Scale-up and Testing of Advanced Materials from the BATT Program

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Overview

Timeline

- October 2009
- September 2013
- 65 % Complete

Budget

- Total project funding
  - DOE share = 100%
  - Contractor share = 0%
- Funding received in FY10
  - $240 k
- Funding for FY11
  - $240 k

Barriers

- Barriers addressed
  - Performance
    - Energy density
- Targets
  - 207 Wh/l

Partners

P.I.s	Companies
G. Ceder (MIT)	Nippon Denko
B. Lucht (URI)	NEI
M. Doeff (LBNL)	HydroQuebec
H. Wu (ANL)	Daikin, America
W. Chen (ANL)	

Relevance

Objectives

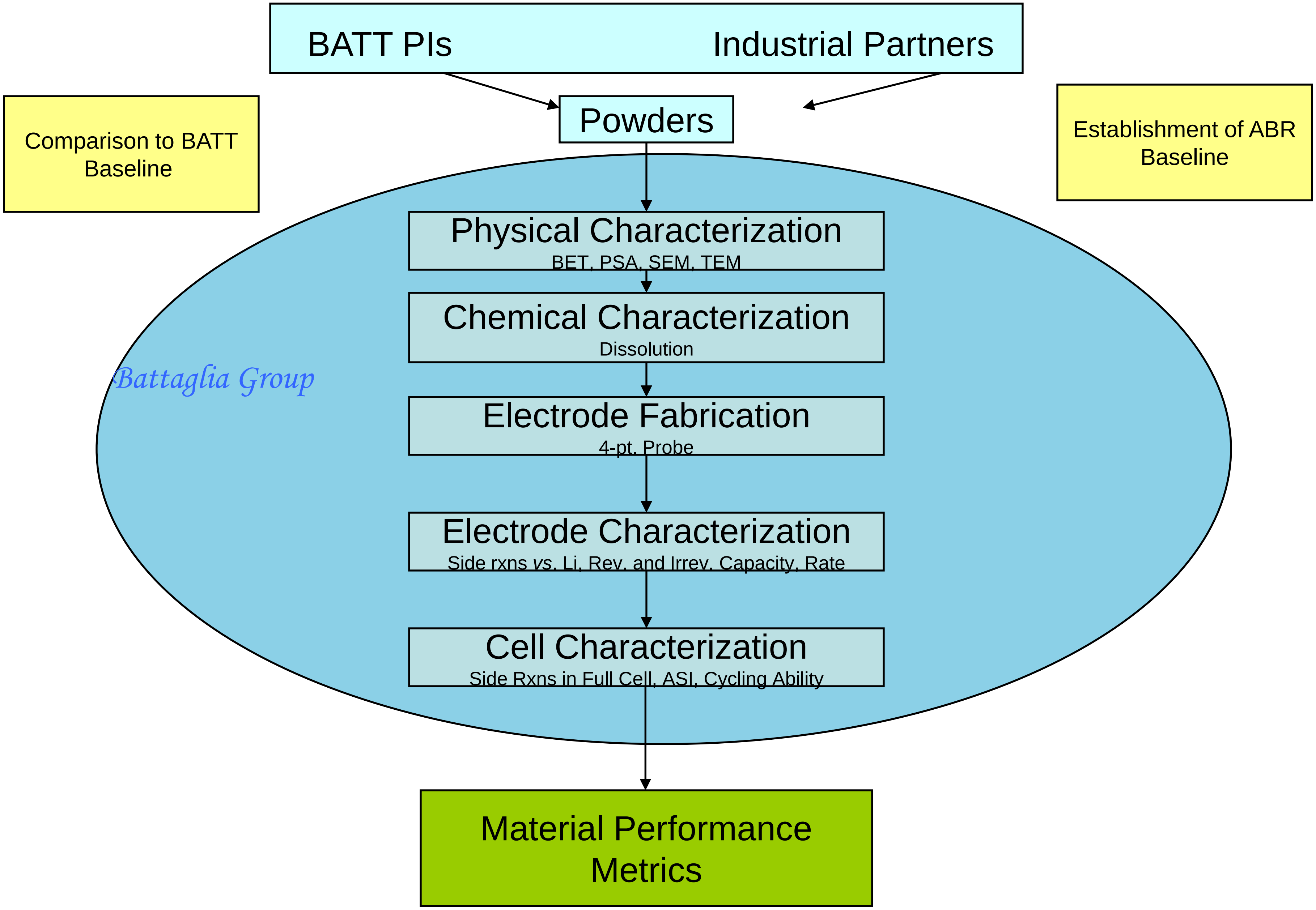
Scale-up and Test Materials from BATT

- General
  - Establish a baseline for new materials relevant to ABR projects.
  - Obtain BATT materials that have demonstrated initial performance better than the BATT-baseline (Gr./NCM).
  - Scale-up those materials if the cognizant BATT PI cannot.
  - Make and test the electrodes and compare to the baseline.

- Specific to 2010/11
  - Emphasis on establishing a $LiNi_{1/2}Mn_{3/2}O_4$ material for the ABR High Voltage Electrolyte Development Project.
  - Evaluated a water-based binder system for the Gr./$LiFePO_4$ cell to address the environmental issues associated with NMP.

To assist developers, this project focuses on a few key problems; a baseline will assist in initiating and comparing experiments.

Approach/Strategy



DOE Reportable Milestones

Deliverable: Battery design, performance, and cycling characteristics of three materials will be reported on at the DOE Merit Review. June 2011. On schedule

Technical Accomplishments and Progress:
1. Correlate Performance to Physical Characteristics

H. Zheng

Performance of Several Graphitic Anode Materials

	MCMB	*OMAC*	*SMG-N*	*SMG-Ns15f*	*SMG-A*	*MAGD15*	*MAGD5*	*CGP-G8*
Q_r (mAh/g)	297-306	345-358	335-351	338-363	322-359	320-360	335-352	313-318
η (%)	92.9-93.4	88.76-90.82	89-91%	88.8-90.2	85.1-88.2	86.8-89	77.3-81.7	93.4-93.7
Rev. specific cell capacity (mAh/g) based on graphite wt.	276 y	322 0.86 y	315 0.87 y	326 0.85 y	321 0.86 y	323 0.85 y	312 0.88 y	287 0.96 y
Rev. cell capacity w/ 1Ah cath. (mAh)	0.93 x	0.90 1.03 x	0.90 1.03 x	0.89 1.04 x	0.87 1.07 x	0.88 1.06 x	0.80 1.16 x	0.93 1 x
Marching (%) *(none < 1)*	~0.5 x	0.5-0.8 1.3 x	0.04-1.2 1.6 x	0.7-2.0 2.8 x	0.6-1.0 1.6 x	0.6-1.2 3.4 x	1.5-2 1.8 x	~0.3 0.6 x
Rate Capability	Moderate go	Poor no go	Poor no go	Poor no go	Moderate go	Moderate go	Good go	Good go
Cycling ability*	400	400	400	400	400	400	400	400
Cumulative Cost Score *(low is good)*	1*1*(0.9+0.1y) **1**	1.03*1.3*(0.9+.1*0.86) **1.3**	1.03*1.6*(0.9+0.1*0.87) **1.6**	1.04*2.8*(0.9+0.1*0.85) **2.8**	1.07*1.6*(0.9+0.1*0.86) **1.7**	1.06*3.4*(0.9+0.1*0.85) **3.5**	1.16*1.8*(0.9+0.1*0.88) **2.1**	1*1*(0.9+0.1*0.96) **1.0**

A library of physical data exists for each material as well, including BET, PSA, SEM, and XRD

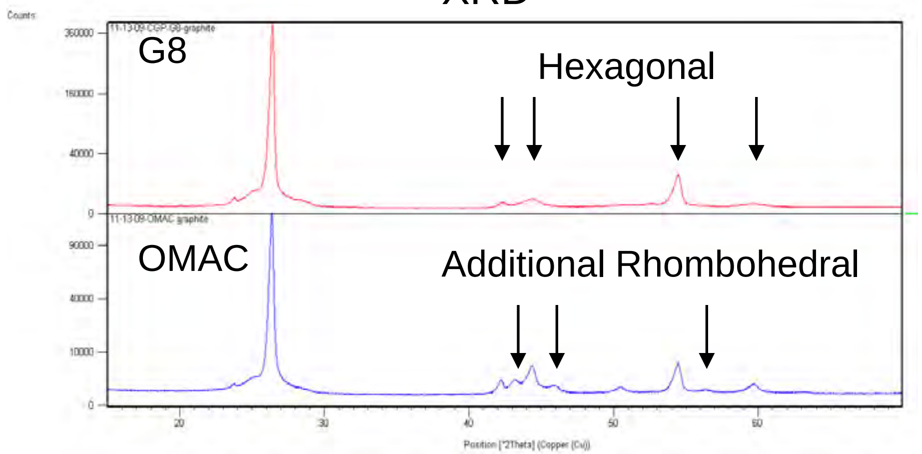
These data were presented at last year’s review; this year we sought correlations between performance and material characteristics.

Technical Accomplishments and Progress:
1. Correlate Performance to Physical Characteristics

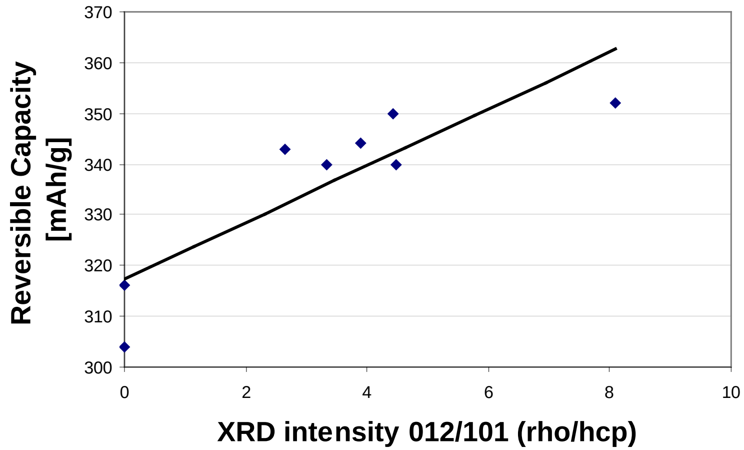
A. Bello

Data Correlation

XRD



Rev. Capacity *vs*. Lack of Graphitization



Covariance	data set 1	data set 2
0.41	rho012/hcp101	Cost score
-0.41		Rate capacity [mAh/cm^2]
0.86		$Q_{rev.}$ [mAh/g]
-0.41		1st cycle eff. [%]
0.43		$\Delta Q/Q_{rev}$ [frac. cap. shift %]
0.15		Rate capacity x $size^2$

Two significant correlations were found:

1. Rate capability increased with smaller particle size.
2. Reversible capacity increased with decreasing graphitization.

Correlation 2 suggests that the high-capacity materials are a combination of soft and graphitic carbon.

Technical Accomplishments and Progress:

2. Identify a $LiNi_{1/2}Mn_{3/2}O_4$-spinel baseline for the high-voltage-electrolyte effort

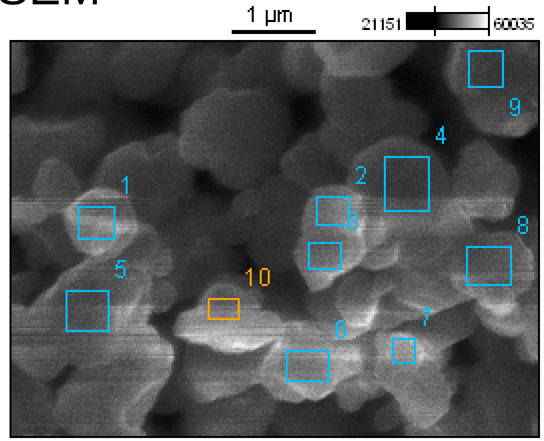
NEI's and Nippon Denko's Materials

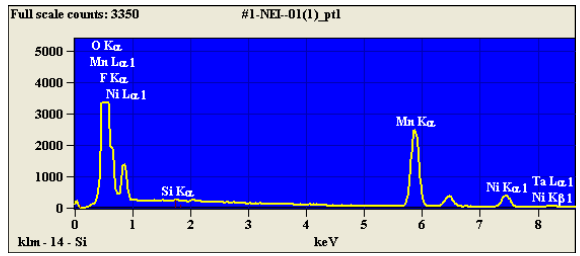
X. Song

SEM

EDX

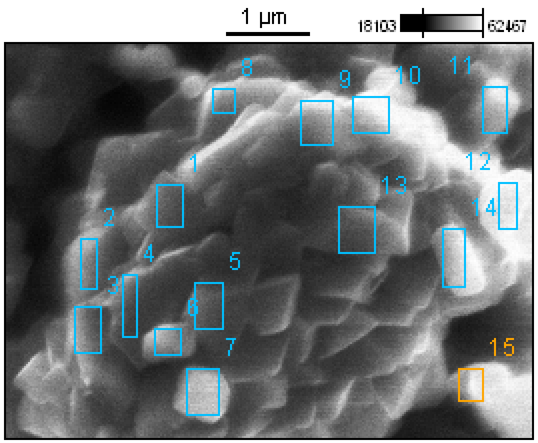
#1-NEI--01(1)

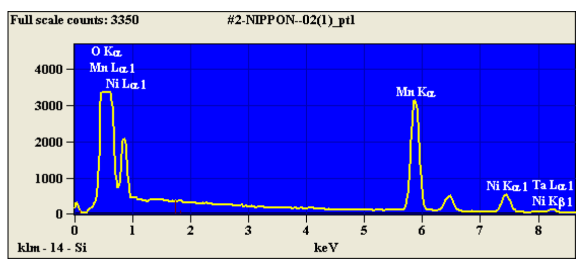




	O-K	Mn-K	Ni-K
#1-NEI--01(1)_pt1	67.82	21.50	6.21
Average after Neglecting Max/Min	67.84	22.53	6.54
Ideal atomic fractions of $Ni_{0.5}Mn_{1.5}O_4$	66.70	25.00	8.30

#2-NIPPON--02(1)





	O-K	Mn-K	Ni-K
#2-NIPPON--02(1)_pt1	73.39	20.74	5.87
Average after Neglecting Max/Min	70.31	22.44	6.19
Ideal atomic fractions of $Ni_{0.5}Mn_{1.5}O_4$	66.7	25.0	8.30

Materials are very similar with regard to morphology and atomic composition.

Technical Accomplishments and Progress:
2. *Identify a $LiNi_{1/2}Mn_{3/2}O_4$-spinel baseline for the high-voltage-electrolyte effort*

Transition Metal Solubility

X. Song

Dissolution experiments
- 5 g of powder in 15 g of electrolyte
- At 55°C for 1 week
- No Ni found in solution.

Supplier	Material	% Mn lost form oxide
NEI	$LiNi_{0.5}Mn_{1.5}O_4$	0.046
Nippon Denko	$LiNi_{0.5}Mn_{1.5}O_4$	0.082
Toda (Mn-spinel)	$Li_{1.15}Mn_{1.85}O_4$	0.104

The amount of Mn is material dependent.

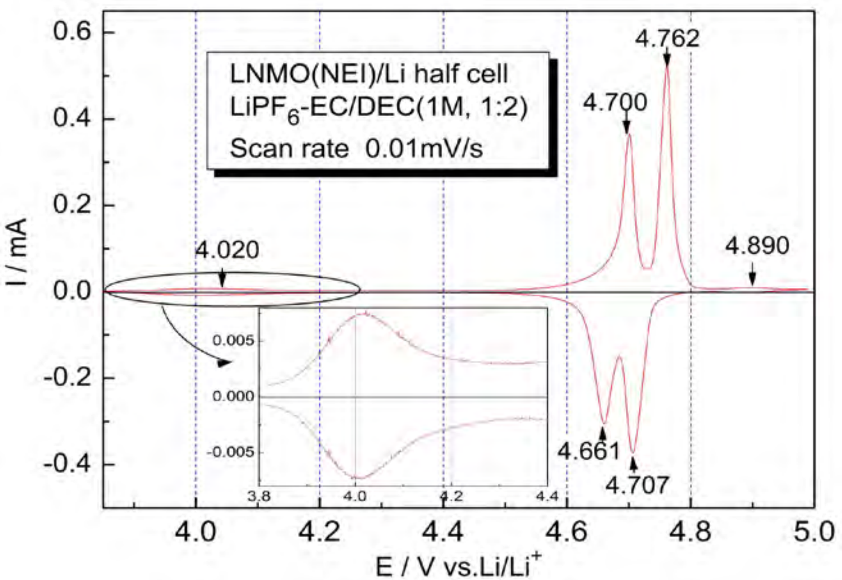
Technical Accomplishments and Progress:

2. Identify a $LiNi_{1/2}Mn_{3/2}O_4$-spinel baseline for the high-voltage-electrolyte effort

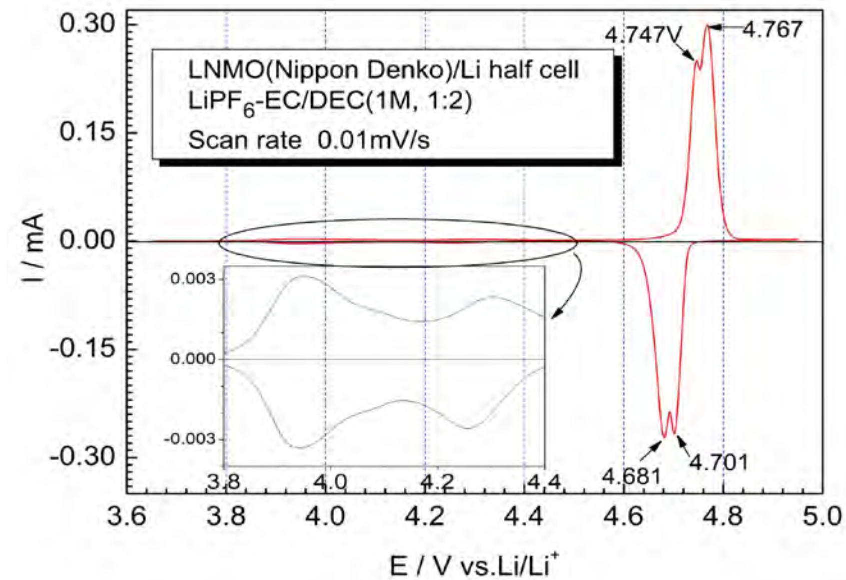
CVs (0.01 mV/s)

Y. Fu

NEI



Nippon Denko

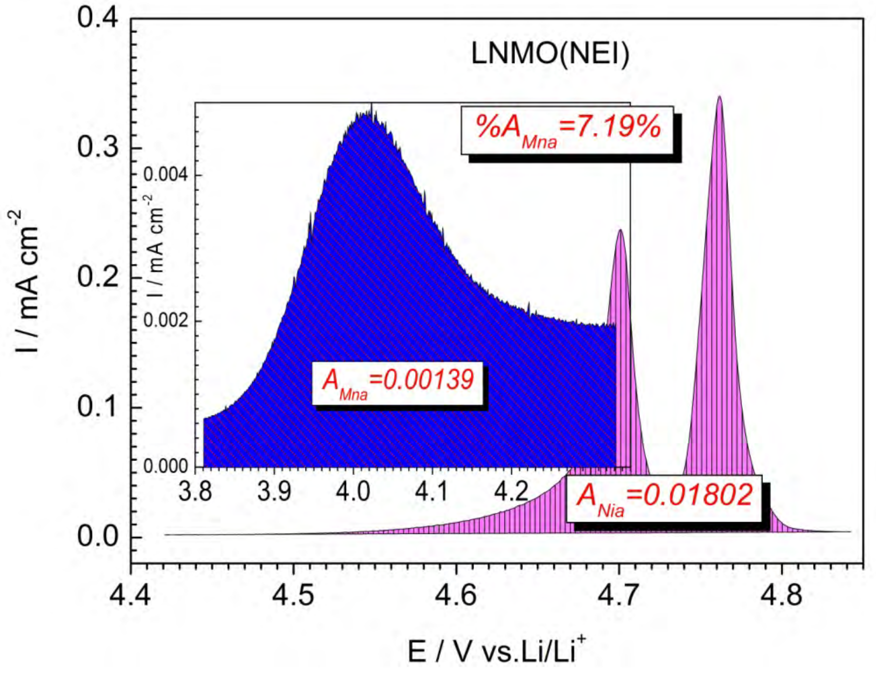


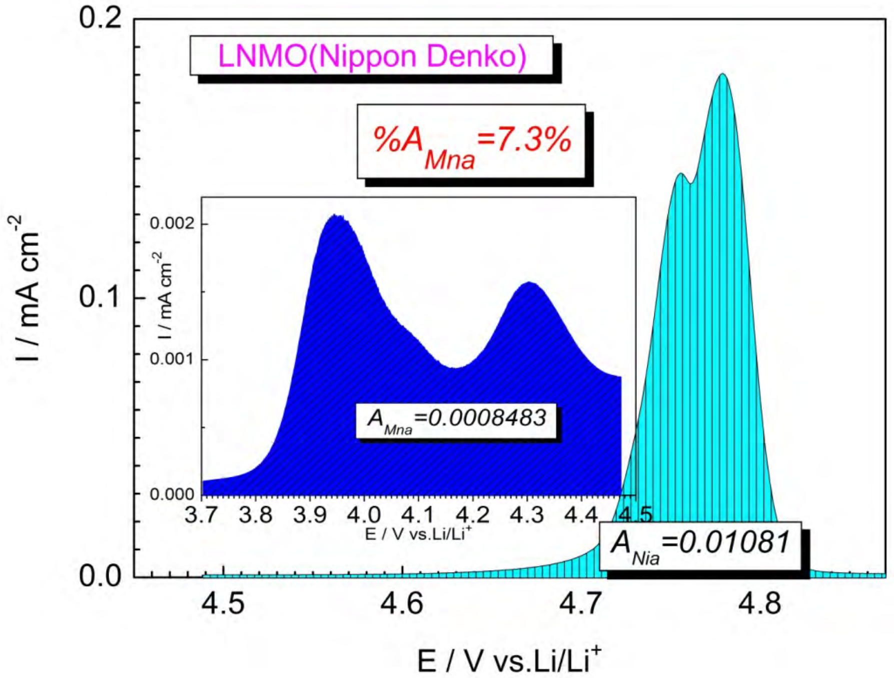
The NEI and Nippon Denko spinels show some differences for both oxidation and reduction potentials.

Technical Accomplishments and Progress:
2. Identify a $LiNi_{1/2}Mn_{3/2}O_4$-spinel baseline for the high-voltage-electrolyte effort

Capacity Breakdown

Y. Fu





The fraction of capacity at upper and lower potentials is the same for each spinel.

Technical Accomplishments and Progress:
2. Identify a $LiNi_{1/2}Mn_{3/2}O_4$-spinel baseline for the high-voltage-electrolyte effort

Y. Fu

Summary Table

Material	Dissolution 1week at 55°C (%)	Ni/Mn ratio EDX (0.33)	Low voltage capacity (%)	1st cycle loss (%)	Rev. Cap. (mAh/g)	Cycling eff. vs. Li in EC:DEC (%)
NEI	0.046	0.291	7.2%	18.4	128.1	5.0
Nippon Denko	0.082	0.276	7.3%	7.9	111.5	4.8
ANL data Enerdel electrodes				10.3	117	

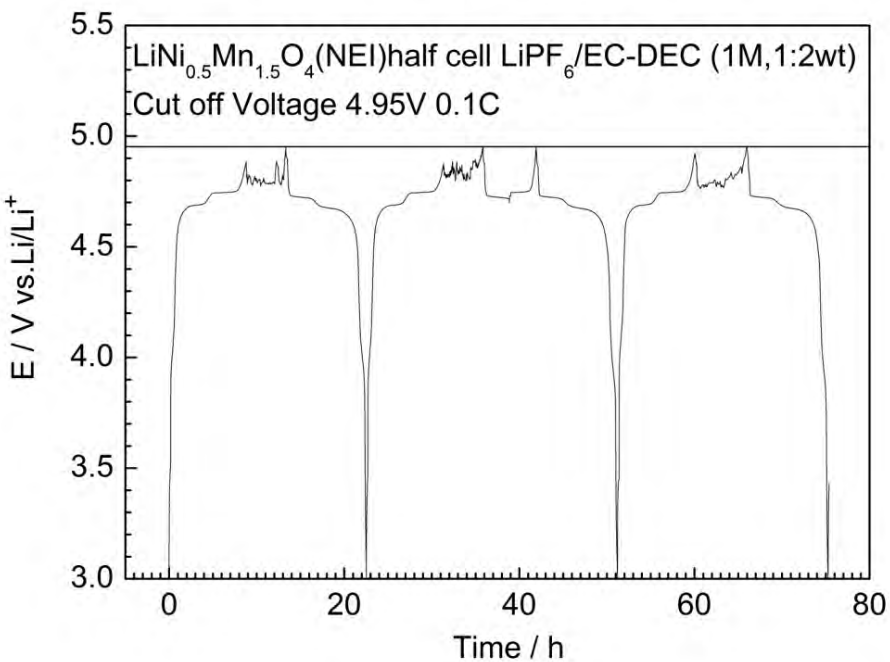
Initial results indicate that the physical and chemical characteristics of the two spinel materials are similar. The electrochemical performance differs.

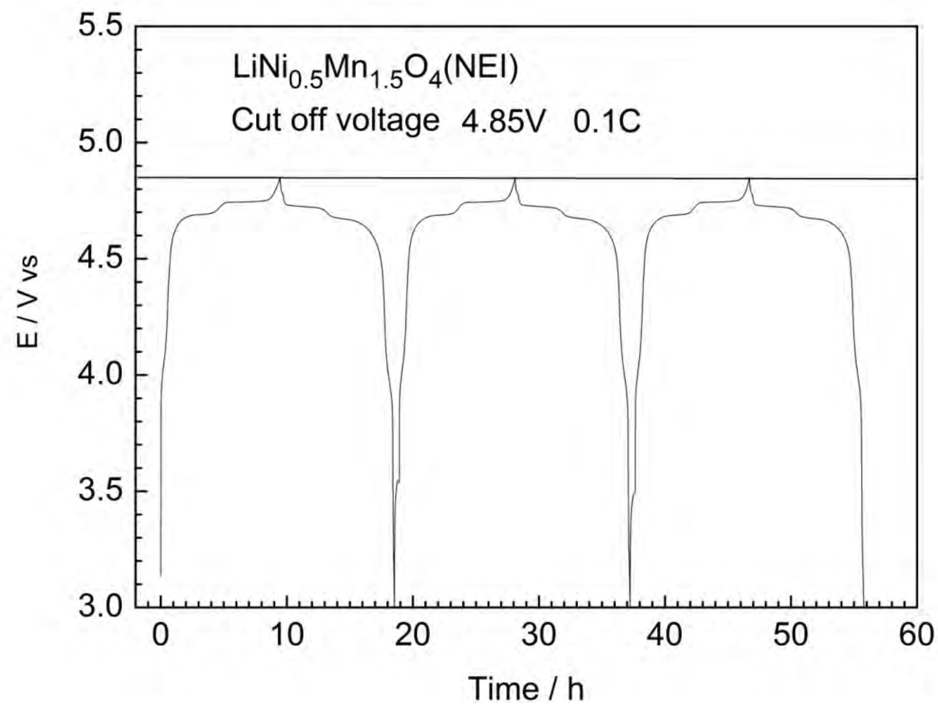
Technical Accomplishments and Progress:

2. Identify a $LiNi_{1/2}Mn_{3/2}O_4$-spinel baseline for the high-voltage-electrolyte effort

Y. Fu

Effect of Cut-Off Voltage





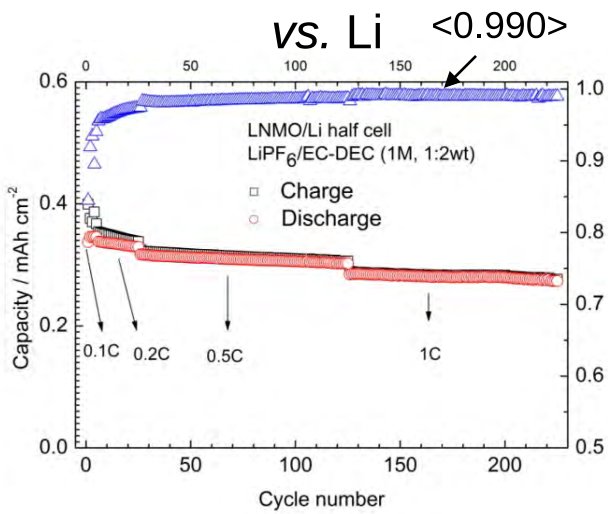
Too high of a cut-off voltage (>4.95 V) leads to electrolyte instability.

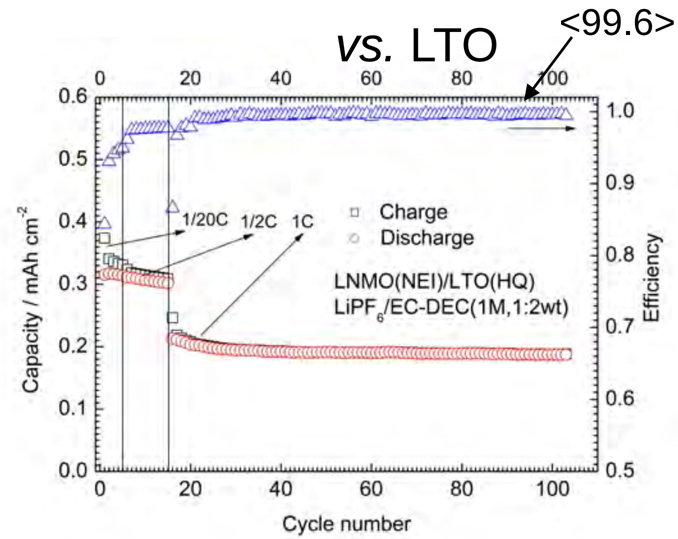
Technical Accomplishments and Progress:

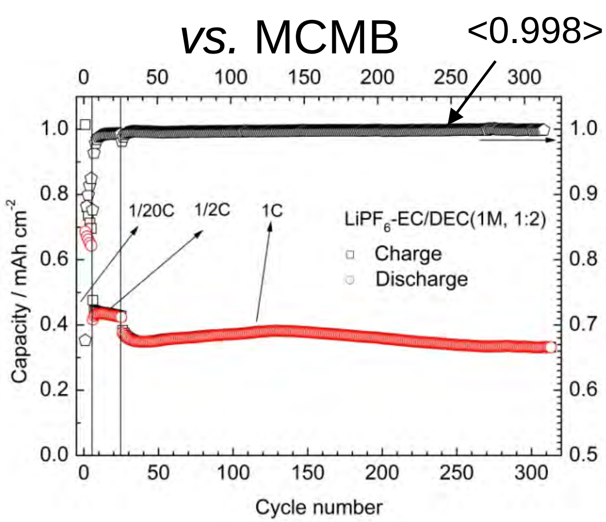
2. *Identify a $LiNi_{1/2}Mn_{3/2}O_4$-spinel baseline for the high-voltage-electrolyte effort*

Y. Fu

Cycle Performance







- The cycling *vs.* Li was unsatisfactory:
  - capacity decay, efficiency *ca*. 98%

- The cycling *vs.* LTO ($Li_4Ti_5O_{12}$) improved, compared well to literature.

- The cycling *vs.* MCMB is promising, but showed some peculiarities typical for cells with this anode.

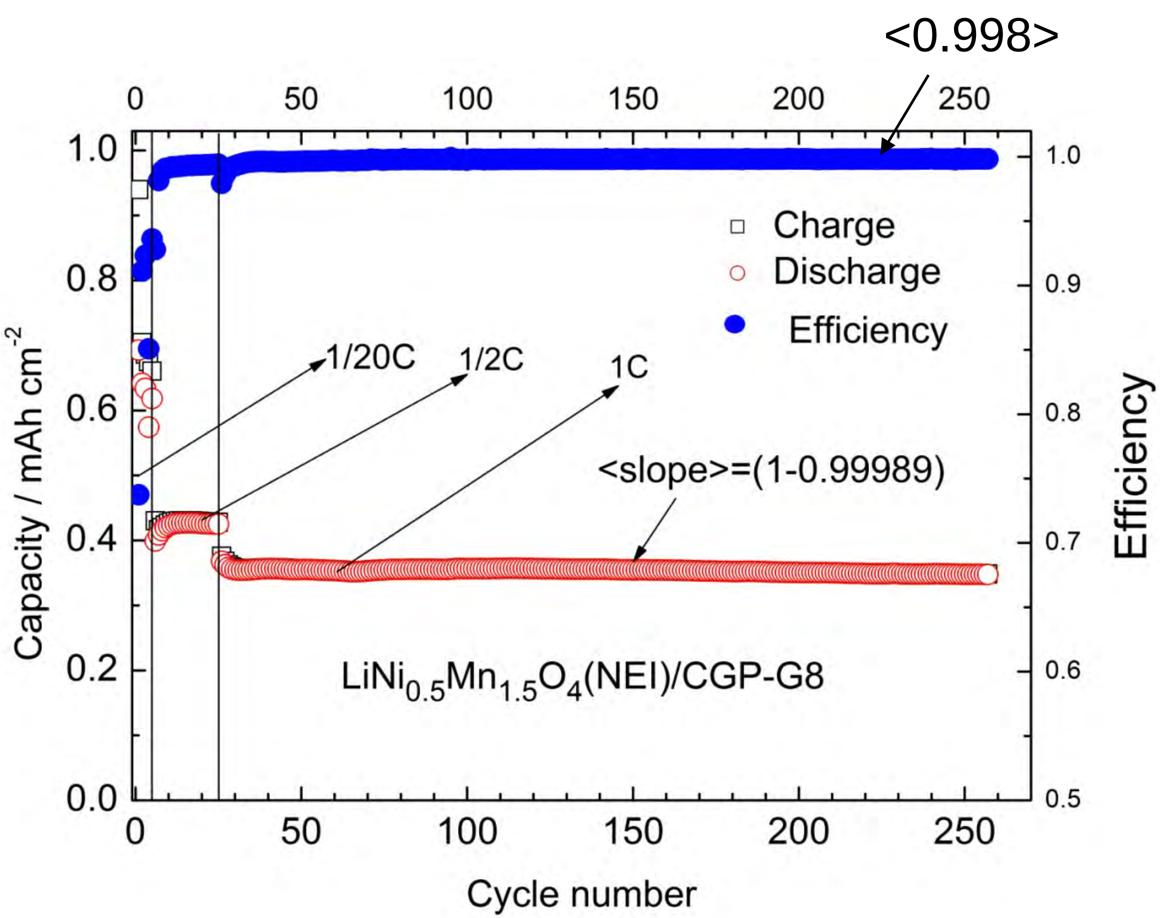
LTO electrodes supplied by HydroQuebec

Technical Accomplishments and Progress:

2. *Identify a $LiNi_{1/2}Mn_{3/2}O_4$-spinel baseline for the high-voltage-electrolyte effort*

Y. Fu

Cycling of CGP-G8/NEI



The energy density is 76% greater than the LTO based cell!

Cycling *vs*. CGP=G8 is very encouraging…. however

- These electrodes are of low loading.
- Cell impedance trends need to be studied.
- The coulombic efficiency may not be high enough.
- Why is there a large drop in capacity from C/20 to C/2?
- Why is there a decline in capacity in the first few cycles?
- Is there gassing?
- Why is G8 different than MCMB? Does this arise from an interaction with the cathode?

Technical Accomplishments and Progress:
3. Improved Cell Performance w/ Aqueous-based PAAX binders

J. Chong
X. Song

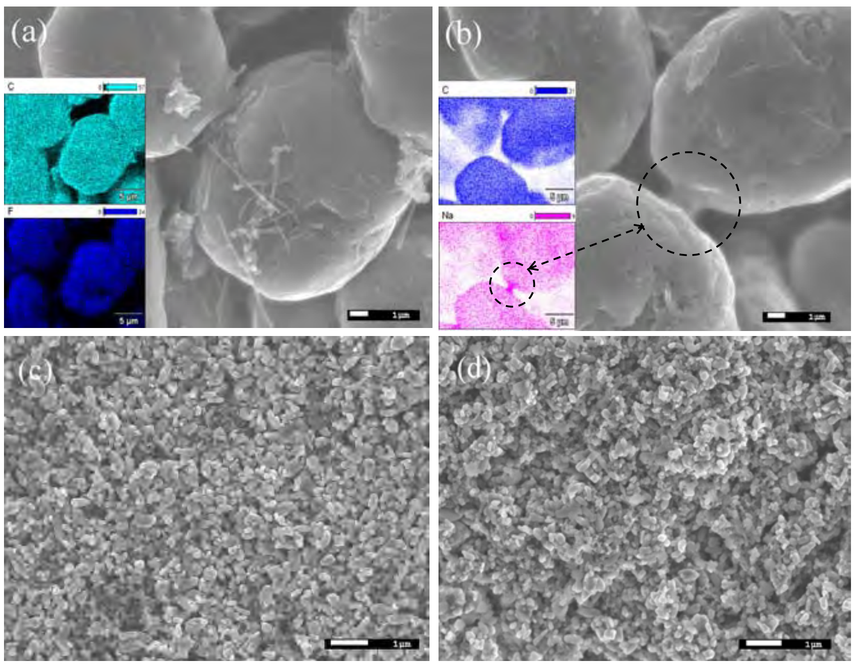
Electrodes of PAANa *vs.* PVDF

PAAX = polyacrylic acid and its salts

PVDF | PAANa

SNG

$LiFePO_4$



Anodes (SNG: Surface modified Natural Graphite from HydroQuebec)

- On a 1 micron scale, the anodes look similar except for polymer bridging w/PAANa
- Bridging also seen with other PAAX binders.

Cathodes (C/LiFePO4 from HQ)

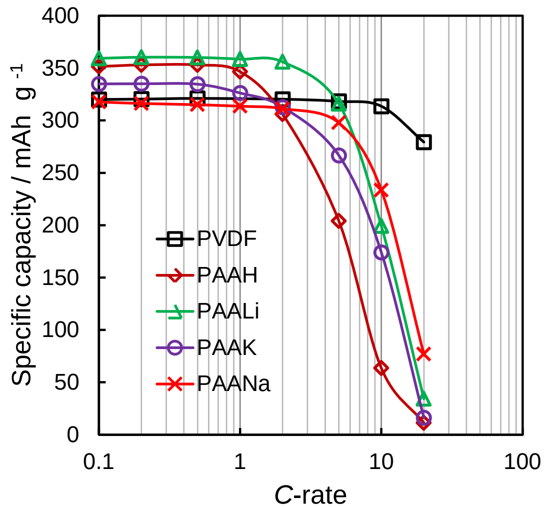
- At a 10 micron scale, the cathodes appear to be very similar.

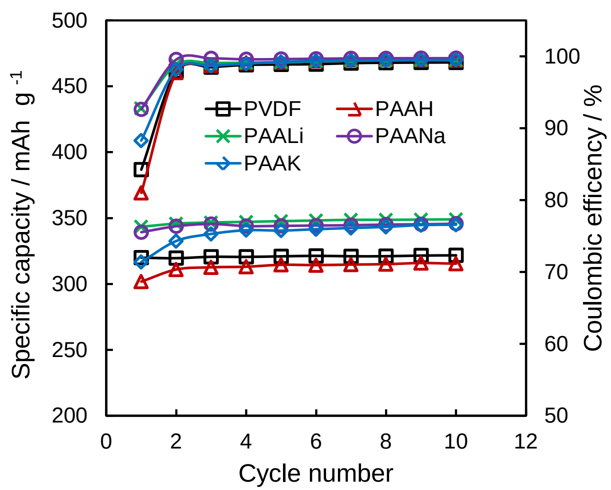
Technical Accomplishments and Progress:
3. Improved Cell Performance w/ Aqueous-based PAAX Binders

J. Chong

Rate Capability, Efficiency, Specific Capacity

90% SNG + 10 % Binder





- PVDF shows the best rate capability
  - Absorbs organic liquids more readily
- All show good coulombic efficiency and initial cycling stability.
- PAALi and PAANa show reasonable rate capability, high specific capacity, and the lowest 1st cycle irrev. capacity loss

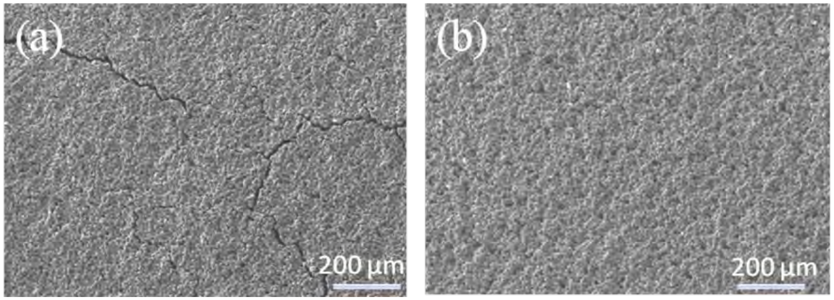
PAALi was chosen for further study to avoid introducing sodium ions into the cell

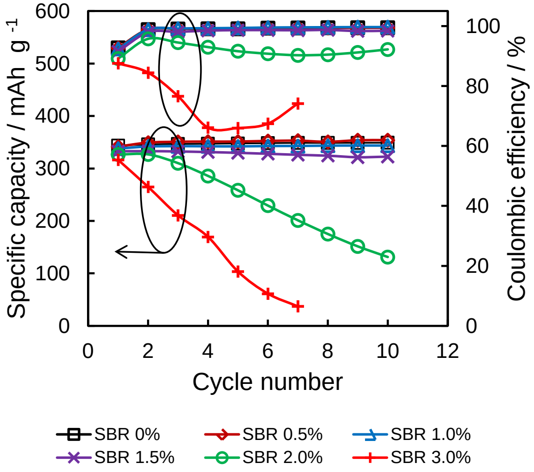
Technical Accomplishments and Progress:
3. Improved Cell Performance w/ Aqueous-based PAAX Binders

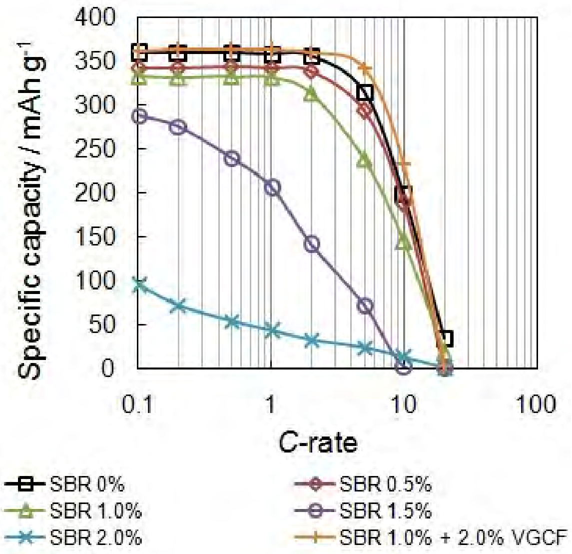
J. Chong
X. Song

Further Modification of PAALi Electrodes

PAALI PAALI + SBR







- On a 200 micron scale, macro-cracks are visible immediately after the drying step.
- One solution to this is the addition of SBR.
- The addition of SBR dramatically reduced the conductivity of the electrode (not shown).
- Above 1% SBR had a negative impact on cell stability and efficiency.
- The poor conductivity was remedied by the addition of VCGF (vapor-grown carbon fibers).

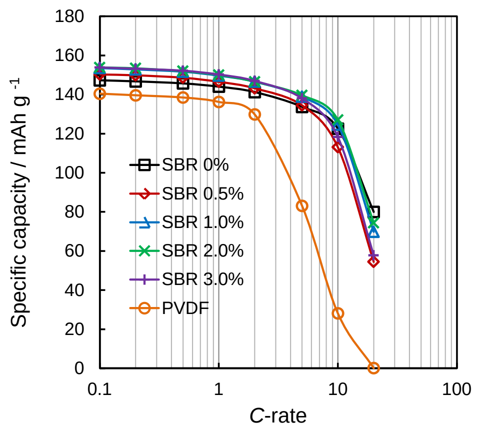
Technical Accomplishments and Progress:

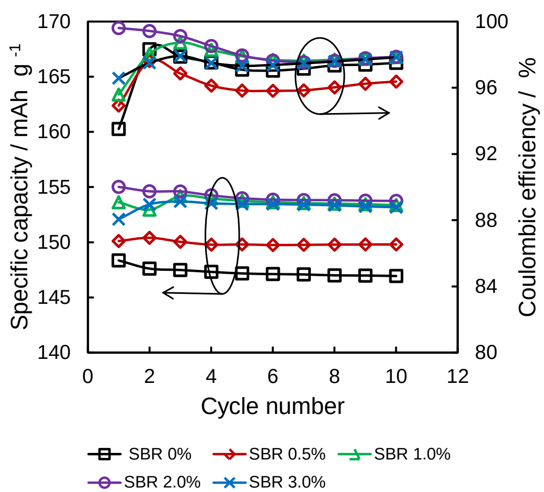
3. Improved Cell Performance w/ Aqueous-based PAAX Binders

J. Chong

Cathodes w/PAALi and SBR

82% LiFePO4 + 10% PAALi/SBR + 8% AB





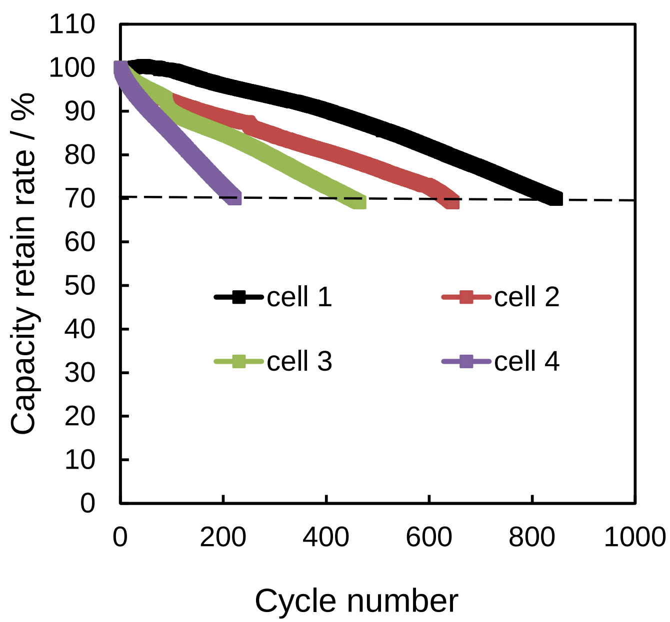
To overcome the poor conductivity of $LiFePO_4$, acetylene black was introduced; anode results suggested that PAALi is a good candidate.

- Rate capability independent of amount of SBR; better than PVDF.
- Coulombic efficiency and specific capacity negatively impacted with 0% < SBR < 2%
- We selected 1% SBR to evaluate full-cell cycle-life performance.

Technical Accomplishments and Progress:
3. Improved Cell Performance w/ Aqueous-based PAAX Binders

J. Chong

Full Cell Cycling



Cell 1: anode: 9% PAALi/1% SBR/2% VGCF/88% SNG12
cathode: 9% PAALi/1% SBR/8% AB/82% $LiFePO_4$
Cell 2: anode: 9% PAALi/1% SBR/90% SNG12
cathode: 10% PVDF/8% AB/82% $LiFePO_4$
Cell 3: anode: 10% PAALi/90% SNG12
cathode: 10% PVDF/ 8% AB/82% $LiFePO_4$
Cell 4: anode: 10% PVDF/2% AB/2% VGCF/86% SNG12
cathode: 10% PVDF/8% AB/82% $LiFePO_4$

Cell 1 entirely based on PAALi.
Cell 4 entirely based on PVDF.
Cells 2 thru 4 have PVDF cathodes.

- The substitution of PAALi for PVDF in the anode increased the cycle life from 223 to 446
- The addition of SBR increased the cycle life to 646
- The addition of VCGF and the substitution of a PVDF cathode with a PAALi cathode further increased the cycle life to 823.

Cells fabricated entirely from water-based polymer slurries can result in better overall performance.

Collaborations and Coordination with Other Institutions

Companies

- Received material from NEI
- Received material from Nippon Denko
- Recently received powders of $LiNi_{1/2}Mn_{3/2}O_4$ from HydroQuebec.
- Expect to receive a new baseline material from NEI through Y.-M. Chiang (MIT)
- Expect to receive new, high-voltage electrolytes from Daikin, Japan

Universities and National Laboratories

- Recently received a laminate of $LiM_xNi_yMn_zO_4$ from ANL and their testing results
- Expect to receive a new $LiNi_{1/2}Mn_{3/2}O_4$ material from G. Ceder's Group (MIT).
- Expect to receive a new $LiNi_{1/2}Mn_{3/2}O_4$ material from A. Manthiram's Group (UT).
- Will be testing a new Ti-substituted NCM material from M. Doeff (LBNL).

Each supplier will receive feedback on their respective materials.

Proposed Future Work

- Identify next-generation baseline material for the high-voltage-electrolyte project
- Collect $LiNi_{1/2}Mn_{3/2}O_4$ from different sources
    - From companies: NEI, Nippon Denko
    - From BATT: Ceder (MIT), Manthiram (UT), Cabana (LBNL), Zhang (PNNL)
    - Collect physical, chemical, and electrochemical characterization data from all sources
    - Correlate chemical and electrochemical data to physical data (BET, PSA, SEM, EDX, XRD)
- Evaluate candidate high-voltage electrolytes
    - From companies: Daikin
    - From within ABR: JPL, ARL
    - From within BATT: Lucht (URI), Angell (UA), Zhang (PNNL)
    - Collect physical, chemical, and electrochemical characterization data from all sources
    - Correlate electrochemical performance data to the chemical and electrochemical characterization data (viscosity, transport properties, voltage stability)

Summary

We have extensive capabilities to provide comprehensive evaluations of new battery materials for transportation applications

- Through a rigorous, multi-criteria analysis CGP-G8 was selected as the BATT baseline graphite. Further analysis revealed that a high fraction of hexagonal structure may be critical to its performance.
- NEI's and Nippon Denko's cathode materials are undergoing extensive evaluations. NEI's material cycles extremely well against CGP-G8. Further work is needed to confirm performance at higher loadings.
- A preliminary study using polyacrylic acid salt binders suggests that it could be possible to prepare high-quality electrodes from aqueous slurries having performance similar to those using PVDF.