Maximizing Energy Density of Electrochemical Capacitors: from Proof of Concept to Reliable Manufacturing

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Improved Electrochemical Systems Needed to Bridge the Power-Energy Gap

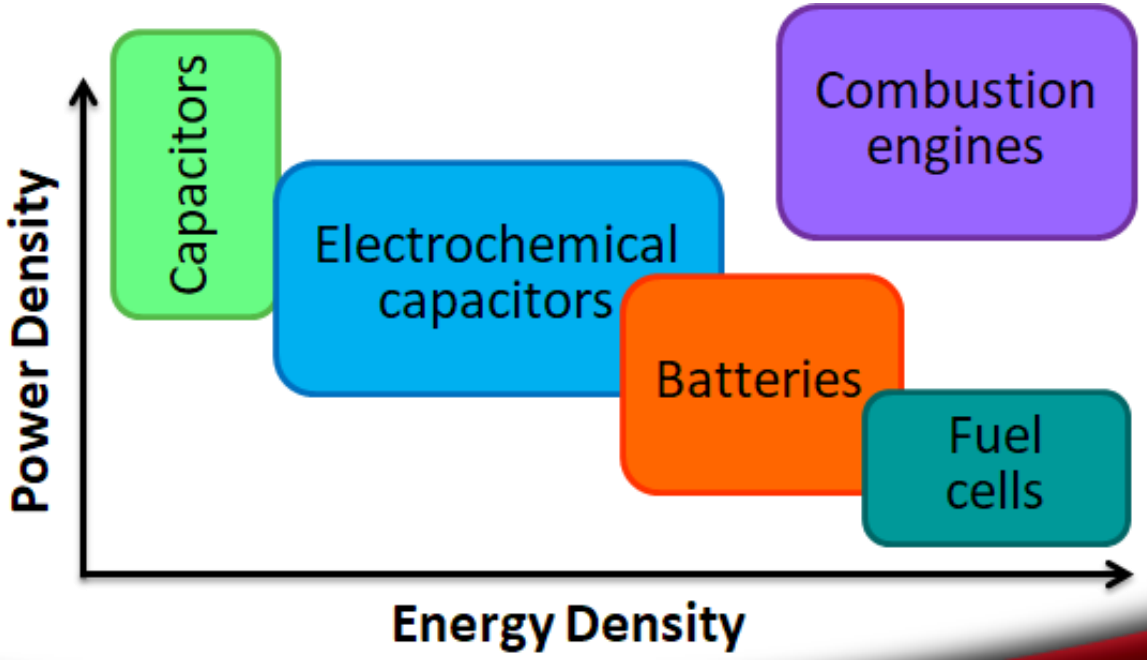
Power dense: electrostatic capacitors achieve

- High rate, short duration power delivery capability
- Surface area driven charge storage
- Extremely long cycle life

Energy dense: fuel cells, batteries

- Provide slower rate, longer power delivery capability
- Volumetric, RedOx reaction-based storage
- Limited life

Improved ultracapacitor:
Increase energy density without sacrificing the power density



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Strategies to Increase Capacitor Energy Density

Increase Active Surface Area

- Nanostructured carbons
  - CNTs
  - Graphene
- New biologically derived carbons
- Optimize pore spacing and distribution

Increases specific capacitance

Linearly increases specific energy

Increase Voltage Window

- Room temperature ionic liquids
- Deep eutectic electrolytes

Specific energy increases by voltage squared

Incorporate Faradic Charge Storage

- Incorporate surface active species
- RedOx species - pseudocapacitance
- Asymmetric electrodes
- Hybrid electrodes

Reduces cycle life but adds volumetric density

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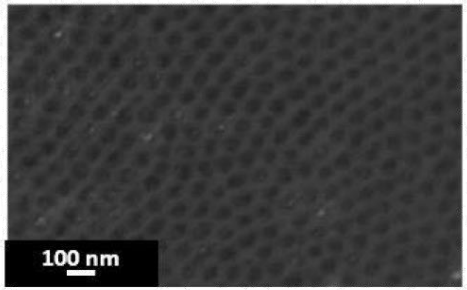
Our Approach: High Surface Area Electrode with Increased Voltage Window

Template Grown Aligned CNTs

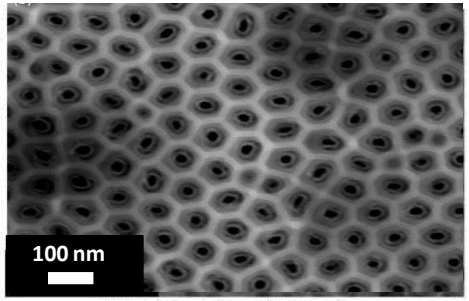
- AAO template precisely controls pore dimensions – diameter, spacing, and length
- High quality CNTs deposited through CVD into the pores
- High surface area vertically aligned CNTs with removal of AAO
- Directed charge transport

Ionic Liquid Electrolyte

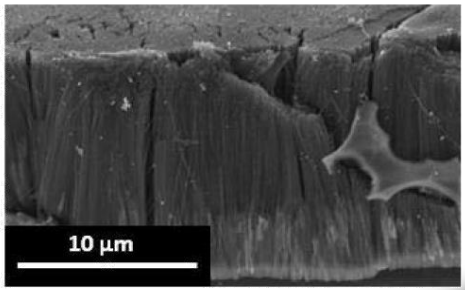
- Maximize the voltage window
- Increased temperature stability
- Wider applicability of the capacitor in hostile environments



(a) Not etched



(c) Etched for 110 min



(c) Cross section of etched template

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Templated Growth Process to Densely Packed Vertically Aligned CNT Electrodes

Highly Controlled AAO Template Formation

Step 1. Controlled voltage and temperature during anodization of aluminum to form a precise nanoporous array

Aluminum Substrate

Self-ordered, uniform alumina pores form during controlled aluminum oxidation

Depth of ordered porous array of aluminum oxide is controlled by the charged passed

Step 2. Voltage step-down + wet chemical etch used to remove thin insulating barrier layer that forms at the base thus exposing the conductive aluminum

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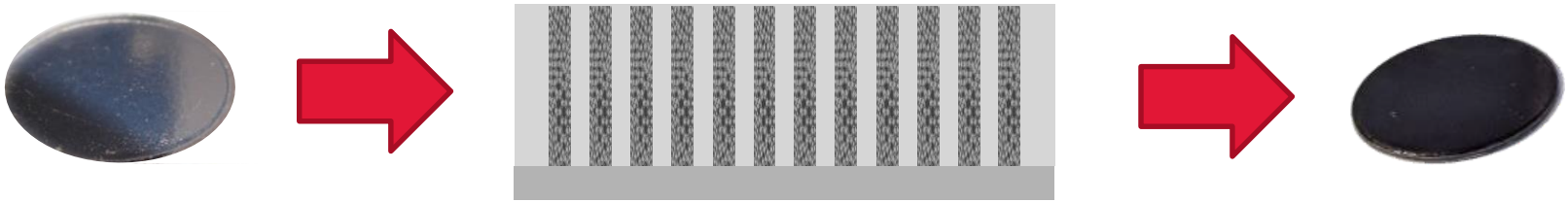
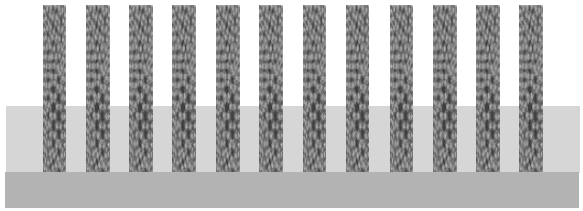
Scalable Growth of Reproducible Vertically Aligned CNT Electrodes

Step 3. Chemical vapor deposition growth of CNTs inside the pores provides controlled diameter, spacing and length



Step 4. Chemical etch of aluminum oxide barrier layer to expose additional surface area of the CNTs



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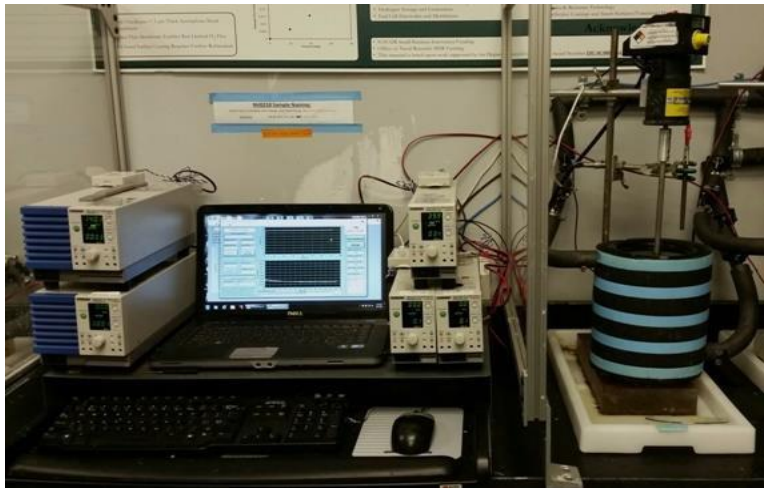
Proof of Concept: Single Sided Disk Scale Cell Fabrication



- **Developed small area holders for controlled one side anodization of disk electrodes**
- **Template dimensions controlled by**
  - Pore size and spacing by acid choice, voltage and temperature
  - Depth controlled by the charge passed
- **CNTs grown at temperatures below the aluminum melting point of 670°C**

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Initial Testing Lessons

- **CNT Electrode Fabrication by CVD in the Templates**
  - Standard Catalyzed growth problematic and hard to scale
    - Catalyst electrodeposited
    - CNT growth had poor reproducibility for small disk electrodes
  - Uncatalyzed CNT growth within the template showed good uniformity and scalability
- **Initial cell testing in in coin cells and H-cells**
  - Testing in the electroanalytical and coin cells
    - Cells hard to assemble with ridged backing
    - Large volume of electrolyte to electrode area
  - Allowed testing of a range of electrolytes including ionic liquids

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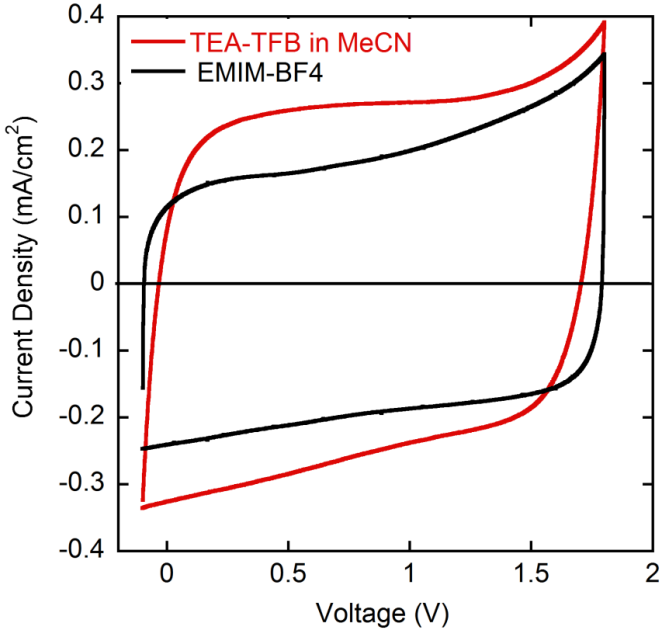
Cyclic Voltammogram Shows Good Capacitance Behavior

- **Cyclic voltammetry shows good behavior**
  - Current rise with increasing voltage, not symmetric on negative sweep
  - Ionic liquids and acetonitrile based electrolytes work well



Cells needs to be scaled and fabricated into a practical device configuration

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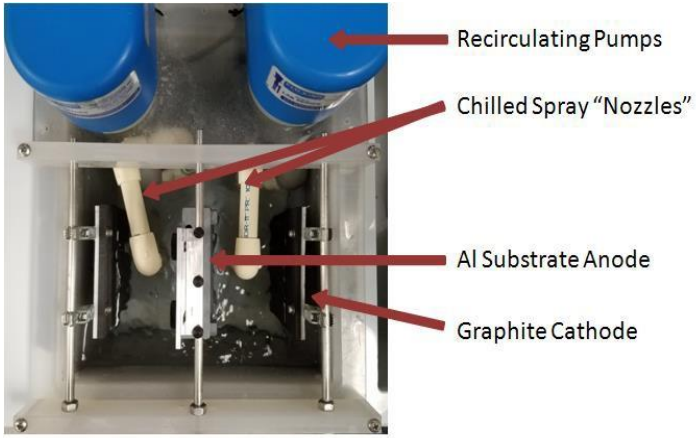
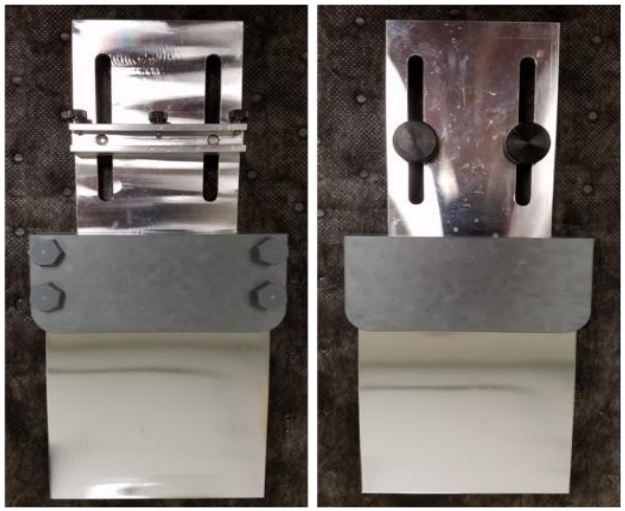
Scaling Towards Practical Manufacturing

- The cross sectional area and both sides need to be anodized
  - Optimized the bath design to anodize and cool with directed mixing jets
  - Developed holders to allow access to both sides equally



Chilled Electrolyte Bath



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Scaling CVD Growth to Two Sided and Multiple Electrode Sheets

- Designed a holder to allow CVD growth of both sides of the electrodes
- Multiple electrodes can have growth at the same time
- Electrodes can be packaged into pouch cells for testing

Increase area by a factor of 50 with no loss of reproducibility

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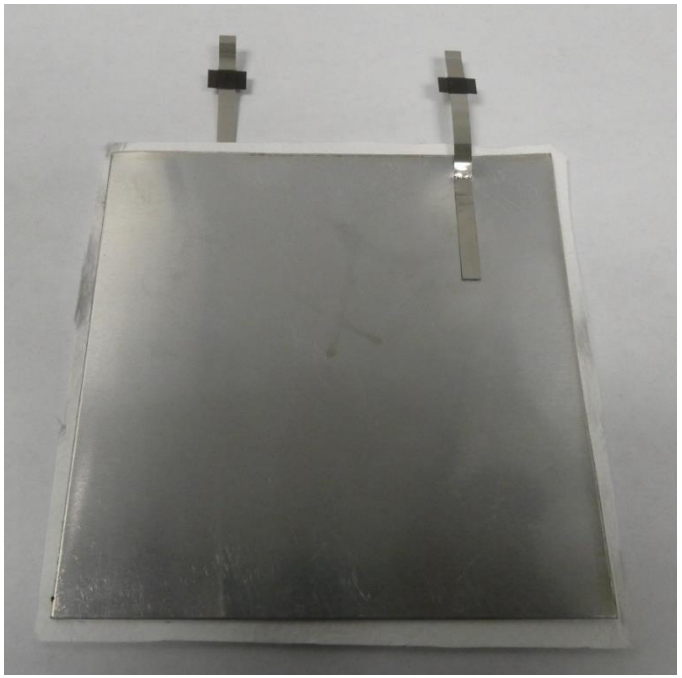
Pouch Cell Fabrication and Testing of Scaled Capacitor

Step 4. Electrodes packaged into pouch cells for testing



Small electrolyte volume for electrode area gives more representative testing of behavior

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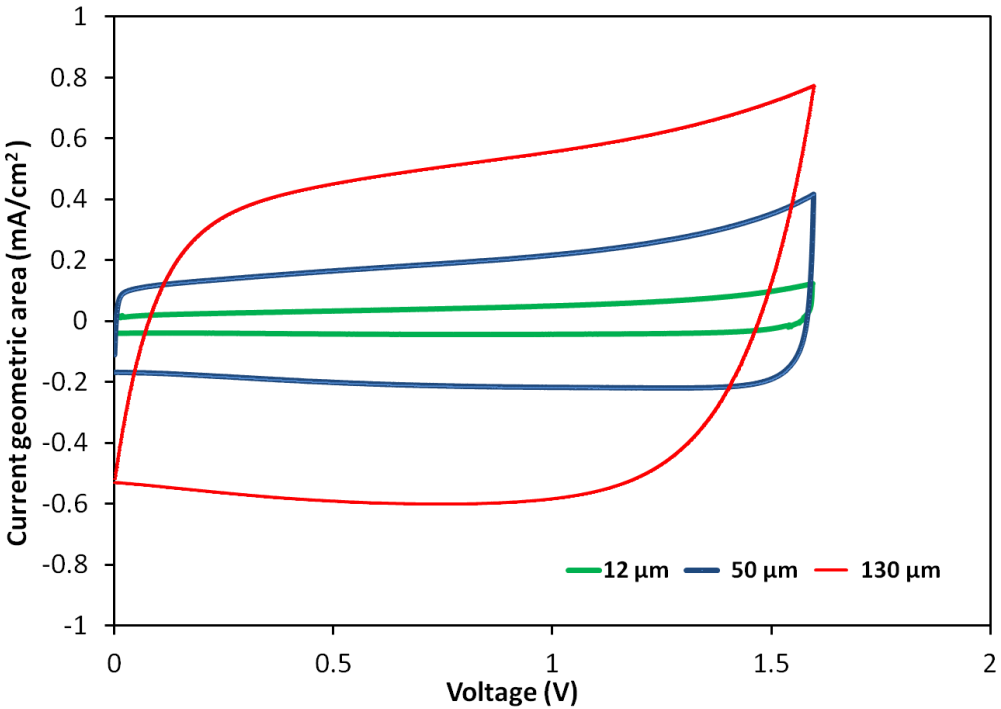
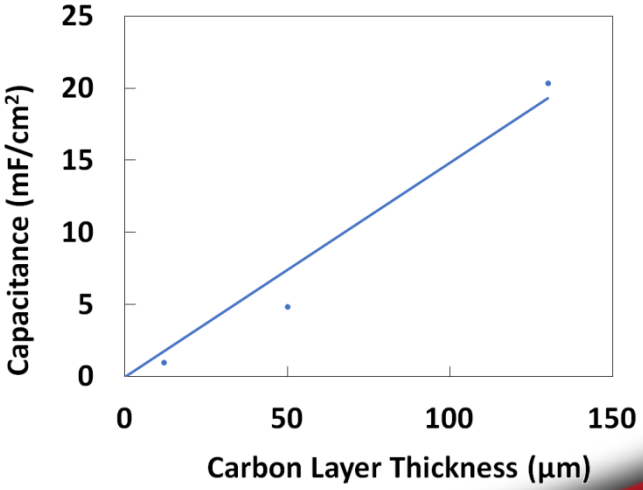
Increased Capacitance by increasing Template Thickness



Cyclic Voltammetry at 100 mV/s with EMIM-BF4 electrolyte

- Varied AAO template thickness from 12 to 130 μm with same pore size
- Measured capacitance showed a linear response



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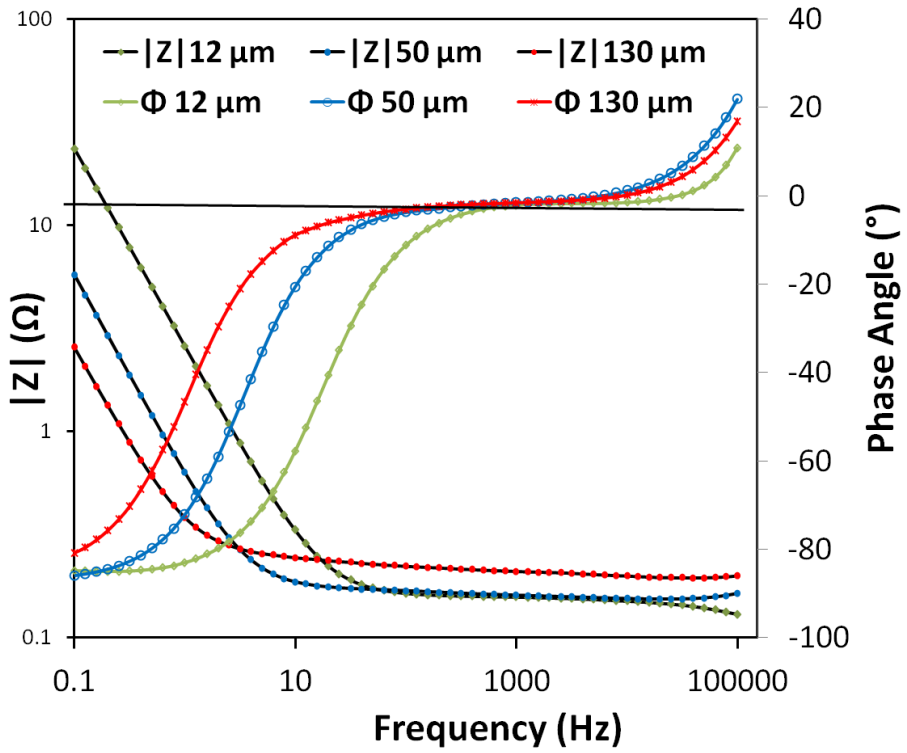
Capacitor Impedance of Cells Dependance on Thickness

- All CNT pore lengths show similar capacitive behavior
- Longer pore shows a shift to lower frequencies as expected due to diffusion limitations



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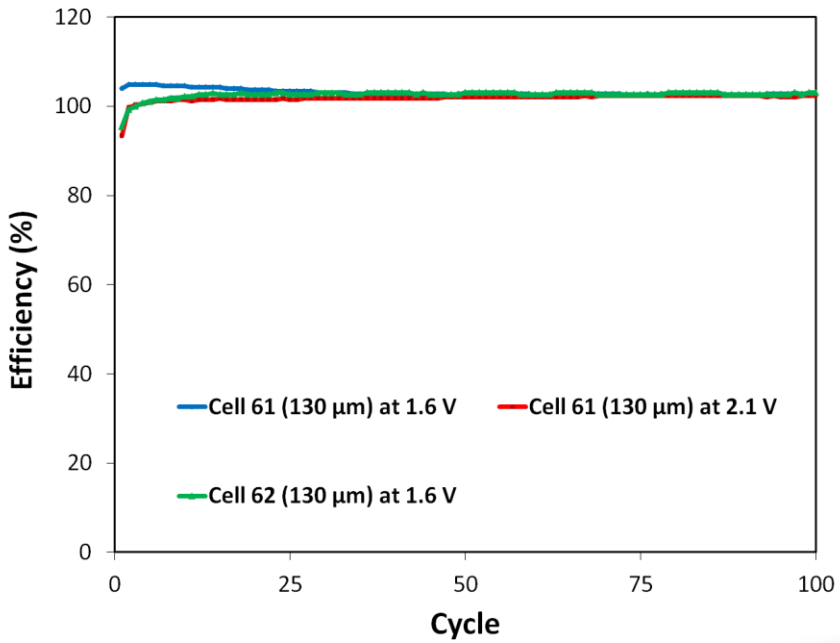
Durability

- Extended galvanic cycling used to evaluate the faradaic efficiency as a measure of the cyclability
  - High efficiency throughout 100 cycles
  - Stable 100% faradic efficiency obtained after some initial cycling
- Additional long term testing planned – as the area is scaled up and we move to multicell packaged devices



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Conclusions

- **Process scaled well maintaining performance and reproducibility for small disk to large area duel sided electrodes**
- **Scaling up required iterative process and adjustments to each step to maintain reproducibility**
- **Capacitance scaled with template thickness with consistent behavior and rate changes based ion diffusion onto pores**
- **Cells show good durability**
- **Future steps:**
  - Increasing active surface area
  - Minimize internal resistance to maximize power density
  - Fully packaged multielectrode cells

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Thank you

Any questions?

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