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Ordered and Ultra-High Aspect Ratio Nanocapillary Arrays as a Model System

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Schwartz, Gregory E. Chester, and
Justin J. Hill

**AIR FORCE TEST CENTER
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228th ECS Meeting

Wednesday, October 14 2015

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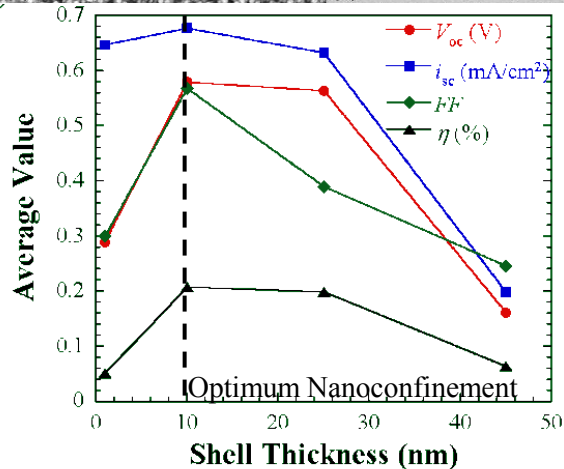
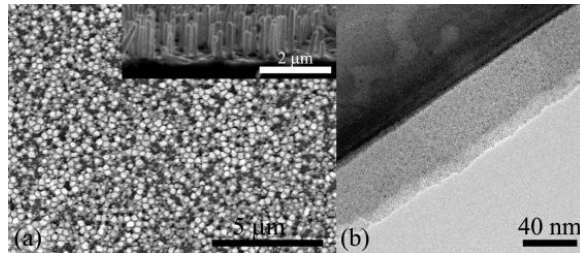
Agenda

- ▶ **AAO: Diverse Nano Applications**
- ▶ **Theoretical Considerations**
- ▶ **Characterizing Ultra-Deep AAO**
- ▶ **Future Work**

Materials Science & Engineering – Energy Conversion

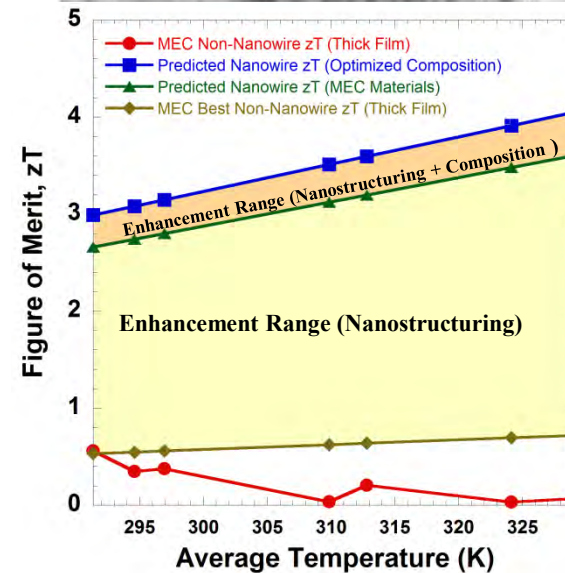
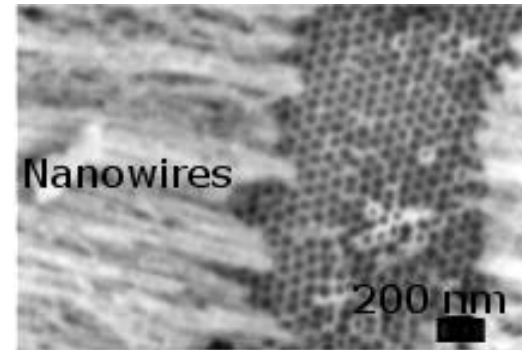
Solar Cells

Photoelectrochemical Light/Electrical Conversion



Thermoelectrics

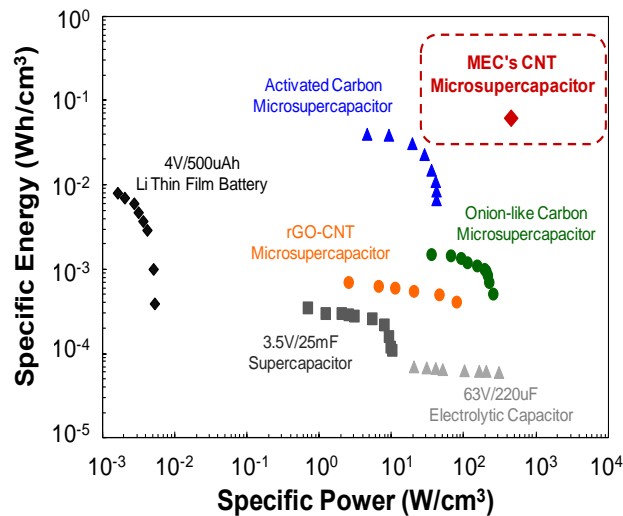
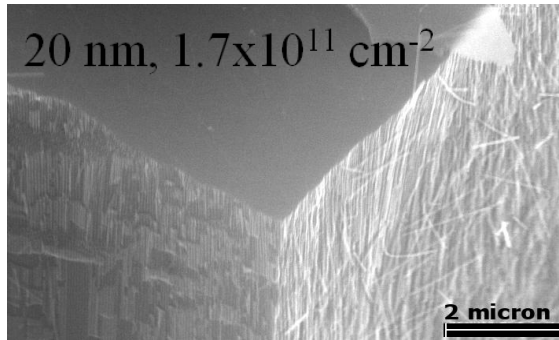
Solid-State Heat/Electrical Conversion



*Mainstream leverages
 nanomaterials to
 enhance technologies
 based on bulk materials*

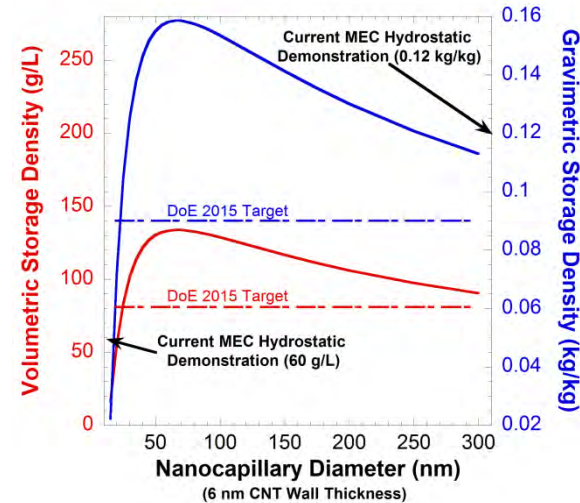
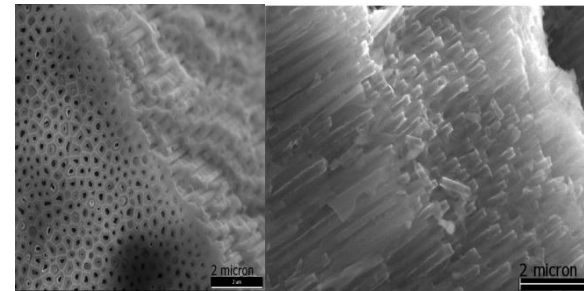
Ultracapacitors

Electrochemical Energy Storage



Nanocapillaries

Hydrogen & Oxygen Storage



Thermodynamic

- Joule Heating
- Uneven Temperature Distribution

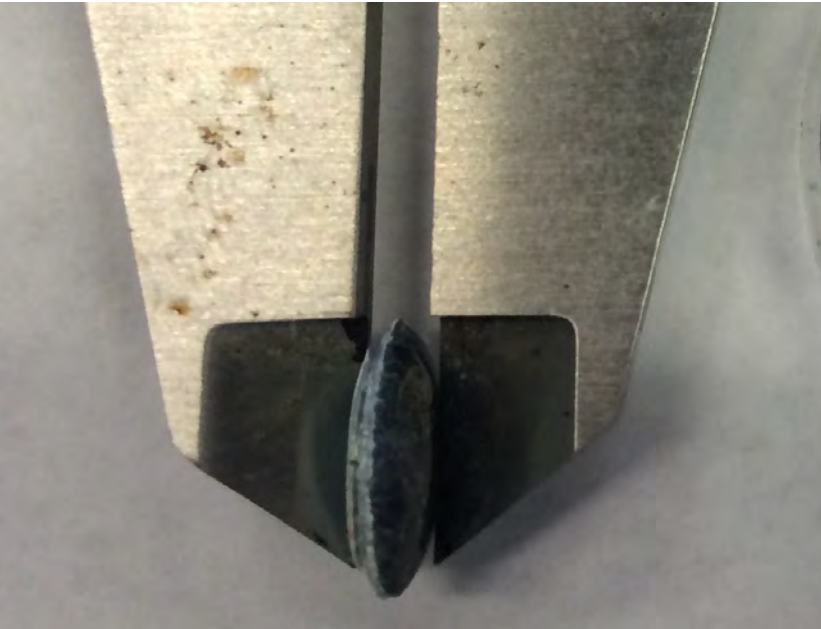
Kinetic

- Al₂O₃ Dissolution
- Side Reactions
- Stress-inhibited kinetics

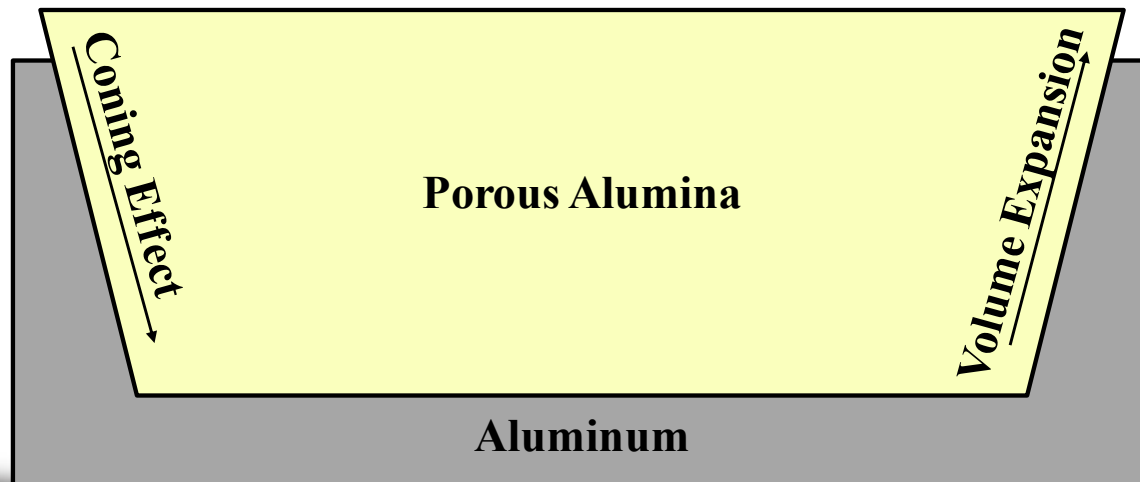
Transport

- Convective Dead Zones
- Concentration Polarization
- High-Field Ionic Conduction

Issue: Conical Anodization

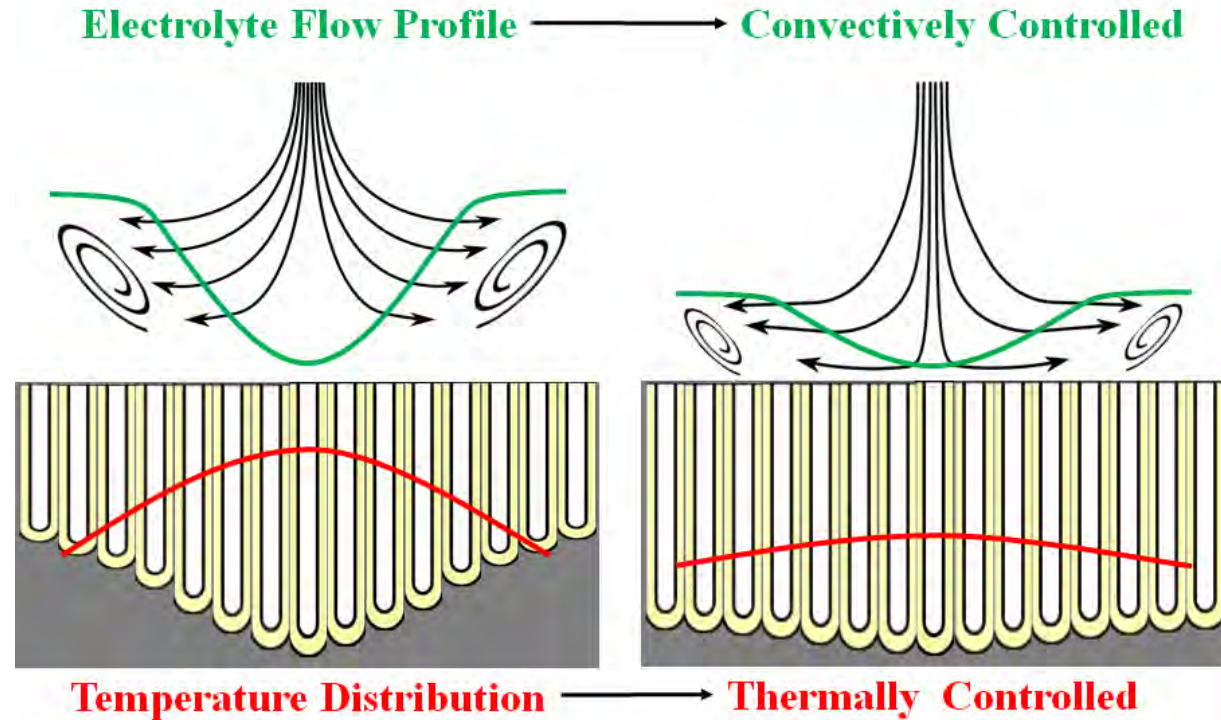


- ▶ Decrease storage volume
- ▶ Mechanical instability
- ▶ Causes:
- ▶ Leakage, stress-inhibited kinetics, uneven temperature distribution

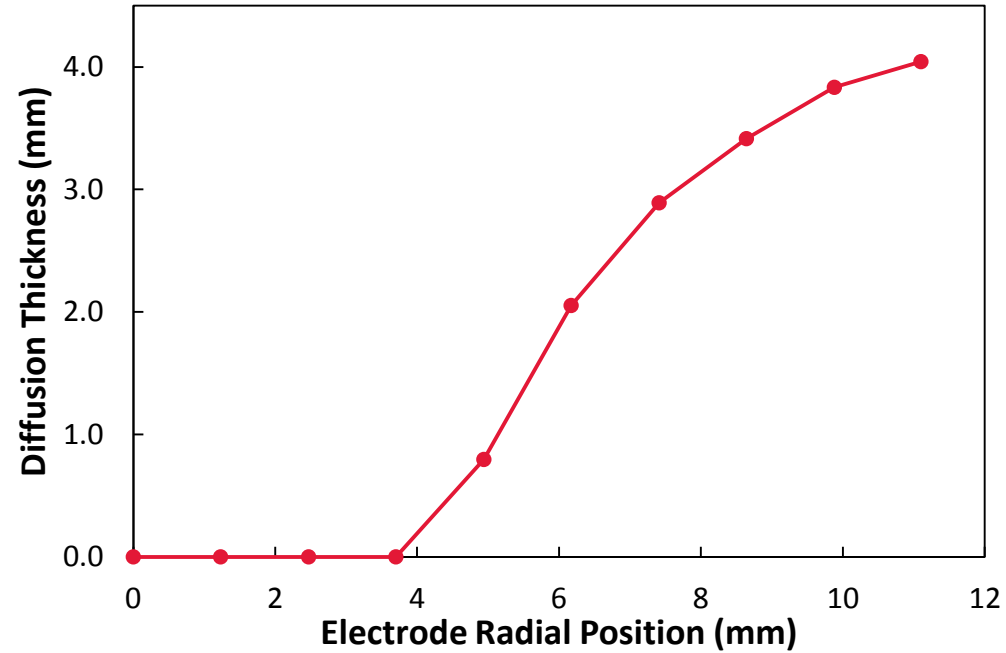
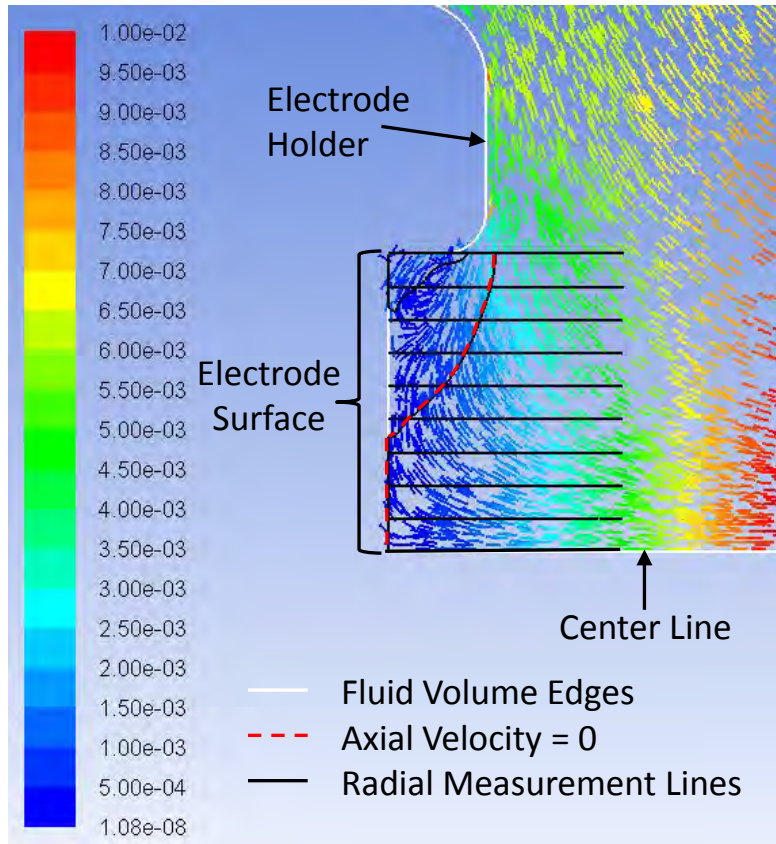


CPE Mitigation Schemes

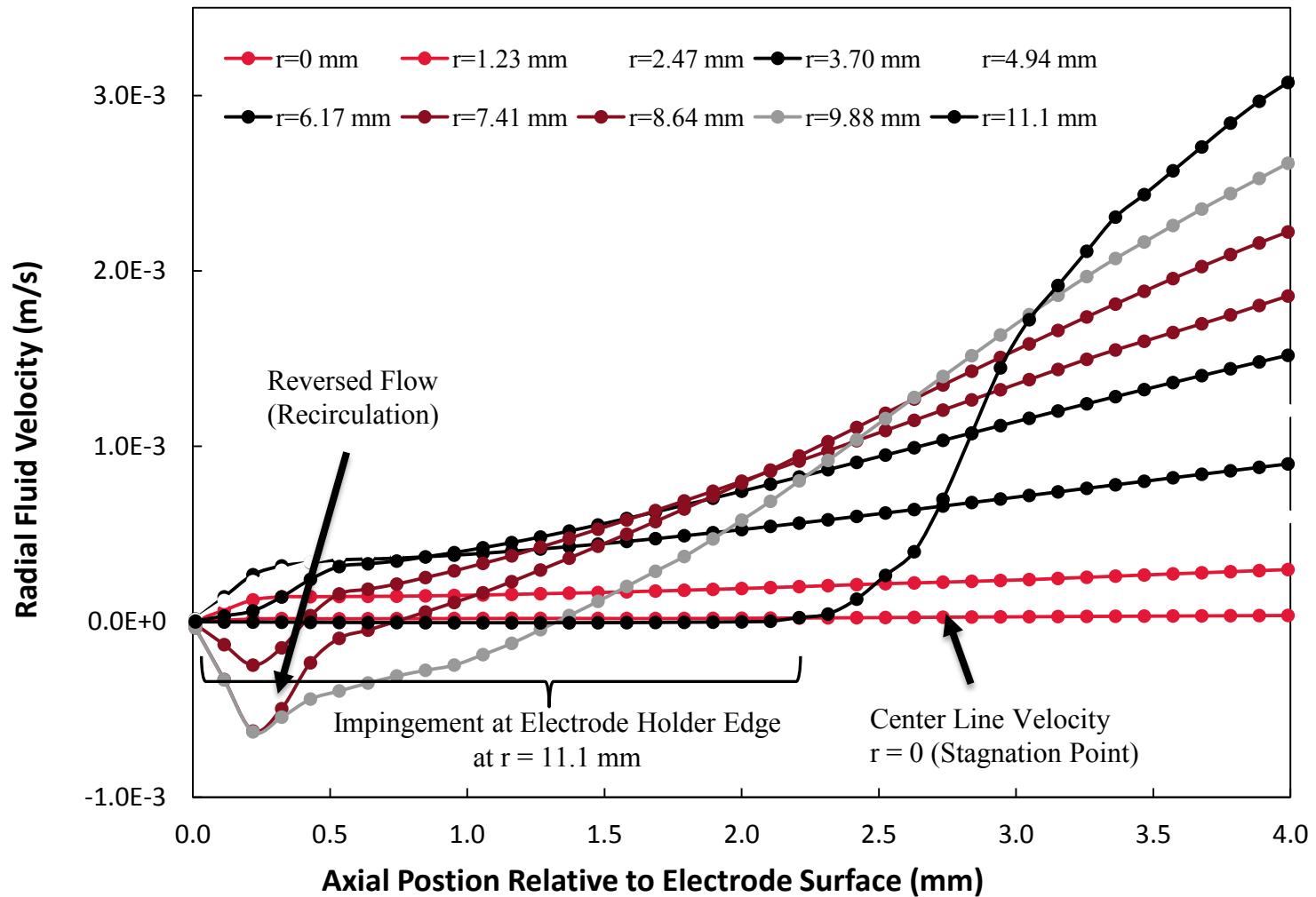
- ▶ Control thermal and flow profile -> even anodization
- ▶ Maximize gas storage volume
- ▶ Rate of anodization benefits



Fluid Flow and Diffusion Layer



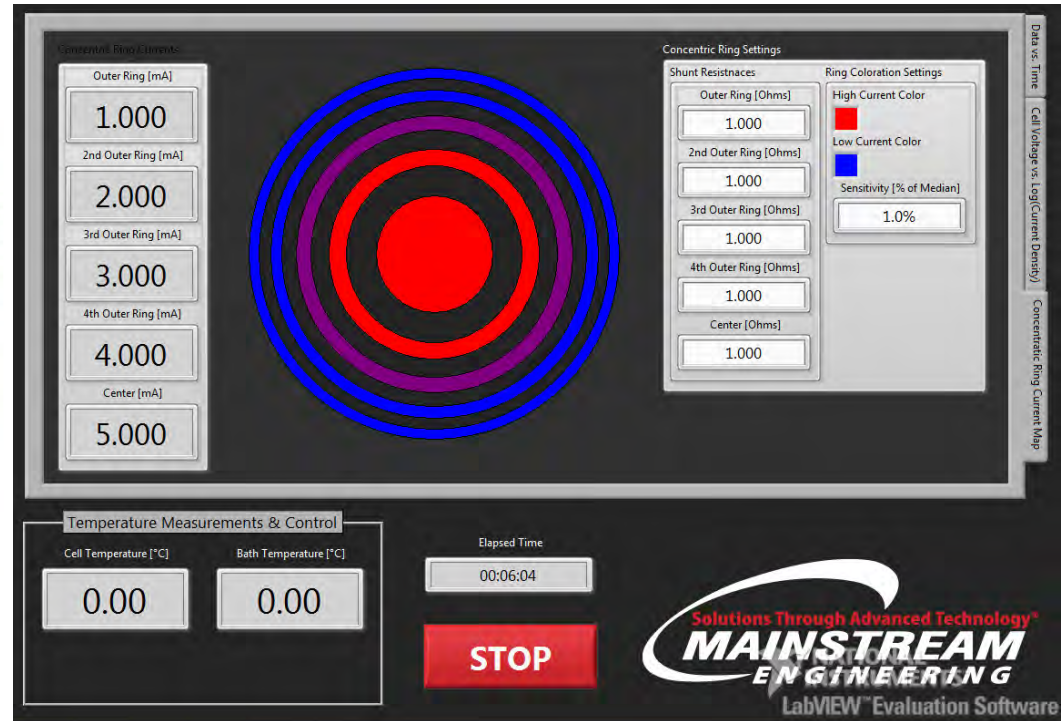
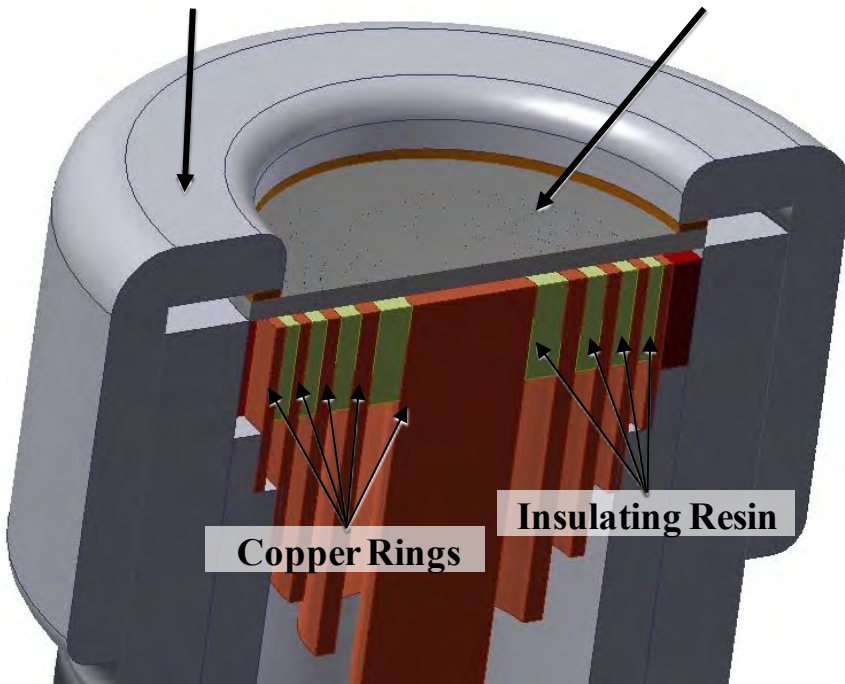
Fluid Flow Profile



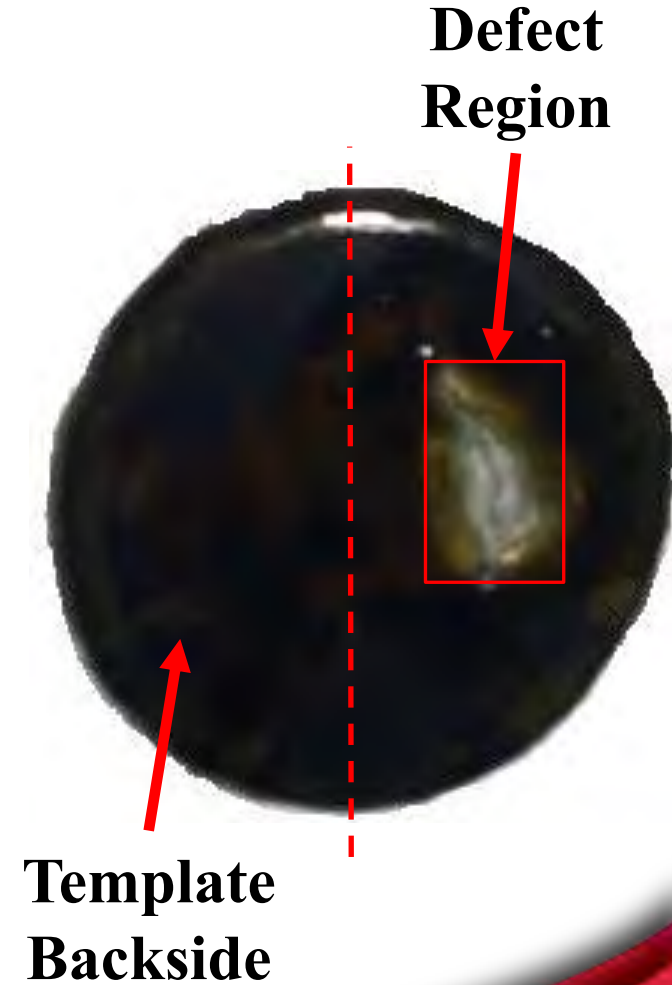
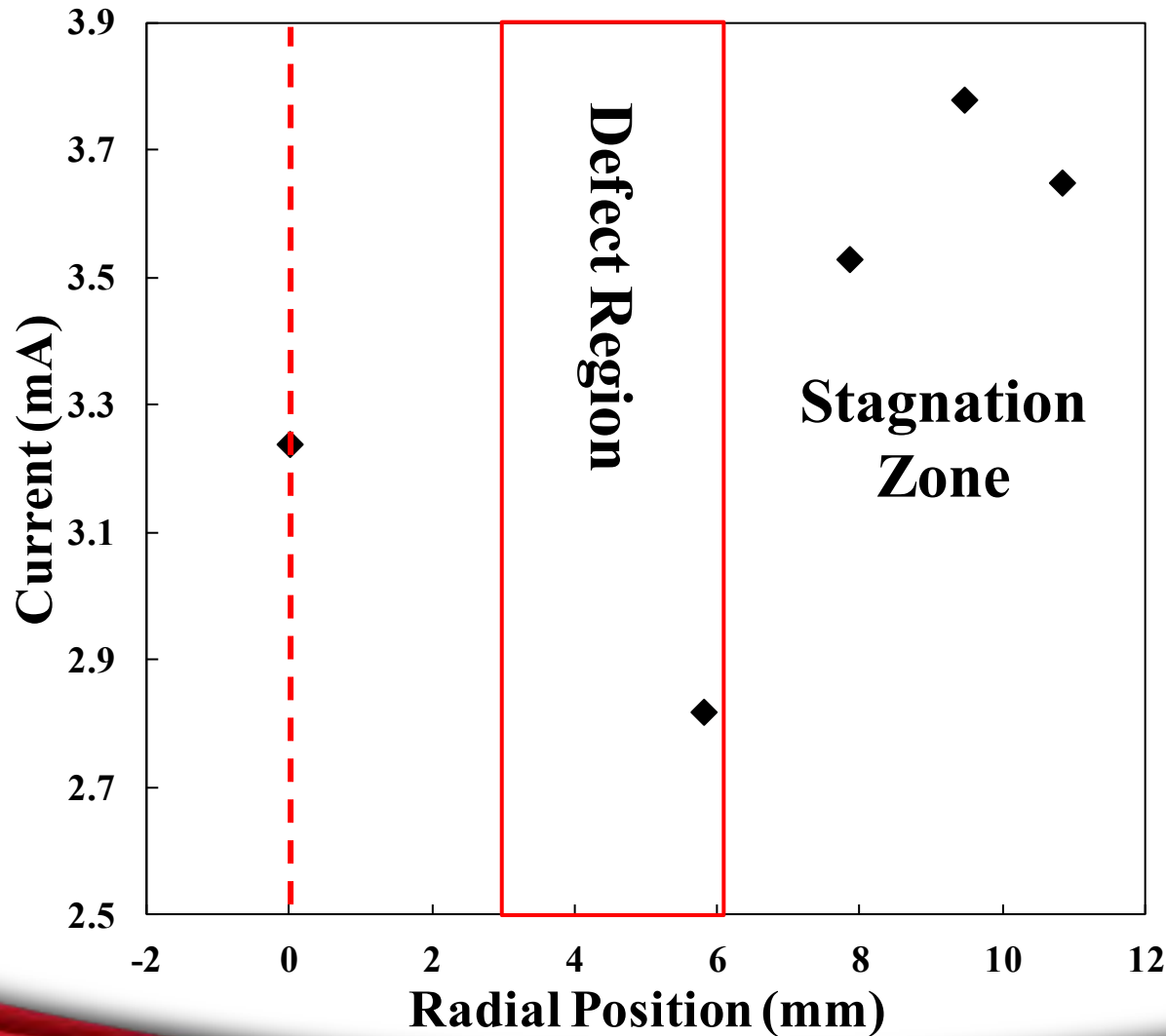
Current Mapping Hard Anodization

Teflon Holder

Aluminum Sample

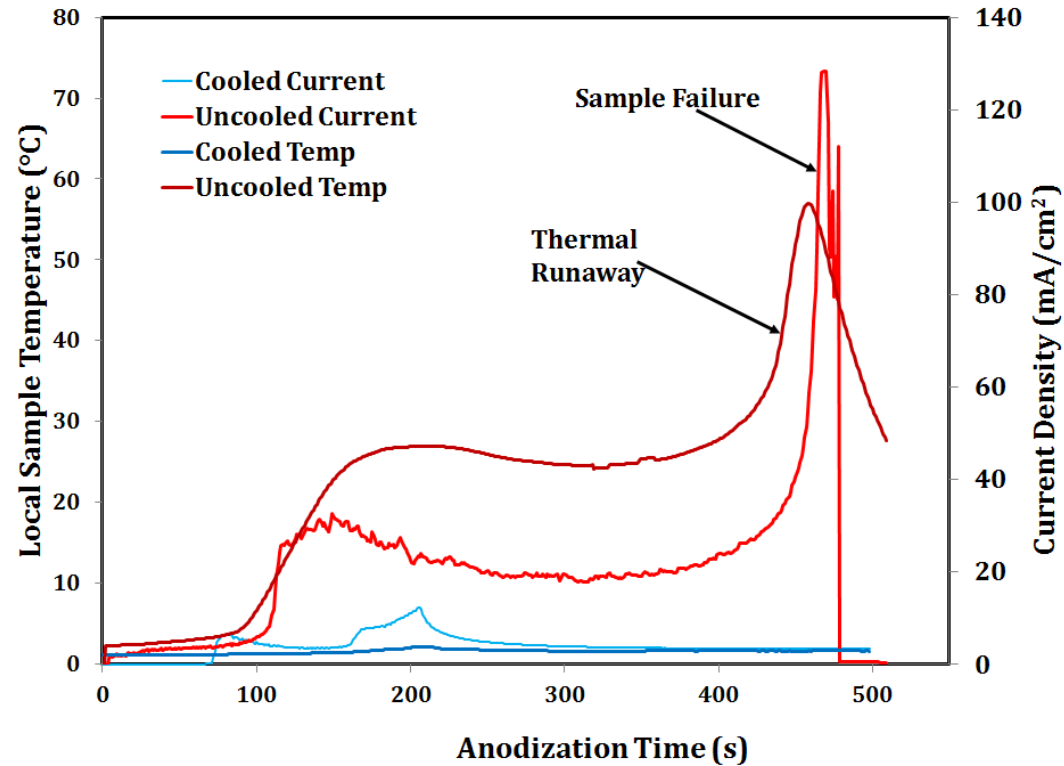


Defect Detection



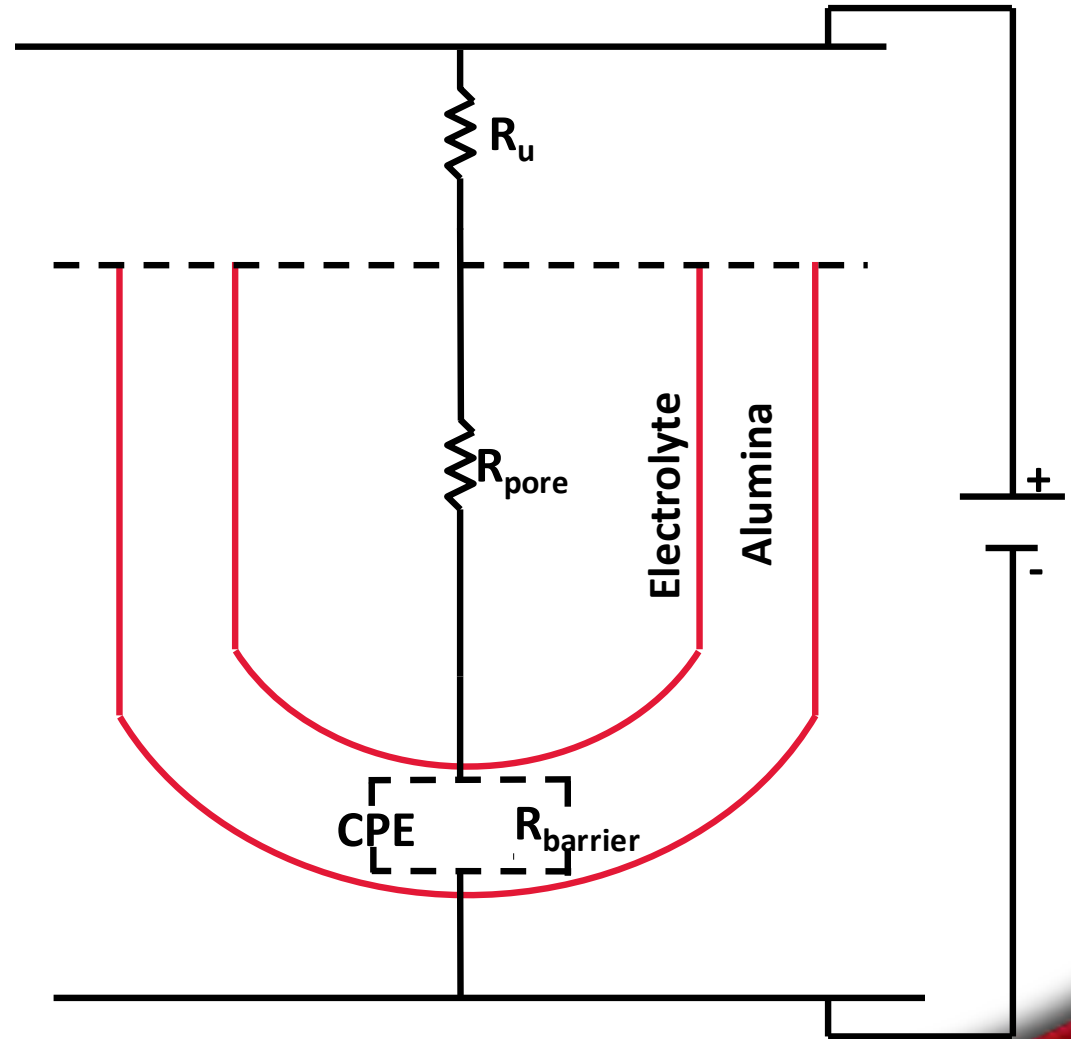
Preventing Thermal Failure

- ▶ **Hard Anodization can reach up to 86°C locally!**
- ▶ **Initial thermal failure common and costly**
- ▶ **Two step anodization increases production complexity**
- ▶ **Answer: thermal control system**



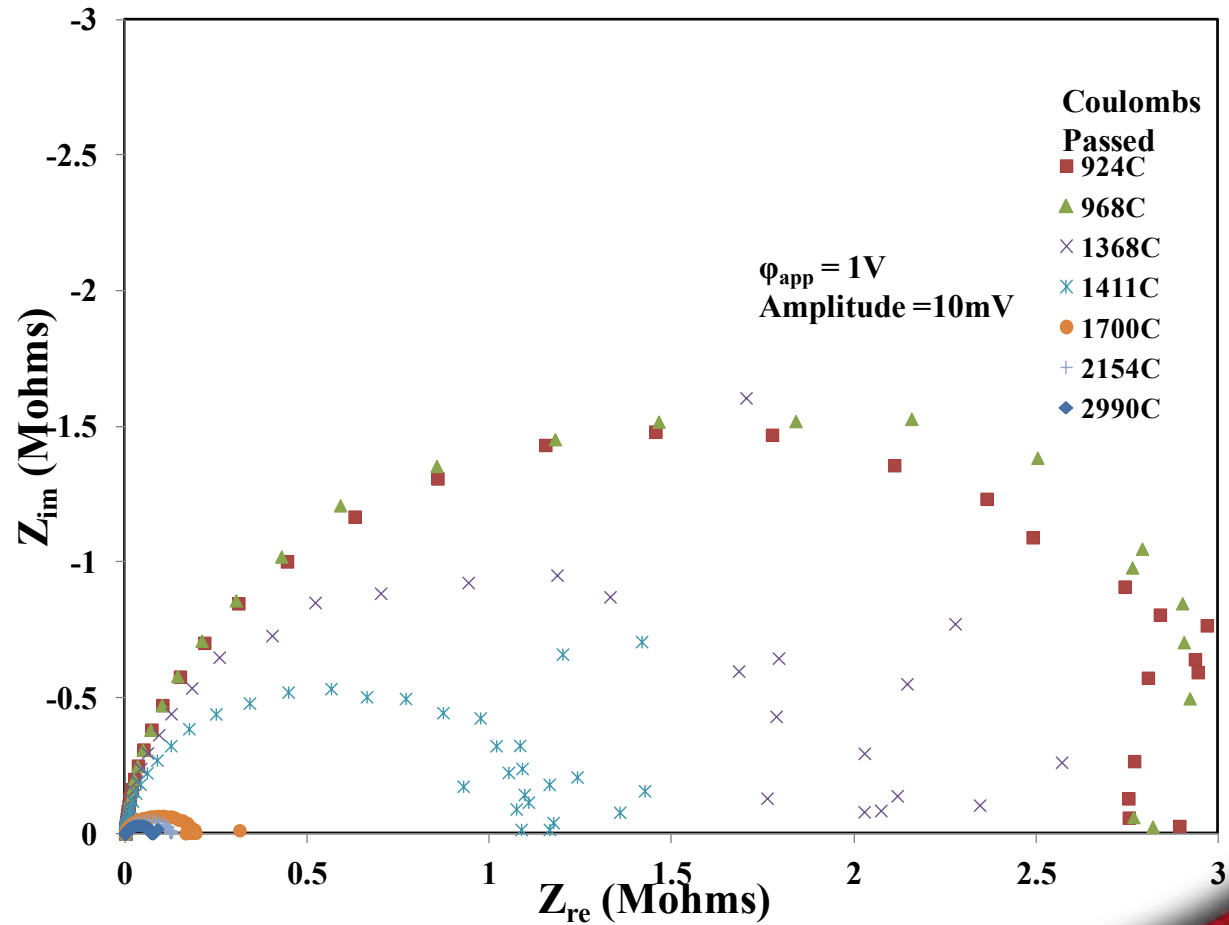
Template Equivalent Circuit

- ▶ Bounded Warburg Diffusion
- ▶ Constant Phase Element
- ▶ *Indicates compositional dependence unevenly distributed*



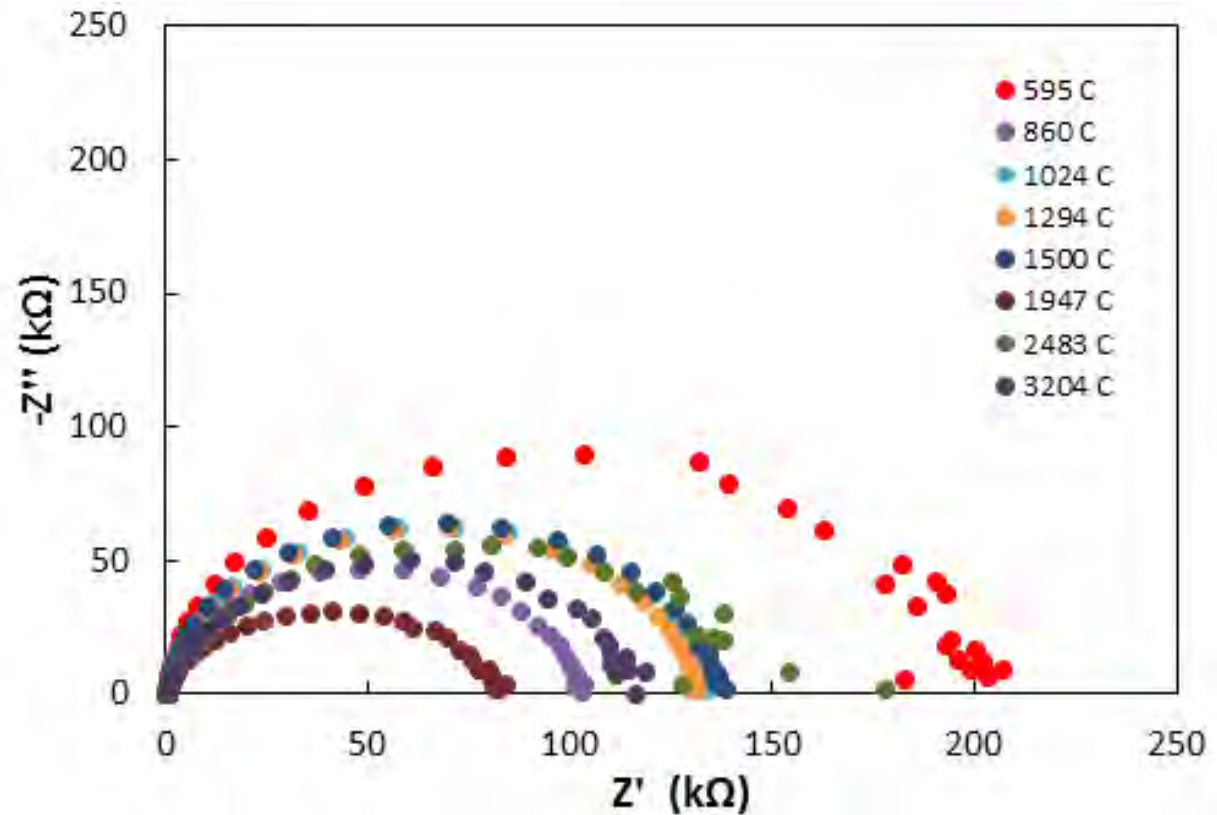
EIS Failure Mode Detection

- ▶ Large drop in charge transfer resistance
- ▶ Solution resistance increases ~depth
- ▶ CPE coefficient increased 3-fold
- ▶ *Indicates sample failure due to leaking*



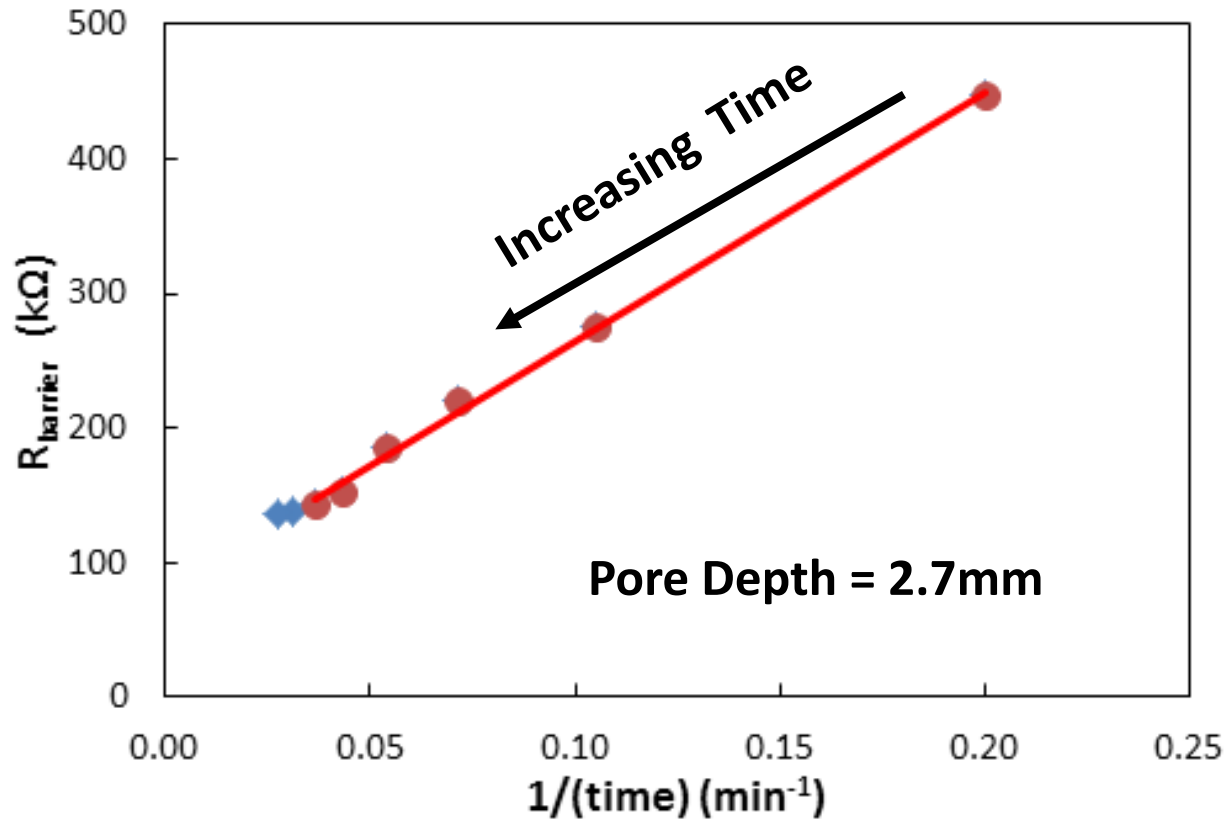
EIS Analysis of Deep Arrays

- ▶ Charge transfer resistance varies due to impurities
- ▶ Solution resistance increases ~depth
- ▶ Weak increase in CPE Coefficient



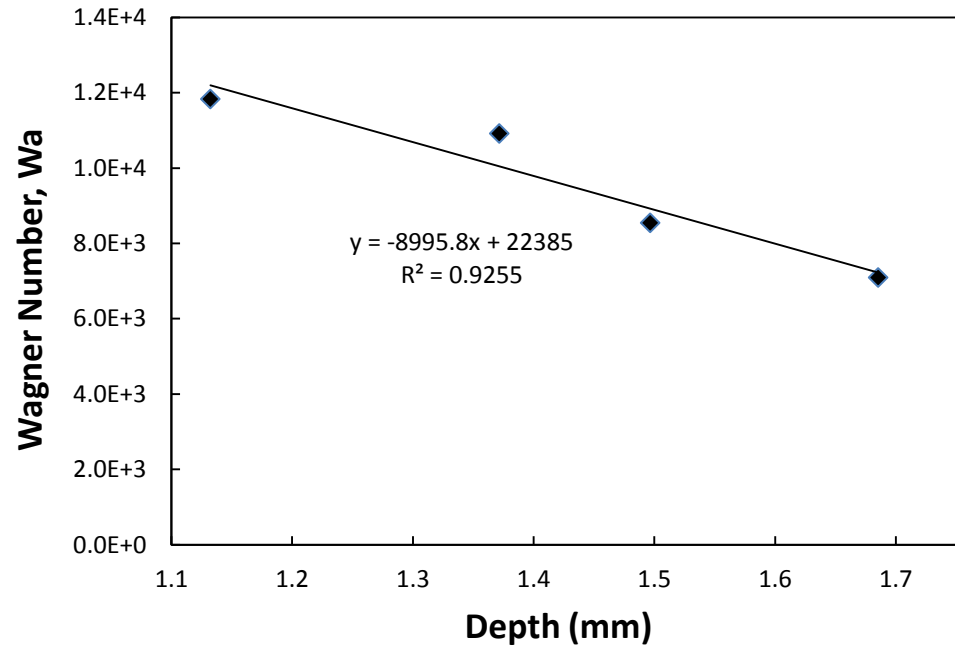
Barrier Layer Relaxation

- ▶ 30 minute relaxation time
- ▶ 4-fold shift in low frequency impedance
- ▶ *Significant concentration gradient established during anodization*



Changes in Electrode Geometry

- ▶ $W_a \gg 10$
- ▶ *Significant change in electrode geometry vs depth*



Summary

- ▶ **Technological progression → doorway to future innovations**
- ▶ **Creative test methods → model progression, failure identification**
- ▶ **Complex thermal/electrochemical dependence**
 - ▶ **Rate-inhibiting concentration gradient established**
- ▶ **Small environmental gradients effect long-term anodization**
- ▶ **Deep pore feasibility dependent on time/cost and anodization bath design**

Questions?

