Interfacial Processes in EES Systems Advanced Diagnostics

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Project ID# ES085

Overview

Timeline

- PI participates in the BMR Program since 1999
- This project was recompeted in FY15 and renewed in FY16 as part of Ni-rich high-voltage cathode project.

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

- FY16 funding $440K
- FY15 funding $500K
- FY14 funding $500K
- FY13 funding $500K

Partners

- 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, H. Bechtel, C. Ban, B. McCloskey
- IMN : D. Guyomard
- MEET : M. Winter
- University of Maryland: B. Eichhorn, A. Jarry
- U. S. Army Research Laboratory, Kang Xu

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. Build and test binder- and carbon-free model NMC electrodes. **Status completed** (December, 2014).
2. Complete preliminary characterization of interfacial activity of the baseline NMC material in organic carbonate electrolytes. **Q3 status on schedule**.
3. Complete preliminary characterization of interfacial activity of the baseline NMC material in organic carbonate electrolytes. **Q3 status on schedule.**
4. Go/No-Go: Demonstrate feasibility of *in situ* near-filed FTIR microscopy and spectroscopy to study interfacial phenomena at Li-battery electrodes. Criteria: Stop development of near-field and LIBS techniques, if the experiments fail to deliver adequate sensitivity. **Q4 status on schedule.**

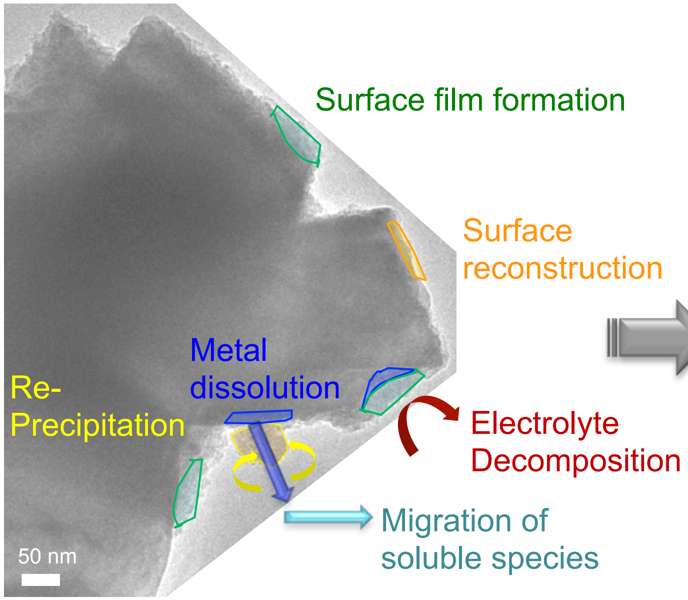
Interfacial Activity of High-Voltage Cathodes

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.

1. Perform *in situ* measurements on composite cathodes and model thin-film or single particle electrodes.
2. Investigate molecular “shuttle” phenomena in Li-ion cells and assess their impact on the cell electrochemical performance.
3. Obtain detailed insight into detrimental processes at electrode/electrolyte interfaces of high voltage Ni-rich NMC-type cathode materials.

Interfacial Reactivity of High-Voltage Cathodes



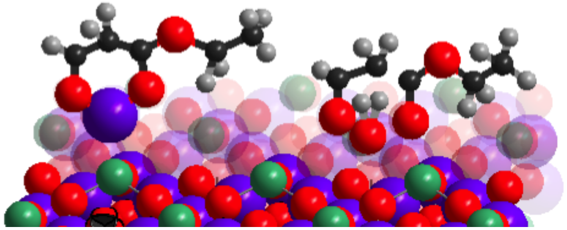
Adapted from J. Vetter, et al,, *J. Power Sources*, 2005, **147**, 269-281

Is there a direct correlation between metal dissolution, oxygen loss, surface reconstruction and surface film formation?

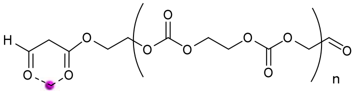
1. A. Jarry et al., JACS, 2015, **137**, 3533-3539.
2. N. S. Norberg et al.,, Electrochem. Commun. 34, 29-32, (2013)
3. M. Moshkovich et al.,, J. Electroanal. Chem., 2001, **497**, 84-96.
4. S. E. Sloop et al.,, *J. Power Sources*, 2003, **119–121**, 330-337.
5. Lin et al., Nat. Com. 2014

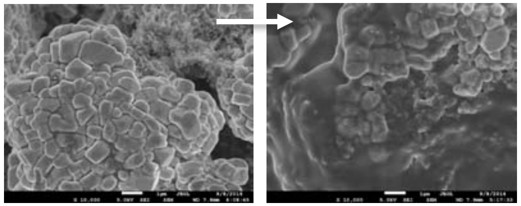
1. Solvents oxidation[1]

2. Metal dissolution[1]

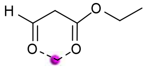


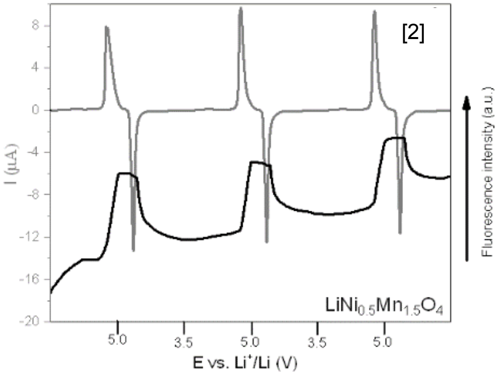
3. Fluorescent Surface film formation[1-4]

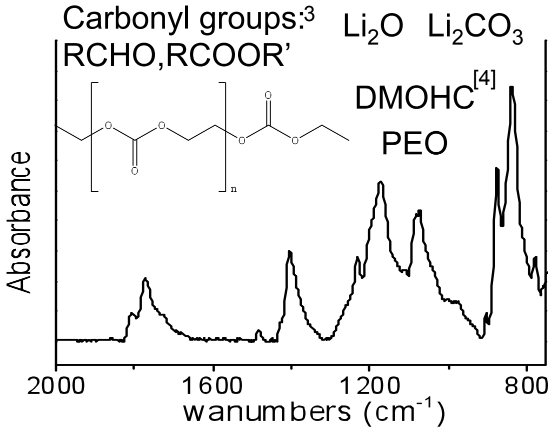




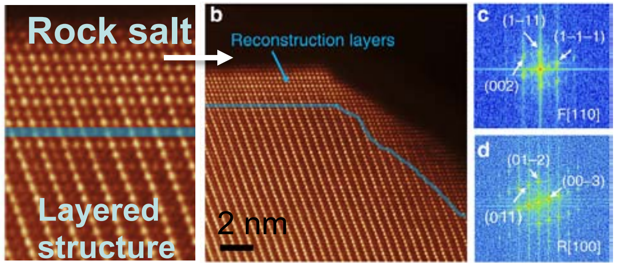
3. Migration of soluble species[1,2]





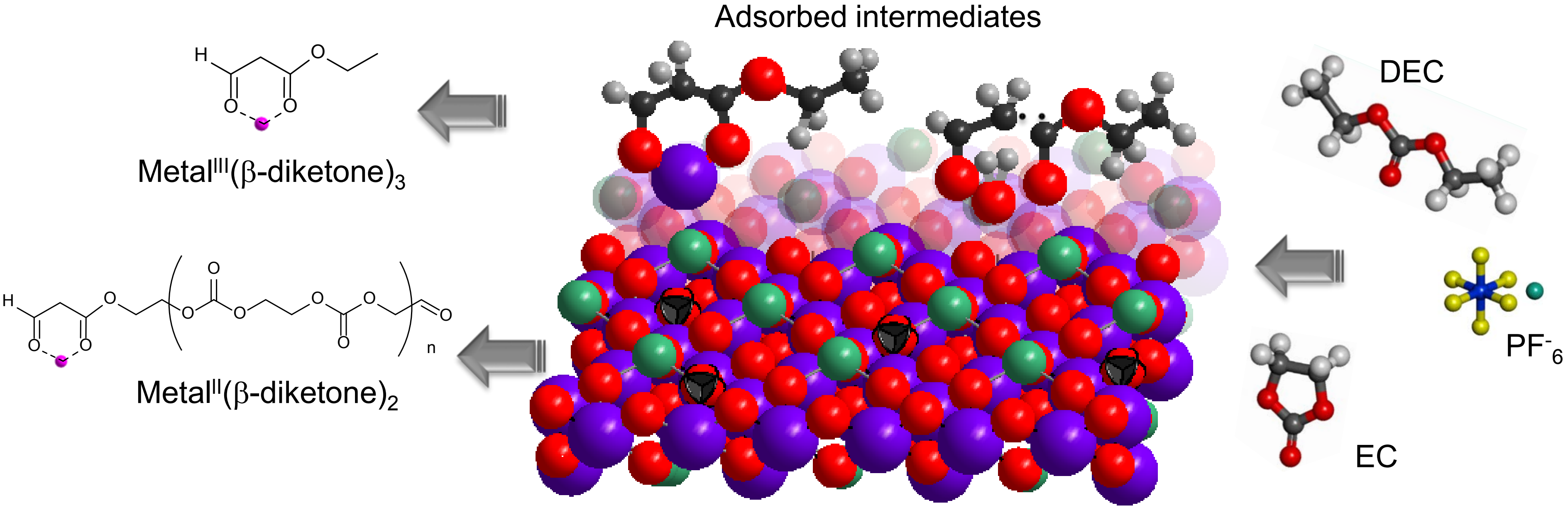


5. Surface reconstruction[5]



Surface Reactivity of High-Voltage Cathodes

Solvent oxidation at transition metal oxide surface is enhanced by surface oxygen vacancies and results in metal dissolution via the formation of fluorescent Metal(β-diketone) complexes.



(111) $Li_xNi_{0.5}Mn_{1.5}O_{4-\delta}$ > 4.2V

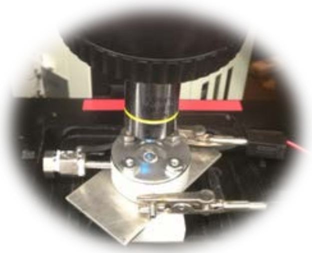
- Oxidation of EC and DEC leads to formation of Metal(β-diketone) fluorescence complexes. Polymer side-chain propagation occurs during EC decomposition.
    - EC oxidation produces high molecular weight $Metal^{II}$(*β*-diketone) complexes which contribute to the build-up of a surface film at the cathode surface.
    - DEC oxidation leads to formation of $Metal^{III}$(*β*-diketone) fluorescent complexes with short side chains which dissolve in the electrolyte.
- These mechanisms of metal dissolution are both enhanced by the continuous creation of oxygen vacancies which will most likely result in surface reconstruction processes.

A. Jarry, S. Gottis, Y.-S. Yu, J. Roque-Rosell, C. Kim, J. Cabana, J. Kerr and R. Kostecki, *Journal of the American Chemical Society*, 2015, **137**, 3533-3539.

Metal Dissolution/Fluorescence Complex Formation at Transition Metal Oxide Cathodes

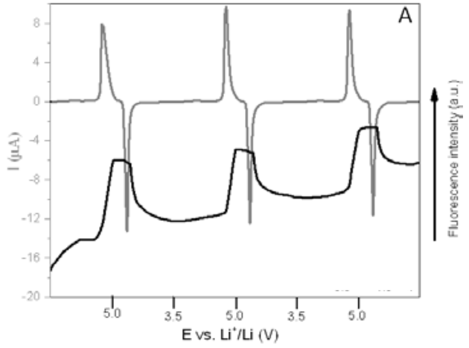
Current and fluorescence intensity monitored during cycling at 0.05 mV/s; binder- and carbon-free electrodes; 1 M $LiPF_6$ in EC/DEC 1:2 wt.

1 mol L^{-1} $LiPF_6$ in EC/DEC (1/2 weight ratio)

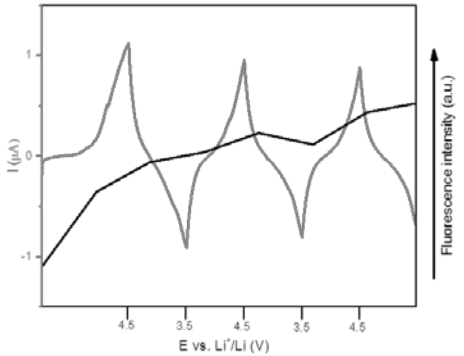


Powder pressed into Al foil as working electrode

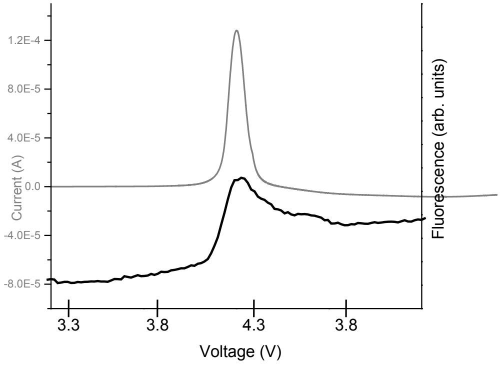
$LiNi_{0.5}Mn_{1.5}O_4$



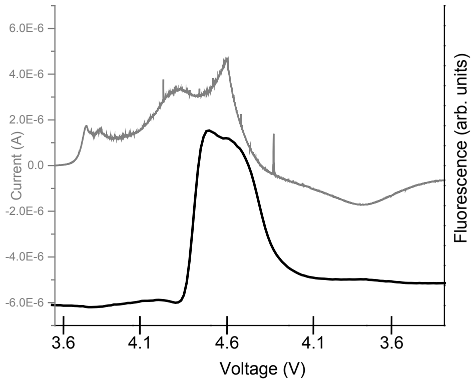
$LiMn_2O_4$



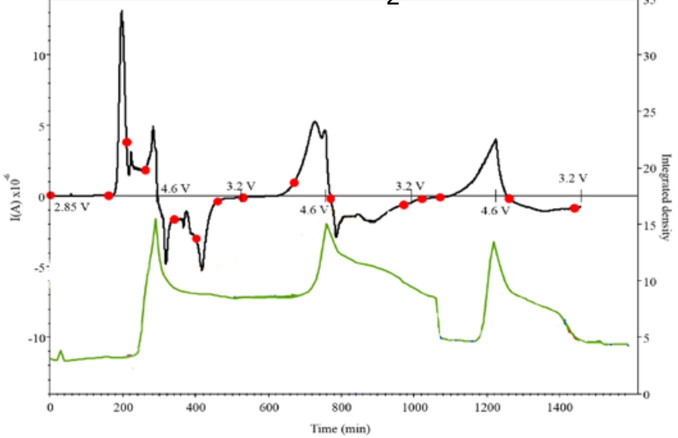
$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC)



$Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$



$LiCoO_2$

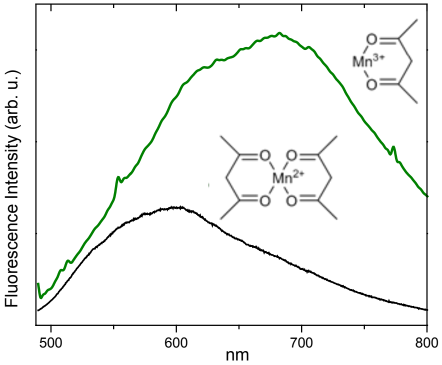


- Formation of fluorescent species is a common phenomenon observed at all transition metal oxide surface during cycling at high potentials.
- Fluorescence rise coincides with Li^+ removal and results in solvent oxidation and metal dissolution.
- The decrease of the fluorescence suggests the existence of a variety of fluorescent species with different molecular weight and solubility.

Metal Dissolution Rate in Organic Carbonate Electrolytes

Fluorescence signal originates mainly from oxidation of **DEC** rather than **EC**.
Fluorescence quantum yield of $Mn^{III}(\beta\text{-diketone})_3$ is much higher than $Mn^{II}(\beta\text{-diketone})_2$.

Mn(β-diketone) complexes



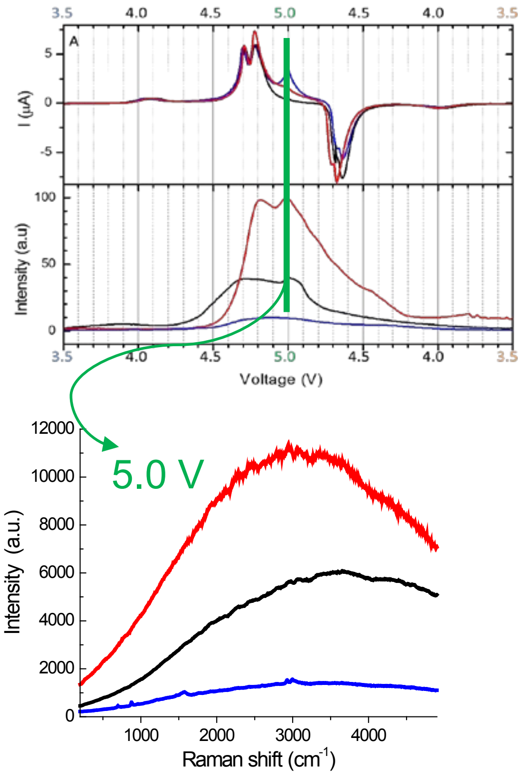
Binder- and carbon-free electrodes cycled
at 0.05 mV/s in 1 M $LiPF_6$,

— EC/DEC (1:2)

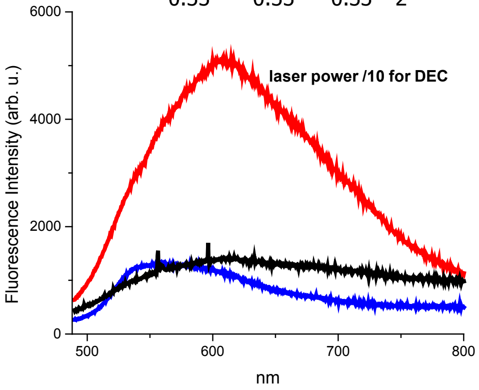
— EC

— DEC

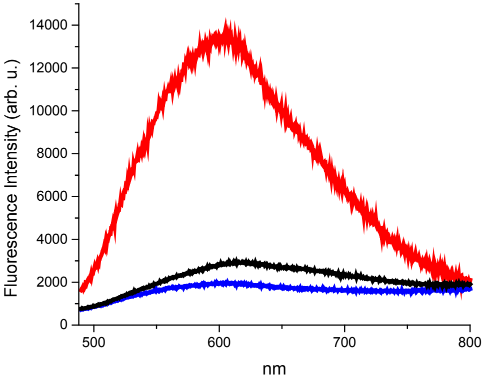
$LiNi_{0.5}Mn_{1.5}O_4$



$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$



$Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$



- ICP measurements revealed that the amount of metal dissolution was twice as fast in DEC electrolyte by a than EC.
- The build-up of the surface film with EC is likely to inhibit metal dissolution process.

Collaboration with B. McCloskey (LBNL/UC Berkeley) and P. Moreau, IMN (France)

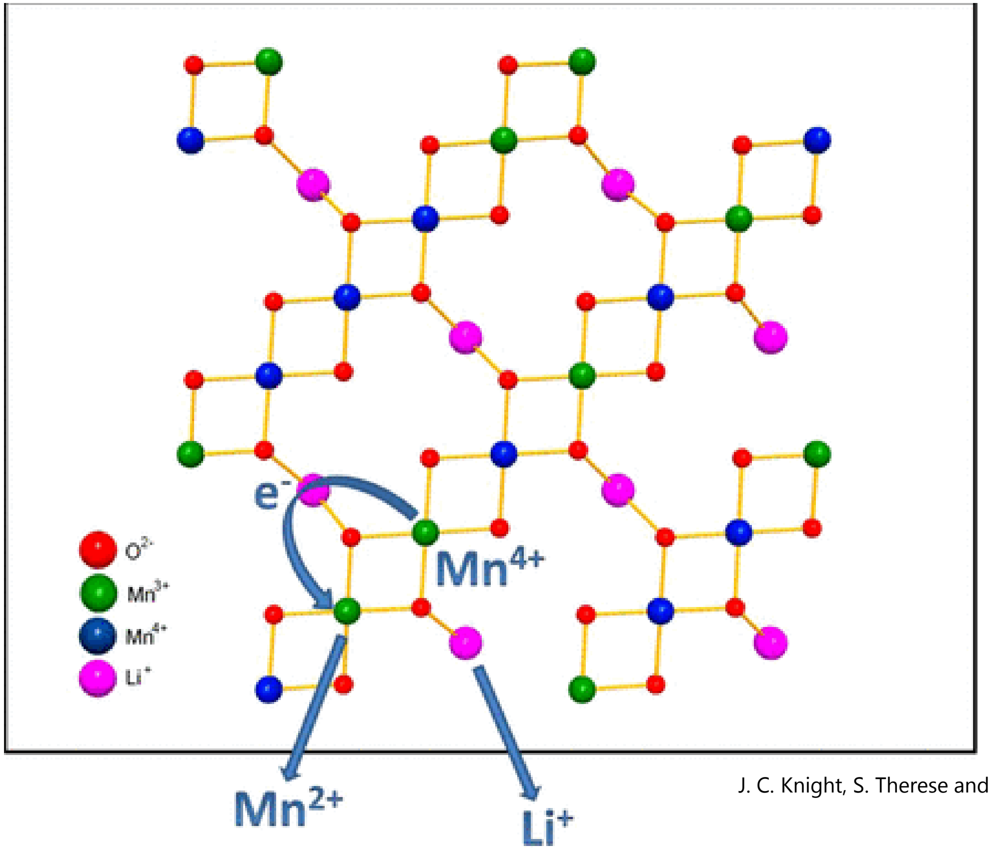
Metal Dissolution From Transition Metal Oxide Cathodes

Hunter proposed a disproportionation reaction under acidic conditions during delithiation, suggesting the release of free Mn^{2+} ions in the system

$$2\,Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$$

J. C. Hunter, *Journal of Solid State Chemistry*, 1981, **39**, 142
M. M. Thackeray et al., *Materials Research Bulletin*, 1984, **19**, 179

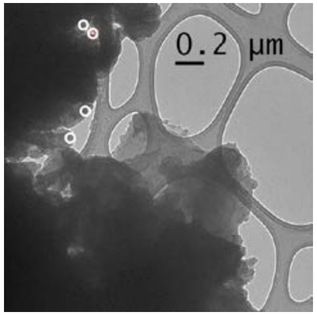
$$2\,LiMn_2O_4 \rightarrow 3MnO_2 + \boxed{MnO + 2Li_2O} \xrightarrow[\text{Aqueous solution}]{\text{HF}} Mn^{2+}$$

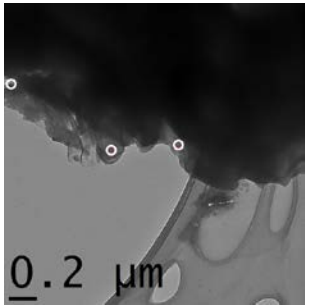


J. C. Knight, S. Therese and A. Manthiram, *J. Electrochem. Soc.*, 2015, **162**, A426

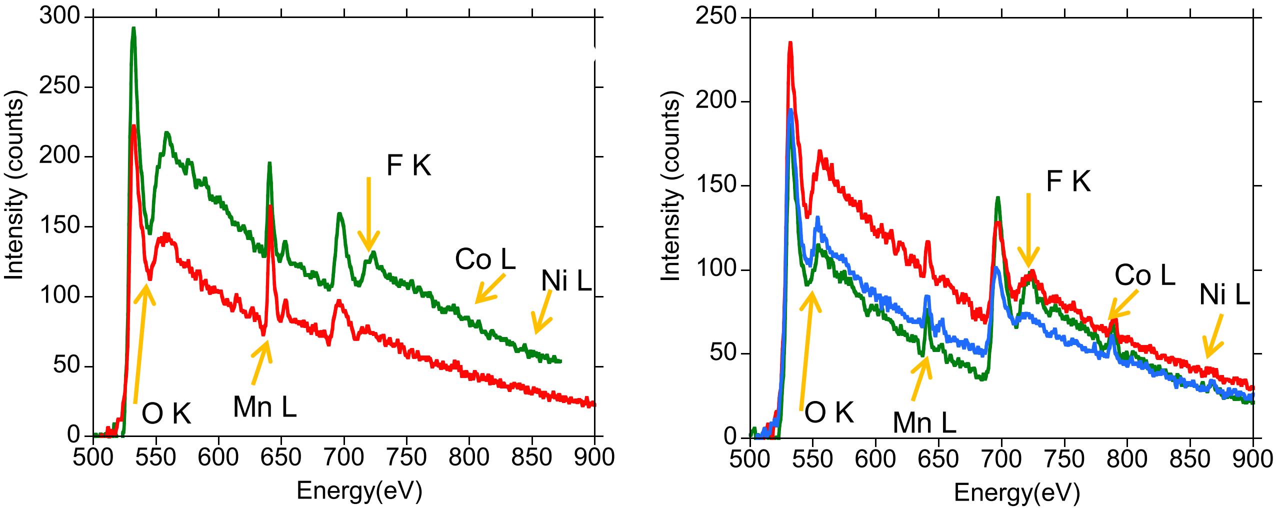
Electrolyte Oxidation Products Distribution in NMC/Graphite Cell

Dissolved of Mn^{II}, Mn^{III}, Co^{II} and Ni^{II} β-diketone complexes are incorporated in the solid electrolyte interphase (SEI) layer at the graphite negative electrode.





Graphite/NMC/1 M $LiPF_6$ salt in EC/DEC (1/2 by wt.) coin cells cycled between 4.3-2.8V 800 times



Areas with high Mn content

Areas with high Co and Ni content

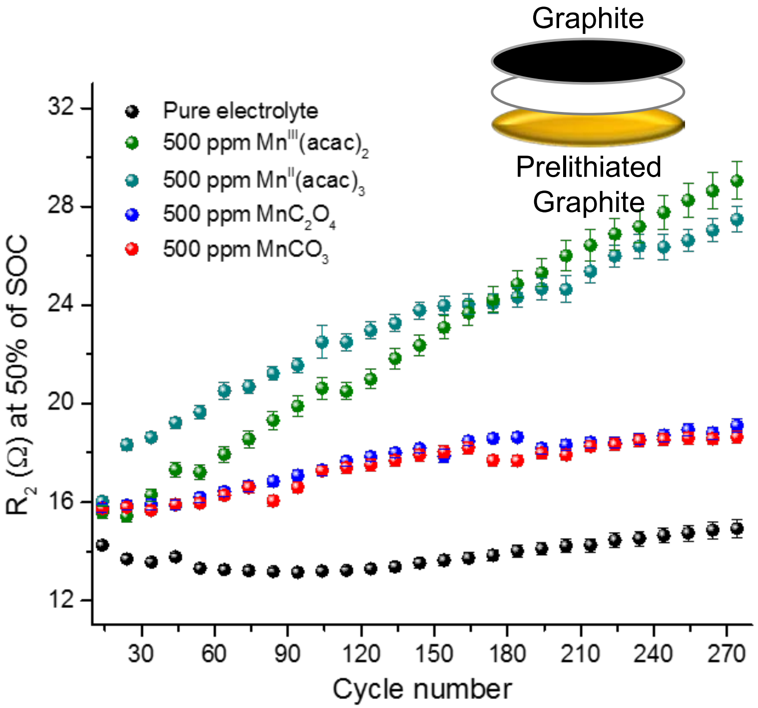
- Mn^{II} and Ni^{II} , Co^{II} complexes, oxalates and carbonates were detected in the graphite anode SEI layer by XAS.
- Distribution of Mn^{II} and Ni^{II} , Co^{II} compounds in the SEI layer varies strongly with location.

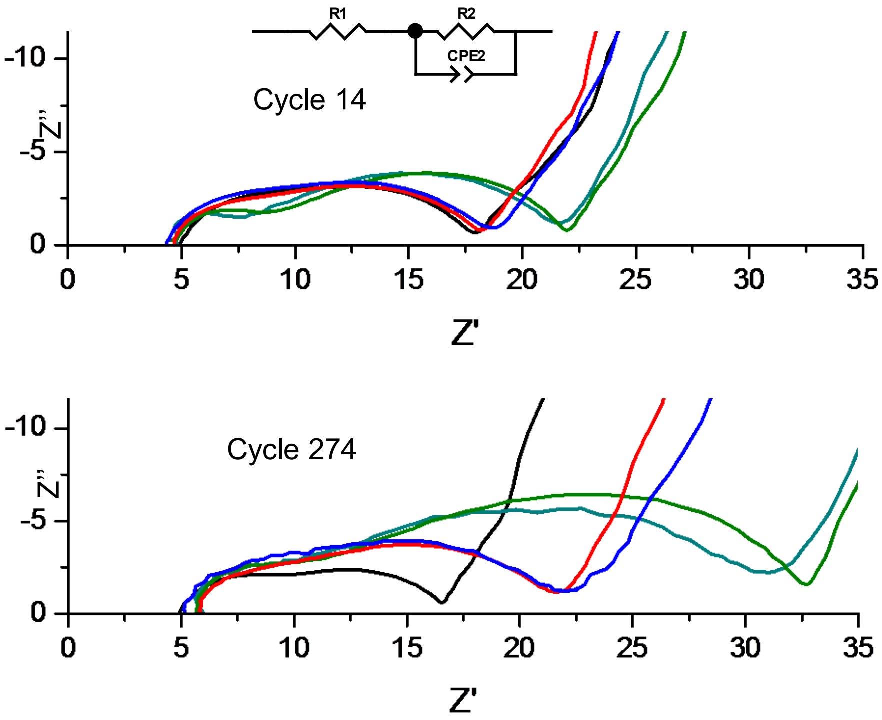
Collaboration with P. Moreau, IMN (France)

The Effect of $Mn^{II/III}$(β-diketone) Coordination Complexes on 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.

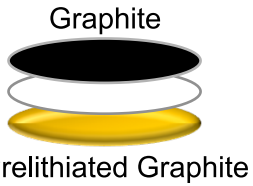
Graphite symmetric cell filled with 1 M $LiPF_6$, EC/DEC (1:2) spiked with 500 ppm of $Mn^{II/III}$ compounds.





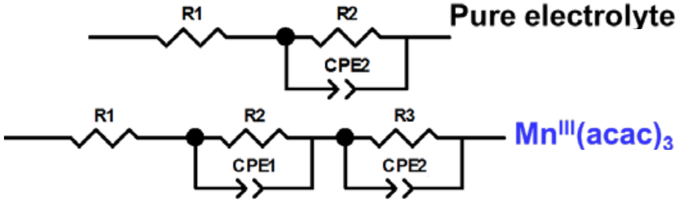
- β-diketone complexes are responsible for the observed impedance increase of the graphite anode (Mn poisoning).
- Slight impedance increase is also observed in the presence of Mn^{II} carbonate and Mn^{II} oxalate.

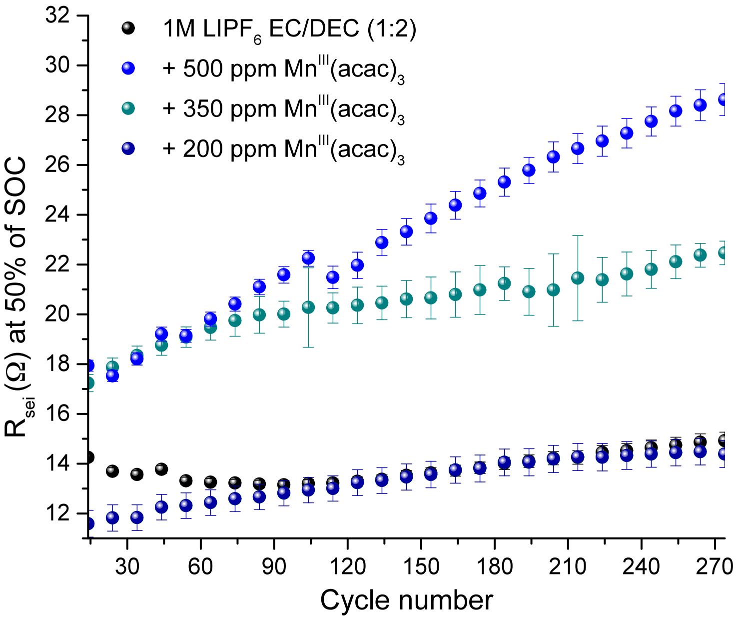
The Effect of $Mn^{II/III}$(β-diketone) Concentration on Li^+ Transport in the SEI Layer

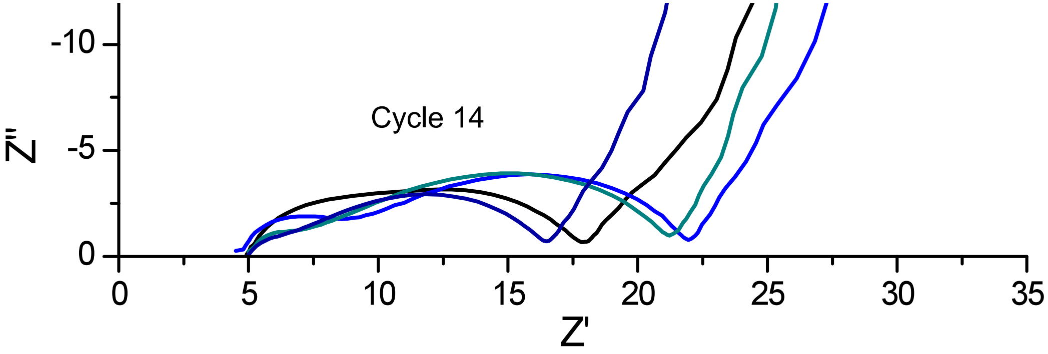


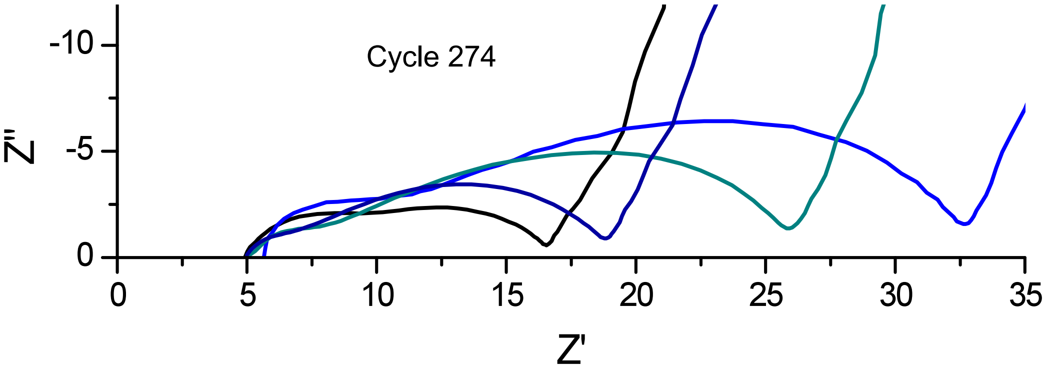
Electrolyte : 1 M $LiPF_6$
in EC/DEC 1:2
with or without
$Mn^{III}(acac)_3$

Equivalent circuit models used to represent interfacial processes at 50% of SOC



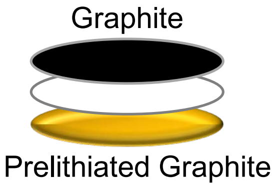






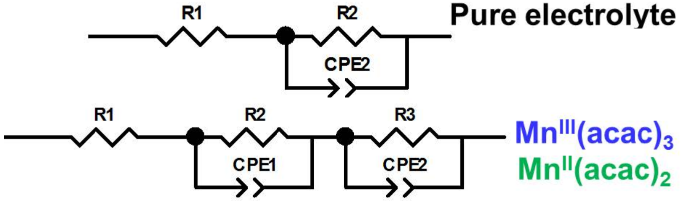
- Progressive deposition of $Mn^{II/III}$(β-diketone) within SEI results in impedance rise.
- Strong effect of $Mn^{II/III}$(β-diketone) concentration on the electrode/cell impedance

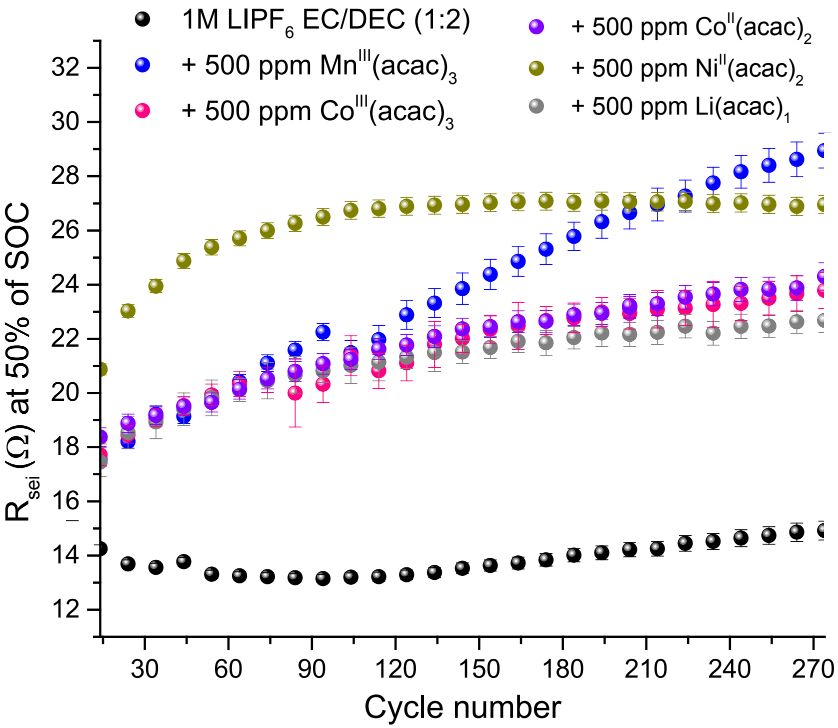
The Effect of β-diketone Ligands on Li$^+$ Transport in the SEI Layer

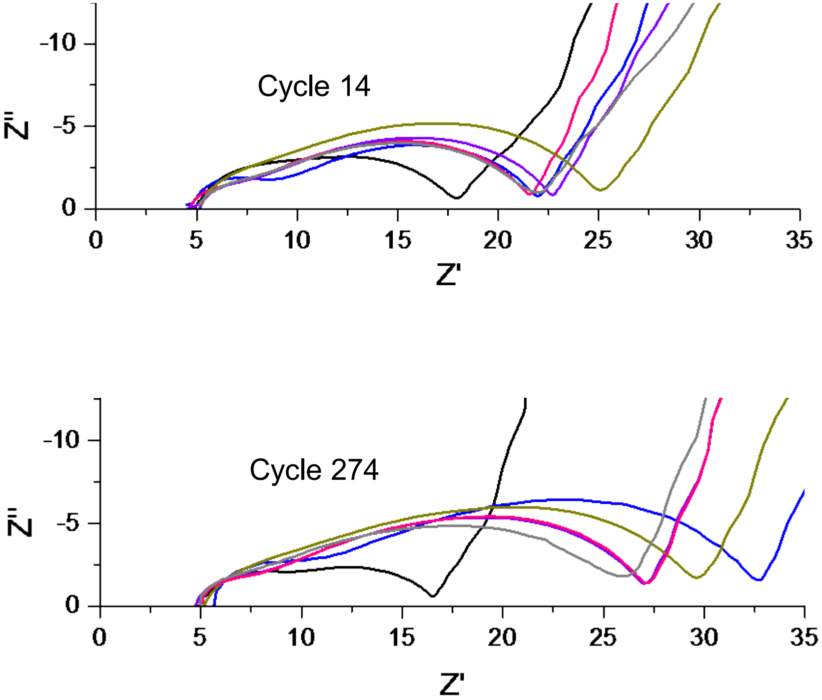


Electrolyte : 1 M LiPF$_6$
in EC/DEC 1:2
with or without
M^{n+}(acac)$_n$

Equivalent circuit models used to represent interfacial processes at 50% of SOC



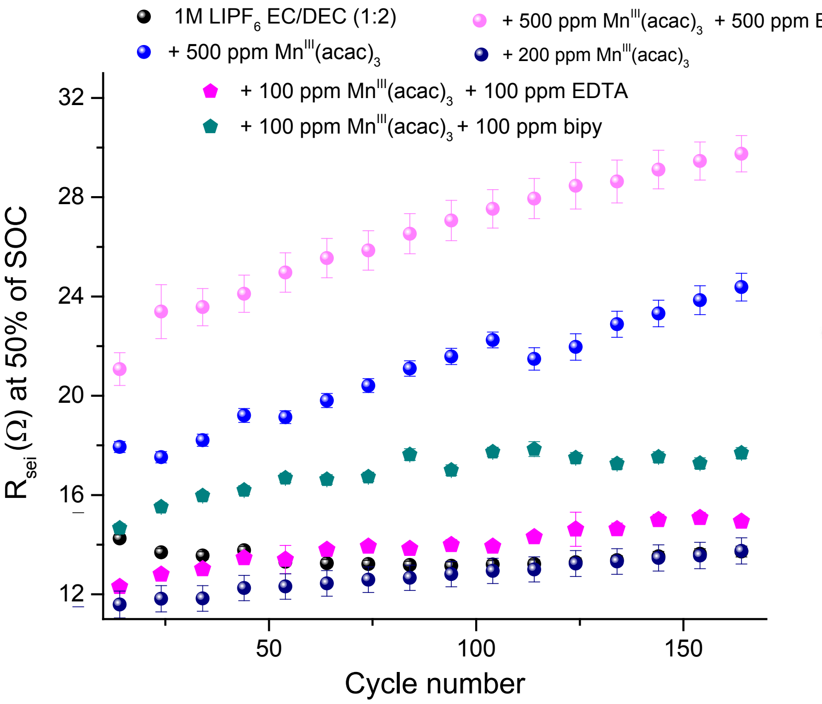


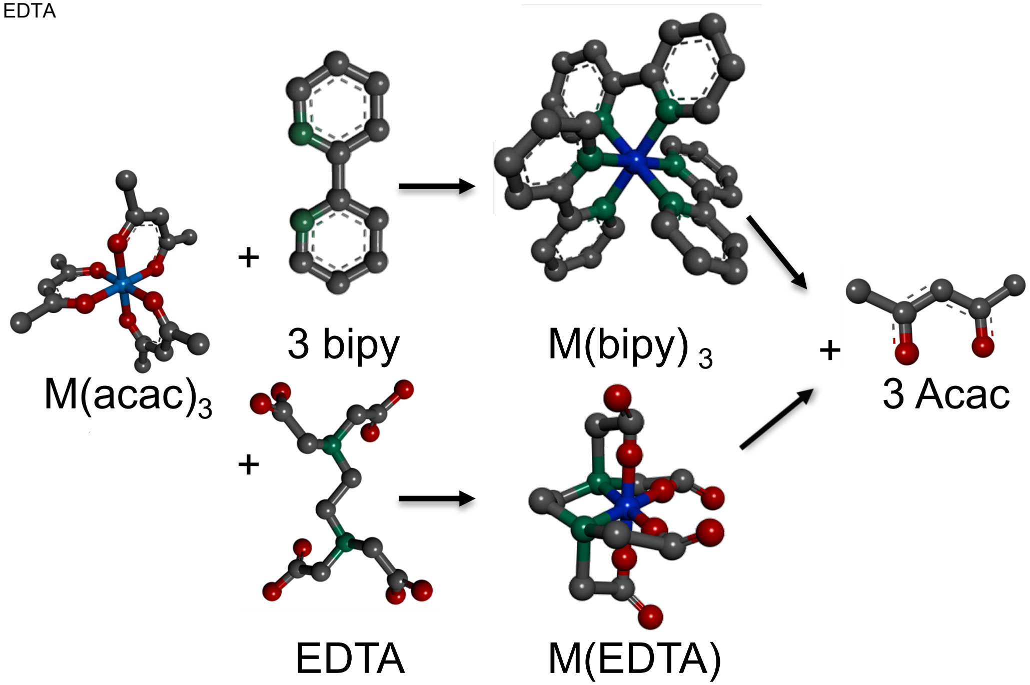


Impedance rise is observed with all M^{n+}(acac)$_n$ complexes (M =Mn, Co, Ni and Li) with the strongest detrimental effect with Mn^{III}(acac)$_3$ and the fastest with Ni^{II}(acac)$_2$

The presence of acetylacetonate ligands in the system results in impedance rise, independently of the central atom of the coordination complex.

The Effect of β-diketone Ligands on Li^+ Transport in the SEI Layer





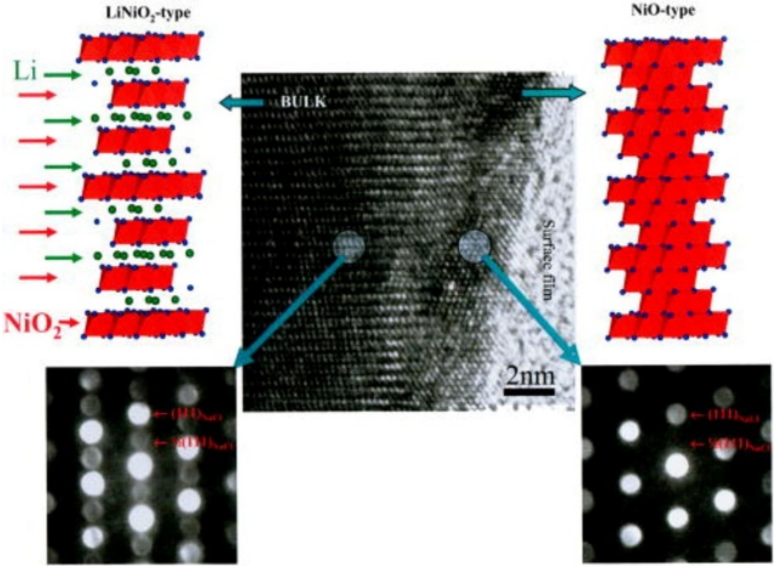
- The detrimental effect of $Mn^{III}(acac)_3$ is enhanced in the presence of EDTA and bipyridine chelating agents.
- EDTA and bipyridine are strong complexing agents which initiate ligand substitution to form very stable Mn EDTA and birydine complexes.
- This reaction initiates a release of β-diketone ligands in the system, enhancing its "poisoning" effect on SEI, even with a very low $Mn^{III}(acac)_3$ initial concentration.

*Collaboration with B. Eichhorn, A. Jarry (*Dept. of Chemistry & Biochemistry, University of Maryland*) and* Kang Xu *(*U. S. Army Research Laboratory)

Surface Reconstruction in Transition Metal Oxides

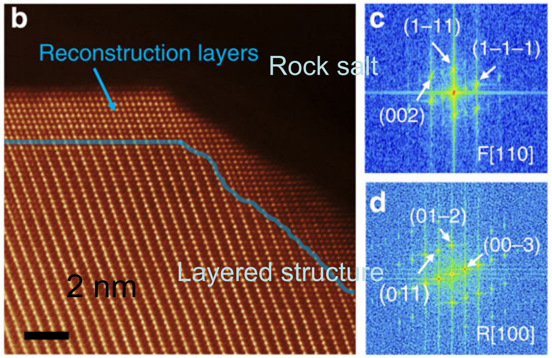
- *Surface reconstruction at transition metal oxide surface i.e., layered-spinel-rock salt structure transformation, is a common surface degradation processes in Li-ion cathode oxide materials.*
- *The thickness of the surface layer observed depends on particle surface facet, electrolyte exposure time and cycling regime.*
- *The rock salt surface layer is usually associated with battery failure due to its higher resistance to Li^+ transport.*

$LiNi_{0.8}Co_{0.2}O_2$

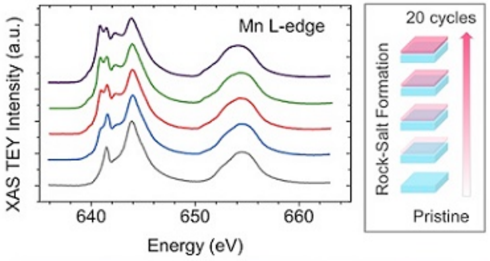


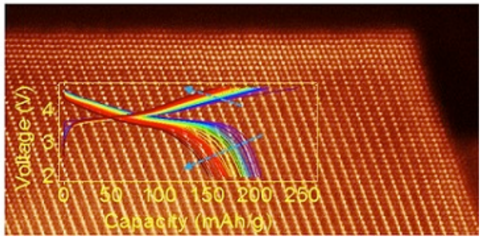
Abraham et al., JES 2003

$LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$



Lin et al., Nat. Commun. 2014



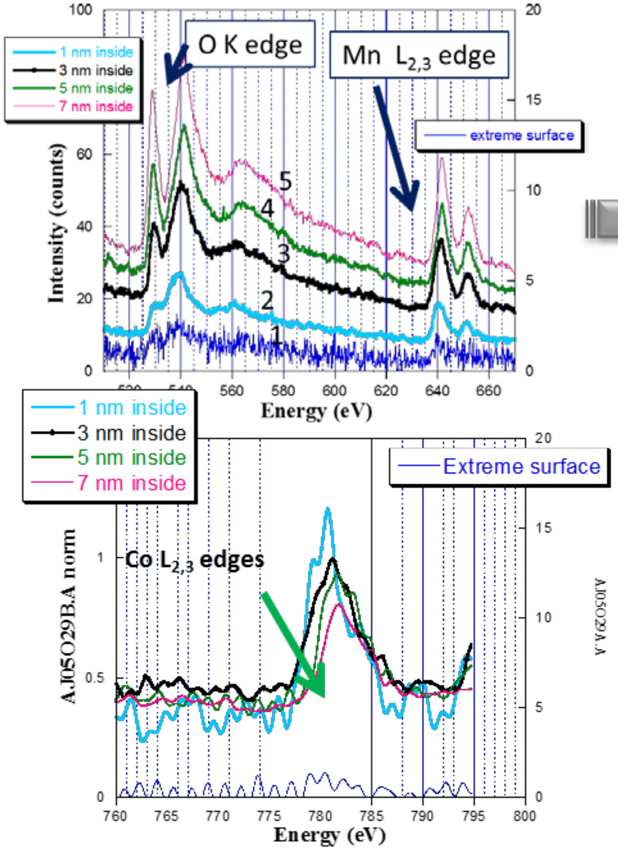


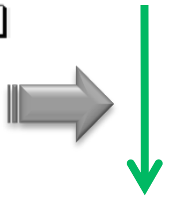
EELS Study of Surface Reconstruction in NMC

Surface reconstruction of NMC is usually associated with a metal reduction at the surface and change in oxygen environment. Both phenomena can be probed using Electron Energy Loss Spectroscopy (EELS) (Mn L_3/L_2 edge ratio determines Mn oxidation state).*

Binder- and carbon-free NMC (111) electrodes cycled in Swagelok vs. Li up to 4.4-2.8V with 1 M $LiPF_6$, EC, DEC or EC/DEC (1/2 wt.)
EELS performed at low temperature using a vacuum transfer sample holder on non washed sample)

EELS spectra (DEC)

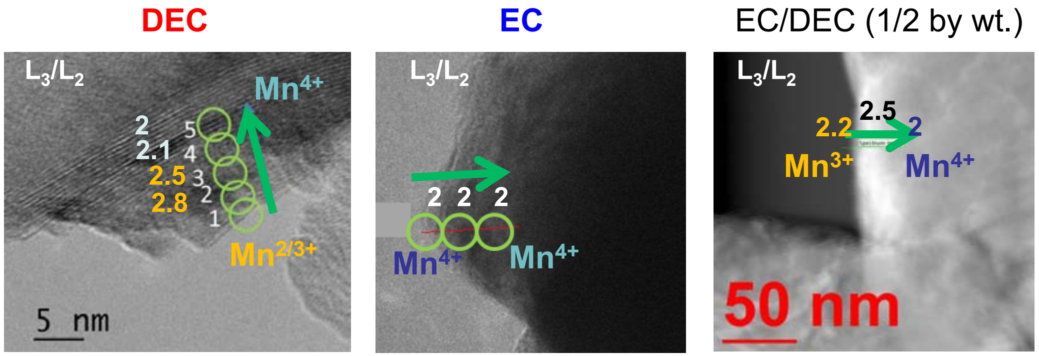




Surface

~10 nm inside

STEM image of the probed areas



DEC

EC

EC/DEC (1/2 by wt.)

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

- Mn oxidation state decrease observed at the surface of NMC is most likely linked with rock salt formation.
- These structural changes are easily identifiable in DEC electrolyte whereas in EC they are hard to find.

Summary I

1. X-ray absorption, optical fluorescence spectroscopy and imaging experiments demonstrated that solvent oxidation at transition metal oxide surface is enhanced by surface defects such as oxygen vacancies and results in metal dissolution via the formation of fluorescent Metal(β-diketone) complexes.
2. We have demonstrated that formation of fluorescent species is a common phenomenon observed in transition metal oxides cathodes during cycling at high potentials.
3. Fluorescence signal originates from oxidation of linear carbonate esters. Oxidation of EC results in the formation of a surface film containing species with longer side chains which inhibit further metal dissolution.
4. Surface reconstruction in $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ surface and rock salt structure formation is more pronounced in linear carbonate ester-based electrolytes.
5. Formation of Mn^{III}/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 as well as surface reconstruction and relates to 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 complex and interrelated mechanism of interfacila phonemena at high-voltage cathodes.

Interfacial Activity of Silicon Anodes

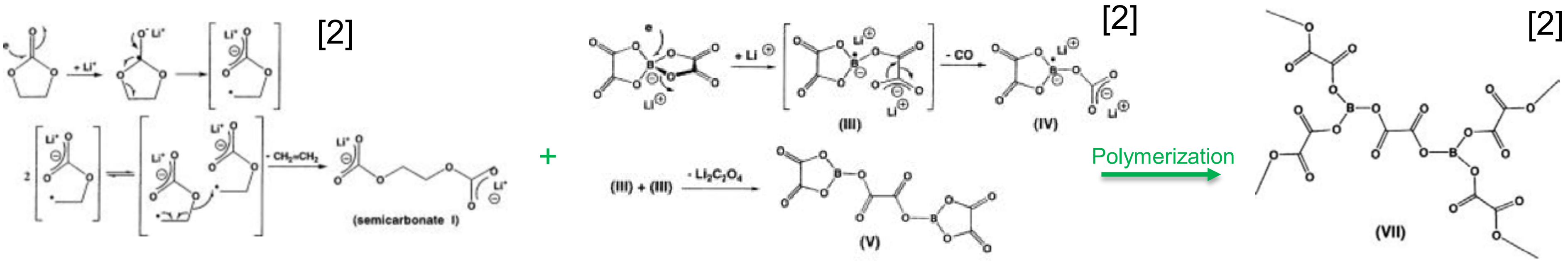
Approach

Identify and study root causes of interfacial instability and mechanisms of degradation of Si anodes in organic electrolytes.

1. 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.
2. Assess impact of interfacial phenomena on the Si anode on the electrochemical performance and lifetime of Li-ion cells

The Effect of LiBOB on SEI Properties Si Anodes

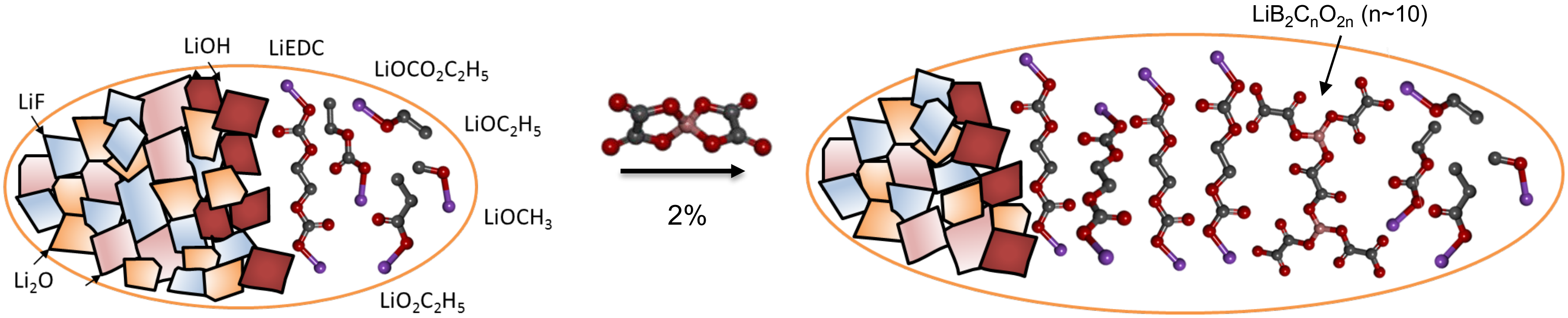
LiBOB additive improves cycling performance of silicon in $LiPF_6$-based electrolytes.[1] The SEI contains stable oligomers such as $ROCO_2Li_2$ and $LiB_2C_nO_{2n}$ (n~10).[2-4]



LIEDC

$LiB_2C_nO_{2n}$ (n=6)

$LiB_2C_nO_{2n}$ (n=10)



Schematic SEI without additive

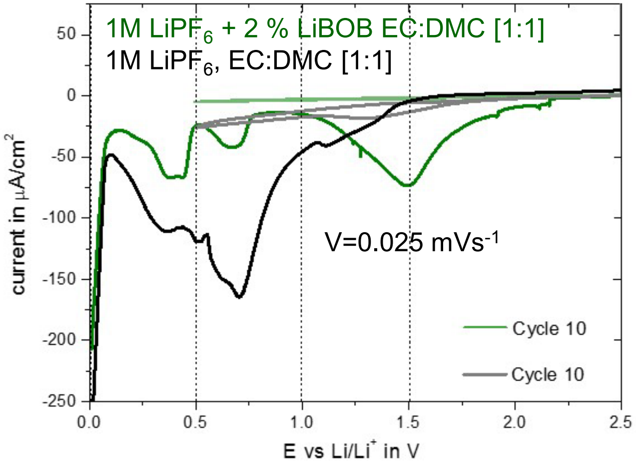
Schematic SEI with LIBOB additive

1. S. Dalavi et al., J. Electrochem. Soc., 159 (2012) A642
2. K. Xu et al.,, Electrochemical and Solid-State Lett., 2003, **6**, A144
3. G. V. Zhuang et al., Electrochem. Solid State Lett., 2004, **7**, A224
4. L. Larush-Asraf et al., J. Power Sources, 2007, **174**, 400

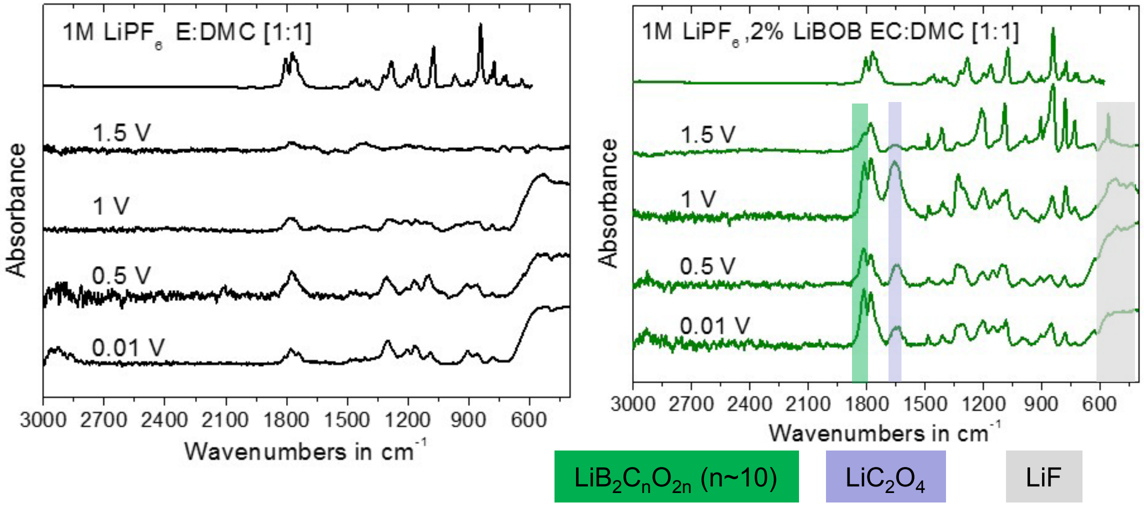
The Effect of LiBOBe Additive on Si Interfacial Instability

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

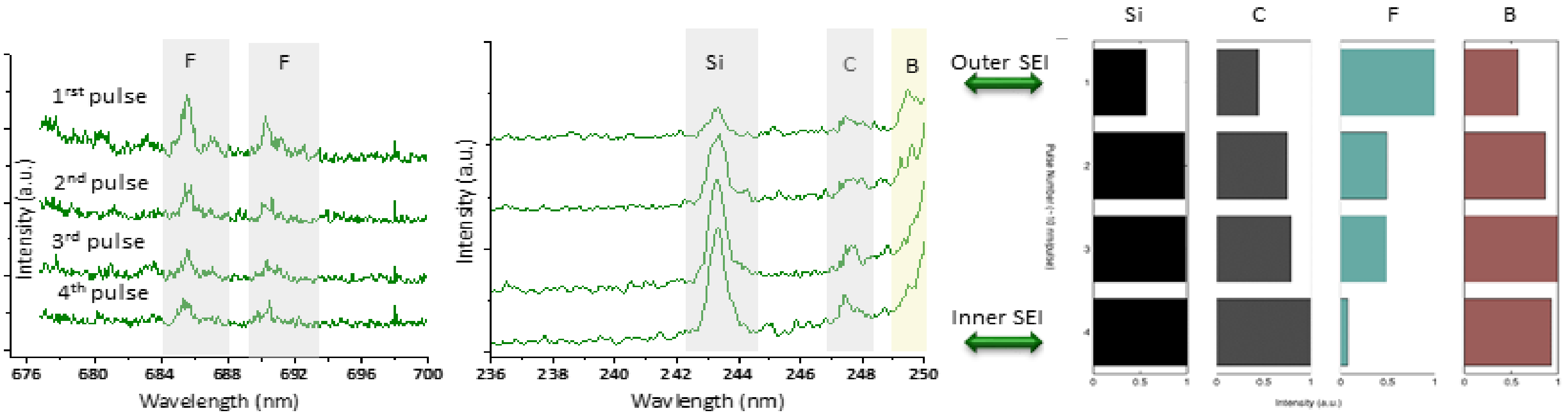
CVs of Si(111) wafer electrode



FTIR of Si(111) wafer electrode



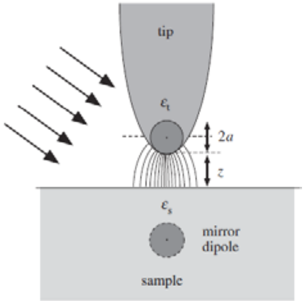
LIBS depth profiling of Si(111) at 0.01 V

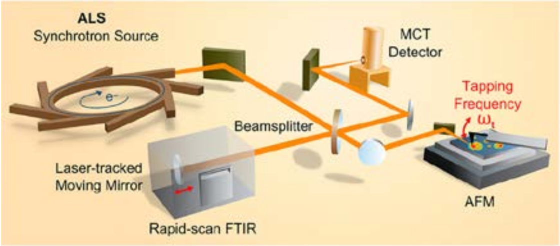


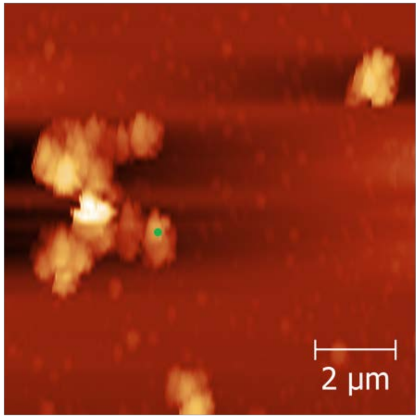
Collaboration with V. Zorba, LBNL

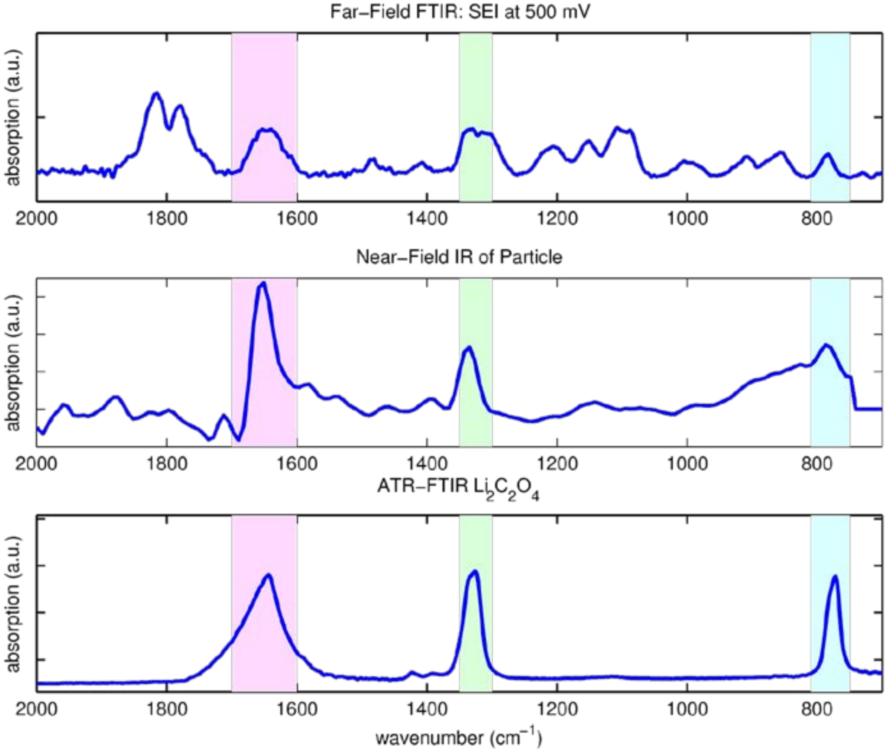
Synchrotron IR Near-Field Spectroscopy of the SEI on Si(111) Electrode

Si(111) wafer at 0.5 V in 1M $LiPF_6$ + 2 % LiBOB, EC:DMC [1:1]









- Local spectra of the SEI layer on Si(111) were obtained at deeply subwavelength (~20 nm) resolution.
- LiC_2O_4 identified in the far- and near-field FTIR spectra.

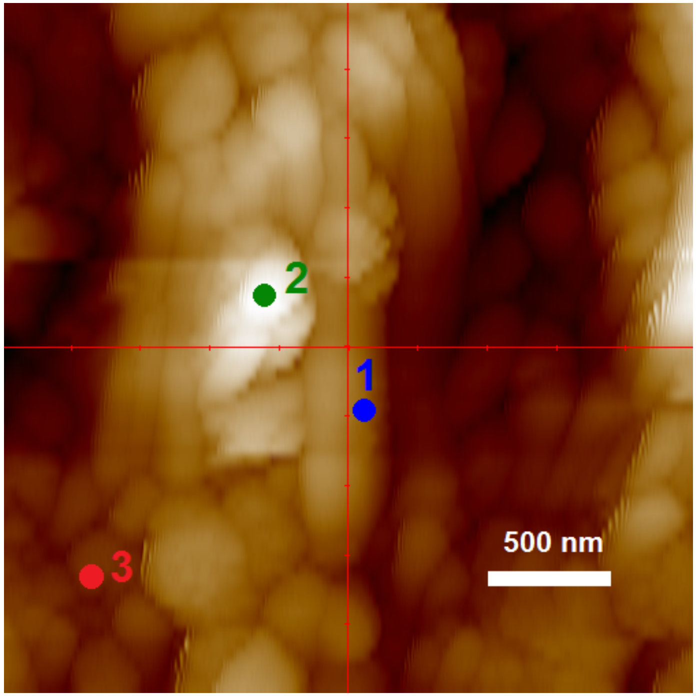
Near-field IR spectroscopy can resolve spectra of individual particles for SEI basic building blocks identification at nanometer scale.

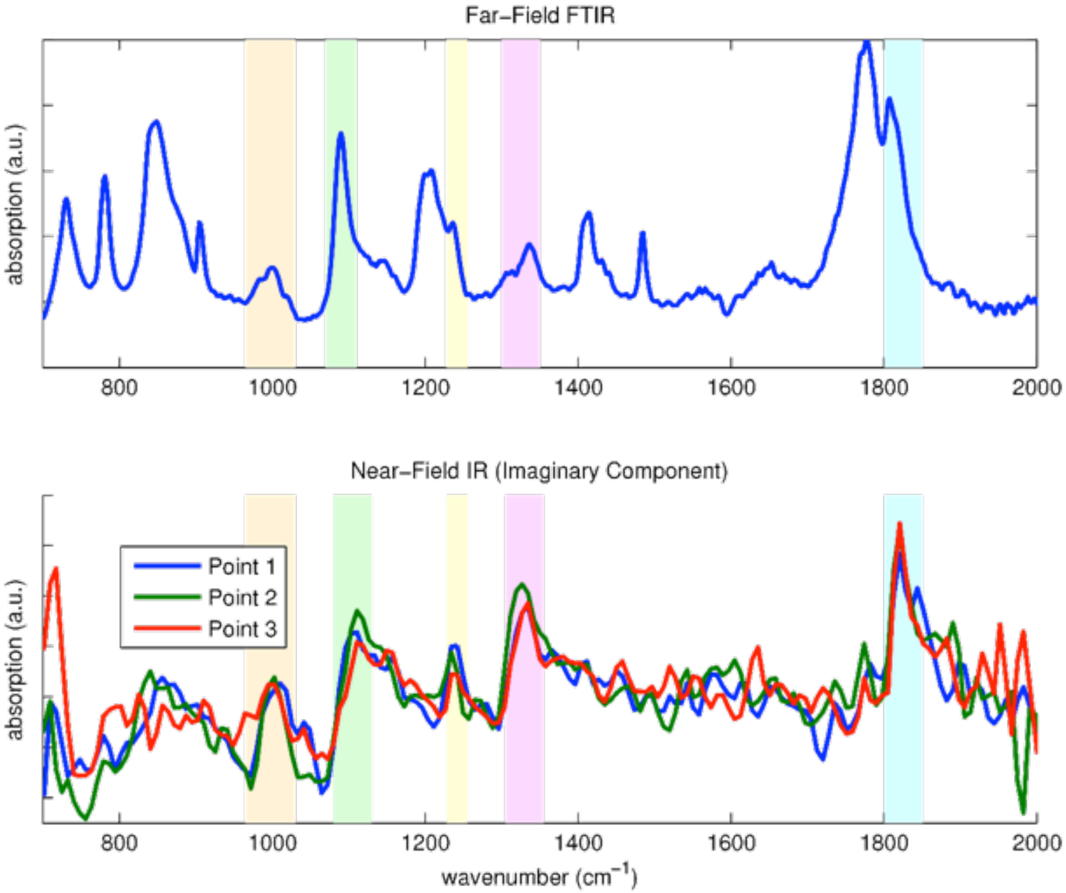
Collaboration with H. Bechtel, ALS/LBNL

Spectral Individuation of the LiBOB-Induced Passivation Film on Si-111 by Near-Field IR Spectroscopy

Si(111) wafer at 1.5 V in 1M $LiPF_6$ + 2 % LiBOB, EC:DMC [1:1]

Topography



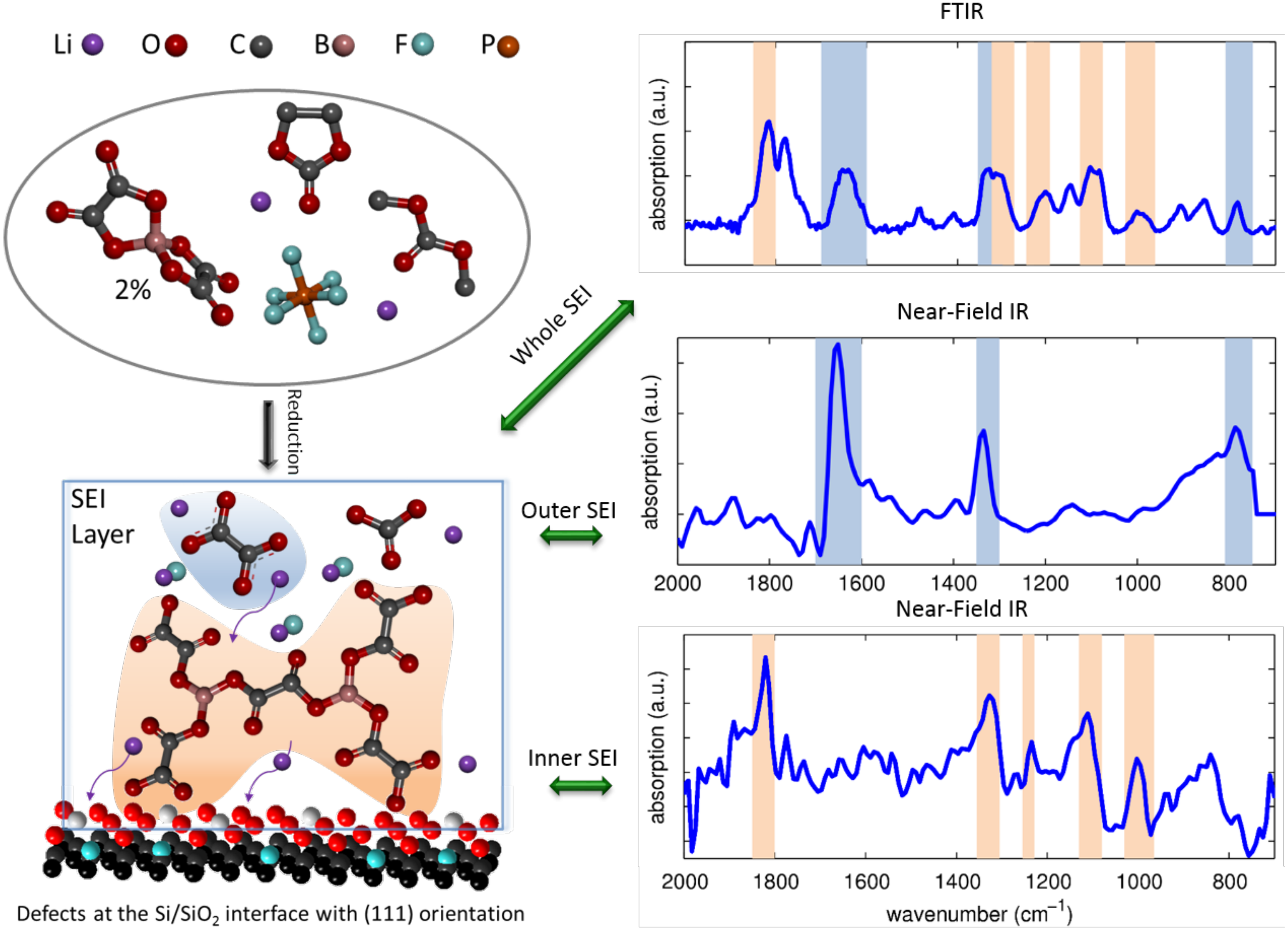


- High lateral and axial resolution of the near-field optical probe enable spectral and chemical selectivity to select out peaks associated with a single compound
- Matching early-stage near- and far-field IR spectra allows isolation of the passivating oligomer $LiB_2C_nO_{2n}$, confirms its presence in the “inner SEI”, establishes structure-function relationship

K. Xu et al.,, *Electrochemical and Solid-State Letters*, 2003, **6**, A144-A148..

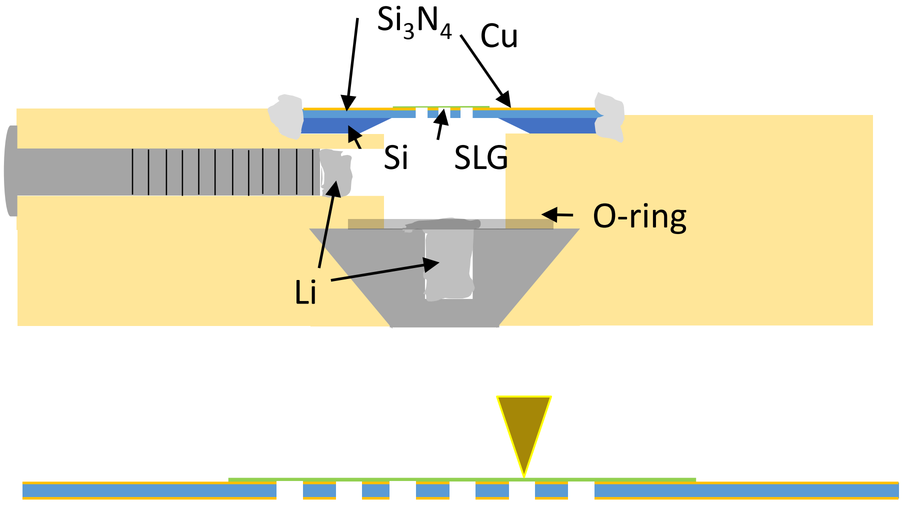
Collaboration with H. Bechtel, ALS/LBNL

Model of the SEI on Si Anodesing Standard Electrolyte with LiBOB Additive

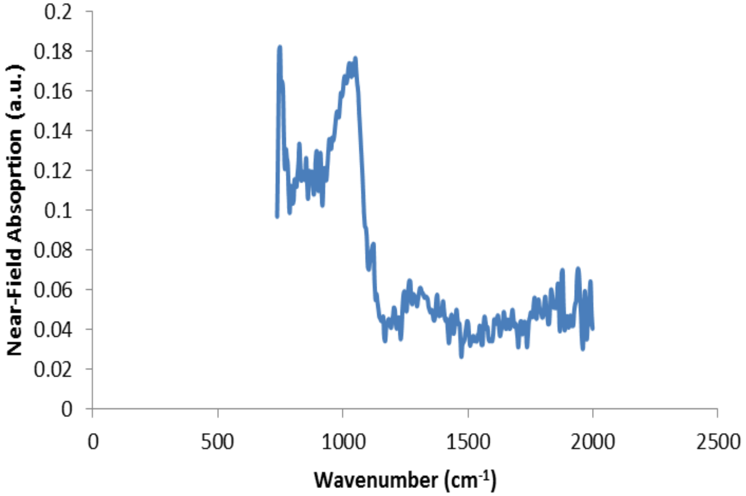


- Model validation using near-field spectroscopy demonstrates how traditional and next-generation techniques can be combined to understand SEI nanostructure

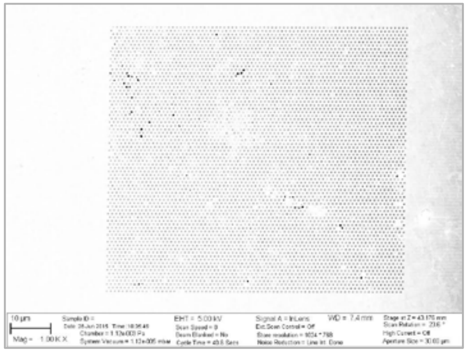
Development of *in situ* Near-Field Imaging for Electrode Surface Films

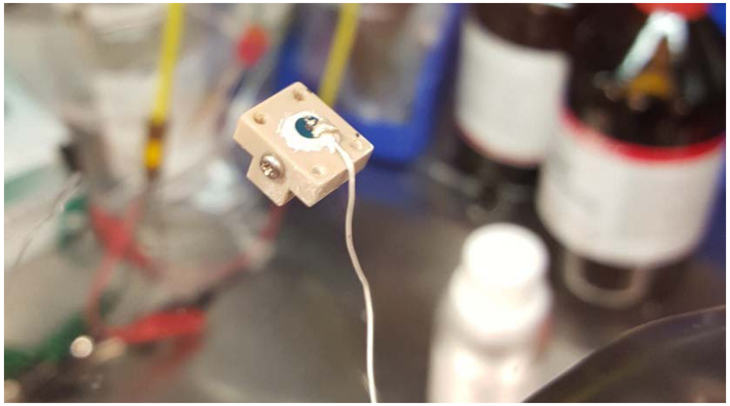


Single-Layer Graphene Membrane Suspended on Perforated Cu-Coated Silicon Nitride Chip



Near-field tip capable of measuring SiO_2 absorption spectrum through graphene layer





- Developing transmembrane imaging with graphene can avoid pitfalls of liquid cell usage
- Graphene useful as a model electrode for SEI growth on graphite

Collaboration with M.Salmeron, LBNL

Summary II

- A combination of traditional (cyclic voltammetry, FTIR) and next-generation (near-field IR, LIBS) techniques were used to identify the role of LiBOB additive in stabilizing the SEI on Si electrodes
  - An oligomeric “inner SEI” composed of $LiB_2C_{10}O_{20}$ forms early (>1.5 V) and is responsible for passivating the Si surface
  - The “outer SEI” consists of compounds including LiF and $Li_2C_2O_4$, which do not clearly contribute to SEI functionality

- Near-field spectroscopy established for the first time as a technique for identifying functional components of the SEI film. Results are in accordance with data provided by other methods and establish new information (spatial localization of compounds) unachievable by other methods

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 is ABMR program lead
- ABMR Cathode and Anode Task Groups
    - ANL, LBNL, SUNY, UP, HQ, NREL and UU

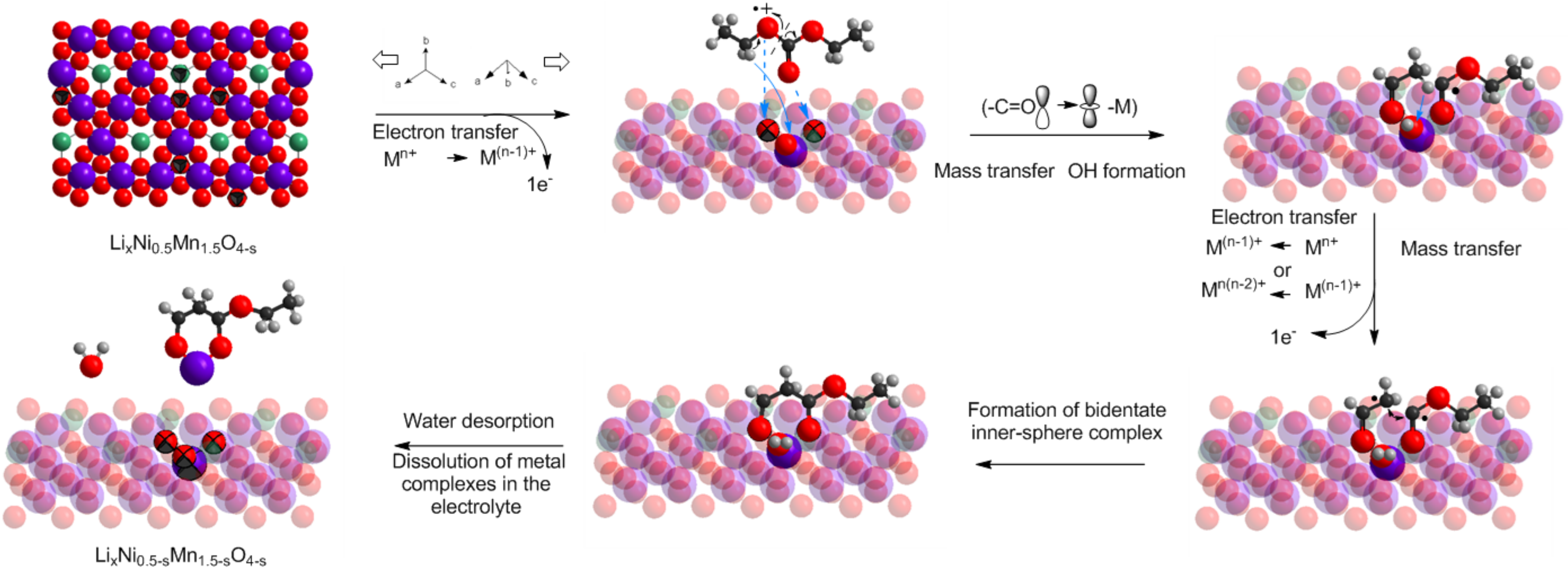
  (G. Chen, J. Kerr, V. Battaglia, M. Doeff, K. Persson, V. Zorba, W. Yang, C. Ban, N. Balsara, B. Mc Closkey)

- 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
- B. Eichhorn, A. Jarry, University of Maryland
- Kang Xu, U. S. Army Research Laboratory

Technical Back-Up Slides

The Mechanism of Formation of Metal Complexes at the $LiNi_{0.5}Mn_{1.5}O_4$ Cathode. 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 $Li_xNi_{0.5}Mn_{1.5}O_{4-s}$.
- DEC oxidation occurs via two proton coupled electron transfer (PCET) associated with ligands adsorption.



$Li_xNi_{0.5}Mn_{1.5}O_{4-s}$

Electron transfer

$M^{n+} \rightarrow M^{(n-1)+}$

$1e^-$

$(-C{=}O \rightarrow -M)$

Mass transfer OH formation

Electron transfer

$M^{(n-1)+} \leftarrow M^{n+}$

or

$M^{n(n-2)+} \leftarrow M^{(n-1)+}$

$1e^-$

Mass transfer

Formation of bidentate inner-sphere complex

Water desorption

Dissolution of metal complexes in the electrolyte

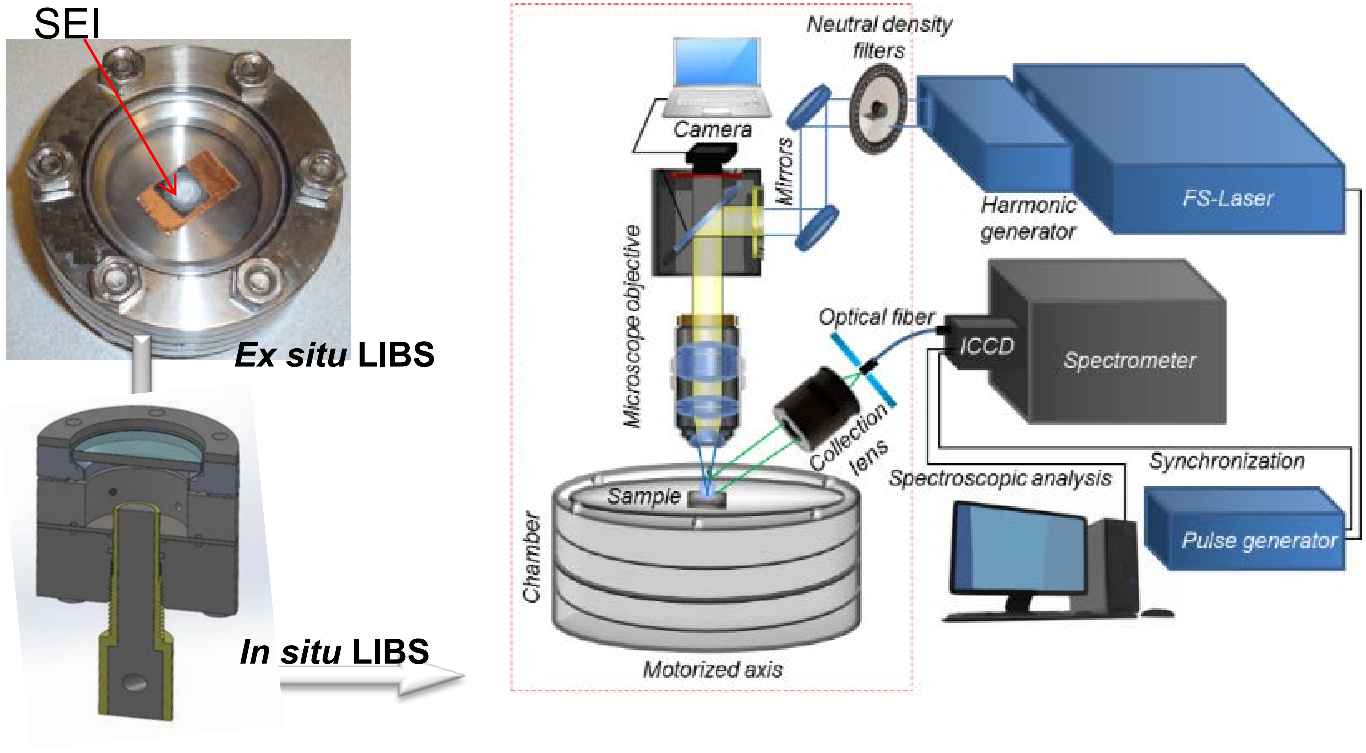
$Li_xNi_{0.5-s}Mn_{1.5-s}O_{4-s}$

- DEC oxidation occurs preferentially at E>4.2 V at Mn^{4+} surface sites.
- DEC oxidation leads to formation of Mn(β -diketone) fluorescent complexes and water.
- Mn(β -diketone) fluorescence complexes with short side chains are soluble in the electrolyte.

A. Jarry, S. Gottis, Y.-S. Yu, J. Roque-Rosell, C. Kim, J. Cabana, J. Kerr, R. Kostecki, Journal of the American Chemical Society, 137 (2015) 3533

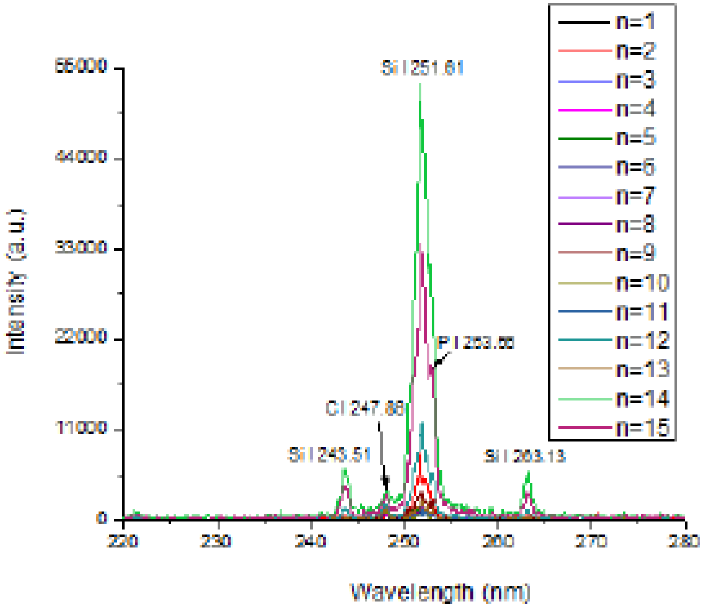
Laser Induced Plasma Spectroscopy for Energy Applications

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

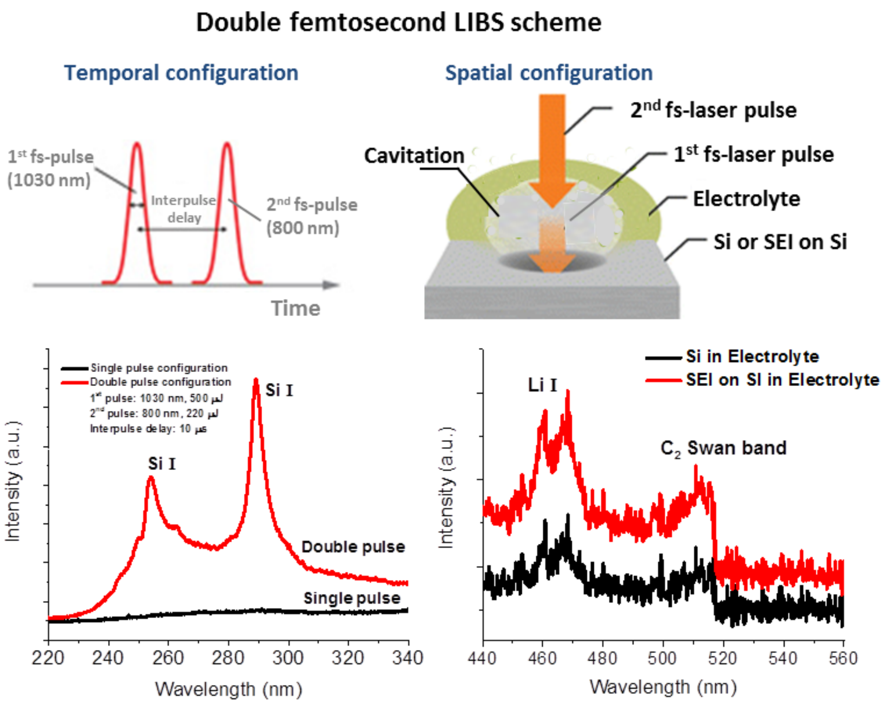


- *In situ* capabilities for probing compositional variations during cycling in real time
- Elemental, molecular and isotopic analysis
- Ability to probe compositional variations with depth (depth profiling) with high resolution

In situ LIBS Measurements of the SEI on Si Electrode



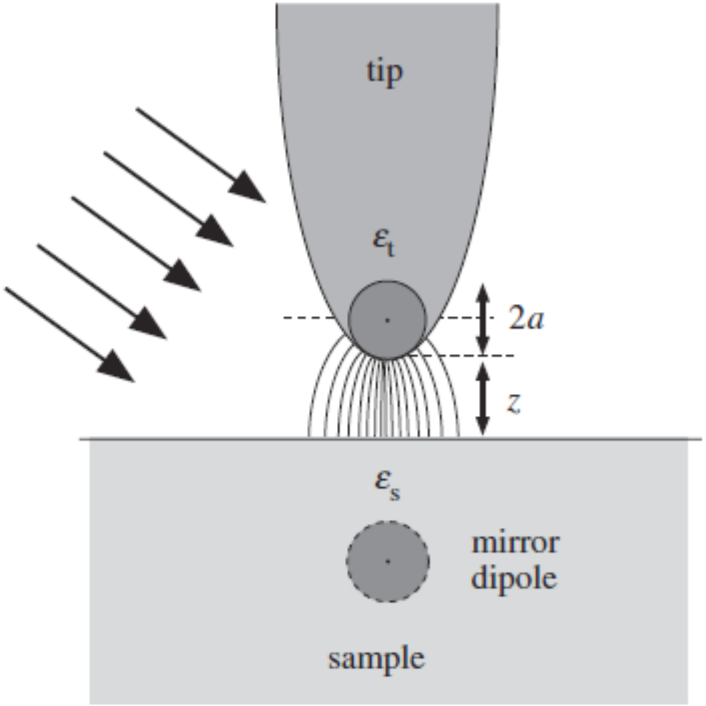
(100) Si wafer with 1M $LiPF_6$ EC:DEC [1:2] electrolyte

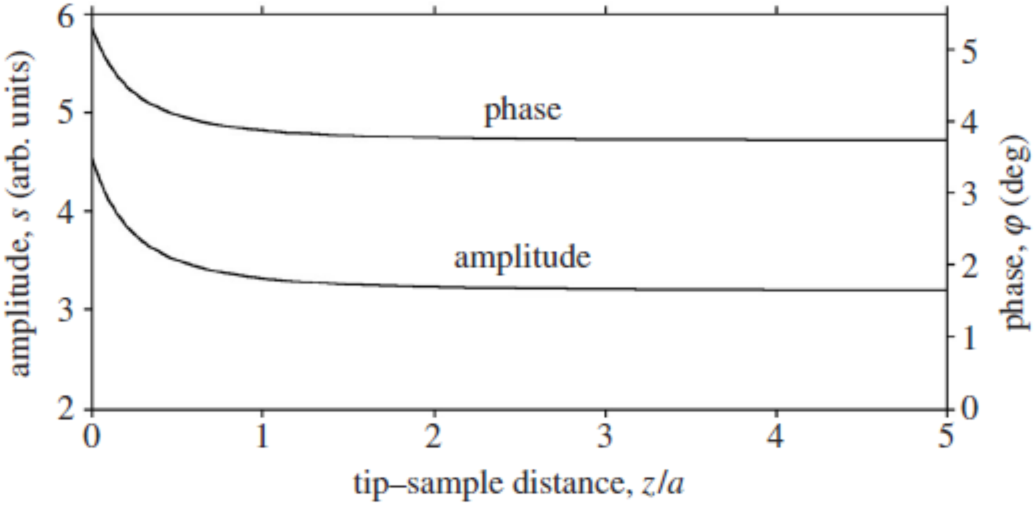

Double femtosecond LIBS scheme

(100) Si wafer with 1M $LiPF_6$, 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





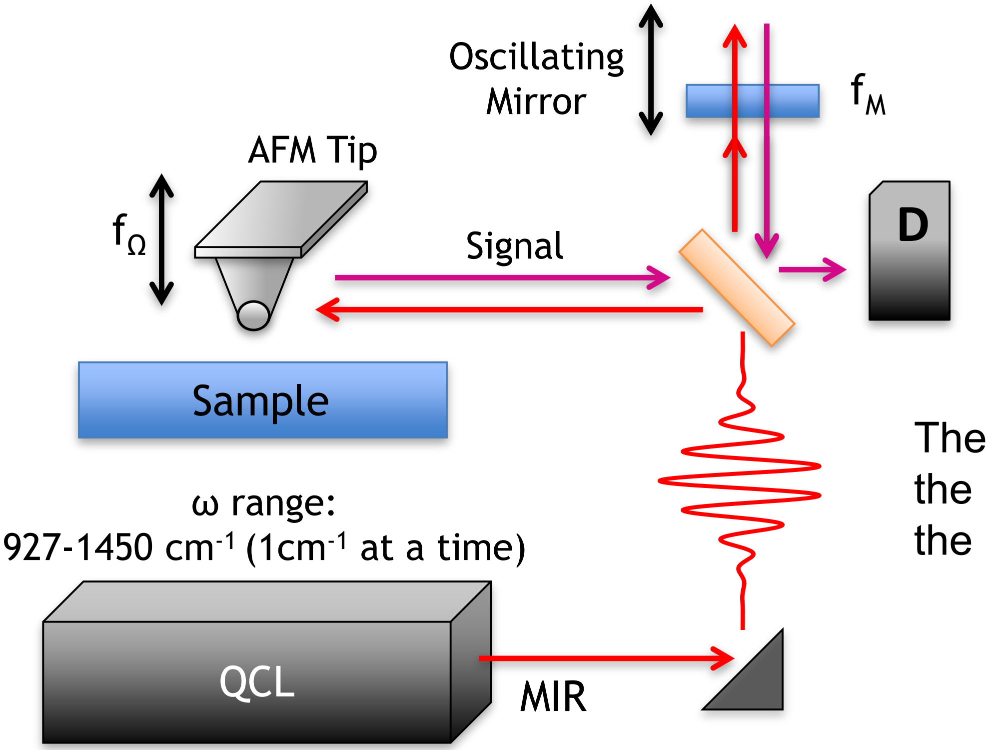
Keilmann, Hillebrand, Phil. Trans. Royal Society 362(1817):787–805 (2004)

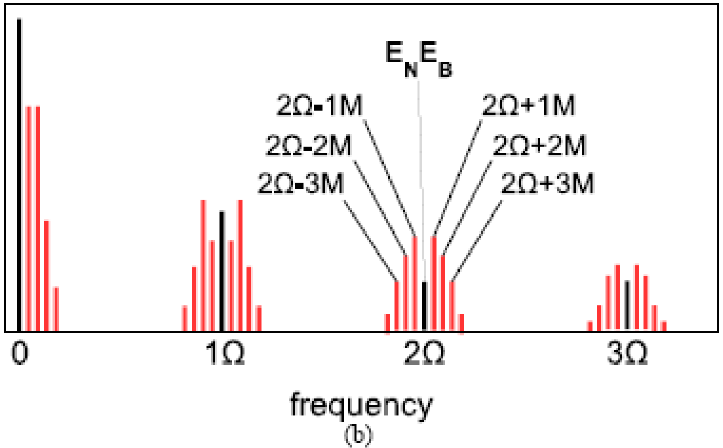
$$\alpha = 4\pi a^3 \frac{\boxed{\varepsilon_t} - 1}{\boxed{\varepsilon_t} + 2}. \qquad \beta = \frac{\boxed{\varepsilon_s} - 1}{\boxed{\varepsilon_s} + 1} \qquad \alpha_{\text{eff}} = \frac{\alpha(1+\beta)}{1 - \alpha\beta/(16\pi(a+\boxed{z})^3)}.$$

- 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

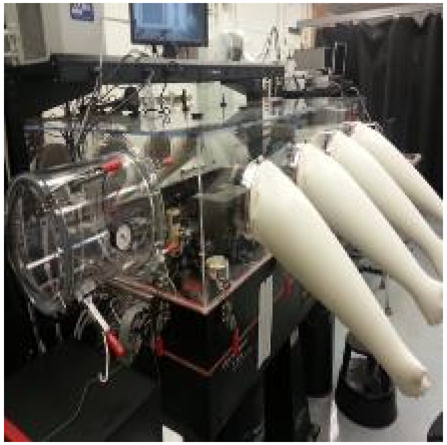
Experimental Setup





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 = 300Hz) and on the oscillating AFM tip (f_Ω = 300KHz).

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).