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

Mitchell L. Solomon, Philip Cox, Nicholas R. Schwartz, Gregory E. Chester, and Justin J. Hill

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<td>Nanocapillary arrays are attractive structures for many applications due to the relative ease and scalability of the self-assembly process of their formation. The high surface area-to-volume ratio of these structures can benefit a wide range of energy technologies such as photovoltaics, electrochemical capacitors and batteries, as well as a range of chemical technologies such as separations, storage and catalyst scaffolding. We are currently demonstrating their utility for high density storage of gases such as hydrogen and oxygen. Their high aspect ratio and ordered arrangement is advantageous for low-cost, bottom-up, templated nanostructure growth and ordered assembly at the device scale. Assembly of nanostructures the device scale in the absence of a templating structure, while maintaining the benefits of a nanomaterial, is often the dominant technical hurdle for implementation of nanomaterials into technologies. In previous work we have used AAO templating to maintain nanostructure benefits for photoelectrochemical cells with areas exceeding several square centimeters. Furthermore, the confined radial dimension of nanocapillaries can be used to synthesize molecularly confined or form quantum confined nanostructures. We have shown these effects benefit to improve double layer capacitance, as well as improving the figure of merit in nanostructured thermoelectrics. Specifically of interest in this discussion is the formation and deep pore growth of anodized aluminum oxide (AAO)-based nanocapillary arrays as the basis for high density, safe and high rate gas storage devices. The target is to grow these ordered nanocapillary structures to centimeters in length while maintaining a uniform 100 nm nanocapillary diameter and an overall structure that is 100’s cm² in area. In order to produce these materials quickly, a hard anodization approach is used. Probing the limits of the fabrication has highlighted a fascinating system of interdependent length scales, transport and thermal processes, and current-potential distributions. Potentiostatic and linear sweep potentiometry during deep nanocapillary growth will be presented. Electrochemical impedance spectroscopy (EIS) of the electrolyte and within oxide barrier layer will be discussed; particularly the constant phase element dispersion behavior during deep nanocapillary growth that exemplifies this as a model electrochemical system for porous electrodes. Particularly the EIS response of the system during nanopore growth and its implications of growth mechanism and modes of failure will be presented. A discussion of the implementation of the experimental design and other factors will be discussed elsewhere.</td>
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<td>Nanocapillaries, templates, hydrogen storage, oxygen storage, electrochemical self-assembly, electrochemical gas compression, nanotechnology, carbon nanotube, nanoparticle, membrane electrode assembly, anodized aluminum oxide, nanocapillary arrays</td>
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Mitch Soloman, Phillip Cox, Nick Schwartz, Greg Chester & Justin J. Hill

228th ECS Meeting
Wednesday, October 14 2015

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Agenda

- AAO: Diverse Nano Applications
- Theoretical Considerations
- Characterizing Ultra-Deep AAO
- Future Work
Mainstream Engineering

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

20 nm, $1.7 \times 10^{11}$ cm$^{-2}$

Nanocapillaries
Hydrogen & Oxygen Storage

Specific Energy (Wh/cm$^3$)
Specific Power (W/cm$^3$)

- Activated Carbon Microsupercapacitor
- MEC’s CNT Microsupercapacitor
- rGO-CNT Microsupercapacitor
- 4V/500uAh Li Thin Film Battery
- 3.5V/25mF Supercapacitor
- 63V/220uF Electrolytic Capacitor

Volumetric Storage Density (g/L)
Gravimetric Storage Density (g/kg)
Nanocapillary Diameter (nm)
(6 nm CNT Wall Thickness)

Current MEC Hydrostatic Demonstration (0.12 kg/kg)
Current MEC Hydrostatic Demonstration (60 g/L)
DoE 2015 Target
Thermodynamic
- Joule Heating
- Uneven Temperature Distribution

Kinetic
- $\text{Al}_2\text{O}_3$ 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

Electrode Holder
Electrode Surface
Center Line

Fluid Volume Edges
Axial Velocity = 0
Radial Measurement Lines

Diffusion Thickness (mm)

Electrode Radial Position (mm)
Fluid Flow Profile

Reversed Flow (Recirculation)

Impingement at Electrode Holder Edge at r = 11.1 mm

Center Line Velocity r = 0 (Stagnation Point)
Current Mapping Hard Anodization

Teflon Holder

Aluminum Sample

Copper Rings

Insulating Resin
Defect Detection

Defect Region

Stagnation Zone

Template Backside

Radial Position (mm)

Current (mA)

Defect Region

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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

\[ Z_{\text{im}} \text{ (Mohms)} \]
\[ Z_{\text{re}} \text{ (Mohms)} \]

\[ \Phi_{\text{app}} = 1 \text{V} \]
\[ \text{Amplitude} = 10 \text{mV} \]
EIS Analysis of Deep Arrays

- Charge transfer resistance varies due to impurities
- Solution resistance increases ~depth
- Weak increase in CPE Coefficient
30 minute relaxation time

4-fold shift in low frequency impedance

- **Significant concentration gradient established during anodization**

![Graph showing the relationship between barrier layer relaxation and time.](image)

Increasing Time

Pore Depth = 2.7mm
- $W_a \gg 10$
- **Significant change in electrode geometry vs depth**

\[ y = -8995.8x + 22385 \]

$R^2 = 0.9255$
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?