Screen Electrode Materials & Cell Chemistries and Streamlining Optimization of Electrode

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Vehicle Technologies
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Vehicle Technologies Program

Overview

Timeline

- Start – Oct. 2008
- Finish – Sep. 2014
- ~45% Complete

Budget

- Total project funding in FY2010
  - –Screening: $350K
  - –Streamlining: $300K

Barriers

- An overwhelming number of materials are being marketed by vendors for Lithium-ion batteries.
- No commercially available high energy material to meet the 40 mile PHEV application established by the FreedomCAR and Fuels Partnership.
- The impact of formulation and fabrication on performance of electrode materials with a broad variation of chemical and physical properties.

Partners and Collaborators

- Andrew Jansen (Argonne National Laboratory)
- Sun-Ho Kang (Argonne National Laboratory)
- Dennis Dees (Argonne National Laboratory)
- Jai Prakash and Aadil Benmayza (Illinois Institute of Technology)

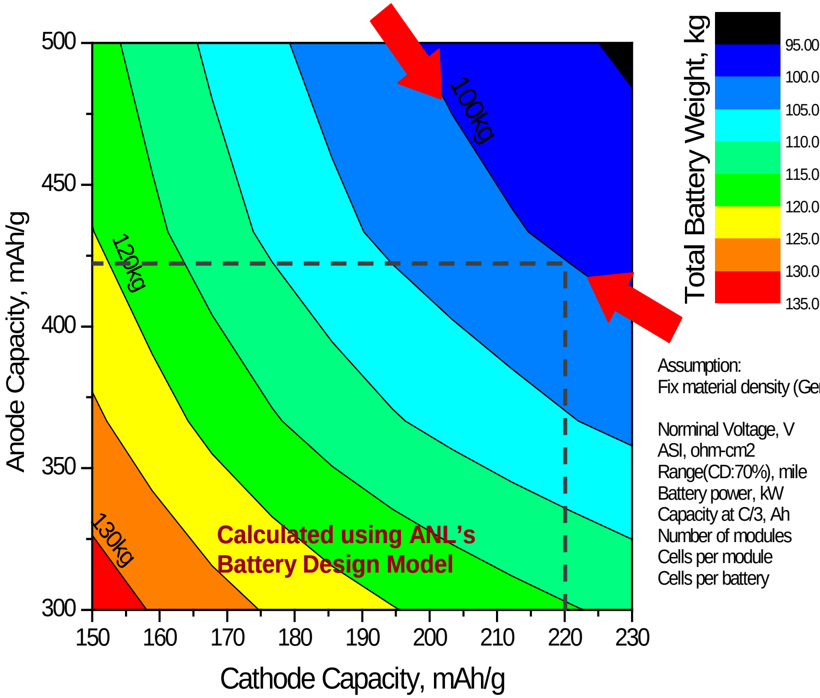
Project I: Objectives of Material Screening

- To identify and evaluate low-cost cell chemistries that can simultaneously meet the life, performance, abuse tolerance, and cost goals for Plug-in HEV application.
- To enhance the understanding of advanced cell components on the electrochemical performance and safety of lithium-ion batteries.
- Identification of high energy density electrode materials is the key for this project.

Battery System Level

100 Wh/kg 145 Wh/L	70% → PHEV	145 Wh/kg 207 Wh/L

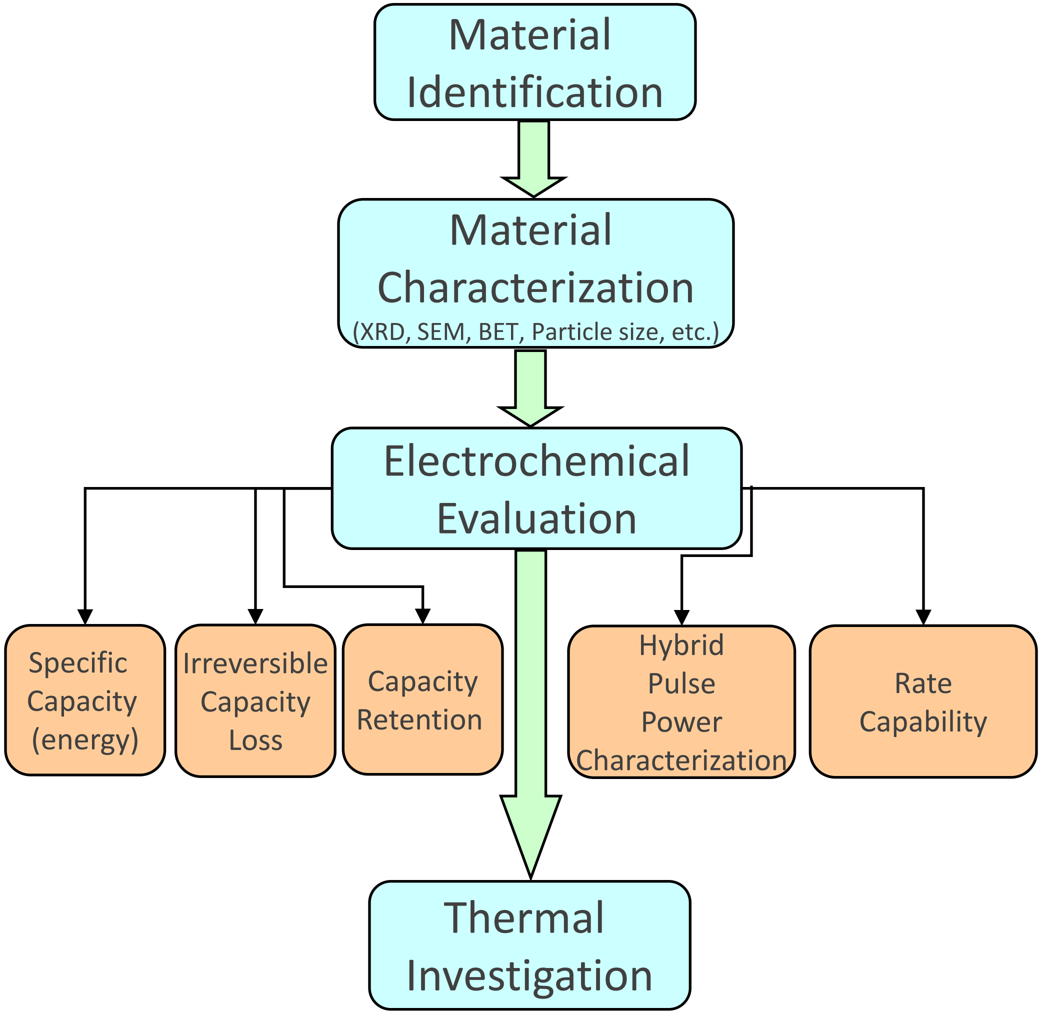
Material Requirements



Assumption:
Fix material density (Gen2)

Norminal Voltage, V	3.6
ASI, ohm-cm2	50
Range(CD:70%), mile	40
Battery power, kW	50.0
Capacity at C/3, Ah	60.0
Number of modules	7
Cells per module	12
Cells per battery	84

Approach: Test Protocol Development



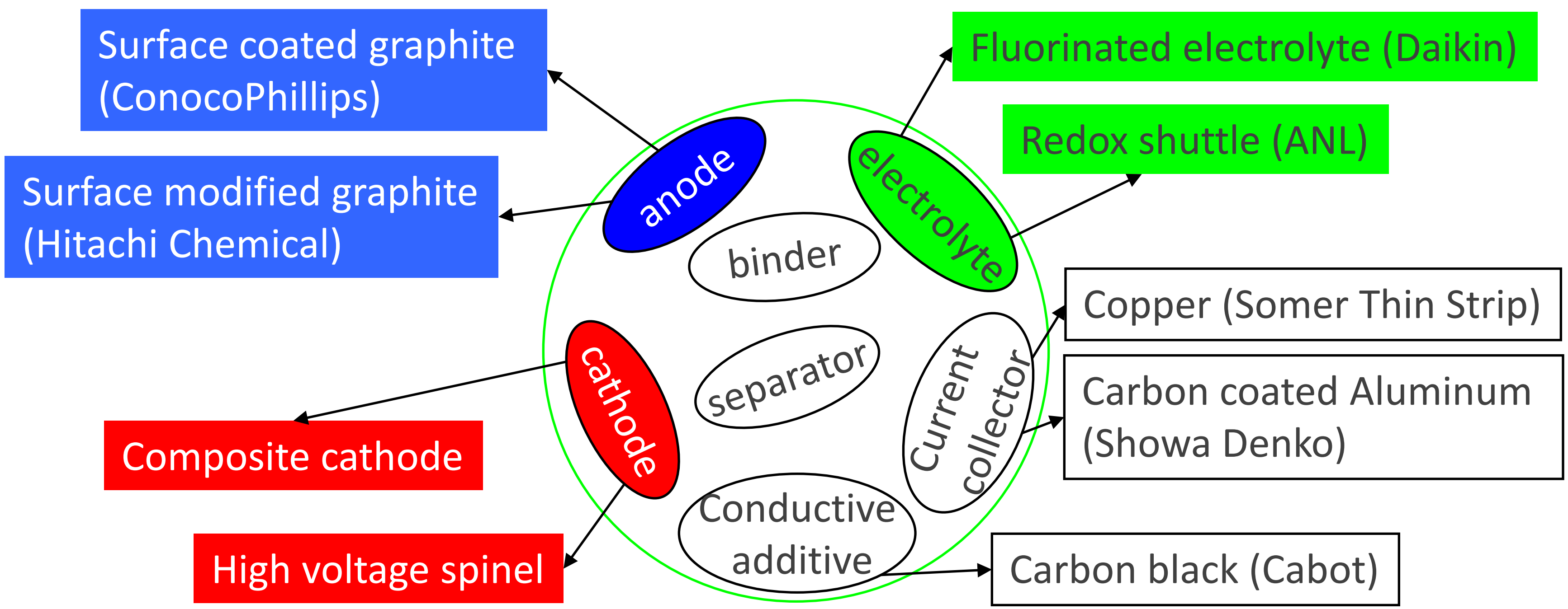
- Test protocol has been defined in "Battery Test Manual for Plug-in Hybrid Electric Vehicles" by INL 2010.
- Accordingly, test procedure and method have been translated to fit the material screening purpose.

USABC Requirements of Energy Storage Systems for PHEV

Characteristics at EOL (End of Life)		High Power/Energy Ratio	High Energy/Power Ratio
Reference Equivalent Electric Range	miles	10	40
Peak Pulse Discharge Power (10 sec)	kW	45	38
Peak Regen Pulse Power (10 sec)	kW	30	25
Available Energy for CD (Charge Depleting) Mode, 10 kW Rate	kWh	3.4	11.6
Available Energy for CS (Charge Sustaining) Mode	kWh	0.5	0.3
Maximum System Weight	kg	60	120
Maximum System Volume	Liter	40	80

Technical Accomplishments

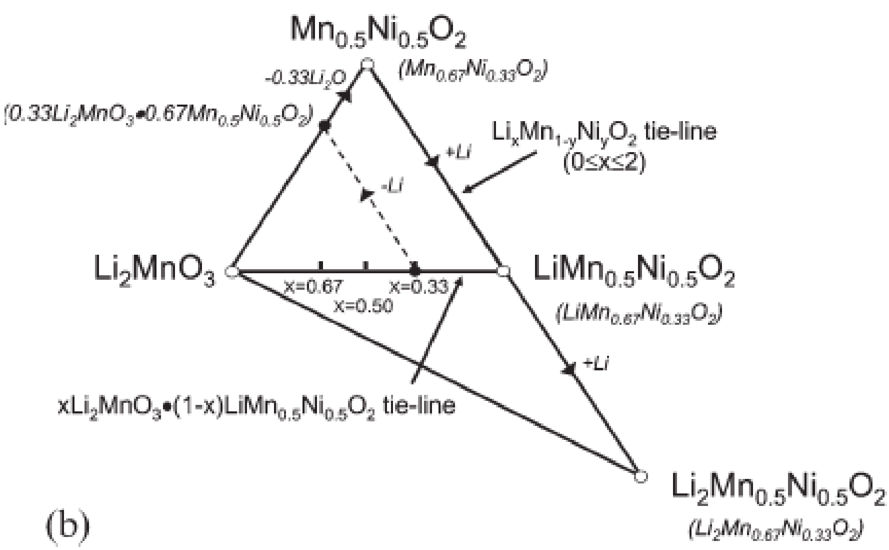
- Several high energy electrode couples, surface treated natural graphite and composite cathode materials, have been identified and studied.
  - Test results have been reported to suppliers.
  - Information is also delivered to cell fabrication team under ABR program (A. Jansen)
- Other cell components, such as electrolyte, redox shuttle, conductive additive, binders, etc., are also investigated.

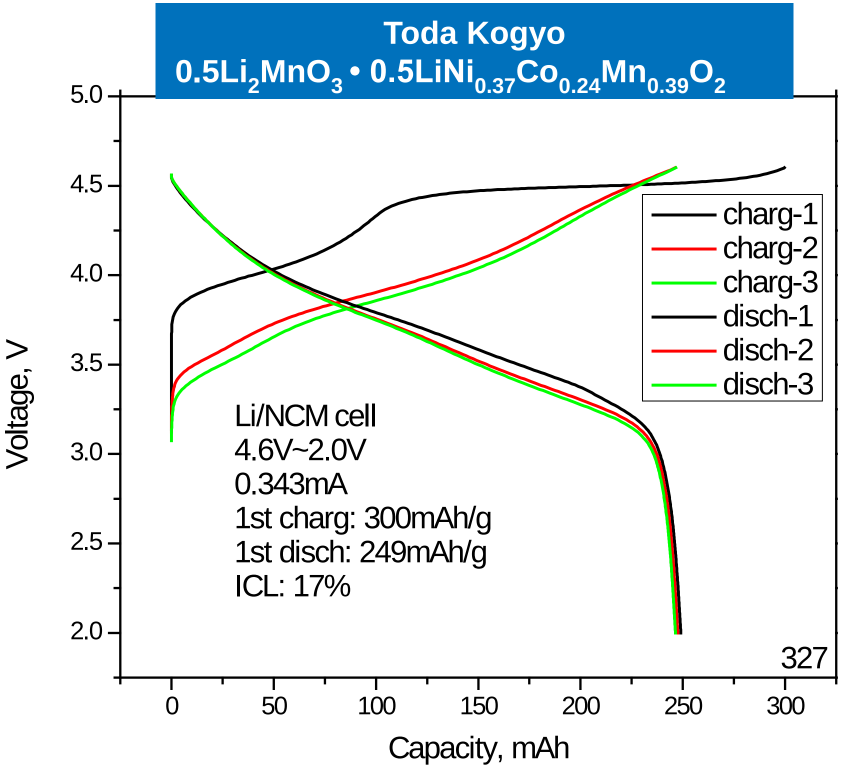


Highlight 1: Composite Cathode Materials

$(1-x)Li_2MnO_3 \bullet xLiMO_2$ cathode materials, where M is a collection of transition metals and the average oxidation state of M is trivalent, have been used to increase the energy density for advanced batteries.

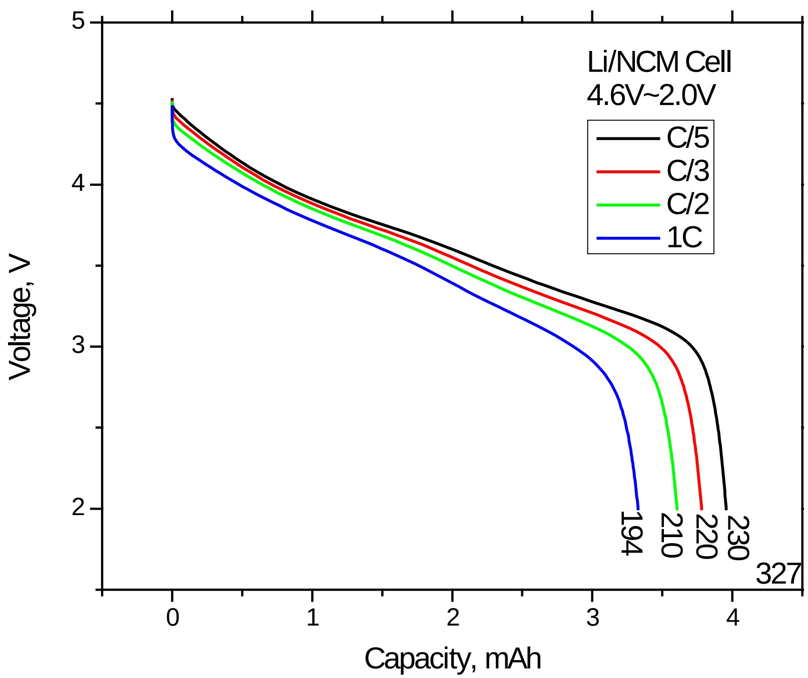
The boost in energy density is due to the electrochemical activation of Li_2MnO_3 domains in the composite material.

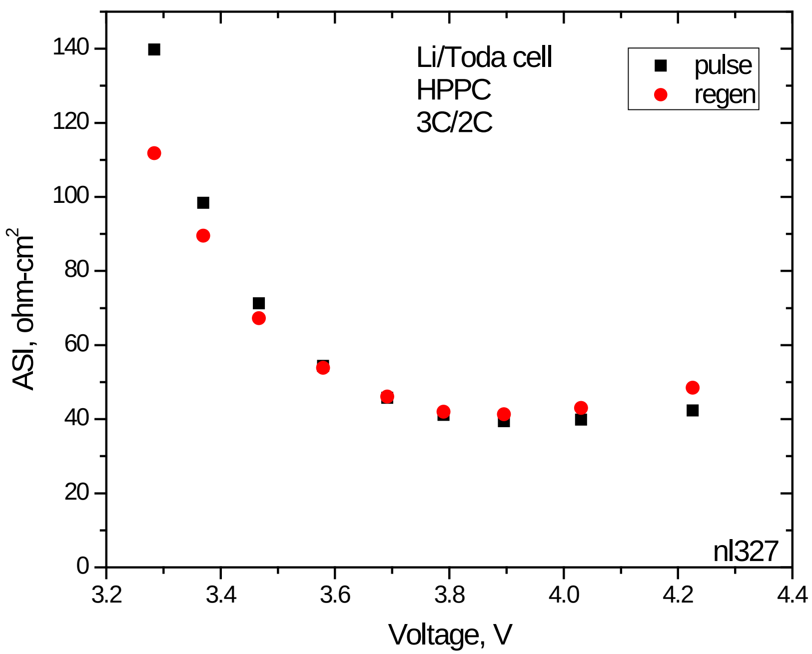




		C/10	C/3
Average voltage	V	3.64	3.58
Specific capacity	mAh/g	246	222
ICL	%	17	
Energy density	mWh/g		
full cycle	4.6~2.0	897	790
Capacity retention	% (50 cyc)		90

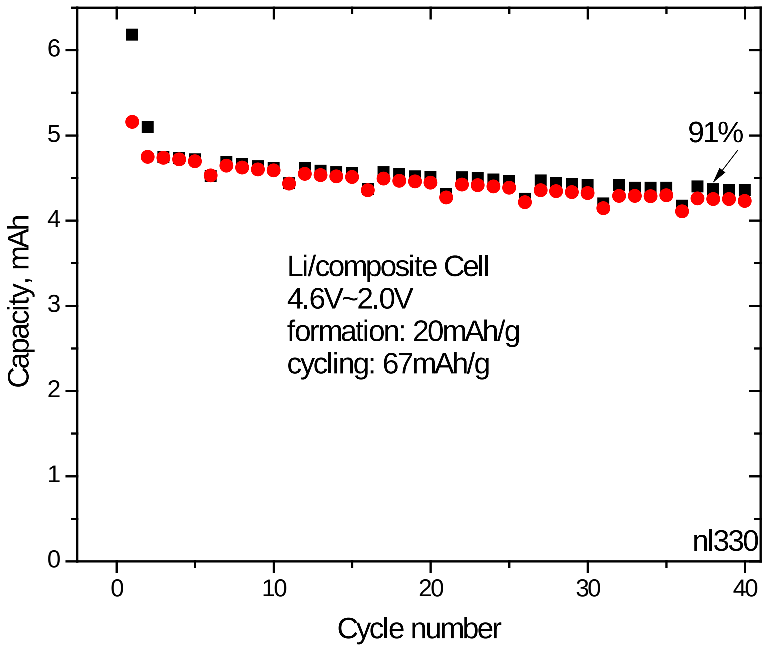
Rate Performance of Composite Cathode Material

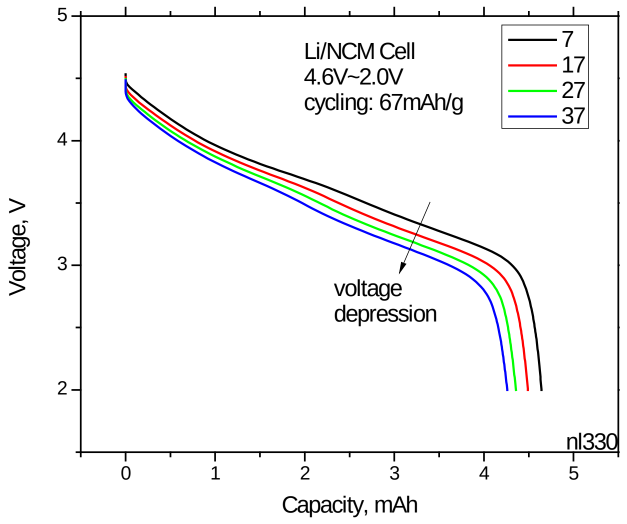


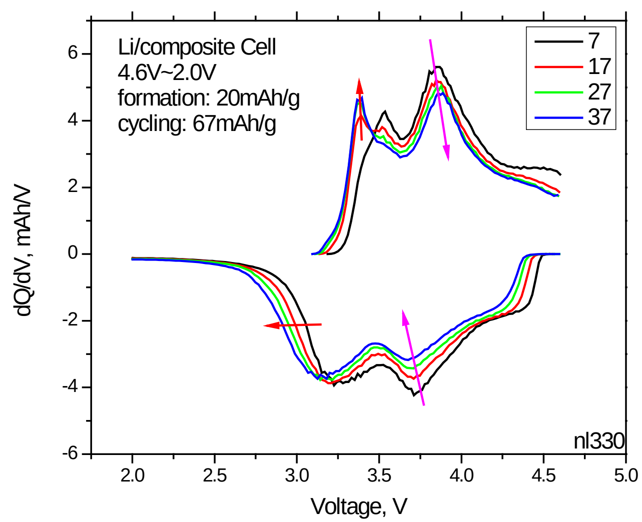


- Excellent rate performance up to 1C with 194 mAh/g.
- Small impedance during HPPC between 10% and 70% DOD.

Voltage Depression of Composite Cathode Material

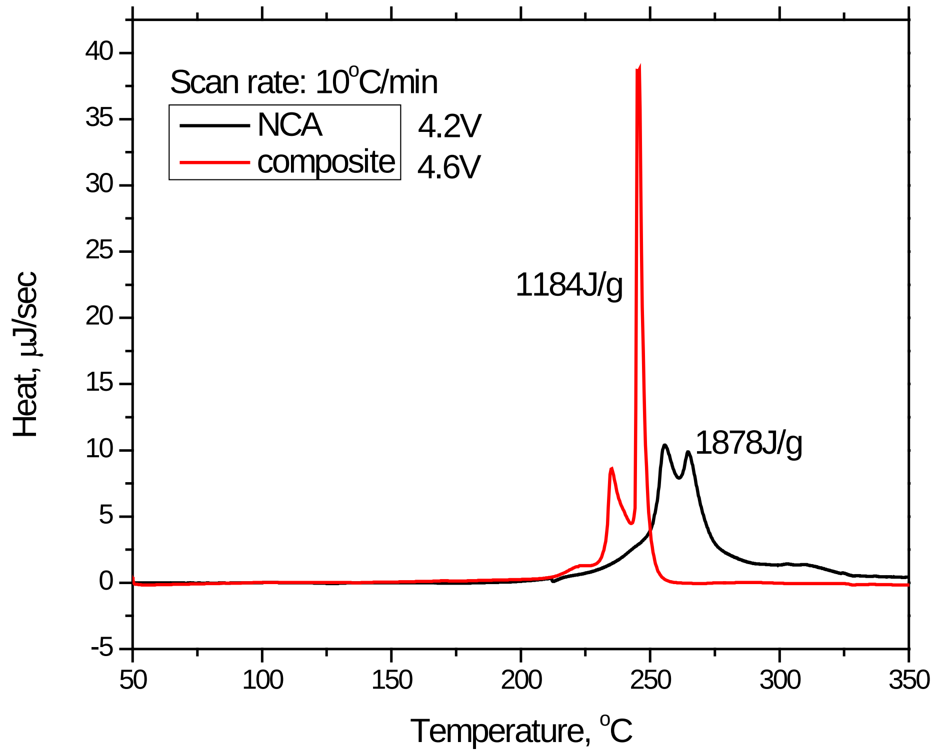






- Composite cathode material shows very good capacity retention during cycling.
- However, voltage depression during cycling was observed, which may affect the energy density.

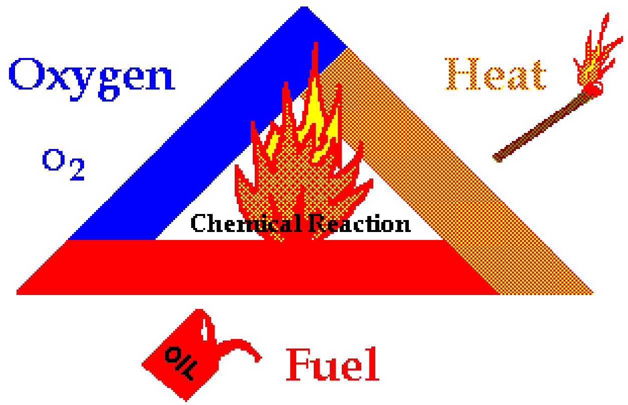
Thermal Property of Composite Cathode



- DSC results indicates that the on-set temperature of exothermic reaction of the fully charge composite is 215°C, same as $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ at 4.2V.
- The total heat generation of fully charged composite is about 1184J/g, which is less than $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ at 4.2V.

Highlight 2: Fluorinated Electrolyte from Daikin

$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$



Electrolyte=Solvent + Salt

- High Current Overcharge
- High Temperature

Fluorinated electrolyte may address safety concerns caused by heat and pressure build-up within the cell and the flammable electrolyte, since it has:

- Higher operational voltage window
- Lower reactivity to anode and cathode
- Thermally stable

Pros and Cons of Fluorinated Electrolyte

Electrolyte composition:

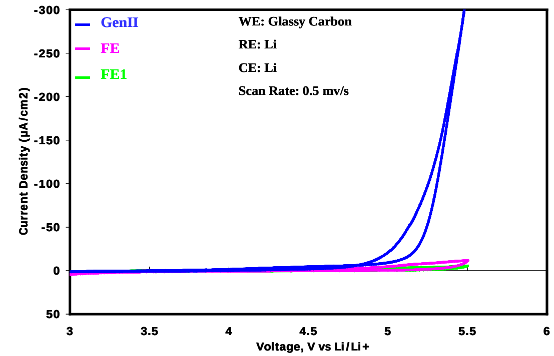
Gen II: 1.2 M LiPF6 EC/EMC (3/7)

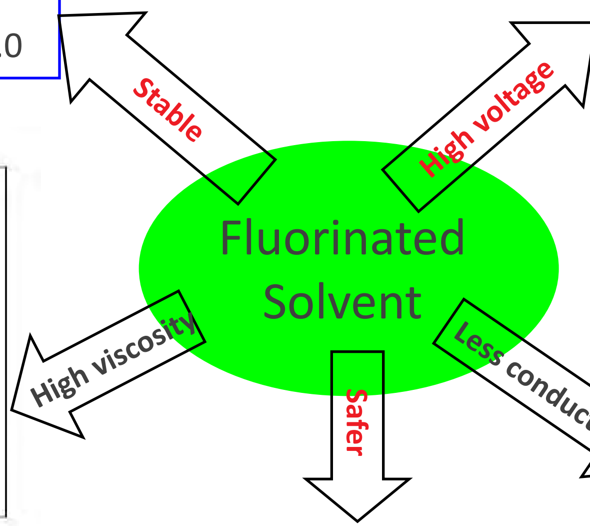
FE1: 1.2M LiPF6 FEC/EMC (3/7)

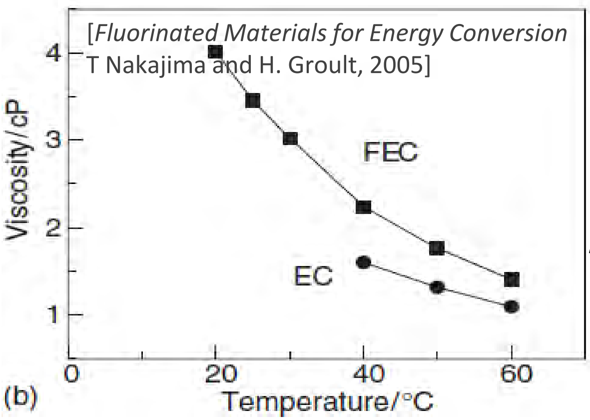
C-H : Binding energy: 417kJ/mol

C-F : Binding energy: 486kJ/mol

Electron negativity: H /2.1; F/4.0

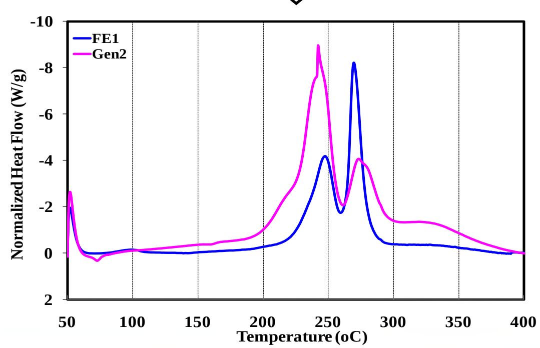




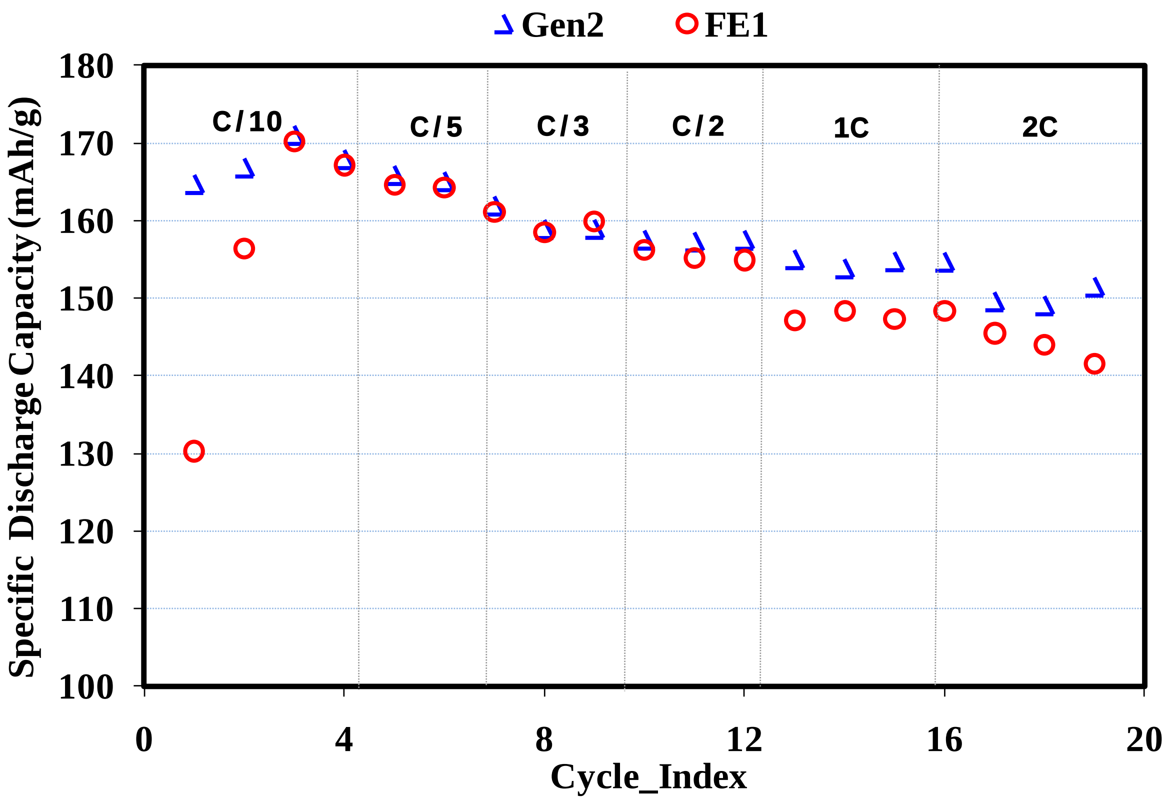


Electrolyte conductivity

Electrolyte		Conductivity (mS/cm)
GenII	1.2M LiPF6 in EC/EMC (3:7)	8.2
FE1	1.2M LiPF6 FEC/EMC(3:7)	4.8

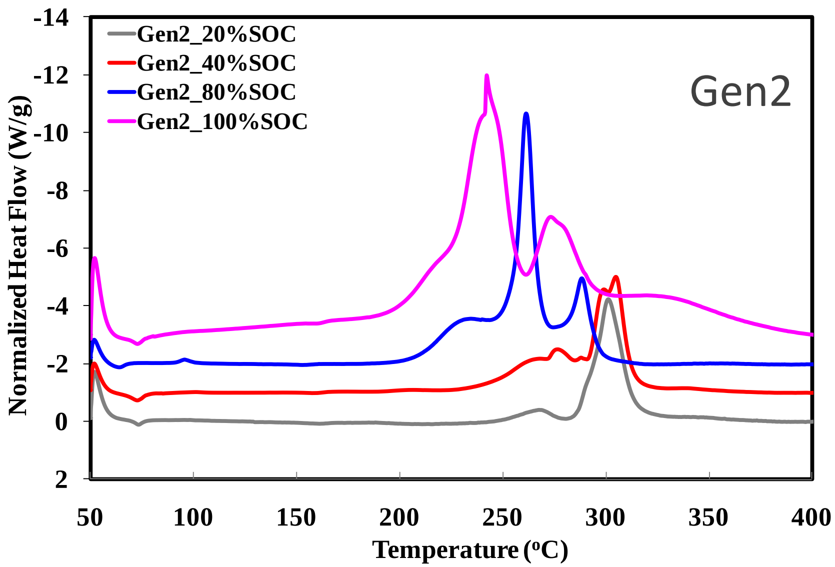


Rate Performance of Fluorinated Electrolytes

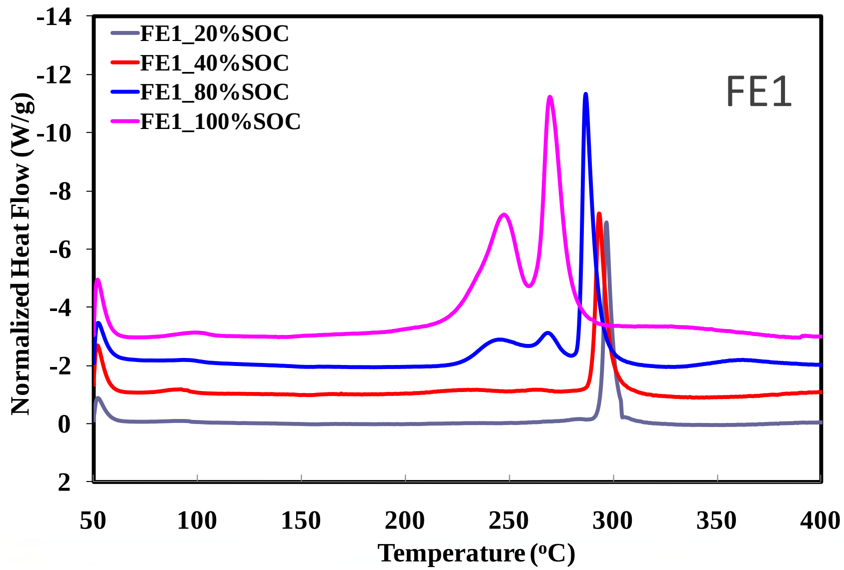


- Comparable performance at lower rates.
- At high rates especially at 1C and 2C the cathode with Gen2 electrolyte shows better performance than FE1.

DSC Results of Fluorinated Electrolyte



	Onset Temperature (˚C)		ΔH(J/g)	
State of charge (%)	Gen2	FE1	Gen2	FE1
100	206	220	1183	1009
80	209	232	1100	788
40	238	273	624	243
20	252	280	394	240



- Higher on-set temperature and less total heat generation were observed to FE1 electrolyte at various state of charge compared to Gen2 electrolyte.

Summary

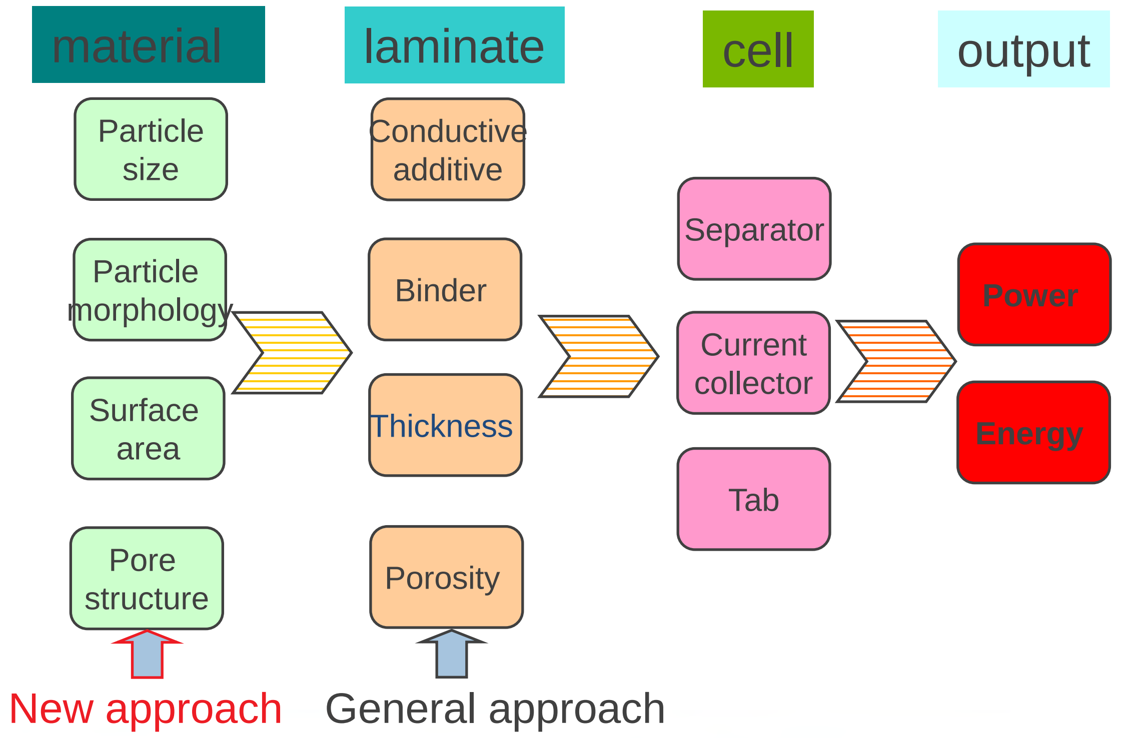
- Composite cathode materials $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.37}Co_{0.24}Mn_{0.29}O_2$
  - Deliver 897Wh/kg, more than 70% of conventional $LiCoO_2$.
  - Good rate performance: 210mAh/g @ C/2.
  - Area specific impedance is about 40 ohm-cm^2 at 50% DOD.
  - 91% capacity retention within 40 cycles.
  - Less heat generation at fully charged state compared to NCA.
- Daikin's Fluorinated ethylene carbonate (FEC)
  - Less capacity is delivered @ 1C due to low conductivity of FEC.
  - DSC results indicate better thermal stability at various state of charge.
- Surface modified graphites from various vendors have been investigated. They all show high capacity, good rate capability and thermal stability and will be used for cell build at ANL.
- Other cell components, such as redox shuttle, binder, separator, carbon additive, current collector have been studied.

Future Plans

- To continue to search and evaluate the high energy density electrode couples to meet the **performance and cost goal** for PHEV applications.
  - $(1\text{-}x)Li_2MnO_3 \bullet xLiMO_2$
  - Surface modified graphite
  - Silicon and its composite
  - Hard carbon (Kureha)
- Other available cell chemistries for lithium battery
  - Electrolyte, additives, redox shuttles
  - Separators
  - Current collector
  - Binder
  - Conductive additives
- Support electrode and cell build project under ABR program
  - Electrode thickness
- Support material scale up program at ANL

Project II: Objectives and Approach of Streamlining the Optimization of Electrode

- To establish the scientific basis needed to streamline the lithium-ion electrode optimization process.
  - To identify and characterize the physical properties relevant to the electrode performance at the particle level.
  - To quantify the impact of fundamental phenomena associated with electrode formulation and fabrication (process) on lithium ion electrode performance.

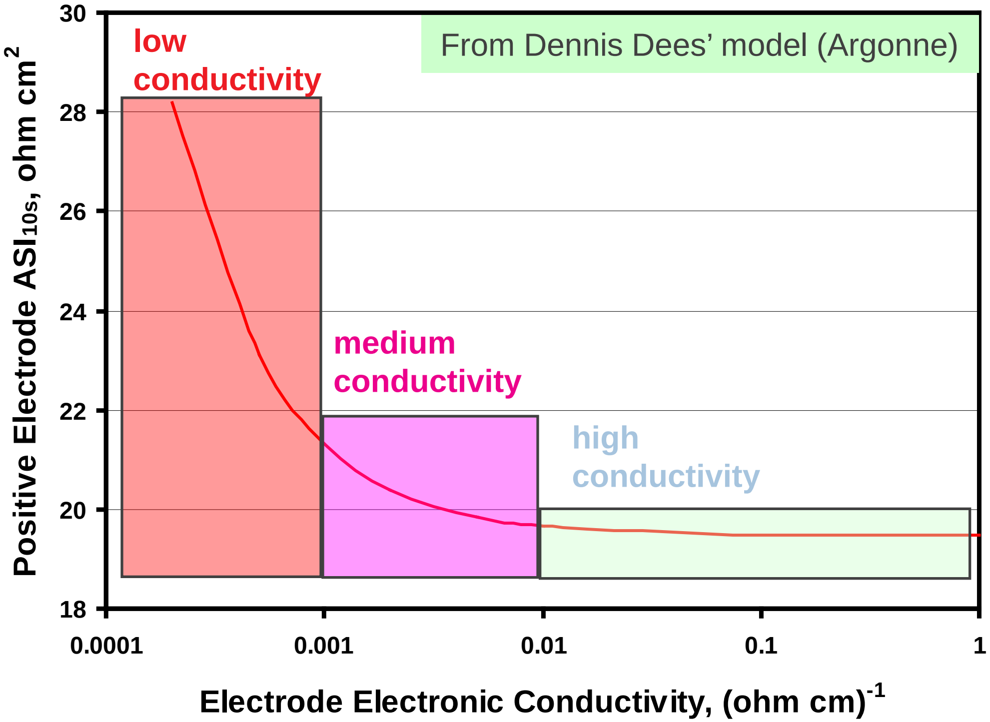


Technical Accomplishments

- Single particle conductivity was found to be higher than powder conductivity in general. The contact resistance between particles should be addressed for electrode optimization.
- Composite electrode made of 0%, 1% and 3% carbon coated $Li_{1+x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) was intensively investigated. Interfacial resistance was found to be dominant for the composite electrode using aluminum substrate.
- Nano electrical imaging was carried out on composite electrode to better understand the conductive network. It was found that the full utilization of conductive carbon additives is necessary to reduce the content of carbon and improve conductivity.

Impact of Electrode Electronic Conductivity

– Impedance Simulation of Gen 3 (NCM) Positive Electrode 5C HPPC

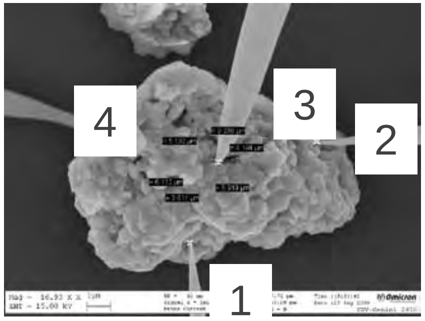


Together with the electrolyte conductivity, the composition of the conductive additive should be tailored to meet the power and energy requirements of lithium ion batteries.

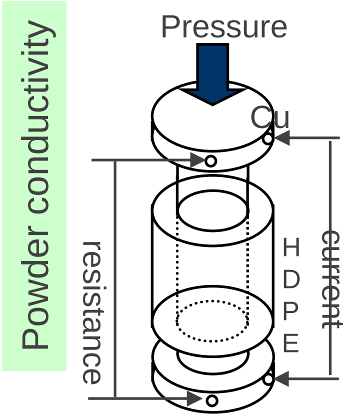
- >0.01 (ohm cm)$^{-1}$: electronic conductivity is much greater than the ionic conductivity and does not impact electrode impedance
- 0.001-0.01 (ohm cm)$^{-1}$: electronic conductivity is comparable to the ionic conductivity
- <0.001 (ohm cm)$^{-1}$: electronic conductivity is much less than the ionic conductivity and significantly impacts electrode impedance

Electronic Conductivity Investigation

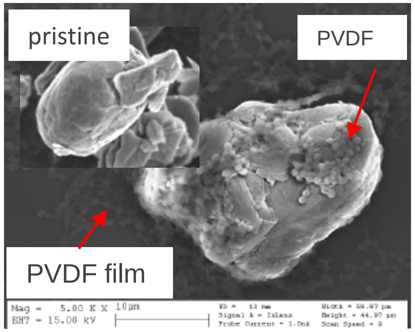
Single particle conductivity > Powder conductivity > Binder conductivity



Single particle conductivity by Nano-probe SEM



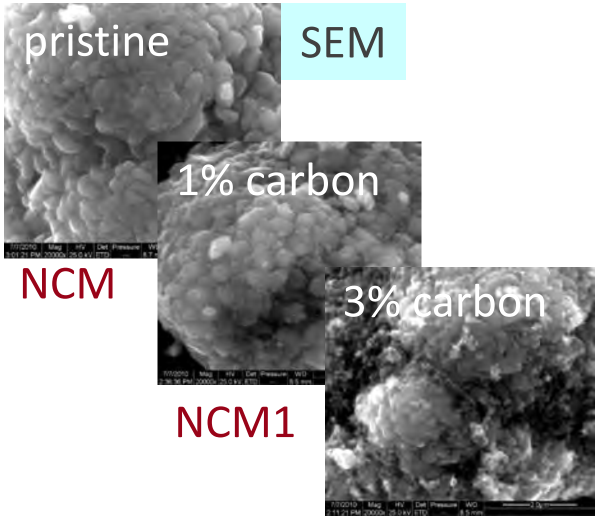
Schematic diagram of powder conductivity measurement apparatus



- Single particle and powder conductivity measurements demonstrate that contact resistance is the key for conductivity of composite electrode.
- In order to address the interfacial resistance between the particle, and current collector, carbon coated $Li_{1+x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ has been studied.

Effects of Carbon Coating on Morphology of $Li_{1+x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM)

SEM

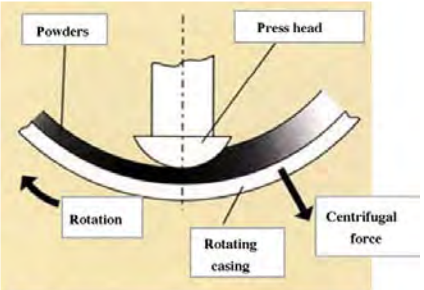


NCM

NCM1

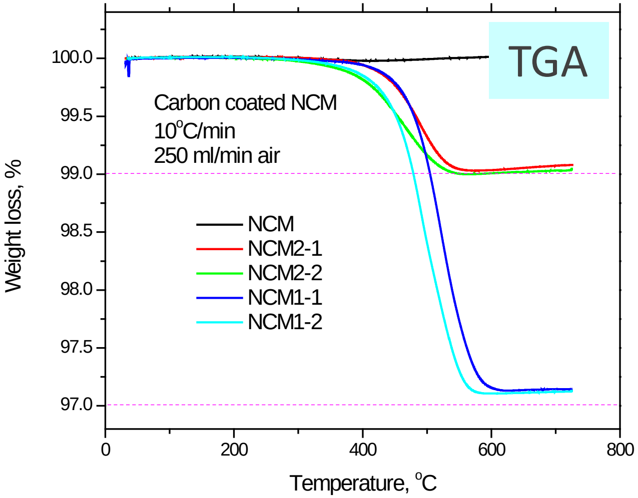
NCM3

Hosokawa

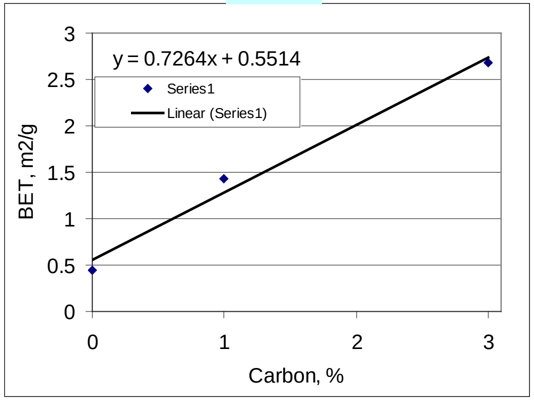


- The powders are subjected to a centrifugal force and are securely pressed against the inner wall of rotating casing.
- The powders are further subjected to various mechanical forces, such as compression and shear forces, as they pass through a narrow gap between the casing wall and the press head.
- As a result, smaller guest particles are dispersed and bonded onto the surface of larger host particles without using binder of any kind.

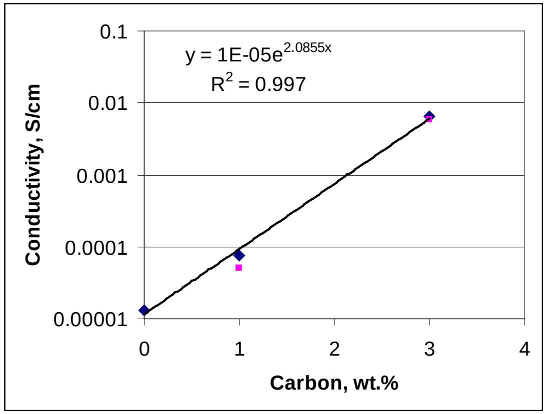
TGA



BET



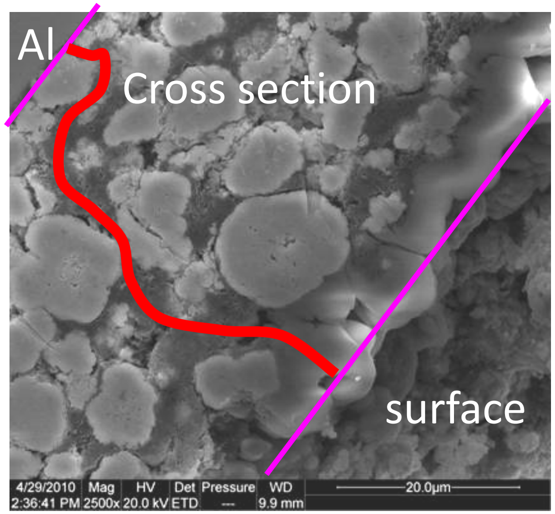
Conductivity



Cross Section of NCM Electrode

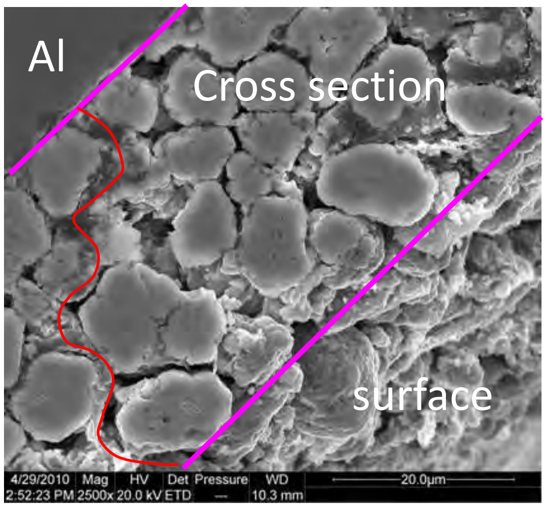
NCM/CB/PVDF
84/ 4 /4

NCM0-24



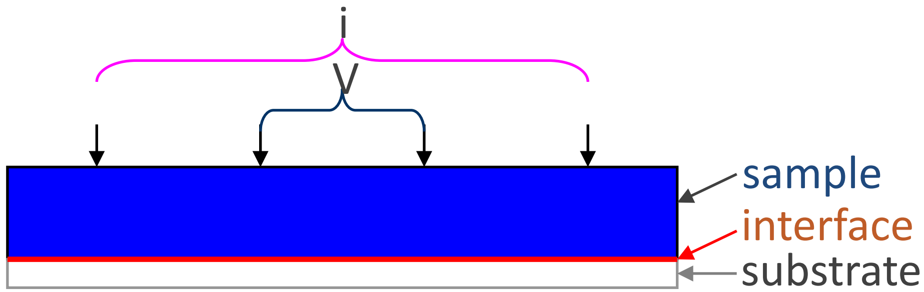
NCM3(w/3%cb)/CB/PVDF
87/ 1 /4

NCM3-04

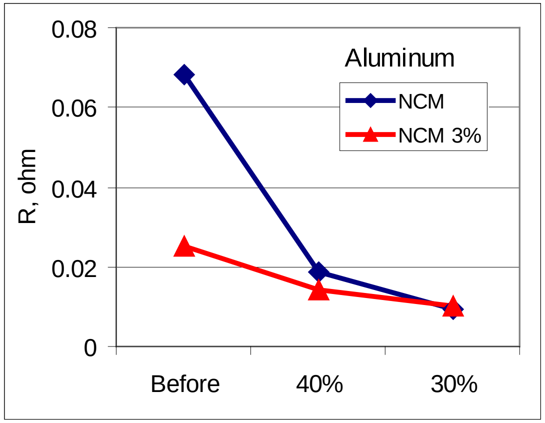


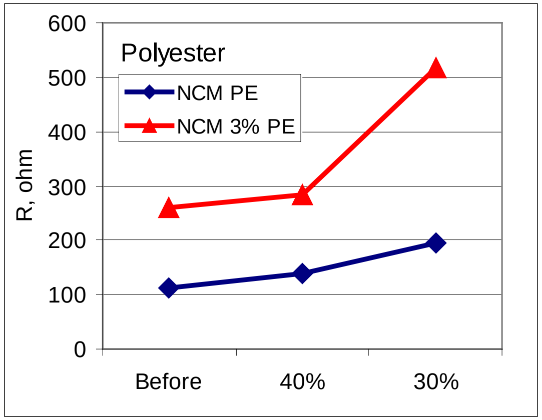
- Continuous carbon pathway was observed for NCM0 with 4% carbon additive.
- But, little or longer pathway for NCM3 electrode with only 1wt% additional carbon additives.

Electrode Conductivity by 4 Probe Method



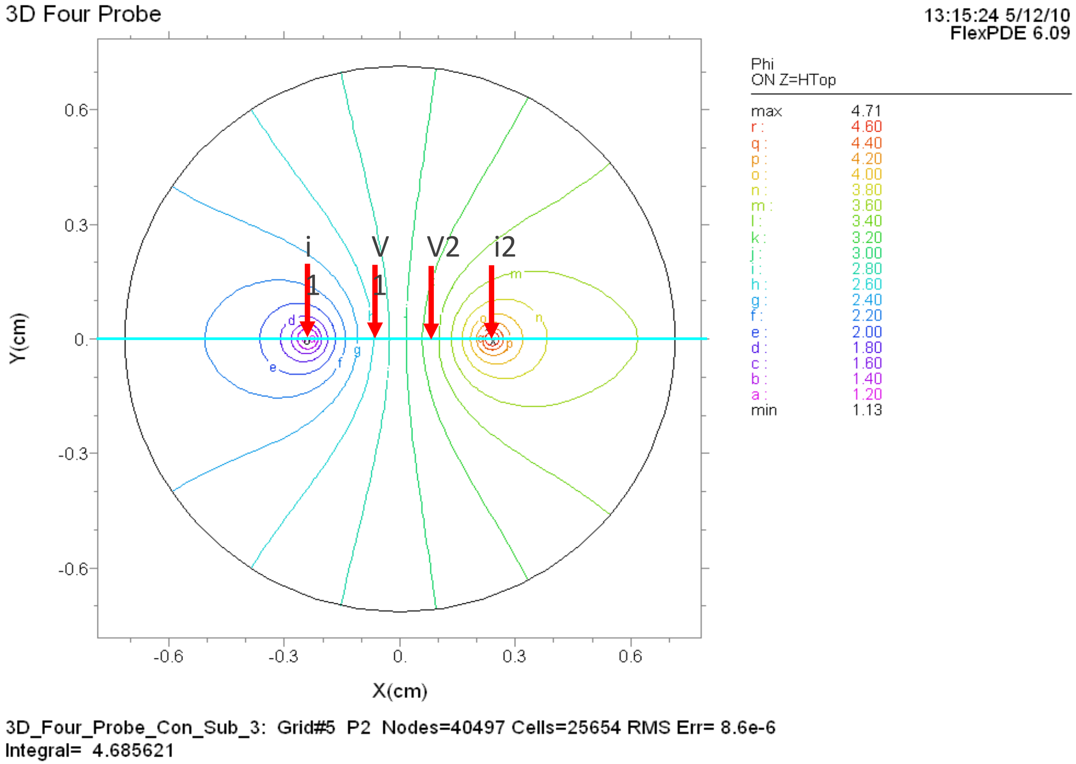
- **Electrode composition***:
  - Active: 84%,
  - SFG-6: 4%
  - Carbon: 4% (*including coated carbon);
  - PVDF: 8%

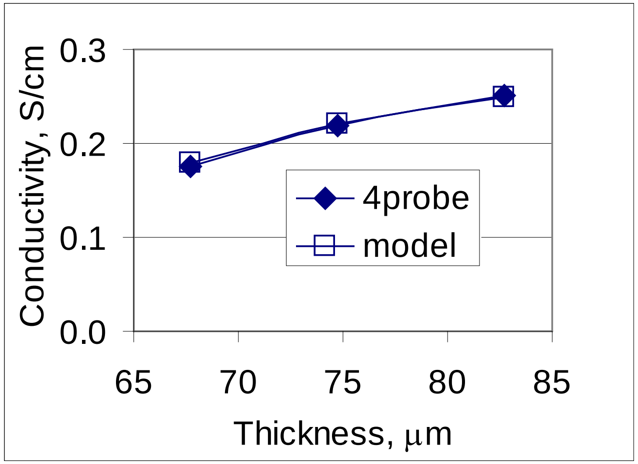




- The resistance of the NCM3 electrode with 1wt% additional carbon on aluminum foil shows less resistance before calendering. Resistances of both electrodes NCM0 and NCM3 on aluminum decreases after calendering.
- For the electrode on polyester substrate, the sheet resistance of the NCM3 electrode is higher. The electrode sheet resistance increases after calendering for both NCM0 and NCM3.
- Therefore, interfacial resistance is dominant for the composite electrode using aluminum substrate. The contact resistance between the particles and substrate was small for carbon coated sample.

4 Probe Modeling of Composite Electrode

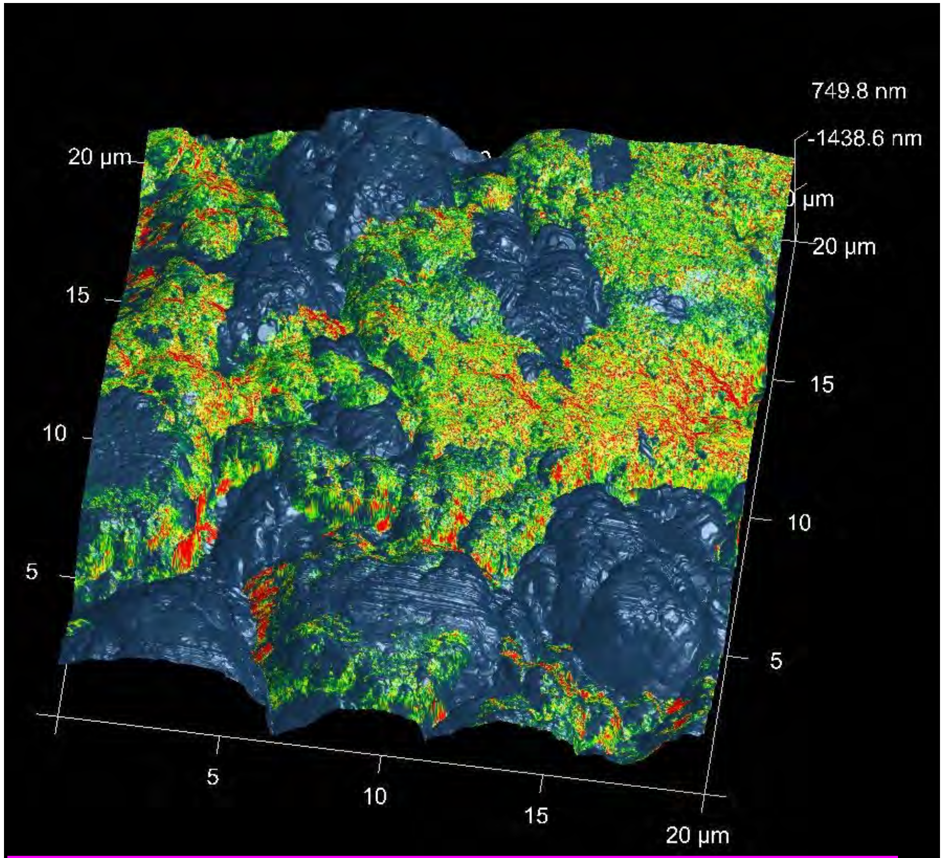




Errlim = 0.00001
Rcontact = 0.5 ohm-cm2
Rinterface = 10000 ohm-cm2
conductivity = 0.221 S/cm

- The conductivity calculated from modeling is consistent to the 4 probe measurement.
- The validated model will be used to determine the interfacial resistance between the composite layer and substrate.

Nano-Electrical Imaging of Electrode using AFM



Current: purple/pink < green < yellow < red

- 3% carbon coated NCM + 4% carbon + 7% PVDF
- Higher current indicates higher conductivity.
- There are two distinct regions in the image: isolated blue rocky-like (NCM) and continuous patches (CB + PVDF).
- The conductivity various with CB/PVDF region, which should be further studied.

AFM by Bruker (Veeco)

Summary

- The electronic conductivity of composite electrode made of carbon coated NCM was intensively investigated.
  - The composite electrode with carbon coated particles has better interfacial conductivity between composite layer and substrate, but higher sheet resistance compared with uncoated particles.
  - The electrode with uncoated particles has lower interfacial conductivity but higher conductivity within the composite sheet.
  - The 4 probe model was validated and the interfacial resistance will be studied.
- Nano electrical image indicates that the carbon additive is not fully utilized to form the conductive matrix.

Future Plans

- Carbon coating impact on the cathode performance will be continued.
  - The amount of coating, additional carbon additive, and binder effect will be investigated.
  - This 4 probe modeling will be utilized to study the interfacial resistance.
- Electrode optimization on electronic conductivity will be address through
  - Percolation theory
  - Optimization of composite electrode conductivity

Contributors and Acknowledgments

Argonne National Laboratory

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