

Novel Electrolytes and Additives

Project Id: ES023

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Overview

Timeline

- Start date: FY09
- End date: On-going
- Percent complete:
 - project on-going

Budget

- Total project funding
 - 100% DOE
- FY09: \$200K
- FY10: \$300K

Barriers

- Performance
- Calendar/Cycle Life
- Abuse tolerance

Partners

- Argonne colleagues
- University of Rhode Island
- CSIRO, Australia
- Kevin Gering, Idaho NL
- Industrial collaborators



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:
 - Low Cost, non-toxic, non-flammable
 - Non-reactivity with other cell components
 - Wide electrochemical stability window, 0 to >5 V
 - Wide temperature stability range, -30 to +50 °C
 - Excellent ionic conductivity to enable rapid ion transport
 - Negligible electronic conductivity to minimize self-discharge
 - Stability over the 10y battery life

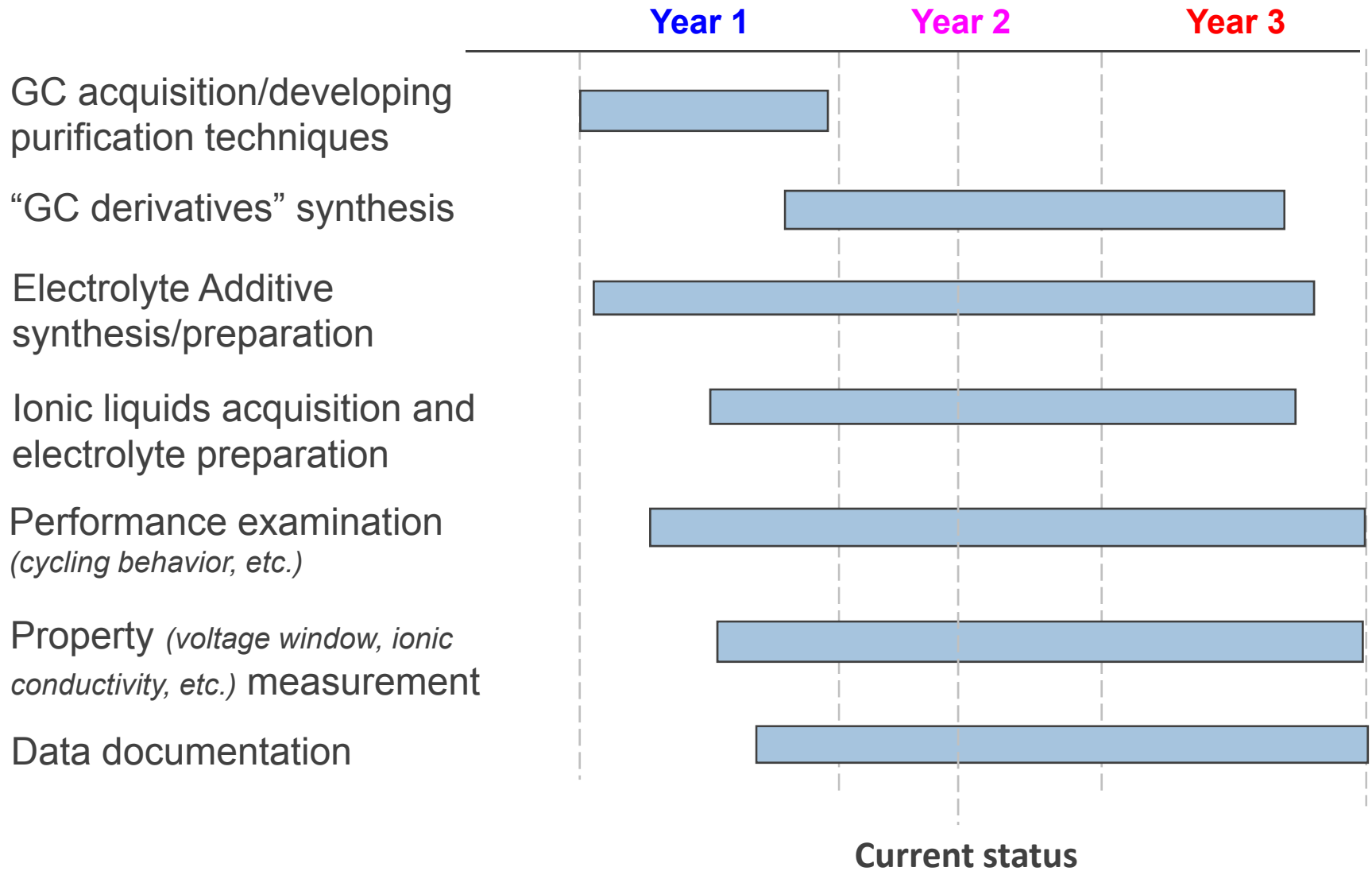


Approach

- 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 may include unsaturated ethers, vinyl silanes, and other compounds.
- Examine room-temperature ionic-liquids (RTIL), and mixtures of RTIL and organic electrolytes, to enable high-safety, high-performance batteries.
- Recommend promising electrolytes and electrolyte additives for use in ABRT cells (calendar life and safety studies)



Milestones

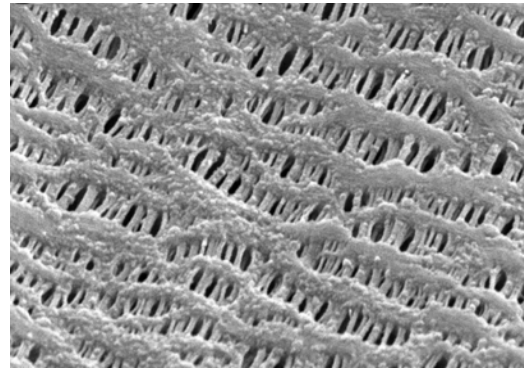


Technical Accomplishments

- ❑ Investigation of GC-based electrolytes
 - ✓ Examined performance/cycling behavior of electrolyte mixtures containing various Li-salts
- ❑ Developed techniques to replace the H (in the OH of GC) with other species, and conducted experiments with these “GC-derivative” solvents
 - ✓ Examined performance/cycling behavior of electrolyte mixtures
- ❑ Identified new electrolyte solvents and electrolyte additives that can enhance cell life
 - ✓ Effects on cell performance, life, and safety are being determined
- ❑ Electrochemical studies with ionic liquids
 - ✓ Examined electrode performance/cycling behavior



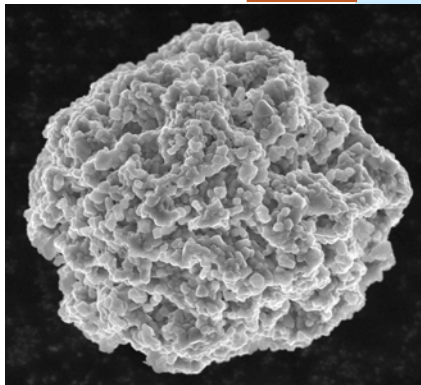
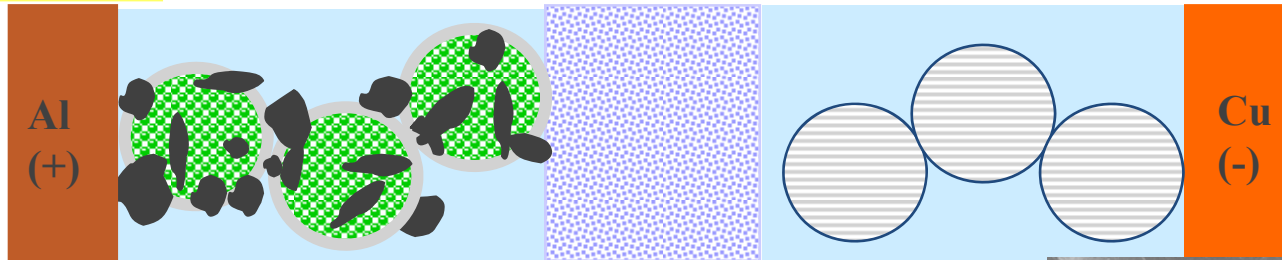
Point of Reference - Electrode and Electrolyte Chemistries



Celgard separator
25 μm thk

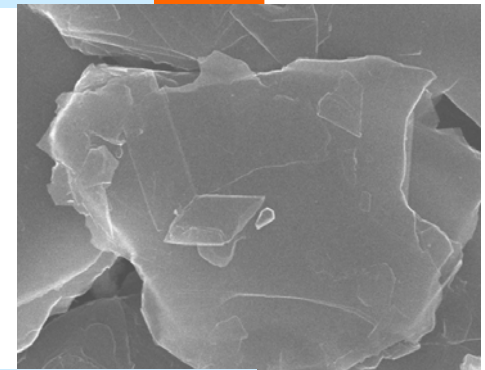
Gen2 Cathode
35 μm thick coating

Gen2 Anode
35 μm thick coating



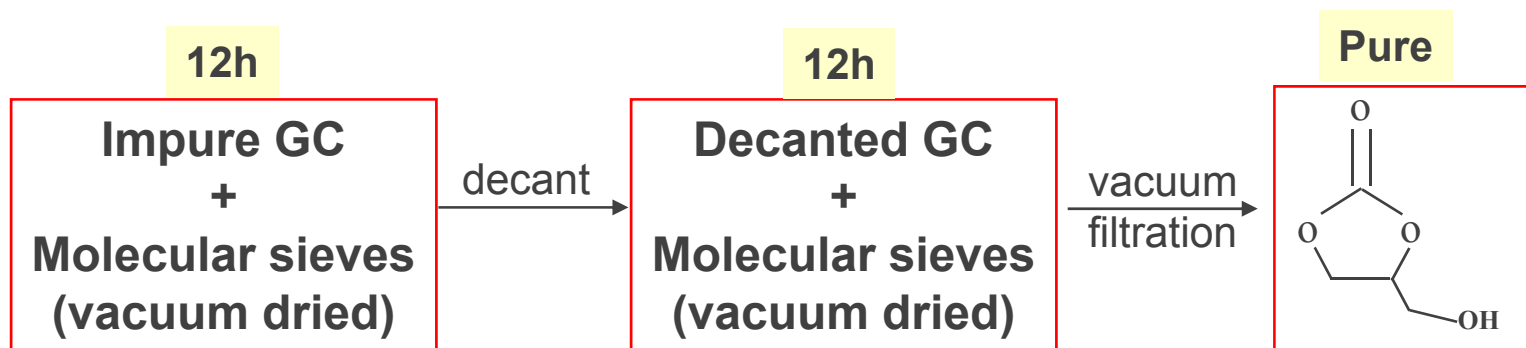
$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$
Particle size $\sim 5 \mu\text{m}$

Gen 2 electrolyte
EC:EMC (3:7 by wt.) + 1.2M LiPF_6



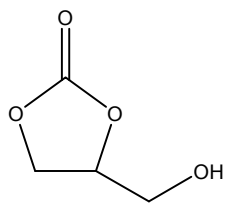
Mag-10 graphite
Particle size $\sim 5 \mu\text{m}$

Glycerol Carbonate from a commercial manufacturer was dried and purified before use in cells

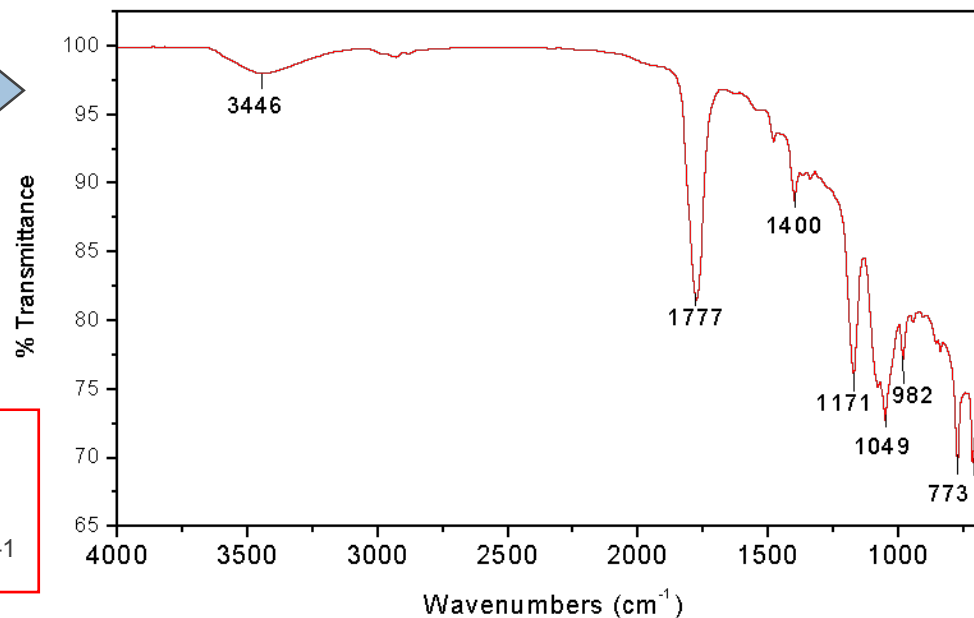


GC drying/purification was conducted in an Ar-atmosphere glove box

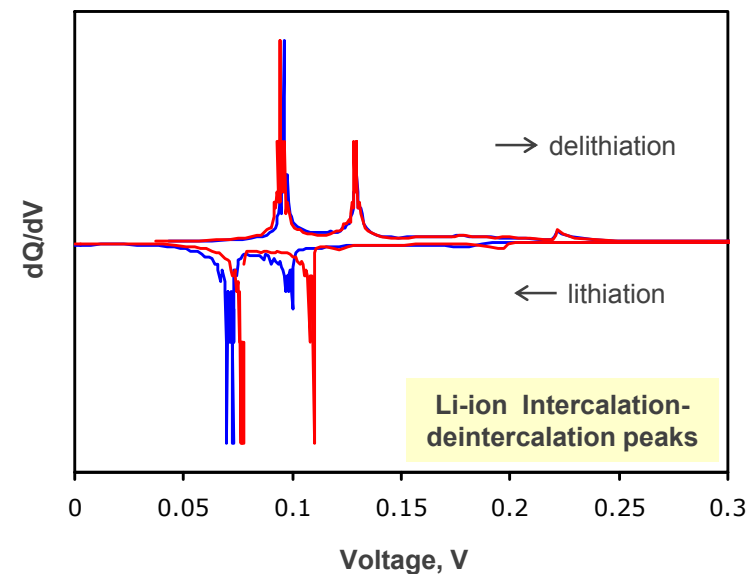
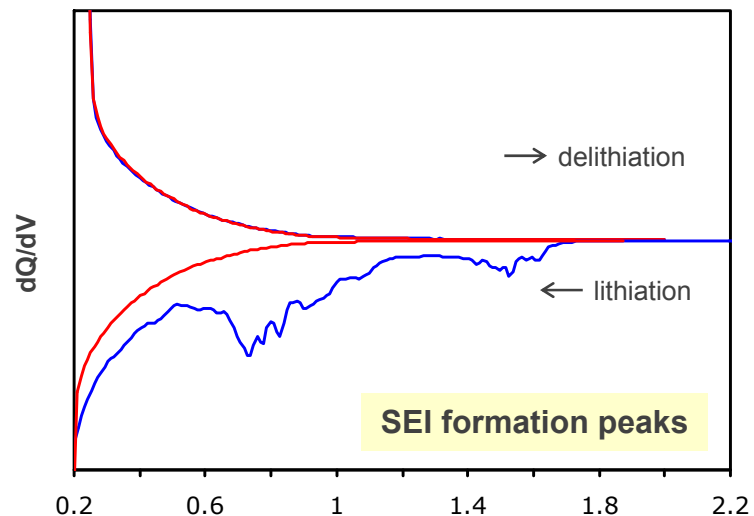
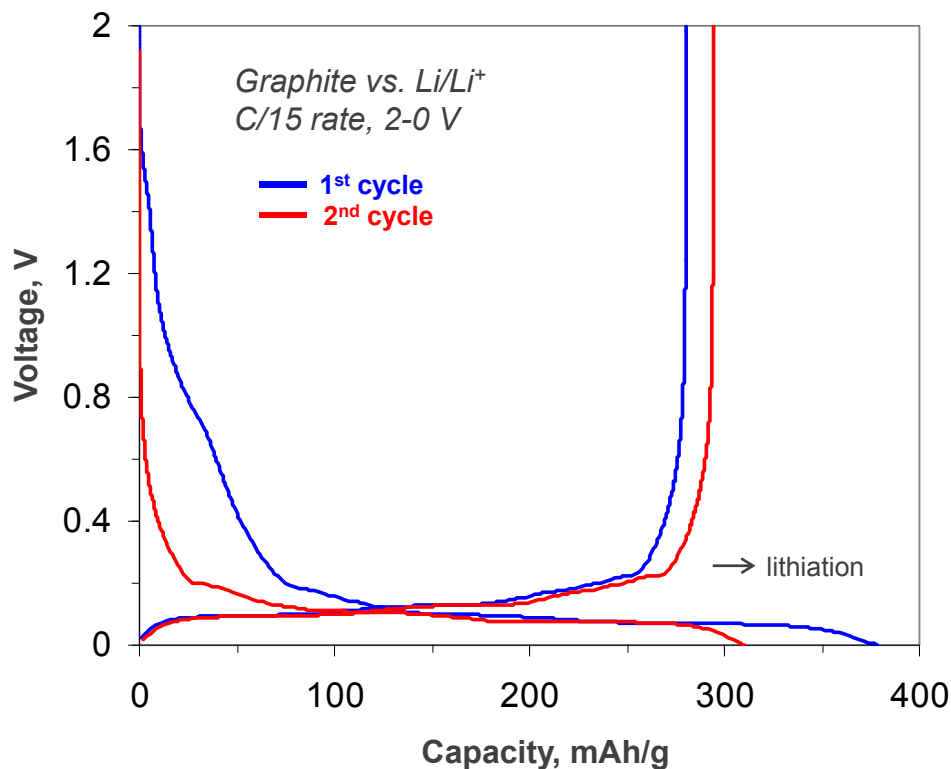
FT-IR spectrum of
glycerol carbonate



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

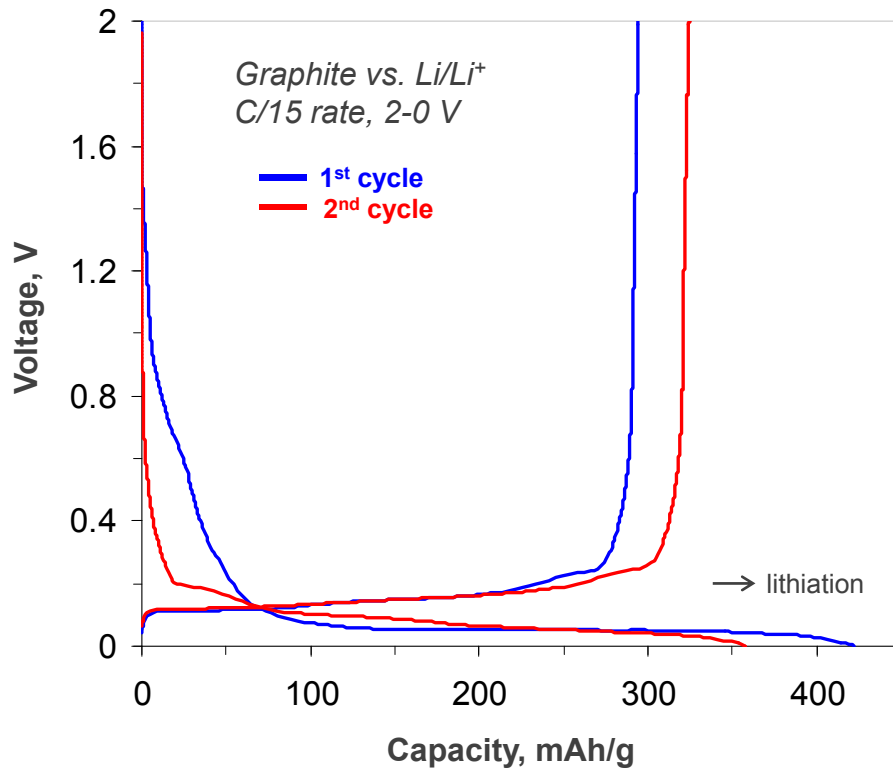


Graphite Electrode - 1.2M LiPF₆ in GC:DMC (2:8)

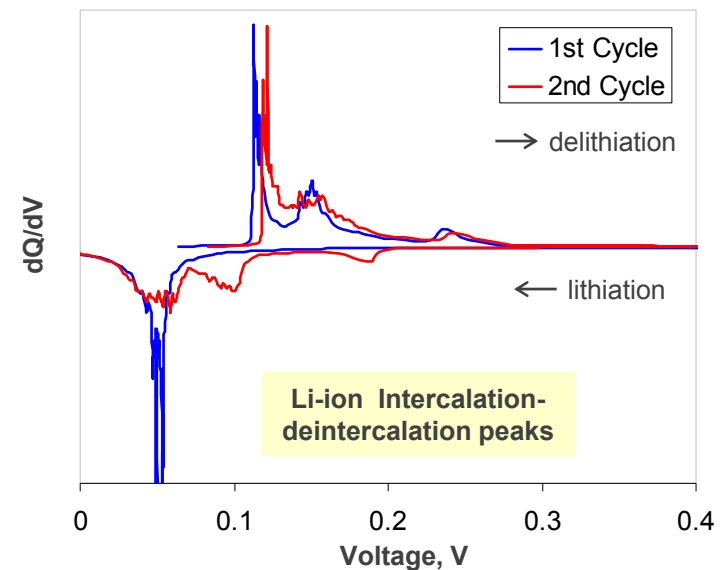
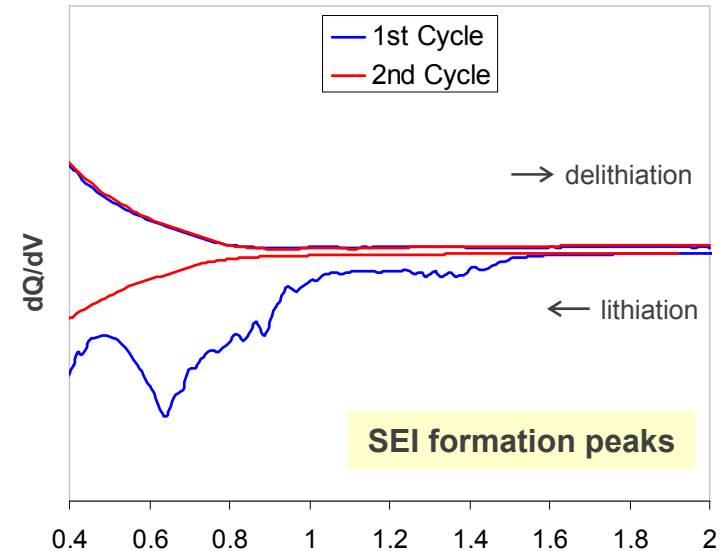


Graphite electrodes can be cycled in GC-based electrolytes. The SEI that forms apparently protects the graphite from solvent intercalation.

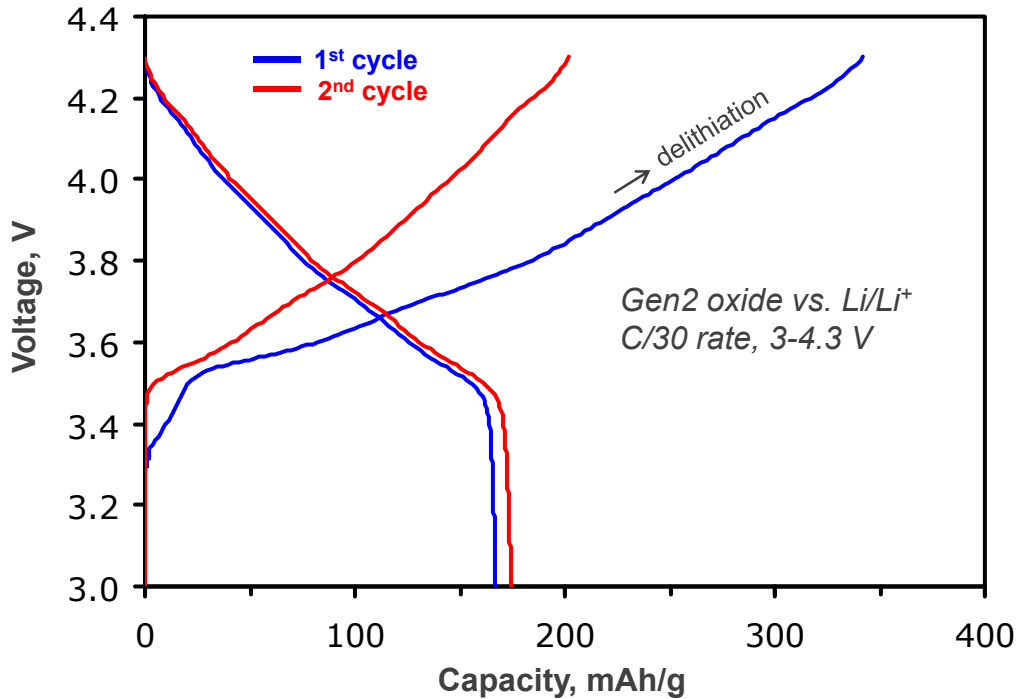
Graphite Electrode - 1M LiBF₄ in GC:DMC (2:8)



Graphite electrodes can be cycled in LiBF₄-based electrolytes. The SEI that forms apparently protects the graphite from solvent intercalation.

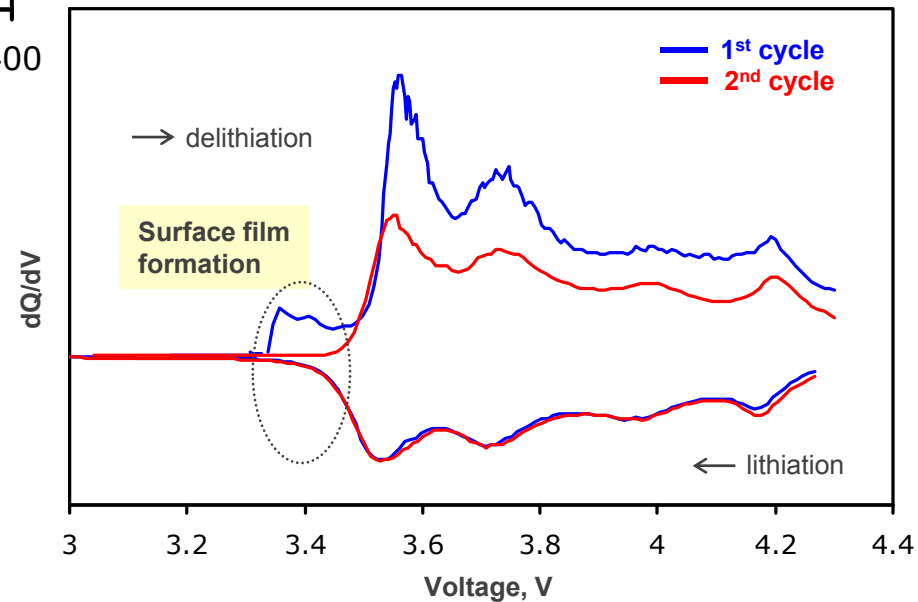


Oxide Electrode - 1.2M LiPF₆ in GC:DMC (2:8)

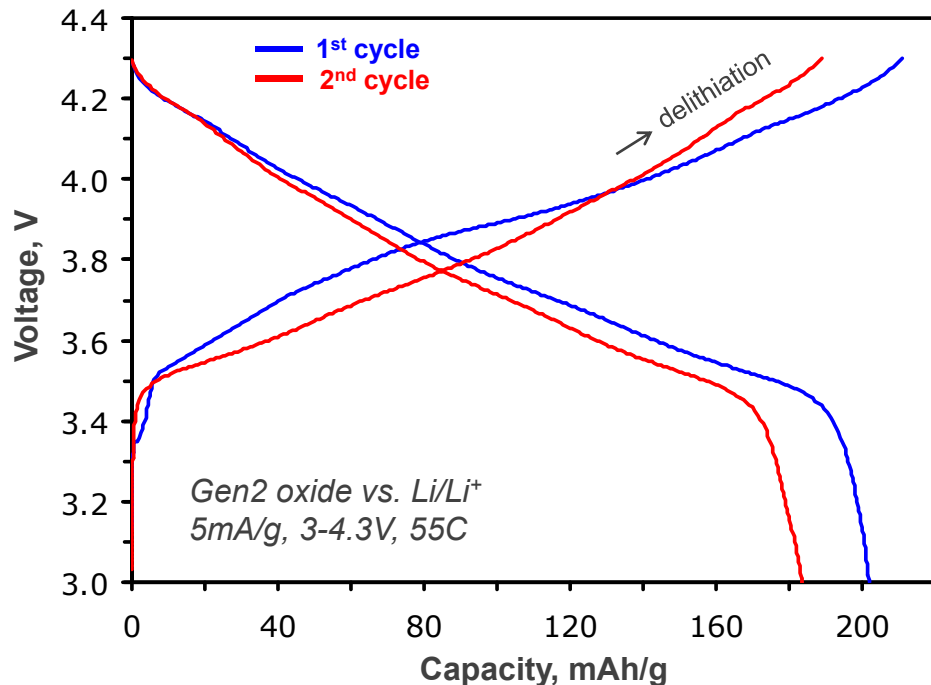


Oxide electrodes can be cycled in GC-based electrolytes. But, significant lithium consumption occurs during the first cycle. Later cycles show reasonable data.

Lithium is consumed during the first charge cycle to form a surface film on the oxide electrodes. (Significant Li consumption is not observed for EC-based electrolytes.) The GC apparently oxidizes during the first cycle, but not in subsequent cycles.

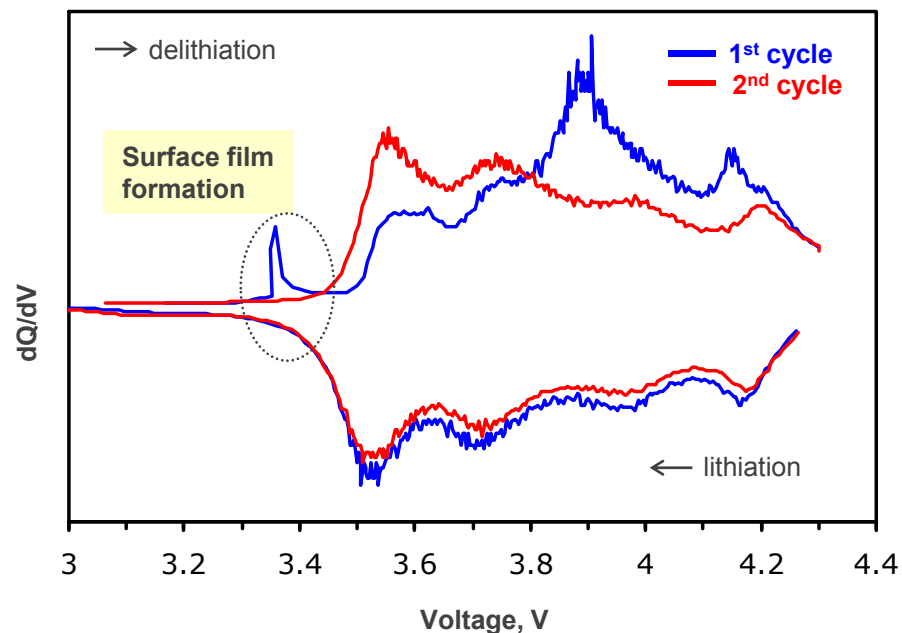


Oxide Electrode - 1M LiBF₄ in GC:DMC (2:8)

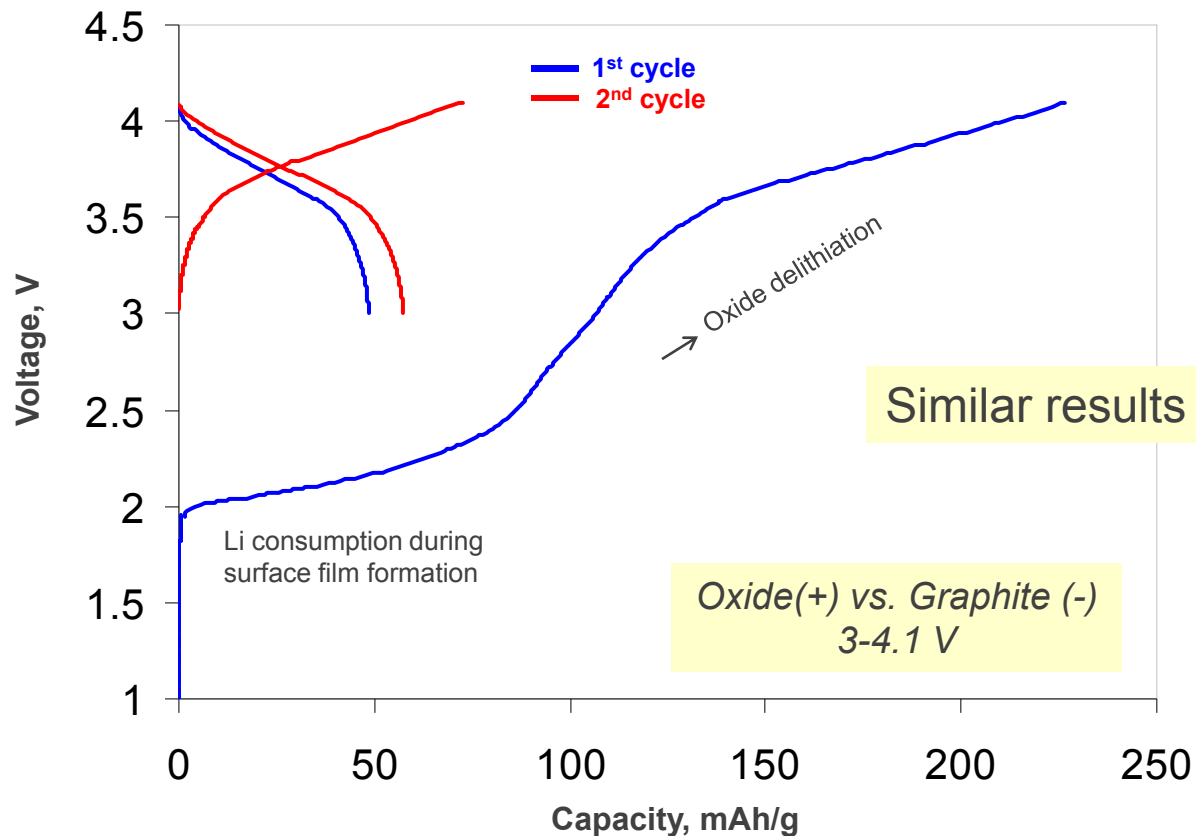


Lithium is consumed during the first charge cycle to form a surface film on the oxide electrodes. (Significant Li consumption is not observed for EC-based electrolytes.) The GC apparently oxidizes during the first cycle, but not in subsequent cycles.

Oxide electrodes can be cycled in GC-based electrolytes. Lithium consumption during the first cycle is smaller than that for LiPF₆ electrolytes. Later cycles show reasonable data.

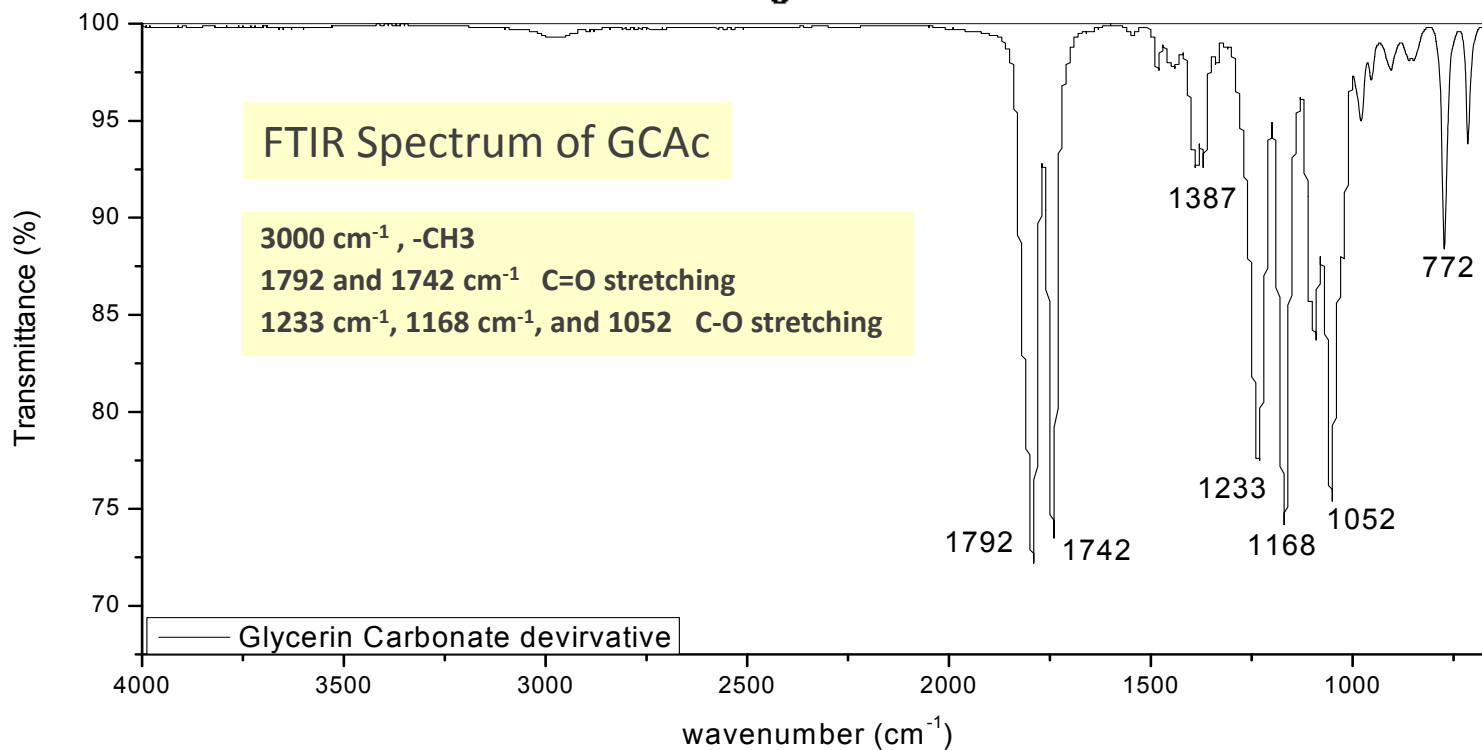
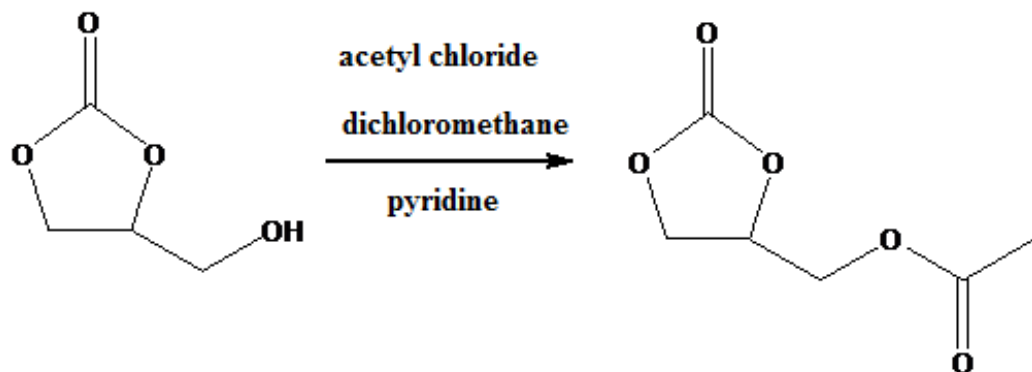


Oxide/Graphite Cell - 1.2M LiPF₆ in GC:DMC (2:8)

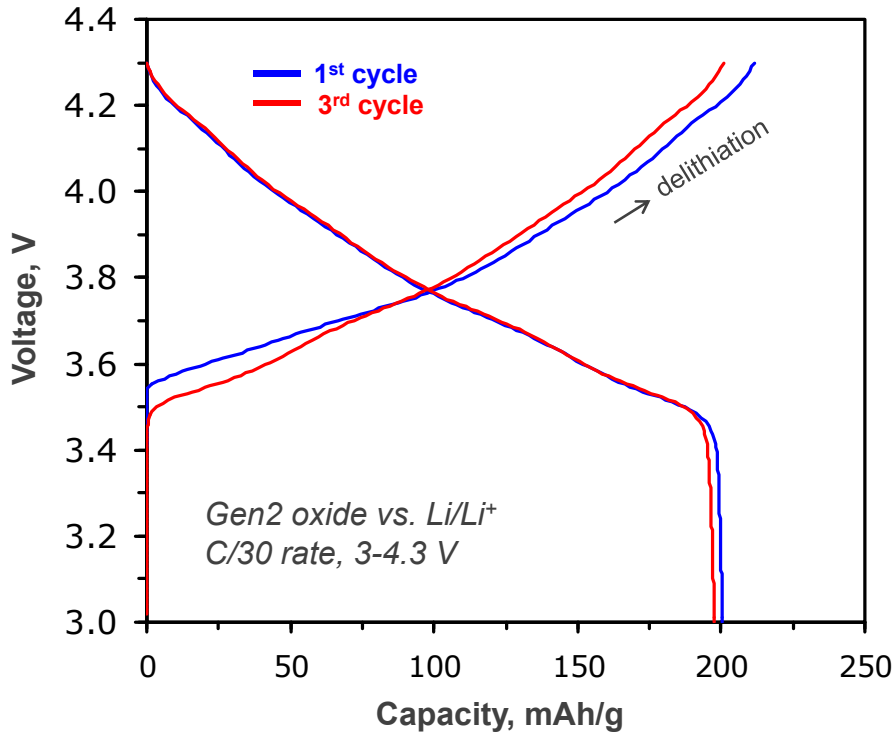


Lithium consumption during GC oxidation depletes Li-inventory in full cell. Therefore, full cell cycling behavior is not good

Preparing the methyl ester version of GC (aka GCac)

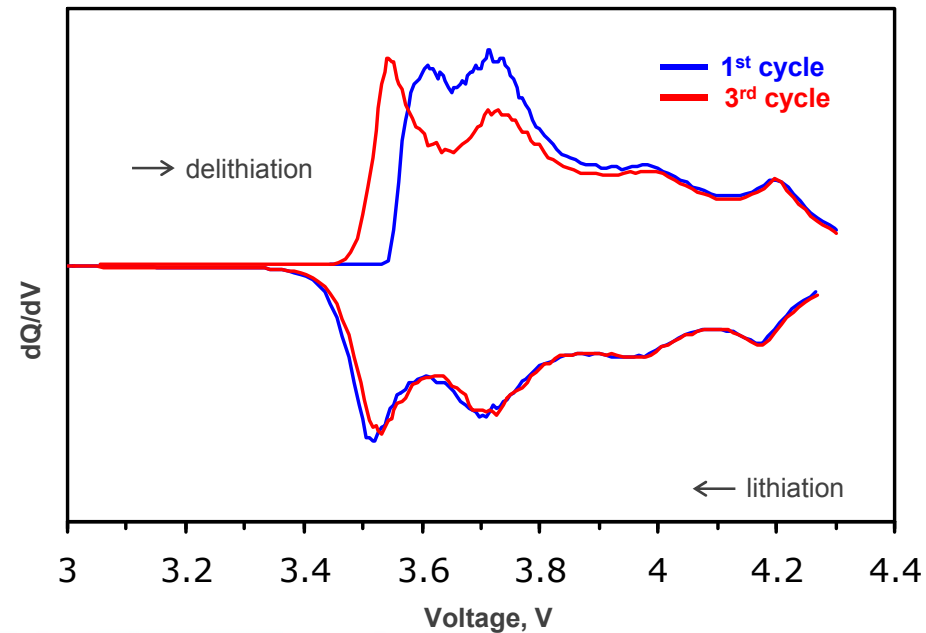


Oxide Electrode - 1.2M LiPF₆ in GCAC:DMC (2:8)

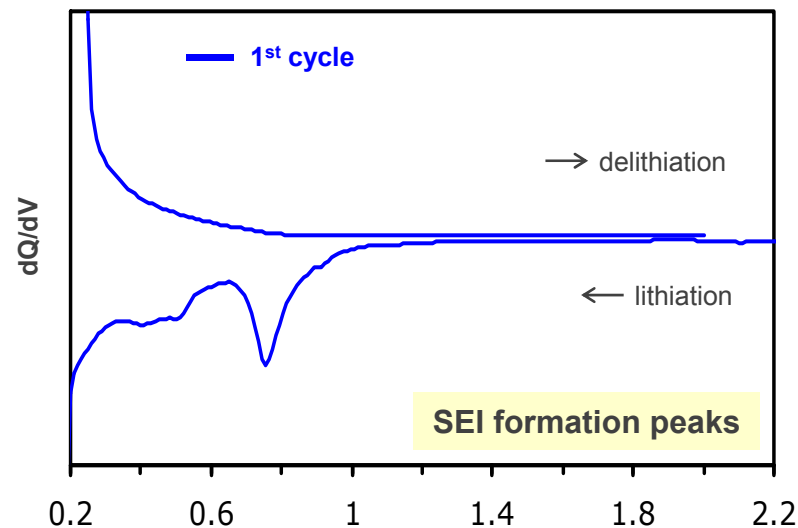
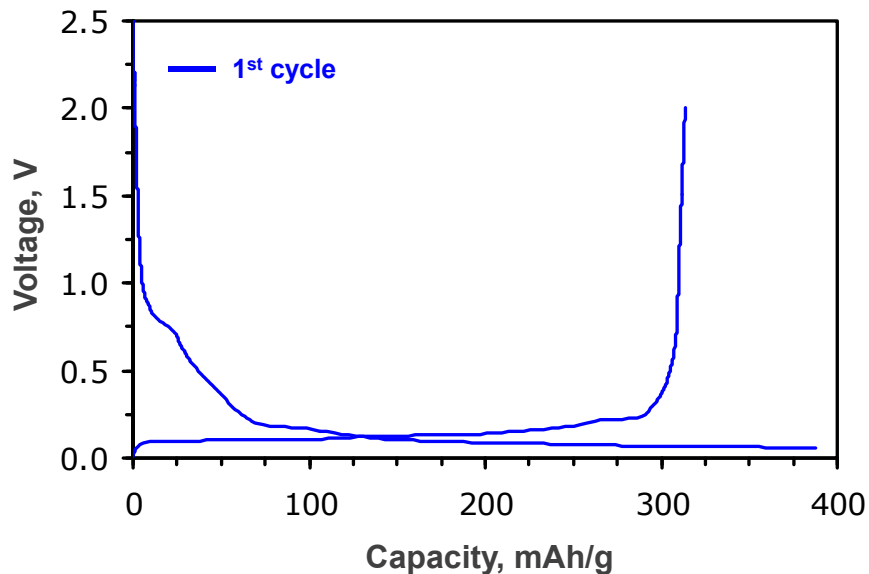


Oxide electrodes can be cycled in GCAC-based electrolytes

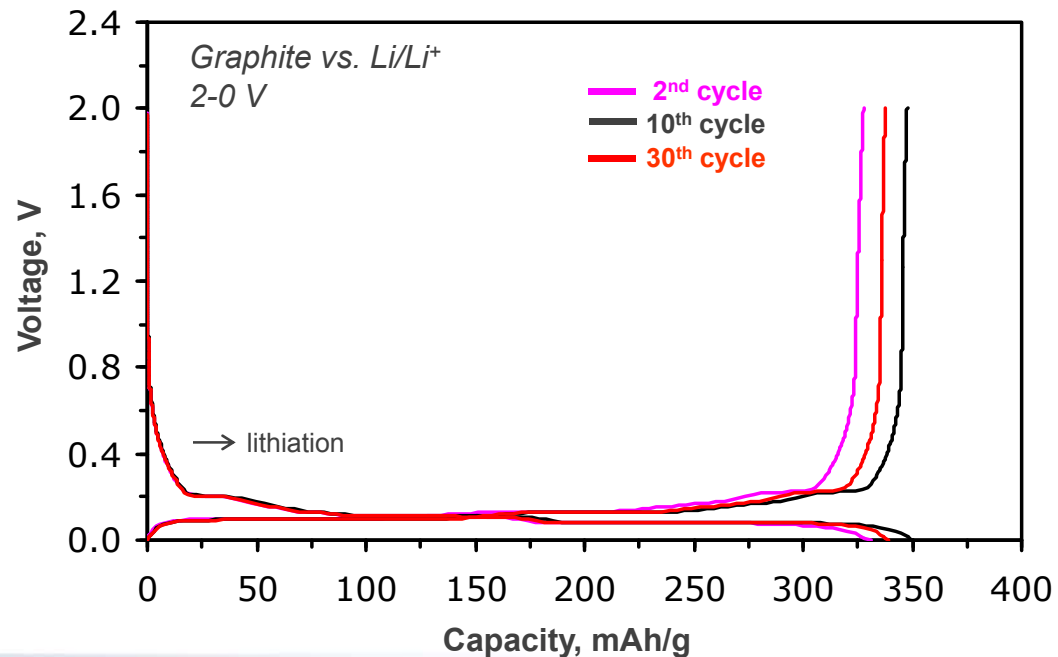
The lithium consumption observed for GC-based electrolytes is NOT seen in GCAC-based electrolytes.



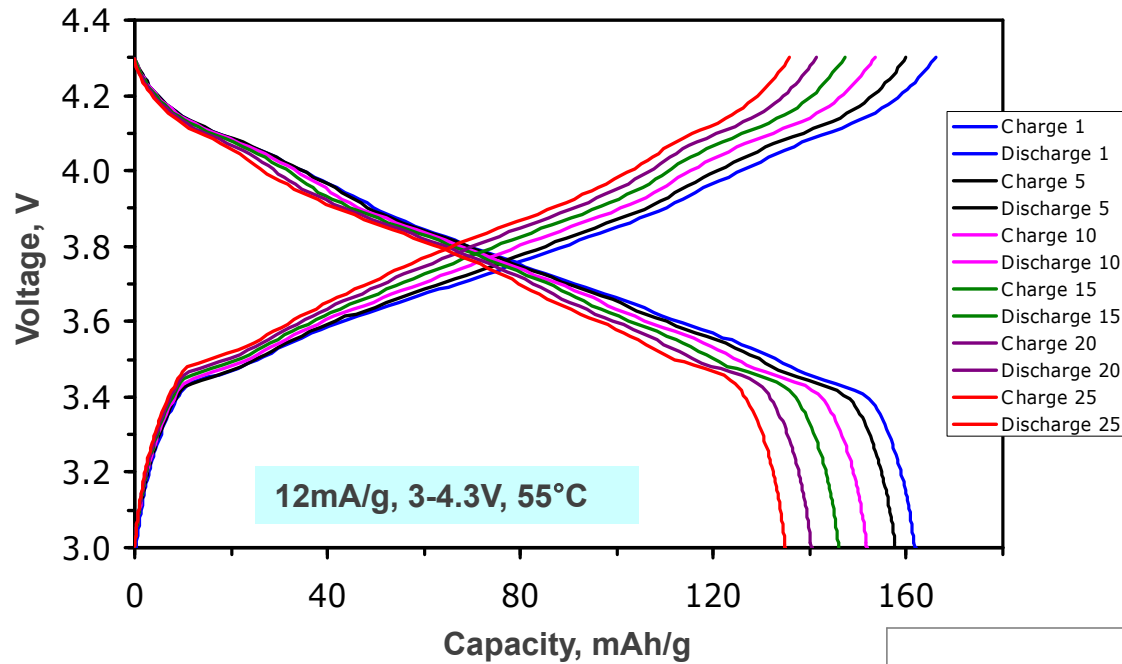
Graphite Electrode - 1.2M LiPF₆ in GC:DMC (2:8)



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

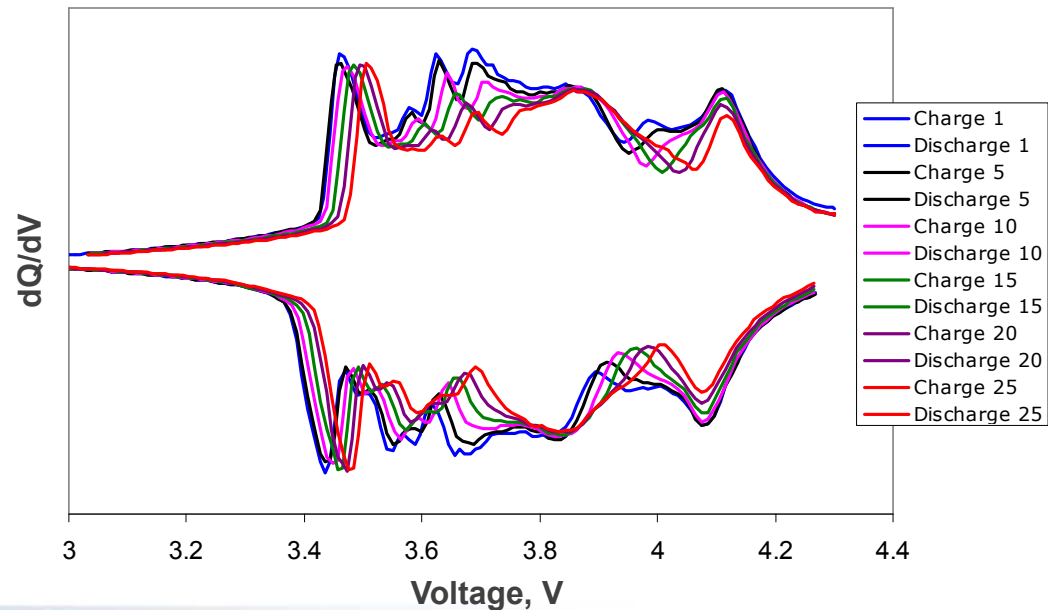


Oxide/Graphite Cell - 1.2M LiPF₆ in GCAC:DMC (2:8)

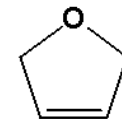


Oxide/Graphite (Full) cells show reasonable cycling behavior in GCAC-based electrolytes

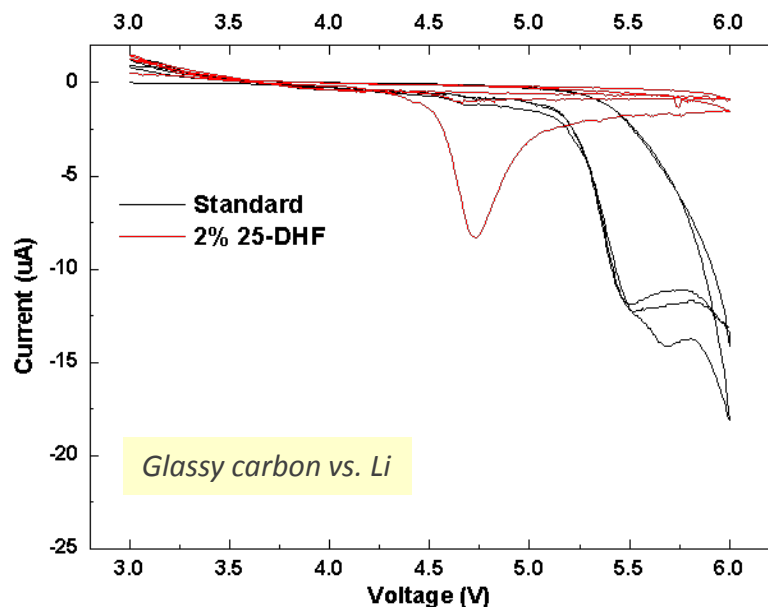
Capacity retention is better when upper voltage is limited to 4V. This observation suggests that the electrolyte oxidizes at higher voltages (> 4V).



2,5 DHF showed promise as an electrolyte additive in early tests

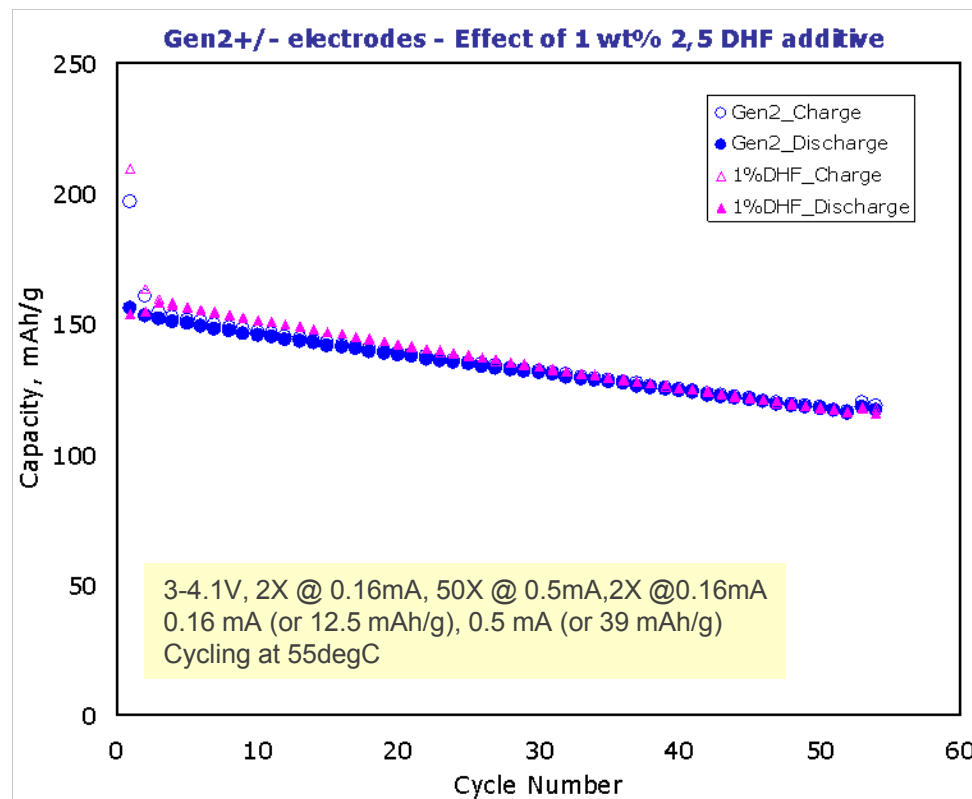


2,5-DiHydroFuran

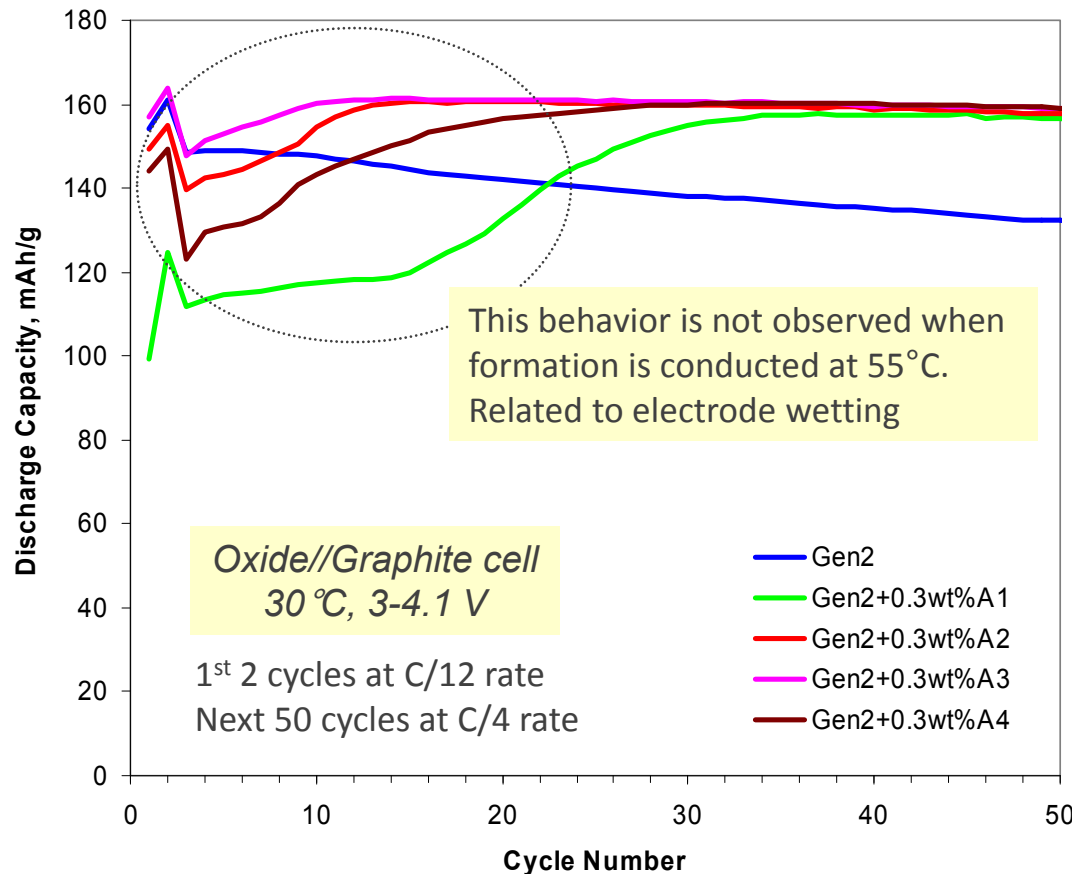


Baseline electrolyte: stable to 5.2V vs. Li
2%DHF-added electrolyte: 4.75V vs. Li peak
2,5 DHF is oxidized at high voltages
Additive could form passivation layer on positive electrode

Capacity data from the cells are similar. 2,5DHF addition to Gen2 electrolyte does not seem to have a beneficial effect on cell capacity retention. Conclusions from tests conducted in NMC(+)//Gr(-) were similar.



A new family of electrolyte solvents/additives has been identified - performance and life tests are in progress

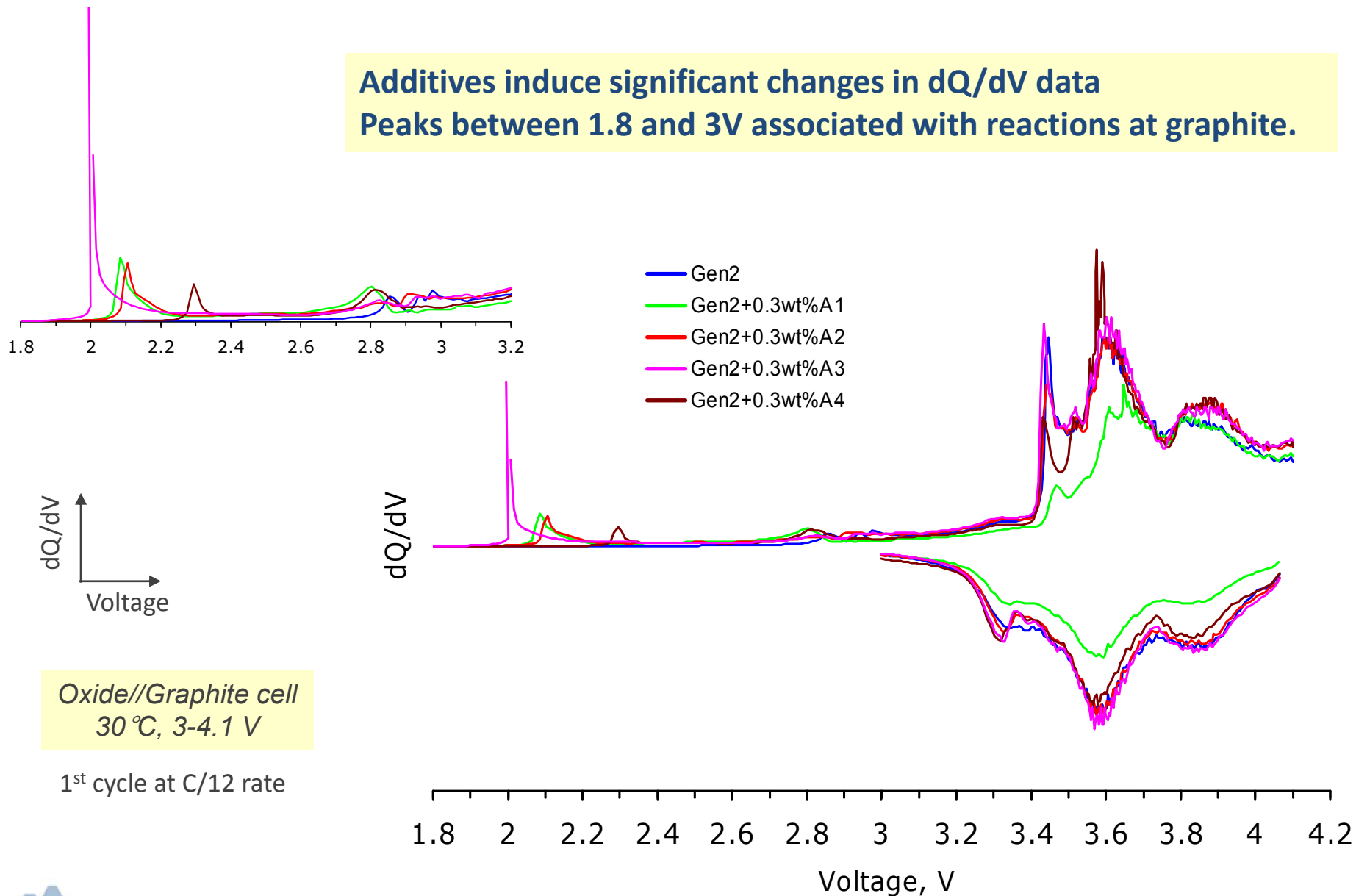


Compounds A1, A2, A3 and A4 are derived from the same family of compounds. They are also being evaluated as solvents

Small additive concentrations (0.3 wt%) improve capacity retention. Cells containing higher concentration (3 wt%) show lower capacity and poorer capacity retention. Of the above, A3 appears to be the best candidate.

dQ/dV data - Effect of Additives (see previous slide)

Additives induce significant changes in dQ/dV data
Peaks between 1.8 and 3V associated with reactions at graphite.

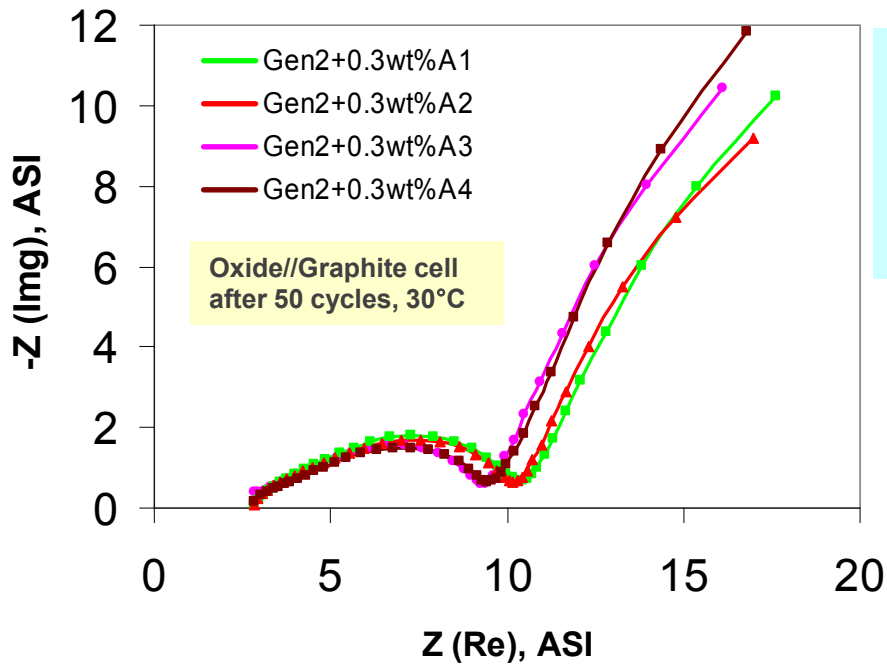


Oxide//Graphite cell
30 °C, 3-4.1 V

1st cycle at C/12 rate

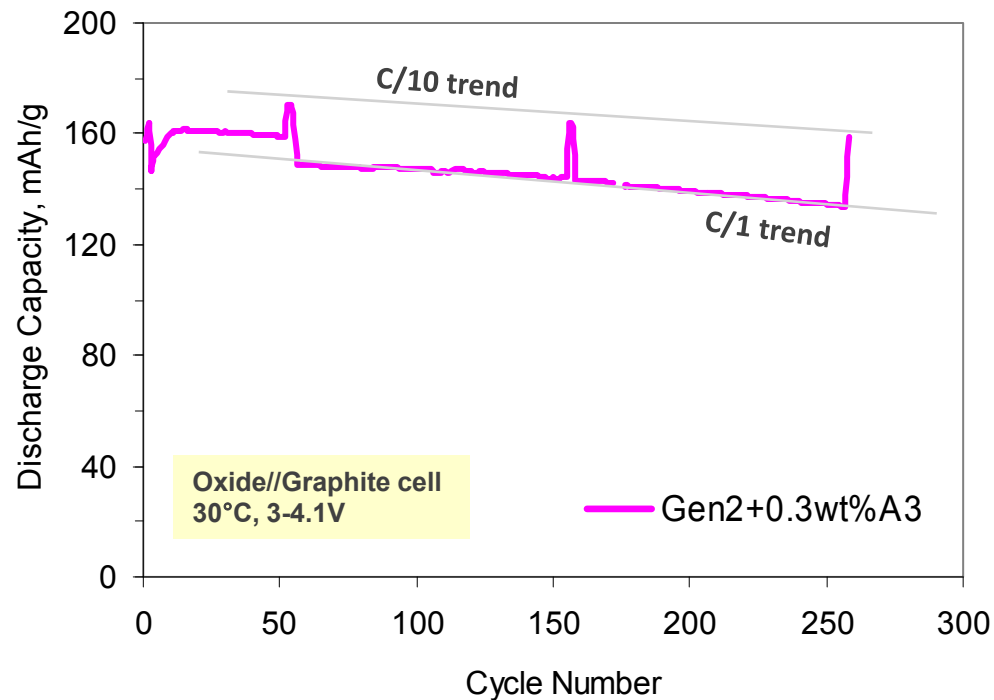


Effect of additives on cell impedance and long-term cycling behavior



Impedance of cells containing additives are comparable or better than that of cells with Gen2 electrolyte.

Long-term cycling behavior of cells, both at RT and at higher temperatures is currently being evaluated.



Ionic Liquid Electrolytes

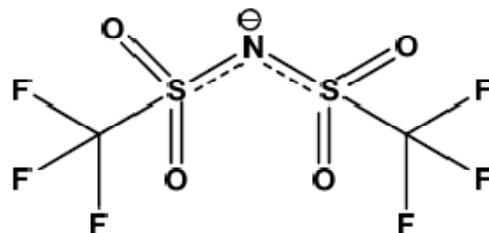
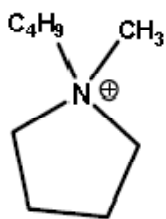
P_{14} TFSI = N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide

P_{13} FSI = N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide

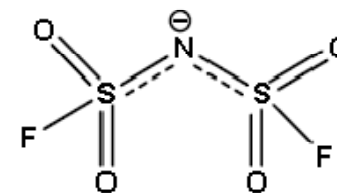
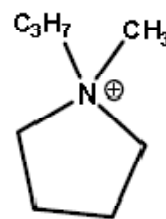
Salt

LiTFSI

LiFSI



P_{14} TFSI



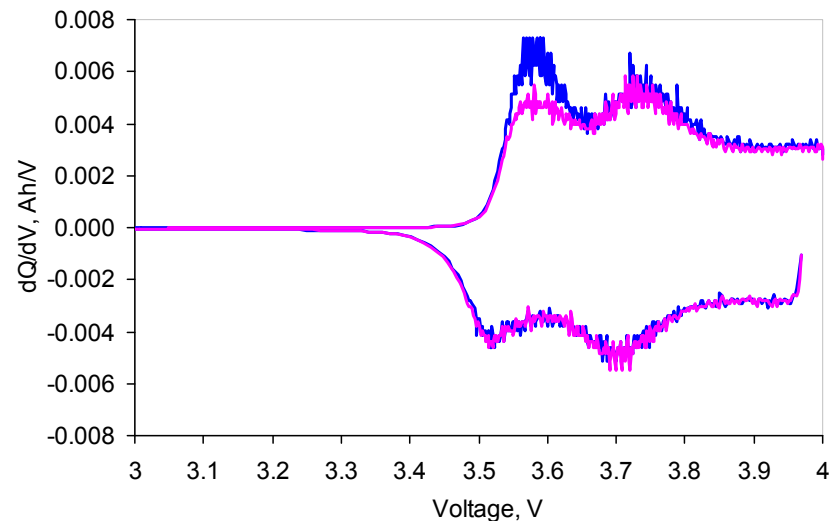
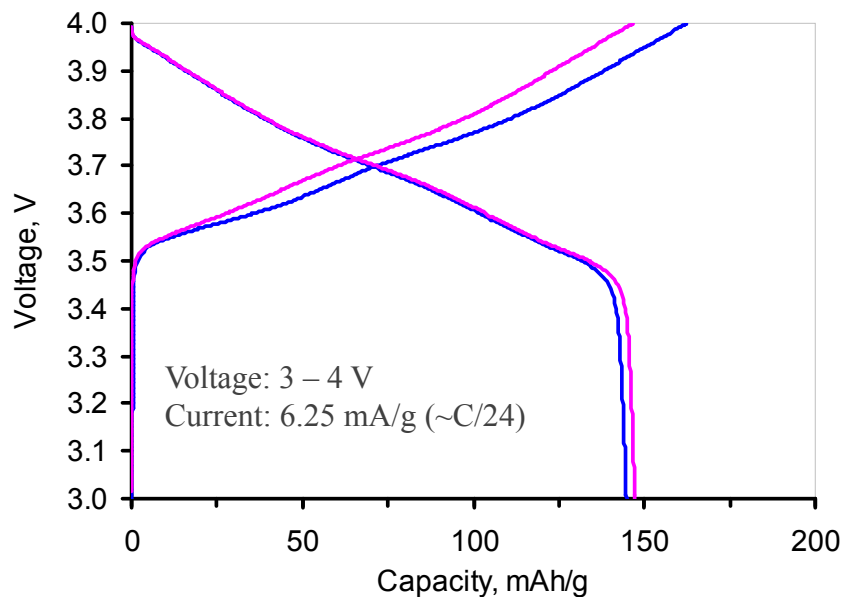
P_{13} FSI

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}

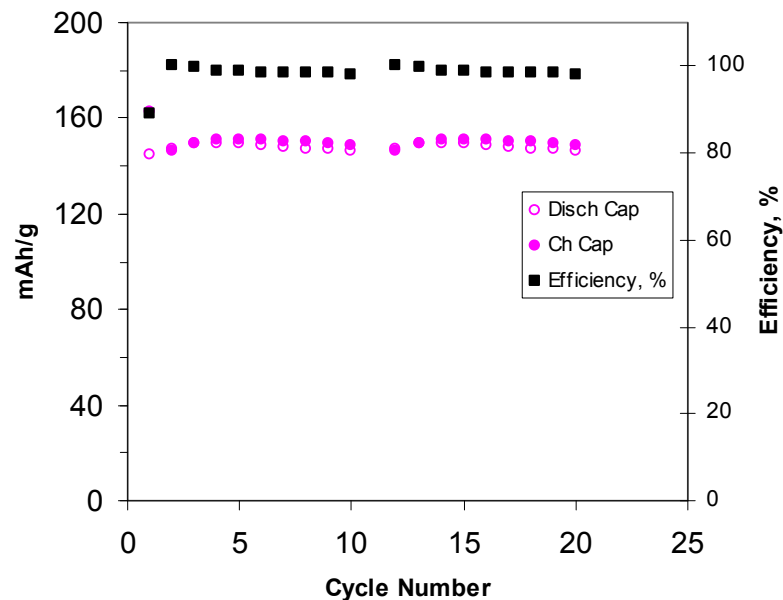
Electrolytes were dried at 50°C for 48h (in a vacuum oven located inside a glovebox) before use.



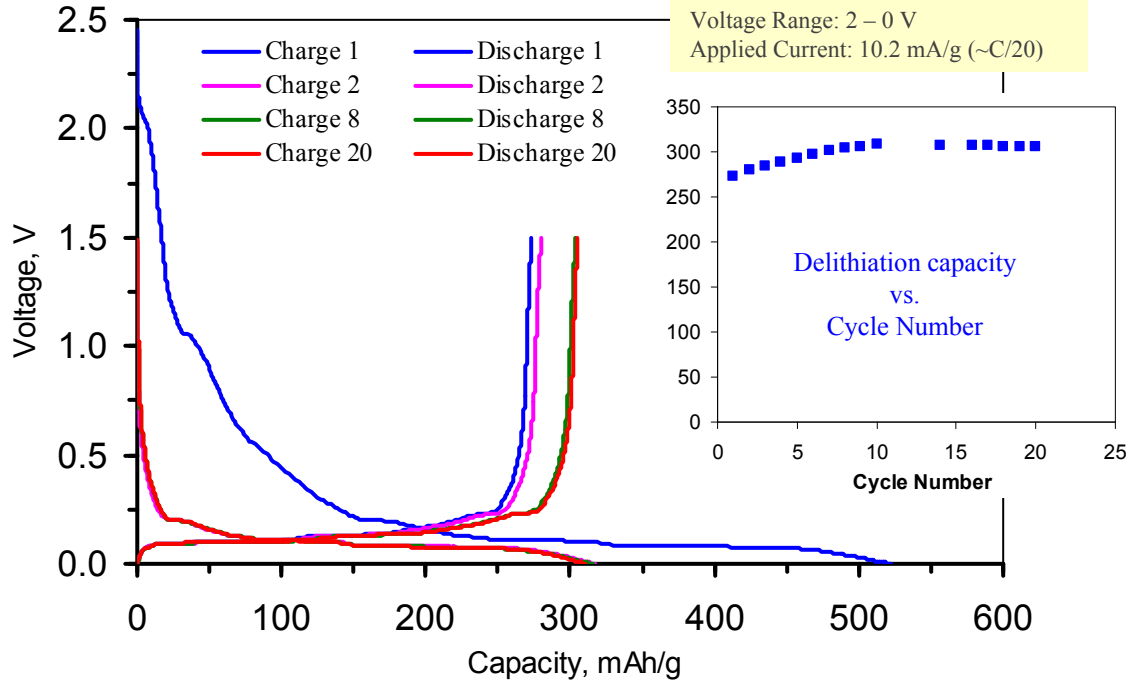
Oxide(+)//Li cell with P14 electrolyte, tested at 55°C



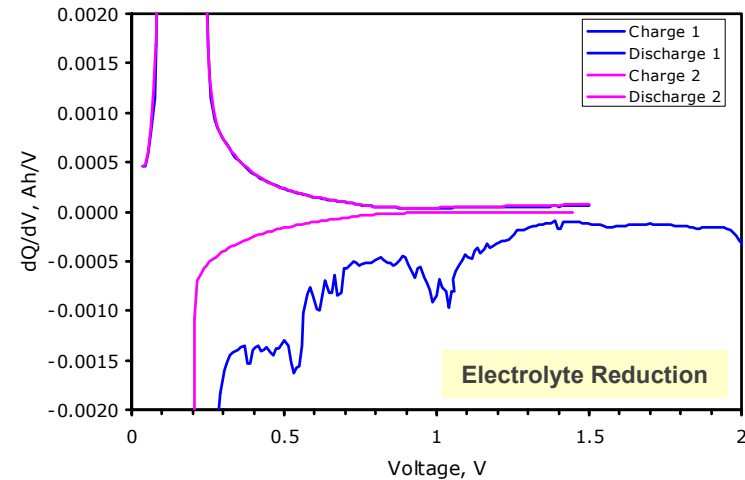
- The NCA electrode cycled well in the 3-4V range; the capacity values and dQ/dV plots are as expected.
- The cells retained their original capacity after 20 cycles at 55°C.
- We did not test cells at higher voltages, i.e., >4V vs. Li.



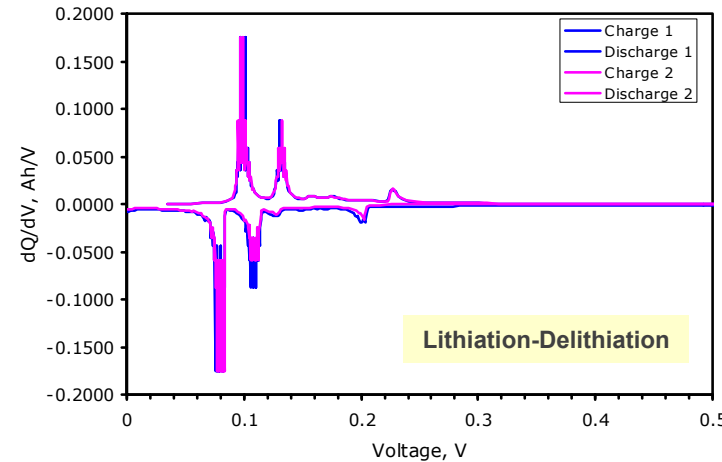
Graphite(-)//Li cell with P13 electrolyte, tested at 55°C



Electrolyte reduction starts \approx 1.5V. Seen only in 1st cycle.



1. Cell delithiation capacities increased during the early cycles and steadied around 300 mAh/g. These cells can be cycled more than a hundred times.
2. Electrochemical eff. during first cycle is \sim 52%, 2nd cycle is \sim 90% and $>$ 99% after 10 cycles. SEI formation during early cycles consumes significant amounts of Li.



Graphite staging behavior is as expected.



Ionic Liquids Study Summary

P14_TFsi - worked well in NCA(+)/Li cell, 3-4V, gave expected capacity

P14_TFsi - cell worked, in Graphite/Li cell, 1.5-0V, but capacity less than half of expected value

P14_TFsi - NCA(+)/Gr cell, poor electrochemical behavior

P13_Fsi - worked well in Graphite/Li cell, 1.5-0V, 3-4V, gave expected capacity, cell can be cycled more than a hundred times

P13_Fsi - NCA(+)/Li cell did not work – electrolyte apparently degrades >3.5V

P13_TFsi - NCA(+)/Gr cell, poor electrochemical behavior



Summary and Future Work

- 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
- We will continue our investigations of novel solvents that include glycerol carbonate (GC), and modifications thereof, which includes
 - Preparation of compounds derived from GC
 - Performance/cycling behavior of various solvent-salt electrolyte mixtures
 - Properties (*electrochemical stability window, temperature stability, etc.*) of “promising” electrolytes
- Develop criteria to identify new electrolyte additives that can enhance cell life by protecting electrode surfaces from reactions with the electrolyte
 - Examine multifunctional additives that can simultaneously affect both positive and negative electrodes
- Continue studies on ionic liquids and on mixtures of ionic liquids and conventional electrolytes
 - Examine electrode performance/cycling behavior under PHEV conditions



Related Publications and Presentations

1. Electrolytes For Lithium And Lithium-Ion Batteries

Argonne Invention Report, ANL-IN-10-003

2. Electrolytes For Lithium And Lithium-Ion Batteries

Argonne Invention Report, ANL-IN-08-071

3. Electrochemical Behavior of electrolytes based on glycerol carbonate and related solvents

Abraham et al., manuscript in preparation

