Novel Electrolytes and Additives

Project Id: ES023

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This presentation does not contain any proprietary or confidential information
Overview

Timeline
- Start date: FY10
- End date: On-going
- Percent complete: - project on-going

Budget
- Total project funding - 100% DOE
  - FY10: $300K
  - FY11: $300K

Barriers
- Performance
- Calendar/Cycle Life
- Abuse tolerance

Partners
- Argonne colleagues
- Purdue University
- University of Rhode Island
- Kang Xu, ARL
- JPL colleagues
- Industrial collaborators
Project Objectives - Relevance

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.

- To enable commercialization of safe, 40-mile range, Li-ion based PHEV batteries with calendar life that exceeds 10 years.

- To identify and synthesize electrolyte components (solvents, salts, additives) that are compatible with electrodes relevant to the ABR program.

- To evaluate performance of these electrolyte components in ABR cells.

- To identify electrolyte performance mechanisms – the knowledge can be used to design improved electrolyte systems for transportation applications.
Approach

**Target Compounds Identification and Acquisition**
- Organic Chemistry
  - Chemical libraries
  - Organic synthesis

**Electrochemical Performance Evaluation and Surface Analysis**
- Electrochemistry
  - Electrochemical cycling
  - AC Impedance
  - Cyclic Voltammetry

**Lead Candidates Identification and Modification**
- Organic Chemistry
  - Chemical libraries
  - Organic synthesis

**Analytical Chemistry**
- X-Ray Photoelectron Spectroscopy
- FTIR & Raman Spectroscopy
- NMR Spectroscopy
- Mass Spectroscopy
Technical Accomplishments and Progress

- **Identified new family of heteroaromatics substituted carboxylic ester-based compounds as electrolyte additives**
  - Determined effects on cell performance and calendar life
  - Argonne filed a USA Patent Application based on these compounds (ANL-376, Cheng, G.; Abraham, D.P., 2010, September 23)
  - Recommended list of electrolyte additive compounds for scale-up

- **Investigating the relationship of additive structure to characteristics of surface films at both positive and negative electrodes**
  - Currently examining the effect of SEI composition/morphology on interactions with Li-ion.

- **Designed and synthesized various GC-derivative compounds including alkyl ethers, carboxylic esters, and alkyl carbonates**
  - Examined performance/cycling behavior of these compounds, both as co-solvents and as electrolyte additives
  - Argonne filed a USA Patent Application (ANL-368, Serial No. 12/910,549) and is in the process of filing another non-provisional patent application (ANL-382, Argonne Invention No. ANL-10-093) based on data from these compounds
Baseline Chemistry used for electrolyte evaluation

- **Positive Electrode:**
  - 84% Fuji CA1505 (NCA)
  - 4% SFG-6 + 4% carbon black
  - 8% PVDF binder (KF1100)

- **Negative Electrode:**
  - 92% Mag-10 Graphite (Gr)
  - 8% PVDF binder (Kureha#C)

- **Baseline Electrolyte (Gen2):**
  - 1.2 M LiPF₆ in EC/EMC (3:7)

- **Typical cycling range:**
  - Positive: 3 – 4.3V vs. Li
  - Negative: 2 – 0 vs. Li
  - Full Cell: 3 – 4.1V
Examples of heteroaromatic compounds examined as electrolyte additives for Lithium Batteries

- Methyl Picolinate (MP)
- Ethyl Nicotinate (EN)
- Methyl Isonicotinate (MIN)
- Methyl-1-methylpyrrole-2-carboxylate (MMPC)
- 2-Ethyl furoate (2-EF)
- 3-Ethyl furoate (3-EF)
- 2-Ethyl thiophenecarboxylate (2-ETC)
- 3,4-diethyl pyridine Carboxylate (3,4-DEPC)
- 3,4-pyridinedicarboxylic anhydride (3,4-PyDCA)

Merits of picolinates and their derivatives

- Compounds are relatively
  - low cost ($0.3 - $4/g)
  - non-toxic (Chromium picolininate is used as a nutritional supplement, nicotinate is derived from tobacco)
  - flash points > 90 C
NCA+/Gr- cell - Effect of Additive Structure

• Small amounts (0.3 wt%) of MP, EN and MIN addition to baseline electrolyte improves capacity retention. MIN appears to be the best performer based on initial capacity loss.
• Small structural changes cause significant impact on initial cycling behavior – further studies can provide information on the effect of molecular structure on SEI characteristics.

![Graph showing discharge capacity and impedance](image)

- Small amounts (0.3 wt%) of MP, EN and MIN addition to baseline electrolyte does not significantly alter cell impedance.
- The graphite SEI generated by MP may have the strongest interaction with the Li-ion, which may explain why the compound displays the widest mid-frequency arc.
Initial Cycling Behavior of NCA+/Gr- cell: Effect of Formation Cycle (0.3wt% MP in baseline electrolyte)

Cells with 0.3 wt% MP in baseline electrolyte show relatively lower initial capacity when formation is conducted at 30°C. The initial capacity is significantly higher when formation is conducted at 55°C.

For cells with the MP electrolyte additive, the one formed at 55°C shows a lower impedance than the one formed at 30°C.
Mechanistic Hypothesis

The SEI generated by the various additives is expected to bear signatures of the corresponding lithium-additive complexes. Stronger SEI/Li\(^+\) interaction may cause higher impedance. The “initial induction period” reflects changes in SEI characteristics during cycling.
All additives with possible intramolecular bidentate binding site for Li-ion exhibit a long "initial induction period" during cycling.

Different heteroatoms have different binding affinities to the Li-ion; N and S binding to the Li-ion appears stronger than O.
Specific capacity during the initial cycles improves significantly when the two possible binding sites for the Li-ion are moved away from each other, avoiding the stronger intramolecular interaction with the Li ion.

Small additions of MIN, PyDCA, and 3-EF (0.3wt%) to the baseline electrolyte improve cell capacity retention compared to the baseline electrolyte in the first 150 cycles.
Cells with 0.3wt% MIN additive show lower impedance increase after 100 cycles at 1C rate than cells with the baseline electrolyte.
Philosophy Behind Study of GC derivatives
- A Good System to Explore Novel Electrolytes

- What is Glycerol Carbonate (GC)?
  Glycerol Carbonate is just an oxygen-substituted Propylene Carbonate!

- What makes GC a good system to study?
  GC can be easily derivatized/modified. Therefore, it provides an excellent platform to study bi-/multi-functional electrolytes.

- Why its important to study bi-/multi-functional electrolyte systems?
  SEI formed by EC is good but not perfect, therefore electrolyte additives are often required. It is reasonable to believe that a better SEI can be achieved by introducing extra functionalities into the molecule.

Note: PC cannot be cycled with graphite anode but GC can.

Note: X can be any functional group thanks to modern organic synthesis techniques.
Previously reported - GC and GCME data

- Cell containing 1.2M LiPF$_6$ in GC:DMC=2:8 can be cycled with graphite anode.
- Surface film formation at the first cycle on oxide electrode indicates oxidation of GC.

- Cell containing 1.2M LiPF$_6$ in GCME:DMC=2:8 can be cycled with both graphite and oxide electrodes.
Evolution towards Glycerine Carbonate Methyl Carbonate (GCMC)

- GC can be cycled with graphite anode without exfoliation!
- However, oxidation potential of GC is low due to the free hydroxyl group.

- Protection of free hydroxyl group in GC improves the cathodic stability significantly.

Glycerol Carbonate

Glycerine carbonate methyl ester

Glycerine carbonate methyl carbonate (GCMC)

Ethylene carbonate (EC) + Dimethyl carbonate (DMC)
Synthesis and NMR Characterization of GCMC

Glycerol Carbonate (1eq) + Methyl Chloroformate (1.25eq) → Glycerine carbonate methyl carbonate (GCMC)

0 °C and then Reflux

\[
\begin{align*}
\text{Glycerol Carbonate} \quad & \quad \text{Methyl Chloroformate} \quad & \quad \text{Glycerine carbonate methyl carbonate (GCMC)} \\
\end{align*}
\]

\[
\begin{align*}
\text{1H NMR} \quad & \quad \text{13C NMR} \\
\end{align*}
\]

Collaboration with Dr. Kang Xu, ARL
GCMC can be used as a co-solvent – data shown below is from cells that do not contain EC.

1.2M LiPF$_6$ in GCMC:EMC=1:6 wt%

Collaboration with Dr. Kang Xu, ARL
GCMC can also be used as an electrolyte additive - data below is from NCA+/Gr- cells with 5wt% GCMC in baseline electrolyte

1st 2 cycles at C/12 rate
Next 50 cycles at C/4 rate
Then 100 cycles at C/1 rate

Capacity, mAh/g

Cycle Number

AC impedance data show that impedance of GCMC-bearing cells is similar to that of cells with baseline electrolyte during the first 50 cycles – the impedance is higher after longer term cycling (150 cycles)
Other promising GC derivatives are also being examined as electrolyte additives - data below is from NCA+/Gr- cells

The additive-containing cells have a slightly higher impedance than the baseline cells. However, cell impedance is unchanged after 50 cycles at C/4 rate.

Cells containing 3wt% of additives A and B showed almost no capacity loss after 50 cycles at C/4 rate. Long-term cycling is in progress.
Collaborations

- **Partners**
  - Purdue University (A. Wei et al.)
    - Collaboration to synthesize derivatives of glycerol carbonate and other promising electrolyte additive compounds
  - University of Rhode Island (B. Lucht et al.)
    - Collaboration to determine changes at the electrode-electrolyte interface using surface analysis techniques.
  - Colleagues at Labs (ARL, JPL)
    - Collaboration to evaluate electrolyte additives or solvents to facilitate/accelerate the development process.
  - Industry Colleagues
    - Collaborations to evaluate novel compounds in ABR cells

- **Technology Transfer**
  - Knowledge generated during the course of our studies is shared with colleagues in US battery industry through presentations, articles, and reports
Work in Progress/Future Work

- Continue exploration of novel electrolyte additives based on our approach: screening, testing, analyzing and optimizing. Our next experiments will be on electrodes identified for the next set of ABR PHEV cells. These experiments will include:
  - Electrolyte stability studies at voltages >4.5V using high-energy NMC layered electrodes
  - Electrolyte stability studies at voltages >4.8V using LiNi_{1/2}Mn_{3/2}O_4 spinel electrodes

- Conduct surface characterization of formed and cycled electrodes to:
  - Understand composition/constitution of “stable” electrode passivation layers
  - Determine oxidation/reduction pathways that lead to “stable” passivation layers
  - Optimize and design better candidates to meet cost, calendar life and safety requirements of batteries for PHEV applications.

- Continue investigations of glycerol carbonate (GC) derivatives:
  - Systematically changing functional group on GC results to effect changes in electrochemical behavior. Charting the structure – activity relationships will yield the mechanistic understanding required to design better electrolyte systems

- 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
Summary

- The objective of this study is to identify and develop novel electrolyte additives and electrolyte solvents to improve the electrochemical performance and calendar life of lithium-ion cells for PHEV applications.
- Our approach is to conduct systematic investigation of promising candidates, such as heteroaromatic compounds and derivatives of glycerol carbonates, by employing synthetic organic chemistry, electrochemical testing, and surface analysis techniques.
- We have identified a new family of heteroaromatics-substituted carboxylic ester-based electrolyte additives/co-solvents. Small additions (~0.3 wt%) of these compounds, which include methyl picolinate (MP), methyl isonicotinate (MIN), 3,4-diethyl pyridinecarboxylate (3,4-DEPC), 2,3-pyrazinedicarboxylic anhydride (2,3-PzDCA), etc. to the baseline electrolyte (1.2M LiPF₆ in 3EC:7EMC) improves capacity retention of NCA(+)//graphite(-) cells.
- We have conducted extensive investigations on compounds derived from glycerol carbonate (GC). Our data show that cells with 5wt% GCMC (Glycerol Carbonate Methyl Carbonate) as an additive to the baseline electrolyte exhibit improved long-term cycling performance. Noted that GCMC can be used as a replacement for Ethylene Carbonate (EC) in the electrolyte. Alkyl ether derivatives of GC have also been evaluated as electrolyte solvents or co-solvents. Noted that the secondary functional group on the molecules has a significant effect on electrochemical performance.