September 17, 2024

Methods of Modifying Structures of Lead Acid Battery Active Materials

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ELBC
16–19 September
Milan, Italy 2024

Background

- Both positive and negative electrodes in lead acid batteries are porous electrodes. Battery performance strongly depends on pore structures.
- Most of those electrodes begin with paste mixing: leady oxide, additives, water, and sulfuric acid were mixed into paste, followed by grid pasting, curing, and formation.
- For 3BS based paste formula, by varying the paste composition, pore structures are mainly decided after paste mixing.
- Another way of modifying pore structure is to control the 4BS crystal size and amount after curing.
- 4BS crystal growth can be affected by two ways: thermodynamically and kinetically.

Background

THERMODYNAMIC WAY: Change soluble Pb concentration

- Two ways to change soluble Pb concentration in paste: temperature and pH
- As shown in the figure, total soluble lead in aqueous solution with SO_4^{2-} is strongly pH related. It is the lowest around pH 9.3. Further from this pH, the higher the solubility.
- Below pH 9.3 4BS is not stable, above this pH, 4BS is stable.
- Increase paste pH, should increase the concentration of soluble lead, increase the supply of material for 4BS growth.

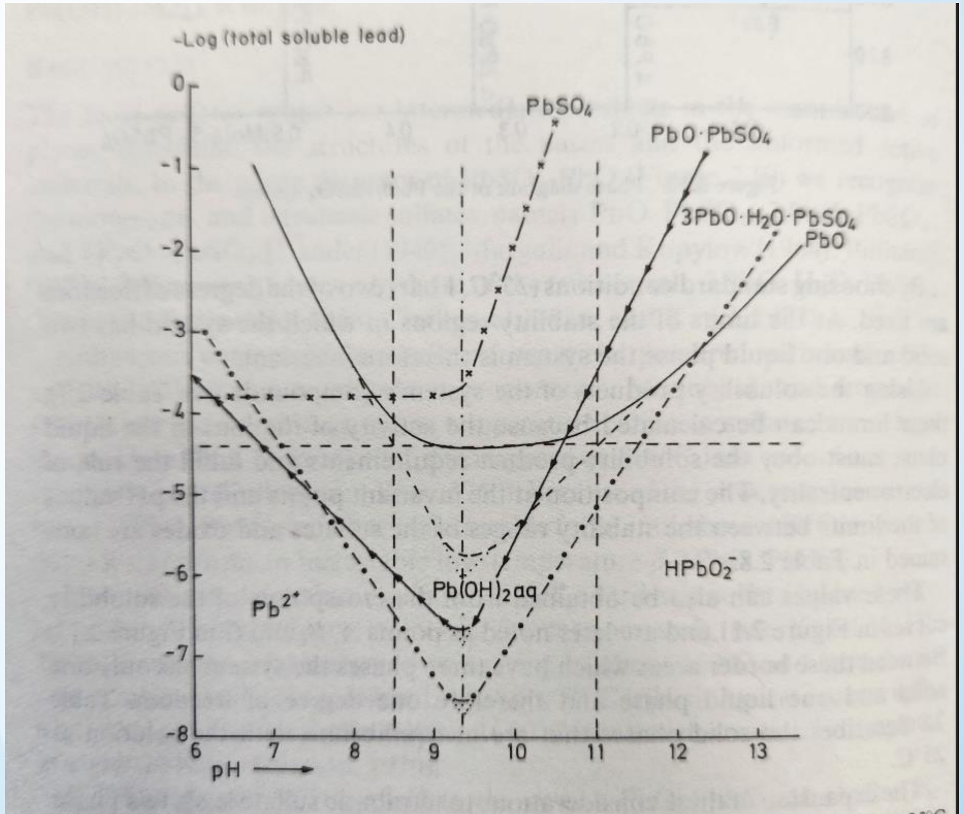


Figure 2.11 Solubility of sulfate-containing components and tetragonal Pb(II) oxide at 25°C and a sulfate ion activity of 10^{-4} as a function of the pH value of the solution.

Lead Acid Batteries, Hans Bode, 1977, p30

Background

<u>KINETIC WAY: Change the rate of soluble lead reaching 4BS surface</u>

- Temperature affects the diffusing rate of soluble lead
- Surface area of 4BS crystals
- Electro-Osmotic Pumping*: movement of liquid by electro-osmotic flow
- Steric Hndrance: slows down the soluble lead reaching 4BS crystal surface
  - Some inert materials block the ways of mass transfer in wet paste, like red lead in the paste
  - Some molecules absorb onto the surface of leady material, preventing soluble lead material from leaving the surface of raw material and reaching the surface of 4BS crystals

*S.V. Baker, P.T. Moseley, A.D. Turner, J. Power Sources 27 (1989) 127–143.

Test Plan: 2 Phases

Phase I: 4BS Crystal Growth Curing Study

- 5% H_2SO_4 in paste, 1.0% SureCure 100 (SC100) 4BS seeds as control, adding other additive to make paste.
- pH agent is a chemical material that can increase paste pH when added to the paste in a small amount.
- β-PbO is the less stable isomorphic phase of PbO in room temperature, it is supposed to be higher solubility than α-PbO in room temperature.
- Lignosulfonate are widely used in expander formulas. There are reports that Vanisperse prevent 4BS crystal growth in negative plates. In this presentation, we report the effect of Vanisperse A (Van A) and Vanisperse HT-1 (HT-1) on 4BS growth and electrochemical performance in positives.
- Curing: 55°C, ~99% RH 48 hours followed by 60°C drying for 24 hours.

Mix ID	4BS seeds	4BS seeds%	Other additive	Other additive%
SC100	SC100	1.0%	none	0.0%
SC+pH agent	SC100	1.0%	pH agent	0.1%
SC+β-PbO	SC100	1.0%	β-PbO	10.0%
SC+Graphite	SC100	1.0%	Graphite	1.0%
SC+Van A	SC100	1.0%	Vanisperse A	0.1%
SC+HT-1	SC100	1.0%	Vanisperse HT-1	0.1%

Test Plan: 2 Phases

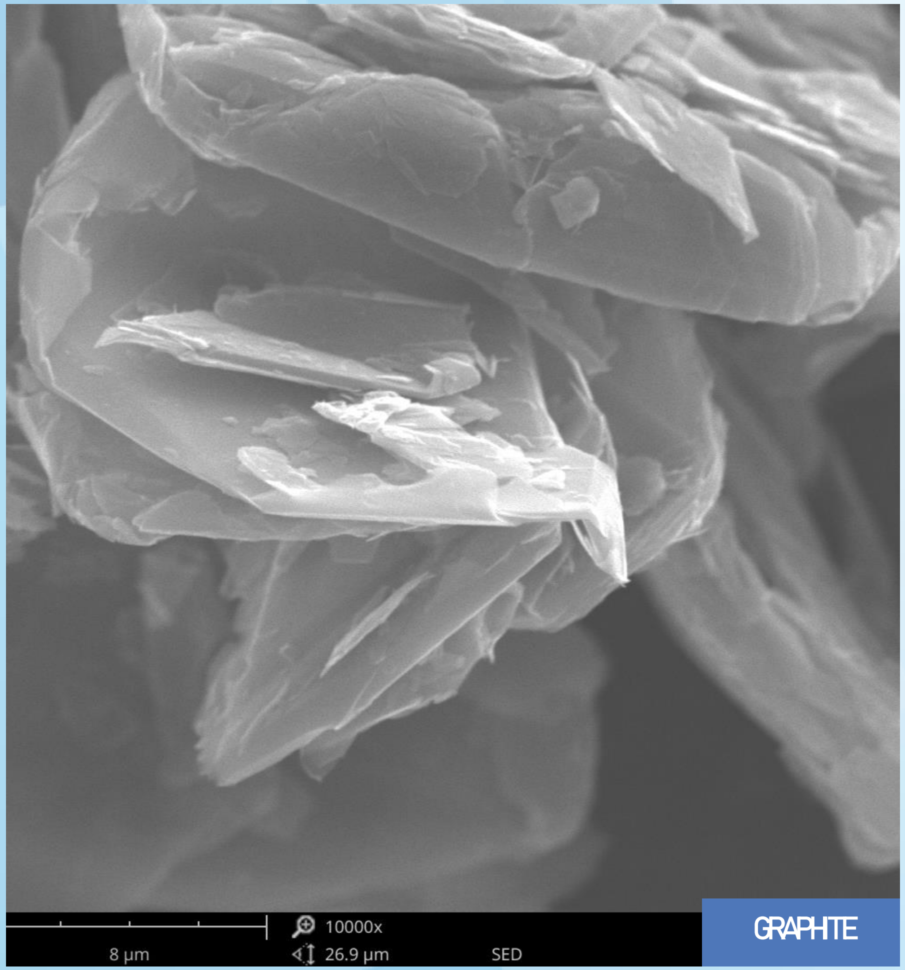
Phase II: Cell Test

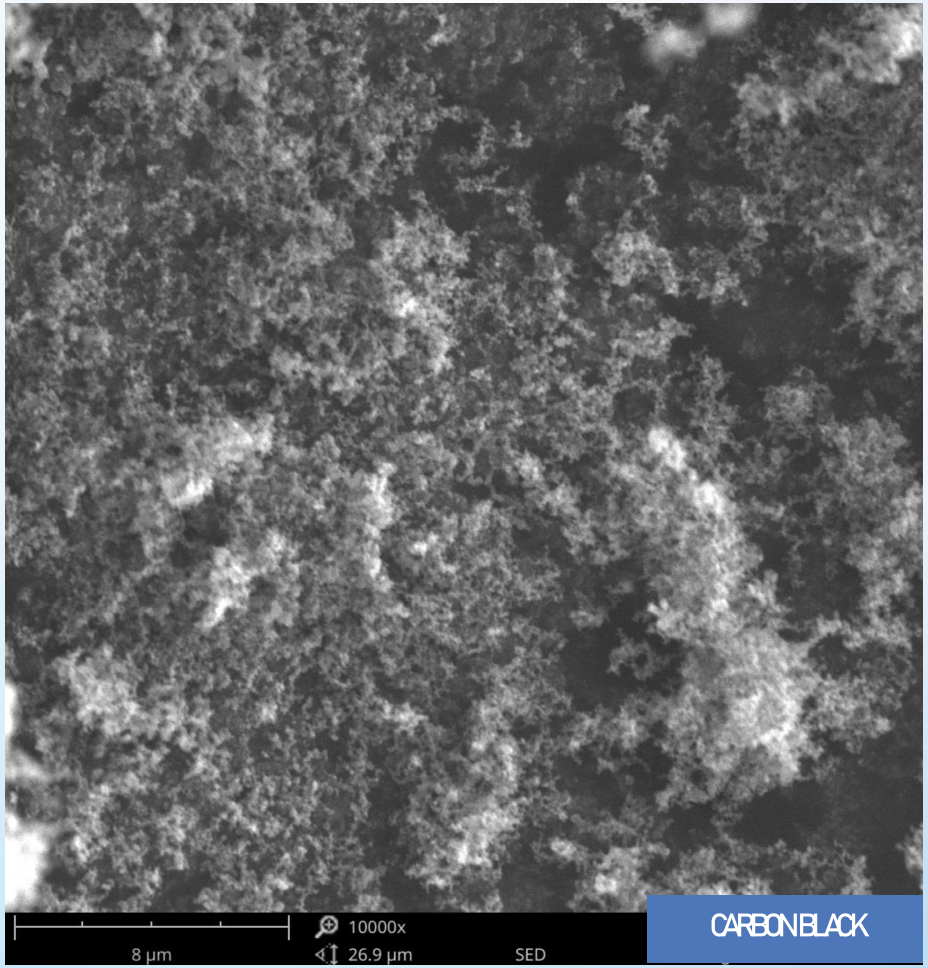
- Same paste formula and curing profile as Phase I except the difference in "other additive", details listed below:
- Those pasted plates used as positives, 2P3N cell structure.

Cell formation
C20
CCA-1
Reserve Capacity 1
CCA-2
Reserve Capacity 2
Gassing Test
qDCA Test
Peukert Test

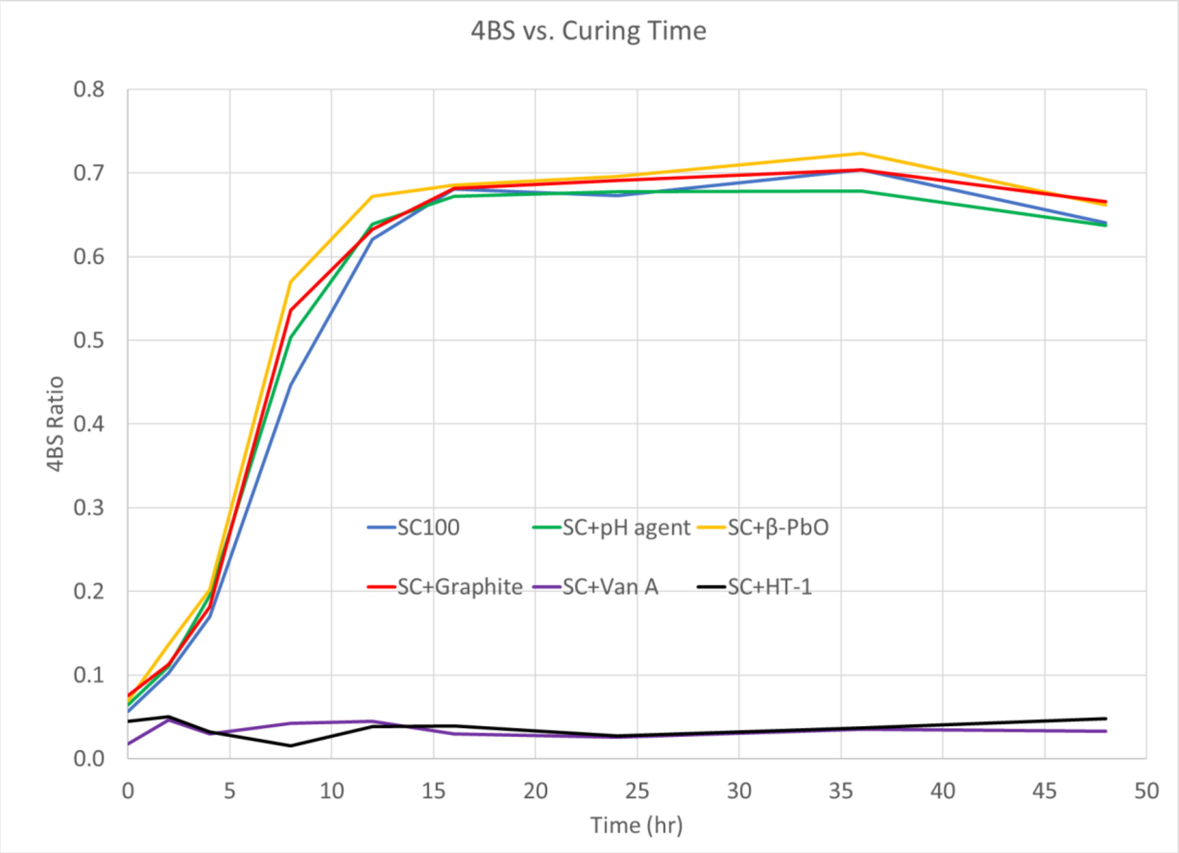
Mix ID	4BS seeds	SC100	Other additive	Other additive
3BS	none	0.0%	none	0.0%
4BS	SC100	1.0%	none	0.0%
SC+pH agent	SC100	1.0%	pH agent	0.1%
SC+β-PbO	SC100	1.0%	β-PbO	10.0%
SC+Graphite	SC100	1.0%	Graphite	1.0%
SC+Van A	SC100	1.0%	Vanisperse A	0.1%
SC+HT-1	SC100	1.0%	Vanisperse HT-1	0.1%
SC+CB	SC100	1.0%	Carbon Black	1.0%

SEM: Graphite vs. Carbon Black





Phase I: Cured AM Analysis- 4BS vs. Curing Time



SOME OBSERVATIONS:

- Very little change in 4BS contents with SC+Van A and SC+HT-1 pastes during curing.
- 4BS finished growth in first 12 to 16 hours of curing for SC100, SC+pH agent, SC+β-PbO and SC+Graphite paste.
- In the first 12 hours of curing, 4BS in SC+pH agent, SC+β-PbO and SC+Graphite paste are higher than 4BS in SC100 paste.

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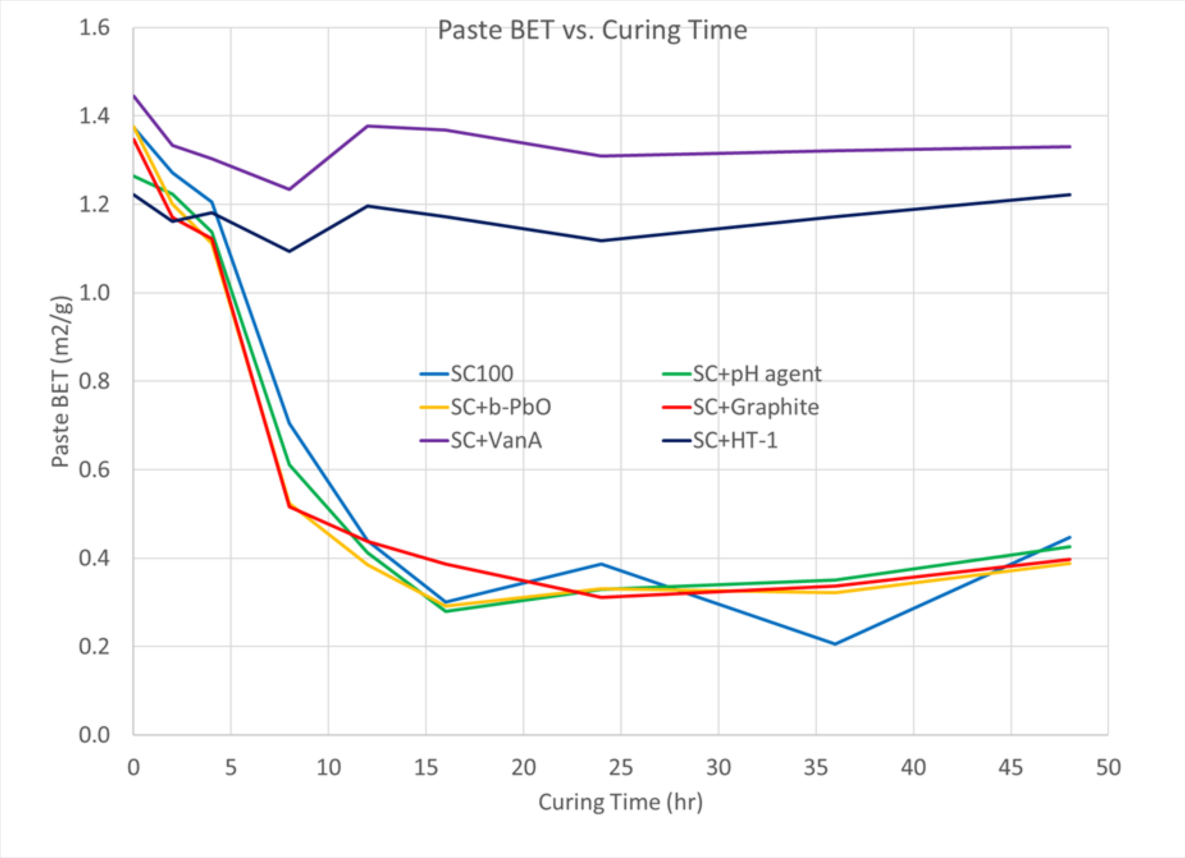
Phase I: Cured AM Analysis- BET vs. Curing Time



SOME OBSERVATIONS:

- Very little change in BET of SC+Van A and SC+HT-1 pastes during all 48 hours of curing.
- BET of all the four 4BS pastes reduced in first 16 hours of curing.
- BET of SC+HT-1 paste is lower than that of SC+Van A paste during all 48-hour curing period.
- From time 2 to 12 hours of curing, BET of SC+pH agent, SC+β-PbO and SC+Graphite pastes are lower than that of SC100 paste.

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Phase II: Cell Test Paste pH

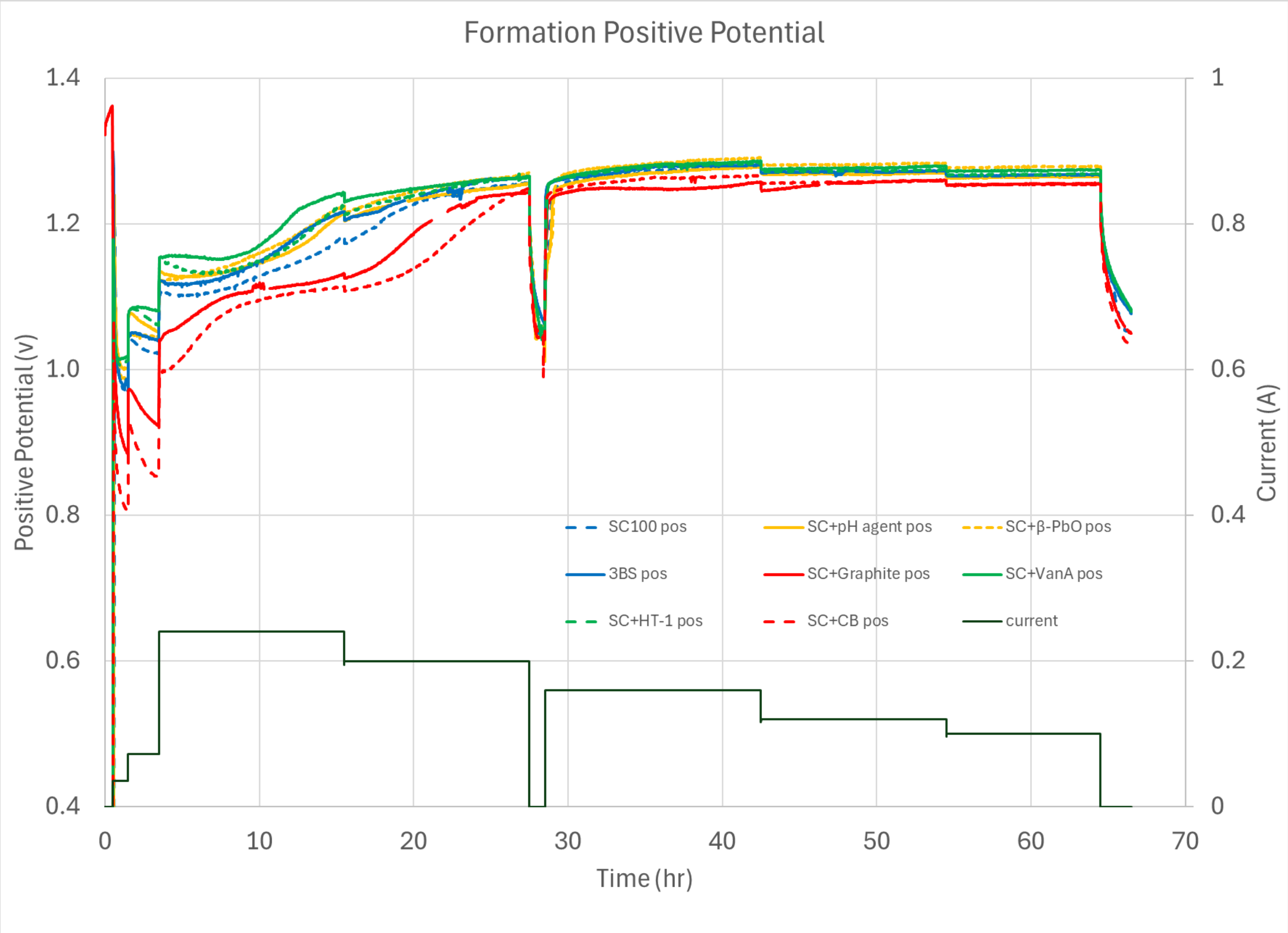
To test the electrochemical performance of these additives, 2nd batch of pastes were made. Paste formula and its pH was listed below:

SOME OBSERVATIONS:

- 0.1% of pH agent significantly increased the pH of paste.
- 10% β-PbO (total oxide: 10% β-PbO + 90% of leady oxide) can slightly increase paste pH
- Both Vanisperse A and Vanisperse HT-1 can increase pH of the paste.
- Graphite and carbon black showed little effect on paste pH

Mix ID	SC100	Other additive	PH
3BS	0.0%	0.0%	10.29±0.03
SC100	1.0%	0.0%	10.25±0.01
SC+pH agent	1.0%	0.1%	10.91±0.02
SC+β-PbO	1.0%	10.0%	10.39±0.01
SC+Graphite	1.0%	1.0%	10.26±0.01
SC+Van A	1.0%	0.1%	10.64±0.02
SC+HT-1	1.0%	0.1%	10.72±0.01
SC+CarbonBlack	1.0%	1.0%	10.35±0.01

Phase II: Cell Test Cell Formation



Formation was performed in 40°C water bath.

SOME OBSERVATIONS:

Comparing to no additives

- pH agent and β-PbO show very similar positive potential/polarization as no other additives (3BS and SC100).
- Graphite and carbon black in positive paste can reduce formation positive potential/polarization.
- Vanisperse A and HT-1 in positive paste increase positive potential/polarization during formation.

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Phase II: Cell Test Cell Formation

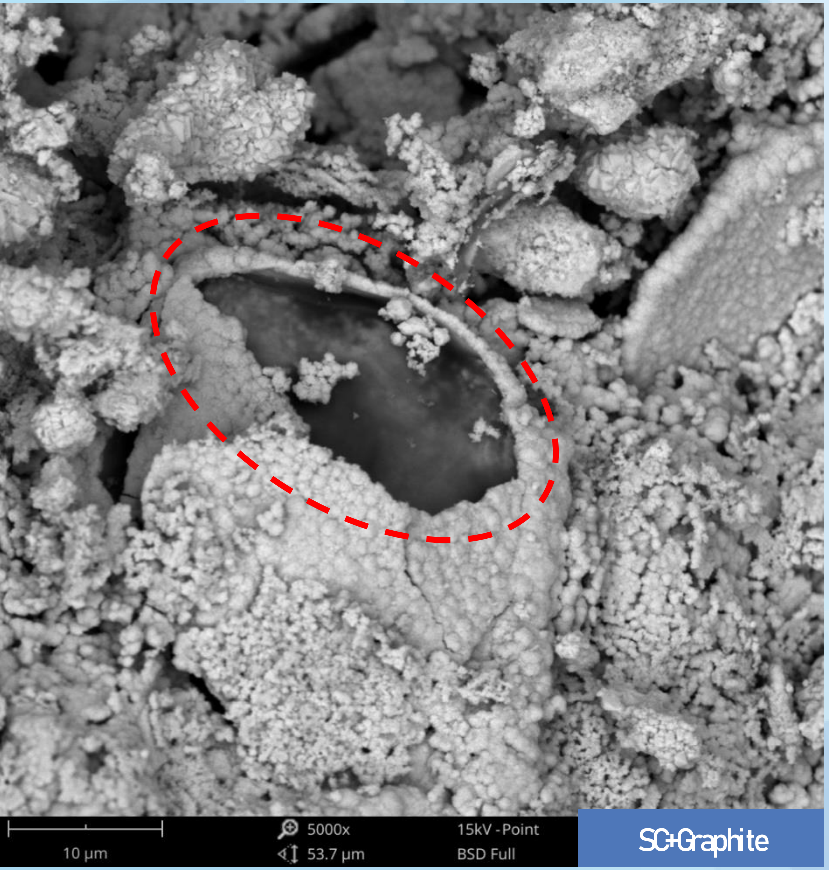
After formation, positive plates were washed acid free, dried for material analysis.

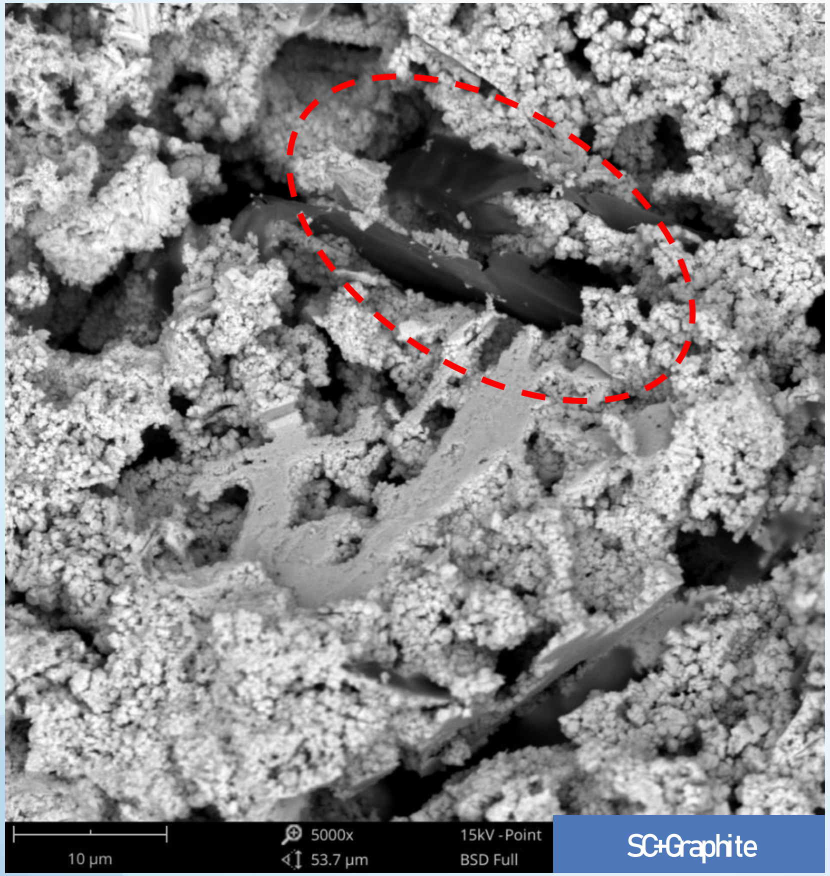
SOME OBSERVATIONS:

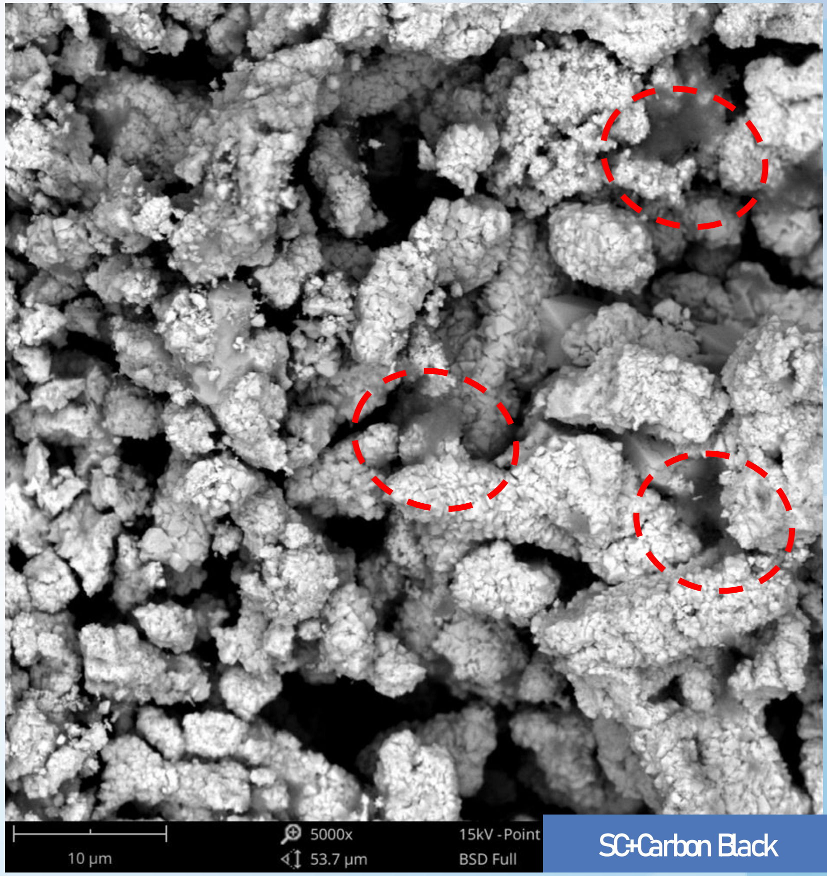
- Graphite and carbon black in positive paste can increase α-PbO_2 in positive plates after formation.
- Vanisperse A and HT-1 in positive paste don't show effect on α-PbO_2 in positive plates after formation.

Paste	α-PbO	α-PbO2	β-PbO2	PbSO4	BET (m2/g)
3BS	8.0%	12.8%	79.0%	0.2%	3.60
SC100	10.3%	17.7%	72.1%	0.0%	5.00
SC+pH agent	9.0%	9.2%	81.9%	0.0%	5.78
SC+β-PbO	5.7%	9.7%	84.6%	0.0%	5.41
SC+Graphite	5.3%	24.6%	69.7%	0.4%	3.73
SC+Van A	7.5%	14.3%	77.0%	1.2%	5.57
SC+HT-1	5.7%	15.7%	77.6%	1.0%	4.42
SC+CB	1.9%	23.9%	72.6%	1.7%	3.78

Phase II: Cell Test – After Formation PAM SEM







SOME OBSERVATIONS:

- Graphite and carbon black were observed in after formation PAM
- In some SEMs, graphite was observed encapsulated in a shell by active material, while no such phenomena was observed with carbon black plate.

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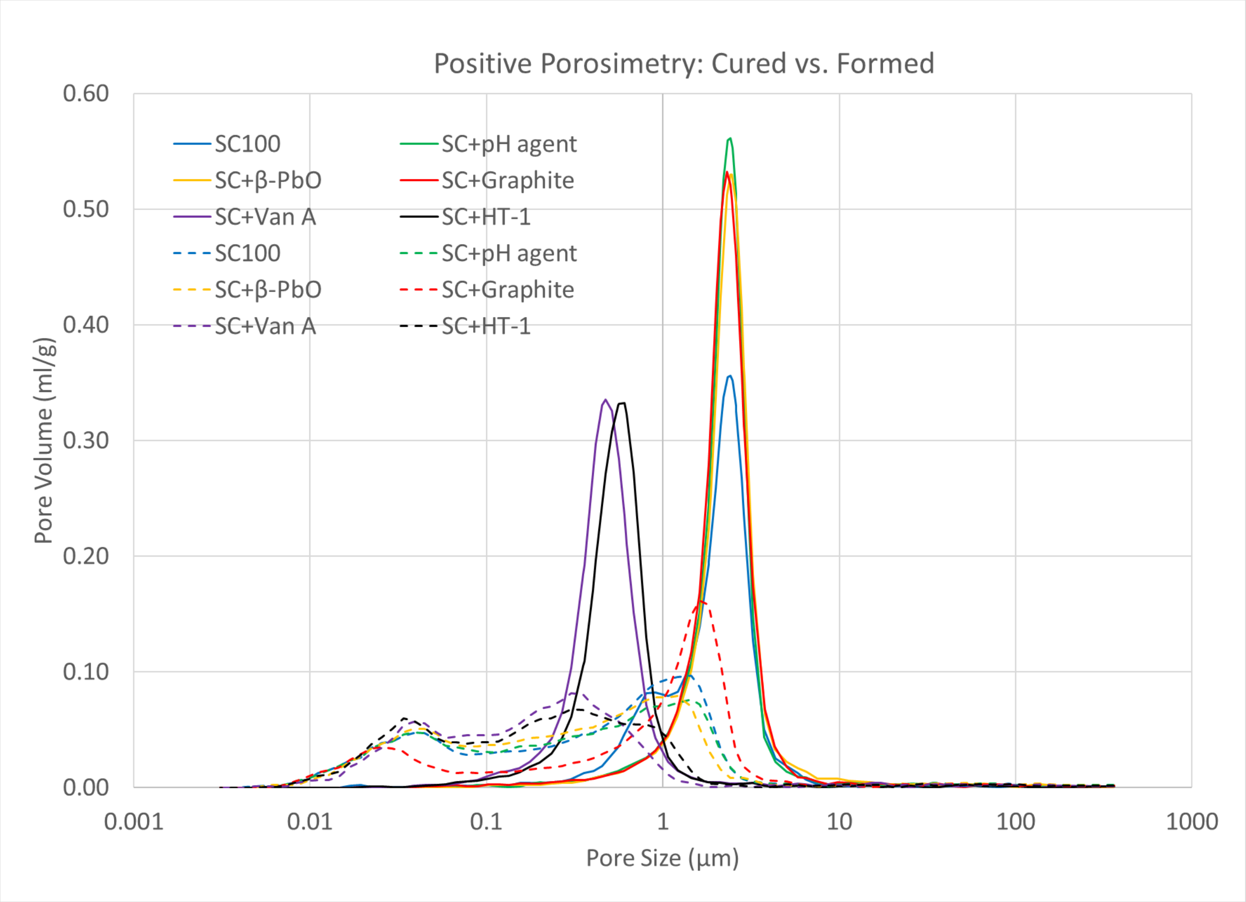
Hg Porosimetry: Cured vs. Formed



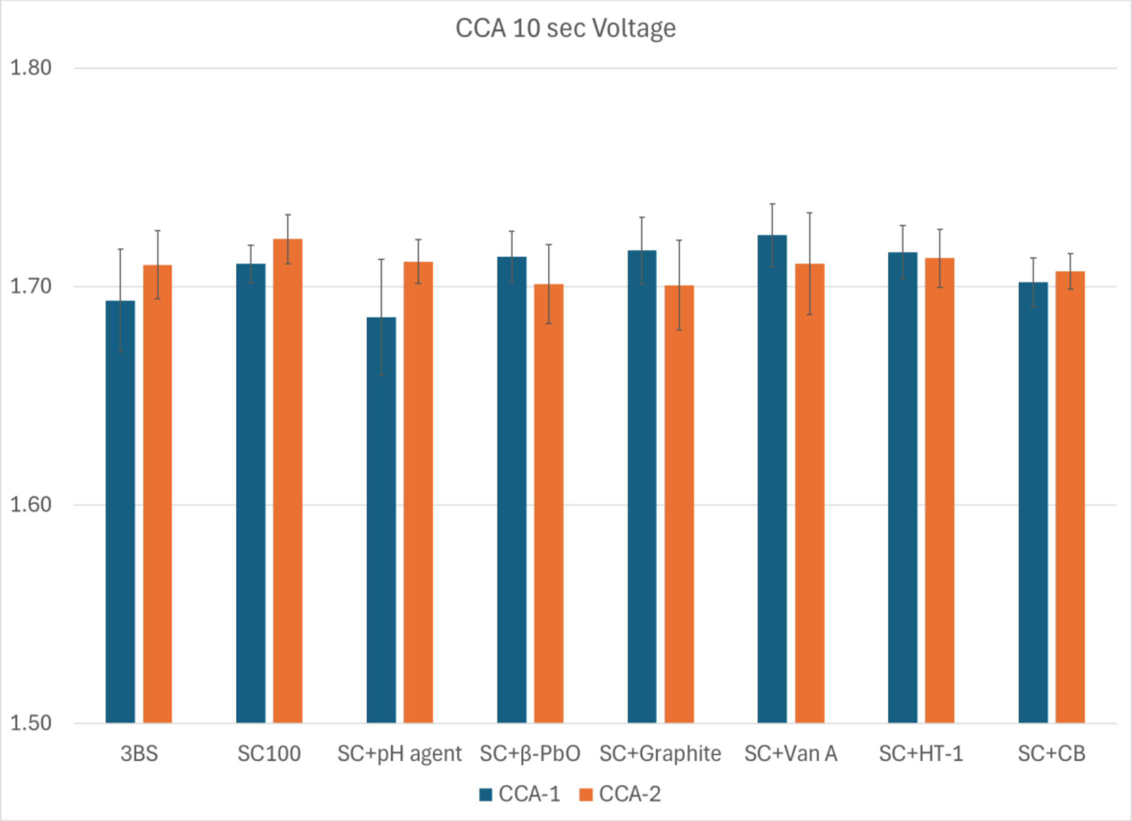
Cured PAM: Solid lines

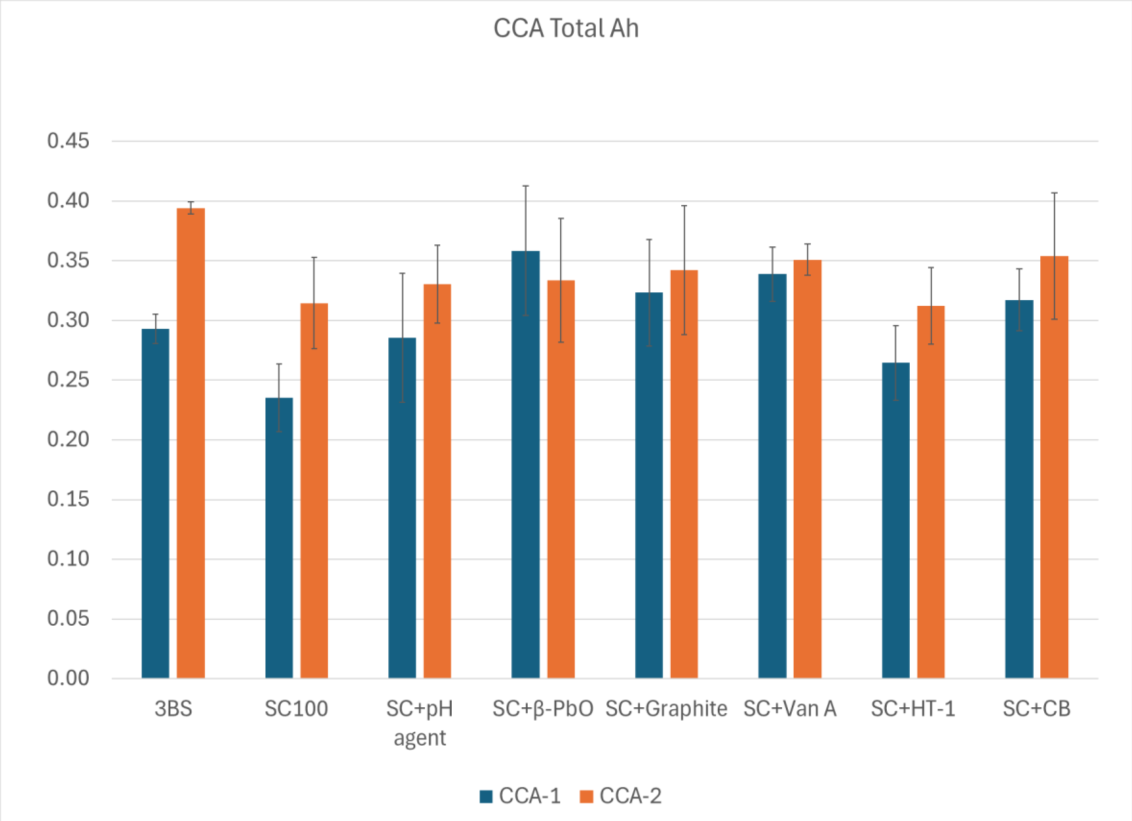
Formed PAM: dashed lines

SOME OBSERVATIONS:

- Overall, larger pores in cured pastes lead to larger pores in formed AM.
- Increased pore size in formed SC+Graphite PAM implies other contributions from graphite: partial oxidation.
- Similar to cured pastes, pore distribution of SC+HT-1 showed more pore volume in large pore area than that of SC+Van A

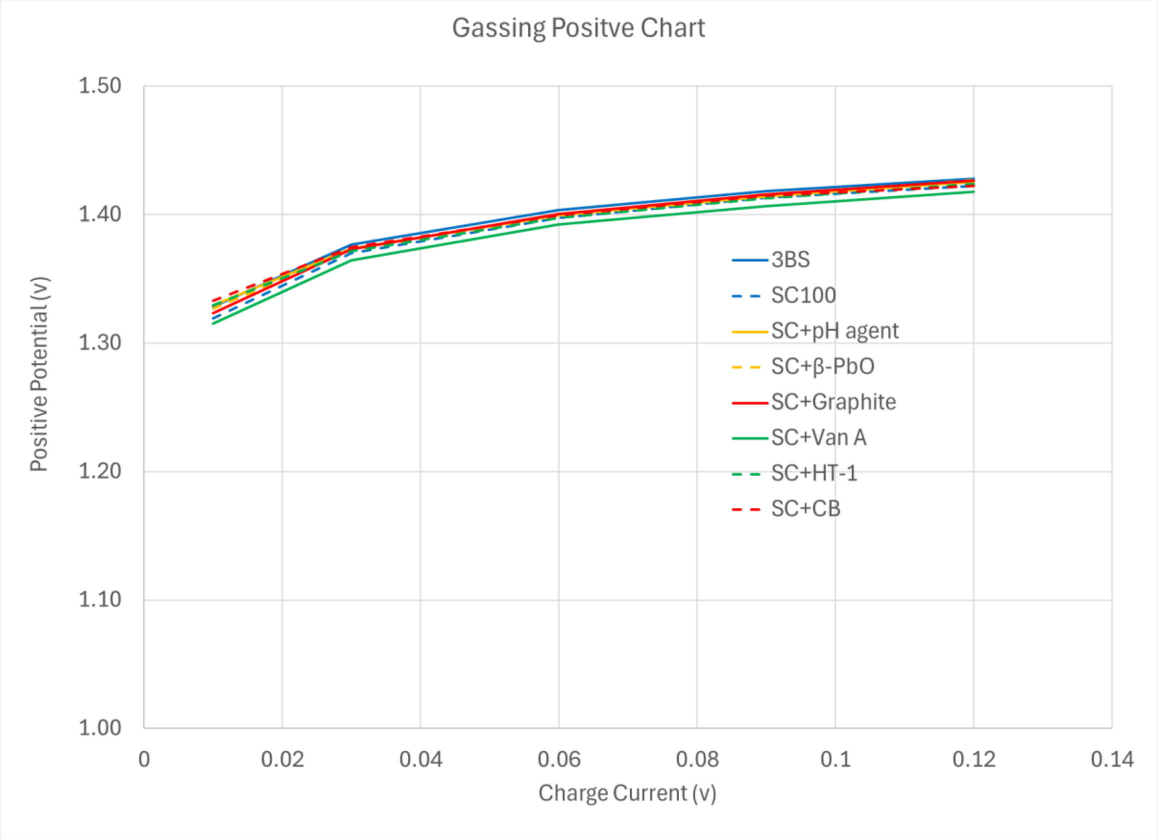
Phase II: Cell Test – CCA Test

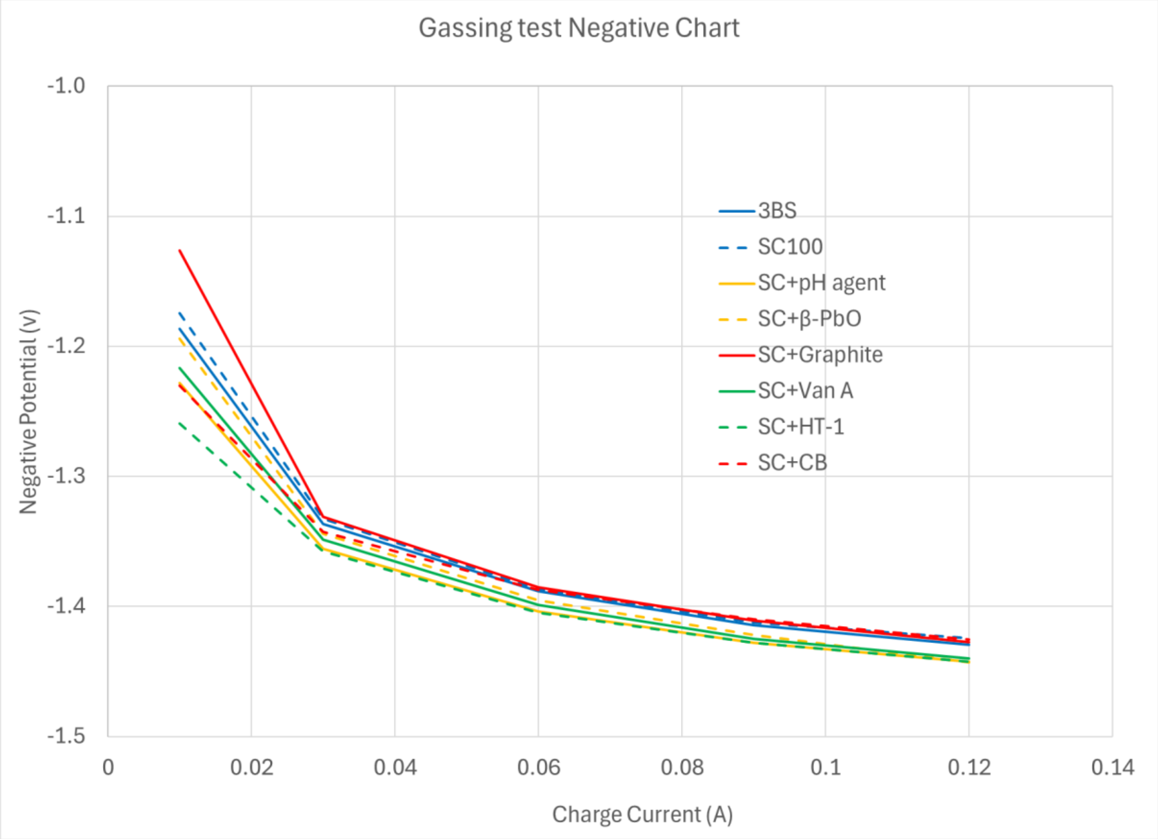




- All positives showed very close CCA 10 sec voltage.
- Considering test variation, it's hard to draw conclusion on total CCA discharge Ah.

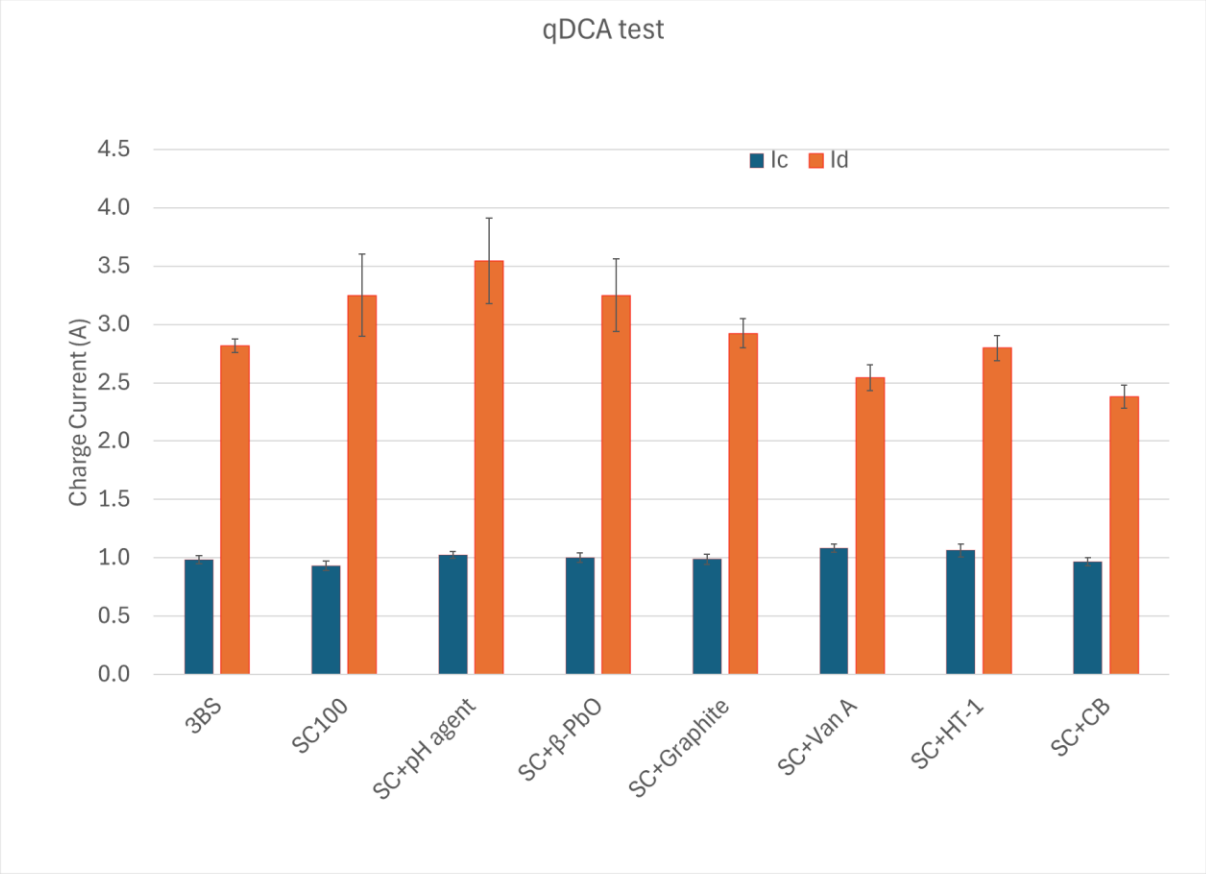
Phase II: Cell Test – Gassing Test





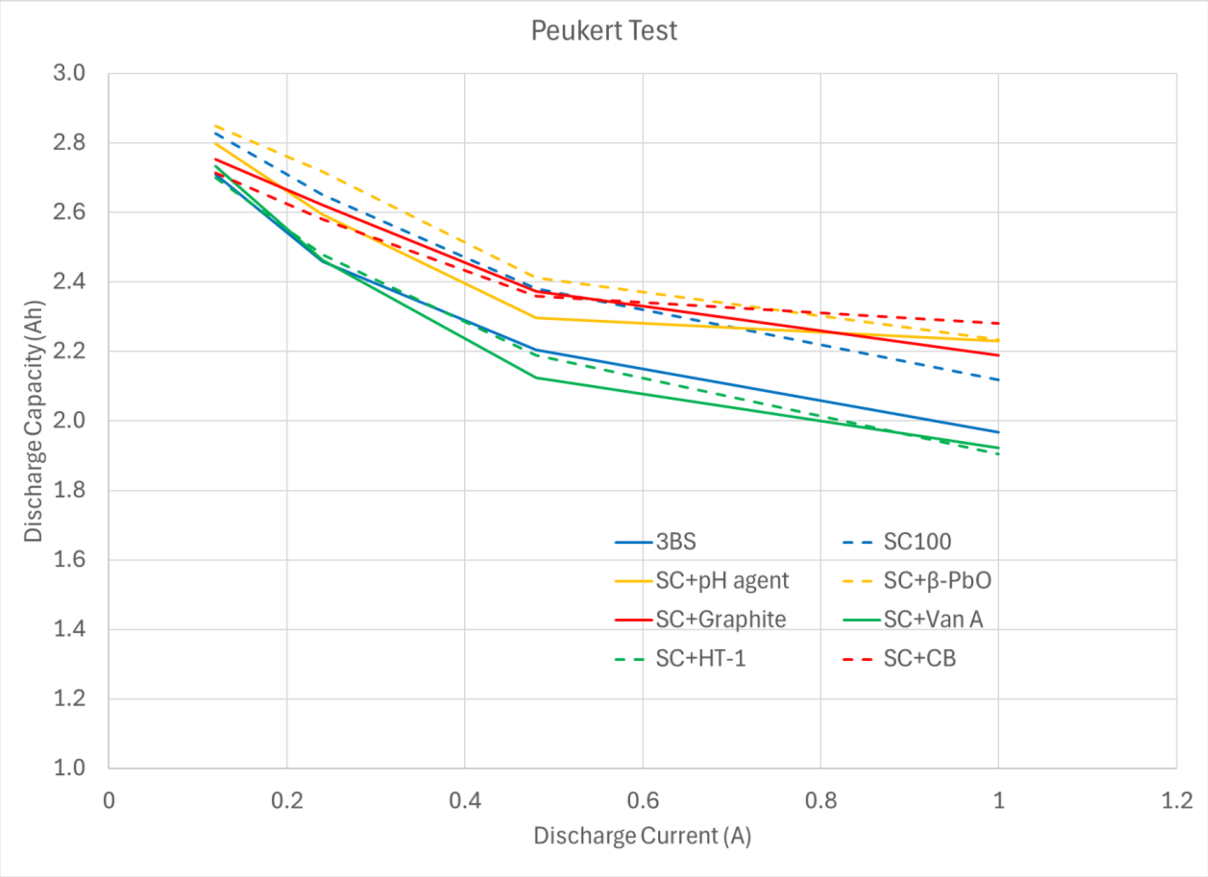
- Very little difference between positive potentials during gassing test.
- The difference between negatives is more significant than positives.
- 0.1% Van A and HT-1 in positive plates can slightly increase the polarization of negative plates in gassing stage.

Phase II: Cell Test – qDCA Test



- SC100, SC+pH agent and SC+β-PbO showed better qDCA performance.
- Larger pores seems to help qDCA (Id), while high α-PbO_2 does not.

Phase II: Cell Test – Peukert Test



- After previous tests (C20, 2 Reserve Capacities, gassing and qDCA), clearly 3BS pastes (3BS, Van A and HT-1) showed lower capacities in higher discharge current than other 4BS pastes (SC100, SC+pH agent, SC+β-PbO, SC+Graphite, SC+carbon black). This probably means larger pores in those 4BS plates is advantageous for high power performance.

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Conclusions

Paste Mixing and Curing:

- Small amount of chemicals can significantly increase paste pH
- pH agent, β-PbO can accelerate 4BS crystal growth. This means increasing paste pH/solubility of leady material can help 4BS crystal growth.
- Graphite increased 4BS growth may imply other mechanism on crystal growth, may be due to electro-osmotic pumping or others.
- Van A and HT-1 can increase paste pH, but they still inhibit 4BS crystal growth. This implies surfactant that can strongly adsorb onto the surface of leady material can significantly inhibit crystal growth. This can guarantee zero 4BS in cured positive paste, achieve more process tolerant, low energy consumption, worry free production.
- 4BS seeds, surfactants can be used to modifying active material pore structure.

Conclusions

Cell Test:

- Adding conductive agent in positive paste like graphite and carbon black can reduce formation polarization, increase α-PbO_2 content in formed PAM.
- Surfactants like Van A and HT-1 in positive paste increase the positive plate polarization in formation.
- After formation, there is still some graphite and less carbon black left in positive plates.
- In formed PAM, graphite was observed encapsuled in shells, while no such phenomena was observed with carbon black plate.
- Addition of SC100, pHagent, β-PbO, graphite, carbon black, Van A and HT-1 in positive showed little effect on positive gassing potential.
- Addition of Van A and HT-1 in positives can slightly increase negative plates gassing polarization. This may imply that some surfactant came out from positive and adsorbed by negative.
- Larger pores created by 4BS crystals help high current performance and qDCA (Id).

Summary

Methods of Modifying Active Material Structures:

- Modifying the crystal size/pore structure of AM in curing:
  - Varying paste formula like water, acid, additives.
  - Temperature (paste mixing, curing).
  - 4BS seeds particle size, loading, etc.
  - Additives that affect 4BS crystal growth (pH, surfactants, etc.).
- Modifying crystal size/pore structure of AM in formation
  - Formed AM structures partially inherited from cured paste.
  - Formed AM structures partially from modifying of formation process (change formation efficiency at stage I and stage II).
  - Formed AM structures partially from other contributions like pore creation agent like carbon materials.

Thank You for Your Attention!

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