Review of the Limits of Structural Optimisation of PAM
– Performance, Costs, and Environmental Aspects

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ELBC Conference, Milan, Italy

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Agenda

- Targets & Introduction
- PAM: Updated Formation Study*
- PAM: Limits of Porosity, Structural Stability
- Carbon Dioxide (CO_2) Mitigation, Process Time Reduction
- Coupling of Parameters - *Balancing a Battery*
- Findings & Summary

* The first part of the formation study was presented at the ELBC 2022

Introduction

Targets: Analyse the Limits of the Positive Active Mass (PAM) in terms of:

- Effective Formation by addition of RL or RL+
- Understand the limits of porosity in cured and formed PAM
- Optimisation potential in PAM
- *Balancing of PAM and NAM in a cell – impact on performance*
- Impact of RL and RL+ on Energy Footprint and Costs in Battery Formation

Study Elements:

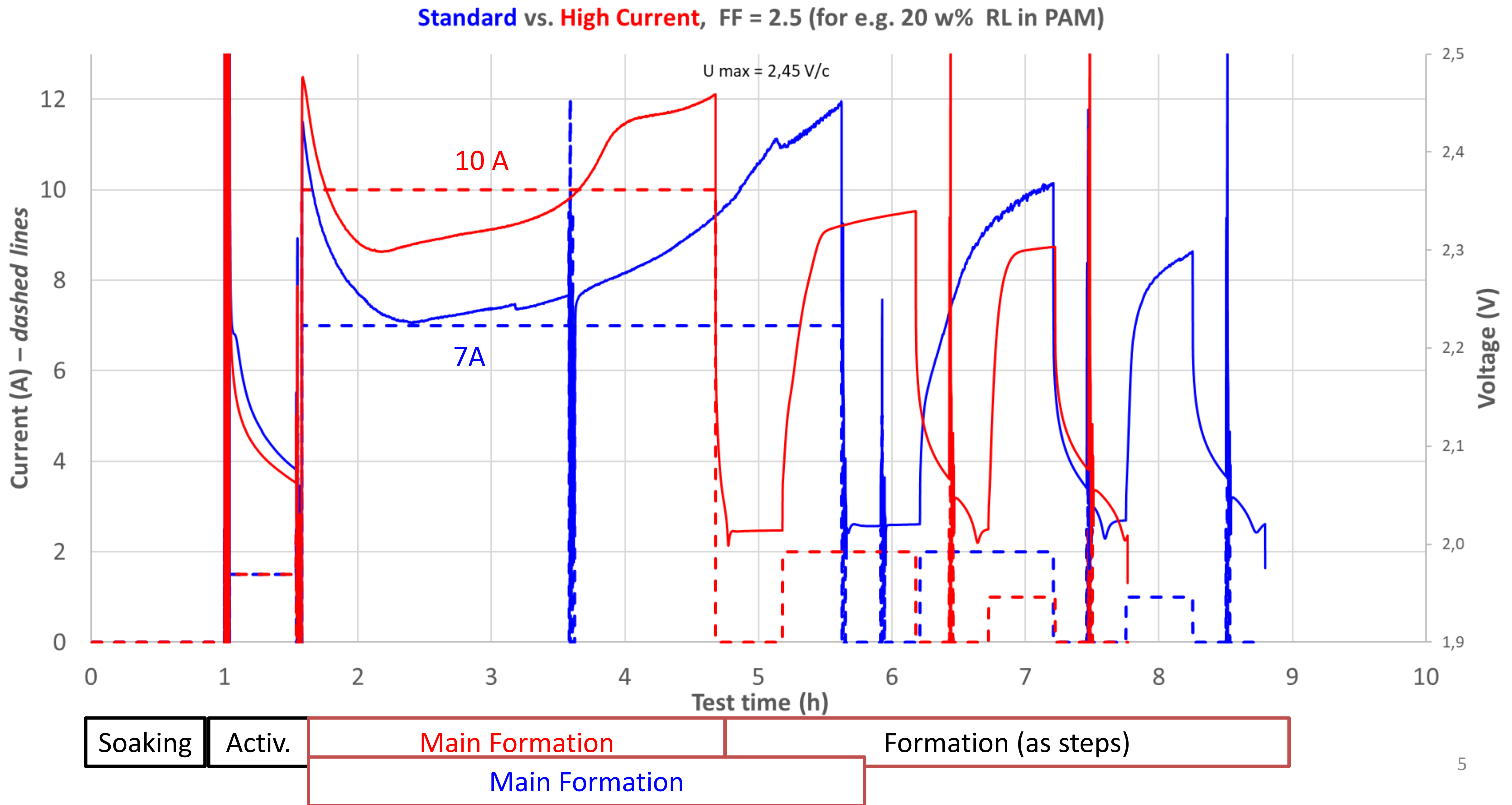
- Formation study with RL and RL+ @45°C
- Capacity study based on PAM porosity
- Relevance of NAM structure

Formation Study

- PAM Mixes:
  - **Red lead (RL)** with d50 = 4.5 µm and Lead dioxide (PbO_2) 25 to 27%
  - **Red lead: *0% = Reference*, 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, 25 wt.%, 50 wt.% …**
  - Comparison of cured positive active masses (PAM): **tri-basic (3BS)** vs **tetra-basic (4BS)**
  - *Comparison of “test” set-ups: 2V with 1p/1n vs. 1p/2n and 2p/1n*

- Conditions of the Formation study:
  - A *high-efficiency* formation profile was used, and the formation factor (FF) was varied
  - A second *fast formation* was tested, and results were compared
  - Testing of initial C20 / C5 capacity and initial capacity evolution
  - The impact of the negative plate was investigated

Formation Profiles



Formation Factor & Formation Energy

$$\textbf{Formation Factor (nominal)} = \frac{\text{Formation Charge (Ah)}}{\textbf{Nominal}\text{ Capacity (Ah)}}$$

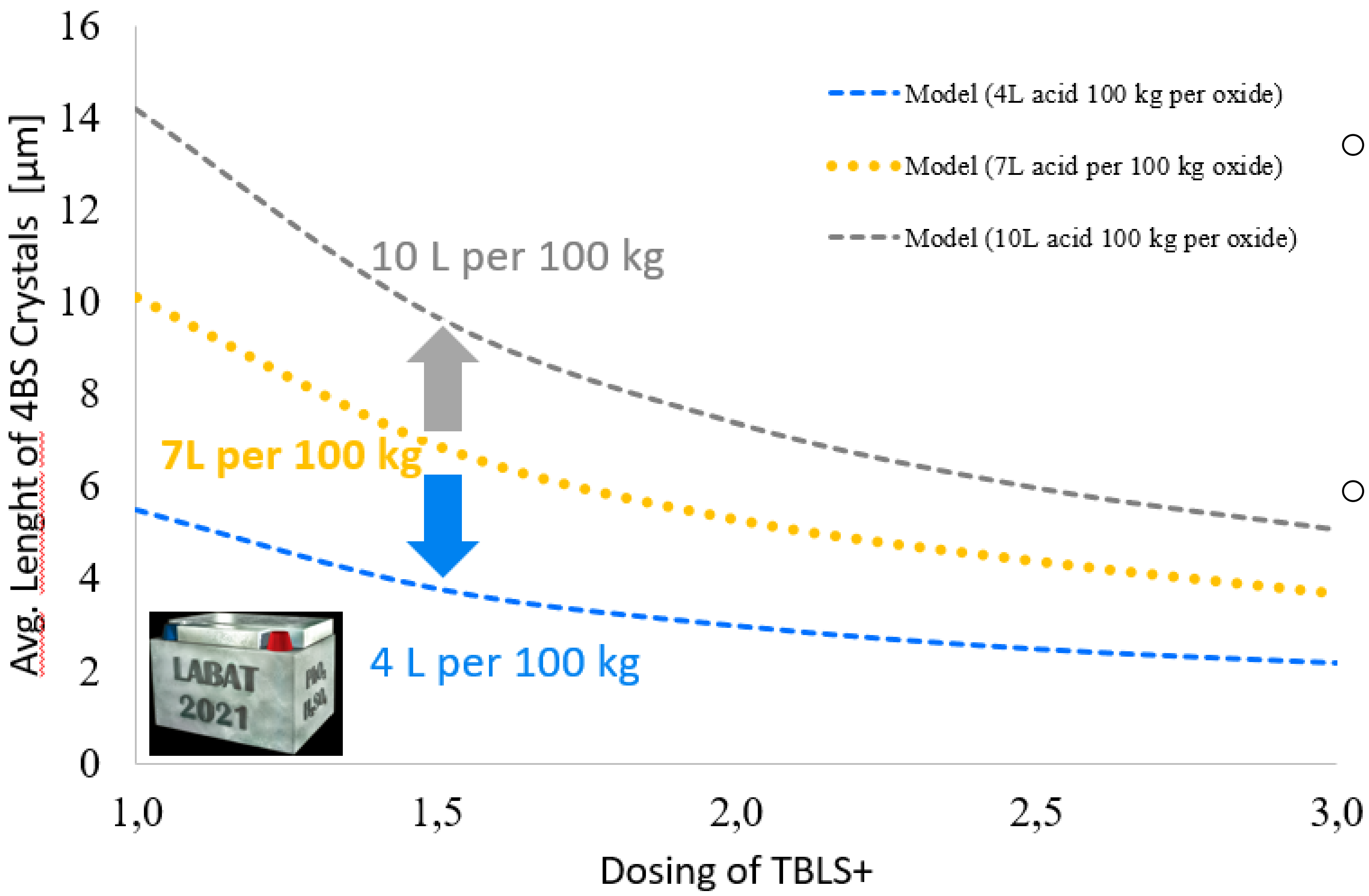
There are two different definitions of the formation factor: **nominal capacity-based** and **actual capacity-based**. Depending on the definition, mass utilisation affects the formation factor.

This study focuses on the specific formation energy calculated in **Wh per gram of dry unformed (DuF) PAM**. The values shown are also **normalised to** a **PbO_2** content of **85%** in formed PAM.

$$\textbf{Formation Energy (specific)} = \frac{\text{Formation Energy (Wh)}}{\textbf{Weight of PAM (DuF) in g}}$$

4BS Seeding and Structure

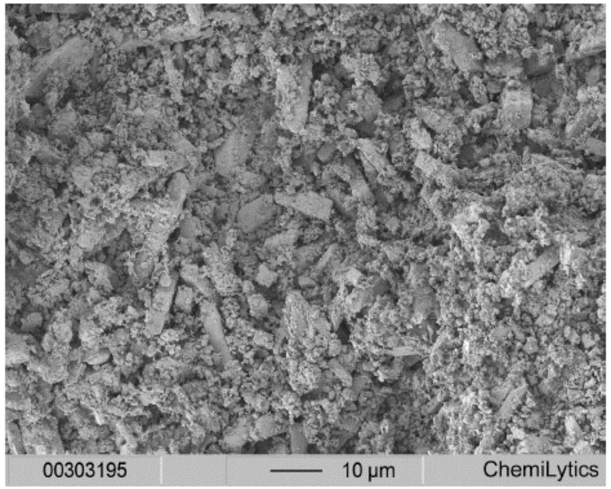
4BS Crystal Size based on a simple Seeding Model

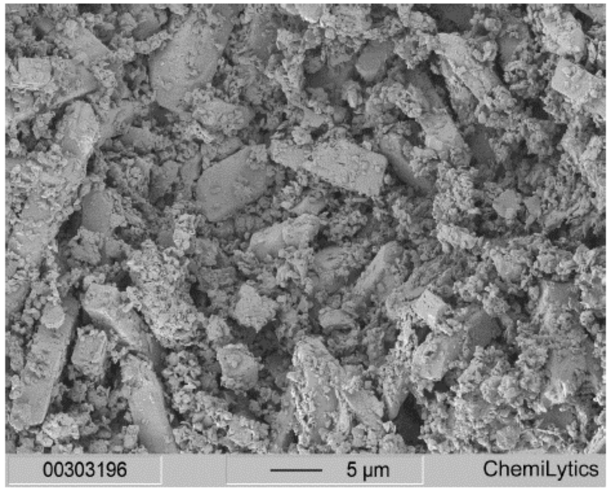


- 4BS crystal size with <u>constant TBLS+ dosing</u> is *increasing* with an *increasing* amount of used sulphuric acid
- and vice versa

PENOX — RL+ creates Tetrabasic (4BS) Structure

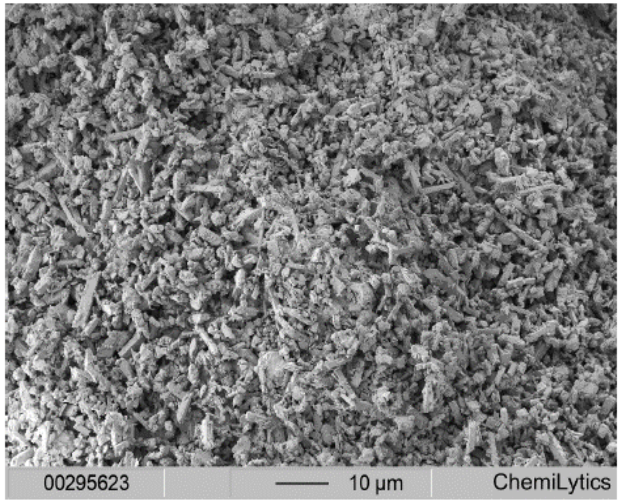
0.15% 4BS seeds

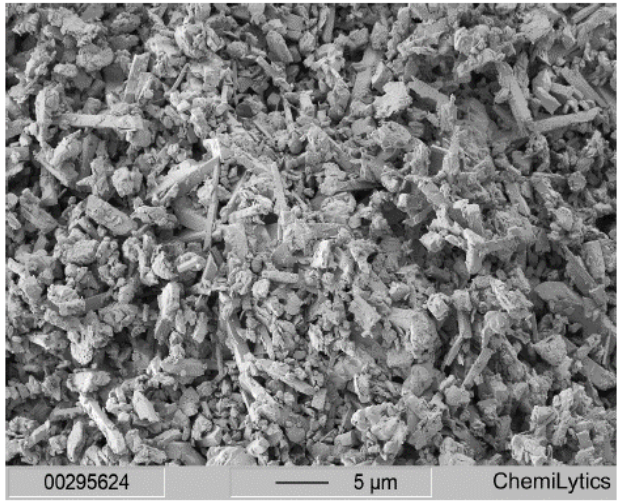




Battery Oxide weight%	Red Lead weight%
90%	10% RL+

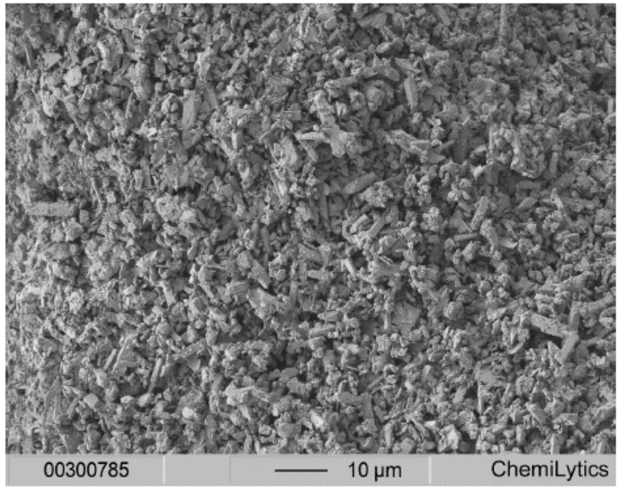
0.38% 4BS seeds

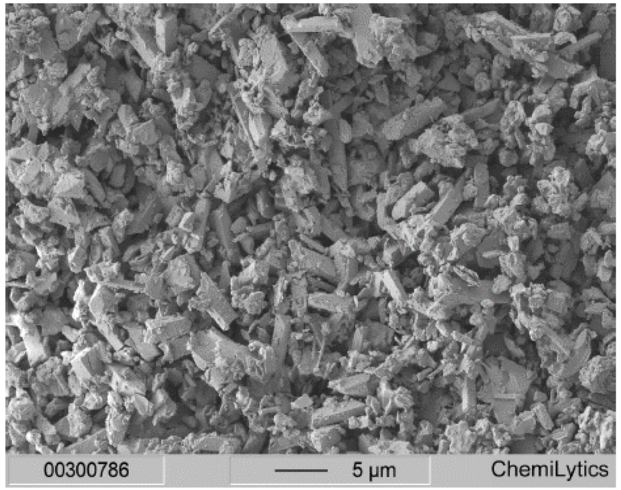




Battery Oxide weight%	Red Lead weight%
75%	25% RL+

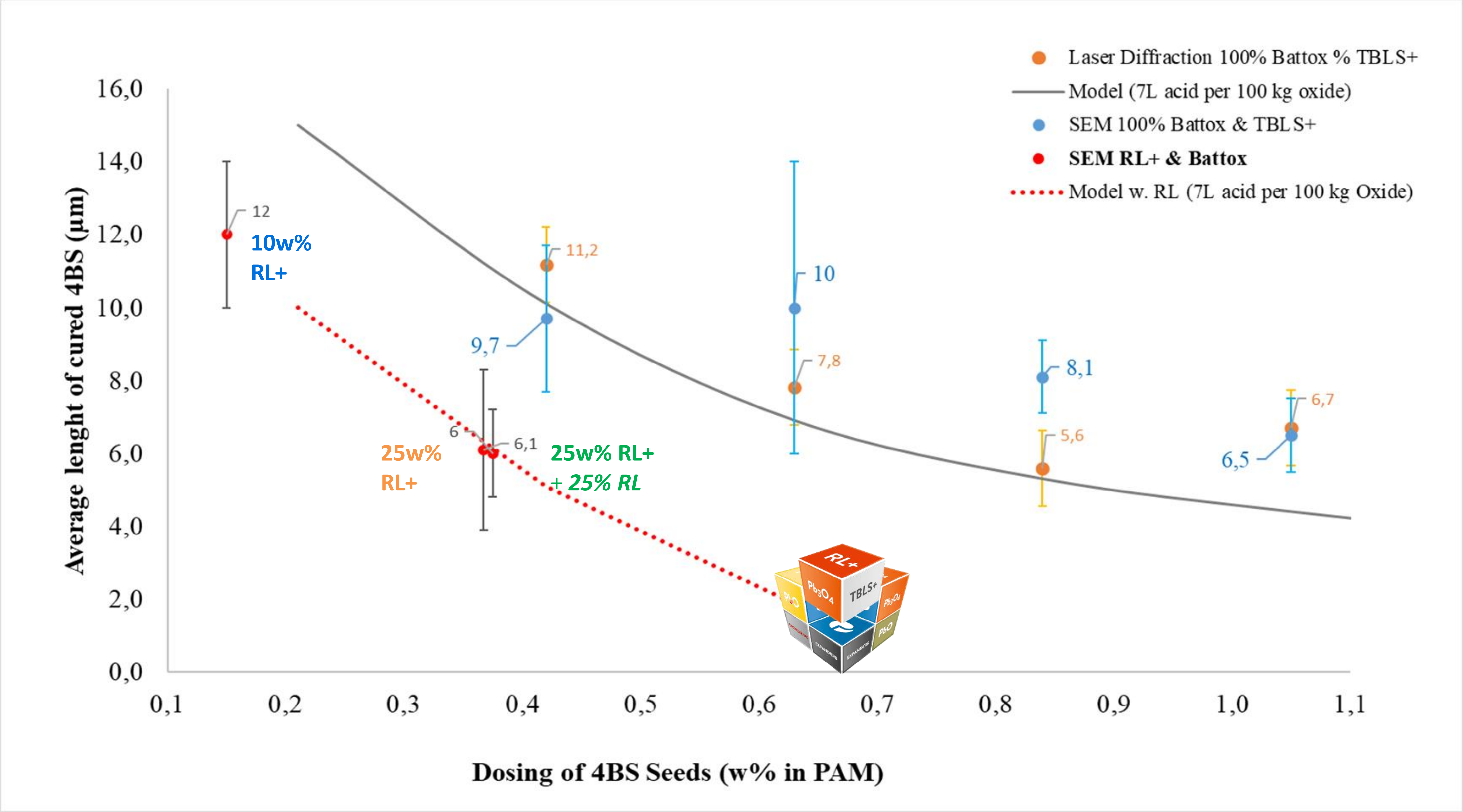
0.38% 4BS seeds



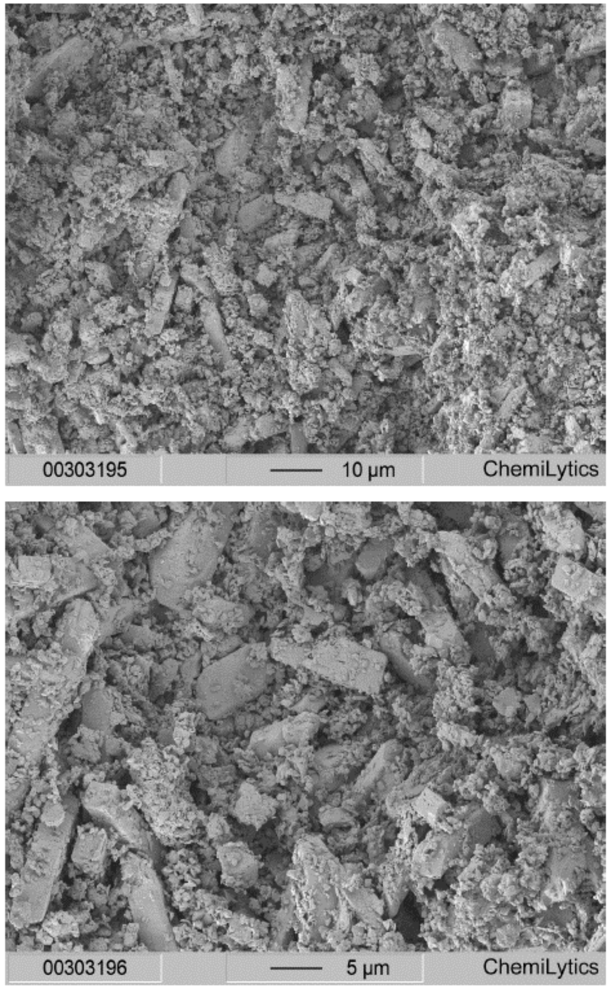


Battery Oxide weight%	Red Lead weight%
50%	25% RL+ & 25% RL

RL+ vs. TBLS+ and Impact on 4BS Structure



4BS & Porosity → Effect on Performance



Battery Oxide weight%	Red Lead weight%
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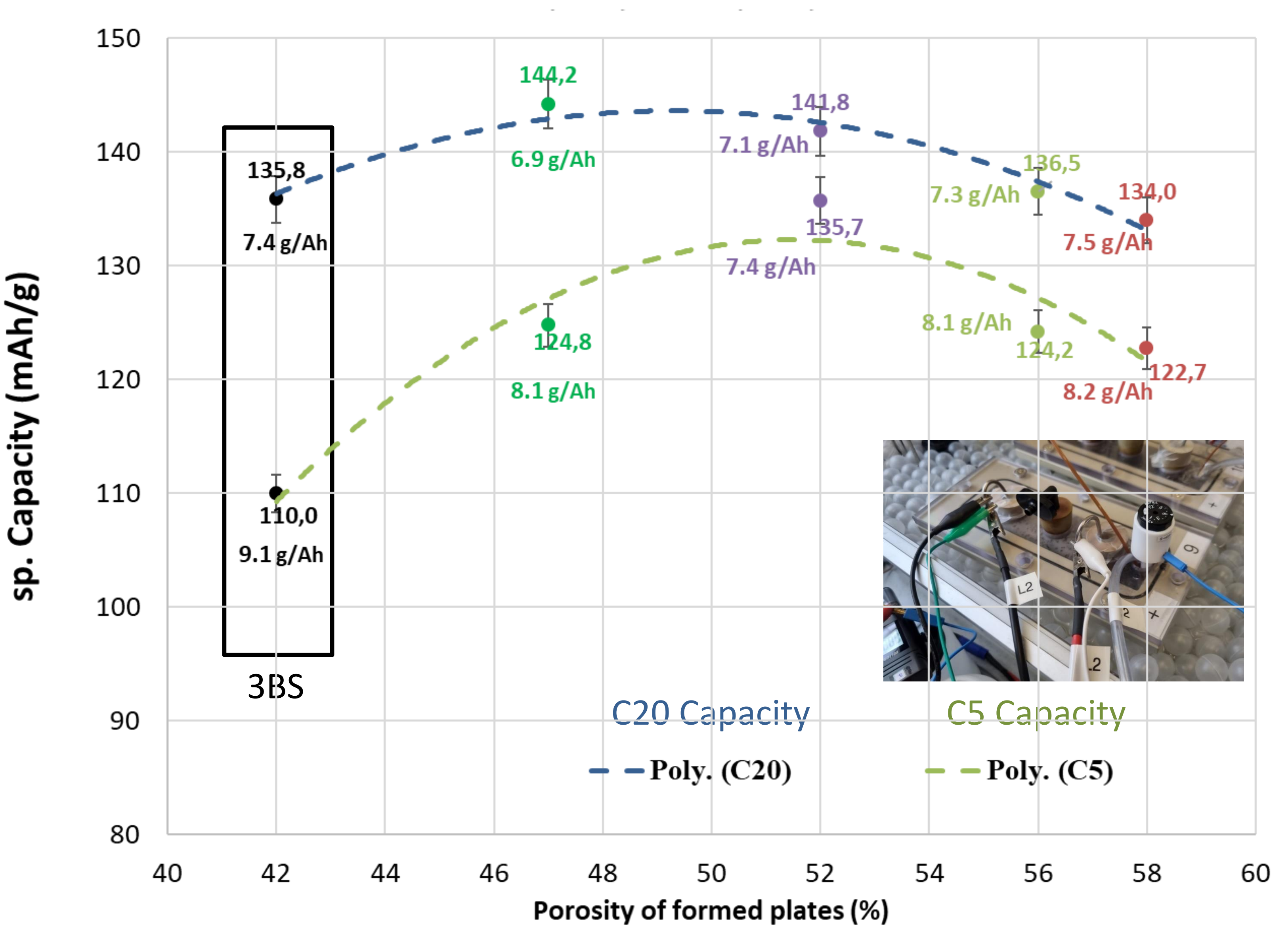


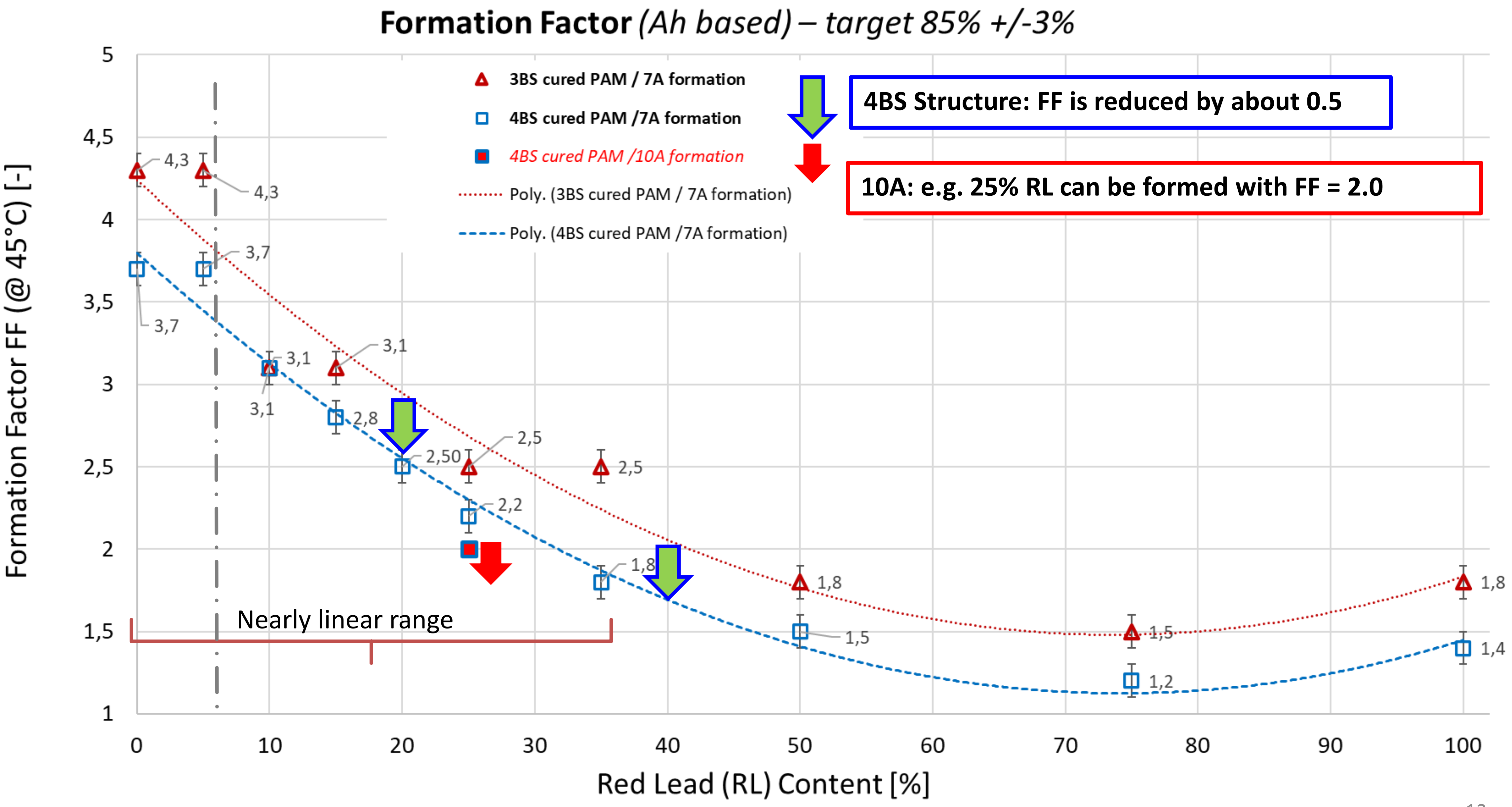
RL+ & Structure → Effect on Performance

- **Using RL+ allows control of the growth of tetrabasic crystals during the curing**
- **Using RL allows for the reduction of formation energy by increasing conductivity. Initial conductivity is enlarged by a "templating effect" of RL forming active PbO_2**
  - Mixing of RL+ and RL allows to achieve the optimal structure for the PAM
  - Please remember that RL needs to be decomposed to PbO_2 during soaking!

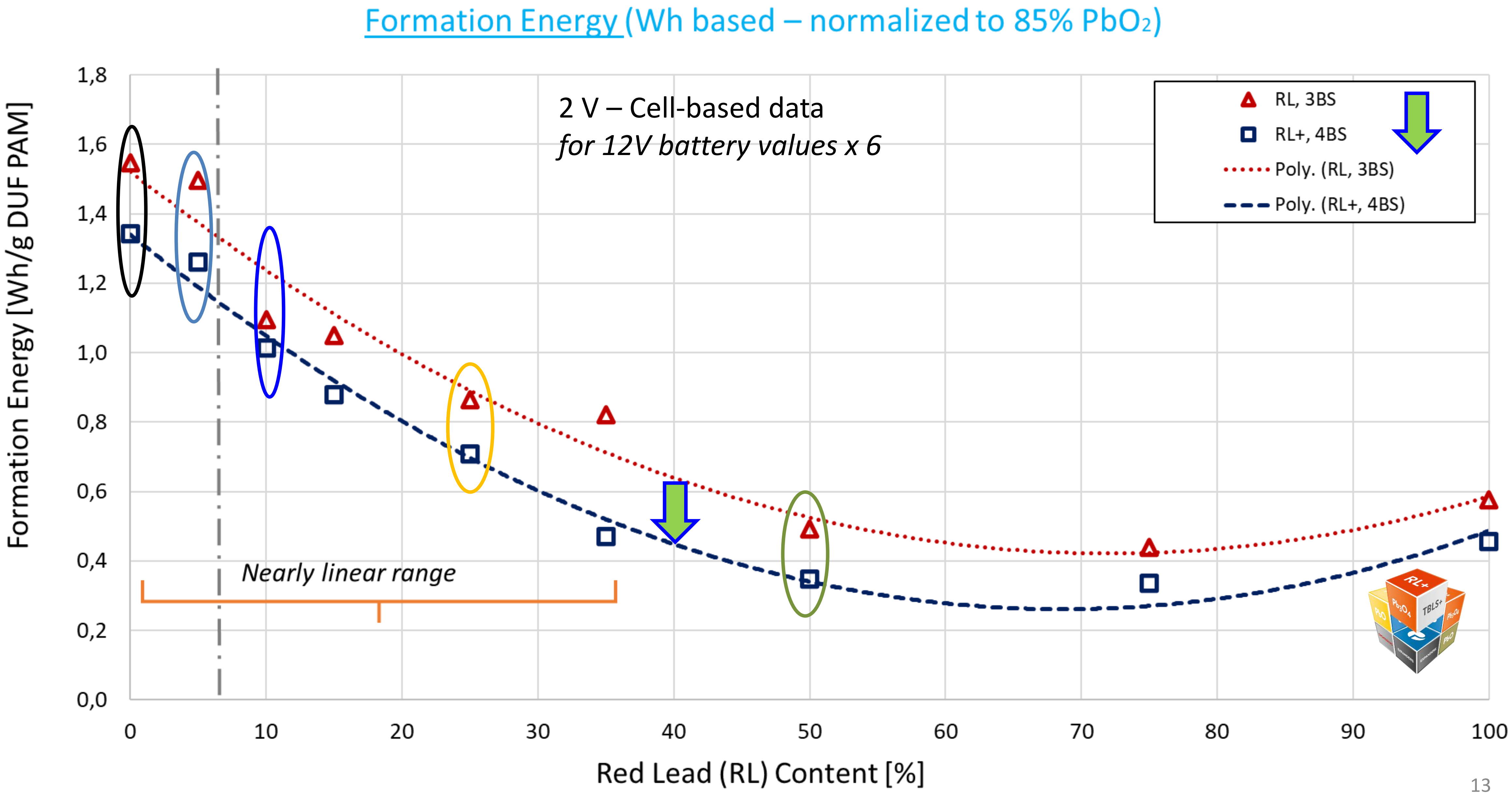
  - Larger 4BS crystals (>>30 µm) require more formation energy
  - Smaller 4BS crystals (< 10 µm) create a less stable structural template – PENOX investigated with 100% DoD testing the cycle life durability
  - Optimum size is about 10 to 20 µm in length of 4BS in cured PAM

  - Plate capacity is highest for about 50% of porosity in the formed PAM
  - Higher porosity than 50% decreases the specific capacity
  - PENOX laboratory 2V cell (1p 2n) was reaching **144 mAh per g PAM = 6.9 g/Ah**

Formation Factor @45˚C



Formation Energy @45˚C



Findings in Formation Study

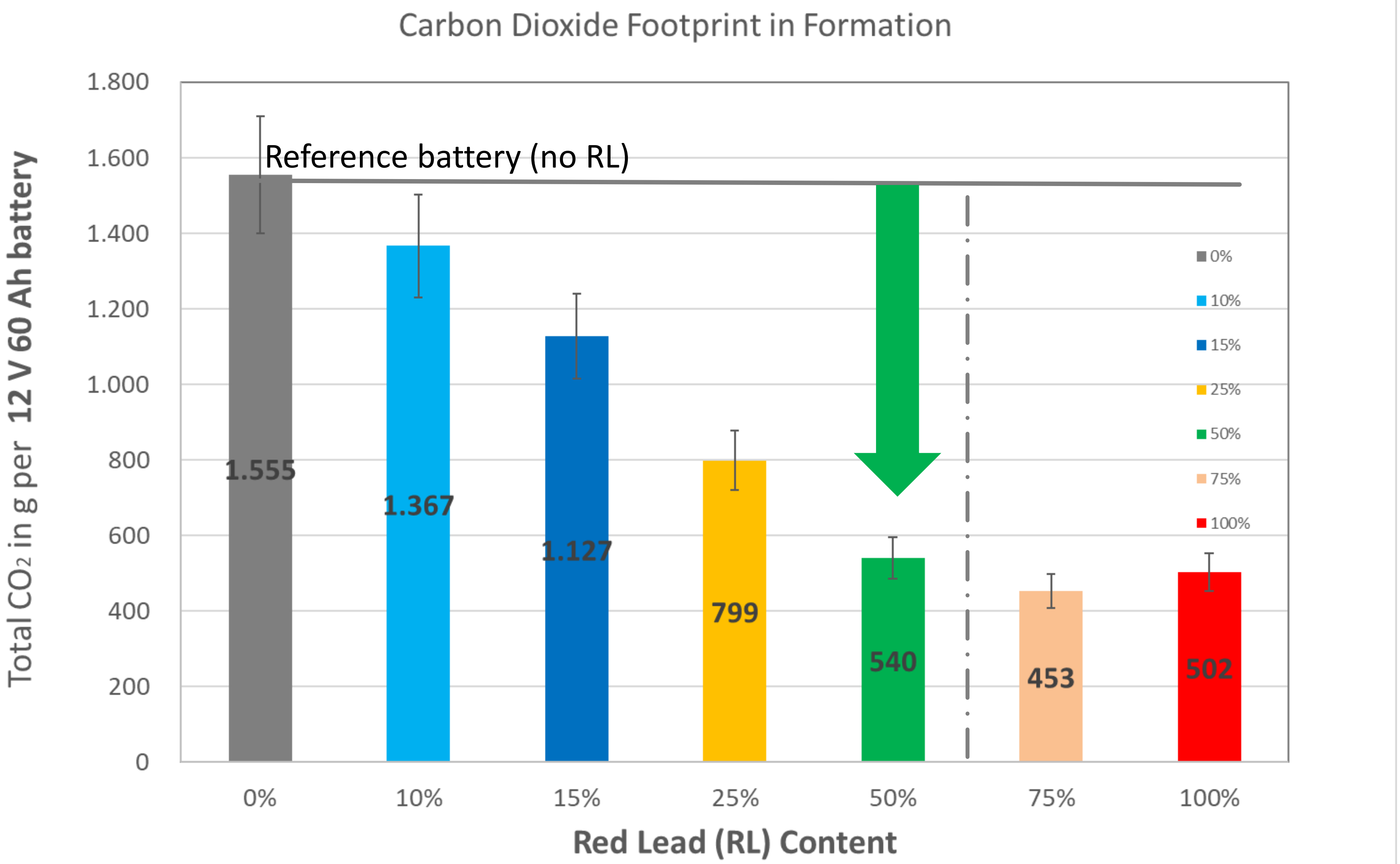
Formation of the **reference cells (w/o RL)** requires a formation factor (FF) of about **3.7 (4BS) to 4.3 (3BS)**

- **Red Lead** allows reducing the formation energy
- **Red Lead** allows to form faster and to maintain a high energy efficiency at a higher current
- **With RL+** (or TBLS+®) the formation energy is reduced in addition by **about 0.2 Wh per g PAM** (this equals about 20% for **25wt.%** of **RL+** used)

The effect of **RL/RL+ content is linear up to about 30 wt.% RL.**

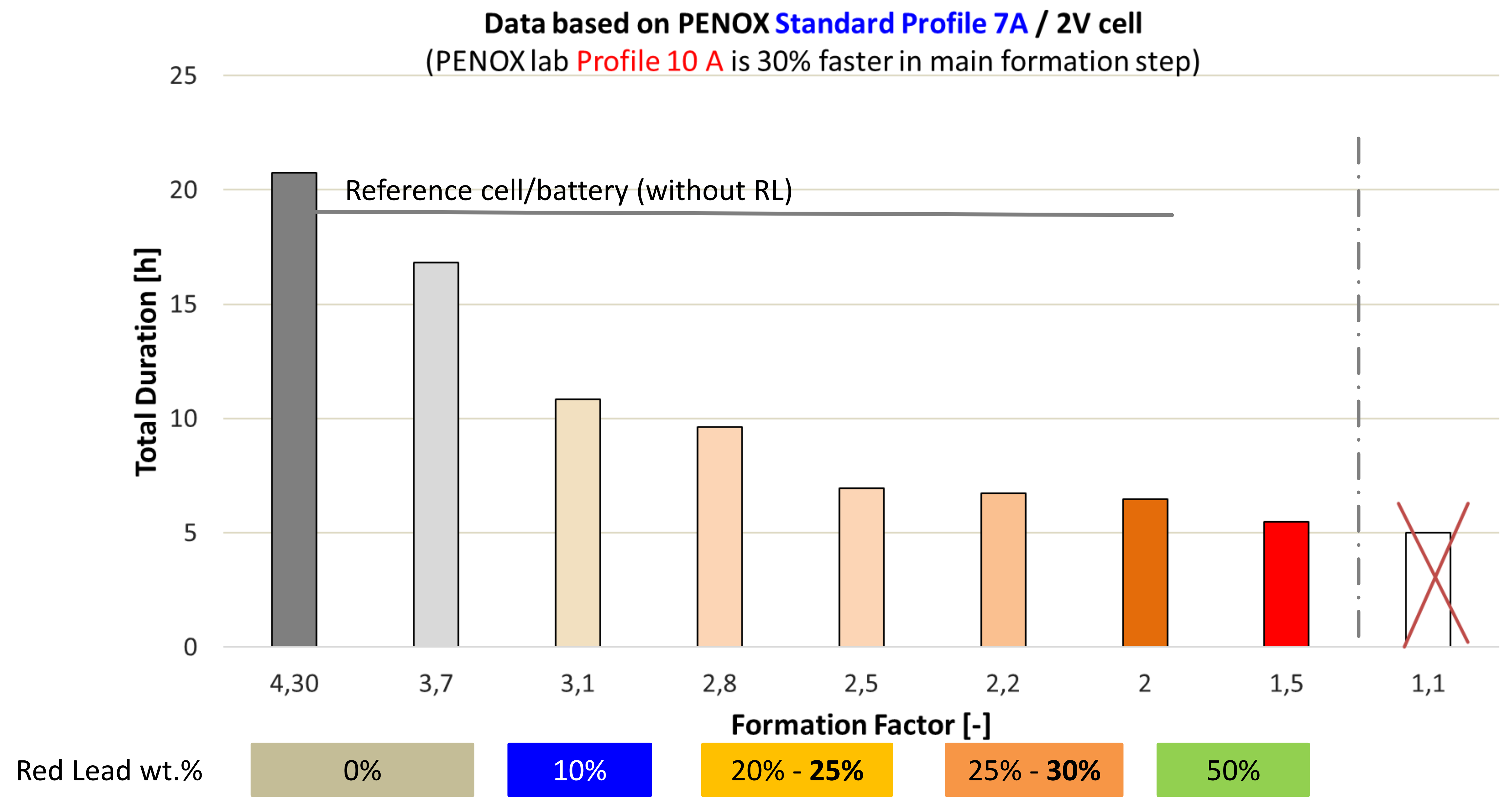
- **10% RL** content allows a formation factor of **3** - **a reduction of about 25% (based on FF = 4.3)**
- **25% RL** content allows a formation factor of **2.5** - **a reduction of about 40%**
- **50% RL content** allows a formation factor of **1.5** - **a reduction by more than 50%**

Formation Efficiency & CO_2 Emissions



(CO2 emission data is based on EU energy mix with 450 g CO2 per kWh)

Impact of RL on Formation Time

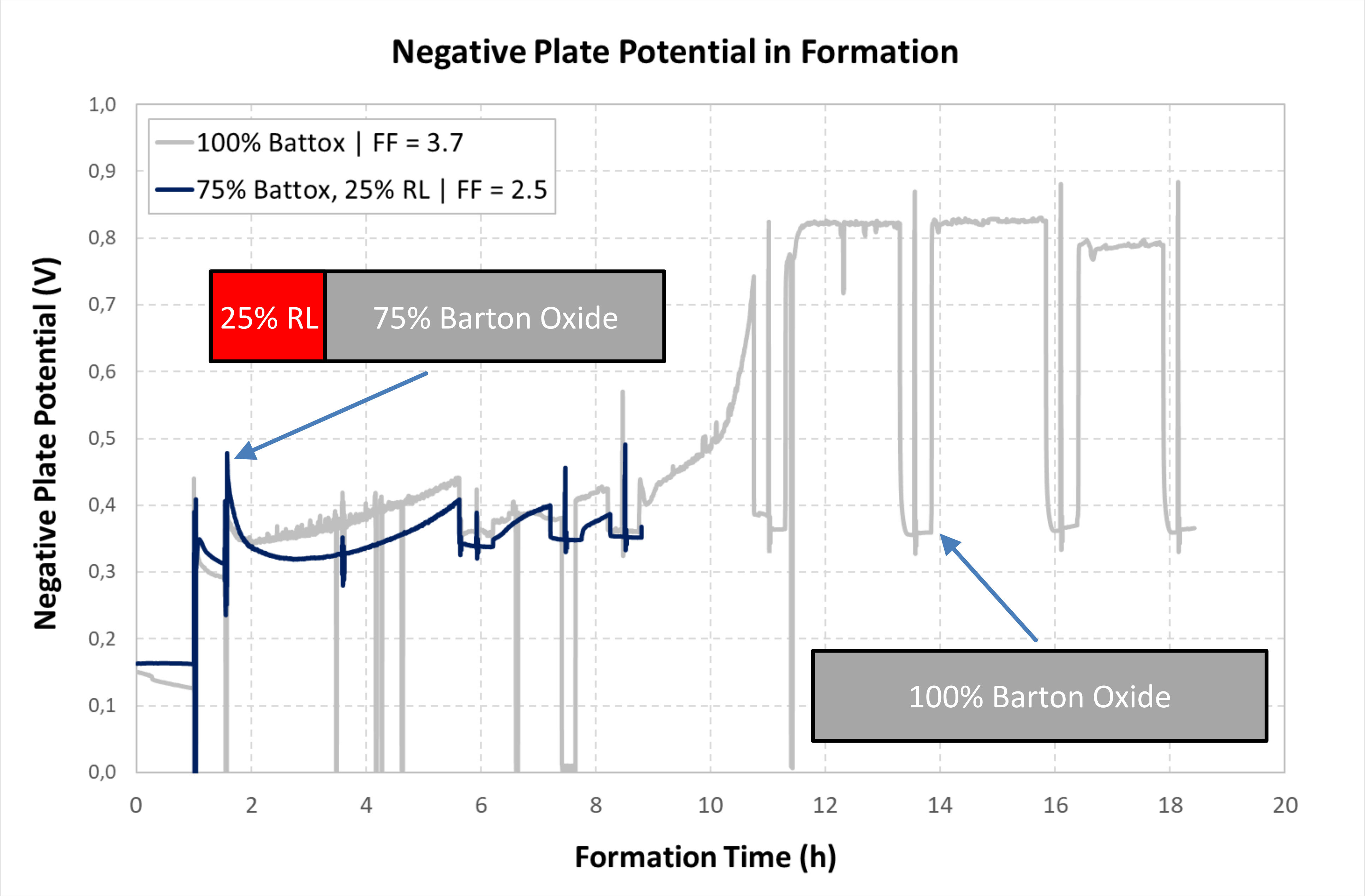


Summary & Outlook

- The impact of **RL** on formation energy and time was systematically investigated
- 4BS cured structure shows a surprisingly constant down-shift by about **2 Wh per kg of PAM** in a 2V cell – *about **1.7 kWh per 60 Ah 12 V (E20 = 0.72 kWh) automotive battery,** e.g. **25 wt.% RL+***
- **RL+**, which combines the function of RL and 4BS, is a cost-effective functional material.
- Using a **4BS structure** allows **higher mass utilisation than a 3BS structure.** *However, the maximum is reached for a **porosity of about 50 %** of the formed positive active mass*.

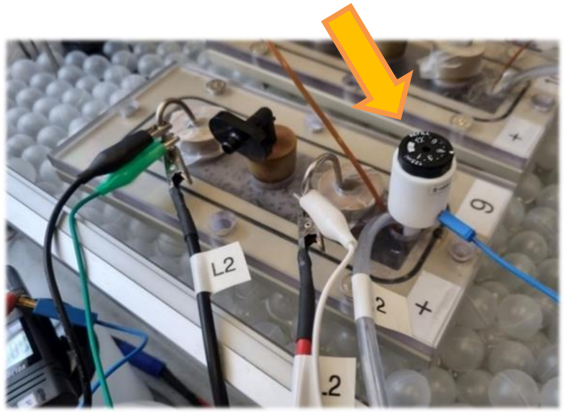
- **BALANCING the Battery: The NAM performance needs to be improved**

Balancing a Battery: NAM Polarisation



- More **RL** results in less „stress“ for the negative electrode.
- This leads to a better-balanced formation.

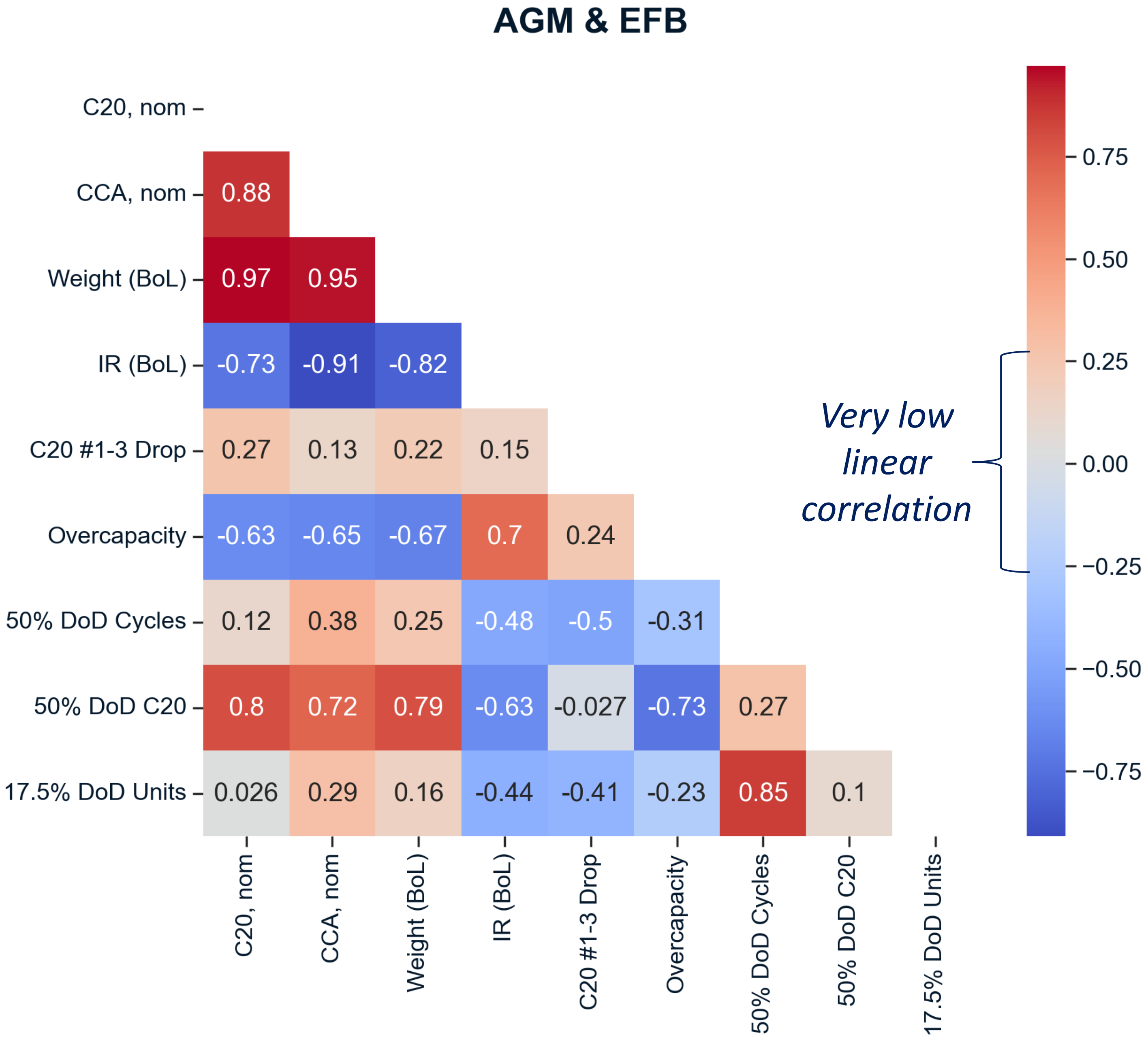
The reference potential was measured for the negative electrode with a reversible hydrogen electrode (RHE).



- **PENOX is aware of the NAM limitation and is working to improve its performance:**
  - Mass transport of the reaction partners – *especially by optimising the porous electrode structure*
  - Local solubility of the lead sulphate for higher charge acceptance
  - Plate conductivity at low SoC

Typical Parameter	PAM	NAM	Comment & Ideas
Paste density:	4.0 to 4.4 g/cm^3	4.2 to 4.4 g/cm^3	Lower density (< 4 g/cm^3) can be stabilised by e.g. AEROXIDES
Porosity **cured AM (water)**:	35 to 45%	30 to 40%	Higher values – either low density AM or 4BS structure in curing
Porosity **formed AM (water)**:	45 to 55%	40 to 45% (50%)	Porosity in NAM can be increased
Pore diameter **formed AM (Hg-Poro):**	3BS: 0.3 to 0.4 µm 4BS: 0.6 to 1.0 µm	3BS: 0.2 to 0.4 µm	Pore diameter in NAM is typically lower compared to PAM – ***except when using special lignin types or 4BS curing***
BET (N2 based):	5 to 10 m^2/g	1.5 to 2.5 m^2/g	BET surface is much lower for NAM

Balancing a Battery – “Performance Pattern”



- It is interesting to study the correlation of electrical parameters
- The left side shows a teaser of the joint work with Austrian Battery Research (ABR)

Please join the presentation of:

Micha Kirchgeßner, Martin Wieger et al. on

Thursday - 19th Sep, **9:20am – 9:40am**

Automotive Lead-Acid Batteries – A Review and “Outside View” on the Perspective for Automotive Batteries

BoL = Beginning of Life
IR = Internal Resistance

Technical Papers by PENOX 2023-2024

PENOX

November 2023

Red Lead as a Key Factor for Higher Efficiency in the Formation of Lead-Acid Batteries

Micha Kirchgeßner, Rainer Bußar, Hamid Ramianpour, PENOX GmbH (D)

The Importance of Formation Efficiency

Energy efficiency has become a critical topic for the European battery industry, especially given the energy price increase scenarios since 2022. Environmental protection efforts are also an essential driver toward lower energy consumption in the formation process, as this process step consumes most electrical energy in a battery plant. As the lead-acid industry is expected to keep a significant share of the global battery market, despite current challenges by other battery chemistries, improving the energy efficiency of the lead-acid battery production process remains highly relevant. [1]

Upcoming: Review of the Limits of Optimisation of PAM using RL and functionalised RL+

– Performance, Costs, and Environmental Aspects

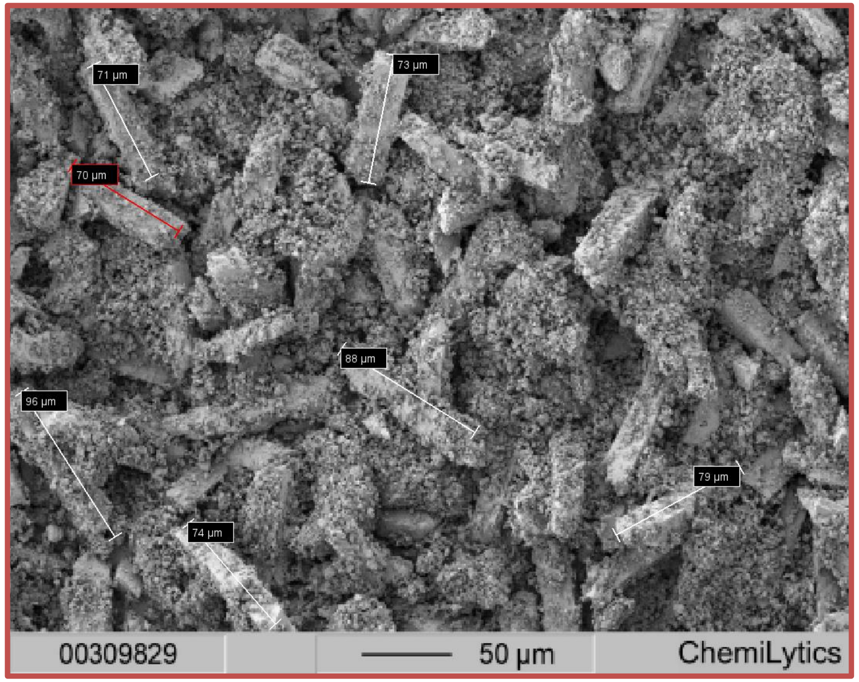
Technical paper as a follow-up of the ELBC 2024

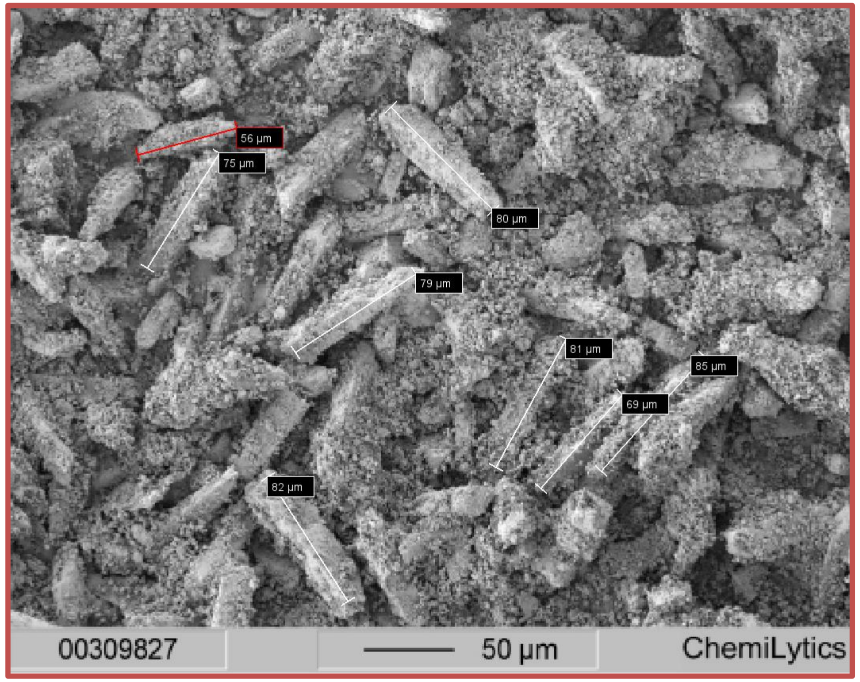
R&D Team & Center in Germany

Thank you for your kind interest

Appendix
- Slides for discussion -

Example: 4BS with very large Crystals





Size (SEM): 75 µm +/- 10 µm

Due to non-ideal seeding and thus, too large crystal growth

Standard 4BS structure (~10 µm) vs. 4BS structure with ~70 µm

Date	Trial	MIX Composition	RL / RL+	4BS	H2O Poro	FF	PbO2 in den Platten (%)		AV
08.2024	**Test 19**	**80%Battox; 20% RL+ @ 45°C**	20	94,3	50,2	**2,5**	85,4	84,2	**84,8**
08.2024	**Test 19**	**80%Battox; 20% RL @ 45°C**	20	24,3	44,4	**2,5**	65,1	62,2	**63,7**

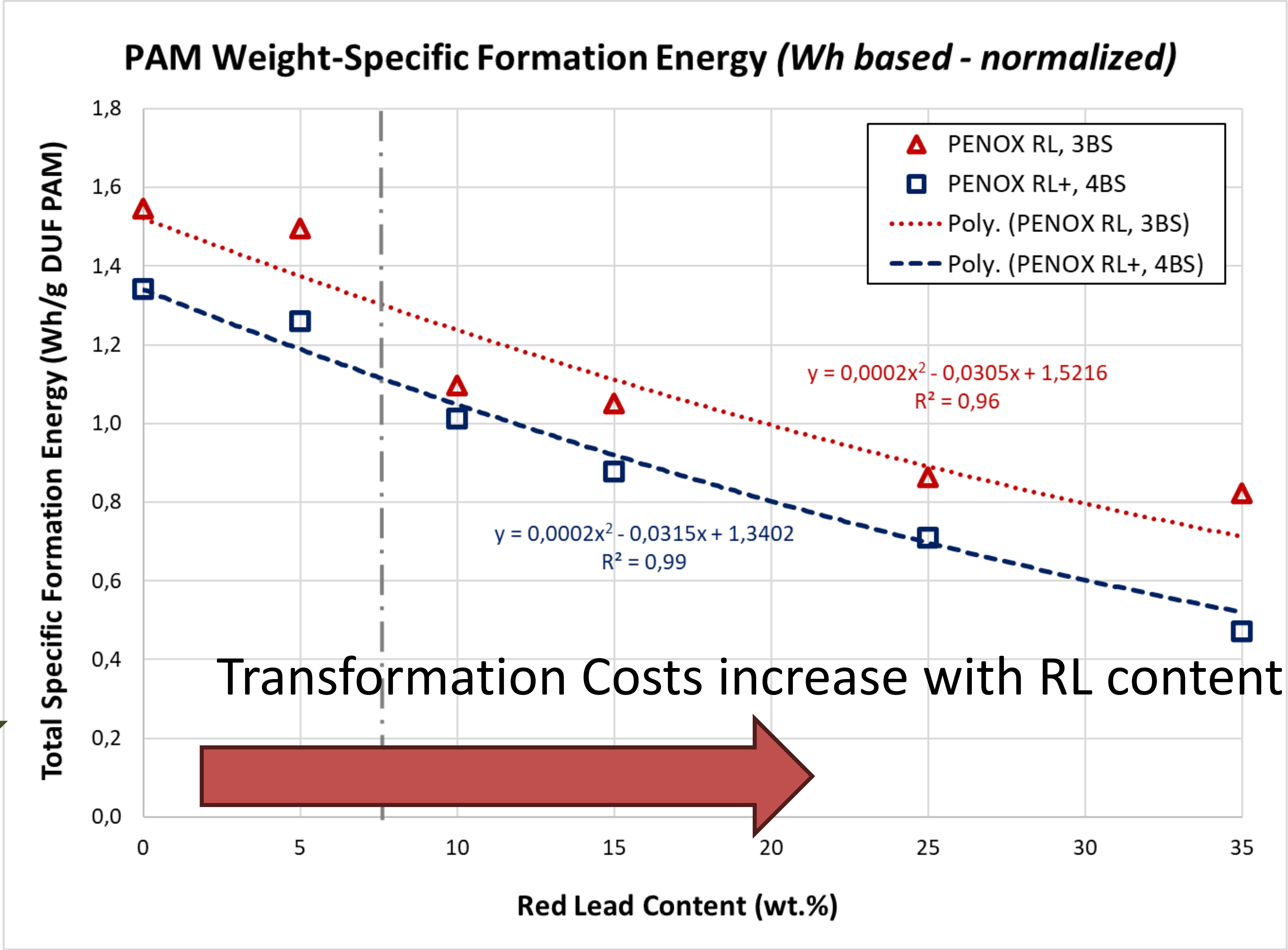
Large 4BS crystals >30 µm require much higher formation energy!
Correct Dosing of 4BS from TBLS+® and RL+ is very important!

PENOX Formation Energy & Costs (0 to 35 w% RL, 2V Cell)

Energy Costs & Process Time decrease

NO RL is a

Non-economic option

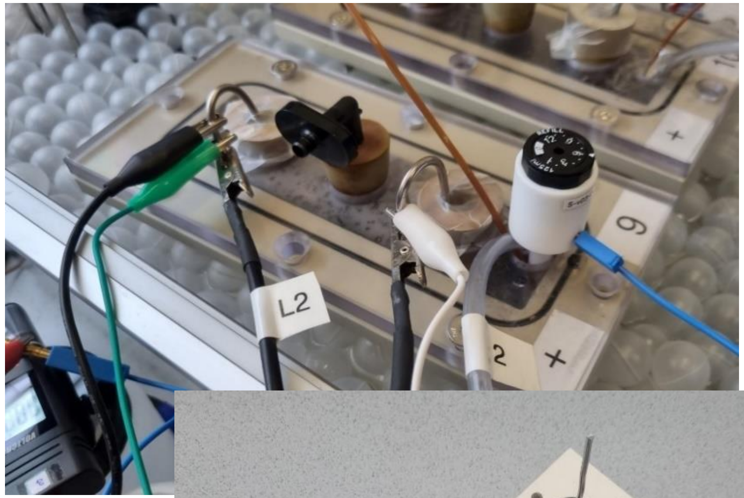


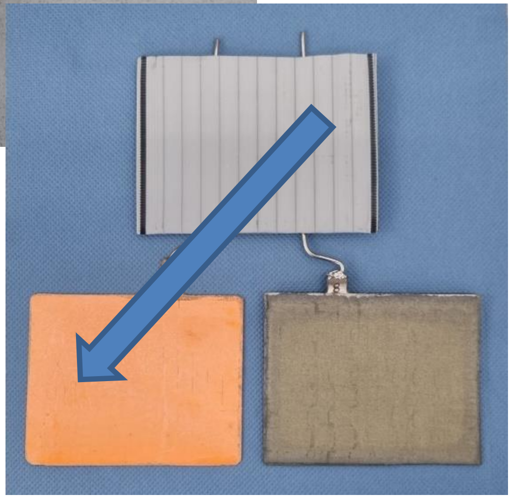
Transformation Costs increase with RL content

Test Setup in PENOX Laboratory

- Cell Set-up:
  - 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

- Variation of the reference:
  - 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 focuses on PAM. PENOX is comparing, e.g. (5p/4n), for a more exact data comparison.