Electrochemistry Discovery Laboratory:

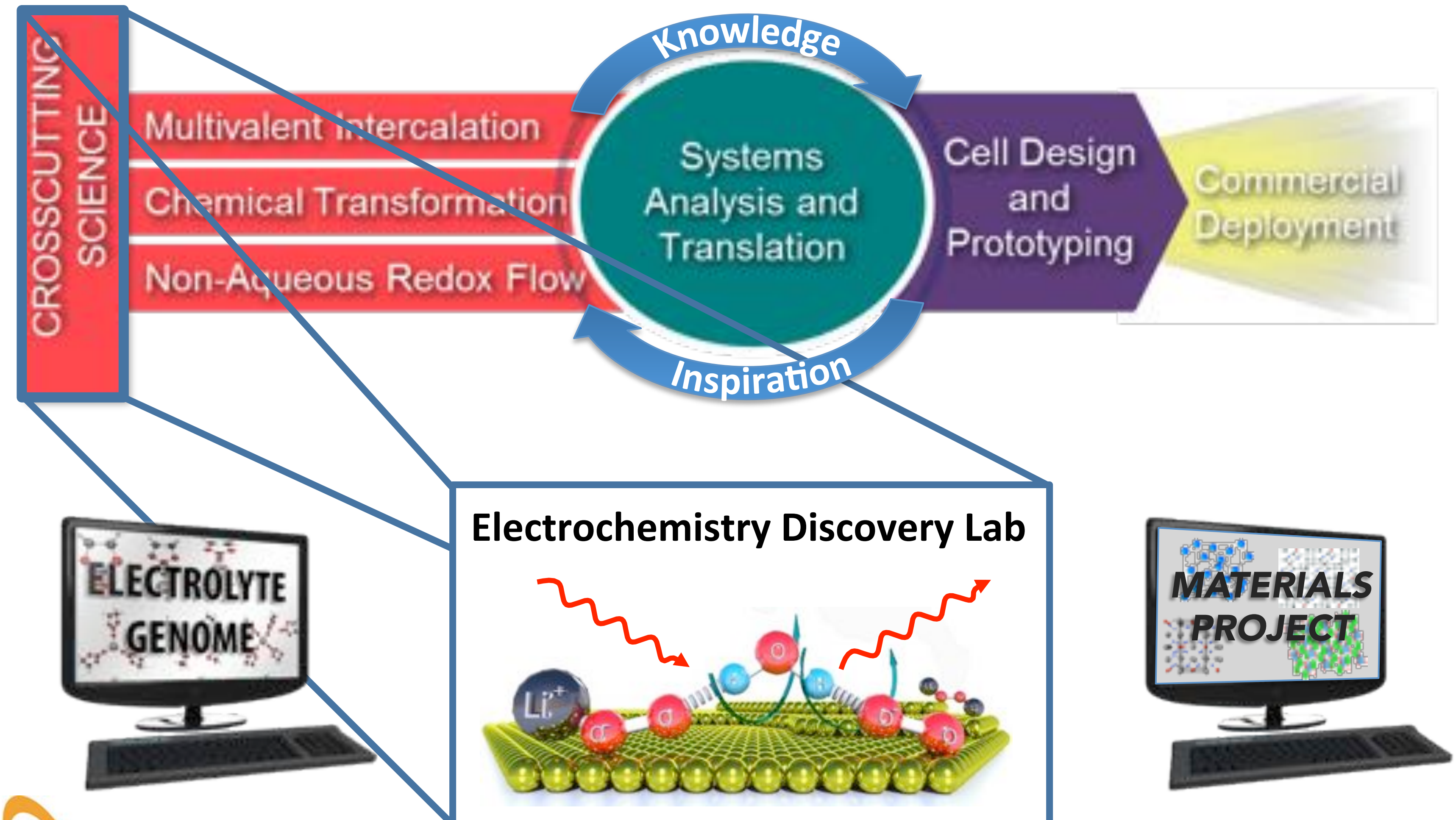
Exploring Energy Conversion and Storage at Atomic and Molecular Levels

Justin Connell

PSE Open Mic: JCESR Special Series
August 27, 2015

The Electrochemistry Discovery Laboratory

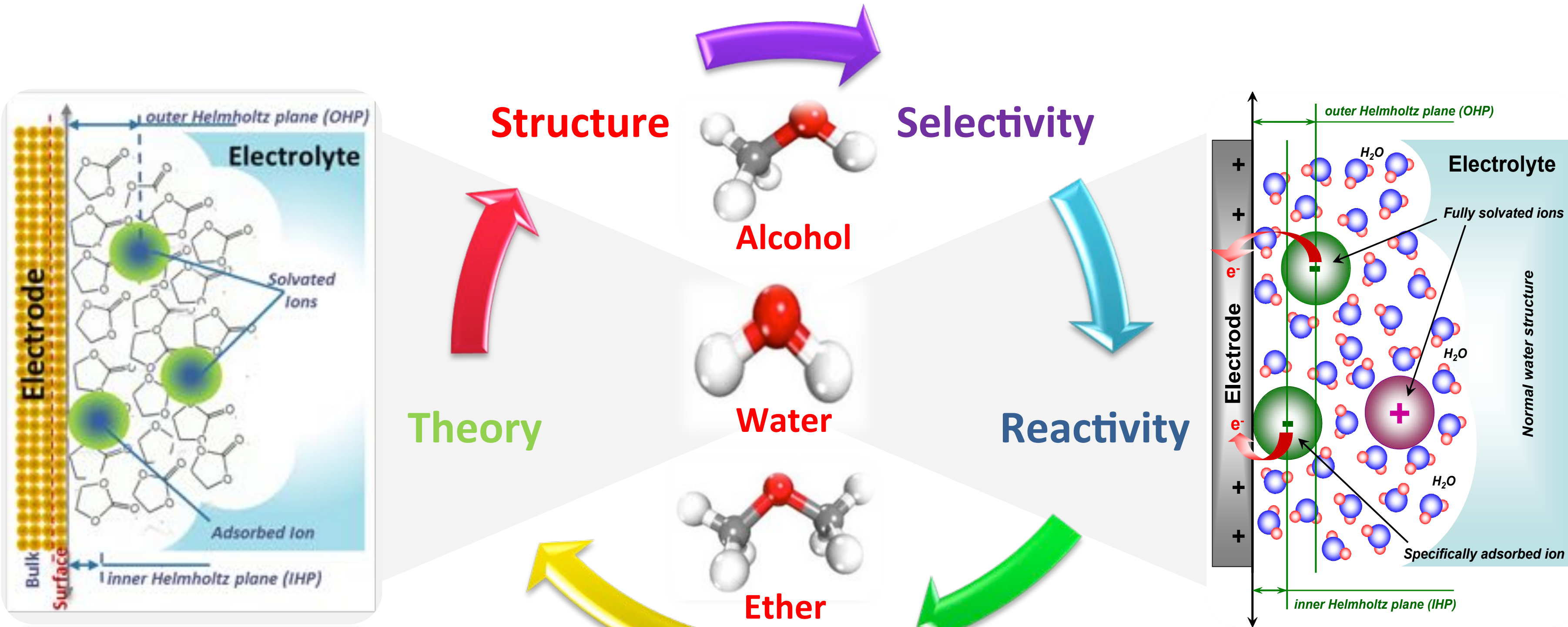
A focal point for fundamental (divergent) and applied (convergent) collaborative research within JCESR



EDL Grand Challenge

Understanding Stability, Reactivity and Selectivity of Beyond Li-Ion Electrochemistry

ATOMIC-MOLECULAR LEVELS | STRUCTURE-FUNCTION RELATIONSHIPS | APPLIED RESEARCH

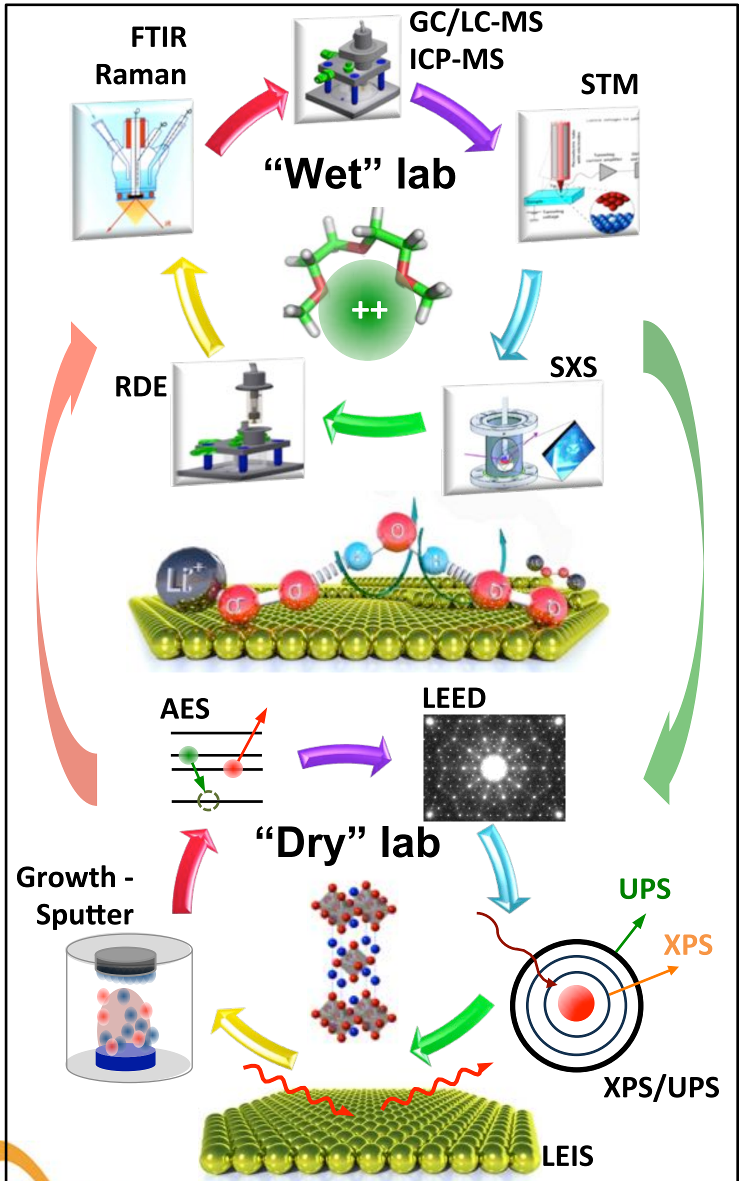


Organic electrolytes **Aqueous electrolytes**

Building a bridge between water-based and organic-based interfaces

JCESR

From Aspiration to Realization



EDL Mission

Understanding functional properties of new materials and electrochemical interfaces at atomic and molecular levels for beyond Li-ion energy storage applications

What is the EDL?

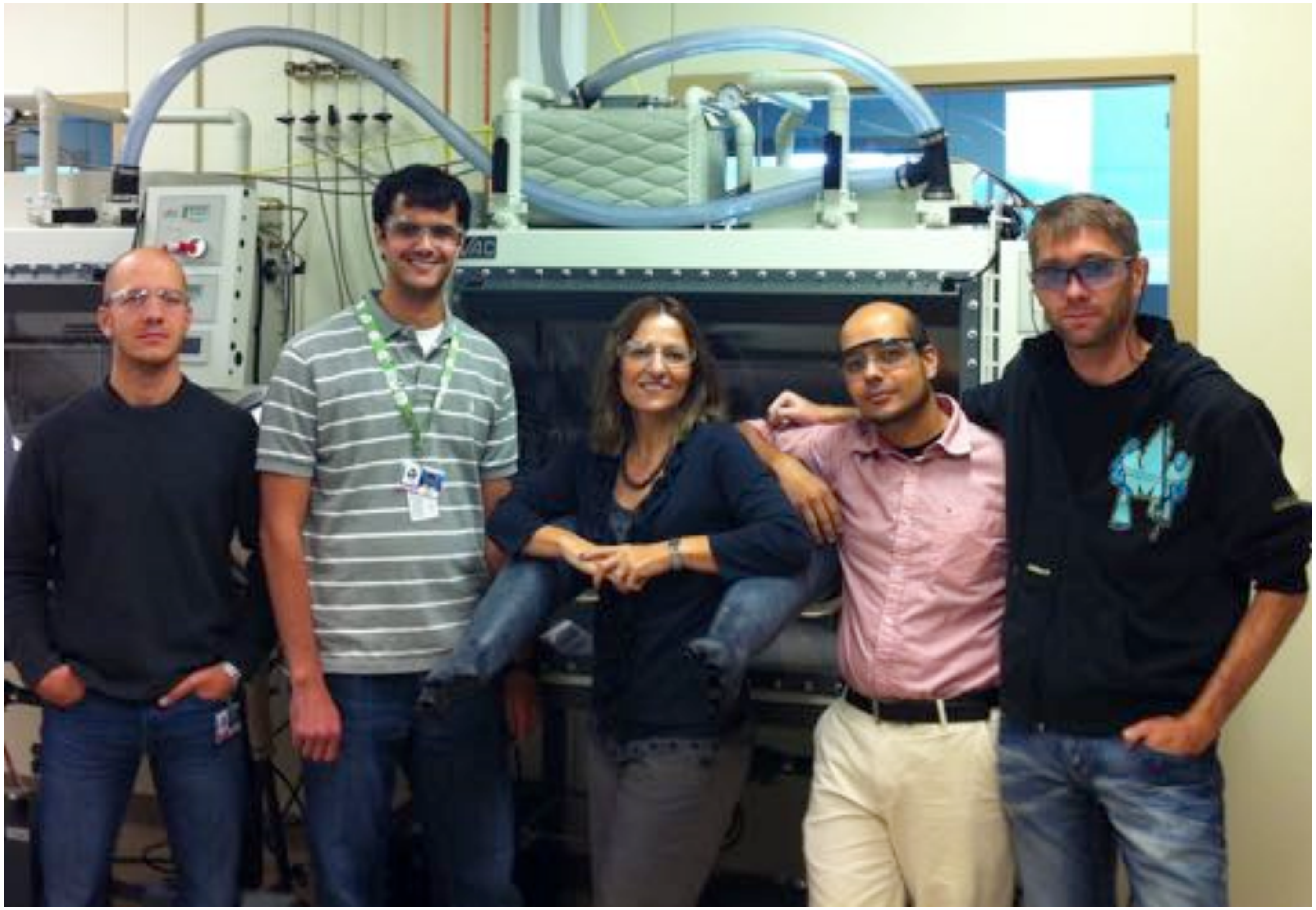
JCESR facility with two primary components:

- **"Wet" Electrochemical Lab** with electrolyte synthesis and purification capabilities, analytical characterization tools, in situ vibrational spectroscopy, and electrochemical testing stations
- **"Dry" Electrochemical Lab** with multiple ultra-high vacuum surface characterization tools and thin film deposition capabilities

Why is the EDL Unique?

- One-of-a-kind combination of *ex situ* and *in situ* experimental tools, in collaboration with computation, for translating fundamental insight into prototypes that achieve JCESR's cost and performance goals
- Focal point for collaboration between the various partner institutions of JCESR

Who we are



Left to right: Bostjan Genorio, Justin Connell, Sanja Tepavcevic, Pietro Papa Lopes, Dusan Strmcnik

Wet Electrochemical Lab

Design:

- Three core functions:
  - **Synthesis and purification** to develop impurity-free electrolytes with sub-ppm H_2O concentration
  - **Electrochemical testing and benchmarking** of electrolytes synthesized in the EDL and elsewhere
  - ***In situ* vibrational spectroscopy** to monitor electrolyte decomposition, as well as intermediate and product formation during electrochemical cycling

Wet Electrochemical Lab

Capabilities:

- **(Electro)chemical Characterization**
  - Gas and Liquid Chromatography
  - GC-Triple Quadrupole Mass Spectrometer
  - GC/LC Time of Flight Mass Spectrometer

Wet Electrochemical Lab

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- **(Electro)chemical Characterization**
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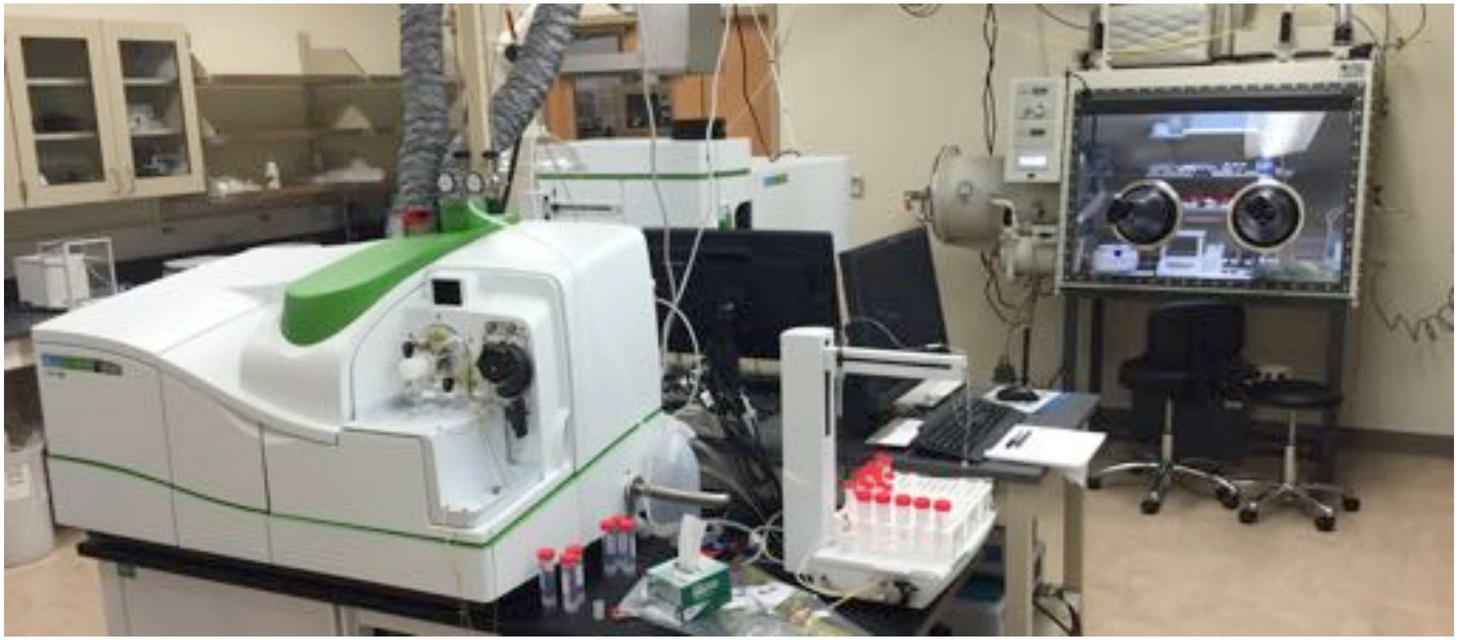
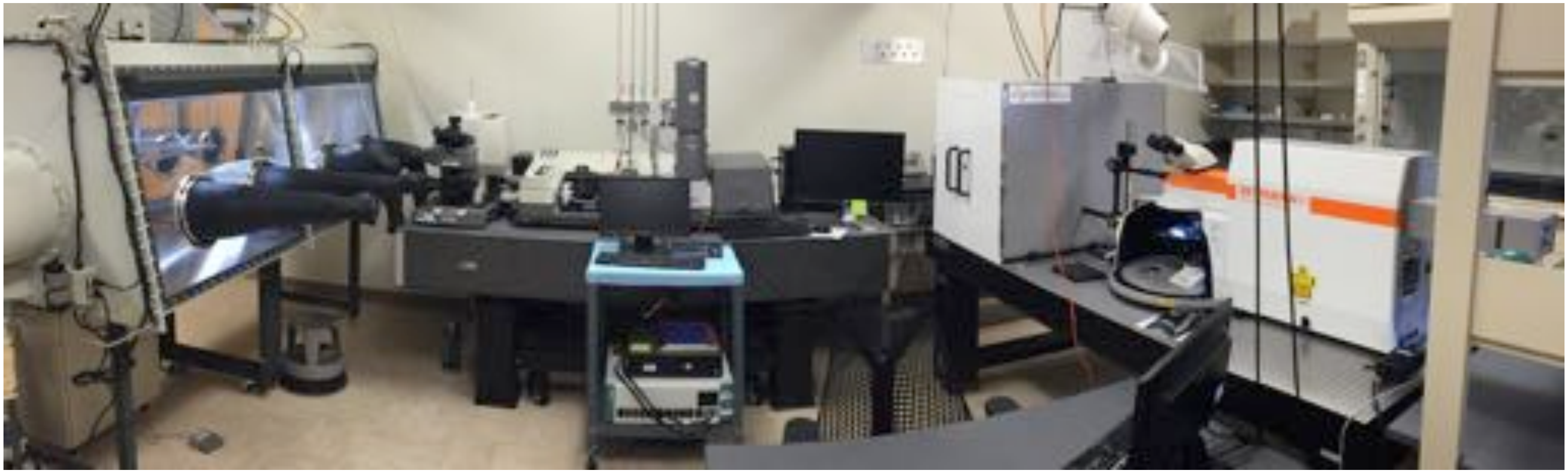
  - GC/LC Time of Flight Mass Spectrometer
  - Inductively Coupled Plasma Mass Spectrometry/Optical Emission Spectroscopy
  - Electrochemical Stations with Rotating (Ring) Disk Electrode Setup



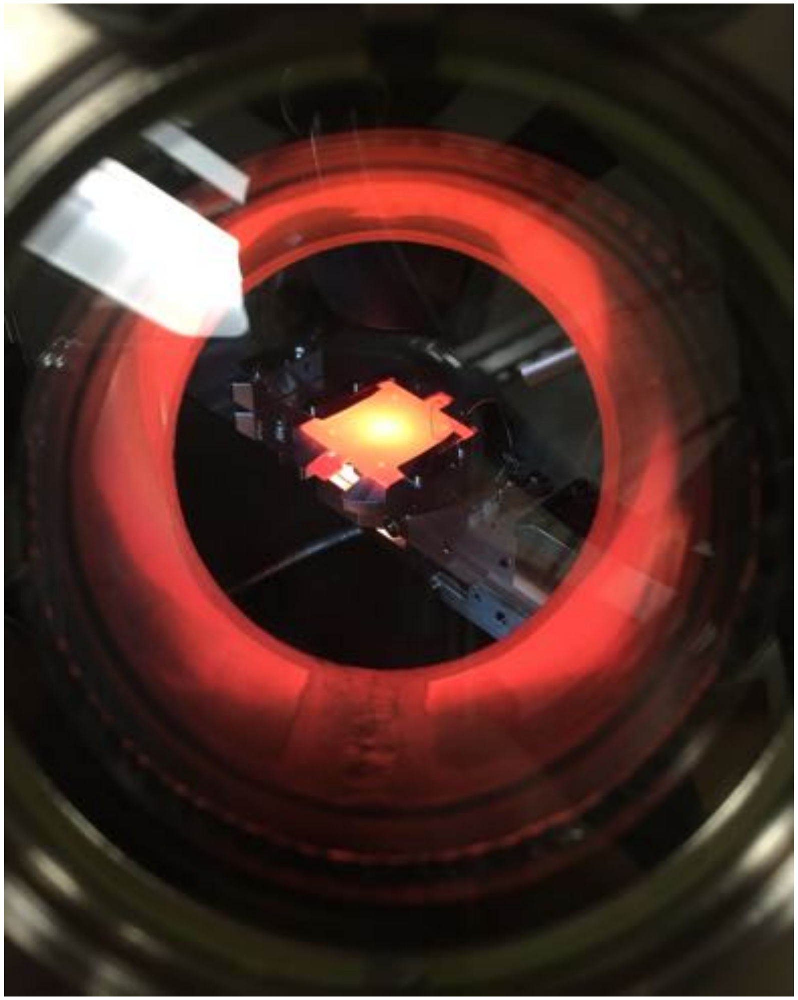
Wet Electrochemical Lab

Capabilities:

- **(Electro)chemical Characterization**
  - Gas and Liquid Chromatography
  - GC-Triple Quadrupole Mass Spectrometer
  - GC/LC Time of Flight Mass Spectrometer
  - Inductively Coupled Plasma Mass Spectrometry/Optical Emission Spectroscopy
  - Electrochemical Stations with Rotating (Ring) Disk Electrode Setup
- ***In Situ* Vibrational Spectroscopy:**
  - Confocal Raman Spectroscopy
  - Fourier Transform Infrared Spectroscopy (both in glove box and in ambient)



Dry Electrochemical Lab

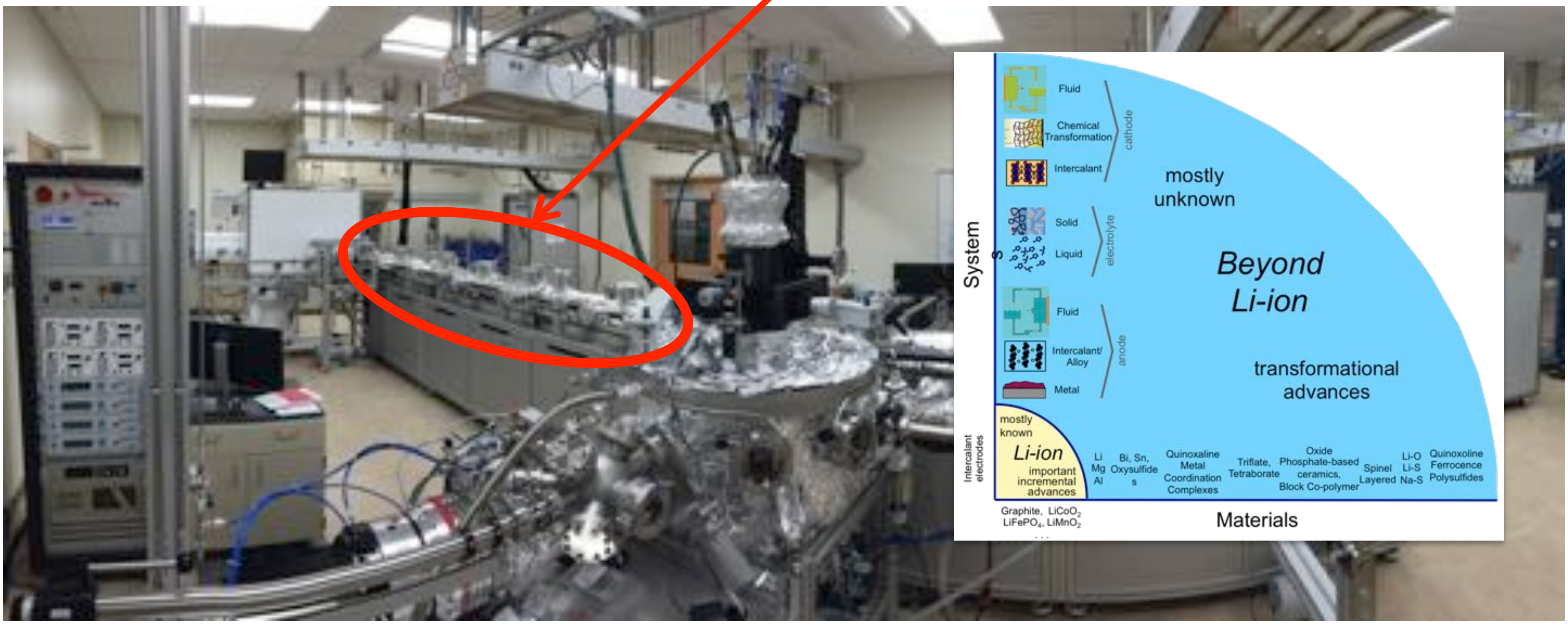


Design:

- Multi-module integrated UHV system to enable the synthesis of well-characterized model thin film and bulk electrode surfaces
- All modules connected by central linear transfer system to enable transfer between modules without exposing samples to ambient
- 3 modules:
  - **Synthesis Module** – deposit thin film electrode samples (metals, metal oxides and complex metal oxides)
  - **Characterization Module** – characterize electrode composition/structure from first monolayer to "bulk"
  - **Sample Inlet/Preparation Module** – direct outlet to glove box to directly input samples from UHV into electrochemical environments

Multi-Module UHV System

Opportunity for future expansion of capabilities



Which new capabilities will be developed depend partially on inputs from Materials Project and Electrolyte Genome

Accessing the EDL

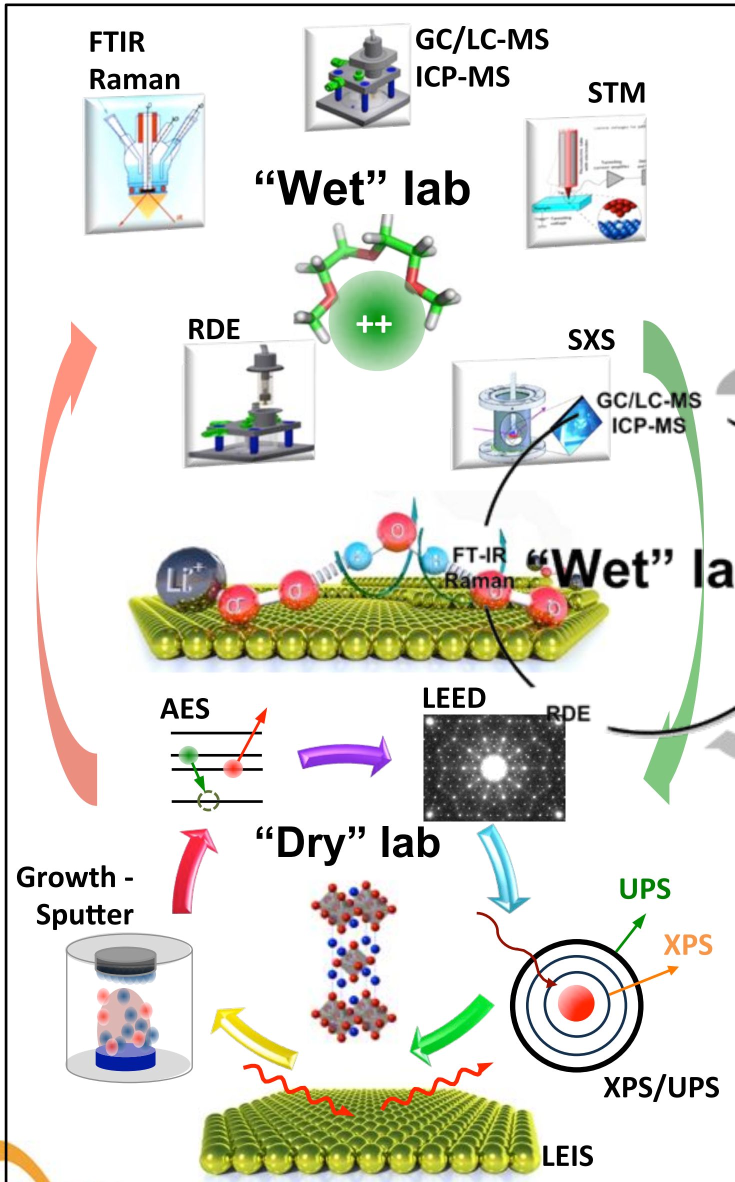
- Develop project scope and schedule
- Visit EDL website and fill out proposal template

  www.jcesr.org/EDL
- Submit proposal template to JCESR-EDL@anl.gov
- Proposal evaluated by EDL staff within 2 weeks
- If accepted, develop visit timeline with EDL staff

Visiting the EDL

- All visitors receive Argonne safety training through JHQ system
- First Tuesday orientation at ANL (cybersecurity, ANL-specific training, etc…)
- On-the-job training with EDL staff
  - Lab-specific orientation
  - Basic operating procedures
  - Demonstrate proficiency with requested instrumentation
- Independent work begins

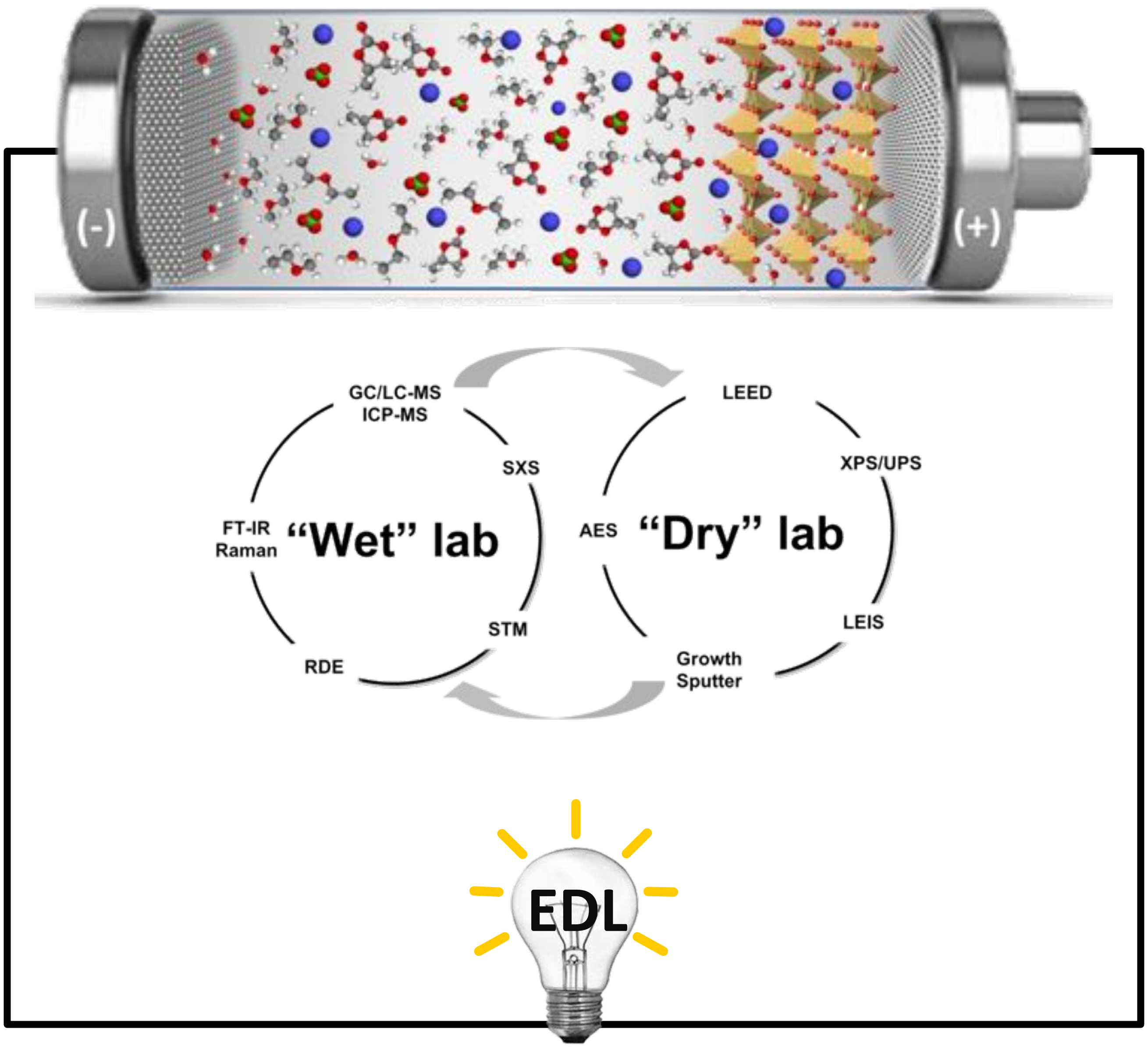
Putting it all Together



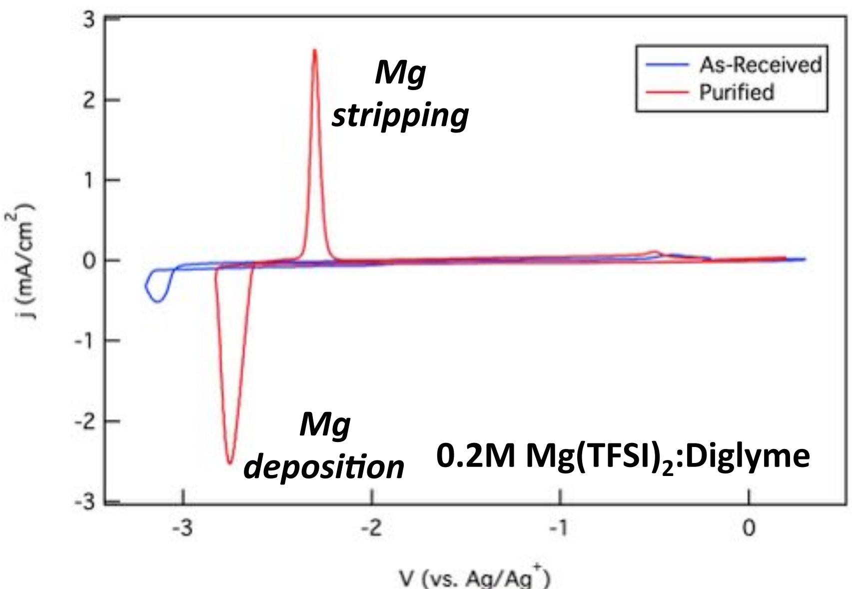
- Developing structure-reactivity-stability relationships is critical to successfully designing beyond Li-ion technologies
- There is much to learn about impurities and defects in organic electrochemistry
- The EDL is positioned to develop this knowledge using the wide array of capabilities that have been developed

JCESR

Control Impurity Content (H_2O; ROH)



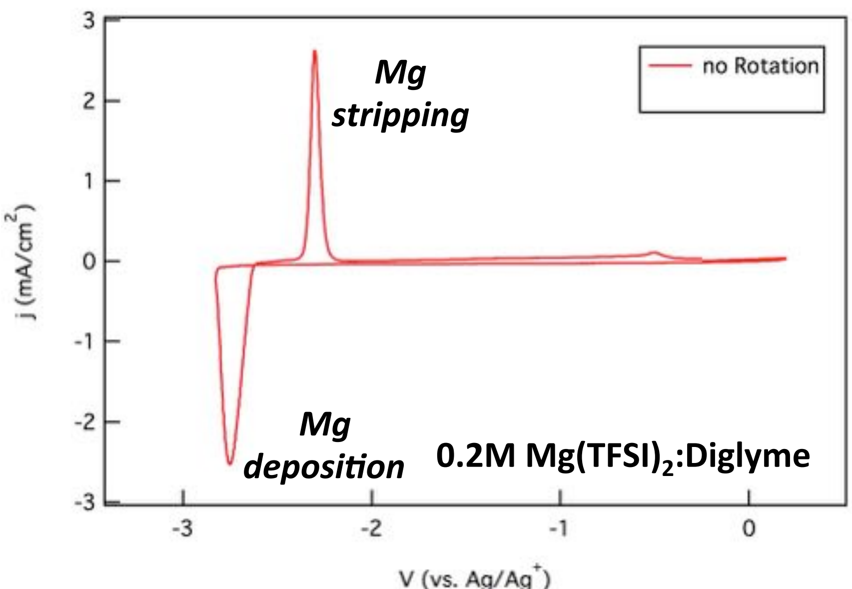
Controlling Impurity Content



- Developing ultrapure electrolytes
  - Solvents with <0.2 *parts-per-million* H_2O and <10 *parts-per-billion* of trace metals
  - Utilize Wet Lab analytical capabilities identify any residual organic species
- Impact on Mg deposition at the anode
  - Reversible deposition/stripping is key to battery performance
  - Purified solvent enables reversible deposition and stripping

N. Hahn, B. Genorio, J. Connell, D. Strmcnik

Controlling Impurity Content



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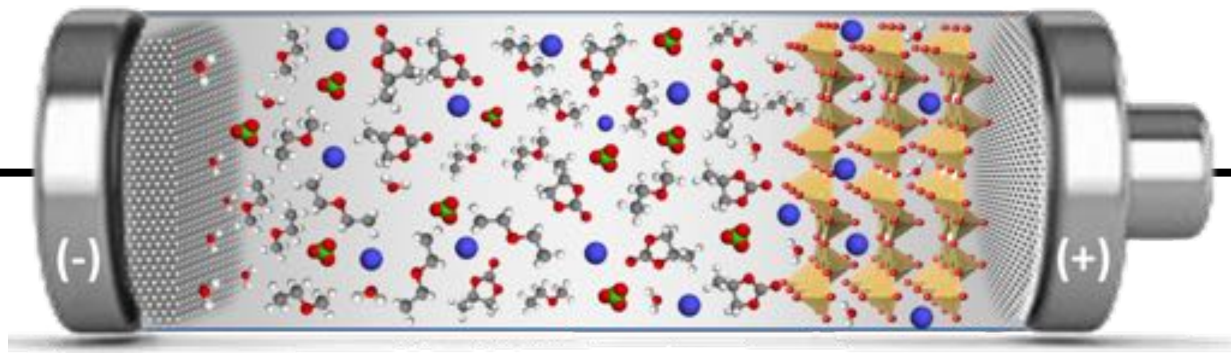
  - Utilize Wet Lab analytical capabilities to identify any residual organic species
- Impact on Mg deposition at the anode
  - Reversible deposition/stripping is key to battery performance
  - Purified solvent enables reversible deposition and stripping
  - Salt is a major source of impurities as well
  - Understanding deposition/stripping is critical for all metal anode systems for beyond Li-ion electrochemistry (Ca^{2+}, Zn^{2+}, Li^+, etc…)

N. Hahn, B. Genorio, J. Connell, D. Strmcnik



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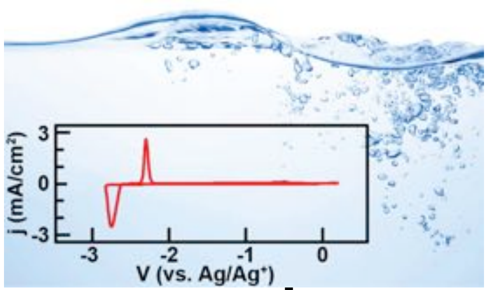
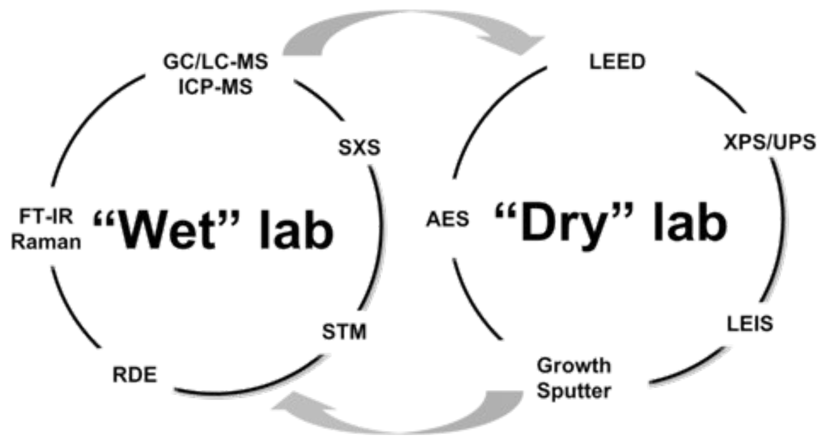


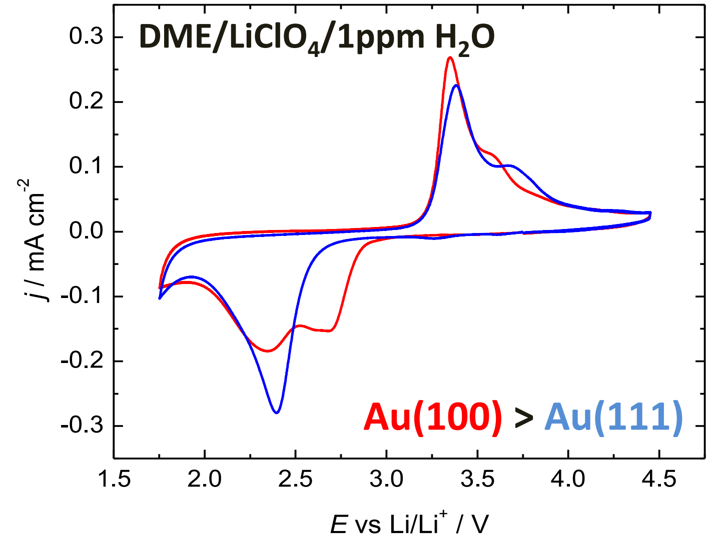
Chemical Transformations

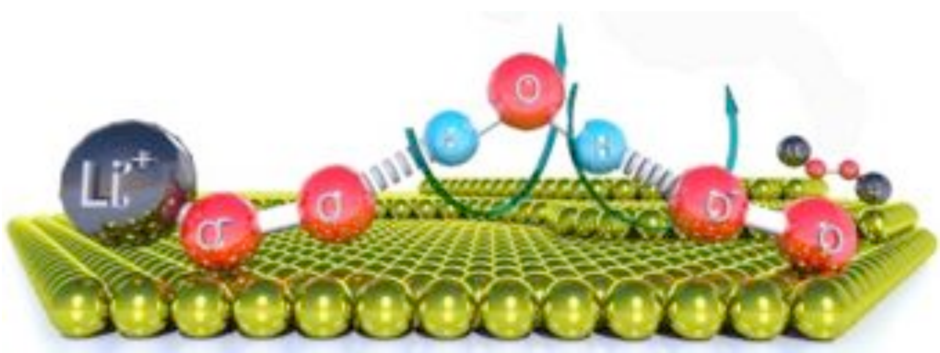


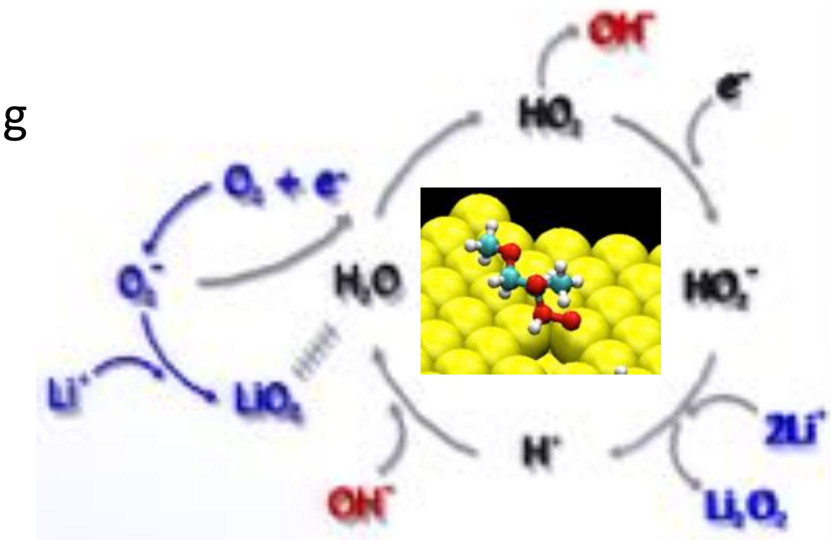
Understand Role of Impurities (H_2O; O_2^{-}; HO_2^{-})

Understanding Role of Impurities

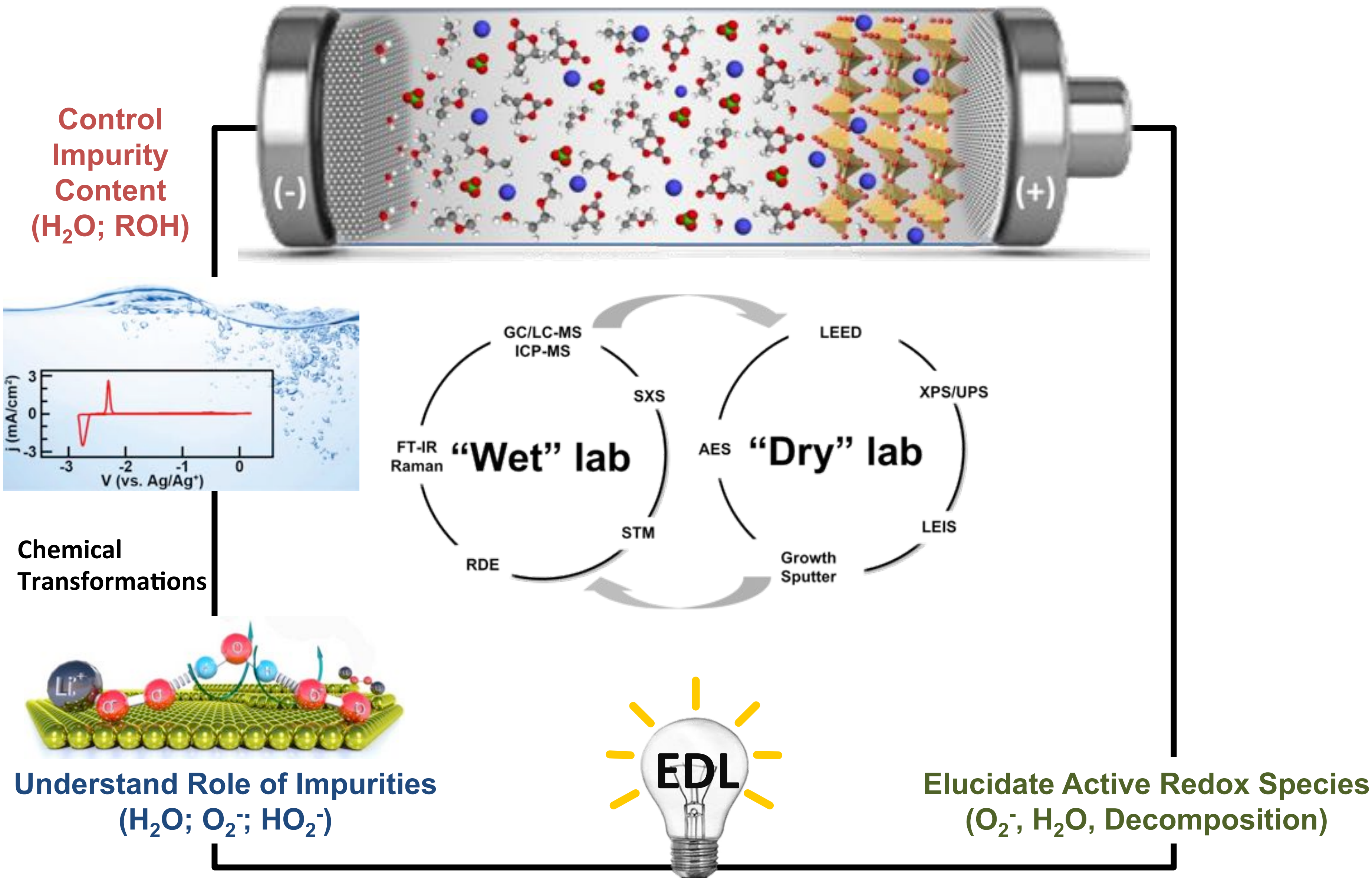
- Li-O_2 is a dramatic example of the impact of impurities on electrochemical performance
  - First example of structure sensitivity in organic electrochemical system
  - Even 1 ppm H_2O acts as both a promoter and a catalyst in this system
  - Combination of experiment and simulations leads to mechanistic insight
- Li-O_2 is also an example of the power of experiment and technoeconomic modeling







K. Harrison, C. Diesendruck, R. Assary, J. Jirkovsky, *et al. Under Review*

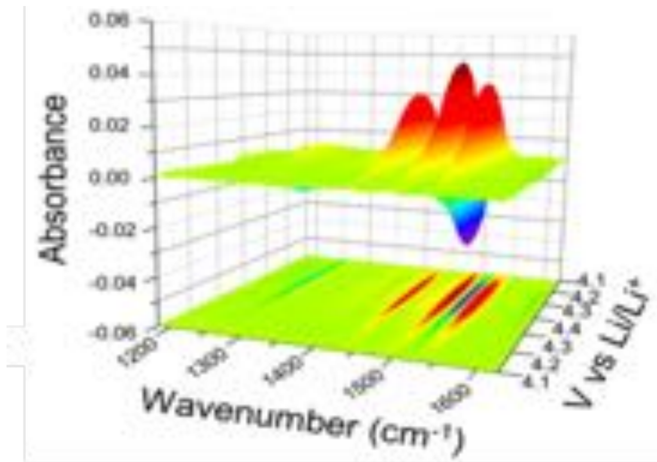

(-)
(+)
Control Impurity Content (H_2O; ROH)
j (mA/cm²)
3
0
-3
-3
-2
-1
0
V (vs. Ag/Ag⁺)
Chemical Transformations
Li⁺
GC/LC-MS
ICP-MS
SXS
FT-IR
Raman
"Wet" lab
RDE
STM
LEED
XPS/UPS
AES
"Dry" lab
LEIS
Growth
Sputter
EDL
Understand Role of Impurities
(H_2O; O_2^-; HO_2^-)
Elucidate Active Redox Species
(O_2^-, H_2O, Decomposition)

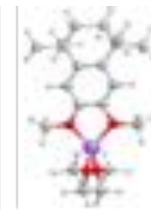
JCESR

Elucidating Redox-Active Species

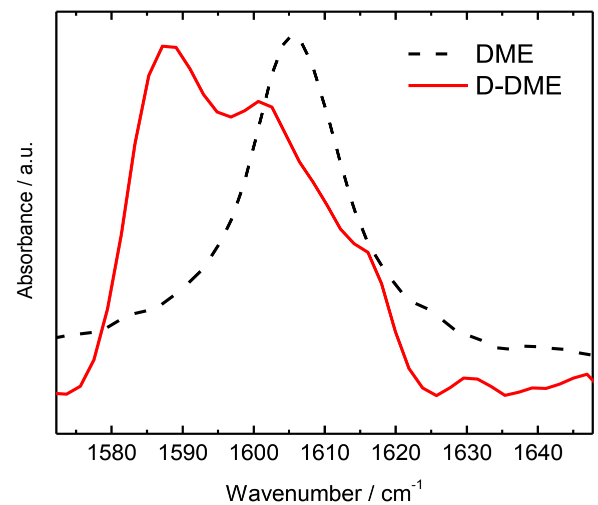
- Lifetime of redox-active molecules for flow batteries
  - *In situ* FTIR shows dynamic changes in redox active molecules
  - DFT provides mechanism of charging

Charge/Discharge of ANL RS-21

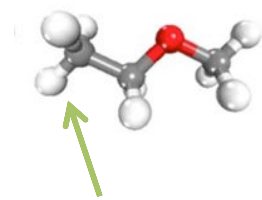




- Decomposition of electrolyte
  - FTIR of isotopically labeled dimethoxyethane (DME) identifies decomposition mechanism
  - Wet Lab analytical capabilities enable further understanding of electrolyte decomposition

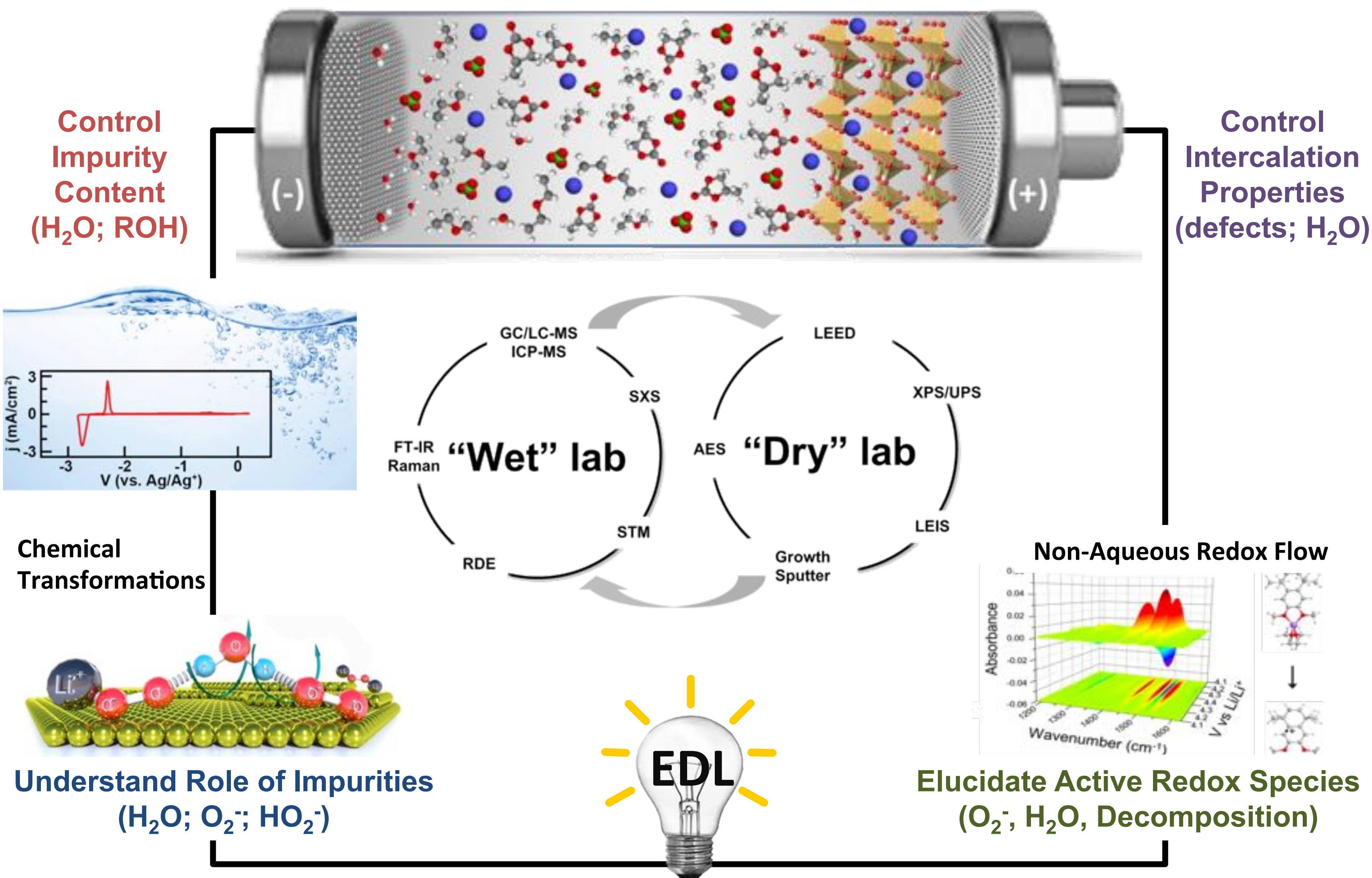


FTIR of DME/$TBAPF_6$ on Au



Nucleophilic attack of α C-H bond by O_2^-

EDL + E. Carino, F. Brushett, J. Moore, K. Zavadil, L. Curtiss



Control Impurity Content (H2O; ROH)
(-)
(+)
Control Intercalation Properties (defects; H2O)
j (mA/cm²)
3
0
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-2
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V (vs. Ag/Ag⁺)
GC/LC-MS
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SXS
FT-IR
Raman
"Wet" lab
STM
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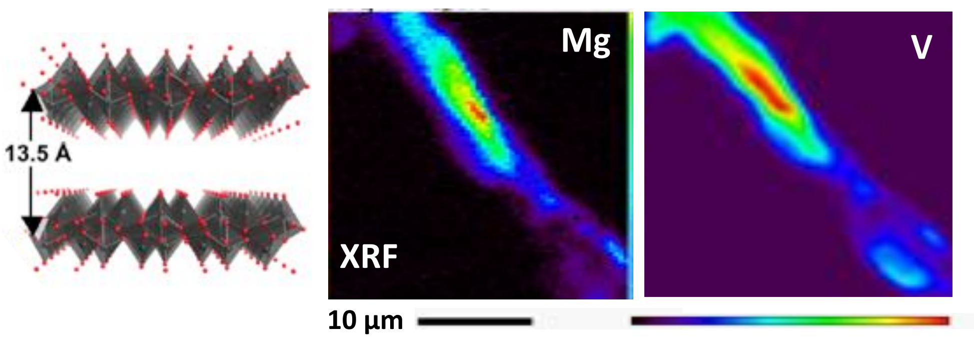
LEED
XPS/UPS
AES
"Dry" lab
LEIS
Growth
Sputter
Chemical Transformations
Li⁺
Non-Aqueous Redox Flow
Absorbance
Wavenumber (cm⁻¹)
V vs Li/Li⁺
EDL
Understand Role of Impurities (H2O; O2⁻; HO2⁻)
Elucidate Active Redox Species (O2⁻, H2O, Decomposition)

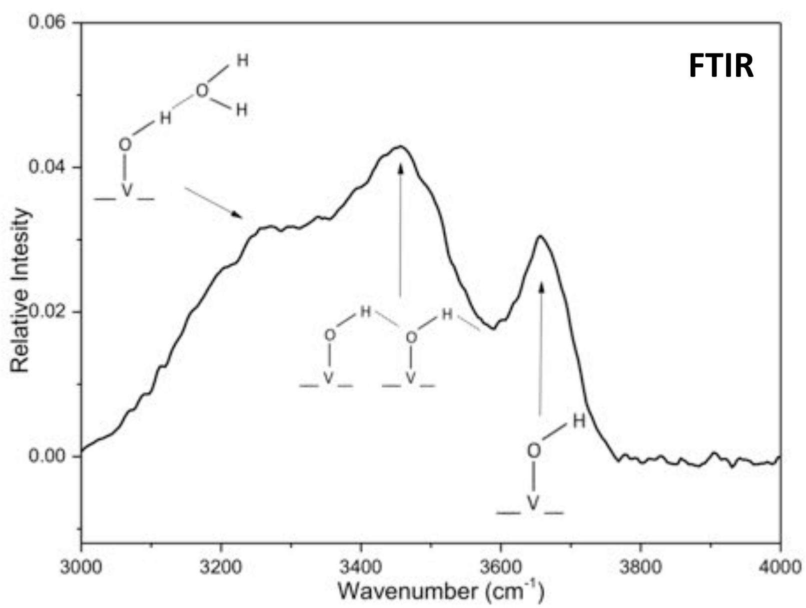
JCESR

Controlling Intercalation Properties

Intercalation vs. Adsorption



Adsorbed vs. Structural OH

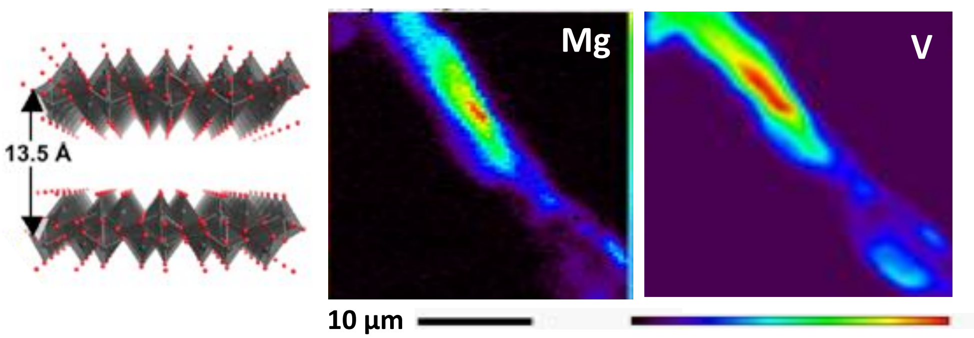


- Cathode materials are extremely sensitive to impurities and defects
  - Amorphous, bilayer V_2O_5 reversibly intercalates Mg ions, crystalline, orthorhombic V_2O_5 does not
  - Intercalation is due to structural water (OH) bonded in between the layers

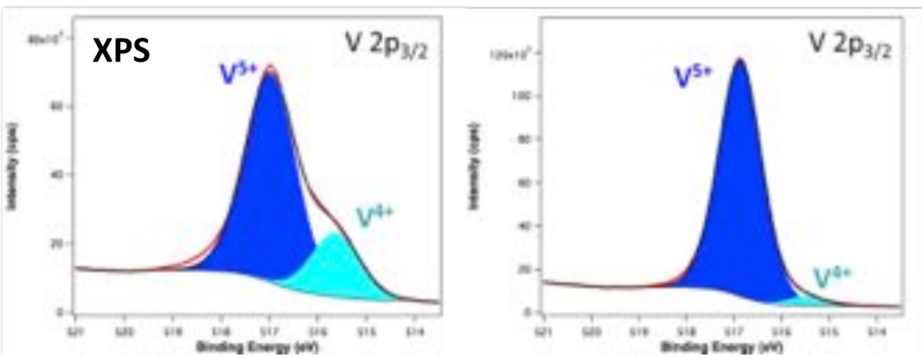
Tepavcevic *et al. ACS Nano* (2015)

Controlling Intercalation Properties

Intercalation vs. Adsorption



Impact of Defect Content



Bilayer V_2O_5 **Amorphous V_2O_5**

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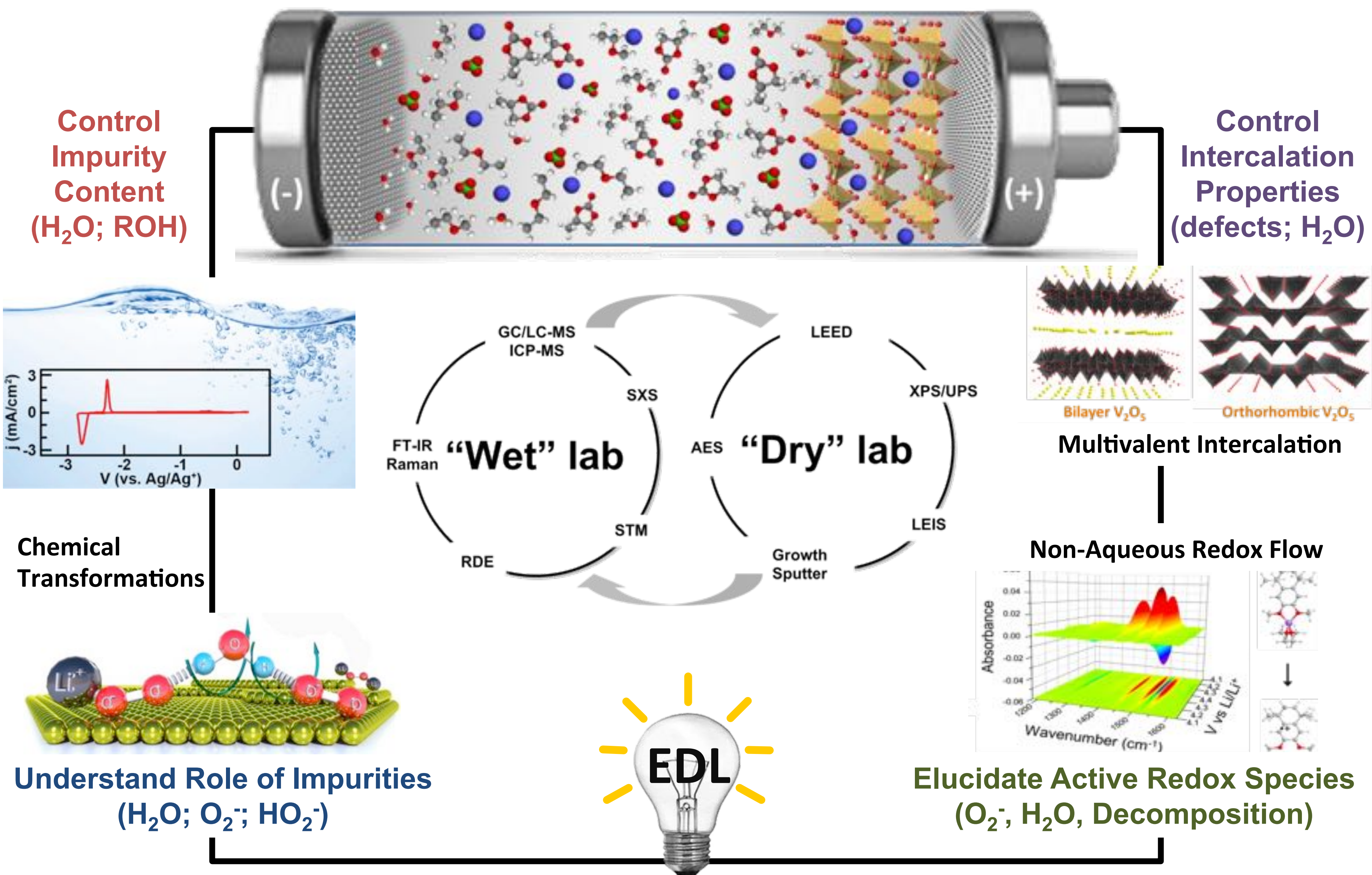
  - Amorphous, bilayer V_2O_5 reversibly intercalates Mg ions, crystalline, orthorhombic V_2O_5 does not
  - Intercalation is due to structural water (OH) bonded in between the layers
  - Independently controlling defect content enables better understanding of the impact of defects vs. structure on performance
- Connecting EDL capabilities with APS and ALS

Tepavcevic *et al. ACS Nano* (2015)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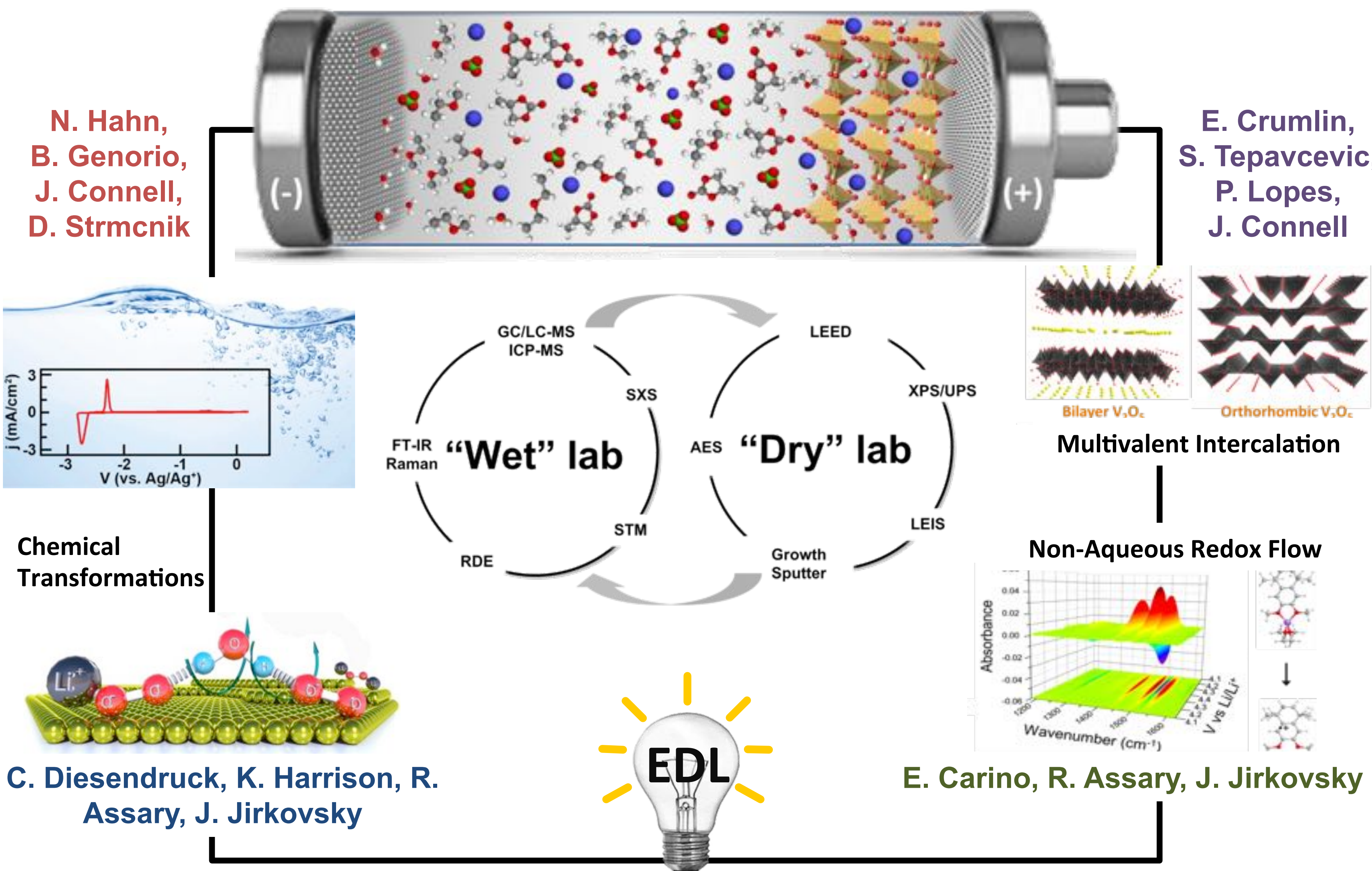
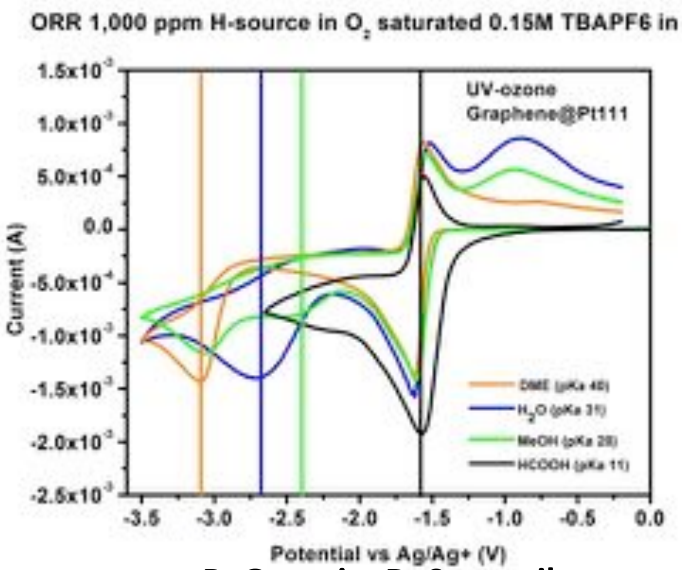
JCESR

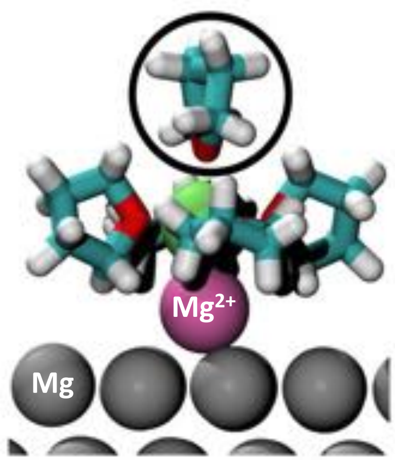


Institutions: ANL/APS, SNL, MIT, UIUC, LBNL/ALS

Continuing Divergent Research Efforts



B. Genorio, D. Strmcnik



J. Connell, Electrolyte Genome, Materials Project

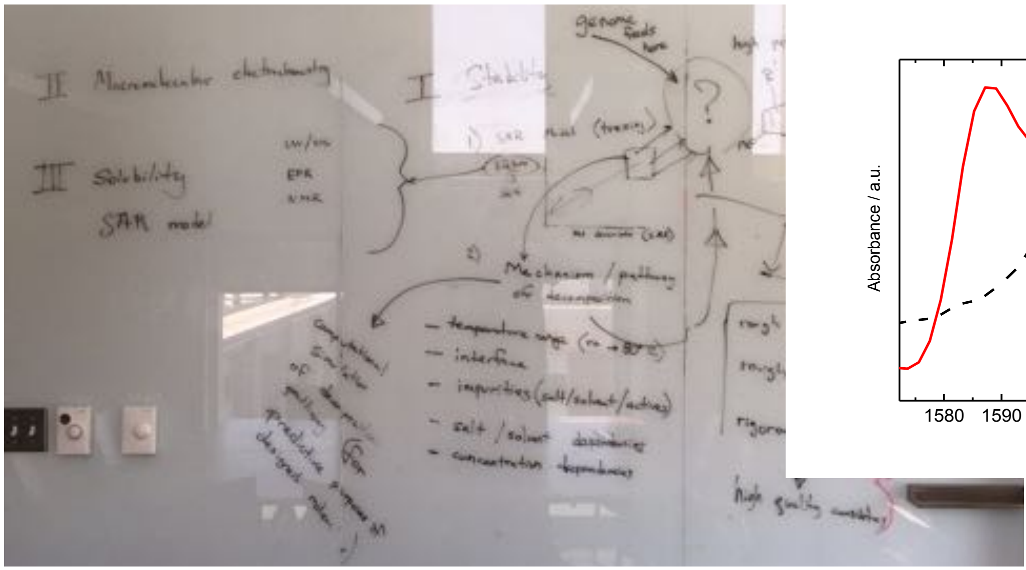
- Assessing impact of alcohols
  - Increasing pK$_a$ increases rate of formation of aggressive radical species
  - Better understanding the role of common impurities is key to enhanced performance

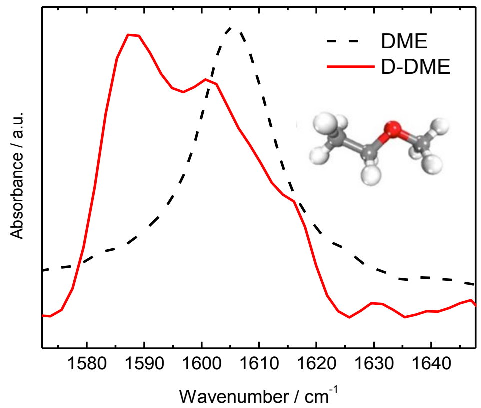
- Connecting further with computation to understand Mg deposition/stripping
  - Well-defined surfaces synthesized in UHV enable direct input into simulation
  - Can connect insights from model single crystal systems to real materials

Canepa *et al. Chem. Mater.* **29** (2015) 3317

Connecting with Convergent Research (Sprints)

- Non-Aqueous Redox Flow (ANL, UIUC, MIT, U Michigan)
  - Evaluate families of redox-active molecules to understand **stability** of the electrolyte and develop a unified Structure-Activity Model
  - Developing uniform electrochemical testing procedures to facilitate cross-institutional collaboration and streamline data integration into model
- Chemical Transformations (UIUC, SNL)
  - Consolidate efforts to understand Mg ion speciation at electrochemical interfaces
  - Utilize EDL capabilities to connect fundamental understanding to real electrolyte systems





Summary and Future

- The EDL houses a wide variety of capabilities that are available for use by the entire JCESR community
- EDL-led efforts have already enabled a deeper understanding of the effects of impurities and defects on electrochemical performance
- Connecting these capabilities with theoretical efforts will enable the development of a multiscale model of the electrochemical behavior of beyond Li-ion technologies