

FUNDAMENTAL STUDIES - UNDERSTANDING THE DISCHARGE MECHANISM AND CAPACITY LIMITS OF LEAD ACID BATTERY ELECTRODES



FREDERICK AGYAPONG-FORDJOUR
Postdoctoral Scientist

CAILIN BUCHANAN
Postdoctoral Scientist

CRYSTAL FERELS
Postdoctoral Scientist

NIKHIL CHAUDHARI
Graduate Researcher

PIETRO PAPA LOPES
Staff Scientist

OUTLINE

The good; **Lead (Pb)**

The bad; **Long**

Duration Storage,

The ugly; **Technical
Challenges.**

Investigating
discharge
mechanism: **CVs**
and **ICP-MS.**

Benchmarking
performance through
PbSO₄ formation
dynamics and the
discharge capacity
limits (Peukert
relationship studies)

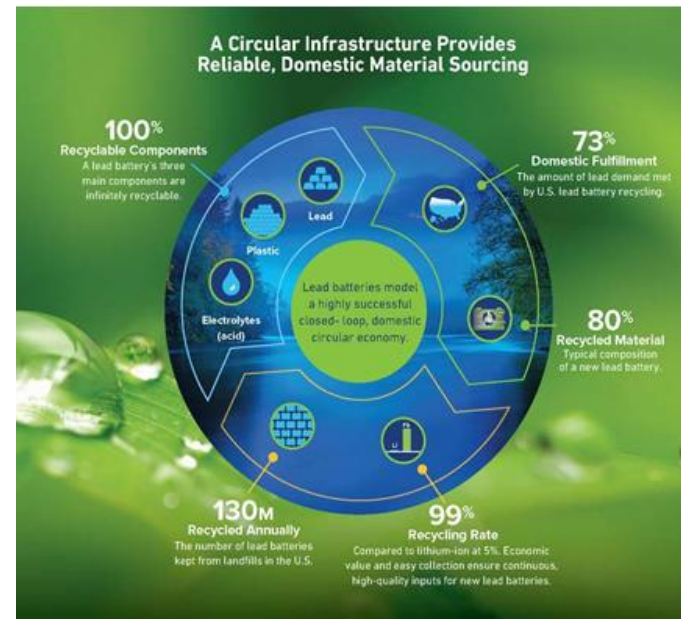
LEAD-ACID BATTERY TECHNOLOGY MEETING GROWING DEMAND AND PERFORMANCE NEEDS

Domestic manufacturing and Recycling

- North American lead battery manufacturing supplies 90% of North American demand.
- Robust infrastructure to ensure sustainability.
- 99% recyclability ensuring a domestic circular economy and independence.

Research driving performance improvements

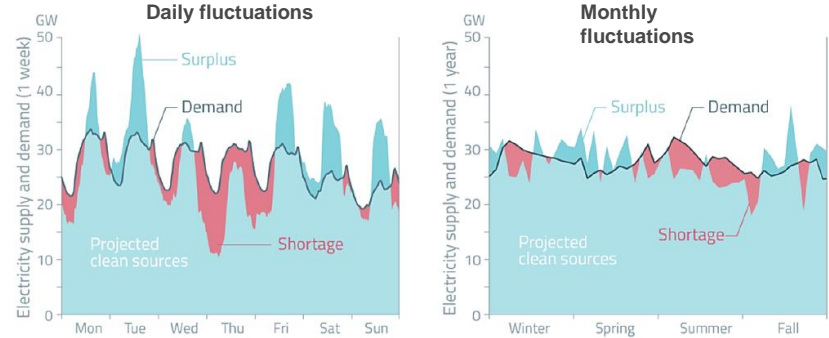
- Increase material utilization (> 40%).
- Low cycle life: Understanding interrelation between materials & processes



The electrochemical and chemical processes that comprise lead acid charging and discharging must be deeply understood

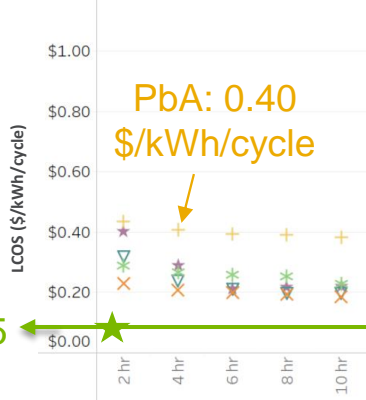
LONG DURATION ENERGY STORAGE (LDES) REQUIRES SIGNIFICANTLY CHEAPER STORAGE THAN STATE OF ART

- 26% of green house gas are emitted from Electricity generation
- Solar and wind can help decarbonize **but are intermittent**



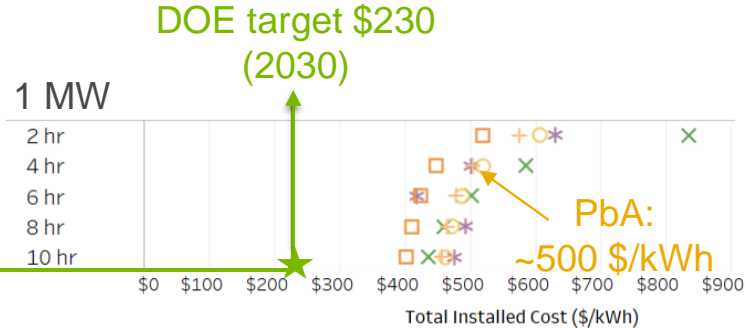
Future Cleantech Architects LDES fact sheet (2022)- fcarchitects.org

- Lithium-ion LFP
- Lithium-ion NMC
- Lead Acid
- Vanadium Redox Flow
- Zinc
- PSH
- CAES
- Gravitational
- Thermal
- Hydrogen



DOE Target \$0.05 (2030)

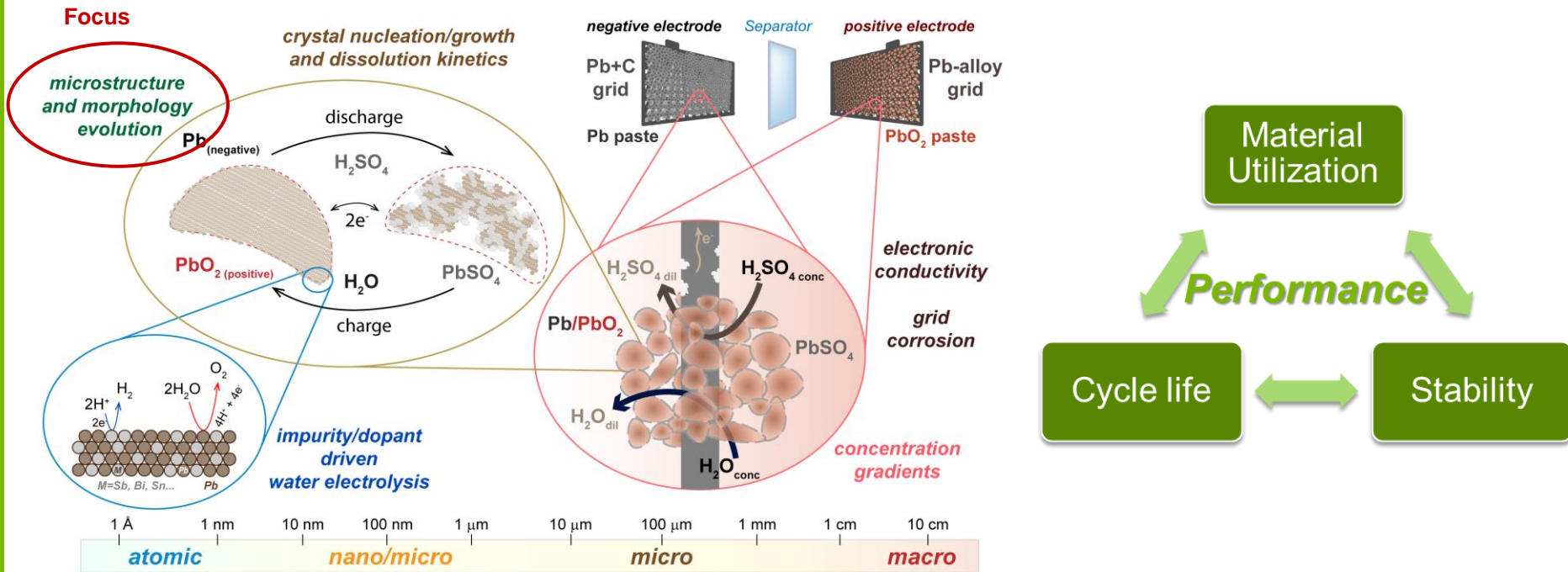
1 MW



DOE 2022 Grid Energy Storage Tech. Cost & Performance Assessment.

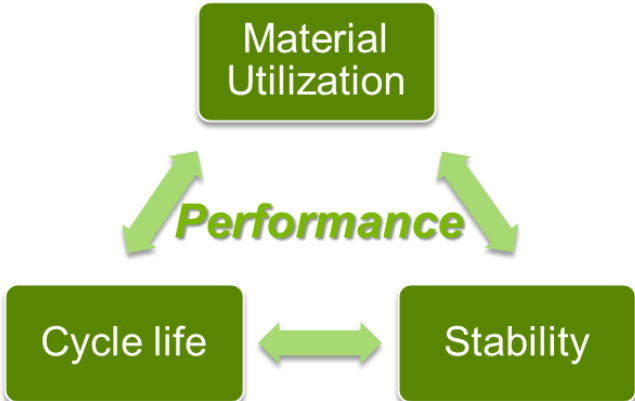
- Lithium-ion LFP
- Lithium-ion NMC
- Lead Acid
- Vanadium Redox Flow
- Zinc
- PSH
- CAES
- Gravitational
- Thermal
- Hydrogen

LEAD ACID BATTERY ELECTROCHEMISTRY



Lopes P. P. et al., *Science* **2020**, 369 (6506), 923-924

What are the fundamental limits of the discharge reaction on the electrodes?

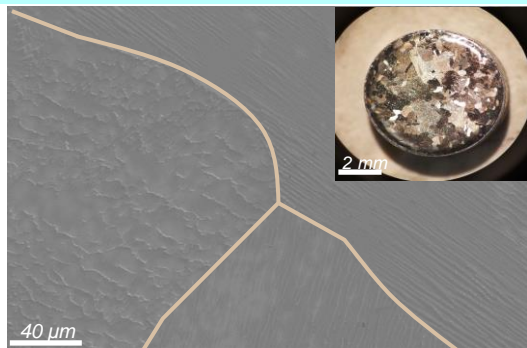


ESTABLISHING REPRODUCIBLE NEGATIVE AND POSITIVE ELECTRODES

A NOVEL, TWO-STEP ELECTROPOLISHING METHOD FOR ACHIEVING A FLAT, POLISHED Pb SURFACE

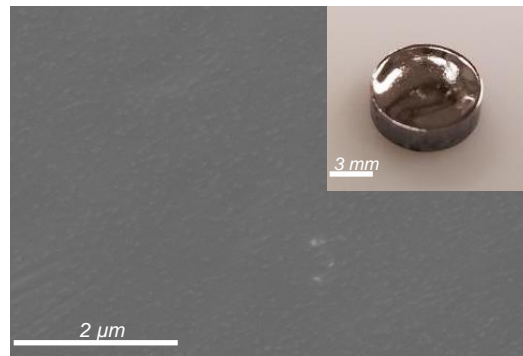
Electrochemical polishing process of Pb (99.9999%) disk:

1. **Grain polish** – low current etching, 5 minutes
2. **Fine polish** – high current etching, 30 seconds
3. **Rinse in H₂O**
4. **Dry with Argon**

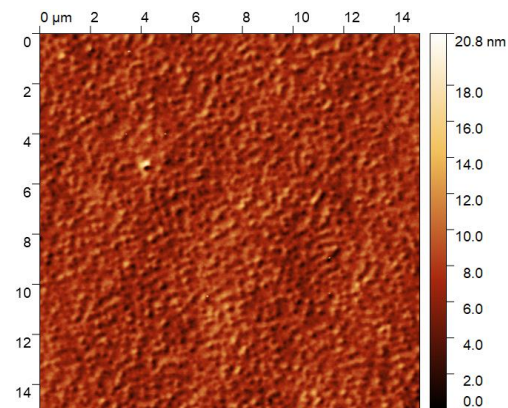


Scanning electron microscopy (SEM) of **grain-polished** Pb

Flat Pb surface possible via E-polishing



SEM of fine-polished Pb disk



AFM shows a small degree of roughness, ~20nm

MAKING LEAD DIOXIDE INTERFACES

Experimental Protocol

WE: Glassy Carbon (mirror polished
0,05um alumina, IPA/H₂O sonication)
CE: Graphite rod
RE: Hg/HgSO₄ (double junction + bridge)

Electrodeposition:

[Pb²⁺]: 0.1M

Electrolyte: 0.1M HClO₄

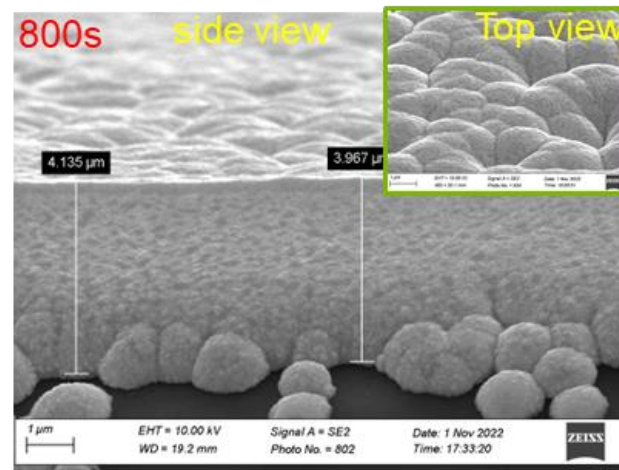
Constant current deposition: 2.16 mAcm⁻²

Electrode rotation: 1600 rpm

Deposition time: 800s

Target film thickness: 4um

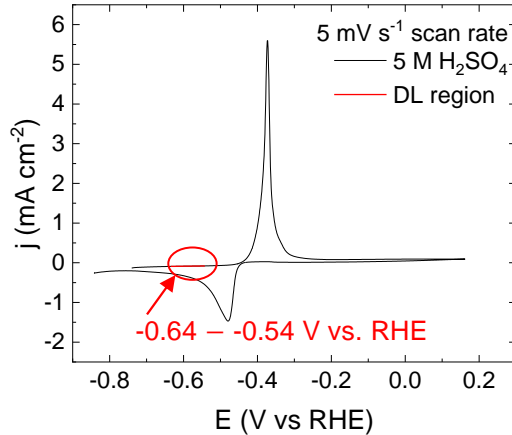
H₂O rinse after deposition before (20s)
transferring to H₂SO₄ containing cell



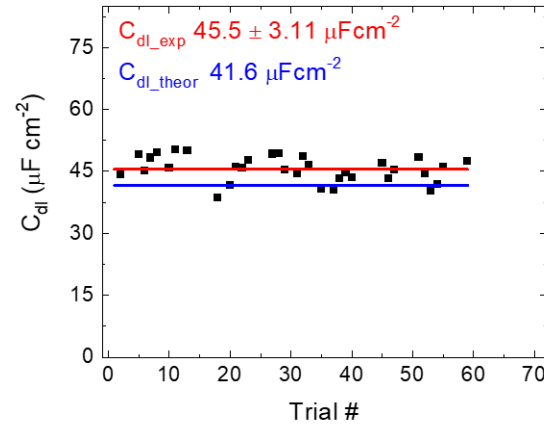
Deposition of PbO₂ from
soluble Pb²⁺ solutions (pH ~
0.7) to form a well-defined
positive active material

PB - DOUBLE LAYER CAPACITANCE IS USED TO MEASURE REPRODUCIBILITY OF POLISHING TECHNIQUE

Entire CV to determine non-Faradaic region for C_{dl} measurements



Comparing average experimental C_{dl} to theoretical



- **Working electrode:** Mirror polished Pb RDE
- **Counter electrode:** Graphite rod
- **Reference electrode:** Hg/Hg₂SO₄ in sat'd K₂SO₄

Avg NAM- C_{dl} value agrees well with theoretical C_{dl}

Reproducibility similarly confirmed from 0.5 – 5 M H₂SO₄

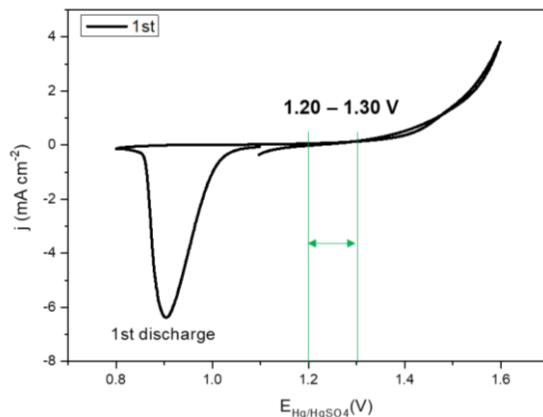
Theor:
$$\frac{1}{C_{dl_theor}} = \frac{1}{C_H} + \frac{1}{C_{GC}}$$

Helmholtz cap.

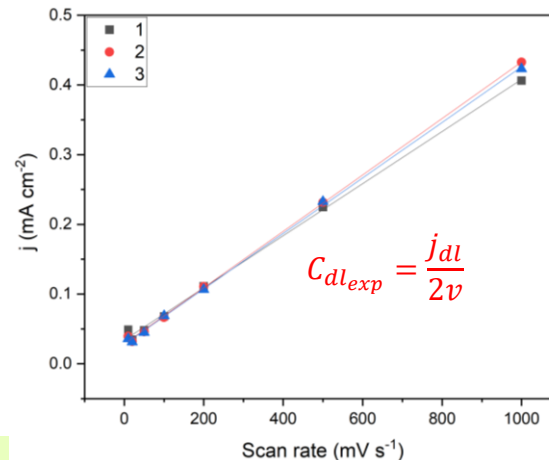
Gouy Chapman cap.

PbO₂ - DOUBLE LAYER CAPACITANCE IS USED TO MEASURE REPRODUCIBILITY OF E-DEPOSITION TECHNIQUE

Entire CV to determine non-Faradaic region for C_{dl} measurements



Linear fits of scan rate (ν) data for 5 trials in 5 M H₂SO₄



- **Working electrode:** Mirror polished Pb RDE
- **Counter electrode:** Graphite rod
- **Reference electrode:** Hg/Hg₂SO₄ in sat'd K₂SO₄

Avg PAM-C_{dl} value 392 ± 1.62 μF cm⁻² indicate higher surface area, consistent with SEM images

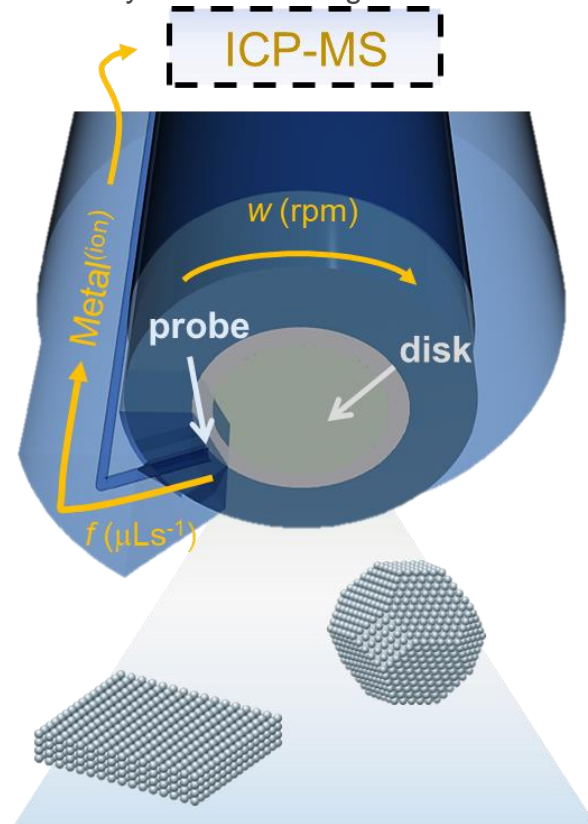
We can discharge and charge both flat Pb and electrodeposited PbO₂ to enable us to identify the mechanism controlling discharge capacity and recharge rates.

PROBING THE DISCHARGE MECHANISM

STATIONARY PROBE ROTATING DISK ELECTRODE (SPRDE)



Stationary Probe Rotating Disk Electrode



In situ dissolution monitoring reveal dynamics of surface stability in real time and at sub monolayer levels

Continuous real time monitoring of species generated at electrode surface

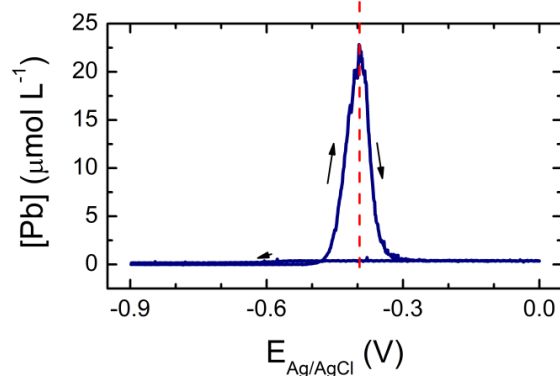
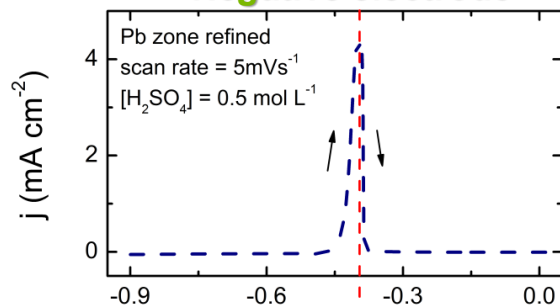
DISCHARGE PROCESS: LEAD DISSOLUTION – LEAD SULFATE PRECIPITATION

Method: Cyclic voltammetry (CV) coupled with *in situ* inductively coupled plasma mass spectroscopy (ICP-MS)

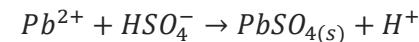
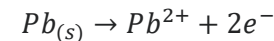
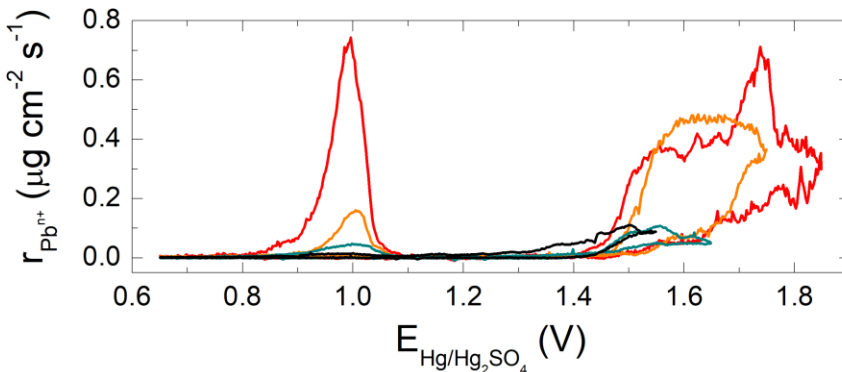
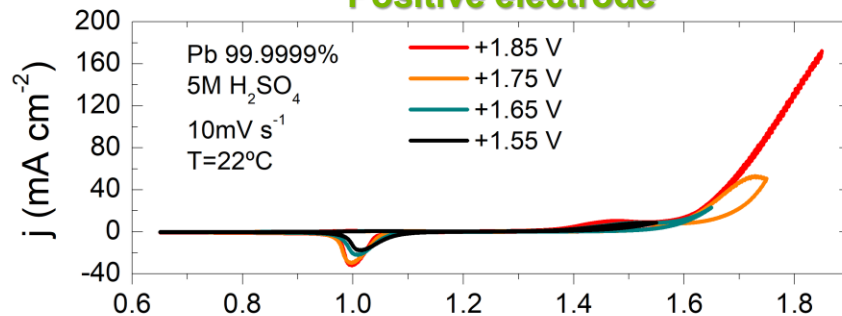
Dissolution of lead is the first step during PbSO_4 formation, generating lead ions right at the surface

Maximum Pb concentration outside diffusion layer is close to Pb solubility limit in sulfuric acid

Negative electrode

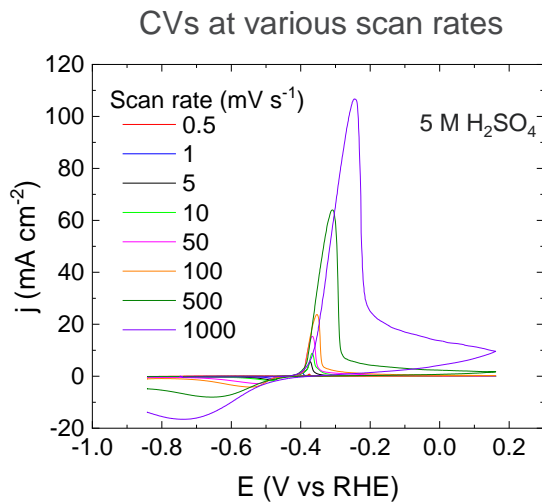


Positive electrode



Electrodes discharge limitations due to surface passivation

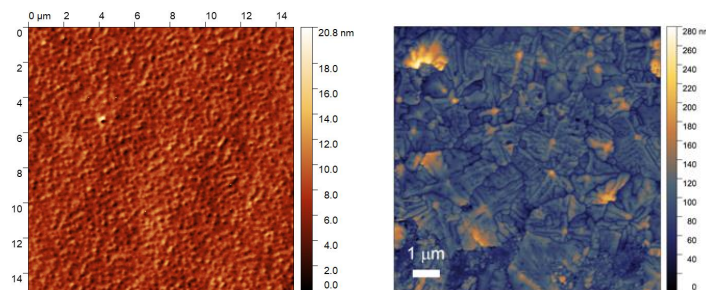
PB - PROBING THE LINK BETWEEN MORPHOLOGY & PERFORMANCE: PbSO₄ CRYSTAL SIZE IS DEPENDENT ON SCAN RATE



Faster scan rates = higher peak currents + more positive discharge potentials

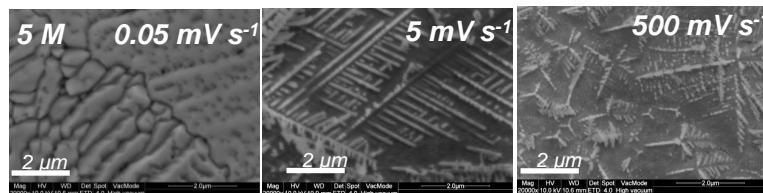
Passivation is faster at faster scan rates

AFM of polished Pb AFM of discharged Pb (5 mV/s)



PbSO₄ layer formed on Pb surface after discharge

SEM of discharged Pb

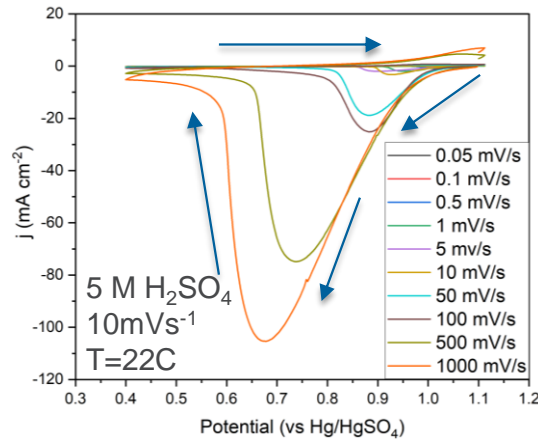


Faster scan rates result in smaller, more uniform crystals

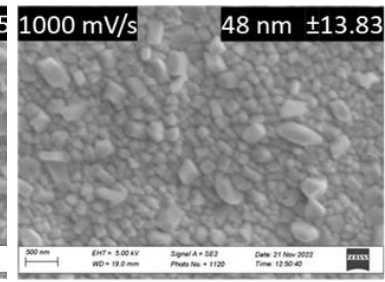
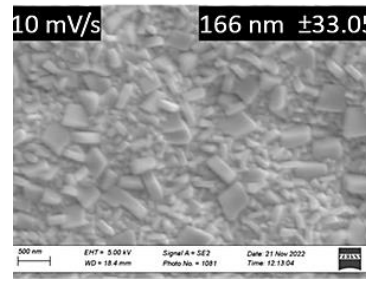
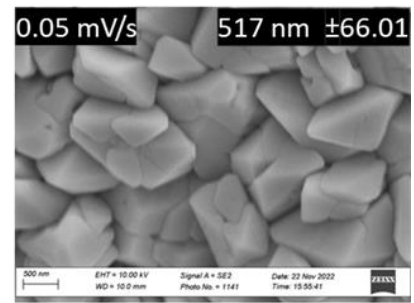
PbO₂ - PROBING THE LINK BETWEEN MORPHOLOGY & PERFORMANCE: PbSO₄ CRYSTAL SIZE IS DEPENDENT ON SCAN RATE

Experimental Protocol

WE: PbO₂/Glassy Carbon
CE: Pb 99.9999% foil
RE: Hg/HgSO₄ (double junction + bridge)
Hold at OCV (~1.1 V) for 300s before discharge



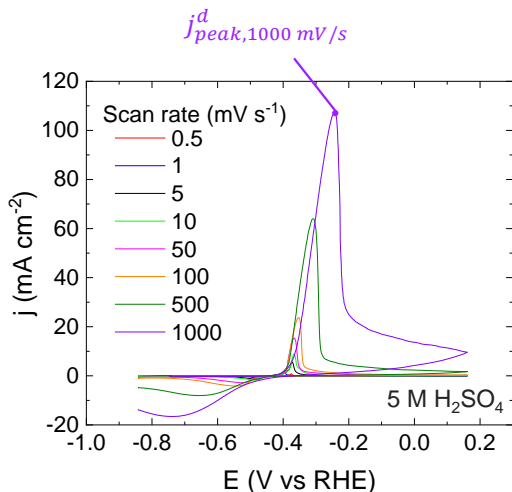
SEM of discharged PbO₂



Faster scan rates result in smaller, more uniform crystals similar to what was observed on NAM.

Key difference is the morphology of PbSO₄ crystals

PB- PROBING THE LINK BETWEEN MORPHOLOGY & PERFORMANCE: PbSO₄ CRYSTAL SIZE, SCAN RATE, H₂SO₄ CONCENTRATION, DISCHARGE CAPACITY

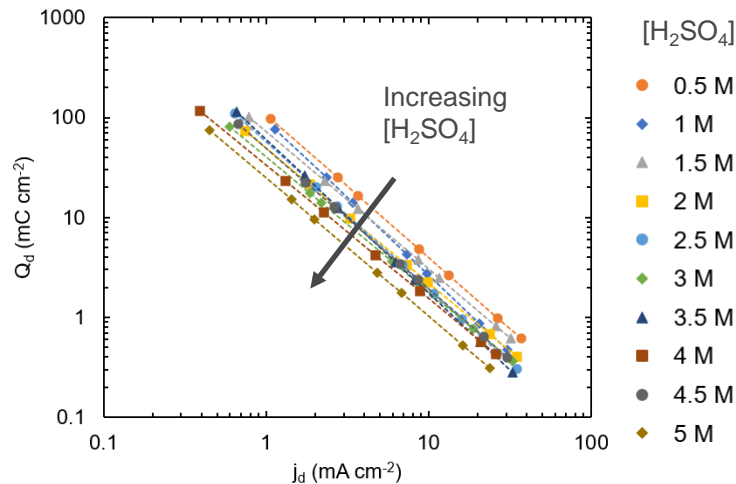


To determine discharge capacity, Q^d

$$Q^d (\text{mC cm}^{-2}) = \frac{\int_0^{j_a} j_{peak}^d dV}{v}$$

Peukert analysis to quantify performance

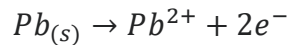
$$\bar{Q} = \bar{Q}^0 j^{-0.5}$$



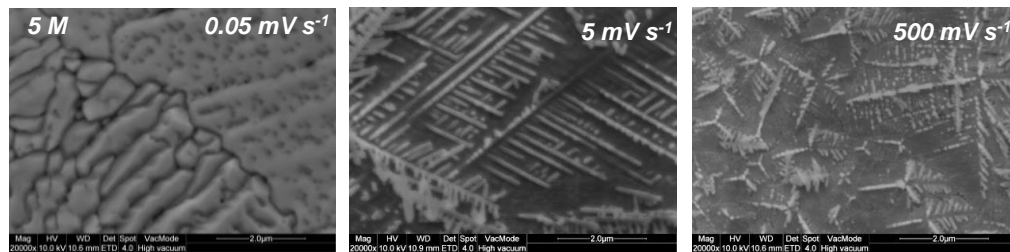
Intrinsic discharge capacity decreases with increasing H₂SO₄ concentration.

PB- PROBING THE LINK BETWEEN MORPHOLOGY & PERFORMANCE: $PbSO_4$ CRYSTAL SIZE, SCAN RATE, H_2SO_4 CONCENTRATION

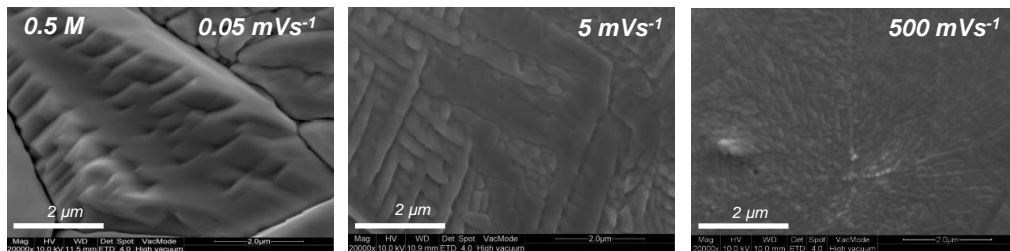
H_2SO_4 concentration will affect HSO_4^- transport and $PbSO_4$ crystal growth



SEM of discharged Pb at 5 M H_2SO_4

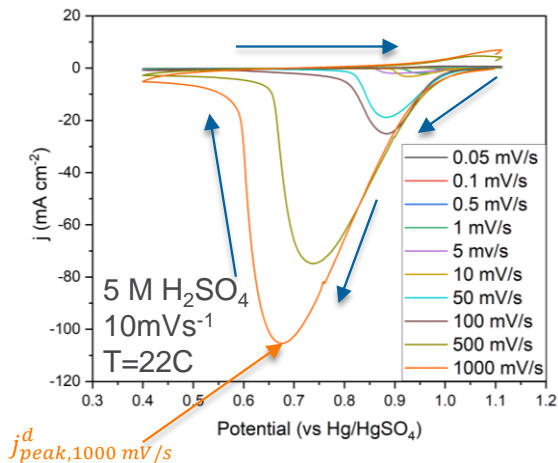


SEM of discharged Pb at 0.5 M H_2SO_4



Lower H_2SO_4 concentration results in larger $PbSO_4$ crystals

PbO₂- PROBING THE LINK BETWEEN MORPHOLOGY & PERFORMANCE: PbSO₄ CRYSTAL SIZE, SCAN RATE, H₂SO₄ CONCENTRATION, DISCHARGE CAPACITY

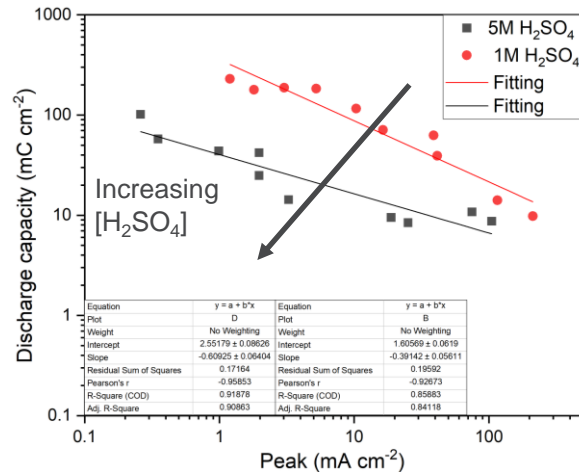


To determine discharge capacity, Q^d

$$Q^d (\text{mC cm}^{-2}) = \frac{\int_0^{j_a} j_{peak}^d dV}{v}$$

Peukert analysis to quantify performance

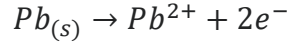
$$\bar{Q} = \bar{Q}^0 j^{-0.5}$$



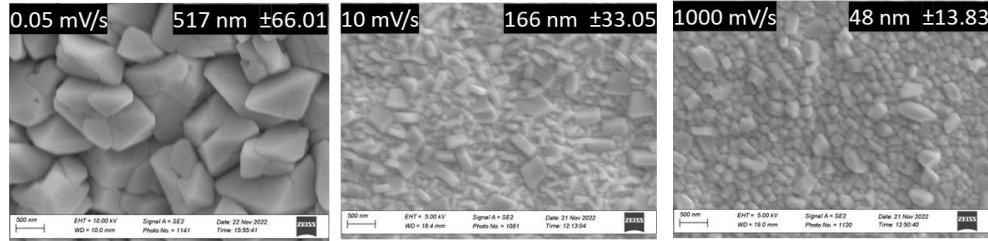
The intrinsic discharge capacity decreases with increasing H₂SO₄ concentration for PbO₂.

PbO₂- PROBING THE LINK BETWEEN MORPHOLOGY & PERFORMANCE: PbSO₄ CRYSTAL SIZE, SCAN RATE, H₂SO₄ CONCENTRATION

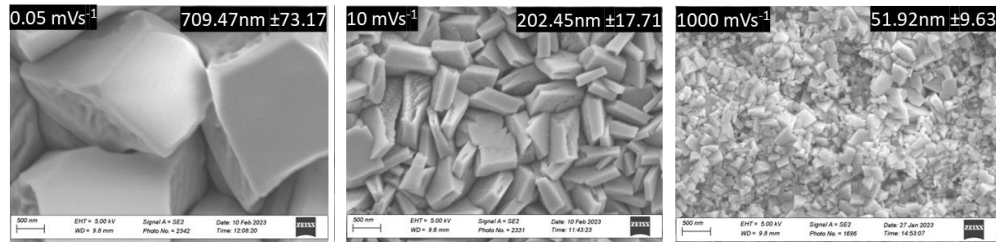
H₂SO₄ concentration will affect HSO₄⁻ transport and PbSO₄ crystal growth



SEM of discharged Pb at 5 M H₂SO₄

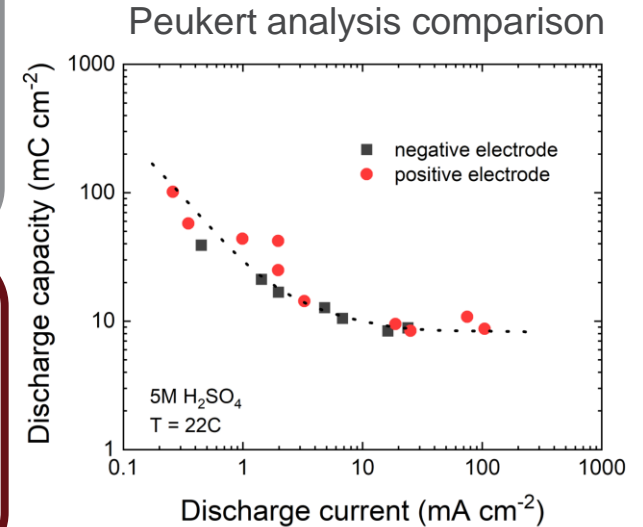
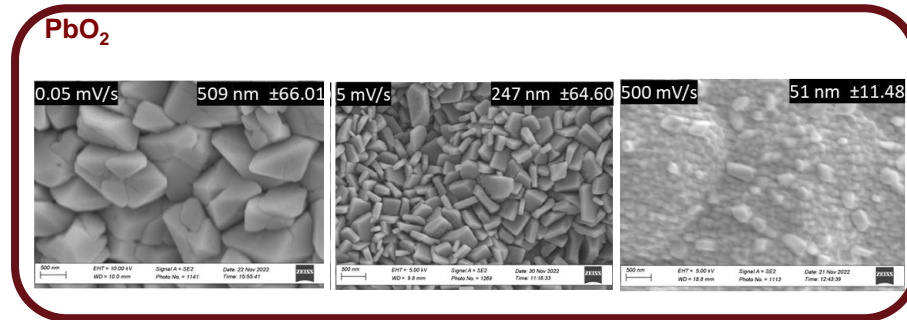
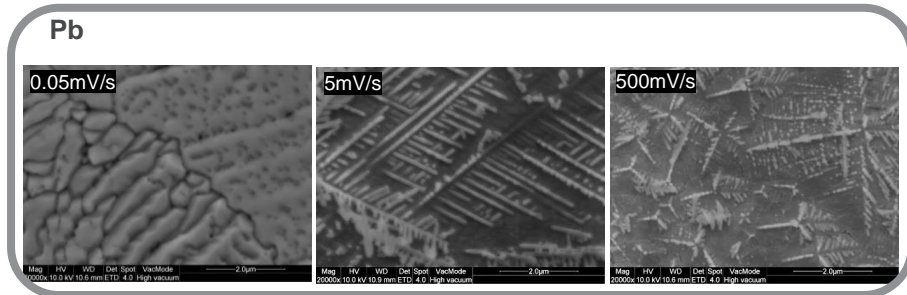


SEM of discharged Pb at 1 M H₂SO₄



PB & PBO₂ DISCHARGE CAPACITY/CURRENT CURVES

Comparison of SEM of discharged in 5 M H₂SO₄



At the fundamental level, the mechanism controlling the discharge capacity on the negative versus positive seems to be the same - PbSO₄ nucleation and growth dynamics.

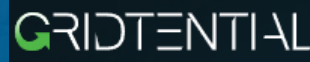
Difference in electrode surface area should impact how much capacity is accessible for your battery

SUMMARY AND OUTLOOK

- Discharge mechanism and limits to discharge capacity seems depend on the nucleation and growth dynamics of the PbSO_4 layer.
- Revealed relationship between electrochemistry and PbSO_4 morphology as they relate *via* dissolution, nucleation and growth dynamics. Solubility is an important parameter controlling size of PbSO_4 particles
- Control over PbSO_4 particle size and morphology as you cycle the battery is key to increasing cycle life and material utilization and meeting DOE target.
- Fundamentally, nucleation and growth dynamics of PbSO_4 controls the discharge capacity of both electrodes – big opportunities for the design of electrodes, expanders, both at the NAM and PAM to improve materials utilization.

Peukert Relationship (discharge)
Particle Size + Faceting (charge)

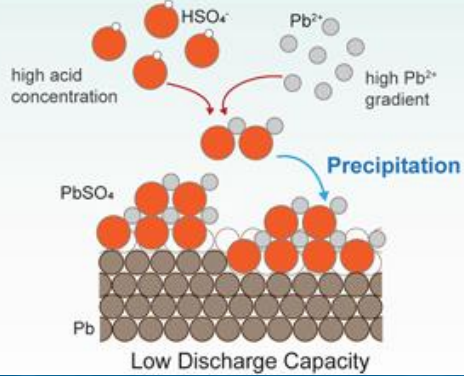
ACKNOWLEDGEMENTS



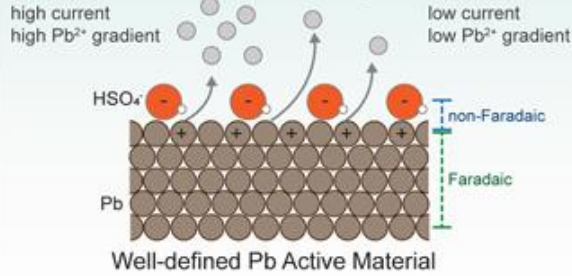
This work was supported by the Lead Battery Science Research Program (LBSRP).

b Nucleation and Growth (fast)

Fast Discharge / High Current

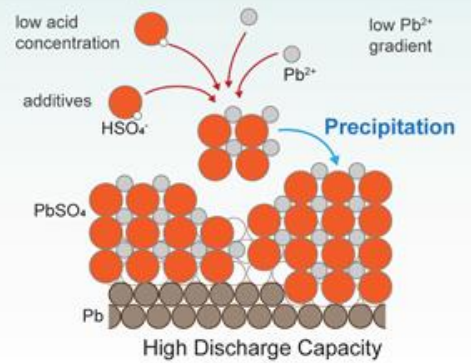


a Dissolution



c Nucleation and Growth (slow)

Slow Discharge / Low Current



J power sources 615 (2024) 235100

THANK YOU FOR YOUR ATTENTION

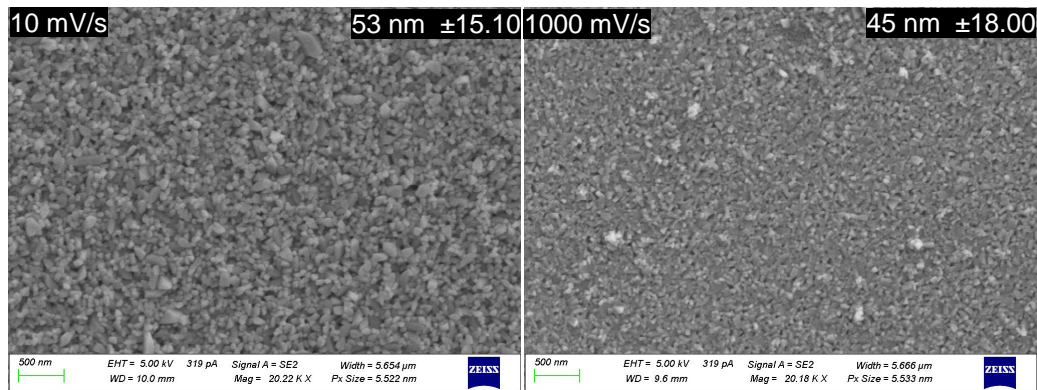
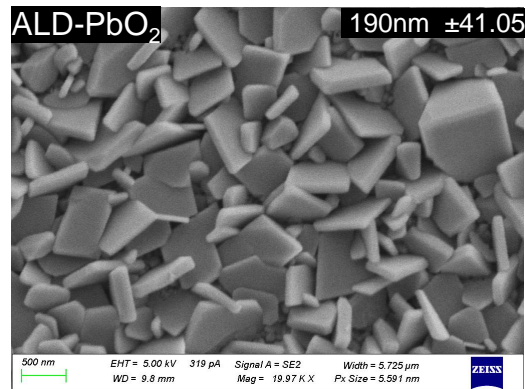
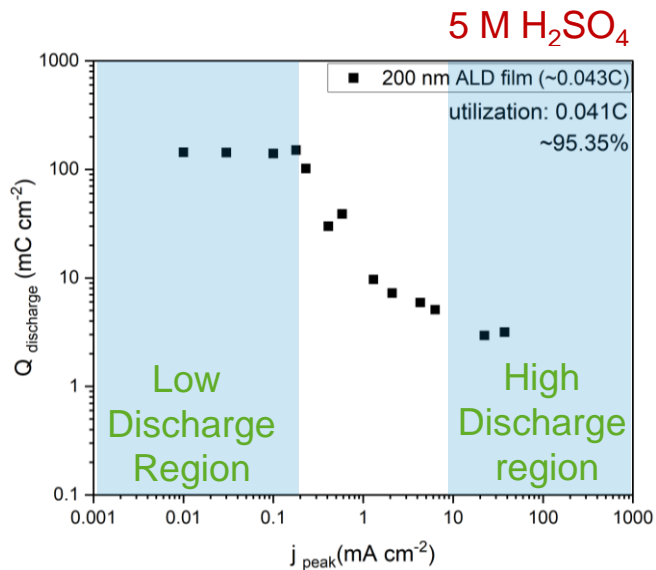
If anyone is hiring for a position that suits my background and experience : otford1@gmail.com

SCAN ME



Extras

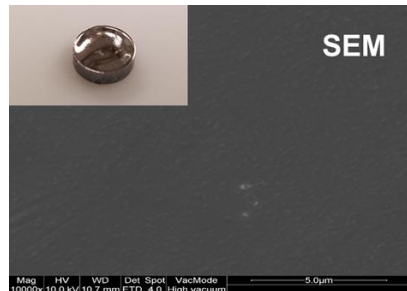
PEUKERT RELATIONSHIP PLATEAU FOR ALD-PbO₂



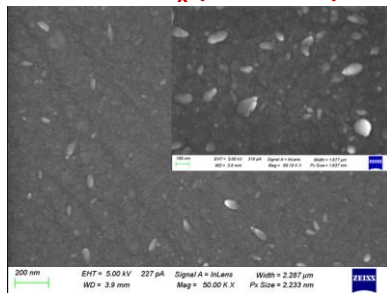
Discharge capacity plateau in ALD PbO_x
due to active material limitation
(~200nm) at low discharge currents.

THE ROAD FROM FLAT TO PASTED ELECTRODE

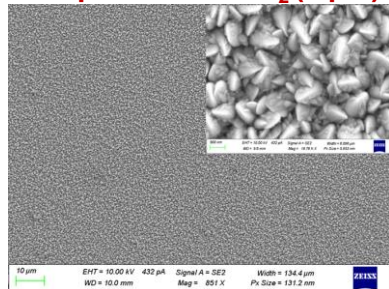
Flat Pb electrode



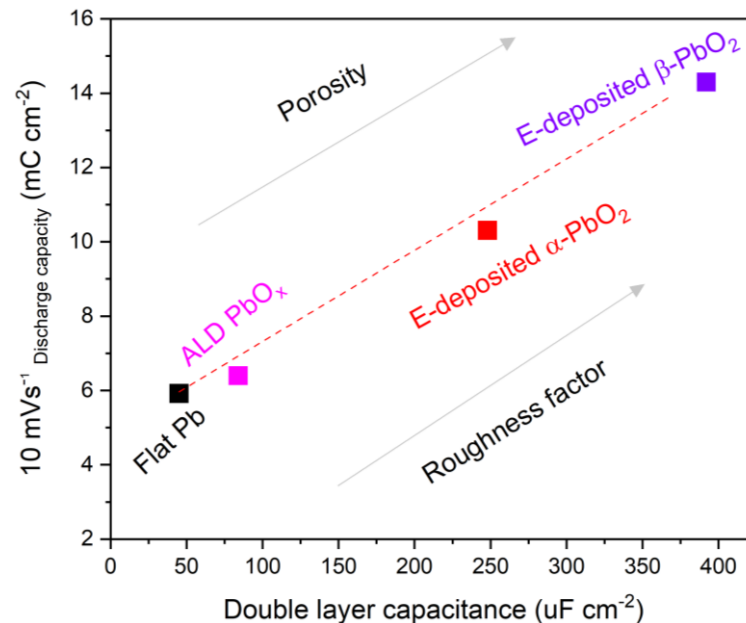
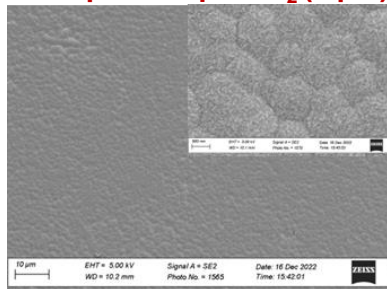
ALD PbO_x (~ 200 nm)



E-deposited α-PbO₂ (4 μm)



E-deposited β-PbO₂ (4 μm)



Beta PbO₂ shows higher ECSA which translate into higher discharge performance. Likely contributing factors **porosity** and **particle size**.