SFU SIMON FRASER UNIVERSITY
DEPARTMENT OF CHEMISTRY

Modeling of Ultrathin Catalyst Layers in Polymer Electrolyte Fuel Cells

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Overview

- Proton Transport in Ultrathin Catalyst Layers
- Single Pore Model
  - Metal phase surface charge density
  - Steady state model
  - Impedance variant
- EIS of 3M Nanostructured Thin Films - Challenges

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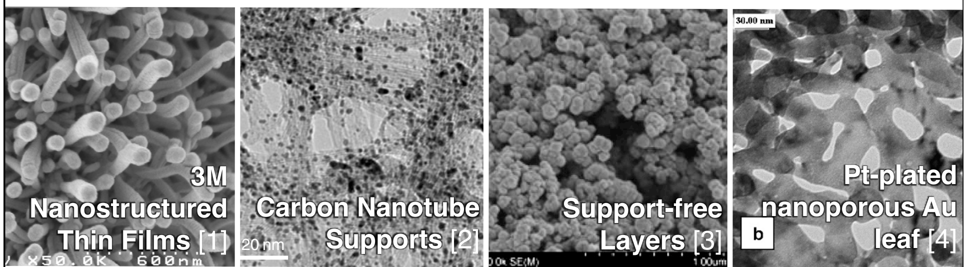
Ultrathin Catalyst Layers (UTCLs)



- Variety of Materials and Structures
  - Pore structure: random or ordered
  - Catalyst support: CNTs, whiskers, support-free, etc.
  - Pt: nanoparticles or continuous film
- Ionomer-free
- Thickness 20nm-1µm

[1] M. K. Debe *et. al.*, *JPS.* 161, 1002 (2006)
[2] JM Tang *et al.*, *Aust. J. Chem.* 2007, 60, 528–532
[3] M. Saha *et al.*, *EA.* 51, 4680 (2006)
[4] R. Zeis *et al.*, *JPS,* 165 (2007) 65-73

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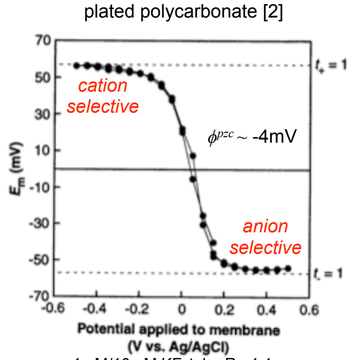
Proton Transport in UTCLs

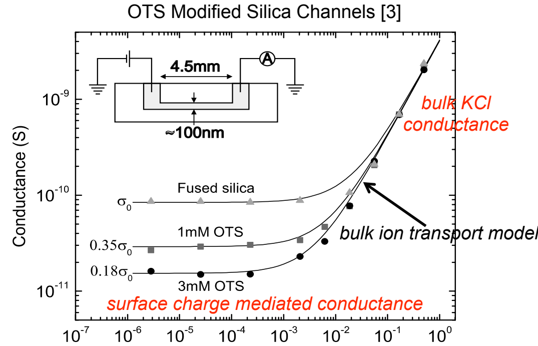
1) Bulk proton transport controlled by surface charge [1]

Ion-selective Au plated polycarbonate [2]



1mM/10mM KF, tube R ~1.1nm

OTS Modified Silica Channels [3]



2) Surface transport of protons [4]

[1] Daiguji, *Chem. Soc. Rev.* **39**, 901, (2010) [2] Nishizawa *et al.*, *Science*, (1995) **268**, 700
[3] Stein *et al.*, *PRL*, **93**, 035901, (2004) [4] Sinha *et al. JES*, **158** (7) B831 (2011)

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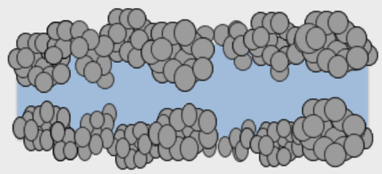
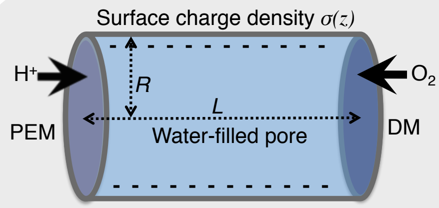
Single Pore Model of UTCLs



Active Regions: water-filled nanopores with heterogeneous Pt/support surfaces



Model system: water-filled, cylindrical nanopore with charged, smooth Pt walls

Metal potential ϕ^M → Current density j

Continuum Approach

Metal potential ϕ^M

↕ *Stern Electric Double Layer Model*

Surface charge density $\sigma(z)$

↕ *PNP (H^+ Transport)*
Fick's Law (O_2 Transport)

Reactant and potential distributions
$\phi(\mathbf{r}),\ c_{H+}(\mathbf{r})\ ,\ c_{O2}(\mathbf{r})$

↕ *Butler Volmer ORR Kinetics*

Local current density $j(z)$

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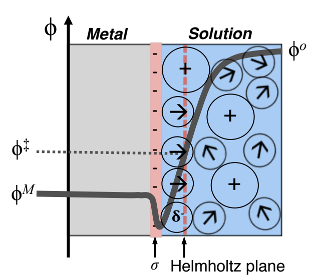
Pore Wall Surface Charge Density

➢ To relate electrode potential ϕ^M and σ, apply Stern Model:



$$\sigma(z) = \int_{\phi^{pzc}-\phi^o}^{\phi^M-\phi^\ddagger} C_H(\phi^M-\phi^\ddagger)' d(\phi^M-\phi^\ddagger)'$$

Helmholtz capacitance C_H
Potential of zero charge ϕ^{pzc}
Helmholtz plane potential $\phi^\ddagger$

➢ Boundary condition for potential at pore wall:

$$\varepsilon \partial_r \phi \Big|_{r=R} = C_H \left[(\phi^M - \phi^\ddagger) - (\phi^{pzc} - \phi^o) \right]$$

Neglected in [1]. Parametrizes metal|solution interfacial structure

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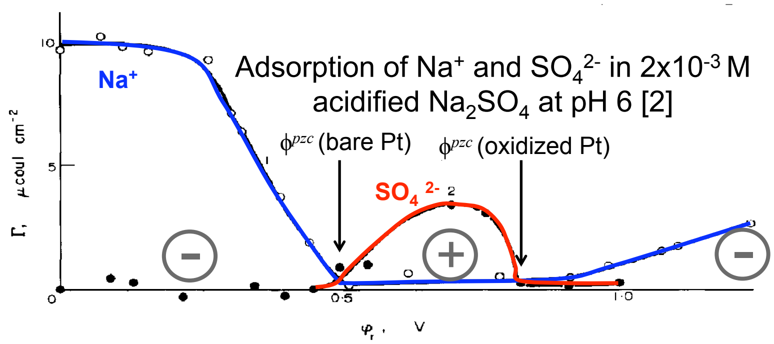
[1] Bazant *et al, JEC,* 500(2001) 52–61; *PRE* **83**, 061507 (2011)

Charging of Oxide-covered Pt

- Specific adsorption can alter the ϕ^{pzc} [1]



- Consider range of Pt ϕ^{pzc}: 0.3-1.0V_{SHE} [3-5]

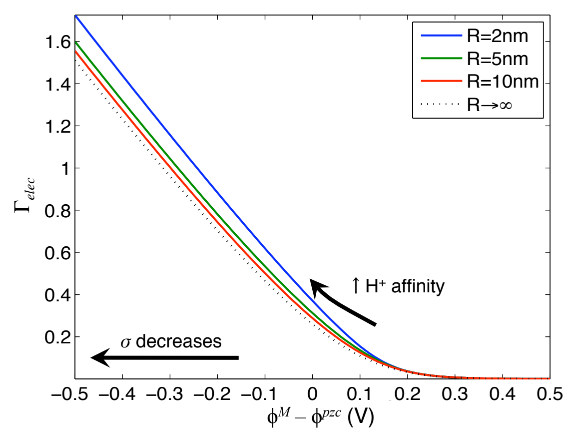
[1] Schmickler, *Interfacial Electrochemistry 2nd ed*, 2010. [2] Kolotyrkina, Petrii, Kazarinov, *Elektrokhimiya* **10**, 1352 (1974))
[3] Climent *et. al. Russ. J. Elec.* 42, 1145 (2006). [4] Hamm *et al., JEC*, 414, 85 (1996). [5] Pajkossy *et. al., EA*, 46, 3063 (2001).

The Impact of $\phi^M - \phi^{pzc}$

Effectiveness Factor of Pt Utilization:

$$\Gamma = \frac{\int_0^L j(z)dz}{-j^o \exp(-\frac{\alpha F \eta_c}{R_g T}) \cdot L} \approx \Gamma_{elec}\Gamma_{O_2}$$

Separable into electrostatic and O_2 contributions, due to small proton flux



Pore H^+ concentration is tuned by $\phi^M - \phi^{pzc}$

Chan and Eikerling, *JES,* **158**(1), B18 (2011).

Oxygen Diffusion Limitations

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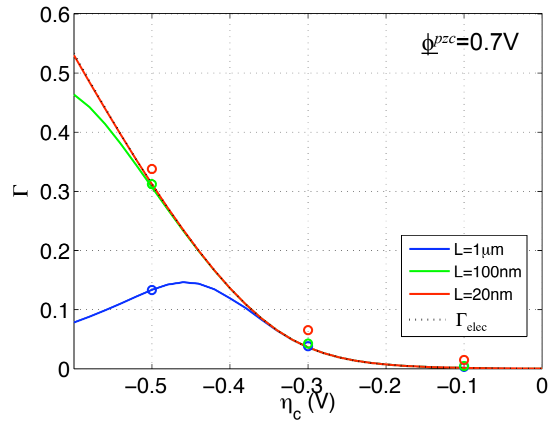
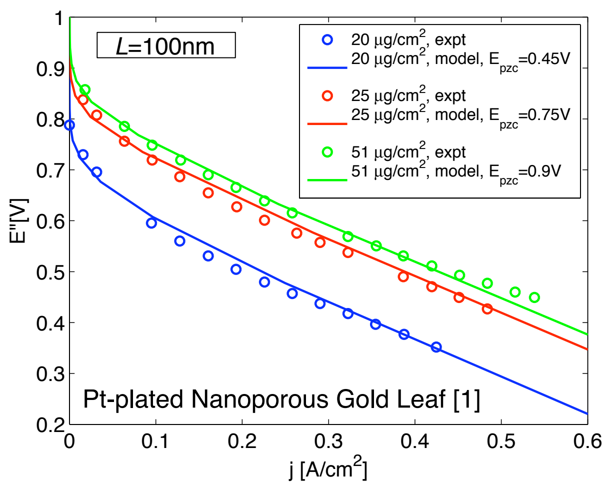


Diffusion of oxygen through water-flooded pores

Chan and Eikerling, *JES,* **158**(1), B18 (2011).

Polarization Curves



Trends reproducible from shifts in ϕ^{pzc}; cannot separate electrostatic and kinetic contributions → Impedance model

[1] R. Zeis *et al.*, *J. Power Sources,* 165 (2007) 65-73

Impedance Model: Analytical Solutions

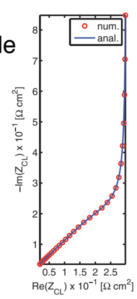
1. High aspect ratios $R << L$
2. Steady state proton and potential distributions are z-independent

- 1D, coupled ODE system in H^+ and O_2 concentrations
- Analytical solutions & circuits in 4 limiting cases
- Verify with full numerical solutions

Chan and Eikerling, *JES,* 159(2), B155, 2012

Impedance Model: Limiting Cases

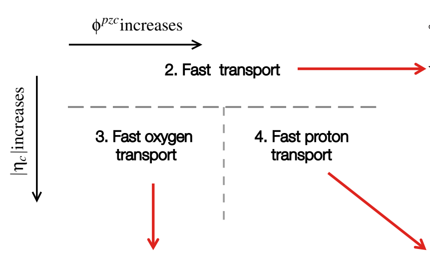
(1) Blocking electrode limit



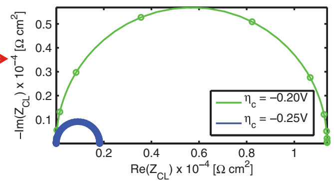
Chan and Eikerling, *JES,* 159(2), B155, 2012

Impedance Model: Limiting Cases

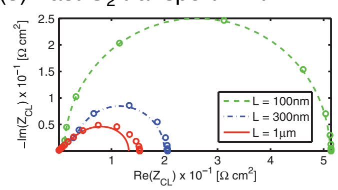
O_2-fed electrodes



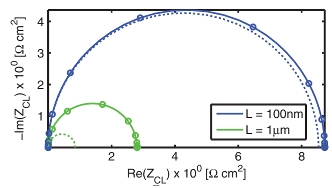
(2) Fast transport limit



(3) Fast O_2 transport limit



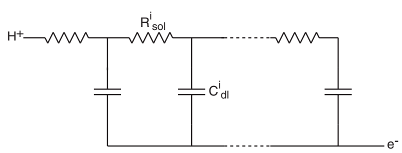
(4) Fast H+ transport limit



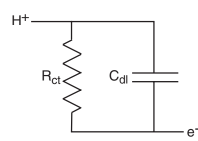
Chan and Eikerling, *JES,* 159(2), B155, 2012

Impedance Model: Limiting Cases

(1) Blocking electrode limit



(2) Fast transport limit



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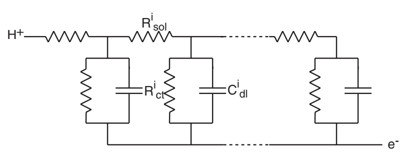
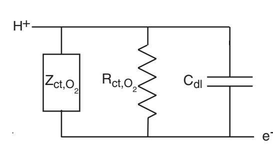


(4) Fast H+ transport limit



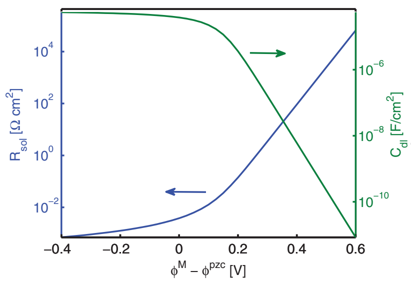
Electrostatics: R_{sol}, C_{dl} Kinetics: R_{ct} Mass Transport: $R_{ct,O2}$

Chan and Eikerling, *JES,* 159(2), B155, 2012

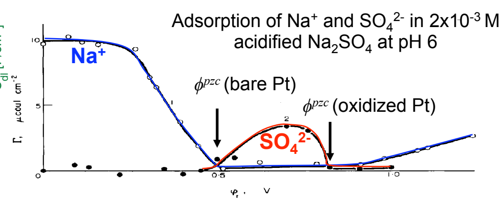
UTCL vs. CCL: Potential Dependence of R_{sol}

- Tunability of proton conductivity with surface charge density

Simple Stern Model Prediction



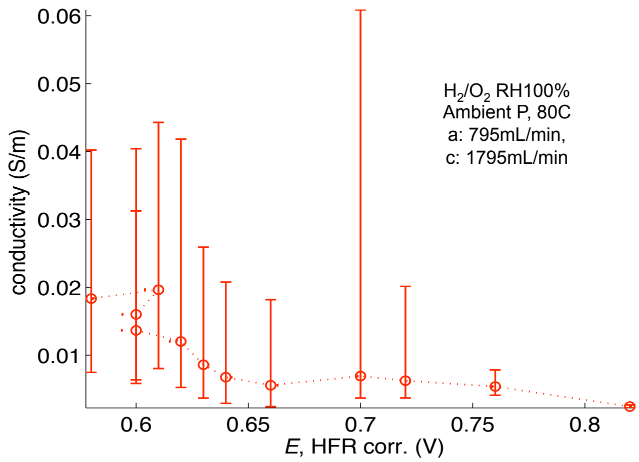
Pt: Impact of oxide on charging properties



Ongoing 3M NSTF EIS Experiments

- Zhong-Xie (NRC-IFCI), Max Cimenti (AFCC)
- Objectives
  - Model evaluation of proton transport mechanism
  - Tool for materials selection
- Challenges
  - Thermal cycle break-in (liquid flushing)
  - High $f = O$(100kHz) required due to high ω_{crit}
  - Fitting errors increased by L, HFR, $C_{PEM|UTCL}$

Proton Conductivity – *Preliminary Results*



- Conductivity is on the same order as that for Pt Black [1]

[1] Thompson and Baker, *ECST*, (1) 709, 2011

Conclusions and Outlook

Steady state model

- Importance of surface charge density, ϕ^{pzc}

Impedance model

- Separation of electrostatic, kinetic, transport contributions
- Evaluation of proton transport mechanism

Challenges

- Systematic set of experimental impedance data (NRC-IFCI/AFCC)
- Pt oxide formation and a corresponding shift in ϕ^{pzc}

Acknowledgements

NSERC CRSNG

NRC·CNRC Institute for Fuel Cell Innovation

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