Final Technical Report

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3. Provide an executive summary, which includes a discussion of 1) how the research adds to the understanding of the area investigated; 2) the technical effectiveness and economic feasibility of the methods or techniques investigated or demonstrated; or 3) how the project is otherwise of benefit to the public. The discussion should be a minimum of one paragraph and written in terms understandable by an educated layman.

Executive Summary

The chemical reactions that occur in batteries are complex, spanning a wide range of time and length scales from atomic jumps to the entire battery structure. The NECCES team of experimentalists and theorists made use of, and developed new methodologies to determine how model compound electrodes function in real time, as batteries are cycled. The team determined that kinetic control of intercalation reactions (reactions in which the crystalline structure is maintained) can be achieved by control of the materials morphology and explains and allows for the high rates of many intercalation reactions where the fundamental properties might indicate poor behavior in a battery application. The small overvoltage required for kinetic control is technically effective and economically feasible. A wide range of state-of-the-art operando techniques was developed to study materials under realistic battery conditions, which are now available to the scientific community.

The team also investigated the key reaction steps in conversion electrodes, where the crystal structure is destroyed on reaction with lithium and rebuilt on lithium removal. These so-called conversion reactions have in principle much higher capacities, but were found to form very reactive discharge products that reduce the overall energy efficiency on cycling. It was found that by mixing either the anion, as in FeOF, or the cation, as in $Cu_{1-y}Fe_yF_2$, the capacity on cycling could be improved.

The fundamental understanding of the reactions occurring in electrode materials gained in this study will allow for the development of much improved battery systems for energy storage. This will benefit the public in longer lived electronics, higher electric vehicle ranges at lower costs, and improved grid storage that also enables renewable energy supplies such as wind and solar.

4. Provide a comparison of the actual accomplishments with the goals and objectives of the project.

This section of the report is divided into three parts, addressing the three overarching goals of the NECCES EFRC.

Goal 1: Understand the transformations that occur in an electrode composite structure, from the atomistic level to the macroscopic level, throughout the lifetime of the functioning battery.

The major present effort under this goal is associated with the application of the characterization tools developed in the first three+ years of the proposal to functioning batteries using the model compounds identified for the intercalation and conversion reactions mechanisms. The goals and actual accomplishments are documented below.

- Advance *in situ* NMR and MRI to study dynamic processes and structures.
    - Continued to push the development of *in situ* methodologies with a particular focus on NMR of paramagnetic materials and magnetic resonance imaging. Applied to investigate two-phase vs. solid solution reactions (NMR)
    - Obtained first MR images of supercapacitors. Mapped electrolyte concentrations.
    - Developed the theory associated with the rf interaction with metals (in this case a lithium meal anode). This understanding is required to optimize the MRI images from metal containing samples such as batteries.
- Design an electrochemical cell for in-situ synchrotron measurements use.
    - Designed, optimized and implemented an electrochemical cell suited for various synchrotron-based operando measurements on intercalation and conversion materials, using *ex situ* and *in situ* measurements at various beamlines of the APS. This AMPIX cell is now being used extensively not only by us, but also by JCESR.
    - Cell used for Pair-Distribution-Function (PDF) Analysis and Small-Angle Scattering to probe local and intermediate range structure changes in FeOF.
    - Cell used to show solid solution behavior during cycling of olivine at high rates by in situ XRD methods. Data could be modeled only with an interface between two phases (LFP and FP) that is larger than the size of the particles themselves confirming that a distribution of cell parameters exists within the electrode.
    - Determine the influence of the electrochemical cell design and experimental conditions (stack pressure, conductivity and incident X-ray beam energy) on the precision and reliability of synchrotron-based *operando* X-ray measurements were carried out.
        - The uniformity of the cycled electrode state in the Argonne-designed operando cell has been compared to electrodes cycled within cells that replicate the deficiencies of alternative operando cells.
        - Without either uniform stack pressure or conductive windows, the material under the window (being probed by the X-ray beam) is in a different state to the rest of the electrode, which could generate misleading results in other cell designs.
        - Developed and optimized the heating assembly to allow better control and monitoring of the reaction temperature in up to 12 cells under an inert-gas atmosphere. Increased longevity of the cells and reduction of the AMPIX operation cost by implementation of the chemically and mechanically resistive PEEK material as the insulating body parts.
- Adapt and employ in-situ near-field optical micro-spectrometry and imaging to electrode materials interfaces and interphases at subwavelength resolution.
    - A synchrotron-based near-field IR spectroscopy experimental setup at the Advanced Light Source, LBNL has been successfully applied to detect chemical species in the SEI layer at 20 nm spatial resolution.

- Develop novel *in situ* methodologies for X-ray based spectroscopy and imaging techniques
    - Developed the *operando* 2D FFTXM-XANES setup, and defined time-efficient collection protocols for 3D FFTXM-XANES in secondary, nanostructured spherical particles of $LiFePO_4$

Goal 2: Identify the key parameters that are required to optimize intercalation reactions in electrodes. (What are the ultimate limits to intercalation reactions, the core of today's batteries?)

The major effort for this goal continues to be placed on the model compound $LiFePO_4$, with lesser effort on related and next generation materials, such as vanadyl phosphate. We continue some work on the cross-over materials, such as SnCo, that exhibit both intercalation and conversion behavior.

The Olivine Model Compound

- Develop theoretical models and experiments to understand the diffusion mechanism in $LiFePO_4$. Determine which reaction mechanism for LFP/FP intercalation is correct and over what length and time scale. We adopted a multi-tool approach, using particles that range from nanometers to microns in size.
    - *ex situ* near-field IR microscopy and spectroscopy, micro-raman, and optical spectroscopy successfully used to study phase distributions in micron-sized single Li_xFePO_4 particles at different stages of delithiation.
    - A preliminary mechanism of single crystal LFP delithiation from the STEM/EELS studies was proposed, which is consistent with LBNL Raman mapping.
    - Used high rate experiments with the AMPIX cell (NECCES development at ANL) to observe the solid solution reaction for the first time in LFP. Performed detailed modeling of X-ray data to separate effects from strain/small domains from a distribution in Li concentrations.
    - NMR experiments probing the interaction between particles, focusing on small (nanometer-sized) crystals, have shown that rapid exchange with the electrolyte occurs. This work is in close collaboration with modeling groups so the rates extracted from NMR are being directly input into continuum modeling studies.occurs.
    - Developed a Kinetic Monte Carlo model capable of simulating the intercalation kinetics in small (~20 nm) particles.
    - Developed a model for the equilibration and open circuit voltage (OCV) for a multiple-particle system considering Li exchange between particles to explain slow equilibration and anomalous OCV in LiFePO4. Conducted phase field simulations of Li concentration evolution in a cell containing many LiFePO4 nanoparticles, based on the model of a solid-solution reaction mechanism. The simulation results show that, under certain conditions, phase separation during (de)lithiation proceeds by groups of particles, whereby multiple particles rapidly (de)lithiate, reversing the process for other particles. The manuscript of this work is in preparation. Used model to explain LFP-FP phase front progression in whole electrode, as determined

    by in situ XRD studies of electrode reactions in a standard coin cell.
  - Computed the anisotropic interfacial energies (including long range stress contributions) of the $LiFePO_4/FePO_4$ interface and its effect on nucleation morphology. Integrated efforts to include the elastic-strain effect into the phase morphology evolution in micron-scale $LiFePO_4$; this modeling is closely linked with the experiments underway and will guide them. Further work has focused on calculations of interfacial energies.
  - A major accomplishment of this reporting period has been to cut (FIB) the large single crystals down from mm to micron sizes to allow the electrochemistry of different facets to be studied. Ionic and electrical conductivity measurements are in progress. We expect to be able to determine the defects in these crystals.
  - Understood the role of substituents and defects on the thermodynamics and kinetics behavior of LFP:
  - Explored temperature-dependent limits of solid solutions of olivine and sarcopside phases.
    - Determined that aliovalent substitution on the Fe site change the equilibrium thermodynamics, by increasing the single phase regions and lowering the temperature, and therefore the energy, for complete solid solution in Li_xFePO_4.
    - Showed that aliovalent substitution, such as V on the Li site, occurs by displacement of some Fe to the Li site with the V residing on the Fe site. The iron on the Li sites is clustered as the rate capability is not impacted, but the capacity is.

Related and next generation Materials

- Explore the next generation of battery materials based on the understanding gained with the EFRC.
  - Synthesized large crystals of LiFeBO3 and other LiMBO3 materials, and characterized their electrode behavior
  - Elucidated the reaction mechanism for LiFeBO3 and an understanding of how the degraded phase that forms readily during electrode manufacture (and on exposure to air) contributes to the electrochemical properties of this material. Demonstrated that degradation of LiFeBO3 involves Fe transfer to Li site.
  - The effect of temperature on the superstructure found in this material involving Li ordering has been determined by using both in-situ diffraction methods and high temperature NMR. Proved that modulation in pristine LiFeBO3 is occupancy-driven and not displacement-driven.
  - Used symmetry modes to continuously refine LiFeBO3 transition between LT and HT form. Used advanced diffraction analysis to determine temperature-dependent energies for (1) Li chain ordering [~100 meV] and (2) Li site exchange [~10 meV]
  - High voltage borates, LiMnBO3 and LiCoBO3 (LCB) have been investigated to increase the energy density of this system. Prepared ultra-thin (~20 nm) films of LiCoBO3; demonstrated electrochemical inactivity of phase
- Synthesize a new class of polyanion compounds containing the anion (PO3)4N7:
  - These have been characterized and patents filed.

- Initiate study of several two electron systems
    - Several polyanion compounds containing V and/or Mo have been synthesized; the vanadium compounds have very interesting and complex chemistry, and in addition are showing extended reversible reaction with lithium.

Cross-Over Materials

- Explore cross-over materials that show a mix of intercalation and conversion.
    - Complete the study of the crossover material, SnCo by end of year 5. Both ex- and in-situ studies were performed.
    - Model SnCo compounds were synthesized and characterized for comparison with material from the SONY Nexelion cell.
    - XAS studies have shown different behavior for Sn and Co on reduction.
    - TEM showed a change in the spatial arrangements of the Sn/Co on lithiation.
    - The carbon component was found to be a critical electrochemically-active component. *Ex situ* and *in situ* studies are underway to resolve the differences.

Goal 3: Determine how to achieve total control over a conversion reaction, over the entire lifetime of the working battery, by deriving an understanding of the relevant chemistries that occur at the molecular (atomic) level and that involve control of the morphology and microstructures of the composite

The major effort under this goal continues to be placed on the iron model compounds, FeF_2, FeOF and FeF_3 and mostly on FeOF in the last 12 months. The three sub-goals and accomplishments are listed below.

- Identify the phase transformations in (including the morphology and chemistry evolution) in the FeF_2, FeOF, and FeF_3 model materials.
    - Conversion materials, by the inherent nature of the reaction result in a repetitive formation and reformation of phases. Given that in most systems this converted phase is a 1-2nm metal crystallite, it is of utmost importance to establish whether the crystallites evolve and if they do so as a function of kinetic parameters such as rate and temperature. This is critical, as we know that the fine crystallites are key to reversibility and also to lithium transport at the interfaces of the material. We are well on the way to establishing with certainty the evolution of morphology of conversion materials as a function of cycle number, rate and temperature. The reactions occurring in the complex FeOF are now much better understood by using of a combination of tools, including in-situ pdf, TEM and magnetism.
- Understand the details of hysteresis and charge transport.
    - All conversion materials exhibit considerable hysteresis. This is true for the chalcogenides along with the fluorides investigated for positive electrode materials in this EFRC effort. Some intercalation reactions were also found to show high hysteresis. In all these cases the cause of the hysteresis was identified by the reaction following different routes on lithium reaction vs lithium removal. Copper titanium

  - sulfide was used as one model compound, which showed convincingly that the slow diffusion of one component is the cause of the hysteresis.
  - Despite this hysteresis conversion materials were found to exhibit >99% coulombic efficiency. Our goal is therefore to determine how to control the reaction route to minimize hysteresis.
  - A combination of modeling and TEM studies have shown fast lithium diffusion along grain boundaries.

- Understand and control the nanostructure of the conversion cathode
  - The NECCES effort has been the first to reveal that a very large part of the failure mode of conversion material cycling rests not in the fundamental instability of the reconversion mechanism, but rather a complex interaction with the electrolyte. Indeed, we identified that reaction products can become part of the conversion chemistry well within the subsurface of the conversion material itself. In addition we have identified reformulation of electrolytes, which demonstrate very significant enhancement of the electrochemistry of a BiF_3 conversion model material. Moving forward we wish to establish whether this mechanism is generic within all conversion materials or whether there are complex interactions, which are more material specific. Having established proof of the importance of the interaction with modest characterization (microscopy, FTIR, XPS), we move forward with more advanced characterization tools to fully explore the low cost iron based fluoride and oxyfluoride conversion materials.

5. Summarize project activities for the entire period of funding, including original hypotheses, approaches used, problems encountered and departure from planned methodology, and an assessment of their impact on the project results. Include, if applicable, facts, figures, analyses, and assumptions used during the life of the project to support the conclusions.

Goal 1: Understand the transformations that occur in an electrode composite structure, from the atomistic level to the macroscopic level, throughout the lifetime of the functioning battery.

The major effort under this goal is associated with the application of the characterization tools developed in this project to the model compounds identified for the intercalation and conversion reactions.

- *In situ* TEM imaging of all-solid-state model battery system:
  - Focused ion beam (FIB) fabrication of micro- and nano-battery with good electrochemical activity achieved.
  - Ex situ STEM/EELS studies of the nano-batteries indicate an interface limited lithium transport. Cathode/electrolyte interface shows accumulation of lithium, while the anode/electrolyte interface was broad with elements inter-diffused.
- Local electrode atom probe tomography (LEAP/APT):
  - A systematic APT study on single crystal LiFePO4 was performed as a reference/standard material of lithium battery cathode materials.
  - UV and green laser assisted APT experiments were carried out and established that UV laser is compatible with Li-containing materials.

- *In situ* TEM-EELS studies of conversion and intercalation materials
    - Designed and built an *in situ* cell for TEM imaging electron diffraction and electron energy-loss spectroscopy measurements at single nanoparticle resolution
- *In situ* NMR methodologies for paramagnetic materials and magnetic resonance imaging
    - Developed an NMR based approach to monitor Li exchange between particles within a composite electrode. Applied this methodology to LiFePO4.
    - Developed a methodology to investigate paramagnetic battery materials by *in situ* NMR spectroscopy.
    - Applied MRI methods to investigate lithium dendrite formation and supercapacitors.
    - Developed comprehensive method for tracking SEI formation by NMR spectroscopy and the spatial connectivity between different components.
- *Ex situ* and *in situ X-ray* spectroscopy and diffraction measurements and PDF Analysis of novel electrode materials
    - Implemented and optimized a heating assembly to allow cycling under non-ambient temperature conditions and kinetic studies on various battery systems
    - Developed multiplexing experimental setup that allows up to 12 cells to be run simultaneously for X-ray measurements.
    - Implemented a new “radial” cell design that allows *in situ* depth profiling measurements of electrodes.
- New class of scanning near- and far-field optical probes to study EES materials
    - Ultrafast laser induced breakdown spectroscopy was successfully developed and applied to perform depth-profiling of SEI layers in ambient pressure/temperature conditions.
    - Developed tomographic near-field IR imaging capabilities for micro-and nanometer scale samples.

Goal 2: Identify the key parameters that are required to optimize intercalation reactions in electrodes. (What are the ultimate limits to intercalation reactions, the core of today’s batteries?)
The Model Compound: Olivines

- Demonstrated the power of 2D transmission X-ray microscopy coupled with X-ray absorption near edge spectroscopy, both in full field and scanning modes (FFTXM- and STXM-XANES), to gain insight into the progress of the transformation from $LiFePO_4$ to $FePO_4$.
    - Observed a complex behavior, proposed to result from a combination of kinetic and thermodynamic limitations. Macroscopic defects, possibly induced by the synthesis process, dominated the kinetics of the phase transition within the crystals.
- Near-field IR microscopy has been successfully applied to small LFP particles at different stages of delithiation and revealed coexistence of LFP and FP in a single particle and no detectable contributions from any intermediate phases. The approach was combined with near-field IR spectroscopy, the method allowing tomographic analysis of the phase propagation mechanism in the Li_xFePO_4 crystal.
    - PR elipsommetric optical data on $LiFePO_4$ that combined with a computing effort at Cambridge, allowed analysis of the near-field data.

- *In situ* quick x-ray absorption spectroscopy has been developed for studying the kinetics of lithium battery materials during the electrochemical (or chemical) delithiation.
    - The progression of the phase front of LFP has been investigated by depth profiling the electrode by using high-energy synchrotron radiation that can penetrate through a coin cell. Used continuum modeling calculations to help explain LFP-FP phase front progression in whole electrode.
- Determined through first–principles (DFT) calculations the anisotropic interfacial energies (including long range stress contributions) of the $LiFePO_4/FePO_4$ interface and its effect on nucleation morphology and integrated with phase field modeling to understand morphology of phase transformation and nucleation of second phase. Demonstrated that interfacial energy between LFP and FP in the ac plane is lower than previously thought. Suggests interfaces may exist in a plane previously not considered to any considerable degree in most experimental and theoretical work.
- A joint theory and NMR study on $LiFe_{1-y}Mn_yPO_4$ developed a new protocol for assigning NMR resonances (in this case 31P NMR) to specific local environments. Hyperfine shifts for different P-O-M "pathways" were extracted from calculations, which were used as initial inputs with which to fit the experimentally obtained spectra. A single set of parameters could be used to fit all members of the $LiFe_{1-y}Mn_yPO_4$ solid solution with y = 0, 0.25, 0.5, 0.75 and 1.0, indicating very little structural distortions across the solid solution. This is in marked contrast to the $LiMg_{1-y}Mn_yPO_4$ series. A similar approach is being used to investigate the $LiCoPO_4$ series following Li removal: the structure of $Li_{2/3}CoPO_4$ was solved via a combination of diffraction, NMR and calculations. Decomposition of Li_xCoPO_4 has been investigated by NMR and the phases are found to be extremely unstable.
- Prepared samples of intermediate phase $Li_{0.6}FePO_4$ and determined the superstructure periodicity

  Used Scanning Transmission X-ray Microscopy (STXM) image LFP/FP interfaces in nano- sized particles. Different sizes of LFP particles after half delithiation were examined by both STXM and STEM/EELS
- High-resolution images on the cracking in different particle sized LFP were analyzed. The relationship between the amount of crackings and the particle size after delithiation has been proposed.
- Demonstrated that vanadium substitution at the Fe site of $LiFePO_4$ is possible.
    - It leads to enhanced solid solution behavior upon Li removal in both Li-rich and Li poor phases, reducing lattice mismatch. Vanadium substitution also decreases the solid solution formation temperature and the voltage gap between the open circuit voltage on charge and discharge. This increased single-phase-like behavior explains the enhanced kinetics of substituted $LiFePO_4$ and is consistent with a pseudo single- phase reaction mechanism (aka disordered lithium lattice).
    - In Li-poor phases, Fe+V >1, the iron was found to reside on the Li-sites forming sarcopside clusters. Although this reduces the capacity it was found to increase capacity retention at high rates
- Shown similarly that Co substitution in LFP extends solid solution limits on either end, but the reaction in this case proceeds via an intermediate phase
- Demonstrated that Mg substitution leads to a complete single phase reaction; similar behavior is observed for the simferite phase.

- An intergrowth between $LiFePO_4$ and the mineral sarcopside has been identified by its characteristic diffraction reflections, by NMR spectroscopy and by electrochemical behavior. This might have major implications for the electrochemistry of metal-rich olivines
- Thermal stability studies of delithiated phases have shown that the crystallinity and thermal behavior of $MnPO_4$ is strongly influenced by the nature of the carbon coating. Results confirm our earlier suggestion that contradictory results on thermal decomposition of Mn- rich olivine phosphates can be explained by uncontrolled moisture exposure and variations in the nature of carbon coating. Local structural distortion induced by Jahn-Teller effect around delithiated $Li_{1-x}MnPO_4$ cathode material has been studied by Mn K-edge EXAFS analysis.

Related and Next Generation Materials:

We continued exploring related and potential next generation materials.

- Obtained detailed understanding of LiFeBO3 (de)lithiation reaction mechanism.
- Discovered new polyanion materials, which were termed "cubicons" on the basis of their cubic crystal structures. The materials combine high rate behavior with moderate capacities:
  - Demonstrated Na-ion batteries with Na3TiP3O9N cathodes (~60 mAh/g, ~2.8 V) and identified 3D Na-ion diffusion pathways and activation energies in this phase
  - Demonstrated Li-ion batteries with Li2Fe2P3O9N cathodes (~140 mAh/g, ~3.2 V)
  - Carried out *in situ* neutron diffraction studies to determine mechanism of Li/Na ion exchange in assorted nitridophosphate compounds
  - Evaluated temperature-dependent thermal parameters to rapidly screen ionic mobility in a variety of nitridophosphate compounds
- Developed novel layered Na-ion cathode system (~140 mAh/g, ~3.4 V)
- Explored several metal phosphates that look promising for the intercalation of two lithium ions, thus substantially increasing the capacity. Very little is understood on the impact on the crystalline lattice on that amount of lithium being inserted. This approach ahs the advantage over using the 2 electron Mg ion in that today's anodes and electrolytes can be used.
  - Two molybdenum phosphates have been studied. Both showed disappointing degrees of lithiation.
  - In contrast vanadyl phosphate, VOPO4 readily reacts with more than one Li ion leading to capacities in excess of 250 mAh/g. We are exploring the reaction mechanism and note that the lithium intercalation reaction steps appear to be different that the lithium removal reaction sequence particularly at higher rates.

Crossover Materials: SnCo

The synthesized crystalline SnCo ($Sn_3Co_3C_4$) was examined in detail and compared directly against the amorphous SnCo, which has been commercialized by Sony. The combined studies by magnetism, NMR and XAS reveal the involvement of Co-rich phase segregation for lithation insertion; they also suggest the importance of structure variables, particularly the finite size, for SnCo anode materials. .

- SnCo

  - Both XAS and magnetic studies detected the segregation of metallic Co upon lithation of $Sn_3Co_3C_4$, similar to that of the Sony SnCoC.
  - In contrast to the reversibility demonstrated by the Sony SnCoC during electrochemical cycling, XAS showed an irreversible change in the structure and electronic properties of the $Sn_3Co_3C_4$ materials during the 1st and 2nd cycles.
  - The intensity of a XAS peak for $Sn_3Co_3C_4$, mainly related to the coordination between Co and metal, increases greatly during the delithiation process of 2nd electrochemical cycle. This change is very probably due to the growth or agglomeration of crystalline Co particles.
  - This comparative study between the crystalline and nanonized "amorphous" SnCo materials demonstrates the importance of finite size and size control for the reaction of lithium cycling with the SnCo material.
- Sn and Ge
  - Motivated by the unexpected NMR signals obtained from the Li_xSn phases obtained in the Sn system, we compared Sn electrochemistry with Ge electrochemistry to explore size effects on lithiation mechanism; identified all the major phases formed in the Ge system by using XRD, PDF and NMR.

Goal 3: Determine how to achieve total control over a conversion reaction, over the entire lifetime of the working battery, by deriving an understanding of the relevant chemistries that occur at the molecular (atomic) level and that involve control of the morphology and microstructures of the composite

- **Phase transformation in FeF_2, FeOF, and FeF_3 model materials:**
  - This has been a main goal of the thrust throughout the EFRC period. The phase reactions have been investigated in detail using XRD and SAED to track phaseformation and evolution. Further details of the structural interactions were obtained by the use of EXAFS and PDF to gain insight into the local structure and coordinating specie interaction lengths. Both of these techniques were investigated in-situ and operando. PDF was accomplished in the AMPIX cells that were designed and developed within the NECCES EFRC program at Argonne. Oxidation state was investigated through the use of XANES EELS mapping and Fe Mossbauer). Morphology evolution of the phases was investigated using in-situ and ex-situ HRTEM, magnetic measurements and also SAXS Electrochemically, the FEOF based materials show significantly improved performance relative to the pure fluorides of FeF_2 and FeF_3. As such, it was of importance to use this milestone to identify key differences in the phase evolution. A number of distinct contrasts in phase evolution were identified. During lithiation within the conversion segment of the FeF_2 and FeF_3 materials, LiF and Fe evolve in a relatively straight-forward multiphase reaction. This is in sharp contrast to the FeOF material, which prenucleates the formation of a rocksalt phase containing Li, Fe, O and possibly F before the Fe is nucleated and converted from the host structure. This rocksalt phase plays a key role in maintaining a very near amorphous phase evolution of rutile upon delithiation. This is in contrast to the much more crystallized rutile phase that is formed during the reconversion back to FeF_2 and FeF_3 in the pure fluorides. All

techniques including theoretical calculations confer on this finding and also the much improved reversibility of the FeOF conversion reaction. Although the key finding seems to be established, we have a desire to get much improved spectroscopic evidence of what the light elements are doing such as Li, O, and F. The question relates to whether the composition of both the rocksalt and rutile phases are static or do they change as a function of lithiation/delithiation. There is high resolution electrochemical evidence suggesting that the composition may be dynamic.

  - In order to better understand the iron-based compounds some scoping experiments were performed on CuF_2 and a mixed $[CuFe]F_2$. A detailed analysis of pure CuF_2 with PDF, XAS, XRD and NMR showed clearly that Cu^{1+} and Cu^{2+} ions dissolve (forming species such as CuF_4^{3-} and CuF_6^{4-}) that compete with reconversion. The mixed fluoride showed much improved reversibility.

- **Understand Details of Hysteresis and Charge Transport**
  - ***Electronic and Ionic Transport:*** A full story regarding electronic transport has crystallized. The fundamental question is how does the electron transport through a conversion reaction product of 2-3M LiF and 1M Fe to the reaction front. Based on densities, the amount of Fe to support electronic conductivity is questionable unless some sort of self wiring of nanostructures occurs. Indeed, we have found conclusively that the latter does indeed occur. In-situ TEM and ex-situ STE have clearly shown that the Fe within a crystallite forms in a 1-2nm dimension and is interconnected with a textured progression through one crystallite of the host fluoride. To support whether the localized interconnection is on the crystallite scale, magnetic measurements were incorporated to measure the blocking temperature at which the paramagnetic moment of the nanostructures ceases, which is directly related to the extent of the interacting/interconnected Fe network. The sizes were found to be on the order of 10-20nm, consistent with the size of the originalcrystallite suggesting that the 1-2nmFe nanoparticles are networked throughout the crystallite. In order to evaluate if this percolation translates to appreciable electronic conductivity, electronic conductivity was measured for converted FeF_2 films place interdigitated arrays. The conductivity was found to be very significant, on the order of 1 S/cm. To prove that the electronic conductivity was sufficient to support electrochemical conversion over longer distances than the previous 20nm activity limit, vertical pore nanostructures were fabricated which caused electronic conductivity to be forced over a length scale >700nm while having a 5x shorter distance for Li-ions. Indeed, the electronic conductivity supported the reaction suggesting electronic conductivity is not the leading cause of sluggish kinetics in conversion materials and that the conversion products self form into a percolated
    electronic network. This then leads to the question of ionic transport. Variable charge MD simulations support that the fast diffusion path for Li^+ ions is the defect region formed between the LiF and Fe within the conversion products. Ion diffusivities in the form of boundary mobilities were established for all the model materials (FeF_2, FeF_3 , and FeOF) showing that mobility is quite slow on the order of 10-18 cm^2/s.
  - ***Hysteresis****:* Hysteresis was investigated in detail utilizing high resolution PITT and reverse scan PITT techniques to separate the intrinsic hysteresis from kinetic

polarization. Results show clearly that all the conversion materials show very low hysteresis, at least for the first half, of the reconversion (delithiation) sweep as the potentials were near the thermodynamic potentials. Much lower intrinsic hysteresis was calculated for the FeOF materials. This was associated with a more symmetric like reaction profile for the FeOF conversion/reconversion reaction.

- **Understand and Control of the nanostructure of the conversion cathode.**
    - The role of electrolyte interaction, reaction products and phase incorporation was earlier completed and reported for the BiF_3 model material. For the Fe based model materials the data gives evidence for the presence of Fe oxidation into solution that becomes incorporated into the FeF_2 cathode interphase layer and creates a cation deficient rutile as evidenced by EELS/TEM, XAS, electrochemistry and NMR. As also noted above for CuF_2 the electrolyte is a major player in the reaction mechanism and reversibility. However, substitution of part of the Cu by Fe significantly changes the solubility and enhances the reversibility of the reaction.

The Future: Planned Activities for the “Renewal” Project

Intercalation Reactions

The ultimate limits of intercalation reactions were identified, and the renewal project will address how to “Close the Gap” between the attained capacities and the ultimate limits of intercalation reaction. The major emphasis is on the layered oxides and on materials that can react with two lithium ions per transition metal redox center. The latter complements the effort by JCESR where magnesium is being studied to attain two electrons per transition metal.

Conversion Reactions

The study of conversion reactions will be discontinued under DOE-EFRC funding. Efforts will be continued under DOE-EERE-BMR funding.

5. Schedule Status. List milestones, anticipated completion dates and actual completion dates.

The design of the next generation of rechargeable batteries requires both the development of new chemistries and the fundamental understanding of the physical and chemical processes that occur in these complex systems. Progress towards identifying the most efficient mechanism(s) for electrical energy storage and the ideal material combination(s) to achieve **this goal**, requires that we address a series of key, basic research issues. In particular, we need to need to develop a **fundamental understanding of how battery materials function and what structural/electronic properties limit their performance**. The mission of the NECCES EFRC is to understand how fundamental chemical reactions occur at electrodes and to use this knowledge to design new chemical energy storage systems.

NECCES has three 5 Year Research Goals, which are supported by a number of milestones. These three Goals are:

1. Understand the transformations that occur in an electrode composite structure, from the atomistic level to the macroscopic level, throughout the lifetime of the functioning battery.

2. Identify the key parameters that are required to optimize intercalation reactions in electrodes. (What are the ultimate limits to intercalation reactions, the core of today's batteries?)
3. Determine how to achieve total control over a conversion reaction, over the entire lifetime of the working battery, by deriving an understanding of the relevant chemistries that occur at the molecular (atomic) level and that involve control of the morphology and microstructures of the composite

Milestones:

Major Goal 1

Year 3 milestones

- Produce pure defect-free olivine (lithium iron phosphate, $LiFePO_4$) crystals as a pure model compound for *in-situ* studies of intercalation reactions.
  - Goal accomplished
    - Produced flux-grown olivine (lithium iron phosphate, $LiFePO_4$) crystals with antisite defects below the detection limit as a pure model compound for *in-situ* studies of intercalation reactions.
- Find some model cathode compounds for conversion reactions.
  - Goal accomplished
    - Characterized the phase progression and reversibility of structural changes for iron oxyfluorides (FeF_y, and FeOF), and establish these cathode materials as model compounds for conversion reactions.
- Develop *in situ* metrologies to probe the structural, phase, and compositional changes of the model compound in functioning batteries.
  - Goal accomplished
    - Probed the structural, phase, and compositional changes of the model compound in functioning batteries using newly developed *in situ* metrologies: *in situ* total scattering experiments to assess local structure *(*PDF), magnetic resonance imaging, X-ray Raman scattering, and X- ray absorption near-edge structure/transmission X-ray microscope.

Year 4 milestones

- Advance *in situ* NMR and MRI to study dynamic processes and structures
  - Goal accomplished
    - NMR and magnetic resonance imaging successfully applied to paramagnetic materials and to the study of lithium deposition.
- Develop electrode level modeling
  - Goal accomplished
    - Computed the anisotropic interfacial energies (including long range stress contributions) of the $LiFePO_4$/$FePO_4$ interface and its effect on nucleation morphology.

Year 5 milestones

- Develop the tools to determine the transformations that occur in an electrode composite structure, from the atomistic level to the macroscopic level, throughout the lifetime of the functioning battery

    - Goal continuing under “renewal” EFRC.
- Document and transfer the characterization methodology and electrode mechanism understanding to the community, including the JCESR Hub
    - Goal accomplished
        - Designed, tested and used in-situ electrochemical cell for APS beam-line. This system has been published and transferred to JCESR.

Major Goal 2

Year 3 milestones

- Develop theoretical model(s) that explains high rate for nanosized olivine particles
    - Goal accomplished
        - Identified a single phase reaction mechanism
        - Identified overpotential as controlling reaction path.
        - Identifying suitable experimental tests of models.
- Determine whether aliovalent doping is possible for Fe in $LiFePO_4$
    - Goal accomplished
        - Showed that doping of olivine on the Fe site enhances reaction kinetics.
- Identify some crossover materials that exhibit both intercalation and conversion chemistries to build a bridge between them.
    - Goal accomplished
        - Identified tin cobalt carbon (SnCoC) and FeOF as crossover materials that exhibit both intercalation and conversion reactions for study.
        - Demonstrated why hybrid reactions of the crossover material FeOF perform better than pure conversion of isostructural FeF_2 reaction kinetics.

Year 4 milestones

- Identified experiments to test different theoretical models for $LiFePO_4$ reaction
    - Goal underway
        - Single particle, and electrode level studies underway with a variety of spectroscopic and synchrotron X-ray based techniques
- Determine why substitution improves the kinetics of $LiFePO_4$
    - Goal accomplished
        - Showed that doping of olivine on the Fe site increases the single phase regions
        - Showed that doping on the Li site also increases the kinetics of reaction, but substantially reduces the capacity. This suggests that the excess iron forms clusters, as in sarcopside
- Determine what “FeOF” really is
    - Goal accomplished

        - Indications that particles of FeOF have an oxygen-rich surface surrounding a fluorine-rich core, which form several phases on reaction and FeOf is not-reformed on charging.
- Complete the study of the crossover material, SnCo, thereby determining how critical is intercalation in the initial steps of conversion reactions.
    - Goal underway
        - Both ex- and in-situ studies are being performed since the present measurements are conflicting.

Year 5 milestones

- Complete the identification of the key parameters that are required to optimize intercalation reactions in electrodes using $LiFePO_4$ as the model.
    - The key parameter identified is the ability to react by a single-phase mechanism, which can be obtained by applying an overpotential in the case of $LiFePO_4$. The single phase can also be obtained by cation substitution,
- Identify systems where control of kinetic vs. thermodynamic pathways result in improved performance.
    - The Olivine system is the model system where kinetic control of the reaction pathway results in much improved reaction rates. For the “renewal” project the system LixVOPO4 was identified as a possibility where x can be as high as 2 and where kinetic control may be important.
- Define what are the ultimate limits to intercalation reactions, based on both experimental and theoretical approaches.
    - These have been determined to be around 350 Wh/kg and 1 kWh/liter in actual cells. See Chemical Reviews, 114, 11414, 2014.

Major Goal 3

Year 3 milestones

- Determine role of metal diffusivity in conversion reactions
    - Goal accomplished
        - Showed that a low diffusion metal (M) in MF_2 is needed to maintain the nanostructure, and therefore the reversibility. Thus FeF_2 is reversible whereas copper (Cu) in CuF_2 diffuses much faster, forming large particles that cannot be easily dissolved.
        - Theoretical studies on a structure-retaining cathode ($CuTi_2S_4$) predicted that Ti_2S_4 will form and the copper will very slowly re-insert into the lattice.
- Develop a tool to observe conversion reactions in real-time
    - Goal accomplished
        - Developed unique *in situ* transmission electron microscopy/ scanning tunneling microscopy characterization that showed, in real-time, the

        - formation of iron nanoparticles, < 5 nm, on reaction of lithium with FeF_2.
  - Determine what caused capacity fade in conversion electrodes
    - Goal accomplished
      - Determined that large capacity fade is predominantly due to surface decomposition of certain electrolytes and subsurface diffusion of the reaction products.
- Year 4 milestones
  - Identify Phase transformation in FeF_2, FeOF, and FeF_3 model materials
    - Goal accomplished
      - The phase progression has been successfully mapped for FeF_2 and the highly complex FeOF model materials.
  - Determine impact of substitution of some of the Fe in FeF_2
    - Goal accomplished
      - Copper successfully introduced into the lattice of FeF_2
      - Copper significantly reduces the discharge overpotential of the FeF_2.
      - However, copper in pure CuF_2 dissolves in electrolyte forming complex anionic species that compete with the conversion reaction on charging
  - Understand Details of Hysteresis and Charge Transport
    - Goal partially accomplished
      - Transport through the conversion reaction has been successfully modeled by MD simulations which demonstrate high mobility of Li ions through Fe: LiF grain boundary regions
  - Investigate role of Electrolyte on the control of the nanostructure.
    - Goal partially ccomplished
      - Electrolyte has been shown to influence in a very direct way the electrochemical performance of conversion positive electrodes. This is due to a combination of catalysis leading to electrolyte formation and high voltages leading to its anodic destruction and consumption by the conversion chemistry

Year 5 milestone

- Determine how to achieve total control over a conversion reaction, over the entire lifetime of the working battery. This will be achieved by deriving an understanding of the relevant chemistries, of those that occur at the molecular (atomic) level to those that involve control of the morphology and microstructures of the composite.
  - Publications now essentially complete on control of conversion reactions.

6. A description of any product produced or technology transfer activities accomplished during this reporting period:

***<u>Publications</u>*:** All peer-reviewed publications have been uploaded to the energyfrontier.us website. There are around 100 publications total, and contain some publications completed under the “continuation” award # DE-SC0012583.

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a. Networks or collaborations fostered:

Meng group's (UCSD) STEM/EELS work was carried out in collaboration with Dr. Miaofang Chi from Oak Ridge National Laboratory. The group has built a long-term relationship with the ShaRE facility in ORNL, which has the most up to date microscopes. In addition, as part of the group's atom probe tomography project a strong collaboration with D. K. Schreiber and D. E. Perea both at Pacific Northwest National Lab and R. L. Martens at University of Alabama, Tuscaloosa were established and will continue in the future as well.

b. See the attached "Disclosures and Patents Table"

7. For projects involving computer modeling, provide the following information with the final report:

a. Model description, key assumptions, version, source and intended use;

The Thornton group developed three sets of simulation codes in NECCES. The first is the smoothed-boundary-method electrochemical simulation (SBMES) code for simulating the lithiation/delithiation dynamics in the particle and microstructure levels. This code solves the coupled continuum-level electrochemical governing equations for (1) Li transport and (2) current continuity in electrode particles, (3) salt concentration evolution and (4) current continuity in electrolyte, and (5) the Butler-Volmer equation for the electrochemical reaction rate at the particle-electrolyte interfaces. This code is applicable to simulate the dynamics in all intercalation materials, with simulation parameters of the corresponding materials. A special version of the code was employed to study the metastable-solid- solution transformation of LFP, in which $LiFePO_4$ (LFP) particles were assumed to be a Li solid solution. The second code uses the porous electrode theory (PET) to simulate the charge/discharge dynamics of a coin cell with a LFP cathode. The third code is the phase field modeling (PFM) of Li-$CuTi_2S_4$ displacement reaction, in which Li, Cu and vacancies are the three diffusing species in the Ti_2S_4 host crystal. Each of Li and Cu concentration evolutions are modeled by a Cahn-Hilliard equation, with a free energy landscape and diffusivities constructed based on the ab initio calculated parameters by Van der Ven group in NECCES.

Van der Ven and his group develop the CASM software package (A clusters approach to statistical mechanics), which automates first-principles statistical mechanical calculations to predict finite temperature thermodynamic and kinetic properties of multi-component crystalline solids. The approach relies on the automated construction of effective Hamiltonians that describe configurational (e.g. due to Li-vacancy disorder) as well as vibrational degrees of freedom in crystalline solids. The CASM software, relying on crystallographic group theory, automates and manages high throughput density functional theory calculations and uses the results to parameterize an algorithmically constructed effective Hamiltonian. CASM then constructs Monte Carlo and kinetic Monte Carlo codes highly optimized for the particular first-principles parameterized effective Hamiltonian to predict thermodynamic properties and diffusion coefficients. The code is currently used within Van der Ven's group and a group of beta testers. It will ultimately be released as an open source code to the general public.

b. Performance criteria for the model related to the intended use;

The continuum-level electrochemical simulations track the concentration evolution of Li, instead of atomic phenomena. The length scale for simulations is from tens of nanometers to a few millimeters. The time scale is from seconds to a few hours. Currently, the module for simulating Li salt concentration in the electrolyte uses the binary dilute electrolyte model, which simplifies the ionic diffusivities as constant values, independent of salt concentration. However, such a constraint can be removed when the data for concentration-dependent ionic diffusivities is available.

The CASM software organizes and runs high throughput DFT calculations and subsequently collects the results to parameterize effective Hamiltonians. This first stage of the workflow is limited by the time and computational requirements of the particular DFT calculations. Upon parameterization of an effective Hamiltonian, the next step involves extensive Monte Carlo and kinetic Monte Carlo simulations to calculated thermodynamic and kinetic properties. A particular project (e.g. the prediction of the voltage and Li diffusion coefficient of an intercalation compound) will take several months as the DFT calculations for each structure can take minutes to days and several hundred of such calculations are required. The fitting procedure of the effective Hamiltonians, while highly automated, must occur iteratively to improve the description. Monte Carlo simulations will also require days to weeks to ensure highly accurate thermodynamic and kinetic averages.

c. Test results to demonstrate the model performance criteria were met (e.g., code verification/validation, sensitivity analyses, history matching with lab or field data, as appropriate);

The SBMES code was tested with materials parameters of $LiCoO_2$. The predicted cell performance is in good agreement with experimental data. The SBMES code for simulating metastable solid-solution transformation of LFP predicted a sequential interparticle phase transformation, which agreed with experimental observations in the literature. The PET simulations of the LFP coin cells agreed with experimental measurements performed by the Grey group in NECCES. The simulation of Li-$CuTi_2S_4$ displacement exhibited an asymmetry in reaction paths between lithiation and delithiation. The result is consistent with the voltage hysteresis reported in the literature.

The cluster expansion code has been thoroughly tested by comparing Monte Carlo results with model systems having analytical solutions, both for equilibrium properties and diffusion coefficients. The codes have also been tested against similar codes developed by other groups. A series of self tests have been developed, which are checked after every upgrade of the software package. Van der Ven and his group are currently developing methodologies and accompanying infrastructure to perform sensitivity analysis and error propagation.

d. Theory behind the model, expressed in non-mathematical terms;

The electrochemical dynamics is described by the thermodynamics and kinetic of materials, as well as the electrochemistry at interfaces. The mechanisms include the Li transport and electron transport within the particles, Li-ion transport and current continuity in the electrolyte, and the intercalation reaction rate at the particle-electrolyte interfaces.
The CASM software connects accurate first-principles electronic structure calculations (primarily DFT based) at zero Kelvin to macroscopic thermodynamic and kinetic properties at finite temperature. The approach relies on statistical mechanics using Monte Carlo simulations to calculate thermodynamic and kinetic averages. The approach relies on rigorous effective Hamiltonians to extrapolate computationally expensive first-principles energies within Monte Carlo simulations.

e. Mathematics to be used, including formulas and calculation methods;

The electrochemical dynamics in a cell involve strongly coupled physical mechanisms that occur within complex microstructures. The smoothed boundary method uses a continuous domain parameter to define the particle geometries, which takes a uniform value within the particles and another uniform value within the electrolyte. Thus, the regions, where the value of the domain parameter transitions, indicate the particle-electrolyte interfaces. This technique allows us to straightforwardly couple the physical mechanisms that occur in the particles and in the electrolyte through the reaction flux at the particle-electrolyte interfaces.

The classical electrochemical governing equations are reformulated into their corresponding SBM version. These new equations are solved using the finite difference method. The equations for Li concentration evolution in the particles, such as the Fickian diffusion and the Cahn-Hilliard equations, are solved using the Euler explicit time stepping scheme. The equation for Li salt concentration evolution, the Fickina diffusion equation, in the electrolyte is solved using a fully implicit time-stepping scheme. The time-independent equations, such as the Laplace equation for the electrostatic potential field in the particle and the Poisson's equation for the electrostatic potential field in the electrolyte, are solved using the alternating-direction-line-relaxation (ADLR) method.

The approach relies on effective Hamiltonians such as a cluster expansion to describe configurational degrees of freedom and lattice dynamical Hamiltonians to describe vibrational excitations (either within the harmonic approximation, or including anharmonic excitations). Monte Carlo tools (primarily metropolis algorithm) simulate the probability distribution from statistical mechanics to calculate thermodynamic averages. Kubo Green equations are evaluated in kinetic Monte Carlo simulations to calculate Li diffusion coefficients.

f. Whether or not the theory and mathematical algorithms were peer reviewed, and, if so, include a summary of theoretical strengths and weaknesses;

The theory and mathematical algorithms involved in the work have been published in peer-reviewed journals. The method developed by the Thornton group provides a powerful tool for simulating particle-to-cell-level electrochemical dynamics. This tool is flexible to extend to simulate many Li intercalation materials. Possible improvement of the code includes (1) a module of Li salt concentration evolution in concentrated electrolyte (instead of dilute), and (2) a module of diffusion along the particle-particle interfaces in dense particle agglomerate. In addition, the theory and mathematical tools have been published in peer-reviewed journals, either by Van der Ven and his students/post docs or by others.

g. Hardware requirements; and

The SBMES code is developed for running on high performance cluster computers using message-passing-interface (MPI) parallel computing. The code is written in Fortran 90. In addition, high performance cluster computers using message-passing-interface (MPI) parallel computing is required for the high throughput DFT calculations.

h. Documentation (e.g., users guide, model code)

The code is current developed in house in the Thornton group, and used by the members of the group. The documentation is included as comments within the code.
The code for the Van der Ven group is being developed on github. Doxygen is used to

structure and convert comments in the software to understandable documentation for other software developers. Documentation directed at users is being developed. The software also has interactive documentation, which provides instructions at every stage of the calculation process.