

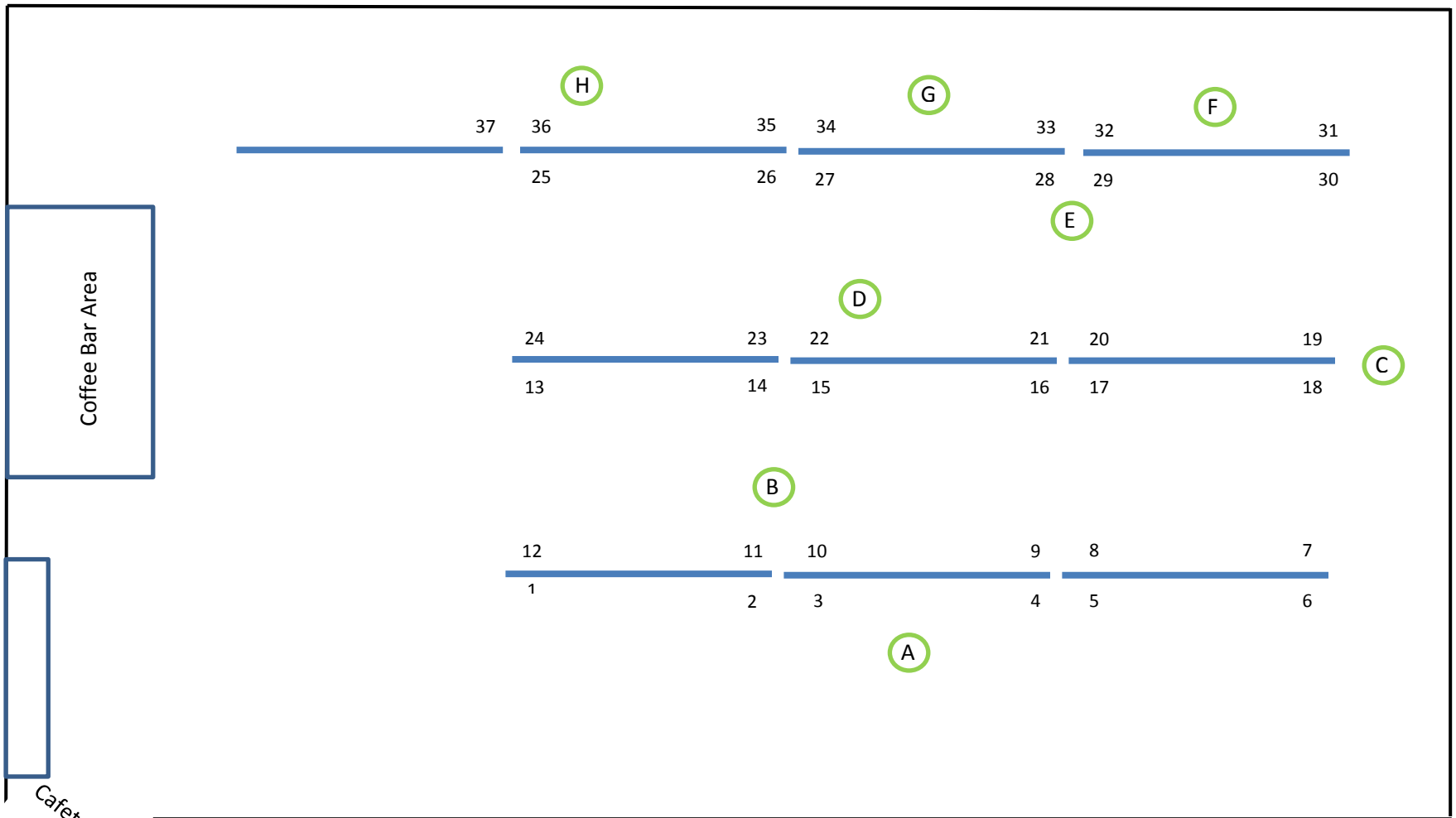


CalCharge



CalCharge Kickoff Event
Lawrence Berkeley National Laboratory
May 3, 2013
Poster Session Abstracts

Window wall, facing the Bay



KEY TO MAP

- (A) Li-ion Batteries Materials
- (B) Advanced Diagnostics
- (C) Theory and Mathematical Modeling
- (D) Lithium Metal Batteries
- (E) Li/Sulfur and Li/Air Batteries
- (F) Sodium and Magnesium Batteries
- (G) Flow Batteries and Fuel Cells
- (H) Energy Storage/Grid Integration

1 Influence of particle morphology on structural evolution and electrochemical performance of $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$ cathode

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The lithium and manganese rich layered oxide family, of general formula $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$ (M = Mn, Co, Ni), are subject of intense investigation due to their high capacity. They have capacities exceeding 200 mAh g^{-1} , well above commercial layered oxide such as LiCoO_2 , which makes them attractive for high energy applications. These materials have a complex structure, generally expressed in the notation of $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ (M = Mn, Co, Ni), and they also have an activation plateau near 4.6 V in which oxygen is presumably removed from the bulk and structural changes are induced. These changes are poorly understood, and there is strong interest in gaining insight in the mechanisms involved so that electrode cycle life and rate capability can be improved. Of particular interest are the structural and morphological changes during delithiation and relithiation. Most synthesis methods, such as the hydroxide precipitation followed by annealing at high temperature around 1000°C , yield aggregated particles with significant inhomogeneity that often complicates the interpretation of experimental results. Our approach is to synthesize large and well-formed crystals to gain a better understanding of the changes that occur during the extraction and insertion of Li. By tuning the molten-salt synthesis conditions, such as the flux, precursor salts, temperature and time, layered $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ were obtained in plate, needle-like, micron and submicron size polyhedron shapes. Chemical and electrochemical methods were used to extract and insert lithium into these oxide crystal samples. Structural and morphological evolutions were evaluated by *in situ* and *ex situ*

XRD, electron microscopy and X-ray absorption spectroscopy. The effect of the morphology on the rate capability and lithium diffusion coefficient will be discussed, as well as the changes in structure during charge and discharge.

2 Anatase TiO_2 colloidal nanocrystal-based architectures: models to assess the role of porosity and nanocrystal morphology in Li battery electrode

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In the context of energy storage, our present research focuses on investigating how nanocrystals (NCs) can be efficiently used as active material in electrodes for lithium ion battery. The high surface area of the nanoparticles suggests an extended contact with the electrolyte and their small dimension shortens the diffusion path of both lithium ions and electrons. Combined, these two features should lead to a significant improvement in the overall charge and discharge rates of the battery.¹ However, when introduced in conventional electrodes (i.e. randomly packed active particles with carbon and a binder) NCs tend to form aggregates. It causes a loss of the nanosize benefit and it also prevents any conclusion about the actual electrochemical behavior of the NCs themselves.

In a previous work, we proposed a unique way to create tridimensional (3D) organized porous architectures of various colloidal nanocrystals by exploiting specific interactions between the bare surface of ligand stripped- NCs and a

specifically designed block-copolymer.² In the context of the present study, 3D ordered NCs based-architectures are key because they represent a unique tool to discriminate the NCs' contribution to the battery performances from the contribution of the NCs' packing. Using the well-controlled architecture, we can therefore compare the electrochemical behavior of a large panel of NCs of different size, shape and composition for the same open architecture.

This way, we were able to study the influence of the NCs morphology on the electrochemical behavior of the anatase TiO₂ nanoparticles. Anatase TiO₂ is a well-studied lithium insertion material, so our results can be compared with rigorous theoretical analysis of the anisotropic strain induced by lithiation, the facet-dependence of lithium insertion reactions, and the crystallographic direction-dependent lithium diffusion constant.³ On this rigorous basis, the lessons learned about the relationship between architecture and electrochemical characteristics can suggest design rules also for other insertion electrode materials.

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Understanding Limitations in NMC Electrode

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The layered Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ (NMC) cathode system has been modeled with the aim of predicting the performance at high rates. While the macro-homogeneous models can describe the behavior of battery electrodes at low rates, further increase in current leads to significant deviation in the model predictions when compared to experimental data. The purpose

of this study is to understand the cause for these deviations.

Experiments were performed on NMC electrodes in a half-cell configuration with a Li-metal counter electrode. The results obtained from the thin and thick NMC electrode showed that at low rates (less than 1C) the system is limited to the solid phase of the active material. This is evident in the end-of-discharge capacity that gradually decreases with increasing rates which reflects the decreasing of the diffusion coefficient of lithium in the solid particles toward the end of discharge. As the discharge rate was increased further, the thicker electrodes showed a rapid capacity loss, suggesting the change in the electrode limitation as the thickness increases. Further analysis of the data suggests that the limitation occur in the electrolyte phase within the porous electrode, and not the Li-metal electrode.

Modeling results show that at rates larger than 1C the calculated electrode potentials and capacity deviate from the experimental data. The prediction of the model can be improved by using appropriate effective transport properties that describe the transport of ionic species in the solution phase of the porous electrode. Therefore, understanding the electrode structure, i.e., the porosity and tortuosity, and the electrolyte transport properties is required to accurately predict the electrode capacity as well as the potential at high rates.

Tuning Battery Voltage with Surface Chemistry

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The ability to tune the electrochemical potential of a battery electrode material without changing its composition would yield an immediate increase in battery energy density by

increasing the discharge voltage. By using dipolar molecules to functionalize the surface of an electrode, it may be possible to achieve such voltage modulation, changing the discharge potential by as much as 1V per electrode. We present a preliminary study of the surface chemistry of titanates, which points the way toward controlling the electrochemical potential to produce higher-energy batteries without requiring new materials development.

5 Applications of Stabilized Lithium Metal Powder (SLMP) in Lithium-ion Batteries

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With increasing demanding of energy, it becomes more and more important to find alternative energy sources beyond fossil fuels. Batteries, especially lithium ion batteries (LIB), provide unique advantages with their high energy densities (up to 150 Whkg⁻¹). To meet the requirement for applications in electric vehicle (EV) and hybrid electric vehicle (HEV), it is desirable to develop high energy density and low cost materials. With current Li-ion technology, lithium in the cell is limited from cathode material, e.g., LiCoO₂ etc., and electrolyte. Solid-Electrolyte Interphase (SEI) formation during initial cycles consumes lithium and results partial capacity loss irreversibly. The incorporation of stabilized lithium metal powder (SLMP), developed by FMC corporation, into anode has been suggested to overcome the irreversible capacity loss, and increase the capacity by 5~10%. Moreover, some non-lithiated materials with high specific capacities can be used as cathode materials if coupled with pre-lithiated anodes. With this strategy, the full cell energy density can be significantly improved.

In this report, we demonstrate the application of SLMP in anode materials. To apply SLMP into the anode electrodes, two strategies have been applied: SLMP was either added into electrode slurry for film casting, or sprayed directly on top of anode laminate. The prelithiated anodes were allowed to rest for different time periods before cycling. Without any low C-rate formation, the cycling results suggest that the anode prelithiation can help the development of SEI.

To conduct the comparison study, CGP-G8 graphite from Conoco Phillips was homogenized with styrene-butadiene rubber (SBR), acetylene black (AB) and SLMP in toluene to make slurry as the ratio of (88% CGP-G8, 5% SBR, 5% AB, 2% SLMP). With the incorporation of SLMP, the open circuit potential dropped quickly from 2.3V to 0.1 V, indicating the partial lithiation of graphite. Half cell performance for SLMP-lithiated graphite anodes with different resting time indicate that the cell without resting has significant capacity drop during the first 10 cycles. With increasing of the resting time, cell capacity of the first cycle increased by up to 10%, and became stable with resting time of 4 days or more. Moreover, the capacity decay is slower with longer resting time and the fading rate tends to stabilize with resting time of 4 days or more. This very likely reveals the SEI formation process, indicating the full development of SEI on SLMP-lithiated graphite with long enough resting time. Development of such SEI (using SLMP method) is equivalent to the slow formation protocols used in regular lithium ion cells.

6 Conductive Polymer Binder for High Capacity Lithium Battery Electrodes

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A new conductive polymer binder is developed for solving the long-standing volume change issue for high capacity materials in lithium battery electrodes. Through synthesis modification, spectroscopy, and simulation techniques the electronic structure and polarity of the polymer was tailored favorably to enable in situ lithium doping. The composite electrodes based on Si particles and this polymer, without any conductive additives, exhibit so far the best performance in several critical aspects for commercial applications, including high capacity, long-term cycling, low over potential between charge and discharge, and good rate performance.

Improved conductive carbon additives for high-energy lithium-ion batteries

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Small-sized lithium ion batteries for portable electronic devices are considered a mature technology, large-scale electric storage devices for transportation applications still require significant improvements of the battery energy density to cost ratio. One promising approach involves development of positive electrode materials that can store more charge and/or operate at higher potentials. e.g., $\text{Li}[\text{Mn}_{1/2}\text{Ni}_{1/2}]\text{O}_2$ y $\text{LiCoO}_2 \cdot z \text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ ($x + y + z = 1$), $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

Carbon black (CB) conductive additives are key components of all Li-ion composite cathodes. CB additives primary role is to enhance electronic percolation in the composite and reduce ohmic resistance of the electrode. Interestingly, carbon black additives constitute the majority of the electrode surface area. Unfortunately, at high potentials CB becomes electrochemically active toward electrolyte oxidation and anion intercalation, which results

in material degradation, surface layer formation, electrode impedance rise and battery failure.

This work focuses on the electro-catalytic properties of carbon blacks and remedies to mitigate their interfacial activity in high-energy Li-ion systems. A thermal treatment to suppress CB electrochemical activity in organic electrolytes and to inhibit adverse side effects was developed and tested both with model and commercial materials. This innovative process was successfully optimized and evaluated for a commercial carbon black powder, which was then used as conductive additive in state-of-the-art high-energy composite cathodes. The new improved CB additives help to suppress unwanted side-processes and improve cycling performance and lifetime of composite high-energy positive electrodes. .

Acknowledgments

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Effect of VC in Graphite / NMC cells

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Degradation at the electrode surface is one of the major reasons behind the capacity fade in a well-made battery. The addition of electrolyte additives is known to alter the surface and rate of intercalation and side-reactions. In particular, VC has been studied extensively for different lithium ion chemistries and is shown to improve coulombic efficiency of different electrodes. In this study, the effect of vinylene carbonate (VC) as an electrolyte additive in a graphite/NMC 333 (lithium-nickel-manganese-cobalt oxide) cell was investigated. A three- electrode cell configuration was used to understand the

performance of individual electrodes at different discharge rates in the presence of VC and compare it with neat electrolyte. Such a study shows that the addition of VC improves the rate performance especially at moderately high rates. It was also observed that the rate of side reactions was decreased with the addition of VC. Despite these important performance improves, it was interesting to find that there was no significant improvement in the cycling performance even though there was significant improvement in columbic efficiency. This suggests that columbic efficiency may not always be a perfect indicator of the expected lifetime of a cell.

Battery Diagnostics Across Different Time and Length Scales

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Significant improvements in energy density, safety performance, and lifetime of lithium-ion batteries are necessary to allow their rapid adoption for automotive applications. The electrode/electrolyte reactions can have a large impact on the performance of Li-ion batteries, and therefore, an understanding of them is critical to the development of new electrodes and electrolytes. *In situ* techniques that probe the interfacial phenomena on electrodes provide real-time information on surface reactivity and avoid any concerns related to surface composition change through sample preparation for ex situ techniques.

In situ and ex situ Raman, fluorescence, FTIR spectroscopy and standard electrochemical techniques are effective method to evaluate the degradation processes and their possible implications on the battery electrochemical performance. A custom-designed in situ spectro-electrochemical cell with a 1 μm spatial

resolution was used to carried out In situ fluorescence /raman measurements during cycling of Li-ion model cells with different chemistries to monitor and characterize the electrode/electrolyte interactions. Variations in fluorescence intensity and FTIR spectrum are used to provide insights into the sources of electrolyte decomposition and the extent of passivation of the electrode with cycling. The chemical cross-talk in a battery is also evaluated, with fluorescence measurements providing a localized probe of the formation and diffusion of decomposition products between the cathode and the anode in a full cell. Surface structural changes were probed by Raman.

In situ ellipsometry and AFM measurements on B-Sn polycrystalline and single crystals surfaces show the development of a surface electrolyte interphase (SEI) layer at potentials well above lithiation. Both the kinetics of formation and the structure of the SEI were revealed to be extremely sensitive to the crystal orientation exposed to the electrolyte. Furthermore, the formation of soluble electrolyte decomposition products that tend to dissolve and diffuse away delay considerably the formation of an effective SEI layer.

By overcoming the diffraction limit normally encountered in microspectroscopy (Fourier-transform infrared (FTIR) and Raman), scattering-type near-field scanning infrared microscopy (NSOM) is capable of providing chemical mapping at high spatial resolution without beam damage. Applied for the first time to energy storage material, the NSOM technique reveals new insights in the phase equilibria in micron-sized Li_xFePO_4 single particles. A novel phase distribution pattern involving coexistence of two phases within a single particle has been demonstrated in this study by exploring tomographic capabilities of NSOM through lightning rod model and point-by-point spectra inversion. These results open a new chapter in material characterization by providing a non-destructive, table-top tomographic technique with fast acquisition

time and high sensitivity to local material properties, rather than elemental composition.

10 *In Situ* Fluorescence Spectroscopy of Interfacial Processes in High-Voltages Cathodes

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Significant improvements in energy density, safety performance, and lifetime of lithium-ion batteries are necessary to allow their rapid adoption for automotive applications. One approach is to find and develop cathode materials with higher operating potentials. Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes with a redox potential of 4.7 V vs. $\text{Li}^{+/0}$ and a capacity of 148 mAh/g are an attractive alternative to conventional layered cathodes LiCoO_2 and LiFePO_4 . However, these high operating voltages are at the edge of the thermodynamic stability window for standard carbonate-based electrolytes, and surface/decomposition reactions between the electrode and electrolyte can have a significant influence on the performance and lifetime of the battery. A fundamental understanding of the physical and chemical processes that govern the complex electrode/electrolyte interactions is fundamental to the development of new battery materials.

In this work, the interfacial reactivity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ single crystals with preferred surface crystalline orientation was probed using *in situ* Raman and fluorescence spectroscopies. Charge-discharge processes in Li-ion cells are accompanied by growth of a large fluorescence background from the surfaces of electrodes and the electrolyte. This strong fluorescence signal can be used to sense and characterize

degradation processes and soluble reactions products that diffuse into the electrolyte.

In situ fluorescence and Raman measurements were carried out during cycling of Li-ion model cells of different chemistries. The intensity of the fluorescent background tends to grow with prolonged electrode polarization/cycling measurements. It has been shown that $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at various states of charge and other composite electrode components do not produce a fluorescent signal. The fluorescence observed provides a direct evidence for the presence of decomposition products formed on the surface of the electrode. *In situ* fluorescence and Raman investigations on a carbon and binder-free $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode demonstrated that $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ that oxidation of Ni is a source of electro-catalytic decomposition of the electrolyte, that much of these decomposition species dissipate or dissolve into the electrolyte or degrade after formation, and hence, that they do not form a stable surface layer on the bare cathode surface during initial cycles.

The formation of photo luminescent active species is not only determined by the materials and the electrolyte but also varies strongly with the crystalline orientation of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ surface.

11 *In-Situ* Lithium Ion Concentration Profiles with Sub-Micron Spatial Resolution via Confocal Raman Microscopy

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Lithium ion transport is the fundamental process behind the function of lithium ion batteries, yet there is little agreement on the value of the diffusion coefficient of lithium ions.

To help resolve this issue, we propose the use of confocal Raman microscopy to perform *in situ* measurements of lithium ion concentration profiles in liquid electrolytes with sub-micron spatial resolution and temporal resolution as fast as 100 ms. In our first experiment, we measure the lithium ion concentration profile in a polarized Li/LiPF₆/Li symmetric cell with one-dimensional lithium ion transport. Future work will be focused on measuring concentration profiles in more complicated geometries.

12 Soft X-ray Spectroscopy for Li-ion Battery Materials

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High performance new materials are essential for renewable energy research and technology. The growing global energy consumption and consequent environmental threats demand us to develop and utilize more efficient approaches to discover such materials, to explore their fundamental properties, to reveal the correlation between these properties and device performances for further material optimization. Synchrotron-based X-ray spectroscopy is one of such incisive experimental tools that can directly probe the key electronic states relevant to the performance of a variety of energy conversion and storage devices such as batteries, catalysis, solar cells, and fuel cells.

Here, we will present our recent studies on the electronic structures of some Li-ion battery materials at the Advanced Light Source (ALS) in Lawrence Berkeley National Laboratory (LBNL) to demonstrate the capability of soft X-ray spectroscopy for battery research. By means of elemental- and orbital-sensitive X-ray absorption (XAS) and X-ray emission (XES) spectroscopies, we are able to depict both unoccupied and occupied states in the vicinity

of the Fermi level, in particular the transition-metal (TM) 3*d* states and anion *p* states associated with Li diffusion, phase transformation, redox process, and safety issue of 3*d*-TM cathode compounds. In addition, the newly developed *in situ* and *operando* instrumentations for soft X-ray spectroscopy empower us to capture the dynamic information of a battery under operating conditions, and will open new directions to reveal more emergent phenomena in electrochemical systems.

13 *Operando* NEXAFS Spectroscopy for Studying Electrochemical Processes in Energy Related Materials

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The hunt for the source of green energy is ever increasing quest of mankind. Based on the same, various electrochemical techniques have been developed in order to generate and store solar energy. The water splitting reaction found in plant photosynthetic machinery is supposed to play pivotal role in this regard by generating hydrogen out of water and store solar energy in the hydrogen bond in the form of chemical energy. Following this path, various energy generating materials have been screened and applied accordingly to produce green energy. Hematite is one such material believed to play significant role in photoelectrochemical-solar-hydrogen production. The water splitting efficiency of hematite is relatively low but it stills a better candidate from the light absorptive and stability perspective. However a detail understanding of the photoelectrochemical process in hematite at molecular scale is very important in order to learn the shortcomings at electronic structure. *Ex-situ* synchrotron XAS technique has already been applied by the author in order to understand the changes in electronic structure

in post photoelectrochemically process film treated under different applied potential. In the next step, to monitor the processes in operando condition, we have employed NEXAFS spectroscopy in an atmospheric pressure chemical vapor deposited (APCVD) Si - hematite film on Silicon nitride substrate. The newly developed ISSAC (in situ advanced absorption cell) end station at BL 6. 3.1 allow us to carry the XAS study in a specially designed liquid flow cell under high vacuum condition with a base pressure of 1×10^{-8} Torr. The idea behind applying such method is to understand the physical chemistry of underlying phenomenon associated with the photoelectrochemical process at the semiconductor - electrolyte interface. The objective of our study was to probe the formation of hole at SC interface and to understand the nature of holes with NEXAFS spectroscopy by looking into the VB of semiconductor. For the experiment, we have used a specially designed liquid flow cell able to operate in UHV condition. The X - ray spectra have been taken during chronoamperometric condition (fixed bias) and exposure of AM 1.5 solar simulated white lights. The analysis of X - ray spectra at O K edge revealed two new spectral features evolved before the pre edge that on increasing the bias and light on condition at around 300 mV. We validated these as an O 2p hole transition into the charge transfer band and an Fe 3d type hole into the upper Hubbard band [1]. In the next step, we also tried to study the role of co - catalyst treatment on the efficiency of photoanode. In order to validate the experiment, we feed very dilute amount of cobalt chloride solution into the electrochemical cell and did NEXAFS study of the cobalt chloride electronic structure. The changes in shape of the spectrum theoretically ascribed to the weight of the transition matrix element in different crystal symmetries [2].

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Ambient-Pressure X-ray Photoelectron Spectroscopy (APXPS) for in-situ CO Oxidation Reaction Study and Liquid Electrolyte Electrochemical Process

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SnO_x promoted platinum-based catalysts are found to be active towards low-temperature CO oxidation reaction, which is an important reaction in many processes, especially the oxidation of ethanol into CO₂ that can be found in the anode surface of a direct alcohol fuel cell. However, neither SnO_x nor Pt has comparable activity towards COR. The mechanism of the increased activity of Pt/SnO_x towards COR is still in question. In an effort to understand the mechanism on this increased activity, recent study on “inverse” catalyst system of SnO_x nanoparticles on Pt single crystal was conducted. We have conducted *in-situ* measurement of CO oxidation on “inverse catalysts” composed of SnO_x nanostructures supported on Pt(111) using near ambient pressure X-ray photoelectron spectroscopy (XPS) and high pressure scanning tunneling microscopy (STM). Nanostructures of SnO_x were prepared by depositing Sn on Pt(111) pre-covered by O₂ layers at low temperature. Ambient-pressure XPS data show that the prepared SnO_x nanoparticles are highly reduced, with Sn(II)O being the dominant oxide species. In-situ study of SnO_x/Pt(111) showed that for lower coverage of SnO_x (0.25 ML), Sn(II)O amount decreased as the surface was heated under CO gas at 445 K, while Sn(0) amount is increased. Meanwhile for the higher coverage (1.0 ML), the decrease of Sn(II) is followed by the increase in the Sn(IV) amount. STM images show that at 0.25 ML SnO_x are small islands nanoparticles that are randomly

placed on the substrate. However, at 1.0 ML the island size and density grow. The in-situ surface characterization data will be combined with previously reported catalytic study of SnO_x/Pt towards COR to help better understand the mechanism of this reaction.

We also report on the construction of a new ambient-pressure XPS (APXPS) system which will allow the use of synchrotron source to analyze processes that occur on the solid-liquid interface region of different system of interest. The new APXPS system is located in bending magnet beamline 9.3.1 in Advanced Light Source. This beamline operates at photon energy of 2.5 keV to 5.5 keV. The use of “hard” X-ray source will allow one to analyze surfaces with higher penetration depth. With this energy range, double layer region of a thin-film of liquid on a solid surface can be analyzed. *In-situ* surface characterization of Pt foil as an electrode in KF electrolyte under electrochemical treatment is possible with the use of this new hard x-ray APXPS system. Cyclic voltammetry of Pt foil in KF electrolyte was recorded inside the APXPS chamber at elevated pressure (near KF vapor pressure). XPS shows that the cation to anion ratio in the double layer region of KF electrolyte and Pt surface interface is dependent of the applied voltage. This study shows the ability to follow the process that occurs in the double layer region and on the electrode surface using hard x-ray APXPS technique. This development will benefit many studies related to materials discovery in energy related research.

15 Overview of Battery Characterization Techniques

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Li-ion batteries are complex multicomponent electrochemical systems that incorporate widely dissimilar phases in physical and electrical contact. Electron and ionic transfer across solid-solid, solid-liquid interfaces and within each of constituent phases determine the behavior of the composite electrodes and the electrochemical performance of the entire battery system. The gradual degradation of lithium-ion batteries limits the performance of portable electronic devices and presents a significant barrier for commercial applications.

Thorough understanding of the battery cell mode of operation cannot be gained solely through testing commercial-type devices. Complex phenomena in battery cells cannot be analyzed in detail unless they are isolated and studied separately. In order to determine such factors that control the function and operation of battery cells, Electrochemistry Diagnostics Group at LBNL, builds and analyzes model systems that are directly relevant to the challenges of the battery technology and allow identification of processes that determine and control cell performance.

Apart from building model systems that isolate/amplify certain factors determining cell characteristics, we are also developing new diagnostic techniques/configurations that would allow fast and straightforward identification of analytes as well as observation of the material *in situ*, as it is operating in an electrochemical cell.

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16 3D Chemical Imaging of Li-ion Battery Materials and Interfacial Layers with Ultrafast Laser Spectroscopy

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Next-generation ultrafast laser-based technologies combined with optical emission and ICP-ToF-Mass Spectroscopy are used for chemical imaging of battery materials across different length scales commensurate with battery component characterization needs. These include electrode/electrolyte interfaces, electrolytes in bulk and thin film configurations, cathodes, and anodes. High-sensitivity, spatially resolved chemical analysis (2D and 3D) is demonstrated for Li-ion battery systems with depth resolution down to the nanometer scale. These ultrafast laser technologies represent highly versatile tools with expanded abilities for the development of large-capacity Li-ion batteries for electric and hybrid vehicle applications.



In-operando X-ray absorption spectroscopy of germanium anodes for lithium ion batteries

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Rechargeable lithium ion batteries (LIBs) are currently the preferred energy storage devices in portable electronics. Currently, the universally-used anode material in LIBs is carbon, due to its fairly high capacity of 372 mAhg⁻¹ and rate capability. However, in order to extend the use of LIBs to electric vehicles, larger capacities are necessary. Group VI-based

materials, such as silicon and germanium, are attractive alternatives to carbon as anode materials mainly due to their high theoretical energy densities (4200 mAhg⁻¹ and 1600 mAhg⁻¹ for silicon and germanium respectively). In particular, germanium has the added advantage of higher Li-ion diffusivity (400 times higher than in silicon), which makes it an attractive candidate for fast-charging applications. In order to develop next-generation and fast-charging anode materials, it is important to understand the interaction between Li and Ge. However, the (de)lithiation mechanism of Ge is not widely studied. In this work, we use in-operando X-ray absorption spectroscopy (XAS) to study the (de)lithiation mechanism in Ge anode material. We will show that crystalline Ge becomes amorphous after the first charge/discharge cycle. Additionally, detailed changes in the XAS spectra during the lithiation process will be discussed.



The Materials Project – A Materials Design Platform

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Today, it takes 18 years on average from materials conception to commercialization. Unless we implement new approaches to the materials discovery and development process, we cannot expect to have a significant impact on our energy economy in the 20-30 year time frame needed to address the climate issues. One of the foremost reasons for the long process time in materials discovery is the lack of comprehensive knowledge about materials, organized for easy analysis and rational design. Materials innovation today is largely done by intuition and based on the experience of single investigators. Google has demonstrated the value of organizing data and making the data available and searchable to large communities. The Materials Project (www.materialsproject.org) aims to leverage the information age for materials using the only

tool that can efficiently scan multiple materials properties in a reasonable amount of time: computations.

Through our project, both experimentalists and theorists have materials properties of all known inorganic compounds and beyond at their fingertips to scan, analyze and provide inspiration for novel materials development. We are continuously calculating and updating our database as well as our analysis tools and web site. To date, we have successfully computed and imported > 30,000 inorganic compounds into the database, which can now be freely accessed and searched over through the web interface. Examples of successful in silico materials design projects for energy storage as well as demonstration of existing capabilities at the Materials Project will be presented. We are adding another capability tailored to specific collaborations and industrial partners which includes a private sandbox for target compounds and calculations which leverages the large data set from the public resource but the keeps data specifically computed for the project private. This resource enables consulting and computations on demand services.

19 Modeling stresses in active material/binder/conductive additive systems

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Mechanical stress due to lithium insertion and removal can be an important cause of battery degradation, particularly for active materials such as silicon, which can experience enormous volume changes during a charge/discharge cycle. In porous electrodes, the volume changes of active material particles also cause displacement and generate stress in the surrounding composite of binder and conductive material. Stress-related damage to the active material, surrounding composite, and to the interfaces between these regions can

result in electrical isolation and capacity loss.

Simulations incorporating large-deformation solid mechanics were performed for two-dimensional model systems consisting of active material undergoing lithium insertion and removal, in contact with the surrounding composite. Stresses were calculated throughout both regions and at their interface.

These simulations were performed under the assumption that the system remains undamaged; while these simulations cannot show accumulation of mechanical damage, it is expected that damage is likely to occur under conditions in which computed stresses exceed yield stresses of the active material, or of the composite, or for the interface between the two regions. Similarly, one can perform ensembles of simulations in order to find conditions under which stresses remain small and damage is unlikely to occur.

20 Hard X-ray tomography as a non-destructive technique to study the growth of lithium dendrites in lithium polymer batteries

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Failure caused by dendrite growth in high-energy-density, rechargeable lithium-ion batteries with lithium metal anodes has

prevented the widespread use of these batteries in a variety of applications ranging from consumer electronics to electric vehicles. Efforts to solve the lithium dendrite problem have all focused on preventing the growth of protrusions from the anode surface. Synchrotron hard X-ray micro-tomography experiments reported in this poster show that during the early stage of dendrite development, the bulk of the dendritic structure lies within the electrode. The portion of the dendrite protruding into the electrolyte increases upon cycling until it spans the electrolyte thickness causing a short circuit. Contrary to conventional wisdom, these results suggest that efforts to prevent dendrite formation should focus on inhibiting the development of cavities in the lithium electrode, and not on suppressing protrusions into the electrolyte.



Strategies for Lithium Stabilization in Novel Electrochemical Systems.

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In order to achieve high energy density batteries for future applications, improvements in the anode performance are necessary. Lithium metal anodes display as much as 3860 mAh g⁻¹ in Li-air batteries compared to conventional graphite anodes 372 mAh g⁻¹. In the past, lithium metal anodes were beset with issues such as poor cycle life due to electrode surface morphological changes during deposition/dissolution cycles. Formation of mossy and dendritic growths of lithium can compromise cell integrity, lead to short circuits and subsequently to a thermal run-away of the system. To overcome these issues, our studies focus on the development of protective ceramic membranes and cross-linked siloxane containing polymers acting as protective coatings

Additionally, solid state inorganic electrolytes were investigated as promising candidates for the development of artificial charge transport interfaces in lithium batteries. Here, the focus of the research was on NASICON type electrolytes such as OHARA® glass, lithium lanthanum zirconium oxide (LLZO) a garnet type material and lithium metaborates (LiBO₂). These compounds with their high chemical stability and reasonable lithium ion conductivity are seen as promising candidates in this field.

Impedance spectroscopy was applied to investigate the lithium-ion transfer across the solid/liquid electrolyte interface. Furthermore, lithium ion solvation and desolvation processes at the interface were investigated using a four-electrode Devanathan-Stachurski symmetrical AC impedance cell. To determine between interface and bulk effects, separate investigations utilizing gold, aluminum and lithium cobalt oxide electrodes, which were deposited directly onto the materials, were performed. Utilizing this approach, impedance spectra can distinguish between the contributions of bulk and grain boundaries from liquid interfacial regions. These results indicate that the composition of the solid/liquid interface greatly affects the Li-ion transfer process not only in the locally but in the whole system.

In a second approach, a study of Lithium electrodes coated with siloxane polymers in bis(trifluoromethanesulfonyl)imide (LiTMFSI) based electrolytes solvents have been carried out. Spectroscopic tools such as *in situ* FTIR demonstrate that lithium metal quickly decomposes conventional carbonate-based electrolytes to form a complex SEI layer. By variation of the siloxanes according to alkyl group to n = 1, 2, 3, and 4 (CH₃O(CH₂CH₂O)_nCH₃) improvements of the behavior were achieved and a correlation of coating thickness to surface layer dissolution elucidated. These surface layers were thoroughly investigated using techniques such as AFM, Raman, FTIR and standard electrochemical spectroscopy. By combining the electrochemistry and the

structural behavior of the samples a relationship between the surface structural and morphological changes, the surface interfacial behavior, and the electrochemical performance of Li-metal anodes was determined.

22 Quantifying polarization losses at single ion conductor (ceramic)/ liquid electrolyte interface

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Single Ion conductor solid electrolytes such as OHARA[®] glass ($\text{Li}_{1+x+3z}\text{Al}_x(\text{Ti,Ge})_{2-x}\text{Si}_{3z}\text{P}_{3-z}\text{O}_{12}$) are being considered for protection from dendrites in Li metal batteries. Previous studies¹ have shown using AC Impedance spectroscopy that a high-energy barrier exists at the OHARA[®] /liquid electrolyte interface. Such a charge transfer resistance has been attributed to Li+ solvation/desolvation. To further investigate this phenomenon, a custom diffusion cell was designed where OHARA[®] glass ceramic was sandwiched between two independent compartments in a Li-Li symmetric cell. Two different concentrations (0.5M and 1M) of LiPF₆ in EC:DEC (1:1) were used as the electrolyte. Experiments were performed with and without the OHARA[®] in the cell to quantify the polarization loss at the OHARA[®] /liquid electrolyte interface.

Theory: When a constant current is passed through the Li-Li symmetric cell with a single-ion conductor (SIC) in the middle, only Li+ passes through from one compartment to the other. In order to maintain electro-neutrality, the flux of Li+ at the SIC /liquid electrolyte interface has to be equal to the constant current being maintained in the cell. As a consequence, in a Li-Li symmetric cell of length 'L' with a SIC in the middle, the concentration profiles of Li+ in each compartment would be that of a Li-Li symmetric cell of length 'L/2'.

Therefore, in principle, if there is no polarization loss at the single ion conductor (ceramic) / liquid electrolyte interface and current is passed for a short period of time (semi-infinite boundary condition maintained), then the voltage difference between the working and counter Li electrodes should be the sum of: (a) potential drop in a Li-Li symmetric cell without the SIC; (b) Ohmic drop through the SIC; (c) concentration over potential right next to either sides of the SIC/liquid electrolyte interface

Experiments: First, a formation protocol for the two Li metal electrodes was established to ensure stable cycling. Thereafter, the cell potential was measured at different current densities in the Li-Li symmetric cell for two cases: (a) with the OHARA[®] glass in the middle; (b) without OHARA[®] glass in the middle. The polarization loss for the case with glass was much higher than what was expected from theory (as explained above). Also, this experiment was performed for 0.5M and 1M electrolyte concentration. For the same current density, polarization losses at the OHARA[®] /liquid electrolyte interface for 1M were higher than that for 0.5M. Both these results suggest that: (a) polarization loss at the OHARA[®] /liquid electrolyte is significant; (b) interfacial effects are concentration dependent.

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23 Multifunctional Binder-Electrolyte for Use in Lithium Battery Cathodes

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Redox reactions that occur at the electrodes of batteries require transport of both ions and electrons to the active centers. This brings significant complications not only because it

requires that the active centers be located at the junctions of conduction pathways, but also because the materials that transport ions and electrons are vastly different. Here, we report on the synthesis and characterization of a block copolymer, poly(3-hexylthiophene)-*b*-poly(ethylene oxide) (P3HT-PEO) that exhibits simultaneous ionic and electronic conduction, as determined by a combination of ac impedance spectroscopy and dc measurements. We discovered that the addition of LiTFSI to P3HT homopolymer results in a roughly 400-fold increase in electronic conductivity at high salt concentrations. By combining this result with measurements of electronic conductivity of P3HT-PEO copolymers with and without salt we estimated the extent to which LiTFSI partitions between the P3HT and PEO microphases. Using the P3HT-PEO polymer as binder material in a lithium battery cathode showed specific capacities that are within experimental error of the theoretical capacity of the battery. The ability of P3HT-PEO to serve all of the transport and binding functions required in a lithium battery electrode is thus demonstrated.

24

Nanostructured block copolymers for use in solid-state lithium metal batteries

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Nanostructured block copolymers (BCPs) with a mechanically robust block and an ion-conducting block doped with a lithium salt have

proven promising for use as electrolytes in rechargeable lithium metal batteries. These materials exhibit high ionic conductivity at elevated temperatures, excellent stability against lithium metal, and the ability to retard dendrite growth. Using these BCPs as electrolytes to create completely dry solid-state lithium metal cells offers the possibility of very high energy density system with no volatile components. The conductivity of these materials has been studied as a function of molecular weight and morphology. These materials have also been cycled in symmetric lithium metal cells, as well as full electrochemical cells with lithium metal as the negative electrode and several different active materials in the positive electrode.

25

TiO₂-SEO Block Copolymer

Nanocomposites as

Solid-State Electrolytes for Lithium Metal Batteries.

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There is considerable interest in developing solid electrolytes for rechargeable lithium batteries as they have the potential to increase both energy density due to incorporation of a lithium metal anode and safety of batteries due to the fact that they are nonflammable. Block copolymers with a mechanically hard non-conducting block and a soft ion-conducting block provide an avenue for obtaining highly conducting rigid solids. In this study we add surface-functionalized TiO₂ nanoparticles to a mixture of polystyrene-*block*-poly(ethylene oxide) and bis(trifluoromethane)sulfonimide lithium salt. The presence of BF₄⁻ moieties on

the surface of the particles was essential for obtaining macroscopically homogeneous electrolytes; macrophase separation was observed with the same nanoparticles with surfaces covered with oleic acid. The stability of these composite electrolytes against lithium metal electrodes was tested in symmetric lithium-composite electrolyte-lithium cells. The surprising result was that electrolytes with 24 wt % nanoparticles exhibited optimum stability; the amount of charge passed before dendrite formation was observed in the optimized composite electrolyte was a factor of five larger than that of the neat block copolymer electrolyte. Both tensile and shear moduli of the electrolytes were non-monotonic functions of particle concentration with peaks in the vicinity of 17 to 20 wt %. In addition, the electrolytes with 24 wt % nanoparticles were optically transparent, and exhibited a uniform morphology when examined by scanning electron microscopy (SEM). In contrast, electrolytes with 12 and 28 wt % nanoparticles were opaque, and TiO₂ clusters were evident in SEM images.

26 Improved Sulfur/Lithium Sulfide Nanocomposite Electrodes for Next-Generation Lithium Cells

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A new generation of batteries with a capability of at least 400 Wh/kg is urgently needed since current lithium ion cells are reaching their maximum energy storage capability (~200 Wh/kg). The lithium/sulfur cell, with a theoretical specific energy of 2680 Wh/kg, is an attractive candidate. However, its rapid capacity decay owing to polysulfide dissolution requires good protection of the cathode materials before it can be commercialized. In our research, we are working on improving the performance of the Li/S cell by modifying the

active material structure, electrolyte and binder. For the sulfur electrode, graphene oxide and other carbon materials with various surface functional groups are used as a component of nanostructured composite electrode materials. With the help of these functional groups as well as a new binder, nanostructured sulfur can be retained during cell cycling. The latest results show that the new C-S materials are exhibiting a capacity higher than 800 mAh/g(sulfur) even after cycling for 1000 times. For Li₂S as the starting material, structured nanoparticles that contain carbon or other conductive materials are under evaluation. Recent results show that the capacity fading of Li₂S electrodes can be alleviated using carbon. In addition to these experiments, simulations of the Li/S cell are being performed. The computational model includes a description of electrochemical kinetics, mass and charge transport in the electrolyte as well as the formation of solid phases. Different reaction mechanisms can be chosen to represent the operation of Li/S cells. Simulated results include charge and discharge curves, concentrations of dissolved ions and polysulfides, volumes of solid and liquid phases in different regions of the cell as well as electrochemical impedance spectra. These results facilitate the interpretation of experimental results. The refinement and validation of the model based on our most recent data is the subject of ongoing studies.

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Molecular Dynamics modeling of Solution phase lithium sulfur chemistry and first-principles interpretation of associated X-ray spectroscopy

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Lithium-sulfur batteries are attractive alternatives to current lithium-ion technology due to the relative abundance of sulfur and a significantly higher theoretical energy density[1]. However current prototypes suffer from poor cycling performance, assumed to be due to the dissolution of polysulfide anions in the electrolyte, away from electrochemically active regions, thereby reducing the amount of active sulfur. As a step towards rational design strategies for optimizing battery performance, we employ ab-initio molecular dynamics simulations and a rigorous statistical mechanics formalism[2] to access the free energy of Li₂S_x species in an molecular model of a polymeric solvent at room temperature. Our approach allows for the exact inclusion of entropic and quantum-chemical effects, which we find to be crucial to explore the speciation of polysulfide of various lengths (two to eight S atoms). In addition, to interpret measurements made at the Advanced Light Source, we also simulate the X-ray characterization of each species by calculating the associated Li and S K-edge Near-Edge X-ray Absorption Spectra from first principles using the eXcited electron and Core-Hole (XCH) approach[3] in combination with molecular dynamics sampling and accurate spectral alignment appropriate to solution phases[4].

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Ex-Situ and In-Situ soft X-Ray Spectroscopy Characterization of Lithium-Sulfur Batteries Towards High Capacity and High Cycle Life

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Elemental sulfur (S) is suggested to be a very attractive cathode material for high-specific-energy rechargeable lithium batteries. In this study, graphene oxide-sulfur (GO-S) nanocomposite was used for lithium/sulfur cells in ionic liquid-based electrolytes with a stable cycling of more than 200 cycles. The chemical change of cathode materials has been monitored by the electronic structure and chemical bonding evolution of cathode using near edge X-ray absorption fine spectroscopy (NEXAFS). After cycling, besides the appearance of lithium polysulfide, the bonds between S atoms and GO are partially weakened, leading to the formation of lithium sulfide, lithium sulfite, lithium sulfate and Li-S-C complex with additional lithium atoms reacting with carboxyl and oxhydryl groups in GO-S. The formation of these chemical species may lead to the reduction of capacity and cycle life of the lithium/sulfur

batteries. Thus, understanding the chemical role of the oxygen content in such cathode may help to further improve the battery performance.

29 **In Situ Ambient Pressure X-ray Photoelectron Spectroscopy Studies using Solid-State Lithium-Oxygen Batteries**

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To reverse the negative impact induced by our large consumption of fossil fuels, alternative energy storage technology is needed to level our power grids, store excess energy from wind and solar power, and drive our cars. Currently we are reaching the limits of Li-ion battery storage capabilities and need to explore new battery systems, such as Li-air (O₂) batteries, which are capable of reaching the long-term needs of our society. However Li-air batteries have suffered from large capacity fading and reversible inefficiencies requiring new techniques like ambient pressure X-ray photoelectron spectroscopy (APXPS) at Lawrence Berkeley National Laboratory's the Advanced Light Source to be utilized to enhance our understanding of how Li-air batteries operate so that we can develop new strategies to overcome these challenges. In this work we developed a solid-state thin film Li-air battery with an exposed working electrode that can be used with APXPS to examine *in situ* chemistry of lithium intercalation under ultra high vacuum (UHV) as well as lithium-oxygen electrochemical reaction products formed in 5 μm of oxygen. This work will show the reversible lithium peroxide formation and decomposition

in situ using a solid-state cell, which help to provide new insights into the lithium-oxygen reaction mechanisms.

30 **In situ X-ray studies of Li-S batteries**

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We will present recent *in situ* transmission X-ray microscopy (TXM) and X-ray diffraction (XRD) work on Li-sulfur batteries. High resolution TXM allows for direct studies of morphology changes during operation, while XRD probes the structural evolution.

With its high specific capacity (1673 mAhg⁻¹), sulfur is an attractive Li-ion battery cathode material. However, due to the solubility of the higher order polysulfides, Li-S batteries suffer from capacity fading and loss of active material. We will present results from *in situ* TXM studies showing the localization of higher order polysulfide on the cathode throughout the discharge cycle despite their high solubility in the electrolyte. These results contradict *ex situ* SEM and EDS studies on similarly prepared cathodes.

31 **New materials based on a layered sodium titanate for dual electrochemical Na and Li intercalation systems†‡**

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The electrochemical properties of materials derived from $\text{NaTi}_3\text{O}_6(\text{OH})\cdot 2\text{H}_2\text{O}$ have been investigated for the first time. The parent compound has a corrugated layered structure consisting of $\{\text{Ti}_6\text{O}_{14}\}^{4-}$ units with hydrated sodium cations and protons in the interlayer spaces. Upon heating to 600°C , water is removed irreversibly, the interlayer distances become smaller, and connecting bonds between the octahedral layers form. It was found that this material can reversibly intercalate both lithium and sodium. The initial specific discharge capacities, as measured in half-cells, varied with the state of hydration and the nature of the counter-electrode (Na or Li). The electrochemical potential showed a non-linear sloping dependence with degree of intercalation, indicative of a solid-solution mechanism of intercalation. The process was centered at a low average potential of about 0.3V vs. Na or Li, the lowest ever reported for titanate-based Li hosts. The dehydrated compound showed better cycling reversibility than the as-made material. The high capacity, low voltage, and high density of this compound, in comparison to carbonaceous materials, make a compelling case for its development as an anode material, for both lithium and sodium ion batteries.

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Initial studies on interpreting X-ray absorption spectra of Chevrel Phases

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Chevrel phases ($\text{M}_x\text{Mo}_6\text{T}_8$, T=S, Se, Te) have recently gained interest because of the high mobility of the M cations, which makes them

useful as cathode materials in rechargeable Mg batteries, where Mg ions are intercalated in a three-dimensional network of cavities formed between Mo_6T_8 clusters. X-ray absorption spectroscopy (XAS) can provide information about the local electronic structure of an atom by exciting core level electrons to unoccupied states. First-principles calculations are carried out to predict and interpret XAS spectra of the Chevrel phase host compound and different stages of the Mg intercalated compound. After finding the relaxed ground state structure within the density functional formalism and including a Hubbard correction term (DFT+U), XAS spectra are calculated in the eXcited electron and Core Hole (XCH) approximation. In this scheme, the excited states appearing in the transition matrix elements are modeled by a pseudopotential with a core hole and including an excited electron in the system. To include finite-temperature effects, Ab-Initio Molecular Dynamics (AIMD) is used to sample different configurations of the system and average over their corresponding spectra. The calculated XAS spectra are expected to serve as a guideline in understanding the changes in the electronic structure of the system during the intercalation process.



Hydrogen-Bromine Flow Battery for Grid-Scale Energy Storage

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Redox flow batteries (RFB) are getting attention as promising candidates for grid-scale energy storage and load leveling including renewable-generation firming. However, due to challenging issues such as low cell performance, durability and high electrolyte cost, their widespread adoption has not occurred. To solve

those issues, we have been developing a flow battery system by utilizing hydrogen and bromine as reactants which are earth-abundant and cheap, but highly active and reversible.

A cost analysis study has demonstrated that a key driver to decrease system cost is to increase cell power. To achieve this high performance, the optimal RFB subcomponents' structure and composition were developed from experimental works. In this poster, detailed experimental methods and results as well as modeling works will be addressed to describe how to develop first-in-class RFB performance.

34 Water Uptake in Fuel-Cell Catalyst Layers

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Proton-exchange-membrane (PEM) fuel cells offer the prospect of supplying clean electrical power for a wide variety of systems including portable electronic devices and vehicles. Ion-conductive polymers are commonly used as the PEM to provide and maintain a conductive nanostructural pathway for protons in the presence of water during operation. Ion-conductive polymers also play a critical role in the catalyst-layers (CLs) where they act as binders as well as proton conductors.

Achieving proper water management in PEM fuel cells has direct impact on device performance and continues to pose challenges. While modeling can help with the optimization, there is a lack of knowledge of the underlying physics of water uptake in the catalyst layer (CL), where the structure and scale of interest differs significantly from that for the PEM. Specifically, the issues of liquid-water capillary uptake and the state and water content and

uptake of the ionomer film remain not well understood. In this poster, results from characterization techniques including ionomer water content and capillary pressure versus saturation are presented. In addition, morphological and transport studies of ionomer thin-films as proxies for catalyst-layer ionomer are discussed.

Water uptake in the catalyst-layer samples (both in-house and commercially made by Ion Power) is determined as a function of humidity and temperatures using dynamic-vapor-sorption equipment. All the CL samples absorb significantly less water compared to the bulk ionomer membranes. Moreover, CL ionomer uptake was observed to increase with increasing loading of Pt, especially at lower humidities, however it is still substantially lower than bulk membrane. To study the capillary properties, capillary pressure – saturation curves are determined. Results suggest a similar effect of Pt on improved hydrophilicity in CL, which also appear to be more hydrophilic than gas-diffusion layers depending on the fabrication method and existence of cracks. The effect of Pt is shown through grazing-incidence small-angle X-Ray scattering (GISAXS) studies to be related to the different polymer morphology where the changes in the orientation of hydrophilic water domains with respect to the surface control the water ingress.

35 Develop charge and discharge profiles for stationary battery applications

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Recent economic and building concerns raise interest to use batteries for stationary storage applications. Stationary batteries, combined with PV and other distributed-energy resources can be part of different energy strategies such

as load shifting or CO₂ reduction. However, it is not possible to isolate batteries from building energy flows and other distributed energy resources and study them apart as they interact with each other. To consider this effect and give advice on energy strategies in commercial buildings, the distributed-energy resources customer adoption model (DER-CAM), formulated as a mixed-integer linear program, has been developed by Lawrence Berkeley National Laboratory. DER-CAM minimizes annual building energy costs, CO₂ emissions or multiple objectives and produces technology neutral optimal results for investment decisions and operational schedules. As a flexible tool, it gives the opportunity to develop charge and discharge profiles for stationary batteries operating in different environments (different building types, different climate zones...). Such profiles can then be used for battery design and testing procedures.

Los Angeles Air Force Base Vehicle to Grid Pilot Demonstration

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Electrification of non-tactical vehicle fleets represents a key efficiency, environmental, and energy security objective for DoD. Among other planned demonstrations, a mixed purpose and duty approximately 40-vehicle 100% plug-in electrical vehicle (PEV) test fleet will be deployed at the Los Angeles Air Force base (L.A. AFB) beginning in mid-2013. Unique to DoD's program, while parked on base, these vehicles will be offered into the California Independent System Operator (CAISO) regulation market. If

selected by CAISO, it will be able to modulate the charging and discharging of the fleet to assist it maintain a stable and secure grid in the state. Revenue from this ancillary service (AS) market will reduce the fleet's operation cost to DoD. The PEVs, the necessary charging stations, and other infrastructure, as well as basic logistics, will be primarily provided by the DoD, and the California Energy Commission is also supporting the project. Several key additional capabilities will be added by the Berkeley Lab led team to demonstrate the full capabilities and requirements of cost effective all-electric fleets with vehicle-to-grid participation. First, the PEVs will be given additional fleet management capabilities. Second, optimization capability will ensure that the highly complex task of scheduling charging and discharging of vehicles can be achieved such that energy costs are minimized and the benefits from participation in grid AS markets are all jointly considered and the best overall bids submitted and scheduling implemented. Third, receipt and fast response to grid instructions as well as settlement of revenues from V2G will be enabled through use of the OpenADR protocol. And finally, the integration of PEVs into the wider base energy system will be analyzed to examine their potential role in base microgrids, which bridges this project to another key DoD security objective.

Bosch's eMobility software together with DER-CAM will be installed on a server at the base, but outside its firewall. eMobility provides fleet management capabilities to base dispatchers and directly controls charging and discharging of the fleet. Akuacom uses an existing secure remote Demand Response Automation Server to deliver CAISO instructions using OpenADR, a widely used protocol for delivering grid signals to controlled loads. Actual bidding and settlement with CAISO can only be executed by an approved Scheduling Coordinator, in this case Southern California Edison, which is also the local distribution company serving the L.A. AFB. DER-CAM forecasts available battery capacity as well as available charge-discharge

capability and develops AS bids into the Reg.U+D market. Participation in the Reg.U-D requires fast (4 seconds) response to signals, so passage of data to eMobility is continuous. Note that the scheduling has two components. First, the purchase of energy for the vehicles should be achieved at minimum cost. Second, the ability of batteries to rapidly charge or discharge can be sold to CAISO as an AS to assist with its grid control. Vehicle charge-discharge schedules are implemented accordingly, providing necessary information to drivers and fleet managers.

37 Buildings to Grid Integration and Electric Vehicles

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Electrification of buildings and electrical vehicle fleets represents a key efficiency and energy security objective for the Federal and State Agencies. Among planned demonstrations by LBNL, a mixed purpose and duty 40-vehicle 100% plug-in electrical vehicle (PEV) pilot test fleet will be deployed at the Los Angeles Air Force base (L.A. AFB). There are many buildings to grid integration activities in the State of California to address peak load and renewable integration issues. The L.A AFB work in particular will add key capabilities to project to demonstrate the full electric grid integration of all-electric fleets. First, the PEVs will be given additional fleet management capabilities. Second, optimization capability will ensure that the highly complex task of scheduling charging and discharging of vehicles can be achieved such that energy costs are minimized and the benefits from participation in grid demand response and ancillary services markets are all jointly considered and the best overall bids submitted and scheduling implemented. Third, receipt and fast response to grid instructions as well as settlement of revenues from grid service

provision will be enabled through use of the OpenADR protocol. And finally, the integration of PEVs into the wider base energy system will be analyzed to examine their potential role in base microgrids, which bridges this project to another key DoD security objective. Such concepts are have evolved from the experiences of Buildings to Grid research.

PEVs can create both costs and non-transportation benefits. Vehicle charging can be costly if not scheduled well relative to the prevailing utility tariff and other constraints, while the fast responding energy storage capability of vehicle batteries can provide valuable services to help satisfy building and local base energy requirements. Further, while vehicles individually are not large electricity loads or sources, when aggregated or when integrated with the buildings at which they are interconnected, they can become a controlled entity able to ameliorate the effects of variable local resources and loads, and provide DR and ancillary services service to the local utility and the wider power system around it.