X·CEL
eXtreme Fast Charge Cell Evaluation
of Lithium-ion Batteries

ELECTROLYTE DESIGN FACTORS TO ENABLE FAST-CHARGE AND MITIGATE LITHIUM METAL DEPOSITION

Project ID: BAT471

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

Overview (entire XCEL program)

Timeline

- Start: October 1, 2017
- End: September 30, 2021
- Percent Complete: 75%

Budget

- Funding for FY20 – $5.5M

Barriers

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

Partners

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

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Relevance

Impact

Battery Extreme Fast Charge (XFC) conditions create new demands that call for re-evaluation of battery materials. To meet VTO XCEL 10-minute XFC goals while using thicker electrode laminates, we are investigating new XFC electrolytes that will enable improved XFC performance in tandem with next-generation XCEL electrodes.

Objectives

- Using modeling and testing techniques, identify new XFC electrolytes that
  - Exhibit higher conductivity and diffusivity over larger range of salt concentration,
  - Require lower lithium desolvation energy,
  - Enable more effective electrode wetting through lower surface tension and viscosity,
  - Produce stable, low-impedance passivation films (SEI) on electrodes,
  - Reduce resistance tied to concentration polarization,
  - Work well in tandem with the thicker Round-2 (R2) electrodes,
  - Act to mitigate the initiation of lithium metal deposition on the anode.

(relevant to section III.2.c in Electrochemical Energy Storage Technical Team Roadmap)

Milestones

Month/Year	Description of Milestone	Status	Lead Lab
June 2020	Identify & optimize best electrolyte composition and accompanying formation process.	On Schedule; possible delay	INL
Subtasks			
June 2020	Apply modeling (AEM) to derive electrolyte properties and support next-tier electrolyte formulations.	On Schedule	INL
June 2020	Perform coin cell testing/screening on candidate electrolyte systems.	On Schedule	INL
June 2020	Develop approach to model wetting of electrodes using electrolyte with high local salt concentrations.	On Schedule	NREL
March 2020	Collaborate with CAMP Facility on optimized formation protocol, wetting parameters, cell assembly, and electrolyte sharing.	Completed	CAMP
June 2020	Produce >300 mL of best electrolyte(s) and deliver to CAMP Facility.	Probable delay tied to lab shut-down (COVID-19)	INL
Sept. 2020	Collaborate with UC Berkeley (McCloskey) on cell outgassing.	On Schedule	UC Berkeley

Approach

THROUGH COMPUTATIONAL MODELING* AND CELL TESTING WE SEEK TO IDENTIFY ELECTROLYTES FOR XFC APPLICATIONS THAT

- Increase conductivity (decrease resistivity) past the BL EC-EMC (3:7) + 1.2M $LiPF_6$.
- Increase species diffusivity to mitigate polarization effects (for ions *and* solvent).
- Maintain good conductivity and diffusivity even in polarized regions.
- Decrease the lithium desolvation burden (required time and energy).
- Increase salt content as feasible.
- Keep t_+ at reasonable levels (say, ≥ 0.4)
- Decrease EC content, yet avoid excessive ion association.
- Achieve balance between surface tension and surface adhesion (wetting).
- Decrease the onset of lithium metal deposition at anode.
- Critical metric: insure good SEI attributes (stable, low-impedance).

Electrolyte development is done in tandem with new electrode designs to insure compatibility. Ultimate validation is performed in pouch cells made by CAMP.

New formulations are comprised of multi-solvent mixtures that yield lower viscosity (e.g., linear carbonates, esters, nitriles, flame retardant, and SEI additives (VC, FEC, $CsPF_6$ etc.)). Mixed salts are considered to enhance performance and SEI.

* INL: Advanced Electrolyte Model (AEM); NREL: High Throughput Screening followed by DFT/MD

Technical Accomplishments and Progress

EXAMPLES OF AEM-GUIDED FORMULATIONS

Electrolytes B8 , B13 and B21 are examples of AEM-designed electrolytes that have shown excellent performance in coin cells to meet or exceed BL performance. B26 is an example of a next-tier optimized system.
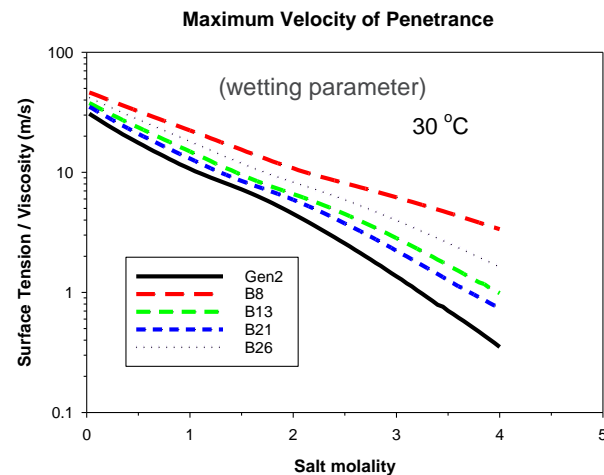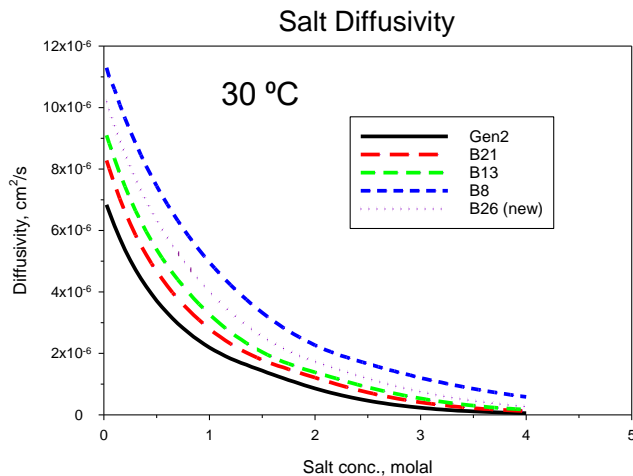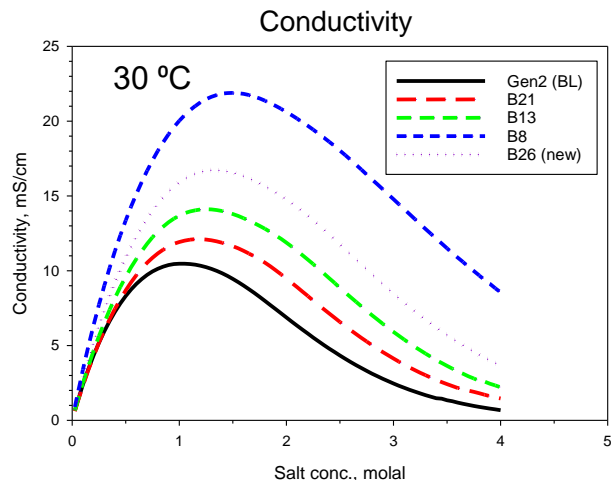
Gen2: EC:EMC (30:70) + LiPF$_6$
B8: EC:DMC:EA:PN:TMP (15:30:20:20:15) w/ (4%VC, 3%FEC) + LiPF$_6$
B13: EC:DMC:EP:EF:TMP (20:30:30:10:10) w/ (3%VC, 3%FEC) + LiPF$_6$
B21: EC:EMC:EP:EF:TMP (20:35:25:10:10) w/ (3%VC, 3%FEC) + LiPF$_6$
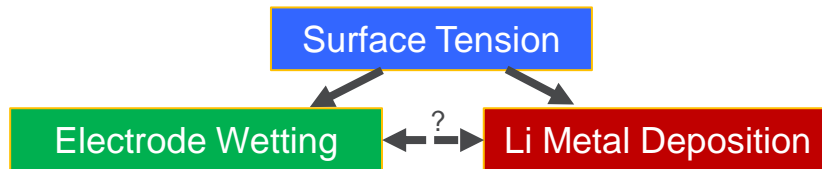B26: EC:DMC:DEC:EP:PN (20:40:10:15:15) w/ (3%VC, 3%FEC) + LiPF$_6$
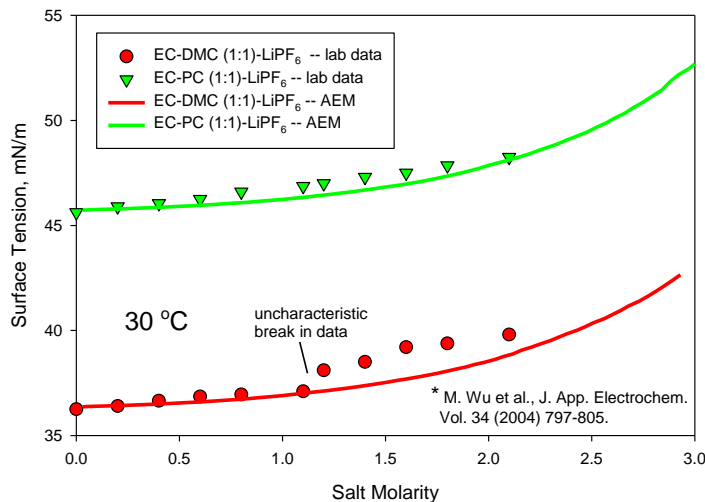
Formulations are geared toward NREL performance recommendations

Surface Tension Predictions

- New molecular-based model for surface tension was added to AEM to support electrode wetting studies at ANL (Dees).

- AEM reveals that surface tension becomes non-linear at higher salt conc., with consequences foreseen under conditions of conc. polarization, wherein the liquid permeation into pores can shift due to the locally higher surface tension at higher salt content.
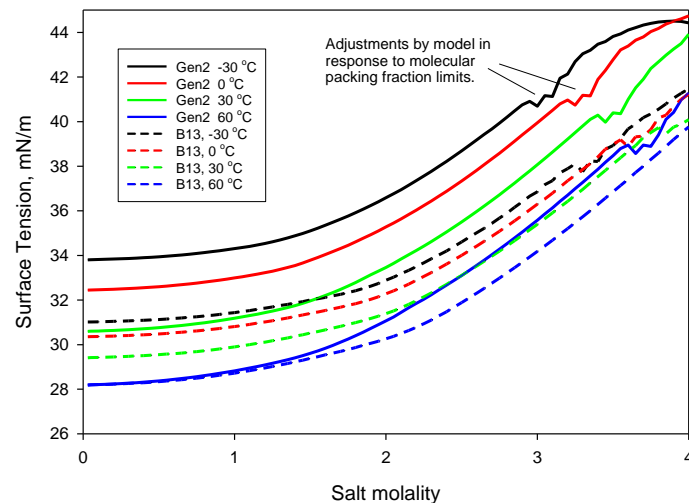

Surface Tension

Electrode Wetting ⬌ ? ⬌ Li Metal Deposition

Comparison of Surface Tension values:
lab measurements* versus AEM predictions

- EC-DMC (1:1)-LiPF$_6$ -- lab data
- EC-PC (1:1)-LiPF$_6$ -- lab data
- EC-DMC (1:1)-LiPF$_6$ -- AEM
- EC-PC (1:1)-LiPF$_6$ -- AEM

30 °C

uncharacteristic break in data

* M. Wu et al., J. App. Electrochem. Vol. 34 (2004) 797-805.

Surface Tension, Gen2 vs 'B13' Electrolyte

- Gen2 -30 °C
- Gen2 0 °C
- Gen2 30 °C
- Gen2 60 °C
- B13, -30 °C
- B13, 0 °C
- B13, 30 °C
- B13, 60 °C

Adjustments by model in response to molecular packing fraction limits.

Surface tension can be used within porous structure models to determine liquid permeation rates, capillary pressures, etc.

B13 is a low-viscosity electrolyte blend for fast-charge conditions.

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Technical Accomplishments and Progress, cont.

## Time Required for Electrolyte to Fill 10-micron Capillaries of Various Radii as f(salt conc.): Gen2 vs B13
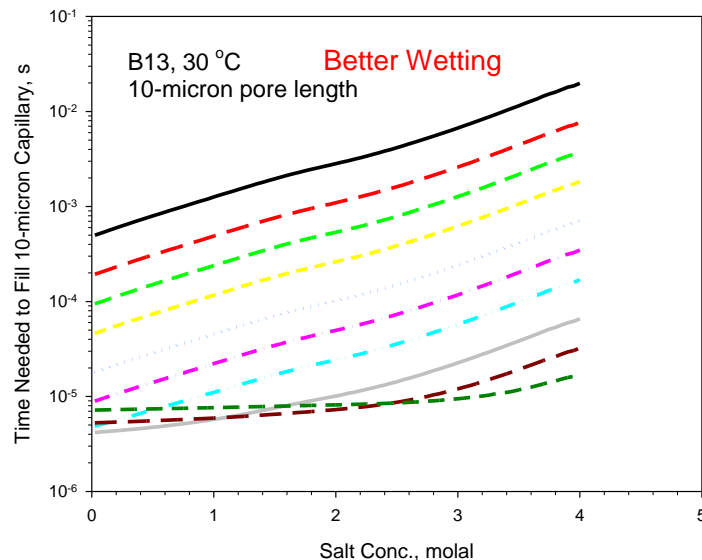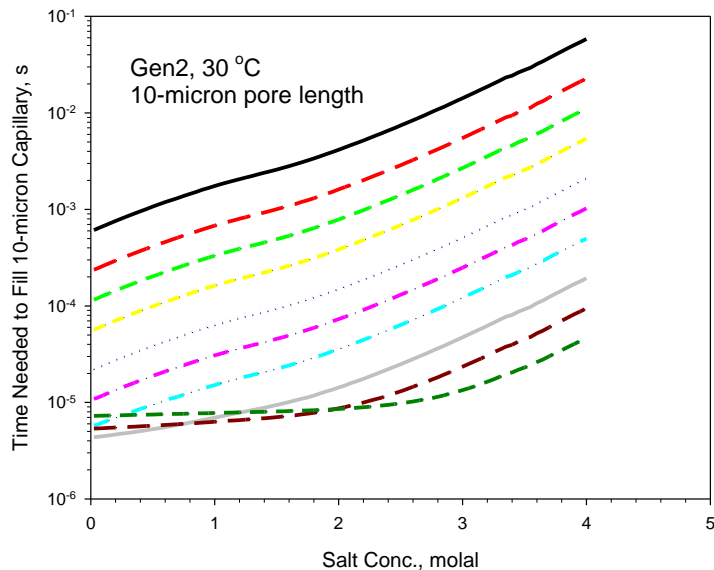
Bosanquet Equation:

$$\frac{d}{dt}\left(\pi r^2 \rho x \frac{dx}{dt}\right) + 8\pi\eta x \frac{dx}{dt} = 2\pi r\gamma\cos\theta, \qquad a = \frac{8\eta}{\rho r^2}$$

$$x^2(t) - x^2(0) = \frac{2b}{a}\left[t - \frac{1}{a}(1 - e^{-at})\right] \qquad b = \frac{2\gamma\cos\theta}{\rho r}.$$

→ B13 permits quicker permeation (by ≈2-4x) of electrolyte through porous structures.
→ Future work will mimic electrode cases: consider porous networks with differing pore dimensions, various degrees of connectivity, and trapped gas. Collaboration between INL-ANL-NREL.

δ_+ δ_-
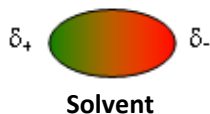
Solvent

The negative dipole is generally more sharply defined.

High Anode Charge Rates lead to local surface fields that can cause solvent disruption, reorientation, repulsion, local nano de-wetting, and preferred routes for Li$^+$ migration...

...producing conditions favorable for lithium metal deposition.

Electron leakage through SEI.
- At defect or heterogeneity sites.
- Worse at high XFC current densities?
- Is leakage more likely during ohmic heating at the SEI at high rates?

Areal variance in current density during XFC.
- What magnitude variance at microscale is due to local heterogeneities?
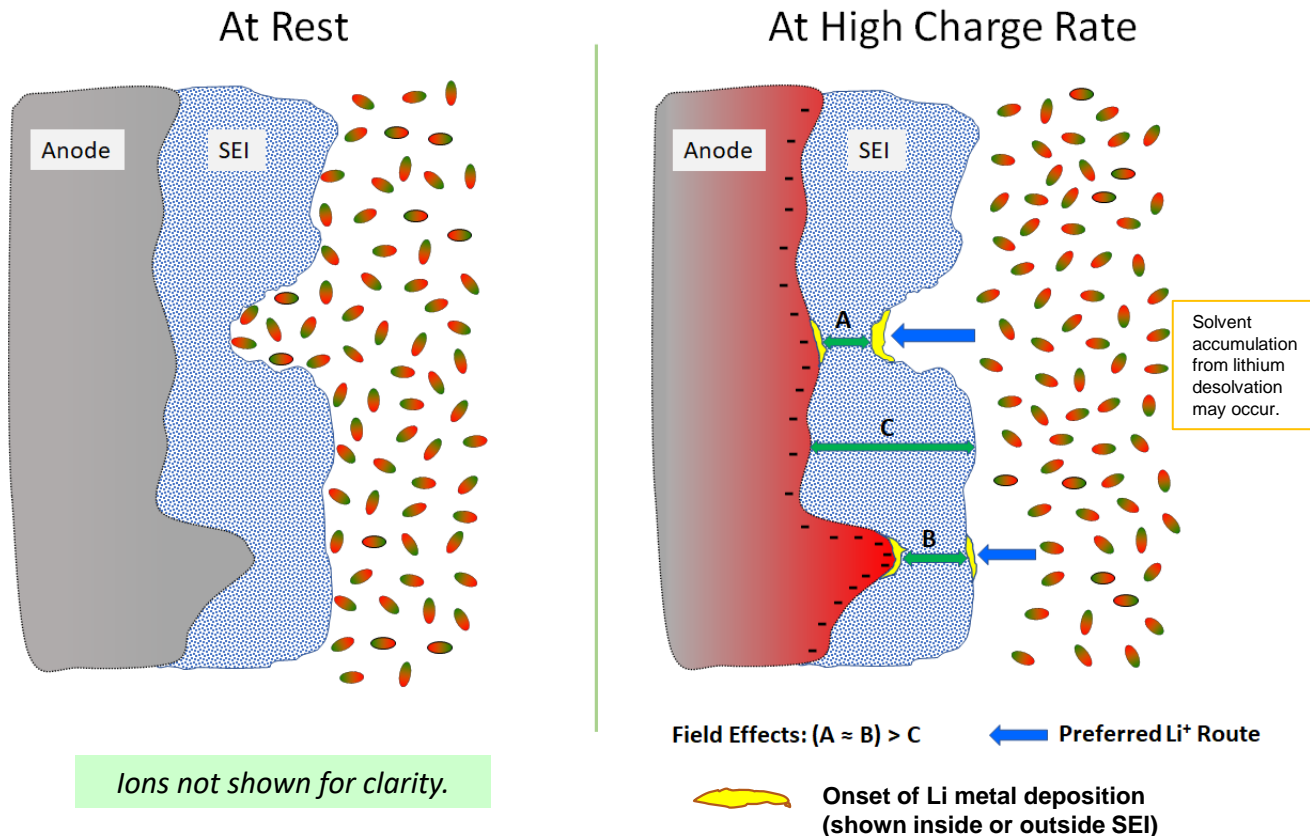
Concentration polarization at anode during XFC.
- Will alter the electrolyte properties within electrode double layers.
- How do the altered properties contribute to lithium reduction at the anode surface?
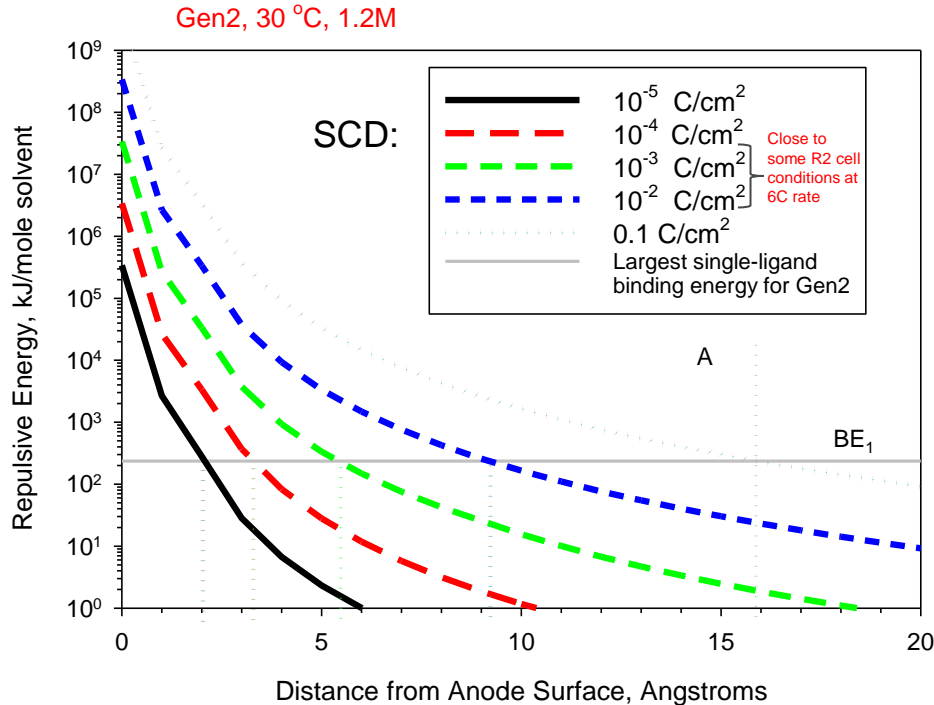
Multiple permittivity effects.

How XFC conditions and electrolyte influence the onset of lithium metal deposition….

At Rest

At High Charge Rate

Anode   SEI

Anode   SEI

A

C

B

Solvent accumulation from lithium desolvation may occur.

Field Effects: (A ≈ B) > C   ⬅ **Preferred Li$^+$ Route**

Ions not shown for clarity.

🟡 **Onset of Li metal deposition (shown inside or outside SEI)**

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Solvent Repulsion from Anode Surface as a Function of Surface Charge Density (SCD)

Gen2, 30 °C, 1.2M

SCD:

- 10^{-5} C/cm^2
- 10^{-4} C/cm^2 — Close to some R2 cell conditions at 6C rate
- 10^{-3} C/cm^2
- 10^{-2} C/cm^2
- 0.1 C/cm^2
- Largest single-ligand binding energy for Gen2

Repulsive Energy, kJ/mole solvent

Distance from Anode Surface, Angstroms

A

BE$_1$

Repulsive Force at 0.01 C/cm^2

- EC
- EMC
- Approx. single-ligand binding energy w Li$^+$

EC experiences higher repulsive force than EMC due to its larger dipole moment.

Better Performance

Repulsive Force, kJ/mole solvent

Distance from Anode Surface, Angstroms

Larger SCD produce greater regions of solvent response/reorientation/repulsion ('A') with corresponding decrease of permittivity.

This creates a region of "unprotected" lithium that can encourage lithium metal deposition at the anode surface. Shorter repulsive distances are better.

Loci of surface heterogeneities where surface charge is locally higher will worsen this process and become initiation sites for lithium metal deposition.

A: Region of probable solvent repulsion from surface at the shown surface charge density, where Li$^+$ is acted on more by the SCD than solvent dipoles.

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Cell Formation Performance

with selected XFC electrolytes
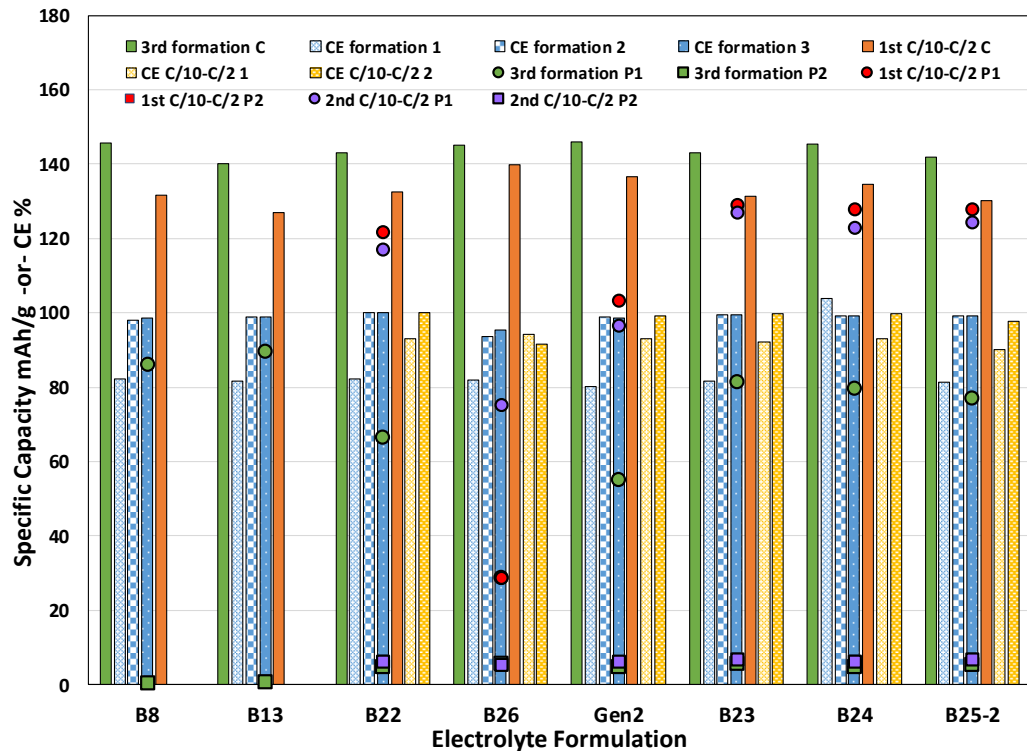
SUMMARY OF BEST CANDIDATES PLUS BL

Gen2 (BL): EC:EMC (30:70, mass) + 1.2m LiPF$_6$

B8: EC:DMC:EA:PN:TMP (15:30:20:20:15) w/ (4%VC, 3%FEC) + 1.25m LiPF$_6$

B13: EC:DMC:EP:EF:TMP (20:30:30:10:10) w/ (3%VC, 3%FEC) + 1.25m LiPF$_6$

B22: EC:DMC:DEC:TMP:EF:EP=20:20:15:10:10:25 w/ (3%VC, 3%FEC) + 1.5m LiPF$_6$

B23: B8 with 0.01M CsPF6

B24: B13 with 0.01M CsPF6

B25: B22 with 0.01M CsPF6

B26: EC:DMC:DEC:EP:PN (20:40:10:15:15) w/ (3%VC, 3%FEC) + 1.25m LiPF$_6$

Of these candidates, the following will be tested in CAMP pouch cells: B8, B13, B22, B24, B26.

CE:
cycling efficiency (ratio of discharge to charge capacity)

P1:
post-discharge polarization

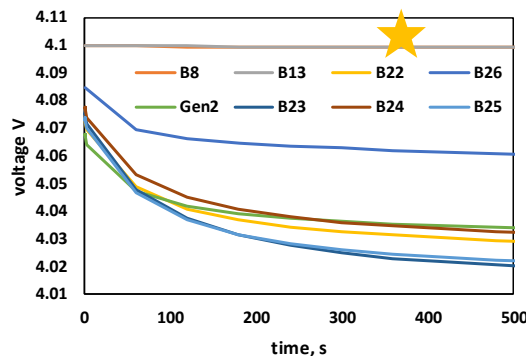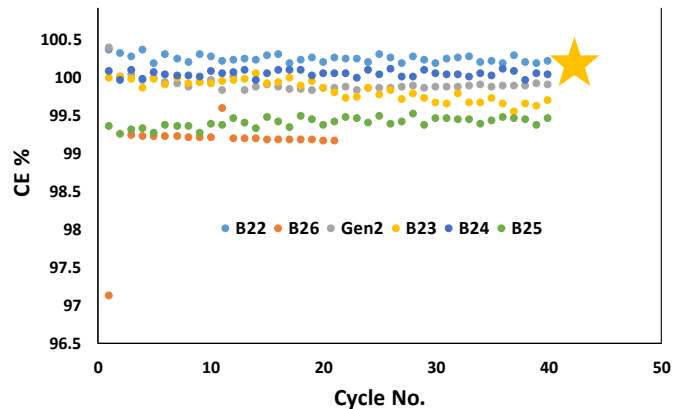**P2**:
post-charge polarization

Vacuum step in coin cell assembly reduces cell variability and increases capacity retention.
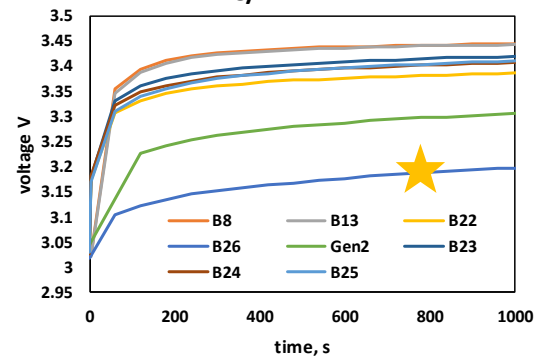
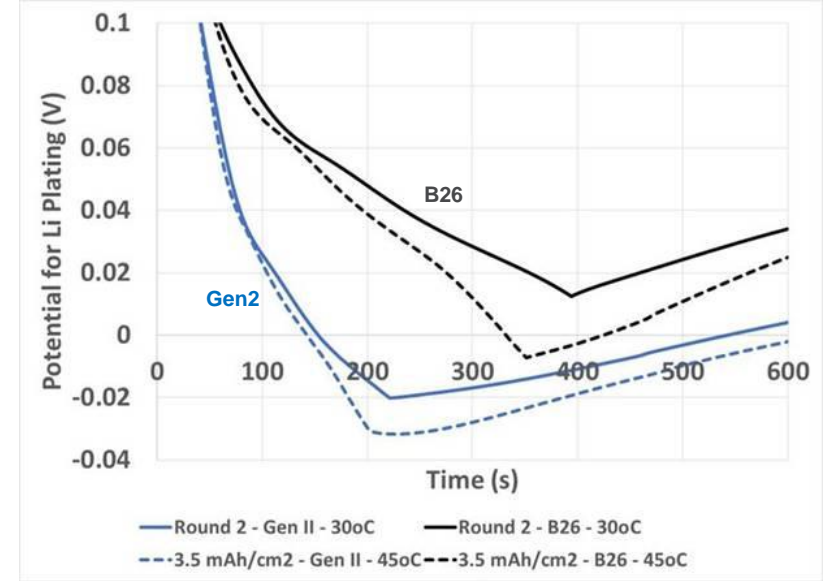# Cell Post-formation Performance
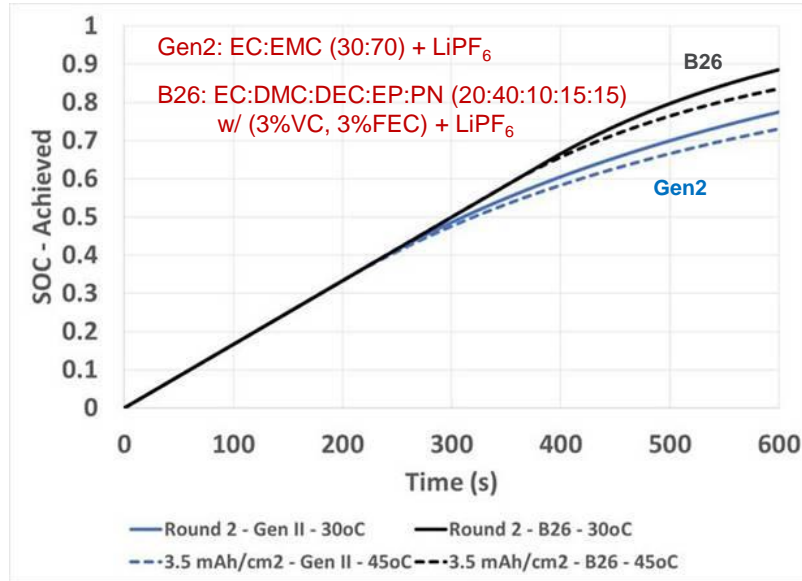
Improvement past Gen2 BL is seen (⭐)
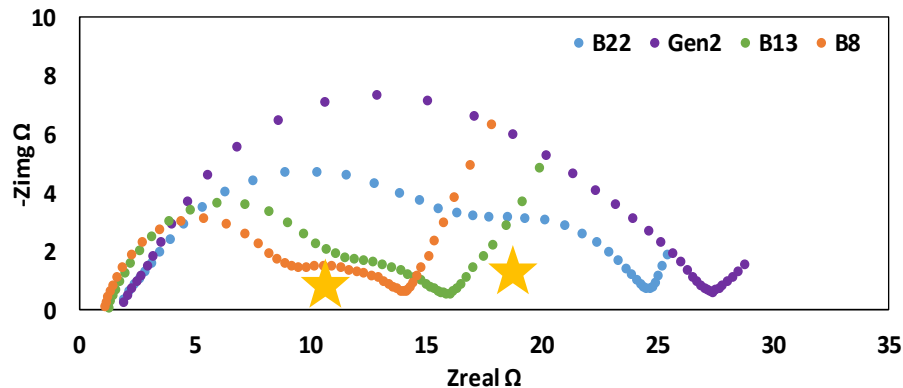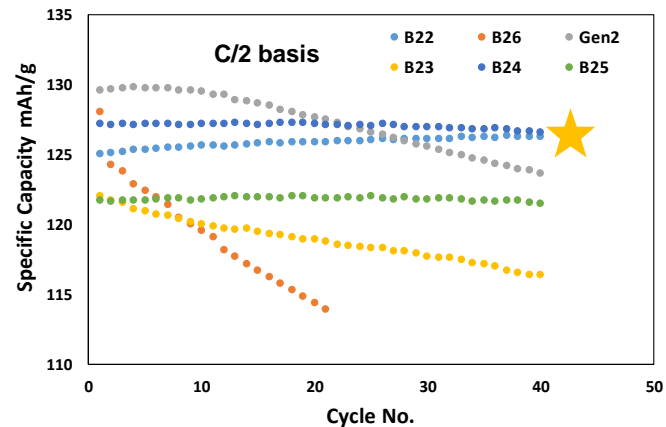
Charge Acceptance and Lithium Deposition

(6C CCCV Simulations)
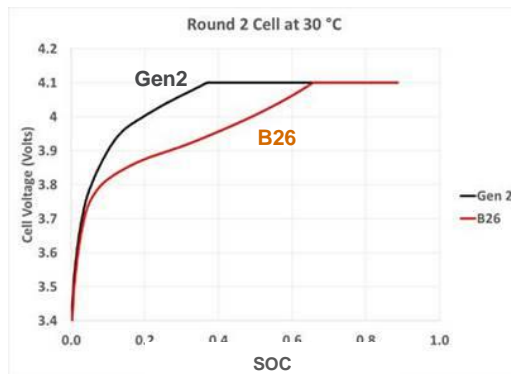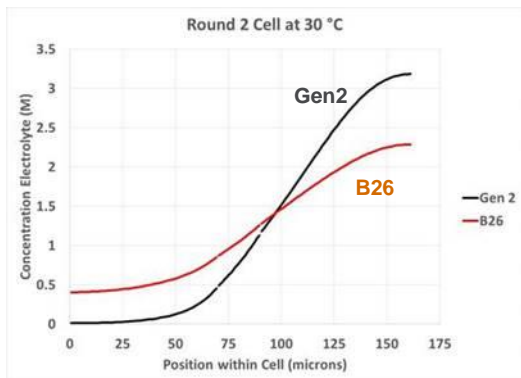
Plots courtesy of NREL (A. Colclasure)

- **For 70 micron electrodes:** B26 should eliminate Li plating and increase SOC for 10 minute capacity (from ~80 to 90%).

- **For 100-micron electrodes:** B26 should reduce Li plating and increase SOC for 10 minute capacity (from ~72 to 83%).
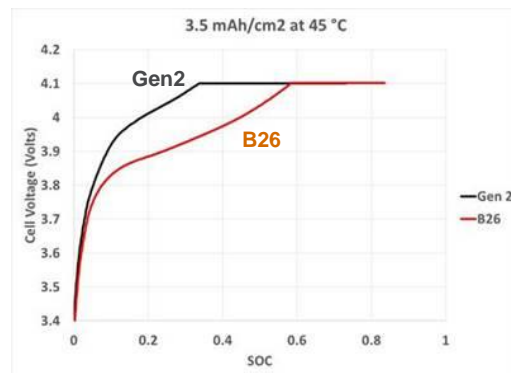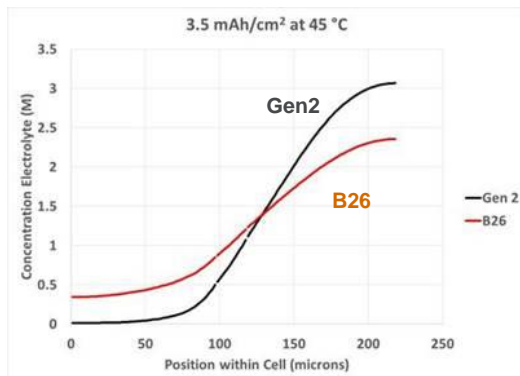
(6C CCCV Simulations, Part 2)

70-micron electrodes, 30 ºC

100-micron electrodes, 45 ºC

- Based on simulations at NREL, concentration polarization and voltage shown at end of CC charge segment (roughly 210-220 seconds for Gen2).

- **B26 reduces polarization across the cell**, allowing
  - lower resistances at the extremes,
  - quicker recovery between cycles,
  - gain of SOC delta of about 0.25 by end of CC.

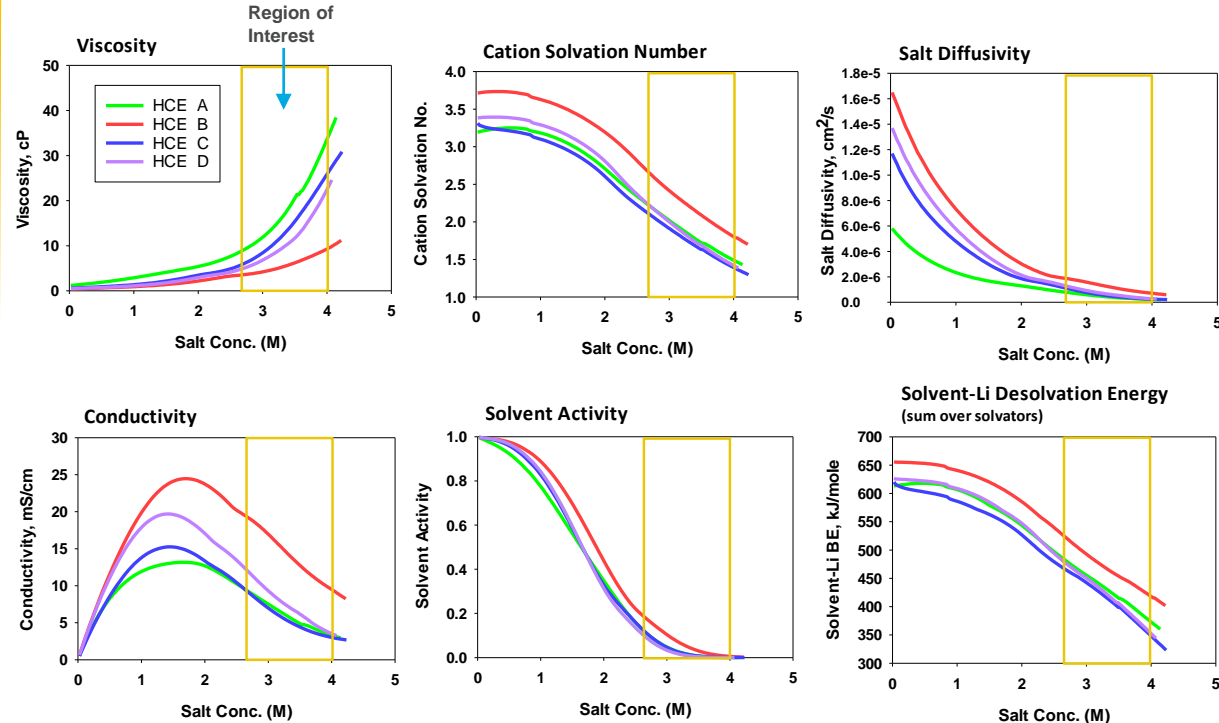*Plots courtesy of NREL (A. Colclasure)*

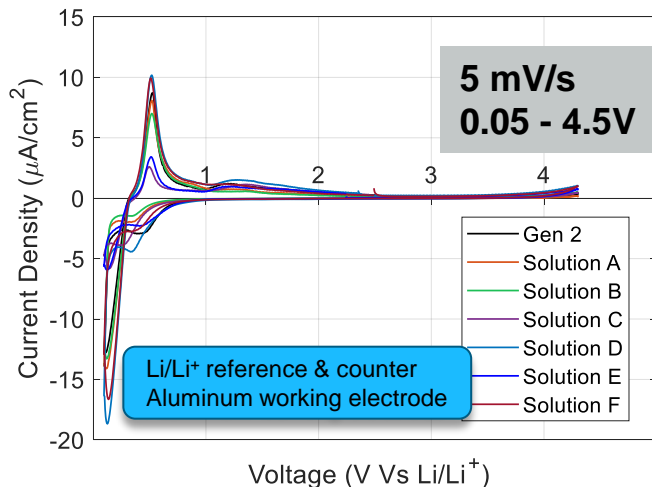# Highly Concentrated Electrolytes (HCE)
XFC Applications

HCE Attributes:

- Generally have 3-5 Molar (M) salt,

- Decrease of solvation number per lithium,

- Corresponding drop in lithium desolvation energy requirements,

- Higher salt content helps moderate concentration polarization,

- Surface tension is greater at higher salt content (helps mitigate Li metal deposition),

- Voltage stability is improved through low solvent activity (nearly all solvent is coordinated with ions),

- Ion hopping is more likely as a transport mechanism (very efficient),

- Valid for current 532 and 622, 811 cathodes (high salt content drops solvent reactivity and gas formation)

- AEM is accurate for HCE conditions.

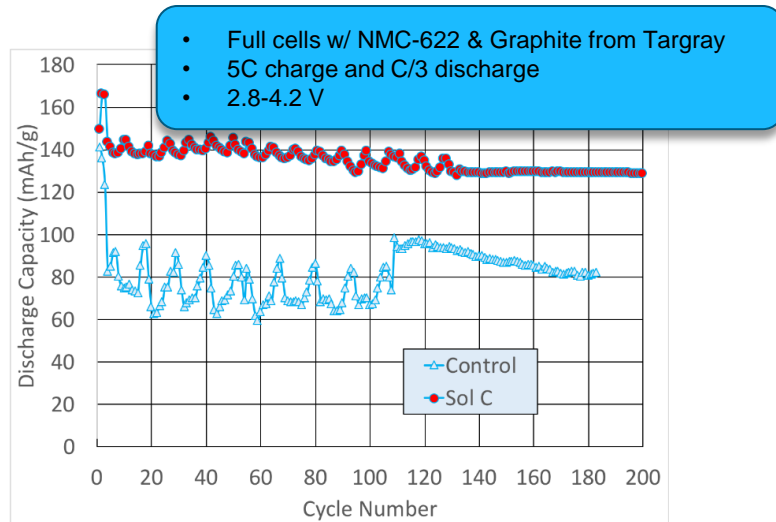*Prescreening via AEM has produced HCE candidates for cell testing:*

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Electrochemical Performance (NREL)

5 mV/s
0.05 - 4.5V

Li/Li+ reference & counter
Aluminum working electrode

- Gen 2
- Solution A
- Solution B
- Solution C
- Solution D
- Solution E
- Solution F

- Continuum models at the cell level identified target properties for electrolyte:
  - 2x diffusivity
  - Li^+ conductivity > 5 mS/cm
  - Transport number > 0.75
- A high-throughput computational screening of over 500000 entries resulted in 6 possible solvents that meet several of these metrics.
- These 6 solvents (labeled A through F) were subject to experimental evaluation.

- Full cells w/ NMC-622 & Graphite from Targray
- 5C charge and C/3 discharge
- 2.8-4.2 V

- Although several of the recipes showed higher initial capacity compared to the baseline, only Solution C retained performance with cycling.
- We are currently performing cell-teardowns to analyze degradation mechanisms on the other formulations.
- The initial high throughput screening did not consider degradation-related parameters (except the oxidation and reduction potentials); so the next round of analyses will inform modification of the functional groups.

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Early ab initio Results (NREL)

GAS PHASE SOLVATION ENERGIES

All binding energies calculated at M062x/6-311G(2d,d,p) in the gas phase

Lower values infer a lower cost of lithium desolvation at the electrode.

Molecule D
TAN
-46.5 kcal/mol

OSF
Molecule B
-21.3 kcal/mol

Molecule F

Li^+ (not to scale)

OHD
-31.0 kcal/mol

OCN
Molecule C
-36.9 kcal/mol

EMC
-38.9 kcal/mol

EC
-45.7 kcal/mol
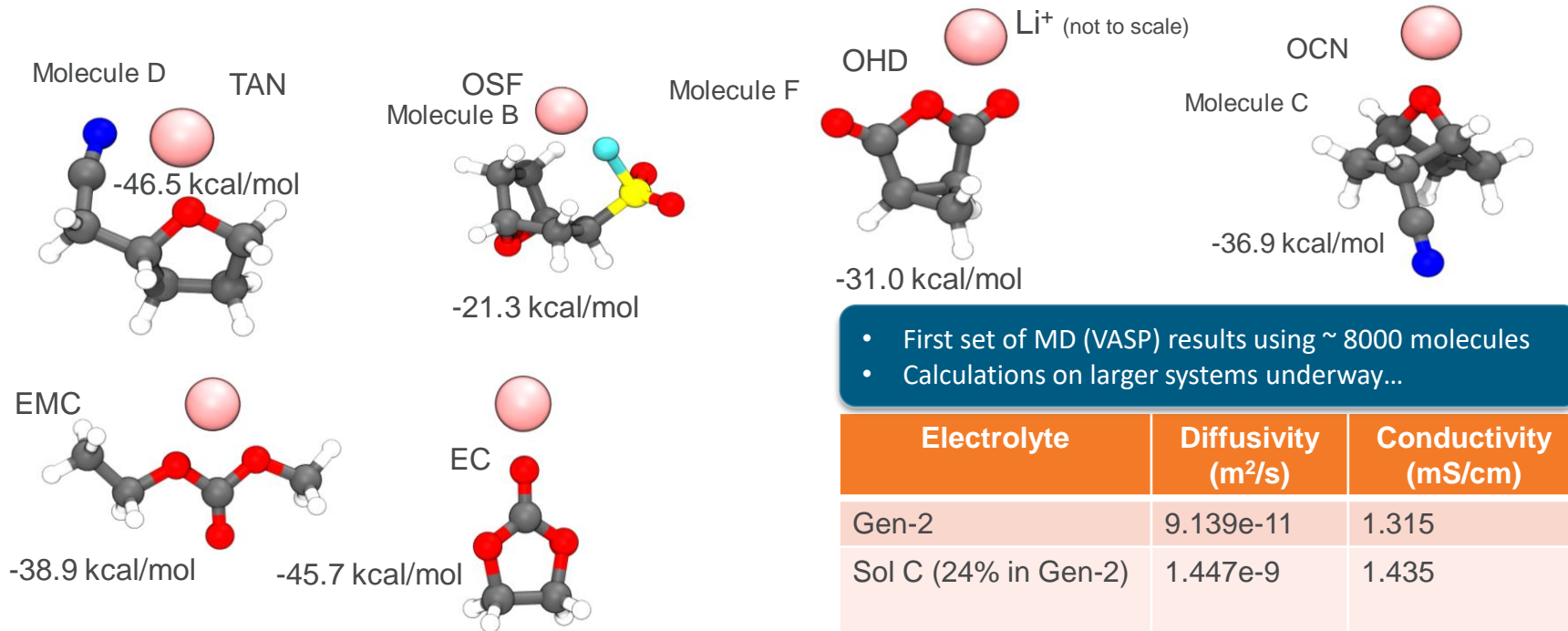
- First set of MD (VASP) results using ~ 8000 molecules
- Calculations on larger systems underway…

Electrolyte	Diffusivity (m²/s)	Conductivity (mS/cm)
Gen-2	9.139e-11	1.315
Sol C (24% in Gen-2)	1.447e-9	1.435
Sol F (30% in Gen-2)	6.886e-10	1.949

Figures courtesy of V. Bharadwaj (NREL)

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Responses to Previous Year Reviewers' Comments

This project was not reviewed last year

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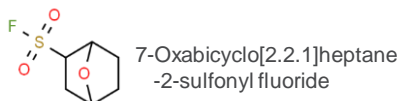# Collaboration and Coordination

- **ANL (A. Jansen, A. Dunlop, D. Dees)**
  - Cell formation and wetting procedures; CAMP cells
  - Surface tension predictions and electrolyte wetting models
  - Electrolyte transport properties for XFC candidates
- **NREL (S. Santhanagopalan, A. Colclasure)**
  - Modeling and testing new electrolyte solvents
  - Electrolyte transport properties for XFC candidates
  - Impact of electrolyte on the initiation of Li metal deposition at anode
  - Anode heterogeneity effects involving electrolytes
- **ORNL (S. Allu)**
  - Initiation and growth of Li metal deposition at anode
- **UC Berkeley (B. McCloskey, E. McShane)**
  - DEMS testing for gas formation from new XFC electrolytes
- **INL (N. Gao, S. Kim)**
  - Cell assembly, testing and data coordination
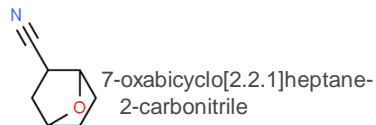
Remaining Challenges and Barriers

- **Discovery of viable XFC electrolytes requires thorough testing and validation**
    - Many-faceted performance and life requirements make implausible a single drag-and-drop solution for electrolytes. Combination of models + testing is imperative to utilize limited resources.
- **Consideration of diverse solutions is justified, but is resource intensive**
    - Examples: testing XFC electrolytes with 1-1.2M salt versus highly concentrated systems with 3-5M salt; testing multiple SEI additive combinations.
- **Bridging the physics, distances and timescales of various models is a critical endeavor**
    - Example, incorporating the molecular scale information from AEM is not readily done within macroscale models.
- **More granularity and understanding is needed regarding processes and their consequences in electrode double-layer (DL) regions during XFC**
    - Examples: electrolyte properties change in DL due to concentration polarization; solvent accumulation in/near DL due to lithium desolvation.
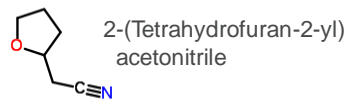
Proposed Future Research

- NREL compounds have been down-selected for inclusion in AEM calculations. A suite of transport and thermodynamic properties will be generated, then performance assessed via NREL cell models.
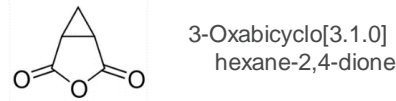

7-Oxabicyclo[2.2.1]heptane-2-sulfonyl fluoride

Solution B: 30% in Gen 2

7-oxabicyclo[2.2.1]heptane-2-carbonitrile

Solution C: 24% in Gen 2

2-(Tetrahydrofuran-2-yl)acetonitrile

Solution D: 30% in Gen 2

3-Oxabicyclo[3.1.0]hexane-2,4-dione

Solution F: 30% in Gen 2

- Complete XFC electrolyte benchmark testing in CAMP R2 pouch cells
  - INL Systems will include formulations B8, B13, B22, B24, B26, as well as selected HCE systems.
  - Collaborate with NREL on modeling and cell testing of their compounds (above) to achieve optimized formulations.

- Demonstrate generalized model for tracking solvent accumulation at anode from Li desolvation
  - Will reveal the connection between charge rate and detrimental solvent accumulation.

- Confirm the mechanistic role of electrolyte in lithium metal deposition at the anode during XFC.

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

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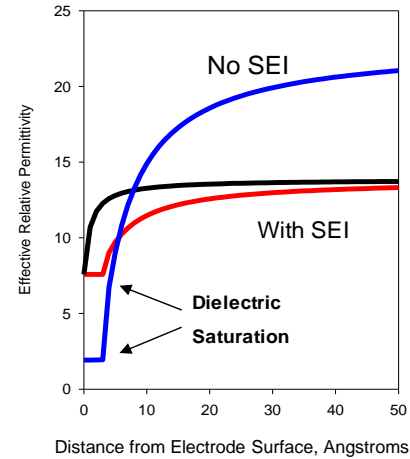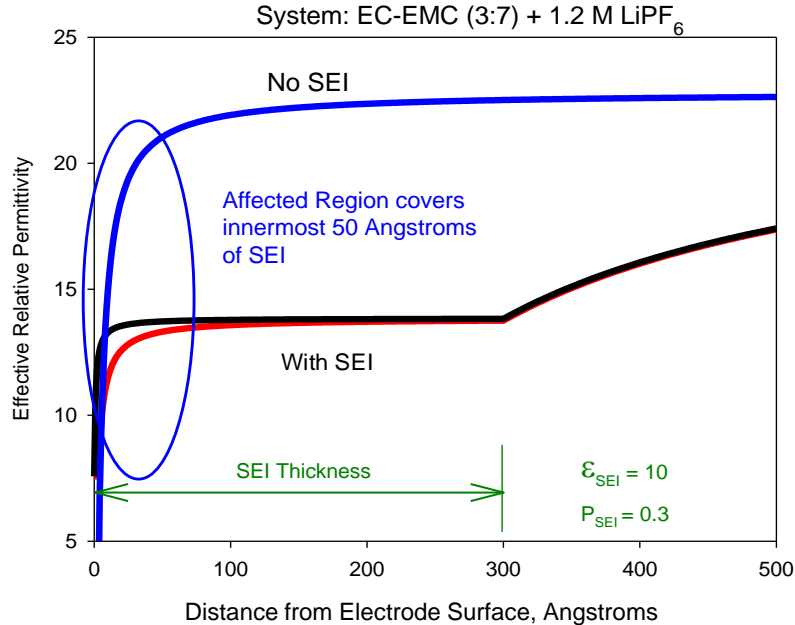
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Summary

- Extreme Fast-charge (XFC) electrolytes have been identified and validated through modeling and cell testing. The down-selected systems perform better than the Gen2 baseline in terms of interfacial impedance and lesser voltage polarization following cell charging.

- These low-viscosity electrolytes have high conductivity and diffusivity and are designed to alleviate common weaknesses of conventional systems.

- Combined modelling (NREL + AEM) demonstrate that INL XFC electrolytes enable more complete charging and decreased risk for Li metal plating.*

- Electrolyte solvents have been identified by NREL that show promise in terms of increased voltage stability and decreased solvation energy with lithium ions.

- Early work has identified mechanisms by which the combination of a high field at the anode surface with the neighboring electrolyte influence the onset of lithium metal deposition under XFC conditions.

X-CEL
eXtreme Fast Charge Cell Evaluation
of Lithium-ion Batteries

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

VEHICLE TECHNOLOGIES OFFICE

TECHNICAL BACKUP SLIDE

Calculated Permittivity over Distance from Anode Surface During Charge (running average over distance from surface)

System: EC-EMC (3:7) + 1.2 M LiPF$_6$

Note that the bulk electrolyte permittivity is already at its true reduced value due to dielectric depression at the bulk salt concentration. The surface charge adds to the overall electronic field experienced by the solvent, and hence further reduces permittivity.

At Surface Charge Density of 10^{-4} C/cm^2
At Surface Charge Density of 10^{-8} C/cm^2
At Surface Charge Density of 10^{-4} C/cm^2, no SEI