Enhanced Power Systems Through Nanotechnology

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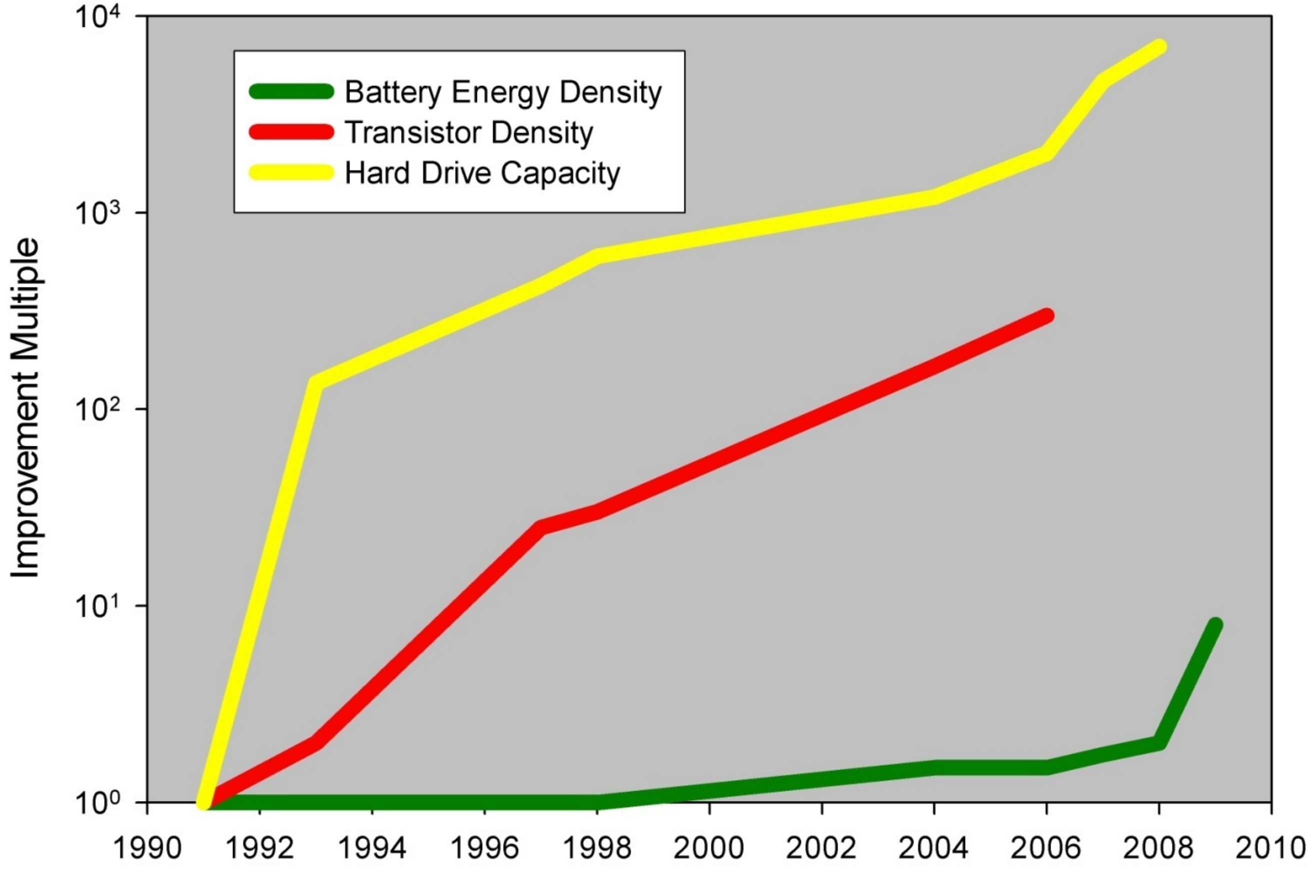
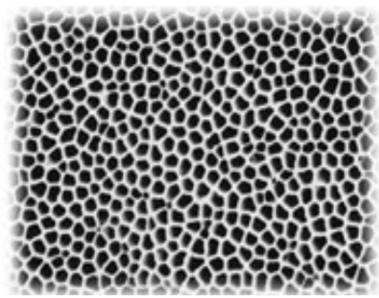
The Movie, “Fantastic Voyage”

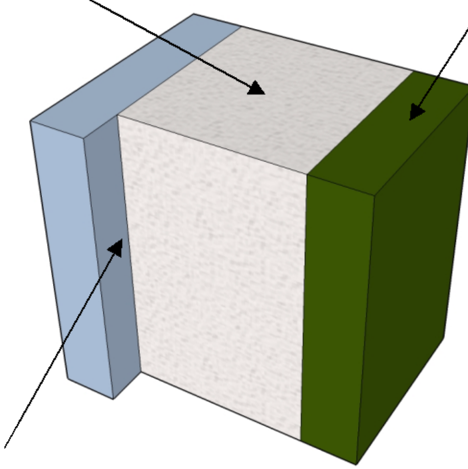
- SYNOPSIS: A medical team is shrunken down to microscopic size and transplanted into the body of an important scientist, so they can remove a life-threatening blood clot from his brain.

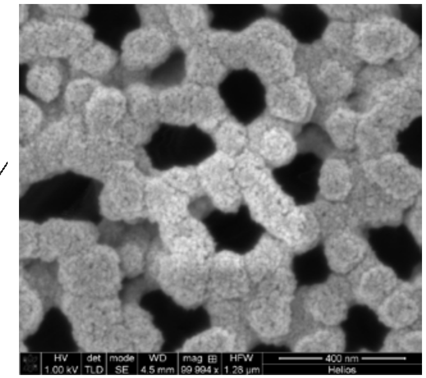
Battery Capacity Has Not Kept Up With Needs



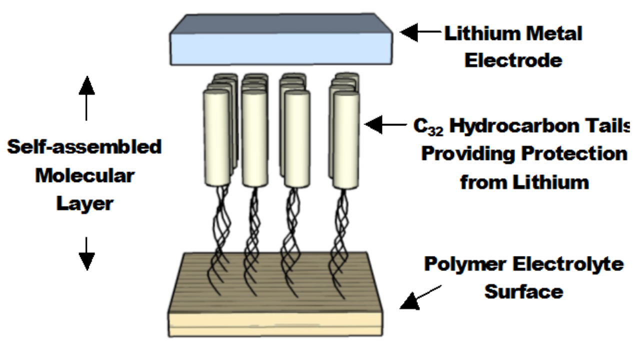


Enhance Electrolyte Performance with Nanostructure



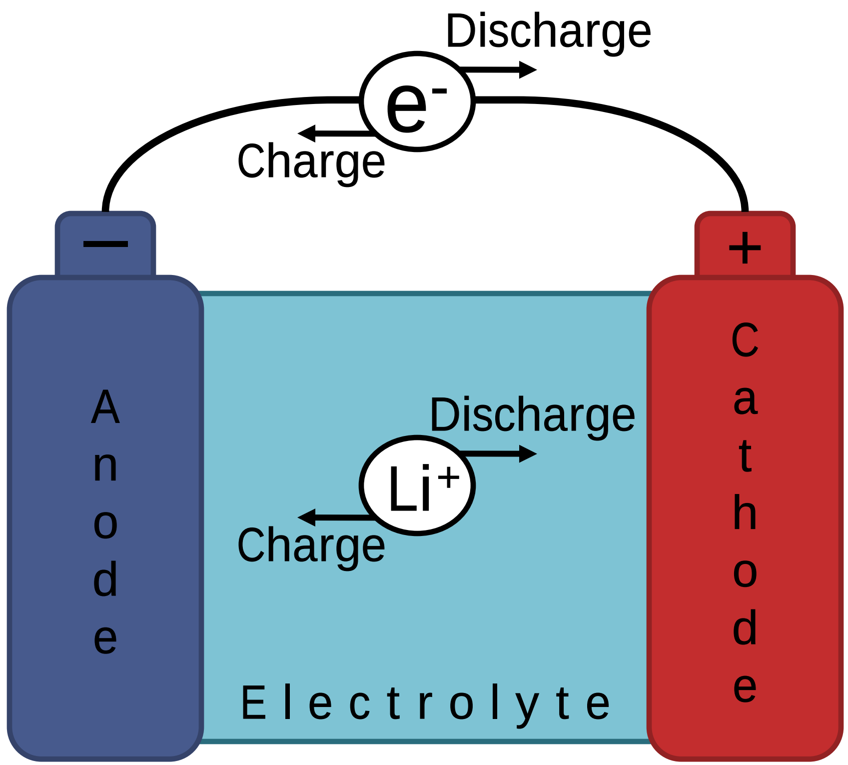


Enhance Electrode Performance with Nanostructure



Stabilize Electrode/Electrolyte Interface with Self-Assembled molecular layer

Secondary Battery Chemistry

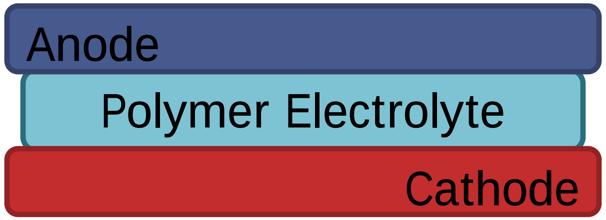


Electrode designations are based on Discharge operations

Lithium Battery Systems

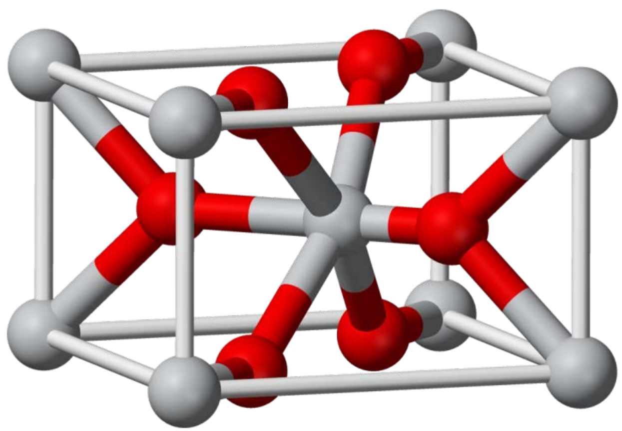
- Lithium metal: uses Li metal anode
  - Safety hazards!
    - Moisture
    - Dendrite formation
- Lithium-ion: no Li metal present
  - Li^+ insertion materials:
    - Anode: Graphite or SnO_2
    - Cathode: $LiCoO_2$ or $LiMnO_4$
- Lithium-ion polymer: polymer electrolyte

This work focuses on the anode material



Tin IV Oxide, SnO_2

- Higher capacity than graphite
  - 781 $mAhg^{-1}$ versus 370 $mAhg^{-1}$
- Safer than lithium anode
  - Li^+ insertion material
  - Alloys with Li up to $Li_{22}Sn_5$
- Forms the nanobasket structure



- Suffers from mechanical degradation due to swelling/contraction upon Li insertion/removal
  - Nanostructuring may help relieve this stress.

Electrochemistry of SnO_2 Anode

<u>Electrode Activation:</u>

- Reduction of SnO_2 to Sn and Li_2O
  - $SnO_2 + 4Li^+ + 4e^- \rightarrow Sn + 2Li_2O$ (irreversible)
  - Only occurs during first charge cycle.
  - Forms small clusters of Sn atoms in Li_2O matrix.

<u>Cycling Capacity:</u>

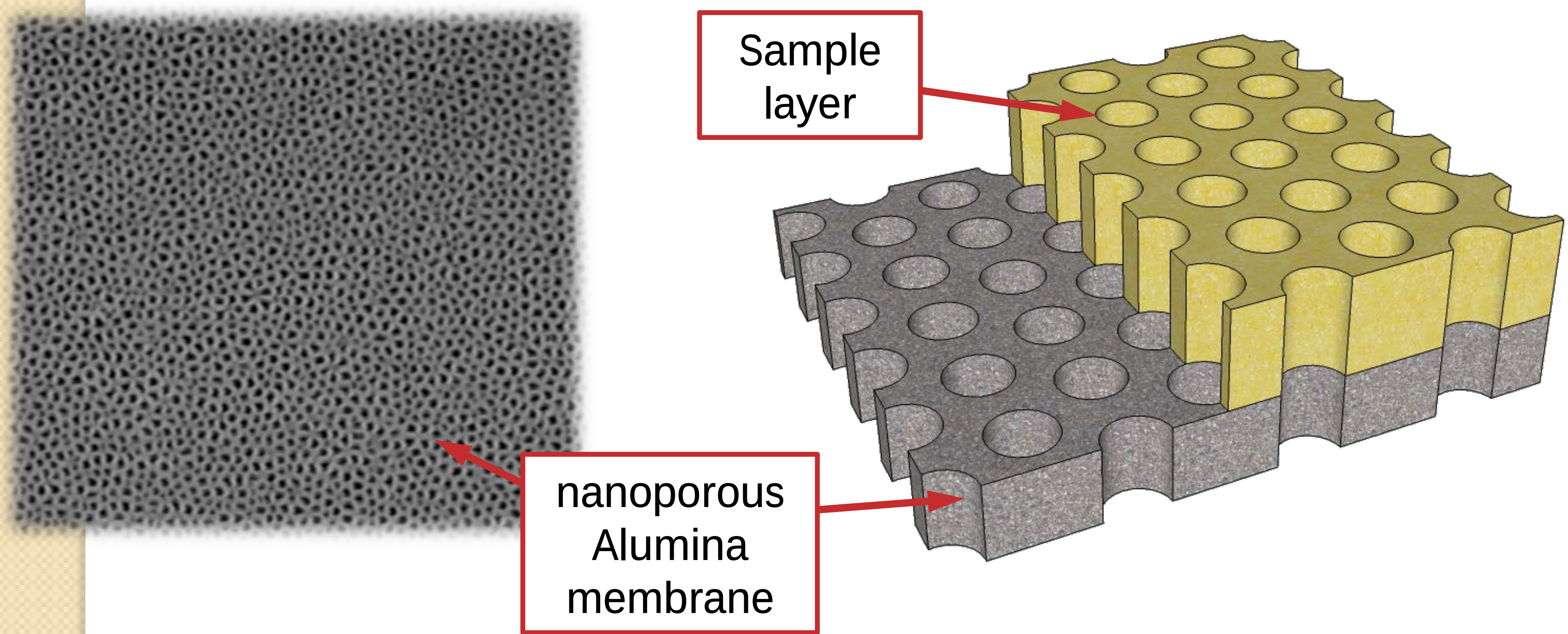
- Alloying/dealloying with Lithium
  - $Sn + xLi^+ + xe^- \leftrightarrow Li_xSn$ (max = 4.4 Li:Sn)

Maximum theoretical capacity based on $Li_{4.4}Sn$ ($Li_{22}Sn_5$):

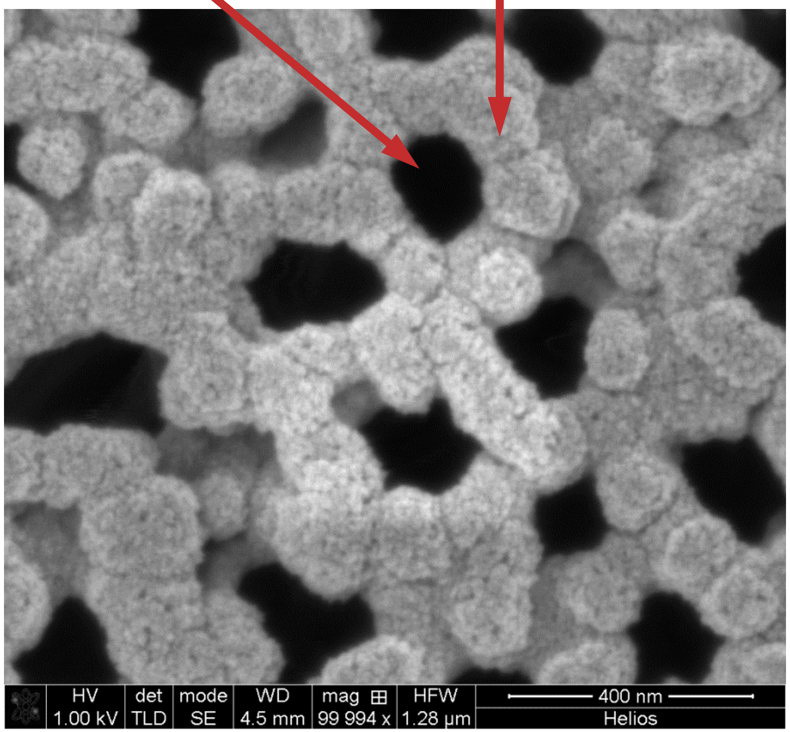
- 781 $mAhg^{-1}$

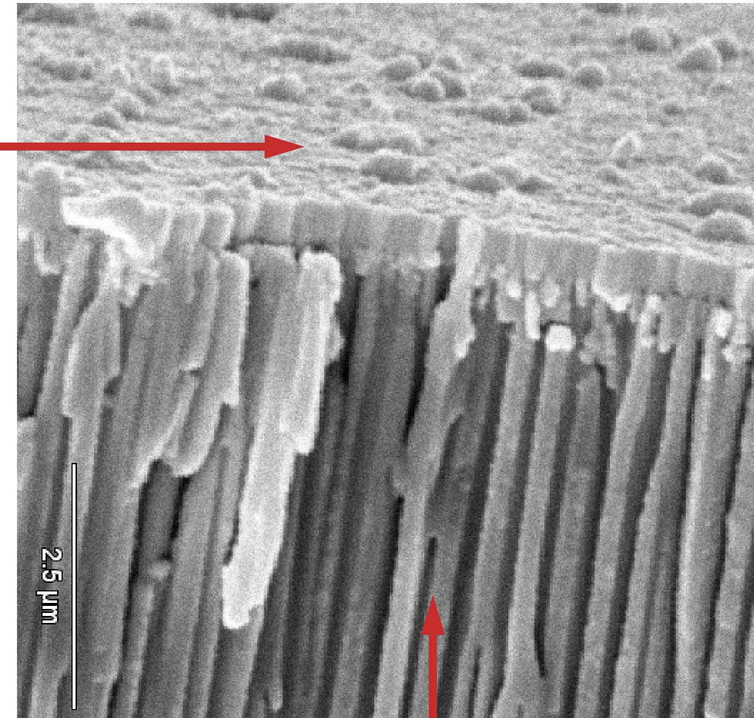
SnO_2 Nanobaskets

- Novel self-assembled structures produced by RF magnetron sputtering onto nanoporous membranes.
- Sample material collects on pore walls, forming hollow columns as thickness increases.



SnO_2 Nanobaskets: SEM





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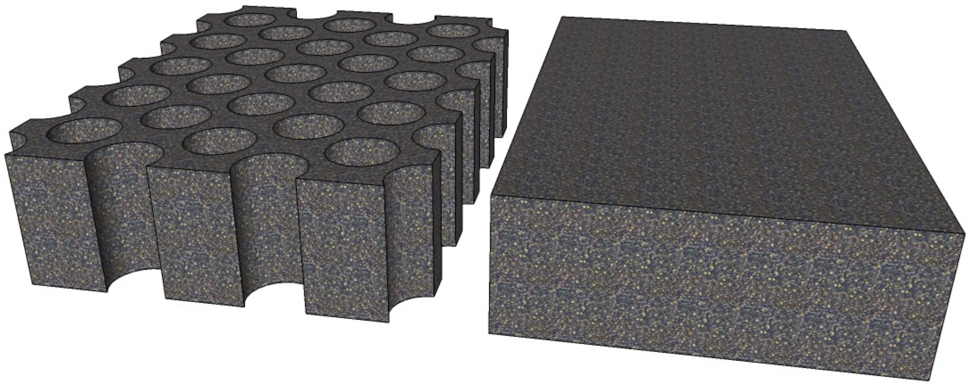
P. L. Johnson and D. Teeters, “Formation and Characterization of SnO_2 Nanobaskets,” *Solid State Ionics*, **177**, 2821 (2006).
M.R. Smith and D. Teeters, Interfacial Storage of Lithium in the Nanostructure of SnO2 Nanobaskets for Capacities Exceeding Theoretical Values, *Solid State Ion*. (2012), doi:10.1016/j.ssi.2011.11.022

Why Nanostructure?

- <u>Increase surface area</u>.
  - More active material is accessible
  - Faster kinetics
  - Reduces resistance
- Reduce the path lengths ions must travel.
  - Faster kinetics
  - Higher material efficiency
- Alleviate mechanical stress.
  - Enhances cycle life and electrode lifespan



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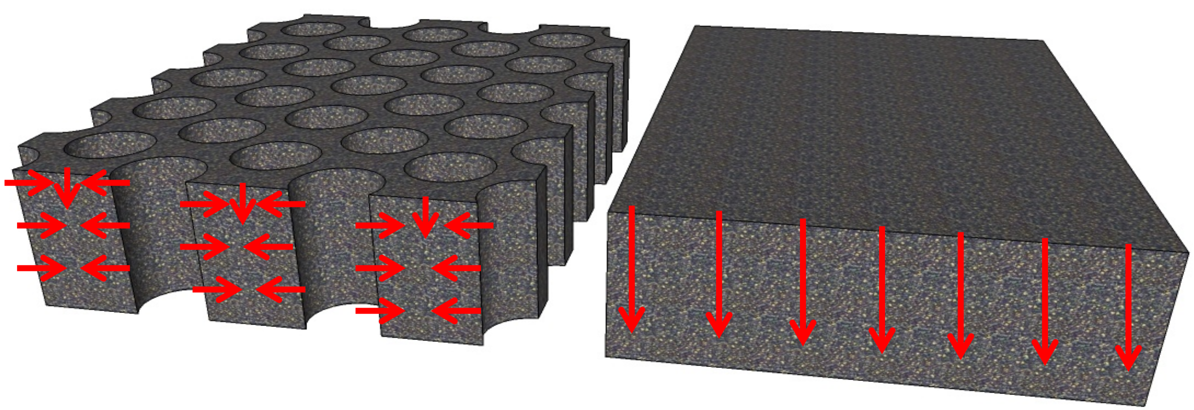
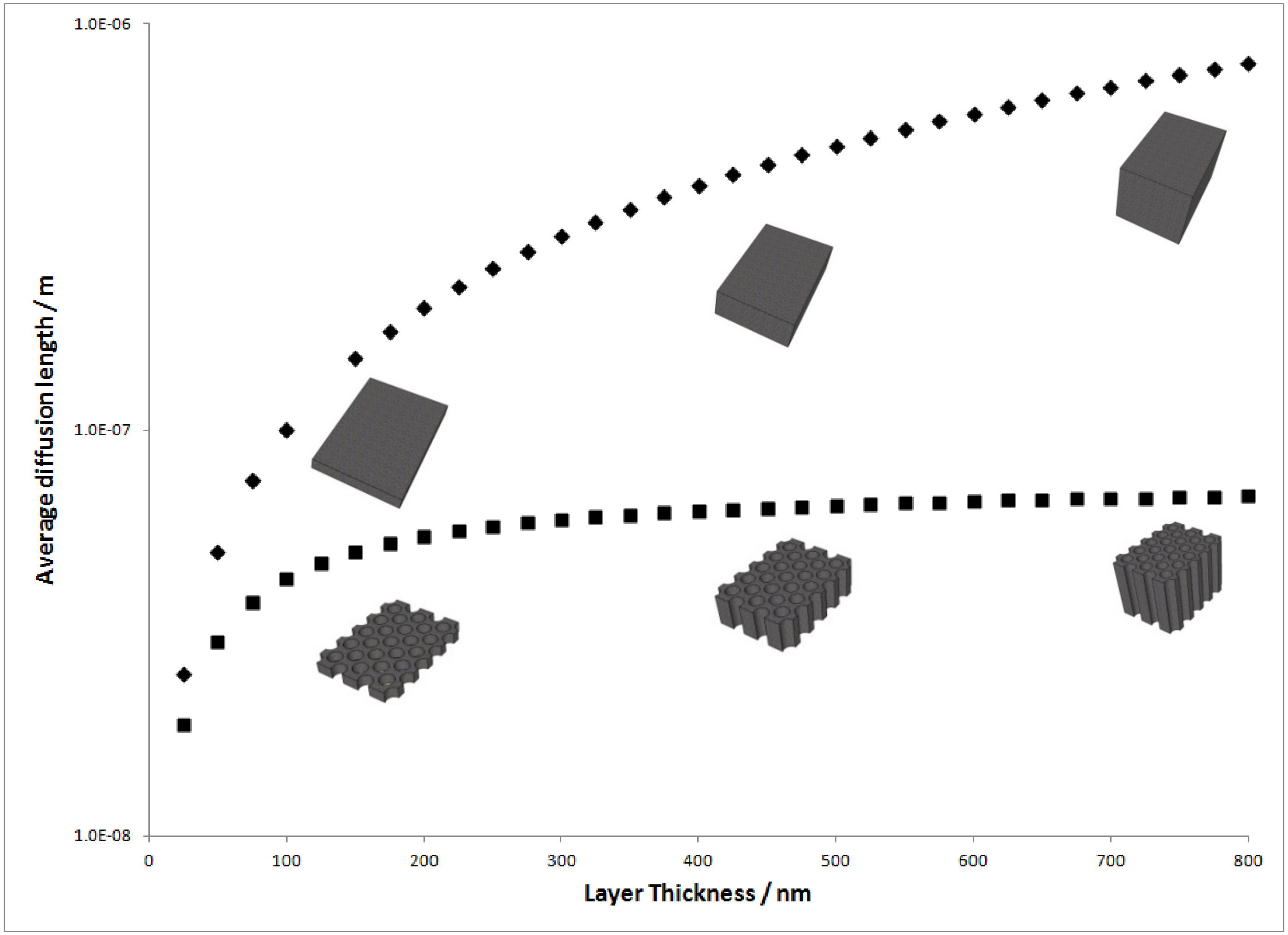


Diffusion Length (calculated)



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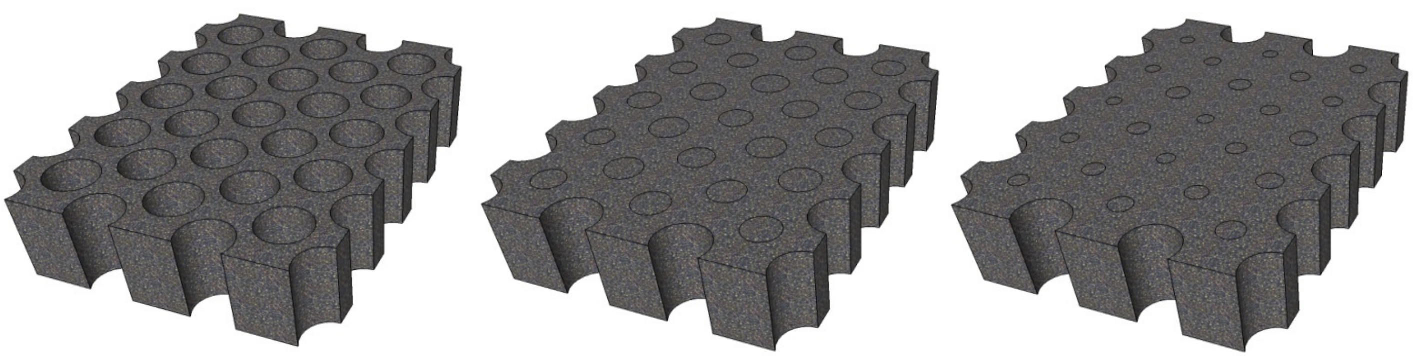


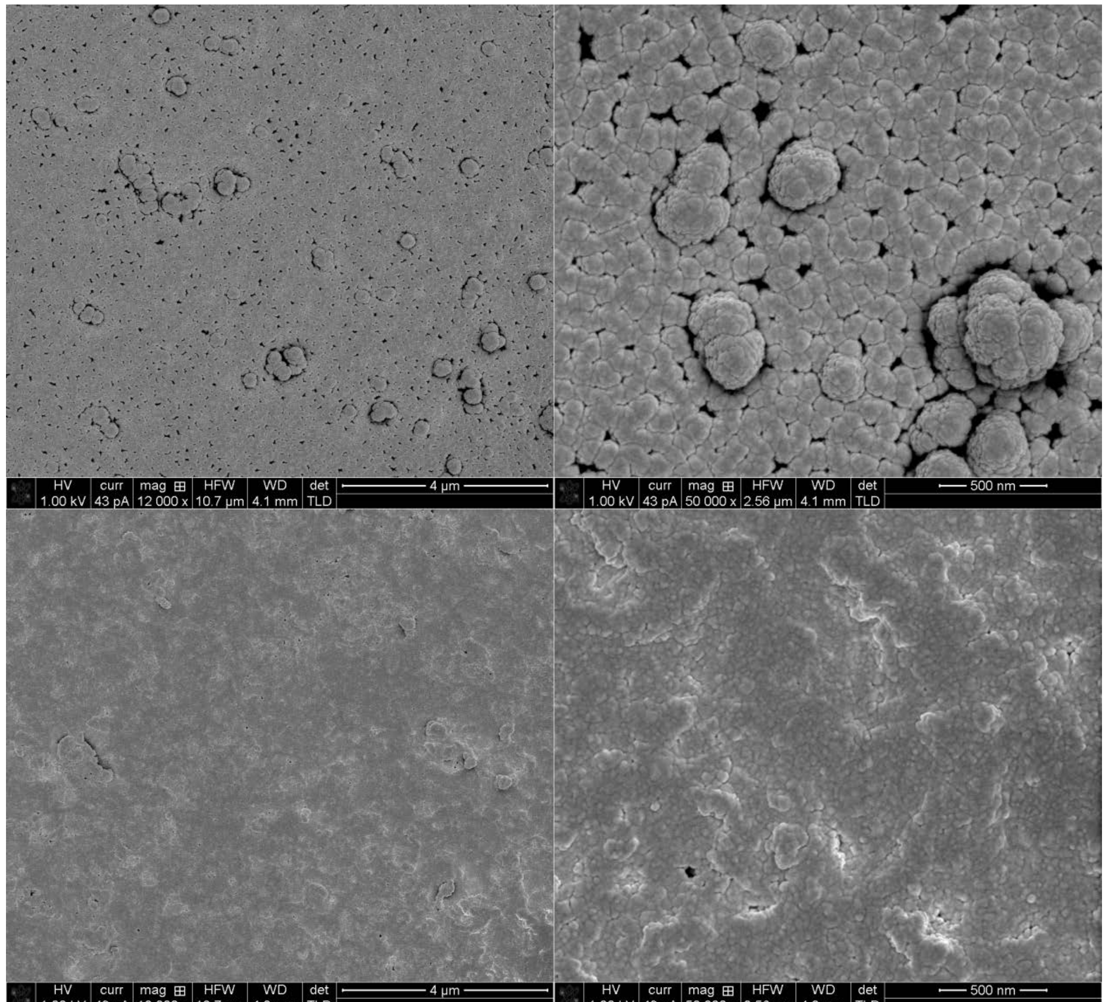
Expansion with Lithium Insertion

10.7 µm HFW

2.56 µm HFW

As prepared

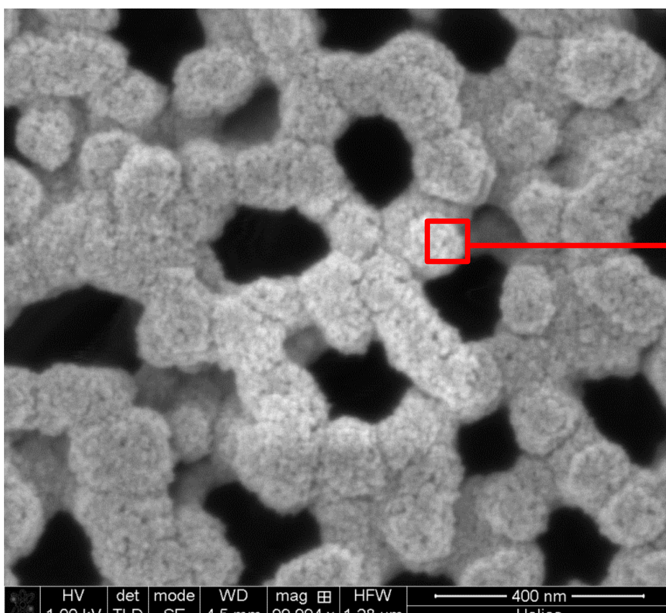
Charged with Lithium



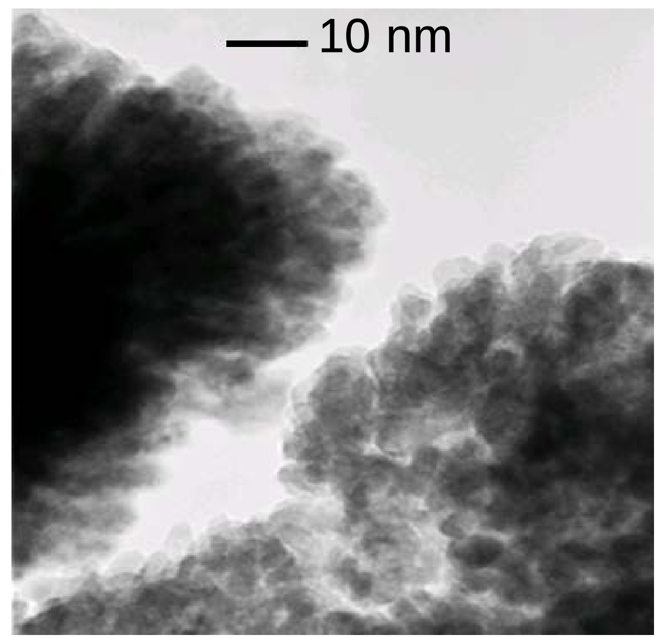
The porous nature of the nanostructure helps accommodate the swelling upon insertion of Lithium

Two-fold Nanostructuring

- 1. Nanobasket hollow column structure
- 2. Nanoparticle substructure
  - Particles on the order of 2-4 nm in diameter
  - Confirmed by Raman and TEM
- Gives an extremely high surface area

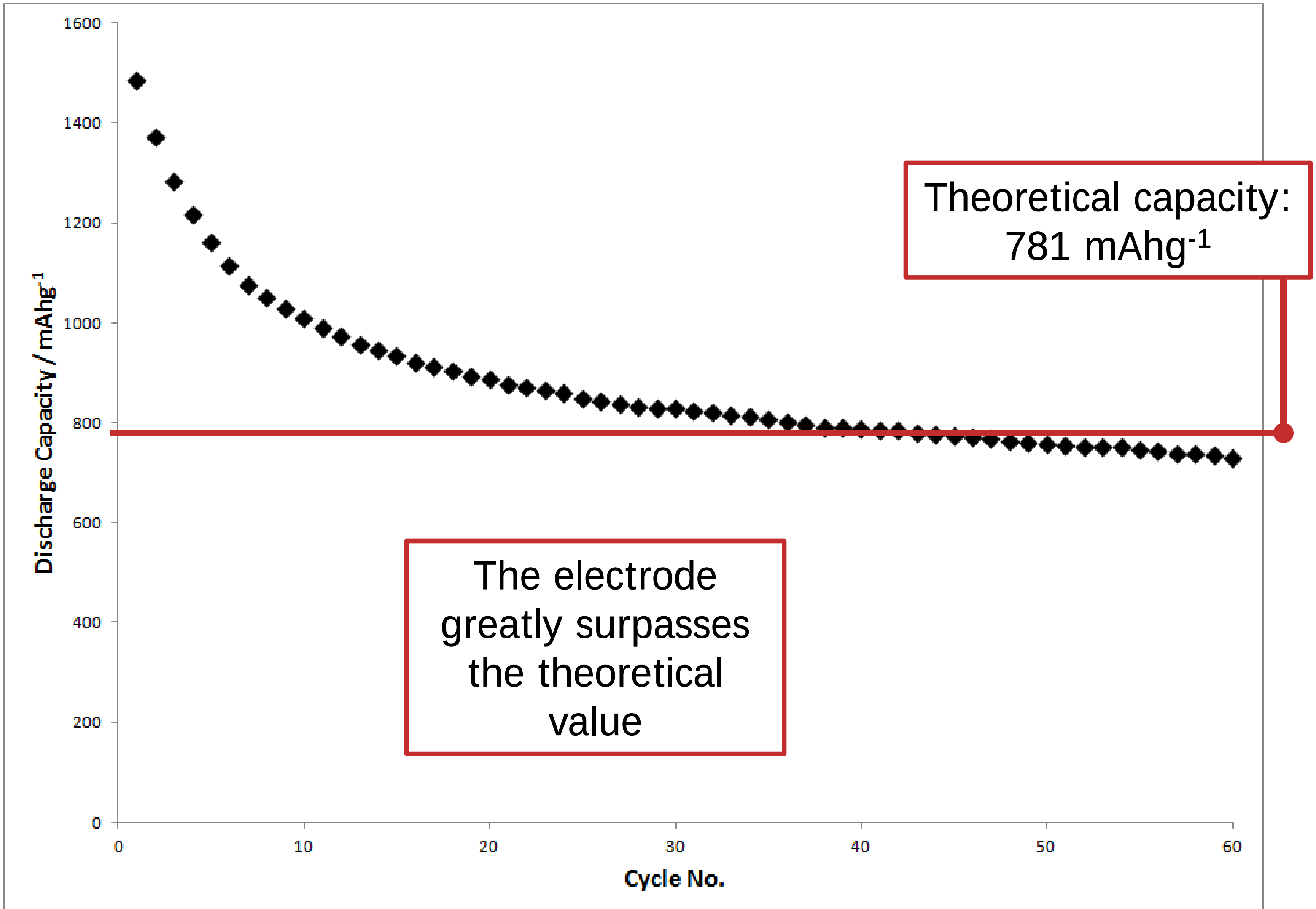


SEM



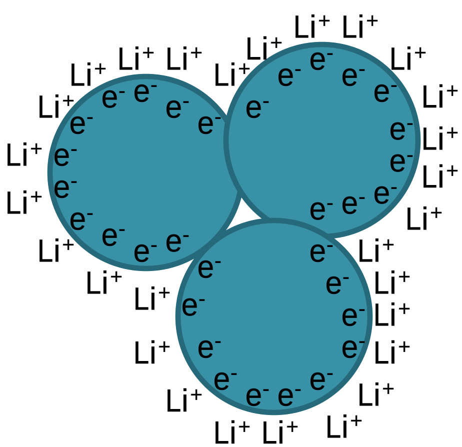
TEM

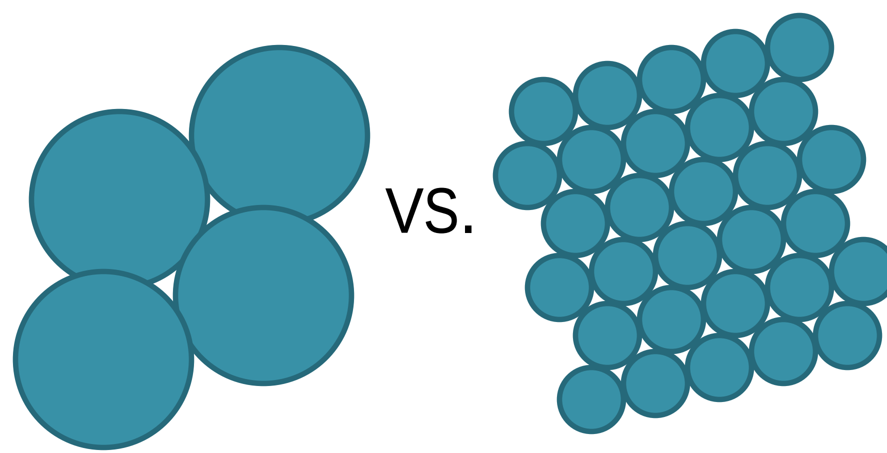
SnO_2 on Cu-coated AAO



Interfacial Charging

- Maier describes a phenomenon termed **interfacial charging**, where extra Li^+ collect at the grain boundaries.
  - → Produces hybrid battery- and capacitor-like properties.
  - → Blurs the line between battery and capacitor.
- Nanobaskets, being nanostructured and composed of a secondary nanoparticle substructure, have an extremely high surface area and therefore a great potential for interfacial storage of lithium.
  - Confirm via annealing studies.





Interfacial Charging

- To investigate the possibility of interfacial charging, samples were annealed in order to soften the sample layer, causing the nanoparticles to coalesce.
  - Raman spectroscopy has shown that such annealing eliminates the 2-4 nm nanoparticle substructure.
  - This would eliminate the added surface area of the electrode without affecting its chemical composition.
- Therefore, any changes to electrode performance should be due to the reduced surface area.

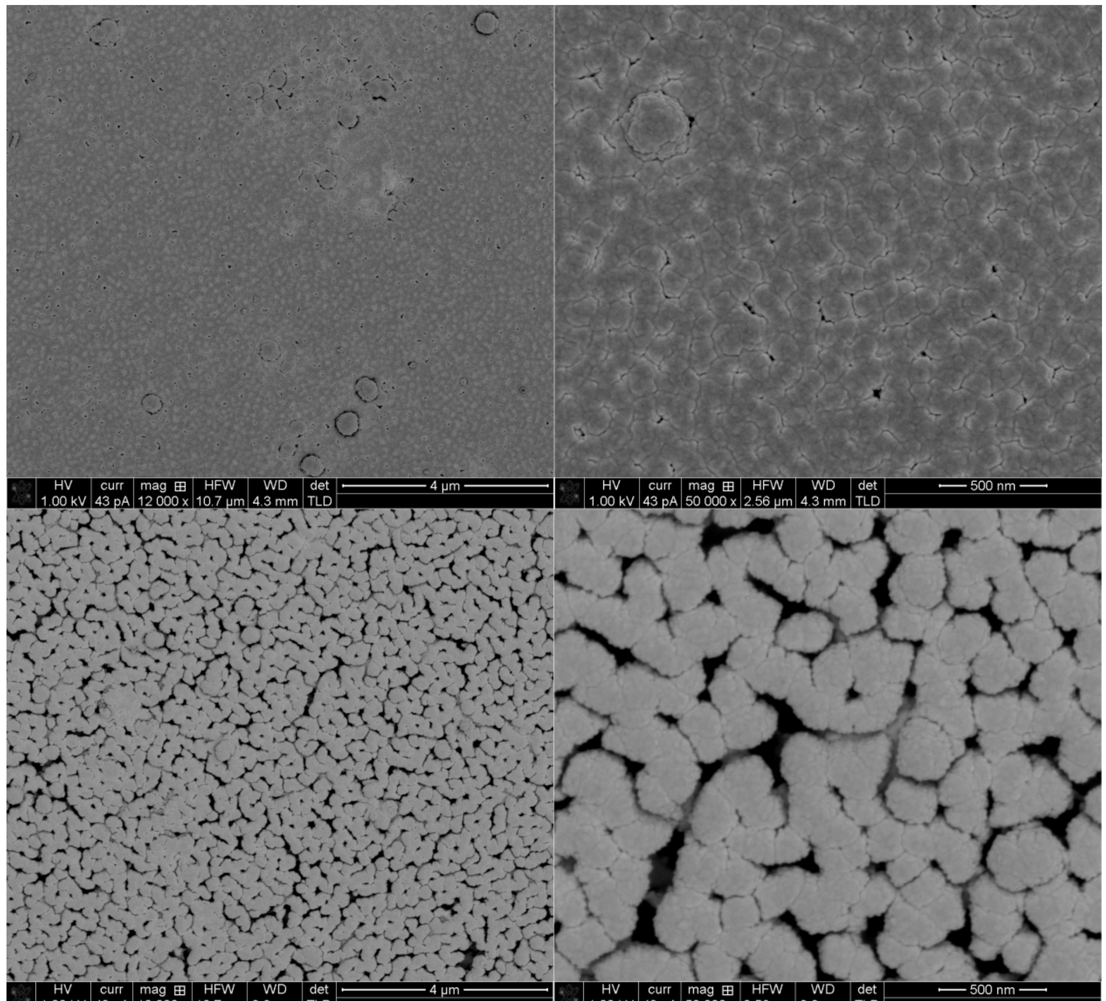
- Samples of SnO_2 were annealed in a Lindberg tube furnace at approximately 500°C for 5 hours.

500 °C for 5 hours

10.7 µm HFW | 2.56 µm HFW

As prepared

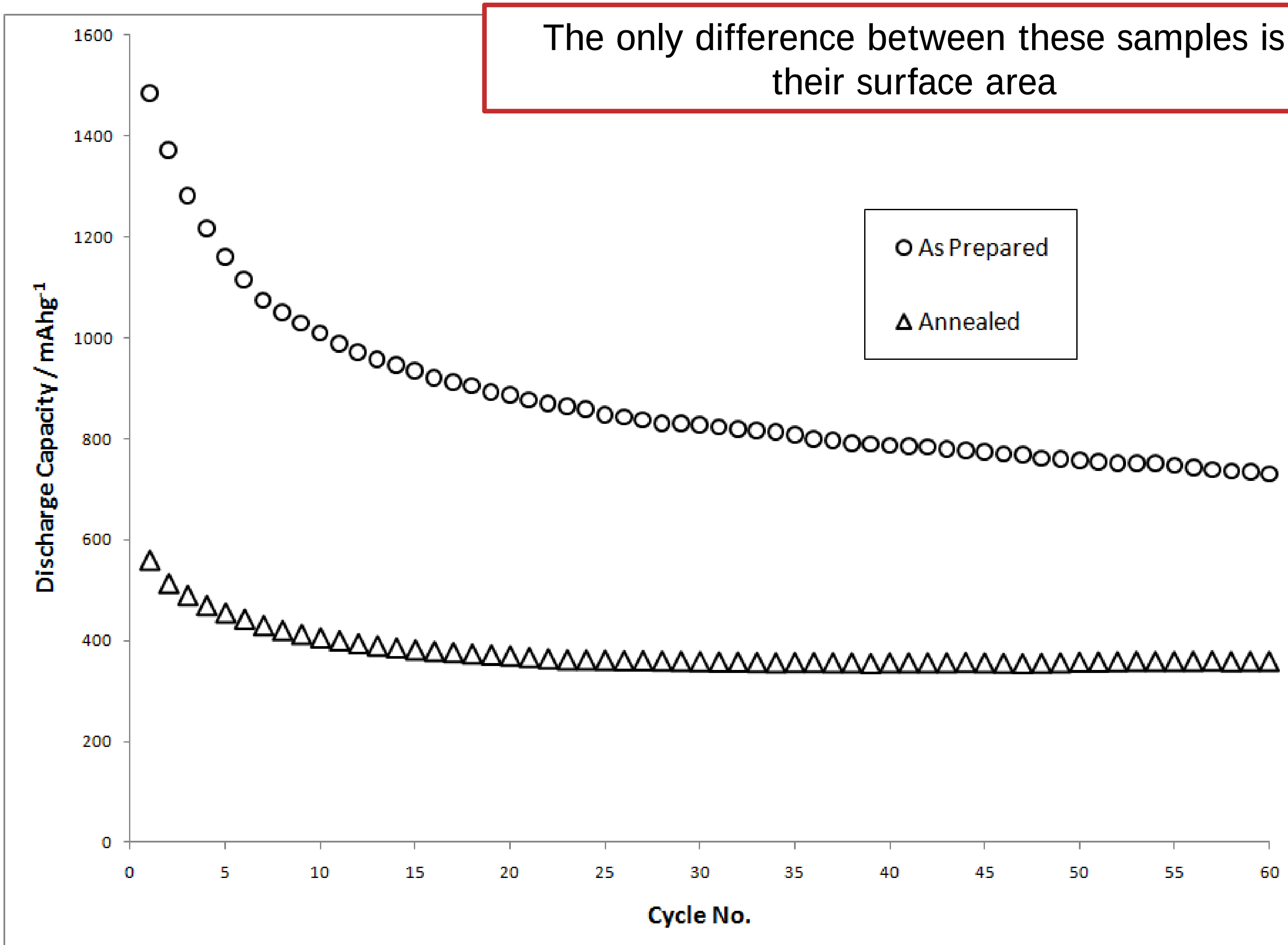
Annealed



The nanostructure seems to open up as the nanoparticles coalesce into the compact bulk form

Results for Annealing Study

The only difference between these samples is their surface area



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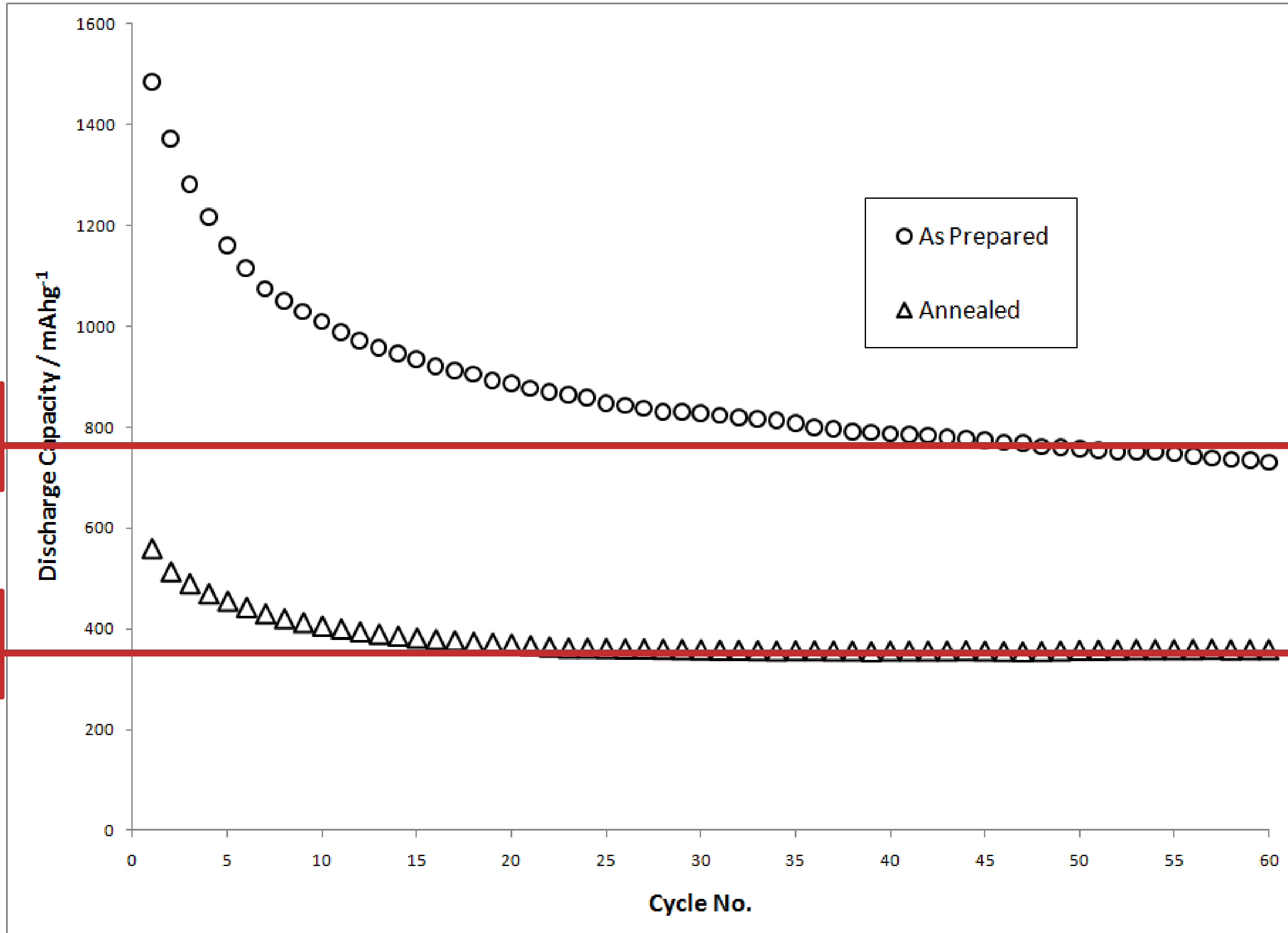


SnO_2
781 $mAhg^{-1}$

Graphite
370 $mAhg^{-1}$

Pseudocapacitance

- SnO_2 nanobasket electrodes exhibit hybrid battery-pseudocapacitor behavior.

Battery	?	Capacitor
Chemical charge storage	~	Physical charge storage
Higher capacity	←	Lower capacity
Slower rates of charge/discharge	→	Faster rates of charge/discharge
(Higher energy density)	~	(Higher power density)
Eventual breakdown	→	Virtually limitless cycle life
Very little self-discharge	←	Exponential rate of self-discharge

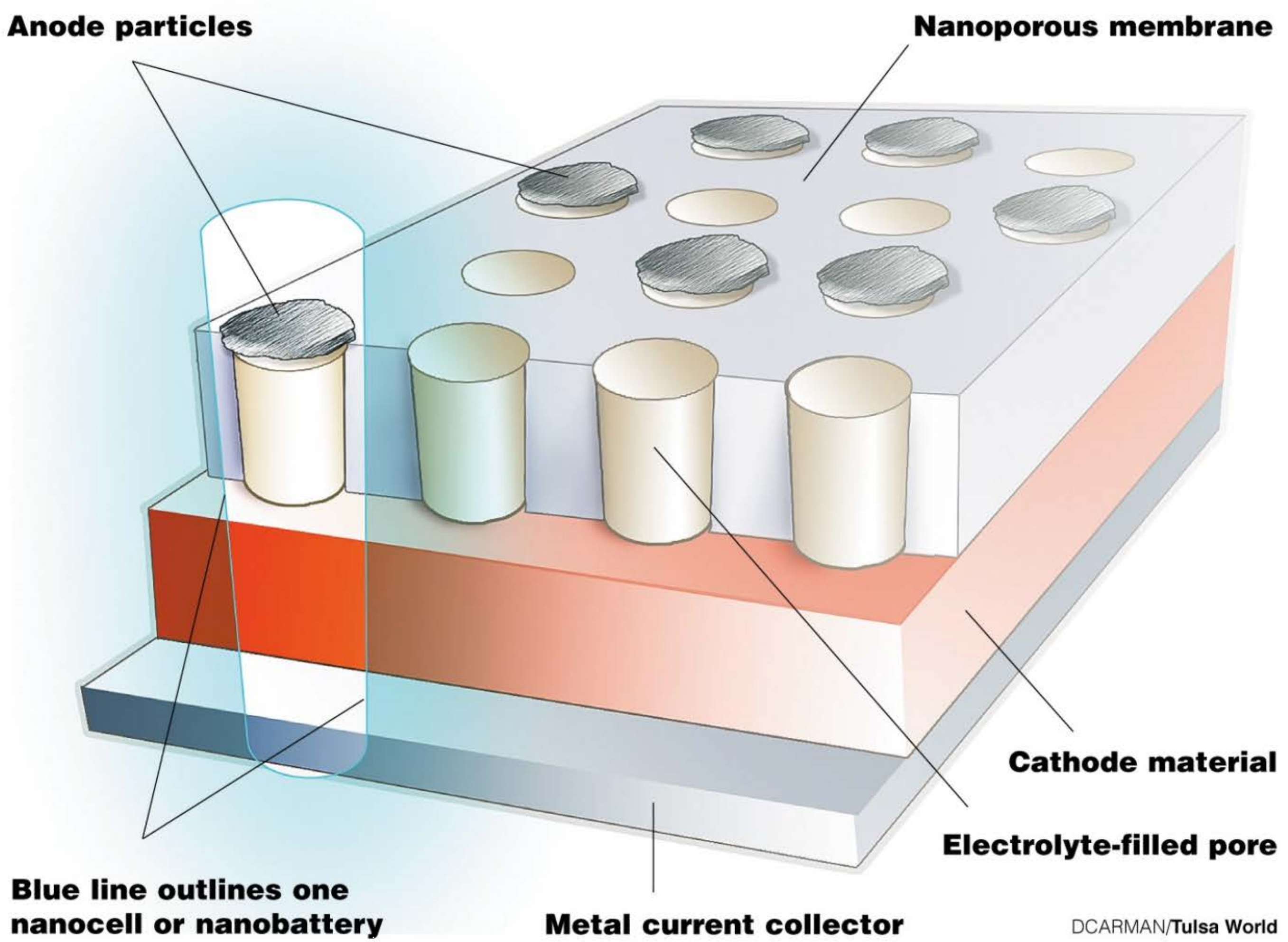
Conclusions: Nanotechnology Can Be Used to Greatly Improve Battery Performance

- SnO_2 anode greatly enhanced by nanostructuring.
  - Nanobasket open-pore structure
  - Nanoparticle substructure
- Extreme surface area allows for significant interfacial mass storage of lithium at the phase boundaries.
  - Greatly increases capacity
- Cycle life enhanced by modifying operating range.
  - Avoids significant aggregation of Sn atoms
- Possesses hybrid battery-pseudocapacitor behavior
  - Due to interfacial charging
  - Demonstrated by GITT
- Exhibits superior diffusion properties.

Present Day Nanosubmarine

- Only half a millimeter in diameter and four millimeters in length, a tiny submarine manufactured by the Duisburg,Germany-based micromechanics firm microTEC is indeed small enough to cruise through an artery. It is shown in an actual artery in the picture below.

Nanobatteries



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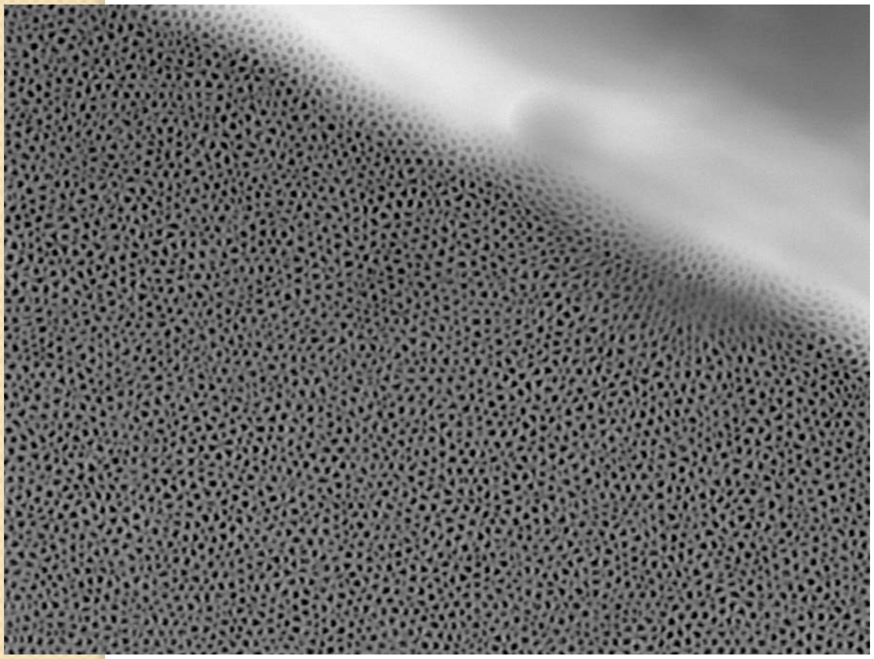
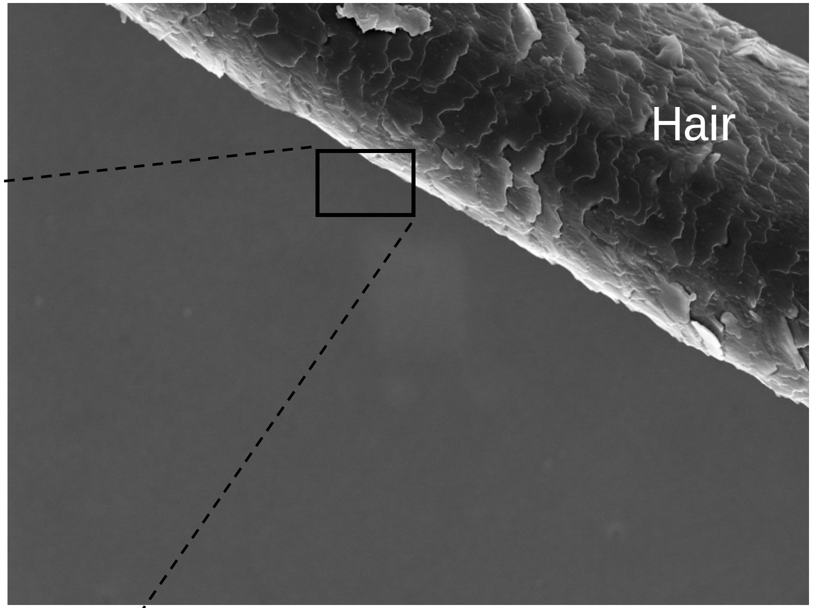
240 Nanobatteries Can Fit into the Diameter of a Human Hair





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