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Novel electrolytes and electrolyte additives for PHEV applications

Project Id: esp_15_abraham

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Vehicle Technologies Annual Merit Review and Peer Evaluation

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Vehicle Technologies Program

Overview

Timeline

- Start date: FY09 (new project)
- End date: On-going
- Percent complete:

  - project on-going

Budget

- Total project funding

  - 100% DOE
- FY09: $200K

Barriers

- Performance
- Calendar/Cycle Life
- Abuse tolerance

Partners

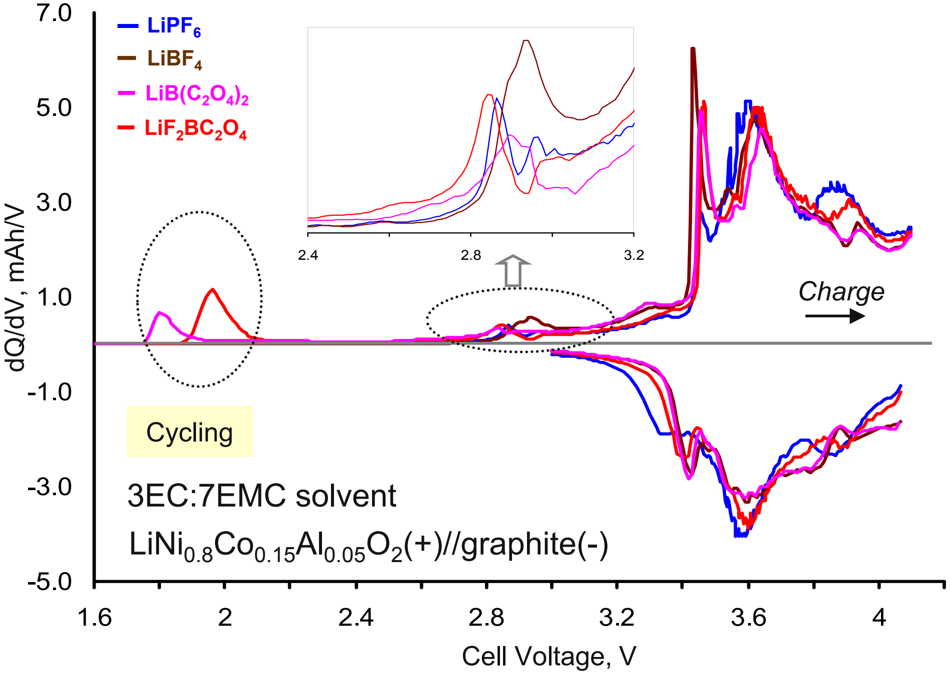
- Argonne colleagues
- University of Rhode Island
- CSIRO, Australia

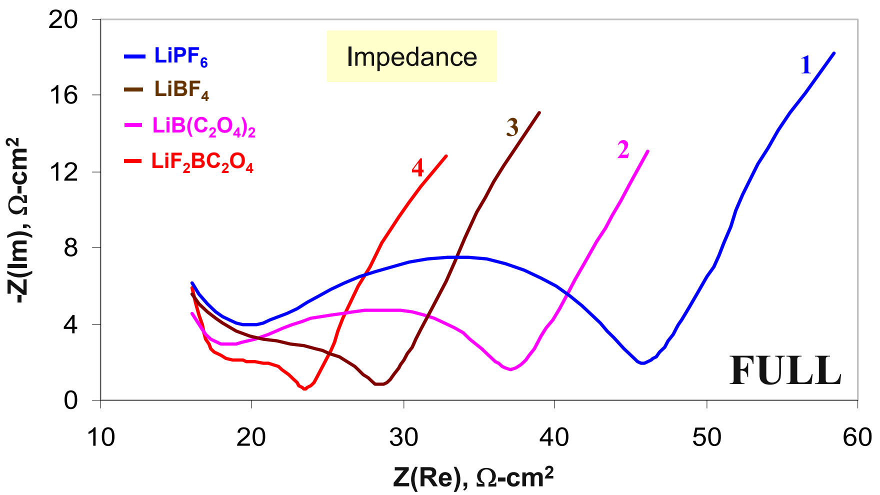
Objectives

Performance, calendar-life, and safety characteristics of Li-ion cells are dictated by the nature and stability of the electrolyte and the electrode-electrolyte interfaces.

- Our goal is to develop novel electrolytes and electrolyte additives for PHEV batteries. An ideal electrolyte would display the following characteristics:
  - ✓ Wide electrochemical stability window, 0 to >5 V
  - ✓ Wide temperature stability range, -30 to +50 °C
  - ✓ Non-reactivity with other cell components
  - ✓ Excellent ionic conductivity to enable rapid ion transport
  - ✓ Negligible electronic conductivity to minimize self-discharge
  - ✓ Stability for over 5000 deep-discharge cycles
  - ✓ Stability over the 10y battery life

Background – Related Work





- Performance *(capacity, impedance)* and aging behavior of various layered-oxide and graphite-based electrodes have been examined in various electrolyte system, as part of ATD cell diagnostics. Some of these electrolytes contained the following:
  - *Solvents: EC, PC, EMC, etc.*
  - *Salts: $LiPF_6$, $LiBF_4$, $LiB(C_2O_4)_2$, $LiF_2BC_2O_4$, etc.*
  - *Additives: VC, VEC, Li-salts, etc.*
- Composition and morphology of electrode surface films (SEI) formed after formation cycling, and after long-term aging, have also been studied.

Approach

- Investigate novel electrolytes that include glycerol carbonate, and modifications thereof. The modified glycerol carbonates will include methyl ethers, ethyl ethers, and oligoethylene oxide ethers.

- Investigate electrolyte additives designed to react and stabilize the cathode surface to improve cell calendar life. The additives include unsaturated ethers, polyunsaturated alanes, and vinyl silanes.

- Examine room-temperature ionic-liquids (RTIL), and mixtures of RTIL and organic electrolytes, to enable high-safety, high-performance batteries.

Milestones

GC acquisition/developing purification techniques

"GC variants" synthesis

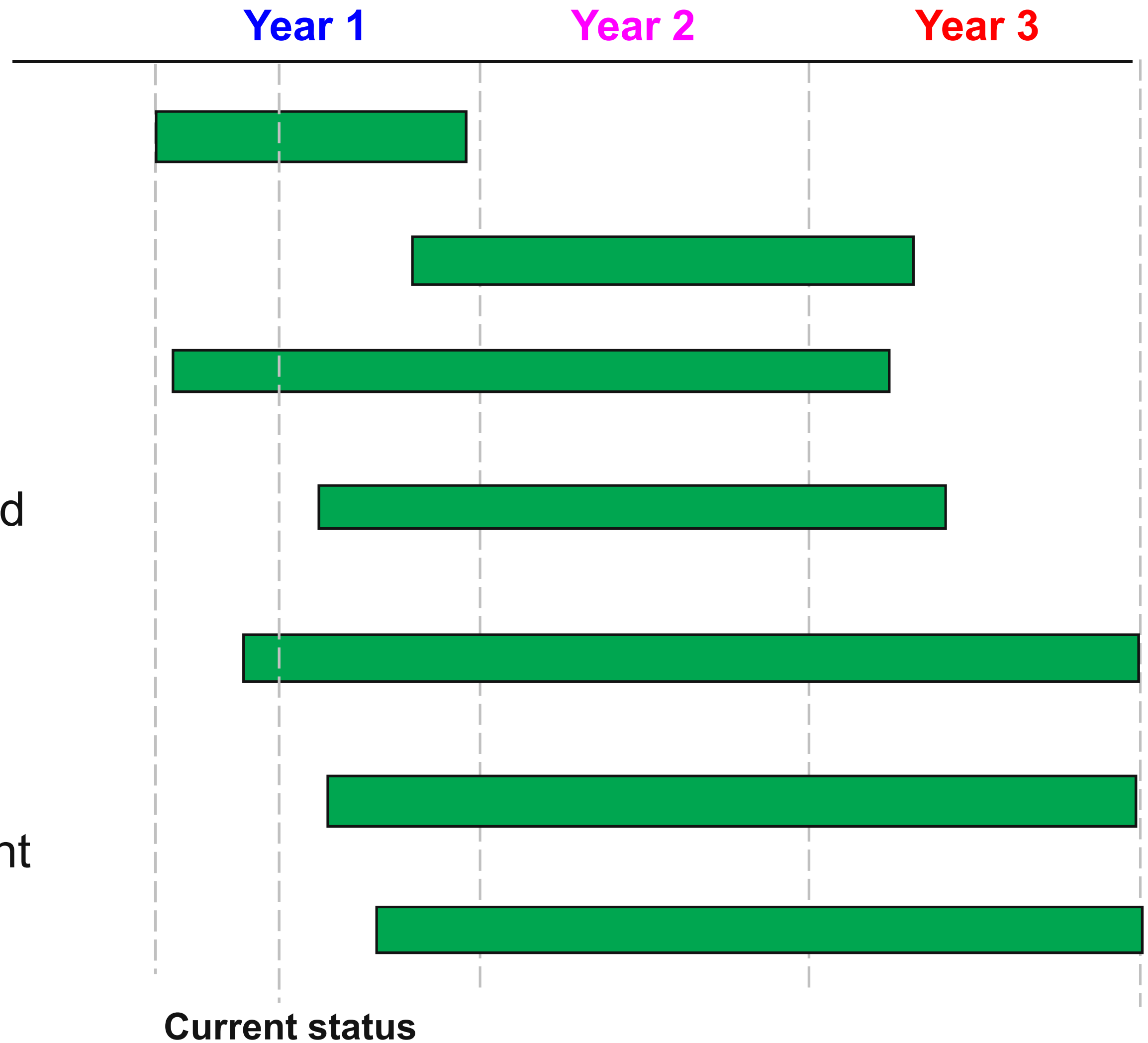
Electrolyte Additive synthesis/preparation

Ionic liquids acquisition and electrolyte preparation

Performance examination *(cycling behavior, etc.)*

Property *(voltage window, ionic conductivity, etc.)* measurement

Data documentation



- Promising electrolytes and electrolyte additives will be recommended for use in ABRT cells for life- and safety- studies

Progress – Glycerol Carbonate (GC) can be a potential low-cost substitute for currently used lithium-battery solvents

- ❑ Obtained GC from a commercial manufacturer
  - ✓ Electrochemical tests conducted with the electrolytes prepared with this “as-received” solvent show poor performance
    - − According to manufacturer spec sheets, the GC is only 93.5% pure (the remaining 6.5% includes alcohol and moisture impurities, which are known to be detrimental in lithium-ion cells).
  - ✓ Techniques to dry/purify GC are being developed.
  - ✓ Initial electrochemical tests conducted with electrolytes prepared using the “dry/purified” GC solvent shows promising results for both graphite-negative and oxide-positive electrodes.

Progress – Glycerol Carbonate Purification

12h

Impure GC
+
Molecular sieves
(vacuum dried)

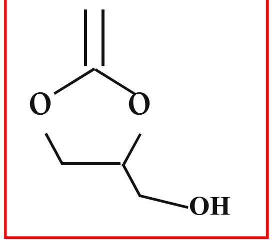
decant →

12h

Decanted GC
+
Molecular sieves
(vacuum dried)

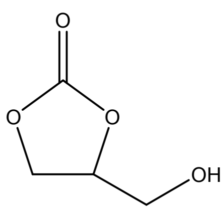
vacuum filtration →

Pure

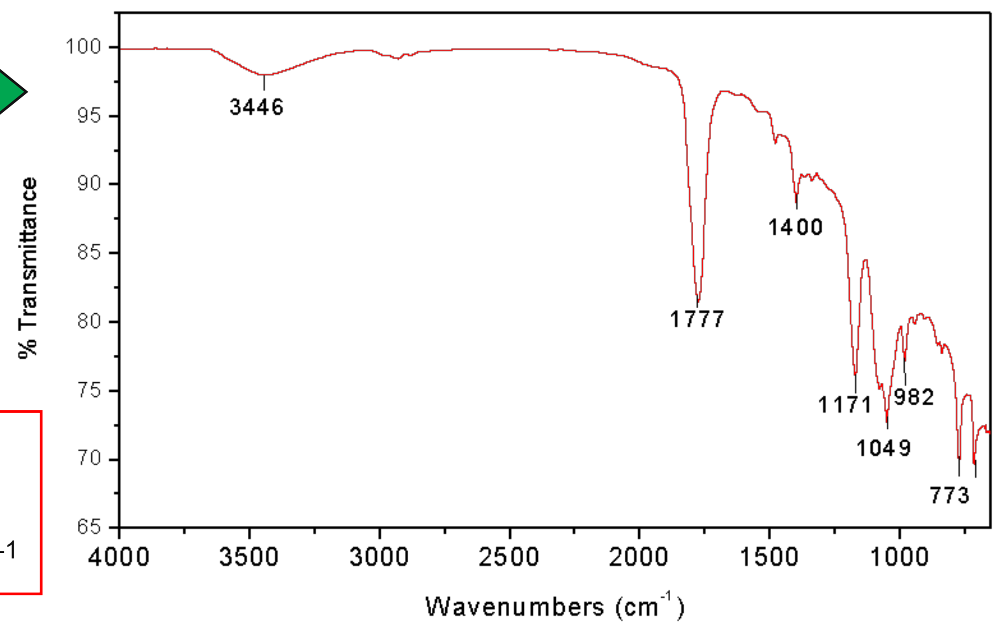


GC drying/purification was conducted in an Ar-atmosphere glove box

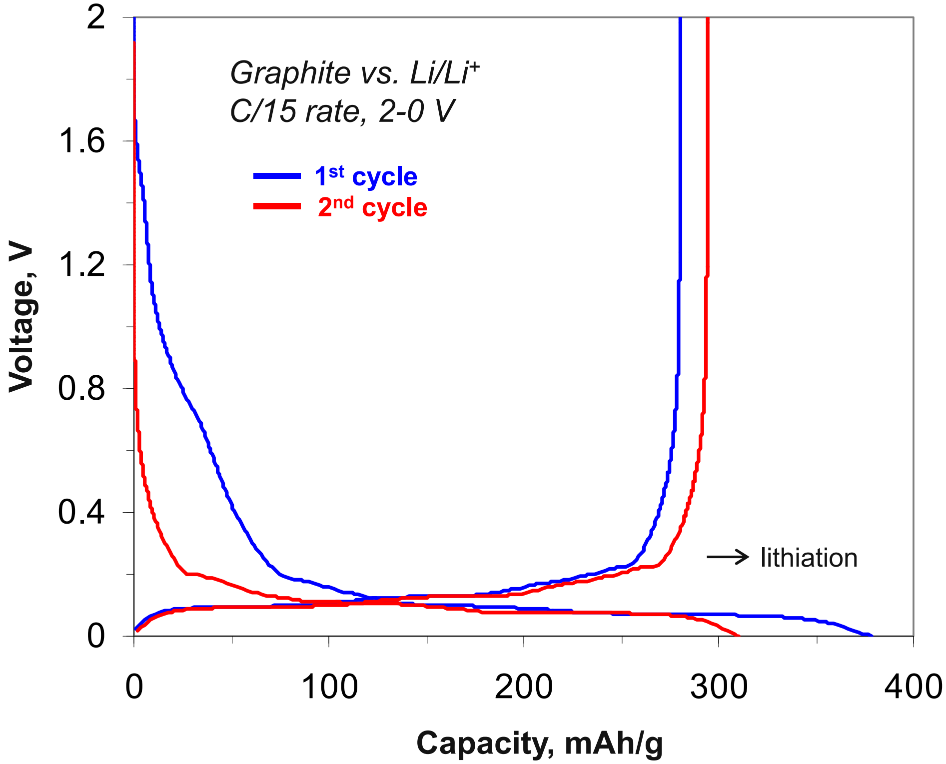
FT-IR spectrum of glycerol carbonate

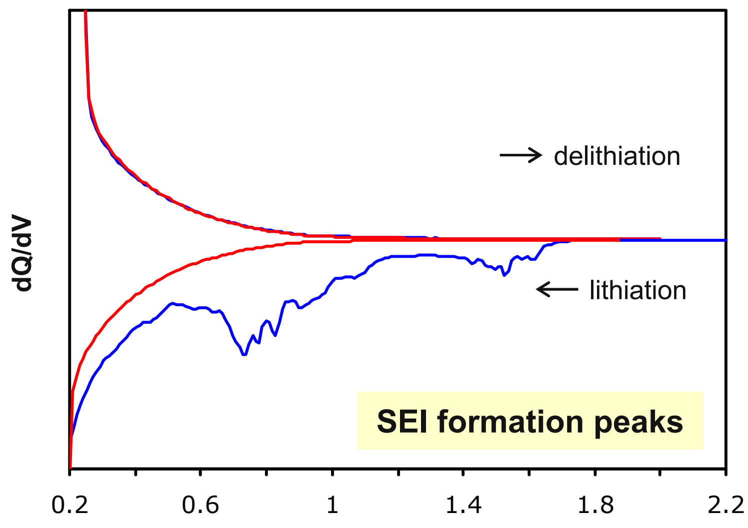


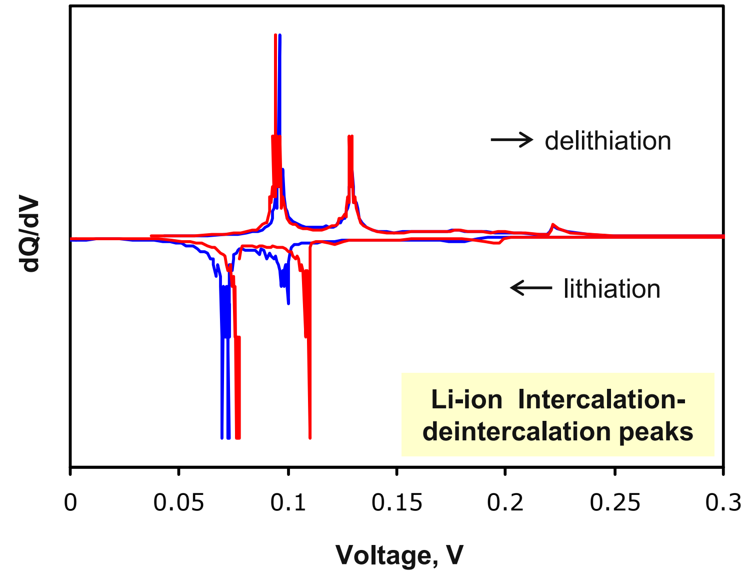
O-H stretching: 3446 cm^{-1}
C=O stretching: 1777 cm^{-1}
C-O stretching: 1171 cm^{-1}, 1049 cm^{-1}



Preliminary Data – Glycerol Carbonate based electrolyte





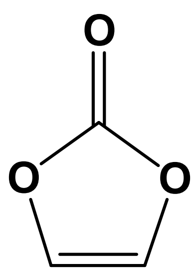


Graphite electrodes can be cycled in GC-based electrolytes. The SEI that forms apparently protects the graphite from solvent intercalation. SEI formation mechanisms will be determined later.

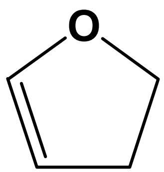
Progress – Electrolyte Additives

An ideal electrolyte additive would passivate and protect the electrode surfaces from further reactions with the electrolyte

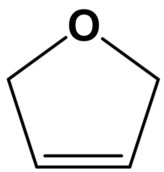
- PHEV testing conditions include wider voltage windows and greater SOC-swings (than HEV test conditions). Hence, reactions at the positive electrode-electrolyte interface are expected to have a significant impact on cell performance and life.
  - ✓ We are investigating the effect of additives that are designed to react on the surface of the cathode to produce a thin lithium-ion conductive layer that stabilizes the electrolyte against further oxidation. Some of these additives are shown below.



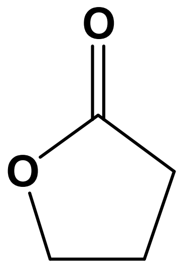
Vinylene Carbonate



2,3-DiHydroFuran

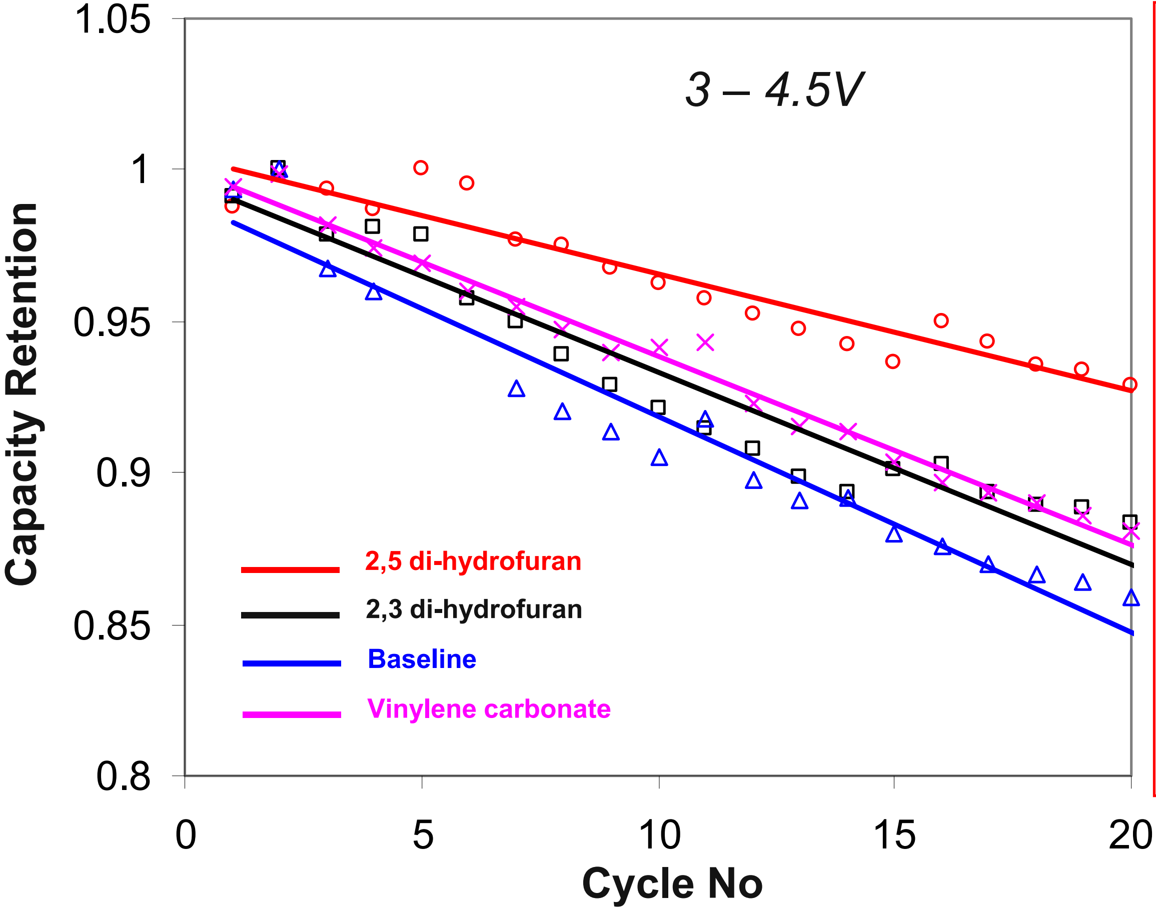


2,5-DiHydroFuran



GBL

Results – Electrolyte Additives



<u>Experiments conducted in cells with</u>

Pos: $Li(Ni_{0.8}Co_{0.2})O_2$

Neg: MCMB graphite

Baseline electrolyte:

EC:DEC:DMC + 1M $LiPF_6$

Small amounts of 2,5 DHF, 2,3 DHF and VC were added to the baseline electrolyte.

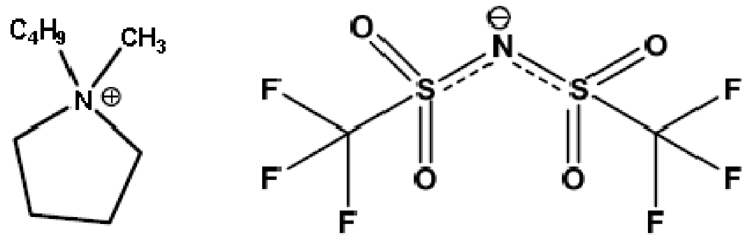
Cycling was conducted between 3 and 4.5V to increase the rate of electrolyte oxidation at the positive electrode.

- These initial data indicate that small additions of 2,5 DHF, 2,3 DHF and VC to the baseline electrolyte can improve cell life.

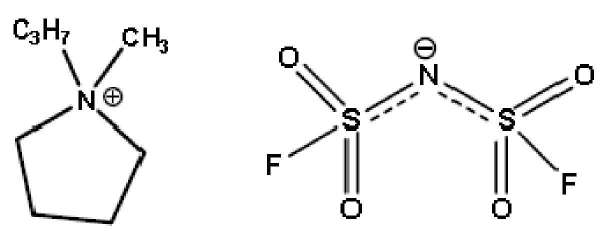
In progress – Ionic Liquids

P_{14}TFSI = N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide
P_{13}FSI = N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide

Salt
LiTFSI
LiFSI



P_{14}TFSI



P_{13}FSI

Density ($gmol^{-1}$)	280	180
MP (°C)	12	5
Viscosity ($mm^2.s^{-1}$)	138	37
Diffusion ($m^2.s^{-1}$)	1.47×10^{-11}	3.44×10^{-11}

Experiments with graphite-negative and oxide-positive electrodes are planned and results will be reported when available

Future Work

- Continue investigation of GC-based electrolytes
  - ✓ Examine performance/cycling behavior of electrolyte mixtures containing various Li-salts.
  - ✓ Determine properties (*electrochemical stability window, temperature stability, etc.*) of “promising” electrolytes.
- Develop techniques to replace the H (in the OH of GC) with other species, and conduct experiments with these novel “GC-variant” solvents.
  - ✓ Examine performance/cycling behavior of electrolyte mixtures containing various Li-salts.
- Identify new electrolyte additives, and continue studies on existing additives, that can enhance cell life by protecting the electrode surfaces from reactions with the electrolyte
  - ✓ Effects on performance, life, and safety will be determined
- Initiate electrochemical studies with the ionic liquids
  - ✓ Examine electrode performance/cycling behavior

Summary

- Novel electrolytes need to be developed to meet the cost, calendar life and safety requirements of batteries for PHEV applications. These batteries may be deep-discharged > 5000 times during the lifetime of the automobile and should have a calendar life of more than 10 years.

- Our approach is to (i) develop novel electrolytes that include glycerol carbonate (GC), and modifications thereof, (ii) examine electrolyte additives that can enhance cell life by protecting the electrode surfaces, (iii) investigate the use of ionic liquids to enable high-safety batteries.

- Our initial studies have focused on developing techniques to prepare high-purity glycerol carbonate. Electrochemical data obtained with these GC-based electrolytes appear promising. Experiments with electrolyte additives designed to protect the positive electrode also show promise.

- We plan to continue studies with GC-based electrolytes, with electrolyte additives and with ionic liquids, and initiate work to identify/test other potential electrolyte systems.