

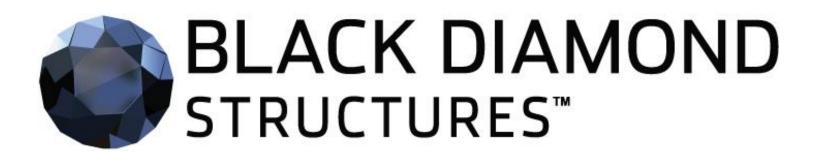
# **MOLECULAR REBAR<sup>®</sup>:**

### Formulated Discrete Carbon Nanotube (dCNT) Additives

Dr. Jeremy P. Meyers, Steven W. Swogger, Dr. Nanjan Sugumaran, Dr. Paul Everill



### Who We Are



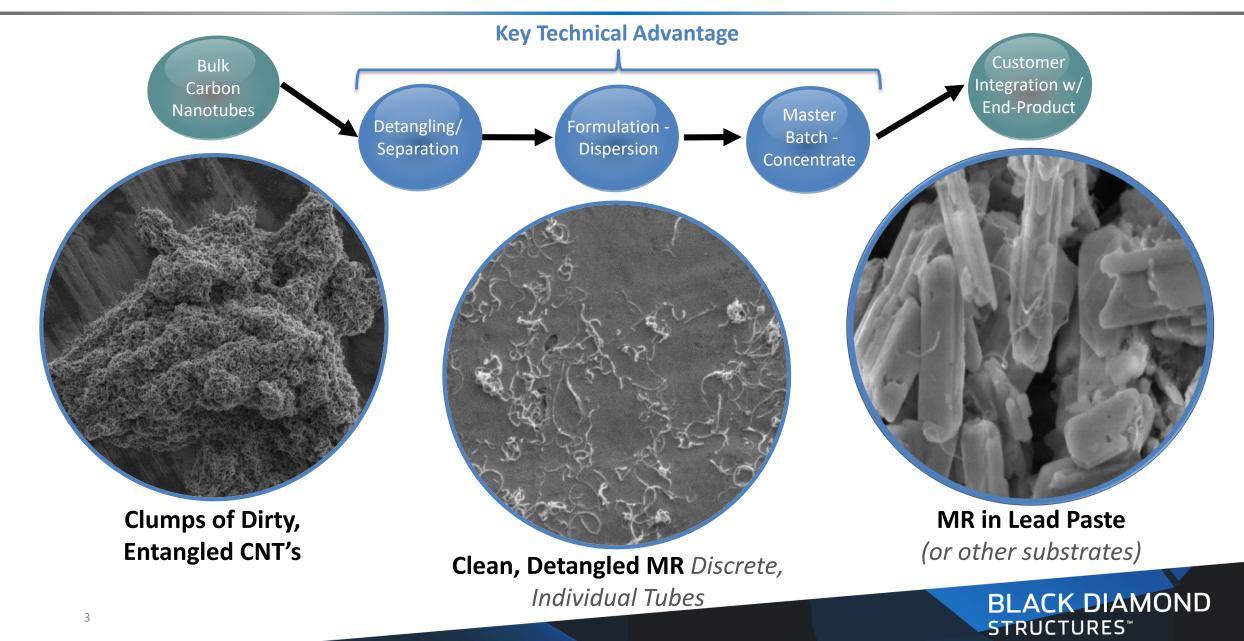
**Black Diamond Structures** is a developer, manufacturer, and marketer of innovative nanomaterial products and solutions based on revolutionary discrete carbon nanotube (dCNT) technology, **MOLECULAR REBAR**<sup>®</sup>



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## **Detangling Traditional CNT into MOLECULAR REBAR**



• For carbon compounds to be effective, they must fully integrate with the lead system; they must not simply be "along for the ride"



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- MOLECULAR REBAR<sup>®</sup> products are formulated for this level of paste integration to maximize benefits

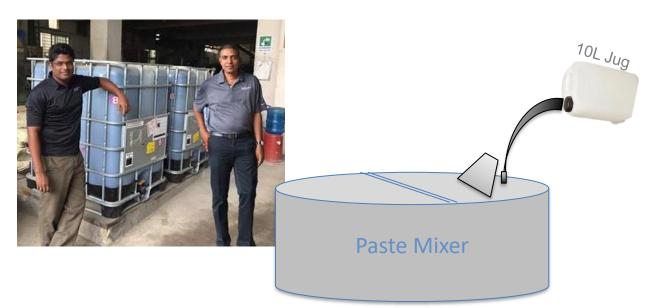


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  - No capital expenditures or modifications to pasting lines required.
- MOLECULAR REBAR<sup>®</sup> have specific affinity for lead oxide allowing them to integrate effectively
  - Carbon poorly integrates into paste mixtures
  - Discrete CNTs associate with lead oxide and are easily cleared from aqueous mixtures



Carbon does not integrate with lead or acid Paste Mixer

Lead & Dilute Acid

MOLECULAR REBAR<sup>®</sup> integrated into the lead

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10L Jug

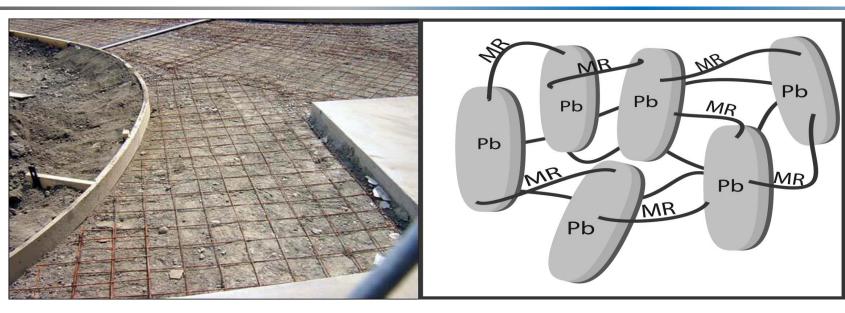
### **MOLECULAR REBAR®** Integrate with PbO in H<sub>2</sub>O/Acid

### Molecular Rebar® Cleared Homogenous Acid + 10 g Mixture PbO 100% Lead/MR (100%) MR in dilute H<sub>2</sub>SO<sub>4</sub> Post Add of PbO 9

- MOLECULAR REBAR<sup>®</sup> uniformly mixes with water and acid in battery paste.
- MR is strongly attracted to the lead as automotive-grade lead oxide is added to mixtures of MR and water or acid
- MR has significant interaction with lead, water, and acid

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### Not Another Carbon: Unique Form & Function



- MR acts a a physical and rheological modifying agent, its form and function are unique from Carbon; "Rebar Effect"
- Benefits of MR are no derived primarily from surface area, hence addition rates at 10% of less of Carbon

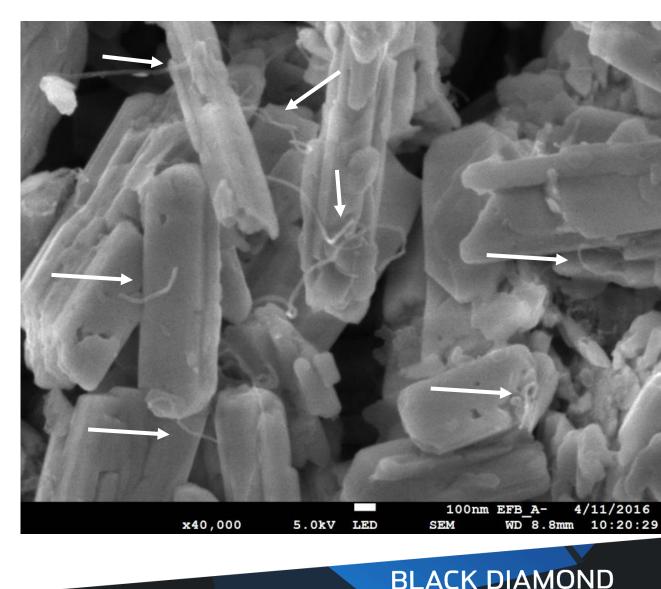
- THE		Pb	pb	
	Pb			
A MAN				arbon

- Carbon has an important role in conductivity and is necessary in a lead acid battery
- Its interactions and purpose are different than MR

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### **Not Another Carbon: Unique Form & Function**

- MR products are formulated for ease of use and incorporation
  - No processing issues or the resulting performance issues (density, plate consistency, etc.)
  - Can be used alongside carbon, expander, other solutions with additional and even corrective benefits.
- MR creates a network of individual nanotubes reinforcing the plates, adding lasting strength and durability



### **Consistent Benefits of MOLECULAR REBAR® Across Applications**

### • More Efficient Charging with dCNT

- Reduced Recharge Times
- More Consistent Capacity & Charge Acceptance
- Allows Charging at Higher Rates without Transition to Gassing

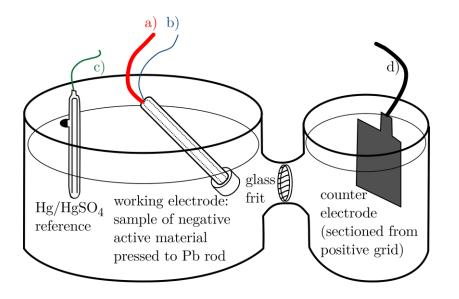
### Improved Maintenance of the Micro-Structures

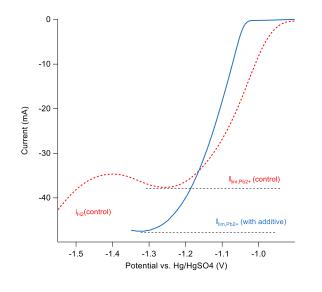
- Sustains a more Effective Conversion of Active Material
- Reduces and Suppresses Irreversible Sulfation
- Observed both Chemical and Mechanical Improvement



## Finding Transition from Pb Charging to H<sub>2</sub> Evolution

• Linear Sweep Voltammetry:





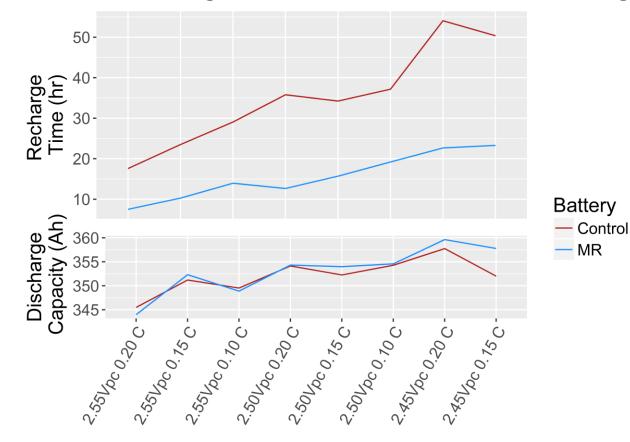
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 Pb charging can sustain higher limiting current with MOLECULAR REBAR<sup>®</sup> in NAM paste, either by promoting diffusion or attacking PbSO<sub>4</sub> particles.

## **Recharge Time Reduction + Capacity Retention**

#### Significant reductions in recharge time across numerous conditions/application charging conditions



#### Various V/i Charge Profiles to 115% after C-20 Discharges

Reduction in time versus Control to return 115% of the C20 Capacity of sets of 3ct 6V 500Ah Flooded batteries.

- MR has a major impact on charging from 90% SOC and beyond
- MR prolongs the Constant Current portion of charging
- MR increase the Current in the Constant Voltage portion of charging
  - Even with much faster Ah return the conversion efficiency is high as shown by the maintained capacity.

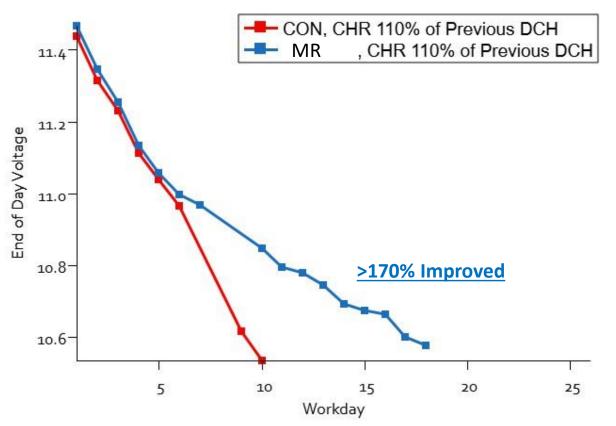
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### **Improved Charge Efficiency**

Lab Simulation Testing: Fixed Ah Input (110%)



The batteries are discharged for a "workday" using 10 cycles or "trips," each with five 10min discharges followed by a 10min rest, resulting in > 80% DOD over a 10-hour duration. Recharge is the same for all batteries and either 8-hours or 10-hours each workday. 12V 80Ah Flat Plate Batteries

- All batteries charged to 110% of the Ah discharged during the workday cycle; 115% is recommended, simulation intentionally undercharged
- MR batteries converted more of the 110% Ah Input back into useable capacity and 70% more cycles
- MR Improves charge efficiency



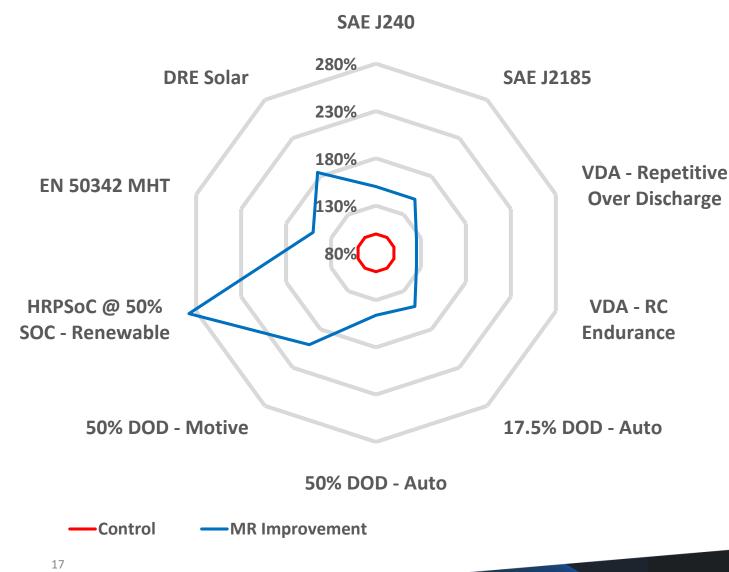
## More Efficient Charging with MOLECULAR REBAR®

- More Efficient Charging with MOLECULAR REBAR®
  - Reduced Recharge Times
  - More Consistent Capacity & Charge Acceptance
  - Allows Charging at Higher Rates without Transition to Gassing



## **Preserving Microstructure for Reliable Performance**

### **Customer Provided Durability Focused Cycle Tests**



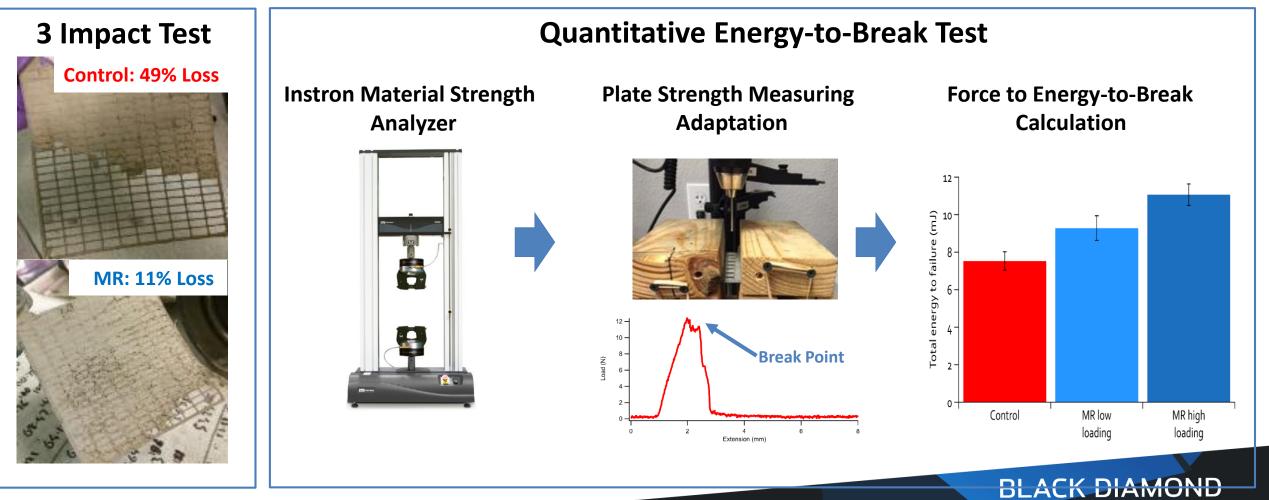
- MR strengthens and maintains the microstructure of the Negative and/or Positive Active Material
- The added Mechanical Integrity & Durability through MR addition can be seen through extended cycle life in many tests by reducing or preventing:

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- Active Material Shedding
- Active Material Growth
- Sulfation
- Grid Corrosion

### **Increased Plate Durability**

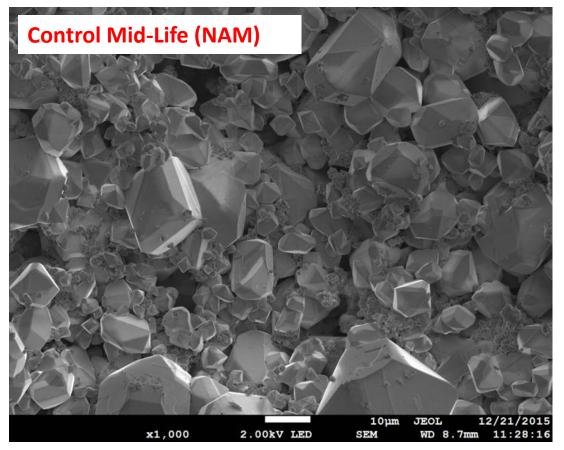
- MR the increase the strength of the active material, reinforcing the lead matrix
- Qualitative and Quantitative tests indicate increased strength of the micro-structure



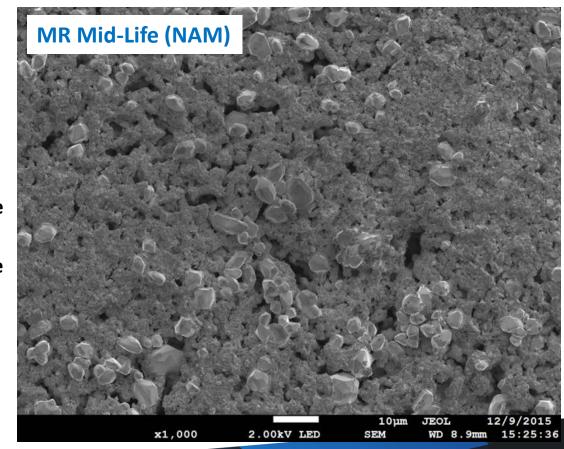
## **Retaining Microstructure in PSoC Cycling**

#### • After >4 Months of intensive PSOC cycling:

- MR decreases sulfate crystal size and frequency allowing the majority of the plate to remain as active sponge lead
- Plates are noticeably stronger to the touch upon teardown; dCNT strength benefits retained through life



Micrographs at 1000x resolution illustrate MR's ability to ensure uniform NAM crystal structure even after > 4 months of cycling

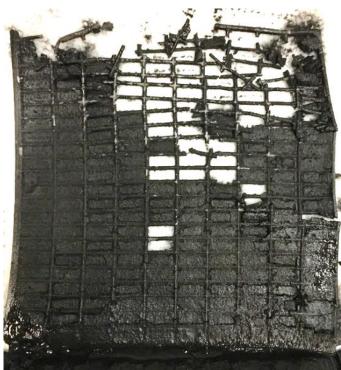


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### **Retained Structure at End of HOT Cycle Life**

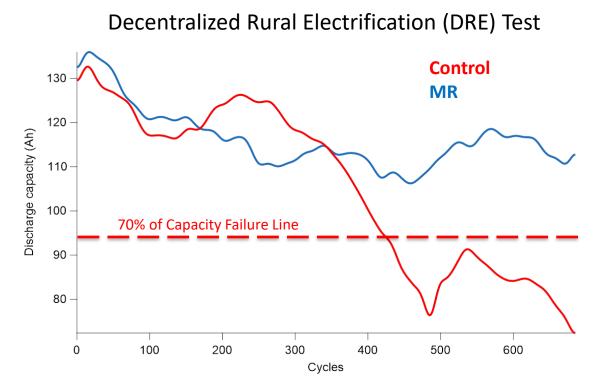
- SAE-J240 @ 70C = High-temperature, abusive study mimicking automotive battery operating conditions
- Altered Failure Modes:
  - Control batteries failed by NAM growth, shorting, PAM collapse
  - Batteries with MR completed 60% more cycles and the active material is better intact with less corrosion
    Control Positive
    MR Positive







### Synergy of Efficient Charging + Reliable Microstructure



Step	Mode	Protocol	Cycles	Potential Failure			
1	Preparation	1) Fully charge the battery					
		2) Discharge at C/10 A till 10.5V					
2	Undercharge cycles	1) Charge at C/10A till 14.1V		Acid stratification			
		2) Rest for 3 hrs	5	Sulphate growth			
		3) Discharge at C/10A till 10.5V	5				
		4) Rest for 3 hrs		AM shedding			
3 Overc		1) Charge at C/10A till 120% Capacity		Corrosion			
		2) Death fair 2 hins		Active Material loosening			
	Overcharge cycles	2) Rest for 3 hrs		Sulphate growth			
		3) Discharge at C/10A till 10.5V		Active Material shedding			
		4) Rest for 3 hrs		Waterloss			
R	Repeat sequences 2 and 3 until discharge capacity in overcharge cycle drops below 70% of C/10 capacity						

- DRE test replicates failure modes seen in real applications
  - Water loss, corrosion, sulphation, active material shedding
- Each cycle lasts ~24 hours
- MR is taking in more Ah per charge without increasing water loss
- MR delays long-term failure modes, extends lifetime >50%
  - Control fails at 425 cycles. MR capacity has stabilized after initial break-in and continues to cycle without degradation beyond 550 cycles

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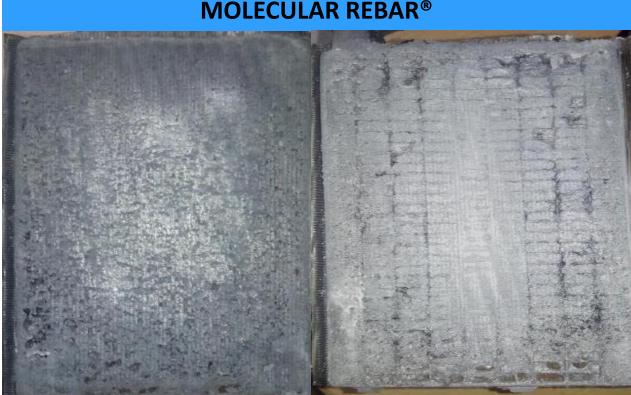
## MR Suppress Sulfation, Maintain Capacity

• DRE Test (Negative Plate Tear Down Plates)

#### Control



- Non-uniform material utilization
- Material soft and puffing/falling out
- Heavily sulfated surface
- Large insulative Sulphate crystals

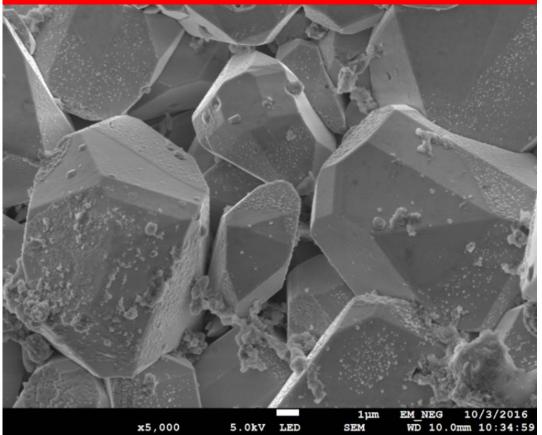


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- Smaller and uniformly sized crystals
- Shiny surface, plate still usable
- No sulfate present on surface

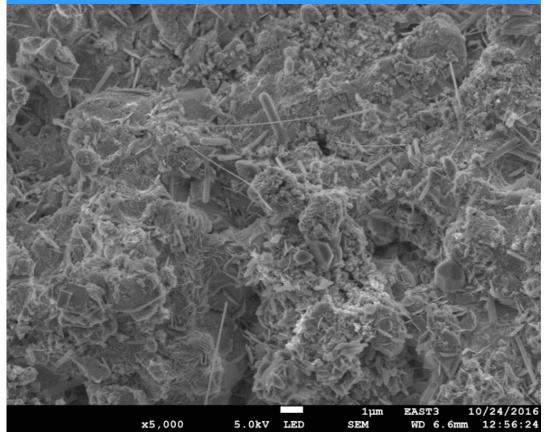
### **MR Preserve Microstructure throughout Life**





- Non-uniform material size
- Major lead sulfate crystal growth





- More uniform material size
- Minimal lead sulfate crystal growth

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### **MOLECULAR REBAR® Summary**

- MOLECULAR REBAR<sup>®</sup> products made of dCNT are designed to be easily be incorporated into industrial pasting lines with minimal to no changes to recipes or equipment.
- MOLECULAR REBAR<sup>®</sup> Provide Similar Benefits Across Applications
  - More Efficient Charging with MOLECULAR REBAR<sup>®</sup>
    - Reduced Recharge Times
    - More Consistent Capacity & Charge Acceptance
  - Improved Maintenance of the Micro-Structures in PAM and NAM
    - Sustains a more Effective Conversion of Active Material
    - Reduces and Suppresses Irreversible Sulfation