

Interfacial Processes in EES Systems Advanced Diagnostics

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Overview

Timeline

- PI participates in the BMR Program since 1999
- This project was recompeted in FY12 and renewed in FY13

Barriers Addressed

- Low Li-ion battery energy density, and calendar/cycle lifetimes for PHV and EV applications
- Inadequate cell/electrode impedance that limits power and affects system safety

Budget

- FY14 funding \$500K
- FY13 funding \$500K
- FY12 funding \$520K

Partners

- ABMR Cathode and Anode Task Groups
 - ANL, ALS, LBNL, SUNY, UP, HQ, NREL and UU
 - G. Chen, J. Kerr, V. Battaglia, M. Doeff, K. Persson, V. Zorba, W. Yang, H. Bechtel, C. Ban, B. McCloskey
- V. Srinivasan and M. Foure (LBNL) are ABMR program lead and program manager, respectively
- IMN : Prof. D. Guyomard
- MEET : Prof. M. Winter

Relevance : Objectives

1. Provide critical understanding of basic principles that govern the function and operation of active materials, composite electrodes and Li-ion battery cells that is necessary for successful implementation of high energy density materials in Li-ion cells for PHEVs and EVs .
 - Establish direct correlations between electrochemical performance, interfacial phenomena, surface chemistry, morphology, topology and degradation mechanisms of ABMR baseline materials, electrodes and cells.
2. Propose and evaluate remedies to interfacial and materials instability e.g., artificial surface coatings (e.g., ALD) and/or structures, novel electrode architectures, electrolyte additives etc.
2. Develop, adapt and employ unique experimental techniques and methodologies to guide development of novel EES materials, electrodes and battery systems.
 - Obtain detailed insight into the dynamic behavior of molecules, atoms, and electrons at electrode/electrolyte interfaces at resolution that is adequate to the size and function of basic chemical or structural building blocks

Milestones

1. Determine the mechanism of transition metal dissolution in high-energy Li-ion cathodes (December, 2014)
 - **Accomplished on time.** Formation of fluorescent Ni^{II} and $\text{Mn}^{\text{II/III}}$ complexes originated from electrochemical oxidation of DEC and EC at the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ electrode at potentials > 4.2 V by proton coupled electron transfer, propagation mechanism and ligands adsorption/desorption on surficial metal sites.
2. Resolve SEI layer chemistry of coated Si single crystal and thin film anodes (March, 2015)
 - **Accomplished on time.** *In situ* studies revealed that alucone coating and additive affect the nature and kinetics of surface reactions and leads to the formation of a better passivation surface film.
3. Determine the mechanism of SEI layer poisoning by Ni and Mn coordination compounds (collaboration with the Bryan D. McCloskey). (June, 2015)
 - **Status on schedule.** Demonstrated that presence of fluorescent metal complexes in the SEI inhibit Li^+ transport.
4. Demonstrate feasibility of *in situ* near-field and LIBS techniques at Li-ion electrodes (collaboration with Vassilia Zorba). “Go/no-go” decision: Stop development of near-field and LIBS techniques, if the experiments fail to deliver adequate sensitivity. (September 2015)
 - **Status on schedule**

Interfacial Activity of High-Voltage Cathodes

Approach

- Apply *in situ* and *ex situ* Raman, fluorescence, FTIR, x-ray absorption spectroscopy/microscopy and standard electrochemical techniques to probe and characterize material, electrode and cell degradation processes.
- Perform *in situ* measurements on composite cathodes and model thin-film or single particle electrodes.
- Investigate molecular “shuttle” phenomena in Li-ion cells and assess their impact on the cell electrochemical performance.

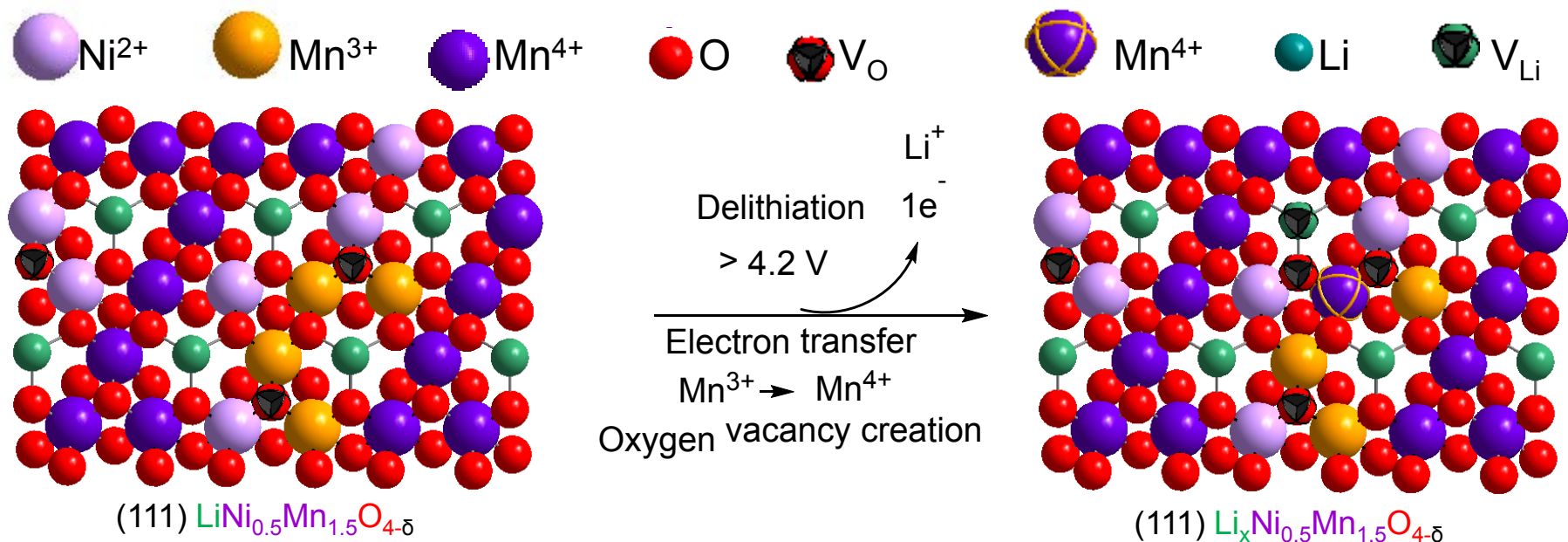
Accomplishments

- Determined the mechanism of transition metal dissolution in LMNO and LMNCO electrodes and chemical cross-talk in high-energy Li-ion cells.
 - Electrochemical oxidation of carbonate esters at transition metal oxide surface electrode leads to formation of β -diketones ligands and Co^{II} , Ni^{II} , $\text{Mn}^{\text{III/IV}}$ complexes.
 - Insoluble $\text{Me}(\beta\text{-diketone})$ complexes form a surface film, which may create electronic and/or ionic barriers in composite cathodes.
 - Soluble $\text{Me}(\beta\text{-diketone})$ complexes diffuse toward the anode, react with and/or get incorporated in the SEI layer (SEI Mn/Ni/Co poisoning).
 - $\text{Me}(\beta\text{-diketone})$ complexes in the SEI layer impede Li^+ transport in the anode.

Reactivity of $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ Surface

Surface reactivity of LMNO spinel leads to electrolyte decomposition, O_2 evolution, surface conversion to rock salt and Mn, Ni dissolution.

- Oxygen vacancies are preferentially surrounded by Ni^{2+} and Mn^{3+} with highly occupied $\text{Mn}^{3+} e_g$ energy level.*
- Li^+ deintercalation preferentially occurs in the vicinity of oxygen vacancies and it is coupled with Mn^{3+} oxidation to Mn^{4+} rather than a Ni^{2+} oxidation to $\text{Ni}^{3+/4+}$.**



Mn^{4+} active redox centers surrounded by two oxygen vacancies at (111) $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ facets are responsible for the observed surface reactivity.

*Sushko, P. V.; Rosso, K. M.; Zhang, J.-G.; Liu, J.; Sushko, M. L. *Advanced Functional Materials* **2013**, 23, 5530

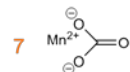
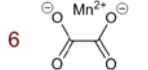
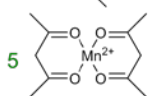
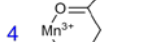
Kumar, N.; Leung, K.; Siegel, D. J., *J. Electrochem. Soc.* **2014, 161, E3059-E3065.

Electrolyte Oxidation Products in LMNO/Graphite Cell

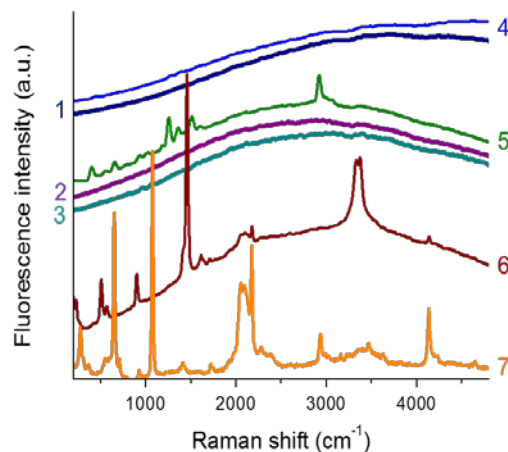
1 LMNO cathode

2 Separator

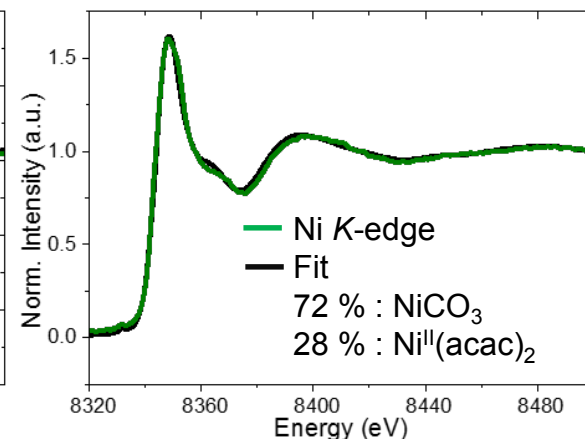
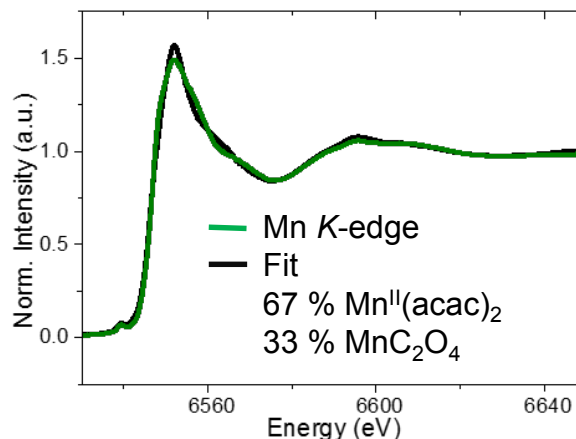
3 Graphite anode



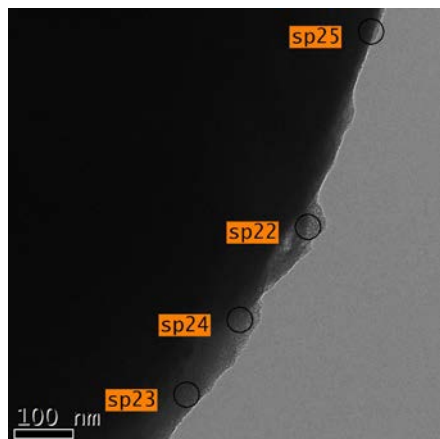
Optical Fluorescence Spectra



X-ray Absorption Spectra of the Graphite Anode



EELS of the Graphite Anode



	F/O	Mn^{2+}/O	L_3/L_2
SP22	1.19	0.12	3.9
SP23	0.93	0.12	4.2
SP24	0.87	0.08	5
SP25	0.78	0.05	4.9

L_3/L_2 ratio: Mn^{4+} (2.1) ; Mn^{3+} (2.2-2.6) ; Mn^{2+} (4.2-5.3)
Z.L. Wang et al. Micron, 31, 355 (2000)

- Omnipresent fluorescence in Li-ion cells is consistent with the presence of Mn^{II} and Mn^{III} β -diketone complexes.
- Mn^{II} and Ni^{II} complexes, oxalates and carbonates were detected in the graphite anode SEI layer.
- Distribution of Mn^{II} and Ni^{II} compounds in the SEI varies strongly with location.

The dissolved of Mn^{II} , Mn^{III} and Ni^{II} β -diketone complexes are incorporated in the solid electrolyte interphase (SEI) surface layer at the graphite anode.

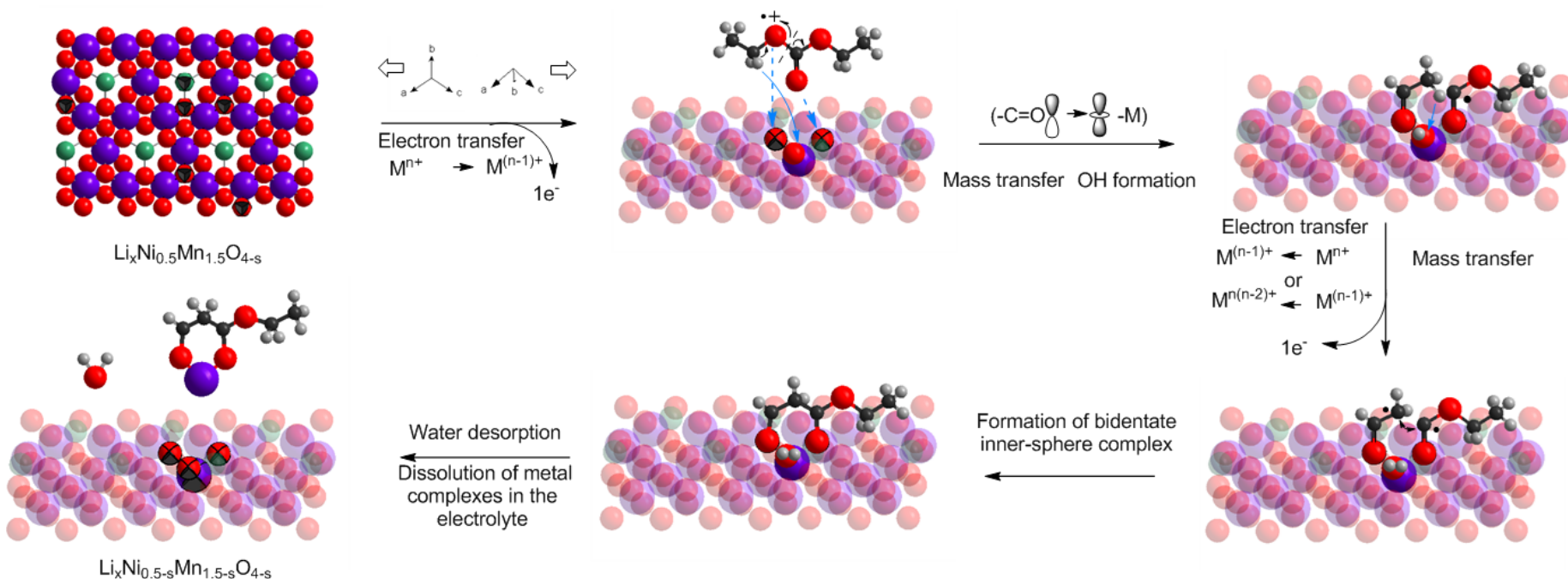
This is contrary to the postulated Mn electroplating or Mn^{2+} free ions incorporation in the SEI.

Collaboration with J. Roque-Rosell, ALS/LBNL and P. Moreau, IMN (France)

The Mechanism of Formation of Mn and Ni β -diketone Complexes at $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode

Part 1. Oxidation of DEC

- Oxidation potential of DEC decreases from 5.7 to 4.2 V in the presence of PF_6^- anions and surface defects in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_{4-s}$.
- DEC oxidation occurs via two proton coupled electron transfer (PCET) associated with ligands adsorption.

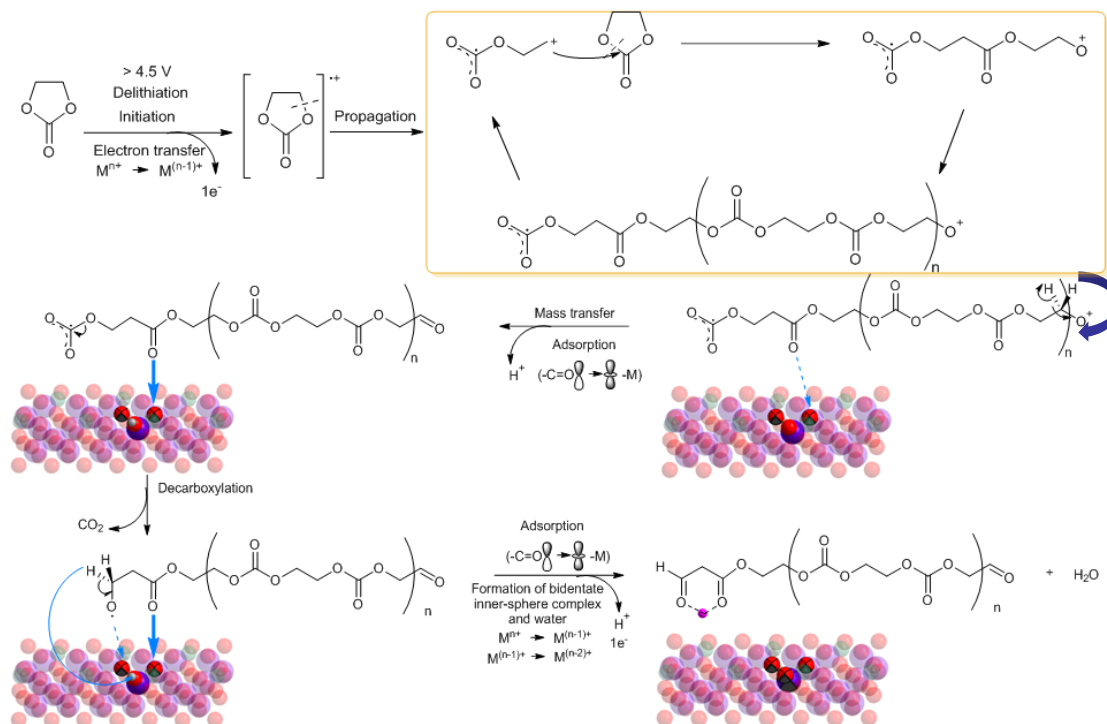


- DEC oxidation occurs preferentially at Mn^{4+} surface sites at $E > 4.2$ V.
- DEC oxidation leads to formation of $\text{Mn}(\beta\text{-diketone})$ fluorescent complexes and water.
 - Subsequent water oxidation can be responsible for the observed O_2 evolution
- $\text{Mn}(\beta\text{-diketone})$ fluorescence complexes with short side chains are soluble in the electrolyte.

The Mechanism of Formation of Mn and Ni β -diketone Complexes at $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode

Part 2. Oxidation of EC

- EC oxidation occurs preferentially at Ni^{4+} sites in the presence of oxygen vacancies at the LMNO surface.
- EC oxidation occurs via two PCET reactions, β -diketone ligand adsorption and polymer side-chain propagation.

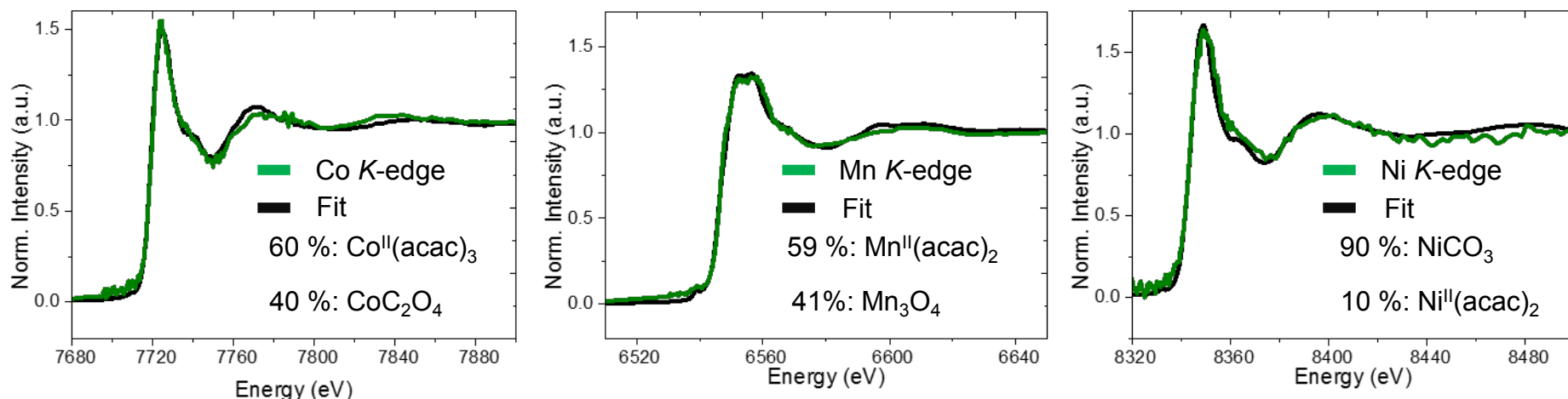


- EC oxidation leads to the formation of insoluble $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}(\beta\text{-diketone})$ and $\text{Ni}^{\text{II}}(\beta\text{-diketone})$ fluorescent complexes with long polymer side-chain.
- Decarboxylation reaction of EC is also valid for the mechanism of formation of Mn/Ni oxalates and Mn/Ni carbonates, which are found among electrolyte decomposition products.

Electrolyte Oxidation Products in LMNCO/Graphite Cell

Surface point defects at transition metal oxides e.g., LMNO, LCO, LMO, LNO, NMC can catalyze organic solvents oxidation and formation of metal complexes with β -diketones ligands.

X-ray Absorption Spectra of the Graphite Anode



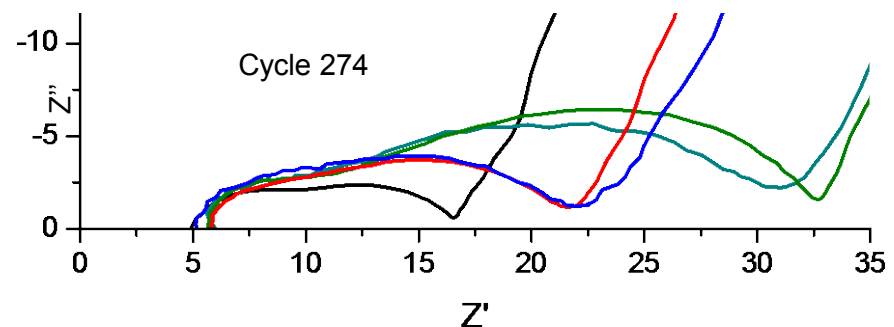
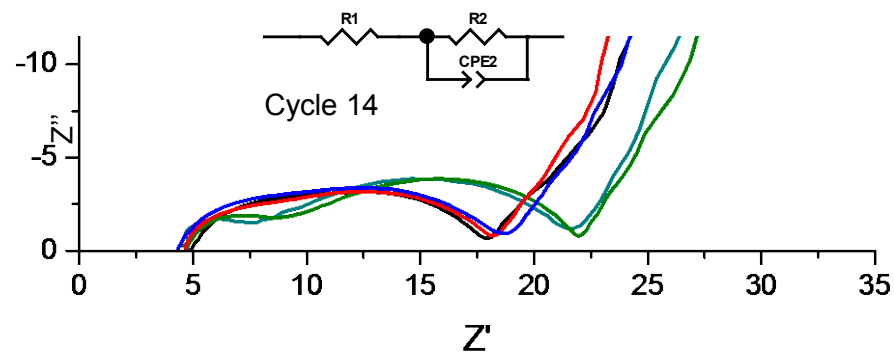
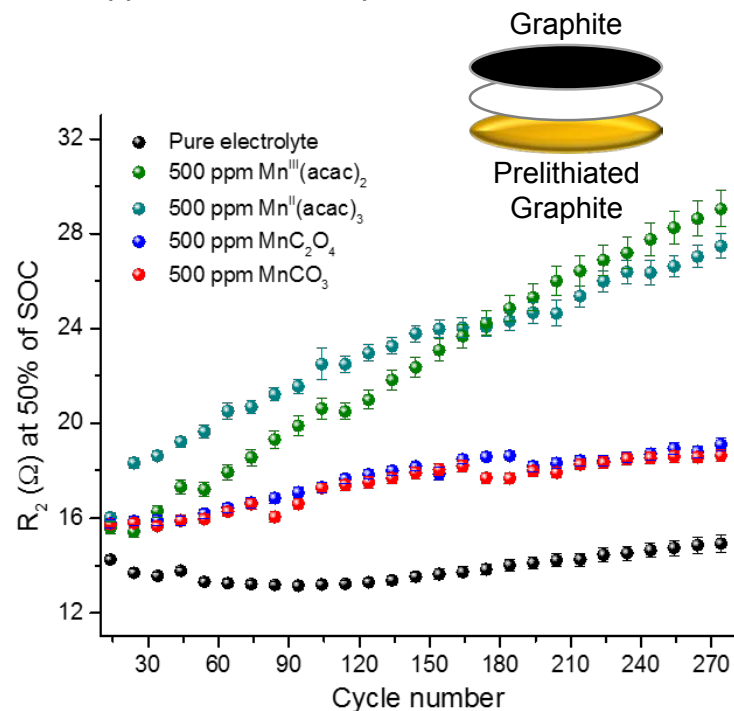
Electrochemical oxidation of DEC and EC at the $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ electrode leads to the formation of fluorescent Ni^{II}, Co^{II} and Mn^{III/IV} complexes with β -diketones ligands and Ni^{II}/Mn^{II} oxalates and carbonates.

Formation of Mn^{III/IV}/Mn^{II}, Co^{II} and Ni^{II} complexes on transition metal oxide cathodes in organic carbonate electrolytes is responsible for Mn, Co and Ni dissolution and relates to the observed failure modes in Li-ion batteries.

The Effect of $\text{Mn}^{\text{II/III}}$ (β -diketone) Coordination Complexes on the Li^+ Transport in the SEI Layer

Fluorescent β -diketone complexes produced on the cathode may be used as a unique probe into the mechanism of Li^+ transport across the solid electrolyte interphases in Li-ion anodes.

Graphite symmetric cell filled with 1 M LiPF_6 , EC/DEC (1:2) spiked with 500 ppm of $\text{Mn}^{\text{II/III}}$ compounds.



- β -diketone complexes are responsible for the observed impedance increase of the graphite anode (Mn poisoning).
- Slight impedance increase is also observed in the presence of Mn^{II} carbonate and Mn^{II} oxalate.

Summary I

- X-ray absorption, optical fluorescence spectroscopy and imaging experiments demonstrated that electrochemical oxidation of DEC and EC at the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ electrode at potentials > 4.2 V leads to the formation of fluorescent Ni^{II} and $\text{Mn}^{\text{III/IV}}$ complexes with β -diketones ligands and Ni^{II} and Mn^{II} oxalates and carbonates.
 - Stepwise and all-concerted proton-coupled electron transfer reaction mechanism, which lead to metal complexes and water formation at the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ surface, are proposed.
 - The rate of these reactions is enhanced by the continuous creation of oxygen vacancies. The adsorption of β -diketone chelate ligands at $\text{Ni}^{\text{IV}}/\text{Mn}^{\text{IV}}$ surface sites greatly facilitates Ni/Mn removal from the crystalline lattice and is primarily responsible for the observed Ni/Mn dissolution.
 - The postulated heterogeneous catalysis mechanism accurately describes interfacial processes on a larger class of $\text{Li}_x(\text{Ni}_a\text{Mn}_b\text{Co}_c)\text{O}_y$ -type cathodes and links it with the observed failure modes in Li-ion batteries.

This study not only determines the mechanism of transition metal dissolution but it can also offer unique insight into the mechanism of Li^+ transport across the solid electrolyte interphases in Li-ion systems.

Interfacial Activity of Silicon Anodes

Approach

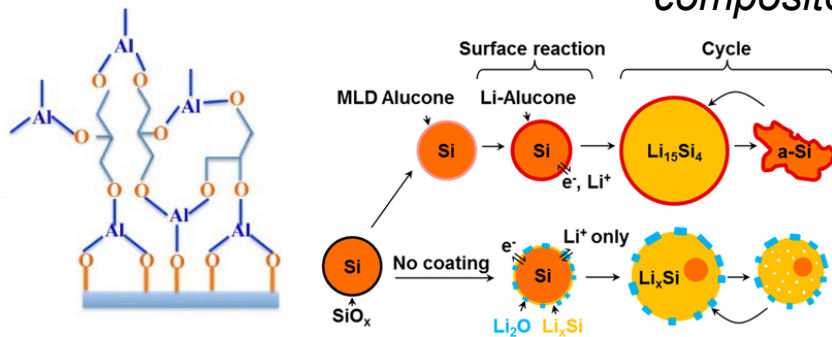
- Identify and study origins of interfacial instability, and mechanisms of degradation of Si anodes in organic electrolytes.
 - Carry out *in situ* measurements on model single crystal Si electrodes at a spatial resolution that corresponds to the size of basic chemical or structural building blocks in the SEI layer.
 - Assess impact of interfacial phenomena on the Si anode on the electrochemical performance and lifetime of Li-ion cells

Accomplishments

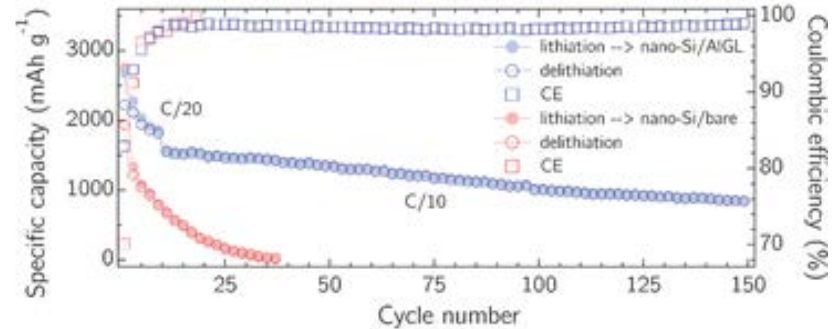
- Si anode interfacial instability can be only partially mitigated by artificial surface coatings (e.g., alucone/ALD) and electrolyte additives.
- Near-field IR spectroscopy and imaging of the SEI layer on Si anodes show the nanoscale chemical and structural inhomogeneity of the film.
- Determined the mechanism of SEI Formation on a Si electrode in the presence of VC and FEC additives (not shown here, see publication list)
- Determined the mechanism of interactions between CMC binder and silicone (not shown here, see publication list)
- Demonstrated feasibility of *in situ* Laser Induced Breakdown Spectroscopy (LIBS) to study depth profile of the SEI layer.

The Effect of Alucone Coating on Si Interfacial Behavior

Alucone coating of helps improve cycleability and coulombic efficiency of nano-Si composite electrodes

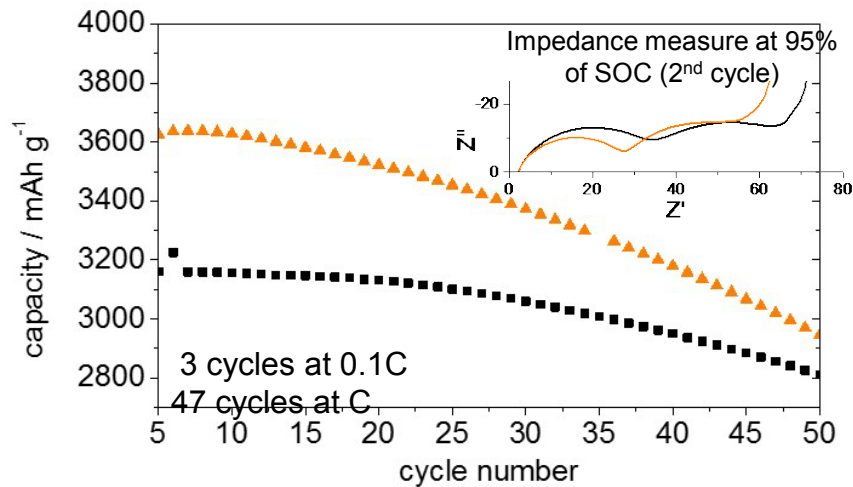


Y. He et al., ACS Nano, 8 (2014) 11816-11823.

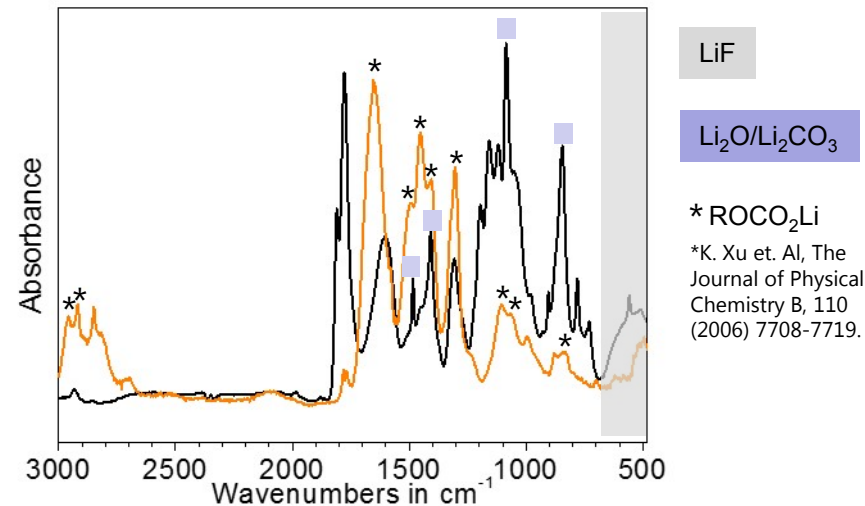


D. Piper et al., Advanced Materials, 10 (2014) 1596-1601.

Si 100 nm thin-film electrode (uncoated; 8 nm Alucone) in 1M LiPF₆, EC:DEC [1:2]



FTIR spectra of Si electrode after 50 cycles



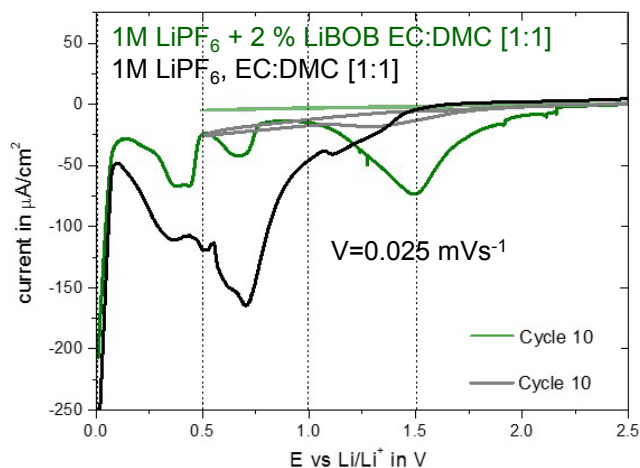
Si/alucone electrode produces an SEI layer with high ratio of organic compounds (ROCO₂Li), which improves cycling performance of the Si nano-composite electrode.

The Effect of Electrolyte Additives on Si Interfacial Behavior

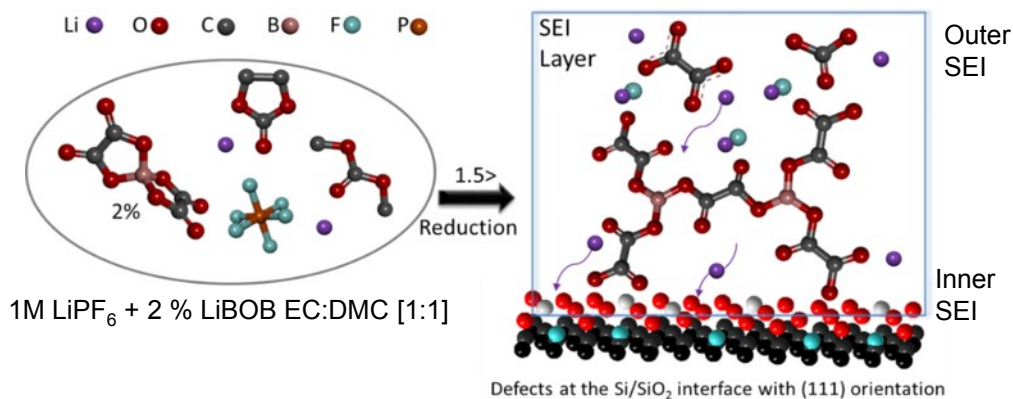
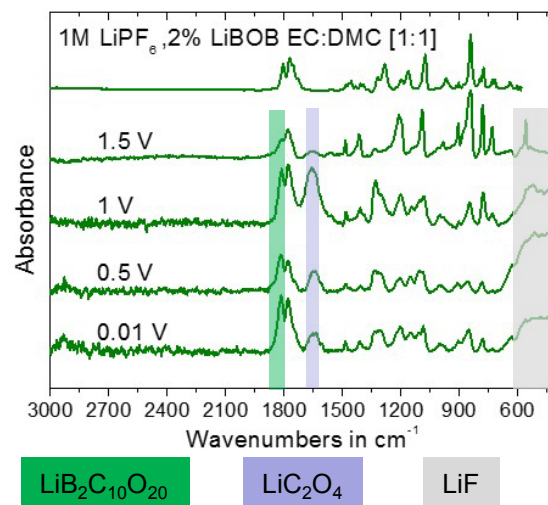
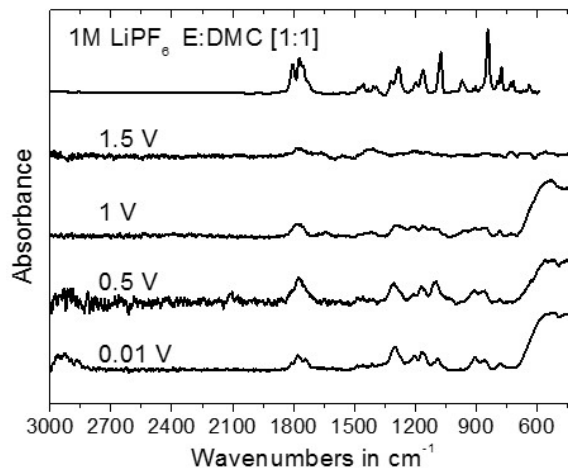
Lithium bisoxalatoborate (LiBOB) additive in LiPF_6 -based electrolytes helps improve cycling performance of silicon thin film anodes

S. Dalavi et al., J. Electrochem. Soc., 159 (2012) A642

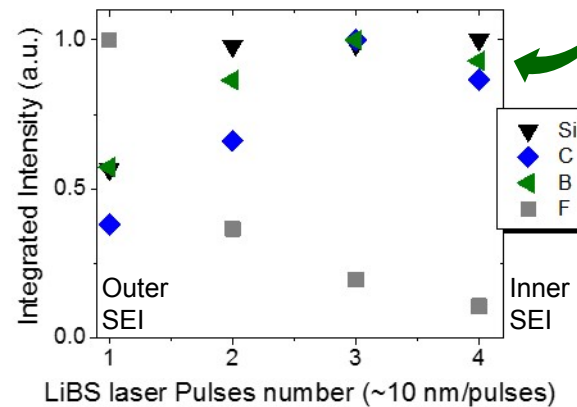
Si(111) wafer electrode



FTIR spectra of Si(111) electrode



Ex situ LIBS depth profiling of Si(111) at 0.01 V

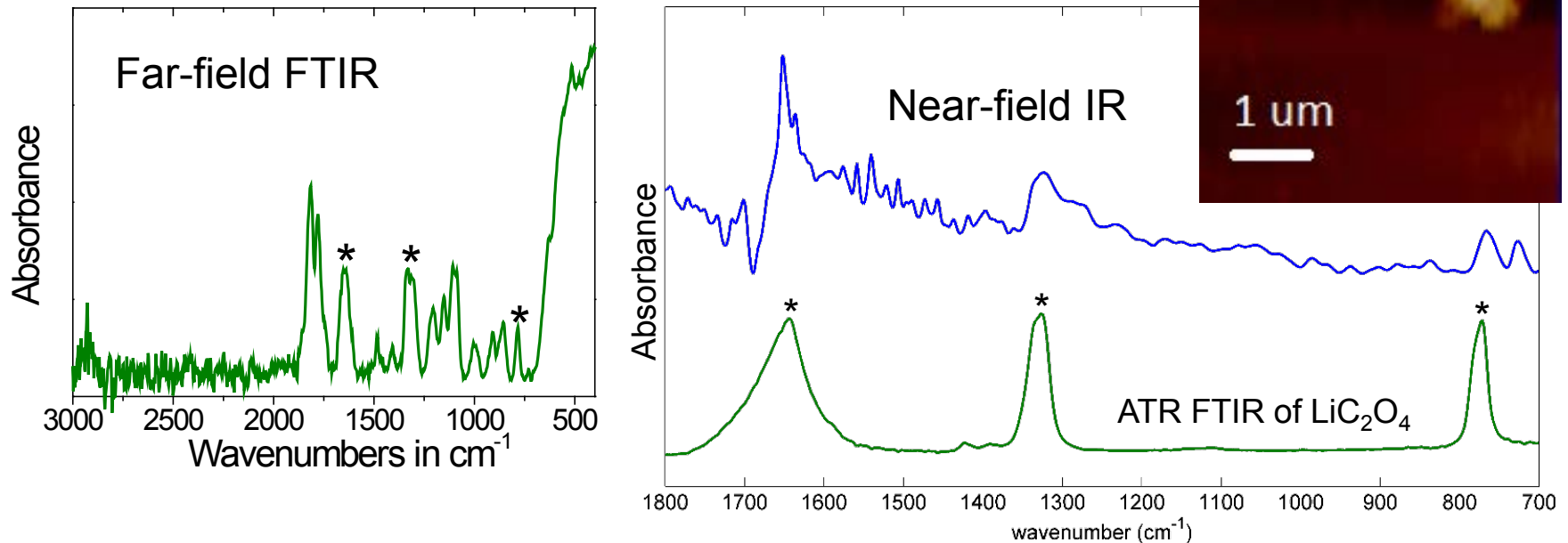


LiBOB additive promotes early formation of an oligomer-based surface film at the silicon surface. This “inner” SEI layer inhibits further electrolyte reduction.

Collaboration with V. Zorba, LBNL

Synchrotron IR Near-Field Spectroscopy of the SEI on Si(111) Electrode

Si(111) wafer at 0.5 V in 1M LiPF₆ + 2 % LiBOB, EC:DMC [1:1]

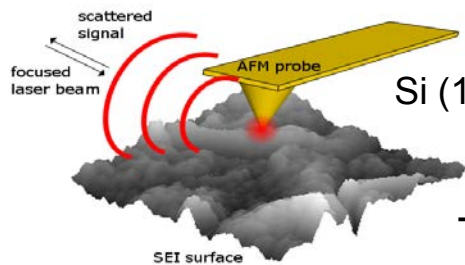


- Local spectra of the SEI layer on Si(111) were obtained at deeply subwavelength (~20 nm) resolution.
- LiC₂O₄ was identified in the far- and near-field IR spectra.

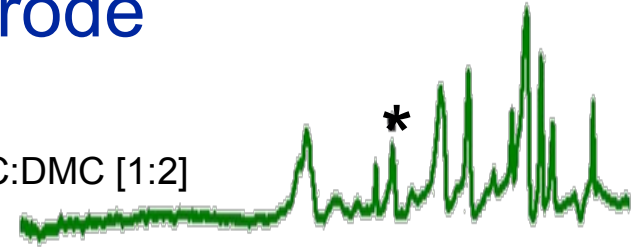
Near-field IR spectroscopy can resolve spectra of individual particles for the SEI basic building blocks identification at nanometer scale.

Single-Wavelength Near-Field Imaging of the SEI on Si(111) Electrode

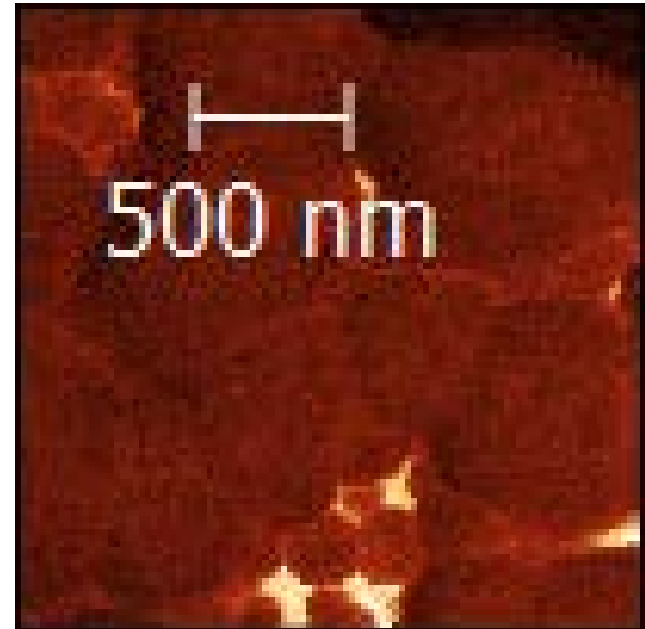
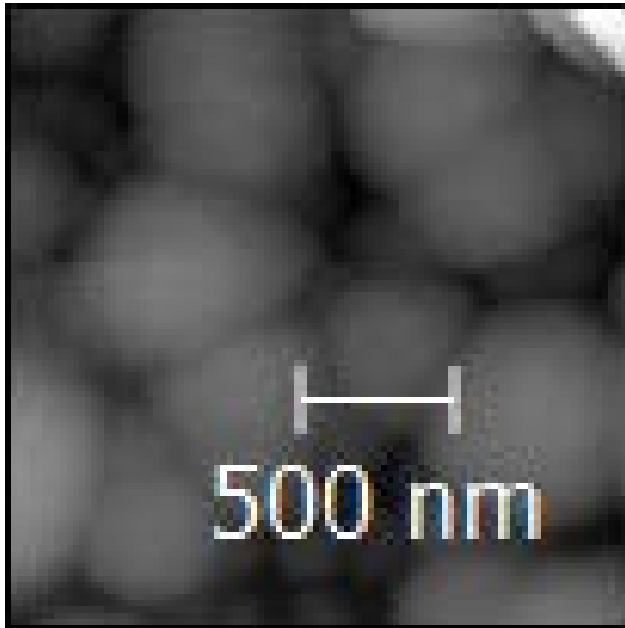
NF-IR Imaging



Si (111) at 1.5 V in 1M LiPF₆ + 2 % LiBOB, EC:DMC [1:2]



*v_{asym} O-C=O in ROCO₂Li at 1412 cm⁻¹



- *Ex situ* near-field IR imaging has been performed in N₂-filled environmental chamber.
- NF-IR images of the SEI layer on Si revealed inhomogeneous distribution of the electrolyte decomposition products at nanoscale.

Summary II

- *In situ* and *ex situ* characterization studies of the Si electrodes showed that the nature and kinetics of interfacial phenomena are strongly dependent of the electrode surface structure, artificial coatings and electrolyte additives.
 - Alucone coating shifts the composition of the SEI toward higher content of organic compounds (ROCO_2Li), which improve the cycling performance of the Si nano-composite electrode.
 - LiBOB additive promotes early formation of an oligomer-based ($\text{LiB}_2\text{C}_{10}\text{O}_{20}$) surface film at the silicon surface. This “inner” SEI layer inhibits further electrolyte reduction.
- Feasibility of *in situ* LIBS measurements for elemental depth profiling of the SEI layer on Si wafer electrodes was demonstrated.
- Near-field IR spectroscopy and imaging of the SEI local composition on Si anodes was demonstrated for the first time.
 - NF-IR images of the SEI layer on Si revealed inhomogeneous distribution of the electrolyte decomposition products at nanoscale.
 - Clear variations in IR contrast correlated to specific features in topography.
 - Preliminary identification of the SEI chemical building blocks was achieved.

Remaining Challenges and Barriers



1. The Li-ion cathode is a major determinant of cost and energy density in lithium-ion batteries. To realize further gains, the specific energies of cathodes must be improved.
2. Cathode structural disorder, interfacial instability and the tendency to convert to spinel or rock salt phases during cycling need to be remedied to achieve energy density, lifetime and safety goals.
3. These failure modes must be addressed through diagnostic studies to guide development of next generation robust cathode materials.

Future Work

- Apply advanced characterization techniques to obtain detailed insight into detrimental processes at electrode/electrolyte interfaces of high voltage Ni-rich NMC-type cathode materials.
- Determine and remedy electrochemical performance limiting factors and degradation mechanisms under cycling conditions.
 - Determine origins of structural instabilities of the high Ni content electrodes, particularly formation of inert spinel and rock salt phases during cycling, oxygen loss, transition metal dissolution, and formation of resistive interphases and surface films at cathode electrolyte interfaces (CEI).
- Work closely with ABMR PIs to establish clear connections between diagnostics, theory/modelling, materials synthesis, and cell development efforts.
- Develop and apply novel innovative experimental methodologies to study and understand the basic function and mechanism of operation of materials, composite electrodes, and Li-ion cells for PHEV and EV applications.

Collaboration and Coordination with Other Institutions

This work has been performed in close collaboration with:

- V. Srinivasan and M. Foure (LBNL) are ABMR program lead and program manager, respectively
- ABMR Cathode and Anode Task Groups
 - ANL, LBNL, SUNY, UP, HQ, NREL and UU
(G. Chen, J. Kerr, V. Battaglia, M. Doeff, K. Persson, V. Zorba, W. Yang, C. Ban, N. Balsara, B. Mc Closkey)



- H. Betchel and J. Roque-Rosell – Advanced Light Source, LBNL
- Prof. D. Guyomard, Dr. P. Moreau - Institut des Matériaux Jean Rouxel Nantes (IMN)
- Prof. M. Winter – Münster Electrochemical Energy Technology



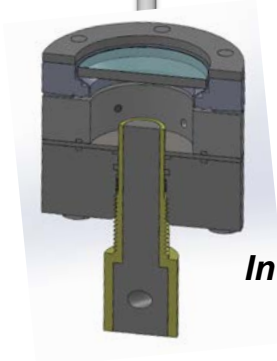
Technical Back-Up Slides

Laser Induced Plasma Spectroscopy for Energy Applications

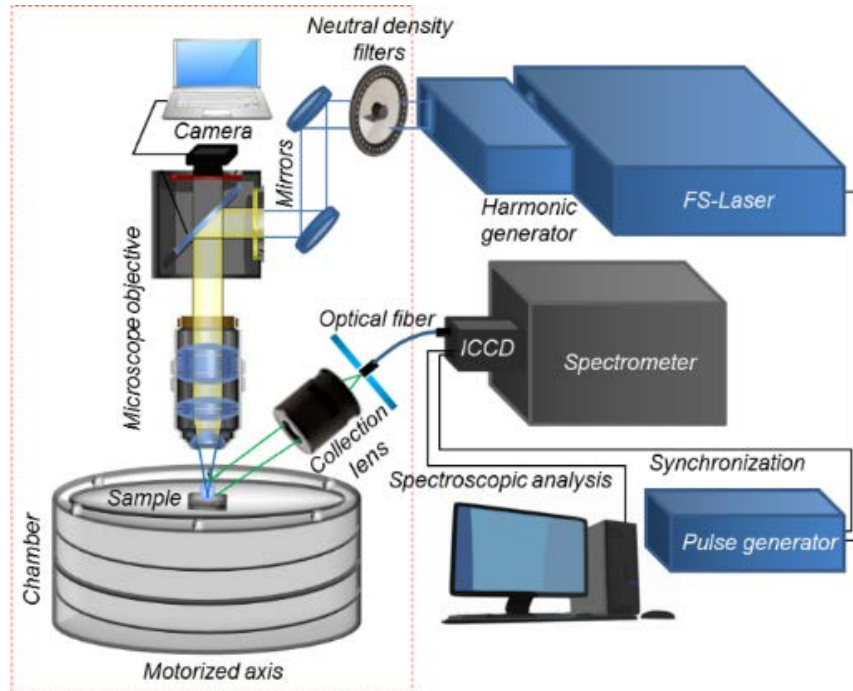
All-optical technique: Excitation and detection based on light (photons)



Ex situ LIBS

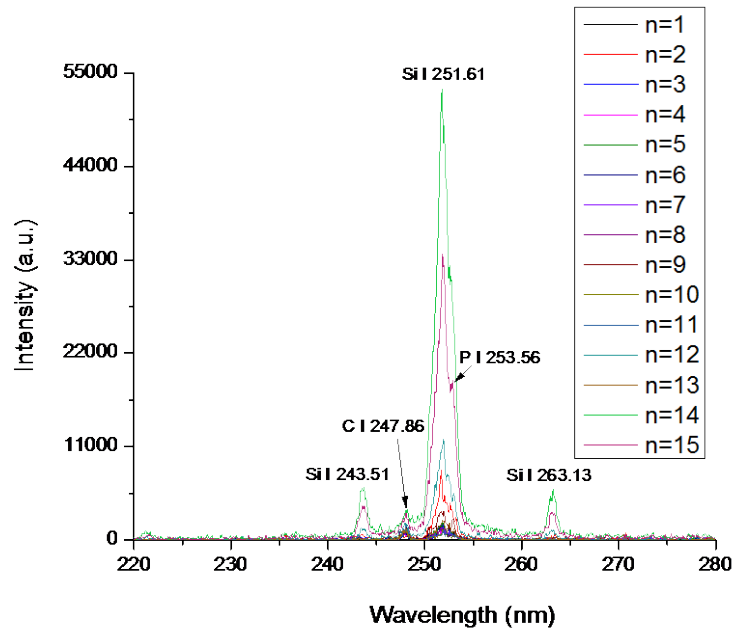


In situ LIBS



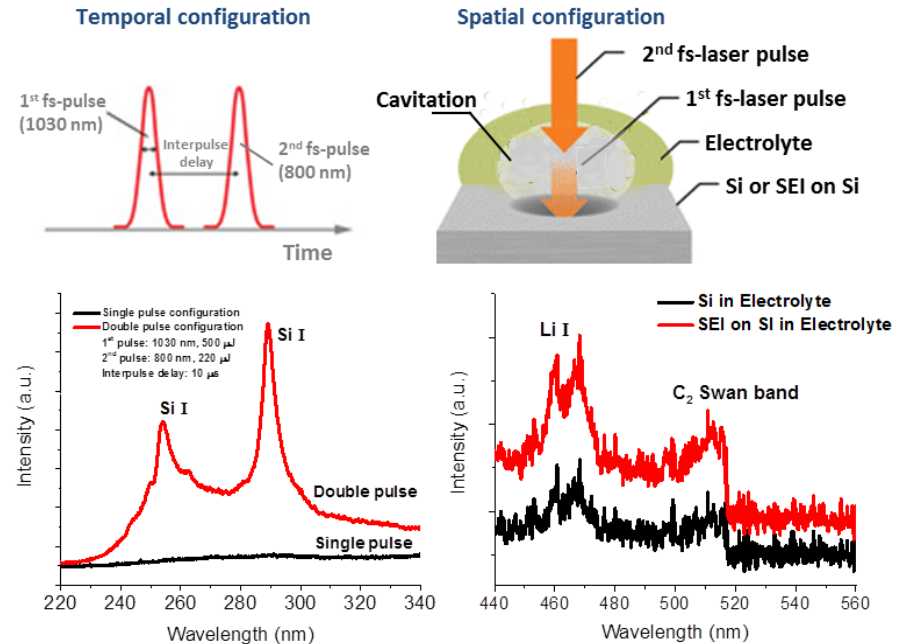
- *In situ* capabilities for probing compositional variations during cycling in real time
- Elemental, molecular and isotopic analysis
- Ability to probe compositional variations with depth (depth profiling) with high resolution

In situ LIBS Measurements of the SEI on Si Electrode



(100) Si wafer with 1M LiPF₆ EC:DEC [1:2] electrolyte

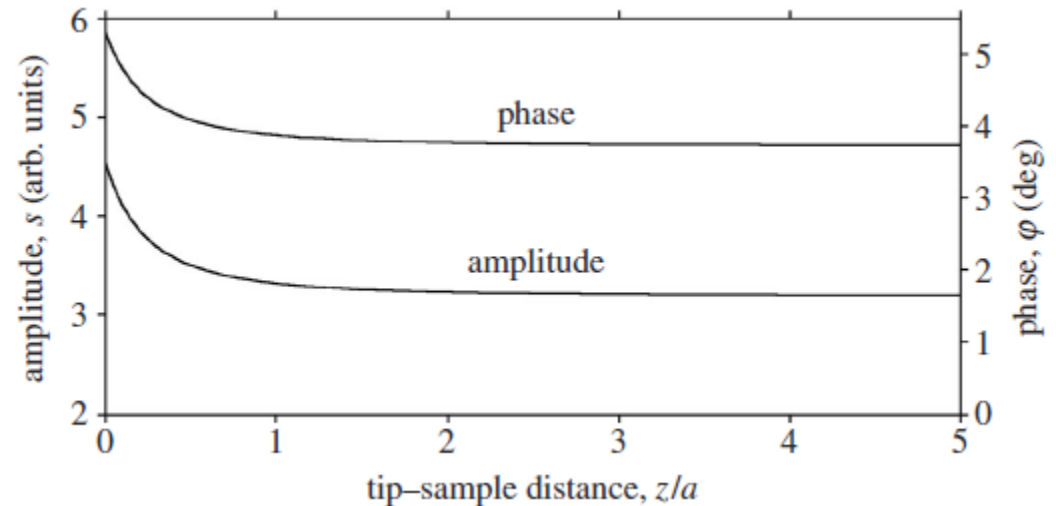
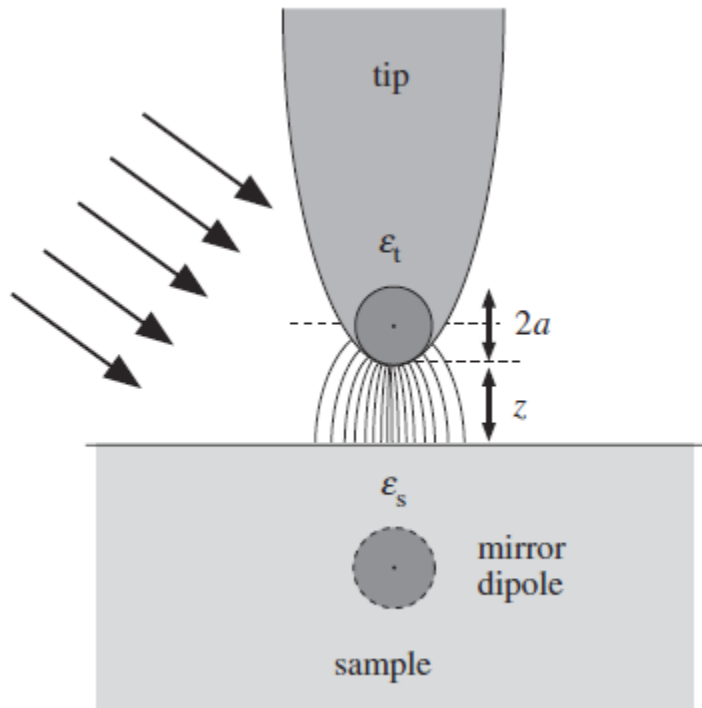
Double femtosecond LIBS scheme



(100) Si wafer with 1M LiPF₆, DEC electrolyte

Signals characteristic for C, P, Li and H were detected *in situ* from the SEI layer on Si(100) wafer electrode upon femtosecond laser double-pulse excitation.

Near-Field EMF Coupling



Keilmann, Hillebrand, Phil. Trans. Royal Society 362(1817):787–805 (2004)

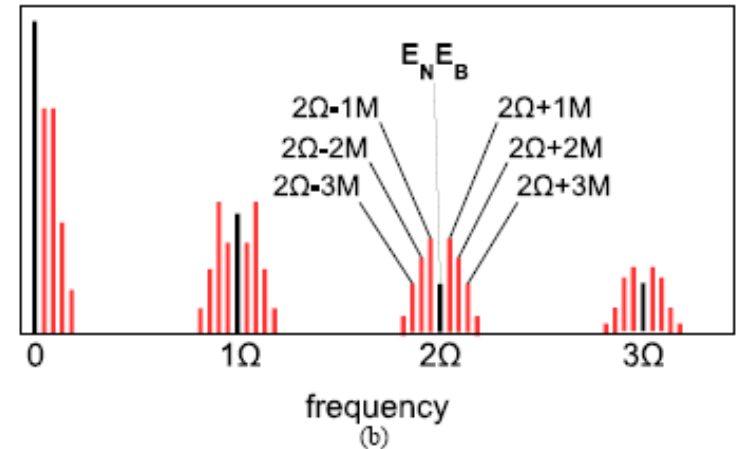
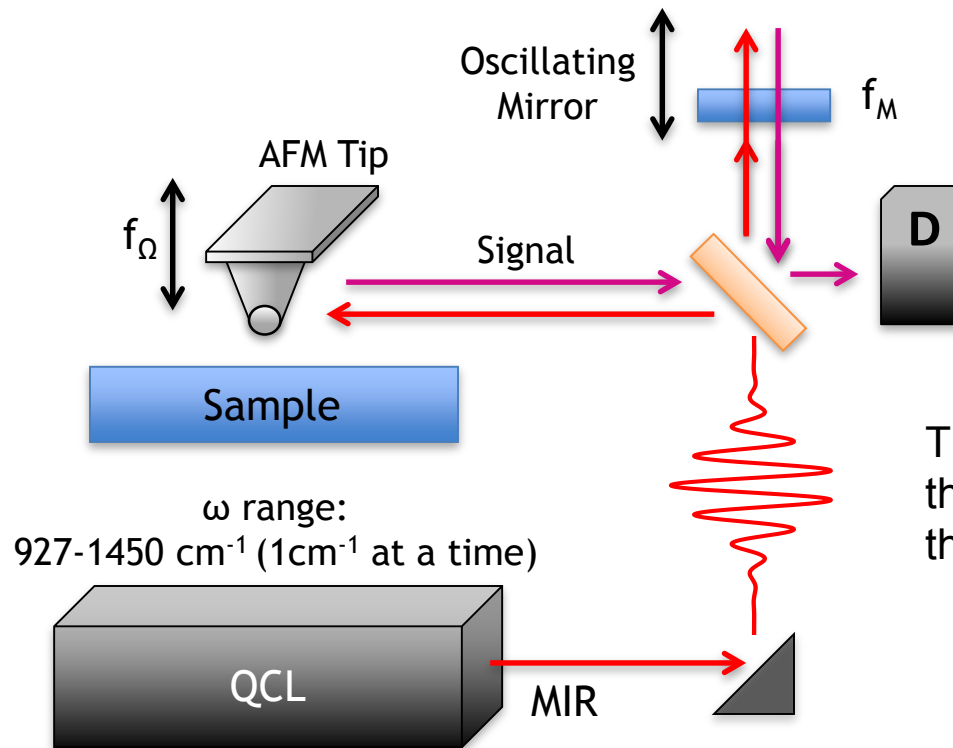
$$\alpha = 4\pi a^3 \frac{\epsilon_t - 1}{\epsilon_t + 2}$$

$$\beta = \frac{\epsilon_s - 1}{\epsilon_s + 1}$$

$$\alpha_{\text{eff}} = \frac{\alpha(1 + \beta)}{1 - \alpha\beta/(16\pi(a + z)^3)}$$

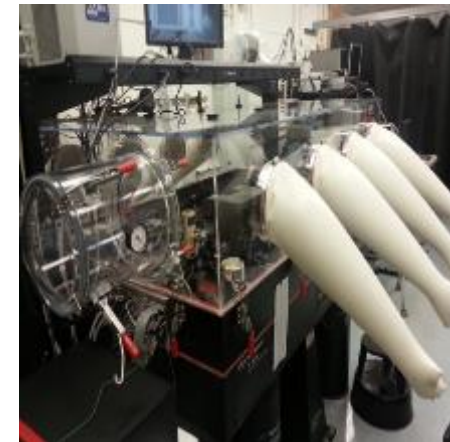
- The nonlinear dependence $\alpha_{\text{eff}}(z)$ is used to eliminate unwanted ‘background’ scattering which generally dominates the detected signal.
- The focused laser beam illuminates a greater part of the tip shaft which typically extends 10 μm from the cantilever, and also the sample.

Near-Field IR Microscopy/Spectroscopy Experimental Setup



The demodulation of the detector output at a the side frequency $fn, m = n\Omega + mM$ provides the near-field signal amplitude and phase Om .

N_2 -purged enclosure



Laser beam focused on a vibrating mirror M (phase modulated reference beam at $f_M = 300\text{Hz}$) and on the oscillating AFM tip ($f_\Omega = 300\text{KHz}$).

Background-free near field signal within an integration time of 6.5 ms (up to 1.6 s) allowing fast raster scan imaging (~ 150 pixels/ s).