Stability of cathode/electrolyte interfaces in high voltage Li-ion batteries

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Project ID # BAT311

Overview

Timeline

- Start: October 2018
- End: September 2021
- Percent complete: 10%

Budget

- Total project funding
  - DOE share: 1.5M
- FY 19: $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

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.*

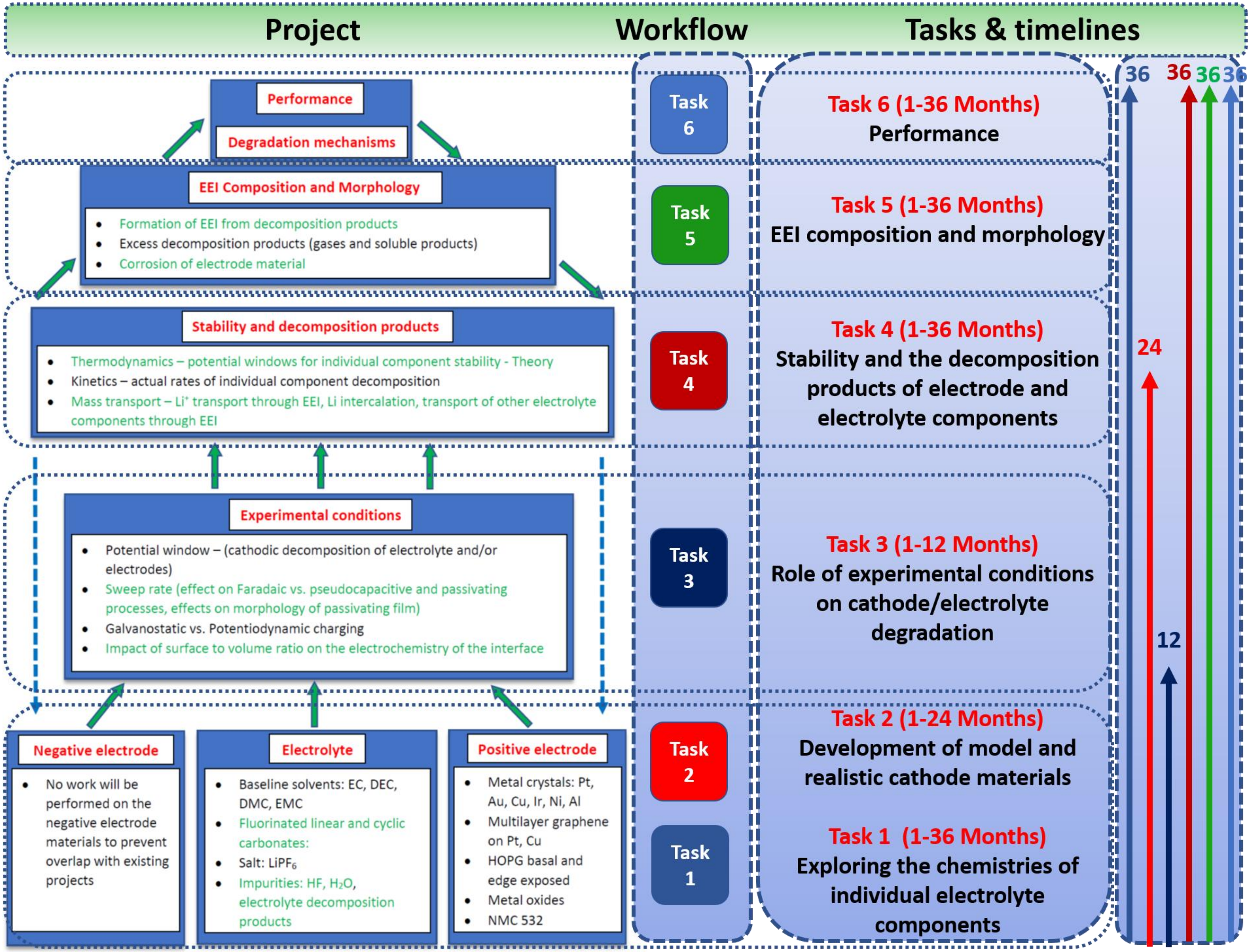
Specific goals

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

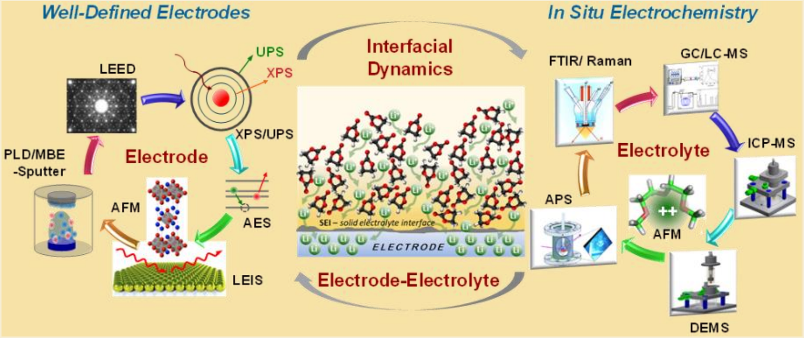
Positive electrode

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

Workflow	Tasks & timelines
Task 6	**Task 6 (1-36 Months)** Performance
Task 5	**Task 5 (1-36 Months)** EEI composition and morphology
Task 4	**Task 4 (1-36 Months)** Stability and the decomposition products of electrode and electrolyte components
Task 3	**Task 3 (1-12 Months)** Role of experimental conditions on cathode/electrolyte degradation
Task 2	**Task 2 (1-24 Months)** Development of model and realistic cathode materials
Task 1	**Task 1 (1-36 Months)** Exploring the chemistries of individual electrolyte components

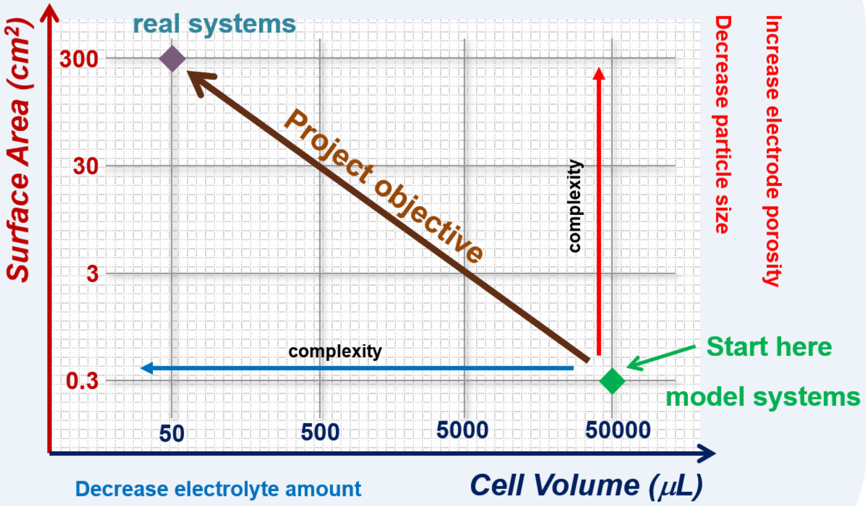
Approach

- *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*

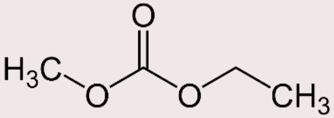
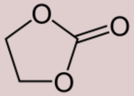
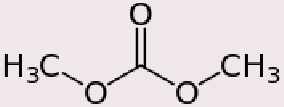
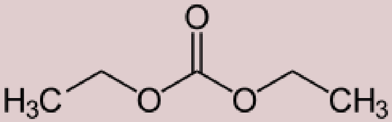


Milestones

Milestone #	Milestone	Date	Status
M.1	First extensive electrolyte analysis performed on EC and EMC based electrolyte using GC-MS, ICP-MS, F ISE and Karl-Fischer	(Mar 2019)	Complete
M.2	Establish the SPRDE-ICP-MS methodology for operation in organic carbonates	(Mar 2019)	Complete
M.3	Perform first electrochemical characterization of EC/EMC based electrolytes on metal cathodes	(Jun 2019)	Complete
M.4	Perform first thermodynamic stability window calculations for EC, EMC based electrolytes	(Jun 2019)	In progress
M.5	Build OEMS capability and perform first measurements	(Jun 2019)	In progress
M.6	Perform first electrochemical characterization of EMC based electrolytes on multi-layer graphene and HOPG	(Jun 2019)	In progress
M.7	Establish the role of experimental conditions in electrolyte/cathode degradation	(Sep 2019)	Future work
M.8	Perform first electrochemical characterization of EC and EMC based electrolytes on TMOs	(Sep 2019)	In progress
M.9	Perform first characterization of solid, liquid and gaseous decomposition products of EC and EMC on different cathode materials	(Sep 2019)	Future work
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)	Future work
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)	Future work
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	Perform first electrochemical characterization of fluorinated EC and EMC based electrolytes on metal cathodes	(Sep 2020)	Future work

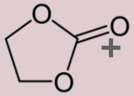
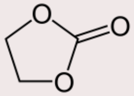
Accomplishments

Extensive electrolyte analysis: LP57 ($LiPF_6$ in EC/EMC) M.1

Compound	Formula	Concentration range	Analysis method used
EMC – Ethyl-methyl carbonate		1 mol/L	spec
EC – Ethylene carbonate		1 mol/L	spec
DMC – dimethyl carbonate		10^{-3} mol/L	GC/MS w/ dynamic headspace analyzer
DEC – diethyl carbonate		10^{-3} mol/L	GC/MS w/ dynamic headspace analyzer
Lithium hexafluoro phosphate	**$LiPF_6$**	1 mol/L	spec
Water	**H_2O**	10^{-4} mol/L	Karl-Fischer
Hydrofluoric acid	**HF**	10^{-3} mol/L	Fluoride Ion selective electrode
Carbon dioxide	**CO_2**	10^{-4} mol/L	GC/MS w/ dynamic headspace analyzer

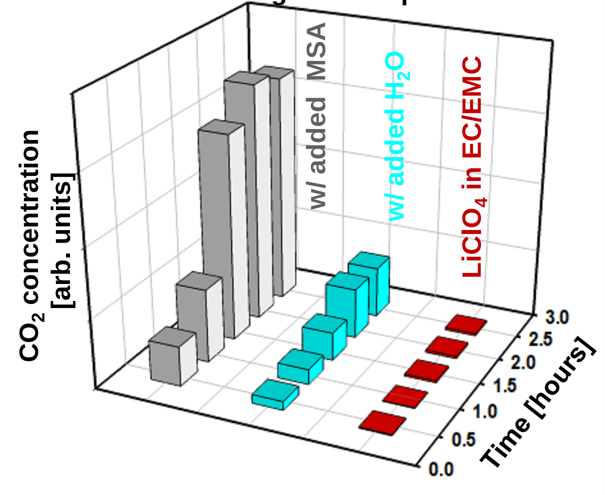
Accomplishments

Chemical processes in LP57

Compound	Reaction	Comments
$LiPF_6$	$LiPF_6 \rightarrow LiF + PF_5$ $PF_5 + H_2O \rightarrow POF_3 + 2HF$	Water quantitatively reacts with $LiPF_6$ to form HF. (Shown in published data – not this project)
EC – Ethylene carbonate	 + $H_2O \rightarrow CO_2 + (CH_2OH)_2$	Water reacts with EC at elevated temperatures to form CO_2 and ethylene glycol (This project)
EC – Ethylene carbonate	 + $H^+ \rightarrow CO_2 + (CH_2)_2O$	Strong acids react with ethylene carbonate to form CO_2 and most likely ethylene oxide (This project)

The standard battery electrolyte possesses rich chemistry even in absence of cathode material or electrochemical driving force. The above list is not exhaustive and we continue to strive to explore more possible reactions.

While HF is not a strong acid, protons can be generated in electrochemical oxidation of the solvent. These access protons can enter into further chemical decomposition reaction(s) with the solvent. Methane-sulfonic acid (MSA) was added to the electrolyte to purposefully introduce protons and extensive decomposition was observed.



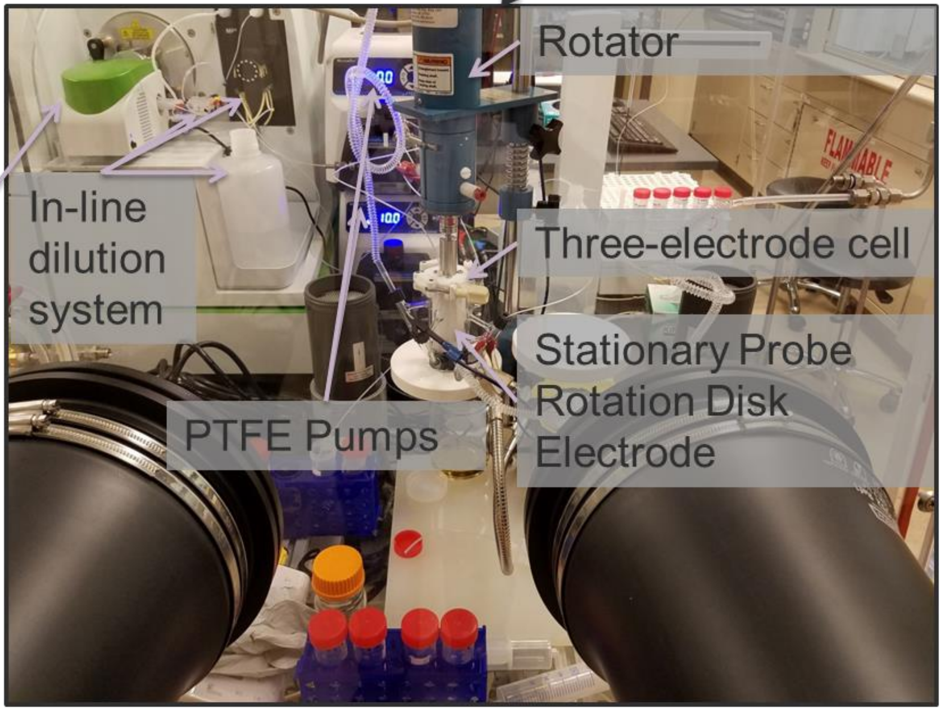
CO_2 evolution from chemical reaction of solvents with strong or weak proton donors

Accomplishments

Establish SPRDE-ICP-MS methodology for operation in LiB electrolytes M.2

- *Stationary probe rotating disk electrode (SPRDE), connected to ICP-MS targets in-situ dissolution of metals form the electrode material*
- *In situ* monitoring allows for independent determination of electrochemical currents and dissolution processes;
- High sensitivity of ICP-MS provides element-specific information with low detection limits to observe the early onset of dissolution processes;
- In turn, this provides information about failure mechanism;

Acrylic Glove-Box
$O_2 < 2ppm$
$H_2O < 1ppm$

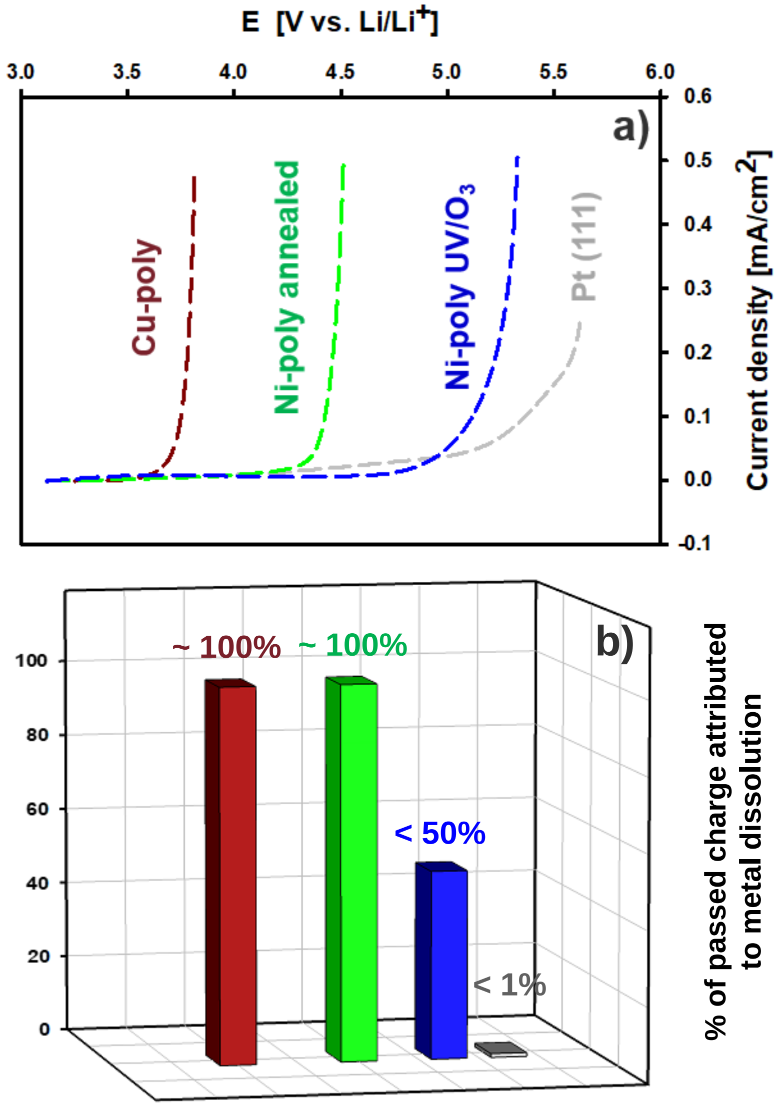


ICP-MS Temperature Controlled Sample Introduction System

Accomplishments

Perform first electrochemical characterization of EC/EMC based electrolytes on metal cathodes M.3

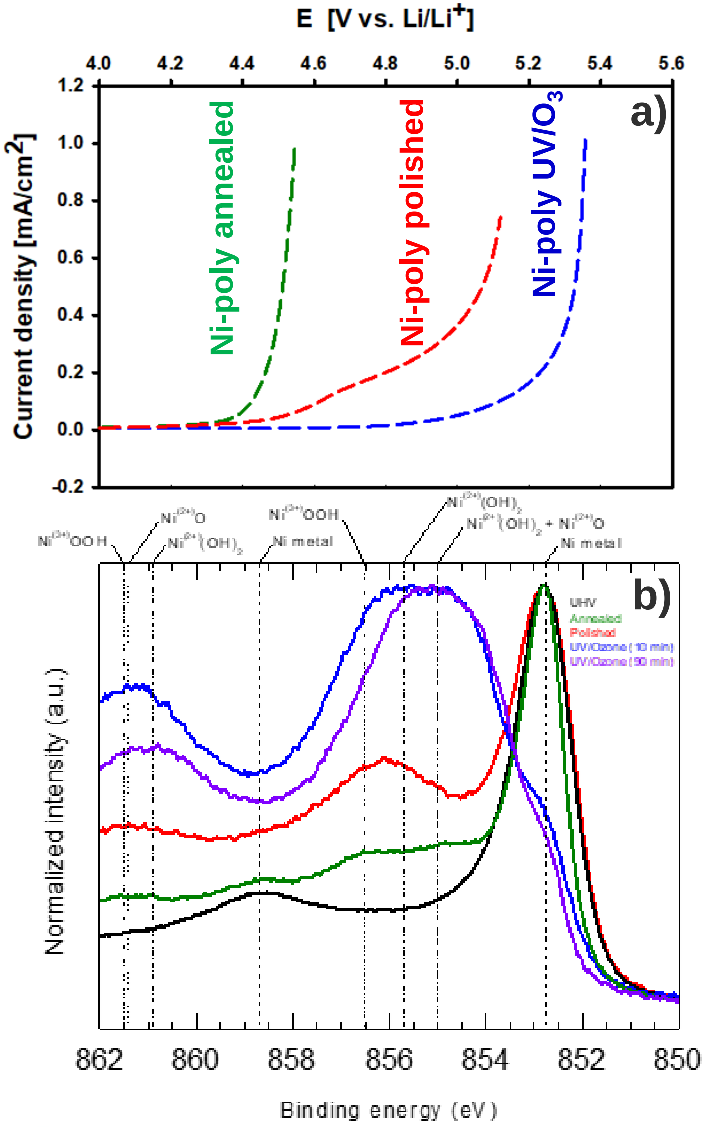
- *Complexity of real battery electrolyte-cathode interface is extremely high and involve, among others, Li$^+$ intercalation-deintercalation, cathode material dissolution and electrolyte decomposition*
- *We are trying to develop simpler systems, where these processes can be studied separately in order to understand them better*
- *In Figure a), we show 4 different interfaces, where the observed current density corresponds from exclusively electrode material dissolution to exclusively electrolyte decomposition. The amount of charge associated with metal dissolution is shown in Figure b), suggesting that solvent is stable beyond 5 V.*
- *These interfaces allow for independent study of various processes, but also provide test systems for our analytical tools.*



Accomplishments

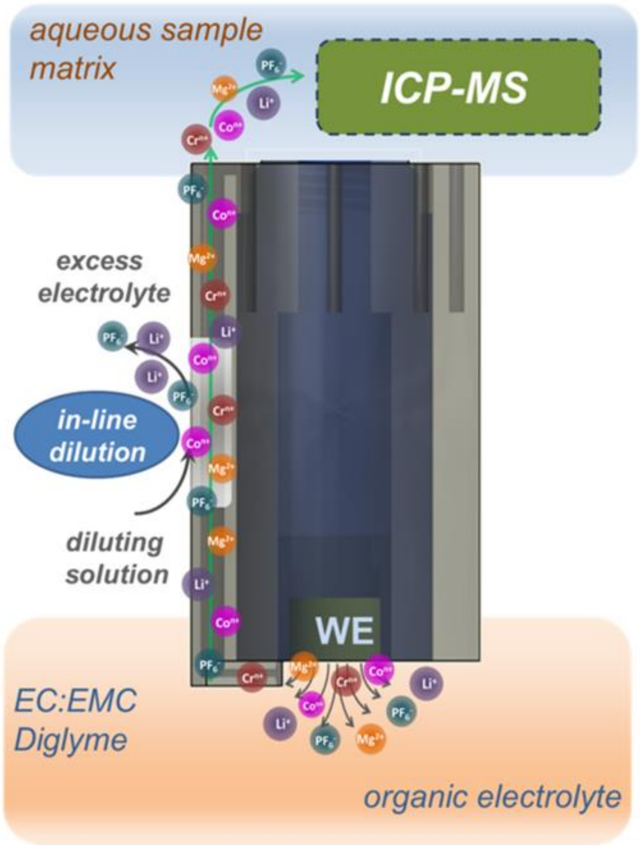
Perform first electrochemical characterization of EC/EMC based electrolytes on metal cathodes M.3

- ❑ *We can increase the complexity of the model systems by controlling the surface chemistry of the electrode material.*
- ❑ *This was done for nickel electrodes, which were terminated in various ways, from completely metallic to completely oxidized as seen in the XPS spectra of the nickel surfaces (Figure b)*
- ❑ *The resulting electrochemical response displayed almost a 1V difference in reaction overpotential (Figure a))*
- ❑ *As determined with the ICP-MS analysis, the entire passed charge corresponded to Ni dissolution on the annealed surface compared to only half on the UV/O_3 treated surface.*

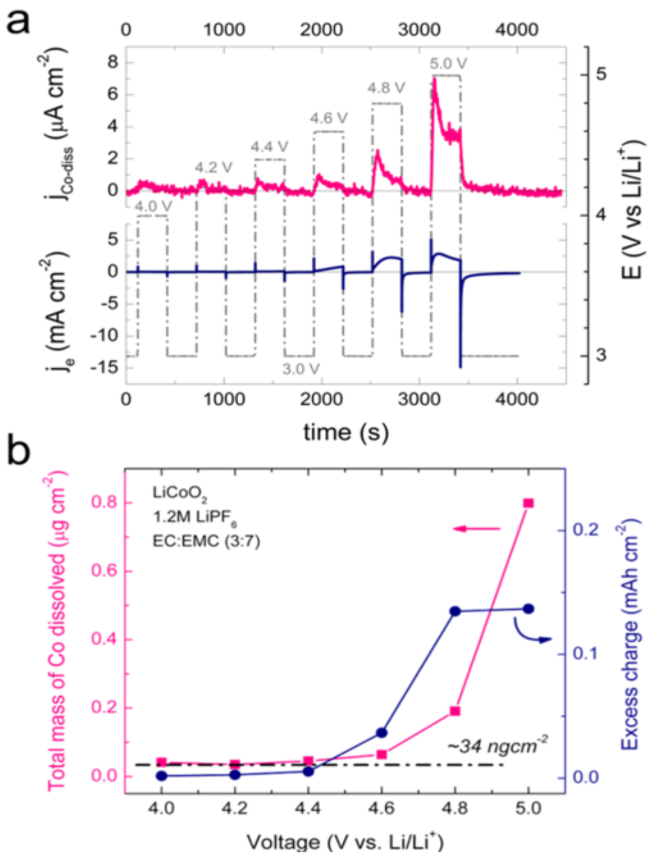


Accomplishments

Perform first electrochemical characterization of EC and EMC based electrolytes on TMOs M.8



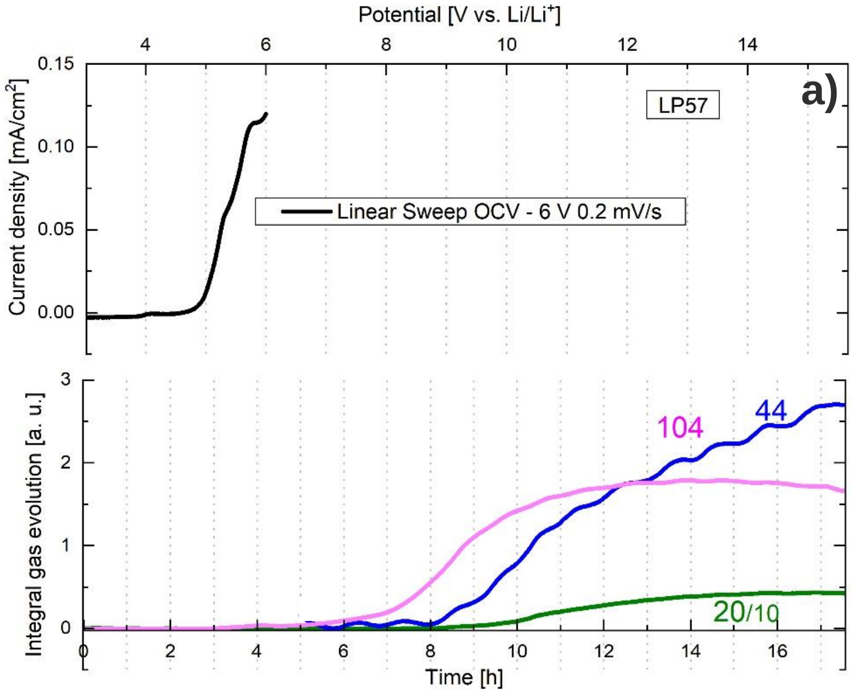
Schematic of the Stationary Probe Rotating Disk Electrode (SPRDE) system coupled to an Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

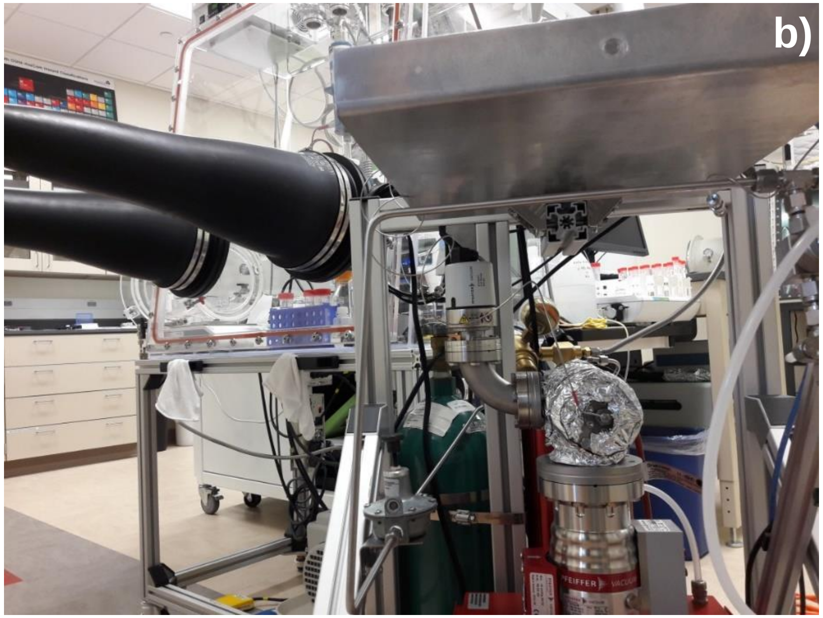


a) *In situ* dissolution currents for Co ion dissolution (magenta) from $LiCoO_2$ in 1.2M LiPF6 in 3:7 EC:EMC b) total mass of Co dissolved in each potential step window (left axis) and corresponding excess positive charge measured on the disk (right axis).

Accomplishments

Build OEMS capability and perform first measurements M.5





- *We have built OEMS capability (Figure b), which is close to operational*
- *Carbon Super C65 was used as a test cathode sample to measure electrolyte decomposition.*
- *The electrochemical response and some typical LP57 decomposition products, e.g. HF, POF_3 and CO_2 are shown in (Figure a)*
- *The last remaining issue with the setup (remedy in progress) is the delayed response of the mass spectrometer due to the dead volume of the capillary connecting the OEMS cell and the mass spec.*

Response to previous year reviewers' comments

This is a new project

Collaborations

ANL, CSE: Zhengcheng(John) Zhang,

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

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*

- *Breach the gap between theoretical predictions and experiment*
- *If individual interface components' electrochemistry can be isolated, we can bring it much closer to computational efforts*

- *Breach 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*

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*
- *Based on experimentally identified decomposition products and computational efforts, propose the electrolyte decomposition mechanism 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*

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*
- *NO computational method mimics real conditions and data on model systems is scarce*
- *The complexity of the model systems is also high*
- *Selecting the "correct" interfaces to isolate individual degradation processes is key to successful application of our approach*

- *Our data so far suggests that the common LiB electrolyte solvents (EC and EMC) are electrochemically reasonably stable on transition metals beyond 5 V.*
- *We have yet to determine a potential electrocatalytic effect in solvent decomposition*
- *On nickel, and possibly cobalt and manganese, the surface termination plays a major role in cathode/electrolyte degradation*
- *The solvent itself is not very stable against chemical attack from weak or strong proton donors.*