Designing Better Batteries at the Nanoscale

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Nanostructures for Electrical Energy Storage
A DOE Energy Frontier Research Center

NEES major research areas
T1 - Nanostructure Interface Science
T2 - Mesoscale Architectures & Ionics
T3 - Nanostructure Degradation Science
T4 - Solid State Energy Storage

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Electrical Energy Storage (EES)

Today’s technology is **inadequate** ... an impediment to

- More efficient use of **conventional sources**
- Wide adoption of **renewable energy**

*Storage is the “currency” of the energy economy*

Analogous to economic marketplace: €, $, ¥, ...

Improved storage technology ➔ high liquidity of energy, efficient energy utilization
Electric vehicles, renewable sources, grid management, ...
Energy Storage for Dynamics of Energy in a Changing World

Electricity grid – today and tomorrow – must contend with changing supply and demand on multiple time scales

Renewables require storage to match disparate time frames of supply vs demand, also on multiple time scales

Both pose critical needs for

- *Increased electrical energy storage capacity*
- *Storage technology capable of managing high power*
- *Robust solutions (i.e., cycle life) at low cost*
Nanostructures for Energy Storage

**Today's EES**
- AAO-ALD embedded metal-insulator-metal device

**Future EES**
- Free-standing MnO$_2$/PEDOT coaxial nanowires
  Liu and Lee, JACS (2008)

- Electrostatic capacitors

- Electrochemical capacitors

- Li ion batteries

**1-D MWCNT random network current collector under ALD c-V$_2$O$_5$ ion storage layer**
Chen, ACS Nano (2012)
Limitations of Today’s Batteries

Ion motion is slow in & out of storage material

Long, tortuous transport paths for electrons & ions

Limited interfacial contact between electrode components and with electrolyte interface

Materials cannot hold enough ions

Ion cycling in & out alters storage material

Binder, separator, & electrolyte add weight & volume

Battery degrades with time

Serious safety concerns

\[ \tau = \frac{l^2}{2D} \]

\( \tau \) = transport time

\( l \) = diffusion length

\( D \) = diffusion coefficient

Designing Better Batteries

**Improve by:**
- Simple, short charge transport pathways
- Easy access from electrolyte
- Stable electrodes for charge cycling
- Less peripheral material
- Materials and structure for safe operation

**Nanostructured systems designed for**
- **ion transport & storage**
- **electron transport**
- **mechanical stability during charge/discharge cycling**
Why Nano?

Build on a wealth of advances in synthesis & characterization at the nanoscale for profound improvements in ...

Materials for higher performance ion storage and transport
  Nanoscale synthesis ➔ better electrode materials & electrolytes

NOT the focus for NEES

Structures & architectures for efficient multifunctionality
  Design, synthesis processes, integration, and novel characterization
  Ion transport & storage, electron transport, chemical/mechanical stability

NEES’ overarching focus

➢ Understand electrochemistry at nanoscale, in **model** nanostructures

➢ Explore nanostructure approaches as candidates for next-generation storage
**Why Nanostructures?**

*Thin layers of ion storage materials*, with large surface area

- facile ion access to storage material
- fast ion transport in thin storage layers

*Current collector materials* intimately contacting all ion storage materials

- fast electron transport

→ heterogeneous, multifunctional

**Robust designs** to accommodate volume change upon ion exchange

- robustness during charge/discharge cycling

**Dense packing** of nanostructures

- high volumetric energy density

→ cycle life

→ energy
High storage performance ➔

**pack the nanostructures at high density - “forests”**

New phenomena emerge at high power, high aspect ratio, dense packing

*Ion depletion, transport limitations*

*Electron transport resistance*

*Influence of surface charge*

...
Templating by Nanoporous Anodic Aluminum Oxide (AAO)

AAO membranes produced by two-step anodic oxidation of Al:

1st anodization (const V, T; 10+ hrs)
Dissolution of anodic oxide
2nd anodization (const V, T: time for depth)

Self-assembled, high density hexagonal array of cylindrical pores
Pore diameter 15-300 nm
Pore depth 0.1-30 μm
Aspect ratios 200-1000


*Animations by Israel Perez
Atomic Layer Deposition (ALD)

- Reactive CVD precursors alternately and separately exposed to surface
- Self-limiting adsorption/reaction
- Monolayer thickness control
- Superb conformality and uniformity

Thickness control

Conformality

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AAO-ALD for MIM Electrostatic Supercapacitor

**ALD MIM layers:**
- Top electrode: TiN 12.6nm
- Dielectric: Al₂O₃ 6.6nm
- Bottom electrode: TiN 5.6nm

Aspect ratios 200-1000 (depth/width)
ALD conformality >93% in all layers
100 billion nanocapacitors per square inch

**AAO nanopores**
- 60nm dia, 1-10μm deep

**SEM images**

“All-in-one” Nanopore Battery

Fabricate ultrasmall nanopore battery (~1 femtoliter)
1 million - 1 billion nanobatteries in a grain of sand!

Testbed for ionics & electrodics

Is smaller better?

Use AAO & ALD

Nanopore battery array
$2 \times 10^9$/cm$^2$

Cross section of single-pore battery

- V$_2$O$_5$ cathode
- Prelithiated V$_2$O$_5$ anode
- Ru current collector
- Electrolyte

Cross Section View

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Energy Storage in Nanopore Batteries

Striking performance in capacity, power, and cycling

Rubloff & Lee groups (UMD)
Chanyuan Liu et al, Nat Nano (2014)

Achieves full theoretical capacity of the $V_2O_5$ active storage material

Capacity retention ~50% at 150C cf. 1C

smaller can be better!

Excellent at high power
➡ Integrated current collector
➡ Open access from nanotubular electrodes

Excellent at extended cycling
➡ Nanotubular design
➡ Uniform functional layers

Rubloff & Lee groups (UMD)
Chanyuan Liu et al, Nat Nano (2014)
ALD Nanostructures Lab (ANSLab)

- Custom electrochemical cell enabling post-cycling disassembly and electrode surface analysis in-situ
- Real-time, in-situ sensing
  Spectroscopic ellipsometry
  Downstream mass spec

**Full device fabrication, testing, and materials/surface analysis pre/post cycling, without air exposure**

- Inert ambient glove box
- Battery assembly/disassembly
- Electrochemical testing
- ALD (thermal, plasma, ozone)
  MnO₂, Al₂O₃, TiO₂, TiN, AlN, & combinations
- ALD-1 Glove box
- Custom electrochemical cell enabling post-cycling disassembly and electrode surface analysis in-situ

**Surface analysis**
- Kratos Ultra DLD
- Mono-XPS, mapping/imaging (3-15µ)
- SEM, scanning Auger (100-200nm)
- Depth profiling (Ar, coronene)
- UPS, ISS
Leveraging AAO-ALD for Solid State Batteries

**Electrostatic Nanocapacitor**

- **Top electrode:** TiN 12.6nm
- **Dielectric:** Al₂O₃ 6.6nm
- **Bottom electrode:** TiN 5.6nm
- **Aspect ratios:** 200-1000 (depth/width)

**Key challenges:**
- Highly conformal solid electrolyte
- Synthesis of interdigitated structures
- Design → key questions of mesoscale architecture

**Crucial component** – solid electrolyte, nonflammable

**3-D Solid State Nanobattery**

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3D cathodes on MWCNT sponge

- Conformal ALD $V_2O_5$ coating
- Compressed for battery test
- MWCNT/$V_2O_5$ core/shell

- $H_2O$ based ALD $V_2O_5$ coated on CNT
- Uniform coating $\rightarrow$ core/shell structure
MWCNT / $\text{V}_2\text{O}_5$ Core/Shell Sponge Electrodes

- **ALD $\text{V}_2\text{O}_5 \rightarrow$ high capacity, good cycling (1,2 Li)**
  
<table>
<thead>
<tr>
<th>#Li per V2O5</th>
<th>Voltage range</th>
<th>Crystalline (VTOP/ozone)</th>
<th>Amorphous (VTOP/H2O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.0-2.6</td>
<td>127 mAh/g</td>
<td>89 mAh/g</td>
</tr>
<tr>
<td>2</td>
<td>4.0-2.1</td>
<td>283 mAh/g</td>
<td>219 mAh/g</td>
</tr>
<tr>
<td>3</td>
<td>4.0-1.5</td>
<td>320 mAh/g</td>
<td>320 mAh/g</td>
</tr>
</tbody>
</table>

- **MWCNT sponge $\rightarrow$ high surface area current collector and scaffold**
- **450X areal capacity cf. planar**

Hu, Rubloff, Lee groups (UMD)
Architectures for Multifunctional Nanostructures

While scaffolds may be random in 3-D, effective electrode structures formed on them must be regular/well-defined 1-D nanostructures to achieve required multifunctionality.
Nanostructure Assemblies Offer Diverse Architectures

“regular”

“random”

“hierarchical”

Zhang et al, Nat Nanotech (2011)
Conclusions

• **Nanostructures ➔ next-generation energy storage**
  – High power at high energy density
  – Stability and capacity retention during charge/discharge cycling
  – Possibly, improved safety

• **Heterogeneous nanostructures for multifunctional behavior**
  – Highly controlled, precision nanostructures as model systems
  – Understand electrochemistry at nanoscale, in nanostructures
  – Provide guidelines for nanostructured energy storage

• **Mesoscale architectures of nanostructures**
  – Dense nanostructure arrays required
  – Numerous architectures available ➔ electrochemical performance ?
  – New phenomena at the mesoscale – e.g., ionics
  – Statistics of massive assemblies ➔ defects, outliers, degradation