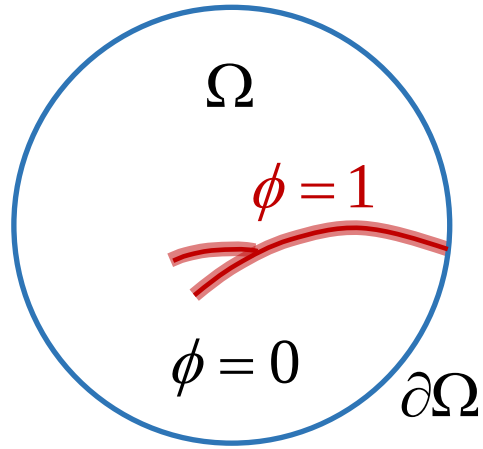
Total free energy for the phase-field fracture model:

$$F = \int_{\Omega} [\, f_{\text{elas}}(\phi) + f_{\text{frac}}(\phi)] d\Omega$$

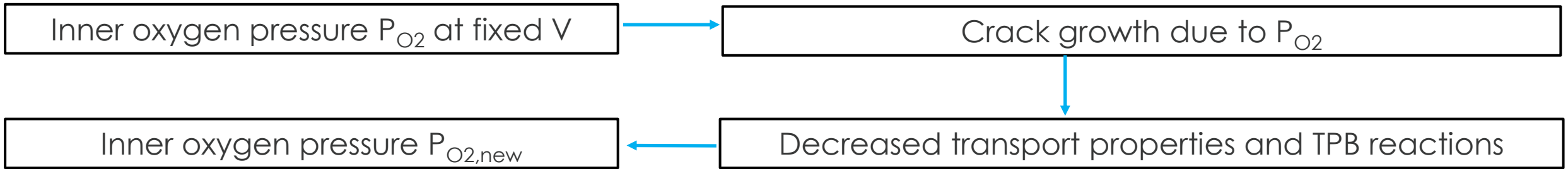
The elastic energy f_{elas} is the driving force of crack growth and may decrease after crack growth.

The fracture energy f_{frac} represents the fracture surface energy due to crack growth.

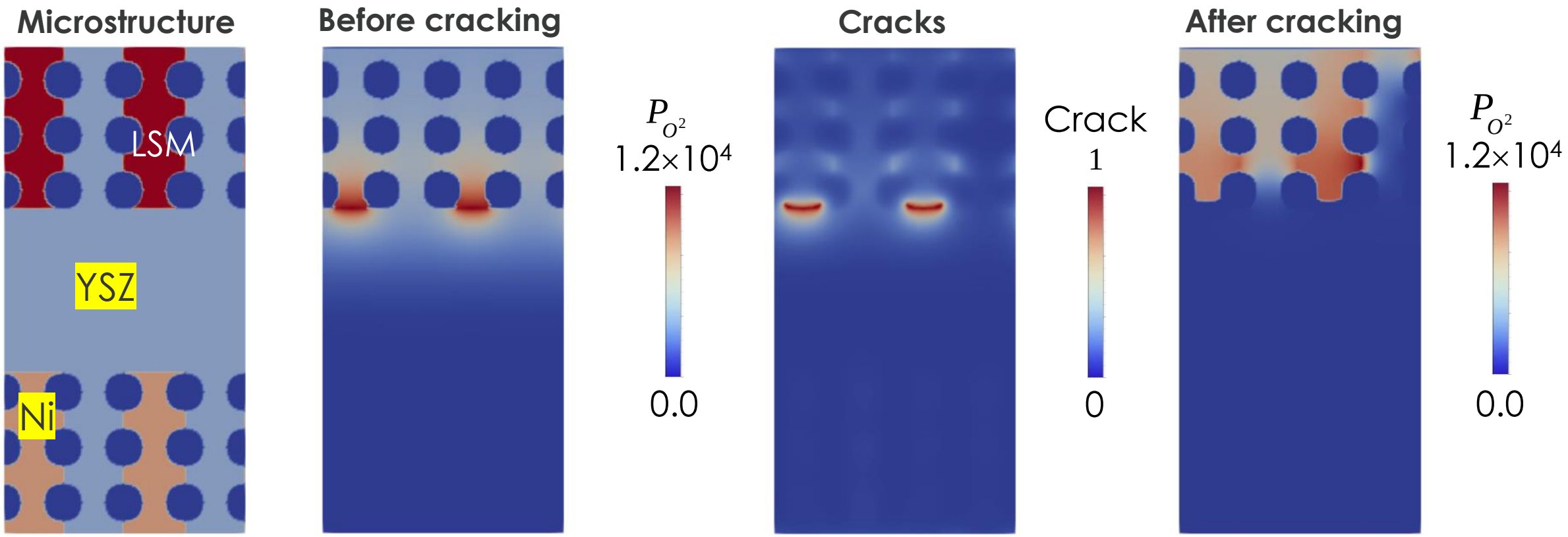
Cracks



Coupled performance-crack model at fixed voltage



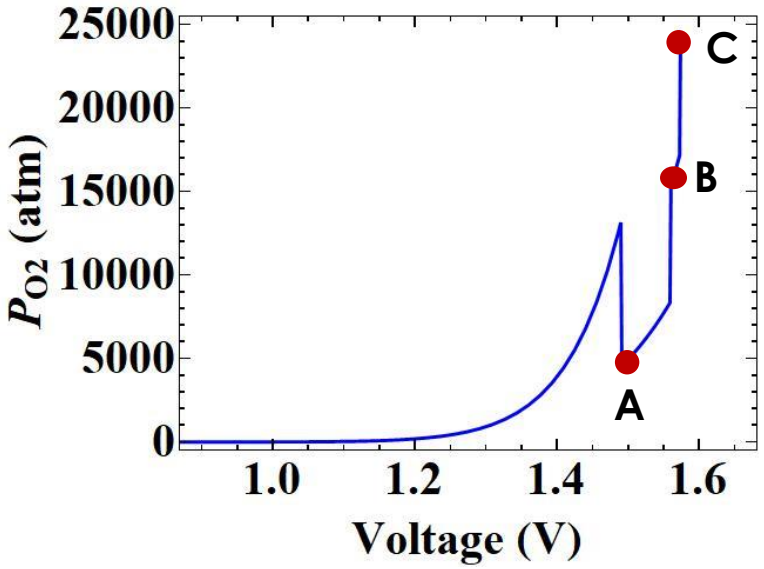
Coupled Performance-Fracture Model at Fixed Voltage

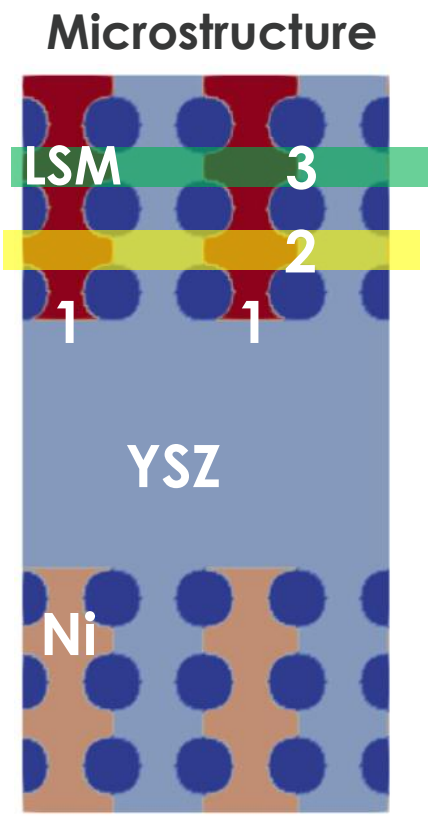


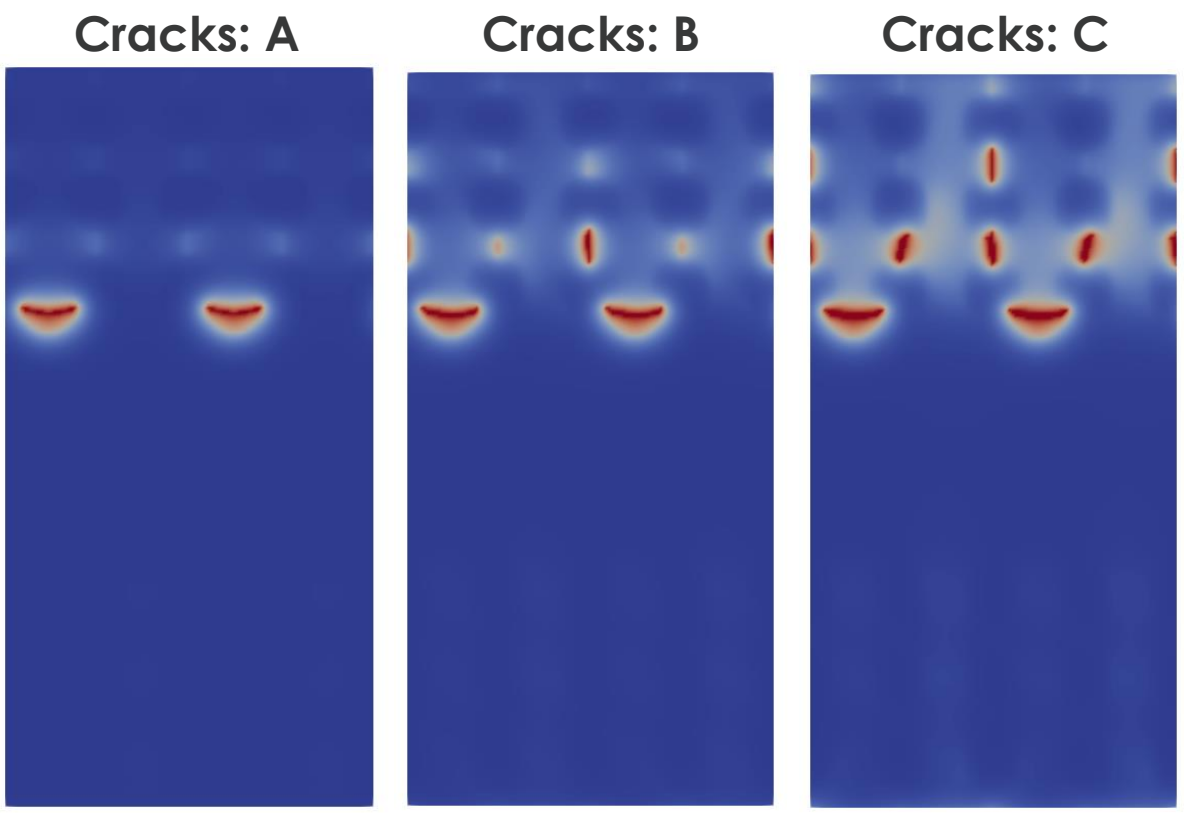
The simulation is performed at V=1.47 V.

After cracking, the maximum of oxygen pressure is achieved inside the OE, which suggests layer-by-layer cracking.

Crack Growth in LSM-based Cells Under Changing Voltage







After crack growth at the OE-EL interface, the maximum of oxygen pressure is achieved at the LSM-YSZ interface inside the OE. Then layer-by-layer cracking is observed.

Conclusions

Conclusions from the parametric studies of inner oxygen pressure in LSM-based cells:

1. Different from the conclusions by Virkar et al. and Zhang et al., increasing the electronic conductivity of YSZ cannot decrease inner oxygen pressure from our simulation results.
2. Under potentiostatic operation, the following conditions are favored: (1) smaller ionic conductivity of YSZ in the electrolyte and HE; (2) larger ionic conductivities of LSM and YSZ in the OE; (3) thicker electrolyte; (4) thicker OE; and (5) thinner HE.
3. Under galvanostatic operation, the following conditions are favored: (1) larger ionic conductivity of YSZ in the electrolyte and OE; (2) larger ionic conductivity of LSM; (3) thinner electrolyte; and (4) an intermediate thickness of the OE.

Conclusions from the coupled performance-fracture model:

1. Crack growth is induced at the interfaces with high inner oxygen pressure.
2. After crack growth, the inner oxygen pressure is redistributed. Simulation results suggest layer-by-layer cracking in the LSM-based cells.

Acknowledgments

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Thanks for your attention!

Questions?

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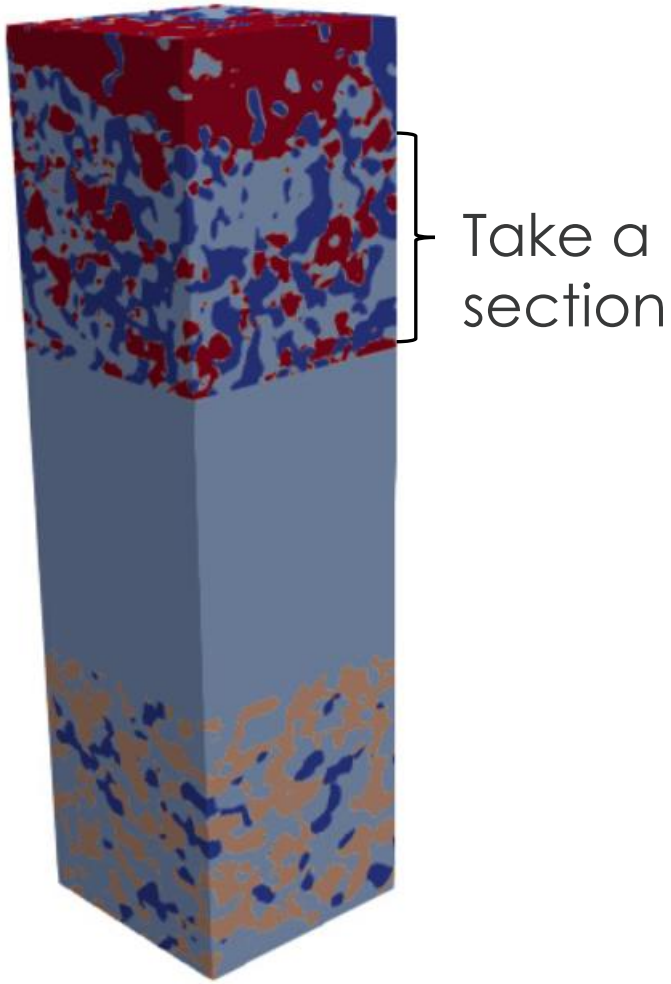
Backup Slides

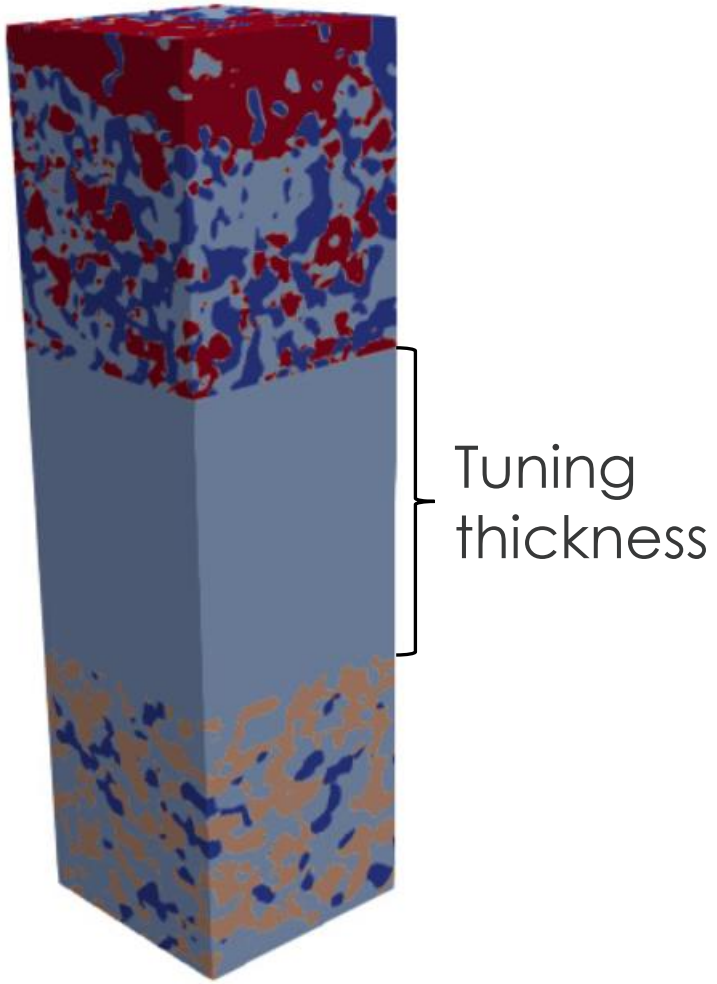
Tuning the Thickness of the Electrode/Electrolyte

NATIONAL ENERGY TECHNOLOGY LABORATORY

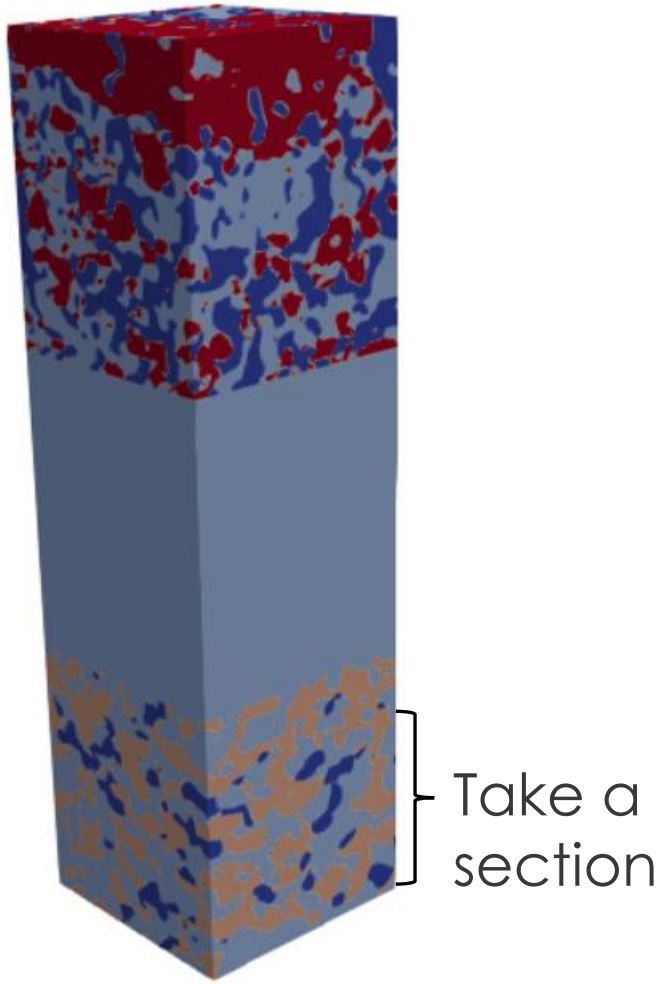
Tuning OE thickness



Tuning electrolyte thickness



Tuning HE thickness



Extend Virkar's Model by Incorporating the Microstructures

Chemical reaction $\frac{1}{2}O_2 + 2e' \leftrightarrow O^{2-}$

Conduction equation for oxygen ions $0 = \nabla \cdot [-\sigma_{O^{2-}}(\xi_i)\nabla\phi_{O^{2-}}] - i_F$

Conduction equation for electrons $0 = \nabla \cdot [-\sigma_{e^-}(\xi_i)\nabla\phi_{e^-}] + 2i_F$

The source term at TPB: Butler-Volmer Equations

$$i_{F,c} = i_{0,c}\left(\frac{P_{O_2}^{\text{Pore}}}{P_{\text{ref}}}\right)^{0.25}\left\{\left(\exp\left[-\frac{\alpha n F \eta_c}{RT}\right] - \exp\left[\frac{(1-\alpha) n F \eta_c}{RT}\right]\right\}\right.$$

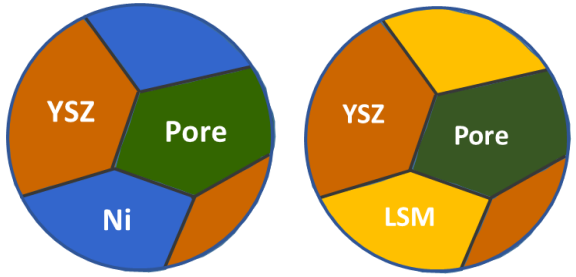
Local overpotential at TPBs $\eta_c = -\phi_{O^{2-},YSZ} + \phi_{e^-,LSM} - \frac{RT}{4F}\ln\frac{P_{O^2}^{\text{Pores}}}{P_{O^2}^0}$

Gas diffusion within the pores is neglected

Inner oxygen pressure $P_{O_2} = P_{O_2}^0 \exp\left[\frac{4F}{RT}(\phi_{e^-} - \phi_{O^{2-}})\right]$

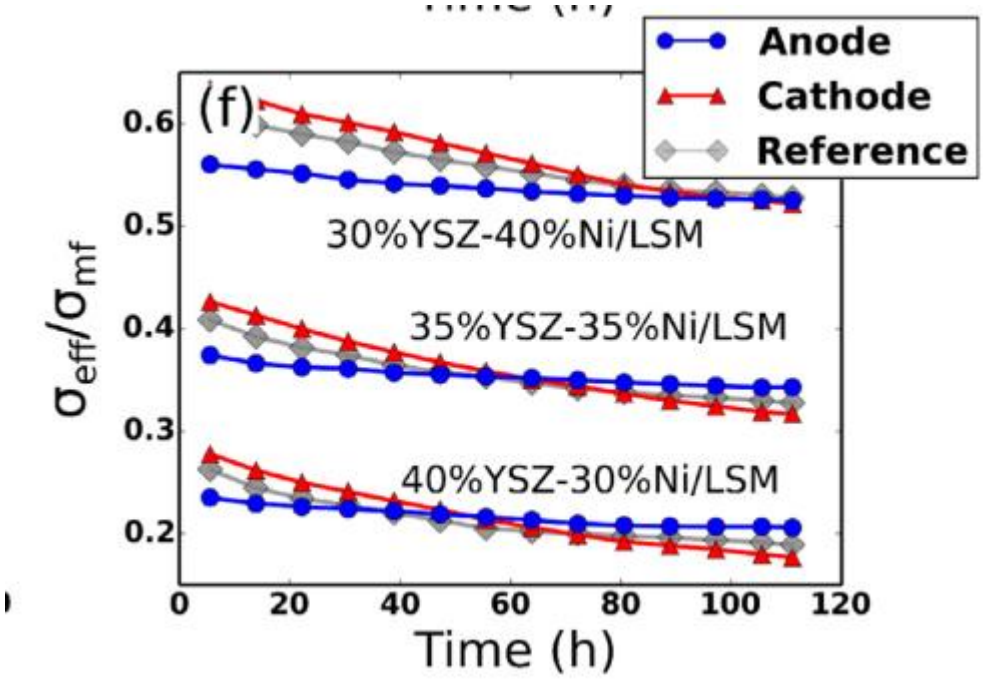
JECS, 166 (2019) F1275-F1283.

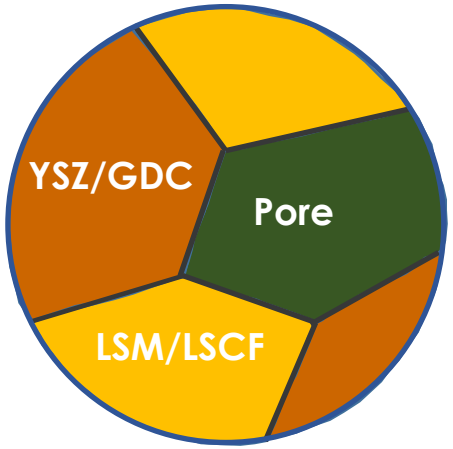
HE and OE microstructures

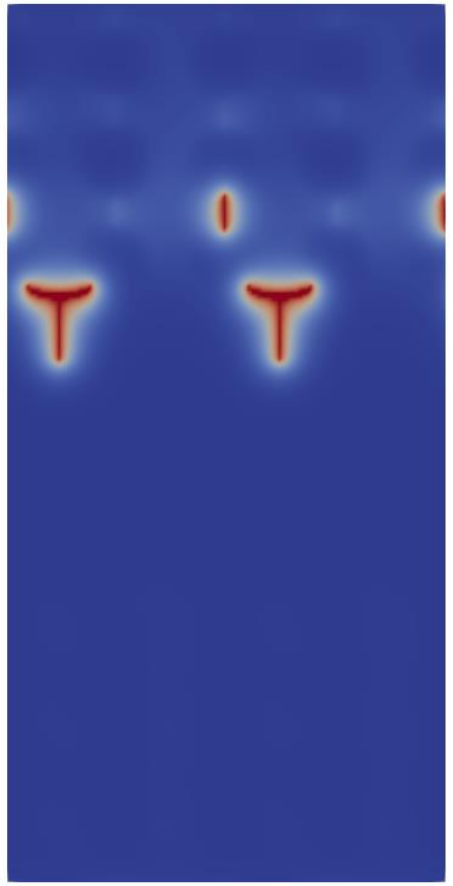


Tao Yang *et. al Int. J. Electrochem. Sci.*, 12 (2017) 6801 – 6828.

Effective Conductivity of the Electrodes





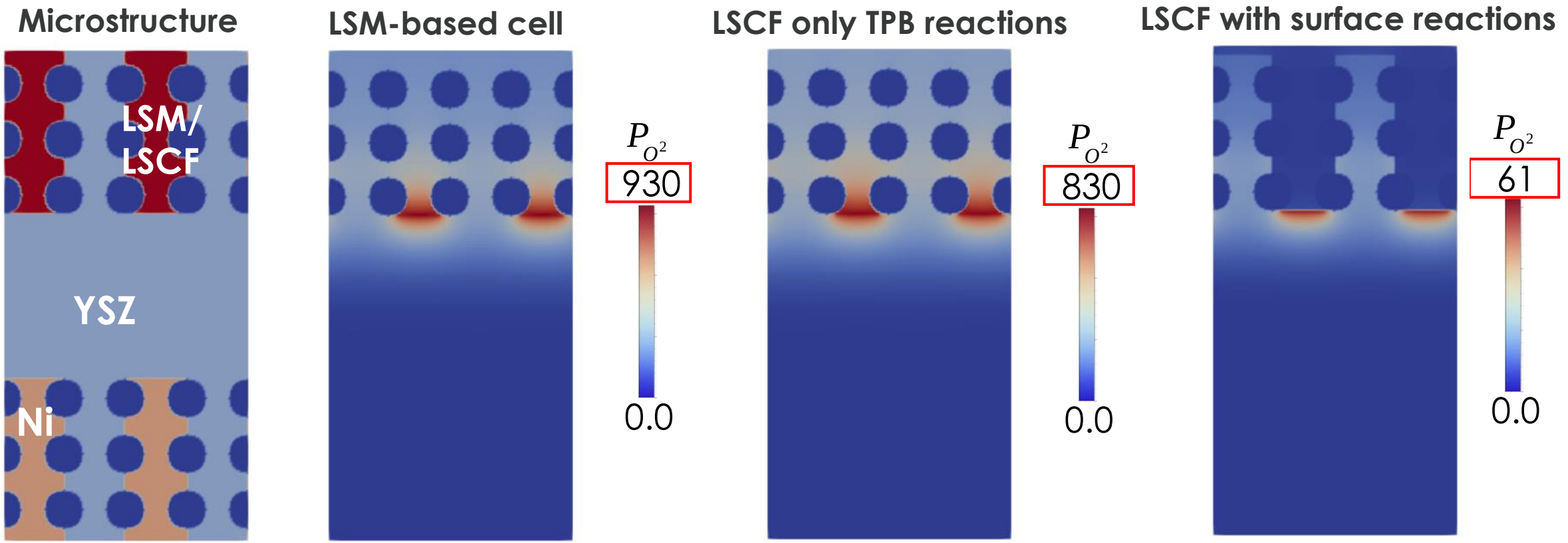


From Y. Lei et al./Journal of Power Sources 345 (2017) 275-289.

Oxygen Pressure in LSM- and LSCF-Based ells

Vcell=1.3 V, $i_0^{\mathrm{NiYSZTPB}} = 2.345\times10^{-3}\ \mathrm{A\cdot m^{-1}}$ $i_0^{\mathrm{LSMYSZTPB}} = 2.247\times10^{-4}\ \mathrm{A\cdot m^{-1}}$ $i_0^{\mathrm{LSCFYSZTPB}} = 2.247\times10^{-4}\ \mathrm{A\cdot m^{-1}}$

$i_0^{\mathrm{LSCFSurface}} = 2.0\times10^{-4}\ \mathrm{A\cdot m^{-1}}$ $i_0^{\mathrm{LSCFYSZInterface}} = 3.0\times10^{-4}\ \mathrm{A\cdot m^{-1}}$



Oxygen pressure is lower in LSCF-based cells than that in LSM-based cells.