DETERMINATION OF ELECTROCHEMICAL PERFORMANCE, AND THERMO-MECHANICAL-CHEMICAL STABILITY OF SOFCS FROM DEFECT MODELING

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OBJECTIVES

1. Provide fundamental relationships between SOFC performance and operating conditions (T, P_{O2}, V, etc..)
2. Experimentally verify models and devise strategies to obtain relevant material constants
3. Extend models to:
   - Thermo-mechanical stability
     - Fracture toughness
     - Elastic modulus
   - Thermo-chemical stability
     - Pore formation and reactions at cathode/electrolyte interface
   - Multilayer structures
     - Interfacial defect concentration, etc.
4. Incorporate microstructural effects such as grain boundaries and grain-size distribution
5. Assemble software package for integration into SECA failure analysis models

DEFECT EQUILBIRIA

Electron-Hole Pair Formation

$$null \leftrightarrow e' + h^{\bullet}$$

$$K_i = c_e c_h = N_v N_c \exp\left(-E_g / k_B T\right)$$

External Equilibria

$$O_O^{\times} \leftrightarrow V_O^{\bullet\bullet} + 2e' + \frac{1}{2}O_2$$

$$K_r = c_V c_e^2 P^{\frac{1}{2}} = K_r^* \exp\left(-\Delta G_r / k_B T\right)$$

Internal Equilibria

$$O_O^{\times} \leftrightarrow V_O^{\bullet\bullet} + O_i''$$

$$K_f = c_V c_I$$

KEYS

(1) Defect Triads vs. Defect Pairs (Brouwer)

$$c_e + c_A = 2c_V$$

$c_e = 2c_V$ …Region I

$c_A = 2c_V$ …Region IIa

(2) Limiting Case

$$P >> 4^{-4} K_r^2 c_V^{-6}$$

DEFECT EQUILIBRIA - BROUWER APPROACH

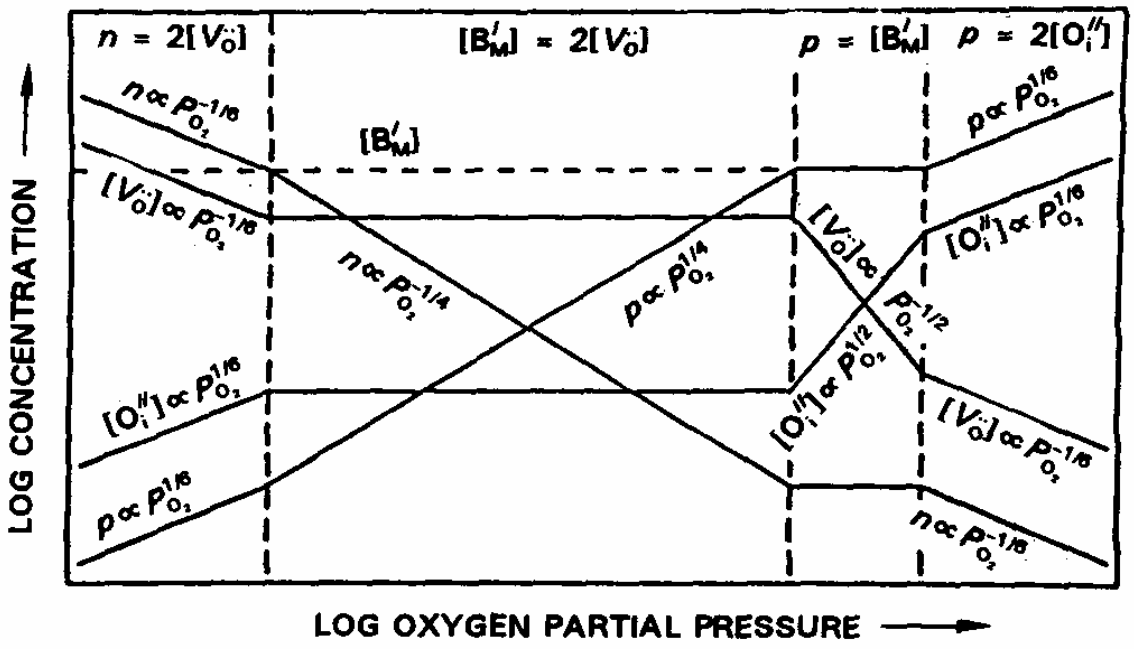
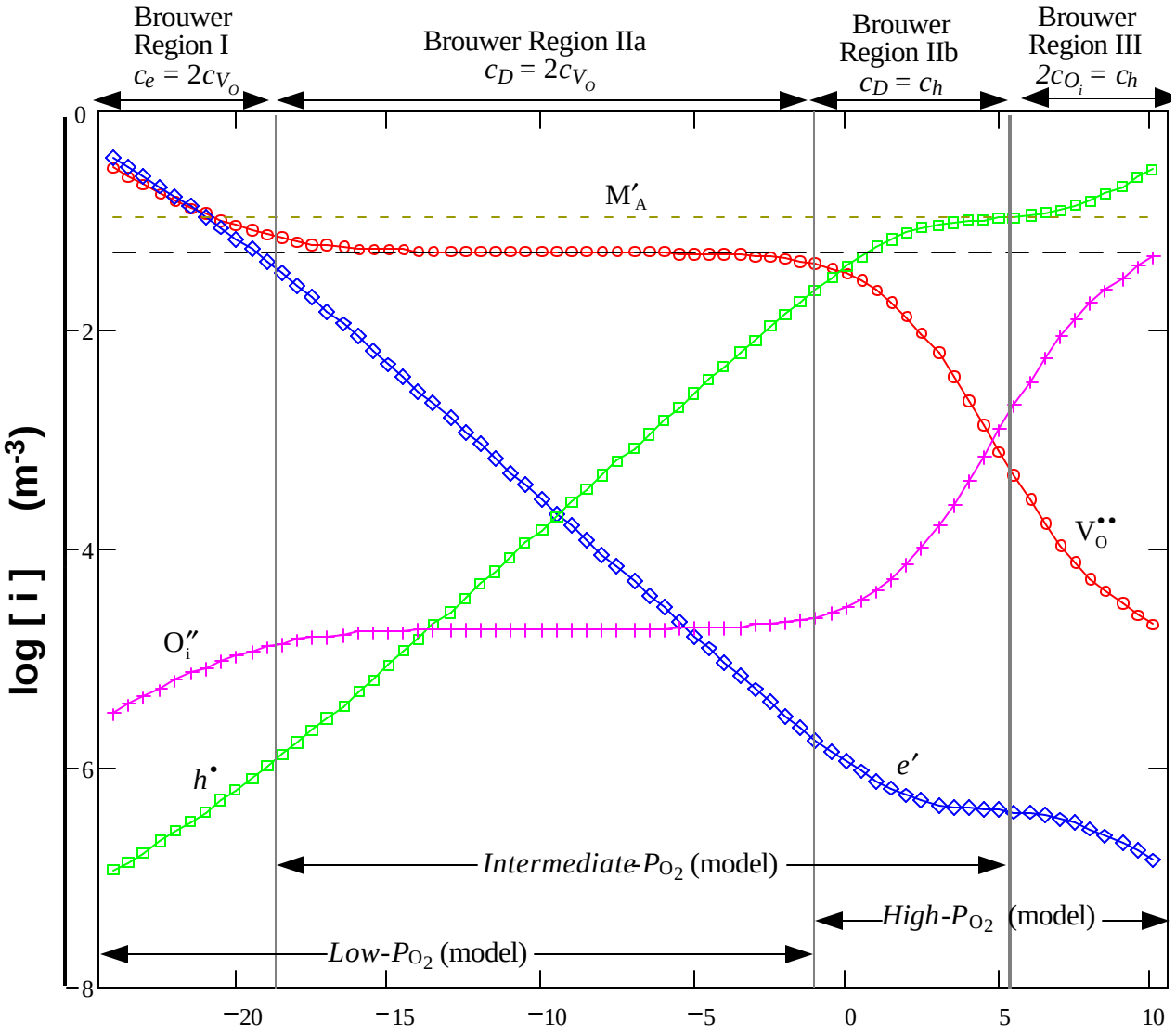
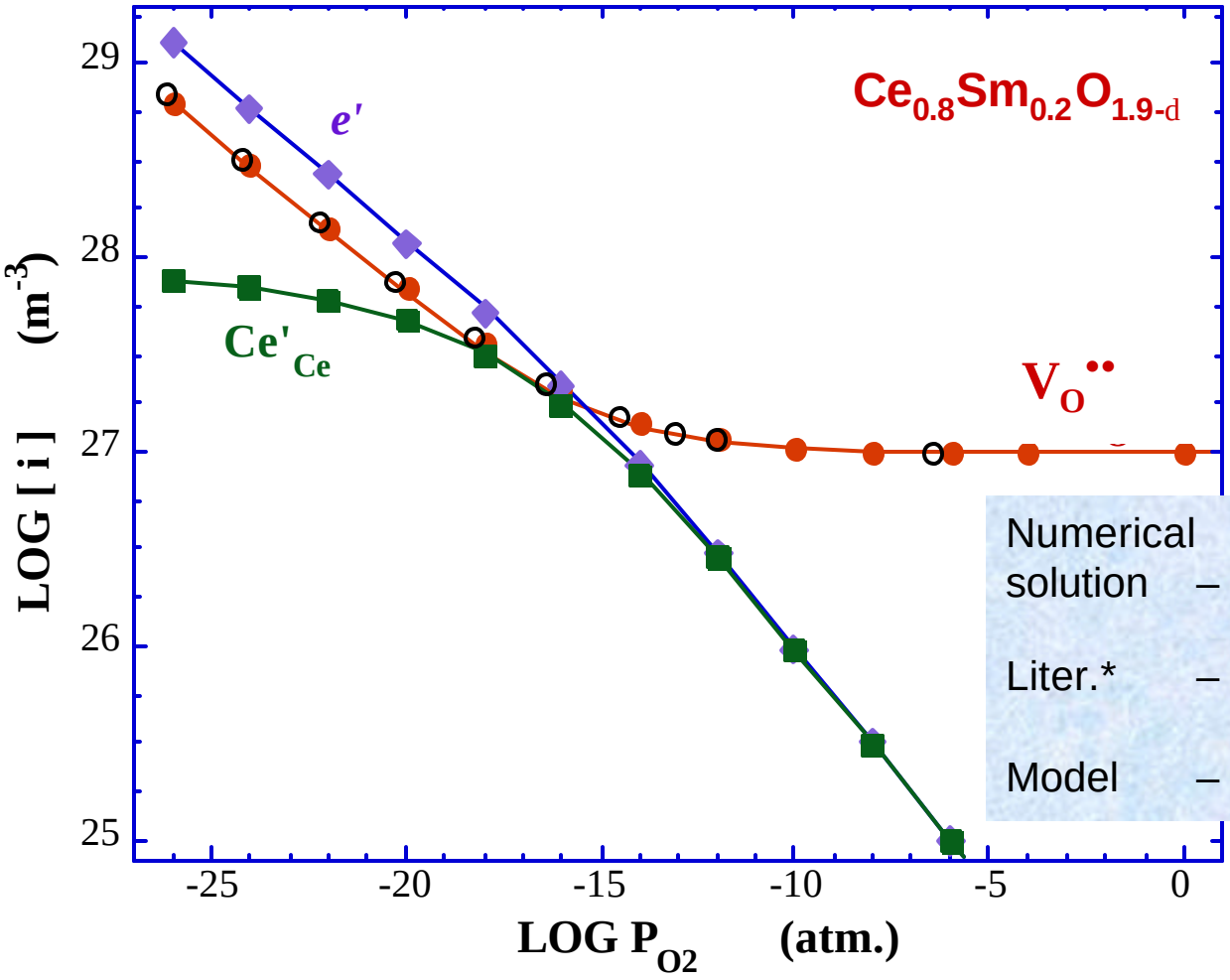


Figure 3.3. *Variation of defect concentration as a function of oxygen partial pressure for a MO_2-B_2O_3 system [3.17]*

DEFECT EQUILIBRIA - MODEL RESULTS (FLUORITE)



COMPARISON OF DEFECT MODEL WITH NUMERICAL SOLUTION



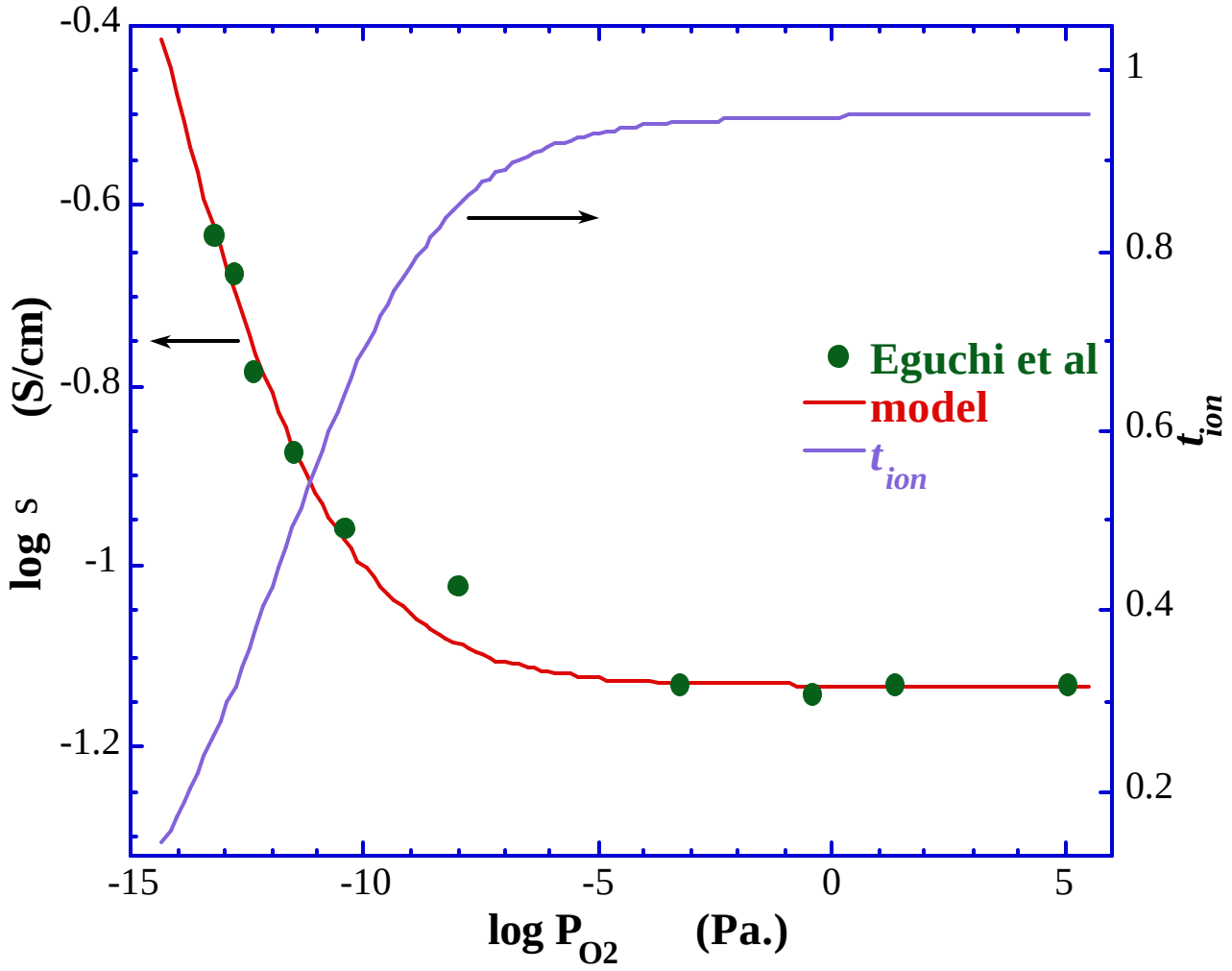
Numerical solution – closed symbols

Liter.* – open symbols

Model – lines

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

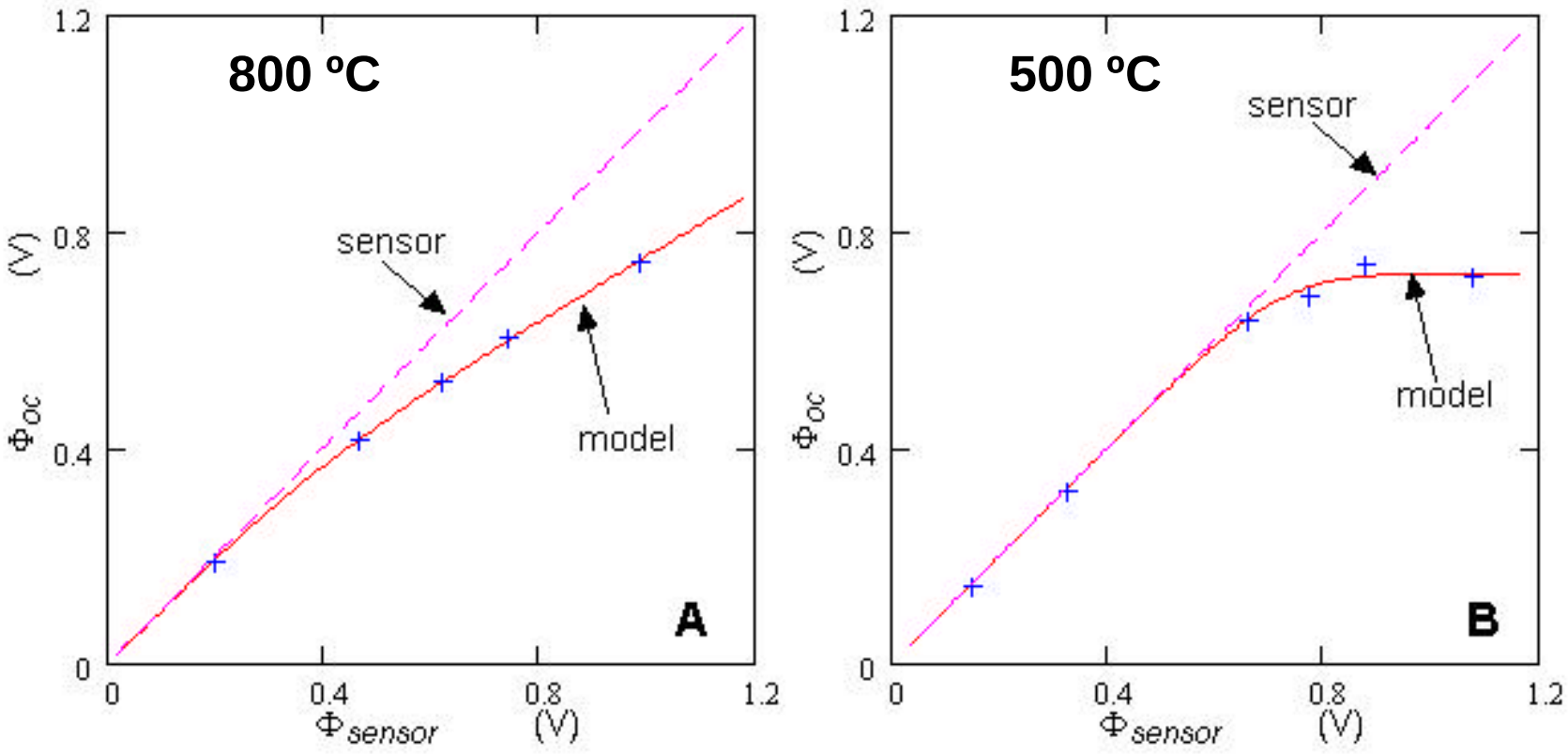
FIT OF DEFECT MODEL TO CONDUCTIVITY DATA*



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

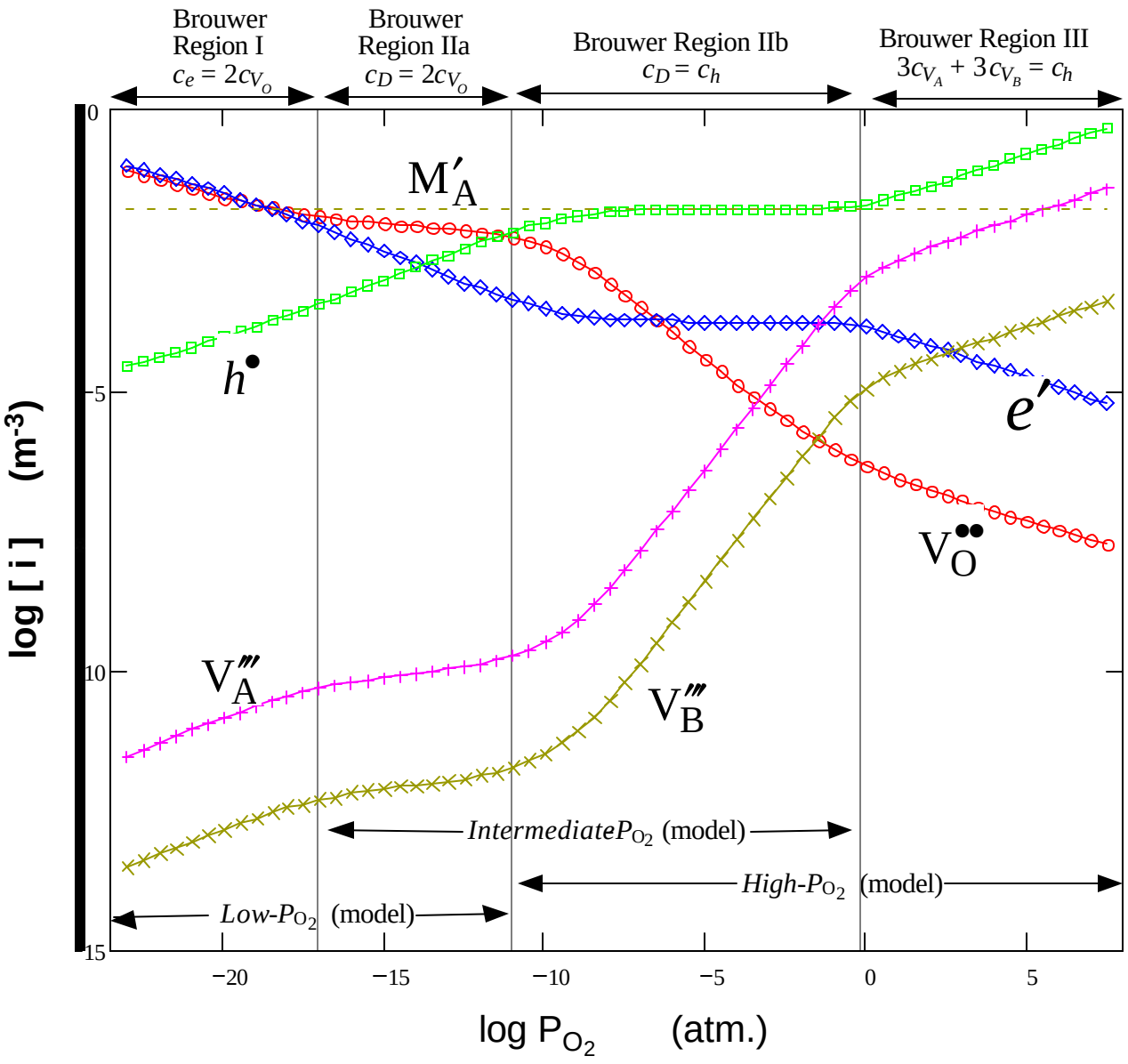
OPEN CIRCUIT (F_{oc}) vs. NERNST (F_{sensor}) POTENTIAL FOR SDC SOFC

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

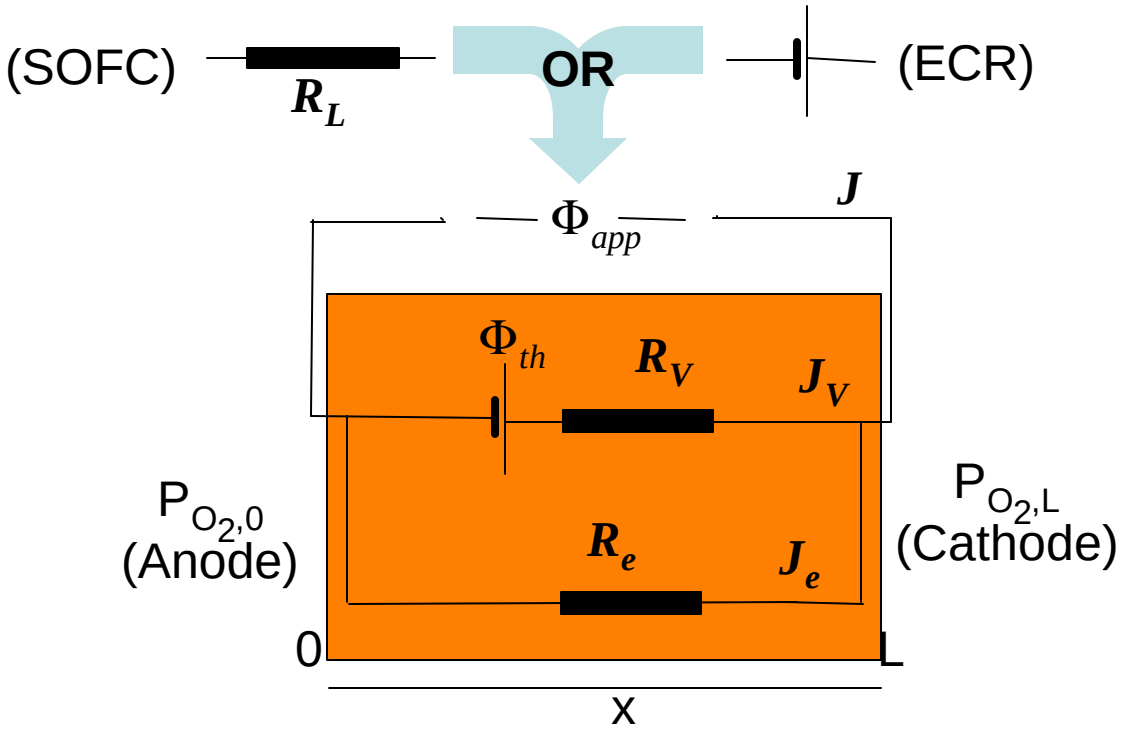


H_2/H_2O (CO/CO_2), Pt/ SDC / Pt, Air

DEFECT EQUILIBRIA - MODEL RESULTS (PEROVSKITE)



ELECTROCHEMICAL PERFORMANCE



$$J = \left(\bar{t}_{ion}\Phi_{th} - \Phi_{app}\right)\bar{\sigma}_{tot}L^{-1} = \eta\bar{\sigma}_{tot}L^{-1}$$

overpotential, $\eta = \bar{t}_{ion}\Phi_{th} - \Phi_{app}$

FUNDAMENTAL EQUATIONS & DEFINITIONS

j	flux
J	current
c	concentration
ϕ	potential
z	charge num.
q	elec. charge
σ	conductivity
u	mobility
D	diffusivity
L	thickness
k_B	Boltz. const.
Φ_{th}	Nernst poten.
Φ_{app}	exter. potential
T	temperature

Subscripts

V	O_2 vacancies
e	electrons

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 $$\overline{\sigma}_i^{-1} = L^{-1} \int_0^L \left[\sigma_i(x)\right]^{-1} \cdot \mathrm{d}x$$

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

Local equilibrium

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

LINEAR POTENTIAL MODEL

For $\nabla j_i = 0$,

$\nabla c_V \sim 0$

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

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

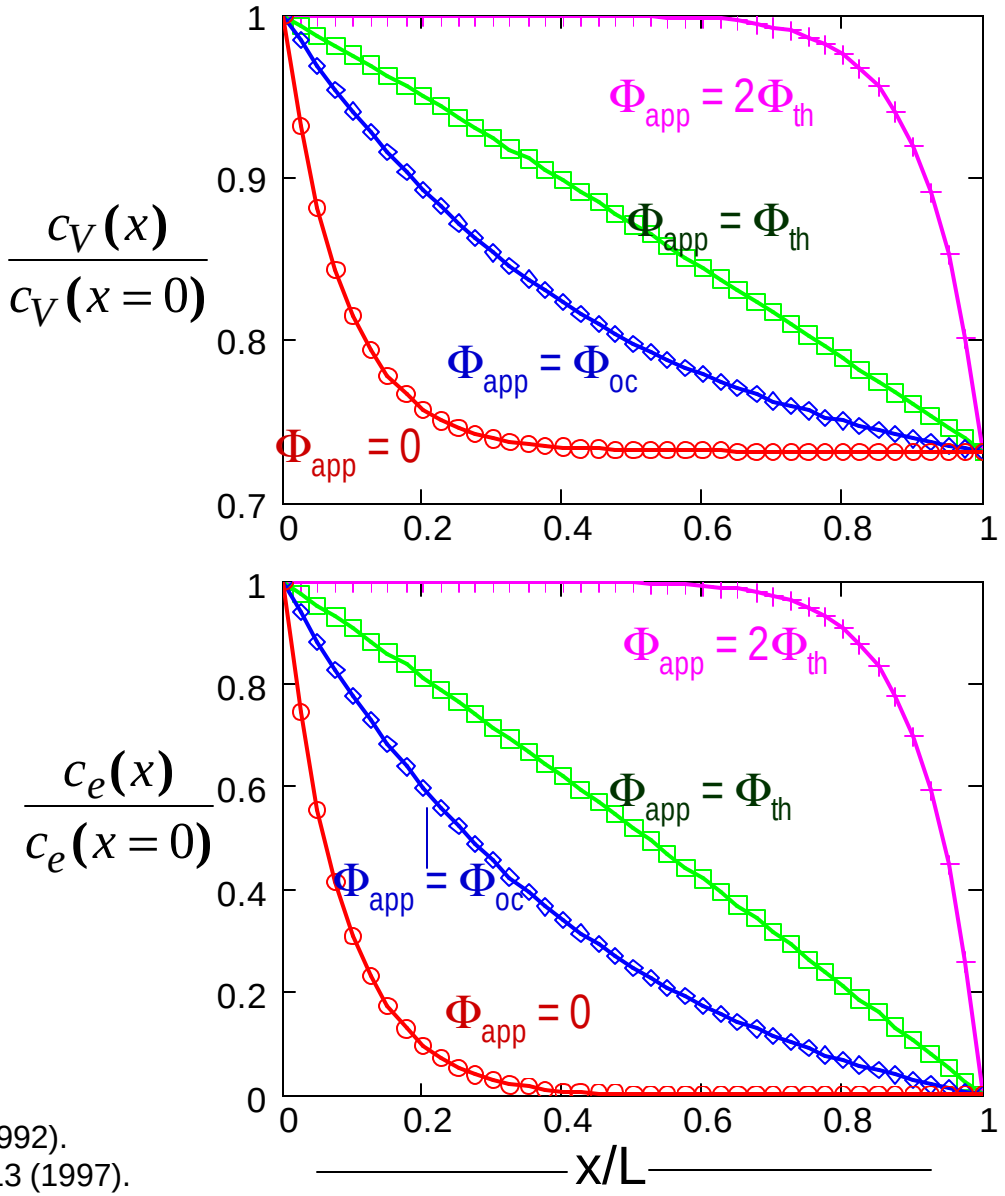
Ionic transference number

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

LINEAR POTENTIAL MODEL: DEFECT CONCENTRATION PROFILES

Fixed Boundary Conditions

Concentration profiles are similar to those produced from the models of Riess and Liu.



I. Riess, *Solid State Ionics* **52** 127 (1992).
M. Liu, *J. Electrochem. Soc.* **144** 1813 (1997).

BOUNDARY CONDITIONS

$$a_{O_2}(\Delta\phi) \sim \exp(B \cdot \Delta\phi)$$

Anode: $\Delta G_r = \Delta G_r^{oc} - q\eta$

Cathode: $\Delta G_r = \Delta G_r^{oc} + q\eta$

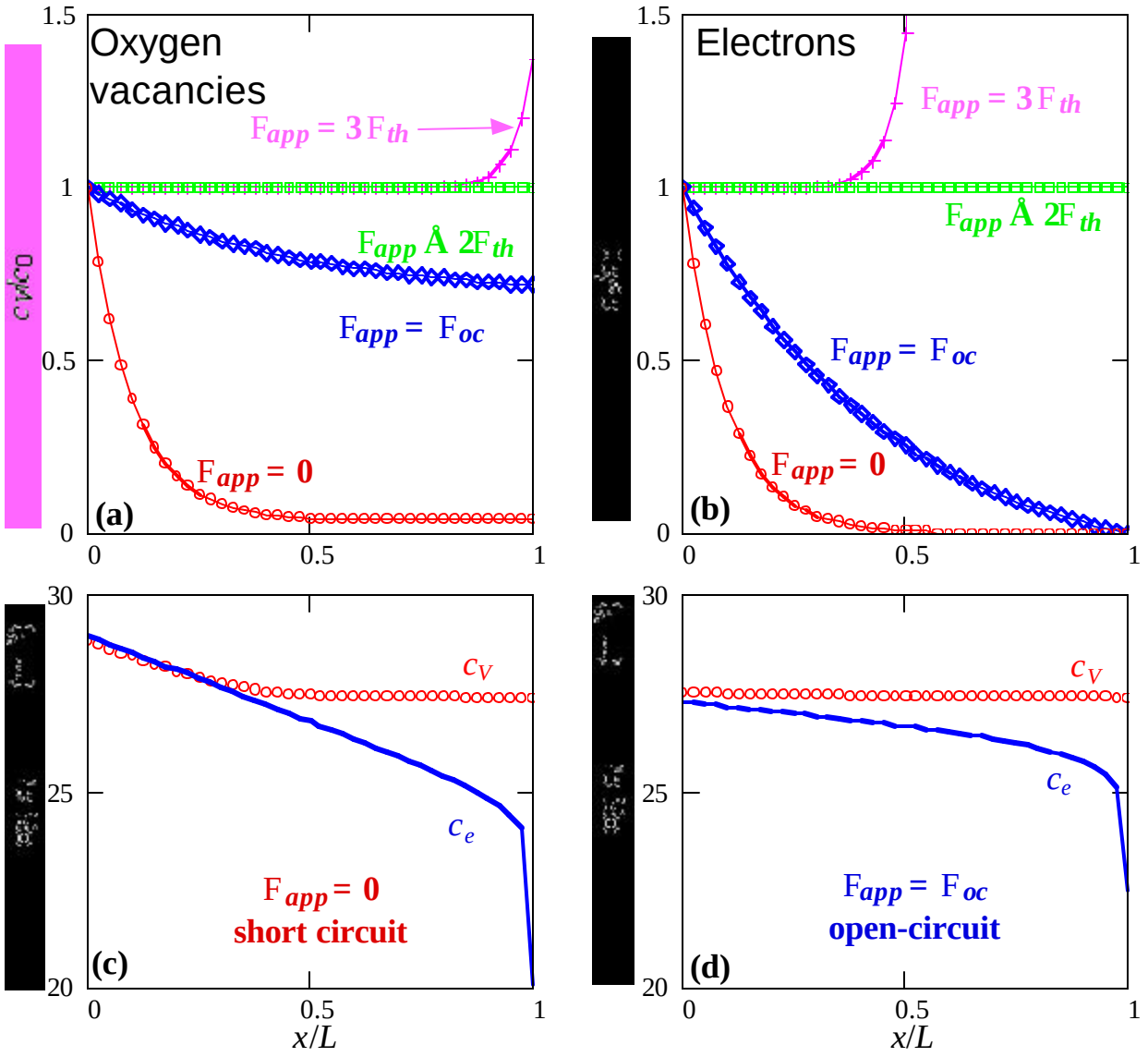
$$K_r = \exp\left(-\frac{\Delta G_r}{k_B T}\right)$$

$$c_V = \left[\frac{3\alpha}{4} K_r^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}} + \left(\frac{c_A}{2}\right)^{\frac{3}{2}}\right]^{\frac{2}{3}}$$

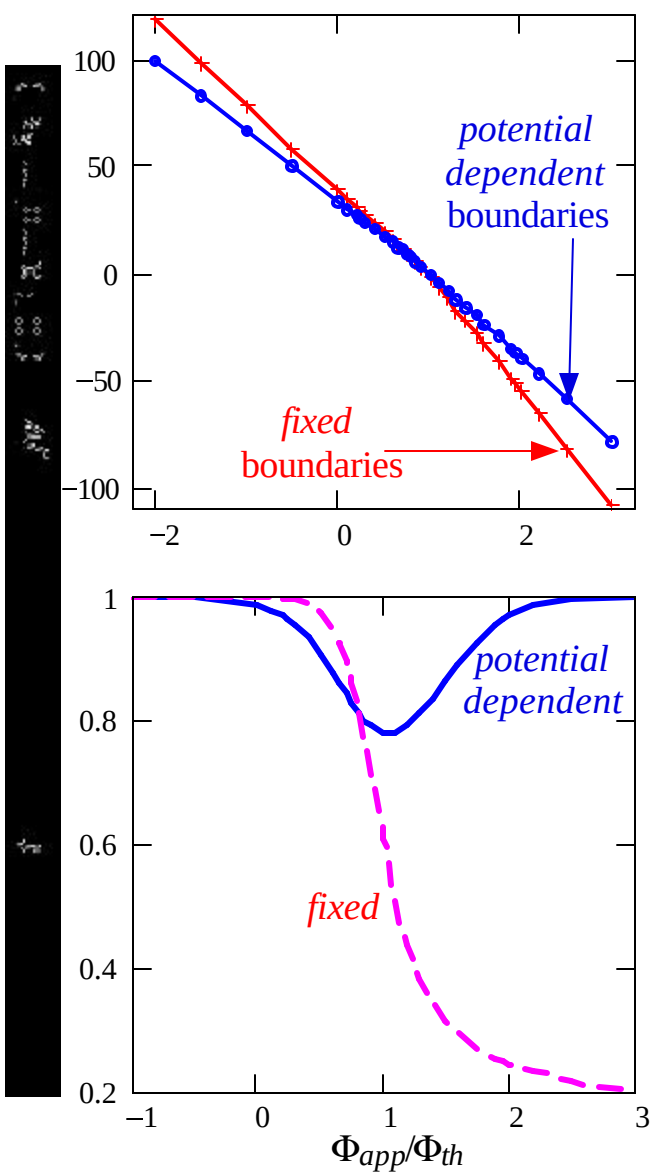
$$c_e = \alpha K_r^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}} c_V^{-\frac{1}{2}}$$

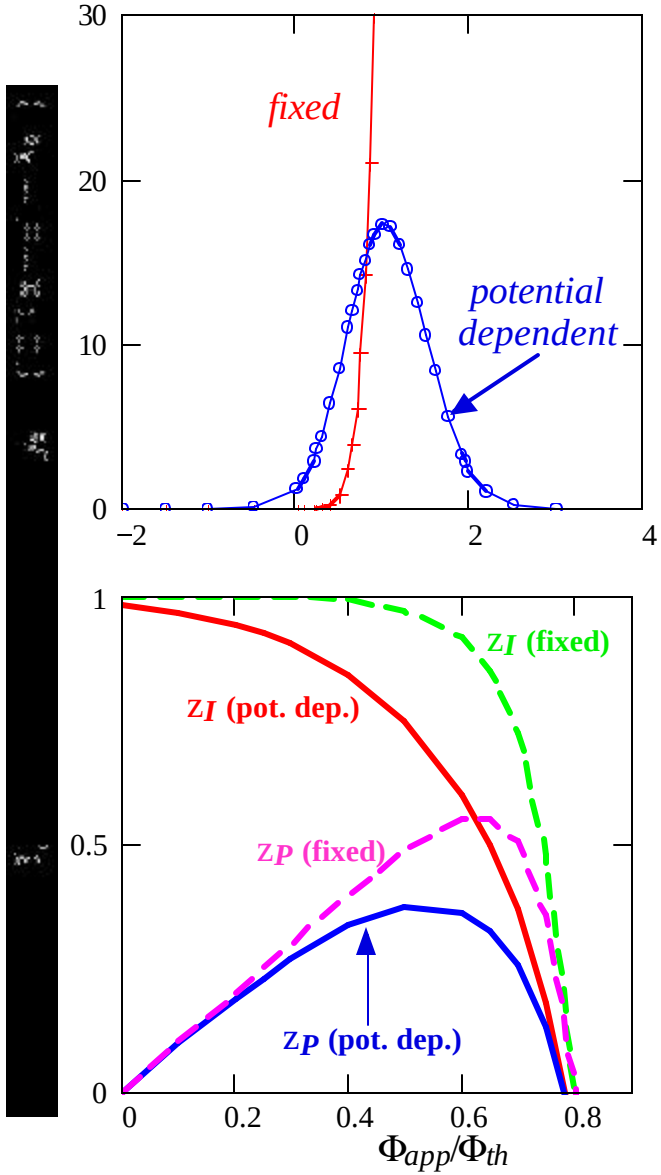
LINEAR POTENTIAL MODEL: DEFECT CONCENTRATION PROFILES

Potential-Dependent
Boundary Conditions



LINEAR POTENTIAL MODEL: FLUX, TRANSFERENCE NUMBER & EFFICIENCY





SUMMARY OF MODEL - PART 1

1. Fixed boundary conditions assume boundary concentrations are independent of an applied potential. Potential-dependent boundary conditions allow boundary concentrations to vary with an applied potential.

2. Employing fixed boundary conditions results in overestimation of the (ionic) oxygen vacancy flux, SOFC current and power efficiencies.

3. For *perfect* ionic or electronic conductors, the same results are obtained with fixed or potential-dependent boundary conditions.

NON-LINEAR POTENTIAL MODEL

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

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

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

$$\nabla^2\phi = \lambda \nabla^2 c_V \quad \text{——} \quad \nabla J = 0 \ \& \ \nabla j_i = 0$$

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

(Nernst-Planck + current equation)

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

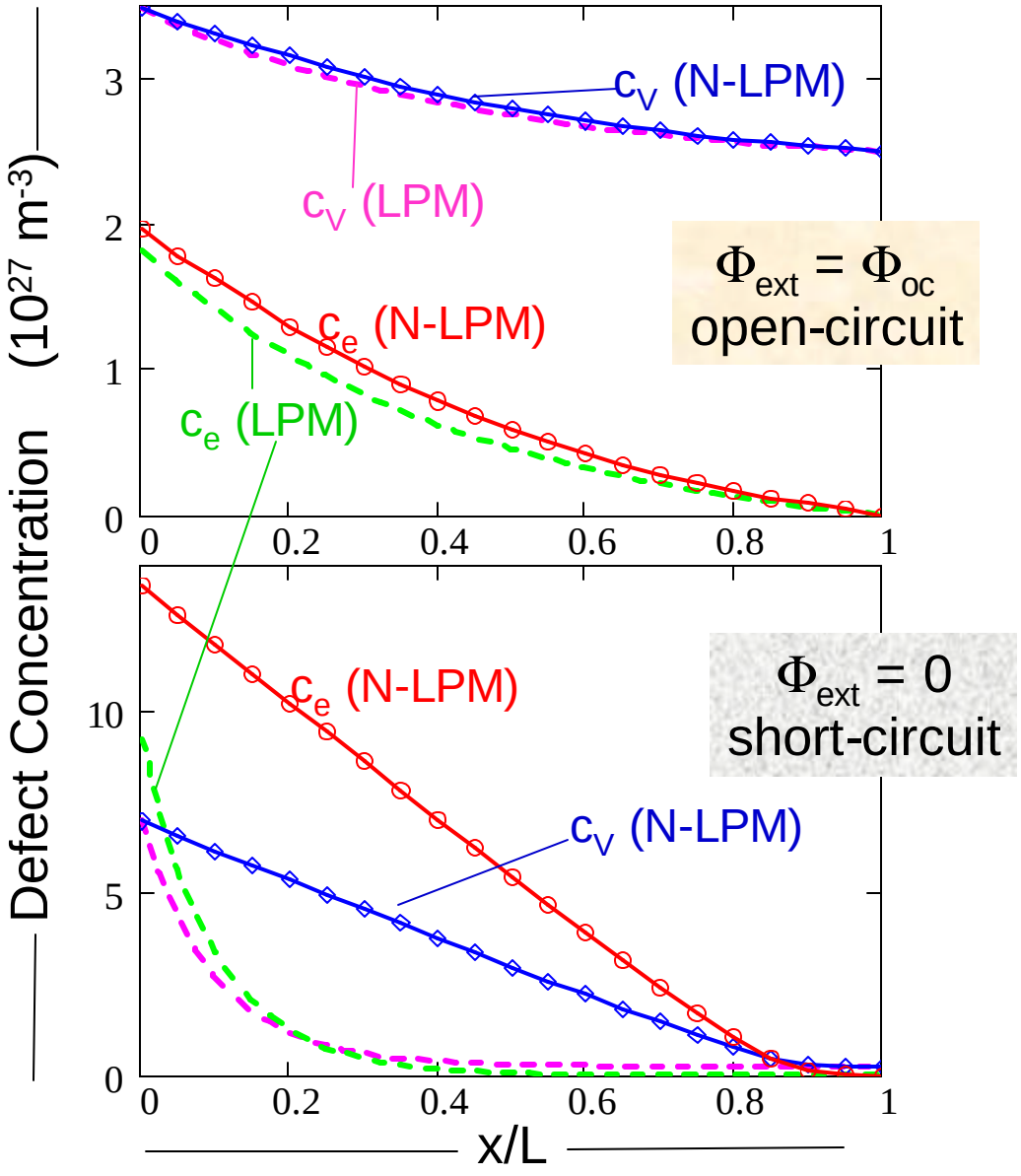
$$c_V(x) - c_{V_0} - \frac{(D_V\gamma - j_V)c_A}{6D_V\gamma} \cdot \ln \frac{6D_V\gamma c_V(x) - j_V c_A}{6D_V\gamma c_{V_0} - j_V c_A} = -\gamma x \quad \text{.....} \quad \text{(B)}$$

(A) – (B)

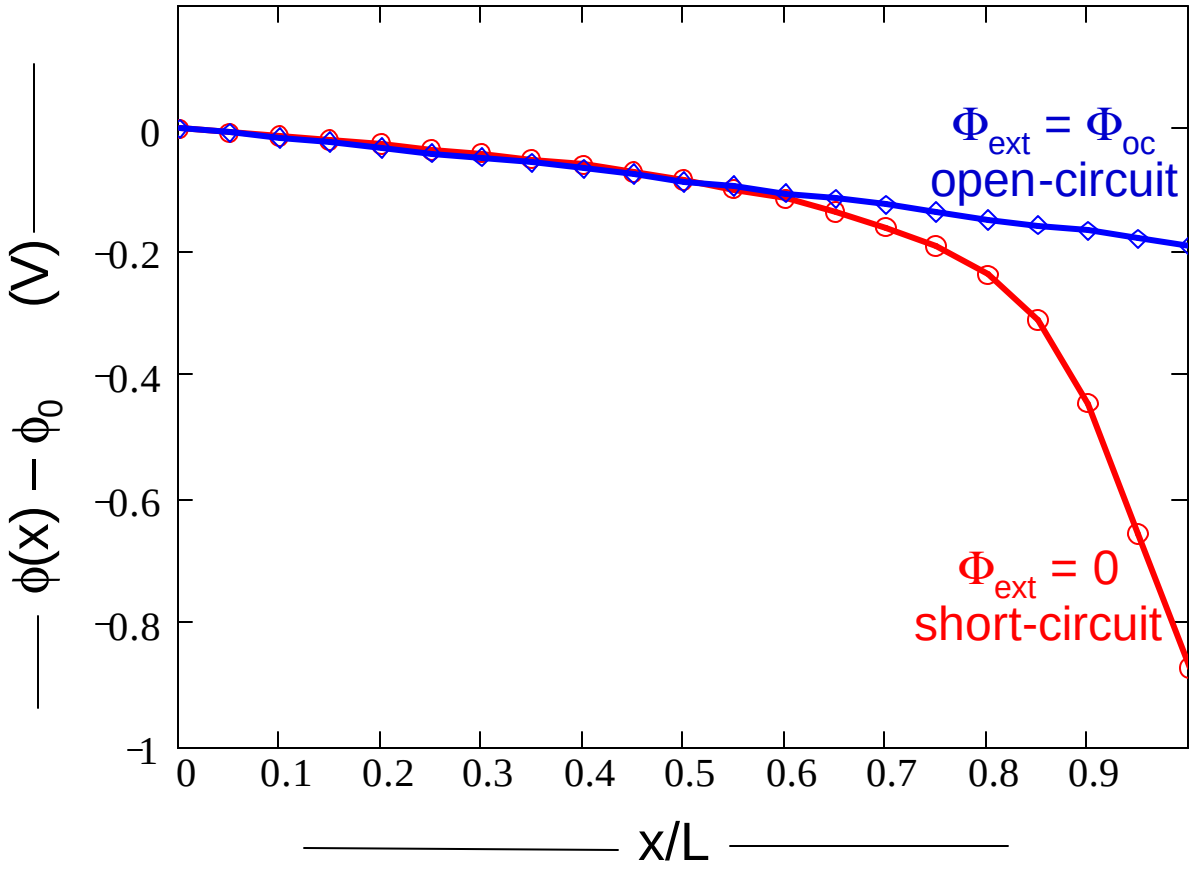
$$\phi(x) = \phi_0 - \frac{(D_V\gamma - j_V)k_B T}{z_V q D_V \gamma} \cdot \ln \frac{6D_V\gamma c_V(x) - j_V c_A}{6D_V\gamma c_{V_0} - j_V c_A}$$

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

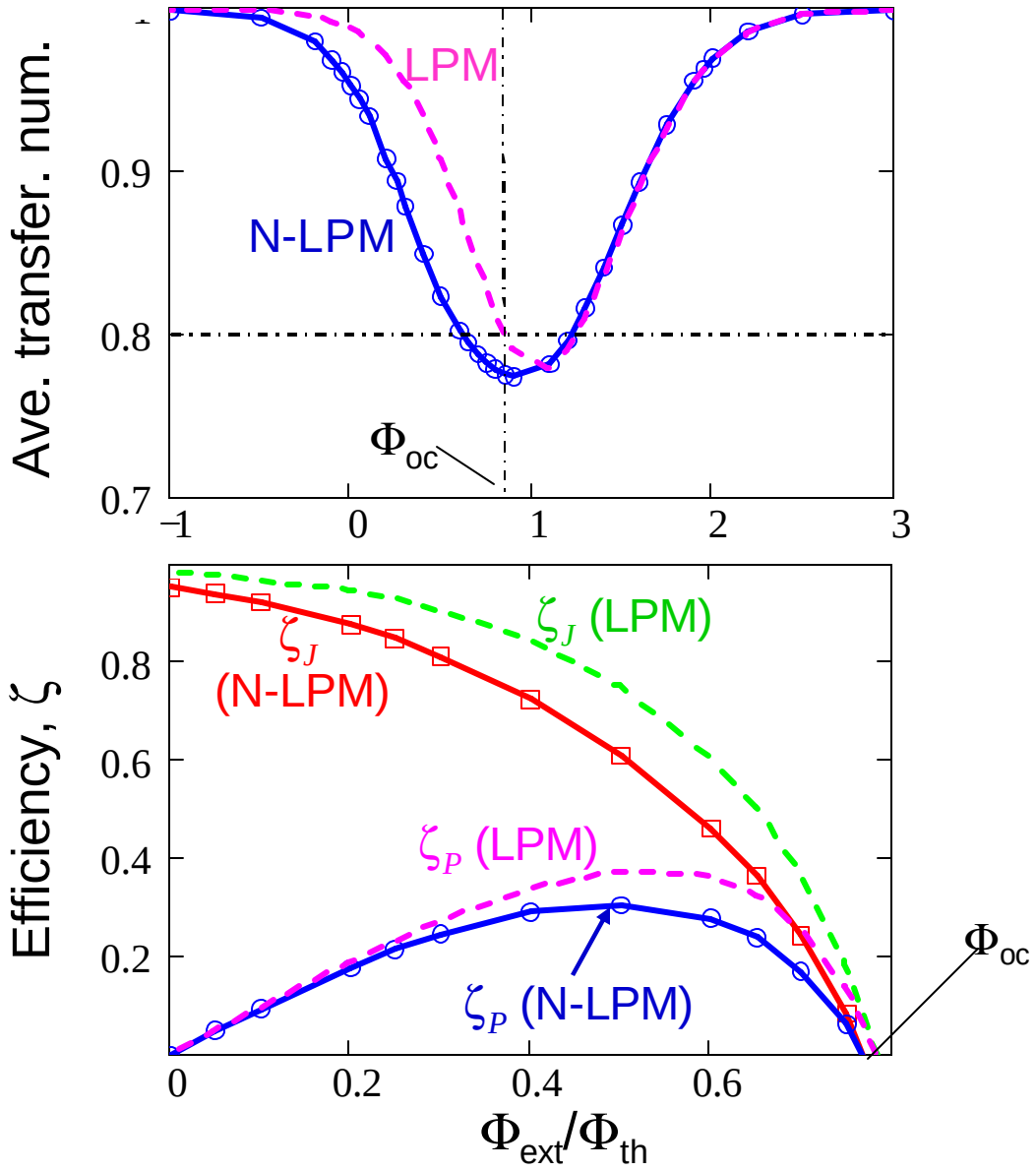
NON-LINEAR POTENTIAL MODEL: DEFECT CONCENTRATION PROFILES



NON-LINEAR POTENTIAL MODEL: POTENTIAL DISTRIBUTION



NON-LINEAR POTENTIAL: TRANSFERENCE NUMBER & EFFICIENCY



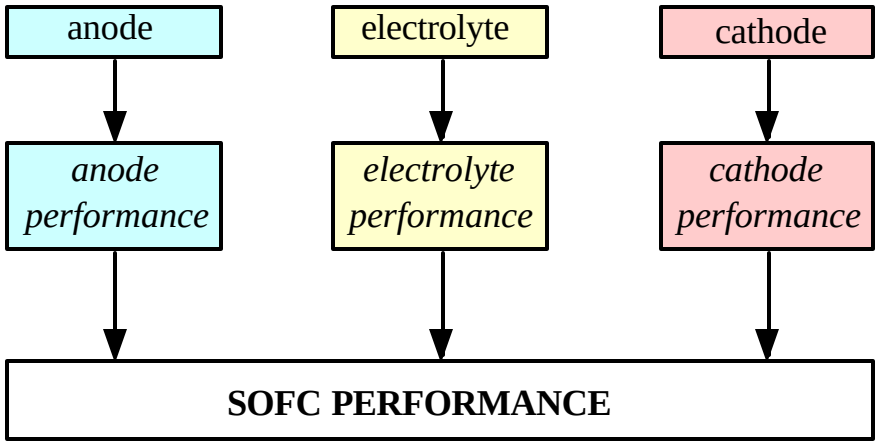
SUMMARYOF MODEL - PART 2

1. Assuming a linear potential distribution forces the *predicted* performance of the MIEC to mimic that of a “perfect” ionic conductor causing the overestimation of SOFC current and power efficiencies.

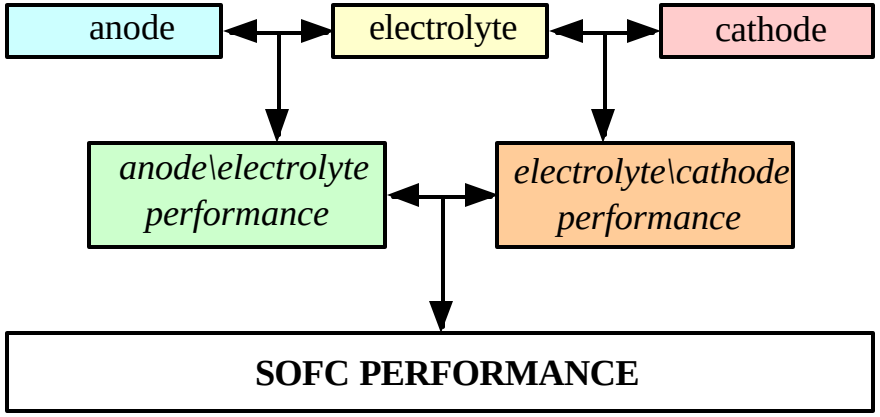
2. The assumption of a linear potential distribution becomes more justifiable as $\Phi_{ext} \rightarrow \Phi_{oc}$ (i.e., in open-circuit conditions) and is least justifiable when $|\Phi_{ext}| \rightarrow |\Phi_{oc}|$.

EXTENDING MODEL TO MULTILAYERED SOFC ARCHITECTURE

Present Approach



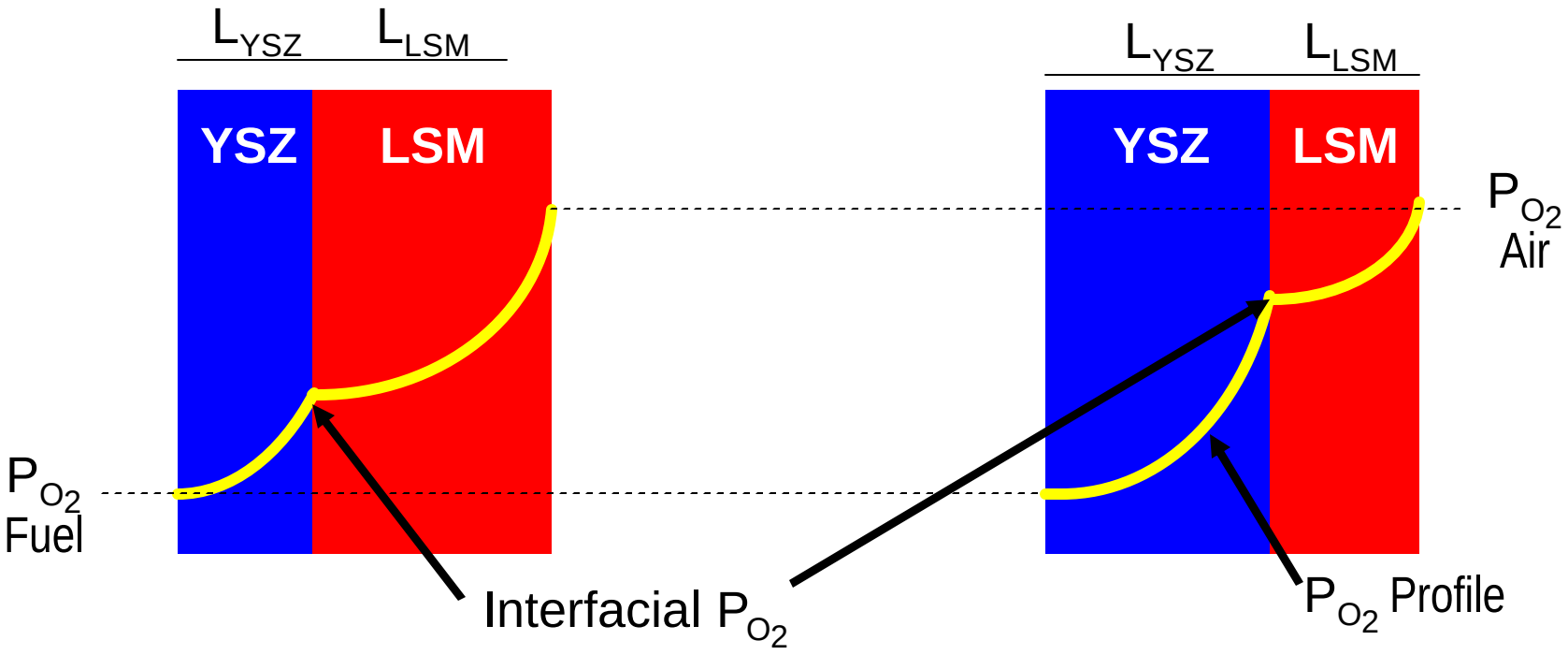
Proposed Approach



ELECTROLYTE/CATHODE INTERFACE

$$La_{1-y}Sr_yMnO_{3-\delta} + \delta ZrO_2 + \frac{3\delta}{2} O_O^{\times} \rightarrow La_{1-y-\delta}Sr_yMnO_{3-\delta} + \frac{\delta}{2} La_2Zr_2O_7 + \frac{3\delta}{2} V_O^{\bullet\bullet} + 3\delta e'$$

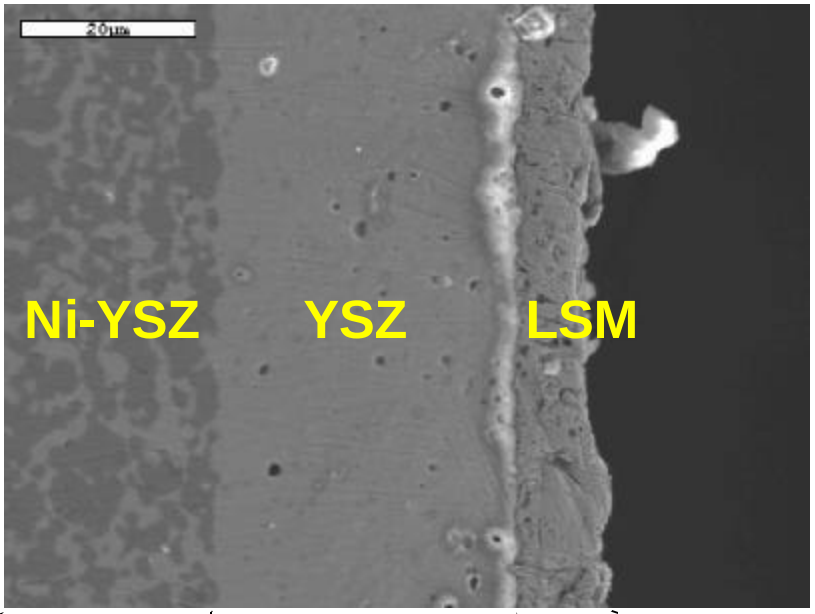
$$K \approx \left[La_2Zr_2O_7\right]^{\frac{\delta}{2}} \left[V_O^{\bullet\bullet}\right]^{\frac{3\delta}{2}} \left[e'\right]^{3\delta} = K_2 \left[La_2Zr_2O_7\right]^{\frac{\delta}{2}} P_{O_2}^{-\frac{3\delta}{4}}$$

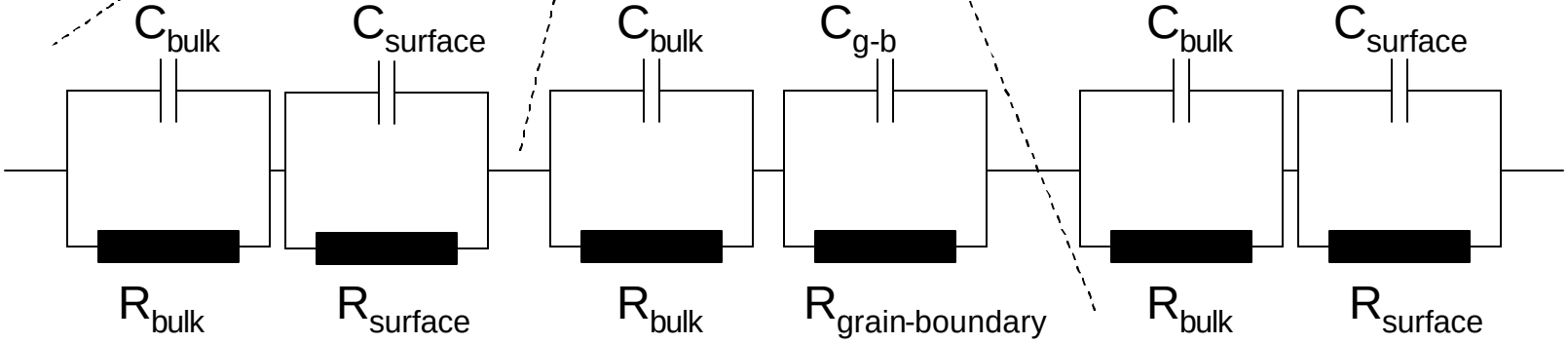


TRANSIENT EFFECTS

$R \equiv f(P_{O2}, c_i, \Phi_{ext}, K)$

$C \equiv f(P_{O2}, c_i, \Phi_{ext}, K)$





EXTENSION OF MODEL TO THERMO-MECHANICAL PROPERTIES

$$E_{bond} \sim (1 - mn^{-1})Ba^{-m}$$

*where B, n and m are empirically determined constants and m < n.

also

$$Y \sim a^{-(m+3)} \quad \text{and} \quad K_{IC} \sim Y^{1/2}a^{-3/2}$$

&

$$a \sim c_V$$

$$Y(x)/Y^{\circ} \approx \left(\sqrt[m+3]{Y^{\circ}}\, b_1 c_V(x) + 1 \right)^{-(m+3)}$$

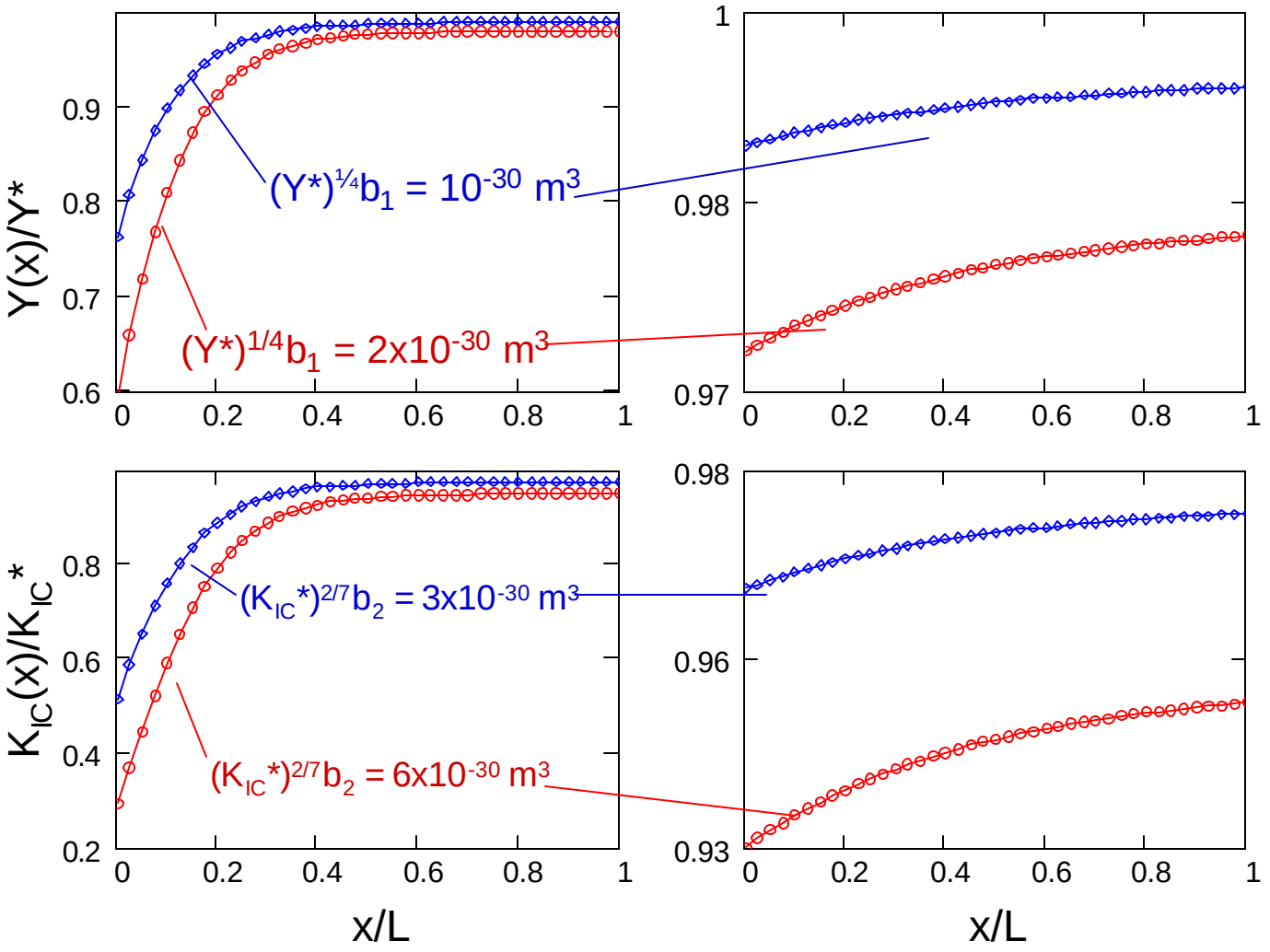
$$K_{IC}(x)/K_{IC}^{o} \approx \left(\sqrt[m+6]{\left(K_{IC}^{o}\right)^2}\, b_2 c_V(x) + 1 \right)^{-\frac{m+6}{2}}$$

* M. Barsoum, in Fundamentals of Ceramics (McGraw-Hill, 1977).

SPATIAL VARIATION OF ELASTIC MODULUS (Y) & FRACTURE TOUGHNESS (K_{IC})

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

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



TASKS TO BE PERFORMED FOR PHASE 1

1. Complete continuum-level electrochemical model (CLEM) with a non-linear Galvani potential and potential-dependent boundary values.

2. Develop a software package for CLEM to integrate into SOFC performance models used by NETL, PNNL, ORNL and the SECA industrial teams.

3. Extend CLEM to thermo-mechanical and thermo-chemical properties.

4. Experimentally determine SOFC related time constants from R-C circuit analysis of cathodes, electrolytes and anodes for use in evaluating the effect of voltage transients from the power conditioning equipment on failure mechanisms and other time dependent properties. These will then be integrated into the model in Phase II.