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Streamlining the Optimization of Li-Ion Battery Electrodes

<u>Wenquan Lu</u> & <u>Sun-Ho Kang</u>

Electrochemical Energy Storage

Chemical Sciences and Engineering Division

Argonne National Laboratory

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Vehicle Technologies Program

Overview

Timeline

- Project start date
  - Oct. 2008
- Project end date
  - Sep. 2014
- Percent complete
  - <8%

Budget

- Total project funding for FY09
  - DOE: $300K

Barriers

Development of a safe cost-effective lithium-ion battery for a PHEV with a 40 mile all electric range that meets or exceeds all performance goals.

- Establishing the interdependence of lithium ion electrode performance and the specifics of the fabrication process.
- Reducing the complexity of the optimization process caused by the broad range of active materials, additives, and binders.
- Quantifying the impact of fundamental phenomena on electrode performance.

Objectives of This Study

- 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.

Approach

- Characterize the physical properties of individual components of composite electrodes for lithium ion batteries.

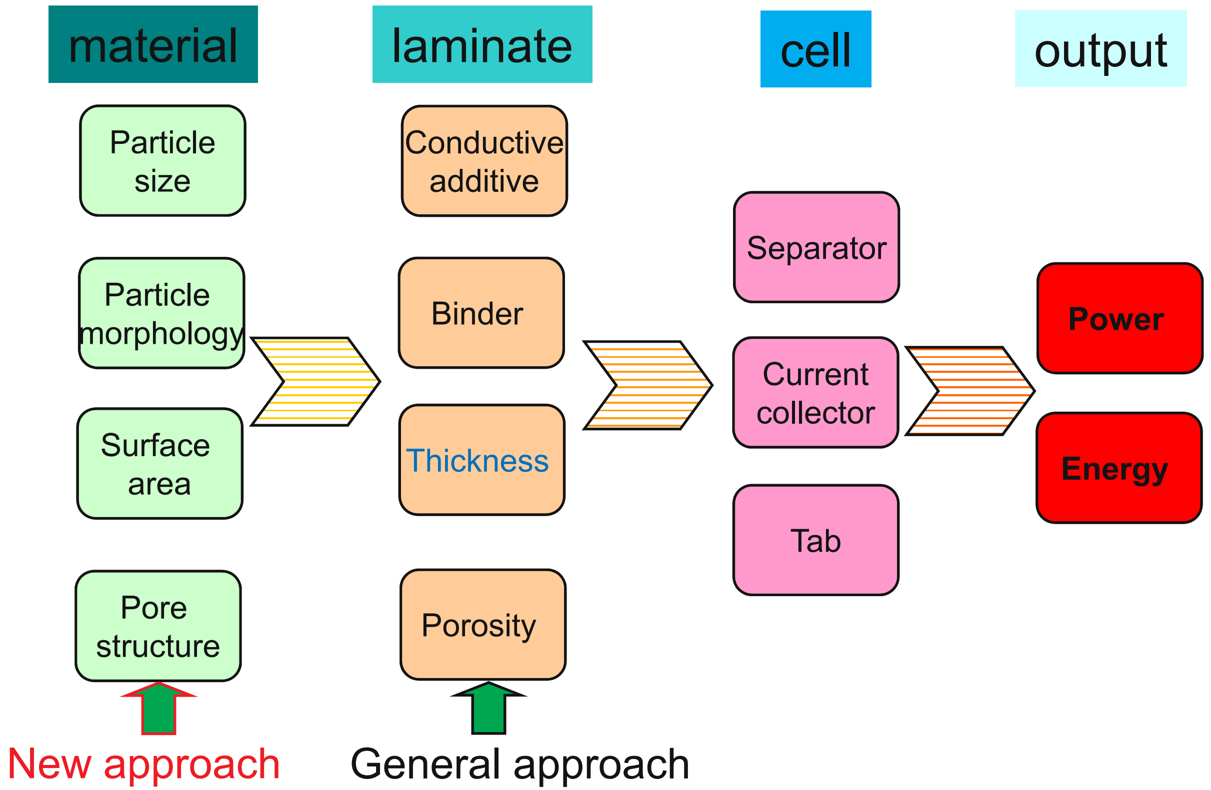
- Initial focus will be to investigate electrode electronic conductivity and cell performance affected by electrode composition and processing.

- Develop models to help quantify the impact of fundamental phenomena on electrode performance.

Technical Accomplishments

- New approach to streamline the optimization of electrode is identified.
- Significant impact of electrode processing on the electrochemical performance of lithium ion battery is 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.
  - Conductivity range of various active electrode materials examined
  - Conductivity of $LiFePO_4$ carbon blends determined.

Streamlining the Optimization of Electrode



- General approach has been to optimize the electrode by varying the conductive additive and binder to overcome the percolation threshold at laminate level.
- Streamlining the optimization of electrode requires a new approach to establish the scientific basis at the particle level.
- The process effect on the electrode optimization will be investigated.

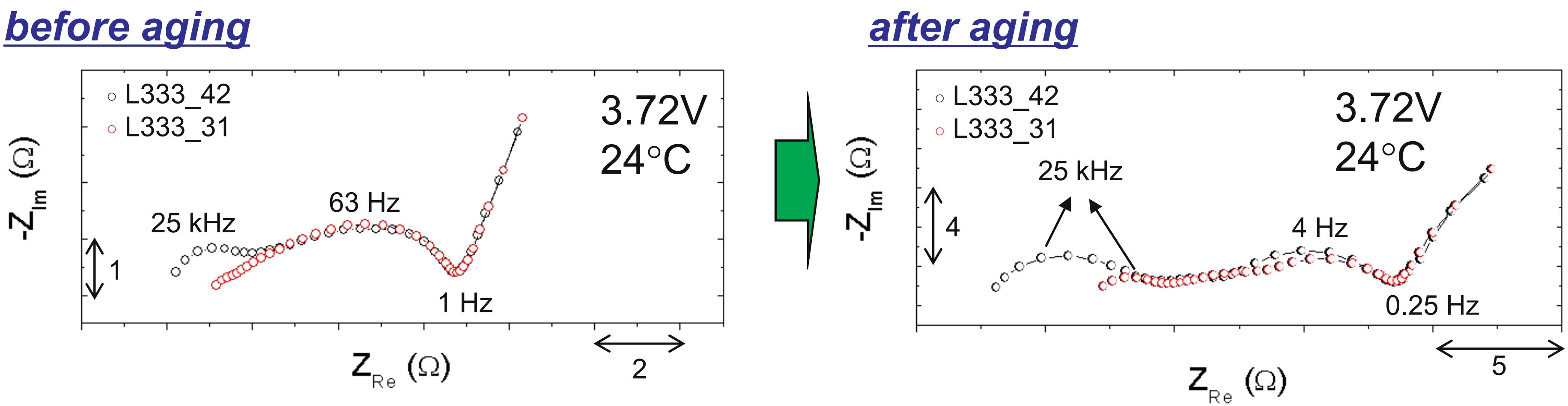
Physical Property Variation of Electrode Materials

- The broad range physical properties of active materials for both anode and cathode is one of driving forces to initiate this project.
- Fundamental understanding of the material properties is critical for electrode optimization.

characteristics	unit		low	high
density	g/ml	tap	<1	3
		true	0.5	9
particel size	μm		0.1	100
surface area	m^2/g		0.1	100
porosity	%			
conductivity	S/cm		1.00E-09	1.00E-02

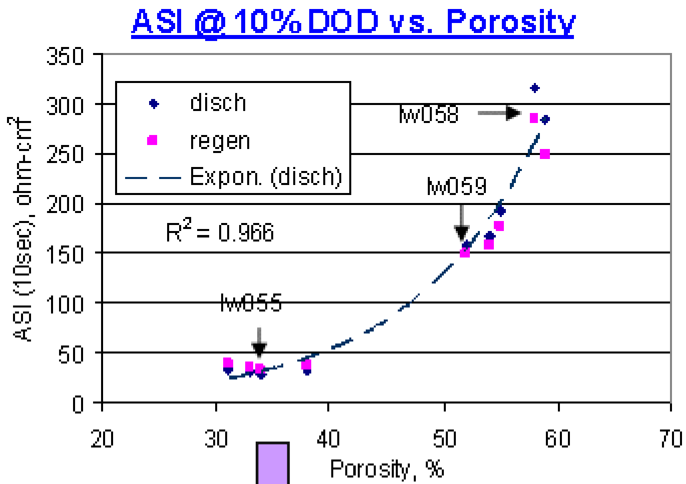
Process Effect on $Li_{1.05}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.95}O_2$ Electrode

- Electrode: L333_42 (42% porosity) and L333_31 (31% porosity)
- Cell impedance change before and after 55 °C aging (3.6-3.9 V, 2 mA, 200 cycles)

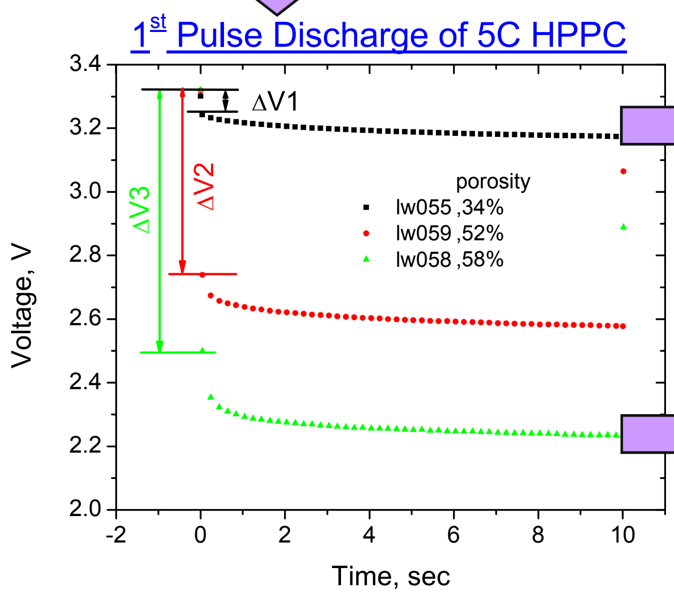


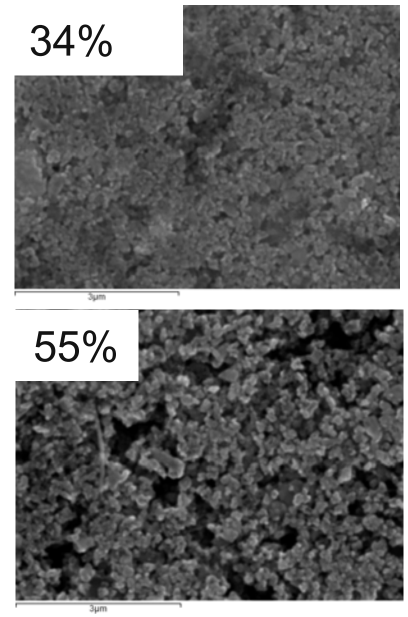
- Similar impedance behavior (in terms of characteristic frequency and impedance arc size) before and after aging at mid- and low-frequency ranges.
  - *Note: The impedance spectra were shifted with reference to low-frequency minimum (1 Hz before aging and 0.25 Hz after aging) for easy comparison.*
- Significant difference at high-frequency range (25 kHz) depending on the electrode porosity.
  - This frequency range is from electronic contribution (not ionic).
  - The increase in high-frequency impedance will affect d.c. pulse power.

Process Effect on Olivine Electrode



- The ASI of electrode with nano size $LiFePO_4$ is significantly reduced by harder calendering – resulting the lower electrode porosity.
- The SEM image indicates that the better electronic contact between particles in the lower porosity electrode might be reason to improve the power performance of the cell.





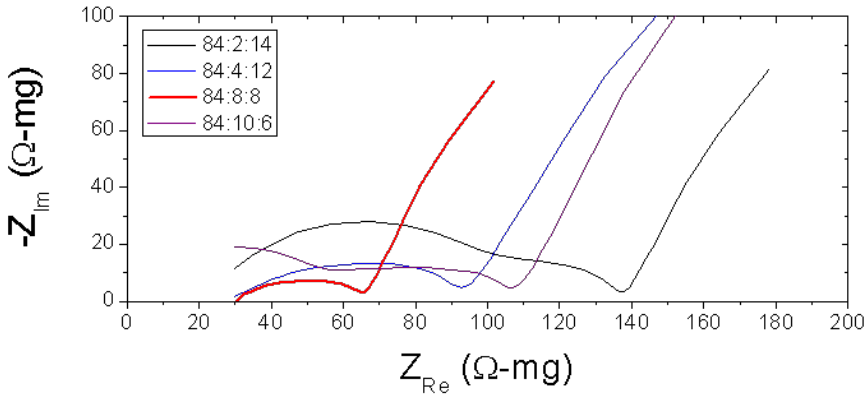
Physical properties:
Particle size:
D50 = 1.4 μm
Surface area:
23.9 m^2/g
Tap density:
0.44 g/cm^3

Olivine electrode:
C-$LiFePO_4$: 84wt.%
SFG-6: 4wt.%
CB: 4wt.%
PVDF: 8wt.%

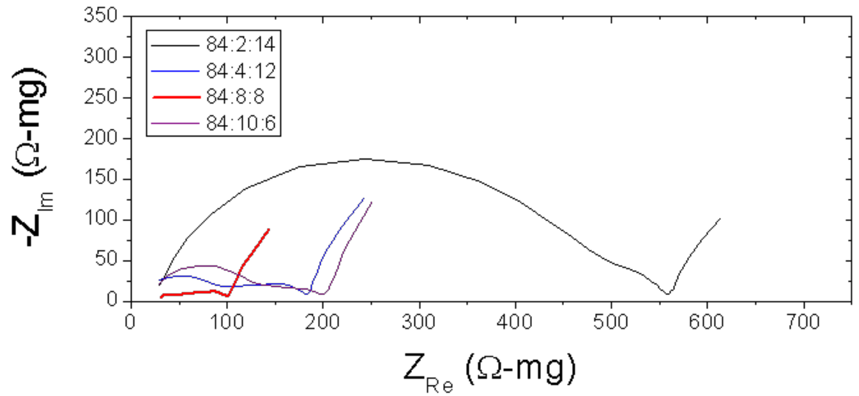
Electrode Composition Effect on Impedance

- Electrodes with different oxide(L333):carbon(Super P):binder(KF1100) ratios were prepared and the effect of electrode composition on the cell impedance behavior was studied (constant porosity, 35%).

before aging

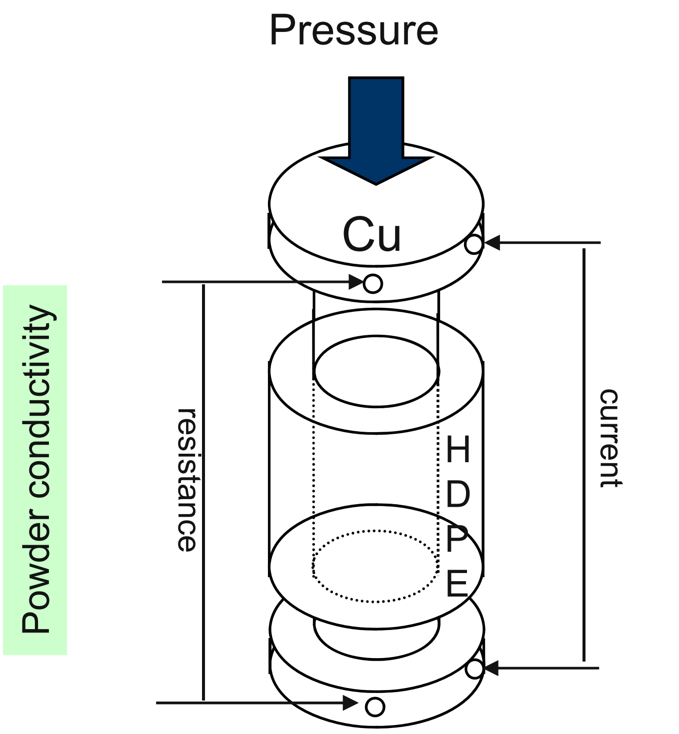


after aging

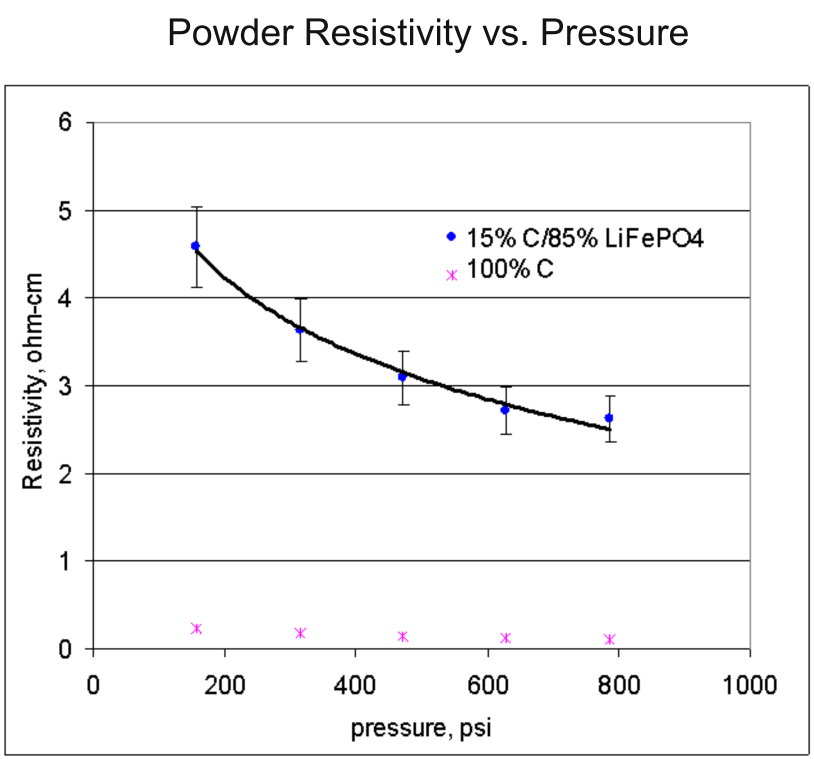


- Oxide:carbon:binder ratio critically affect the cell impedance and its aging behavior.
- Our data, so far, indicates that electrodes with 84 wt% oxide, 8 wt% carbon, and 8 wt% PVdF binder show the lowest initial impedance and lowest impedance after aging for L333.

Preliminary Proof of Design for Conductivity Measurement

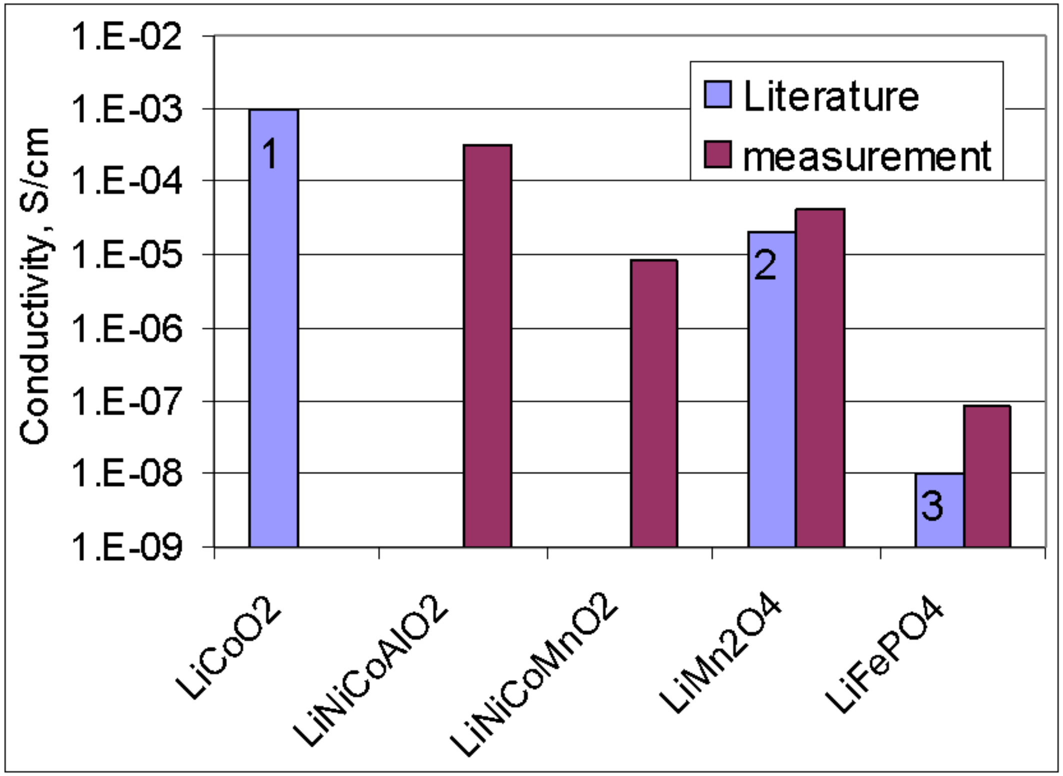


Schematic diagram of powder conductivity measurement apparatus



- Electronic conductivity of powder can be measured under various pressures using the apparatus.
- The measured powder resistivity decreases within a magnitude from low to high press pressure.

Conductivity Variations of Cathode Materials

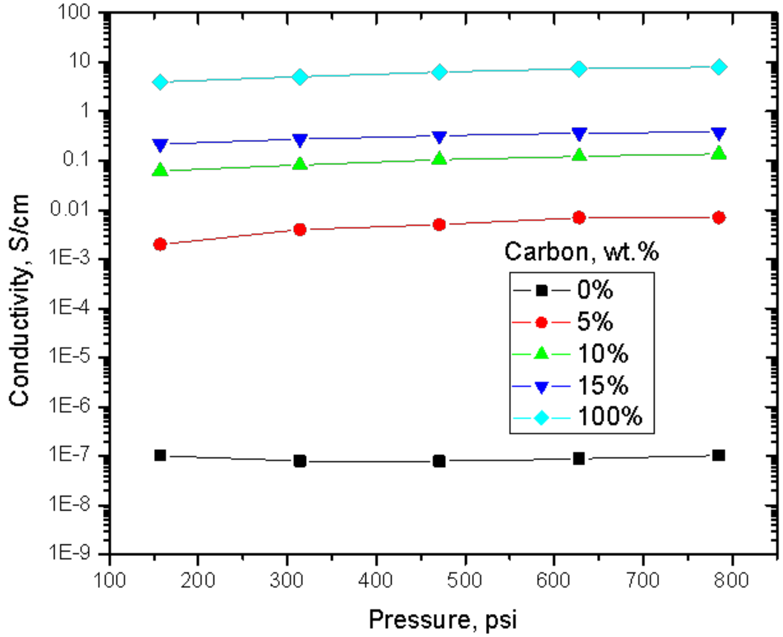


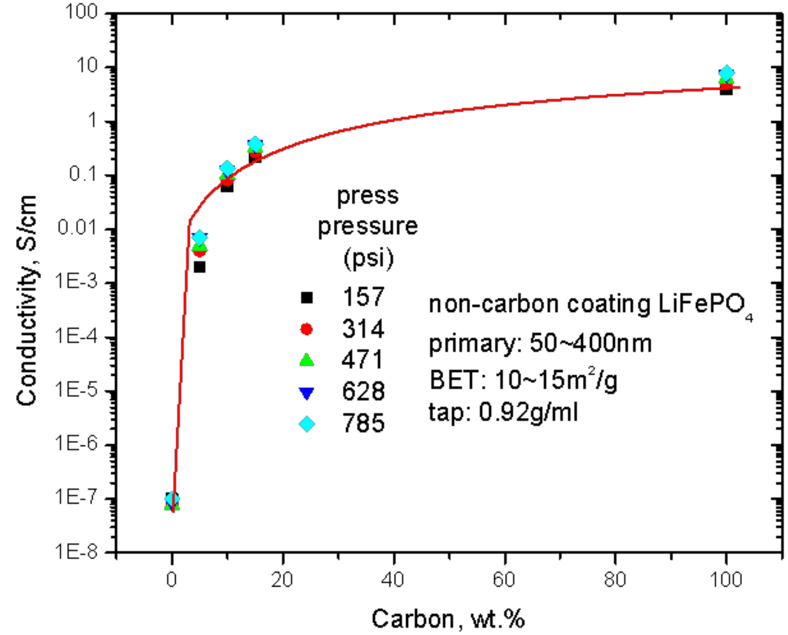
Cathode materials:
LiNiCoAlO2: $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$
LiNiCoMnO2: $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$
LiFePO4: no carbon coating

1. Tukamoto, H. & West, A.R. J. Electrochem. Soc. 144, 3164–3168 (1997).
2. Kawaia, H., Nagatab, M., Kageyamac, H., Tukamoto, H. & West, A. R. Electrochim. Acta 45, 315–327 (1999).
3. Chung, S.-Y., Bloking, J.T. & Chiang, Y.-M. Nature Mater. 2, 123–128 (2002).

- The measured conductivities of electrode materials are consistent with literature results.
- Electronic conductivity variation of different electrode materials indicates different electrode formulations are needed for optimized electrodes.

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

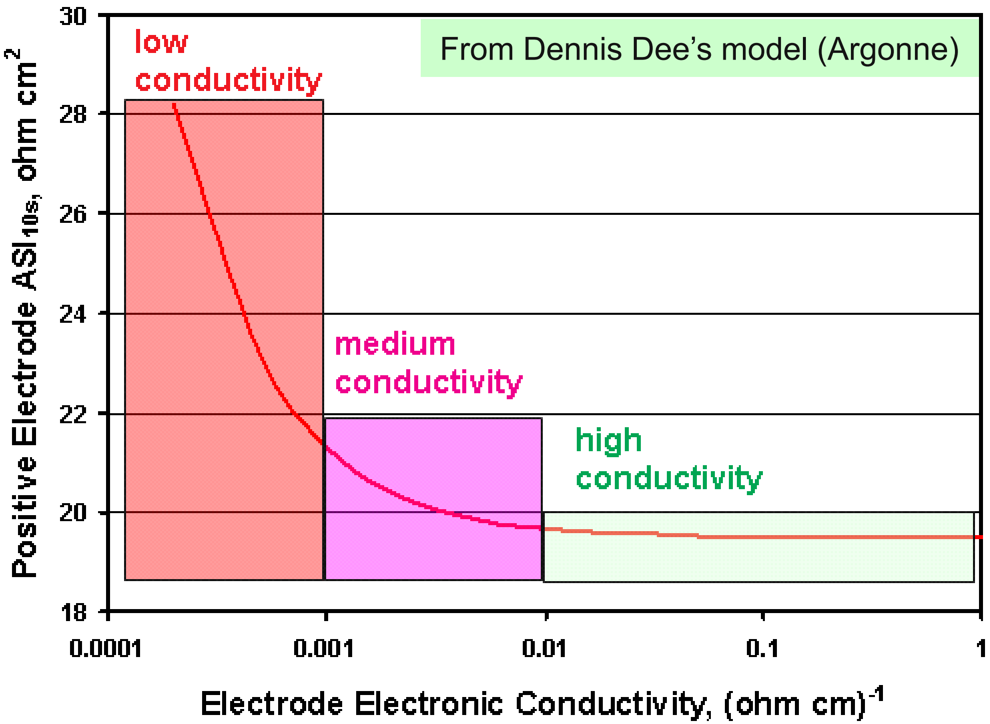




- Electronic conductivity increases with increasing the conductive additive, especially at low additive composition.
- 5 wt.% carbon additive can improve the powder conductivity of non-carbon coated $LiFePO_4$ from ~10^{-7} to ~10^{-3} S/cm.

Impact of Electrode Electronic Conductivity

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



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

Future Plans

- Electronic conductivity characterization
  - Various active materials
  - Blend of active material, carbon, and binder
  - To break down the contact resistance of particle to particle, and particle to current collector
- Physical properties characterization of active materials, including morphology, particle size and distribution, surface area, and pore structure.
- Process effect on electrode conductivity
  - Four point probe method
  - Electrochemical impedance spectroscopy (EIS)
  - HPPC pulse performance
- Correlate electrode material properties with electrochemical performance

Summary

- A new approach will be used to establish the scientific basis for streamlining the optimization of electrode.
- Electrode processing is found to have significant impact on electrode performance
  - High frequency arc of NCM electrode, related to the electronic conductivity.
  - High power performance of carbon coated nano size $LiFePO_4$ electrode with better electronic conductivity (low porosity).
- The electronic conductivity of electrode materials can be measured using home-made apparatus.
  - Broad range of electronic conductivities of various cathode materials was validated, indicating the necessary of electrode optimization.
  - The conductivity of $LiFePO_4$/carbon blend shown the conductive additive (carbon) effect.
  - Simulation of Gen 3 positive electrode 5C HPPC discharge impedance shows the effect of electronic conductivity.

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