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_{O_2}, V, etc..)
2. Develop transient (time dependent) transport model
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. Experimentally verify models and devise strategies to obtain relevant material constants
6. Assemble software package for integration into SECA failure analysis models

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

3. Model transient behavior of defects in SOFCs.

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

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

CONTINUUM LEVEL ELECTROCHEMICAL MODEL - Defect Equilbiria

Features of the Defect Model

- Continuous functions for the defect concentrations vs. discontinuous “piecewise” Brouwer approach.
- Dependent on thermodynamic quantities, namely the mass-action constants (K’s).
- Quantitative for any SOE/MIEC.
- Derived from fundamental thermodynamic equations.

Electron-Hole Pair Formation

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

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

External Equilibria

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

$$K_r = c_V c_e^2 P_{\mathrm{O_2}}^{\frac{1}{2}} = K_r^* \, \mathbf{exp}\left(-\Delta G_r / k_B T\right)$$

Internal Equilibria

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

$$K_f = c_V c_I$$

Defect Triads (CLEM)	**vs.**	**Defect Pairs (Brouwer)**
$c_e + c_A = 2c_V$		$c_e = 2c_V$ …Region I
Limiting Case		$c_A = 2c_V$ …Region IIa
$P_{\mathrm{O_2}} >> 4^{-4} K_r^2 c_V^{-6}$		

DEFECT EQUILIBRIA - BROUWER APPROACH

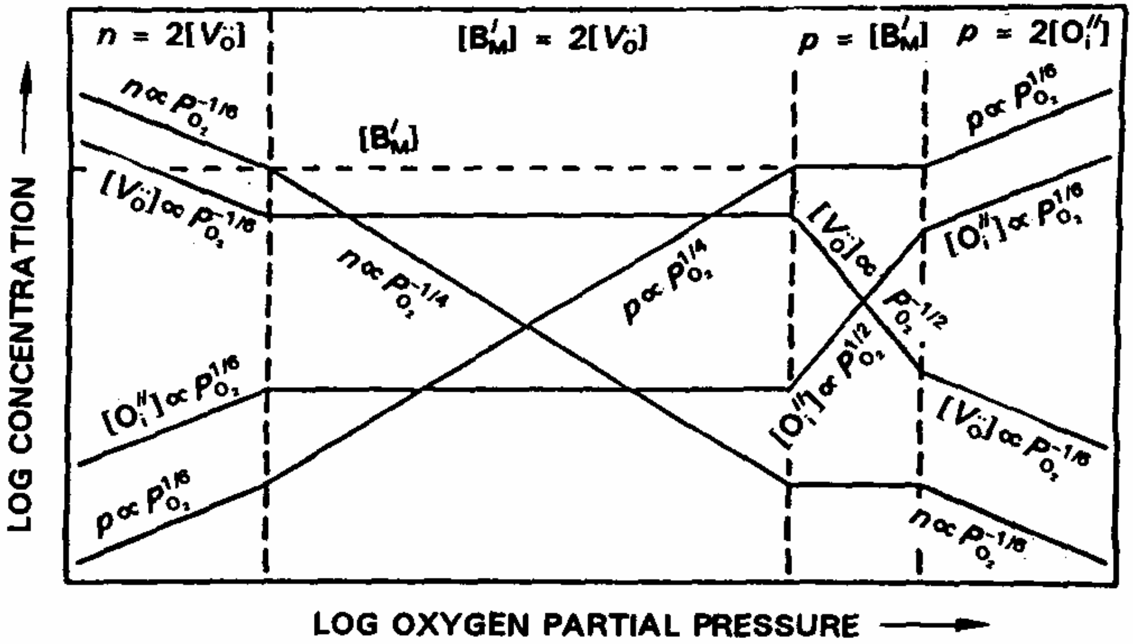
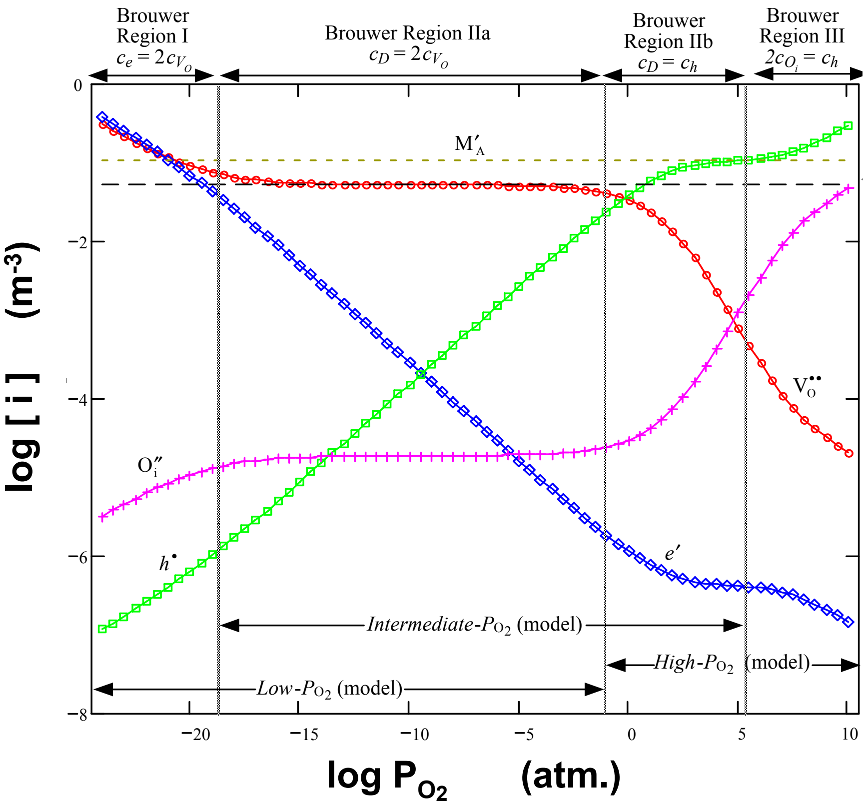


Figure 3.3. *Variation of defect concentration as a function of oxygen partial pressure for a* MO_2-B_2O_3 *system [3.17]*

CONTINUUM LEVEL ELECTROCHEMICAL MODEL - Defect Equilibria

FLUORITE



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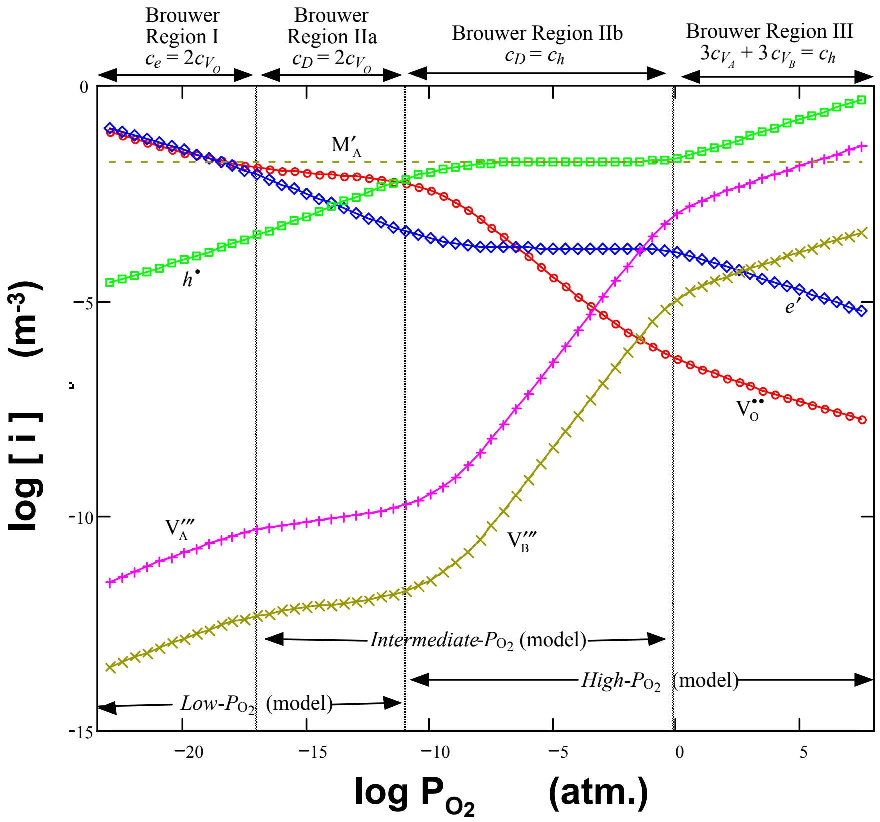
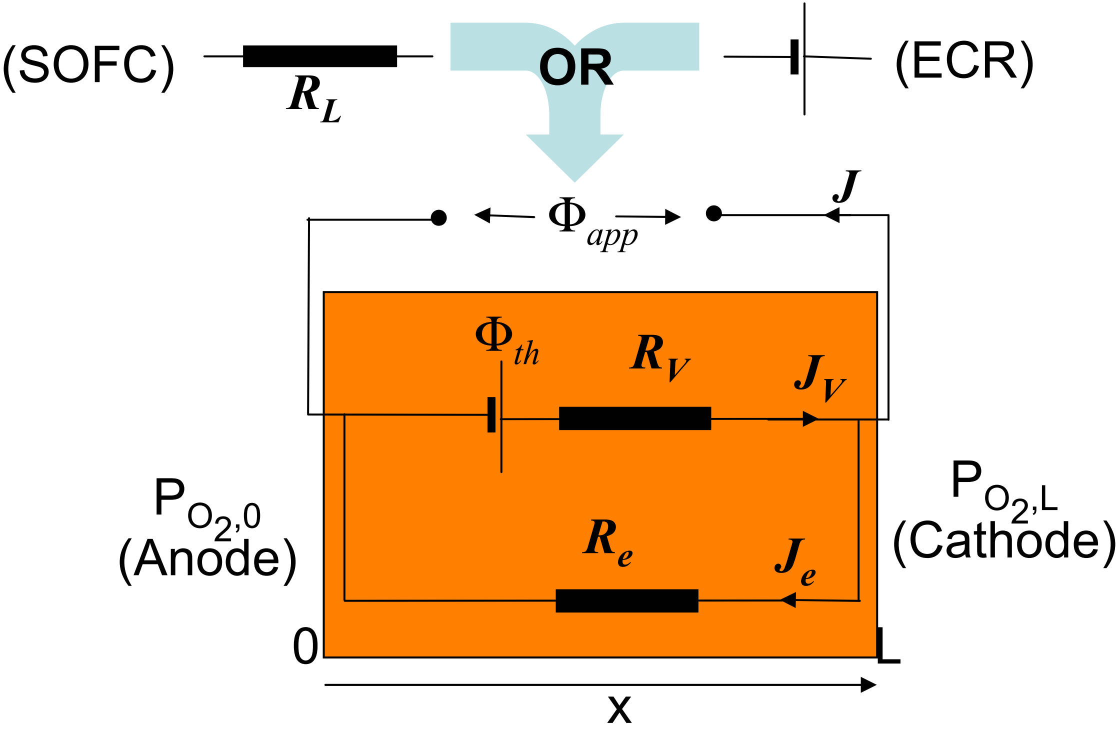


Verified Continuum Level Electrochemical Model:

- vs. other models[1]
- vs. conductivity[2]
- vs. OCP

1. O. Porat and H. L. Tuller, *J. Electroceramics* **1** (1997) 42; 2. Eguchi et al, *Solid State Ionics* **52** (1992) 265.

CONTINUUM LEVEL ELECTROCHEMICAL MODEL - Electrochemical Performance



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

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

FUNDAMENTAL TRANSPORT 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 $$\sum_i z_i c_i = z_V c_V + z_A c_A + z_e c_e \approx 0$$

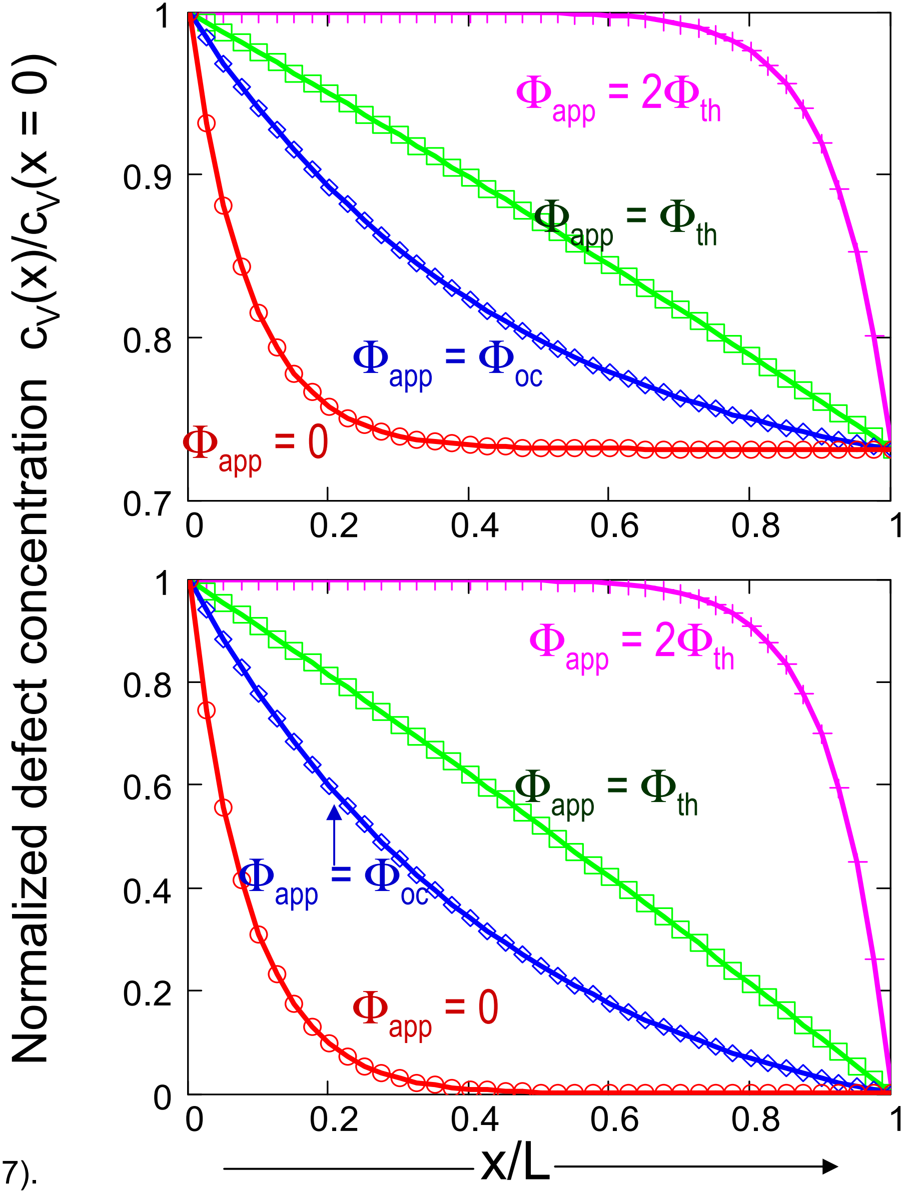
Local equilibrium

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

LINEAR POTENTIAL MODELS: DEFECT CONCENTRATION PROFILES

Fixed Boundary Conditions

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



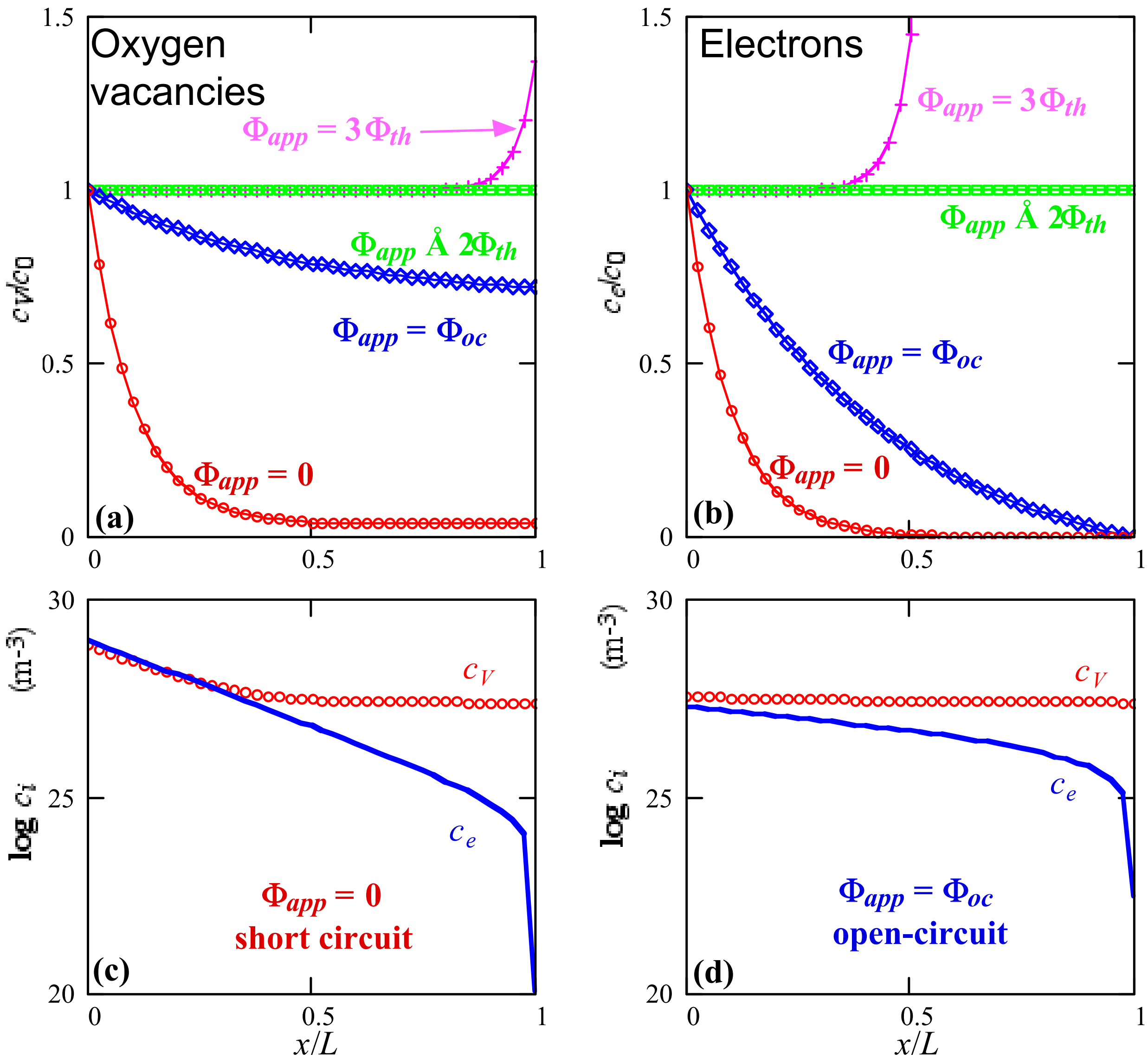
Oxygen vacancies

Electrons

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

LINEAR POTENTIAL MODEL: DEFECT CONCENTRATION PROFILES

Potential-Dependent Boundary Conditions



NON-LINEAR POTENTIAL MODEL

We have addressed the short comings of the linear potential models with fixed boundary conditions (independent of applied potential) by developing a continuum level electrochemical model that:

- *allows* the Galvani potential to be non-linear
- incorporates potential dependent boundary conditions.

The key features employed in the development of the model are that:

- in steady-state the gradient of the flux is zero (i.e., $\nabla j_i = 0$)
- the divergence of the current is always zero ($\nabla J = 0$)
- the free energy of formation for defects at the gas-solid interface has both a chemical (from the chemical potential) and an electrical component (from the overpotential)

CONTINUUM LEVEL ELECTROCHEMICAL MODEL/NON-LINEAR POTENTIAL MODEL

The fact that the gradient of both the (total) current and the flux of any species is zero is used to obtain two separate (but related) differential equations equations.

Each differential equation is solved and the results compared to generate the model

$\nabla J = 0$ & $\nabla j_i = 0$

$$\frac{(z_V u_e j_V - u_V j_e)c_V - j_V u_e c_A}{z_V(z_V - z_e)c_V - c_A} = \frac{qD_eD_V}{k_BT}\nabla c_V$$

$$\nabla^2\phi = \lambda\nabla^2 c_V$$

$$c_V(x) - c_{V_0} - \frac{\phi(x) - \phi_0}{\lambda} = -\gamma x$$

$$c_V(x) - c_{V_0} - \frac{(D_V\gamma - j_V)c_A}{z_V(z_V - z_e)D_V\gamma} \cdot \ln\frac{z_V(z_V - z_e)D_V\gamma c_V(x) - j_V c_A}{z_V(z_V - z_e)D_V\gamma c_{V_0} - j_V c_A} = -\gamma x$$

$$\gamma = \frac{\phi_L - \phi_0}{\lambda L} - \frac{c_{V_L} - c_{V_0}}{L} \qquad \lambda = \frac{(z_V - z_e)k_BT}{z_e q c_A}$$

Galvani potential

$$\phi(x)=\phi_0-\frac{\left(D_V\gamma-j_V\right)k_BT}{z_VqD_V\gamma}\cdot\mathbf{ln}\frac{z_V\left(z_V-z_e\right)D_V\gamma c_V(x)-j_Vc_A}{z_V\left(z_V-z_e\right)D_V\gamma c_{V_0}-j_Vc_A}$$

Electronic flux

$$j_e=j_V\frac{z_V^2}{z_e^2}\left(\frac{1}{\bar{t}_{ion}}-1\right)\left(\frac{k_BT\,\mathbf{ln}\left(c_{e_L}/c_{e_0}\right)+z_eq\Delta\phi}{k_BT\,\mathbf{ln}\left(c_{V_L}/c_{V_0}\right)+z_Vq\Delta\phi}\right)$$

Oxygen vacancy flux

$$j_V=-\frac{\left(z_V-z_e\right)qD_eD_V\gamma}{k_BT}\left[u_e-u_V\frac{z_V}{z_e^2}\left(\frac{1}{\bar{t}_{ion}}-1\right)\left(\frac{k_BT\,\mathbf{ln}\left(c_{e_L}/c_{e_0}\right)+z_eq\Delta\phi}{k_BT\,\mathbf{ln}\left(c_{V_L}/c_{V_0}\right)+z_Vq\Delta\phi}\right)\right]^{-1}$$

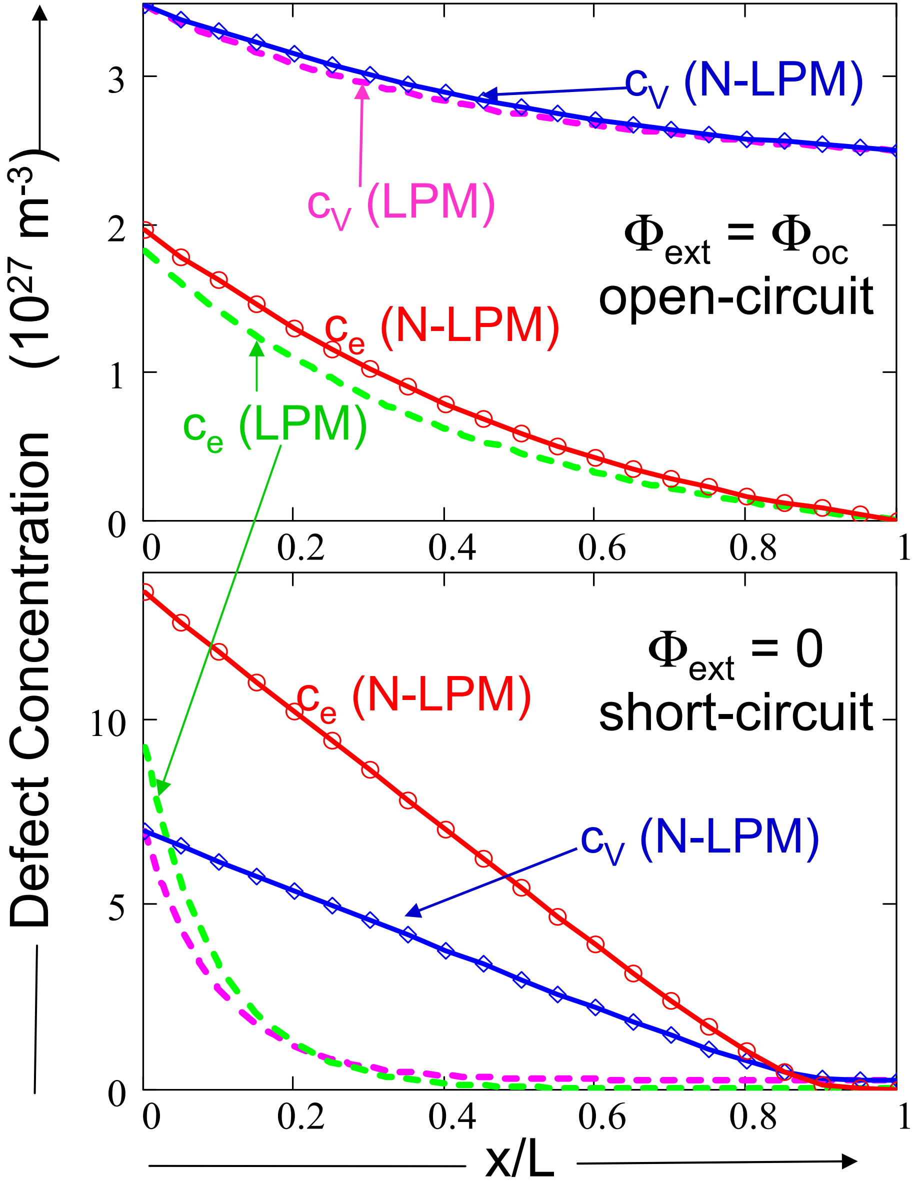
NON-LINEAR POTENTIAL MODEL: DEFECT CONCENTRATION PROFILES

- In *open-circuit* there is little difference between LPM and N-LPM.

- $\nabla^2\phi \propto \nabla(\nabla c_V)$, so as $\nabla c_V \rightarrow 0$, ϕ becomes a linear function of *x*.

- Significant difference between LPM and N-LPM in *short circuit* conditions where $|\nabla c_V| >> 0$.

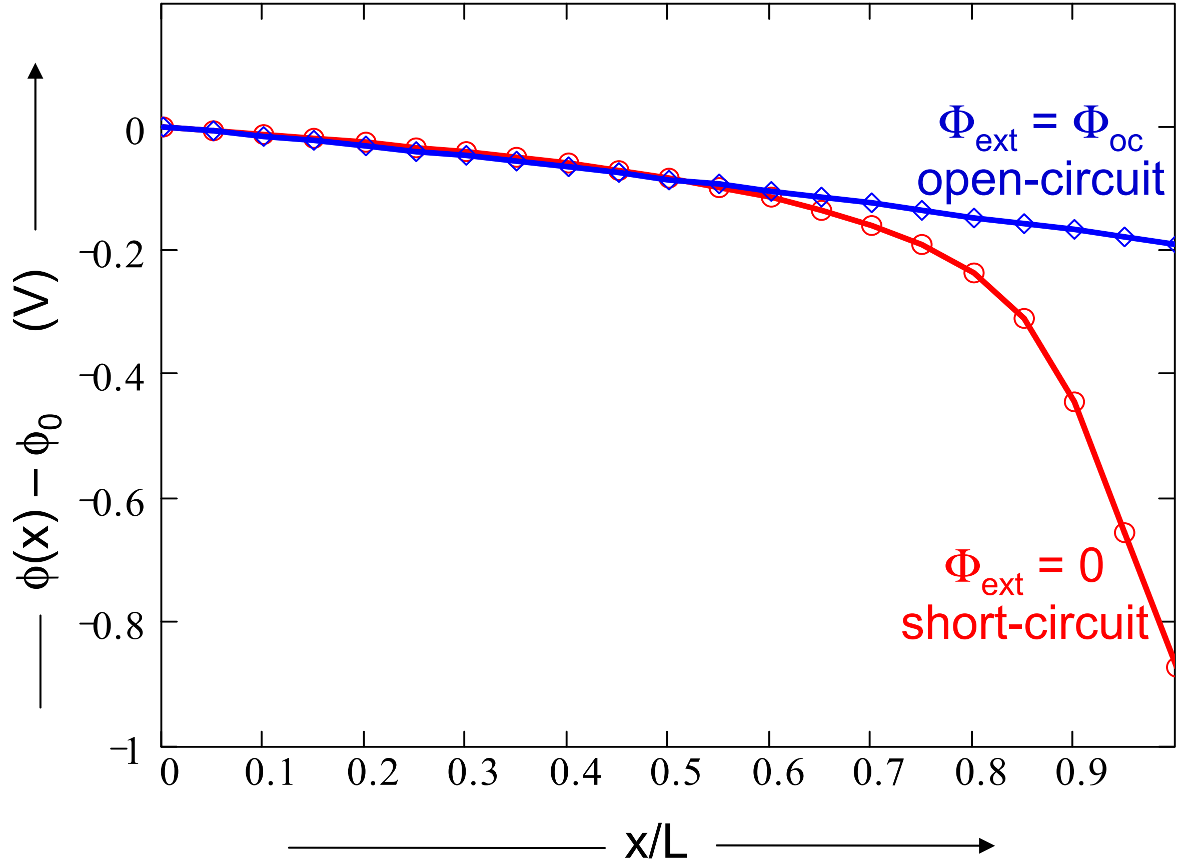
- Concentration gradients are not confined to the “near-boundary” areas for N-LPM.



NON-LINEAR POTENTIAL MODEL: POTENTIAL DISTRIBUTION

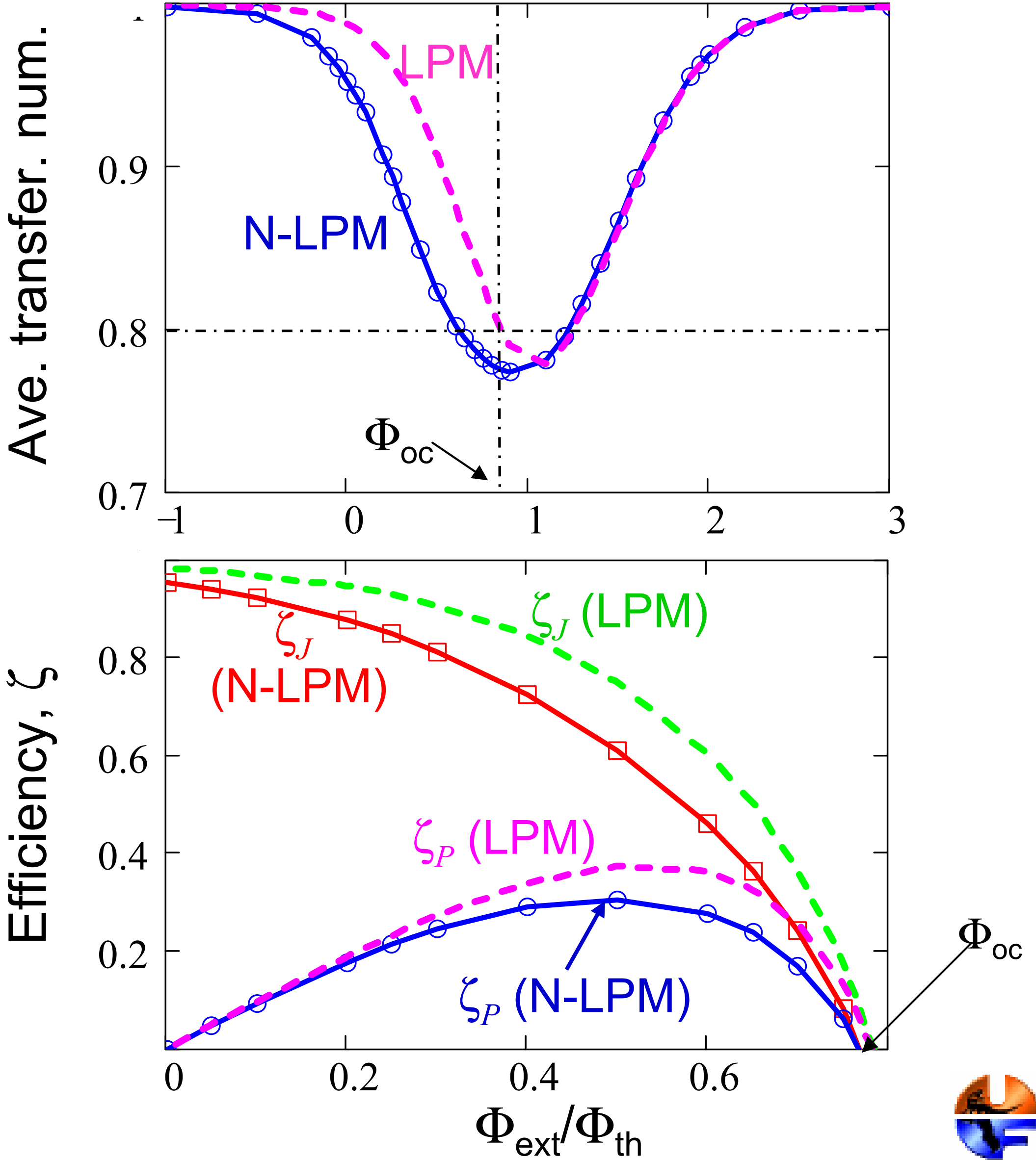
- The non-linearity of $\phi(x)$ increases as Φ_{ext} moves away from Φ_{oc}.

- In open-circuit conditions the Galvani potential ($\Delta\phi$) approaches zero. Hence, $\nabla^2\phi$ also goes to zero and the electric field ($\nabla\phi$) approaches linearity.

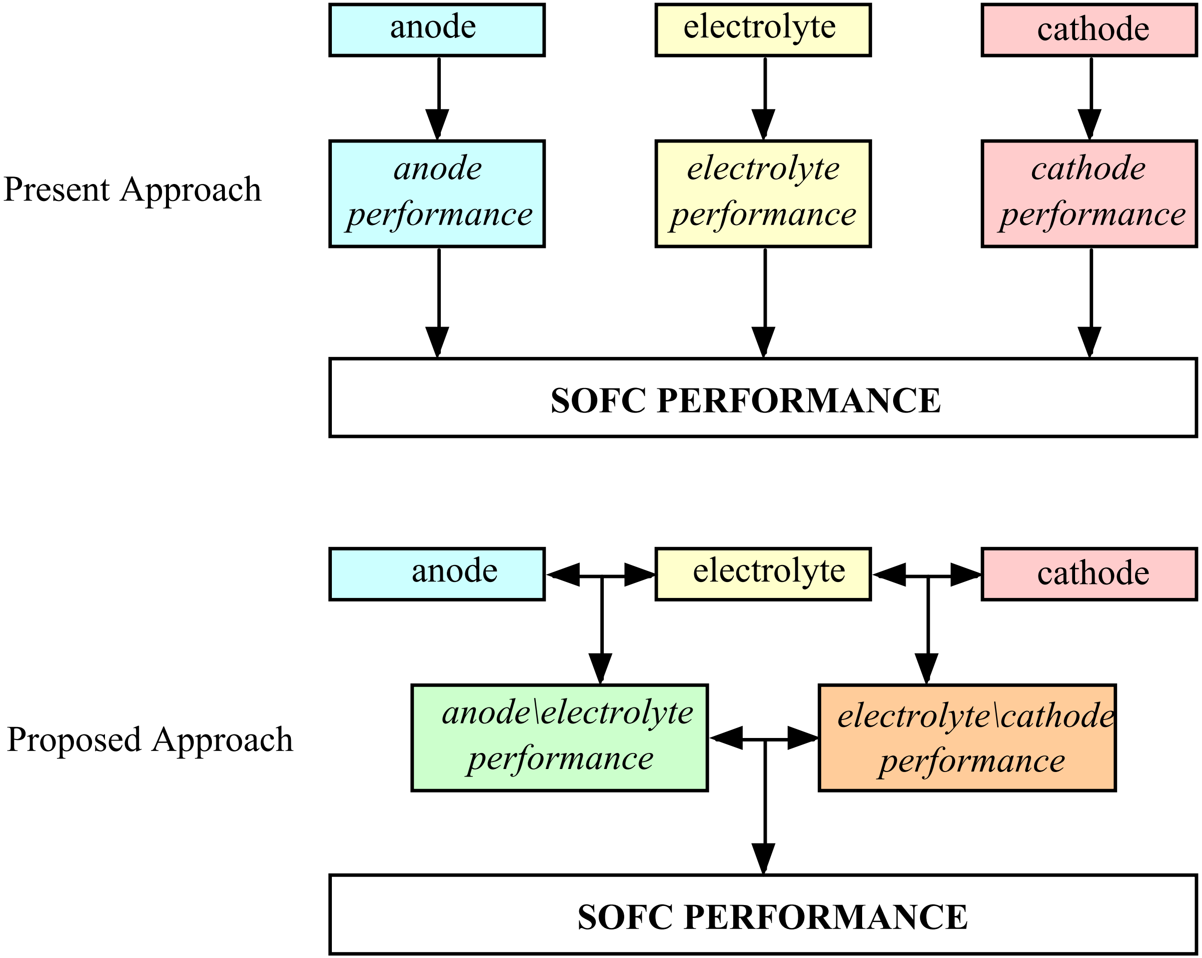


NON-LINEAR POTENTIAL: TRANSFERENCE NUMBER & EFFICIENCY

- The N-LPM doesn’t “force” $\nabla c_V \approx 0$, thereby (falsely) suppressing the electron concentration. Consequently, a reduced transference number and power and current efficiency is observed.



EXTENDING CONTINUUM LEVEL ELECTROCHEMICAL MODEL TO MULTILAYERED SOFC ARCHITECTURE



Present Approach

anode

electrolyte

cathode

anode performance

electrolyte performance

cathode performance

SOFC PERFORMANCE

Proposed Approach

anode

electrolyte

cathode

anode\electrolyte performance

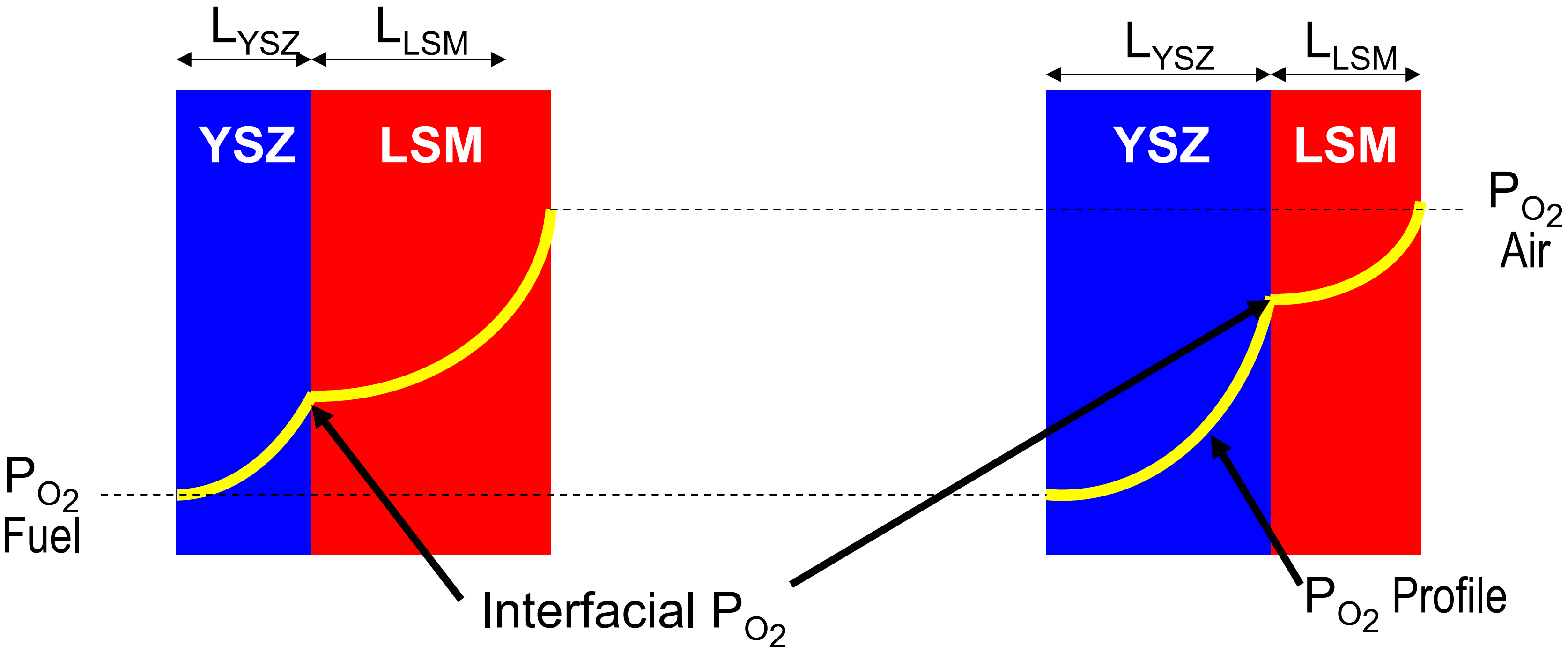
electrolyte\cathode performance

SOFC PERFORMANCE

EXTENSION OF CONTINUUM LEVEL ELECTROCHEMICAL MODEL TO THERMOCHEMICAL STABILITY: Electrolyte/Cathode Interface

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

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



EXTENSION OF CONTINUUM LEVEL ELECTROCHEMICAL MODEL TO THERMO-MECHANICAL PROPERTIES

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

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

also

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

&

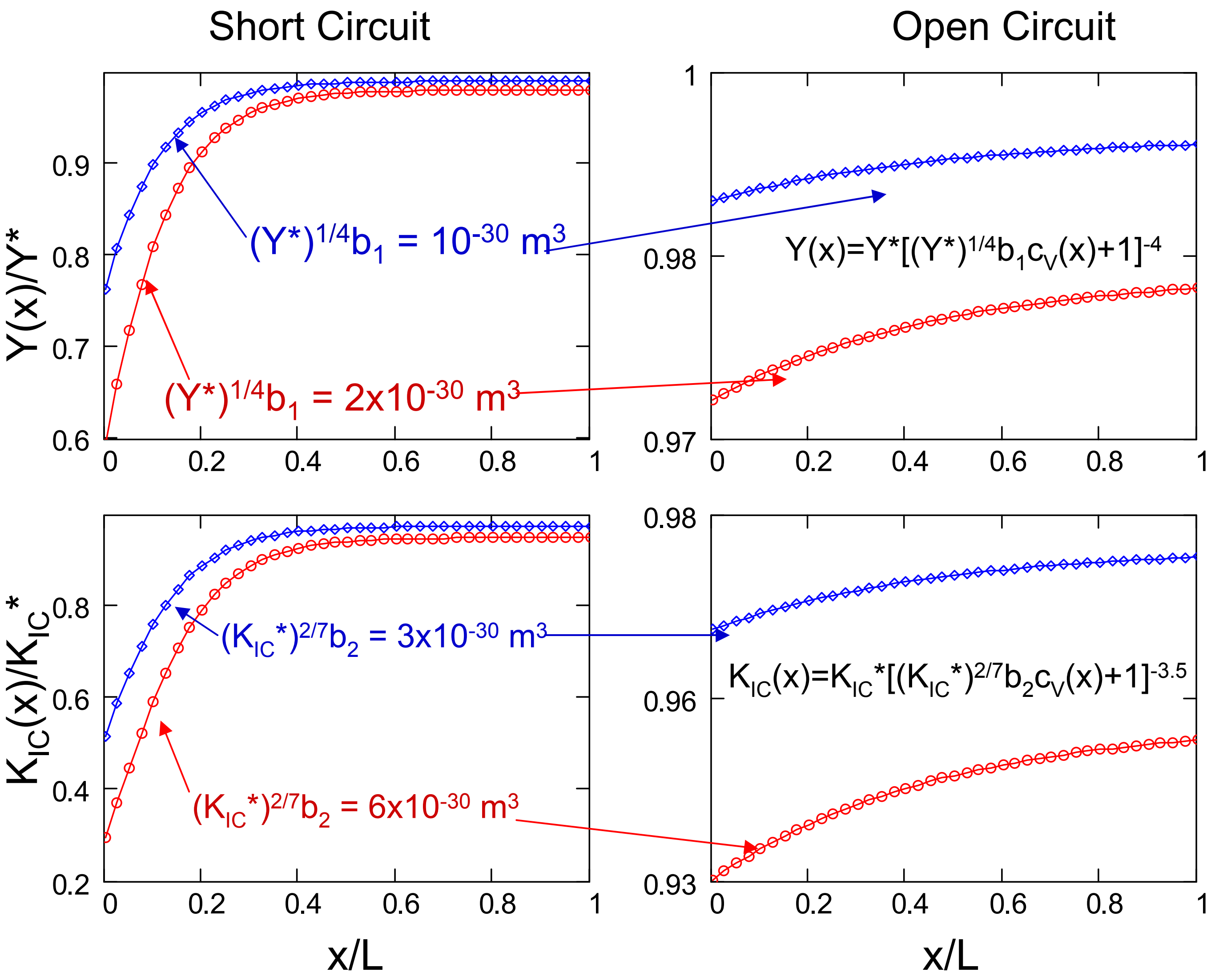
$$a \sim c_V$$

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

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

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

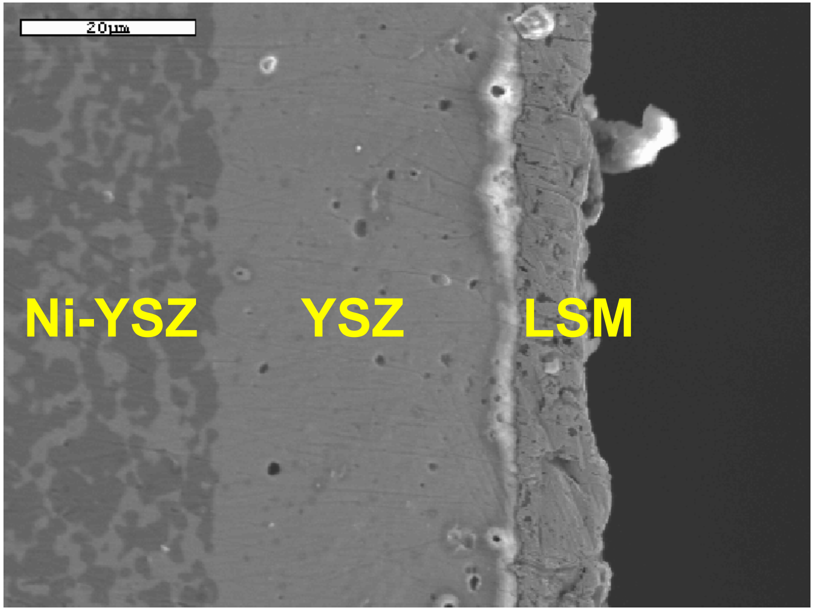
SPATIAL VARIATION OF ELASTIC MODULUS (Y) & FRACTURE TOUGHNESS (K_{IC})

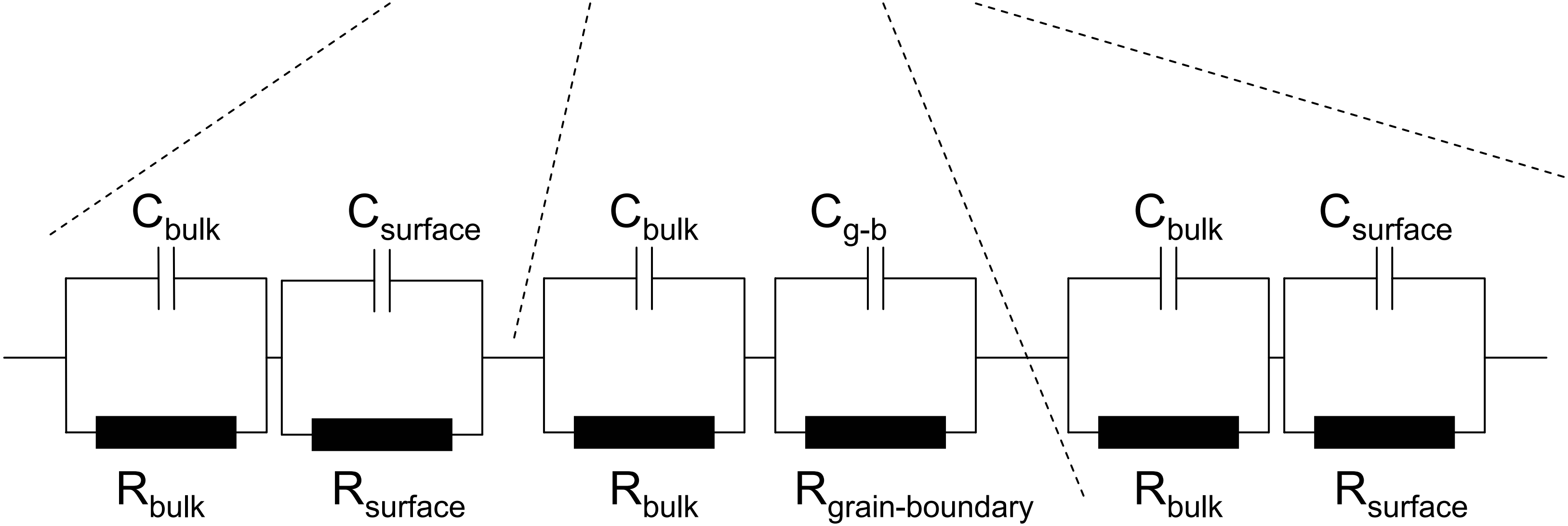


TRANSIENT EFFECTS

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

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





TRANSIENT TRANSPORT MODEL FOR ZIRCONIA

Nernst-Planck flux equation

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

Material balance equation

$$\frac{\partial c_i}{\partial t} = -\nabla j_i$$

Current equation

$$J = q \sum_i z_i j_i$$

Equations for flux, material balance, current and charge neutrality are manipulated to obtain expressions for the rate of change of defect concentration.

$$\frac{\partial c_V}{\partial t} = \frac{D_e D_V}{z_e D_e - z_V D_V} \left[(z_e - z_V) \nabla^2 c_V + z_e c_A \frac{q}{k_B T} \nabla^2 \phi \right]$$

$$\frac{\partial c_e}{\partial t} = \frac{D_e D_V}{z_e D_e - z_V D_V} \left[(z_e - z_V) \nabla^2 c_e + z_e z_V c_A \frac{q}{k_B T} \nabla^2 \phi \right]$$

And an expression for the electric field as a function of defect concentrations.

$$\nabla \phi = -\frac{J + (z_V q D_V \nabla c_V + z_e q D_e \nabla c_e)}{q(z_V u_V c_V + z_e u_e c_e)}$$

In order to obtain a tractable solution at this time we will consider generally two types of conductors

1. Good ionic conductors where $\nabla c_V = 0$ and $c_V >> c_e$ (e.g. YSZ).
2. Good electronic conductors where $\nabla c_e = 0$ and $c_e >> c_V$ (e.g. LSM).

Specifically, here we consider zirconia

For zirconia

$$\nabla c_V \approx 0 \qquad z_V c_V \approx c_A$$

$$c_V >>> c_e \qquad \sigma_V >> \sigma_e$$

Therefore

$$\nabla\phi \approx -\frac{J + z_e q D_e \nabla c_e}{q\left(z_V u_V c_V\right)} \quad \rightarrow \quad \nabla^2\phi \approx -\frac{z_e D_e}{u_V c_A}\nabla^2 c_e$$

$$\frac{\partial c_V}{\partial t} \approx 0$$

$$\frac{\partial c_e}{\partial t} = \frac{\left(z_V - z_e\right)D_e D_V + D_e^2}{z_V D_V - z_e D_e}\nabla^2 c_e = \alpha^2 \nabla^2 c_e$$

TRANSIENT EFFECTS ON DEFECT CONCENTRATION - using Fourier series

CASE 1: Introduction of a P_{O_2} gradient

Here we consider what happens when a zirconia electrolyte is first placed into a P_{O_2} gradient.

$$c_e(x,t) = \sum_{n=1}^{\infty} \frac{2\left(\left(-1\right)^n c_{e,L}^{\infty} - c_{e,0}^{\infty} + c_e^{0}\right)}{n\pi} e^{-\alpha^2\left(\frac{n\pi}{L}\right)^2 t} \mathbf{sin}\frac{n\pi}{L}x + \frac{c_{e,L}^{\infty} - c_{e,0}^{\infty}}{L}x + c_{e,0}^{\infty}$$

$$\phi(x,t) = \frac{2D_e}{u_V c_A} \sum_{n=1}^{\infty} \frac{\left(-1\right)^n c_{e,L}^{\infty} - c_{e,0}^{\infty} + c_e^{0}}{n\pi} e^{-\alpha^2\left(\frac{n\pi}{L}\right)^2 t} \mathbf{sin}\frac{n\pi}{L}x + \frac{\phi_L^{\infty} - \phi_0^{\infty}}{L}x + \phi_0^{\infty}$$

CASE 2: Changing the load resistance and/or the applied potential.

Here we consider what happens when the load resistance or an applied potential is changed for a zirconia electrolyte already operating in a P_{O_2} gradient

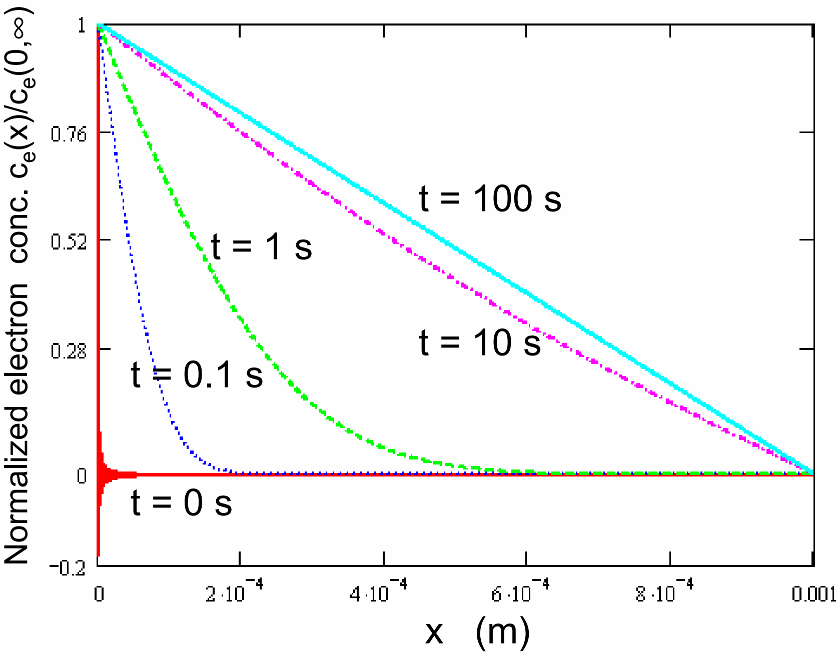
$$c_e(x,t) = \sum_{n=1}^{\infty} \frac{2\left[\left(-1\right)^{n-1}\left(c_{e,L}^{0} - c_{e,L}^{\infty}\right) + \left(c_{e,0}^{0} - c_{e,0}^{\infty}\right)\right]}{n\pi} e^{-\alpha^2\left(\frac{n\pi}{L}\right)^2 t} \mathbf{sin}\frac{n\pi}{L}x$$

$$+\frac{c_{e,L}^{\infty} - c_{e,0}^{\infty}}{L}x + c_{e,0}^{\infty}$$

$$\phi(x,t) = \frac{D_e}{u_V c_A} c_e(x,t)$$

CASE 1

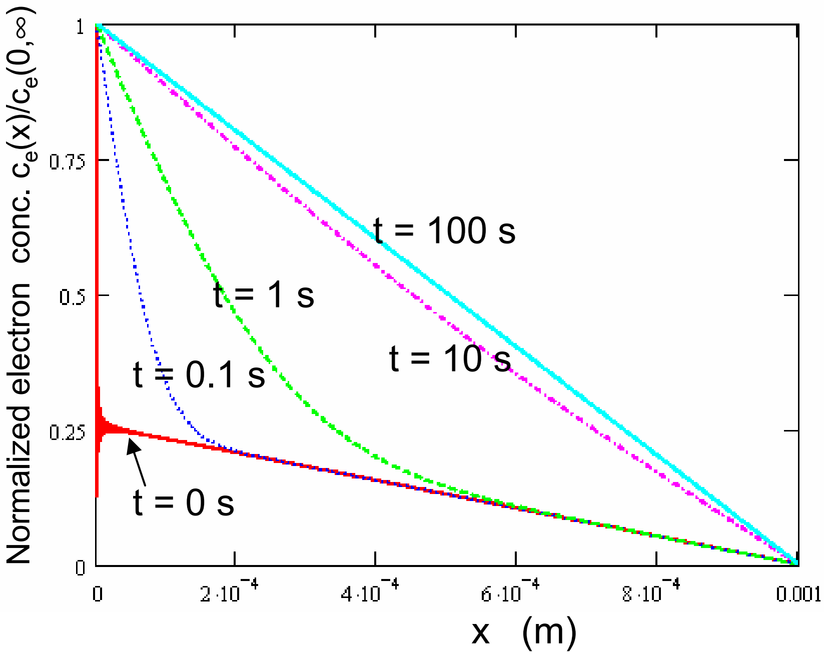
Introduction of a P_{O_2} gradient



Before the zirconia electrolyte is introduced to a P_{O_2} gradient (i.e., at t = 0), the concentration distribution is flat. After the P_{O_2} gradient is introduced, a new concentration distribution gradually established.

CASE 2

Changing the P_{O_2} gradient, applied potential or load resistance

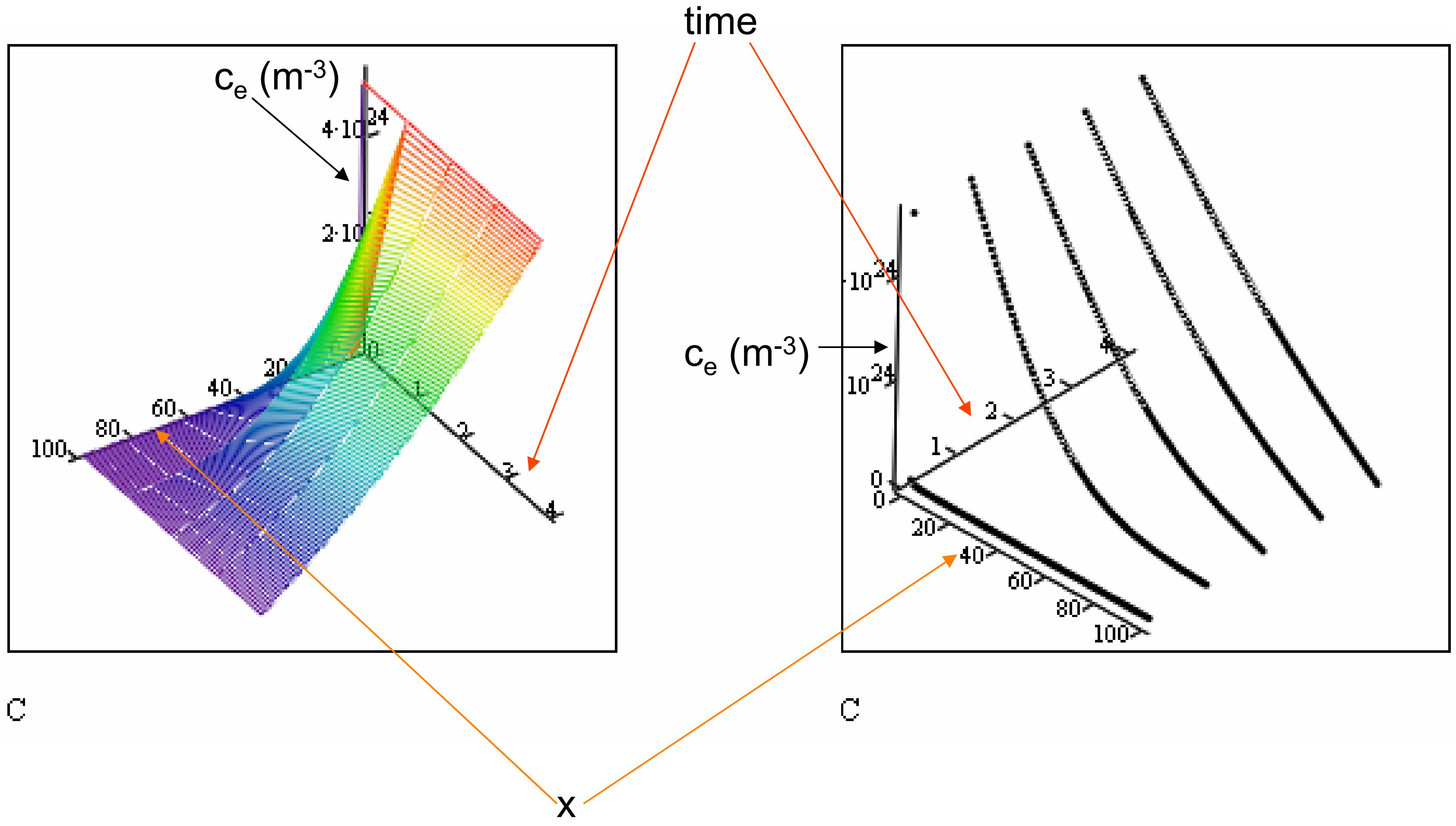


After the boundary concentrations are perturbed a new concentration distribution gradually established.

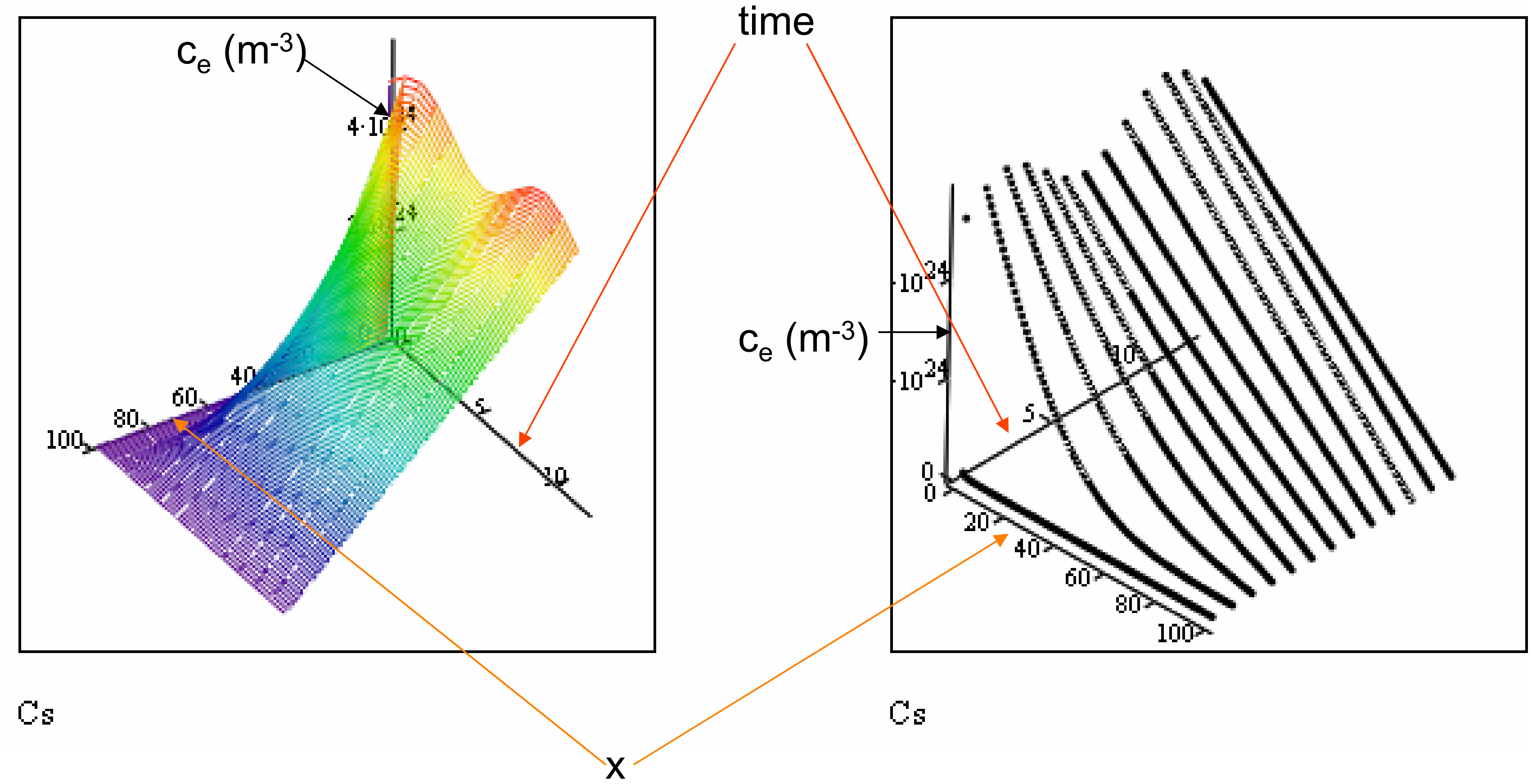
For the above processes, the time constant, τ,

- $\tau \propto 1/L$ (steady-state achieved more rapidly for thinner electrolytes)
- $\tau \propto D_e$ (rapid electron diffusion helps system to reach steady-state

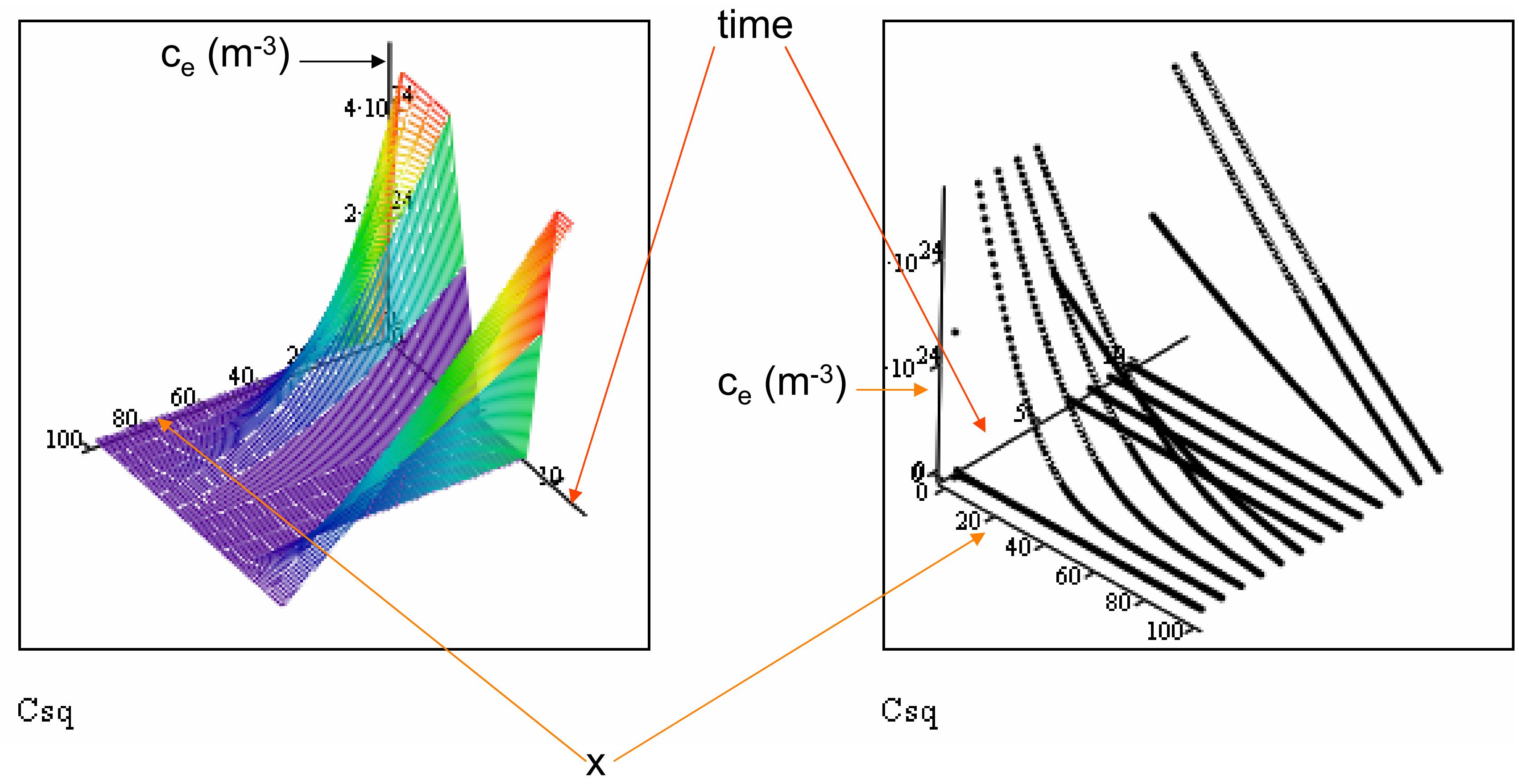
CASE 1: Introduction of a P_{O2} gradient



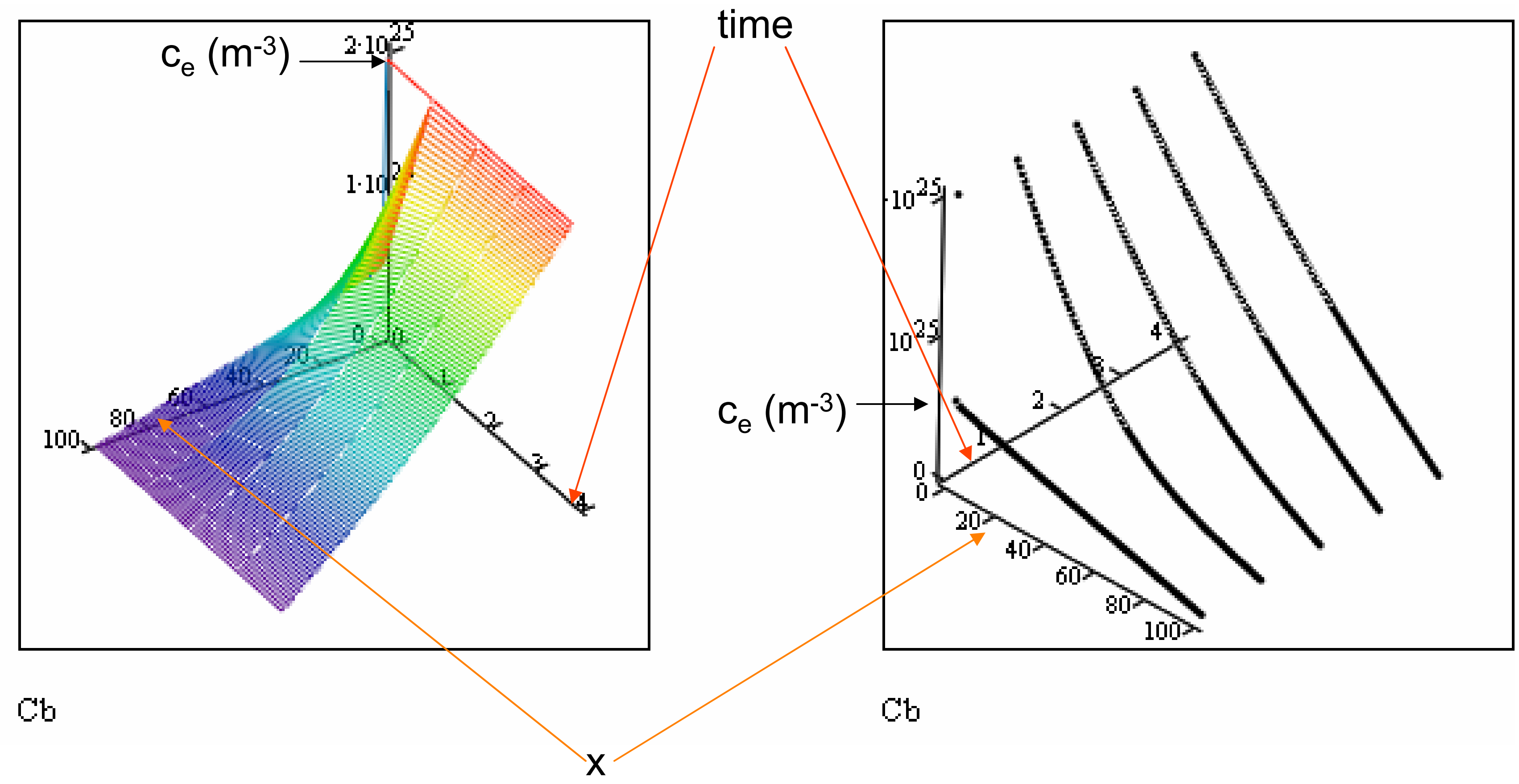
CASE 1 + Sinusoidal variation



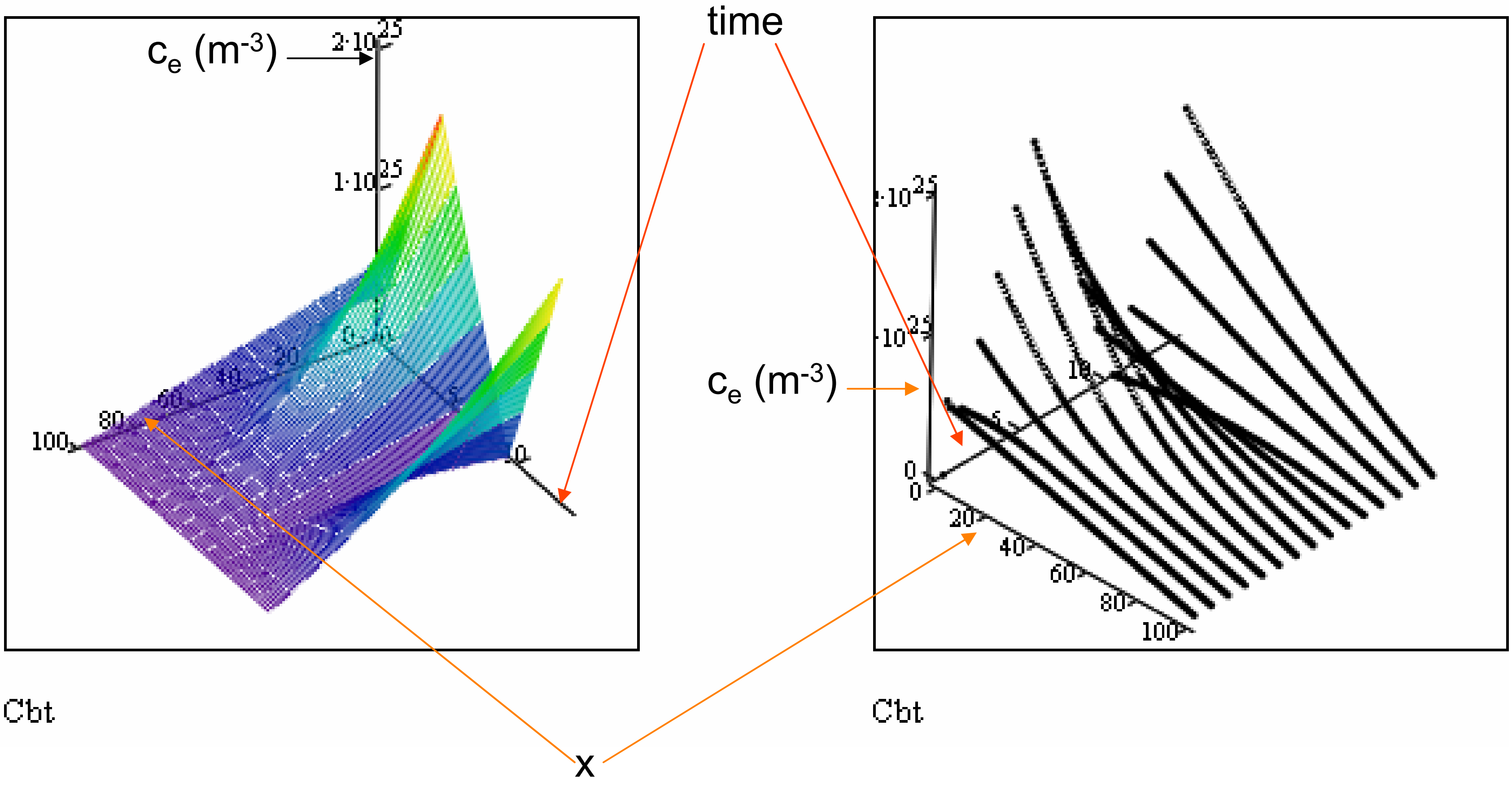
CASE 1 + Square-wave variation



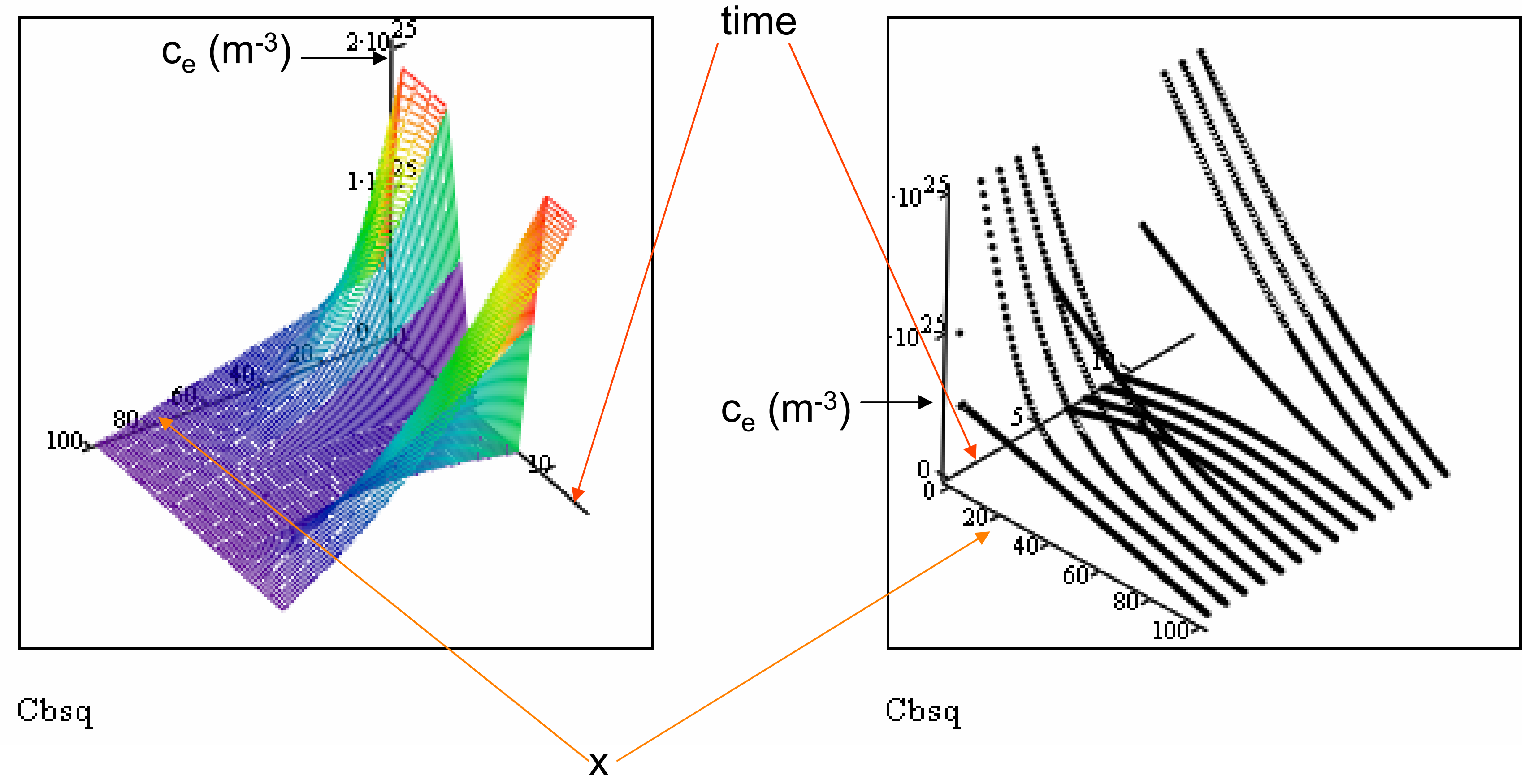
CASE 2: Changing the P_{O_2} gradient/applied potential/load resistance



CASE 2 + Triangular-wave variation



CASE 2 + Square-wave variation



CONCLUSIONS

We have developed a continuum level electrochemical model from which we can obtain

1. Continuous equations relating defect concentration to oxygen potential
2. Assumption free equations for the:
    - Spatial distribution of ionic and electronic defects
    - transport properties
    - power and current efficiency of SOFC electrolytes
3. Thermo-chemical stability
4. Thermo-mechanical properties
5. Time evolution of the transport properties of oxide ion conducting materials.

APPLICATION TO SECA TEAMS

- Developed spatial relationships that can be used to model:
  - Electrochemical performance
  - Interaction between materials
    - Phase instability ->performance degradation
  - Lattice expansion and Mechanical properties
    - Delamination -> mechanical failure

- Extended model to transient behavior to determine effect of:
  - Air/fuel compositional changes (start-up)and perturbations
  - Load changes
  - Thermal cycling

- Based on fundamental thermodynamic constants:
  - Can be applied to any material set and geometry