UNDERSTANDING AND MITIGATING INTERFACIAL REACTIVITY BETWEEN ELECTRODE AND ELECTROLYTE

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2021 DOE Vehicle Technologies Office Annual Merit Review
June 21, 2021

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OVERVIEW

Timeline
- Start: October 2018
- End: September 2021
- Percent complete: 60%

Budget
- Total project funding
  - DOE share: 1.5M
- FY 2021: $500K

Barriers
- Barriers addressed:
  - Performance
  - Life
  - Abuse tolerance
Existing and High voltage (>4.5 V) cathode-electrolyte chemistries of Next-gen Li-ion have life and performance issues that are not well understood on the fundamental level

Partners
- Interactions/ collaborations
ANL, CSE: Zhengcheng Zhang,
Fluorinated electrolytes
SLAC: Mike Toney
Molecular level understanding of interfaces
RELEVANCE

General Objective
• Develop fundamental mechanistic understanding of the principles that govern the decomposition and properties of cathode/electrolyte interfaces and relate them to the performance of high voltage Li-ion cells.

Specific goals
• Develop a methodology and tools for the investigation of the degradation of cathode-electrolyte interfaces using fundamental science-based strategy. (Developed RRDE method for proton detection in carbonate solvents, Built OEMS capability and validated the method)
• Develop an in-depth understanding of degradation mechanisms of existing and novel carbonate solvent-based electrolytes on well-defined model surfaces, followed by real cathode materials (NMC). (Gained insight into carbonate decomposition mechanism, Developed a detailed map of reactions for the decomposition of the solvent, electrolyte and cathode material following carbonate solvent electrooxidation)
• Identify stable electrolyte/electrode interfacial components for Next-gen LiB

Impact
• This project will have an impact on the DOE EERE Office Program, which recognizes that “Achieving the potential of next-generation lithium ion battery chemistries relies on understanding of the underlying chemistry and physics of the cathode interface”.
• It addresses key barriers for Next-gen LiB as defined in the recent U.S. Drive Roadmap: Performance, Life and Abuse Tolerance
APPROACH

- Develop a methodology, tools and systems for the investigation of the degradation of cathode-electrolyte interfaces using fundamental science-based strategy.

- Extend the state of the art of understanding how individual components of the cathode-electrolyte interface behave at potentials relevant for high-voltage Li-ion batteries on model systems.

- Implement this knowledge into the real next generation high-voltage cathode materials and electrolytes.
<table>
<thead>
<tr>
<th>Milestone #</th>
<th>Milestone</th>
<th>Date</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>M.8</td>
<td>Establish the role of experimental conditions in electrolyte/cathode degradation</td>
<td>(Sep 2019)</td>
<td>Complete</td>
</tr>
<tr>
<td>M.10</td>
<td>Perform first characterization of solid, liquid and gaseous decomposition products of EC and EMC on different cathode materials</td>
<td>(Sep 2019)</td>
<td>Complete</td>
</tr>
<tr>
<td>M.11</td>
<td>Conclude identification of decomposition mechanism of EC and EMC on model and real systems – decide on most compatible set of electrolyte/cathode material</td>
<td>(Jan 2020)</td>
<td>Partially complete</td>
</tr>
<tr>
<td>M.12 SMART</td>
<td>Prepare set of coin cells for testing of EC and EMC chemistry impact on battery performance – decide go/no go on compatibility of electrolyte - cathode material</td>
<td>(Jan 2020)</td>
<td>Delayed</td>
</tr>
<tr>
<td>M.13</td>
<td>Perform first thermodynamic stability window calculations for fluorinated EC, EMC based electrolytes</td>
<td>(Jun 2020)</td>
<td>Complete</td>
</tr>
<tr>
<td>M.14-15</td>
<td>First extensive electrolyte analysis performed on fluorinated EC and EMC based electrolytes using GC-MS, ICP-MS, F ISE and Karl-Fischer</td>
<td>(Jun 2020)</td>
<td>Complete</td>
</tr>
<tr>
<td>M.16-19</td>
<td>Perform electrochemical characterization of fluorinated EC and EMC based electrolytes on different electrode materials</td>
<td>(Jan 2021)</td>
<td>Partially Complete</td>
</tr>
<tr>
<td>M.20</td>
<td>Perform first characterization of solid, liquid and gaseous decomposition products of fluorinated EC and EMC on different cathode materials</td>
<td>(Jun 2021)</td>
<td>Partially Complete</td>
</tr>
<tr>
<td>M.21</td>
<td>Conclude identification of decomposition mechanism of fluorinated EC and EMC on model and real systems</td>
<td>(Sep 2021)</td>
<td>Future work</td>
</tr>
<tr>
<td>M.22 SMART</td>
<td>Prepare set of coin cells for testing of fluorinated EC and EMC chemistry impact on battery performance – decide go/no go on compatibility of electrolyte/cathode material</td>
<td>(Sep 2021)</td>
<td>Future work</td>
</tr>
</tbody>
</table>
ACCOMPLISHMENTS

Approach development – Bridging the gap between model and real systems - one of critical assumptions

Gap between model and real systems is caused in part by vastly different experimental conditions (specifically surface to volume ratio of different measuring platforms).

Our data is collected over the range of 5 orders of magnitude in surface-volume ratio across the 4 different cells we use in our investigation.

The data shows good correlation among various systems.

Vastly different cell setups in terms of surface/volume ratio show almost identical responses for same electrolyte and electrode material combination.

Flooded cell (50 mL), Milli-cell (5 mL), OEMS cell (500 µL), Micro-cell (100 µL), are utilized to reach a desired level of complexity.
ACCOMPLISHMENTS

Formation of proton in electrooxidation of solvents  Task 1, M.10

- First step in electrooxidation of solvent is removal of electron with concomitant or subsequent proton abstraction
  - For the first time, we are able to track the formation of protons during solvent oxidation with our recently developed RRDE method – our measurements indicate that (solvated) proton formation is common to all solvents and is stable on the timescale of days
  - For EC, proton formation is observed as early as 4 V indicating solvent oxidation at potentials relevant for LiB.
  - As one of the main products of solvent oxidation, proton and its interaction with the components of the LiB was carefully investigated

EC $\rightarrow$ EC$^+$ $\Delta G$ EC$^+$ + H$^+$

$E_{\text{ox}}$ – oxidation potential

$\Delta G_{H,S}$ – free energy of proton removal

EC

$E_{[\text{V vs. LiLi}^+]}$

Current density [mA/cm$^2$]

Disk

Protons are detected on the ring

Ring

Oxidized [Co ppm]

Proton:Electron Ratio

$E_{[\text{V vs. LiLi}^+]}

0.5

0.6

0.7

0.8

0.9

1.0

$\Delta G$ $E_{\text{ox}}$ $E_{\text{ox}}$ - e$^-$
ACCkPLISHMENTS
Interaction of proton with solvent - EC  Task 1, M.11

• 3mM concentration of H⁺ was achieved by electrooxidation of LiClO₄/EC electrolyte on Pt

• Gradual discoloration of solution is observed over course of 100+ hours

• DHS-GC-MS after 100 hours reveals presence of CO₂, oxirane, methyl-dioxolane and dioxane

• OEMS measurement in same electrolyte during electrooxidation. Evolution of CO2 and production of ethylene oxide is confirmed.
ACCOMPLISHMENTS

Interaction of proton with solvent - EC – mechanism  Task 1, M.11

- Protonation of EC’s carbonyl group triggers ring opening and release of CO₂. Proton is reintroduced in the electrolyte – i.e., serves as a catalyst for the reaction.

- The remaining part of the molecule forms oxirane (monomer) or 1,4-dioxane and 2-methyl-1,3-dioxolane (dimer).

- The reaction rate for this reaction is \( r = k[EC][H^+] \).

- Reaction rate constant \( k = 1.3 \times 10^{-5} \text{ s}^{-1} \)
ACCOMPLISHMENTS

Interaction of proton with LiPF$_6$ electrolyte

- 3 mM proton concentration is generated by electrolyte oxidation on Pt electrode.
- Proton reacts quantitatively with PF$_6^-$ anion to produce HF.
- $\text{H}^+ + \text{PF}_6^- \rightarrow \text{HF} + \text{PF}_5$

Ion-selective fluoride electrode is used to monitor the HF concentration in the 1M LiPF$_6$ electrolyte in the 5 mL cell.

Reaction rate constant $k = 4.3 \times 10^{-5}$ s$^{-1}$

- In the OEMS cell HF and POF$_3$ are detected, consistent with PF$_6^-$ degradation, closely following the oxidation current.
ACCOMPLISHMENTS

Interaction of proton with cathode material – NMC 622

• 3 mM proton concentration is generated by LiClO₄/EC electrolyte oxidation and brought in contact with 30 mg of NMC

• Proton reacts with NMC

\[ \text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2 + 4\text{H}^+ \rightarrow \]

\[ \text{Li}^+ + 0.6\text{Ni}^{2+/3+} + 0.2\text{Mn}^{4+} + 0.2\text{Co}^{3+} + 2\text{H}_2\text{O} \]

• Reaction rate constant

\[ kA = 1.7 \times 10^{-5} \text{ s}^{-1} \]

• RDE is used to monitor changes in proton concentration with time

• We attribute the initial fast decrease of [H⁺] to the reaction with Li₂CO₃, always present in the NMC

• ICP-MS is used to track the transition metal concentration in the electrolyte

• Note that reaction rate depends on the surface area A of NMC
ACCOMPLISHMENTS

Summary - proton interaction with electrolyte and cathode Task 1, M.11

| Compound                          | Reaction                              | Reaction Rate | Comments                                                      |
|-----------------------------------|---------------------------------------|---------------|                                                              |
| LiPF₆                             | LiPF₆ + H⁺ → HF + PF₅                 | 4.3*10⁻⁵ s⁻¹  | Proton can react with electrolyte to form HF                 |
| NMC                              | LiTMO + 2H⁺ → Li⁺ + TM⁺⁺ + H₂O        | 1.7*10⁻⁵ s⁻¹  | Proton can react with LiTMO to form water and transition metal cations |
| EC – Ethylene carbonate or other organic carbonates | + H⁺ → CO₂ + ethers +H⁺ | 1.3*10⁻⁵ s⁻¹ | Strong acids catalyze ethylene carbonate decomposition to CO₂ and another reactive species |

Proton is by far the most detrimental species in LiB. It is the product of solvent oxidation which can occur as early as 4 V vs. Li/Li⁺. Proton can be detrimental to solvent, electrolyte and cathode material. The rate constants for proton reaction with the solvent, NMC and LiPF₆ are all in the same order of magnitude so none of the processes can be neglected.

Preventing proton creation or mitigating its presence are two approaches that can be used in addressing cathode interface durability issues.

A method for proton detection and quantification is key to investigating the extent of its effect on LiB components.
ACCOMPLISHMENTS

Electrochemical oxidation of EC  
Task 1,4 M.11,13

- Based on RRDE data and DFT, we propose 3 possible paths for solvent oxidation
- For most carbonate solvents, the proton to electron ratio at high current densities hovers around 1:2

**Path A**
Formation of **radical cation**, $E_{ox}$ is rate determining. Unstable, CO one of most likely products per literature

**Path B**
Formation of **radical** species and proton, $E_{ox}$ or $\Delta G_{H-S}$ is rate determining. Unstable, $CO_2$ one of most likely products per literature. Need combination of path A and B to explain proton:electron ratio

**Path C**
Formation of **carbocation** and proton, $E_{ox}$ or $\Delta G_{H-S}$ is rate determining. Can explain proton:electron ratio, potentially stable with anion stabilization.
The premises of using fluorinated solvents is based on their supposed higher stability towards electrooxidation. DFT suggests 0.2 V and 0.5 V higher $E_{ox}$ for FEC and DFEC vs EC, respectively.

Experimentally, however, we observe **no stabilization effect** in fluorinated solvents. The main electroreduction process (high current densities) actually commences at 0.1 and 0.2 V lower potentials for FEC and DEFC compared to EC.

This suggests that the deprotonation ($\Delta G_{H-S}$) and not the electron transfer ($E_{ox}$) is rate determining.

A possible explanation for beneficial effects of the fluorinated solvents might be in the low current density potential range (more relevant for LIB operation), where we see very small amount of protons created compared to other solvents.
ACCOMPLISHMENTS

Electrochemical oxidation of VC  

- VC has the lowest oxidation potential of all organic carbonates investigated in our study, ~1 V lower than EC.

- The experimentally observed oxidation potential matches qualitatively with DFT calculated $E_{ox}$, suggesting that the electron transfer is rate determining.

- In accord with path A, we observe the lowest proton:electron ratio of all solvents at high current densities and the highest level of CO evolution of all tested solvents.
ACCOMPLISHMENTS

Electrochemical oxidation of solvents - summary

Stability order of cyclic organic solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ΔE_{ox}</th>
<th>ΔG_{H-S}</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1FEC</td>
<td>0.2</td>
<td>-0.1</td>
</tr>
<tr>
<td>2FEC</td>
<td>0.5</td>
<td>-0.4</td>
</tr>
<tr>
<td>VC</td>
<td>-1.5</td>
<td>2.7</td>
</tr>
<tr>
<td>PC</td>
<td>-0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

- Experimental data and theory suggest different rate determining steps for electrooxidation of various cyclic carbonates – either deprotonation or electron transfer
- Main electrooxidation process does not corroborate higher stability of fluorinated solvents. Possible effect of impurities at lower potentials may need to be explored
RESPONSE TO PREVIOUS YEAR REVIEWERS’ COMMENTS

This project was not reviewed in FY2020.
COLLABORATIONS

ANL, CSE: Zhengcheng (John) Zhang, Dr. Zhang is supplying us with clean fluorinated electrolytes

SLAC: Mike Toney, Dr. Toney and his team are exploring similar phenomena on the fundamental level with x-ray based characterization. We are hoping to benefit from each-others approaches and findings. So far, only some information exchange about our programs has taken place.
REMAINING CHALLENGES AND BARRIERS

- The complexity of the cathode/electrolyte interface is high even on the model systems
- Identify electrode material / electrolyte couples that exhibit single predominant degradation process, such that the chemistry and/or the electrochemistry of the individual components can be isolated
- Bridge the gap between theoretical predictions and experiment
- If individual interface components’ electrochemistry can be isolated, we can bring it much closer to computational efforts
- Bridge the gap between model and real systems
- By understanding the chemistry/electrochemistry of individual components on model interfaces and gradually increasing the complexity of the system, we hope to better understand the real one
- Further develop tools for the analysis of the interface, especially for the soluble degradation products

The challenges/barriers marked with ✓ have, at least in part, been resolved in the current FY cycle
## PROPOSED FUTURE WORK

- Test performance of coin cells with a known amount of protons introduced to cyclic and linear carbonate-based electrolytes. [M.12]
- Perform NMR on oxidized carbonate-based electrolytes [M.10, M.20]
- Investigate the degradation behavior of fluorinated solvents [M.21]
- Run computations for various material/electrolyte combinations [M.4 and M.13]
- Based on experimentally identified decomposition products and computational efforts, propose the electrolyte decomposition mechanism [M.11, M.21]
- Prepare or synthesize and characterize transition metal and transition metal oxides with various surface composition/termination [M.8]
- Identify decomposition products on TM and TMO surfaces and propose an electrolyte/cathode material degradation mechanism [M.9-10, M.19]
- Test performance of coin cells with a known amount of protons introduced to fluorinated carbonate-based solvents [M.22]

The work marked with ✓ has been done in part in the current FY cycle.

Any proposed future work is subject to change based on funding levels.
SUMMARY

❑ To date, fundamental understanding of the degradation processes on cathode/electrolyte interfaces in LiB remains elusive
❑ The complexity of the real systems is too high for ANY analytical tool to resolve
❑ Selecting the “correct” interfaces to isolate individual degradation processes is key to successful application of our approach

❑ Proton is generated as one of the products during solvent oxidation
❑ RRDE offers an elegant way to monitor the production and quantification of protons
❑ Proton can attack the solvent, electrolyte or cathode material, with rate constants within same order of magnitude, so none of these processes can be neglected

❑ RRDE, OEMS and DFT offer mechanistic insights into electrochemical oxidation of solvents. Three possible paths are proposed with either electron transfer and/or proton abstraction as rate determining
❑ Experimentally, fluorinated solvents do not show higher stability as suggested by DFT. The order of stability, determined experimentally is VC<<DFEC<FEC≈PC<EC
❑ At “lower” potentials (4-5 V), impurities may play a role in improved performance of fluorinated solvents