The Abdus Salam
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2269-10

Workshop on New Materials for Renewable Energy

17 - 21 October 2011

Advancing electrocatalysis in intermediate temperature fuel cells

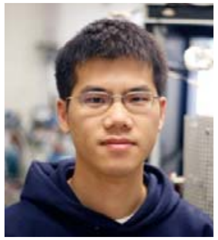
Sossina M. HAILE

California Institute of Technology
Steele Laboratories, Materials Science
Pasadena
U.S.A.

Strada Costiera 11, 34151 Trieste, Italy - Tel.+39 040 2240 111; Fax +39 040 224 163 - sci_info@ictp.it

Advancing Electrocatalysis in Intermediate Temperature Fuel Cells

1. Oxide Electrocatalysts more Active than Pt
2. Diffusion-limited Electrodes
3. Butler-Volmer Kinetics at the Nanoscale



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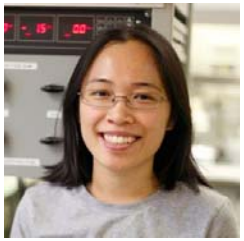


Workshop on New Materials for Renewable Energy

October 17-21, 2011, Trieste, Italy

Fuel Cell Types

Corrosive liquids

Types differentiated by **electrolyte**, temperature of operation

Portable

Stationary

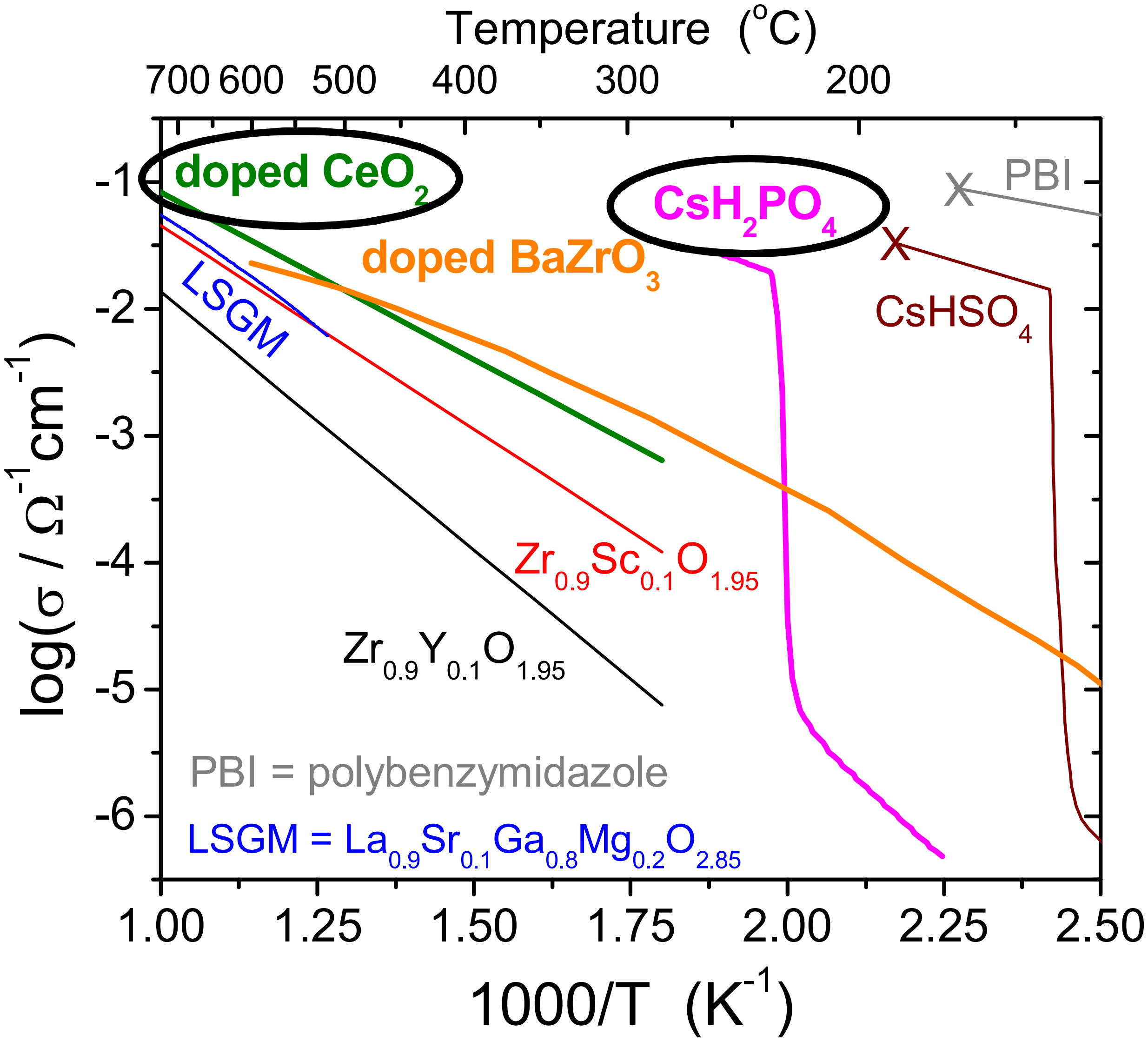
Type °C	**PEM** 90-110	**AFC** 100-250	**PAFC** 150-220	**MCFC** 500-700	**SOFC** 700-1000
Fuel	H_2 + H_2O	H_2	H_2	HC + CO	HC + CO
Electrolyte *Ion*	Nafion $H_3O^+ \downarrow$	KOH $OH^- \uparrow$	H_3PO_4 $H^+ \downarrow$	Na_2CO_3 $CO_3^{2-} \uparrow$	$Y\text{-}ZrO_2$ $O^{2-} \uparrow$
Oxidant	O_2	O_2 + H_2O	O_2	O_2 + CO_2	O_2

Fuel flexibility, efficiency →

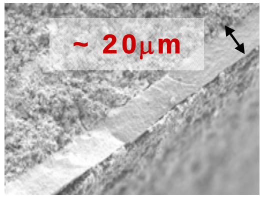
← Easy thermal cycling

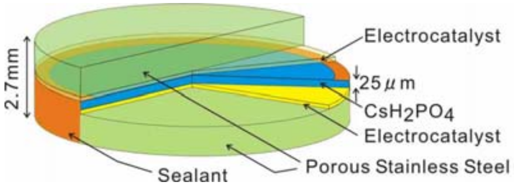
Target regime

Candidate Solid Electrolytes



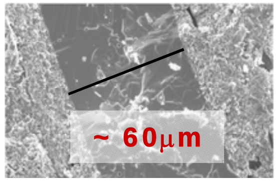
Performance Limitation

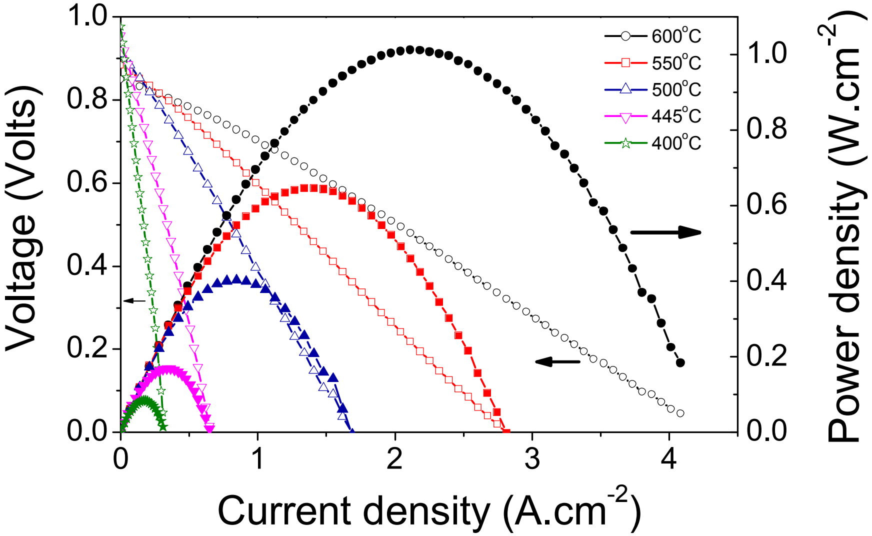


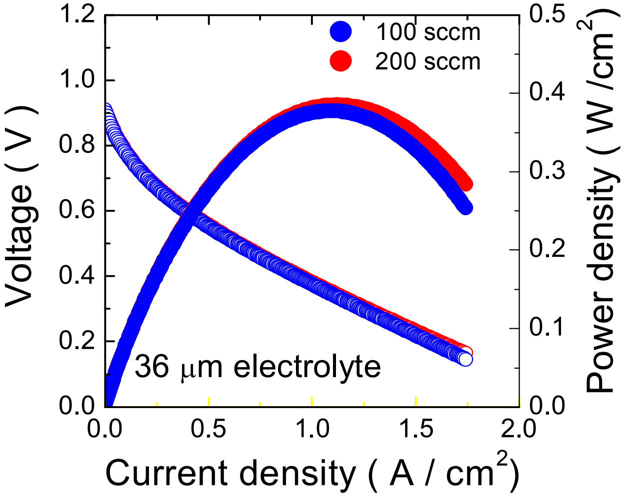


- Thin-electrolyte cells prepared
- Such cells are electrode limited
  - Ceria fuel cell – anode
    - Ceria-nickel composite
  - CsH_2PO_4 fuel cell – electrodes
    - CsH_2PO_4-carbon-Pt composite

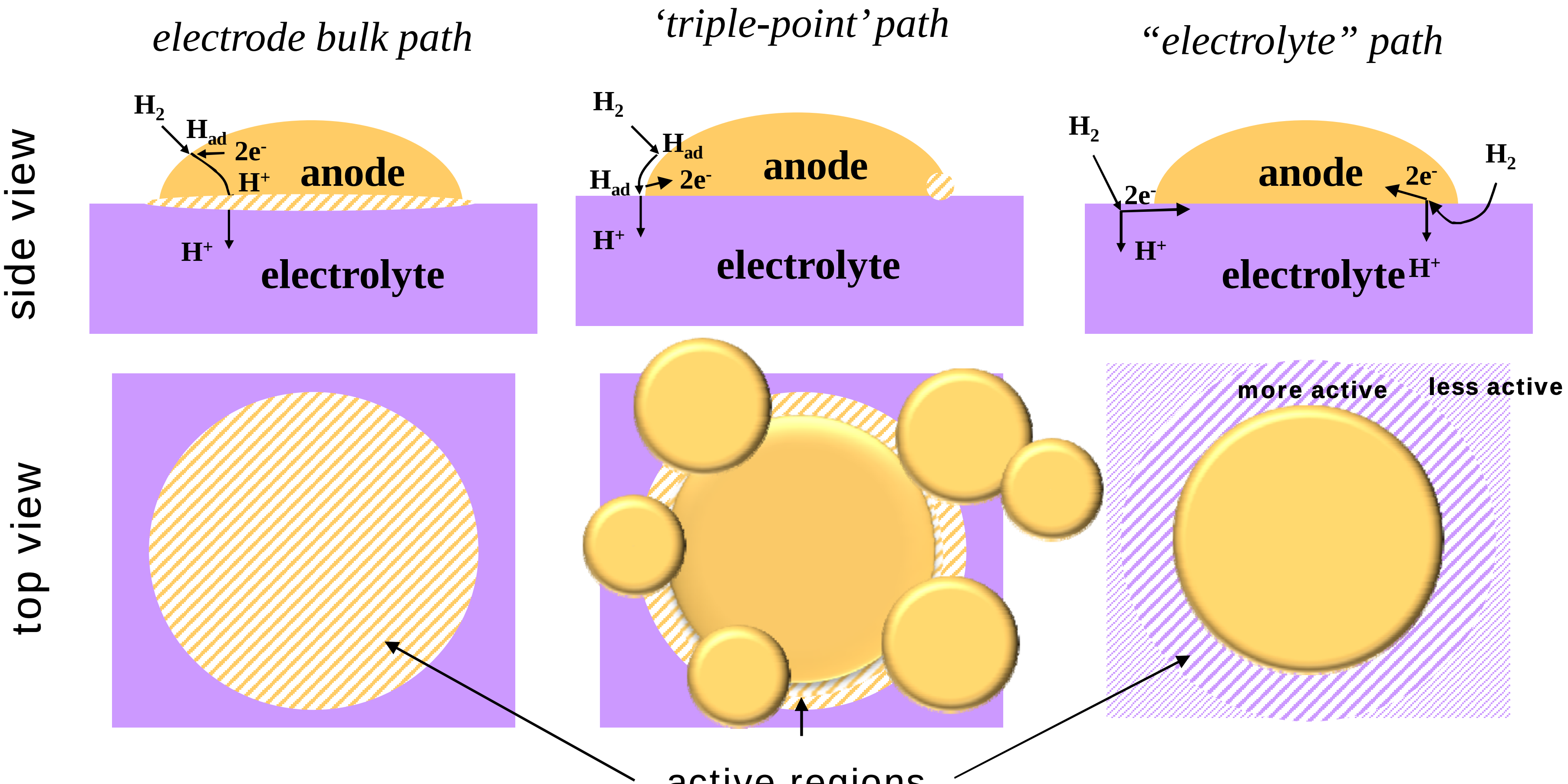
- Where is the active site?







Electrochemical Reaction Pathways



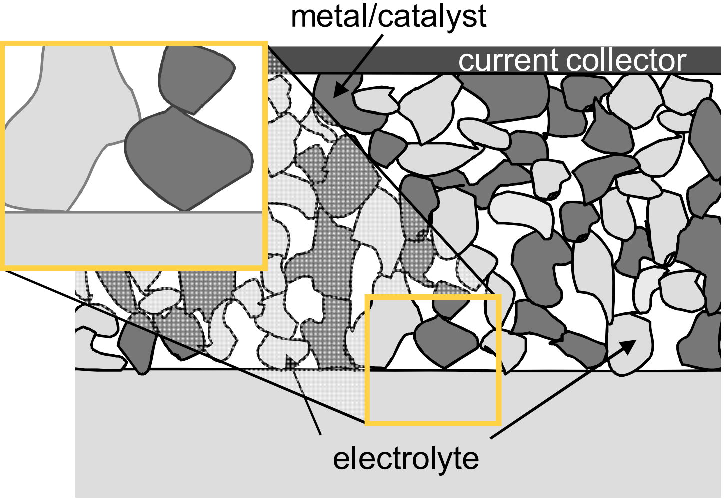
active regions

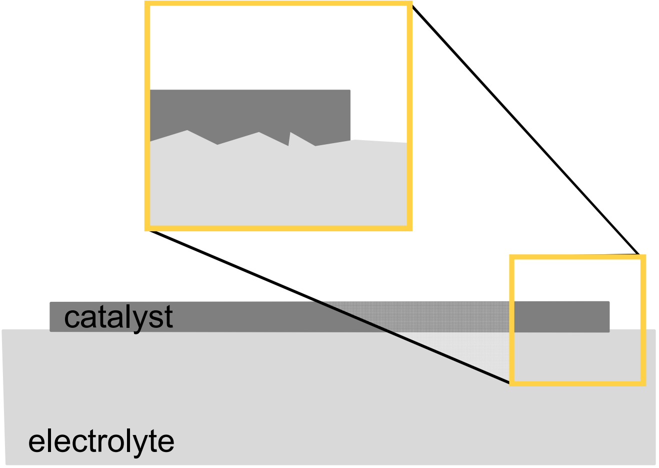
connected in 3-D to the exterior circuit

must know pathway to design optimal electrode architectures

Identifying Active Interfaces

- Patterned metal current-collectors/electrodes by photolithograpy



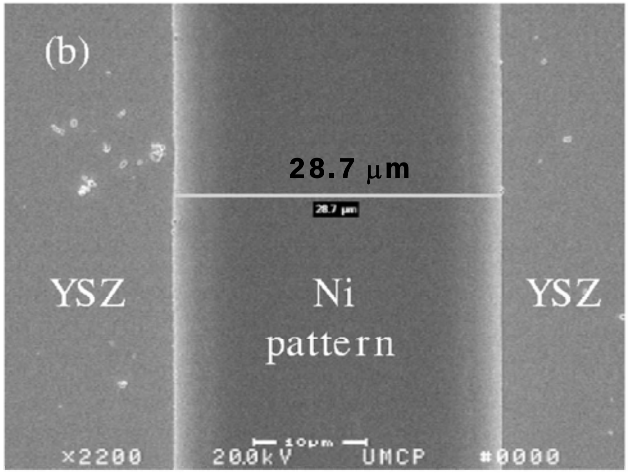


- Nanoscale electrode by conducting AFM

State-of-the-Art: Patterned Structures

- Patterned metal current-collectors/electrodes increasingly pursued for quantitative studies
- Typically degrade during experimentation

as-deposited (sputtered, 125 nm)

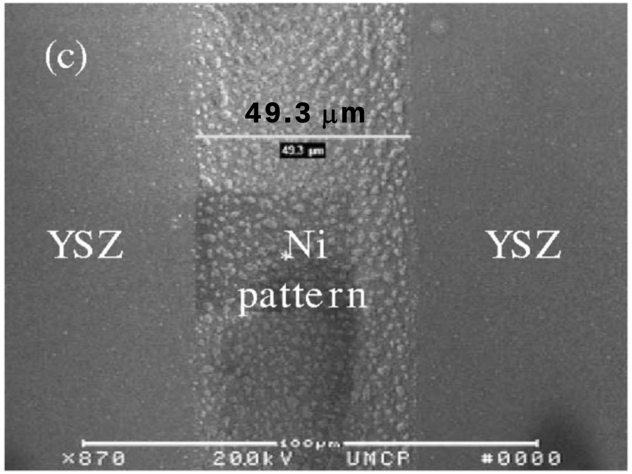


on (100) single crystal $Zr_{0.92}Y_{0.08}O_2$

T = 750-850 °C

H_2, CO atm

post evalution

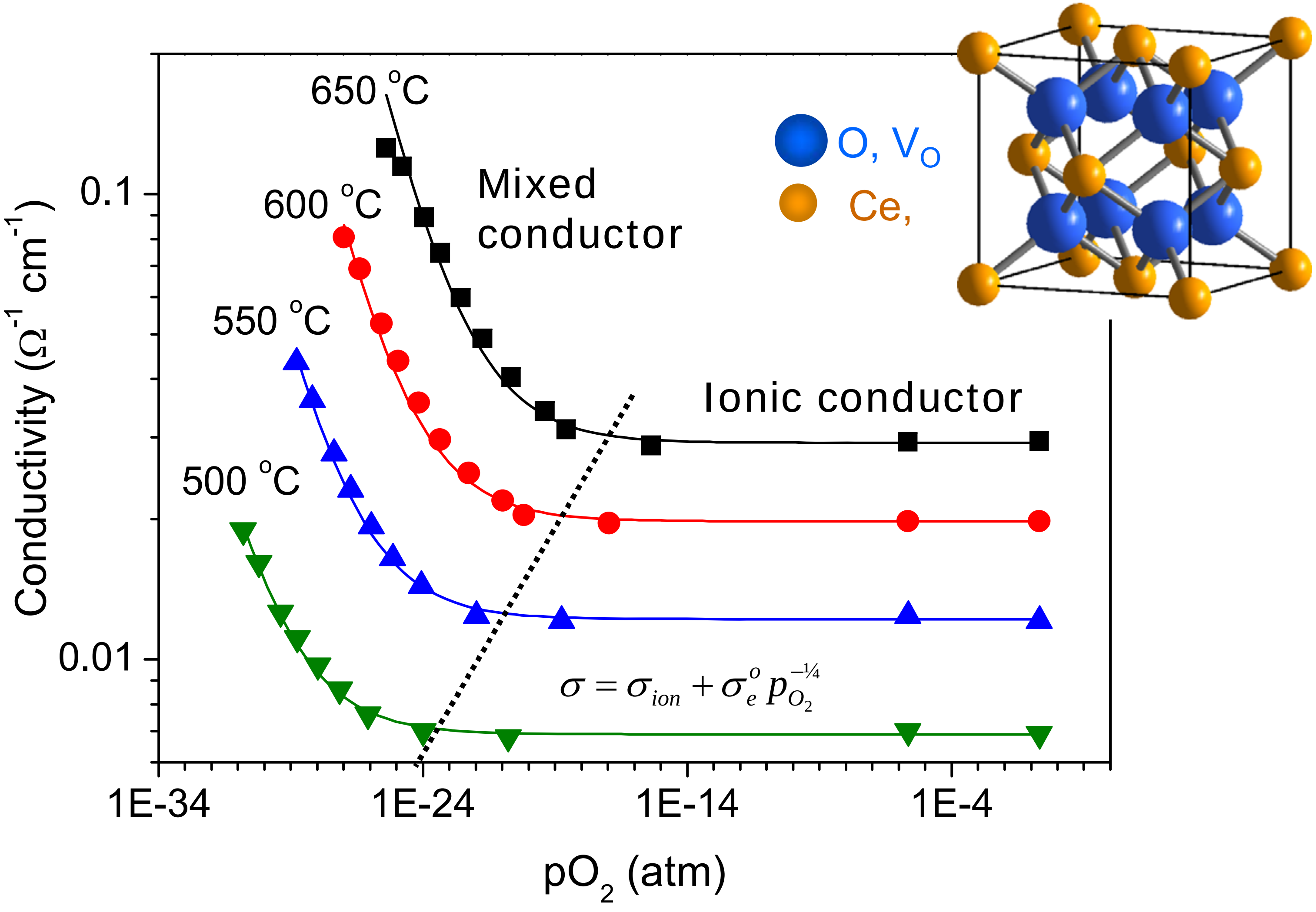


A. M. Sukeshini, B. Habibzadeh, B. P. Becker, C. A. Stoltz, B. W. Eichhorn, and G. S. Jackson, *J. Electrochem. Soc.* **153** A705-A715 (2006).

This work: Part I

- Patterned metal current collectors on doped ceria
    - Thermal stability
        - Thick films; well-defined edges
- Hydrogen electro-oxidation
- Objective:
    - Determine if the oxide surface plays a role in the electro-oxidation

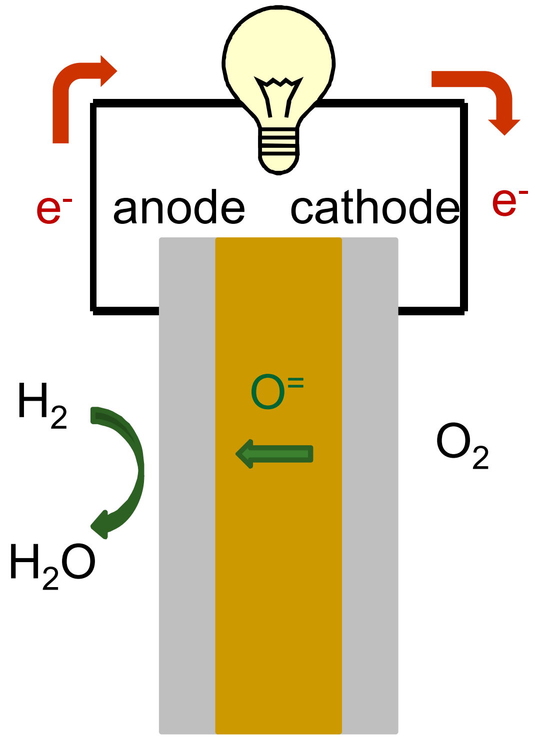
Ceria as Both Anode & Electrolyte



W. Lai, S. M. Haile. J. Am. Ceram. Soc., **88** 2979 (2005)

Ceria in Fuel Cell Anodes

- General observation of improved activity
  - Resistant to carbon deposition
  - Redox tolerant
  - Impregnate Ni/YSZ anodes with ceria
  - Replace YSZ with ceria
  - Doped or undoped
- Oxide apparently plays a direct role in electrocatalysis

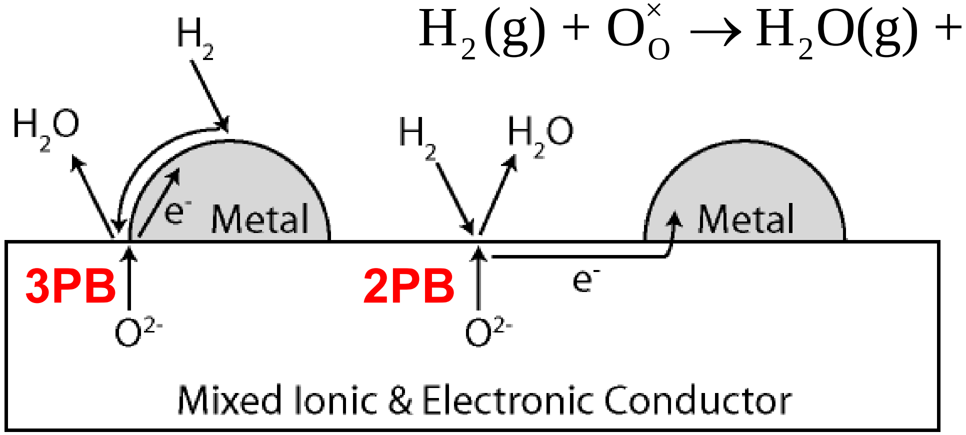


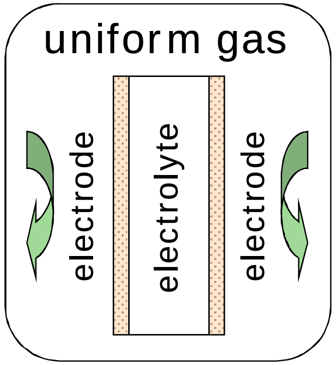
Anode reaction:

$H_2 + O^= \rightarrow H_2O + 2e^-$

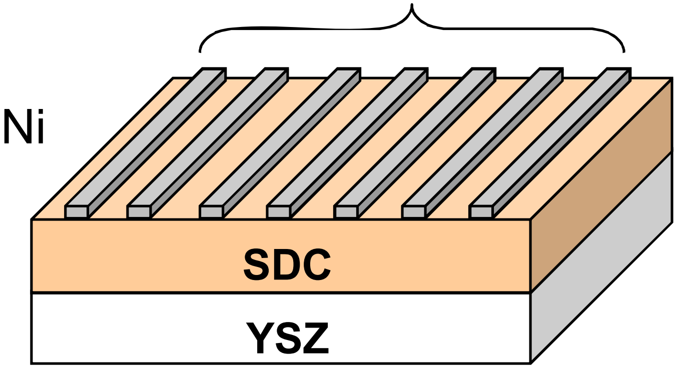
Identifying Active Sites

$$H_2(g) + O_O^{\times} \rightarrow H_2O(g) + V_O^{\bullet\bullet} + 2e'$$





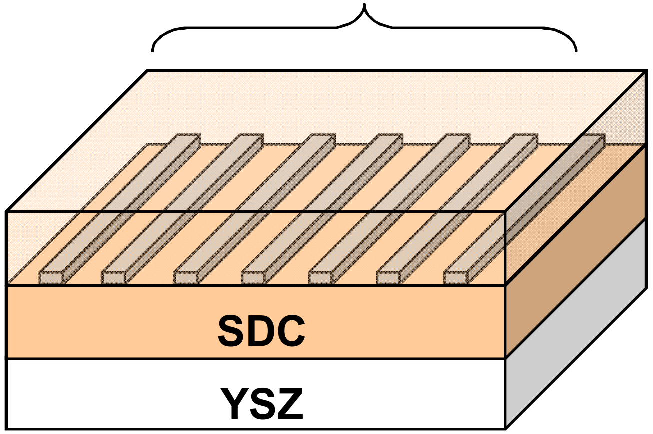
Patterns interconnected



Pt & Ni

Vary 3PB and 2PB reaction site densities independently

Patterns embedded and interconnected

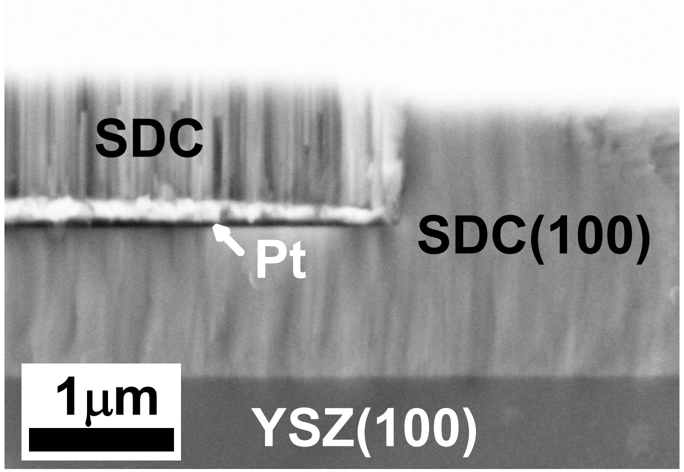


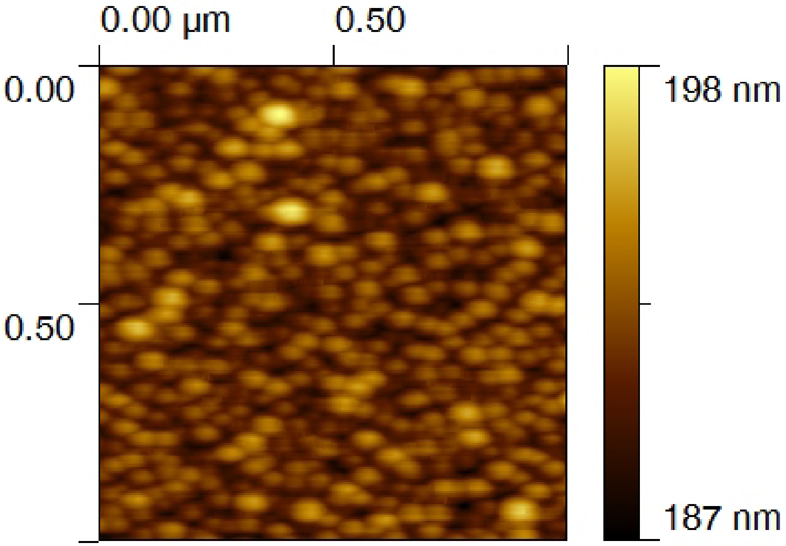
Pt only

Single, fixed geometry

Film Growth by PLD

- Highly oriented/epitaxial SDC on single crystal YSZ
  - (100), (110) & (111)
- Composition as desired
- Low pO_2 gives high density



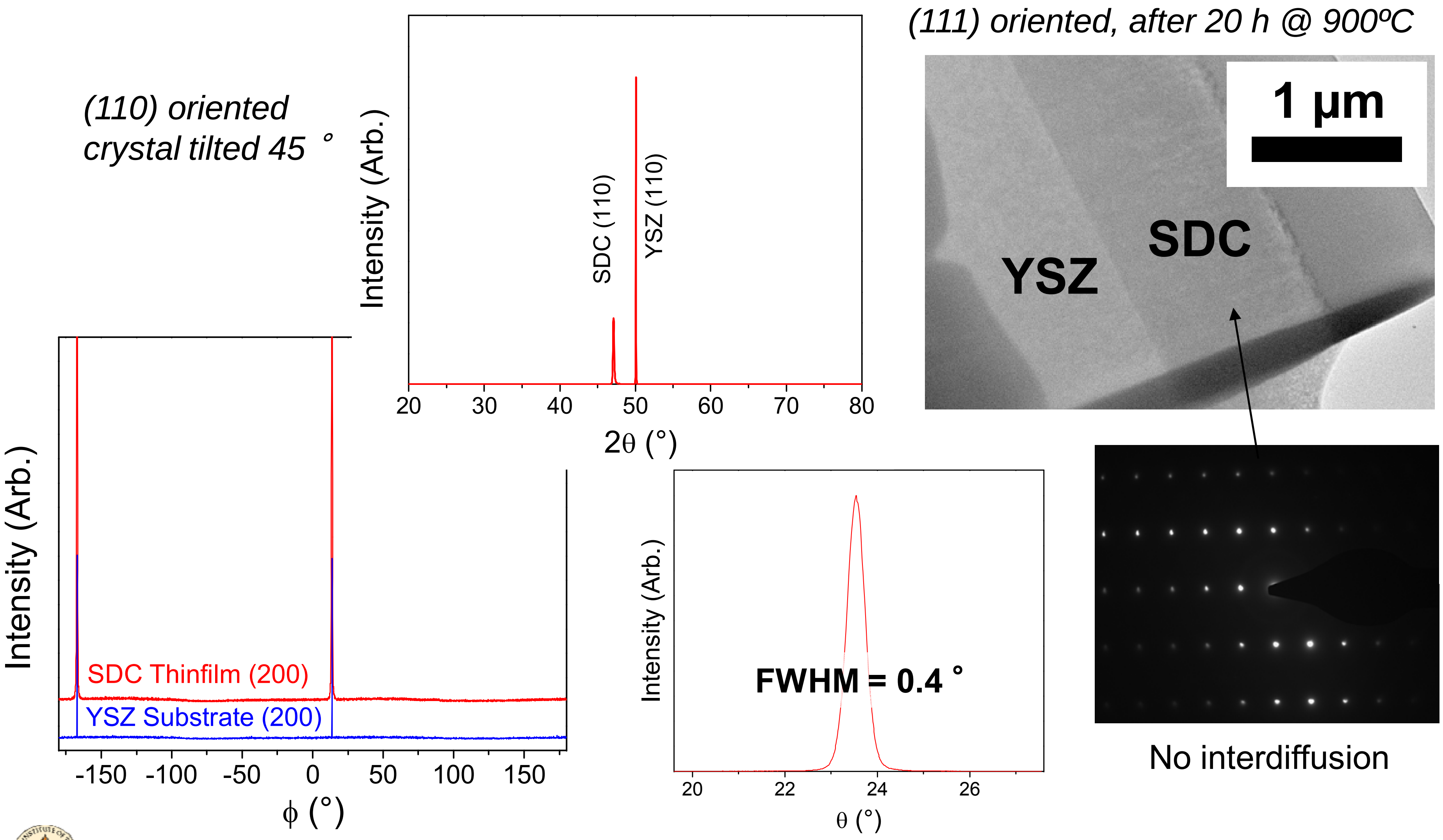


rms roughness: 1.41 nm

Typical Deposition Conditions

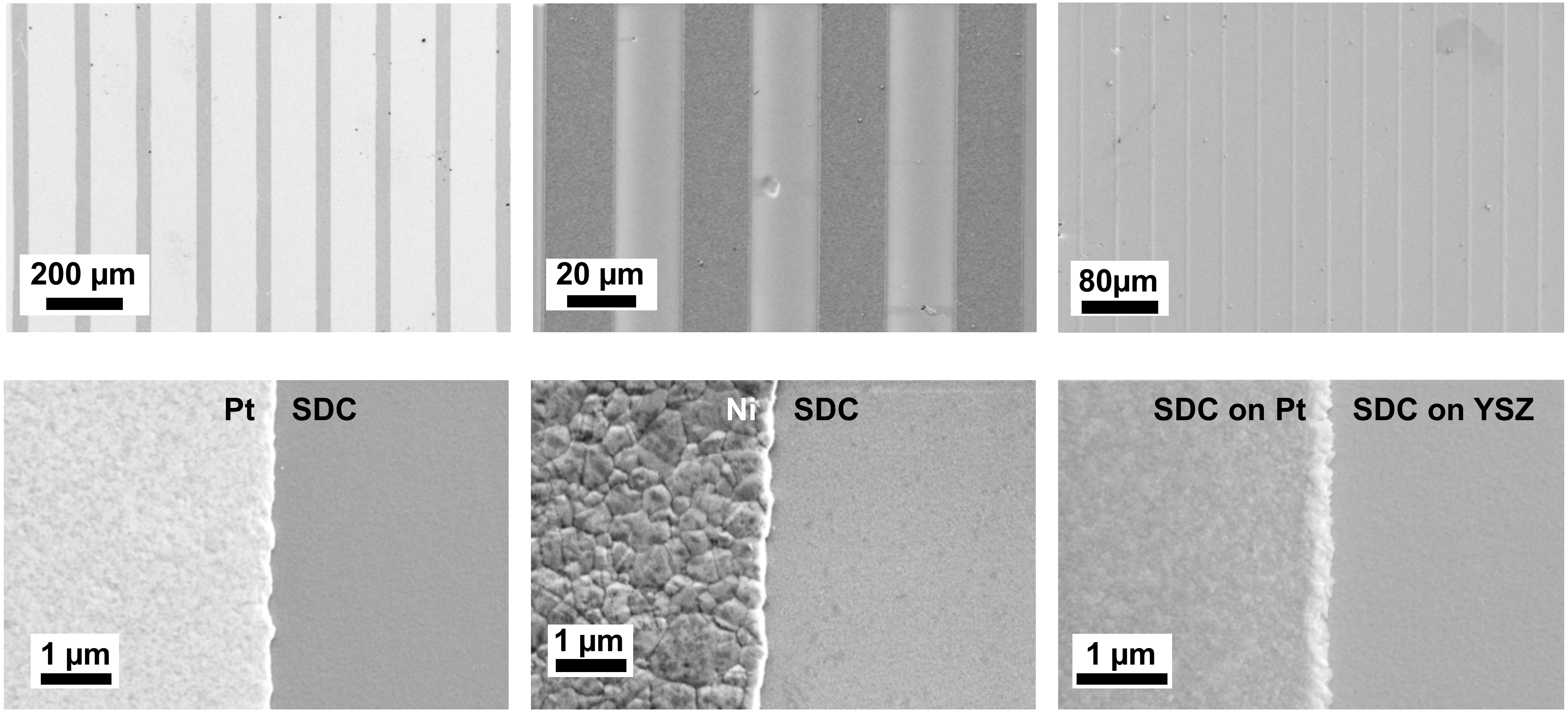
Laser Energy	300 mJ
Substrate Temperature	650 ºC
Pulses	100k @ 20 Hz
Oxygen Partial Pressure	20 – 100 mTorr

Film Quality and Stability



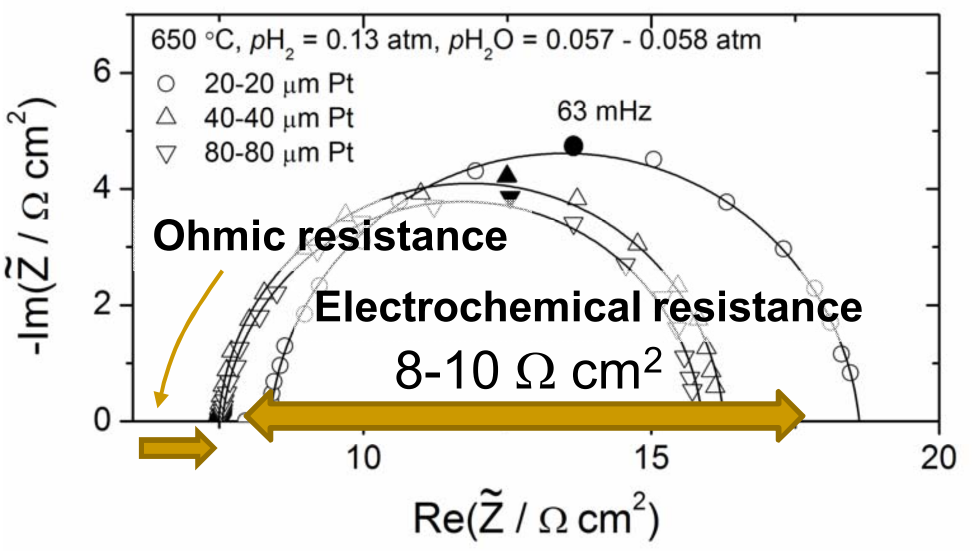
Metal Patterns by Photolithography

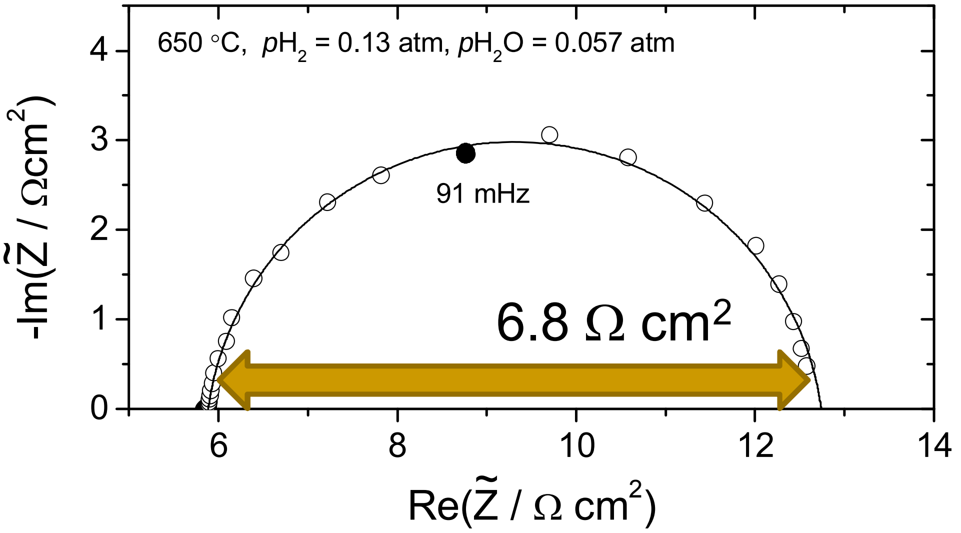
Exposed Pt | Exposed Ni | Embedded Pt



After electrochemical characterization at 650 °C under H_2-H_2O-Ar

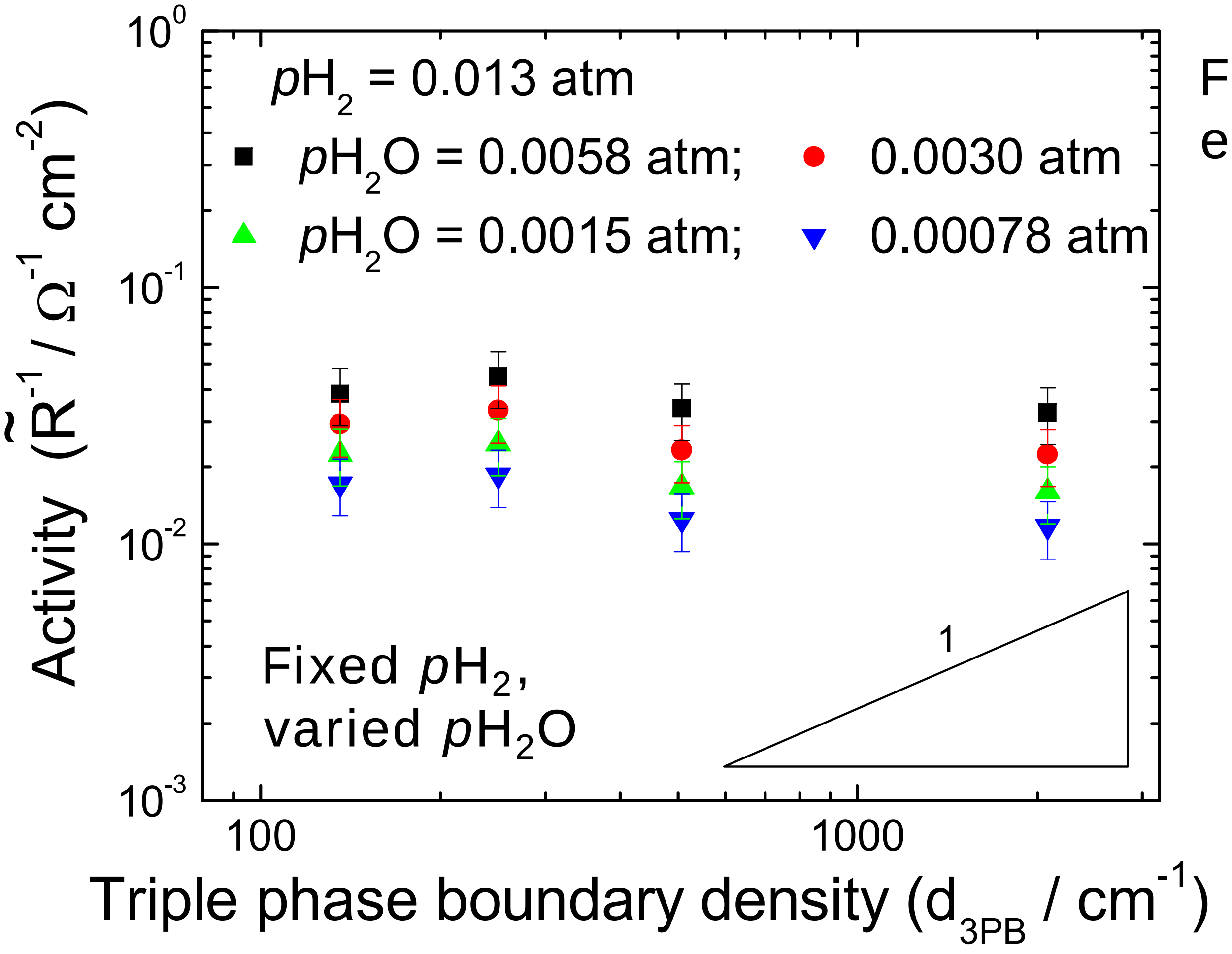
Impedance Response





- Exposed Patterns
  - Fixed SDC/Pt ratio
  - 3PB density varied
  - Approximately constant
- Embedded Pattern
  - *Higher* activity
  - Pt 3PBs are not playing a role!

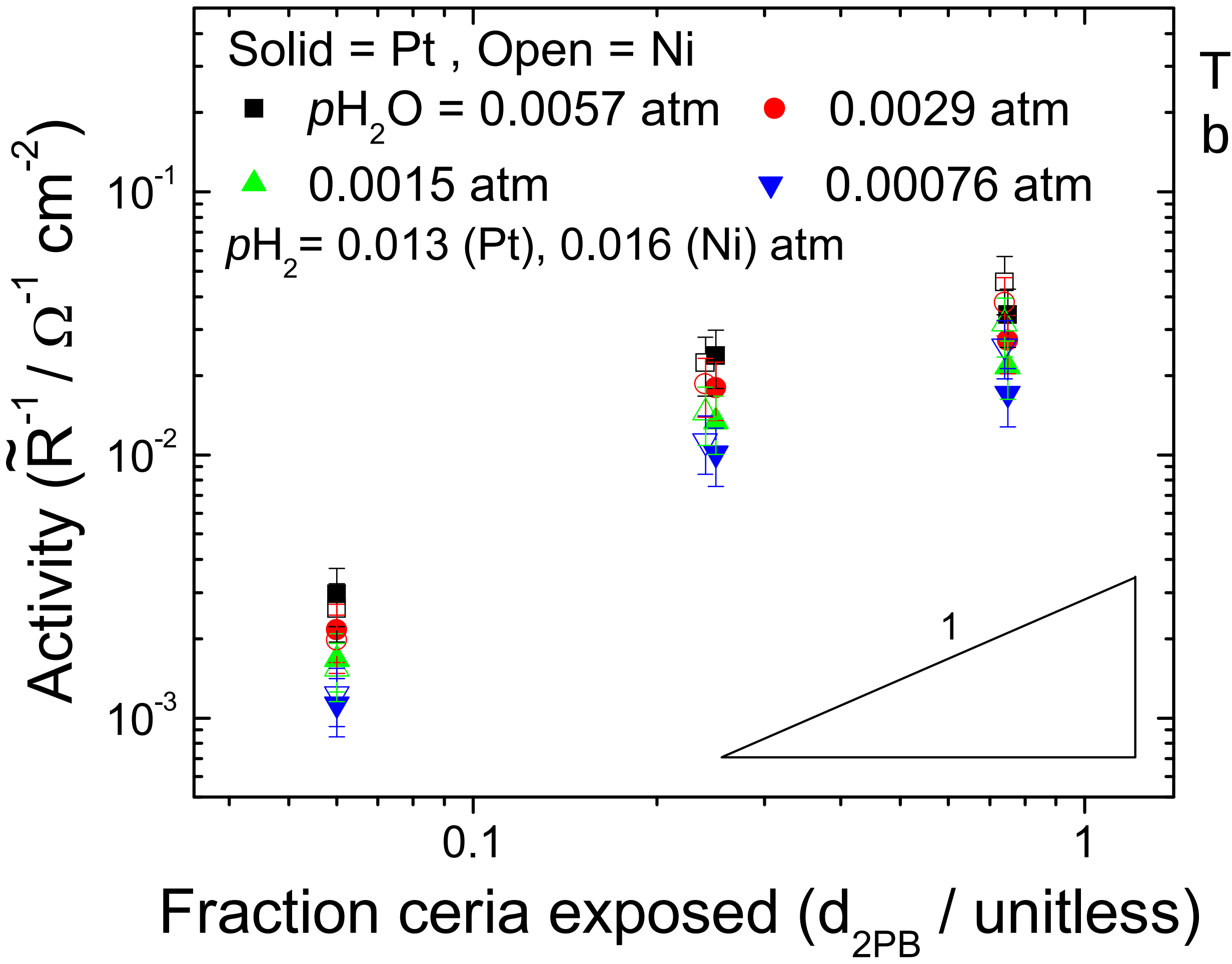
Dependence on Features Sizes



Fraction ceria exposed = 0.5

- Activity is **independent** of 3PB density
- Pt and Ni are essentially identical (not shown)

Dependence on Features Sizes

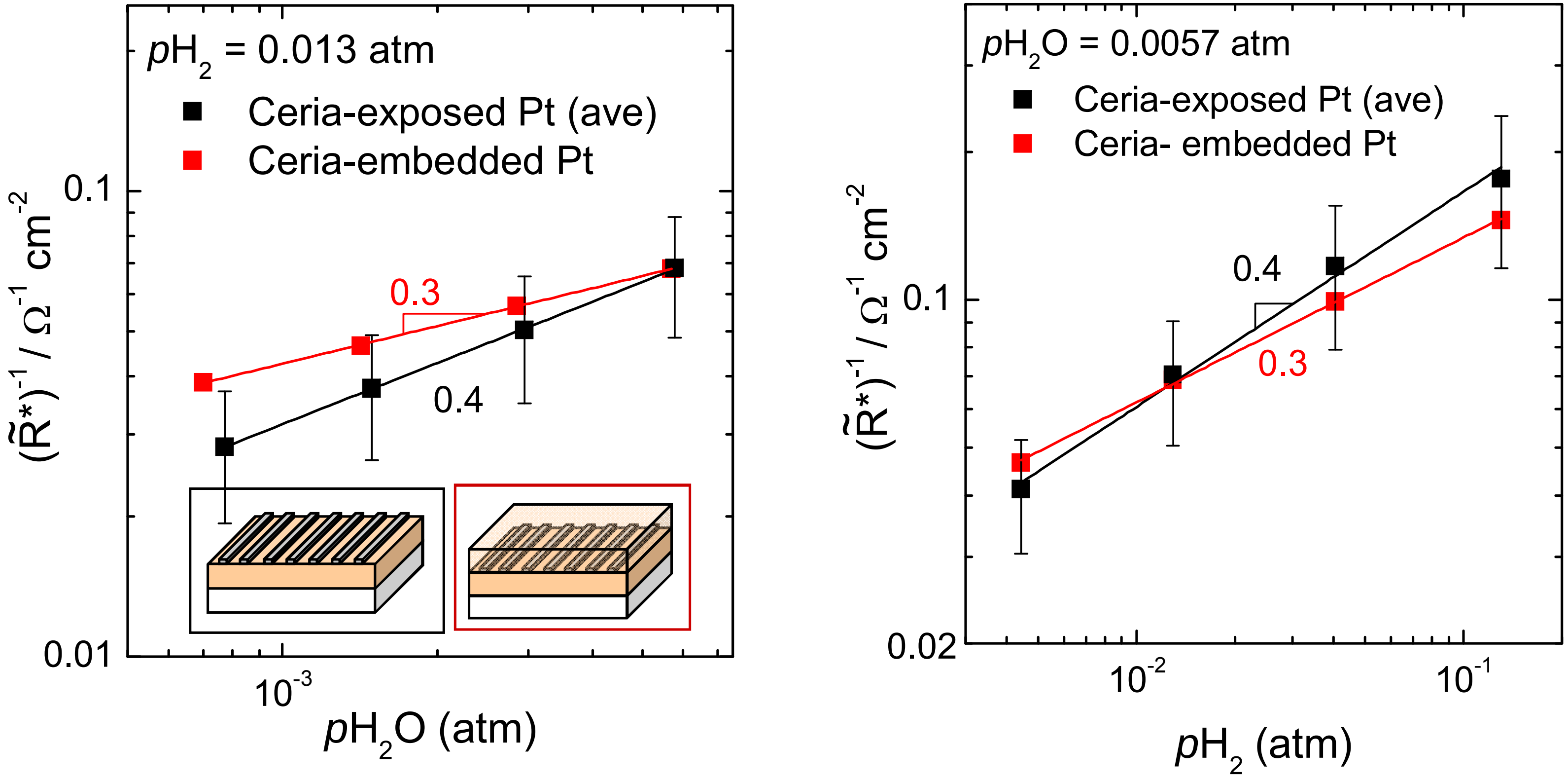


Triple phase boundary density = 125 cm^{-1}

Fixed pH_2, varied pH_2O

- Activity is **proportional** to ceria exposure
- Pt and Ni are essentially identical

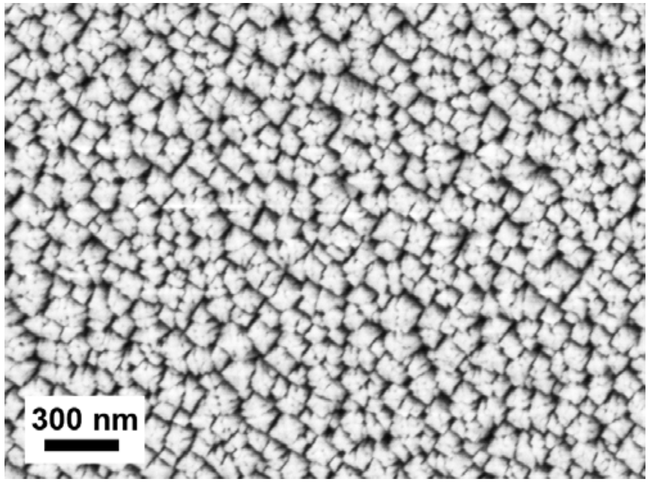
Activity Normalized to Ceria (2PB)

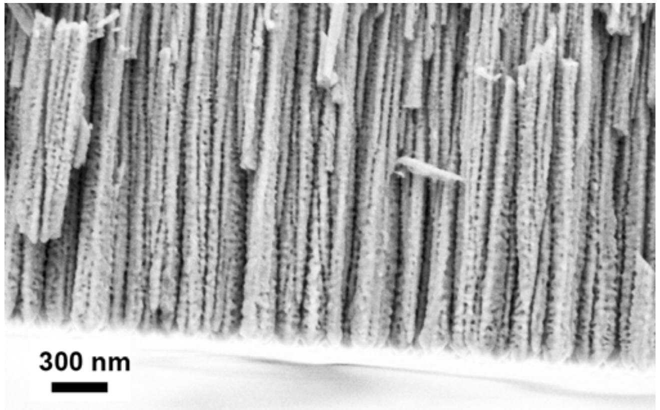


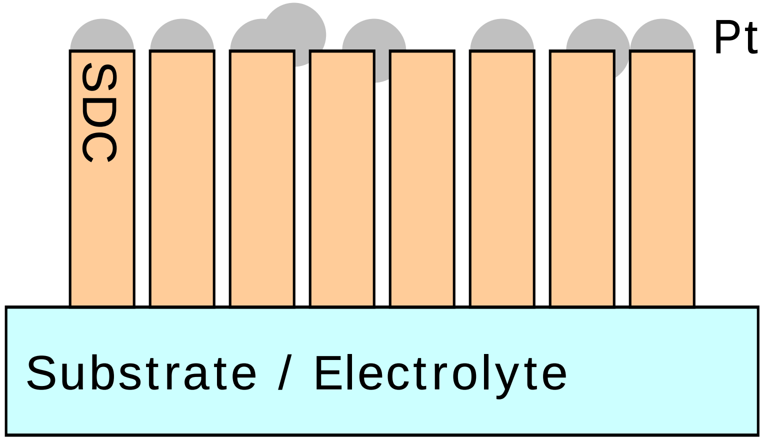
- All data collapse to a single curve
  - Ceria is more active than Pt! 100 μm electron transport
- Extrapolate to fuel cell conditions (pH_2 = 1, pH_2O = 0.03 atm)
  - Predict 1 Ωcm^2 at 650 °C for a flat (!) electrode

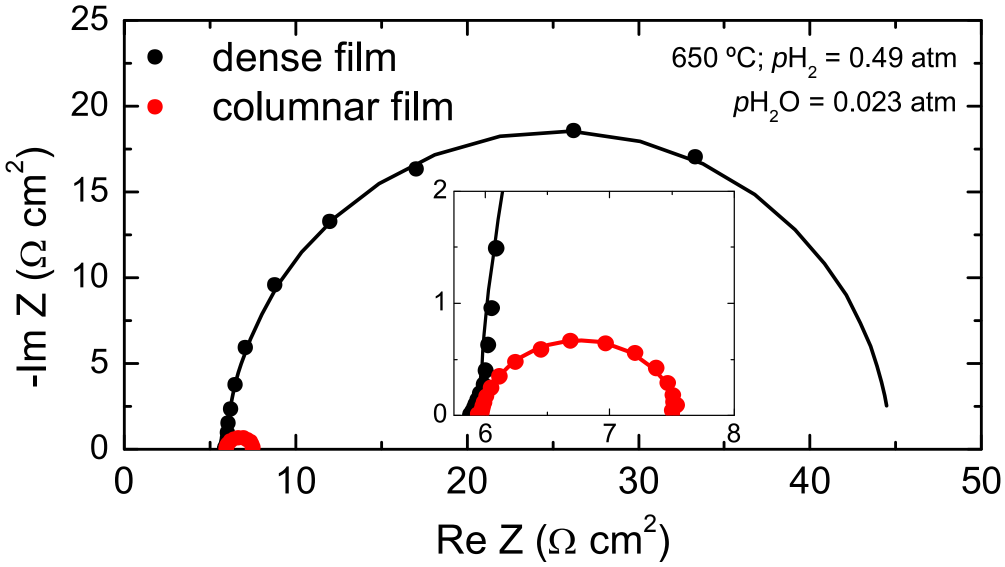
Structuring for Higher Activity

PLD film, pO_2 = 100 Torr,









W. C. Chueh, Y. Hao, WooChul Jung and S. M. Haile., under review, *Nat. Mat.*

Intermission

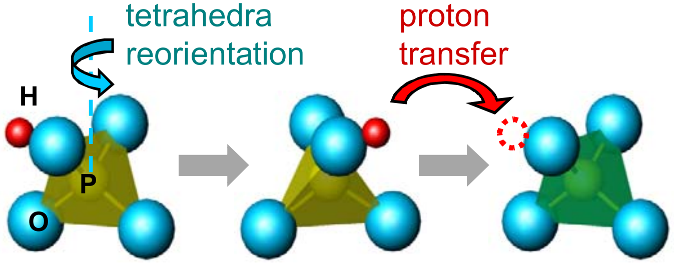
- Ceria has high inherent activity for hydrogen electro-oxidation
- Values are comparable or better than the most promising oxide anodes
- At the length scales accessible by photolithography, triple phase boundaries are negligible
  - Pt and Ni are essentially identical
- Electron transport over long (μm) distances through ceria occurs
- Freed of the ‘tyranny’ of the triple phase boundaries, a plethora of anode designs can be considered

This Work: Part II

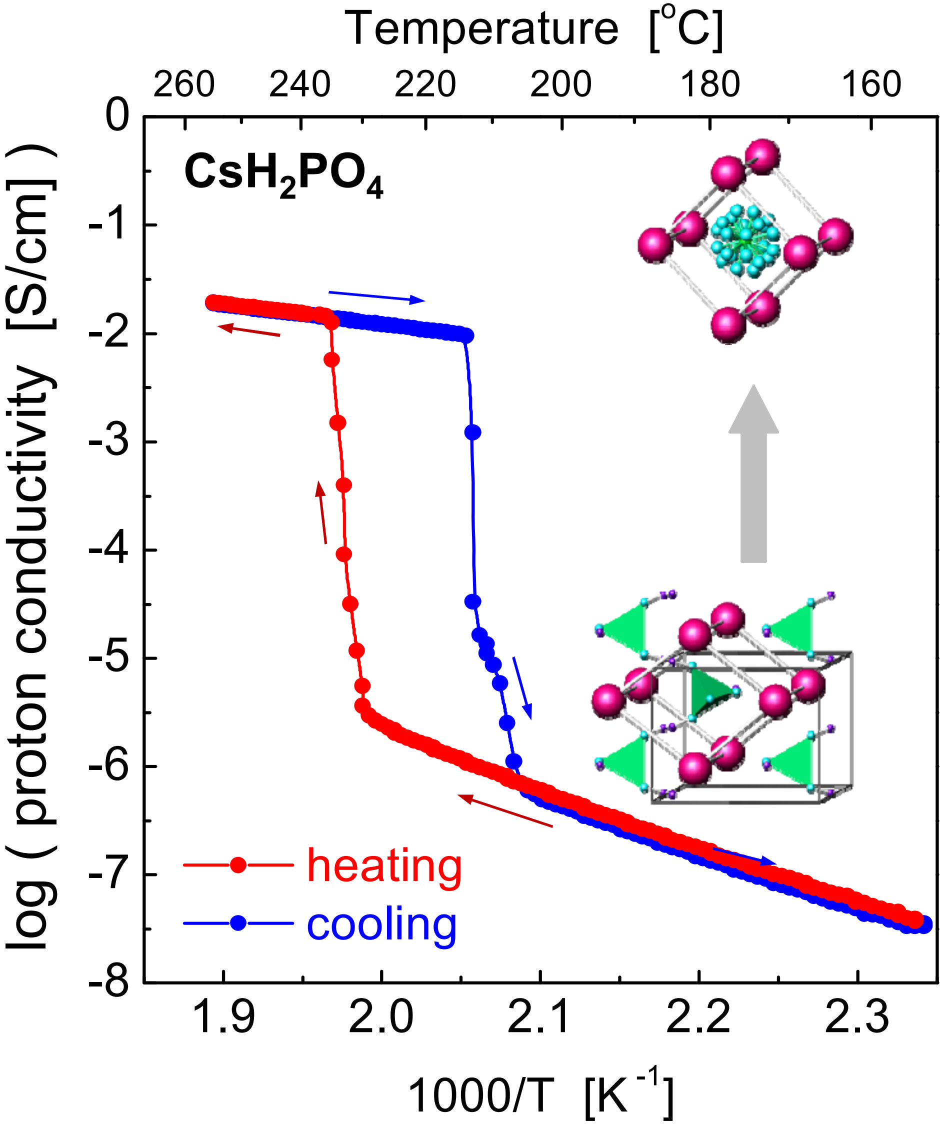
- Geometrically defined Pt current collectors on CsH_2PO_4, a superprotonic solid acid conductor
- Hydrogen electro-oxidation
- Objective:
  - Determine reaction pathway
  - Determine geometry independent triple-phase boundary resistance (per unit length)

Solid Acid Family of Compounds

- Acid salts
- MH_2XO_4, $MHXO_4$, $M_3H(XO_4)_2$
  - M = Cs, K, Rb, NH_4
  - X = S, P, Se, As
- “Superprotonic” transport



- CsH_2PO_4 is best choice for fuel cell electrolyte
  - Operate at T > 230 ºC
  - Humidify atmosphere



S. M. Haile. *Materials Today* **2003,** 24-29
M. W. Louie, M. Kislitsyn, K. Bhattacharya and S. M. Haile. *Solid State Ionics* **2010,** 181(3-4), 173-179

Technology Development Path

2001

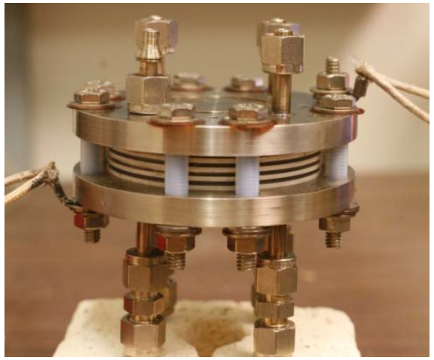
2004

Dane

Calum

Stable electrolyte

2007



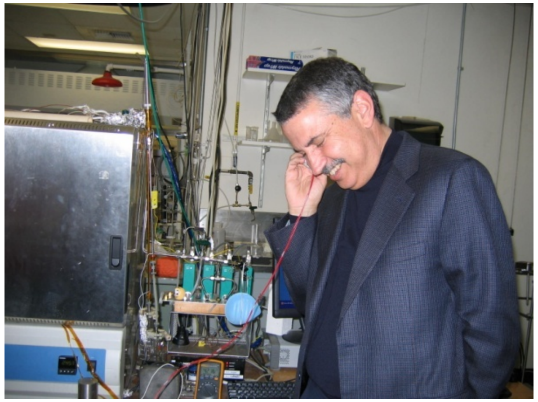
$15m in VC funds

Manufacturability

Durability

SUPERPROTONIC

2007



Tom Friedman talking on SAFC powered cell phone

2008

2008

2” MEA
20 cell stack
60 W net

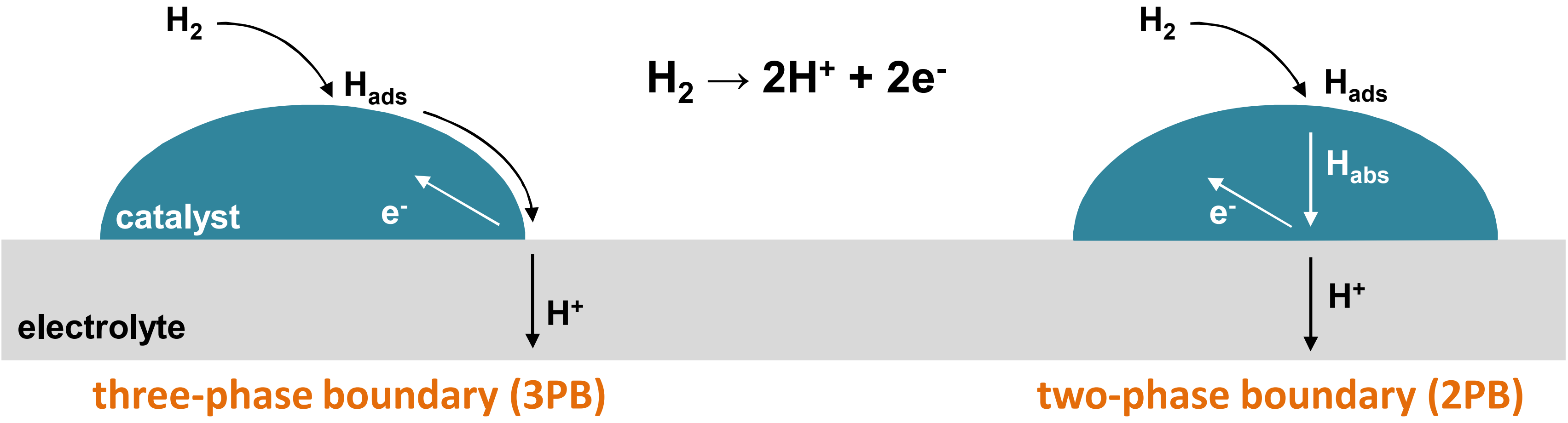
SAFCell, Inc.

2011...??

5” MEA
60 cell stack
1.4 kW net

Electrochemical reaction pathways

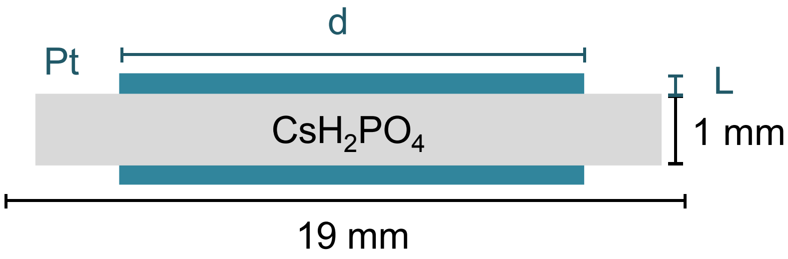
- Ions, electrons, adsorbates, gaseous/aqueous species interact across multiple phases

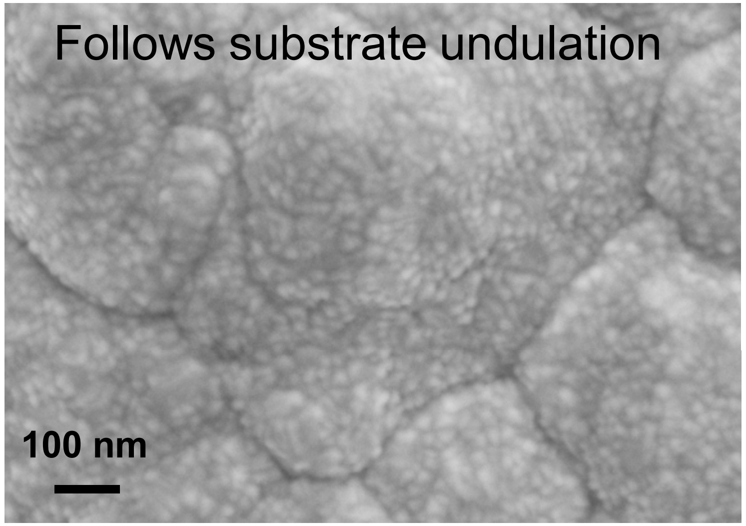


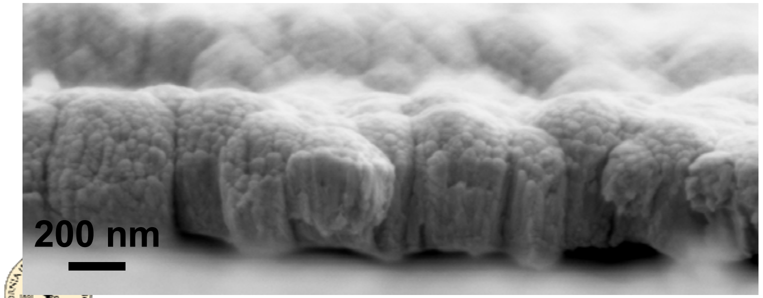
$$H_2 \rightarrow 2H^+ + 2e^-$$

- Kinetic parameters → choose electrode components and design structure

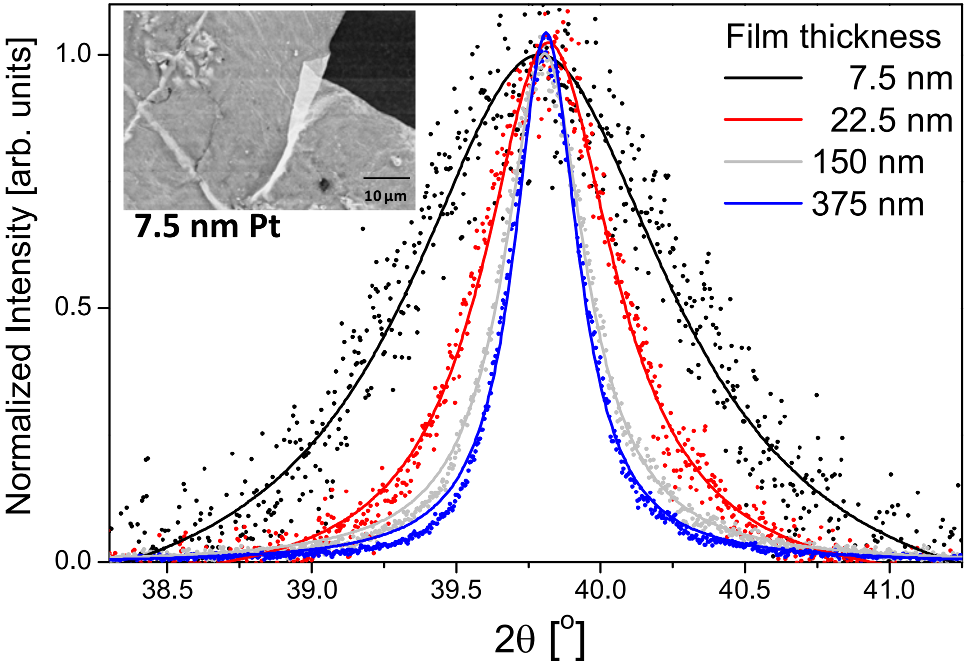
Pt | CsH_2PO_4 | Pt Symmetric Cells




Follows substrate undulation



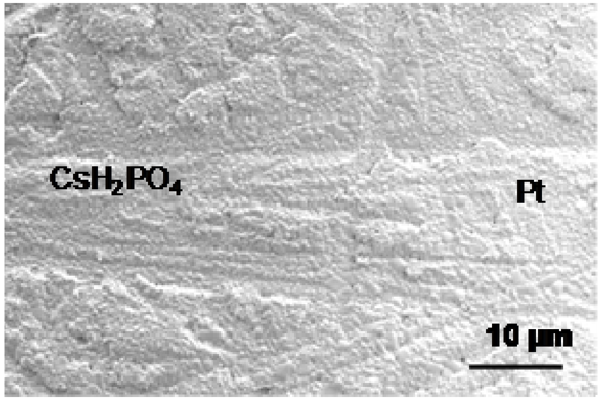
- Thin film Pt electrodes
  - Polycrystalline CsH_2PO_4 substrates
  - Deposition time → film thickness
    - 7.5 to 375 nm
  - Shadow-mask → film diameter
    - 1.3 to 19 mm

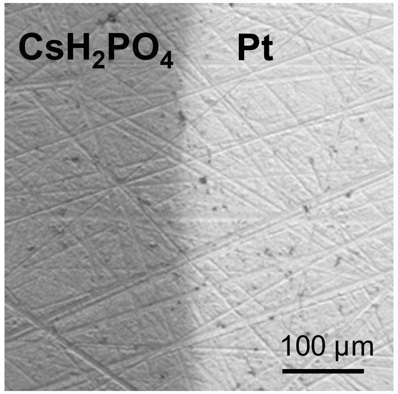


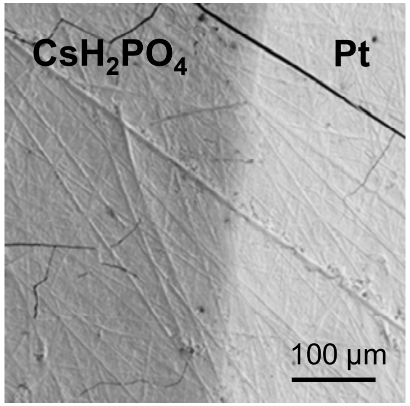
M. W. Louie, K. Sasaki and S. M. Haile. *ECS Trans*, **13**(28), 57-62 (2008)
M. W. Louie and S. M. Haile, *Eng. Env. Sci.* **4** (10), 4230-4238 (2011)

Challenging Characteristics

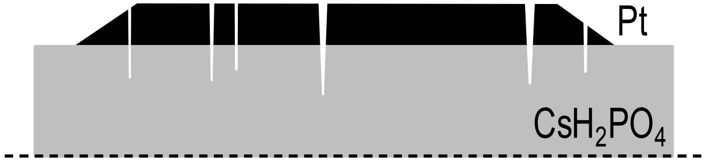
- Sputter deposition with shadow masks
  - Shallowly defined edges, sloped region ~40 μm, $<$ 10% of total




as-deposited


***after* transition**

- Deposition on undulating surface
  - Suggests thickness variation; on smooth surface ± 2%
- Phase transformation of CsH_2PO_4
  - Generation of microcracks, transmitted to Pt; 9 ± 4 mm/mm^2

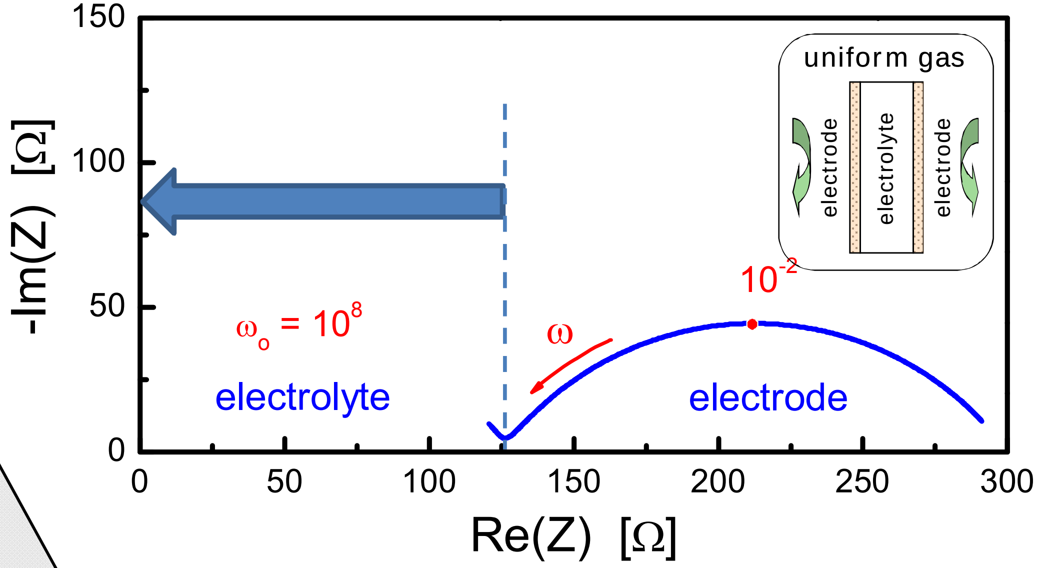


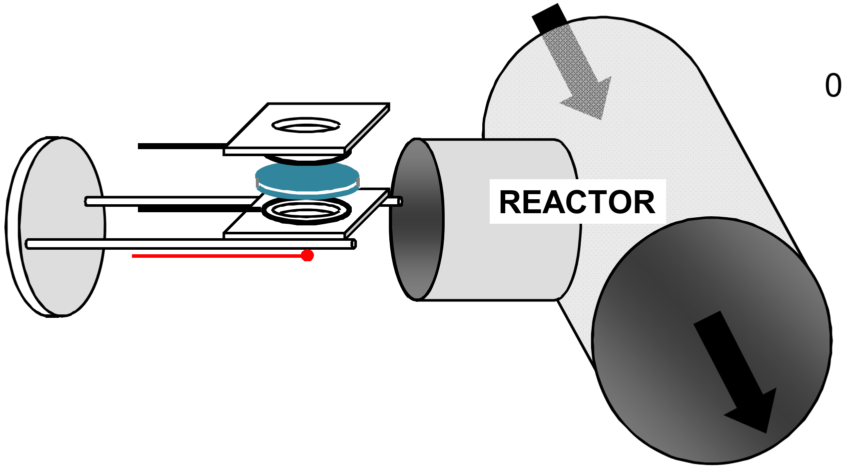
- Sputter deposition
  - Possible inherent porosity

Electrochemical Measurements

- Current collectors
  - Toray carbon paper
- Conditions
  - 200–250 °C
  - 0.06–0.5 atm H_2
  - 0.3–0.5 atm H_2O
  - No gradient

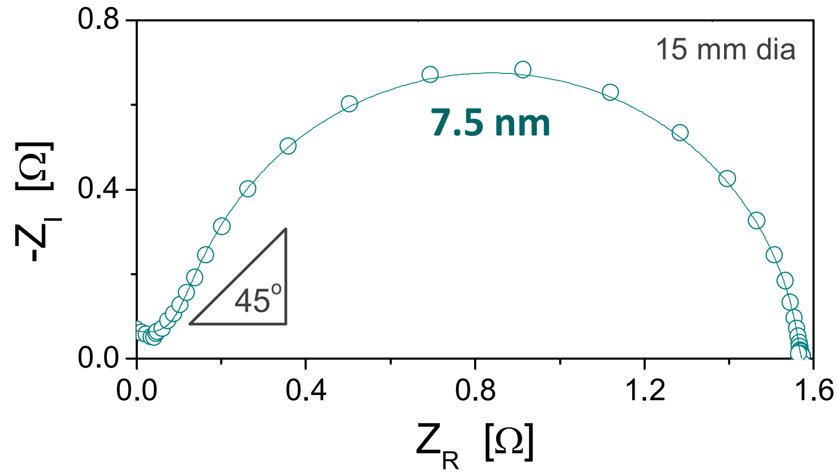
- Zero bias impedance
  - 0 ± 10 mV
  - 1 MHz – 100 mHz

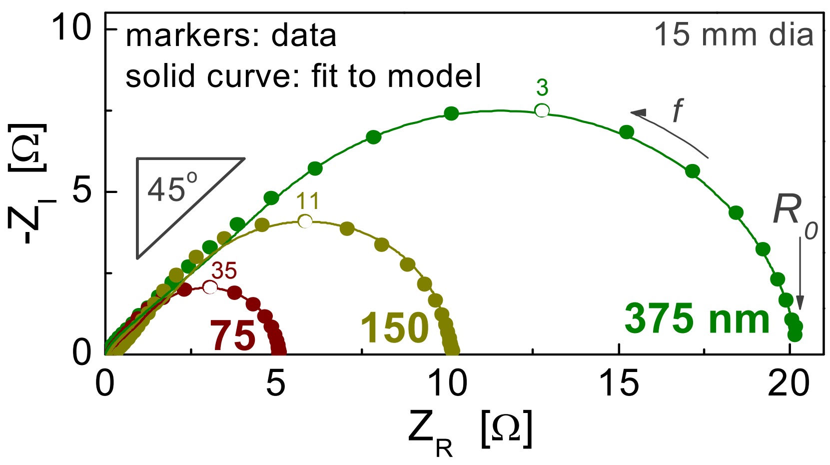




- Subtract ohmic contributions

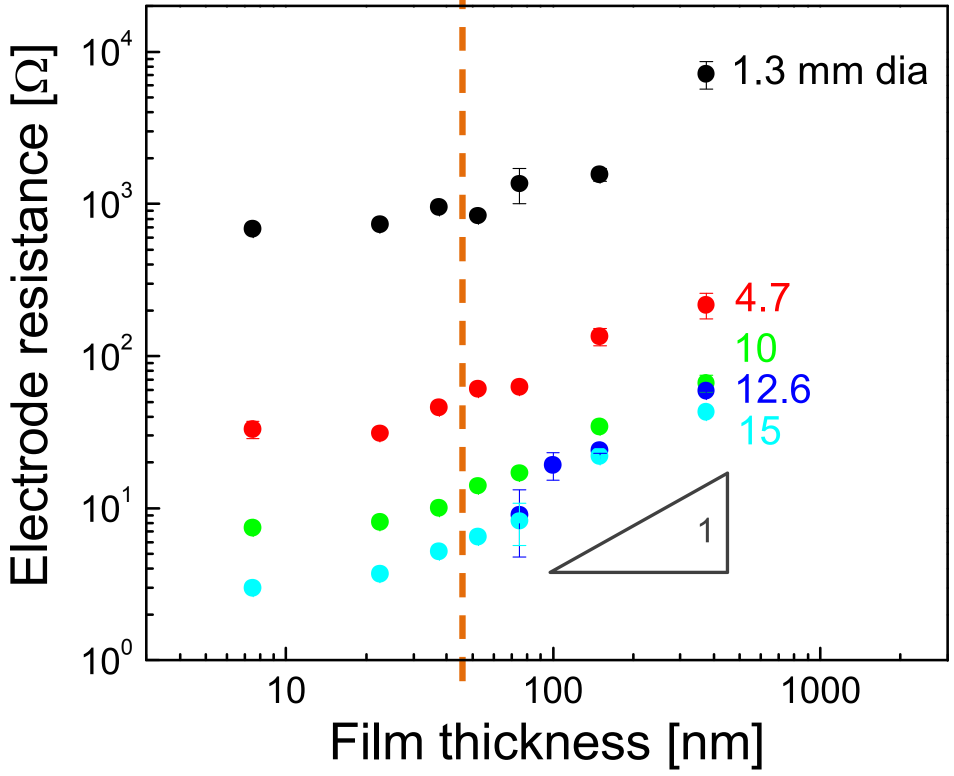
Thickness Dependence of Response





Regime II

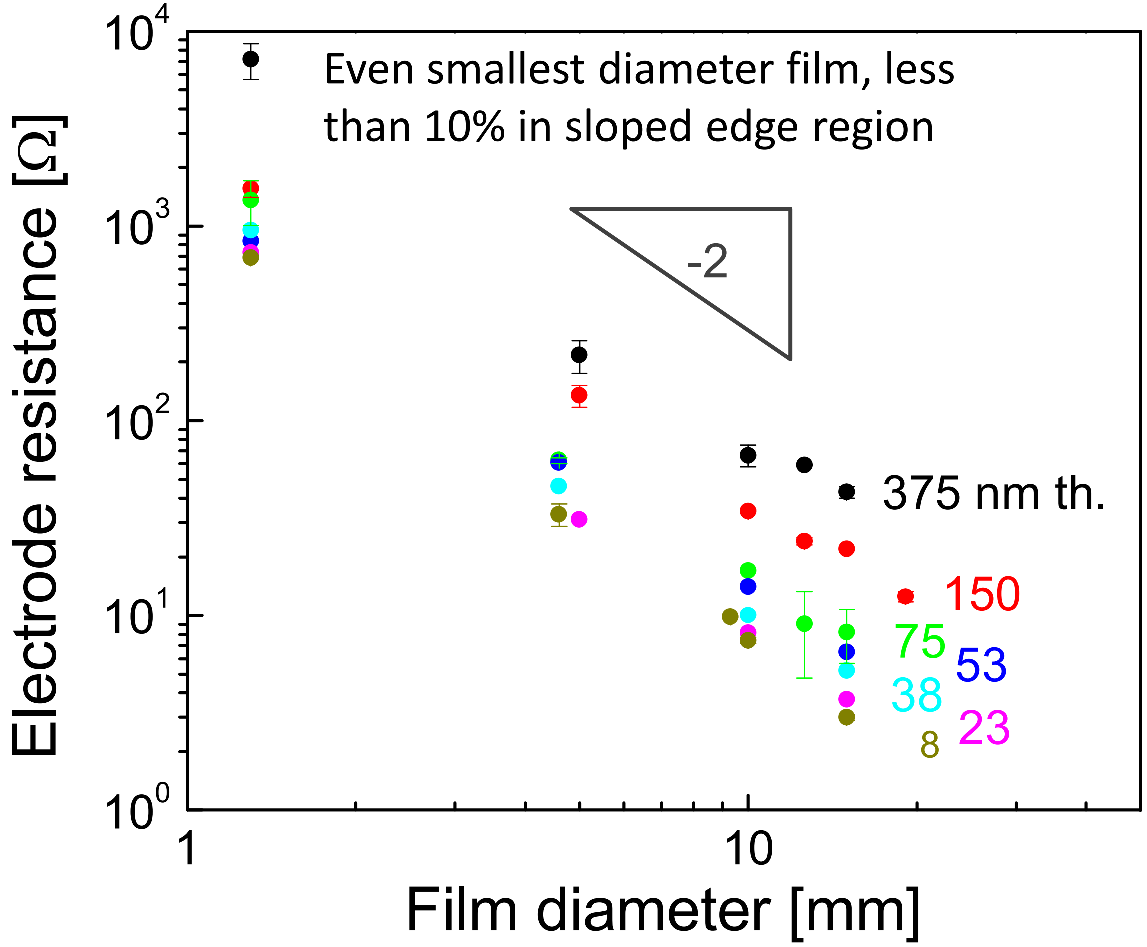
Symmetric Arc
WEAK Thickness
Dependence



Regime I

Asymmetric Arc
STRONG Thickness
Dependence

Diameter Dependence of Response

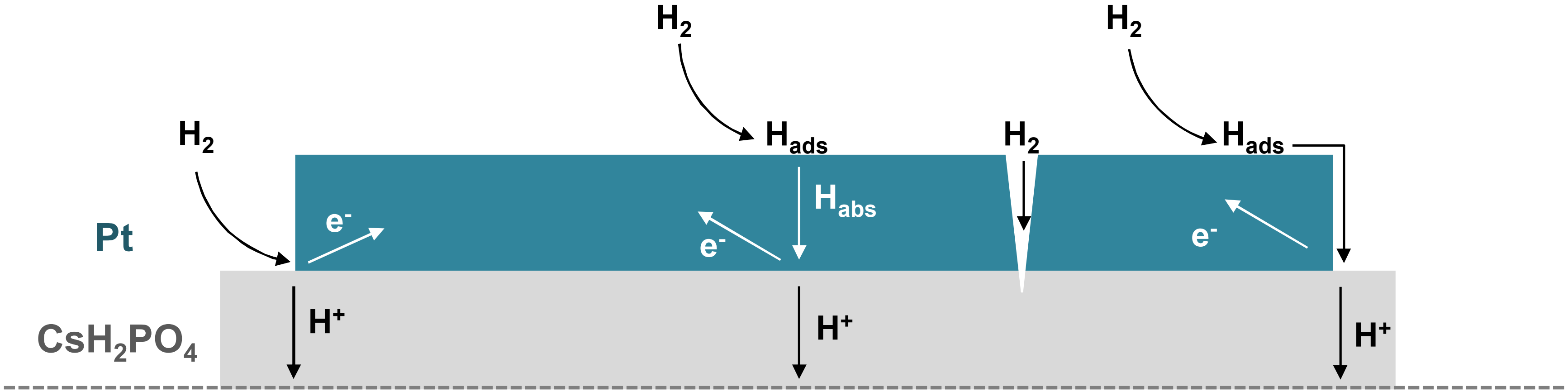


Even smallest diameter film, less than 10% in sloped edge region

Electrode resistance $\propto$ d^{-2}

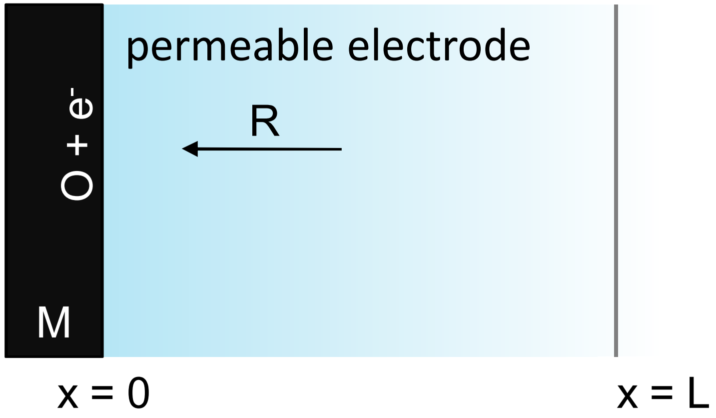
Regime I: Thick Pt Films

- Thickness and area-dependent electrode process
- Half tear-drop, Warburg arc

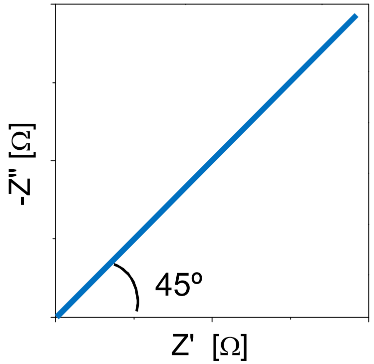


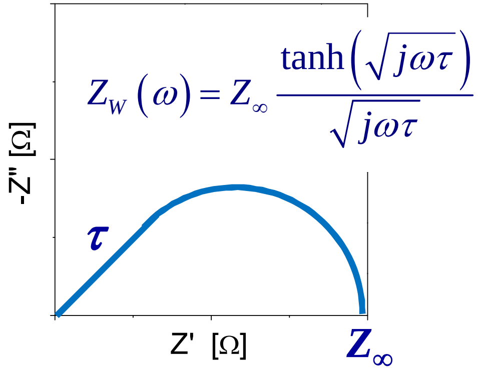
- Implies rate-limiting process is diffusion!
- Warburg arc in Nyquist plot is a feature of diffusion
- What kind of diffusion?

Warburg Diffusion

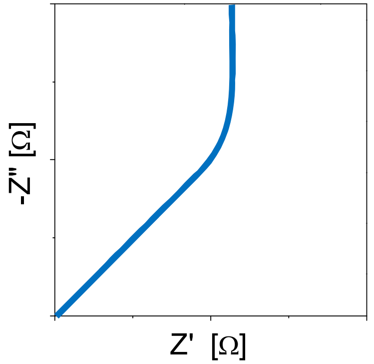


$$\frac{\partial c_i}{\partial t} = D\frac{\partial^2 c_i}{\partial x^2}$$





$$Z_W(\omega) = Z_\infty \frac{\tanh\left(\sqrt{j\omega\tau}\right)}{\sqrt{j\omega\tau}}$$

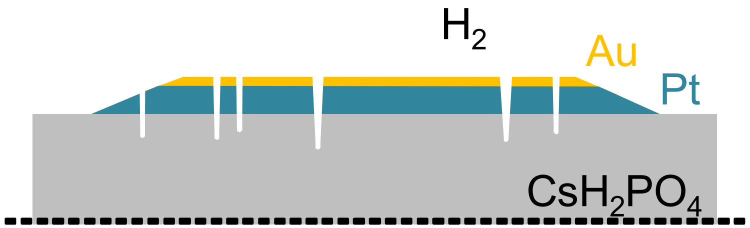


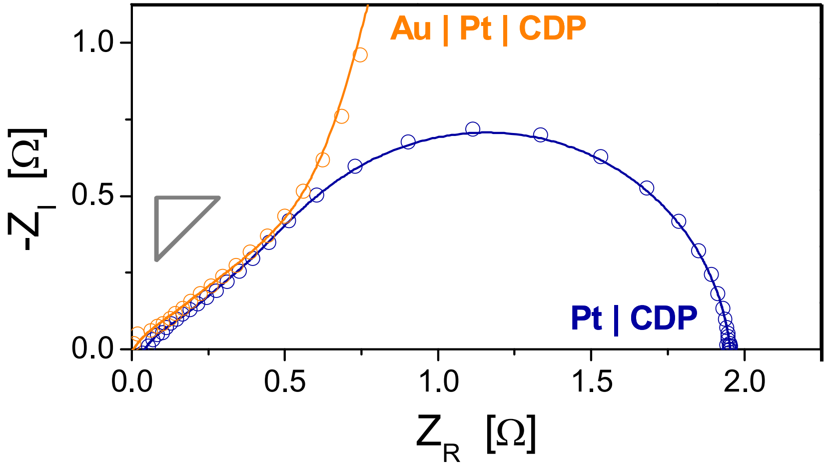
Boundary conditions

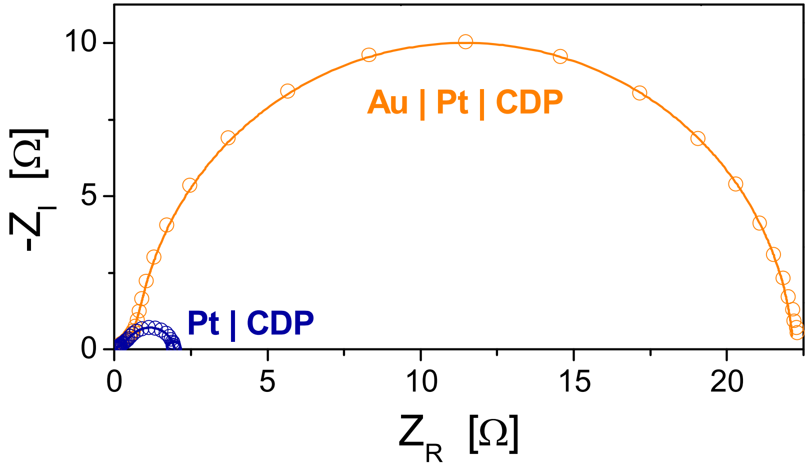
- Infinitely fast charge transfer at x = 0
- For semi-infinite diffusion, x = ∞
- For bounded diffusion @ x = L
  - Reversible electrodes (fast supply of R)
  - Irreversible “blocking” electrodes

Regime I: Thick Pt Films

- Diffusion with reversible bounds
  - Gaseous? Pore walls? Bulk?







- Diffusion process remains
- Large blocking arc

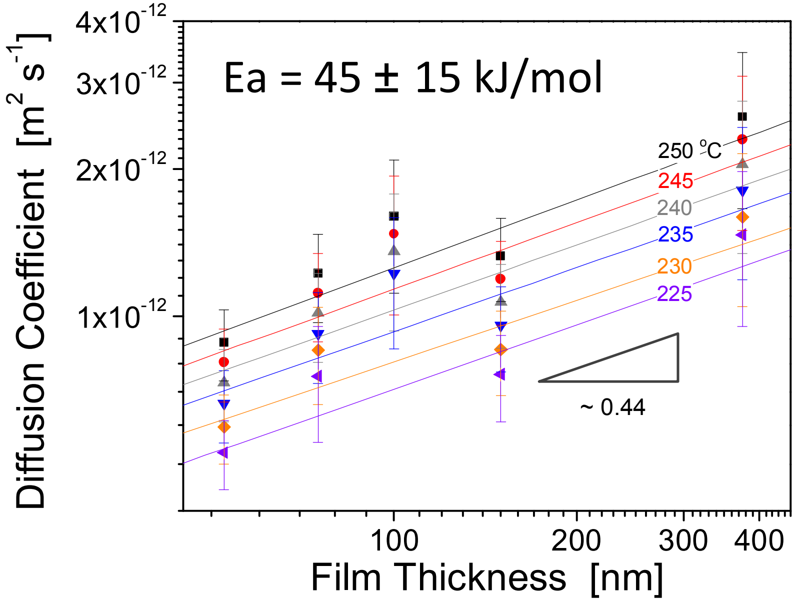
→ Pathway involves metal|gas interface, followed by diffusion

→ H_2(g) through pores negligible

Quantitative Analysis of Diffusion

$$Z_W(\omega) = Z_\infty \frac{\tanh\left(\sqrt{j\omega\tau}\right)}{\sqrt{j\omega\tau}}, \qquad \tau = \frac{L^2}{D_H}, \qquad Z_\infty = \frac{A}{L}\frac{k_b T}{(ez)^2 c_H D_H}$$

Finite-length Warburg equation

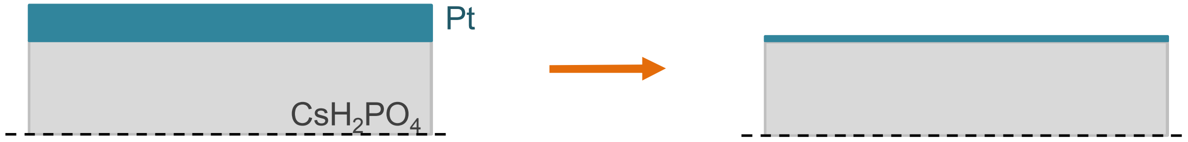


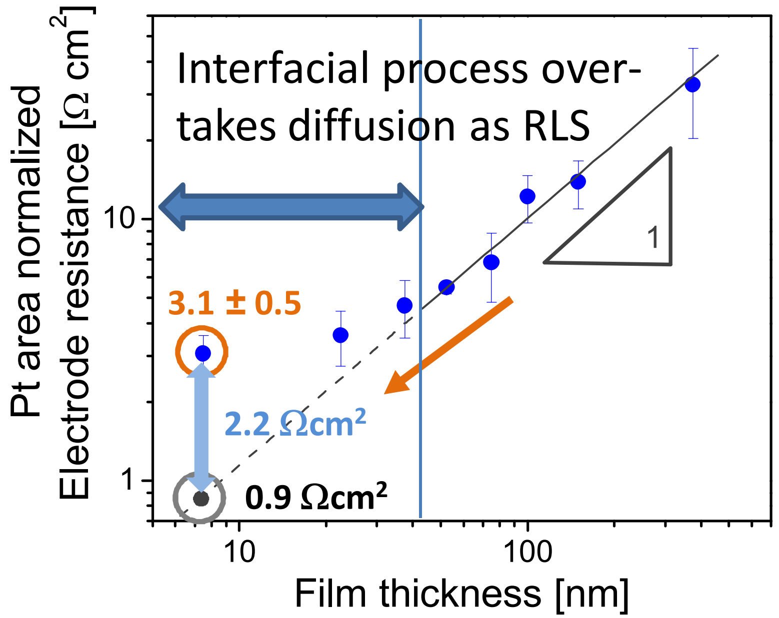
T [°C]	D_H [$\times10^{-12}$ m^2 s^{-1}]	c_H [$\times10^{-4}$ H/Pt]
250	1.6 ± 0.7	2.4 ± 0.8
225	0.9 ± 0.5	2.8 ± 0.8

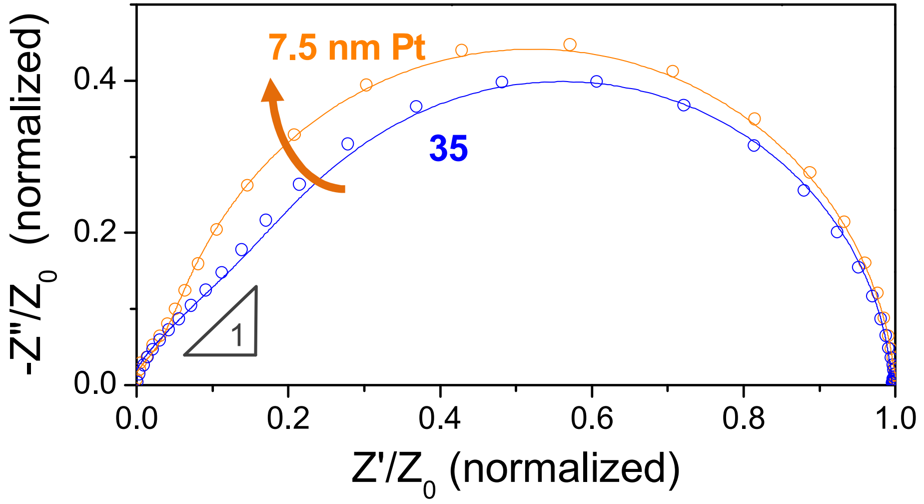
Apparent grain size dependence of D_H

Consistent with interstitial hydrogen diffusion

Regime II: sub-30 nm Pt Films







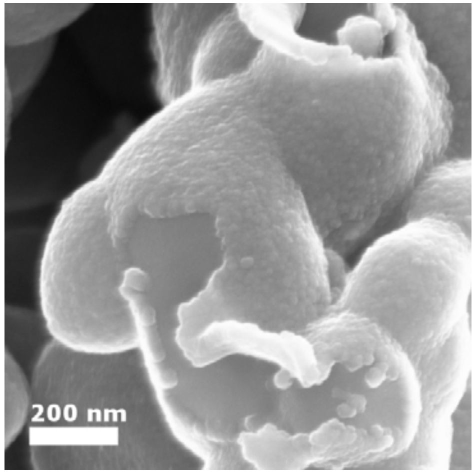
- Decreasing thickness will provide limited benefit
- Reaction resistance is 71% of total for 7.5 nm films
- Stability challenge: thinner films coarsen

Implications for Solid Acid Fuel Cells

Anode performance comparison

Electrodes	**Resistance** $\Omega\ cm^2$	**Pt loading** mg/cm^2	**Loading-normalized performance** *S/mg*
8 nm Pt film (*sputter depos.)*	3.1 ± 0.5	0.017	19

- Improved utilization of Pt
- 50-fold increase in surface area
  - 0.06 Ωcm^2; 0.85 mg/cm^2
- Scalable strategies for nanoparticle synthesis, Pt incorporation
  - Electrospray deposition, Pt-AcAc CVD



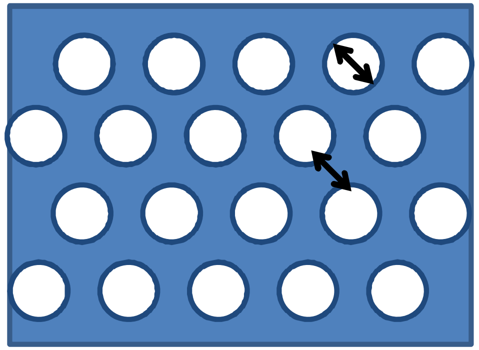
A. B. Papandrew, C. R. I . Chisholm, R. A. Elgammal, M. M. Ozer and S. K. Zecevic. *Chem Mat* , accepted

[1] A. Varga, N. A. Brunelli, M .W. Louie, K. P. Giapis and S. M. Haile. *J Mater Chem* **2010**, 22(3), 1186-1194

[2] S. M. Haile, C. R. I Chisholm, K. Sasaki, D. A. Boysen and T. Uda. *Faraday Discuss* **2007**, 134, 17-39

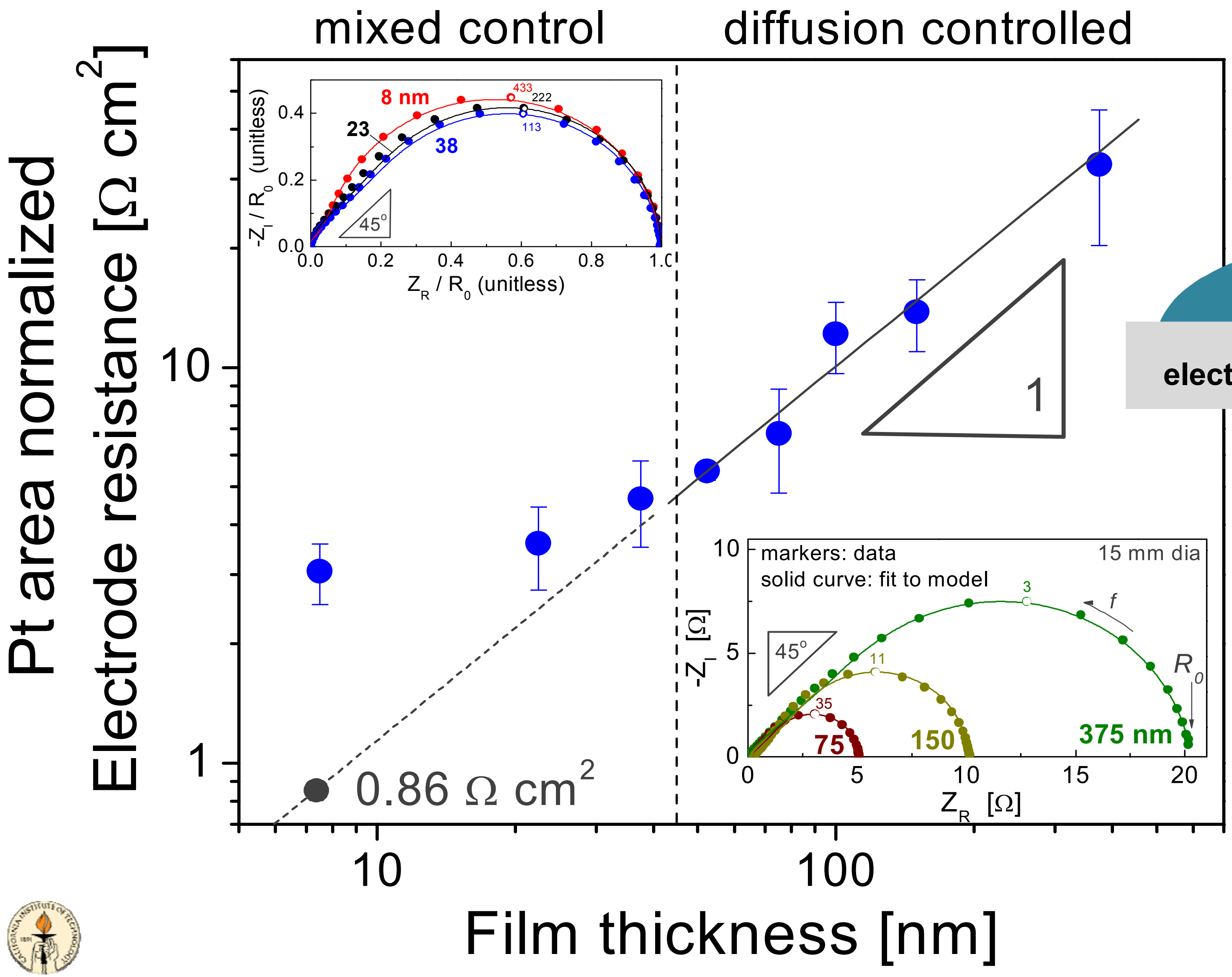
Implications for Solid Acid Fuel Cells

- Is there a role for triple phase boundaries?
- Geometry utilized disfavors TPBs (too few)
- Au overlayer blocks two-phase pathway
  - Permits estimation of lower bound resistivity: 41 kΩ cm
- Consider geometry required for comparable activity from TPBs and two-phase pathway
  - Porous, 7.5 nm thick film
  - Area/perimeter = 7.6 μm
  - Finer structure required if ρ(TPB) exceeds lower bound

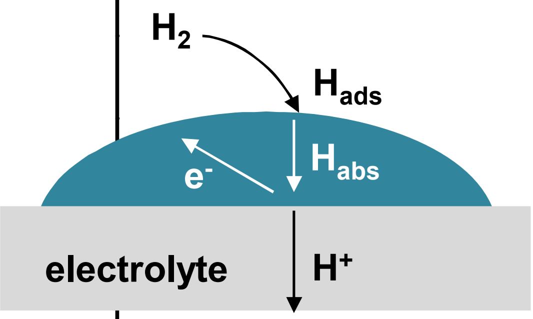


~9 μm

Summary: 2-Phase Pathway Dominates



$H_2 \leftrightarrow 2H^+ + 2e^-$

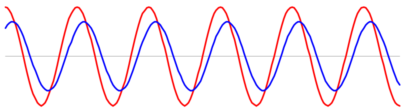


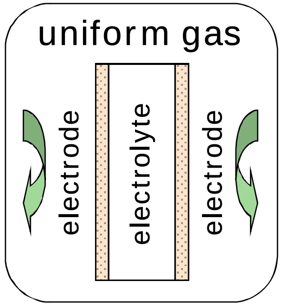
This work: Part III

- Geometrically **asymmetric, nanoscale** Pt current collectors on $CsHSO_4$, a surrogate superprotonic solid acid conductor;
  - Superprotonic transition at 141 ^{o}C
- Oxygen electro-reduction
- Objective:
  - Uncover nanoscale heterogeneity in electrode kinetics
  - Ultimately, if such heterogeneities exist, design electrodes that maximize high activity sites

Challenge of Symmetric Cells

$$Z(\omega) = \frac{V(\omega)}{I(\omega)}$$

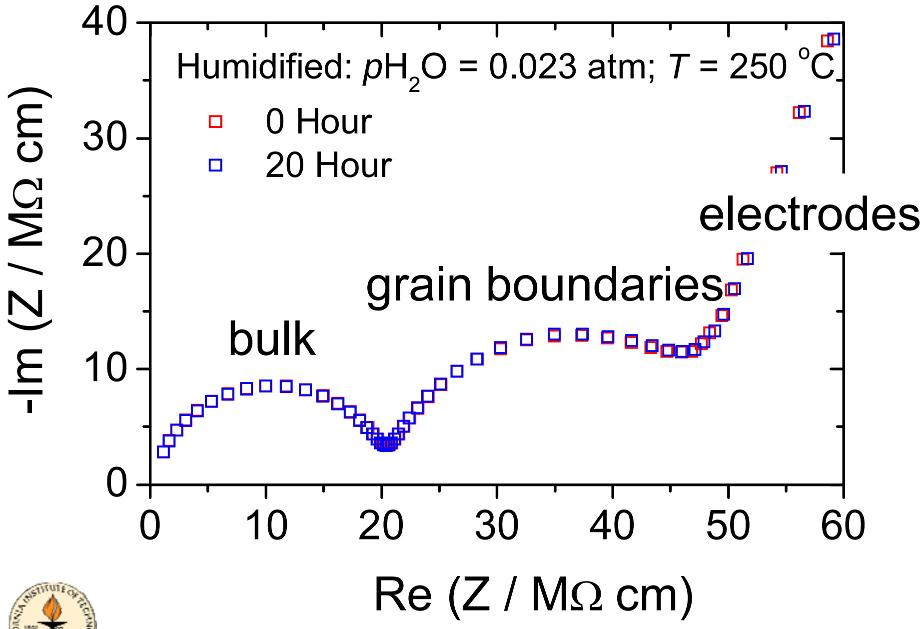


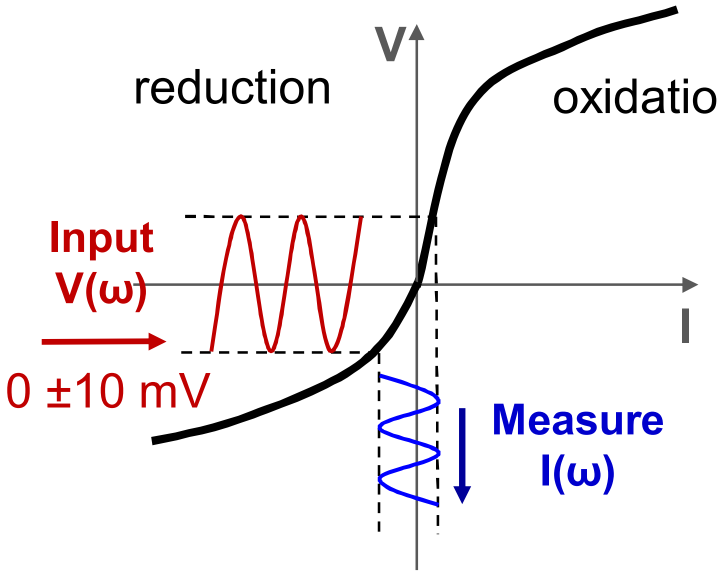


Bulk: linear and symmetric (Ohm’s law)

Grain boundaries and **electrodes**

Non-linear and asymmetric





measure

$$\langle R \rangle = \frac{\Delta V}{\Delta I}$$

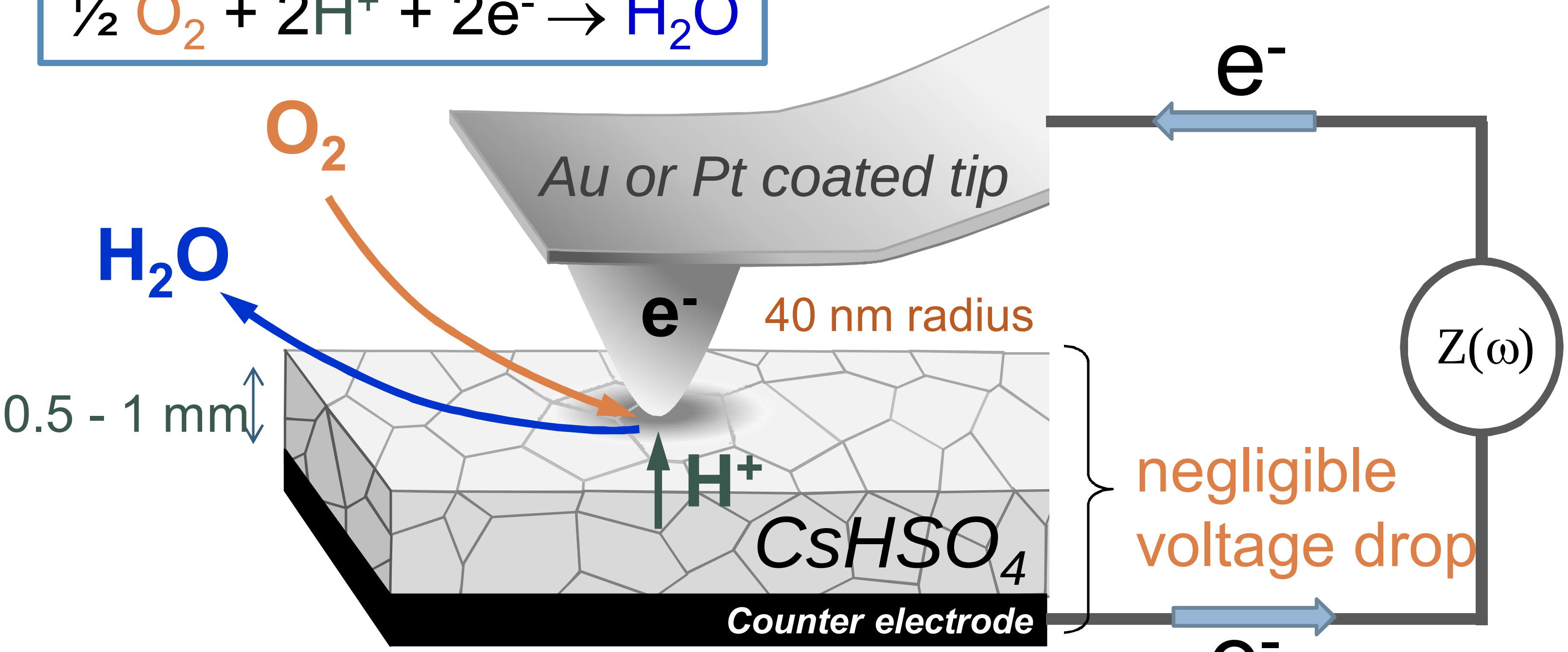
want

$$R(I) = \frac{\partial V}{\partial I}$$

Nanoscale Electrodes

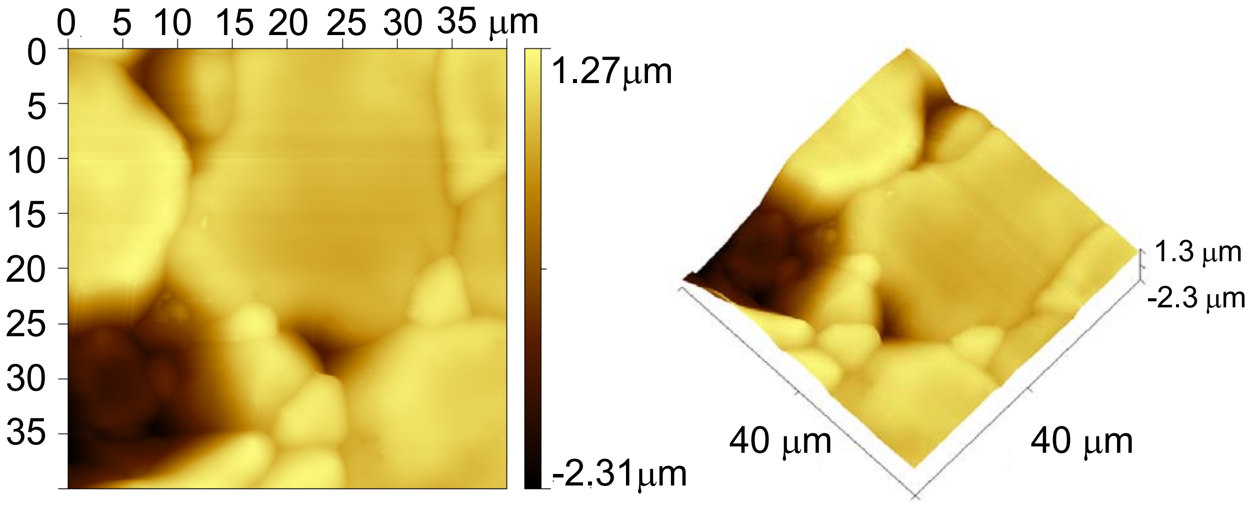
- ☐ Asymmetric geometry isolates electrode behavior
- ☐ Objective: identify highly active sites/features

$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$



$H_2O \rightarrow \frac{1}{2} O_2 + 2H^+ + 2e^-$

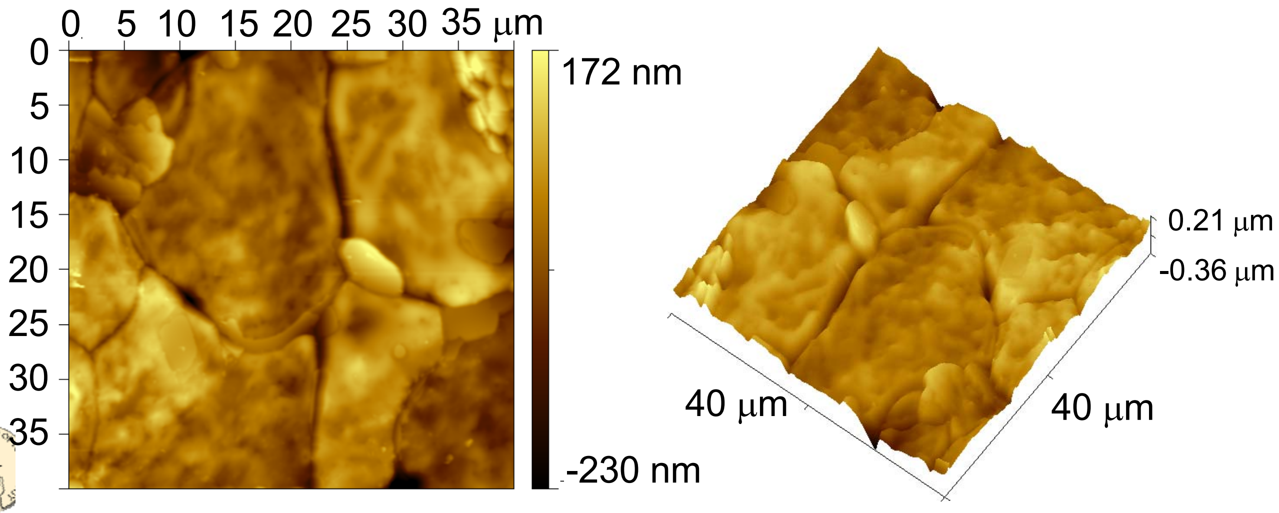
Typical Surface Features



CsH_2PO_4 (CDP)

T_{SP} = 228 °C

Active humidification required for operation



$CsHSO_4$ (CHS)

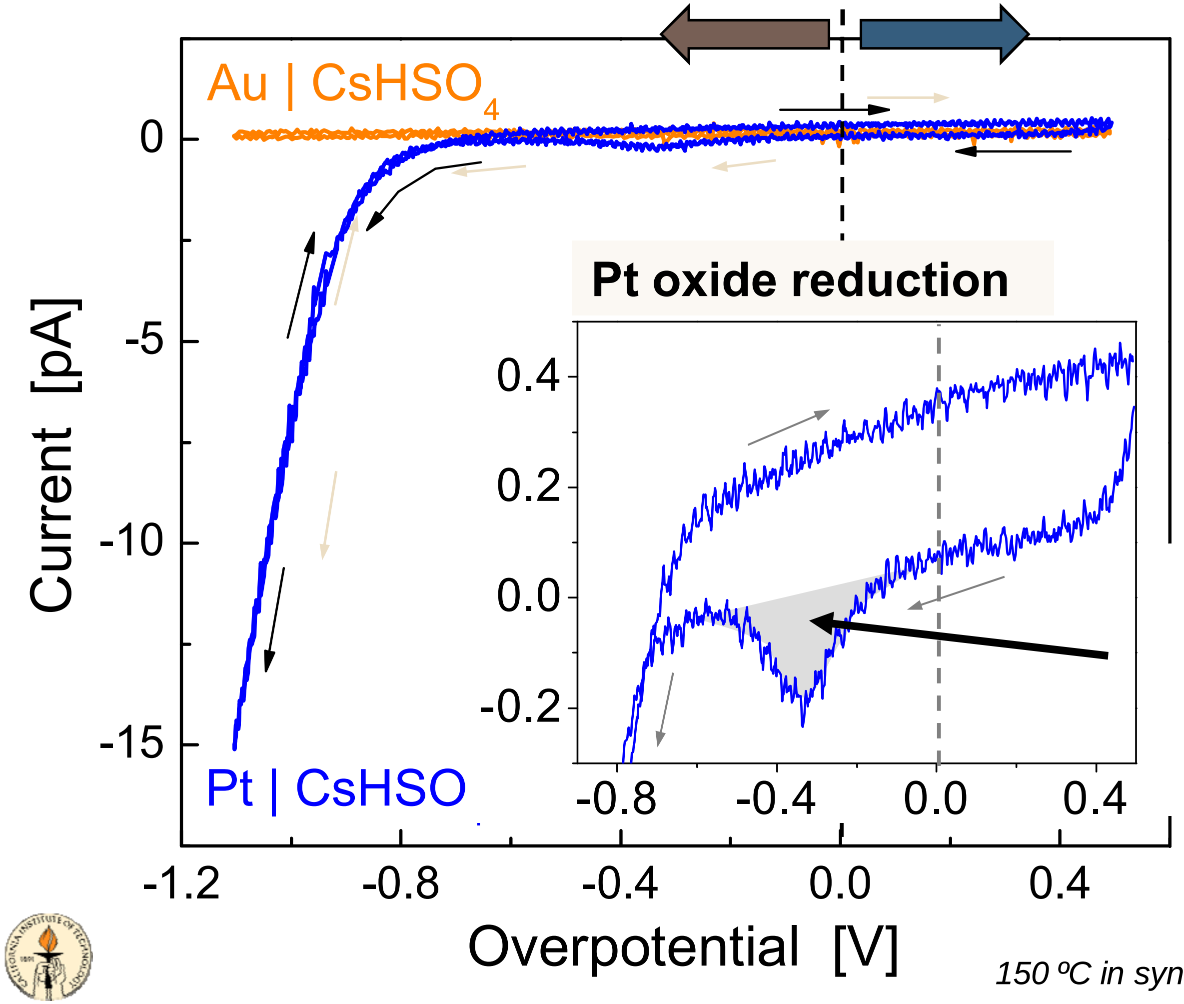
T_{SP} = 141 °C

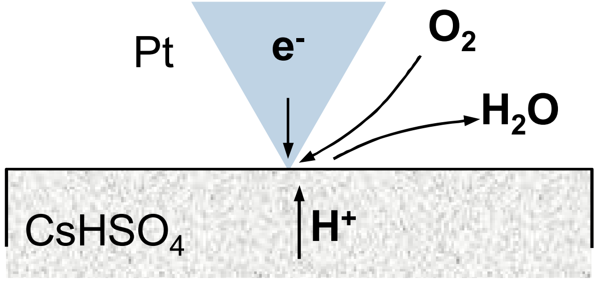
No such requirement

Pt | $CsHSO_4$

$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$





Onset ~ -0.1 V, PtO or PtO_2

e.g. PtO

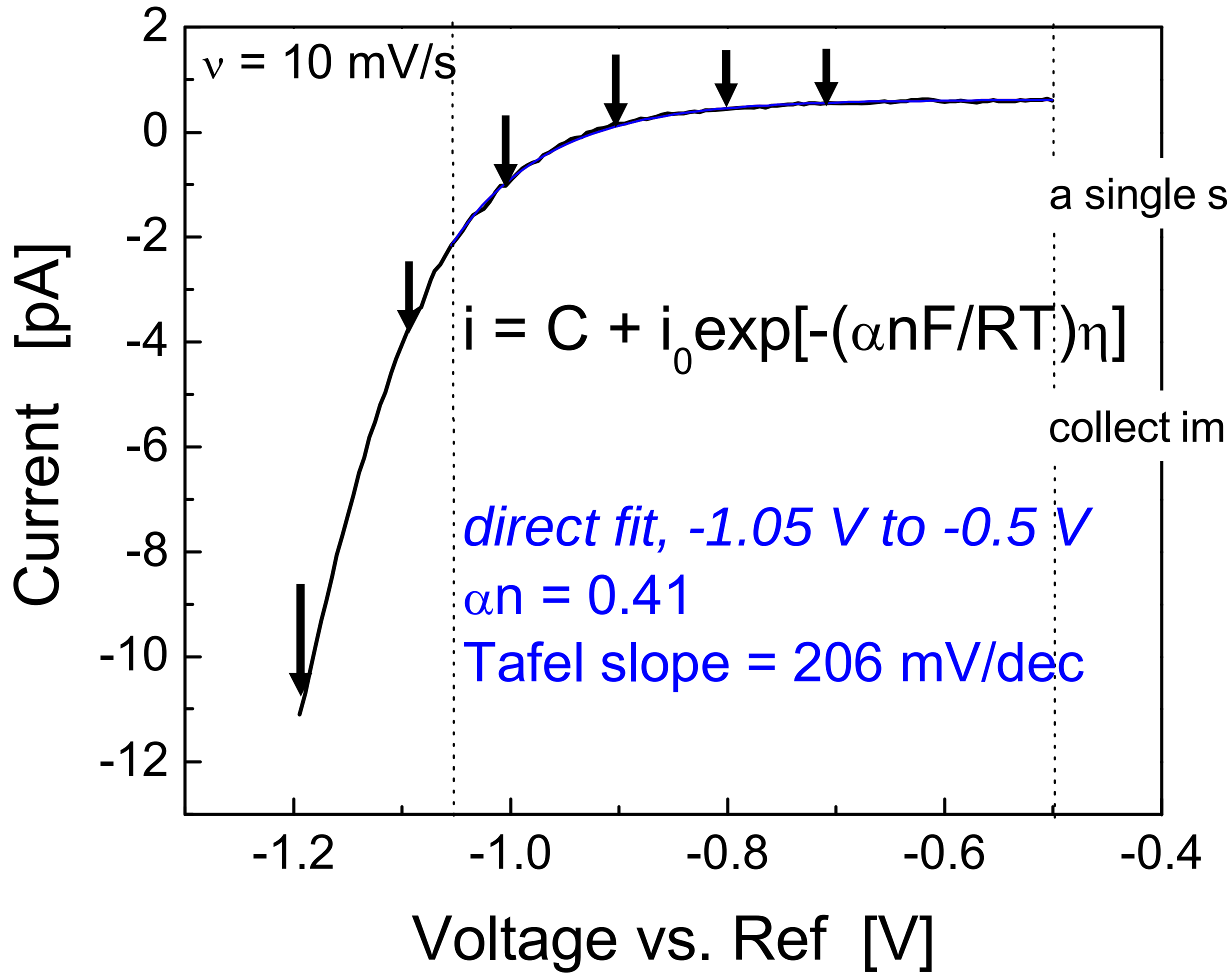
$PtO + 2H^+ + 2e^- \rightarrow Pt + H_2O$

Peak area ~ 5×10^{-13} C

150 ºC in syn. air w/ ~0.03 atm H_2O, 100 mV/s, ~0.3 µN

Oxygen electroreduction on Pt

T_{surf} ~ 150 °C, ambient air, pO_2 = 0.21 atm, pH_2O = 0.02 atm, Force ~ 1.4 uN



$i = C + i_0 \exp[-(\alpha n F/RT)\eta]$

direct fit, -1.05 V to -0.5 V

$\alpha n = 0.41$

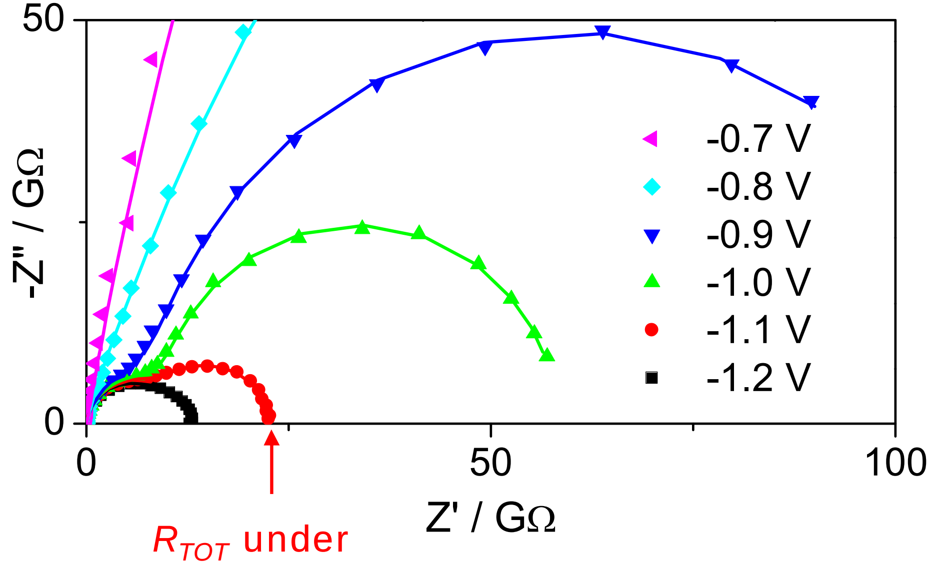
Tafel slope = 206 mV/dec

a single step / process?

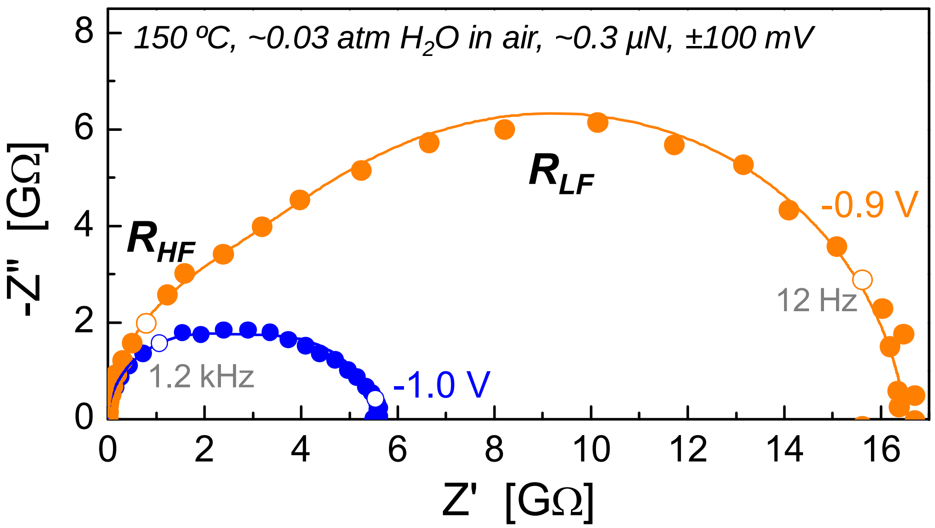
collect impedance spectra

Oxygen electroreduction on Pt

- Impedance spectra under bias
  - *Two processes visible*
  - *Spectra measurable only where current is sufficient*
  - *Different tips display similar, not identical, features*

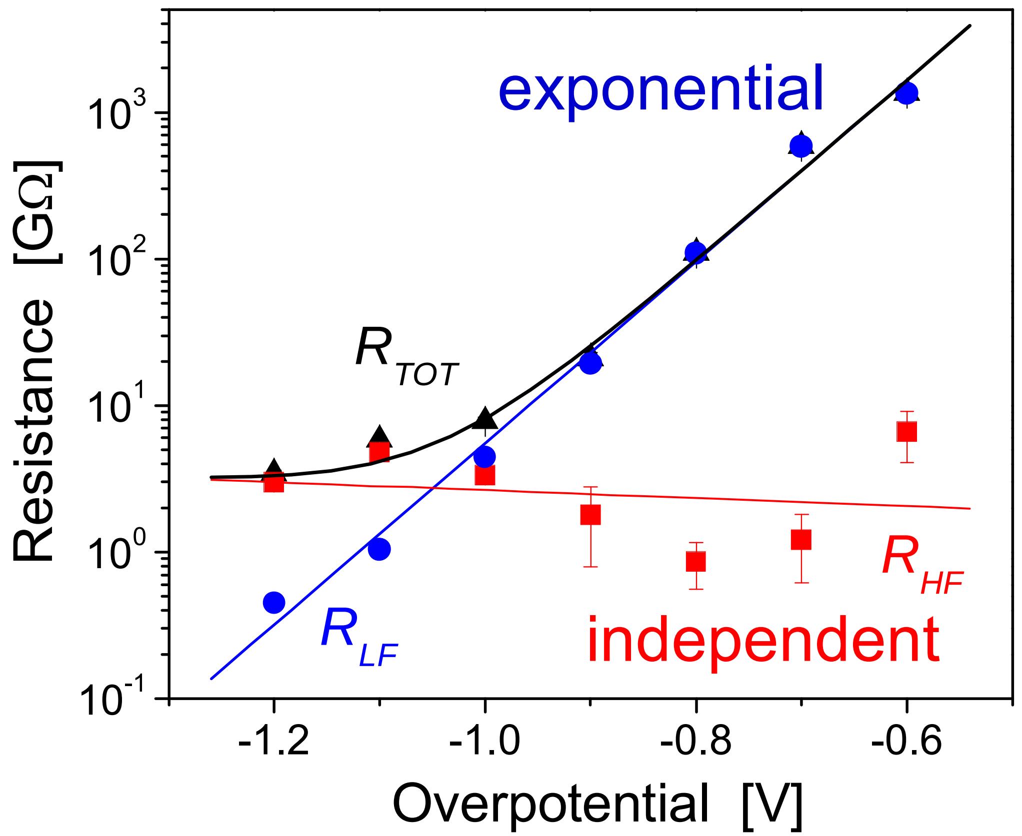


R_{TOT} under -1.1 V bias


150 ºC, ~0.03 atm H_2O in air, ~0.3 µN, ±100 mV

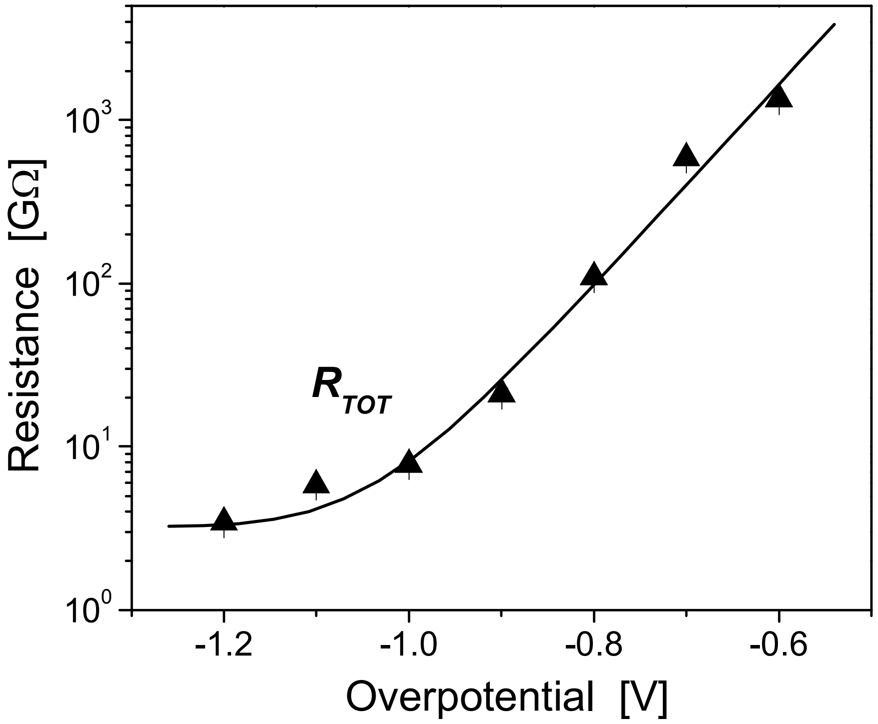
- ☐ Multiple processes hidden in d.c. measurement
- ☐ High ω arc is ~bias independent, low ω arc ↓ with ↑ bias

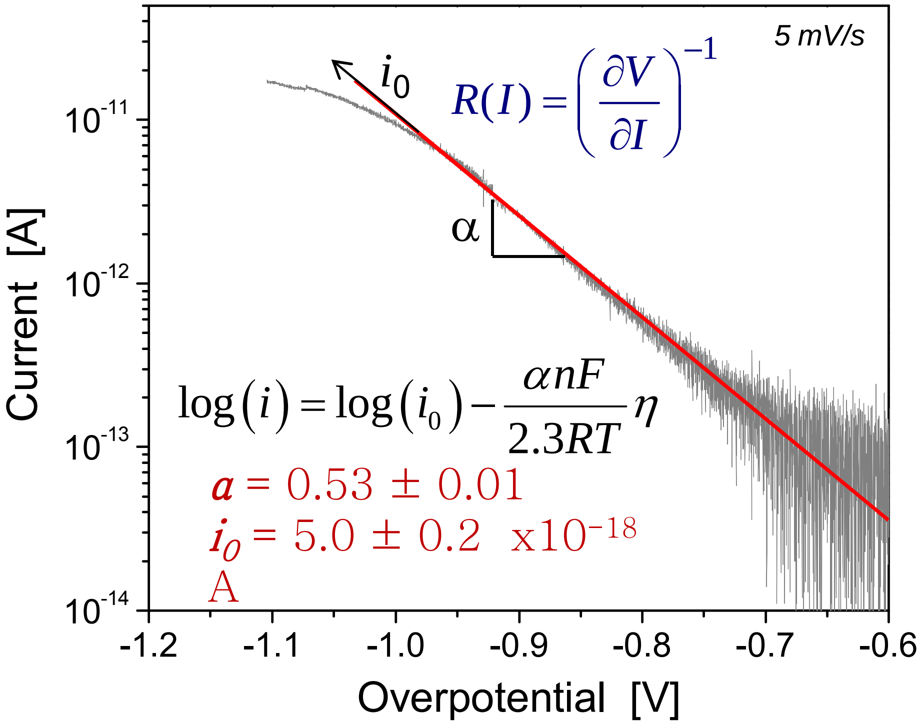
Analysis of Oxygen Electro-reduction



- R_{LF}
  - Tafel-like behavior
  - Dominates at small η
- R_{HF}
  - Ohmic behavior
  - Dominates at large η
- R_{TOT}
  - Too large at small η
  - Reflects R_{HF} at intermed

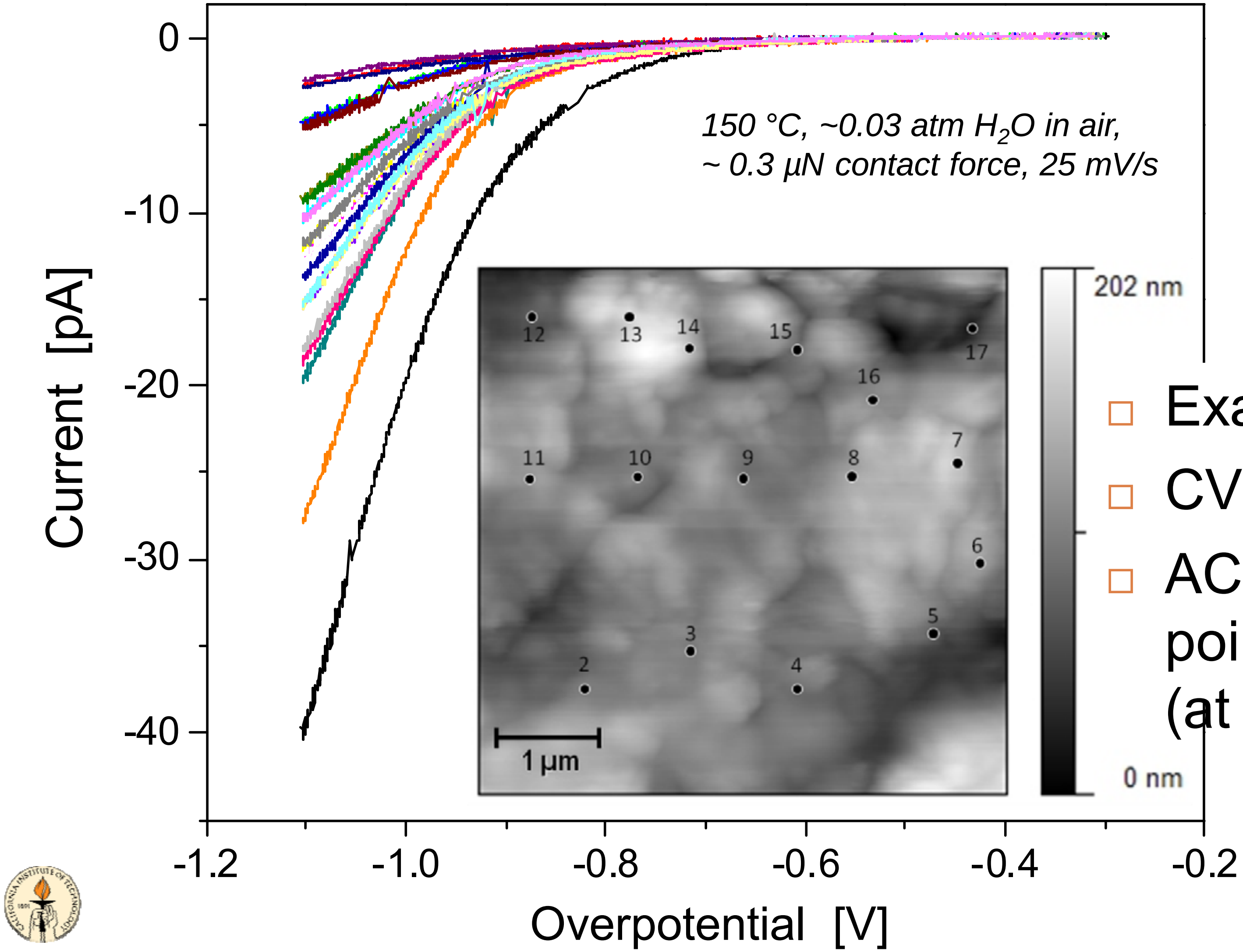
DC vs. AC Response





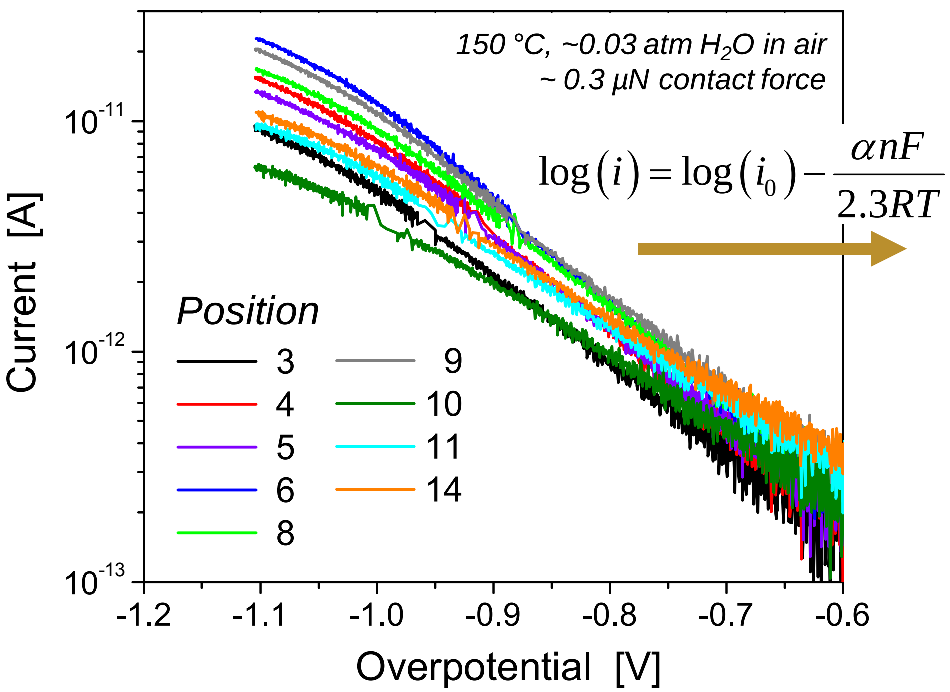
- Agreement between AC and DC
  - DC for quantitative analysis, AC for clarification
- Linear regime dominates voltage range of interest
  - Butler-Volmer kinetics for charge transfer

Spatial Variation of Electrocatalysis



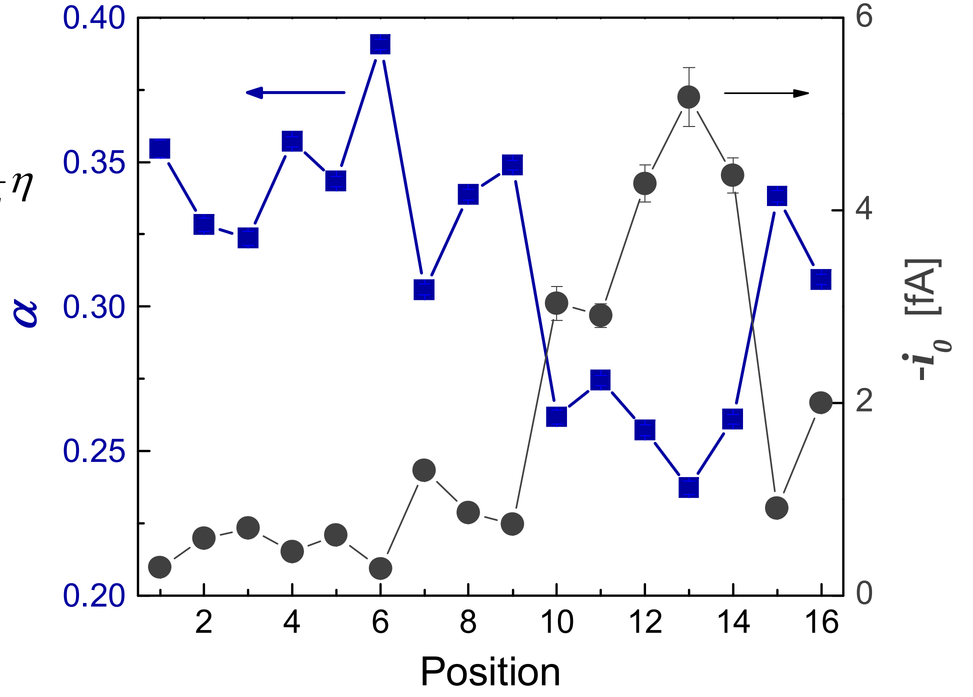
- □ Example scan
- □ CV at 16 positions
- □ ACIS at select points
  (at -1 and -0.9 V)

Spatial Variation of Electrocatalysis

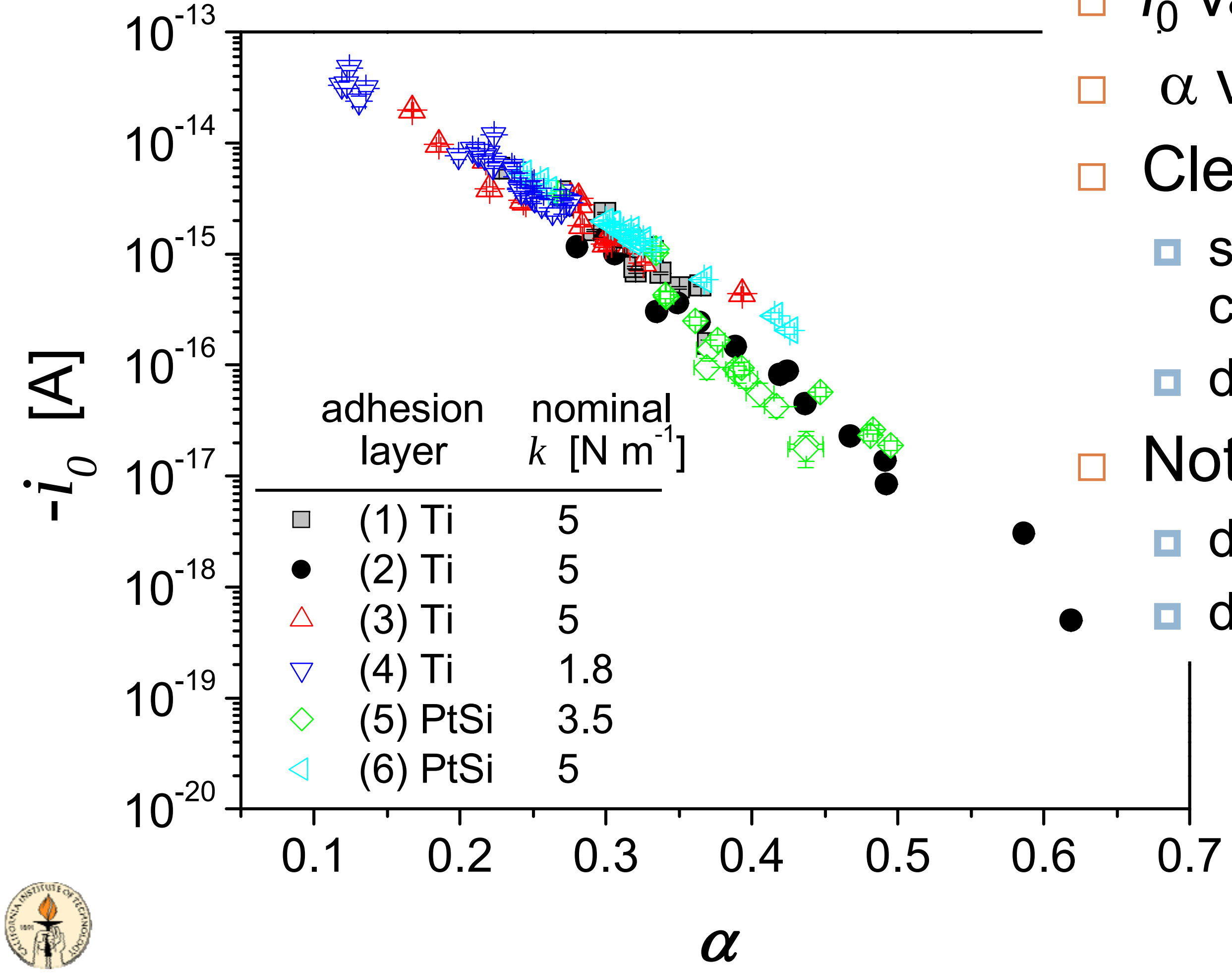


150 °C, ~0.03 atm H_2O in air
~ 0.3 μN contact force

$$\log(i) = \log(i_0) - \frac{\alpha n F}{2.3RT}\eta$$

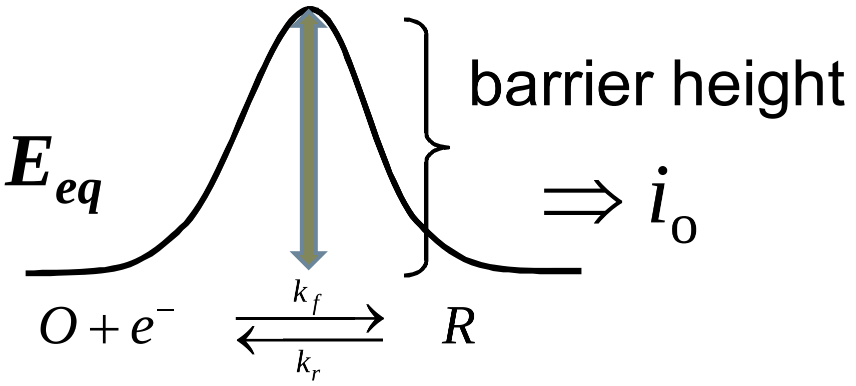


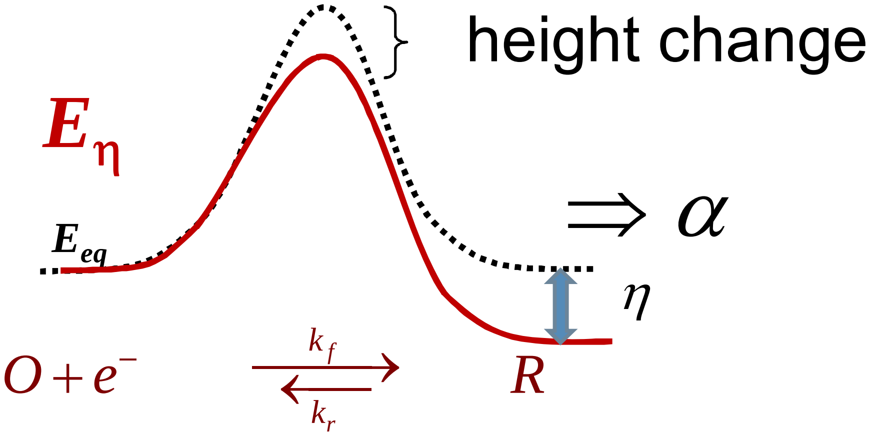
Unexpected Correlation



- i_0 varies by 10^5
- α varies from 0.1 to 0.6
- Clear correlation
  - six different tips, chemistries
  - different force constants
- Not due to
  - differences in force
  - differences in contact area

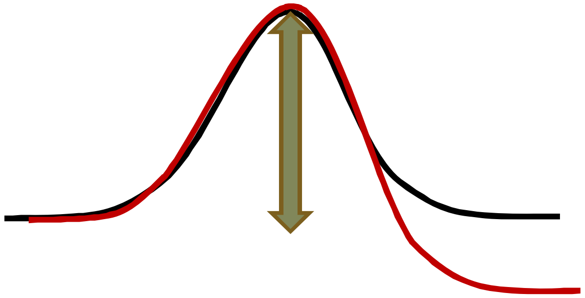
Physical Interpretation





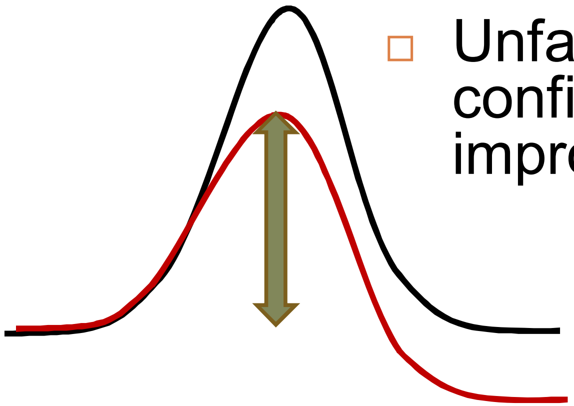
Two extremes

- Large i_o, small α



- Favorable configuration does not improve under bias

- Small i_o, large α



- Unfavorable configuration improves

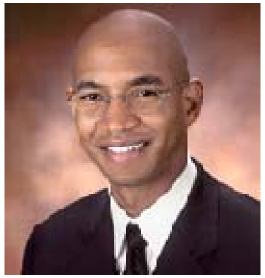
Summary

- Ceria-metal anode composites are dominated by activity of the oxide component
  - Not triple-phase boundary limited
- Pt anodes in solid acid fuel cells show high solubility and diffusivity of Pt
  - Not triple-phase boundary limited
- Pt AFM tip cathodes on solid acid electrolytes reveal spatial heterogeneity
  - Correlation between exchange current and asymmetry factor qualitatively explained
  - Atomistic picture? Universality? Usefulness?

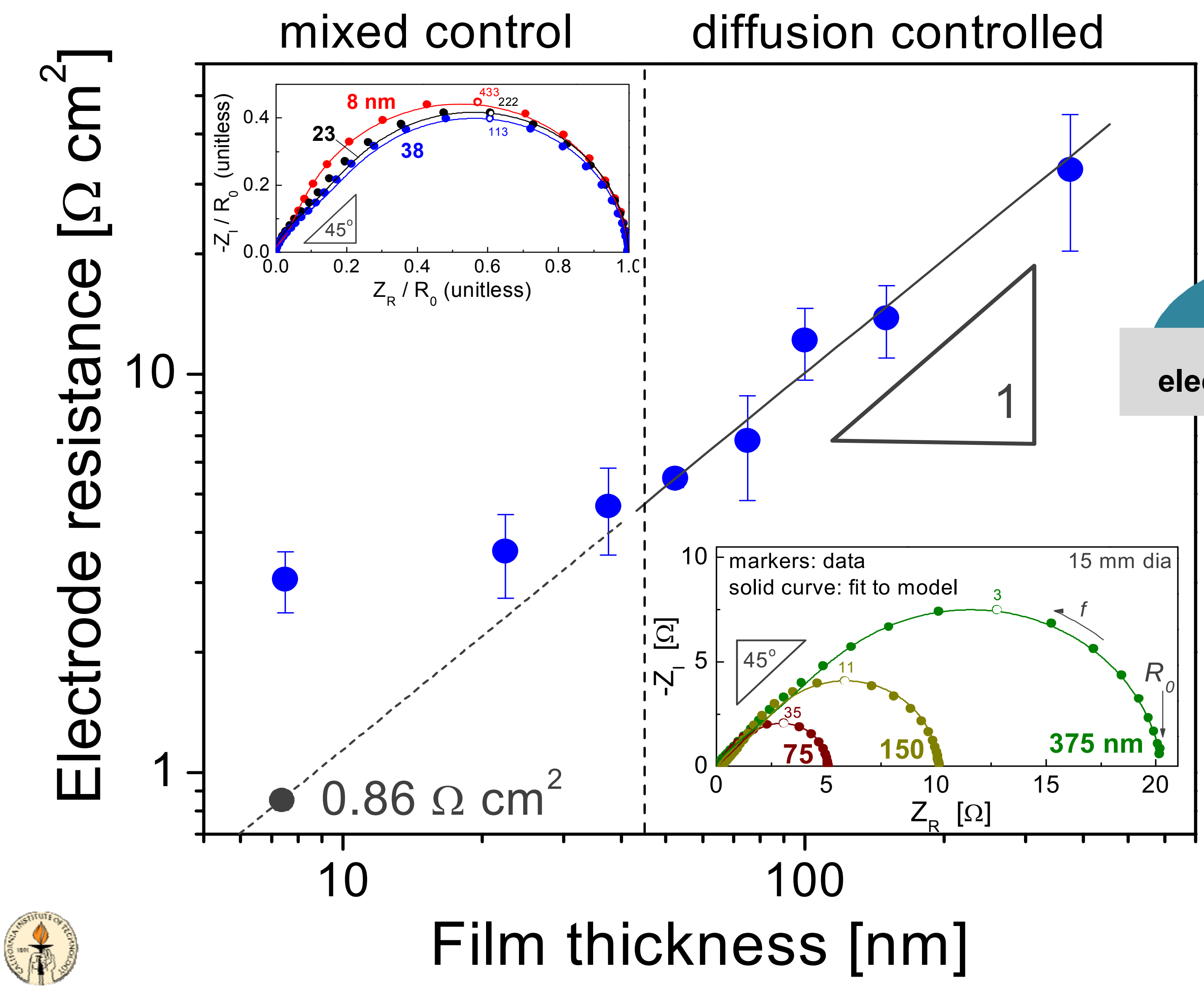
Acknowledgements

- US National Science Foundation
  - Solid State Chemistry Program
  - Ceramic Science Program
  - Materials Research Science & Engineering Centers
  - Graduate Research Fellowship Program
- Gordon and Betty Moore Foundation
- Stanford Global Climate and Energy Program
- Dr. William C. Chueh, Dr. Mary W. Louie
- Prof. Adrian Hightower

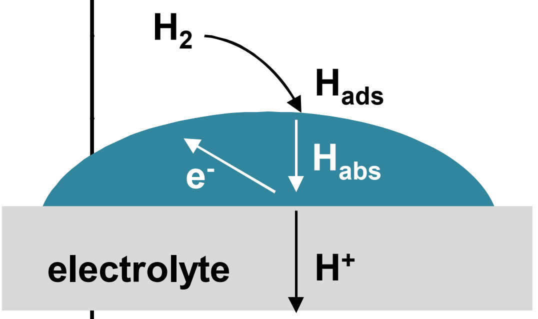
Prof of Engineering, Harvey Mudd College
Caltech Ph.D.



Summary: 2-Phase Pathway Dominates

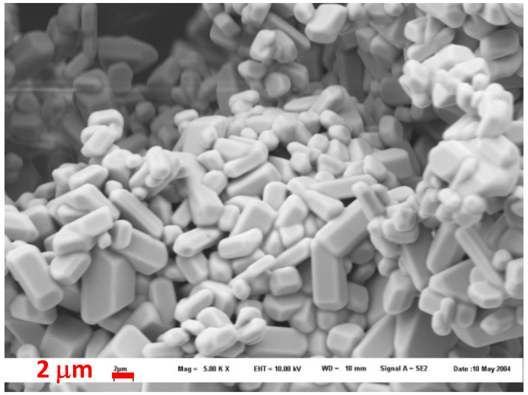


$H_2 \leftrightarrow 2H^+ + 2e^-$

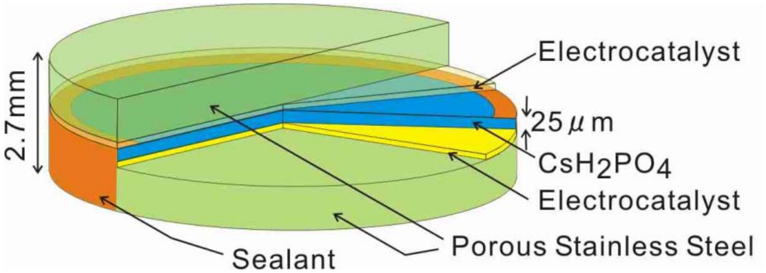


Fuel Cell Operation

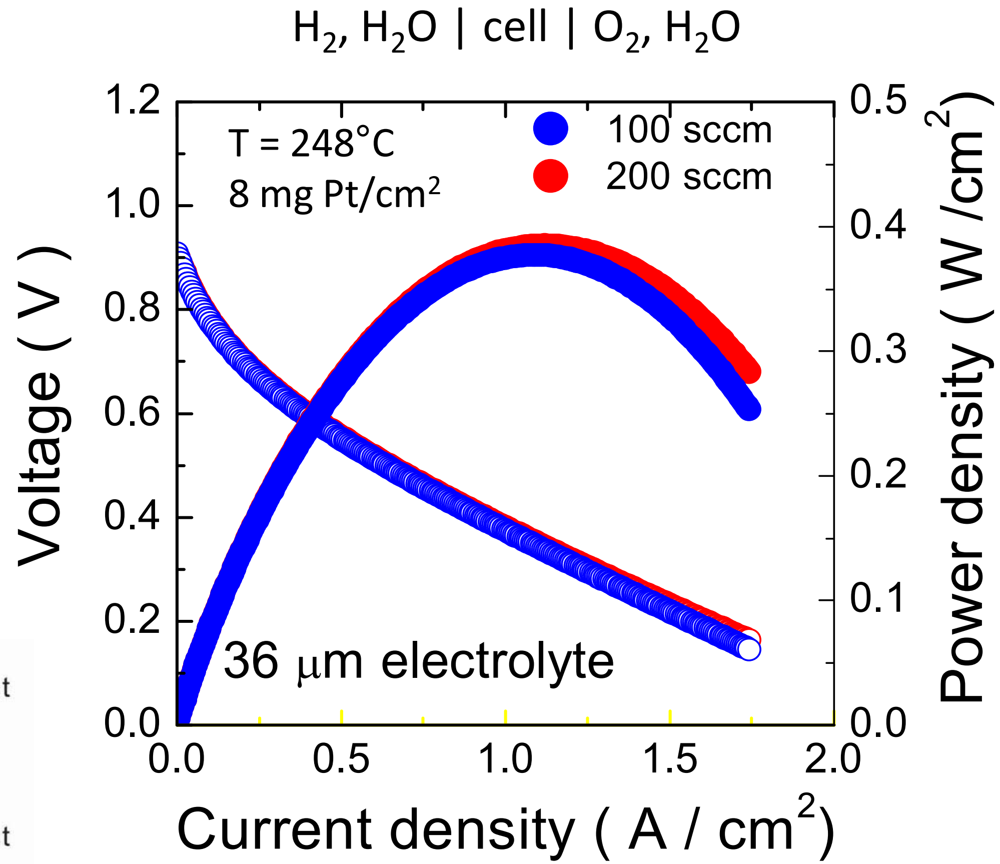
Fine CsH_2PO_4



Slurry deposit



10-40 μm pores, ~40% porosity

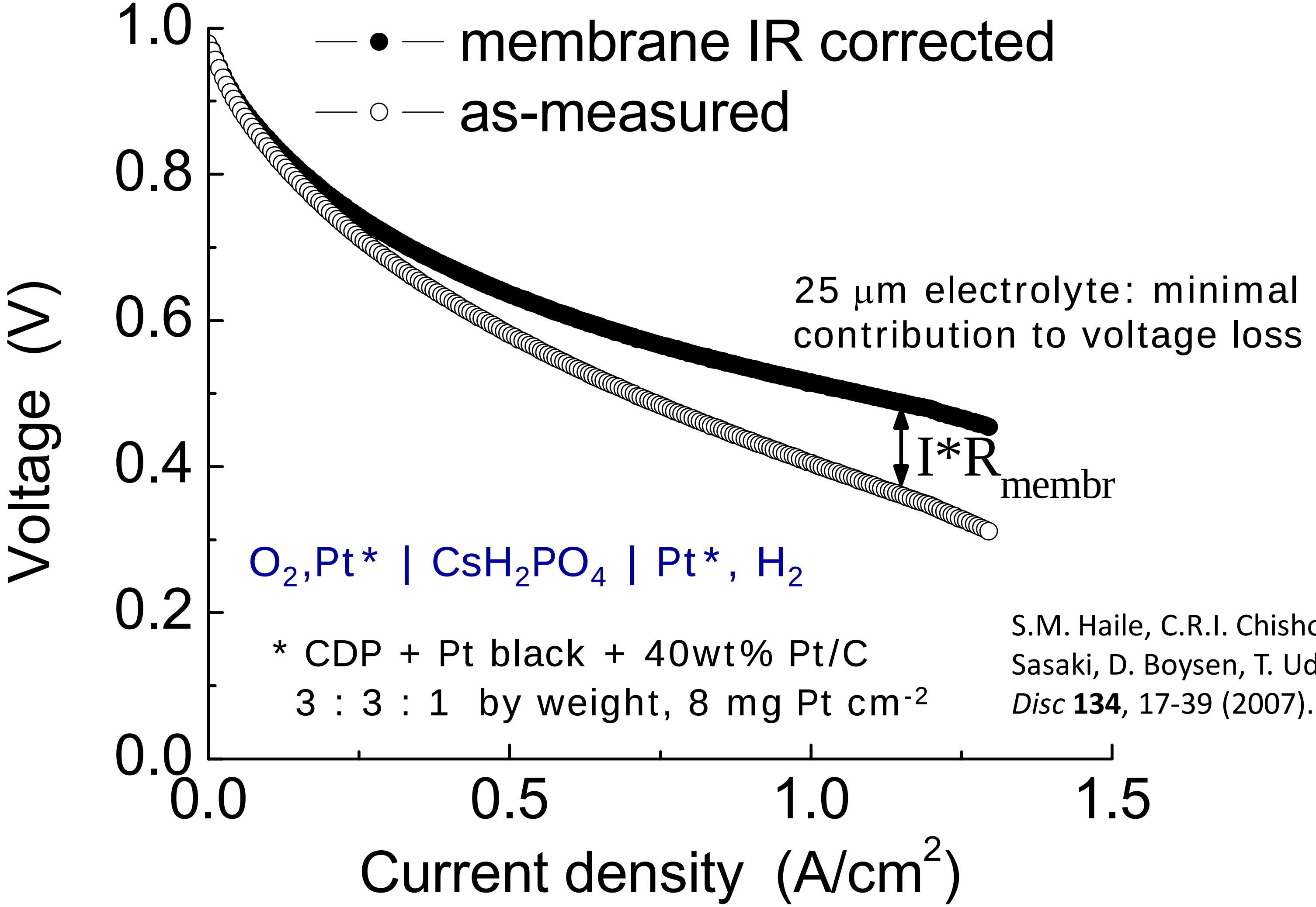


T. Uda & S.M. Haile, *Electrochem & Solid State Lett*. **8** (2005) A245-A246

Open circuit voltage: 0.9-1.0 V *Peak power density: 285-415 mW/cm²*

Electrocatalyst: CDP + Pt black + 40wt% Pt/C = 3 : 3 : 1 by weight

Electro-catalysis as Rate-limiting Step



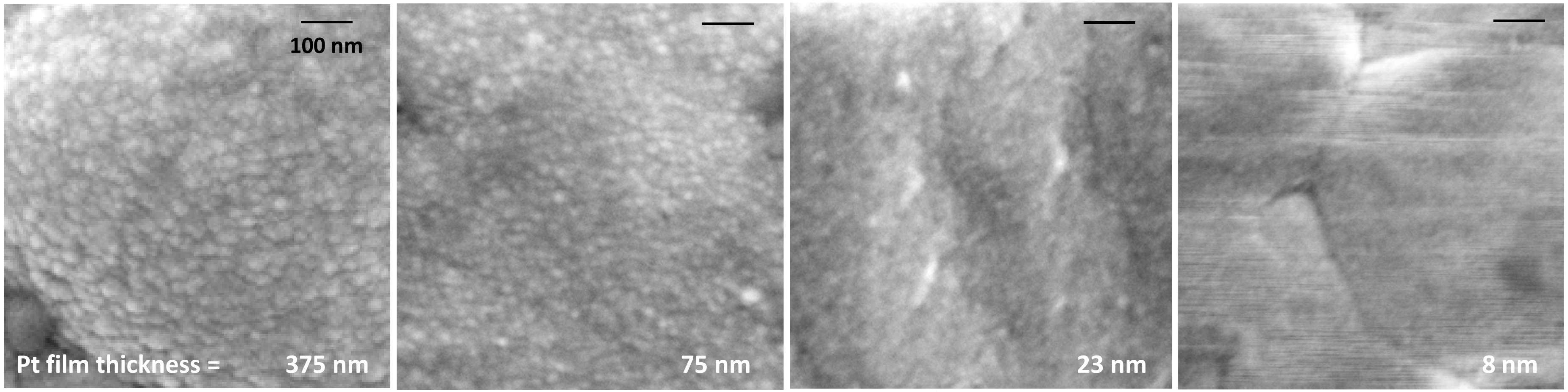
25 μm electrolyte: minimal contribution to voltage loss

O_2,Pt* | CsH_2PO_4 | Pt*, H_2

* CDP + Pt black + 40wt% Pt/C
3 : 3 : 1 by weight, 8 mg Pt cm^{-2}

S.M. Haile, C.R.I. Chisholm, K. Sasaki, D. Boysen, T. Uda, *Faraday Disc* **134**, 17-39 (2007).

Film morphology by SEM



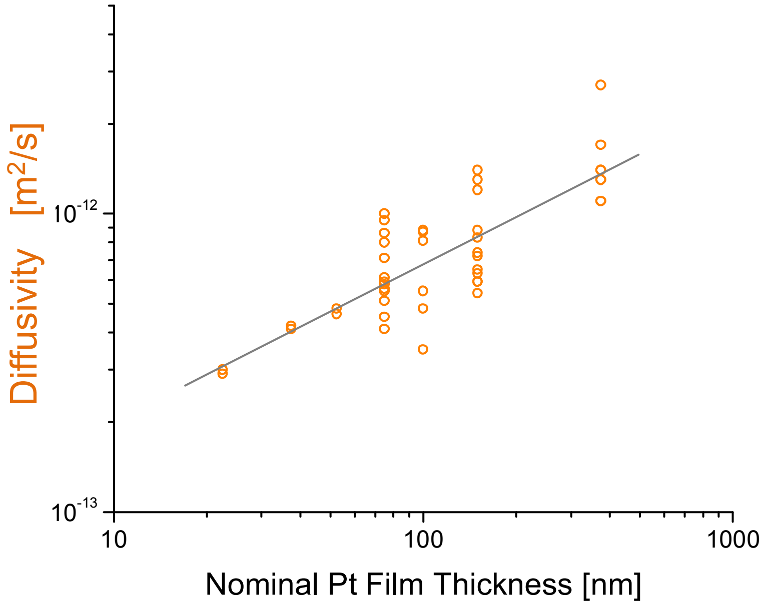
Trap density (N_t) ↑ Apparent diffusivity (D_{app}) ↓

Site fraction occupied by H

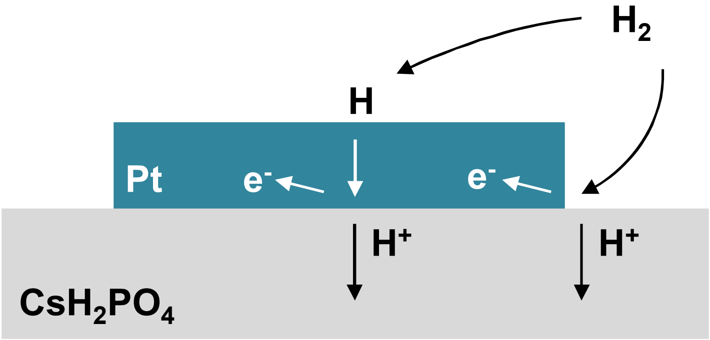
$$D_{app} = D_L \frac{\theta_L N_L}{\theta_t N_t} \qquad N_t, \theta_L, \theta_t \ll 1$$

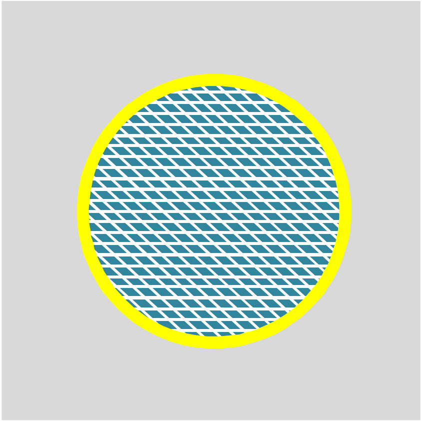
perfect lattice

$\frac{\#\ \text{sites}}{\text{vol}}$

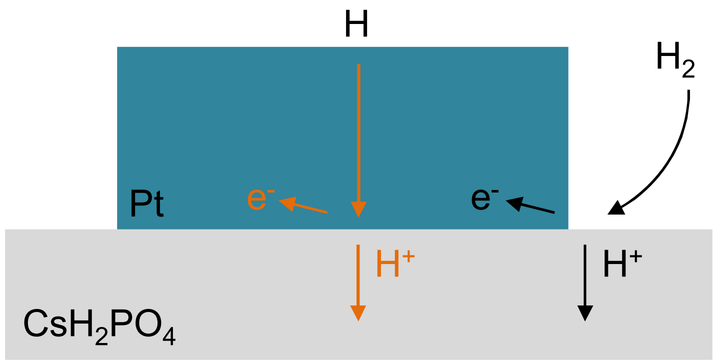


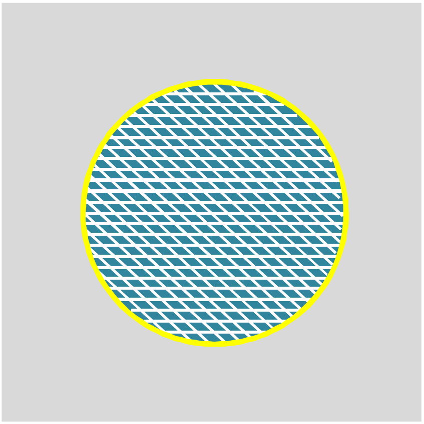
Implications: 2PB vs. 3PB Pathway

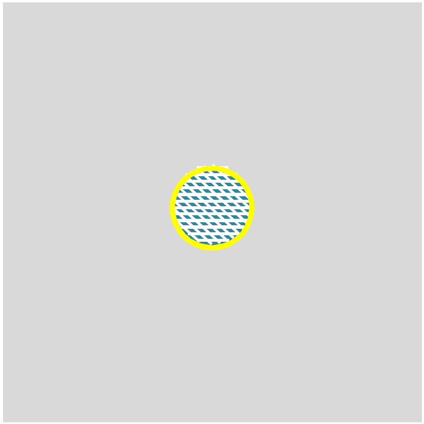




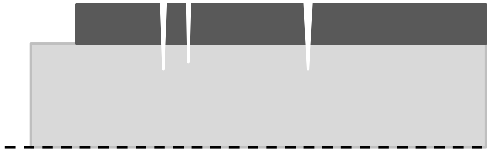
- 2PB pathway can occur with Pt catalysts!
- New geometry for electrodes, not based on nanoparticles





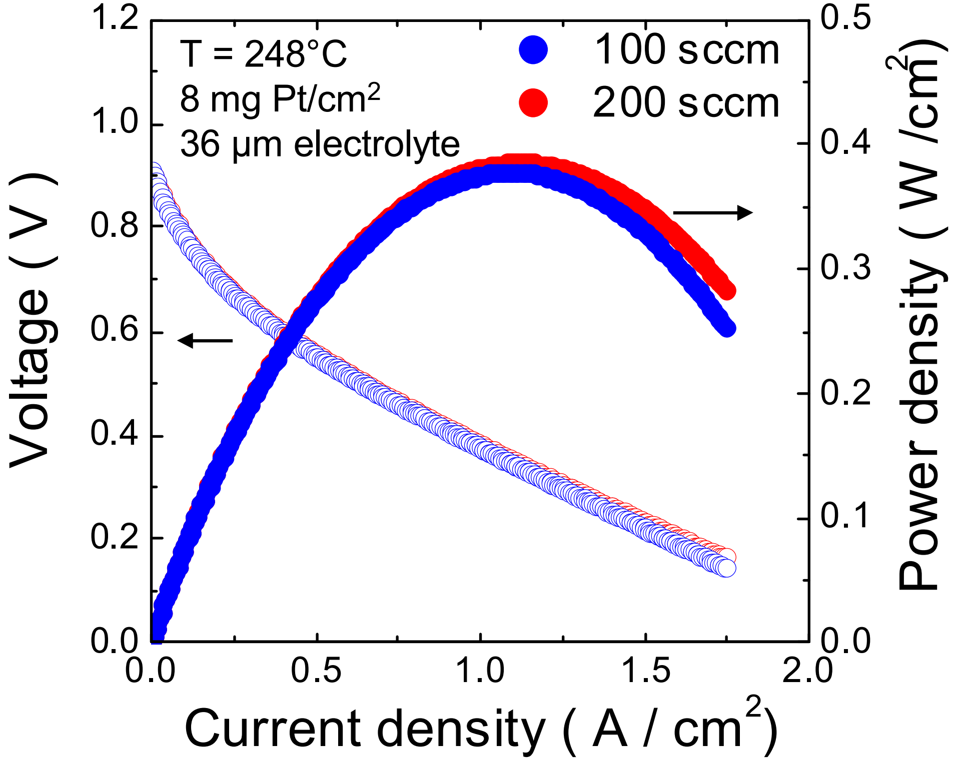


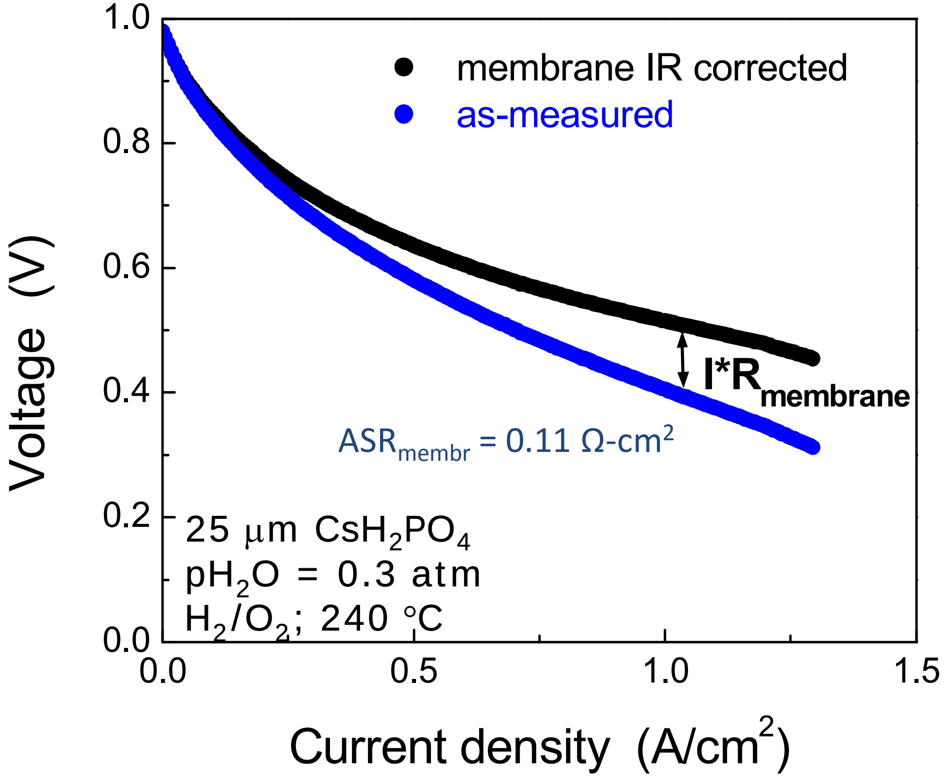
d ≤ 400 um (actual value TBD)



Performance of Solid Acid Fuel Cells

0.3 atm H_2O, H_2 | cell | O_2, 0.3 atm H_2O



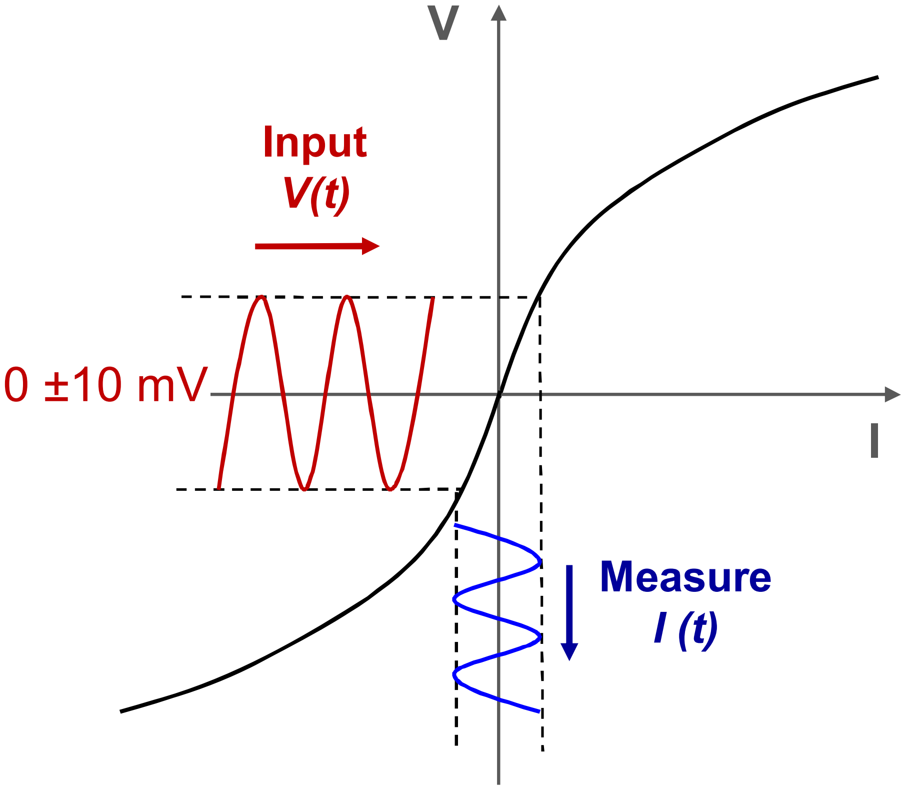


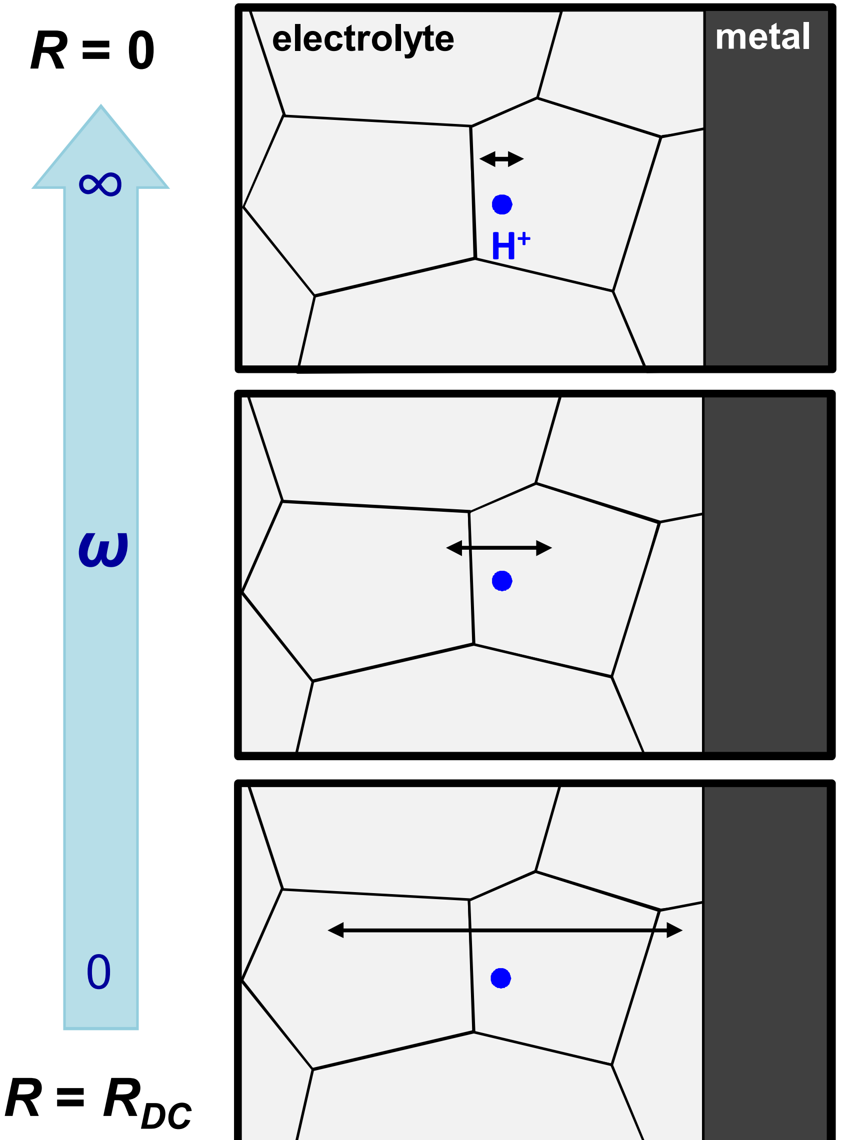
Faraday discussions

Open circuit voltage: 0.9-1.0 V
Peak power density: 285-415 mW/cm^2

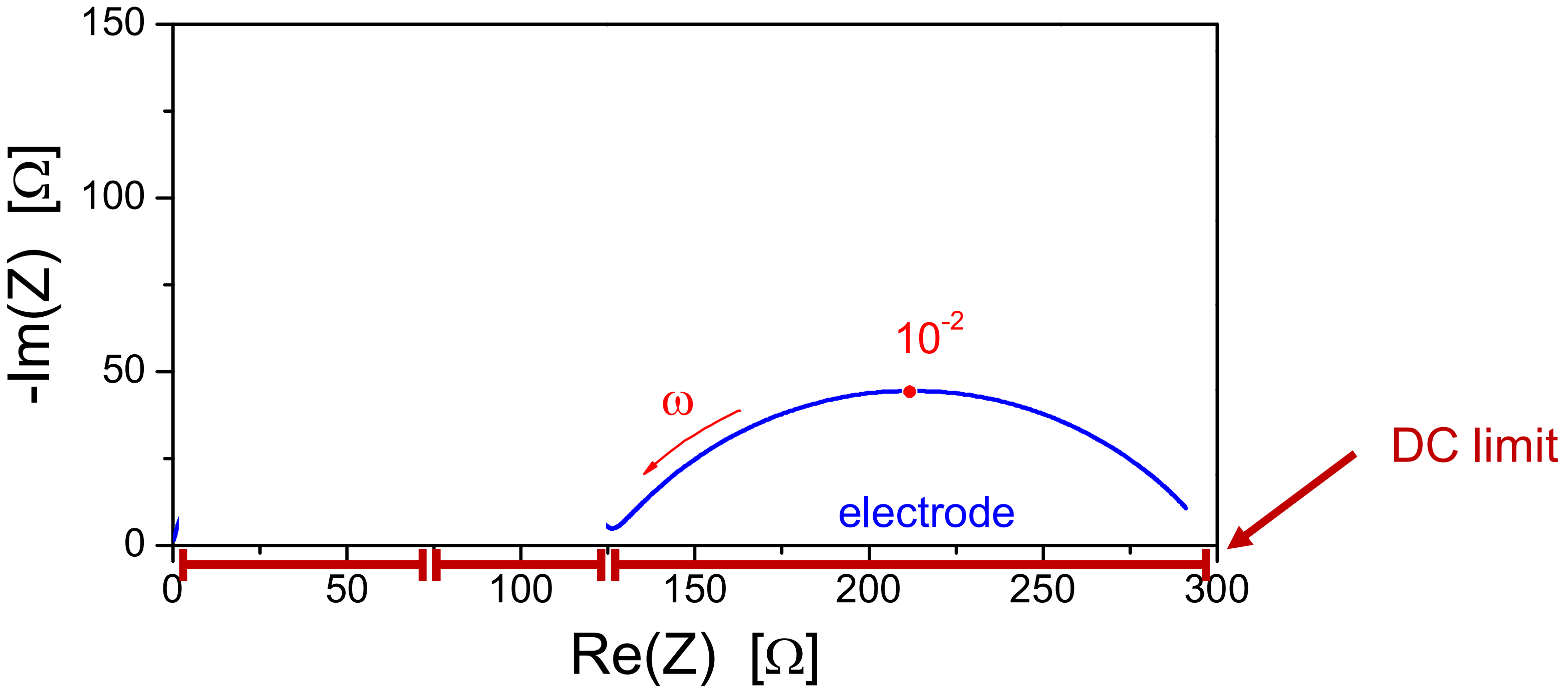
T. Uda & S.M. Haile, *Electrochem & Solid State Lett*. **8** (2005) A245-A246

AC Impedance Spectroscopy

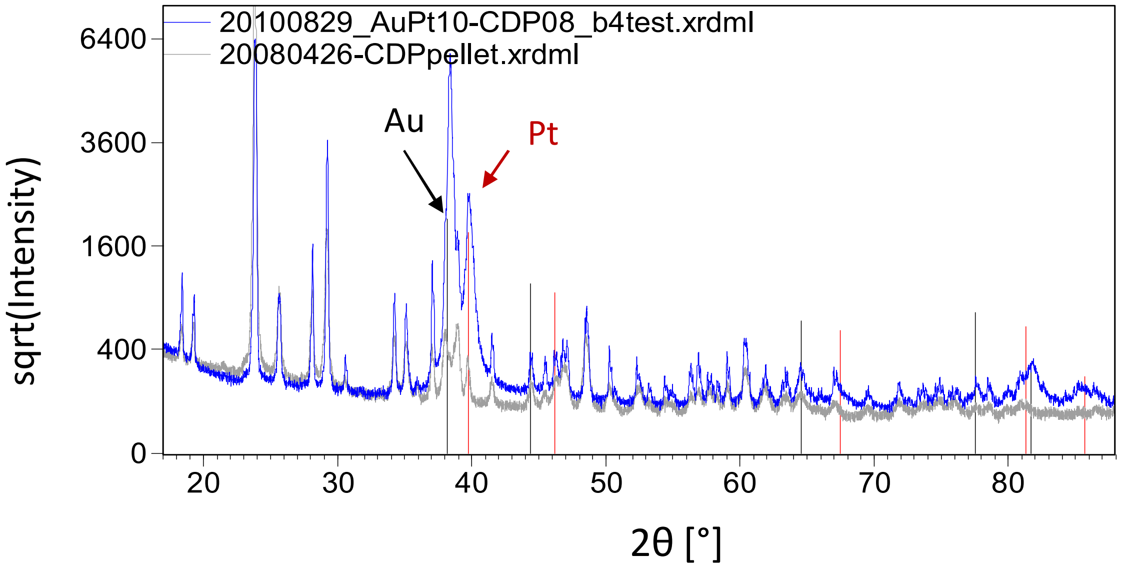


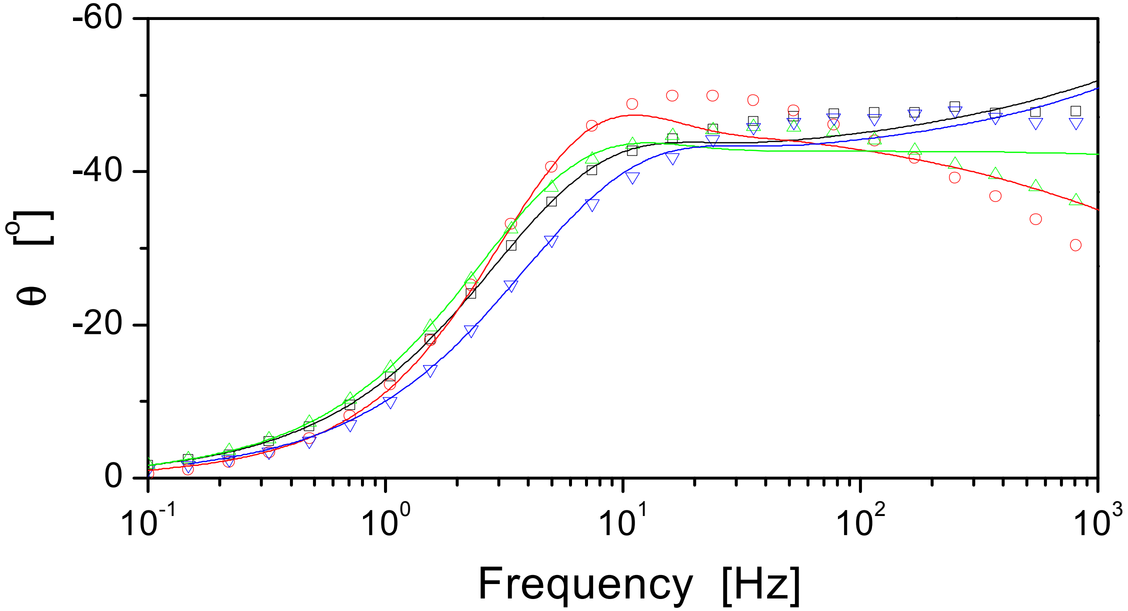


ACIS: Nyquist plot

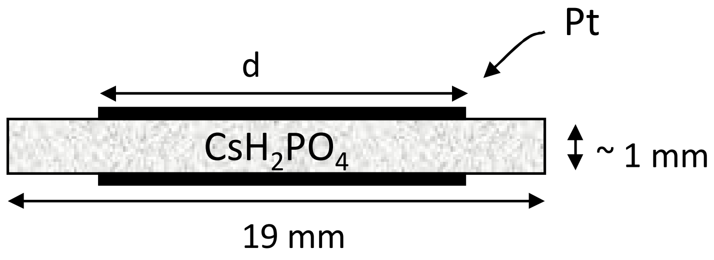


Separate electrochemical reaction steps
with different characteristic times

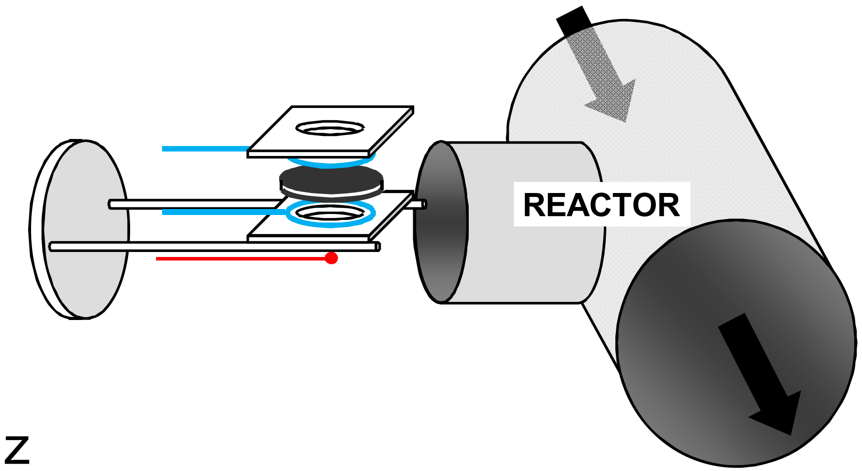

20100829_AuPt10-CDP08_b4test.xrdml
20080426-CDPpellet.xrdml
Au
Pt
sqrt(Intensity)
6400
3600
1600
400
0
20
30
40
50
60
70
80
2θ [°]


-60
-40
-20
0
θ [°]
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
Frequency [Hz]

Platinum symmetric cells



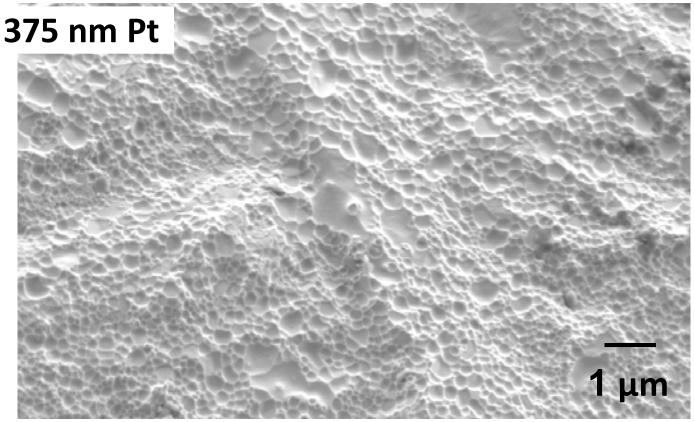
- Cell fabrication
  - CsH_2PO_4 polycryst disc: densified, sanded, rinsed, treated at ~100 °C
  - Shadow masked (1-19 mm diameter)
  - Magnetron sputter deposition @ RT



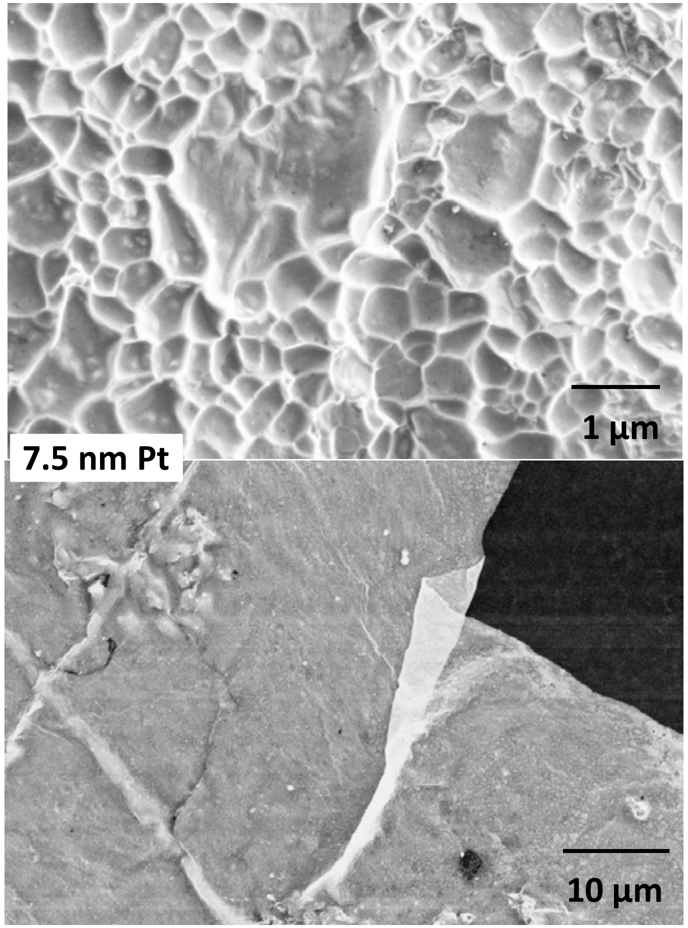
- Electrochem. characterization
  - 200-250 °C, $H_2/H_2O/Ar$
  - 0.06-0.5 atm H_2, 0.3-0.5 atm H_2O
  - ACIS , 0 ± 10 mV, 1 MHz – 100 mHz

- Resistance at OCV → indication of activity
- Examine dependence on pH_2, pH_2O, T, geometry

375 nm Pt



7.5 nm Pt



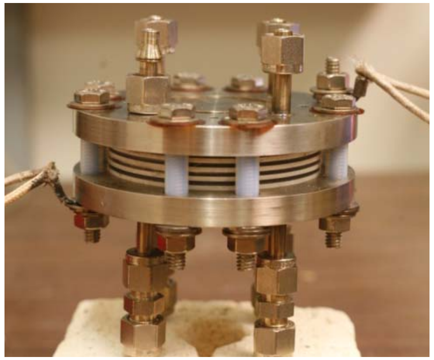
From Breakthrough to Product

2001

Calum

Dane

2007



SUPERPROTONIC

2011

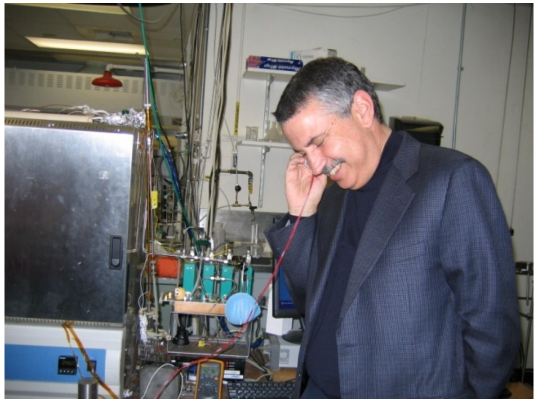
5” MEA
60 cell stack
1.4 kW net

2008

2” MEA
20 cell stack
60 W net

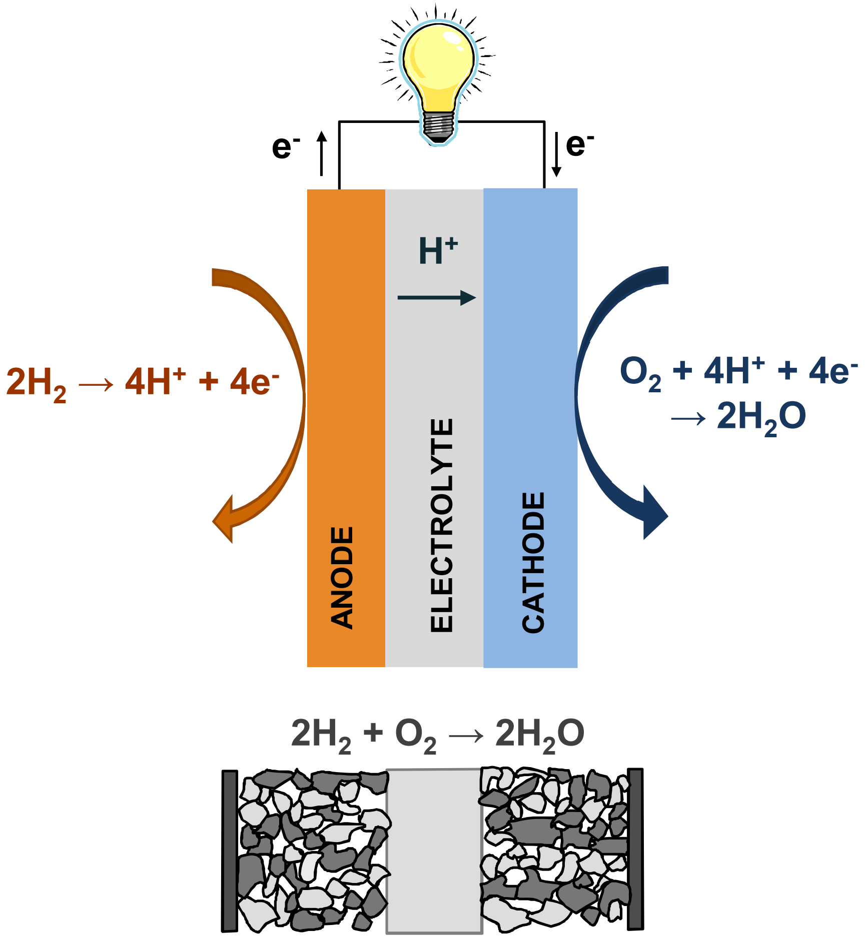
SAFCell, Inc.

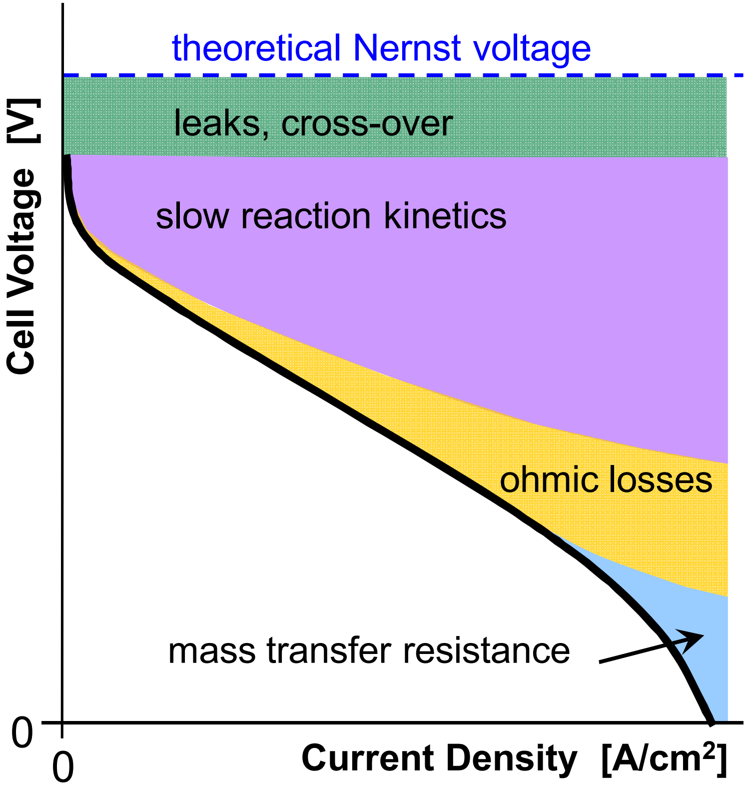
2007



Tom Friedman talking to his wife on an SAFC powered cell phone

Fuel Cell Basics



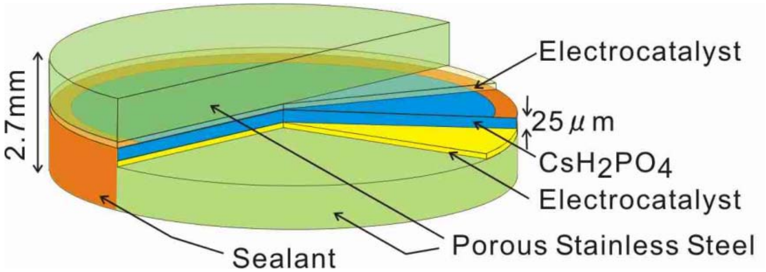


$$E = E_{eq} - \boxed{E_L} - \boxed{\eta_{act}} - \boxed{\eta_{iR}} - \boxed{\eta_{MT}}$$

Material Requirements

- Ion-conducting, dense electrolyte membrane
- Porous, electron- and ion-conducting electrodes

Performance of Solid Acid Fuel Cells



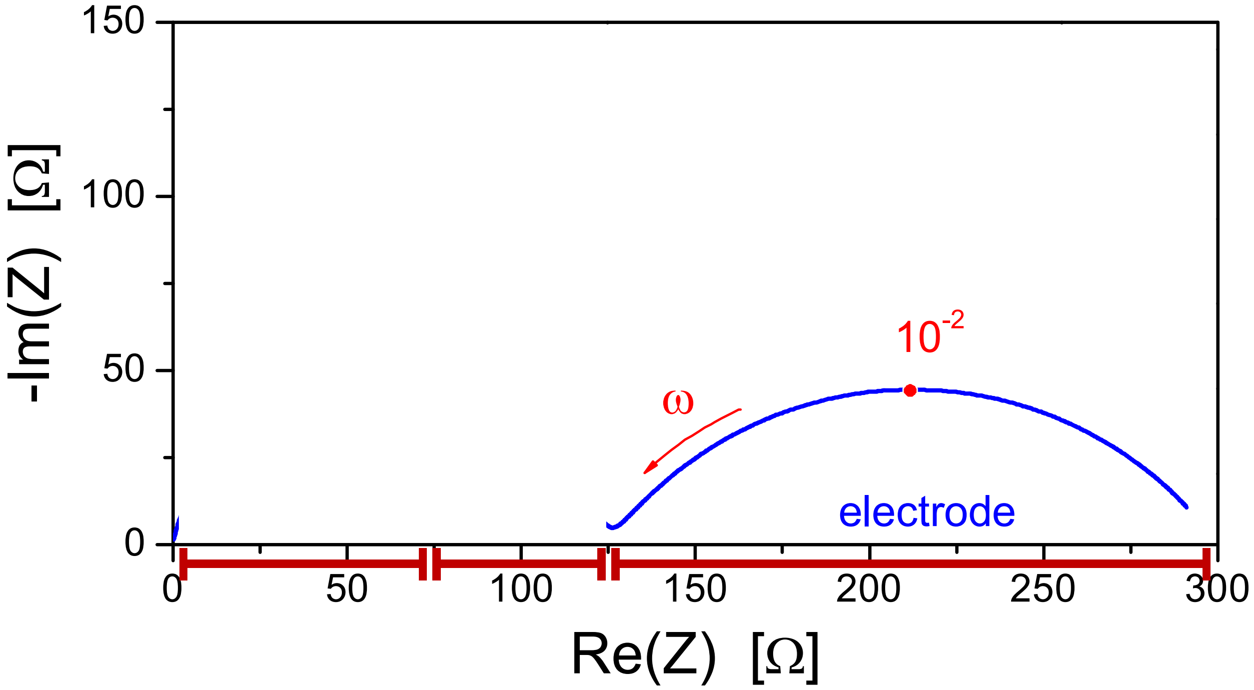
- 400 mW/cm^2 peak power density (H_2 | cell | O_2 at 248 ºC)
  - Thin CsH_2PO_4 layer
  - Composite electrodes w/ Pt loading ~ 8 mg/cm^2

- Overpotentials at electrodes are limiting

T. Uda and S.M. Haile. *Electrochem Solid State Lett* **2005,** 8, A245-A246
S. M. Haile, C. R. I Chisholm, K. Sasaki, D. A. Boysen and T. Uda. *Faraday Discuss* **2007**, 134, 17-39

AC Impedance Spectroscopy

Separate electrochemical reaction steps with different characteristic times

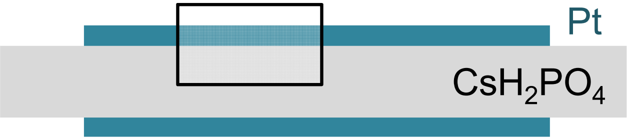


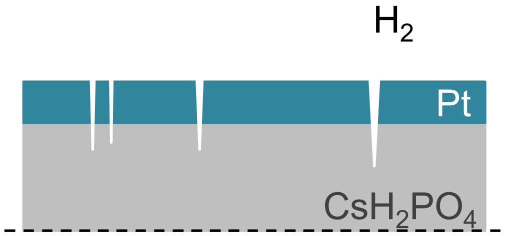
- Resistance near equilibrium gives indication of electrode activity
- 0 ± 10 mV, 1 MHz – 100 mHz

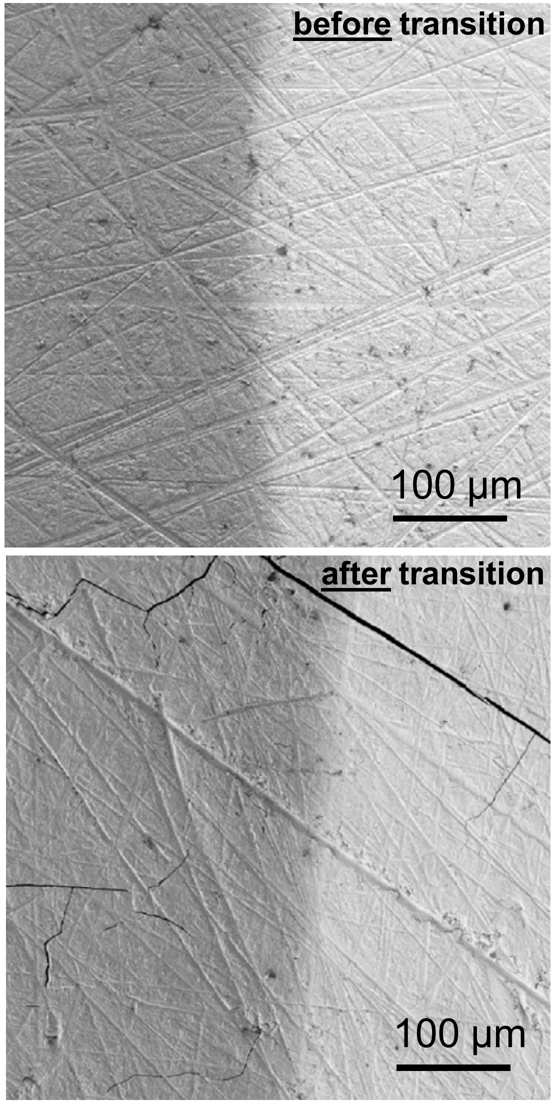
Pt | CsH_2PO_4 | Pt Symmetric Cells

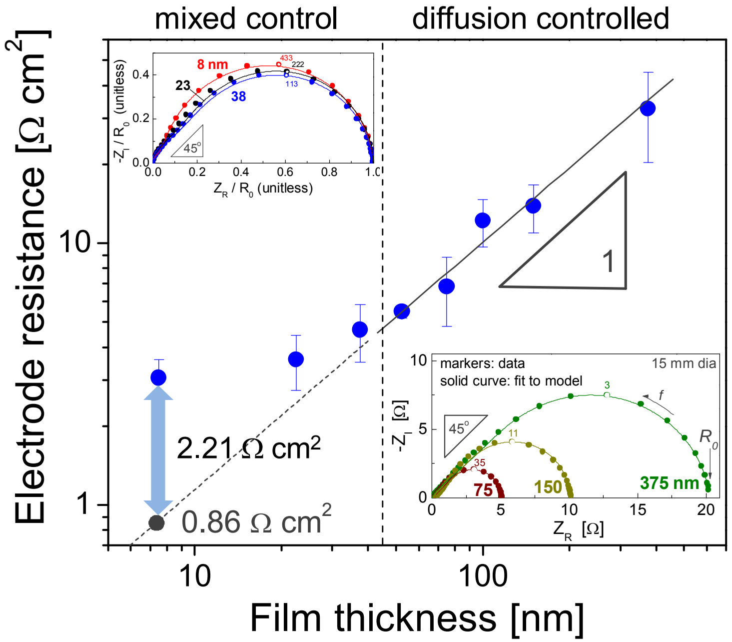
- Environmental conditions
  - 200–250 ºC
  - 0.06–0.5 atm H_2
  - 0.3–0.5 atm H_2O

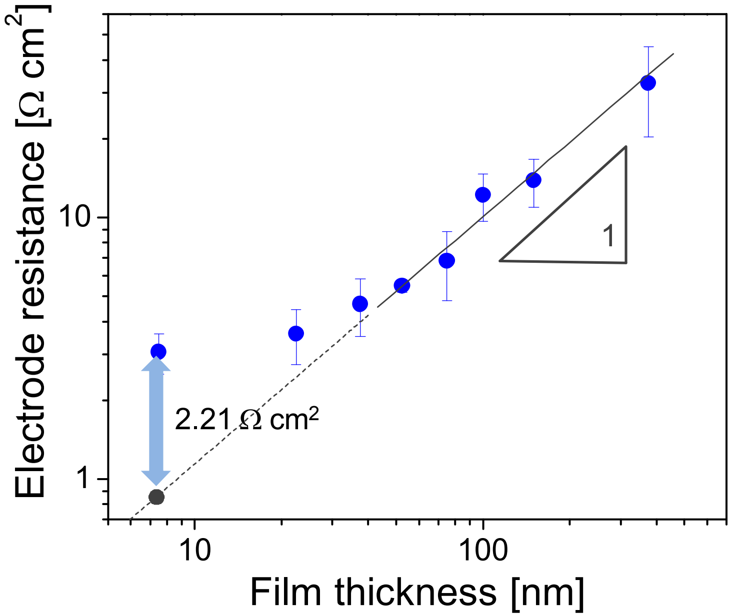
- CsH_2PO_4: phase transformation
  - Generation of microcracks
  - Crack length density: 9 ± 4 mm/mm^2

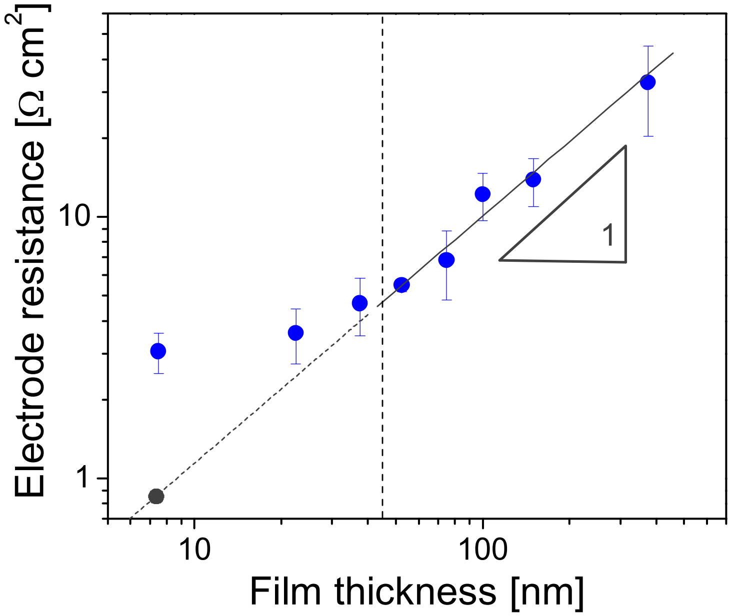







mixed control
diffusion controlled
Electrode resistance [Ω cm2]
Film thickness [nm]
1
10
10
100
2.21 Ω cm2
0.86 Ω cm2
1
-Z_I / R_0 (unitless)
Z_R / R_0 (unitless)
0.0
0.2
0.4
0.6
0.8
1.0
8 nm
23
38
433
222
113
45°
markers: data
solid curve: fit to model
15 mm dia
-Z_I [Ω]
Z_R [Ω]
0
5
10
15
20
3
11
35
75
150
375 nm
f
R0
45°


Electrode resistance [Ω cm2]
Film thickness [nm]
1
10
10
100
2.21 Ω cm2
1


Electrode resistance [Ω cm2]
Film thickness [nm]
1
10
10
100
1