WE START WITH YES.

Stabilizing Cathode/Electrolyte Interphase by New Electrolyte Design

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Project ID # BAT374

Overview

Timeline

- Project start: Oct. 1, 2018
- Project end: Sept. 30, 2021
- Percent complete: 60%

Budget

- Total project funding
  - 100% DOE funding
- Funding for FY 2020: $250 K

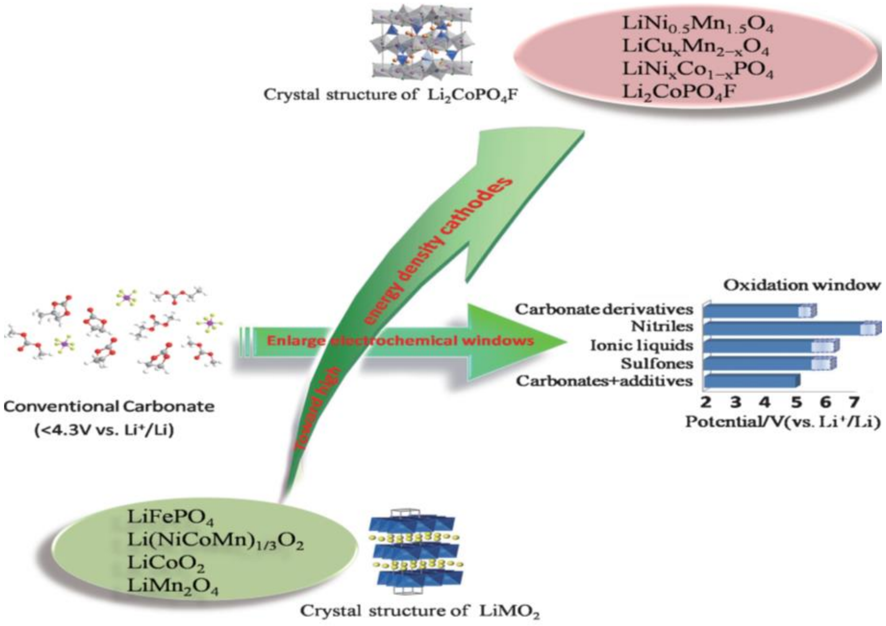
Barriers

- Cycle and calendar life – Next generation high energy density batteries
- Thermodynamic stability at cathode/electrolyte interphase
- Abuse Tolerance

Partners

- Daimler/Mercedes-Benz
- US Army Research Laboratory
- Northern Illinois University
- Argonne National Lab - MERF
- Lydall Performance Materials
- Leading Organization: ANL

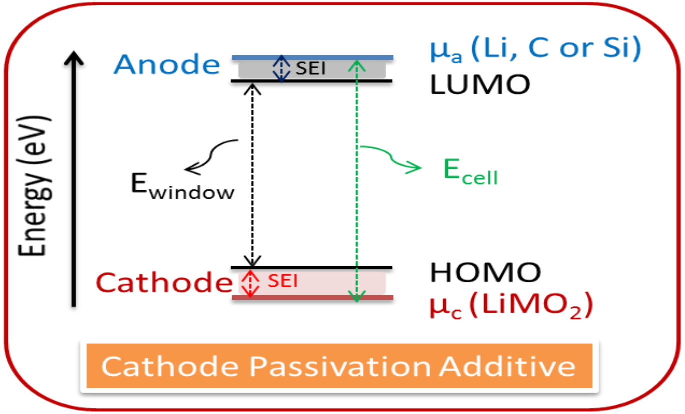
Relevance - Project Objectives



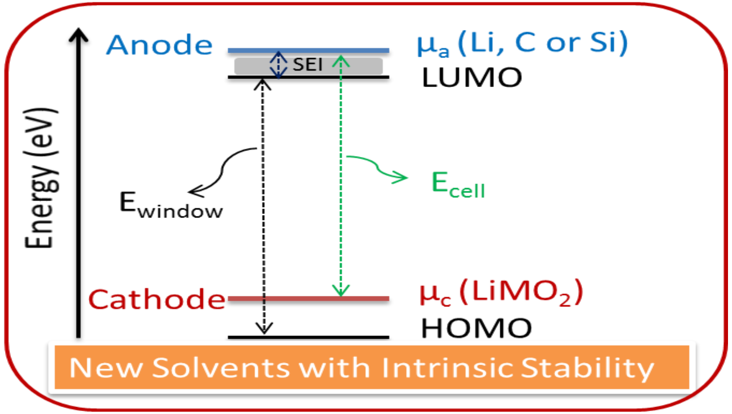
- Next-generation lithium-ion battery requires high-voltage high-energy density for long-range electric vehicle applications.
- Cathode materials with high voltage (> 4.3 V) and high capacity (>200 $mAhg^{-1}$) with low cost are greatly demanded.
- The performance of high-voltage high-energy cells are compromised due to the instable cathode/electrolyte interphase caused by the decomposition of electrolytes and transition metal dissolution-diffusion-deposition cycle.
- The objective of this project is to design and develop stable electrolyte materials that can thermodynamically stabilize the cathode/electrolyte interphase.
- The new electrolyte materials could tolerate high charging voltages (>5.0 V *vs* Li^+/Li) of the Ni-rich, low-Co cathodes and are compatible with other cell components.

Technical Approach and Strategy

Electrolyte Additives



Electrolyte Solvents



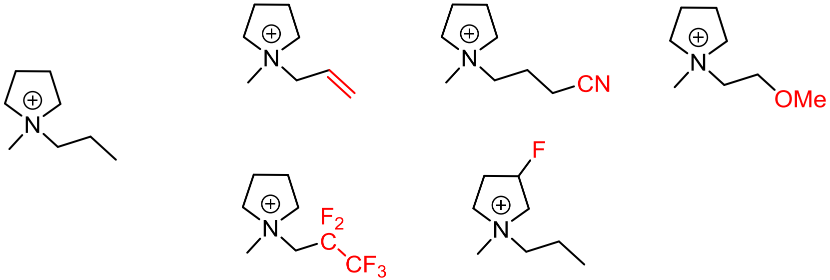
- ✓ Molecular design of additives that could be oxidatively decomposed and deposited on the surface of cathode forming a cathode-electrolyte-interphase (CEI) to provide kinetic stabilization at the cathode/electrolyte interphase at high voltages.

- ✓ Design and develop new electrolyte solvents to provide thermodynamic stability at cathode/electrolyte interphase at high voltages.

Technic Accomplishments and Progress

Design and synthesis of pyrrolidinium-based Deep Eutectic Solvents (DES)

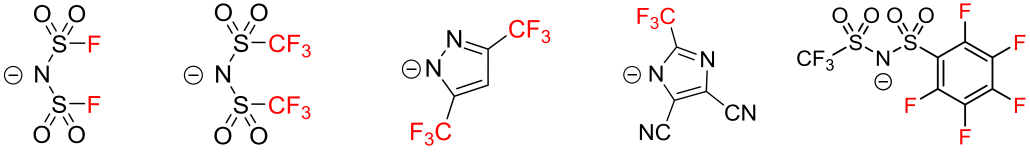
Cation



Improve viscosity
Additives for CEI/SEI

Improve high voltage stability

Anion

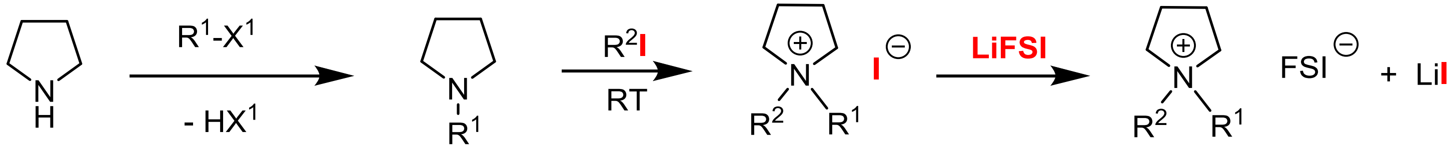


FSI TFSI TFPI TDI FAST

New lithium salts
with organic anions

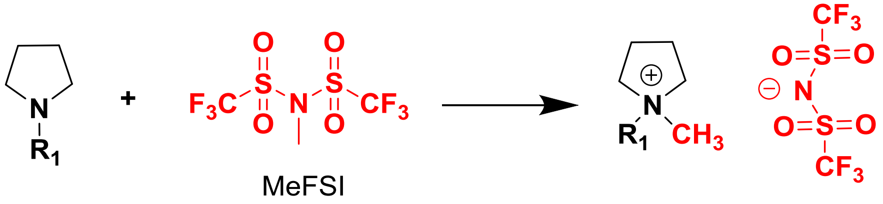
One-Step Synthesis of Functionalized DES: High Purity, Low Cost

Traditional synthesis of ionic liquid (IL):



- Multiple steps, labor intensive
- Possible halide contamination
- Li salt availability and purity

New synthesis of DES: Halide-free

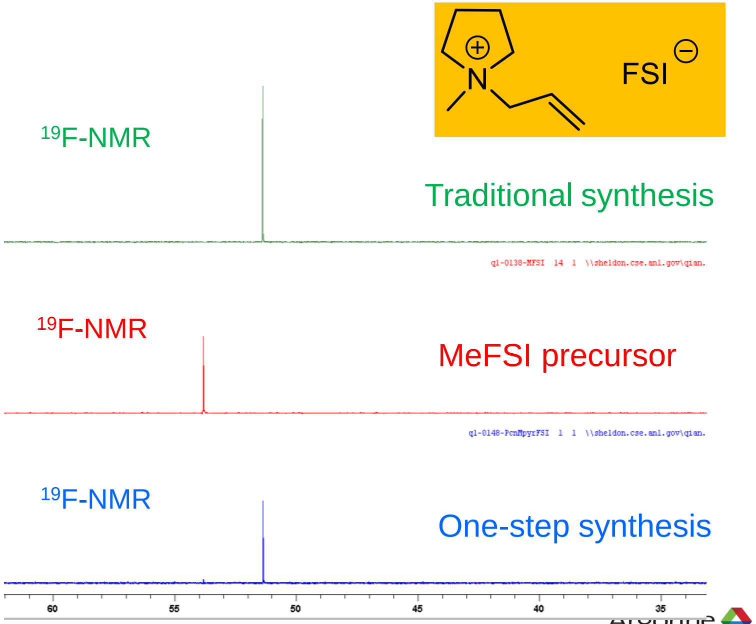


✓ One step synthesis: green chemistry

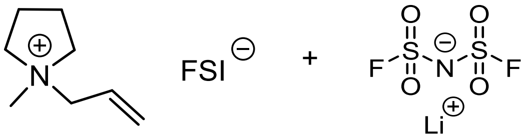
✓ Halide-free synthesis

✓ Ultra-high purity starting material

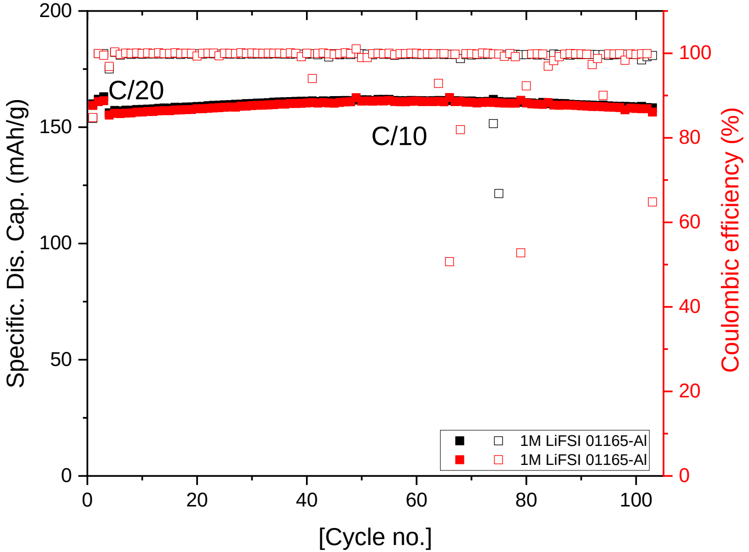
✓ MERF: scale-up of MeFSI

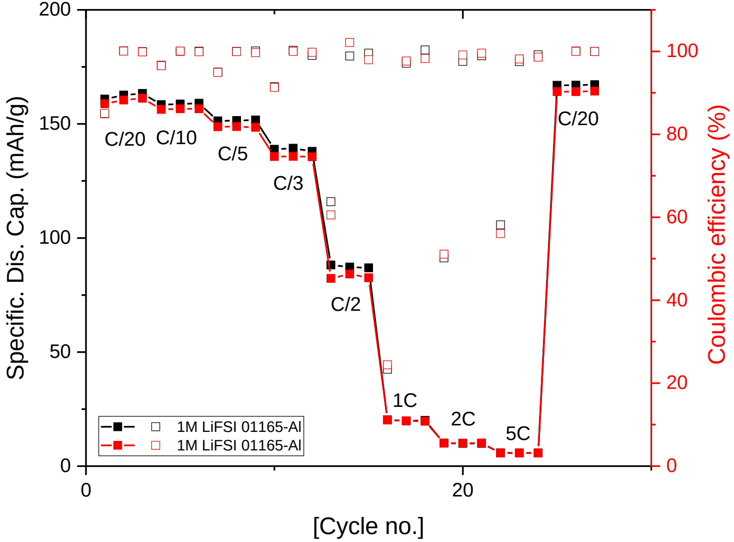


1.1 Allyl-Functionalized DES AMpyrFSI: Rate Capability



- Cell setup: NMC532/Li cells
- Voltage window: 4.3-3.0 V
- Electrolyte: 1 M LiFSI AMpyrFSI





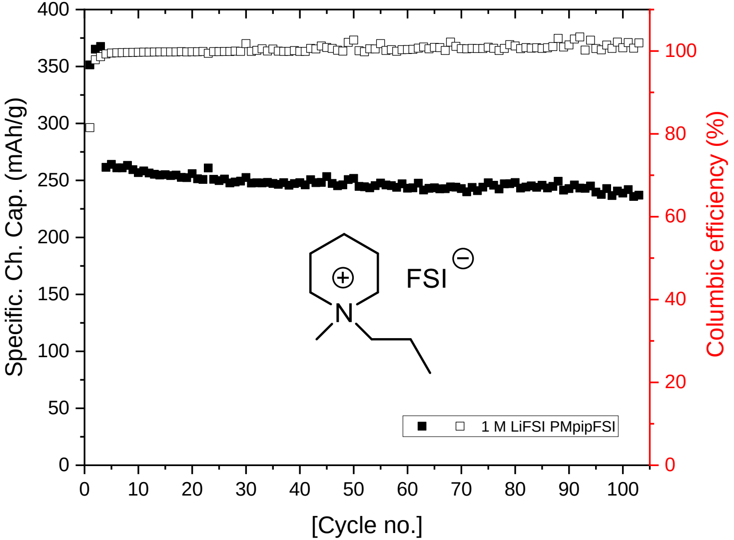
❑ Ally-substituted pyrrolidinium bis(fluorosulfonyl)imide DES (AMpyrFSI) was synthesized by one-step reaction.

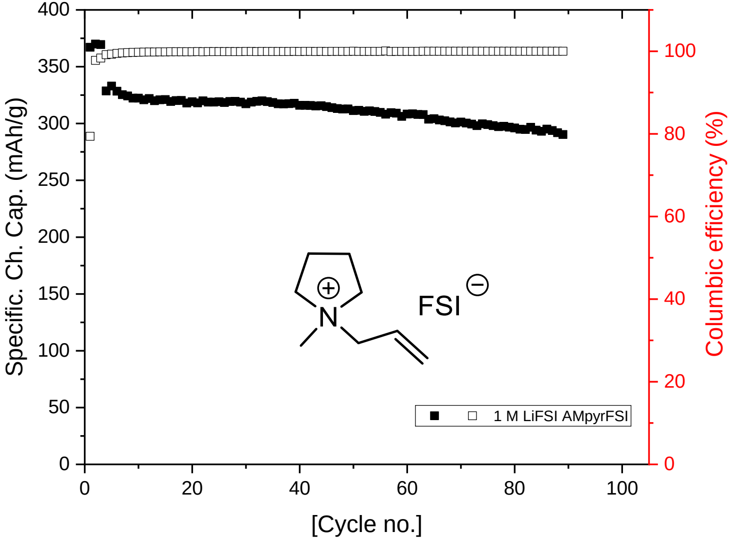
❑ New electrolyte is highly compatible with NMC cathode and Li metal.

❑ The functionalized AMpyrFSI showed improved C-rate capability owing to its lower viscosity and higher conductivity.

1.2 Allyl-Functionalized DES AMpyrFSI: SEI Formation Capability

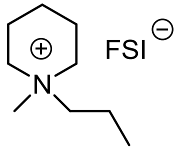
- Cell setup: Graphite/Li cells
- Voltage window: 1.5 - 0.01V
- Electrolyte: 1 M LiFSI AMpyrFSI
- 3 cycles @ C/20, then 100 cycles @ C/10

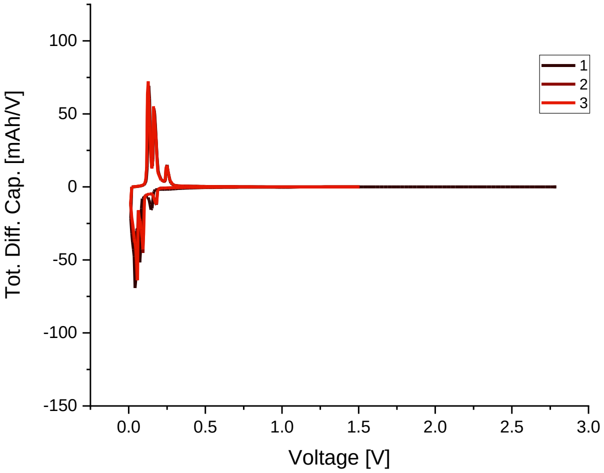


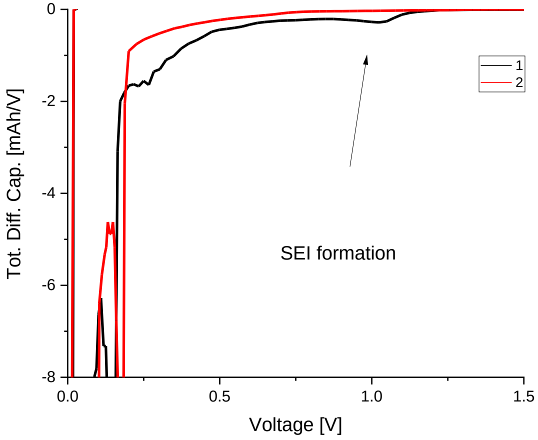


- ❑ Allyl-substituted DES showed improved SEI formation capability on graphite anode.
- ❑ The SEI formed by the reductive decomposition of AMpyrFSI is thinner and less resistive than that formed by the unsubstituted pyrrolidinium DES.

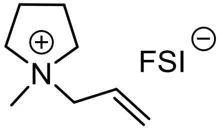
1.3 Allyl-Functionalized DES AMpyrFSI: dQ/dV of Graphite/Li Cell

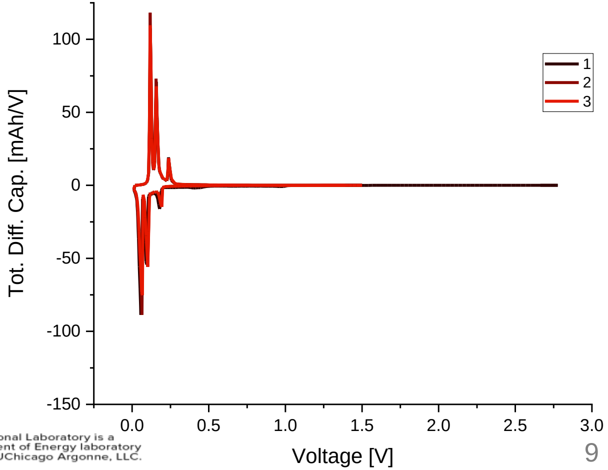


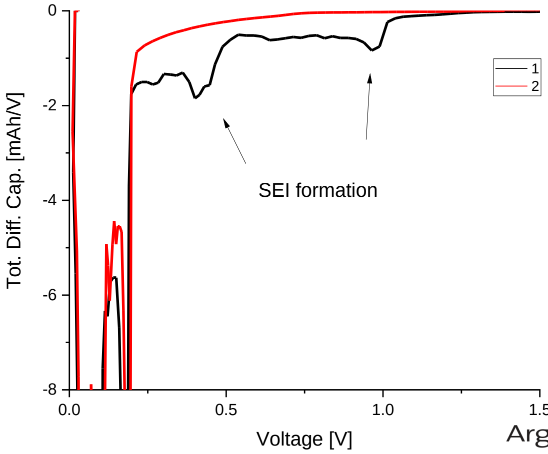




SEI formation



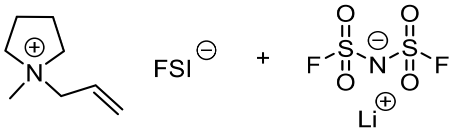


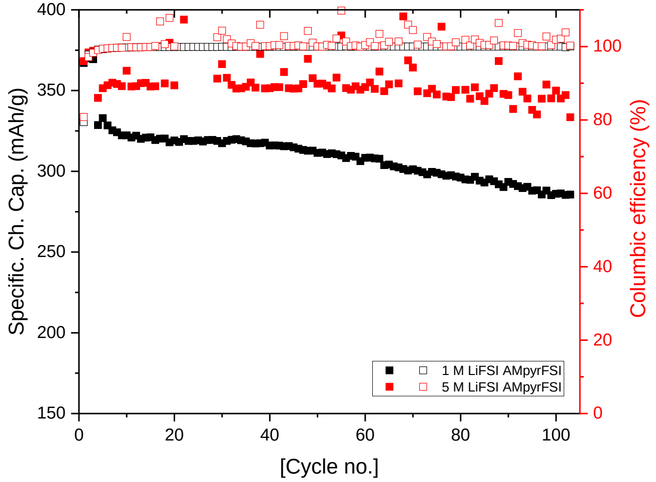


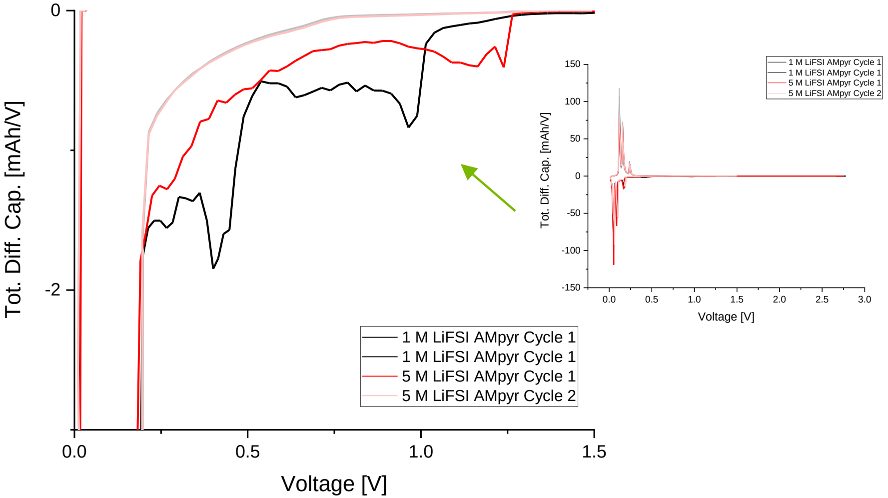
SEI formation

1.4 Allyl-Functionalized DES AMpyrFSI: Salt Concentration and SEI

❑ Cell setup: Graphite/Li half cells
❑ Cycling window: 1.5-0.01 V
❑ LiFSI concentration: 1 M and 5 M

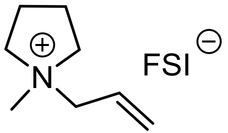




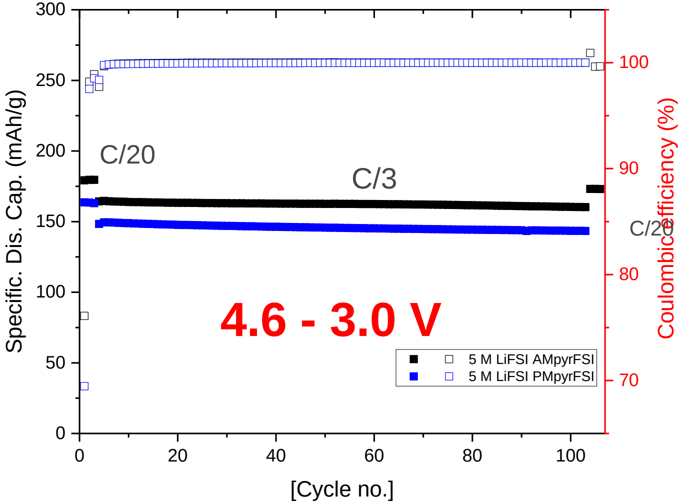

dQ/dV profiles

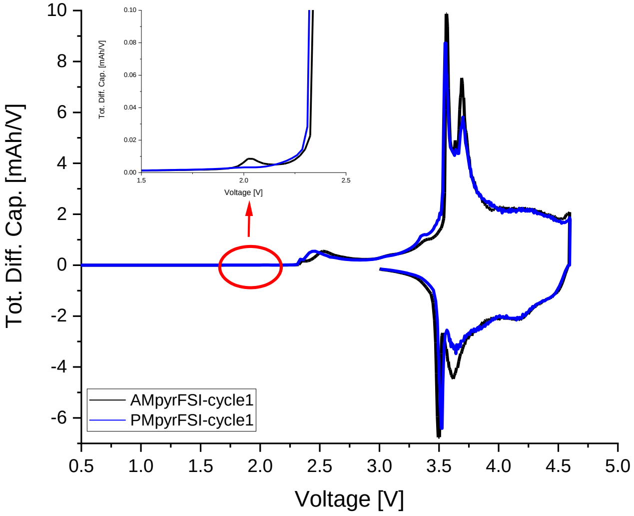
❑ Allyl group also participates in the SEI formation process as observed in 1 M LiFSI AMpyFSI.
❑ High LiFSI salt concentration alter the SEI formation process and helps form a less resistive SEI.
❑ High LiFSI salt concentration improved the initial capacity and capacity retention of graphite/Li cells.

1.5 Allyl-Functionalized DES AMpyrFSI: NMC/Graphite High Voltage Cell Performance



AMpyrFSI *vs* PMpyrFSI

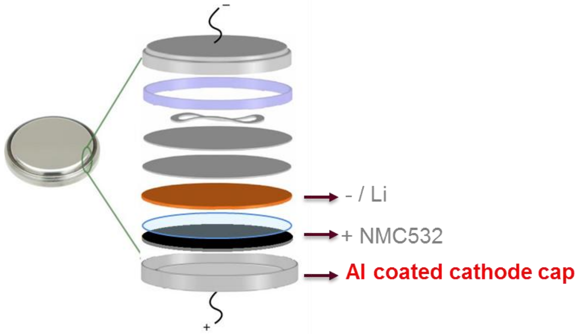


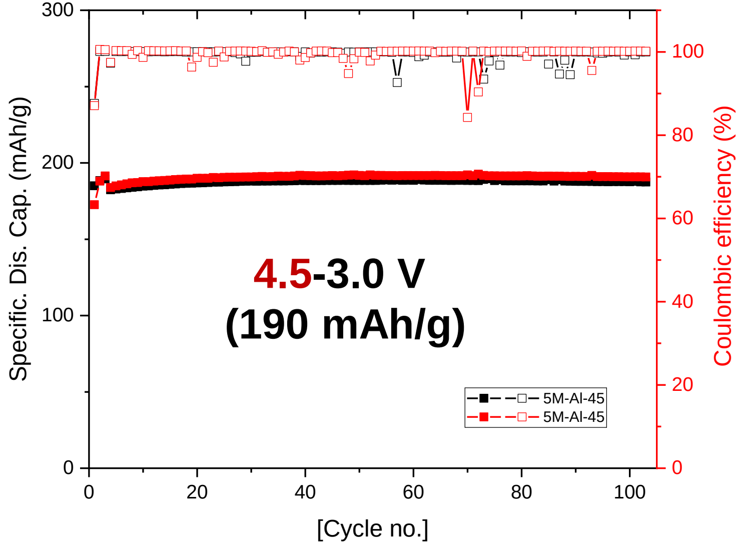


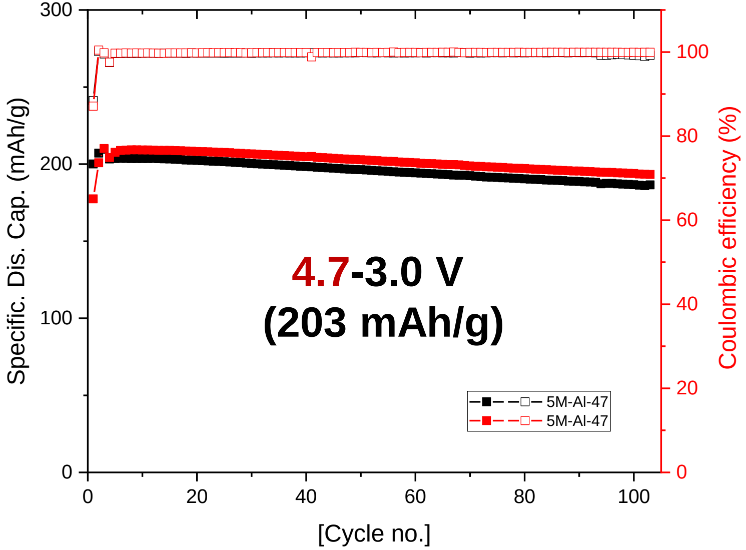
- First cycle Coulombic efficiency: 76% *vs* 69% (AMpyrFSI *vs* PMpyrFSI)
- SEI formation of AMpyrFSI prevents further electrolyte decomposition and active Li$^+$ loss.
- Post-test analysis on cycled graphite anodes is in process (SEM, XPS, ICP-MS).

2. Super Concentrated DES

5 M LiFSI in $PM_{pip}FSI$







- 5 M LiFSI PMpipFSI electrolyte showed exceptional capacity retention with close to 100% CE.
- This electrolyte also supports 4.7 V NMC532/Li cell. However, the rate capability needs to be improved.

2.1 Super Concentrated DES: Effect of Diluent

☐ Super-concentrated FDES shows good cycling stability
☐ Due to the high viscosity, its C-rate capability is low

☐ Design idea: adding appropriate diluent to lower the E_a of the lithium ion transfer:

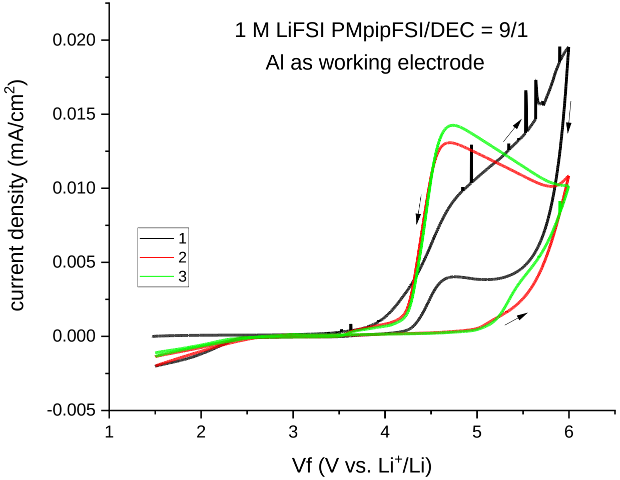
✓ Organic carbonates

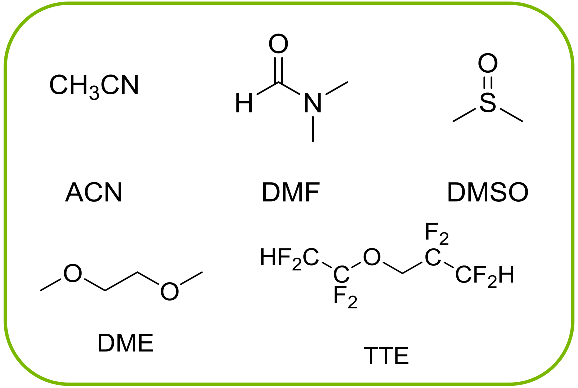
✓ Polar solvents: ACN, DMF, and DMSO

✓ Chelating solvent: DME

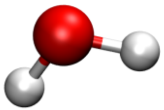
✓ None-solvating solvent: fluorinated ether (TTE)

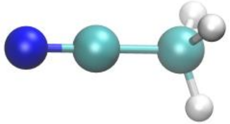
✓ Water (H_2O)

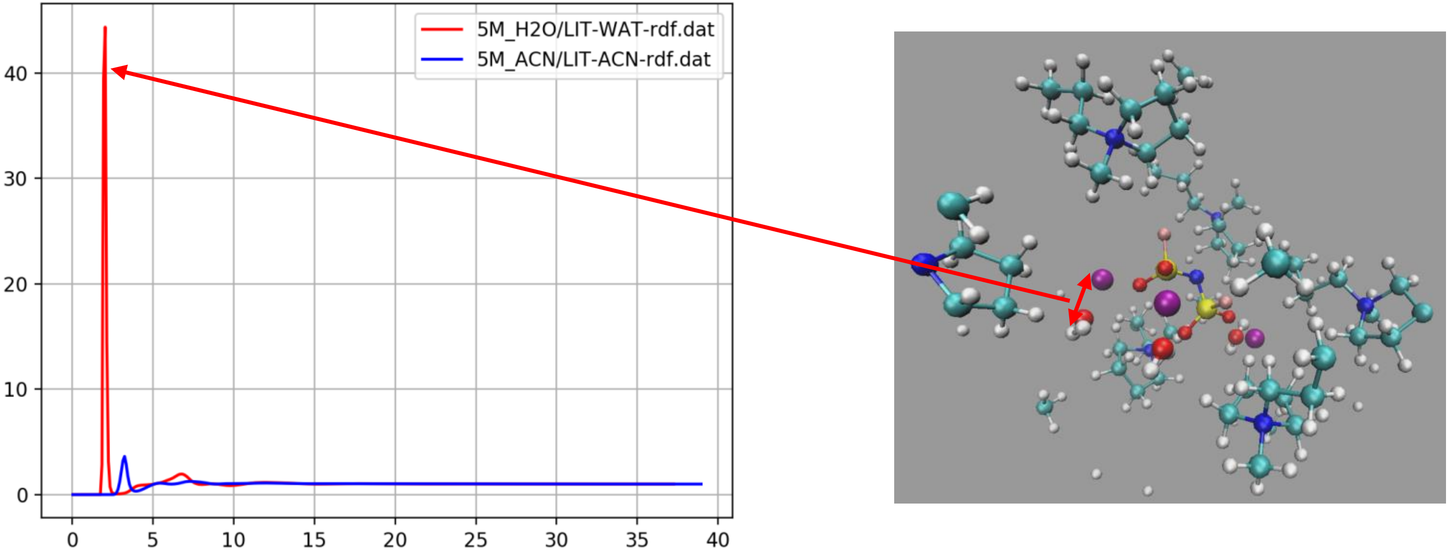




2.2 Super Concentrated DES: MD Simulation of Polar Solvents


Water(H_2O)


Acetonitrile (ACN)

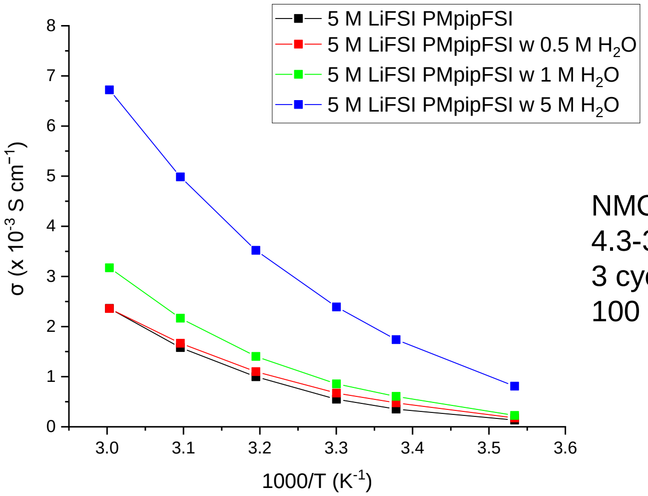


- ☐ H_2O: strong coordination with Li^+; potentially enhances Li^+ transport (high entropy).
- ☐ ACN: weak coordination with Li^+.

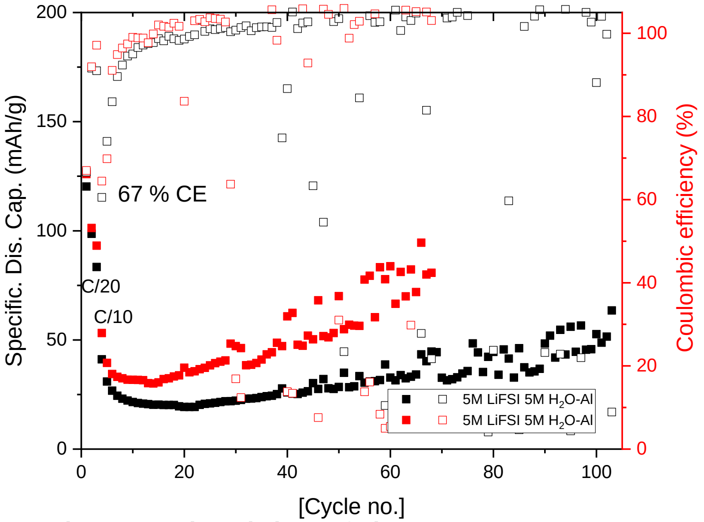
2.3 Super Concentrated DES: H_2O as Diluent with High Concentration

PMpipFSI-H_2O Calculated absolute value

LiFSI \ H2O	5 M	2 M	1 M	0.8 M	0.5 M	0.2 M
1 M	56279 ppm	23298 ppm	11787 ppm	9451 ppm	5928 ppm	2380 ppm
5 M	38339 ppm	15697 ppm	7911 ppm	6338 ppm	3971 ppm	1592 ppm

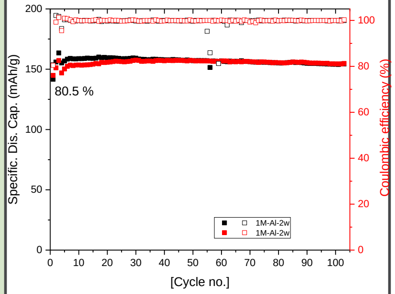
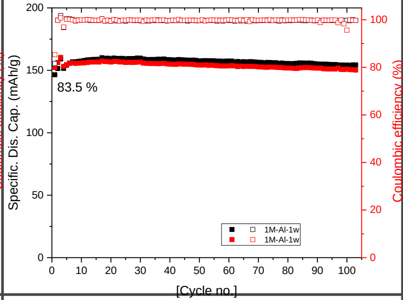
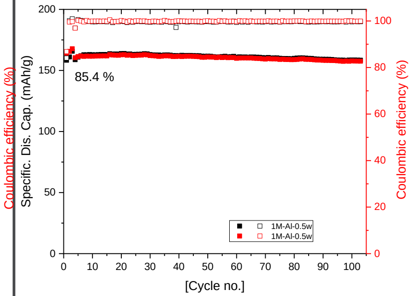
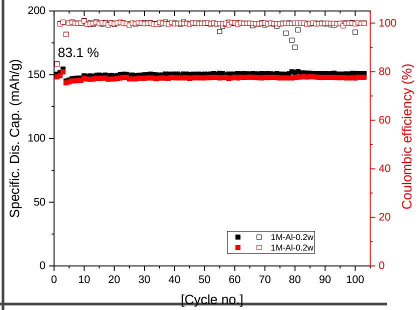
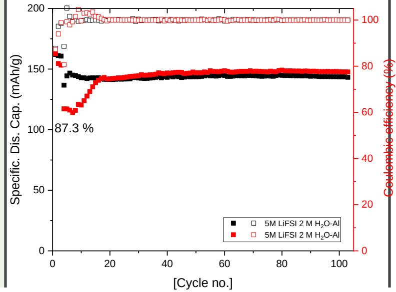
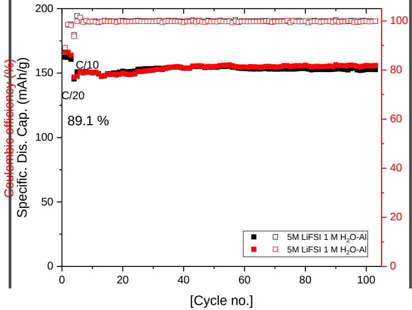
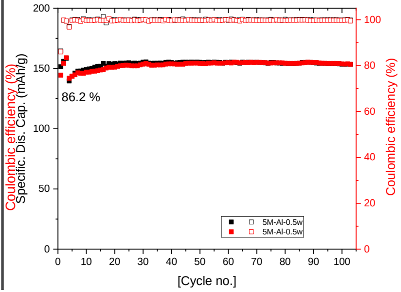
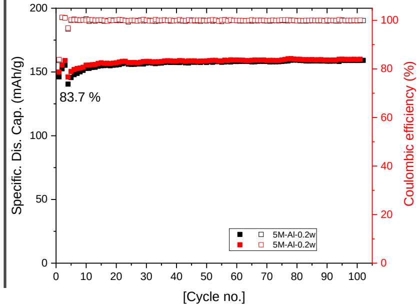


NMC532/Li half cell,
4.3-3.0 V
3 cycle @ C/20 as formation
100 C/10 cycles



- Introduction of H_2O as diluent to 5 M LiFSI PMpipFSI increases the conductivity of the DES.
- However, 5 M H_2O couldn't support stable cycling of NMC532/Li cell.

2.4 Super Concentrated DES: Low Concentration H_2O

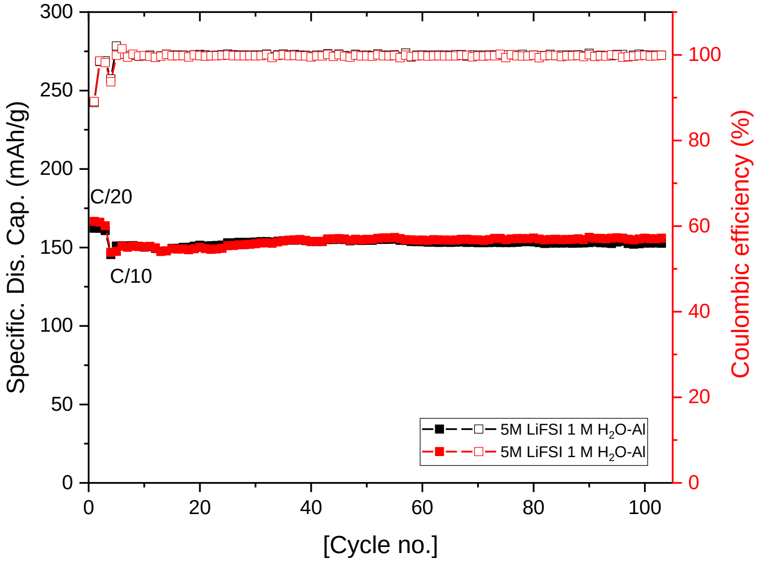
H_2O / LiFSI	2 M	1 M	0.5 M	0.2 M
1 M				
5 M				

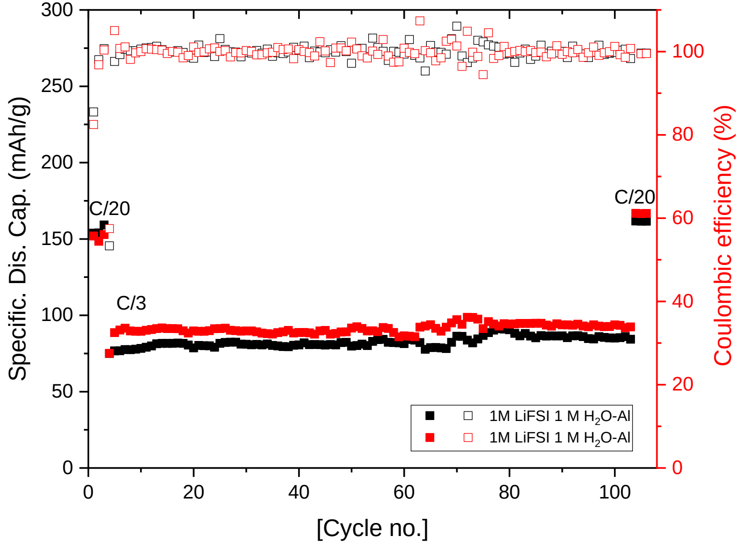
- ❑ With less than 2 M H_2O (< 20000 ppm), NMC532/Li cells perform very similar in 1 M or 5 M LiFSI.
- ❑ 1st cycle CE varies from 80 to 90% with no obvious trend with H_2O concentration or LiFSI concentration.
- ❑ Low concentration of H_2O is compatible with NMC532 cathode and Li anode.

2.5 Super Concentrated DES: H_2O Concentration on Cell Performance

NMC532/Li, 4.3-3.0 V

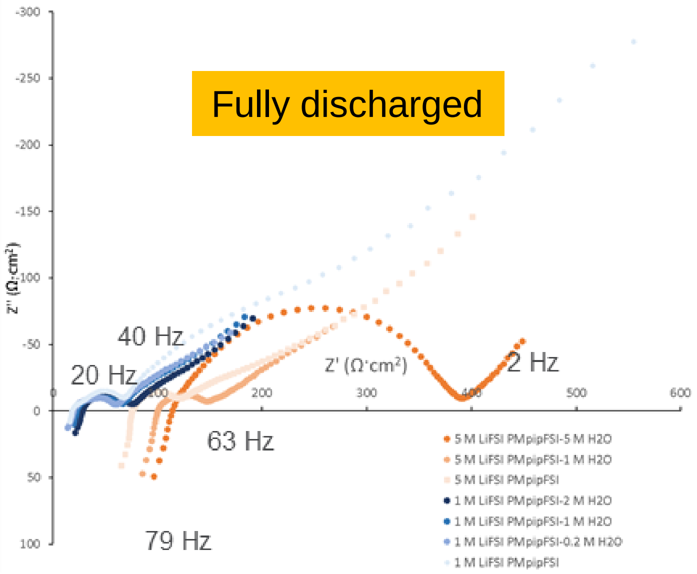
5 M LiFSI PMpipFSI - 1 M H_2O *vs* 1 M LiFSI PMpipFSI - 1 M H_2O

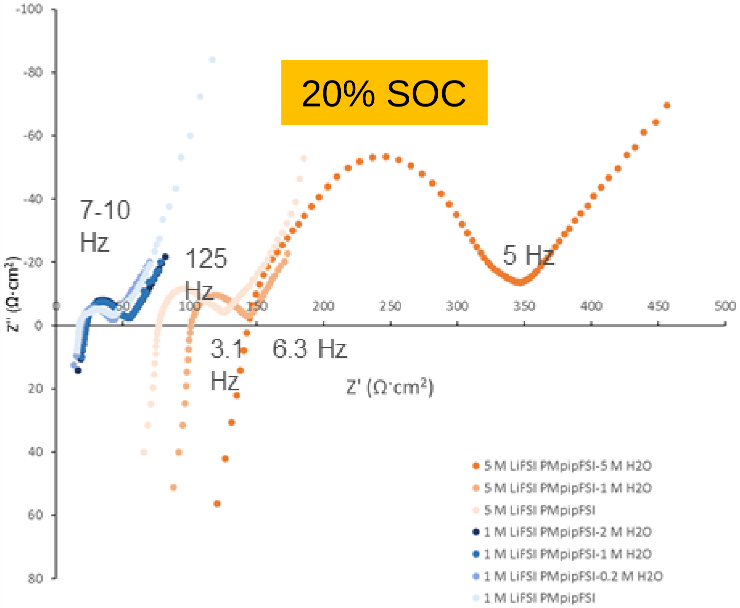




2.6 Super Concentrated DES: Interfacial Impedance (EIS)

- Cells were tested after 100 cycles at two different state of charge (SOC).
  - 5 M LiFSI PMpipFSI with 5 M H_2O: high resistance buildup causes cell failure.
  - With no more than 2 M H_2O (< 20000 ppm), the interface impedance is similar regardless of LiFSI concentration.

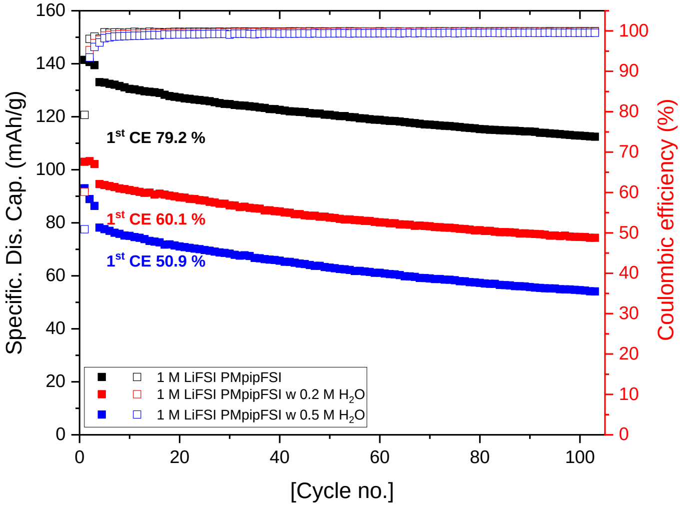




2.7 Super Concentrated DES with H_2O: Full Cell Performance

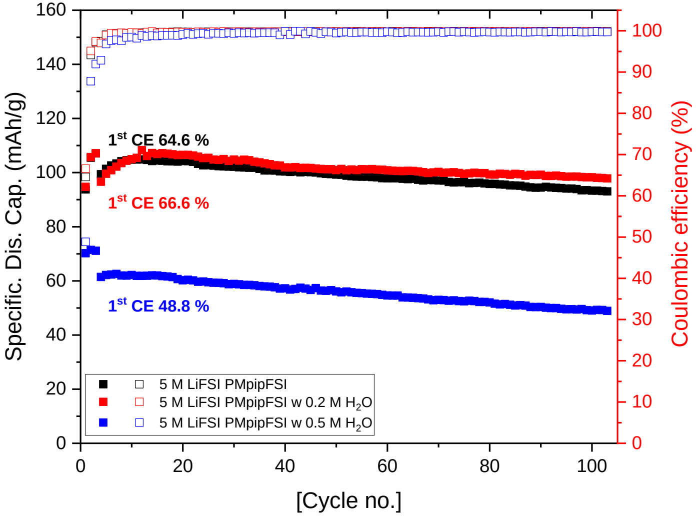
- In NMC532/graphite full cell, H_2O degrades the cycling performance with increased H_2O concentration.
- H_2O decomposition causes active Li trapping on the graphite anode.
- 5 M LiFSI with 0.2 M H_2O showed same cycling stability with that without water.

1 M LiFSI



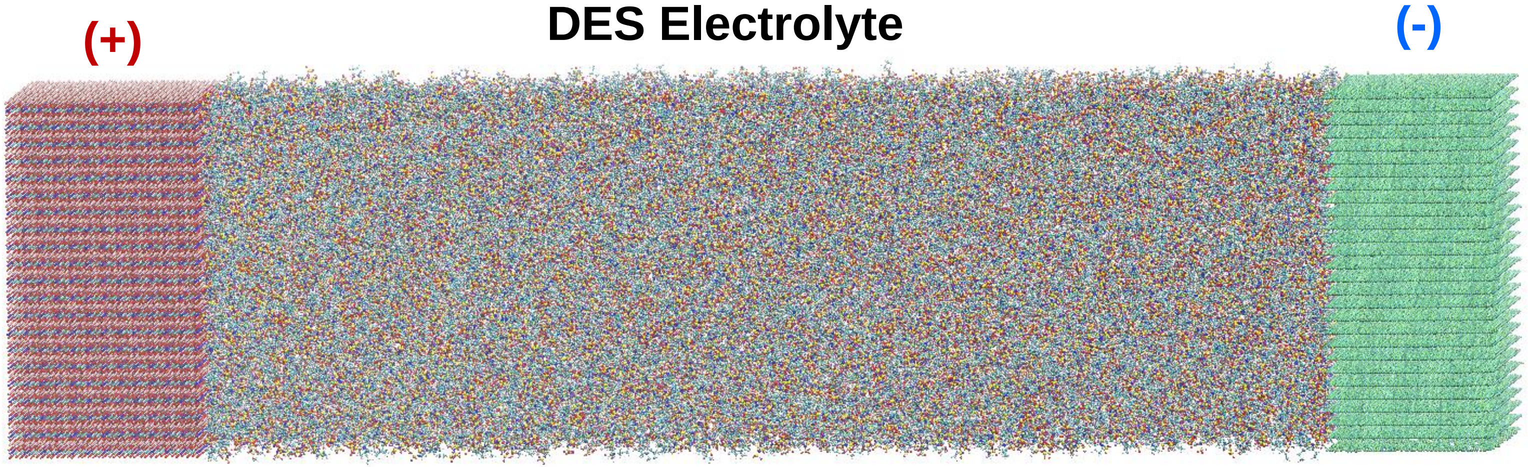
Testing condition:
NMC532/Graphite
4.2-3.0 V
C/20 formation
C/10 cycling

5 M LiFSI



2.8 Super Concentrated DES with H_2O: MD Simulations

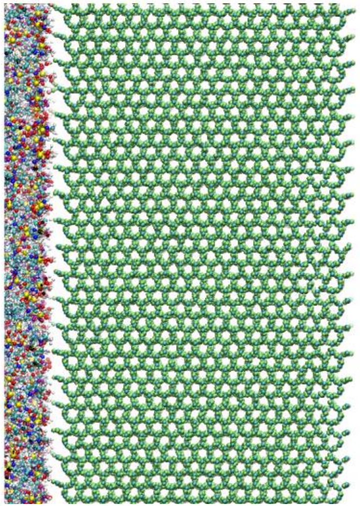
Modeling electrode/electrolyte interface
using real cathode NMC532 and Graphite anode



- **Parameterization**: Partial charges of cathode fitted from electrostatic potential of 2 × 2 × 2 cell with DFT calculation (CP2K); universal Force Field (UFF) for Van Der Waals force of electrodes; GAAMP force field for ionic liquid and lithium ion.
- **Electrolyte phase**: Simulation cell dimension ~300 Å x 100 Å x 100 Å, ~350,000 atoms.
- **Entire cell dimension**: ~500 Å x 100 Å x 100 Å including 100 Å vacuum and 100Å electrodes to make isolated electrode/electrolyte battery system; ~500,000 atoms.
- **MD simulation**: Ensemble run of 16 independent trajectories with NAMD.

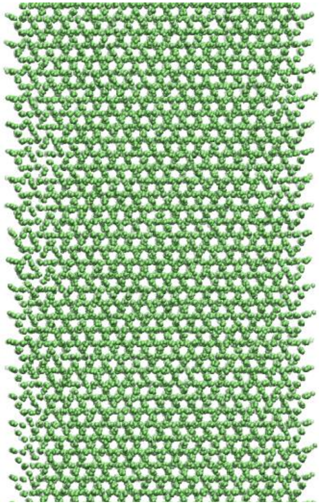
Graphite anode modeling

DES/Graphite



Carbon +
Conduction electrons

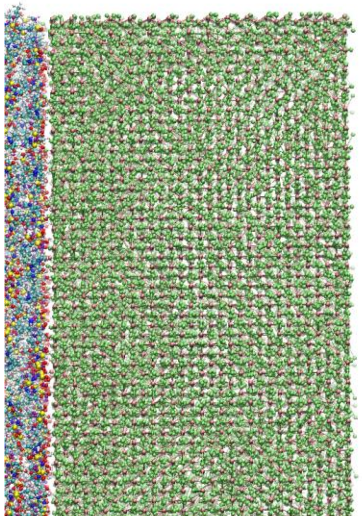
Induced charges on graphite



Conduction electrons

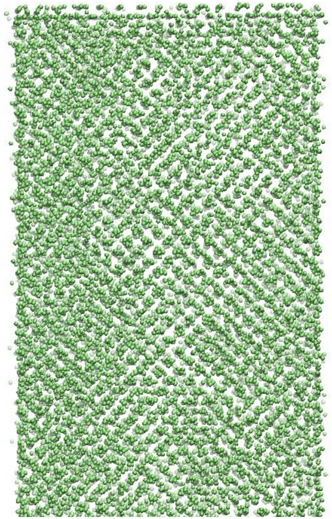
Li-metal anode modeling

DES/Li



Lithium +
Conduction electrons

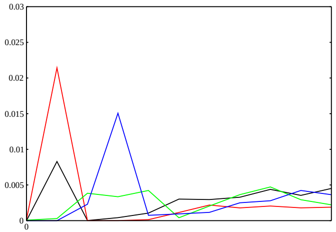
Induced charges on Li



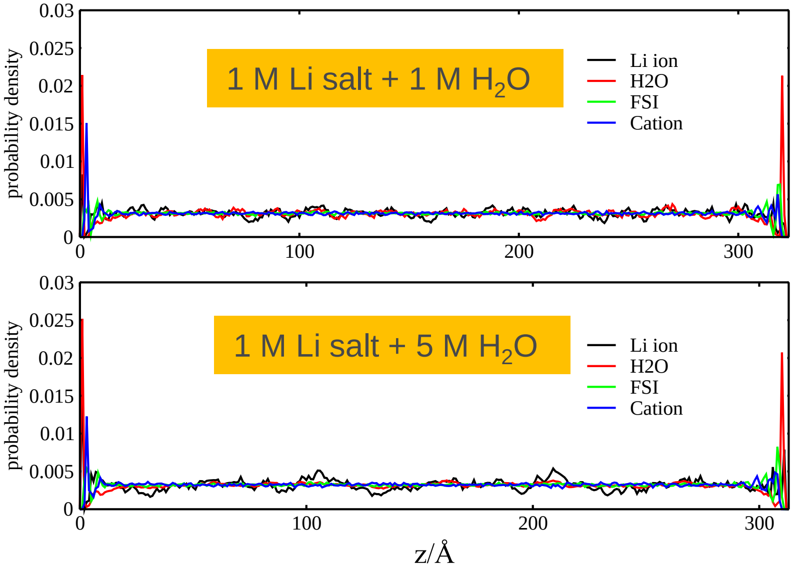
Conduction electrons

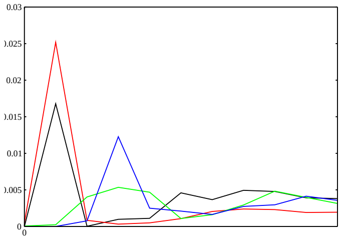
- Polarizable potential for Gr and Li anode that consists of Lennard-Jones potential and a harmonically coupled core-shell charge pair for every metal atom.
- Conduction electrons model surface charge induced by electrolyte at graphite/electrolyte and lithium/electrolyte interface.

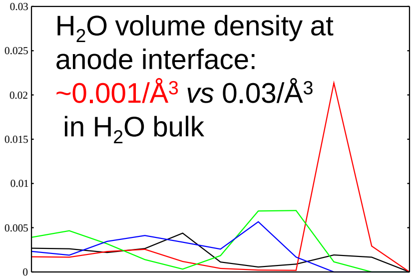
H_2O Effect on Electrode/Electrolyte Interface Structure



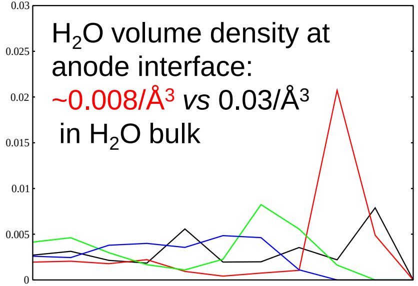
Density distribution profile between cathode and anode



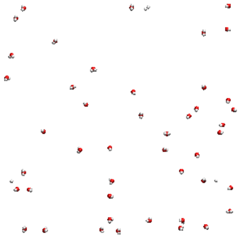




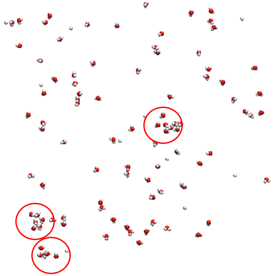
H_2O volume density at anode interface: ~0.001/Å^3 *vs* 0.03/Å^3 in H_2O bulk



H_2O volume density at anode interface: ~0.008/Å^3 *vs* 0.03/Å^3 in H_2O bulk



Snapshot of H_2O



- ☐ DES electrolyte ion distribution at electrode interface: significantly high Li^+ and cation at NMC surface, and high FSI^- density on Gr and Li.
- ☐ H_2O does not considerably affect interfacial structure/distribution of Li^+ and molecular layering of FSI^- & cation, explaining why with increasing H_2O content no considerable benefit for capacity.
- ☐ At 5 M H_2O for either 1 M or 5 M LiFSI, the surface H_2O are agglomerated and its density is close to natural H_2O bulk, causing instability at the surface of the anode.

Responses to Previous Year Reviewers' Comments

(1) The reviewer remarked that, in general, the approach is good as it potentially allows for the drop-in solutions for the industry. Since this is new project, the reviewer suggested it might be a good time to consider objectives that, if met, offer practical solutions. For example, the reviewer proposed first identifying the cathode compositions that offer the highest energy densities at the industry acceptable voltages (safety) and then investigating new electrolyte solutions to improve interface stability and cell's longevity. The reviewer wrote that the concern is that going to high voltages (please define) might be a logical path, but it might not be practical for many reasons for EV applications.

Response: Thanks for this reviewer's comments. Following the reviewer's comments, our plan is to switch from NMC532 to NMC811 as baseline cathode for this electrolyte project. Also, the anode passivation study will switch from Li metal and graphite to silicon. Actually, the compatibility of the new electrolyte with Si anode has started.

(2) Remarking that low-cost halide-free synthesis of LiFSI sounds interesting, the reviewer would like to have heard more about plans on this.

Response: Thanks for the good words on our one-step synthesis method. Since the proprietary one-step synthesis is halide-free with extremely high purity, all the electrolyte solvents will be prepared using this new method. Literature reports contradicting results for the same electrolyte system which might be caused by the purity level of the solvents especially ionic liquid-based and deep eutectic solvent-based.

(3) The reviewer remarked there is excellent work on identifying and addressing challenges associated with the use of the new materials. The reviewer said it will be interesting to see if there is a dependency of the transition-metal dissolution as a function of composition (Ni-content) versus the standard electrolyte used today.

Response: Thanks for this reviewer's suggestion. The transition metal dissolution was deeply suppressed by using the DES-based electrolyte compared with the standard electrolytes due to its highly ordered structure at high salt concentration and lack of solvation power to dissolve TM ions.

Collaboration and Coordination with Other Institutions

Dr. Jason Croy – Argonne National Laboratory, *Cathode materials*

Dr. Wei Jiang – Argonne Leadership Computing Facility, *MD simulation*

Dr. Krzysztof Pupek – Argonne National Laboratory, *DES Precursor*

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

Dr. Tao Xu – Northern Illinois University, *Self-assembled monolayers*

Dr. Peter de Wit – Lydall Performance Materials (Netherlands), *Separator*

Dr. Caroline Cloutier – Daimler AG, *Performance validation*

Remaining Challenges and Barriers

- ✓ Sluggish Li^+ transport in super-concentrated deep eutectic solvent-based electrolytes, and still low C-rate or power capability.
- ✓ Resilient SEI formation on the graphite anode by the reductive decomposition of tailored functional groups of DES electrolytes.
- ✓ SEI with low interfacial impedance and fast Li^+ transport kinetics.
- ✓ Mechanism of ion transport at the electrode/electrolyte interface and in the bulk for the DES with various diluents.
- ✓ Discovery of new DES-based electrolytes that are highly pure, low cost, and high-voltage stability in high energy EV batteries.

Proposed Future Research

- Continue studying the high voltage stability of allyl-functionalized AMpyrFSI DES based electrolyte in Li-ion cells using high nickel NMC811 cathode and 5-V LNMO spinel cathode coupled with a silicon or Si/graphite anode.
- Post-test analysis of the cathode-electrolyte-interface (CEI) and graphite SEI formation using HRTEM, FT-IR, XPS.
- Design and synthesize DES with new functional groups that could lead to low viscosity, high Li^+ transference number, capability of SEI formation, and high power performance.
- Continue to investigate super concentrated DES electrolyte with H_2O as diluent with a target to enable the high voltage cell using a graphite anode.
- Analyze the exposure time of the super concentrated electrolyte in open air and validate its electrochemical performance in full cell.
- Post-analyze the impact of H_2O on the interfacial stability using SEM/EDS, depth-profiling XPS and HRTEM.
- Continue to investigate and simulate super concentrated DES electrolytes with other diluents especially at the electrode interface and the correlation with its electrochemical performance.

Summary

- Ally-substituted pyrrolidinium bis(fluorosulfonyl)imide DES (AMpyrFSI) was synthesized by one-step reaction; the new electrolyte is highly compatible with NMC cathode, Li metal anode and graphite anode.
- The functionalized AMpyrFSI showed improved C-rate capability owing to its lower viscosity and higher conductivity and improved SEI formation capability on graphite anode.
- The SEI formed by the reductive decomposition of AMpyrFSI is thinner and less resistive than that formed by the unsubstituted pyrrolidinium DES. SEI formation of AMpyrFSI prevents further electrolyte decomposition and active Li^+ loss.
- Introduction of H_2O as diluent to 5 M LiFSI PMpipFSI increases the bulk electrolyte conductivity. However, 5 M H_2O couldn't support stable cell cycling in NMC532/Li cell.
- With less than 2 M H_2O (< 20000 ppm), NMC532/Li cells perform very similar in 1 M LiFSI or 5 M LiFSI PMpipFSI.
- 1st cycle CE varies from 80 to 90% with no obvious trend with H_2O concentration or LiFSI concentration; low concentration of H_2O is compatible with NMC532 cathode and Li anode.
- H_2O does not considerably affect interfacial structure/distribution of lithium ion and molecular layering of FSI and cation, explaining why with increasing H_2O content no considerable capacity gain.
- Interface structure of DES + lithium salt: significantly high lithium ion density at cathode surface; high cation density on cathode surface; high FSI (anion) density on anode surface.
- At 5 M H_2O for either 1 M or 5 M lithium ion electrolytes, the high surface density of H_2O close to natural H_2O bulk, tending to break formation of SEI, and react with surface Li metal.