

10.00am

Advanced High Energy and High Power Battery Systems for Automotive Applications

Khalil Amine

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Abstract

To meet the high-energy requirement that can enable the 40-miles electric drive Plug in Hybrid Electric Vehicle (P-HEVs), long range electric vehicle (EV) and smart grid, it is necessary to develop very high energy and high power cathodes and anodes that when combined in a battery system must offer 5,000 charge-depleting cycles, 15 years calendar life as well as excellent safety characteristics. These challenging requirements make it difficult for conventional cathode materials to be adopted in P-HEVs and EVs. In this talk, we report several high-energy systems that offer the potential of enabling next generation PHEVs and EVs. After a brief description of lithium ion battery concept, we will disclose several strategies to increase significantly the energy density of lithium battery through the development of novel functional materials. We will also describe some new approaches to improve the cycle life and safety of lithium batteries using advanced nanocoating at the particle level and functional electrolyte additives that play a significant role in stabilizing the interfaces during battery operation and abuse.

Biography

Dr. Khalil Amine is a Senior Fellow Scientist and the Manager of the Advanced Lithium Battery Technology group at Argonne National Laboratory, where he is responsible for directing the research and development of advanced materials and battery systems for HEV, PHEV, EV, satellite, military and medical applications. He is the founder and lead organizer and chair of the International Conference on Advanced Lithium Batteries for Automotive Applications. Among his many awards, Dr. Khalil is a 2003 recipient of Scientific America's Top Worldwide Research 50 Research Award, a 2009 recipient of the US Federal Laboratory Award for Excellence in Technology Transfer, and is the three-time recipient of the R&D 100 Award. In 2010, he was awarded the ECS Battery Technology award and the International Battery Association award. He holds or has filed over 120 patents, patent applications and has over 254 publications. From 1998-2008, Dr. Khalil was the most cited scientist in the world in the field battery technology.

Advanced High Power and High Energy battery chemistries for Automotive Applications

Khalil Amine, Ph.D

Argonne National Laboratory

US Department of Energy

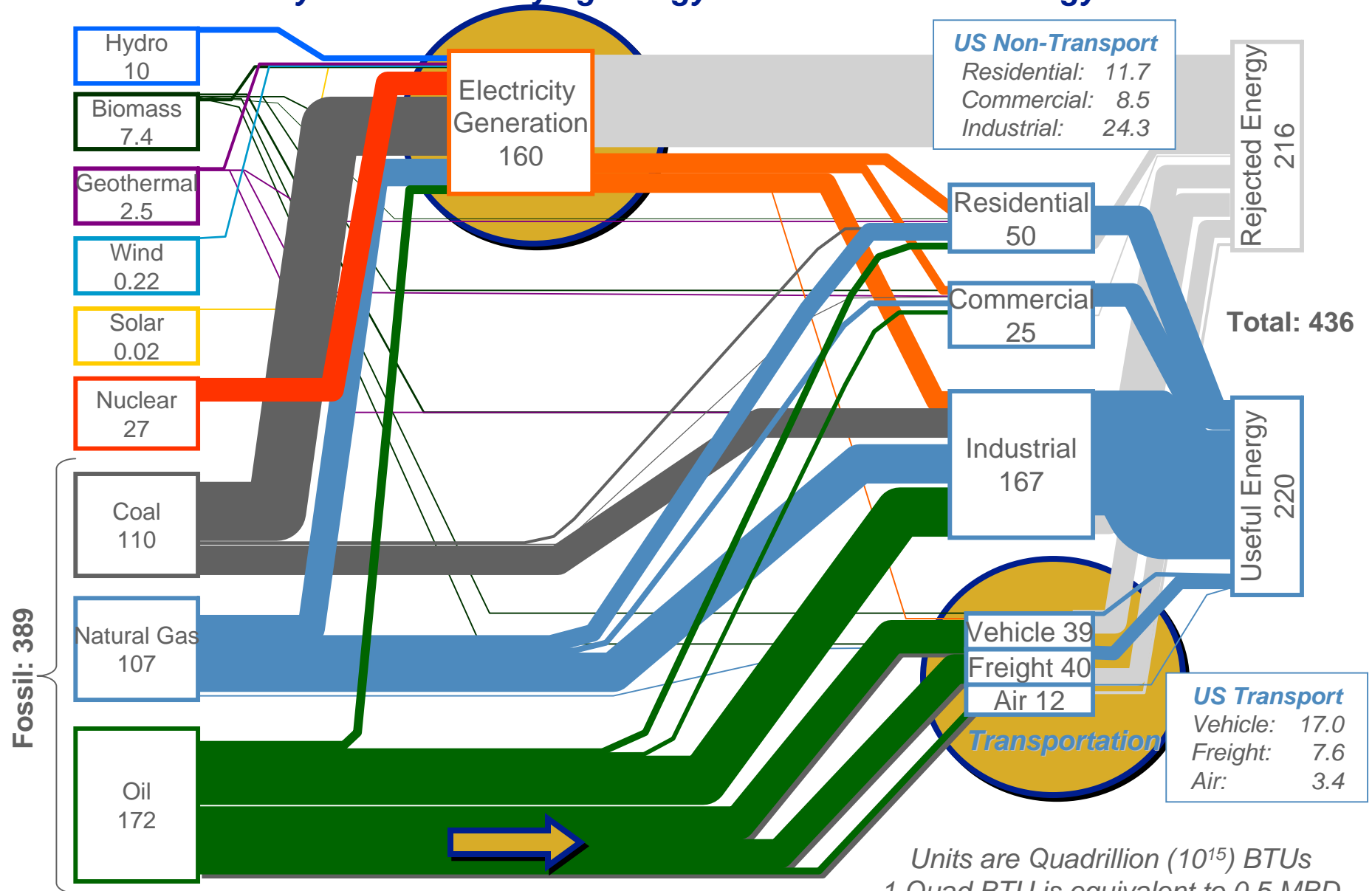
Acknowledgments:

***H.Wu, Z. chen, . Belharouak, G. Koeing, Z. Zhang, L. Curtiss, Y.K. Sun,
J. Lu; P. Du; A. Abouimrane, J. Moore; Y. Qin; T. Tan, N. Ota***

***Tien Duong, Peter Faguy and D. Howell, Vehicle Technology program,
US Department of Energy***

2005 Global Human-Activity Energy Flows

- ➔ *Transportation the only major industry dependent on only 1 energy supply chain*
- ➔ *Electricity serves as unifying energy carrier for diverse energy resources*



Source: Lawrence Livermore National Laboratory

Units are Quadrillion (10^{15}) BTUs
 1 Quad BTU is equivalent to 0.5 MBD

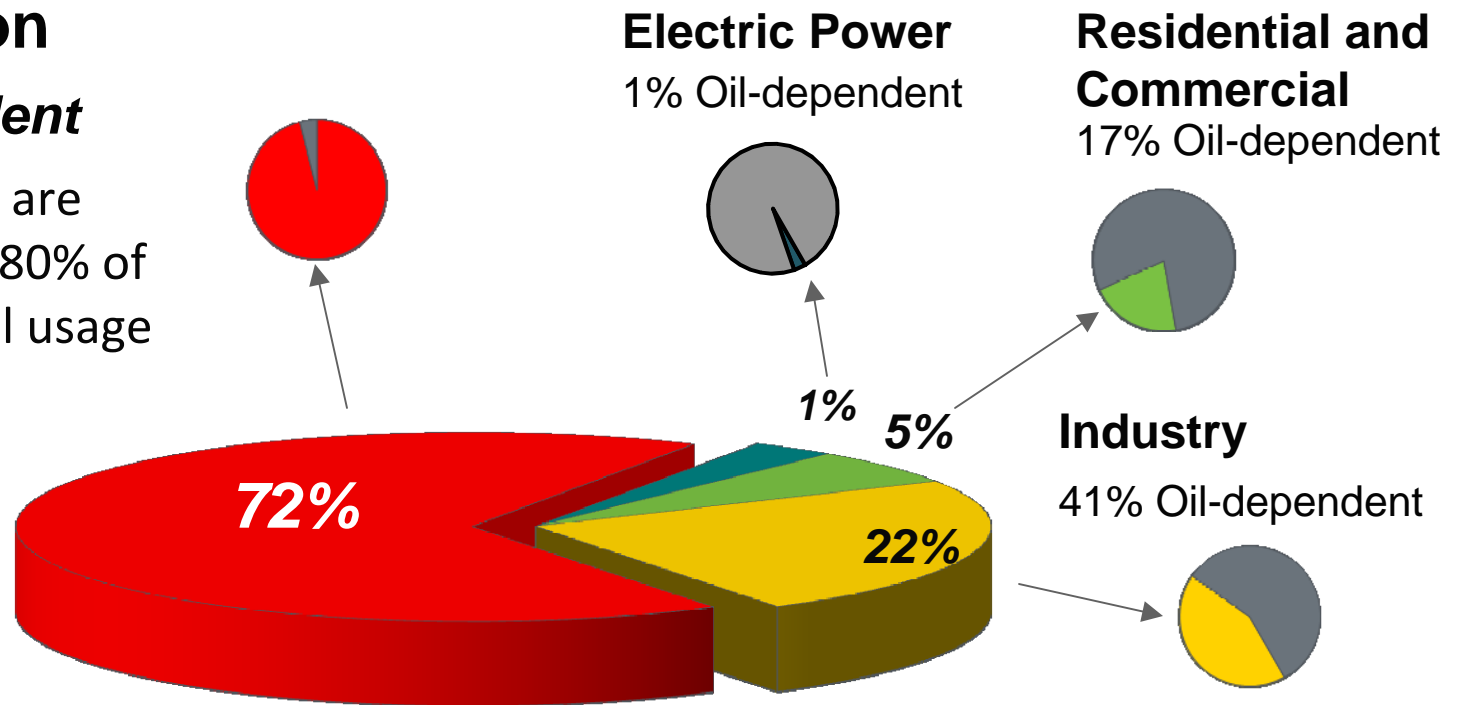
U.S. Oil-dependence is Driven by Transportation

U.S. Oil Consumption by End-use Sector 19.1 Million Barrels per Day (2010)

Transportation

94% Oil-dependent

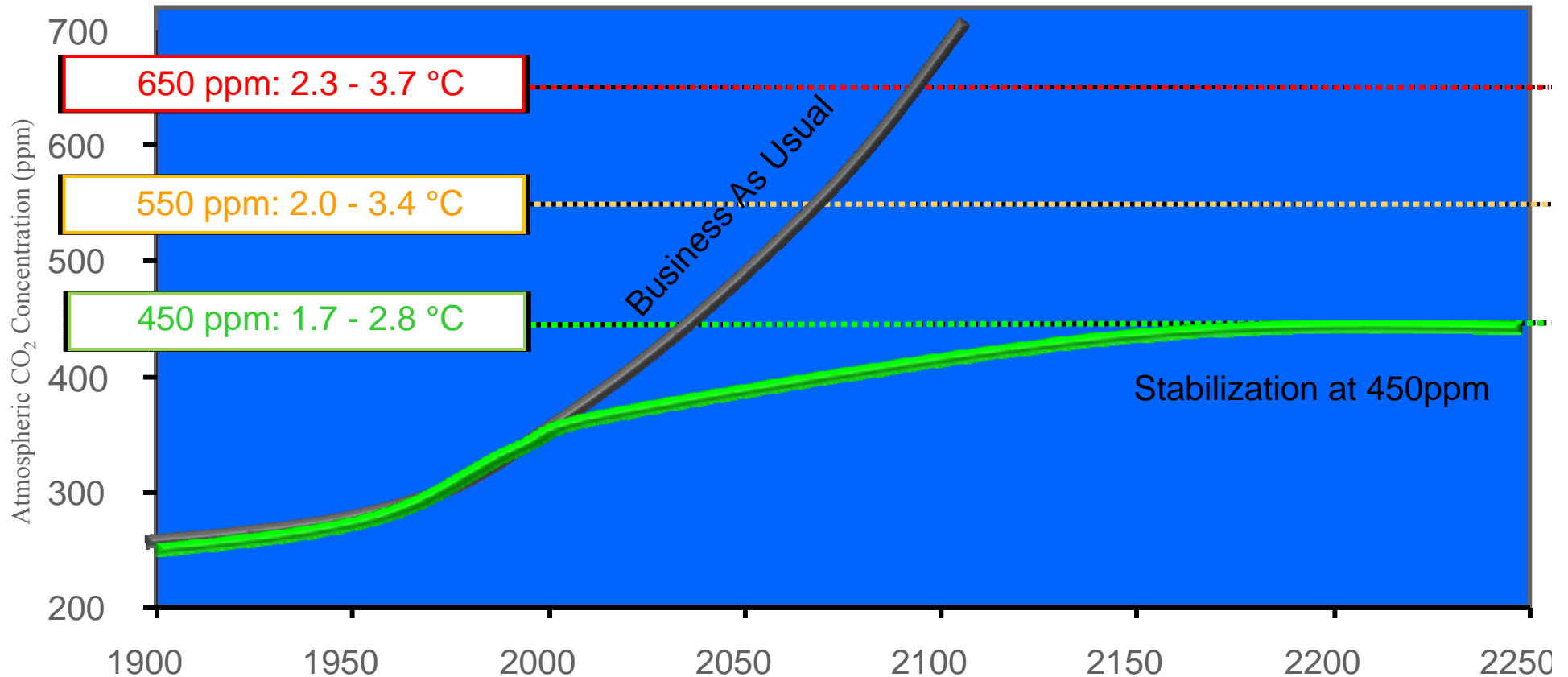
- On-road vehicles are responsible for ~80% of transportation oil usage



Source: DOE/EIA Annual Energy Review, April 2010



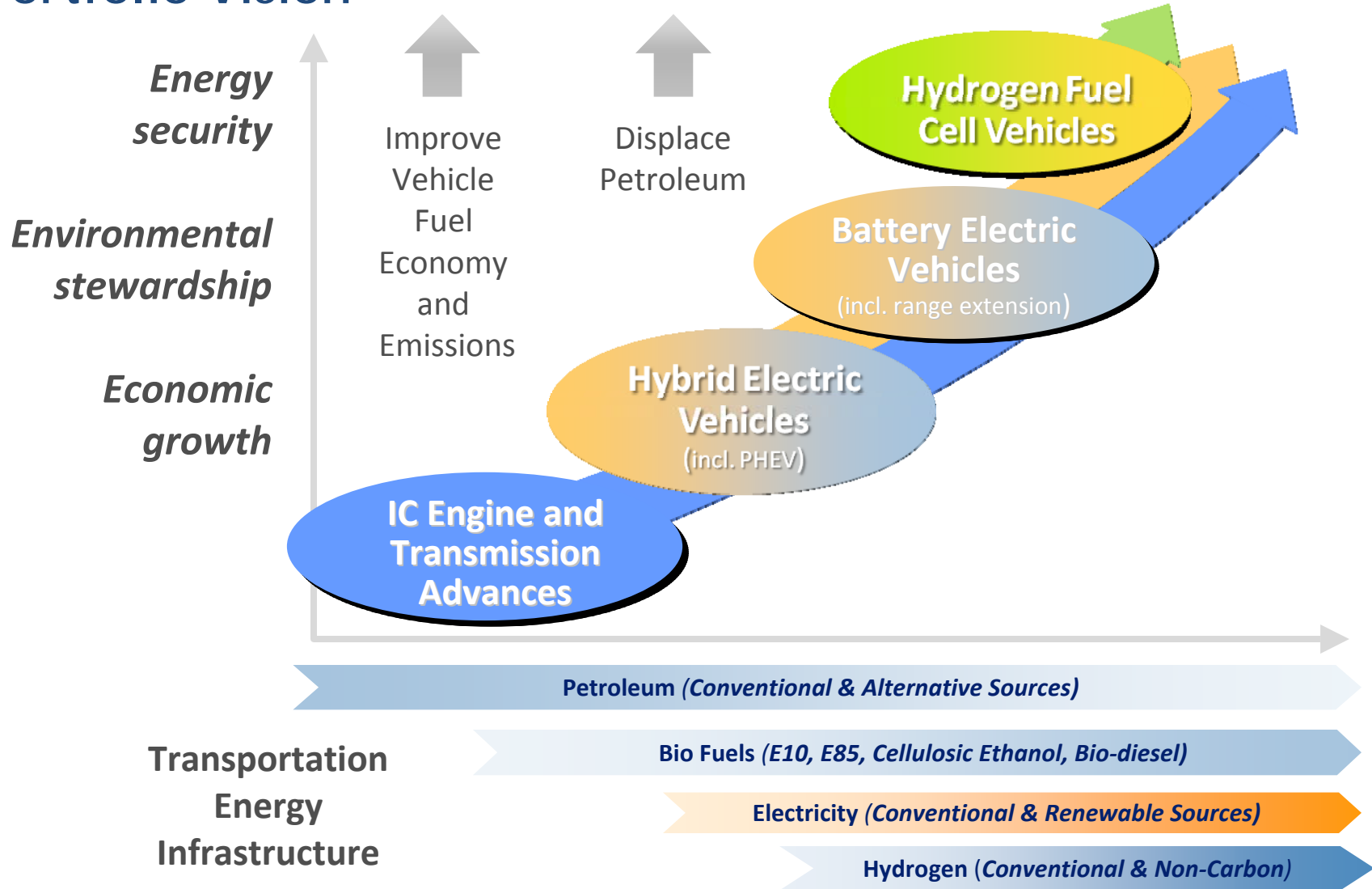
CO₂ Reduction Glidepath – Long Term Vision



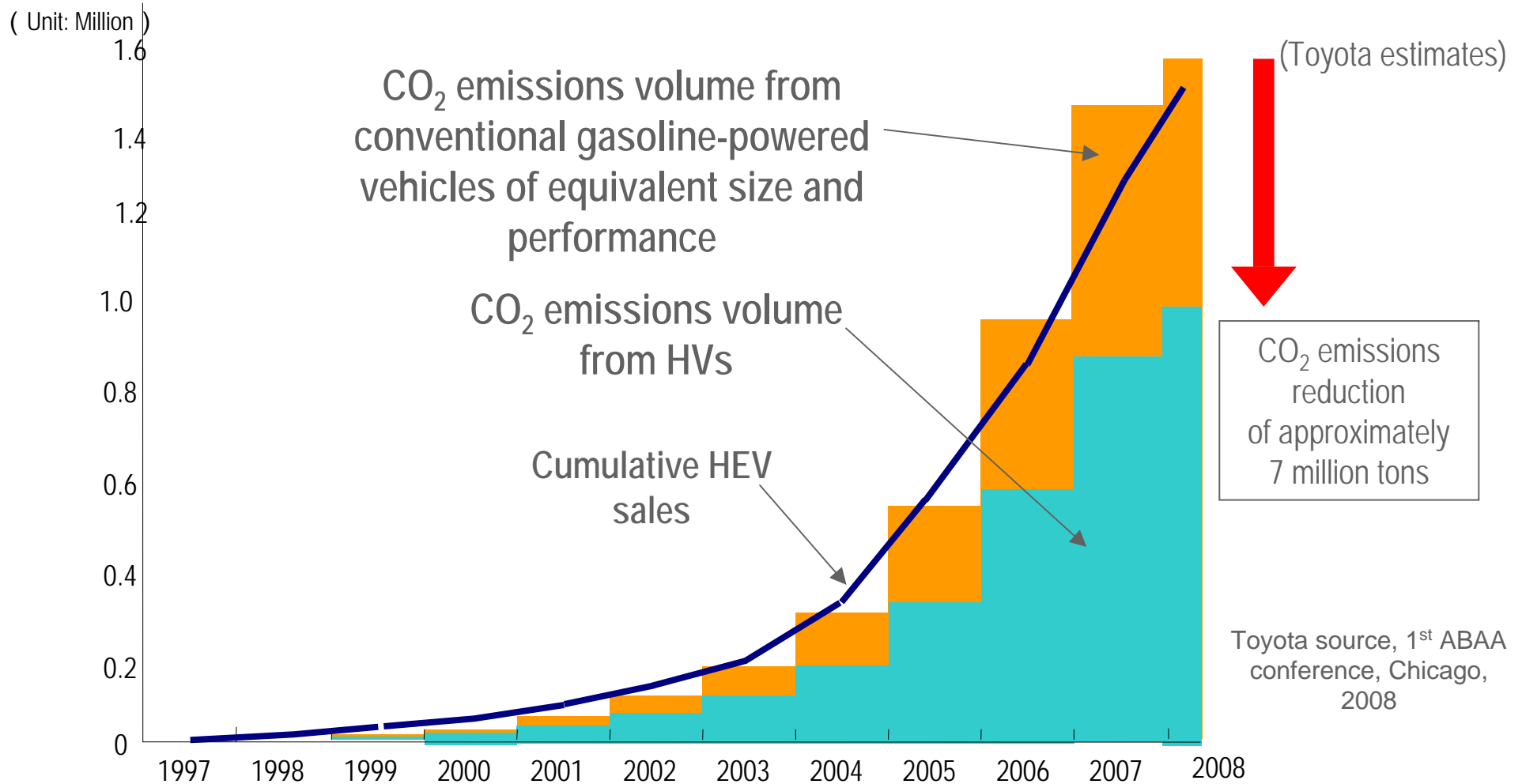
- Simply “not getting worse” is not good enough
- Customers globally expect more fuel efficient / low CO₂ vehicles
- This is a long-term commitment for a sustainable future



Government-Industry Partnership: Advanced Propulsion Portfolio Vision



Effect on CO₂ Emissions Reduction through Sales of 1.5 Million HEVs



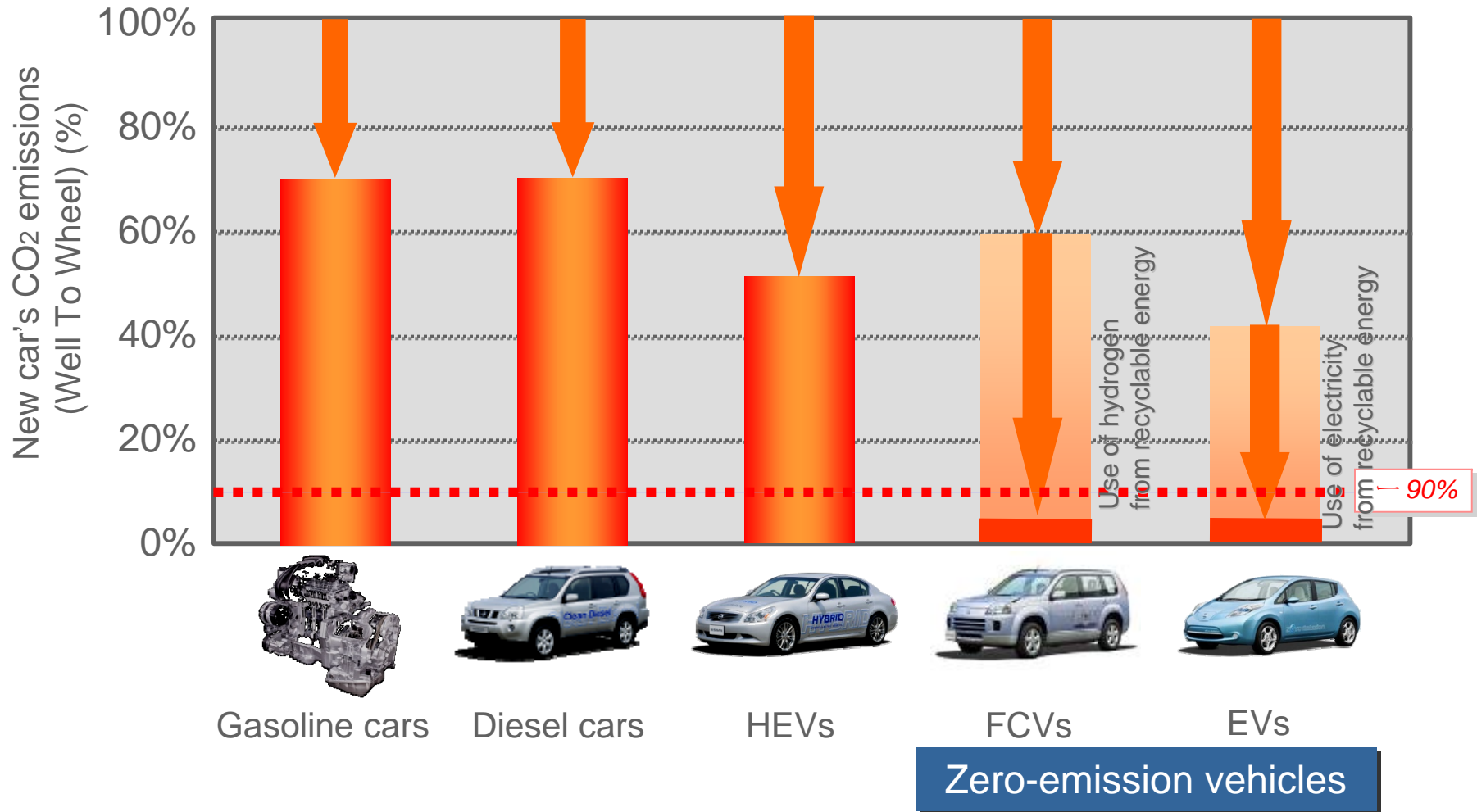
Cumulative CO₂ emissions volume = No. vehicles sold × driving distance × fuel efficiency × CO₂ emissions factor

CO₂ emissions reduced by approximately 7 million tons due to sales of 1.5 million HEVs

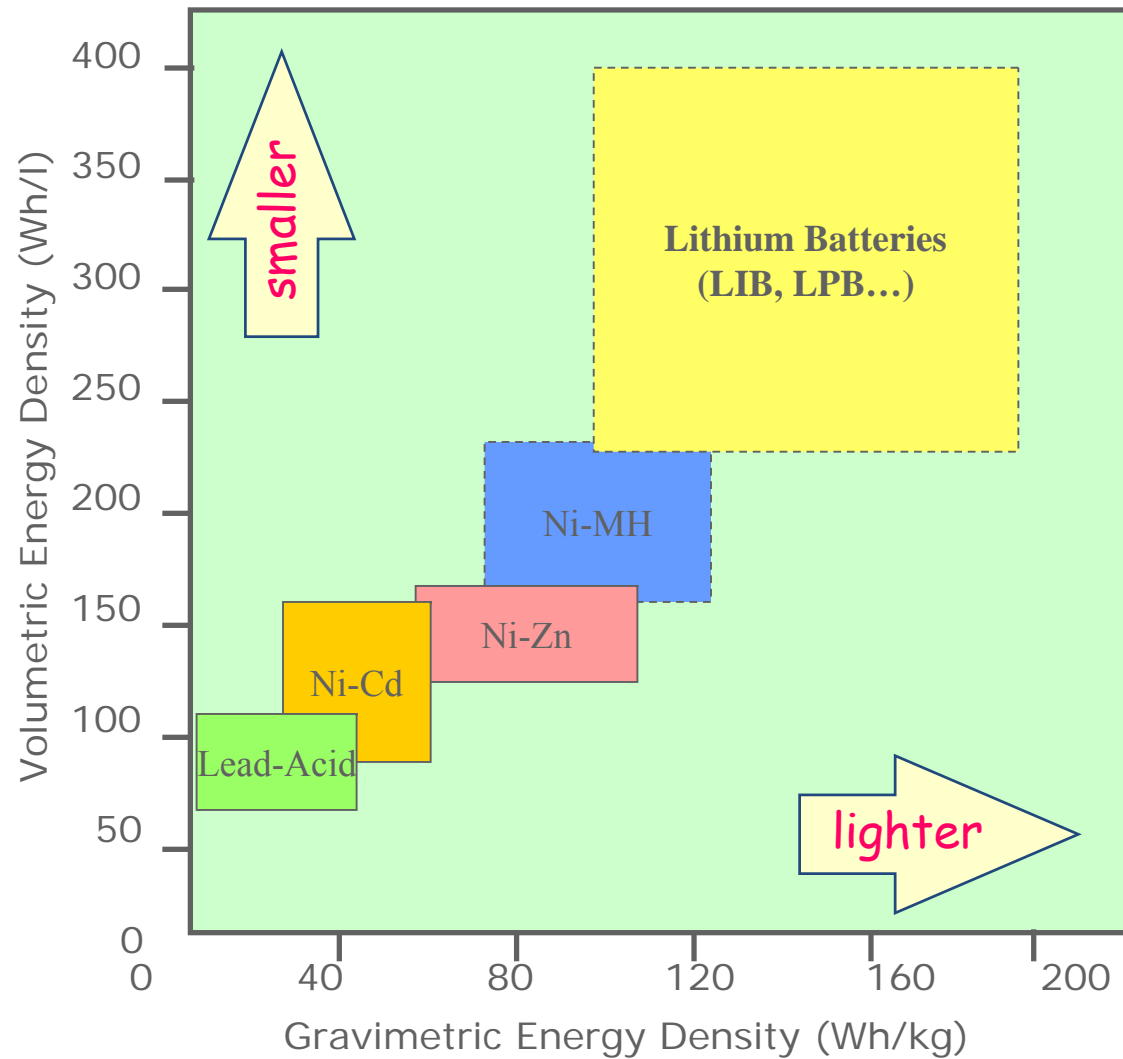


Environment : Electric Powertrain for CO₂ Reduction

- Ultimate goal of Zero-emission vehicles and clean energy

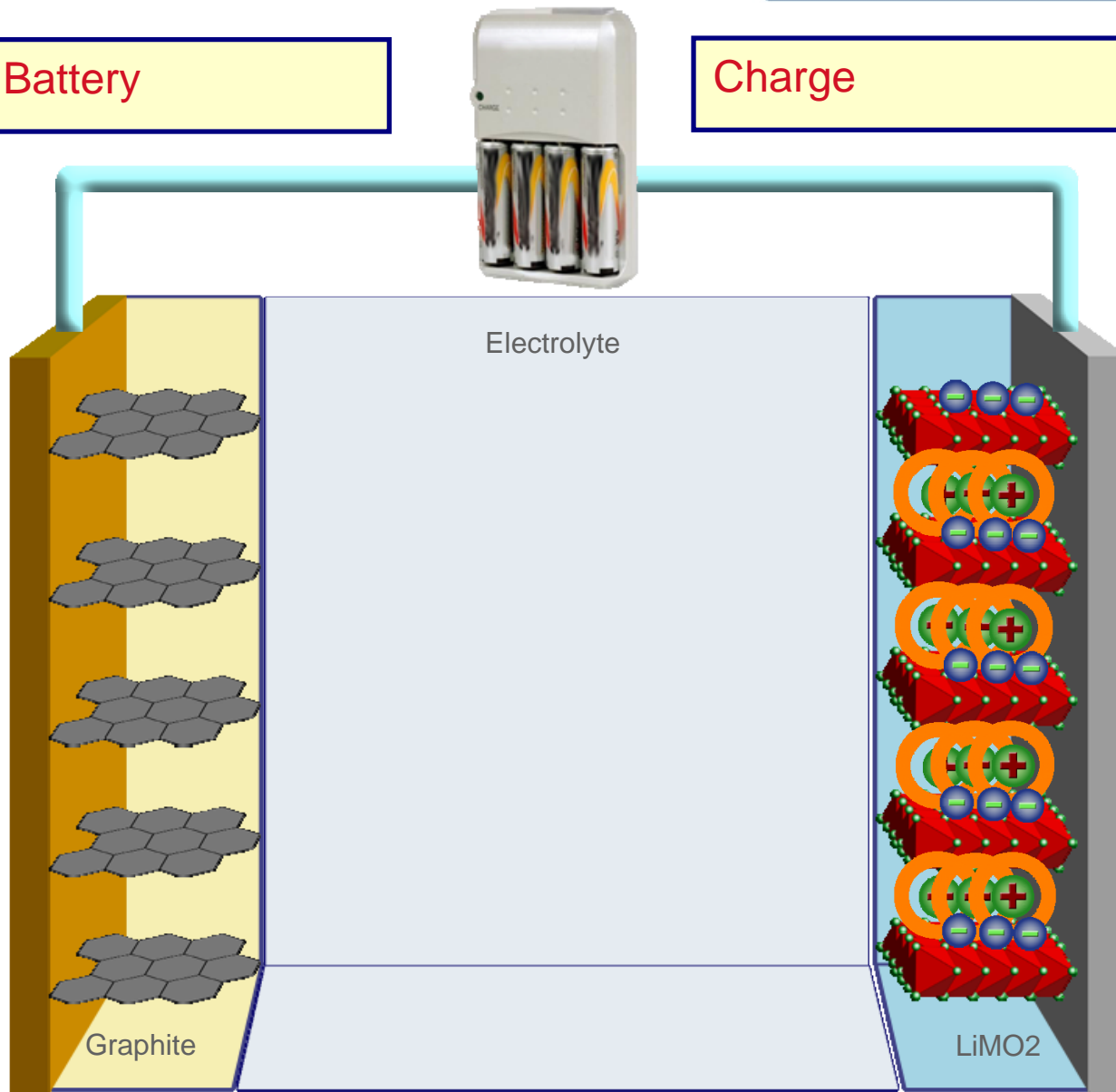


Why Li-ion cells for Transportation (HEVs, PHEVs, EVs)? Higher cell voltage & higher energy/power densities



Lithium-Ion Battery

Charge

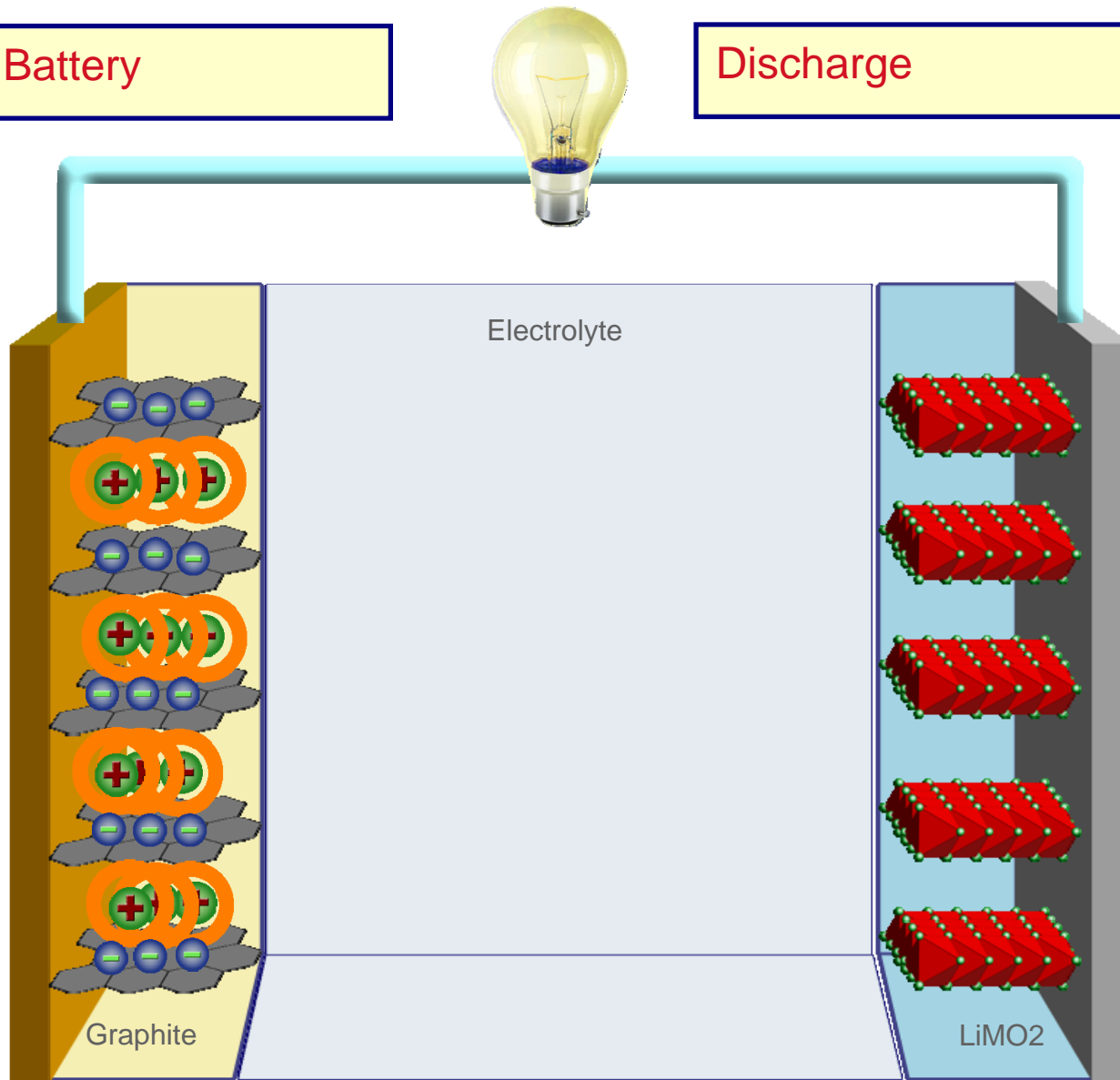


SEI

SEI

Lithium-Ion Battery

Discharge



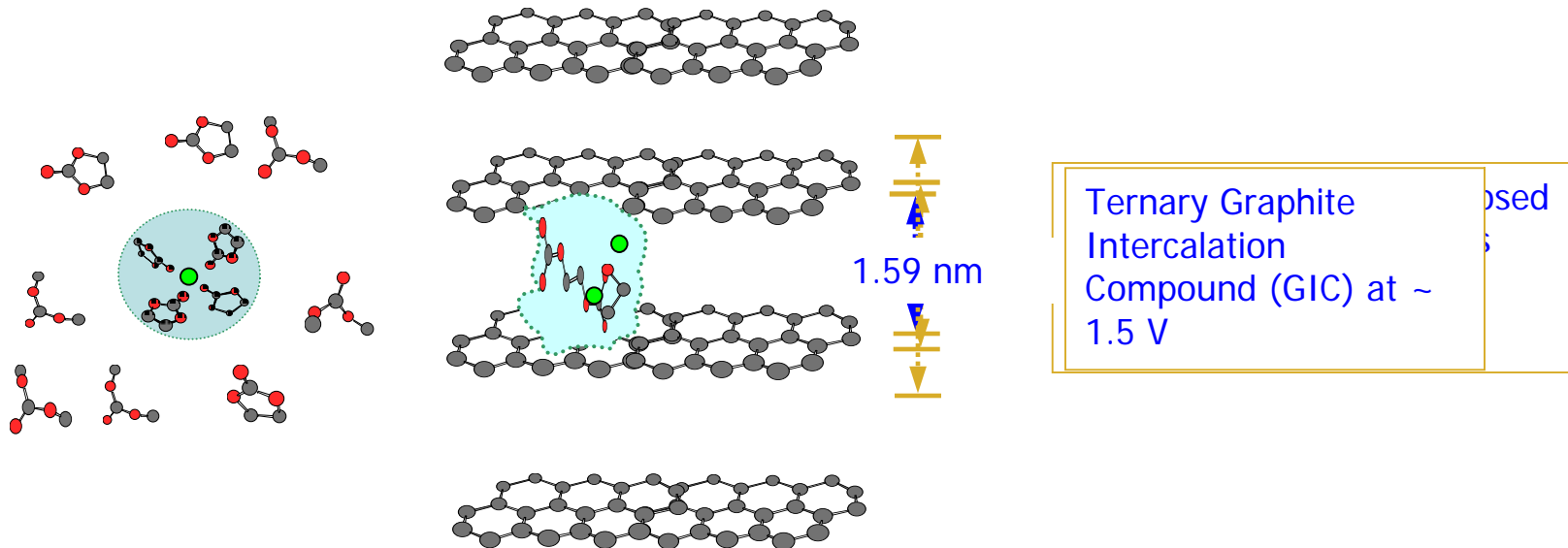
SEI

SEI

Importance of Solid Electrolyte Interface in stabilizing the system

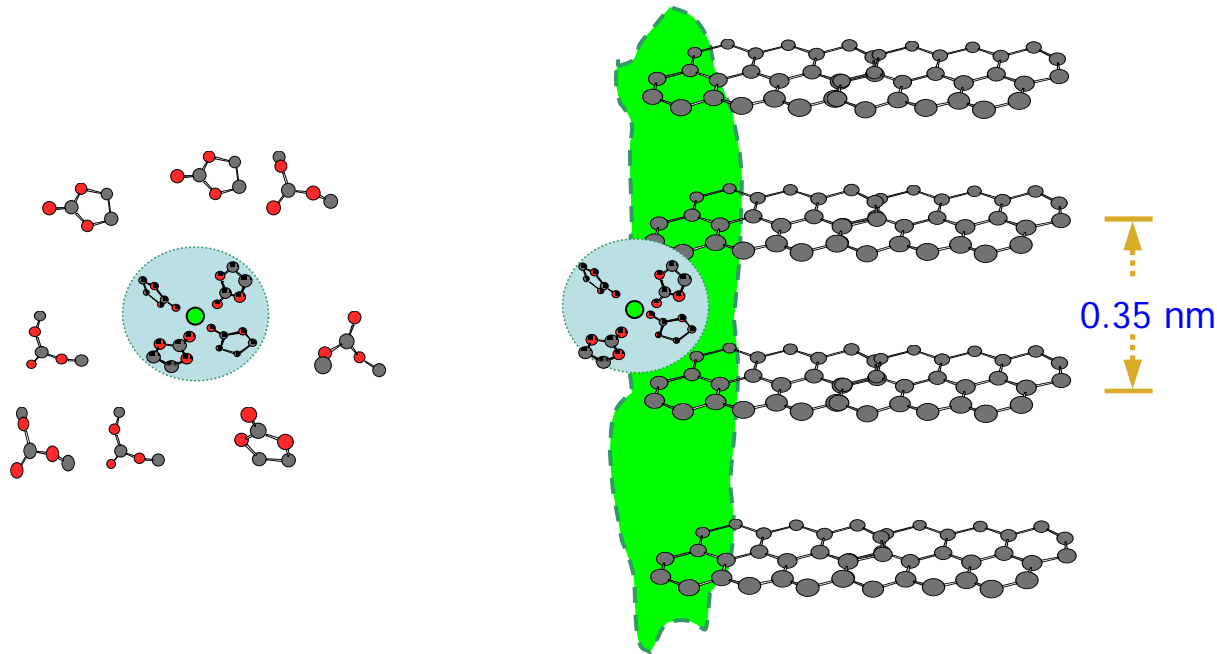
"Solvation-Sheath" Model for SEI Formation

1. Lithium ion is solvated by EC when moving from cathode to graphite anode
2. Below 1V, EC solvent start decomposing and leads to an SEI at the edge of graphite



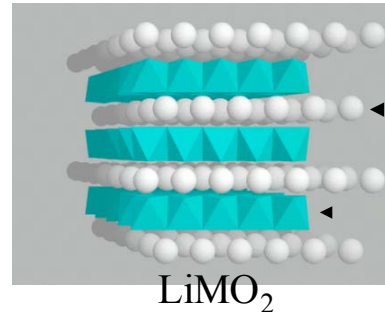
Importance of Solid Electrolyte Interface

Once SEI is formed, all solvated Li^+ must experience a desolvation process



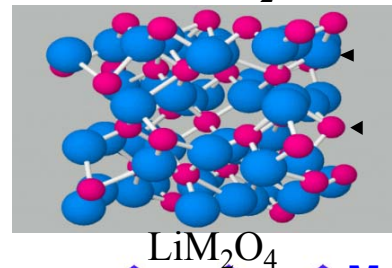
Present Lithium Battery Technologies

Layered
Oxides 2-D



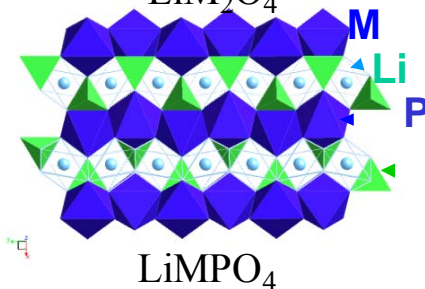
Capacity 150 mAh/g
 $V = 3.6 \text{ V}$

Spinel Oxides
3-D



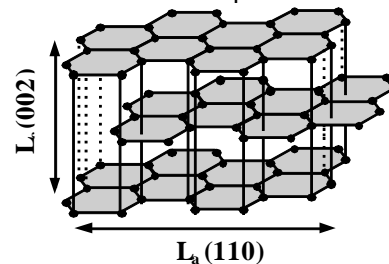
Capacity 100 mAh/g
 $V = 3.8 \text{ V}$

Polyanions,
Olivines 1-D



Capacity 150 mAh/g
 $V = 3.3 \text{ V}$

Current Anode LiC_6
372 mAh/g



Capacity 372mAh/g
 $V = 0.2 \text{ V}$

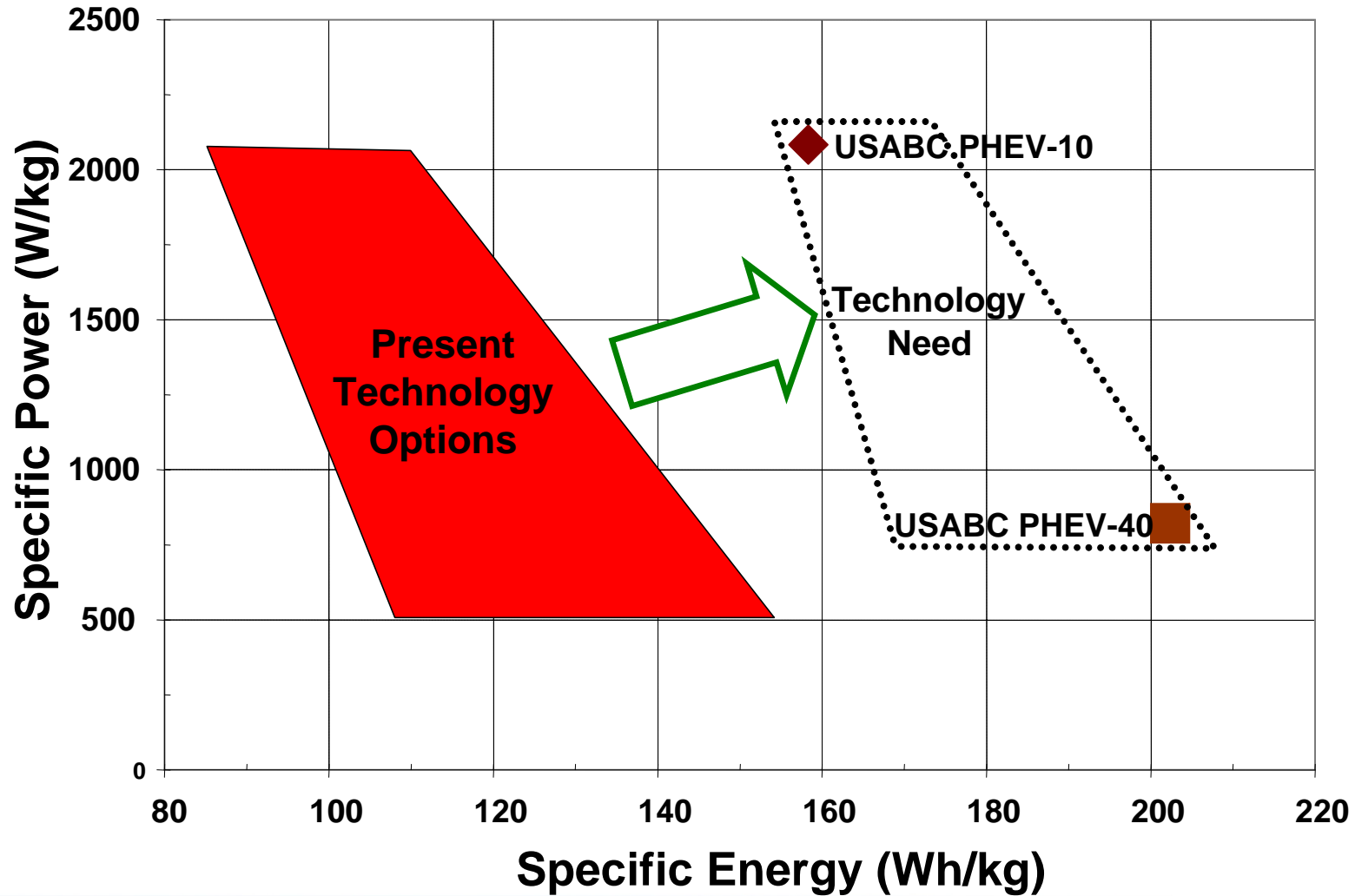


Chevy Voltage Battery Technology

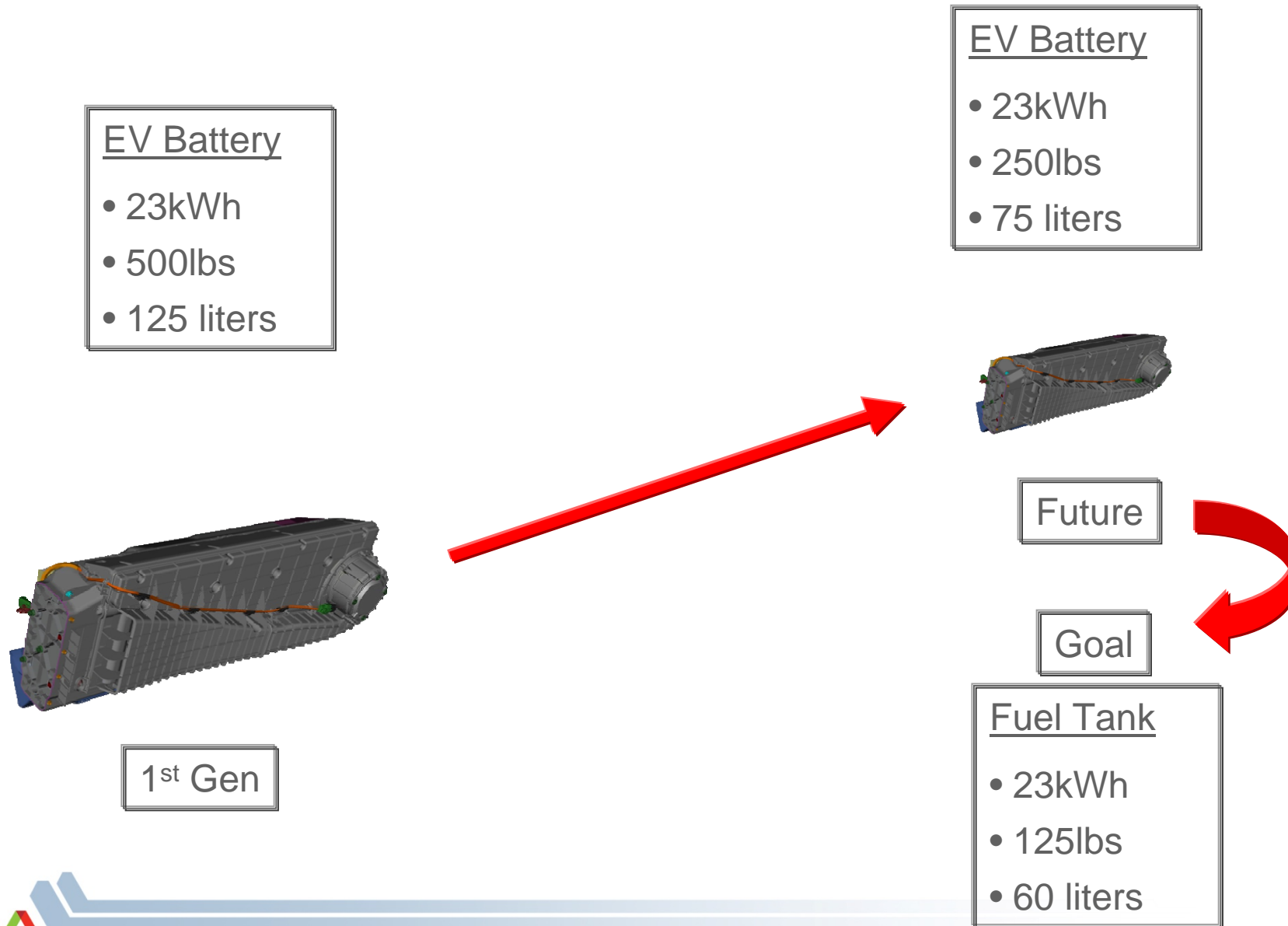
- Chevy Volt uses Argonne's LiMn_2O_4 /NMC material technology
- Chemistry is based on low Energy LiMn_2O_4 spinel
- Battery is very large and costly



High Energy Battery Systems are Needed to Reduce Vehicle Cost



Battery Technology Energy Evolution



Next Generation lithium ion batteries

>250-400 mAh/g
3X current cathode
3.5 – 5.0 volt

Next Generation
Cathode

Non flammable & high
Voltage Electrolyte

Next Generation
electrolyte

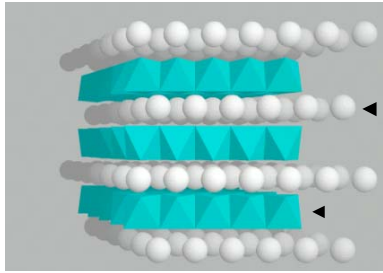
> 1000 mAh/g
3X current anode
0 – 0.5 volt

Next Generation
anode

Electrode interface
stabilization

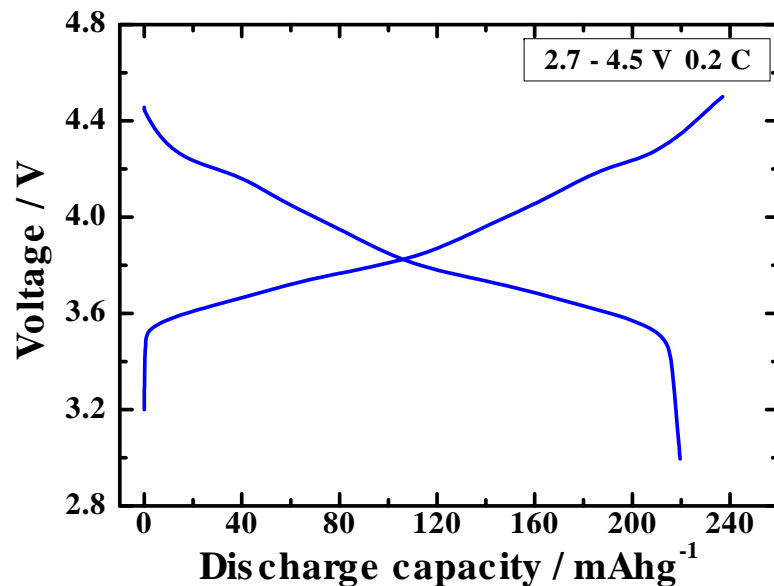


Increase capacity of conventional cathodes by operating at high voltages (250wh/kg)

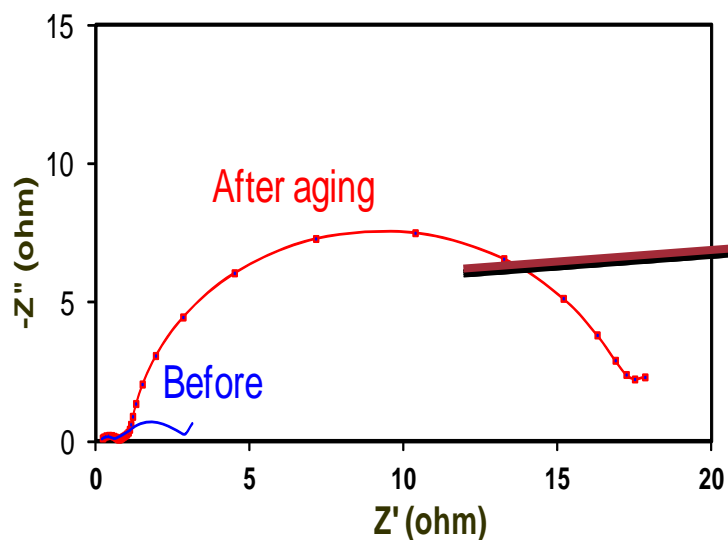


NCA provide 150 mAh/g at cut off voltage of 4.1V

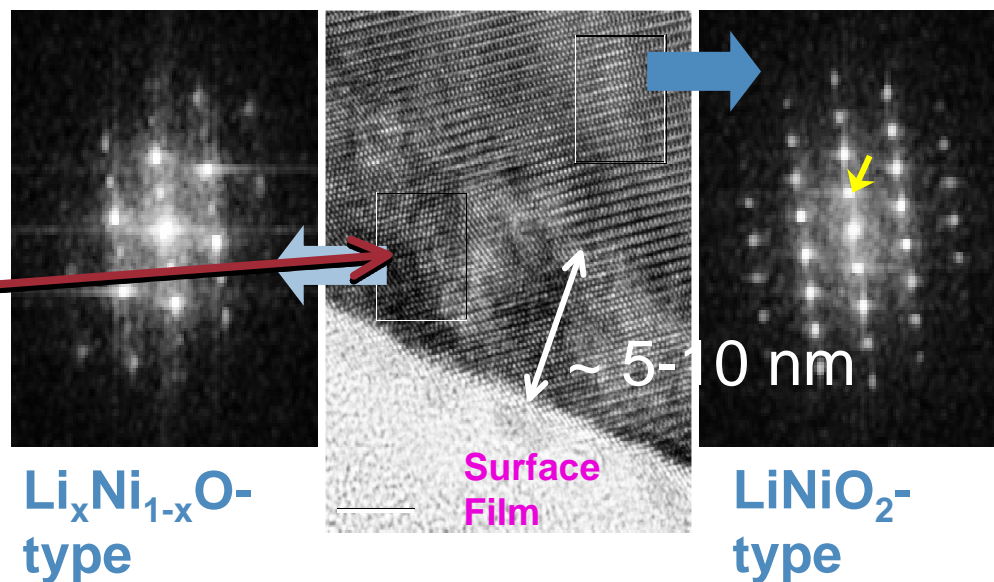
At 4.5V, NCA provide 220mAh/g capacity but poor cycle life



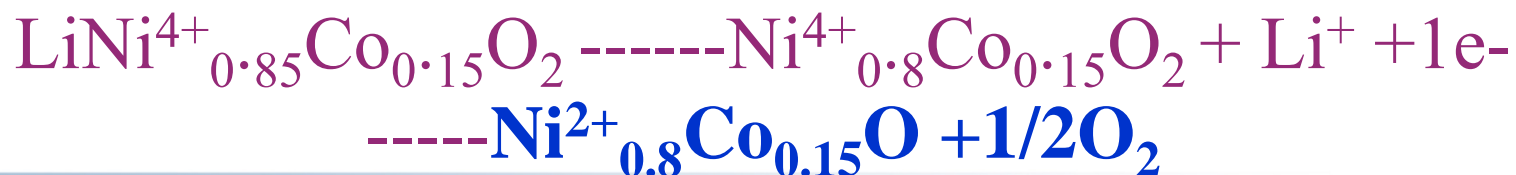
Surface reactions is the cause of power and capacity fade in NCA at high voltages



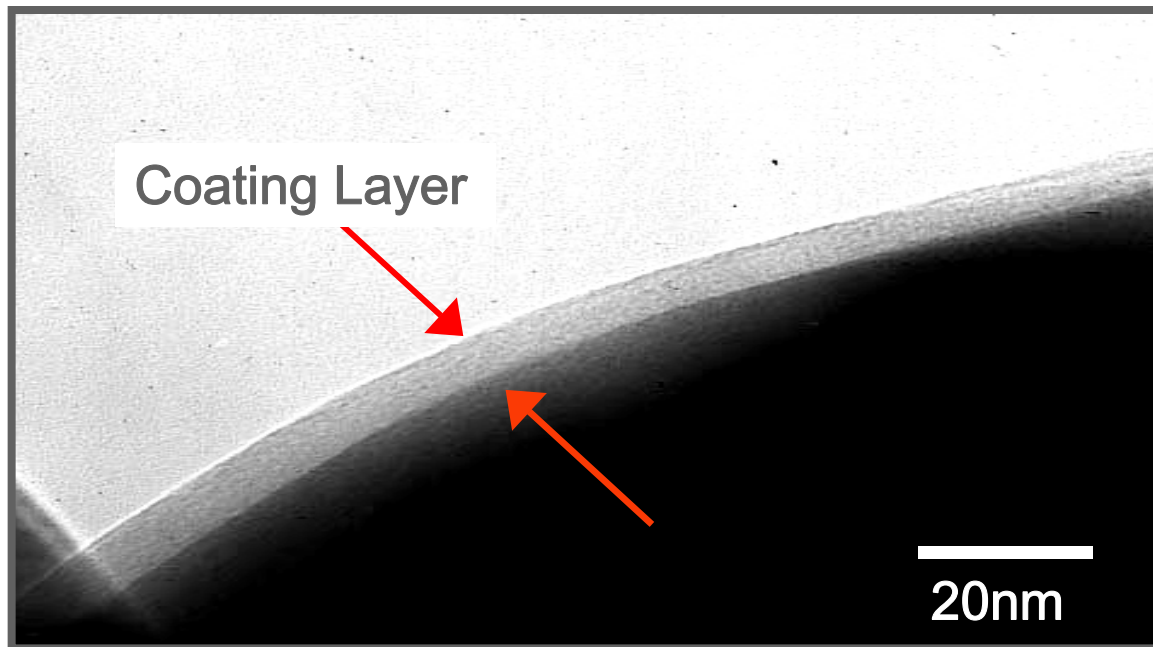
AC impedance of aged NCA/Graphite cell (55°C) using reference electrode



HRTEM of aged NCA electrode



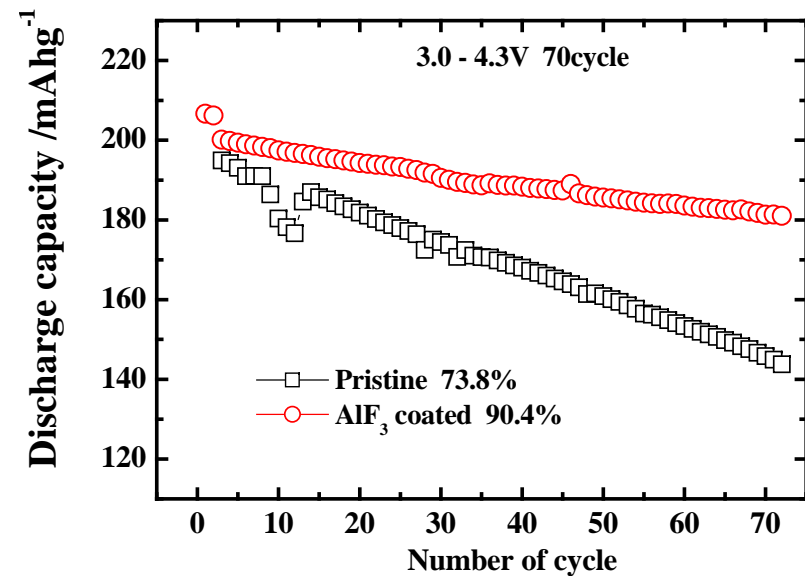
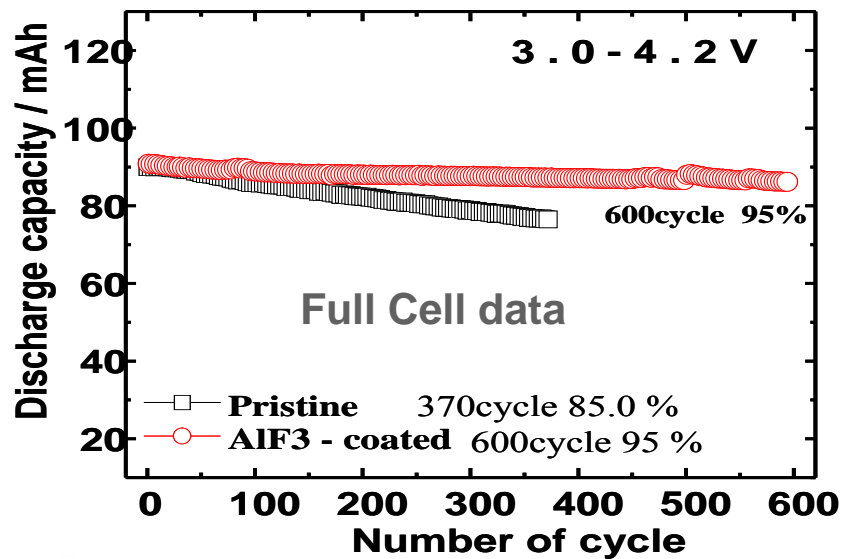
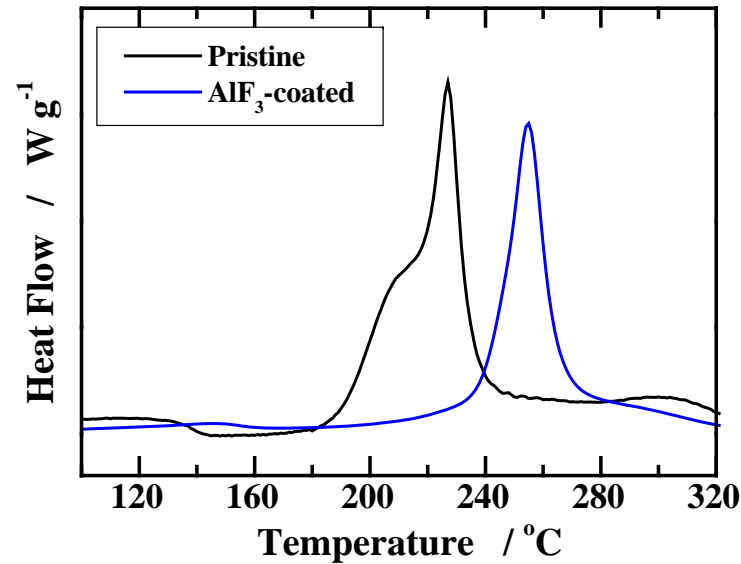
Coating the cathode particle with AlF_3 can improve the safety of the lithium battery



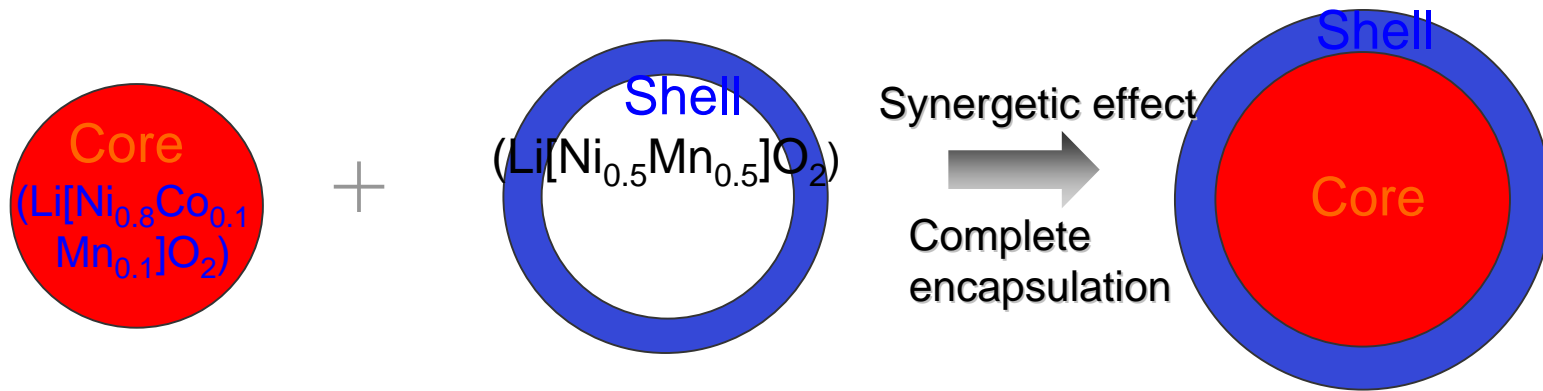
Coating thickness is very uniform and less than 8nm



AlF₃-coated on Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O₂ (NCA)



Concept of Core-Shell type Cathode

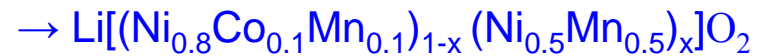


- High capacity. (200 mAh/g)
- Poor thermal stability.
- Structurally unstable due to reactive Ni⁴⁺.

- Good thermal stability.
- Low capacity. (150 mAh/g)

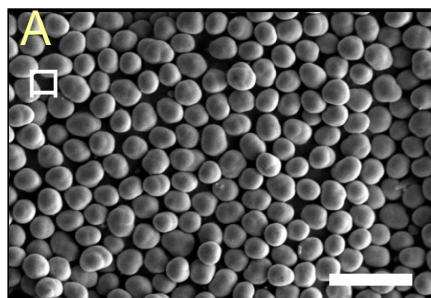
➤ High Energy density and low cost.

➤ Good thermal stability.

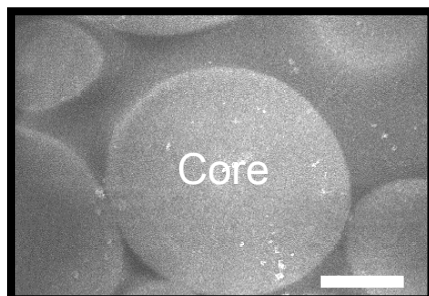


Synthetic Route

STEP I



50 μm

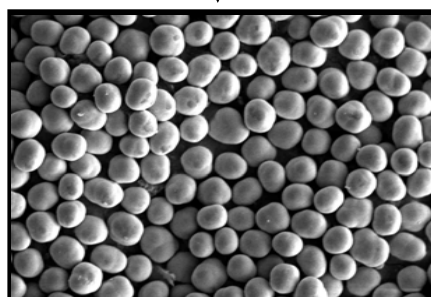


5 μm

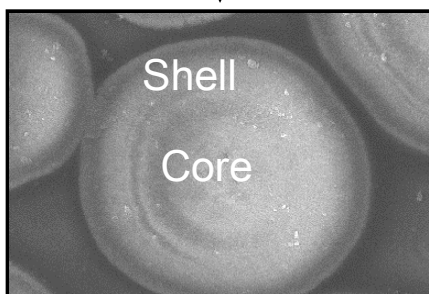
$[\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}](\text{OH})_2$
co-precipitation



STEP II



50 μm



5 μm

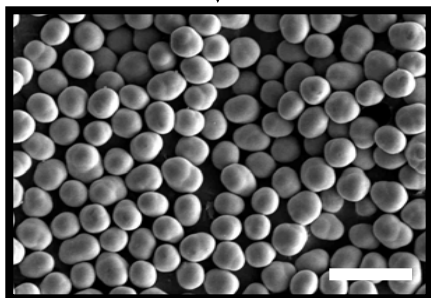
Encapsulation of
 $[\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}](\text{OH})_2$ core by
 $[\text{Ni}_{0.5}\text{Mn}_{0.5}](\text{OH})_2$ shell
via co-precipitation



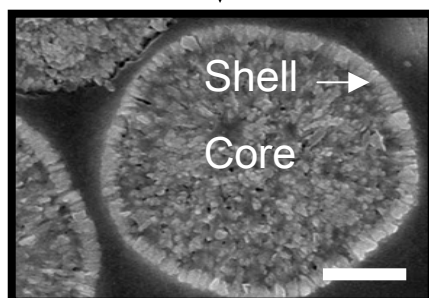
Formation of core-shell hydroxide
 $[(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})_{1-x}(\text{Ni}_{0.5}\text{Mn}_{0.5})_x](\text{OH})_2$



STEP III



50 μm



5 μm

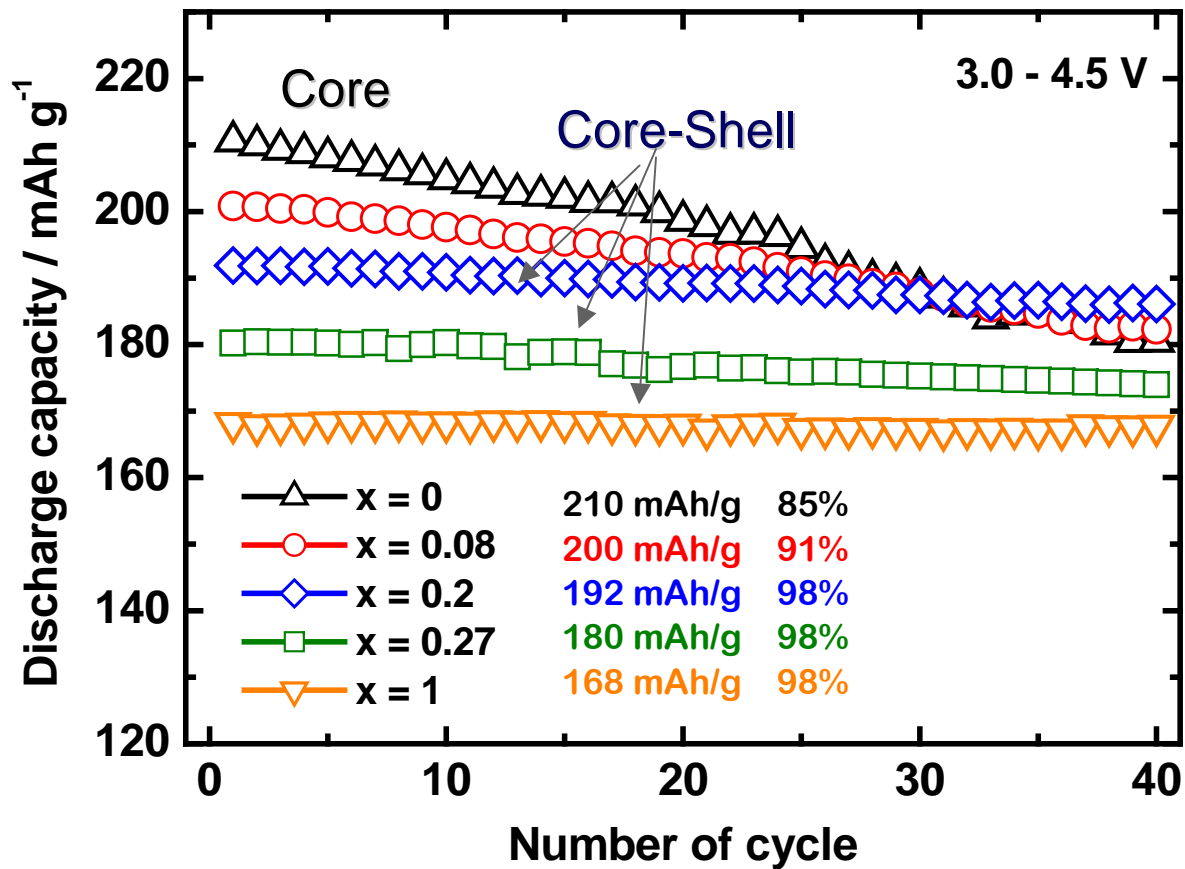
Incorporation of Li salt
by calcination at high temperature



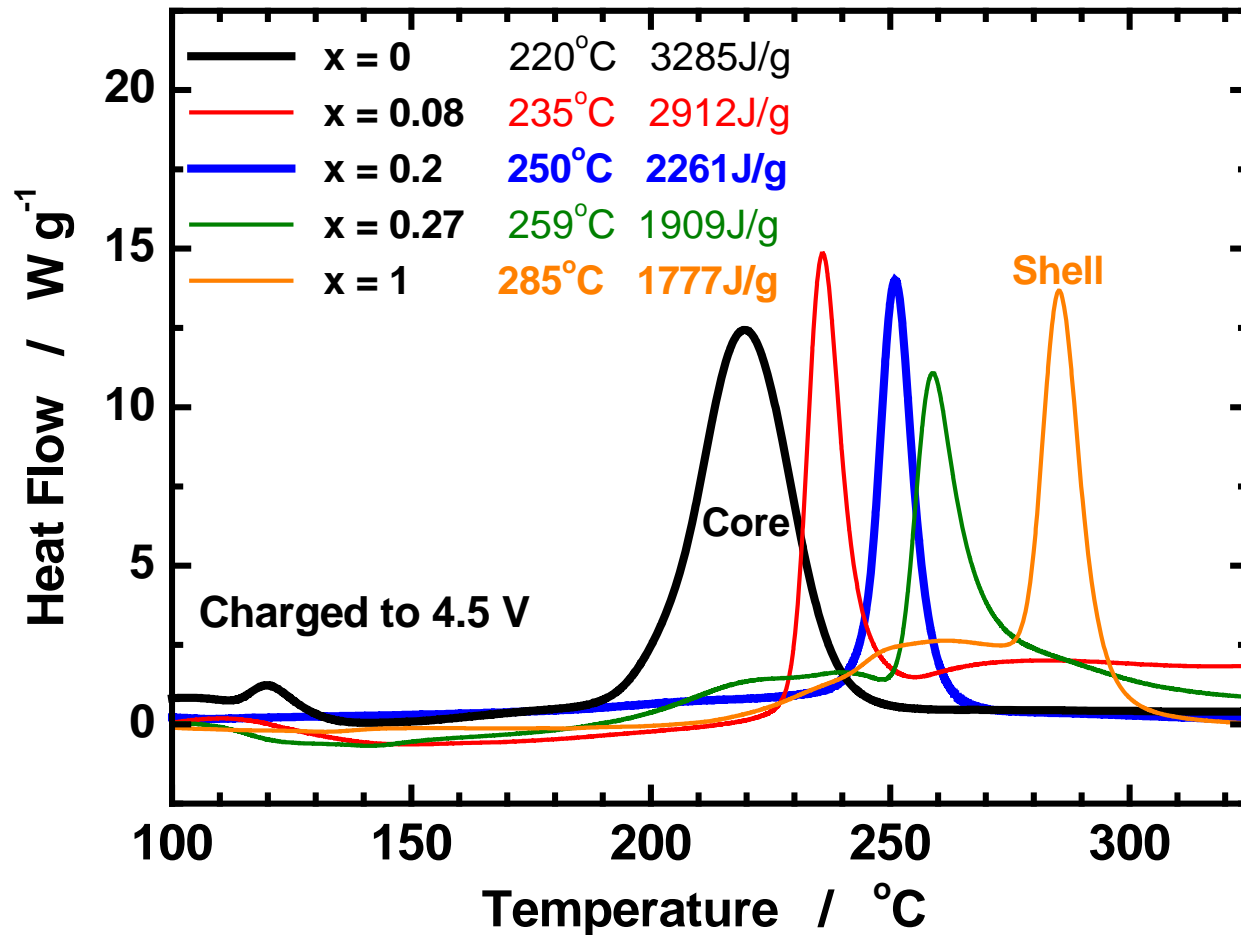
Formation of spherical core-shell
 $\text{Li}[(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})_{1-x}(\text{Ni}_{0.5}\text{Mn}_{0.5})_x]\text{O}_2$



Cycling Performance of Core-Shell $\text{Li}[(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})_{1-x}(\text{Ni}_{0.5}\text{Mn}_{0.5})_x]\text{O}_2$



DSC Profiles of Core-Shell $\text{Li}[(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})_{1-x}(\text{Ni}_{0.5}\text{Mn}_{0.5})_x]\text{O}_2$

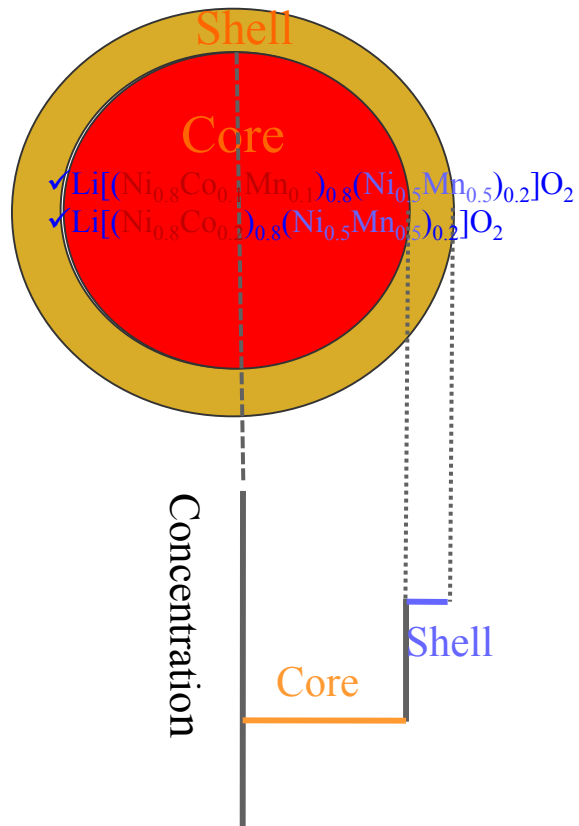


➤ Simple encapsulation of the core by shell give rise to a significant increase onset Temperature and reduction of heat generation

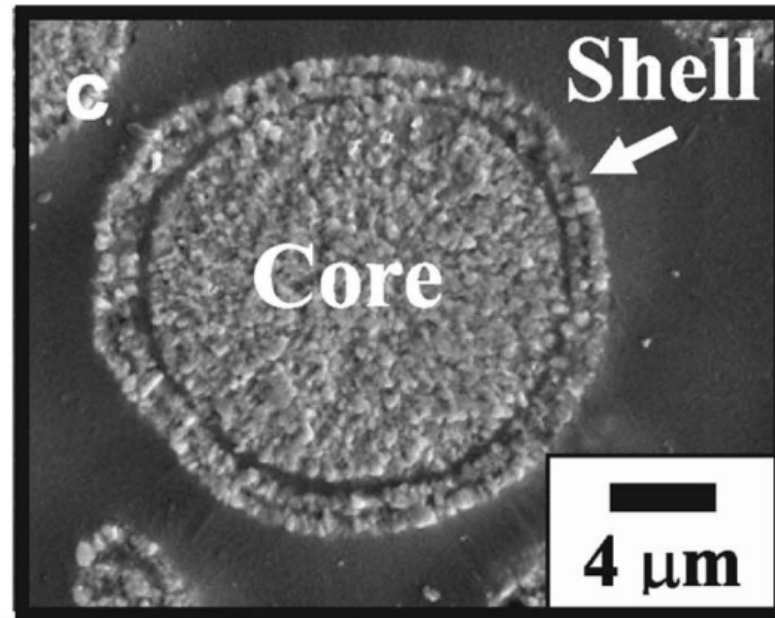
➤ The thermally stable outer shell $\text{Li}_{1-x}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ suppresses the oxygen release from the highly delithiated $\text{Li}_{1-x}[\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}]\text{O}_2$

Problems of Core-Shell materials

Core-Shell



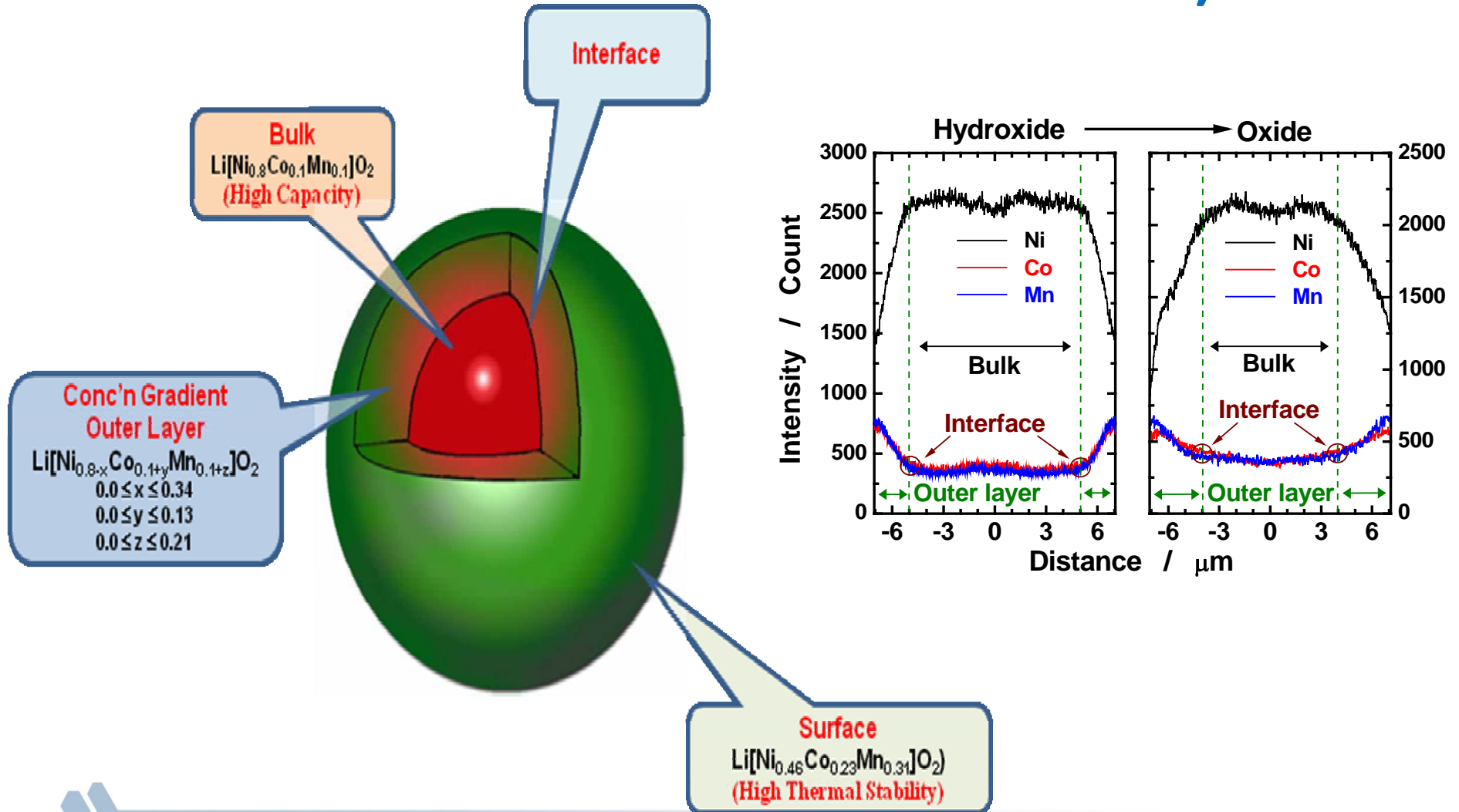
Core-Shell after cycling



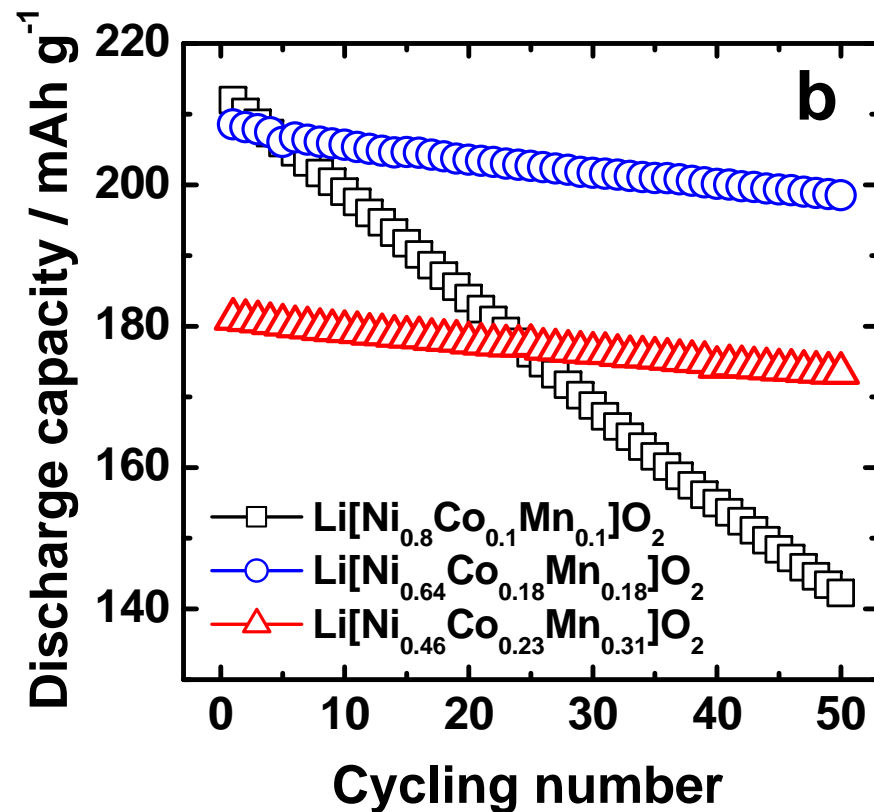
- ✓ Abrupt composition change of transition metal at interface between core and shell.
 - ✓ Separation between core and shell; different volume change (Core: 9%, Shell: 2%)
- lead to poor electrochemical performances.



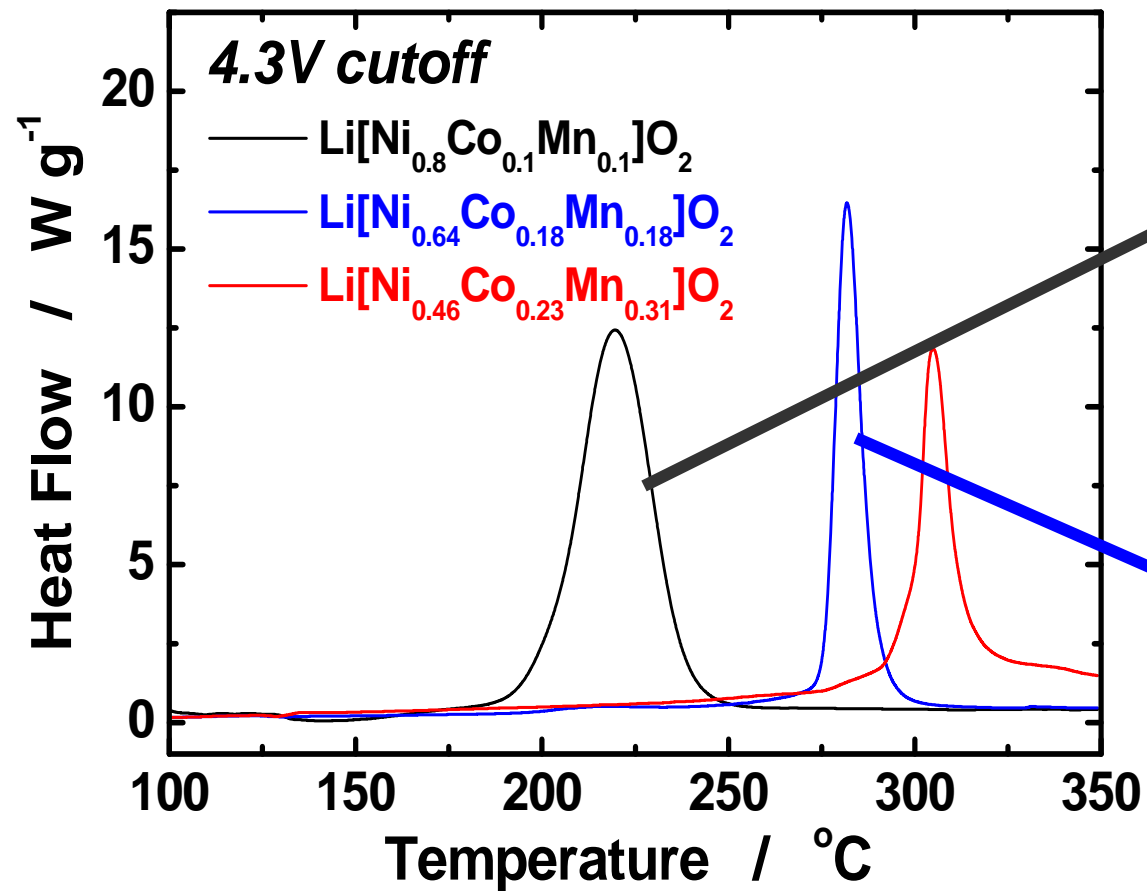
Using Functional material design (Gradient concentration material to mitigate a mismatch between core & shell)



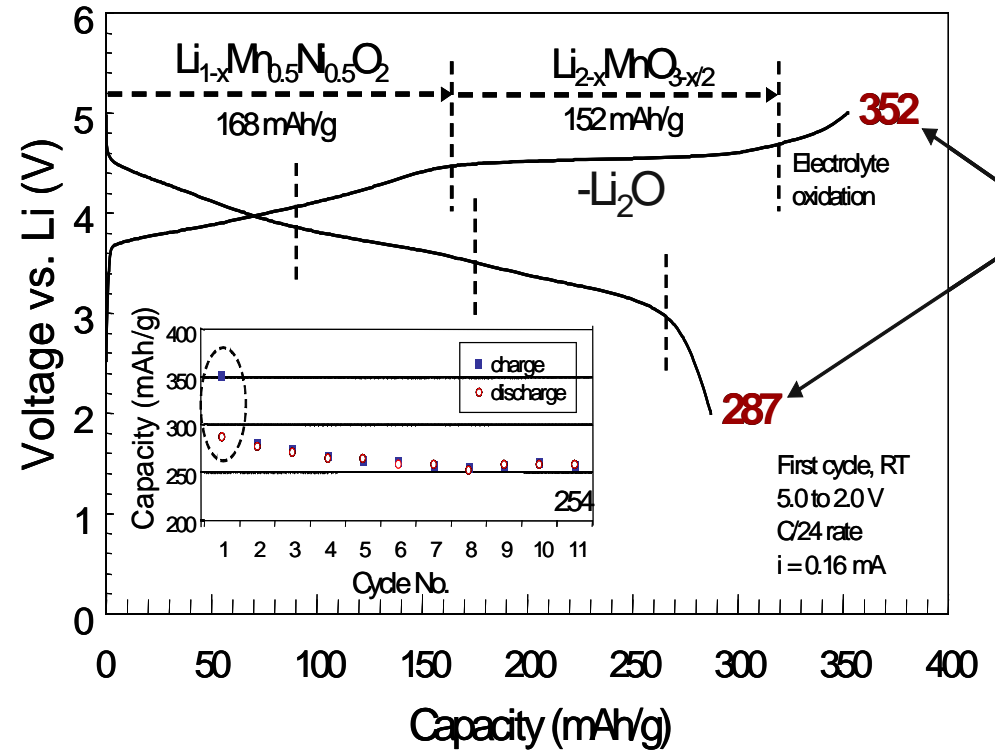
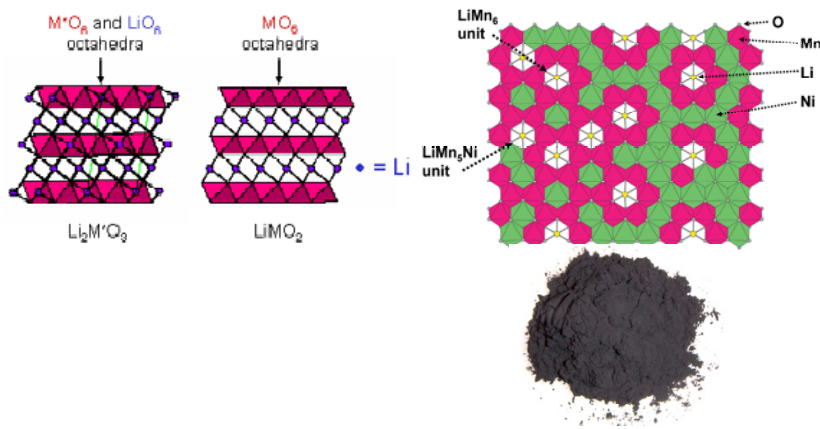
Comparison of safety & cycling performance of gradient concentration material ($\text{LiNi}_{0.64}\text{Co}_{0.18}\text{Mn}_{0.18}\text{O}_2$) $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (bulk composition) and $\text{LiNi}_{0.46}\text{Co}_{0.23}\text{Mn}_{0.31}\text{O}_2$ outer surface composition)



Differential Scanning Calorimetry (DSC) of fully Charged Core and Continuous Gradient Material



ANL's High Energy composite electrode $[x\text{Li}_2\text{MnO}_3 \bullet y\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2]$ (300wh/kg)

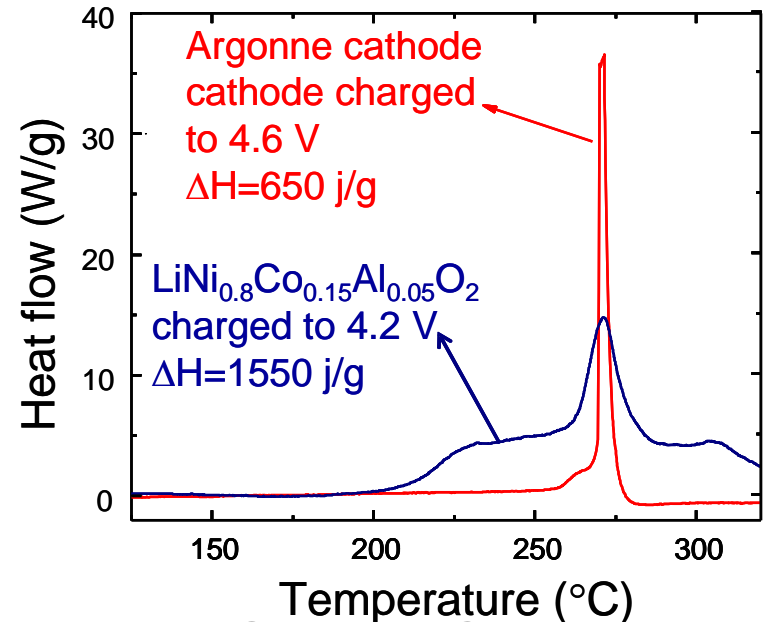
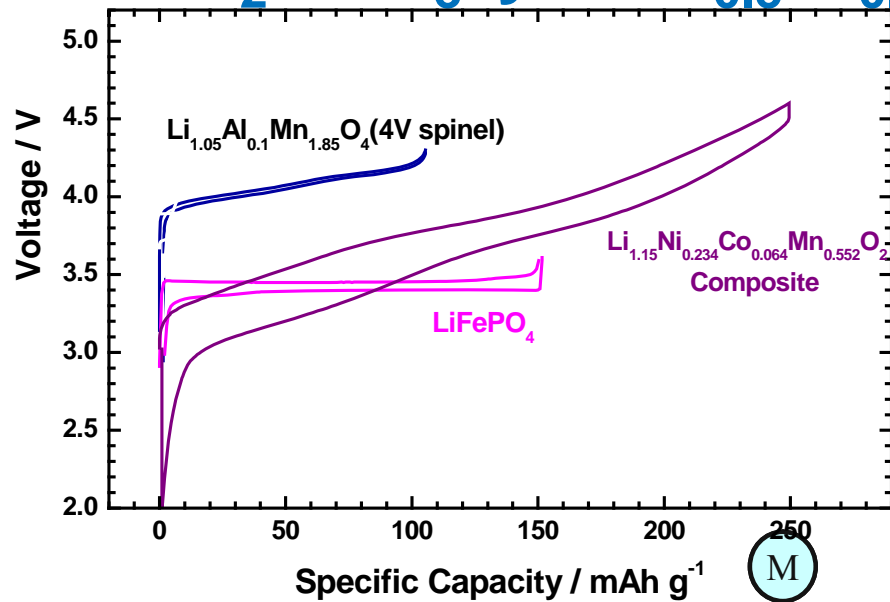


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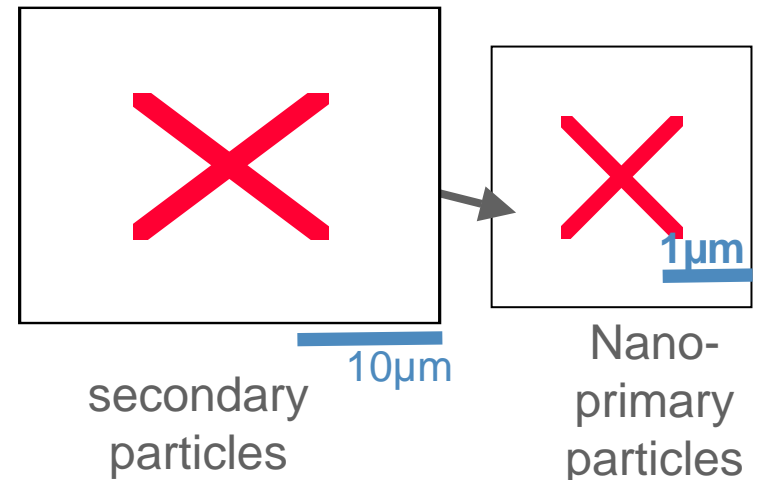
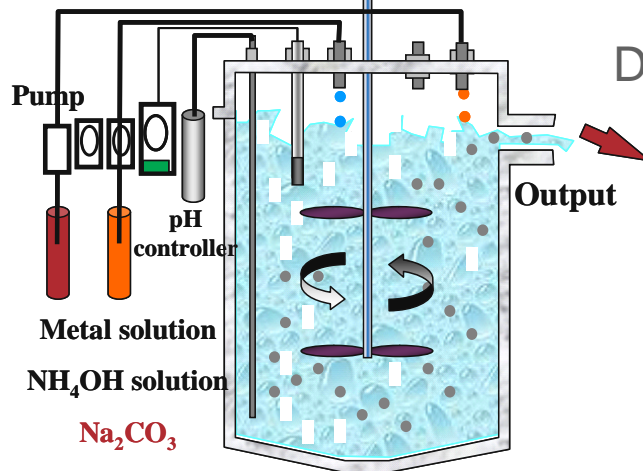
- [K. Amine, 2009 R&D 100 award](#)
- [Licensed to Toda America, BASF, Envia and NanoeXa, LG & GM](#)

ANL High Energy Composite Electrode

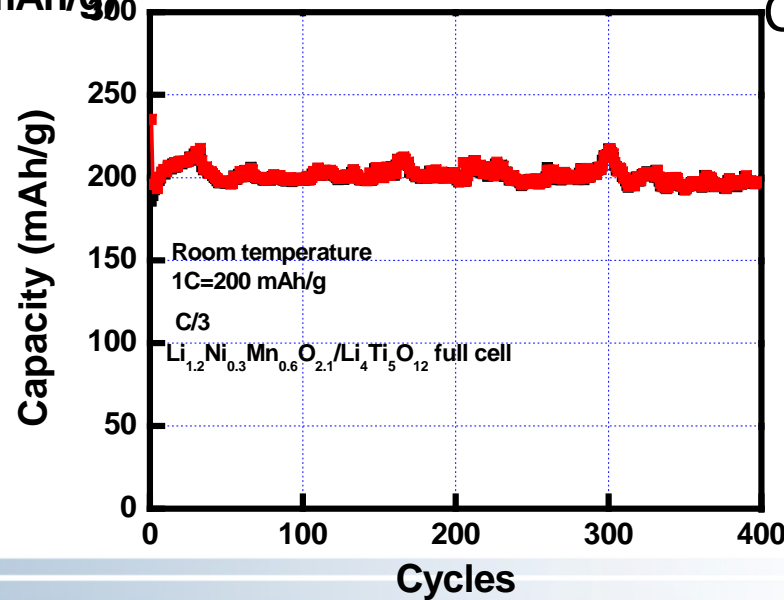
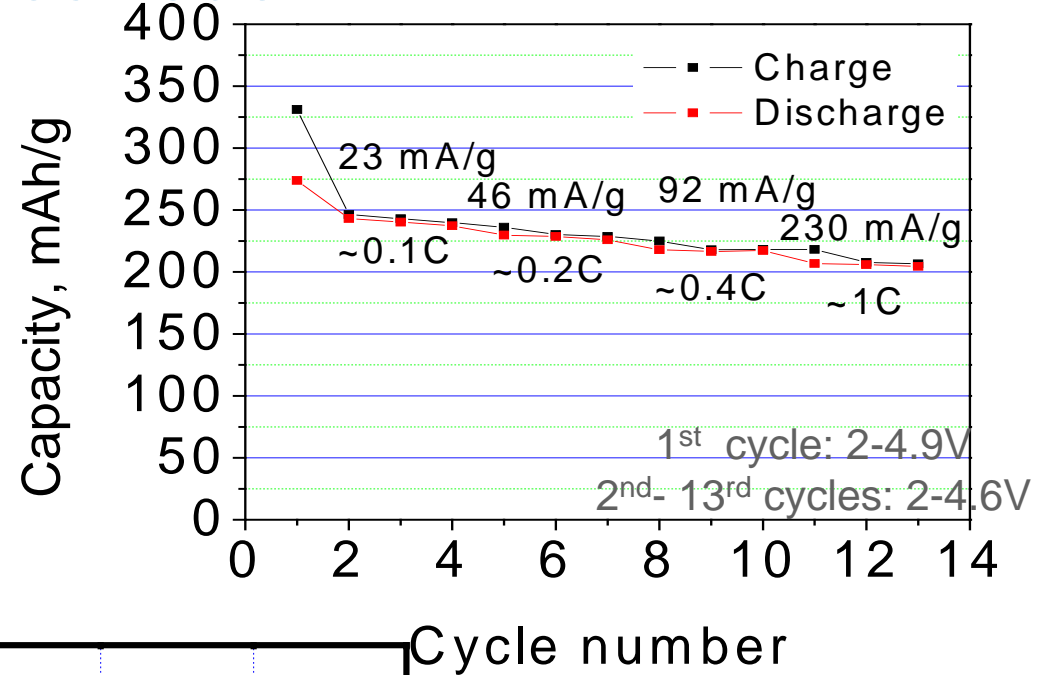
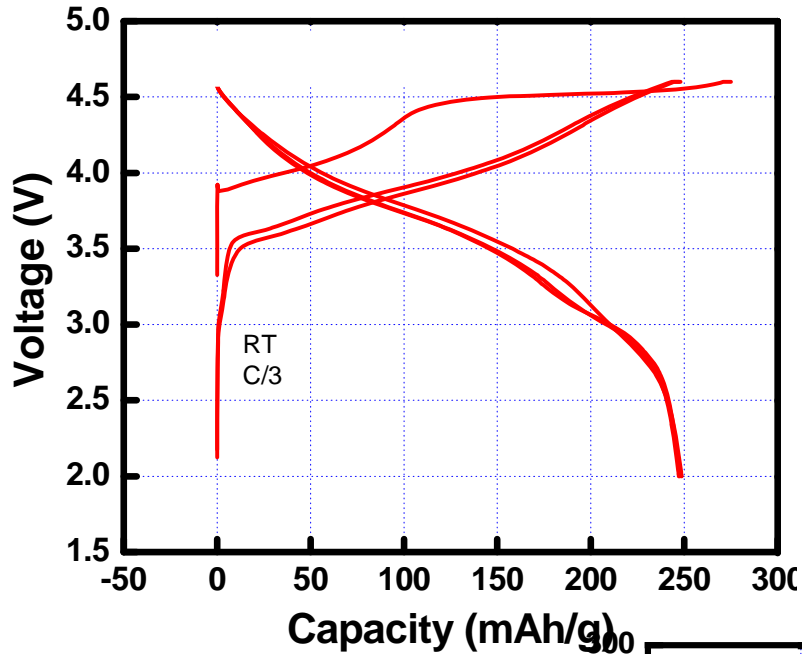
$x\text{Li}_2\text{MnO}_3 \cdot y\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ for PHEV-40 & EVs



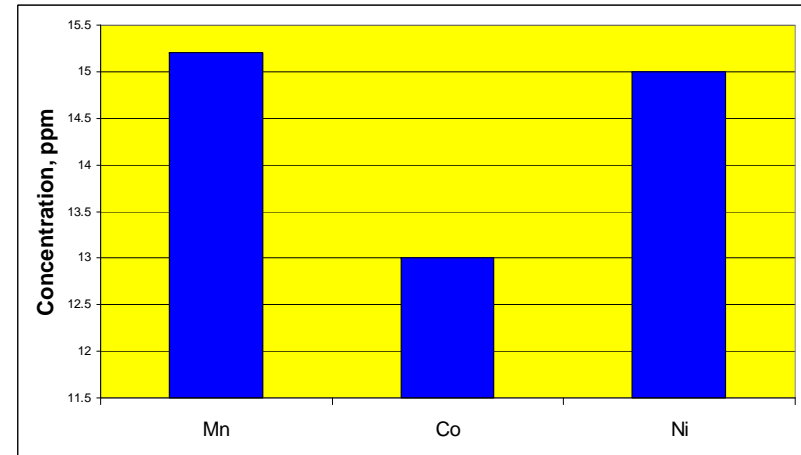
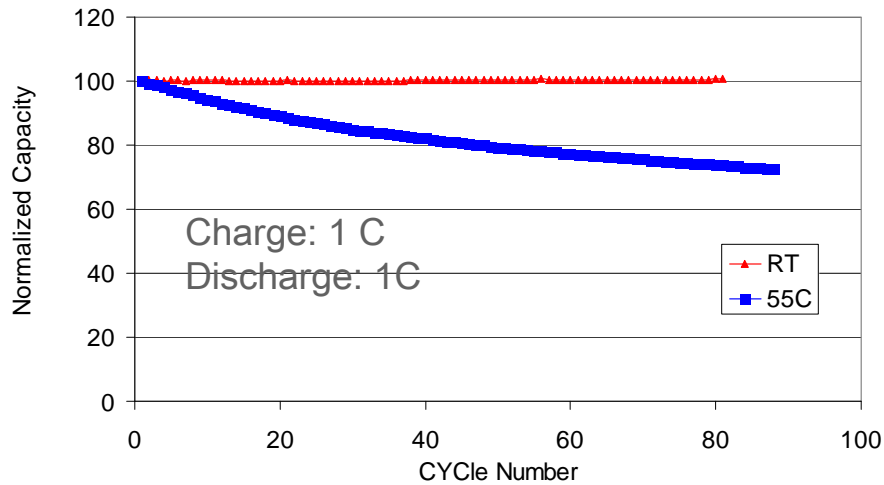
Differential Scanning Calorimetry test



Electrochemical behaviors of ANL composite electrode

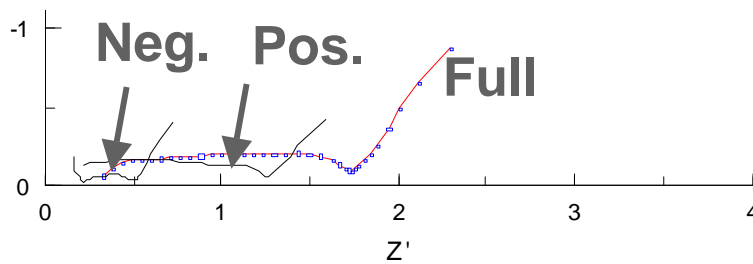


Issue with NMC/Graphite cell at Elevated Temperature

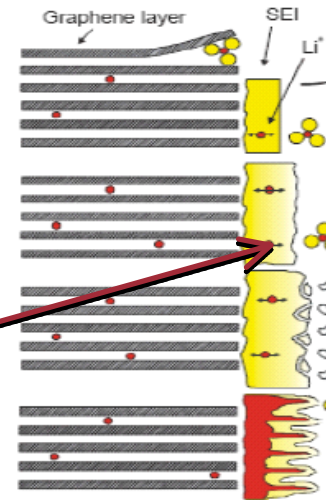
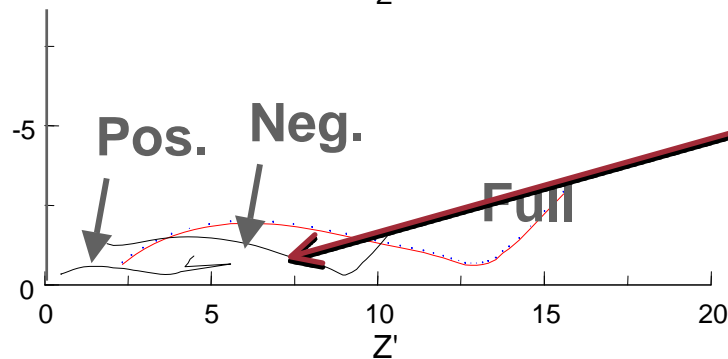


Mn, Ni and Co dissolution

1st cycle



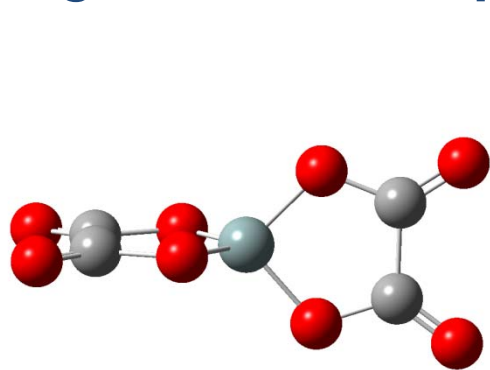
25th cycle



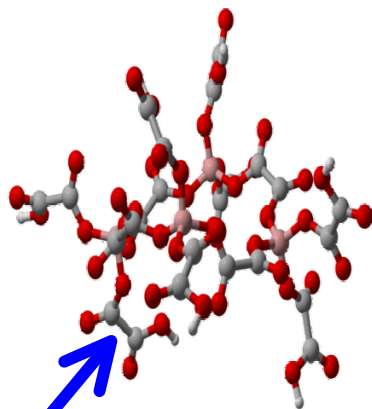
Mn, Ni metal act as a catalyst in the decomposition of the SEI



LiBOB additive forms a stable SEI, resulting in a significant improvement in the cell performance

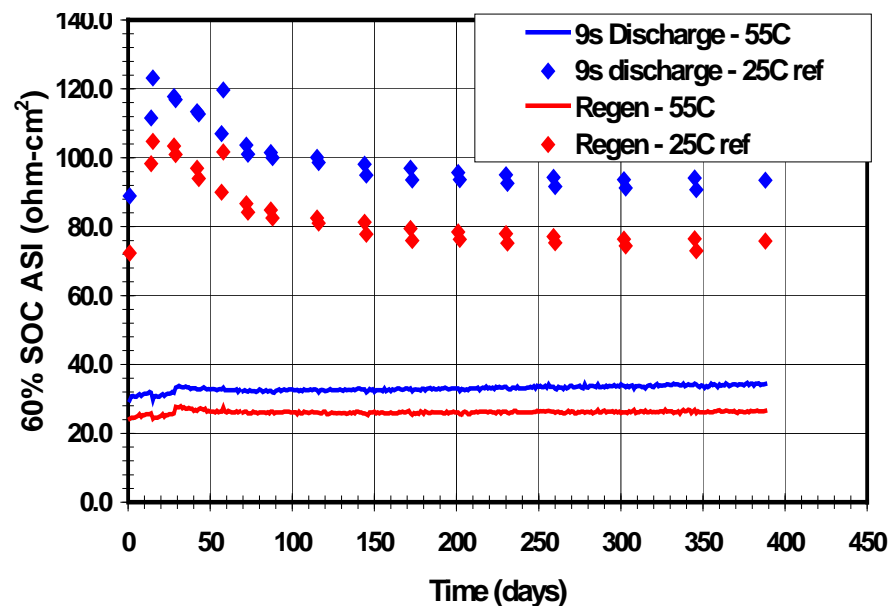
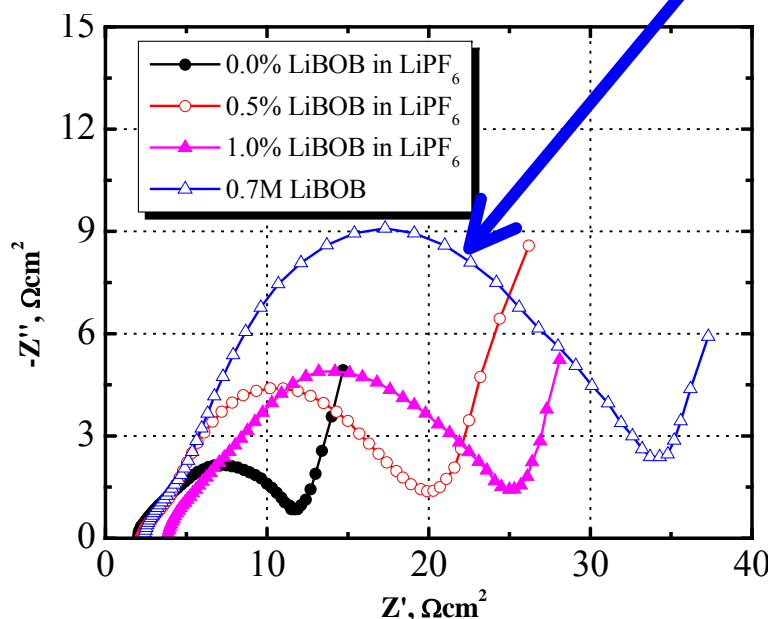


BOB⁻, B(C₂O₄)₂⁻



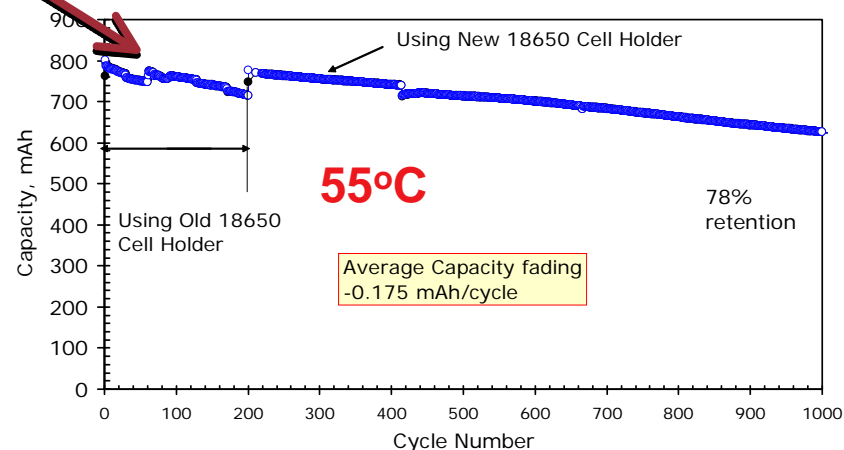
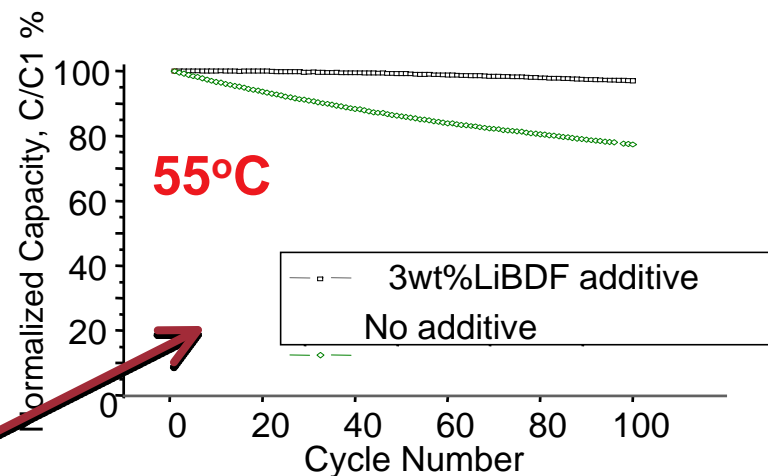
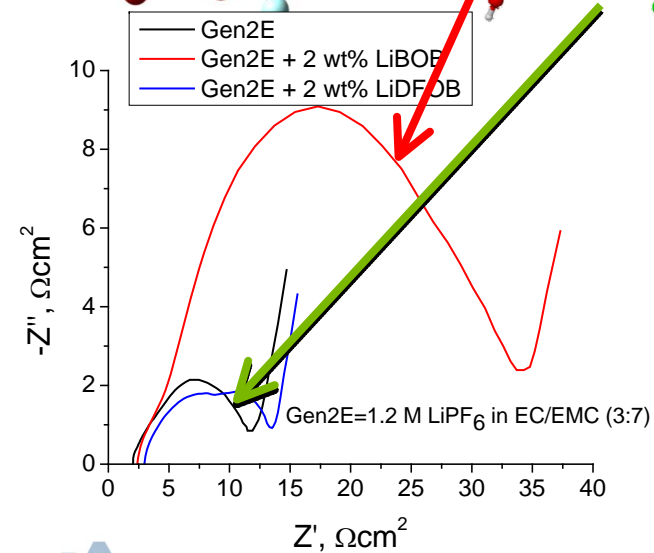
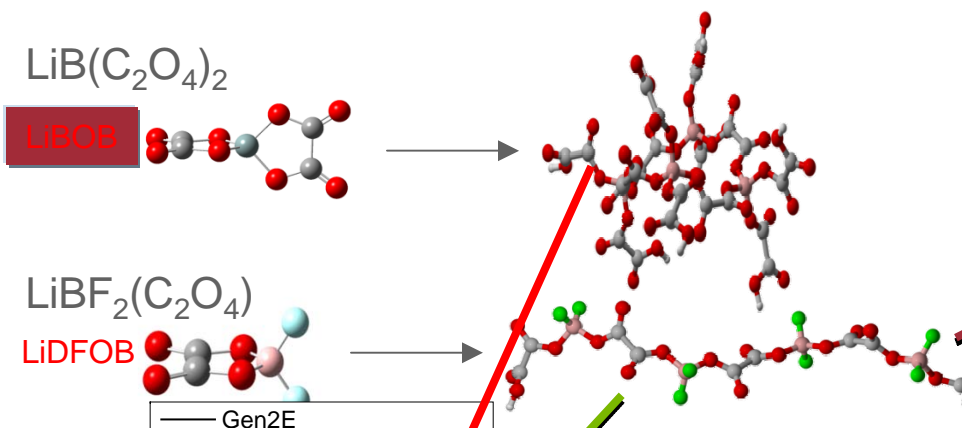
BOB tetramer structure

Density functional calculations show the LiBOB 3-D polymeric structure growth.

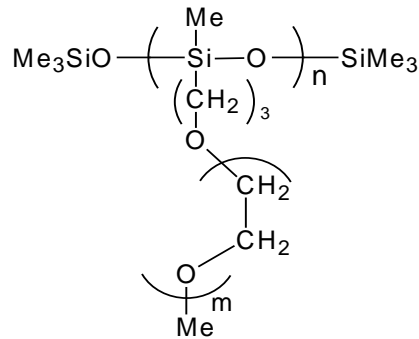


Stabilizing the Interface using Functional Electrolyte Additives for Life & Safety improvement

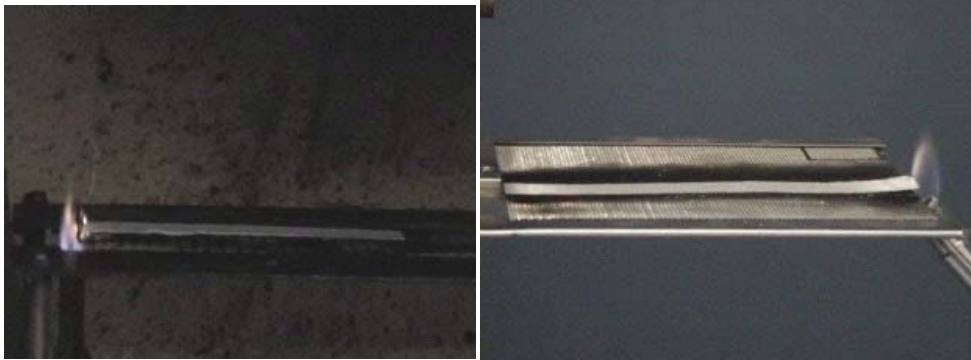
- Density functional calculations show that putting fluorines on the LiBOB additive (lower reaction) prevents 3-D polymer growth



New ANL's High Voltage and Stable Siloxane Electrolyte for EV Applications

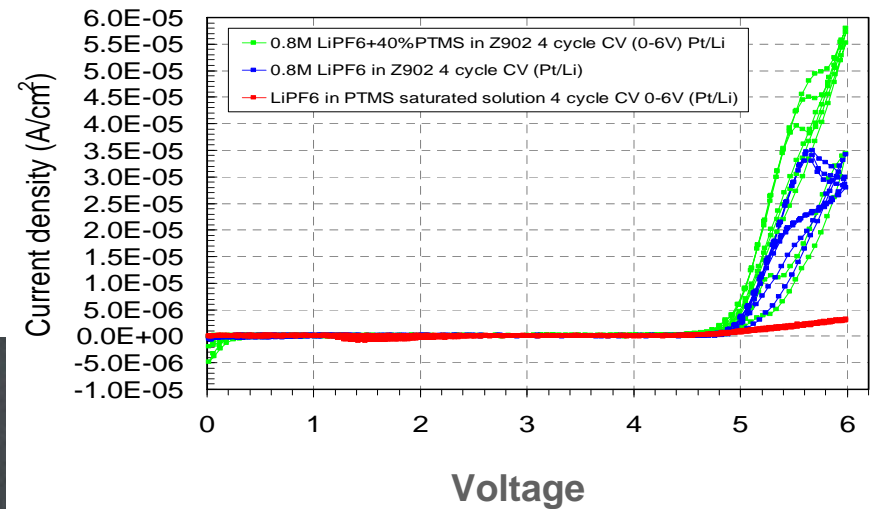


Conductivity = 1.23×10^{-3} S/cm
Voltage >5.0V



**Carbonate
electrolyte**

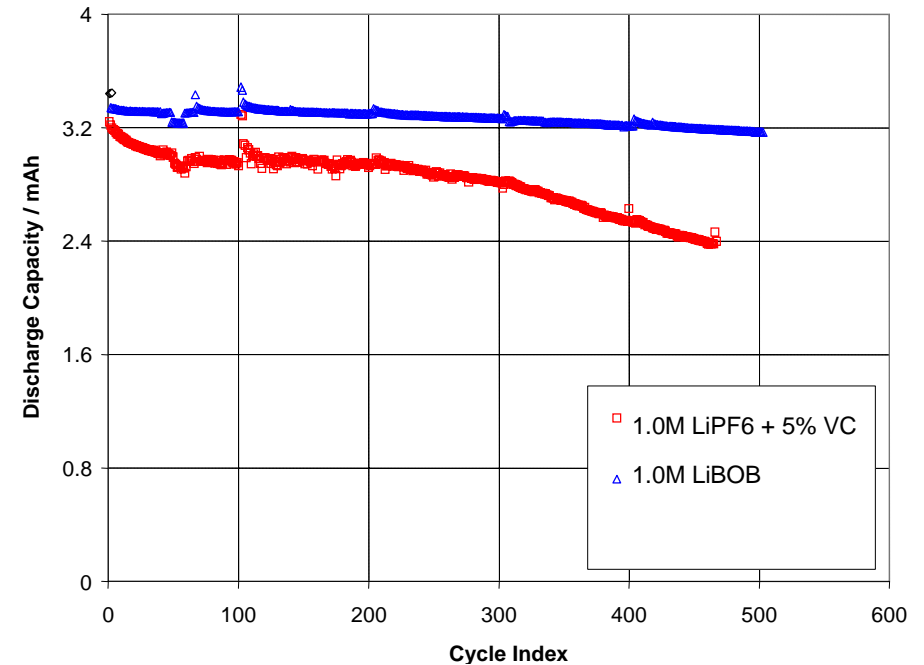
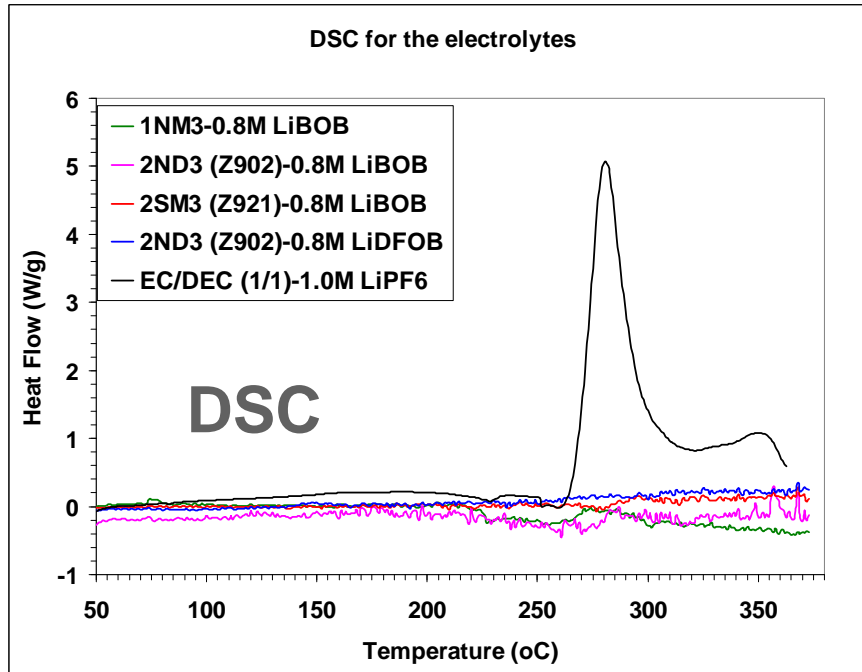
**Siloxane
electrolyte**



**Siloxane electrolyte exhibits high
voltage stability**



Cycle Performance Of the Siloxane Electrolyte using NMC/graphite system



Siloxane shows no reactivity with electrolyte at high temperature

Cells based on siloxane shows outstanding cycleability at 4.2V and 55°C



Spark ignition test under cell heating

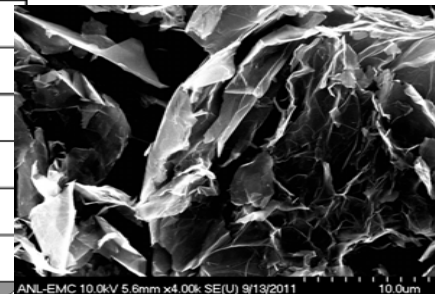
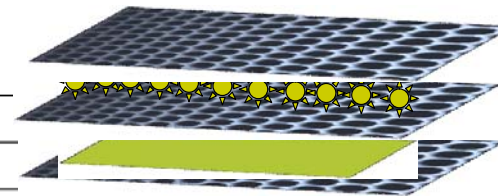
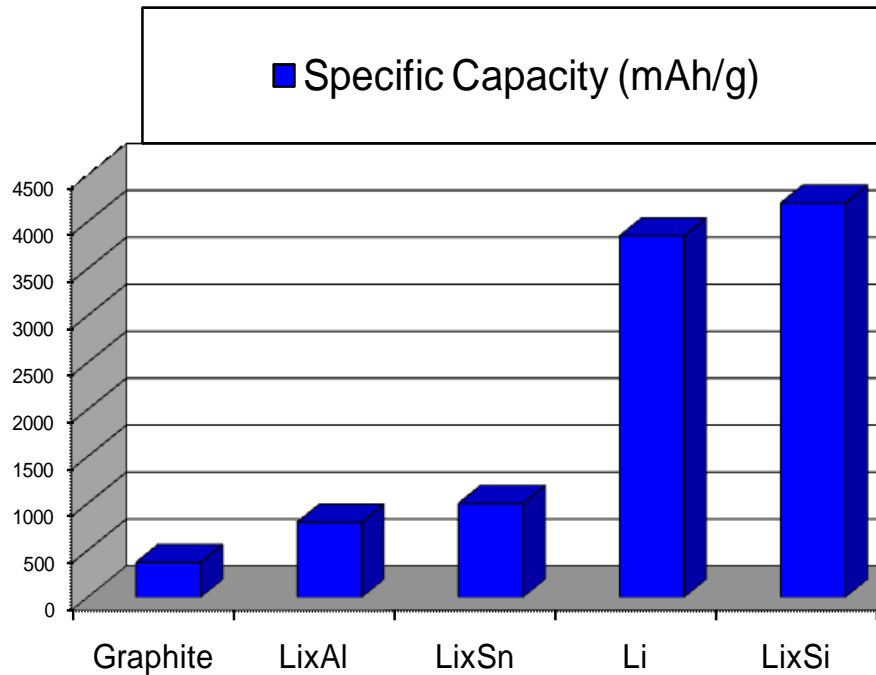
(Standard Electrolyte)



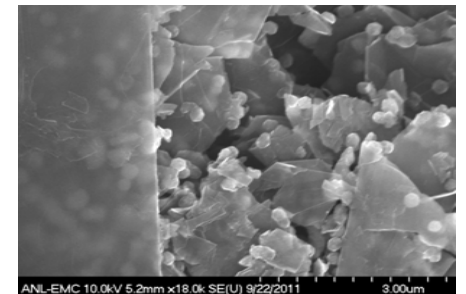
Siloxane Electrolyte



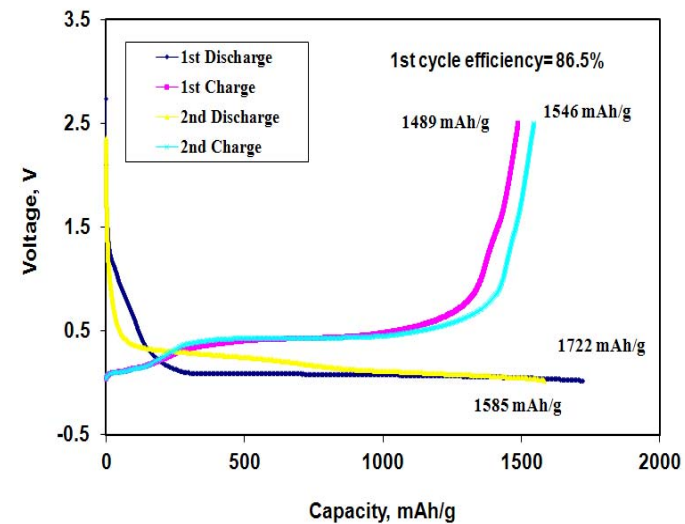
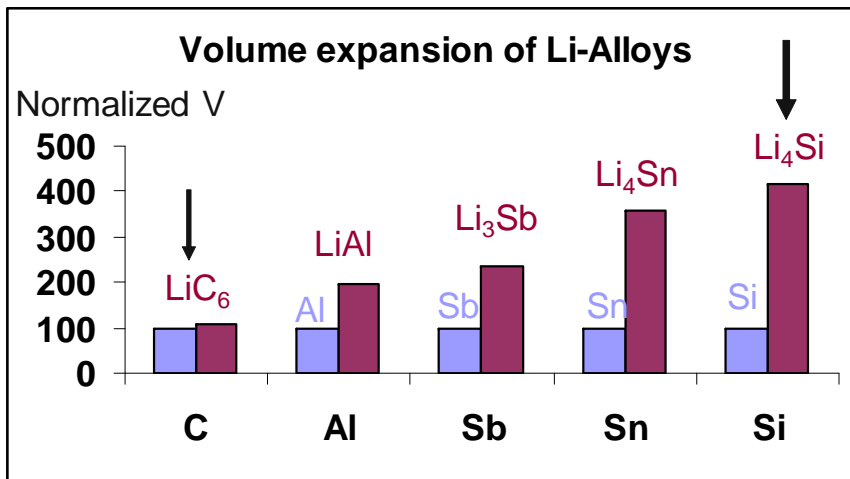
Very High Energy Si-based Anodes



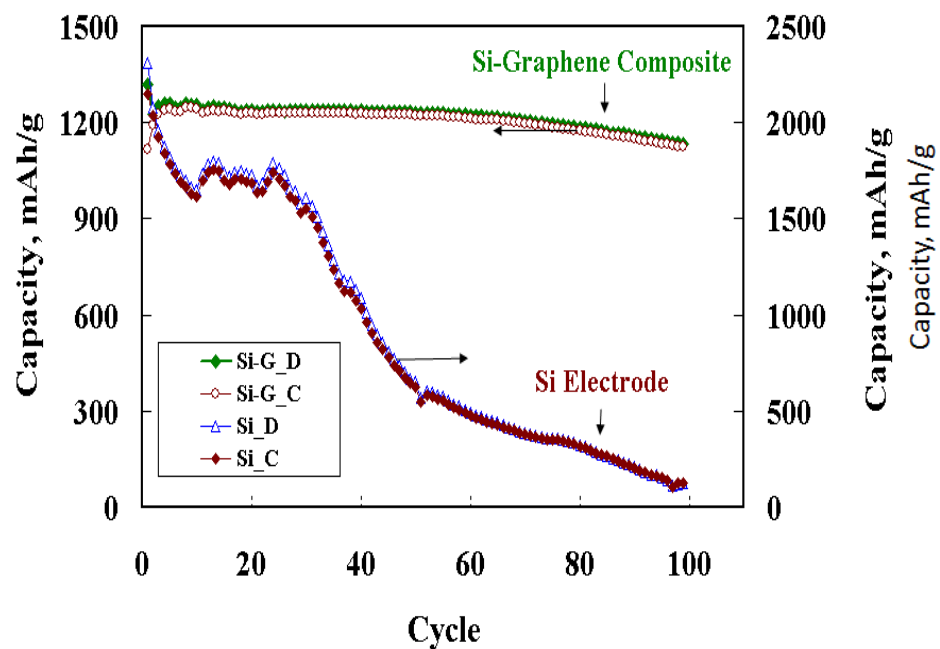
Graphene



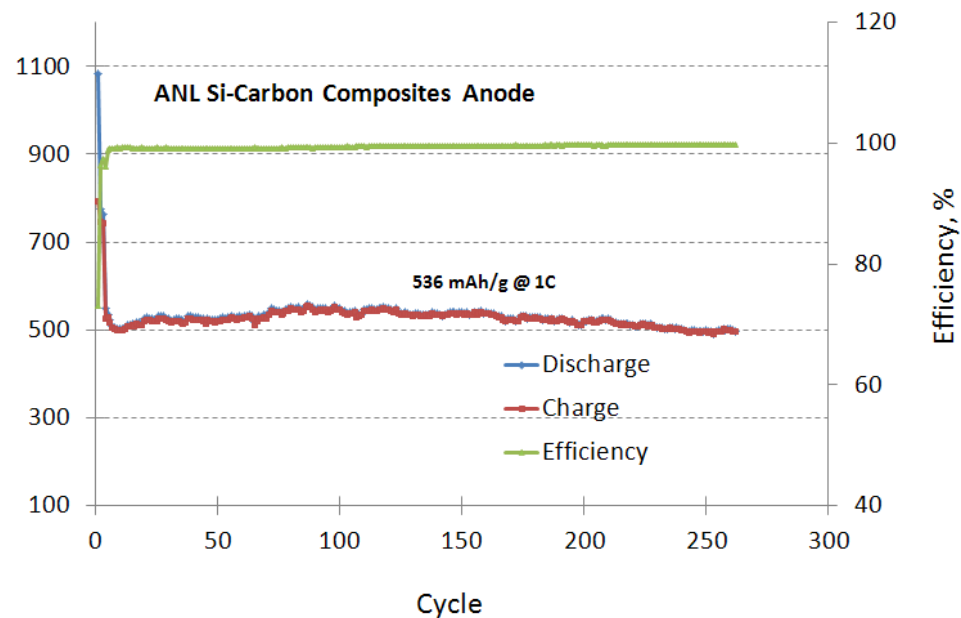
Si-Graphene



Cycling Performance at Different rates



C/5 rate



1C rate



Conclusions

- ✓ Argonne is investigating a whole range of battery chemistries for smart grid, HEVs, PHEVs and EVs
- ✓ ANL new composite electrode and Gradient materials have a strong potential to enable long range EVs and next generation low cost Chevy Volt.
- ✓ Surface nano-coating of cathodes and electrolyte additives can allow for increase energy, improve cycle life and safety

