I. Introduction, Background and Progress:

The mission of the Energy Materials Center at Cornell (emc^2) was to achieve a detailed understanding, via a combination of synthesis of new materials, experimental and computational approaches, of how the nature, structure, and dynamics of nanostructured interfaces affect energy conversion and storage with emphasis on fuel cells, batteries and supercapacitors. Our research on these systems was organized around a full system strategy for:

- the development and improved performance of materials for both electrodes at which storage or conversion occurs
- understanding their internal interfaces, such as SEI layers in batteries and electrocatalyst supports in fuel cells, and methods for structuring them to enable high mass transport as well as high ionic and electronic conductivity
- development of ion-conducting electrolytes for batteries and fuel cells (separately) and other separator components, as needed
- development of methods for the characterization of these systems under operating conditions (operando methods)

Generally, our work took industry and DOE report findings of current materials as a point of departure to focus on novel material sets for improved performance. In addition, some of our work focused on studying existing materials, for example observing battery solvent degradation, fuel cell catalyst coarsening or monitoring lithium dendrite growth, employing in operando methods developed within the center.

The emc^2 addressed the goal statements above with coordinated and well integrated teams individually focused on (a) discovery and synthesis of novel materials, (b) operando analytical characterization of existing and novel systems, and (c) novel theoretical approaches as unique, ultra-precise interrogation methods to understand analytical and electrochemical observations.

The fundamental challenges and scientific research goals that we have addressed include:

Fuel Cells: (ᴍ) Higher performance electrocatalysts for fuel cells (ᴍ) Alkaline membranes for fuel cells that exhibit high conductivity for OH^- ions and long term durability (ᴍ) Conducting and stable (non-carbon) electrocatalyst supports with initial emphasis on nitrides and oxides.

Batteries: (ᴍ) Nanostructured materials for battery applications (ᴍ) Achieving high energy density and long term stability in Li/S batteries (ᴍ) Fundamentally understanding and eliminating unstable electrodeposition and dendrite growth to enable the use of metal anodes in batteries (ᴍ) Enabling “beyond lithium” secondary battery systems including those based on Na, Mg and Al (ᴍ) High performance supercapacitors integrating double layer and pseudocapacitive storage.

Theory: (ᴍ) *In silico* design, synthesis and characterization of organic materials for battery and supercapacitor applications (ᴍ) Developments of joint density functional theory (JDFT) for the *ab initio* description of electronic systems in contact with molecular liquids, GASP (generic algorithm for structure prediction) and other methodologies, and their application to energy conversion and storage systems (ᴍ) Development of microscopic effective theories (METs) for the study of electrocatalysis.

During the past 5 years we made great strides in the development of better performing ORR electrocatalysts [I.1-I.6], alkaline membranes [I.7-I.9] and catalyst supports [I.10-I.15]. We also made significant advances in anodes,

which followed our early work [I.16, I.17] on ordered intermetallic phases [I.18-I.22] and was later coupled to our combinatorial efforts [I.23-I.27]. We identified a number of anode electrocatalysts with enhanced performance towards oxidation of formic acid [I.28-I.30], and other small organic molecules [I.18, I.21, I.31].

Our work on batteries was characterized by highly integrated efforts such as the "Li/S Initiative" which helped provide the fundamental knowledge base required to enable such a technology [I.32-I.37]. We have carried out extensive work on oxide-based and metallic anode materials [I.38-I.45] whose performance and stability could be dramatically enhanced by nanostructuring and surface modification. We have made detailed mechanistic studies, using *operando* X-ray based methods, of conversion materials such as Mn_3O_4 [I.43] and germanium nanowires during the charge/discharge processes [I.46-I.48].

We carried out extensive computational and experimental/synthetic work on the use of organic, inorganic and carbon-based systems for batteries and supercapacitors [I.49-I.59]. This enabled the development of well-defined design criteria and performance metrics.

The work on complex oxides impacted both fuel cells and batteries and was closely coupled to our theoretical and computational studies. One of the main accomplishments, which involved a very close coupling of theory and experiment, dealt with the effects of epitaxial strains for tuning energy levels and band gaps, using $SrTiO_3$ as a test case, which provided a great deal of insight [I.60, I.61].

In the area of theory and computation, we made great strides in developing and utilizing JDFT [I.62-I.64] for computational electrochemistry, and in a genetic algorithm for structure prediction (GASP) [I.65] for materials prediction and microscopic effective theories (METs) for the study of electro- and photo-catalysis.

In the area of novel experimental methods, we made tremendous progress in the development of *in situ* and *operando* methods including advanced X-ray based methods [I.18, I.21, I.25, I.43, I.66], multidimensional DEMS (differential electrochemical mass spectrometry) for fuel cells and batteries [I.67-I.71], conducting probe and other AFM based methods [I.72], advanced TEM methods [I.1, I.4, I.6, I.22, I.33-I.37, I.73-I.76] including *in situ*/*operando* electrochemical liquid cells [I.76] and specimen-chamber-free SEM (air SEM).

Name	Department	Expertise
Héctor Abruña	CCB	Electrochemistry
Lynden Archer	Chem. E.	Transport in hybrid materials
Tomás Arias	Phys.	Theory
Joel Brock	App. Phys.	X-ray methods
Geoff Coates	CCB	Polymer synthesis
Frank DiSalvo	CCB	Solid state materials
William Dichtel	CCB	Organic/inorganic synthesis
James Engstrom	Chem. E.	Surface science
Craig Fennie	App. Phys.	Theory
Emmanuel Giannelis	Mat. Sci.	Composite materials
Tobias Hanrath	Chem. E.	Nanomaterials
Richard Hennig	Mat. Sci.	Computational Mat. Sci.
Lena Kourkoutis	App. Phys.	Cryo-TEM
John Marohn	CCB	Scanned probe methods
David Muller	App. Phys.	Electron microscopy
Jiwoong Park	CCB	Spectral imaging
Richard Robinson	Mat. Sci.	Nanomaterials synthesis
Darrell Schlom	Mat. Sci.	MBE deposition
Jin Suntivich	Mat. Sci.	Time-resolved stimulated Raman spectroscopy
Bruce VanDover	Mat. Sci.	High throughput methods
Ulrich Wiesner	Mat. Sci.	Block co-polymers
David Zax	CCB	Solid state NMR

Table I.1: emc² Affiliated Faculty

We had a world-class interdisciplinary research team that encompassed all the relevant fields and expertise necessary to aggressively pursue our research agenda. The team included faculty from Chemistry and Chemical Biology; (CCB), Physics; (Phys.), Materials Science; (Mat. Sci.),

Chemical Engineering; (Chem-E.) and Applied Physics; (App. Phys.) The specific faculty involved, their affiliation and general areas of expertise are presented in Table I.1. The PIs have a long history and proven record of effective collaborations. Of the 17 original faculty, 14 have collaborated with 2 or more other center members on EFRC funded publications, and 6 of our 10 most cited papers are collaborations. In addition, we have 46 publications with 2 or more PIs as co-authors.

II. Detailed Achievements

A. Fuel Cells:

A. ORR Electrocatalysts: We have studied, in detail, the ORR with electrocatalysts based on core/shell structures of Pt with first row transition metals including Fe, Co, Ni and Cu. [FC.1-FC.6] Through the use of electron microscopy with elemental mapping (**Muller**), we have established that, in all cases, the active form of the catalyst is composed of a core/shell structure in which the core is composed of Pt/(Fe, Co, Ni or Cu) and the shell is a Pt layer 2-3 atoms thick [FC.5]. In the case of Pt_3Co we showed that there are significant differences in stability and activity depending on whether the core is an alloy (disordered) or an ordered intermetallic (which has a slightly smaller lattice constant) [FC.1]. In fact, the catalyst is more active (>300%) and the activity is maintained over much longer times only when the core is ordered [FC.1]. (Fig. FC-1)

Dealloying of Pt-metal catalysts can enhance electrocatalytic activity over pure Pt, and the resulting structure and composition are a function of the starting catalyst composition, the method of dealloying, the initial crystal structure (random alloy or ordered intermetallic), and the morphology of the dealloyed product. In the case of Cu_3Pt we have compared the effects of dealloying by electrochemical and chemical means. While both methods give rise to materials that exhibit higher activity than Pt/C, chemical dealloying (in nitric acid) gave rise to more active and more durable (stable activity) electrocatalysts [FC.1-FC.7].

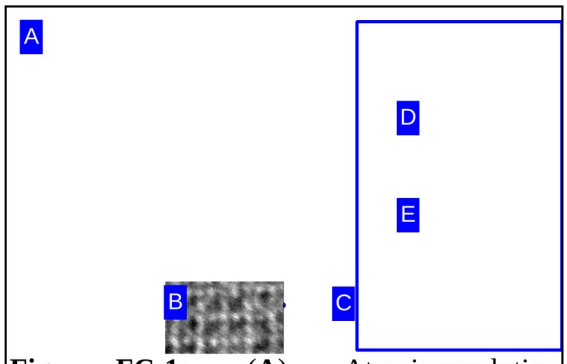

Fig. FC-1: (**A**) Atomic-resolution ADF-STEM image of Pt_3Co/C-700 (ordered intermetallic core). The inset shows the projected unit cell along the [001] axis. (**B**) A crop of the super lattice feature from (**A**). (**C**) Simulated ADF-STEM image of $L1_2$ ordered Pt_3Co along [001]. (**D**) ORR polarization curves in O_2-saturated 0.1 M $HClO_4$, Rotation rate, 1600 rpm; Sweep rate, 5 mVs-1. (**E**) Mass activities for Pt/C, disordered Pt_3Co/C-400 and ordered Pt_3Co/C-700 at 0.85 and 0.9 V.[Ref FC.1]

Muller and **Abruña**, using a TEM grid as the working electrode in an electrochemical cell and combining it with newly developed, atomic-resolution electron spectroscopy techniques [FC.8], and 3D imaging by electron tomography [FC.9], have shown that Pt-Co fuel cell catalysts coarsen during potential sweeps between +0.6 V to +1.0 V for 30,000 cycles (simulating the life of an operating fuel cell). For example, in Fig. FC-2, gold-colored clusters show the starting position of a Pt_3Co nanoparticle catalyst, and the red-colored clusters show their final positions and shapes. Our results indicate that while both Ostwald ripening and coalescence play important roles in the loss of catalytic activity, the latter appears to play a dominant role on carbon supports [FC.8].

Muller and Abruña designed and are exploiting a novel electrochemical TEM liquid cell (Fig. FC-3) to determine the fundamental limits of operation and degradation of catalyst nanoparticles and their supports, and especially the interaction between supports and nanoparticles. Preliminary *in situ* electron microscopy during electrochemical cycling suggests that the carbon support corrodes most rapidly at the nanoparticle contact, and at constrictions. Such *operando* studies are critical for understanding corrosion processes and increasing durability and represent one of the Center's unique capabilities.

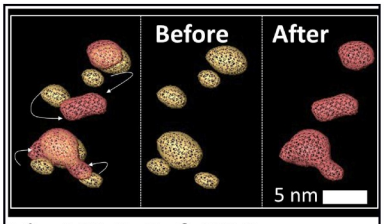

Fig. FC-2: Ref. FC.9

The above findings on Pt alloys and compounds are exciting and suggest new possibilities in catalyst design.

B. Combinatorial search of anode materials: We have developed high throughput combinatorial methods to accelerate the discovery of electrocatalysts with emphasis on anodes. **Abruña, DiSalvo, Hennig** and **van Dover** developed methods to deposit (via multi elemental sputtering onto 3" Si wafers) compositionally graded thin films and to electrochemically characterize the entire films to identify compositions that are most active for the oxidation of small organic molecules such as methanol and ethanol. A systematic study of Pt doped with Sn, Ta, W, Mo, Ru, Fe, In, Pd, Hf, Zn, Zr, Nb, Sc, Ni, Ti, V, Cr, or Rh, revealed high activity toward MeOH oxidation for the Pt-In, Pt-Sn and Pt-Zn systems at unexpectedly low doping concentrations (~3%). These materials exhibited activity comparable to the well-known Pt-Ru system at 30% Ru [FC.10]. We believe that such activity is due, at least in part, to the nature of surface oxides formed under the operating conditions.

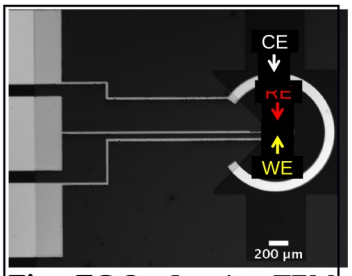

Fig. FC-3: *In situ* TEM electrochemical cell.

A study of Pd-Rh-Ta phases demonstrated the importance of electrochemical pretreatment to activate the surface [FC.11]. After a short bias to negative potentials, a Pd-Rh-Ta ternary system exhibited high activity for methanol oxidation. These observations raise fundamental questions about the surface composition, structure and chemistry that underlie the observed activity, and suggest that the development of lower-cost/high-performance catalysts is possible [FC.12].

As part of the combinatorial efforts, we developed a scanning minicell that allows for the electrochemical interrogation of specific areas within a combinatorial library while retaining the integrity of the sample. We have also developed a novel and highly efficient method for rapidly mapping structural information to reveal known phases and new phases in combinatorial films using high-energy synchrotron X-rays [FC.13]. Most recently, we designed, built and installed a holder for sputtering metal thin films onto an array of 16 glassy carbon slugs allowing for the generation of an array of metal compositions. Once sputtered, the glassy carbon slugs can be inserted into an interchangeable-disk/ring electrode tip allowing rigorous RDE and RRDE examination of the catalyst films.

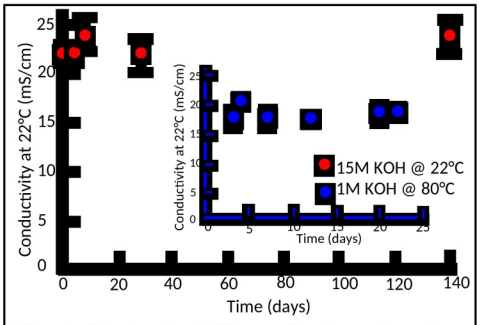

Fig. FC-4: Stability of phosphonium polymer under basic conditions.

C. Alkaline membranes: **Coates** and **Abruña** have developed several classes of alkaline anion exchange membranes (AAEMs) that exhibit high hydroxide conductivity, while maintaining their robust mechanical strength [FC.14-FC.17]. Cross-linked polymer networks that contain trimethyl ammonium cations were prepared via ring opening metathesis polymerization (ROMP) from a bifunctional cyclooctene monomer and cyclooctene (COE). Remarkably, the optimized polymer had ionic conductivity comparable to Nafion®, the predominant PEMFC electrolyte. These polymers are readily soluble in organic solvents, but insoluble in water, which make them ideal candidates for both polymer electrolyte membranes and for the ionomer-catalyst inks needed to fabricate a fuel cell.

However, recent reports highlighted the facile degradation of ammonium cations under basic conditions [FC.18] and the investigation of other cationic moieties was pursued [FC.19]. We developed a new class of AAEMs that consisted of tetrakis(dialkylamino)-phosphonium cations appended to polyethylene. Polymers containing the phosphonium cations had high conductivity and did not exhibit measurable degradation after being subjected to 15M KOH for 20 weeks or 1M KOH at 80 °C for 22 days, as shown in Fig. FC-4.

We also investigated the sensitivity of membrane conductivity and durability to the reaction of OH^- with CO_2, to generate carbonate (CO_3^{2-}). We studied carbonation/anion-uptake in a quaternary ammonium based AAEM using the electrochemical quartz crystal microbalance (EQCM) technique, by monitoring changes in the resonant frequency (Δf) and the motional resistance (ΔRm) of the resonator. Changes in Δf and ΔRm indicated the incorporation of CO_3^{2-}/$HCOO^-$ into the film and that both could readily displace OH^- from the film. However, the anion exchange between CO_3^{2-}/$HCOO^-$ and OH^- was found to be reversible and there was no carbonate precipitation [FC.20].

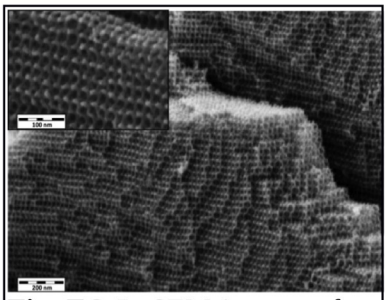

Fig. FC-5: SEM images of an ordered mesoporous nitride prepared from a triblock polymer – oxide precursor by ammonolysis.

D. Catalyst supports: Carbon supports corrode in operating fuel cells [FC.21], and although the corrosion rate can be slowed by adding system controls, catalyst supports that have lower corrosion rates than carbon will be required for long-lasting fuel cells. **DiSalvo**, **Wiesner** and **Abruña** have found that doped transition metal oxides and nitrides show considerable promise as conducting catalyst supports. We developed two routes to such mesostructured materials using block co-polymers (Fig. FC-5) or packed polymer sphere opals as templates to produce a variety of mesoscale morphologies, or by nitriding oxides without organic templating [FC.22-FC.26].

Transition metal nitrides are especially promising as supports since they have conductivities that are 3 or more orders of magnitude higher than carbon black, and since they are already known to be durable as coatings on fuel cell bipolar plates [FC.27]. Our initial corrosion studies of nitrides immersed in aqueous acids or bases at 80 °C have shown low or negligible corrosion rates, depending upon nitride composition. However, both pH and the acid anion play active roles [FC.26]. When Nafion is dissolved in an alcohol/water solution, to mimic the fuel cell environment, corrosion rates are zero within experimental error (currently at less than 1 Å of surface nitride lost or converted/day).

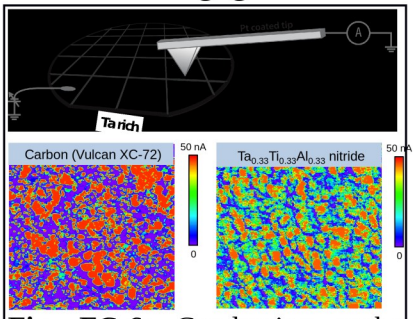

Fig. FC-6: Conducting probe AFM schematic and conductance maps for Vulcan XC-72 and a $Ta_{0.33}Ti_{0.33}Al_{0.33}$ nitride.

Initial screening of composition-spread thin nitride films containing 3 metals, by both corrosion tests and by conductive probe atomic force microscopy (cp-AFM by **Marohn**), showed improved performance over simple binary compositions and with conductances comparable to that of Vulcan XC-72, the standard fuel cell carbon support (Fig. FC-6) [FC.28].

E. Theory: **Hennig** and **Arias** have developed atomic level understanding of the observed behavior at fuel cell electrodes. The intent was to develop theory that would generate predictive insights that will provide guidelines for the design of better catalyst/support systems. DFT calculations (**Hennig**) provide insights into the changes of bulk and surface electronic states as a function of composition and structure. The unique JDFT developed by **Arias**, allowed the calculation of surface electronic states and chemical reactions in contact with a supporting electrolyte.

B. Batteries and Supercapacitors:

Developing efficient electrical energy storage technologies [B.1-B.6] batteries [B.2-B.4] and supercapacitors [B.5, B.6]) is a national imperative in our transition towards a sustainable energy portfolio. Grid integration of inherently intermittent renewable energy resources and broad deployment of electrified transportation are critically dependent on advances in performance, durability, safety, and cost of electrical energy storage [B.1]. Breakthroughs in battery performance are predicated upon coordinated improvements in anode, cathode and electrolyte materials, as well as improved fundamental understanding of and control over metal insertion and charge transfer and transport in the electrodes and electrolyte. Structural changes must be understood and controlled to achieve the required step-change advances in performance, cost, and lifetime. Future technologies must also utilize more earth-abundant materials to manage cost and to ensure deeper market penetration. We see tremendous opportunities in moving “beyond lithium” as well as the use of sodium, magnesium, aluminum and other metals. Even modest changes in performance and lifetimes in storage technologies based on any of these chemistries would result in dramatic changes in the electrical energy storage technologies landscape.

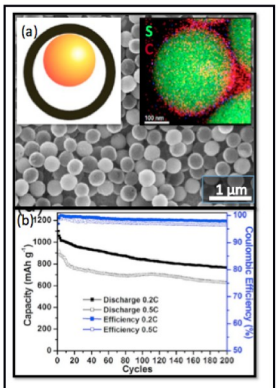

Fig. B-1: (a) Sulfur-based cathodes based on yolk-shell structures (b) Charge/discharge profiles.

For supercapacitors, their capacity can be dramatically enhanced by utilizing the so-called “pseudocapacitance” along with the electrochemical double layer (EDL) capacitance [B.7]. The discovery and development of new materials capable of storing multiple electrons per formula unit and/or lower mass per electron transferred (providing high capacity), with fast charge transfer kinetics (and thus high power), made of abundant/inexpensive elements, and that can be tuned by synthesis, are already having an impact [B.6]. Sophisticated strategies based on self- and directed- molecular assembly for configuring these materials into explicit, three-dimensional architectures are expected to lead to supercapacitors with storage capacities that rival those of today’s batteries, but capable of very fast charge/discharge rates.

Our team integrated researchers with complementary expertise in materials synthesis, structural and chemical analysis of interfaces, electro- chemical characterization of batteries and battery components and computation and simulation of the delicate interplay between materials and interfaces. A unique strength of our approach is the synergistic

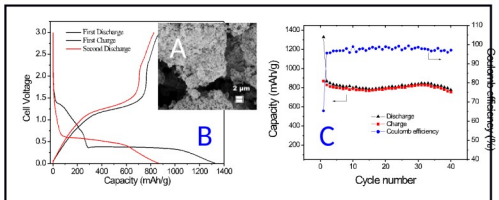

Fig. B-2: Nanostructured Mn_3O_4 anodes: (A) SEM, (B) voltage-capacity, and (C) cycling performance. Ref. B.23

integration of research on all battery components in *one team at one location* with a history of successful collaborations.

A. Cathodes: One of the most attractive candidates for next-generation electrical energy storage is the Li/S system by virtue of the high theoretical capacity of the sulfur cathode, 1675 mAh/g and energy density of the Li/S system (2.6 kWh/kg). To realize such a capacity reversibly, safely and over long times, the cathode must be structured to ensure electrical contact to the sulfur, while polysulfides formed during cycling remain immobilized. We organized a center-wide integrated effort, the "Lithium Sulfur Initiative", to address these challenges. Our advances in creating nanostructured sulfur-based cathodes include: cross-linked polyacrylonitrile/Li_2S_x carbon composites, [B.8] Li_2S in a porous carbon matrix, [B.9] hollow carbon@sulfur composites, [B.10] polyaniline coated yolk-shell structures, [B.11] (Fig. B-1) and amylopectin wrapped graphene oxide/sulfur composites [B.12]. Electrochemical characterization of these nanostructured sulfur composites revealed dramatic improvements in cycling performance for over 200 cycles and stable charge capacities in excess of 750 mAh/g at 0.2C [B.12]. We also found that the solvent plays a key role on the electrochemical performance of the Li-S battery cathode. X-ray absorption spectroscopy revealed that reduced sulfur species chemically react with carbonate-based solvents, making this class of solvents inappropriate for elemental sulfur cathodes of lithium batteries [B.13].

We have integrated computational methods and advanced *operando* X-ray diffraction and absorption spectroscopy to better understand the fundamental electrochemical mechanisms in Li/S charge/discharge processes [B.14]. We coupled insights from these experiments with statistical mechanics and *ab initio* calculations to predict equilibrium composition and structure of Li-S [B.15]. (See Theory section) Coupling sulfur-composites to hierarchical carbon architectures presents a promising route to create 3-D structures that mitigate dendrite formation. Previous work to create 3-D gyroids from block-copolymers [B.16] and mesoporous carbon foams [B.17, B.18] has demonstrated refined structure control spanning several length-scales and establishes a promising point-of-departure for the work discussed below. We also demonstrated how computational screening and design can be integrated with synthesis and ultimately electrochemical characterization to accelerate the discovery of high-performance organic materials for electrical energy storage [B.19-B.22].

B. Anodes: Our advances in developing next-generation anode materials and understanding their electrochemical performance have leveraged access to unique *operando* characterization expertise established in the center. We have created nanostructured Mn_3O_4 anodes with high capacity and cycling performance [B.23] (Fig. B-2) and unraveled the mechanistic complexity of the conversion reaction in Mn_3O_4 anodes using operando X-ray diffraction and absorption spectroscopy [B.24]. (See also Section E) Similarly, *operando* X-ray diffraction and extended X-ray absorption fine structure (EXAFS) spectroscopy provided new insights into the evolution of the structure of Ge nanowire anodes during cycling with lithium [B.25]. We have developed scalable fabrication

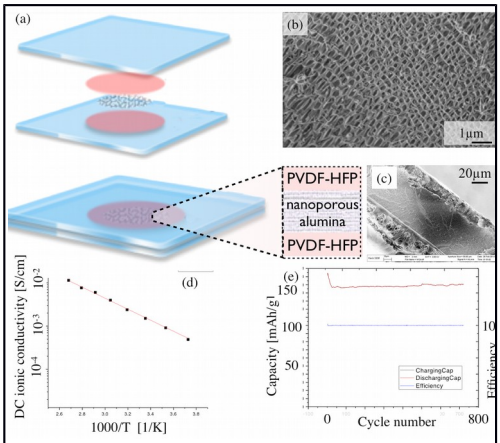

Fig.B-3: (a) Schematic of a laminated nanoporous electrolyte/separator. SEM images of (b) internal layer and (c) cross-section. (d) ionic conductivity of the laminated electrolyte/separator infused with propylene carbonate/LiTFSI (e) Cycling performance for a Li/electrolyte laminate/$Li_4Ti_5O_{12}$ cell.

methods to create Si nanowire anodes directly on Cu current collectors [B.26]. We synthesized Si-C nanocomposites and analyzed their application as anodes in Li-ion batteries [B.27]. We have demonstrated the synthesis and characterization of high voltage spinel anode materials based on carbon coated $Li_4Ti_5O_{12}$ [B.28] and the fabrication of carbon/Co_3O_4 nanocomposites, [B.29] Co_3O_4 needles, [B.30] TiO_2 hollow nanoparticles, [B.31] and coaxial SnO_2@carbon hollow nanospheres [B.32]. Battery research in emc^2 was integrated in a workflow and feedback loop connecting initial materials discovery in the lab to development of nanofabrication methods at commercially relevant scales. The latter was evidenced by our demonstration of how novel electrode materials can be deposited on the current collector via electrophoretic deposition [B.32].

C: Electrolytes and separators: Realization of reliable next-generation secondary batteries, such as Li-S will require advances in understanding and controlling of electro-deposition at the lithium anode. Despite intensive studies, there are no general strategies for producing a lithium anode that can be cycled stably and safely. Motivated by theory, we created a family of structured electrolytes based on hard nanoparticles grafted with oligomers and salts [B.33]. These hybrid particles spontaneously assemble to form porous media electrolytes with high Li^+ transference numbers and are found to suppress Li dendrite nucleation [B.34]. We have advanced this concept to produce nanoporous electrolyte-separator membranes comprised of laminated polymer/alumina nanoporous structures infused with a liquid electrolyte (Fig. B-3) and demonstrated stable cycling for more than 1000 cycles in lithium cells [B.35]. These ideas have most recently lead to the creation of novel nanoporous hybrid electrolytes based on mixed salts, which when deployed in symmetric lithium batteries yield cells that show no evidence of short circuits over hundreds of cycles.

C. Complex Oxides:

The overarching goal of this thrust was to understand and control, via atomic-scale materials engineering, the interplay between the diverse microscopic degrees of freedom prevalent in complex oxide systems in order to create new "designer" heterostructures for electrocatalysts, conductive supports for fuel cell electrocatalysts, cathodes and supercapacitors for energy storage, i.e., to create a "*new energy materials by design*" paradigm.

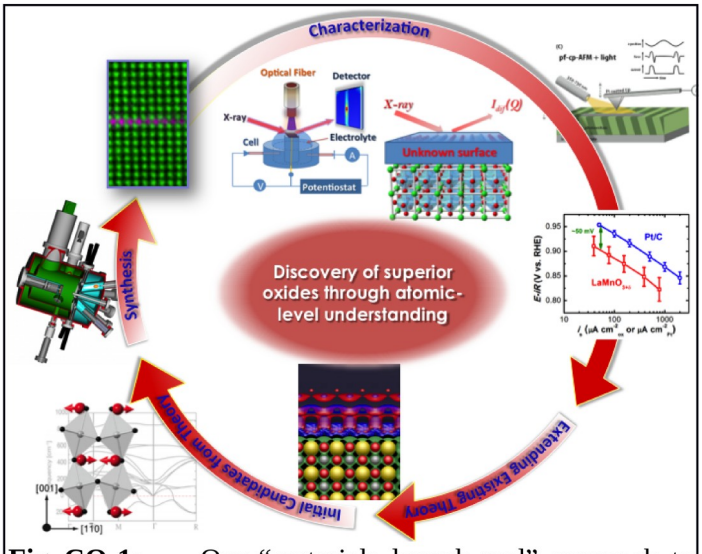

Fig. CO-1: Our "materials launch pad" approach to understand and create new "designer" heterostructures for electrocatalysts. The collaborative network pictorially represented has been shown to work in our existing EFRC.

Complex oxide materials are essential to numerous energy generation, storage, and conversion functions within fuel cells, batteries, and supercapacitors. Crucial atomic-level knowledge of the structure of the active surfaces of complex oxides under conditions of use *(operando)* remains

elusive and largely unknown, yet all theoretical/computational models rely on this knowledge as a staring point. Knowing the real surface structure and how it interacts with surrounding fluids, ions, and gases is a challenge that, today, is beyond any one theoretical or experimental technique. Removing the limitations arising from such lack of information, however, would facilitate the deliberate (non-Edisonian) identification and design of superior materials for energy applications. This would enable emerging "*materials-by-design*" methodologies to be applied to the development of superior complex oxides that could dramatically enhance the performance of numerous energy generation and storage technologies. Our approach to develop the key structure-function understanding that links the active structure to the relevant electrochemistry calls for close integration of theory, synthesis, and characterization into a "materials launch pad," thereby closing the loop that often exists between the powerful theoretical and computational methods that model chemical reactions on *idealized* single-crystal surface structures and the characterization of polycrystalline materials under *real* electrochemical conditions (Fig. CO-1).

A unique aspect of this materials launch pad was our ability to synthesize, with atomic precision, atomic-scale, single-crystal materials via molecular-beam epitaxy (MBE), and to characterize and theoretically model (See Theory Section below) these materials under electrochemically relevant conditions. Materials synthesized via bulk techniques often contain many kinds of surfaces, grains, defects, etc., thereby complicating the extraction of the key features relevant to the electrochemistry. Our thin film approach opens up new routes to understanding the key structure-function relationships (that are not possible with bulk techniques) by providing "control knobs" to tune and control the structure of a material. This not only allows for the systematic exploration of structure-function relationships that are not easily extracted from bulk polycrystalline materials, but also of phases/structures that do not exist in the bulk phase diagrams of materials. For example, using these materials "control knobs" the relevant electrochemical structure-function relationships can be determined as a function of (1) crystallographic orientation and (2) controlled perturbations of the atomic spacing, *e.g.*, via strain. These structure and performance data are compared with calculations from *ab initio* theoretical methods that are able to accurately model electrochemistry between a known surface and a surrounding fluid (*e.g.*, water). This closed loop approach allows us to clearly identify the key structural features existing under real electrochemical conditions. With such understanding an interesting question arises—can we turn around and design a material/surface that optimizes these key features, e.g., can we actually identify/design a material that is naturally "loaded" or "trained," with the characteristics that would make it an effective electrocatalyst?

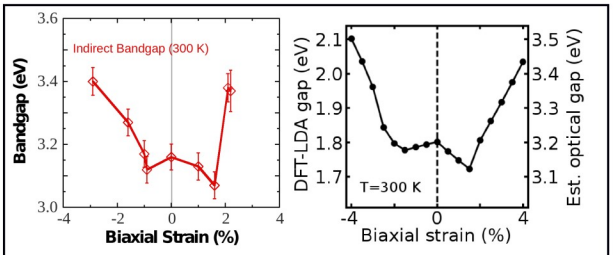

Fig. CO-2: A comparison of the effect of biaxial strain on (001) $SrTiO_3$ from experiment (left) and theory (right). In extending the first principles calculations to room temperature, Ref. [CO.4] was used.

Our programmatic focus was to identify

and investigate complex oxides for (1) electrocatalysts that can replace platinum in the oxygen reduction reaction (ORR) of fuel cells, (2) conductive supports for fuel cell electrocatalysts that are stable at high potentials; (3) cathodes in lithium-ion, and "beyond lithium" (i.e., Na, Mg, Al) batteries; and (4) supercapacitors for energy storage.

Our integrated approach to understanding and designing new atomic-scale materials relevant for electrochemical applications was a bold, fresh approach, and one that, we successfully showed to work in unraveling the details of photocatalysis on the surface of $SrTiO_3$. The discovery of $SrTiO_3$ as an extremely stable photocatalyst [CO.1] dates back almost 4 decades to shortly after the discovery of anatase (TiO_2) for this use [CO.2]. $SrTiO_3$ had the key advantage that water splitting of both oxygen and hydrogen occured without the need of an applied voltage [CO.1]. Its optical gap (3.2 eV), however, is too large for efficient light harvesting of the solar spectrum. As a starting point, we had proposed a new route, via strain engineering, to alter the band gap and band edges of $SrTiO_3$, and made various predictions (**Fennie**) using chemically intuitive structures, albeit ignoring the real electrochemical environment in use (See Theory Section for additional details) [CO.3]. Next, we synthesized (**Schlom**) and structurally characterized (**Muller**) the epitaxially stained $SrTiO_3$ thin films that our theory team suggested, and measured the optical gaps at room temperature in air. The agreement between the prediction and our experiments was quite remarkable (Fig. CO-2).[i]

Next, we studied $SrTiO_3$ under real electrochemical conditions (**Abruña**, **Brock**). What we found experimentally was something that could not be described by our previous theory, which had assumed the chemically intuitive vacuum structure. Turning back to theory, this time modeling the real water-$SrTiO_3$ interface structure using JDFT, we found that the activated surface of $SrTiO_3$ has a structure akin to anatase [CO.5]. We found a strong tendency for water to structure ("freeze") at the interface, and remarkable agreement, *without any adjustable parameters*, between our predicted and the observed X-ray crystal truncation rod (CTR) data (Fig. CO-3). The real water-$SrTiO_3$ interface was completely devoid of strontium and it appears that the role of the $SrTiO_3$ is simply to alter the lattice spacing of the anatase-like surface layer performing the photocatalysis, thus enabling water splitting to take place in the absence of an applied bias. Based on this approach we were able to: (✓) Employ theory as a guide to experiment and understand how strain, orientation, and dimensionality can be used to control the band gap and band edge energies of $SrTiO_3$ in order to establish general design rules for making a better photocatalyst (**Fennie**, **Schlom**) [CO.3, CO.6] and (✓) determine the surface structure of single-crystal (001)

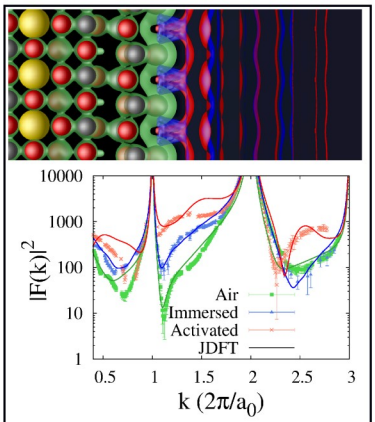

Fig. CO-3: JDFT prediction and experimental determination of the microscopic structure of the water/$SrTiO_3$ interface. Density map of activated surface (top): atomic locations (balls), electron density (green), oxygen site density (blue), proton site density (red). CTRs (bottom): parameter-free predictions (curves), experiment (data with error bars). From Ref. [CO.5]

$SrTiO_3$ in water under photocatalytic operating conditions using CTR diffraction analysis (to determine the electron density) in an electrochemical cell at Cornell's synchrotron (**Brock**, **Abruña**) in combination with JDFT (**Arias**) that accurately included water to narrow down and identify the only surface structure compatible with both theory and experiment under operating conditions (of particular importance were electrode potential induced changes in the surface structure), thereby further refining the design rules for making a better photocatalyst.

D. Theory:

The Energy Materials Center at Cornell (emc^2) experienced returns on its investment in its theoretical and modeling efforts exceeding even the original high expectations. As the description of the other thrusts attest, these efforts were transformative of energy-science over the entire purview of the Center, from batteries to complex oxides to fuel cells. We also opened new vistas in the underlying fundamental theories of energy-materials performance including development of the first practicable, first principles *ab initio* approach to electrochemical interfaces based on JDFT; development of the novel, genetic algorithm for structure prediction (GASP) tuned specifically to explore the stoichiometric phase spaces relevant to batteries and pseudocapacitors; and development of new microscopic effective theories (METs) for design and continuous tuning of novel electro- and photo- catalysts. Such game-changing progress was uniquely enabled by a center like the emc^2 to focus fundamental theorists on the pertinent energy-specific issues.

Indeed, we made significant progress in meeting the research challenge to "develop and employ theoretical and modeling platforms to understand the fundamentals underlying interfaces and their relationships to energy generation, conversion, and storage." As mentioned above, our theoretical/modeling efforts were deeply integrated into all ongoing science efforts within the emc^2. This section focuses on the transformative theory/modeling platforms developed by the Center and how these platforms specifically impacted energy-science, in general, and Center activities, in particular.

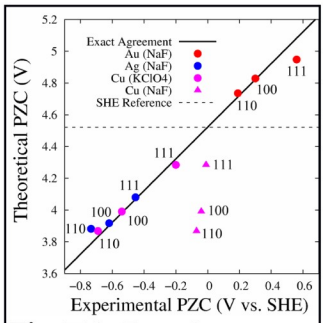

Fig. T-1: Experiment vs. Theory for potentials of zero charge E_{PZC}.

A: Joint density-functional theory (JDFT): Among the greatest interfacial challenges in energy science, from a theory modeling point of view, is the interface between a solid system and a liquid electrolyte. Predictive *ab initio* electrochemistry, JDFT, gives a fully rigorous and, in principle, exact treatment of the free-energy and ensemble averages associated with thermodynamic equilibrium between a liquid electrolyte environment and a system described at the quantum level in terms of *only* the electron density of the quantum system and the atomic site densities for the species comprising the electrolyte [T.1, T.2]. This approach dramatically reduces the computational complexity of sampling the phase space of species configurations in the electrolyte environment. With emc^2 support, this approach was developed from proofs of underlying theorems and a few demonstration calculations [T.1, T.2] into a complete framework for *ab initio* electrochemical calculations [T.3-T.10]. This included the generation of (**XX**) new, accurate classical DFTs to describe the liquid water and other solvent environments [T.6, T.7]; (**XX**) much more accurate coupling functionals between the liquid and the electronic system [T.8], with much clearer understanding of the roles of electrostatic, cavitation and van der Waals interactions [T.4, T.11]; (**XX**) development of a hierarchy of different levels of approximation

suited to enabling a much wider range of studies (full JDFT [T.8], non-local linear response JDFT [T.11], and non-linear PCMs (Polarizable Continuum Models) [T.4]). It also generated, a clear understanding of the proper thermodynamic mapping between electrochemical observables (*e.g.*, electrode potential) and their corresponding *ab initio* computables (*e.g.*, "Fermi level"), enabling studies of the impact of the applied potential on electrochemical processes [T.3]. The value of these developments is evident from the Center-wide impact that JDFT had, enabling calculations that would otherwise have been impossible or inaccurate with state-of-the-art methods.

These developments were made available to the wider community through the Center-sponsored JDFTx software package [T.10]. We also implemented JDFT extensions into the widely used density-functional code VASP [T.12], with all software and associated documentation freely available as a VASP code module [T.13].

1.Fundamental electrochemical phenomena: We validated our JDFT *ab initio* approach against experimental measurements of a number of fundamental electrochemical phenomena. Fig. T-1 compares our predictions to experiment for the potentials of zero charge (PZCs) of the low index faces of a series of metals. The data falling near the solid line of unit slope shows that we obtain excellent agreement (better than 0.1 eV), sufficient to allow our *theory* to establish that one set of *experim*ental results for Cu (in $KClO_4$ electrolyte) were reliable, whereas another set of experiments (using NaF) were not [T.3].

JDFT also predicted the structure of the electrochemical double layer to sufficient accuracy to allow predicting the voltage dependence of differential capacitances. Fig. T-2 compares the predictions of various theories; full JDFT (red), standard PCM (magenta), Gouy-Chapman-Stern model (green), Gouy-Chapman-Stern with best-fit parameters of highly unphysical values (blue). Only JDFT simultaneously demonstrates the correct minimum capacitance value, minimum width and steep potential rise. Competing, state-of-the-art approaches (magenta) show no trace of these phenomena.

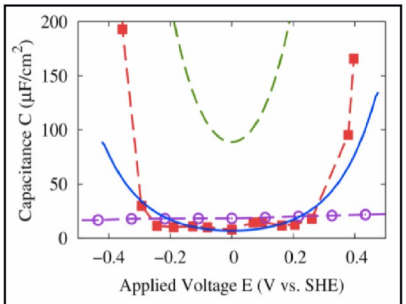

Fig.T-2: Differential capacitance versus applied potential for different computational models.

Finally, JDFT accurately predicted, from first principles, phenomena such as the underpotential deposition of Cu on Pt [T.14]. In all of these examples, we could compare the results of our calculations directly with experiment, providing unambiguous testing and validation.

2. JDFT enabled science: (ᵡᵡ) *Solid-liquid interfaces:* Such interfaces are at the heart of virtually all electrochemical systems and energy generation and conversion technologies and generally present a major challenge to many materials simulation methods. A realistic first-principles computational study of such systems entails the inclusion of solvent effects. We applied JDFT to study the effects of solvent on the surface energies of different facets of metallic and semiconducting nanocrystals [T.12, T.15] and found that solvation reduced the surface energies of the nanocrystals. (ᵡᵡ) *Dendrite formation:* In collaboration with the **Archer** group, and in an effort to determine the role played by diffusion on the maximum current density prior to dendrite onset in Li metal anodes, we carried out a JDFT study of Li diffusion on typical anode SEI surfaces in electrolyte [T.16], including LiOH and, for electrolytes containing fluoride, LiF. We found a 0.13 eV lower barrier to diffusion for Li on LiF, corresponding to a *two-order of magnitude* increase in the diffusion constant, consistent with the empirical

Species	Vacuum (Theory); [eV]	Solvated (Theory); [eV]	Solvated (UV-vis); [eV]
SO_4^{-2}	3.4	7.1	
$LiSO_4^-$	4.4	6.3	6.2
Li^+	9.2	8.9	
LiOH	5.4	5.9	6.1

Table T-1: Computed HOMO-LUMO excitation gaps for various species.

observation that smoother regions on cycled electrodes are richer in F [T.17]. These results open the possibility for suggesting specific electrolyte chemistries to protect against dendrite formation in Li and likely other metal anodes. (ᵡᵡ) *Operando interpretation of electron absorption in Li-ion batteries:* In close collaboration with the **Muller** group, **Arias** computed the HOMO-LUMO excitation gaps for a series of aqueous-solvated sulfate ions (Table T-1) to allow interpretation of spatio-temporal variations in EELS signatures near operating electrodes (Table T-1) [T.4, T.18]. We identified $LiSO_4^-$ as the source of the observed absorption while ruling out other competing species (HSO_4^-, Li^+, LiOH, H_3O^+).

B. Grand-Canonical Genetic Algorithm for Materials Prediction: Knowledge of a material's atomic structure is a prerequisite to computational materials studies. With this knowledge, standard theoretical methods will yield chemical, electronic and optical properties. Thermodynamic stability of a material phase requires it to be not only the (free) energy minimum for a given composition, but also lower in energy than any mixture of competing phases. Multicomponent structure prediction thus requires a search over the entire composition space, amounting to computing the complete phase diagram. Toward this end, we developed a grand-canonical genetic algorithm (GASP), which searches simultaneously over compositional and geometrical degrees of freedom [T.19]. Our method was unique in utilizing information from favorable local compositions, achieving far greater efficiency than previous methods. We disseminated this new approach through the GASP software package [T.20], which was interfaced to a number of energy and local optimization codes and included comprehensive documentation and tutorials.

(ᵡᵡ) *First principles prediction of Li-Si phase diagram*: The Li-Si materials system holds promise for use as an anode in Li battery applications. Using GASP we have determined the charge capacity, voltage profiles, and energy storage density of this system *ab initio*, without adjustable parameters or any experimental input. Fig. T-3 shows our results for the stable and metastable Li-Si phases likely to form during the charging and discharging processes, with *ab initio* molecular dynamics employed to study the amorphous phases [T.21]. We observed, in agreement with experiment, that the formation of amorphous Li-Si only slightly increases the anode potential. Additionally, the genetic algorithm identified a previously unreported member of the Li-Si binary phase diagram (Li_5Si_2) which is stable at 0 K with respect to previously known phases and is closely related to the partially occupied Li_7Si_3 phase.

C. Microscopic effective theories (METs): electro- and photo-catalysis by design: Control over the electronic structure, conduction/valence band edges and band gaps, is fundamentally interesting and technologically relevant in numerous energy related applications. Our objective was to achieve this control by elucidating the fundamental principles governing the relationships between atomic-scale structure and the macroscopic behavior of complex bulk, thin film, and heterostructured materials. Understanding how the composition, symmetry, geometry, and topology of crystalline motifs influence the interplay among the active degrees-of-freedom and manifests itself in macroscopic materials behavior affords the opportunity to design, *in silico*, properties and functionalities. Our approach

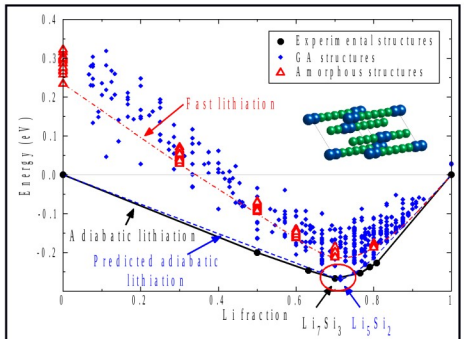

Fig. T-3: GASP search of low-energy structures in the Li-Si system. GASP identified a previously overlooked member of the Li-Si phase diagram; Li_5Si_2.

combined microscopic Hamiltonians/models with fundamental principles of solid-state chemistry and first-principles simulations to produce *microscopic effective theories* (METs), which enable this kind of understanding and material design.

1.Strain tuning**:** While chemical substitution has been extensively employed as a means of tuning the electronic structure of complex oxides, it often has unintended consequences. Unlike chemical doping, epitaxial strain has the potential to avoid nanoscale disorder and instead provide a homogenous sample. Moreover, our METs indicated that strain altered the overlap of neighboring orbitals, affecting the balance between electron hybridization and Coulomb repulsion, thus opening the possibility of tuning the band gap and redox potentials of a material. While it is very difficult to change the lattice constant of a bulk material, thin films can be strained considerably by coherent epitaxy to a substrate with a different lattice constant.
(ᵡᵡ) *$SrTiO_3$:* $SrTiO_3$ has been explored in solar water splitting applications due to its favorable energy levels and stability against degradation. However, its indirect optical gap (3.2 eV) is too large for efficient light harvesting of the solar spectrum. Using our MET approach, we proposed a new route, anisotropic strain and ferroic distortions, for altering the band gap and band edges of $SrTiO_3$. Symmetry arguments indicated that while anisotropic strain in the absence of ferroic distortions reduces the gap, ferroic distortions increase it, as confirmed in *ab initio* calculations (Fig. CO-2) [T.22]. In addition, band edge energies, important for electro- and photocatalysis, can be controllably raised or lowered by hundreds of mV relative to vacuum. Moreover, our new, symmetry-analysis approach allowed us to show that thin films of $SrTiO_3$ biaxially strained in the (111) plane instead of (100) would indeed have considerably reduced gaps relative to bulk. This prediction is also consistent with our experimental results. The successes of METs for predicting such trends suggests well-defined routes for tuning the electronic structures of pyrochlore oxides.
(ᵡᵡ) *Bismuth Pyrochlores***:** Moving to more complex materials with even more opportunities for achieving novel, desired properties, we next considered an entirely different family of non-perovskite heterostructures based on Bi-Pyrochlores. As mentioned in the fuel cells and complex oxides sections, these materials show great promise as potential ORR electrocatalsts in alkaline media and their study is part of our proposed research for the next five years. In this context, we have already carried out computational studies on a number of bismuth pyrochlore compounds including $Bi_2Ti_2O_7$, $Bi_2Hf_2O_7$, $Bi_2Sn_2O_7$ and $Bi_2Pb_2O_7$ and the effects of strain. We believe that the lessons learned from these studies, as well as those on $SrTiO_3$, will provide the foundation for the design of pyrochlore-based electrocatalysts.

E. Novel *in situ* and *Operando* Methods:

A major challenge in the development of new electrochemical energy storage and conversion materials is understanding their fundamental mechanisms of operation and degradation. Their microscopically inhomogeneous nature calls for characterization tools that provide *operando* and localized information from individual grains and particles, as well as real-time monitoring of representative ensembles to connect fundamental physico-chemical properties with

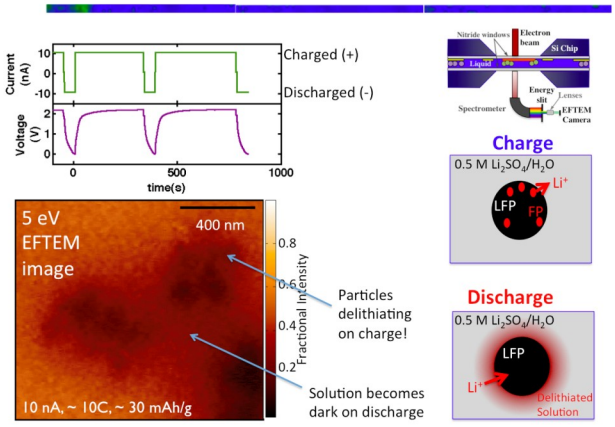

Fig. M-2: EFTEM monitoring of lithiation/delithiation dynamics in $LiFePO_4$.

electrochemical behavior and device performance. Consequently, we emphasized and invested a great deal of resources in the development of novel *operando* techniques, which are providing unprecedented insights into the mechanisms of operation and degradation of fuel cell and battery materials. These include: (ᴥ) Large area X-ray detector and *in situ* electrochemical cells for real-time X-ray synchrotron studies (ᴥ) Dual-electrode DEMS providing the equivalent of rotating ring disk electrode voltammetry with mass spectrometric detection [M.1]. (ᴥ) Scanning DEMS combined with scanning electrochemical microscopy for screening combinatorial libraries [M.2]. (ᴥ) DEMS cell for lithium ion batteries [M.3]. (ᴥ) Confocal Raman with *in situ* electrochemical cell (ᴥ) Polarization modulation FT-IR with *in situ* cell [M.4]. These techniques, now part of our experimental facilities portfolio. We also developed atomic-resolution mapping of composition and bonding by STEM, used in thrusts A and C for Pt-M catalysts [M.5-M.7] and strained oxides [M.8,-M.11].

More recently, we have focused on the development of *operando* electron microscopy (SEM, TEM) methods to span length scales from the atomic to the macroscopic. We studied the coalescence of fuel cell electrocatalysts (Fig. M-1) and the lithiation dynamics of $LiFePO_4$ (Fig. M-2).

IV. Summary:

Our work over the past 5 years has enabled a detailed understanding, via a combination of synthesis of new materials, experimental and computational approaches, of how the nature, structure, and dynamics of nanostructured interfaces affect energy generation, conversion and storage with emphasis on fuel cells and batteries. We structured our center into highly collaborative and integrated research thrust efforts and composed of world-class researchers with a well-established history and proven record of effective collaborations. Our research objectives were guided by the Grand Challenges articulated in DOE's report "Directing Matter and Energy: Five Challenges for Science and the Imagination;" the BES workshop reports in the *Basic Research Needs* series, as well as challenges identified in "*Computational Materials Science and Chemistry: Accelerating Discovery and Innovation through Simulation-Based Engineering and Science and From Quanta to the Continuum: Opportunities for Mesoscale Science.*

i**References ****References are organized by individual sections. **Bold** indicates work supported by emc^2.

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II. Detailed Achievements

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