Gas Transport and Electrochemistry in Solid Oxide Fuel Cell Electrodes

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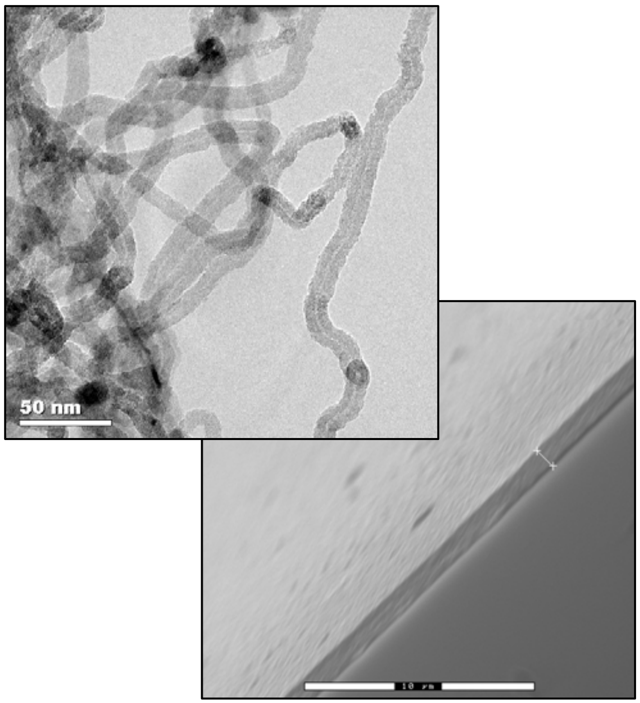
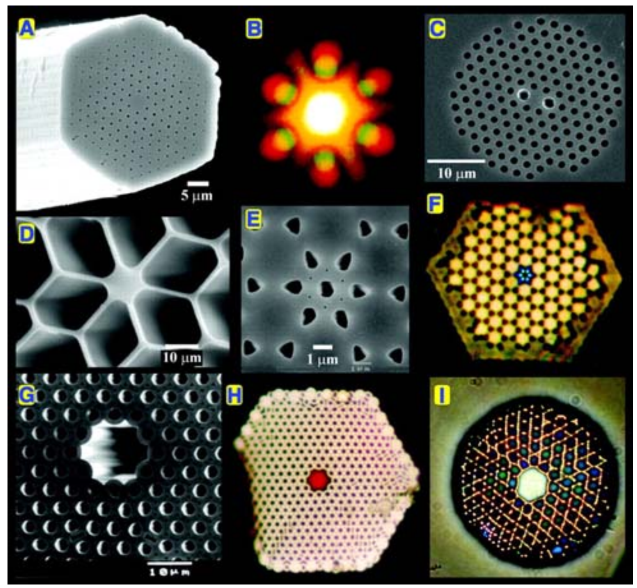
Overview of Research Activities

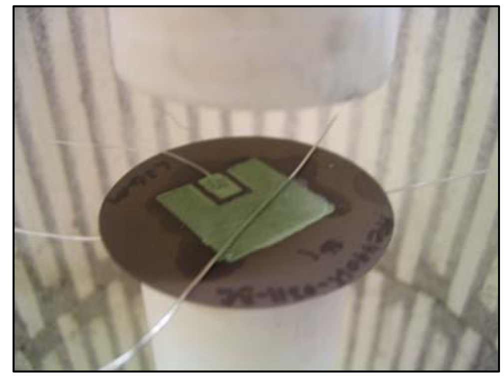
- **Heat & Mass Transfer with Chemical Rxns:**

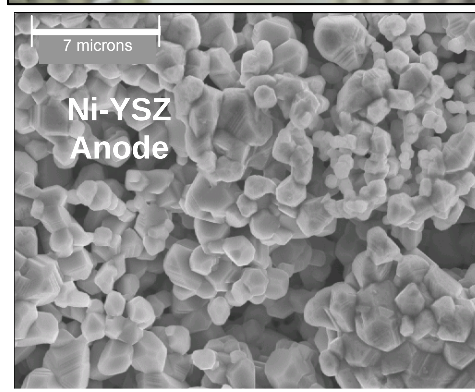
CVD Nanomaterials | Photonics | Fuel Cells





*P. Russell, Science **299**:358, 2003.*

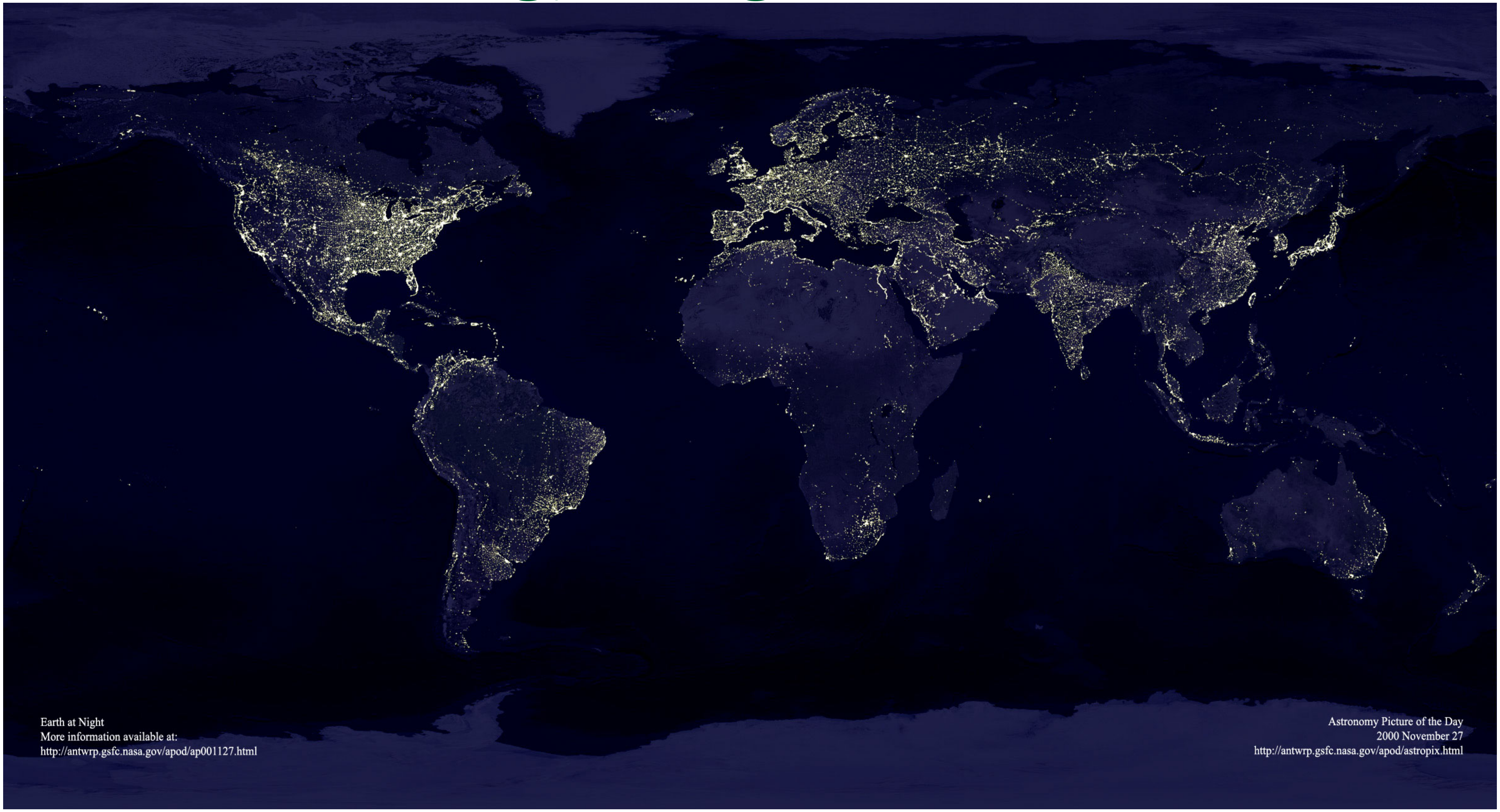




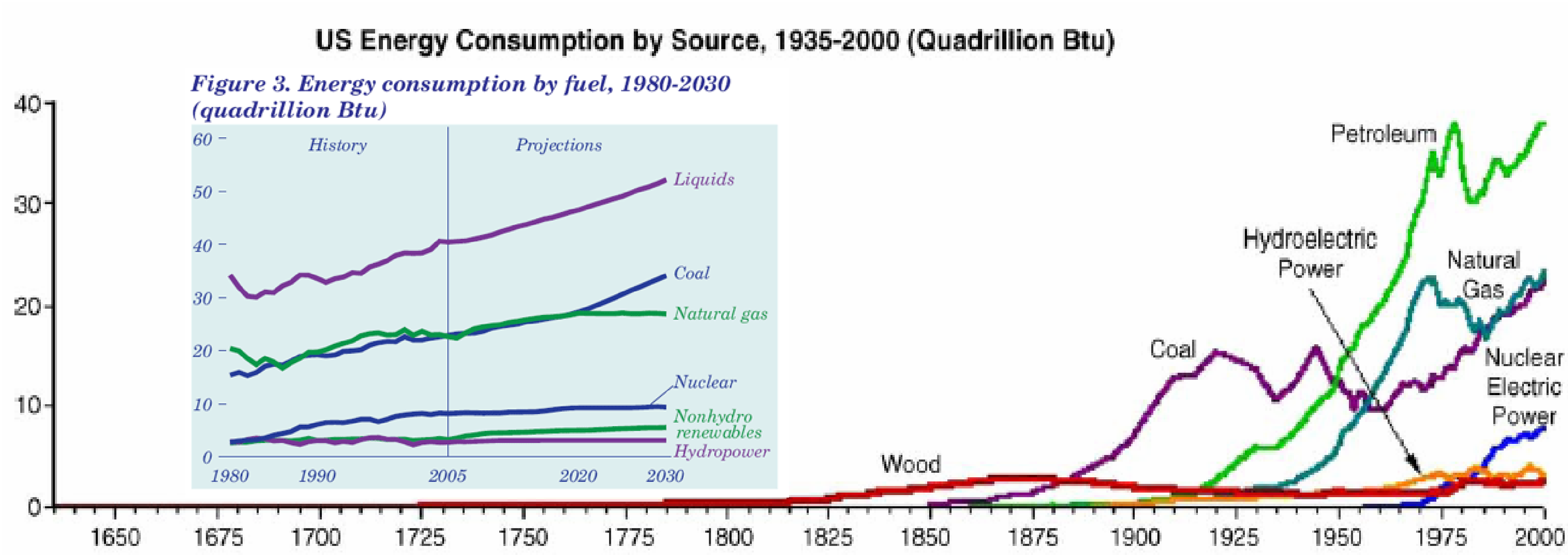
Outline

- Introduction – Energy Conversion
- Fuel Cell Background & Motivation
- Imaging & Analysis at the Pore Level
  - Pore Imaging
  - Gas Transport
  - Electrochemistry
- Electrode Microstructure and Grading
- Conclusions & Future Research Plans

Global Energy Usage

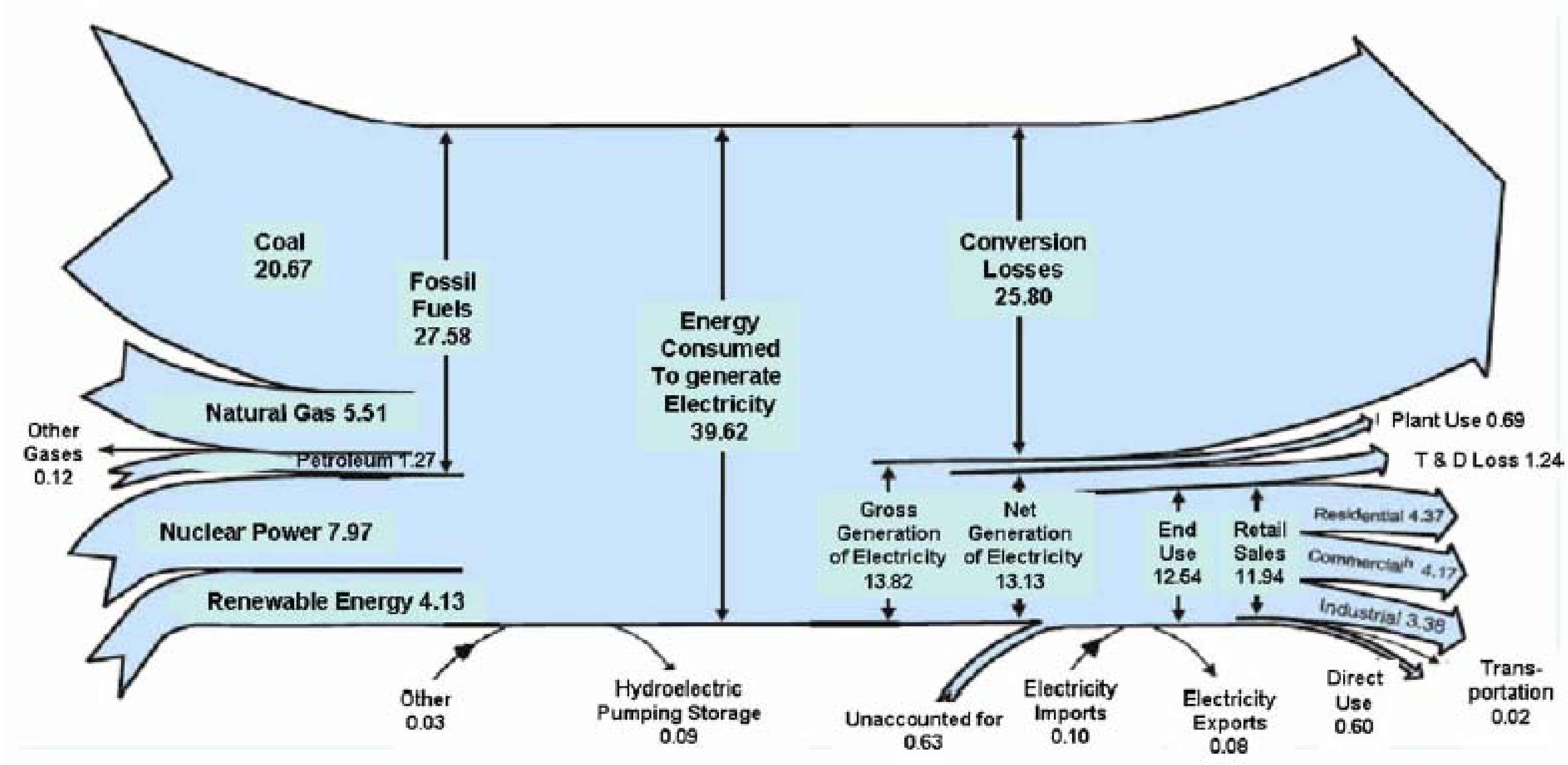


U.S. Energy Usage



Energy Information Association Annual Energy Outlook, DOE/EIA Report # 0383, 2007.
C. Song, *Catal. Today* **115**:2-32. 2006.

Energy Conversion Efficiency



US Power Plants, 2003, in quadrillion BTU
C. Song, *Catal. Today* **115**:2-32. 2006.

Energy Conversion Technologies

- **For Fossil Fuels:**
  - **SOA: Heat Engines**
    - **Steam Cycles**
    - **Gas Turbines**
    - **Internal Combustion**
  - **Fuel Cells?**

High Electrical Efficiency
Fuel Flexibility
Scalable

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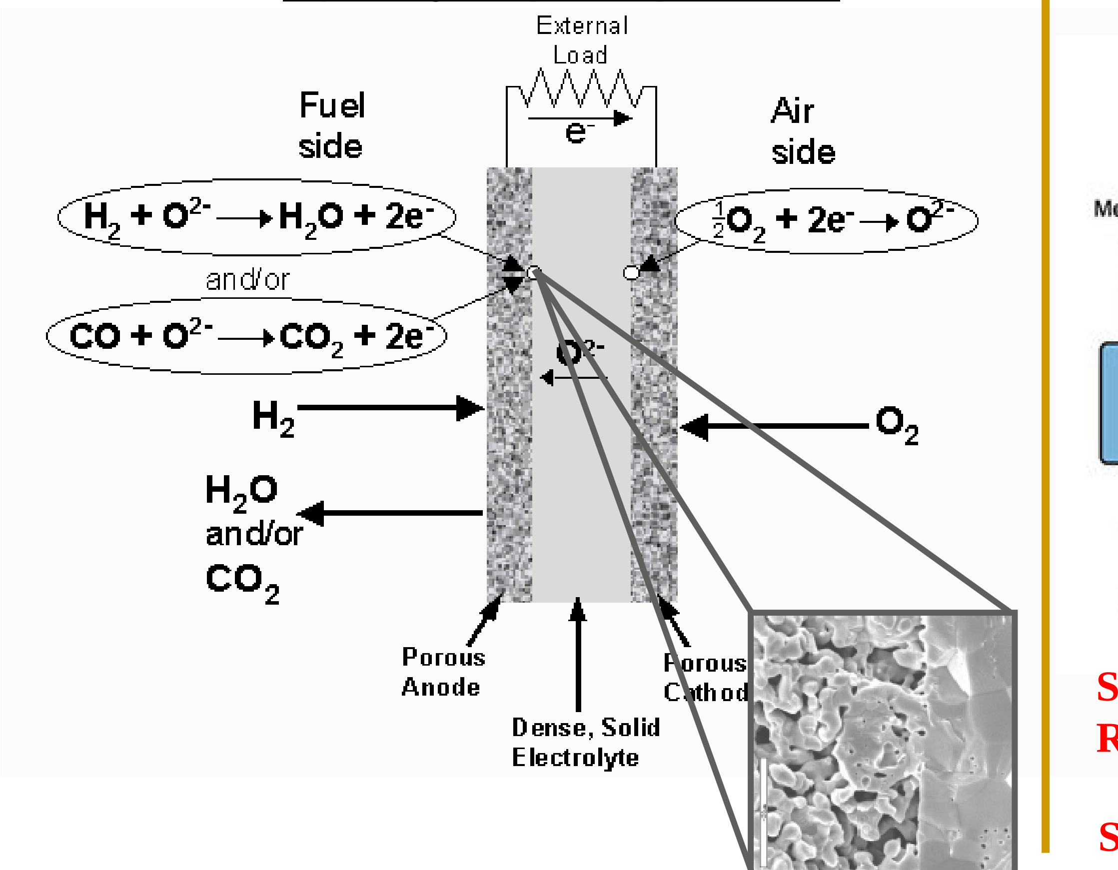
Types of Fuel Cells

Fuel Cells	Electrolyte	Operating Temperature ℃	Fuel Supply	Applications
Alkaline (AFC)	circulating liquid or matrix	50-250	Hydrogen or NH_3-Cracker	small units, up to automobiles
Proton Exchange Membrane(PEM)	immobilized, acidic	60-100	Hydrogen or Converter	small units, up to automobiles
Phosphoric Acid (PAFC)	concentrated acid gel	175-200	Hydrogen or Converter	Power Plants 50 to 200 kW
Molten Carbonate (MCFC)	Li/Na-carbonate melt	600-1000	Selected fuel or Converter	Power Plants up to 1 MW
Solid Oxide (SOFC)	ceramic Zr/Y-oxides	650-1000	All Fuels, direct feed	Small to large Power Plants

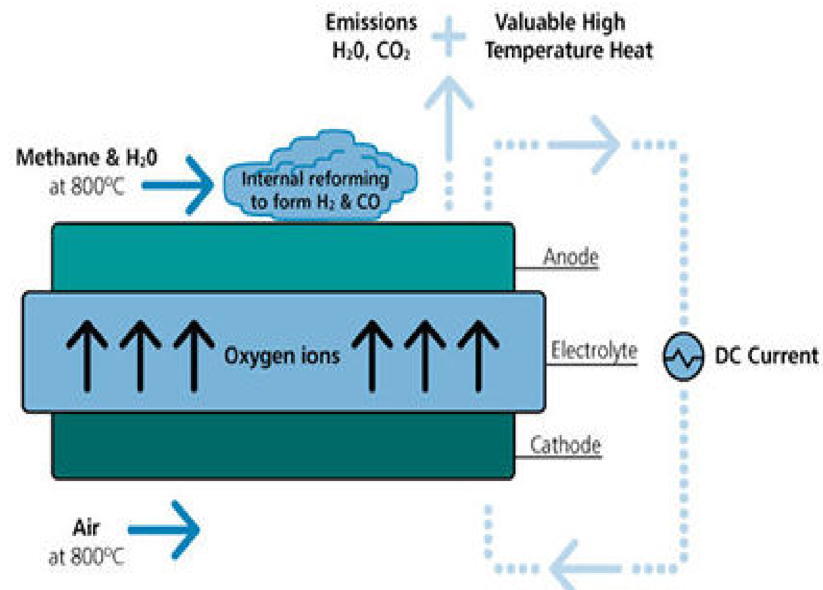
Solid Oxide Fuel Cell

Hydrogen (& CO) Fueled



from http://www.thirdorbitpower.com/SOFC_mech.html

Internal Reforming



Steam Reforming

$$CH_4 + H_2O \Leftrightarrow 3H_2 + CO$$

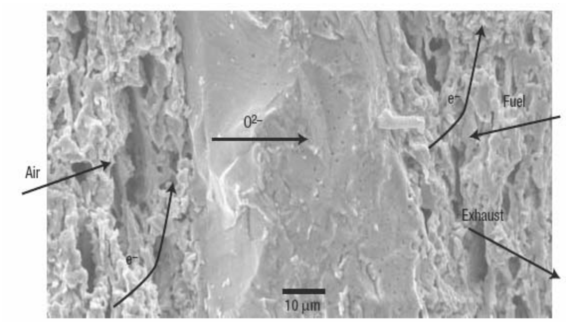
Shift Reaction

$$CO + H_2O \Leftrightarrow H_2 + CO_2$$

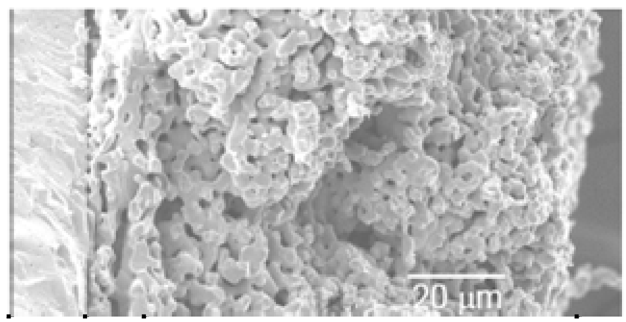
How, specifically, can we design fuel cell microstructure to optimize performance and durability?

Design Input → **Electrochemistry** → **Materials** → **Design** → **Fabricate** → **Test**

Previous Generation SOFC → **Current Generation SOFC** → **Next Generation**



Atkinson et al., Nature Mat. **3**:17-27, 2004.



$La_{0.3}Sr_{0.7}TiO_3$ current collector

Porous YSZ-active region

YSZ electrolyte

Gorte et al., 2006

?

Modeling Tool needed to Determine Optimal Microstructure.

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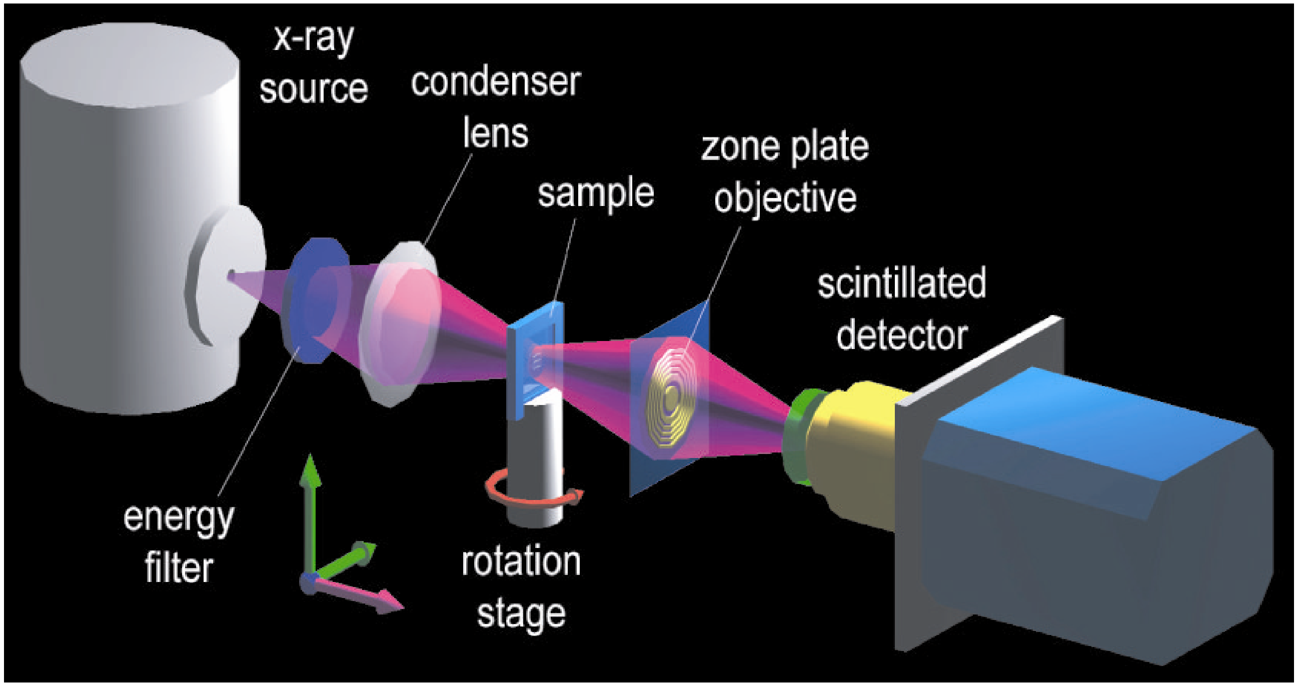
SOFC Pore Structure Imaging

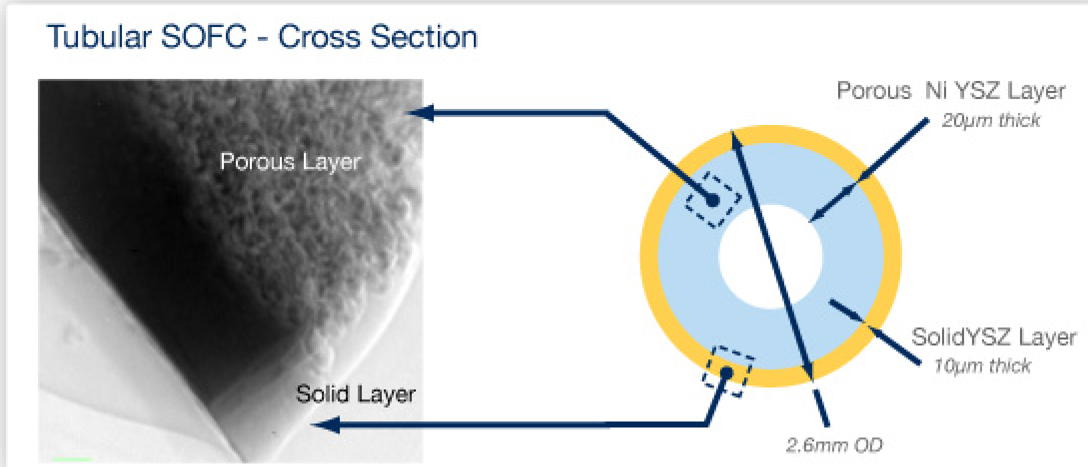
X-Ray Microtomography (XMT)

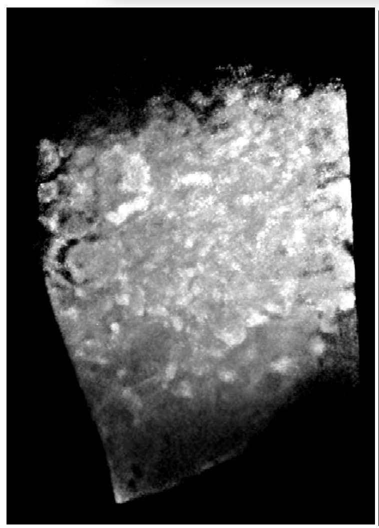
- Non-destructive tomography capable of reconstructing 3-D pore structure.
- X-rays penetrate sample, which is mounted on a rotation stage, and pass through a scintillation screen. The 2-D slice is captured by a camera.
- The sample is rotated through 180 degrees where each slice is captured at specified angle intervals and reconstructed into a 3-D volume of the pore structure.

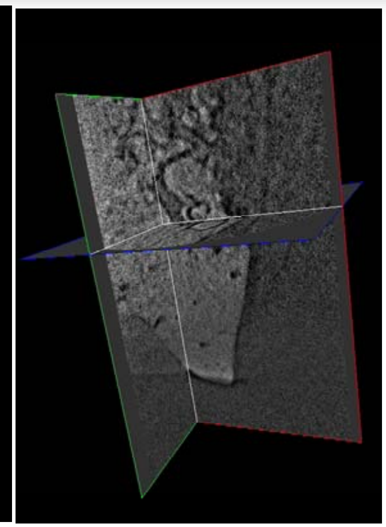


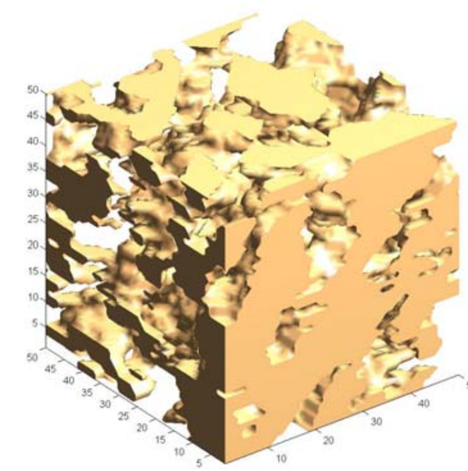
SOFC Pore Structure Imaging – cont’d

- **XMT Experiment details**
  - Xradia (Concord, CA)
  - 8 keV copper source
  - 181 projections at 300 sec per projection
  - 22.6 μm field of view
  - 50 nm resolution
  - 3-D tomographic reconstruction

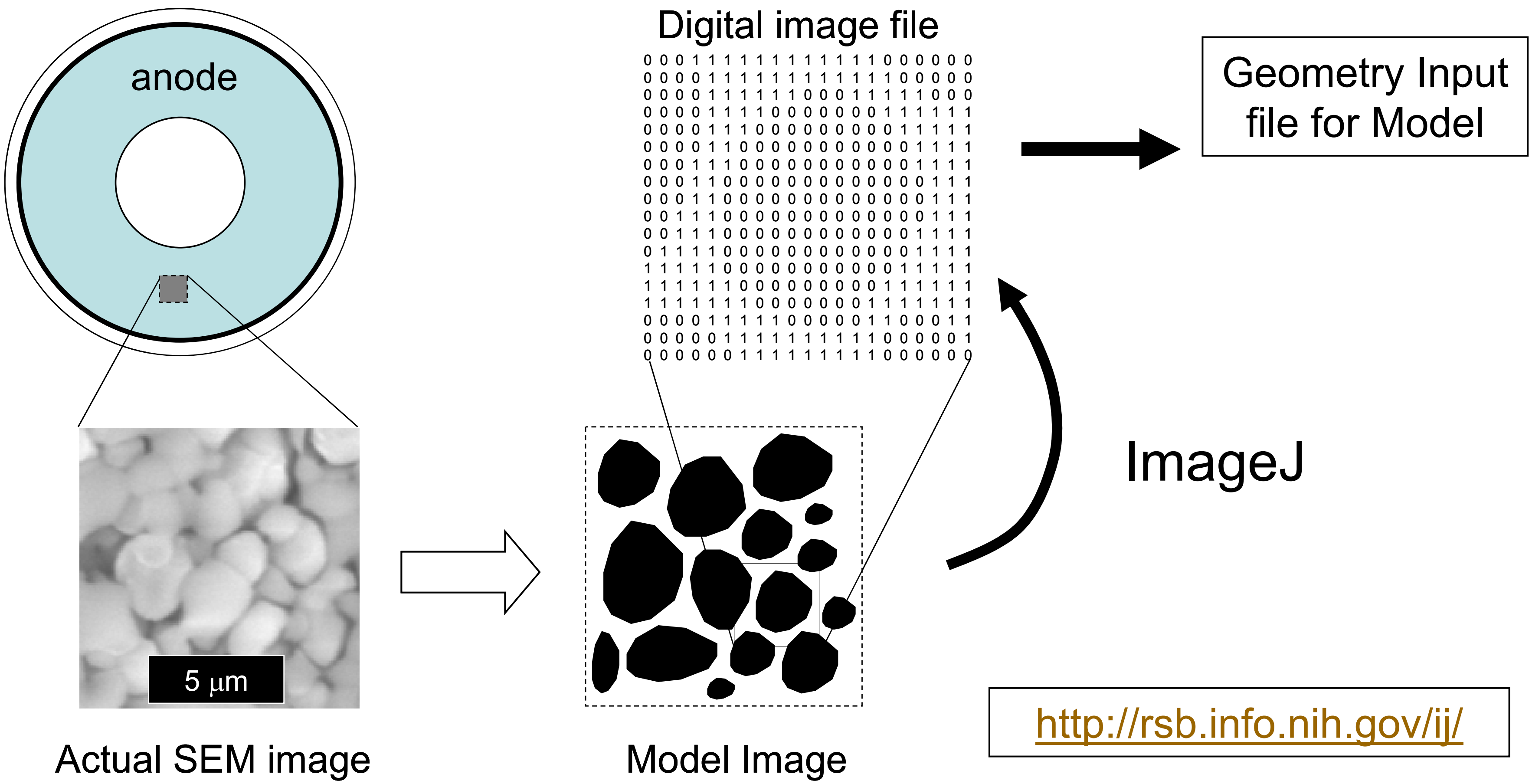








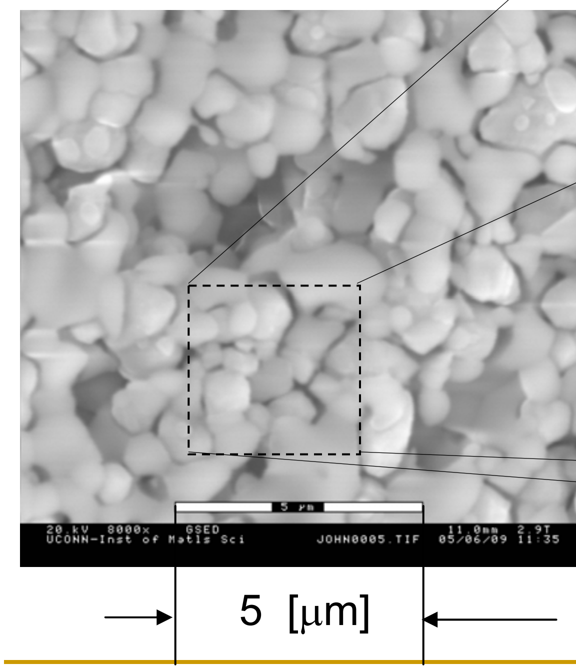
Imaging Processing and Modeling

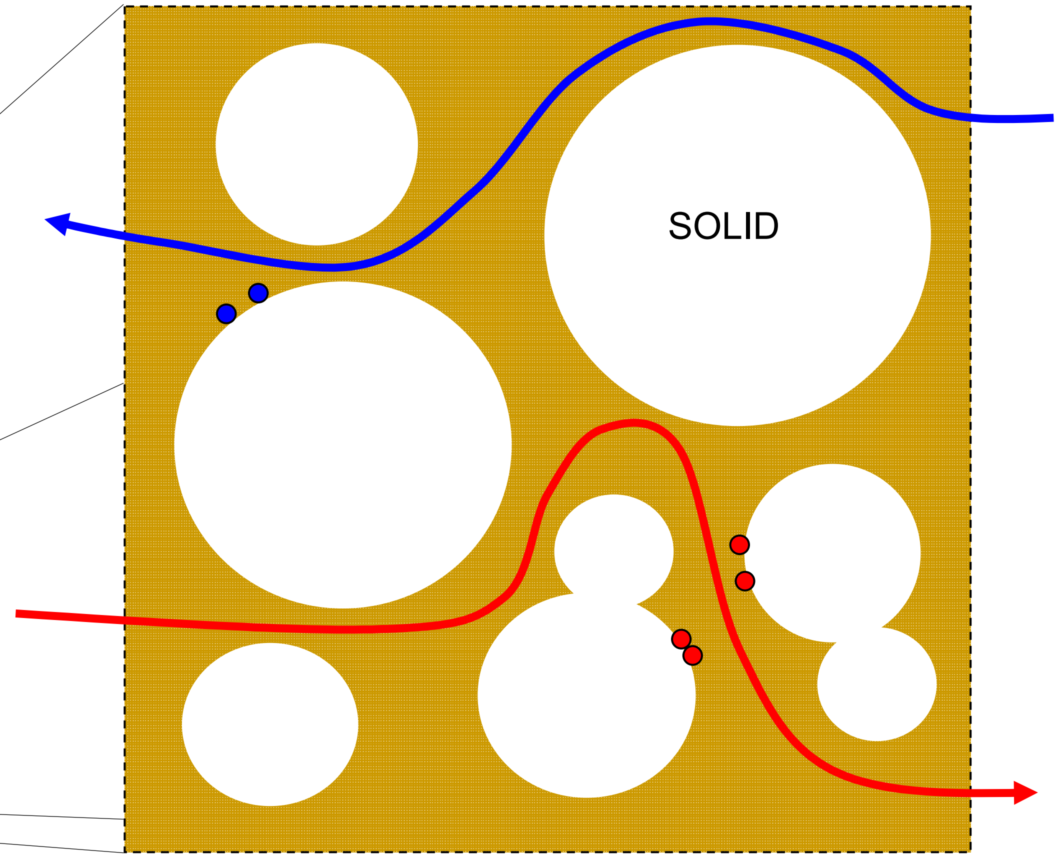


A.S. Joshi, W.K.S. Chiu, et al., 9th AIAA-2006-3820, 2006.

Modeling Challenges

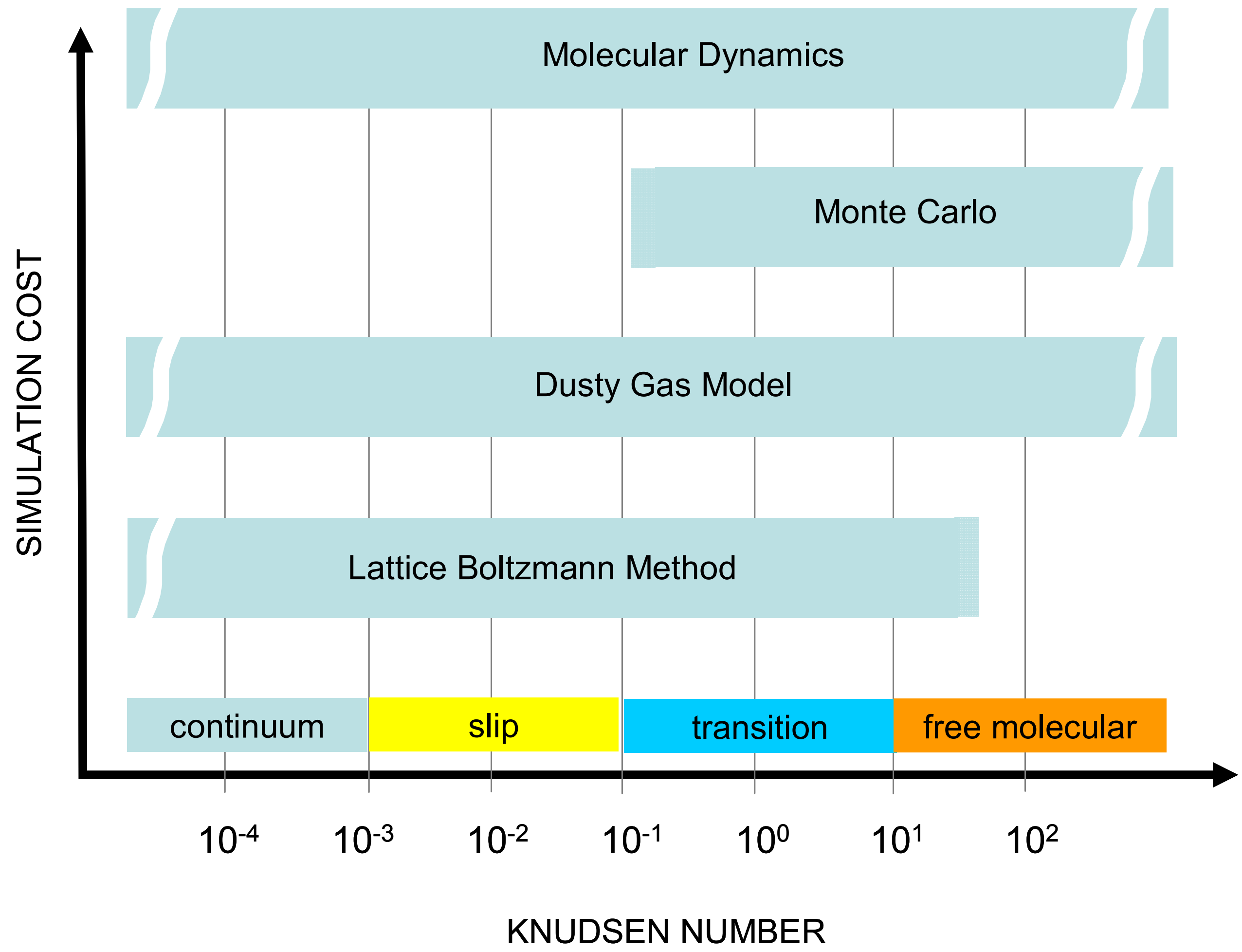
- Gas diffusion occurs at high temperature and through micron size pores. Continuum theory is no longer valid.
- Gas particles can get adsorbed on the solid material.
- Complex structure.





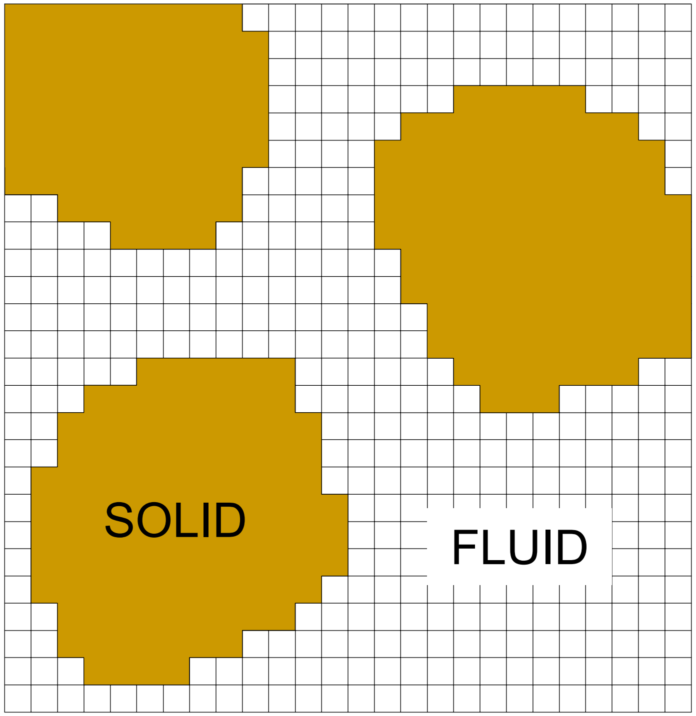
Chemical reactions among gas components need to be included for the case of internal reforming and at the TPB.

A Comparison of Modeling Approaches



Lattice Boltzmann Method (LBM)

- Historically derived from the lattice gas cellular automata
- LBM is a numerical approximation to the Boltzmann equation



- Multiple species
- Complex geometry
- Parallel algorithm
- Wall interactions
- Non-continuum regime

M.E. McCracken M. E. and J. Abraham, *Phys. Rev. E*, 71:046704. 2005.

Basic LBM Algorithm: Stream and Collide

$$n_{i,\mathbf{r}+\mathbf{e}_i}^{\sigma,\,n+1} = n_{i,\mathbf{r}}^{\sigma,\,n} - \Omega_{i,\mathbf{r}}^{\sigma,\,n}$$

new time level

species

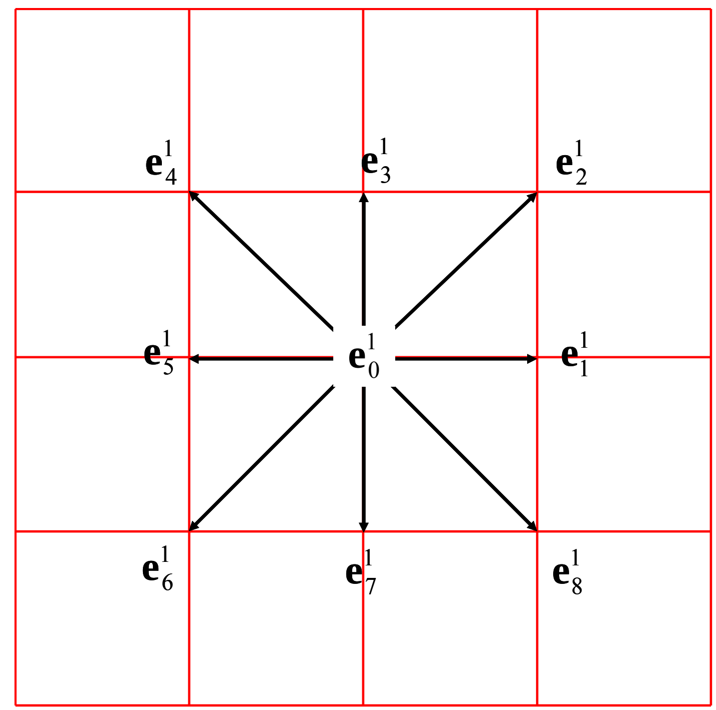
old time-level

discrete velocity

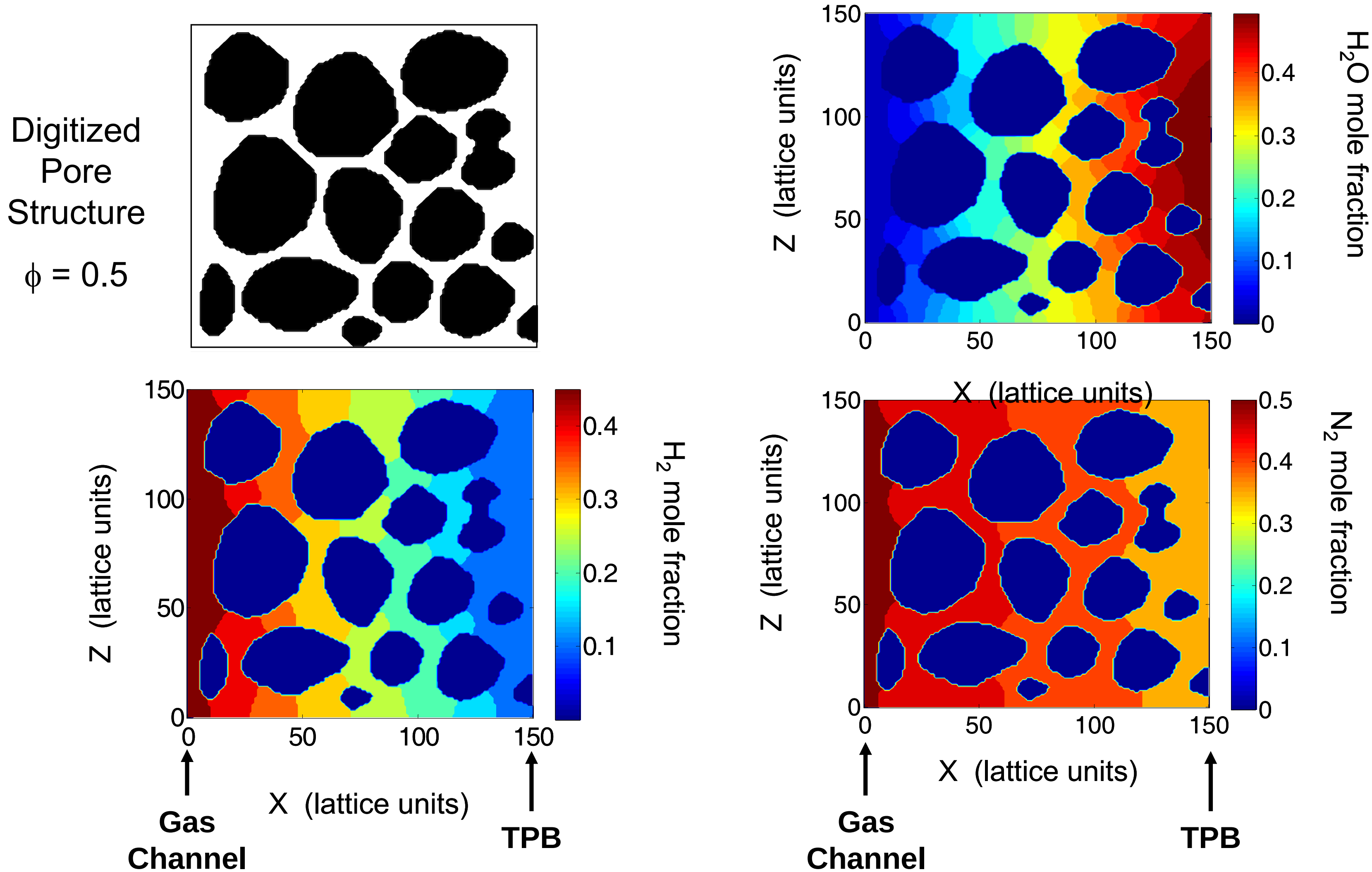
direction

velocity distribution function

BGK collision term



Multi-Component Gas Transport in a SOFC Anode



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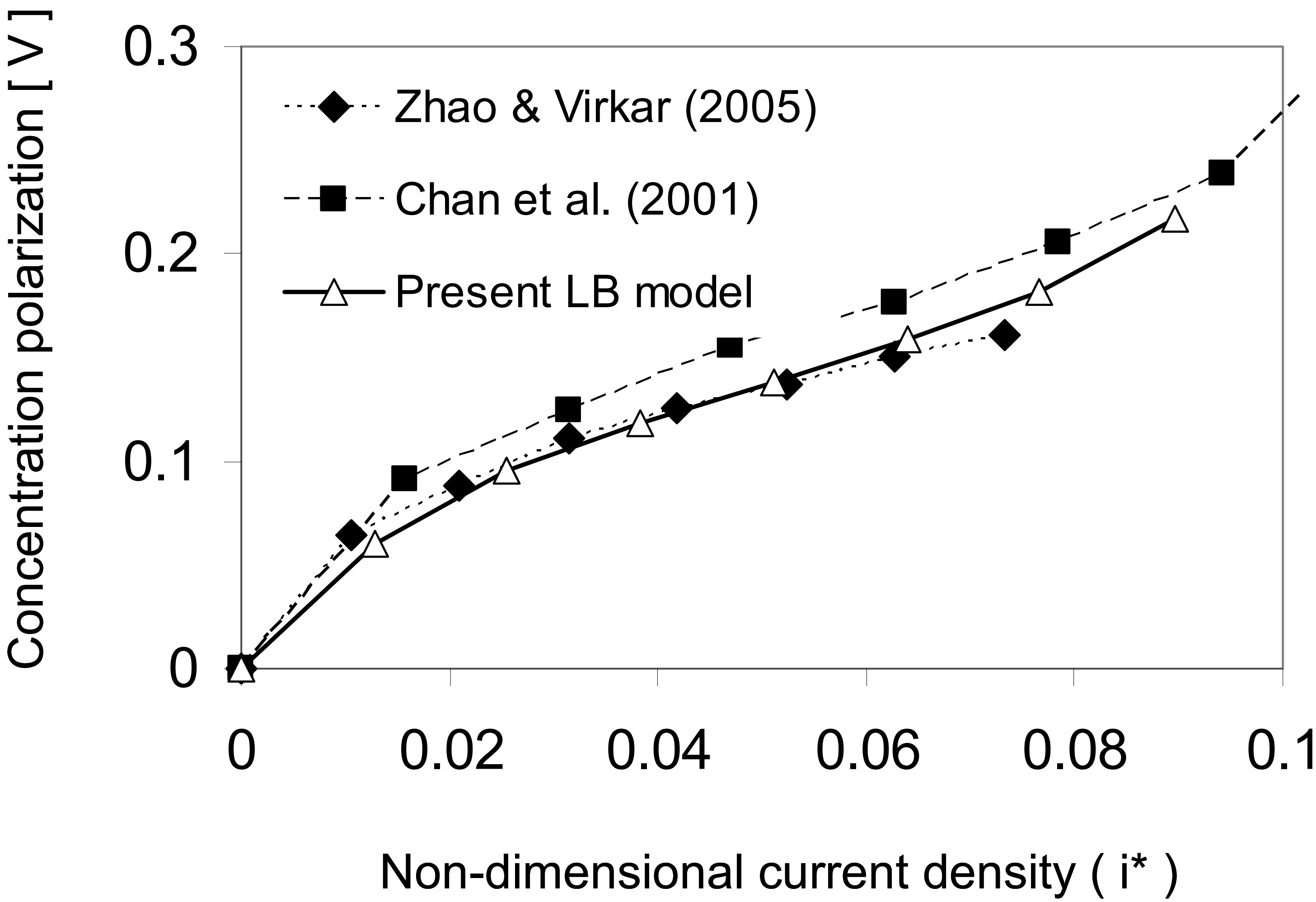
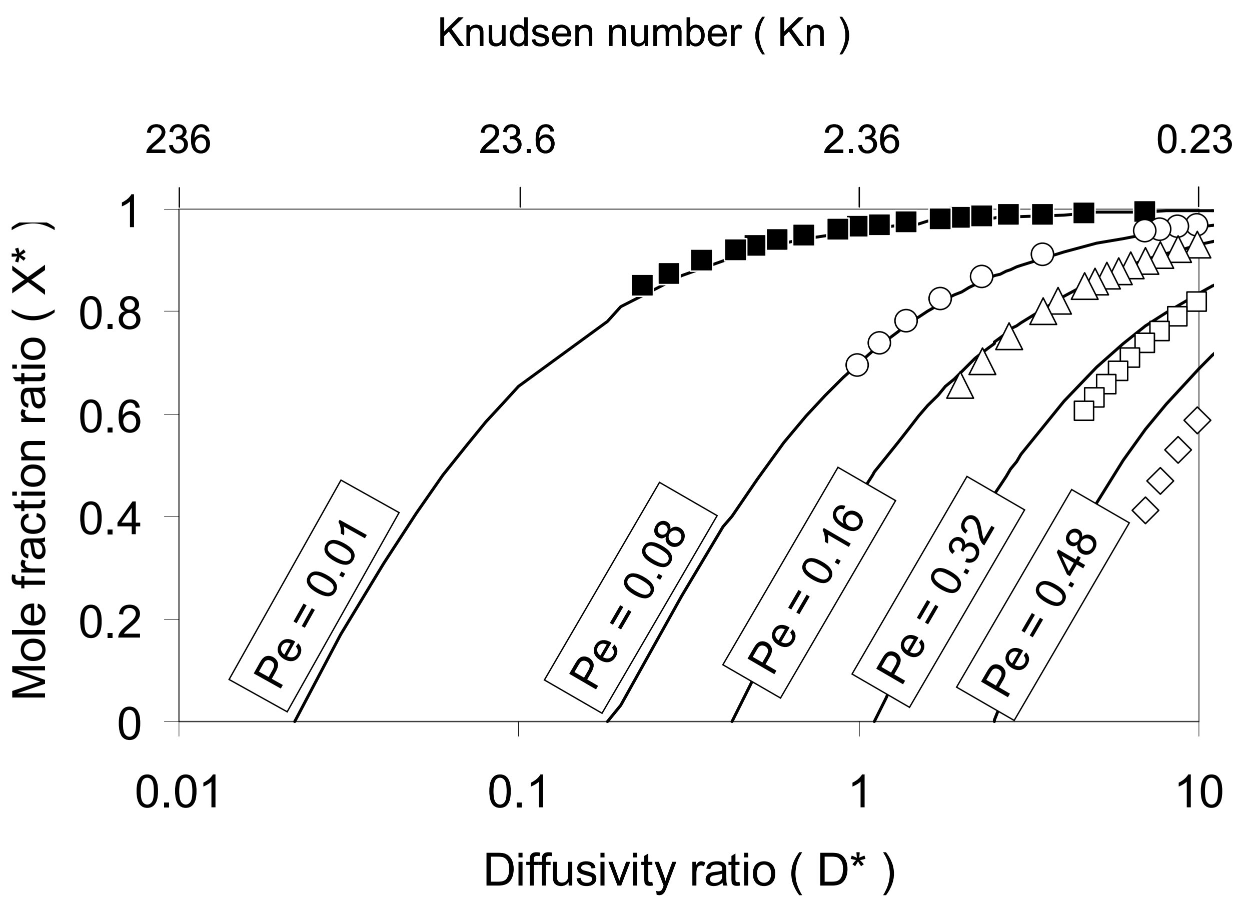
A.S. Joshi, W.K.S. Chiu, et al., *J. Power Sources*, accepted, 2006.
A.S. Joshi, W.K.S. Chiu, et al., 42nd Power Sources Conference, pp. 131-134, 2006.

LBM Validation



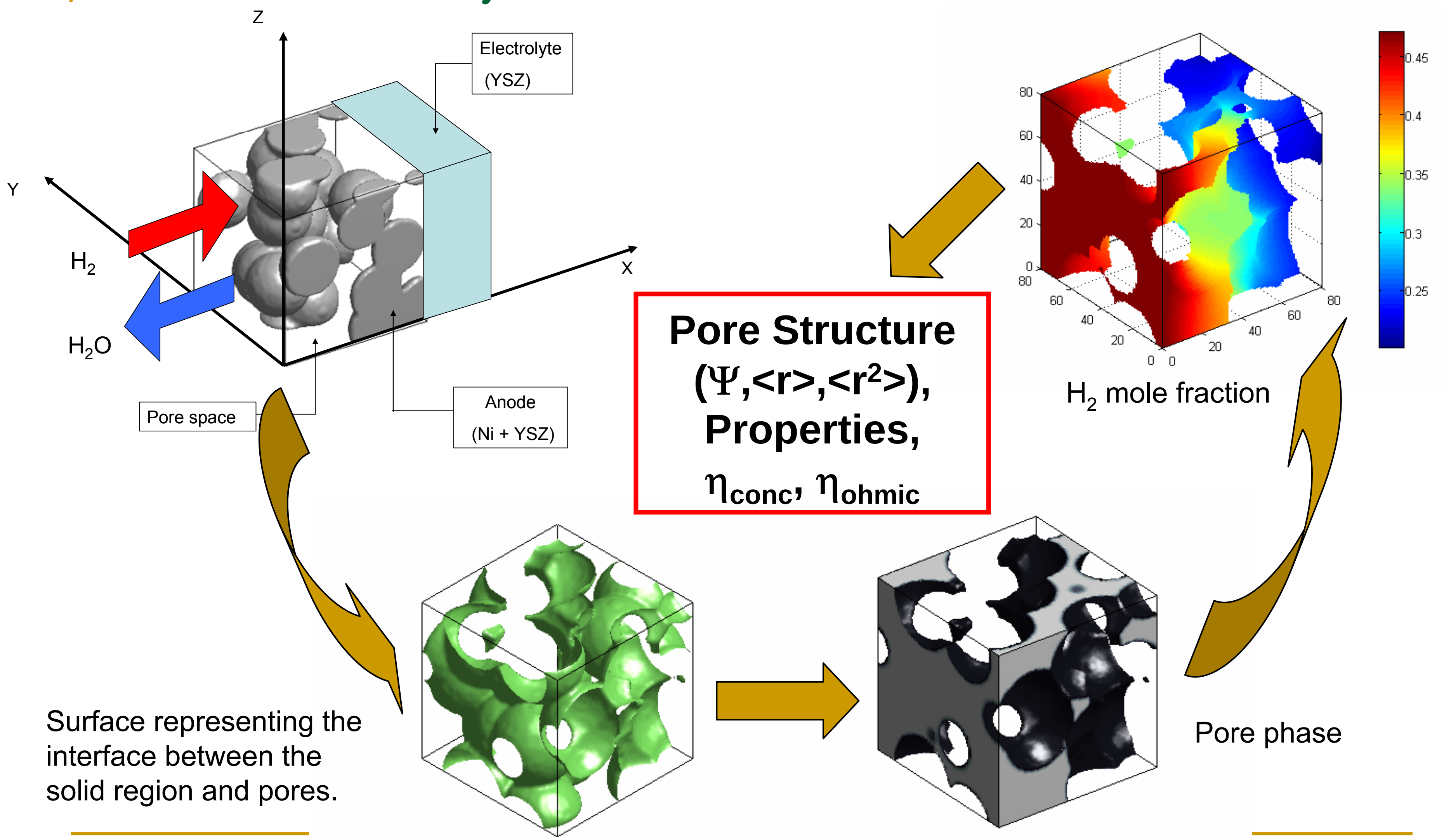
LBM Validation – cont'd.



LBM: data points **Dusty Gas**: solid lines

A.S. Joshi, W.K.S. Chiu, et al., ASME IMECE2006-13620, 2006.

3D LBM Analysis of a SOFC Anode



Electrochemical Reaction Kinetics in a SOFC Anode

Global Reaction: $H_2^g + O^{2-}_{electrolyte} \rightarrow H_2O^g + 2e^-_{Ni}$

$k_{+/-\#}$:	Reaction rate
S:	Surface vacancy
$X \bullet S$:	Surface species
$V_o^{\cdot\cdot}$:	Oxygen vacancies
O_o^x:	Oxygen ion

The Gauckler Reaction Mechanism:

$$H_2(g) + 2S \xleftrightarrow{k1,k-1} 2H \bullet S$$

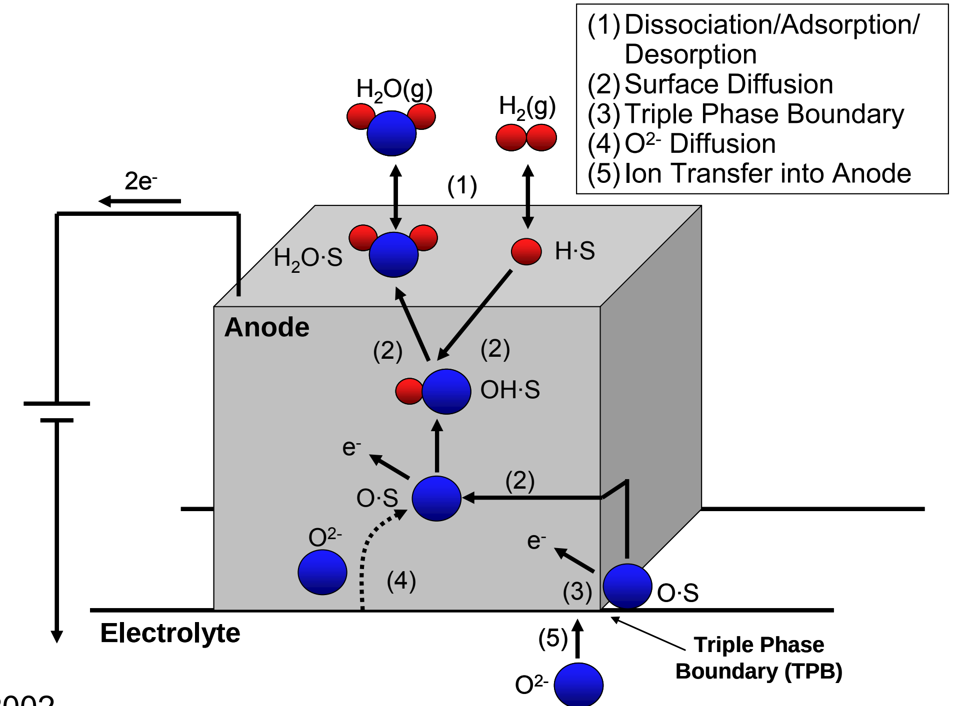
$$H_2O(g) + S \xleftrightarrow{k2,k-2} H_2O \bullet S$$

$$O \bullet S + H \bullet S \xleftrightarrow{k3,k-3} OH \bullet S + S$$

$$H_2O \bullet S + O \bullet S \xleftrightarrow{k4,k-4} 2OH \bullet S$$

$$H_2O \bullet S + S \xleftrightarrow{k5,k-5} OH \bullet S + H \bullet S$$

$$O_O^x + S \xleftrightarrow{k6,k-6} O \bullet S + V_O^{\cdot\cdot} + 2e^-_{Ni}$$



A. Bieberle and L.J. Gauckler, *Solid State Ionics.* **146:** 23-41, 2002.

Electrochemical Model Rate Equations

- Traditional analysis requires selection of single rate limiting step and equilibration
    - Langmuir-Hinshelwood type rate equation
- Approach breaks down when reaction mechanisms contain steps that occur at similar rates
- For proposed mechanism requires solution to set of (4) coupled non-linear, stiff differential-equations

$$\frac{\partial \theta_H}{\partial t} = \left(2k_1\theta_V^2 - 2k_{-1}\theta_H^2 - k_3\theta_H\theta_O + k_{-3}\theta_{OH}\theta_V + k_5\theta_{H_2O}\theta_V - k_{-5}\theta_{OH}\theta_H\right)$$

$$\frac{\partial \theta_{H_2O}}{\partial t} = \left(k_2\theta_V - k_{-2}\theta_{H_2O} + k_{-4}\theta_{OH}^2 - k_5\theta_{H_2O}\theta_V - k_{-5}\theta_{OH}\theta_H\right)$$

$$\frac{\partial \theta_{OH}}{\partial t} = \left(k_3\theta_H\theta_O - k_{-3}\theta_{OH}\theta_V + 2k_4\theta_{H_2O}\theta_O - 2k_{-4}\theta_{OH}^2 + k_5\theta_{H_2O}\theta_V - k_{-5}\theta_{OH}\theta_H\right)$$

$$\frac{\partial \theta_O}{\partial t} = \left(-k_3\theta_H\theta_O + k_{-3}\theta_{OH}\theta_V + -k_4\theta_{H_2O}\theta_O + k_{-4}\theta_{OH}^2 + k_6\theta_V + k_{-6}\theta_O\right)$$

$$1 = \theta_V + \theta_H + \theta_{OH} + \theta_{H_2O} + \theta_O$$

θ_i: Species Surface Coverage

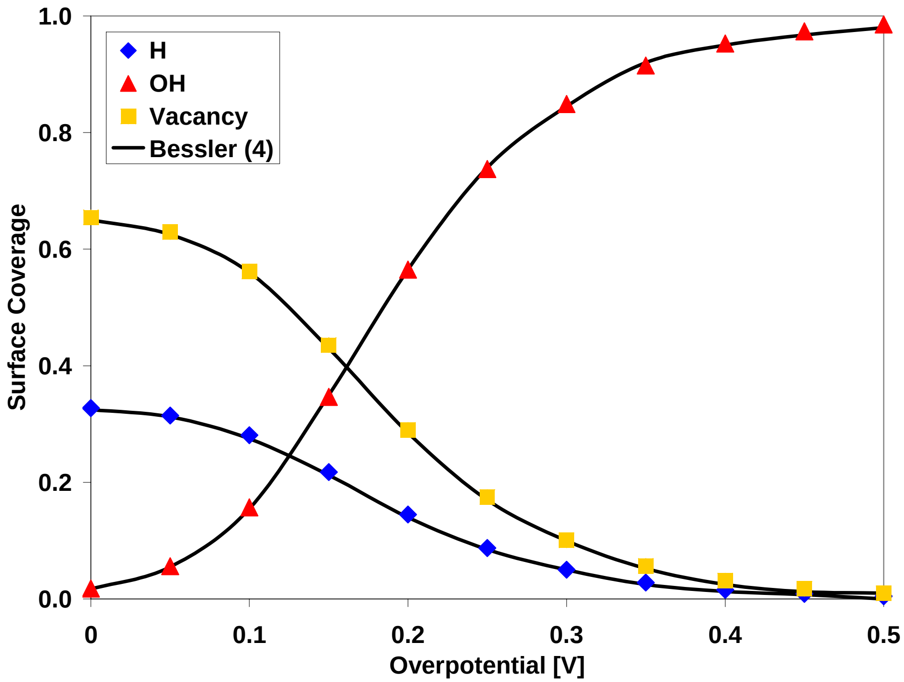
$$k_6 = k_6^o \cdot \exp\left(\beta \frac{2F}{RT}\eta\right)$$

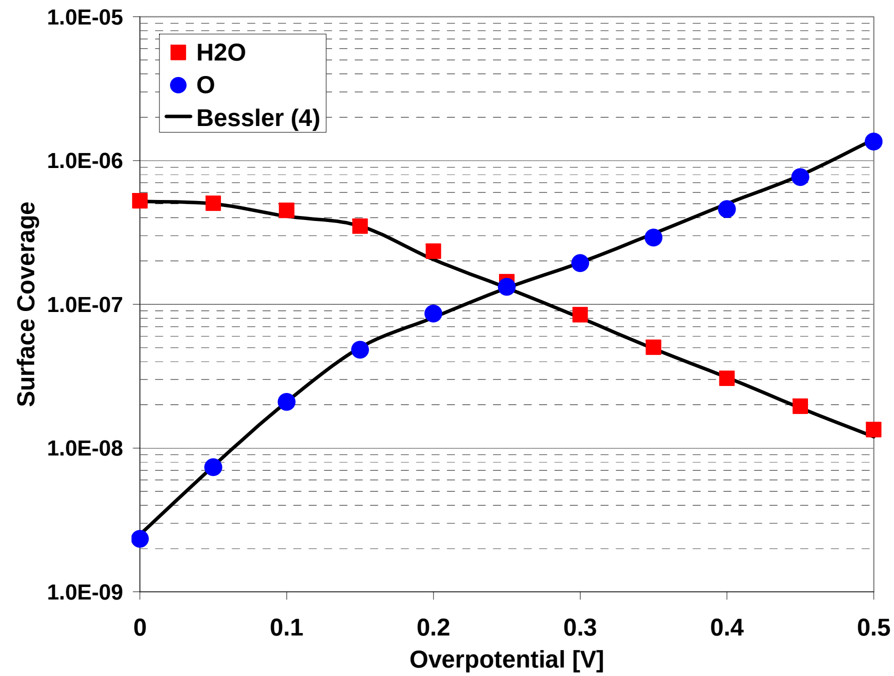
$$k_{-6} = k_{-6}^o \cdot \exp\left(\left(\beta - 1\right)\frac{2F}{RT}\eta\right)$$

$$i = 2F\frac{N_o}{N_A}\left(k_6\theta_V - k_{-6}\theta_O\right)$$

$$\vec{J} \bullet \vec{n} = \frac{i}{2F}$$

Validation of Reaction Kinetics Function





$$H_2^g + 2S \xleftrightarrow{k_1, k_{-1}} 2H \bullet S$$

$$H_2O^g + S \xleftrightarrow{k_2, k_{-2}} H_2O \bullet S$$

$$O \bullet S \xleftrightarrow{k_3, k_{-3}} OH \bullet S + S$$

W.G. Bessler, *Solid State Ionics* 176:997-1011, 2005.

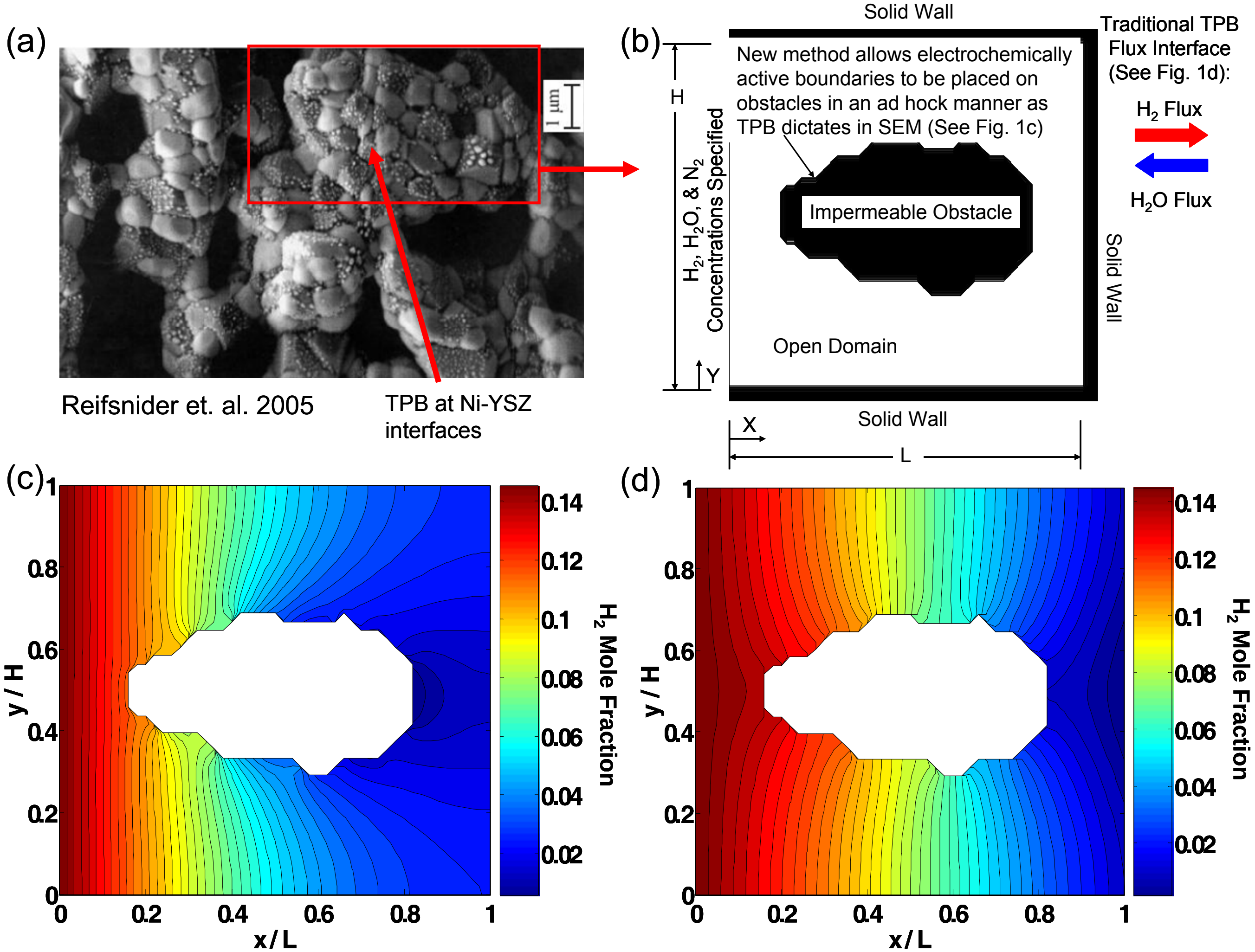
$$H_2O \bullet S + O \bullet S \xleftrightarrow{k_4, k_{-4}} 2OH \bullet S$$

$$H_2O \bullet S + S \xleftrightarrow{k_5, k_{-5}} OH \bullet S + H \bullet S$$

$$O_o^x + S \xleftrightarrow{k_6, k_{-6}} O \bullet S + V_o^{\cdot\cdot} + 2e_{NI}^-$$

K. N. Grew, W. K. S. Chiu, et al., ASME IMECE2006-13621, 2006.

Electrochemistry & Gas Transport in a SOFC Anode



$$\eta_{act}$$
$$k_{+/-\#}$$
$$\theta_i$$

K. N. Grew, W. K. S. Chiu, et al., ASME IMECE2006-13621, 2006.

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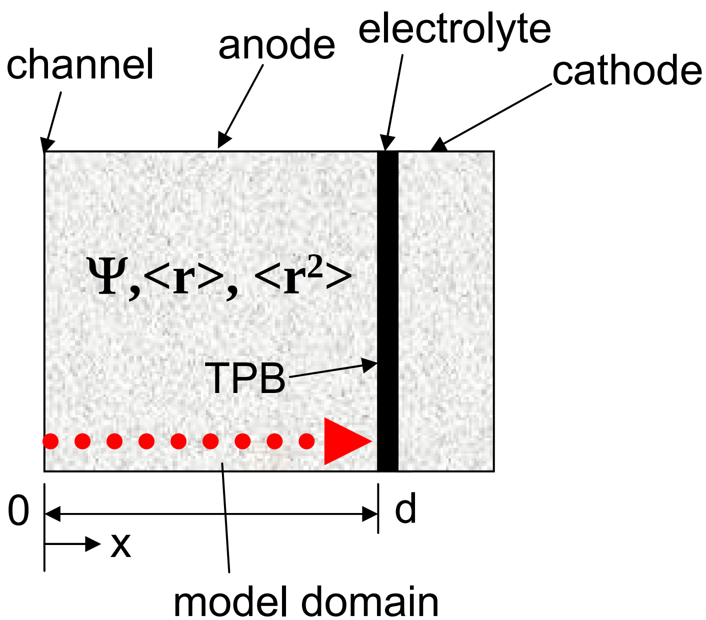
Electrode Microstructure

- Structure can be described by three parameters:

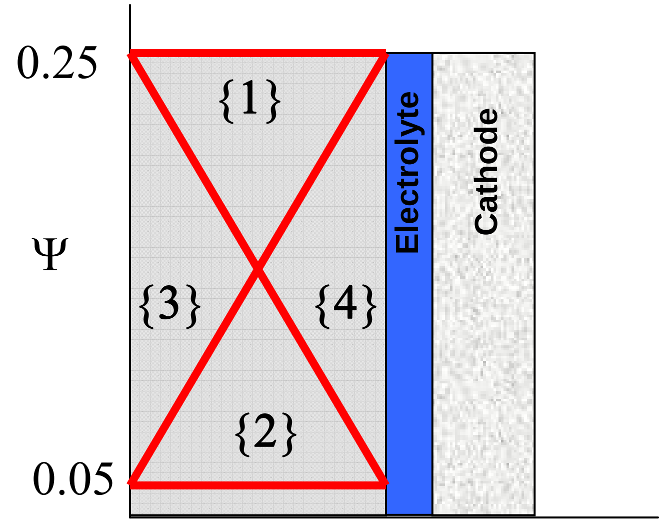


- Ψ – Structural Parameter (ε/τ)
  - Porosity: $0 \leq \varepsilon \leq 1$
  - Tortuosity: $\tau \geq 1$
  - ~10X as important upon performance as other parameters in conditions studied.
- $\langle r \rangle$ – Average pore radius
- $\langle r^2 \rangle$ – Pore radius distribution

Pore-Level Analysis $\Rightarrow$ Properties, η_{act}, η_{ohmic}, η_{conc}

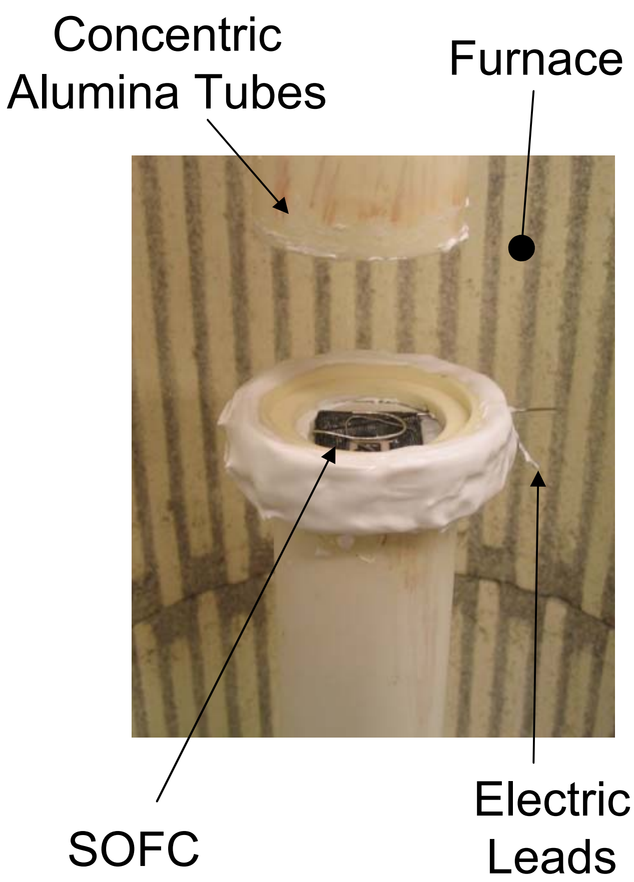
Effect of Grading Electrode Microstructure

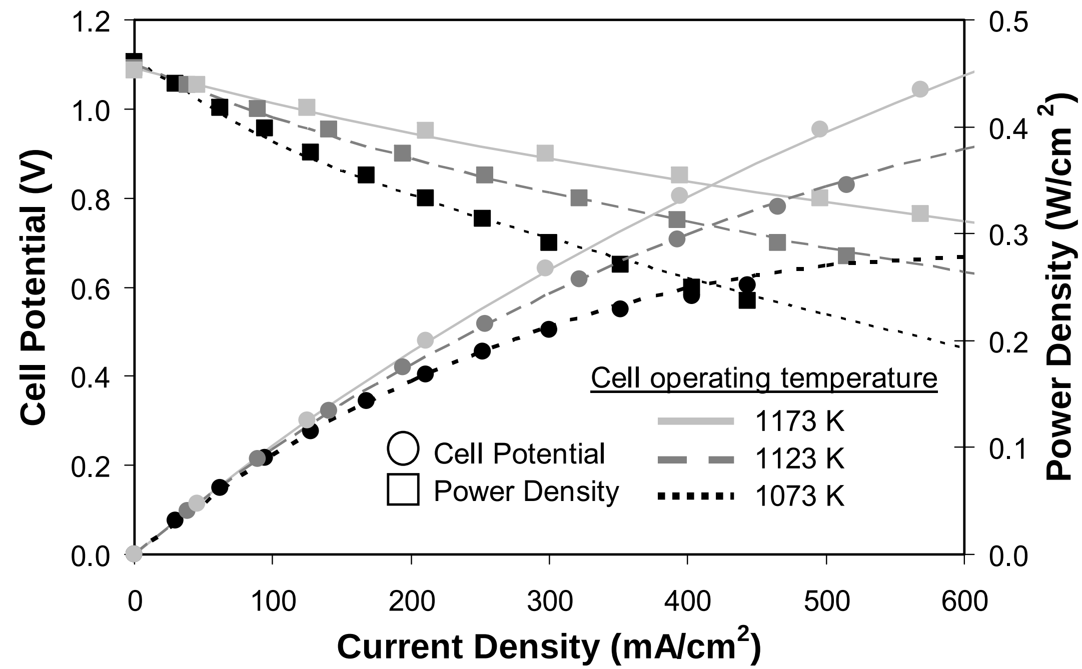
- Performance evaluated with alternative anode designs
  - Two fuel streams
    - Diluted hydrogen - Conditions near cell outlet
      - 10% H_2 – 3% H2O – balance inert gas
    - Partially reformed methane with internal reforming- Approx. cell inlet
      - 10% H_2 – 49% CH_4 – 30% H_2O – 6% CO – 5% CO_2



  - Four microstructure cases
    - {1} - Ψ is a constant high value of 0.25
    - {2} - Ψ is a constant low value of 0.05
    - {3} - Ψ is high at the TPB and low at the gas supply channel 0.25 -> 0.05
    - {4} - Ψ is low at the TPB and high at the gas supply channel 0.05 -> 0.25

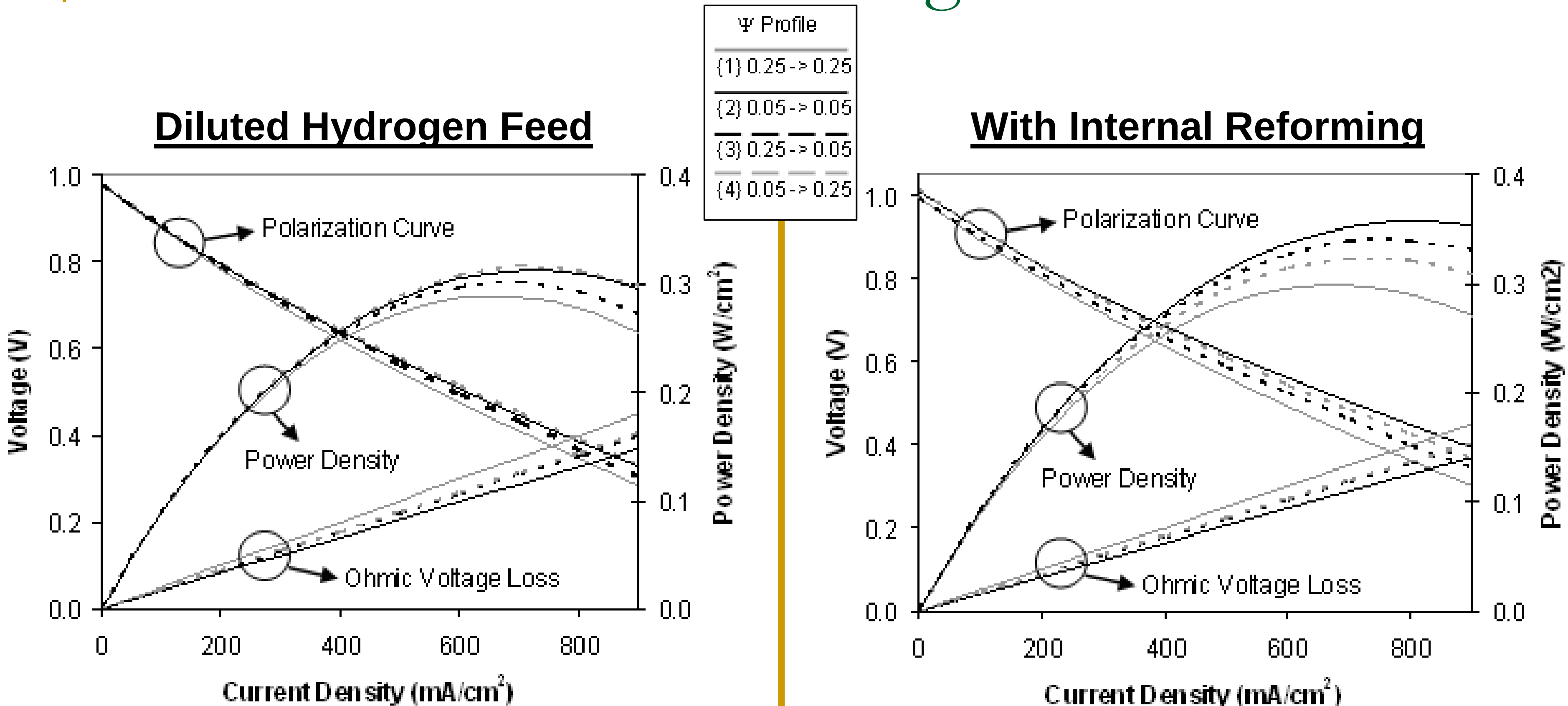
Model Validation by Experiments





E. S. Greene, W. K. S. Chiu, A. A. Burke and M. G. Medeiros, *42nd Power Sources Conference*, pp. 451-454, 2006.

Effect of Electrode Grading on Performance



E. S. Greene, W. K. S. Chiu and M. G. Medeiros, *J. Power Sources* 161:225-231, 2006.

SOFC Performance Correlations

$$Da = \frac{\tau_{diffusion}}{\tau_{reaction}} = \frac{R_{EC} d^2}{D_{H_2} C_{H_2}}$$

Curve Fits

Da ~ d$^{1.79}$

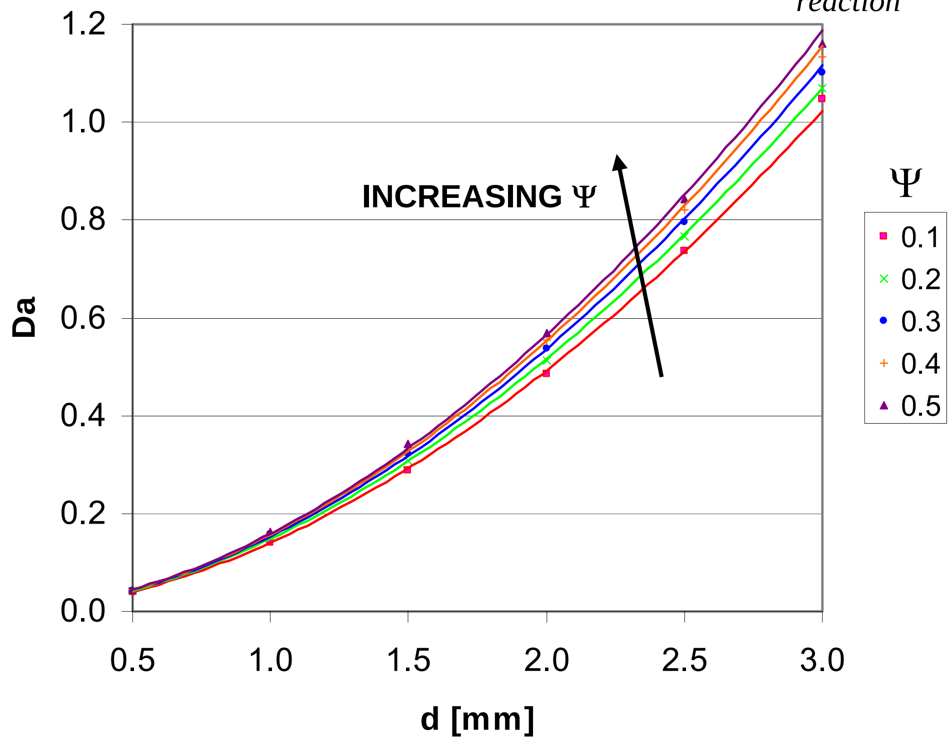
$R^2 = 0.999$

Da ~ $\Psi^{0.357}$

$R^2 = 0.998$

- **Displays prevalently kinetically limited characteristics (Da<1)**

- **Exponent of power law fits display larger sensitivity of Da to d than Ψ**



E.S. Greene, M.G. Medeiros and W.K.S. Chiu, *J. Fuel Cell Sci. Tech.* 2:136-140, 2005.

Conclusions

- SOFC is promising energy conversion device.
- Performance strongly dependent on electrode microstructure.
- Presented modeling/experimental approach to analyze and design SOFC electrodes.
- Optimized fuel cell electrodes can provide a durable high efficiency energy conversion technology for our society.

Acknowledgements

- Sponsors
  - Office of Naval Research
  - Army Research Office
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  - NexTech Materials
  - Xradia
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  - Andrew C. Lysaght
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