The role of additives in Auxiliary and Energy Storage Batteries

21st Asian Battery Conference / Borneo, September 2025

Content

Introduction

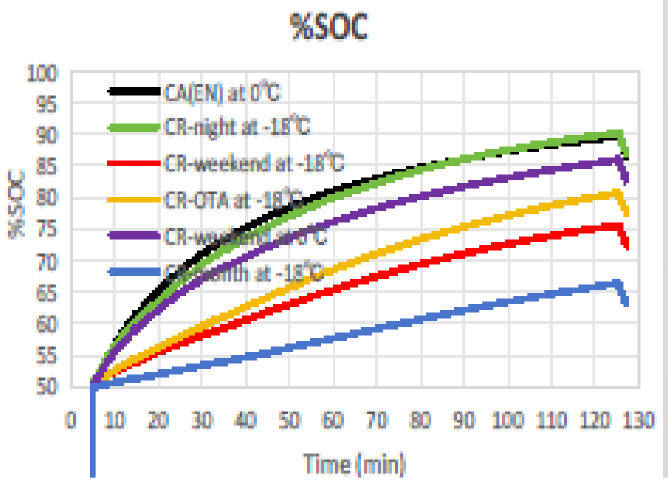
- The development of new type of automotive and energy storage systems could represent a significant market opportunity for lead batteries.
- Both applications require fast **Charge Recovery (CR)**, particularly under partial state of charge (<50%) and very low temperatures (up to -18ºC).
- The latest IEC draft for auxiliary and backup batteries include new tests to measure the State of Charge (SoC) and State of Function (SoF).
- Several battery makers are providing new data under different test conditions that are showing interesting (but not always expected) test results.
- **The role of additives is key to improve charge recovery and determine the feasibility of lead battery for new applications.**

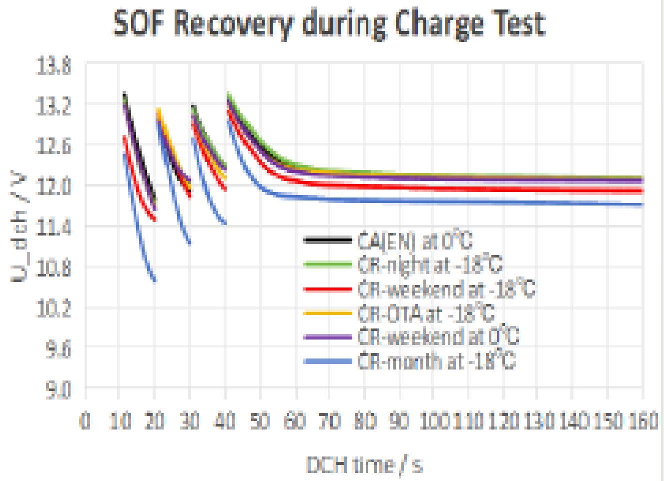
Content

Charge Recovery

SoC (% Charge) vs SOF (Discharge Voltage)

- Charge recovery tests of automotive flooded batteries were done in different environmental conditions:
  - ✓ Charge Acceptance (CA) at 0ºC (standard IEC 60095-1 test).
  - ✓ Charge Recovery (CR) at -18ºC (new IEC 60095-8 draft).
- As expected, the new charge recovery test (at very low temperature) is very demanding for lead acid batteries.
- Longer rest period (supporting key-off loads) reduce further the charge recovery due to lead sulfate recrystallization.
- Quite interesting is to observe that despite the low Ah charge recovered (%SoC), the discharge voltage is still very high.
- **State of Function (SoF) is maintained along the discharge, even with the minimal charge previously recovered.**



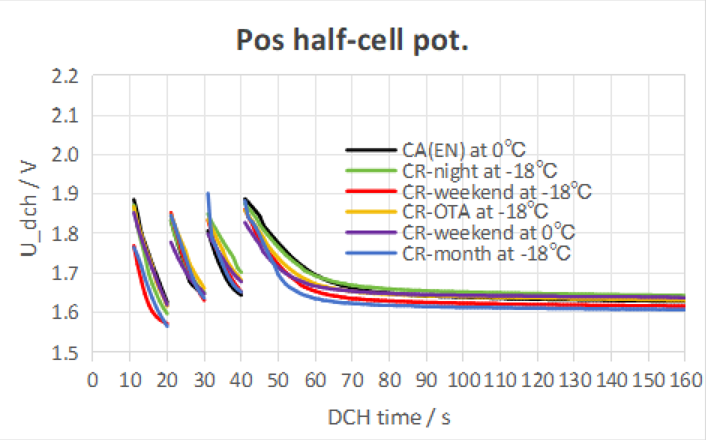


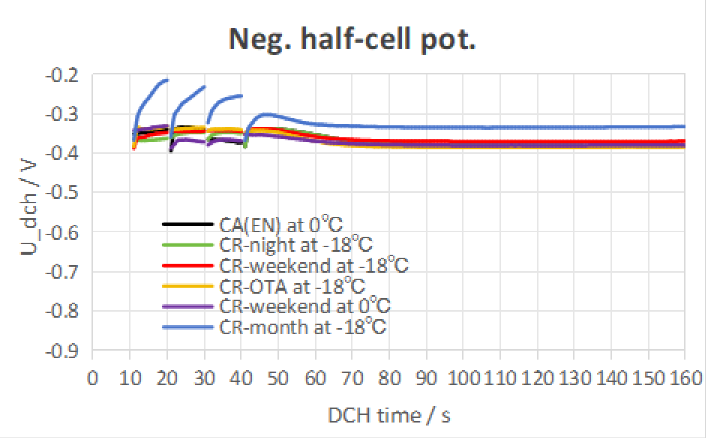
E. Karden, Camel tests / CBI-ALBA workshop, Turin (2025)

Charge Recovery

Positive vs Negative Potential

- Further details of the charge recovery behavior can be obtained by measuring the half cell potentials.
- SOC recovery at very low temperature (-18ºC) is quite limited, but SOF is very fast even after long rest periods.
- The positive potential is quite high during short pulses (pseudo-capacitor) and maintains the SOF for longer periods (plateau).
- However, under the most demanding conditions (CR-month at -18ºC), the negative plate is strongly polarized.
- **The root cause for low charge recovery was negative plate polarization that limit the charge current.**





Content

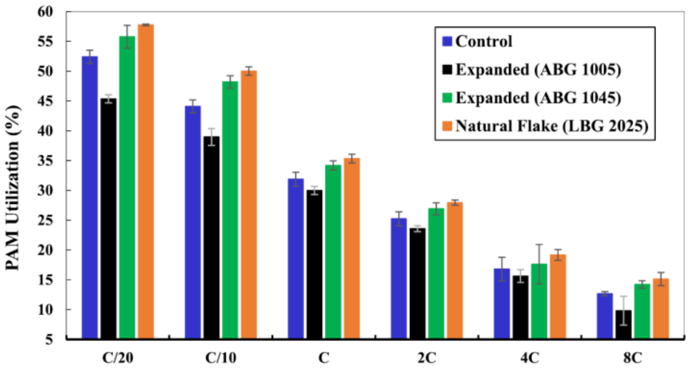
Positive Active Material Additives

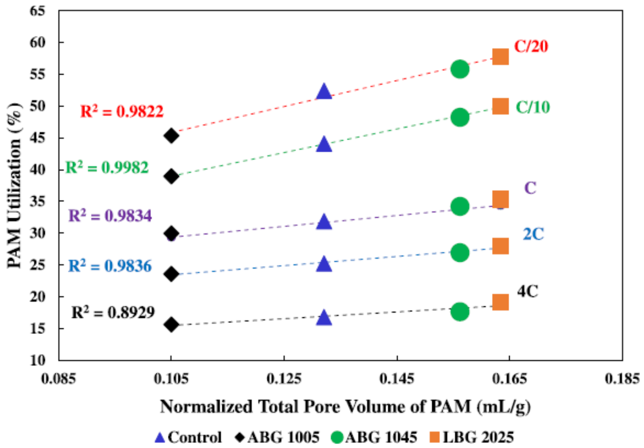
- The use of different types of additives in the positive plate have been investigated extensively with limited success up to now.
- **Carbon** materials (Graphite) are not fully stable in the highly oxidative conditions of the positive plate but creates additional porosity that increases the capacity.
- **Silica** compounds increase surface area and high-rate performance, maintaining the PAM microstructure along the life.
- **Nanomaterials** (Carbon Nanotubes, Graphene) modify the active material microstructure, improving the access of acid to the internal part of the active material.
- **An overview of the most recent publications show that PAM additives are still an interesting research topic for automotive and industrial lead batteries.**

PAM additives

Expanded Graphite (EG)

- Currently used in the negative plate, EG can also be used as a conductive additive for the positive plate.
- Two EG samples (with different particle size and crystallinity) were recently investigated as positive additives.
- PAM utilization can be improved with expanded or natural flake graphite, due to the conductivity and acid supply enhancement.
- A direct correlation exist between PAM utilization and total pore volume, but not with the electrical resistance.
- **Particle size and crystallinity seems to be more important than the electronic conductivity of the expanded graphite.**





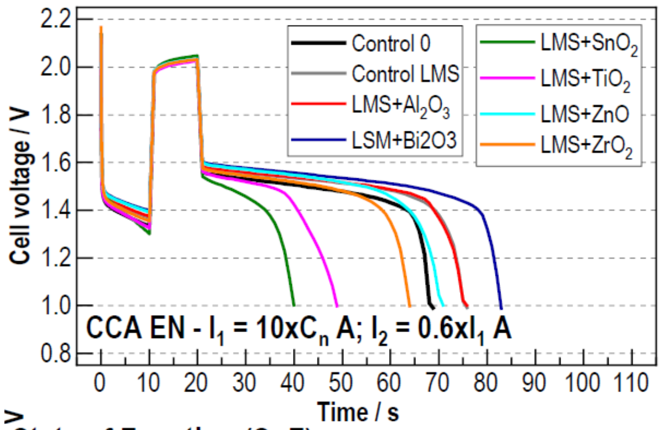
J. Kosacki et al. / Journal of The Electrochemical Society, 2021 168 120540

PAM additives

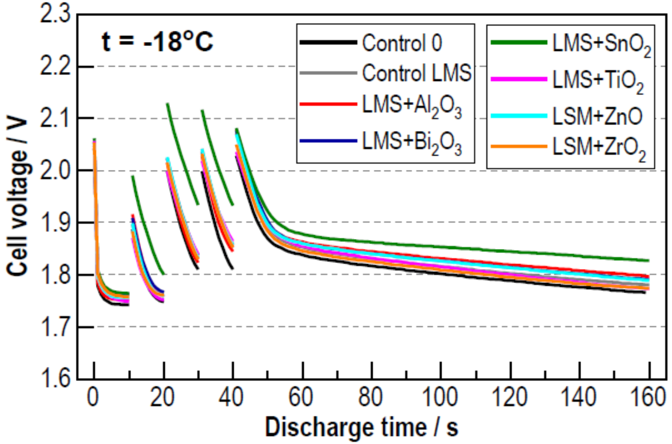
Lead Monosilicate (LMS) compounds

- LMS additives increase the PAM surface area, improving the high-rate capacity.
- On the other hand, some metallic oxides (like Al_2O_3, Bi_2O_3, SnO_2, TiO_2, ZnO & ZrO_2) may also improve performance and cycle life of lead acid batteries.
- Preliminary cell tests of doped LMS (+ Bi_2O_3) in PAM show an increase of cold-cranking ability.
- On the other hand, the voltage in discharge (SoF) after charge recovery tests is significantly increased with doped LMS (+SnO_2) in the PAM.
- **Combining LMS with select metallic oxides may improve both high-rate performance and charge recovery.**

Cold-cranking ability test (CCA @-18°C)



State of Function (SoF)

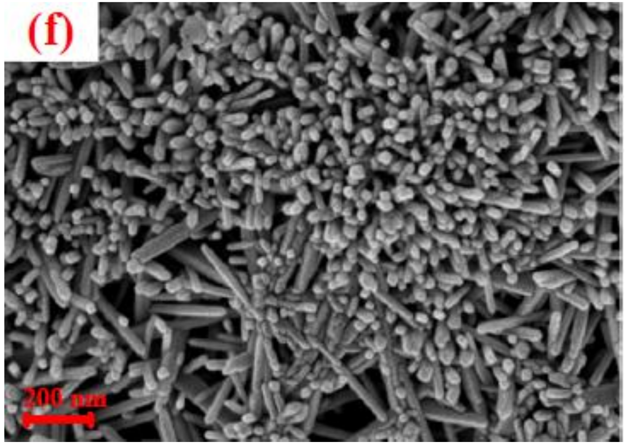


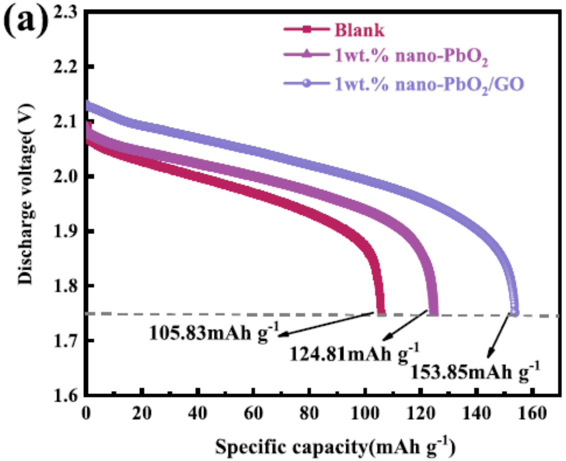
P. Nikolov, BAS-Hammond / CBI European Workshop, Turin (2025)

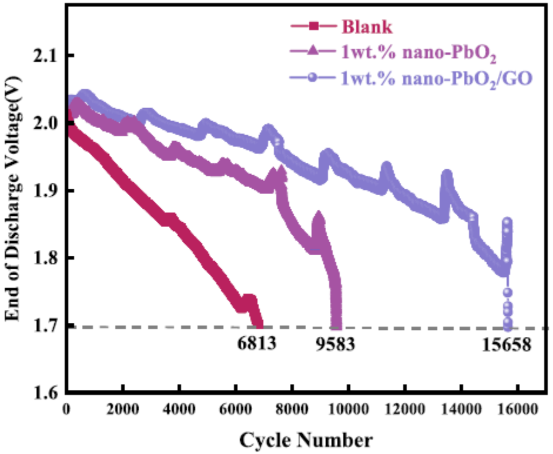
PAM additives

Graphene Oxide (GO)

- The addition of GO to PbO_2 electrodes promotes the formation of a dendritic 3D rod-like PAM structure, that inhibits the growth of bulky $PbSO_4$ particles.
- GO additive significantly improves the specific capacity and cycle life at partial state of charge.
- **The dual functions of GO (as nucleating and conductive additive) modify the PAM microstructure and reduce sulfation.**







L. Ren et al. / Colloids and Surfaces A: Physicochemical and Engineering Aspects 676 (2023) 132303

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3. PAM additives
4. **NAM additives**
5. Summary and outlook

Negative Active Material Additives

- Expander formulations are key to obtain the negative surface area needed for high-rate performance and maintain it along the cycle life.
  - ✓ **Barium sulfate** crystals act as nucleating agents for lead sulfate precipitation.
  - ✓ **Carbon** materials reduce hydrogen overvoltage allowing higher charge current.
  - ✓ **Lignin** is adsorbed on the carbon surface, helping to maintain NAM surface area.
  - ✓ **Lead Monosilicate** increase the surface area with little effect on the NAM porosity.
- **NAM additives play a key role in charge recovery as they control the negative overpotential, allowing to increase the positive plate state of charge.**

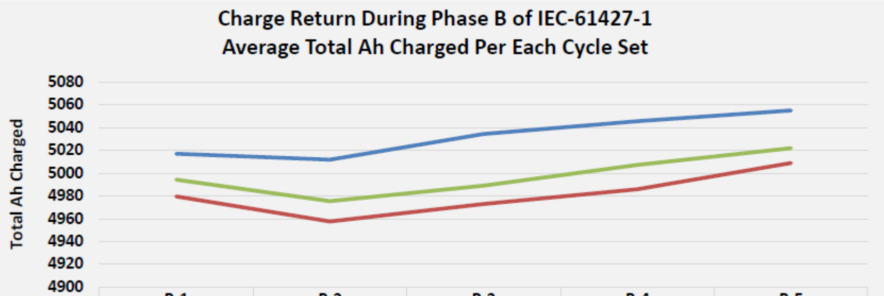
NAM additives

Barium Sulphate

- Industrial scale batteries were built with the same expander composition, except the $BaSO_4$ particle size.
- Cycle Life Testing were made under IEC-61427-1 cycle life norm (for solar application).
- The average charged capacity showed that HU-N accepts more charge, possibly due to smaller lead sulfate crystal produced by $BaSO_4$ nanoparticles.
- The improved Ah charged per cycle support stable discharge capacity at partial state of charge.
- **Small $BaSO_4$ crystals may also improve charge return and cycle life of energy storage batteries.**

Recommended BaSO4 Material	Supplier	Material Type	Details
EWO	Sachtleben	Standard (control)	Wet Milled Mined Material
PB-08	XinMei	Sub Micron	Uncoated Precipitated Material
HU-N	Venator	Nano	Uncoated Nanomaterial

% Versus Oxide	Expander Components			
	BaSO4	Carbon (Ace-Black)	Lignin (Van-A)	TOTAL
	0.70%	0.50%	0.20%	1.4%



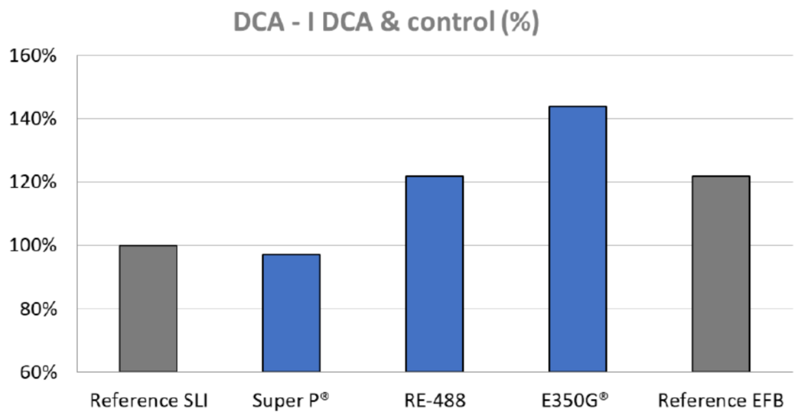
	B-1	B-2	B-3	B-4	B-5
HU-N	5017.0	5011.8	5034.3	5045.6	5055.1
PB-08	4979.6	4957.6	4972.8	4985.9	5008.9
EWO	4994.3	4975.4	4989.0	5007.2	5021.9

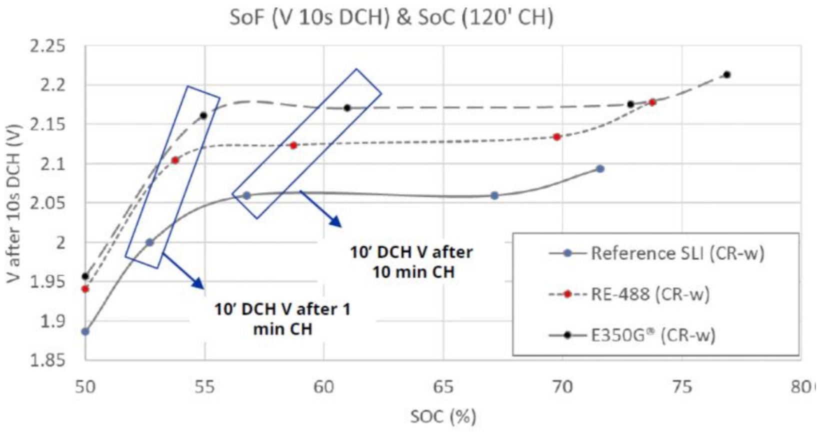
T. Wojcinski, Hammond / CBI technical meeting, Nashville (2024)

NAM additives

Carbon

- Charge acceptance is strongly related to carbon material properties (surface area and chemistry).
- New carbon materials have been developed to fulfill both the automotive starter and auxiliary battery requirements.
- Medium surface area carbon black (130-150 m2/g) represent a good compromise between dynamic charge acceptance (DCA) and reduced water loss.
- High surface area carbons (>300 m2/g) produce a strong impact on state of function and charge recovery.
- **Carbon materials are key to achieve the fast charge recovery demanded by new applications.**



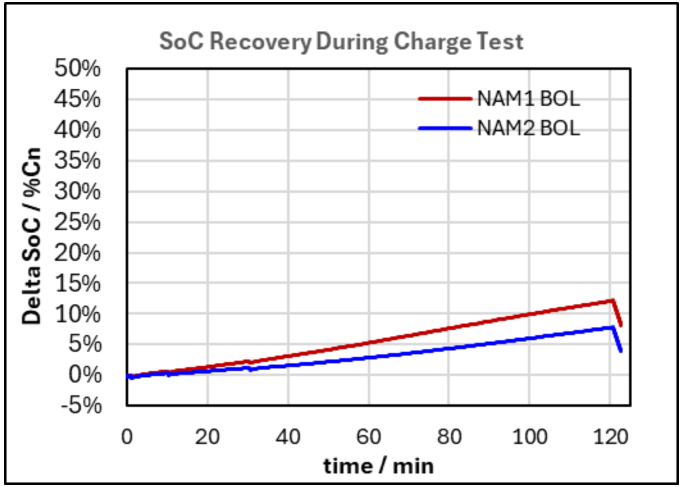


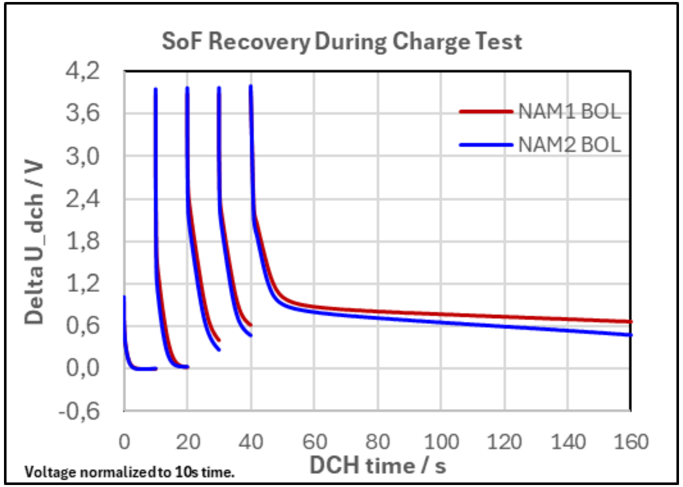
P. Garcia, Imerys / 19th European Lead Battery Conference, Milan (2024)

NAM additives

Expander formulation

- Charge Recovery tests were performed on AGM batteries with two different negative formulations:
  - ✓ NAM 1: Optimized to increase Charge Recovery (CR)
  - ✓ NAM 2: Optimized for cold cranking ability (CCA)
- The expander formulation introduced in the NAM 1 significantly improved Charge Recovery (SoC) and discharge voltage (SoF).
- However, highly demanding requirements for cold cranking time (NAM 2), limit the possibilities to improve charge recovery.
- **Optimizing the expander formulation for each application is key to develop new auxiliary and energy storage batteries.**



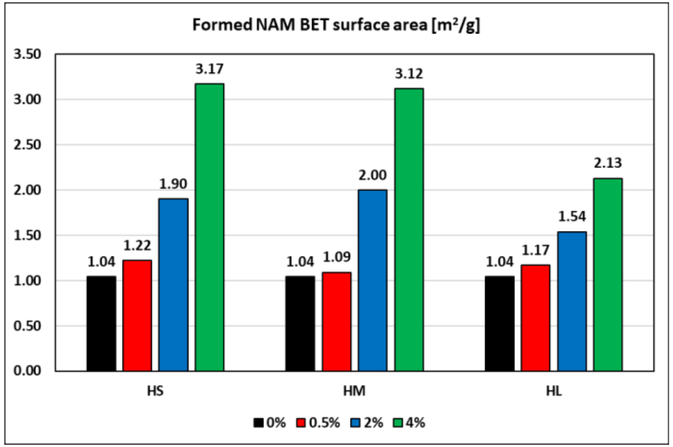


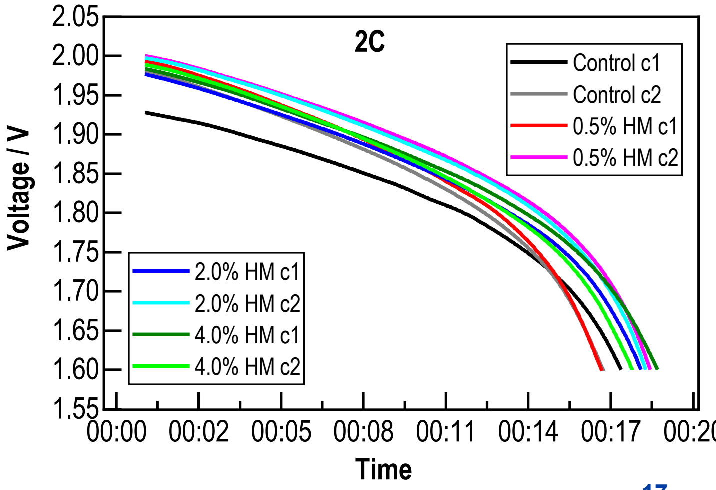
Ian Wolfe, East Penn / CBI-ALBA Workshop, Turin (2025)

NAM additives

Lead Monosilcate (LMS)

- LMS increase the NAM surface, with a clear effect of dosage (0.5<2<4%), but less significant of particle size.
- The effect on BET surface area is related to the high surface area silica produced by reaction of LMS with sulfuric acid.
- Low-rate capacity is usually limited by the positive plate porosity, but surface area determine the high-rate performance (2C) of negative limited designs.
- **LMS increases the surface area of the negative plate and may improve the high-rate performance of auxiliary and energy storage batteries.**





M. Robotti, Hammond / 19th European Lead Battery Conference, Milan (2024)

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Summary

- Carbon materials:
  - ✓ Graphite produces PAM expansion, increasing initial capacity and cycle life.
  - ✓ Carbon increase NAM surface and reduce overpotential, allowing fast charge recovery.
- Expander formulations:
  - ✓ High surface area Carbon (and small particle size $BaSO_4$) increase NAM surface area.
  - ✓ Optimizing charge recovery with new expander formulations may allow to fulfil the highly demanding auxiliary and energy storage battery requirements.
- Silica compounds:
  - ✓ Lead Monosilicate increase surface area, improving cold cranking and high-rate capacity.
  - ✓ Doped silica compounds improve cold cranking (CCA) and discharge voltage (SoF).
- Nanomaterials:
  - ✓ Graphene Oxide improves capacity and reduce sulfation by nucleating a conductive 3D microstructure inside the PAM.

Outlook

- NAM:
  - ✓ Optimize NAM expander formulations to improve fast charge recovery, while maintaining other automotive requirements (for instance: cold cranking duration >30 s).
  - ✓ Investigate NAM surface area enhancers (like Carbon or Silica compounds) to comply with the new auxiliary and energy storage requirements.
- PAM:
  - ✓ Optimize PAM porosity and composition with new types of Carbon or Synthetic Graphite.
  - ✓ Investigate doped Silica compounds (Bi, Sn) and Nanomaterials (CNT, GO) effects on PAM microstructure along the cycle life.

Thank you for your attention