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CHANGES IN PAM COMPOSITION AND MORPHOLOGY DURING FORMATION AND CYCLING MEASURED BY IN SITU XRD



TIM FISTER,¹ TIFFANY KINNIBRUGH,² KEVIN KNEHR,¹ MOHAMMED EFFAT,¹ JAE JIN KIM,¹ SEONGJUN KIM,² JUAN GARCIA,¹ HAKIM IDDIR,¹ ZHENZHEN YANG,¹ JULIAN KOSACKI,³ MATTHEW SPENCE³

- 1. Argonne National Laboratory, Chemical Sciences and Engineering Division
- 2. Argonne National Laboratory, X-ray Science Division
- 3. Clarios, Glendale WI





INTRODUCTION



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RIPENING IN LEAD BATTERIES

Negative sulfation: similar issues in the positive?

- Grain growth is often ignored in the positive since the initial PbO₂ particle size is very nanoscale...
 - ...BUT: we find that PbO₂ crystal size *increases* rapidly during cycling (especially at high depth-of-discharge)
 - This leads to reduced conductivity, mechanical integrity associated with PAM softening/shedding. (related to "Kugelhaufen effect", "agglomeration of spheres," etc).
 - This process is reminiscent of PbSO₄ ripening during PSOC cycling, i.e. sulfation.
 - PbO₂ also becomes increasingly stoichiometric (freshly formed electrodes have PbO_{1+x} and Pb_{1-x}O₂H_y species)
- Big question: why is PbO₂ nanoscale after formation and can this inform how we cycle batteries?

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OUR APPROACH High energy synchrotron XRD

XRD is ideal tool to study crystallization:

- Refinements: electrode speciation
- Change in lattice constants: defects
- Line-shape: crystal domain size









OUR APPROACH High energy synchrotron XRD

XRD is ideal tool to study crystallization:

- Refinements: electrode speciation
- Change in lattice constants: defects
- Line-shape: crystal domain size
- Background: related, in part, to acid species

Not covered today, but in addition to electrode species, we can quantify the amount of electrolyte and its local concentration







OUR APPROACH High energy synchrotron XRD

XRD is ideal tool to study crystallization:

- Refinements: electrode speciation
- Change in lattice constants: defects
- Line-shape: crystal domain size
- Background: related, in part, to acid species

Our in-situ cells:

- Plante cell: controlled acid conditions
- Pasted cells: closer to commercial products...









OUTLINE

- Diffraction maps from commercial plates after formation: Effect of acid SG, temperature, soak time, and current density
- Changes in speciation and particle size after formation, initial cycling, and deep cycling.
- Positive-limited cells during cycling
- Plante cells: effect of acid SG on α, βPbO₂ activity and crystal structure changes from stoichiometric PbO₂.
- Summary





CHANGES IN PAM SPECIATION DURING FORMATION AND CYCLING



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CLARIOS CELLS 2N/1P test cells

- Three electrode cells using commercial SLI plates (plates are 90-100 g active material)
- PE separator
- 235 mL acid
- Cells were formed and PAM electrodes were vacuum sealed (in acid) and measured within 1-2 days (negligible self-discharge)



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DESIGN OF EXPERIMENT

Formation variables, cycling

- Initial formation variables: soak time, soak/formation temperature, acid SG, current density
 - Most important variables: acid SG and formation temperature
 - Focused on cells formed in 25C and 60C in 1080 and 1280 formation (and cell formed in neutral SG).

Cell #	Fill acid Temp C	Fill Cell Temp	Fill Acid SG	Pickle time, hr	Formation Temp	Current Density
F1	-18	-18	1.28	1	25	std
F3	25	25	1.28	1	25	std
F5	40	25	1.28	1	25	std
F7	25	25	1.08	1	25	std
F9	25	25	1.08	1	60	std
F11	25	25	1.18	1	60	std
F13	25	25	1.28	1	60	std
F15	25	25	1.28	1	25	low
F17	-18	-18	1.08	1	25	low
E10	25	25	60g/LNo2SO4	1	25	etd

Cell	Fill	Fill Acid	Pickle	Form	Current			
#	Temp	SG	time, hr	Temp	Density	Stop Point	Beamtime	Measurement
G1	25	1.28	1	25	std	After Formation (repeat)	Feb 10-12	After formation
G2	25	1.28	1	25	std	After RC conditioning cycles	Feb 10-12	After 5 cycles
G3	25	1.28	1	25	std	Spare (ANL in situ cell)	Feb, April	Spare (at ANL)
G4	25	1.28	1	25	std	After 2 months Cycling 80%DoD	April 4-5	After 2 months cycling
P1	25	1.28	0.25	25	std	After Formation (short pickle)	Feb 10-12	Short pickle
G5	25	1.08	1	25	std	After Formation (repeat)	Feb 10-12	After formation
G6	25	1.08	1	25	std	After RC conditioning cycles	Feb 10-12	After 5 cycles
G7	25	1.08	1	25	std	Spare (ANL in situ cell)	Feb, April	Spare (at ANL)
G8	25	1.08	1	25	std	After 2 months Cycling 80%DoD	April 4-5	After 2 months cycling
P2	25	1.08	0.25	25	std	After Formation (short pickle)	Feb 10-12	Short pickle
G9	25	1.08	1	60	std	After Formation (repeat)	Feb 10-12	After formation
G10	25	1.08	1	60	std	After RC conditioning cycles	Feb 10-12	After 5 cycles
G11	25	1.08	1	60	std	Spare (ANL in situ cell)	Feb, April	Spare (at ANL)
G12	25	1.08	1	60	std	After 2 months Cycling 80%DoD	April 4-5	After 2 months cycling
P3	25	1.08	0.25	60	std	After Formation (short pickle)	Feb 10-12	Short pickle
G13	25	1.28	1	60	std	After Formation (repeat)	Feb 10-12	After formation
G14	25	1.28	1	60	std	After RC conditioning cycles	Feb 10-12	After 5 cycles
G15	25	1.28	1	60	std	Spare (ANL in situ cell)	Feb, April	Spare (at ANL)
G16	25	1.28	1	60	std	After 2 months Cycling 80%DoD	April 4-5	After 2 months cycling
P4	25	1.28	0.25	60	std	After Formation (short pickle)	Feb 10-12	Short pickle
G17	25	1.00*	1	25	std	After Formation (repeat)	Feb 10-12	After formation
G18	25	1.00*	1	25	std	After RC conditioning cycles	Feb 10-12	After 5 cycles
G19	25	1.00*	1	25	std	Spare (in situ cell)	Feb, April	Spare (at ANL)
G20	25	1.00*	1	25	std	After 2 months Cycling 80%DoD	April 4-5	After 2 months cycling
P5	25	1.00*	0.25	25	std	After Formation (short pickle)	Feb 10-12	Short pickle





MACROCELL FORMATION

Variation with fill temperature, form temperature, SG, and current

Maps of XRD fits to Pb, βPbO₂, PbSO₄, αPbO, and αPbO₂.



MAPS Summarizing 19844 pts

 Use lead and overall signal maps to create 'regions of interest' (ROIs) corresponding to the overall electrode, the lead grid, and the active material that does not overlap the grid.





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SUMMARY Overall composition Summary of fits for each

First row includes all points on the electrode map.

map:

- Second row includes points in grid region of interest (ROI), about 37% of points.
- Last row are points not overlapping grid. Pb signal here represents free lead signal.



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RESULTS **SG/T** matrix

Temperature, acid SG most important variables:

- Temperature crucial for converting PbO to PbSO₄ during soak.
- Electrolyte alkalinity at start of formation determines αPbO_2 content.

1080SG

Slowest conversion of PbO

to PbSO₄. Due to slow

after soak does not

charge: PbO surface

conversion to PbSO₄.

converted to $PbSO_4$.

Inefficient formation, lowest-capacity cell.

25C

60C

conversion, acid remains

acidic and residual PbO

convert to PbO2. Start of

During discharge, surface

PbO_x reduces and can be

PbSO₄. PbSO₄ in alkaline

pH at start of charge and

converts to αPbO₂. This

 βPbO_2 growth. (reason for

enhanced αPbO_2 near grid

in factory plates since PAM

formation propagates from

grid). Largest PbO₂ crystals

due highest solubility during

lowers pH, leading to

charge.

after formation (mol%) 0 0 00 0 00 11% oPbO2 46% aPbO Composition a oxidizes (to PbO_x), stopping 36% BPbO2 4% Ph G5: 25C 1.08SG formed after formation (mol%) Faster conversion of PbO to 37% oPbO2 8% oPbO

43% BPbO2

10% Pb

G9: 60C

1.08SG

formed

Composition a

0

PbSO₄ (though slows with time as acid SG is reduced). Due to high starting SG: electrolyte remains acidic and only βPbO_2 produced during formation. Amount of PbO strongly affected by soak time (see short soak P-series tests). Fastest conversion of PbO to PbSO₄ during soak. For these cells, acid is not neutralized. leading to highest βPbO₂ content at end of formation and highest initial capacity.

Lower-pH: faster

conversion of PbO to

1280SG



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DESIGN OF EXPERIMENT Formation variables, cycling

- Initial formation variables: soak time, soak/formation temperature, acid SG, current density
 - Most important variables: acid SG and formation temperature
 - Focused on cells formed in 25C and 60C in 1080 and 1280 formation (and cell formed in neutral SG).
- Cycling:
 - Replace formation acid with 1280SG
 - "Conditioning:" 100% DOD, 5 cycles (5A = C/1.5), increase in capacity
 - "Cycling:" 80%DOD, ~50 cycles (0.75A = C/20), decrease in capacity
 - "End of life" (not shown).

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EXAMPLE G9-12

1080+60C formation

- After formation: high αPbO_2 content, especially near grid.
- After 5 conditioning cycles: 10% conversion of αPbO_2 to βPbO_2 .
- Near end-of-life: almost entirely βPbO_2 . Some PbO, αPbO_2 remaining near grid.



SPECIES Analysis of 206,550 XRD patterns

- Despite having very different compositions after formation, all batteries approach similar composition after 20-30 cycles.
- αPbO₂ more resilient than PbO during this process.







MORPHOLOGY: CRYSTALLITE SIZE Scherrer equation

- Particle size ~ λ /(FWHM resolution)
- Resolution from Pb lines (~0.018 deg)
- Particle size maps using βPbO₂ 110 line
 - Particle ripening with cycling
 - Increasing heterogeneity, larger particles at top of cell.





PARTICLE SIZE MAPS Changes in βPbO₂ with cycling

Right: evolution of particle size distribution using histogram of βPbO_2 crystal size over entire plate.

- After formation, βPbO₂ is extremely nanoscale and uniform over plate.
 - Exceptions are high-T samples, especially in dilute (i.e. high solubility) conditions.
- Cycling leads to rapid ripening of the βPbO₂. Distribution becomes more heterogeneous, with larger crystals near top (where electrolyte is more dilute).
- The particle size distribution, using entire map as input, is another way to show this trend (note that size is reported on log-scale).







IN SITU CYCLING: POSITIVE LIMITED CELL



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OPERANDO CYCLING Cells, cycling

- NPN cells using DUF Clarios plates. Previously discussed June 2023. Two cells were cycled in situ:
 - G7: Formed in 1080+25C = high α PbO
 - G11: Formed in 1080+60C = high αPbO_2 .
- Acid was switched to 1280 for cycling; cells were precycled 5 times.





Using "conditioning" cycles from Spence: 5A discharge/3A charge (130%). Incorporated 45 min. rests to obtain a fully charged/fully discharged map for each cell. First three cycles ~65% DOD, last three cycles at 100%DOD.

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MAPS: G11 (HIGH αPbO₂ ELECTRODE) Overall phase fractions

- Maps include all three electrodes (2 neg, 1 pos)
- Example, at start.
 - ~2/3 of the signal is from the negative electrodes (i.e. Pb).
 - Plates are not perfectly aligned (see sides). PAM grid is visible in PbO, PbO₂ maps.
 - Some variation in PAM species signal (more αPbO_2 at top)





MAPS: G11 Overall phase fractions

Similar phase fractions as previous analysis.

- PbSO₄ content consistent with cell utilization.
- See α→βPbO₂ conversion over 6 cycles.





CELL MAPS G11: 65%DOD cycling

- Compositions similar to previous analysis.
- One new finding: αPbO₂ is active during discharge *and* charge...







CELL MAPS

G11: 100%DOD cycling

- Compositions similar to previous analysis.
- One new finding: αPbO₂ is active during discharge and charge...



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G11: SOC Overall trends

- Pb, βPbO₂, and PbSO₄ proportional to linear changes in SOC (below 100%SOC).
- Gradual consumption of αPbO and αPbO₂.
- Unlike previous analysis, we can resolve some reversibility in αPbO₂...



β - vs α-PbO₂ ~60% DOD: a closer look

For this plot: normalize to initial wt% to understand utilization of each species.

- Both PbO₂ phases are active, but much higher utilization for βPbO₂: ~35% vs. ~5-10% for αPbO₂.
 - In other words: only ~15-20% charge carried by αPbO_2 at 60% DOD.

β - vs α-PbO₂ 100% DOD: a closer look

For this plot: normalize to initial wt% to understand utilization of each species.

- Both PbO₂ phases are active, but much higher utilization for βPbO₂: ~50% vs. 11% for αPbO₂.
 - In other words: 22% charge carried by αPbO_2 at 100% DOD.
- Growth/dissolution rate of βPbO₂ is largely linear with SOC. This is NOT the case with αPbO₂.
 - Dissolution (charge) and growth (discharge) is faster at low SOC

β - vs α-PbO₂ 100% DOD: a closer look

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- Both PbO₂ phases are active, but much higher utilization for βPbO₂: ~50% vs. 11% for αPbO₂.
 - In other words: 22% charge carried by αPbO_2 at 100% DOD.
- Growth/dissolution rate of βPbO₂ is largely linear with SOC. This is NOT the case with αPbO₂.
 - Dissolution (charge) and growth (discharge) is faster at low SOC
- Conversion of $\alpha \rightarrow \beta PbO_2$ 130% faster at 100%DOD than 65%DOD.

DEEP DISCHARGE:

Simulating 5A discharge at 1.280 SG

- June 2023: Knehr/Effat simulation of 1280 2N/1P cell at 5 A:
 - **PAM is acid limited** at 7.3 Ah (100%DOD) at 5 A.
 - Near end of discharge PAM is at neutral (or even alkaline!) pH:
 - Lower SG

RIPENING

βPbO₂ crystallite size

- See consistent shrinking/growing of PbO₂ during discharge and charge.
- Ripening (i.e. growth over repeated cycles) is faster at 100%DOD.
 - Effect is most pronounced near the top of the battery.
 - Better charge acceptance (PbSO₄ growth) at bottom of plate could be related to smaller PbO₂.

PLANTE CELLS AT HIGH POTENTIALS: CONTROLLED pH AND DYNAMIC DEFECTS

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IN SITU STUDIES: PLANTE CELLS

X-ray scattering from a lead surface

- Example: APS, 13BMC
- Energy = 28 keV (λ = 0.43 Å)

Beam defining optics, slits, detectors

Sample (echem cell) Detector (Pilatus1M)

Potentiostat

OVERVIEW

Cycling at well defined acid concentrations

- Higher acid SG (first cycles): changes mostly from βPbO₂, similar difference in α/β activity as pasted cells.
- Note that αPbO₂ is still active during discharge and charge (same as paste results)
- Neutral acid conditions: 50/50 α/β PbO₂.
- Alkaline conditions (not shown): only αPbO₂.

1080SG 2mV/s Changes in crystal structure

In addition to composition, changes in *crystal structure* (lattice constants) was found during cycling. These changes are likely due to lattice defects.

- In general, βPbO₂ deviates 'pure' (stochiometric) values, especially at end of charge, at high potential.
 - Deviation is consistent with Pb vacancies (DFT)

c" lattice parameter

Tetragonal (rutile) βPbO₂

"a" lattice parameter

Similar changes found in 1240 and 1000SG samples.

COMPARISON WITH PREVIOUS LITERATURE Individual lattice constants

Defects in PbO₂ were previously characterized using NMR and neutron diffraction:

Summary of neutron scattering literature:

- Squares = chemical βPbO₂
- Circles = electrochemical βPbO₂
- Numbers = degree of cycling.

Main trends:

- Cycling leads to more stoichiometric PbO₂.
- High variability in a and c lattice constants between studies...

COMPARISON WITH PREVIOUS LITERATURE Individual lattice constants

- Clear trends can be found by looking at the *ratio* of the a- and c-lattice constants ('tetragonality').
 - Chemical PbO_2 = low tetragonality (~1.463)
 - Ex situ electrochemical PbO₂
 = higher tetragonality (~1.466)
 - In situ cycling (previous pasted cells): 1.468
 - In situ Plante studies:
 1.466 1.47 (higher at high potential)
- Exact Pb, H occupancy not known: still need neutrons!

SUMMARY AND MECHANISMS: pH, SPECIES, DEFECTS, STRAIN, AND RIPENING

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SUMMARY: SPECIES α vs βPbO₂, residual PbO

- During cycling, both α and βPbO₂ are active, with increased αPbO₂ activity at higher pH.
 - High $βPbO_2$ content = higher initial capacity, but poor cycle life.
 - Managing DOD and charge/discharge rates important for preserving αPbO_2
- During formation, local alkalinity most present in low SG or at high temperature, which promotes PbO + HSO₄⁻ → PbSO₄ + OH⁻ conversion.
- During charge (during formation or cycling), PbO in PAM is resistant to dissolution.
 - Likely due to surface PbO_{1+x} layer that resembles corrosion layer species (litharge-like PbO_{1.5} and PbO_{1.67}: Kinnibrugh, Inorganic Chem. 2024).
 - Evidence: PbO lattice *expansion* during charge, deviating from stochiometric litharge

Change in PbO_{1+x} during cycling for cell G7 (high PbO content). Note the change in clattice constant, consistent with oxidation of PbO to PbO_{1+x} (litharge c = 5.01 Å)

DEFECTS

Guidance from DFT

- Thermodynamics: relatively low energy barriers for lead vacancies in both α- and β-PbO₂.
 - H⁺ concentration is variable, likely varies during cycling with potential.
 - Defects give higher electronic conductivity.
 - Defects favored at high potential and high pH (low SG)
- Kinetics (AIMD):
 - Defect energetics smaller at surface than in bulk: likely a growth defect
 - H⁺ mobility much higher in β-PbO₂ than α-PbO₂, but largely localized to Pb vacancy.

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EFFECT ON CRYSTAL SIZE

Lattice defects (strain) prevents ripening

Lattice defects and particle size are interconnected:

- Correlation: Pb vacancies (and H interstitials) likely form during growth; smaller particles = more defects.
- Causation: defects lead to localized lattice strain within PbO₂. Strain and chemical mismatch inhibits further growth, leading to smaller particle size.
 - Higher current, temperature, and acid SG during charge also contributes to particle size (from formation study).
 - Deep discharge helps release/remove defects. Since PbO2 is never fully dissolved during discharge, heterogeneous nucleation can lead to progressive ripening (analogous to sulfation during PSOC cycling).

Future *coherent* diffraction in the \$815M APS Upgrade is the perfect technique for measuring lattice defects and strain.

Coherent diffraction reconstructions of PbSO₄ nanoparticles (Suzana, Papa Lopes). Can we do similar things for PbO₂?

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