# Micro Scale Dynamic Modeling of LSM/YSZ Composite Cathodes

S. Raju Pakalapati[1,2], Kirk Gerdes[1], Harry Finklea[1,2], Mingyang Gong[1,2], Xingbo Liu[1,2], Ismail Celik[1,2]
[1]National Energy Technology Laboratory, Morgantown, WV
[2]National Institute for Fuel Cell Technology, West Virginia University, Morgantown, WV

## Introduction

- Activation of Oxygen Reduction Reaction (ORR) in cathode is a major source of loss for low temperature SOFCs.
- Knowledge of the kinetics of oxygen reduction and their dependence on the microstructure will lead to better cathode designs
- Two possible parallel pathways could contribute to ORR on LSM-YSZ cathodes.
  - 2PB pathway and 3PB pathway.
- A micro-scale computational model is developed for composite LSM/YSZ cathodes which takes into account the effect of microstructure.

## Model Description

- LSM, YSZ and pore phases are assumed to be completely percolated and treated as superimposed continua
- Governing equations for charge and mass transfer are solved in each phase.
- Effective transport coefficients are used and the effect of micro-structure is taken into account through averaged parameters.
- A multi-step charge transfer reaction mechanism with parallel 2PB and 3PB pathways.

### Reaction Mechanism:

$$(S1)\quad \frac{1}{2}O_2 + S \leftrightarrow O_{ad}$$

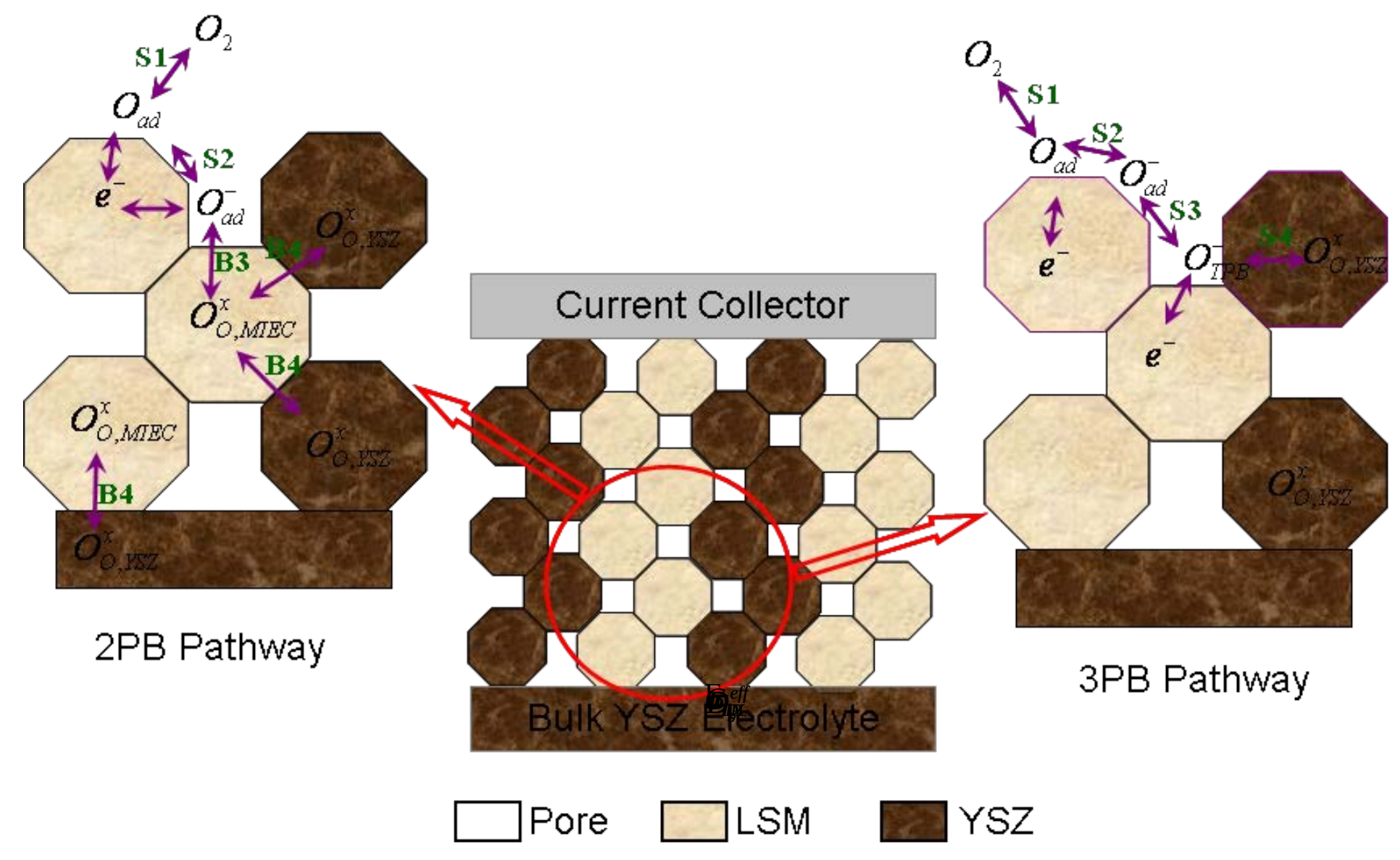
$$(S2)\quad O_{ad} + e^- \leftrightarrow O_{ad}^-$$

$$(S3)\quad O_{ad}^- \leftrightarrow O_{TPB}^-$$

$$(S4)\quad O_{TPB}^- + e^- + V_{O,YSZ}^{**} \leftrightarrow O_{O,YSZ}^x + S$$

$$(B3)\quad O_{ad}^- + V_{O,MIEC}^{**} + e^- \leftrightarrow O_{O,MIEC}^x$$

$$(B4)\quad O_{O,MIEC}^x + e^- + V_{O,YSZ}^{**} \leftrightarrow O_{O,YSZ}^x + V_{O,MIEC}^{**}$$



## Model Equations

Gas species transport ($O_2$)

$$\varepsilon\frac{\partial n_{O_2}}{\partial t} = \nabla\left(D_{O_2}^{eff}\nabla n_{O_2}\right) - r_{ads}$$

Coverages Transport (O, $O^-$,$O^-_{TPB}$)

$$\frac{\partial\theta_i}{\partial t} = \nabla\left(D_{\theta_i}^{eff}\nabla\theta_i\right) + r_i$$

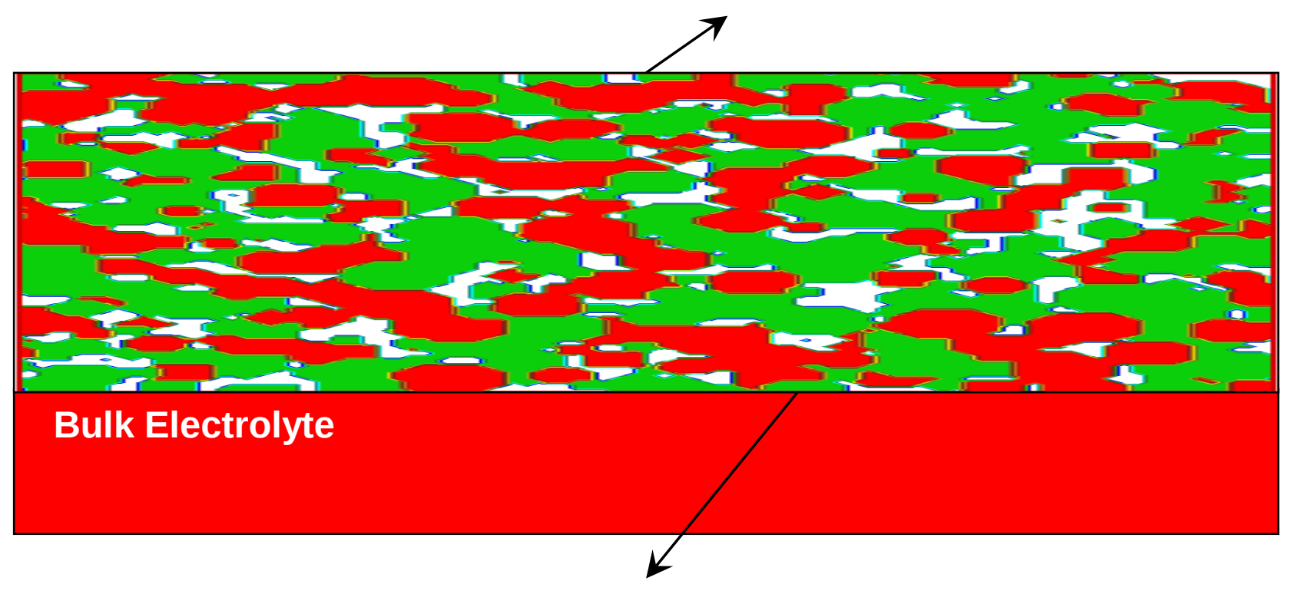
Vacancies Transport ( $C_{V,MIEC}$ , $C_{V,YSZ}$)

$$\frac{\partial C_V}{\partial t} = \nabla\left(D_{C_V}^{eff}\nabla C_V\right) + r_{C_V}$$

Charge Transport

$$C_{DL}\frac{\partial(\Delta\varphi)}{\partial t} = \nabla\cdot\left(\sigma_i\nabla(\Delta\varphi)\right) - i_F$$

**C/Air interface**
**Ionic current = 0, Electronic potential prescribed, Oxygen concentration prescribed, and flux of all Other species (coverages and vacancies) is zero**

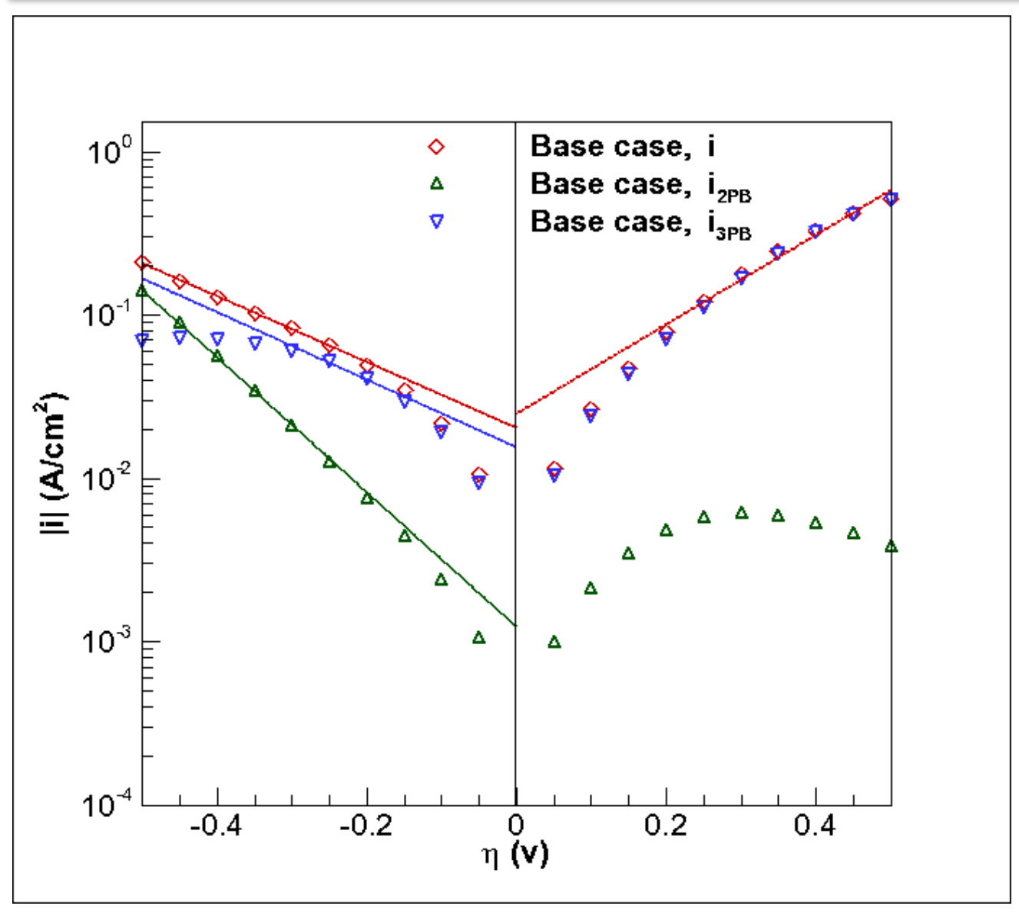


**C/E Interface**
**Electronic current = 0, Ionic potential prescribed, YSZ oxygen vacancy is prescribed, All other fluxes are zero**

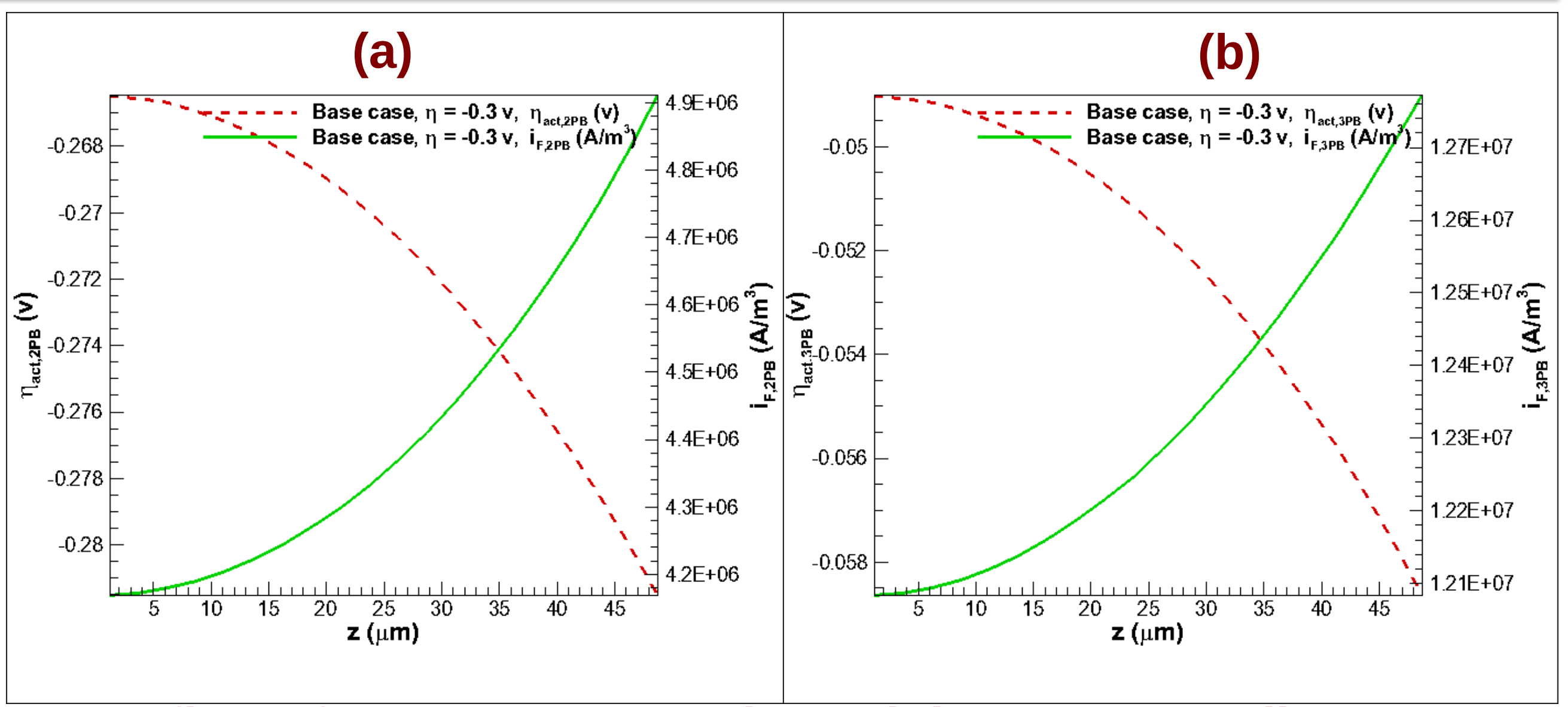
### Model Parameters

| rameter | Value | Units | Description |
|---|---|---|---|
| $a_{LY}$ | $1\times10^6$ | $m^{-1}$ | Specific LSM/YSZ interface area |
| $a_{LP}$ | $1\times10^6$ | $m^{-1}$ | Specific LSM/Pore interface area |
| $\Gamma$ | $1\times10^{-5}$ | mol $m^{-2}$ | Active site density on LSM |
| $\sigma_i$ | 2.6 | $\Omega^{-1}m^{-1}$ | Conductivity of YSZ |
| $C_{DL}$ | 0.1 | F $m^{-2}$ | Double layer capacitance of LSM/YSZ interface |
| $D_s^{eff}$ | $1\times10^{-10}$ | $m^2$ $s^{-1}$ | surface diffusion coefficient |
| $D_b^{eff}$ | $1\times10^{-10}$ | $m^2$ $s^{-1}$ | bulk diffusion coefficient |
| $C_{O^-_{Eq}}$ | $1\times10^{-6}$ | mol $m^{-2}$ | Equilibrium concentration of surface $O^-$ ions |
| $\theta_{O,Eq}$ | 0.01 | no units | Equilibrium concentration of surface O ions |
| $C_{V,LSM,Eq}$ | $1\times10^{-1}$ | mol $m^{-3}$ | Equilibrium concentration of vacancies in LSM |
| $C_{V,YSZ,Eq}$ | $5\times10^3$ | mol $m^{-3}$ | Equilibrium concentration of vacancies in YSZ |
| $k_{S1}^-$ | $1\times10^4$ | $s^{-1}$ | Backward reaction rate constant for reaction S1 |
| $r_{S2,0}$ | $5.0\times10^{-4}$ | mol $m^{-2}$ $s^{-1}$ | Equilibrium exchange rate for reaction S2 |
| $k_{S3}$ | $1\times10^1$ | $s^{-1}$ | Forward reaction rate constant for reaction S3 |
| $r_{S4,0}$ | $1.0\times10^{-3}$ | mol $m^{-2}$ $s^{-1}$ | Equilibrium exchange rate for reaction S4 |
| $r_{B3,0}$ | $5.0\times10^{-4}$ | mol $m^{-2}$ $s^{-1}$ | Equilibrium exchange rate for reaction B3 |
| $r_{B4,0}$ | $1.0\times10^{-4}$ | mol $m^{-2}$ $s^{-1}$ | Equilibrium exchange rate for reaction B4 |

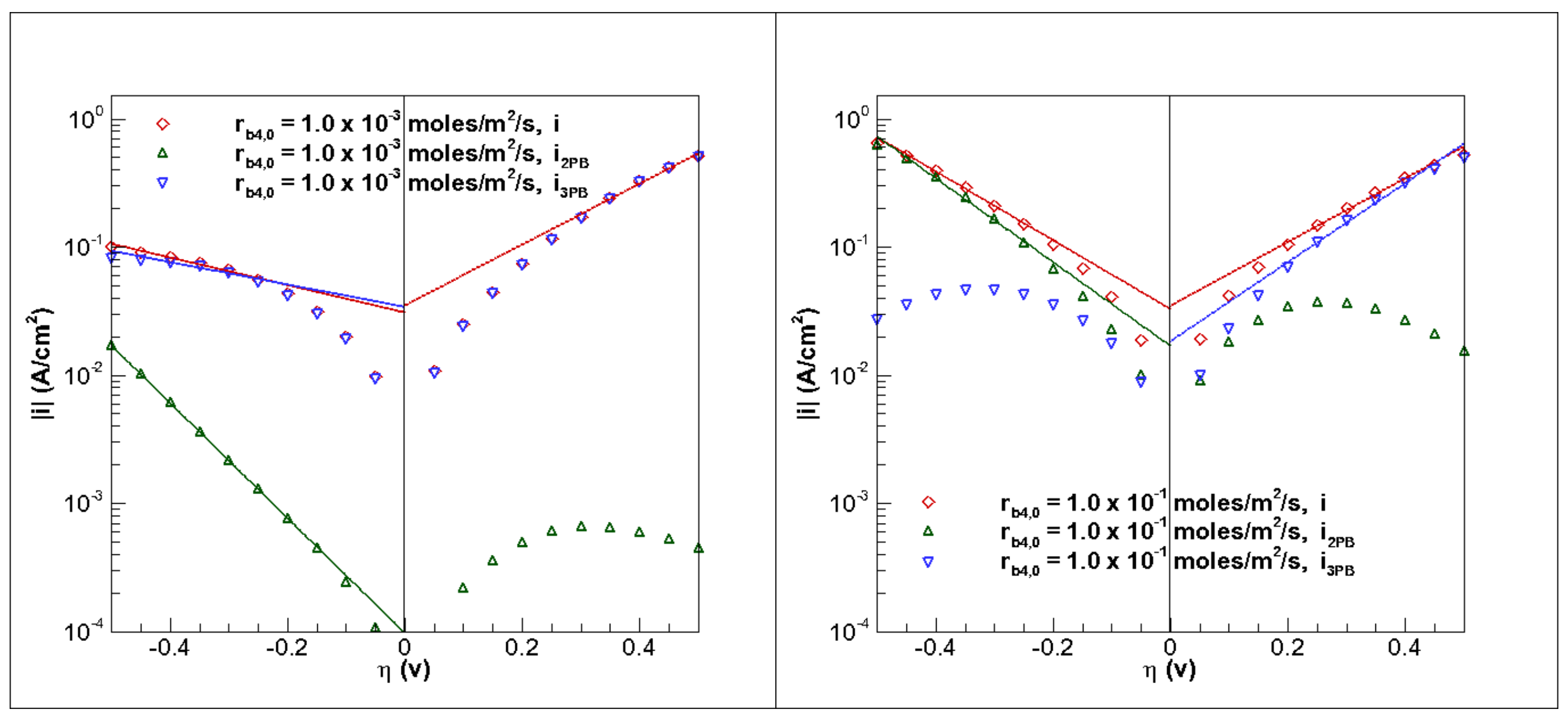
## Results



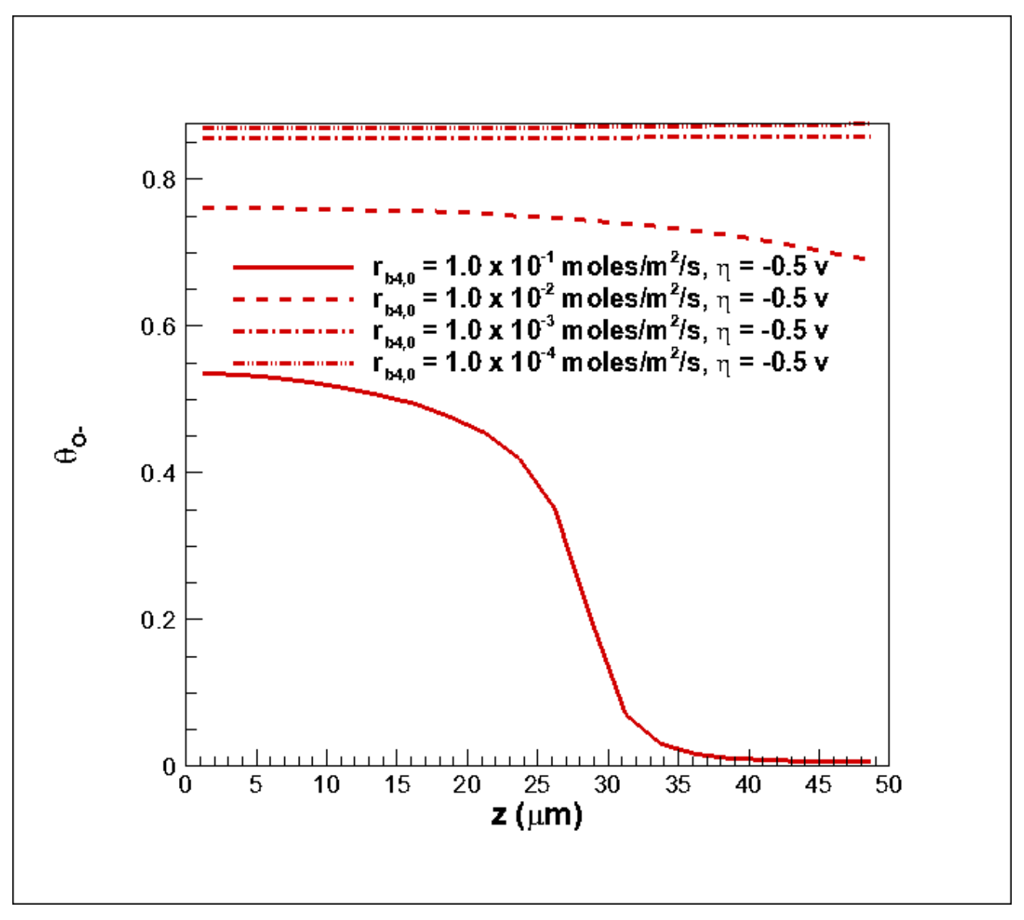
**Predicted polarization curve along with 2PB and 3PB contributions for the base case.**



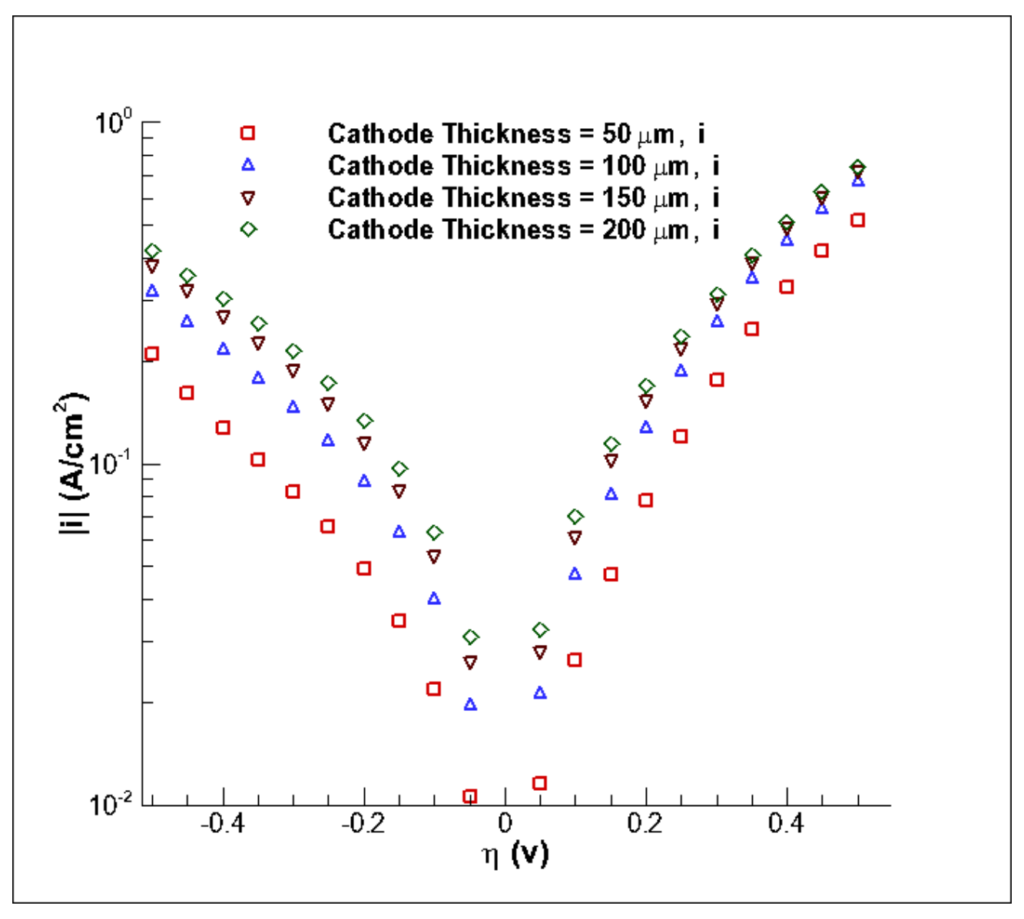
**Profiles of local over-potential and the corresponding local volumetric charge transfer rates at an applied over-voltage of -0.3 V for (a) 2PB mechanism and (b) 3PB mechanism**



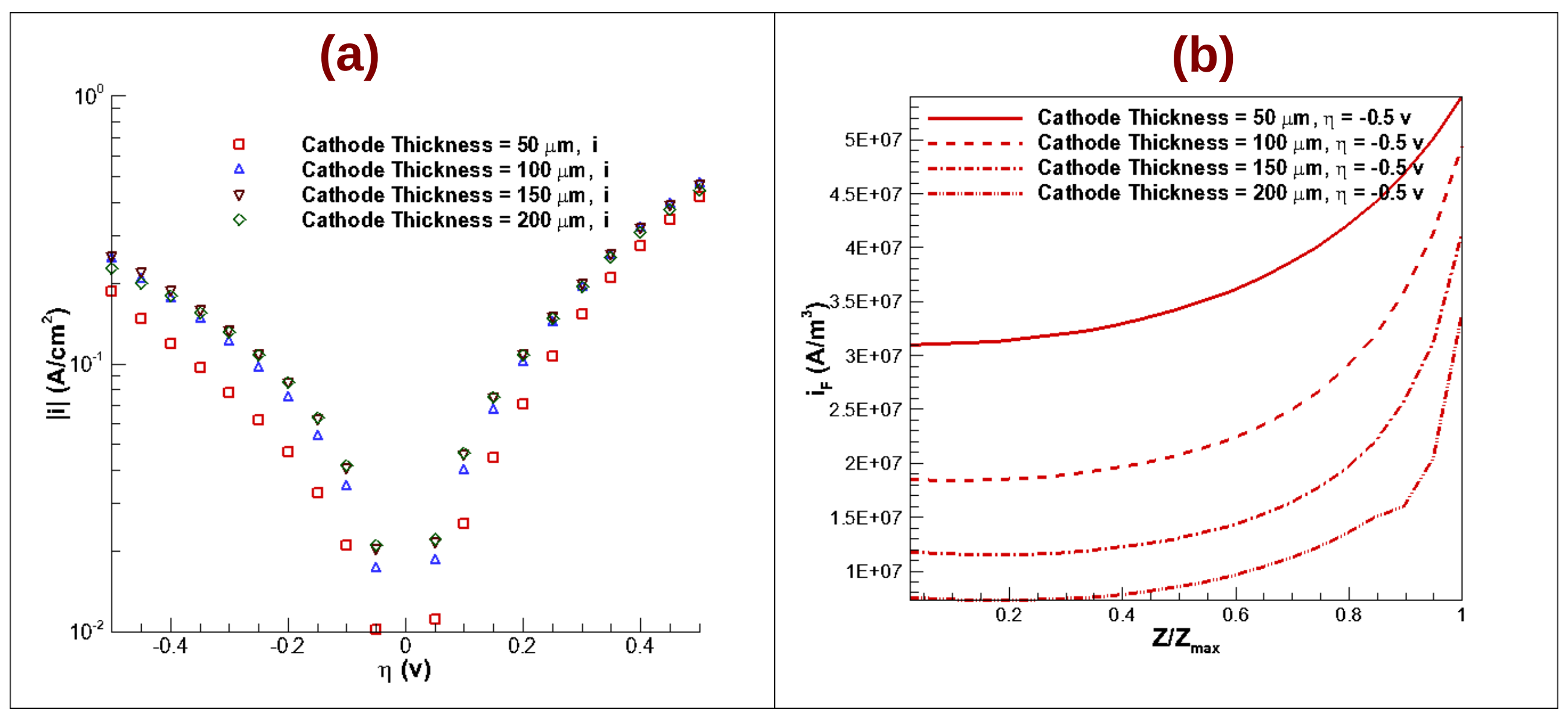
**Predicted polarization curves for different values of $r_{b40}$**



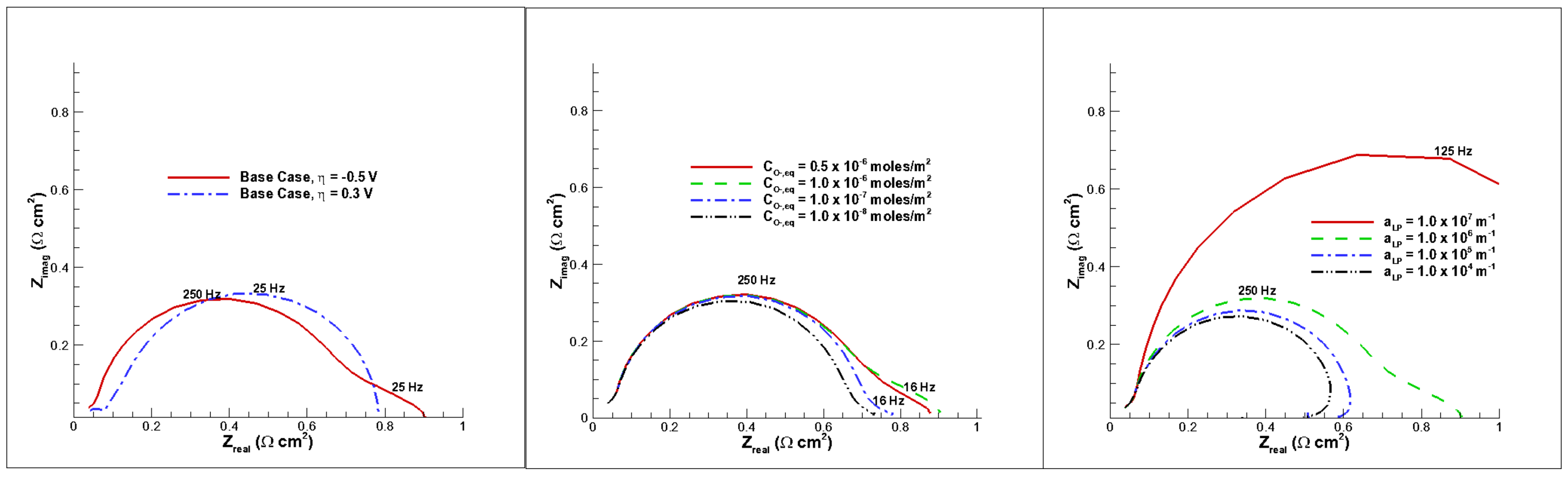
**Profiles along the cathode thickness of coverage of $O^-$ surface species for different values of $r_{b40}$**



**Effect of cathode thickness on polarization curve**



**Effect of cathode thickness when porosity is increased linearly from the cathode surface to the active interface: (a) polarization curves (b) profiles of faradaic current.**



**Predicted impedance curves for different parametric cases**

## Conclusions

- A micro-scale model with parallel pathways for ORR is developed for cathode.
- The model predicts local distributions of thermodynamic and electrochemical parameters along with polarization and impedance curves.
- The relative contributions from 2PB and 3PB pathways to the total current could be sensitive to operating conditions as well as cathode microstructure .
- The model exhibits physically plausible sensitivity to the model parameters and showed good qualitative agreement with experimental polarization data

## ACKNOWLEDGEMENT

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## CONTACT

**Dr. Ismail Celik, MAE Department**
**West Virginia University, Morgantown, WV.**
**Ph: 304 293 3209 Fax: 304 293 6689**
**Email: ismail.celik@mail.wvu.edu**
**URL: http://nift.wvu.edu/**

**NATIONAL ENERGY TECHNOLOGY LABORATORY**

Albany, OR • Fairbanks, AK • Morgantown, WV • Pittsburgh, PA • Sugar Land, TX