High Voltage Electrolyte for Lithium Batteries

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Argonne National Laboratory

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Project Overview

Timeline

- Project start date: FY10 (new project)
- Project end date: FY14
- Percent complete: 10%

Barriers

- Conventional carbonate based electrolyte decomposes at 4.5V
- Low voltage operation limit energy density both volumetric and gravimetric.

Budget

- Total project funding
  - 100% DOE funding
- Funding for FY11: $200K

Partners

- US Army Research Lab
- Center of Nanoscale Materials (ANL)
- DaikinÈ Chemical Company
- EnerDelÈ Company
- Project Lead – Zhang & Amine

Objective

- To develop an electrolyte with wide electrochemical window that can provide stable cycling performance for 5V cathode materials recently developed for high energy and high power lithium ion battery for PHEV and EV applications.

- FY10's objective is to identify and synthesize several solvent systems as possible candidates for high voltage electrolytes.

Approach

Silane/Sulfone Approach

- ✓ Investigate linear and cyclic sulfones as electrolyte solvents using high voltage spinel $LiNi_{0.5}Mn_{1.5}O_4$ cathode and lithium titanate oxide anode;
- ✓ Formulate various electrolytes with hybrid sulfone/silane solvents.

Fluorinated Ester/Ether Approach

- ✓ Synthesize and formulate various fluorinated ester or/and fluorinated ether/carbonate electrolytes;
- ✓ Synthesize and formulate sulfone/silane/ flourinated tertiary electrolytes.

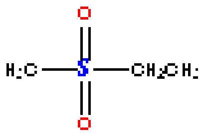
Ionic Liquids Approach

- ✓ Design, synthesize functional ionic liquids with functional groups.

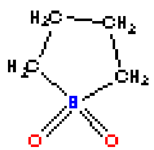
Electrochemical Characterizations/Evaluations

- ✓ Evaluate electrolyte performance with high voltage cathodes.

Achievements and Progress



EMS (mp=35°C)



TMS (mp=23°C)

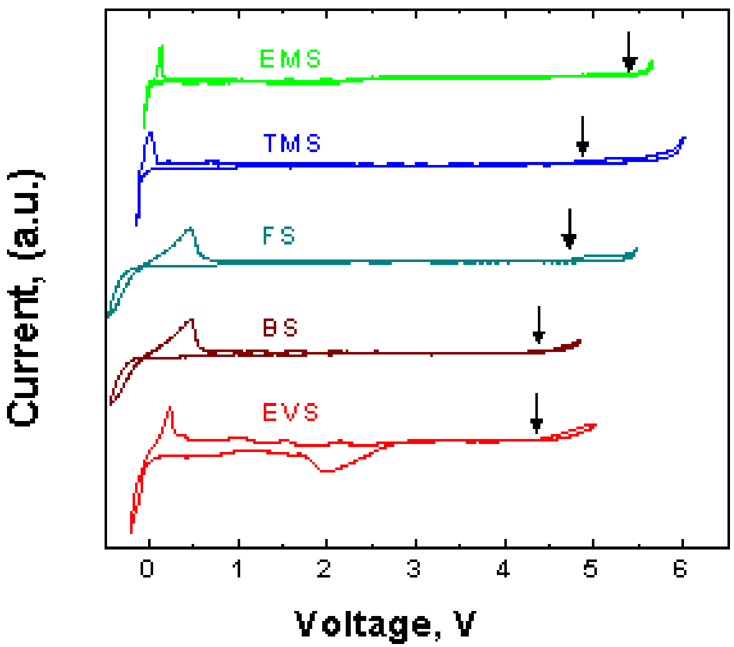


Fig.1. CV profiles of 1.0M LiTFSI/Sulfone electrolytes.

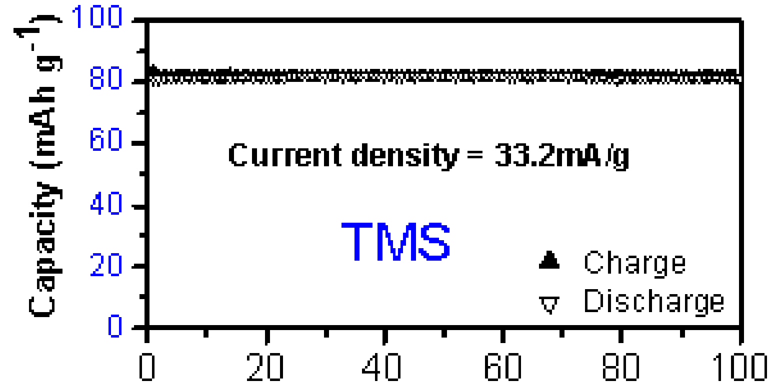


Fig.2. Cycling performance of TMS/1M LiTFSI electrolyte in $LiMn_2O_4$/LTO cells. No capacity fade for 100 cycles.

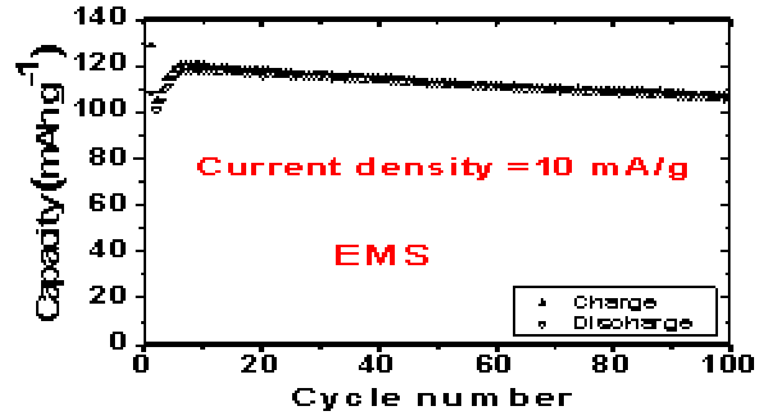
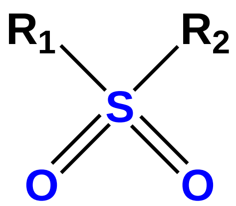


Fig.3. Cycling performance of EMS/1M LiTFSI electrolyte in $LiNi_{0.5}Mn_{1.5}O_4$/LTO cells. Capacity rising in first 10 cycles is due to the electrode and separator wetting issue.

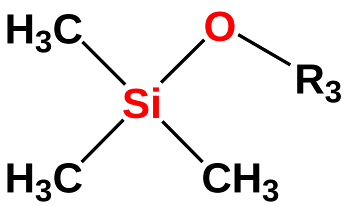
Sulfone/Silane Hybrid Electrolyte

- ✓ Sulfone based electrolyte showed excellent cycling performance in $LiMn_2O_4$/LTO and $LiNi_{0.5}Mn_{1.5}O_4$/LTO cells. 1.0M LiTFSI TMS or EMS electrolytes achieved 100 cycles with no capacity fade for $LiMn_2O_4$/LTO chemistry.
- ✘ Sulfone based electrolyte has an issue of wettability with polyolefin separators and electrode. Good performance was achieved by using glass fiber separator and a formation step.
- ✘ Sulfone based electrolyte performance deteriorates when cycled with high C-rate.
- ✘ Sulfone based electrolyte is not compatible with graphite-based anode - No SEI formation.



Sulfone

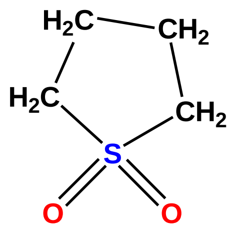
- ✓ High oxidation potential
- ✓ High to medium ionic conductivity
- ✓ Low cost
- ✘ High melting point for symmetrical sulfones – narrow liquid-phase temperature
- ✘ High viscosity compared with carbonate electrolyte



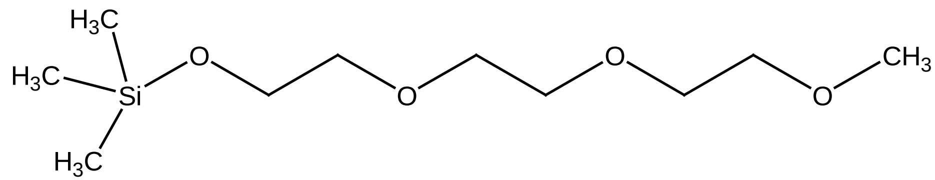
Silane

- ✓ Medium wide electrochemical window
- ✓ High ionic conductivity
- ✓ Non-flammability
- ✓ Excellent wetting property
- ✓ Wide liquid-phase temperature (-40~200°C)
- ✓ Low viscosity-comparable with carbonate electrolyte

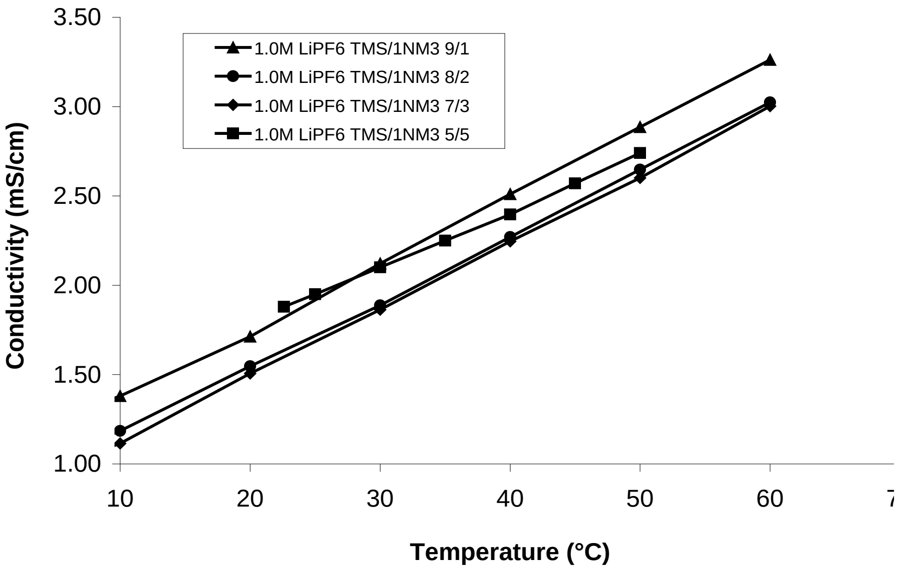
Tetramethylene sulfone (TMS)/Silane (1NM3)



TMS



1NM3



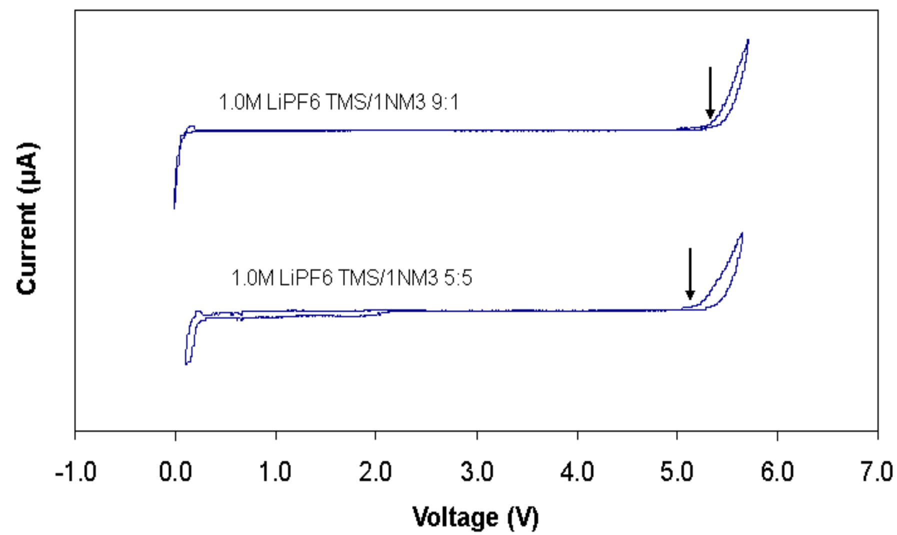
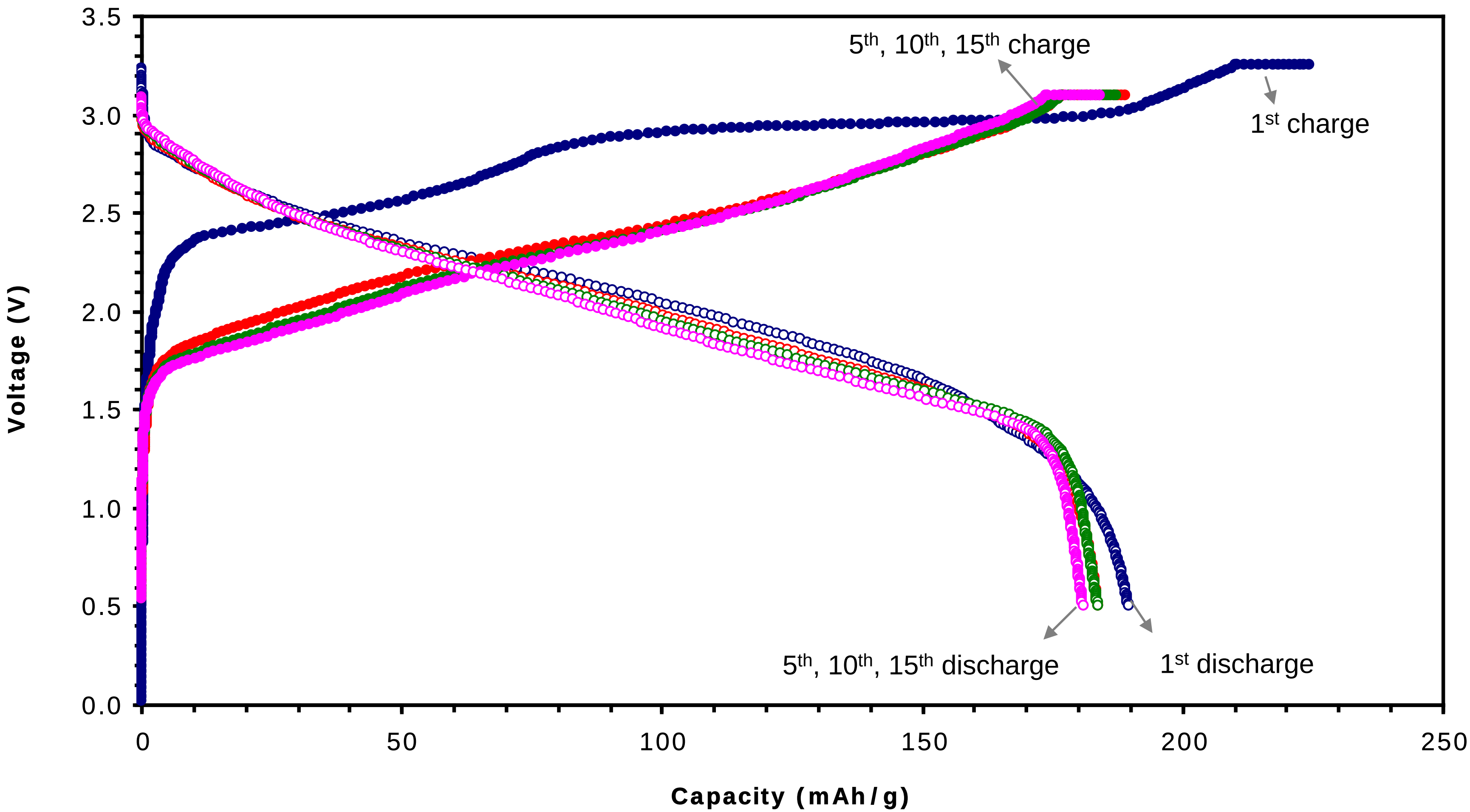


Fig. (left): Ionic conductivities versus temperature for 1.0M $LiPF_6$ TMS/1NM3 hybrid electrolytes (Left).
Fig. (right): Cyclic voltammograms of 1.0M $LiPF_6$ TMS/1NM3 electrolytes with weight ratios of 9:1 and 5:5.

Charge/Discharge Profiles for $Li_{1.2}Ni_{0.15}Co_{0.10}Mn_{0.55}O_2$/LTO Cell Using 1.0M $LiPF_6$ TMS/1NM3 (5/5) Electrolyte

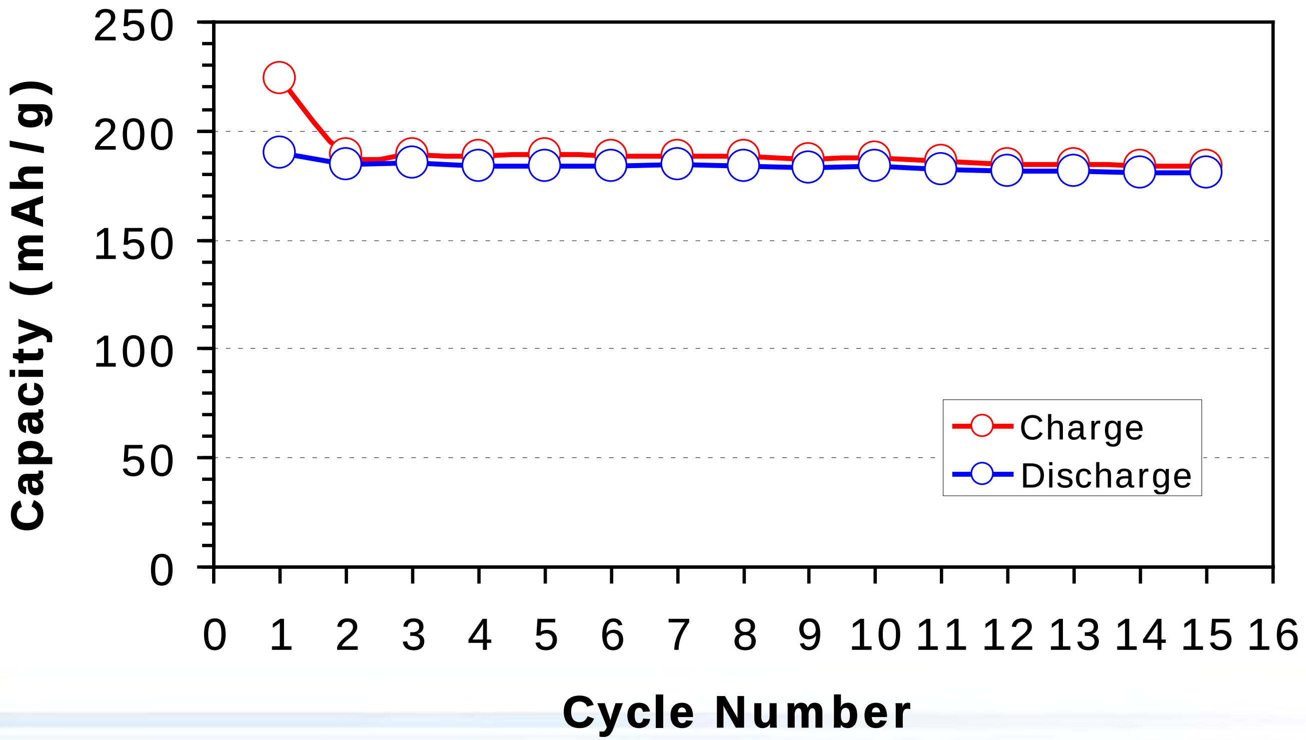


1st cycle charged to 3.25V as activation step;

2nd and the subsequent cycles are regular cycling: 0.5~3.1V, C/20 at room temperature

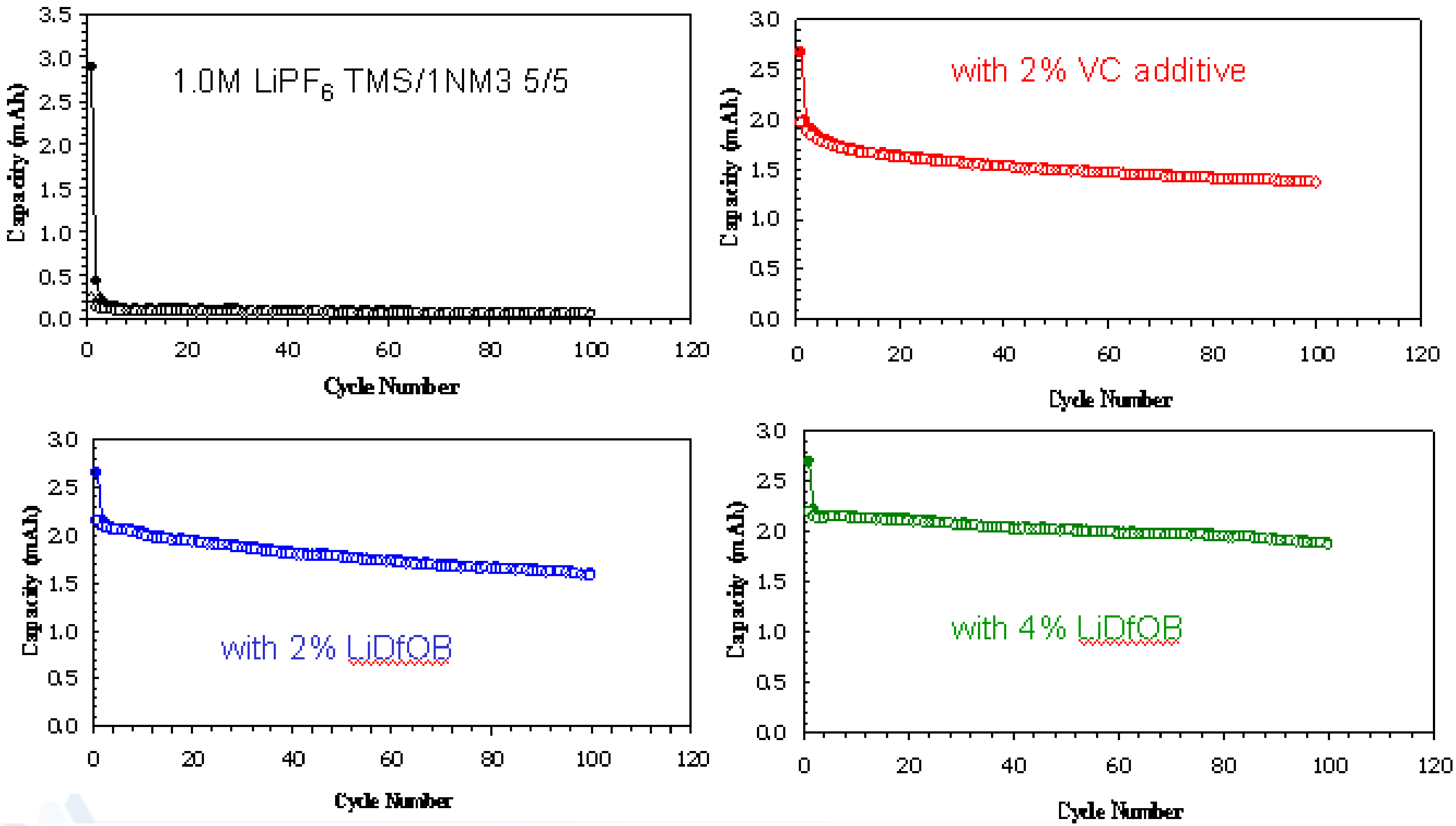
Charge/Discharge Profiles for $LiMn_2O_4$/LTO and $Li_{1.2}Ni_{0.15}Co_{0.10}Mn_{0.55}O_2$/LTO with 1.0M $LiPF_6$ TMS/1NM3 (5/5) Electrolyte

High voltage Cathode: $Li_{1.2}Ni_{0.15}Co_{0.10}Mn_{0.55}O_2$
Anode: LTO
Electrolyte: 1.0M $LiPF_6$ TMS/1NM3 (5/5)
Separator: Celgard 2325
Cut off voltage: 0.5~3.1V,
Charge discharge current: C/20

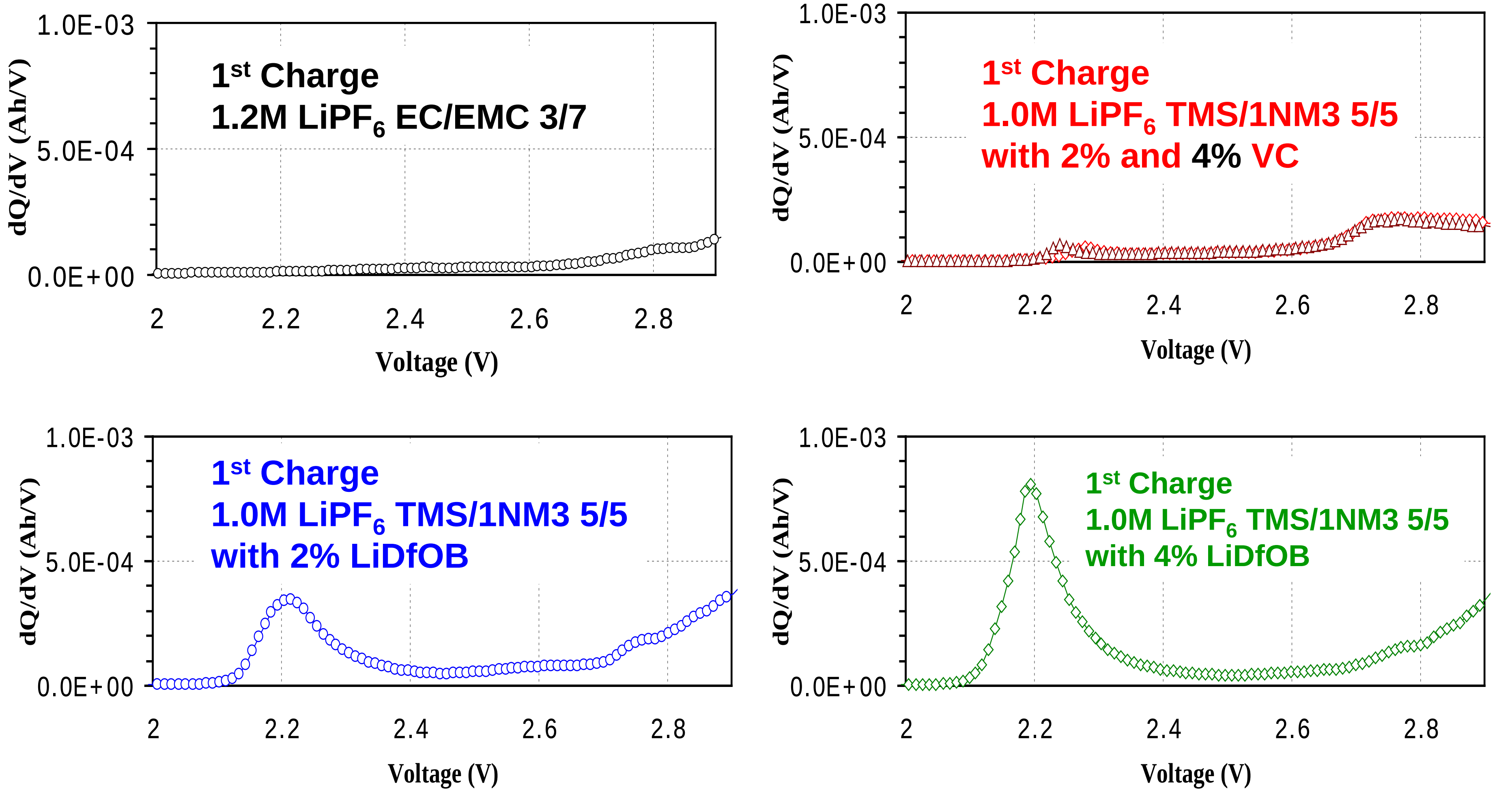


Cycling Performance Using Graphite Based Anode with Electrolyte 1.0M $LiPF_6$ TMS/1NM3 5/5

Evaluated by $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$/MCMB graphite Chemistry

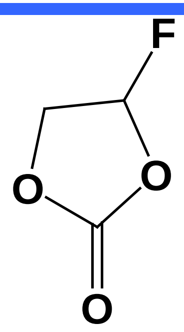


Differential Capacity (dQ/dV) Profiles of Electrolyte 1.0M $LiPF_6$ TMS/1NM3 with and w/o Additives

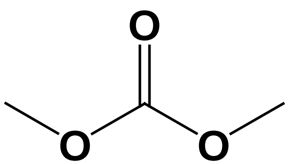


dQ/dV data support the Formation of New Solid Electrolyte Interphase on Graphite Anode

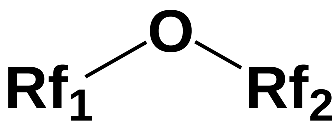
Fluorinated Solvents as High Voltage Electrolyte



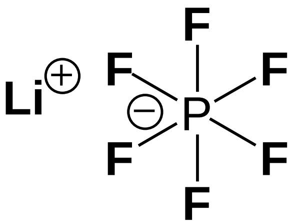
FEC



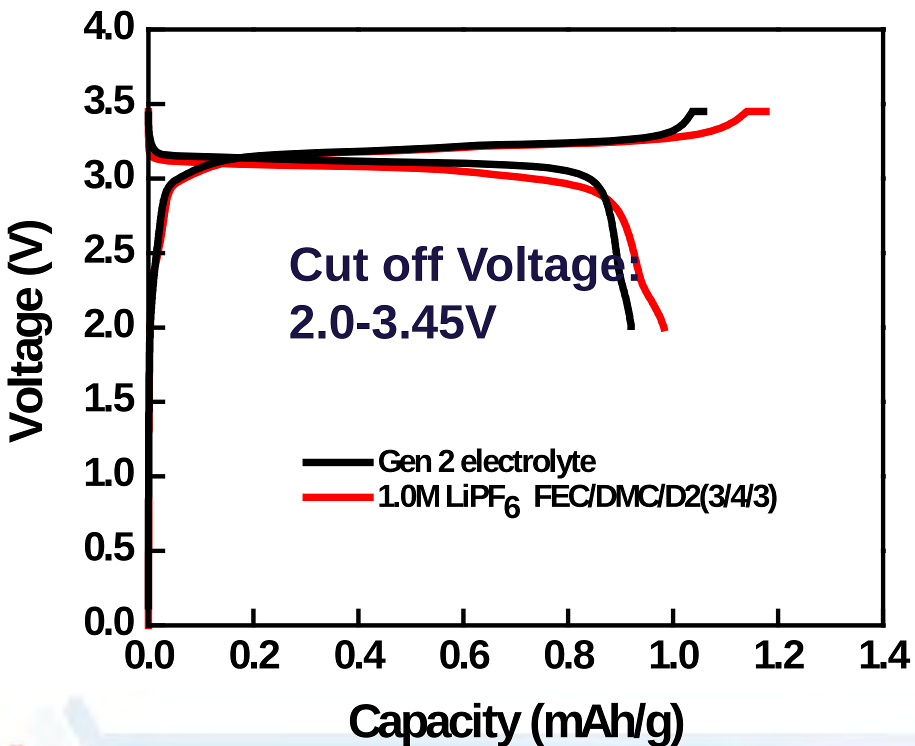
DMC



D2



$LiPF_6$



1st charge/discharge profile

Cathode: $LiNi_{0.5}Mn_{1.5}O_4$

Anode: $Li_4Ti_5O_{12}$

Electrolyte: 1.0M $LiPF_6$
FEC/DMC/D2 =3:4:3 (volume)

Fluorinated Solvents as High Voltage Electrolyte

Cathode: $LiNi_{0.5}Mn_{1.5}O_4$
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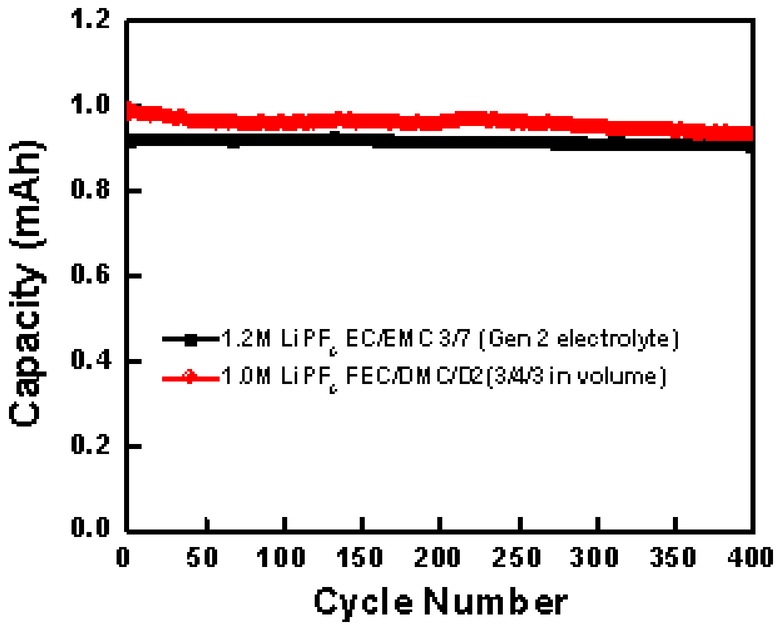
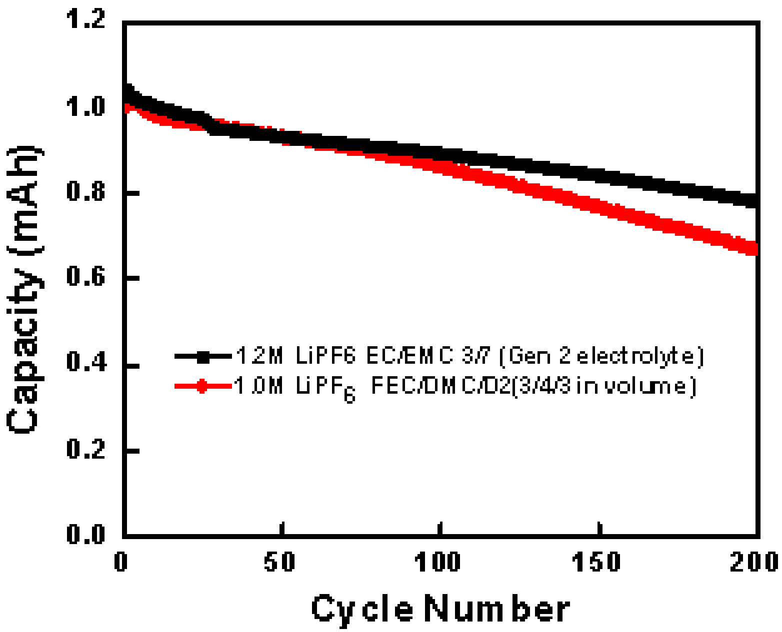
FEC/DMC/D2 =3:4:3 (volume)

1C cycling at 25°C



1C cycling at 55°C

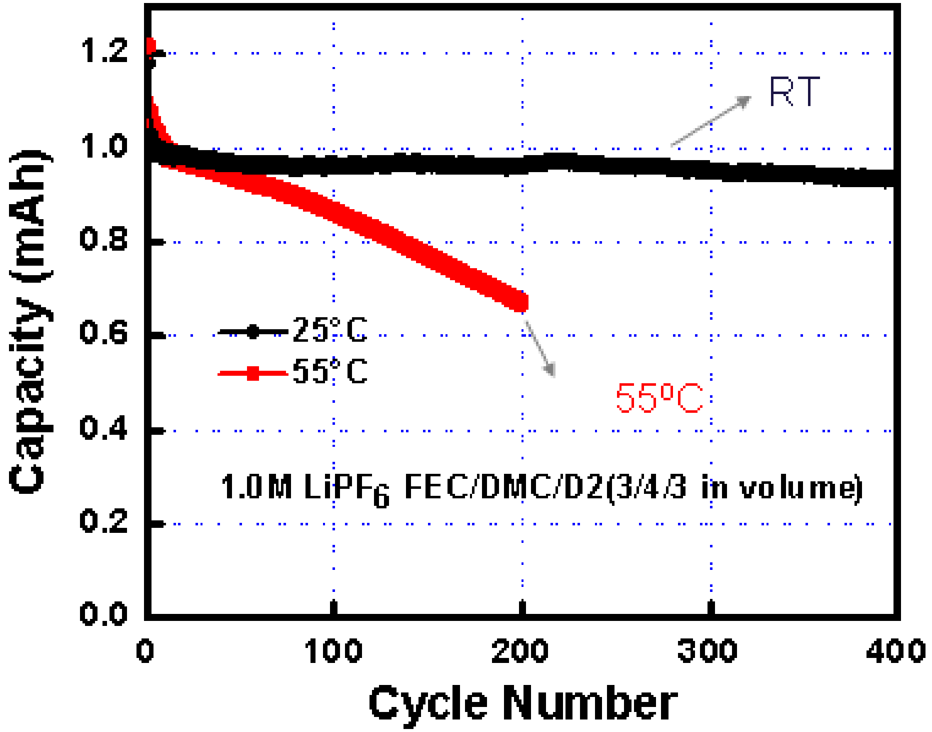


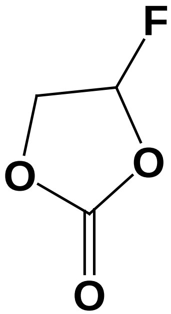
Mixture of fluorinated ester and ether electrolyte showed excellent ambient cycling performance, How ever the high temperature started to degrade after 100 cycles due to the instability of the fluorinated ester.

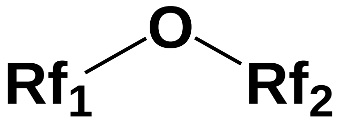
Accelerated Cycling Performance at RT and 55ºC

To increase the thermal stability and reactivity

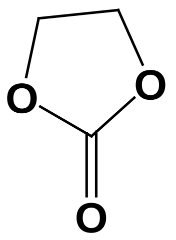
Comparison of cycling stability at RT and 55ºC with 2C charge/discharge rate



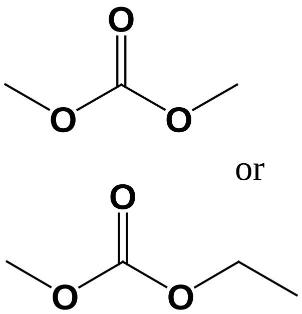




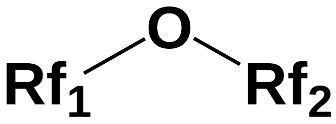
Fluorinated Solvents as High Voltage Electrolyte



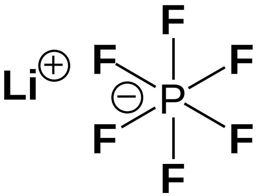
FEC



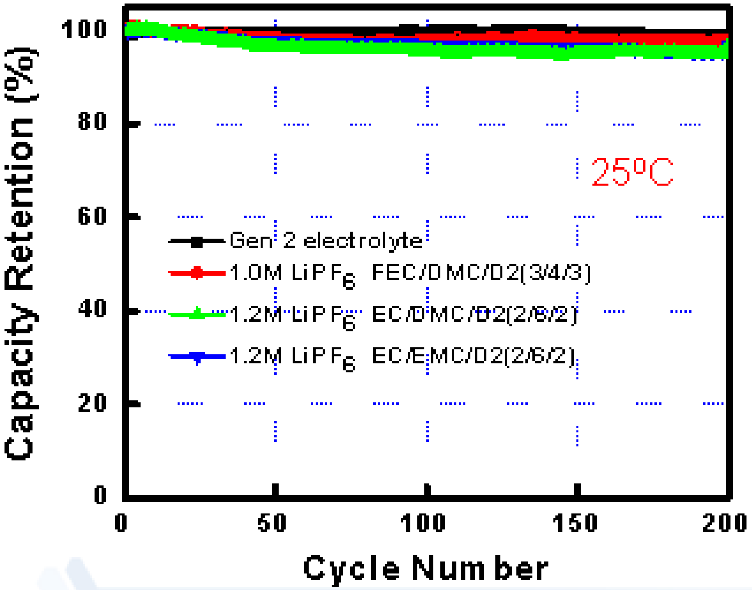
DMC/EMC

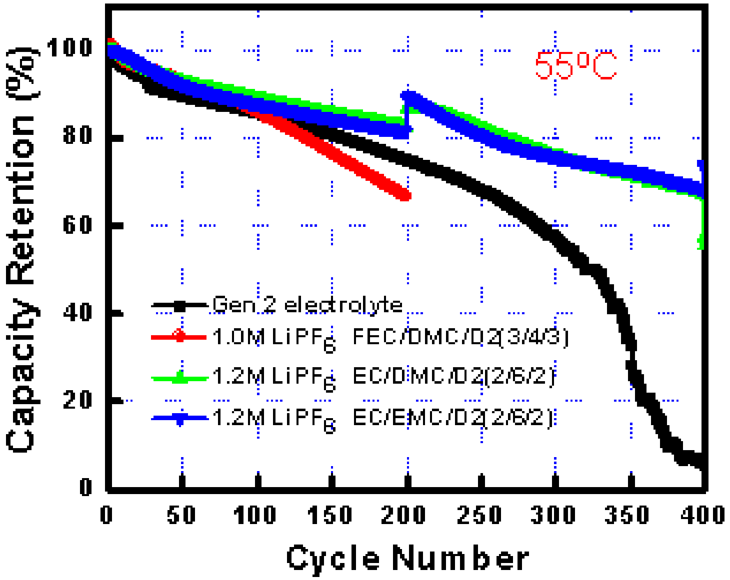


D2



$LiPF_6$





Collaboration and Interactions

- **US Army Research Laboratory**

  - Dr. Richard Jow and Dr. Kang Xu for technical and information exchanges;

- **Center of Nanomaterials -Argonne National Laboratory**

  - Dr. Larry Curtiss for calculation of reduction/oxidation potentials of solvents by quantum chemical methods;

- **Daikin Chemical Company**

  -Dr. Meiten Koh for the supply of FEC and D2 solvents and material synthesis discussions.

- **EnerDel**

  - Dr. Yumoto and Naoki for high voltage spinel cathode and LTO anode and technical discussions.

Proposed Future Work

- ✓ Further explore sulfone/silane hybrid electrolytes
- ✓ Further explore the fluorinate ethers/carbonate hybrid electrolytes;
- ✓ Investigate the sulfone/fluorinated hybrid electrolytes;
- ✓ Continue exploring formulations based on silane/fluorinated solvents hybrid electrolyte;
- ✓ Evaluate the battery cycling performance of these high voltage electrolytes at 55^oC using LiNMO/LTO chemistry;
- ✓ Study their impact on calendar and cycle life of lithium ion battery;
- ✓ Investigate their impact on safety of lithium ion battery.

Summary

- Sulfone/Silane hybrid system shows an increase in a voltage window stability *vs*. Sulfone only;
- Performance of Sulfone/Silane hybrid system using high voltage composite layered electrode shows good cycling stability;
- New additive were developed for sulfone/silane hybrid electrolyte system to enable their use in graphite anode;
- Fluorinated ether mixed with conventional electrolyte shows excellent cycling performance both at room and high temperature using high voltage LNMO spinel system as cathode and LTO as anode.