

FOUR YEARS OF  
**Nanostructures for  
Electrical Energy  
Storage**

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A DOE ENERGY FRONTIER  
RESEARCH CENTER

# PRECISION + STRUCTURE



Office of  
Science

**NEES**  
NANOSTRUCTURES for ELECTRICAL ENERGY STORAGE

## PRECISION + STRUCTURE

**ON THE COVER:**  
**A BEADED-STRING ANODE**  
INTERFACES ARE CRITICAL TO MULTIFUNCTIONAL, HETEROGENEOUS NANOSTRUCTURES. NEES RESEARCHERS DISCOVERED THAT THEY COULD CREATE A ROBUST HETEROSTRUCTURE WITH A CARBON NANOTUBE CURRENT COLLECTOR AND LOCALIZED “BEADS” OF SILICON TO HOLD AND RELEASE LITHIUM IONS DURING CHARGING AND DISCHARGING. BY CONTROLLING CARBOXYLIC ACID GROUPS ON THE CARBON, THEY COULD DEPOSIT SILICON AS BEADS AT THESE REGIONS, MAINTAINING ELECTRICAL CONTACT FROM THE CNT TO THE SILICON BEADS WHILE THE BEADS EXPAND AND CONTRACT DURING LITHIUM ION CYCLING. THIS SOLVES A FUNDAMENTAL PROBLEM ASSOCIATED WITH HIGH ENERGY DENSITY SILICON ANODES.

Making battery electrodes out of nanostructures is widely seen as the avenue to next-generation electrical energy storage, because the design of nanostructures offers higher power at high energy and improved stability during charge cycling of ions in and out of the storage electrode materials. Storage devices require ions and electrons to be transported from anode to cathode during discharge, with the ions migrating inside the battery through an electrolyte while the electrons provide electricity outside the battery.

Nanostructured electrodes must be multifunctional, providing storage electrode accessibility to electrolyte ions, thin storage layers for fast ion transport, good connection to conductors for the electrons, and stability and safety of the structures while ions cause expansion, contraction, and distortion of storage layers. Achieving this multifunctionality requires an intense focus on the **structure** of nanoelectrodes, which are necessarily heterogeneous—made of multiple materials. Structure is the primary focus of the NEES EFRC.

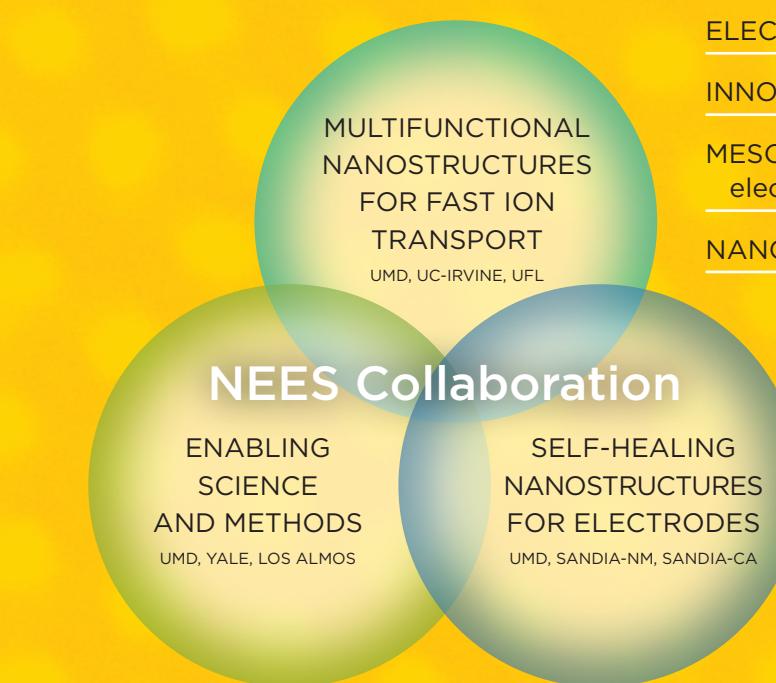
NEES seeks to understand and master electrochemical storage at the nanoscale through highly controlled model systems—experimental and computational—as the approach through which fundamental science can be learned. This places a premium on **precision** techniques for making these nanostructures, on diagnosing their properties and behavior, and on testing the inferences made through computational sciences.

# Introduction

**NANOSTRUCTURES FOR ELECTRICAL ENERGY STORAGE** (NEES) is an Energy Frontier Research Center (EFRC) supported by the U.S. Department of Energy's Office of Science. NEES takes on fundamental challenges in energy storage through experimentation and discovery at the nanoscale.

The Center synthesizes and studies heterogeneous nanotubes, nanowires, nanoparticles, and thin films in regular, precise geometries and configurations. **Founded in 2009**, the Center strives to understand how properties such as geometry, orientation, and interfaces of structures and their aggregates determine the performance of lithium-ion batteries and capacitors in order to achieve next generation energy storage technologies. Heterogeneous nanostructures combine different materials to satisfy simultaneous **electrical, mechanical, and electrochemical challenges**. By focusing directly on structure of multifunctional nanoelectrodes and using a limited number of prototypical materials, **NEES develops underlying science needed to design new nanostructure-based architectures for energy storage**.

The **21 senior investigators** and **35 students and research associates** of NEES have easy access to broad expertise and profound resources. NEES catalyzes innovative research by bringing together young and experienced researchers from **four universities** and **two DOE national laboratories** to create an environment of scientific stimulation and collaboration that is essential for major breakthroughs. In the past four years, NEES made significant advances, most notably in:



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# New strategies FOR NANOSTRUCTURE SYNTHESIS



**WITH EXPERTISE** in both established and cutting-edge techniques of nanoscience, NEES creates major advances in energy storage research by carefully synthesizing different materials to produce controlled, heterogeneous nanostructures. To grow materials into well-controlled geometries and bring together heterogeneous components at interfaces. NEES employs “bottom-up” techniques including self-assembly, conformal deposition for self-aligned structures, and self-limiting processes, all of which exploit natural phenomena at the nanoscale. Multiple steps carried out in appropriate sequence are essential to realize precision energy storage nanostructures, particularly when arranged in dense “forest” architectures.

NEES uses a variety of synthesis techniques. Vapor-liquid-solid catalytic growth provides ultra-pure silicon, germanium, and related anodic nano-wires and carbon nanotubes. Lithographically patterned nanowire electrodeposition, developed by NEES, employs clever modification of optical lithographic

patterning to create millimeters-long metallic nanowires, followed by electrodeposition of cathodic oxides (for instance, manganese oxide) to form nanowires with height and width superbly controlled within one or two nanometers. Tobacco mosaic virus—shaped like a nanotube with precise dimensions of 14 nanometers' outer diameter, 4 nanometers' inner diameter, and 300 nanometers long—are used as super-precise scaffolds for battery nanostructures.

Self-assembly is also exploited to create nanopore templates through controlled anodization of aluminum to form aluminum oxide with ordered nanopore arrays ranging within 50-200 nanometers wide and 10-50 micrometers deep, achieving a depth/width from 200-1000 nanometers. Using atomic layer deposition or electrochemical deposition with the nanopore templates, high-density vertical arrays of nearly identical nanowires or nanotubes can be formed from metal, polymer, oxides, or combinations of them, while the deposition conditions determine the shape of the nanostructures.

## ELECTRODE/ELECTROLYTE

# Interfaces

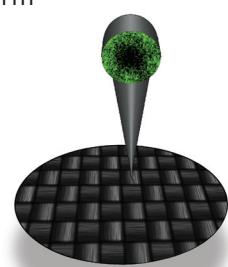
## ELECTROCHEMICAL INTERACTIONS

at the electrode/electrolyte interface are important generally, but especially so for nanostructured approaches because of the large electrode surface areas involved and the high surface-to-volume ratios that result.

Using powerful computational methods and novel experiments, NEES examines electrode-electrolyte interfaces to understand chemical and structural changes that affect how these systems transport and store charge.

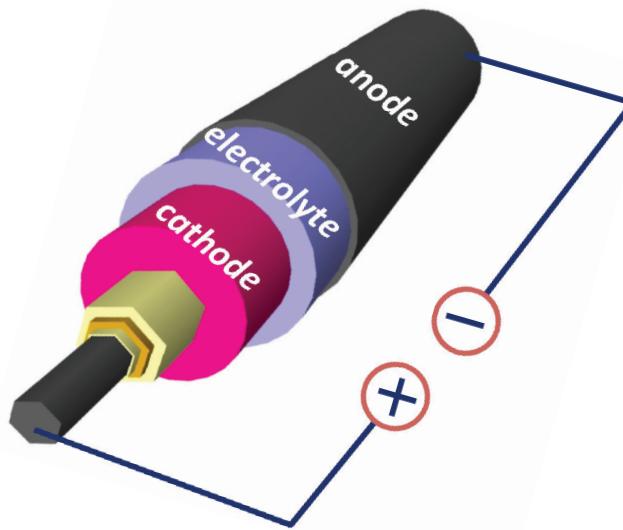
In lithium-ion batteries, the chemical transformation at the interface between an organic electrolyte and an electrode (especially an anode) can lead to the formation of a complex interfacial layer, called the solid electrolyte interphase (SEI). The SEI layer plays a critical role in battery electrochemistry, protecting the anode surface from aggressive chemical attack and suppressing electronic transport that would spur further SEI growth. However, the formation of the SEI consumes lithium from the electrolyte and decreases the battery efficiency. Using DFT calculations, NEES has analyzed the interaction between a common electrolyte (ethylene carbonate) and a common anode (carbon), identifying the electron transfer reaction that leads to decomposition of the ethylene carbonate and ultimately to SEI formation. For a prototype cathode material (manganese spinel), the ethylene carbonate molecule begins to destabilize as it approaches the surface even before any electron transfers across

the interface. NEES has extended this work, along with experimental counterparts, to investigate how ultrathin  $\text{Al}_2\text{O}_3$  layers deposited by ALD can act as “artificial SEI” layers to nearly extinguish electron transport to the electrolyte, thereby preventing ethylene carbonate breakdown and lithium consumption. The notion of synthesizing artificial interlayers engineered to fulfill specific functions represents a powerful approach to future battery design.



Lithium-sulfur batteries, attractive for their high energy density, pose different challenges in interface science. During discharge, lithium ions from the anode react with the sulfur cathode to form polysulfides. Of these, higher order polysulfides dissolve from the electrode surface into the electrolyte rather than store charge at the cathode, thus losing capacity. NEES researchers have identified several nanostructure-based solutions to this degradation mechanism, including: thermal reaction to transform the lithium sulfate products to insoluble species; binding the sulfur to stable carbon materials that serve as scaffolds for the cathode; and trapping dissolved polysulfides in an ALD  $\text{Al}_2\text{O}_3$ -coated activated carbon cloth between the electrodes, so that they can be returned to the cathode during recharge.

# NEES Publishes in Top Journals



# Innovative

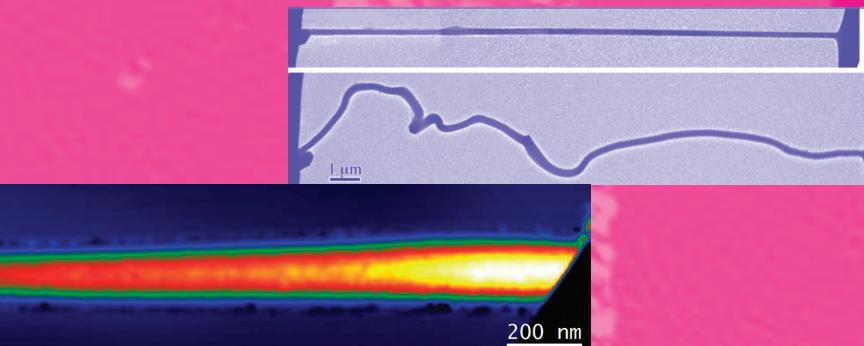
## THE NEES EFRC HAS DEVELOPED

innovative platforms for ultra sensitive and precise measurements at the nanoscale. In the journal *Science* in 2009, NEES pioneered a unique electrochemical cell configuration to reveal lithiation/delithiation mechanisms in individual nanostructures comprised of elemental or heterogeneous nanowires. Real-time imaging by high resolution TEM at the nanoscale was first achieved using ionic liquid electrolyte compatible with the vacuum environment and then with solid electrolyte formed on the lithium anode, providing detailed mechanistic understanding of nanostructure electrochemistry. Continuing in situ TEM work employs a novel device to use dielectrophoresis to steer and attach individual nanostructures to nanoelectrode probes. This structure can be employed in concert with a wet-cell microchip inside the TEM to expand the work to conventional organic electrolytes while achieving much higher spatial resolution than commercially available TEM devices. Led by NEES researchers, the wet cell microchip is the latest in a series of Discovery Platforms that serve as user facilities produced at the Sandia-Los Alamos Center for Integrated Nanotechnologies (CINT). Recently NEES has been a leader in developing TEM electron holography

to visualize electrostatic potential distributions surrounding nanostructures, investing in this capability to obtain voltage maps of electrochemical nanostructures during operation.

Other experimental platforms in NEES probe the limits of energy storage down to single nanometers or to individual defects. Single-nanowire electrochemical measurements have recently been achieved in the TEM. A field-effect transistor platform configured with a carbon nanotube channel and a manganese oxide ion storage coating detects, with high sensitivity, the electronic resistance between the carbon current collector and the oxide storage material. Long cathodic  $\text{MnO}_2$  nanowires controlled in cross-sectional dimensions and shape with LPNE serve as horizontal platforms for studying the limits of electrochemical storage capacity down to tens of nanometers. These configurations invite a variety of new ways for researchers to interrogate electrochemical storage at the nanoscale. UHV surface science environments have enabled synthesis of single-crystal  $\text{MnO}_2$  nanoparticles grown at step edges of highly ordered pyrolytic graphite surfaces. This allows scanning probe microscopy methods in both UHV and wet electrochemical conditions to probe nanoscale electrochemical behavior as lithium is introduced at specific sites.

## EXPERIMENTAL PLATFORMS



# IMPACTOR

34-14

PERCENT OF TOTAL  
PUBLISHED ARTICLES: 22%

Nature Materials  
Science  
Nature Nanotechnology  
Advanced Materials  
Nano Letters

13-10

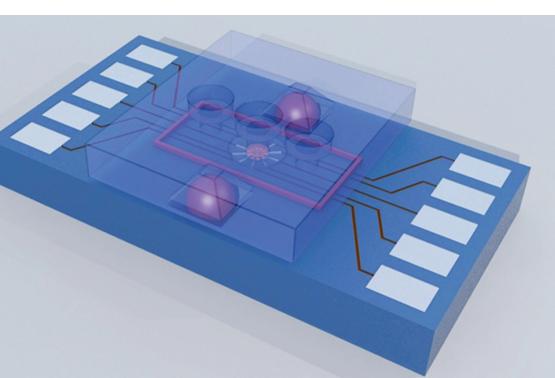
PERCENT OF TOTAL  
PUBLISHED ARTICLES: 24%

ACS Nano  
Advanced Energy Materials  
Advanced Functional Materials  
Journal of the American  
Chemical Society  
Energy & Environmental Science  
Nature Communications

9-5

PERCENT OF TOTAL  
PUBLISHED ARTICLES: 25%

Small  
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Chem Mat  
Chemical Comm  
J Phys Chem Lett  
J of Mat Chem  
Nanoscale  
Carbon  
J Power Sources  
MRS Bulletin  
Electrochemistry  
Comm  
J Phys Chem C  
Analyst  
Nanotechnology



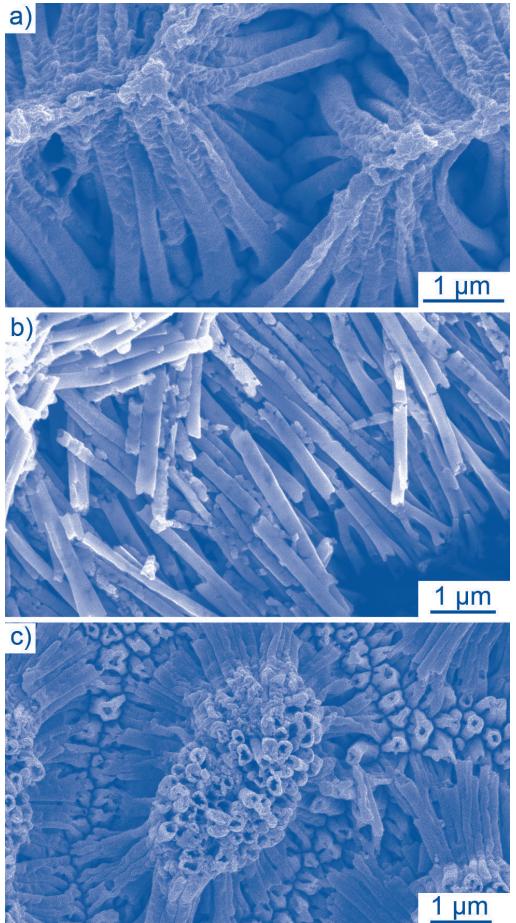
4-3

PERCENT OF TOTAL  
PUBLISHED ARTICLES: 19%

Electrochimica Acta  
Physical Review B  
Phys Chem Chem Phys  
J Electrochem Soc  
Mater Lett  
J Applied Physics  
Micron  
JVST-A  
Journal of Micromechanics and  
Microengineering  
Proceedings of SPIE  
Nano Energy  
RSC advances

# Mesoscale architectures

## OF ELECTROCHEMICAL NANOSTRUCTURES



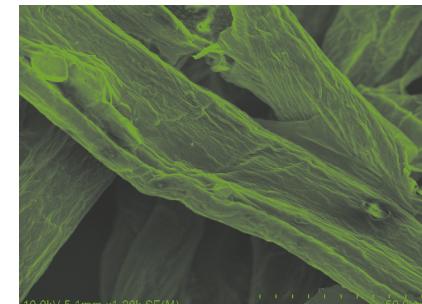
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**NEES'S PRIME FOCUS** has been the synthesis and study of carefully designed, regular, ordered nanostructures to elucidate the science of electrochemistry at the nanoscale. For such nanostructures, performance in electrochemical storage is determined by dimensions and areal density of the nanoelectrodes. NEES has begun to look at other factors that affect storage performance at the mesoscale—namely, hierarchy and randomness—that raise scientific challenges of their own.

NEES has seen that length scale hierarchy can influence energy storage performance. In-situ TEM experiments carried out during lithiation/delithiation of single germanium and silicon nanowires reveals the early formation nanopores inside the nanowires which persist during subsequent cycles—a “pore memory” effect that suggests a persistent internal substructure in the nanoelectrodes. In a different example, researchers discovered ways introduce a spatial fine structure to oxide nanostructures via electrochemical reduction and oxidation, producing nanofibrils or nanoflakes that enhance storage capacity. Nanocrystals within  $\text{MnO}_2$ /PEDOT nanowires and columnar substructures in carbon nanowires influence storage capacity. The possibility of precision synthesis of profoundly hierarchical architectures has been illustrated in virus-templated nanoelectrodes (300 nanometers long) covering microscale pillars made by conventional optical lithography. Together these examples suggest that length scale hierarchy is a useful design tool for nanostructure-

based electrical energy storage, including particularly designs to confront the ion transport considerations in “ionics”.

NEES has also started to explore how the precision nanostructures it has studied behave when arranged in non-regular architectures, such as long nanowire networks that mimic regular nanostructures locally along the nanowire but appear to be randomly arranged in 3D. For example, a significant NEES milestone has been the investigation of cathodic “sponge” architectures in which long multiwall carbon nanotubes form current collectors on which  $\text{MnO}_2$  or  $\text{V}_2\text{O}_5$  layers are conformally deposited as active storage material, using electrochemical or atomic layer deposition. These nanostructured “sponge” cathodes show charge storage and cycling performance at least as high as in regular nanostructure forests. The open structure of the 1D nanowire network provides substantial design flexibility while enabling characterization by techniques such as SEM and TEM. In such architectures, the open volume promotes ion transport in the electrolyte, the nanotubes ensure connectivity to external contacts for electron transport, and the conformal coating of active storage layers provides robust contact to the nanotube conducting scaffold.



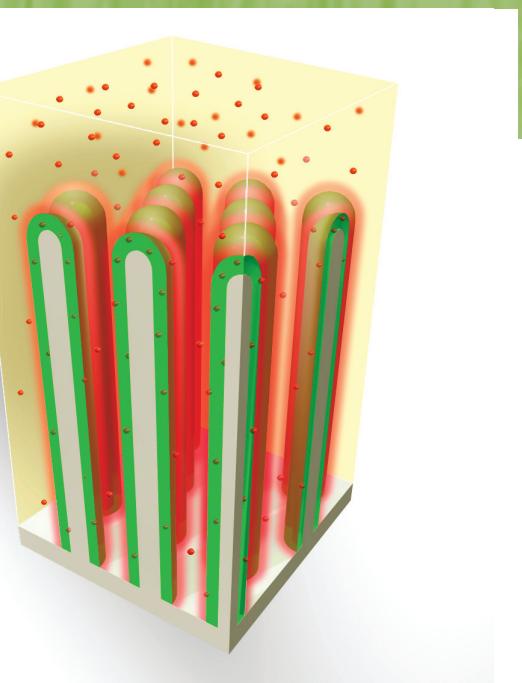
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NEES has also shown that cellulose, the fundamental constituent of paper, can provide both a scaffold for conformal coating by current collecting and active storage layers, and also internal storage spaces for electrolyte within cellulose fibers.

A rich set of scientific challenges surround these mesoscale architectures: synthesis routes needed to make them; characterizing porosity, tortuosity, and new metrics yet to be defined as relevant to understand these structures; identifying what factors gate performance and cycling stability; and assessing what the statistical distribution of local geometries portends for managing defects and degradation phenomena. From a technology perspective, the broad architectural options available at the mesoscale pose challenges in optimizing design and in manufacturability.

# Nanostructure forests

NEW SCIENCE AT THE MESOSCALE



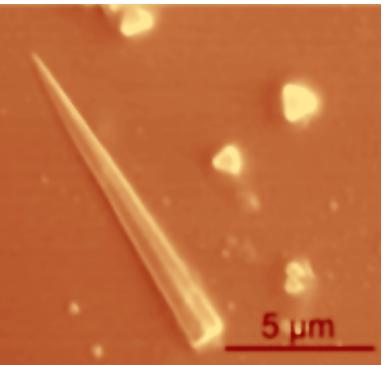
**WHILE NEES' FOCUS** is on design and behavior of heterogeneous nanostructured electrodes, including numerous studies of single nanostructures, the technology payoff comes only when these nanostructures are packed together at high density to achieve high power and high energy per unit volume and weight. These dense "nanostructure forests" present not only high areal density of nanoelectrodes spaced only 50-100 nanometers apart, but also extreme aspect ratios of electrolyte regions between the nanoelectrodes. In such confined environments, ion transport ("ionics") may be limited by the concentration of readily available lithium ions, by slow diffusive transport from the bulk electrolyte, by surface charge or electrokinetic effects at the electrodes, or by the properties of electrical double layers that comprise notable fractions of the inter-electrode region.

Such scientific questions—their importance identified explicitly in the middle of the NEES program—represent new issues emerging as a consequence of mesoscale architecture, strongly dependent on the length scales and orientations of nanostructures in aggregation.

This "ionics" issue couples directly back to the electron transport ("electrodics") aspects of nanostructure design, because changes in ion concentration and transport between nanoelectrodes may alter the balance between ion and electron transport in the heterogeneous nanoelectrodes. In this sense, both ionics and

electrodics reflect the influence of mesoscale architecture for high-density nanostructure forests.

NEES researchers are addressing the ionics issues from several perspectives. One is the study of single tapered nanopores in the limit that electrical double layers overlap at the small end of the pores. In this regime ion current and flow rectification occur, controlled by surface charge on the pore walls. These mechanisms may play a role at somewhat larger interelectrode spacing for nanostructure forests. In a different promising approach, NEES is studying the fundamentals of ion transport in nanofluidic transistor systems, where surface charges and dimensions can be directly controlled. Multiphysics finite element calculations complement this work, along with experimental test sites for single nanoelectrode TEM voltage mapping and electrochemical performance assessments for dense nanowire forests.



## LOOKING BACK + LOOKING FORWARD

NEES' primary intellectual contribution has been its identification and demonstration of the critical role played by **structure**—both nanostructure design and mesoscale architecture. Much of the effort has been to understand the way multifunctionality—ion, electron, electrochemical reactivity, and mechanical stresses—plays out and demands heterogeneous nanostructure configurations. This has stimulated NEES researchers to exploit research skills in precision synthesis and characterization of nanostructures, and to focus on model systems to maximize the insight achieved from experimental and computational studies. Often this has required collaboration between investigators and institutional partners to assemble the combined skills of nanoscience, electrochemistry, and more.

The growing collaborative teamwork of NEES investigators has been largely responsible for the evolution of its research perspective, widening substantially to address structure at the architecture level, engaging random and hierarchical architectures as well as regular versions, and recognizing clearly that these architectural issues highlight the importance of mesoscale science while revealing specific new scientific questions.

The value of nanostructures for a next-generation technology is best measured in mesoscale architectures of heterogeneous nanostructure components. Accordingly, NEES' contribution can be considered as the **science of structure and architecture**, which links new materials to technologies for electrical energy storage.

The NEES team looks forward to the many challenges that remain in establishing structure-related scientific underpinnings for a next-generation electrical energy storage paradigm. Some of these lie in decoding and mastering new storage mechanisms operative in "beyond lithium ion" systems, for which NEES' model systems approach is an asset. Others reside in continuing a focus on mesoscale architectures and on the connectivity it promotes to technology.



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