From Basic To Advanced EFB Design – Function and Limits of Carbon

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Content

Function and Design of EFB Batteries

- EFB Batteries = Enhanced Flooded Batteries
- Introduced first by European Manufactures* as an alternative for AGM Technology**
- Their key-performance parameters are in-between advanced SLI batteries and AGM Batteries – reaching close to AGM performance for Advanced EFB

EFB Batteries are designed for:

- High (50% DoD) cycle life (reg. are 50% DoD, and 17.5% DoD in pSoc)
- High (dynamic) charge acceptance (CA, DCA)
- Operate in "Start-Stop" Applications
- To be more robust as compared to AGM Batteries

EFB technology is presently moving into their *third* design generation called "*EFB+C*"

* EXIDE Technologies was among the first companies developing this technology as "Advanced Flooded" Technology
**AGM Technology was initially developed as a new type of VRLA battery by Hoppecke in Germany in the 1990th

Generations of EFB Batteries

PENOX

„Basic“ EFB

„Advanced“ EFB

Future Designs

Generation „0“ (G0)
- 50 cycles @50% DoD
- pSoC cycling possible
- Initial testing at 20% DoD in pSoC
- Basic Design, gravity casted grids, no compression

EFB Gen.1
- > 100 cycles @50% DoD
- 17.5% DoD: >6 units
- CA: >1/Ah
- DCA: no req.
- Basic Design, improved plate designed, improved separators, slight compression

EFB Gen.2
- > 100 cycles @50% DoD
- 17.5% DoD: >9 units
- DCA: >0.3 A/Ah

- Improved NAM to PAM Ratio
- Use of Carbon in NAM

EFB-Gen.3 / „EFB+ C“
- > 150 cycles @50% DoD
- 17.5% DoD: >12 units; target: >15 units (VW >18 units)
- DCA: >0.4 A/Ah target: >1 A/Ah

- Thin grids with high mass utilization
- **Use of Functional Carbon**

Source of modified image: https://www.iconspng.com/image/121184/car-battery

“Basics” Design Features

- Modern battery designs tend to have a capacity limitation by the PAM
- Space limitations in the battery box shift designs often close to a limitation by the electrolyte (discharge below a density of 1.15 g/cm³ is critical)
- Density of the electrolyte should not be increased above 1.28 g/cm²
- In high temperature applications the electrolyte density is often reduced to about 1.26 g/cm³

- NAM surface is critical for charge acceptance, and designs are mostly based on terminal negative plates (one more negative plate)
- Effective NAM structure requires a min. porosity of 40 % and a min. surface area of 1 m²/g

- PAM porosity (>45%) is supporting mass utilisation. However, for a high cycle life a min. amount of PAM weight is needed.
- ***The battery requires a balanced design in terms of electrolyte, PAM to NAM weight ratio and relative geometric and electrochemical active surface area…***

"Basics"

Cold-Cranking is supported by:

- High surface area of the electrodes (> 1 m^2/g in PAM and >5 m^2/g in PAM) to reduce at a given Ampere rate the specific current density
- Higher acid density will increase the discharge performance, but limits the re-charge
- NAM structure tends to be the parameter critical for performance (as surface is more limited)

Dynamic Charge Acceptance (DCA) is supported by:

- High surface area of the electrodes is supportive (>1.5; better >2 m^2/g in NAM)
- NAM structure is critical for performance – advanced expander mixes supporting an enhanced surface
- Carbon additives are supportive – (loadings of functional carbon between 0.3 w% up to 1.0 w%)

Charge Acceptance (CA) is supported by:

- NAM to PAM ratio is critical (typical 1 : 1.1 up to 1.3)
- NAM structure is critical – advanced expander mixes supporting an enhanced interface with the electrolyte are supportive (both surface and bulk-volume interface)
- Easiest improved by having a higher number of thinner plates (geometric advantage of surface area)
- Functional Carbon additives are supportive, but less as compared to DCA

Basic Design for EFB Batteries

PENOX GmbH R+D Department	Requisitos técnicos da EFB 24.02.2022 – V2.0

Requisitos básicos para

o projeto de um

Bateria EFB

PENOX GmbH
Departamento de I+D
Alemanha

PENOX is supporting customer development activities – Manuscript available on „Basic EFB Design“

Improving Negative Active Mass (NAM)

<u>NAM is benefitting from:</u>

- Expander mixes supporting a higher and stable active electrolyte surface
- Expander mixes supporting a higher porosity with larger average pore structure
- Functional carbon addition adjusted to the type and amount of lignosulfonate*

<u>PENOX (new) directions are:</u>

- **Introducing optimized porosity in cured NAM, stabilized by a tetrabasic (4BS) negative curing**
- PENOX is testing the impact on charge acceptance and dynamic charge acceptance
- Synergy with functional carbon is investigated – a high carbon loading is not linearly related to a DCA performance – *carbon results in issues with water consumption, carbon loss by cycling and is very costly (up to 20k€/t)*

(*Borregaard, ABC 2020)

Improving Pore Structure of NAM

PENOX directions are:

Using a “classical” tri-basic curing (3BS curing)

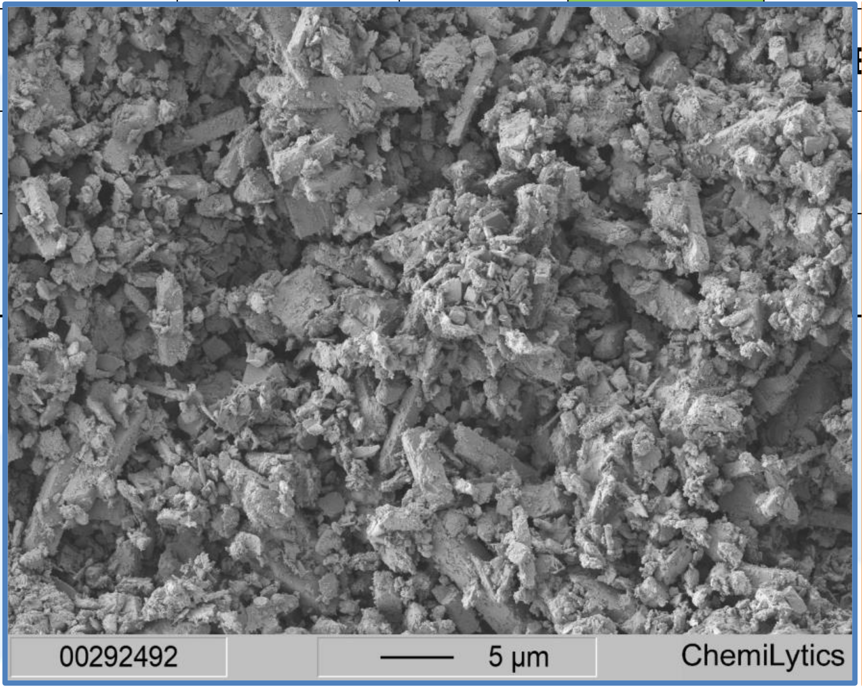
- Using lignosulfonate mixes improving pore structure
- Part of the research started in the AddESun-project (funded by the German ministry of economy)

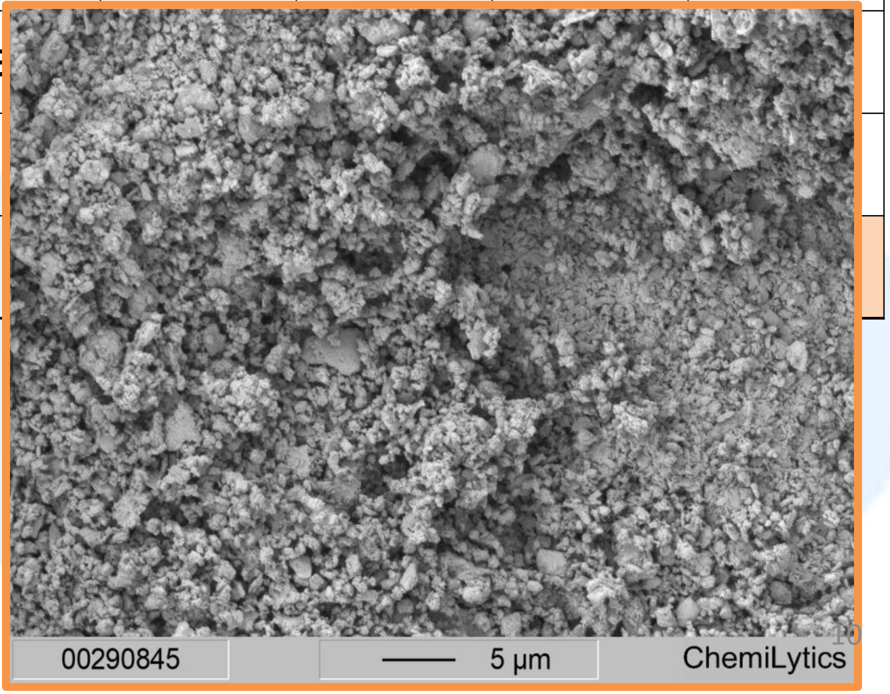
Using a tetra-basic curing (4BS curing)

- Using special PENOX expander mix and TBLS+® to realize a tetrabasic NAM structure

Studies on NAM Structure (3BS vs. 4BS)

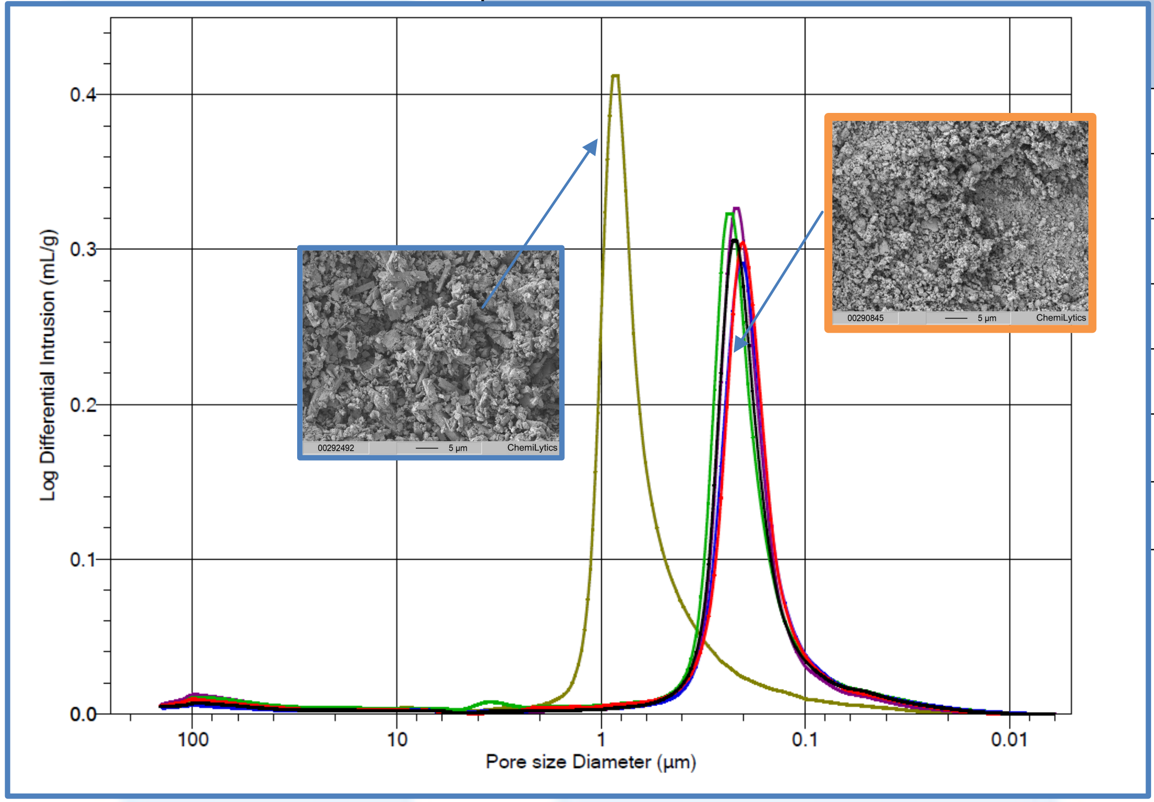
Extract from Testing Series of PENOX									
Parameters			Trial 3		Trial 4		Trial 5		Trial 6
Expander Mix and Carbon Type	Surface Area m²/g	Surface Area eff. m²/g	3BS	4BS	3BS	4BS	3BS	4BS	3BS
Carbon A (0.7%) powder & Lignosulfonate A	165	115	3BS	4BS					
Carbon B (0.7%) dispersion & Lignosulfonate A									
Carbon C (0.14%) dispersion & Lignosulfonate A									
Carbon B (0.7%) dispersion & Lignosulfonate DCA									





Studies on NAM Structure (3BS vs. 4BS)

	Reference	Trial 3		Trial 4	Trial 5
	3BS	3BS	4BS	4BS	4BS
	0.10	0.10	0.13	0.13	0.13
	2.46	2.37	1.12	0.99	0.65
	0.21	0.21	0.78	1.08	1.17
	0.16	0.17	0.38	0.27	0.85
	42.4	**43.4**	**50.6**	**49.2**	**49.9**
	0.310	0.330	0.415	0.380	0.505
	2.4	**2.4**	**1.4**	**1.44**	**1.12**



- All plates with 4BS curing have a higher porosity and higher median pore diameter

- BET surface area is lower for 4BS cured negative plates….

…will it be relevant?

Dynamic Charge Acceptance (DCA)

Expander Mix and Carbon Type	Surface Area m²/g	Surface Area eff. m²/g	Ce (Ah)	Ce/Cn	Ic (A)	Id (A)	Id/Ic	Ir (A)	I DCA (A/Ah)
Carbon A (0.7%) powder & Lignosulfonate A	**165**	**115**	12.71	1.16	3.02	12.27	4.07	11.65	**0.44**
Carbon B (0.7%) dispersion & Lignosulfonate A	**107**	**75**	12.11	1.10	3.73	11.96	3.24	10.66	**0.45**
Carbon C (0.14%) dispersion & Lignosulfonate A	**1485**	**208**	12.14	1.10	4.08	11.83	2.91	11.05	**0.47**
Carbon B (0.7%) dispersion & Lignosulfonate DCA	**107**	**75**	running						

- Target of the market: >1 A/Ah for an EFB battery (Gen 3+)
- Carbon alone will not be able to realize it

- **We found higher I DCA values with a 4BS structure as compared to 3BS structure**
- Low loading with high surface are carbon results in acceptable I DCA values
- Higher loading with high surface-area carbons are expensive and not supporting I DCA as expected

PENOX

Summary - NAM

- Charge acceptance is crucial for 17.5% DoD cycle life
- Carbon additives in NAM are one approach to improve DCA
- BET Surface is not the only relevant parameter => Porosity and pore structure matter as well!
- PENOX aims to realize an synergetic structure based on functional carbon and 4BS curing
- TBLS+® is a potential alternative and synergetic additive for 4BS curing of NAM
    - Increase of the porosity to >45% (as 40% in standard)
    - 3 to 4 times larger pore diameter as compared to the 3BS reference

- **Electrodes with PENOX TBLS+® in NAM showed:**
    - Higher DCA in comparison with reference plates (typical 0.1 up to 0.3 A/Ah)
    - Higher porosity is also an electrolyte reservoir and thus allows better mass utilisation
    - *Higher cycle durability in the 17.5% DoD Test (Ian Klein, ELBC 2020)*

Improving Positive Active Mass (PAM)

PAM is benefitting from:

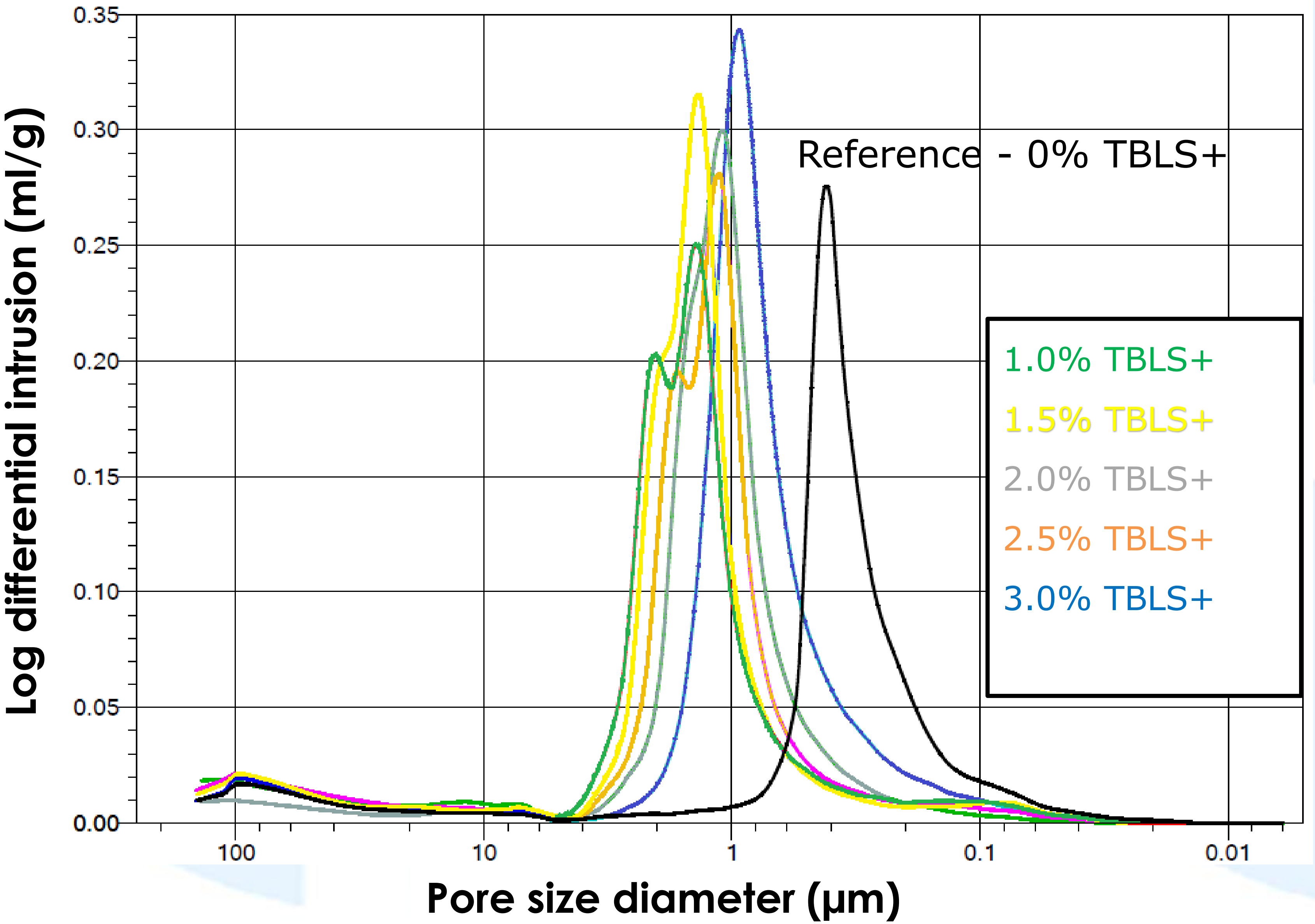
- Optimized mix of leady oxides with a specific distribution of particle sizes – very fine oxides (such as mill oxides) tend to reduce cycle life
- Addition of red lead is supporting the formation efficiency
- Tetrabasic curing (4BS curing) using TBLS+® to optimize the pore structure and thus the mass utilization

PENOX (new) directions are:

- Adjusting crystal size with tetrabasic seeding additives
- Advanced leady oxides for 4BS curing and improved AM structure

- **Introducing new bi-functional oxides such as PENOX RL+**

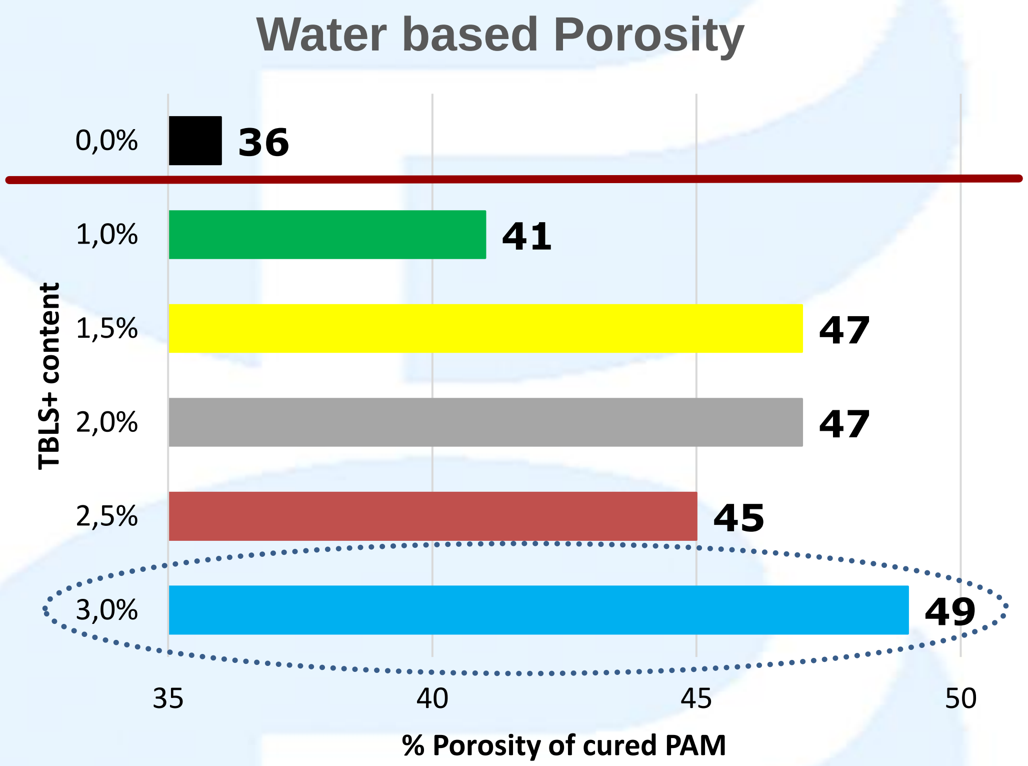
Effect of TBLS+® on the Cured PAM

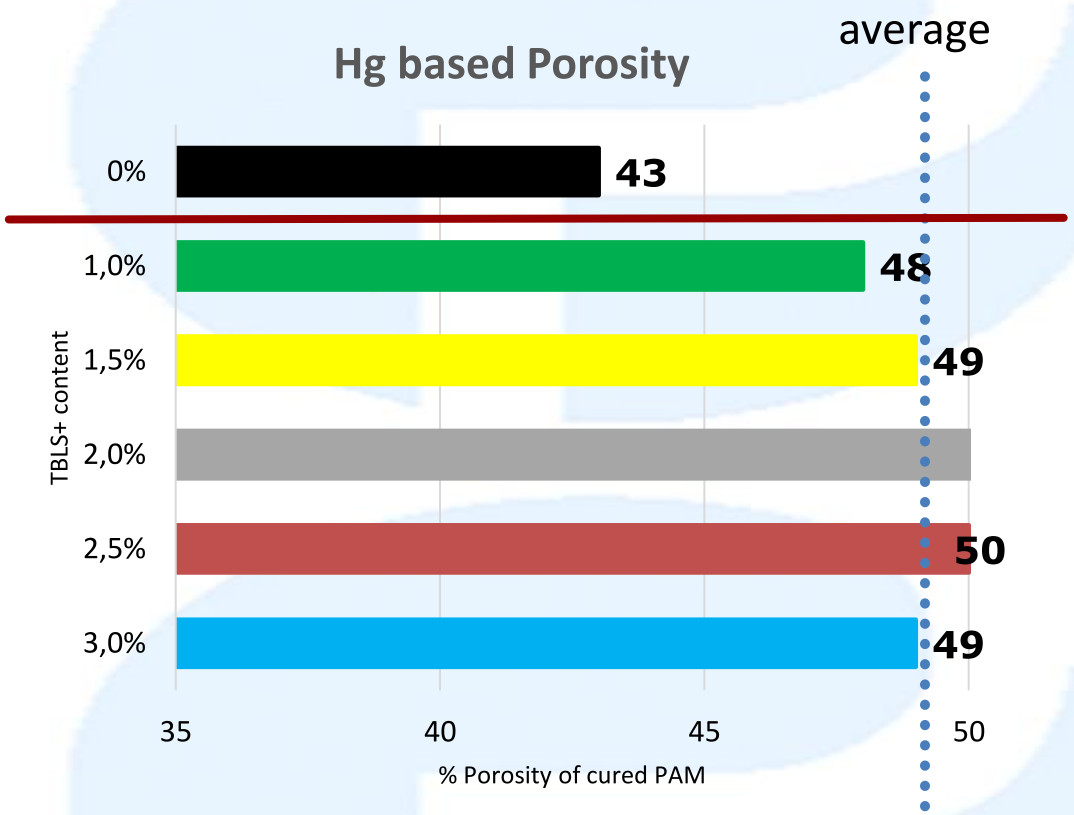


- Reference: 3BS
- Test series with 1 to 3% TBLS+® addition: 4BS

- **Pore diameter and porosity are studied as a function of TBLS+®**

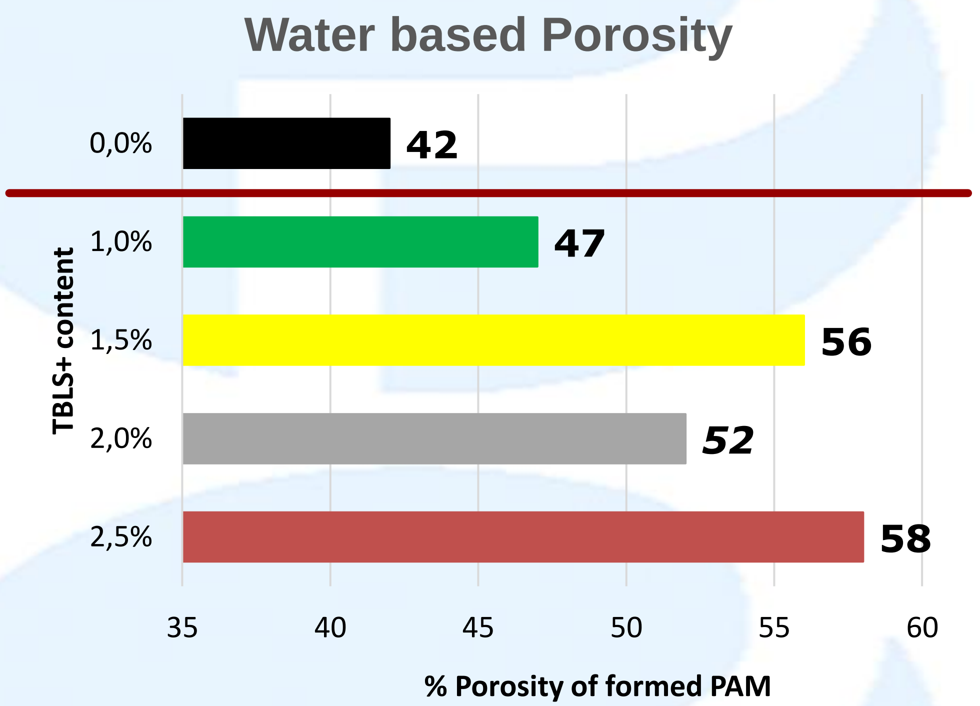
Porosity - Effect of TBLS+® on the Cured PAM

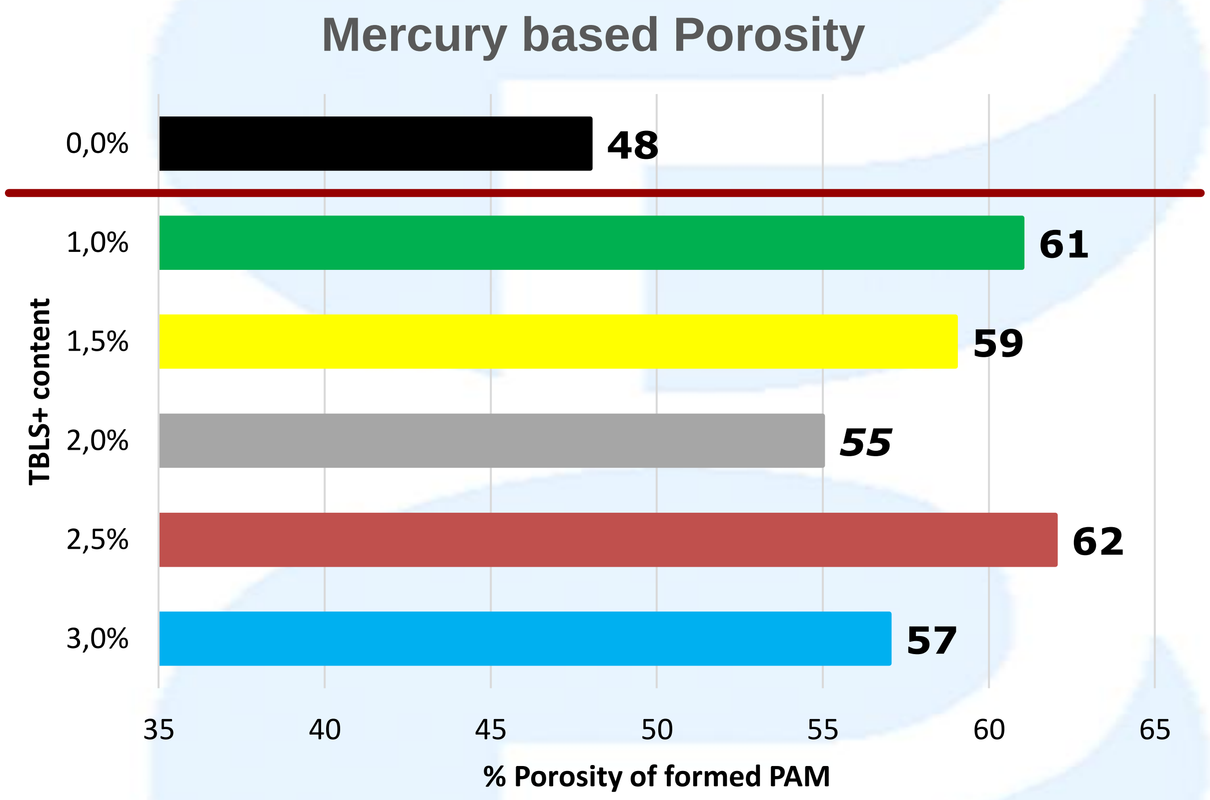




→ Cured electrodes with TBLS+® had 15 – 20% higher porosity than reference electrode

Porosity - Effect of TBLS+® on the Formed PAM





→ Formed electrodes with TBLS+® had min. 14% up to 30% higher porosity than reference electrode

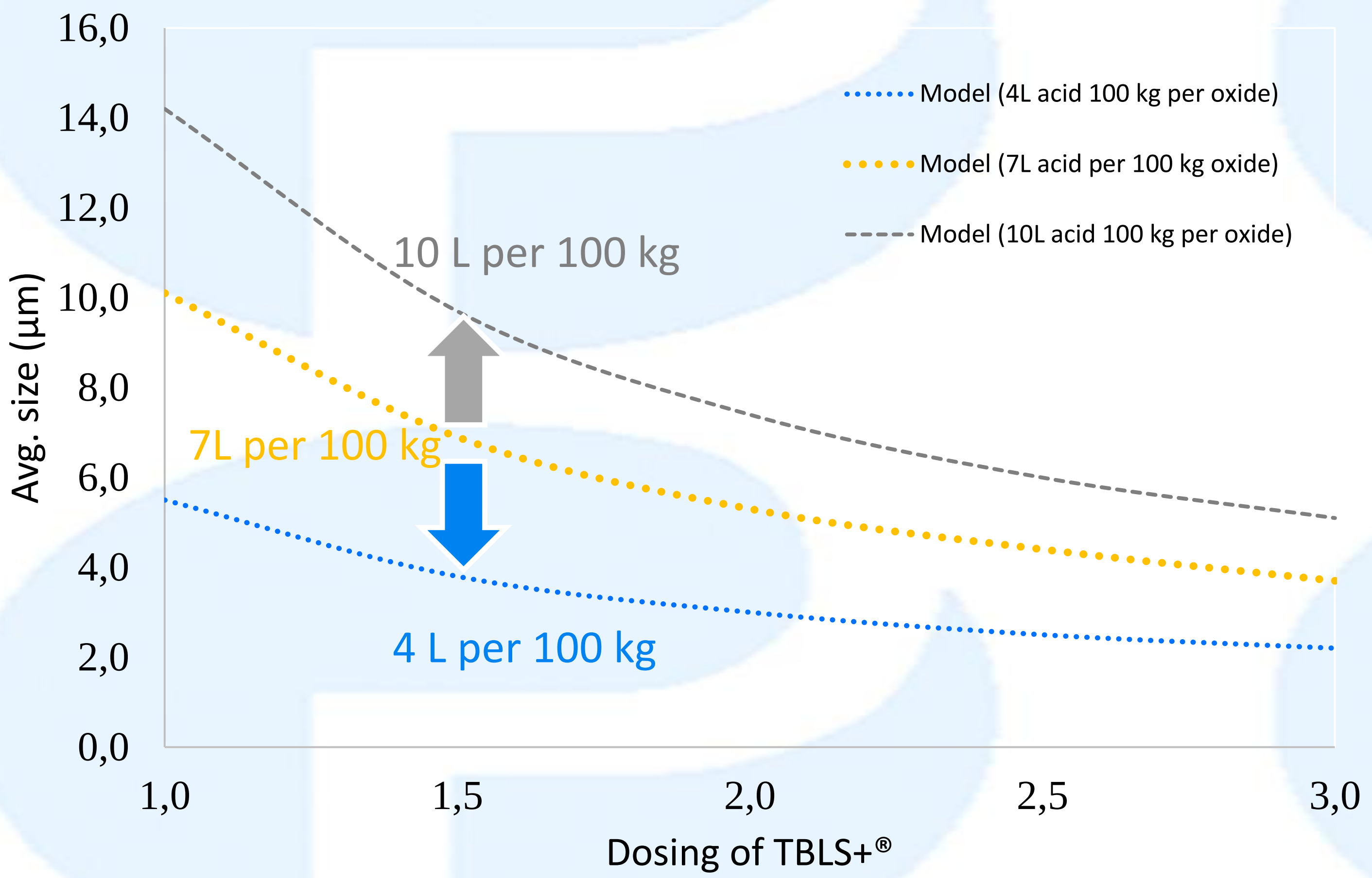
Seeding Model – to understand the Effect of TBLS+®

- Simple model to allow to estimate the optimal TBLS+® dosing in PAM
- Example provided is based on a Acid-to-oxide ratio of **7** litres sulphuric acid per 100 kg of dry lead oxide

Assumptions:

- homogeneous distribution of the seed tetrabasic crystals (d50 0.5 to 0.7 µm)
- homogeneous growth of the seeds during crystallization phase of curing
- The crystal growth aspect ratio locked in x:y:z direction: **1.00: 0.70: 5.00**

Average 4BS Crystal Size based on simple Model

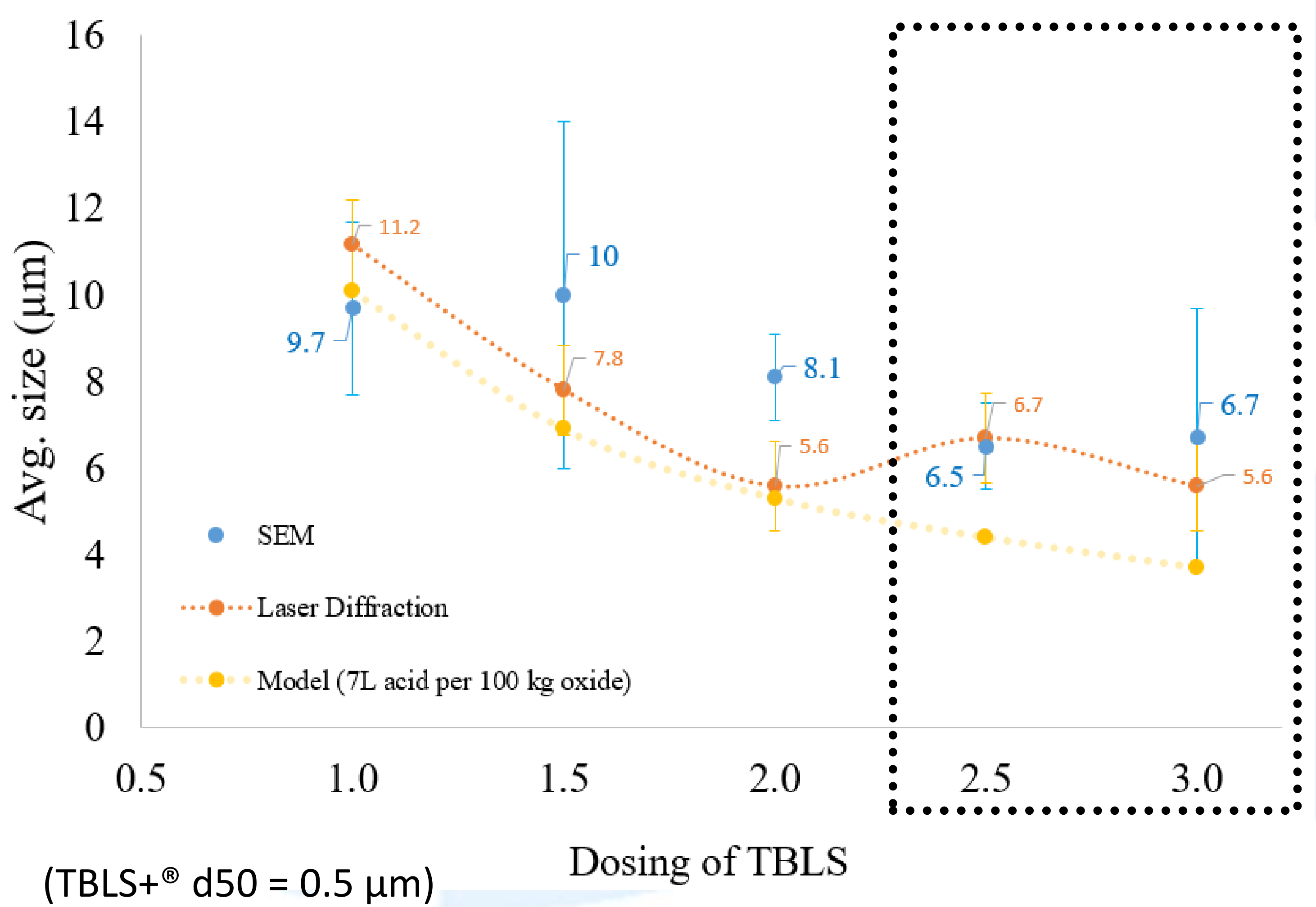


- 4BS crystal size (with constant TBLS+® seeding) is increasing with increasing amount of used sulphuric acid
- and vice versa

(TBLS+® d50 = 0.5 µm)

Comparison of Average 4BS Crystal Size

Comparison based on the Model, SEM, and the Laser Diffractometry (µm)



(TBLS+® d50 = 0.5 µm)

- SEM data is more off
- Laser diffraction gives a reasonable fit with the model

→ Over-dosing (>2.5% TBLS+) results in crystals growing together (in-effective use)

Structural Impact of TBLS+®

- Without TBLS+® and in a 3BS structure the pore diameter is below 1 µm
- TBLS+® shows a significant effect on the porosity of electrodes
- With TBLS+® the crystal size can be systematically controlled (=model)
- **There is, depending on the paste recipe, an optimal dosing of TBLS+®**
- Optimized electrodes with TBLS+® have larger pore diameters: about **4 times**
- Larger pore size results in a higher water porosity of about **20%**
- 4BS crystals for high dosing of TBLS+® (>2%) grow together – *that can result in a structure more similar to lower dosing!*

- **Impact of structural properties on electrical performance was studied**

Impact on Capacity – *Peukert Test*

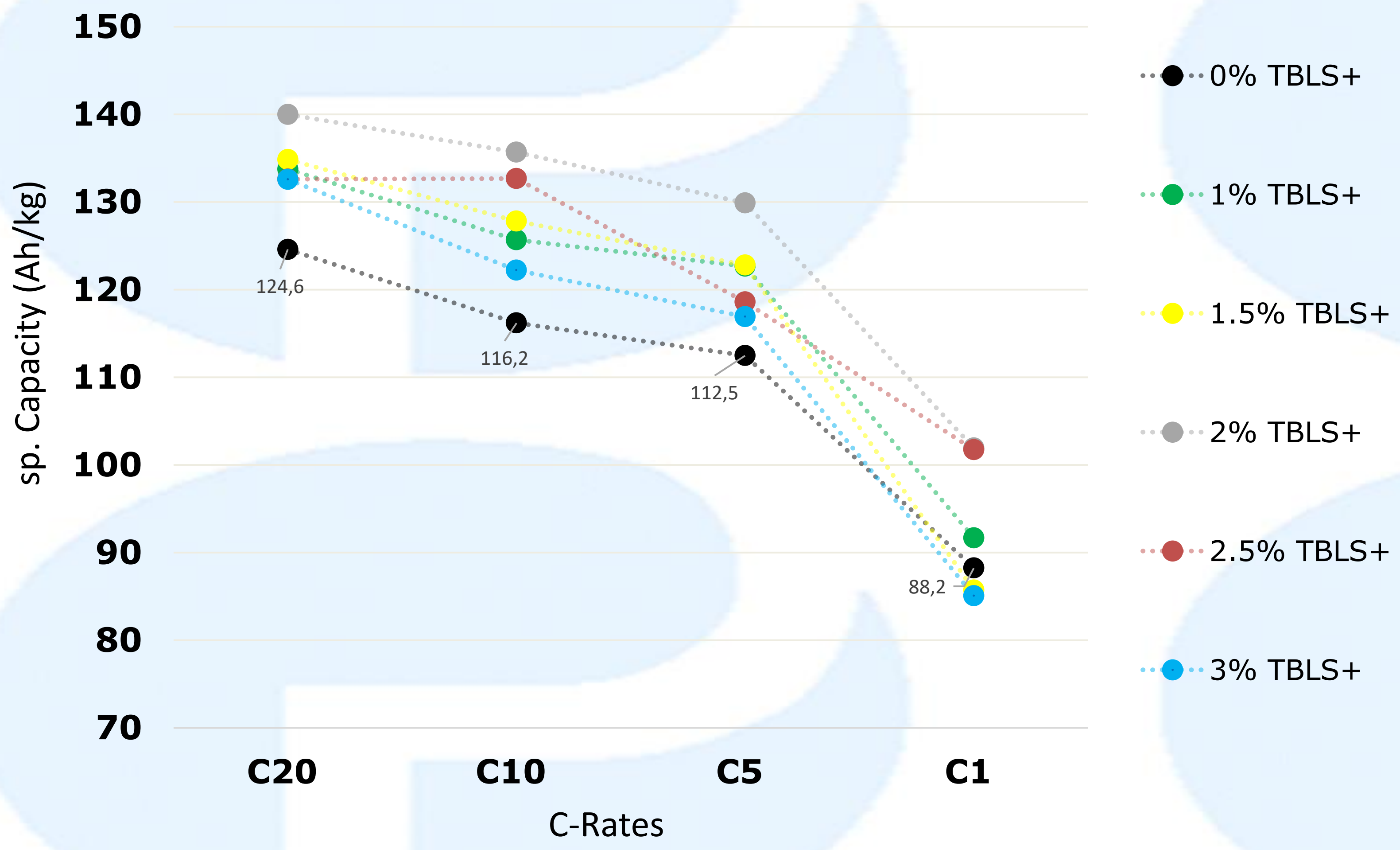
Consists of two parts:

- First run: C20, C5, C10, and C1
- Second run: C5, C20, C1, and C10 (see next slide)

Cn – rated capacity – means measured capacity after n hours of discharge.

Purpose: Check the electrode stability and the accuracy of the capacity value

Peukert Test – Second Run



- Electrodes with TBLS+® showed **10%** larger discharge capacity
- Electrodes with 1.0% and 1.5% TBLS+® have nearly the same capacity in the two runs

Summary - PAM

- TBLS+® in PAM as additive has a significant effect on the structure of electrodes:
  - Increase of the porosity by up to 20%
  - 4 times larger pore diameter as compared to the reference

- Electrodes with TBLS+® showed :
  - Higher formation efficiency
  - Higher and more stable capacity
  - Higher cycle durability in the 100% DoD Test (fast aging test)

Perspective for Battery Additives in EFB

NAM:

- PENOX is offering new EFB expanders to improve the NAM structure
- 4BS curing of NAM is possible using PENOX designed expanders
- 4BS curing is an alternative or supportive concept to improve NAM and safe costs of expensive functional carbons

PAM:

- 4BS curing is an effective concept to improve PAM in EFB batteries
- PENOX is offering new advanced oxides combining the advantage of Red Lead and TBLS+®

=> our new PENOX RL+

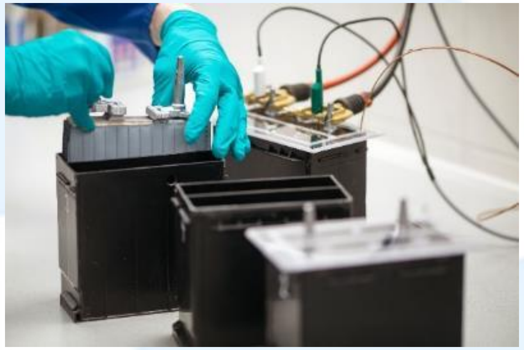
Innovation by PENOX

A New Innovation for the PAM combining Red Lead and TBLS+®

Kindly visit our Booth 104

PENOX

R&D Center in Thuringia, Germany



Thank you for your kind interest!