

Impact of Oxide Coverage on Oxygen Reduction Reaction (ORR) Kinetics in Proton Exchange Membrane Fuel Cells (PEMFCs)

**Nalini P. Subramanian, Thomas A. Greszler,
Junliang Zhang, Wenbin Gu, Rohit Makharia**

General Motors Fuel Cell Activities

Honeoye Falls, NY



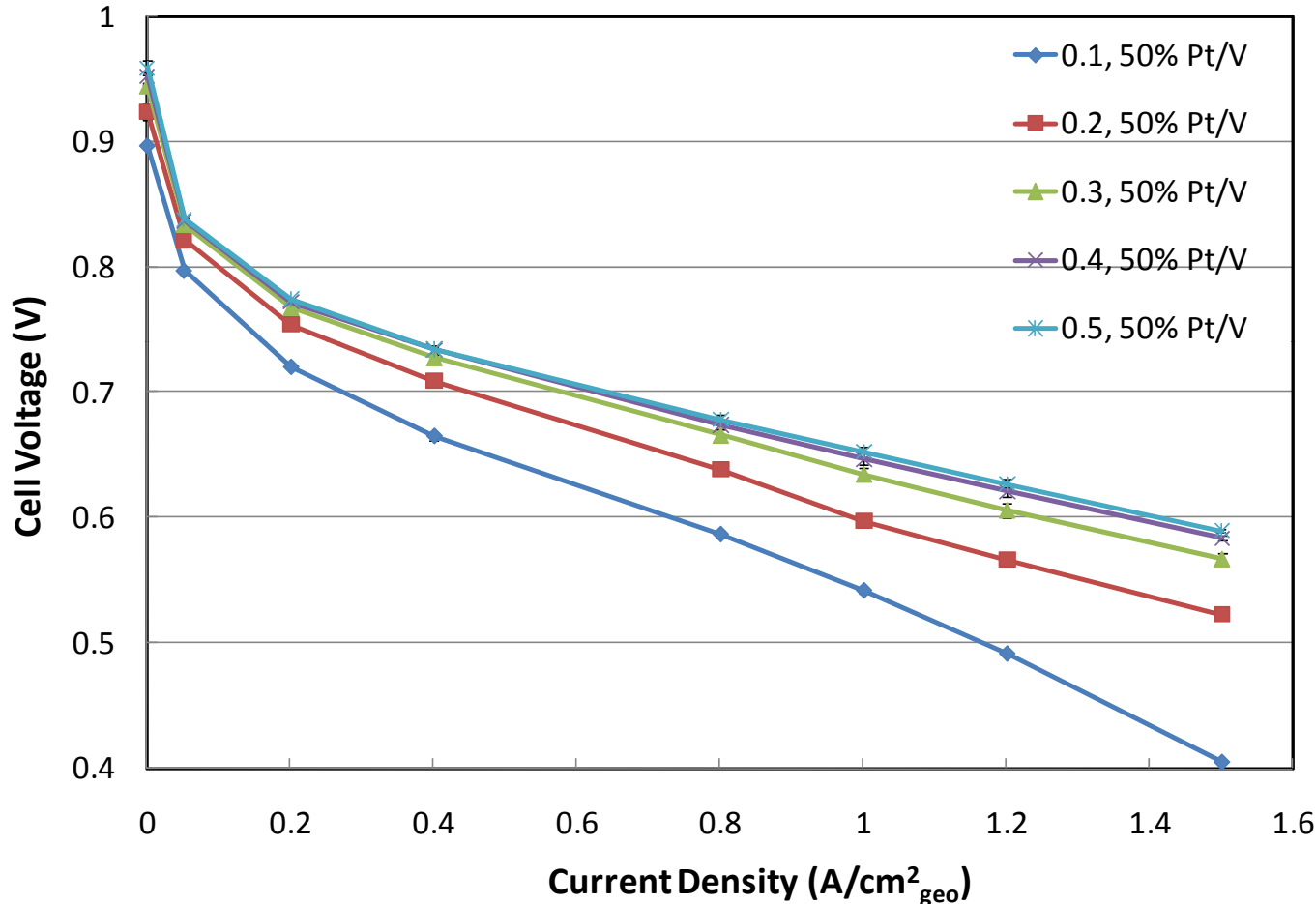
Palm Springs, CA - November 19, 2009

Outline

- High current density/Low cell potential performance issues
- Motivation to study impact of oxide coverage
- Objectives of this study and Experimental details
- Simple vs. Coverage-dependent kinetic models
- Experimental Results – Reaction Order and Tafel Slopes
- Summary and Next Steps

Impact of Pt Loading H₂/Air performance

32% RH in, 80°C, 150 kPa-out, 1.5/2 Stoich, H₂/air



Anode

- 20% Pt/V, 0.05 mg/cm²
- 0.6 Ionomer/Carbon (w/w)

Cathode

- 50% Pt/V, 0.4 mg/cm²
- 0.95 Ionomer/Carbon (w/w)

Membrane

- 25 μm thick, 1000 EW

Diffusion Media

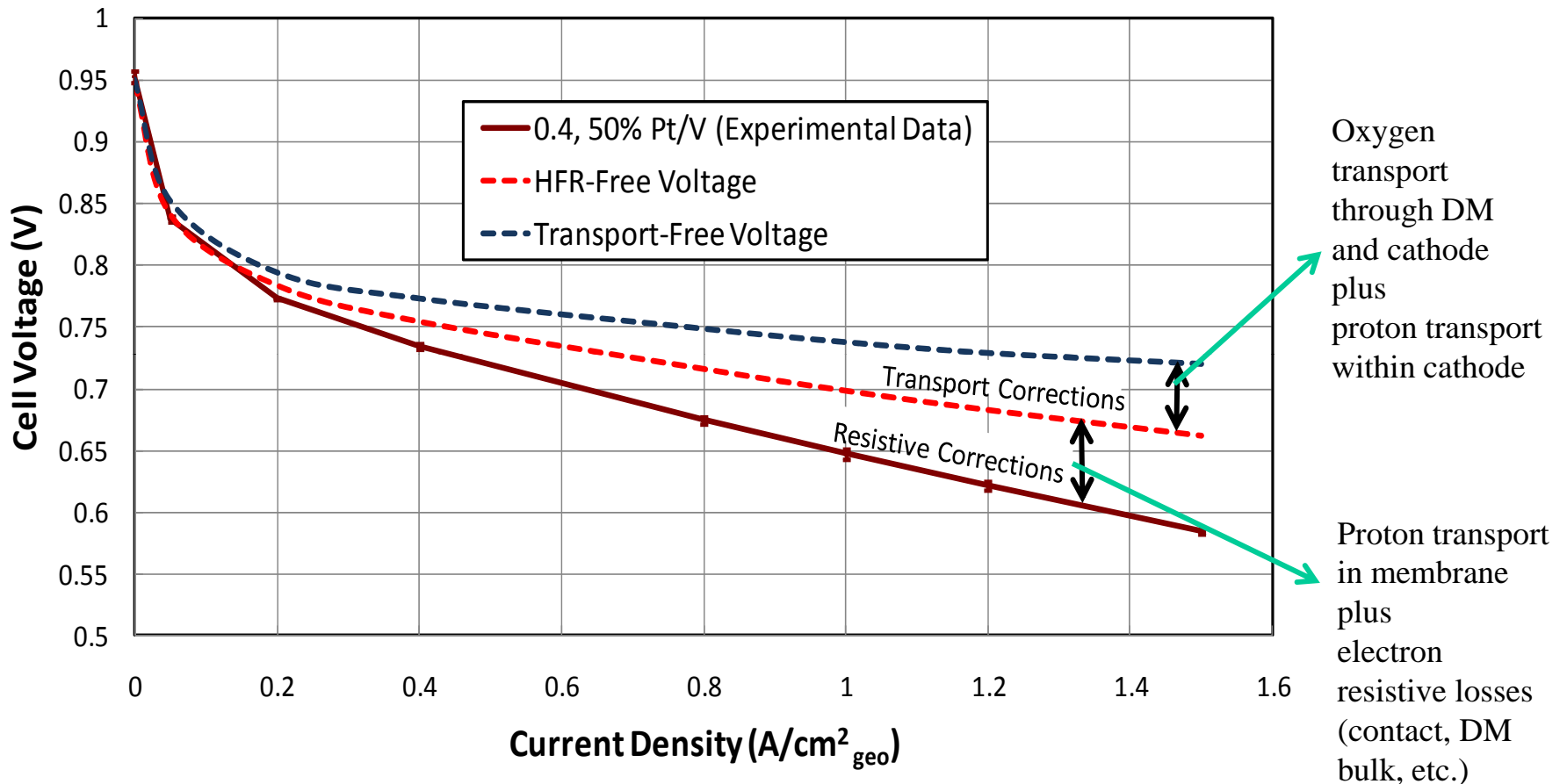
- Carbon paper with micro porous layer
- 200 μm thick

T. Greszler, S. Kumaraguru, N. Subramanian, B. Litteer, Z. Liu and Rohit Makharia, GHT33-2, *Fuel Cell Seminar and Exposition* (2008)



☐ Higher performance loss observed at high current density for low-loaded Pt cathodes

Accounting for Resistive and Transport Losses



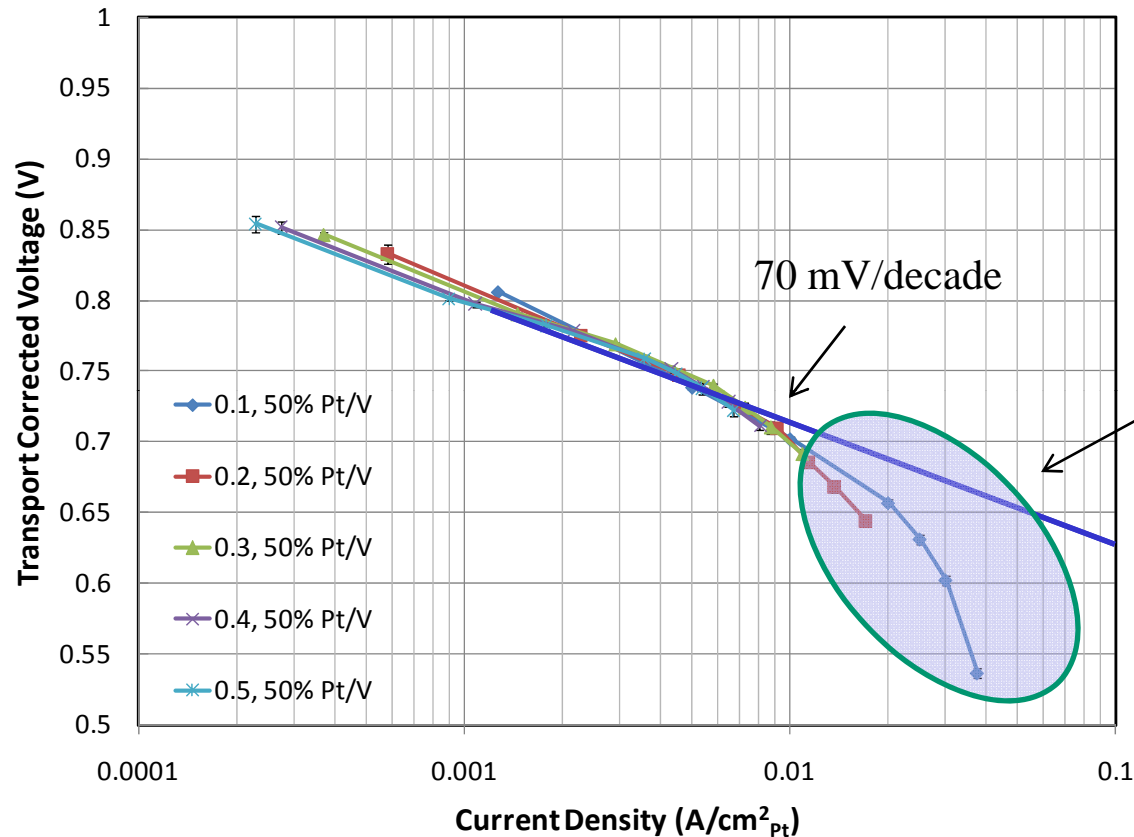
T. Greszler, S. Kumaraguru, N. Subramanian, B. Litteer, Z. Liu and Rohit Makharia, GHT33-2, *Fuel Cell Seminar and Exposition* (2008)

- ❑ Resistive losses are measured with high frequency resistance
- ❑ Bulk Transport losses are determined with 1-D model utilizing measured MEA properties (electrode proton resistance, DM oxygen transport resistance, etc.)

Impact of Pt Loading

Transport-corrected H₂-Air Tafel plot (voltage vs. A/cm²_{Pt})

80°C, 150 kPa-out, 32% RH-in, 1.5/2 Stoich, hydrogen/air



Transition in Tafel slope - Kinetic Change or local transport losses ?

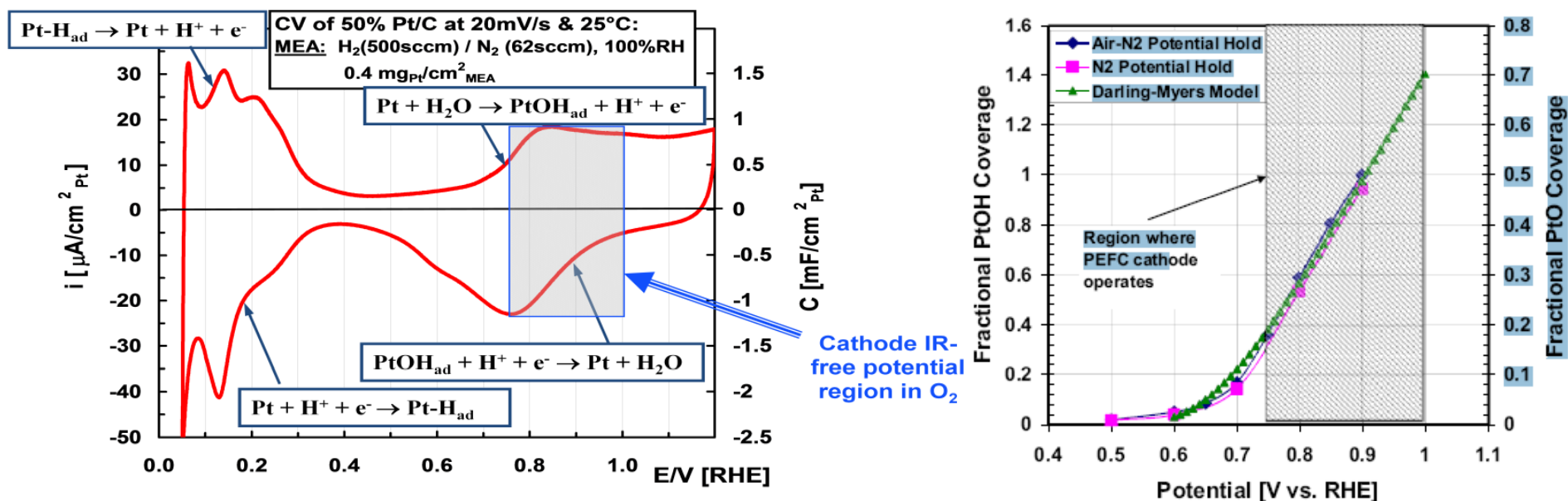
T. Greszler, S. Kumaraguru, N. Subramanian, B. Litteer, Z. Liu and Rohit Makharia, GHT33-2, *Fuel Cell Seminar and Exposition* (2008)

- ❑ Deviation from a 70mV/dec Tafel slope is observed at high current density (or low V)
- ❑ It is unclear if this deviation is related to ORR kinetics or unaccounted transport loss at or near the Pt surface



Motivation to Study Effect of Oxide Coverage

-Potential Dependent Oxide Coverage



- Pt-OH/O coverage varies as a function of potential
- State-of-the-art cathodes operate in a region where Pt is oxidized
- With lower Pt loadings, the potential range of operation is such that the Pt-surface transitions from a nearly oxide-free Pt surface to full or partially covered Pt-surface.
- Are the oxides intermediates? Or poisons?

* M. Mathias, D. Baker, J. Zhang, Y. Liu, and W. Gu, *ECS Transactions*, 13, 129 (2008)

❑ The influence of potential dependent oxide coverage and the role of oxides in reaction mechanism and ORR Kinetics needs to be understood

Treatment of Oxides

- No consensus nor clear understanding of the role of oxides – Intermediates or Poisons?
- Watanabe *et al.*¹ explain the enhanced ORR on Pt-Fe alloy with increased oxygen coverage
- Mathias *et al.*² explain the inductance observed in low frequency impedance using surface poisoning with oxide
- The impact of p_{O_2} on oxide coverage is not well understood.
 - Mathias *et al.*² have shown no effect of air exposure on oxide coverage.
 - But Paik *et al.*³ have reported that O_2 exposure led to a change in the surface coverage.

¹ M. Wakisaka, H. Suzuki, S. Mitsui, H. Uchida, M. Watanabe, *J. Phys. Chem.*, 112, 2750 (2008)

² M. Mathias, D. Baker, J. Zhang, Y. Liu, and W. Gu, *ECS Transactions*, 13, 129 (2008)

³ C.H. Paik, T. D. Jarvi, W.E. O'Grady, *Electrochem. Solid-State Lett.*, 7, A82 (2004)

□ Effect of oxide coverage on ORR and effect of p_{O_2} on oxide coverage not completely understood

Coverage dependent ORR Kinetics

- Simple ORR model

$$I = i_0 p_{O_2}^\gamma \exp\left(\frac{-\beta F \eta}{RT}\right)$$

- Rate expression for ORR including effect of oxide coverage as a poison assuming a Temkin isotherm*

$$I = i_0 p_{O_2}^\gamma (1 - \theta_{ad})^x \exp\left(\frac{-\beta F \eta}{RT}\right) \exp\left(\frac{-\omega \theta}{RT}\right)$$

i_0 -intrinsic exchange current density, p_{O_2} -partial pressure of O_2 , γ -rxn. order for O_2 , β -symmetry factor, θ – surface coverage by adsorbed species, x -no. of Pt-sites occupied by adsorbed species, $\omega\theta$ – parameter characterizing the rate of change of energy of adsorption with surface coverage by adsorbing species, η – overpotential

- Oxide coverage can change the measured/apparent Tafel Slope and reaction order
 - a) Change in oxide coverage as a function of potential (θ)
 - b) Change in energy for adsorption for oxide species with surface coverage ($\omega\theta$)

*N.M. Markovic', H.A. Gasteiger, B.N. Grgur, P.N. Ross, *J. Electroanal. Chem.*, 467, 157 (1999)

□ The exponential and/or the pre-exponential terms can influence changes in apparent Tafel Slope (TS) and/or reaction order

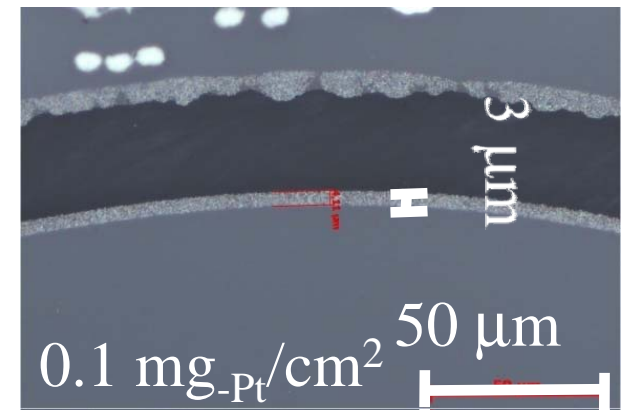
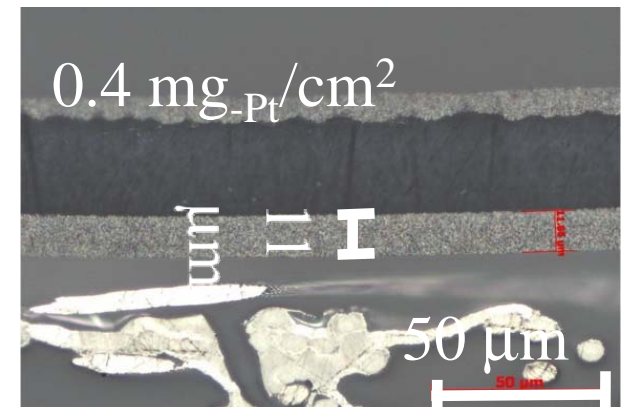
Objectives of this Study

- Obtain low cell potential without operating at high current density (try to minimize transport losses) by significantly reducing the cathode platinum loading and the oxygen partial pressure
- **Vacuum will be used to go to extremely low O₂ partial pressures.** Earlier work in literature achieved lower O₂ partial pressures with dilution* (*M. Uchimura and S.S. Kocha, 214th ECS Meeting, Abstract #914)
- Any transition in Tafel slope, if any, from these experiments should only be due to transition in kinetics
- Influence of oxide coverage on reaction order and Tafel slope will be understood by using the experimental potential dependent oxide coverage and fitting the ORR Kinetic model to experimental performance data at various partial pressures of O₂
- Pt-oxide kinetics can not only be used to predict steady state performance but also transients

Minimizing Transport Effects

- Eliminating Bulk Transport
 - Thin and uniform electrodes
 - Operating in pure O₂ and 100% RH
 - Using straight-through flow fields to reduce pressure drop
 - Operating at 3/10 stoic of H₂/O₂ at 0.4 A/cm²
 - Operating at low current density
- Eliminating Local Transport
 - If local transport is controlling, most of the losses are expected to occur at or near Pt surface
 - Modeling results indicate that even after assuming 100nm of ionomer film over Pt, the pressure drop is not significant across the film

SEM X-Section of MEA



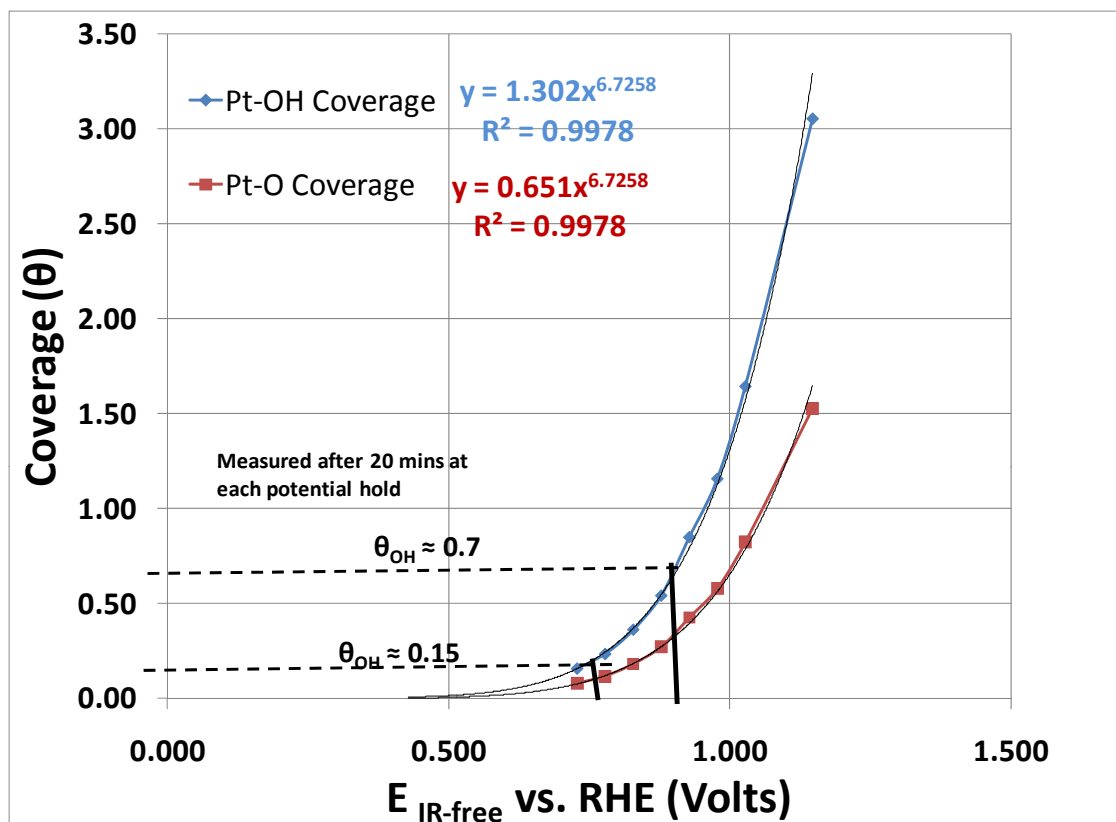
□ Calculations indicate no significant transport limitations – both bulk and local

Experimental Details

- 50 cm² cell
- Cathode - 50% Pt/V, ~0.1/0.4 mg_{-Pt}/cm²_{-MEA}
- Anode – 20% Pt/V, 0.05 mg_{-Pt}/cm²_{-MEA}
- Performance Measurements
 - NRE-211 membrane (25μm thick)
 - 80°C, 100%RH, constant flow 420 and 700 sccm H₂/O₂, p_{O₂}=202,102,62, 32, 15 kPa
 - **0.7 V, 10 mins reduction step before every polarization curve**
 - **Positive scan polarization curves from 0.4 A/cm²-0.02 A/cm²**
 - **20 mins at each current density**
- Oxide Measurements
 - 80°C, 100%RH, H₂/N₂, 10%H₂ in the anode to reduce H₂ cross-over currents
 - Additionally membrane was switched to NRE-212 (50μm thick) to reduce H₂ cross-over
 - **Oxide coverage calculated from negative peaks in the CVs measured at 20 mV/s, after constant potential hold for 20 mins**

❑ Performance measured at various O₂ partial pressures and at current densities at or below 0.4 A/cm²

Oxide Coverage from CVs measured in H₂/N₂



Potential dependent coverage

$$\theta = AE^B_{IR-free}(RHE)$$

Where A=1.302 and B=6.7258 from the experimental data fit assuming Pt-OH

Oxide coverage calculated from negative peaks in the CVs measured at 20 mV/s, after constant potential hold for 20 mins

It is possible to expand the experimental IR-free potential range in performance measurements by varying p_{O_2} and Pt loading

Tafel Slope (TS) and Reaction Order

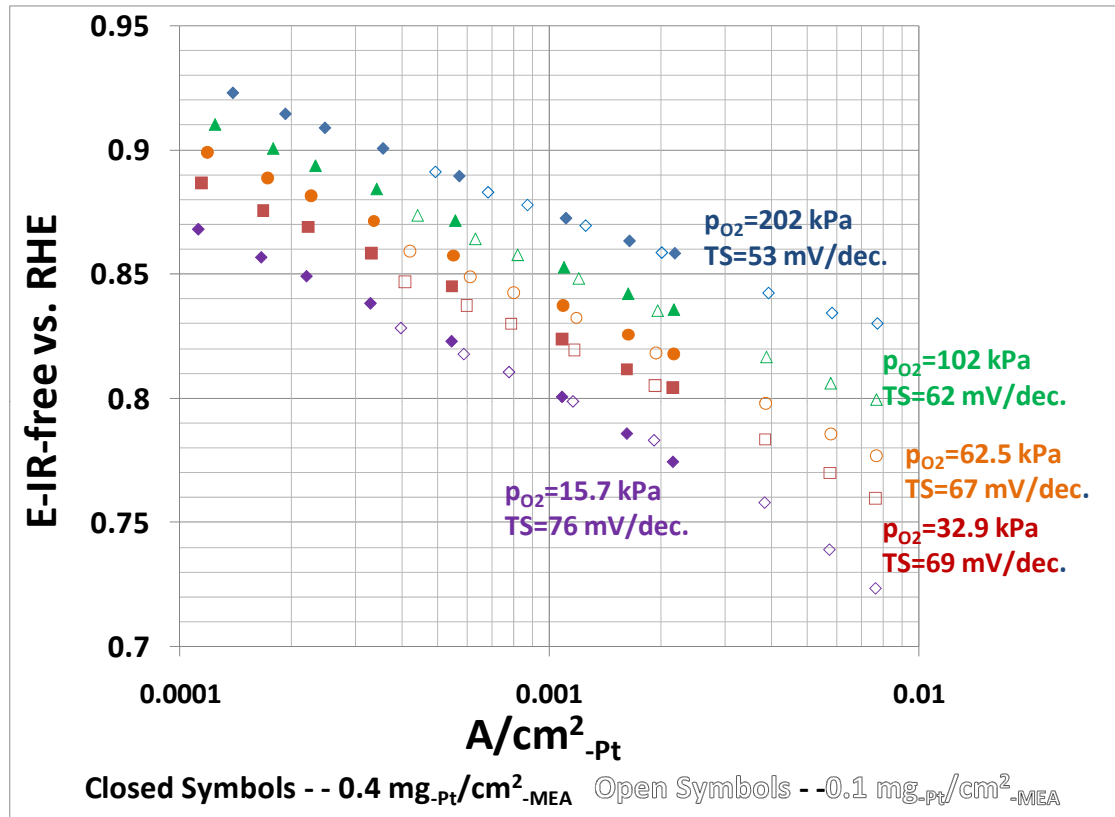
	Simple ORR model*	Coverage dependent ORR model**
Rate expression J	$i_0 p_{O_2}^\gamma \exp\left(\frac{-\beta F \eta}{RT}\right)$	$i_0 p_{O_2}^\gamma (1 - \theta_{ad})^\alpha \exp\left(\frac{-\beta F \eta}{RT}\right) \exp\left(\frac{-\omega \theta}{RT}\right)$
Oxygen Reaction Order $\left(\frac{\partial \log i}{\partial \log p_{O_2}}\right)_{\eta, T}$	γ	$\gamma - \left(\frac{\alpha}{1 - \theta} + \frac{\omega}{RT}\right) \frac{E \theta}{E_{IR-free(RHE)}} \frac{RT}{4F}$
1/(Tafel slope) $\left(\frac{\partial \log i}{\partial E_{IR-free(RHE)}}\right)_{p_{O_2}, T}$	$-\frac{\beta F}{2.303 RT}$	$-\frac{\beta F}{2.303 RT} - \frac{1}{2.303} \left(\frac{\alpha}{1 - \theta} + \frac{\omega}{RT}\right) \frac{E \theta}{E_{IR-free(RHE)}}$

* K. C. Neyerlin, Wenbin Gu, Jacob Jorne, and Hubert A. Gasteiger, *J. Electrochem. Soc.*, 153, A1955 (2006)

** Assuming ω and γ are independent of $E_{IR-free(RHE)}$ $\theta = A E_{IR-free(RHE)}^B$

□ The exponential and the pre-exponential terms can influence changes in apparent TS and reaction order

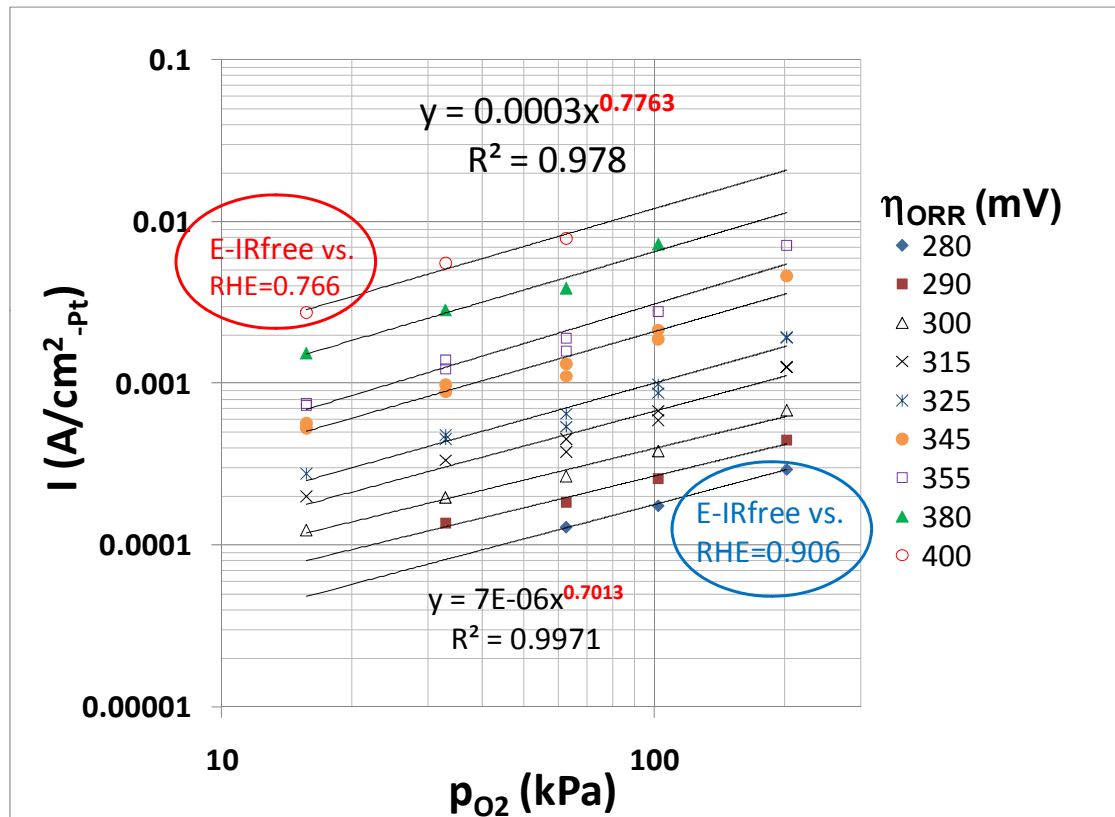
Performance Data in O₂ (voltage vs. A/cm²_{Pt})



- ❑ Both the 0.1 and 0.4 loaded parts fall on the master curve at different p_{O₂}
- ❑ Simple kinetic model with a constant TS cannot be used to predict the data at different p_{O₂}

O₂ Reaction Order

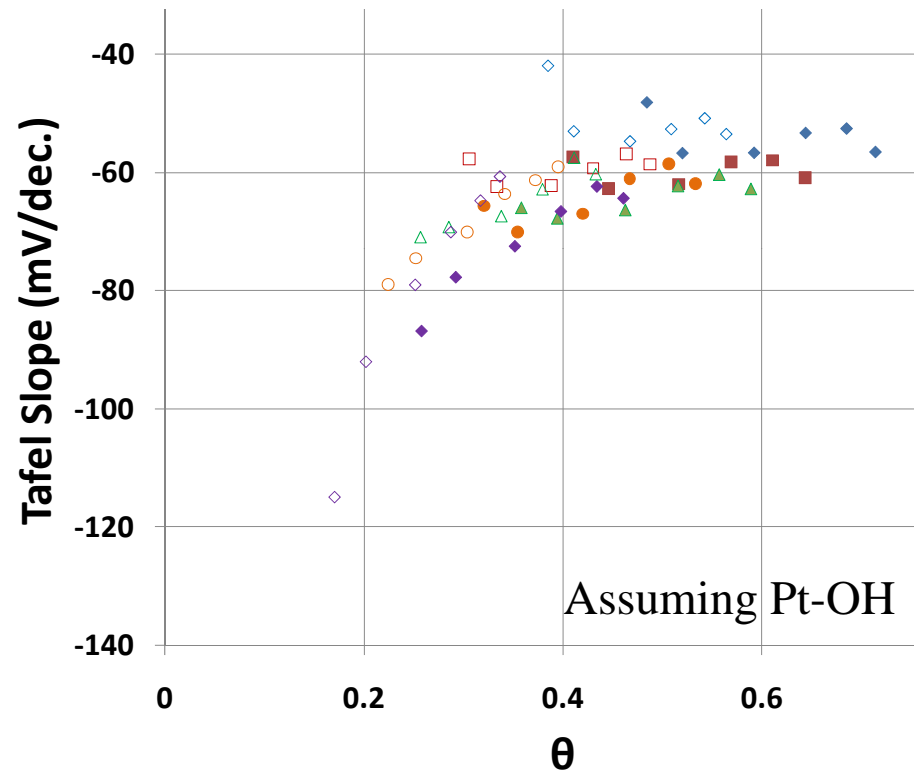
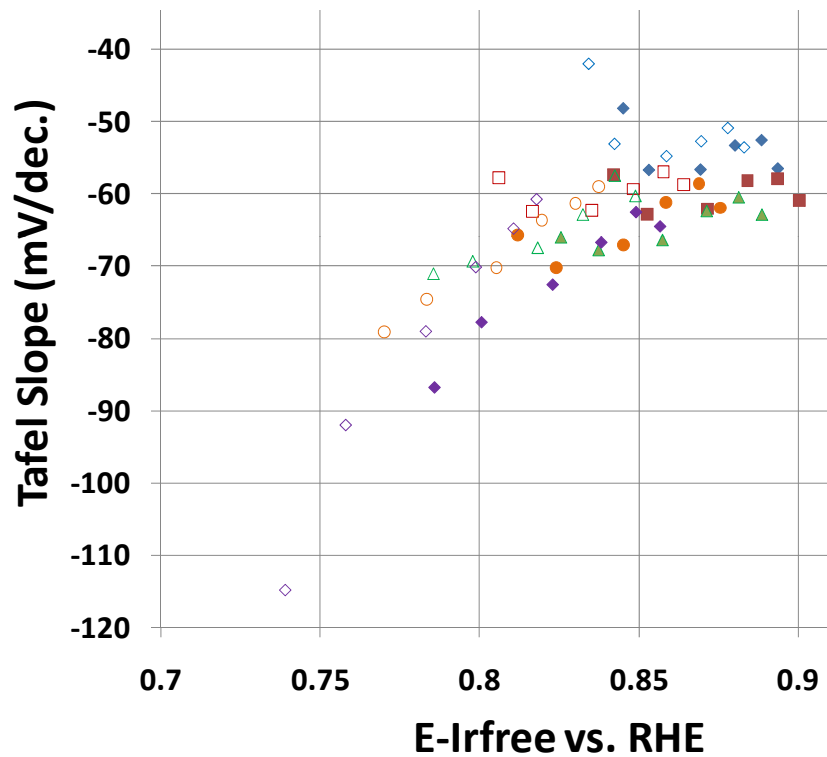
$$\left(\frac{\partial \log i}{\partial \log p_{O_2}}\right)_{\eta, T} = \gamma - \left(\frac{x}{1-\theta} + \frac{\omega}{RT}\right) \frac{E\theta}{E_{IR-free(RHE)}} \frac{RT}{4F}$$



□ For $E_{IR-free(RHE)}$ from 0.766 to 0.906, the apparent reaction order is nearly independent of $E_{IR-free(RHE)}$

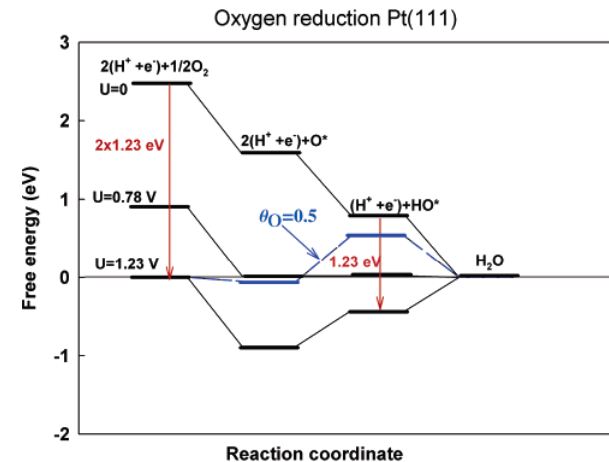
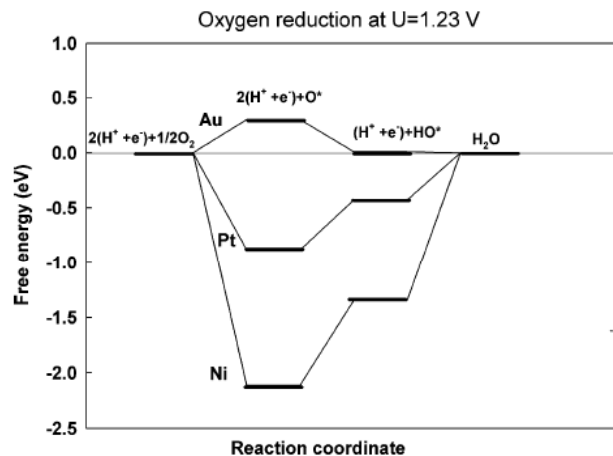
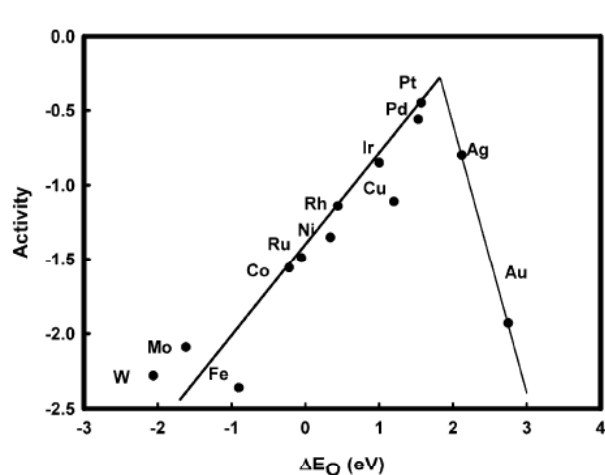
Tafel Slope vs. $E_{IR-free(RHE)}$

$$\left(\frac{\partial \log i}{\partial E_{IR-free(RHE)}} \right)_{p_{O_2}, T} = \frac{\frac{\beta F}{RT} - \left(\frac{\alpha}{1-\theta} + \frac{\omega}{RT} \right) \frac{E\theta}{E_{IR-free(RHE)}}}{2.303}$$



- Apparent TS is not a strong function of p_{O_2} , but a function of $E_{IR-free(RHE)}$ and hence has a correlation to θ
- Higher TS at low θ may explain the high current density/low cell potential performance losses

Reaction Mechanisms



- The “Volcano plot” shows the ORR activity as a function of binding energy of oxygen on metals
- Depending on the binding energy, the energy barriers for the different steps in the reaction mechanism changes¹
- In addition the energy barrier for the different steps changes as a function of potential*
- This suggests that the rate determining step can vary as a function of potential on Pt²

¹ J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jońsson, *J. Phys. Chem. B.*, 108, 17886 (2004)

² J. X. Wang, J. Zhang, and R.R. Adzic, *J. Phys. Chem. A*, 111, 12702 (2007)

Summary and Next Steps

- Reaction order is nearly constant in the potential range studied, i.e., independent of $E_{\text{IR-free(RHE)}}$ and θ
- Tafel slope is a function of $E_{\text{IR-free(RHE)}}$ and hence has some correlation to θ
- Need to incorporate potential dependent reaction mechanisms to explain change in Tafel slopes. This will help understand the performance losses at high current density/low cell potential
- Currently expanding the IR-free potential range by increasing p_{O_2} and by decreasing cathode Pt loading
- In-situ measurements (XANES¹ and XPS²) can provide some information about the nature of the oxide species
- Compare catalysts with differences in Pt-oxide and ORR Kinetics, i.e., Pt vs. Pt-alloys

¹ S. Mukherjee, J. Ziegelbauer, T. Arruda, D. Ramaker, B. Shyam, *Interface*, 17, 46 (2008)

² M. Wakisaka, H. Suzuki, S. Mitsui, H. Uchida, M. Watanabe, *J. Phys. Chem.*, 112, 2750 (2008)

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