ADVANCED RED LEAD USED in BATTERY FORMATION – IMPACT on COSTS, BATTERY LIFE, and ENVIRONMENTAL FOOTPRINT

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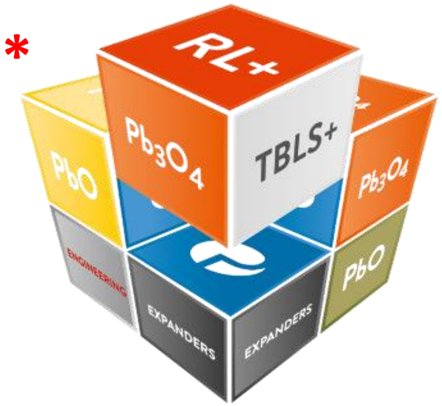
Agenda

- Basics & Introduction
- Formation study* with different types of PENOX Red Lead
- Carbon Dioxide (CO_2) Mitigation, Process Time Reduction
- Findings & Summary

- **“Functional Red Lead” = Red Lead Plus (RL+)****



* First part of the formation study was presented on ELBC 2022
** RL+ was first presented to the battery industry at the FENIBAT 2022

Introduction – Basics of Formation

• Process duration	10 to 20 h (flooded technology)
	>20 to 30 h (AGM technology)
• Formation charge (Ah based related to PAM)	300 to 600 Ah/kg (flooded)
	400 to 500 Ah/kg (AGM Technology)
• **Formation energy (Wh based related to PAM)**	660 to 1300 Wh/kg in **a 2V cell**
	4.0 to 7.8 kWh/kg in a **12V battery**
• *Formation factor*	*3 to 6 depending on technology*
• **Energy costs**	driven by formation efficiency
• **Process costs**	**balanced time vs. efficiency**

The Formation process can be optimized by tuning the key-factors relevant for an effective transformation of the electrical energy into chemical energy in both electrode polarities.

A basic conflict is typically the demand for a fast process and a high energy efficiency

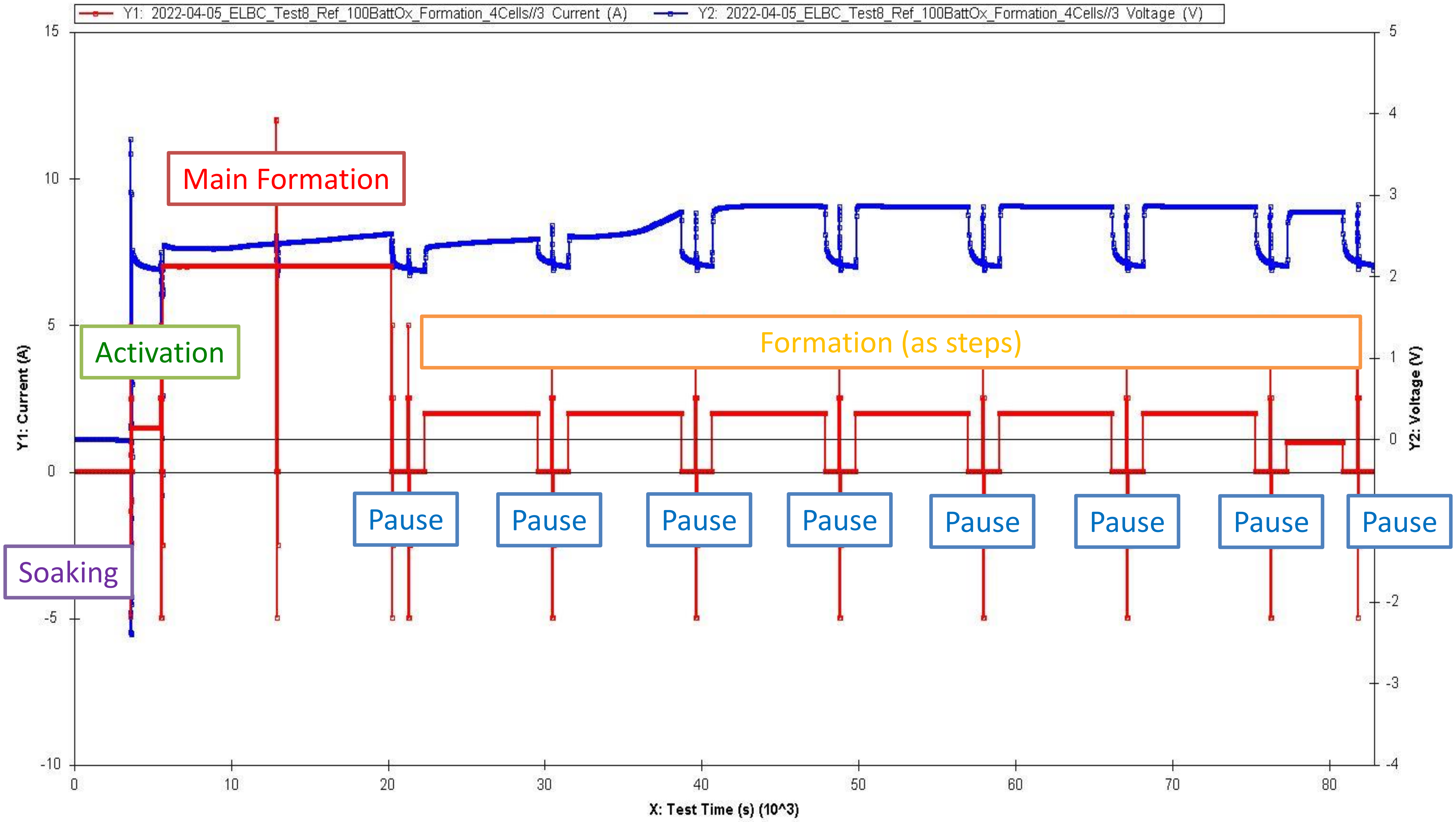
Introduction – Formation Profile

Typical Formation Steps (Flooded Technology*): "two-shot formation" => PENOX Reference Study

- **Soaking** of the cell
  - Depending on plate thickness and electrolyte density max. 1 h – optimum often with 0.5 h
- **Activation** Step
  - Low current density to create a basic conductivity
  - Typical duration 0.5 to 1h with a current of 0.1 to 0.3 A per Ah
- **Main formation** Step with high current
  - High current step with 0.5 to 1 A per Ah – time is limited by the charge acceptance of the NAM
  - Step must be ended before the negative plates show a high over-potential
- **Pause** before following steps with reduced current density
  - Typical rest time is 15 minutes to 0.5h depending on plate thickness to allow electrolyte migration and degassing
- **Formation** Steps with reduced current
  - Typically several steps with reduced current are following

*This profile is based on a flooded cell – in our study we have used 1p / 2n set-up, Electrolyte density is 1.15 g/cm³.

Formation Profile (12.5 Ah Plate)



Comments on AGM Formation

- General Comments on AGM:
  - AGM formation runs much longer – current limitations and pauses in formation are important
  - The formation requires to allow for a specific water loss, to reach the target acid density
  - Control of the plate process, to control the electrolyte contained within the active mass is crucial
  - PENOX believes that Red Lead (RL) is mandatory in PAM to achieve optimal performance for AGM technology
- Investigations:
  - PENOX has studied first the effect of RL in a simplified flooded set-up
  - The impact of the structure of the PAM was investigated (still on-going)
  - However, it became clear that the NAM structure is very relevant as well (new study started)
  - Future updates concerning AGM technology will be posted under: https://penoxgroup.com/ AGM news

Study on Formation Energy

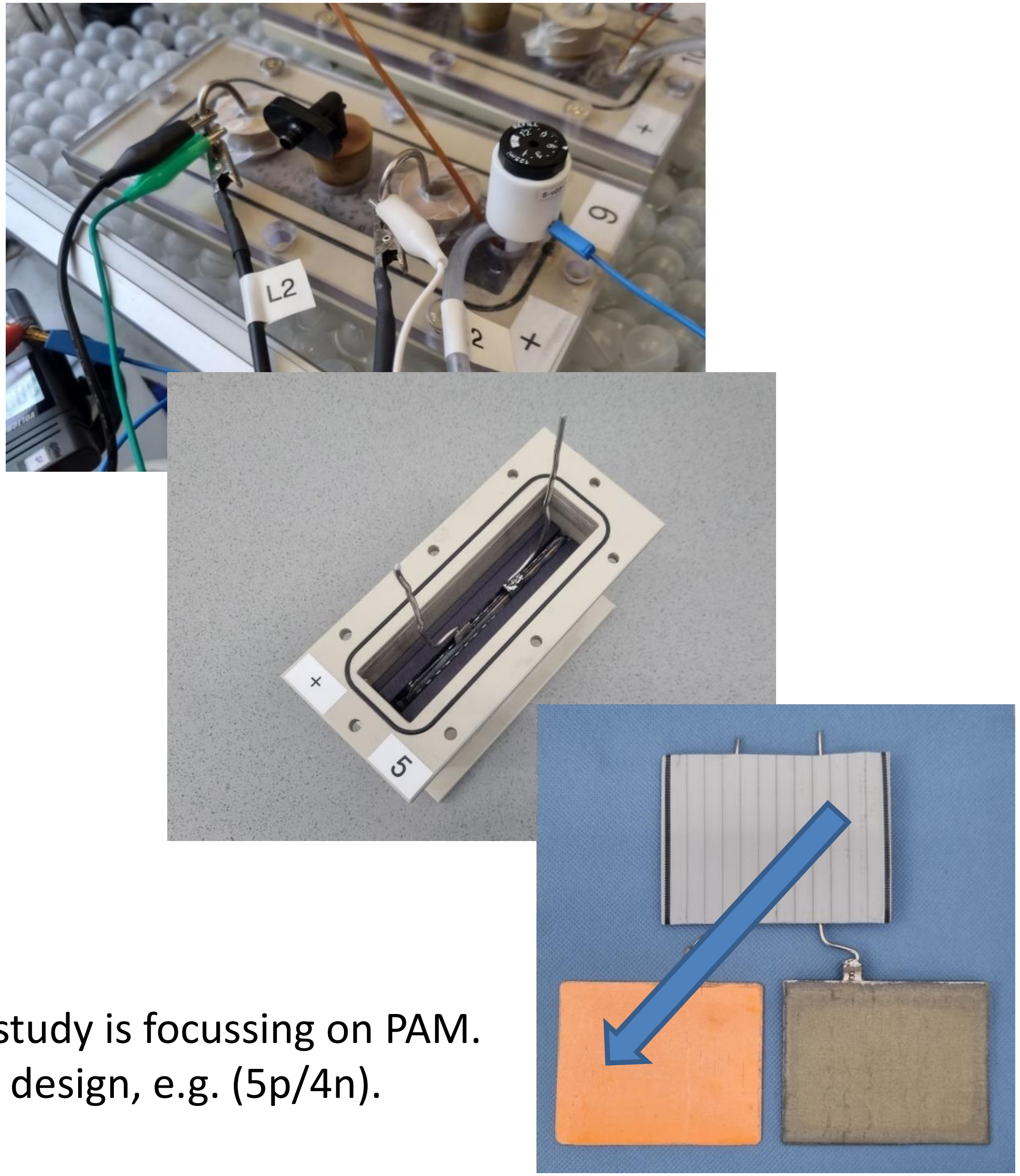
- Systematic testing of PAM mixes with:
  - We used industrial **Red lead (RL)** with d50 4.5 µm and PbO_2 (lead dioxide) 25 to 27%
  - Different contents of **Red lead (RL) 0%, 10%, 25%, 50%, 75% and 100%**
  - Comparison of **tri-basic (3BS)** and **tetra-basic (4BS)** cured positive active masses (PAM)

- Conditions of the RL study:
  - Same formation profile was used, only duration was varied to change the formation factor
  - Formation factor was systematically varied, and the resulting lead dioxide (PbO_2) content analysed
  - Structural investigation of the cured plates (of the formed plates)
  - Testing of initial C20 / C5 capacity and initial capacity evolution
  - Impact of the negative plate was investigated using reference electrodes

Reference System & Cell

- <u>Cell Set-up:</u>
  - Grid technology is gravity cast grids
  - One positive plate (1p) with C20: 12 Ah nominal
  - Two negative plates (2n)
  - PAM : NAM ratio in weight equals: 1 : 1.8*
  - Electrolyte: 300 g, density 1.28 +/- 0.05 g/cm^3
  - C20, **C5** was tested at 20 to 22 °C

- <u>Variation of the reference:</u>
  - M-neg. plate is a ***standard negative***
  - J-neg. plate is a ***negative plate with advanced carbon***



*This high NAM content is reducing the impact of the NAM, as this study is focussing on PAM. PENOX will compare the identified optimal PAM in a normal battery design, e.g. (5p/4n).

Reference System & Cell

Industrial Plate based Reference Systems	Cell Set-up	Structure %	H2O Poro %	Formation Factor	PbO2 Content (%) upper %	PbO2 Content (%) lower %	Average Target: 85 +/- 3 %
Reference 1 (Mill oxide) @25°C	1p2n - M neg.*	**3BS**	40	*2.8*	72.4	69.6	71.0
				3.1	72.0	70.6	71.3
Reference 1 (Mill oxide) @35°C	1p2n - M neg.	**3BS**	40	*2.8*	82.3	80.4	81.4
				3.1	83.0	81.6	82.3
Reference 1 (Mill oxide) @45°C	1p2n - M neg.	**3BS**	40	**2.8**	85.4	83.0	**84.2**
				3.1	91.6	84.4	**88.0**
Reference 2 (Mill oxide) @25°C	1p2n - J neg.**	**3BS**	40	2.8	74.4	69.2	71.8
				3.1	72.0	70.0	71.0
Reference 2 (Mill oxide) @35°C	1p2n - J neg.	**3BS**	40	2.8	81.2	77.5	79.4
				3.1	81.3	78.2	**79.8**
Reference 2 (Mill oxide) @45°C	1p2n – J neg.	**3BS**	40	2.8	87.1	81.8	**84.5**
				3.1	87.3	84.7	**86.0**
References produced in PENOX laboratory							
PENOX Reference 3 (100% Battox PAM) @45°C	1p2n - J neg.	**3BS**	50	2.8	69.8	71.3	70.6
				3.7	84.0	84.0	**84.0**

* M-neg. plate is a ***standard negative (SLI);*** **J-neg. plate is a ***negative plate with advanced carbon (EFB type)***

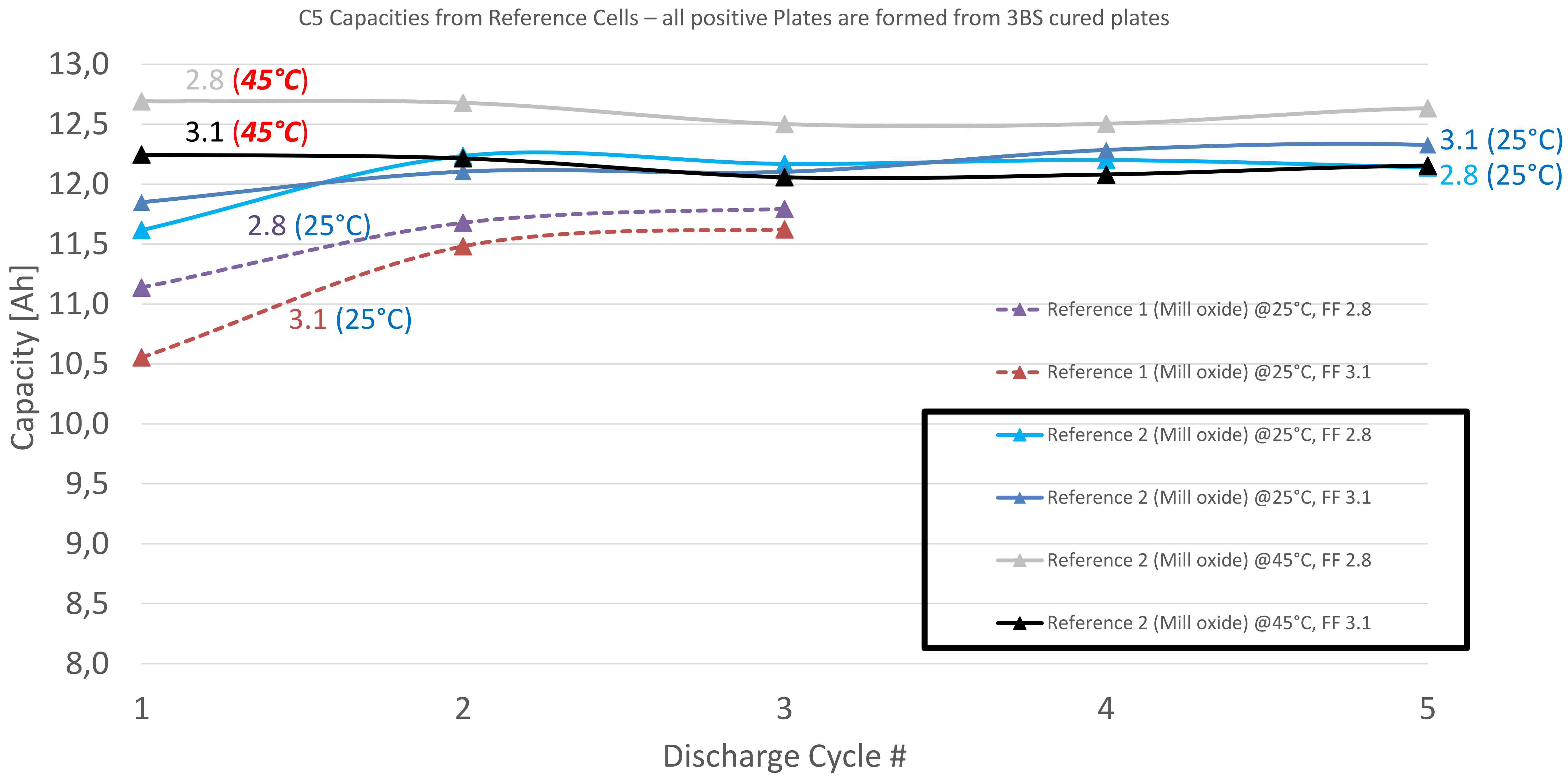
Reference System & Cell

- Formation of the **reference cells** required a formation factor of **3.1 up to 3.7**
- Formation of the **reference cells** required about **420 to 500 Ah per kg** of PAM

- Temperature of 25°C is too low for an effective formation
- **Temperature of 45°C allows a fast formation**

- Evolution of the C5 capacities are shown on the next slide – *please note that for the industrial reference plates we can not know the individual PAM weight – plate weight was measured.*

C5 Capacities (Reference Plates)



For the reference plates only the total plate weights known

Characteristics of Red Lead Plus = RL+

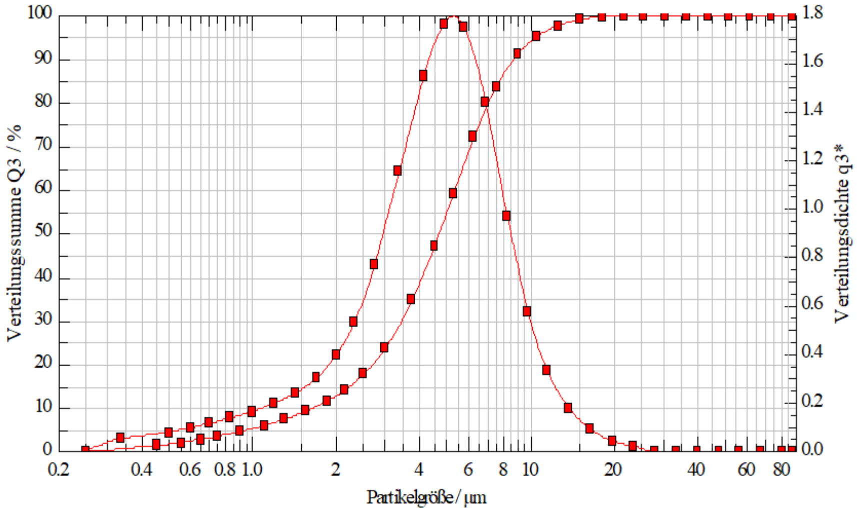
RL+ is an „advanced Red Lead (RL):

- It is free flowing powder similar to normal red lead.
- The particle size distribution (PSD) curve follows the PSD-curve of the standard red lead
- **The surface is coated with tetrabasic seeding crystals**.

RL+ can be produced by PENOX from different types of Pb_3O_4. However, PENOX recommends to use standard industrial grades of RL.

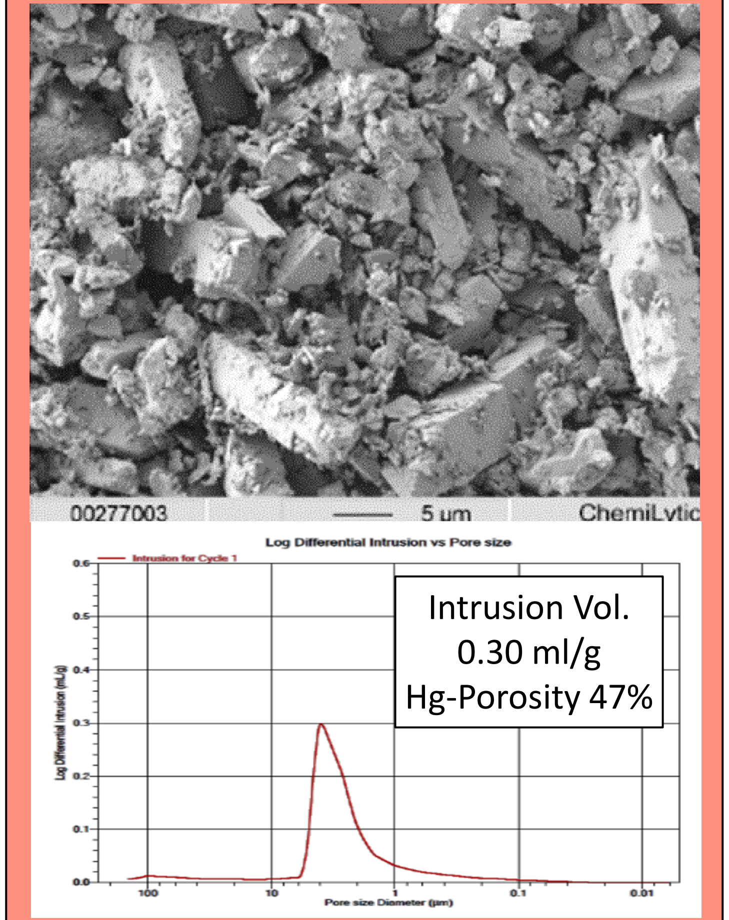
RL+ is available as a standard product with a 4BS content of 1.5 w%.

- Depending on demand different loadings can be produced and made available, up to 5 w% 4BS.

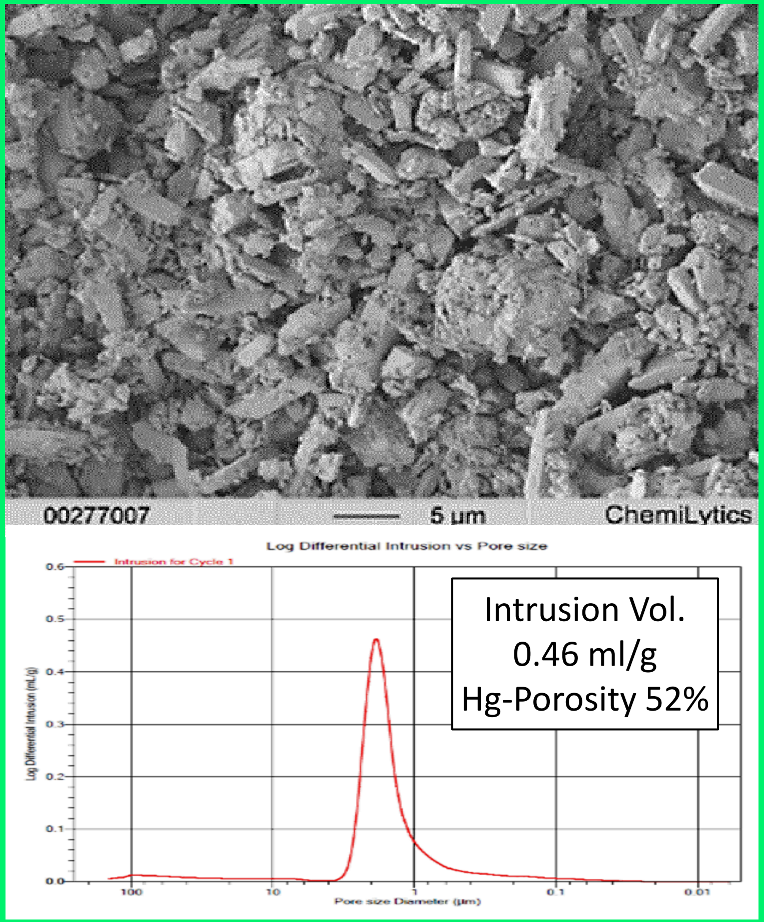


Comparison of 4BS Additives

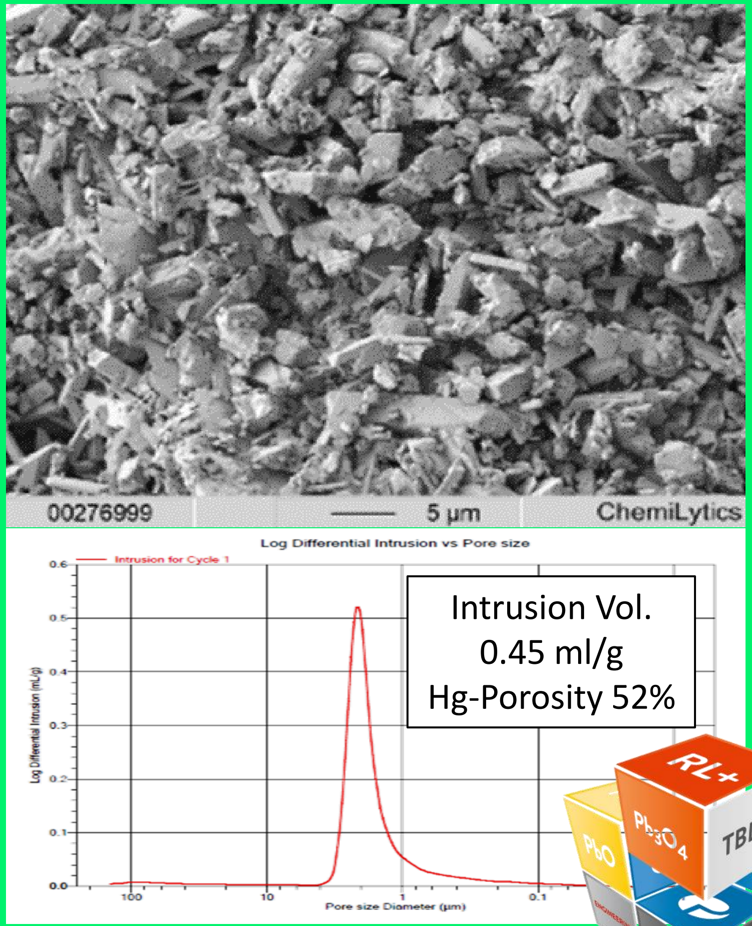
0.5% Powder 4BS seeds

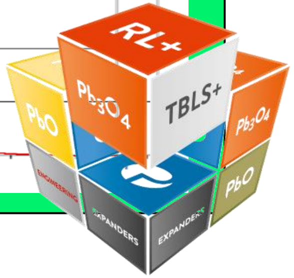


TBLS+® with 0.5%[1] 4BS seeds



RL+ with 0.5% 4BS seeds

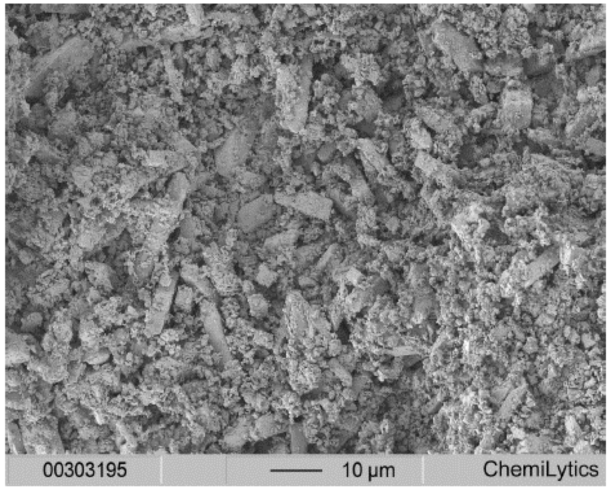


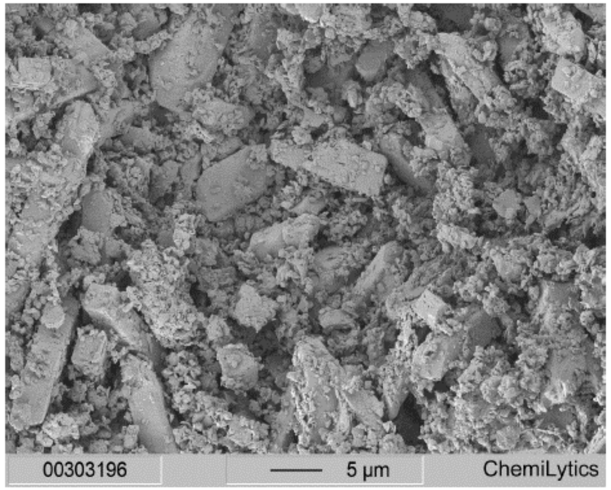


- Coarse (powder based) seeds result in larger 4BS crystals after curing
- TBLS+® contains fine seed crystals with d50 of 0.5 to 0.7 µm, which results in the growth of smaller 4BS crystals
- **RL+ is coated with similar fine 4BS seed crystals, which result in an identical 4BS crystal growth**

RL+ creating 4BS Structure

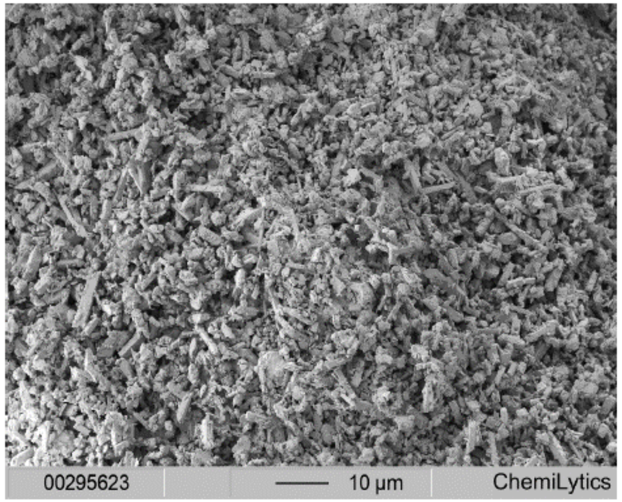
0.15% 4BS seeds

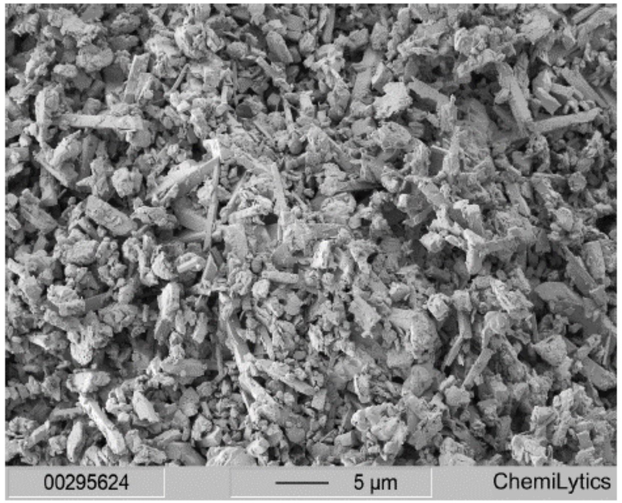




Battery Oxide weight%	Red Lead weight%
90%	10% RL+

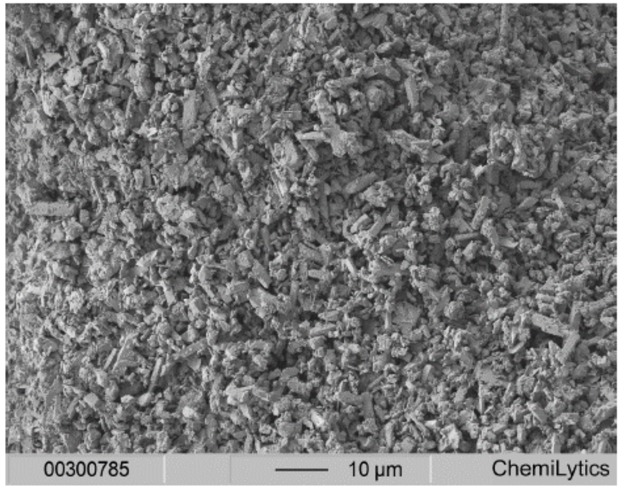
0.38% 4BS seeds

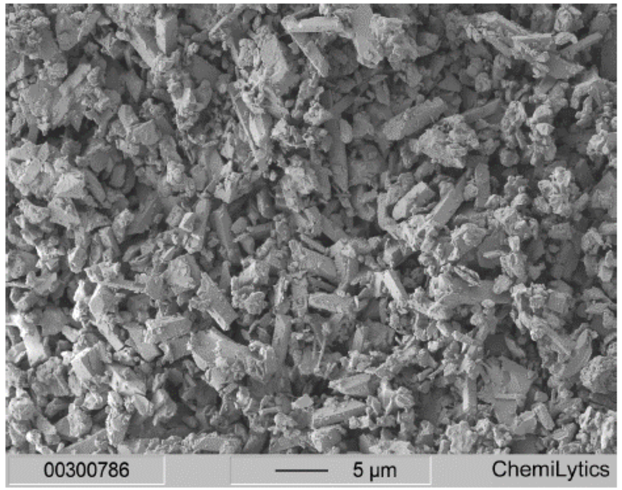




Battery Oxide weight%	Red Lead weight%
75%	25% RL+

0.38% 4BS seeds





Battery Oxide weight%	Red Lead weight%
50%	**25% RL+** & 25% RL

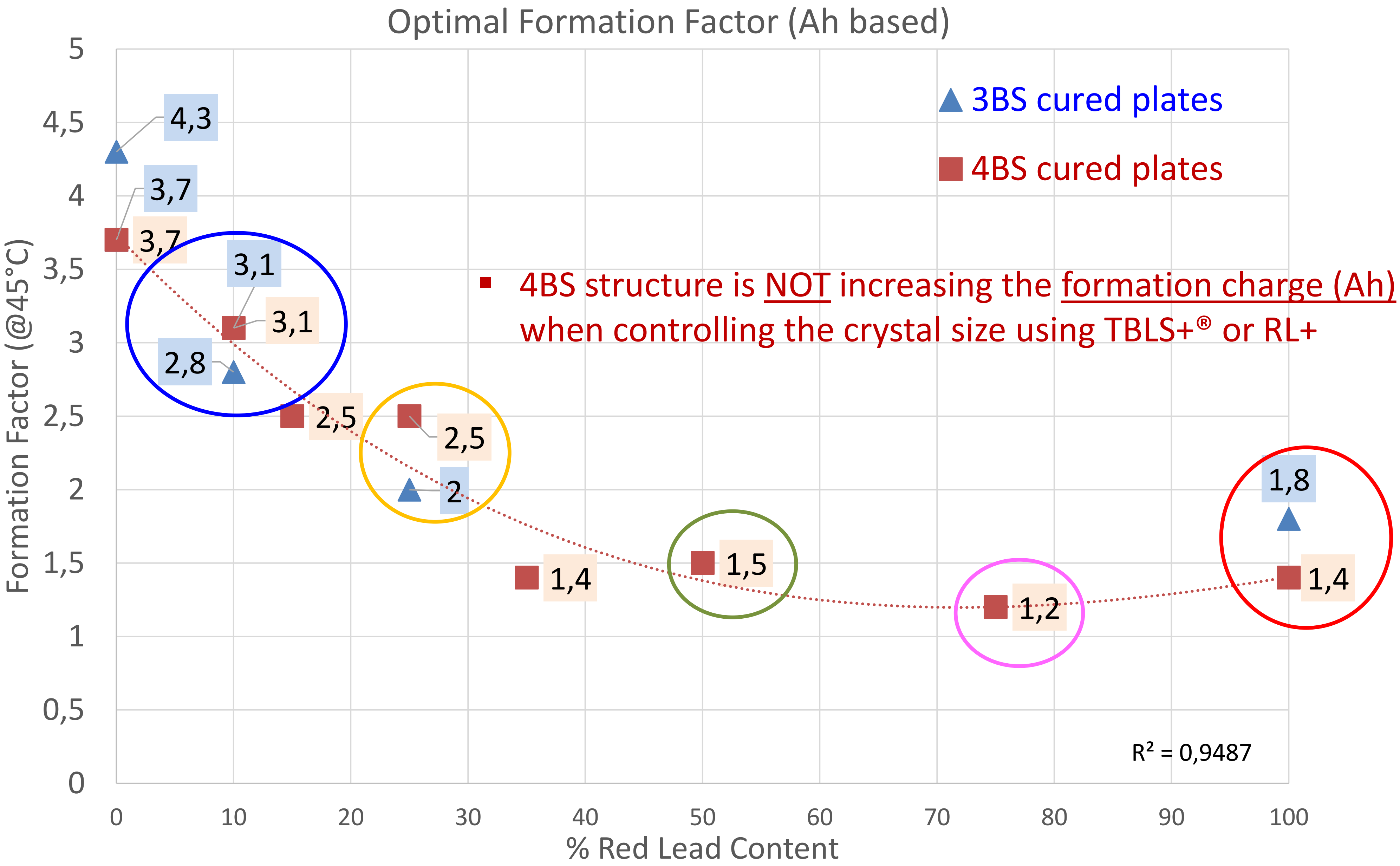
PENOX Impact of RL-Content – 4BS Structure

PAM composition		PAM Structure	H2O Porosity	Formation Factor (FF)	Average PbO2 Target: 85 +/- 3
Battery Oxide weight%	Red Lead weight%	Av. 4BS content	%	(lower is better)	%
100% (Mill oxide)	*0%*	*N/D*	*N/D*	*N/D*	*N/D*
100% (Barton oxide)	0% RL+ *(*1% TBLS+)*	*92.6%*	*49%*	*3.7*	*82.3*
90%	10%	*90.4%*	48%	3.1	85.0
85%	15%	*93.4%*	52%	2.5	85.0
75%	25%	*92.6%*	59%	2.5	87.9
75%	25%	*92.6%*	59%	1.5	80.9
65%	35%	*80.9%*	50%	1.4	81.9
50%	50%	*92.1%*	49%	1.3	80.2
50%	50%	*92.1%*	49%	1.5	88.4
25%	75%	*84.3%*	51%	1.2	85.7
0%	100%	*91.6%*	46%	1.4	84.1

- * 4BS structure is based on 1% of TBLS+ (0.42% of 4BS seeds in PAM) – Reference formation factor is 3.7

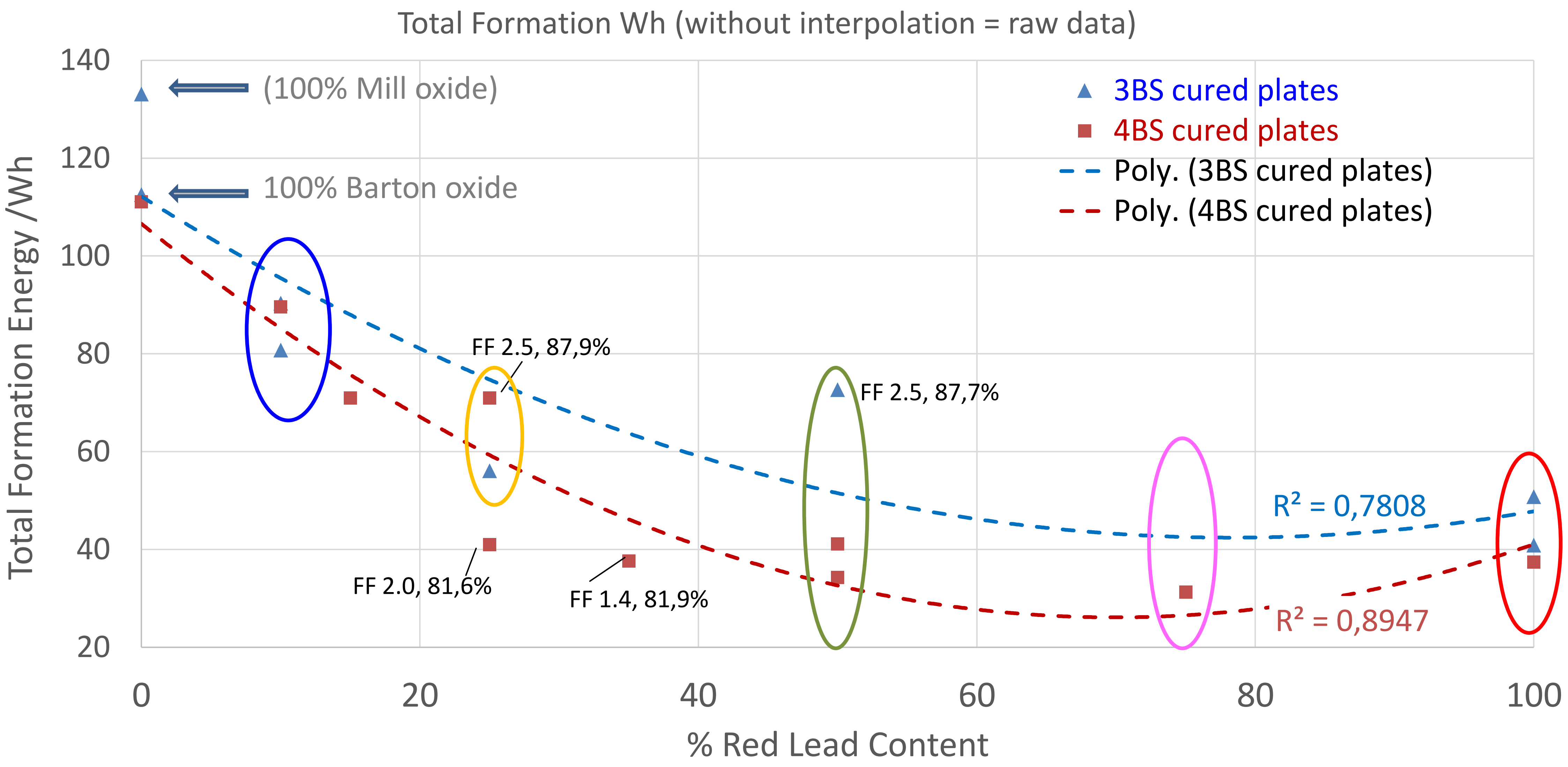
- **Formation factor can be reduced to about 2 for 25% of RL+**
- Formation factor can be reduced to about 1.5 for 50% RL (25% of RL and 25% of RL+)

Formation Factor depending on RL content



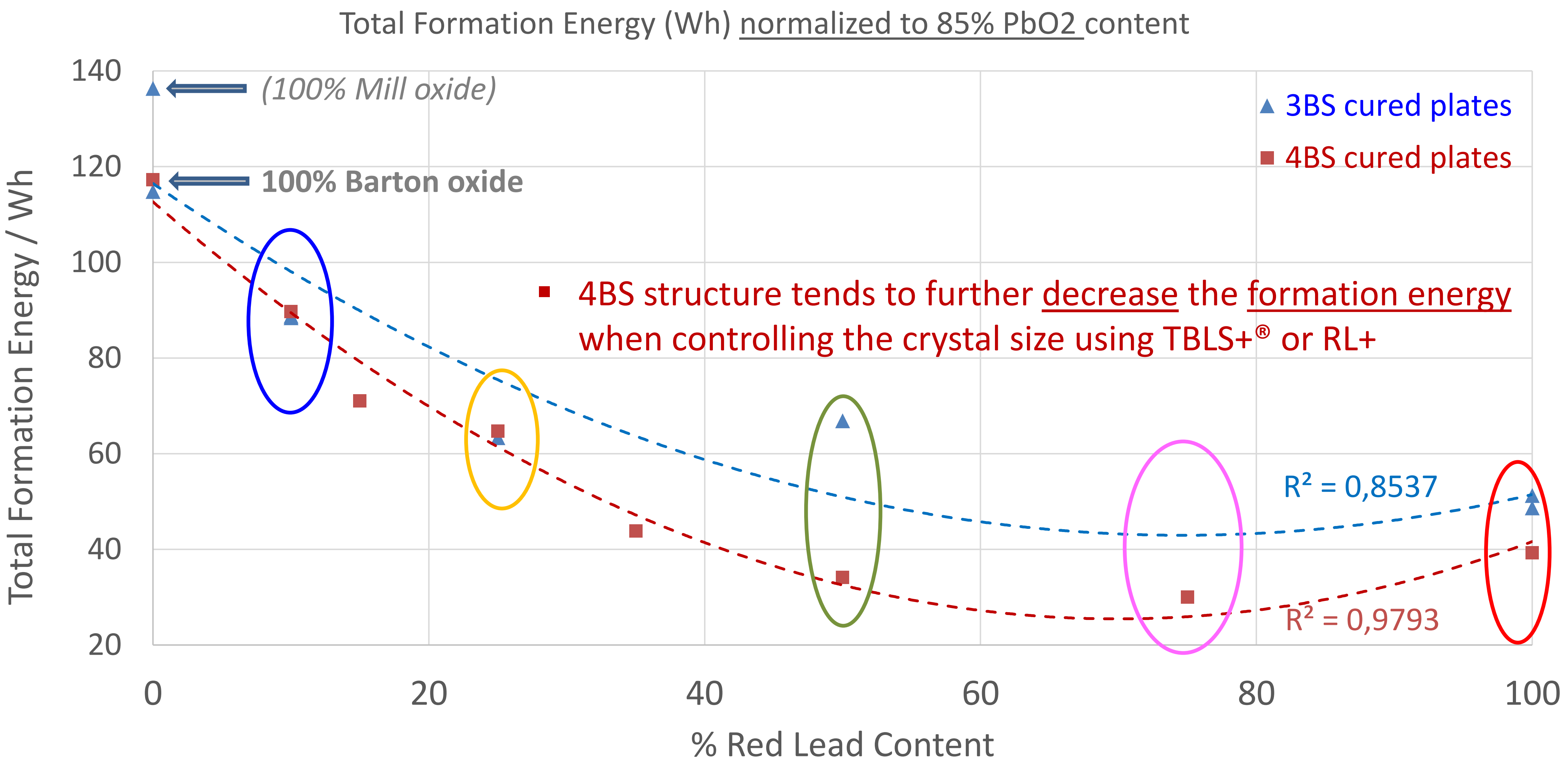
- 4BS structure is NOT increasing the formation charge (Ah) when controlling the crystal size using TBLS+® or RL+

Formation Energy (Wh based)



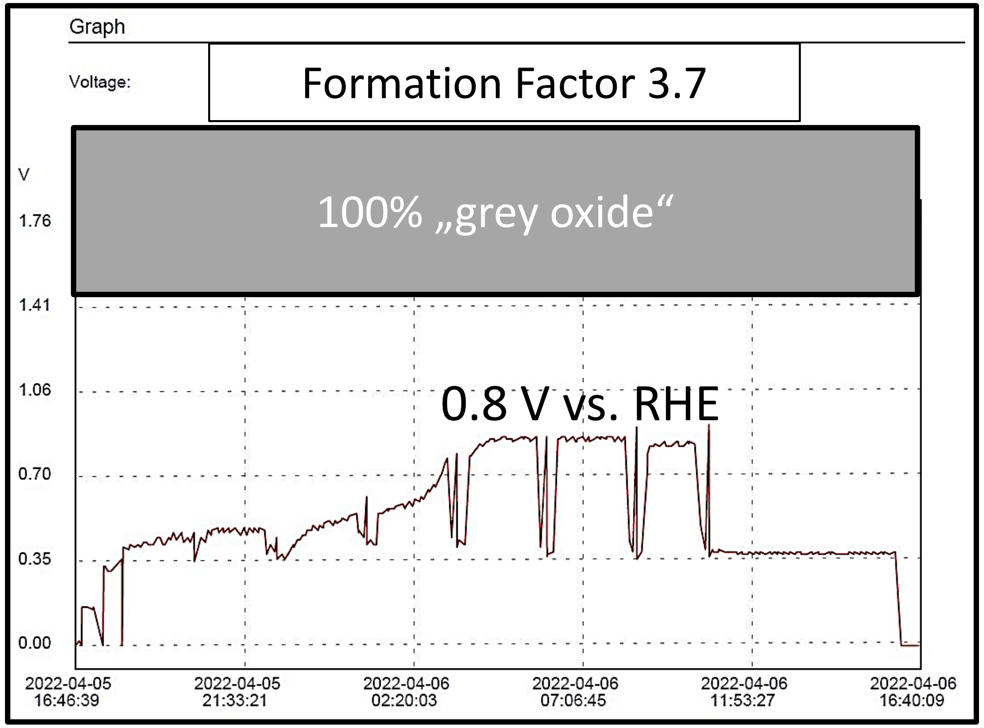
* This data-set requires additional measurements to allow for a better fitting.

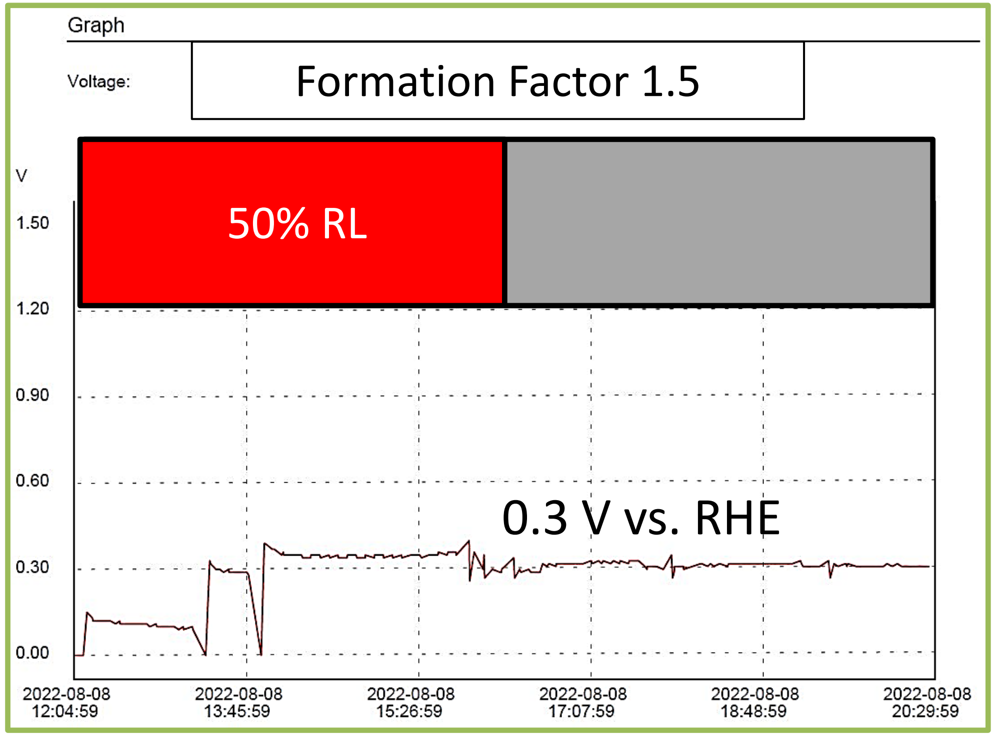
PENOX Formation Energy (Wh based - normalized)

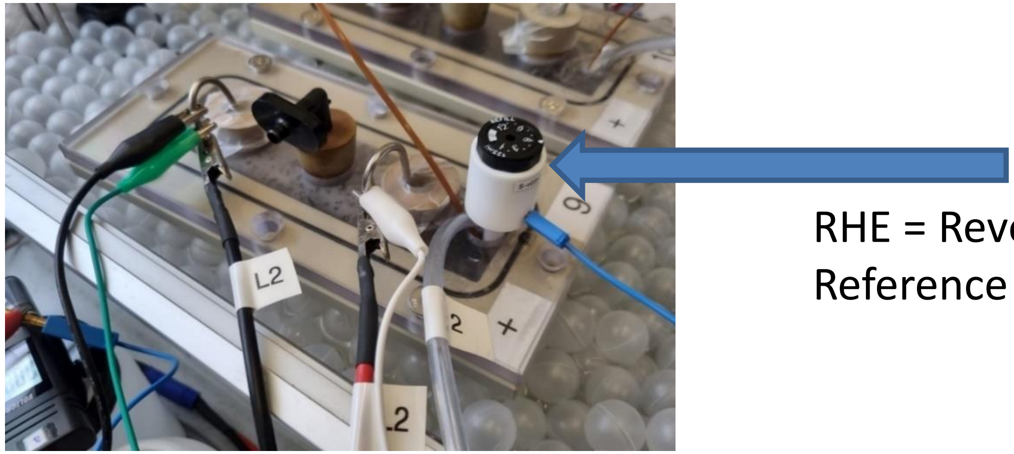


* The formation energy was interpolated to reach 85% of lead dioxide in the PAM.
This interpolation of the 3BS structure will require further refinement based on additional data.

Negative Plate Potential in Formation



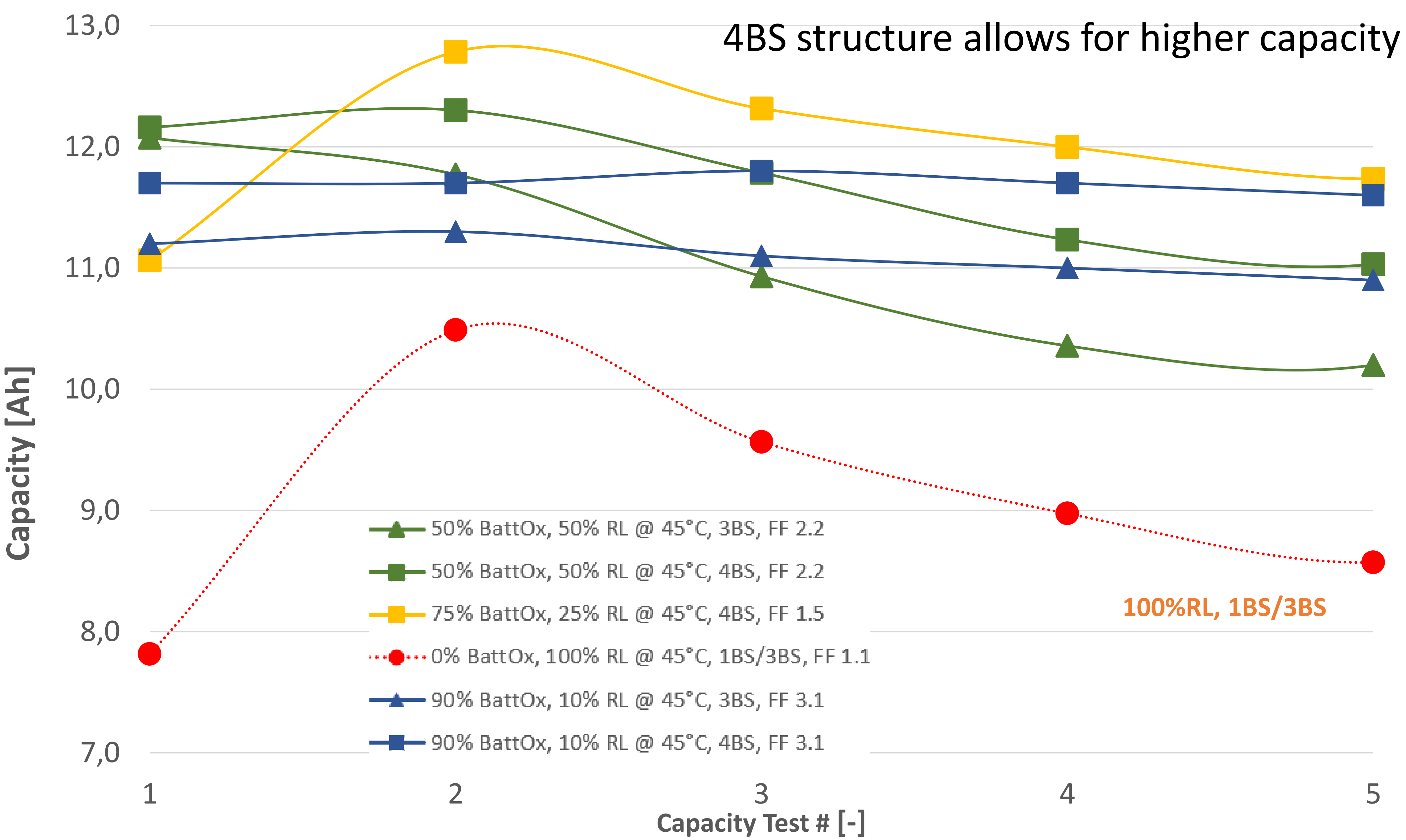




- More RL results in less „stress“ for the negative electrode.
- A better balanced formation.

RHE = Reversible hydrogen electrode
Reference potential for the negative electrode

PENOX C5 Capacities (with RL+ tested @25˚C)



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Findings and Impact

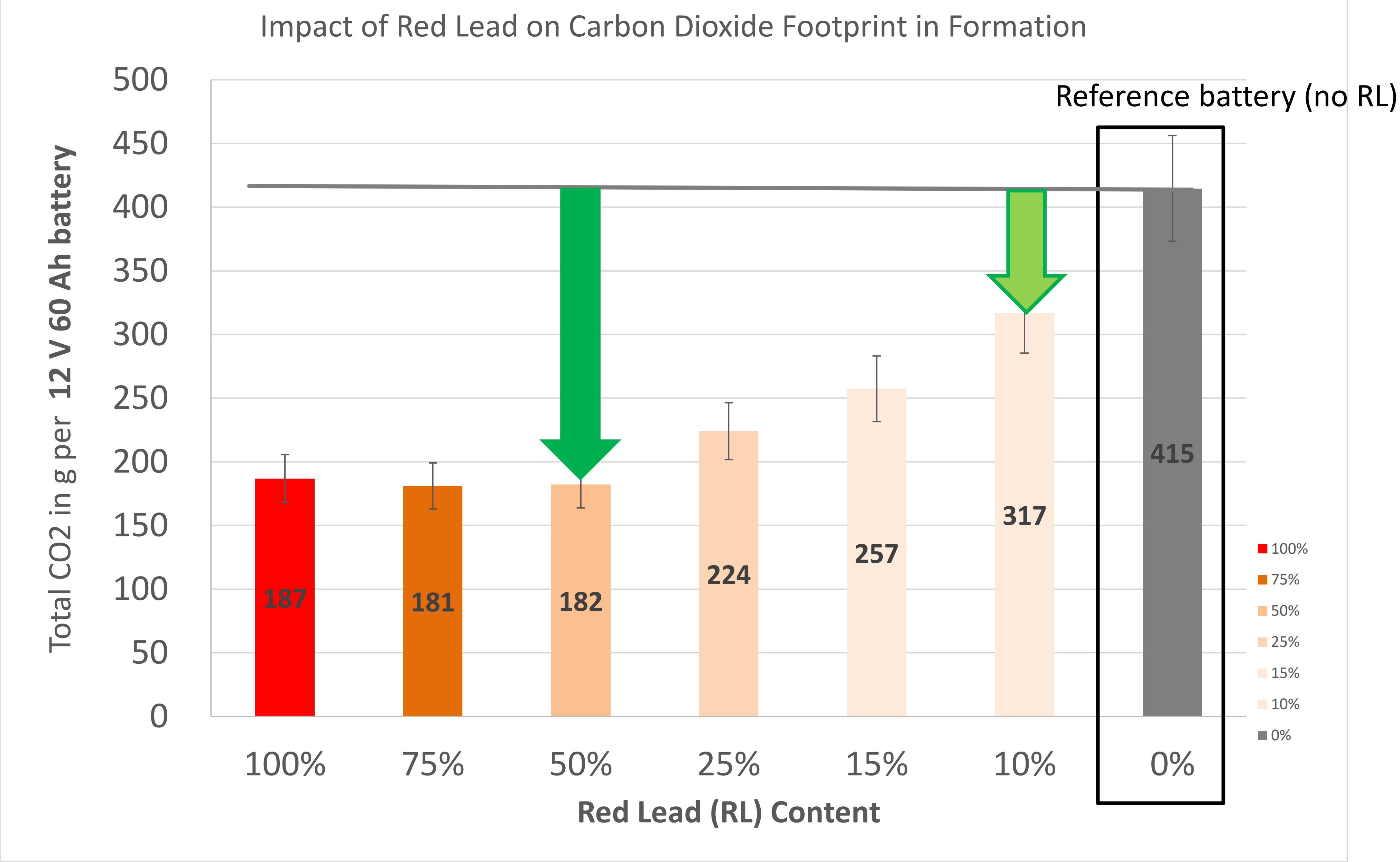
Formation of the **reference cells (only grey lead oxide)** require a formation factor of about **3.7**

Formation of the **reference cells (2V)** require about **420 to 500 Ah per kg** of PAM

- **Red Lead** allows to reduce the formation energy significantly
- The effect of **RL addition is not linear** and there is an economical optimum for the RL content
- **100% RL content** is not allowing for a well developed 4BS structure
- **50% RL content** allows to reduce the formation factor from 3.1 to **1.5** - **a reduction by about 50%**
- **25% RL** content allows to reduce the formation factor from 3.1 to **2** - **a reduction by about 35%**

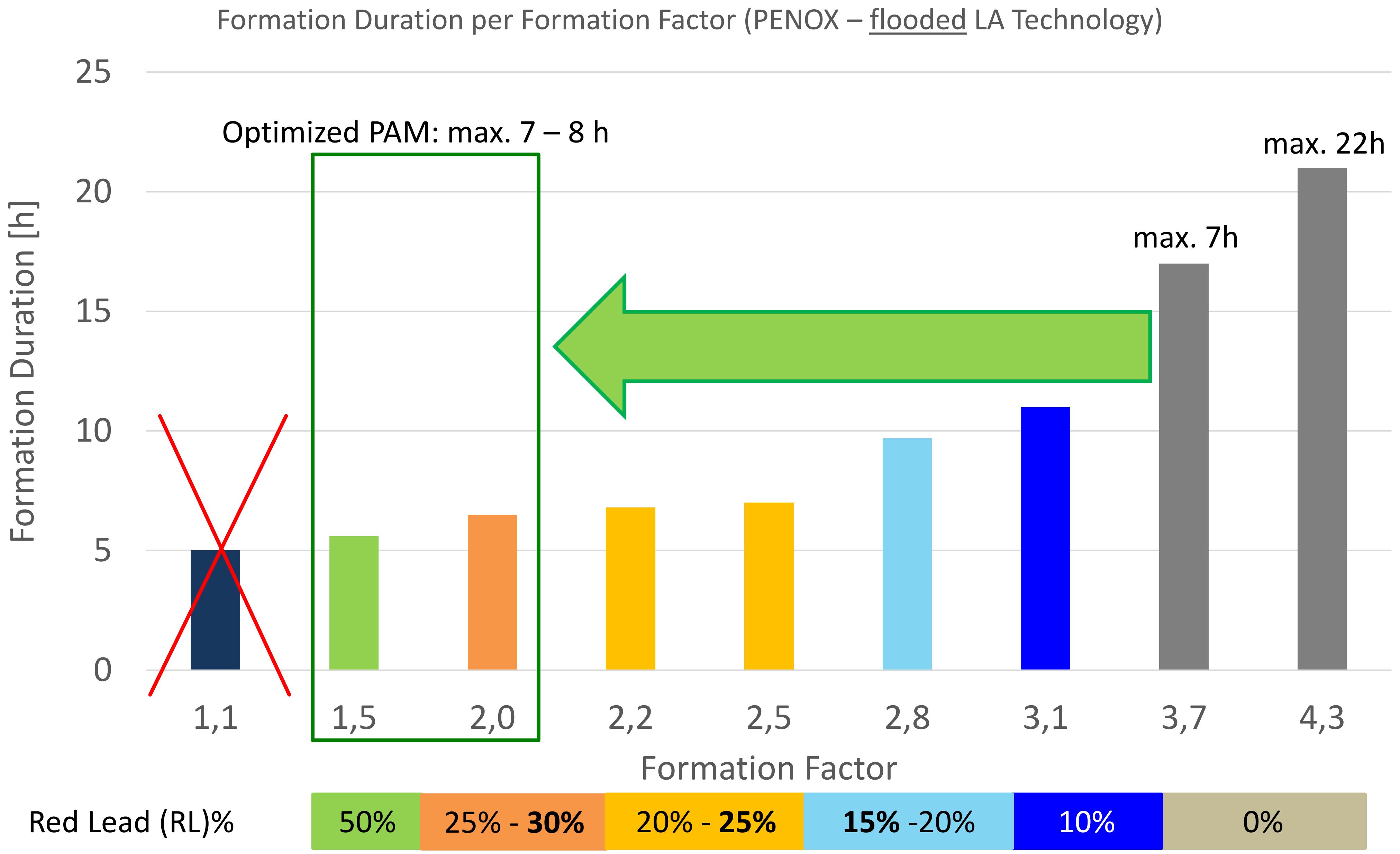
➔ Depending on the relative impact of the electricity costs and the value of process time reduction, there is a specific optimum for the RL and RL+ content.

Impact of Formation Efficiency on CO2 Emissions



(CO2 emission data is based on Brasilian energy mix with 120 g CO2 per kWh)

Impact of RL% on Formation Time



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Summary

<u>Red Lead Industrial Grade and especially RL+ allows for:</u>

- Formation energy **reduced by up to 50% vs. using 100% grey oxide**
- Formation time reduced – depending on the battery technology **by up to 50%**
- **AGM technology has a significant benefit from even small RL content, e.g. 10 w.%**
- **RL+ content can be as low as 10 w.% to achieve a tetrabasic (4BS) structure**
- **RL+ allows for higher mass utilisation – higher capacity with same active mass**
- **RL+ can be mixed with normal red lead (RL), if higher content of RL is beneficial**
- Carbon dioxide foot print is reduced by a more efficient formation:
  - The emission reduction is depending on the carbon dioxide foot print of the electricity generation
  - ***In Brazil with about 120 g CO2 per kWh still a reduction from about 400 g to 200 g for a 12 V 60 Ah battery can be achieved!***

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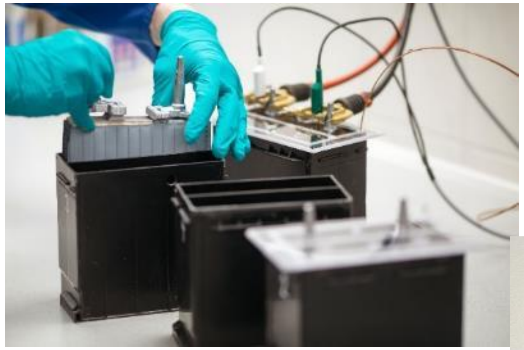
R&D Team & Center in Germany



Thank you for your kind interest!

PENOX Design for Advanced AutomotiveBatteries

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 GmbH
R+D Department

Technical Guideline

08.08.2023 – V2

Minimum and Basic Requirements
Addressed to an AGM Design for
Automotive- and UPS-Batteries

PENOX GmbH

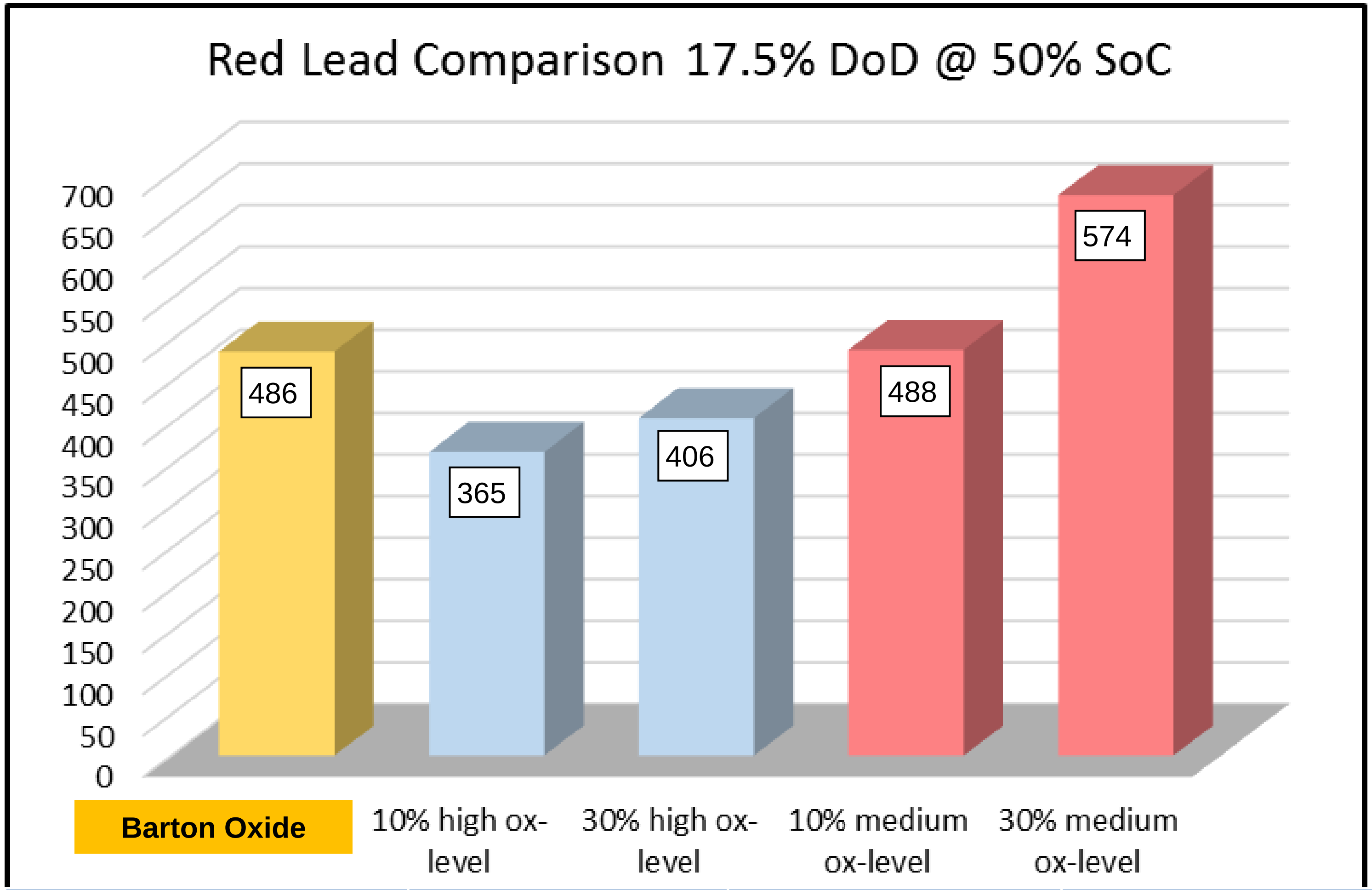
R+D Department

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

NEW Script on AGM Technology and basic consideration in 08/2023 – for FENIBAT 2023

Appendix
- Slides for discussion -

PENOX Impact of AGM Grade RL on Cycle life*



- RL can be highly oxidized, such material is often used in Asia (called "HD" grade)
- RL with lower oxidation is a coarser powder and has a beneficial effect on cycle life

- This effect is eg. seen in a 17.5% DoD test using PENOX AGM grade RL

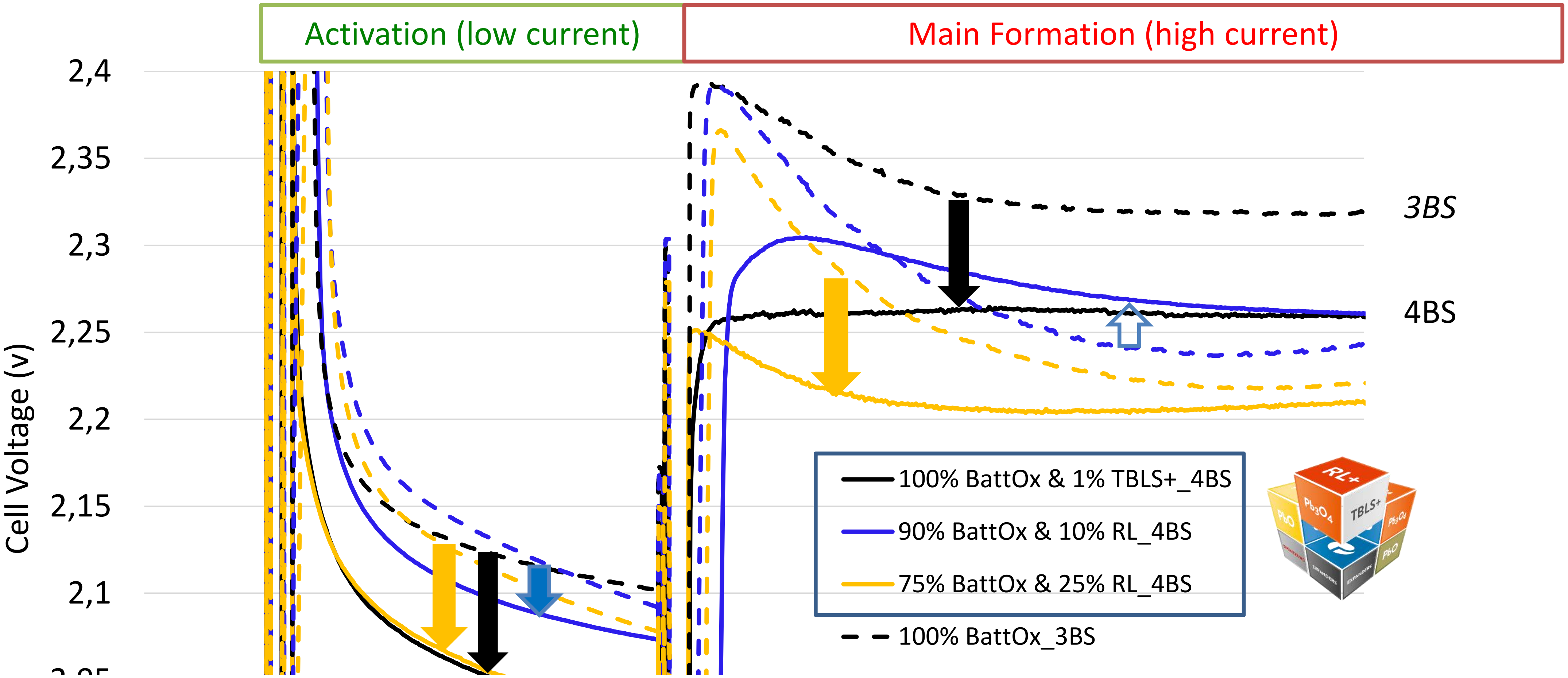
*18th ELBC, Ian Klein et al.

Grades	Pb_3O_4 [%]	PbO_2 [%]	β-PbO (residual) [%]	Acid Absorption[1] [mg acid/g oxide]	D50 [2] [micron]
HD grade RL	>96	>33.5	<4	>170	<2
AGM grade RL	77.4 - 86	28 - 30	14 – 22.6	140 - 180	4.5 – 5.5

Impact on Formation Efficiency

- **Conductivity of the active mass during formation**
  - Cured active masses have a high internal resistance – **RL is increasing the initial conductivity**
- **Current density during a formation step**
  - High current density are impacting both polarities – we need to remember the negative electrode
  - Negative electrodes have a lower surface area with respect to the positive electrode
- **Electrolyte density within the electrode and mass transport**
  - Mass transport is a relevant process during formation
  - Solubility is controlled by local electrolyte density within the active masses
  - Therefore, the structure and porosity of the electrodes are crucial
- **Bulk electrolyte density**
  - Bulk density controls the mass transport of sulfuric acid (generated) within the double-layer and the electrolyte reservoir
- **Temperature of the electrodes**
  - Kinetics are strongly depending on temperature

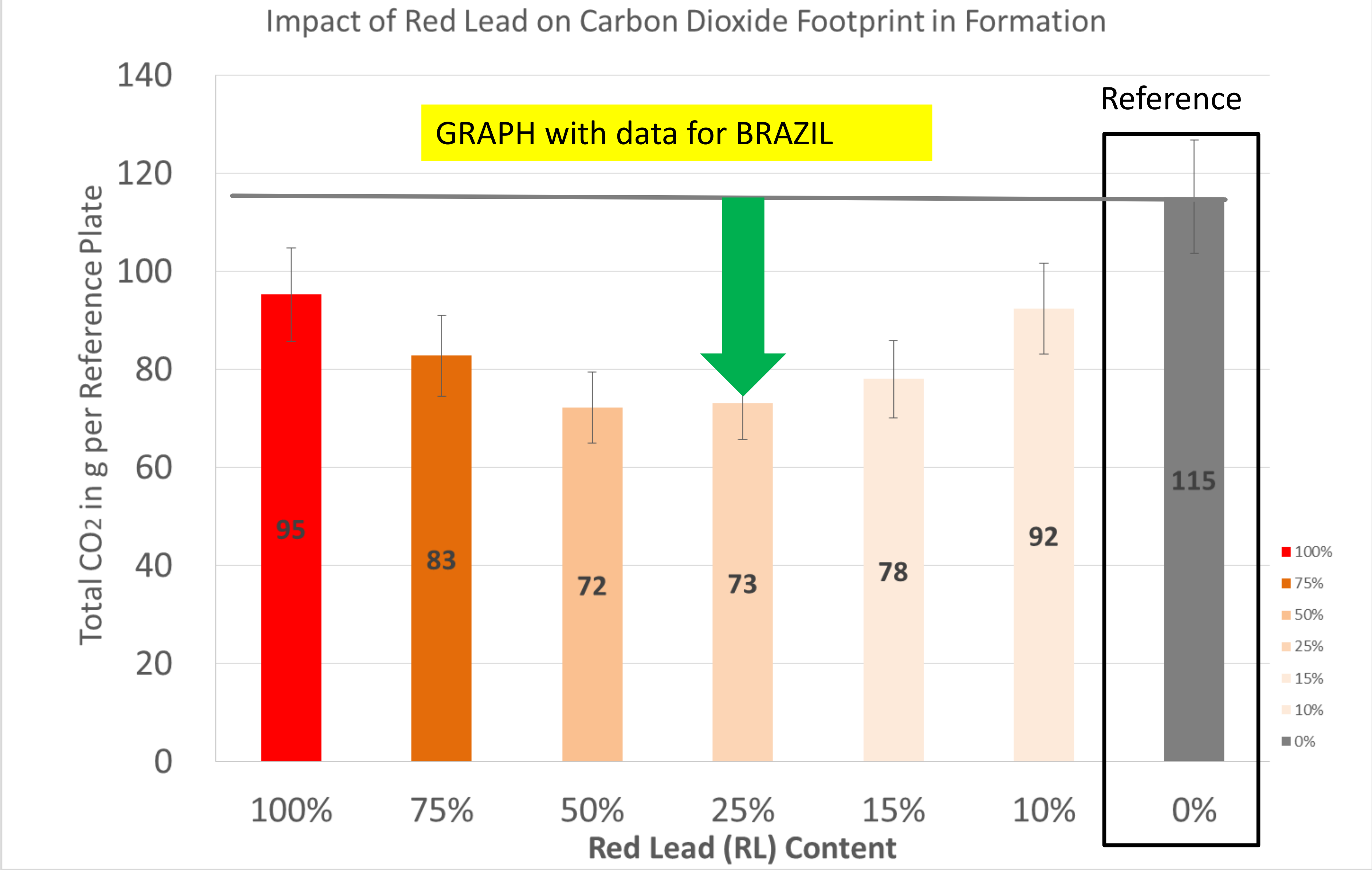
PENOX Voltage Evolution during Formation



4BS structure (based on RL+ or TBLS+®) results in lower cell voltage during formation
=> higher formation energy efficiency in terms of *Wh per kg of AM*

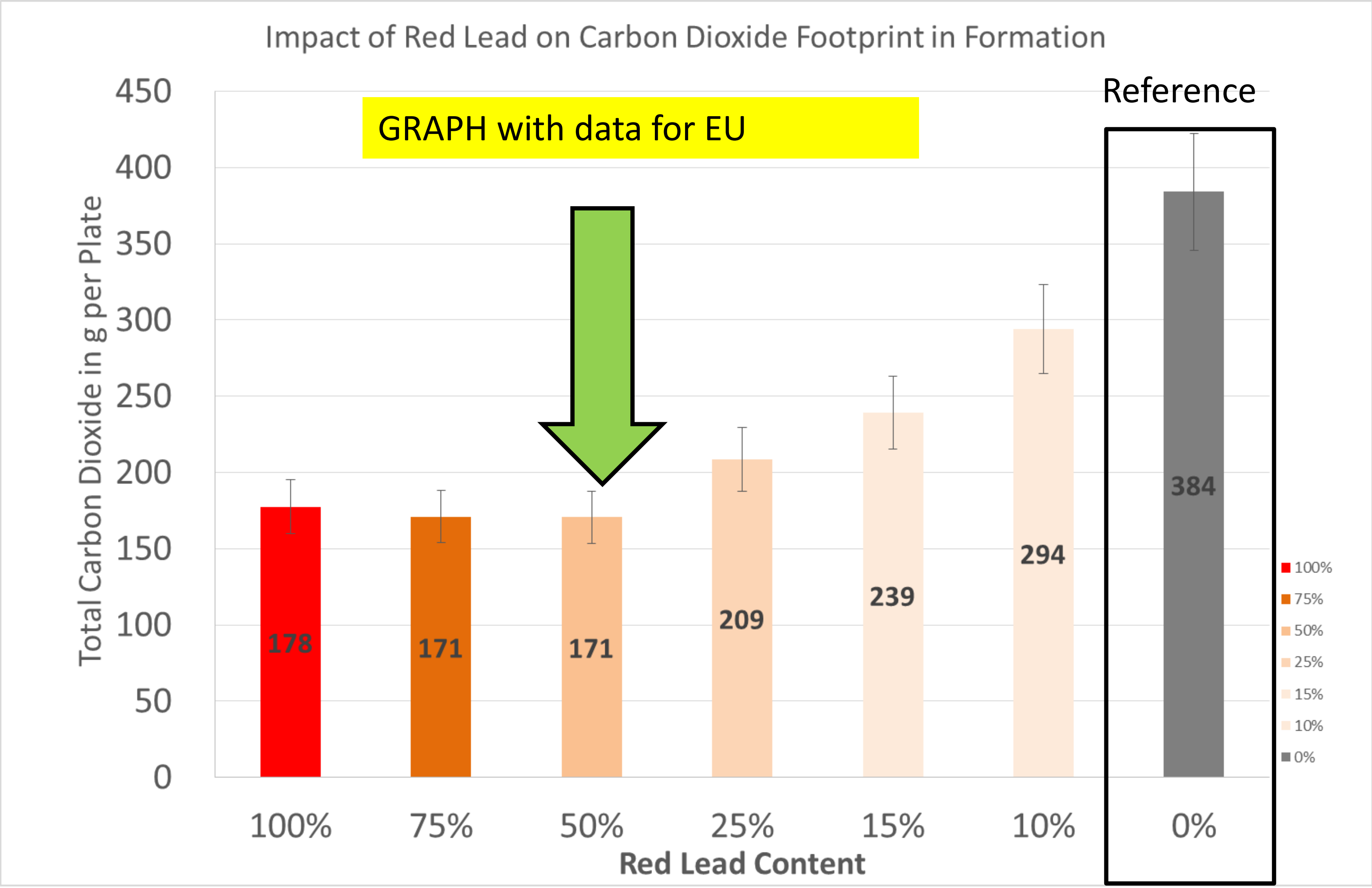
This effect is higher for higher currents used in a formation step!

Impact of Formation Efficiency on CO2 Emissions



(CO2 emission data is based on Brasilian energy mix with 120 g CO2 per kWh of electricity)

Impact of Formation Efficiency on Carbon Dioxide Emissions



(CO_2 emission data is based on EU energy mix with 400 g CO_2 per kWh of electricity)