UF Herbert Wertheim College of Engineering
Department of Materials Science & Engineering
UNIVERSITY of FLORIDA

SWAMP Research Group

Templated Carbon Nanotube Electrodes for On-Chip Electrochemical Double Layer Capacitors

PRESENTED BY

Gibson Scisco

Advised By

Kevin Jones, Kirk Ziegler, Mark Orazem, Simon Phillpot, and Brent Gila

Approved for public release; distribution is unlimited. 412TW-PA- 20509

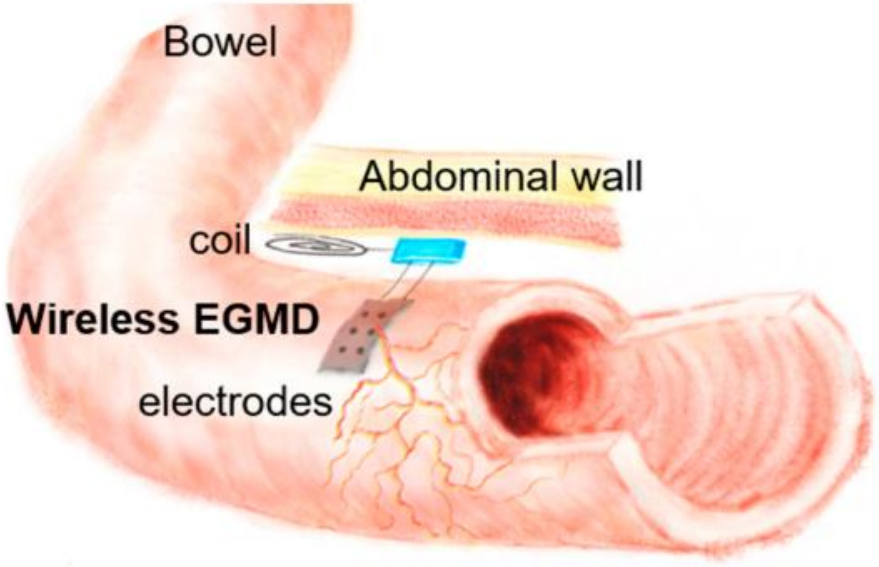
Talk Contents

- Introduction and background
  - Electrochemical double-layer capacitors (EDLCs)
  - Anodized aluminum oxide (AAO)
    - AAO on Si for systems-on-a-chip
  - Ionic liquid (IL) electrolytes
  - Research Objectives
- Results
  - Processing-structure-performance relationships of CNT-AAO-Si EDLCs
  - Electrochemical impedance spectroscopy (EIS) studies of CNT-AAO-Si EDLCs
    - De Levie model of porous electrodes
    - Comparing CPE parameters from CV and EIS
- Conclusions and future outlook

On-Chip Energy Storage Unlocks Internet of Things

- **Engineer better medicines** and **advance health informatics**
  - Implantable devices[1]
- **Restore and improve urban infrastructure**
  - Long-term deployed sensors[2]
- Microbatteries or microsupercapacitors (MSCs)
- Should be compatible with Si processing

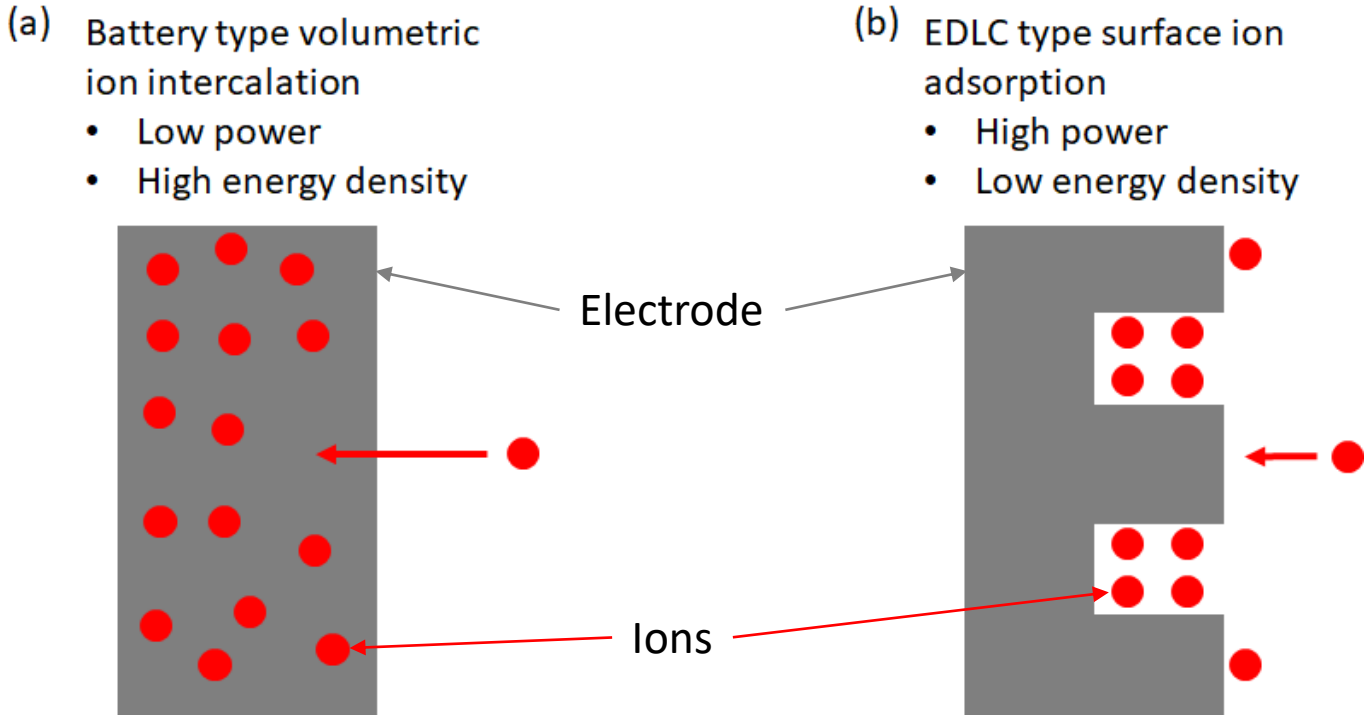
(1)



1. Lo, Y.-K. *et al*. *Micromachines* **9**, (2018)
2. Boukabache, H. et al. Sensors 12, 13617–13635 (2012)

EDLCs and Batteries – Storage Mechanism

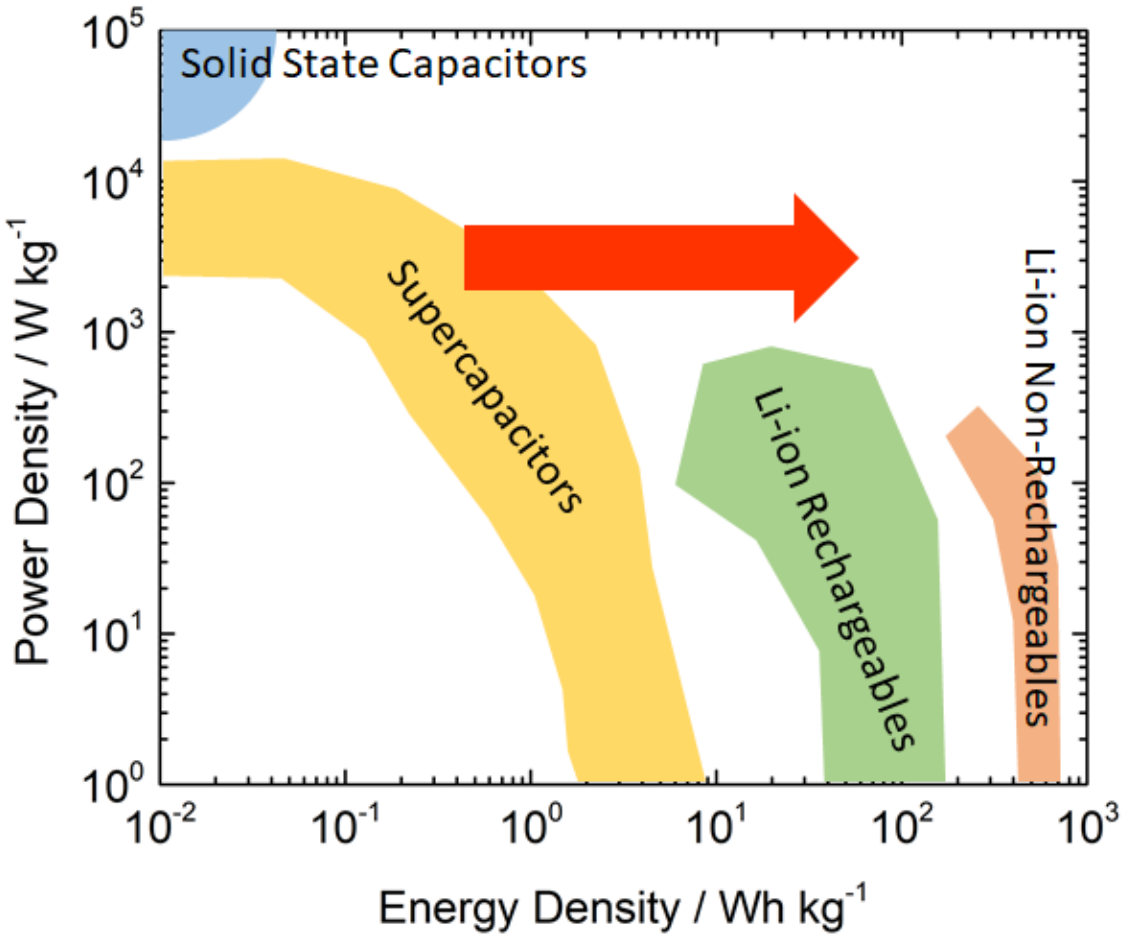
- Battery
  - Irreversible phase changes
  - Swelling/deswelling
  - Cyclability < 10,000 cycles
- EDLC
  - Electrode unchanged
  - Surface adsorption only
  - Cyclability > 100,000 of cycles



How to Increase Energy Density of EDLCs

$$E = \frac{1}{2}CV^2 \qquad C = \frac{\epsilon A}{d}$$

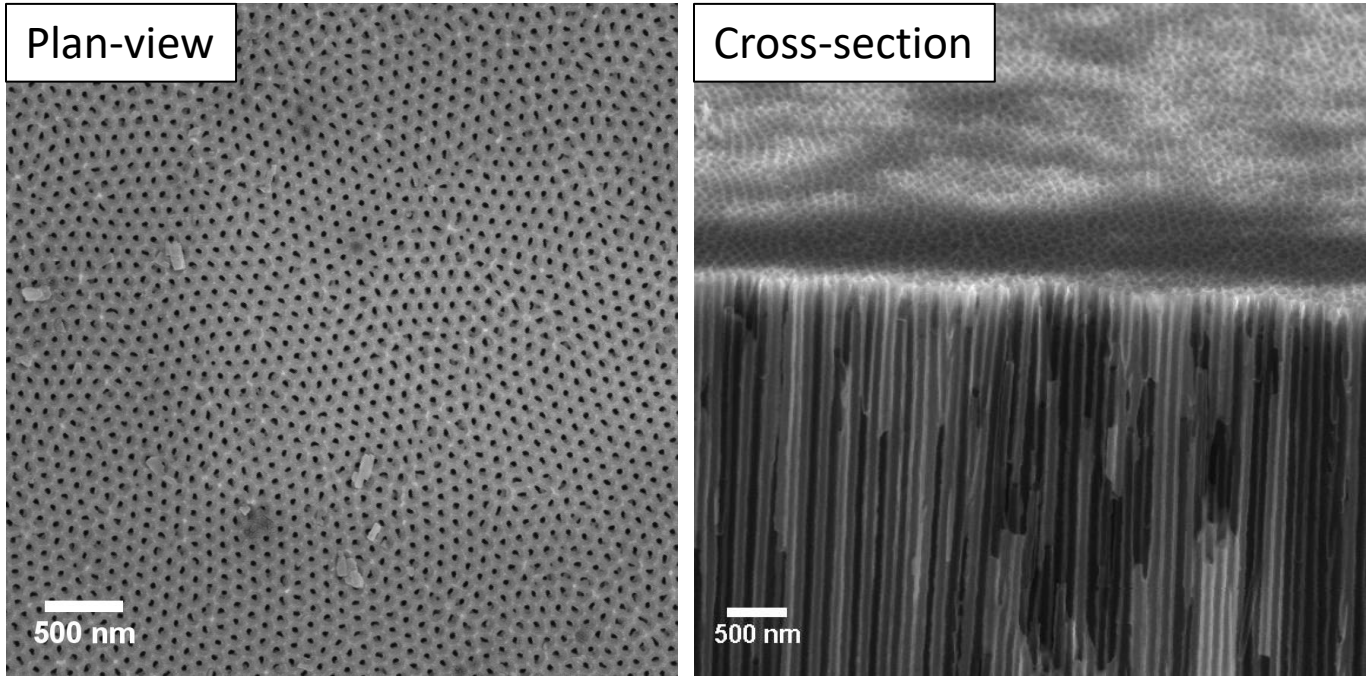
- Increase voltage
  - Aqueous electrolytes < 1.23 V
  - Ionic liquid (IL) > 3 V
- Increase area
  - Porous electrodes
  - Templated carbon nanotubes (CNTs)



Simon, P. & Gogotsi, Y. *Nat. Mater.* **7**, 845–854 (2008).

Anodized Aluminum Oxide (AAO)

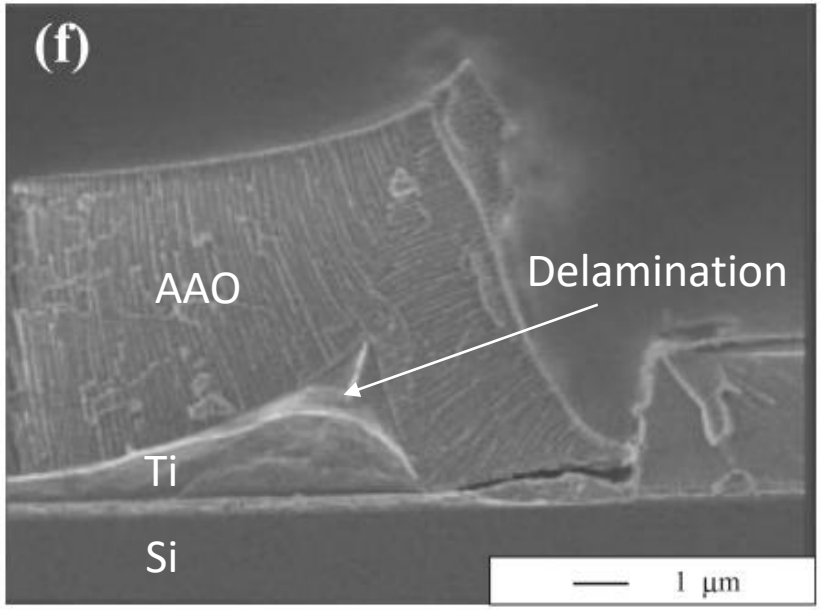
- Porous film of Al_xO_y
- Ordered AAO pioneered in the 1990s by Masuda et al.
- Dimensions controlled by anodization conditions
- This work:
  - 0.3 M oxalic acid, 15 °C, 40 V
  - ~45 nm pore diameter
  - ~1×10^{10} pores cm^{-2}
  - 1.4×10^5 cm^2 cm^{-3}



Masuda, H. *et al.*, *Science*, **268**, 1466–1468 (1995).

AAO on Si

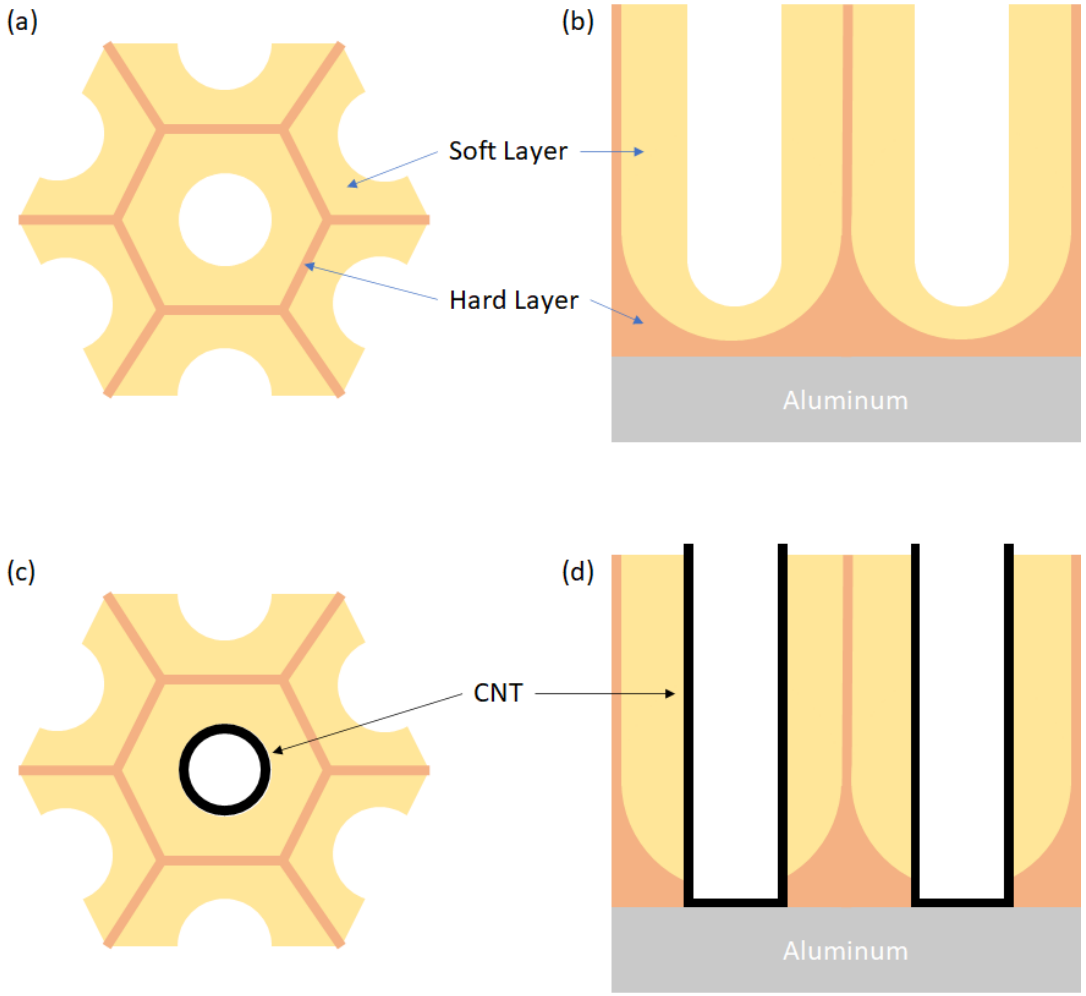
- Deposit Al on Si and anodize
  - Delamination
  - Film thickness variation
- Anodize, remove Al, then transfer
  - Films delicate
  - Adhered through solvent surface tension
- Desired: thick, consistent films, easily handleable, and well-adhered to Si



Rabin, O. *et al*. *Adv. Funct. Mater.* **13**, 631–638 (2003)

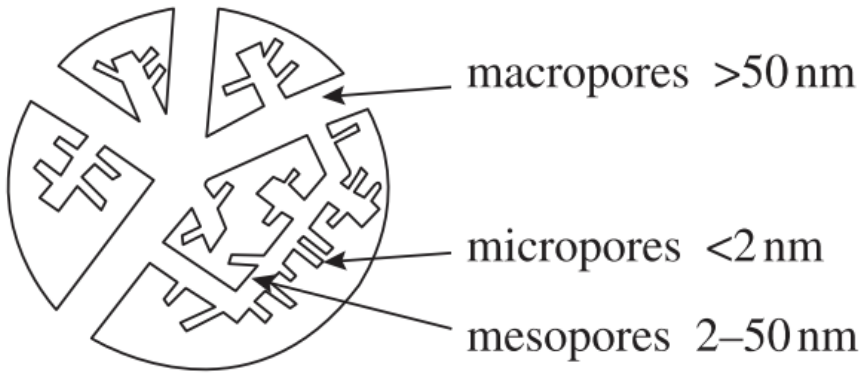
AAO Structure

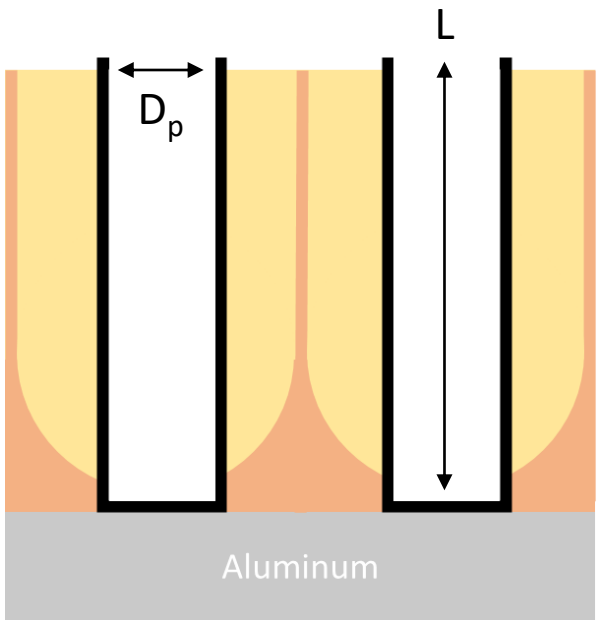
- Soft layer forms at AAO-electrolyte interface
- Hard layer forms at AAO-metal interface
- Chemical vapor deposition (CVD) coats the AAO walls with carbon
  - Not “true” CNT



AAO-Based EDLCs Offer Testbed Device

- Electrochemical models rely on knowledge of electrode dimensions
- Most porous electrodes have a random network of pores which cannot be measured
- AAO has well defined and controllable pore structure
- Possible to use CNT/AAO EDLCs to measure properties of IL electrolytes in a working device



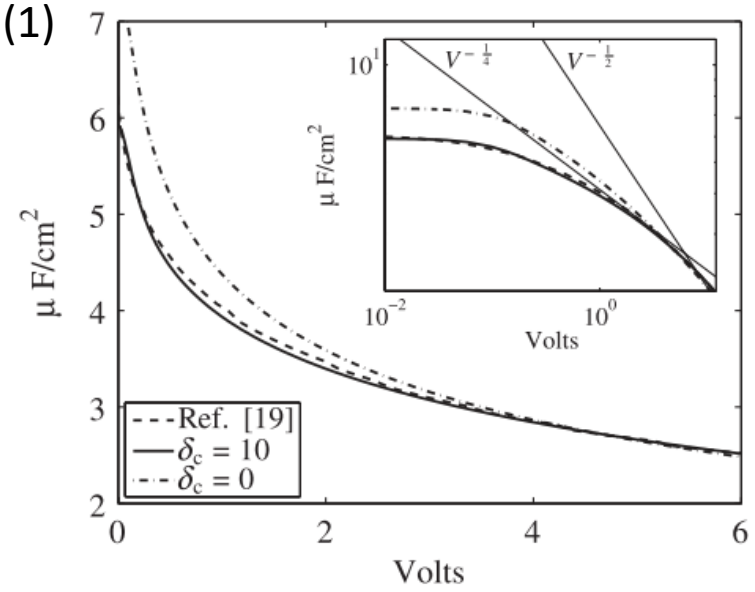


P. Simon and Y. Gogotsi, *Phil. Trans. R. Soc. A*, **368**, 3457–3467 (2010)

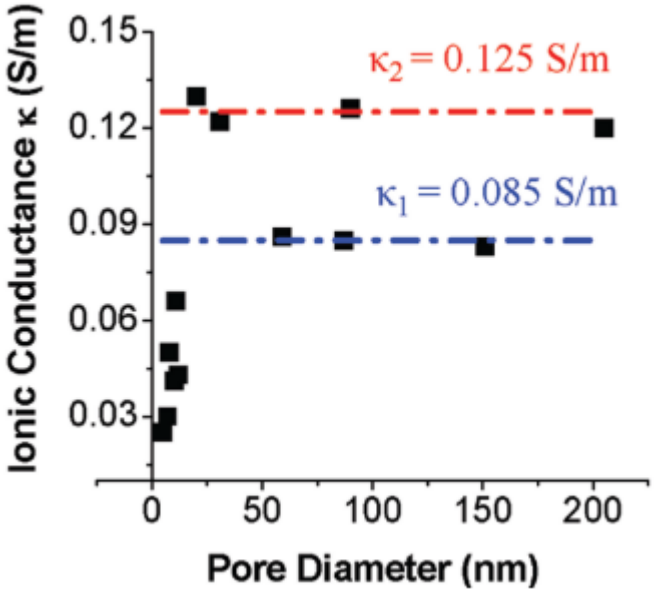
Electric Double Layer in Ionic Liquids

- Lower double layer capacitance than aqueous solutions[1]
  - Ion crowding
  - Overscreening
- Strange effects in nanopores
  - Decreased[2] and enhanced[3] conductance
  - Capillary freezing[4]
- Solvent free ILs should be studied in carbon nanopores for MSC applications

(1)



(2)



1. Bazant, M. Z. *et al. Phys. Rev. Lett.* **106**, 046102 (2011).
2. Davenport, M. et al. Nano Lett. 9, 2125–2128 (2009).
3. Iacob, C. *et al. Soft Matter* **8**, 289–293 (2012).
4. Comtet, J. *et al. Nat. Mater.* **16**, 634–639 (2017).

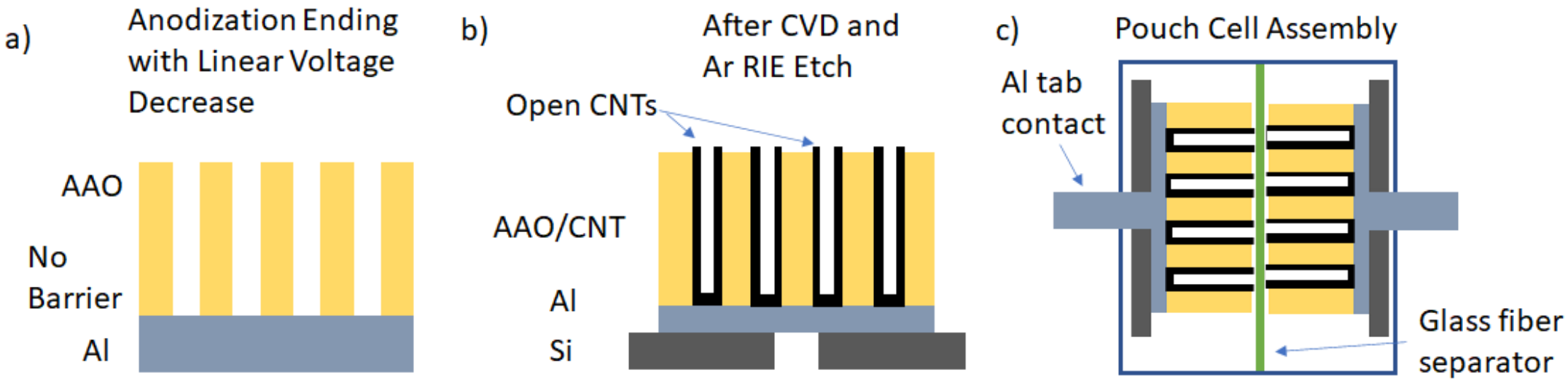
Research Objectives

- Create thick AAO templates on Si to enable AAO-based MSCs
- Explore processing-performance relationships of CNT-AAO EDLCs with neat IL electrolytes
- Study IL behavior in carbon nanopores of EDLCs using electrochemical impedance spectroscopy (EIS)

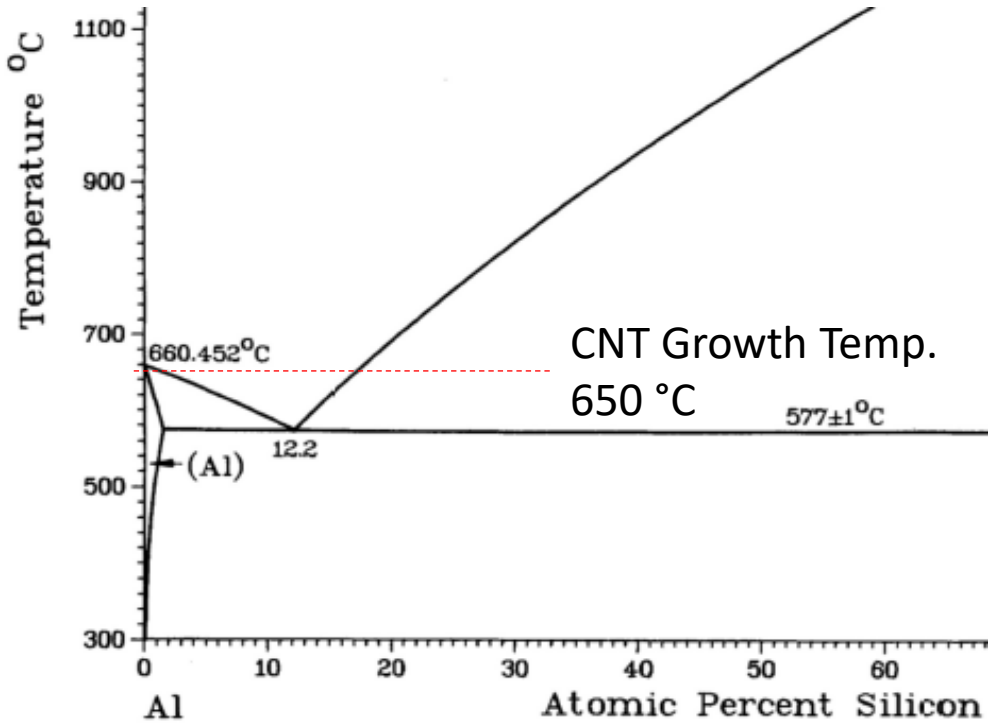
Talk Contents

- Introduction and background
  - Electrochemical double-layer capacitors (EDLCs)
  - Anodized aluminum oxide (AAO)
    - AAO on Si for systems-on-a-chip
  - Ionic liquid (IL) electrolytes
  - Research Objectives
- Results
  - Processing-structure-performance relationships of CNT-AAO-Si EDLCs
  - Electrochemical impedance spectroscopy (EIS) studies of CNT-AAO-Si EDLCs
    - De Levie model of porous electrodes
    - Comparing CPE parameters from CV and EIS
- Conclusions and future outlook

Multi-Step Fabrication Process

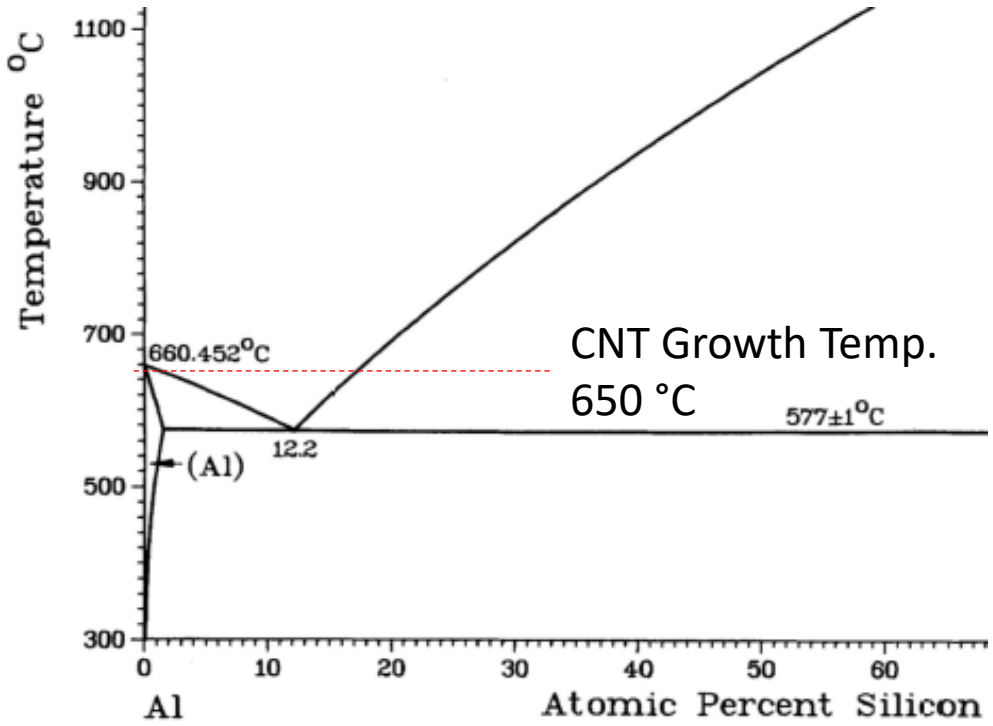


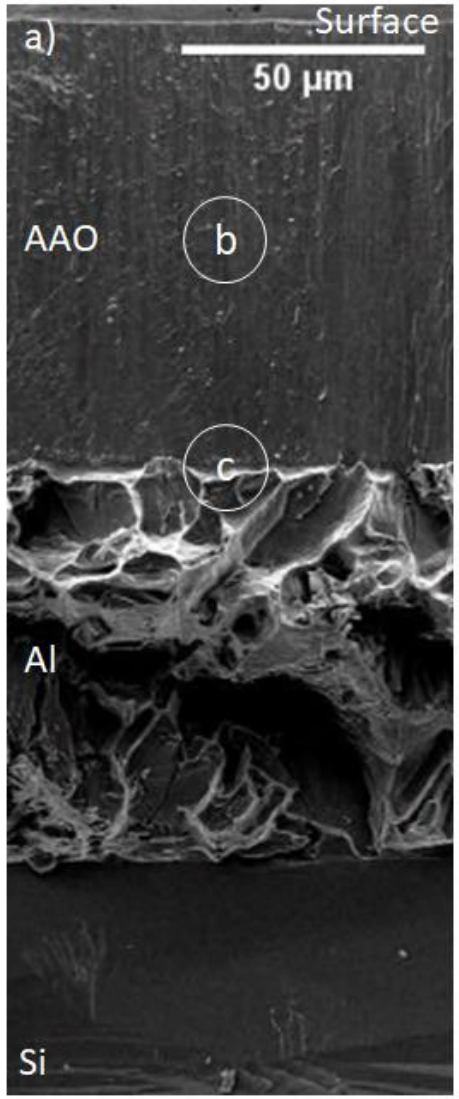
Eutectic Bonding of AAO on Si

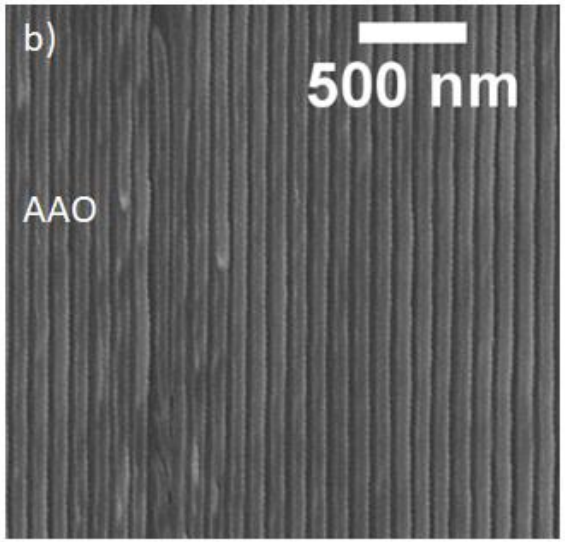


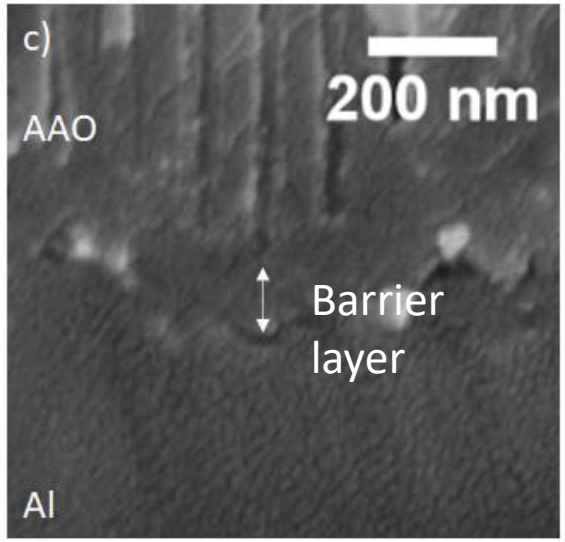
CNT Growth Temp.
650 °C

Eutectic Bonding of AAO on Si







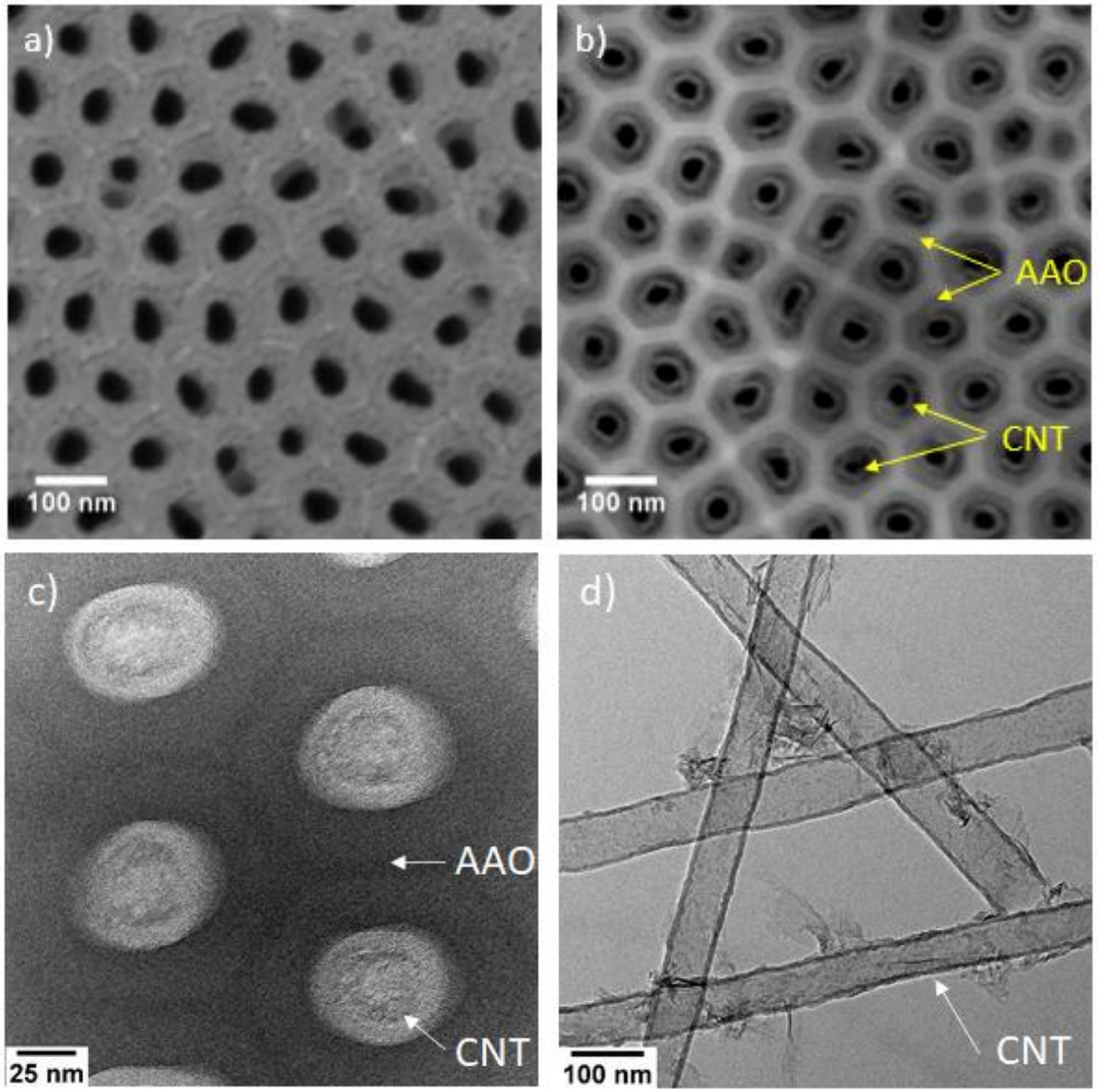


- AAO unchanged by high temperature anneal

Scisco, G. P., *et al. J. Power Sources* **474**, (2020)

Depositing CNTs in AAO

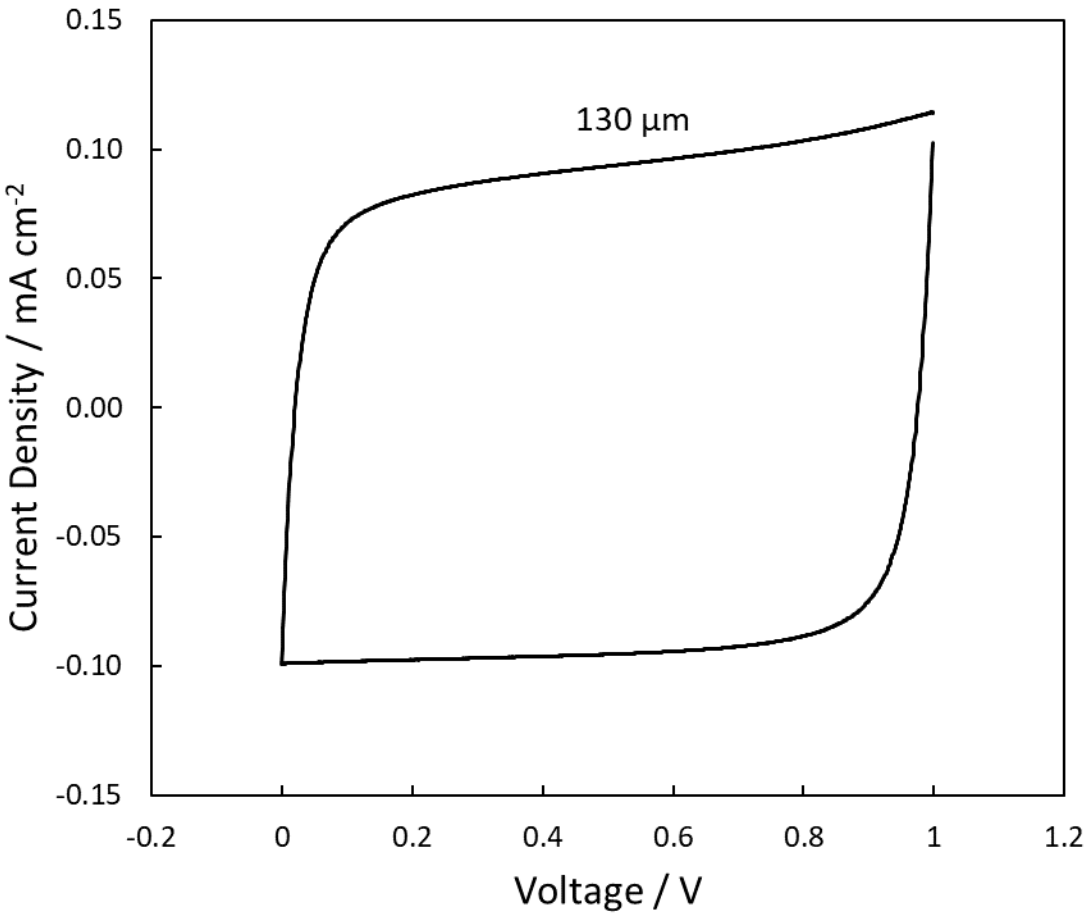
- Pore size before CVD
  - 44.5 ± 6.9 nm
- Pore size after CVD
  - 24.4 ± 4.6 nm
- CNT wall thickness from SEM
  - 10 ± 8 nm
- CNT wall thickness from TEM
  - 9.4 ± 2.8 nm



Capacitance Measured Through Cyclic Voltammetry

- Unable to utilize full IL voltage range due to unwanted reactions above 1 V
- Rectangular CV indicates ideal response
- Capacitance proportional to area under curve

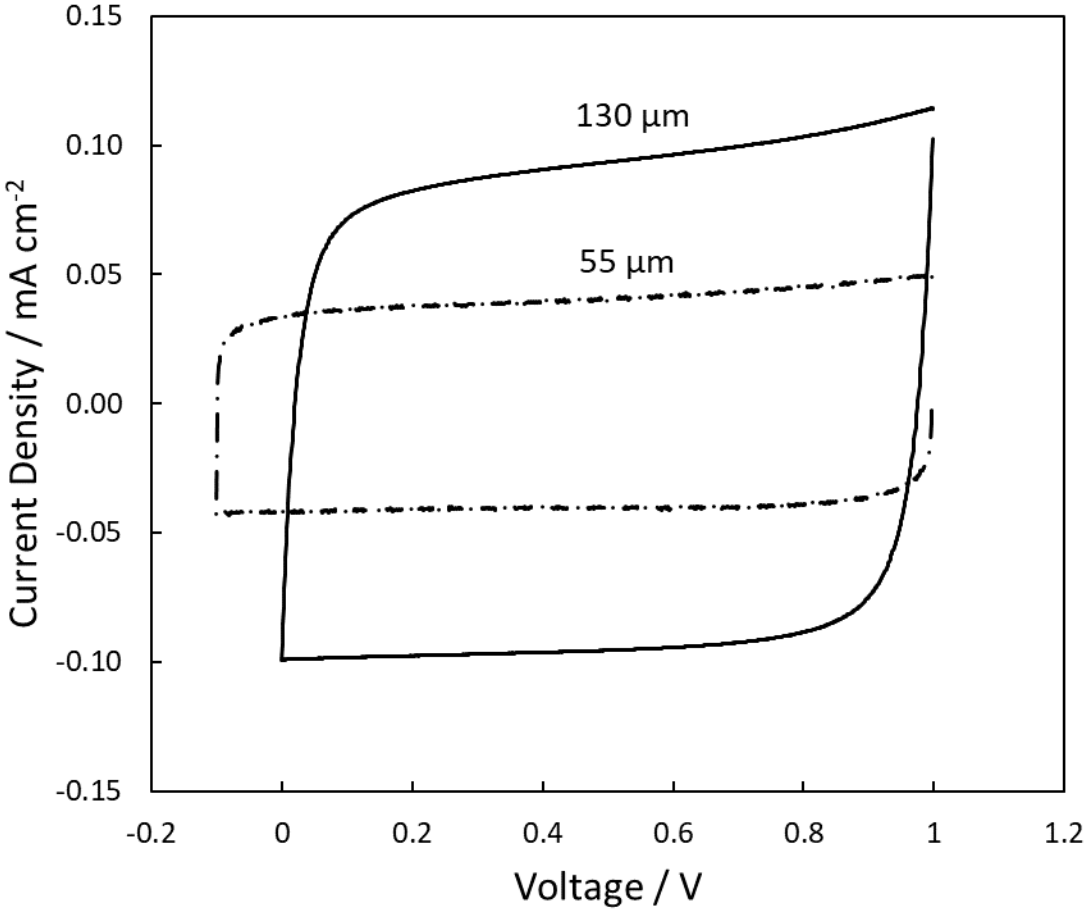
$$C = \frac{\int_{V1}^{V2} di\, dV}{Av\Delta V}$$



Capacitance Measured Through Cyclic Voltammetry

- Unable to utilize full IL voltage range due to unwanted reactions above 1 V
- Rectangular CV indicates ideal response
- Capacitance proportional to area under curve

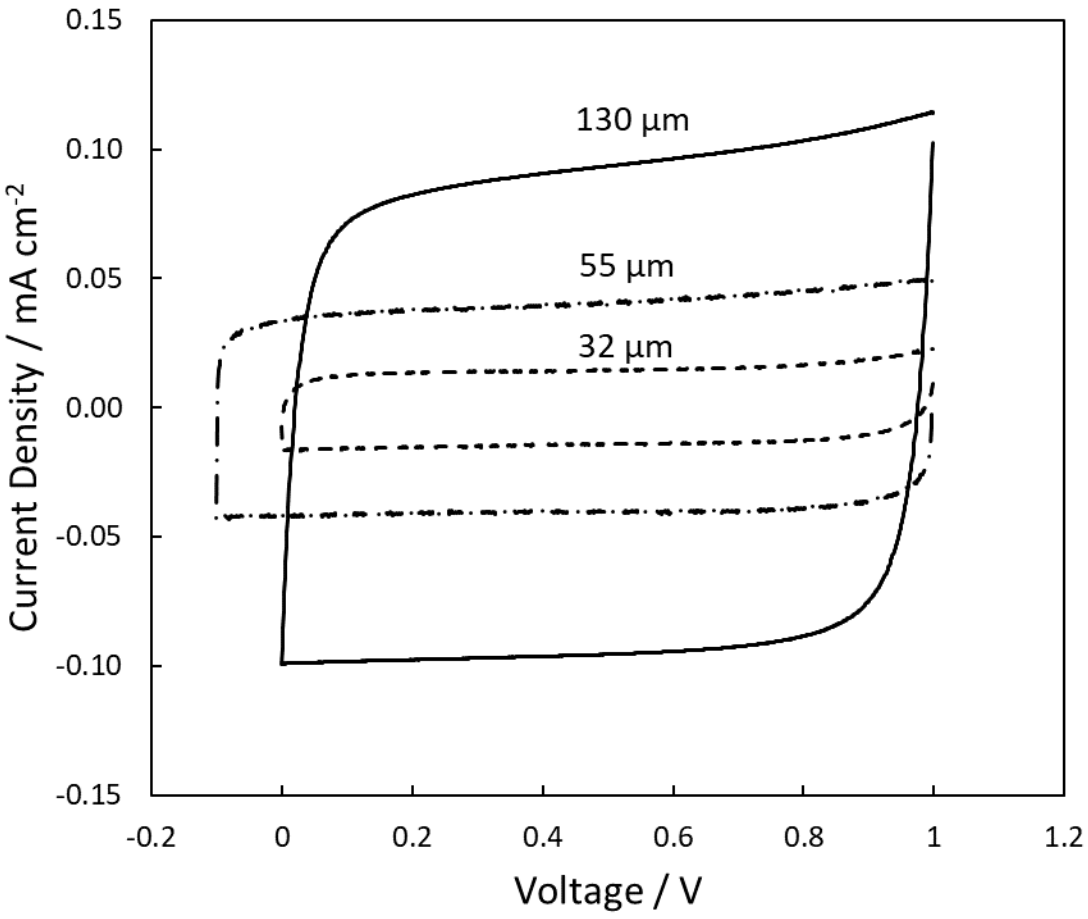
$$C = \frac{\int_{V1}^{V2} di\, dV}{Av\Delta V}$$



Capacitance Measured Through Cyclic Voltammetry

- Unable to utilize full IL voltage range due to unwanted reactions above 1 V
- Rectangular CV indicates ideal response
- Capacitance proportional to area under curve

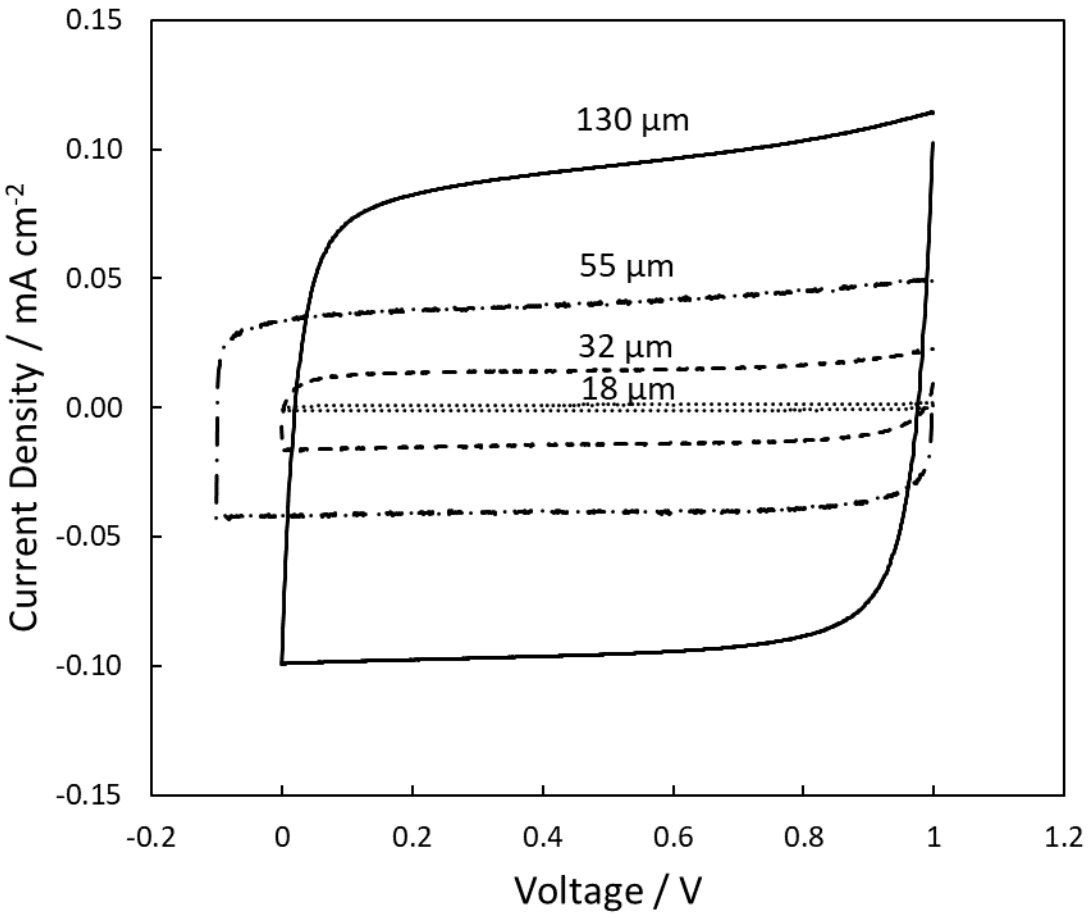
$$C = \frac{\int_{V1}^{V2} di\, dV}{Av\Delta V}$$



Capacitance Measured Through Cyclic Voltammetry

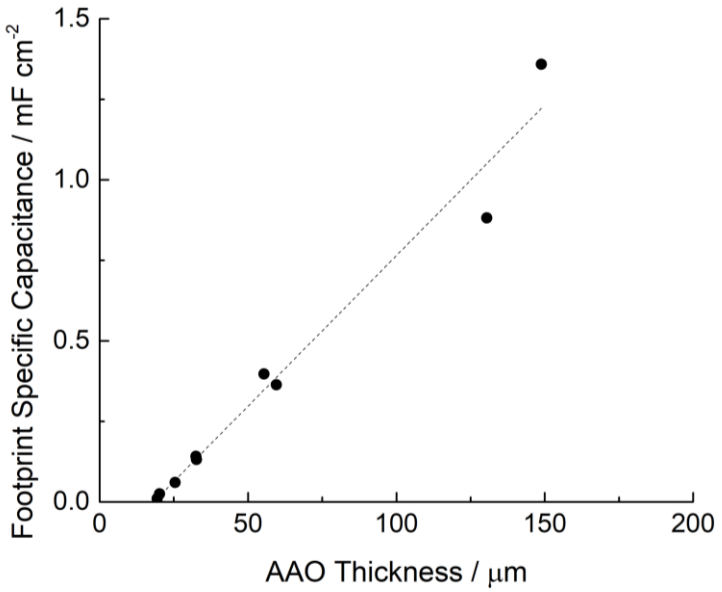
- Unable to utilize full IL voltage range due to unwanted reactions above 1 V
- Rectangular CV indicates ideal response
- Capacitance proportional to area under curve

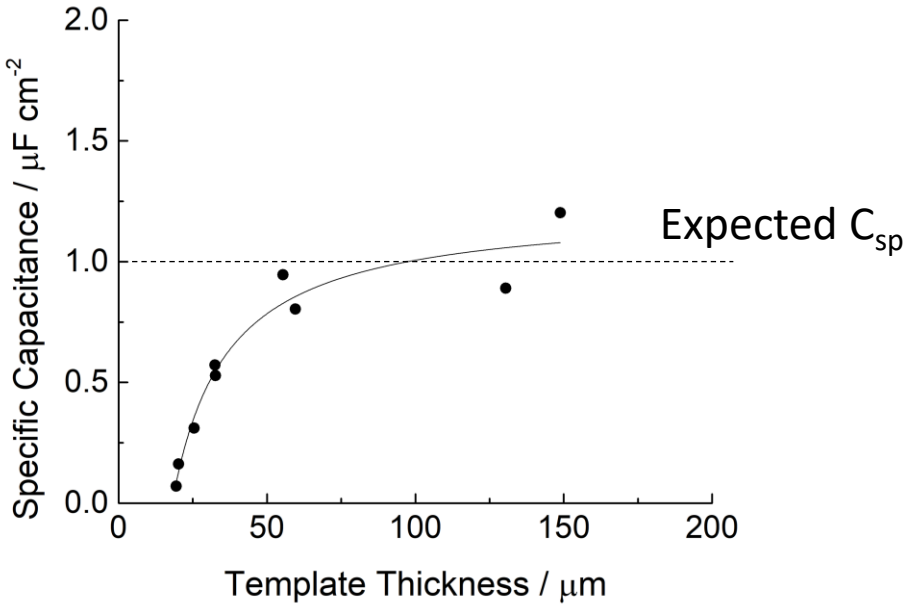
$$C = \frac{\int_{V1}^{V2} di\, dV}{Av\Delta V}$$



CV Indicates Decreased Active Area

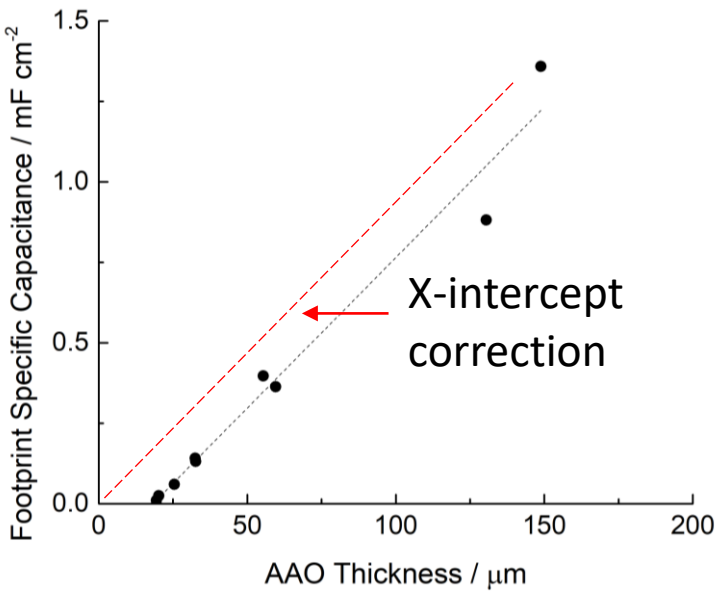
- (a) Calculated capacitance scales linearly with AAO thickness
  - Non-zero intercept at 18.3 µm
  - Equates to 396 cm^2
- (b) Specific capacitance based on porous area

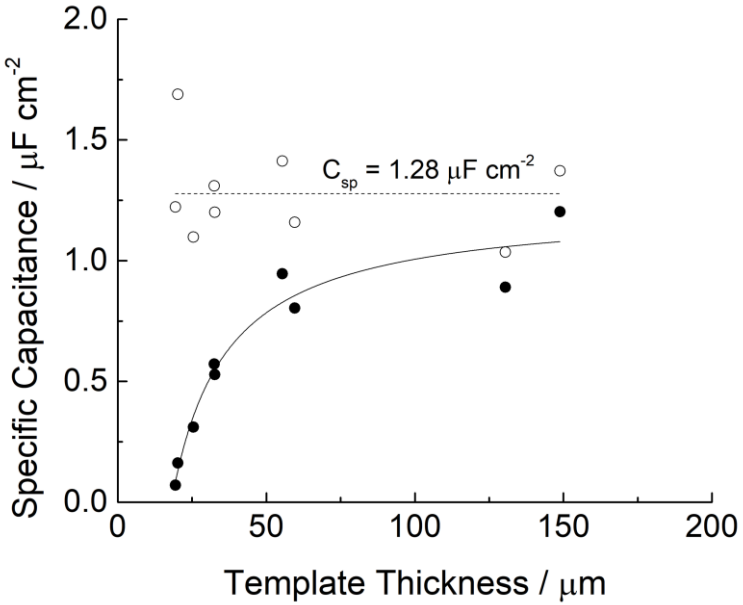




CV Indicates Decreased Active Area

- (a) Calculated capacitance scales linearly with AAO thickness
  - Non-zero intercept at 18.3 µm
  - Equates to 396 cm^2
- (b) Specific capacitance based on porous area
  - Should be flat line near 1 µF cm^{-2}
  - Intercept corrected C_{sp} = 1.28 µF cm^{-2}





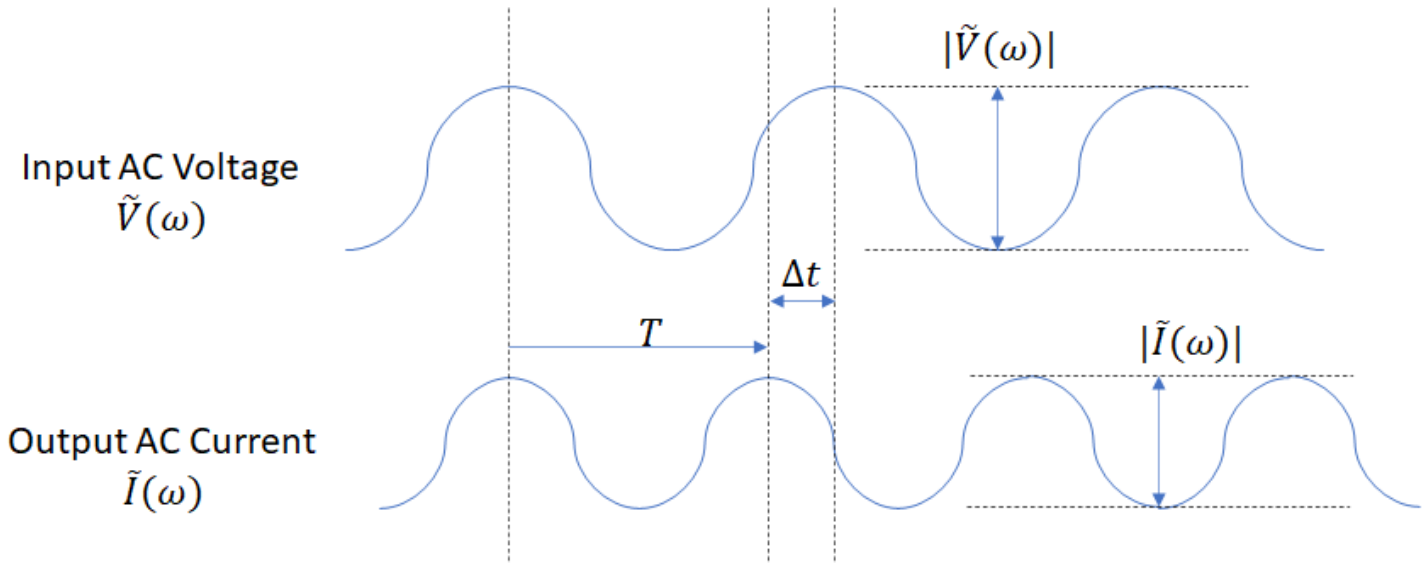
Conclusions from Processing-Performance

- Non-zero intercept of linear capacitance vs AAO thickness
- Correcting for intercept led to more consistent C_{sp}
- Unused portion of electrode
  - Electrolyte wetting
  - Pore blockages
  - High resistance areas
    - Varying resistance carbon
    - Incomplete barrier layer removal

Talk Contents

- Introduction and background
  - Electrochemical double-layer capacitors (EDLCs)
  - Anodized aluminum oxide (AAO)
    - AAO on Si for systems-on-a-chip
  - Ionic liquid (IL) electrolytes
  - Research Objectives
- Results
  - Processing-structure-performance relationships of CNT-AAO-Si EDLCs
  - Electrochemical impedance spectroscopy (EIS) studies of CNT-AAO-Si EDLCs
    - De Levie model of porous electrodes
- Conclusions and future outlook

Electrochemical Impedance Spectroscopy (EIS)



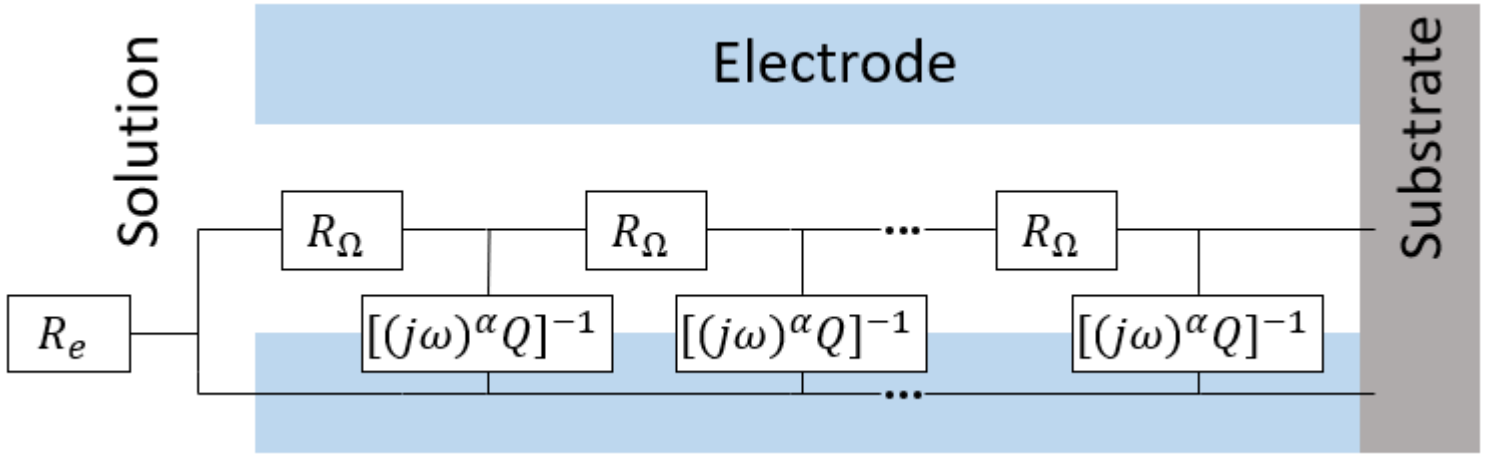
$$V = IR$$

$$\varphi = 2\pi \frac{\Delta t}{T}$$

$$\tilde{Z}(\omega) = \frac{|\tilde{V}(\omega)|}{|\tilde{I}(\omega)|}[\cos\varphi(\omega) + j\sin\varphi(\omega)]$$

De Levie Model of Porous Electrodes

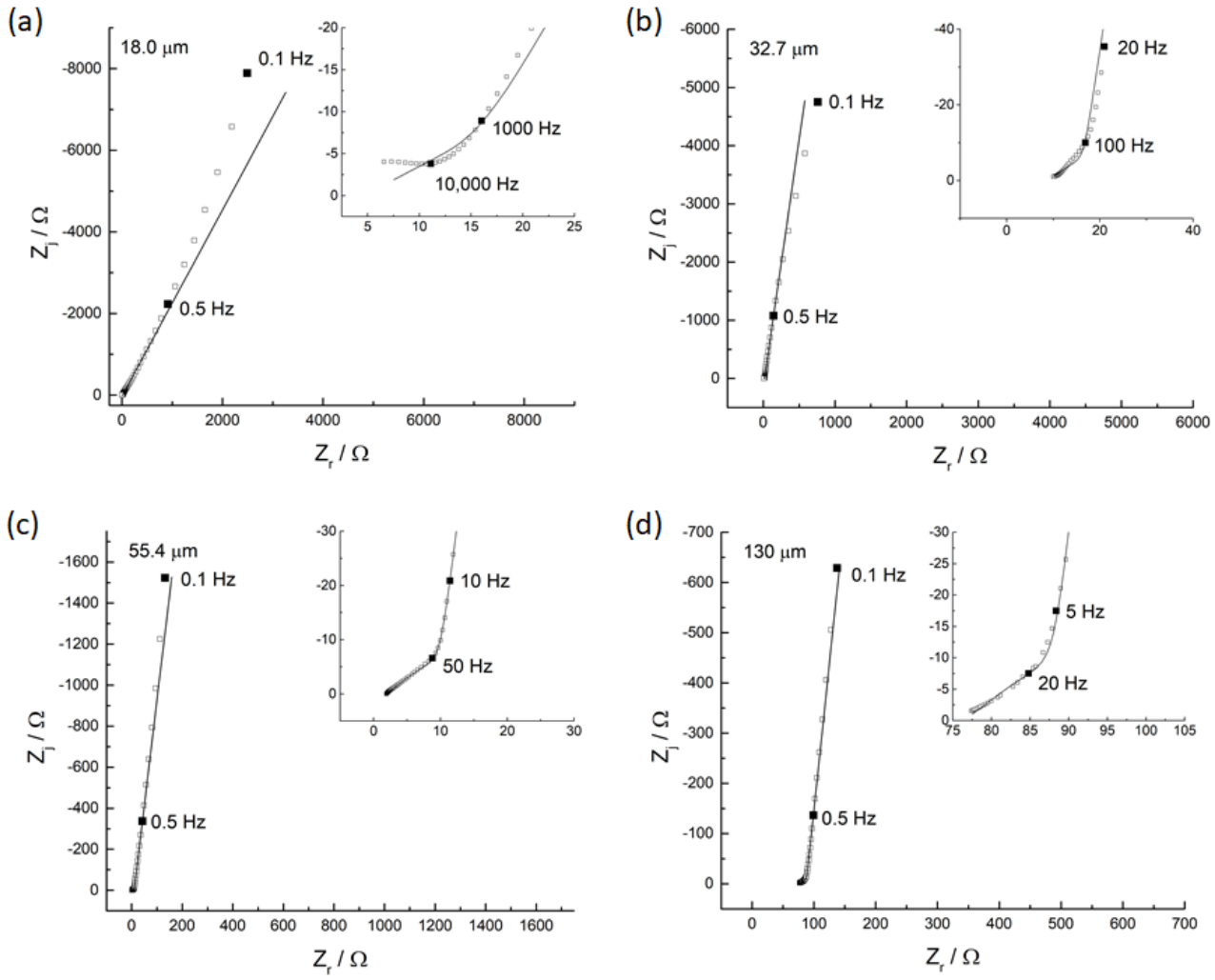
- Ohmic resistance, R_e
- In-pore solution resistance
  - $R_\Omega = \frac{\rho_e L}{n\pi r^2}$
  - ρ_e = solution resistivity in pores
- Non-ideal capacitance modeled as constant phase element
  - $Z = \frac{1}{(j\omega)^\alpha Q}$



EIS Data Well-Fit by De Levie Model

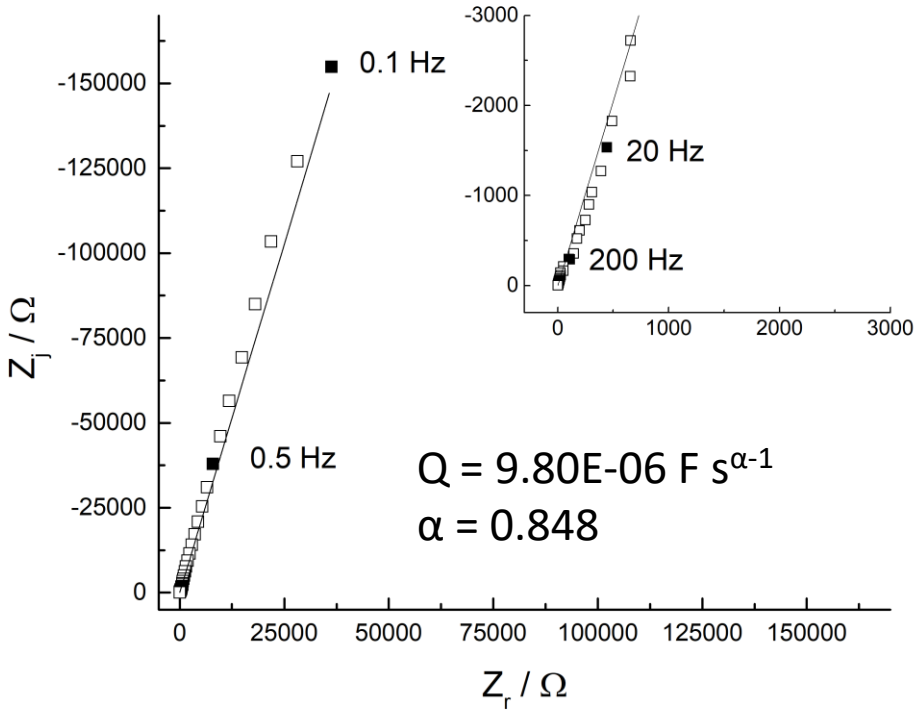
- Good fit found in each case
- Error in fitted values < 6%
- Breakpoint frequency related to penetration depth of AC signal into pores

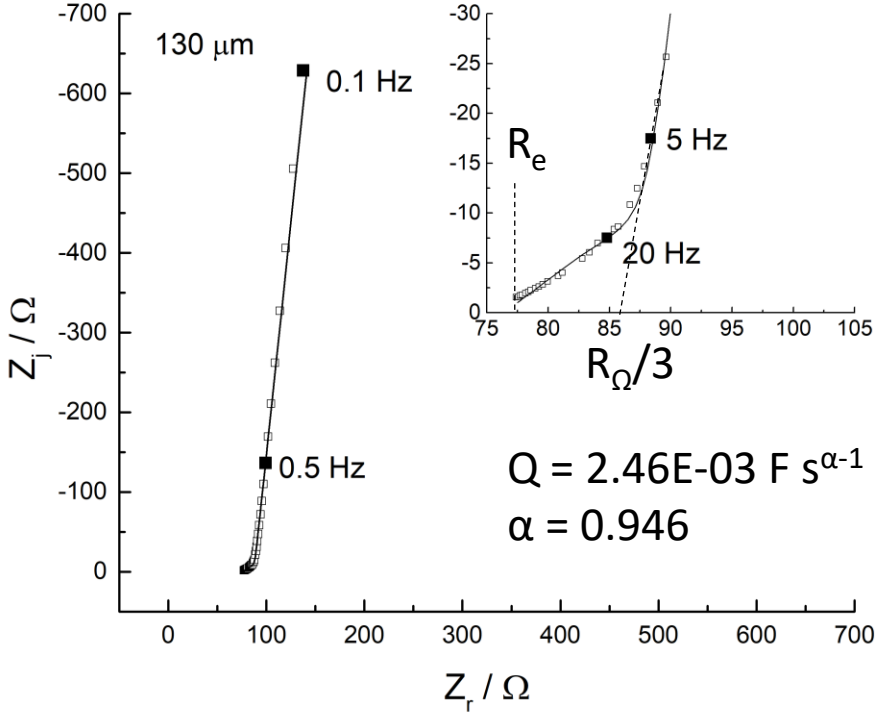
$$\omega_{bp} = \frac{9r}{4\rho_e L^2 C_{sp}}$$



Ratio of Q Gives Active Area

Control



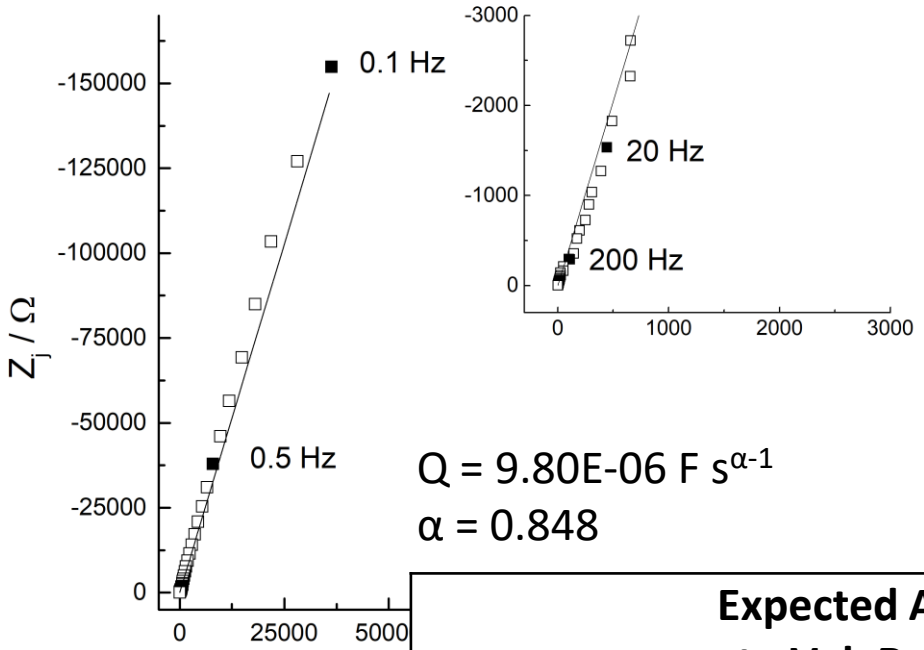


130 µm thick AAO

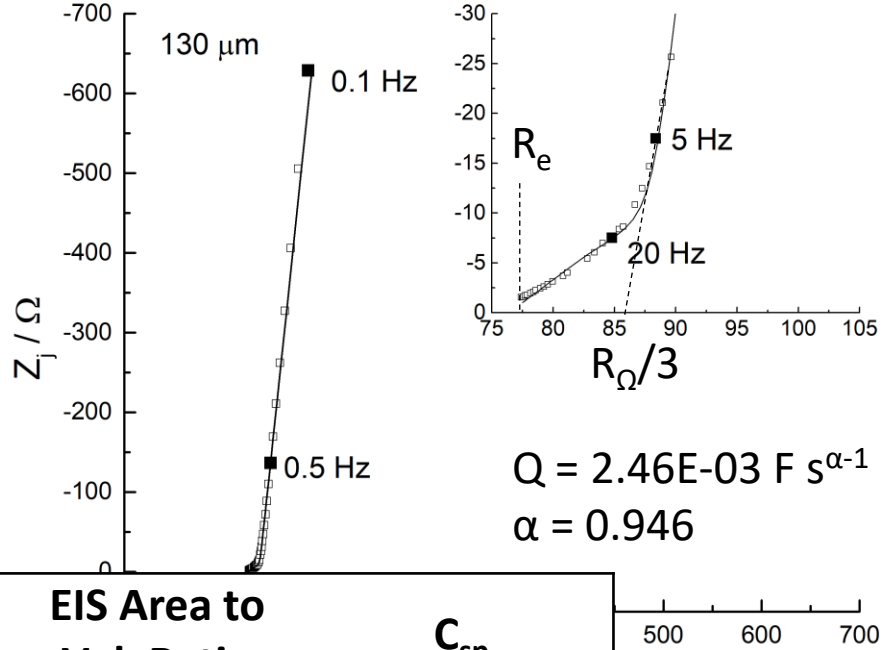
$$C = Q^{\frac{1}{\alpha}}(R_e + R_\Omega)^{\frac{1-\alpha}{\alpha}}$$

Ratio of Q Gives Active Area

Control



Q = 9.80E-06 F $s^{\alpha-1}$
α = 0.848



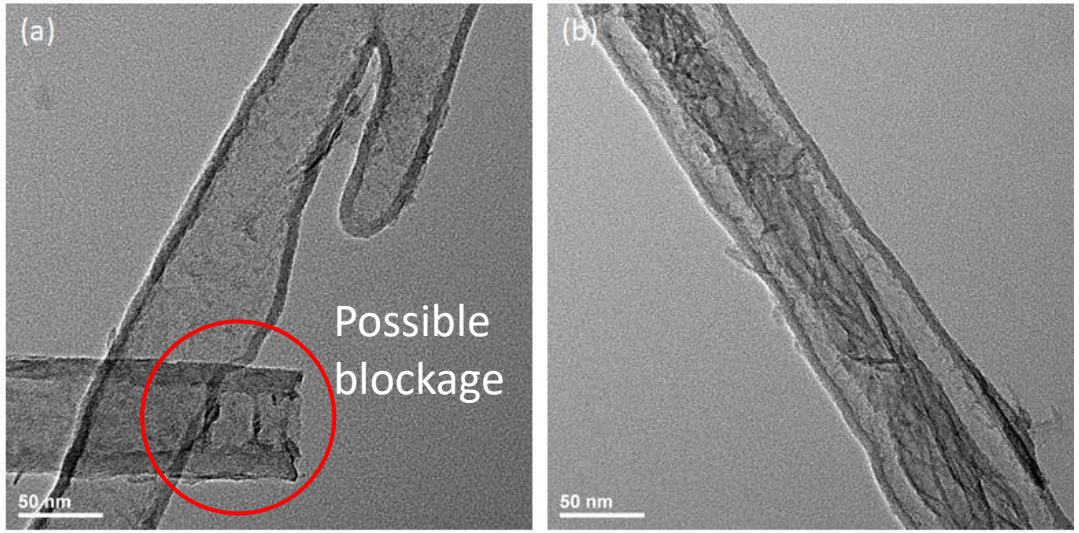
Q = 2.46E-03 F $s^{\alpha-1}$
α = 0.946

130 µm thick AAO

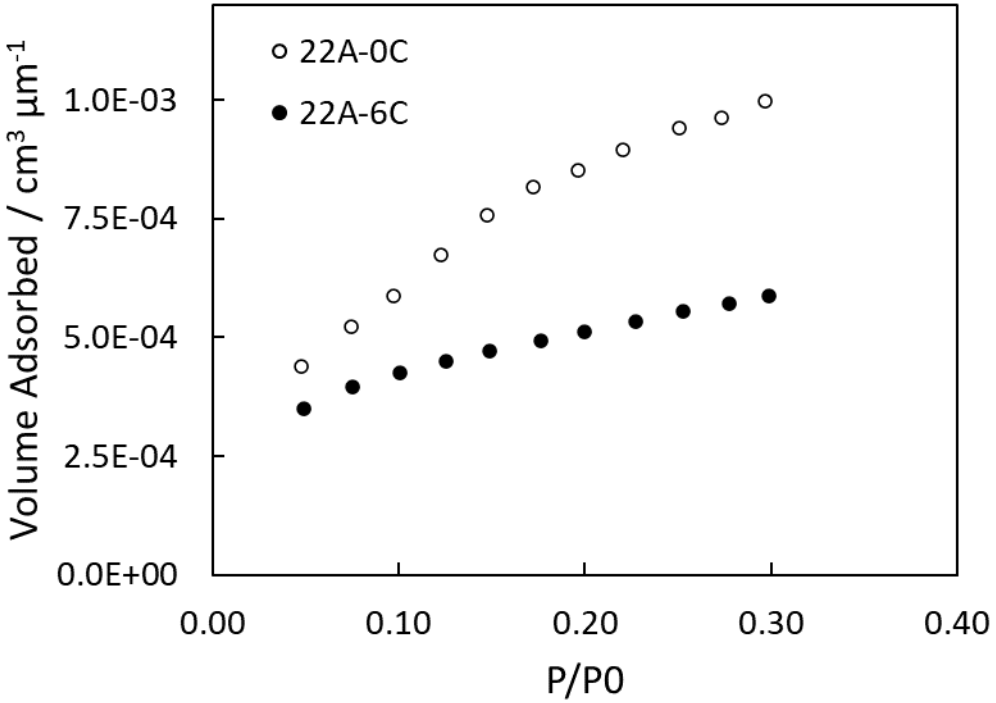
	Expected Area to Vol. Ratio [10^4 cm²/cm³]	EIS Area to Vol. Ratio [10^4 cm²/cm³]	C_{sp} [µF/cm²]
18 µm	7.59	1.97	0.21
32 µm	7.59	1.99	1.13
55 µm	7.59	3.70	1.28
130 µm	7.59	3.84	1.58

TEM Reveals Blocked CNTs

- AAO removed through etching in NaOH
  - Template thickness ~30 µm
  - 75% of area inactive
- 16% of tubes blocked (5/32)
- TEM not indicative of statistics
- CVD reaction rate dependent on accessible area



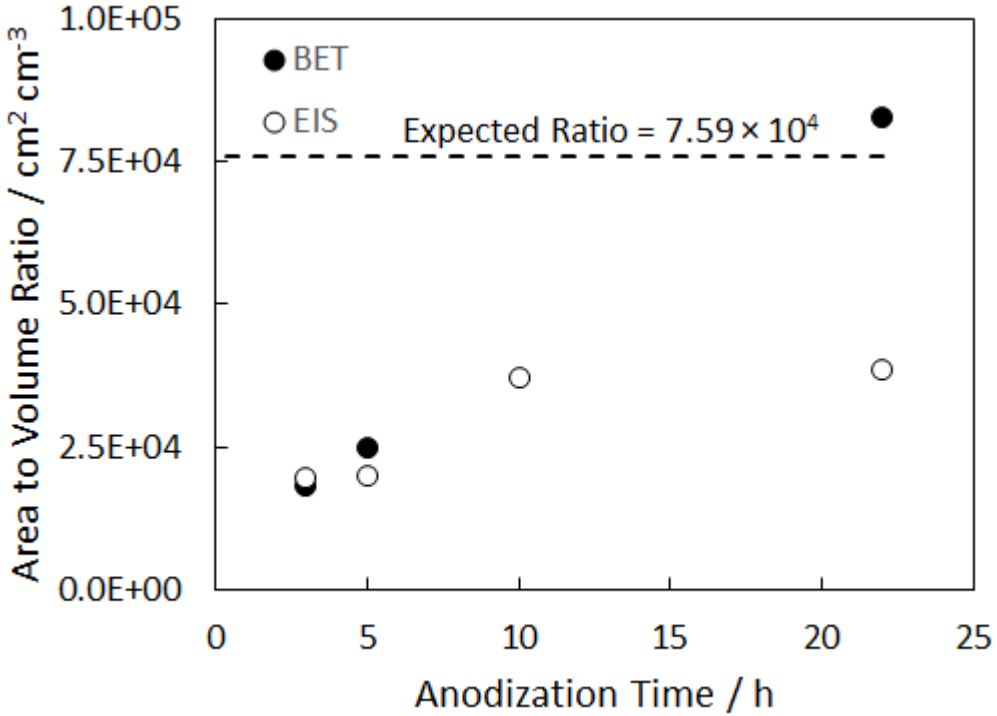
BET Provides Physical Measurement of Accessible Area



	Expected Area to Vol. Ratio [10^4 cm^2/cm^3]	BET Area to Vol. Ratio [10^4 cm^2/cm^3]	EIS Area to Vol. Ratio [10^4 cm^2/cm^3]
AAO only	13.8	15.4	-
~130 µm w/ CVD	7.59	8.28	3.84

- BET agrees with SEM for thickest templates
- Implies that reduction in active area may not be the result of physical blockages

BET Provides Physical Measurement of Accessible Area

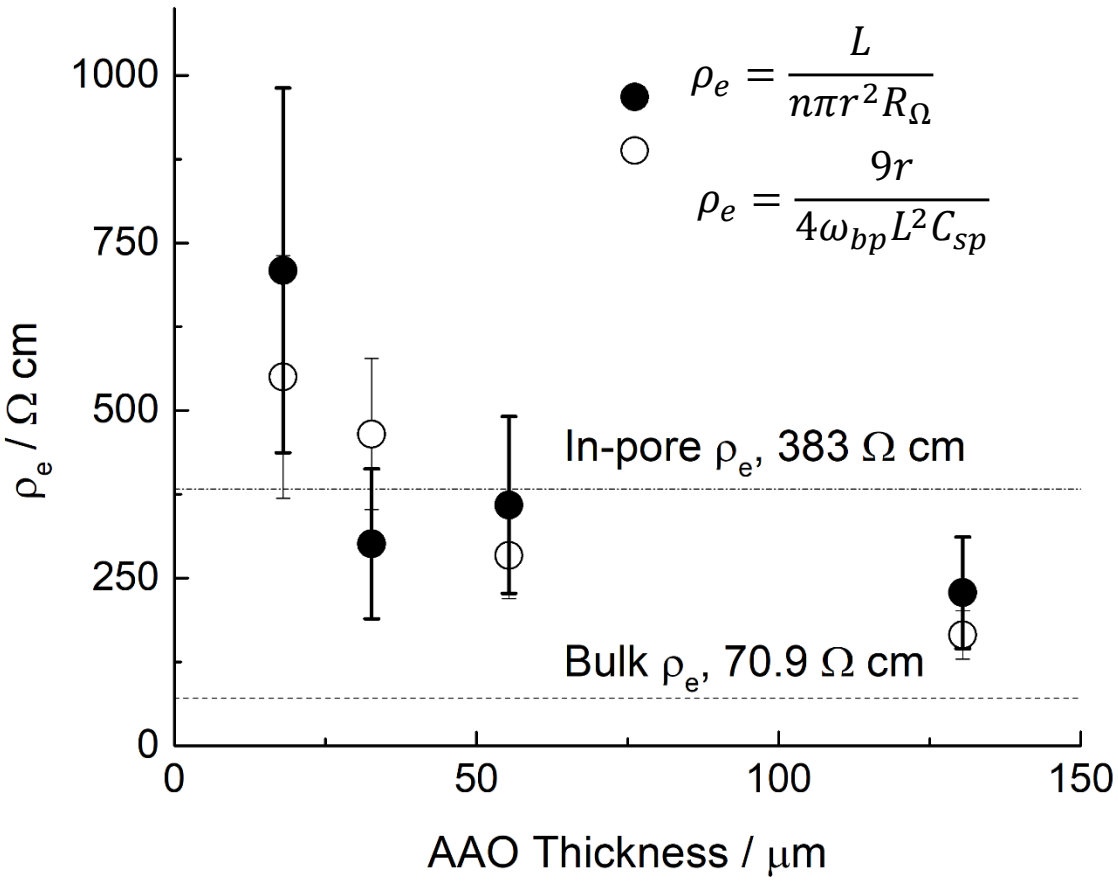


	Expected Area to Vol. Ratio [10^4 cm^2/cm^3]	BET Area to Vol. Ratio [10^4 cm^2/cm^3]	EIS Area to Vol. Ratio [10^4 cm^2/cm^3]
~130 µm w/ CVD	7.59	8.28	3.84
~30 µm w/CVD	7.59	2.49	1.99
~18 µm w/ CVD	7.59	1.82	1.97

- Mechanism of active area reduction depends on template thickness
- Physical blockages in thinner templates
- Electrical blockages in thicker templates

In-Pore Resistivity 5x Greater than Bulk From EIS

- Filled circles: n taken as % of initial value
- Open circles: C_{sp} was corrected for reduced area
- Resistivity of IL was 5 times greater in pores than bulk
- Hydrophilic nanopores shown to be higher resistivity[1]
- Capillary freezing drastically increases IL viscosity under nanoconfinement[2]



1. Iacob, C. *et al*. *Phys. Chem. Chem. Phys.* **12**, 13798–13803 (2010).
2. Comtet, J. *et al*. *Nat. Mater.* **16**, 634–639 (2017).

Conclusions from EIS Study

- EIS offers method to measure electrochemically active surface area
- Active area was determined to be much lower than expected
  - TEM indicated that tubes are blocked during CVD growth
  - BET indicated that electrolyte may not be wetting the electrode
- Resistivity of solvent free IL >4x higher in nanopores up to 25 nm diameter
  - Important for rational design of EDLC pore structure

Overall Conclusions and Future Outlook

- AAO bondable to Si using eutectic reaction
  - Improving integration into Si processing flow
- CNT growth in AAO more complex than simple coating process
  - Effects of anion contamination in AAO
- EIS measured 10x increased resistivity
  - Effect of electrode surface chemistry on IL – carbon interaction

ACKNOWLEDGEMENTS

Ziegler Group, UF CHE
ww2.che.ufl.edu/ziegler