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

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Argonne National Laboratory

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2021 DOE VTO Annual Merit Review

Project ID: BAT520

OVERVIEW

Timeline

- Start: October 1, 2020
- End: September 30, 2023
- Percent Complete: 33%

Budget

- Total project funding for FY21:
  - ANL - $400,000
  - LBL - $300,000
- Presentation:
  - BAT520

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and U.S. DRIVE goals
  - Performance (capacity, energy and power) at low temperatures
  - Abuse tolerance
  - Cost

Partners

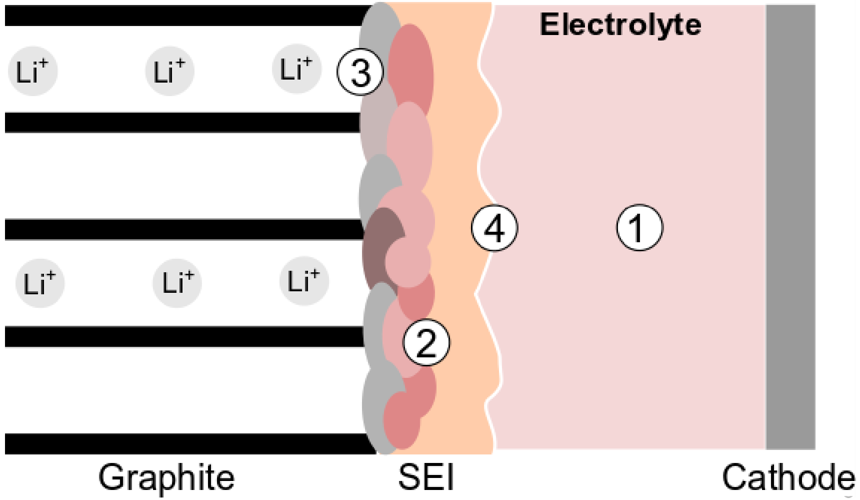
- Lawrence Berkeley National Lab
- Materials Engineering Research Facility - Argonne
- Materials Science Division – Argonne
- Navitas Systems
- Leading Organization: Argonne National Lab

RELEVANCE

The next-generation Li-ion battery for electric vehicles requires not only high-energy high-power density, long cycle life, low cost, and enhanced safety, but also fast charging and superior low temperature (LT) performance, especially in the cryogenic range to -20ºC.

$$\boxed{R_{cell} = R_{bulk} + R_{SEI} + R_{charge\ transfer}}$$

$$\frac{1}{R} = A_o e^{-E_a/RT}$$



Overpotential and lithium plating at subzero temperatures cause low cell performance

1) Low ionic conductivity of the bulk of electrolyte: lithium salt precipitation, low Li^+ diffusivity – high resistance of electrolyte (R_{bulk})

2) High resistance of solid-electrolyte-interface (SEI) (R_{SEI}) formed on graphite anode at low temperature

3) Reduced kinetics of Li^+ intercalation and deintercalation ($R_{charge\ transfer}$)

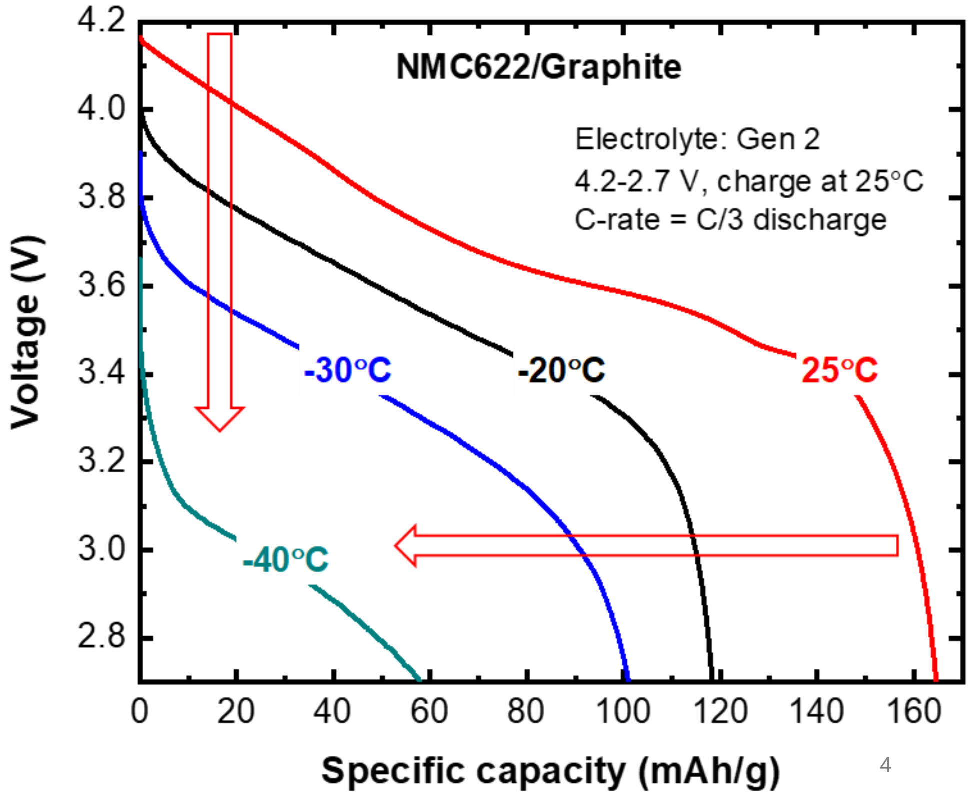
4) Unfavorable Li^+ de-solvation at the graphite/electrolyte interface ($R_{charge\ transfer}$)

5) SEI evolution during low temperature cycling

PROJECT OBJECTIVES

Li-ion battery performance at -40°C ~ 25°C

* Gen 2 EL: 1.2 M $LiPF_6$ EC/EMC (w/w=3/7)

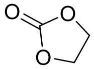
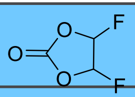
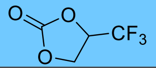
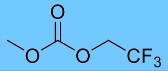
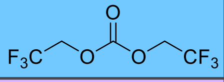
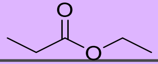
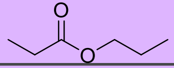
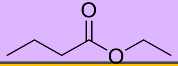


- ✓ With decreasing temperature from room temperature (25°C) to - 40°C, the discharge capacity of lithium-ion battery is significantly reduced up to 65%.
- ✓ Not only discharge capacity, the discharge voltage of the lithium-ion battery also decreases dramatically with decreasing temperature, leading to the loss of overall energy of the battery at subzero temperatures.
- ✓ The objective of this project is to develop new-solvent based next-generation electrolyte materials/formulations that improve the low temperature performance without compromising high-temperature performance and fast charge capability.

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.

Low m.p. Solvents

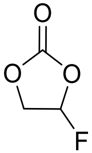
Solvent	Chemical Name	Chemical Structure	M.P. (°C)	B.P. (°C)	Dielectric Constant
EC	Ethylene carbonate		36.4	248	90
DFEC	2,2-Difluoroethylene carbonate		-18.5	-	2.3
TFPC	3,3,3-Trifluoropropylene carbonate		-3	206.6	n.a.
FEMC	2,2,2-Trifluoroethyl methyl carbonate		-66.7	104-106	n.a.
HFDEC	Bis(2,2,2-trifluoroethyl) carbonate		-66.5	118	n.a.
EP	Ethyl propionate		-73.6	98.9	5.8
PP	Propyl propionate		-76	122-124	5.2
EB	Ethyl butyrate		-93	120-121	n.a.
BN	Butyronitrile		-112	115-117	24.8

Fluorinated Carbonates: DFEC, TFPC, FEMC, HFDEC

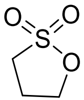
Carboxylate Esters: EP, PP, EB

Alkyl Nitriles: BN

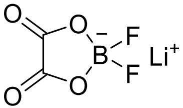
SEI Formation Additives



FEC

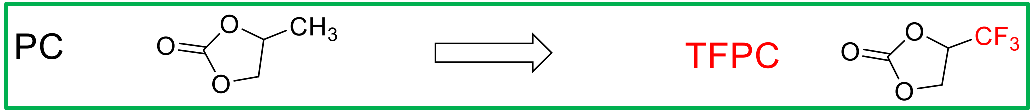


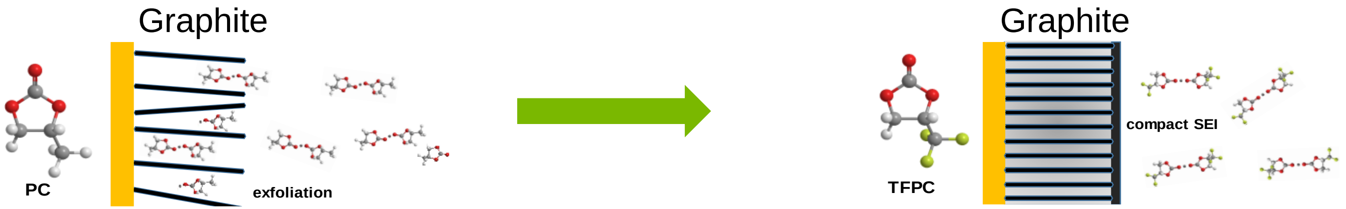
PS

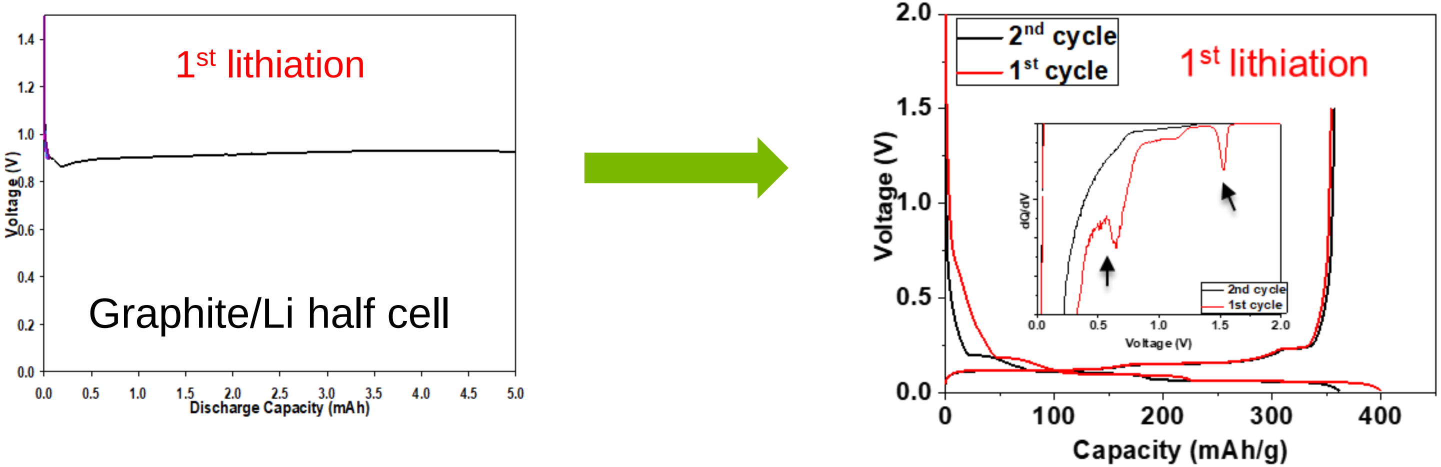


LiDFOB

(1) TFPC (fluorinated PC)-Based Low Temperature Electrolyte (LTE)





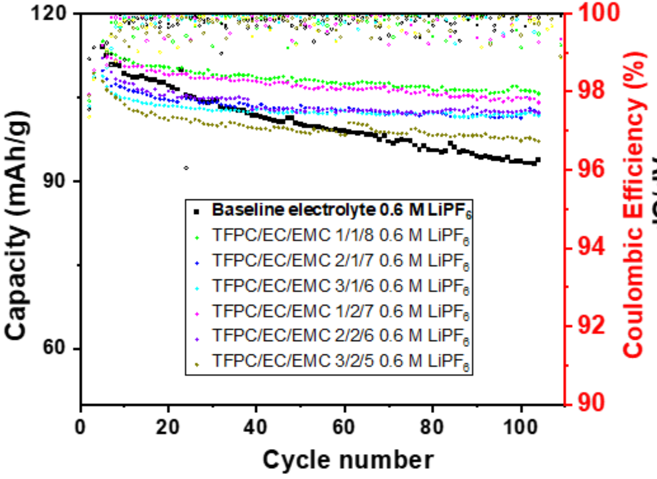


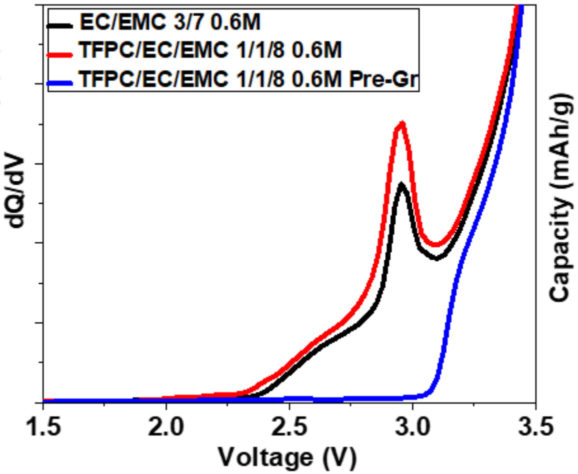
- Although an ideal LT electrolyte solvent, PC-based electrolyte exfoliates graphite anode at 0.9 V *vs* Li^+/Li.
- However, after fluorination, TFPC passivates the graphite surface and enables reversible Li^+ intercalation chemistry.

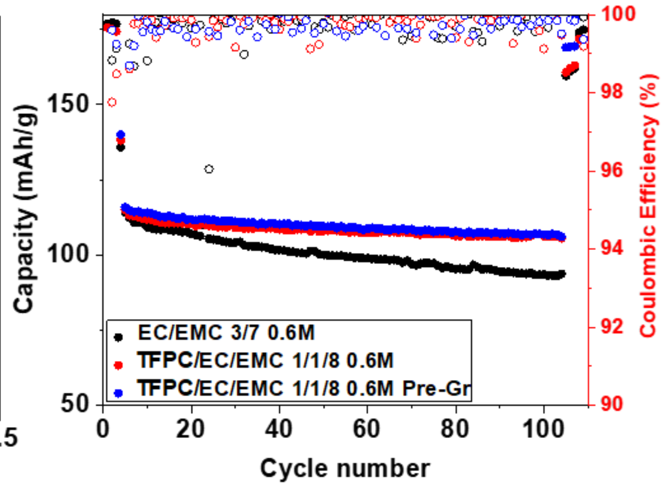
TFPC (fluorinated PC)-Based LTE Cell Performance at -20ºC

NMC622/Graphite Cell
Cutoff voltage: 2.7 – 4.2 V
3 C/20 formation cycles at RT
1 C/20 formation cycle at -20ºC
C/3 cycling at -20ºC

NMC622/preformed graphite cell
Graphite anode was preformed with Gen 2' electrolyte (0.6 M $LiPF_6$ EC/EMC)
Cutoff voltage: 2.7 – 4.2 V
C/3 cycling at -20ºC

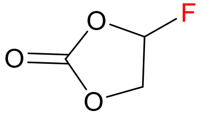




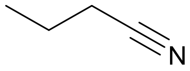


- Up to 30% TFPC, all ternary electrolyte formulations (TFPC/EC/EMC) overperform the Gen 2 baseline electrolyte at -20ºC.
- 10% TFPC shows the best performance: capacity and capacity retention.
- Preformed graphite with Gen 2 electrolyte didn't show advantage in cell performance – electrolyte bulk property dominates.

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



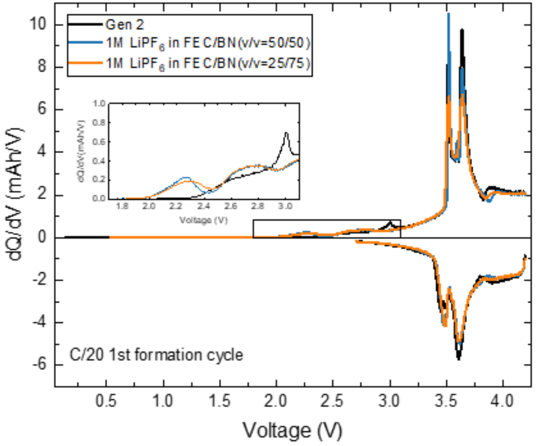
FEC +



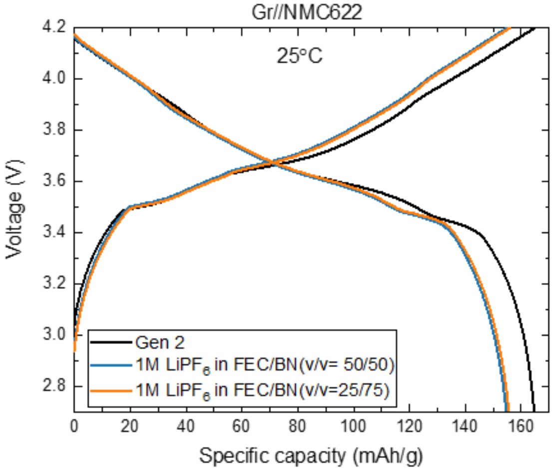
BN

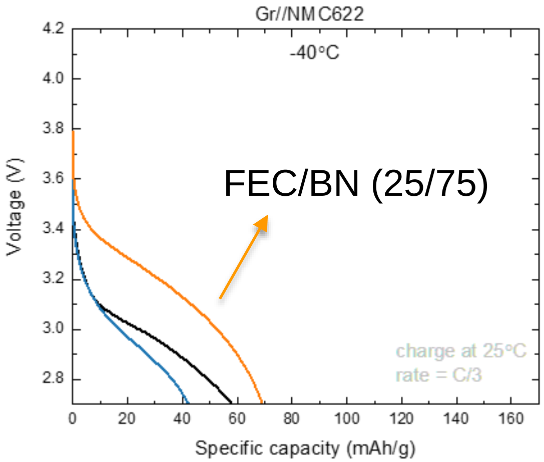
Testing protocol: 2.7-4.2V; C/20 formationX3, C/3 for 1.5 cycles at 25°C; C/3 discharge at -20°C, respectively. 2 cells per electrolyte

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



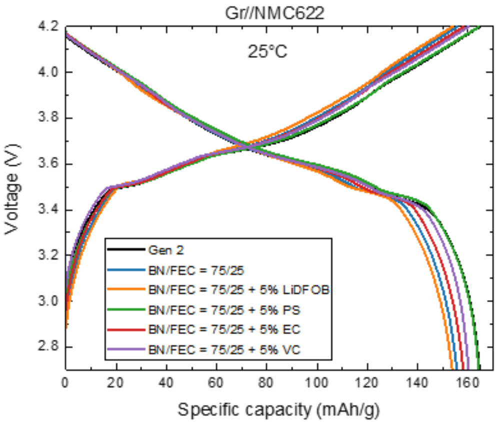
Cell performances at 25 and -20°C with different FEC amount

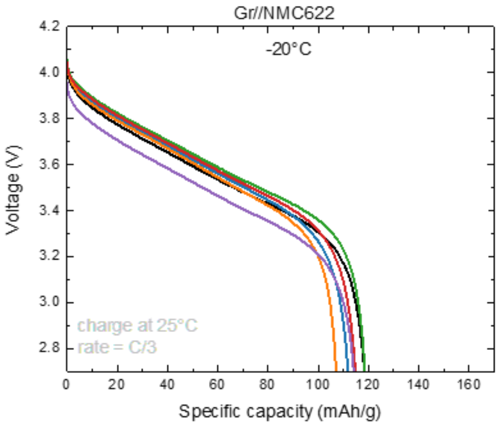


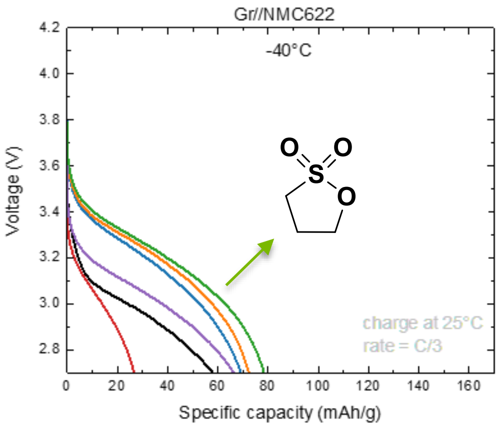


- Large amount of FEC (>10%) is necessary. This is due to the high reactivity of BN at the graphite electrode.
- However, LT performance was compromised if FEC volume ratio is higher than 25%.
- The optimal FEC/BN solvent ratio is 25/75 (v/v).

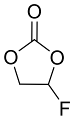
Fluoroethylene Carbonate (FEC)/Butyronitrile (BN) + Tailored Additives



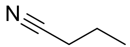




Solvent

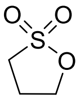


FEC



BN

Additive



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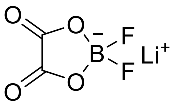
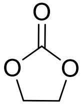
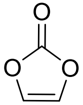


LiDFOB



EC

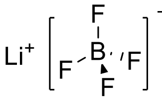


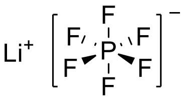
VC

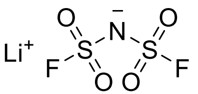
- Tailored for 1.0 M $LiPF_6$ FEC/BN electrolyte system, 1,3-propane sultone (PS) shows the comparable performance with Gen 2 at room temperature.
- Among all the additives studied (LiDFOB, EC and VC), PS shows the best low temperature cell performance at -20ºC and even -40ºC.
- 5% PS additive amount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

Fluoroethylene Carbonate (FEC)/Butyronitrile (BN) + Li Salts

Li Salt:

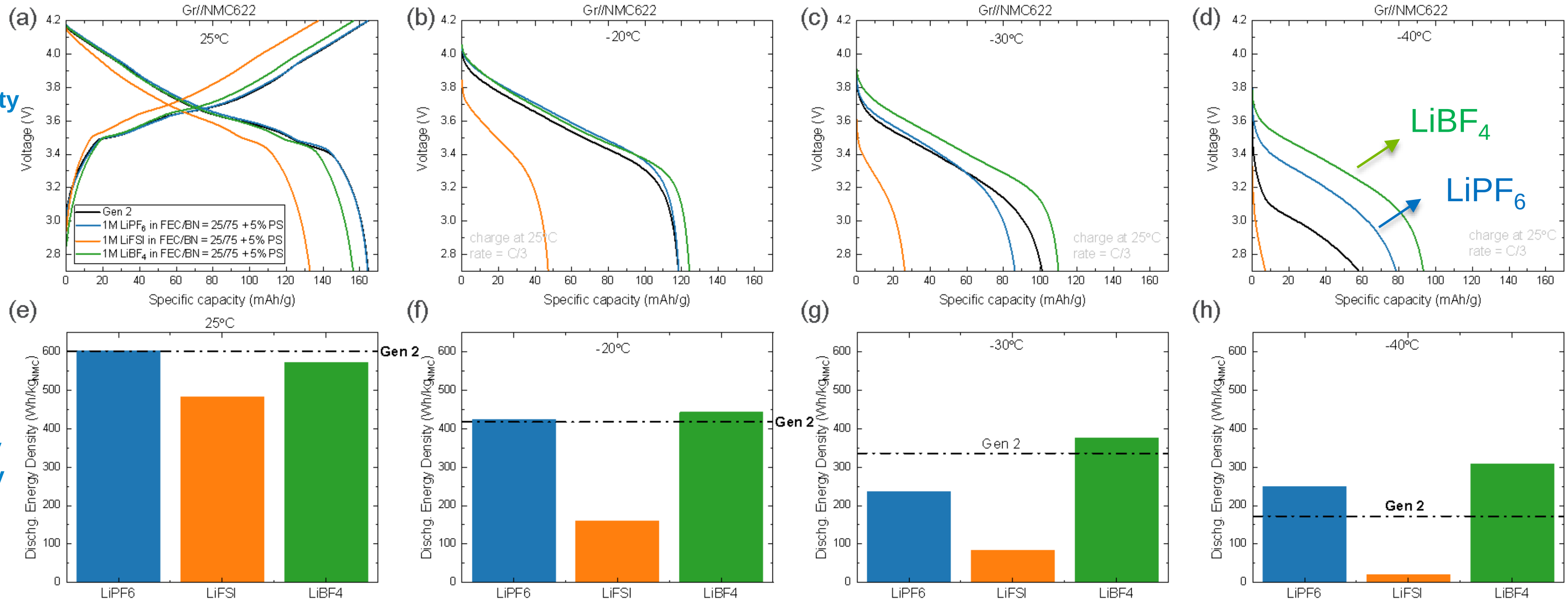

$LiBF_4$


$LiPF_6$


LiFSI

Capacity

Energy density



- LT cell performance (capacity and energy) is highly dependent on the selection of the anion of the lithium salt.
- $LiBF_4$ showed the best better LT performance than $LiPF_6$ and LiFSI salt.
- 1.0 M $LiBF_4$ in FEC/BN (25/75) + 5% PS was selected as the optimal electrolyte for further study.

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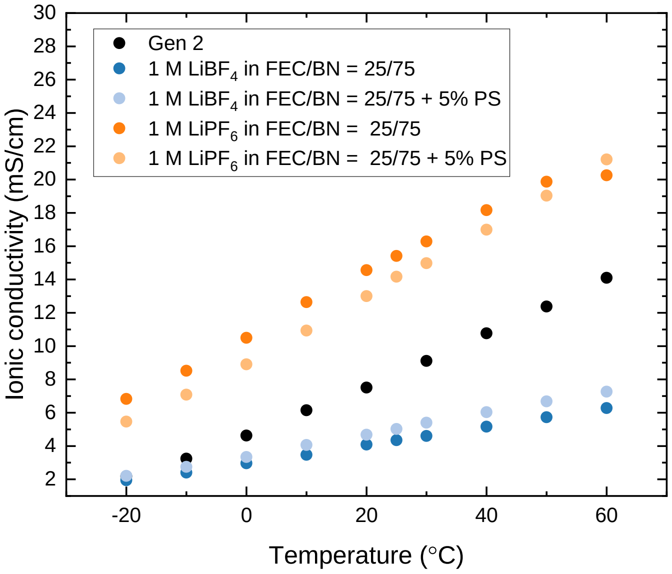
Fluoroethylene Carbonate (FEC)/Butyronitrile (BN) – Ionic Conductivity

Ionic conductivity



Activation energy from VFT equation fitting

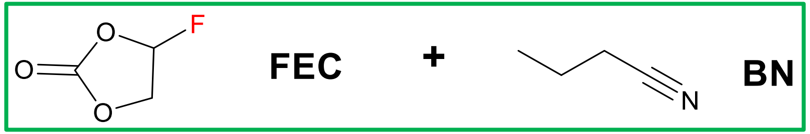
$$\sigma = \sigma_0 T^{-1/2} e^{\left[-\frac{E_a}{R(T-T_0)}\right]}$$

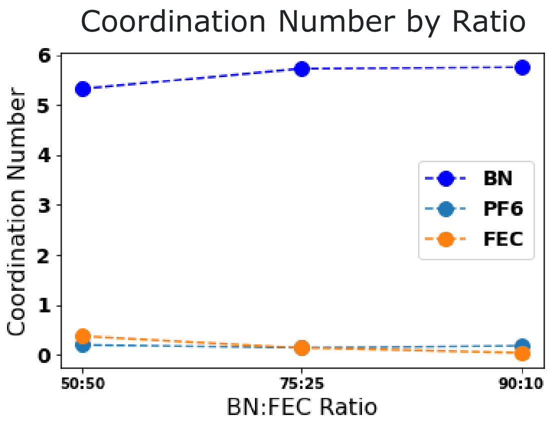
E_a: pseudo-activation energy; σ_0 and T_0: empirical fitting constants

Electrolyte	E_a (kJ/mol)
Gen 2 (Baseline electrolyte)	17 ± 0.2
1 M $LiPF_6$ in FEC/BN (25/75)	13 ± 0.2
1 M $LiPF_6$ in FEC/BN (25/75) + 5% PS	19 ± 0.3
1M $LiBF_4$ in FEC/BN (25/75)	20 ± 0.2
1 M $LiBF_4$ in FEC/BN (25/75) + 5% PS	18 ± 0.3

- 1 M $LiPF_6$ in FEC/BN (v/v = 25/75) had exceptionally high ionic conductivities, *i.e.* 16.0 mS/cm and 7.0 mS/cm at 25°C and -20°C, respectively, much higher than those for 1 M $LiBF_4$ in FEC/BN (25/75).
- Adding 5% PS additive slightly decreases the conductivities of LiPF6 electrolyte but increases for the LiPF4 electrolyte.
- Log σ vs 1/T plots do not exhibit good linear fit. A modified Nernst equation was applied for E_a calculation.

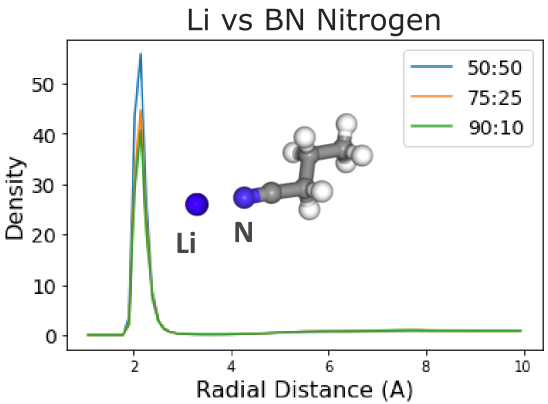
FEC/BN Electrolyte: Coordination and Solvation Structure

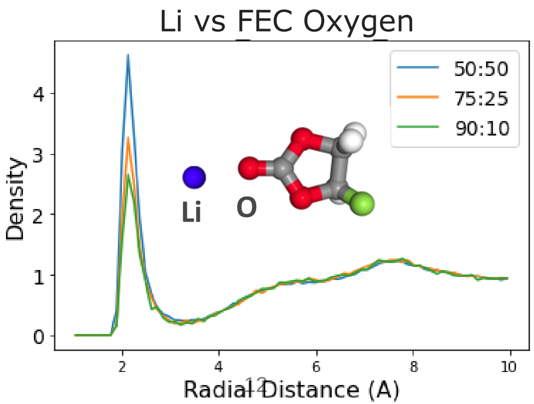


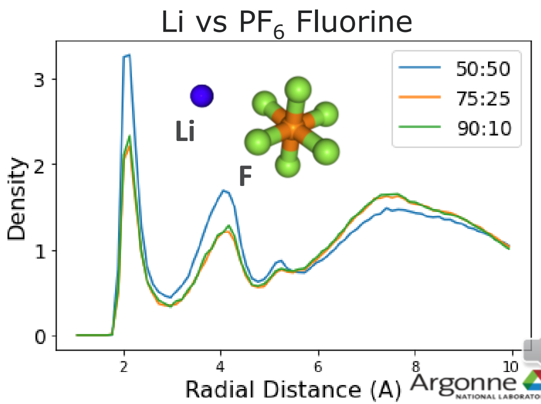


- BN is coordinated strongly through nitrogen and dominates the solvation shell, excluding the presence of other solvents and the anion.
- FEC is coordinated through the carbonyl oxygen, but more weakly than the nitrogen through nitrile group in BN.

Different solvent ratios exhibit similar solvated species, with some differences in relative populations



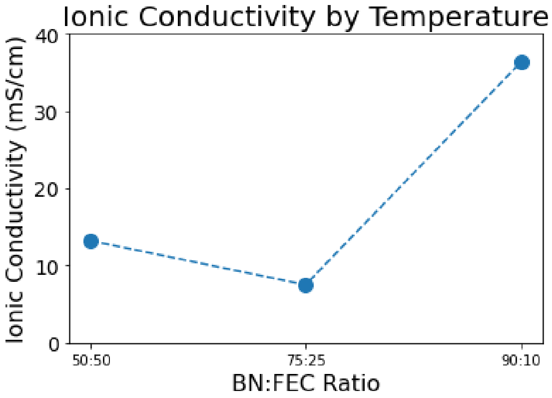


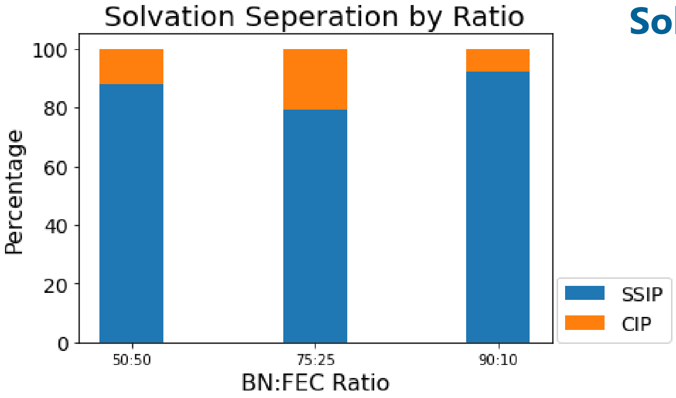


FEC/BN Electrolyte: Solvent Ratio Effect on Ion Pairing and Conductivity

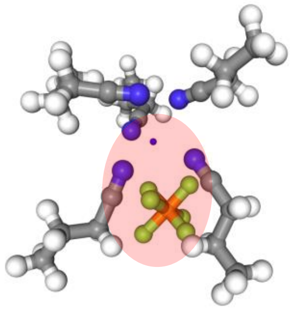
- Despite improved cell performance at LT, the BN/FEC 75:25 ratio has the worst ion transport properties.
- Higher ion pairing in the bulk electrolyte reduces Li^+ mobility and conductivity of the system.

Ionic conductivity shows a minimum at the 75:25 BN:FEC ratio

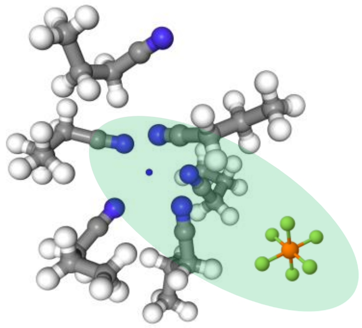




Contact Ion Pair (CIP)



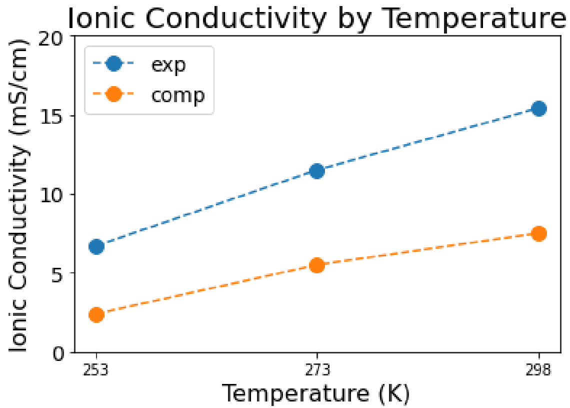
Solvent Separated Ion Pair (SSIP)

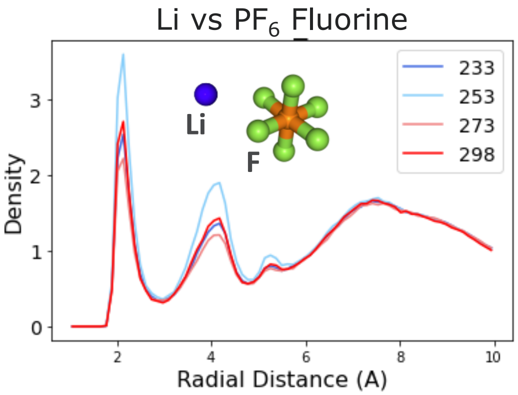


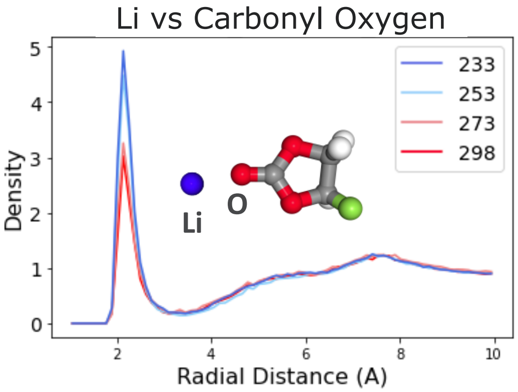
FEC/BN Electrolyte: Temperature Effect on Ion Dynamics and Conductivity

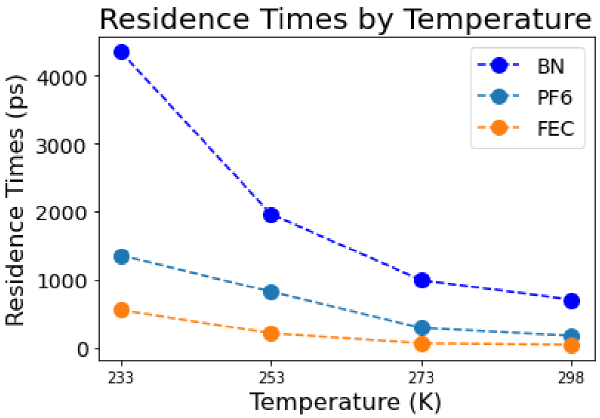
- Conductivity trend is closely reproduced by modeling.
- Residence times rapidly drop as T increases, allowing FEC and PF_6^- to participate in the solvation shell more frequently.
- BN is still the majority component in the solvation shell at all temperatures.

Temperature change does not affect speciation, but they do affect solvation dynamics



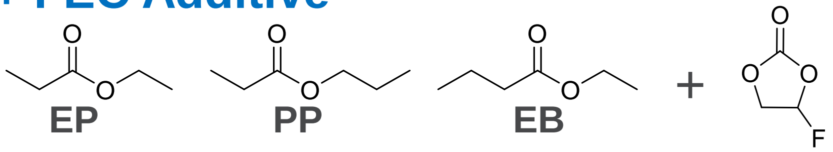






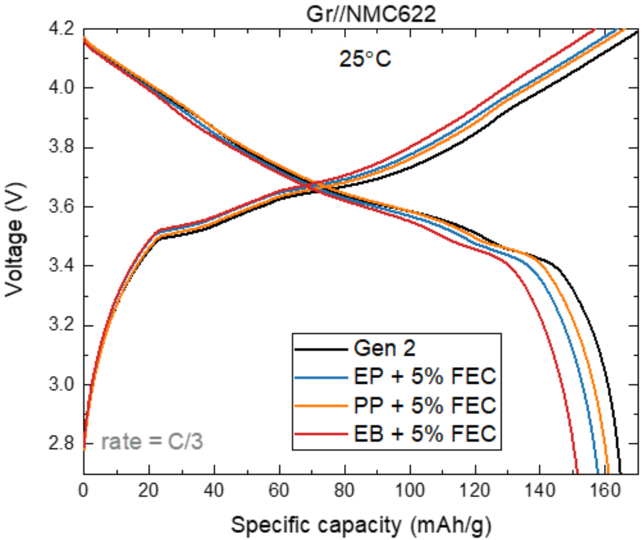
(3) Carboxylate Esters + FEC Additive

Gen 2:
1.2 M $LiPF_6$ EC/EMC
(w/w=3/7)

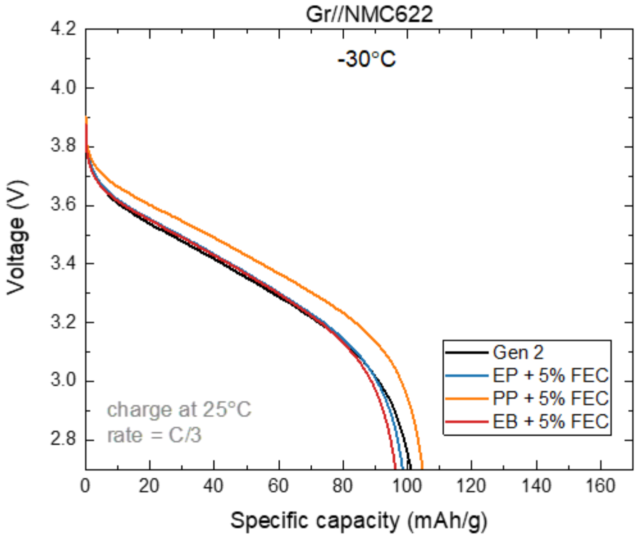


Testing protocol:
2.7-4.2V; C/20 formationx3, C/3 for 1.5 cycles at 25°C;
C/3 discharge at -20°C;
2 cells per electrolyte.

Discharge-charge voltage profile at C/3, 25°C



Discharge voltage profile at C/3, -20°C



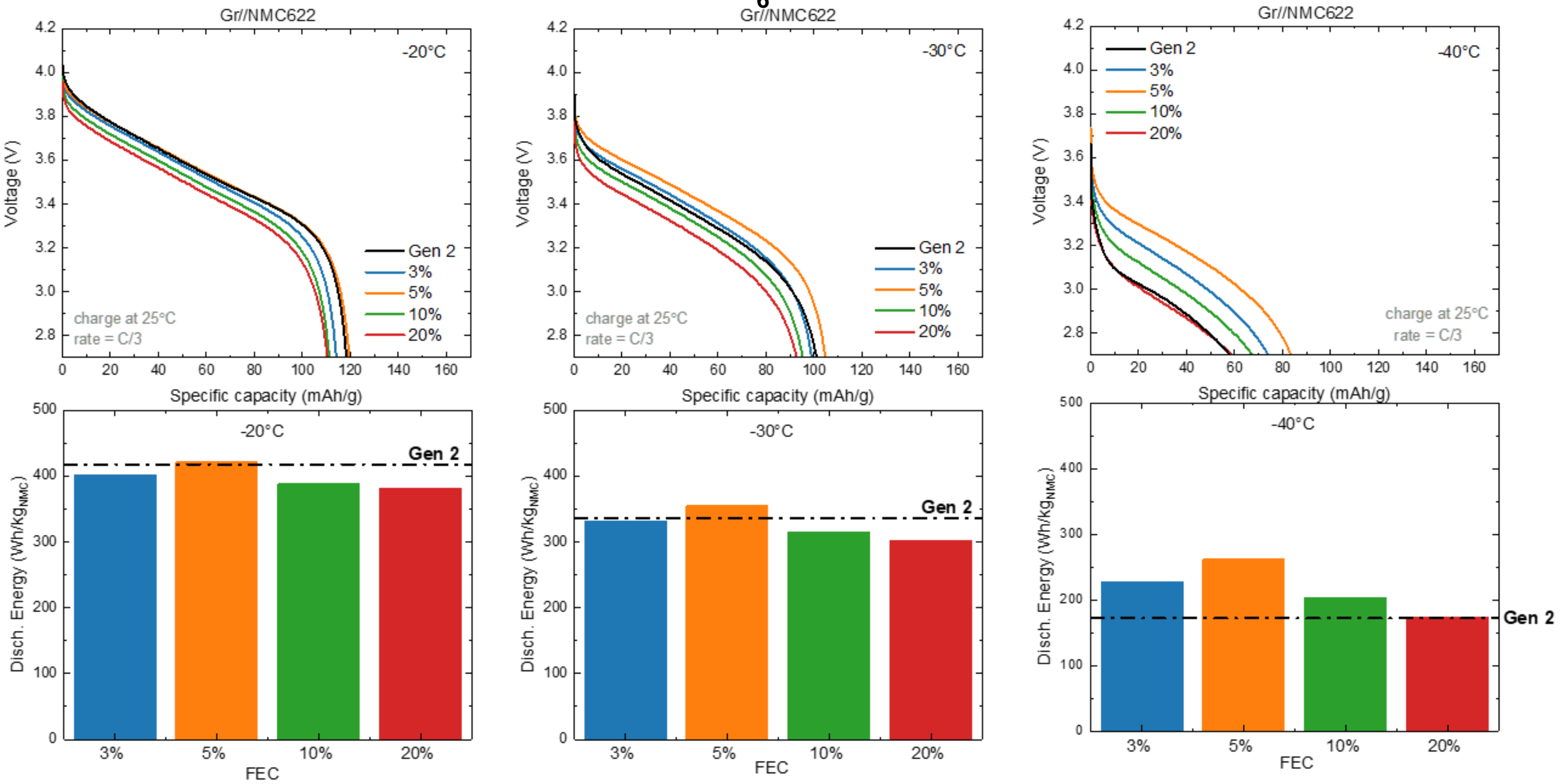
- All carboxylate esters-based electrolytes with FEC as additive showed slightly lower discharge capacities than Gen 2 at 25°C.
- Propyl propionate (PP)-based electrolyte with 5% FEC showed improved capacity and energy at LT such as -30°C.

Carboxylate Esters + FEC Additive: Additive Concentration Effect

Gen 2 vs 1 M $LiPF_6$/PP + x w.t.% FEC

Discharge voltage profile

Discharge Energy



- At LT (-20 °C to -40°C), PP + 5% FEC showed higher discharge capacity and energies than Gen 2.
- At -40°C, all PP-based electrolytes had higher discharge energies than Gen 2.

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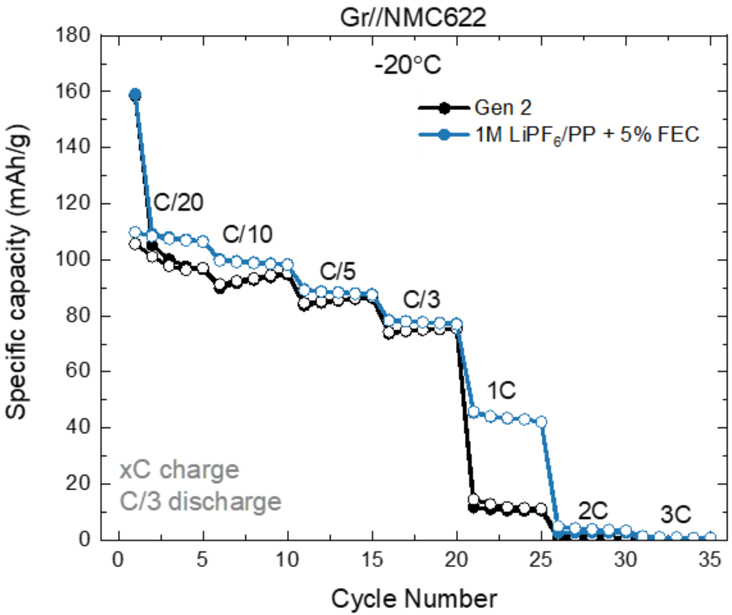
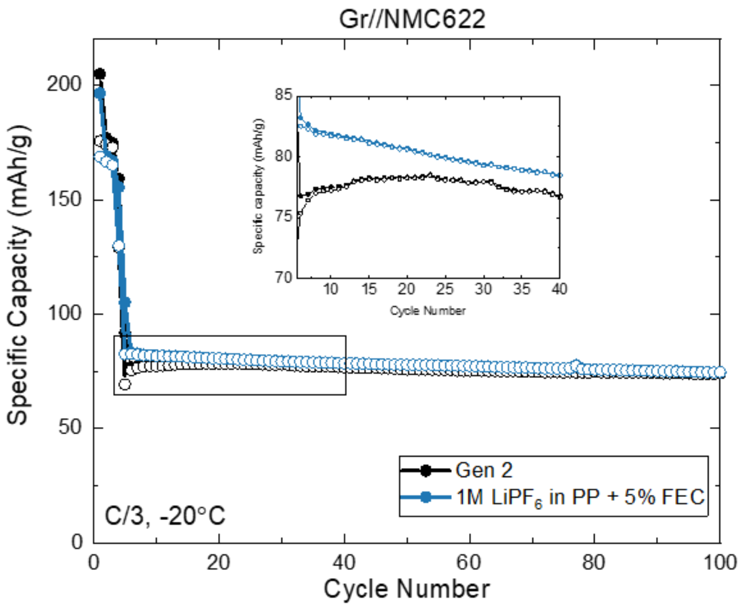
Carboxylate Esters + FEC Additive: C-Rate Capability at LT

Rate performance at -20°C



C/3 cycling at -20°C

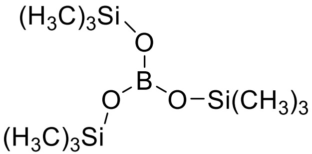


Testing protocol: left figure: 2.7-4.2V; C/20 formationX3 at 25°C, C/20, C/10, C/5, C/3, C, 2C, 3C charge and C/3 discharge, 5 cycles at each charge/discharge rate at -20°; right figure: 2.7-4.2V; C/20 formationX3 at 25°C; C/20x1 and C/3 x 100 cycles at -20°C. 2 cells per EL.

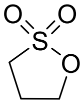
- At -20°C, 1M $LiPF_6$ PP+5% FEC shows improved C-rate capability than Gen 2.
- 1.0 M $LiPF_6$ PP+5% FEC shows slightly higher cycling capacity and comparable cycle life as Gen 2.

Carboxylate Esters + Mixed Additives (FEC + LiDFOB)

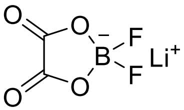
- FEC is the best SEI-forming single additive for PP electrolyte.
- Synergetic effect between FEC and LiDFOB further improves LT performance.



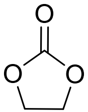
TMSB



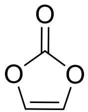
PS



LiDFOB

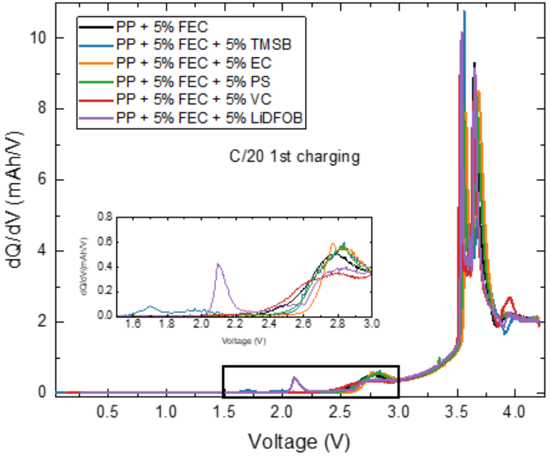


EC

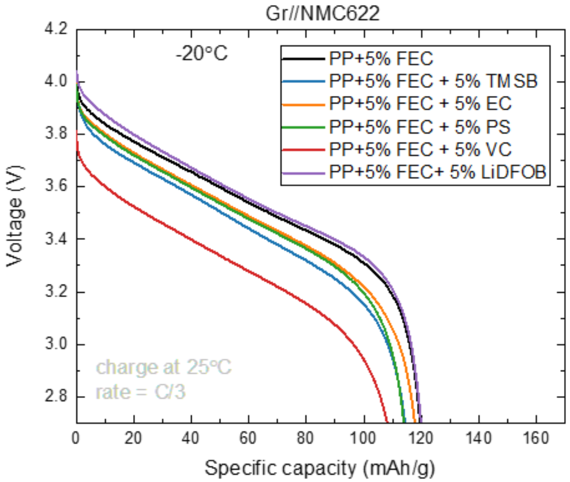


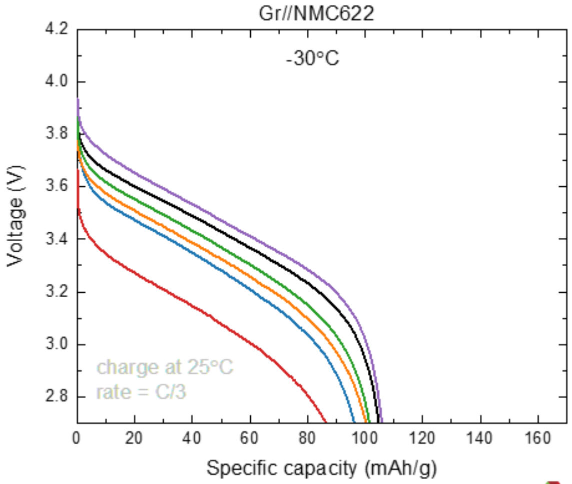
VC

Full cell dQ/dV (1st formation cycle)

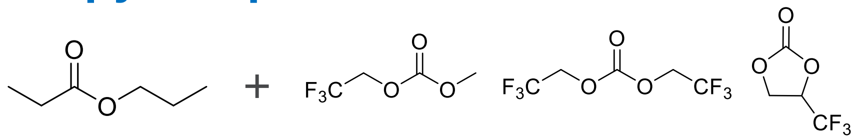


1 M $LiPF_6$/PP + Two Additives





(4) Propyl Propionate + Fluorinated Carbonates – FEMC, HFDEC, TFPC

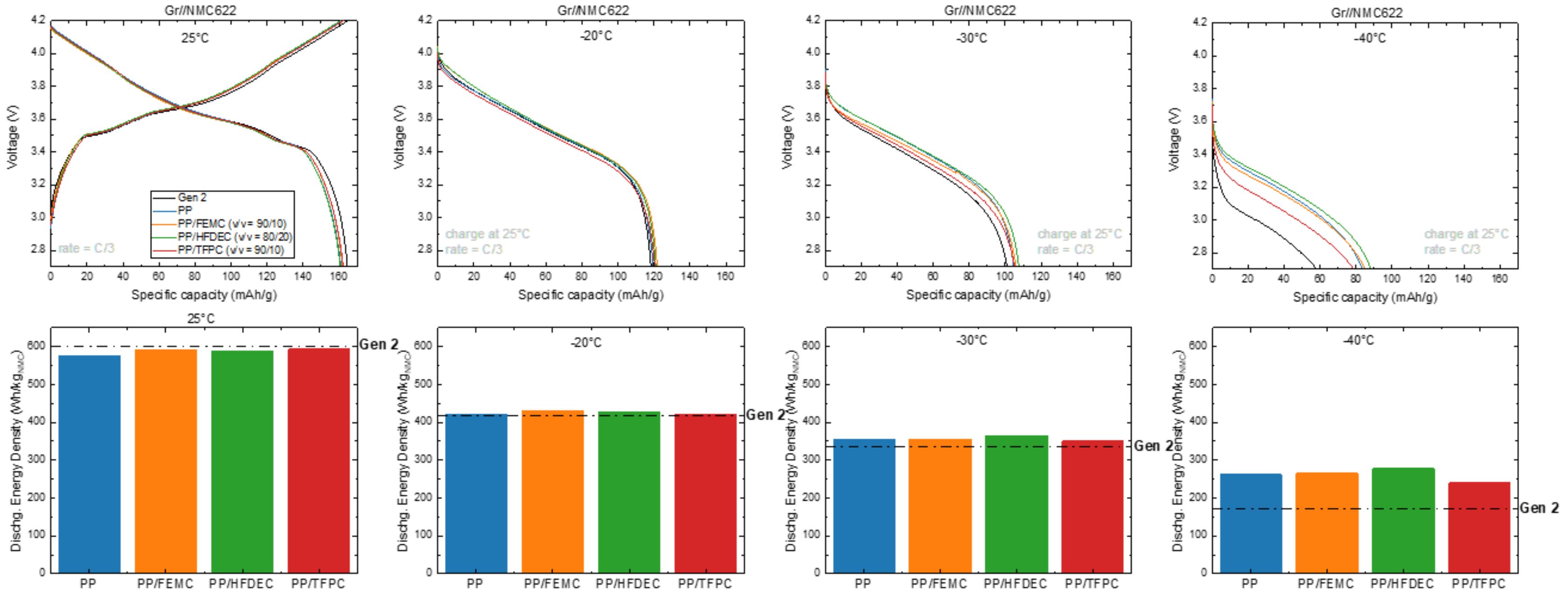


PP FEMC HFDEC TFPC

PP/F-Carbonate Electrolyte: 1 M $LiPF_6$ + 5 w.t.% FEC
Gen 2: 1.2 M $LiPF_6$ EC/EMC (w/w=3/7)

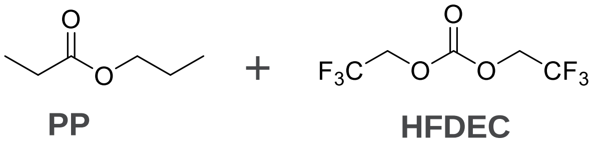
Voltage profile

Discharge energy density

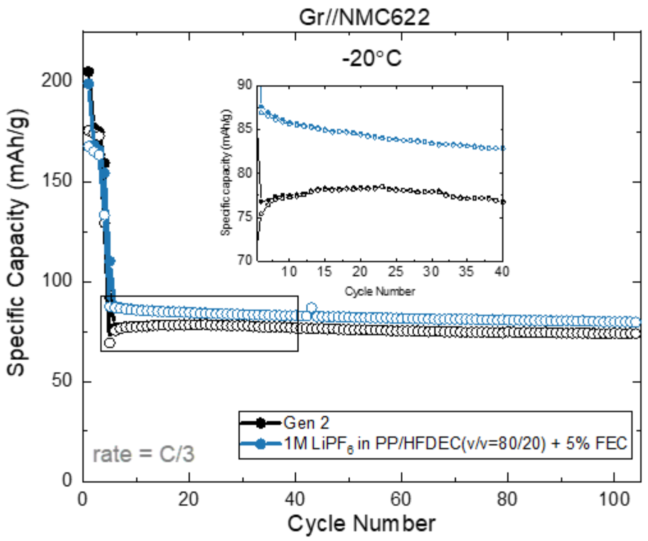


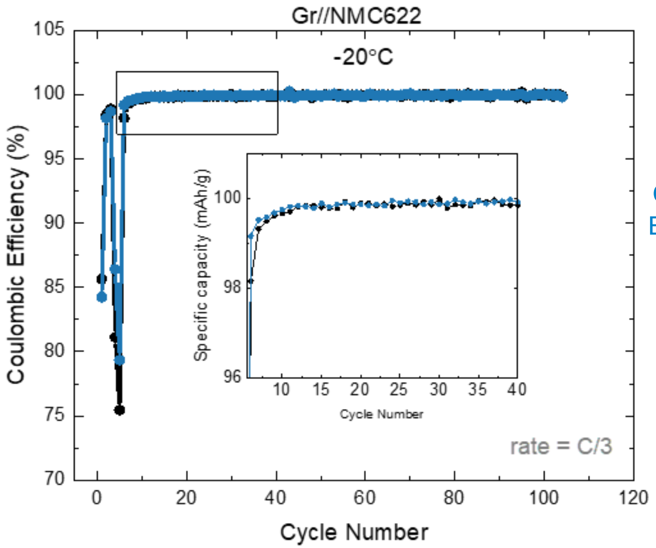
- PP/FEMC(v/v=90/10), PP/HFDE(v/v=80/20), and PP/TFPC(v/v=90/10) is the optimal solvent ratio for LT.
- HFDEC showed the best performance below -20°C among all studied fluorinated carbonate co-solvents.

Propyl Propionate + Fluorinated Carbonates Binary Solvents



Charge/discharge capacities





Coulombic Efficiencies

- At -20^{o}C, 1 M $LiPF_6$ in PP/HFDEC (80/20) + 5% FEC shows improved cycling performance compared with Gen 2.
- Further additive development is needed to improve low and high temperature performance.

RESPONSES TO PREVIOUS YEAR REVIEWER'S COMMENTS

This project was not reviewed last year

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

Kristin Persson – Lawrence Berkeley National Laboratory, Electrolyte simulation

Krzysztof Pupek – MERF, Argonne National Lab, TFPC solvent scaleup synthesis

Sheng S. Zhang – US Army Research Laboratory, Technical discussions

Andy Jansen/Bryant Polzin – CAMP facility, Argonne National Lab, Electrode supply

James Dong – Navitas Systems, LT electrolyte evaluation and testing

REMAINING CHALLENGES AND BARRIERS

- High ionic conductivities of non-traditional LTEs have been achieved by developing new formulations containing fluorinated carbonate solvents and non-carbonate solvents (carboxylate esters – acetate, propionates, butyrate and alkyl nitriles) at subzero temperatures.
- However, the solvent reactivities with graphite anode, *i.e.,* lack of resilient SEI formation for these non-traditional solvents remains a grand challenge to enable long-term cycling performance at lot temperature.
- Exclusive SEI additives tailored for each LTE that could form a low-resistance and high-resilience SEI needs to be identified or designed and synthesized.
- Correlation of electrolyte compositions - solvent/additive/lithium salt – with cell performance at low temperatures.
- Developed LTEs should also perform equally at high temperature performance (>50°C) to meet the USABC electrolyte target.
- Develop effective predictors of electrolyte performance from first-principles calculations.

PROPOSED FUTURE RESEARCH

Continue optimizing LTEs that show improved cell performance at low temperature (-40 ~ -20°C) for long-term cyclability and high temperature (>50°C) performance; Continue developing non-traditional solvent-based LTEs

- ✓ Further optimize additives for the developed highly conductive electrolyte systems to improve long-term cycling performance at low temperatures.
- ✓ Understand the root cause of the anion (BF_4^- vs PF_6^-) effect in the FEC/BN electrolyte system using molecular modeling.
- ✓ Further understand how the bulk properties of electrolyte impact its LT performance.
- ✓ Investigate how the Li^+ desolvation and interaction/deintercalation kinetics impact its LT property by spectroscopic and simulation methods.
- ✓ Post-test analysis to identify the root cause of the degraded cell performance at LTs.
- ✓ Further develop new electrolyte formulations containing different solvent combination, tailored additives and suitable lithium salts.
- ✓ Streamline modeling workflow to enable high-throughput classical modeling work that spans the range of experimental studies.
- ✓ Integrate classical modeling workflow with ab-initio techniques to calculate reduction potentials for relevant molecular clusters.

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

SUMMARY

- ✓ New fluorinated carbonate-based electrolytes, *i.e., t*rifluoropropylene carbonate (TFPC), fluoroethylene carbonate (FEC)/butyronitrile (BN), and fluorocarbonates/propyl propionate (PP) and propyl propionate (PP) solo-solvent, were developed for LT applications which show improved cell capacity and energy at -20°C ~ -40°C compared with Gen 2 evaluated in NMC622/graphite couple.
- ✓ For TFPC-based electrolyte, TFPC added as a cosolvent to the traditional electrolyte significantly improves the cell performance at low temperature.
- ✓ For FEC/BN binary solvent system, the FEC/BN solvent ratio, lithium salt, and SEI additives were optimized to achieve optimal cell performance (capacity, energy and C-rate) at low temperature.
- ✓ Anions of lithium salt significantly affects the low temperature performance for FEC/BN-based electrolytes; $LiBF_4$ outperformed $LiPF_6$ and LiFSI.
- ✓ For fluorinated carbonates/PP-based electrolytes, bis(2,2,2-trifluoroethyl) carbonate (HFDEC) outperformed other fluorocarbonates (FEMC, TFPC, FEC) at -20°C.
- ✓ For FEC/BN binary system, modeling indicates temperature minimally effects solvation structure but substantially changes solvation dynamics.
- ✓ Optimal FEC/BN (25/75) solvent ratio is determined by SEI formation rather than bulk transport property.

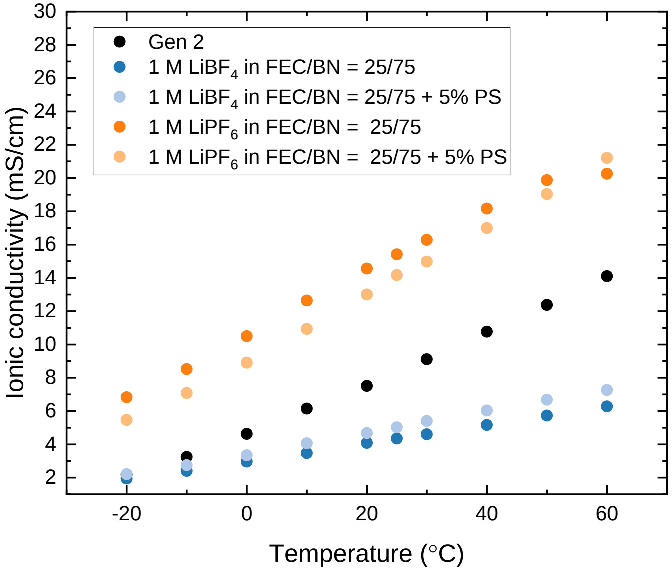
TECHNICAL BACK-UP DIVIDER SLIDE

TECHNICAL BACK-UP SLIDES

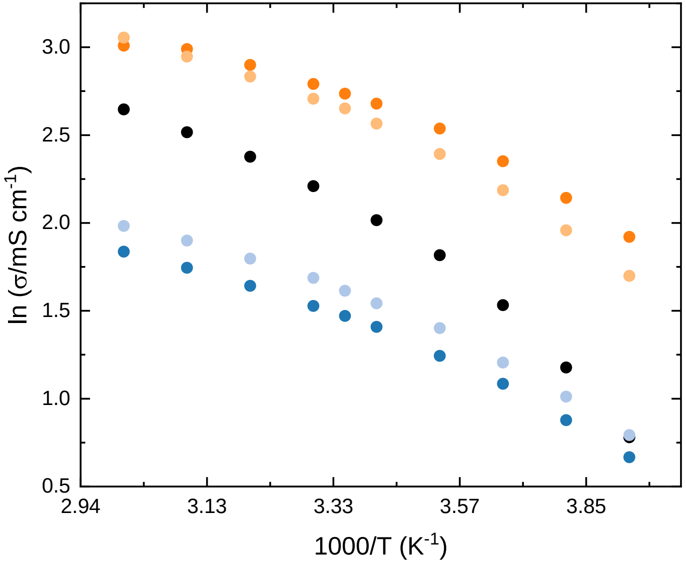
FEC/BN| Electrolyte bulk property: $LiBF_4$ vs $LiPF_6$

- LT performances: $LiBF_4$ is better than $LiPF_6$
- 1 M $LiPF_6$ in FEC/BN (v/v = 25/75) has exceptionally high ionic conductivities, *i.e.* ~16 mS/cm and 7 mS/cm at 25 and -20°C, respectively, which are also much higher than 1 M $LiBF_4$ in FEC/BN (v/v = 25/75)
- Adding PS alters ionic conductivities slightly. The temperature dependence of the ionic conductivity is non-Arrhenius

Ionic conductivity



Arrhenius plot



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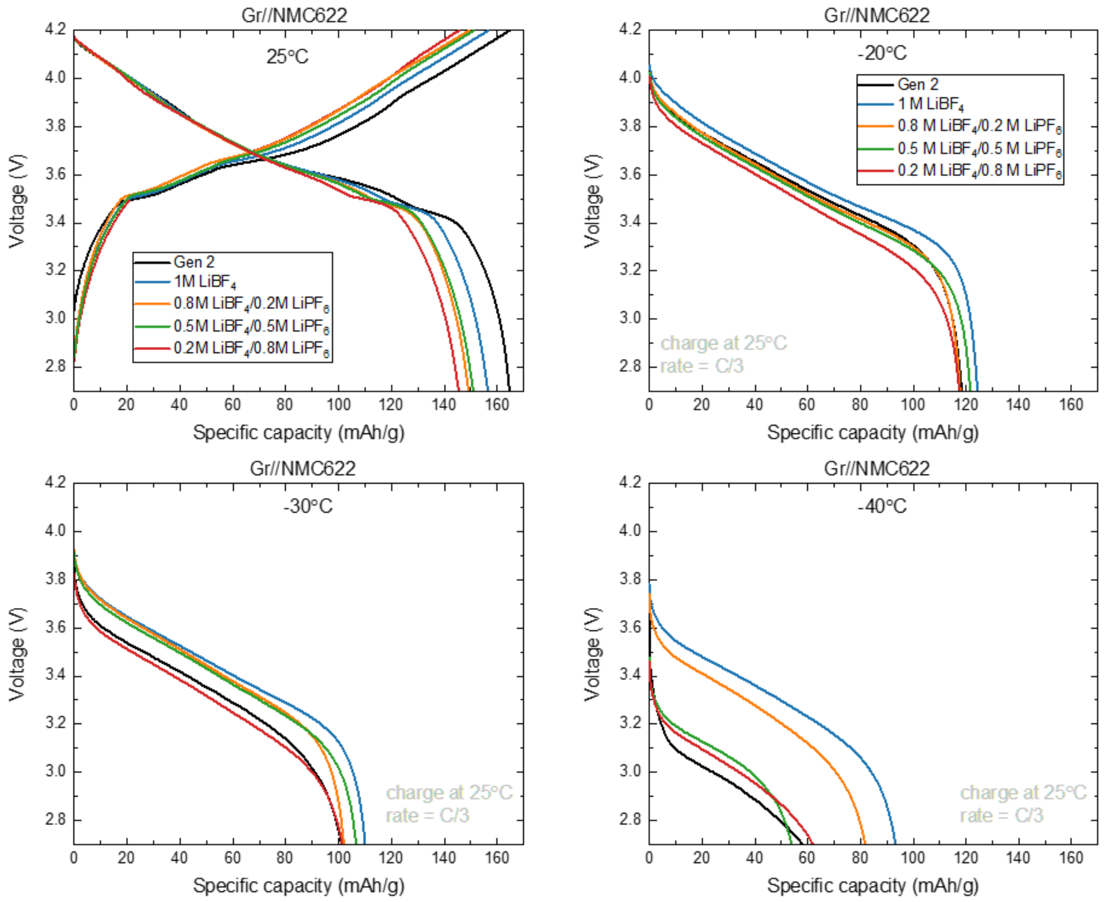
TECHNICAL BACK-UP SLIDES



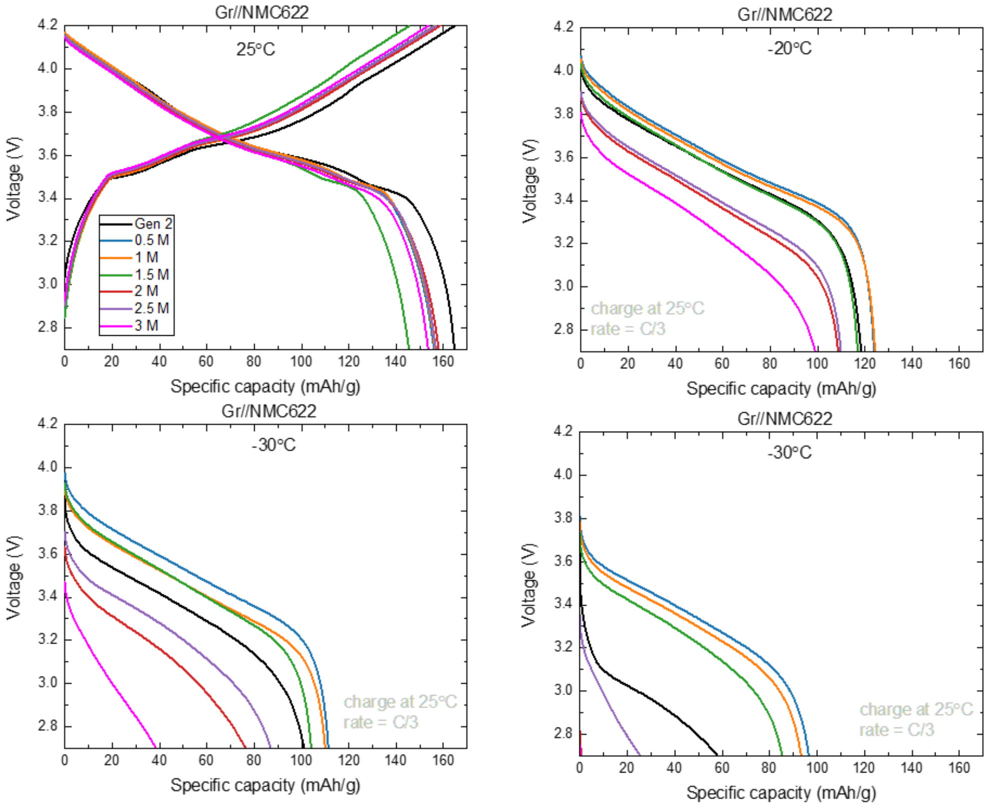
FEC/BN with $LiPF_6$/$LiBF_4$ Mixed Salt

Solvent: FEC/BN (v/v=25/75)

Cycling protocol: 2.7-4.2V; C/20 formationX3, C/3 for 1.5 cycles at 25°C; C/3 discharge at -20, -30, -40°C, respectively. 2 cells per EL. Best cell shown.

- Mixed salt electrolytes showed deteriorated cell performance at both low and room temperatures.
- Single salt electrolyte 1 M $LiBF_4$ is still the best at all temperatures.

TECHNICAL BACK-UP SLIDES



FEC/BN:
$LiBF_4$ concentration effect

Salt: $LiBF_4$
Solvent: FEC/BN (v/v=25/75)

Testing protocol: 2.7-4.2V; C/20 formationX3, C/3 for 1.5 cycles at 25°C; C/3 discharge at -20, -30, -40°C, respectively. 2 cells per EL. Best cell shown.

- $LiBF_4$ concentration impacts the low temperature performance.
- Low $LiBF_4$ concentration which is less than (0.5 M) is beneficial for LT performance.
- However, when concentration is more than 1.5 M, cell performance degrades fast.