Synthesis, Screening, and Characterization of Novel Low Temperature Electrolyte for Lithium-Ion Batteries

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Overview

Timeline
- Start: 10/01/2019
- Finish: 09/30/2022
- Percent completed: 60%

Barriers addressed
- New electrolyte to enable Li-ion batteries to deliver > 70% room temperature capacity at -20 °C while still meeting the fast charge, calendar and cycle life requirement of USABC in temperature range between 30 °C and 60 °C
- To reduce the production cost of a PHEV battery

Budget
- Funding received in FY20 DOE: $1,000k
- Funding received in FY21 DOE: $1,000k

Collaborators
- Stony Brook University
- Pacific Northwest National Laboratory (PNNL)
- Argonne National Laboratory (ANL)
New electrolyte systems with improved low temperature performance are critically needed for lithium-ion batteries (LIBs) to power electric vehicles (EVs). Current lithium-ion batteries (LIB) experience a significant capacity drop down to about one fifth of its room temperature capacity at -30 °C. The widely used LIB electrolytes are almost exclusively based on ethylene carbonate (EC) as a major solvent component due to the high dielectric constant and capability to form good solid-electrolyte-interphase (SEI) on the graphite anode. Unfortunately, EC has a rather high melting point (37 °C), leading to significantly increased viscosity and severely decreased Li+ conductivity at low temperatures. LIB also has high impedance at low temperature due to the sluggish Li+ transport through SEI. These issues cause very low capacity and poor cyclability at low temperature. Therefore, to improve the low temperature performance of LIB, it is critical to develop new electrolyte system that is low in viscosity, high in Li+ conductivity, and able to form stable and low-impedance interphase on both anode and cathode. This consortium, with team members of Brookhaven National Laboratory (BNL), Army Research Laboratory (ARL), University of Maryland (UMD), and University of Rhode Island (URI), address the low temperature electrolyte challenge through integrated approaches of theoretical calculation, electrolyte components design, synthesis, and testing, as well as advanced characterization.

The project objective is to develop next generation electrolyte formulations that enable the Li-ion batteries to deliver >70% of room temperature energy at -20 °C, while still meeting the United States Advanced Battery Consortium (USABC) Operating Environment Conditions (-30 to +52 °C), fast charge capability, calendar life testing at 30, 40, 50, and 60 °C.
<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestones</th>
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<tbody>
<tr>
<td>Dec/2020</td>
<td>Optimization of the TTE-based electrolytes (I); Complete the electrochemical testing of half-cells using Li-NMC532 (or NMC622, NMC811 and NCA) cathodes and TTE-based electrolyte at $-20^\circ$C and at C/3 cycling rate at different area capacities; as well as half-cells using graphite anodes (UMD). Complete MD simulations of temperature dependence of the TTE-based electrolytes (ARL). <strong>Completed.</strong></td>
</tr>
<tr>
<td>Mar/2021</td>
<td>Optimization of the TTE-based electrolytes (II); Complete the first stage electrochemical testing of the full-cells using NMC532 (or NMC622, NMC811 and NCA) cathode and Graphite anode at different area capacities in TTE-based electrolyte at $-20^\circ$C and at C/3 cycling rate. (UMD) <strong>Completed.</strong></td>
</tr>
<tr>
<td>Jun/2021</td>
<td>Complete screening, electrochemical testing, and characterization of electrolytes with low salt concentration for low temperature electrolyte using different solvents, salts and additives for graphite-NMC battery application aiming good low temperature performance and low cost (BNL). Complete DFT calculations of the reduction stability of the electrolyte components (ARL). <strong>On schedule.</strong></td>
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<tr>
<td>Sep/2021</td>
<td>Complete ex-situ surface analysis using combination of XPS, IR-ATR, and SEM for graphite/NMC532 (or NMC622, NMC811 and NCA) full cells using TTE based electrolytes to understand interface structure. Complete the first stage investigation of novel ester based low temperature electrolytes. Complete preparation for two manuscripts for publication (BNL, ARL, UMD, URI) <strong>On schedule.</strong></td>
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Approaches

- Design new electrolyte systems using an integrated approach starting from theoretical calculations such as molecular dynamic (MD) calculations to understand the electrolyte-electrode interphases, the functionalities of solvents, salts, and additives; to predict the Li\(^+\) transport property, electronic structure and SEI formation mechanism of the electrolyte for proposing candidates that have high Li\(^+\) conductivity, good stability, as well as low-impedance SEI.
- Screening new electrolyte systems using various solvents, salts and additives and different combination of them for the best electrolyte candidates to achieve improve low temperature performance while still meeting the fast charge and calendar life testing of USABC.
- Solvent candidates to be explored include ethers, esters, nitriles and their fluorine-substituted derivatives. Salt candidates include lithium tetrafluoroborate (LiBF4), lithium hexafluorophosphate (LiPF6), lithium bis(fluorosulfonyl) imide (LiFSI), lithium bis(trifluoromethanesulfonyl) imide (LiTFSI), lithium bis(oxalato) borate (LiBOB), and lithium difluoro(oxalato)borate (LiDFOB) etc. Additive candidates include vinylene carbonate (VC), fluoro ethylene carbonate (FEC), phosphites, phosphates, sulfones, sultones, and sulfates.
- The new electrolyte system is subject to a series of electrochemical testing and diagnostic studies for performance evaluation and mechanistic studies. These knowledges provide feedback to the theoretical model for better understanding and more accurate predictions.
- New electrolyte systems are subject to a series of characterizations and theoretical calculations such as Infrared and Raman spectroscopies as well as x-ray and neutron pair distribution function (xPDF and nPDF) analysis. The SEI and cathode-electrolyte-interphase (CEI) components are subject to characterizations such as x-ray photoemission spectroscopy (XPS), high energy x-ray photoelectron spectroscopy (HAXPES), resonant inelastic x-ray scattering (RIXS), and x-ray absorption spectroscopy (XAS) to obtain information such as structure, depth-profiling, and chemical distribution.
Approaches using localized high concentration electrolytes and Low Concentration Electrolytes

Electrolytes with various concentrations

Moderate  High Concentration  Low Concentration

Low Concentration Electrolytes (LCE):

**Pro:**
- Low cost, low viscosity

**Con:**
- Low ionic conductivity, solvent-derived SEI

ACS Energy Lett. 2020, 5, 4, 1156–1158
ACS Energy Lett. 2020, 5, 11, 3633–3636
Technical Accomplishments

- Isoxazole (IZ) was discovered by this project to be a promising solvent for low temperature application. At -20 °C, IZ based electrolyte still has a conductivity of more than 10 mS/cm which is comparable to that of conventional electrolyte at room temperature. Unfortunately, when LiPF6, LiFSI, and LiTFSI were used as salts, the cells cannot be charged and discharged, suggesting incapability of forming a stable SEI on graphite anode when IZ is used as the solvent. When LiDFOB was used as salt, the cell can be discharged and charged. Adding FEC as a co-solvent was able to further improve the electrochemical performance of IZ-based electrolyte for the Li||graphite half-cell. Results of this work have been written in a manuscript and submitted to *ACS Applied Materials and Interface* (accepted in May 2021).

- IZ based electrolytes with LiDFOB salt, surface film on graphite electrodes after formation cycling at room temperature and post low temperature cycling at -20 °C was investigated by X-ray Photoelectron Spectroscopy (XPS) in comparison with the graphite anode cycled using baseline electrolyte (1 M LiPF6 in EC-DMC). The results show that thicker solid electrolyte interphase (SEI) was formed on anode cycled the baseline electrolyte than that cycled in IZ-based electrolyte. The XPS spectra for IZ-based electrolyte show clear signal of decomposition products of LiDFOB, while no such signal was observed for the baseline electrolyte, providing evidence about the positive contribution of LiDFOB on the formation of stable SEI on the graphite anode and better electrochemical performance of IZ-base electrolytes. Results are being processed to be submitted to the *Journal of the Electrochemical Society* in May 2021.

- Based on the previous work of UMD team of the all-fluorinated carbonate electrolyte (1.28 M LiFSI in FEC0.1FEMC0.2HFE0.7) (Nature Energy, 4, 882–890(2019)), modification of this electrolyte by removing FEC, replacing expensive FEMC was carried out by using X solvent, and replacing low-boiling point HFE with TTE. The electrochemical performance of graphite anodes in 2.0 M LiFSI-X-TTE and 3.0 M LiFSI-X-TTE electrolytes can provide the same capacity at -20 °C as that at room-temperature capacity at a current rate of 1/5 C. NMC811||Graphite pouch cell at 25 oC in 3.0M LiFSI-X-TTE electrolytes delivers a full capacity at 1/3C with a high-capacity retention of 80% after 100 cycles. In addition, the NMC811||Graphite pouch full cell at a low temperature of -20 °C can also deliver 75% capacity at -20°C at the same rate of 1/3 C the results are being processed and the results will be written to a manuscript to be submitted in FY2021.

- Quantum chemistry (QC) calculations were performed on the TTE, TTE/Li+, FEC/Li+, LiFSI and EC/DMC/Li+/PF6- to validate ability of MD simulations predict baseline properties where ample experimental data are available for validation. An excellent ability of MD simulations using the revised APPLE&P force field to predict the Li+ solvation shell composition, diffusion coefficients of all species and temperature dependence of conductivity. MD simulations of the TTE-based electrolytes are currently initiated based upon initial optimization performed by UMD.

- A review paper has been prepared by the consortium and will be submitted for publication in FY2021.
Technical Accomplishments

- It was discovered that when isoxazole (IZ) was used as main solvent, the ionic conductivity of the electrolyte for Li-ion batteries is more than doubled in a temperature range between -20 °C to 20 °C compared to the baseline electrolyte using ethylene carbonate-ethyl methyl carbonate (EC-EMC).
- Lithium difluoro(oxalato)borate (LiDFOB) salt and fluoroethylene carbonate (FEC) additive were used to form stable solid electrolyte interphase (SEI) on the surface of graphite anode.
- Cells using new electrolyte with 1M LiDFOB in FEC:IZ (1:10, vol%) solvents demonstrated very high 187.5 mAh g\(^{-1}\) reversible capacity at -20 °C while the baseline electrolyte only delivered 23.1 mAh g\(^{-1}\) reversible capacity.

Electrochemical impedance spectroscopy (EIS) of (a) 1M LiPF\(_6\) in EC/EMC (3/7) and (b) 1M LiDFOB in isoxazole/FEC (10/1, vol%) electrolytes and (c) their ionic conductivity at different temperature. (d), (e) Voltage profiles of Li/graphite cell using 1M LiPF6 in EC/EMC (3/7) and 1M LiDFOB in isoxazole/FEC (10/1, vol%) at various temperatures at C/10. (f) Cycling performance of Li/graphite cell using 1M DFOB in isoxazole/FEC (10/1, vol%) at 0 °C using C/10 rate.
The C1s, O1s, F1s, B1s and N1s XPS spectra of the pristine graphite and electrodes cycled using baseline and 1M LiDFOB in IZ/FEC (10/1, vol%) electrolytes show that the formation of an oxalates rich SEI in IZ-based electrolytes might be the main contributor to the enhanced SEI stability and improved cycling performance of the IZ based electrolyte.
## Technical Accomplishments

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Capacity RT (1/5C)</th>
<th>Capacity -20°C (1/5C)</th>
<th>Capacity -40°C (1/20C)</th>
<th>Capacity 60°C (1/5C)</th>
<th>Stable over 4.5 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1# 0.75M LiFSI FEC&lt;sub&gt;0.05&lt;/sub&gt;FEMC&lt;sub&gt;0.25&lt;/sub&gt; TT E&lt;sub&gt;0.7&lt;/sub&gt;</td>
<td>100%</td>
<td>NA</td>
<td>10%</td>
<td>NA</td>
<td>Yes</td>
</tr>
<tr>
<td>2# 1.25M LiFSI in FEC&lt;sub&gt;0.05&lt;/sub&gt;FEMC&lt;sub&gt;0.45&lt;/sub&gt; TT E&lt;sub&gt;0.5&lt;/sub&gt;</td>
<td>100%</td>
<td>83%</td>
<td>10%</td>
<td>100%</td>
<td>Yes</td>
</tr>
<tr>
<td>3# 2M LiFSI in MB&lt;sub&gt;0.5&lt;/sub&gt;TTE&lt;sub&gt;0.5&lt;/sub&gt;</td>
<td>100%</td>
<td>86%</td>
<td>54%</td>
<td>NA</td>
<td>No</td>
</tr>
<tr>
<td>4# 2M LiFSI in DEC&lt;sub&gt;0.5&lt;/sub&gt;TTE&lt;sub&gt;0.5&lt;/sub&gt;</td>
<td>100%</td>
<td>100%</td>
<td>59%</td>
<td>NA</td>
<td>No</td>
</tr>
<tr>
<td>5# 1.33M LiFSI in EMC&lt;sub&gt;0.5&lt;/sub&gt;TTE&lt;sub&gt;0.5&lt;/sub&gt;</td>
<td>100%</td>
<td>100%</td>
<td>78%</td>
<td>100%</td>
<td>Yes</td>
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<tr>
<td>6# 2M LiFSI in EMC&lt;sub&gt;0.5&lt;/sub&gt;TTE&lt;sub&gt;0.5&lt;/sub&gt;</td>
<td>100%</td>
<td>100%</td>
<td>78%</td>
<td>100%</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Technical Accomplishments

Electrochemical performance of cells using TTE based electrolyte in comparison with baseline electrolyte.

Rate capacity and cycle stability of Graphite||Li in 2 M LiFSI in EMC$_{0.5}$TTE$_{0.5}$ electrolyte at the rate of 1/3 C at -20°C.

Rate capacity and cycle stability of NMC811||Li in 2 M LiFSI in EMC$_{0.5}$TTE$_{0.5}$ electrolyte at the rate of 1/3 C at -20°C.

Rate performance and cycle stability of NMC811/G Full cell at 1/3C and Temperature: -20°C.
Technical Accomplishments

Electrochemical performance of NMC811||Graphite Full cells using TTE-based electrolyte

- 68% capacity retention @ 0.2C
- 2.2 mAh/cm²

Capacity retention of NMC811||Gr full cell @ -20°C

Capacity retention of batteries with SE(left) and EITI(right) electrolytes charged at RT(1/3C) and discharged at different T

NMC811/G Full cell
- Rate: 1/3C
- Temperature: 50°C
- Areal capacity: 1 mAh/cm²
Technical Accomplishments

MD Simulations of 2M LiFSI(EMC:TTE) electrolyte

- Salt-rich 6M LiFSI: EMC domain within the high fluidity TTE domain
- Strong ion aggregation: only 1.4% of Li$^+$ solvent separated from FSI$^-$
- No “free” FSI$^-$ (<0.14%)
- Ionicity of 0.1-0.11
- At 333 K, conductivity from MD 2.7 mS cm$^{-1}$ in good agreement with exp. 2.43 mS cm$^{-1}$
- $t_+ > 0.6$ MD (Rolling method), 0.54 exp, UMD

LiFSI reduction and decomposition from DFT

$E_{\text{red}} > 1.5$V

$\Delta G = 0.3$ eV
Collaborations with other institutions and companies

- This project is being carried out through collaborative efforts by a consortium of four institutions including Brookhaven National Laboratory (BNL), Army Research Laboratory (ARL), University of Maryland at College Park (UMD), and University of Rhode Island (URI)

- Collaborations with Argonne National Lab. (ANL)

- Collaboration with Pacific Northwest National Lab. (PNNL)
Proposed Future Work for FY 2020 and FY 2021

- **FY2021 Q3 Milestone:**
  Complete screening, electrochemical testing, and characterization of electrolytes with low salt concentration for low temperature electrolyte using different solvents, salts and additives for graphite-NMC battery application aiming good low temperature performance and low cost. (BNL).
  Complete DFT calculations of the reduction stability of the electrolyte components (ARL).

- **FY2021 Q4 Milestone:**
  Complete screening, electrochemical testing, and characterization of electrolytes with low salt concentration for low temperature electrolyte using different solvents, salts and additives for graphite-NMC battery application aiming good low temperature performance and low cost (BNL).
  Complete DFT calculations of the reduction stability of the electrolyte components (ARL).

**FY2022 work proposed:**

- Further develop the TTE-based electrolyte to meet all the criteria required for low temperature electrolytes.
- Explore the new low temperature electrolyte formulation using low-cost solvents and salts and low concentration electrolytes strategy.
- Carry out characterization studies of the electrolytes developed, analyze the results and write manuscripts for publications in scientific journals.
Summary

Relevance
- To develop next generation electrolyte formulations that enable the Li-ion batteries to deliver >70% of room temperature energy at -20 °C, while still meeting the United States Advanced Battery Consortium (USABC) Operating Environment Conditions (-30 to +52 °C), fast charge capability, calendar life testing at 30, 40, 50, and 60 °C.

Approaches
- Theoretical calculations of the new electrolytes, understanding the electrolyte-electrode interphases.
- Synthesis of new solvents, salts, and additives
- Advanced characterizations of the electrolyte systems in actual battery environments

Technical Accomplishments
- Developed a new novel low temperature system using Isoxazole (IZ) based electrolyte with LiDFOB as salt and FEC as additive showing excellent low temperature performance
- The IZ-based new electrolyte was characterized using XPS spectroscopy and the contribution of LiDFOB salt on stable SEI formation is confirmed in comparison with baseline electrolyte using LiPF₆ in EC-DMC
- New low temperature electrolytes using 2.0 M LiFSI-X-solvent-TTE and 3.0 M LiFSI-X-solvent-TTE have been developed and tested. Graphite anodes provided close to 100% of room temperature capacity when operated at -20 C at a current rate of 1/5C.

Proposed Future work
- Explore the new low temperature electrolyte formulation using low-cost solvents and salts and low concentration electrolytes strategy
- Carry out characterization studies of the electrolytes developed, analyze the results and write manuscripts for publications in scientific journals