Understanding and Mitigating Interfacial Reactivity Between Electrode and Electrolyte

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DOE merit review

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Project ID# ES311

Overview

Timeline

- Start: June 2016
- Finish: 2019
- 15%

Barriers

- Barriers addressed
  - Cycle life
  - Capacity
  - Efficiency

Budget

- Total project funding
  - DOE share: 800 K
  - Contractor 0 K
- FY 16: $ 400 K
- FY 17: $ 400 K

Partners

- Interactions/ collaborations
  - Jun Liu, PNNL
  - Xiangming He, Tsinghua University

Project Objectives and Relevance

- Improve the stability of solid/liquid interfaces in Li-ion batteries from insights into the atomic/molecular processes occurring during cycling.
- The goal is to do this for novel cathodes such as 6:2:2 and 8:1:1 NMC cathodes, which have higher voltage and higher power densities, and for which instabilities of the solid-liquid interfaces will limit cycling
- Development of surface characterization techniques & methods for stabilization of solid/liquid interfaces in lithium ion batteries can lead to enhanced performance and increased safety

Milestones

Month/Year	Milestones
Dec/16	First ex-situ measurements of electrode/electrolyte decomposition products using ICP-MS and GC-MS. Develop protocol for calculating electrochemical reactions at electrolyte-electrode interfaces. ***Completed.***
Mar/17	Build a new set of 16-channel high precision electrochemical measurement system dedicated to this project ***Completed.***
Jun/17	Benchmarking the kinetics of direct electrochemical oxidation of baseline electrolyte at different potentials. ***On schedule.***
Sep/17	*Coupling of ICP-MS with electrochemical cell for the direct in-situ investigation of the metal dissolution from the cathode.* ↪ ***On schedule.***

Strategies

- Apply comprehensive *in situ* characterization and integrated modeling capabilities to understand solid liquid interfaces
  - Initial studies with model systems such as $LiCoO_2$ will be used to establish techniques
  - Novel cathodes such as 6:2:2 and 8:1:1 NMC cathodes will be thoroughly investigated because of their relevance to the DOE program
  - Commercial and highly purified electrolytes comprised of organic solvents, salts and additives will be investigated
- Use the information from these studies to understand the complexities that govern the interfaces and enable advancement far beyond the current state-of-the-art Li-ion systems by discovery of new stable cathode materials, surface protection methodologies, and novel electrolytes

Approach

Systems

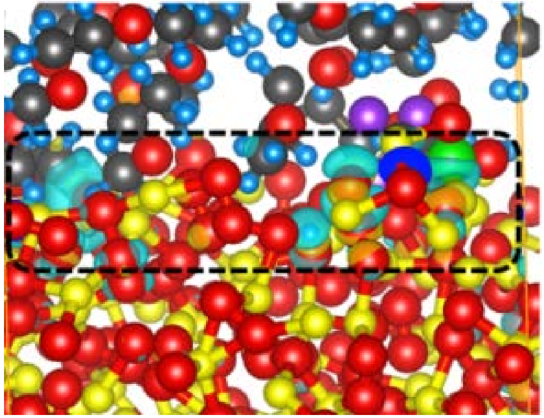
- Cathodes:
  - Model systems such as $LiCoO_2$
  - 6:2:2 and 8:1:1 NMC
- Electrolytes
  - GEN2 1.2 M $LiPF_6$ [EC/EMC (3:7)]
  - Fluorinated and additives

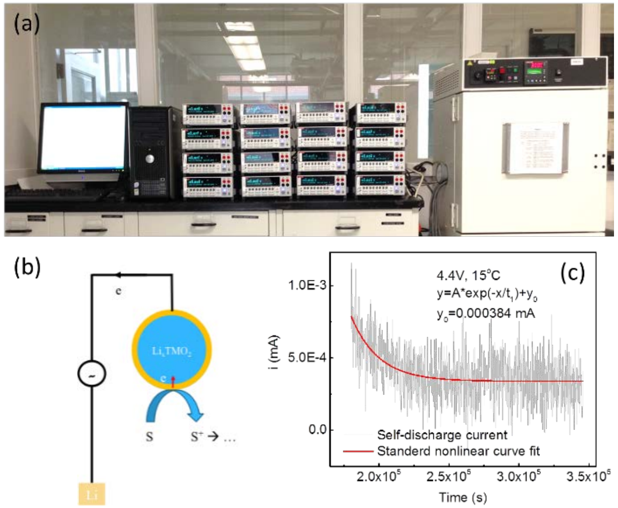
Electrochemical Testing

- High precision electrochemical measurement system dedicated to this project
- A three electrode RDE (rotating disk electrode setup

Gas and Ion Characterization

- Gas Chromatography with Triple Quadrupole Mass Spectrometry (GC-QqQ) in Headspace sampling mode (HS)
- Differential Electrochemical Mass Spectrometry (DEMS)
- Inductively Coupled Plasma with Mass Spectrometry (ICP-MS)

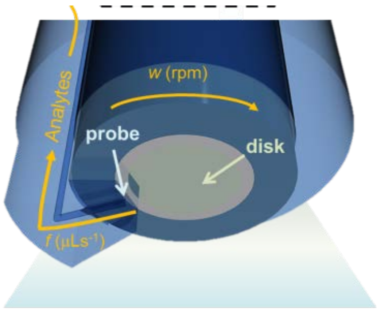




Approach (continued)

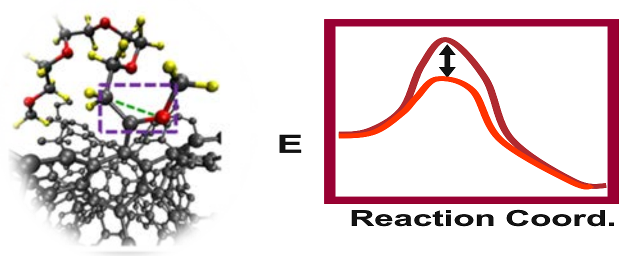
Interface Characterization

- XPS measurement (Advanced Photon Source)
- TEM imaging (ANL Electron Microscopy Center)
- FTIR, Raman
- SEM imaging

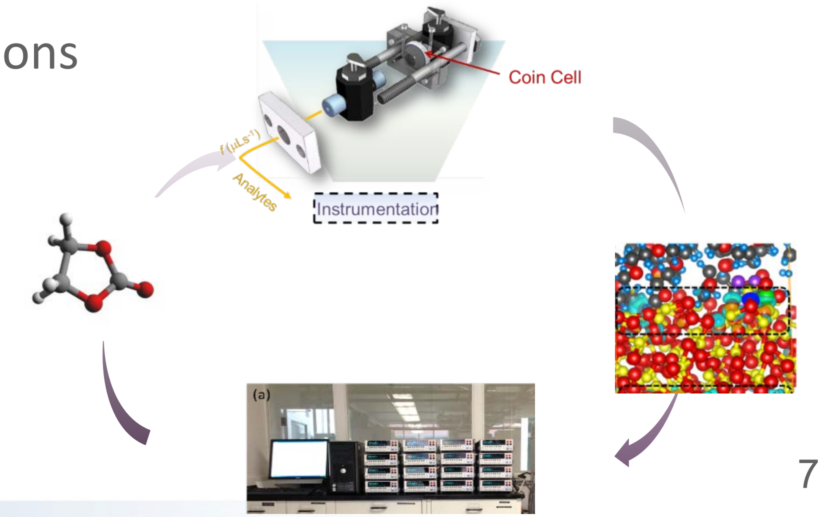


Computational studies

- Periodic, molecular, and cluster calculations using density functional calculations
- Ab initio molecular dynamics simulations
- Reaction energies and barriers for stability screening
- Electrolyte/surface interface simulations

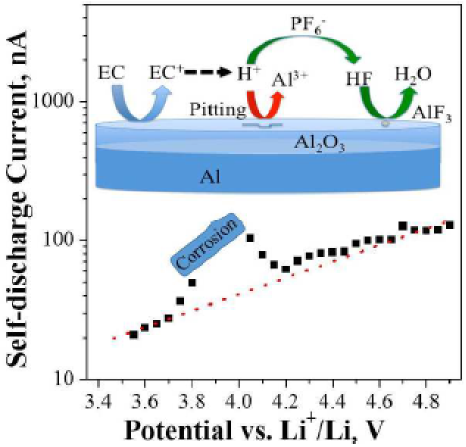


Merging in situ experimental methods with multi-scale simulations for improving interfacial stability



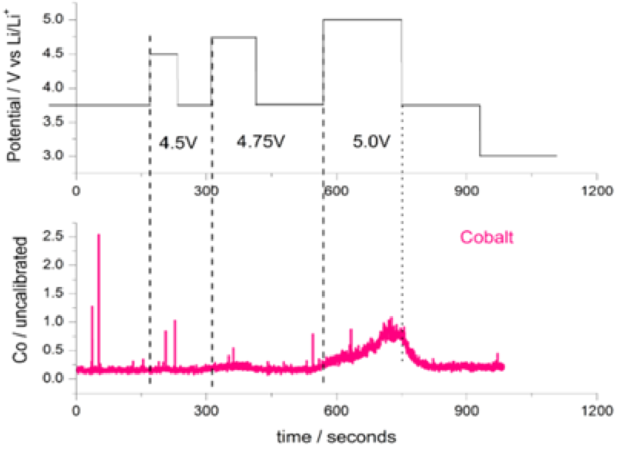
Technical Accomplishments

- Established state-of-the-art experimental technique to investigate at atomic/molecular-levels, the stability of electrochemical interfaces at the electrode in combination with theory

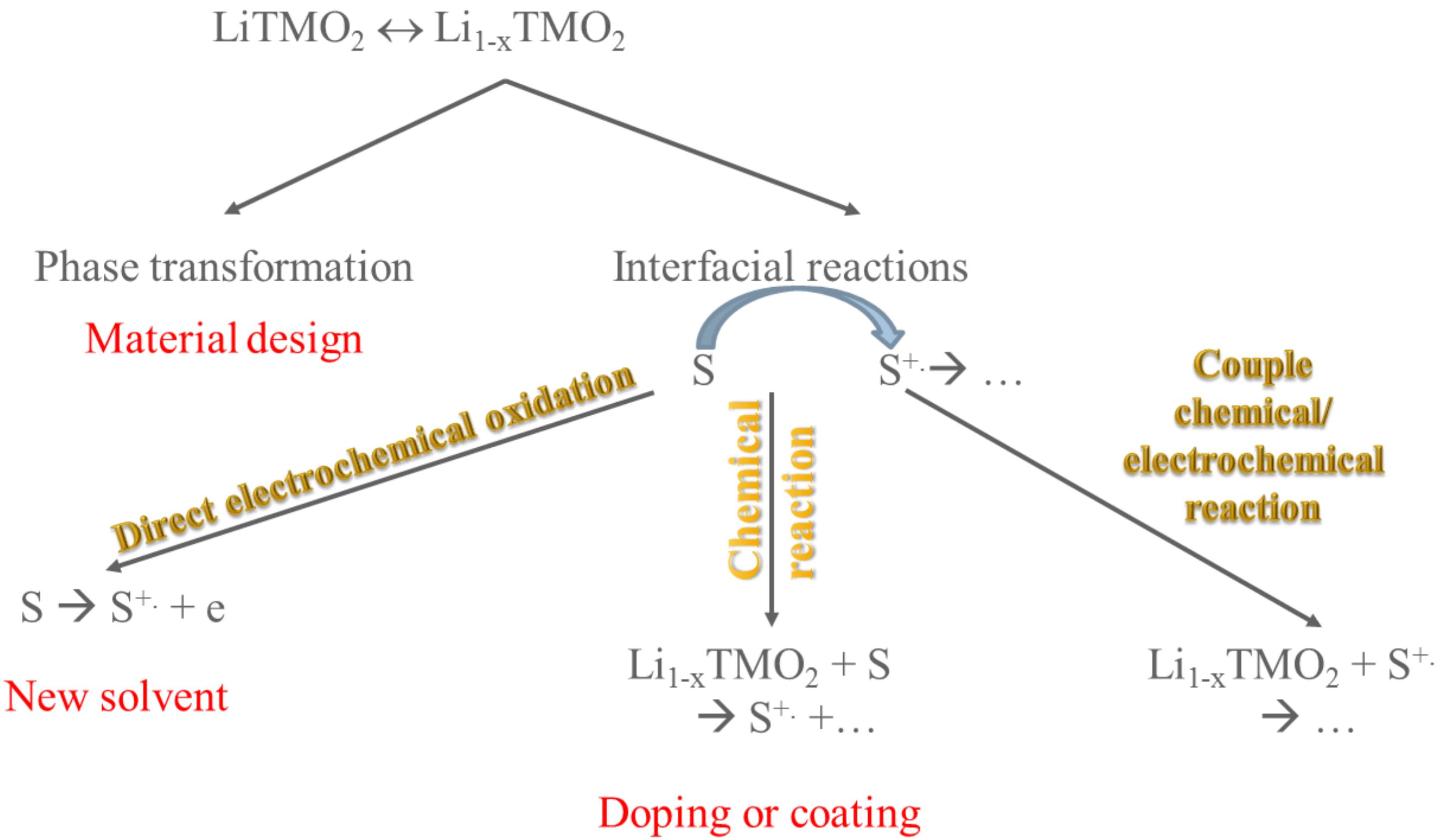


- Investigated the oxidation of EC/EMC electrolyte in the presence of an aluminum current collector and explained the mechanism for instability

- *First-of-its-kind* experiment of *in situ* dissolution of Co from $LiCoO_2$ at higher potentials using a SPRDE-ICP-MS setup.



Possible Li-ion battery degradation mechanisms



$LiTMO_2 \leftrightarrow Li_{1-x}TMO_2$

Phase transformation

Material design

Interfacial reactions

S

$S^{+\cdot} \rightarrow \ldots$

Direct electrochemical oxidation

Chemical reaction

Couple chemical/ electrochemical reaction

$S \rightarrow S^{+\cdot} + e$

New solvent

$Li_{1-x}TMO_2 + S \rightarrow S^{+\cdot} + \ldots$

$Li_{1-x}TMO_2 + S^{+\cdot} \rightarrow \ldots$

Doping or coating

- Initial focus of this project has been on interfacial reactions ($S \rightarrow S^{+} + e$) at the aluminum current collector in Li-ion batteries

Corrosion of Aluminum Current Collector in Li-ion Batteries

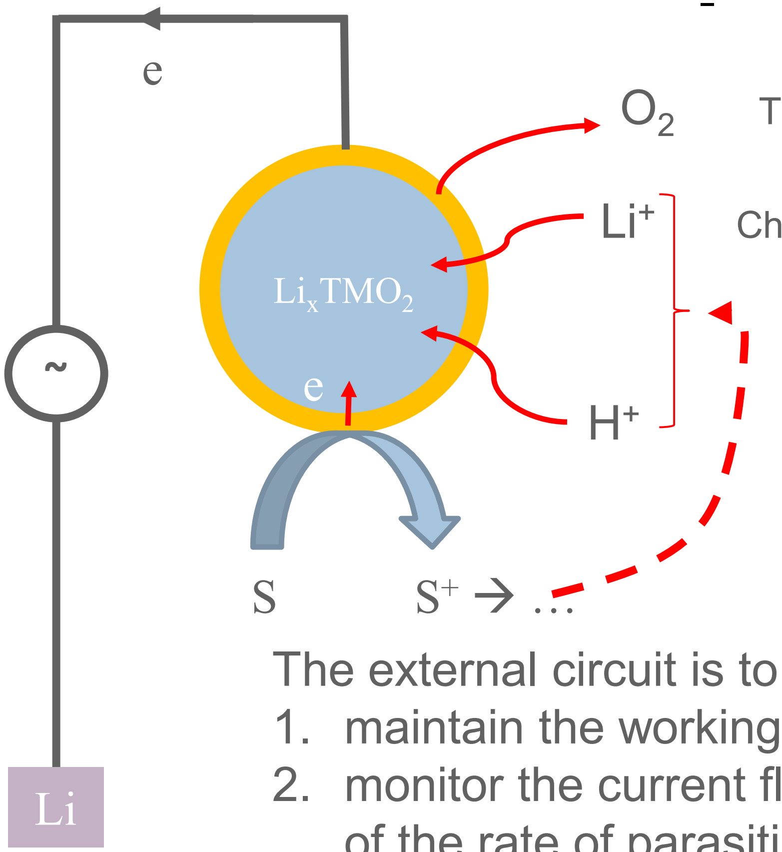
- Corrosion of aluminum current collectors and the oxidation of solvents at a relatively high potential has been widely investigated
  - ➢ An issue for the long-term and stable operation of lithium-ion batteries
- Widely accepted that the naturally generated Al_2O_3 on aluminum foils is not resistive enough against corrosion

<u>Some results related to the corrosion mechanism</u>

1. Decomposition of $LiPF_6$ in the presence of moisture helps to deposit a layer of AlF_3 that physically passivates the aluminum foils
   - ➢ severe corrosion of aluminum foil has been reported in electrolytes using lithium salts with no fluorine
2. High dielectric constant solvents, such as carbonates, prevents the adequate precipitation of ionic compounds such as AlF_3
3. High concentration of free solvent molecules in traditional electrolytes is belived to lift up Al^{3+} from the aluminum foils
   - ➢ superconcentrated electrolytes with no free solvent molecule were reported to prevent the corrosion of aluminum foils

☐ Clearly, a consensus on the corrosion mechanism has not been reached yet

Some typical parasitic reactions involving the cathode (and current collector) and principles for measuring them



Thackeray et. al., *JACS*, 128: 8694 (**2006**).

Chen et. al., *J. Power Source*, 273: 1250 (**2015**).

Chen et. al., *Adv. Ener. Mater.*, 3:729 (**2013**).

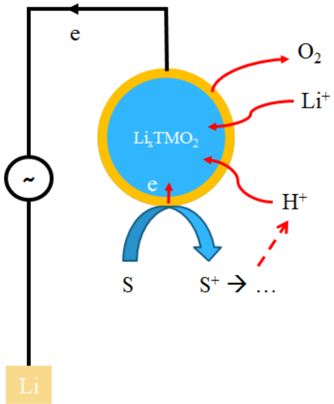
The external circuit is to:

1. maintain the working electrode at a constant SOC
2. monitor the current flow as an quantitative indicator of the rate of parasitic reaction.

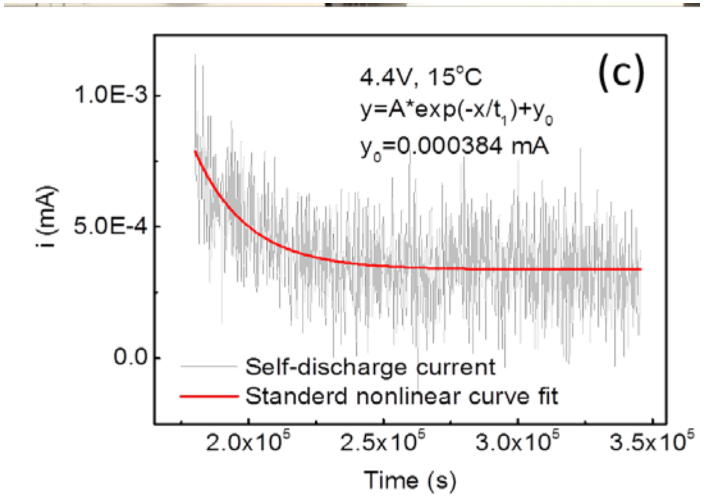
It is of much interest to investigate the parasitic reactions occurring inside lithium-ion batteries. Hence, a high precision electrochemical measurement system was built for this purpose.

Measuring the rate of parasitic reactions

Home-built system for this project (capability to measure to below μA)



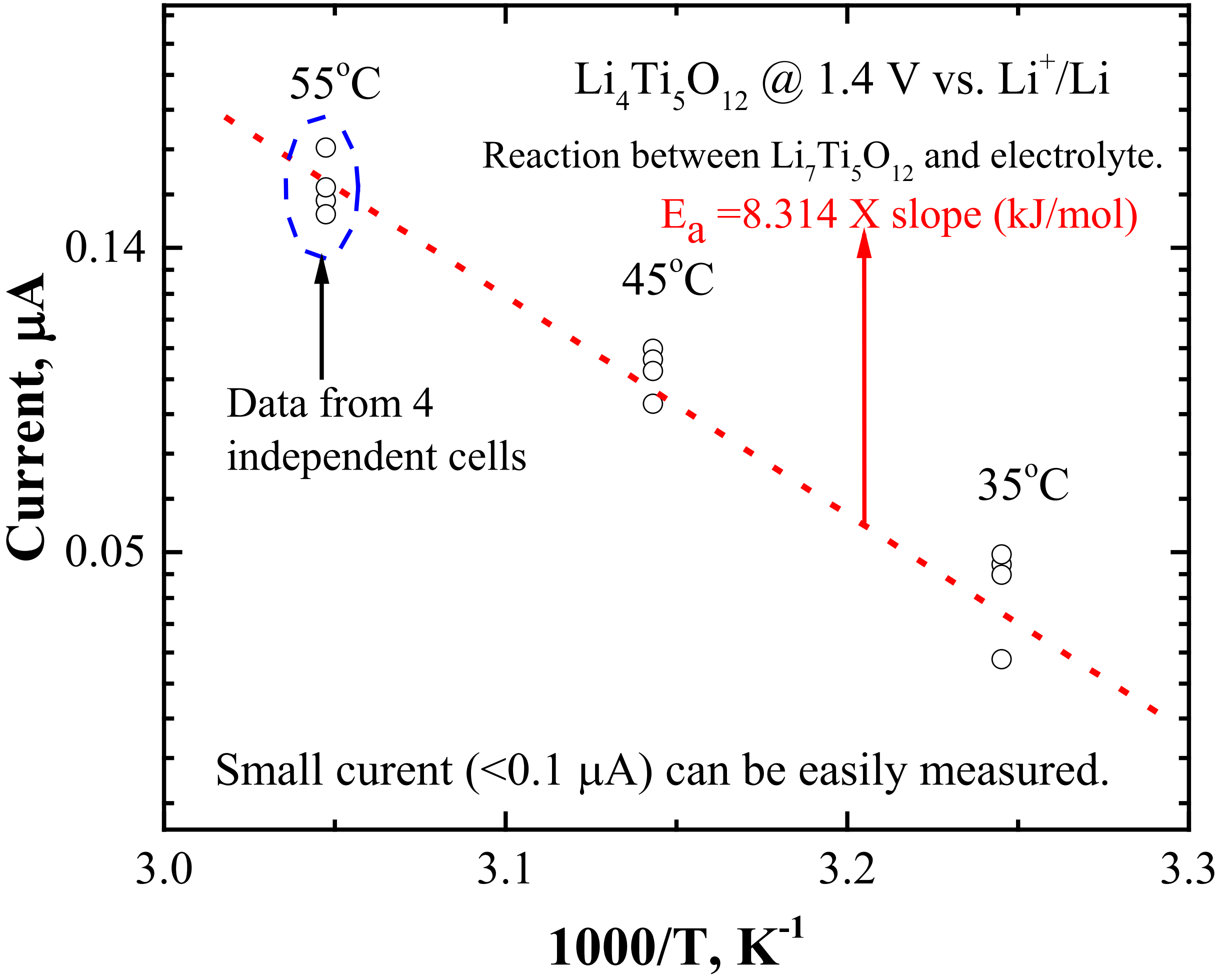
Principle of the new system



Typical raw data from a measurement of $Li_4Ti_5O_{12}$

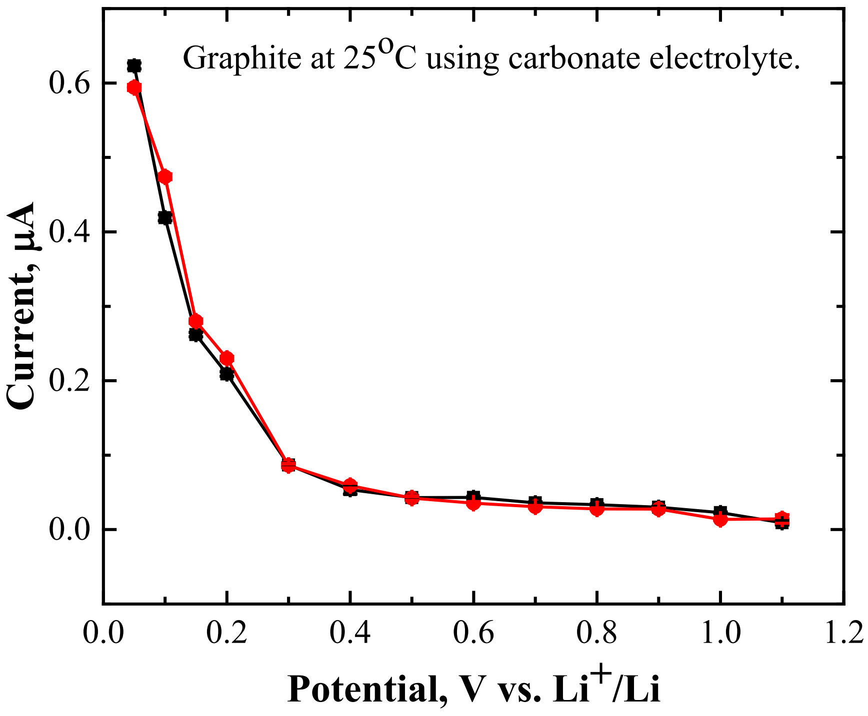
The current measured is a direct indicator of the rate of side reactions between the electrolyte and the working electrode (and current collector).

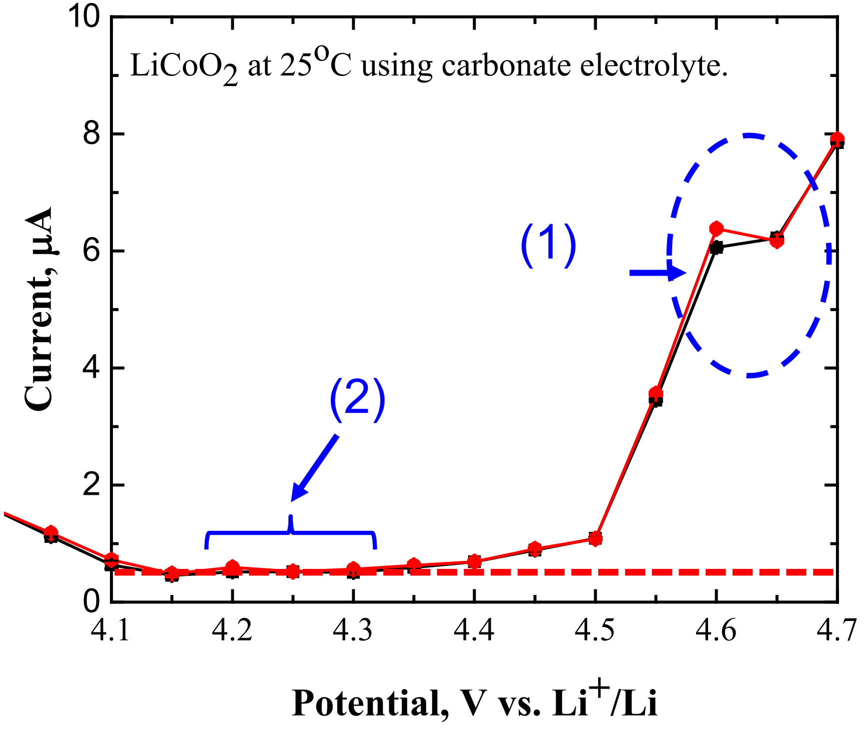
Measuring the rate of parasitic reactions of $Li_4Ti_5O_{12}$



Investigation of known electrodes with the new home-built system

Electrolyte: 1.2 M $LiPF_6$ in EC/EMC (3:7)

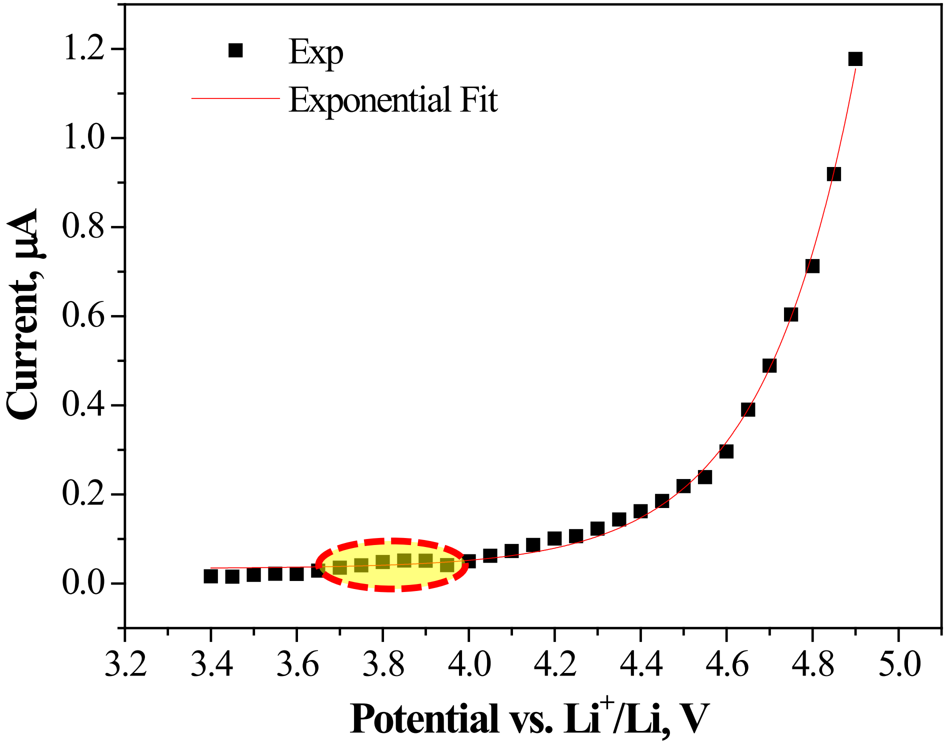




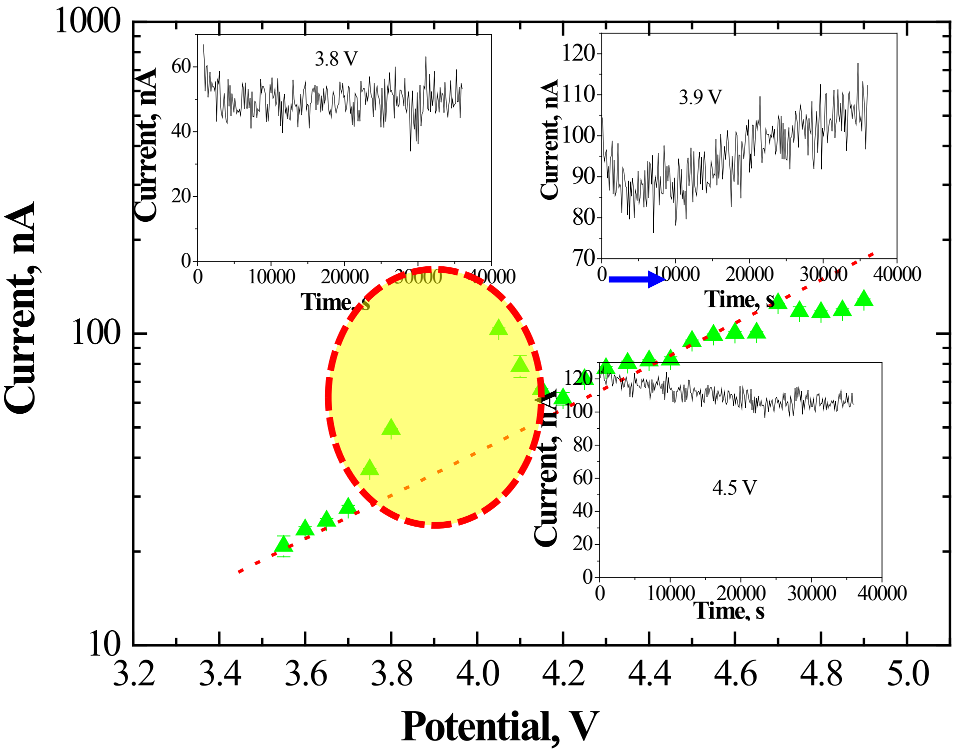
- ➢ The reaction at the anode side agrees roughly with a typical electrochemical reduction reaction.
- ➢ The reaction at the cathode side is complicated: (1) The change of reaction mode at about 4.6 V. (2) A "large" current (0.5 μA) measured in the potential window below 4.3 V.

Investigation of only the Al current collector to find the origin of the initial leakage current (0.5 μA)

Li | $LiPF_6$, EC/EMC | Al/Carbon black

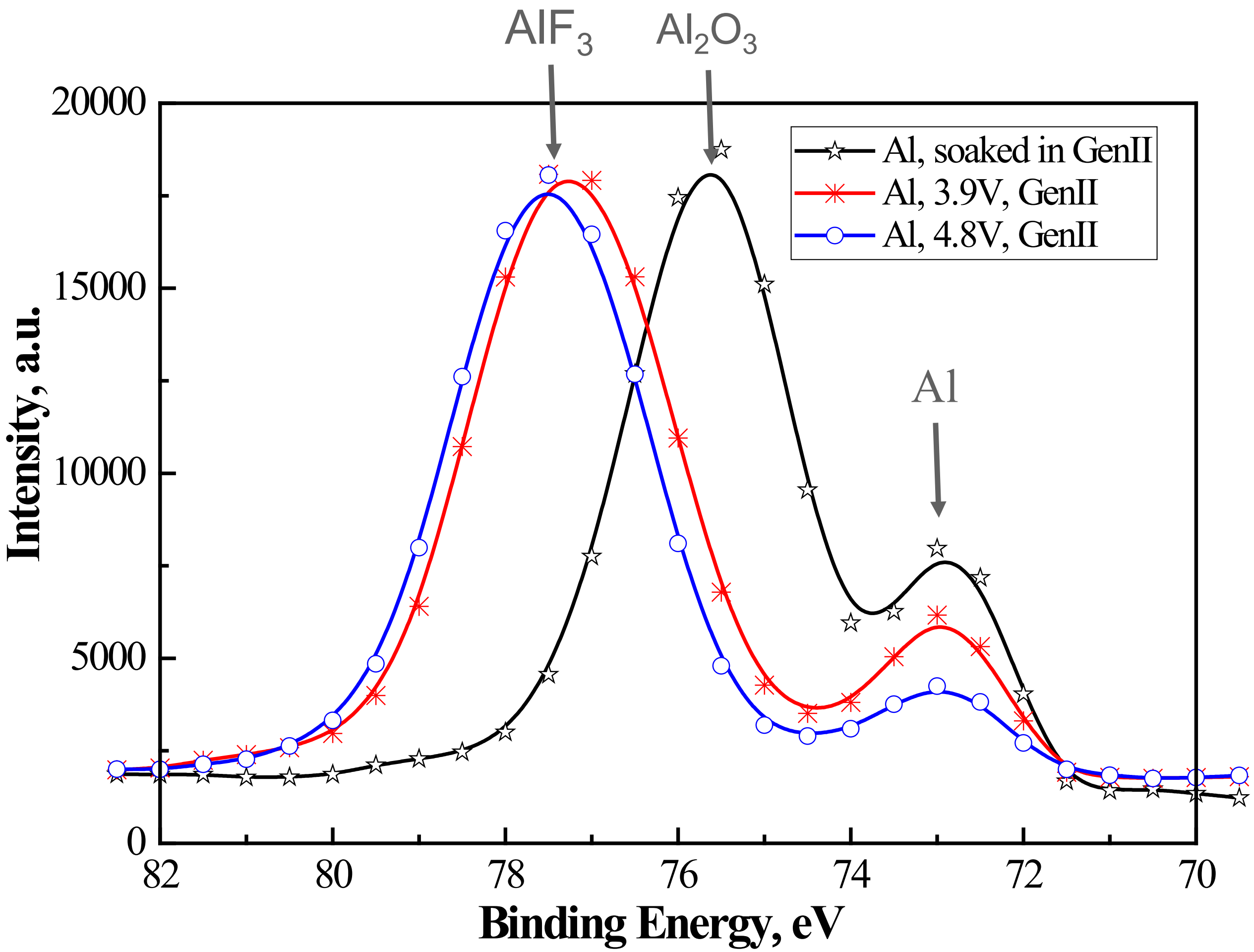


Li | $LiPF_6$, EC/EMC | Al



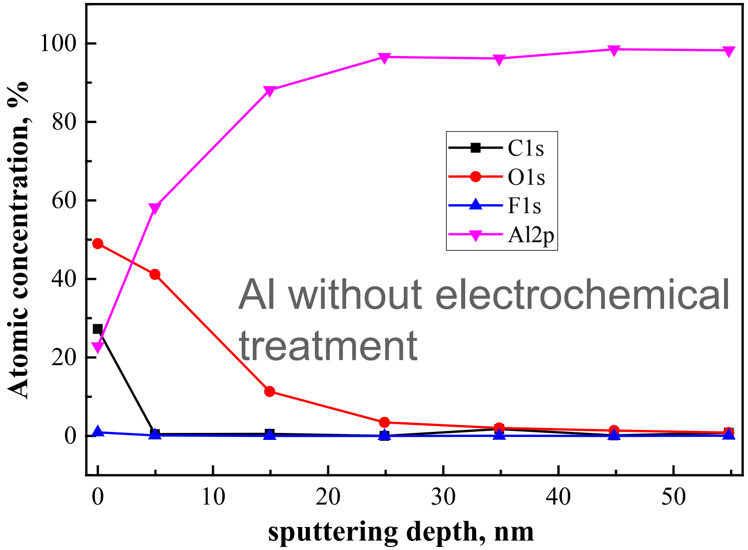
- ➢ Unexpected reaction at a potential as low as 3.8 V.
- ➢ The surface chemistry of Al foil was modified, leading to the increase of the exchange current density at the Al foil (see the increase of current vs. time at 3.9 V).

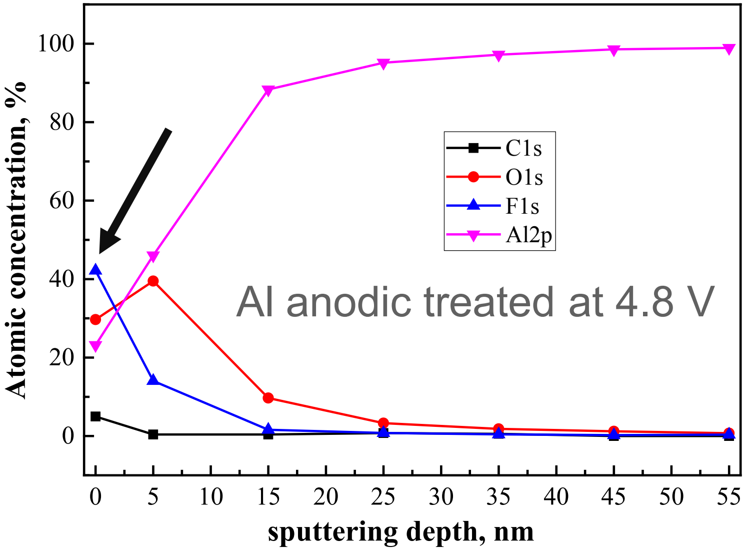
Confirmation of Al surface modification using XPS

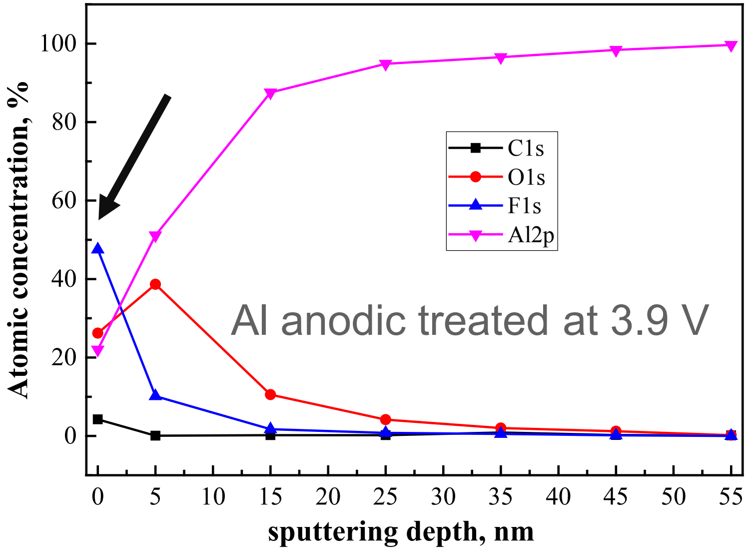


- Soaking Al foil in the electrolyte doesn’t trigger the conversion of Al_2O_3 into AlF_3.
- Conversion of Al_2O_3 to AlF_3 at the potential window ~3.9V.

Depth profile analysis of Al from sputtering and XPS



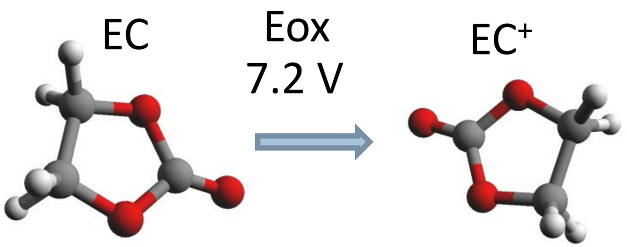




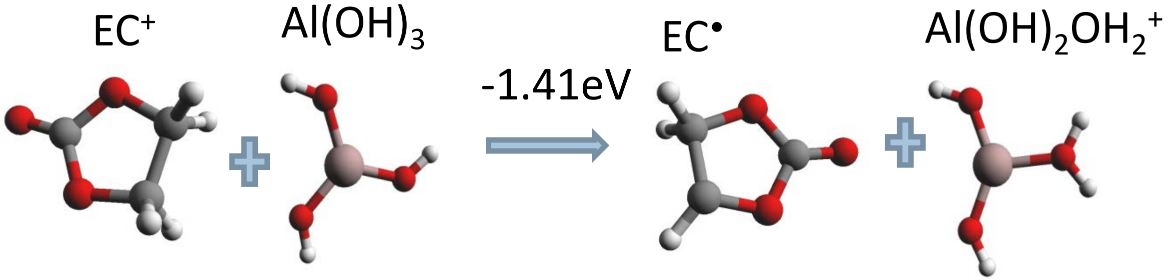
- AlF_3 was not found on the Al foil without electrochemical treatment.
- After electrochemical treatment, a thin layer of AlF_3 (~5 nm) was observed on the surface of Al foil (increase in F1s signal)

Computational studies of EC oxidation on Al using a molecular model

DFT:
B3LYP
PCM



Oxidation of EC and loss of a proton to another EC is favorable with E_{ox} = 5.94 V (Xing and Borodin, PCCP, 2012

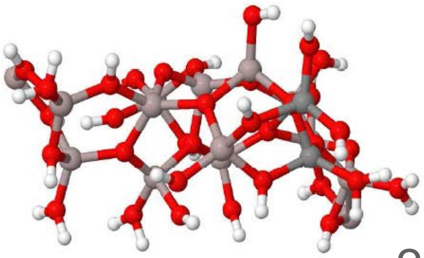


Proton transfer to an OH group coordinated to aluminum can be more favorable

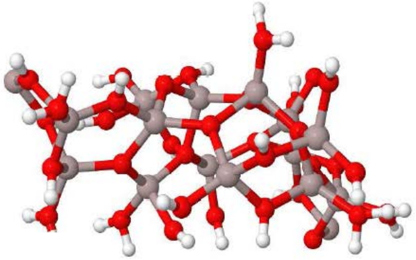
- Our DFT calculations show:
  - Hydroxyl groups coordinated to tetrahedral Al readily accept H$^+$, lowering E_{ox} to 4.75-5.82V depending on Al molecular model
  - Similarly, SH groups coordinated to tetrahedral Al readily accept H$^+$, lowering E_{ox} to 5.21-6.28V.
- Lower oxidation potential in the presence of -OH or -SH groups coordinated to Al indicates feasibility of the proton transfer to alumina in the suggested corrosion mechanism from experiment

Computational studies of EC oxidation on Al usng a surface model

alumina

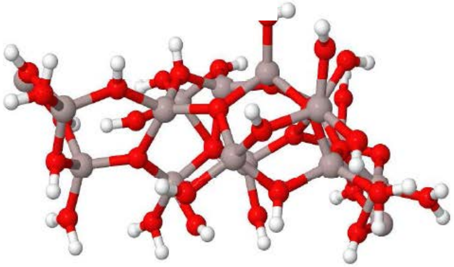


1H



The proton transfer to OH groups (e.g. model 1H) or bridging O (e.g. model 2H) of an amorphous alumina model were considered.

2H

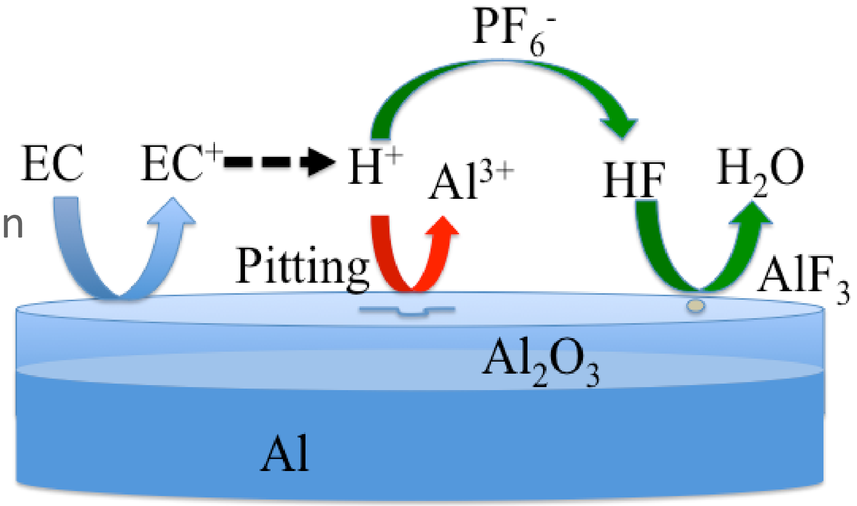


Alumina models: clusters derived from a periodic model of amorphous alumina

- H^+ transfer to alumina results in a lower E_{ox} , about 5.20 – 5.44 V
- These values are consistent with small molecular models of tetrahedral alumina
- Thus, DFT calculations provide support the corrosion mechanism

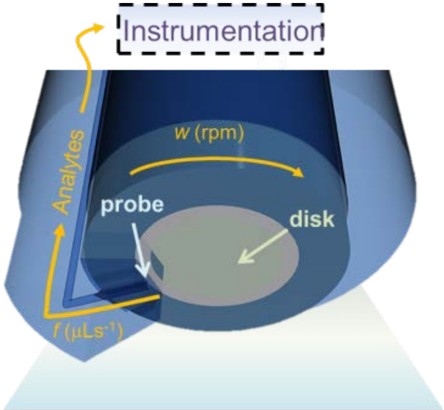
Corrosion of Al: a coupled electrochemical-chemical reaction

- The old wisdom is that trace amounts of moisture in the electrolyte can trigger the decomposition of $LiPF_6$ to generate HF.
- It was demonstrated here that the passivation is triggered during anodic treatment of the aluminum at 3.9 V or higher.
- The corrosion reaction of the aluminum foil is found to be a coupled electrochemical−chemical reaction
- The proton generated from the electrochemical oxidation of electrolyte components leads to thinning of the Al_2O_3 layer
- The proton also promotes the conversion of Al_2O_3 in AlF_3 for more active passivation



Development of a complementary technique for measuring *in situ* dissolution of 3d elements

Concept

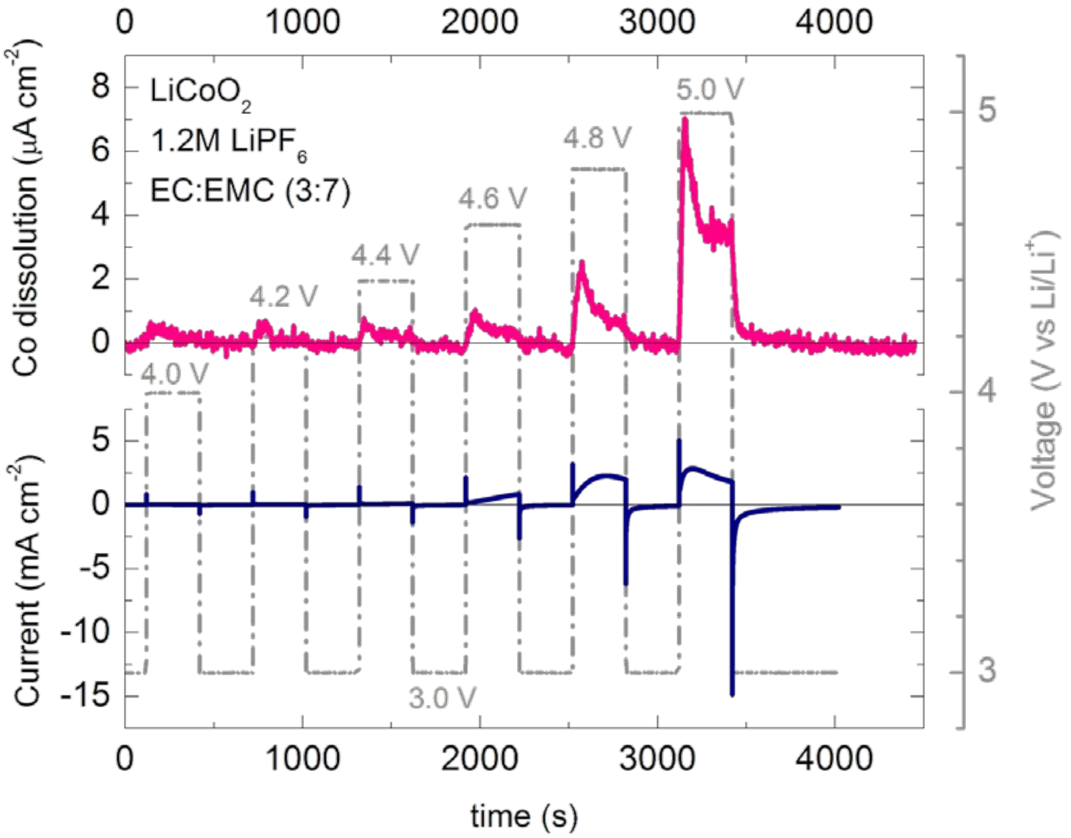


Stationary Probe
Rotating Disk Electrode
(SPRDE)

- ✓ The technique allows for *in situ* metal (Co, Ni, Mn) dissolution measurements, that provides unique 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
- ✓ All of which, in combination with controlled changes in potential/current provides complementary information about failure mechanisms

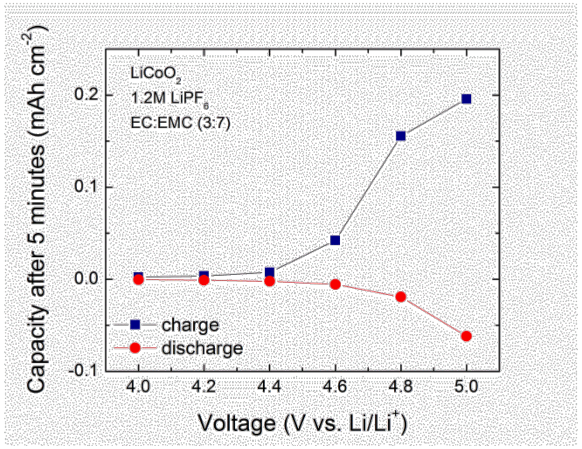
Demonstrating Capability for Monitoring In Situ Cobalt Dissolution from $LiCoO_2$

- Short time potential steps (gray) profile shows simultaneous Co dissolution current (top) and electrochemical current (bottom);
- Early onset of transient dissolution observed at 4.0V;
- Continuous Co dissolution is observed at 4.6V and above;
- Dynamics of charging process easily observed from current vs. time profiles at each hold potential;



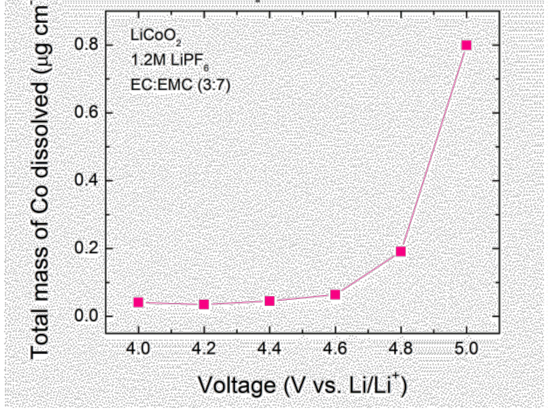
Dynamics of cobalt dissolution from $LiCoO_2$

Deintercalation/intercalation dynamics

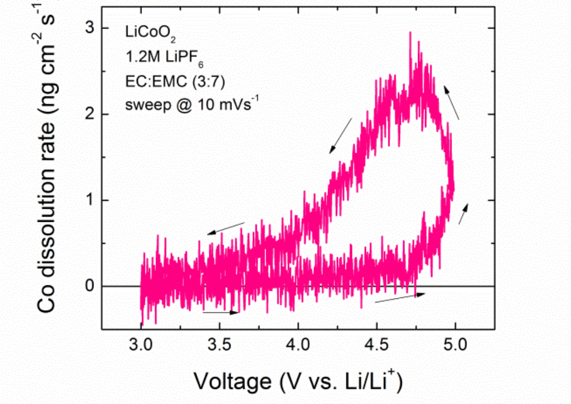


Dissolution dynamics

Step-hold



Potential Sweep



- Capacity is greater at charging than at discharging – related to the kinetics of deintercalation/intercalation processes;
- Dissolution takes place independently from de-intercalation - confirming that is not directly tied to Li^+ removal from the structure but rather some other process;
- However, cobalt ion loss increases exponentially with potential; even during “fast” potential sweep there is dissolution triggered above 4.6V.

Response to last year reviewer's comments

This project is a new start and
no comments from 2016 AMR are available

Collaborations with other institutions and companies

- Jun Liu, PNNL
  - XPS measurements
- Xiangming He, Tsinghua University
  - coatings

Proposed Future Work

- Develop new in-situ diagnostic tools to interrogate solid/liquid surface reaction
- Quantify the impact of voltage, morphology, surface area (porosity) on stability of NMC 6:2:2 for interfacial chemical reactions ($Li_{1-x}TMO_2 + S \rightarrow S^+ +$ …) and understand mechanisms using experiment and theory
- Investigate the impact of surface coatings and doping on Ni-rich cathodes on mitigating the interfacial chemical reactions
- Measure rate of dissolution of Ni, Co and Mn from NMC materials, both 6:2:2 and 8:1:1.
  - use this information for the dissolution of these three components to devise strategies on how to stabilize NMC.

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

Summary

- The corrosion of aluminum foil in nonaqueous electrolytes was revisited using a home-built high-precision electrochemical measurement system.
- The corrosion reaction of the aluminum foil is found to be a coupled electrochemical−chemical reaction
  - the proton generated from the electrochemical oxidation of electrolyte components leads to thinning of the Al_2O_3 layer
  - the proton also promotes the conversion of Al_2O_3 in AlF_3 for more active passivation.
  - DFT calculations are used to derive a mechanism and indicate that there is a lower oxidation potential for the electrolyte near the alumina surface
- In situ dissolution of Co from $LiCoO_2$ at higher potentials was monitored by a new SPRDE-ICP-MS setup.