Electrochemical Input for SOFC Performance Modeling

Summary and Recommendations

Report to DOE/NETL
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by

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- Summary of a report in preparation

OBJECTIVES:

A. Review current literature on electrode kinetics in SOFC

B. Compile electrochemical data relevant for SOFC modeling

C. Recommend a modeling strategy for incorporating electrochemistry

POTENTIAL BALANCE

$$\Delta E = \Delta E^{eq} - jR_{\Omega} - \eta_N + \eta_P$$

ΔE = cell potential under load [V]

ΔE^{eq} = cell equilibrium potential [V]

j = current density [$A \cdot m^{-2}$]

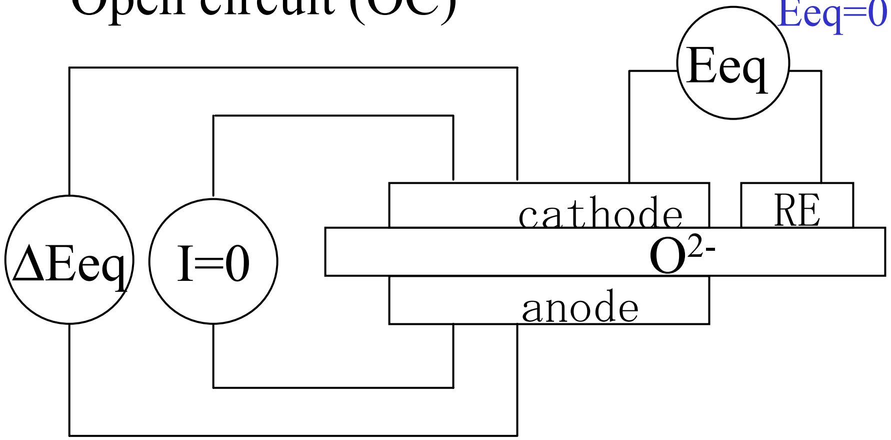
R_{Ω} = ohmic area-specific resistance [$ohm \cdot m^2$]

η_N = NE (or anode) polarization [V]

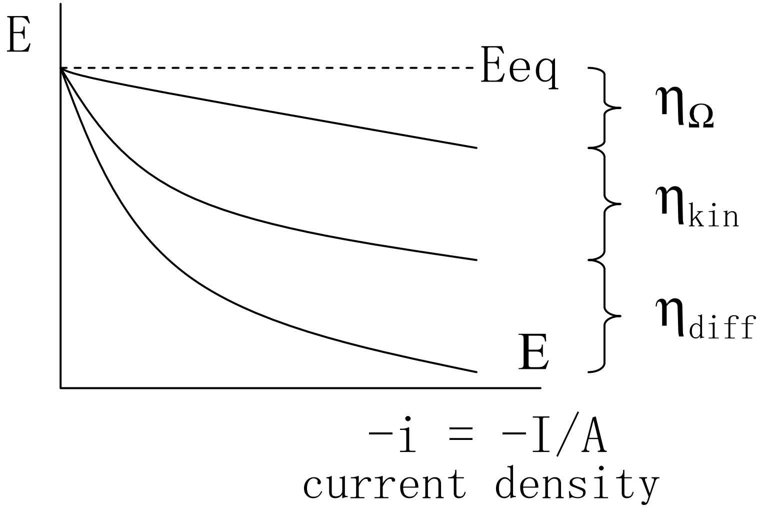
η_P = PE (or cathode) polarization [V]

3-electrode fuel cell

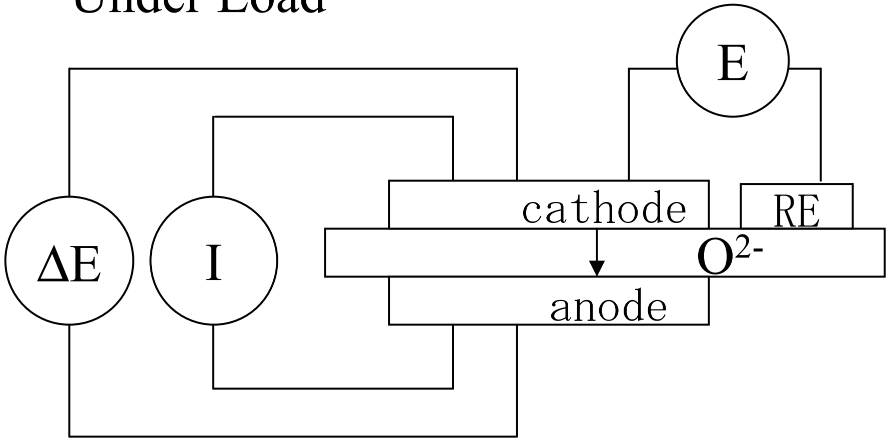
Open circuit (OC)



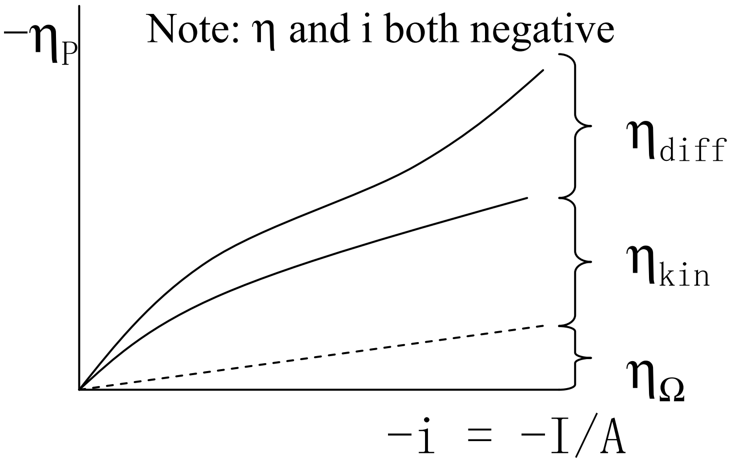
Eeq=0 at OC, if electrode and RE under same gas



Under Load



$E - E_{eq} = \eta =$ “polarization”


Note: η and i both negative

POLARIZATION OR OVERPOTENTIAL η

is the potential driving force for the reaction

- in anodic direction (current and overpotential both positive), or
- in cathodic direction (both negative)

For each electrode

$$\eta = E - E^{eq} \qquad [V]$$

It consists of three contributions:

$$\eta = \eta_{kin} + \eta_{dif} + \eta_{\Omega} \qquad [V]$$

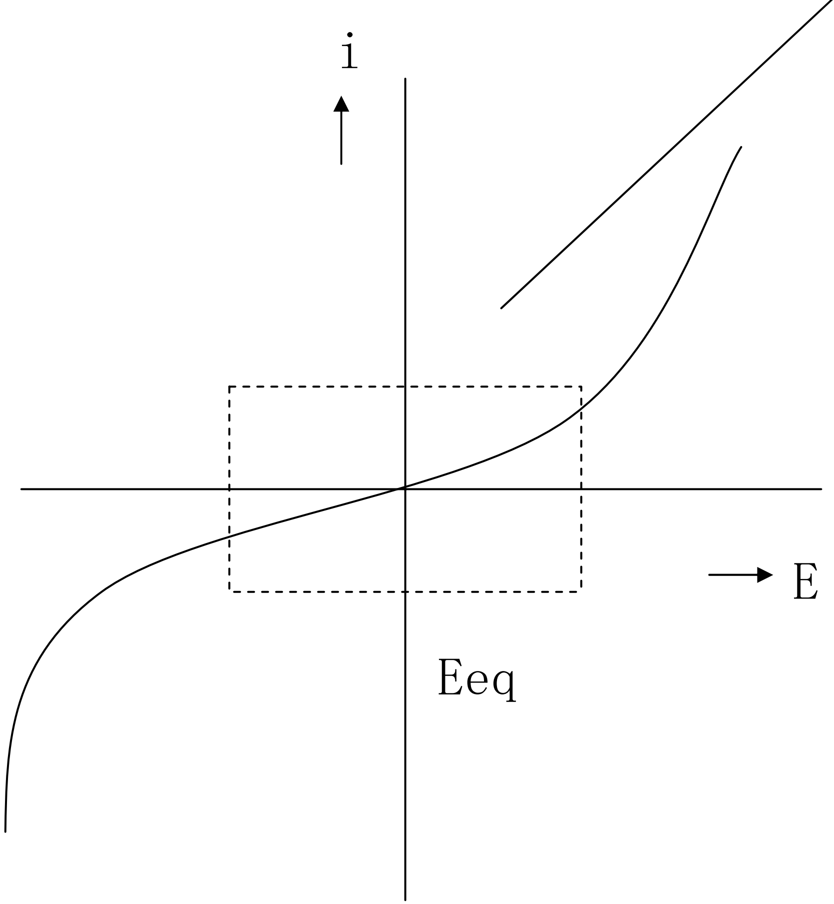
where η_{kin} = kinetic (surface) overpotential

η_{dif} = diffusion (mass transfer, concentration) overpotential

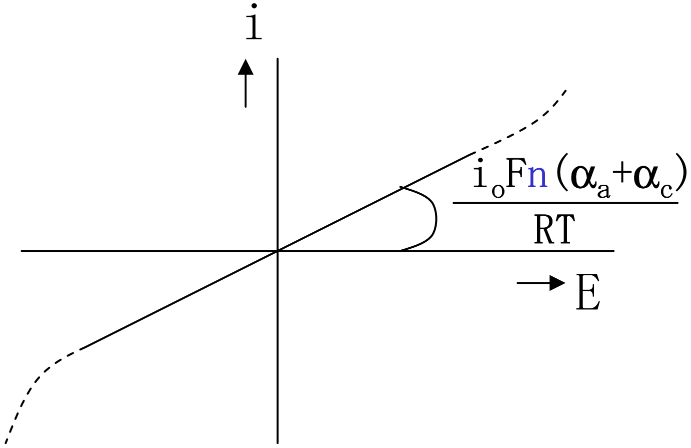
η_{Ω} = ohmic contribution to polarization

η_{kin} represents ELECTRODE KINETIC rate limitation

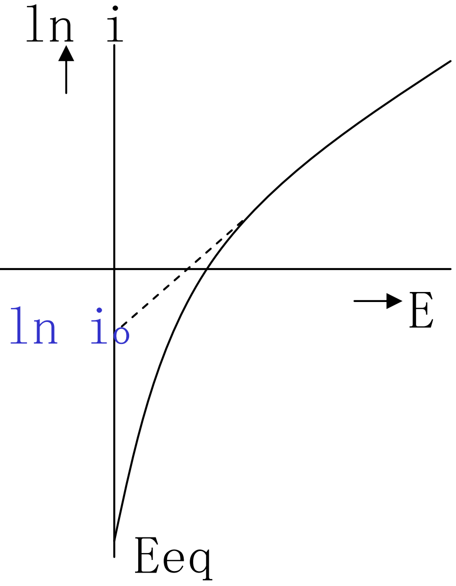
Butler-Volmer equation



Linear equation



Tafel equation (anodic branch)



η_{dif} represents **diffusion (or concentration) polarization**

- due to diffusion (or mass-transfer) resistance

In fuel cell electrodes this resistance is usually understood to be

- *gas-phase diffusion* resistance

But it might include

- *surface diffusion* resistance (of adsorbed electro-active species such as H, OH^-, etc , assumed to participate in the electrode reaction

However, surface diffusion resistance is not easy to distinguish from kinetic resistance

OVERPOTENTIAL

- is actually a *local quantity* (for each point on the electrode/electrolyte interface)
- usually varies from point to point in the depth of a fuel cell porous electrode
- due to non-uniform current distribution
- consequently, local overpotential is difficult to measure

Experimentally, we measure:

POLARIZATION, i.e.,

potential (vs RE) at current tab of an electrode, under load,

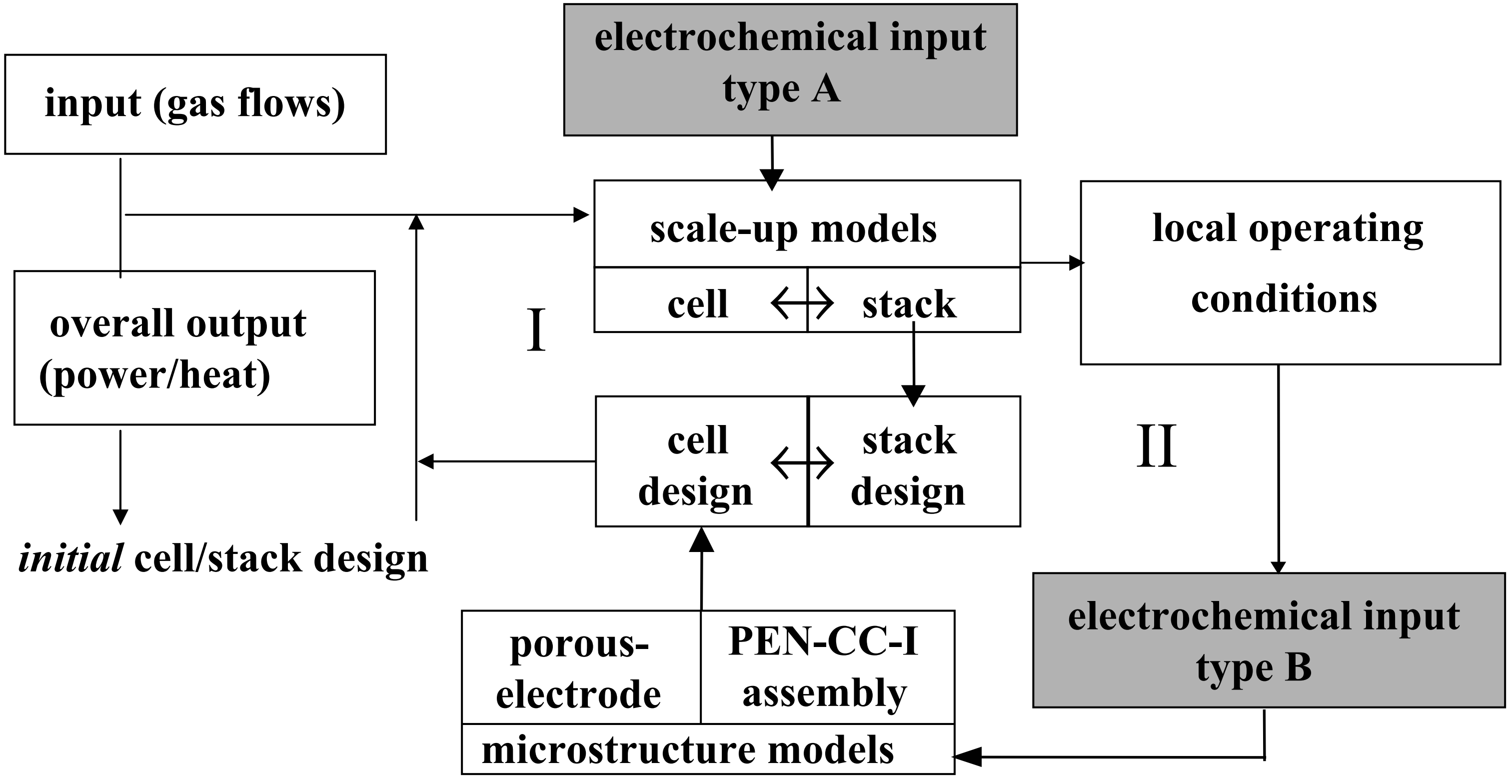
minus

potential (vs same RE) at same current tab, under equilibrium condition (open circuit)

NOTE: *polarization of a fuel cell electrode = sum of*

- *distributed overpotential and*
- *distributed IR-drop*

Flow sheet for SOFC design/performance modeling showing electrochemical input



input (gas flows)

electrochemical input type A

scale-up models

cell ↔ stack

local operating conditions

overall output (power/heat)

I

cell design ↔ stack design

II

***initial* cell/stack design**

porous-electrode

PEN-CC-I assembly

microstructure models

electrochemical input type B

Design process starts from the left and proceeds through cell+stack iteration I, then electrode+cell iteration II within iteration I (if greater accuracy is needed)

This design flowsheet suggests two types of

electrochemical input needed for SOFC modeling

Type A. Input for scale-up modeling of cells and stacks

* *need not be detailed*, mechanistically
* must apply over a range of relevant operating conditions—and correlate i-E behavior with gas composition, temperature, pressure
* may be material/structure specific (and perhaps "laboratory-specific")
* range of validity restricted by application targeted

Type B. Input for modeling electrode performance as f (microstructure)

* may need to contain kinetic (mechanistic) and diffusion details
* may be needed only over certain range of composition and temperature (***depending on feedback from scale-up model***!)
* has a larger "generic content"

Part I. ELECTRODE-KINETICS OF SOFC ELECTRODES

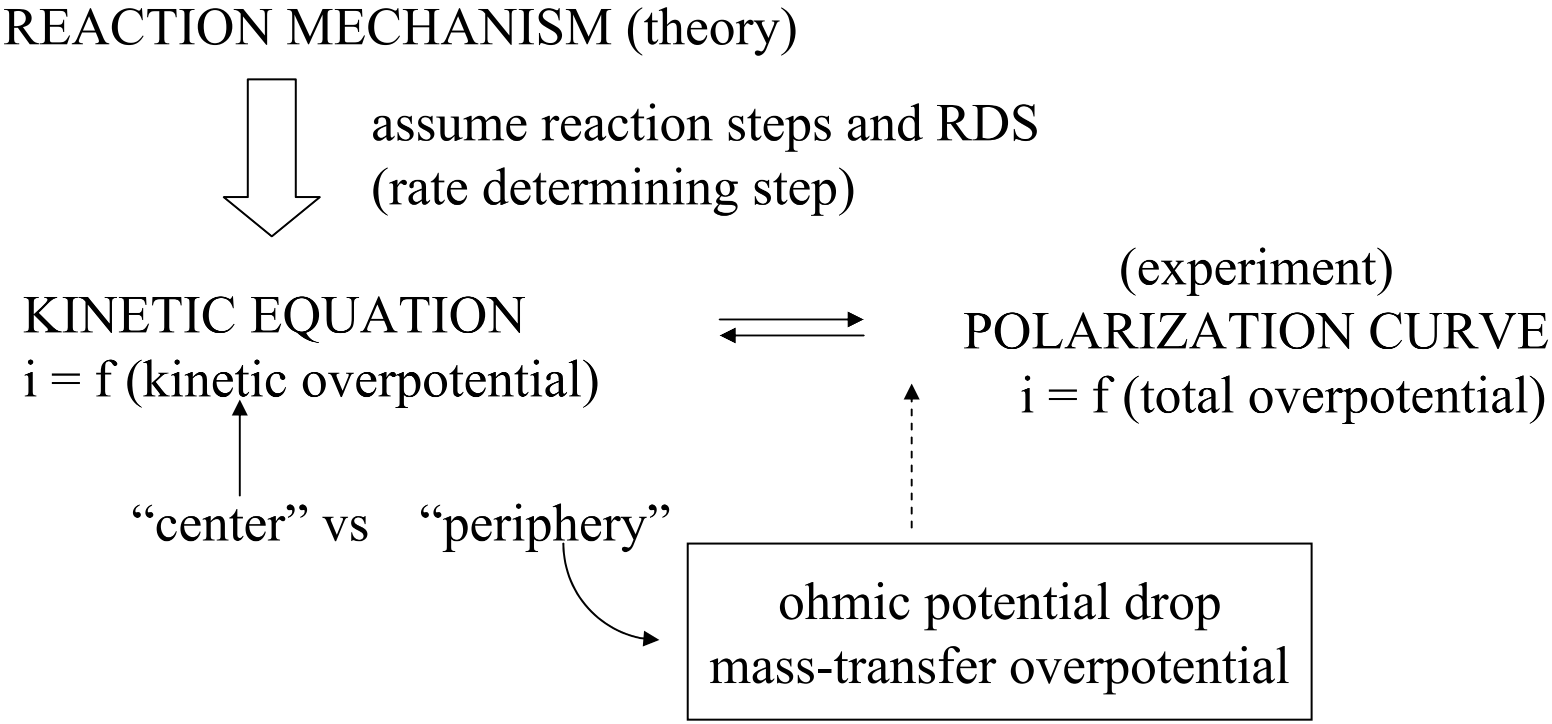
- several hundred references compiled
- key papers identified and reviewed
- divided into 2 distinct periods

1980 – 1995	classical approach
1995 – present	pragmatic approach • emphasizing microstructure

First period – classical approach

- Attempt separation of kinetics/mass transfer/ohmic resistance using reference electrode
- Use of “ideal” electrode materials (Pt, Ni)
- Expression of results in
    - Butler-Volmer formalism
    - reaction mechanism

RELATIONSHIP OF REACTION MECHANISM TO EXPERIMENTAL DATA



REACTION MECHANISM (theory)

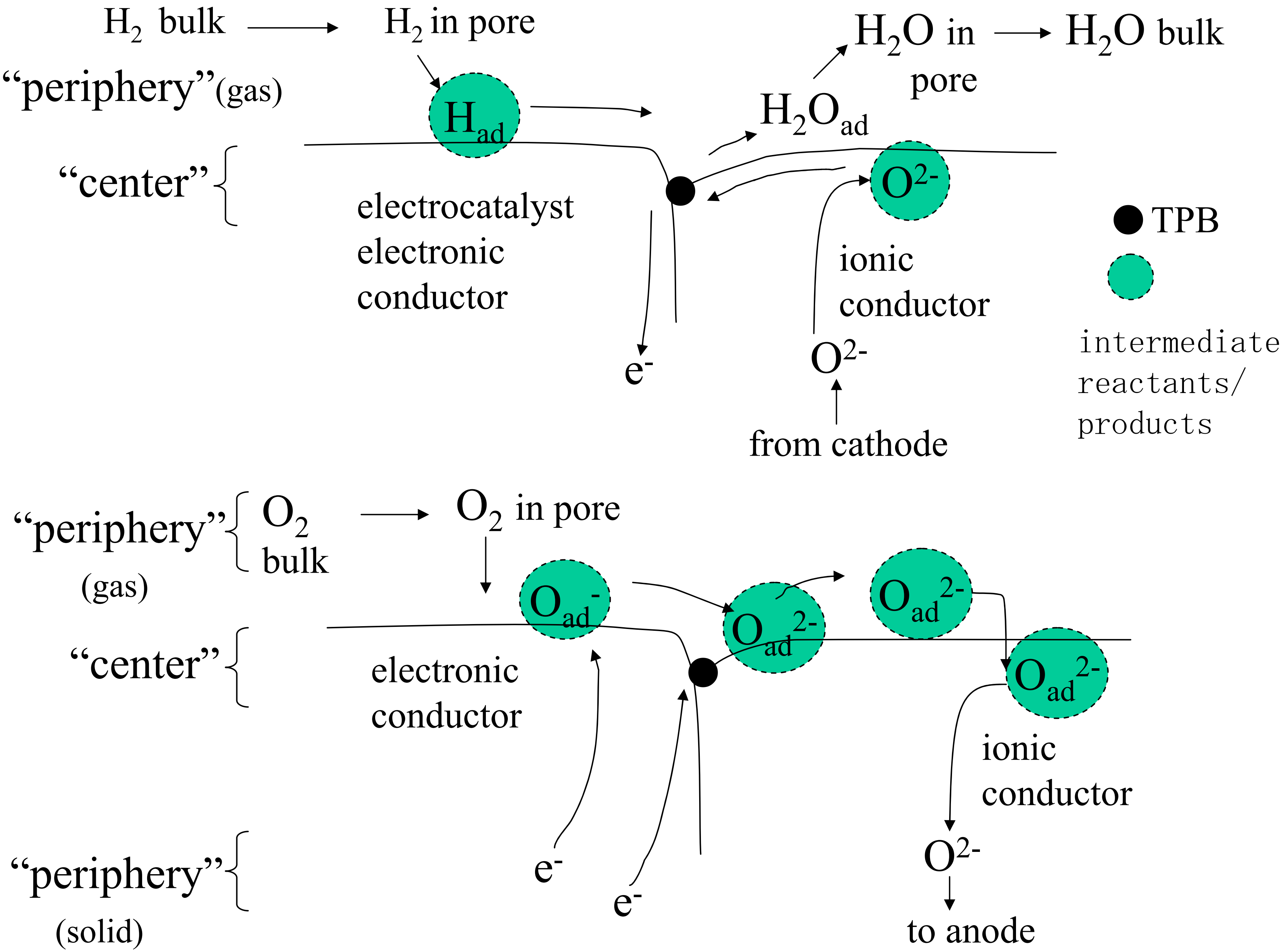
assume reaction steps and RDS
(rate determining step)

KINETIC EQUATION
i = f (kinetic overpotential)

(experiment)
POLARIZATION CURVE
i = f (total overpotential)

“center” vs “periphery”

ohmic potential drop
mass-transfer overpotential



H_2 bulk → H_2 in pore

H_2O in pore → H_2O bulk

"periphery"(gas)

H_{ad}

H_2O_{ad}

"center"

O^{2-}

electrocatalyst electronic conductor

ionic conductor

e^-

O^{2-}

from cathode

● TPB

🟩 intermediate reactants/ products

"periphery" O_2 bulk → O_2 in pore

(gas)

O_{ad}^{-}

O_{ad}^{2-}

O_{ad}^{2-}

"center"

electronic conductor

O_{ad}^{2-}

ionic conductor

"periphery"

(solid)

e^-

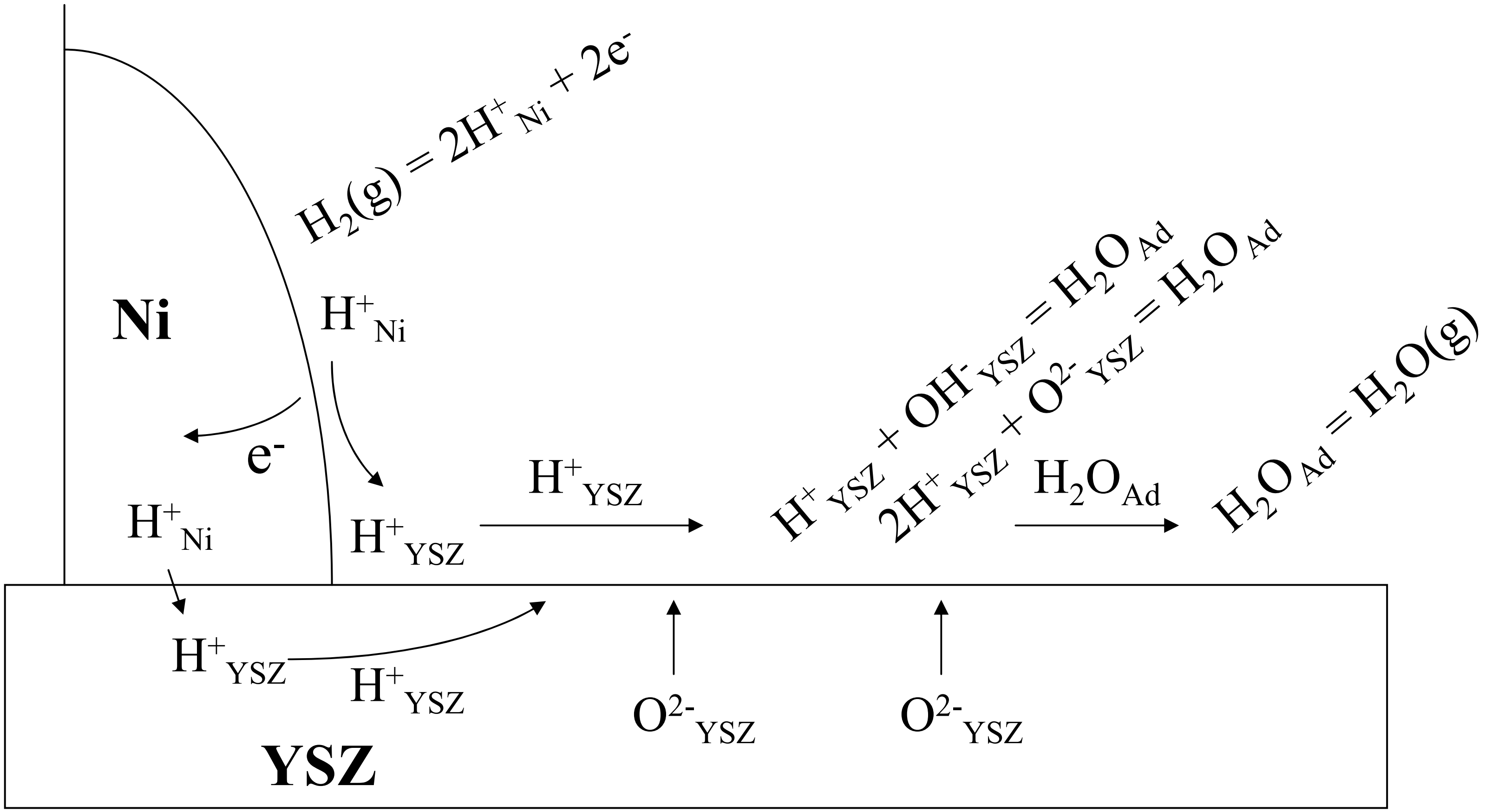
e^-

O^{2-}

to anode

First period – main focus

- **reaction site** : in principle three-phase-boundary (TPB),
  but
  in practice TPB plus adjacent (reaction + diffusion) zone
- possible **reaction pathways**
- appropriate **geometry of test cell** and location of reference electrode (RE)
    - distortion of measurements by inaccurate RE placement
    - non-uniform gas access
    - necessity of small utilization fuel, air



$H_2(g) = 2H^+_{Ni} + 2e^-$

Ni

H^+_{Ni}

e^-

H^+_{YSZ}

H^+_{YSZ}

H^+_{Ni}

H^+_{YSZ}

H^+_{YSZ}

$H^+_{YSZ} + OH^-_{YSZ} = H_2O_{Ad}$

$2H^+_{YSZ} + O^{2-}_{YSZ} = H_2O_{Ad}$

H_2O_{Ad}

$H_2O_{Ad} = H_2O(g)$

O^{2-}_{YSZ}

O^{2-}_{YSZ}

YSZ

Competing reaction paths and transport steps which may occur on the YSZ surface
(from Primdahl, et al.)

First period – conclusions

- kinetics of both H_2 oxidation and O_2 reduction are relatively fast compared to gas phase mass transfer (at least in small test cells)
- surface diffusion, though fast, may determine kinetics

- linear current-overpotential curves expected (RT/F = 60-100 mV) but often not obtained (Tafel slopes reported)
- polarization behavior varies strongly depending on microstructure
- range of i_o values reported → may be due to large variations in l_{TPB} as well as surface diffusion distance
- time-dependence of kinetics (hysteresis at short times, ageing effect at long times)
- contradictory reaction mechanisms adopted by different researchers

All this points to

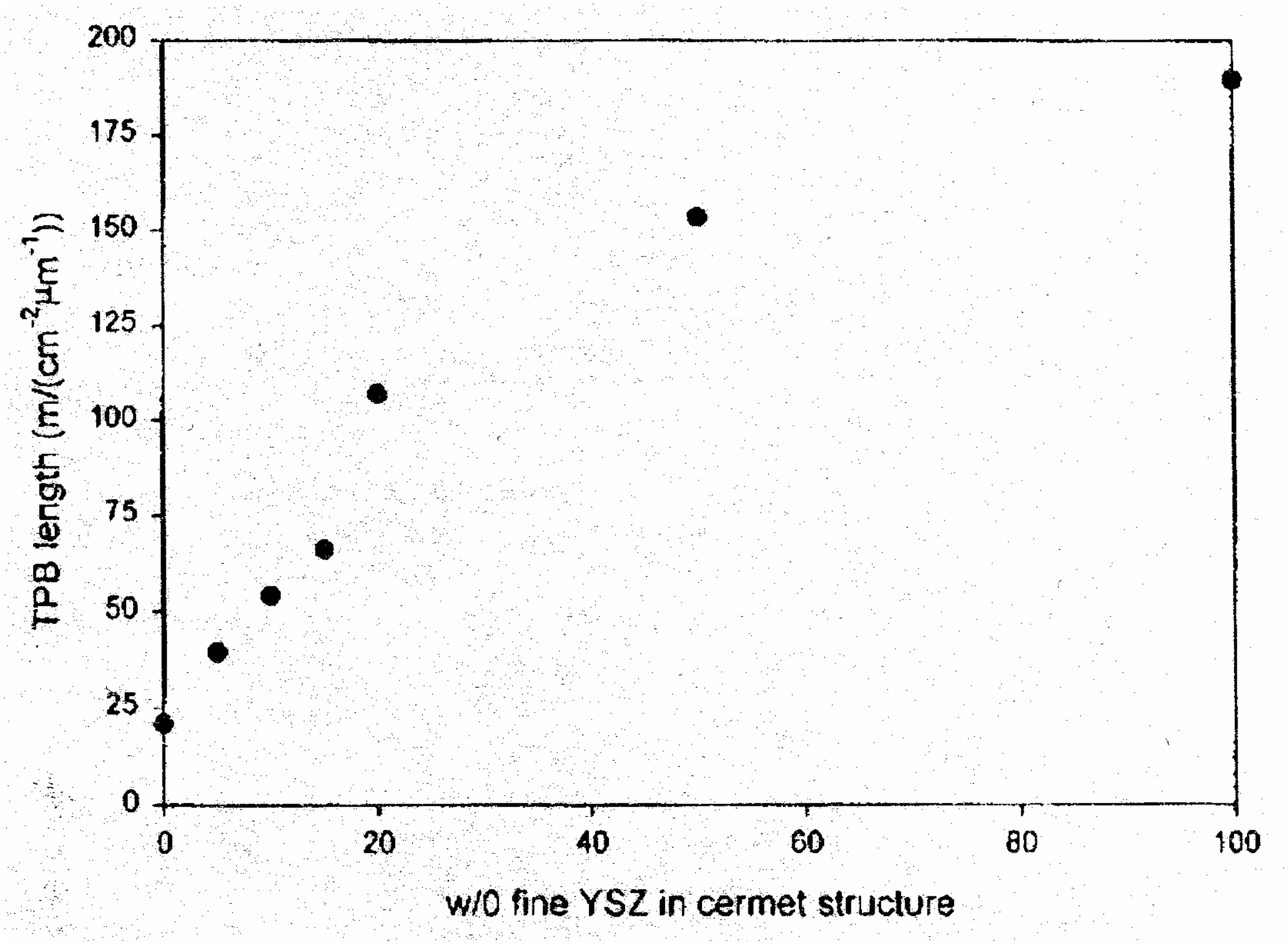
- need for a standardized test cell geometry
- lack of control in microstructure fabrication
- effect of variable operation history.

Second period – main focus

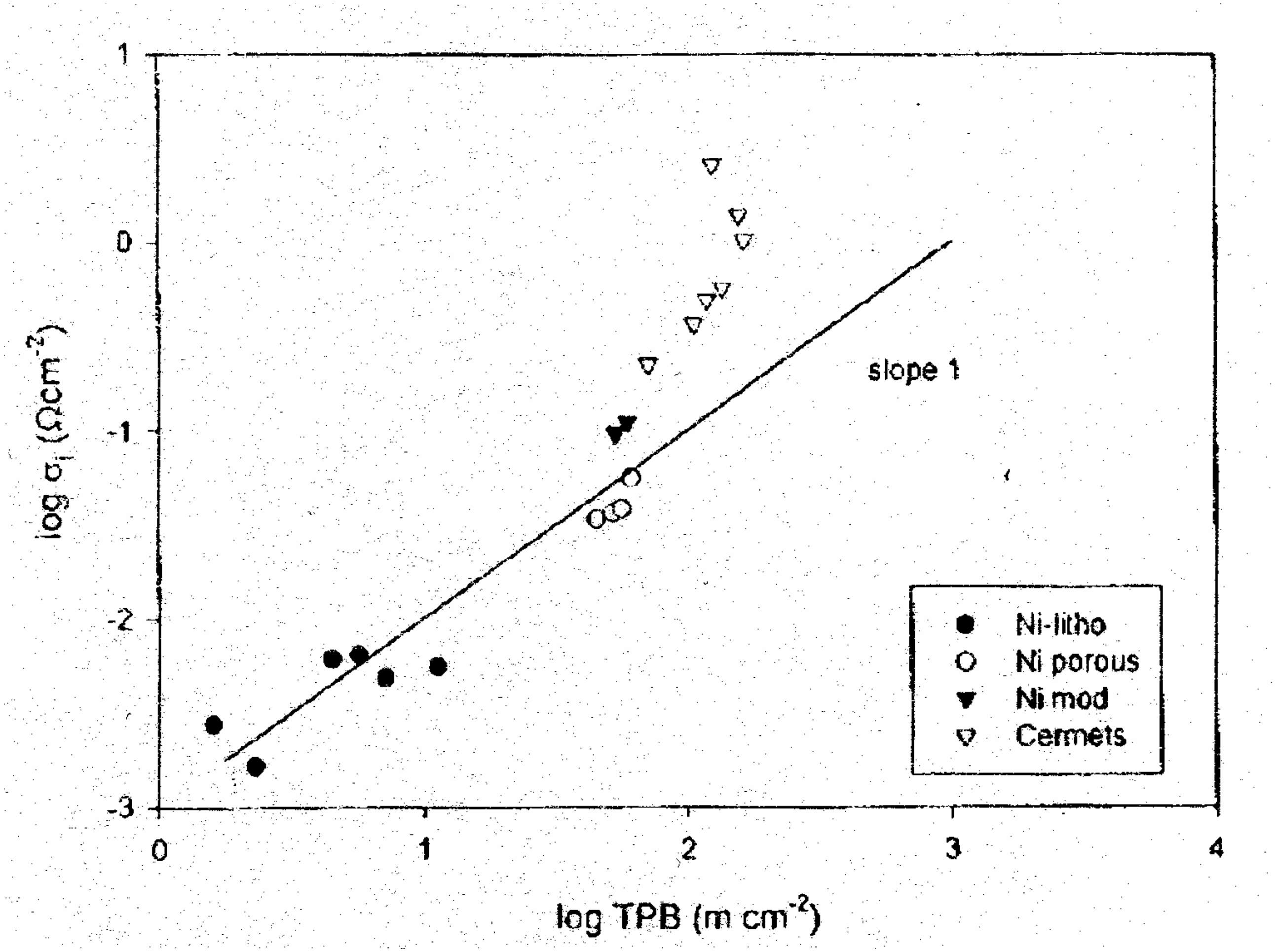
- extensive and systematic studies of microstructure effect on kinetics (de Boer, Primdahl and Mogensen, Jorgensen and Mogensen, Bieberle and Gauckler, Mitterdorfer and Gauckler, van Heuveln)

- adoption of standard test cells
  - thin-electrolyte cells (RE placement sensitive)
  - thick-electrolyte cells (ohmic resistance dominant)

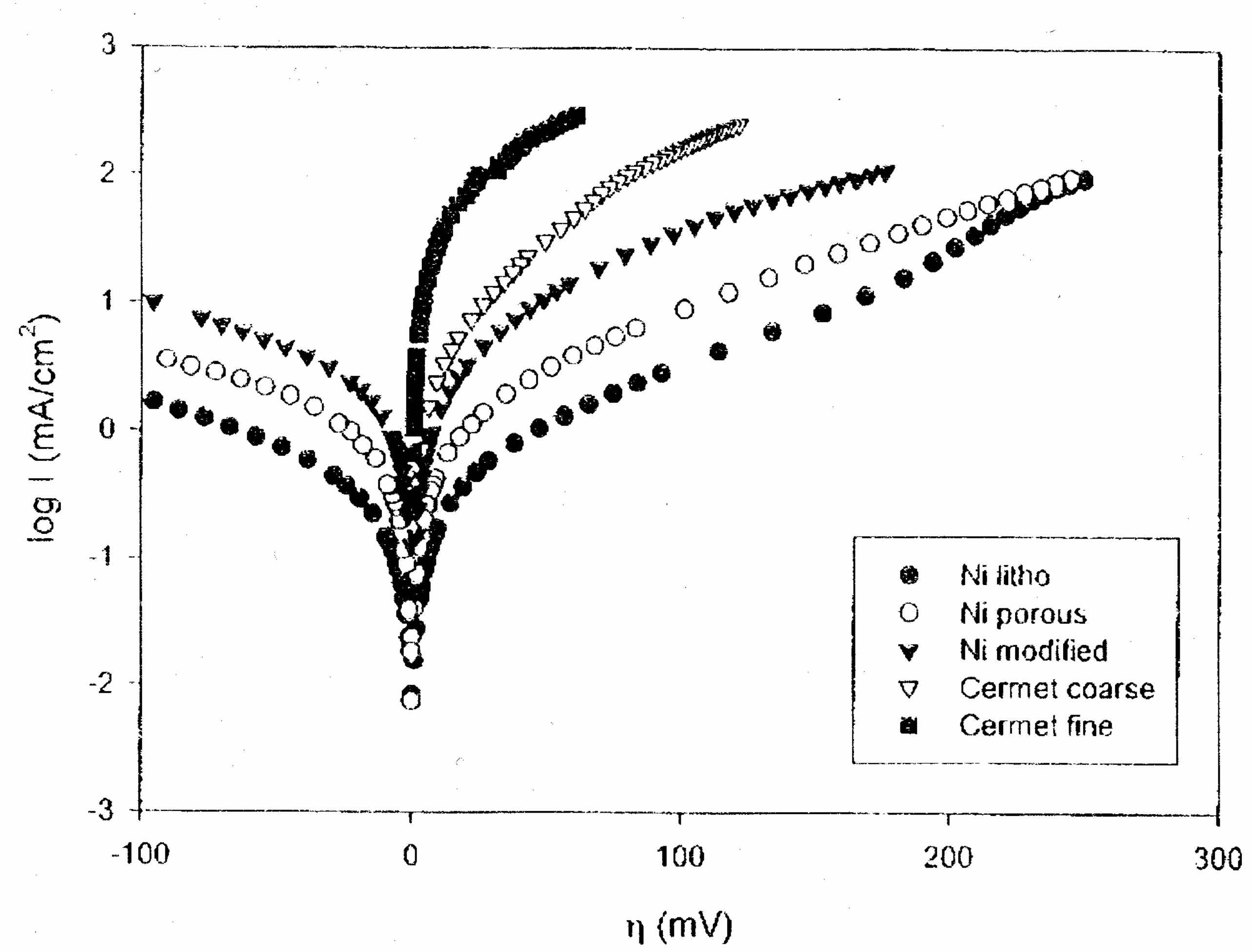
- AC impedance analysis preferred, as non-intrusive technique



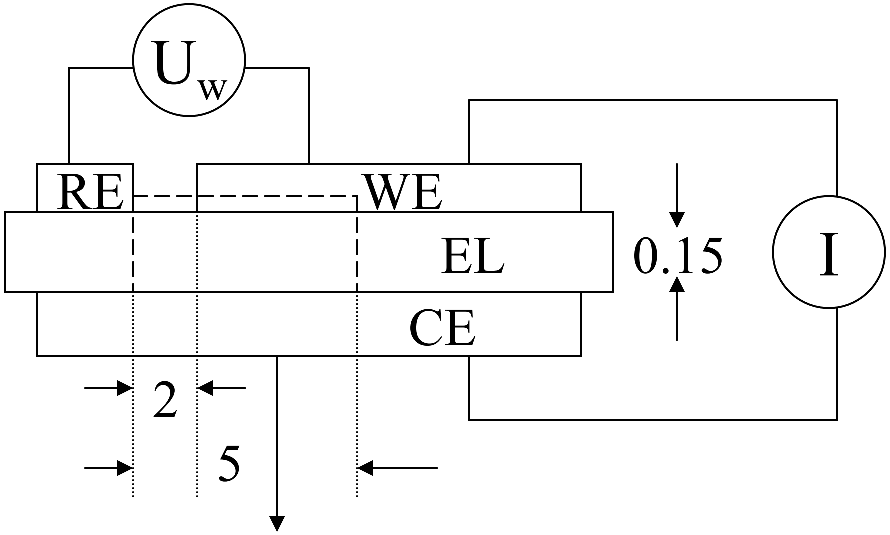
TPB length ($m \cdot cm^{-2} \mu m^{-1}$) as function of w/0 fine YSZ in the cermet structures (from de Boer, et al.)



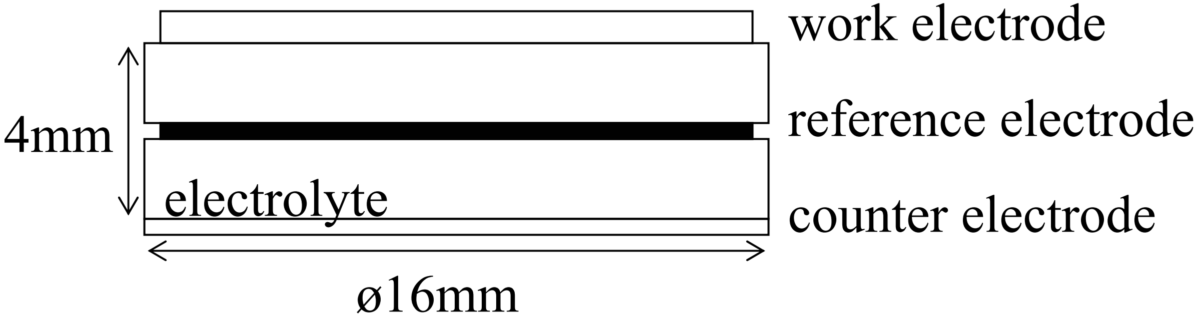
Total electrode conductance for different type of anodes
as function of the measured nickel perimeter
(from de Boer, et al.)



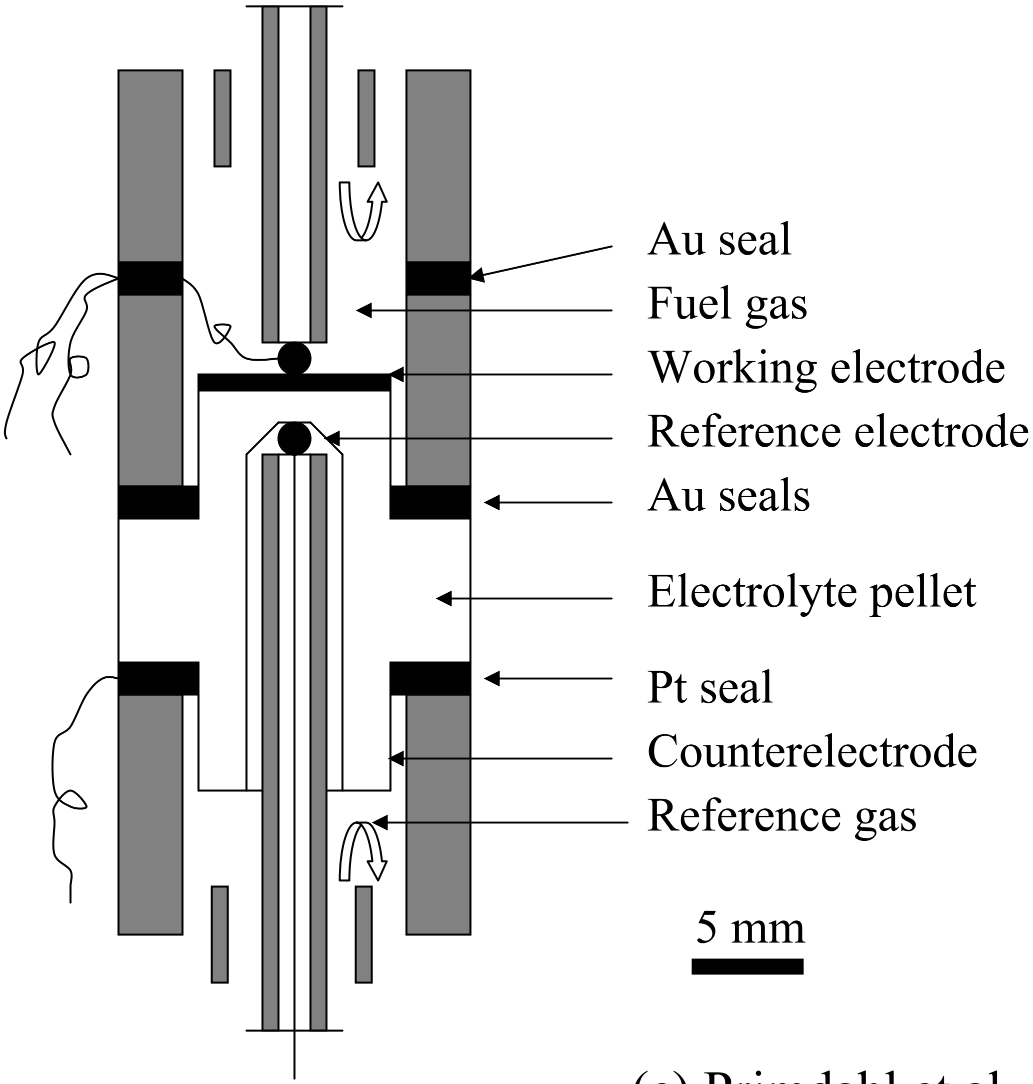
Tafel plots as measured for different anodes under standard conditions (from de Boer, et al.)



(a) van Heuveln et al. (ECN)
Bieberle (TUZ)



(b) de Boer et al. (TUTwenthe)



Au seal

Fuel gas

Working electrode

Reference electrode

Au seals

Electrolyte pellet

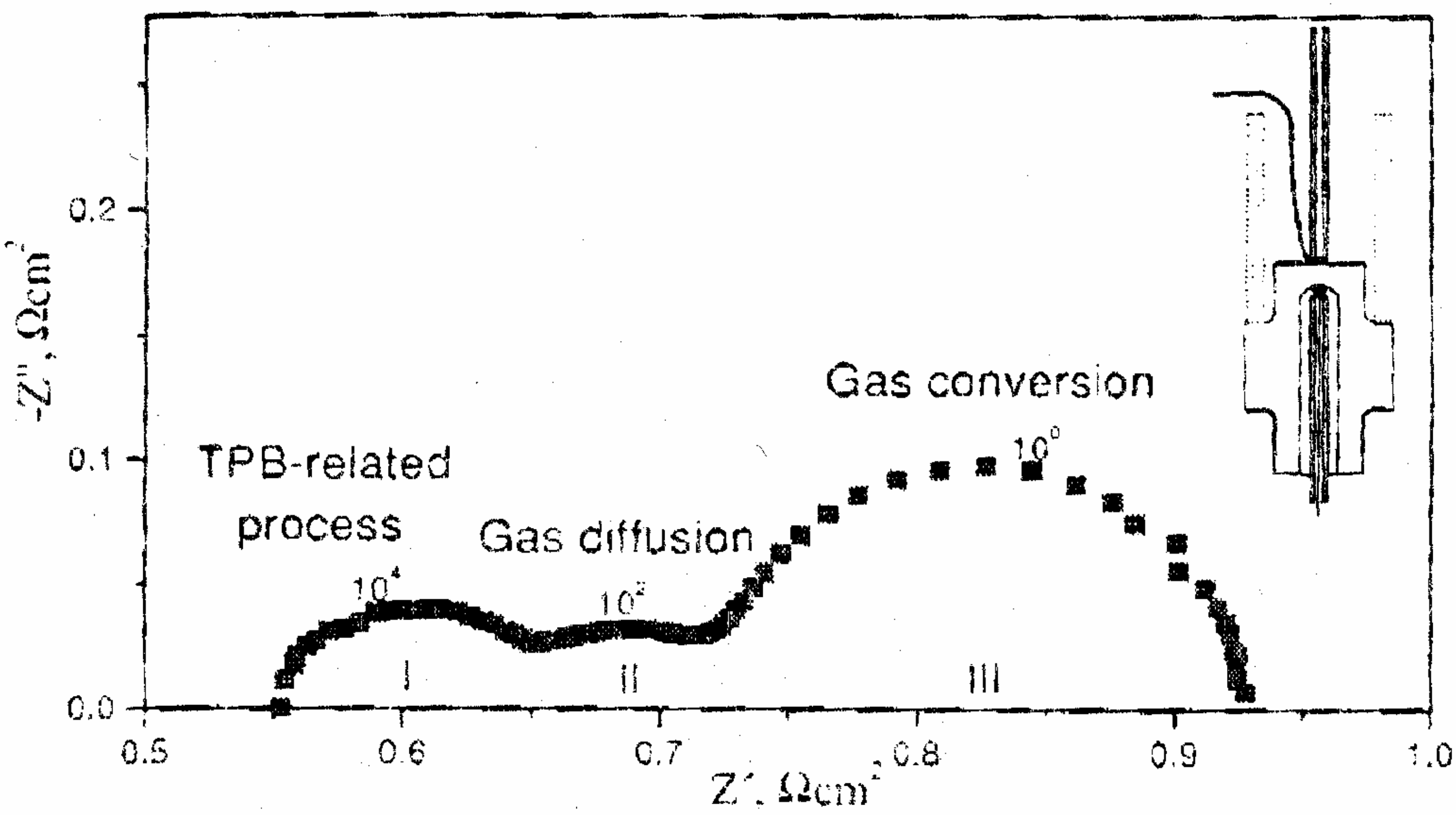
Pt seal

Counterelectrode

Reference gas

5 mm

(c) Primdahl et al. (Risoe)



Impedance spectrum for a Ni/YSZ cermet anode at 1000°C in hydrogen with 3% water at open circuit potential (From Primdahl, et al.)

Second period – conclusions

- AC impedance characteristics show typically 3 semi-circles (some depressed)

- At both anode and cathode the high-frequency resistance R_1 is kinetic in origin, and related to l_{TPB}

- The relationship to l_{TPB} (if known) is <u>not</u> reproducible from one cell to the next → microstructure control at level of pore size (1-10 μm) is not enough. Variability depends probably on purity of materials as well as details of heat treatment.
  Raises the issue of quality control in fabrication, at sub-μm level!

- The middle and low frequency semi-circles are related to gas composition (and utilization) as well as cell geometry – but microstructure at level of 1-10 μm also plays a role

Second period – conclusions (cont'd)

- Analysis of impedance data (reaction orders, etc.) does not indicate a clearly recognizable single RDS (rate-determining step)

- Multi-RDS mechanisms are likely and may require analyzing data by advanced numerical methods (State-space-method etc.-Gauckler et al.)

- The resistance values associated with the high-frequency semi-circle may be useful in porous-electrode modeling as measure of electrode-kinetic resistance, but they appear to be "laboratory-specific".

- Gas composition dependence of kinetic resistance (R_1) is weak, and certainly much weaker than temperature dependence. Mass transfer resistance (R_2 etc) is clearly dependent on gas composition and current load. However, available AC impedance data are not sufficient to quantify this.

RATE PROCESSES IDENTIFIED BY AC IMPEDANCE ANALYSIS IN LSM-YSZ COMPOSITE CATHODES

(based on van Heuveln et al. and Jørgensen and Mogensen)

Freq(Hz)	E_{act}(kJ/mol)	p_{O2}^{-x}	R(Ω-cm^2)	Main influence	Process
10^2-10^4	~100	0	<0.01	microstructure incr w/thickness	transp [O] or O^{2-} between LSM/YSZ
10^{-1}-10^4	~100	0.15-0.5	R_1= 0.02-0.25	freq T-dependent decr w/ length TPB decr w/ current load	ads O_2, surf diff [O] charge transf @TPB “activation”(?)
1-10	~0	0.5-1	R_2=0.01-1	incr w/ current incr w/ decr T_{sinter}	gas-phase diffusion
<1	0	0		inductive	“activation”(?) rel. to TPB structure
				or	
			R_3=0.01-1	capacitive(u_{ox}-dep.)	oxidant utilization

NOTE: In cell and electrode modeling, potential losses due to gas-phase diffusion resistance and fuel/oxidant conversion are automatically included. Therefore, R_2 and R_3 are not relevant as input into cell-electrode modeling.

RATE PROCESSES IDENTIFIED BY AC IMPEDANCE ANALYSIS IN Ni-YSZ CERMET ANODES

(based on de Boer et al., Primdahl and Mogensen, Bieberle et al.)

Freq(Hz)	E_{act}(kJ/mol)	p_{H2}^{-x}	p_{H2O}^{-y}	R(Ω-cm^2)	Main factors	Rate Process
10^3-10^4	~80	0	0	R_1= 0.3-4	microstr.-sensitive decr w/YSZ size indep. of thickness dep. on ageing	charge trf Ni/YSZ between LSM/YSZ
10-10^3	~0	low p_{H2}: 0.1-0.3 high p_{H2}: 1	 1 1	R_2= 0.1-0.2	incr w/current AC imp. may become inductive	gas-phase diffusion some effect of TPB
0.1-10	~0	low p_{H2}: 0.2	 1	R_3= 0.01	incr w/current AC imp. purely capacitive	gas-phase conversion

NOTE: In cell and electrode modeling, potential losses due to gas-phase diffusion resistance and fuel/oxidant conversion are automatically included. Therefore, R_2 and R_3 are not relevant as input into cell-electrode modeling.

PART II. ELECTROCHEMICAL INPUT FOR SOFC MODELING

- More than 100 relevant references compiled
- Key papers identified and reviewed
- Essentially, SOFC modeling started in 1990
  - significant activity still going on in Europe, but most results not published
- Electrochemical input described in the literature is very rudimentary.

(probably, most relevant data for scale-up are proprietary and design-specific.)

A review of the modeling work for SOFC (pre-SECA)

Model developer	Design type	Approach in modeling	Limitations of the model
Debenedetti and Vayenas Massachusetts Institute of Technology (1983)	Monolithic co, cross and counter flow	Steady state model. Heat-, mass- and charge balances solved for unit cells of CSTR type. 2D model	Neglected conductive heat transfer in solid parts of the cell. Adiabatic cell. Neglected activation and diffusion terms. Only H_2 utilized as a fuel.
Ahmed, McPheeters and Kumar Argonne National Laboratory (1993)	Monolithic cross flow	Steady state model. Heat-, mass- and charge balances formulated for homogenized unit cells. 2D model	Neglected conductive heat transfer in solid parts of the cell. Adiabatic cell. Neglected activation and diffusion terms. Only H_2 utilized as a fuel.
Karoliussen Norway Institute of Technology (1993)	Planar co, cross and counter flow the model is flexible with respect to the geometry of the fuel and air channels	Steady state model. Heat-, mass- and charge balances formulated for homogenized unit cells. Internal reforming in the cell. 3D model	Reforming kinetics is only valid for certain anode material. Diffusion losses are neglected.
Achenbach Research Centre Julich (1994)	Planar co, cross and counter flow the model is flexible with respect to the geometry of the fuel and air channels	Time dependent model. Heat-, mass- and charge balances formulated for homogenized unit cells. Internal reforming in the cell. 3D model	Reforming kinetics is only valid for certain anode material. Kinetics of hydrogen oxidation is only valid for certain anode material.
Hendnksen Risoe National Laboratory (1996)	Planar co, cross and counter flow the model is flexible with respect to the geometry of the fuel and air channels	Steady state model. Heat, mass- and charge balances formulated for homogenized unit cells. Internal reforming in the cell. 3D model	Reforming kinetics is Only valid for certain Anode material.
Costamagna Genova University (1998)	Planar circular cell Radial gas flow	Steady state model. Heat-, mass- and charge balances formulated for homogenized unit cells. 2D model	Only H_2 utilized as a fuel.

CELL and STACK MODEL

Basic options for simplification

- one point model (T averaged, $u_{f,ox}$ assumed)
  - $E = E_{eq,in} - u_f i_{max} Z_{avg}(T_{avg}) A$ (1)
  - $eff = E u_f (i_{max} A)/(\Delta H/nF)$ (2)
- T-dependence of local impedance (2D)
  - $E = E_{eq,local} - Z_{local}(T) i_{local}$ (3)
  - $q_{local} = -i^2_{local} Z_{local} + (T\Delta S/nF)_{local} i_{local}$ (4)
  - local heat balance (2-D + b.c.) (5)
  - efficiency (eff) by integration of i (6)
- T-dependence as well as composition-dependence of local impedance (2-D or 3-D)
  - $E = E_{eq,local} - Z_{local}(T, \text{comp.}) i_{local}$ (7)
  - $q_{local} = -i^2_{local} Z_{local}(T, \text{comp.}) + (T\Delta S/nF)_{local} i_{local}$ (8)
  - local mass balance (2-D) (9)
  - local heat balance (2-D or 3-D + b.c.) (10)
  - current continuity (3-D) (11)
  - voltage integration over stack (3-D) (12)
  - efficiency (eff) by integration of i (2-D) (13)
    or voltage (3-D) (14)

What kind of electrochemical input is needed?

- Depends on the scale of the model, therefore on **level of modeling**

level 1	system	modular
level 2	stack	3-D
level 3	(a) cell as layer in stack	2-D
	(b) gas channel/interconnect	2-D or 3-D
level 4	porous electrode	1-D
level 5	materials properties	1-D and molecular

- Of interest for **SOFC scale-up modeling** are :

level 2		stack (2D/3D CFD and thermal modeling)
level 3	(a)	cell as layer in stack (2D)
	(b)	gas channel/interconnect profile (2D/3D)

- Of interest for **optimizing electrode microstructure** are :

level 3	(b)	gas channel/interconnect profile (2D/3D)
level 4		porous-electrode model (1D/2D)

Two types of

electrochemical input needed for SOFC modeling

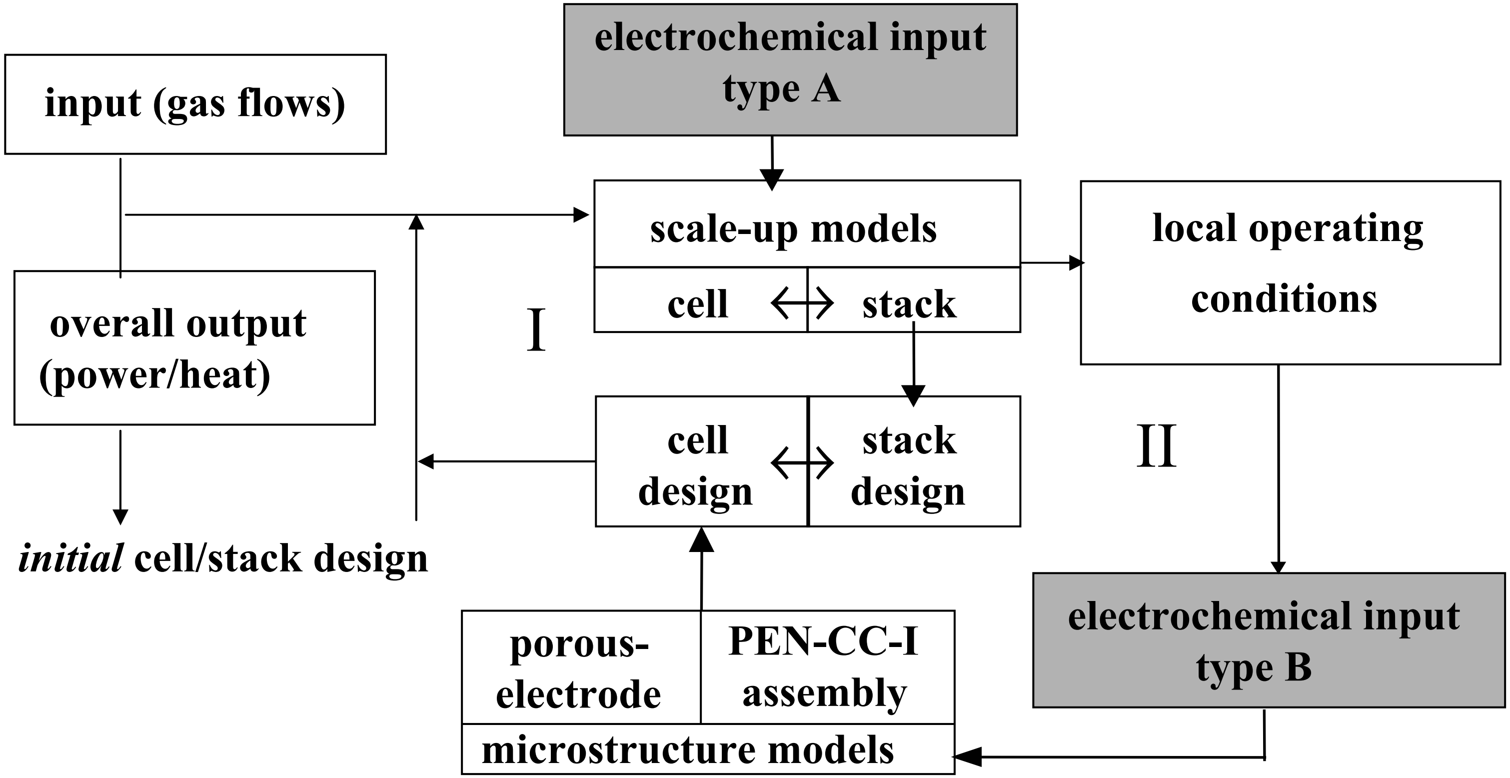
Type A. Input for scale-up modeling of cells and stacks

- _need not be detailed_, mechanistically
- must apply over a range of relevant operating conditions—and correlate i-E behavior with gas composition, temperature, pressure
- may be material/structure specific (and perhaps "laboratory-specific")
- range of validity restricted by application targeted

Type B. Input for modeling electrode performance as f (microstructure)

- may need to contain kinetic (mechanistic) and diffusion details
- may be needed only over certain range of composition and temperature (***depending on feedback from scale-up model***!)
- has a larger "generic content"

Flow sheet for SOFC design/performance modeling showing electrochemical input



input (gas flows)

electrochemical input type A

scale-up models

cell ↔ stack

local operating conditions

overall output (power/heat)

I

cell design ↔ stack design

II

***initial* cell/stack design**

porous-electrode

PEN-CC-I assembly

microstructure models

electrochemical input type B

Design process starts from the left and proceeds through cell+stack iteration I, then electrode+cell iteration II within iteration I (if greater accuracy is needed)

Type-A Electrochemical Input

- Cell and Stack Modeling is best served by Type A input.
  But this is ***not available in the SOFC literature*** – at least not in ready-to-use form.

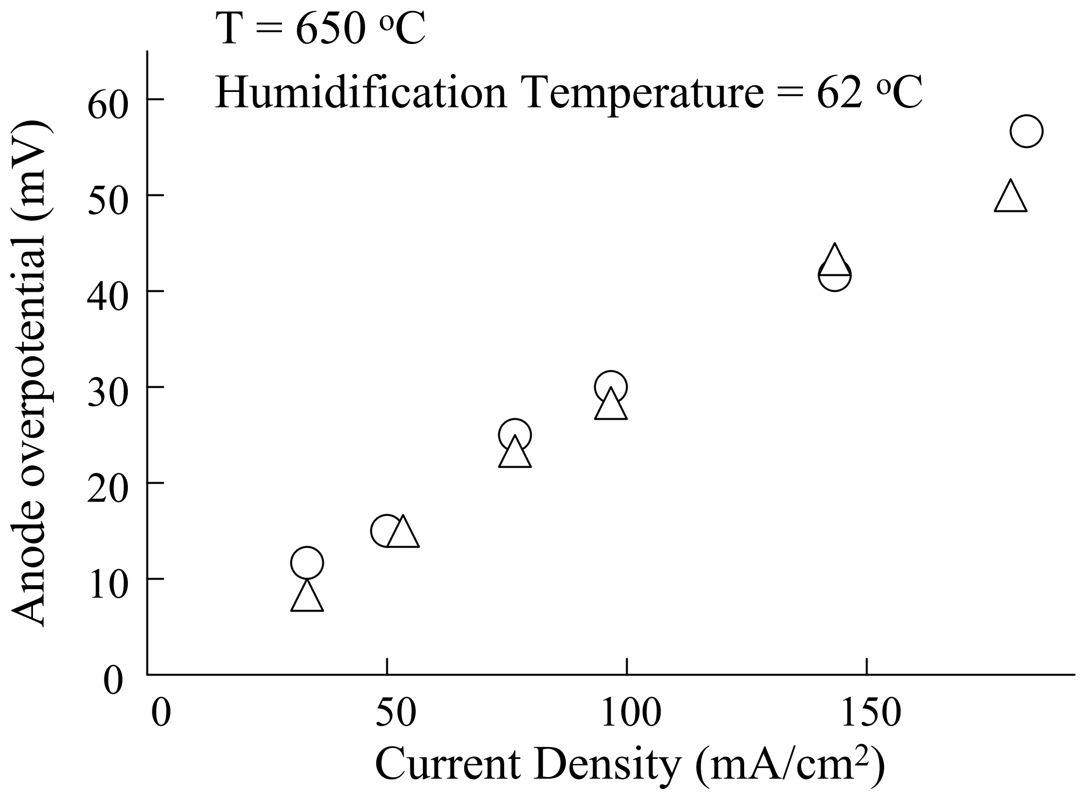
- As an example of this type of input, correlations developed by IIT from polarization measurements on small MCFC test cells are shown.
  Test cells must operate at small utilization and have same cell geometry, materials and electrode microstructure as the full-scale stack.

- In well-performing fuel cells (>500C) , the I-E "curve" is nearly linear.

- Therefore, a "DC impedance", *Z*, can be assigned to each electrode.

- The Z values of each electrode can be correlated with gas composition and temperature.

H_2	CO_2	N_2	He
20	20	60	--
20	20	--	60



Example of Quasi-Linear Electrode (Anode) Performance Characteristic

Example of Linear Regression Analysis of Anode Data (MCFC)

z_{AN} = A exp(Q/RT)
z_{AN} = Anode Resistance at 160 mA/cm^2 (kcal/g-mol)

Gas (Dry)			Q (kcal/g-mol)
H_2	CO_2	N_2	
80	20	--	14.5 ± 1.2
40	20	40	10.9 ± 3.6
40	40	20	14.8 ± 0.95
20	20	60	12.8 ± 1.1
10	20	70	12.0 ± 0.64

Humidification Temperature = 60-64 ^{o}C

Example of Linear Regression Analysis of Anode Data (MCFC)

$$z_{AN} = A(H_2)^a(CO_2)^b(H_2O)^c$$

z_{AN} – Anode Resistance at 160 mA/cm^2 (ohm-cm^2)

Temperature (°C)	a	b	c
600	-0.23 ± 0.01	0.17 ± 0.02	-2.4 ± 0.1
650	-0.45 ± 0.17	-0.33 ± 0.29	-0.8 ± 1.9
700	-0.18 ± 0.19	0.24 ± 0.29	-5.5 ± 0.95

$$z_{AN} = 2.27*10^{-5}(H_2)^a(CO_2)^b(H_2O)^c\exp(Q/RT)$$

a	b	c	Q (kcal/g-mol)
-0.42 ± 0.07	-0.17 ± 0.11	-1.0 ± 0.64	12.8 ± 1.2

NOTE relatively large uncertainties in reaction orders!

Type-B Electrochemical Input

- This input is also important, but more detailed than Type-A.

- Essentially important for
    - anode in IR-SOFC and direct HC operation
    - cathode at high utilization

- R_1 (high-frequency semi-circle) data from AC impedance measurements may be a first-approximation of kinetic resistance

- This information must be combined with porous-electrode modeling to obtain realistic estimates of polarization, CH_4 conversion, etc.

Porous Electrode Model:
1-D macro-homogenous porous-electrode
(1) mass balance

$$D^{E}_{CH_4,m}\frac{d}{dx}\left[\frac{\frac{dC_{CH_4}}{dx}}{1+2X_{CH_4}}\right]-R_{ref}=0$$

$$D^{E}_{CO,m}\frac{d}{dx}\left[\frac{\frac{dC_{CO}}{dx}}{1-2X_{CO}}\right]+R_{ref}-R_{shift}=0$$

$$D^{E}_{H_2,m}\frac{d}{dx}\left[\frac{\frac{dC_{H_2}}{dx}}{1-0.5X_{H_2}}\right]+3R_{ref}+R_{shift}-\frac{\nabla .i2}{2F}=0$$

$$D^{E}_{H_2O,m}\frac{d}{dx}\left[\frac{\frac{dC_{H_2O}}{dx}}{1+X_{H_2O}}\right]-R_{ref}-R_{shift}+\frac{\nabla .i2}{2F}=0$$

$$D^{E}_{CO_2,m}\frac{d}{dx}\left[\frac{\frac{dC_{CO_2}}{dx}}{1-2X_{CO_2}}\right]+R_{shift}=0$$

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Porous Electrode Model: cont.

(2) Charge balance and electrode kinetic expression:

$$\nabla . i1 + \nabla . i2 = 0$$

$$\nabla . i2 = a i_0 \left[\frac{C_{H2}}{C_{H2,b}} \left(1 + \frac{\alpha_c F \eta_s}{RT} \right) - \frac{C_{H2O}}{C_{H2O,b}} \left(1 - \frac{\alpha_c F \eta_s}{RT} \right) \right]$$

(3) Heat balance:

$$\lambda_{avg} \frac{d^2 T}{dx^2} + \frac{i_1^2}{\sigma} + \frac{i_2^2}{\kappa} + \eta_s \nabla . i_2 - \frac{(\nabla . i_2) Q_A}{2F} - R_{ref} Q_{ref} = 0$$

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CH_4-H_2O Reforming rate kinetics

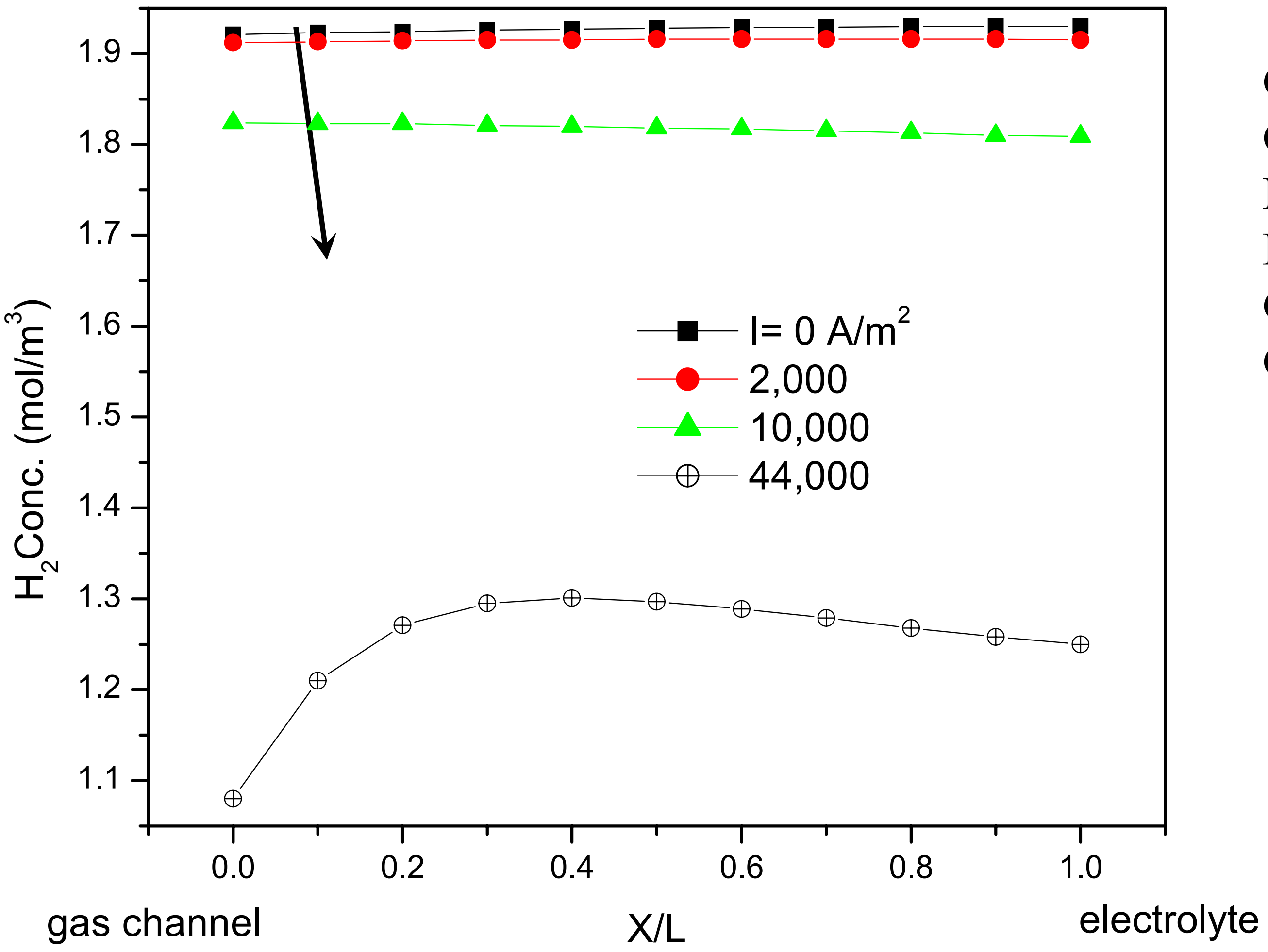
$$r = k p_{CH_4}^{\alpha} p_{H_2O}^{\beta} \quad \text{where} \quad k = A \exp(-\frac{E}{RT})$$

Authors	α	β	A	E kJ/kmole
Lee, et al	1	-1.25	12.09 kmol kg^{-1}_{Ni} s^{-1} $Pa^{0.25}$	9.85×10^4
Parsons, et al	1.25	0	1.43 mol m^{-2} s^{-1} $bar^{-1.25}$	75×10^4
Achenbach, et al	1	0	4274 mol m^{-2} s^{-1} bar^{-1}	92×10^4
Ødegård	1.20	0	6339 mol g^{-1}_{Ni} s^{-1} $atm^{-1.20}$	58×10^4

Porous-Electrode Modeling of IR-SOFC Anode

Effect of Gas Composition

phi(gas)=0.2, phi (Ni)=0.284, phi(ZrO2)=0.516



Gas composition(B)
CH4=0.097
H2O=0.552
H2=0.193
CO=0.049
CO2=0.109

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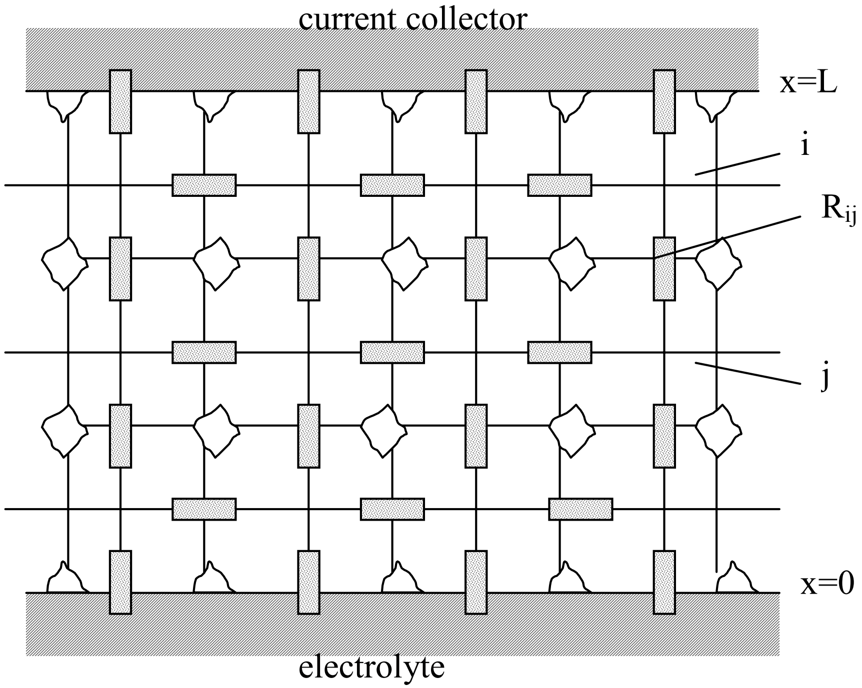
Type-B Electrochemical Input (cont'd)

- A type of input that is useful in micromodeling of composite electrodes is particulate-connectivity (or Monte-Carlo) electrochemical modeling.

Particulate Connectivity Model



A schematic presentation of the composite SOFC electrode. Current collectors are placed at both sides of the lattice. Particles i and j are electrically connected via the resistor Rij = σ_{ij}^{-1}, which depends on the kind of particles occupying these sites. (From Sunde)

PART III.
OVERALL RECOMMENDATIONS FOR SECA MODELING STRATEGY

- Systematic collection of Type-A experimental data for two purposes:
  - Direct use in scale-up modeling
  - Analysis to extract electrode-kinetic or reforming-kinetic data

- Correlation of R_1 data from AC impedance measurements (“laboratory-specific”) with electrode microstructure.

Information such as temperature dependence, gas composition dependence may be shared by SECA community for advancement of the technology

- Application of porous-electrode and composite-electrode (Monte-Carlo type) modeling for microstructure optimization comments welcome !

to

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