



# High Energy Lithium Batteries for PHEV Applications

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# Program Overview

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## Time line

Start Date: Oct. 2013

End Date: Sept. 2015

Status: 75% Completed

## Budget

Total Project Funding:

\$ 3,785,088

Cost Share:

\$ 757,018

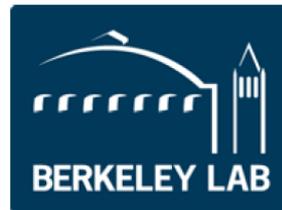
Funding Received:

\$ 2,264,921

## Barriers

- Meeting PHEV power specifications
- Loss of power with cycling
- Cycle and calendar life

## Partners



## Project Lead



# Project Objectives - Relevance

## Goals

Develop a high capacity cathode, and Si-C based anode and integrate them and build high capacity (0.25-40Ah) pouch cells that exceed the ABR minimum target goals for PHEVs

## Relevance

- Identifying the root cause and solving the DC-Resistance rise at low SOC's, enabling the use of the high-energy offered by HCMR™ Li-rich cathode materials

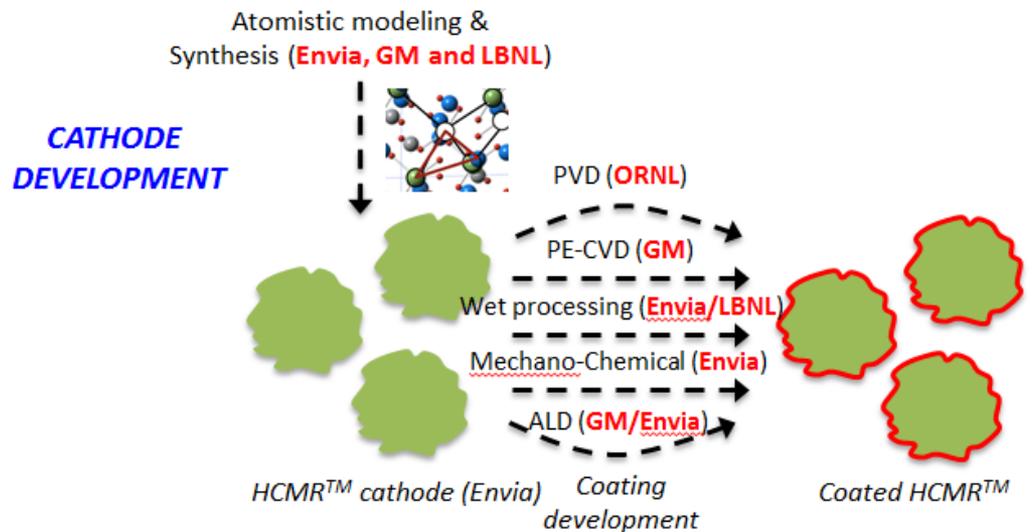
## Project Tasks

- Material development
- Nanocoating engineering
- Atomistic and cell-level modeling
- Material scale-up
- Large cell development
- Large cell testing

## Cell Targets

Characteristics	Unit	PHEV40
Specific Discharge Pulse Power	W/kg	800
Discharge Pulse Power Density	W/L	1600
Specific Regen Pulse Power	W/kg	430
Regen Pulse Power Density	W/L	860
Recharge Rate	NA	C/3
Specific Energy	Wh/kg	200
Energy Density	Wh/L	400
Calendar Life	Years	10+
Cycle Life (at 30° C with C/3 Charge and 1C Discharge rates)	Cycles	5000
Operating Temperature Range	°C	-30 to +52

# Project Development Roadmap

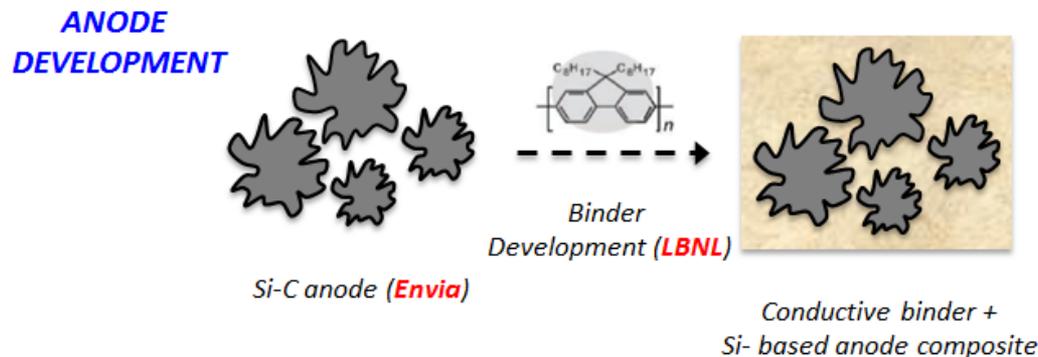


**GOAL:** Develop a **high capacity cathode** and a **Si-C based anode** in order to build high capacity (0.25-40Ah) pouch cells that **exceed the ABR target** goals for PHEV applications.

## CELL INTEGRATION (Envia) & TESTING (All)



High capacity cells to meet PHEV ABR cell targets

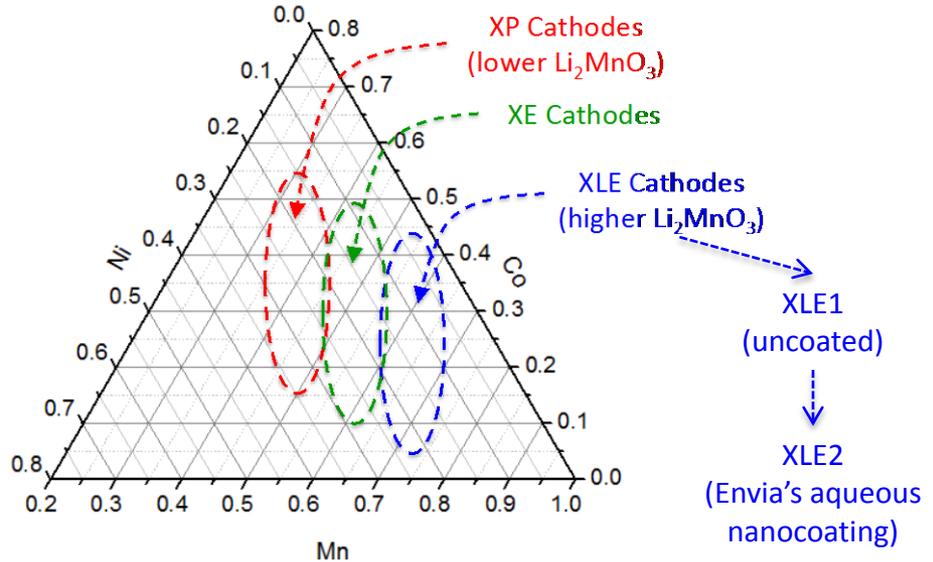
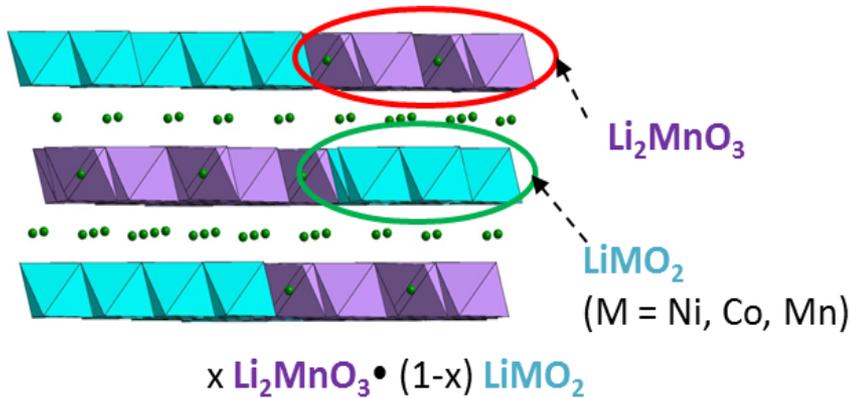


# Project Tasks & Timeline

Task	Sub Tasks	Timeline								
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	
Cathode Development	Composition Engineering	◆(XLE)				◆(XE)				
	Surface coating									
	1. LiPON		→							
	2. ALD			→						
	3. Polymer			→						
	4. Carbon	→					→			
	Atomistic Modeling		→							
	Diagnostic studies		→							
Anode Development	Composition Engineering									
	Binder Development			→						
Cell Development	1. Cell Sizing Studies				→					
	2. 1~50 Ah Cell Builds (Internal)						→			
	4. 1~50 Ah Final Cell Build								→	

# HCMR™ Cathode Introduction

HCMR™ Cathode Phase Diagram



HCMR™ Type	C/10 Capacity Range	Status
	mAh/g (4.6-2.0V)	
XP	200 ~ 220	Commercialization
XE	225 ~ 240	R&D
XLE	240 ~ 280	R&D

HCMR™: High Capacity Manganese Rich

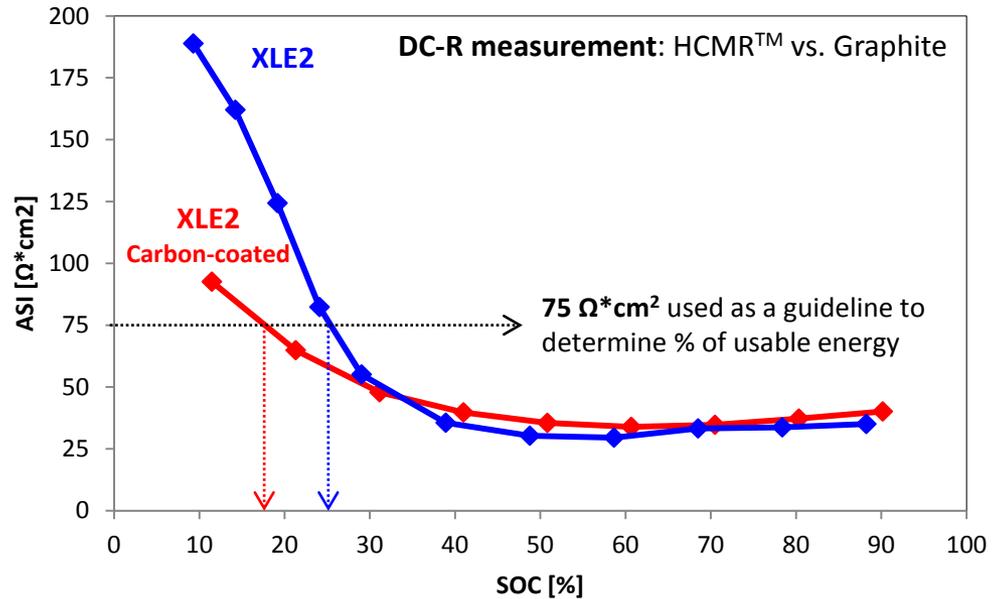
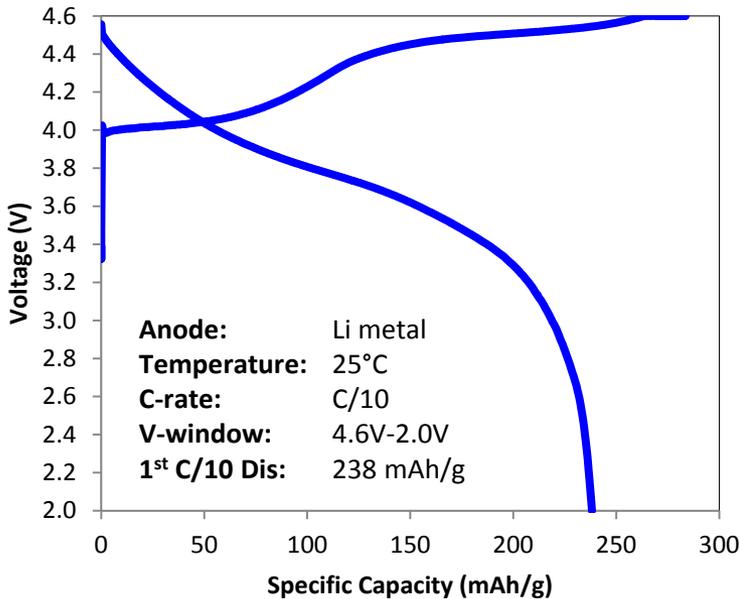
**Key benefits:**

- High Capacity
- Low Cost
- High safety

**Key issues:**

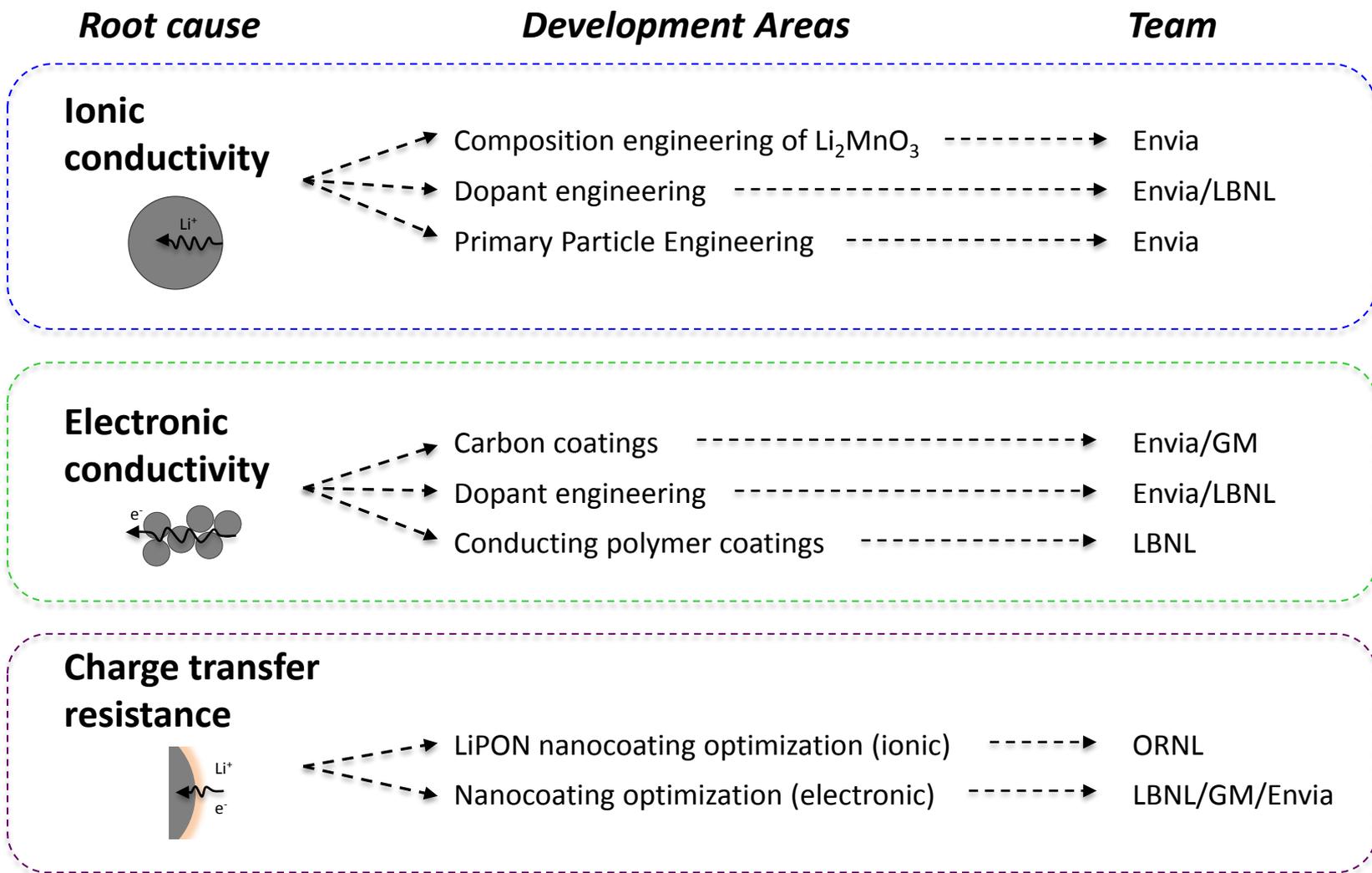
- High DC-Resistance
- Voltage fade upon cycling
- Poor durability

# XLE2 Electrochemical Properties



- DC-R measurement shows that only 75% of the 238 mAh/g initial capacity is usable at the BoL
- Conductive carbon coating increases usable energy, but does not stop DC-R growth with cycling
- Studies to further mitigate DC-R issues take two parallel approaches:
  - Surface coatings: apply electronic, ionic, and surface conductive coatings
  - Diagnostic: identify root-cause for DC-R and DC-R growth

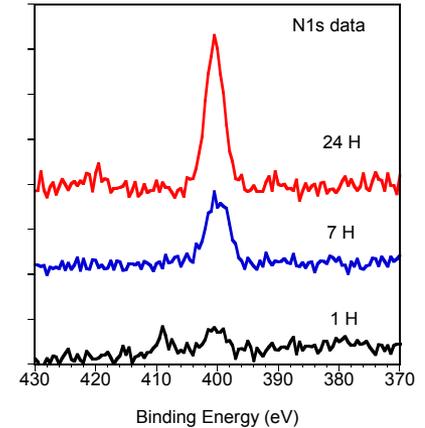
# DC-R Models and Approaches for Improvement



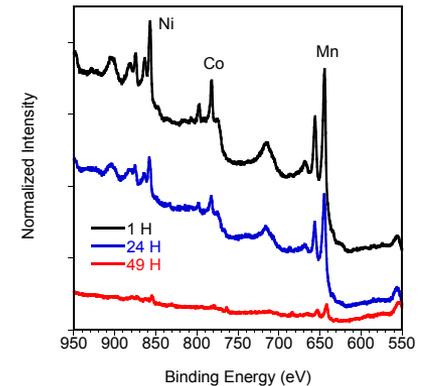
# LiPON-Coated XLE2: Introduction

**Approach: Coating nanometer-thick layer of solid electrolyte, lithium phosphorus oxynitride (LiPON) on HCMR™ cathode powders**

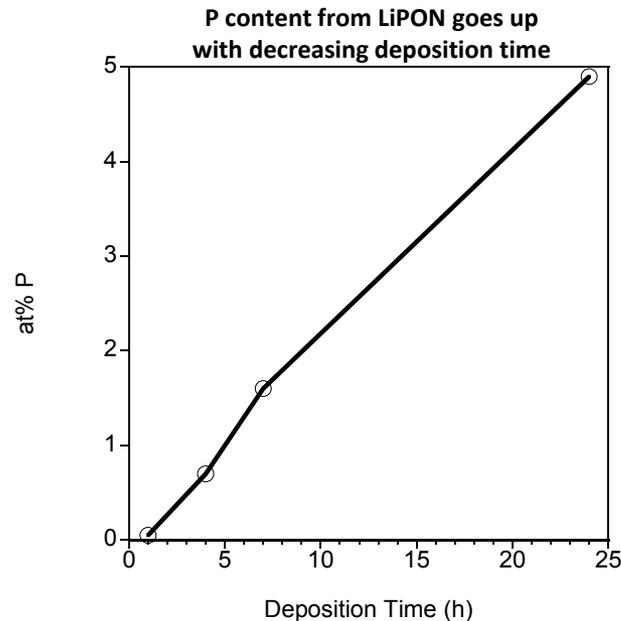
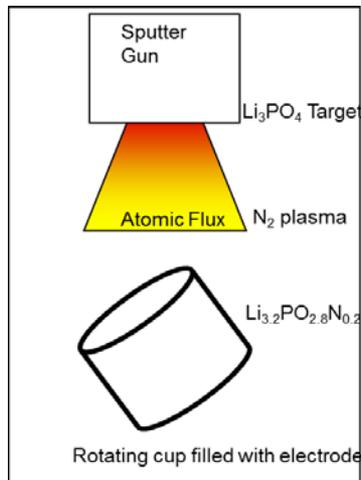
- LiPON was deposited using RF sputtering
- Non-conformal (unlike ALD) but capable to be scaled-up to kilogram level
- Deposition time between 1-3 hours results in good control of coating thicknesses from 0.5 nm to 15 nm
- ICP, XPS techniques used to estimate average LiPON coating thickness



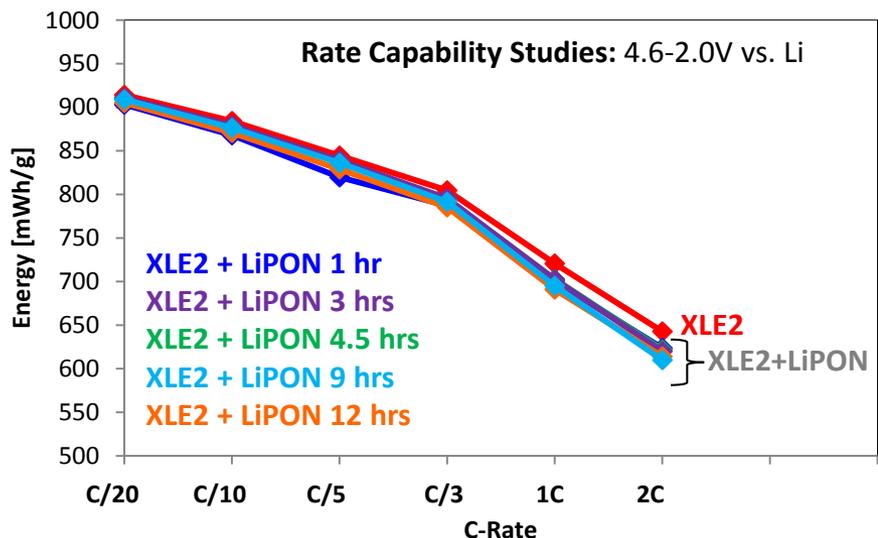
N 1s XPS signal increases with higher deposition time which correlates to higher coating thickness



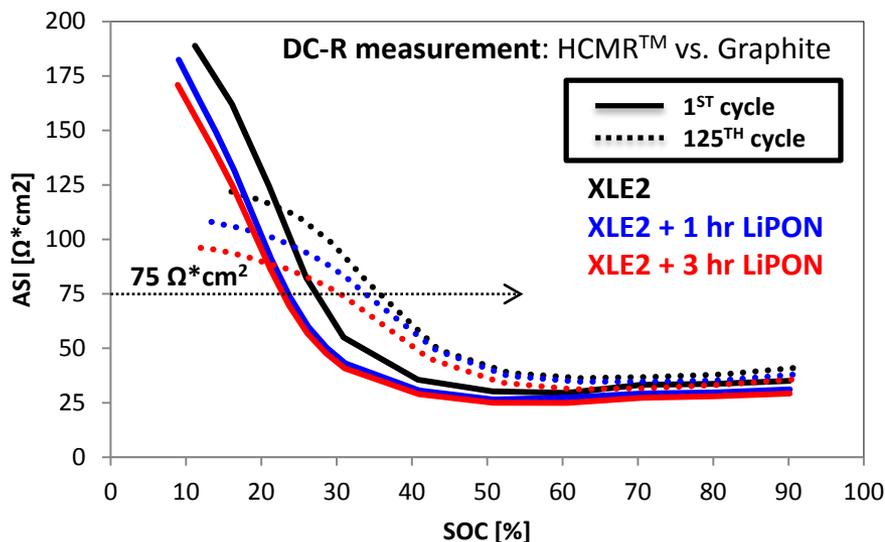
Transition metal core-level signal (Mn,Ni,Co) is attenuated with increasing Lipon thickness



# LiPON-Coated XLE2: Electrochemical Properties



- No change in capacity at C/3; very minimal drop in 1C & 2C capacities
- Thicker coatings show slightly lower average voltage than the XLE2-baseline at 1C & 2C
- Down selected 1h and 3h LiPON-coated XLE2 materials for DC-R studies



- XLE2-baseline and LiPON-coated samples show energy retentions of 86-89% after 125 cycles
- DC-R studies show a loss of 8-10% usable energy after 125 cycles for both XLE2-baseline and LiPON-coated materials

LiPON coating shows NO improvement in DC-R or DC-R growth when compared to the XLE2-baseline

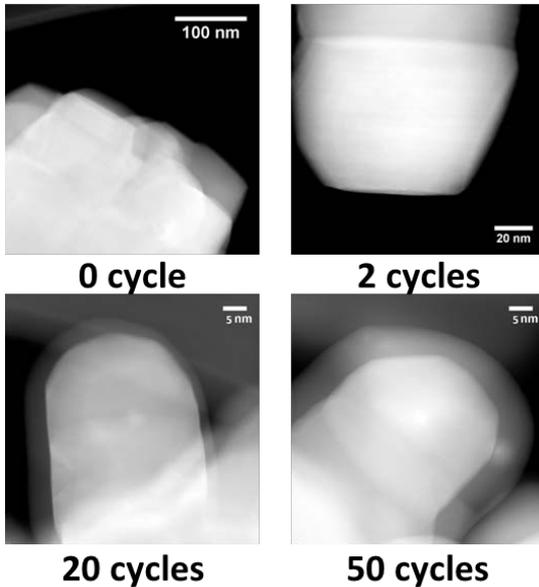
# ALD-Coated XLE2: Introduction

## Approach: Explore different ALD nanocoatings

-  $\text{Al}_2\text{O}_3$ ,  $\text{AlF}_3$ ,  $\text{AlN}$ ,  $\text{ZnO}$ ,  $\text{TiN}$ .

- Optimize ALD conditions for uniform nanocoatings without capacity loss
- Investigate effects of ALD-coated materials on the DC-R of HCMR<sup>TM</sup> cathodes

## Thickness of $\text{Al}_2\text{O}_3$ vs. cycle number



## Functions of surface coating

### Chemical Protection:

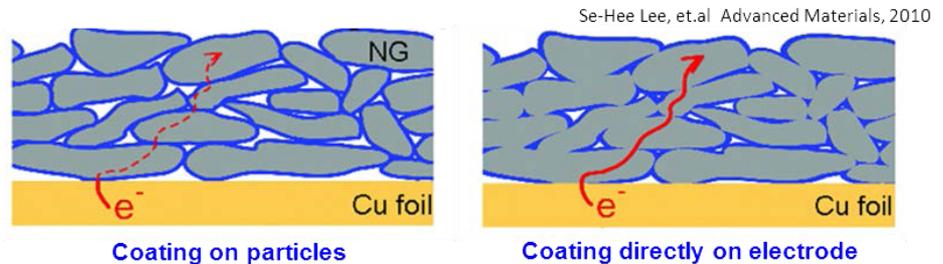
1. HF scavenger
2. Overcharge tolerance
3. Coulomb efficiency

### Mechanical Protection:

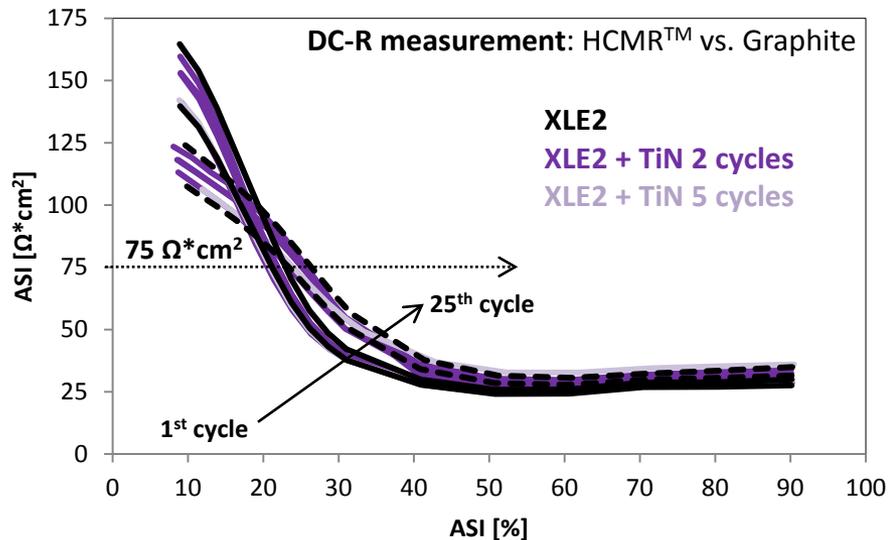
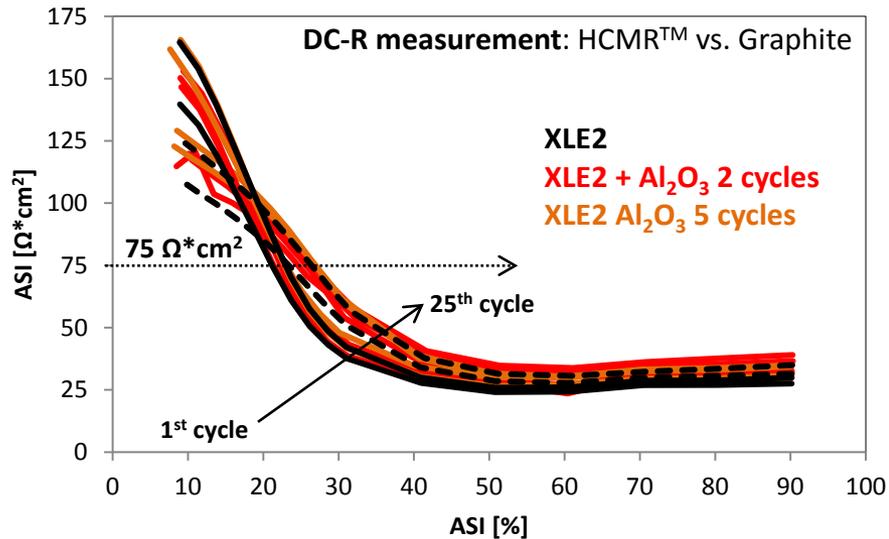
1. Structural stability
2. Stable SEI layer

## ALD coating properties

- Self-limiting sequential surface chemical reaction
- Conformal coating on 3D structure
- Precise thickness control → 1 cycle ~ 1.1 Å layer
- Low temperature deposition
- Two ALD coating techniques: particles vs. electrodes



# ALD-Coated XLE2: Electrochemical Properties



- Several iterations of studies on XLE1 and XLE2 were conducted to investigate ALD coating:
  - Chemistry:  $\text{AlF}_3$ ,  $\text{Al}_2\text{O}_3$ , AlN, TiN
  - Thickness: 2 ~ 20 ALD cycles
  - Process: on powder vs. on electrode
- ALD coatings show no major improvement on the energy nor cycle-life of XLE2 at C/3
- DC-R studies on XLE2 ALD-coated materials investigated the following variables
  - Coating on electrode
  - $\text{Al}_2\text{O}_3$  vs. TiN
  - 2 cycles vs. 5 cycles
- After 25 cycles, the XLE2-baseline and ALD-coated materials show the same 97-99% capacity retention
- Rise in DC-R and DC-R growth (loss of usable energy) is unchanged after applying an ALD coating on XLE2
- DC-R growth remains at 3-4% SOC after 25 cycles

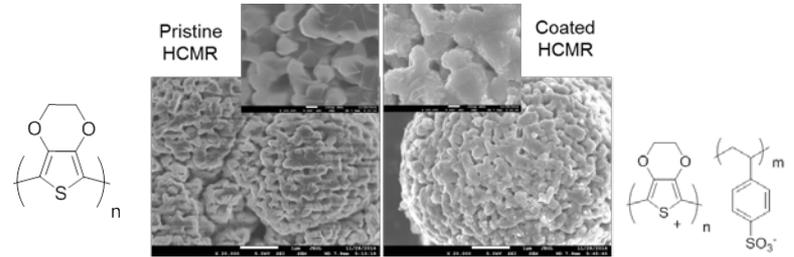
# Polymer-Coated XLE1

**Approach: polymer coating can improve conduction pathways and provide a “breathable” physical barrier between the electrode and the electrolyte**

- Explore different electroactive polymers as HCMR™ cathode coatings
- Develop and optimize coating processes to achieve uniform coating at desirable thickness
- Investigate the effect of polymer coatings on the DC-R of HCMR™ cathodes

## Coating techniques:

- Precipitation of dissolved polymer onto the cathode particles suspended in the solution upon solvent removal
- Chemical polymerization of monomer onto the cathode particles suspended in the solution
- Oxidative polymerization of monomer onto the pre-delithiated cathode particle surface
- Electrochemical polymerization

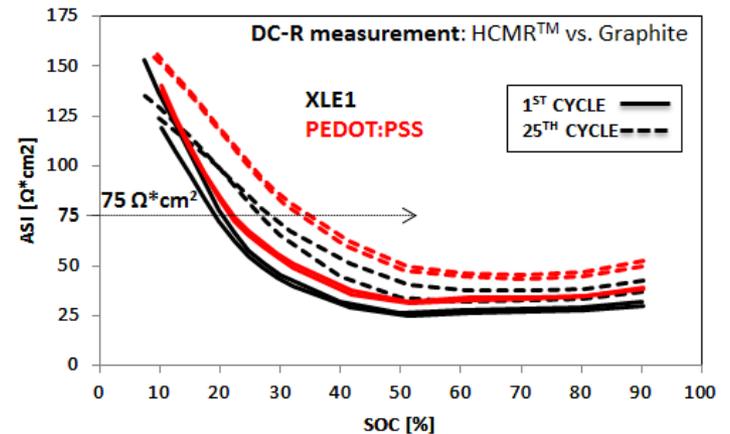


### PEDOT:

Typically insoluble, with low oxidation onset potential for wide operation window with respect to cathode cycling. Can be chemically or electro-chemically polymerized

### PEDOT-PSS:

A soluble polymeric version of the electron-rich EDOT unit. High conductivity-grade are commercially available but it contains PSS counter polyelectrolyte



- Studies performed on XLE1 due to surface passivation of nanocoated material (XLE2)
- Coated materials – poor rate capability
- XLE1-PEDOT:PSS - No benefit in both BoL DC-R and after cycling
- XLE1-PEDOT:PSS – shows more drop in usable energy with cycling than XLE1

# Metal Dissolution Studies

		Mn [ppm]	
		Avg	StDev
XLE1	Control	120	20
	PEDOT	192	20
	PEDOT:PSS	106	1
XLE2	Control	101	21
	1 hr LiPON	118	12
	Al <sub>2</sub> O <sub>3</sub> 2 cycles	74	11
	Al <sub>2</sub> O <sub>3</sub> 5 cycles	66	17
	TiN 2 cycles	113	26
	TiN 5 cycles	113	15

## Full-Cell Metal Dissolution Protocol

- Full-cell vs. Graphite
- Cells stored at 60°C for 7 days at 4.5V
- Mn ppm obtained via ICP-OES

- Low metal dissolution values are correlated with better cycle & calendar life
- Ni and Co are always found to be < 20 ppm
- ALD-Al<sub>2</sub>O<sub>3</sub> (5 cycles) shows the lowest Mn-dissolution numbers

# SOC Investigations: *in-situ* Raman

## Cell set-up:

Electrode: Carbon-Binder free (CBF) XLE2 vs Li/Li<sup>+</sup>

Electrolyte: EC:DEC 1:1  
1 mol/L LiPF<sub>6</sub>

## Electrochemistry:

Cyclic voltammetry

Scan rate: 0.1 mV/s

Cut off voltage: 2.0 V – 4.6 V

## Raman:

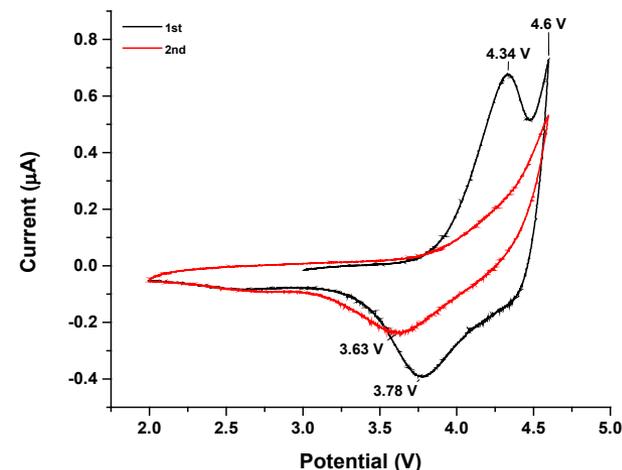
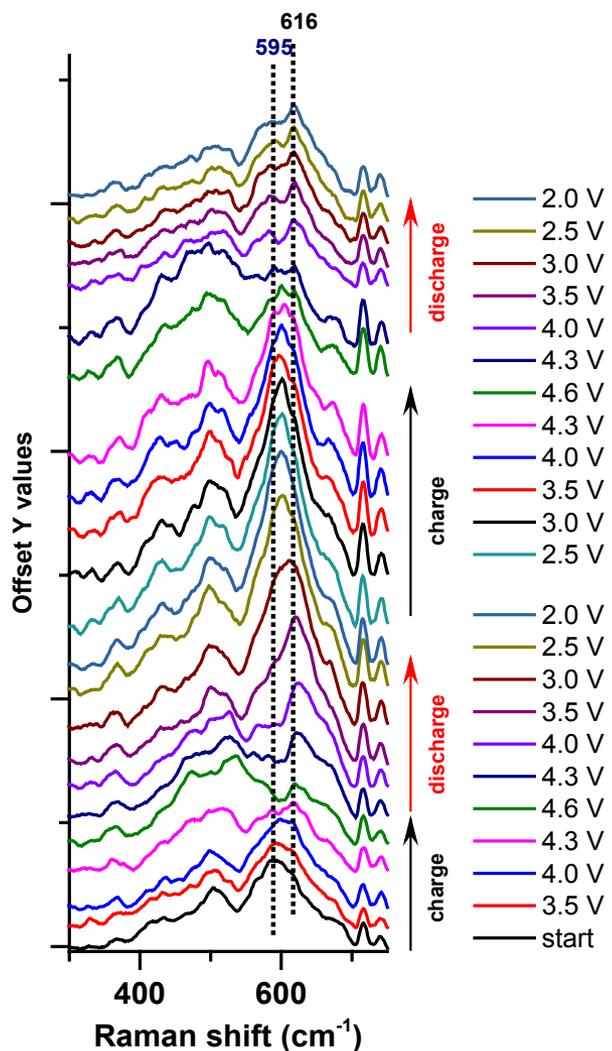
Exc. wavelength: 488 nm

Laser power: 0.55 mW

Magnification: x80

Grating: 1800

- ~498 cm<sup>-1</sup> Ni<sup>2+</sup>-O
- ~562 cm<sup>-1</sup> Ni<sup>4+</sup>-O
- ~600 cm<sup>-1</sup> Mn<sup>3+/4+</sup>-O, Co<sup>3+</sup>-O
- ~651 cm<sup>-1</sup> Mn-O (A<sub>1g</sub>)

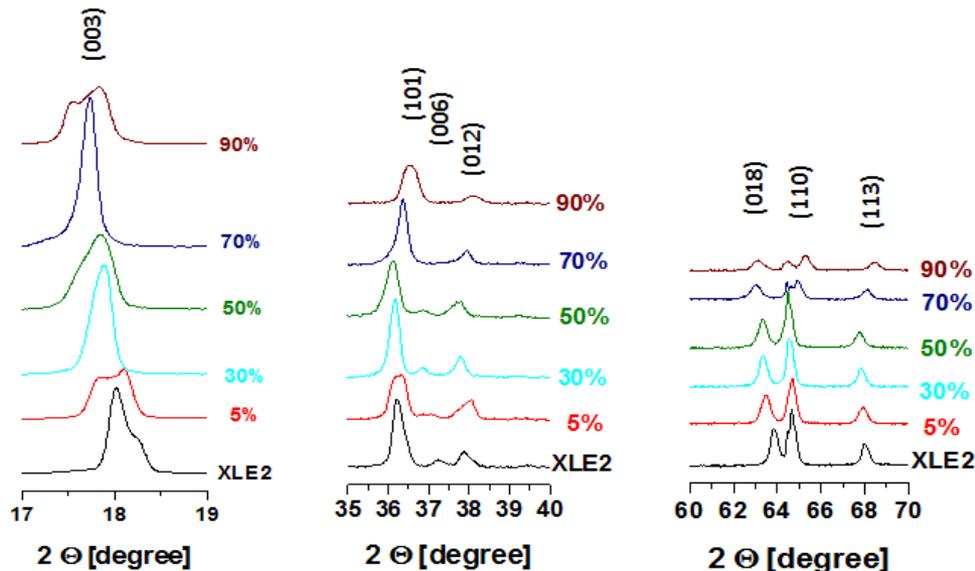
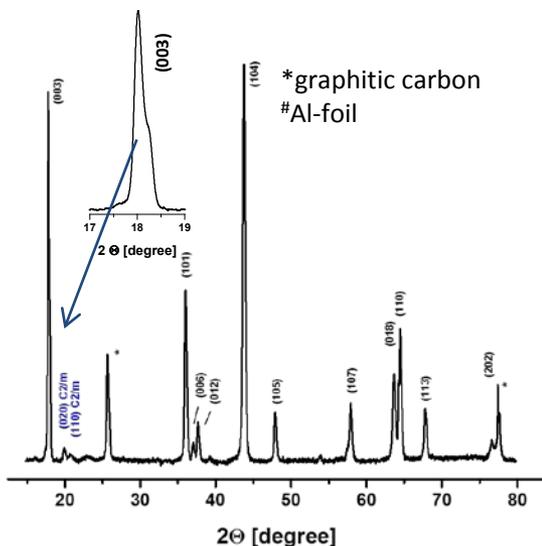


- Oxidation of Ni<sup>2+</sup> to Ni<sup>4+</sup> during delithiation
- Major peak at 600 cm<sup>-1</sup> shifts to higher wavenumbers with cycling as well as intensity increase for shoulder at 650 cm<sup>-1</sup>  
→ sign of the spinel-like structure formation

**Formation of spinel-like structure already visible in first cycles, yet mostly reversible.**

# Diagnostics: XRD

## XLE2 laminate



- Major peaks assigned to rhombohedral/ trigonal phase ( $R\bar{3}m$  space group)
- Lower  $2\theta$  region two weak peaks assigned to monoclinic phase ( $C2/m$  space group;  $Li_2MnO_3$ -like regions)

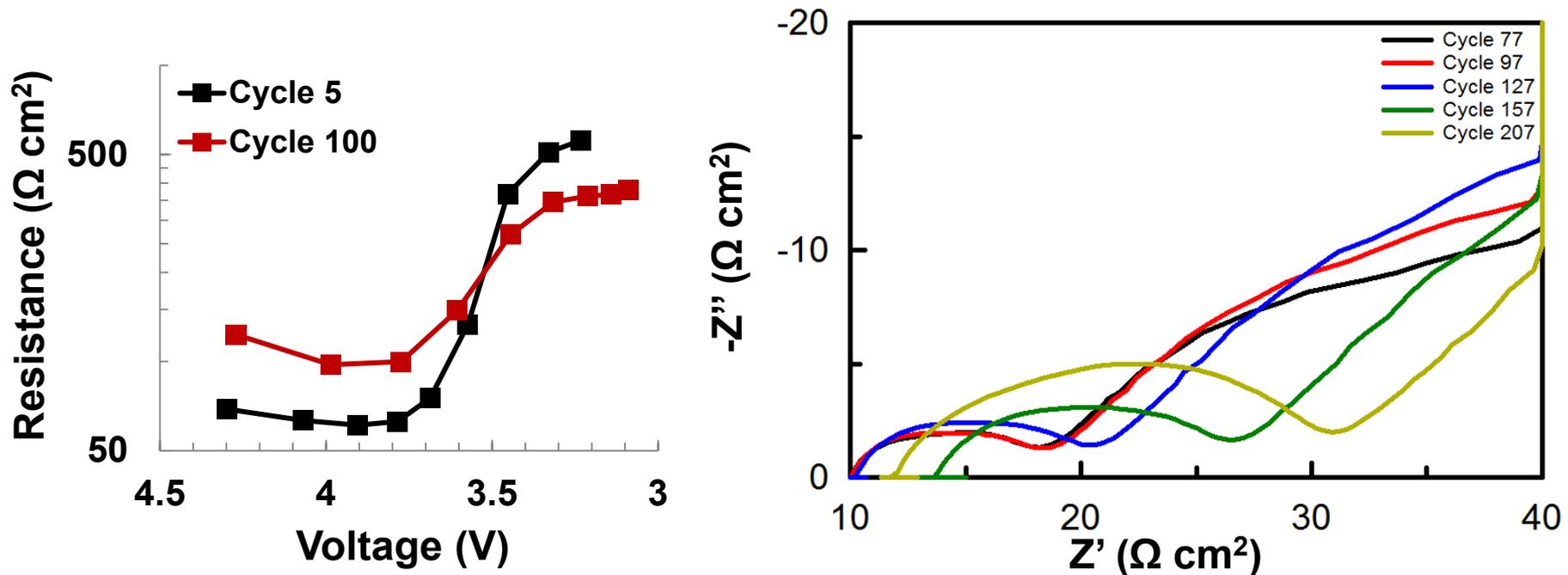
**Shoulder in peak (003) indicates the existence of more than one phase.**

- Shift of (003) peak to lower 2-theta values  
→ lattice expansion along c-axis - due to delithiation, transition metal oxidation and ion radii shrinking
- Shoulder of (003) becomes major peak
- No peaks for monoclinic phase ( $C2/m$ ) after cycling
- (006) signal shifts to lower 2-theta values
- At higher potentials, (101) and (012) are shifted to higher 2-theta  
→ lattice contraction
- (110) and (113) shift at 90% SOC to higher 2-theta values  
→ lattice contraction along a-axis

**Lattice expansion (delithiation) and contraction (lithiation) during cycling along c-axis. Lattice contraction observed at higher potentials (70%/90% SOC) along a-axis.**

# Origins of the DC-Resistance Increase in HCMR™ Cathodes

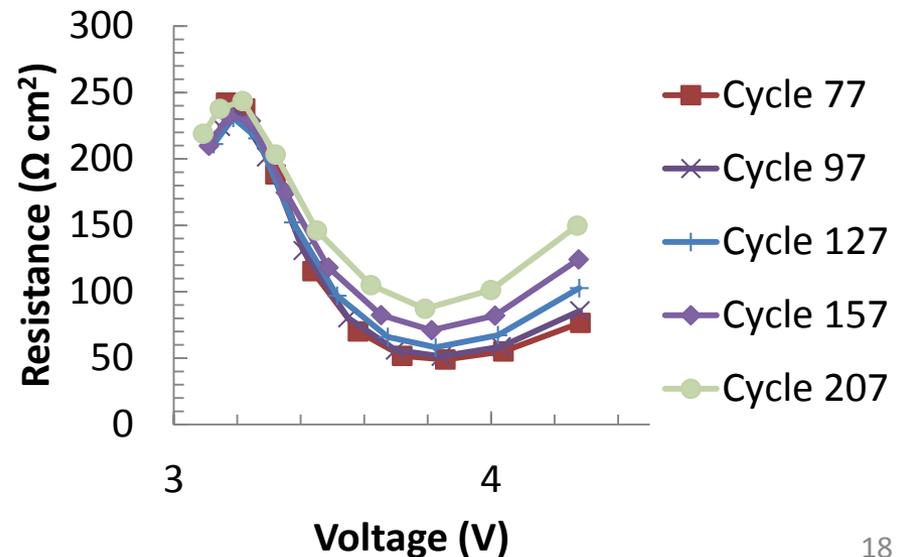
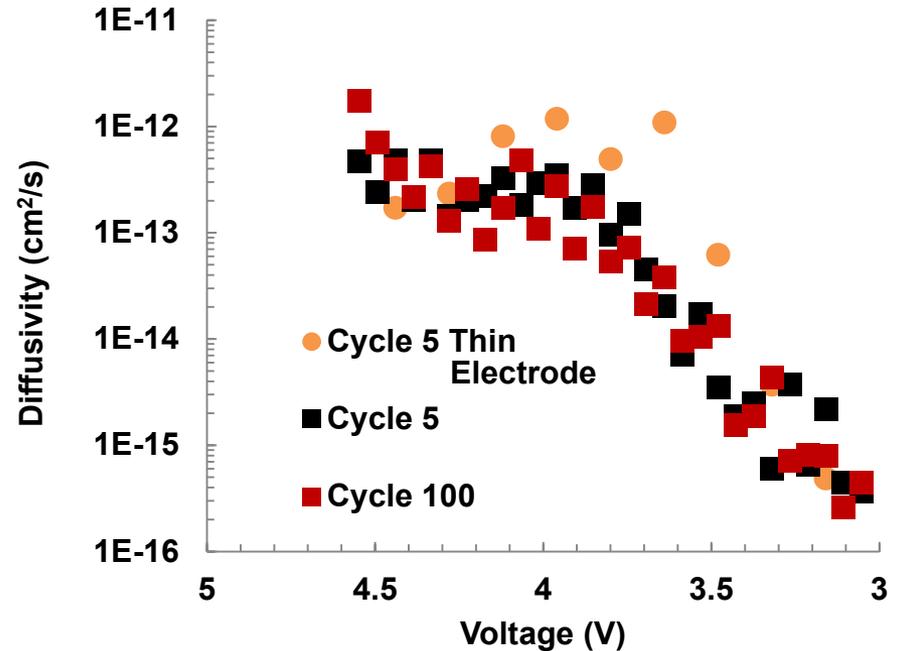
1. Evidence of structural transformation with cycling and proposed strategies using lithium and transition metal substitutions
2. Ionic and electronic barriers at interphases and interfaces
3. Loss of mechanical integrity in HCMR™ material - changes in morphology and topology



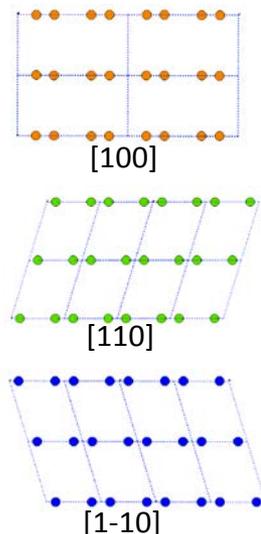
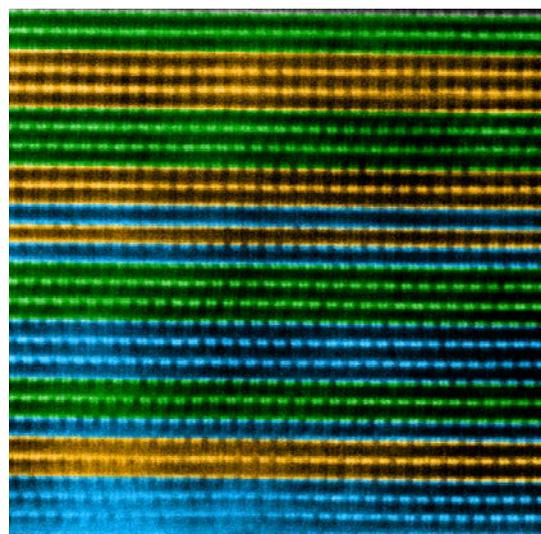
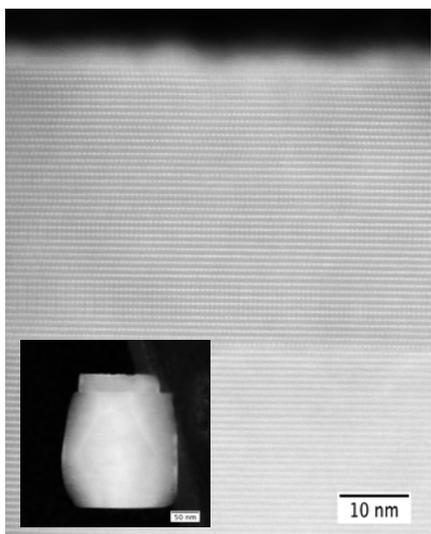
DC-R rises within a cycle and with prolonged cycling

# DC-R Rise Within Each Cycle

- Potentiostatic Intermittent Titration Technique (PITT) was used to measure the diffusivity
  - Diffusivity correlates strongly to voltage and the observed DC-R rise
  - Diffusivity measurement is independent of parameters such as electrode thickness
- DC-R rises with long term cycling
  - Resistive films may build up between the primary particles
  - Evidence of film formation is from growth of resistance at 4.3 V
  - Film formation also seen by FTIR

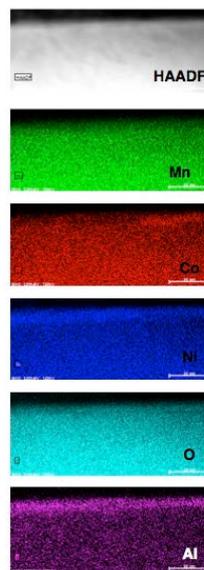
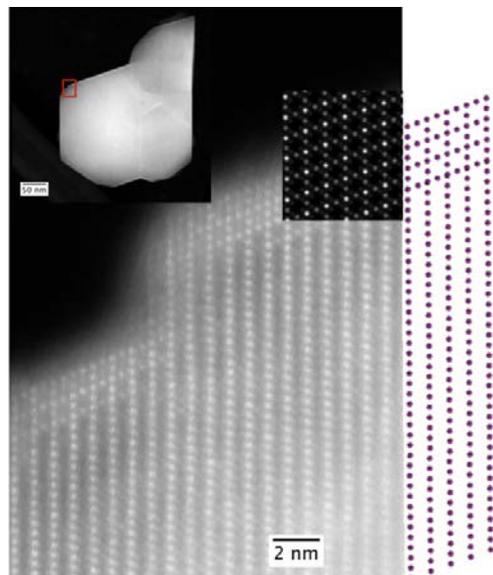
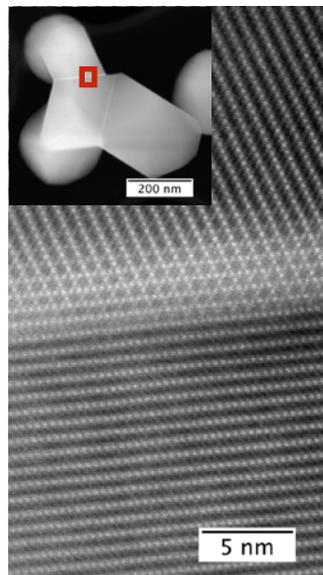


# Bulk & Surface Structure of HCMR™- XLE2 Material



## Bulk

- Li- and Mn-rich transition metal oxides consist of randomly-sized monoclinic domains stacked on (001) planes
- Observed throughout the primary particle  $\diamond$  bulk is made up of a single phase (except for defects and surface layer)
- No segregation of Mn – XEDS

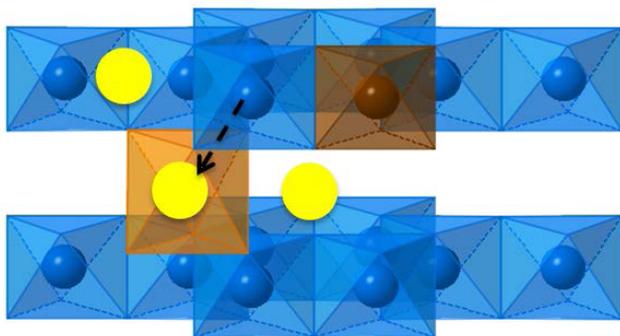


## Surface

- 2-3 nm thick surface layer with a spinel structure was observed on certain crystallographic facets
- These surface layers show segregation of Ni (and some Co) and has lower O concentration

This is a new finding and further work is in progress to understand the structural intricacies of Li-rich NMC materials. For more details, please see Poster **ES258**

# Combinatorial Screening of Doping Candidates



 Li replacement    
  Mn replacement

- $\Delta E = E(\text{after B migration}) - E(\text{before B migration})$
- Mn replacement is more influential than Li replacement on determining if  $\Delta E$  is positive (B migration is unfavorable) or negative (B migration is favorable)

Prototype formula:



A: Na, K, Mg

B: T, V, Co, Ni, W, Ru

Mn migration in  $\text{A}_{0.042}\text{B}_x\text{Mn}_{1-x}\text{O}_3$ , (A: Na or K, B: Co or Ni)

Li-replacement (A)	Mn-replacement (B)	$\Delta E$ (eV) in $x=0.5$	$\Delta E$ (eV) in $x=0.375$	$\Delta E$ (eV) in $x=0.25$
K	Co	2.22	-2.16	-2.67
K	Ni	2.02	1.59	-8.55
Na	Co	0.47	-1.33	-0.68
Na	Ni	1.64	2.44	-7.60

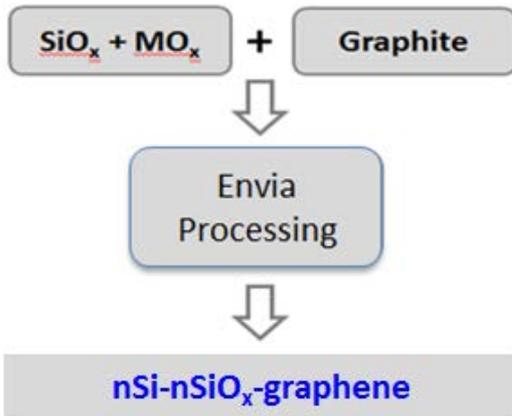
 Resistant to Mn-migration

 Vulnerable to Mn-migration

- To increase the Mn content (to reduce the material cost), K and Ni combination is better choice than K and Co combination.
- Ionic radius:  $\text{Li}^+$  (90 pm),  $\text{Na}^+$  (116 pm),  $\text{K}^+$  (152 pm) – have to maintain the Li-replacements uniformly distributed over the material.

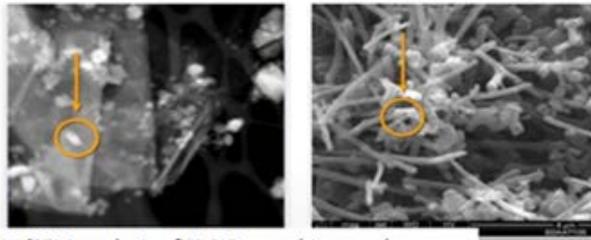
Attempts to synthesize the K and Ni doped  $\text{Li}_2\text{MnO}_3$  compositions suggested by theoretical calculation were NOT successful. Theory to experiment correlation has not been made yet!

# Si-C Anode Development

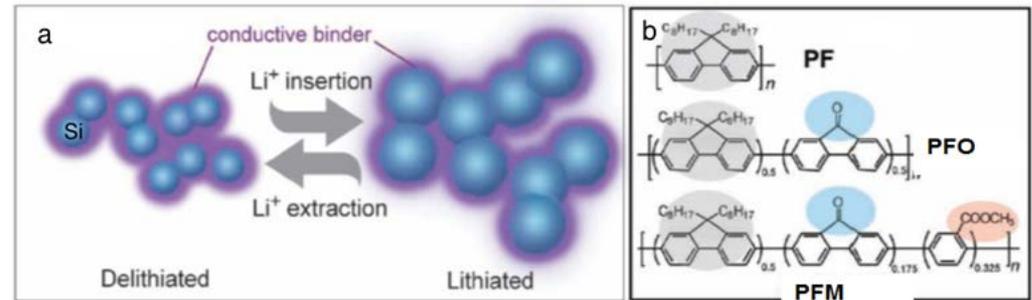
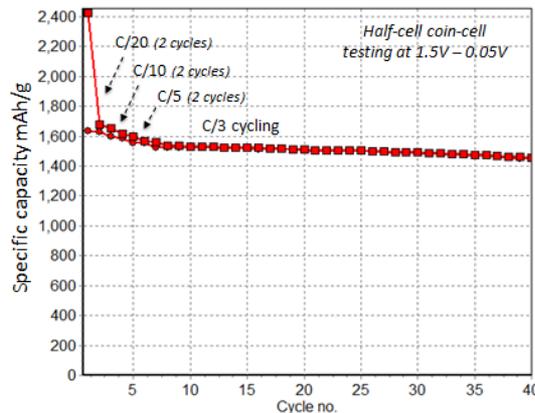


- Envia has developed an anode powder synthesis process using low cost precursors like SiO<sub>x</sub> and graphite
- Process is cheap, scalable and available in kg quantities

*Embedded SiO<sub>x</sub> and Si particles between graphene sheets enhances mechanical stability and resistance against pulverization due to the large Si volume expansion explaining the improved cycle life*



TEM/SEM analysis of Si-SiO<sub>x</sub>-graphite anodes:

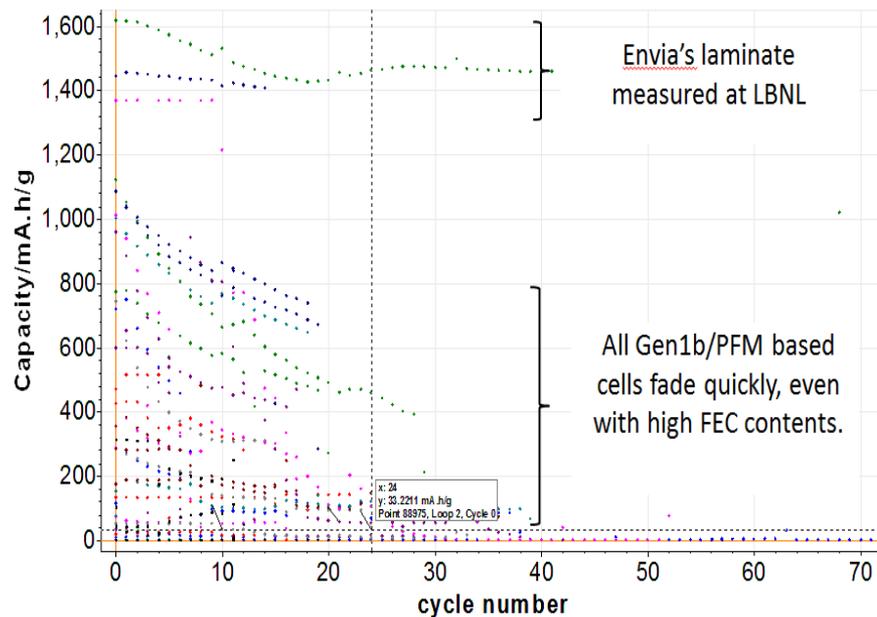
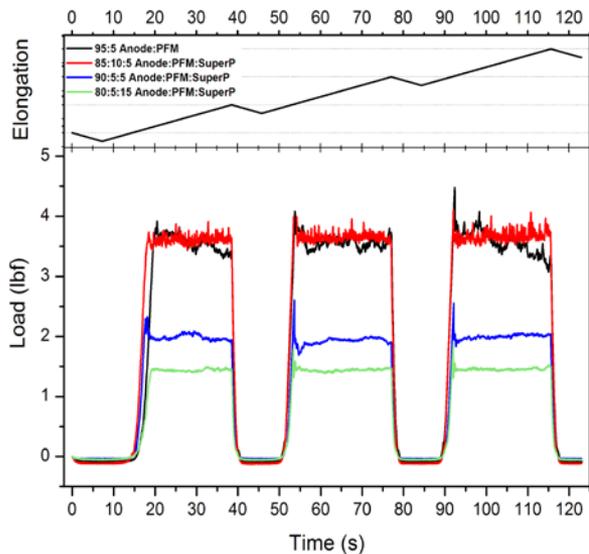


Envia's anode material has been paired with LBNL's conductive binder to enable long cycle and calendar life meeting ABR PHEV goals

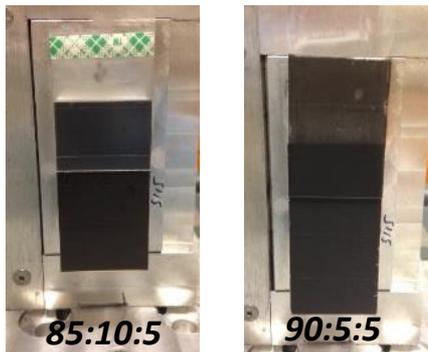
Source: LBNL

# PFM-based Laminates - Adhesion Tests

RS-12-	ratio			
	Gen1b	PFM	Super P	Chlorobenzene
0	95	5	0	1:30
1	90	5	5	1:30
2	85	10	5	1:25
3	80	5	15	1:30

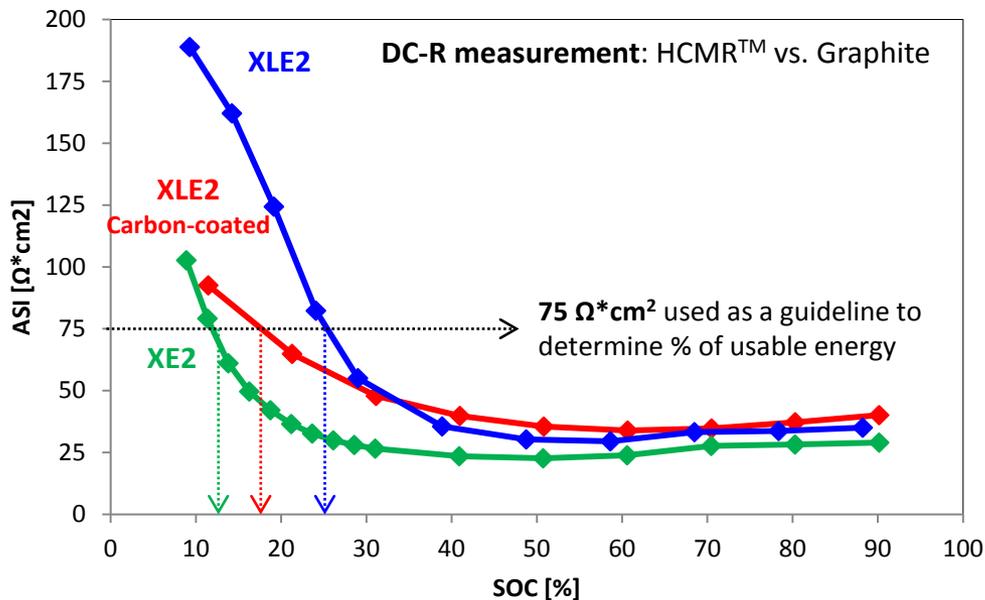
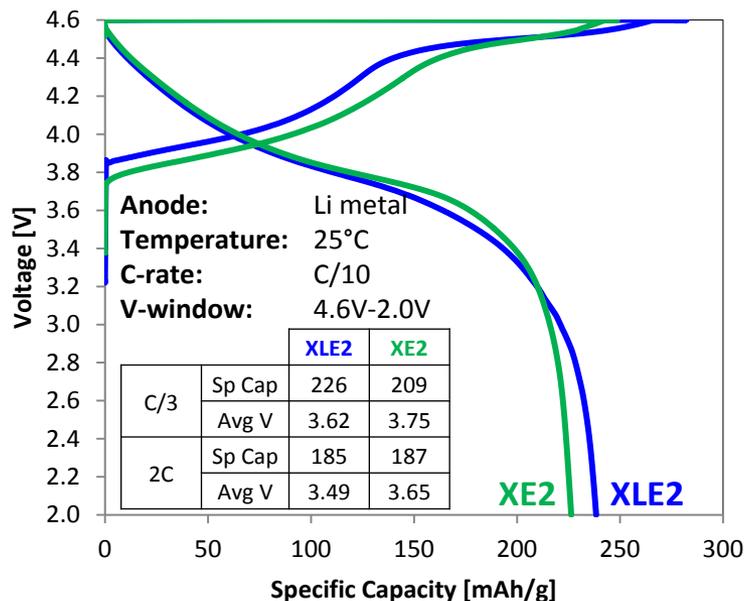
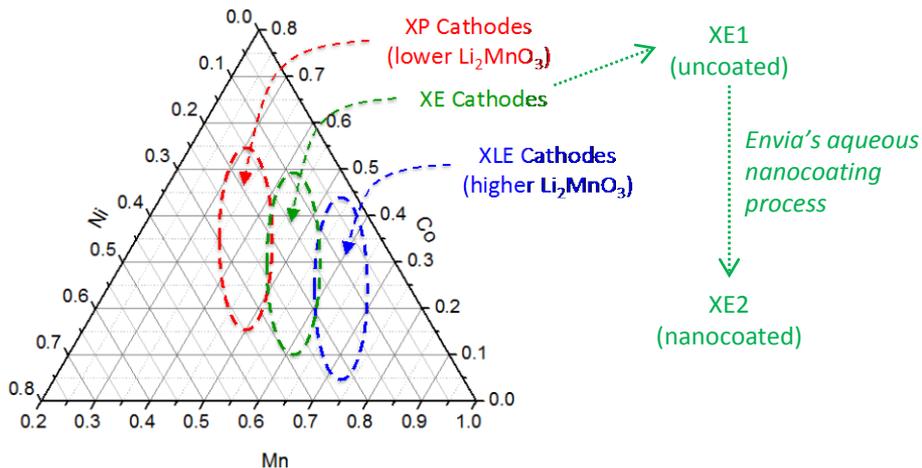


- Laminates fabricated with PFM as binder for Envia's anode show excellent adhesion
- Composition optimization efforts performed on the Gen1b/PFM
- Studied the influence of binder and carbon content, FEC additive, EG chains, particle coatings



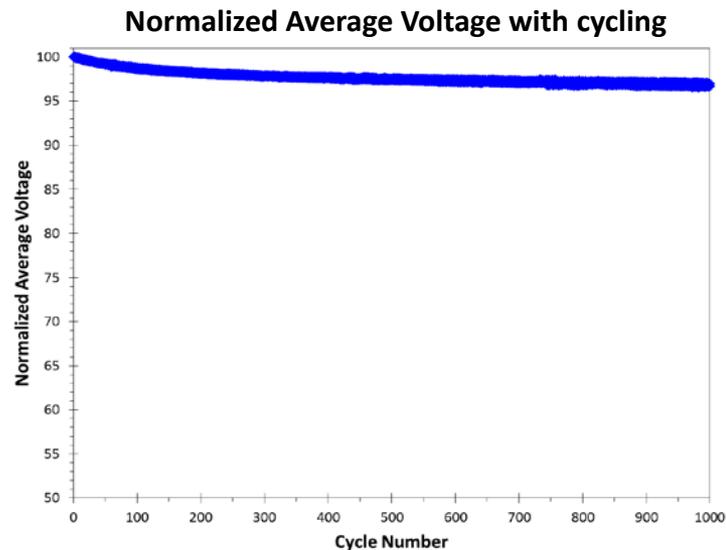
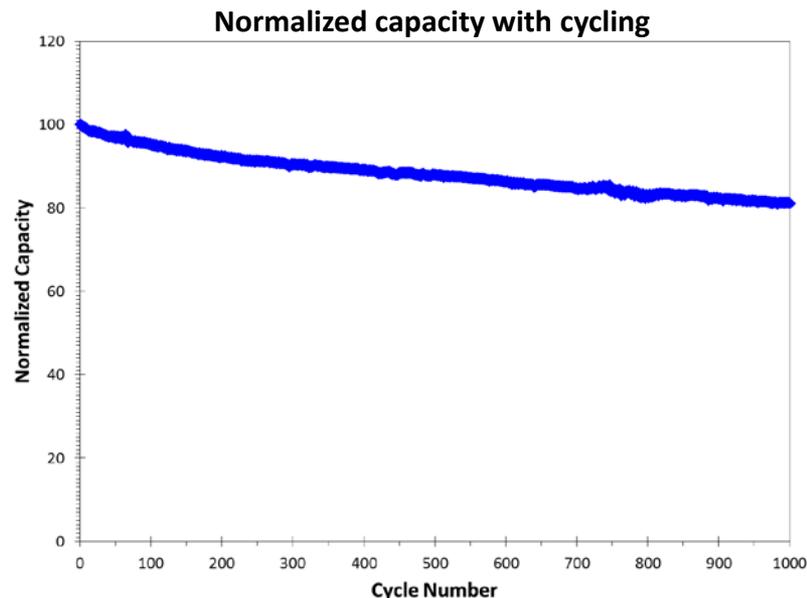
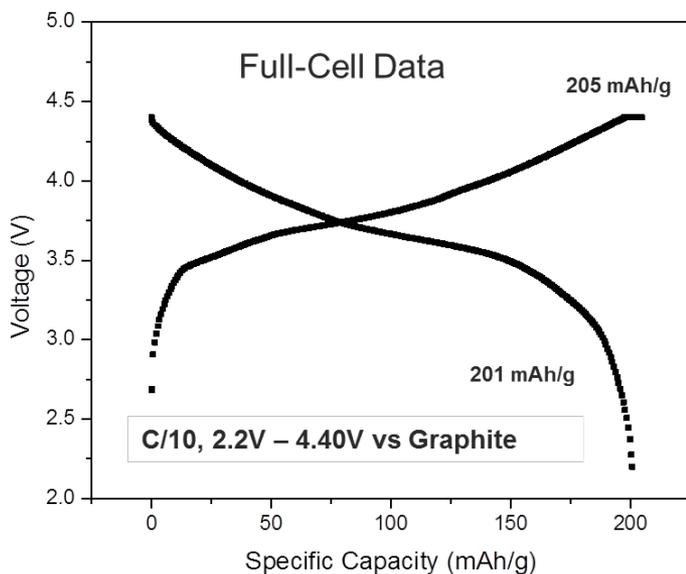
**Using Gen1b (Si-SiO-C), we cannot capitalize on conductivity and strong adhesion of PFM. Performance cannot be matched with Envia's binder**

# Compositional Engineering – XLE to XE



**PHEV cells demand high power – The newly developed composition (HCMR™ XE) is better or on-par in capacity in high rates with higher average voltage than XLE material.**

# HCMR™-XE vs. Graphite



Voltage Window	C/10 (mAh/g)	C/5 (mAh/g)	C/3 (mAh/g)	C/2 (mAh/g)	C/2 Avg. V (V)
2.2-4.4V	201	197	194	191	3.584
2.2-4.35V	196	192	189	185	3.576

# Cell Sizing

## Envia/GM R&D

- Material properties
- Performance

## Cell Suppliers

- Electrode design
- Cell engineering

## GM Product Engineering

- Vehicle requirements
- Cell configuration

**ENERGY SIZING TOOL:**  
Li balance model  $\Rightarrow$  Energy capability

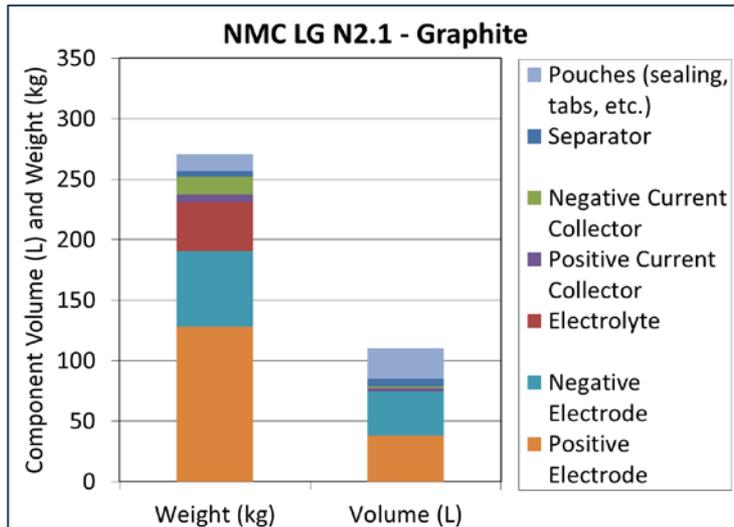
Energy density Wh/L  
Specific energy Wh/kg

## Cathode Design

	"Low"	"High"
Active material %	92	94
Loading, mg/cm <sup>2</sup>	14	18
Porosity %	36	28
Capacity, mAh/g	185	200
<b>SIZING RESULTS</b>		
Cell specific energy, usable Wh/kg	218*	234*
Cell energy density, usable Wh/L	387*	426*

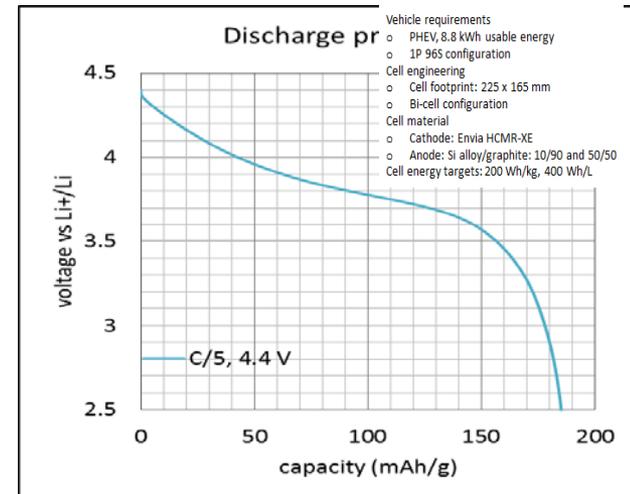
## Component mass

## Component volume



## GM Costing

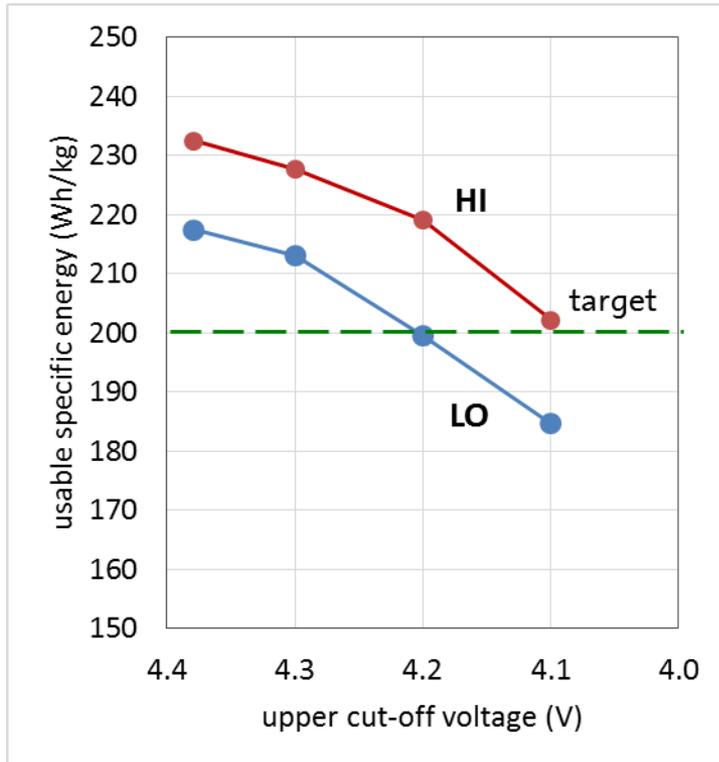
- Cost data
- Battery cost



# Effect of Upper Cut-off Voltage on Cell Energy

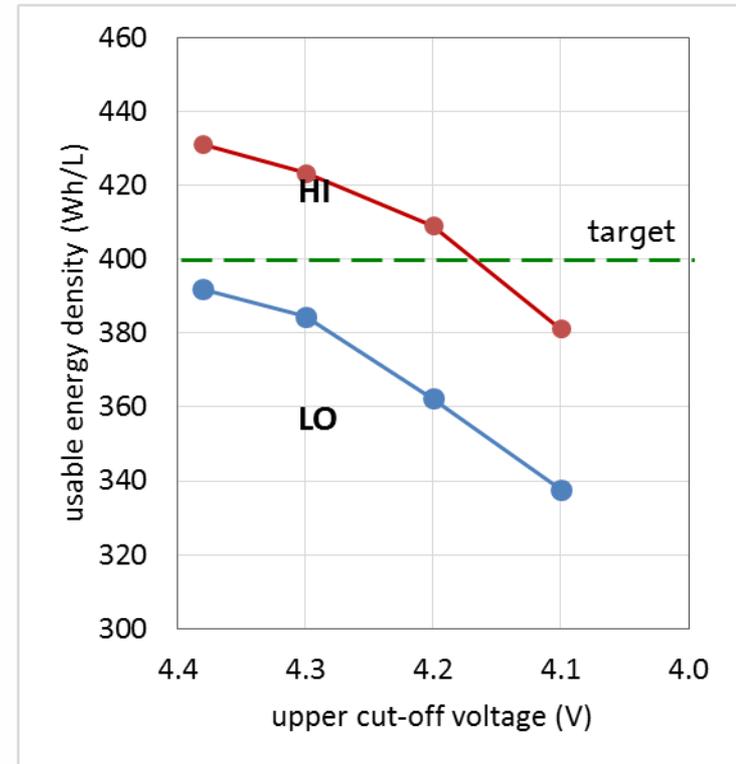
Sizing studies to optimize the upper cut-off window (as low as possible) to get the best energy efficiency with cycling

Specific energy (Wh/kg)



Significant scope for reducing upper cut-off voltage

Energy density (Wh/L)



Limited scope for reducing upper cut-off voltage

HCMR™-XE cathode with 10% Si alloy/90% graphite anode



# Summary

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## Surface Coating Studies

- LiPON coating as well as ALD-driven oxide and nitride coatings does NOT improve DC-R or usable energy both at BoL and with cycling
- Cycling Efficiency and Mn-dissolution numbers improved

## Diagnostic Studies on Origin of DC-R

- Raman spectra indicate prolonged oxidation / reduction of Ni
- *In situ* Raman confirms formation of spinel-like structure by cycling
- STEM studies show (i) Li- and Mn-rich transition metal oxides consist of randomly-sized monoclinic domains stacked on (001) planes and (ii) bulk is made up of a single phase (except for defects and surface layer) - observed throughout the primary particle
- Phase 'change' to one phase with prolonged cycling
- Lattice expansion along c-axis with prolonged cycling



DC-R is caused by changes in cathode material diffusivity due to changes in the lattice parameter during cycling – ***A bulk phenomena not limited to surface!***

**From both diagnostic and experimental studies it is clear that the to improve the DC-R, bulk material has to be modified - Composition engineering, rather than surface modification, is the key!**

# Conclusions, Future Work & Remaining Challenges

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## **Conclusions:**

- HCMR™-XE shows excellent promise with improved DC-R (usable energy)- Future work will shift the baseline from HCMR™-XLE to XE cathode material
- HCMR™-XE shows stable cycling ~ 1000 cycles against graphitic anode with high capacity
- Energy sizing has shown that without approaching higher charging voltages (< 4.3 V) we will be able to meet the ABR target metrics of 200 Wh/kg vs. Si-based anode

## **Future Work:**

- Down select the best composition & nanocoating (mainly focusing on improving the cycle and calendar life) and scale-up for large format cell builds
- Employ promising diagnostic methods to understand the DC-R characteristics of HCMR™-XE compared to the HCMR™-XLE materials
- STEM studies on different Li/M ratio samples to see the change in the structural aspects of Li-rich NMC
- Design cells following the energy sizing results to engineer 200 Wh/kg cells vs. Si-anode to show improved cycle life meeting the PHEV targets

## **Remaining Challenges:**

- Demonstrate 200 Wh/kg & 400 Wh/l in large format cell (20 ~ 50 Ah) using down selected materials with a cycle and calendar life meeting the ABR project goals



# Acknowledgements

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