Impedance Spectroscopy for PEM Fuel Cells

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Electrochemical Impedance Spectroscopy

- Electrochemical technique
  - In-situ
  - transient
  - sensitive
- Measurement in terms of macroscopic quantities
  - total current
  - averaged potential
- Not a chemical spectroscopy

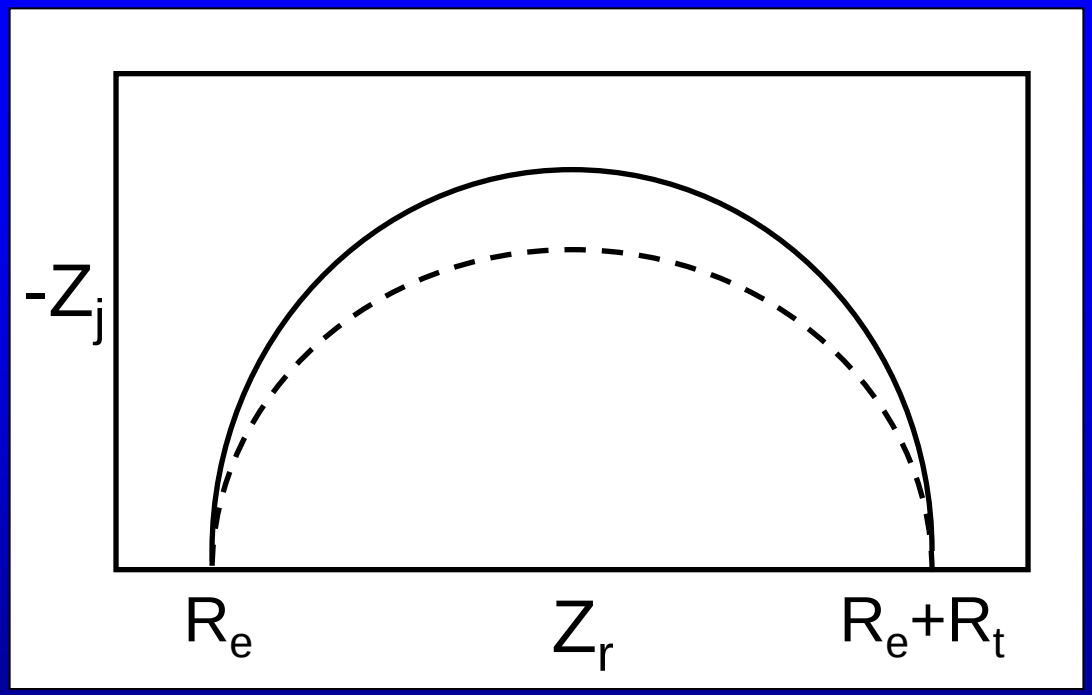
For many systems: EIS yields a physical description

- Electrode-Electrolyte Interface
  - Electrical double layer
  - Diffusion layer
  - Kinetics
- Electrochemical Reactions
- Transport Processes

EIS has a BAD reputation for energy research

- Technique over-sold
- Questionable data
  - Nonstationary behavior
  - Instrument artifacts
  - nonlinearity
- Too much information – technique is too sensitive
- Interpretation in terms of electrical circuits
  - Models not unique
  - Models not connected directly to chemistry/physics
- Nonuniform distributions of reactivity
- Use of a CPE

Constant Phase Element (CPE)

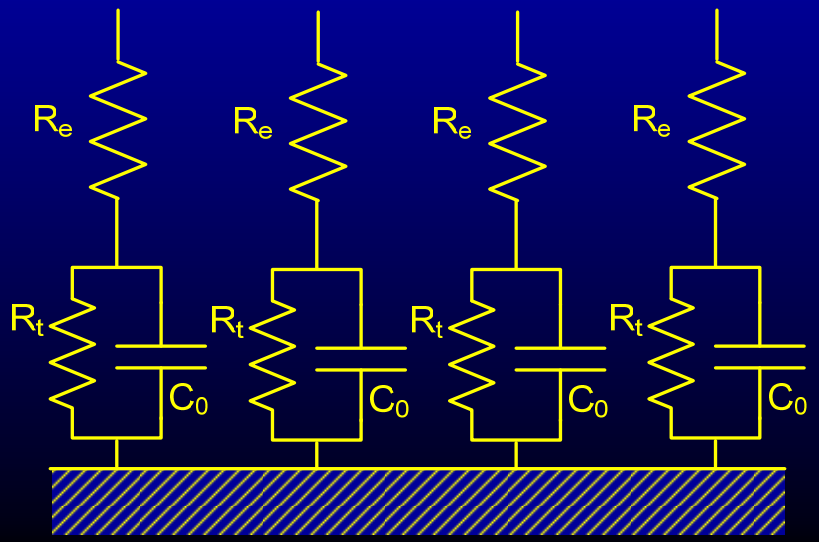


Semi-Circle

$$Z = R_e + \frac{R_t}{1 + j\omega C_0 R_t}$$

Depressed Semi-Circle

$$Z = R_e + \frac{R_t}{1 + (j\omega)^{\alpha} QR_t}$$



CPE caused by distribution of time constants

The CPE is Controversial

L'alliance anti-CPE se noue dans la rue

De nombreux lycéens ont rejoint les cortèges étudiants, hier un peu partout en France, pour protester contre le contrat première embauche. Demain, de nouvelles manifestations auront lieu à l'appel des syndicats de salariés ainsi que des principales organisations lycéennes et étudiantes P.3 à 5

Dans Marseille, hier.

GÉRARD JULIEN/AFP

Liberation 20 March, 2006

Une «crise profonde»

Selon notre sondage, seuls 6% des Français défendent le CPE «en l'état».

La Croix 17 March, 2006

CPE: Contrat Première Embauche

(First Employment Contract, 2006)

CPE: Constant Phase Element

Semi-Circle

$$Z = R_e + \frac{R_t}{1 + j\omega C_0 R_t}$$

Depressed Semi-Circle

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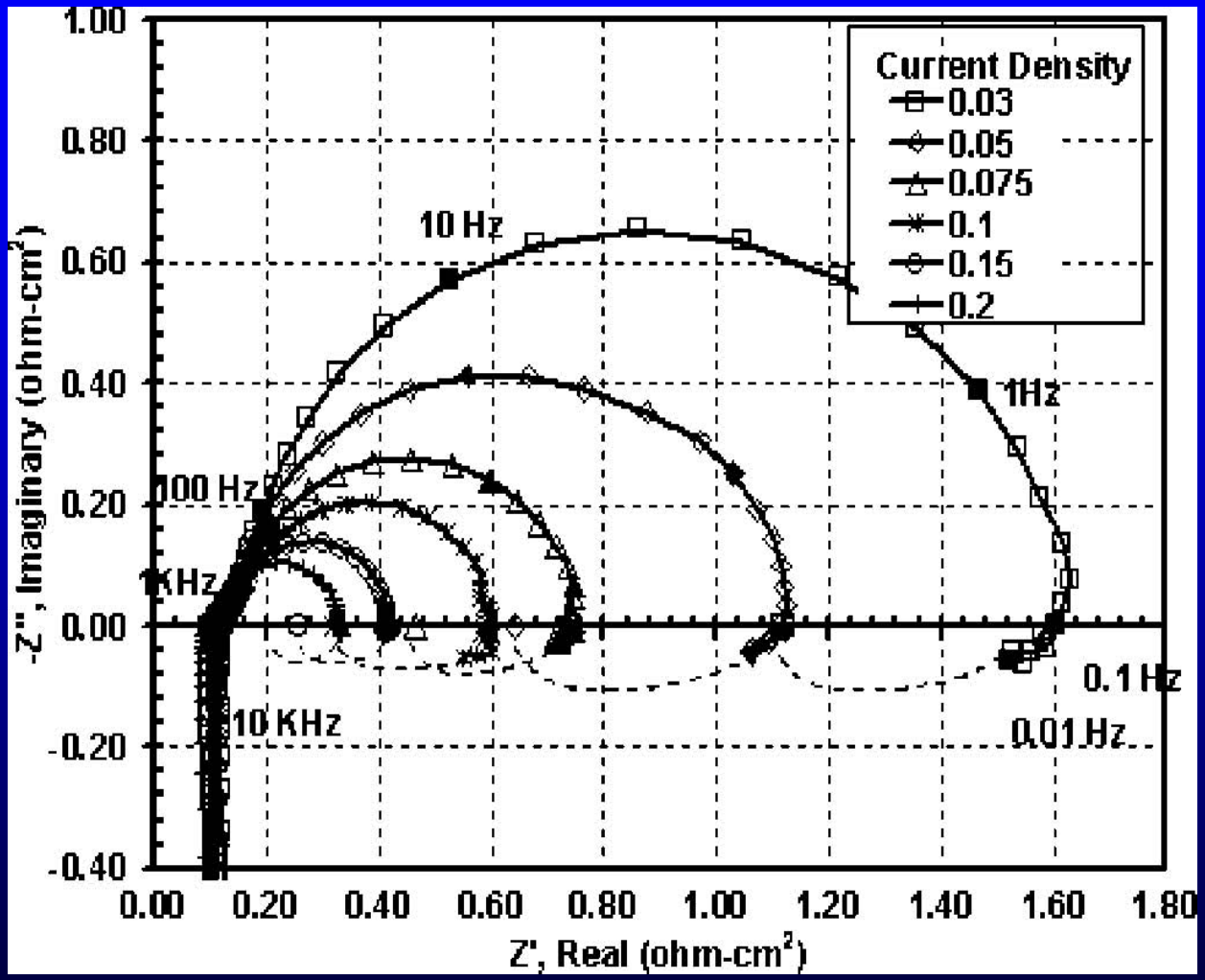
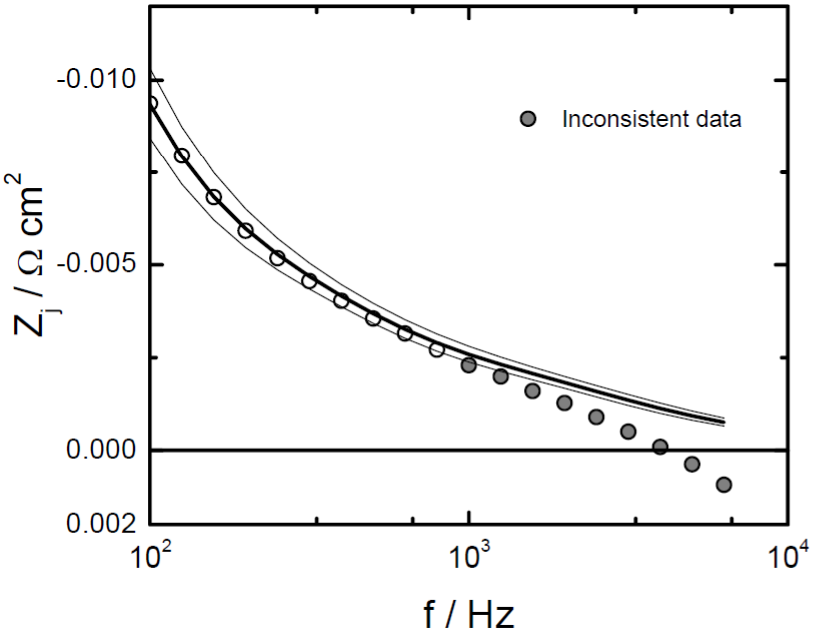
PEM Fuel Cell

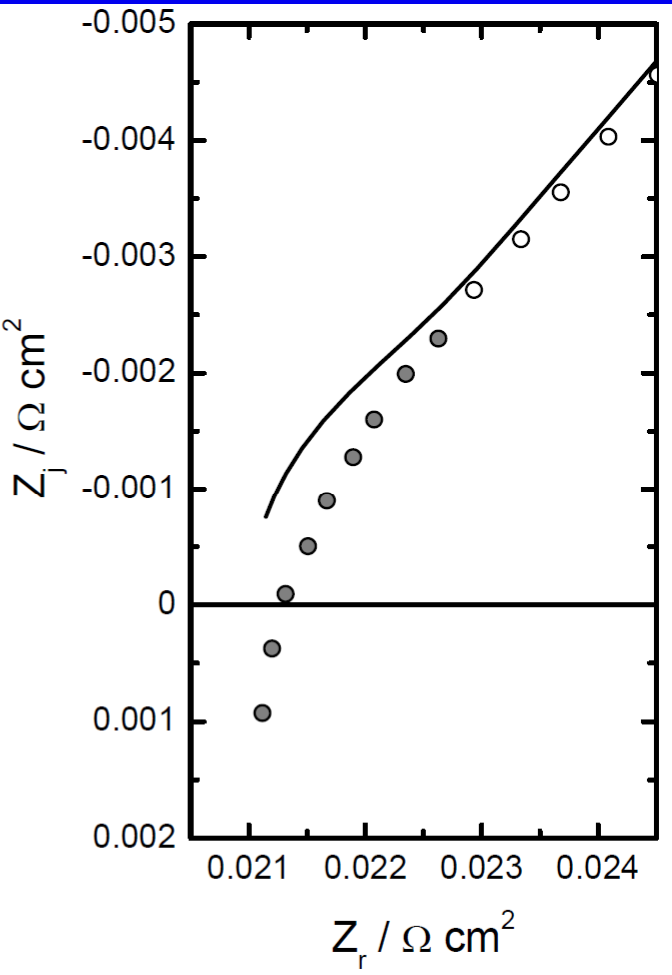


R. Makharia, M. F. Mathias, and D. R. Baker, *J. Electrochem. Soc.*,152 (2005) A970.
S. K. Roy, M. E. Orazem, and B. Tribollet, *J. Electrochem. Soc.*, 154 (2007), B1378.

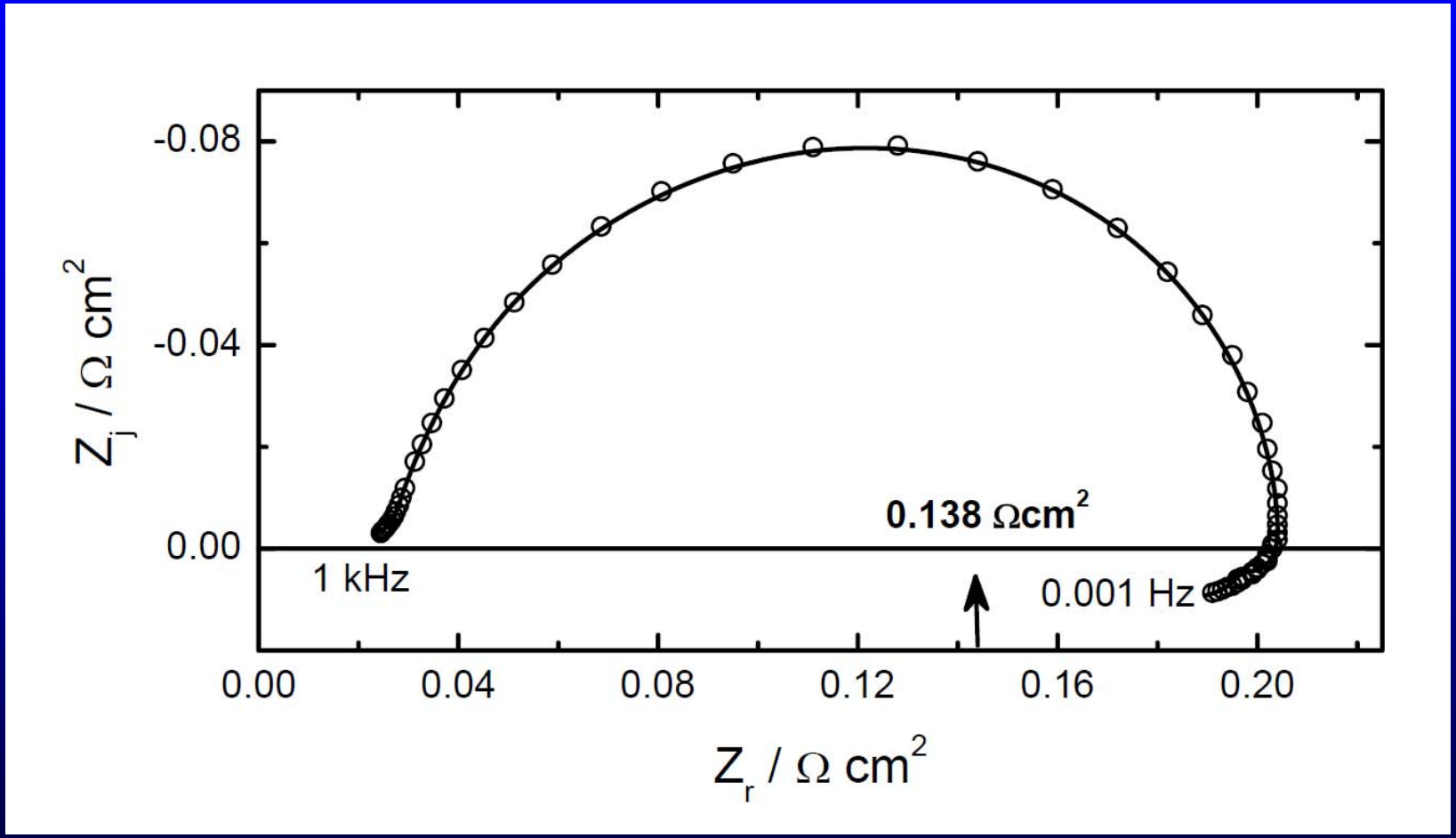
Error Analysis by Measurement Model

High-frequency artifacts extend to negative imaginary values





Impedance Data after Measurement Model Analysis



S. K. Roy, M. E. Orazem, and B. Tribollet, *J. Electrochem. Soc.,* **154** (2007), B1378.
S. K. Roy and M. E. Orazem, *J. Electrochem. Soc.,* **154** (2007), B883.

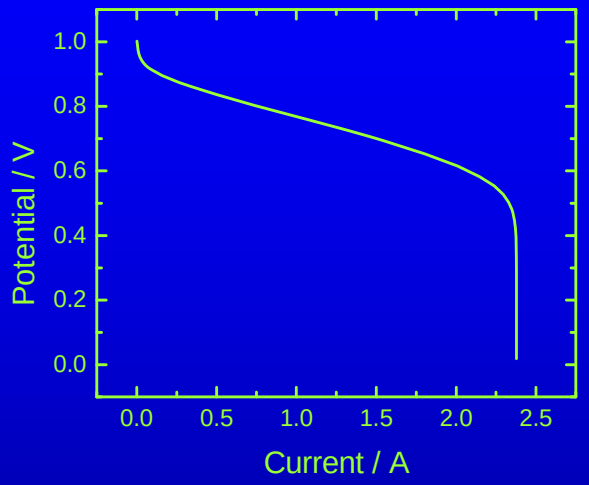
Process Model Development

Steps in Model Development

Reaction Mechanisms

Steady-State Current Expressions

Polarization Curve



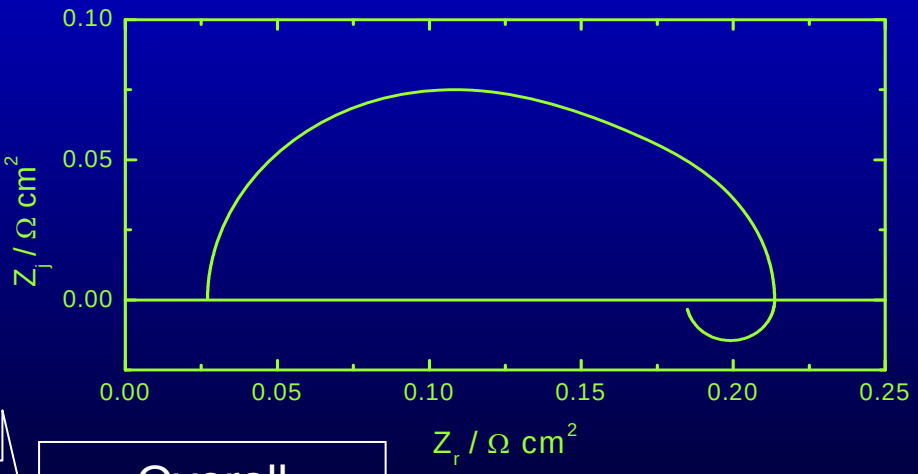
Apply Sinusoidal Perturbation

Faradaic Impedance

Double Layer Capacitance

Electrolyte Resistance

Overall Impedance



Proposed Reaction

- Oxygen Reduction

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

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

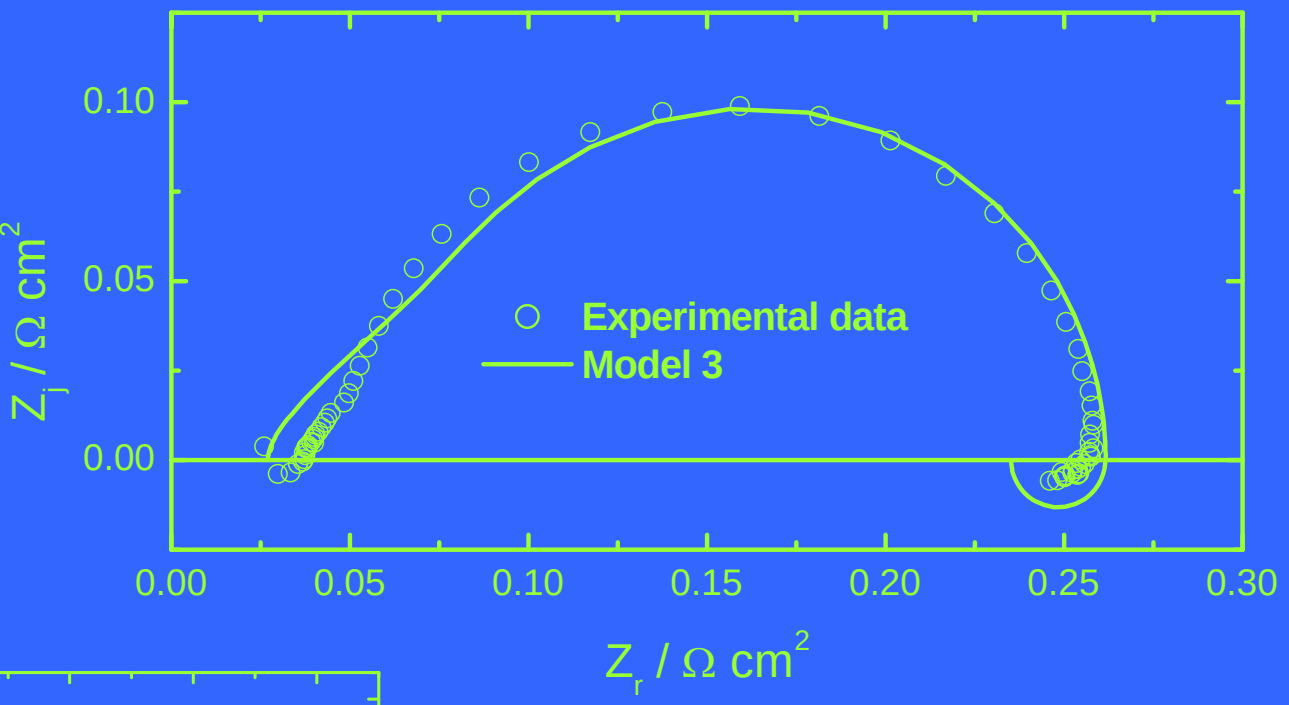
$$PtO + 2H^+ \rightarrow Pt^{+2} + 2H_2O$$

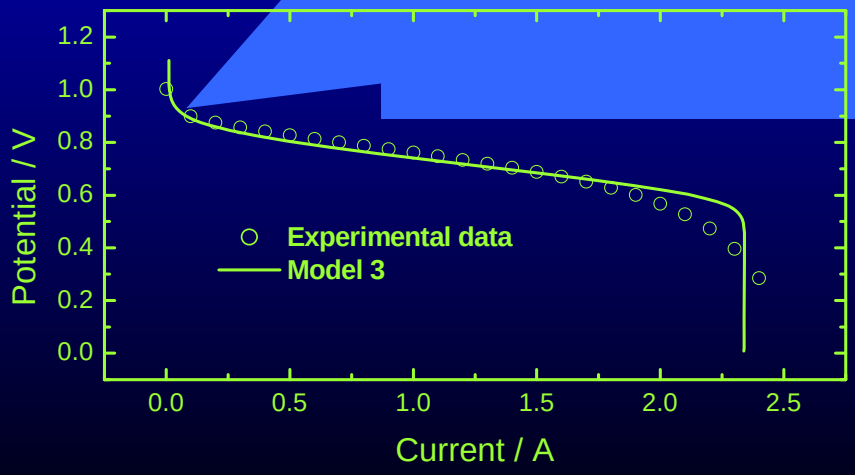
- Hydrogen Oxidation

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

R. M. Darling and J. P. Meyers, *J. Electrochem. Soc.,* 150 (2003) A1523.

Comparison to Data





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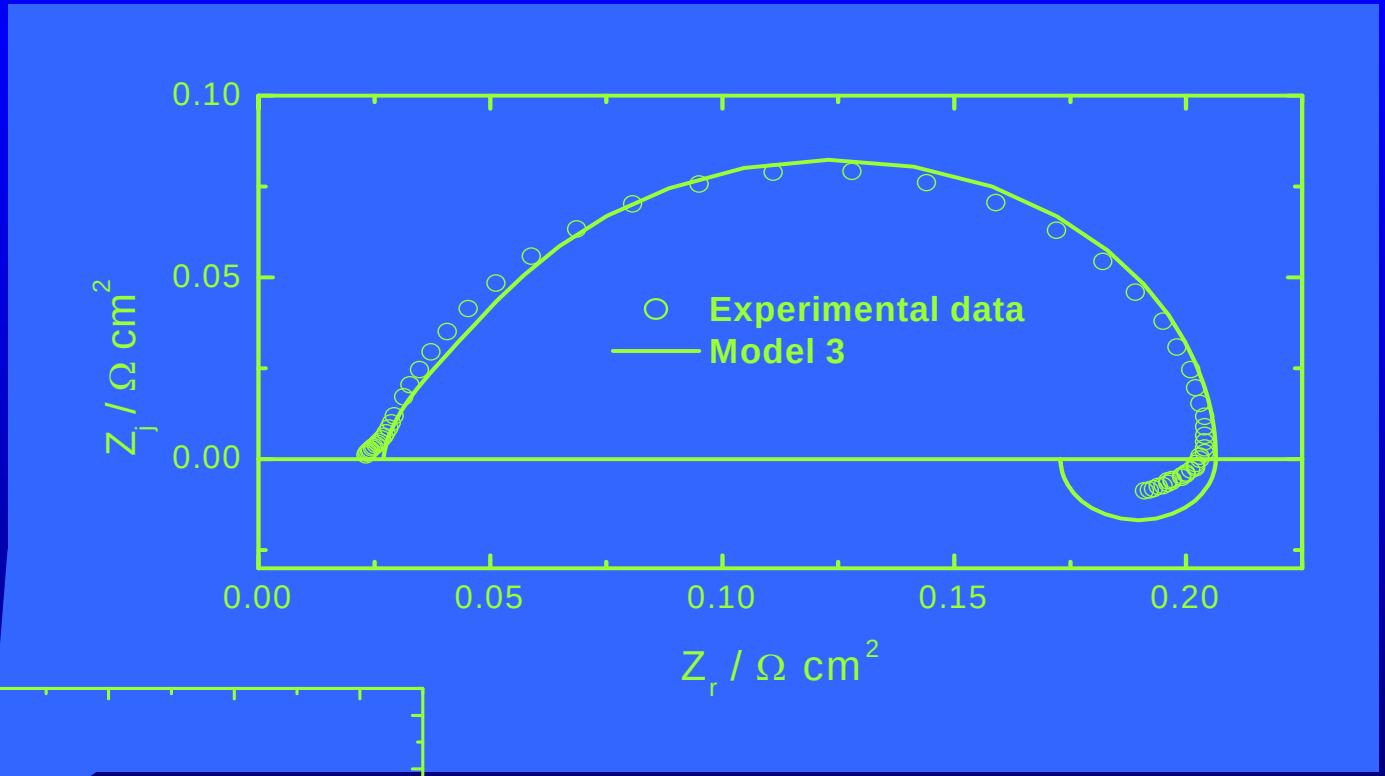

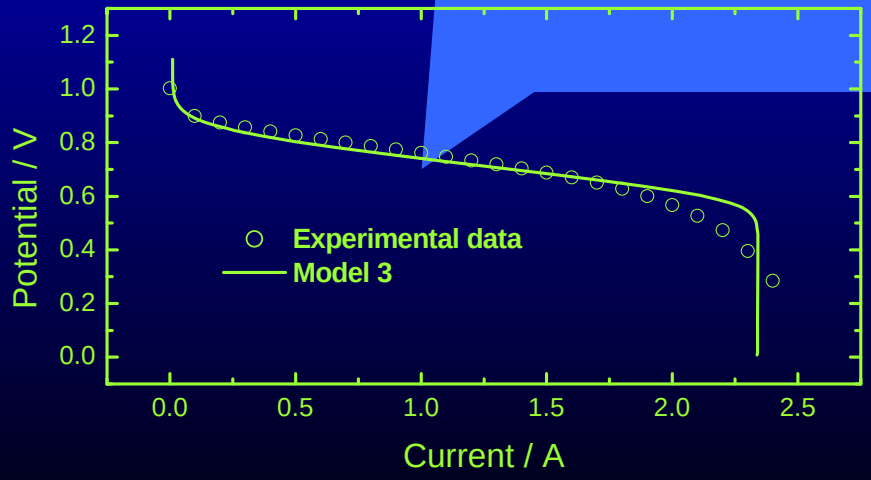

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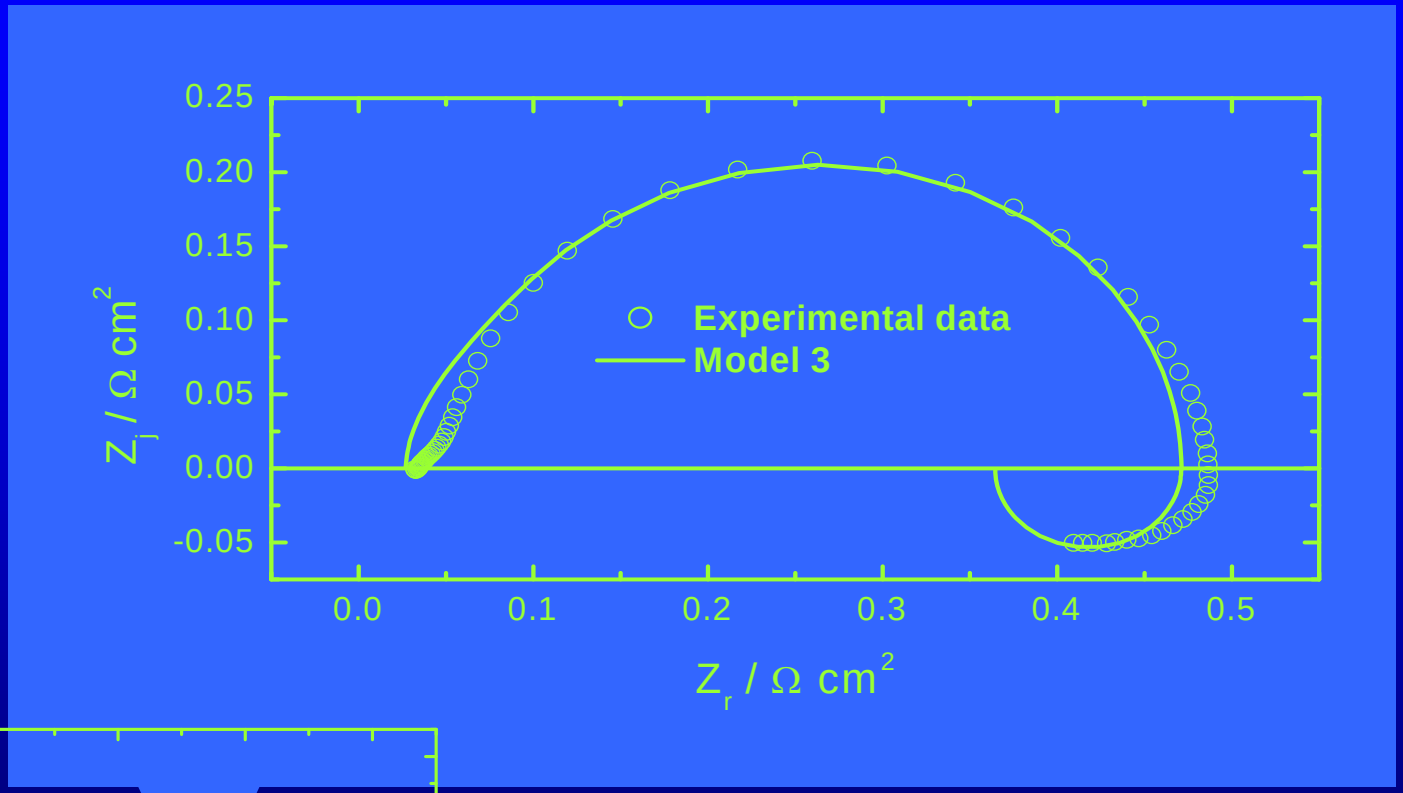
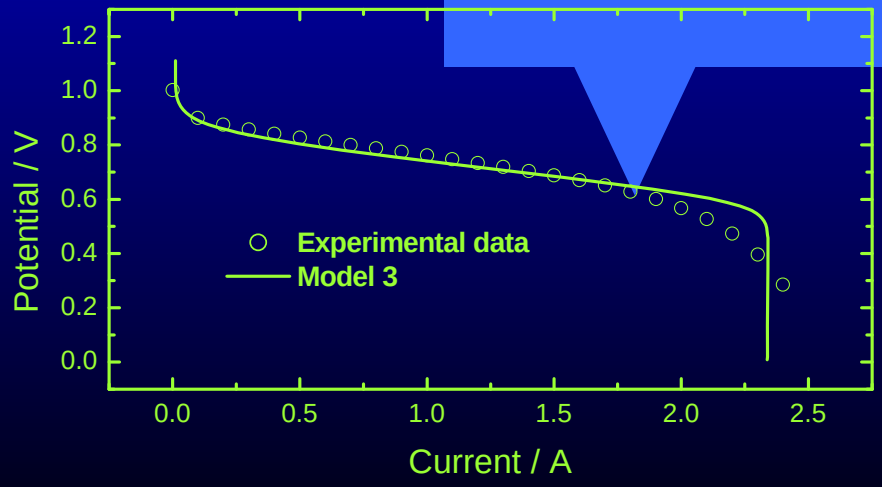


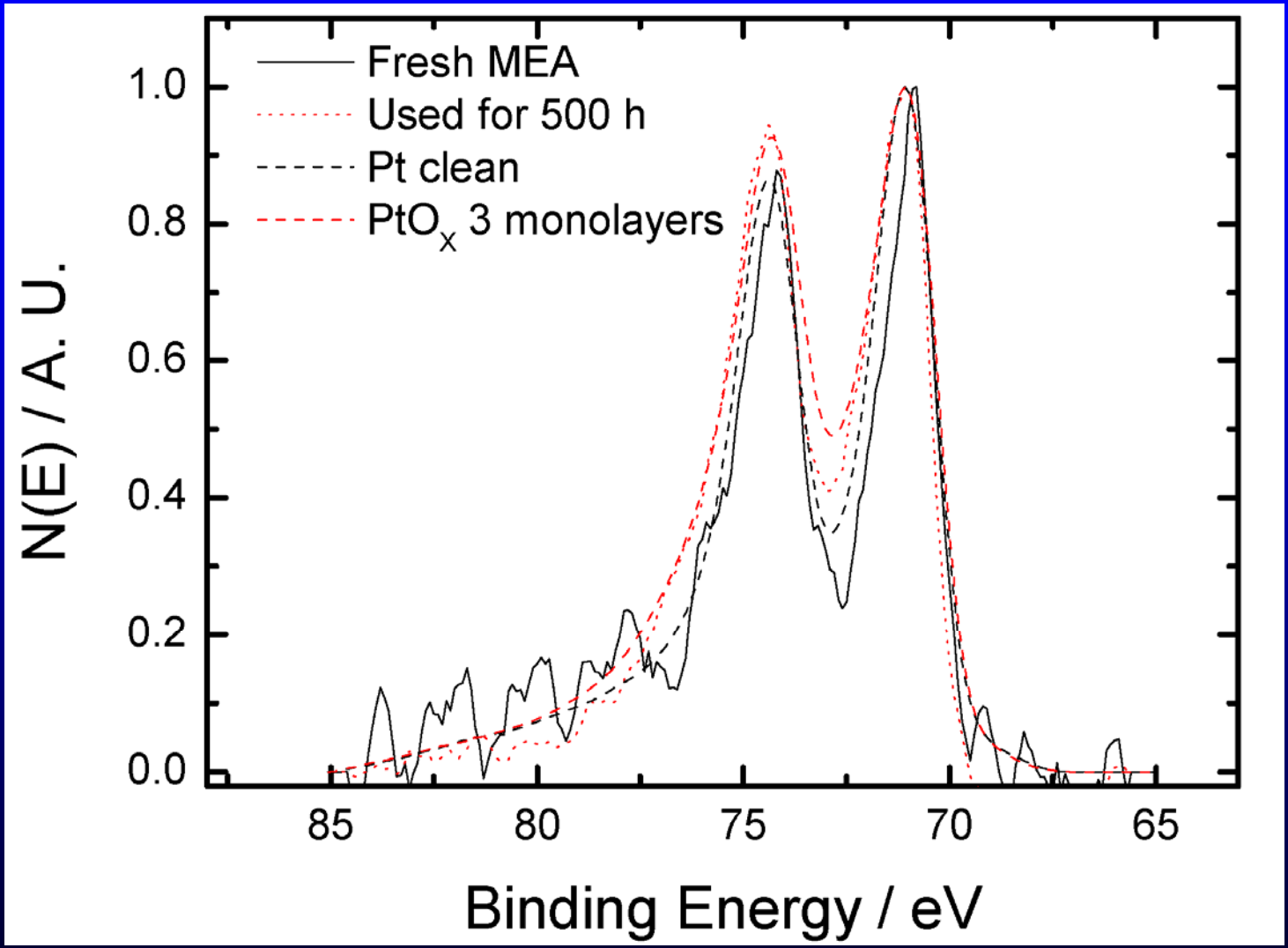


Model development suggests supporting experiments

- Formation of PtO
- Reduction in electrochemically active area
- Dissolved Pt in outflow

S. K. Roy and M. E. Orazem, *J. Electrochem. Soc.,* **156** (2009), B203.
M. E. Orazem and B. Tribollet, *Electrochim. Acta,* **53** (2008), 7360.

Evidence for PtO_x



Helena and Jason Weaver, University of Florida

Electrochemical Impedance Spectroscopy

- Electrochemical Technique
  - In-situ
  - Non-invasive
  - Sensitive to transport, kinetics, surfaces
- Amenable to a Systematic Approach
  - Measurement models
  - Deterministic Models
- Not a Stand-Alone Technique
- Yields Insight
  - Reaction mechanisms
  - Degradation phenomena

Needs/Opportunities for EIS

- Deterministic models
  - reactions
  - transport
  - nonuniform surfaces
- Error analysis
- Correlation to operating conditions
  - noise to flooding/drying
  - features to degradation mechanisms