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ACCELERATING THE INVESTIGATION OF ORGANIC EXPANDER MOLECULES TO UNDERSTAND STRUCTURE-FUNCTION RELATIONSHIPS IN PbA BATTERIES

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Outline

- Background and motivation
- Overview of expanders research program
  - Electrochemical and chemical stability
  - Probing MEM-Pb species interactions
  - Screening electrochemical performance
- Accelerating electrochemical performance screening through automation
- Conclusions

PbA negative electrodes are limited by $PbSO_4$ agglomeration

- Lead acid (PbA) batteries use lead as the negative active material (NAM) and lead dioxide as the positive active material (PAM)
- $PbSO_4$ agglomeration results in NAM failure
  - Loss of electrical contact
  - Low surface area

discharge →

NAM $Pb + SO_4^{2-} \leftrightarrow PbSO_4 + 2e^-$

← *charge*

charge →

PAM $PbSO_4 + 2H_2O \leftrightarrow PbO_2 + H_2SO_4 + 2H^+ + 2e^-$

← *discharge*

Lopes and Stamenkovic. (2020). *Science, 369*(6506), 923-934. Ferels, Chaudhari, Agyapong-Fordjour, Buchanan, and Lopes. (2024). *J. Power Sources, 615*(30), 235100.

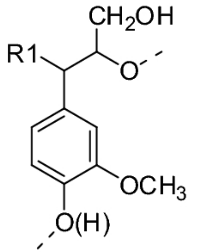
To improve NAM, interactions between expander molecules and Pb species must be understood

Expander molecules

- \+ Increase + maintain surface area, improving discharge performance
- − Typically decrease charge performance, e.g., Vanisperse A® (Van A)

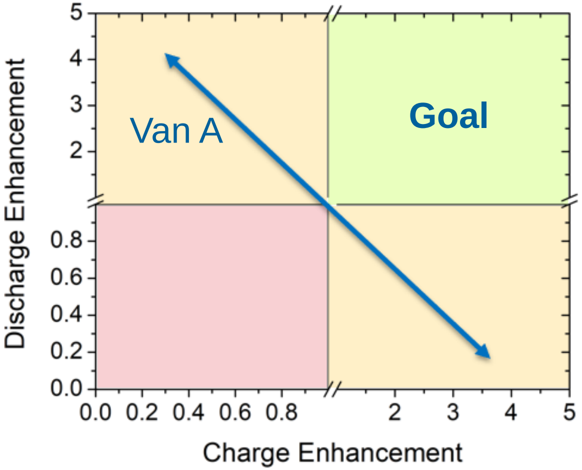
Goal: Design expander molecules that enhance both charge and discharge

- Study interactions via model expander molecules (MEMs)



R1 = OH or SO_3^{2-}

Lignosulfonate molecular structure, a subset of Van A



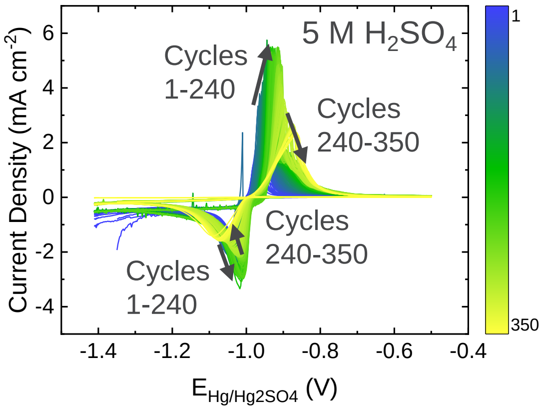
Overview of research collaboration between Argonne, U Toledo, and industry partners

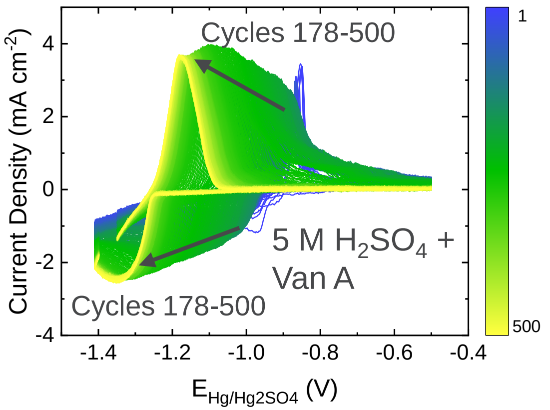
- American Battery Research Group is a Cooperative Research and Development Agreement between Argonne National Laboratory, U Toledo, and industry partners
  - Project has been ongoing for 3 years
- Toolbox developed with techniques to probe
  - Stability
  - Pb-MEM interactions
  - Discharge and charge enhancement factors
- MEMs are proprietary, but methods will be demonstrated using Van A

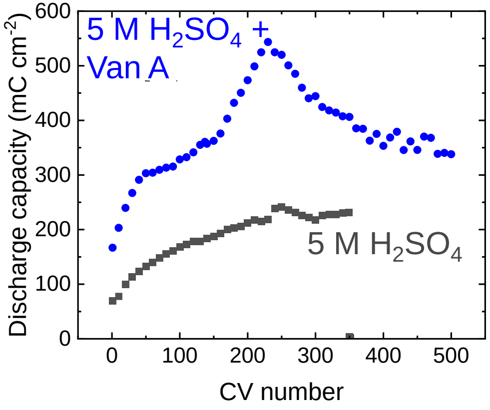
Expanders Research Project Toolbox
Cyclic voltammetry (CV)
Density functional theory (DFT) calculations
Raman spectroscopy
Liquid chromatography mass spectrometry
Affinity column + UV Vis spectroscopy

CVs used to quantify MEM electrochemical stability

- CVs demonstrate gradual loss of electrochemical performance over hundreds of cycles for NAM electrode in 5 M H_2SO_4
  - Van A demonstrates improved discharge performance







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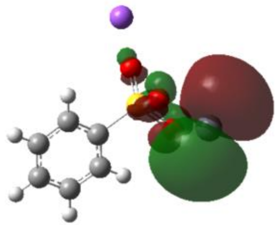
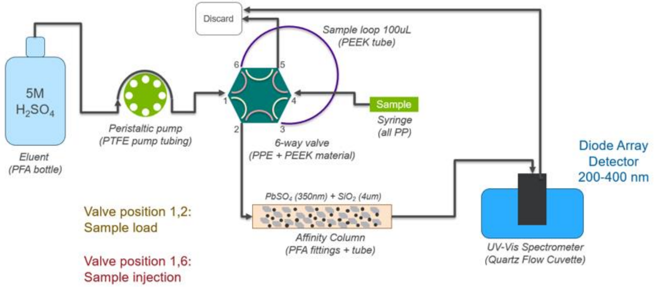
DFT and affinity column are used for probing MEM-Pb species interactions

- DFT calculates highest occupied and lowest unoccupied molecular orbitals (HOMO, LUMO)
  - HOMO: Pb^{2+} interactions
  - LUMO: SO_4^{2-} interactions
- DFT can interpret molecular vibrational information Raman spectroscopy



LUMO of lead benzyl sulfonate from DFT

- Affinity column coupled with UV-Vis detects statistically significant differences in retention time for different MEMs



CVs quantify the MEMs' discharge enhancement factors (DEF) through Peukert equation

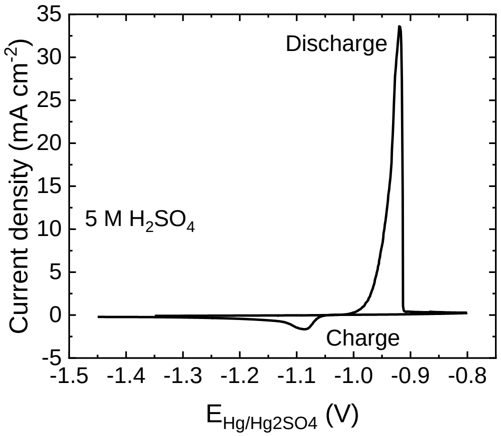
Peukert equation from first principles relates discharge capacity (Q_d) to

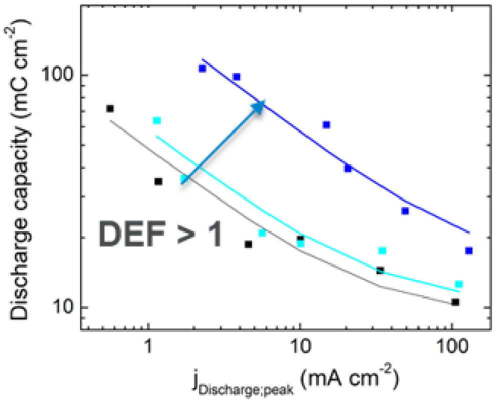
- Pb^{2+} ion gradient,
- $PbSO_4$ nucleation and growth kinetics, and
- HSO_4^- ion gradient as a function of discharge current (j_d)

$$Q_d = (\alpha + \beta j_d)^{0.5} j_d^{-0.5}$$

Discharge performance is fitted with Peukert equation to determine a value for α (intrinsic capacity)

$$DEF = \left(\frac{\alpha_{MEMs}}{\alpha_{baseline}}\right)^{1/2}$$





Buchanan. *Assessing the discharge mechanism & limiting capacity of the negative electrode for the lead acid battery and its implications for LDES economics.* ACS Fall 2023, San Francisco, Paper ID 3931402.

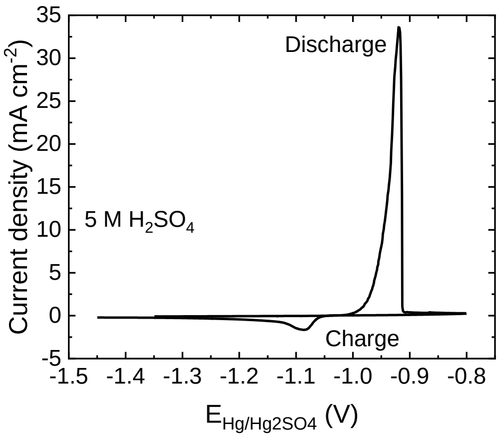
CVs quantify the MEMs' charge enhancement factor (CEF) through kinetic charge acceptance curves

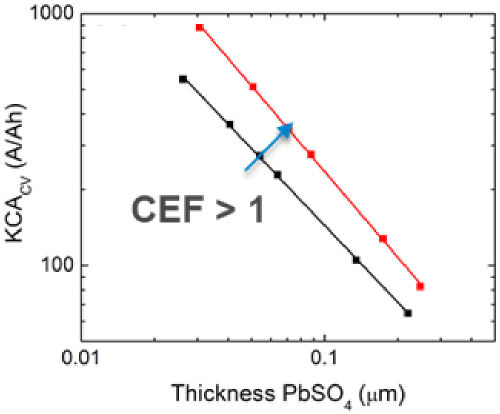
- Kinetic charge acceptance (KCA) curves are used to determine rate of dissolution of $PbSO_4$ particles during charging, k_{dis}

$$KCA_{-1.2\,V} = \frac{j_c(-1.2\,V)}{Q_d} \cong k_{dis}\,\frac{\lambda}{d^m}$$

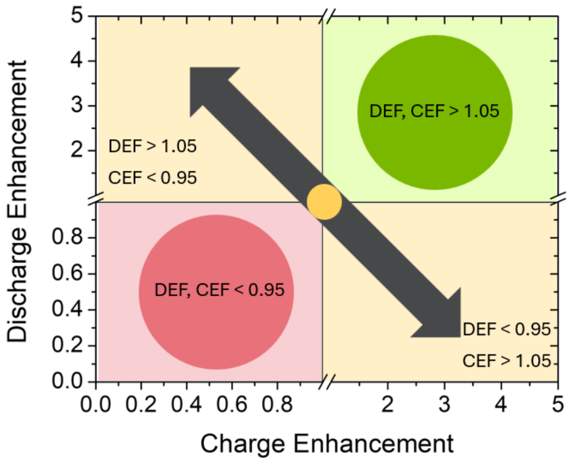
$$CEF = \frac{k_{dis-MEMs}}{k_{dis-baseline}}$$

$$\lambda = \frac{3M}{\pi F \rho}$$



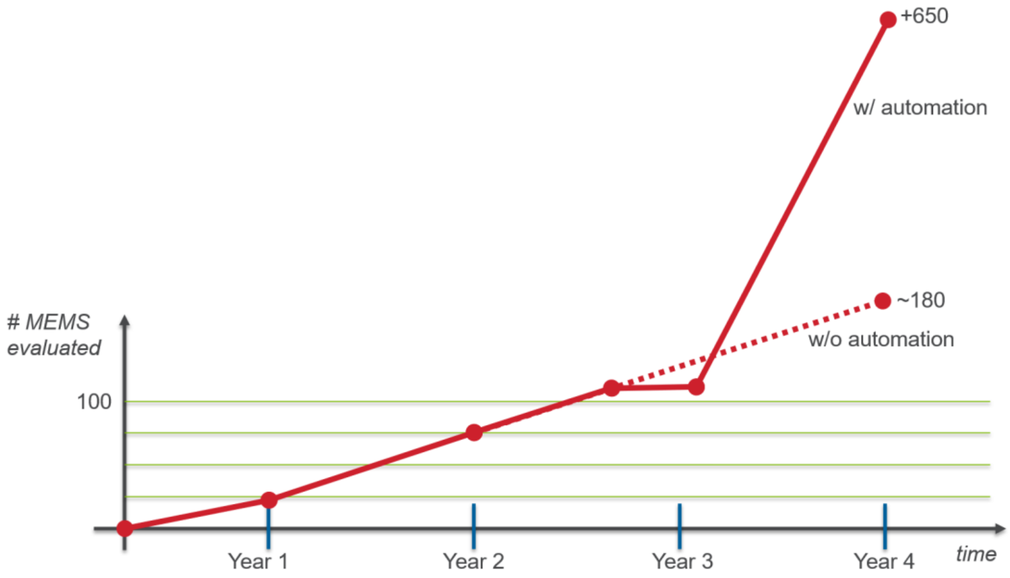


The rate of electrochemical screening must be increased

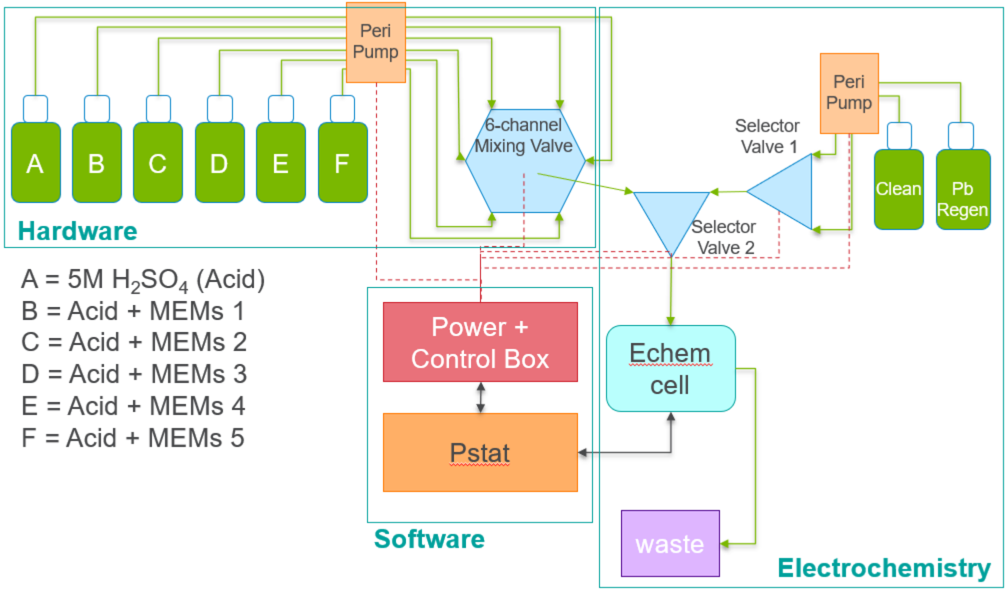


- MEMs are organized by DEF and CEF values into quadrants
- Over the last 3 years, 100+ molecules tested
  - 13% of MEMs are enhancers

- Electrochemical screening can be accelerated through automation



An automated system can be used to screen MEMs more efficiently and enhance reproducibility



A = 5M H_2SO_4 (Acid)
B = Acid + MEMs 1
C = Acid + MEMs 2
D = Acid + MEMs 3
E = Acid + MEMs 4
F = Acid + MEMs 5

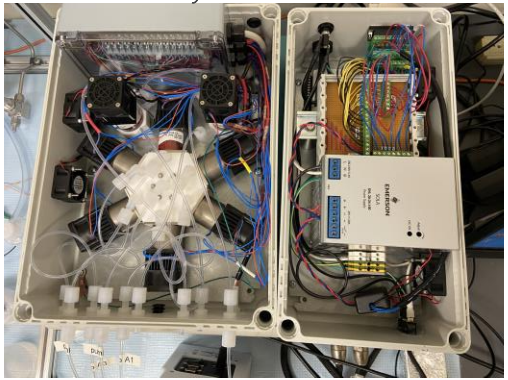
Electrochemical **S**ystem for **M**olecule **A**utomated and **R**apid **T**esting

Design considerations:

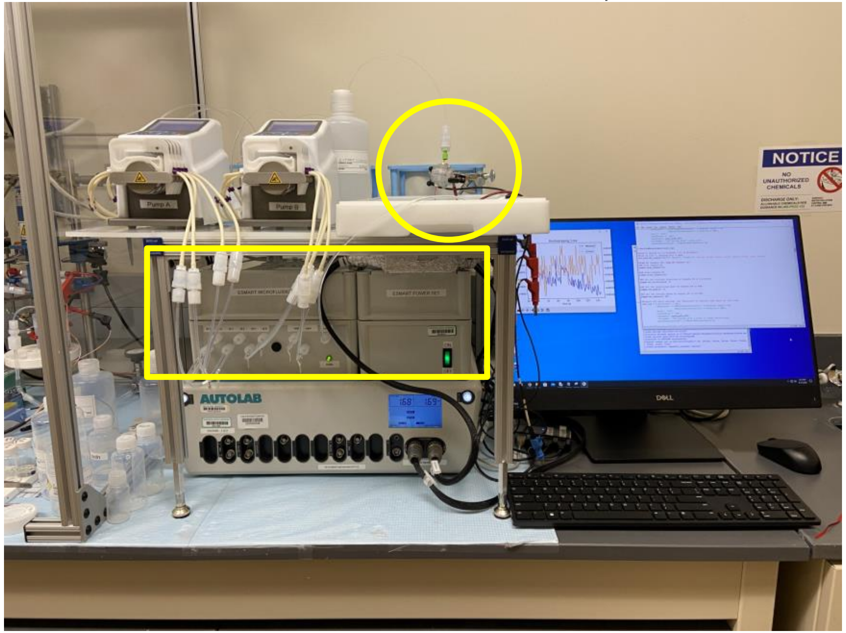
- Mixing up to 6 solutions simultaneously
- Fresh NAM surface via Pb electrodeposition

The E-SMART system will allow for an accelerated pace of MEM electrochemical screening

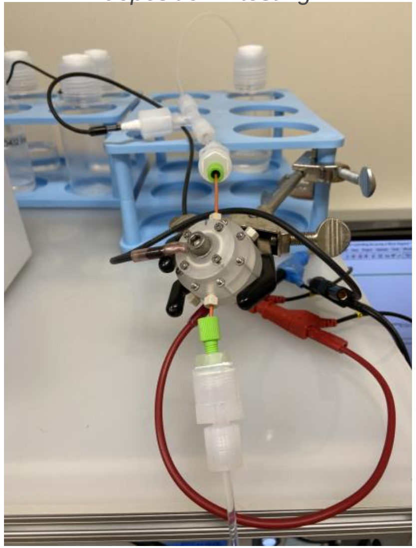
Valves with flow path integrated and circuitry to control valves



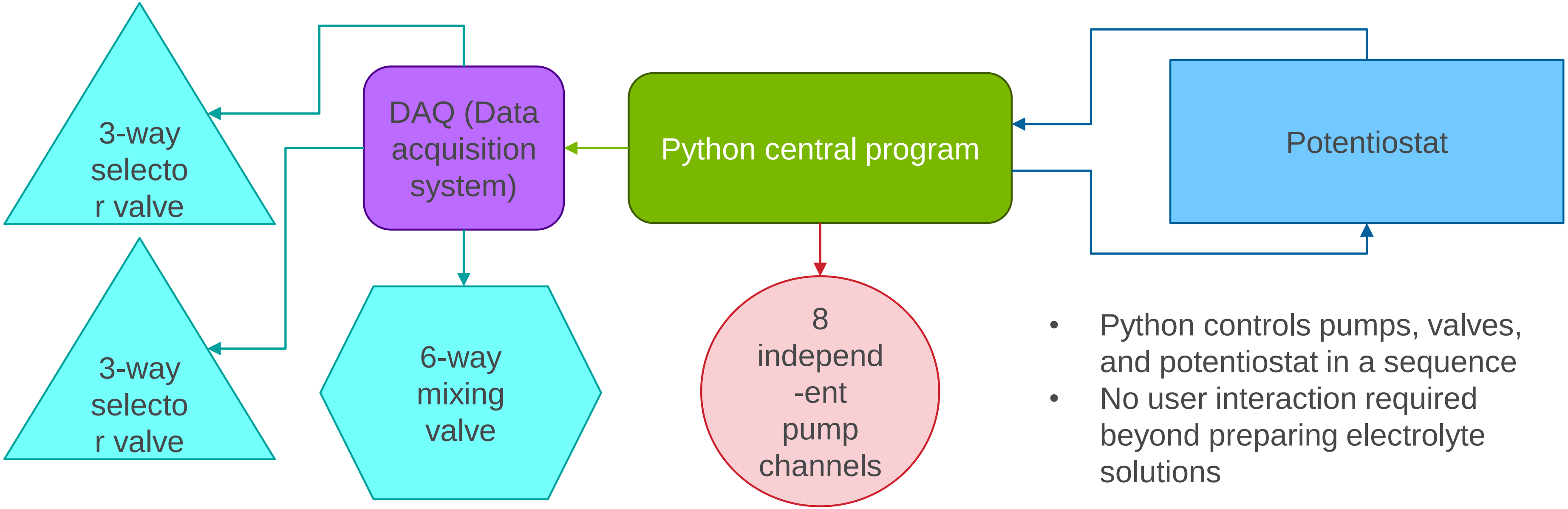
Overview of E-SMART automated system, with 8 independent pump and valve channels for 6 MEM solutions and 1 rinse and 1 deposition solution



Microfluidic cell + in line reference electrode for active material deposition + testing

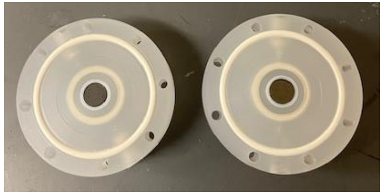


E-SMART system uses one central program to control pumps, valves, and electrochemical testing

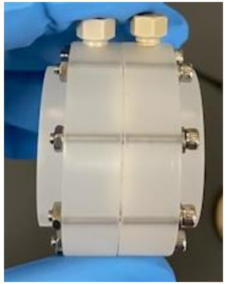


- Python controls pumps, valves, and potentiostat in a sequence
- No user interaction required beyond preparing electrolyte solutions

Flow cell: Active material deposition for electrochemical testing

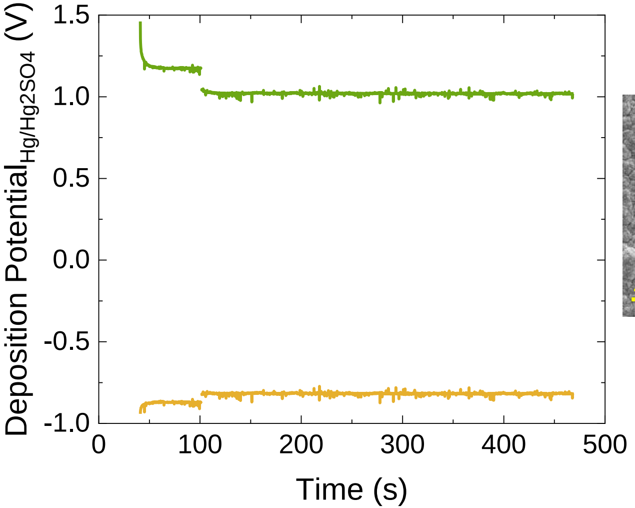


Top view cross section of flow cell with glassy carbon RDEs

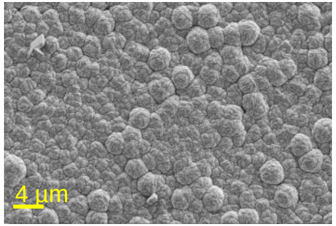


Assembled flow cell

- Developed a protocol for depositing active material from $Pb(ClO_4)_2$ solution using constant current onto glassy carbon rotating disk electrode (RDE) substrates

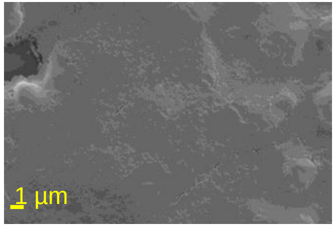


Positive



EHT = 5.00 kV, WD = 10.9 mm, Mag = 2.53 kX

Negative

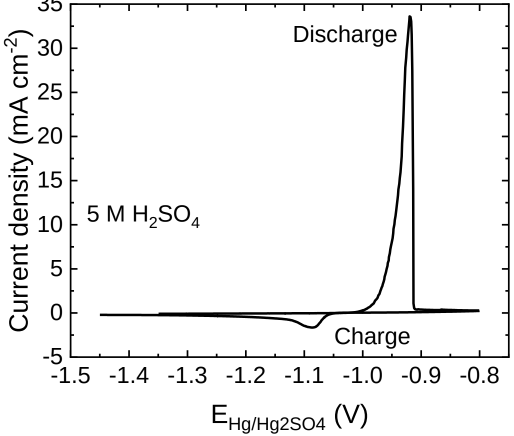


EHT = 3.00 kV, WD = 10.4 mm, Mag = 5.00 kX

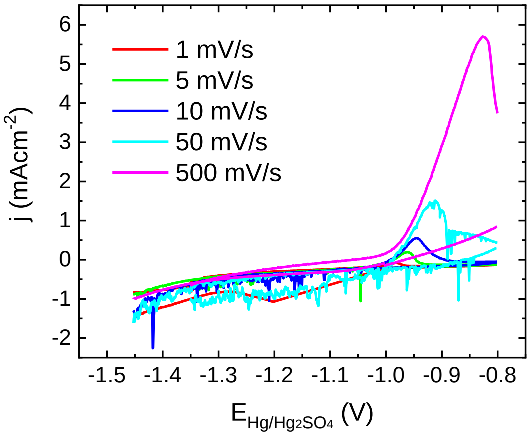
SEM images of PbO_2 and Pb electrodeposited on glassy carbon substrates

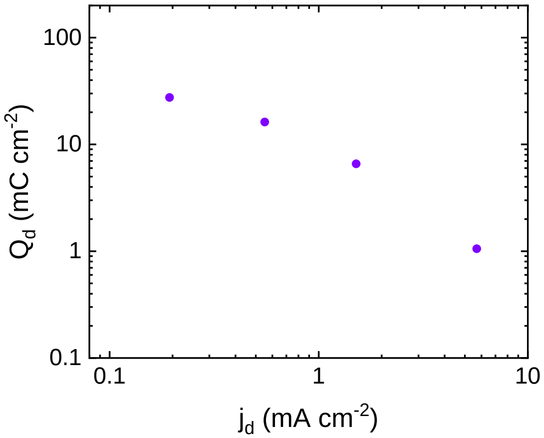
Preliminary results collected on E-SMART system qualitatively agree with previous measurements

Flat lead disk measurements



E-SMART edep measurements





- Characteristic lead discharge and charge peaks observed from electrodeposited material in E-SMART system
- Trend in discharge capacity (Q_d) with current density (j_d) follows Peukert equation

Conclusions

- We have developed a toolbox for testing the electrochemical and chemical stability and charge and discharge enhancement of model expander molecules
- DFT has been used to calculate HOMO and LUMO values and along with the affinity column system will be used to characterize MEM interactions with Pb and $PbSO_4$
- Enhancer MEMs, which improve both charge and discharge performance, have been identified and should be used to identify the design rules for expander molecules
- Automated system for electrochemical testing will accelerate the number of MEMs that can be screened and enhance reproducibility
- Next step: Probe structure-function relationships using DFT and affinity column, and link results to measured electrochemical behavior through statistical analysis approaches

Acknowledgements

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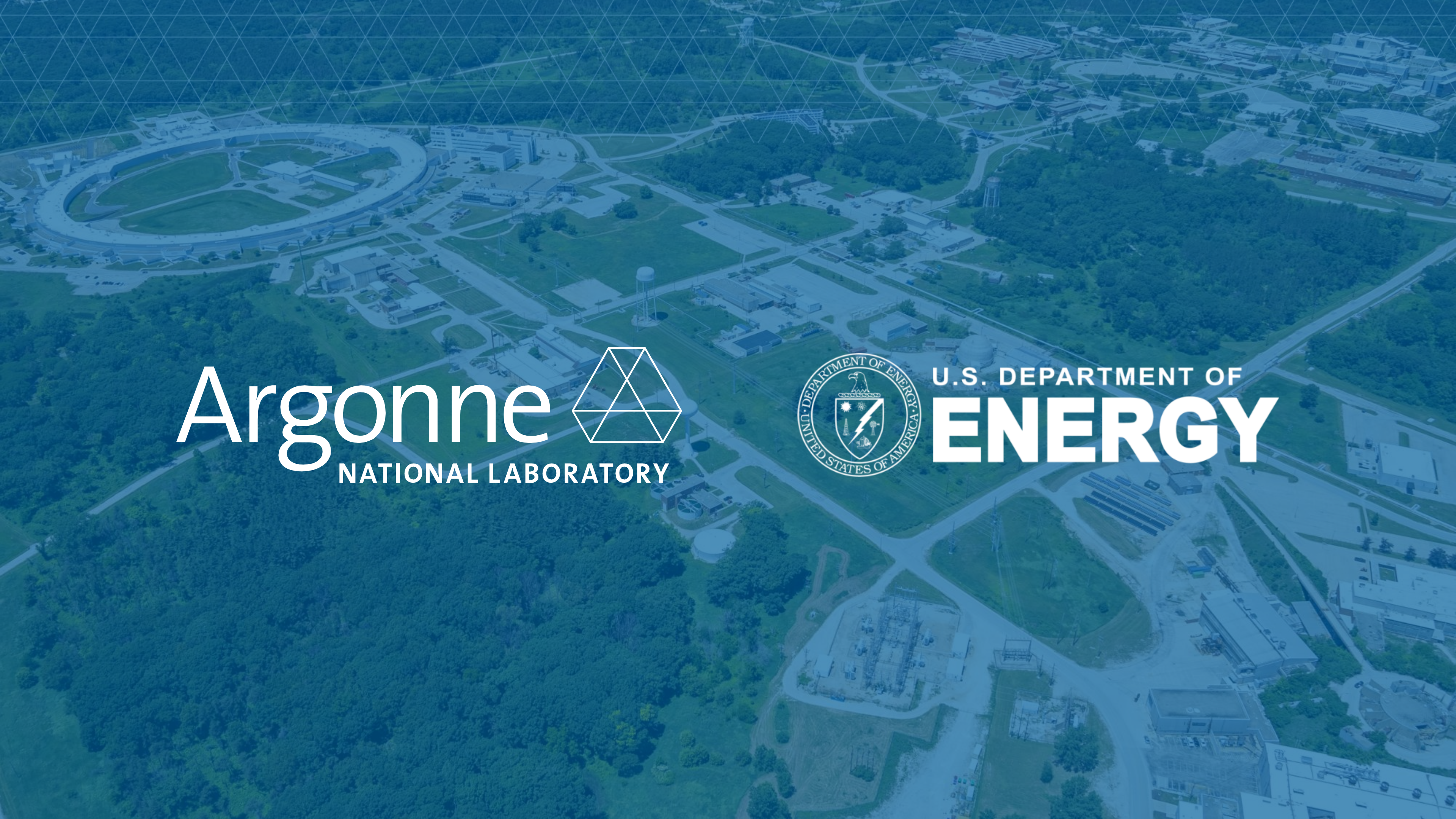
American Battery Research Group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