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

Bryan D. McCloskey, Principal Investigator
Lawrence Berkeley National Laboratory
June 21-25, 2021
Project ID: bat521

Overview

Timeline

- Start Date: Oct. 1, 2019
- End Date: Sept. 30, 2022
- Percent complete: 50%

Budget

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

Barriers Addressed

- Energy Density
- Safety
- Low rate capability
- Low temperature performance

Partners/Collaborators

Kristin Persson, Nitash Balsara, Robert Kostecki, Vincent Battaglia, Wei Tong, Gao Liu
LBNL/UC
Cell Analysis, Modeling, and Prototyping (CAMP) Facility, ANL (Electrode preparation)

Relevance

- At low temperatures (<0 °C), Li-ion batteries achieve only a modest fraction of their room temperature (20 °C) capacity and energy density on discharge.
- For conventional Li-ion battery electrolytes, the modest volume fraction of ethylene carbonate, which is a solid at 20 °C and relatively viscous even at slightly elevated temperature, is problematic for ion transport at low temperatures.
- Furthermore, high resistivity of the solid electrolyte interface and charge transfer kinetics have both been observed to limit discharge rates at low temperatures, although it is not clear if these resistance primarily originate from the anode or cathode.

Objectives 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.

Milestones

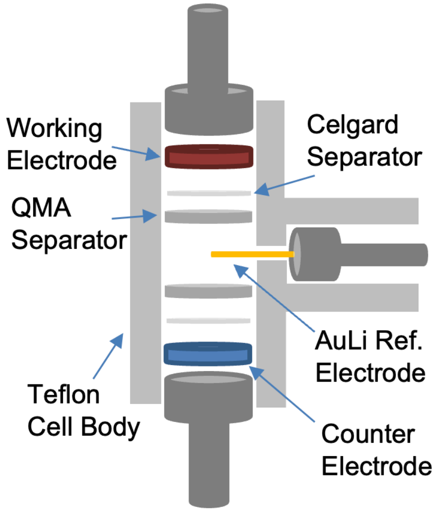
Date	Milestones	Status
December 2020	Complete molecular dynamics simulation studies on influence of temperature on LP57 electrolyte transport/solvation properties.	Completed
March 2021	Complete pouch cell temperature-dependent discharge and impedance analysis of R2 electrodes in LP57 electrolyte with and without butyrolactone substitution.	Completed
June 2021	Complete study on influence of common additives on low temperature discharge capability. Go: continue studies on the best performing additive composition, No-go: all others.	Completed
September 2021	Complete 3-electrode impedance comparison of graphite and NMC electrodes cycled at low and moderate temperature in LP57 with and without additive containing electrolytes.	On track

Approach

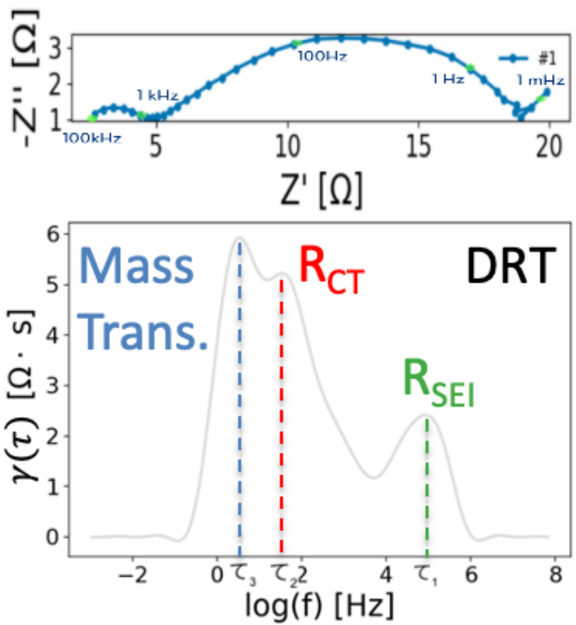
- Electrodes used: 2.9 mAh/cm^2 graphite, 2.5 mAh/cm^2 NMC622 (from CAMP)
- Understand low temperature performance as a function of electrolyte composition
- Electrolyte parameters examined: LiPF$_6$ concentration, additive concentration/composition, substitute GBL for EC (GBL is chemically similar to EC, but has a much larger liquid temperature window).

Techniques utilized:

3-electrode cells to isolate impedances

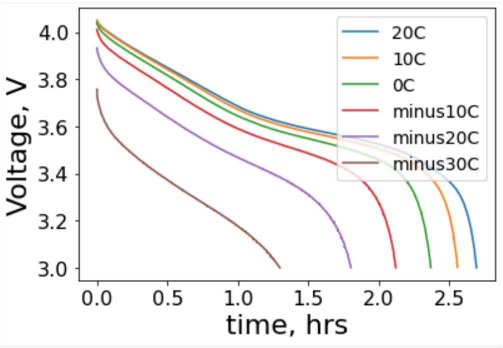


Impedance analysis, Distribution of relaxations (DRT)

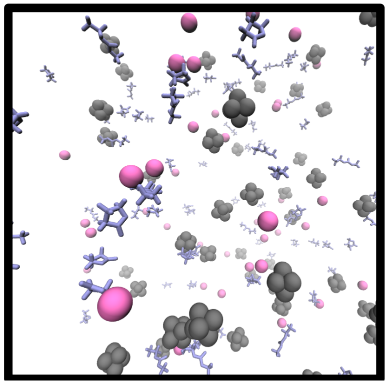


$$Z(\omega) = R_o + Z_{pol}(\omega) = R_o + R_{pol}\int \frac{\gamma(\tau)}{1 + j\omega\tau}d\tau$$

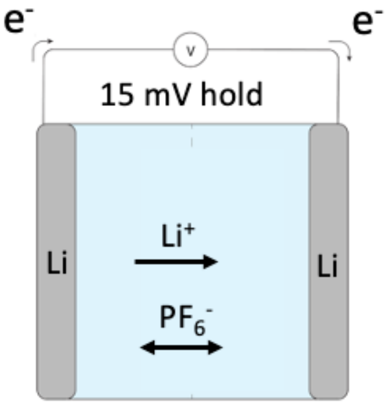
Electrochemical Characterization

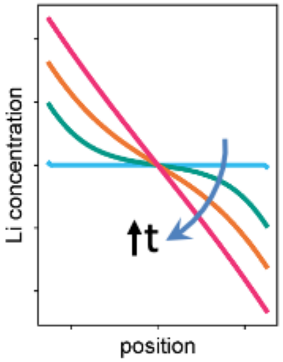


Molecular dynamics simulations



Transport analysis



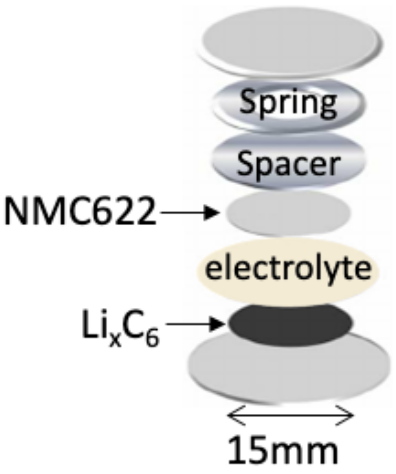


Berkeley UNIVERSITY OF CALIFORNIA

BERKELEY LAB

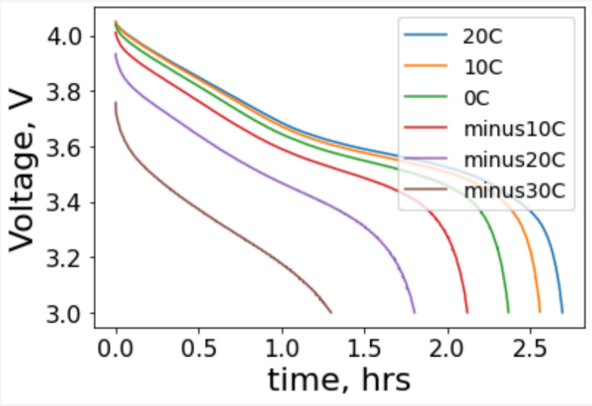
Accomplishment: Baseline cell performance and impedance analysis

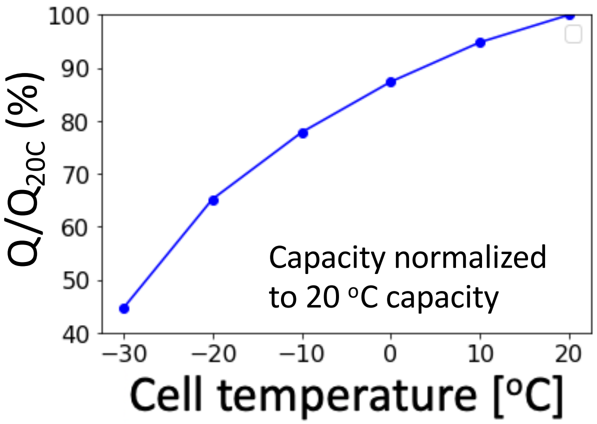
Coin cells



40 µL 1M $LiPF_6$ in
3:7 wt:wt EC:EMC (LP57)
Celgard separator (18 mm dia)
Cell capacity: 4.3 mAh total
1.8 cm^2 electrode area
Formation: 3 x C/10,
3 x C/3 cycles at 20 °C

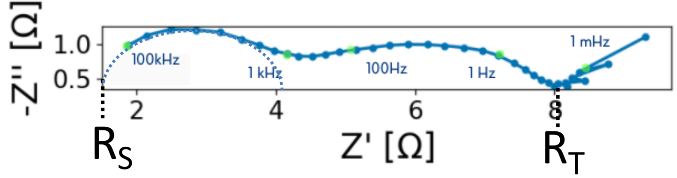
1.4 mA discharge rate (C/3)

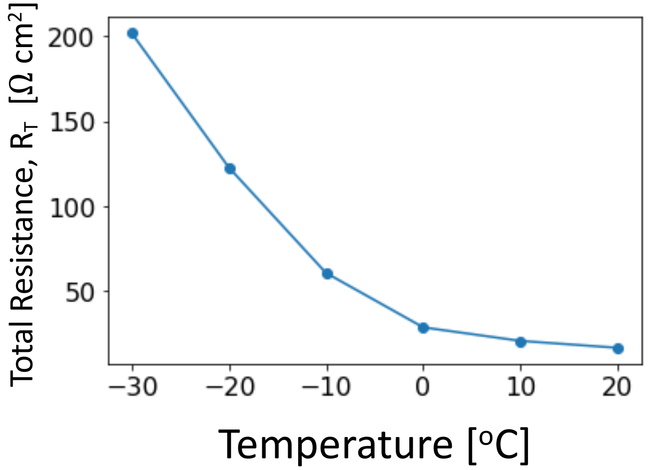




Discharge capacity and average voltage decrease substantially at low temperatures due to high resistances

Cell impedance at 20 °C

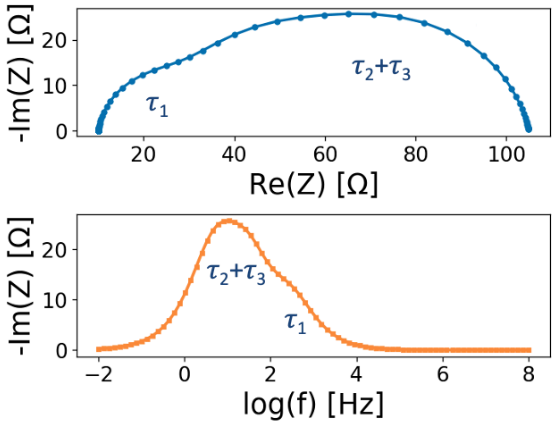




- Cell resistance reported at average cell voltage at each individual temperature
- Impedance collected galvanostatically (during application of discharge current)
- Data satisfies Kramers-Kroenig relations for linearity

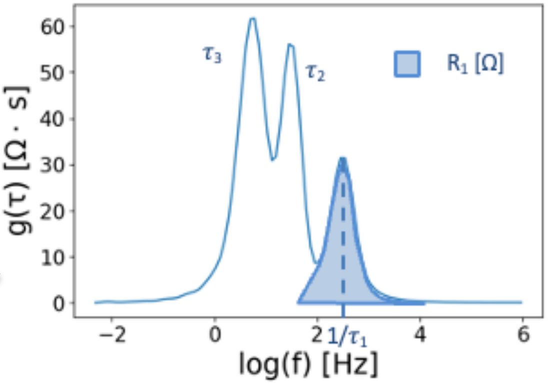
Approach (II): Impedance analysis using distribution of relaxation times (DRT) to resolve processes

- Separating processes by time constants offers better resolution than traditional equivalent circuit fitting
- Impedance associated with mass transport and charge transfer resistance have similar time constants at low temperatures.

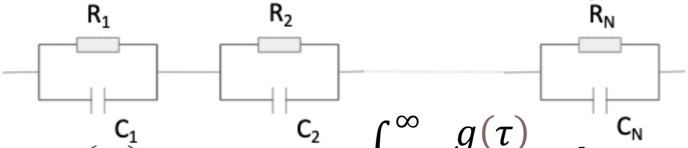


Simulated 3 RC circuit where time constants overlap, make deconvolution difficult

Time transform



Equivalent circuit: Infinite RC elements each with unique time constant, τ_N



$$Z(\omega) = R_s + R_{pol}\int_0^{\infty}\frac{g(\tau)}{1+i\omega\tau}\,d\tau$$

- DRT fits impedance data to an infinite number of RC circuits, each with its own unique time constant, τ.
- Time transform allows the extraction of the distribution of time constants, $g(\tau)$.
- Peaks correspond to dominant system processes

  Integration of peak area gives process resistance

$Z(\omega)$= total system impedance; R_S= cell series resistance; R_{pol}= total polarization resistance;

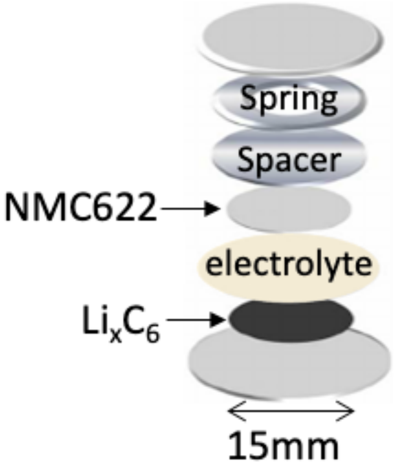
τ = time constant (considered continuous); $g(\tau)$= distribution of time constants

Orazem and Tribollet, *Electrochemical Impedance Spectroscopy*, 2008

Schichlein, et al, *J. of App. Electrochem.* 32 (2002)

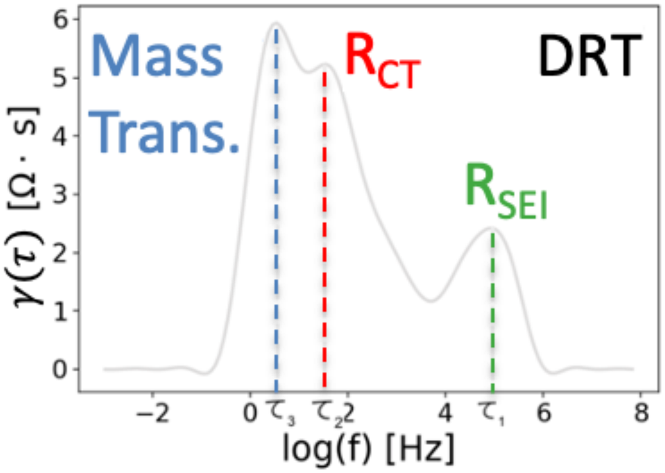
Accomplishment: Galvanostatic impedance to understand origin of resistance rise

Coin cells



40 µL 1M $LiPF_6$ in
3:7 wt:wt EC:EMC (LP57)
Celgard separator (18 mm dia)
Cell capacity: 4.3 mAh total
1.8 cm^2 electrode area

Galvanostatic impedance at
0 °C analyzed using DRT



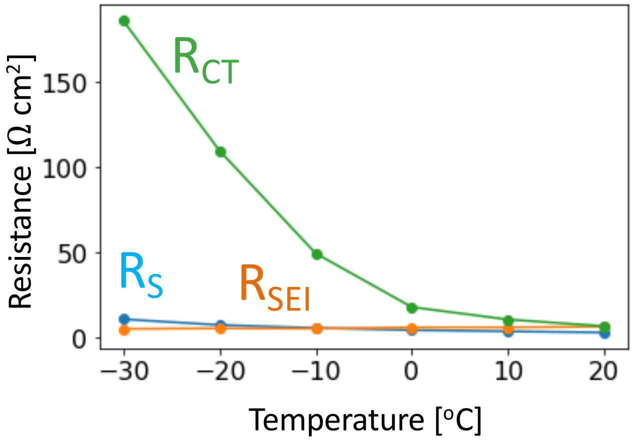
R_{CT} = total cell charge transfer resistance (anode + cathode)

R_{SEI}= total interfacial resistance (SEI + CEI)

Mass trans.= mass transport/ diffusion processes

Peak assignments from prior reports:
J. Power Sources (2021) 496, 229867
J. Power Sources (2015) 282, 335
Electrochimica Acta (2019) 322, 134755

Peak integration

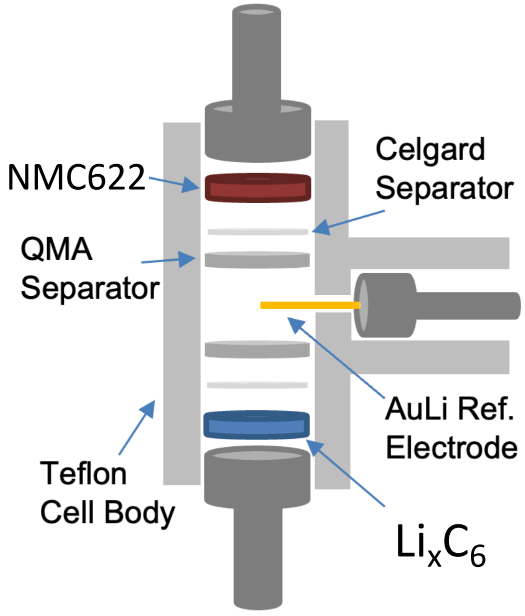


R_S= Electrolyte (series) resistance, from Nyquist plot

The peak ascribed to charge transfer resistance dominates over SEI/CEI and electrolyte transport at low temperatures

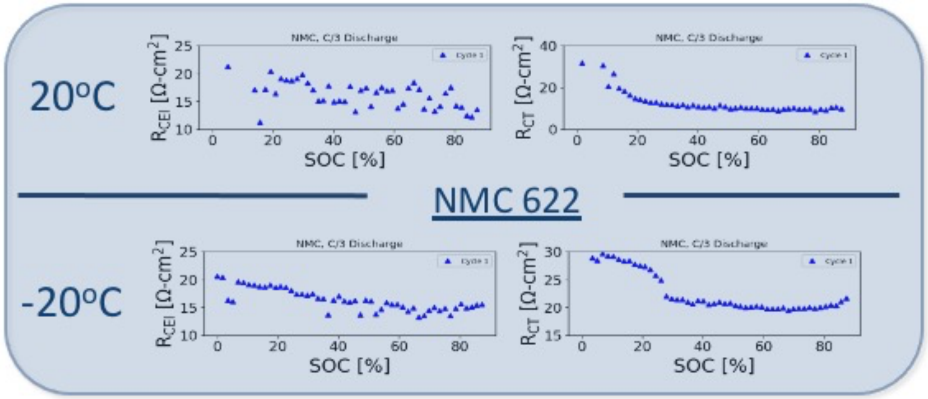
Accomplishment: 3 electrode cell to understand impedance origins at anode and cathode

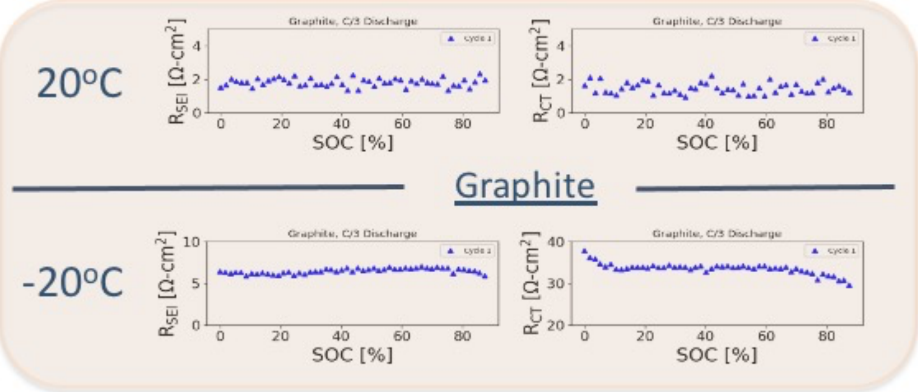
3 electrode cell configuration
Baseline electrolyte (LP57)



Allows deconvolution of resistances at NMC and graphite

Galvanostatic impedance/DRT collected during C/3 discharge at NMC and Li_xC_6 at 20 and -20 °C





Measured at SOC =40%

	$\Omega\ cm^2$	$20\ ^oC$	$-20\ ^oC$
NMC622	**R_{CEI}**	15	17
	R_{CT}	9	22
Graphite	**R_{SEI}**	2	7
	R_{CT}	1.8	35

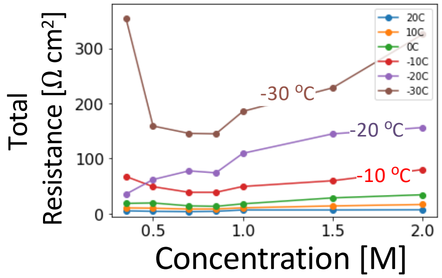
R_{CEI}= cathode-electrolyte interface resistance

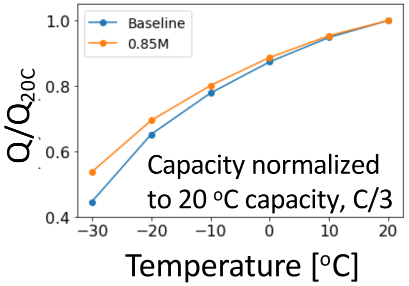
At 20 °C, NMC impedances dominate overall resistance. Comparing −20 to 20 °C, NMC impedance modestly increases, but Li_xC_6 charge transfer resistance dramatically increases.

Accomplishment: Electrolyte concentration and additive influence on cell resistance

- Data collected in full LiC_6-NMC622 coin cells (see first accomplishment slide), galvanostatic impedance

Concentration influence (in 3:7 EC:EMC)



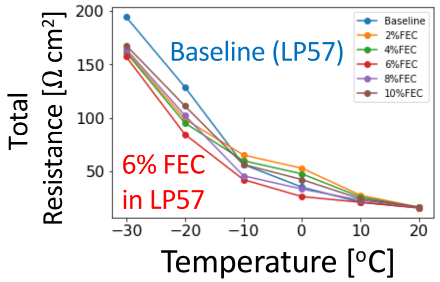


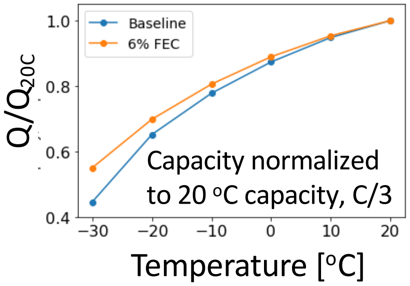
−20 °C	R_{CT} [Ω cm^2]
1 M $LiPF_6$	109
0.8M $LiPF_6$	74

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

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

Fluoro–EC (FEC) influence

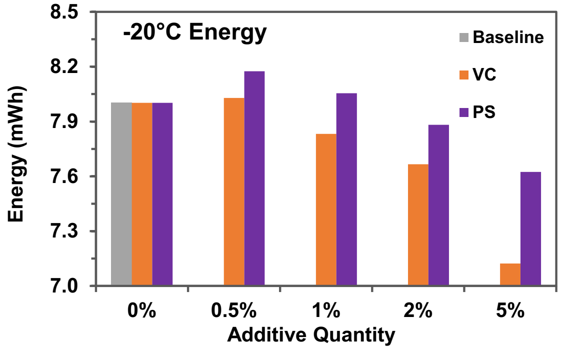


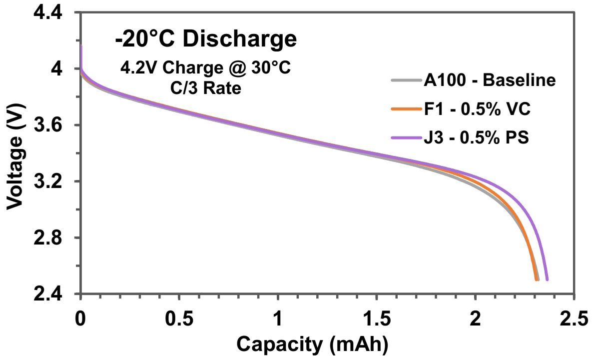


−20 °C	R_{CT} [Ω cm^2]
0% FEC	109
6% FEC	82

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

Vinyl carbonate (VC), propane sultone (PS) influence





VC and PS have minimal effect on R_T and capacity

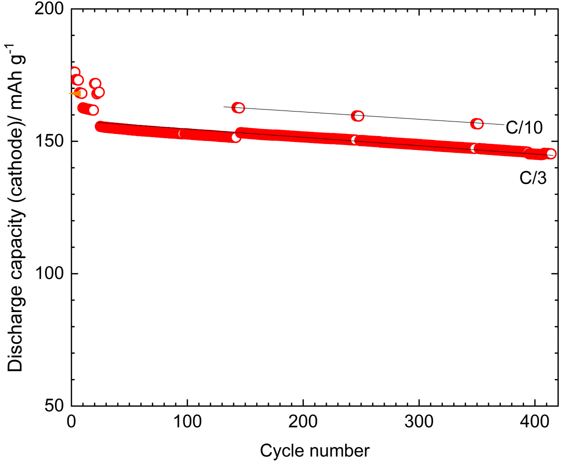
Future work: 3 electrode cell to identify anode/cathode resistances

Accomplishment: Low melting point liquid as co-solvent: γ-butyrolactone (GBL)

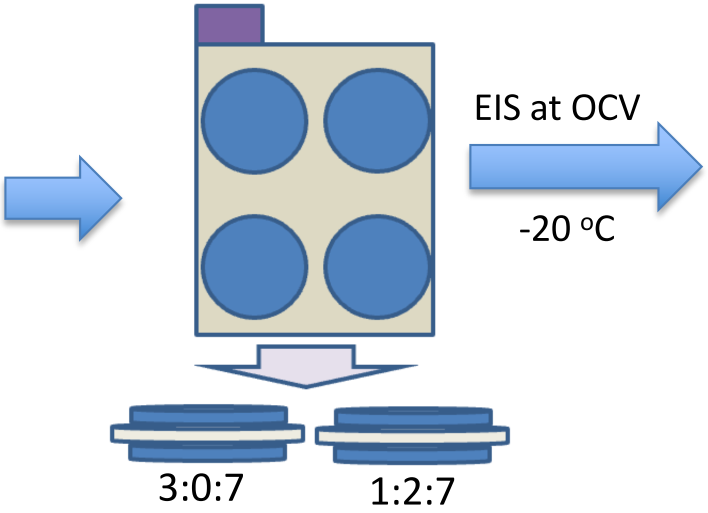
GBL melts at -43 °C and boils at 204 °C; EC melts at 39 °C and boils at 248 °C, EC and GBL are very similar chemically

Does GBL offer any advantage over EC in low temp performance?

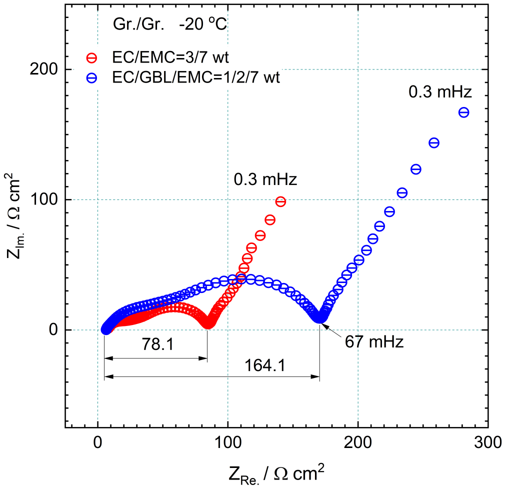
Pouch cell cycled 400 times in LP57 at 20 °C, discharged to 70% SOC on final cycle

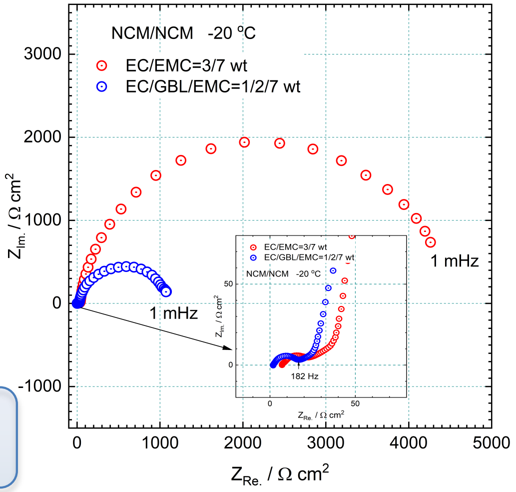


Coin cell electrodes punched out, symmetric Gr/Gr and NMC/NMC cells prepared



EC:GBL:EMC



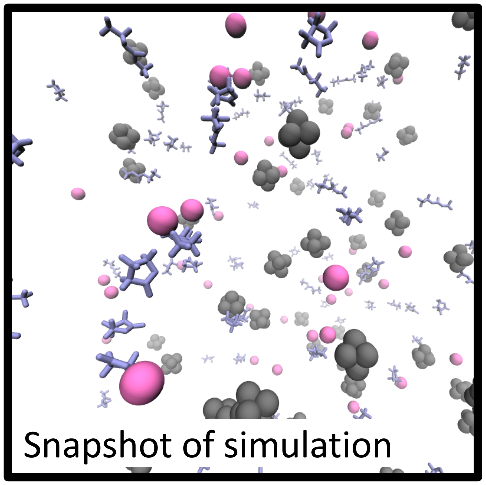


Note: Cells formed with GBL as a co-solvent and no additives form poor SEIs

Modest increase in graphite impedance with GBL as co–solvent, very large decrease in NMC impedance

Accomplishment: Molecular dynamics to understand low temperature transport mechanisms

All results on LP57

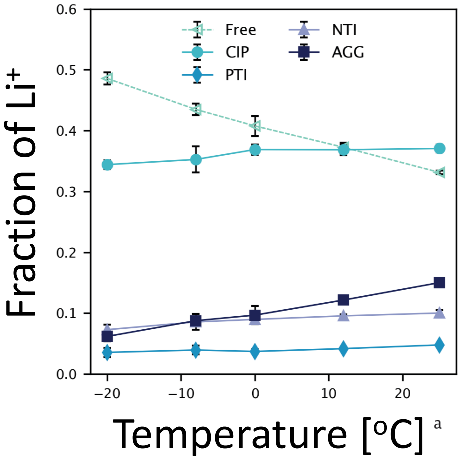


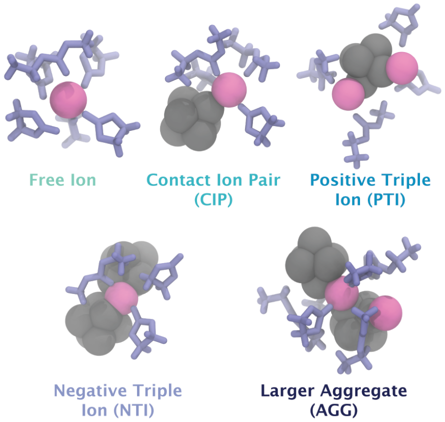
Snapshot of simulation

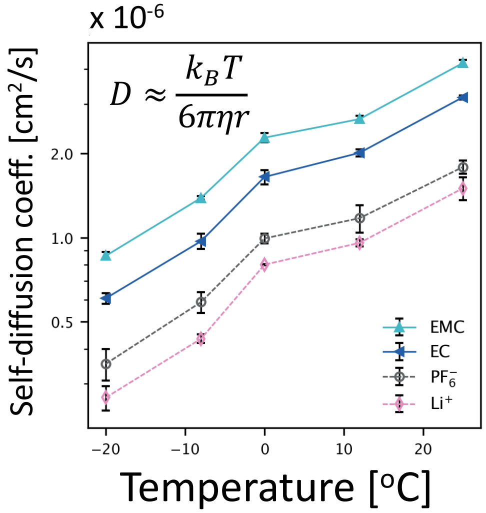
Li$^+$ are pink spheres,

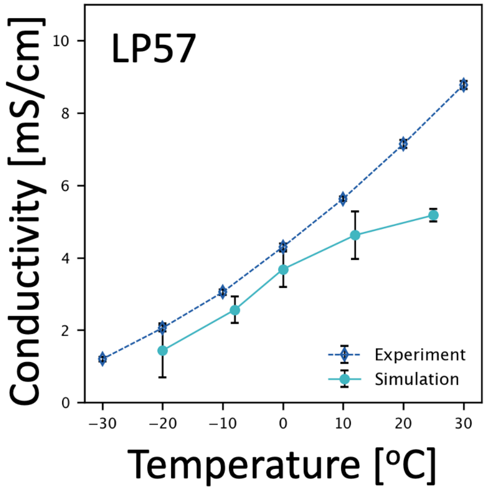
PF_6^- are grey sphere aggregates

Solvents are shown explicitly









Reasonable agreement between experiments and theory

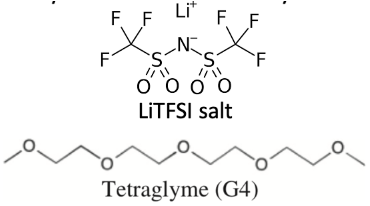
<u>Methodology:</u>

1) Select a system of N particles
2) Initialize positions and velocities of each particle
3) Compute the forces acting on each particle
4) Integrate Newton's equations of motion
5) Advance the simulation in time

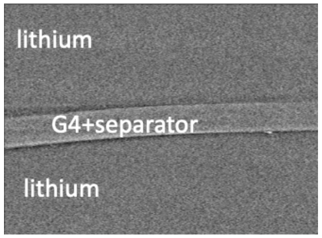
Ion pairing <u>decreases</u> and viscosity increases, with decreasing temperature, results in net conductivity decrease

Accomplishment: Development of experimentation to measure low temperature transport properties of liquid electrolytes

Electrolyte used:

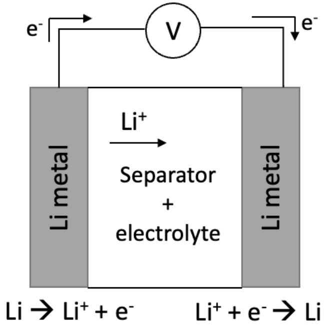


Chosen initially due to known reasonable stability toward Li metal:

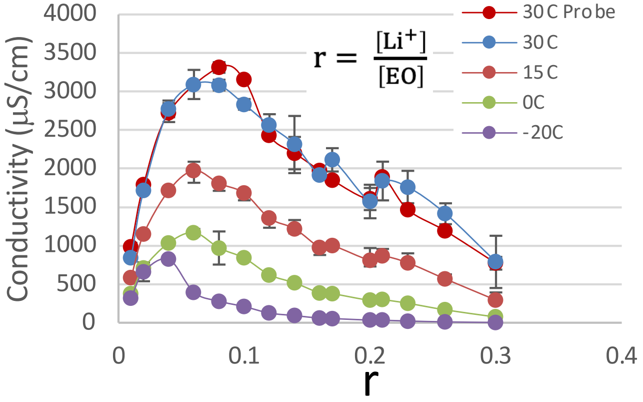


X-ray tomogram after cycling

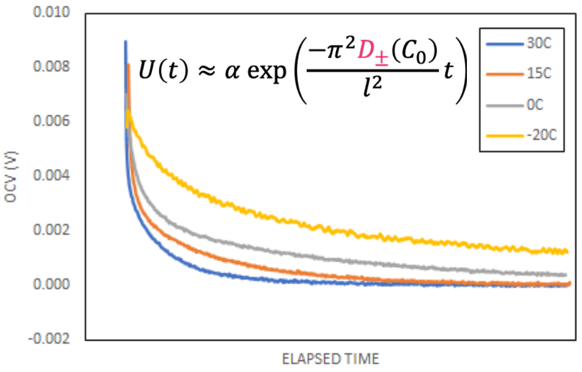
Polarization measurement



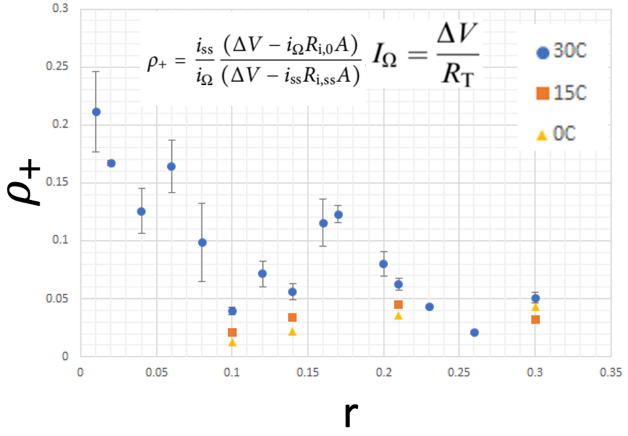
Conductivity in Li-Li symmetric cells



Voltage relaxation after polarization, can relate to salt diffusion coefficient



Current fraction (ρ_+) of initial vs steady-state current during polarization



- Conductivity, restricted diffusion, and polarization measurements to measure current fraction
- Future work: Concentration cells to measure thermodynamic factor to relate concentration and chemical potential gradients
- Combine these measurements with Newman-Balsara theory to fully characterize the transport properties of liquid electrolytes (transference number, diffusion coefficient, conductivity, and thermodynamic factor)
- Future work: extend to LP57 and other liquid compositions

Remaining challenges and barriers

- While GBL clearly improves charge transfer resistance at NMC, it has poor stability at the anode. Can we engineer an additive composition that allows improved anode stability while taking advantage of improved cathode performance?
  - Stability of any other co-solvents/additives will need to be carefully considered
  - We need to continue to develop an understanding of why GBL reduces cathode resistance and link resistance reduction to cell performance
- Additives other than FEC appear to have limited capacity/resistance reduction improvements, likely because charge transfer resistance dominates cell performance (not SEI resistance)
  - The focus of low temperature performance should be on solvent engineering, with additives to improve stability as needed
- Can we accurately measure transport properties in electrolytes that have poor Li metal stability?

Future work

- Why does the addition of GBL reduce cathode impedance?
  - Hypothesis: Solvation of Li^+ influences charge transfer resistance, so examine co-solvents with varying donor numbers: propylene carbonate, acetonitrile, GBL may provide insight
  - Study additives to improve stability of electrolytes with new co-solvents as needed
- Spectroscopic analysis (Raman, infrared) of anodes and cathodes to link interfacial chemical composition to impedance
  - Parameters to be examined: salt concentration, FEC, GBL inclusion
- Gas evolution analysis to understand stability limitations in new electrolyte compositions containing GBL or other co-solvents
  - Additive/salt engineering to improve stability of GBL-containing electrolytes
- Molecular dynamics to understand solvation dynamics of Li^+ in varying salts
  - Important to understand charge transfer kinetics
- Fully evaluate transport properties of new electrolyte compositions as a function of temperature
- Delivery of 100 mAh pouch cells with optimized electrolyte composition to DOE (final deliverable of project)
  - So far, lower concentration $LiPF_6$ (~0.8M) in 3:7 EC:EMC with a few percent FEC likely provides best performance of electrolyte studies so far, but solvent engineering will likely increase performance further

Any future work is subject to change based on funding levels

Summary

- Charge transfer resistance dominates low temperature performance of Li-ion batteries
  - Both anode and cathode charge transfer resistance are large at low temperatures.
- Overall cell impedance optimized at slightly lower salt concentrations (~0.8 M) than LP57
- FEC is the only additive studied so far that appears to reduce cell impedances at low temperatures
- GBL, while unstable at the graphite anode, reduces charge transfer resistance at the cathode when employed as a co-solvent. Further additive engineering is needed to improve stability.
- Ion pairing decreases with decreasing temperature, but viscosity dramatically increases, reducing overall conductivity

Response to previous year's reviewer's comments

- This is the first year that the project has been reviewed