# STABLE HIGH CONDUCTIVITY BILAYERED ELECTROLYTES FOR LOW TEMPERATURE SOLID OXIDE FUEL CELLS

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# WHY LOW TEMPERATURE (< 600 ºC)?

Metallic Interconnects

Lower cost and greater reliability

Easier Sealing

Lower cost and greater reliability

Smaller Thermal Mismatch

Greater reliability → Lower cost

Less Insulation

Lower cost

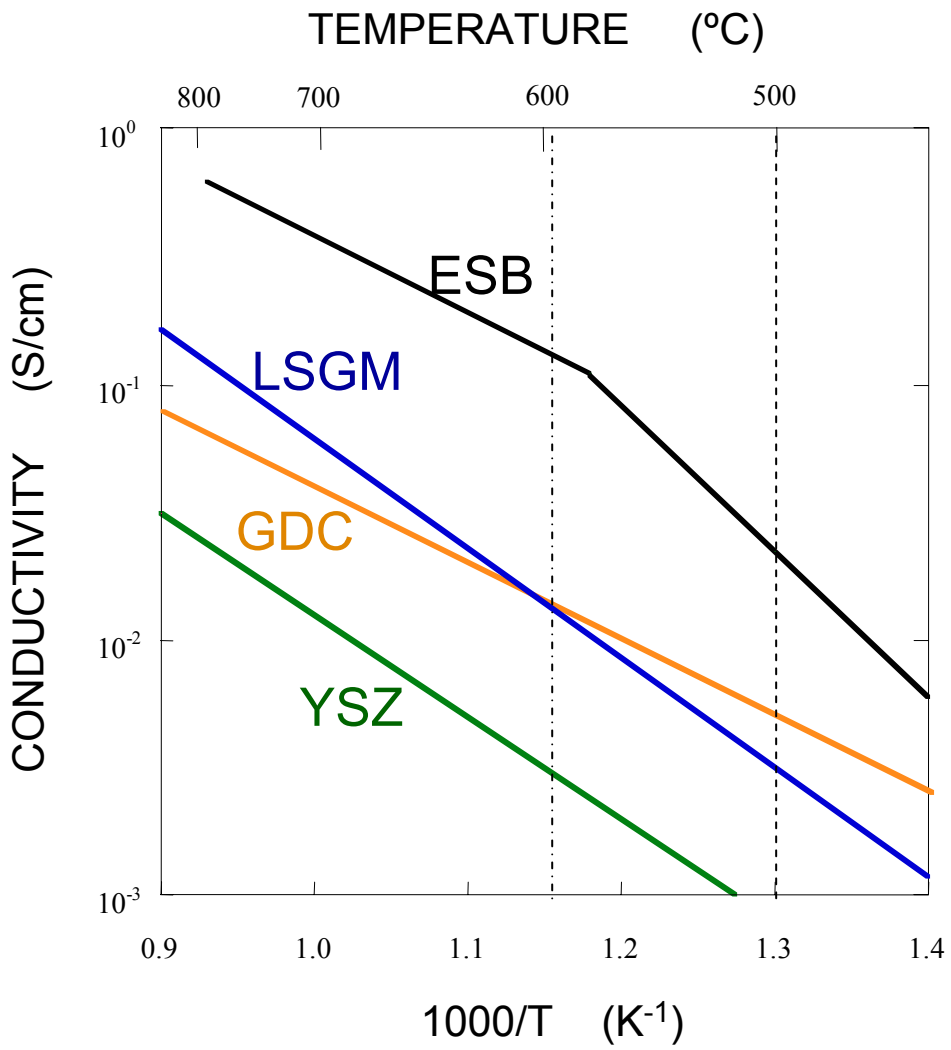
Rapid Startup with Less Energy Consumption

Lower cost and better performance

Stable High Surface-Area Electrodes

Better performance → Lower cost

# CONDUCTIVITY OF VARIOUS ELECTROLYTES



# Ceria-Conductivity & Bismuth Oxide-Structure in Reducing Conditions

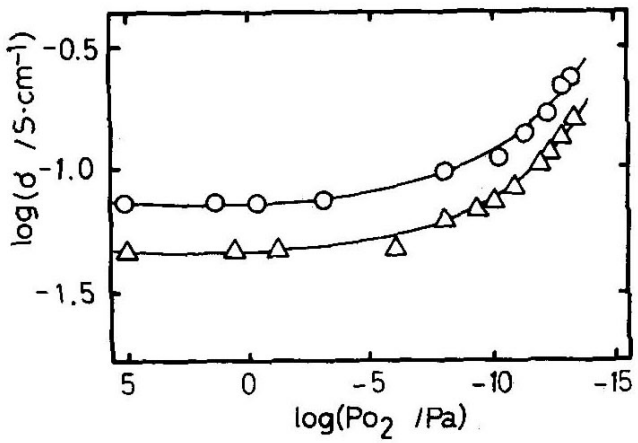



Fig. 6. Electrical conductivities as a function of oxygen partial pressure at 800°C: (○) $(CeO_2)_{0.8}(SmO_{1.5})_{0.2}$; (△) $(CeO_2)_{0.8}(GdO_{1.5})_{0.2}$.

Eguchi, et al., *Solid State Ionics,* **52**, 168 (1992)

Wachsman, et al., *Solid State Ionics,* **52**, 216 (1992)

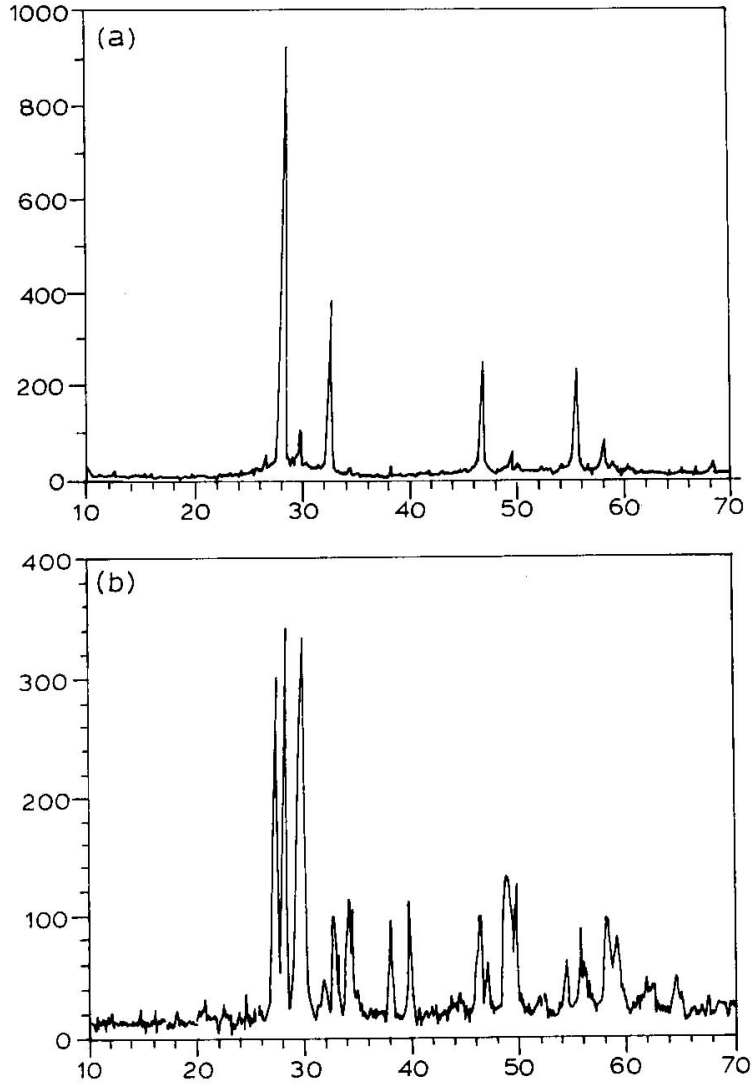



Fig. 4. X-ray diffraction of 20 mol% ESB: (a) as received; (b) annealed 4 h at 700 °C in $H_2/H_2O$ $P_{O_2} = 10^{-21}$ atm).

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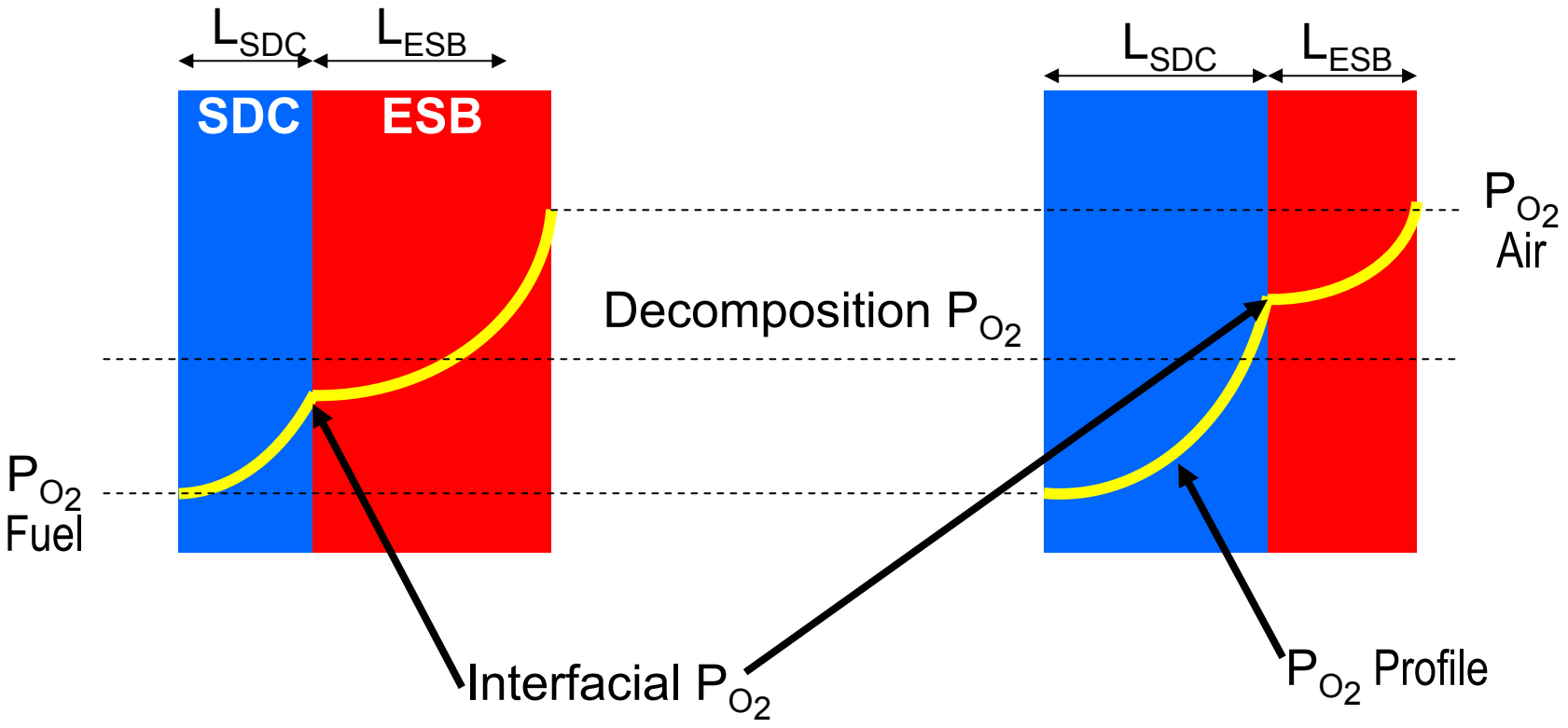
# BILAYER CONCEPT



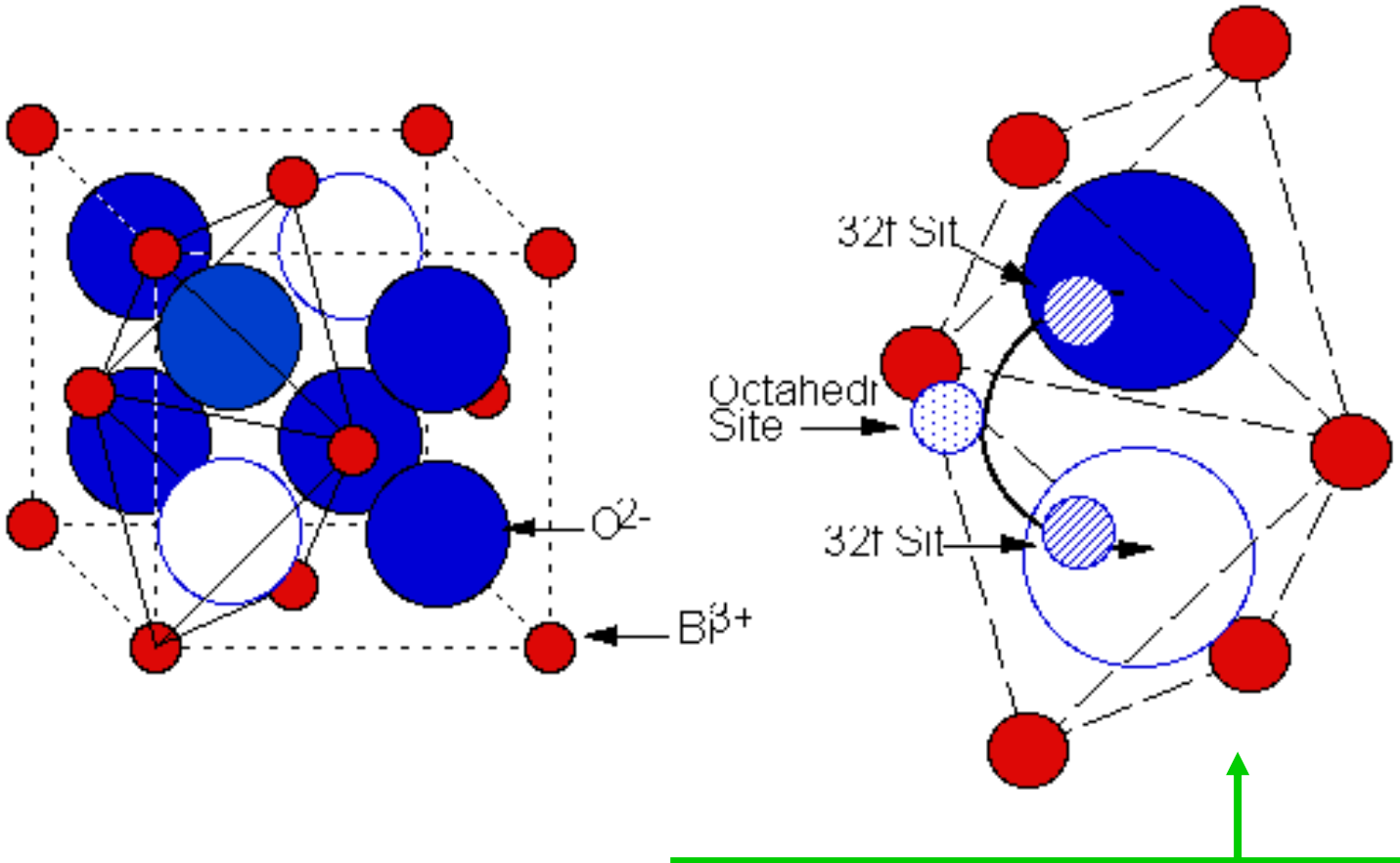

$L_{SDC} / L_{ESB} < \tau_{optimal}$

**ESB decomposes**

$L_{SDC} / L_{ESB} > \tau_{optimal}$

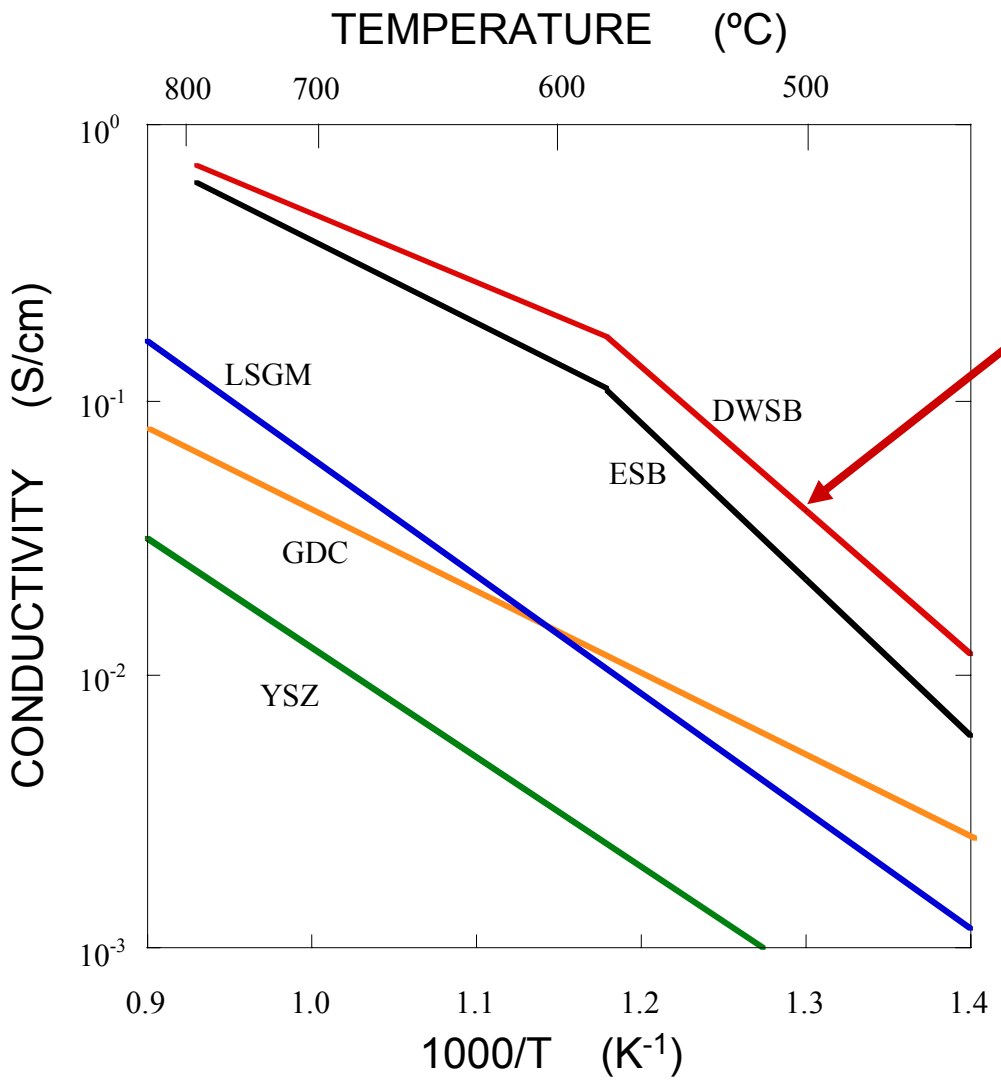
**ESB is stable**

# FUNDAMENTALS OF IONIC TRANSPORT IN FLUORITE OXIDES




Jump from one tetrahedron to an adjacent tetrathedron in <100> direction

# CONDUCTIVITY OF VARIOUS ELECTROLYTES




**New Electrolyte**

# CONDUCTIVITY OF VARIOUS ELECTROLYTES @ 500 ºC

| Electrolyte | Conductivity (S/cm) | ASR ($\Omega \cdot cm^2$) 100 µm thick | ASR ($\Omega \cdot cm^2$) 10 µm thick |
|---|---|---|---|
| YSZ | 0.00046 | 21.74 | 2.17 |
| LSGM | 0.0051 | 1.96 | 0.20 |
| **GDC** | **0.0095** | **1.05** | **0.11** |
| **ESB** | **0.021** | **0.48** | **0.05** |
| **DWSB** | **0.043** | **0.23** | **0.02** |

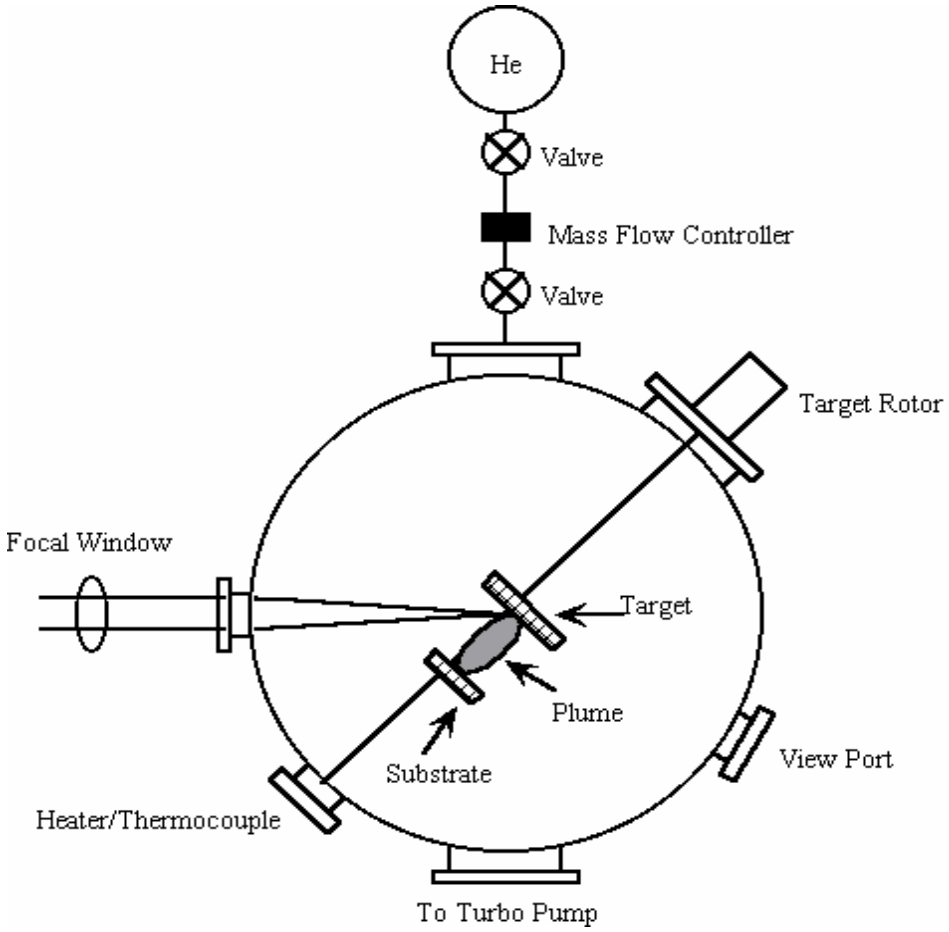
# PULSED-LASER DEPOSITION: PROCEDURE & CHARACTERIZATION

1. ***Pellet Preparation***
   - Solid State Synthesis

2. ***Preparation of Thin Films***
   - Pulsed Laser Deposition (PLD)
   - target: ESB, substrate: SDC

3. ***Microstructural Analysis***
   - Profilometry
   - XRD, SEM, and EDS

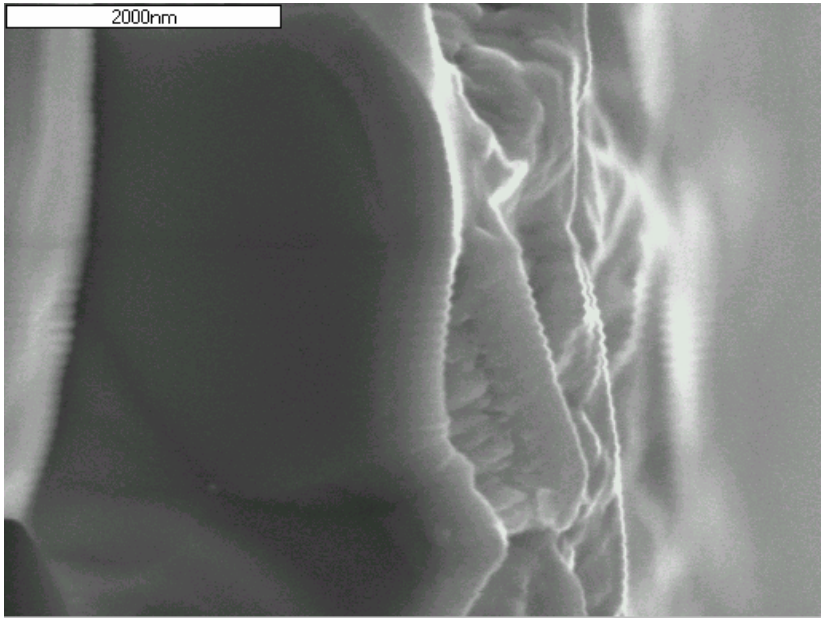
4. ***Electrical Measurement***
   - AC Impedance Spectroscopy
     ( 0.1 - 10MHz: 300 - 800°C)

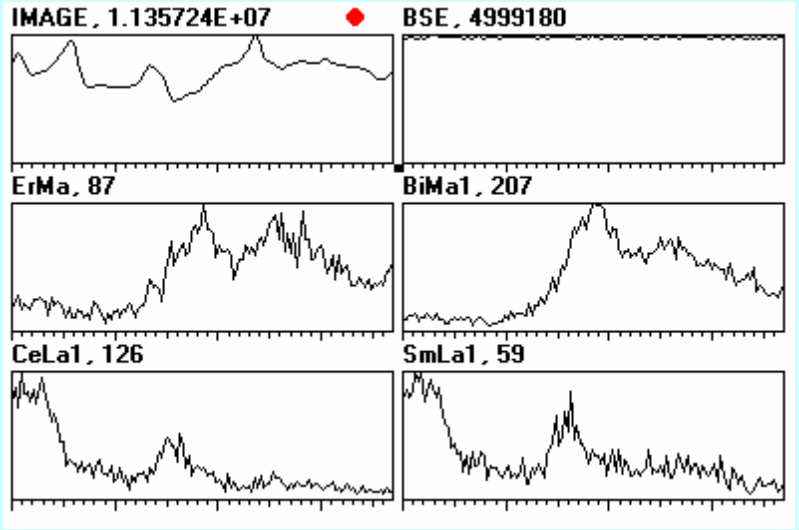



PLD Operation

# Characterization: SDC/ESB bilayer via Pulse-Laser Deposition (PLD)

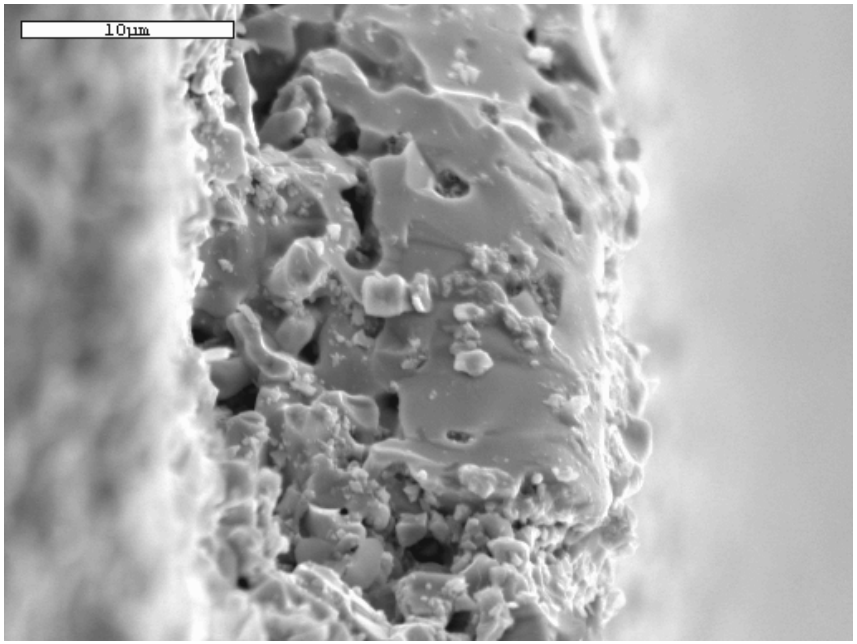
Cross-section SEM micrograph of SDC/ESB bilayer

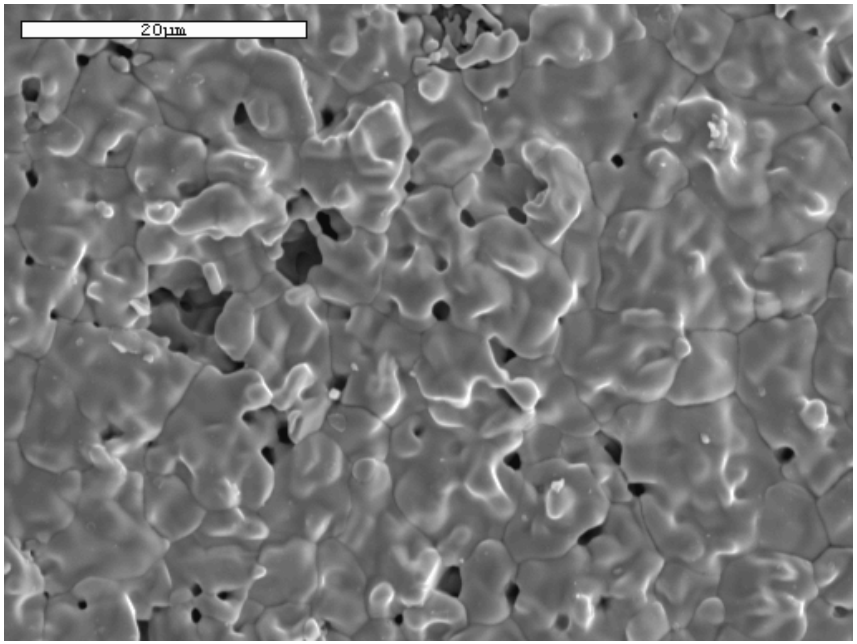



Chemical composition of ESB/SDC bilayer from EDS by X-ray linescan

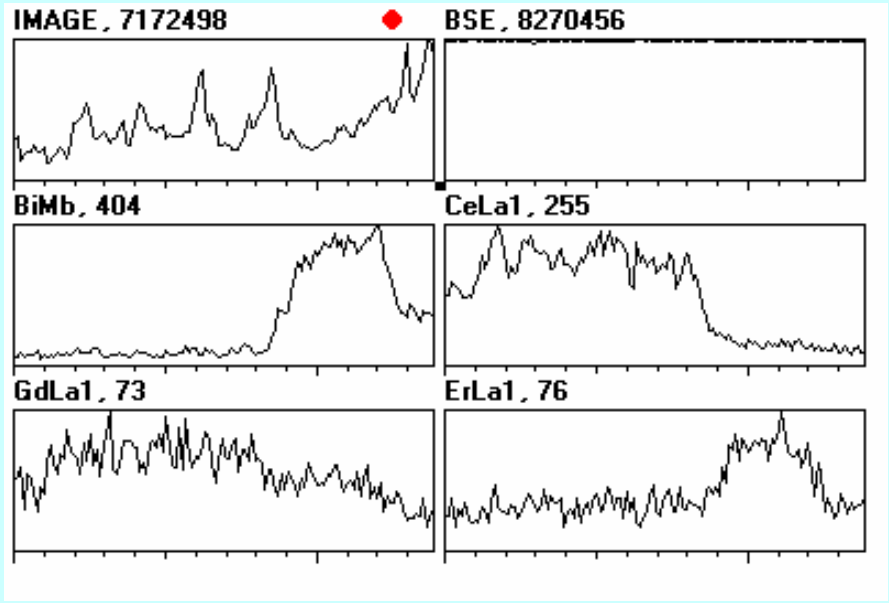
# Characterization: SDC/ESB bilayer via Dip-Coating

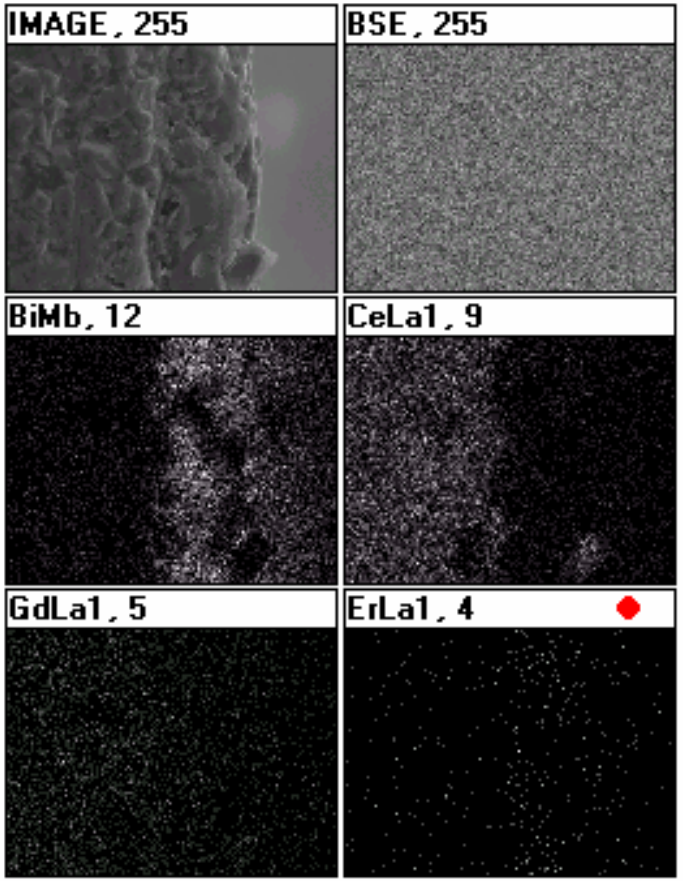



Cross-section and Surface
SEM micrograph of SDC/ESB bilayer

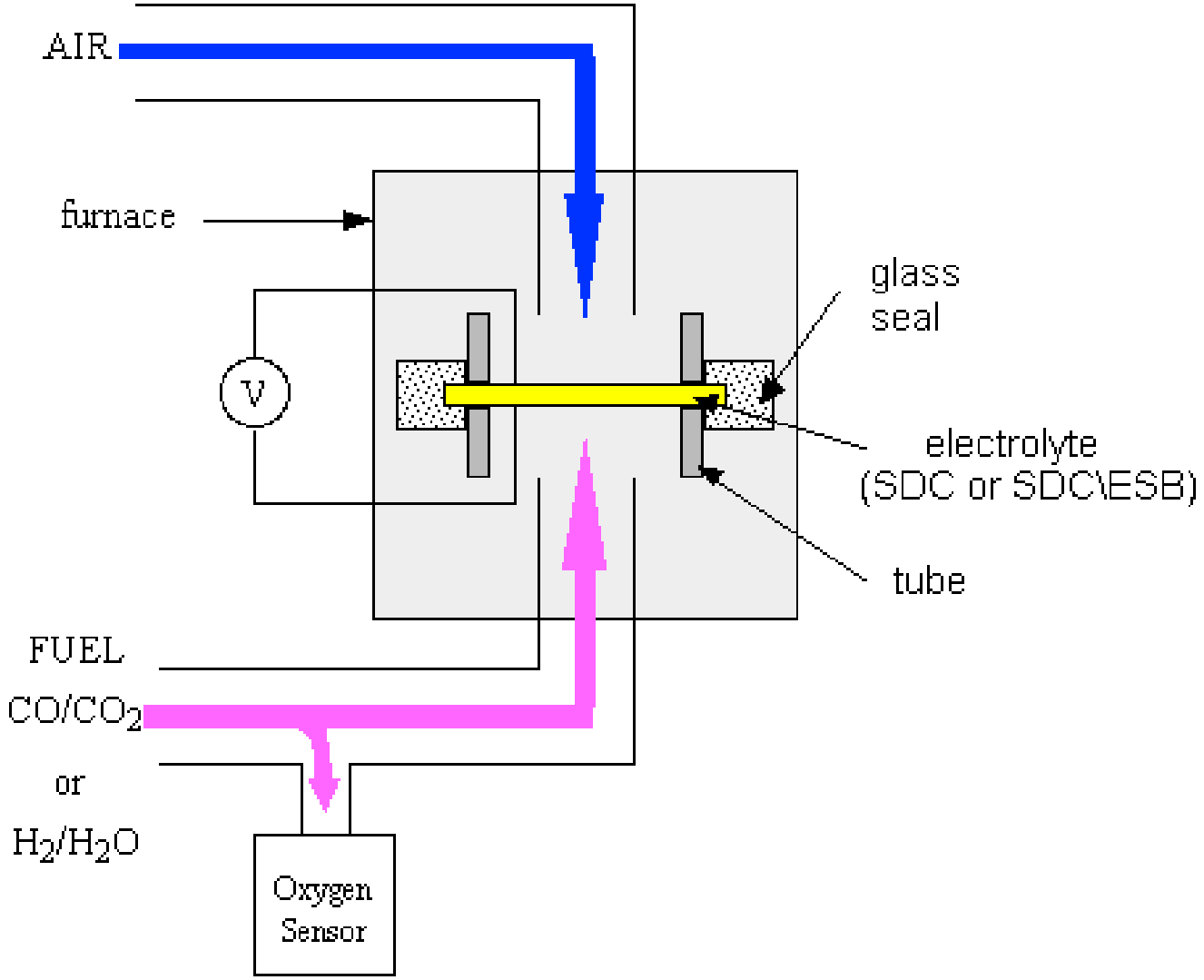
# Characterization: SDC/ESB Bilayer via Dip-Coating



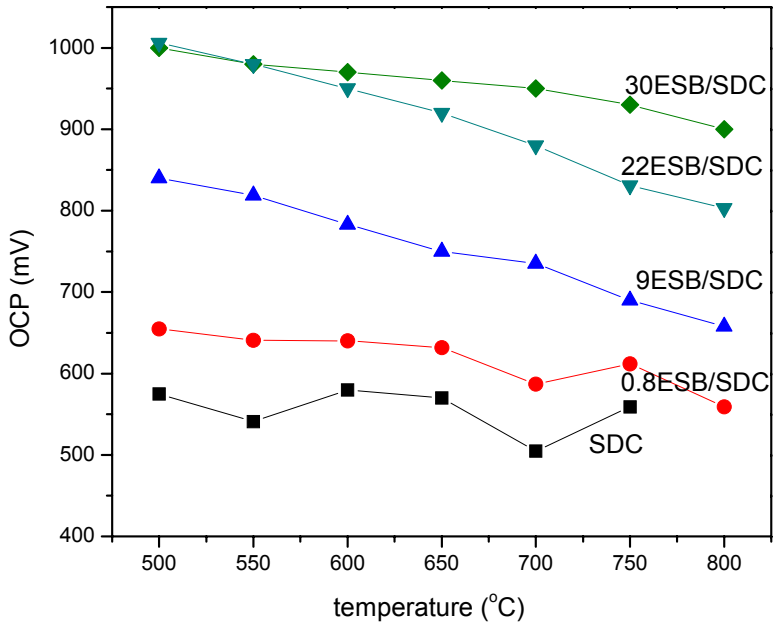



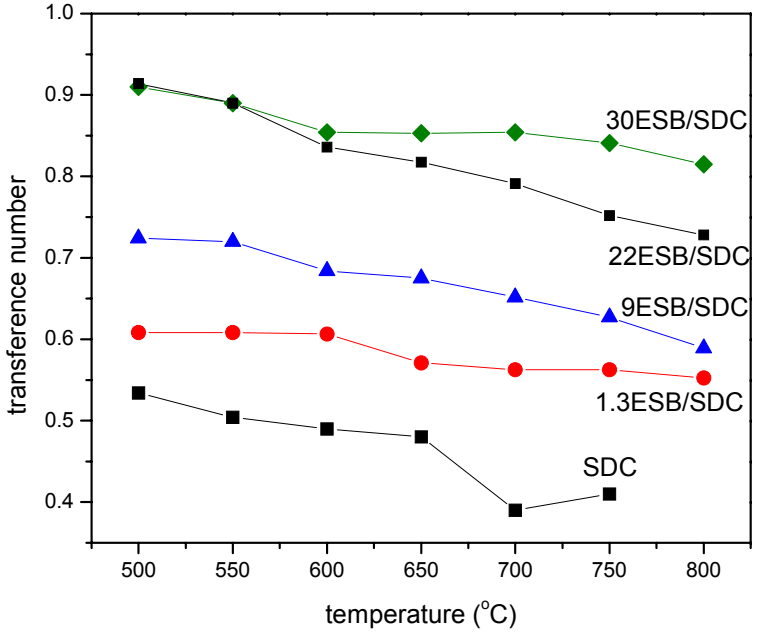

Chemical composition of ESB/SDC bilayer from EDS by X-ray linescan……and mapping

# FUEL CELL TESTING: SCHEMATIC



# Characterization: OCP and $t_i$ vs. Temperature for SDC and ESB/SDC Electrolytes

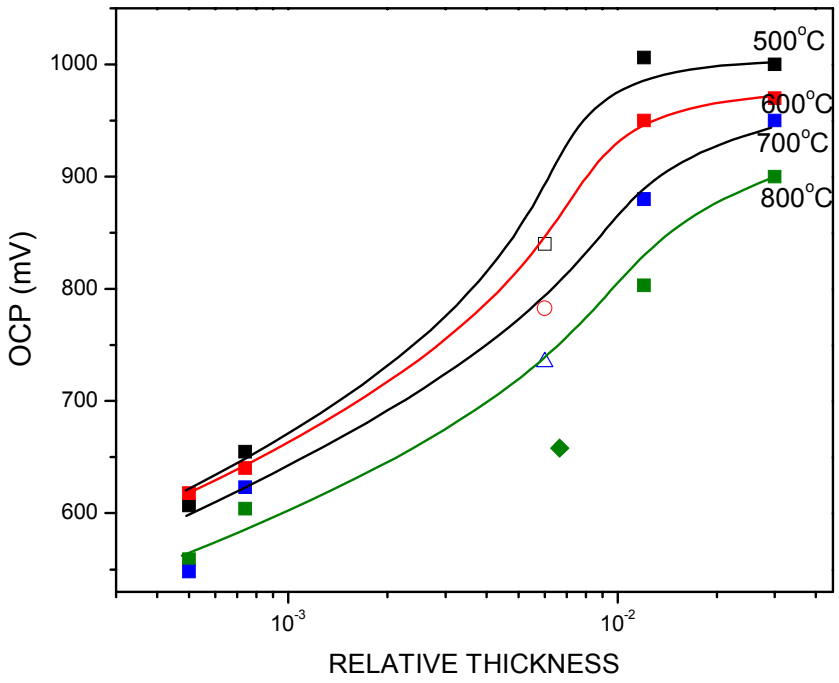


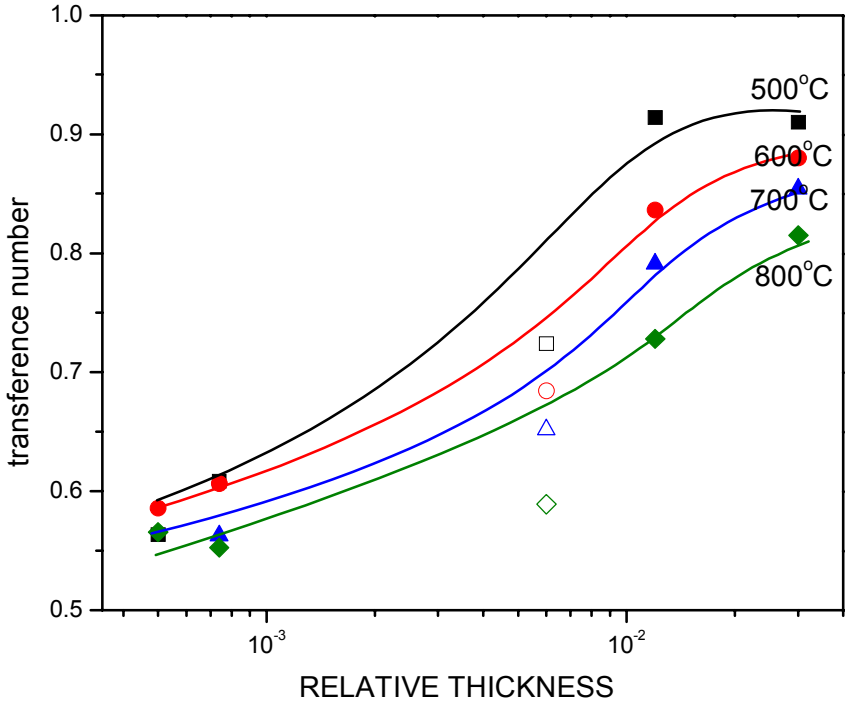




XESB/SDC ≡ X μm thick ESB layer on ~1.5 mm thick SDC substrate

# Effect of Relative Thickness on OCP & $t_i$ for ESB/SDC Bilayer-Electrolyte SOFC

## *with Air at the Cathode and $H_2/H_2O$ at the Anode*




Effect of ESB/SDC *relative thickness* on (a) *open-circuit potential* and (b) *transference number* of bilayer electrolyte SOFC with air on the cathode side and $H_2/H_2O$ on the anode side (open symbols: data obtained with a porous ESB film).

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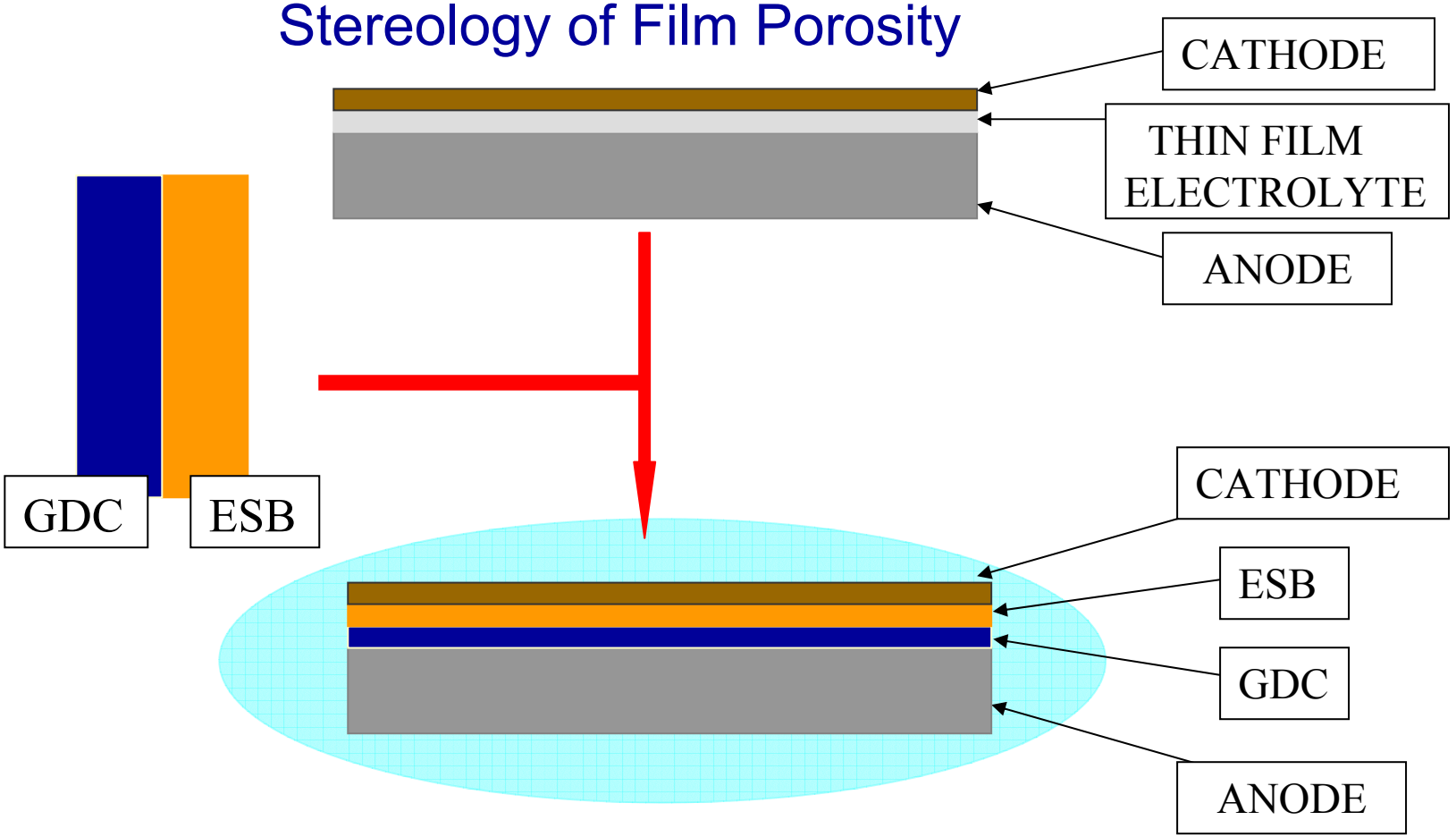
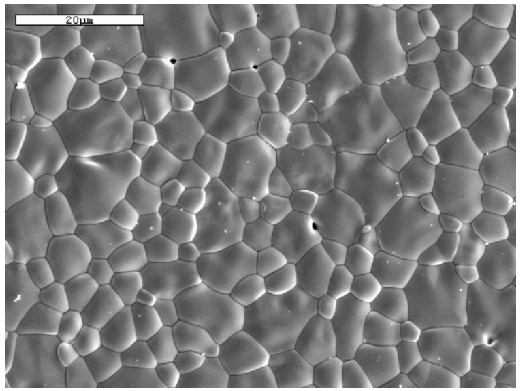
# Electrode supported thin-film electrolyte systems Quantitative Stereology of Film Porosity



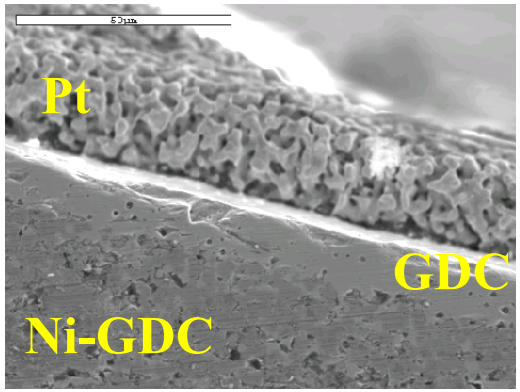
# Thick Film GDC Electrolyte by Colloidal Deposition on Porous Ni-GDC Cermet

Surface



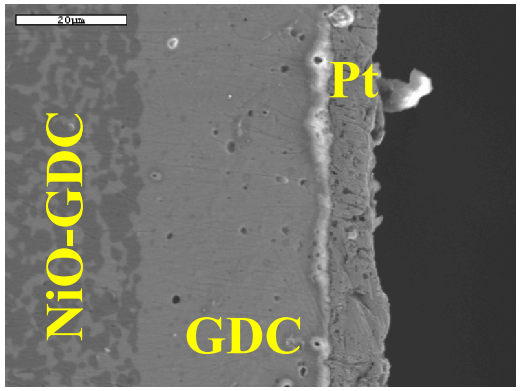
20µm

Cross-section 5coats




50µm

Cross-section 15coats



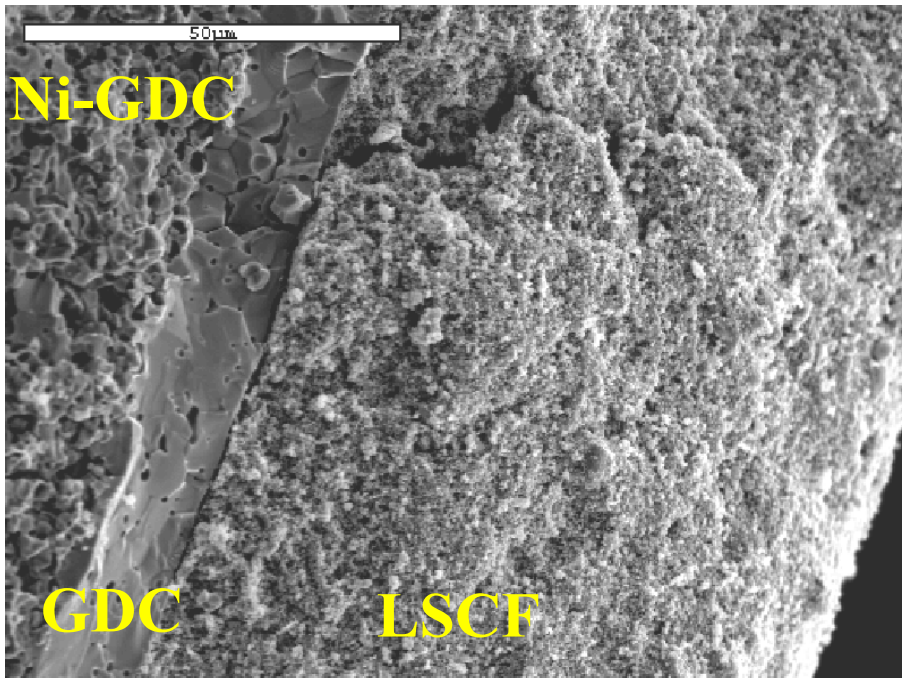

20µm

Sintering Conditions → Pre-sintering: 850°C/4hrs

Final sintering: 1600°C/6hrs

# Fractured Section of Fuel Cell

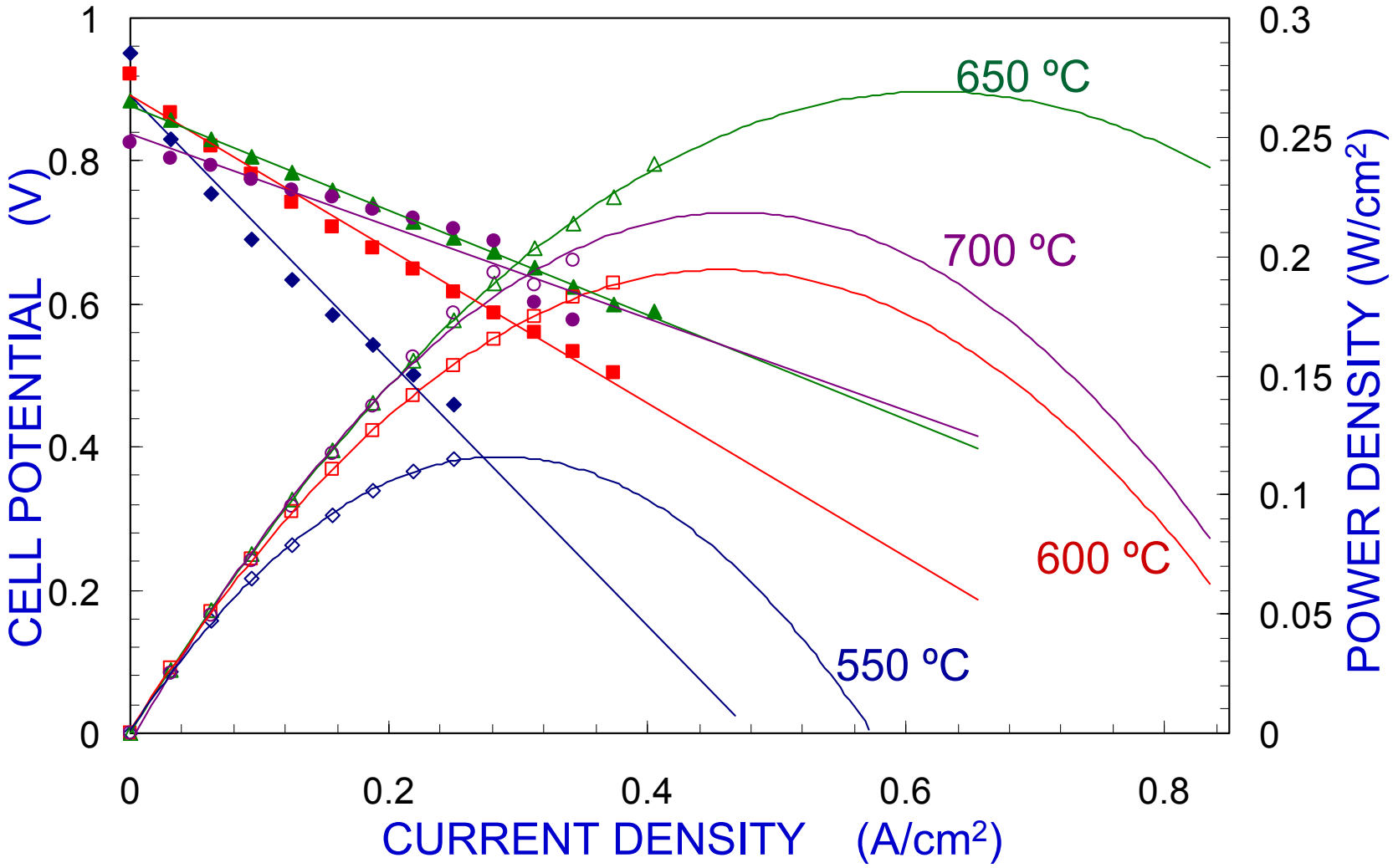
Ni-GDC / GDC(≈15μm) / LSCF(≈85μm)




50μm

# SOFC PERFORMANCE

## $H_2/H_2O$, GDC-Ni / GDC / LSCF, Air

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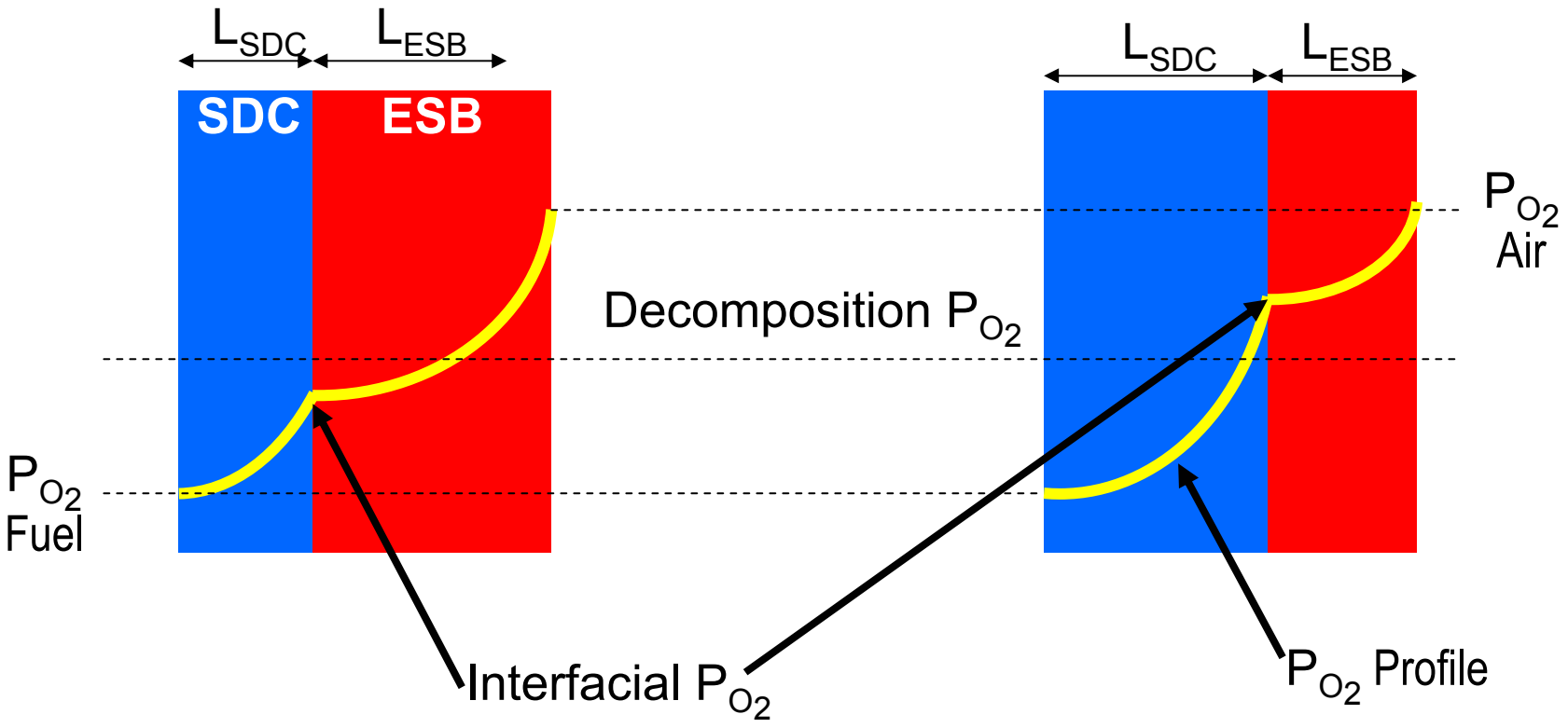
# BILAYER CONCEPT



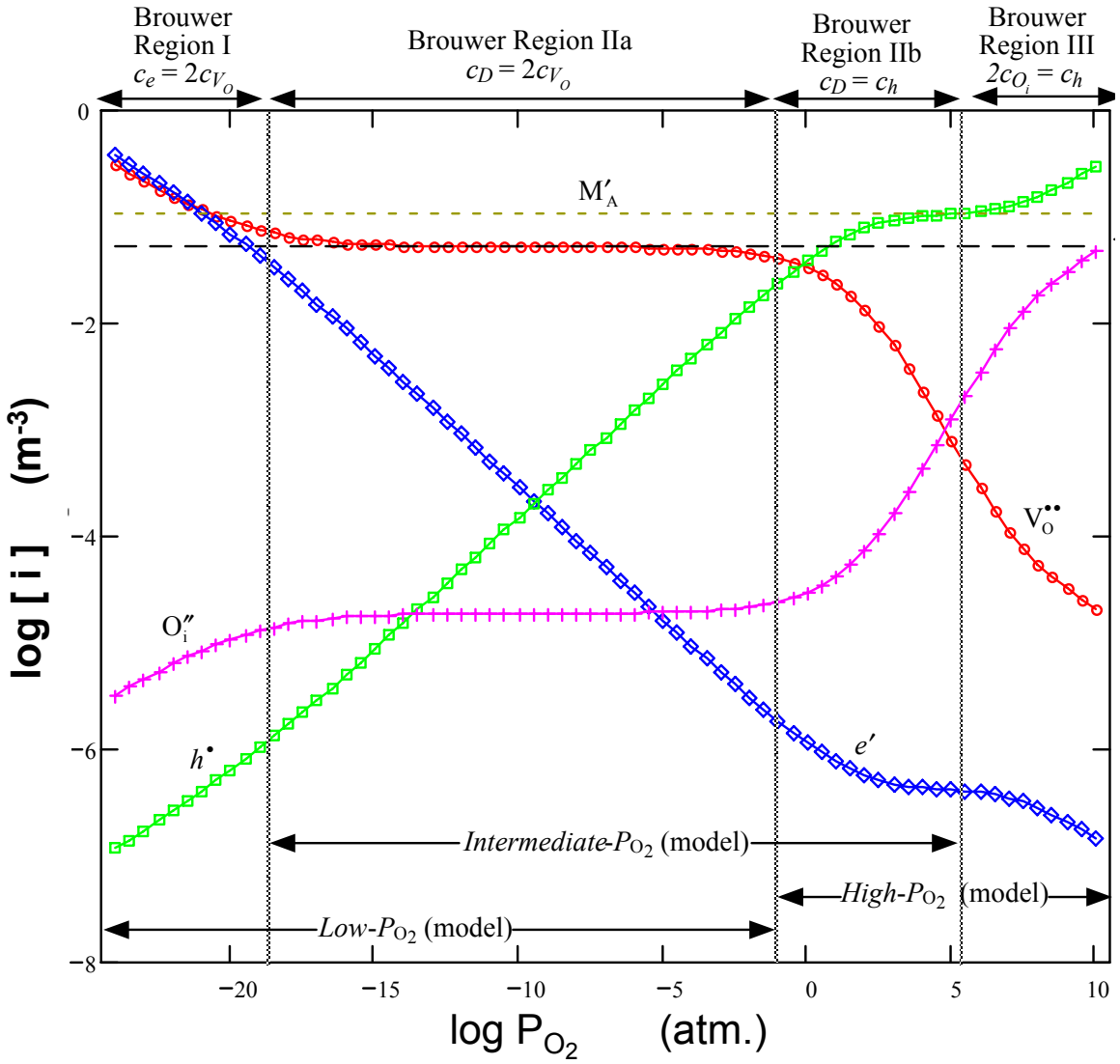

$L_{SDC} / L_{ESB} < \tau_{optimal}$

**ESB decomposes**

$L_{SDC} / L_{ESB} > \tau_{optimal}$

**ESB is stable**

# MODELED DEFECT EQUILIBRIUM DIAGRAM FOR A FLUORITE-STRUCTURED OXIDE

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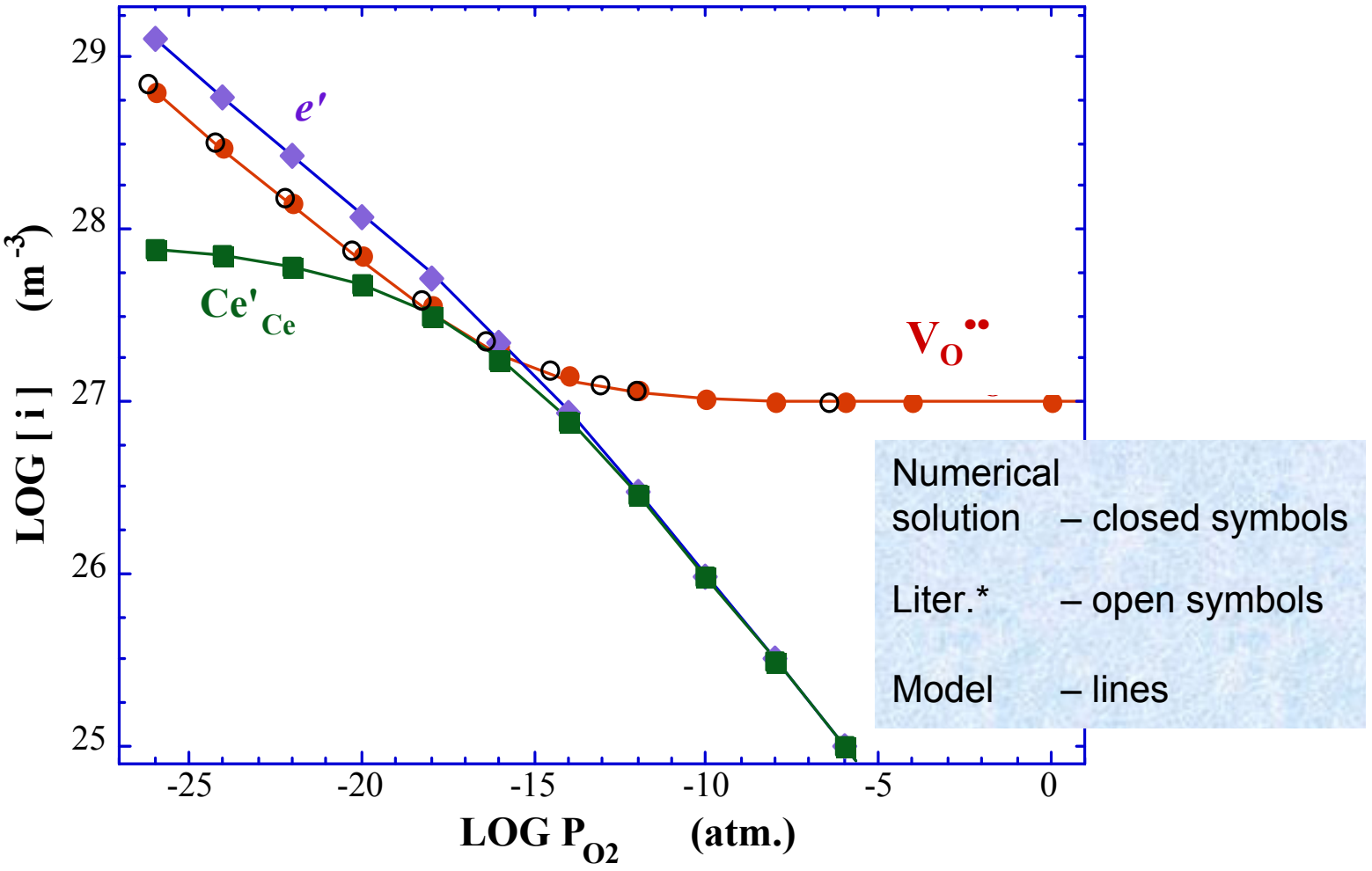
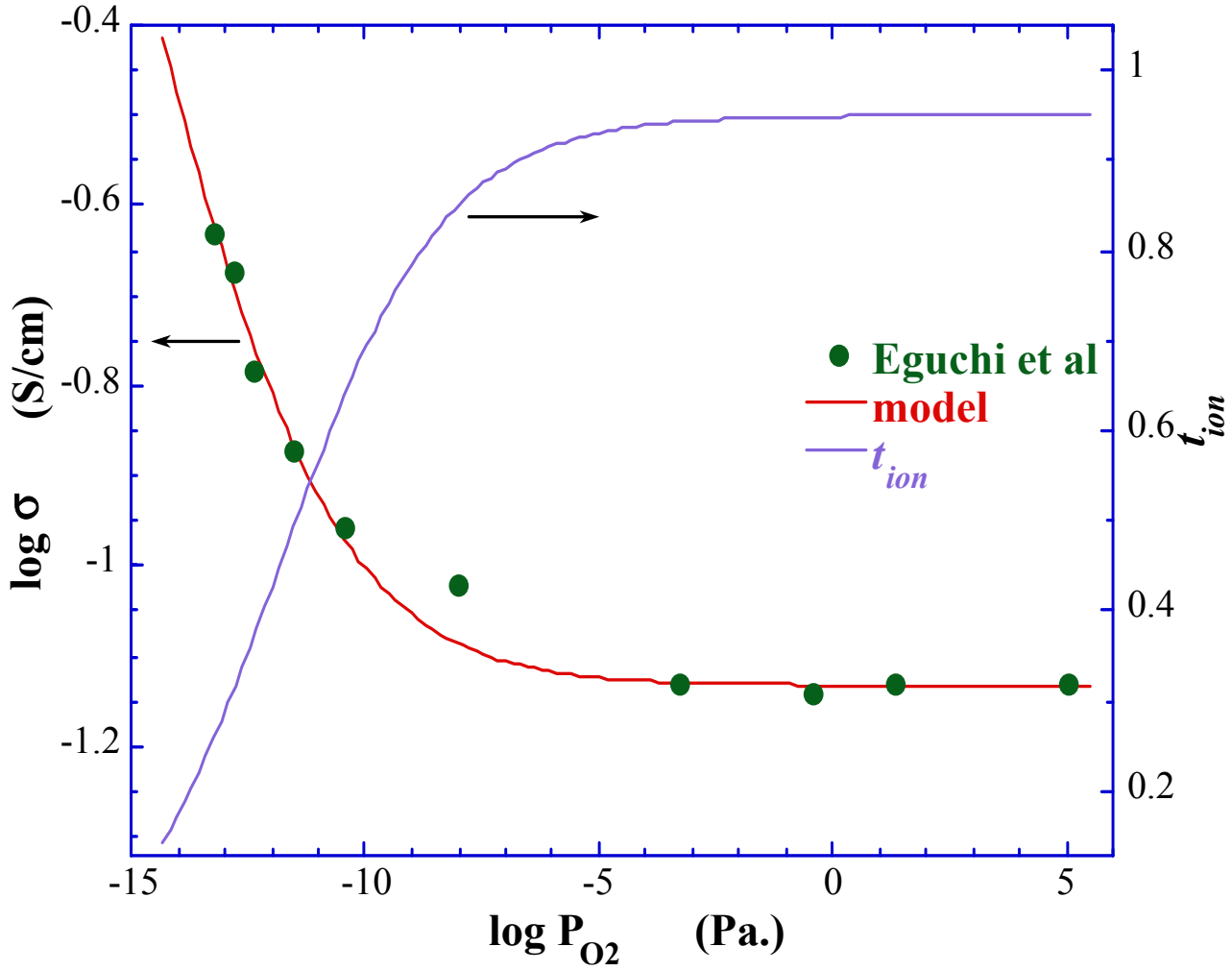
# COMPARISON OF DEFECT MODEL WITH NUMERICAL SOLUTION TO DEFECT EQUATIONS FOR $Ce_{0.8}Sm_{0.2}O_{1.9-\delta}$




* O. Porat and H. L. Tuller, *J. Electroceramics* **1** (1997) 42.

# FIT OF DEFECT MODEL TO CONDUCTIVITY DATA*




* Eguchi et al, *Solid State Ionics* **52** (1992) 265.

# FUNDAMENTAL EQNS. & DEFNS.

Nernst-Planck $$j_i = -D_i \nabla c_i - u_i c_i \nabla \phi$$

Current $$J = \sum_i J_i = q \sum_i z_i j_i$$

Average conductivity $$\overline{\sigma}_i^{-1} = L^{-1} \int_0^L [\sigma_i(x)]^{-1} \cdot dx$$

Charge neutrality $$\sum_i z_i c_i = z_V c_V + z_A c_A + z_e c_e \approx 0$$

Local equilibrium

$$\phi_L - \phi_0 = \Delta\phi = \Phi_{ext} - \Phi_{th} - k_B T (z_V q)^{-1} \ln\left(c_{V_L} / c_{V_0}\right)$$

| | |
|---|---|
| $j$ | flux |
| $J$ | current |
| $c$ | concentration |
| $\phi$ | potential |
| $z$ | charge num. |
| $q$ | elec. charge |
| $s$ | conductivity |
| $u$ | mobility |
| $D$ | diffusivity |
| $L$ | thickness |
| $k_B$ | Boltz. const. |
| $\Phi_{th}$ | Nernst poten. |
| $\Phi_{ext}$ | exter. potential |
| $T$ | temperature |

Subscripts

| | |
|---|---|
| $V$ | $O_2$ vacancies |
| $e$ | electrons |

# LINEAR POTENTIAL MODEL

For $\nabla j_i = 0$,

$\nabla c_V \approx 0$

and/or

$D_e >> D_V$

Defect distribution

$$c_i(x) = \frac{c_{i_L} - c_{i_0}\exp(\beta\Delta\phi) + (c_{i_0} - c_{i_L})\exp(\beta\Delta\phi\, x/L)}{1 - \exp(\beta\Delta\phi)}$$

Defect flux $$j_i(\Delta\phi) = \frac{J_i(\Delta\phi)}{z_i q} = -u_i \frac{\Delta\phi}{L} \cdot \frac{c_{i_L} - c_{i_0}\exp(\beta\Delta\phi)}{1 - \exp(\beta\Delta\phi)}$$

$$\beta = \frac{z_V D_V - z_e D_e}{D_e - D_V} \cdot \frac{q}{k_B T}$$

typically

$$\beta \sim \frac{q}{k_B T}$$

Current efficiency

$$\zeta_J(\Delta\phi) = \frac{J(\Delta\phi)}{J_V(\Delta\phi)} = 1 + \frac{J_e(\Delta\phi)}{J_V(\Delta\phi)}$$

Power efficiency

$$\zeta_P(\Delta\phi) = \frac{J(\Delta\phi)}{J_V(\Delta\phi)} \cdot \frac{\Phi_{ext}}{\Phi_{th}}$$

Transference number $$\bar{t}_{ion}(\Delta\phi) = \left[1 + \frac{J_e(\Delta\phi)}{J_V(\Delta\phi)} \cdot \frac{\ln(c_{V_0}/c_{V_L}) + \beta\Delta\phi}{\ln(c_{e_0}/c_{e_L}) + \beta\Delta\phi}\right]^{-1}$$

# NON-LINEAR POTENTIAL MODEL

$$\nabla^2\phi = \lambda\nabla^2 c_V \quad \leftarrow \quad \nabla J = 0 \;\&\; \nabla j_i = 0$$

$$\gamma = \frac{\phi_L - \phi_0}{\lambda L} - \frac{c_{V_L} - c_{V_0}}{L}$$

$$\lambda = \frac{(z_V - z_e)k_B T}{z_e q c_A}$$

$z_V = 2,\ z_e = z_A = -1$

$$c_V(x) - c_{V_0} - (\phi(x) - \phi_0)/\lambda = -\gamma x \qquad \text{(A)}$$

(Nernst-Planck + current equation)

$$(z_V u_e j_V - u_V j_e)c_V - j_V u_e c_A = \frac{qD_e D_V}{k_B T}(6c_V - c_A)\nabla c_V$$

$$c_V(x) - c_{V_0} - \frac{(D_V\gamma - j_V)c_A}{6D_V\gamma}\cdot \ln\frac{6D_V\gamma c_V(x) - j_V c_A}{6D_V\gamma c_{V_0} - j_V c_A} = -\gamma x \qquad \text{(B)}$$

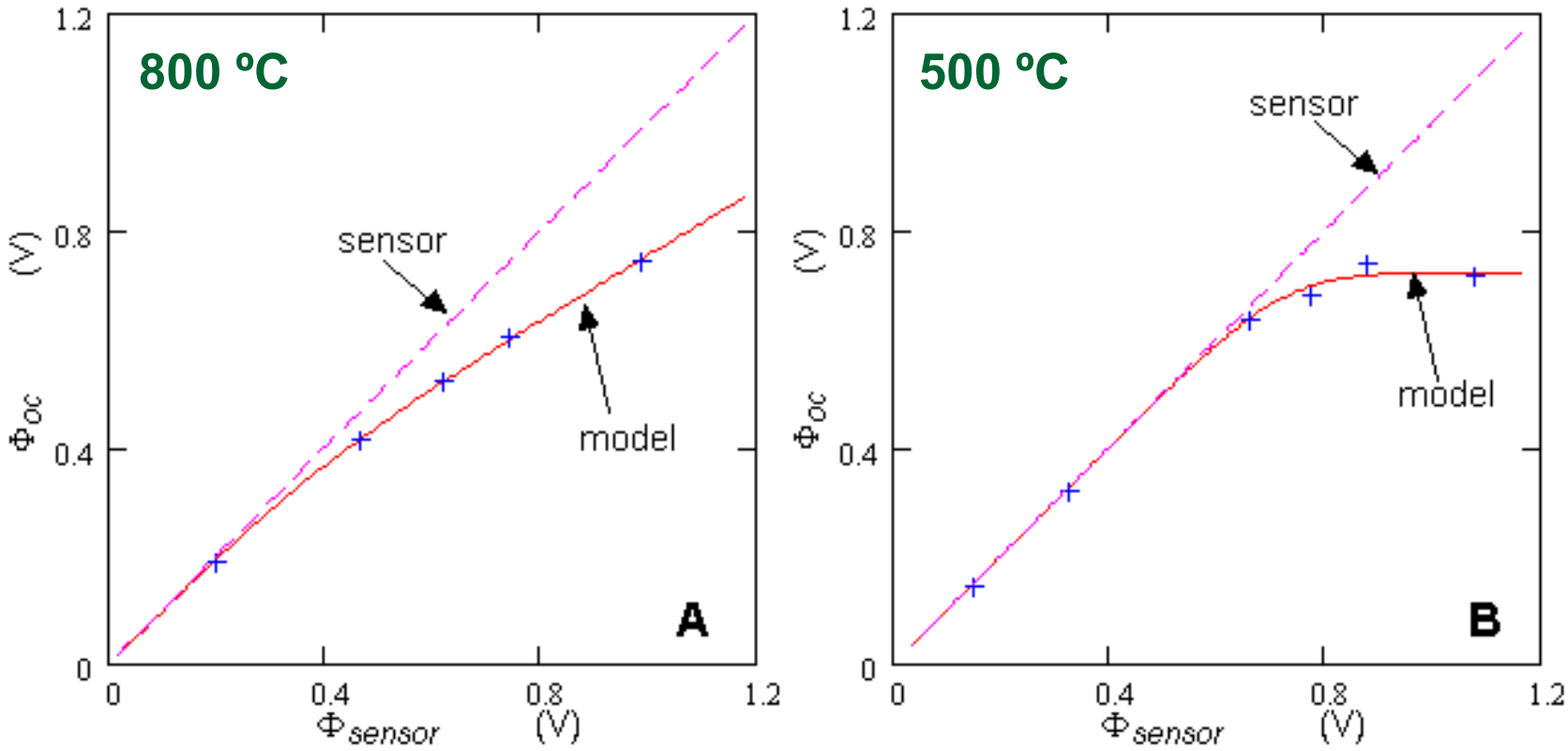
(A) – (B)

$$\phi(x) = \phi_0 - \frac{(D_V\gamma - j_V)k_B T}{z_V q D_V \gamma}\cdot \ln\frac{6D_V\gamma c_V(x) - j_V c_A}{6D_V\gamma c_{V_0} - j_V c_A}$$

$$\gamma = -k_B T\frac{z_V u_e j_V - u_V j_e}{6qD_e D_V}$$

# OPEN CIRCUIT ($\Phi_{oc}$) vs. NERNST ($\Phi_{sensor}$) POTENTIAL FOR SDC SOFC

model (—), expt. data (+), sensor (---)




$H_2/H_2O$ ($CO/CO_2$), Pt/ SDC / Pt, Air

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# Modeling the Relationship between Thickness ratio, Performance and ESB Decomposition Potential

$$J_V^{SDC} = J_V^{ESB}$$

+

$$\phi_L - \phi_0 = \Delta\phi = -\frac{(z_V q D_V \gamma - J_V) k_B T}{z_V^2 q^2 D_V \gamma} \cdot \ln \frac{z_V^2 (z_V - z_{e,h}) q D_V \gamma c_{V_L} - J_V c_A}{z_V^2 (z_V - z_{e,h}) q D_V \gamma c_{V_0} - J_V c_A}$$

$$\gamma = \lambda^{-1} \Delta\phi / L - (c_{V_L} - c_{V_0}) / L = -\frac{z_{e,h} D_{e,h} J_V + z_V D_V J_{e,h}}{z_V (z_V - z_{e,h}) q D_{e,h} D_V}$$

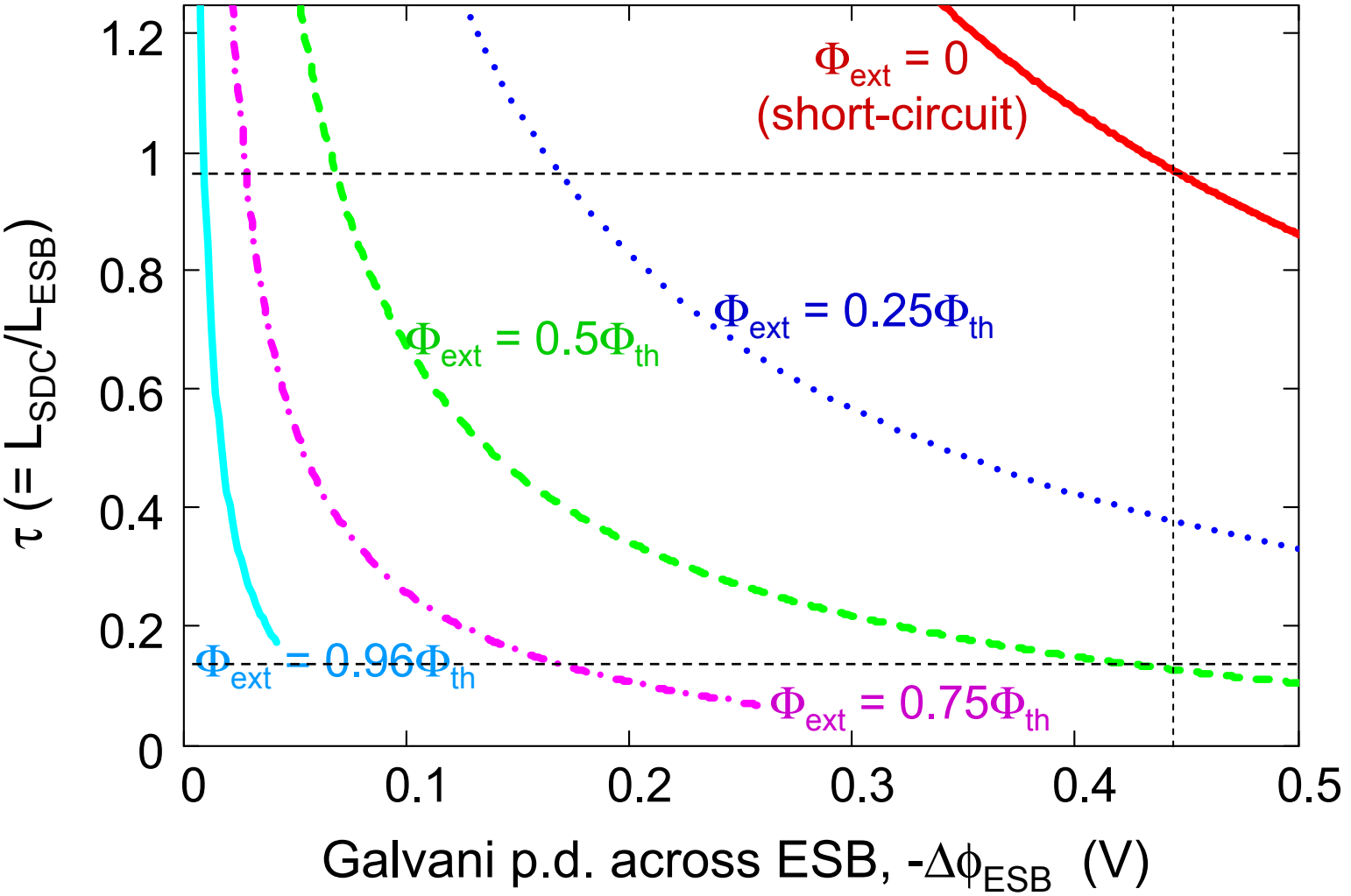
$$\tau_{oc} = \frac{L^{\varepsilon}}{L^{\delta}} = \frac{D_e^{\varepsilon} D_V^{\varepsilon} \left[ \frac{3\left(c_{V_L}^{\varepsilon} - c_{V_0}^{\varepsilon}\right)}{-D_e^{\varepsilon} - 2D_V^{\varepsilon}} - \frac{\left(D_e^{\varepsilon} - D_V^{\varepsilon}\right)c_A^{\varepsilon}}{\left(-D_e^{\varepsilon} - 2D_V^{\varepsilon}\right)^2} \ln \frac{2\left(-D_e^{\varepsilon} - 2D_V^{\varepsilon}\right)c_{V_L}^{\varepsilon} + D_e^{\varepsilon} c_A^{\varepsilon}}{2\left(-D_e^{\varepsilon} - 2D_V^{\varepsilon}\right)c_{V_0}^{\varepsilon} + D_e^{\varepsilon} c_A^{\varepsilon}} \right]}{D_h^{\delta} D_V^{\delta} \left[ \frac{c_{V_L}^{\delta} - c_{V_0}^{\delta}}{D_h^{\delta} - 2D_V^{\delta}} + \frac{\left(D_h^{\delta} - D_V^{\delta}\right)c_A^{\delta}}{\left(D_h^{\delta} - 2D_V^{\delta}\right)^2} \ln \frac{2\left(D_h^{\delta} - 2D_V^{\delta}\right)c_{V_L}^{\delta} - D_h^{\delta} c_A^{\delta}}{2\left(D_h^{\delta} - 2D_V^{\delta}\right)c_{V_0}^{\delta} - D_h^{\delta} c_A^{\delta}} \right]}$$

ε = SDC, δ = ESB

$$\tau = \frac{\frac{q\left(\Phi_{ext} - \Phi_{th}\right)}{k_B T} - \frac{1}{2}\ln\frac{c_{V_L}}{c_{V_0}} - \frac{q\Delta\phi^{\delta}}{k_B T} + 3\left(\frac{c_{V_0}^{\varepsilon}}{c_A^{\varepsilon}} - \frac{1}{2}\right)\left[\left(\frac{c_{V_L}}{c_{V_0}}\right)^{-\frac{1}{2}} \exp\left(\frac{q\left(\Phi_{ext} - \Phi_{th} - \Delta\phi^{\delta}\right)}{k_B T}\right) - 1\right]}{\frac{D_V^{\delta}}{D_V^{\varepsilon}} \cdot \frac{c_A^{\delta}}{c_A^{\varepsilon}} \cdot \left\{\frac{q\Delta\phi^{\delta}}{k_B T} - \left(\frac{c_{V_L}^{\delta}}{c_A^{\delta}} + \frac{1}{2}\right)\left[1 - \exp\left(\frac{q\Delta\phi^{\delta}}{k_B T}\right)\right]\right\}}$$

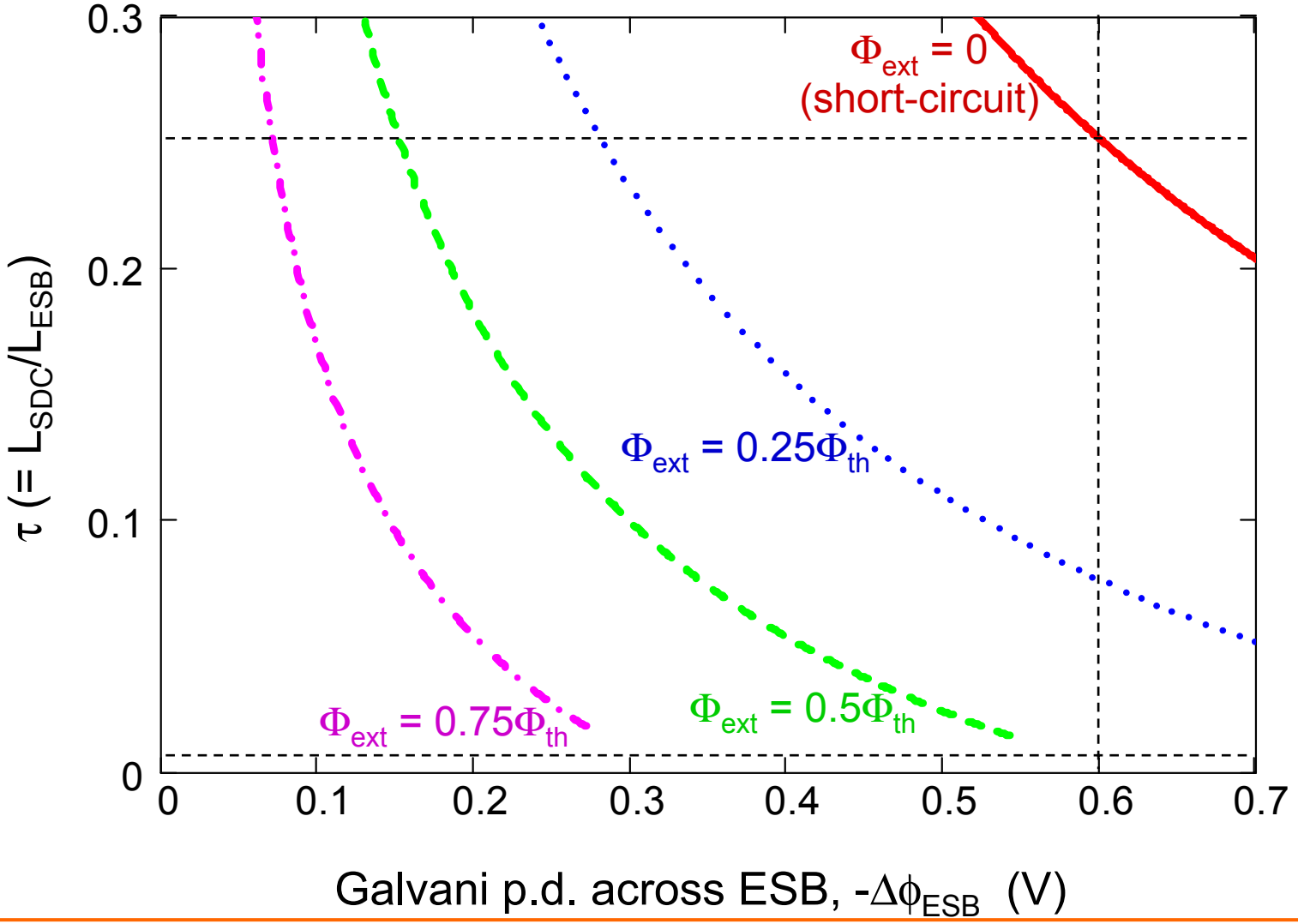
# ELECTROLYTE DESIGN

## Determination of thickness ratio at 800 ºC



# ELECTROLYTE DESIGN

## Determination of thickness ratio at 500 ºC



# RELATIVE THICKNESS ($\tau$) PREDICTED BY MODEL

| | | $\tau$ | $1/\tau = L_{ESB}/L_{SDC}$ | ASR* ($\Omega cm^2$) |
|---|---|---|---|---|
| 800 ºC | short circuit | 0.98 | 1.0 | 0.010 |
| | max. power | 0.14 | 7.1 | 0.003 |
| 500 ºC | short circuit | 0.25 | 4.0 | 0.11 |
| | max. power | **~0.007** | **~140** | **0.05** |

* $L = L_{ESB} + L_{SDC} = 10\ \mu m$

# SUMMARY

Developed Analytical Models for Transport in Oxides

- Based on Nernst-Planck flux equation and defect equilibria (minimal assumptions)
- Determined external equilibrium constant, $K_R$
- Verified transport model for SDC OCP vs. anode $P_{O_2}$
- Verified defect model for SDC conductivity vs. $P_{O_2}$
- Used model to predict SDC/ESB thickness ratio

@500 ºC $140 > L_{ESB}/L_{SDC} > 4$

$0.05\ \Omega cm^2 < ASR < 0.11\ \Omega cm^2$

# SUMMARY-Continued

Fabricated and Tested ESB/SDC Bilayer Electrolytes

- Achieved OCP = 1.00 V and $t_i$ = 0.9
- Demonstrated increasing relative thickness of ESB increases OCP and $t_i$
  - Consistent with bilayer concept
  - Consistent with computer model predictions

Fabricated thin (~10 μm) anode supported GDC SOFCs

-Maximum power density @650 C = 270 mW/cm$^2$

Developed New Bismuth Oxide Electrolyte (DWSB)

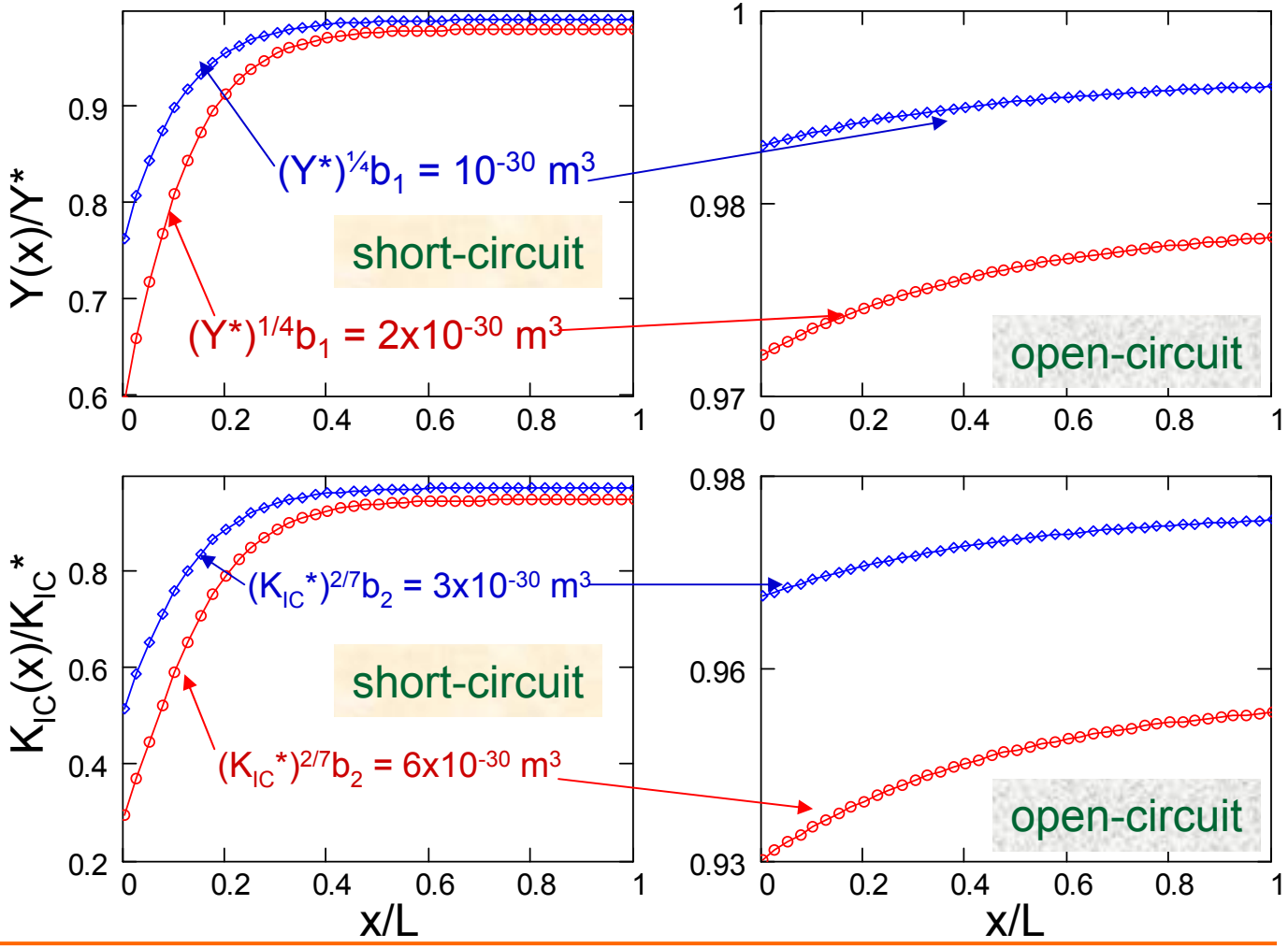
- Highest conductivity of any known electrolyte
  - -0.57 S/cm at 800°C
  - -0.043 S/cm at 500°C

# APPLICABILITY TO SOFC COMMERCIALIZATION

$Y(x)=Y^*[(Y^*)^{1/4}b_1c_V(x)+1]^{-4}$

$K_{IC}(x)=K_{IC}^*[(K_{IC}^*)^{2/7}b_2c_V(x)+1]^{-3.5}$

**SPATIAL VARIATION OF ELASTIC MODULUS (Y) & FRACTURE TOUGHNESS ($K_{IC}$) IN SOFC ELECTROLYTES**

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# Activities for the Next 3 Months…

Develop cathode compatible with $Bi_2O_3$ electrolyte.

Fabricate and test thin anode-supported ESB/GDC SOFCs.