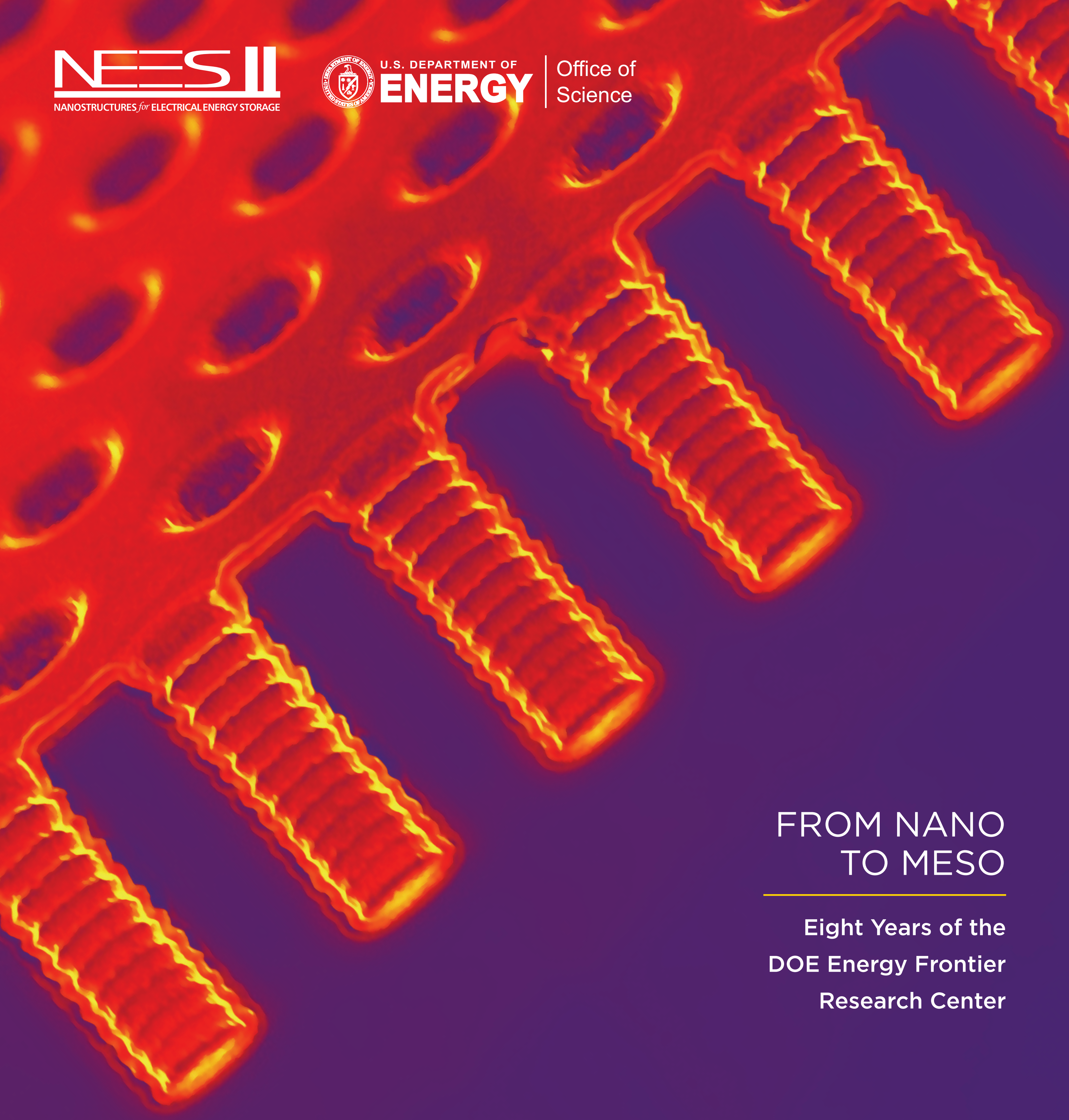
NESS II
NANOSTRUCTURES *for* ELECTRICAL ENERGY STORAGE

U.S. DEPARTMENT OF ENERGY | Office of Science



FROM NANO TO MESO

Eight Years of the DOE Energy Frontier Research Center

PRECISION ARCHITECTURES

Storing electrical energy is a central requirement to balance the energy economy, providing compatibility between where and when sources of energy are available and where and when they are needed by users. Batteries and related energy storage devices thus serve as an energy "bank," receiving and holding energy that is deposited from various sources, and delivering it to various uses when they need to make a withdrawal. Storage saves solar or wind energy when available in abundance, and delivers it back after sundown or when winds are calm. Batteries let us hold energy in electric cars or cellphones and use it when desired. Ideally, storage devices hold huge amounts of energy and yet can deliver that energy at high power. In a more subtle context, storage facilitates smooth management of energy supply and demand variations on the electric grid, and analogously during acceleration and braking in an electric car.

WHY DO WE NEED STORAGE?

Today's rechargeable lithium-ion batteries—and those projected over much of the next decade—cannot meet the energy, power, reliability and safety demands in a growing energy economy. NEES seeks to establish a scientific base to support the paradigm shift in energy storage that is needed.

FROM NANO TO MESO AND BEYOND

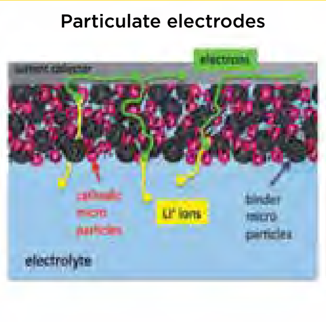
SCIENCE TO ENABLE A NEXT GENERATION OF ENERGY STORAGE

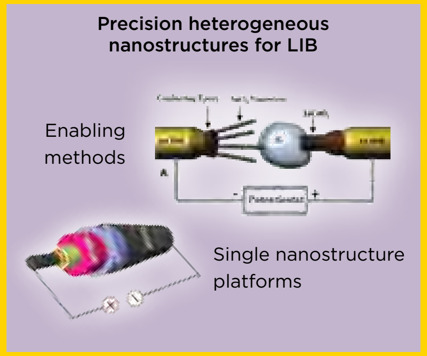
Harvesting, holding, and delivering energy all rely on energy storage science. Batteries and related storage devices depend on both ions and electrons to move through materials and interfaces, providing challenges for materials science and chemistry in unparalleled ways. NEES seeks to understand these phenomena on a firm scientific footing and to develop new concepts to fuel a next generation of energy storage. Our collaboration exploits a significant portfolio of experimental, theoretical, and intellectual resources. NEES achievements to date suggest boundless opportunities to create revolutionary designs for the batteries of the future.

TODAY'S BATTERIES:
- Uncontrolled transport paths
- Excess inactive material
- Safety concerns

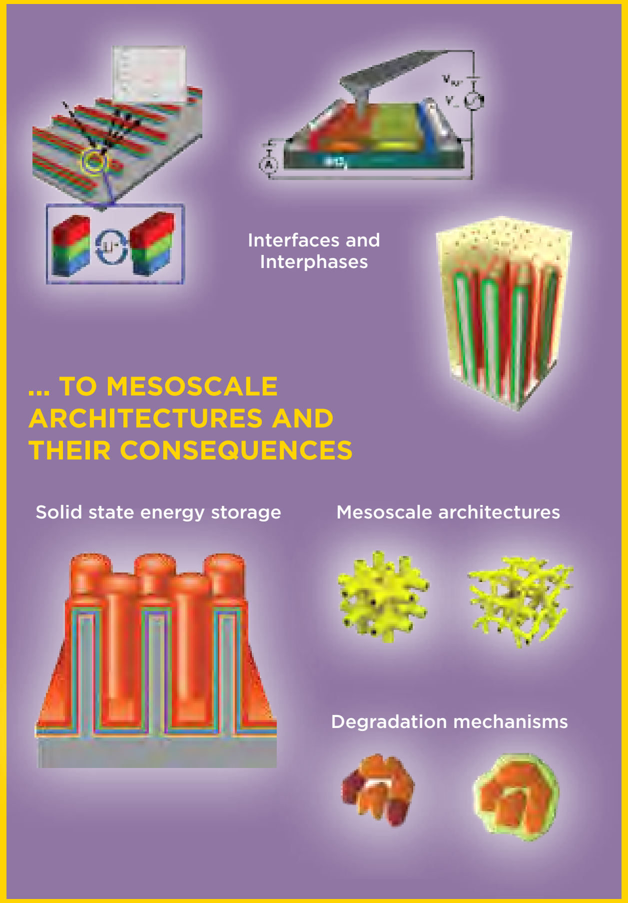
NEES-1:
- Precision nanostructured electrodes
- Heterogeneous, multifunctional
- Electrode/electrolyte interfaces

NEES-2:
- Nanostructures beyond Li-ion
- 3-D mesoscale architectures
- Local consequences (ionics, degradation)
- Rational design of interfaces & interphases





FROM NANOSTRUCTURES ...



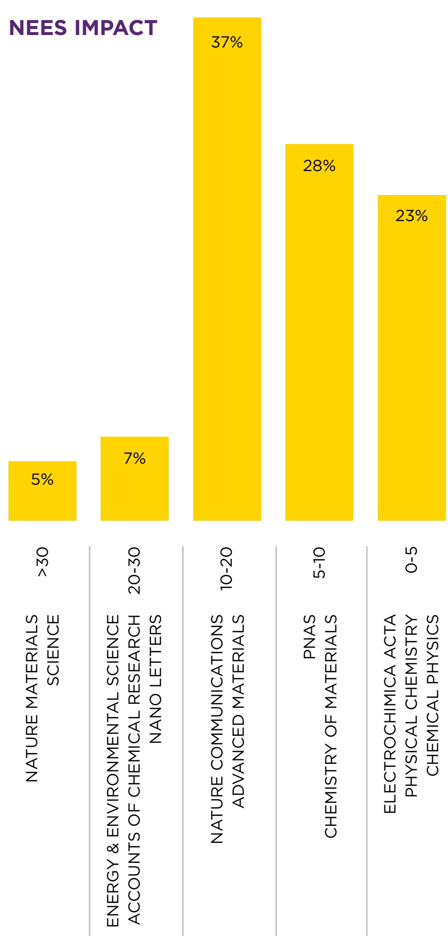
EVOLUTION OF NEES RESEARCH

The **NEES mission** is to reveal scientific insights and design principles that enable a next-generation electrical energy storage technology based on **dense mesoscale architectures of multifunctional nanostructures.** This mission has evolved substantially since NEES began in 2009.

NEES RESEARCH

- An Energy Frontier Research Center (EFRC) supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. Initiated in August 2009 (Phase 1), renewed in 2014 (Phase 2)
- +20 scientists funded in disciplines ranging from chemistry and physics to materials and chemical engineering
- Young energy scientists: graduate/PhD students, undergraduates, postdoctoral researchers
- 7 universities and 2 national lab sites, led by the University of Maryland
- +250 journal publications over 8 years

NEES IMPACT

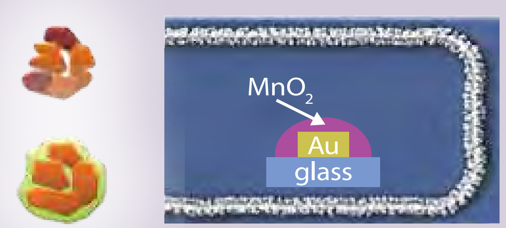


EXAMPLES OF JOURNALS IN THIS RANGE

THRUST 4
SOLID STATE ENERGY STORAGE

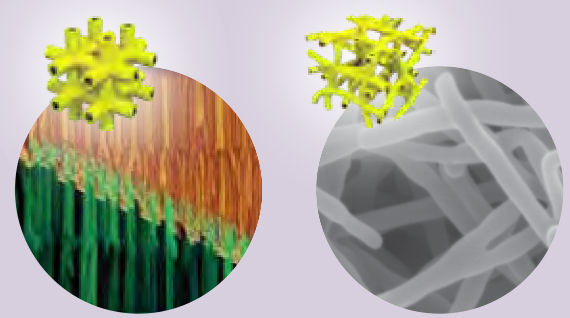
Synthesize solid electrolytes and 3D solid state battery architectures to understand their electrochemical interfaces and consequences for performance of safe energy storage

THRUST 3
NANOSTRUCTURE DEGRADATION SCIENCE



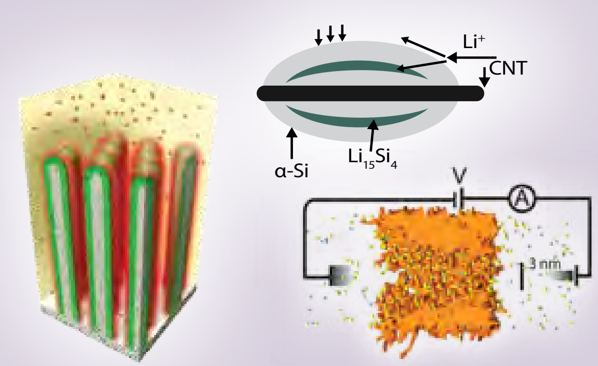
Identify fundamental mechanisms driving nanostructure degradation and failure, and develop methods of mitigation

THRUST 2
MESOSCALE ARCHITECTURES



Synthesize nanostructure assemblies into various architectures to assess the role of mesoscale architecture in realizing energy

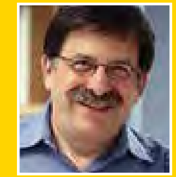
THRUST 1
TRANSPORT IN ELECTROCHEMICAL INTERPHASES



Understand chemical formation of interphase films at electrochemical interfaces and their ion and electron transport

OUR TEAM

MANAGEMENT TEAM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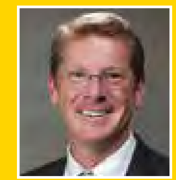
Sang Bok Lee, *UMD*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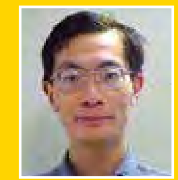
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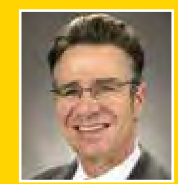
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Chunsheng Wang, *UMD*


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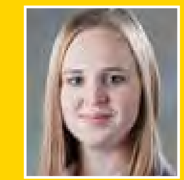
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Janice Reutt-Robey, *UMD*


Yue Qi, *Michigan State*

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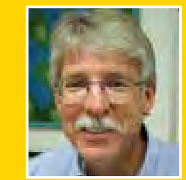
A. Alec Talin, *Sandia, CA*


Bruce Dunn, *UCLA*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AFFILIATES

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Hendrik Bluhm, *LBNL*

Ethan Crumlin, *LBNL*

Kevin Zavadil, *Sandia, NM*

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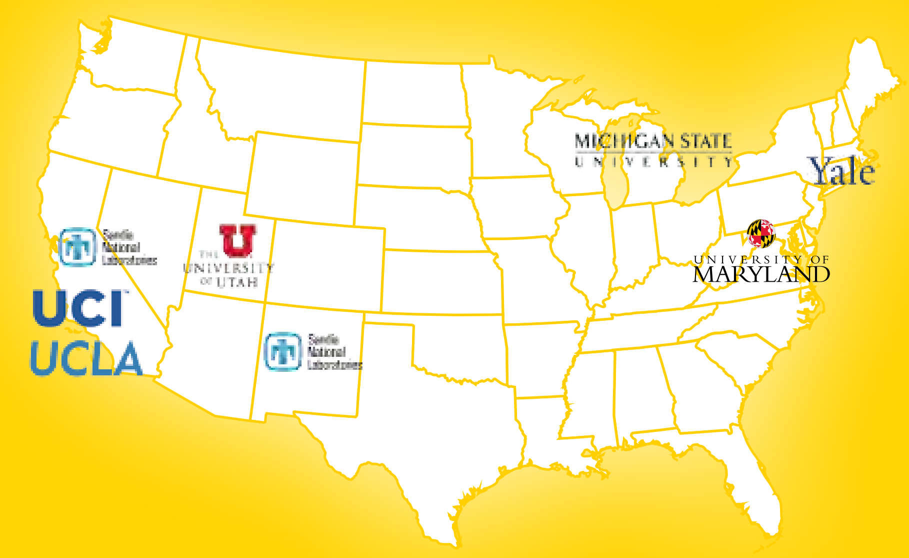
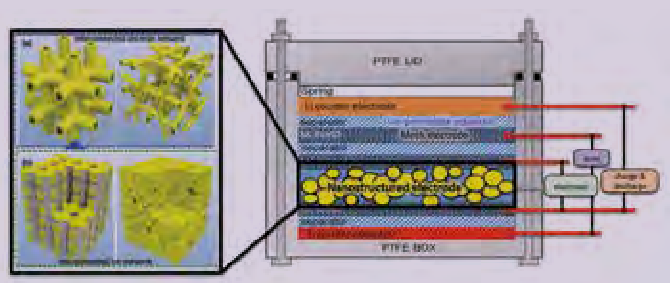


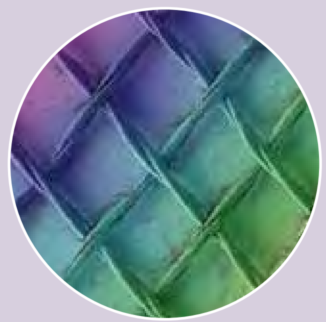
MESOSCALE ARCHITECTURES

NEES' focus on architecture is aimed at understanding the **essential mechanisms underlying electrochemical events and battery performance**—the benefits accessible through nanostructuring and 3D architectures. NEES' research goals differ from that of much of the battery research community, where focus typically lies in understanding and identifying new materials for high performance battery chemistries. One of NEES' research goals is to provide **nanostructure design guidelines** that underscore the importance of electron transport pathways for access to ion storage material, amidst architectures involving porosity and tortuous pathways through random, pseudo-random and regular 3D meso-architectures. Examples include parallel nanowires and nanopores as an ideal case, sponge-like structures assembled in random 3D arrangement, and bio-scaffolds such as cellulose films and natural woods with highly anisotropic mesoscale pore design.

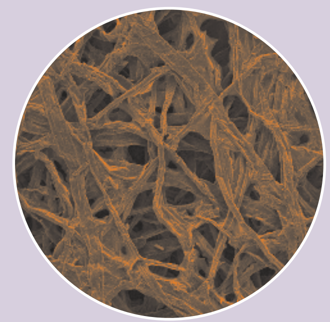
COMPARATIVE ARCHITECTURES

A new electrochemical cell design distinguishes ion versus electron conductivity across a spectrum of meso-scale electrode architectures, offering insights into meso-scale design guidelines and possibly their propensity to initiate degradation.

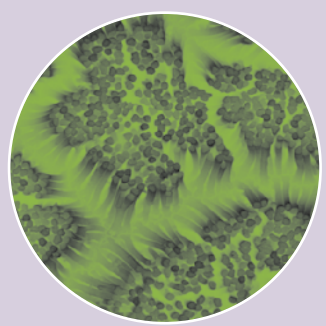




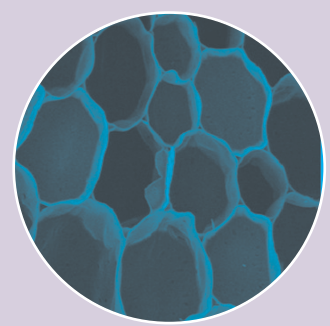
Electrically conductive silicon anode carbon nanotube composite yarn



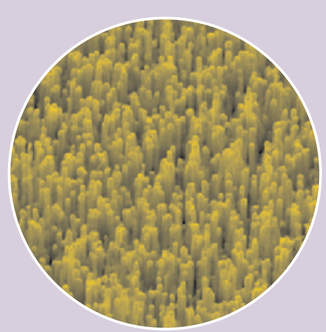
Mesoporous cellulose fibers are functionalized with carbon nanotubes and storage materials.



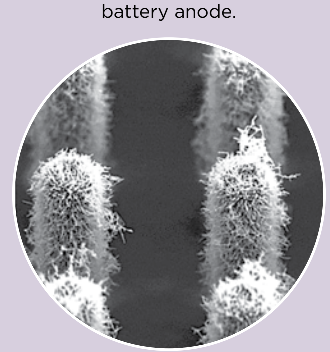
Amorphous MnO_2 cathode nanowire arrays



High-temperature treatment of grass forms carbonized architecture framework for battery anode.



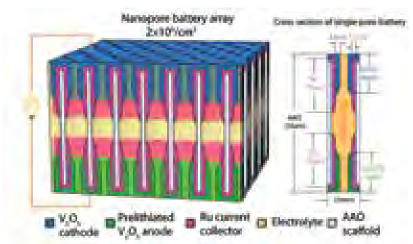
Templated growth of parallel silicon nanowire forest



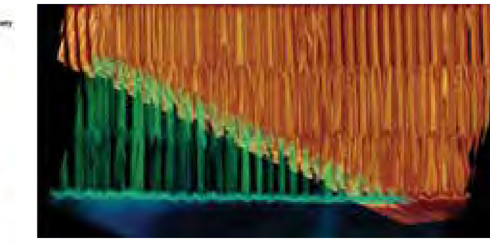
3D virus-templated hierarchical electrodes

Arranging nanostructures into architectures at the mesoscale

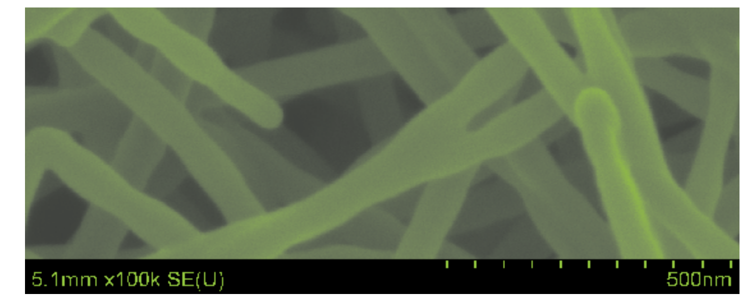
NEES has investigated the performance and stability of precision nanostructures arranged in different architectures, from highly ordered (top left) to random (bottom). Both the dense packing of nanostructures for high energy density and the variability of local geometries in random arrangements may constrain ion and/or electron transport and may introduce sites that initiate degradation and failure. These are central issues of mesoscale science, which NEES seeks to address through comparing such structures, including particularly carefully synthesized models which introduce elements of randomness (interpore connections, top right) in a controlled fashion.



Ordered nanopore battery array, C. Liu et al, *Nat Nanotech* (2014)



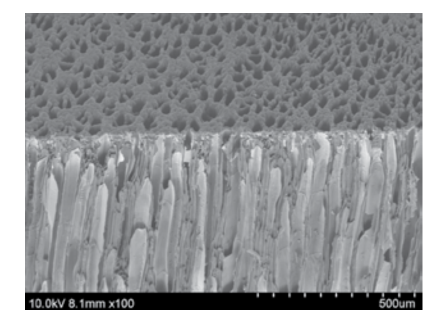
Ordered nanopores with lateral interconnects, Gillette et al, *Physical Chemistry Chemical Physics* (2015)

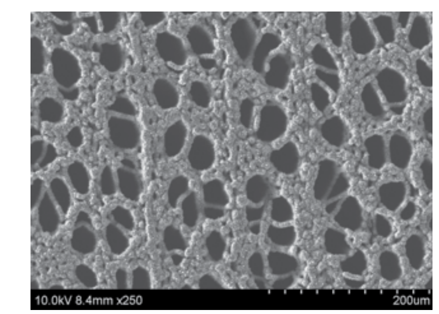


Pseudo-random arrangement of precision nanostructures into 3D "sponge" architectures. Chen et al, *ACS Nano* (2012)

Battery architectures built on natural scaffolds

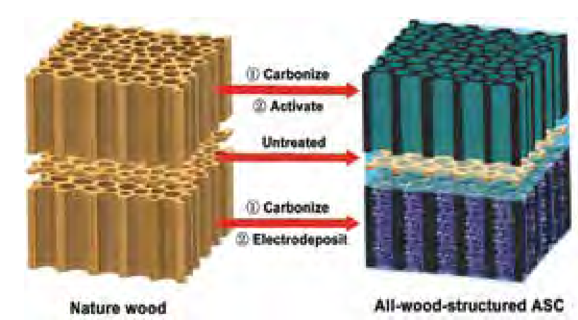
The structure of natural wood involves densely packed micro- and nano-scale pores clustered in different diameters, characteristics well suited to achieving the power-energy benefits of NEES' 3D nanostructure arrays. NEES has developed processes to transform the wood to battery elements, carbonizing and activating it to make a carbon anode, electrodepositing MnO_2 to make a cathode, and retaining the wood as is to make a separator, and finally, demonstrating full battery performance. The benefits of wood's unique 3D anisotropy are showing value across a broad spectrum, including green electronics, biological devices, transparent paper, solar cells, and functional membranes, as well as energy storage.





Above: Cross sectional and top views of wood pores with MnO_2 cathode material added

Below: Natural wood processed to form anode, cathode, and separator for a Li-ion battery. Chen et al, *Energy & Environmental Science* (2017)

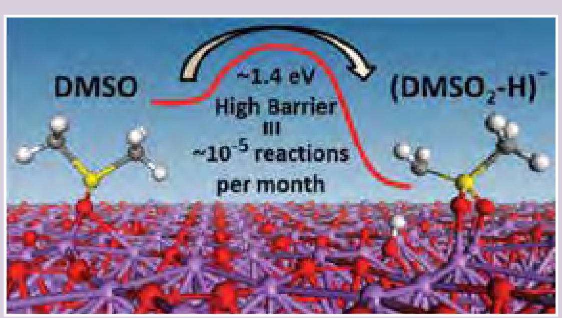


Asymmetric supercapacitor

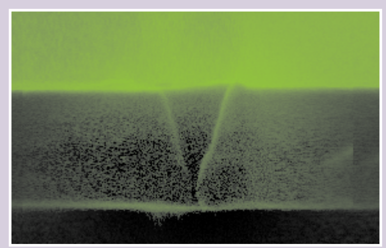
INTERFACES AND INTERPHASES

Building upon its recognized strengths in **synthesis and characterization of heterogeneous nanostructures** and their assembly into meso-architectures, NEES has turned its attention to understanding mechanisms of charge transfer at reactive interfaces, the evolution of new interphase films at these interfaces, and the resulting charge transport through them. This research is advanced by development of **new experimental platforms** and **by modeling and simulation** intimately connected and relevant to the experiments. Experimental platforms push characterization to the deep nanoscale regime, revealing scaling behavior that ultimately controls electrochemical performance of nanostructured environments. Simulations with molecular scale fidelity depict reactions and the comparative kinetics of multiple pathways. The focus on **reactive interfaces and resulting interphases** has generated new directions, exemplified by the creation of an interface-free battery and the intentional formation of artificial interphases that enhance electrode stability and battery capacity with cycling.

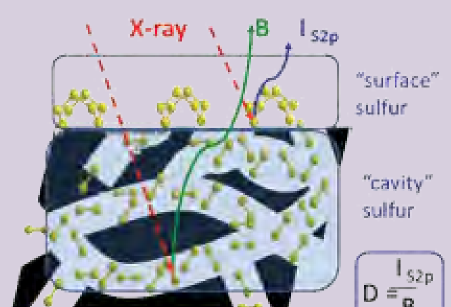
Precision coaxial nanowire as a charge transport testbed.
Corso et al, *Nano Letters* (2014)



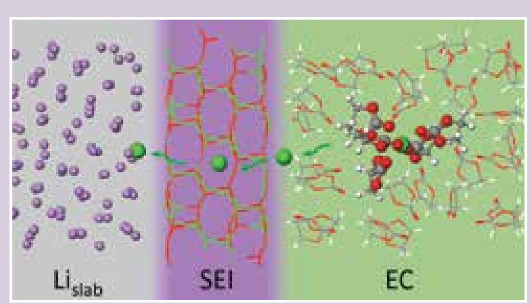
Solvent-electrode surface reaction kinetics.
Schroeder et al, *ACS Appl. Mater. Interfaces* (2015)



Rectification of ion transport through conical nanopores.
Vlassiouk et al, *PNAS* (2009)



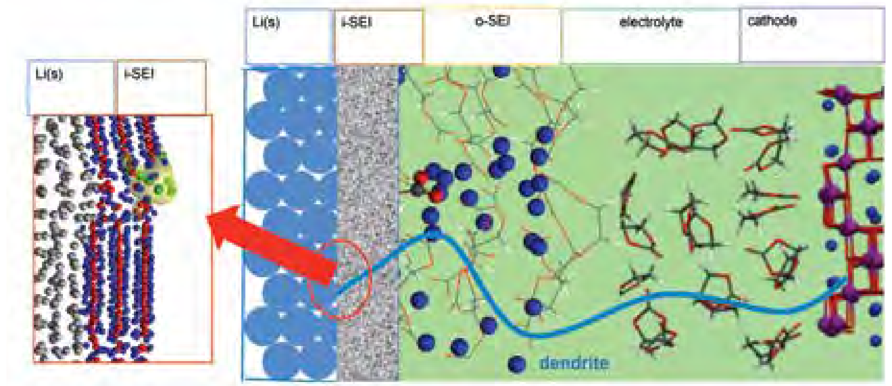
Binding sulfur to carbon nanopore surfaces.
Xu et al, *Advanced Functional Materials* (2015)



Revealing fundamentals of interphase formation.
Li et al, *Accounts of Chemical Research* (2016)

Passivation of reactive Li electrodes

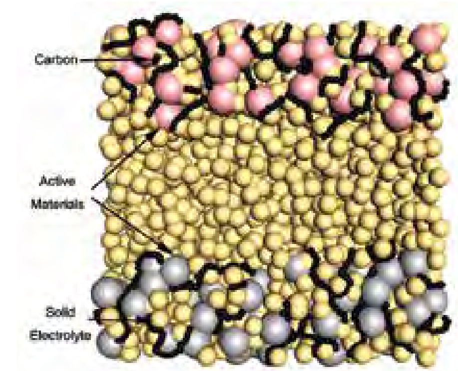
The pervasive growth of solid electrolyte interphase layers in Li-ion batteries provides a complex passivating film containing inorganic Li_2O and LiF (along with organic moeities). Nevertheless Li dendrites can form—risking battery shorting and fire—not only in conventional Li-ion batteries, but surprisingly even in all solid state batteries. Using molecular modeling NEES has identified mechanisms by which dendrite formation can be initiated in the inorganics, particularly Li_2O, where Li atoms enter grain boundaries, provide electron transport paths, and ultimately result in passivation breakdown via Li dendrites. These results inform the design of passivation strategies in all solid state batteries.



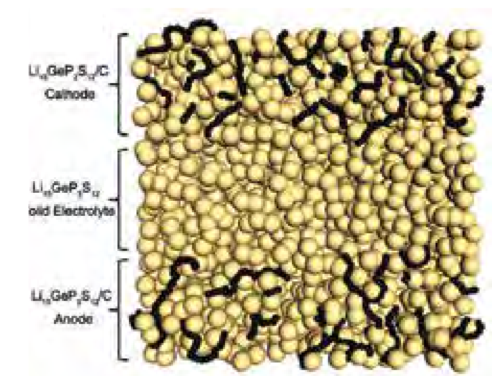
Spatial Heterogeneities and Onset of Passivation. Breakdown at Lithium Anode Interfaces.
Leung and Jungjohann, *J. Phys. Chem. C.* (2017)

Toward a perfect solid state battery

Recognizing the myriad of challenges surrounding interfaces—particularly reactive interfaces that in turn form interphase films—NEES has conceived and demonstrated a solid state battery made from particles of a single material, LGPS. Anode and cathode are formed by incorporation of carbon into those regions, enabling electron transport to support redox reactions in the LGPS itself to provide energy storage functionality. This "single material battery" based on LGPS and carbon effectively avoids interfaces between electrolyte and the electrodes.



Above: Conventional solid state battery
Below: Single-material solid state battery
Han et al, *Advanced Materials* (2015)

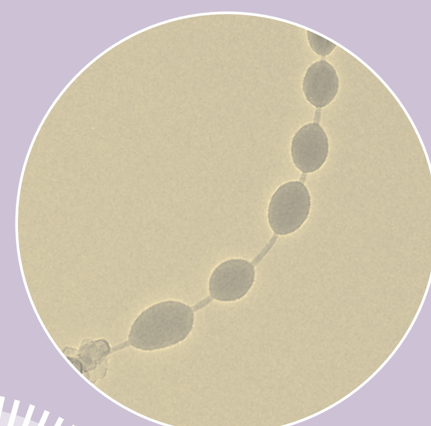


DEGRADATION AND MITIGATION

Nanostructured electrodes enable enhancements in specific power and capacity for battery electrodes due to tremendous surface area and short ion transport pathways compared to their planar electrode counterparts. However, nanostructures may be more susceptible to surface chemical processes (e.g., electrode dissolution, traditional solid-electrolyte interphase formation) and to consequences of cycling-induced structural changes (e.g., nanoelectrode disconnection). In an effort to establish a science of electrochemical nanostructure degradation, NEES has assessed its substantial research results to **identify and categorize degradation mechanisms**—chemical, electrochemical, and mechanical. It has also developed and demonstrated critical mitigation strategies that employ control of interface reactions and creation of interphases in the nanostructured electrodes. Particular effort and success has resulted from close coupling of theory and experiment to understand mechanisms, and to reflect this in design guidelines and predictive degradation models.

Molecular dynamics model enables simultaneous tracking of chemical, structural and mechanical evolution of Si core-shell nanostructured electrode during lithiation. Kim et al, *Physical Chemistry Chemical Physics* (2016)

Inert outer coatings prevent structural instability while enhancing electron transport. Kharki et al, *ACS Nano* (2013)



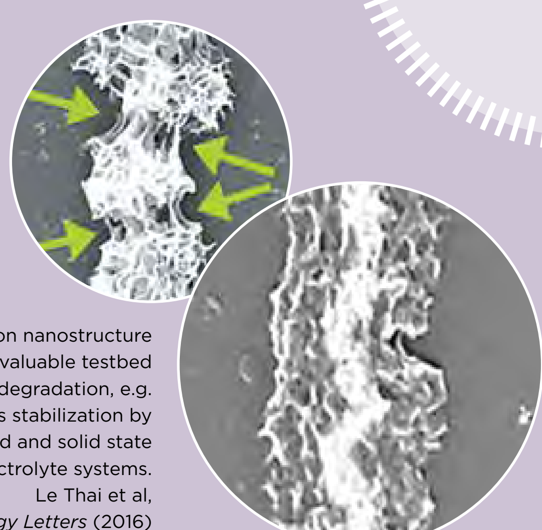
Chemical surface modification enables heteronanostructure designs to accommodate volume expansion & strengthen interface adhesion. Sun et al, *ACS Nano* (2013)

NANOSTRUCTURE DESIGN

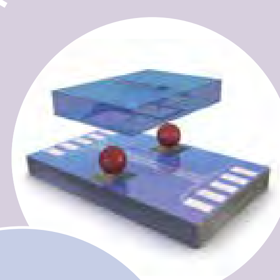
CHEMICAL

MECHANICAL

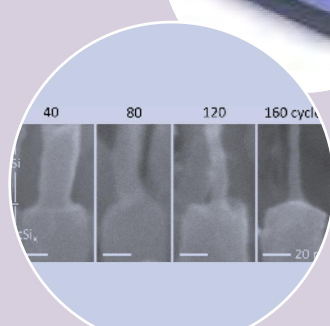
ELECTROCHEMICAL



Precision nanostructure design offers valuable testbed to understand degradation, e.g. nanostructures stabilization by gel for liquid and solid state electrolyte systems. Le Thai et al, *ACS Energy Letters* (2016)



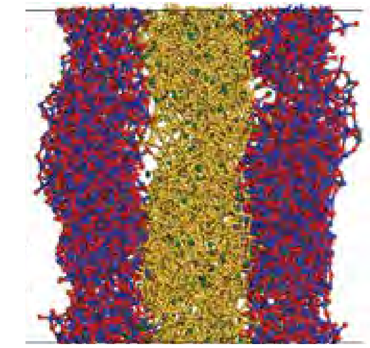
Experimental TEM liquid cell platform provides insights to microstructure formations & propagations in operando. Leenheer et al, *ACS Nano* (2015)



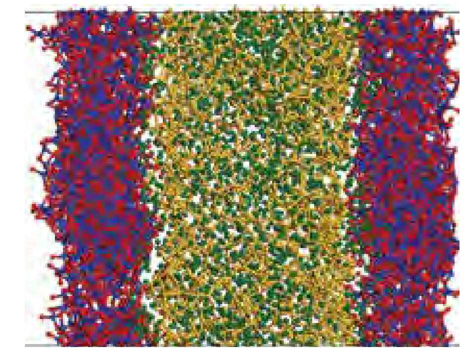
Template-grown parallel silicon nanowires demonstrate spatial nonuniformities leading to predictable locations for accelerated degradation and failure. Cho and Picraux et al, *Nano Letters* (2013)

Delithiation rates alter materials, structures, and their properties.

While silicon is highly desired as a high energy anode, it poses severe degradation problems due to its large 300% volume expansion upon full lithiation. Thin protective layers are a promising approach to mitigate the resulting fracture mechanics problems. Using continuous reactive molecular dynamics simulation of silicon nanowirescoated by either Al_2O_3 or SiO_2, NEES has shown that fast delithiation leaves appreciable lithium inside the nanowire and imposes a radial gradient in mechanical properties, while slow delithiation allows the nanowire to shrink and expel most of the lithium, but leaves defect structures that accelerate subsequent lithiation. These results provide guidelines for design and operation of silicon nanowire-based battery anodes.



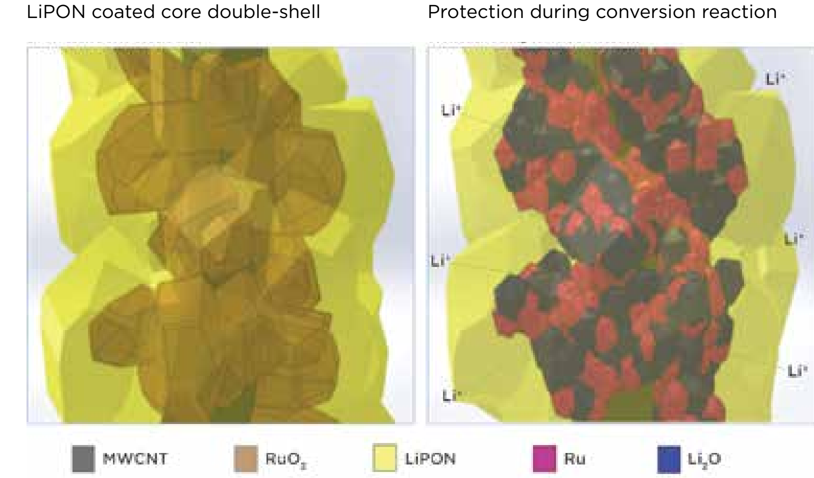
Slow Delithiation



Delithiation rates modify composition, structure, and properties of S_i nanowire anodes with protective coatings. Kim et al, *Nano Letters* (2017)

Managing high chemical reactivity in conversion material electrodes.

Lithiation of high-energy electrode materials commonly causes dramatic chemical reactions with new reaction products that render reversibility (i.e., rechargeability) difficult. Using a model MWCNT@RuO_2 nanostructure, NEES has shown experimentally that a thin protective layer of LiPON dramatically enhances the reaction reversibility during charge/discharge cycles, allowing much more of the energy storage capacity of the nanoelectrodes to be retained. The use of a thin, conformal LiPON protective layer is credited with some of this benefit because the thin LiPON functions as a solid electrolyte in enabling Li-ion transport between electrolyte and electrode.

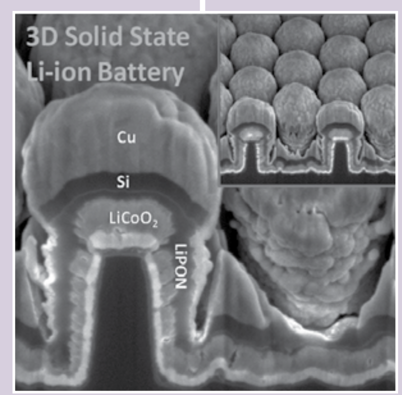


Conformal coatings of LiPON solid electrolyte on model MWCNT@RuO_2 nanoelectrodes. Lin et al, *ACS Nano* (2016)

SOLID STATE ENERGY STORAGE

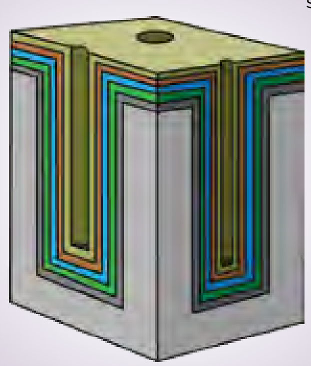
A primary motivation for solid state batteries is to alleviate the safety risks associated with the flammable organic liquid electrolytes commonly used in rechargeable lithium-ion batteries, which have led to widely-publicized fires and explosions. The use of all-solid-state materials also opens the door to significantly greater architectural design flexibility, enabling micro- and nano-electrode structuring in 3D and open-ended battery form factors. NEES research is focused on **electrode and battery architectures** as an overarching theme, seeking to understand key aspects of solid electrode/electrolyte interfaces, including similarities and contrasts with liquid electrolyte/electrode interfaces, and to develop **synthesis approaches for solid state batteries** on nano- and micro- scales. A particular emphasis is the synthesis of solid state electrolytes that can be **deposited conformally over micro- and nano-scale 3D topography** to enable design flexibility and access the benefits of 3D architectures. Exploiting highly conformal atomic layer deposition, NEES has demonstrated solid electrolyte synthesis and its pivotal role in realizing the first fully 3D nanoscale solid state battery array. NEES has also identified distinctly different applications for solid state batteries, exemplified by analog memory devices for neuromorphic computing.

NEES' expertise in precision hetero- nanostructures extends to novel miniature solid state configurations. Ruzmetov et al, *Nano Letters* (2012)

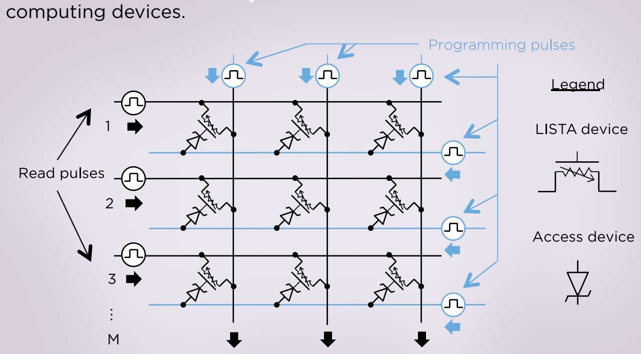


Examining planar and 3D geometries lead to the development of conformal thin-film deposition techniques. Talin et al, *ACS Appl. Mater. Interfaces* (2016)

Highly conforming, nanoscale, ion-conducting thin film is a key enabling factor for high density integrated 3D solid state batteries and for neuromorphic computing devices.



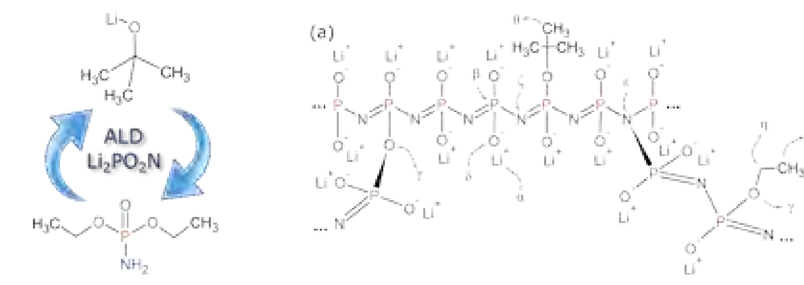
Pearse et al, *Advanced Materials* (submitted)

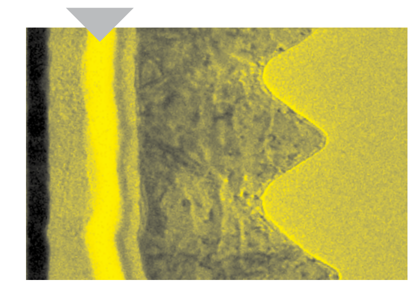


Fuller et al, *Advanced Materials* (2017)

Conformal thin solid electrolyte

Key opportunities in solid state batteries lie in improved safety (no flammable organic electrolyte), self-aligned 3D structures for high power-energy, and—potentially—conformal solid electrolytes thin enough not to limit ion transport in the cell. NEES has developed ALD Li_2PO_2N, a LiPON-like solid electrolyte usable in the 40-100nm thickness range in solid state batteries with challenging 3D topography—significant advances compared to ~1 micron LiPON thickness employed in only planar, not 3D, configurations.



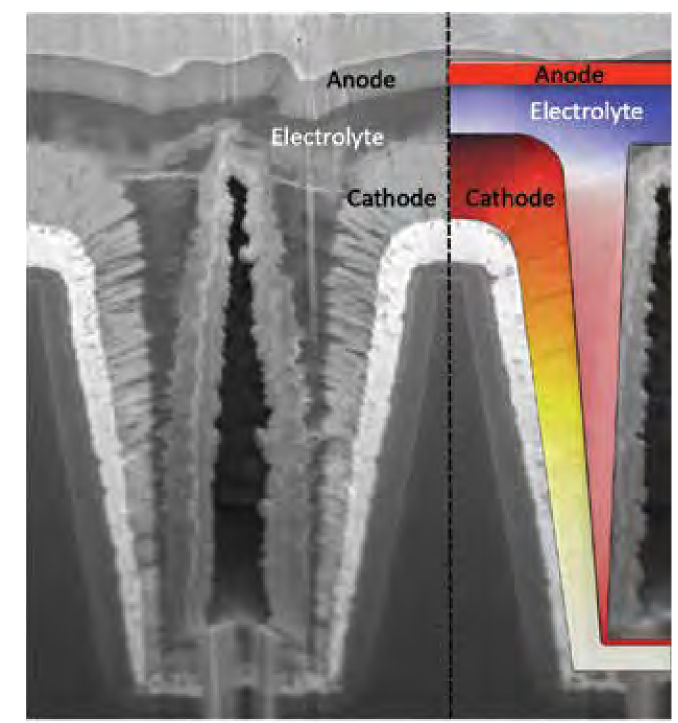


Above: Thermal ALD process for LiPON-like Li polyphosphazene

Right: Thin Li_2PO_2N solid electrolyte in planar solid state battery. Pearse et al, *Chem Mater* (2017)

3D solid state batteries

By distributing a given amount of active electrode material in thinner layers over larger surface area, energy density can be delivered at higher power, thereby achieving significant benefits from using 3D architectures in solid state batteries. NEES has demonstrated pioneering 3D solid state batteries. Sputter-deposited active layers exhibit rough topography and anisotropic materials. Multiphysics simulations show distinctive inhomogeneities during charge and discharge. Conformal ALD layers circumvent these limitations, improving performance and realizing the power-energy benefits of the 3D architecture.



Sputter-deposited solid state battery layers over Si "pillar" scaffold. Talin et al, *ACS Appl. Mater. Interf.* (2016)

NEESCONNECT

WHAT IS NEESCONNECT?

NEESConnect is a community network of early career scientists who share common research interests and expertise in both basic and applied energy research areas.

WHAT IS OUR GOAL?

Our overarching goal is to provide a sustainable program for workforce training and development in all aspects of today's complicated energy landscape—research, teaching, science communications, outreach, energy policy and resources.

CAREER PATHFINDER

(l-r, top row) Erin Cleveland, Xinyi Chen, Stefanie Sherrill Wittenberg; (bottom row) Kostas Gerasopolous, Ashley Predith, Wenbo Yan

NEES hosts informal Q &A discussion forums by inviting alumni student members to talk about their working experiences in the academic, industry and government sectors.

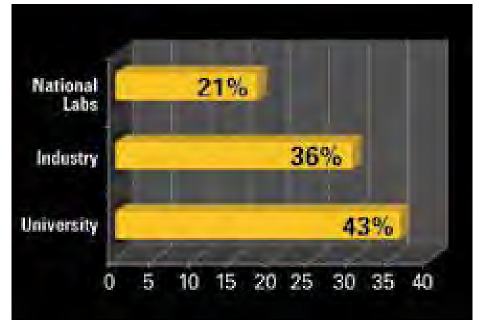
STUDENT OPPORTUNITIES

NEES encourages students to take on roles and initiatives that go beyond their own research environment. They take on active roles

(l-r, top row) Gaurav Jha (UCI), Luning Wang (UMD); (bottom row) David Ashby (UCLA), Emily Sahadeo (UMD)

such as the Student Thrust Leaders to foster leadership skills and the EFRC newsletter writers to sharpen communication skills. EFRC newsletter writer and editorial board member Tim Plett was a student at the University of California, Irvine.

WHERE ARE THEY NOW?



NEES degree-graduates and postdocs make contributions to many sectors of employment.

THE TRAVELLING SCIENTIST

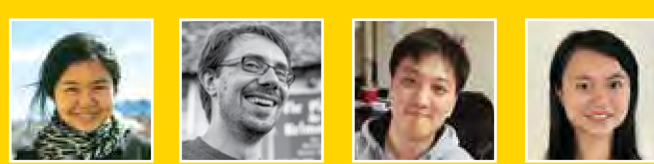
Travel offers early career scientists rewarding opportunities with lasting impacts.

Zoey Warecki, a graduate student at the University of Maryland studying materials science and engineering, spent one month visiting NEES partners at the Center for Integrated Nanotechnologies, part of Sandia National Laboratories. She got hands-on experience with developing and adopting the liquid cell capability for transmission electron microscopy to do battery research.

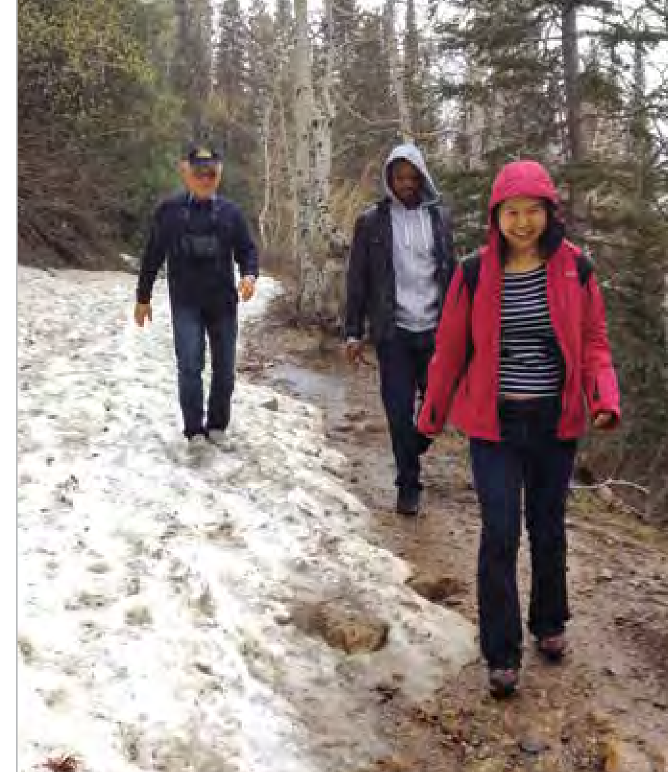
INTEGRATING INNOVATIVE IDEAS

The NEES student team devises new ideas to look at ion transport under confinement in battery research.

The team's expertise converges in thin-film synthesis, semiconductor device fabrication and multiphysics modeling to investigate transport properties in highly confined architectures.



Members: (l-r) Sylvia Xin Li, graduate student, Physics, Yale; Kim McKelvey, postdoctoral researcher, Chemistry, U. of Utah; Nam Kim, graduate student, Chemistry, UMD; Chanyuan Liu, graduate student, Materials Science Eng., UMD.



TRAVEL GRANTS

NEES invests in multi-institutional, cross-disciplinary research collaborations. We create a cooperative learning environment to encourage active exchange of science ideas and best practices, as exemplified by the 2016 NEES Collaboration Travel Grant initiative for early-career scientists.

(l-r) Martin Edwards (U of Utah), Juliette Experton (UFL), Yuxiao Lin (MSU), Zoey Warecki (UMD), Sylvia Xin Li (Yale)

OUTLOOK

NEES has chosen an unusual research pathway to understand the science of electrochemical energy storage, focused on structure (rather than materials) and embodied in the design of multicomponent, multifunctional nanostructures, their dense aggregation into mesoscale architectures, and the consequences that follow. By creating precision nanostructures— through novel synthesis approaches, closely coupled with diverse modeling and characterization methods—NEES has elucidated fundamental science ranging from the balance of ion and electron transport in electrode nanostructures, to the impact of their assembly in larger-scale architectures, to degradation and mitigation phenomena that connect mechanical, chemical, and electrochemical behavior to nanostructure architectural design, and finally to design guidelines that will benefit a next generation energy storage technology.

NEES foresees a bright future for these approaches: dissecting ion and electron transport as manifested in architectures that underscore the importance of mesoscale science and link nanoscience to battery-relevant length scales and behavior; interrogating and representing these behaviors in models with predictive capability; combining modeling and nanoscale synthesis to achieve new levels of storage performance and durability; developing a mechanistic science of degradation which points the way to mitigation strategies; realizing a profoundly safer battery technology; and applying these lessons to application domains beyond energy storage.

TO LEARN MORE VISIT www.efrc.umd.edu

WINNER OF 2017
PEOPLE'S CHOICE AWARD
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Big Things, Small Packages

By Chuck Martin (and the Nano Knights),
NEES Principal Investigator, University of Florida

Big things come in small packages
That's the NEES nano way
We can pulse more power
Than anyone can say

Big things come in small packages
We prove it true at NEES
The architects of nanotech
For your batteries
The architects of nanotech
For your energy needs

Ions, electrons, electrode materials too
How you going to wire them to let the power come through?
3D nanostructuring that's the thing we do
To let the power come through
To let the power come through
Let the power come through!
You best believe here at NEES we let the power come through

Because big things come in small packages
That's the NEES nano way
Delivering the breakthroughs
That lead to a brighter day

Big things come in small packages
We prove it true at NEES
The architects of nanotech
For your batteries
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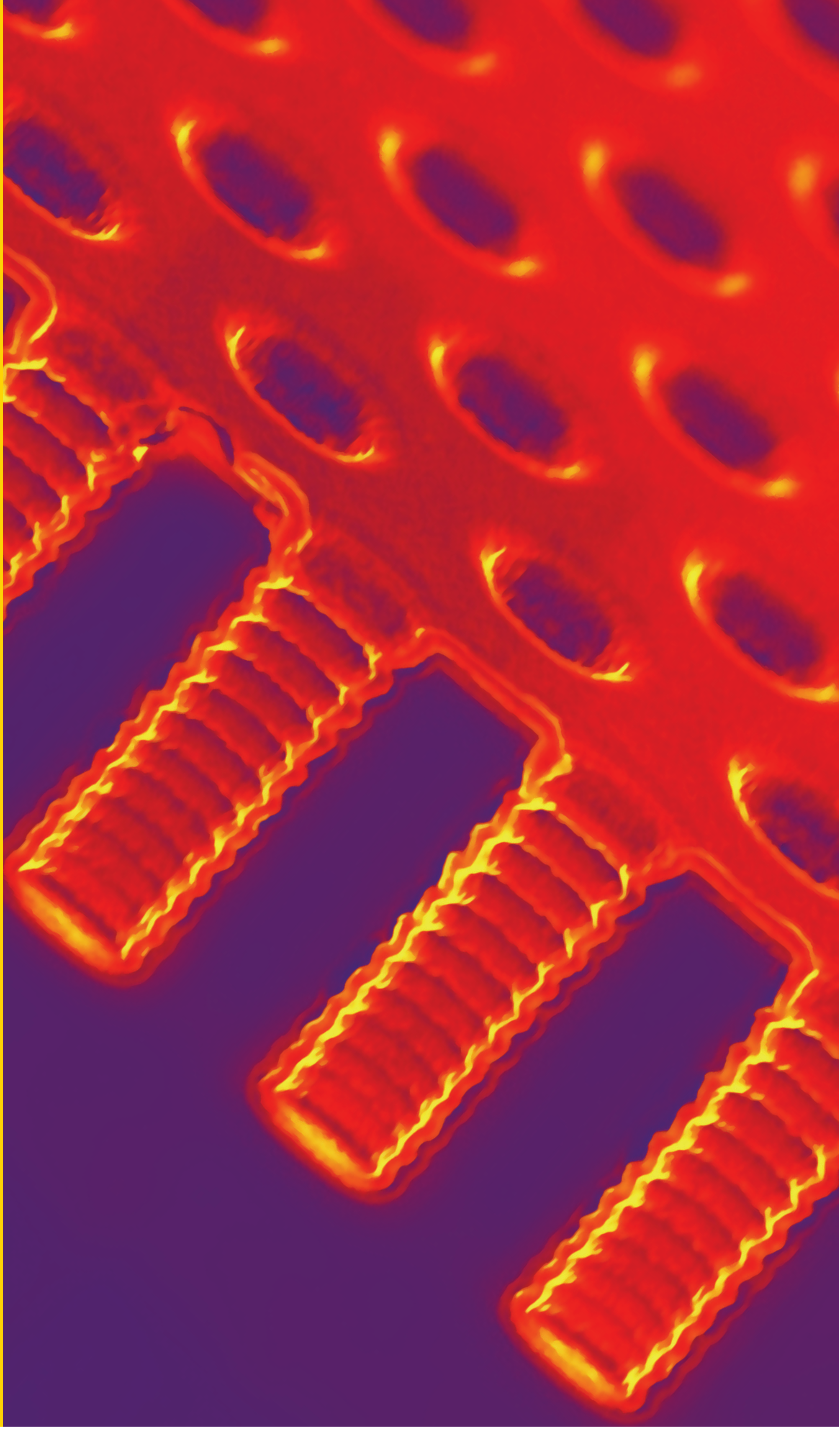
The architects of nanotech
Here at NEES!



NEES II
NANOSTRUCTURES *for* ELECTRICAL ENERGY STORAGE

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UNIVERSITY OF MARYLAND
THE UNIVERSITY OF UTAH
Yale University