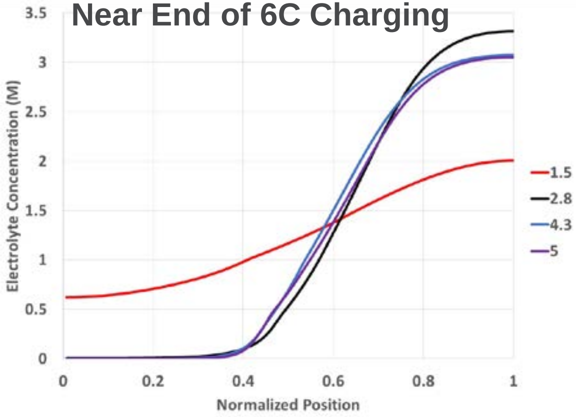
BAT371

XCEL
eXtreme Fast Charge Cell Evaluation
of Lithium-ion Batteries

UNDERSTANDING ELECTRODE SCALE AND ELECTROLYTE EFFECTS DURING FAST CHARGE



Electrolyte Salt Concentration Near End of 6C Charging

DENNIS DEES

Argonne National Laboratory

ANDREW COLCLASURE

National Renewable Energy Laboratory

This presentation does not contain any proprietary, confidential, or otherwise restricted information

OTHER MAJOR CONTRIBUTORS

NREL: Shriram Santhanagopalan
INL: Kevin Gering
Argonne: Daniel Abraham, Ira Bloom, Dave Robertson, Marco Rodrigues

June 12, 2019
Crystal City, VA

OVERVIEW

Timeline

- Start: October 1, 2017
- End: September 30, 2021
- Percent Complete: 37%

Barriers

- Cell degradation during fast charge
- Low energy density and high cost of fast charge cells

Budget

- Funding for FY19 – 6390k
  - ANL – 2400k
  - NREL – 1600K
  - INL – 440K
  - SLAC – 1000K
  - LBNL – 950K

Partners

- Argonne National Laboratory
- Idaho National Laboratory
- Lawrence Berkeley National Lab
- National Renewable Energy Laboratory
- SLAC National Accelerator Lab

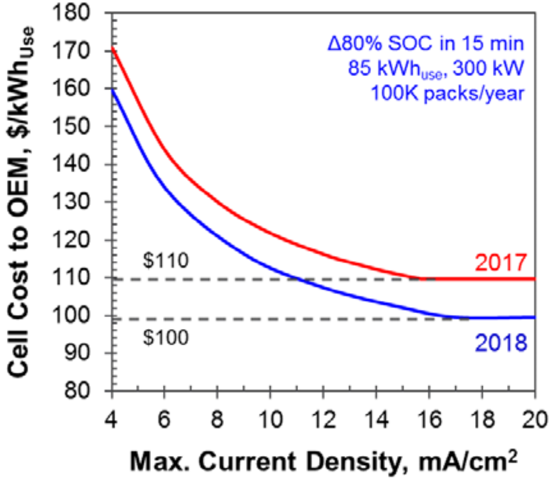
RELEVANCE

Battery Performance and Cost (BatPaC) Model utilized to quantify fast charge challenges.

- The BatPaC model is used to design lithium-ion battery packs and estimate their cost in large volume manufacturing.

- Fast charging BEV battery packs was examined with the BatPaC model.
  - Lithium plating limits the anode thickness and increases pack cost.
  - Cell cost increases nonlinearly with decreasing charging times.
  - Cooling may be needed during charging.
  - Improved electrodes are needed to lower cost.

Gr//NMC622, 168 cells, 315V



- The objective of this effort is to utilize electrochemical models developed to examine transport, reaction, and phase-change in graphite based electrodes and seek solutions for fast charge applications.

- Work is focused on quantifying limitations in the graphite electrode that impact the cell's maximum fast charge capability.

APPROACH

- Macro-homogeneous electrochemical model is used to investigate limitations and further suggest approaches for enabling fast charging for high loading cells suitable for EVs (e.g. tortuosity, temperature, porosity, N/P ratio, next generation electrolytes)
- This electrochemical modeling work builds on earlier successful characterization and modeling studies through extending efforts into fast charge limitations.
- Electrolyte models are used to develop next generation electrolytes with enhanced transport properties.
- Include phase-transition phenomena as well as lithium intercalation for graphite active materials in model to better account for high C-rate performance.

MILESTONES

Related milestones in XCEL

Milestone	Status
Rationalize performance and degradation experimental findings from NREL, ANL and INL using models to explain underlying mechanisms behind observed electrochemical performance and degradation.	On Track
Identify viable electrolyte candidates that would significantly improve transport behavior for fast charge cell performance.	Complete
Short-list electrolyte design space by collecting surface energy data from experimental wetting measurements for promising electrolyte formulations from high-throughput screening.	On Track
Determine phase-change model parameters for Superior Graphite active material.	Complete

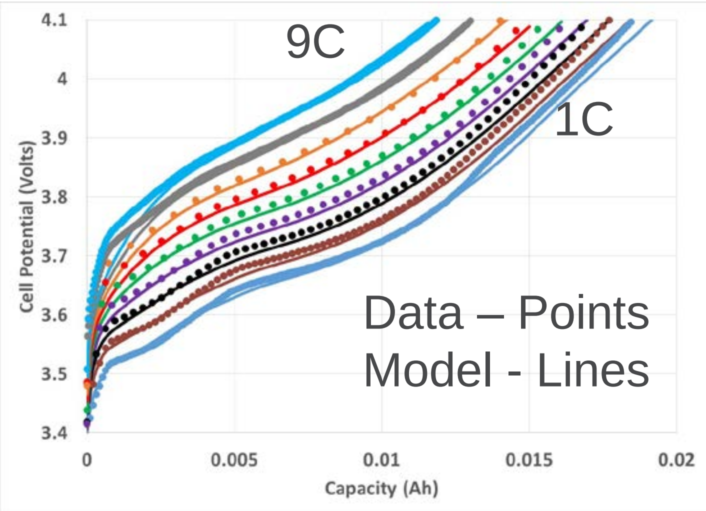
TECHNICAL ACCOMPLISHMENTS AND PROGRESS

- Model used to determine strategies for enabling extreme fast charging at loading of 3 and 4 mAh/cm^2 without lithium plating.
- Elevated Temperature, low tortuosity electrodes, and next generation electrolytes are shown to significantly enhance extreme fast charging capability for thick electrodes and are significant areas of research.
- Initial screening with Advanced Electrolyte Model has produced fast charge electrolytes that exhibit conductivity and diffusivity at least 2-3 times greater than the baseline. Initial cell testing has confirmed validity for some of these electrolytes.
- An electrolyte screening model based on associating physical properties to functional groups was developed to identify next generation electrolytes for fast charge.
- Graphite active material model that includes phase-transition phenomena as well as lithium intercalation utilized to examine graphites over a range of diagnostic studies in half-cells and full micro-reference electrode cells affirms earlier observations of apparent increasing lithium diffusion coefficient with C-rate.

MACROSCALE POROUS ELECTRODE MODELING

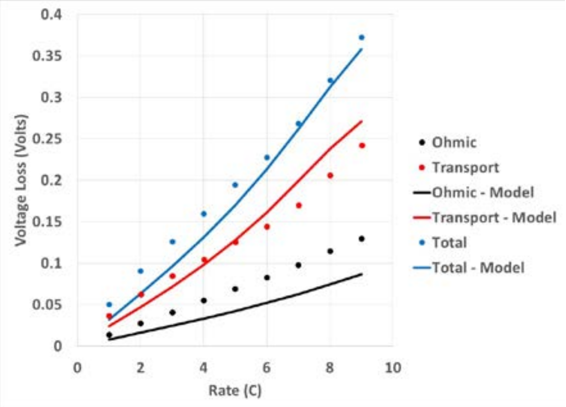
TECHNICAL ACCOMPLISHMENTS AND PROGRESS

DATA AND MODEL PREDICTIONS FOR CELLS WITH LOW LOADING

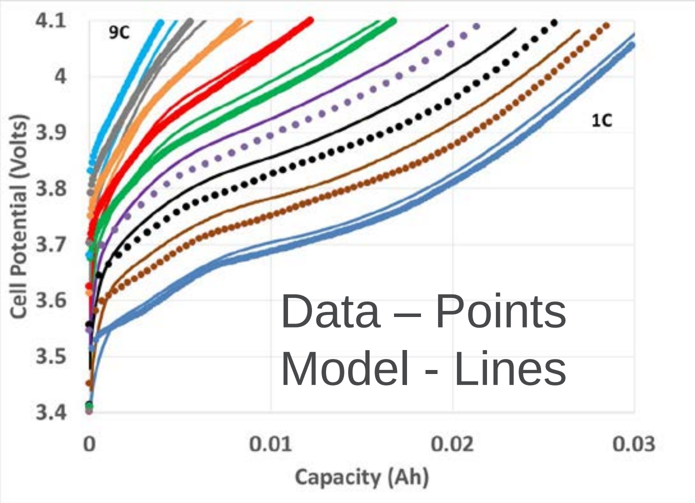


Rate	mAh/g-NMC	SOC
1	128	88
3	118	81
5	108	74
6	103	71
7	97	67
8	90	62
9	82	57

- Electrodes are ~40 microns thick with ~35% porosity (1.5 mAh/cm^2)
- Increases charge rate from 1C to 6C only reduces end SOC from 88% to 71%
- Overpotential increase linearly with rate

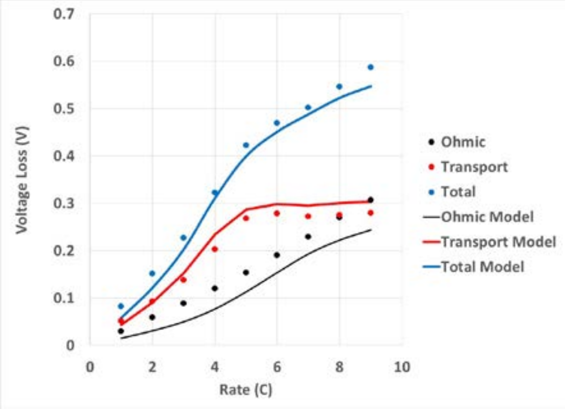


DATA AND MODEL PREDICTIONS FOR CELLS WITH MODERATE LOADING

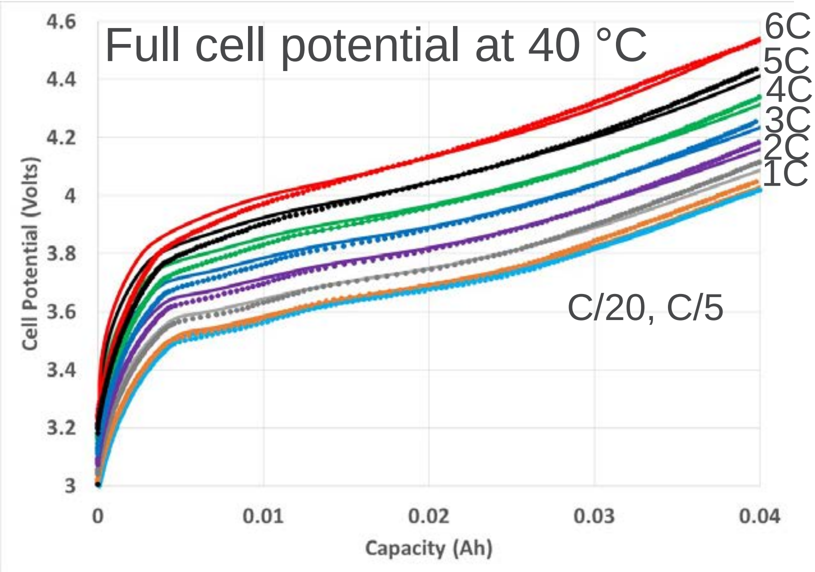


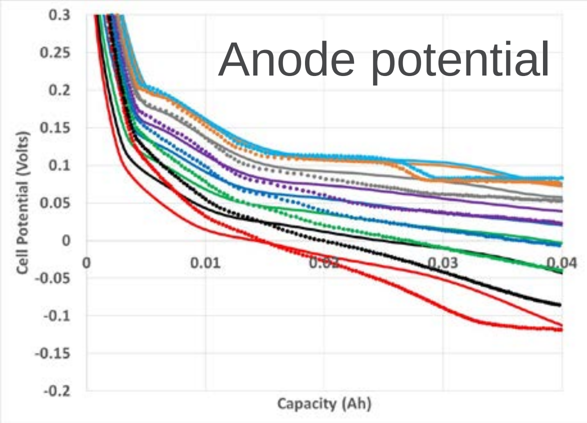
Rate	mAh/g-NMC	SOC
1	134	92
3	112	77
5	73	50
6	51	36
7	35	24
8	24	16
9	17	12

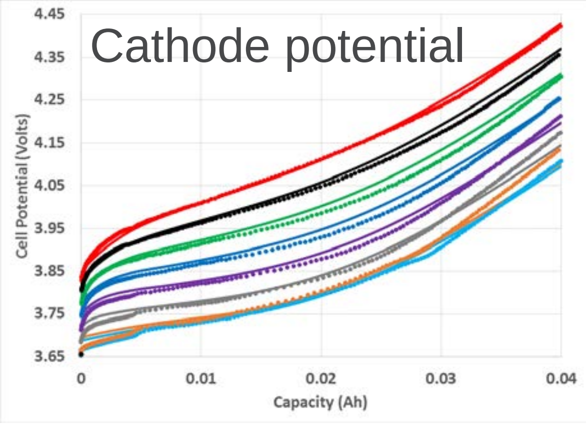
- Electrodes are ~70 microns thick with ~35% porosity (2.5 mAh/cm^2)
- Increases charge rate from 1C to 6C only reduces end SOC from 90% to 35%
- Severe transport losses above 4C



INDIVIDUAL ELECTRODE POTENTIALS DURING CHARGING FOR MODERATE LOADING

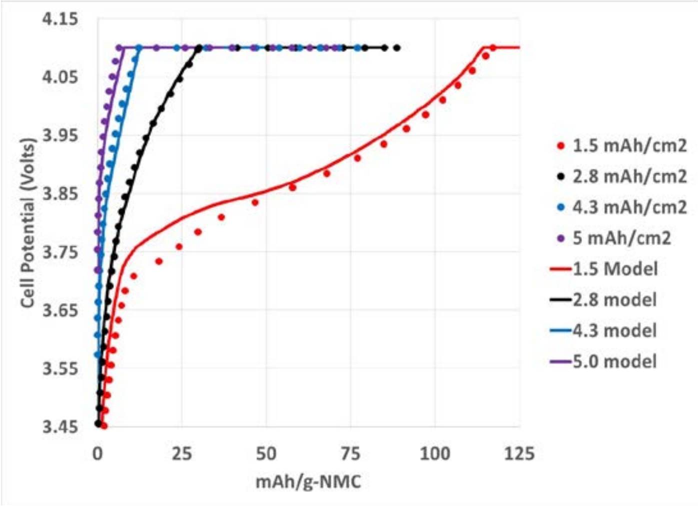




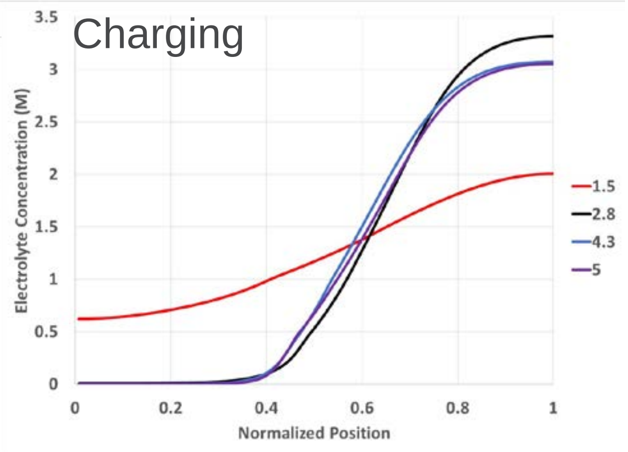


- Electrode potentials measured with copper wire with in-situ plated lithium (Daniel Abraham - ANL)
- Graphite diffusion coefficient seems to be enhanced with rate (model overpredicts low rate graphite performance)

6C CHARGING AS A FUNCTION OF LOADING (1.5-5 mAh/cm^2)



Salt concentration near end of 6C Charging



Loading (mAh/cm^2)	6C CC Only (mAh/g-NMC)	10 minutes Capacity (mAh/g-NMC)
1.5	**115**	**131**
2.8	**30**	**88**
4.3	**12**	**76**
5	**6**	**70**

- Higher loadings
  - Severe electrolyte transport limitations
  - Significant amounts of lithium plating

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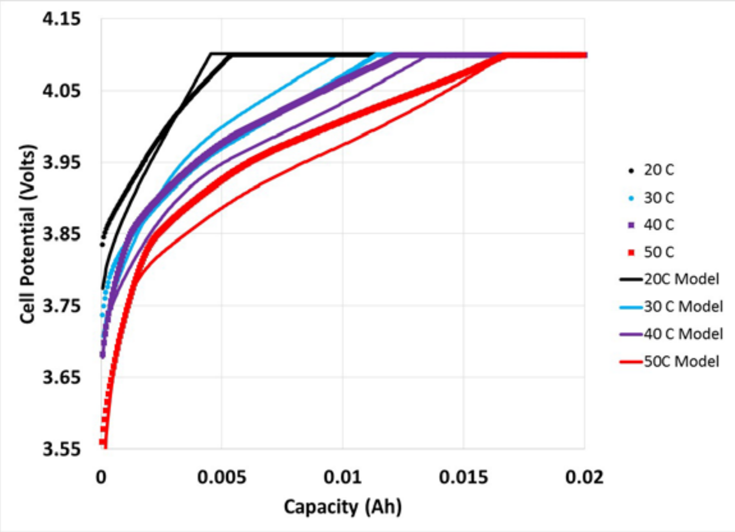
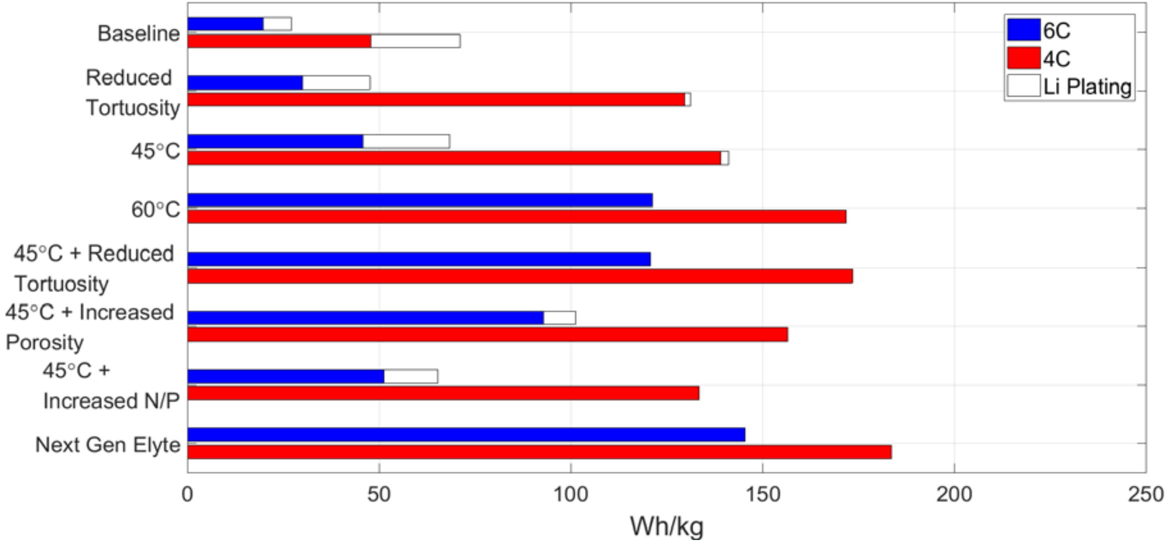
6C CHARGING AS FUNCTION OF TEMPERATURE AT MODERATE LOADING



- Electrodes are ~70 microns thick with ~35% porosity (2.5 mAh/cm^2)
- Increases temperature from 20 to 50°C increases 6C CC capacity from 23 to 71 mAh/g-NMC
- Model best fits data with activation energy for D_S and i_o of 0 kJ/mol
- E_a for D_e and κ of 29 and 15 kJ/mol (Gen2)

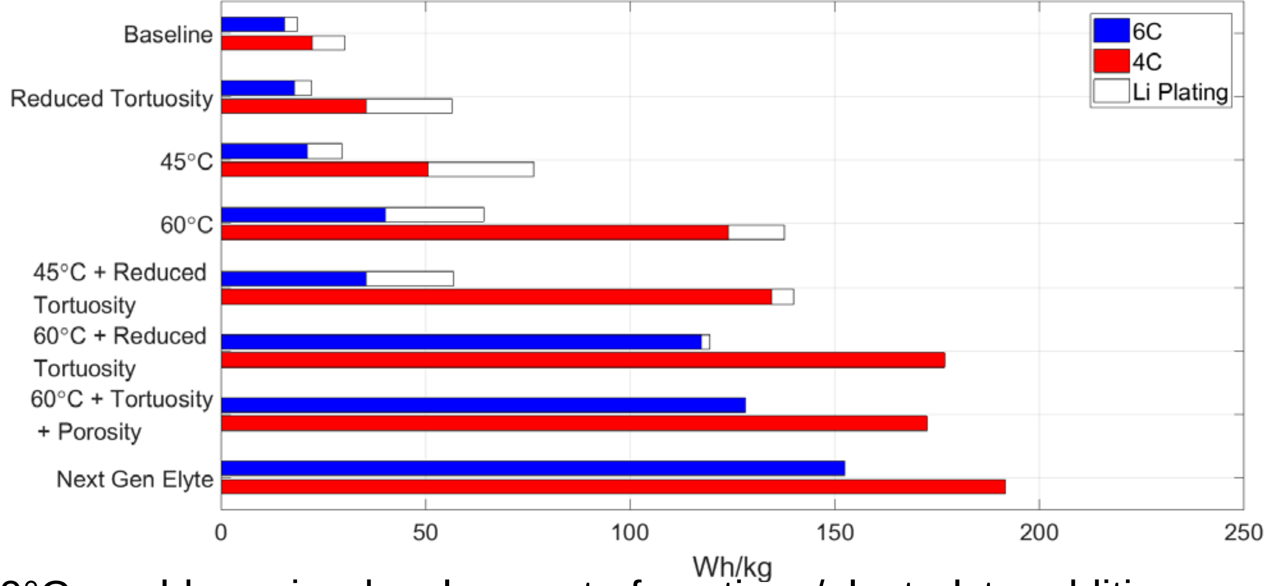
Temperature °C	CC Capacity (mAh/g-NMC)	10 minutes Capacity (mAh/g-NMC)
20	23	91
30	49	107
40	52	109
50	71	118

ENABLING XFC AT LOADING OF 3 mAh/cm^2 (220 Wh/kg CELL; 80 MICRON ELECTRODES)



- Elevated temperature and reduced tortuosity are viable near-term technologies
- Porosity and N/P ratio provide less value and reduce 1C density
- Important to continue research on electrolyte with enhanced transport
  - NGE = 1.8X ionic conductivity, 3X diffusivity, and transference number increased by 0.05

ENABLING XFC AT LOADING OF 4 mAh/cm^2 (230 Wh/kg CELL; 110 MICRON ELECTRODES)



- 60°C would require development of coatings/electrolyte additives
- Important to continue research on electrolyte with enhanced transport
  - NGE = 2X ionic conductivity, 4X diffusivity, and transference number increased by 0.15
  - More important to improve diffusivity/transference number than conductivity

ENABLING FAST CHARGE THROUGH IMPROVED ELECTROLYTES

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

DESIGN OF ALTERNATIVE ELECTROLYTES TO ENABLE FAST CHARGE Li-ION CHEMISTRIES

Idaho National Laboratory (INL) Advanced Electrolyte Model (AEM)

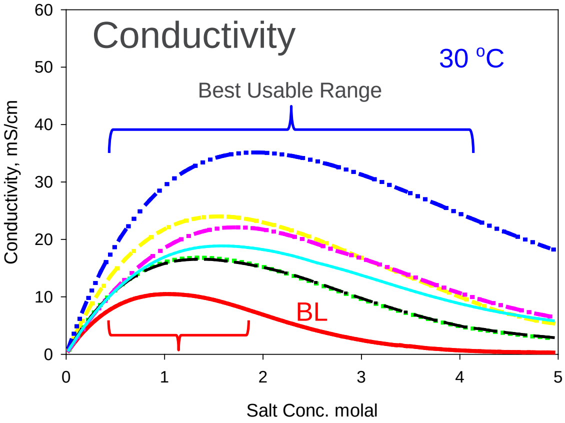
- Approach is to use the INL AEM to investigate new electrolyte goals:
  - Increase Conductivity (decrease resistivity) to increase power.
  - Increase species diffusivity to mitigate polarization effects.
  - Maintain good conductivity and diffusivity even in polarized regions.
  - Decrease the lithium desolvation burden (required time and energy).
  - Keep t_+ at reasonable levels (say, ≥ 0.4)
  - Increase salt content.
  - Decrease EC content, yet avoid excessive ion association.
- Companion Testing: insure good SEI and cycling attributes are achieved.

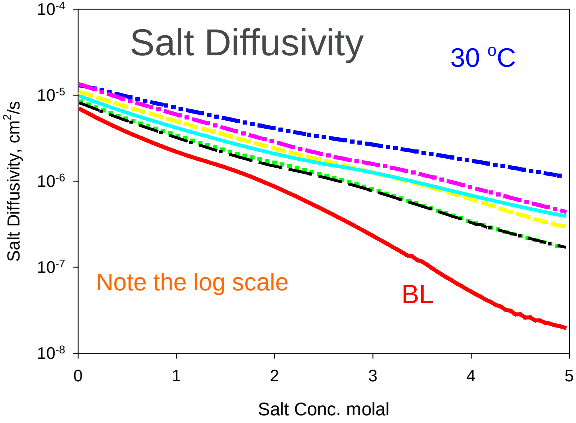
Initial Electrolyte Systems under consideration

━━━━━━	Gen2 BL: EC-EMC (30:70, mass) + $LiPF_6$
▪▪▪▪▪▪▪	EC-DMC-MFA-EA (20:30:20:30) w 3% VC + $LiPF_6$
▪ ▪ ▪ ▪ ▪ ▪	EC-DMC-TMP-PN (15:35:20:30) w 3% VC + $LiPF_6$
▪▪▪ ▪▪▪ ▪▪▪	EC-EF-MFA-PN (10:25:25:40) w 3% VC + $LiPF_6$
▪▪ ▪▪ ▪▪ ▪▪	EC-DME-DMC-MA-EF (15:10:25:25:25) + $LiPF_6$
▪ ▪ ▪ ━	EC-DMC-MFA-EF-TMP (15:25:20:20:20) + $LiPF_6$
━━━━━━	EC-DMC-MFA-EF-TMP (12:25:20:33:10) + $LiPF_6$

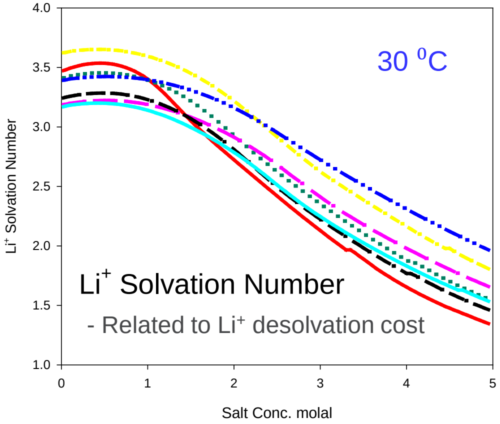
Note that lower amounts of EC are used.

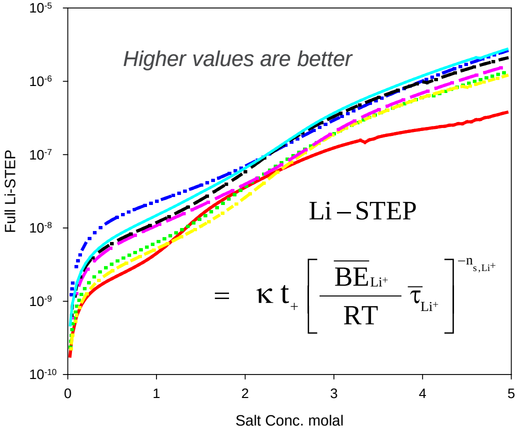
AEM SELECTED ELECTROLYTE PROPERTIES



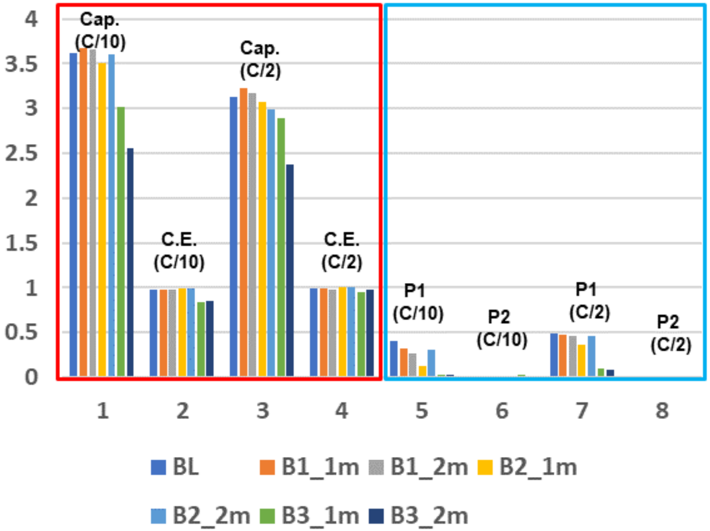


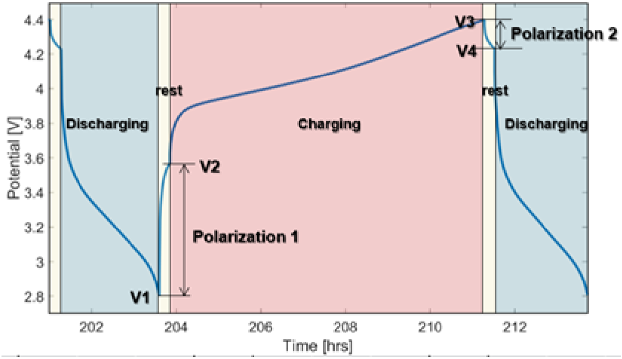
So far, AEM predictions for conductivity are within about 10% variance with most lab data. Validation is ongoing.





POST-FORMATION RESULTS FOR SELECTED FORMULATIONS (1 and 2 molal salt cases)





Separator(5/8”): Celgard 2500

Cathode(9/16”=1.60cm^2): NMC 532
- 3.01 mAh/cm^2 → 3.81577 mAh

Anode(1/2”=1.27cm^2): Superior Graphite
- 2.70 mAh/cm^2 → 4.327274 mAh

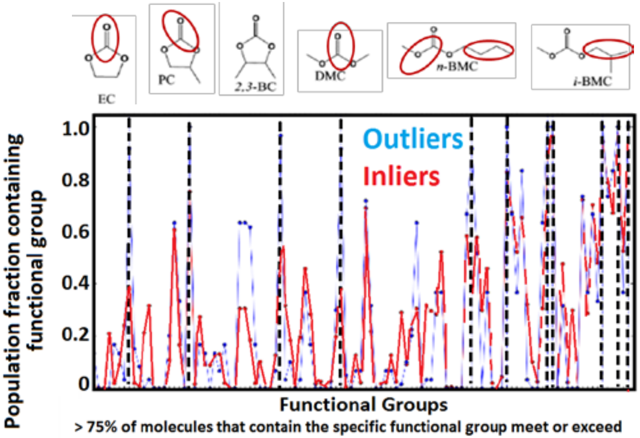
N/P=1.13

- These early results indicate that some of the fast charge electrolytes show better performance than the BL.
- Inclusion of key SEI additives will enable better interfacial stabilization for systems with more volatile solvents.
- Optimization: achieved through iterative linkage of AEM and testing.

ELECTROLYTE SCREENING - MODELING

Mean Sphere Approximation Models Utilized to Connect Physical Properties to Functional Groups

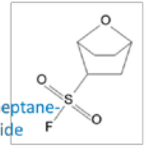
- Model utilized to screen traditional and non-traditional electrolyte solvents.
- Model allows for complex mixtures (e.g. multiple co-solvents, two or more salts, additives, etc.).
- However, not all combinations of functional groups fall into predictable groups.
- Some key observations:
  - Solvents that provide good cation solvation help in meeting diffusivity targets.
  - At high concentrations, number and size of anions control properties like viscosity.
  - Species occupying the “solvation sheath” have limited influence on transport properties.



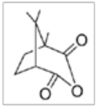
> 75% of molecules that contain the specific functional group meet or exceed target conductivity. The conductivity of the molecule is higher by 25% or more compared to molecule without the functional group - - - - -

- Fused/Bridged bicyclic molecules for solvents

7-oxa-bicyclo-heptane-2-nitrile

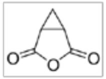


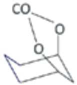
7-oxa-bicyclo-heptane-2-sulfonyl fluoride

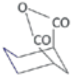


Camphoric Anhydride

1,2-Cyclopropane dicarboxylic anhydride



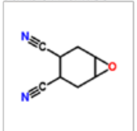


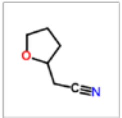


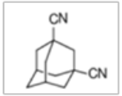
2,4-Dioxabicyclo[3.3.1] nonan-3-one

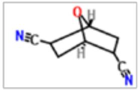
3-Oxabicyclo[3.3.1] nonane-2,4-dione

- Carbonitriles





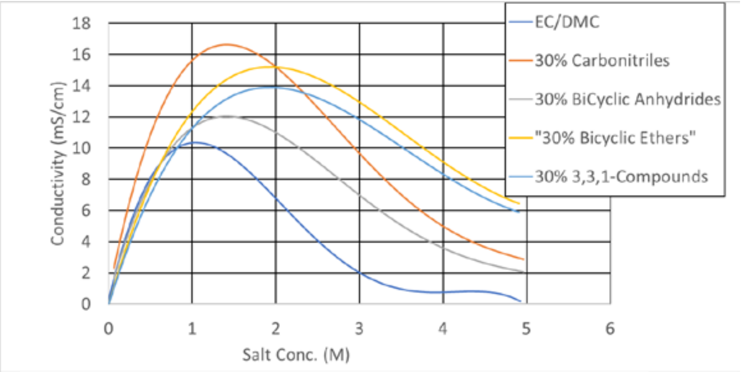


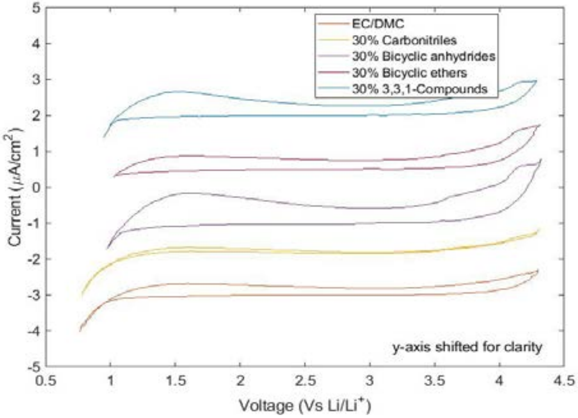


ELECTROLYTE SCREENING - CHARACTERIZATION

Promising electrolytes are formulated and pertinent physical, chemical, and electrochemical properties examined.

- Solubility
- Conductivity
- Viscosity
- Electrochemical window
- Infrared SEI studies
- Interfacial resistance / surface tension





PHASE CHANGE AND DIFFUSION IN GRAPHITE

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

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INCLUDING PHASE CHANGE IN GRAPHITE ELECTRODE ELECTROCHEMICAL MODEL

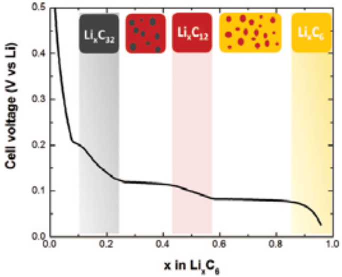
- An electrochemical model that accounts for the diffusion of lithium and the phase changes was developed.
- For simplicity three phases were introduced: LiC_{32}, LiC_{12}, and LiC_6.
- The Avrami equation was used to describe the phase changes.

$$\varepsilon_{s,j} = 1 - \exp(-k' t^n)$$

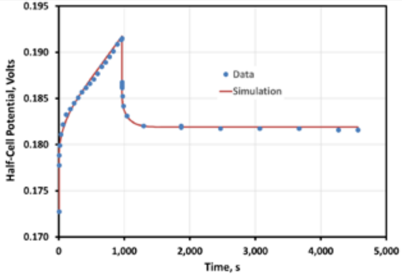
- The model effectively simulates GITT studies and tracks phase changes.
- Diffusion coefficient for the single phases in various of graphites on the order of 10^{-13} cm^2/s, based on graphite active surface area equal to the BET surface area.
- Resulting in a lithiation time constant of several tenths of hours.

Ref: Gallagher, et al., J. Electrochem. Soc.,(2012)

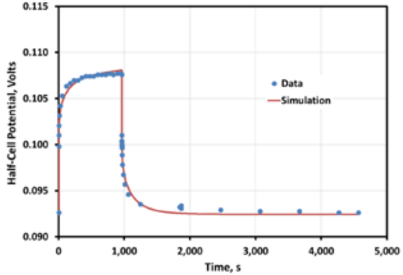
Graphite // Li Half-Cell Slow Charge



GITT Data in LiC_{32} Single Phase



GITT Data in LiC_6-LiC_{12} Phases



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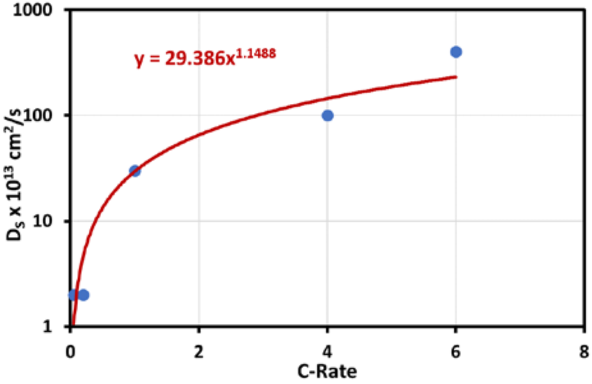
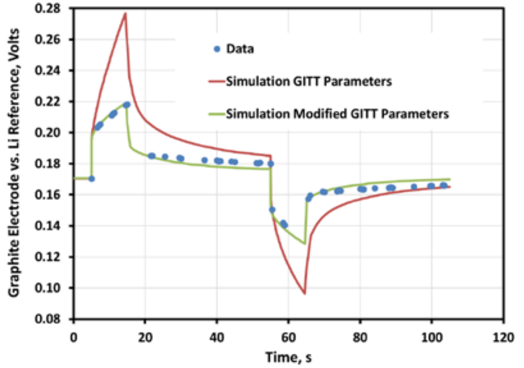
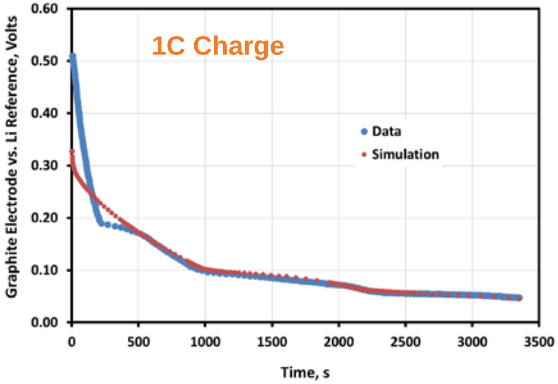
MICRO-REFERENCE ELECTRODE CELL DATA USED TO CONFIRM INCREASING DIFFUSION COEFFICIENT WITH HIGHER CURRENTS

Sample Graphite Electrode Data from NMC // A12 Graphite Reference Electrode Cell

- Reference electrode cell data crucial to establishing diffusion coefficient changes.
- Diffusion coefficient increases an order-of-magnitude from C/20 to 1C.
- Confirmed on multiple graphites.




HPPC-Like 10s 3C Current Pulses



REMAINING CHALLENGES AND BARRIERS

- Optimize and finalize electrolyte formulations through model/test iterations to ensure improved interfacial attributes for electrodes.
- Understand the fundamental phenomena for apparent increase in lithium diffusion coefficient in graphite at higher rates.
- Development of a more detailed SEI model and lithium side reaction for an electrochemical model describing lithium plating.

PROPOSED FUTURE RESEARCH

- Quantify lithium plating model based on in-situ experiments.
- Improve electrolyte properties at high salt concentrations and incorporate promising next generation electrolytes into model.
- Refine active material transport and reaction parameters as a function of temperature.
- Extend cell testing from coin cell to pouch cell architecture; perform rate testing for all viable electrolyte candidates, and document aging trends.
- Study cycling performance under high charge rates for proposed formulations in full cells
- Support diagnostics and characterization efforts.

Any proposed future work is subject to change based on funding levels.

SUMMARY

- Macroscale porous electrode electrochemical model used to examine strategies for enabling extreme fast charging at high loadings without lithium plating.
  - Elevated Temperature, low tortuosity electrodes, and next generation electrolytes are all shown to significantly enhance fast charging.
  - Porosity and N/P ratio provide less value.
- Initial screening with electrolyte models have identified several promising next generation electrolytes.
  - Well established Advanced Electrolyte Model leveraged for present study.
  - Electrolyte screening model based on associating physical properties to functional groups was developed.
- An electrochemical model describing the phase-transition phenomena and lithium intercalation in graphite was utilized to affirm earlier observations of apparent increasing lithium diffusion coefficient with C-rate.

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Five National Laboratories have teamed with other institutions to form this integrated effort focused on enabling fast charge capability.
- This effort is part of a broad range of unified studies (BAT338, BAT339, BAT340, BAT371, BAT383, BAT384, BAT386).

RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

- There are no previous year reviewer comments.

CONTRIBUTORS AND ACKNOWLEDGEMENTS

Andy Jansen
Abhi Raj
Alison Dunlop
Andrew Colclasure
Antony Vamvakeros
Aron Saxon
Bryan McCloskey
Bryant Polzin
Chuntian Cao
Daniel Abraham
Daniel Steingart
Dave Kim
David Robertson
David Wragg
Dennis Dees
Donal Finegan
Eongyu Yi
Eric Dufek
Francois Usseglio-Viretta
Guoying Chen
Hakim Iddir
Hang-Georg Steinruck
Hansen Wang
Ilya Shkrob
Ira Bloom
Jiayu Wan
Johanna Nelson Weker
John Okasinski
Juan Garcia
Kandler Smith
Kaushik Kalaga
Kevin Gering
Marca Doeff
Marco DiMichiel
Marco Rodrigues
Matt Keyser
Michael Evans
Michael Toney
Nancy Dietz Rago
Nitash Balsara
Paul Shearing
Pierre Yao
Ravi Prasher
Robert Kostecki
Ryan Jackman
Sang Cheol Kim
Sangwook Kim
Sean Wood
Seoung-Bum Son
Shabbir Ahmed
Shriram Santhanagopalan
Steve Trask
Tanvir Tanim
Victor Maroni
Vince Battaglia
Vivek Thampy
Wei Tong
Weijie Mai
Wenxiao Huang
William Huang
Yanying Zhu
Yi Cui
Zhenzhen Yang

Argonne NATIONAL LABORATORY

BERKELEY LAB
Lawrence Berkeley National Laboratory

INL
Idaho National Laboratory

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

SLAC
NATIONAL ACCELERATOR LABORATORY

Support for this work from the Vehicle Technologies Office, DOE-EERE – Samuel Gillard, Steven Boyd, David Howell

ESRF
The European Synchrotron

UCL

XCEL
eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

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