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II ACCOMPLISHMENTS: 1. What are the major goals of the project?

Vision

The NEES **vision** has been to reveal a set of scientific insights and design principles that can underpin a next-generation electrical energy storage approach, building on advances in nanoscale science and technology to achieve simultaneous high power and high energy over extended charge/discharge cycling. The vision is motivated by the recognition that scaling into the nm regime opens the door to new physical phenomena and that the tools enlisted in nanoscale research provide major new opportunities for the synthesis not only of materials at molecular scale but for structures at nano scale and above. NEES has translated this vision into its research program based on two observations.

First, while the behavior of ions and electrons in electrolytes and in electrode materials is crucial to electrical energy storage (or more appropriately electrochemical energy storage), it is the transport of ion and electron charge between different structural components of a storage device that ultimately determine its performance. With it well recognized that the choice of electrode materials typically constrain ion transport kinetics as well as maximum ion concentration, the search for better electrode materials has been a primary driver of battery research. At the same time the synthesis of electrodes is typically based on aggregation of particles with varying size, shape, and orientation in the electrode. Togeter with the presence of additional materials to impart electrical conductivity and cohesion to the composite electrode, change in electrode materials is necessarily accompanied by structural changes at the nano/micro scale that are difficult to categorize and manage. From the beginning, NEES' vision has been to create and study simpler, highly controlled spatial arrangements of known materials as battery components (electrodes, current collectors, and electrolyte) and to understand how design and structure above the molecular scale determines the energy storage performance available from known materials.

Second, advances in nanoscience dramatically expanded the portfolio of synthesis methods, structural motifs, and new phenomena available for research. Some of these gave rapid access to new building blocks at the deep nanoscale (e.g.., carbon nanotubes grown by self-assembly, nanoscale arrays formed by electrochemical self-alignment, monolayer films controlled by self-limiting reaction). Such advances served as the enabler for the NEES vision to be pursued experimentally through study of 3D structures created and controlled at the nano, micro, and meso scales. Here, we use meso as in the BES MESO Report[1], implying not only intermediate or varying length scales, but very much the way behavior is influenced by other factors including aggregation of nanocomponents at different densities and spatial configurations, statistical variations in the aggregates, hierarchical architectures in which they can be assembled, or local 3D configurations that result from the architectures.

Goals

Over its life cycle, NEES (www.efrc.umd.edu) has pursued **two overarching goals**:

(1) to understand the scientific fundamentals of electrochemical storage from the nanoscale to the mesoscale

(2) to create and learn from innovative, controlled, heterogeneous nanostructures, where such nanostructures can enable the first goal and serve as models for future paradigms in energy storage.

Specific goals include:

- *Synthesize heterogeneous nanostructures comprised of multiple materials arranged in controlled fashion and characterize their behavior*
- *Demonstrate and elucidate design principles for achieving simultaneous high power and high energy*
- *Develop materials processes which enable precision control of thin layers and 3D structures*
- *Investigate the impact of artificial interphases on electrode stability during ion insertion/deinsertion*
- *Create dense arrays of nanostructures to understand how the architecture of these assemblies, along with nanostructure design, influences energy storage behavior at the mesoscale*
- *Identify and understand the consequences of nanoconfinement and local inhomogeneities in 3D mesoscale arrays*
- *Develop and apply computatioal models to stimulate, guide and interpret experiments*

Scope and evolution

NEES' research scope has been broadly defined by its focus on the **confluence of structure and nanoscience**. The emphasis on structure was driven by two factors: (1) the recognition that battery research has been dominated by discovery and development of electrode and electrolyte materials themselves, with considerably less emphasis or ability to control how these different components are arranged into a functioning energy storage device; and (2) the realization that nanoscience, together with thin film processing, offers profound opportunities to create and control device structures at a level well beyond that employed in conventional batteries.

Accordingly, NEES has concentrated on **precision control of structures** from the deep nanoscale (~1nm) to micro/macro scale, synthesizing thin films and 3D structures as heterogeneous nanostructures both as isolated devices and in massive, often dense arrays. By *heterogeneous* nanostructures, we imply that multiple materials are employed, distinguishing different components of an energy storage device, which in turn is multifunctional in providing for the ion transport, ion storage, electron transport, and charge/discharge cycling stability required for a rechargeable battery. Consistent with its emphasis on structure, NEES strategy has been to employ better known battery materials as models, except where innovation in materials synthesis for precision structures was needed.

The **evolution of NEES' scope** has included transitions from liquid organic electrolytes (the standard in Li ion batteries) to solid electrolytes and from individual heterogeneous nanostructures to mesoscale architectures comprised of dense nanostructure arrays. More specifically, NEES-1 ($14.0M, 2009-2014) focused on the design, synthesis and properties of multifunctional nanostructures made of material structures for ion transport/storage and electron transport, and offering facile ion access from electrolyte. Its renewal as NEES-2 ($11.2M, 2015-2018) evolved the focus to mesoscale counterparts and consequences, embodied in the study of mesoscale architectures, their performance, degradation, and mitigation mechanisms, and how they interact and/or are driven by nanoscale behavior, realized in both liquid and solid electrolyte storage systems.

In the latter stages of NEES-2, NEES increasingly recognized all-solid-state energy storage as a profound trend and a scientific opportunity that raises new fundamental issues, such as electrode/electrolyte interface properties and reactivity, ion transport in solid electrolytes and across interfaces, and interdependence of ion and electron behavior. With its leadership capabilities in thin film fabrication of model solid state nanostructures and corresponding mesoscale architectures, NEES was in a prime position to dramatically advance the understanding of solid state storage. NEES developed a 4-year EFRC renewal proposal "Precision Ion-Electron Control in Solid State Storage (PICS3)" in 2018 focused entirely on solid state storage, retaining about half its PIs, but this was not funded. Instead, NEES received a 2-year extension NEES-2E ($2.0M, 2019-2020), which it has used to focus on completing key directions in precision 3D solid state battery structures and solid electrolytes.

The scientific momentum represented in NEES is continuing. A group of 4 PIs, including 3 from NEES, has proposed and since been awarded a DOE-BES grant ($2.25M, 2020-2023) for "Thin Film Platforms to Advance Scientific Frontiers in Solid State Energy Storage", capitalizing on 3D patterned structures to provide new electrochemical insights. In the 2018 competition and with encouragement from NEES leadership, 4 NEES PIs with excellent strengths in ionics and nanofluidic transport formed a nucleus that led to a new EFRC award to CENT (Center for Enhanced Nanofluidic Transport, https://cent.mit.edu/people/ led by Strano (MIT), with the NEES alums taking roles as Deputy Director and 2 of 3 Thrust Leaders.

II ACCOMPLISHMENTS: 2A. What was accomplished under these goals?

Significant and sustained progress has been made toward these goals during the NEES program 2009-2020. Below we describe selected examples within the contexts of the above goals.

1. Synthesize heterogeneous nanostructures comprised of multiple materials arranged in controlled fashion and characterize their electrochemical behavior

Early NEES work employed various fabrication strategies to create nanostructures combining ion storage components in close contact with electron transport, a prescription seen as essential to high power-energy performance for both anode and cathode materials. NEES work pioneered in-situ TEM, beginning with a single-nanowire lithiation experiment in which Li ions from LixCoO2 cathode were transported through ionic liquid electrolyte to lithiate SnO2 nanowires, with the expansion of materials that occurs being directly observed in real-time video. [2], [3]. Numerous publications from NEES and others followed as the technique was widely adopted. A more direct demonstration of multicomponent nanostructures, also observed by in-situ TEM, was the formation of "Si beads on a CNT string" [4], where a multiwall carbon nanotube (MWCNT) was positioned between electrical probes, with Si beads attached to the CNT. Despite the well-known fragility of Si due to its large volume expansion (400%) upon lithiation, the isolated Si beads could expand and contract upon lithiation from the liquid electrolyte while adhering to the CNT and transporting electrons over the CNT. The development of MWCNT-based yarns and fabrics provides a pathway to larger-scale versions.

NEES has demonstrated a substantial variety of such heterogeneous nanostructures, including: coaxial nanowires of conducting polymer (PEDOT) with oxide cathode (RuO_2) formed by electrochemical deposition (ECD) in anodic Al oxide (AAO) nanopores[5]; "nanostructure forests" creaated by conformal coatings made by atomic layer deposition (ALD) on CNTs[6], Si nanowires, or in nanopore templates; lithographically enabled nanowires of conductors (Au) coated by oxide (MnO_2) using ECD[7]; and heterogeneous nanostructured Ni/V_2O_5 electrodes formed on tobacco mosaic virus particles [8].

2. Demonstrate and elucidate design principles for achieving simultaneous high power and high energy

Normally battery designs involve tradeoffs, the most obvious being power vs energy: for higher energy density, thicker ion storage electrodes are needed, but the slow transport of ions in solids reduces the ability to deliver that energy at high power. *Nanostructure designs offer a solution: (1) ion storage material distributed as thin layers over larger areas that contact the electrolyte; (2) current collecting material for electron transport in intimate contact with ion storage (particularly with 3D electrode arrangements), so that high power is deliverable; and (3) nanoscale structures to achieve some mechanical flexibility to withstand changing stress/strain that results from lithiation/delithiation.*

These design guidelines were demonstrated repeatedly in NEES research. For example, MWCNTs in a random sponge configuration were coated with ~16nm V_2O_5 by an ALD process, yielding ~50nm total thickness to form a nanostructured cathode. [6] Lithiation cycling enabled insertion of 1 or 2 Li per V_2O_5 formula unit with cycling stability >100 cycles, showing stability of the nanostructured design, and ~50X increase in power (current density), at only ~5X cost in capacity/energy.

These guidelines have been reinforced by experiments using regular arrays of precision nanostructures. Li ion nanobattery arrays, using ALD electrodes and current collectors at each end along with liquid organic electrolyte (forming the world's smallest Li ion batteries) [9], [10] show exceptional power-energy performance, losing only 2X in capacity/energy for 150X increase in power, while little capacity fade. Design variations and multiphysics modeling showed the intimate connection of current collectors is essential for the power benefit. 3D solid-state batteries (SSBs) created by ALD multilayers over etched Si pores [11] reinforce guidelines prescribing thin electrode layers with large area contact to both current collectors and electrolyte to achieve high power-energy.

3. Develop materials processes which enable precision control of thin layers and 3D structures

To create nanostructures and architectures in prescribed configurations, NEES research has included development of materials processes for specific properties. The design guidelines above prescribe the use of 3D scaffolds on which battery components should synthesized, but the 3D character - often dramatic in terms of aspect ratios (vertical/horizontal dimensions) requires battery materials to be added by conformal deposition. This has led to NEES development of highly conformal ALD and ECD processes for electrode materials (e.g., V2O5, MnO2, SnO2, RuO2), current collectors (e.g., TiN, Pt, ZnO), solid electrolytes (e.g., LiPON), and insulators (e.g., Al2O3, AlZnO).

NEES research in 3D-SSBs, beginning with NEES' single-nanowire solid state battery in 2012, [12] has placed an emphasis on new synthesis approaches for solid electrolyte materials, including thin layers by low temperature plasma ALD LiPON[13] or medium temperature thermal ALD processes for LiPON[14] and NaPON[15]. Such layers are highly suitable for 3D-SSBs where highly conformal deposition is required and thicknesses can be reduced substantially, to ~30nm. [14] ALD processes, or hybrids thereof, are very suitable for 3D-SSBs or as protection layers on reactive electrodes. Alternatively, NEES has also developed solution-processed ionogel electrolytes[16], comprising a silica matrix filled with ionic liquid electrolyte, with much higher ionic conductivity compatible with thicker electrolyte but essential solid and thin film fabrication of 3D batteries in a 2.5D format. [17]

4. Investigate the impact of artificial interphases on electrode stability during ion insertion/deinsertion

Liquid organic electrolytes can decompose in contact with electrode materials, particularly at high voltage, leading to formation of a "natural" solid-electrolyte-interphase (SEI) layer that offers some protection against further degradation. The SEI is chemically and structurally complex, and it can continue to grow with charge/discharge cycling. Degradation mechanisms can include intrinsic electrode/electrolyte reactions, corrosion involving electrolyte impurities (e.g., H2O) or counterelectrode components (e.g.., Mn dissolution from MnO2 cathodes, polysulfides from S-based cathodes), and structural change in electrodes (e.g., stress/strain from intercalation, conversion reactions) subjected to ion insertion/deinsertion during charge/discharge cycling.

NEES was early in assessing whether a thin protection layer, formed by ALD, could be applied to electrodes before cycling to serve as an "artificial" SEI to more effectively protect against degradation processes. Initial results using Al2O3 ALD layers showed improvement in capacity retention with cycling. Subsequent studies focused on ALD LiPON solid electrolyte, which allowed thicker protection layers because of their higher ionic conductivity. While thermal ALD LiPON is suitable for use with many battery materials, plasma ALD is particularly notable in operating at temperatures sufficiently low to allow direct deposition onto Li metal, as widely sought for a very high energy density anode material. NEES has used ALD[18], electrochemical treatment[19], and hybrid protection layers[20] with some success to protect Li metal anodes. LiPON protection layers have also shown value in stabilizing electrode materials that undergo conversion reactions with Li (e.g., Li + RuO2 => Li2O + Ru), [18] involving dramatic bonding and phase changes that without such protection would show only poor reversibility and capacity retention.

5. Create dense arrays of nanostructures to understand how the architecture of these assemblies, along with nanostructure design, influences energy storage behavior at the mesoscale

From its inception NEES has envisioned that a critical underpinning of energy storage science is how battery components are structured and hierarchically assembled at difference scales of length and functionality. While nanostructure designs may be fixed, arrays of nanostructures (e.g., MnO2 nanowires released from AAO templates, or CVD-grown CNT forests) can involve different densities and configurations of such nanostructures, affecting not only energy density but likely also available power and cycling stability. Hence NEES has been committed to a search for understanding at the mesoscale, where scales from molecular or nano up are important and where practical consequences are determined (i.e., energy, power, and cycling of a battery).

NEES has created a variety of architectures ranging from quite random to highly regular (perhaps even well ordered). Initially this concentrated on single-electrode architectures as evaluated in liquid electrolyte. Randomly arranged MWCNT fibers or yarns, each coated uniformly and conformally with electrode material to produce locally well-defined nanostructures, represent a "random" mesoscale architecture. In contrast, coaxial nanostructures comprised of cathodic oxide and conducting polymer, when synthesized in highly regular, ordered AAO pores, represent a reasonably regular architecture even when the Al2O3 AAO matrix is dissolved to release the nanowires. Both approaches provide locally well-defined nanoscale structures, but assembled into quite different architectures. While harder to control their mesoscale assembly, the more random architectures reflect nanostructure design guidelines, such as maintaining thin ion storage layers for high power, incorporating electron transport layers in close contact with ion storage materials, and increasing nanoelectrode volumetric density to increase capacity and energy density.

NEES employs thin film patterning methods to create highly controlled 3D-SSB architectures as model systems to unravel the behavior of SSB systems. These methods enable design and realization of a wide range of dimensional changes, high aspect ratio scaffolds, and architectural features such as corners and edges where hot spots or other manifestations of nonuniform behavior can be expected as a consequence of 3D designs. Indeed, parallel arrays of 3D-SSBs, measured and modeled, offer significant insight into these factors. Arrays of SSBs formed by sputtering cathode, electrolyte, and anode layers over Si pillar scaffolds to form 2.5D batteries (2.5D since anode is planar). Electrochemical behavior, combined with multiphysics modeling, reveals spatial inhomogeities that occur during charge/discharge as a consequence of the 3D shapes involved, compromising performance. [21] One step in the right direction - using more conformal processes - employed ALD layers deposited into etched pores in Si to form smoother interfaces and thinner solid electrolyte. [11] An alternative step - improving ionic conductivity of the electrolyte - was achieved with ionogel processing. [16] [22]

6. Identify and understand the consequences of nanoconfinement and local inhomogeneities in 3D mesoscale arrays

Understanding the role of 3D architecture means embarking on investigations at the mesoscale, where differing length scales and functionalities are combined into an overall system, with multiple impacts. An immediate example follows from the design guidelines for high power-energy: once design of heterogeneous nanostructured electrodes is finalized, how closely can they be packed to further increase energy density, and at what point do other phenomena become limiting, or significantly adverse?

NEES has pursued several approaches to these questions as directed at the limits of electrolyte nanoconfinement. NEES created and evaluated behavior of massive arrays of individual Li ion batteries in AAO pores with tiny volumes (~1fL each), with liquid electrolyte volumes confined to <200nm dia x 50 μm long, i.e. aspect ratio ~250X. [9], [10]. Observations of exceptional capacity retention at high power and extended cycling show that there is no performance limitation imposed by electrolyte nanoconfinement. Pushing this question further, NEES used microfabrication techniques to create nanofluidic channels 20nm high x 13μm long separation between TiO2 electrodes [23]. Electrochemical measurements and multiphysics modeling suggest that selective ion accumulation occurs when confinement conditions produce Debye layer overlap, leading to power-energy benefits and improved reaction reversibility. Other NEES work has employed single nanopore configurations for research advancements in electroosmotic flow rectification[24]-[26], voltage modulation of ionic conductivity[27], [28], ion transport in solids[29], and development of scanning electrochemical techniques[30].

A different embodiment of nanoconfinement and inhomogeneity is the behavior of ion and electron transport in 3D tortuous pathways, which surely play a role in batteries fabricated from particulate electrodes. Nanoporous AAO provides an excellent starting point for low/zero tortuosity nanochannels, from which NEES has developed synthesis modifications to introduce connections between neighboring channels at chosen points along the channels. [31]. Using ALD V2O5 coating in the networks to form an electrode architecture, the interconnected pores increased capacity and power handling capability, the latter attributed to electronic transport effects within the electrodes.

In creating and assessing different controlled mesoscale architectures (see #5 above), NEES has demonstrated means by which their design and synthesis can be used to vary nanoscale transport pathways, with particular consequences for kinetic response at high power and transient inhomogeneities which follow from that. Comparison of 3D-SSBs fabricated from sputter deposition[21] vs ALD[11] is a good example. In addition to overall design and dimensions, techniques have been demonstrated to alter more subtle structural features, e.g. by using ALD to round corners in a 3D structure. [32]

7. Develop and apply computational models to stimulate, guide and interpret experiments

Computational modeling has played a pervasive role in NEES research, motivating and interpreting experiment throughout. Early work concentrated on initial electrode/electrolyte decomposition reactions, modeled at molecular scale by DFT, for insight into the molecular chemistry which initiates formation of SEI layers in organic liquid electrolyte systems[33], the kinetics of such reactions[34], and the role of thin passivation layers (see #4 above) in suppressing SEI formation[35] on various electrode surfaces.

Whether intentionally created or formed by available oxidation or SEI decomposition reactions, electronically insulating layers are common on electrode surfaces, playing a role in modifying such reactions chemically and electrochemically. Such layers influence voltage gradients across a battery and the resulting stability of liquid organic electrolytes. DFT calculations have shown how SEI growth occurs and at what stage and thickness the likely SEI components suppress or prevent electron tunneling through the layer. [36] Fundamental investigations by NEES have also highlighted the question of how electrostatic energies (voltages) and chemical energies of the materials involved in electrochemical reactions, where these energies respond on different time scales. [37]

In all-solid-state batteries, manifestations of these issues change. Thin electric double layers are replaced by thicker space charge regions in electrolytes and insulating/semiconducting electrodes, and interfacial electrode/electrolyte reactions pose implications for voltage gradients that may affect ion transport as well as electronic interface barriers. Experimental results indicate such reactions [38] [39], while NEES DFT calculations are poised to elucidate contact potentials, electric fields at interfaces, and reaction kinetics. [40], [41]. Extending such studies to address voltage gradients across the multiple interfaces in a full battery is a major challenge. Nevertheless NEES has established an ab initio framework to calculate interface potential drops across a full battery cell in equilibrium and to understand the changes that result from Li ion relocation between the electrodes in concert with electron transfer due to interfacial band-bending changes. [42]

NEES has stimulated a variety of computational approaches that make increasing contact with experiment in 3D-SSBs. Charge/discharge kinetics and the influence of inhomogeneities introduced by 3D architecture have been elucidated by multiphysics modeling[21] [17] and extended to evaluate the consequences in 3D-SSB architectures of stresses induced by interfacial reaction as well as Li ion transfer. [43].

II ACCOMPLISHMENTS: 2B. What are the major remaining challenges?

Despite much progress in NEES and other energy storage research centers and groups, profound challenges remain in the fundamental science which leverages use-inspired goals in energy storage. The 2017 Basic Research Needs (BRN) for Next-Generation Electrical Energy Storage document provides a community consensus on the major challenges through its five Priority Research Directions (PRDs), which are expressed at a high level and accompanied by a selection of significant examples.

Here we share our views on the major remaining challenges from the perspectives of our NEES research experience. We focus mainly on all-solid-state embodiments of electrochemistry for electrical energy storage, consistent with the recent years' concentration in NEES research and with the growing community interest in SSBs. They touch on virtually all five PRDs in the 2017 BRN.

1. Fundamental science of solid state energy storage

Replacing a liquid electrolyte with a solid causes at profound physical changes. One is the constrained nature of **solvation in a rigid atomic surrounding** (as currently emphasized and pursued in JCESR), which determines effective ion charge and transport kinetics in materials and ultimately at interfaces. A second is the **bidirectional interaction between ions and electrons**. Simply stated, electronic structure of the material(s) determines not only band structure but also a host of properties of interfaces (e.g., electrode/electrolyte) - band alignment, space charge length scales and electric fields - which may influence ion transport across these interfaces during charge/discharge cycling. On the other hand, such cycling creates time-varying concentrations of Li (or other ions) that substantially alter electrode materials, leading to changes in band structure and interface barriers. Reconciling and integrating the coordinated behavior of interacting ions and electrons - in bulk materials and at interfaces - represents a crucial theoretical and computational modeling challenge.

2. Computational modeling at the meso scale

Modeling frameworks that account for both ions and electrons in a self-consistent manner could provide a coherent way to address ion transport and interface behavior. But the **real payoff is at the mesoscale**: experimental results (not to mention practical application) are nearly always mesoscale in that they involve multiple material components and the interfaces between them, as well as phenomena and gradients across length scales. NEES has made a good start along these lines, predicting voltage gradients across solid state battery cells in agreement with scanning probe voltage gradient experiments. [42] Calculations also predict reversal of electric fields near the interface with changes in electrode state-of-charge (SOC), not yet measurable experimentally. New **modeling approaches are needed to accommodate distinctly different manifestations of the mesoscale**, involving different length scales, multiple interfaces, spatiotemporal gradients, and 2D and 3D features which induce variation in local properties. Examples include changing gradients across material as lithiation/delithiation occurs, consequences of interphase regions that form by reaction at interfaces, and the impact of 3D features such as modification of interface properties and spatial gradients near electrode edges or corners.

3. Characterization

NEES foresees computational modeling as providing profound leverage to address the fundamental science of solid state energy storage, but **much empirical knowledge required to realize the benefits of modeling is not available**. While impedance spectroscopy (EIS) is routinely employed to estimate interface impedance to ion transport, that comes from a simple electrical analog model that cannot uniquely determine that interface impedance. At the mesoscale the impedance associated with ionic conductivity is distributed spatially and changing during charge/discharge, yet for most materials we do not know how ionic or electronic conductivity depends on SOC nor how sharp gradients in SOC might be. We don’t know band offsets and space charge fields near SSB interfaces. Furthermore, 2D or 3D configurations of batteries - desirable for high power-energy - further complicate the situation. Corresponding knowledge gaps remain with respect to band offsets at interfaces, their impact on ion transport, and their changes with lithiation/delithiation. If we knew such information and could thus inform computational models, our understanding and ability to design energy storage devices would be substantially heightened.

Clearly new approaches to characterization are needed to acquire such kinds of mesoscale information, in particular about interface barriers, evolving distributions of physical properties as SOC varies, and local characterization methods applied to 2D and 3D features. Since condensed phases of material hide buried interfaces from many of our characterization instruments, **major advances in characterization are needed, fostered either by innovation in measurement instruments, fabrication and design of the sample, or both**.

4. Mesoscale design for high power-energy

Aggregation of nano- or even micro-structured components to form an energy storage device presents substantial design, synthesis, and analysis challenges that are in some sense conceptually orthogonal. The **dominant question is how to configure a massive assembly of high power-energy nanostructures** into an effective high power-energy storage device. The design complexity is substantial, where anodic and/or cathodic components are likely to comprise distinct structures of heterogeneous materials for ion and electron transport and there are numerous ways in which these might be located with respect to each other and to solid (or conceivably liquid) electrolyte materials. Intervening interphase layers may be desirable as well. As can be envisioned from considering an interdigitated electrode architecture, the design of 3D energy storage devices may entertain different electrode shapes, different orientation and proximity of anode and cathode nanostructures, and different dimensions of features.

A crucial question is **whether the desired configurations can actually be synthesized**, given techniques available at the time. Different synthesis approaches will certainly impose constraints (e.g. from minimum spacing between electrodes or asperities on the surface). On the other hand, some may open opportunities to tailoring architectures (e.g., rounding edges or corners) for controlling outliers in statistical distributions. NEES and others have created some exemplary architectures[44], [45] [17] [11] [9] as proof-of-concept, which furthermore demonstrated the value of conformal thin film fabrication methods.

Nevertheless, given the large design space for such architectures and the multi-step fabrication sequences required, **multiphysics modeling is an absolute essential to (1) narrow the designs chosen for experimental realization and (2) understand the behavior of the experimental models**. Innovative characterization techniques (above) hold promise for enriching the validity and value of these modeling approaches. Artificial intelligence or machine learning methods can enhance learning from a systematic search of possible designs.

Other aspects of mesoscale design are also critical. **Mechanical behavior** is mesoscale in that forces are distributed through multiple if not all components of a mesoscale system such as a 3D-SSB. At the same time, resulting stress/strain - particularly but not only from charge/discharge cycling - can initiate degradation mechanisms that lead to capacity loss and failure. Materials choices (e.g., inorganic, polymeric) and design of nanoscale structures and mesoscale architectures all influence mechanics and its consequences for energy storage devices. Finally, with large numbers of nanocomponents contributing to a mesoscale device, **statistical variability and outliers or defects** within that distribution have a disproportionate ability to compromise the intended performance of a mesoscale energy storage device. This may be particularly critical in controlled, precision 3D architectures that NEES has pursued to offer high power-energy behavior as sought for energy storage technologies. It is certainly crucial for the majority of battery designs: here electrodes and solid electrolytes are composed of active particles for ion storage, which are partially connected to or enclosed in electron-conducting layers and adhesive materials, posing a challenge to modeling of tortuous networks for both ion and electron flow and the associated statistics.

5. Other domains for research in spatiotemporal electrochemistry

NEES and other groups have demonstrated the benefits of **thin film fabricated energy storage devices** which exploit highly-controlled fabrication of precision 3D structures and architectures. Such thin film fabrication has been the driver and the enabler for some of the most advanced technology available today - in computers, cellphones, displays, and other systems that comprise logic, memory, sensors, actuators, and communications. This raises the question of whether there is a role for thin film fabrication in the world of batteries. Given the demonstration of thin film fabricated battery structures, it seems clear that they can be integrated effectively into electronic systems, potentially influencing such areas as biomedical devices, small satellites in space, or environmenal sensing and security systems. While the underlying science may be no different than that NEES has pursued, these obvious applications of thin film technology may be worthwhile to consider as use-inspired motivations.

At the heart of NEES research has been the challenge to understand and control spatiotemporal electrochemistry in the kinds of 3D structural and architectural configurations that can benefit electrical energy storage in batteries, capacitors, and electronic systems. Here we mention two **other domains that employ redox activity**, but face major challenges to understand and control spatiotemporal electrochemistry, analogous to the goals of NEES and other BES centers.

Redox phenomena, at the heart of electrical energy storage, pose opportunities in other areas of application. Those domains may pose fundamental science questions somewhat differently, but with broad and important consequences. One such arena is in biologically inspired **neuromorphic computing.** With great interest already established in this direction, it is opportune that the very nanostructures pioneered in NEES can serve well as redox memory devices[46]-[48] for neuromorphic computing. [49] In this approach, voltage pulses across a tiny thin film fabricated battery control ion concentration in an electrode, changing the resistance of the electrode material as a nonvolatile analog data in memory. The computing performance of such devices challenges our ability to make very thin battery layers, 2D/3D battery devices, low leakage, and high speed operation - somewhat different metrics that reflect fundamentals of the storage device.

Redox reactions play critical roles in biology, with electrons exchanged through molecular intermediates, and redox biology is important in central metabolism, immunity, etc. This **enables electrochemistry to couple directly to biology** in biocompatible aqueous environments, e.g. by modulating the biological system (actuation) or interrogating it (sensing). [50]-[53]. Configurations of individual electrodes - either isolated in biocompatible solution or incorporated into microfluidic systems - have been utilized for research in biological signaling mechanisms, cell entrapment, small molecule and drug sensing, biopolymer construction, antibody-antigen binding. [54] While it encounters a host of different constraints from energy storage or even redox-based neuromorphic computing, this arena of electrochemistry research offer common ground with issues in liquid electrolyte batteries, e.g. kinetics, diffusion and solvation in biological media, ion diffusivity in biopolymers.

II ACCOMPLISHMENTS: 3. What opportunities for training & professional development has the project provided?

NEES administration. Students and postdocs have long played a strong role in NEES' activities and administration, typically organizing the various thrust teleconferences as well as participating regularly in thrust discussions so that they see a picture of the research well beyond their own work. They conscientiously attended all-hands meetings that feature strategic presentations and discussion as well as specific talks on technical topics. These activities, and particularly their coordinating roles, made them heavily invested in the work of the EFRC. Typically students and postdocs took responsibility to plan the all-hands teleseminars and to maintain the thrust membership lists.

NEESConnect. In order to provide a networking framework within NEES for both current and past student members, NEES developed a variety of activities, known as NEESConnect. The goal was to reinforce communications and collaborations for science exchange, career development and a global understanding of today's energy challenge, and to explore how NEES fits into this bigger picture. NEESConnect met four times a year via teleconferencing, with a senior scientist as advisor to facilitate activities that students and postdocs suggest as topics and activities of interest. Career development discussions have often been a priority, offering students and postdocs guidance on how to prepare for and pursue career paths in industry, government, and university.

Research groups. Though details depend on the individual research group, students and postdocs working on NEES research have been exposed to a broad perspective that informs their view of their future career. Gratifying examples are the numerous cases where NEES students at different sites used their NEES thrust discussions to engage others to form new collaborations.

II ACCOMPLISHMENTS: 4. How have the results been disseminated to communities of interest?

Communication within NEES. Our internal communications have been a high priority, and from time to time we revised our processes to accommodate changes in funded PI groups and reorganization of our thrust areas. We typically scheduled a NEES teleconference each week at the same time, alternating between thrusts and an all-hands teleseminar in a 3-week cycle. Organization, planning, and execution of these teleconferences was done by students and postdocs. Typically the thrust meetings included one or sometimes two presentations and some brief oral updates. The all-hands teleseminar featured a more formal presentation, occasionally by an outside speaker.

NEES meeting. NEES has held one strategy meetiing and one all-hands accomplishments meeting each year, rotating through NEES sites. These typically included a poster contest in which students and research associates presented their most recent results and updates, with poster award categories for: Team Science, in which expertise and effort were spread across the various teams and thrusts of the NEES project; Presentation, where both visual and verbal style were assessed; and Innovation, which valued novelty of approach.

Science highlights. NEES has developed science highlights on a regular basis, in an effort to condense the huge amount of science results into public digestible summary statements with emphasis on accomplishment without losing pertinent scientific details, and to frame its significance and impact in the context that can be understood more readily. These are accessible on the NEES website to reach interested members of the public audience.

NEES publications. NEES has published over 300 journal articles, with the proponderance in journals with very high (15.0 < IF < 39.0) or high 6.0 < IF < 15.0 impact factor. This track record not only shows NEES' high publication productivity, it also demonstrates the importance and impacts NEES researchers have contributed toward an ever-evolving landscape of energy research in materials structures and architectures.

NEES news. The News section http://www.efrc.umd.edu/news/ of the NEES website highlights significant happenings in NEES, ranging from scientific advances to outreach activities to external recognition. Those which originate with a public relations release through the Maryland NanoCenter often elicit news coverage from various media.

Scientific communities. NEES members shared results at scientific meetings of interest, often as invited talks, and to initiate professional focus topics such as in conference symposia. A variety of invited and contributed papers presented at conferences shared the scientific contributions of NEES participants, with regular presence at MRS, ACS, ECS, AVS, and other conferences, complemented by presentations at special meetings.

II ACCOMPLISHMENTS: 5. What do you plan to do during the next reporting period to accomplish the goals?

The NEES EFRC ended July 31, 2020.

V IMPACT: 1. What is the impact on the development of the principal discipline(s) of the project?

NEES research had significant impact on the principal discipline of energy storage in several stages. In the first years NEES demonstrated a variety of heterogeneous nanostructures as nanoscale electrodes comprising distinct materials for electron transport (current collectors) intimately contacting thin ion storage materials, which in turn provided large area access to electrolyte as a source for ion insertion/deinsertion. NEES' focus on nanostructure design to validated design guidelines in terms of structural relationships for battery components, the functionality these relationships impart, and the resulting benefit as **simultaneous high power and high energy**.

From the beginning, **NEES' focus on structure and architecture** has presented the community with a different perspective, where the design of multicomponent nanostructures and their assembly into massive arrays at the mesoscale becomes complementary to and as important as the more traditional focus on choice and discovery of best materials for electrodes and electrolyte. A consequence of nanostructural dimensions and dense packing of nanostructures has been NEES advances in understanding **ionics and electrodics** - the behavior of ions and electrons in highly confined nanoenvironments. The partnership of NEES PIs working in this area initiated the new CENT EFRC (Center for Enhanced Nanofluidic Transport, https://cent.mit.edu/people/ led by Strano (MIT), with the NEES alums taking roles as Deputy Director and 2 of 3 Thrust Leaders.

NEES has been a leader in **solid state energy storage science**, particularly through its focus on precision nanostructures and the power of thin film technology to create precise structures that serve as revealing model systems. Examining these issues caused NEES to recognize and underscore the essential issues that are raised in controlled solid state storage systems, particularly how **interface science of ion and electron environments** interact as electronic structure generates space charge and electric field gradients that influence ion transport, while in turn that very transport – during charge and discharge – modifies electronic band structure, space charge, and voltage gradients.

At the cell level, the patterning and control capability of thin film technology enabled NEES to construct solid state batteries from interdigitated nano/micro electrodes, a striking demonstration realizing the benefits of simultaneous high power and energy in a dense, controlled **mesoscale electrode architecture** beyond anything in the battery research field of which we are aware. Furthermore, NEES demonstrated **new solid electrolyte structures** that expand the design space for solid state batteries; this includes (1) ultrathin conformal solid electrolyte layers of modest ionic conductivity serve as an alternative to much thicker electrolytes requiring very high conductivity; and (2) composite ionogel material involving a porous silica network immobilizing an ionic liquid electrolyte, achieving high ionic conductivity that allows nanostructured electrode(s) in configurations that do not require very thin electrolyte separations. Together these features pave the way for **mesoscale 3D and 2.5D solid state battery prototypes**, which are gaining serious technology interest.

Finally, the ability to synthesize precision 3D structures at the nano and micro scale - a centerpiece for NEES - has recently served to nucleate a new direction for NEES leadership, in which novel 3D structures will be developed to elicit new scientific insights in solid state energy storage, ranging from interfacial energy barriers and the consequences of ion transport across such barriers to diagnostics of 3D-SSB architectures and consequences. This holds promise for enhancing how we understand and can design solid state energy storage devices, an effort now supported by a DOE-BES grant for “Thin Film Platforms to Advance Scientific Frontiers in Solid State Energy Storage”.

V IMPACT: 2. What is the impact on other disciplines?

Energy storage. NEES’ current work has impacting battery technology in several ways. Thin film processes are one of these, where we have seen the application of ALD thin protection layers to a variety of battery technology studies, including its use to mitigate degradation mechanisms in composite electrode systems with both liquid and solid electrolytes. Indeed, projections from NEES solid state battery work promise significant advances in power-energy performance over current commercial thin film solid state batteries.

Electronics. Impacts of NEES’ solid state energy storage research can already be seen in electronics. High performance capacitors and batteries that decouple energy density and power density as developed in NEES are - in an industry-funded collaboration - on their way to use in advanced analog electronics, where 3D structures and controlled conformal synthesis can serve as enablers for Internet-of-Things applications, implanted biomedical devices, and beyond.

Computing. Another area of significant (perhaps even revolutionary) impact is in computing. Talin has adapted NEES' solid state battery configurations to serve as a nonvolatile analog memory device, essentially a redox transistor. Such devices are essential for widespread neuromorphic computing as used in artificial intelligence and machine learning applications. In a redox transistor, a voltage pulse is used to transfer Li ions from one electrode to the other, after which it the information is retained as alkali ion charge. Projections indicate that the precision synthesis of thin electrode and electrolyte layers, the patterning available in thin film fabrication, and the stability of ion charge once transferred into an electrode material all conspire to make this application of a solid state battery very promising.

Cross-disciplinary science. Finally we note the cross-disciplinary impact of NEES research, which has created new perspectives for PI's and their groups which herald from electrochemistry, materials science, solid state physics, materials chemistry, and beyond.

V IMPACT: 3. What is the impact on the development of human resources?

Science communications. NEES students and postdocs have enlarged their professional experience by involvement with Frontiers in Energy Research, DOE EFRC's newsletter and authoring of several articles in it. David Stewart, formerly posdoc and now research faculty, has served ably on the newsletter's editorial board and in management of the Early Career Network.

Career development. A significant fraction of NEESConnect events have been aimed at supporting career development for NEES students and postdocs, sometimes through a seminar and other times through a panel discussion. Some of the NEESConnect activities have mirrored the academic preparation available at UMD Engineering in its Future Faculty Fellow program, in which NEES students have participated.

Leadership development. NEES PI's have also gained experience as thrust leaders and generally as they participate in organizational issues facing NEES, much of which are shared with the PI's. This has also provided opportunity to think about other venues to new roles. A particular example is that of Professor Yue Qi, who has interacted in NEES before and since joining academia. NEES management saw clear signs of leadership in her. When she asked advice about taking on a new role at Michigan State Engineering, we encouraged her. She became the first Associate Dean for Inclusion and Diversity. Most recently she has accepted a chaired position at Brown University. Another example is that of Professor Sang Bok Lee, Deputy Director of NEES, who has taken over Directorship of the Maryland NanoCenter after its founding director Gary Rubloff (NEES Director) stepped down.

IMPACT: 4. What is the impact on physical, institutional, and information resources that form infrastructure?

The NEES EFRC has had a profound impact on the institutional environment at its lead institution, the University of Maryland. The **EFRC assumed a pivotal role in building the UMD research environment as a pillar of excellence in electrochemical and battery science and technology,** where UMD now boasts one of the largest funding bases for such R&D, ranging from BES science to ARPA-E and EERE technology. Another measure of this influence is the founding of the Center for Research in Extreme Batteries (CREB), founded by Chunsheng Wang (UMD, a NEES PI) with partners at ARL and NIST to focus on specific application areas having special requirements (e.g., temperature extremes, biomedical compatibility, etc.). This was followed by the establishment of the Maryland Energy Innovation Institute, designed and funded by the Maryland Governor and legislature and led by NEES Advisory Board member Eric Wachsman.

With the focus of its **solid state storage** thrust and the pivot in direction NEES took in its 2018 EFRC renewal proposal, NEES laid a strong foundation for the growing direction of solid state battery R&D. While NEES' embodiment of this has been focused on thin film synthesis, NEES PI's and their colleagues have also embraced solid state storage in the form of composite electrode and electrolyte materials, thus covering much of the solid state battery landscape.

NEES research was the driving force to create Rubloff's **ALD Nanostructures Laboratory** (ANSLab), designed specifically to address design and synthesis of electrochemical nanostructure and 3D architectures for solid state energy storage, electrode protection layers, selected materials synthesis and characterization of materials in these various structures. ANSLab contains unique facilities configured as an integrated facility comprising ALD/MLD processes for many materials, real-time/in-situ sensing and metrology in ALD using spectroscopic ellipsometry and downstream mass spectrometry, evaporation of alkalis and metals, ion sputtering, a host of surface analysis techniques, and battery assembly, testing, and post-operation forensics. ANSLab has also become a collaborative meeting place, where students and postdocs from several groups work on a steady basis.

V IMPACT: 5. What is the impact on technology transfer?

Impact on Technology Transfer

NEES' research achievements led to a steady increase in technology transfer related benefits, including significant industry-funded partnerships and intellectual property. The expertise and capabilities developed and demonstrated in NEES science have had very substantial benefit in terms of other funded programs - particularly with industry - and in intellectual property and startup opportunities. Here we summarize more recent items along these lines. More details is available from the NEES FY19 annual report.

Industry partnerships

- **SAFT Battery – CWang**. Goal to integrate S-C composite into existing Li-ion battery manufacturing processes, building on NEES advance in transforming long-chain sulfur into short-chain products in microporous carbon, covered with a solid-electrolyte interphase.
- **SAFT Battery - Rubloff**. Goals (1) mitigate LMO-LTO cell degradation using protection layers for start-stop batteries and (2) develop polymer electrolyte (with UMD collaborator Kofinas), protection layers, and cell integration.
- **Unifi Manufacturing, Inc.**; **Milliken & Company - YHWang & Hu.** Goal is "Meta Cooling Textile with Synergetic Infrared Radiation and Air Convection for Bidirectional Thermoregulation" (ARPA-E).

- **Point Engineering Co. (PEC) - Lee.** Goal is continuous production process of large area high quality anodized aluminum oxide (AAO) wafers and their thin film battery and sensor applications.
- **Trinity Rail Group - Hu**. Goal is "Design and Manufacture of Cellulose Nanofiber based Lightweight, Strong and Tough Structural Materials for Vehicle Applications" based on wood nanocellulose fibers developed by NEES.
- **General Motors - Qi.** Collaborates with GM scientists Xingcheng Xiao and Qinglin Zhang on two EERE-BMR awards modeling (1) morphology growth behavior in liquid and solid electrolyte, and (2) electrochemical-mechanical properties of solid electrolyte interphases in Li-metal batteries.
- **Liox Power, Inc. - CWang**. Wang, Liox and Saft seek to develop a 500 Wh demonstration unit for DoE/DoD evaluation, as partner companies on the ARPA-E RANGE project.
- **Murata-IPDiA - Rubloff**. IPDiA (France) is subsidiary collaborating to create very high power electrostatic capacitors, using ALD on AAO templates which in turn are fully integrated onto a Si electronics platform, recently funded (with collaborator McCluskey) for $981,633 over 3 years.
- **SK Innovation/PolyPlus Battery - Rubloff**, **Lee.** Goal is integrating solid electrolyte (sulfide glass with Li metal) into high power Li ion battery system to replace their current separator, funded through (1) SKI Mini-Satellite Lab at UMD and (2) industrial consortium with PolyPlus, together totaling about $600,000/yr.
- **Maryland TEDCO - Rubloff**. Goal is lateral configuration for a 3D solid state battery, comprised of multiple solid state batteries stacked on top of each other, fabricated and wired in a simple manufacturing process. Maryland TEDCO grant $115,000. supports prototyping, IP development, and market and cost analysis.

Intellectual property - patents filed and/or issued:

Here we summarize recent activity for non-provisional patents pending or issued. This does not include provisional applications or invention disclosures.

- **US Patent 8,980,216 - YHWang et al "Covalently Functionalized Carbon Nanostructures and Methods for Their Separation"**. This application was modified on 3/17/2015 and is currently under review. This work addressed the chemical functionalization of carbon nanotubes, a topic central to a sequence of important C-Si nanostructure papers that reflect NEES' insights into interfacial bonding and architecture of heterogeneous, multicomponent nanostructures. It is directed to carbon nanostructures, e.g., carbon nanotubes, methods of covalently functionalizing carbon nanostructures, and methods of separating and isolating covalently functionalized carbon. In some embodiments, carbon nanotubes are reacted with alkylating agents to provide water-soluble covalently functionalized carbon nanotubes. In other embodiments, carbon nanotubes are reacted with a thermally responsive agent and exposed to light in order to separate carbon nanotubes of a specific chirality from a mixture of carbon nanotubes.
- **US Patent 8,912,522 - Rubloff, Lee, et al "Nanodevice Arrays for Electrical Energy Storage, Capture and Management, and Method for their Formation".** This was originally issued on 12/16/2014. Their recent nanopore battery array publication in Nature Nanotechnology in 2014 then stimulated a CIP (Continuation in Part) of 8,912,522 under the same name, involving a Provisional 62/001,995 on 5/22/2014 extending IP coverage to nanostructures

with disconnected electrodes at each end of nanopores through issuance of a follow-on U.S. patent. The CIP has been named a finalist for the University of Maryland's Invention of the Year Award for 2014. Lee and Rubloff are currently exploring options for technology and manufacturing that can exploit the insights of the corresponding EFRC advances. This patent provides broad coverage for a portfolio of two terminal devices (batteries, capacitors, solar cells, thermoelectrics, etc.) which are formed as nanostructured devices in nanopores, allowing contacts at both ends of the pores or contacts brought to the same end. The original patent has been enhanced by a Continuation-in-Part that covers specifically the separated electrode structures in NEES' nanopore battery.

- **US Patent 10,826,065 - Rubloff, Lee, Hu, et al. "Protection Layers for Metal Anodes"**. Non-provisional application was filed 4/5/2017 as PCT/US2015/054083. US patent was issued 11/3/2020 for application 15/517.126. The invention relates to protecting Li and other reactive metal anodes using ALD inorganic layers, with benefit to capacity maintenance during cycling and lowering dry room costs.
- **US Patent Application - Rubloff, Lee, et al. "Staggered-Electrode Solid State Multibattery**. Non-provisional application was filed 1/3/2019. The Staggered-Electrode Solid State Multibattery discloses a multi-layered stack of planar solid state batteries designed for simultaneous high power and high energy, realized using a facile manufacturing process. A provisional 62/613861 was filed 1/5/2018, followed by a PCT application 012180 in 2019 which is pending. The Invention Report Number is 0820102-18-0009.
- **US Patent Application 18/021805 - CS Wang et al. "Low Cost Aqueous Hydrogel Electrolyte Systems with Wide Electrochemical Stability Window"**. Non-provisional application was filed 3/9/2018 as PCT/US2018/021805 and is pending. The invention relates to aqueous batteries that are achieved on hydrogel-like electrolyte systems.

V IMPACT: 6. What is the impact on society beyond science and technology?

Science communications. NEES people contributed articles to Frontiers in Energy Research, DOE EFRC's newsletter, over the years. More recent examples of which are listed below. Young scientists portraying the larger context of their research to a broader community holds promise for development of a more science-literate society.

Tailoring Efficiency: The Molybdenum Disulfide Story, Sahadeo (2018)
https://www.energyfrontier.us/content/tailoring-efficiency-molybdenum-disulfide-story
Meet a Better Battery: All Solid Materials Facilitate Safer Energy Storage, Sahadeo (2018)
https://www.energyfrontier.us/content/meet-better-battery-all-solid-materials-facilitate-safer-energy-storage
What Stress Means for Batteries, Stewart (2019)
https://www.energyfrontier.us/content/what-stress-means-batteries

General Public. The NEES website http://www.efrc.umd.edu/, maintained by the Maryland NanoCenter is a useful portal for information sharing and public relations. Articles intended for the general public are developed in the Maryland NanoCenter in partnership with the NEES Management team. Through this portal, NEES informs the public about Center mission and objectives, activities and announcements of events. It is also used to disseminate NEES news articles, publications and research highlights in order to reach the targeted audience with impactful research progress made in the EFRC.

NEES brochures. NEES continues to disseminate two high quality 8-10 page brochures that depict the achievements and impact of NEES programs. While the brochures were originally intended to inform scientists and program managers about NEES research, NEES recognized the larger value inherent in sharing these with other research institutions, legislators and their staff at the Federal and state level, and a variety of visitors. In 2018, NEES sent 30 brochures to legislators with a cover letter thanking them for their support of science, and updated the campaign by reaching out on Twitter to 14 specific legislators and coordinating with their staffers to publicize the contact between legislators and scientists. Frontiers in Energy Research wrote about the effort in a 2018 article on outreach.

V IMPACT: 7. Foreign Spending.

None.

VI CHANGES/PROBLEMS: 1. Changes in approach and reasons for change

Does not apply.

VI CHANGES/PROBLEMS: 2. Actual or anticipated problems or delays and actions or plans to resolve them

Does not apply.

VI CHANGES/PROBLEMS: 3. Changes that have a significant impact on expenditures

Does not apply.

VI CHANGES/PROBLEMS: 4. Significant changes in use or care of human subjects, vertebrate animals, and/or biohazards

Does not apply.

VI CHANGES/PROBLEMS: 5. Change of primary performance site location from that originally proposed

Does not apply.

VI CHANGES/PROBLEMS: 6. Carryover amount (Mandatory)

There is no carryover, funds have been fully spent at end of grant.

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