Screen Electrode Materials & Cell Chemistries and Streamlining Optimization of Electrode

Presented by Wenquan Lu
Project ID: ES028

Electrochemical Energy Storage
Chemical Sciences and Engineering Division
Argonne National Laboratory
Jun 7th – 11th , 2010

Vehicle Technologies
Annual Merit Review and Peer Evaluation
Washington, D.C.

Vehicle Technologies Program

U.S. DEPARTMENT OF ENERGY

Overview

Timeline

- Start – Oct. 2008
- Finish – Sep. 2014
- ~25% 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)

Part 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.

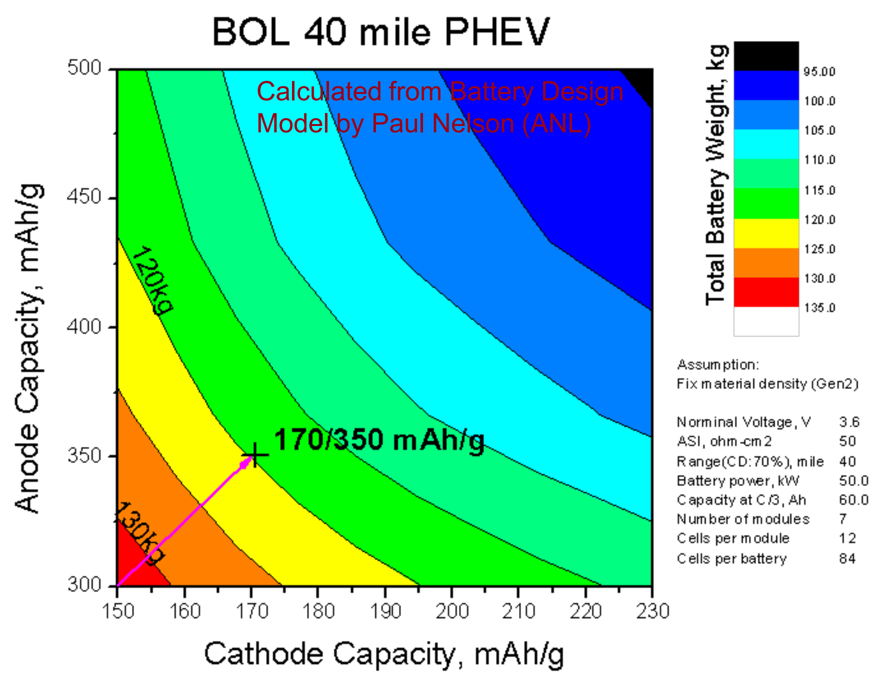
Battery System Level

100 Wh/kg
145 Wh/L

→ 70% **PHEV** →

145 Wh/kg
207 Wh/L

Material Requirements



Part I: Technical Accomplishments

Previous Work

- Test Protocol Development for material screening
- $Li_{1+w}[Ni_xCo_yMn_z]_{1-w}O_2$ (NCM): Toda Kogyo, Japan
- $LiNi_xCo_yMn_zO_2$: SoBright, China
- $LiFePO_4$: Mitsui Engineering Shipbuilding (MES), Japan
- $LiMn_2O_4$: Tronox, USA - *Domestic supplier*

Current Work and Achievement

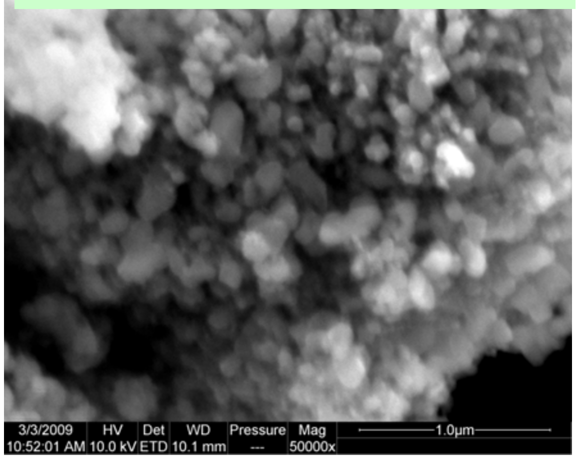
- High energy density $LiMnFePO_4$
- $LiNiCoMnO_2$ from Argonne (S. K. Kang)
- SMG graphite from Hitachi Chemical
- Fluorinated Electrolyte from Daikin
- Other materials tested, but not shown here, include
  - $LiFePO_4$ cathode materials
  - Graphite anode materials
  - Separators

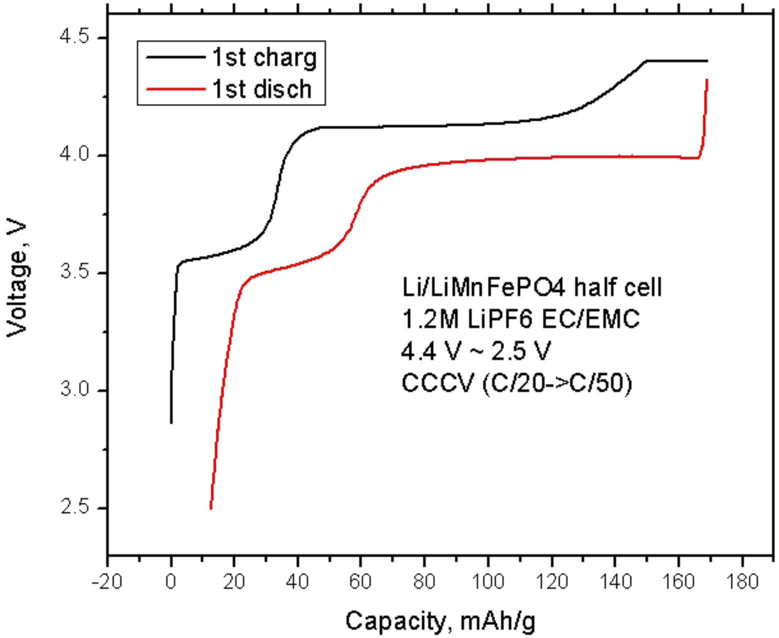
High Energy Density Fe doped $LiMnPO_4$

Olivine Family:
$LiFePO_4$: 3.6 V vs. Li; semiconductor
$LiMnPO_4$: 4.1 V vs. Li ; insulator
$LiCoPO_4$: 4.8 V vs. Li
$LiNiPO_4$: 5.1 V vs. Li

$LiMnPO_4$ has higher specific capacity with appropriate operation voltage window as drop-in replacement of $LiMO_2$.

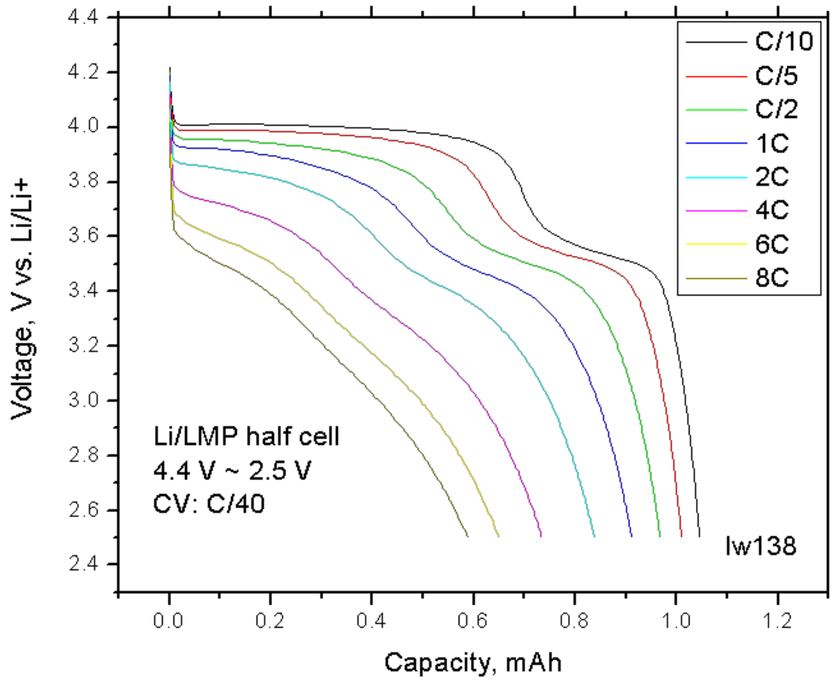
Nanostructure $LiMnFePO_4$

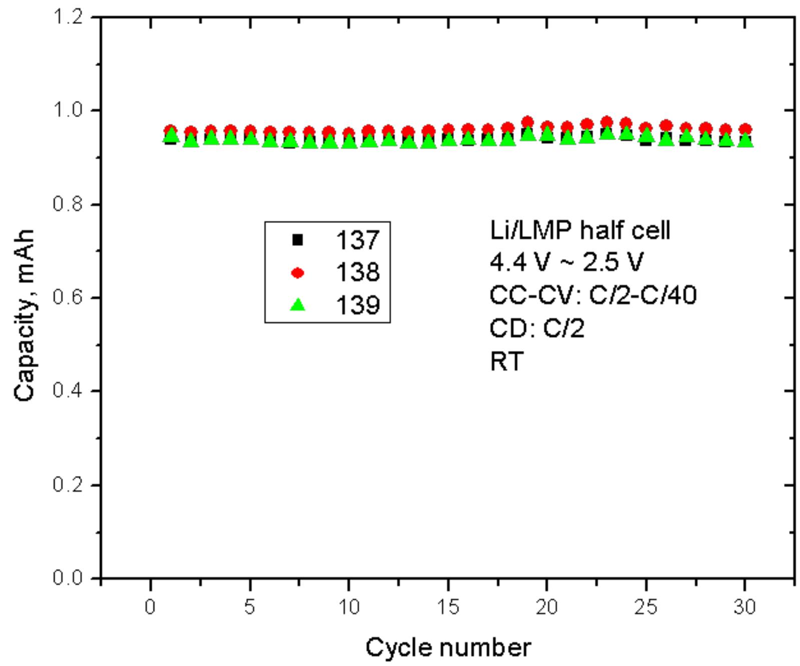




- The two voltage plateaus (two differential capacity peaks) are related to the oxidations of Fe and Mn, respectively.
- The 1st charge capacity is 168 mAh/g, very close to theoretical value.

Rate Capability and Cycling Performance $LiMnFePO_4$





- Under half cell condition, there is about 80% capacity retention at 2C rate.
- The half cell capacity does not fade during cycling at room temperature.

$Li_{1.05}(Ni_{4/9}Co_{1/9}Mn_{4/9})_{0.95}O_2$ from Argonne

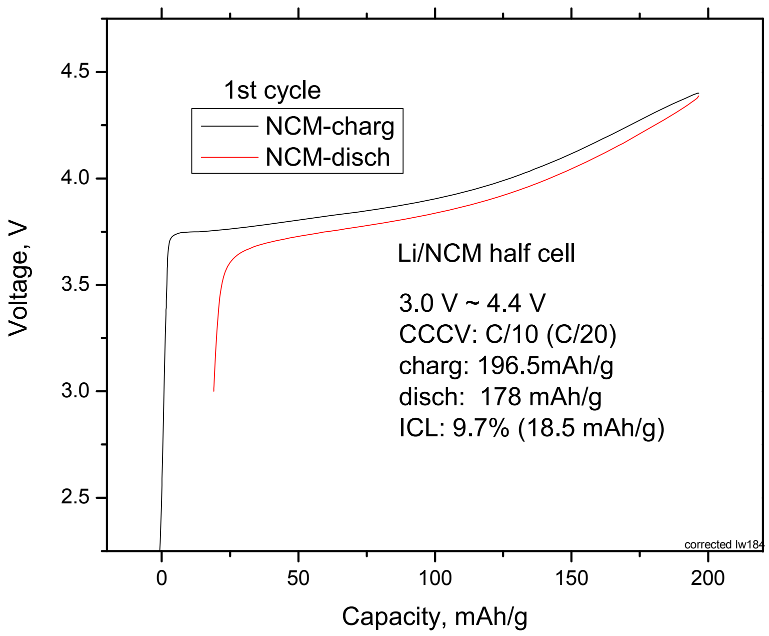
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$

$Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{1-x}O_2$

$Li_{1.05}(Ni_{4/9}Co_{1/9}Mn_{4/9})_{0.95}O_2$

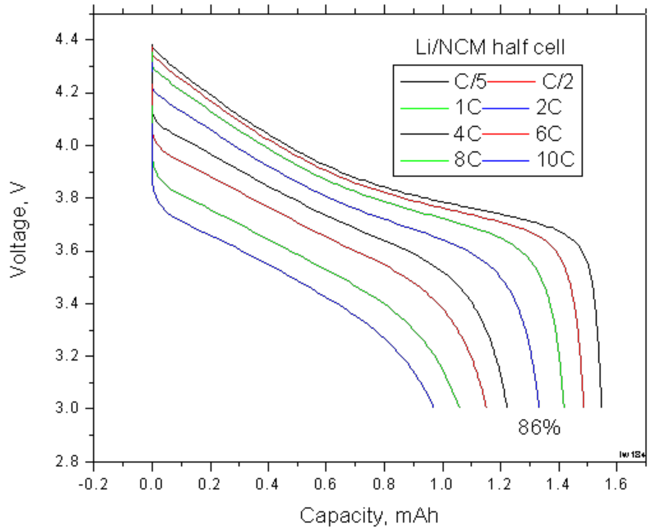
- $Li_{1+a}(Ni_xCo_yMn_z)_{1-a}O_2$ is currently available cathode material with highest energy density.
- $Li_{1.05}(Ni_{4/9}Co_{1/9}Mn_{4/9})_{0.95}O_2$, as one of composite materials, has even less Co content than $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{1-x}O_2$, which can reduce the material cost.

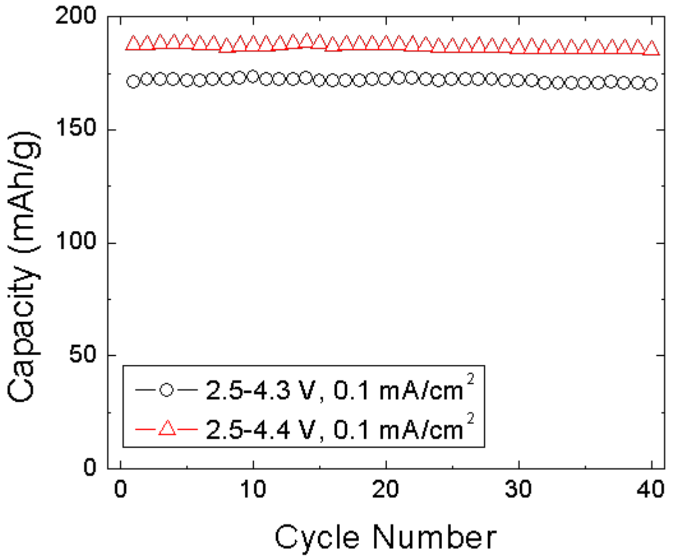
$Li_{1.05}(Ni_{4/9}Co_{1/9}Mn_{4/9})_{0.95}O_2$



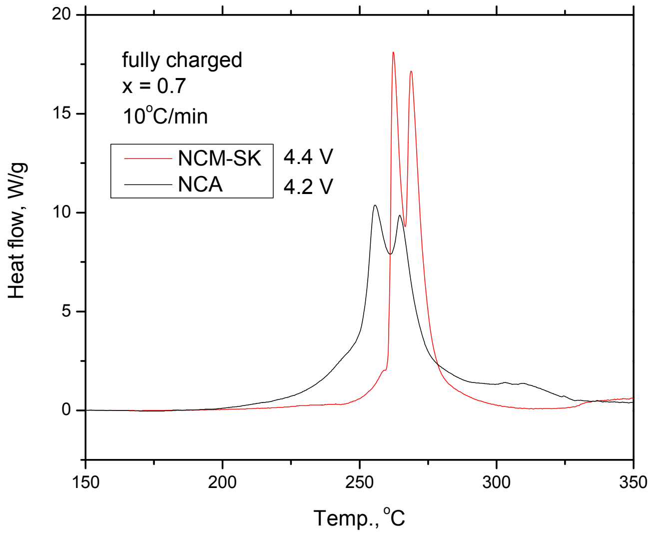
- Moreover, $Li_{1.05}(Ni_{4/9}Co_{1/9}Mn_{4/9})_{0.95}O_2$, has higher specific capacity (~180mAh/g), but less irreversible capacity loss (<10%).

Electrochemical and Thermal Properties of $Li_{1.05}(Ni_{4/9}Co_{1/9}Mn_{4/9})_{0.95}O_2$

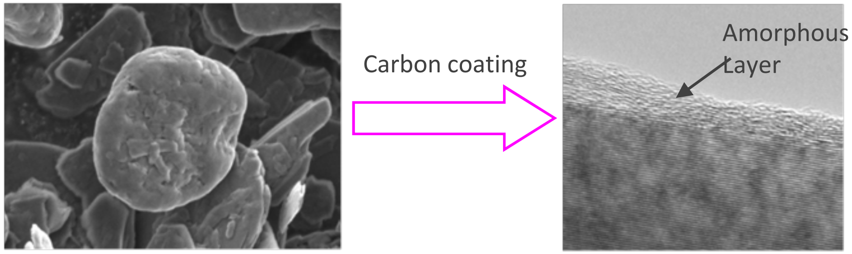




- There is still about 86% capacity retention at 2C rate.
- Excellent cycle of $Li_{1.05}(Ni_{4/9}Co_{1/9}Mn_{4/9})_{0.95}O_2$ is obtained at room temperature.
- More thermally stable than NCA cathode at same state of charge.



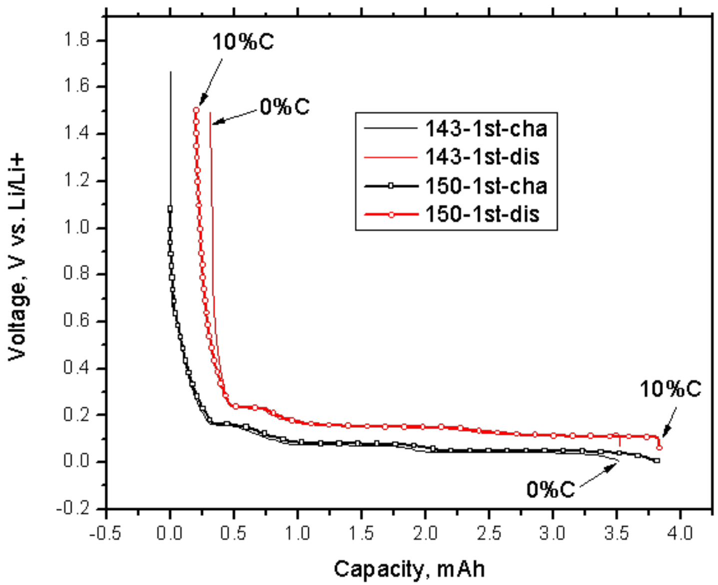
SMG from Hitachi Chemicals



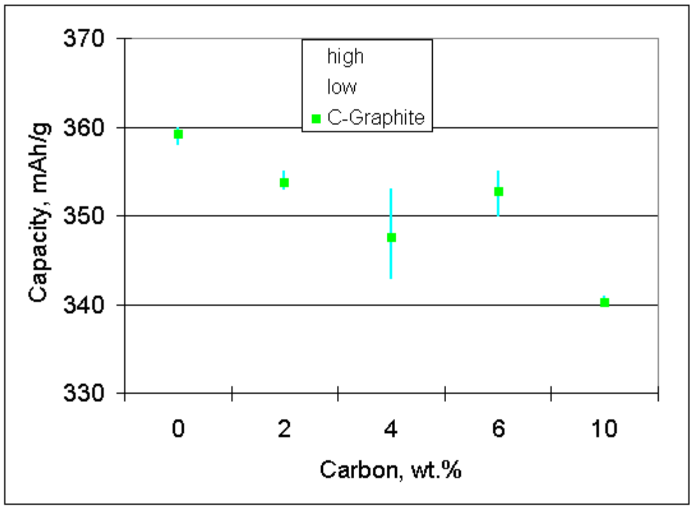
Carbon coating as protective layer :

✓Erase active point
✓Less reactivity with electrolyte
✓Less SEI formation

Voltage Profile

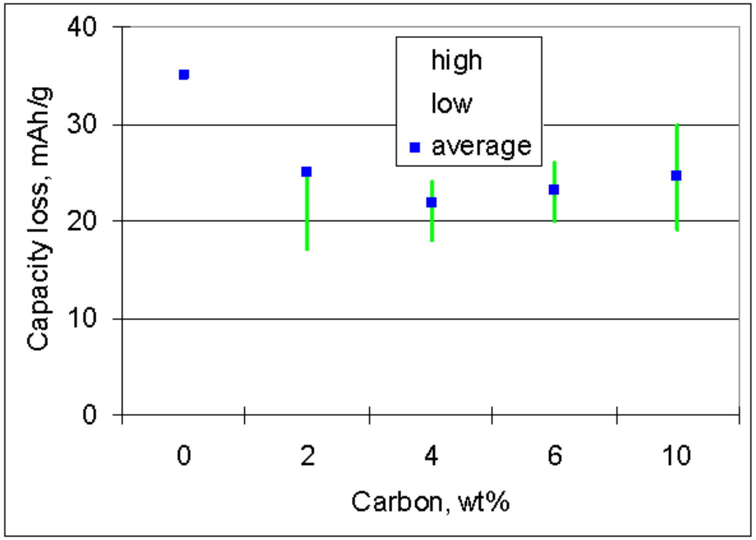


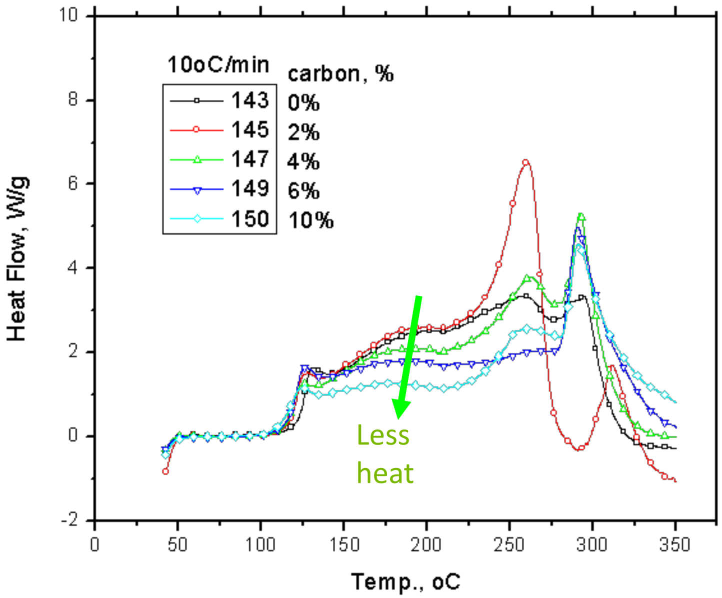
Specific capacity



- Carbon coating on graphite can reduce surface area, provide protective layer.
- There is still about 350mAh/g specific capacity (including carbon) for SMG with up to 6% carbon coating.

Irreversible Capacity Loss and Thermal Stability of Carbon Coated Graphite





- Less irreversible capacity loss for SMG after carbon coating.
- Better thermal stability is observed for the carbon coated graphite.

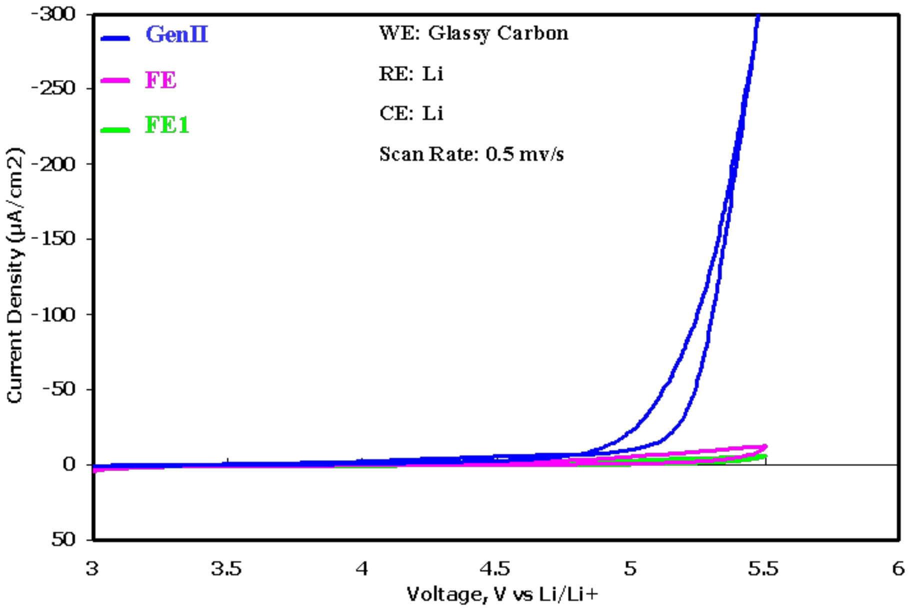
Fluorinated Electrolyte from Daikin

Electrolyte composition:

Gen II: 1.2 M LiPF6 EC/EMC (3/7)
FE: 1.2 M LiPF6 FEC/EMC/D2 (2/4/4)
FE2: 1.2 M LiPF6 D2/EMC (3/7)

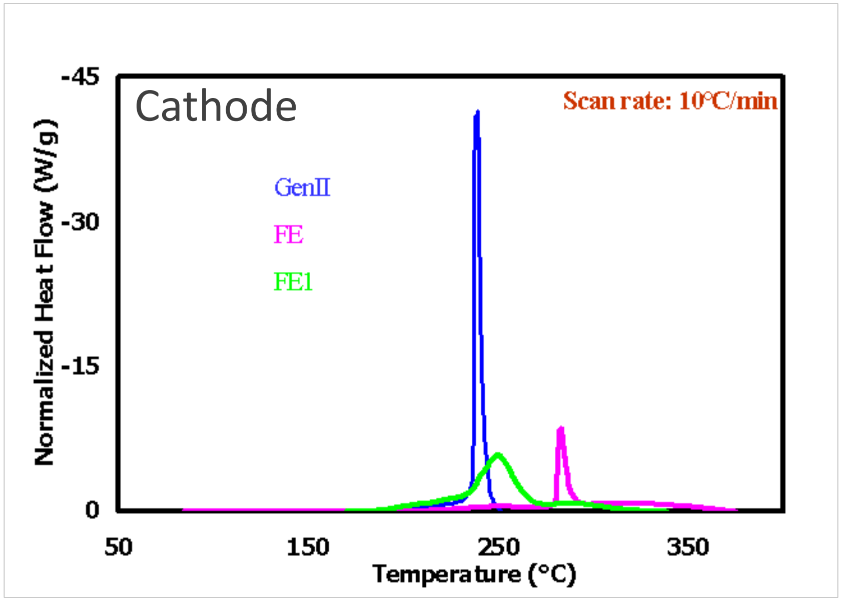
Electrolyte conductivity

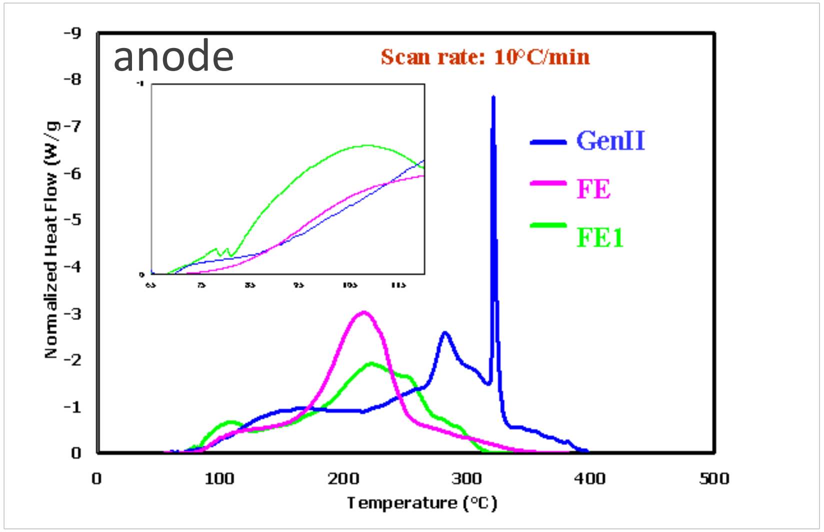
Electrolyte		Conductivity (mS/cm)
GenII	1.2M LiPF6 in EC/EMC (3:7)	8.2
FE	1.2M LiPF6 FEC/EMC/D2 (2:4:4)	7.2
FE1	1.2M LiPF6 FEC/EMC(3:7)	4.8



- The fluorinated solvent reduces the conductivity of the electrolyte.
- The voltage window of the electrolyte is expanded using fluorinated solvents.

Calorimetry Study on Charged Electrodes





Electrolyte	Onset Temperature (°C)	Peak Temperature (°C)	ΔH (J/g)
Gen2	175	239	-1329
FE	211	274	-693
FE1	183	250	-1116

Electrolyte	Onset Temperature (°C)	Peak Temperature (°C)	ΔH (J/g)
GenII	70	320	-332
FE	78	293	-268
FE1	70	217	-306

- The DSC results indicate that the thermal stability of cathode material is improved using fluorinated solvents.
- However, this thermal advantage is not observed for graphite electrode.

Part I: Summary

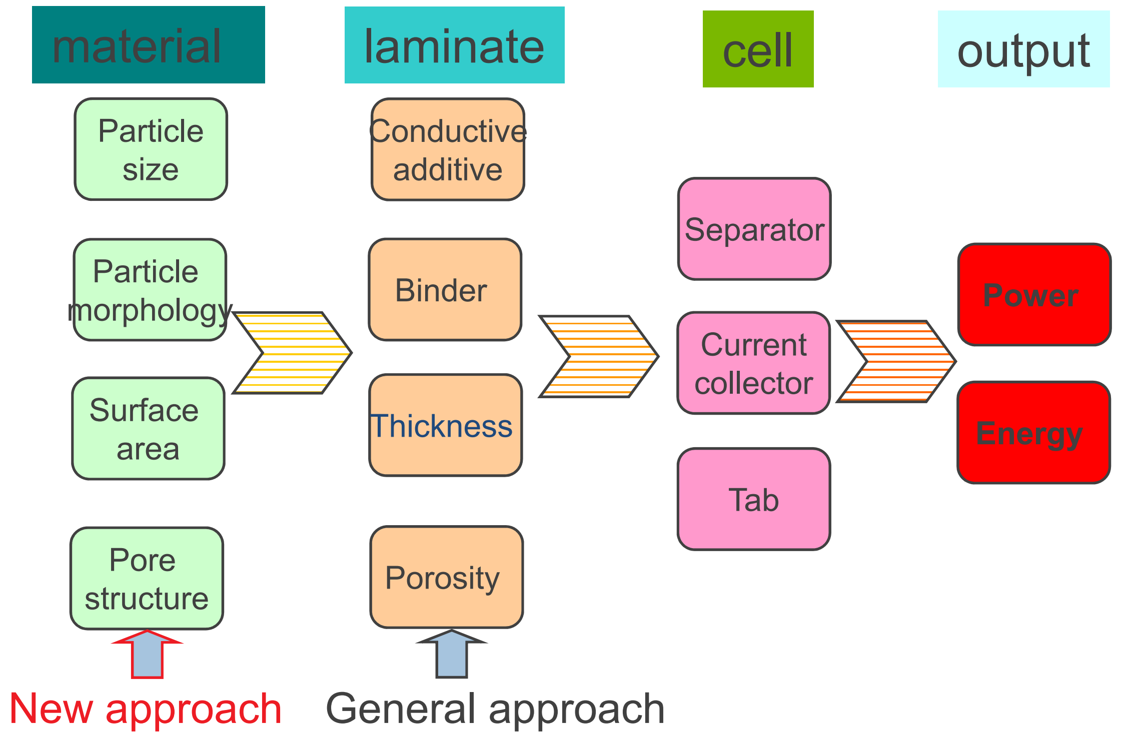
- $LiMnFePO_4$ shows
  - High operational potential, ~4.0 V.
  - high specific capacity: >160mAh/g.
  - ~80% capacity retention at 2C rate.
  - Good cycling performance.
- Argonne's $Li_{1.05}(Ni_{4/9}Co_{1/9}Mn_{4/9})_{0.95}O_2$ shows
  - Low cost with less Co content
  - Higher energy density: ~180mAh/g.
  - Low irreversible capacity loss, <10%.
- Hitachi's SMG has
  - High reversible capacity, ~350mAh/g.
  - Less SEI formation & low impedance
  - Better thermal stability

Future Plans

- To continue the investigation on current available electrode materials and cell chemistries
  - $LiNiCoMnO_2$ (Phoenix)
  - Hard carbon (Kureha)
  - Aqueous binder (SBR)
  - Fluorinated solvent (Daikin)
  - Carbon black (Cabot Corp)
  - Current collectors
- To continue the materials search and evaluation to meet the **performance and cost goal** for PHEV applications.

Part II: Objectives 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

Previous Work

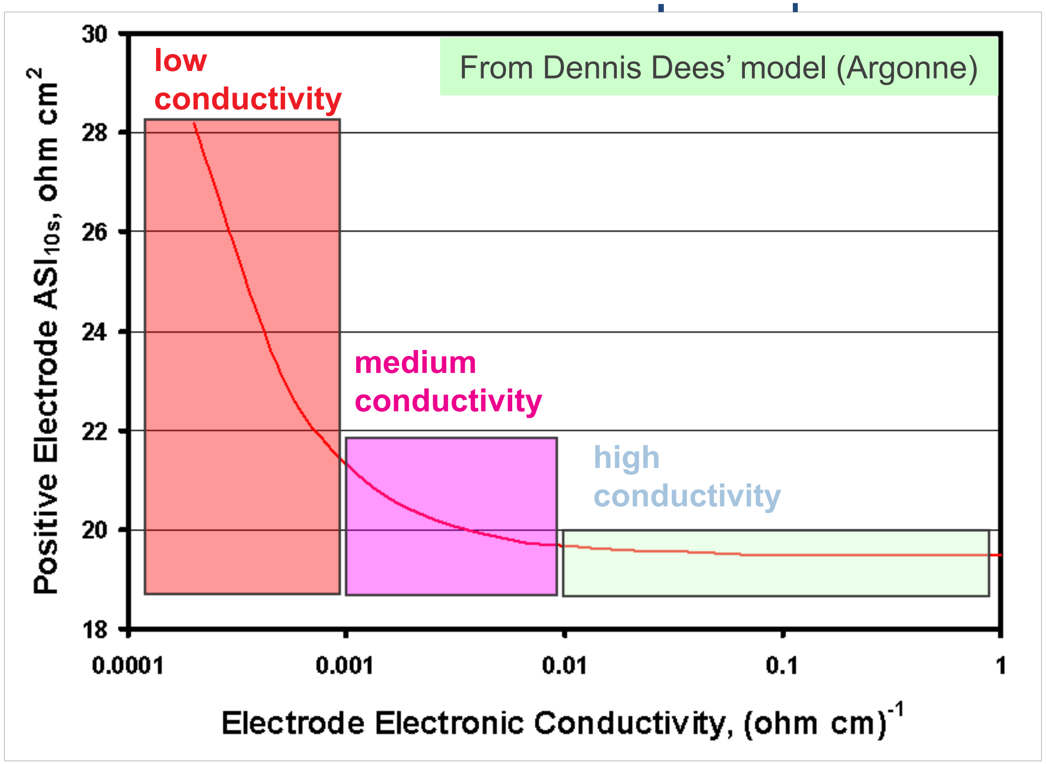
- Significant impact of electrode processing on the electrochemical performance of lithium ion batteries demonstrated.
- Preliminary investigation of electrode composition shows beneficial effect of optimized electrode on cell aging and impedance.
- Electronic conductivities of various active electrode materials (powder) were carried out using in-house developed apparatus.

Current Work and Achievement

- Conductive additive distribution study
- Carbon coating on electronic conductivity of powder
- Electronic conductivity measurement at single particle level.
- Binder effect on conductivity of powder.
- Binder carbon free (BCF) oxide thin film electrode fabrication.

Impact of Electrode Electronic Conductivity

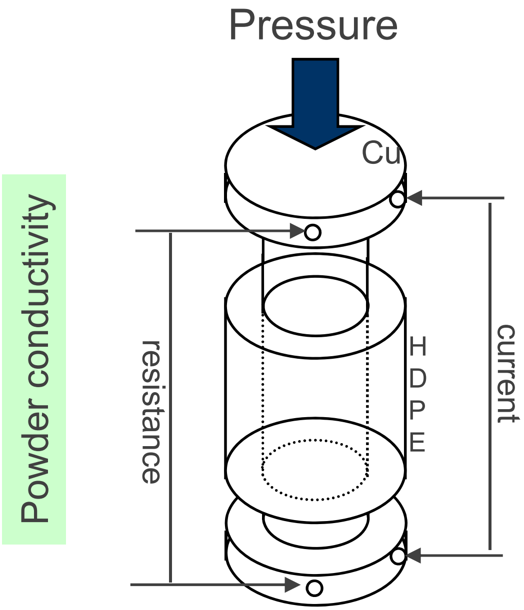
– Simulation of Gen 3 (NCM) Positive Electrode 5C HPPC Discharge



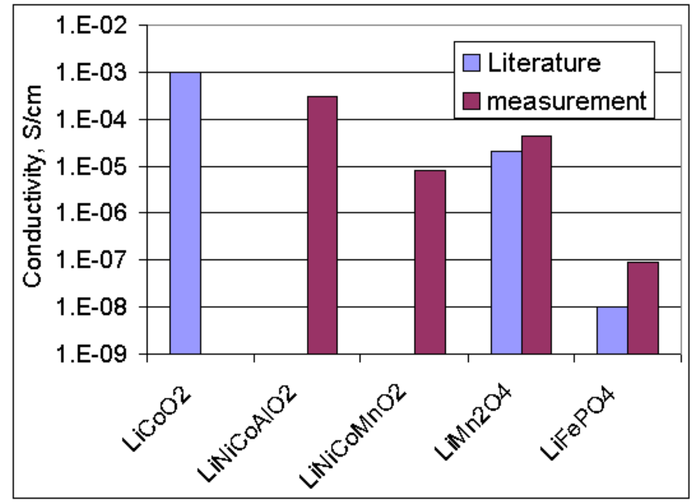
Together with the electrolyte conductivity, the composition of the conductive additive should be tailored to meet the power and energy requirements of lithium ion batteries.

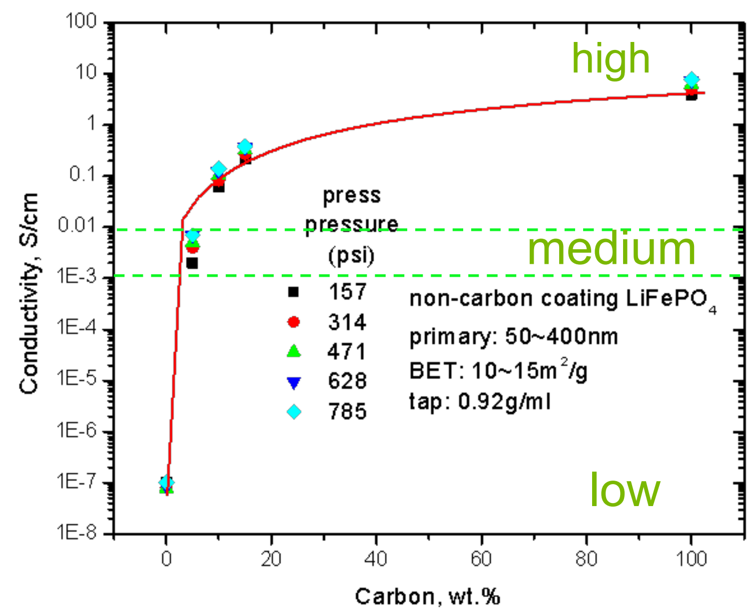
- >0.01 (ohm cm)$^{-1}$: electronic conductivity is much greater than the ionic conductivity and does not impact electrode impedance
- 0.001-0.01 (ohm cm)$^{-1}$: electronic conductivity is comparable to the ionic conductivity
- <0.001 (ohm cm)$^{-1}$: electronic conductivity is much less than the ionic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

Carbon Additive Effect on Conductivity of $LiFePO_4$/Carbon Blend



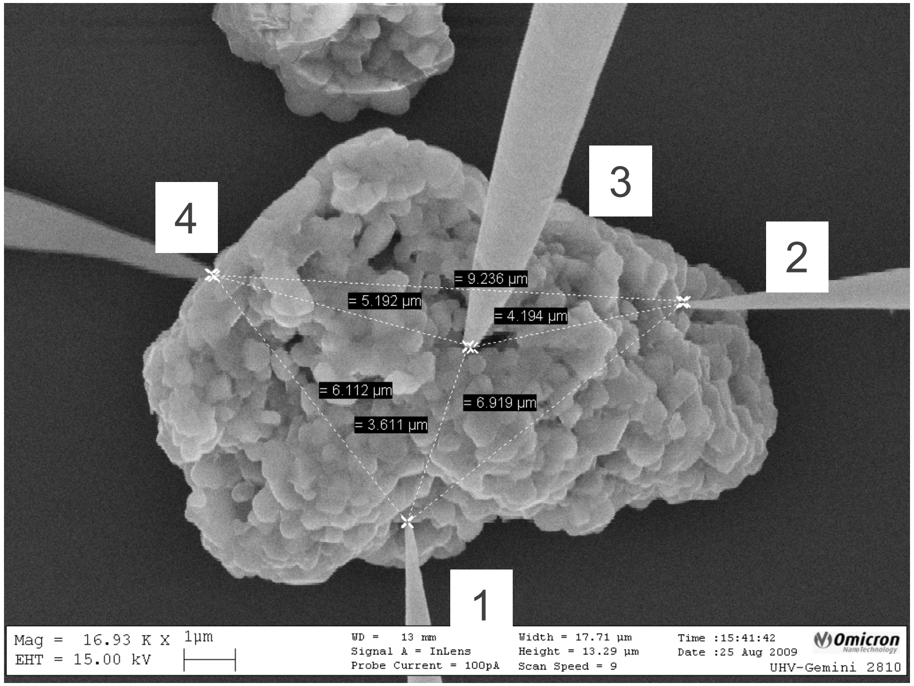
Schematic diagram of powder conductivity measurement apparatus

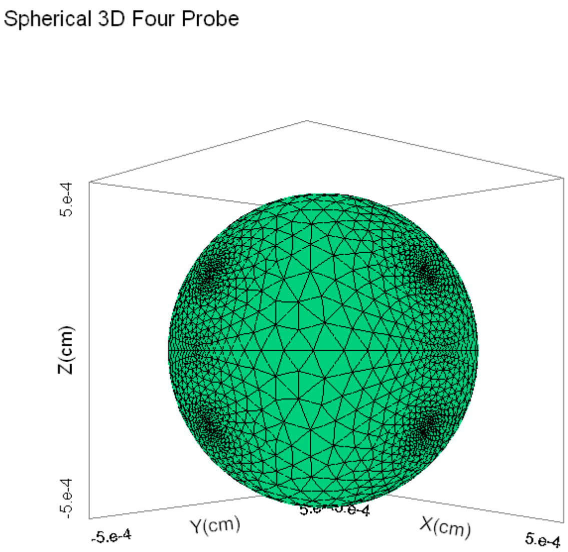




- Electronic conductivity increases with increasing the conductive additive, especially at low additive composition.
- 5 wt.% carbon additive can improve the powder conductivity of non-carbon coated $LiFePO_4$ from ~10^{-7} to ~10^{-3} S/cm.

Conductivity Measurement of Single Particle $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)

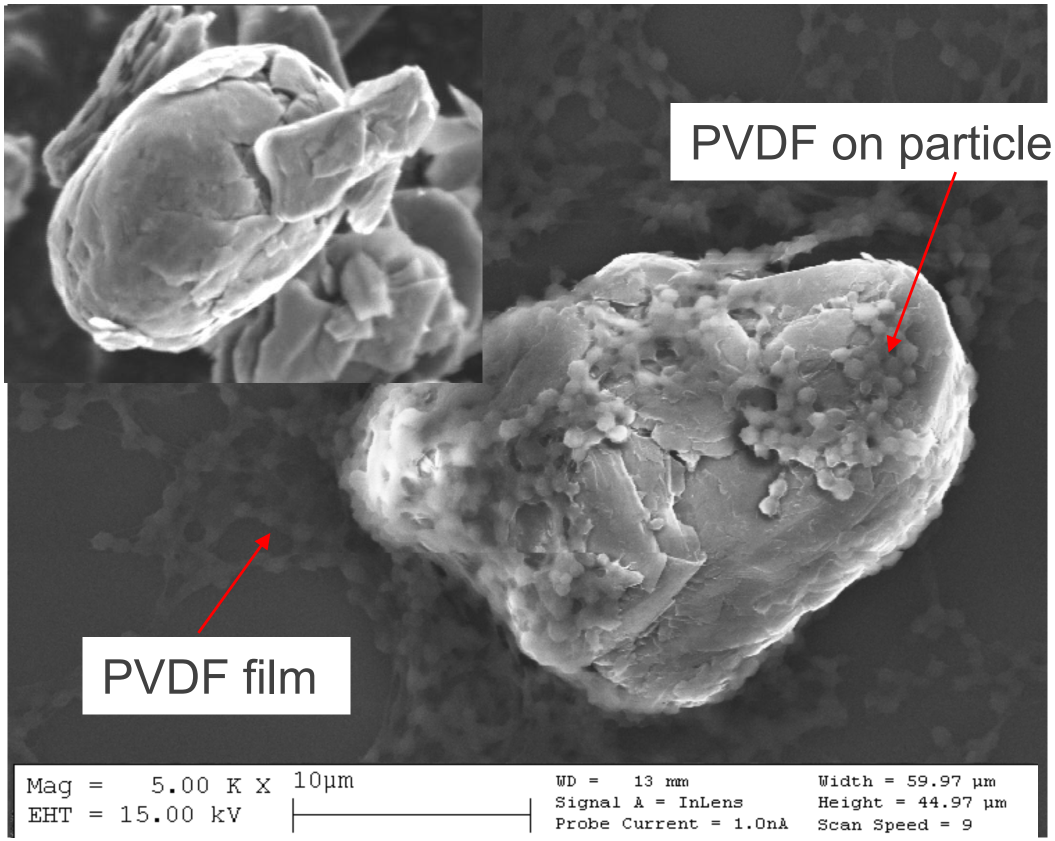




NCAPart5-13 (8-25-2009)

- The calculated conductivity is much higher than that of literature report, even with consideration of the contact resistance.
- The measured resistance for all of the tip pairs are similar.
- The observation above indicates that the contact resistance may be dominant.

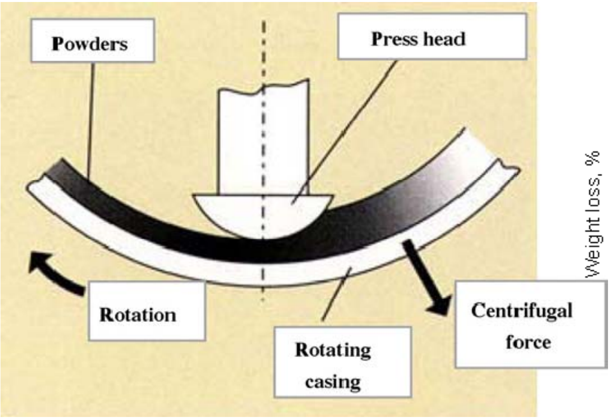
Interaction between Active Material and Binder

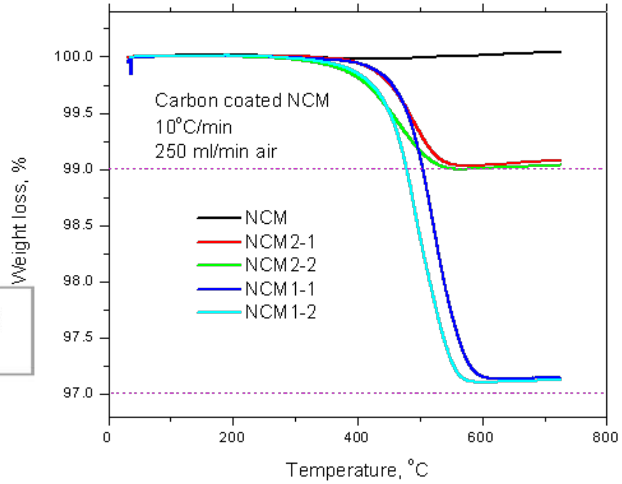


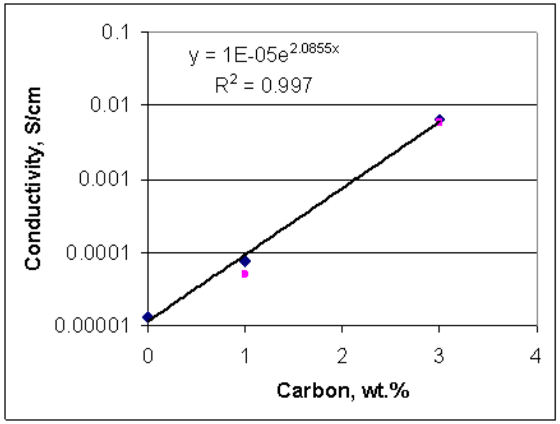
- With high binder/graphite ratio, PVDF binder forms a film on the surface of the graphite particles.
- The binder film was essentially such an electronic insulator with a high electronic resistance that is observed with the 4 probe SEM measurement.

- Four probe measurement on single particles demonstrate that contact resistance is the key for conductivity of composite electrode.

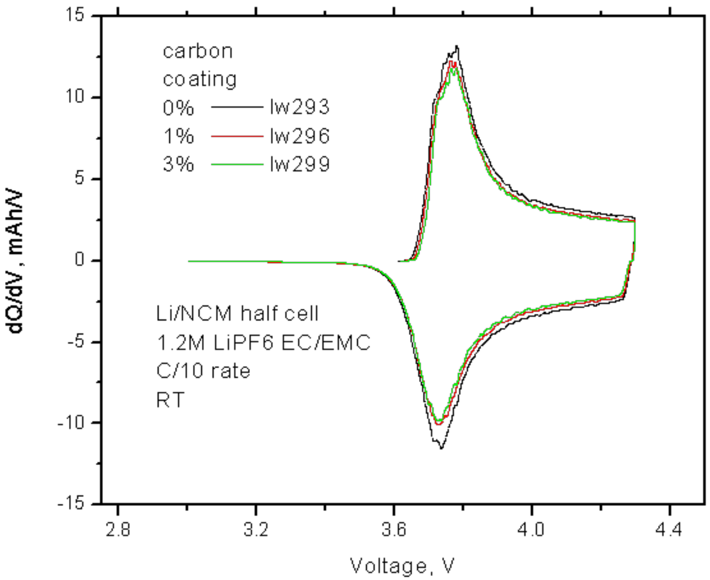
Carbon Coating Effect on Powder Conductivity





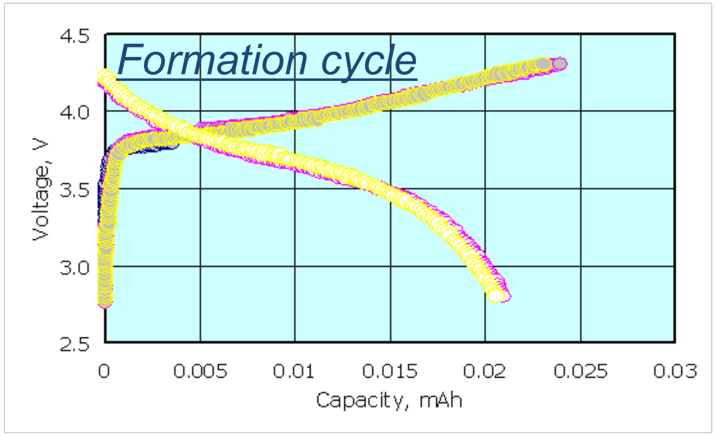


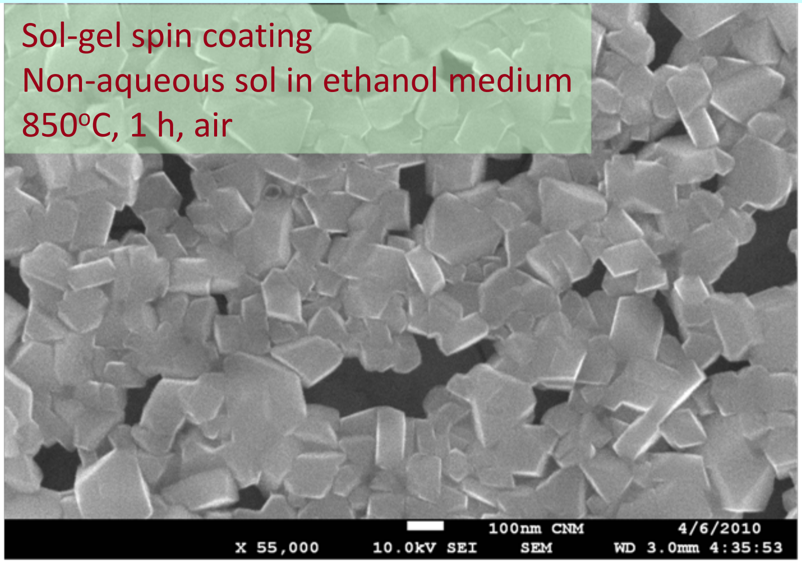
- Carbon coating on metal oxide is prepared.
- TGA results confirmed that right amount of carbon coating is obtained.
- Conductivity of NCM increases exponentially with carbon coating.
- Electrochemical results indicate same electrochemical properties for the NCM with and without carbon coating.
- The power capability and thermal stability will be investigated next.

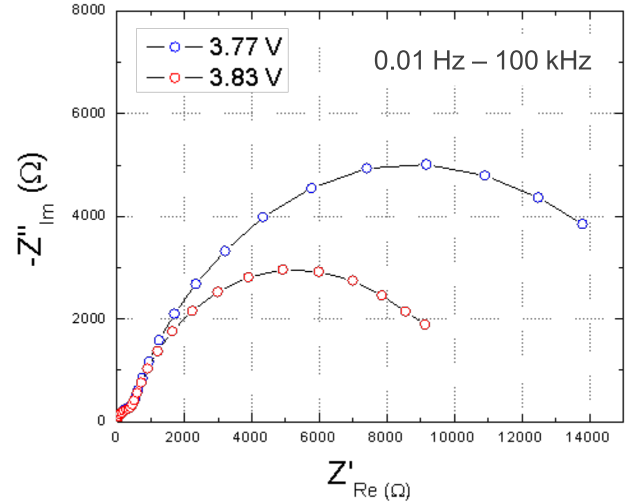


Binder and Carbon Free (BCF) Oxide Film

BCF oxide cathode is two-dimensional analog to the three-dimensional secondary particles for composite electrode, which can provide useful insight into the correlation between active material's particle characteristics and the electrode's electrochemical characteristics without complication from carbon and binder.







- Thin film $LiNiCoMnO_2$ is prepared. Around 100nm particle size is obtained. The electrochemical results indicate layered character.
- Electrochemical impedance spectra is measured and going to be analyzed.
- Different microstructures (particle size) with the same active material loading will be investigated.

Part II: Summary

- Conductivity of single particle has been studied using 4 probe SEM. The results indicate that the contact resistance might be the main contributor to the electronic conductivity of powder materials.
- The 4 probe SEM also shows that the binder is very high insulating material, the binder effect on the conductivity of electrode should be considered.
- Carbon coating on cathode materials (NCM) has been initiated to minimize the conductive additives without scarifying the electrochemical performance.
- Binder Carbon Free (BCF) thin film electrode was fabricated and tested. The electrochemical properties, such as lithium ion diffusion, is under investigation.

Future Plans

- Carbon coating impact on the cathode performance will be continued.
- The contact resistance of particle to particle, and particle to current collector will be investigated.
- Modeling work will be used to predict the optimum amount of carbon additives for cathode electrode.
- Study on the effects of lithium metal oxide particle's physical properties using binder- and carbon free (BCF) thin film will be continued.
  - Particle size, active material loading, and surface area can be controlled (number of coating, annealing temperature, annealing time).

Contributors and Acknowledgments

Argonne National Laboratory

- Nathan Liu
- Jack Vaughey
- Daniel Abraham
- Paul Nelson
- Lynn Trahey
- Khalil Amine
- Gary Henriksen
- Electron Microscopy Center (EMC)
- Center for Nanoscale Materials (CNM)

- Hitachi Chemicals, Japan
- Sumitomo Osaka Cement Co., LTD., Japan
- Mitsubishi Chemical Corp. Japan
- Daikin Inc., Japan
- Porous Power Technology, CO
- Hirose Paper North America, GA
- Exxonmobil Chemical Co., NY
- Somer Thin Strip, CT
- Pred Materials International, Inc., NY
- Hosokawa Micron Corporation, NJ
- Leica Microsystems

Support from David Howell of the U.S. Department of Energy's Office of Vehicle Technologies Program is gratefully acknowledged.