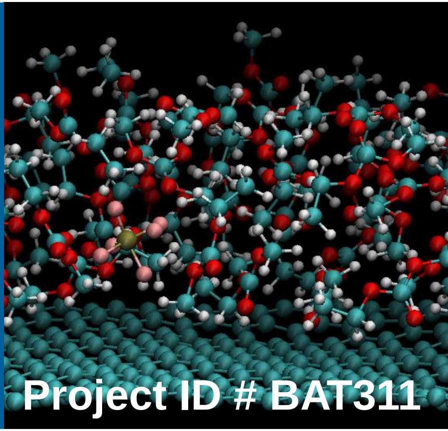
UNDERSTANDING AND MITIGATING INTERFACIAL REACTIVITY BETWEEN ELECTRODE AND ELECTROLYTE


Project ID # BAT311

DUSAN STRMCNIK
Argonne National Laboratory

2020 DOE Vehicle Technologies
Office Annual Merit Review
June 1, 2020

OVERVIEW

Timeline

- Start: October 2018
- End: September 2021
- Percent complete: 30%

Budget

- Total project funding
  - DOE share: 1.5M
- FY 2020: $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.*

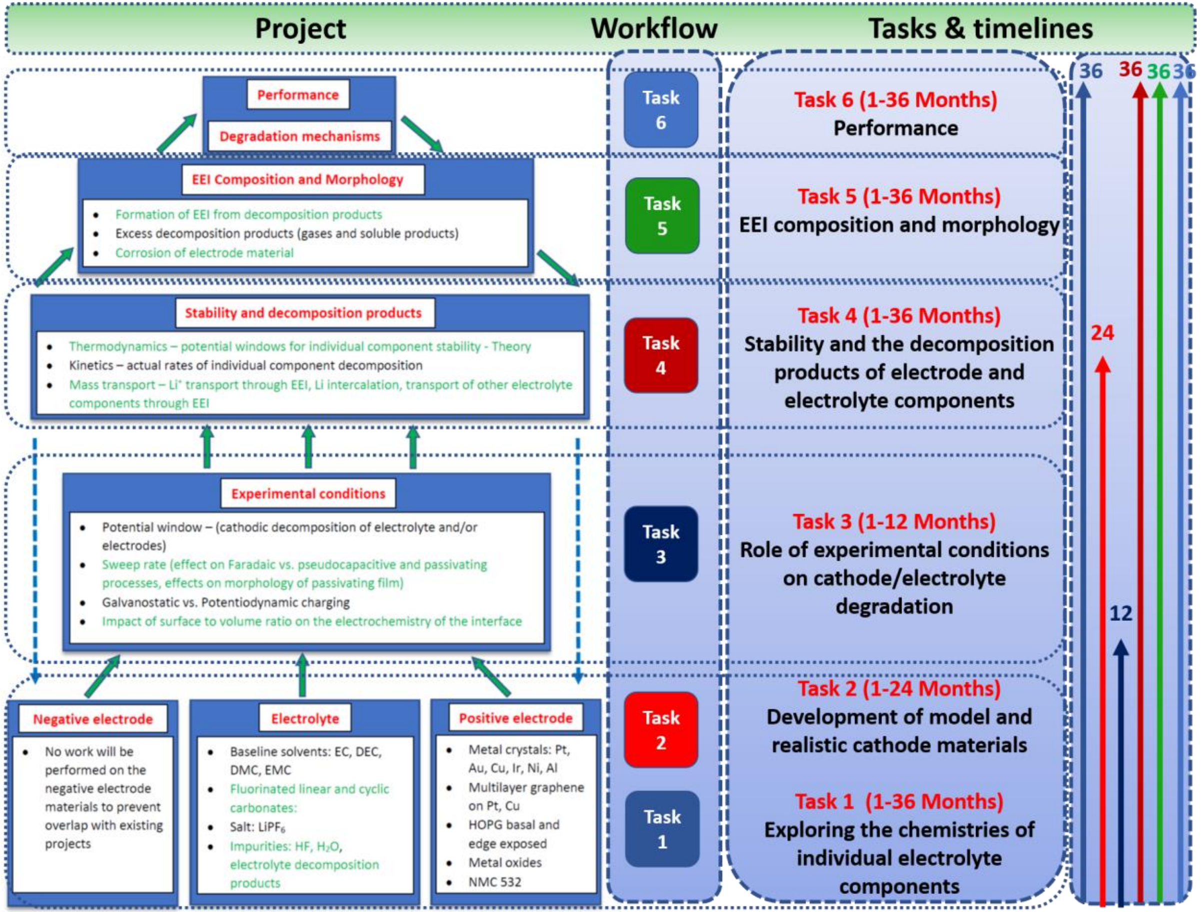
Specific goals

- *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)***
- *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



Project | **Workflow** | **Tasks & timelines**

Performance

Degradation mechanisms

EEI Composition and Morphology

- Formation of EEI from decomposition products
- Excess decomposition products (gases and soluble products)
- Corrosion of electrode material

Stability and decomposition products

- Thermodynamics – potential windows for individual component stability - Theory
- Kinetics – actual rates of individual component decomposition
- Mass transport – Li$^+$ transport through EEI, Li intercalation, transport of other electrolyte components through EEI

Experimental conditions

- Potential window – (cathodic decomposition of electrolyte and/or electrodes)
- Sweep rate (effect on Faradaic vs. pseudocapacitive and passivating processes, effects on morphology of passivating film)
- Galvanostatic vs. Potentiodynamic charging
- Impact of surface to volume ratio on the electrochemistry of the interface

Negative electrode

- No work will be performed on the negative electrode materials to prevent overlap with existing projects

Electrolyte

- Baseline solvents: EC, DEC, DMC, EMC
- Fluorinated linear and cyclic carbonates:
- Salt: $LiPF_6$
- Impurities: HF, H_2O, electrolyte decomposition products

Positive electrode

- Metal crystals: Pt, Au, Cu, Ir, Ni, Al
- Multilayer graphene on Pt, Cu
- HOPG basal and edge exposed
- Metal oxides
- NMC 532

Task 6 (1-36 Months)
Performance

Task 5 (1-36 Months)
EEI composition and morphology

Task 4 (1-36 Months)
Stability and the decomposition products of electrode and electrolyte components

Task 3 (1-12 Months)
Role of experimental conditions on cathode/electrolyte degradation

Task 2 (1-24 Months)
Development of model and realistic cathode materials

Task 1 (1-36 Months)
Exploring the chemistries of individual electrolyte components

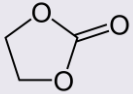
- *Develop a methodology, tools and systems for the investigation of the degradation of cathode-electrolyte interfaces using fundamental science-based strategy.*
- *Extend the state of the art of understanding how individual components of the cathode-electrolyte interface behave at potentials relevant for high-voltage Li-ion batteries on model systems*
- *Implement this knowledge into the real next generation high-voltage cathode materials and electrolytes*

MILESTONES

Milestone #	Milestone	Date	Status
M.3&M.6	Perform first electrochemical characterization of EC/EMC based electrolytes on metal cathodes and on multi-layer graphene and HOPG	(Jun 2019)	Complete
M.4	Perform first thermodynamic stability window calculations for EC, EMC based electrolytes	(Jun 2019)	Complete
M.5	Build OEMS capability and perform first measurements	(Jun 2019)	Complete
M.9	Perform first characterization of solid, liquid and gaseous decomposition products of EC and EMC on different cathode materials	(Sep 2019)	In progress
M.10	Conclude identification of decomposition mechanism of EC and EMC on model and real systems – decide on most compatible set of electrolyte/cathode material	(Jan 2020)	In progress
M.11 SMART	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	(Jan 2020)	In progress
M.12	Perform first thermodynamic stability window calculations for fluorinated EC, EMC based electrolytes	(Jun 2020)	Future work
M.13	First extensive electrolyte analysis performed on fluorinated EC and EMC based electrolytes using GC-MS, ICP-MS, F ISE and Karl-Fischer	(Jun 2020)	Future work
M.15-19	Perform electrochemical characterization of fluorinated EC and EMC based electrolytes on different electrode materials	(Sep 2020)	Future work
M.20-22	Characterize the decomposition products of fluorinated EC and EMC, identify the mechanism and test performance in coin cells	(Sep 2012)	Future work

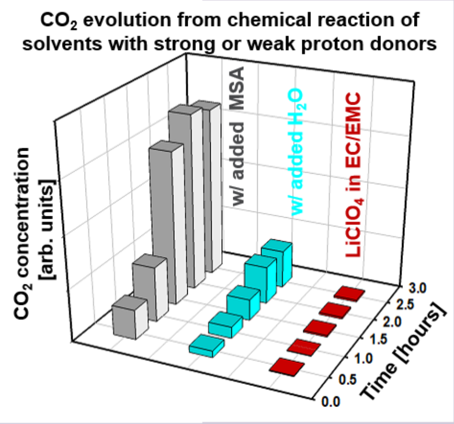
ACCOMPLISHMENTS

Chemical processes in LP57 Task 1, M.1

Compound	Reaction	Comments
$LiPF_6$	**$LiPF_6 + H^+ \rightarrow HF + PF_5$**	Proton can react with electrolyte to form HF
Transition metal oxide	**$TMO + 2H^+ \rightarrow TM^{2+} + H_2O$**	Proton can react with TMO to form water and transition metal cations
EC – Ethylene carbonate or other organic carbonates	 **$+ H^+ \rightarrow CO_2 + (CH_2)_2O + H^+$**	Strong acids catalyze ethylene carbonate decomposition to CO_2 and another reactive species

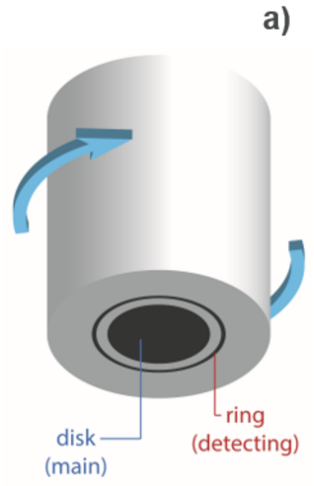
We have established that excess protons can be detrimental to solvent, electrolyte and cathode material. The above reactions are chemical in nature, i.e. can happen in absence of electrochemical driving force – of course after the protons have been formed.

In light of the detrimental nature of the proton, we found it imperative to develop a method for proton detection during electrolyte decomposition.

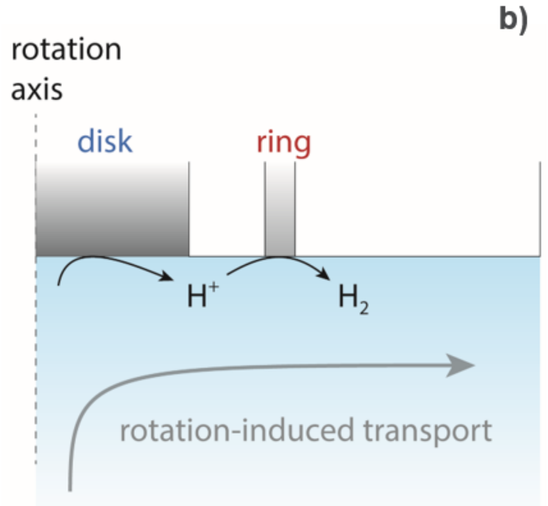

CO_2 evolution from chemical reaction of solvents with strong or weak proton donors

ACCOMPLISHMENTS

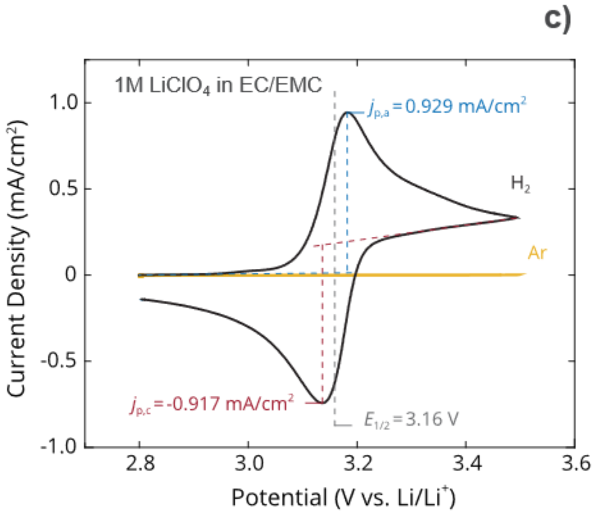
In-situ proton detection during electrolyte oxidation using RRDE Task 5



Our method for proton detection is based on rotating ring-disk electrode **RRDE** electrochemical detection using **Pt ring** as an **amperometric detector**



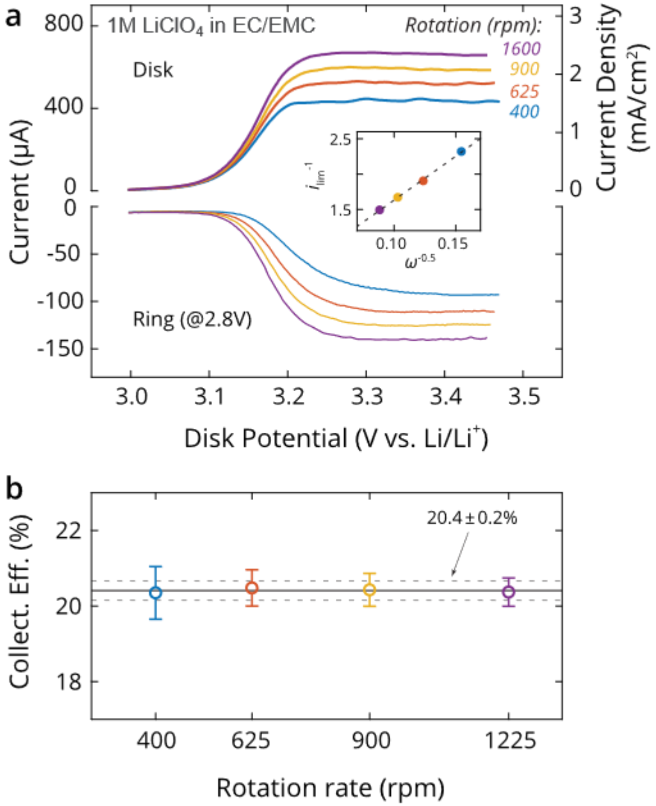
The protons, generated on the disk, are “collected” on the ring via hydrogen evolution reaction HER.



The method was validated using hydrogen oxidation reaction (HOR) to produce protons on the disk, which were then detected on the ring. A typical voltammograms on Pt disk in Ar and H_2 purged solution are shown.

ACCOMPLISHMENTS

In-situ proton detection during electrolyte oxidation using RRDE Task 5



The validation included measurements of polarization curves at 4 different rotation rates on the disk and the corresponding response on the ring.

Disk reaction: $H_2 \rightarrow 2H^+ + 2e^-$

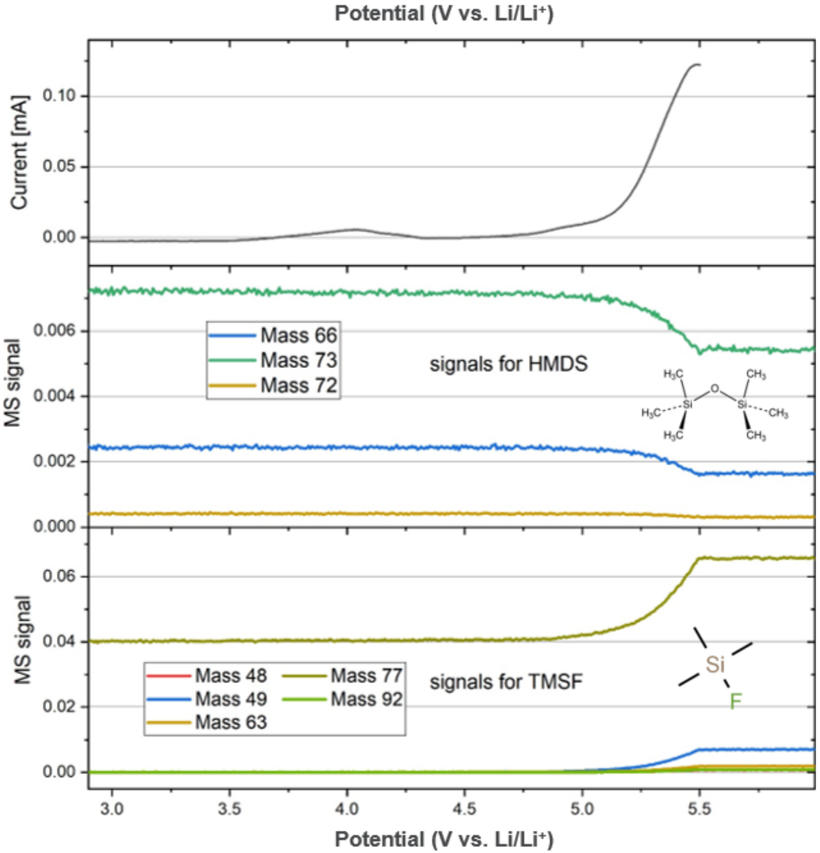
Ring reaction: $2H^+ + 2e^- \rightarrow H_2$

The ring collection efficiency η was measured to be close to 20%, an expected value for the geometry of our RRDE. Furthermore, the same value was obtained with Fc/Fc^+.

These findings confirmed that i) it was possible to use RRDE for proton detection and ii) the protons or protonated species were stable for long enough to travel from the disk to the ring in order to be detected.
Publication in ACS Analytical Chemistry is pending.

ACCOMPLISHMENTS

Validation of OEMS setup Task 5



In FY19 cycle we have built the OEMS capability, which was close to operational. All remining issues have since been resolved.

To test and confirm the proper operation of our setup, we performed electrochemical oxidation of 1M $LiPF_6$/EC/EMC electrolyte with Hexamethyl-disiloxane (HMDS) as additive.

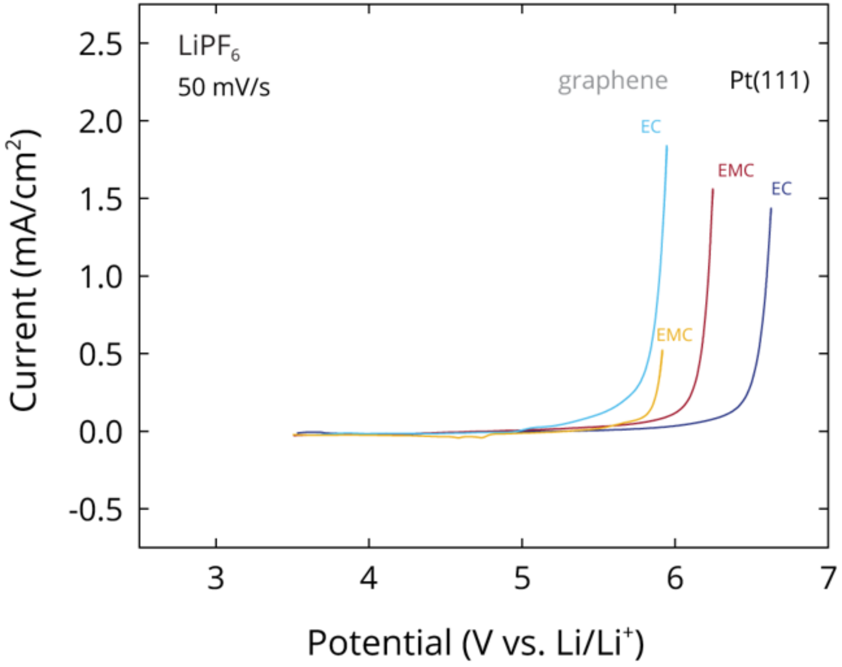
HMDS is known to react with HF produced during electrolyte oxidation, forming trimethylsilyl fluoride (TMSF) and trimethyl silanol:

$$HMDS + HF \rightarrow SiF(CH_3)_3 + Si(CH_3)_3OH$$

HMDS and TMSF both have distinct m/z signals, different from any possible m/z signal from the matrix components. Both the decrease in HMDS and increase in TMSF signals were found to exactly following the current response, giving us great confidence in proper operation of our setup.

ACCOMPLISHMENTS

Role of solvent and electrode material in stability of electrolyte Task 1 M.3,6



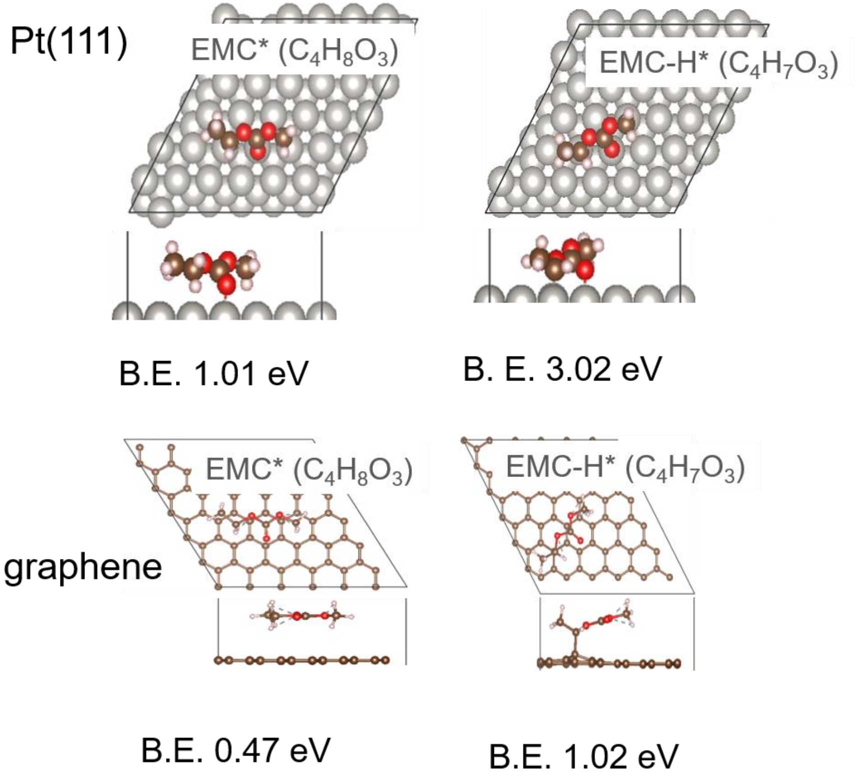
Pt (111) and multi-layer graphene electrodes were chosen as model metal and carbon systems.

When performing electrochemical oxidation of 1M $LiPF_6$/EC and 1M $LiPF_6$/EMC electrolytes on Pt and graphene, we observed that the potential of the main oxidation process, signified by the sharp exponential current increase, depended both on the nature of electrode material as well as on the solvent.

While some studies suggest that the differences in solvent oxidative stability could be linked to the differences in solvent stabilization of the H^+ after the electron transfer, we find it intriguing why these variations would have so significantly different magnitudes on Pt vs. graphene electrodes.

ACCOMPLISHMENTS

Role of electrode material on solvent stability Task 4, M.4



We studied the effect of surface, graphene or Pt, in EMC reactions.

Binding energies (B.E.) for both EMC and EMC-H were calculated.

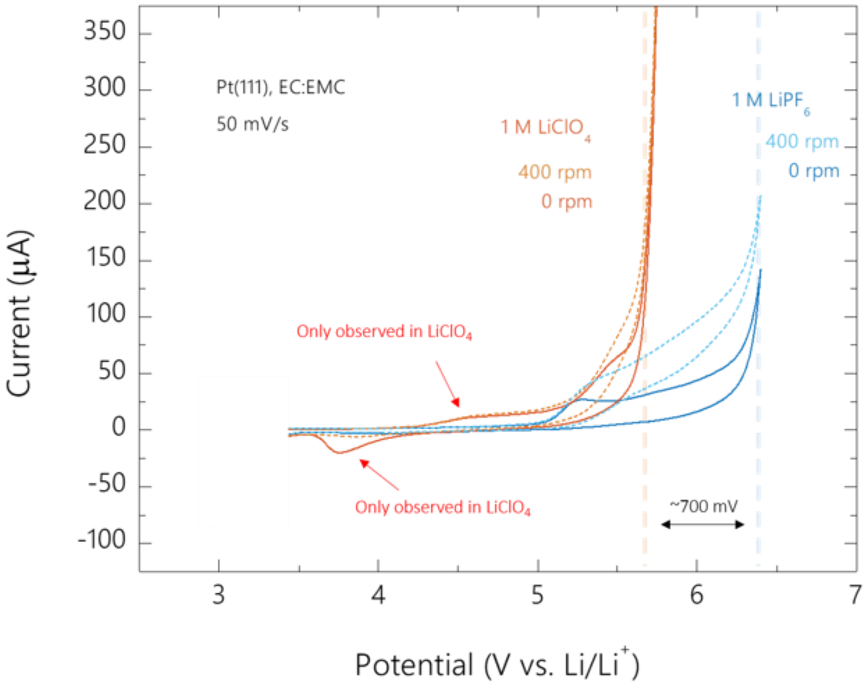
DFT-PBE with periodic boundary conditions was used.
Implicit solvent and vdW was included.

EMC binds stronger to Pt, forming Pt-O bond, than to graphene, forming no chemical bonds. EMC-H binds stronger to each of the surfaces than EMC.

The difference in binding energies points to potential differences in reactivity between EMC (or its fragments) with both surfaces

ACCOMPLISHMENTS

Role of anions and impurities in electrolyte stability Task 1 M.3,6



Anion seems to play an enormous role in the electrooxidation of the solvents – a 0.7 V difference is observed for $LiPF_6$ and $LiClO_4$ based electrolytes on Pt(111) surface.

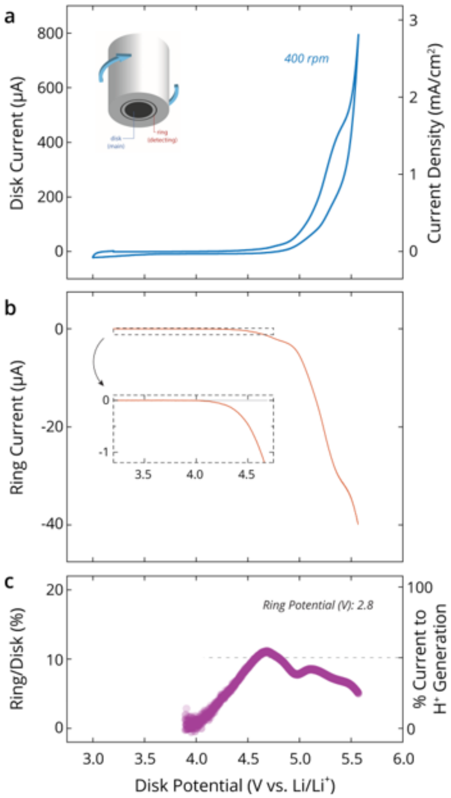
This difference is somewhat smaller on graphene surface (results not shown), but still significant (~200 mV)

Some theoretical studies suggest the differences in solvent oxidative stability could be linked to the differences in anion stabilization of the H^+, none predict differences of this magnitude for the two electrolytes.

Smaller currents observed prior to the main oxidation process are rotation dependent, suggesting possible oxidation due to electrolyte impurities.

ACCOMPLISHMENTS

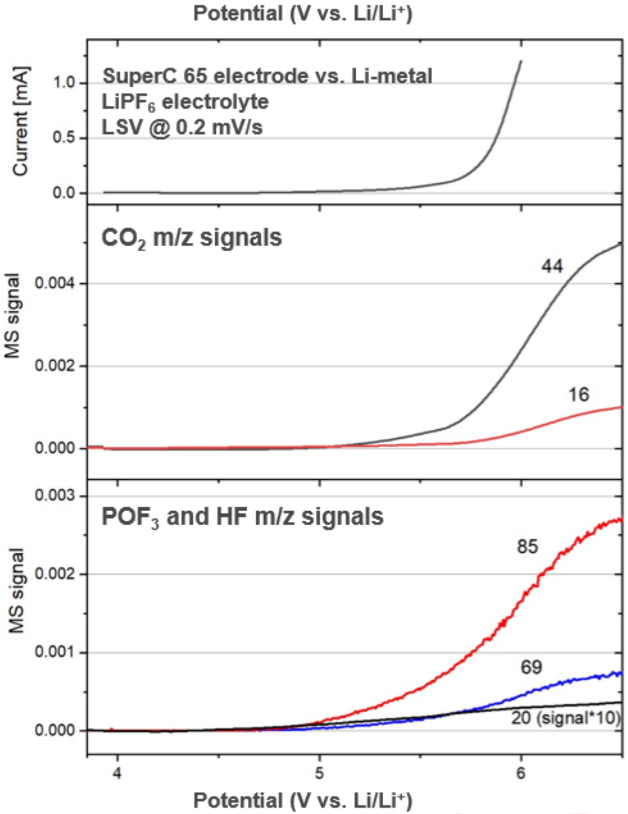
Identification of decomposition mechanism of EC and EMC Task 1 M.10



Extensive electrolyte decomposition is observed positive of 5 V. However, small oxidation currents are observed as early as 4 V. RRDE detects protons or protonated species in this entire range.

In contrast with our validation reaction (HOR), far less than one proton per every exchanged electron is detected in the electrolyte oxidation. This is universally true, regardless of solvent, electrode material etc.

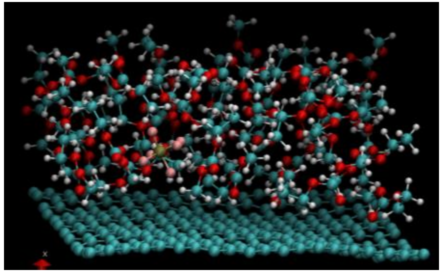
HF and POF$_3$ are detected with OEMS, consistent with PF$_6^-$ degradation, closely following the oxidation current. Somewhat lagging, we also observe the signal for CO$_2$.



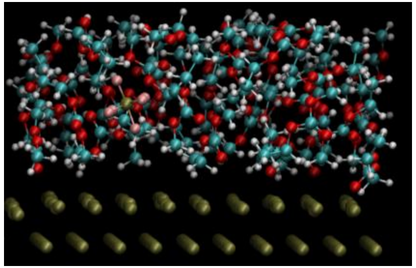
ACCOMPLISHMENTS

Identification of decomposition mechanism of EC and EMC — Task 4 M.4

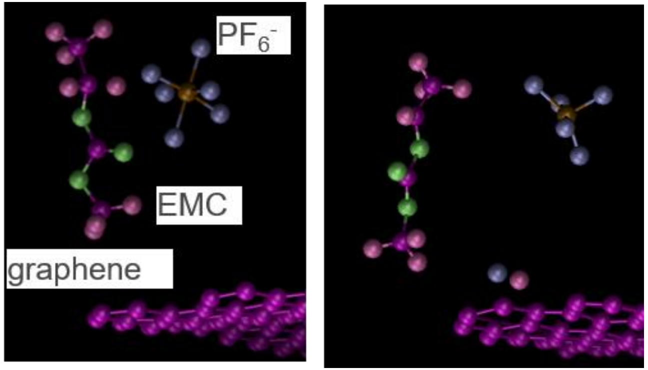
- NVE simulation on different surface
- EMC & PF_6 ion with density of 1.13 g/cm^3 placed on graphene or Pt (111) in a periodic box



EMC on Single-layer graphene



EMC on (111) Pt surface



H is donated from ethyl carbon attached to carbonate group

(Only reacting EMC and PF_6 are shown for clarity)

- HF formation is observed in the AIMD simulation by H abstraction from EMC
- PF_6 molecule is stabilized during this reaction by coordinating with three neighboring EMC molecules, one is H donor
- This suggests that the salt (LiPF6 vs LiClO4) determines pathway for EMC decomposition
- One-proton process of EMC decomposition step was found from AIMD

ACCOMPLISHMENTS

Identification of decomposition mechanism of EC and EMC Task 1 M.10

$$\text{EMC* } (C_4H_8O_3) \longrightarrow \text{EMC-H* } (C_4H_7O_3) + H^+$$

Proton is produced in the electrochemical oxidation of the solvent – EMC is shown as an example. Oxidation currents and protons detected as low as 4 V. Major decomposition commences positive of 5 V.

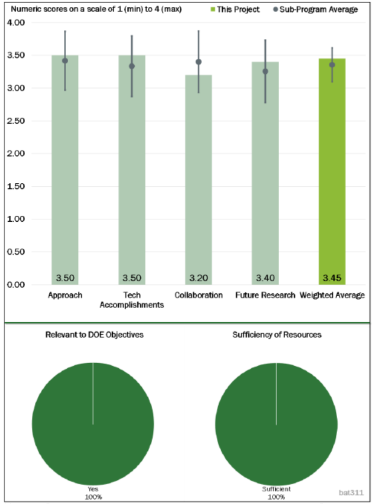
$$H^+ + PF_6^- \longrightarrow HF + PF_5$$

In the case of $LiPF_6$ electrolyte the proton further attacks the PF_6^- to form HF. The POF_3 detected in MS is produced from PF_5 either in the electrolyte or inside the transfer capillary

$$\text{EMC-H* } (C_4H_7O_3) \longrightarrow CO_2 + ?$$

CO_2 is produced in the further decomposition of the carbonate solvent – we only speculate about the possible pathway(s) at this point.

RESPONSE TO PREVIOUS YEAR REVIEWERS' COMMENTS



Most of the comments received for FY2019 were positive and encouraging. There were some specific concerns the reviewers raised, which are addressed below:

"…the PIs should consider strategic inclusion of experiments with coupled, but controlled, parameters to help produce validation data for model development. Bridging the gap between models and experiment is absolutely necessary to make rapid progress here—there are simply too many parameters (e.g., materials and processing variables) to methodically sort through them one at a time with exceptional experimental rigor."

We are aware of the complexity of the problem as well as the possible coupling between effects of many variables. We are attempting to establish global trends across several well defined systems and connect the findings with computational modeling to more quickly sort through possible scenarios. Some of the first "fruits" of this approach are presented in the accomplishment section.

"…it was not clear to the reviewer how the researchers plan to address the possibility of the formation of oligomers or inorganic content upon electrolyte decomposition."

If the compounds are solid and precipitate on the electrode, we have well-established XPS and FT-IRAS methodology in our analytical tool portfolio. For the soluble oligomers, we have the capability of GC-MS and HPLC-MS, the specific methods would, however, need to be developed. For ionic soluble compounds, we've just added a RRDE method for proton detection which gives very useful information about decomposition.

"…the approaches to using Pt or Pt-based materials as the model system seem far away from the real material systems."

We understand and agree with the reviewer but note, that Pt systems are used for method validation, testing the possible electrocatalytic nature of the process as well as excluding electrode degradation processes from investigation of solvent degradation.

RESPONSE TO PREVIOUS YEAR REVIEWERS' COMMENTS

"…Initial reports on metal surfaces show electrochemical trends with the presence of surface oxygen, suggesting that identification of clean and appropriately terminated surfaces relevant to actual cathode materials will be extremely important. Selecting and preparing single-crystal oxide surfaces containing Li+ should be a target."

"focus on metal substrates is understandable in the attempt to use model materials with well-defined surfaces. However, the reviewer added, electrochemistry is surface dependent, so moving toward the metal oxide surfaces is encouraged."

We agree completely with the reviewers. Target are relevant Li-TMO surfaces. However, we cannot make the mistake of moving to TMOs before understanding the electrolyte decomposition on much simpler systems, such as Pt and graphene. The result would be yet another murky speculative report.

"…The reviewer's suggestion is for the PIs to clarify soon which reactions and dynamics appear to be the most important and then focus the future work on those priorities."

We think that the generation of protons and the further reactions of protons with electrode, solvent and electrolyte are the most important processes to understand. This will therefore be our future focus with regards to different solvents, electrolytes and electrode materials

COLLABORATIONS

ANL, CSE: Zhengcheng(John) Zhang,

Dr. Zhang will be providing fluorinated electrolytes in the second phase of the project

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

- ☑ *Choose the best system for isolated study of potential induced solvent decomposition – (likely candidates are Pt, Pt supported multi-layer graphene, Au)*
- ☑ *Devise detection method for H^+ , which is likely product of solvent decomposition*
- ☐ *Develop a small volume cell linked to GC-MS for in-situ detection of soluble products M.9*
- ☑ *Solve remaining issues with OEMS system M.5*
- ☐ *Perform OEMS experiments on other material/electrolyte combinations M.5*
- ☑ *Based on experimentally identified decomposition products and computational efforts, propose the electrolyte decomposition mechanism M.4 and M.10*
- ☐ *Run computations for other material/electrolyte combinations M.4 and M.10*
- ☐ *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 a electrolyte/cathode material degradation mechanism M.9 and M.10*
- ☐ *Test the role of the "main culprits", identified in the degradation of the model interfaces, in the performance of the coin cells M.11*
- ☐ *Start investigating the degradation behavior of fluorinated solvents M.12-14*

The work marked with ✓ has been done 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 generation during solvent oxidation is the most detrimental process for cathode-electrolyte interface*
- ❑ *RRDE offers an elegant way to monitor the production of protons during electrolyte oxidation*
- ❑ *The electrode material, the electrolyte anion and solvent all affect the oxidation potential.*
- ❑ *At “lower” potentials (4-5 V), impurities play a significant role in the observed oxidation currents*
- ❑ *Computational efforts for EMC oxidation suggest proton abstraction after electron transfer is stabilized by HF formation from* PF_6^- *anion.*
- ❑ *OEMS confirms HF formation during electrolyte oxidation.* CO_2 *formation is also detected.*
- ❑ *Experiments show a significant difference between EMC/EC oxidation on graphene and Pt surfaces. Computations suggest differences in reactant and intermediate binding energies might explain the differences in reactivity*