Screen Electrode Materials & Cell Chemistries and Streamlining Optimization of Electrode

Wenquan Lu (PI)

Q. Wu, K. Yassin-Lakhsassi, M. Miranda, T. K. Honaker-Schroeder

Electrochemical Energy Storage
Chemical Sciences and Engineering Division
Argonne National Laboratory

Vehicle Technologies

Annual Merit Review and Peer Evaluation

Washington, D.C.

May 14th – 18th , 2012

Project ID: ES028

Vehicle Technologies Program

Overview

Timeline

- Start – Oct. 2008
- Finish – Sep. 2012
- Future: will continue to support ABR programs
  - ABR facilities,
  - Voltage fade
  - Electrochemical couples

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 Freedom CAR and Fuels Partnership.
- The impact of formulation and fabrication on performance of electrode materials with a broad variation of chemical and physical properties.

Budget

- Total project funding in FY2012:

  Screening: $450K

  Optimization: $300 (No Cost Extension)

Partners and Collaborators

- Cell Fabrication Facility (Andrew Jansen, Bryant Polzin, and Steve Trask, ANL)
- Modeling (Dennis Dees and Kevin Gallagher, ANL)
- Material Development (Christopher Johnson, ANL)
- Materials Engineering Research Facility (Gregory Krumdick, ANL)
- Illinois Institute of Technology (Jai Prakash)

Objectives

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.
- Independent screening tests using standardized test procedures to select promising advanced materials and cell couples for an internal cell build and further testing.
- To enhance the understanding of advanced cell components on the electrochemical performance and safety of lithium-ion batteries.

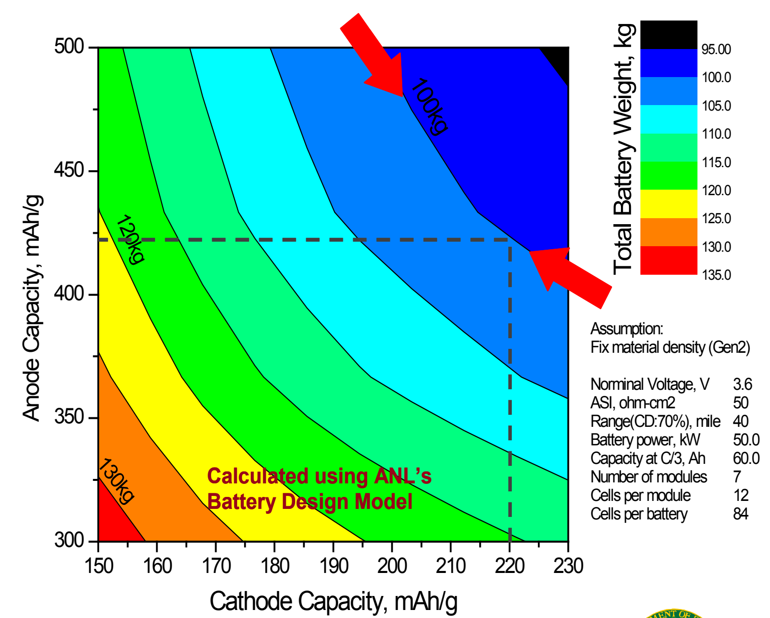
Streamlining the optimization:

- 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.

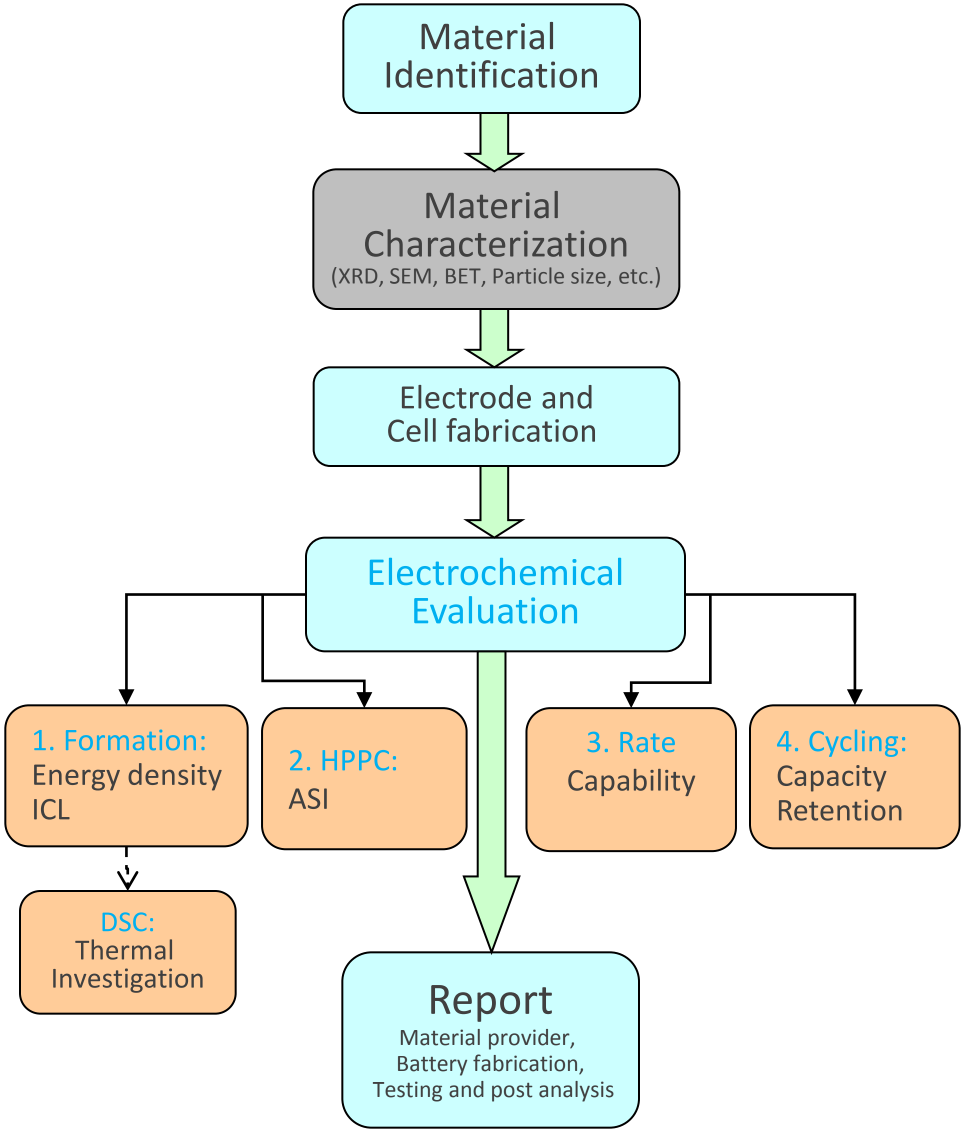
USABC Requirements of Energy Storage Systems for PHEV

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

Material Requirements



Approach: Test Protocol Development



As shown on the left, electrochemical evaluation will be the focus of this project.

In order to conduct the electrochemical characterization for screening purpose, C rate and pulse current was calculated for coin cells according to PHEV 40 requirements.

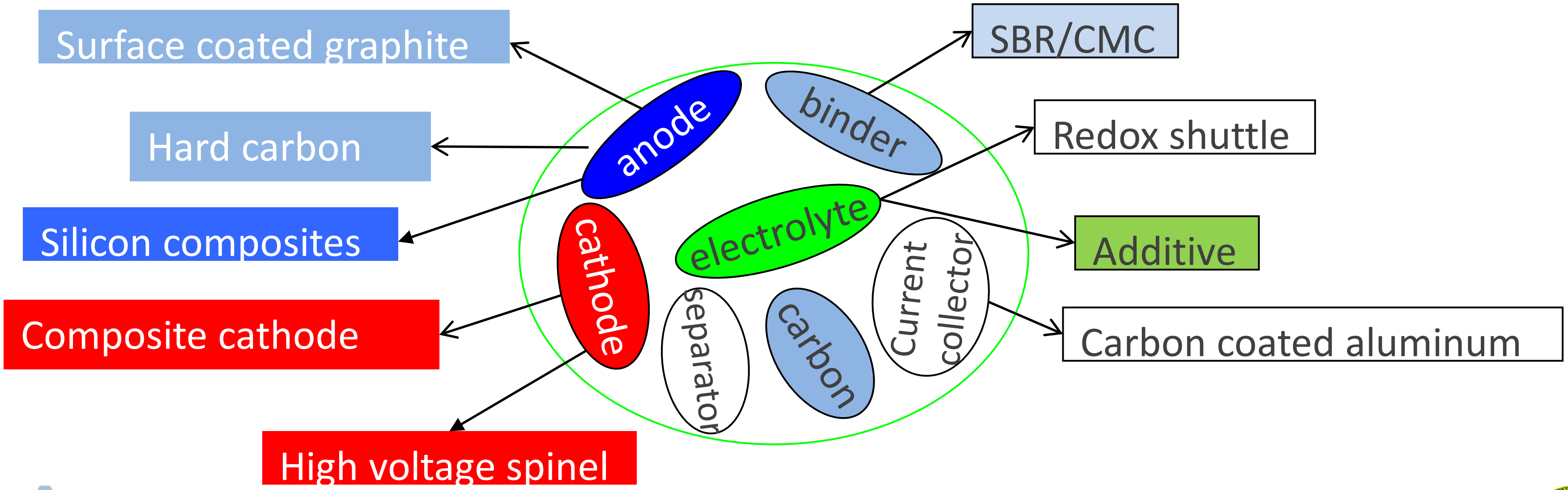
energy kWh		capacity usage 90	80	70	60
capacity retention	90	14.3	16.1	18.4	21.5
	80	16.1	18.1	20.7	24.2
	70	18.4	20.7	23.7	27.6
	60	21.5	24.2	27.6	32.2

CD, ave C/n		capacity usage 90	80	70	60
capacity retention	90	1.4	1.6	1.8	2.1
	80	1.6	1.8	2.1	2.4
	70	1.8	2.1	2.4	2.8
	60	2.1	2.4	2.8	3.2

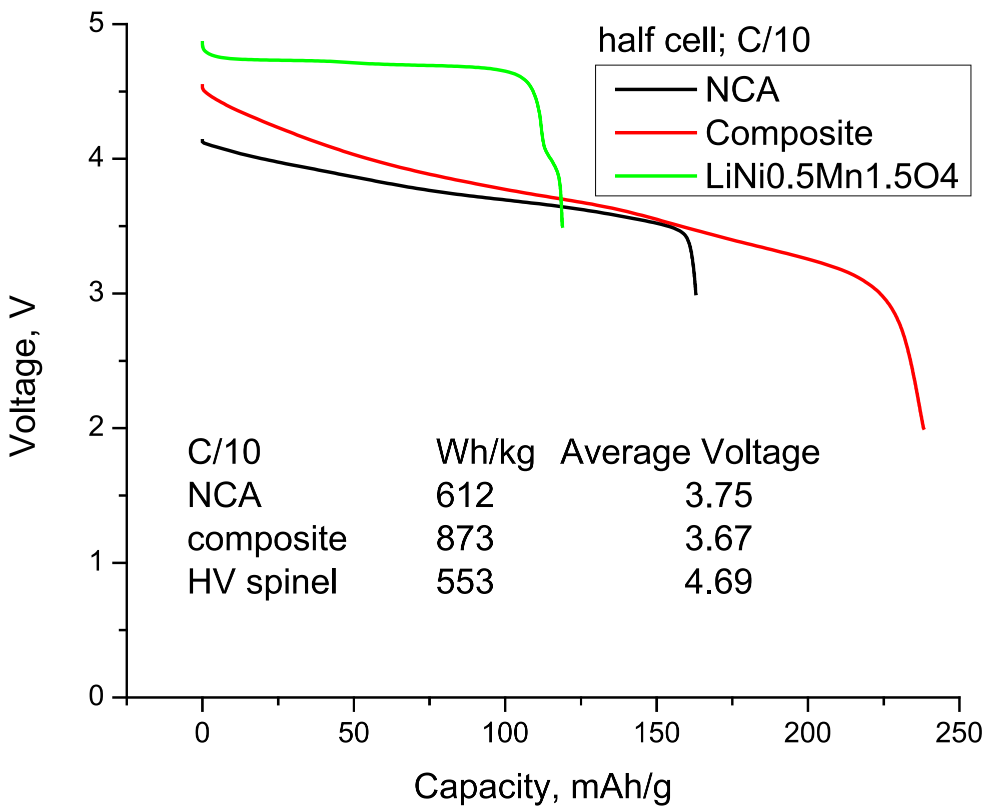
pulse, ave nC		capacity usage 90	80	70	60
capacity retention	90	2.7	2.4	2.1	1.8
	80	2.4	2.1	1.8	1.6
	70	2.1	1.8	1.6	1.4
	60	1.8	1.6	1.4	1.2

Technical Accomplishments

- Several high energy electrode couples, composite cathode materials and silicon composite anode materials, have been identified and studied.
  - Test results have been reported to suppliers.
  - Information was also delivered to the **Cell Fabrication** team and **Materials Engineering Research Facility** under ABR program.
- Other cell components, such as electrolyte and additives, conductive additive, binders, etc., have also been investigated.
- Streamlining the optimization of the electrode:
  - Carbon coating effect on metal oxide was investigated.
  - Formulation optimization on composite cathode material was conducted.
  - Modeling to predict optimum compositions of AM/C/B for high energy.



High Energy Density Cathode



Ref: es111, K. Gallagher, AMR2012

	NCA-G	LNMO-G	LMRNMC-G
Price to OEM, US$	4314	3490	3406
Weight, kg	110	102	92
Volume, L	68	63	61
$/kWh$_{use}$	363	293	286
Wh$_{use}$/kg	108	117	129
Wh$_{use}$/L	176	190	196

LNMO: $LiNi_{0.5}Mn_{1.5}O_4$
LMRNMC: layer-layer composite

Battery packs designed to meet PHEV40 goals
- 17 kWh, 60 kW at [V/U] = 0.8
- Battery pack OCV at 50% SOC = 360 ± 15 V
- **70 % useable capacity**, max power measured at 25% SOC
- (80-96 cells in series)
- 100 μm maximum electrode thickness

- According to the modeling studies, both high energy composite and spinel cathode materials have good chance to meet the PHEV requirements, which are the current focus for material screening.

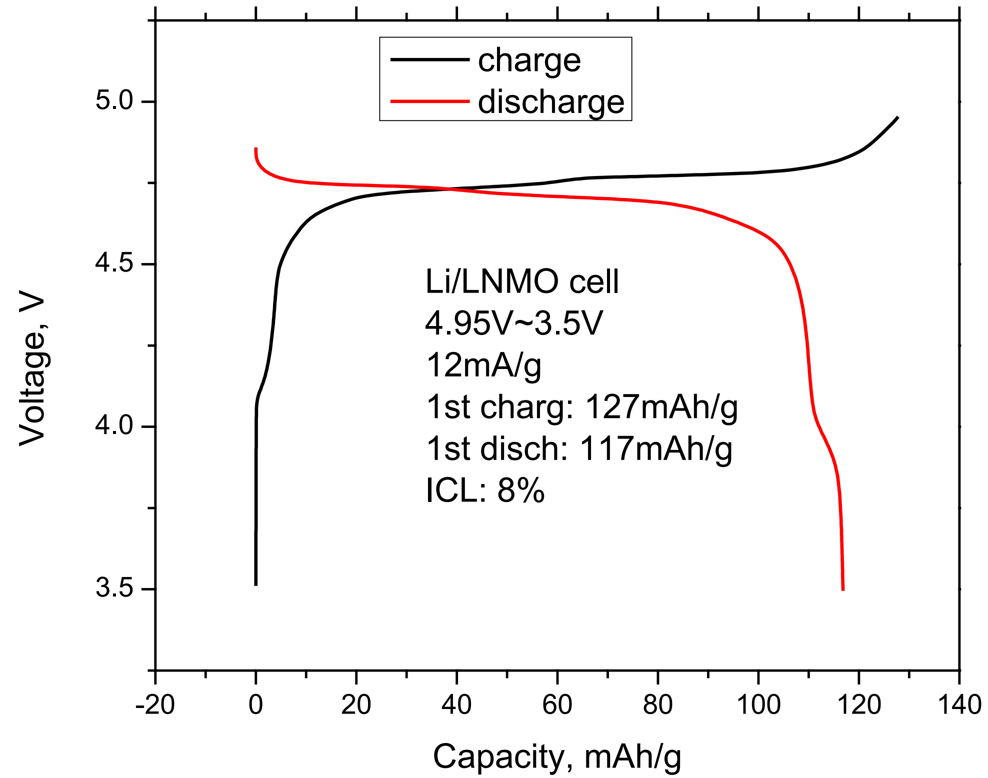
High Voltage Spinel - $LiNi_{0.5}Mn_{1.5}O_4$

- $LiNi_{0.5}Mn_{1.5}O_4$
- Electrochemical reaction:
  - Ni^{3+}/Ni^{4+} and Ni^{2+}/Ni^{3+}
  - Mn^{3+}/Mn^{4+} impurity
- Theoretical capacity:
  - 146 mAh/g
  - Average 4.7V

4.95V~3.5V

		C/10	C/3
Average voltage	V	4.67	4.63
Specific capacity	mAh/g	119	117
ICL	%	91.5	
Energy density	mWh/g		
full cycle		554	545

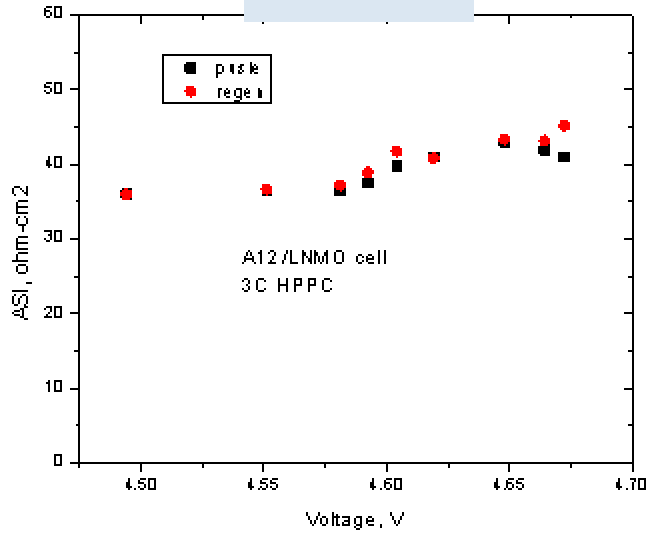
Half Cell Formation



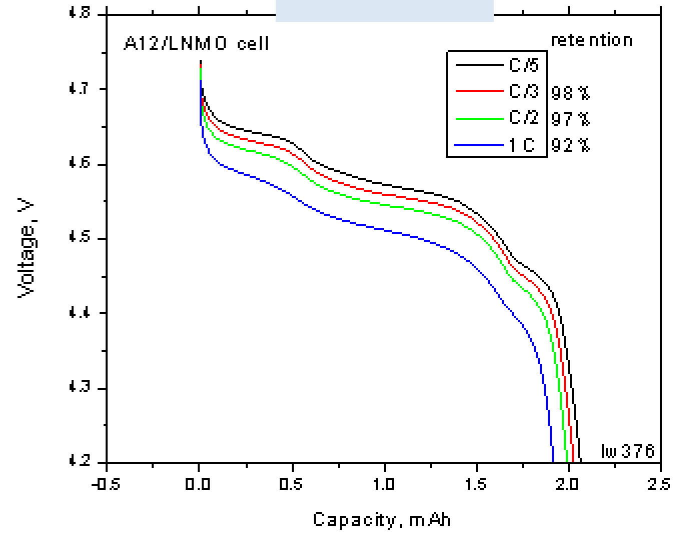
- $LiNi_{0.5}Mn_{1.5}O_4$ shows about 120 mAh/g capacity, which is close to its theoretical capacity. In addition, it shows low irreversible capacity loss.

Electrochemical Characterization of HV Spinel

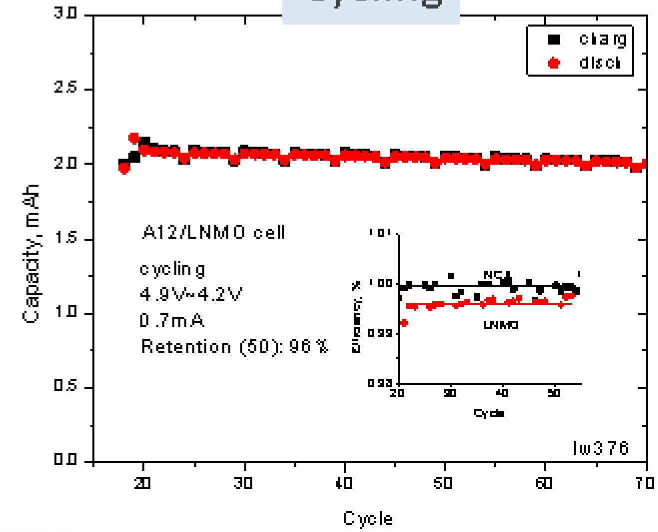
HPPC test



Rate Test



Cycling

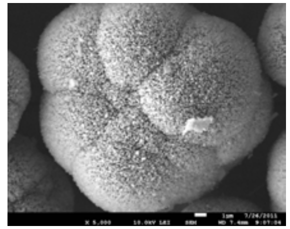


- Relatively constant ASI throughout whole DOD
- Excellent rate performance
- Good cycle life when coupled with either **graphite** or $Li_4Ti_5O_{12}$.
- Lower coulombic efficiency may be related to the electrolyte oxidation.

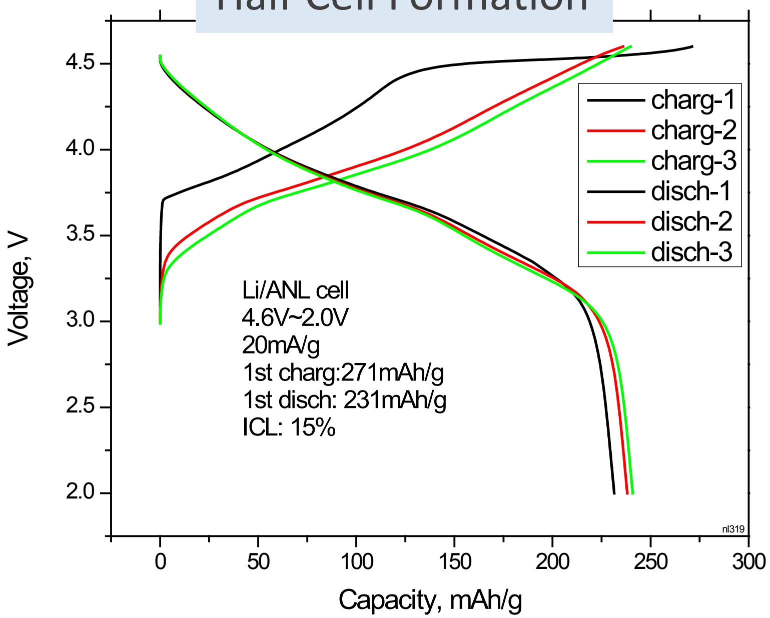
Composite Cathode

$Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$ (H. Wu, ANL)
$1/3Li_2MnO_3 \bullet 2/3LiNi_{0.5}Mn_{0.5}O_2$

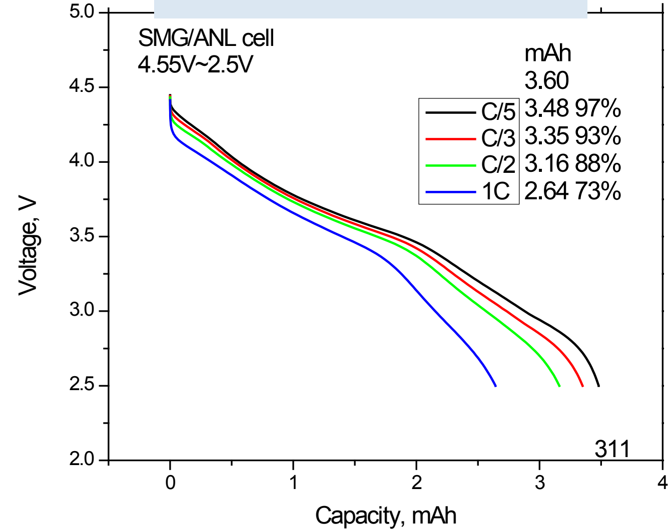
- No cobalt
- Easy to synthesize
- High tap density

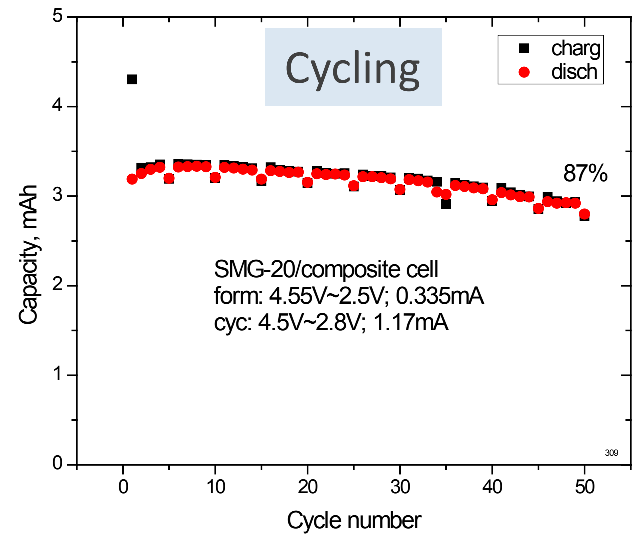


Half Cell Formation



Rate Test of Full Cell

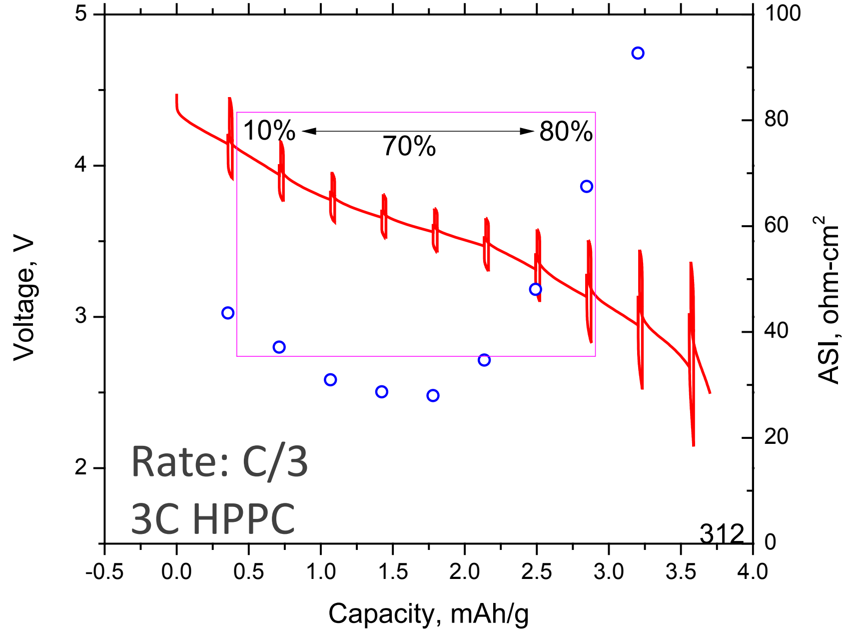




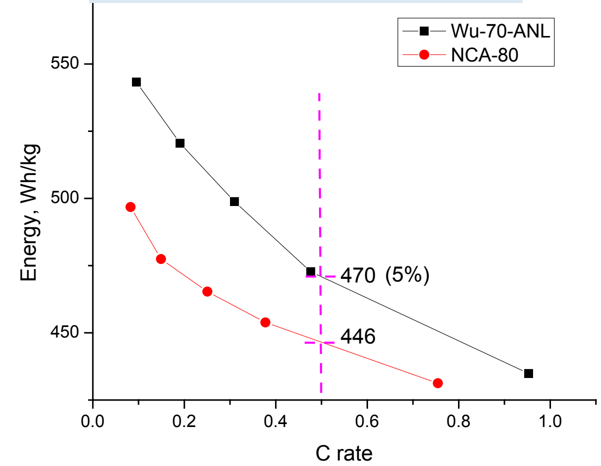
- High energy density, good rate capability, and reasonable cycleability was obtained with this composite material.

Usable Energy of Composite Cathode

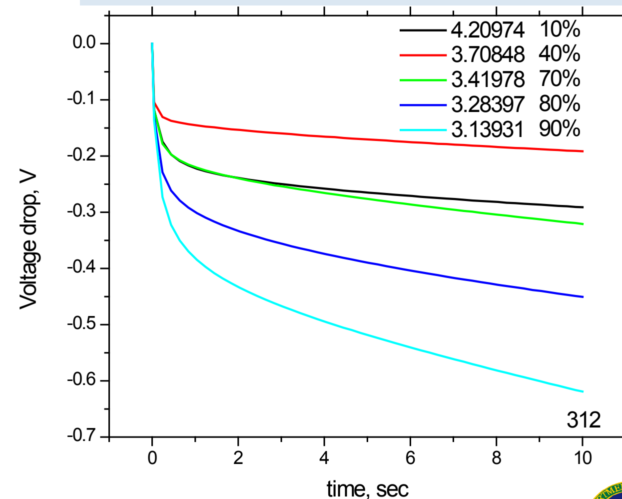
HPPC & ASI of graphite/composite cell



Usable energy vs. rate

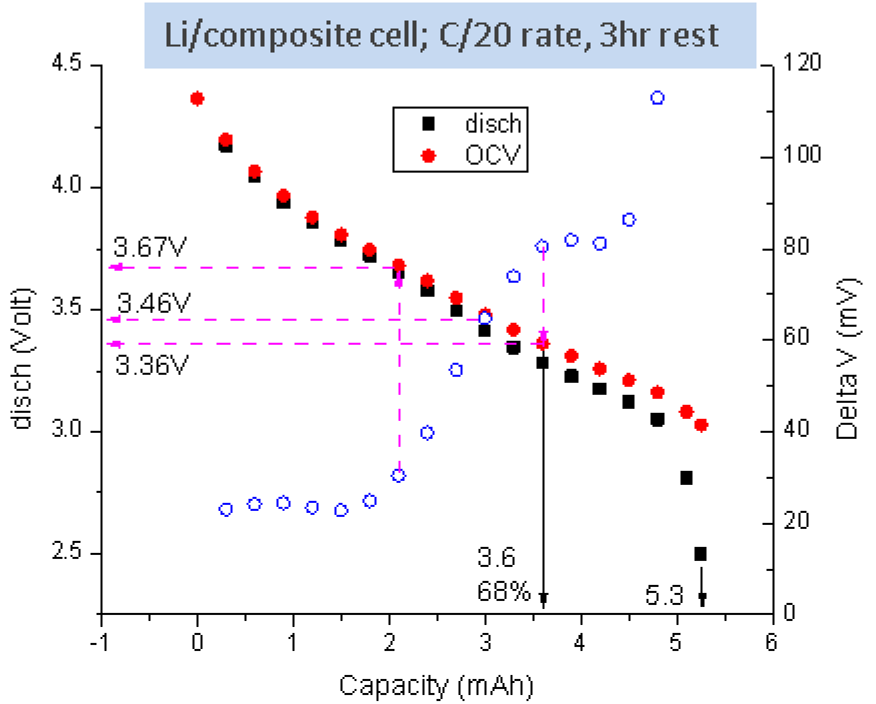


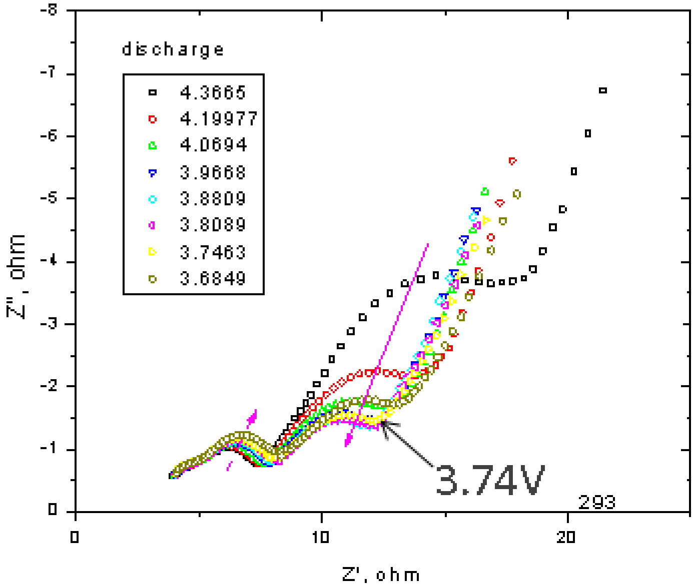
Voltage profile during 10 sec pulse

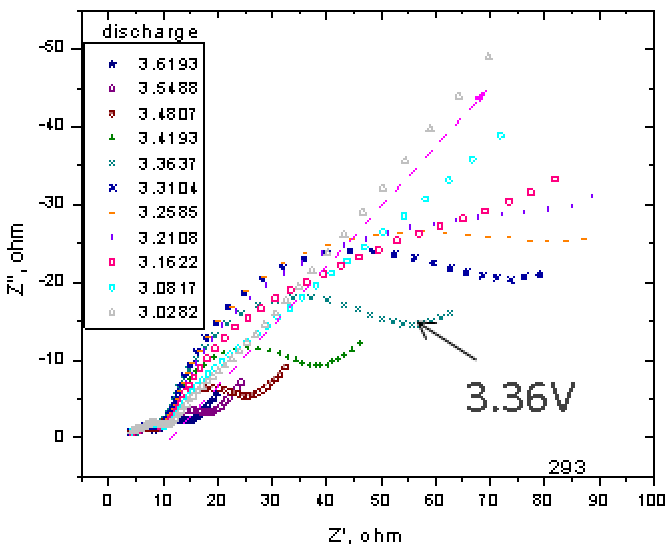


- At 80% DOD, the impedance barely meets the PHEV requirement.
- The usable energy of the electrode affects the energy density of cell system dramatically.
- The voltage response during the pulse discharge indicates that the lithium ion diffusion might cause the higher impedance at high DOD.

Thermodynamics of Composite Cathode - Voltage Fade







- There are two different overpotential regions during discharge process.
- The higher impedance at lower SOC is corresponding to higher overpotential and higher low frequency circlular arc.

Electrode Optimization: Composite Material

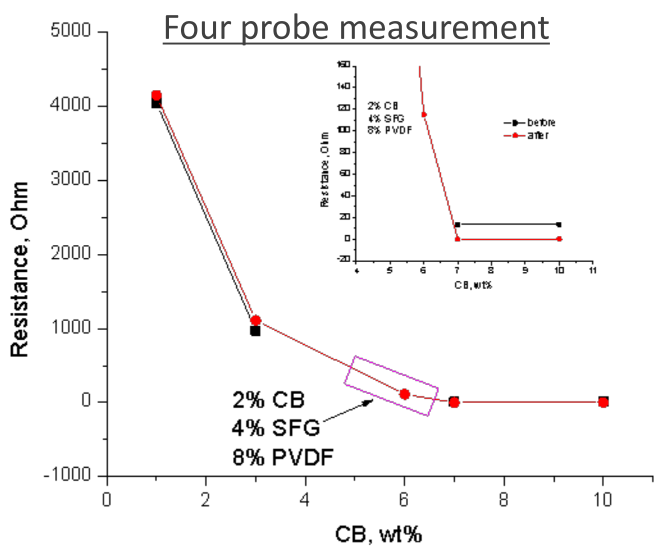
<u>Electrode composition:</u>

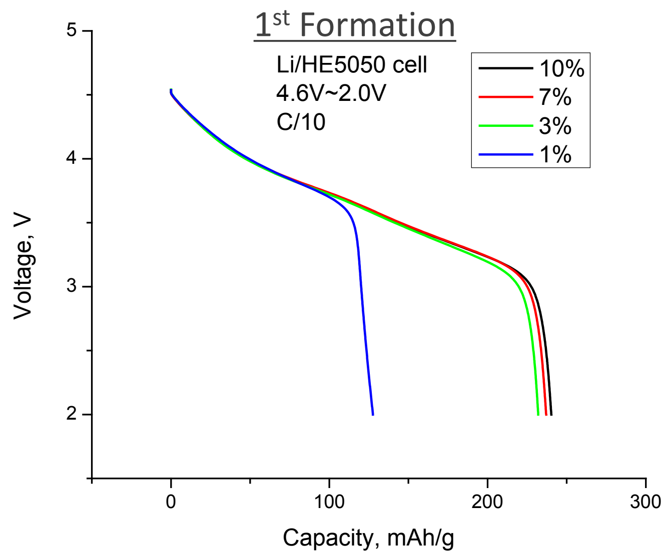
Active: HE5050;

CB/PVDF = 1;

wt.% of CB: 1, 3, 7, 10%

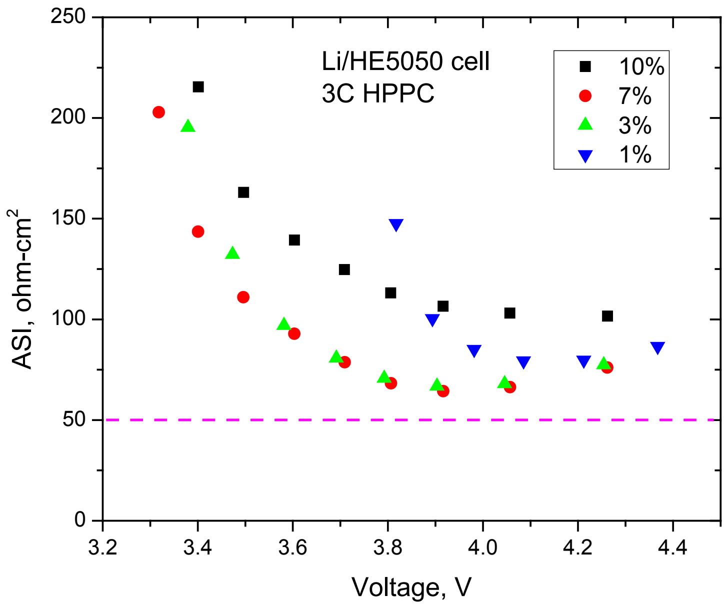
Percent of PVDF (%)	Weight of Electrode (mg)	Weight of Active Material (mg)	Thickness of Electrode (μm)	Area Loading (mg/cm^2)		Volume Loading (g/cm^3)	
				Electrode	Active material	Electrode	Active material
1	18.13	17.77	54	11.33	11.10	2.10	2.06
3	11.52	10.83	31	7.20	6.77	2.32	2.18
7	8.77	7.54	27	5.48	4.71	2.03	1.75
10	8.40	6.72	27	5.25	4.20	1.94	1.56





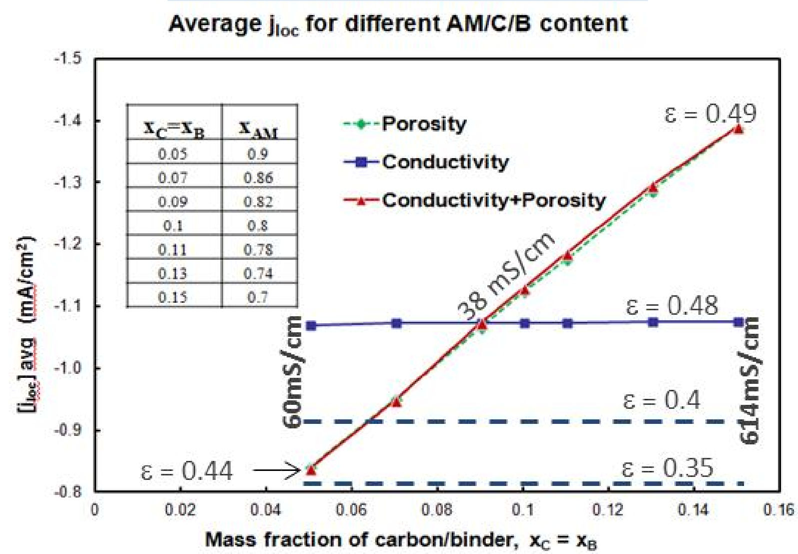
- Laminate with good integrity was made with as little as 3% CB and 3% PVDF, which showed similar performance as laminate with 7% and 10% carbon additives.

Electrode Optimization: Composite Material



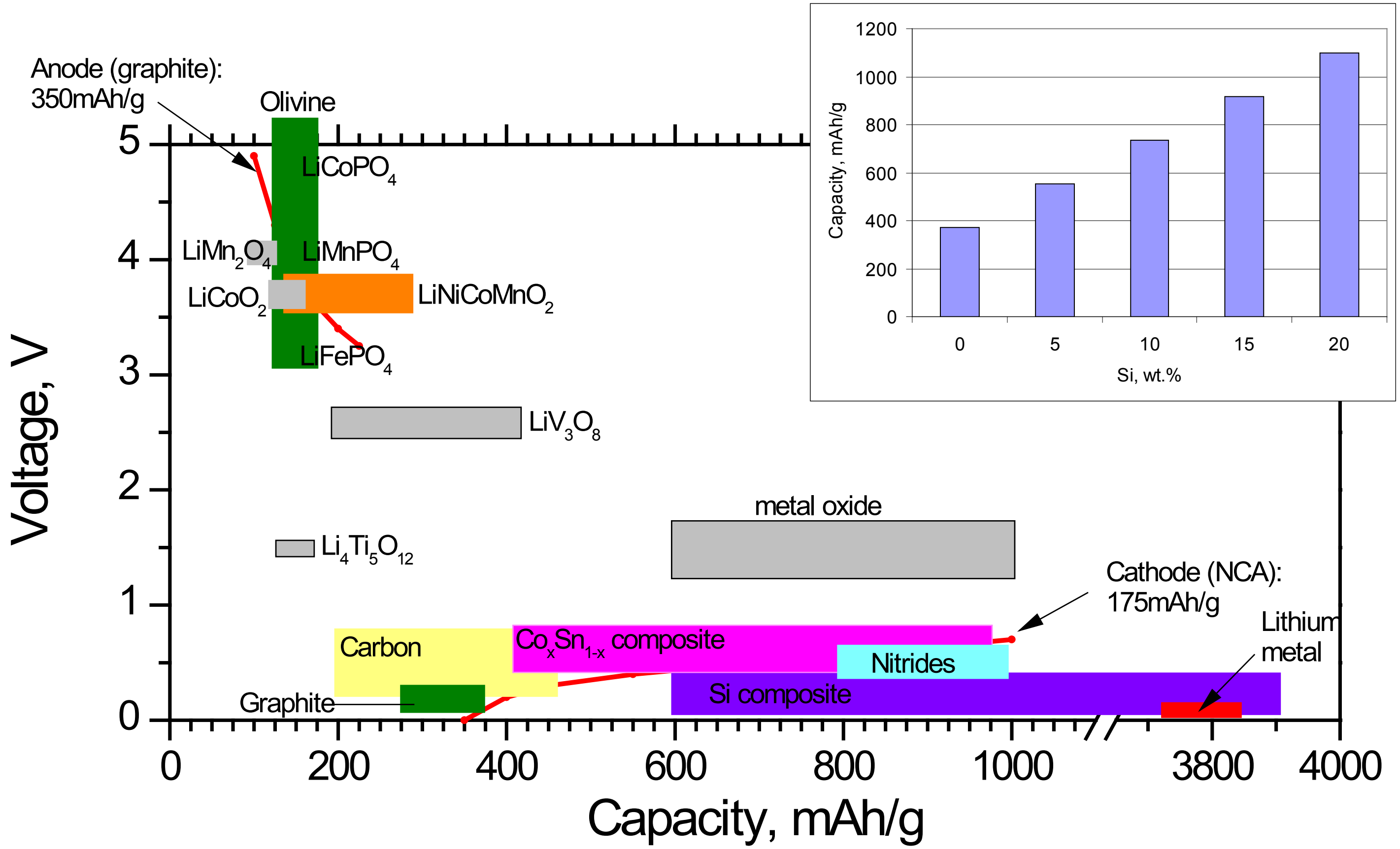
- Hybrid Pulse Power Characterization results showed that the lowest Area specific Impedance (ASI) was obtained for the electrodes with 3% and 7% CB and PVDF.

Optimization modeling by IIT



- According to IIT's optimization model, the electrode porosity is dominant for the cell power performance once the electronic conductivity of the electrode passes the percolation threshold. The electrochemical results are consistent to the modeling prediction.

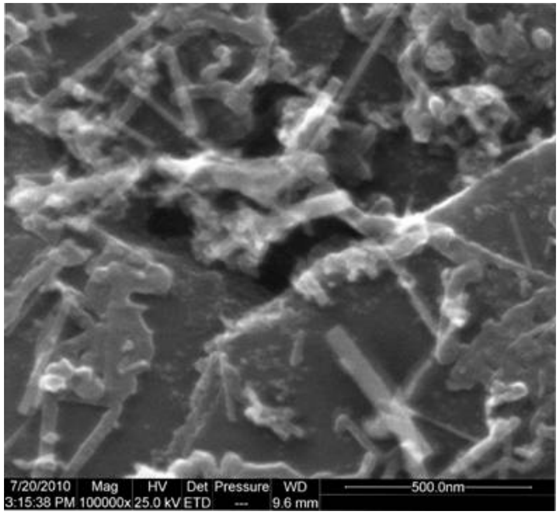
Silicon Electrode and Additives



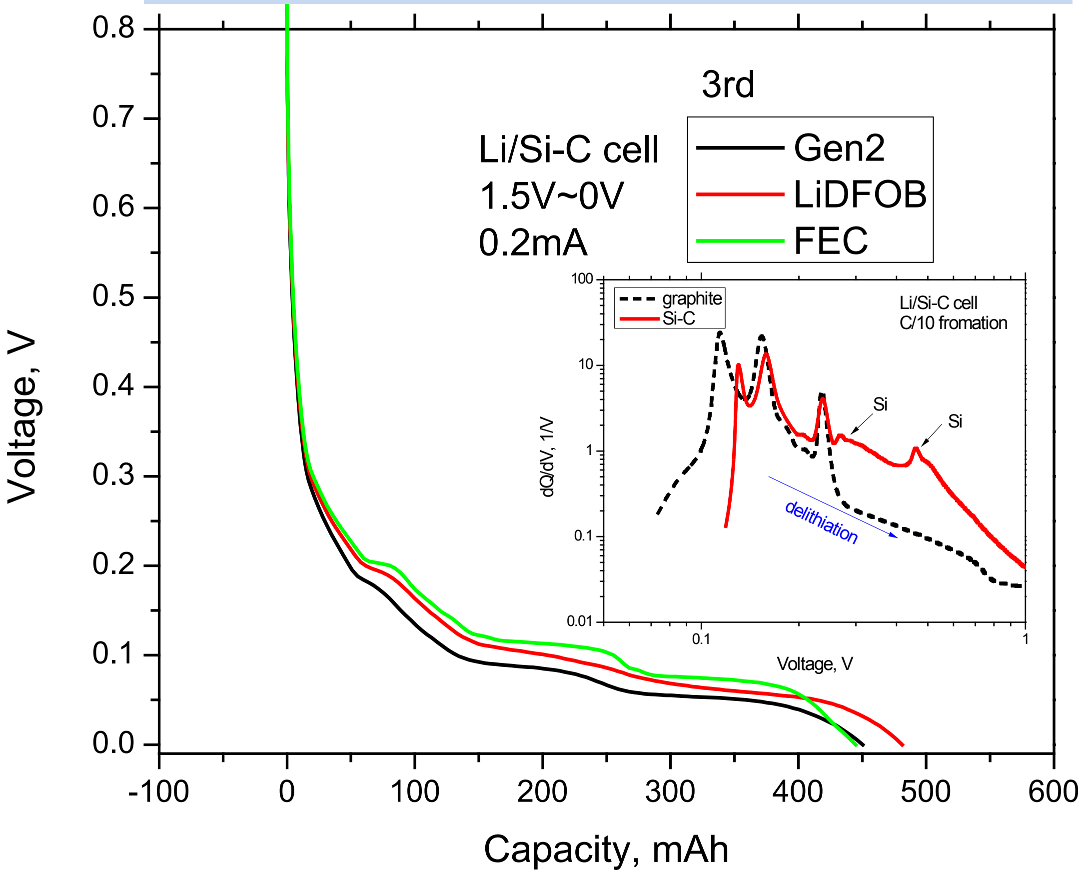
- Silicon composite will better balance the cathode electrode due to its adjustable high capacity.

Si composite Anode

- The reversible capacity of Si composite is as high as 450mAh/g.
- The capacity contribution by silicon composite can be seen from differential capacity plot.
- The additive apparently reduced the overpotential of silicon composite electrode.



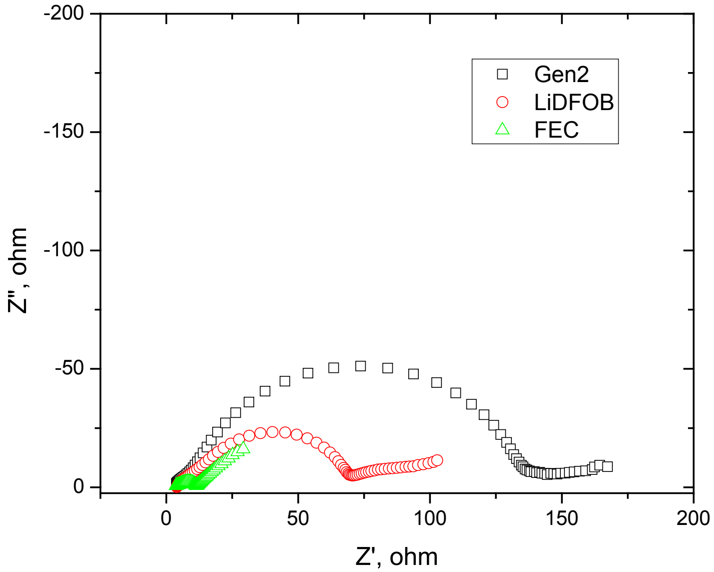
Electrolyte:
Gen2: 1.2M LiPF6 EC/EMC (3/7)
Lithium difluoro(oxalato)borate (LiDFOB): 2% in Gen2
Fluorinated Ethylene Carbonate (FEC): 10% in Gen2



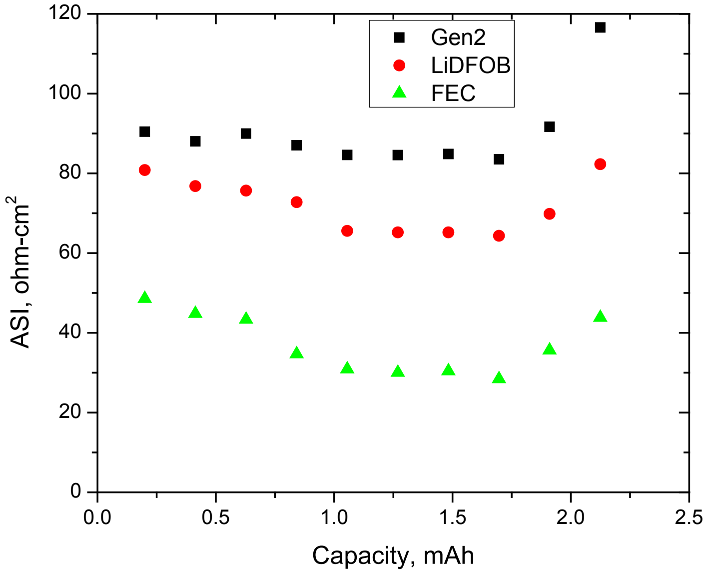
- V. Etacheri, O. Haik, Y. Goffer, G. A. Roberts, I. C. Stefan, R. Fasching, and D.ron Aurbach, Langmuir, 2012.
- H. Nakai, T. Kubota, A. Kita, and A. Kawashima, JES 2011.

Impact of Electrolyte on Cell Impedance

Li/Si-C cell; 50% SOC
5mV; 500kHz~20mHz



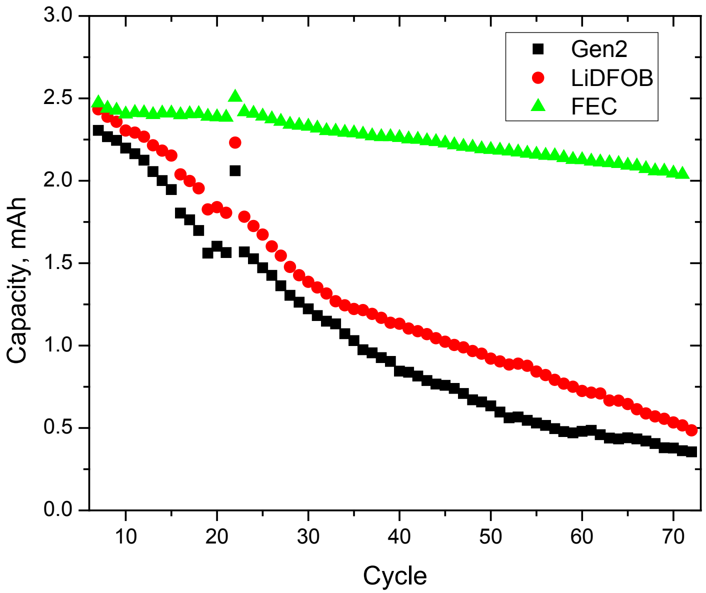
Li/Si-C cell
1C HPPC



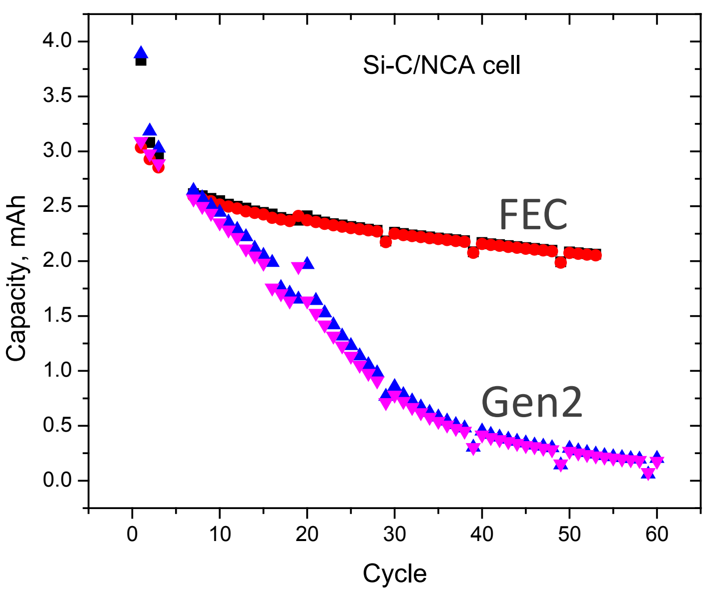
- The lower interfacial resistance due to additives can be further observed from EIS and HPPC test.
- Other researchers found that FEC derived SEI on Si is thinner and more stable compared to EC derived SEI, which can explain the low impedance of Si composite electrode with FEC.

Impact of Electrolyte on Cell Cycle Life

Li/Si-C cell; 1.5V~0V; C/3 rate



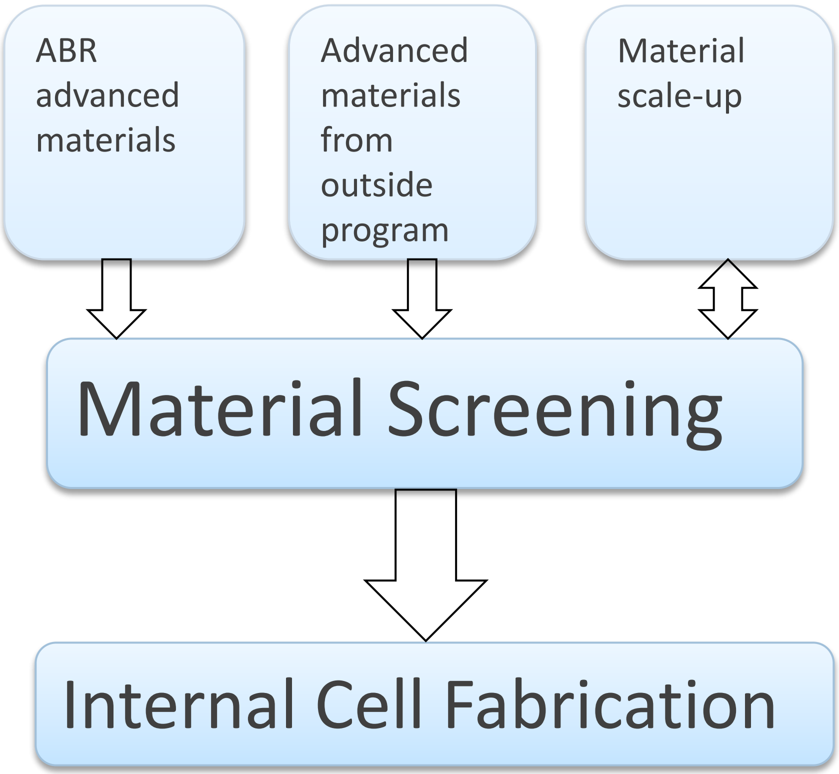
Si-C/NCA cell; C/3 rate



- The cycle life of silicon composite electrode is greatly improved in both half cells and full cells with FEC additive.

Future Plan: Program Transformation

Continue:



Initiate the voltage fade studies:

The new project will focus on thermodynamic investigation of composite material, which is part of core R&D on advanced materials.

Initiate efforts on development of new electrochemical couples.

Summary

- As promising cathode for PHEV application, The electrochemical performance of high voltage spinel, $LiNi_{0.5}Mn_{1.5}O_4$, was characterized. This cathode material shows excellent rate, power, and cycle performance in both half cell and full cell using typical carbonate based electrolyte.

- One of high energy composite cathode materials, $0.33Li_2MnO_3 \bullet 0.67LiNi_{0.5}Mn_{0.5}O_2$,developed at ANL was characterized.
  - This type of cathode material shows highest energy density among its class.
    - Deliver 878Wh/kg at low rate, about 70% more than conventional $LiCoO_2$.
  - Usable energy of current composite material is limited by its high impedance at low SOC.
  - Electrode optimization results demonstrated the possibility to make good composite electrode using low carbon and PVDF binder.

- Si-C composite
  - The 450 mAh/g reversible capacity was obtained from Si-C composite.
  - The impedance originated from SEI was greatly reduced using fluorinated ethylene carbonate (FEC) as additive.
  - The cell cycle life was improved by FEC additive.

- Other cell components, such as redox shuttle, binder, separator, carbon additive have been studied and information was delivered to material supplier and internal facilities.

Contributors and Acknowledgments

Argonne National Laboratory

- Huiming Wu
- Donghan Kim
- Jason Croy
- Ilias Belharouk
- Jack Vaughey
- Daniel Abraham
- Zonghai Chen
- Yan Qin
- Lu Zhang
- John Zhang
- Khalil Amine
- Mike Thackeray
- Gary Henriksen
- Nancy Dietz (Post-test Group)
- Electron Microscopy Center (EMC)

- ConocoPhillips
- Toda Kogyo
- Solvay
- Daikin Inc., Japan
- Pred Materials International, Inc., NY
- Hosokawa Micron Corporation, NJ
- Northwestern University
- Nanosys
- NEI corporation
- JSR
- ZEON

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