Positive Active Mass Additives

Types, Effects, and Mechanism

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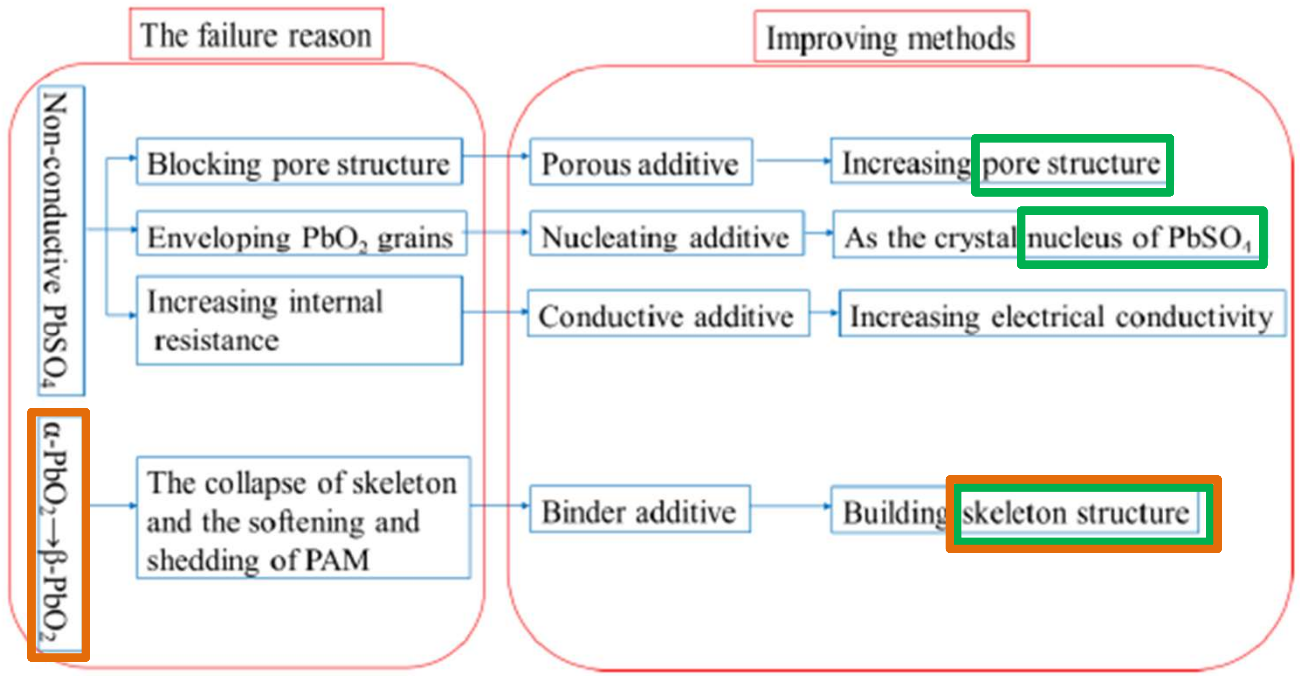
BLACK DIAMOND STRUCTURES™

Positive Plate Improvements Are Required

- **PAM-related failures are intensifying in the field**
  - NAM failure mitigation puts more "pressure" on PAM
  - Higher operating temperatures encourage corrosion
  - H_2O loss / polarization due to Adv. NAM provoke failure
- **Performance can be improved, from the active material perspective, using two general "levers":**
  - **Plate structure**
    - Density, surface area, pore structure, corrosion layer
  - **Plate composition**
    - 3BS/4BS, α/β-PbO_2, $PbSO_4$

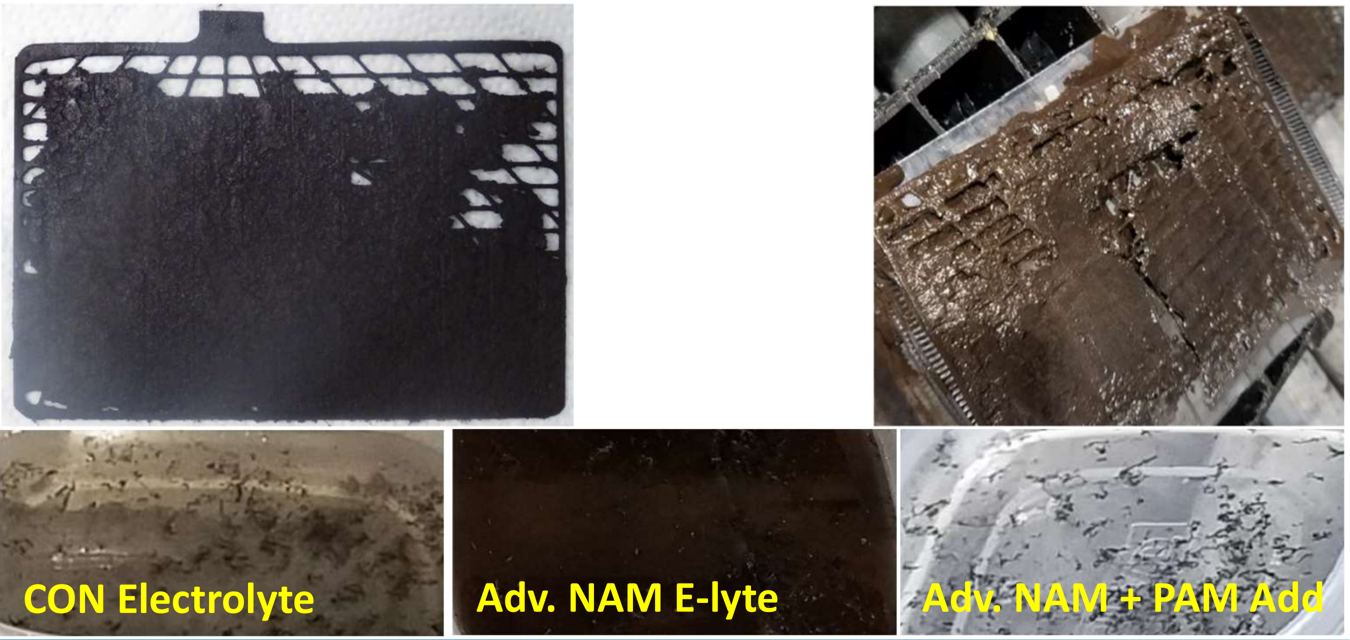
Continued in #401

- **Here, we review additives which may help to control these "levers", and review their potential role in high temp durability and brake energy recuperation**



Ref: Hao. Int. J. Electrochem. Sci. (2018) 13. p2329

Role of Positive Plate in High-Temp Durability



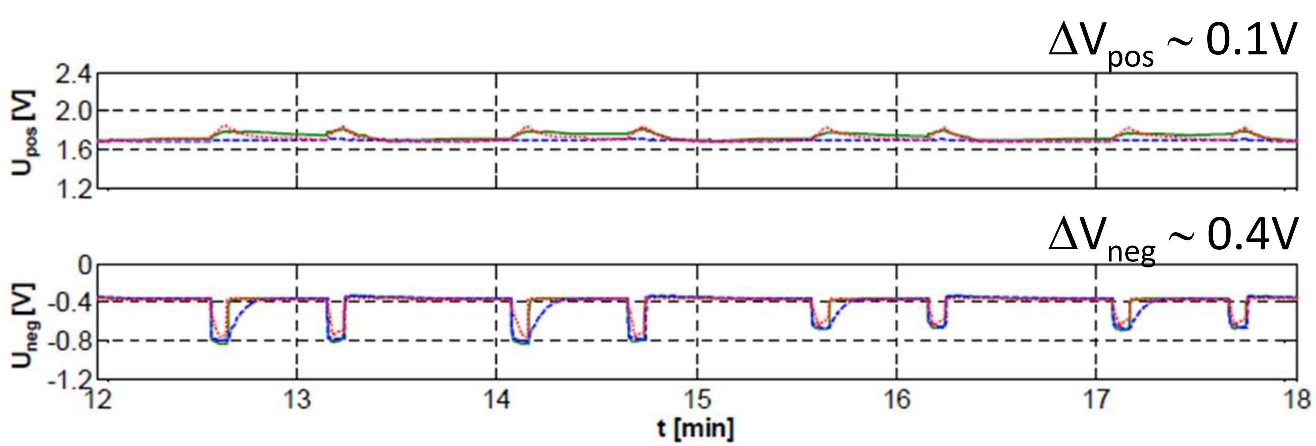
- Role of the Positive Plate in High-Temp Durability
  - **Material Shedding**
    - Can be related to poor crystal connections, swelling
    - Can be related to poor grid-material contact
    - Darkens electrolyte due to sloughed off material
    - Results in capacity loss and failure through shorting, mossing, bridging, increased corrosion

Continued in #404

  - **Corrosion**
    - Electrochemical degradation of the grid itself
    - Related to poor, or imperfect, alloy composition
    - Material can stay intact, but grid collapses
    - Results in capacity loss and failure through grid/tab disconnect, full cell loss (-2 V), shorting, separator oxidation tears

Role of Positive Plate in Brake Energy Recuperation

PAM	EN DCA (A/Ah)	Paste SO_4:PbO Ratio (%)	Paste Density (g/mL)	[4BS] (%)	[3BS] (%)	Pore Area (m^2/g)	Av. Pore Diameter (nm)
1	**0.15**	2.6	4.45	10.3	15.3	1.07	256
2	**0.22**	5.1	3.98	41.2	25.8	0.68	704



Ref: H. Budde-Meiwes, *Doctoral Thesis*, RWTH Aachen

- **Can PAM changes improve Dynamic Charge Acceptance?**
  - In some systems, yes, the positive plate can control Dynamic Charge Performance
  - In BDS' experience with lower-tier, 12 V batteries, drastic PAM changes (with identical NAM plates) drive changes to DCA magnitude (+46%)
- **So, why do we focus on NAM additives?**
  - Polarization of the negative electrode is of a larger magnitude than the positive electrode
  - Suggests that electrode is being exercised more
  - PAM not typically materials limited (higher m^2 than NAM), but could be functionally limited (?)

Effect of NAM Components on the PAM

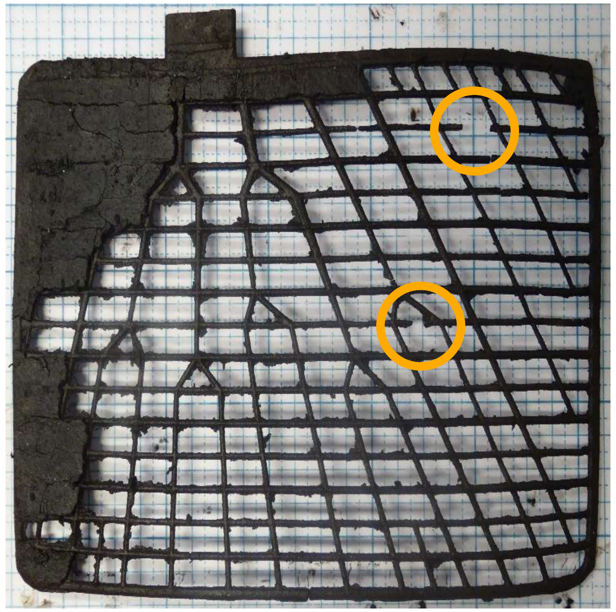
INDIRECT ADDITIVE EFFECTS

Depolarizing NAM Agents

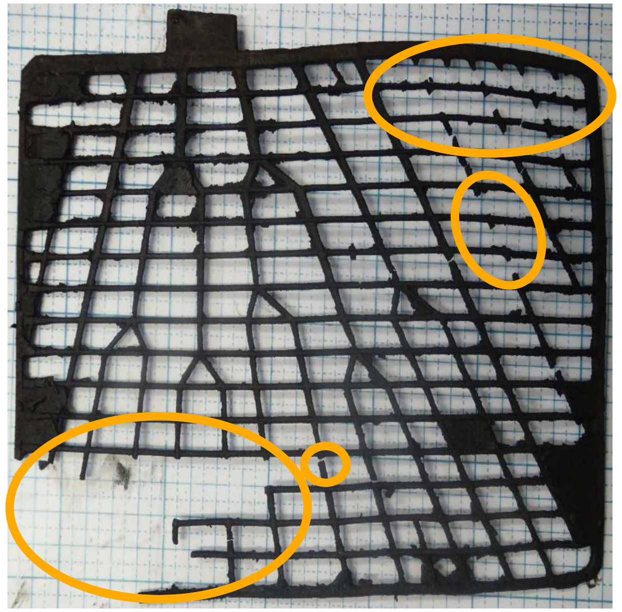
- **Industry has been Negative Plate-focused**
  - Charge Acceptance has been a dominant market driver for the last 10 years due to Start-Stop technology
  - Industry research concentrated on NAM improvements since that electrode is typically charge limiting
- **NAM advancements can increase the occurrence of positive grid corrosion and other PAM-centric failures**
  - Seen heavily in current technical specifications
    - eg. SAE J2801, SAE J240, JIS 5301D LLE, others
  - H_2O loss-induced acid concentration speeds corrosion
  - High-temperature operation intensifies corrosion

PAM Comparison Following 10 Weeks of nKLT (75 °C)

After Key Life Test, Plates are Dropped Once from 1m onto concrete



Low Carbon Sample
80% Active Material Lost
Few, Small Grid Breaks (O)



High Carbon Sample
95% Active Material Lost
Intensified Grid Breaks (O)

Ref: Everill. ABC 2019.

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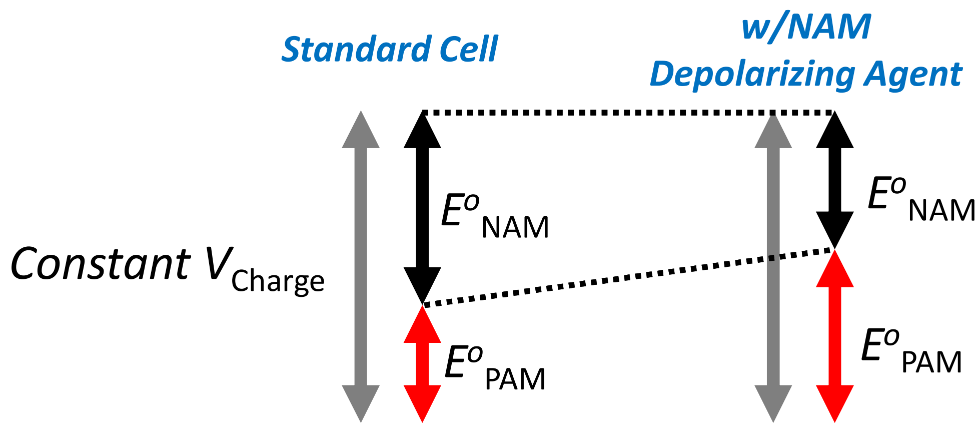
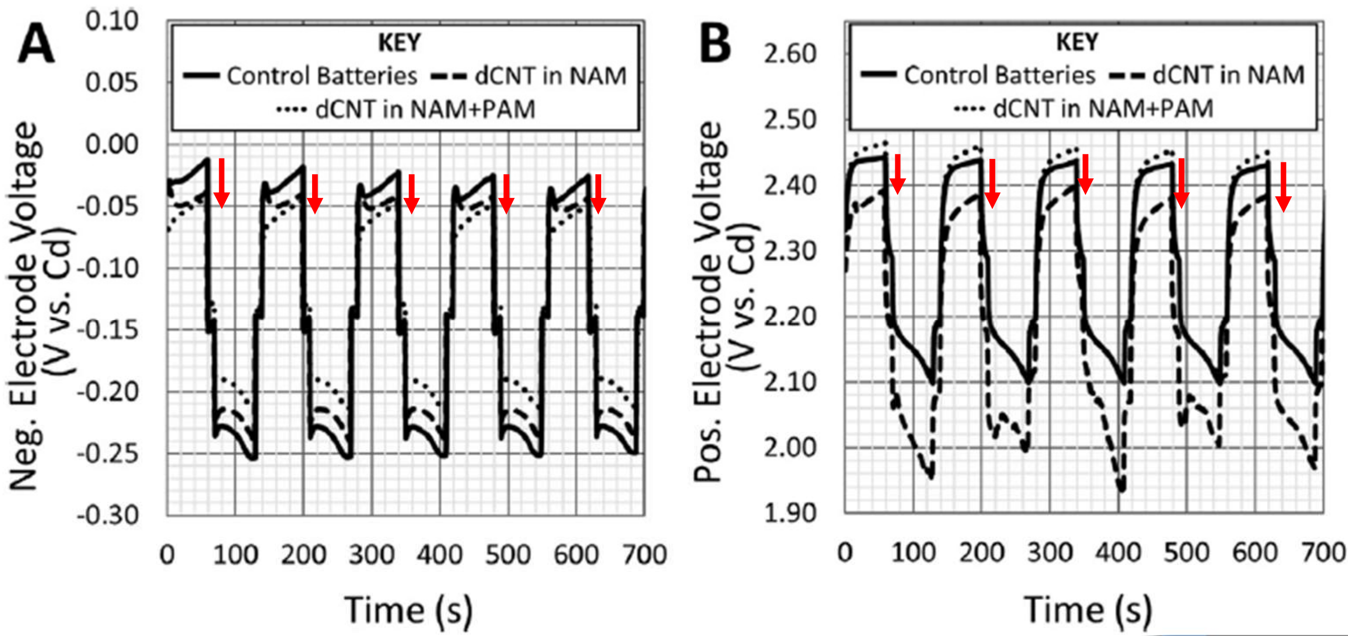
Depolarizing NAM Agents

- **In Constant Voltage charges (>3s brake event):**
  - A depolarized negative plate pushes the positive plate into a different potential window during CV charges
  - In some cases, it can increase utilization:
    - Higher initial capacity, improved capacity retention
  - Can sometimes lead to overworking, shedding
    - Faster shift from αPbO_2 (structural) to βPbO_2 (bulk)

- **In Constant Current charges (<3s brake event):**
  - Depolarization of negative can still influence positive
  - Effects can be seen in reference electrode studies





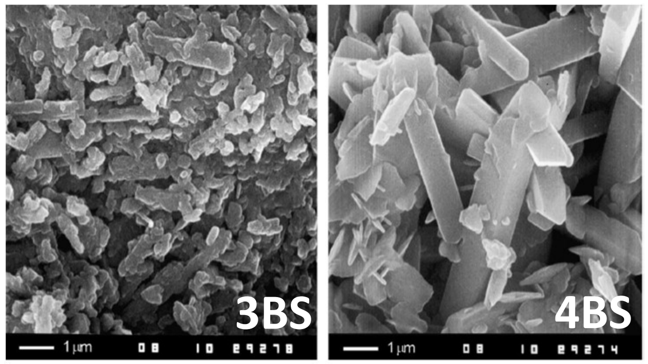
Ref: Sugumaran. Journal Power Sources (2015) 279 p281

Effect of PAM Components

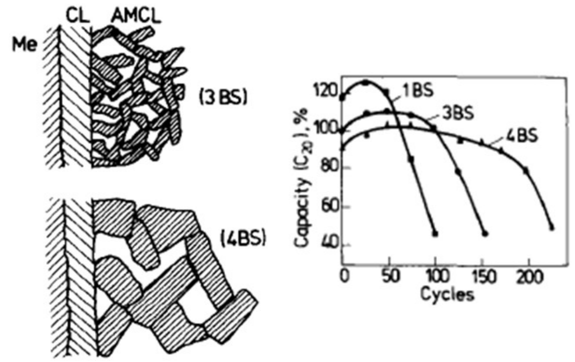
DIRECT ADDITIVE EFFECTS

Tetrabasic Seed Crystal

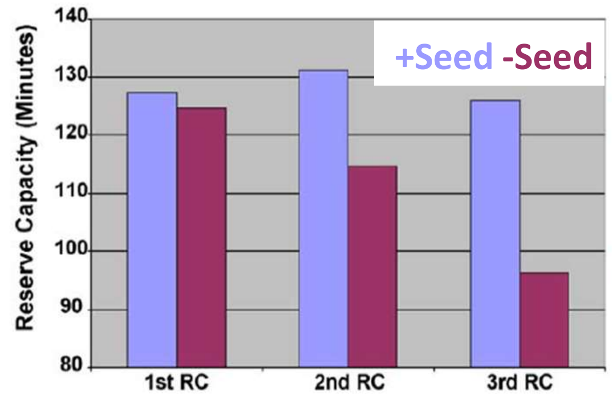
- **Tetrabasic Lead Sulfate ($4PbO \cdot PbSO_4 \cdot H_2O$, "4BS") is a large (>10 μm) crystal grown in specific conditions**
  - Provide strong foundation for active mass which, when formed, favor α-PbO_2 for structural reinforcement
  - Low surface:volume ratio can complicate formation processes which fail to convert the crystal's inner core
  - Low initial capacity, helped w/ ~25% Red Lead (Pb_3O_4)
- **4BS seed control conversion, lowering temp needed for growth, and producing uniform active structure**
  - A templating/nucleation agent
- **Claimed Performance Enhancements:**
  - Improved initial capacity, and consistency through life
  - **HIGH TEMP:** Dependent on many variables
  - **DCA**: Can increase magnitude, no effect on memory
- **Variants:** 0.5-5.0 um crystal sizes, powder or suspension
- **Loading Considerations:** 0.5-2.0% wrt PbO



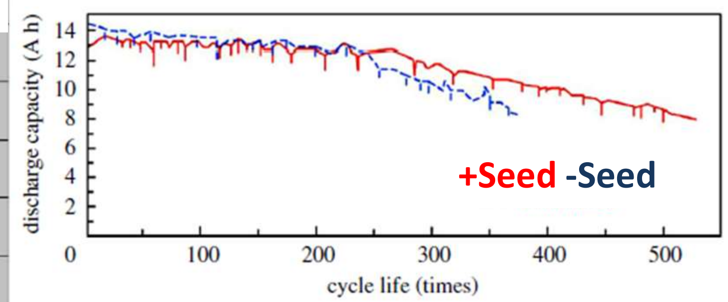
Ref: Pavlov. Lead-Acid Battery: Science and Technology. 2011



Ref: Pavlov. J. Power Sources. (1995) 53 p9



Ref: Boden. J. Power Sources. (2006) 158 p1133

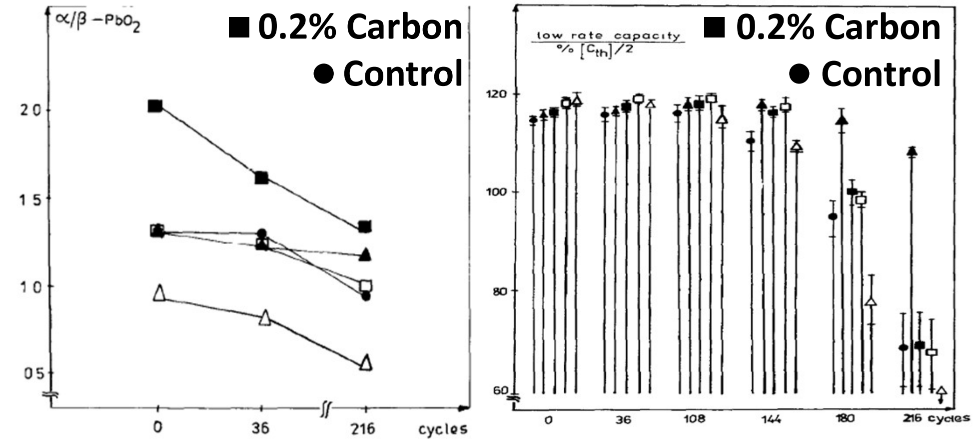


Ref: Kim. Royal Society Open Science. (2019) 6. p190882

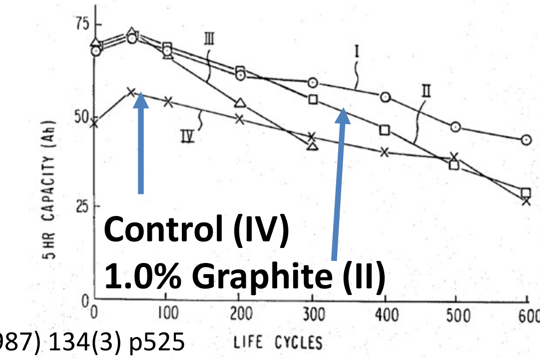
Effect on Meissner's Metrics (See #401)	NOTE: PPT# 401 explores formed plates; cured plate extrapolations not discussed
Crystal Composition	Increases 4BS% cured; Increases αPbO_2 formed
Pore Volume	Increases vs. 3BS; Decreases vs. typical 4BS
Pore Size	Increases vs. 3BS; Decreases vs. typical 4BS
Pore Surface Area	Decreases vs. 3BS; Increases vs. typical 4BS
Acid Access	Increases vs. 3BS; Decreases vs. typical 4BS

Carbon

- **Carbon is infrequently used in the positive active**
  - Oxidative potential eventually converts material to CO_2
- **Early work suggested improvement to electronic and ionic conductivity conveyed from intrinsic material properties, but later work suggested porosity enhancement through oxidation of the particles**
- **Claimed Performance Enhancements:**
  - Altered formation, favoring αPbO_2
  - No significant benefits in some studies (small particles)
  - Improved capacity, cycle life in others (large particles)
  - **HIGH TEMP**: Can limit AM shedding
  - **DCA**: Unknown
- **Variants:** Carbon Black, Acetylene Black, Graphite
- **Loading Considerations:** 0.1-1.0% wrt PbO, affects paste density



Ref: Dietz. Journal of Power Sources (1985) 14. p305



Ref: Tokunaga J. Echem Soc (1987) 134(3) p525

Effect on Meissner's Metrics (See #401)

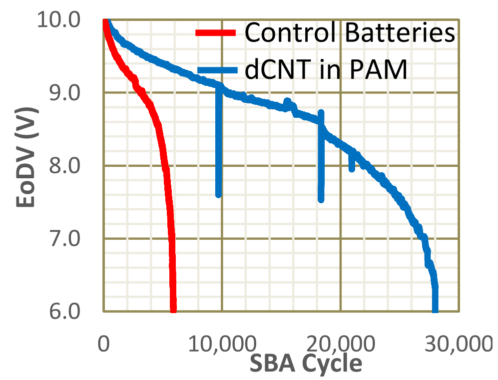
NOTE: PPT# 401 explores formed plates; cured plate extrapolations not discussed

Crystal Composition	Increases α-PbO_2 in formation
Pore Volume	Increases in cured, no change/slight in formed
Pore Size	Increases in cured, no change/slight in formed
Pore Surface Area	No change in cured, no change/slight in formed
Acid Access	Increases

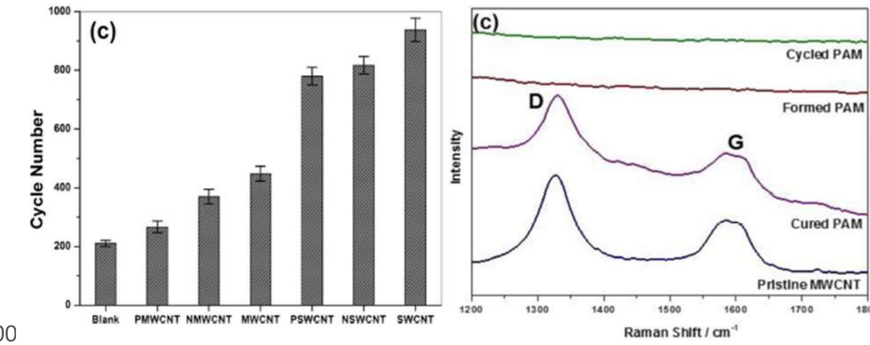
Ref: Lach. J Solid Stata ElectroChem. (2019) 23 p693;

Carbon Nanomaterial

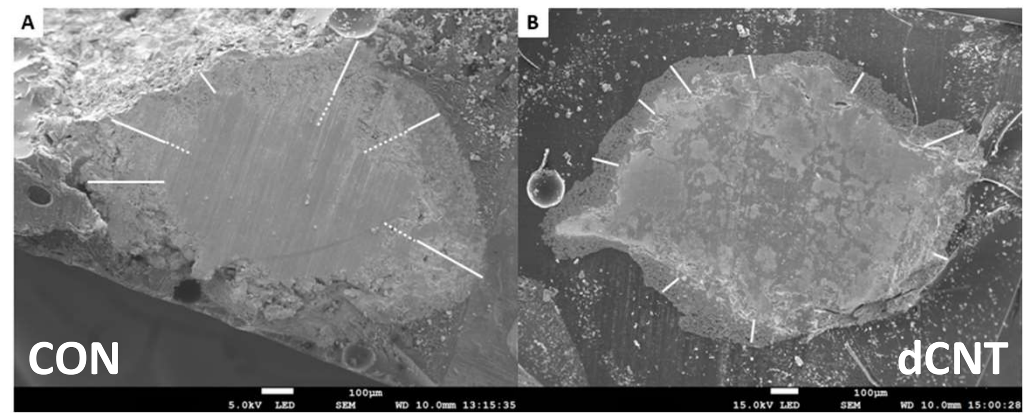
- **Some nanomaterials improve plate structure and battery performance with very low mass addition**
  - Their application was earlier stalled by impurities, cost, aggregation tendency, and handling concerns
- **Two theories of action:**
  1. Stability towards oxidation and persistent inter-crystal connections resulting in conductivity improvements
  2. Uniform structural optimization that bolsters the plate structure and enhances the grid-material interface
- **Claimed Performance Enhancements**
  - Improved cycle life and capacity consistency
  - Improved deep discharge performance
  - **HIGH TEMP**: Some improve corrosion layer and mitigate shedding
  - **DCA**: Some improve conductivity to support better rate
- **Variants:** MOLECULAR REBAR®, Graphene, Single/Multiwall CNT
- **Loading Considerations:** 0.001-0.1% wrt PbO,



Ref: Everill, ELBC 2014.



Ref: Banerjee. J. Electrochemical Society. (2016) 163 (8) pA1518



Ref: Meyers. J. Energy Storage. (2020) 32 p101983

Effect on Meissner's Metrics (See #401)	NOTE: PPT# 401 explores formed plates; cured plate extrapolations not discussed
Crystal Composition	Decreases $PbSO_4$ in cycled plate, can change α/β ratio
Pore Volume	No change
Pore Size	Decrease cured, Increases formed
Pore Surface Area	Increases cured, Decreases formed
Acid Access	Increases

Metal, Metal Salts

KEY: ↑ Increases ↓ Decreases – Not Mentioned

	Loading (% wrt PbO)	Mechanism	Performance	Industry Adoption*	Effect on Meissner's Metrics (See #401)					References
					Crystal Comp.	Pore Vol.	Pore Size	Pore Surf. Area	Acid Access	
Bismuth (Bi)	0.05	Alters crystal morphology, like Sb but w/ lower rates of gassing + self DCH	Improved initial capacity in deep cycling	Zero	?	↑	?	↑	↑	1, 2, 10
Antimony (Sb, or $SbSO_4$)	0.005-0.1	Alters crystal morphology, Arsenic can play a supporting role.	Improved cycle life, less O_2 (Density must be >3.75 g/mL to stop - plating)	Very Low	?	↑	?	↑	↑	3
Sodium (Na, or Na_2SO_4)	0.01-0.05 M	Dissolves in acid increasing pore vol. Reduces 4BS size (+ α/β-PbO_2)	Improved active material utilization, especially in concert with 4BS	Very Low	-	↓	↓	↑	↑	4, 5
Calcium (Ca, or $CaSO_4$)	0.25-2	Believed to be a $PbSO_4$ nucleation agent	Improved HRD voltage esp. cold temperatures, no effect to cycle life	Very Low	?	?	?	↑	↑	4, 6
Tin ($SnSO_4$)	0.1-2.0	Increases *n* in PbO_n around grid to suppress conversion of Pb grid to PbO_x	Mitigate PCL-1 failures and delay corrosion	Very Low	CL	-	-	-	-	7
Barium ($BaSO_4$)	<0.1	4BS nucleation agent, pronounced shedding in non-compressed cells	Improved 4BS conversion, higher αPbO_2, improved cycle life.	Zero	**4BS↑**	↑	↑	↓	↑	8, 9

*Dr. Everill's experience form >165 global manufacturers

Ref:
1 - Lam. J. Power Sources (1998) 73 p36,
2 - Lam. J Power Sources (1999) 78 p139.
3 - Shiomi. US 6,284,411 B1 Patent (2001)
4 - Hao. Int. J. Electrochem. Sci. 13 (2018) 2329-2340
5 - Chen. J. Power Sources (2000) 90(2) p125
6 - Ramanathan. J. Power Sources (1991) 35 p83
7 - Slavkov. J. Power Sources (2002) 112 p199
8 - Dittman. J. Electrochem. Soc (1954) p533
9 - Atlung. J. Power Sources (1990) p131
10 - CSIRO / Pasminco Practice

Metal Oxides

KEY: ↑ Increases ↓ Decreases – Not Mentioned

	Loading (% wrt PbO)	Mechanism	Performance	Industry Adoption*	Effect on Meissner's Metrics (See #401)					References
					Crystal Comp.	Pore Vol.	Pore Size	Pore Surf. Area	Acid Access	
SnO_2 (Tin Oxide)	0.1-2.0	Alters PbO_2 crystal morphology	Improves formation efficiency and initial capacity	Very Low	PbO_2 ↑	↑	-	↑	↑	1, 2, 3
Sb_2O_3 (Antimony trioxide)	0.05-0.3	Improves active material-grid binding in Ca-alloy grids	Improved initial capacity, Improved corrosion resistance (PCL-1)	Near Zero	CL	↑	-	↑	↑	4
Pb_3O_4 (Red Lead)	20-30	Provides alternate chemical route to PbO_2 (Pb_3O_4 + H_2O_4 → PbO_2 + $\beta PbSO_4$)	Improves formation efficiency and initial capacity, important w/4BS	High w/ 4BS Users	PbO_2 ↑	-	-	-	-	5
Ti_4O_7 (Titanium Oxide)	0.2-0.5	Increases the overpotential of the gassing reaction	Decreased H_2O loss, improvement in active material utilization	Near Zero	-	-	-	↑	-	1
Diatomite ($SiO_2 \cdot nH_2O$)	3.0	Increase in porosity with no change to mechanical strength or composition	Improved capacity and utilization	Near Zero	PbO_2 ↑	↑	-	-	↑	2
Bi_2O_3 (Bismuth Oxide)	0.02	Increase in porosity as the Bi dissolves and leaves pore structure behind	Improved initial capacity	Near Zero	PbO_2 ↑	↑	-	-	↑	2

*Dr. Everill's experience form >165 global manufacturers

Ref:
1 - Pavlov. Lead Acid Batteries (2011) p351
2 - Hao. Int. J. Electrochem. Sci. 13 (2018) 2329-2340
3 – Hariprakash. J. App. Electrochem (2004) 34 p1039'
4 – Zhou. Chinese J. of Power Sources (2009) 4 p291
5 – Ferg J. Power Sources (2006) 155 p428

Go to www.menti.com and use the code 29 03 75 8

Mentimeter

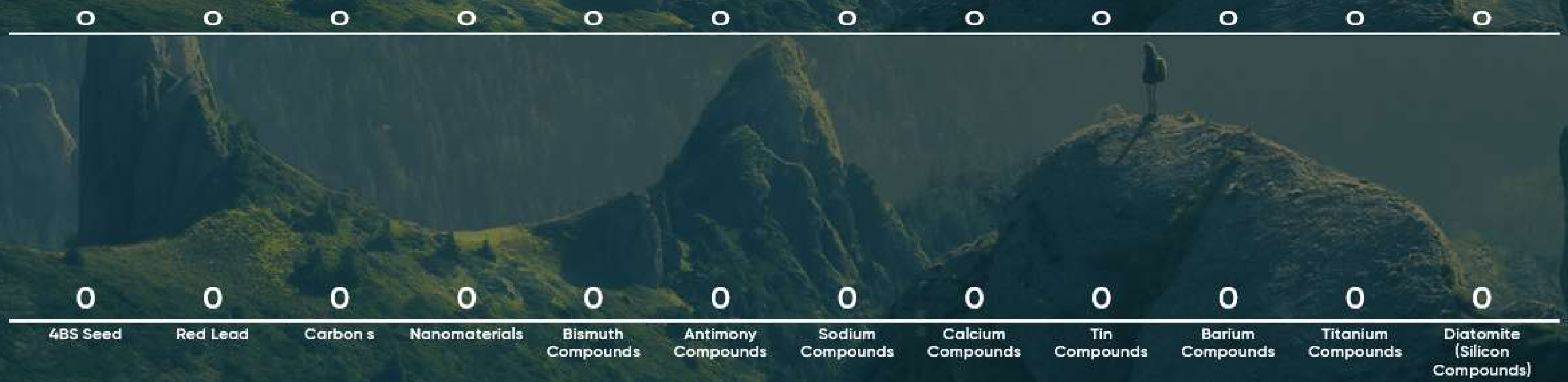
402-1: I apply, or have applied in the past, the following PAM additives:

4BS Seed	Red Lead	Carbons	Nanomaterials	Antimony Compounds	Bismuth Compounds	Sodium Compounds	Calcium Compounds	Tin Compounds	Titanium Compounds	Diatomite (SiO2) Compounds
0	0	0	0	0	0	0	0	0	0	0

Go to www.menti.com and use the code 29 03 75 8

Mentimeter

402-2: The following additives performed as marketed in my systems

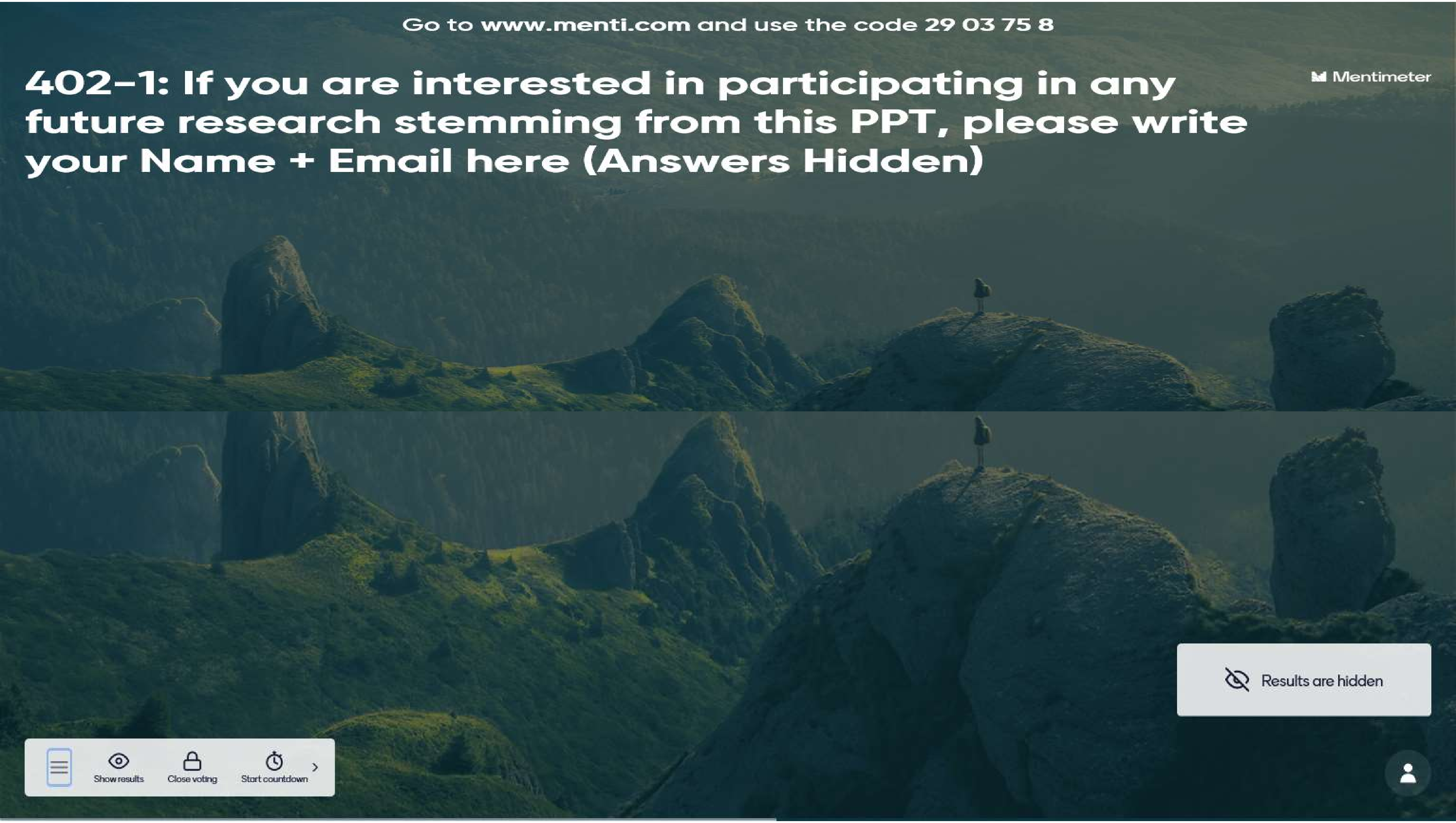


Wrap-Up and DCA/High Temperature Report Card

- **Positive plates can limit advanced automotive batteries due to shedding, corrosion, or as an inhibitor of DCA**
- **To alleviate these limitations, additives should be applied to target user-defined, optimal PAM structure:**

PAM Additive	Primary Effect(s)	Effect on DCA Magnitude	Effect on DCA Memory	Effect on High-Temperature Failure Modes
Tetrabasic Seed	Morphology	Can Improve	?	Reduced shedding
Carbon	Conductivity, Porosity	?	?	?
Nanomaterials	Morphology, Porosity Corrosion Layer	?	?	Some reduce shedding, corrosion
Metal, Metal Salts	Morphology, Porosity	?	?	Some reduce corrosion
Metal Oxides	Morphology, Porosity, Conductivity	?	?	Some reduce corrosion, water loss

PAM additives are much less understood, studied, or available than NAM additives, which warrants further investigation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402-1: If you are interested in participating in any future research stemming from this PPT, please write your Name + Email here (Answers Hidden)
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Results are hidden
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