MATERIALS BENCHMARKING ACTIVITIES FOR CAMP FACILITY

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Chemical Sciences and Engineering Division
Argonne National Laboratory

Vehicle Technologies
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Project ID: ES028

OVERVIEW

Timeline

- Start – Oct. 1st 2014
- Finish – Sep. 30th 2017

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE/USABC goals
  - Cost,
  - Performance.
- High energy active material Identification and evaluation

Budget

- Total project funding in FY2016: $350K (as part of CAMP effort)
- 100% DOE

Partners and Collaborators

- The Cell Analysis, Modeling, and Prototyping (CAMP) Facility (Andrew Jansen, ANL)
- Materials Engineering Research Facility (MERF) (Gregory Krumdick, ANL)
- Post Test Analysis Facility (Ira Bloom, ANL)
- Industries, Research institutions, and Universities

RELEVANCE

- An overwhelming number of materials are being marketed/reported by vendors/inventors for Lithium-ion batteries, which are needed to be validated for xEV applications.
- CAMP Facility was established at ANL to provide a realistic and consistent evaluation of candidate chemistries. In order to utilize the facility more efficiently and economically, the cell chemistries will be validated internally to determine if they warrant further consideration.
- The benchmarking (validation) activities will not only benefit the CAMP Facility, but also provide an objective opinion to the material developer. Moreover, the better understanding of the active materials at cell system level will support the material development efforts.

OBJECTIVES

- 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.
  - High energy active materials for both anode and cathode are focus of this project.
- To enhance the understanding of advanced cell components on the electrochemical performance and safety of LIB.
- To support the CAMP Facility for prototyping cell and electrode library development, also the MERF facility for material scale up.

APPROACH AND STRATEGY

- To collaborate with material developers and leverage ANL's expertise in electrode design and cell testing.
- Any cell chemistry, which has impact on the cell performance, will be validated, mainly in terms of
  - Electrochemical performance,
  - Electrode optimization,
  - Thermal stability.
- The electrochemical performance will be validated using coin type cells under test protocol derived from PHEV 40 requirements.

USABC Requirements of Energy Storage Systems for PHEV

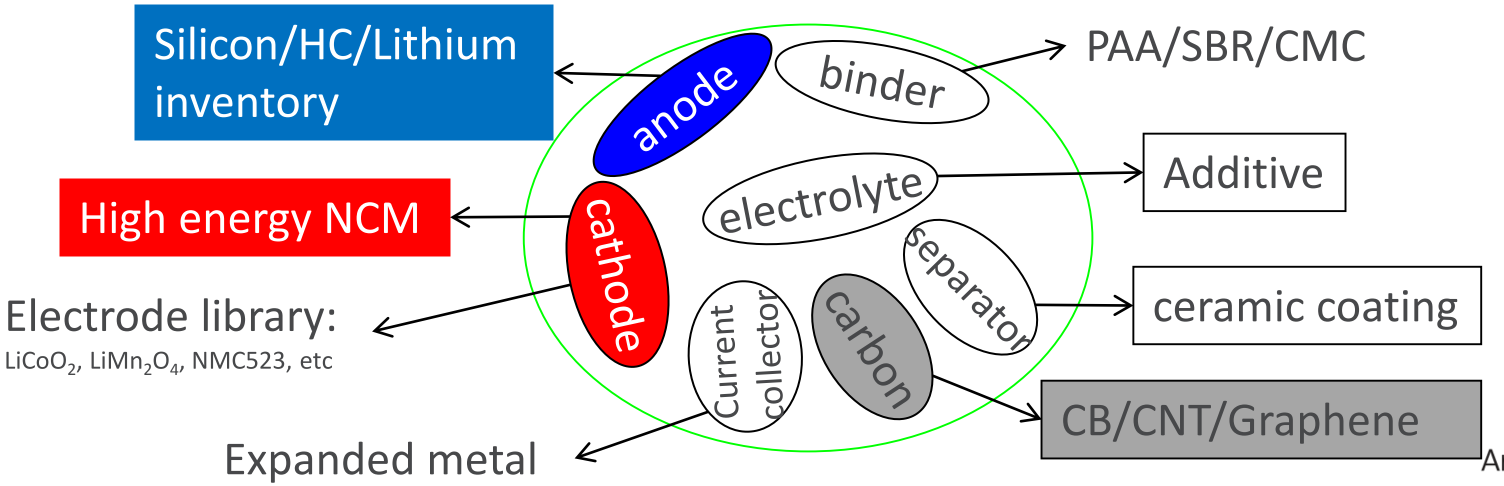
USABC Requirements of Energy Storage Systems for PHEV			
Characteristics at EOL	Unit	PHEV-20 mile	PHEV-40 mile
Reference Equivalent Electric Range	miles	20	40
Peak Discharge Pulse Power (10 sec)	kW	37	38
Peak Regen Pulse Power (10 sec)	kW	25	25
Available Energy for CD (Charge-Depleting) Mode	kWh	5.8	11.6
Available Energy for CS (Charge-Sustaining) Mode	kWh	0.3	0.3
Maximum System Weight	kg	70	120
Maximum System Volume	L	47	80

Test Protocol development

- In order to conduct the electrochemical characterization of the battery chemistries for Applied Battery Research for Transportation (ABR) program, C rate and pulse current was calculated for coin cells according to PHEV 40 requirements.

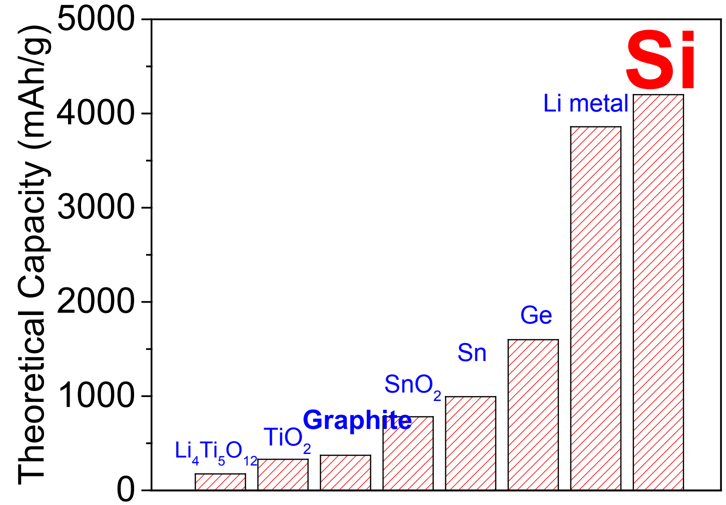
TECHNICAL ACCOMPLISHMENTS AND MILESTONES

- Studied lithium inventory effect on high energy, but low coulombic efficiency anode.
- Worked on advanced conductive additives to promote high energy and high power LIB.
- Explored high energy cathode materials and their thermal stability.
- Other cell components, such as electrolyte and additives, conductive additive, separators, binders, etc., have also been investigated.

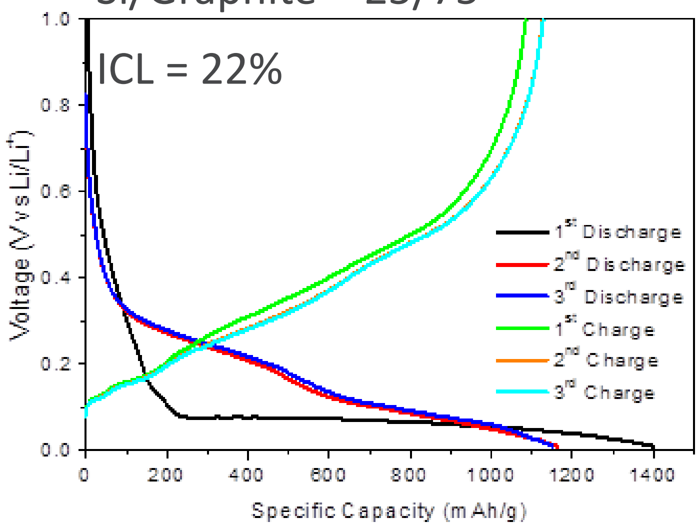


IRREVERSIBLE CAPACITY LOSS (ICL) OF HIGH ENERGY ANODE

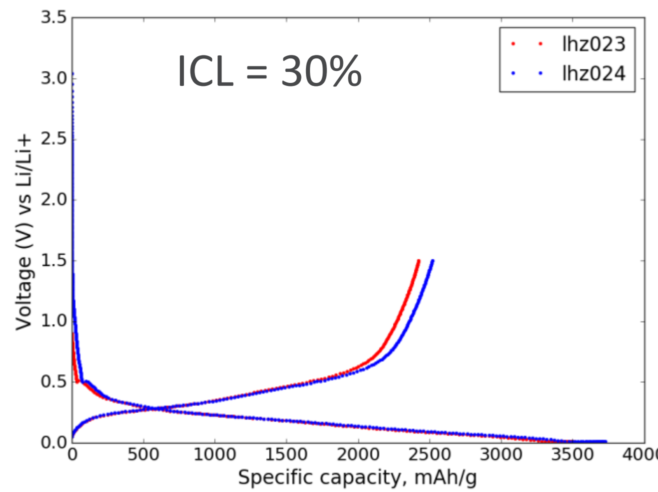
- Silicon can provide high capacity, but
  - Several issues need to be addressed.
  - One of them is large ICL, regardless of its form: Si, Si/graphite blend, or SiOx.



Si/Graphite = 25/75



SiOx



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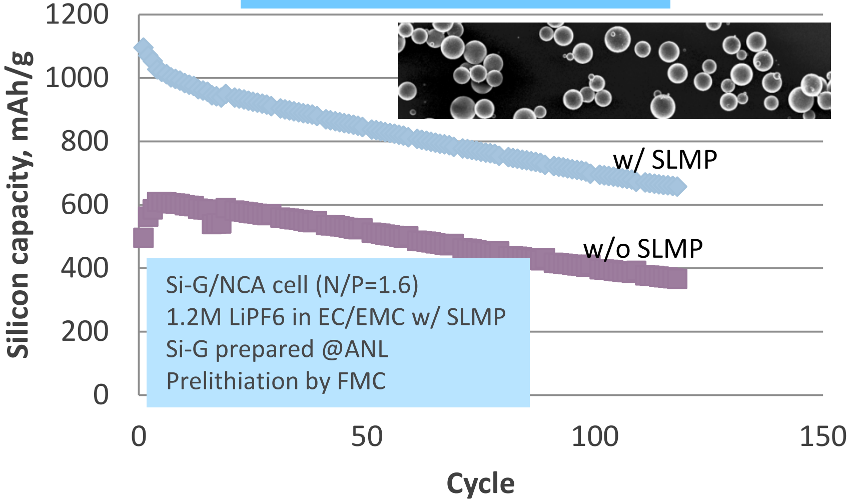
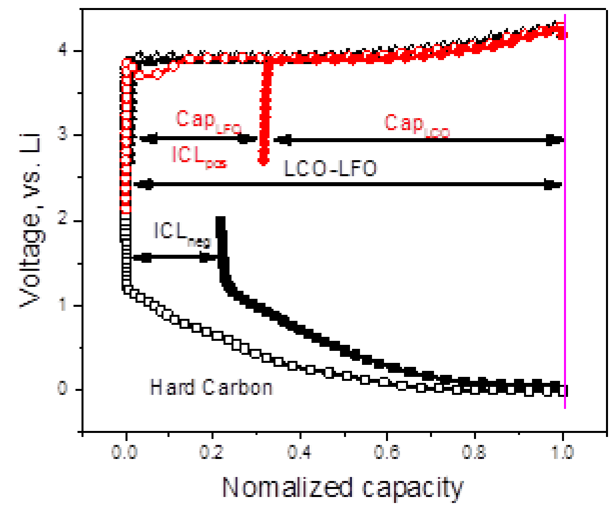
LITHIUM INVENTORY FROM ANODE OR CATHODE

Lithium from anode



Lithium from cathode



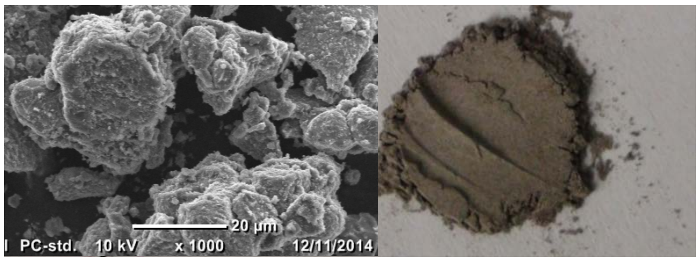
- Prelithiation of anode using lithium powder apparently can mitigate the ICL during 1st cycle.
- Challenge is to apply and activate the lithium powder on anode.

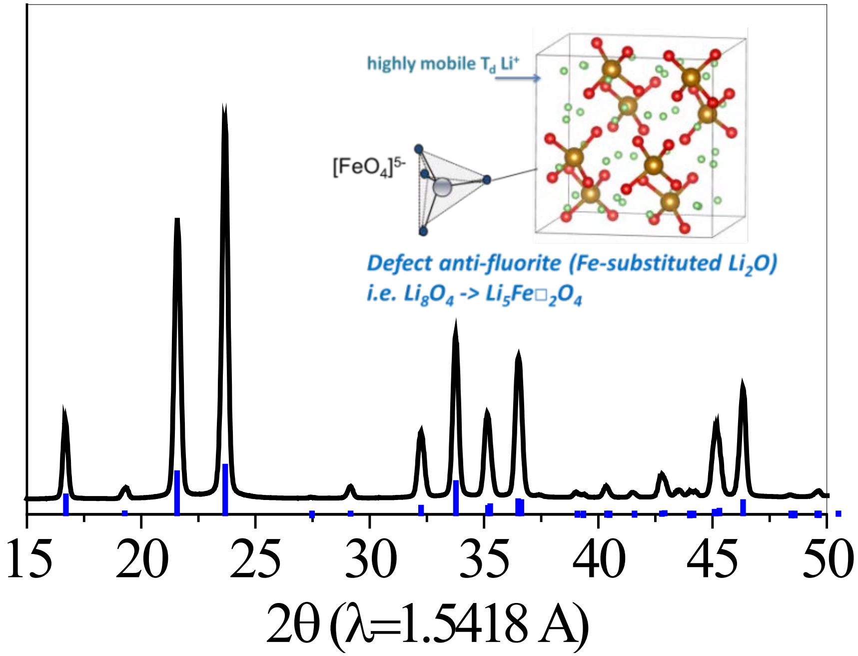
- How about blending lithium inventory into cathode electrode during slurry preparation?
  - Pros: drop in replacement.
  - Cons: adding dead weight.

LITHIUM RICH Li_5FeO_4 DEVELOPED

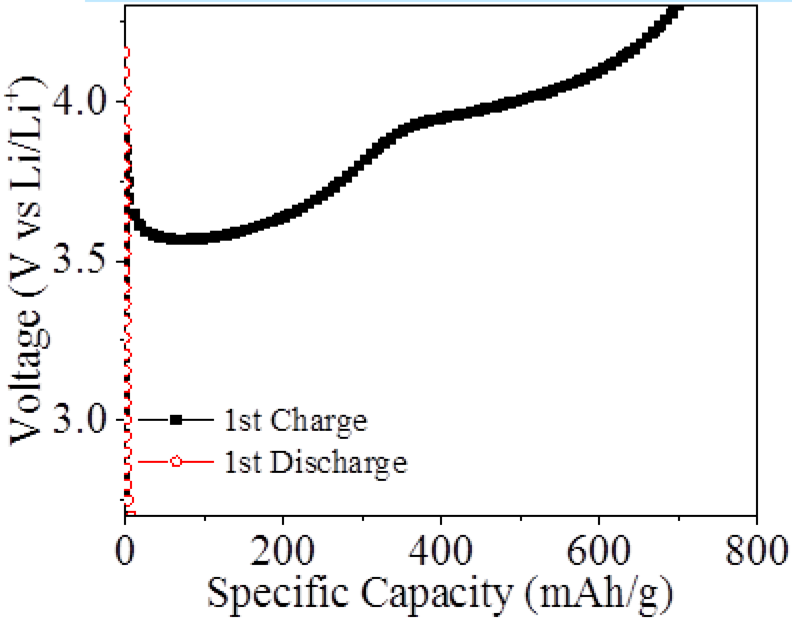
BY C. JOHNSON GROUP, ANL

Li_5FeO_4 powder





Charge/discharge of Li/LFO half-cell



- Very high lithium content:
  - 867 mAh/g if remove all 5 lithium. 760mAh/g was achieved in the lab.
  - Irreversible within normal operational voltage window.

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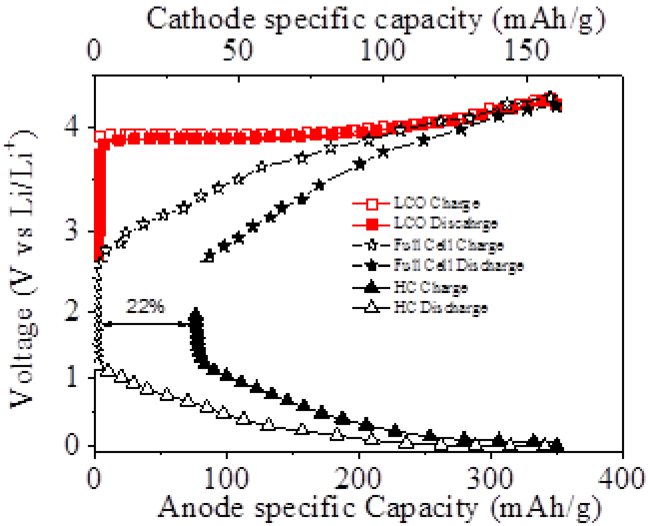
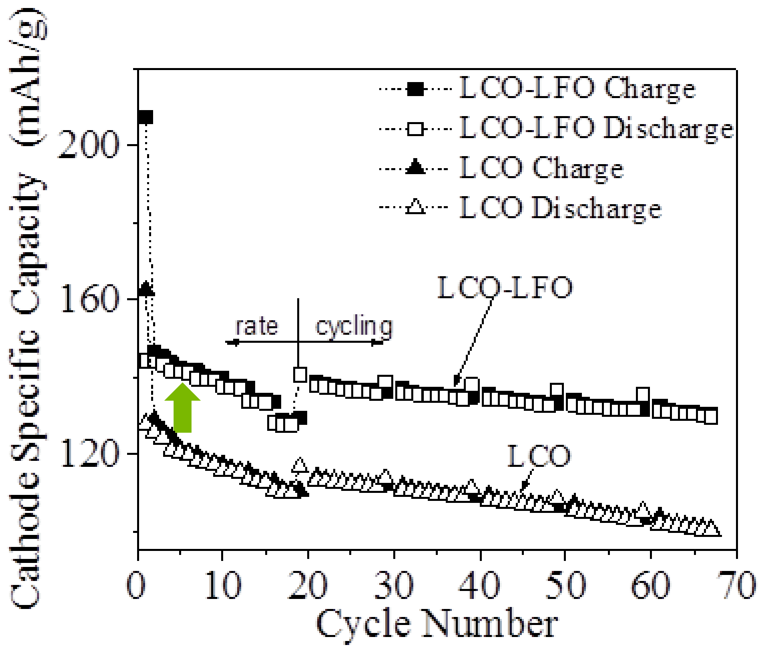
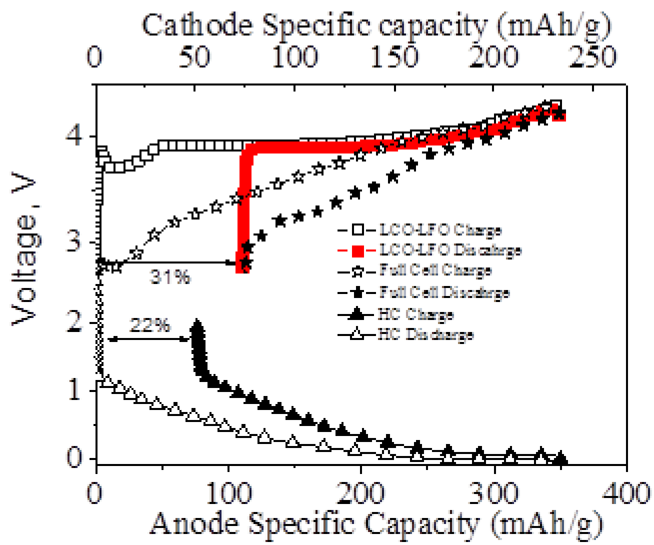
Li_5FeO_4 EFFECT ON HARD CARBON AND $LiCoO_2$ ELECTRODE COUPLE

HC vs. LCO/LFO (0wt.%)





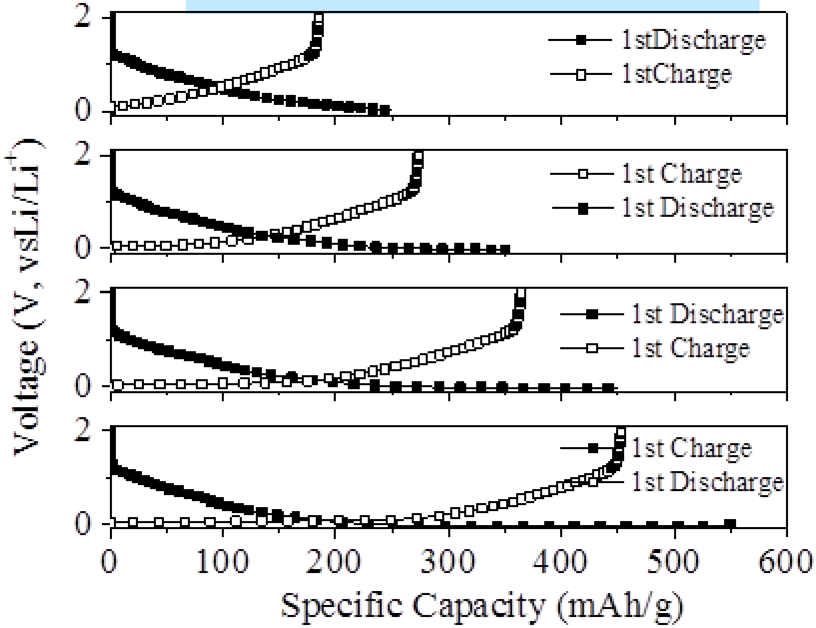
HC vs. LCO/LFO (7wt.%)



- 7wt.% LFO in cathode can prevent sacrificing of valuable cathode material to compensate the ICL on negative electrode.
- The reversible capacity of cathode increases from 121mAh/g of LCO only to 144mAh/g of LCO/LFO(7wt.%) in full cell using Hard Carbon (HC) as anode.

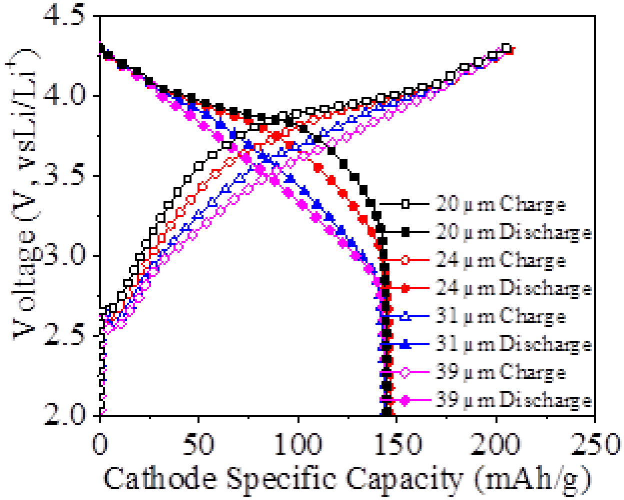
ENERGY DENSITY IMPROVEMENT BY MAXIMIZING HC CAPACITY

Voltage profiles of Li/HC half-cells with various cut-off voltages

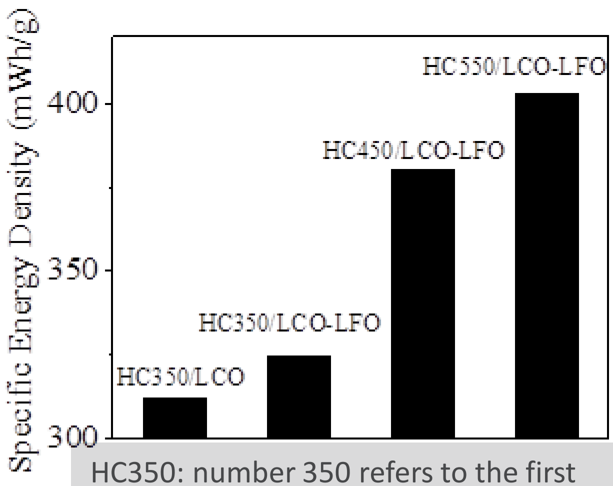


- More capacity can be achieved by lowering cut-off voltage for HC.
- The energy density of full cell can increase from 325Wh/kg to 400Wh/kg by utilizing more capacity from HC.

HC/LCO-LFO full cell



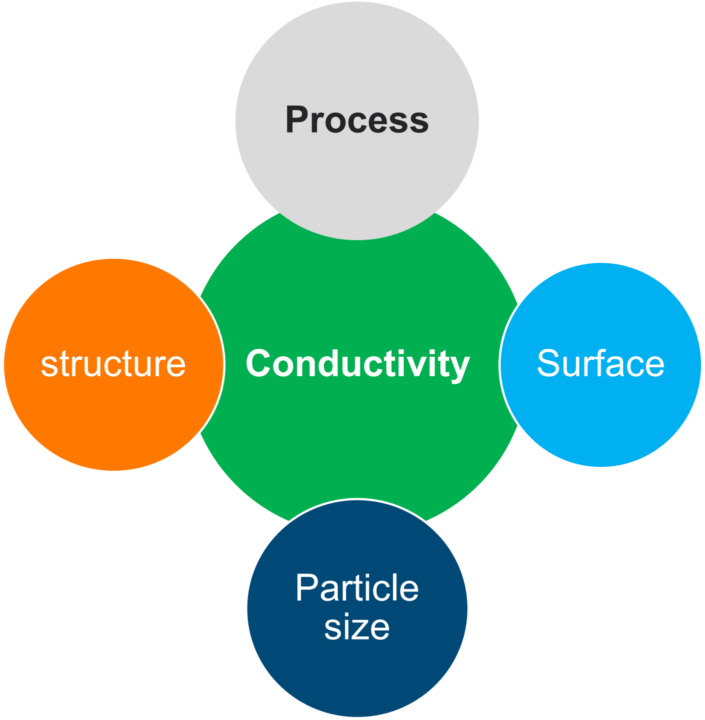
Increasing HC capacity usage by lowering its loading (thickness)



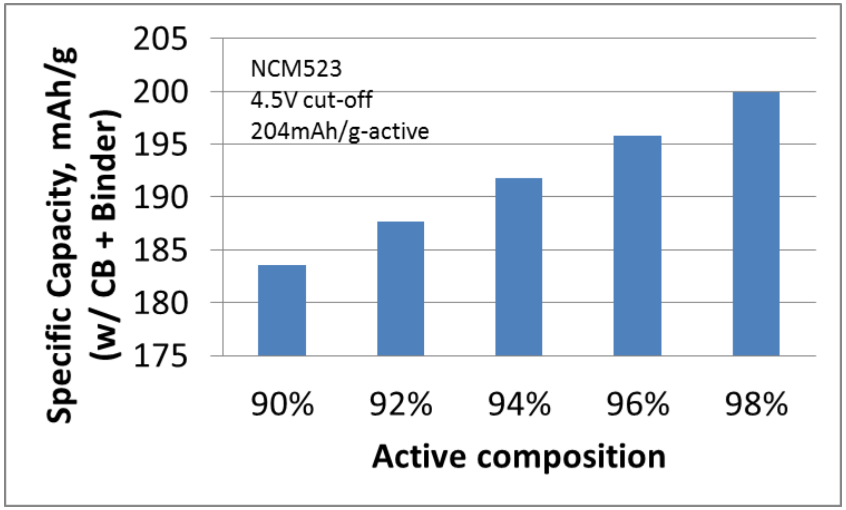
HC350: number 350 refers to the first lithiation capacity of HC (mAh/g).

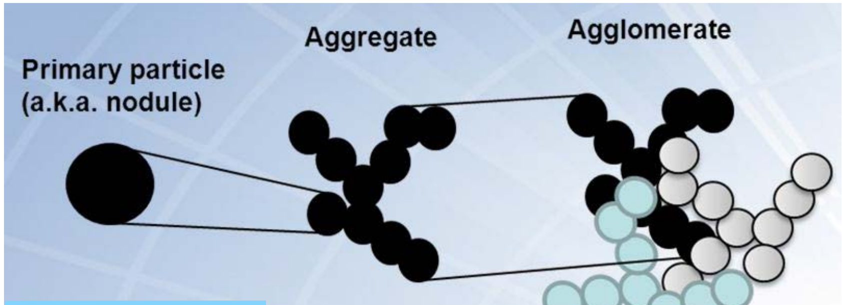
CONDUCTIVE ADDITIVE DEVELOPMENT
COLLABORATION WITH CABOT

- Great challenge on high energy active materials forces optimization of whole cell system, including electrode optimization.



Carbon additive effect on electrode capacity





Provide by Cabot

1. A. Mdarhri et. al., Electronic conduction and microstructure in polymer composites filled with carbonaceous particles, J. Appl. Phys. Vol. 112, p034118 (2012). threshold volume fraction = 8vol.%.
2. Electrode Fabrication and Materials Evaluation, Vince Battaglia, 2008 DOE Merit Review, Washington DC.

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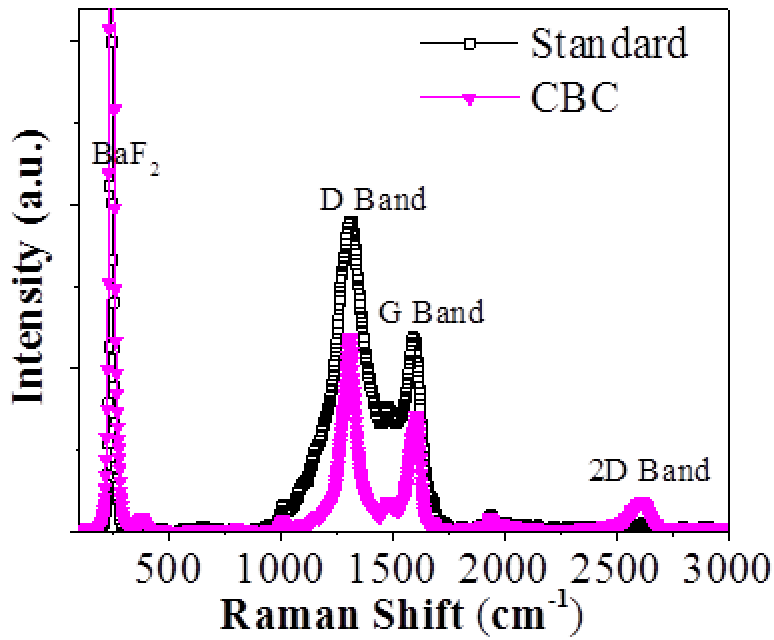
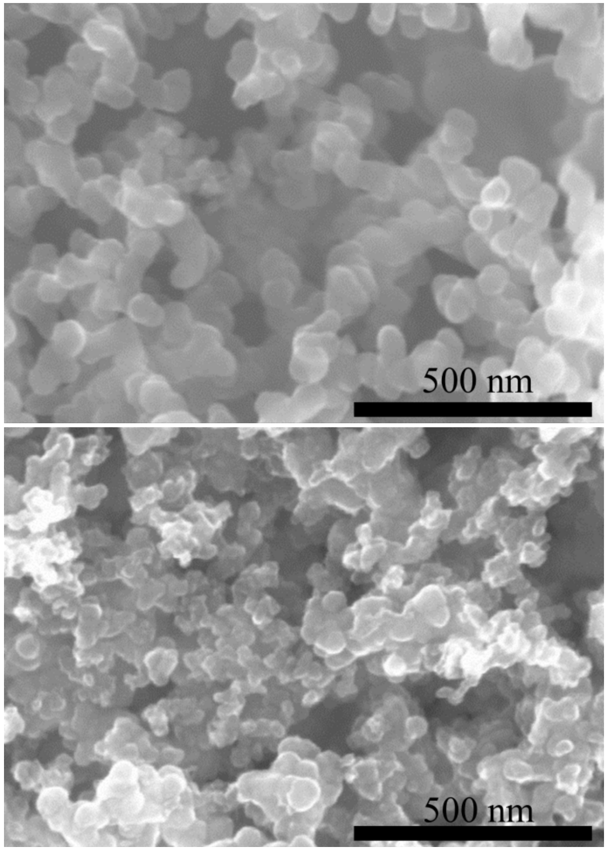
SURFACE TREATED CARBON BLACK FROM CABOT (CBC)

Sample ID	Lot#	Amount	N2 BET SA	OAN
		g	m2/g	ml/100g
CBC	84633	~100	90-100	140-170





- Carbon black developed at Cabot with balanced particle size, structure, and graphitized surface.

CARBON BLACK DISTRIBUTION IN NCM523 COMPOSITE ELECTRODE

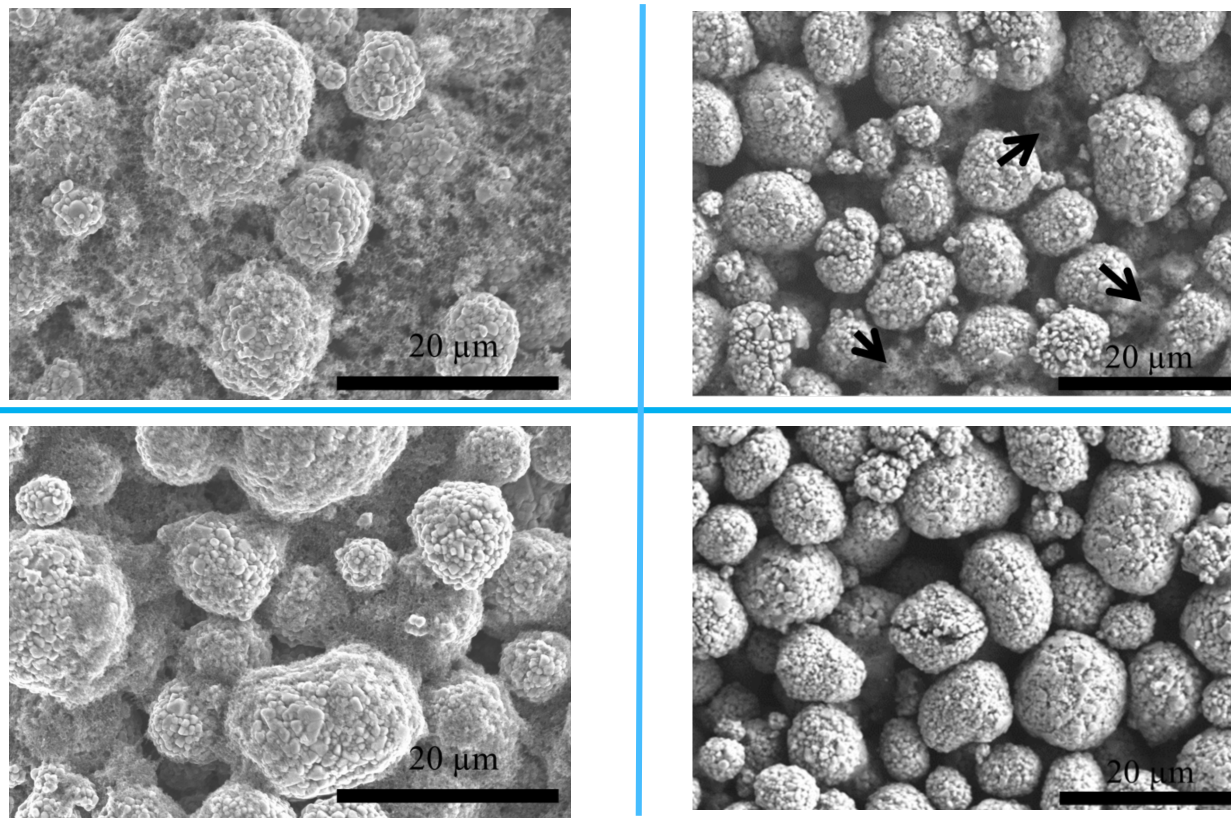
5wt.% CB

1wt.% CB

standard

CBC

Carbon black from Cabot



- Better dispersion was observed in NCM523 electrode when 1wt.% Cabot carbon black was used.

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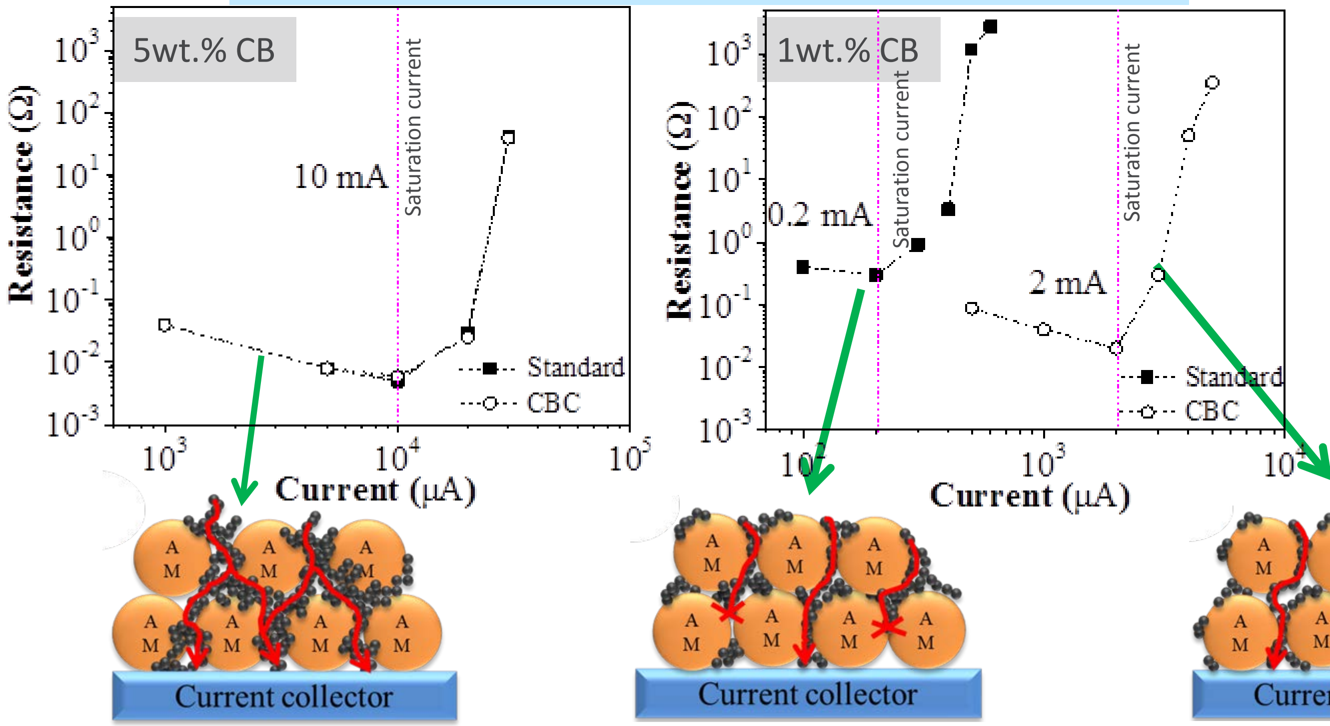
NON-LINEAR CONDUCTIVITY OF NCM523 COMPOSITE ELECTRODE

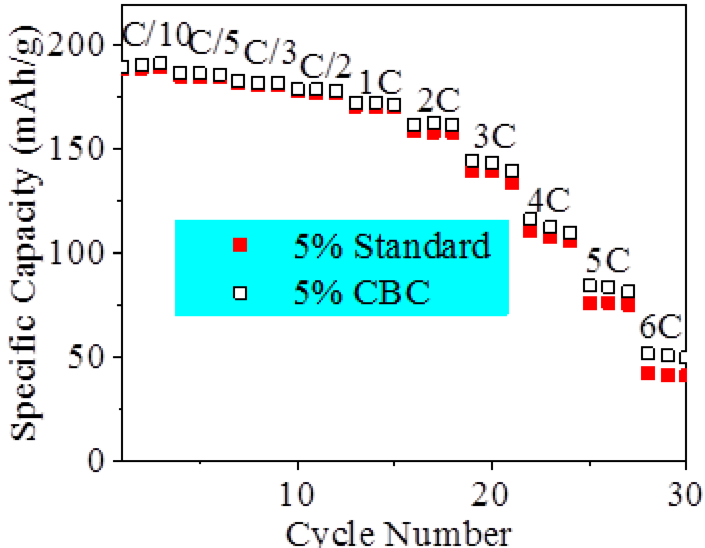
Non-linear conductivity of NCM523 electrode

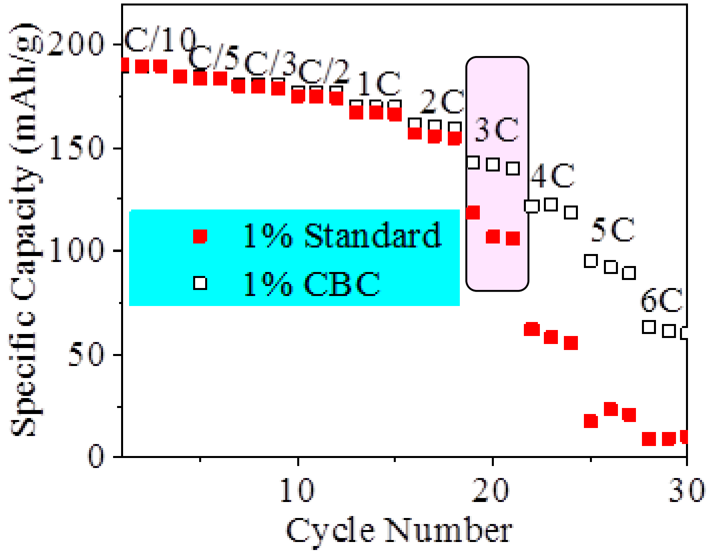


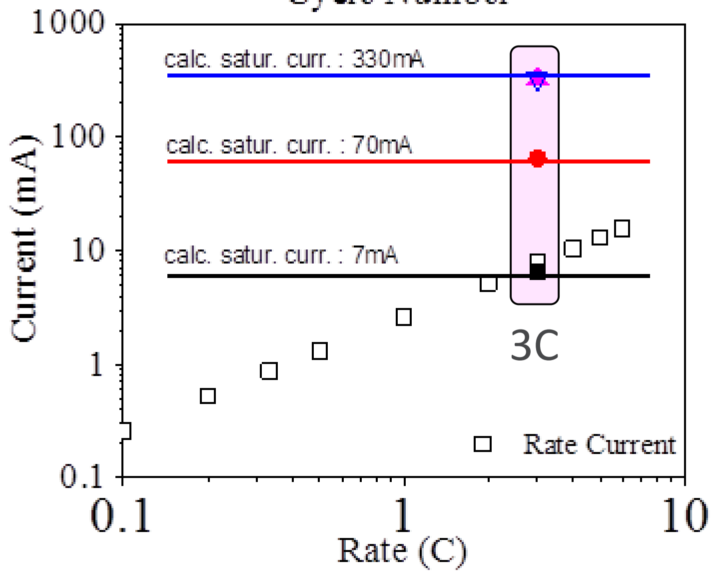
- Non-linear conductivity was observed for NCM523 composite electrode. The saturation current was determined from 4-point probe measurement.
  - High carbon content (5%): As high as 10mA saturated current was observed regardless which carbon black was used.
  - Low carbon content (1%): Higher saturated current (2mA) was obtained for electrodes using 1% Cabot carbon black.

RATE PERFORMANCE OF NCM523 COMPOSITE ELECTRODE

Rate performance of Li/NCM523 half cell

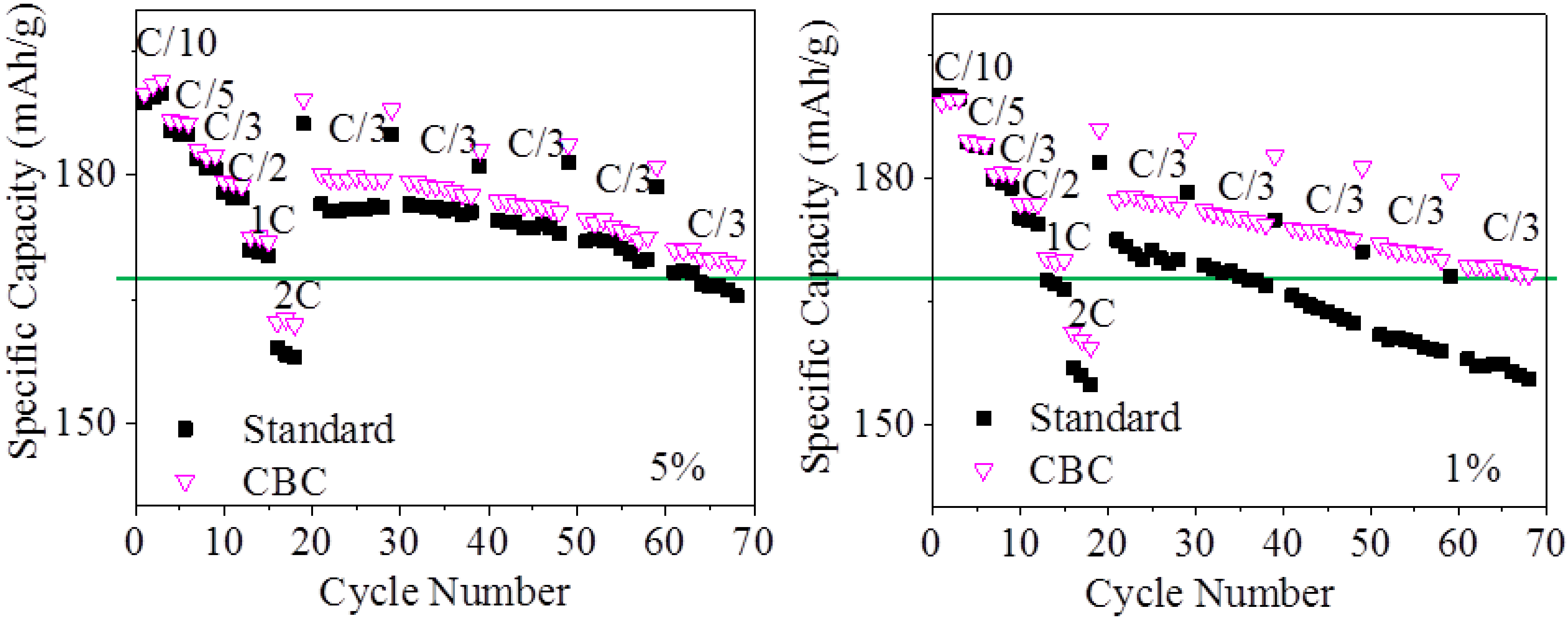






- Same rate performance was obtained for the electrodes using 5% of either carbon black.
- Rate performance separation started from 3C discharge rate when 1% carbon black was present in NCM523 electrode.

CYCLE PERFORMANCE OF NCM523 COMPOSITE ELECTRODE



- For NCM523 electrode with high carbon content (5%): Similar cycle performance was obtained regardless of carbon black.
- For NCM523 electrode with low carbon content (1%): Better cycle performance was observed for the electrode using Cabot carbon black.
- No discernable cycle performance difference was observed for NCM523 electrodes with 5% and 1% Cabot black.

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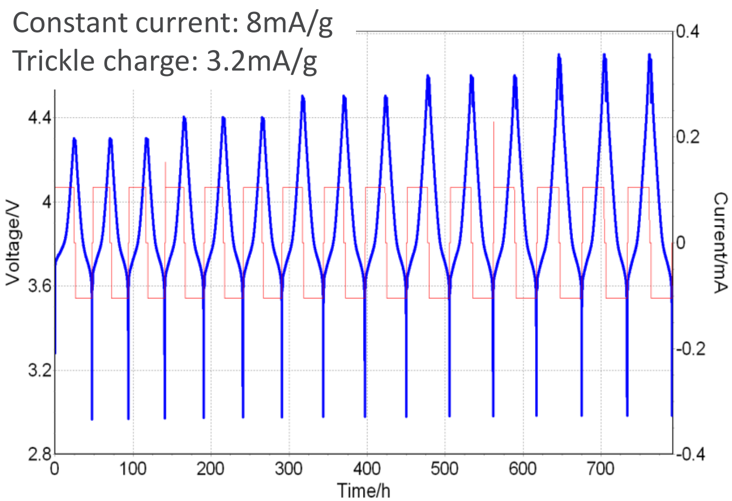
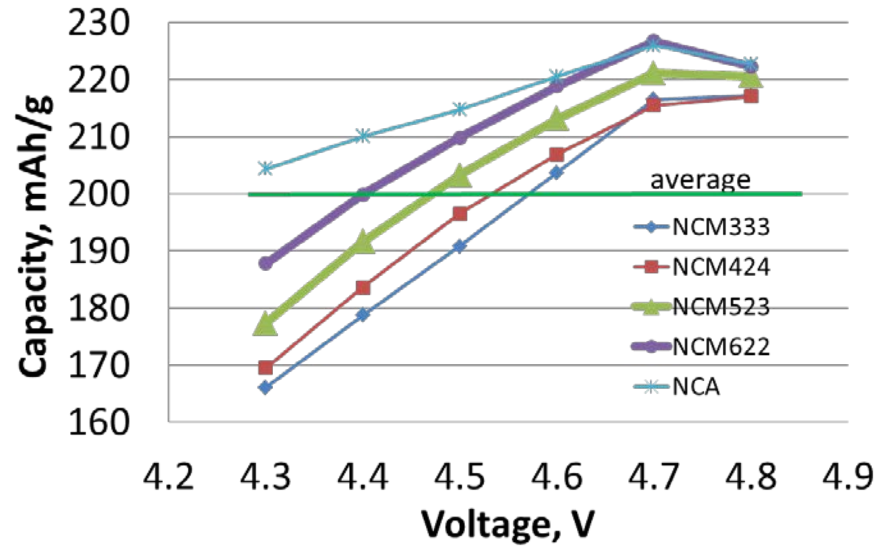
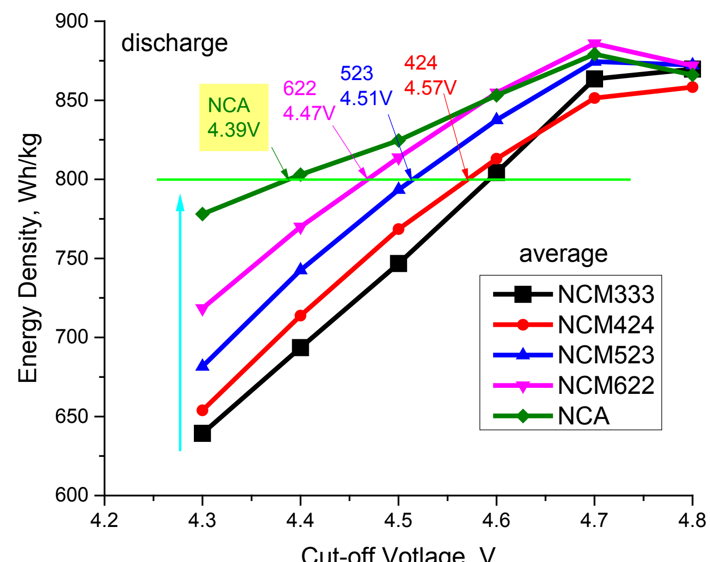
HIGH ENERGY NICKEL RICH TRANSITION METAL OXIDE CATHODES





- Energy density of NCM increases with increasing Ni content.
- The Ni content effect on energy rise is more profound with lower cut-off voltage.
- Regardless of Ni content, the maximum energy density was observed at 4.7V.
- The selected Ni rich cathode materials are being studied with HE-HV project.



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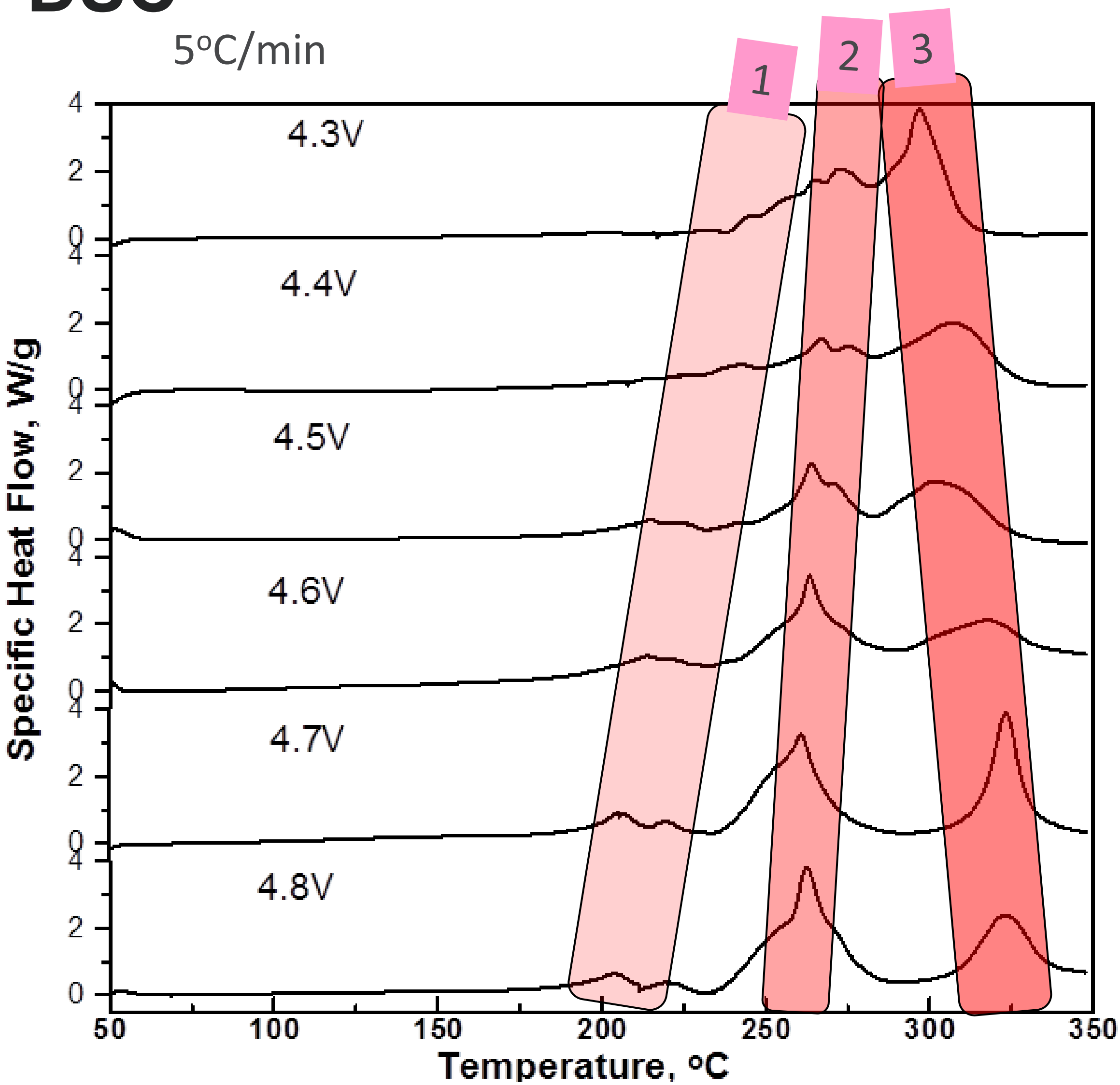
THERMAL INVESTIGATION OF NCM523 USING DSC



- Three groups of exothermic events were observed at low (1), middle (2), and high (3) temperature range.
- On-set temperature of low exotherm decreases with increasing cut-off voltages.
- On-set temperature of middle exotherm decreases with increasing cut-off voltages.
- On-set temperature of high exotherm increases with increasing cut-off voltages.

FUTURE PLAN

- High energy electrode materials
  - Continue to search and evaluate high energy density anode/cathode materials, as they become available.
  - Surface modification effect on electrochemical performance of high energy materials will be explored.
  - Continue the thermal investigation on high energy cathode materials.
- Electrode optimization:
  - Cabot carbon black has been requested and electrodes and pouch cells will be fabricated and tested at CAMP Facility.
  - SWCNT and graphene conductive additive will be explored to further improve the electrode performance.
- Continue to work closely with research institutions and industrial suppliers to enable the LIB technology for PHEV+EV applications.

SUMMARY

- Lithium inventory material (Li_5FeO_4) was successfully blended into positive electrode to address the ICL of the negative electrode.
  - The higher energy density and good cycle performance was achieved using HC/LCO-LFO electrode couple.
- The comparable rate and cycle performance were obtained for NCM523 electrode with 1wt.% carbon black provided by Cabot, which can increase the capacity of cathode as a whole (including carbon and binder) up to 8%.
  - We also observed the non-linear conductivity of composite electrode, which will aid the electrode design according to the requirements.
- High energy cathode materials, including nickel rich lithium transition metal oxides, were studied.
  - High nickel content leads to high capacity with lower cut-off voltage.
  - The relationship between the thermal stability and state of charge was established for NCM523 with various cut-off voltages.

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RESPONSE TO PREVIOUS YEAR REVIEWER'S COMMENTS

- No comments provided from previous review for this project.
- See general comments about CAMP Facility in ES030 presentation.

CONTRIBUTORS AND ACKNOWLEDGMENTS

Industries

- BMW (German)
- Cabot corp. (USA)
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- OSiAlC (USA)
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- PPG (USA)
- ShanShan (China)
- ShuangAo (China)
- Sinode (USA)
- Superior Graphite (USA)
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Facilities

- Advanced Photon Sources
- Electron Microscopy Center
- Material Engineering Research Facility (MERF)
- Post Test Analysis Facility

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Research institutes

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