Vehicle Technologies Office

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BAT477: Overview of the Liquid Electrolytes Program

Wednesday, June 23, 2021

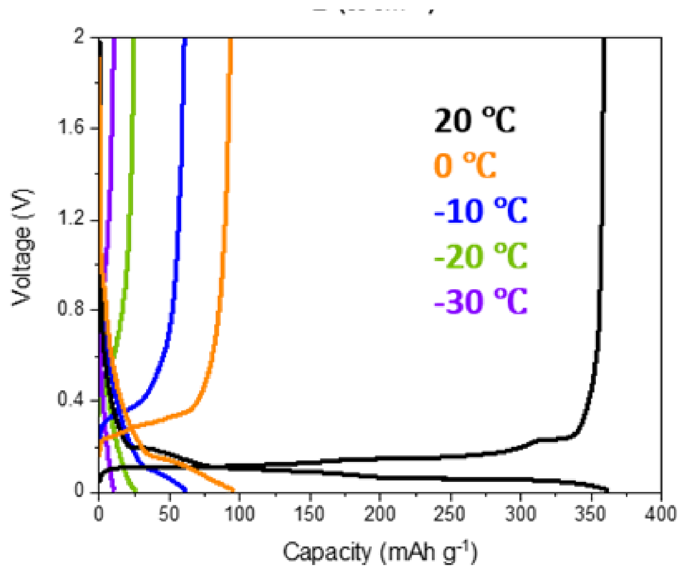
Mallory Clites, PhD. (DOE)

Overview

- Current Challenges for Li-ion Battery Liquid Electrolytes
- FY 2019 Lab Call for Advanced Li-ion Liquid Electrolytes
- Lab Call Projects Funded
- Timeline of Work
- Project Highlights
- Takeaways
- Posters at AMR
- Questions

Challenges with Liquid Electrolytes

- **Energy density** – liquid electrolytes often limit the voltage range, limiting energy density
- **Safety** – flammability of liquid electrolytes can affect safety concerns
- **Rate capability** – Fast charging performance can be limited by liquid electrolytes
- **Low temperature performance** – freezing points of solvents as well as viscosities, resistivities, and other parameters at low temperature affect capacities
- **High temperature performance** – volatility of solvents affect high temperature performance



Voltage profiles of Li/graphite cell using 1M LiPF6 in EC/EMC (3/7)

Xiao-Qing Yang et al. 2021. AMR Presentation - BAT519.

FY 2019 Lab Call for Advanced Li-ion Liquid Electrolytes

Low temperature performance

- Li-ion batteries achieve only a fraction of room temperature capacity and energy density on discharge at lower temperatures
- Traditional liquid electrolytes contain ethylene carbonate, which is a solid at 20 ^{o}C
- High resistivity of the solid electrolyte interface and charge transfer kinetics can limit discharge rates at low temperatures

Objectives

Develop next generation electrolyte formulations that enable the Li-ion batteries to deliver >70% of room temperature energy at -20 °C

While still meeting:

- United States Advanced Battery Consortium (USABC) Operating Environment Conditions (-30 to +52 °C)
- Fast charge capability
- Life cycle performance
- Calendar life performance

Timeline of Work

- Lab Call was announced in April 2019
- Three lab call projects were awarded in August 2019
- Projects began in October of 2019
- Projects are scheduled to be completed in September 2022

Lab Call Projects Awarded

Synthesis, Screening, and Characterization of Novel Low Temperature Electrolyte for Lithium-Ion Batteries

BAT519

Lead: Xiao-Qing Yang
Brookhaven National Lab

Enyuan Hu
Brookhaven National Lab

Kang Xu and **Oleg Borodin**
Army Research Lab

Chunsheng Wang
University of Maryland at College Park

Brett Lucht
University of Rhode Island

Fluorinated Solvent-Based Electrolytes for Low Temperature Li-Ion Batteries

BAT520

Lead: Zhengcheng (John) Zhang
Argonne National Laboratory

Kristin Persson
Lawrence Berkeley National Laboratory

Krzysztof Pupek
MERF, Argonne National Lab

Sheng S. Zhang
US Army Research Laboratory

Andy Jansen/Bryant Polzin
CAMP facility, Argonne National Laboratory

James Dong
Navitas Systems

Ethylene Carbonate-Lean Electrolytes for Low-Temperature, Safe, Lithium-Ion Batteries

BAT521

Lead: Bryan McCloskey
Lawrence Berkeley National Laboratory

Nitash Balsa,
Robert Kostecki,
Vincent Battaglia,
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Project Highlights:

BAT519 **Synthesis, Screening, and Characterization of Novel Low Temperature Electrolyte for Lithium-Ion Batteries**

Lead: Xiao-Qing Yang
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Brett Lucht
University of Rhode Island

Budget

- Funding received in FY20
  DOE: $1,000,000
- Funding received in FY21
  DOE: $1,000,000

Timeline

- Start: 10/01/2019
- Finish: 09/30/2022
- Percent completed: 60%

Approach

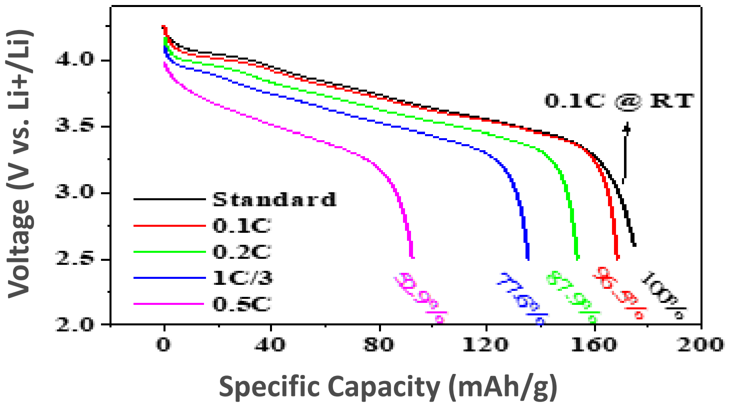
- Combine molecular dynamic (MD) calculations with synthesis, characterization, and testing to screen new solvent, additive, and salt combinations for improved low-temp performance
- Predict the Li^+ transport property, electronic structure and SEI formation mechanism of the electrolyte for proposing candidates that have high Li+ conductivity, good stability, as well as low-impedance SEI.

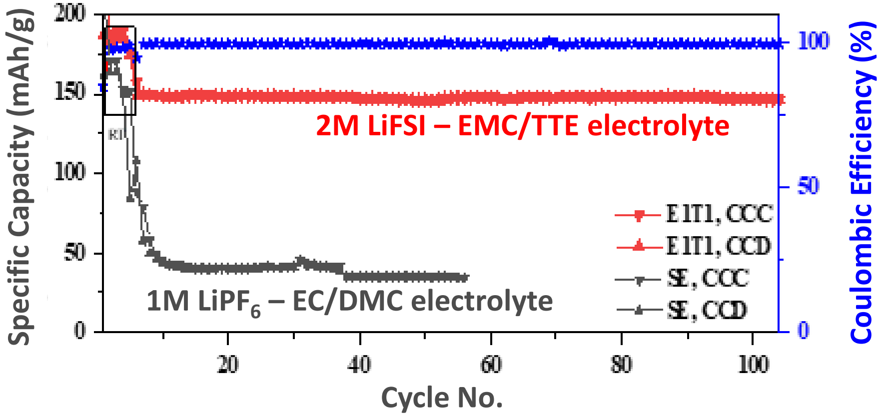
Project Highlights:

BAT519 Synthesis, Screening, and Characterization of Novel Low Temperature Electrolyte for Lithium-Ion Batteries

- Solvent candidates include ethers, esters, nitriles and their fluorine-substituted derivatives
- Salt candidates include lithium tetrafluoroborate ($LiBF_4$), lithium hexafluorophosphate ($LiPF_6$), lithium bis(fluorosulfonyl) imide (LiFSI), lithium bis(trifluoromethanesulfonyl) imide (LiTFSI), lithium bis(oxalato) borate (LiBOB), and lithium difluoro(oxalato)borate (LiDFOB) etc.
- Additive candidates include vinylene carbonate (VC), fluoro ethylene carbonate (FEC), phosphites, phosphates, sulfones, sultones, and sulfates.

Rate Performance and Cycle Stability of NMC811-Graphite Full Cells at 1/3C and -20C





Xiao-Qing Yang et al. 2021. AMR Presentation - BAT519.

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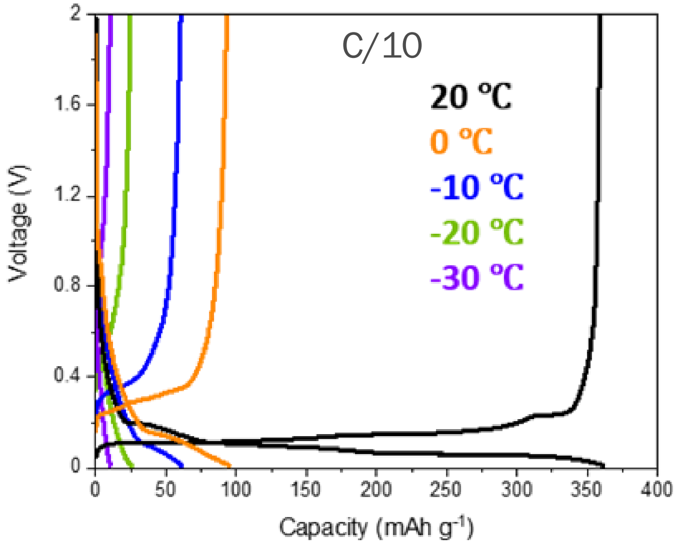
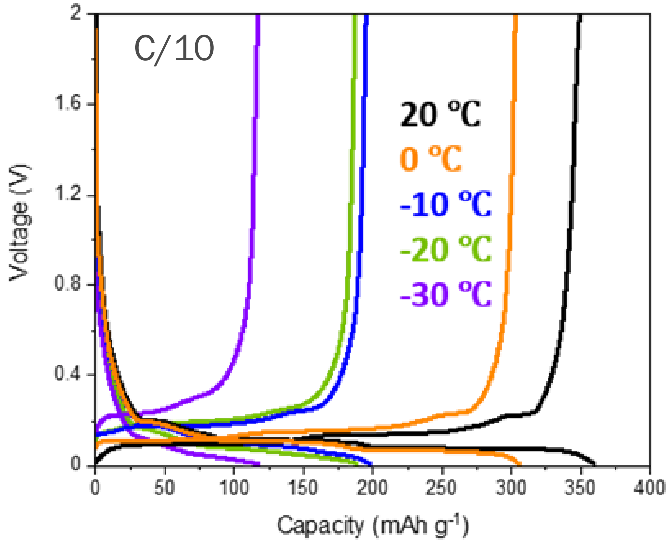
Project Highlights:

BAT519 **Synthesis, Screening, and Characterization of Novel Low Temperature Electrolyte for Lithium-Ion Batteries**



Voltage profiles of Li/graphite cell using 1M LiPF6 in EC/EMC (3/7)



Voltage profiles of Li/graphite cell 1M LiDFOB in isoxazole/FEC (10/1, vol%)

Xiao-Qing Yang et al. 2021. AMR Presentation - BAT519.

- When isoxazole (IZ) was used as main solvent, the ionic conductivity of the electrolyte for Li-ion batteries is more than doubled in a temperature range between -20 ^{o}C to 20 ^{o}C compared to the baseline electrolyte using ethylene carbonate-ethyl methyl carbonate (EC-EMC)
- Lithium difluoro(oxalato)borate (LiDFOB) salt and fluoroethylene carbonate (FEC) additive were used to form stable solid electrolyte interphase (SEI) on the surface of graphite anode
- Cells using new electrolyte with 1M LiDFOB in FEC:IZ (1:10, vol%) solvents demonstrated very high 187.5 mAh g^{-1} reversable capacity at -20 ^{o}C while the baseline electrolyte only delivered 23.1 mAh g^{-1} reversible capacity.

Project Highlights:

BAT520 **Fluorinated Solvent-Based Electrolytes for Low Temperature Li-Ion Batteries**

Lead: Zhengcheng (John) Zhang
Argonne National Laboratory

Kristin Persson
Lawrence Berkeley National Laboratory

Krzysztof Pupek
MERF, Argonne National Lab

Sheng S. Zhang
US Army Research Laboratory

Andy Jansen/Bryant Polzin
CAMP facility, Argonne National Laboratory

James Dong
Navitas Systems

Budget

- Total project funding for FY21:
  ANL - $400,000
  LBL - $300,000

Timeline

- Start: 10/01/2019
- Finish: 09/30/2022
- Percent completed: 50%

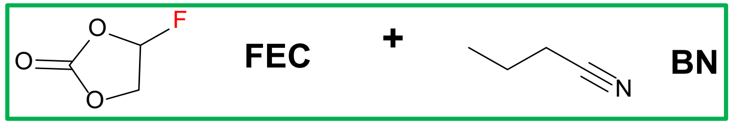
Approach

- Low melting point (m.p.) fluorinated carbonates (linear and cyclic) as well as extremely low m.p. carboxylate esters and alkyl nitriles as mixed solvents to improve the low ionic conductivity at subzero temperatures.
- Development of tailored SEI formation additives to stabilize the graphite anode surface with low resistance.

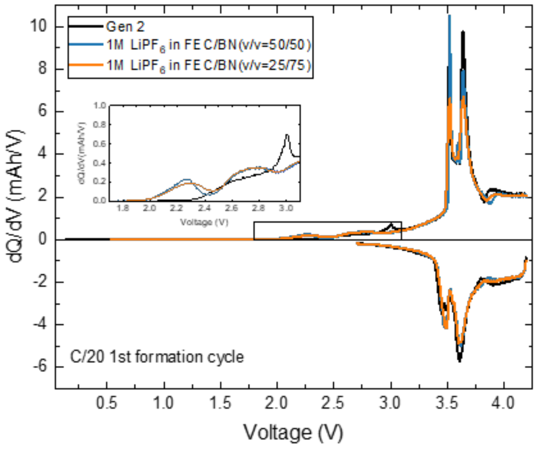
Project Highlights:

BAT520 **Fluorinated Solvent-Based Electrolytes for Low Temperature Li-Ion Batteries**

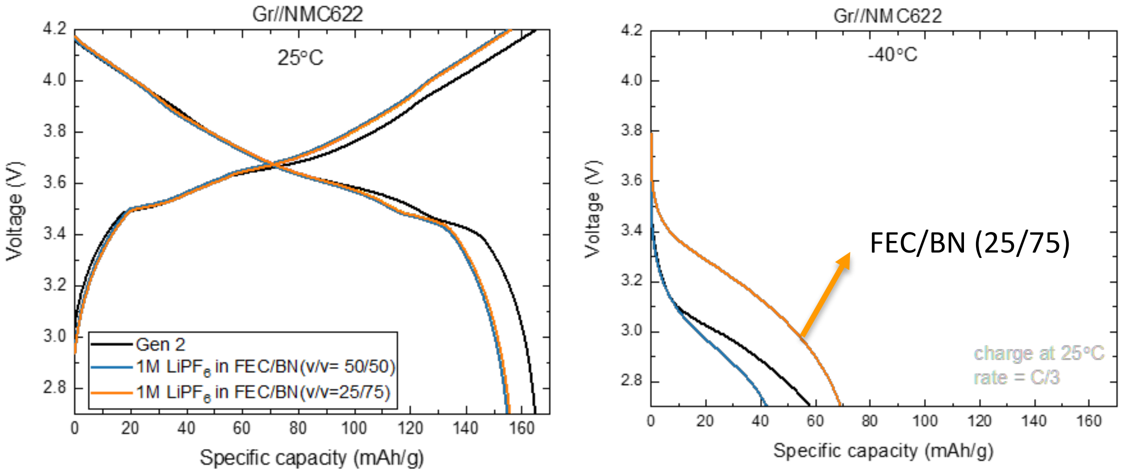
Fluoroethylene Carbonate (FEC)/Butyronitrile (BN) Binary Solvents



Full cell dQ/dV (C/20 1st formation cycle)



Cell performances at 25 and -20°C with different FEC amount



- Large amount of FEC (>10%) is necessary. This is due to the high reactivity of BN at the graphite electrode
- Low-temperature performance was compromised if FEC volume ratio is higher than 25%
- An optimal FEC/BN solvent ratio found of 25/75 (v/v)

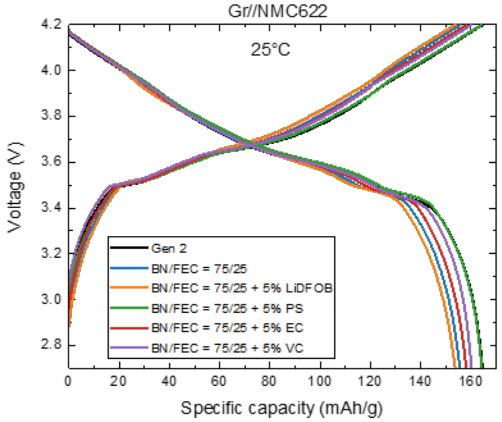
Testing protocol: 2.7-4.2V; C/20 formationX3, C/3 for 1.5 cycles at 25°C; C/3 discharge at -20°C, respectively. 2 cells per electrolyte

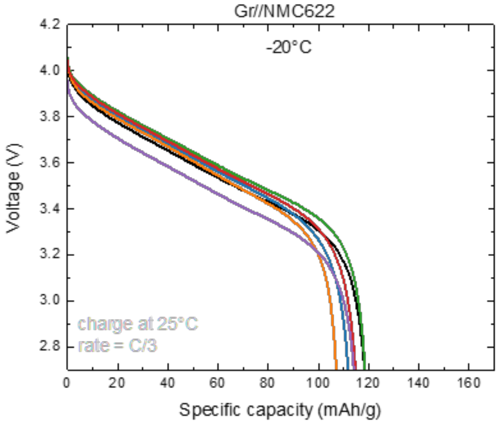
Zhengcheng Zhang et al. 2021. AMR Presentation - BAT520.

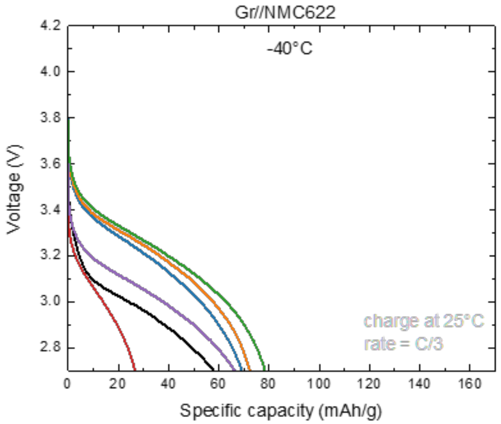
Project Highlights:

BAT520 **Fluorinated Solvent-Based Electrolytes for Low Temperature Li-Ion Batteries**

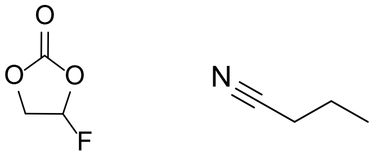
Fluoroethylene Carbonate (FEC)/Butyronitrile (BN) + Tailored Additives





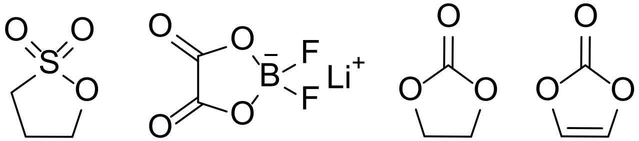


Solvents



FEC BN

Additives



PS LiDFOB EC VC

- Tailored for 1.0 M $LiPF_6$ FEC/BN electrolyte system, 1,3-propane sultone (PS) shows the comparable performance with Gen 2 at room temperature.
- Among all the additives studied (LiDFOB, EC and VC), PS shows the best low temperature cell performance at -20°C and even -40°C.
- 5% PS additive amount is optimal - 1.0 M $LiPF_6$ FEC/BN (25/75) + 5% PS

Zhengcheng Zhang et al. 2021. AMR Presentation - BAT520.

Project Highlights:

BAT521 **Ethylene Carbonate-Lean Electrolytes for Low-Temperature, Safe, Lithium-Ion Batteries**

Lead: Bryan McCloskey
Lawrence Berkeley National Laboratory

Nitash Balsa,
Robert Kostecki,
Vincent Battaglia,
Wei Tong,
and **Gao Liu**
Lawrence Berkeley National Laboratory

Budget

- Total budget (3 years): $2350K
- FY21 funding: $650K

Timeline

- Start: 10/01/2019
- Finish: 09/30/2022
- Percent completed: 50%

Approach for FY21

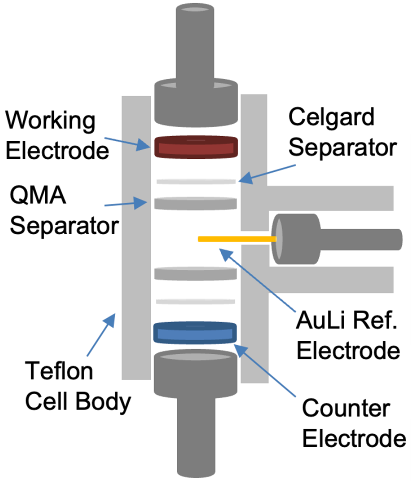
- Understand the origin of resistances within Li-ion batteries at low temperature.
- Understand the influence of electrolyte composition on these resistances and battery performance:
  - Baseline cell: graphite-NMC622 with 1M $LiPF_6$ in 3:7 EC:EMC (ethylene carbonate:ethyl methyl carbonate), LP57
  - Substitute γ-butyrolactone (GBL) for EC (GBL has a larger liquid temperature window than EC)
  - Fluorinated EC (FEC), propane sultone (PS), and vinyl carbonate (VC) used as additives at various concentrations
  - $LiPF_6$ concentration
- Establish molecular dynamics simulations to understand temperature trends in electrolyte transport
- Establish experimental transport characterization techniques for liquids at low temperature.

Project Highlights

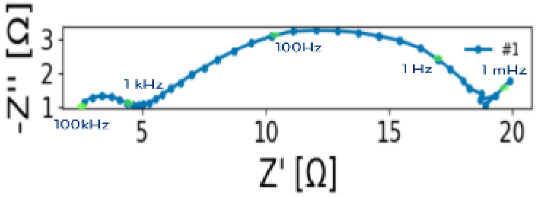
BAT521 **Ethylene Carbonate-Lean Electrolytes for Low-Temperature, Safe, Lithium-Ion Batteries**

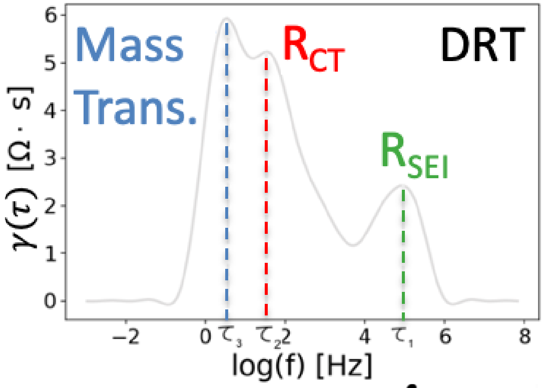
Techniques utilized:

3-electrode cells to isolate impedances



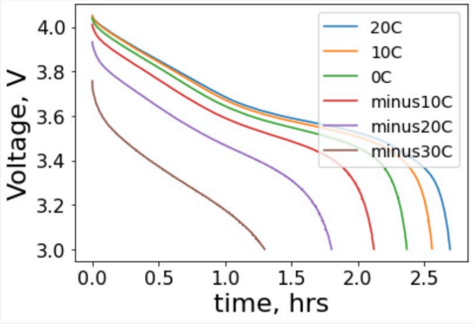
Impedance analysis, Distribution of relaxations (DRT)



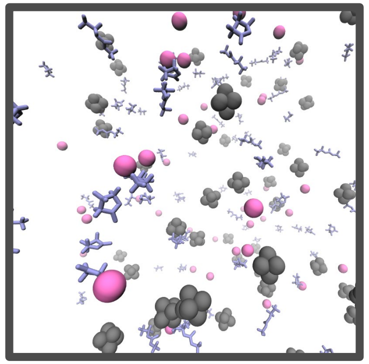


$$Z(\omega) = R_o + Z_{pol}(\omega) = R_o + R_{pol}\int \frac{\gamma(\tau)}{1 + j\omega\tau} d\tau$$

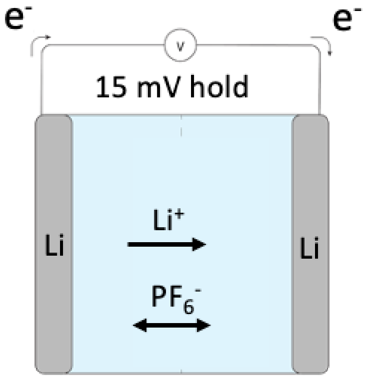
Electrochemical Characterization

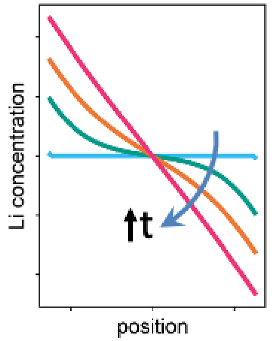


Molecular dynamics simulations



Transport analysis





- Electrodes used: 2.9 mAh/cm2 graphite, 2.5 mAh/cm2 NMC622 (from CAMP)
- Understand low temperature performance as a function of electrolyte composition
- Electrolyte parameters examined: LiPF6 concentration, additive concentration/ composition, substitute GBL for EC (GBL is chemically similar to EC, but has a much larger liquid temperature window)

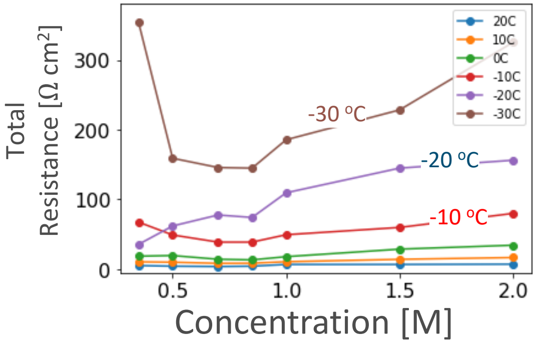
Bryan McCloskey et al. 2021. AMR Presentation - BAT521.

BAT521 Ethylene Carbonate-Lean Electrolytes for Low-Temperature, Safe, Lithium-Ion Batteries

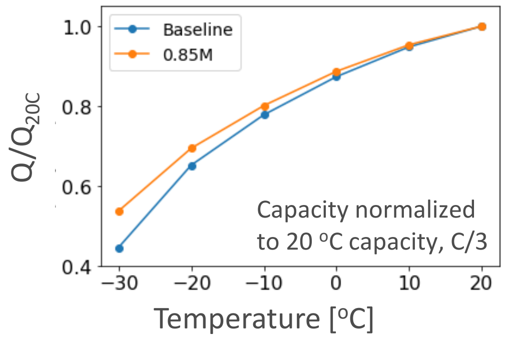
Electrolyte concentration and additive influence on cell resistance

Data collected in full LiC_6-NMC622 coin cells

Concentration influence (in 3:7 EC:EMC)

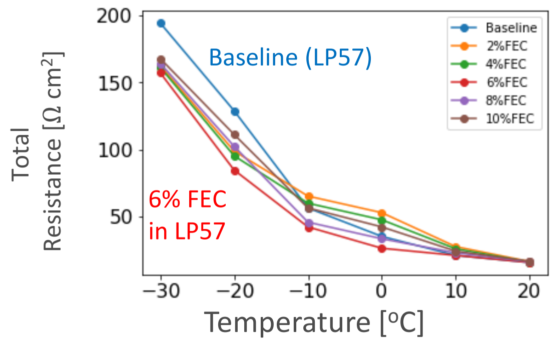


–20 °C	R_{CT} [Ω cm^2]
1 M $LiPF_6$	109
0.8M $LiPF_6$	74

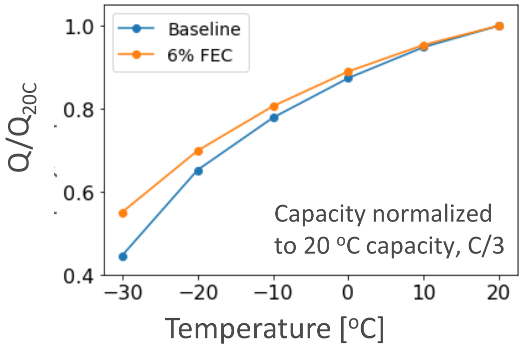


Low temp R_T optimized at ~0.8 M $LiPF_6$, driven by reduction in overall R_{CT}

Fluoro-EC (FEC) influence



–20 °C	R_{CT} [Ω cm^2]
0% FEC	109
6% FEC	82



R_{SEI} and R_S are only very slightly affected by concentration and FEC

FEC has no influence on R_T above 0 °C, reduces R_T below 0 °C, with 6 wt% showing optimal performance

Bryan McCloskey et al. 2021. AMR Presentation - BAT521.

Takeaways

- All three lab projects are focusing on improving low temperature performance of liquid electrolytes while maintaining avg. temperature, rate capability, and cycle life performance
- Each program is taking a different approach to improving performance, including different salt, solvent, and additive combinations, EC-lean chemistries, as well as fluorinated chemistries
- Each program is interested understanding the “why” behind the performance, and fully characterizing all mixtures
- Each program is using realistic cathode and anode pairs and cell formats
- Each program has demonstrated marked improvement above baseline Gen 2 electrolyte in their respective system

Poster Presentation at This Year's AMR

Synthesis, Screening, and Characterization of Novel Low Temperature Electrolyte for Lithium-Ion Batteries

Lead: Xiao-Qing Yang
Brookhaven National Lab (BNL)

BAT519

Friday June 25, 2021
8:00 am

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BAT521

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Thank You

Questions?