Electrolytes in Support of 5 V Li-ion Chemistries

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Overview

Timeline

- Start: Sep 2008
- End: Sep 2011
- 80 % complete

Budget

- Total project funding
  - DOE $600K
- Funding received in FY08/09
  - $400K
- Funding for FY10
  - $200K

Barriers

- SOA electrolytes based on Carbonate Solvents decompose below 4.5 V;
- Sulfone-based solvents showed anodic stability up to 5.8 V but:
  - SEI chemistry from reduction of sulfones does not provide protection of graphitic anodes
  - Most sulfones are viscous liquids with m.p. near RT.
- Lack of a reliable 5 V cathode as characterization platform.

Partners

- Argonne National Laboratory
- SAFT Batteries
- Rutgers University

Milestones

- **Sep 2009:**
  - **Synthesize sulfone based solvents with and without unsaturated bonds and evaluate their electrochemical properties**
  - **Synthesize ARL proprietary additives for both sulfone- and carbonate-based electrolytes**
- **Sep 2010:**
  - **Formulate new electrolyte compositions**
  - **Explore additives that passivates cathode surfaces at high voltages**
  - **Diagnostic studies: surface characterization and SEI chemistry**

Objectives

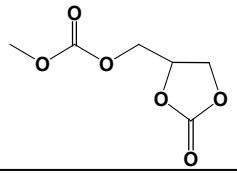
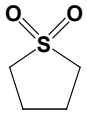
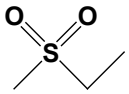
- **Develop high voltage electrolytes that enable the dreamed 5 V Li Ion Chemistry**
  - **Energy density:**
    - **New chemistries for HEV/PHEV**
  - **“Energy Quality”:**
    - **Energy form**
    - **Conversion efficiency**
    - **Potential at which energy is delivered**

Approach

- **Sulfone-approach**
  - Synthesize and characterization of unsymmetric and unsaturated sulfones
  - Formulate electrolytes using sulfones as co-solvents and additives
- **Carbonate-approach**
  - Synthesize and characterization of ARL-proprietary compounds
  - Formulate electrolytes using ARL-proprietary compounds as co-solvents and additives
- **Electrochemical characterization of new electrolytes on various 5 V cathode surfaces**

Technical Accomplishments

- **Synthesized new sulfone solvents and ARL-proprietary additives.**

Solvent	Structure	Melting Point (oC)	Boiling Point (oC)	LUMO* (eV)	HOMO* (eV)	Reduction Potential (vs. Li+/Li)	Oxidation Potential (vs. Li+/Li)
LLC		80		0.87/0.72	12.95/12.89	1.33±0.11	7.85±0.04
ARL1~5							
SL		35		0.87/0.65	11.55/11.58	1.34±0.02	6.23±0.03
EMS		36.5		0.90/0.72	11.87/11.66	1.26±0.02	6.32±0.03

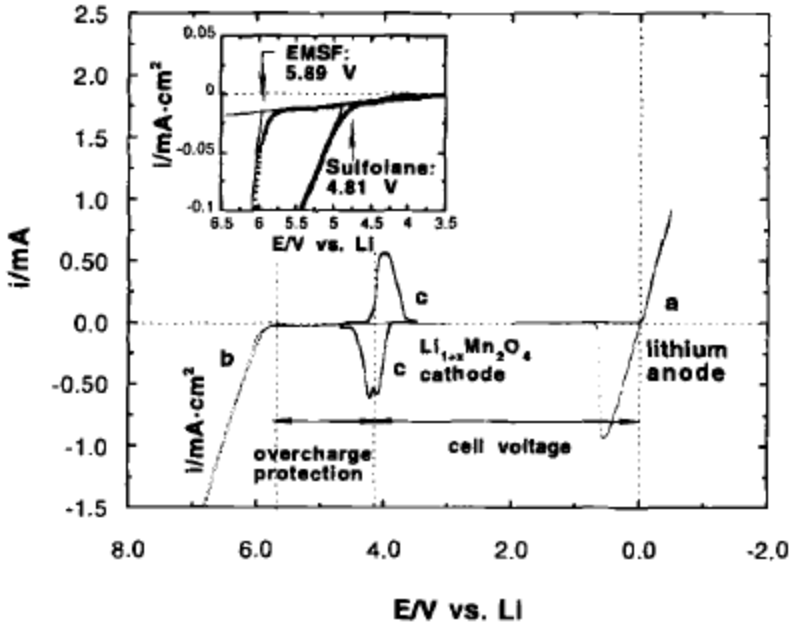
*** LUMO/HOMO and projected decomposition potentials were computed by Prof. J. Klauda at UMD**

Technical Accomplishments

- Over 80 electrolyte compositions formulated and evaluated on a 5 V cathode
- Incremental improvements with sulfone-based electrolytes
- Significant improvements with carbonate-based electrolytes using ARL-additives
- Challenges:
  - Absence of a reliable 5 V cathode surface
  - NCA and NMC (as surrogate cathodes)
  - $LiCoPO_4$
  - Spinel $LiNi_{0.5}Mn_{1.5}O_4$

Approach 1: Sulfone-based

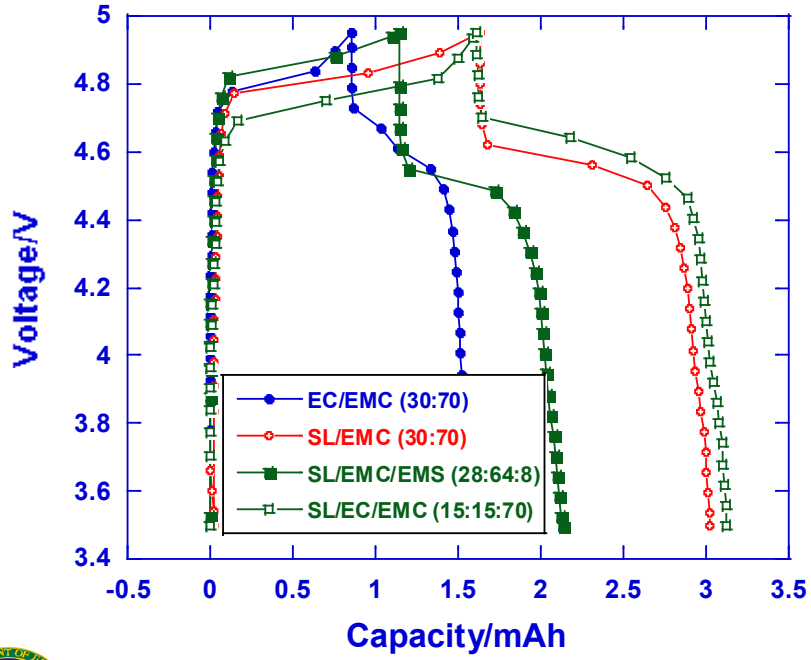
- **Carbonate solvents oxidatively decompose below 4.5 V**
  - **Depending on cathode surface**
  - **Data collected on non-porous electrodes unreliable**
- **Sulfone exhibited highest anodic decomposition limit:**
  - **5.8 V on spinel $Li_{1+x}Mn_2O_4$**
  - **Linear sweep on composite cathode surface**
    - **step forward than non-porous surfaces**
    - **But not sufficient to meet the high standard for battery cycling**

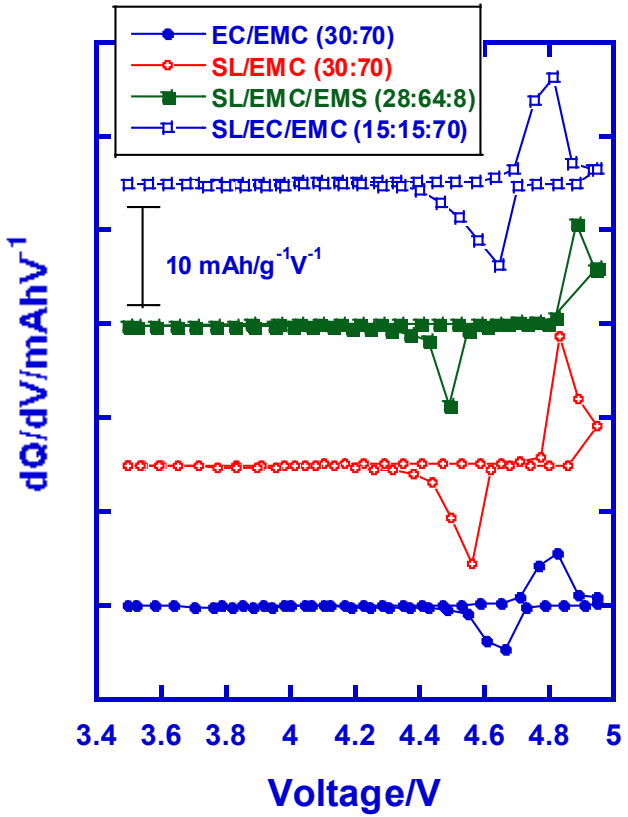


K. Xu, C. A. Angell, JES, 1998, 145, L70

Approach 1: Sulfone-based

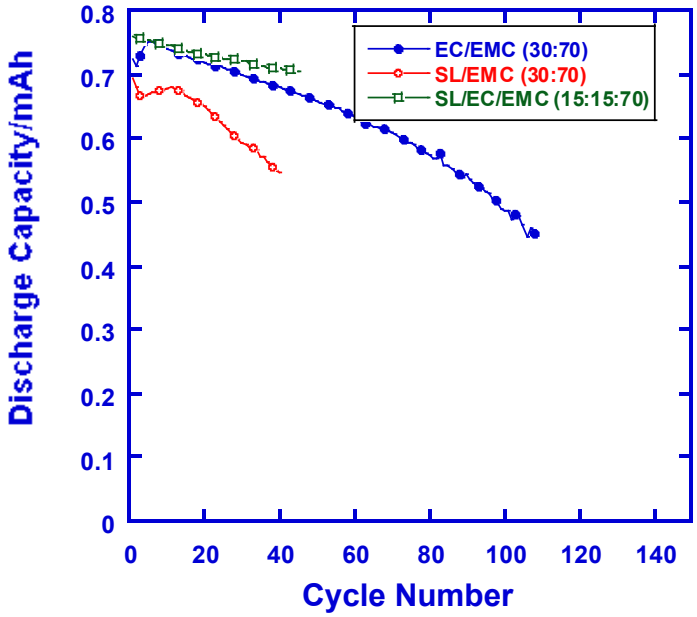
- Formulations with SL as co-solvents replacing carbonates
- Voltage profile on Spinel $LiNi_{0.5}Mn_{1.5}O_4$ showed expected redox couple around 4.7 V
- Large voltage hysteresis associated with SL due to high impedance
- EC still an indispensable component

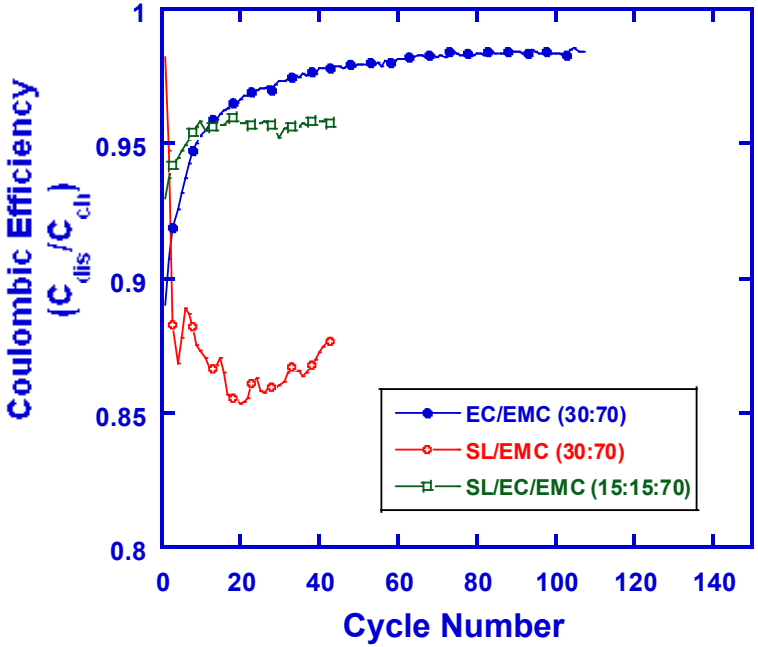




Approach 1: Sulfone-based

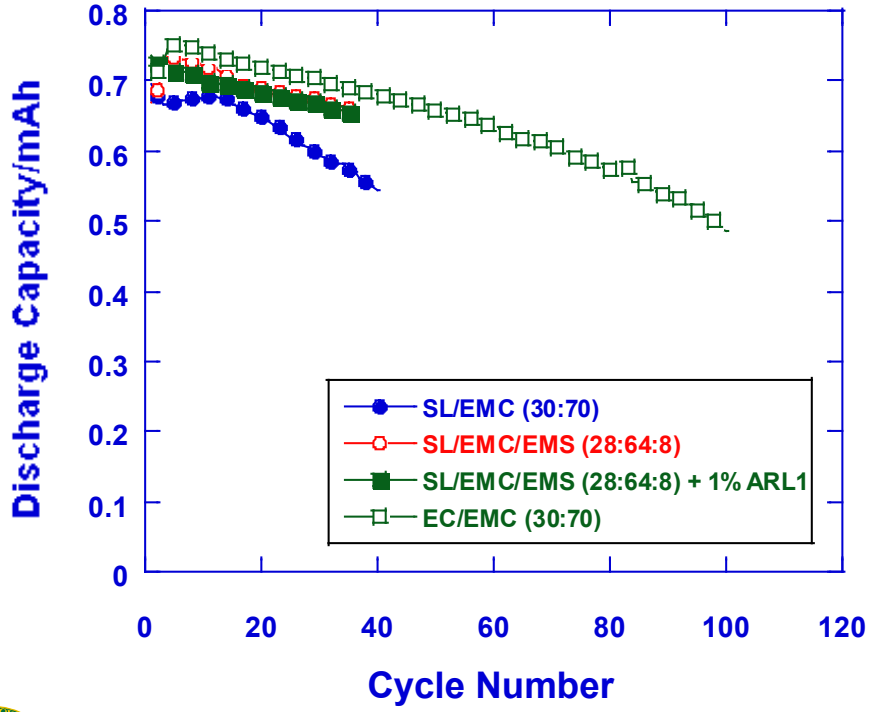
- Capacity in all cases fades rapidly upon cycling
  - Coulombic efficiency < 1.0 indicating sustaining oxidation of solvents
  - Anodic stability at >4.5 V a severe challenge
- SL/EC/EMC performs better than others
  - Co-presence of SL and EC might contribute to the passivation of cathode surface
  - None of the compositions tested meets expectations

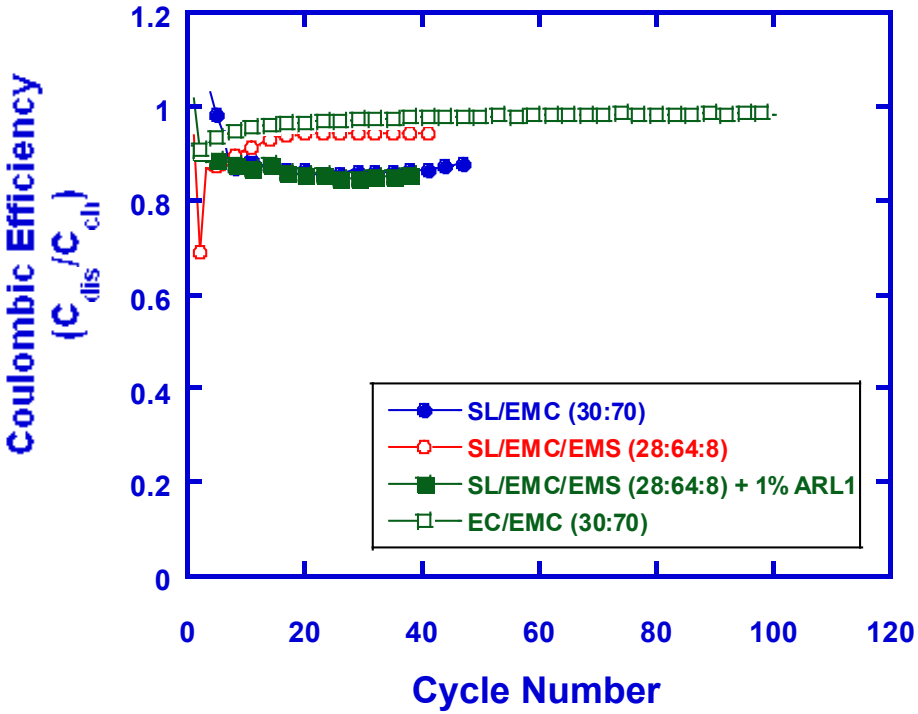




Approach 1: Sulfone-based

- **Effect of EMS and additive ARL1**
  - **Presence of EMS seems to help stabilize cathode surface**
  - **Improved capacity retention and Coulombic efficiency ~ 1.0 indicating mitigated solvents oxidation on cathode**
  - **None of the compositions tested meets expectations**

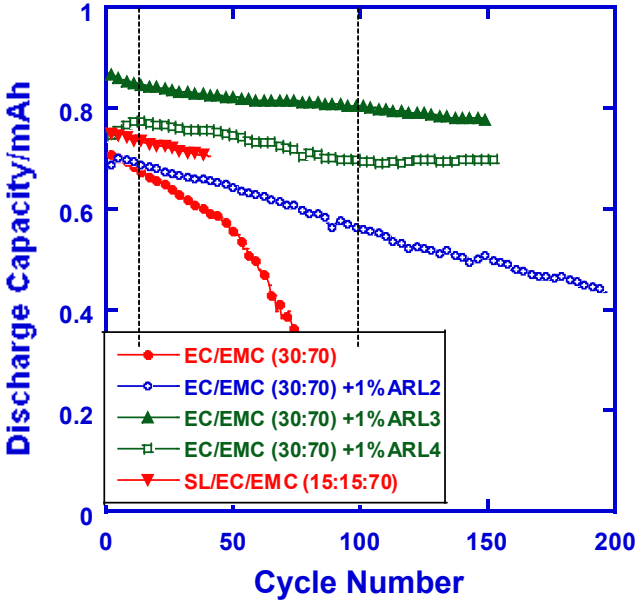


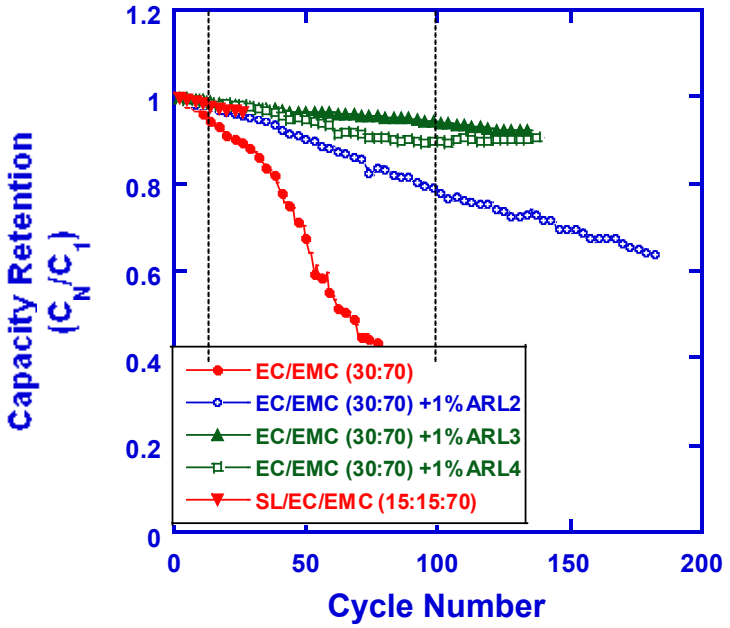


Approach 2: Additive-based

5 ARL additives in Base Formulation 1.0 m $LiPF_6$/EC/EMC (30:70)

- Base formulation with high EMC ratio for low temperature
- ARL additives kept at 1% wt
- Various degree of improvement
- ARL3 out-performs all other additives
  - Small voltage drop indicating less resistive SEI
  - Slow capacity fading (7% capacity loss at 80th cycle vs. ~50% for base formulation)

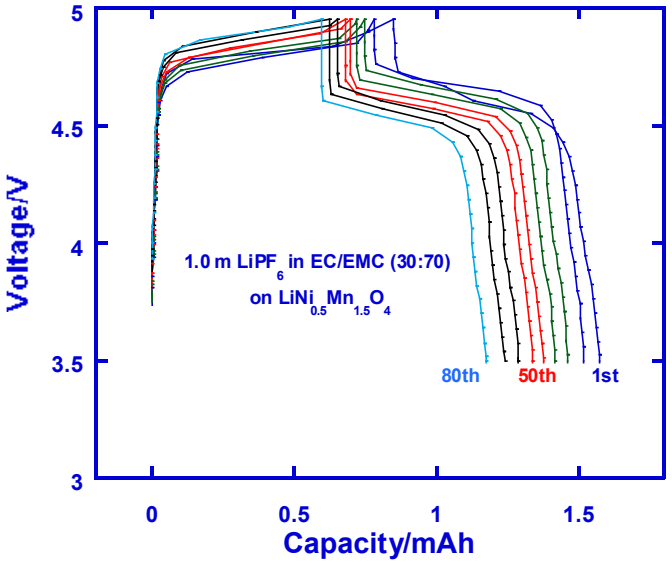


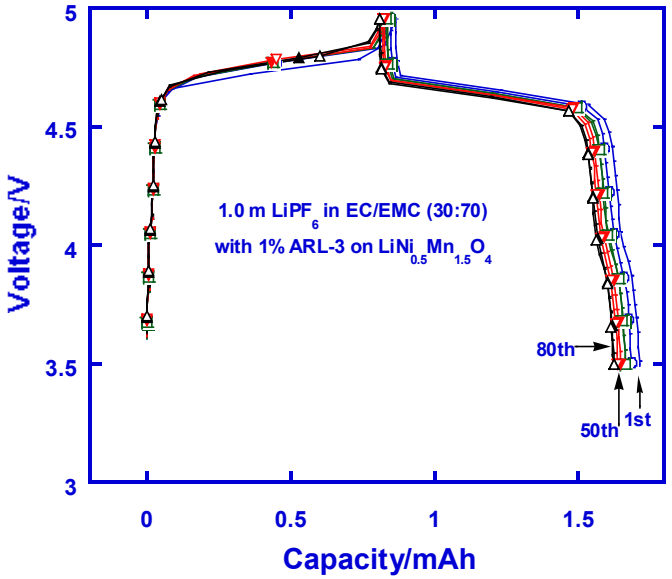


Approach 2: Additive-based

Only 1% ARL3 in Base Formulation 1.0 m $LiPF_6$/EC/EMC (30:70) makes significant difference

- Higher capacity utilization
- Smaller hysteresis between charging/discharging processes
- Much slower fading rate



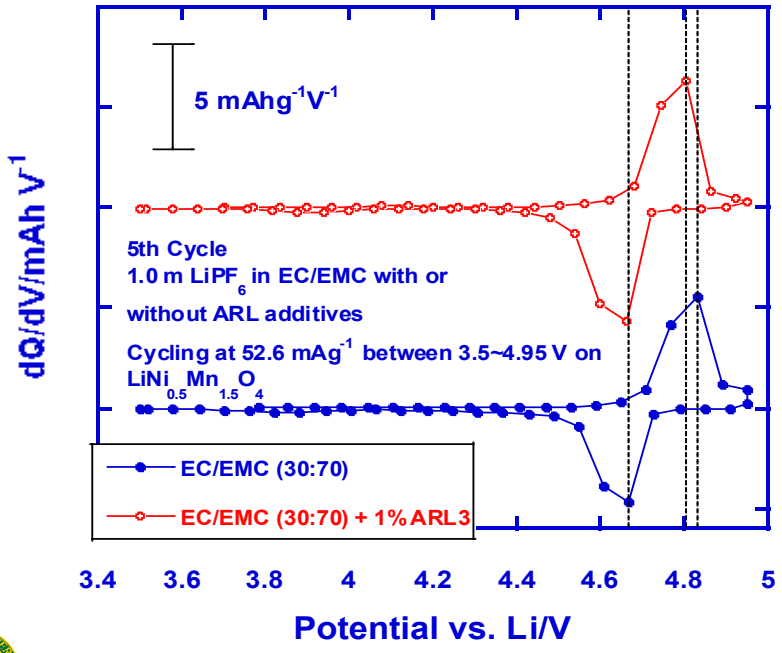


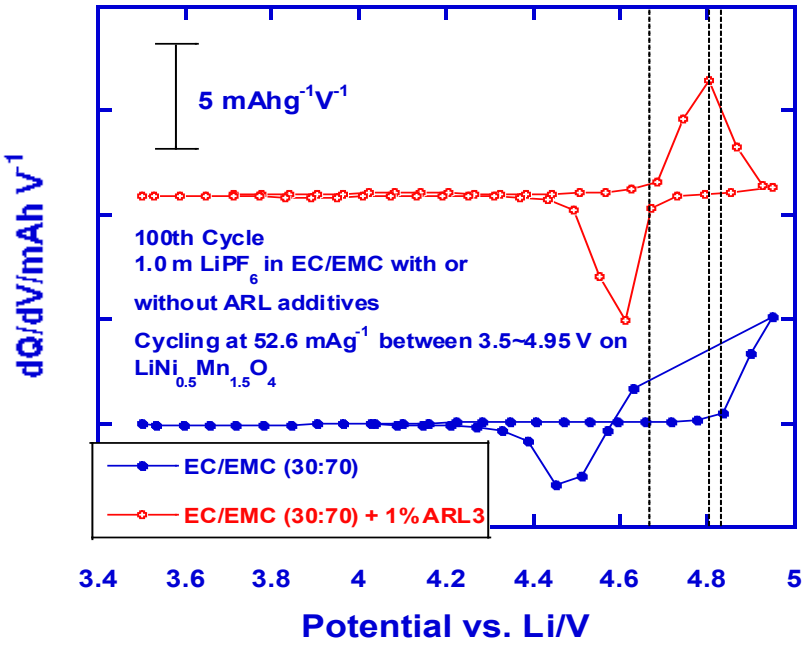
ARL3 must be involved in a novel interphasial chemistry to stabilize $LiNi_{0.5}Mn_{1.5}O_4$ surface

Approach 2: Additive-based

Differential capacity vs. Voltage Plots

- 2 separate peaks corresponding to Ni^{2+}/Ni^{4+} redox chemistry
- Little difference at early cycles between control electrolyte and ARL3-containing electrolyte
  - Smaller peak separation with ARL3 presence
- Pronounced difference at 100th cycle





Future Work

- **Optimization of carbonate-based electrolytes**
  - **Focuses on performances at elevated temperatures**
  - **Studies on impedance in combination of interphasial chemistries**
- **Characterization and diagnostic studies**
  - **XPS, XRD, EIS, SEM/TEM**
- **Design and synthesis of new ARL additives**
  - **Further improvements are expected with new additive structures**

Summary

- **Advances have been made in the efforts to develop high anodic-stability electrolytes with sulfones**
  - **However, sulfones as a major solvent components raise other issues, such as SEI chemistry on graphitic anode, negative impact of its viscous nature on ion transport and electrode wetting, etc**

- **Significant improvement has been made in the additive approach, where carbonate-based electrolytes have been enabled to support the 5 V Li ion chemistry with a spinel cathode**
  - **Further improvements are being made to optimize the performance;**
  - **Surface analysis on-going will reveal fundamental understanding on mechanism and interphasial chemistry.**