502

# Negative Active Mass Additives

## Types, Effects, and Mechanism

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BLACK DIAMOND
STRUCTURES™

# When We Last Spoke…

- **We probed aspects of “Dynamic Charge Acceptance” (DCA)**
  - A term describing the responsiveness of batteries held at Partial State of Charge to short, intense energy pulses mimicking operation of a start/stop automotive battery
    - Ex. EN 50432-6 DCA Protocol, Run-In DCA

- **We investigated “levers” which could manipulate DCA magnitude**
  - State of Charge (SoC) interrogated → higher starting SoC lowers $I_C/I_D/I_R$, lower SoC increases $I_C/I_D/I_R$
  - Voltage administered during pulses → 16 V provides higher $I_C/I_D/I_R$ vs. 14.8 V
  - Rest period duration → 20 h pre-qDCA rest provides slight improvement on $I_C$ vs. 72 h

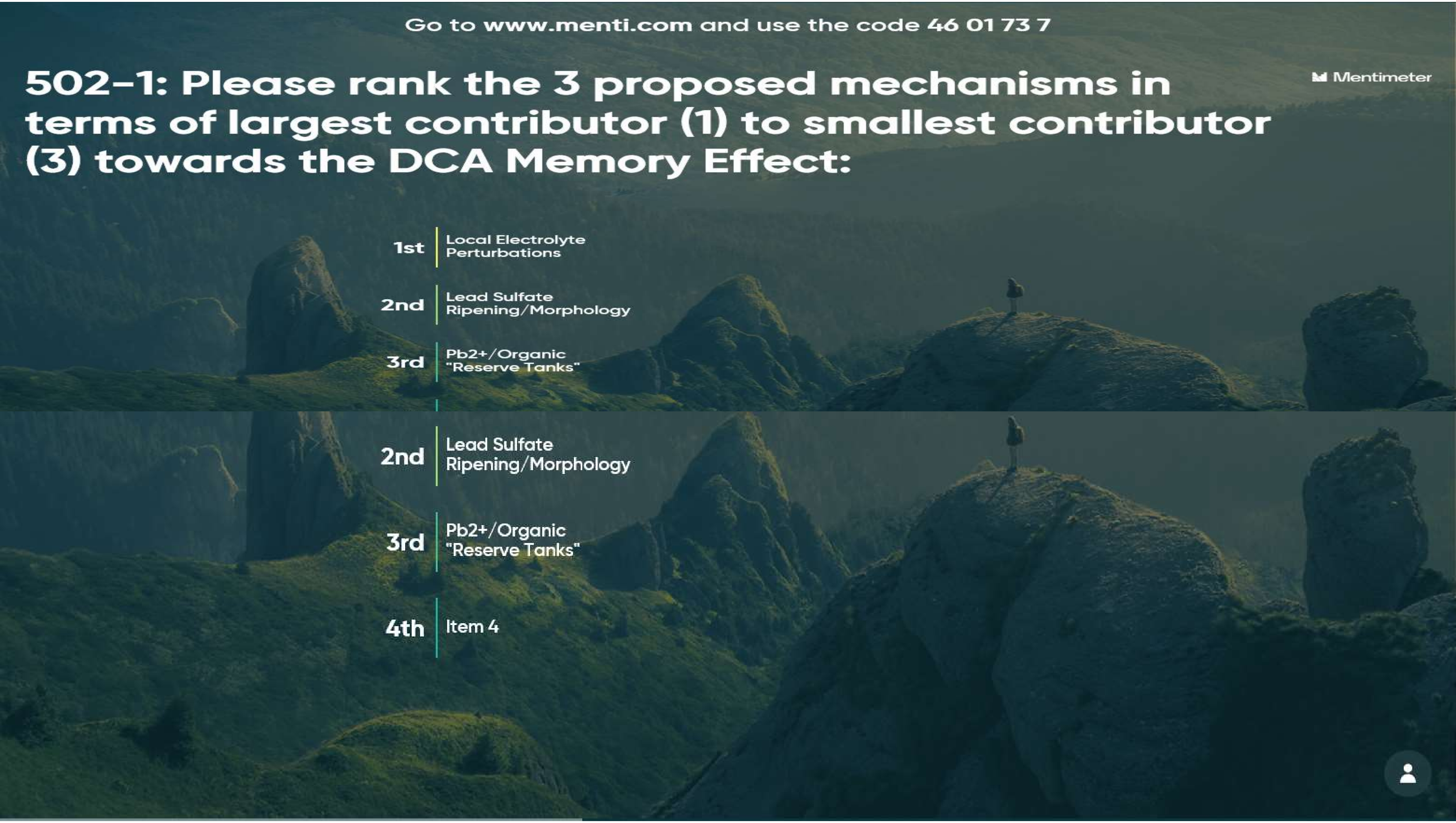
**Continued in #512**

- **We defined the concept of “DCA Memory” and explored three theories of its origin**
  - DCA magnitude is inextricably linked to the process which came before → the battery “remembers” what it just did
    - Measuring DCA post-discharge (ex. $I_D$) typically provide a 3-5X higher value than measuring post-charge (ex. $I_C$)

1. Local Electrolyte Effect as cause → Pockets of low/high SG enable/limit charge reactions
2. Lead Sulfate Ripening as cause → A hardening of crystals and passivation of their activity
3. Perturbation of $Pb^{2+}$ as cause → An expanded role for organics in $Pb^{2+}$ diffusion and storage

**Continued in #515**

**Continued in #514**



Go to www.menti.com and use the code 46 01 73 7

Mentimeter

# 502-1: Please rank the 3 proposed mechanisms in terms of largest contributor (1) to smallest contributor (3) towards the DCA Memory Effect:

| | |
|---|---|
| 1st | Local Electrolyte Perturbations |
| 2nd | Lead Sulfate Ripening/Morphology |
| 3rd | Pb2+/Organic "Reserve Tanks" |

| | |
|---|---|
| 2nd | Lead Sulfate Ripening/Morphology |
| 3rd | Pb2+/Organic "Reserve Tanks" |

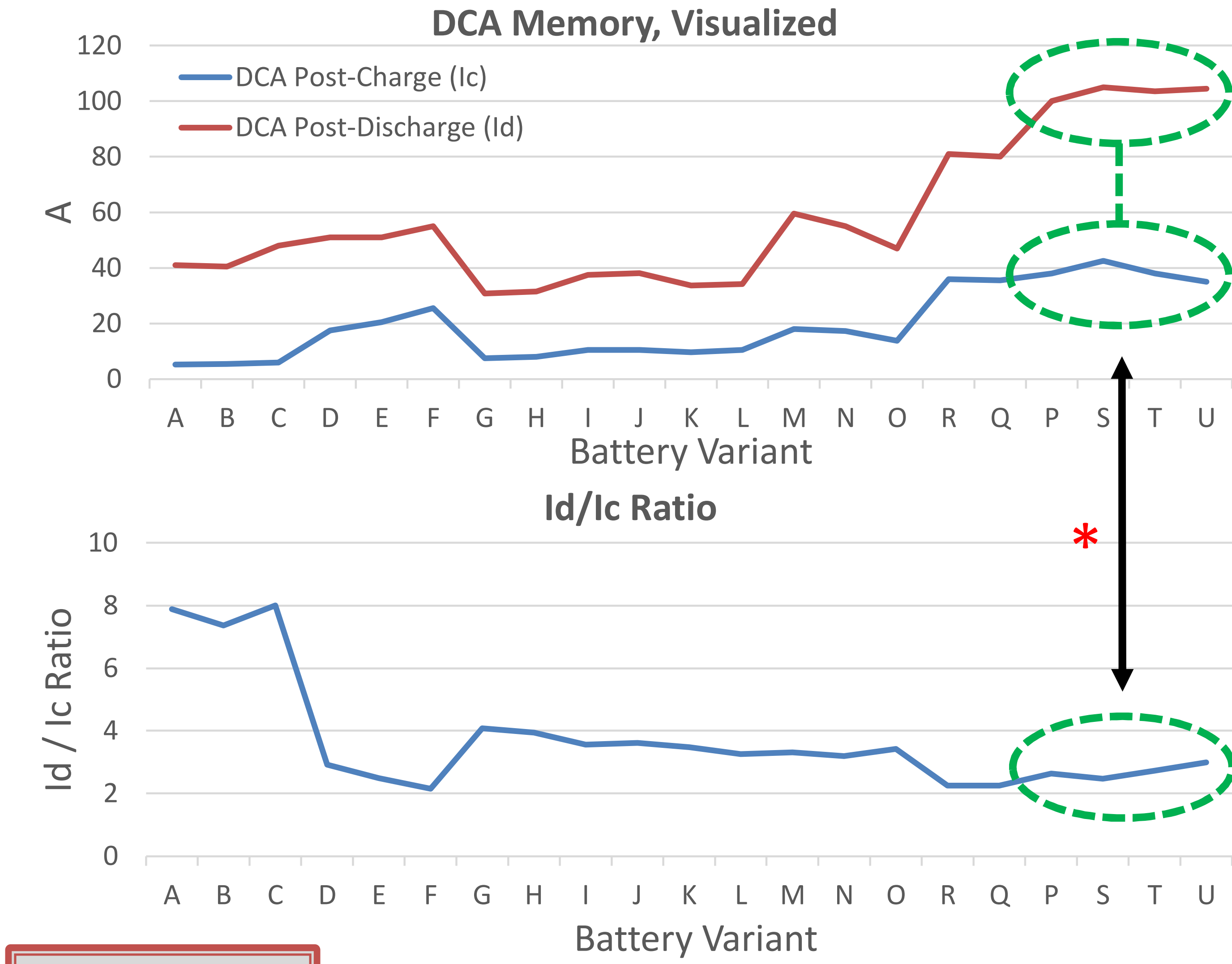
4th Item 4

# Why Seek the Origin of DCA Memory, and How?

- **The goal *is not* understanding the mechanism…**
  - …it is a step towards the goal

- **The goal *is* harnessing the knowledge to make a battery perform like it just discharged, every charge**
  - $I_D >> I_C$, always
  - The best batteries in BDS’ experience have low $I_D$:$I_C$ (*)
    - And high magnitude of $I_C$ and $I_D$
  - How can a charged plate be structurally engineered to perform like a discharged plate?

- **What tools can we use to reach our goals?**
  - Smart, out-of-the-box engineering
  - Battery management system optimization
  - Careful review of structure-function relationships
  - ***…and Additives!!***



Continued in #501

Go to www.menti.com and use the code 46 01 73 7

# 502-2: In my experience with the following batteries designs, the ratio of Id/Ic is closest to:

Ic is nearly equ
EFB / EFB+C
VRLA
Id is nearly !

# Our Additive Addiction: Lead is Not Enough

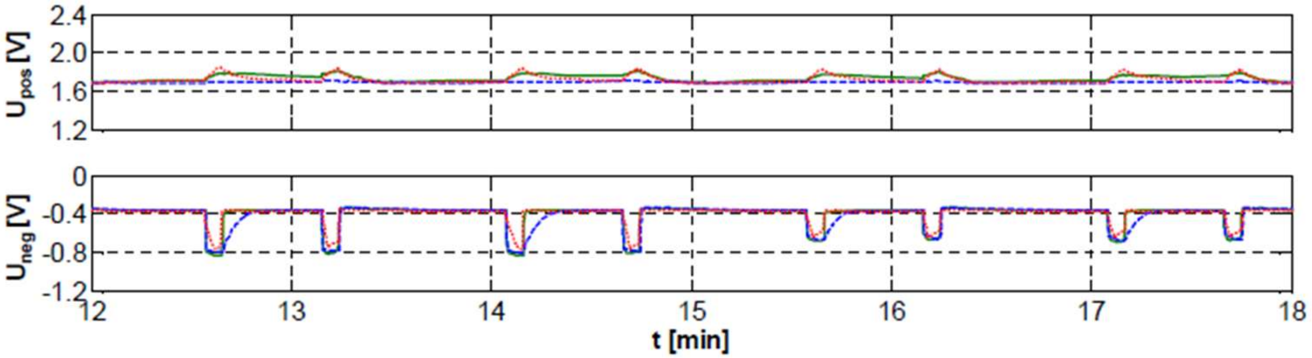
- Historically, four additives were used in the Negative Active Mass (NAM), all of which diversified over time:

| NAM Additive | Typical Loading% (wrt PbO) | Historical Usage | Contemporary Usage |
|---|---|---|---|
| **Carbon** | 0.1-5.0 | A pigment to visually differentiate positive and negative plates; not a performance additive | A hotly discussed and highly diversified performance additive offering functional gains across many applications |
| **Organics** | 0.1-0.5 | Added to the NAM by accident as leachate from wooden battery cases, lifecycle crashed without its presence during shift to plastic | Innovations led to optimized/modified natural products and more tailored prescription of those solutions in balance with other components |
| **Barium Sulfate** | 0.5-2.0 | Nucleation agent facilitating growth of lead sulfate of small size during discharge | Diversification of grades, which now include the nanoscale, to improve discharge performance, recover from discharge, and CCA |
| **Fiber**<br>*(Not Discussed Here)* | 0.01-x.xx | Added as a rheological paste strengthening agent during drying with no chemical or electrochemical performance inferred | Custom lengths/widths are prepared for various crystal compositions and end needs including long-term plate robustness in cycling |

***In the following slides, we explore modern NAM additives, their theorized mechanism of action, and their potential role in defining DCA Memory***

# For DCA, Are Additives Deployed to the Right Plate?

- **Reference electrode studies of DCA indicate a controlling role for the negative electrode**
  - Polarization of the negative electrode is of a larger magnitude than the positive electrode



$\Delta V_{pos} \sim 0.1V$

$\Delta V_{neg} \sim 0.4V$

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

  - Global research aimed at improving DCA magnitude or understanding DCA Memory has focused on NAM

Continued in #402

- **Still, in some cases, the positive electrode is capable of dramatically limiting DCA performance**
  - In BDS' experiments with full-scale 12 V batteries, PAM changes (NAM identical) can drive changes to DCA Magnitude

| | EN DCA (A/Ah) | Paste $SO_4$:PbO Ratio (%) | Paste Density (g/mL) | [4BS] (%) | [3BS] (%) | Pore Area (m²/g) | Av. Pore Diameter (nm) |
|---|---|---|---|---|---|---|---|
| PAM 1 | 0.15 | 2.6 | 4.45 | 10.3 | 15.3 | 1.07 | 256 |
| PAM 2 | 0.22 | 5.1 | 3.98 | 41.2 | 25.8 | 0.68 | 704 |

# Structure-Function Relationships in Pb-Acid Battery

- **Nature is governed by Structure/Function relationships; DCA performance and memory must be no different. Understanding/manipulating NAM STRUCTURE to provide the FUNCTION we desire is central to this Breakout:**

Continued in #501/515

**Sulfate Crystal Morphology ⟷ Chargeability**

- Small crystals (<100 nm) charge very efficiently since Pb$^{2+}$ solubility is less limiting around them
- Medium (>100 nm) to large (>>100nm) crystals differ less in Pb$^{2+}$ solubility, but can be “hard”/pacified or block pores
- Can we use additives to maintain smaller, uniform, reversible crystal morphology throughout life?

Continued in #525 / #401

**Pore Structure ⟷ Acid Access + Utilization**

- Typical NAM pore diameter is $\sim$1 $\mu$m which sterically hinders the growth of very large sulfates in the interior
- Tight pores present a mass transfer limitation for $SO_4^{2-}$ and can result in basification if $H^+$ diffuse out, forming $\alpha$PbO
- Can we use additives to manufacture and maintain an experimentally defined “optimal” pore structure?

**Surface Area ⟷ Reactivity**

- Large, “sluggish” $PbSO_4$ have low surface area, providing less physical pace for electrochemistry / mass transfer
- High Pb surface area increases performance, but too high increases self-discharge
- Can we use additives to lock the structure of sponge Pb and $PbSO_4$ through life?

# Carbon – Basics

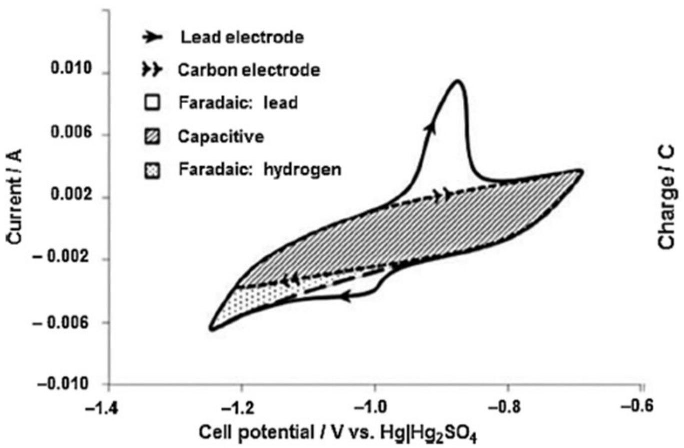
Continued in #524

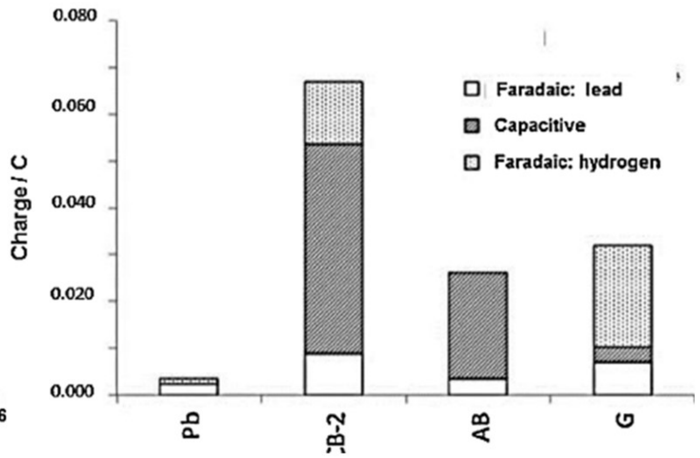
- **Variants**
  - Carbon black, acetylene black, graphite, expanded graphite,
- **Loading Considerations**
  - 0.1-2% wrt PbO
  - Limited by paste processing concerns (additional water/lower density/hard to mix)
  - Limited by excessive hydrogen evolution driven by often high impurities and external surface area
    - Offset with specific surface chemistry (ex. acidic), pre-adsorption of Pb, improvement of Pb/C contact
- **Performance Effects (Varies by Product)**
  - Improved static/dynamic charge acceptance in multiple specifications resulting in improved microcycling/PSoC durability
  - CCA performance can be decreased due to adsorption of the system's organic component which can be balanced out
  - Increased water loss with some products due to impurities, surface area, or promotion of hydrogen evolution reaction

***"Carbon is one of the significant 'levers' for increasing NAM charge performance, yet there is no strong consensus as to what carbon's role is" – Shane Christie, ArcActive***

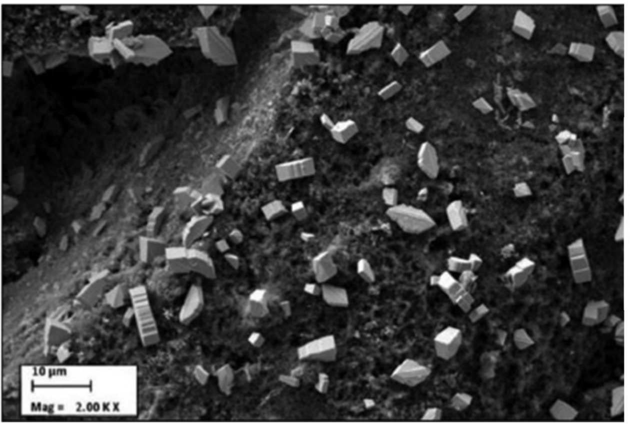
Ref: Moseley, J., Rand. D. A. J., Davidson, A., Monahov, B. Energy Stor. 19 (2018) 272-290; Bozkaya. AABA 2018

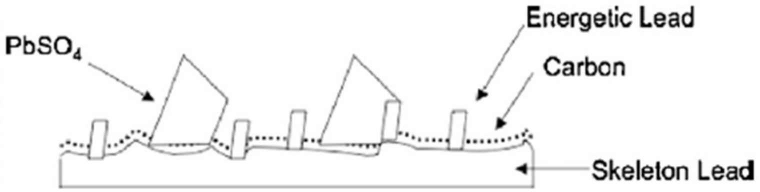
# Carbon – Theories of Function (1/2)





Ref: Jaiswal, J. Energy Storage. 1 (2015) 14-21



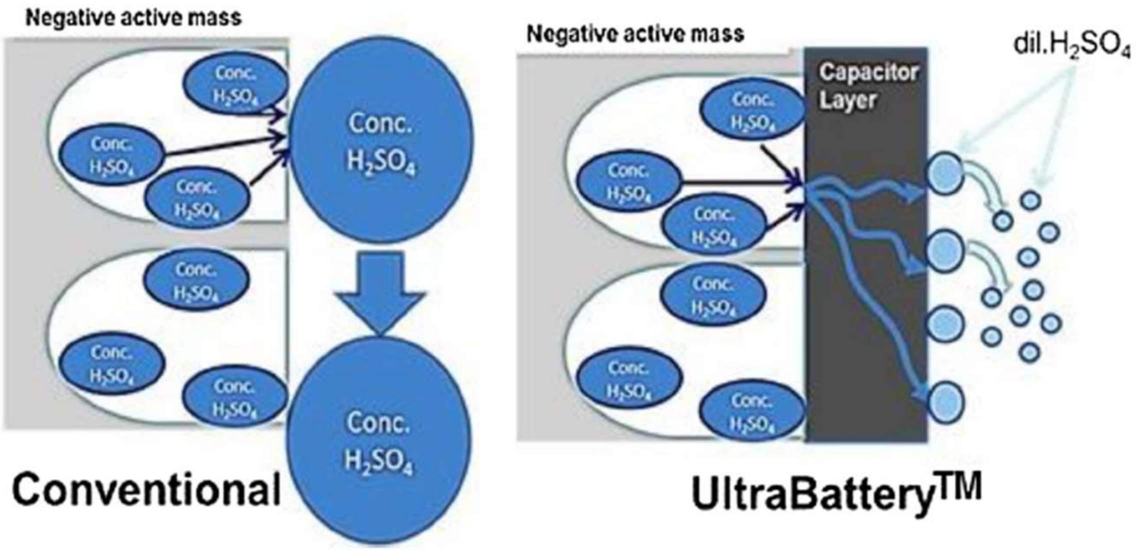


- **Electronic Enhancement**
  - – Carbon could act as capacitor, absorbing current during/after CHR, transferring to Pb soon after
    - Surface area ↑, Capacitance ↑
    - Would play a role in charging schemes resulting in rapid voltage changes when capacitance can build
  - – Carbon enhances utilization of the active mass in CHR and DCH through improved electronic conductivity
  - – Time constant not long enough to account for DCA Memory which can be on the order of weeks

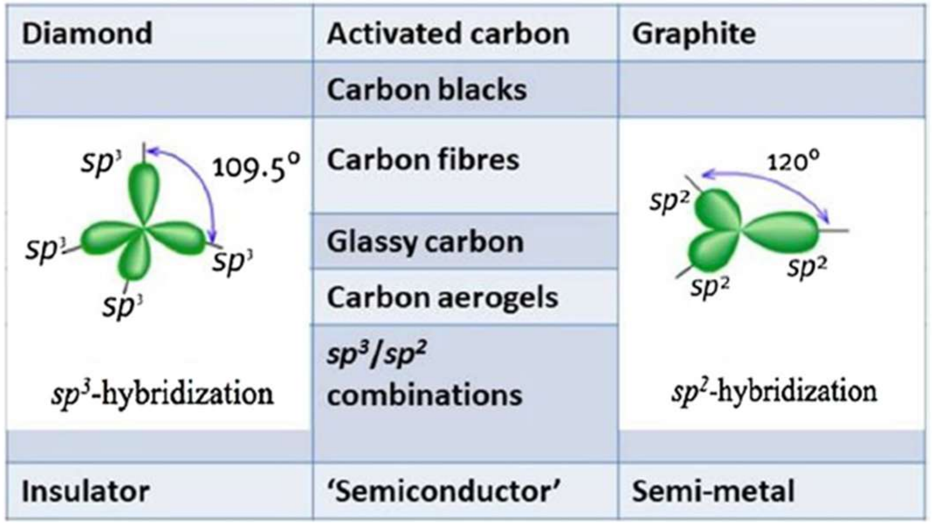
- **A New Electroactive Surface**
  - – Carbon provides a 2nd surface for $Pb^{2+}$ deposition reactions expanding electrode capability
  - – Two roles: 1) Functions as capacitor in <5 s charge time and, 2) Nucleation site in >10 s charge time
  - – Intimate contact required

Ref: Moseley, J., Rand. D. A. J., Davidson, A., Monahov, B. J. Energy Stor. 19 (2018) 272-290;
Samuelis, ABC (2015)

# Carbon – Theories of Function (2/2)



Ref: Furukawa, in Lead-Acid Battries for Future Automobiles (2017)



| Diamond | Activated carbon | Graphite |
|---|---|---|
| | Carbon blacks | |
| $sp^3$-hybridization | Carbon fibres | $sp^2$-hybridization |
| | Glassy carbon | |
| | Carbon aerogels | |
| | $sp^3/sp^2$ combinations | |
| Insulator | 'Semiconductor' | Semi-metal |

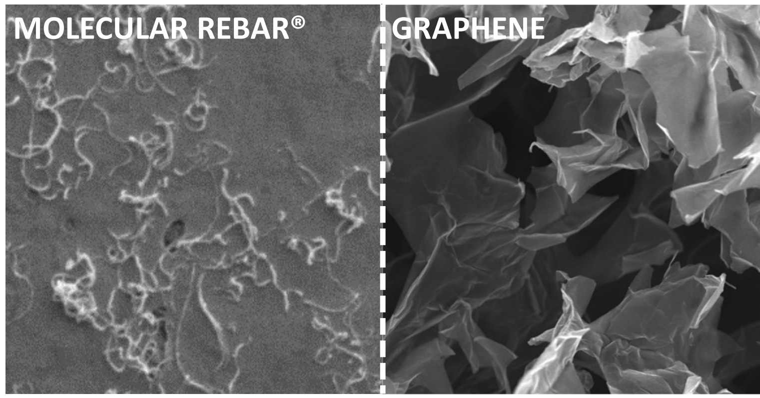
Ref: Moseley, J., Rand. D. A. J., Davidson, A., Monahov, B. , J. Energy Stor. 19 (2018) 272-290; Moseley, J. Power Sources. 191 (2009) 134-138

Continued in #501/515

- **Physical Effects**
  - Carbon provides steric hindrance reducing sulfate size
  - Increasing the porosity of the NAM to improve supply of electrolyte (possibly with "Electroosmotic pumping")
  - Increasing tortuosity of acid path to bulk attenuates stratification (ex. UltraBattery capacitor)
- **Alternative Mechanisms:**
  - Intercalation of $H^+$ in graphite, analogous to graphite's $Li^+$ intercalation in li-Ion cells, to improve conductivity
  - Carbon as oxygen scavenger, reducing sulfation by replacing one use of PAM-supplied oxygen for another:
    - $\frac{1}{2} O_2 + Pb + H_2SO_4 \rightarrow PbSO_4 + H_2O$ = sulfation
    - $2 O\cdot + C \rightarrow CO_2$ = gas loss, carbon degradation

# Nanomaterials – Basics

Continued in #524

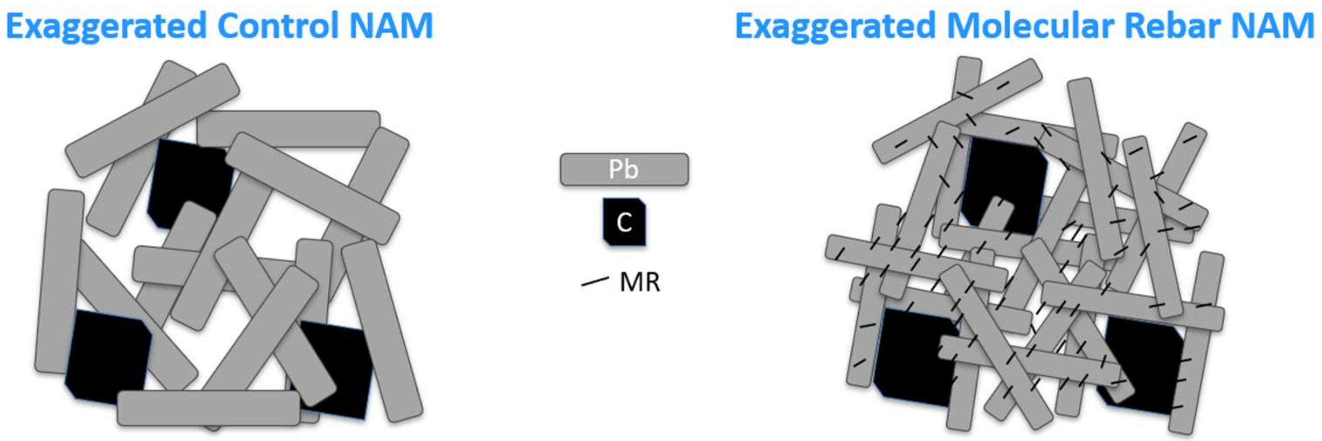


- **Variants**
  - MOLECULAR REBAR®, Multi- or Single-walled carbon nanotubes, graphene
- **Loading Considerations**
  - 0.01-0.75% wrt PbO
  - Unformulated materials present handling/safety issues, high aggregation tendency
  - Non-purified forms prone to excessive hydrogen evolution driven by presence of residual catalysts and high surface area
    - Offset by purification techniques, high materials efficiency (low loading levels), and surface modifications
- **Performance Effects (Varies by Product)**
  - Improved dynamic charge acceptance in multiple specifications resulting in improved microcycling/PSoC durability
  - Enhanced material strength and robustness when uniformly incorporated
  - Combination of physical reinforcement and electrical performance improvement permits reduction in overbuilding
  - Enhanced CCA performance with some varieties

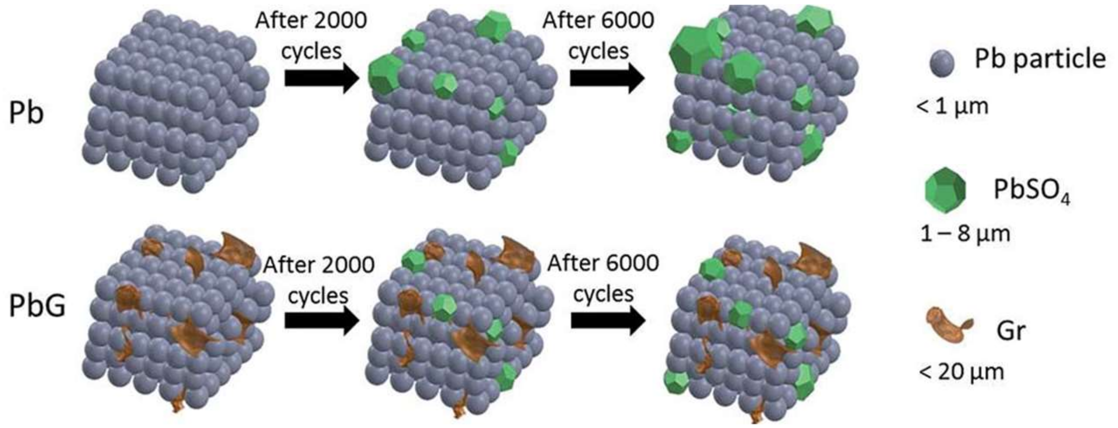
***"…Nanomaterials… may be very promising due to their ordered structure, high chemical stability, and high intrinsic electrical conductivity" – Dr. Anjan Banjeree, Bar-Ilan University***

# Nanomaterials – Theories of Function

- **MOLECULAR REBAR® (NAM)**
  - Crystal packing rearrangement to provide:
    - Higher surface area
    - Thinner, more numerous pores (no density chang
  - Strength reinforcement by bridging crystals
  - Steric hindrance and restriction of growth of $PbSO_4$
  - May also pay a role in improving $Pb^{2+}$ availability



- **Graphene Mechanism**
  - Some propose it merges organic + carbon capabilities:
    - Improved electroactive surface area for adsorption/desorption of $Pb^{2+}$ (charge transfer), similar to proposed for organics
    - Double layer capacitance and enhanced conductivity, similar to proposed for carbon



Ref: Yeung, RSC Adv.. (2015) 5, 71314; Kumar RSC Adv. (2014) 4, 36517

# Organics – Basics

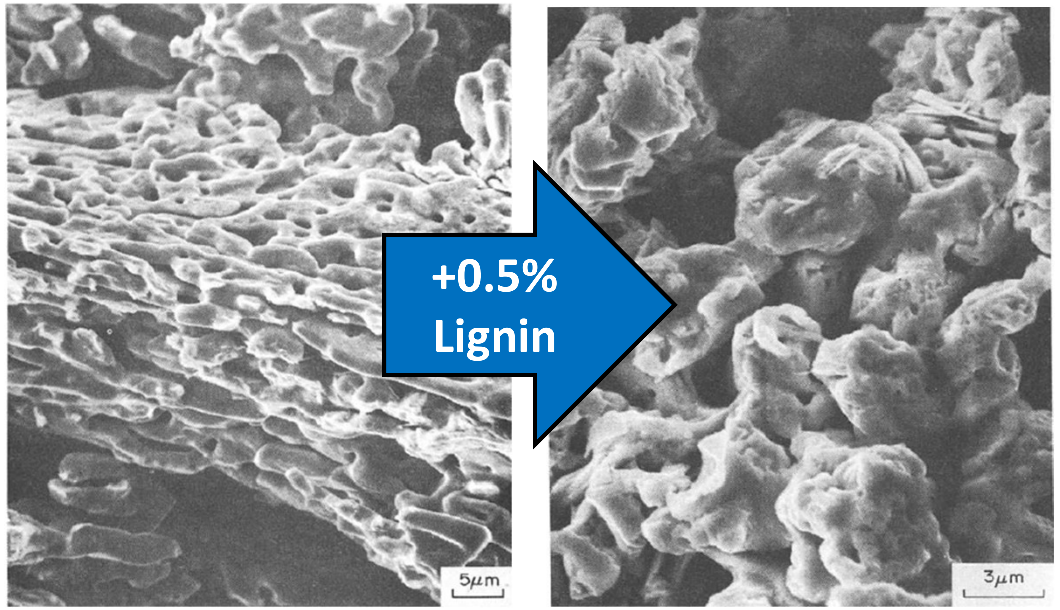
Continued in #524

- **Variants**
  - Vanisperse(s), Indulin, Humic Acid, Kraftplex, Napthalene Sulfonates
- **Loading Considerations**
  - 0.1-0.5% wrt PbO
  - High loading provides enhanced CCA + lower $H_2O$ loss, sacrificing charge acceptance
  - Low loading provides enhanced charge acceptance, sacrificing CCA and cycle life
- **Performance Effects (Varies by Product)**
  - Increased cycle life in most testing protocols and applications
  - Increased dynamic charge acceptance when used at minimal/optimal concentrations
  - Effects in high temperature cycling vary by variety, with some forms being less stable to heat
  - Overloading passivates lead surface with thick organic layer. Optimal loading should produce an incomplete monolayer.

***"Organics are a necessary evil. They are fundamental for long life and low water loss, yet they corrupt charge acceptance and can be difficult to balance with other additives"***
***– Dr. Nanjan Sugumaran, Independent Consultant***

# Organics – Theories of Function

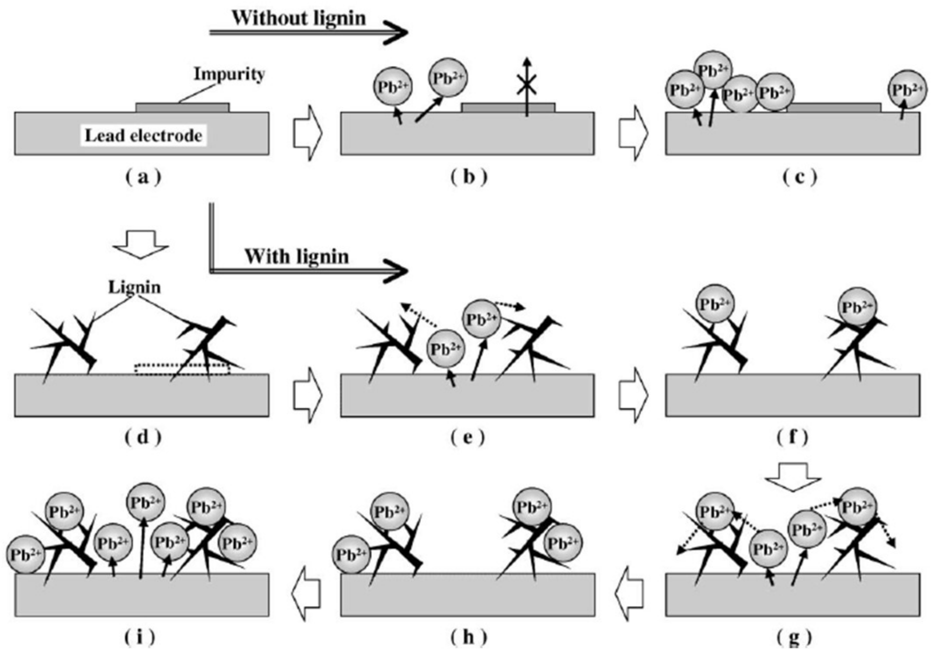
- **Surface Complexity Enhancing Agent**
  - Increases active surface area of the negative plate
  - Creates complex, arborescent Pb structures
  - Addresses surface simplification by favoring “tubiform excrescences”, rather than monodirectional growth



**Growing Monocrystal** **Multiple Growing Crystals**

Ref: Simon. Electrochemica Acta (1974) p739-743

- **$Pb^{2+}$ Dispersing/Reservoir-Building Agent**
  - Bind and redistribute $Pb^{2+}$, scattering it across surface to shepherd crystal growth complexity
  - Binds $Pb^0$/PbO/$Pb^{2+}$ more effectively than $PbSO_4$
  - Keeps [$Pb^{2+}$] available to reaction, chemistry dependent



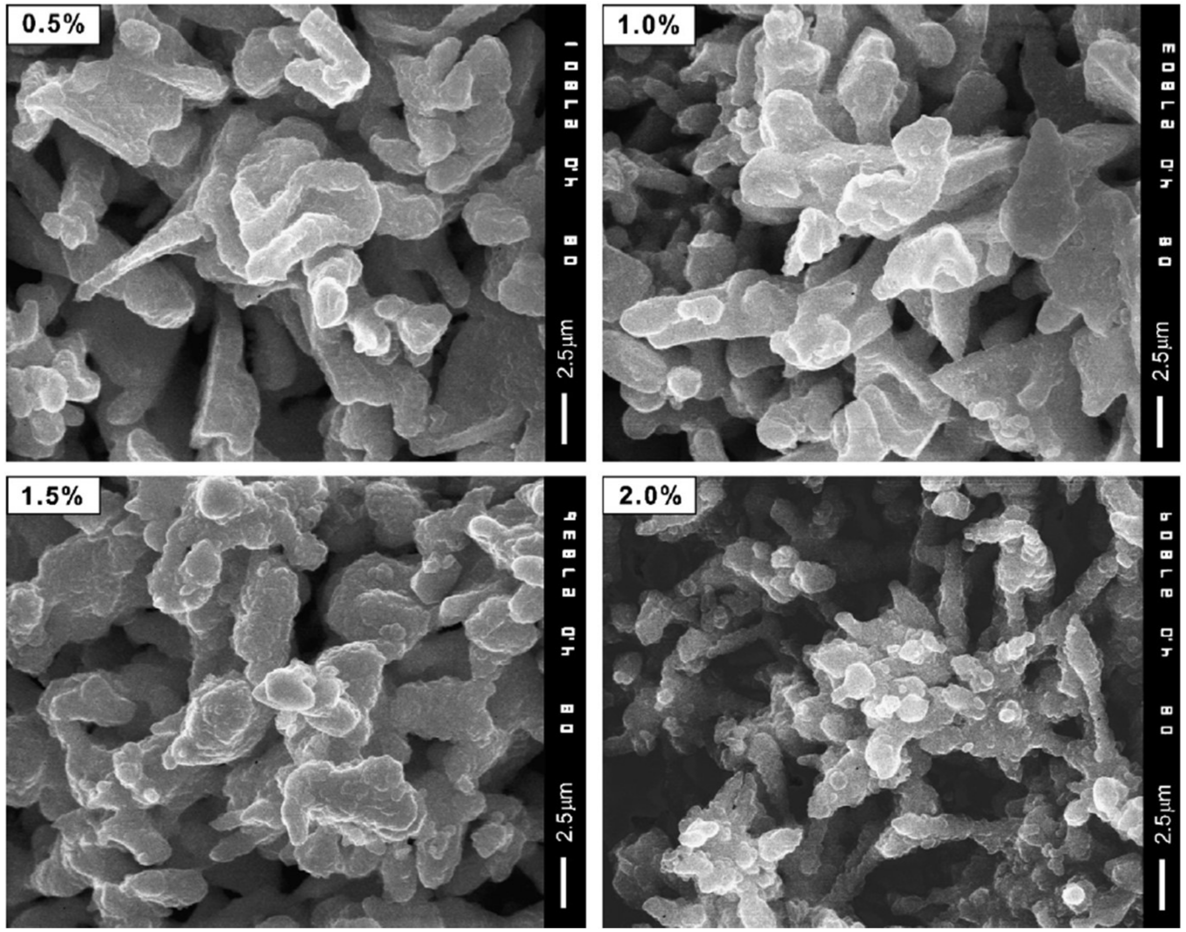
Ref: Ban. Journal of Power Sources. (2002) 107. p167-172; Mryvold Jornal of Power Soruces (2003) 117 p187

# Barium Sulfate – Basics

- **Variants**
  - <0.1 μm, 0.1-0.5 μm, 0.02-0.08 μm
- **Loading Considerations**
  - 0.5-2.0% wrt PbO
  - Heavily application dependent, deep cycle batteries typically favoring more
- **Performance Effects (Varies by Product)**
  - Improved cyclability
  - Improved CCA recovery

# Barium Sulfate – Theories of Function

- **Lead Sulfate nucleation agent**
  - Isomorphous with certain habits of $PbSO_4$ (template)
  - Lowers overpotential of $PbSO_4$ nucleation, easing its formation
  - Not electroactive or dissolvable
- **Necessity?**
  - In cycling, or at least <98% SoC, $PbSO_4$ is present in higher quantities than $BaSO_4$ so the nucleation agent is already already present in the “natural” form
- **Agglomeration problems with nanoBa?**



Ref: Pavlov. J. Power Sources. (2010) 195 p4435

# Wrap-Up and DCA/High Temperature Report Card

- Negative plates play key roles in defining DCA magnitude, but advanced designs can provoke high temp failure
- A diversification in the additive space aims to provide the industry with the tools it needs to stay competitive:

| PAM Additive | Primary Effect(s) | Effect on DCA Magnitude | Effect on DCA Memory | Effect on High-Temperature Failure Modes |
|---|---|---|---|---|
| **Carbon** | Conductivity, Porosity | Increase | ? | Neutral, some exacerbate failure |
| **Nanomaterials** | Morphology, Porosity | Increase | ? | Some improve |
| **Organics** | Morphology | Decrease | ? | Can reduce water loss |
| **Barium Sulfate** | Morphology | Can Increase | ? | ? |

***Global research collaborations can help define balance in these additives, understand DCA Magnitude/Memory origin, and move the industry forward***

**Honorable Mentions:**
Titanium oxide: poor conductor that can still sterically hinder the lead sulfate
Bismuth sulfide: HER reduction agent

Go to www.menti.com and use the code 46 01 73 7

# 502-3: Please place each NAM additive on the chart to reflect your understanding of its effects on each variable

Mentimeter

1 Carbons
2 Nanomaterials
3 Organics
4 Barium Sulfate

3 Organics
4 Barium Sulfate