# Developing Scanning Electrochemical Microscopy (SECM) for Cathode Interfaces

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National Renewable Energy Laboratory
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2020 Annual Merit Review and Peer Evaluation Meeting

Project ID # bat410

# Overview

## Timeline

- Project start date: 10/1/2018
- Project end date: 9/30/2021
- Percent complete: 50%

## Budget

- Total project funding: $ 1.1M
  - DOE share: $1.1 M
  - Contractor share: N/A
- Funding for FY 2019: $200K
- Funding for FY 2020: $450K

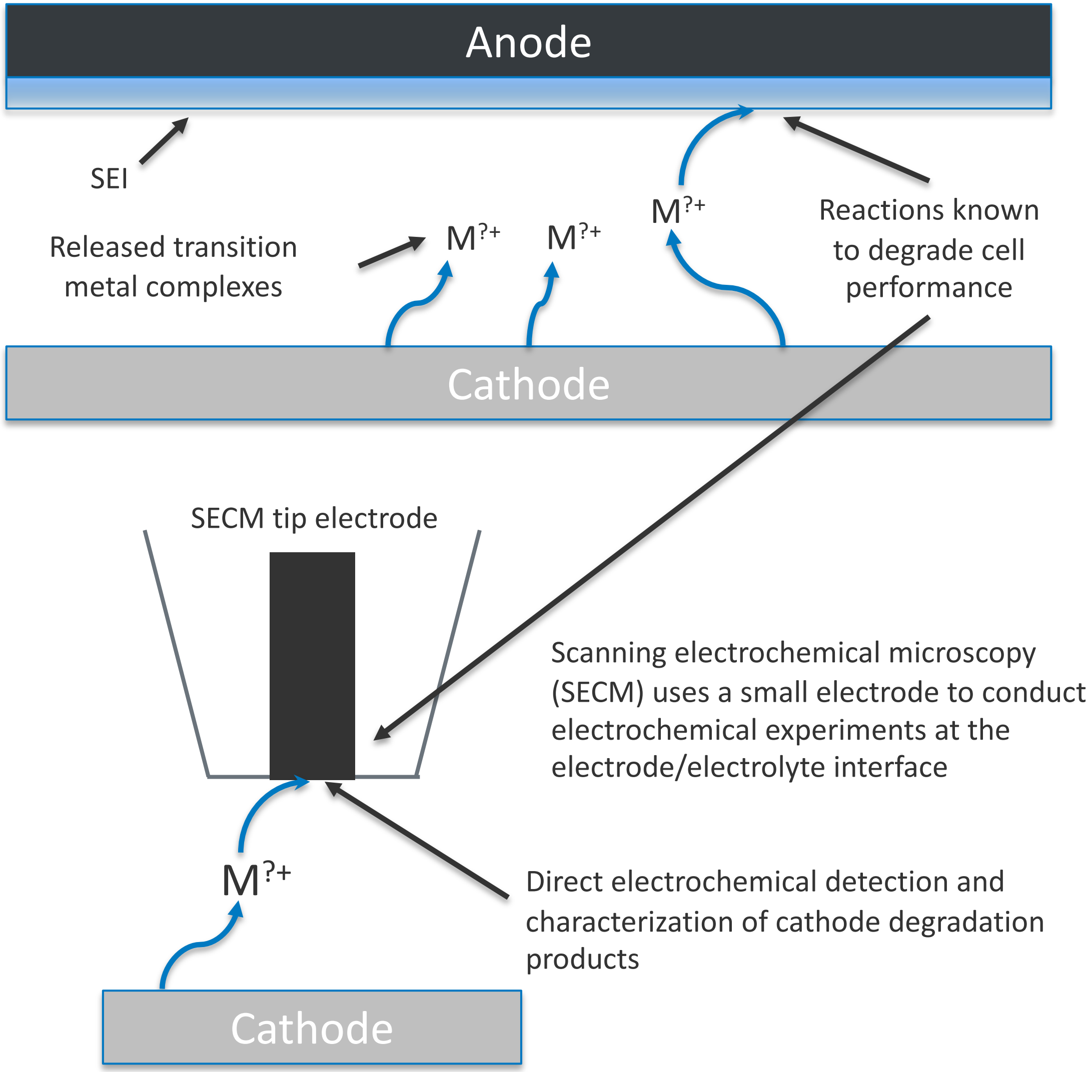
## Barriers

- Barriers addressed
  - Performance
  - Life
  - Cost

## Partners

- New Mexico State University
- Oregon State University
- University of Houston – Clear Lake
- SLAC
- LBNL (developing)
- Argonne NL (developing)

# Relevance



- Metal ion complexes formed from cathode degradation are known to diffuse through cells depositing at the anode SEI leading to decreased performance.
- The precise properties of these degradation products and their interactions at the anode surface are still poorly understood.
- Studies of metal complex/SEI interactions often rely on the introduction of model metal ion compounds.
- Here we focus on electrochemical characterization of degradation from a variety of model cathodes as a function of electrolyte composition using the Scanning Electrochemical Microscope (SECM).
- We also compare the properties of cathode degradation to commonly used model compounds.

# Approach: SECM Background

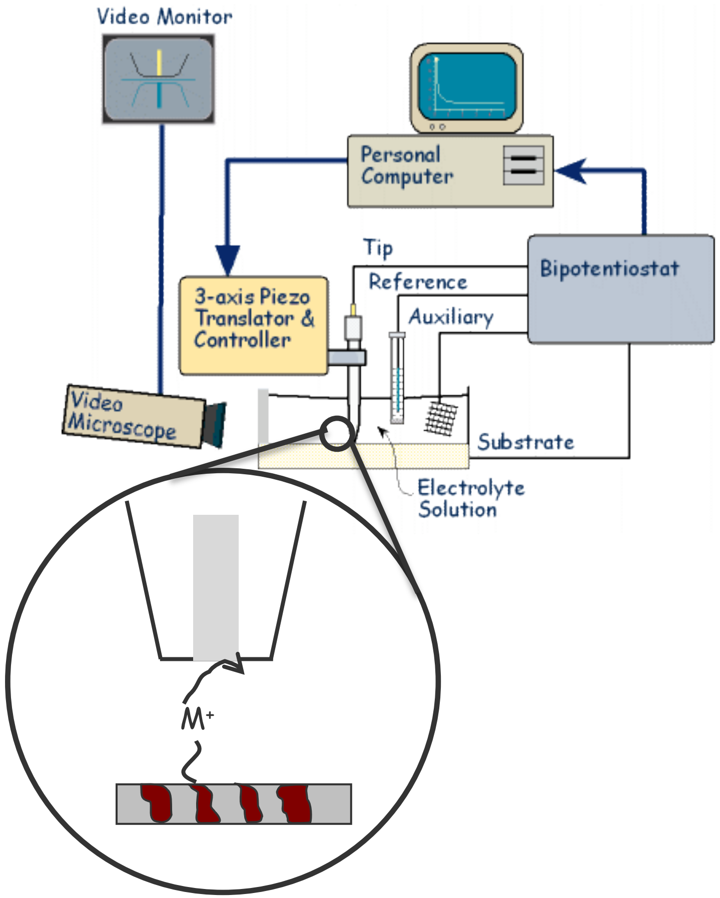
Scanning Electrochemical Microscopy (SECM) as well as other electrochemical probe microscopies enable a myriad of techniques for in-situ analysis of processes occurring at the electrode/electrolyte interface.

The scanning probe in the SECM method is a small (μm-nm diameter) electrode that detects electrochemical reactions.

Tip and substrate voltages are controlled vs. the same reference and counter electrodes in a four-electrode cell show to the right

The method enables direct characterization of electrochemical processes occurring between the probe “tip” electrode and an underlying substrate in an active electrochemical cell.

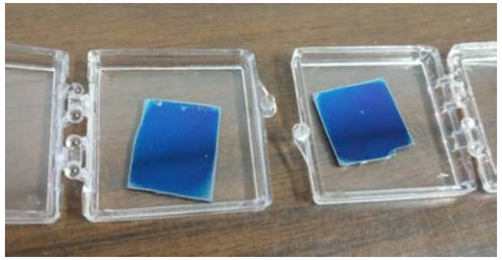
Imaging capabilities allow spatial observation of surface processes.



Scanning Electrochemical Microscopy; Bard, A.J., Mirkin, M.V., Eds.; CRC Press: Boca Raton, Fl, 2012

# Approach: Project Overview

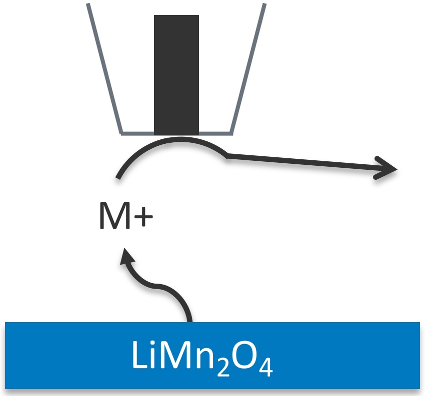
Studies based on model cathode materials building up to the analysis of NMC cathodes

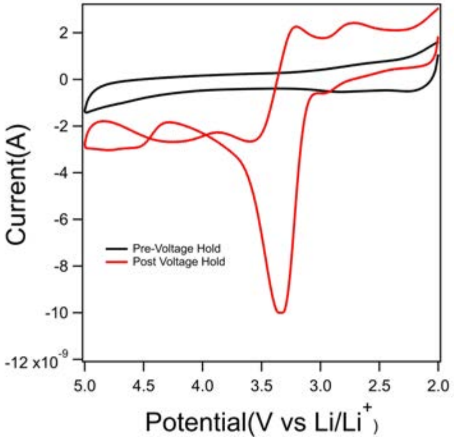


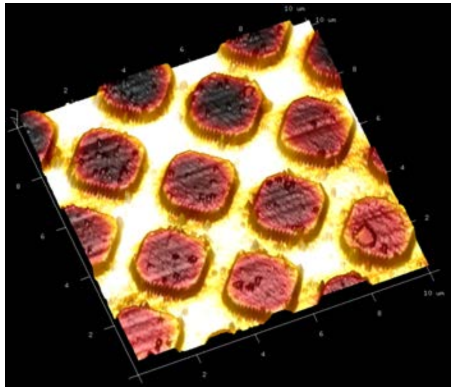
Planned model cathode experimental progression

$LiMn_2O_4 \rightarrow LiNi_{0.5}Mn_{1.5}O_4 \rightarrow$ NMCs

Electrochemical analysis of degradation products in varied model electrolyte systems







High resolution AFM-SECM to image variations in degradation product properties as function of surface morphology and structure

**Developing in FY20 based on FY19 review input**

Integration with complementary diagnostics

- Inductively Coupled Plasma (ICP) Spectroscopy
- Electron Paramagnetic Resonance (EPR) Spectroscopy
- FTIR/Raman Spectroscopy (developing)
- Fluorescence Microscopy (developing)

# Milestones

**FY19**

- SECM design and installation
- Development of model cathodes
- Initial studies of Mn dissolution from $LiMn_2O_4$ (LMO)

**FY20**

- Complete studies of LMO
- Studies of dissolution from $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO)
- Installation of AFM/SECM system

**FY21**

- Studies of dissolution from NMC cathode family
- High resolution imaging of degradation with AFM/SECM

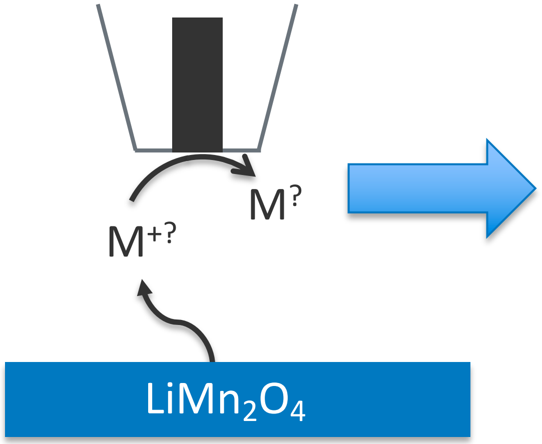
| FY20 Milestone Name/Description | End Date | Type | Status |
|---|---|---|---|
| **Summary report on work to date on Mn dissolution from LMO with varied electrolyte systems including initial examination of single crystal substrates** | 12/31/2019 | Quarterly Progress Measure (Regular) | Complete |
| **Submission of manuscript on SECM studies of Mn dissolution from LMO in various electrolytes to peer reviewed journal** | 3/31/2020 | Annual Milestone (Regular) | Complete |
| **Summary report on initial studies of degradation of LNMO substrates** | 6/30/2020 | Quarterly Progress Measure (Regular) | On-going |
| **Submission of manuscript on SECM studies of Mn dissolution from single crystal LMO materials** | 9/30/2020 | Quarterly Progress Measure (Regular) | On-going |

# Approach: SECM Generation/Collection Voltammetry

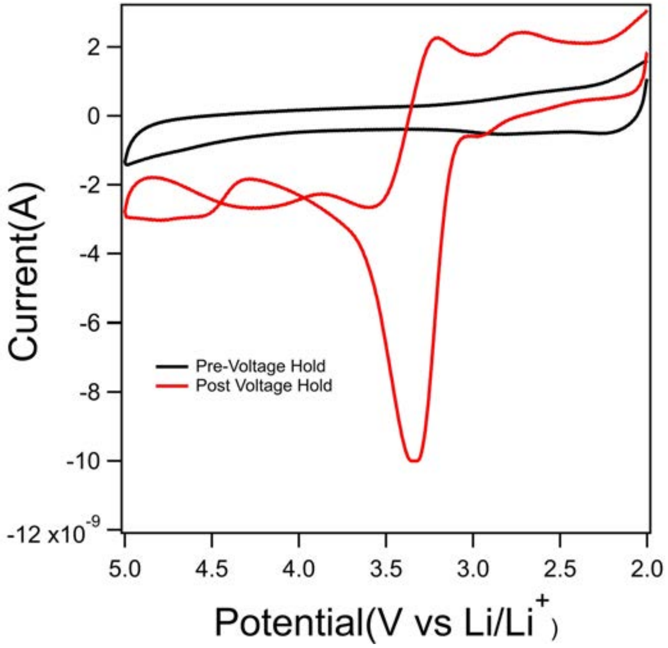
- Our primary analysis method for this work combines cyclic voltammetry with the generation/collection (G/C) mode of SECM.

- In G/C mode SECM, a species is generated at the substrate and then detected (collected) at the tip.

- Combining this with cyclic voltammetry (CV) conducted near the substrate surface allows characterization of the electrochemical properties of evolving species analogous to the rotating ring disk electrode (RRDE) experiment.



Tip: 25 um Pt Disk
Substrate: LMO on Stainless steel
RE: Li/Li+
CE: Pt



Various electrolyte formulations studied
*Salts*: $LiClO_4$, $LiPF_6$, LiTFSI
*Solvents*: propylene carbonate*, ethyl methyl carbonate, ethylene carbonate

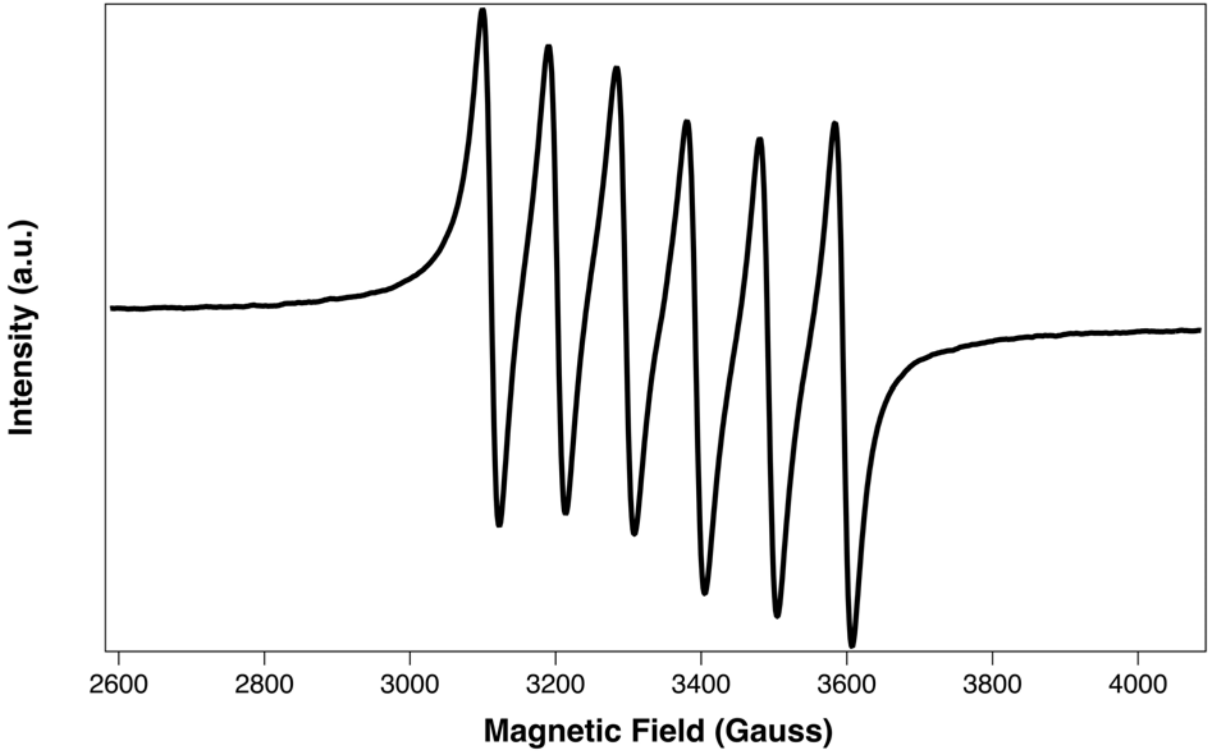
*Propylene carbonate was used due to being a single component and having low volatility.

- Data to the right shows CV data collected at a 25 μm Pt tip placed ~ 20 μm above a model LMO sample. An initial scan was collected prior to starting high voltage (4.5V) holds at the LMO. A subsequent scan was collected after a five-hour voltage hold and clearly shows signal due to cathode degradation.

# Technical Accomplishment: Detection of Mn Oxidation State Ratios

In addition to our G/C SECM voltammetry method and based on feedback from previous reviewers, we are adopting a procedure reported by Banerjee et al. to determine the relative concentrations of $Mn^{2+}$ and $Mn^{3+}$ species with a combination of Inductively Coupled Plasma (ICP) and Electron Paramagnetic Resonance (EPR) Spectroscopies.

EPR for manganese(II) acetylacetonate in EC/EMC $LiPF_6$



- ICP is used to obtain total Mn concentration
- EPR is capable of detecting and quantifying $Mn^{2+}$
- The balance of total Mn is assumed to be in the $Mn^{3+}$ state

Completed work:

- ICP determination of total Mn concentration
- Confirmation of $Mn^{2+}$ by EPR

Pending work:

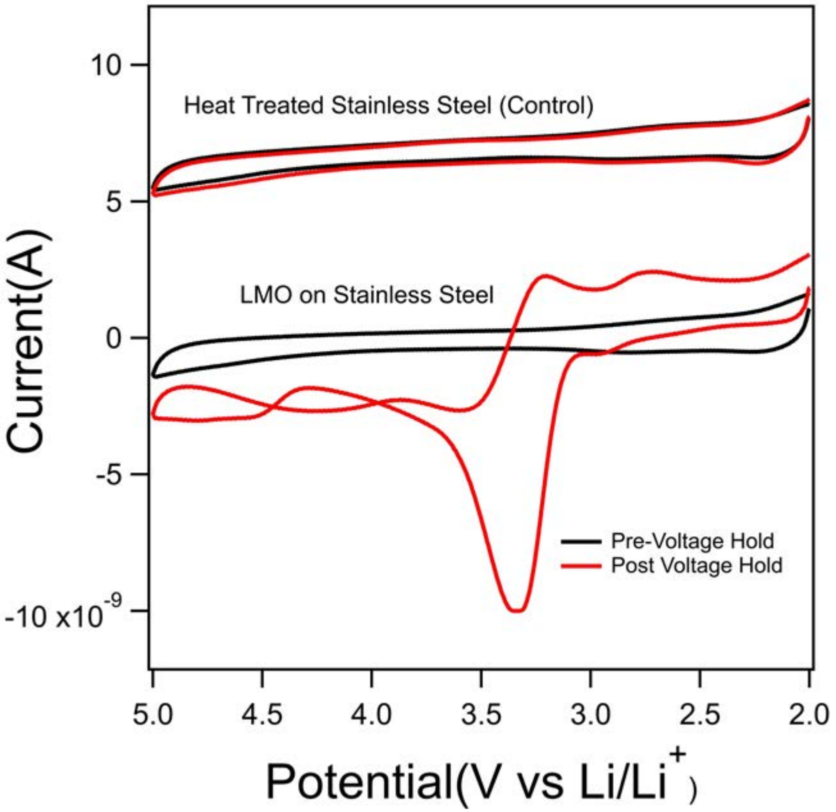
- Quantitation of $Mn^{2+}$ via EPR

Pairing additional analytical techniques with our SECM based methods helps clarify some of the ambiguity that can be inherent electrochemical detection methods when taken alone.

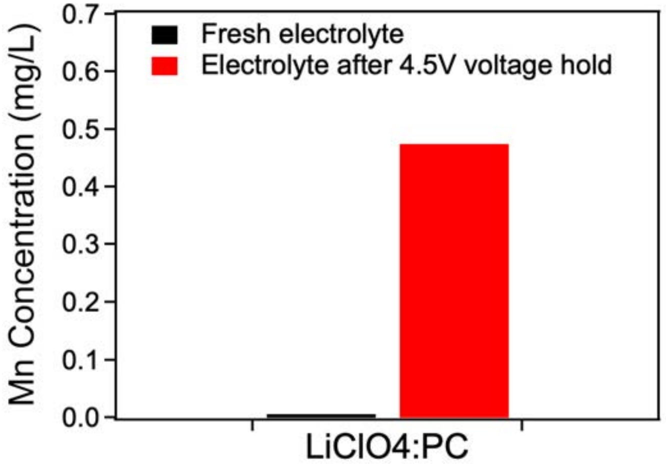
Banerjee, A. et al. J. Am. Chem. Soc. 2017, 139, 1738-1741

# Technical Accomplishment: Detection of Mn Oxidation State Ratios

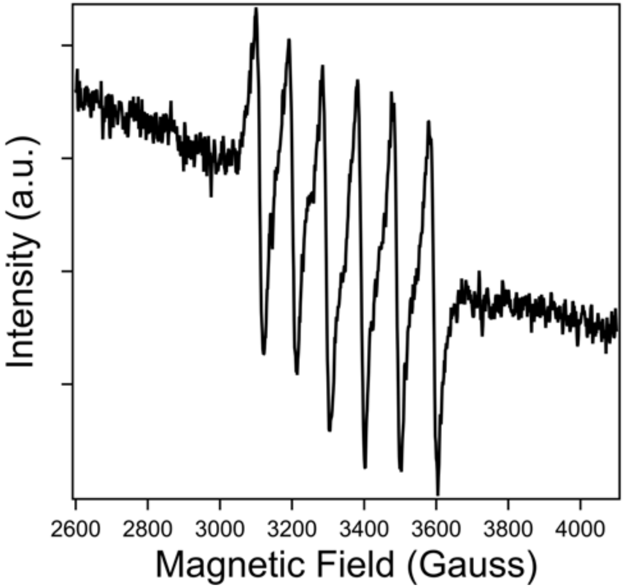
G/C SECM voltammograms collected before and after at 5 hour 4.5V hold at the substrate. Tip - 25 μm Pt disk; scan rate - 1V/s; d = 20 μm



ICP-AES for Pre- and Post-Voltage Hold 1M $LiClO_4$



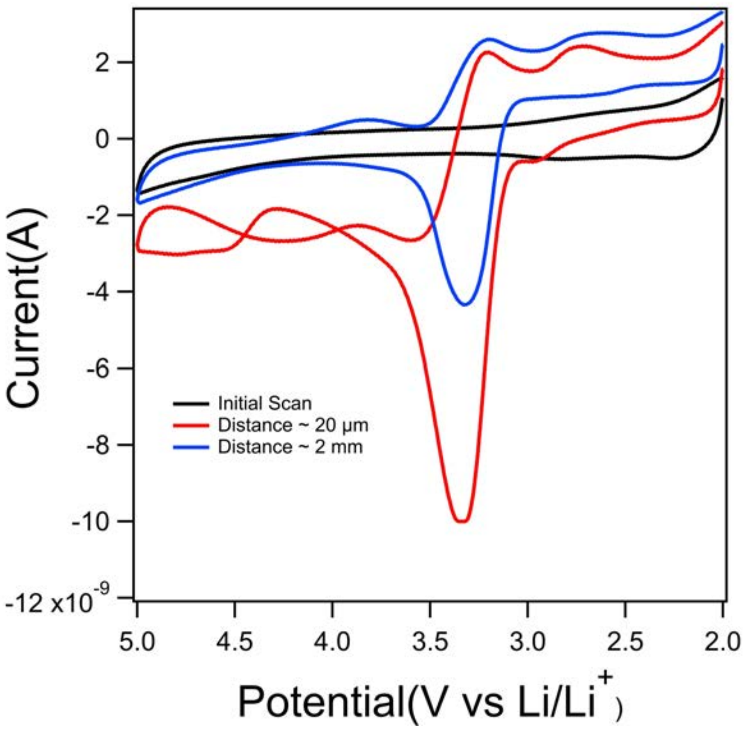
RT EPR for Post-Voltage Hold 1M $LiClO_4$



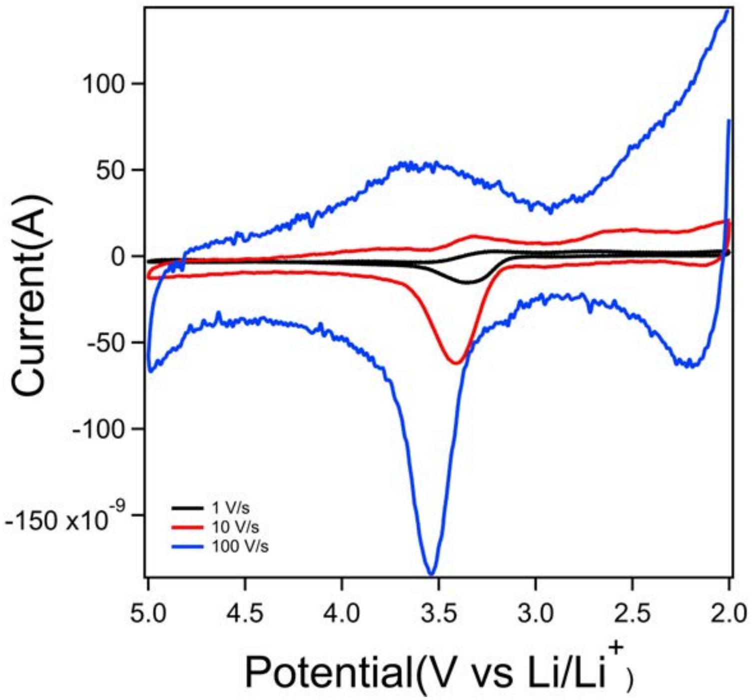
- G/C SECM data was collected for Mn dissolution from LMO occurring in 1M $LiClO_4$ and propylene carbonate before and after a 5-hour voltage hold at 4.5Vm (LMO)
- Control experiments confirm voltammetric signature observed is due to LMO
- ICP and EPR confirm the presence of $Mn^{2+}$ but cannot rule out $Mn^{3+}$ at present pending EPR quantitation experiments
- Three electron transfer reactions are observed for at ~ 2.8V, 3.4V and 4.5V
- Strong asymmetry between oxidation and reduction peaks for 3.4V species indicates irreversibility or catalytic effect
- Species generated at 4.5V appears to be unstable

# Technical Accomplishments: Voltammetric Characterization of LMO Degradation Products

G/C SECM voltammograms collected with the tip positioned near (~20μm) and far (~2mm) from the underlying substrate after a 5 hour 4.5V hold



G/C SECM voltammograms collected at varied scan rates with the tip positioned near (~20μm) the substrate after a 5 hour 4.5V hold



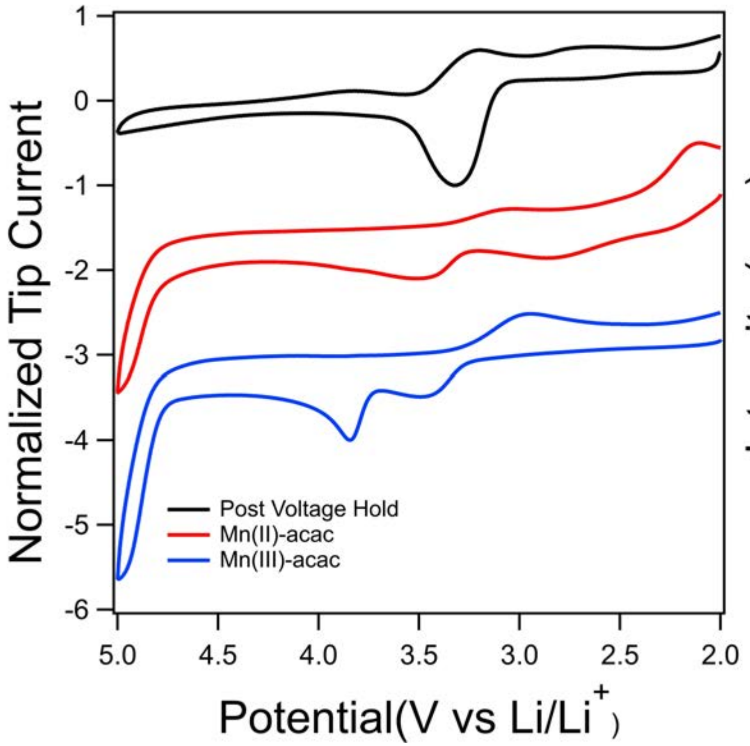
- Variations in tip to substrate distance can reveal insights to surface reactivity.
- G/C SECM-CV studies at varied scan rates can be used to characterize kinetics of associated electron transfer reactions.
- Amplification of the oxidation current when near the surface likely due to interactions with substrate.
- The 4.5V process is eliminated above 10V/s.
- Minor shifts in peak position for the 3.4V process even at 100V/s

- The amplification of the oxidation current observed in the data on the left likely indicates that the nearby substrate remains highly reactive to the oxidation product even at open circuit
- Scan rate dependence shows that the reaction above 4.5V is kinetically slower than that observed at 3.4V
- Minor shift in peak position for the 3.4V process with scan rate indicative of fast reaction kinetics

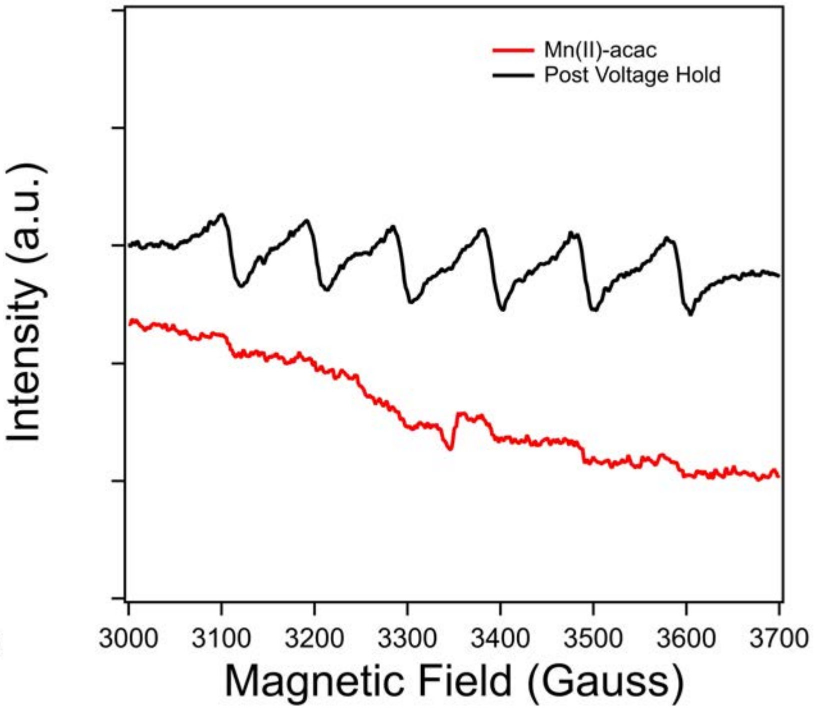
Methods developed here will be employed to study more complex and battery relevant species

# Comparison of Degradation Products to Common Model Compounds

G/C SECM CV data compared to CV's of model compounds collected in standard three electrode cells all in 1M $LiClO_4$:PC



Comparison of EPR data for post voltage hold solution and model $Mn^{2+}$ salt in 1M $LiClO_4$:PC

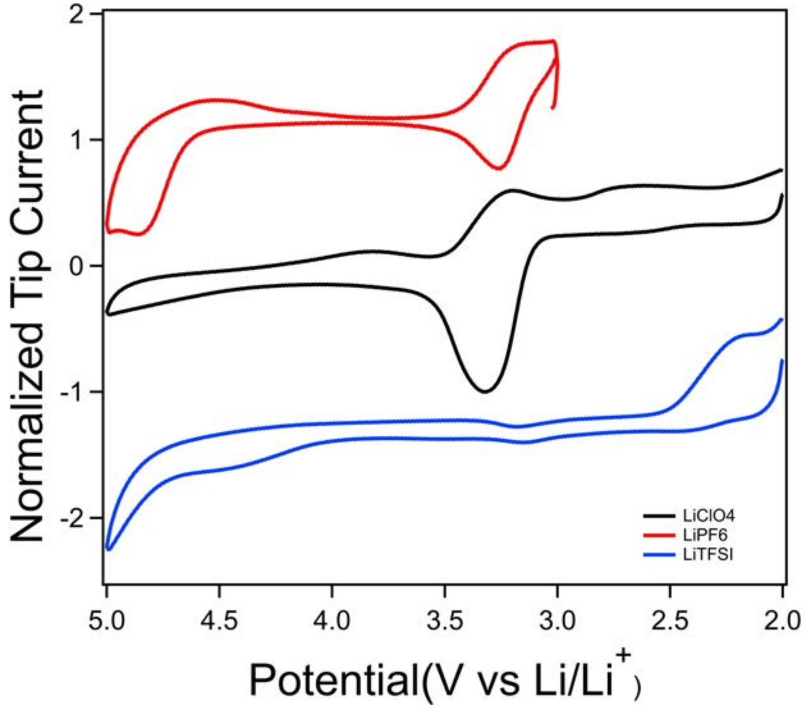


- Acetylacetonate (acac) complexes were chosen due to previous use as a model for Mn dissolution studies.
- ICP confirmed the presence of Mn in all examined solutions.
- EPR showed $Mn^{2+}$ present after high voltage hold, but not in the $Mn^{2+}$ model salt solution.
- Planned experiments will also examine Mn–$ClO_4$, –$PF_6$ and –TFSI model salts.

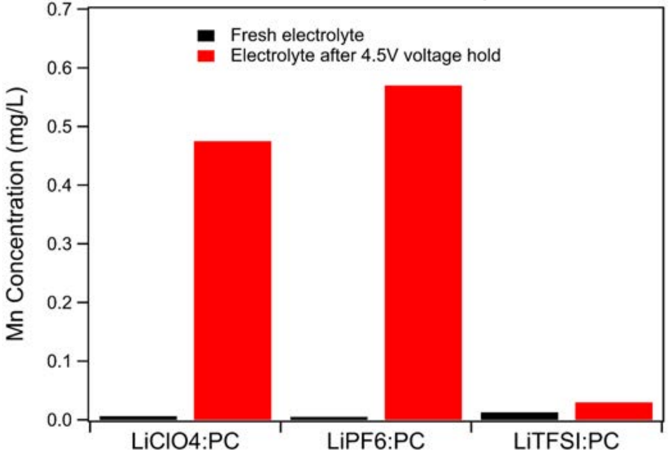
- Above data shows that neither $Mn^{2+}$ or $Mn^{3+}$(acac) complexes in 1M $LiClO_4$ match the observed signature for degradation products detected in G/C SECM experiments
- Absence of EPR signal for model $Mn^{2+}$(acac) system, even after ICP confirmed presence of Mn, demonstrates that $Mn^{2+}$(acac) complex does not appear to be stable in $LiClO_4$:PC electrolyte
- Lack of stability for the model salt is possibly due to a change in the Mn coordination environment or chemical oxidation to $Mn^{3+}$

# Impact of Anion Identity on LMO Degradation Products

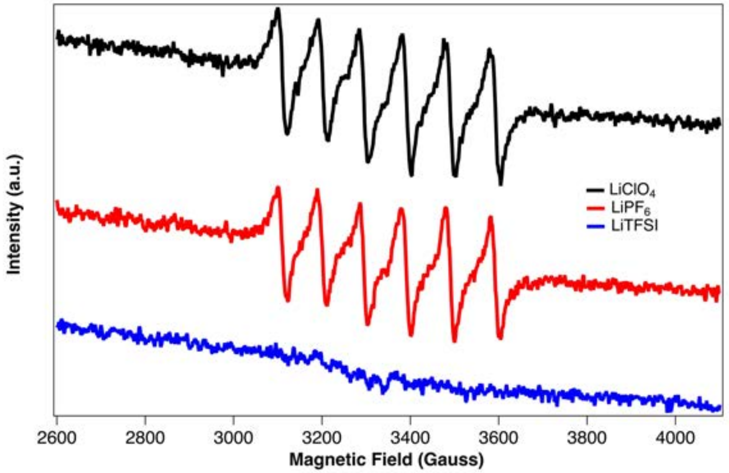
G/C SECM voltammograms collected after a 5-hour voltage hold at 4.5V for model electrolytes with varied anions



ICP measured Mn concentration for various electrolyte solutions after LMO voltage hold



EPR for various electrolyte solutions after LMO voltage hold



LMO degradation products were examined in three model electrolytes.

- 1M $LiClO_4$ in propylene carbonate
- 1M $LiPF_6$ in propylene carbonate
- 1M LiTFSI in propylene carbonate

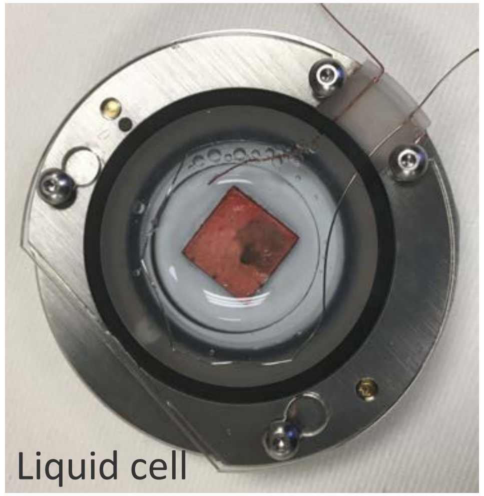
- Both $LiClO_4$ and $LiPF_6$ appear to show a similar redox reaction occurring at ~ 3.4V
- $LiPF_6$ appears to show a more reversible process than $LiClO_4$
- $LiPF_6$ also shows a second, more stable redox reaction above 4.5V
- ICP and EPR confirm the presence of $Mn^{2+}$ in the $LiClO_4$ and $LiPF_6$ solutions
- Limited Mn dissolution appears to be observed for the TFSI system

This data shows that the electrochemical properties of the LMO degradation products varies with the identity of the electrolyte anion. This is complementary to recent observations that anion identity impacts reactivity of metal complexes at the SEI interface.

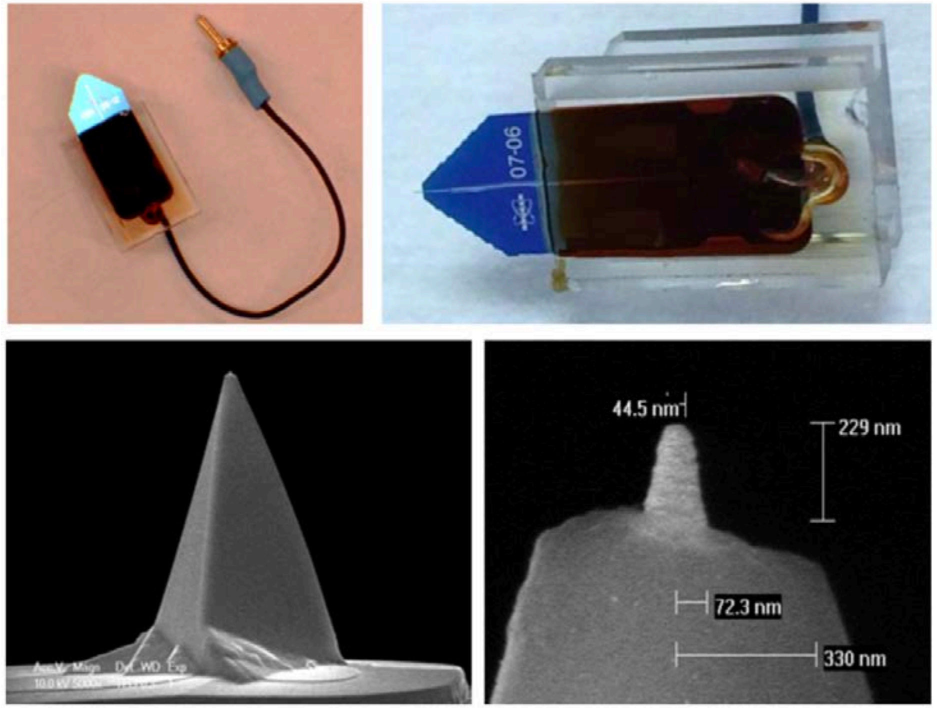
# New capability - Atomic force microscopy-based scanning electrochemical microscopy

Capability Highlights:

- High spatial resolution: ~150-200 nm
- Liquid cell enables in-situ imaging of surface morphology and cyclic voltammetry simultaneously
- Housed in a glove-box facilitating air-free measurements



Liquid cell



Nanofabricated microelectrode probe is ~50 nm at tip apex.

Status Update:

- Successfully in-situ imaged surface morphology of patterned surface
- Successfully implemented model electrochemical reaction of electrodepositing copper on Graphite

Next Steps:

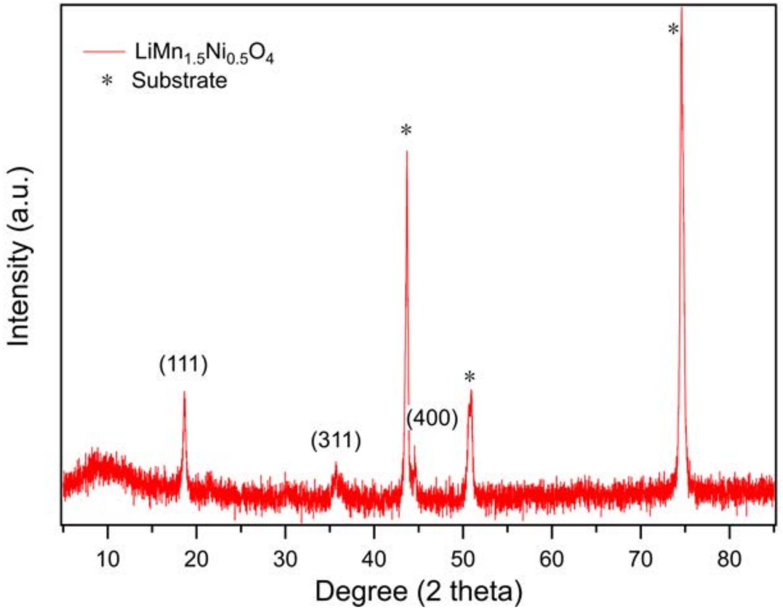
- In-situ image LMO film deposited on a silicon substrate.
- Elucidate surface morphology as a function of applied bias on LMO.
- Elucidate LMO morphology changes resulting from systematic CV

The AFM/SECM system is installed and initial experiments currently underway

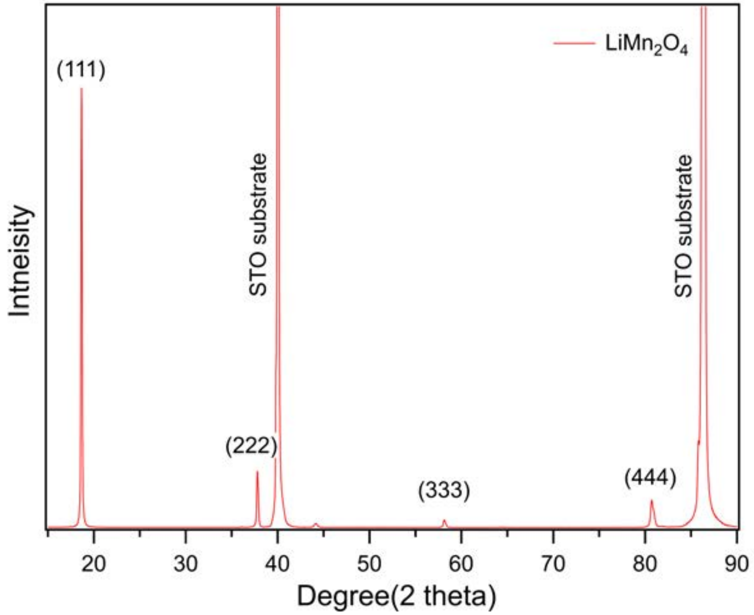
# Model Cathode Development

- Polymer Assisted Deposition (PAD) is a solution-based process for forming a variety of metal oxides
- We have used this to produce all model cathodes to date
- FY20 effort has focused on synthesis of $LiNi_{0.5}Mn0_{1.5}O_4$, $LiMn_2O_4$ and NMC 532 thin films for future studies as well as partner laboratories
- Electrochemical characterization of these materials is on-going

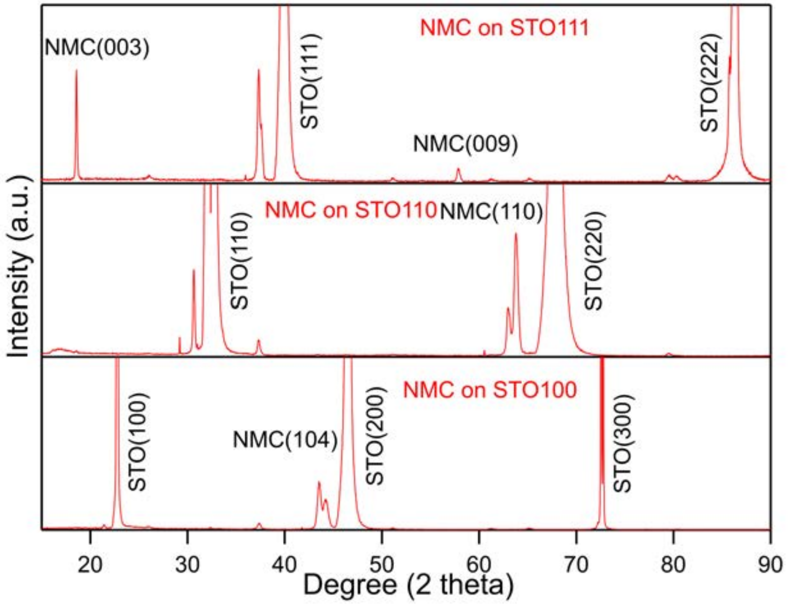
$LiNi_{0.5}Mn0_{1.5}O_4$



$LiMn_2O_4$ (111)



NMC 532



The PAD method allows a high degree of flexibility in producing a wide variety of model cathode films for further study

We have developed and are confirming methods to produce needed model cathodes for FY20 and FY21 work

We have also been approached by partner laboratories (SLAC) and are supplying them with required samples

# Responses to Previous Year Reviewers' Comments

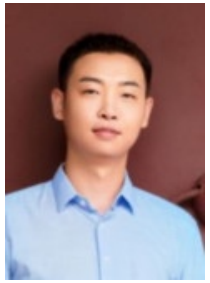
- The most significant suggestion from last year's review panel was the addition of complementary analytical techniques to the project. Reviewers noted that electrochemical results in and of themselves can be ambiguous about the identity of the detected species. We agree with the reviewers and are in the process of bringing additional methods on board as well as building collaborations to address this need. Data presented here included ICP and EPR studies which are newly added this year. We are currently working with internal and approaching external collaborators to bring in spectroscopic methods.

- Our FY19 reviewers also expressed concern about the resolution of traditional SECM methods. This is being addressed by the addition of our new AFM/SECM instrument which enables resolution down to 200 nm. It is also important to note that the SECM is a more versatile tool than just a scanning probe microscope. The data presented here is focused on using the method to understand the fundamental electrochemical processes occurring at the interface rather than focused on imaging methods. We will use the information presented here to inform imaging experiments that can now be conducted at high resolution.

- FY19 reviewers also called out the need for increased collaborations to bring further value to this effort. We have actively engaged a broader group of researchers, for the moment, predominantly at NREL. We are currently reaching out to the Argonne cathode project teams as well as collaborators at LBNL to bring in additional diagnostic methods. We have also begun collaborations with SLAC, initially focused on characterization of our single crystal model cathodes and will continue to expand this partnership through the remainder of the project. In addition, we have begun discussions with and are co-advising a visiting professor with NREL's modeling teams to add this capability to our project portfolio.

# Collaboration and Coordination

| Collaborator | Entity | VTO | Description |
|---|---|---|---|
| SLAC | National Laboratory | Yes | Characterization of single crystal model cathode materials |
| Argonne NL (developing) | National Laboratory | Yes | Discussing integration with the Argonne led cathode research under VTO |
| LBNL (developing) | National Laboratory | Yes | Approaching researchers at LBNL regarding inclusion of fluorescence microscopy to pair with SECM imaging |
| New Mexico State University | University | No | Fabrication of model cathode materials and experimental SECM work |
| Oregon State University | University (SULI) | No | Fabrication and characterization of SECM tip-based anodes |
| University of Houston | University | No | Design of novel electrochemical cells for AFM/SECM |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NREL

# Remaining Challenges and Barriers

- Our largest remaining challenge is related to the ability to detect varied degradation products as our model cathodes become more complex. The approach we have taken is designed to allow us to mitigate this risk. This is the primary reason that we are working with simplified model cathodes as well as starting with the simplest (Mn dissolution from LMO) system. We will ramp up complexity of the cathode slowly by moving to the LNMO system next and then to the NMC's.
- Another challenge is integrating broader capabilities that can be paired with our electrochemical techniques. As discussed, we have begun work with EPR and ICP to complement existing methods in FY20. We will require further partnerships to bring alternative techniques on board, including spectroscopic methods and modeling. We are aggressively engaging with potential partners within the VTO program in order to mitigate this risk.

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

# Proposed Future Research

- Our initial choice of PC as our electrolyte solvent was in order to limit evaporation of the electrolyte in our open SECM cell. The common Gen2 electrolyte is volatile. We are currently working to produce an enclosed SECM cell based on existing designs that will limit solvent loss so that we can continue studies with the EC/EMC electrolyte blends.
- We are currently beginning work into studying dissolution processes at LNMO after building our base of knowledge on the simpler LMO material. We will continue this work as we move toward the more commercially relevant NMC cathodes.
- Focus on NMC materials is expected to progress from lower Ni content to higher (NMC532, NMC622 and NMC 811) as has been consistent with much of the cathode research under the VTO program.
- In the remainder of FY20 we will complete the ramp up of the AFM/SECM system and begin work on high resolution imaging of cathode degradation. This will initially focus on LMO and be informed by the results presented here and then translated to additional model cathodes.
- We seek to take advantage of the ability to produce epitaxial films of model cathodes for our studies in order to try to tie surface structure to degradation properties. This work will begin in FY20 and continue into FY21.
- In FY20-FY21 we also plan to begin work on alternative SECM tips to the currently used platinum. We plan to develop at least one new tip that can mimic anode behavior and can give a more direct snapshot of precisely how degradation products interact with the anode SEI interface.
- Beyond, FY21 we seek to develop additional forms of SECM that can help deconvolute some of the detailed mechanisms of cathode degradation. We are interested in developing multifunctional SECM tips that can simultaneously detect and image the presence of HF near the electrode surface while conducting analysis of evolved metal complexes.

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

# Summary

- This work has shown the ability to detect and characterize cathode degradation products in-situ at the cathode/electrolyte interface via SECM.
- Methods for assessing the electrochemical properties of cathode degradation products has been demonstrated using Mn dissolution in 1M $LiClO_4$, 1M $LiPF_6$ and 1M LiTFSI in propylene carbonate. These methods will be employed to study the properties of degradation products from interactions with various other electrolyte samples.
- The properties of cathode degradation products are shown to vary based on the composition of the electrolyte and reveal a complex and rich chemistry occurring at the electrode/electrolyte interface.
- The apparent impact of the electrolyte anion is complementary to other recent studies indicating similar impact on SEI interactions with cathode degradation products.
- A more complete understanding of the electrochemical properties of actual cathode degradation products will help inform studies to suppress cell performance degradation.

# Thank You

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