The Development of Structure Activity Relationships for Advance Cell Chemistries within the ABR Program

Robert Kostecki
Lawrence Berkeley National Laboratory
Berkeley, California 94720

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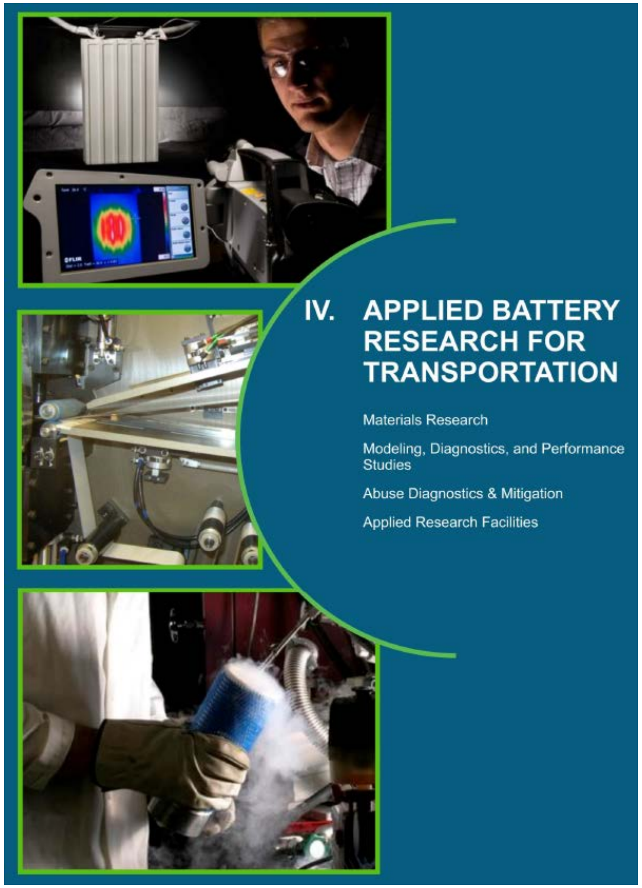
Project ID# ES176

Applied Battery Research for Transportation
Overview

The ABR program is focused on materials and cell couples for high energy batteries for use in PHEV40 light-duty vehicles. The key barriers are:

- High cost
- Insufficient energy density to meet the 40 mile all electric range
- Limited calendar and cycle life
- Insufficient tolerance to abusive conditions
- Operation between -30ºC and +52ºC



IV. APPLIED BATTERY RESEARCH FOR TRANSPORTATION

Materials Research

Modeling, Diagnostics, and Performance Studies

Abuse Diagnostics & Mitigation

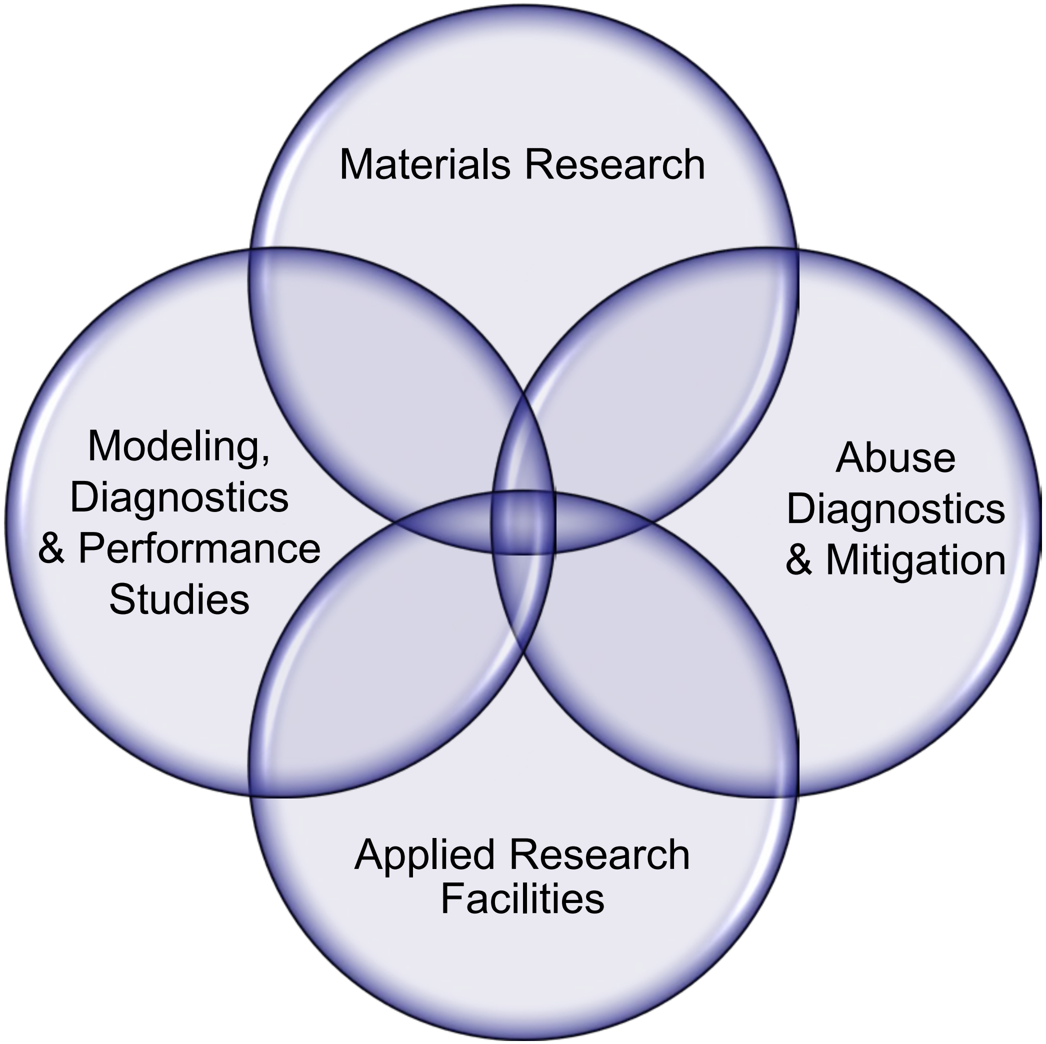
Applied Research Facilities

- ➢ *Develop higher energy materials, higher voltage electrolytes, combined into more optimal cell chemistries that are more stable and long-lived*
- ➢ *Understand and enhance the abuse tolerance of the individual materials, components, and cell chemistries*

Program Mission and Goals

Address scientific and engineering barriers to the commercialization of electrochemical energy storage systems for PHEVs

Problem-centric R&D philosophy with near-term technology development targets



Materials Research

Modeling, Diagnostics & Performance Studies

Abuse Diagnostics & Mitigation

Applied Research Facilities

Characterization of Energy Storage Systems

➢ Materials Characterization

- Unravel structure-property relationship from the sub-atomic to macro-composite system levels.
- Determine key material parameters and their implications for material stability and rate performance.
- Understand dynamic phenomena in electrode active materials and electrolytes

➢ Interfacial Phenomena

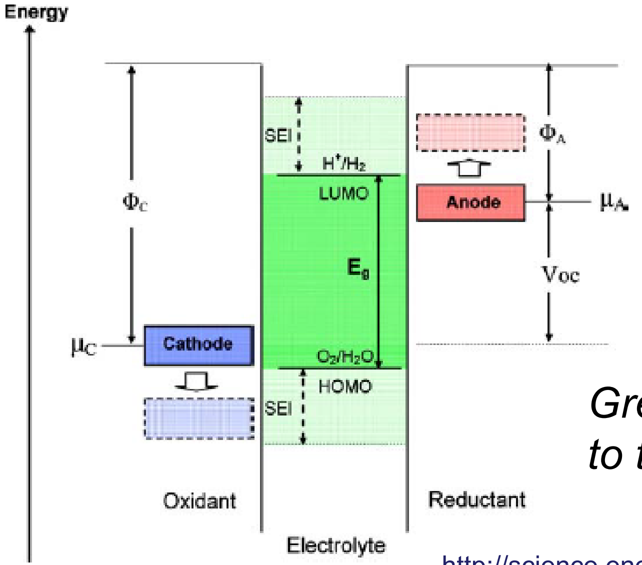
- Advance molecular-level surface electrochemistry to sense the identity or chemical functionality and spatial arrangement (orientation) of surface species at the surface with no interference from the electrolyte
- Probe and characterize charge transfer and mass transport processes
- Understand the thermodynamic, structural, mechanistic and dynamic aspects of interfacial reactions at atomic- and nano-scale

Surface sensitivity of electrochemical reactions has been known and studied for five decades!

“Preparation of Spherical Single Crystal Electrodes for Use in Electrocrystallization Studies”, D.K. Roe and H. Gerischer, *J. Electrochem. Soc.,* **110**, 350, 1963; followed by work by Anson, Bard, Bockris, Budevski, Clavilier, Convay, Faulkner, Fawcett, Heineman, Hubbard, Kolb, Lipkowski, Murray, Nagy, Ross, Scherson, Wieckowski, Will, Winograd, Yeager and many others.

“…there are many fundamental gaps in understanding the atomic- and molecular level processes that govern operation of EES devices…Fundamental research is critically needed to uncover the underlying principles”

http://www.sc.doe.gov/bes/reports/files/EES_rpt.pdf



Greater understanding of the interface contribution to the kinetic stability of the system is needed

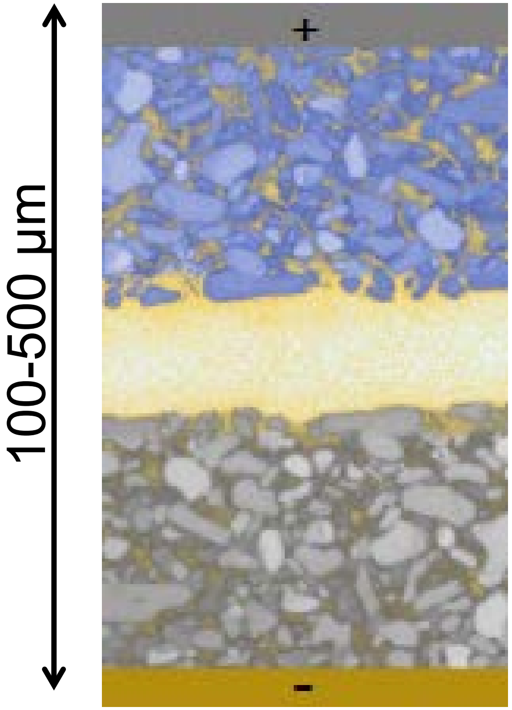
http://science.energy.gov/~/media/bes/pdf/reports/files/setf_rpt.pdf

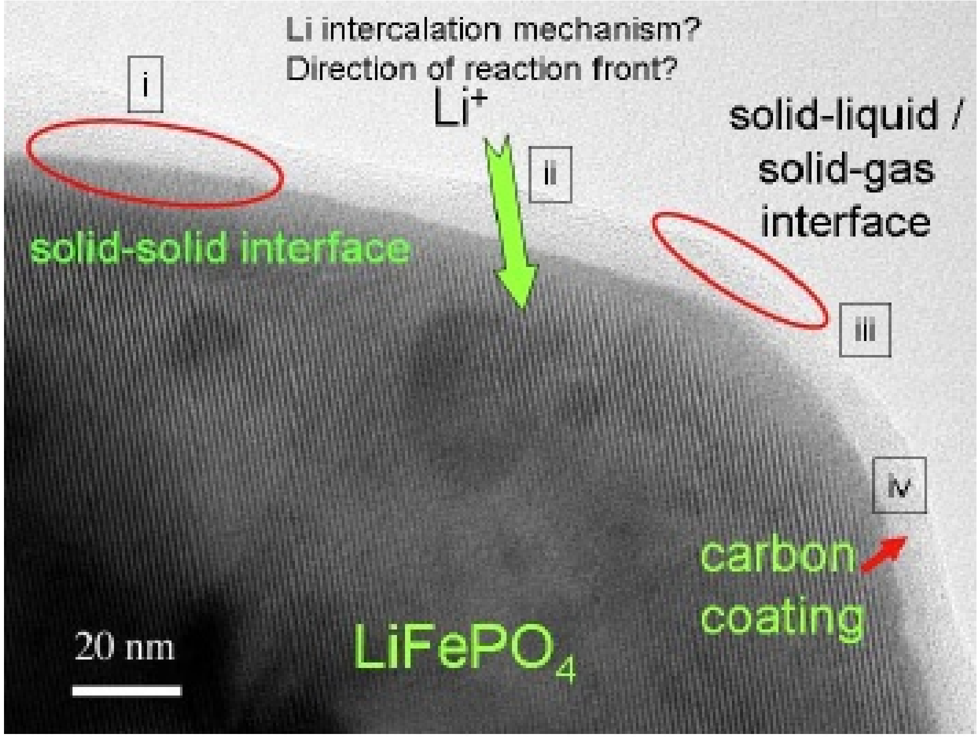
The key enabling factors for an effective strategy for characterization of battery systems includes:

1. The use of model electrodes with structurally well defined surfaces
2. Development and application of novel *in situ* structure- or molecule-specific methods
3. Implementation of new theoretical concepts in the modeling of solid-liquid interfaces

Morphology and Topology of Li-cell

H. Gabrish, UNO

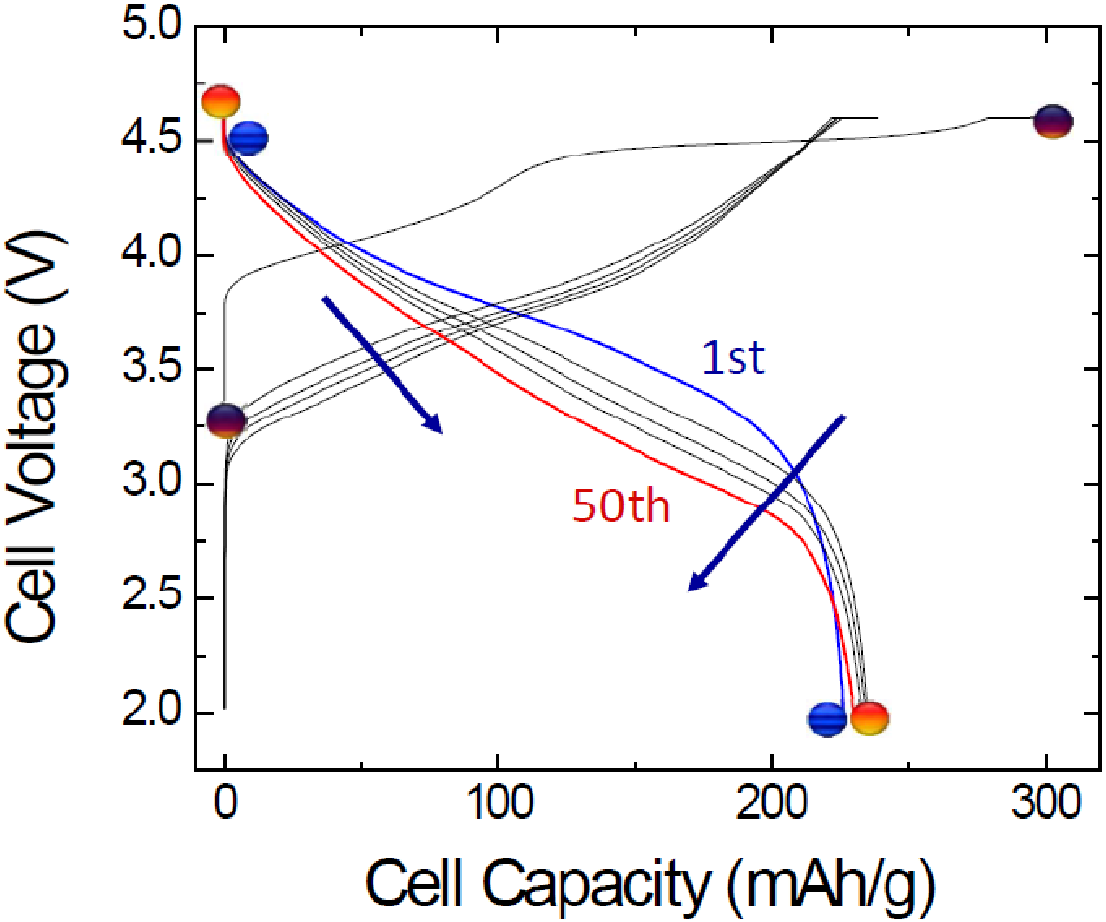




- A battery system involves interactions among various states of matter.
- A simple electrode design must be meticulously optimized for every active material chemistry, particle size, morphology and topology.

The influence of electrode surface structure on electrochemical reaction rates and mechanisms is a major challenge in battery research where electrodes with inherent structural heterogeneities are used ubiquitously

Voltage Fade in LMR-NMC

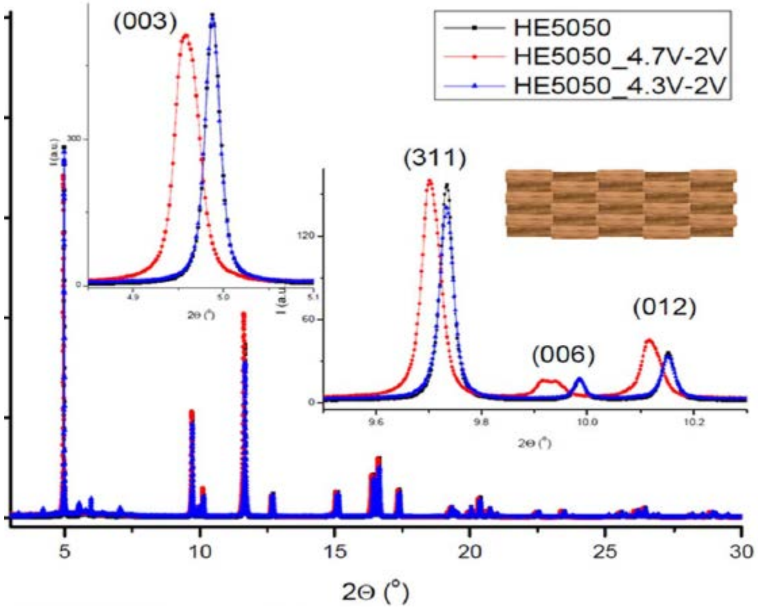


- ● Structure before and after activation?
- ● Structural difference after 1st cycle charge/discharge below and above 4.5 V?
- ● Structural difference before (1 cycle) and after (50 cycles?) voltage fade?

- Anthony Burrell, DOE-AMR 2012: ES161

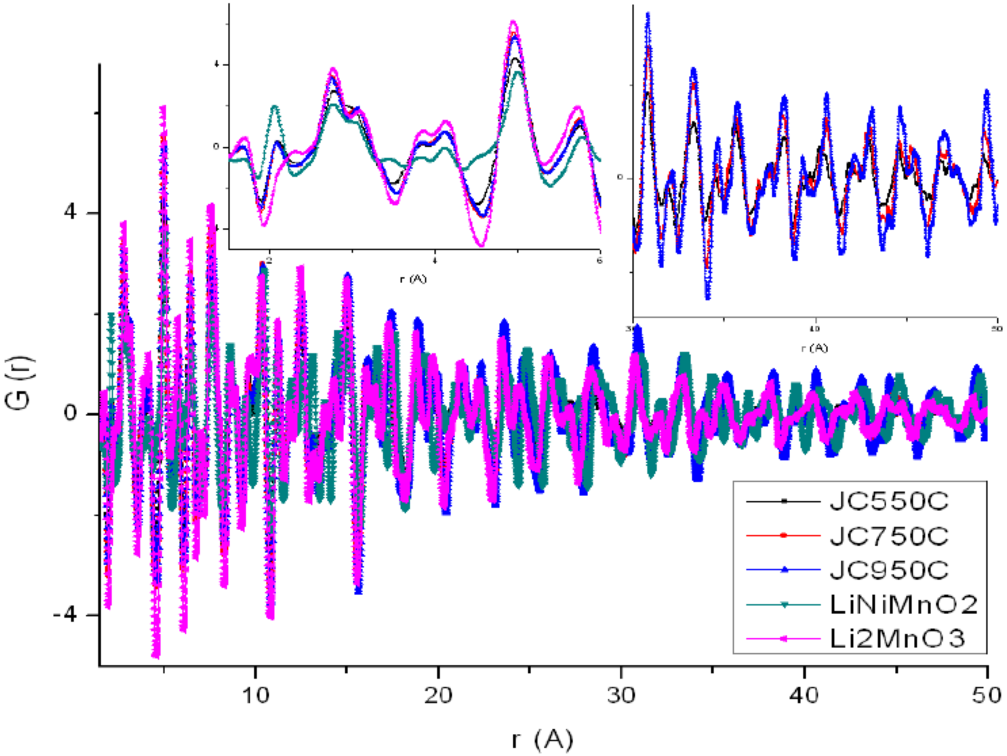
XRD and NPDF of LMR-NMC

M. Balasubramanian et al.



The activated electrode (4.7V-2V) becomes structurally heterogeneous or phase separate

Two similar interconnected layered structures with 0.26% misfit along c-axis and 0.16% within the layers



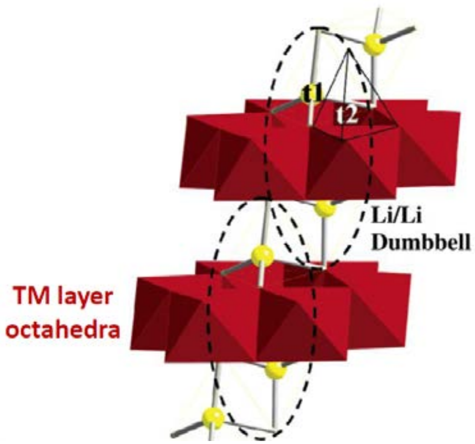
NPDF showed that both the *local structure* and *long-range structural coherence* plays an important role in the electrochemical performance

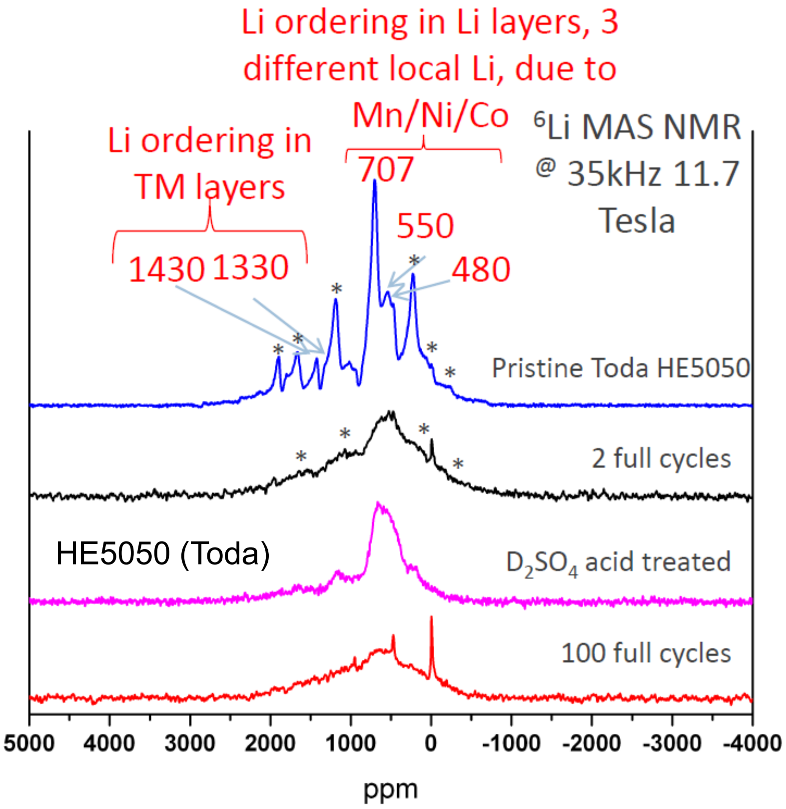
^{6}Li NMR Studies of LMR-NMC

Argonne NATIONAL LABORATORY

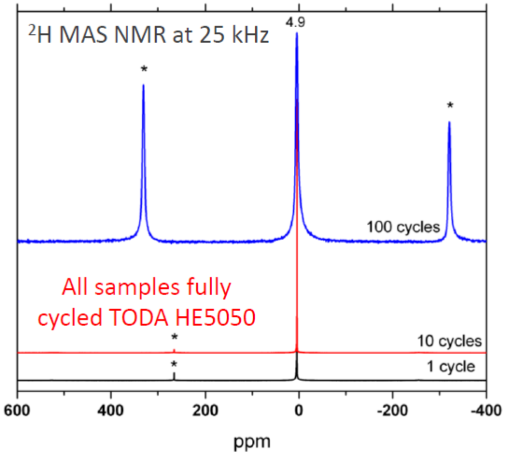
J. Vaughey et al.

Origin of the excess capacity ?
Li_{th} – dumbbell configuration





- No structural ^{2}H detected after cycling
- Significant accumulation of diamagnetic (surface) deuterium bearing species consistent with SEI build-up



- Loss of local ordering in Li and TM layers for Li and transition metals. TM migration
- Oxygen loss and formation of defect sites, stacking faults, lattice shearing
- Formation of a spinel-like structure

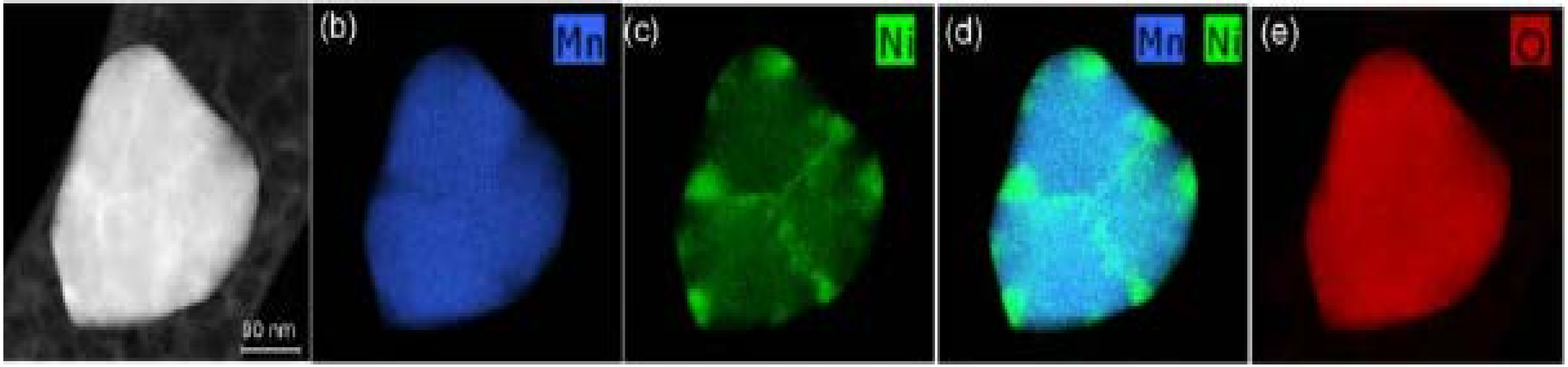
- These structural rearrangements are also reflected at the surface
- Changes in electrochemical activity toward the electrolyte may be expected

Surface Segregation of Ni in $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ Particles

Pacific Northwest
NATIONAL LABORATORY

Argonne
NATIONAL LABORATORY

J. Zhang, K. Amine et al.



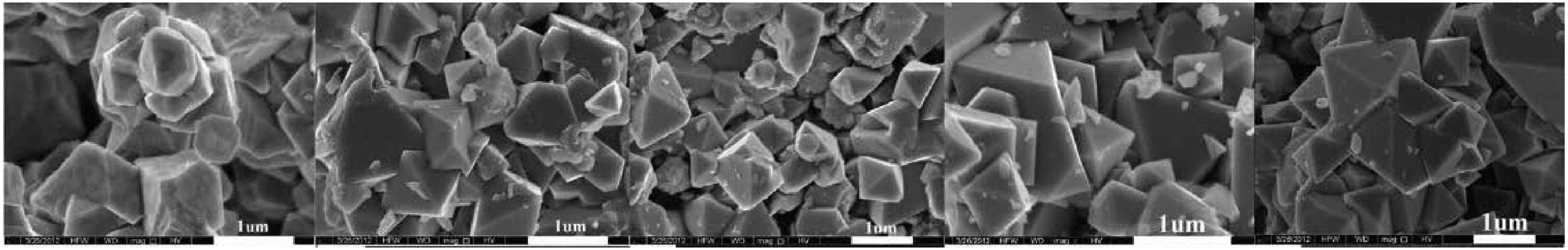
- Ni segregates at surfaces and boundaries
- Ni segregation may impact the Li diffusivity

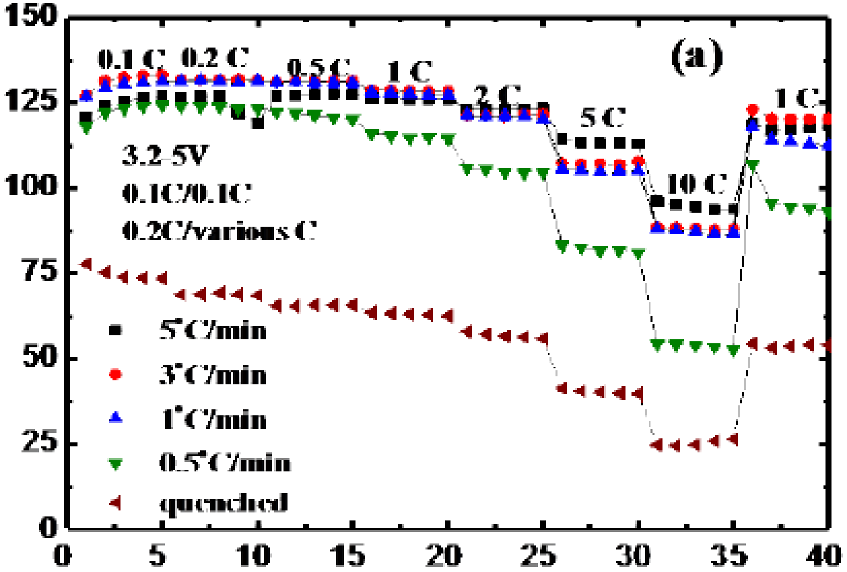
What is the effect of Ni-rich surface on the electrocatalytic activity of LMR-NMC electrode?

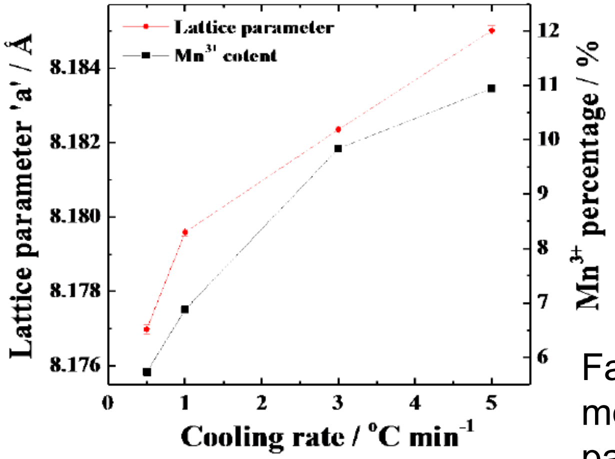
Morphology and Structure of $LiMn_{1.5}Ni_{0.5}O_4$ Spinel

The Effect on Interfacial Stability and Rate Performance

Pacific Northwest National Laboratory
Brookhaven National Laboratory
J. Zhang,
X-Q. Yang et al.


Quenched 5ºC/min 3ºC/min 1ºC/min 0.5ºC/min





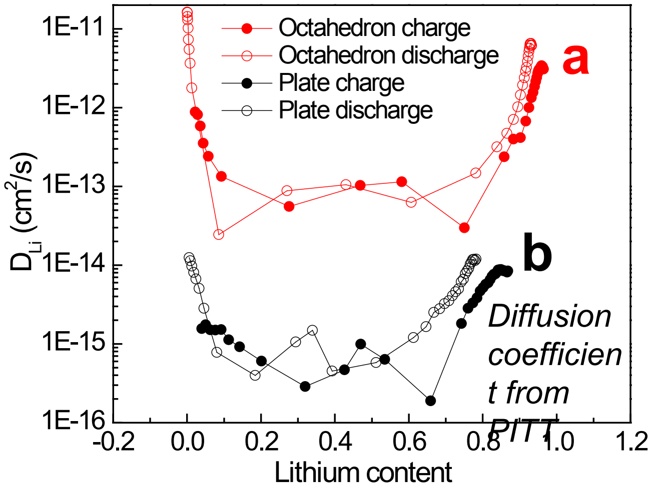
Faster cooling generates more Mn^{3+} lattice parameter increases

Presence of disordered phase improves rate capability and long-term cycling stability

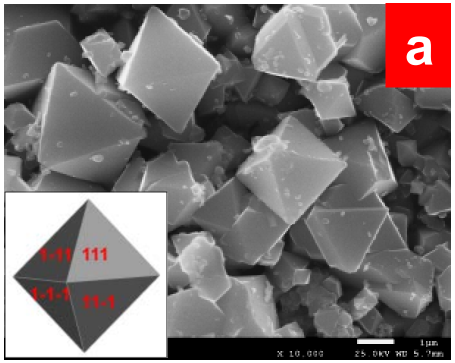
Does the particle morphology and surface crystalline orientation of $LiMn_{1.5}Ni_{0.5}O_4$ affect the electrochemical response?

Single Crystal Diagnostics $LiMn_{1.5}Ni_{0.5}O_4$ Spinel

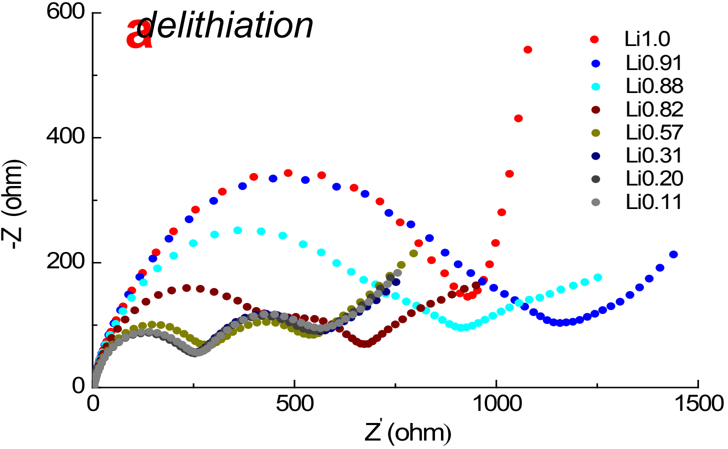
G. Chen
ES037

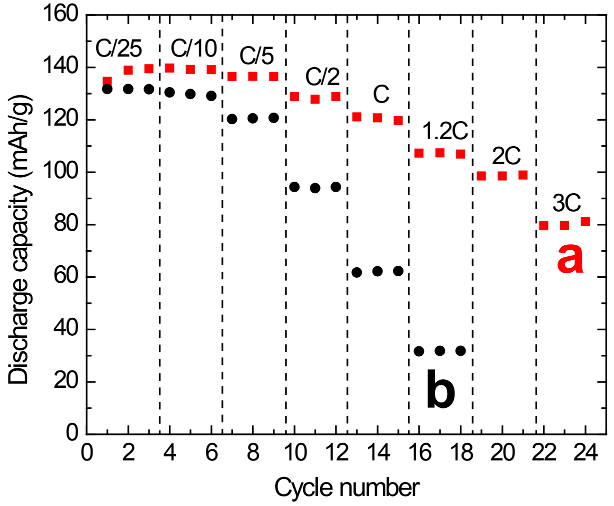


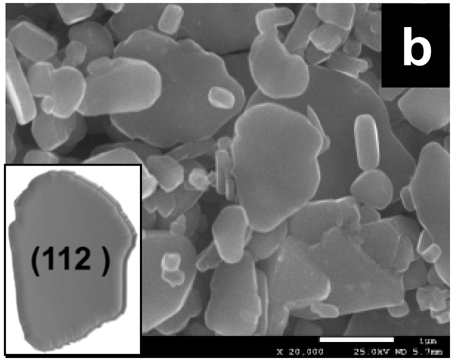
Diffusion coefficient from PITT

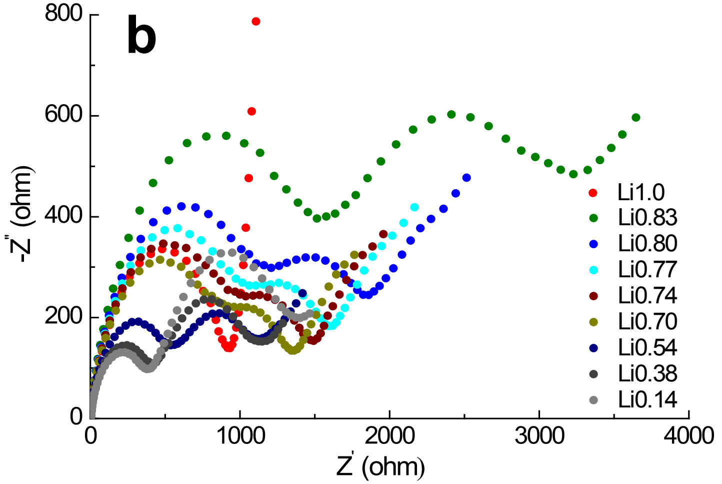


AC impedance from first delithiation





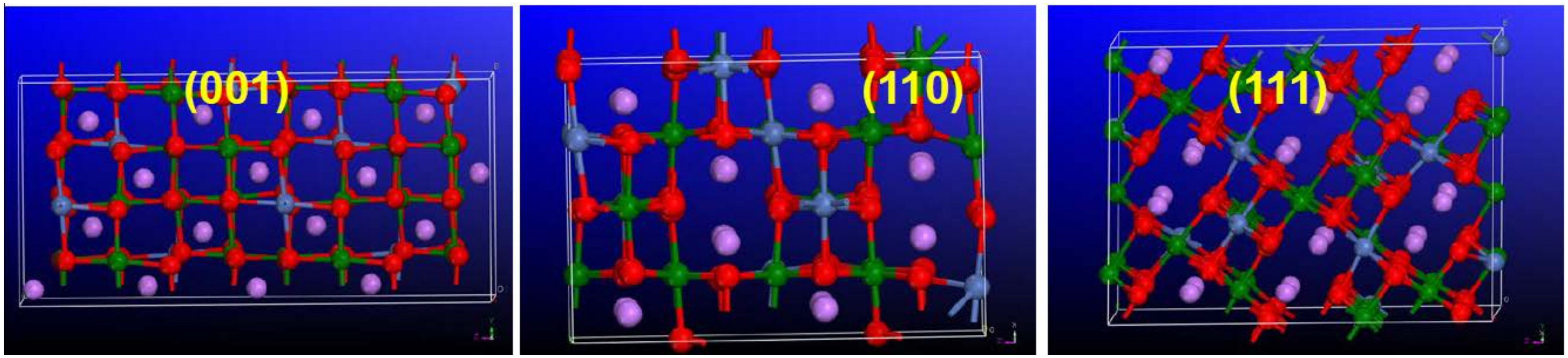




Particle morphology and surface crystalline orientation are critical for superior rate capability and interfacial stability – higher rate and lower reactivity on (111) surface facets

Ab-Initio DFT Calculations on Electrode Surfaces and Molecular Dynamics Simulations of Interfacial Phenomena

D. Bedrov, F. Liu
O. Borodin
ES058



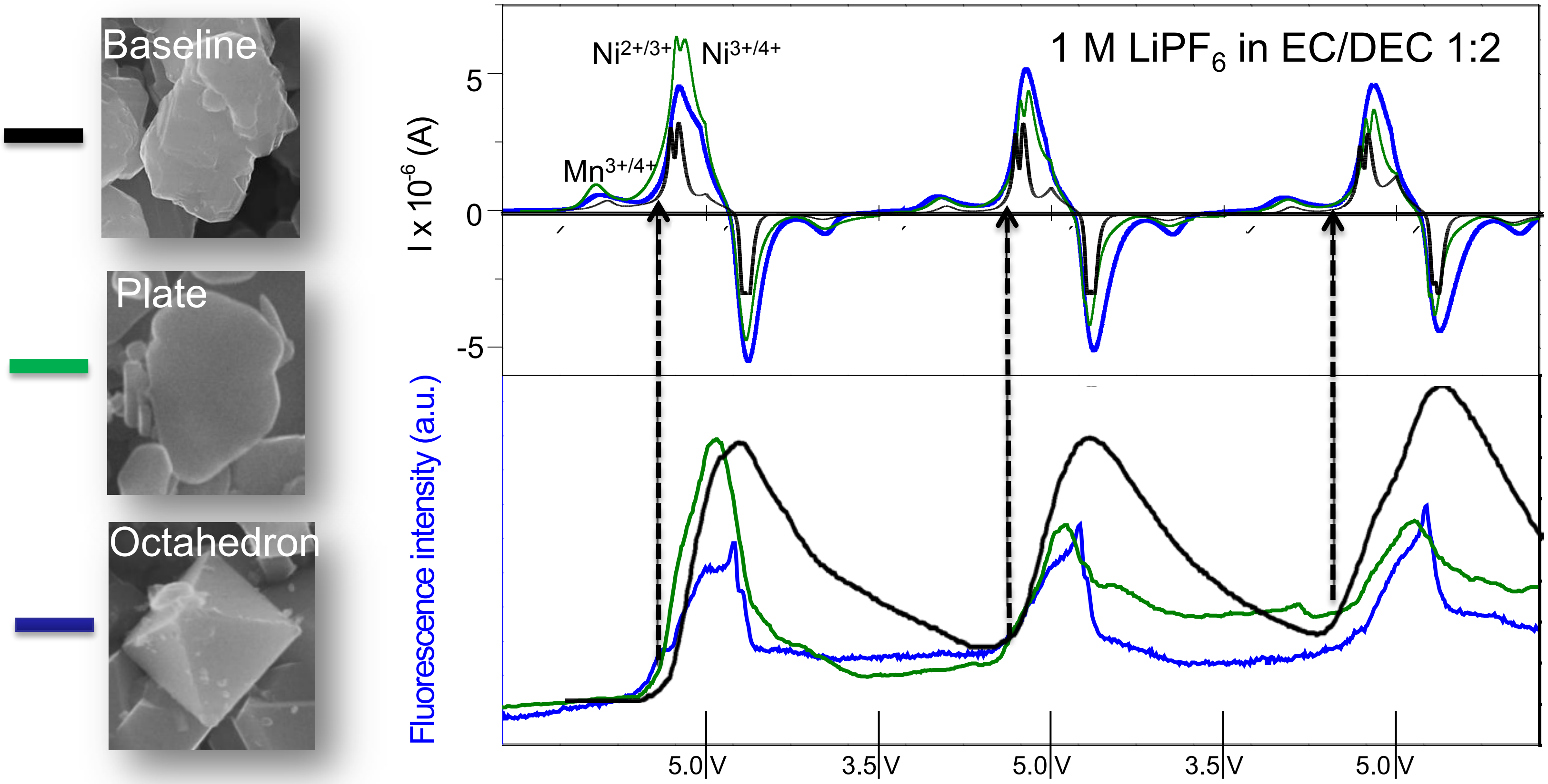
Surface Energies (Stoichiometric,meV/Å²)

	$LiNi_{0.5}Mn_{1.5}O_4$							
Surface Configurations	(001)		(110)		(111)			
	1	2	1	2	1	2	3	4
	64.89	114.73	94.10	90.74	188.42	86.48	129.31*	109.31*

(001) surface is more stable than (111) and (110) surfaces, which is in contradiction with experimental observations!

Single Crystal Diagnostics $LiMn_{1.5}Ni_{0.5}O_4$ Spinel

R. Kostecki
ES033



- The rate of electrolyte decomposition varies strongly with the crystalline orientation of LMNO surface and the electrode potential
- Electrolyte oxidation products on LMNO platelets tend to passivate the active material better than octahedrons during the initial charge/discharge cycles

Electrolyte decomposition at high potentials occurs at Ni^{n+} sites

LiPON Coated LMR-NMC

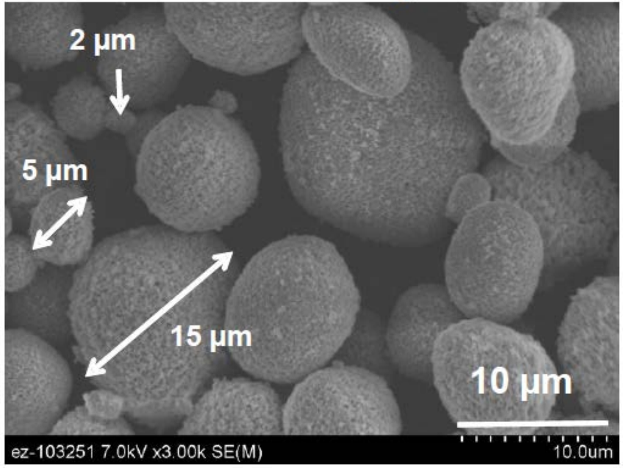
The Effect on Interfacial Stability and Rate Performance

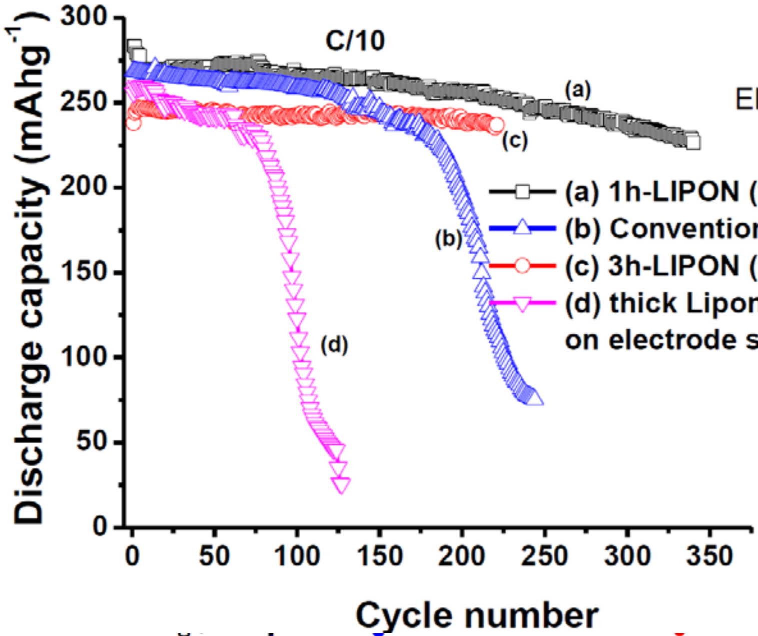
Oak Ridge National Laboratory

J. Nanda et al.

$Li_{1.2}Mn_{0.525}Ni_{0.175}Co_{0.1}O_2$

$0.6Li(Li_{1/3}Mn_{2/3})O_3$-$0.4Li[Mn_{0.3}Ni_{0.45}Co_{0.25}])O_2$

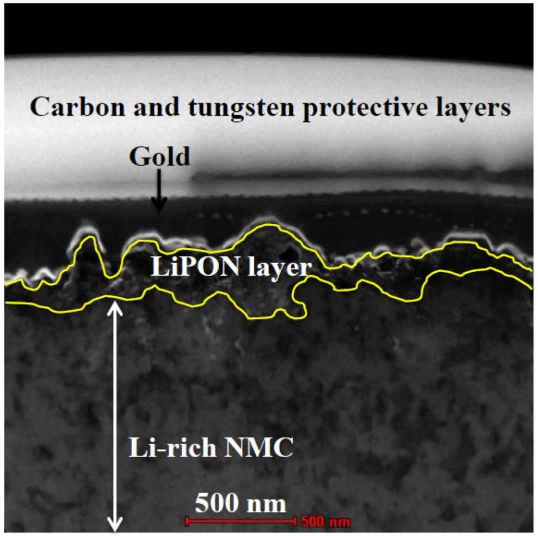


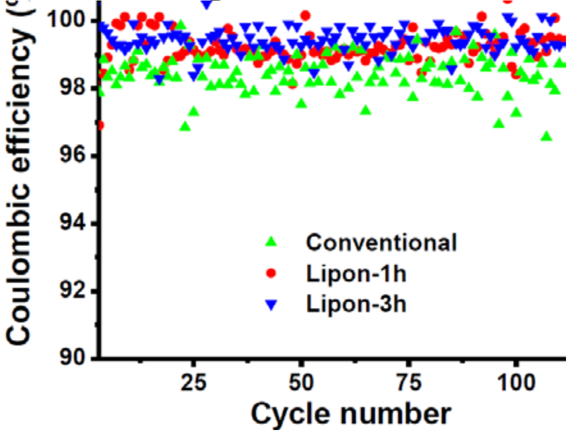


Cycling window

4.9 – 2.5 V

Electrolyte : 1.2 M $LiPF_6$ in EC: DMC (1: 2 w/w)



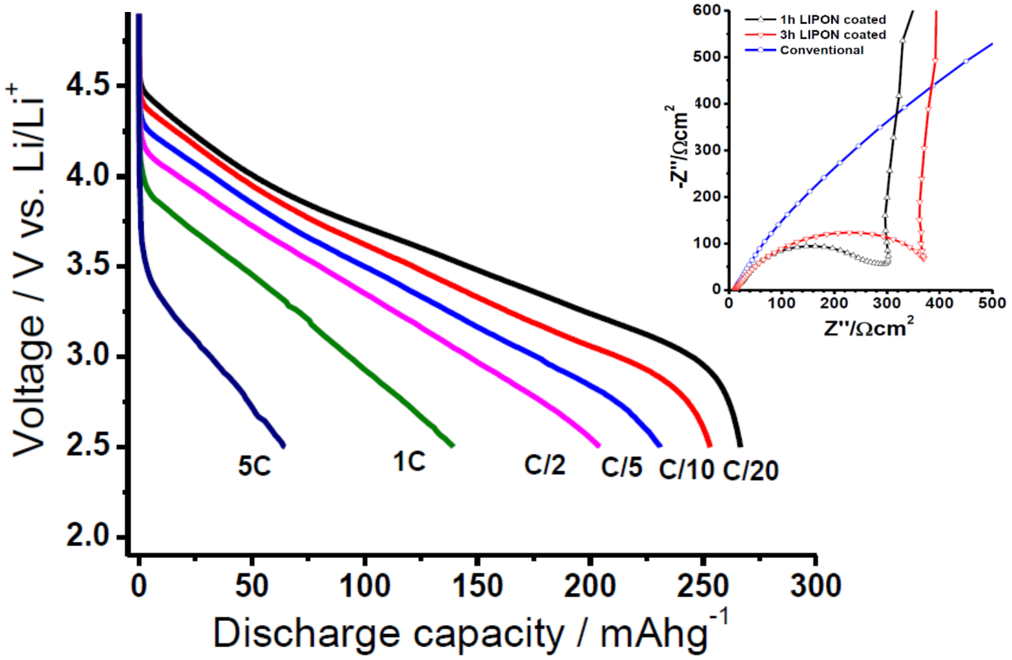


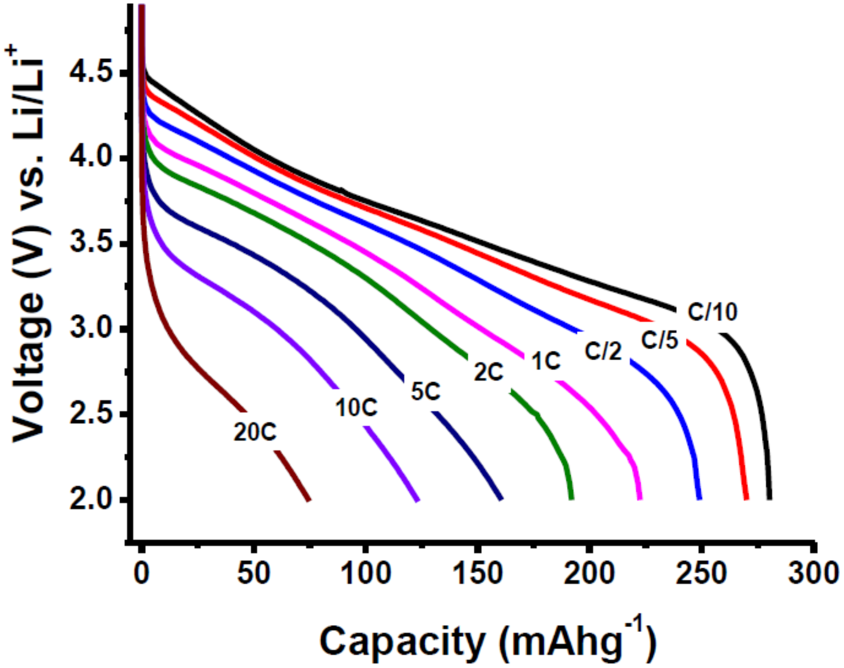
Electrochemical tests show that LiPON layer can improve the interfacial stability of LMR-NMC

LiPON Coated LMR-NMC

The Effect on Interfacial Stability and Rate Performance

J. Nanda et al.





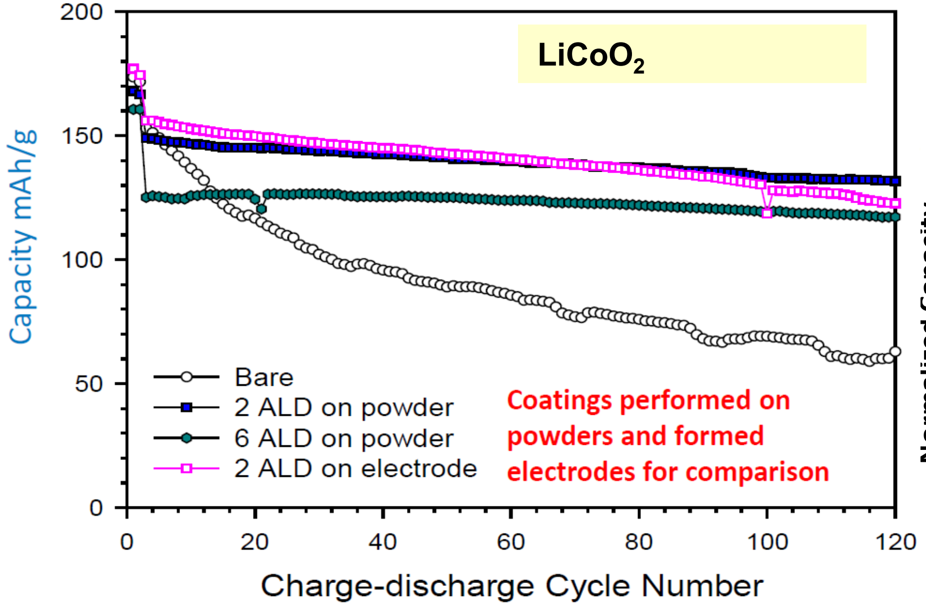
Significant improvement in C-rate performance

- Less electrolyte degradation in presence of LiPON?
- Less surface film formation upon high V cycling?
- Better charge transfer kinetics at interface?

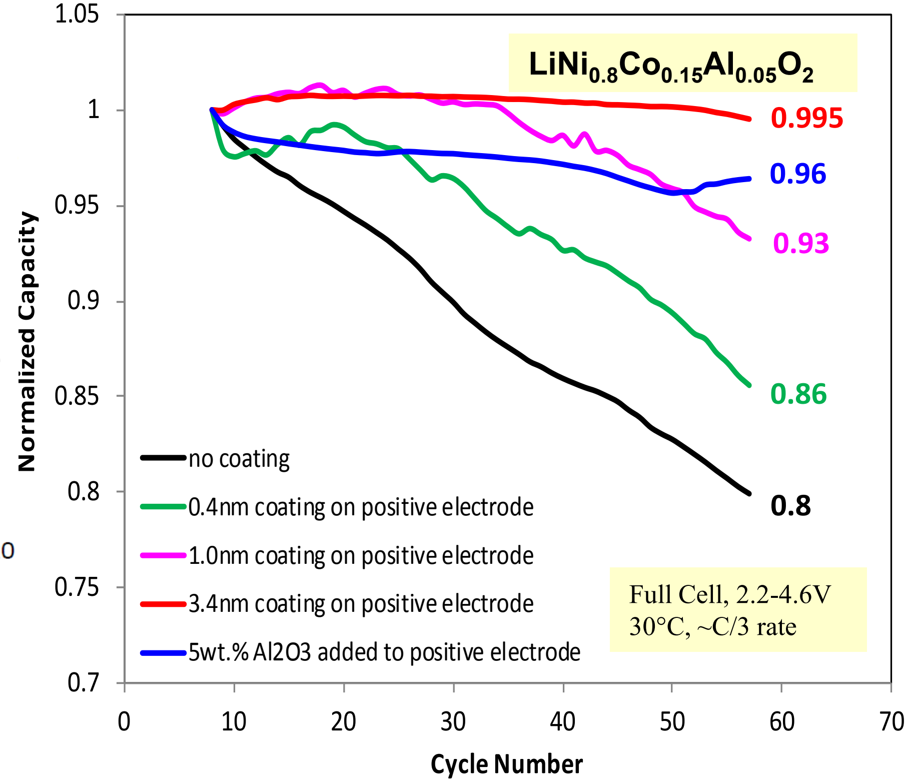
LiPON coating does not prevent voltage fade

Effect of Alumina-Coating and/or Addition in $LiMeO_2$ Positive Electrodes

Argonne NATIONAL LABORATORY
NREL NATIONAL RENEWABLE ENERGY LABORATORY
D. Abraham
R.C.Tenent



Coatings performed on powders and formed electrodes for comparison

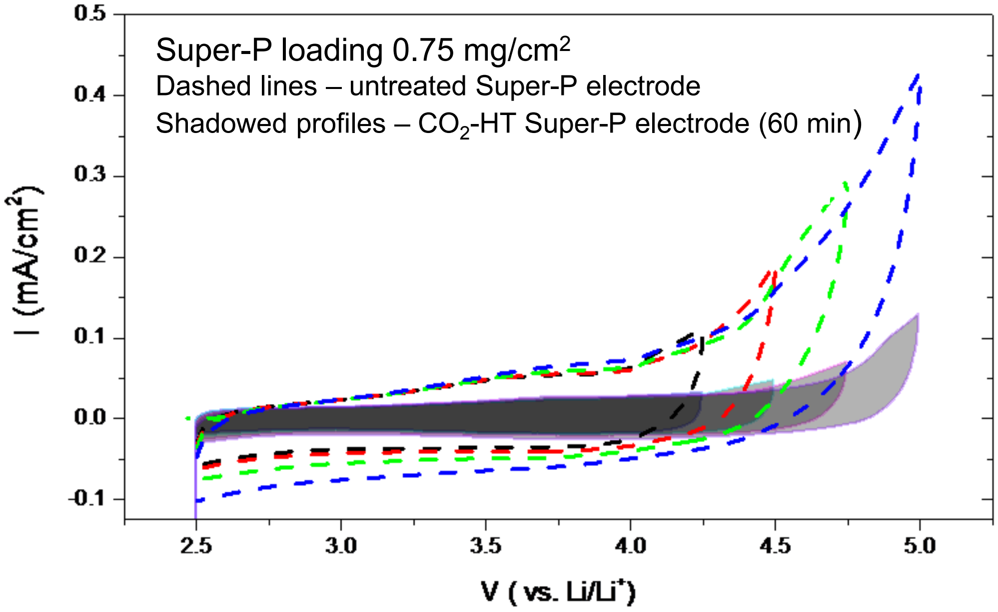


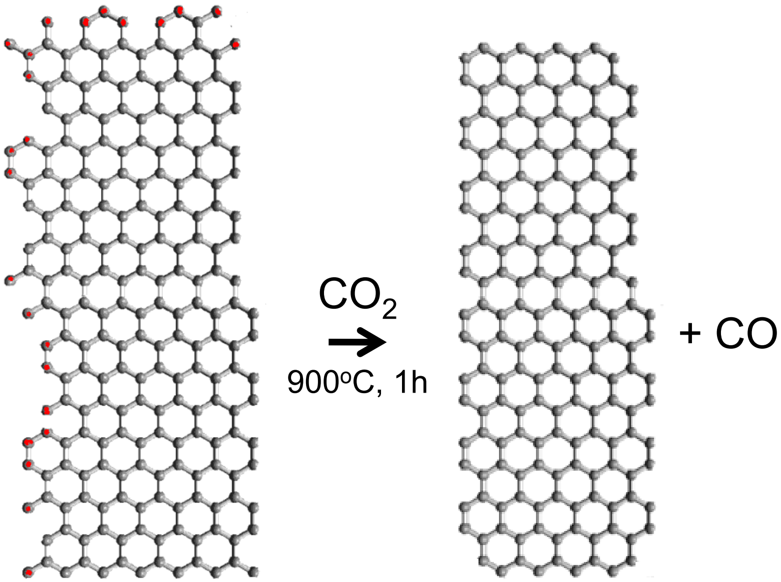
Full Cell, 2.2-4.6V
30°C, ~C/3 rate

Alumina reduces dissolution of Mn, Ni, and Co from the positive electrode by acting as an HF-getter. Incorporation of Al-bearing species may further help stabilize the SEI

Electrochemical Activity of CB Additives

Berkeley Lab
R. Kostecki

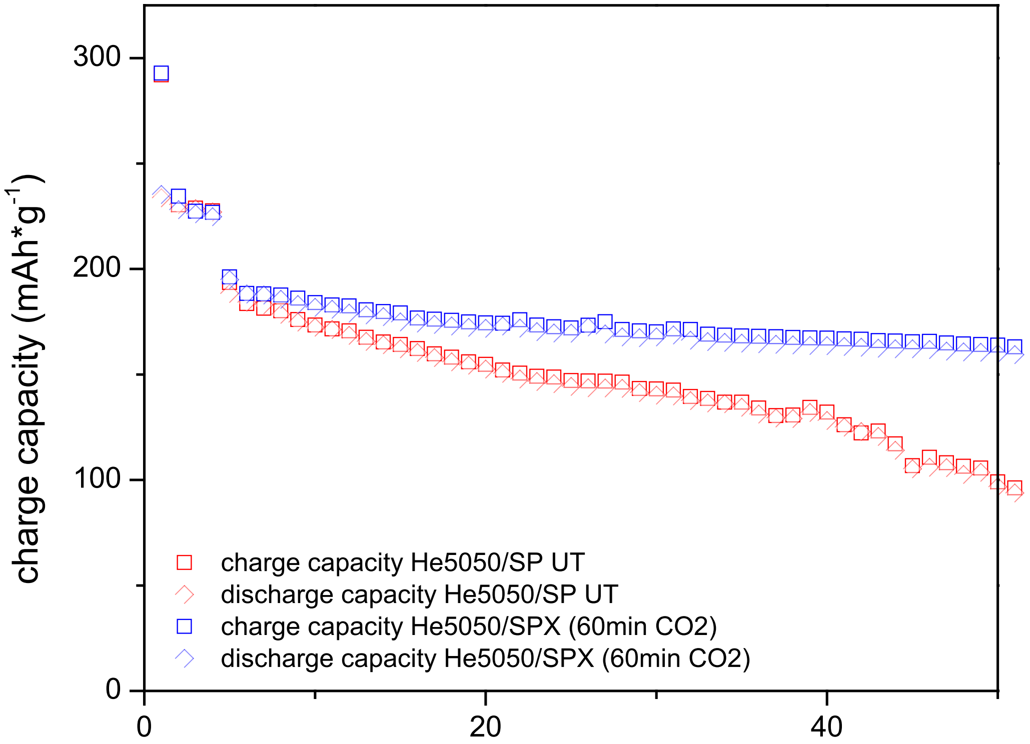




- Electrolyte oxidation on carbon black additives contributes to coulombic inefficiency of limits the use of high-voltage cathode materials
- Heat-treatment leads to synproportionation reaction of carbon edge atoms and CO_2 whereas bulk structure remains unaffected
- Higher onset potential for electrolyte decomposition for the CO_2 surface-treated carbon black electrode
- Lower electrolyte reduction current at comparable mass loading and similar surface area

Modified Carbon Black Additives for Improved High-Energy Cathodes

R. Kostecki, V. Battaglia
B. Polzin



Electrode composition

- 88% $Li_{1.2}Ni_{0.15}Co_{0.10}Mn_{0.55}O_2$ (Toda He 5050)
- 8% PVdF (KF-1100, Kureha Co. Ltd)
- 4% Super-P Li pristine/CO_2-treated

Mass loading

9.35 mg/cm^2 for treated
8.32 mg/cm^2 for pristine
7.44 mg/cm^2 for ABR baseline (SAFT)

Cycling

4xC/12 and 50xC/3 (210 mAh/g)

Composite cathodes with modified carbon black additive display superior cycling performance and better capacity retention than baseline electrodes

Patent application submitted; received LBNL Tech Transfer grant to commercialize the technology – work is ongoing

Summary

- Inorganic and organic electrolyte decomposition products form at the cathode and dissolve in the electrolyte
- Electrolyte decomposition at high potentials occurs at Ni^{n+} sites
- Insoluble electrolyte decomposition products form electronic and ionic barriers in composite cathodes and contribute to the impedance rise in Li-ion cells
- Adequate particle morphology is critical in achieving optimal rate capability and stability of the high-voltage Li-ion materials
- Electrolyte additives, surface coatings could be effective strategies to reduce surface reactivity of high-voltage cathodes

“With this underpinning knowledge, wholly new concepts in materials design can be developed for producing materials that are capable of storing higher energy densities and have long cycle lifetimes”

Future Work

- Develop and apply innovative *in situ* and *ex situ* diffraction, spectroscopic and imaging methodologies to study basic function and mechanism of interfacial processes on model well-defined Li-ion battery materials as well as composite cathodes
- Encourage and initiate relevant efforts in theory development and modeling of electrochemical interfaces in Li-ion systems
- Establish direct correlations between electrochemical performance, interfacial phenomena, surface chemistry, morphology, topology and degradation mechanisms
- Unveil the structure and reactivity at hidden or buried interfaces and interphases that determine battery performance and failure modes
- Understand the underlying principles that govern these phenomena and develop effective remedies to enable high energy density materials in Li-ion cells for PHEVs and EVs.
- Cooperate with JCESR Hub, BATT Program and relevant Energy Frontiers Research Centers to investigate the effect of material structure, morphology on formation of stable surface/SEI layers

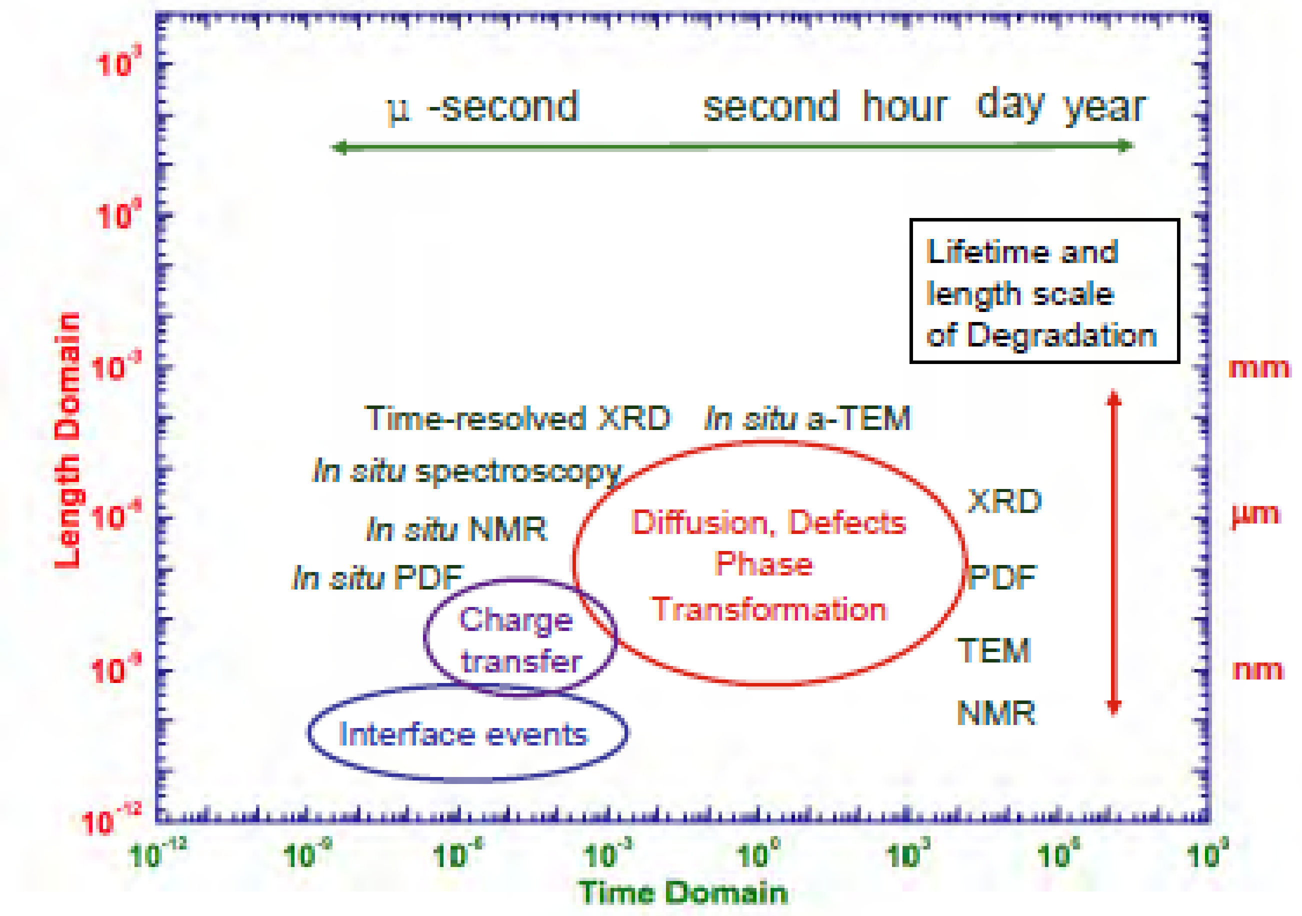
Technical backup slides

EES Analytical Tools – Basic Parameters

Sensitivity, Selectivity, Specificity

Spatial, Temporal and Energy Resolution

In situ probing/monitoring



Report of the Basic Energy Sciences Workshop for Electrical Energy Storage
http://www.sc.doe.gov/bes/reports/files/EES_rpt.pdf