Time-Dependent Modeling of MIECs

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Motivation

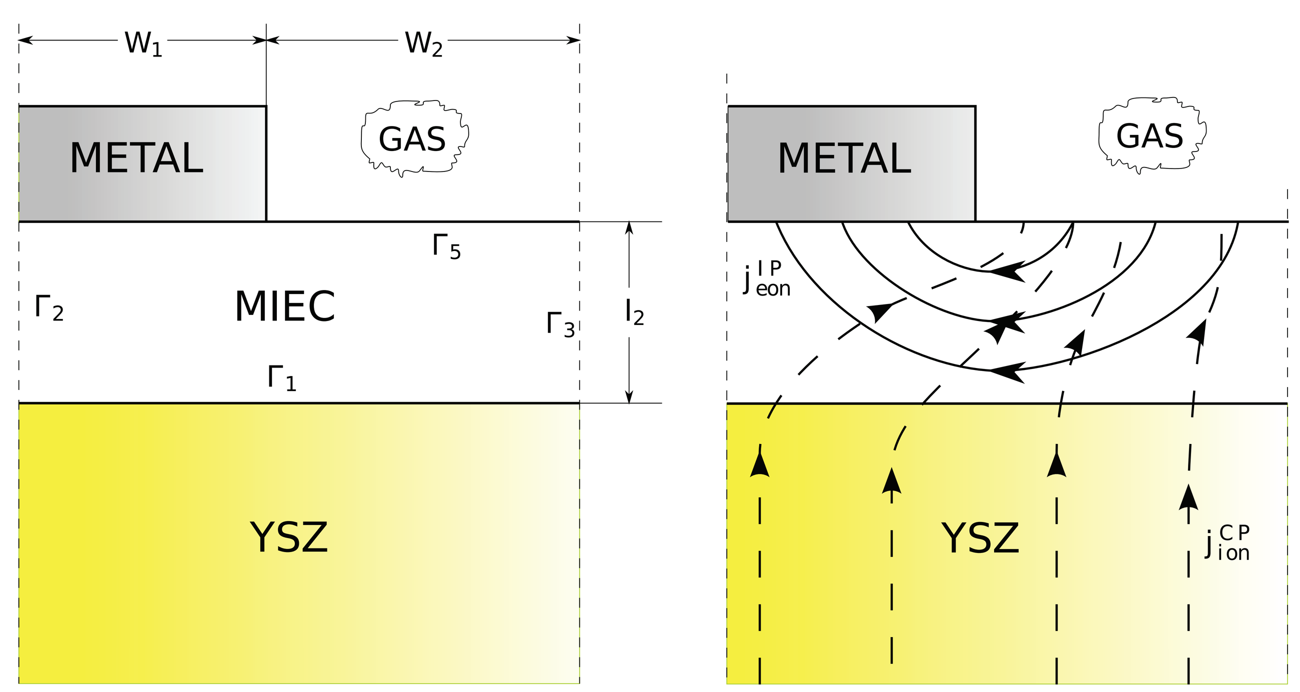
Mixed ionic electronic conductors (MIEC) are currently of great interest for SOFC applications. For example, ceria-containing anodes can be operated directly on hydrocarbons without coking and without suffering from sulfur poisoning. In addition, they can be used at lower temperatures than Ni/YSZ cermets. In order to design, optimize, and characterize MIEC electrodes, it is useful to have models to aid in interpreting experimental results.

Introduction

In this work, we present a linear, time-dependent model for the study of MIECs. This model allows us to compute in time and space species concentrations, electric potential and currents.

Systems Studied

We model a YSZ slab (thickness 1mm) placed between two MIEC thin films (approx 1µm thick) with patterned metal electrodes. The MIEC is immersed in a reducing atmosphere consisting of H_2O/H_2 and a noble gas. The system is symmetric.



Our Model

We solve Drift-Diffusion + Poisson eqn.s (notation ref.s 1 and 2)

$$\triangle \phi = -\frac{\rho}{\varepsilon}$$

$$\partial_t c_{eon} + \nabla \cdot \left(-D_{eon} c_{eon} \nabla \frac{\tilde{\mu}_e}{k_b T} \right) = 0$$

$$\partial_t c_{ion} + \nabla \cdot \left(-D_{ion} c_{ion} \nabla \frac{\tilde{\mu}_v}{k_b T} \right) = 0$$

Definitions:

$B =$ dopant concentration; $\tilde{\phi} = \frac{e\phi}{k_b T}$

$c_{eon} = \bar{n}Bn =$ polaron conc.; $c_{ion} = \bar{p}Bp =$ vacancy conc.

$\tau_n = \frac{l_c^2}{D_{eon}}$; $\tau_p = \frac{l_c^2}{D_{ion}}$

$\tau_n^\star = \frac{\tau_n + \frac{\bar{n}}{4\bar{p}}\tau_p}{1 + \frac{\bar{n}}{4\bar{p}}}$; $\tau_\phi^\star = \frac{\tau_p - \tau_n}{1 + \frac{4\bar{p}}{\bar{n}}}$

$\tilde{\mathbf{x}} = \frac{x}{l_c}$; $\tilde{t} = \frac{t}{\tau_n}$

We use the following math procedure (ref.s 3 and 4):

1. We perform a regular perturbation using small bias approximation (linearize equations);
2. We Fourier transform the equations obtained;
3. We do a singular perturbation with boundary layer corrections (Debye length is small but the thickness is small too);
4. We solve the equations such that H^1 discretization errors (error in both fluxes and potentials) can be bounded rigorously

BULK:

$$i\omega\tau_n^\star \hat{n}^{(1)} - \triangle \hat{n}^{(1)} = 0$$

$$i\omega\tau_\phi^\star \hat{n}^{(1)} - \triangle \hat{\phi}^{(1)} = 0$$

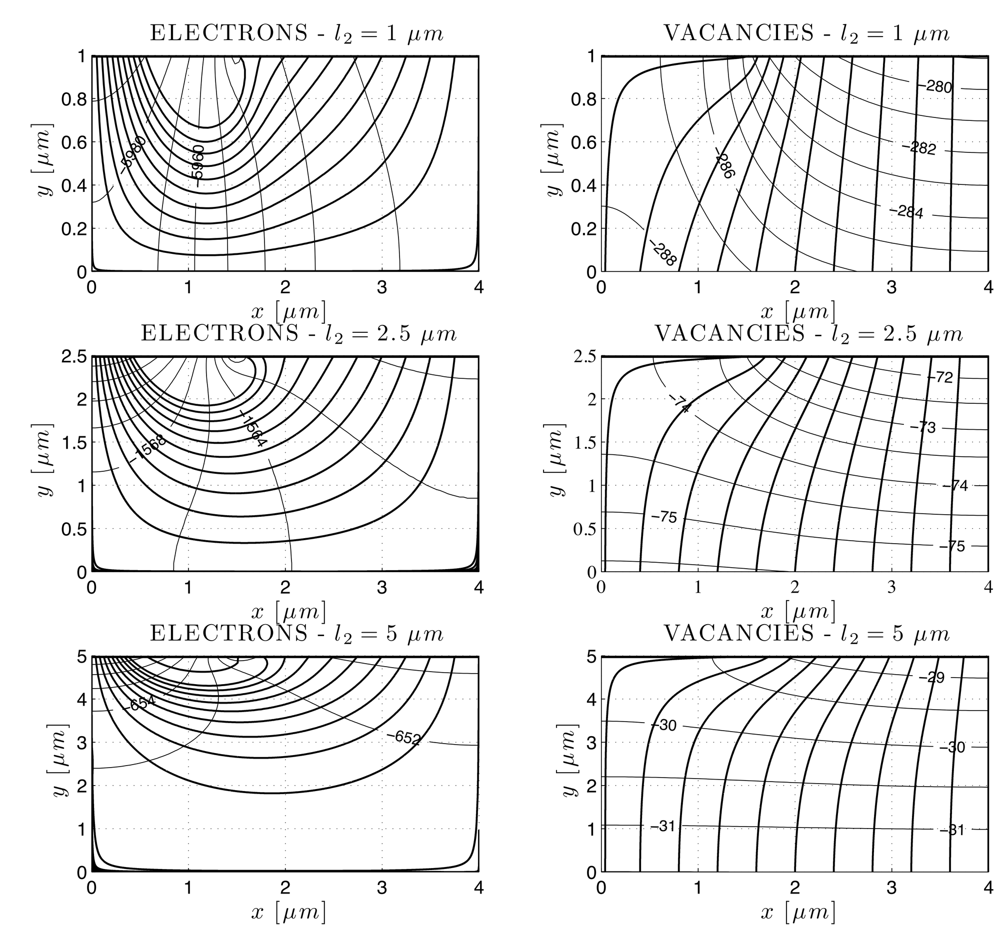
BCs at gas|MIEC

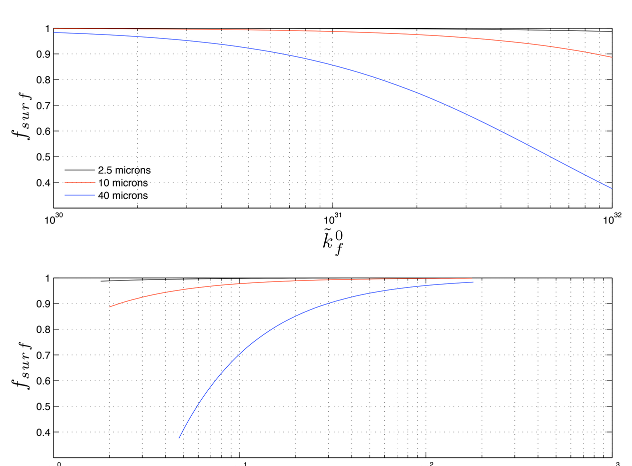
locally two processes in parallel:
1. injection of electrons and vacancies (Resistor)
2. double layer (Capacitor)

$$Z_{\text{gas}|\text{MIEC}} = \frac{1}{\frac{1}{\frac{1}{2}\left(1+\frac{W_1}{W_2}\right)\frac{U_T}{e\boxed{k_f}\tilde{p}_{H_2}}} + i\omega \frac{\boxed{C_Q}}{U_T\left(1+\frac{c^0_{eon}}{4c^0_{ion}}\right)}\frac{1}{1+\frac{W_1}{W_2}}}$$

Steady State Results (Samarium Doped Ceria)

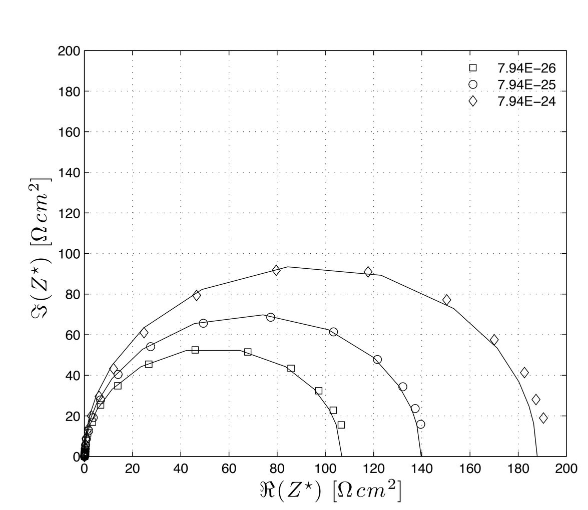
No parameter fitting (all data from ref. 1) We recover plausible behavior for fluxes and potentials.





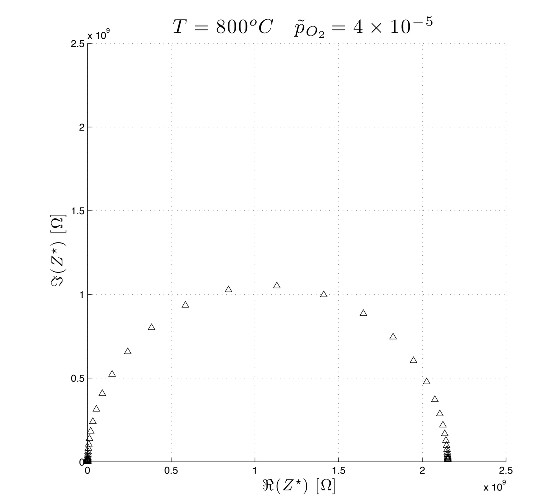
Behavior of the Area Specific Resistance Polarization (ASRP) depends upon MIEC|metal and MIEC|gas width.
($f_{surf} = R_{surf}/ASRP$; $f_{surf} = 1 \Rightarrow$ surface dominated ASRP)

Time Dependent Results

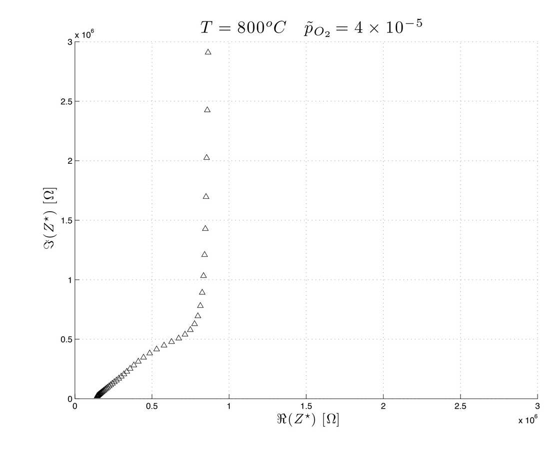


We recover RC behavior for SDC thin films. Good match with recent experimental results of Chueh et al. (ref. 5).

LSM behavior matches well the experimental results for microelectrodes (ref. 6) (Note: computation in cylindrical coordinates)

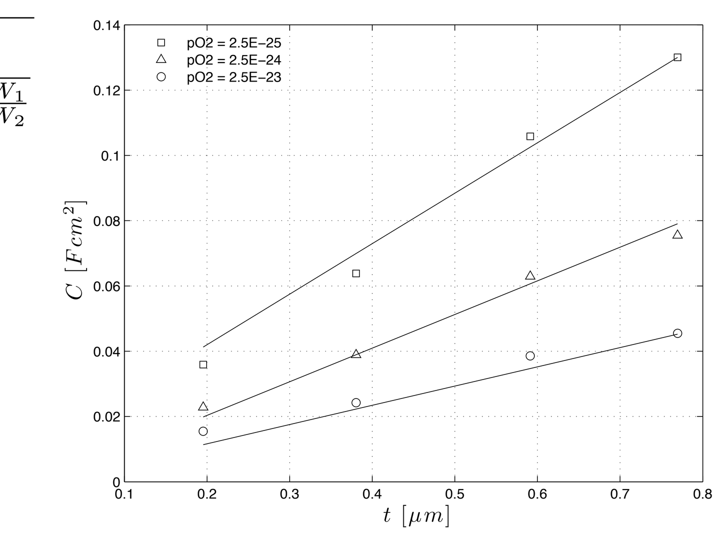


Low frequency



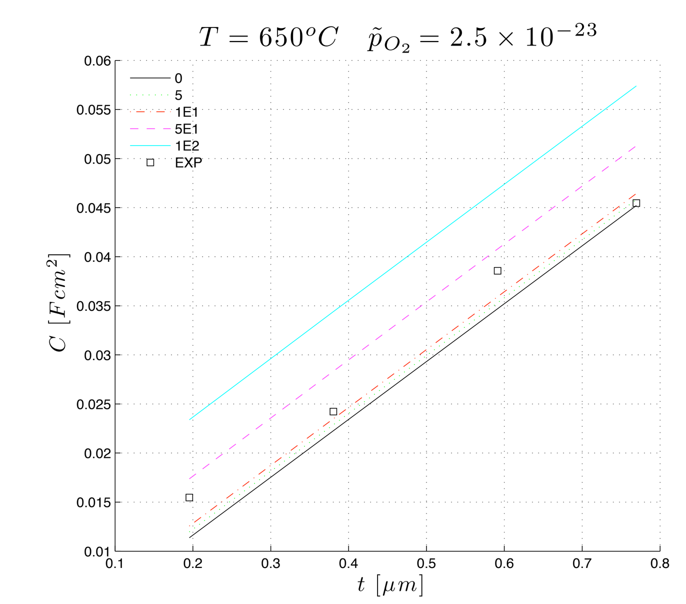
High frequency

Chemical Capacitance (SDC)



Good match with capacitance results reported in ref. 5. $C = C_{chem} + C_{surf}$

If reactions are slow (k_f small) then capacitance of interface is additive w.r.t. chemical capacitance



Ongoing Work

- extension of the model to 3D
- inclusion of non-neutrality and roughness effects (boundary layers and multiscale solutions)
- comparison of the model with non-linear experiments to be run in collaboration with S.M. Haile @ Caltech and W. Lai @MSU
- exploration of quantum effects (semiconductors)

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