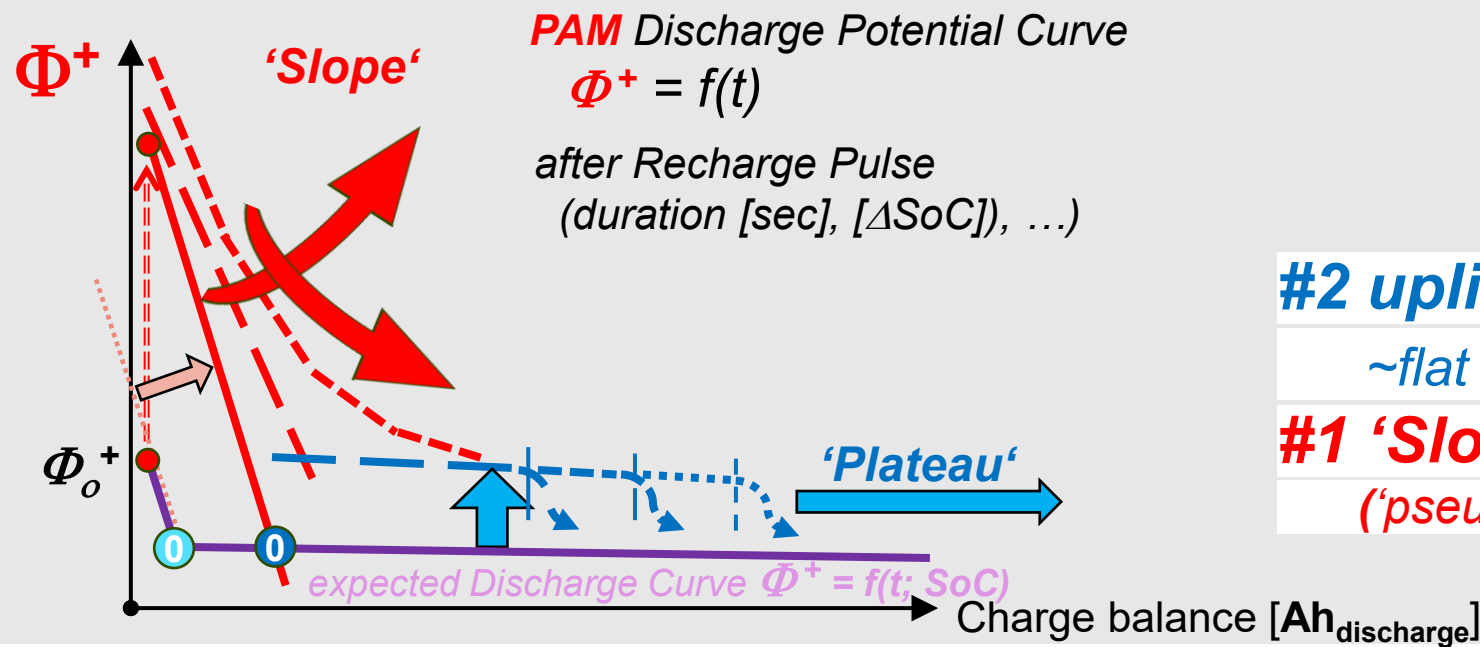




#2 uplift of discharge potential
 ~flat 'elevated **Plateau**'

#1 'Slope'
 ('pseudo-capacitor'-like)



CR11: Understanding PbO_2 structure: fast SoF recovery @ PSoC

bottom-up analysis and hypotheses on 'improved' DIScharge Characteristics

after previous (partial) REcharge

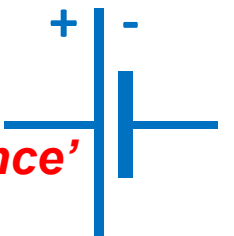
Dr. Eberhard Meissner

– Battery Specialist –

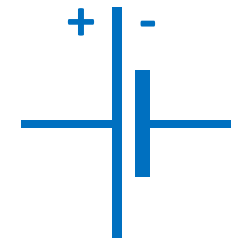
260520 high pos. electrode polarization η^+ essential
 → create 'fresh' PbO_2 with high surface energy

⇒ Application Relevance: what to do now ?

⇒ **uplift of 'elevated Plateau'**
 ⇒ **increase of 'pseudo-capacitance'**



CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



Content – Part 1: Look inside the Nutshell !



Content – Part 2: Application Relevance



Content – Part 3: Questions & Perspectives



CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



Content – Part 1: Look inside the Nutshell !



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CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses

Part 1: look inside the Nutshell !

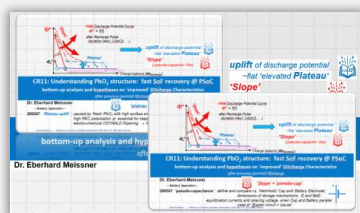


‘elevated discharge Plateau’ AND ‘high pseudo-cap’

REMEMBER: both effects located at **POSITIVE** electrode of battery !

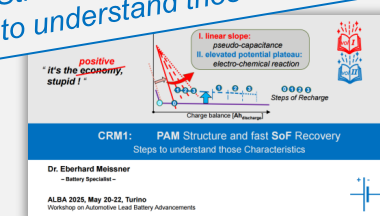
for details: [cf. presentations from WEBINAR 1 \(7 May 2026\):](#)
Decyphering recovery of pulse performance

Model description

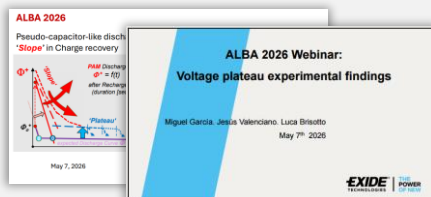


1. **PAM potential uplift**
[Structures and mechanisms that govern it \(Eberhard Meissner\)](#)
2. **PAM pseudo-capacitance**
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cf [P18] E.Meissner, ALBA Torino 2025, CRM1
“**PAM** Structure and fast **SoF** Recovery:
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Experimental Support, Evidence & early Quantification

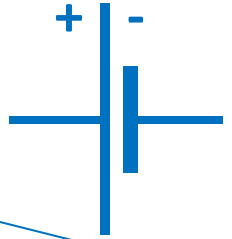


1. **PAM potential uplift**
[New experimental findings \(Miguel Garcia\)](#)
2. **PAM pseudo-capacitance**
[New experimental findings \(Jibo Zhang\)](#)

+ TODAY !

[More presentations at](#)
ALBA2026 Sessions CRP + CR1 + CR2

CR: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



Mechanisms behind ‘uplift of discharge Plateau’

a) origin of ‘uplift’ – basics from thermodynamics; surface energy

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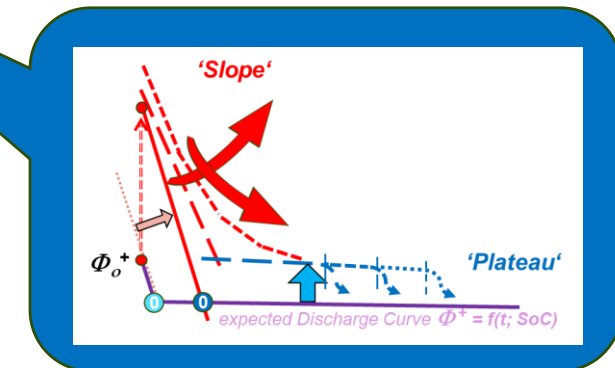
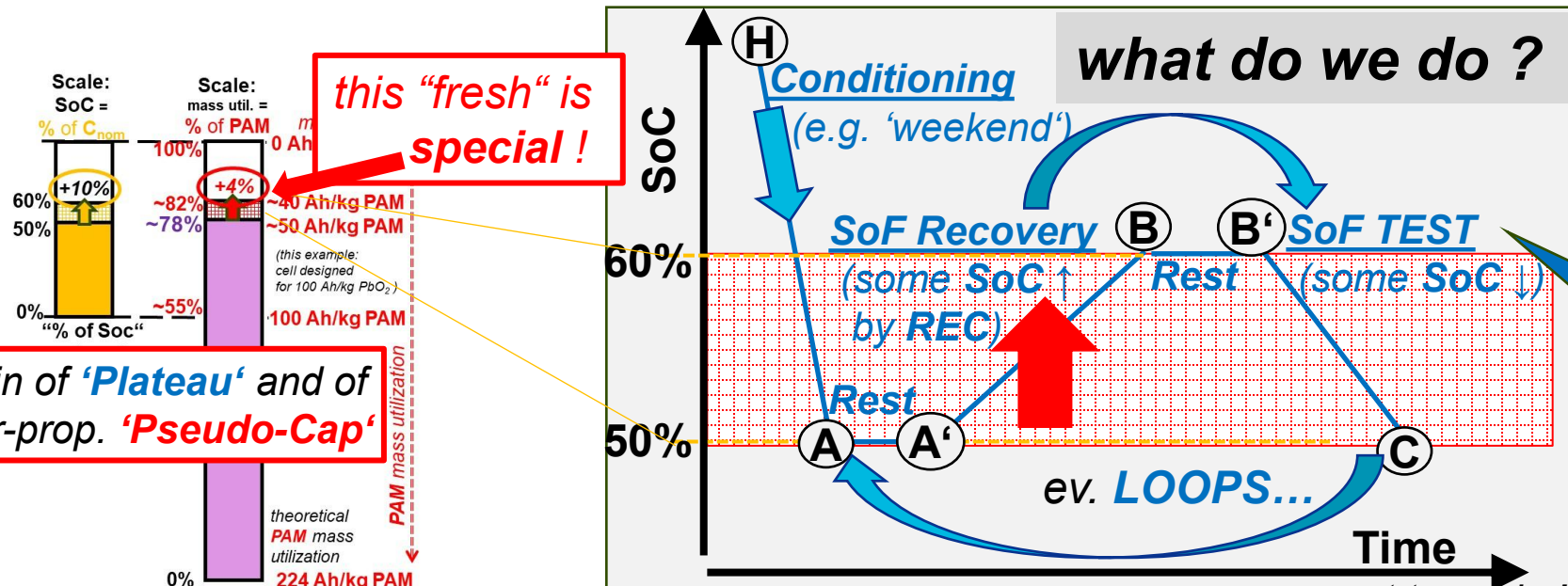
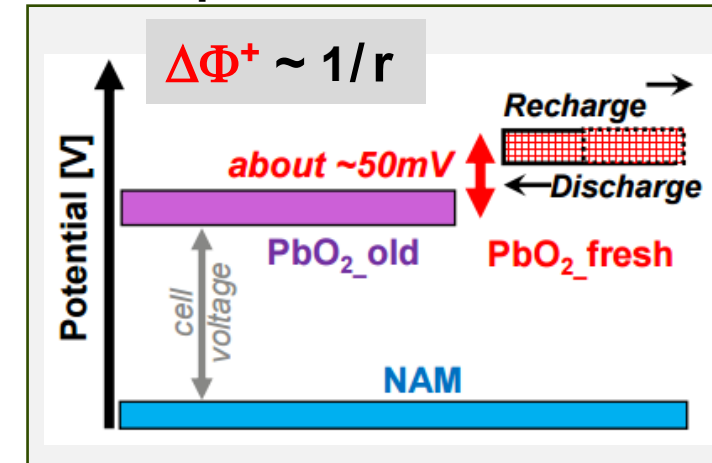
Lessons learned from ALBA2025 Torino (cf. presentation CRM1 E.Meissner [P18])

‘uplift of discharge Plateau’ after previous RECharge seamless understood due to ‘Laplace Pressure’,

if “**freshly**” created PbO₂ particle surfaces @RECharge = electro-deposition !

have a **higher surface energy** σ [J/m²] than the “**old**” PbO₂ particles

e.g. **fine** PbO₂ particles (nano << 20 nm; cf. electro-catalysts)



CR: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



Mechanisms behind ‘uplift of discharge Plateau’

a) origin of ‘uplift’ – basics from thermodynamics; surface energy

Upon RECharge, ‘fresh’ PbO₂ material is electrodeposited from solution

our Target: create ‘fine’ PbO₂ particles
(*nano-sized*, high surface energy $\sigma \rightarrow$ high Laplace pressure $\rightarrow$ higher potential)

for a high ‘*discharge Plateau uplift*’

Classical Nucleation Theory (CNT), applied to electrodeposition

rule of thumb: **high PAM polarization η^+ !** [18]

$\Rightarrow$ **more** nuclei, **finer** structure of deposit, **less regular** crystallinity

$\Rightarrow$ **leading to** (II.) ‘plateau uplift’ and

(I.) ‘increase of pseudo-capacitance’

- **create** very fine PbO₂ nuclei
- **mitigate / impede / limit** further growth of such fresh PbO₂ nuclei when **REC** continues
- **stabilize** fine PbO₂ particles in (short) rest periods (*against coarsening by electro-chemical OSTWALD ripening*)



CR: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



Mechanisms behind ‘uplift of discharge Plateau’

b) ‘fine PbO₂ particles’ generated by diffusion-controlled nucleation @REC

Why ‘high positive electrode polarization η^+ ’ ?

Low polarization η^+ : **kinetic control**

High polarization η^+ : **diffusion-control**

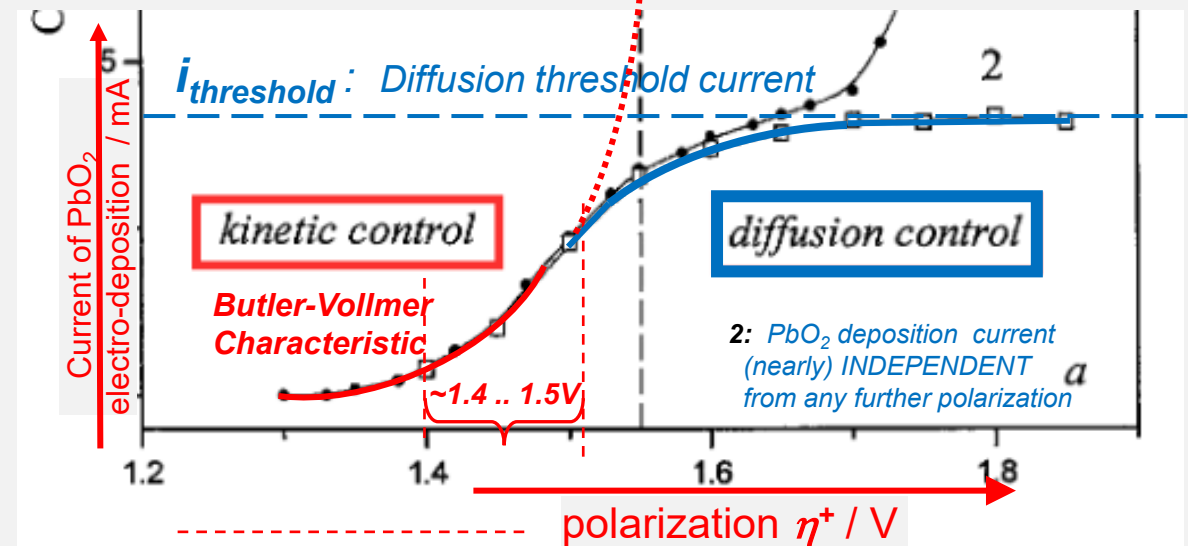
PbO₂ deposition rate levels off:

→ $i_{\text{threshold}}$ = Diffusion threshold current

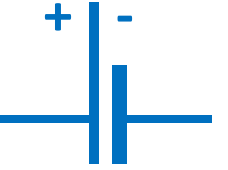
⇒ deposition **current** CANNOT be increased
by even higher **polarization η** ! “supply chain” issue

⇒ **operating condition to create nano-sized PbO₂ nuclei !**

Deposition rate $i = f(\text{polarization } \eta^+)$



CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



in a Nutshell: fresh PbO₂ with **BOTH** '*elevated discharge Plateau*' AND '*high pseudo-cap*'

Polarization of substrate: Recharge = creation of NEW (additional) PbO₂ material by electro-deposition

IF polarization η^+ is **LOW** already existing (mainly coarse) PbO₂ particles continue to grow even more

IF polarization η^+ is **HIGH**

initially **HIGH η^+**

⇒ **small nuclei**

⇒ new "**fine particles**" with **high surface energy σ** ,

i.e. with an elevated equilibrium potential Φ^+

⇒ '*elevated discharge Plateau*'

continuously **HIGH η^+**

⇒ **limited growth** of nuclei, uniform size

HIGH η^+ at end of **REC**

→ "**fine PbO₂ particles**": high surface area, many dangling bonds, open structure / high disorder

⇒ promoting "*pseudo-cap*" -type mechanisms

⇒ **large capacitance C of pseudo-cap**

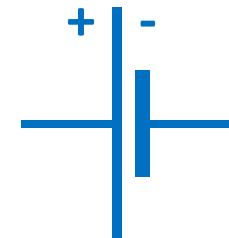
⇒ **pseudo-cap C charged to high potential**

⇒ **much charge Q at high potential**

⇒ stabilizes '*elevated Plateau*' for some Pause

⇒ **a '*high*' and '*long*' Slope**

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



Part 1: look inside the Nutshell !

Part 2: Application Relevance



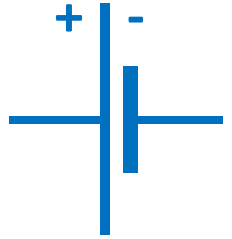
- Opportunity from Fast SoF Recovery - Benefits to expect
- Pre-Requisites to
 1. Generate the Effects
 2. (temporary) Maintain the Effects
 - What we have in place already !
- ToDos to be addressed now

Part 3: Questions & Perspectives

- PERSPECTIVES for more *uplift of 'elevated Plateau'* ?
- PERSPECTIVES for higher *C* of *'pseudo-cap'* ? *[F/g of 'freshly deposited' PbO₂]*
- PERSPECTIVES to utilize effects at Temp >0°C ?

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses

Part 2: Application Relevance



Opportunity from Fast SoF Recovery - Benefits to expect

potential uplift $\sim +50\text{mV} / \text{cell} = \sim +300\text{mV} / 12\text{V batt}$

potential slope $\sim 300 \rightarrow 0\text{mV} / \text{cell} = \sim 1'800 \rightarrow 0\text{mV} / 12\text{V batt}$

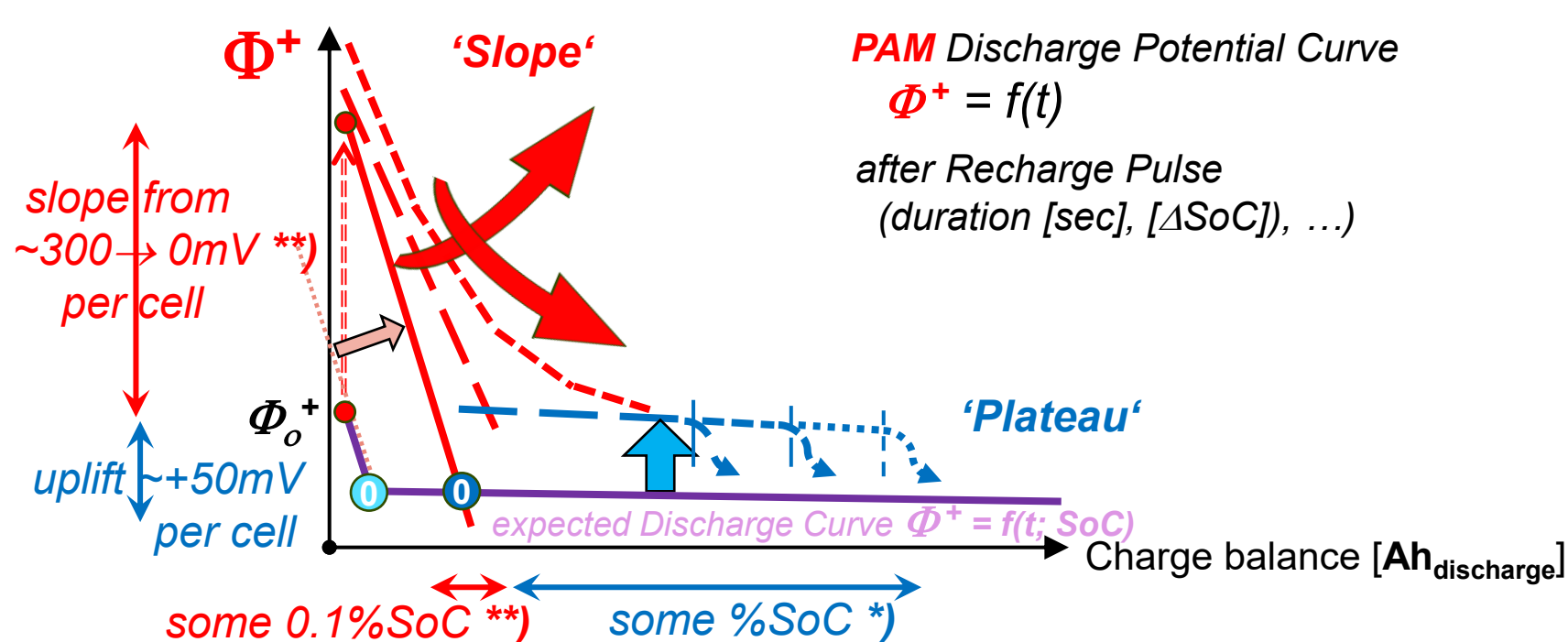
vs. **standard potential**

0mV

capacity [Ah / SoC] : some %SoC *)

capacity [Ah / SoC] : some 0.1%SoC **)

capacity [Ah / SoC] : = actual SoC

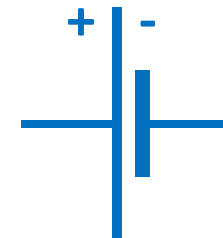


***) depends on REC [Ah] pattern**

*****) depends on operating history
and REC pattern**

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses

Part 2: Application Relevance



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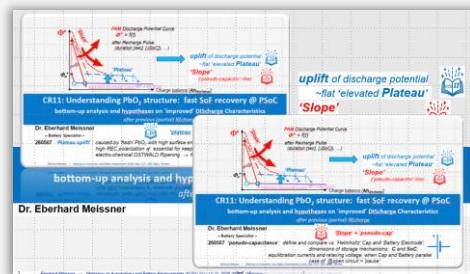
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What we have in place already !

Model description



cf. presentations from **ALBA2026 WEBINAR 1** (7 May 2026):

Decyphering recovery of pulse performance

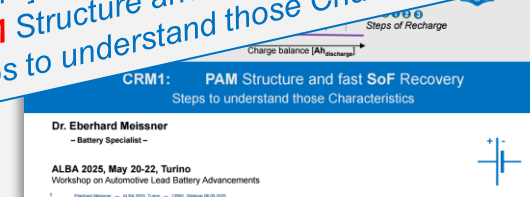
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Structures and mechanisms that govern it (Eberhard Meissner)

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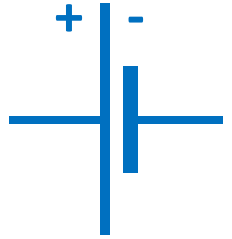
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ALBA2026 Sessions CRP + CR1 + CR2

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses

Part 2: Application Relevance



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vs. **standard potential** 0mV

capacity [Ah /SoC] : some %SoC *)

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capacity [Ah /SoC] : = actual SoC

in BACKUP material:

- **experimental observations**

- **how to use ? ideas for realization with AUX**

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses

Part 2: Application Relevance What did we observe so far ('engineering')

High PAM Potential @REC / Polarization η^* is decisive - it is not primarily + Δ SoC (inducing pore acid S.G. increase)

η^* higher by e.g. +100mV $\uparrow$ method: different means at NAM design
marginal benefit from higher + Δ SoC
effect of η^* dominating vs. effects from absolute SoC or + Δ SoC

for 1) PAM Potential 'plateau uplift' @DIS
by several +10mV $\uparrow$, typ. +50mV $\uparrow$ - but not much more
REST PERIOD before DIS: minor impact on 'plateau uplift'
SoC(pseudo-cap) $\uparrow$ $\Rightarrow$ SoC(PAM) plateau (t-DIS >> 10sec) up

2) PAM Potential 'Slope' @DIS changes
a) flattening, i.e. C(pseudo-cap) $\uparrow$ up to 2x larger
b) curvature, i.e. even higher C when slope approaching 'plateau'
c) higher start, i.e. SoC(pseudo-cap) (pseudo-cap) $\uparrow$ >> 100mV $\uparrow$

REST PERIOD before DIS: marginal impact on C (steepness of 'Slope')
but voltage level (t-DIS < 10sec) down: SoC(pseudo-cap) $\downarrow$ $\Rightarrow$ SoC(PAM)
Pseudo-Cap C with both DIS and REC: similar C values

mechanisms / effects always active - technical realization / use more easy at low .. medium Temp $\checkmark$

(1) sufficient power required for REC at High Polarization η^* (2) limited parasitical reactions (O₂, H₂)
(3) kinetics of electro-chem. OSTWALD Ripening of nano-scale PbO₂ nuclei (survival of 'plateau uplift' and 'pseudo-cap')

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses

Part 2: Application Relevance How to make use of ? Ideas for realization with AUX

Benefit of high Polarization η^* to keep PbO₂ structure 'healthy' in PAM well known (at least since 1980ies/1990ies)
e.g.: E. Meissner, Influence of recharge potential and acid concentration on the discharge behaviour of PbO₂ electrodes, JPS 46 (1993) 231-238
E. Meissner, How to understand the reversible capacity decay of the lead dioxide electrode, JPS 78 (1999) 99-114, REVIEW, many [refs.]

historical Hurdles to realize / use / establish: technical - limited understanding - 'emotional' acceptance

- may require high recharge power to drive rate of electro-deposition of PbO₂ into Pb²⁺ transport limitation
- may require high recharge voltage for battery (connected to the whole low-voltage power system, incl. light bulbs)

concerns from vehicle makers:

- cost for larger alternator; more torque feedback to crankshaft $\Rightarrow$ customer discomfort (when w/o engine control unit)
- primitive alternator voltage control only (historical: control from temperature at the alternator)
- compatibility with existing standardized electronics $\Rightarrow$ COST: established technical standards for voltage.

concerns from battery makers:

- fear for gas evolution (O₂, H₂) $\Rightarrow$ battery dryout; fear for grid corrosion; fear to lose credibility (old narratives ...)

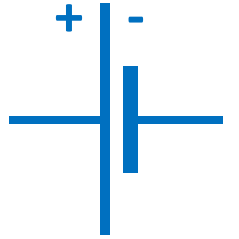
concerns from whole community (establishment): fear from any CHANGE

by 2026: NO more light bulbs; BMS measures temp. + batt. voltage precisely at terminals; easy voltage control from DC/DC for AUX battery, situation-dependent recharge control (e.g. high REC power ONLY @emergency, @lower temp., ...)

$\Rightarrow$ Vehicle makers: consider this approach - just doing for AUX! OR any technical hurdle overlooked?

$\Rightarrow$ Battery makers: facilitate for moderate temp. (not only for LOW) by improving CA of neg. electrode, limiting H₂ gassing
EM personal view: for fast SOF recovery, limited 'new' perspectives for PAM modification
cf. strategies presented

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



Part 2: Application Relevance



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Pre-Requisites

1. Generate the Effects

(recent) battery recharge at sufficient high rate to reach **high positive electrode polarization**

target: PAM recharge main reaction is **diffusion limited**, i.e. **REC current** $i \rightarrow i_{threshold}$

A) have (sufficiently) **powerful recharge** power source

easy at low Temp (i.e. low $i_{threshold}$)

B) **know** about actual $i_{threshold} = f(T, SoC; operat. history)$

e.g. store in lookup-table in BMS

C) **realize** (a) by **battery design**

reduce neg. electrode polarization at given REC current i

(b) by vehicle **system design**

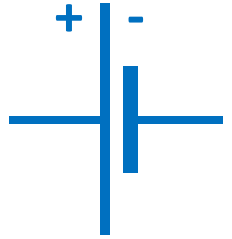
increase REC voltage → **16V** (short-term, when needed)

(c) **both** (a) + (b)

may extend applicability also when Temp is less low !

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses

Part 2: Application Relevance

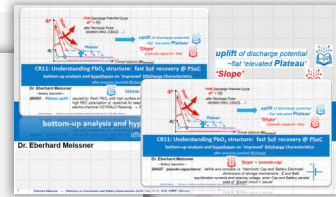


More experimental work needed
for **QUANTIFICATION**

For Basics about ion depletion and $\rightarrow i_{\text{threshold}}$,
cf presentations from **WEBINAR 1** (7 May 2026):
Decyphering recovery of pulse performance

1. PAM potential uplift

Structures and mechanisms that govern it (Eberhard Meissner)



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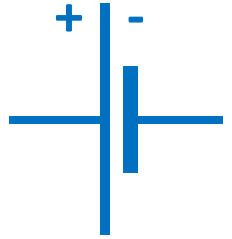
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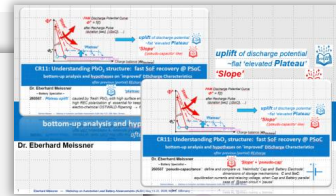


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Diffusion threshold current $i_{\text{threshold}}$ of **Pb²⁺** depends on

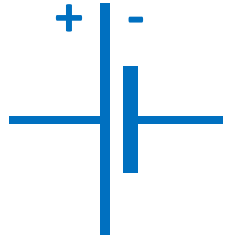
- **PbSO₄** dissolution speed = $f(\text{Temp}, \text{particle size}, \text{facet} \dots)$
- **PbSO₄** solubility $c_s = f(\text{Temp}, \text{e'lyte conc} \sim \text{SoC})$
- **PbSO₄** diffusibility $D = f(\text{Temp}, \text{e'lyte conc} \sim \text{SoC})$
- (average) distance **PbSO₄** $\leftrightarrow$ location of electro-deposition
- tortuosity / porosity of **PAM** structure = $f(\text{SoC}, \text{operating history})$

$\Rightarrow$ **Temp + SoC (indirectly) key influence factors for $i_{\text{threshold}}$!**

More experimental work needed
for **QUANTIFICATION**
probably **much of behavior is generic**,
some aspects **product-specific**,
others **depend on operational history**

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses

Part 2: Application Relevance

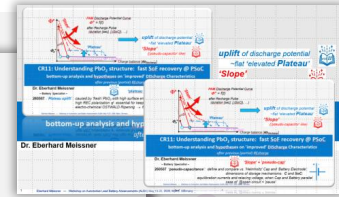


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may extend applicability also when Temp is less low !

alternative designs for lower REC
polarization of **neg. electrode**

cf. 4C_CR26_260430_ZHANG

cf. 4A_CR18_260428_NIKOLOV

a)

b)

2. Using 16,2V during recharge
anticipates the SOF 10'@15V

2. Faster SOF recovery using 16,2V

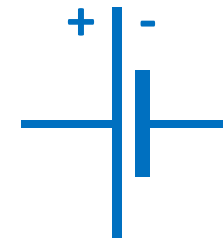
3. 6' at 16,2V reaches the SOF10
min @15V

from 53_SO23_260430_Cavendish.pdf

elevated REC voltage ~16V already tried out !

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses

Part 2: Application Relevance



1. Generate the Effects

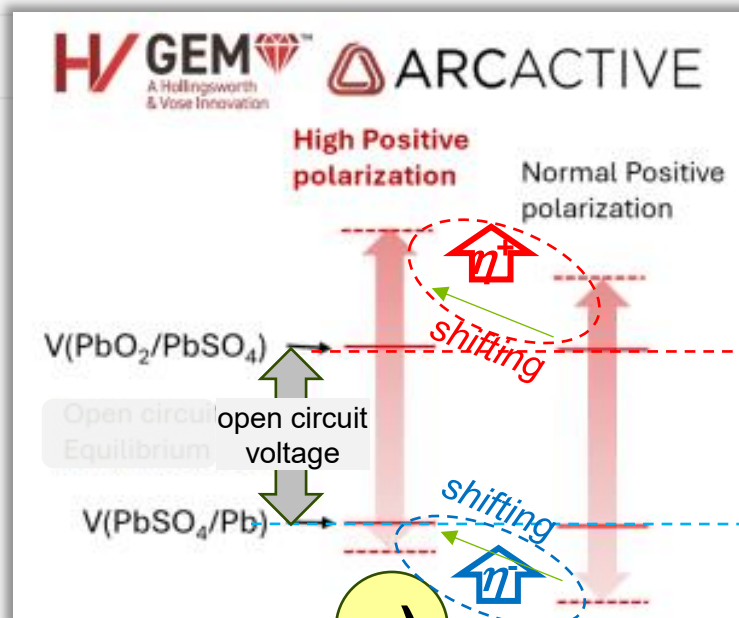
Strategies for 'high positive electrode polarization η^+ ' upon REC

a) Battery Design

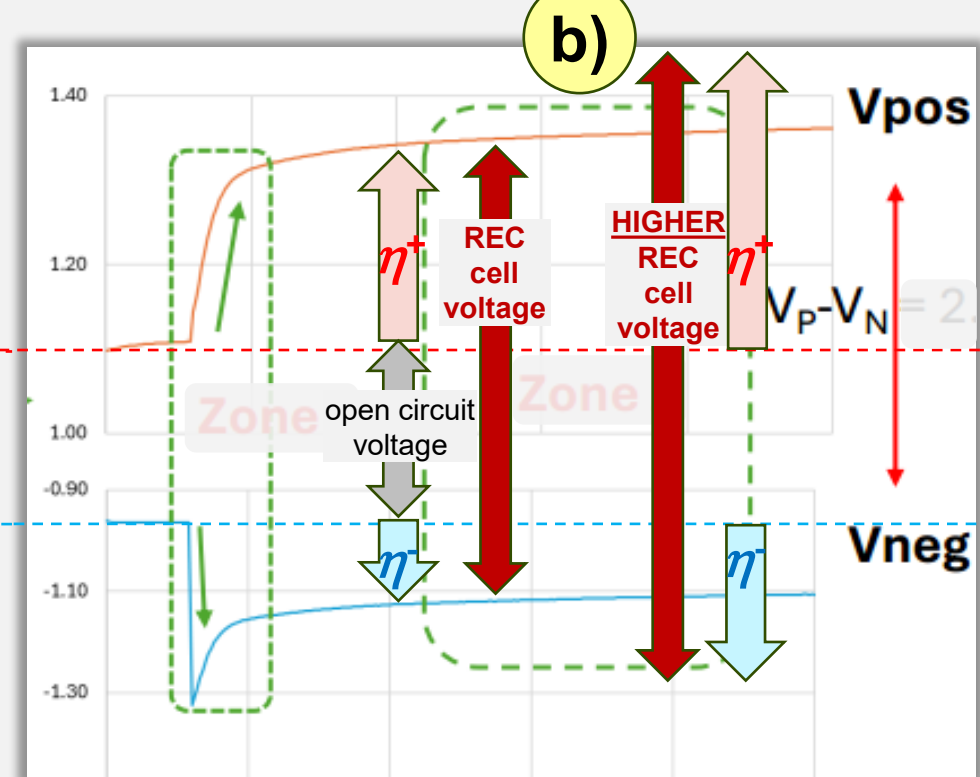
reduce η^-
→ shifting split of cell voltage @REC towards higher η^+
(at a certain given REC charge voltage)

b) System Design

increase
REC cell voltage



a)



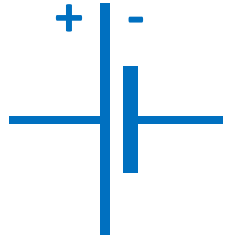
b)

Figs. using 4C_CR26_260430_Zhang.pdf by AA + H&V
Optimizing voltage distribution in Charge Recovery by GEM negative electrodes

alternative designs for lower REC polarization of neg. electrode
cf. 4C_CR26_260430_ZHANG
cf. 4A_CR18_260428_NIKOLOV

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses

Part 2: Application Relevance



1. Generate the Effects

Strategies for 'high positive electrode polarization η^+ ' upon REC

b)

System Design

increase

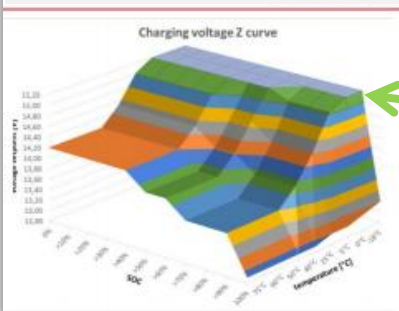
REC cell voltage

Traditional **concerns** against high **REC cell voltage**

vehicle: light bulbs voltage fluctuation
 NO LONGER NOT with AUX

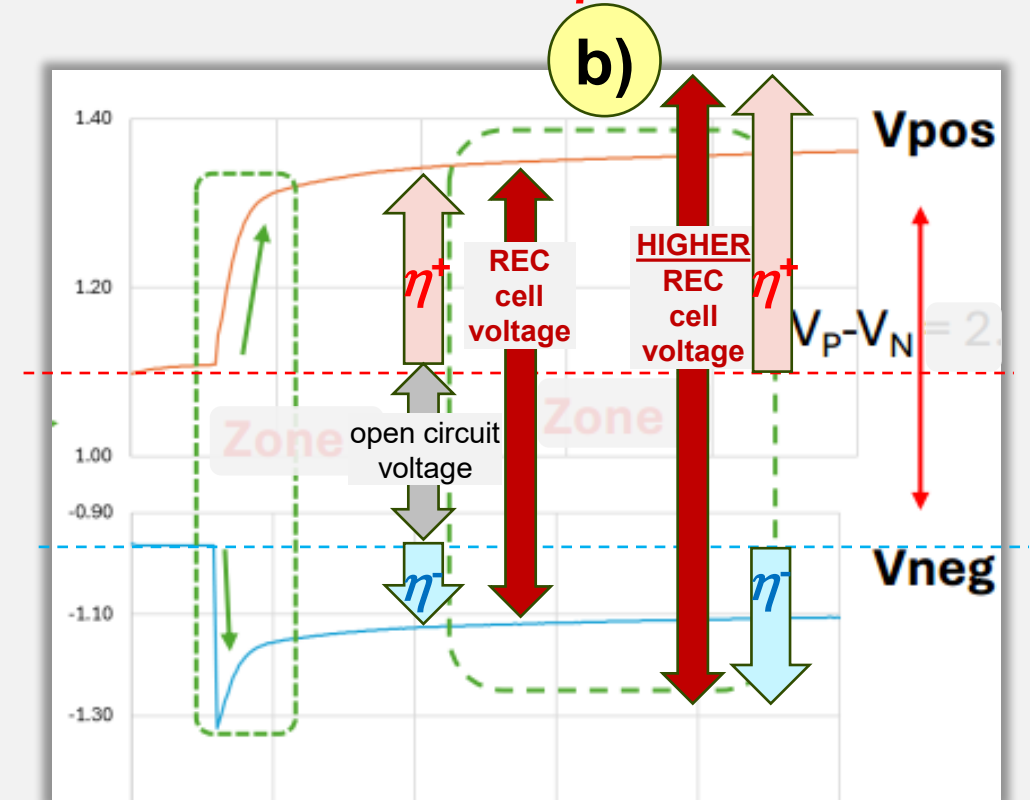
battery: more water loss + corrosion
 but NOT within short periods at low Temp
 (when needed)

cf. example from
64_SO25_260430_Mauer.pdf



Standards allow for voltage up to 16.0 V !

WHY to curtail Z-curve for low Temp already at 15.2V ?



CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



Part 2: Application Relevance



Opportunity from Fast SoF Recovery - Benefits to expect

.....
Pre-Requisites

1. Generate the Effects

.....

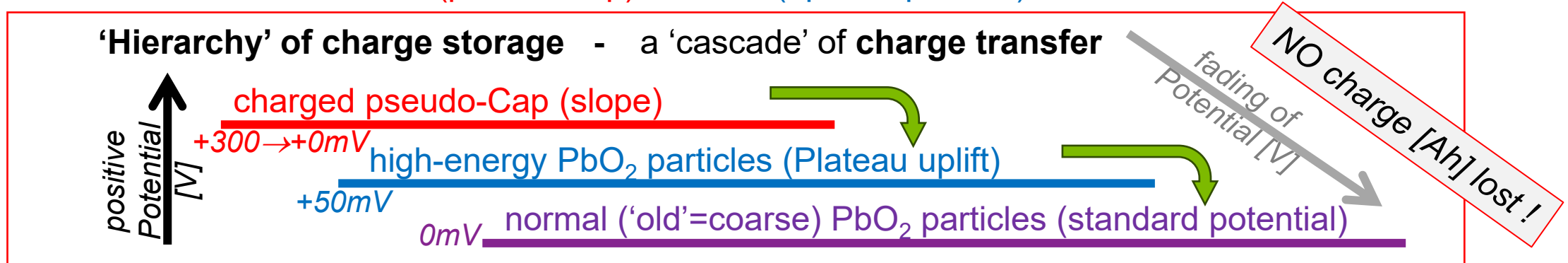
2. (temporary) **Maintain the Effects**

*N.B. various mechanisms induce **fading** of 'slope' and of 'uplift'*

period τ (pause) since end of (recent) recharge should be **short** !

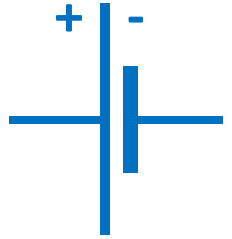
Quantification needed to roughly predict **kinetics of charge transfer reactions**

SoC(pseudo-cap) → **SoC**(uplifted plateau) → 'standard' **SoC**



CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses

Part 2: Application Relevance



Early experiments in place on charge transfer from
SoC(pseudo-cap) → **SoC(uptified plateau)**

cf. presentations from
ALBA2026 Sessions CRP + CR1 + CR2

GAP: further systematical experiments needed

What we have in place already !

cf. presentations from **WEBINAR 1** (7 May 2026):

Decyphering recovery of pulse performance

1. PAM potential uplift

[New experimental findings \(Miguel Garcia\)](#)

2. PAM pseudo-capacitance

[New experimental findings \(Jibo Zhang\)](#)

2. (temporary) **Maintain the Effects**

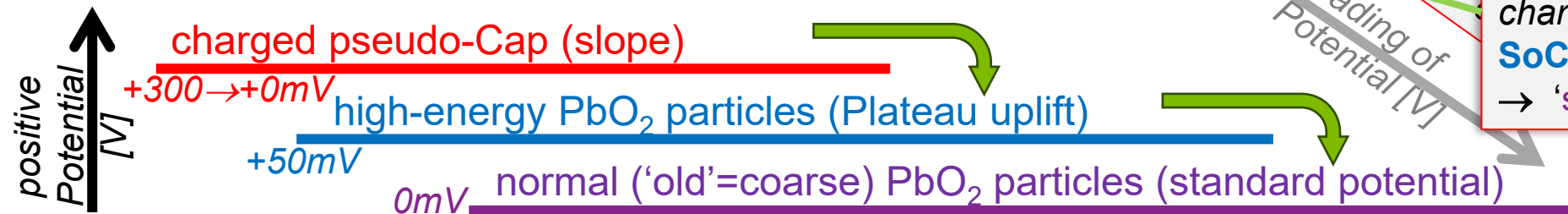
N.B. various mechanisms induce **fading** of '**slope**' and of '**uptified**'

period τ (pause) since end of (recent) recharge should be **short** !

Quantification needed to roughly predict **kinetics of charge transfer reactions**

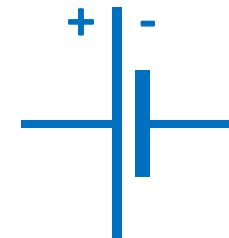
SoC(pseudo-cap) → **SoC(uptified plateau)** → '**standard**' **SoC**

'Hierarchy' of charge storage - a 'cascade' of charge transfer



GAP: NO systematical experiments so far on charge transfer from **SoC(uptified plateau)** → '**standard**' **SoC**

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



Part 1: look inside the Nutshell !

Part 2: Application Relevance

- Opportunity from Fast SoF Recovery - Benefits to expect
- Pre-Requisites to
 1. Generate the Effects
 2. (temporary) Maintain the Effects
 - What we have in place already !
- ToDos to be addressed now

Part 3: Questions & Perspectives



- PERSPECTIVES for more **uplift of 'elevated Plateau'** ?
- PERSPECTIVES for higher **C** of **'pseudo-cap'** ? *[F/g of 'freshly deposited' PbO₂]*
- PERSPECTIVES to utilize effects at Temp >0°C ?

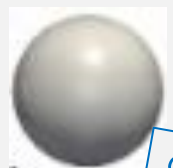
CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses

Part 3: Questions & Perspectives

(1) any PERSPECTIVES for more uplift of 'elevated Plateau'?

observed: *potential uplift* $\sim +50\text{mV} / \text{cell} = \sim +300\text{mV} / 12\text{V batt}$

ΔV = (change of molar) volume
 F = Faraday Constant $n = 2$
 σ = surface energy r = 'radius'
assuming particle as naive 'smooth ball'



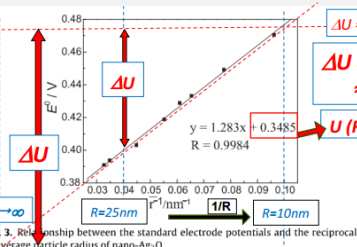
potential uplift (CNT)

$$\Delta\Phi^+ = 2 \cdot \sigma \cdot \Delta V_m / r / n \cdot F$$

cf [P18] E.Meissner,
ALBA Torino 2025, CRM1

Quantification

example: **Ag₂O**
(particle radius R)



$$\Delta U \approx (0.476\text{V} - 0.355\text{V}) \approx 121\text{mV}$$

$$\Delta U = U(R=10\text{nm}) - U(R \rightarrow \infty) \approx 121\text{mV}$$

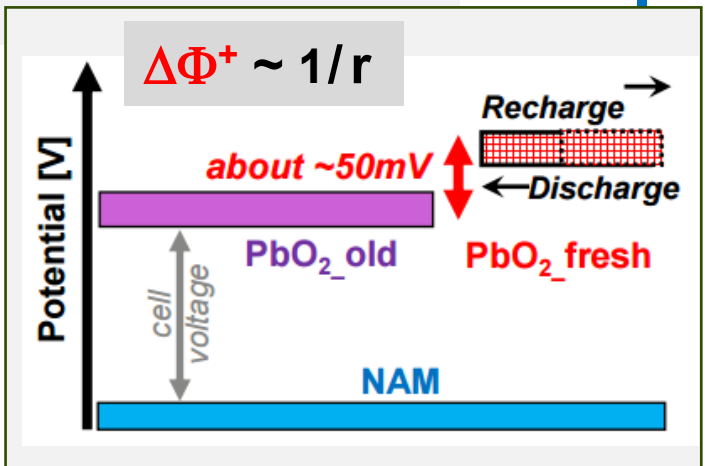
$$U(R \rightarrow \infty) \approx +0.3485\text{V}$$



Experiment: potential increase with nano-Ag₂O

$\Rightarrow$ by $\approx +121\text{mV}$ particles $R \approx 10\text{nm}$ vs. flat surface ($R \rightarrow \infty$)

$\Rightarrow$ by $\approx +75\text{mV}$ particles $R \approx 10\text{nm}$ vs. particles $R \approx 25\text{nm}$



$\Delta\Phi^+$	0mV	20mV	50mV	100mV	200mV
crit. Radius r_{crit} (if $\sigma = 1\text{J/m}^2$)	infinite	13nm	5nm	2.5nm	1.3nm
equiv. number of PbO ₂ unit cells	infinite	~ 25	~ 10	~ 5	~ 2.5

what we observe

NOT a naive 'smooth surface'

Question (1) translates into

(1a) can we expect to *generate* even finer nuclei
and to *stabilize* (=limit further growth) such fine particles?

hypothetical PbO₂ nano-particles needed for $\Delta\Phi^+ > \sim 50\text{mV}$
comprize only low number of **PbO₂ unit cells** (size $\sim 0.5\text{nm}$);
Laplace equation no longer applicable (NO 'smooth surface')



cherry



blackberry

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses

Part 3: Questions & Perspectives

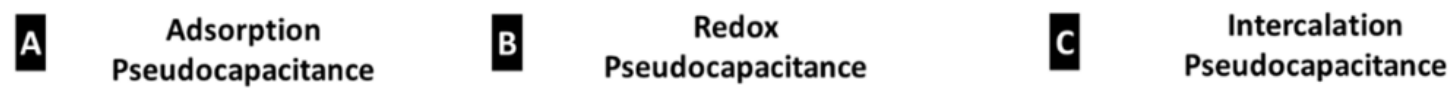


(2) any PERSPECTIVES for higher C of **'pseudo-cap'**?

observed: $C_{pseudo} \sim 12-26 \text{ F/g}$ of 'fresh' PbO₂

'pseudo-cap' may comprise SEVERAL mechanisms !

cf [P18] E.Meissner,
ALBA Torino 2025, CRM1



Contribution to 'pseudo-capacitance'

'nano-sized' vs. 'coarse'

NOT just simple narrative: *'fines have larger SSA [m²/g]'*

particle surfaces not smooth: **steps** and **kinks**, dynamic re-organization

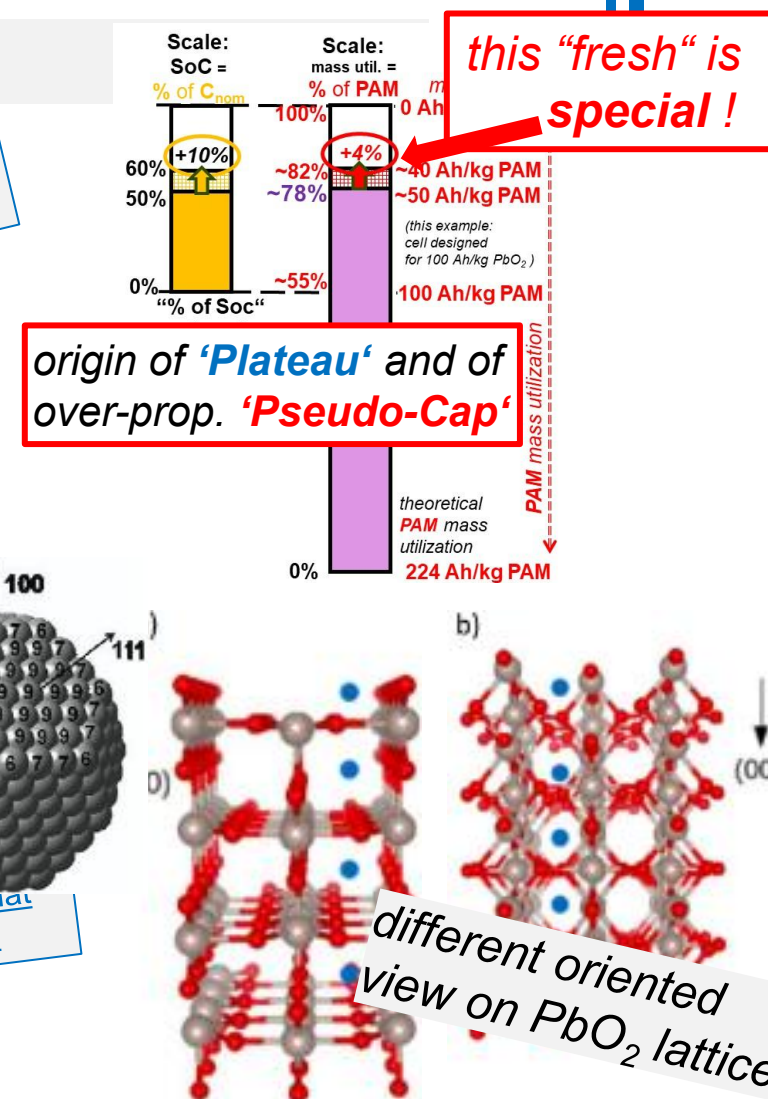
Facets ! different properties of lattice surfaces / planes:

- **mobility** / diffusion of species (e^- , H^+ , OH^- , $O \dots$) depend on orientation
- surface energies $\sigma_{[h,k,l]}$ (Wulff's Law) $\rightarrow$ **local potential**
- **dangling bonds** $\rightarrow$ adsorption of species

WEBINAR 1 (7 May)
2. PAM pseudo-capacitance
Structures and mechanisms that
govern it (Eberhard Meissner)

Question (2) translates into

(2a) can we generate even more 'opportunities' for mechanisms contributing to spec. **'pseudo-capacitance'** [F/g] than with the finest, most disordered PbO₂ nano-particles we know about ?



any ordering $\rightarrow$ facetting (Wulff's Law) will reduce dangling bonds, etc .

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses

Part 3: Questions & Perspectives



WEBINAR 1 (7 May 2026):
2. PAM pseudo-capacitance
Structures and mechanisms that
govern it (Eberhard Meissner)

(3) any PERSPECTIVES to utilize effects at Temp > -18°C / > 0°C ?

observed: most work -18°C, some 0°C;
PhD thesis G.Pilatowicz 2017

cf [P18] E.Meissner,
ALBA Torino 2025, CRM1

Diffusion threshold current $i_{\text{threshold}}$ of Pb²⁺ depends

- PbSO₄ dissolution speed = $f(\text{Temp}, \text{particle size}, \text{facet} \dots)$
- PbSO₄ solubility $c_s = f(\text{Temp}, \text{e'lyte conc} \sim \text{SoC})$
- PbSO₄ diffusibility $D = f(\text{Temp}, \text{e'lyte conc} \sim \text{SoC})$
- (average) distance PbSO₄ $\leftrightarrow$ location of electro-deposition
- tortuosity / porosity of PAM structure = $f(\text{SoC}, \text{operating history})$

$\Rightarrow$ **Temp + SoC (indirectly) key influence factors for $i_{\text{threshold}}$!**

diffusion-control

e.g. **factor >10 at $\Delta T = +44^\circ\text{C}$**
with NEG Pb electrode

N.B. -18°C $\rightarrow$ +25°C = +43deg

$$i_{\text{threshold}} \sim D \cdot c_{\text{sat}} / \delta_{\text{average}}$$

D = Pb²⁺ diffusibility

c_{sat} = Pb²⁺ saturation conc.

δ_{average} = average Pb²⁺ diffusion path length
= $f(\text{operat. history; PAM recipe ?})$

mechanisms effective also at **higher Temp.**,
but **faster fading kinetics** may be a hurdle for use

At Temp > ~0°C, *more and more difficult to realize*

- high PbO₂ deposition rate $\rightarrow \sim i_{\text{threshold}}$
- 'high positive electrode polarization η^+ '

because

(i) $\rightarrow i_{\text{threshold}}$ increases dramatically with Temp

AND

(ii) more concern at higher Temp about

- increased corrosion
- increased O₂ evolution / water loss

when REC cell voltages were applied

as needed to drive such high $i \rightarrow i_{\text{threshold}}$

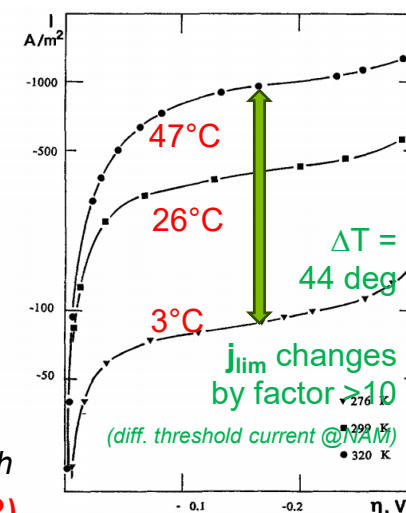


Fig. 1. Cathodic polarization curves for the same electrode at different temperatures.

J. Electrochem. Soc. 135 (1988) 1613-1618
Simonsson Eklund Lindgren Kinetics of the
Porous Lead Pb Electrode in the Lead-Acid Battery

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



Part 1: look inside the Nutshell !

Part 2: Application Relevance

Part 3: Questions & Perspectives

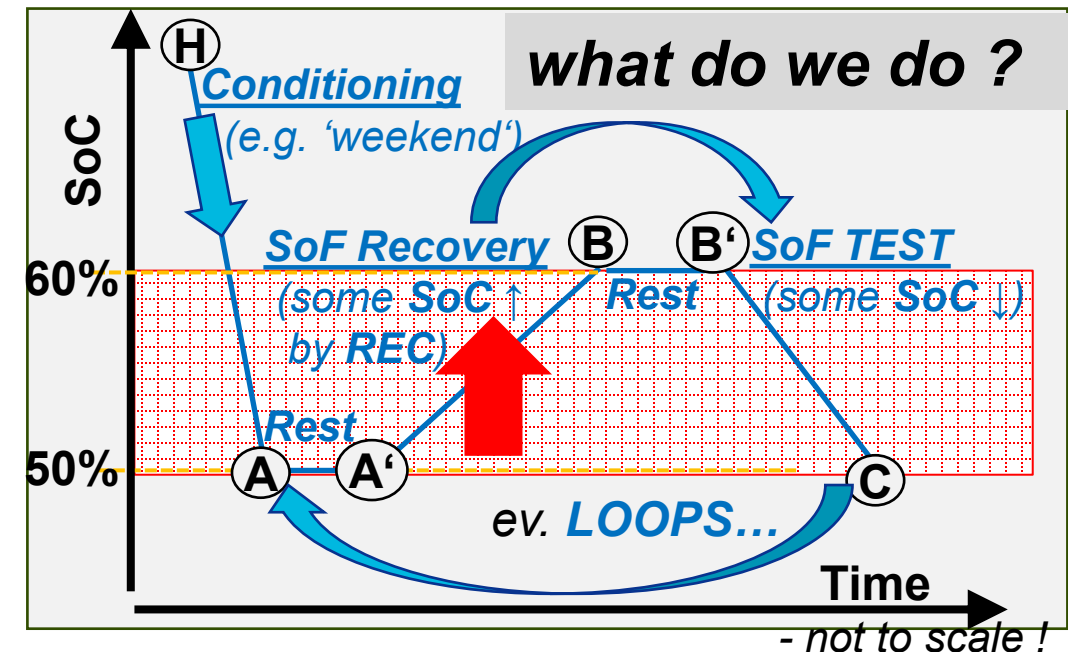
Summary - Conclusions



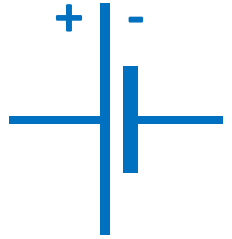
- ✓ mechanisms of **fast SoF recovery** identified
 - located at **PAM** - *structure of fresh PbO₂*
 - **one** root cause - *'nano-scale' PbO₂ particles created when pos. polarization is HIGH @REC*
 - **two** features: **'uplift'** + **'high pseudo-cap'**

- ✓ in place: consistent experimental verification
- ☑ only sparse initial quantification; @low Temp

- ! investigations done so far under **favourable conditions**:
 - *conditioning by low-rate discharge @low Temp*
 - *REC at low Temp → high polarization easy to achieve*
 - *short (or even no) rest period before SOF TEST*



CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



Part 1: look inside the Nutshell !

Part 2: Application Relevance

Part 3: Questions & Discussion

Summary



mechanism

- located
- one roc
- cre
- two



in place: con



only



investigations done so far under **favourable conditions**:

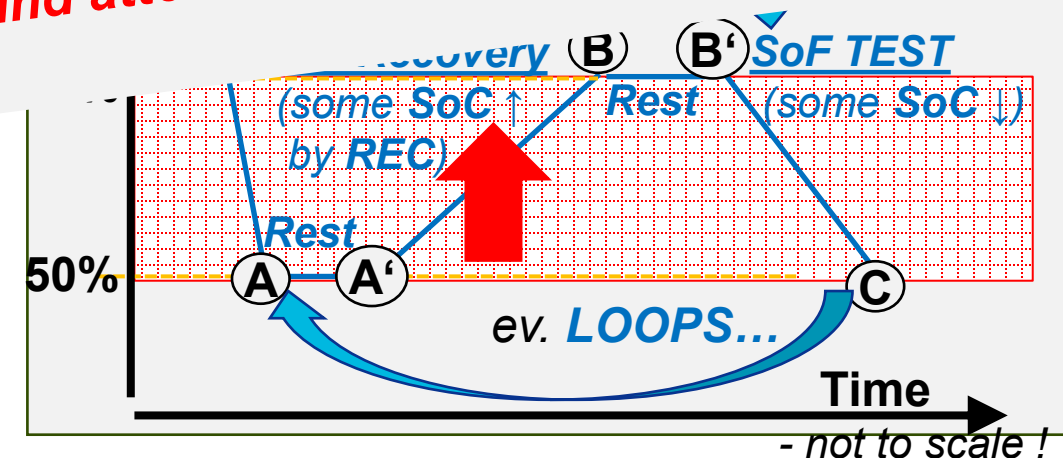
- conditioning by low-rate discharge @low Temp
- REC at low Temp → high polarization easy to achieve
- short (or even no) rest period before SOF TEST

A helpful co-incidence:
at LOW TEMPERATURES - just when needed **MOST** -
Fast SoF Recovery can be **Realized** the easiest
and **Benefits** are most prominent !

⇒ **let's try out the limits !**

Thank you for your kind attention !

we do ?



CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



How to make use of ? ideas for realization with AUX ('engineering')

Benefit of high **Polarization** η^+ to keep **PbO₂** structure 'healthy' in PAM well known (at least since 1980ies/1990ies)

e.g. *E.Meissner, Influence of recharge potential and acid concentration on the discharge behaviour of PbO₂ electrodes, JPS 46 (1993) 231-238*
E.Meissner, How to understand the reversible capacity decay of the lead dioxide electrode, JPS 78 (1999) 99-114, REVIEW, many [refs.]

historical **Hurdles** to realize / use / establish: *technical - limited understanding - 'emotional' acceptance*

- may require high **recharge power** to drive rate of electro-deposition of **PbO₂** into **Pb²⁺** transport limitation
- may require high **recharge voltage** for battery (*connected to the whole low-voltage power system, incl. light bulbs*)

concerns from **vehicle makers**:

cost for larger alternator; more **torque** feedback to crankshaft $\Rightarrow$ customer **discomfort** (when w/o engine control unit)
primitive alternator voltage control only (historical: control from *temperature at the alternator*)

compatibility with existing standardized electronics $\Leftrightarrow$ **COST** ; established technical **standards** for voltage

concerns from **battery makers**:

fear for gas evolution (O₂↑, H₂↑) $\Rightarrow$ battery dryout; **fear** for grid corrosion; **fear** to lose credibility (*old narratives ...*)

concerns from **whole community** (establishment): **fear** from any CHANGE

by **2026**: NO more light bulbs; BMS measures temp. + batt. voltage precisely at terminals; easy voltage control from DC/DC for AUX battery, situation-dependent recharge control (e.g. *high REC power ONLY @emergency, @lower temp., ...*)

$\Rightarrow$ **Vehicle makers**: consider this approach - just doing for AUX ! OR any technical hurdle overlooked ?

$\Rightarrow$ **Battery makers**: facilitate for moderate temp. (*not only for LOW*) by improving CA of neg. electrode, limiting H₂↑ gassing
EM personal view: for fast SOF recovery, limited 'new' perspectives for PAM modification cf. strategies presented

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



What did we see – how to make use of ? ('engineering')

High PAM Potential @REC / Polarization η^+ is decisive - *it is not primarily $+\Delta\text{SoC}$ (inducing pore acid S.G. increase)*

η^+ higher by e.g. +100mV $\uparrow$ *method: different means at NAM design*
marginal benefit from higher $+\Delta\text{SoC}$
effect of η^+ dominating vs. effects from absolute SoC or $+\Delta\text{SoC}$

[CR26_260426_ZHANG p.14 \(lower right\)](#)

[CR18_260428_NIKOLOV p.7, 10 \(short REC +2-3% sufficient\)](#)

[CR13_26xxyy_GARCIA](#)

for **1) PAM Potential 'plateau uplift' @DIS**

by several +10mV $\uparrow$, typ. +50mV $\uparrow$ - but not much more

REST PERIOD before DIS: *minor impact on 'plateau uplift'*

$\text{SoC}(\text{pseudo-cap}) \downarrow \Rightarrow \text{SoC}(\text{PAM}) \uparrow$ *plateau (t-DIS $\gg$ 10sec) up*

[CR13_26xxyy_GARCIA](#)

[CR18_260428_NIKOLOV p.6; CR26_260426_ZHANG p.9](#)

[CR18_260428_NIKOLOV p.8 \(lower left\)](#)

[CR18_260428_NIKOLOV p.9 \(2min of OCV REST\)](#)

2) PAM Potential 'Slope' @DIS changes

a) flattening, i.e. $\text{C}(\text{pseudo-cap}) \uparrow$ *up to 2x larger*

b) curvature, i.e. even higher C when slope approaching 'plateau'

c) higher start, i.e. $\text{SoC}(\text{pseudo-cap}) (\text{pseudo-cap}) \uparrow \uparrow \gg 100\text{mV} \uparrow$

[CR26_260426_ZHANG p.10](#)

[CR13_26xxyy_GARCIA](#)

[CR26_260426_ZHANG p.10](#)

REST PERIOD before DIS: *marginal impact on C (steepness of 'Slope')*

but voltage level (t-DIS $<$ 10sec) down: $\text{SoC}(\text{pseudo-cap}) \downarrow \Rightarrow \text{SoC}(\text{PAM}) \uparrow$

[CR18_260428_NIKOLOV p.8 \(lower left\)](#)

[CR18_260428_NIKOLOV p.9 \(2min of OCV REST\)](#)

Pseudo-Cap C with both DIS and REC : $\sim$ similar C values

[CR14_260428_HAMMOUCHE p.2 lower Figs \(@overcharge\)](#)

[CR15_26xxyy_WIRTH \(@REC phases vs. @DIS phases\)](#)

mechanisms / effects always active - *technical realization / use more easy at low .. medium Temp*

(1) sufficient power required for REC at High Polarization η^+ (2) limited parasitical reactions ($\text{O}_2 \uparrow$, $\text{H}_2 \uparrow$)

(3) kinetics of electro-chem. OSTWALD Ripening of nano-scale PbO₂ nuclei (*survival of 'plateau uplift' and 'pseudo-cap'*)

CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses

+
-
BACKUP

OUTLOOK to complexity ('science')

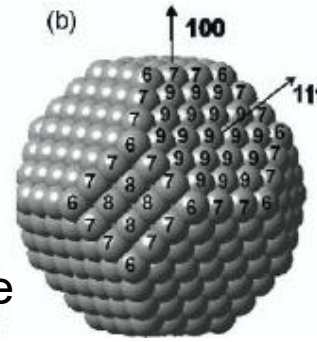


naive macro-homogeneous vision:

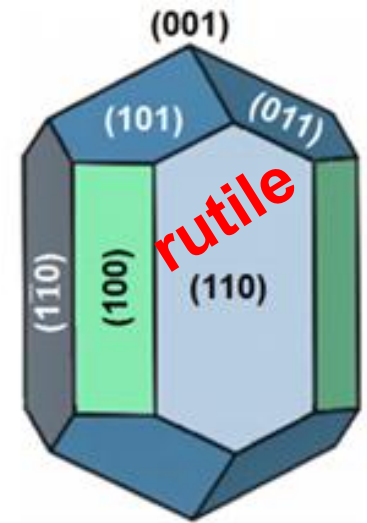
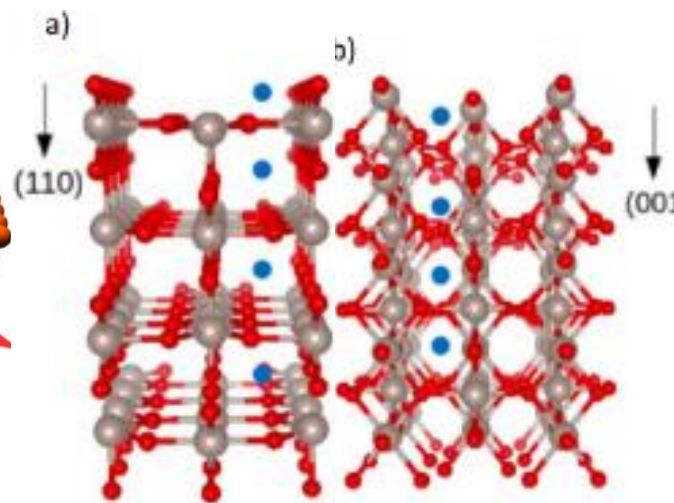
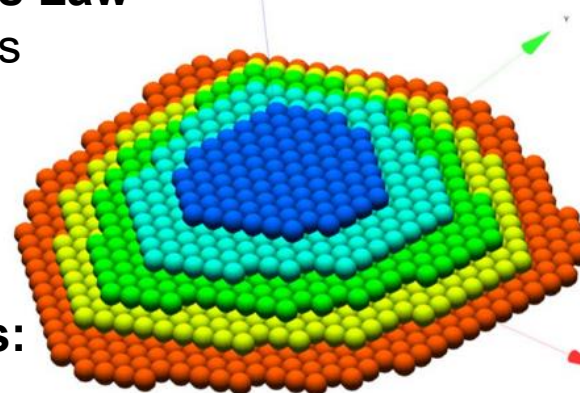
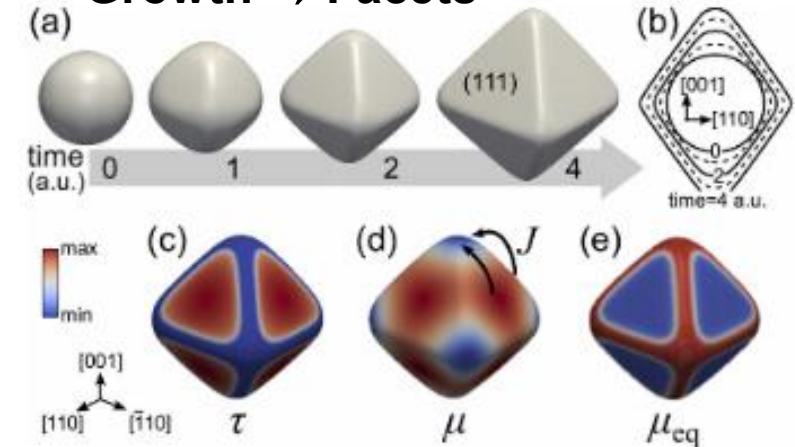
- small ball-shaped nuclei, smooth surface

Reality:

- nano-particles larger by **factor 10-20** only than PbO₂ unit cell
- formation of **facets**, with DIFFERENT **surface energies** $\sigma_{[h,k,l]}$ according to **WULFF's Law**
- **steps** and **kinks** on surfaces
- dynamic re-organization of lattice surfaces
- different properties of lattice **surfaces** and **planes**:
 - surface energies $\sigma_{[h,k,l]}$
 - dangling bonds → adsorption of species
 - mobility / diffusion of species (e^- , H^+ , OH^- , O ...) depends on orientation



Growth → Facets



N.B. generic figures taken from literature; NOT all specific to PbO₂

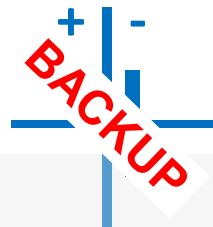
CR11: References to Conference Presentations addressing topics in this context & Key messages and caveats



- [P1] E.Meissner @ Workshops “High-Temperature Durability Tests for Advanced Lead–Acid 12-V Batteries”
- Kloster Eberbach, Germany, Jan 2017 - Alcalá de Henares, Spain, May 2018 - Bruges, Belgium, May 2019 - virtual, Nov 2020 - Bergamo, June 2022
- *Oxygen transport and storage in flooded cell, [Lit. from 1950-1990ies], intermediate O_2 storage buffer reduces water loss in PSoC operation*
- [P2] E.Meissner, “Origin of the DCA Memory Effect: Rôle of Ostwald Ripening and re-crystallization”; Presentation #515 at EFB Virtual Workshop *), Nov. 2020
- *Ostwald Ripening may change structure and distribution of $PbSO_4$ within porous NAM mass*
- [P3] E.Meissner, “NAM Classics: is low DCA caused by Ostwald ripening?”, Presentation #501 at EFB Virtual Workshop *), Nov. 2020 ;
- *consequences from Ostwald-Froehlich Relationship and Lifshitz-Slyozov-Wagner (LSW) Theory, applied to $PbSO_4$ in NAM; Modelling of NAM Recharge;*
- *Recommendation to design a fine pore structure for NAM, to give no room for growth of coarse $PbSO_4$ crystals*
- *finding from literature that some NAM structures comprising advanced carbon additives show such (1) finer pore structure and also (2) a higher DCA*
- [P4] E.Meissner, “Compare morphology & material parameters of Positive vs. Negative Active Mass”, Presentation #401 at EFB Virtual Workshop *), Nov. 2020
- *other than NAM, REcharge kinetics of PAM does not degrade; PAM pores are finer than NAM pores by about one order of magnitude*
- [P5] E.Meissner, “Interaction of Main Reactions and Side Reactions at Pos. and Neg. Electrodes”, presented at 17ELBC, virtual, Sept. 2020
- *within NAM, SoC may be locally inhomogeneous over plate (in z- and x-direction, i.e. over electrode height, over electrode depth) ;*
- *active materials Pb, H_2SO_4 , PbO_2 each have individual SoC; NAM has usual the LOWEST SoC: $SoC(Pb) < SoC(H_2SO_4) < SoC(PbO_2)$*
- [P6] E.Meissner, “Lead-Acid Battery Side Reactions - Asymmetry at Pos. and Neg. Electrodes”, presented at 16ELBC, Vienna, Sept. 2018
- *simple Ah tracking does not represent a “true” SoC value due to various side reactions, incl. oxygen cycle;*
- *Oxygen Cycle in both VRLA and flooded L/A batteries is coupling positive and negative electrode side reactions*
- [P7] E.Meissner, “Lead-Acid Battery L/A Batteries in PSOC Operation: a challenge for NAM recharge”, presented at 11LABAT2021, virtual, June 2021
- *at PSoC, Ostwald Ripening of $PbSO_4$ impedes Pb^{2+} supply for recharge by (1) crystal coarsening (less solubility) (2) relocation of $PbSO_4$ (farer distance)*
- [P8] E.Meissner, “Particle Size and Surface Shape of Active Materials: Impact from Free Surface Energy”, presented at 11LABAT2021, virtual, June 2021
- *Free Surface Energy of solid/electrolyte interface is decisive for shape and structure of battery materials - essential for battery characteristics and function*
- [P9] E.Meissner, “Battery Micro-Cycling in Start/Stop Operation: O_2 Intermediate Storage Acting as a Charge Buffer”, presented at AABC Europe, Wiesbaden Jan. 2020
- *dynamic battery operation: $i_{O_2-red}@NAM$ NOT synchronous to $i_{O_2}@PAM$; O_2 recombined at NAM generated MUCH EARLIER at PAM & stored intermediately*

*) Full Title of series of **EFB Workshops** and **ALBA Workshops**, organized by CENELEC and Consortium of Battery Innovation:
“Automotive Lead Battery Advancements”; June 2022 (Bergamo), June 2023 (Wolfsburg; comprising preceding Webinars), June 2024 (Paris) , May 2025 (Turino)
“DCA and Heat”: Testing Charge Acceptance and High Temperature Durability for Adv. Lead 12 V Batteries”; Jan 2017 (Eberbach), May 2018 (Alcala), May 2019 (Bruges), May+Nov 2020 (virtual)

CR11: References to Conference Presentations addressing topics in this context & Key messages and caveats



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“DCA and Heat”: Testing Charge Acceptance and High Temperature Durability for Adv. Lead 12 V Batteries”; Jan 2017 (Eberbach), May 2018 (Alcala), May 2019 (Bruges), May+Nov 2020 (virtual)

[P10] E.Meissner, “Oxygen Cycle in Lead-Acid Batteries: Implications from Inhomogeneous O_2 Reduction Reaction at **NAM**”, presented 12AABC Europe, Mainz June 2022
- charge acceptance of **NAM** degraded by O_2 recombination at **NAM** in PSoC duty (O_2 reduction during non-charge phases enhances Ostwald Ripening of $PbSO_4$)

[P11] E.Meissner, “Mechanisms and morphology limiting charge acceptance // CA limitations – literature & interpretation of new findings”,
Presentation #2B3 at EFB Workshop “High-Temperature Durability Tests for Advanced Lead–Acid 12-V Batteries: ALBA”, Bergamo, July 2022 *)
- literature survey & summary of key insights and implications from recent years about DCA of **NAM**, O_2 Reduction Reaction, **Ostwald**, SoC imbalance

[P12] E.Meissner, “Oxygen Reduction Reaction promoting Ostwald Ripening of $PbSO_4$ Crystals at **NAM** Electrode Surface”, presented at 18ELBC, Lyon, Sept. 2022
- O_2 reduction preferably at **NAM** geometrical surface; local discharge promotes $PbSO_4$ Ostwald Ripening and imbalance $SoC(Pb) < SoC(H_2SO_4) < SoC(PbO_2)$

[P13] E.Meissner, “The Big Short Challenge - why no metal-metal short”, Presentation at ALBA Webinar “1 Big Short Challenge”, 24 Jan 2023 *)
- no persistent high current-shorts in LAB, as metallic shorts (direct metallic contacts between positive and negative metal parts) cannot persist in LAB

[P14] E.Meissner, “Dynamics of Electrode Reactions upon Battery Charging”, Presentation W35a_Meissner.pdf at ALBA Webinar “3 Recharge Kinetics”,
8 Jun 2023; ALBA Workshop Wolfsburg, June 2023 *)
- Multiple Reactions simultaneously at same Electrode: Differences between **PAM** and **NAM** upon recharge (main reaction, gas evolution, **capacitance**)

[P15] E.Meissner, “Recharge of LAB - kinetics, dynamics, charge efficiency; Discussion of Experiments & Takeaway”, Presentation W35b, Webinar Wolfsburg, 2023 *)
- summary from various Authors: **PAM** potential stabilized against fast fluctuations by **PbO₂ pseudo-capacity**; no corresponding effect with **NAM**

[P16] E.Meissner, “Understanding fast transient SOF recovery at onset of battery recharge”, Presentation CR03 at ALBA Workshop, Paris, June 2024 *)
- **PbO₂ pseudo-capacitance**: experimental findings, quantification, mechanism, consequences for stabilizing **PAM** potential against fast fluctuations $\Rightarrow$ **SoF**

[P17] E.Meissner, “A fresh look at the Negative Active Material: three types of electrochemical reaction occurring simultaneously in the same location”, presented at 19ELBC, Milan, Sept. 2024; - besides **NAM** main reactions, H_2 reduction and esp. O_2 reduction have to be considered, with different distributions in space and time

[P18] E.Meissner, “**PAM** Structure and fast SoF Recovery - Steps to understand those Characteristics”, Presentation CRM2 at ALBA Workshop, Turino, May 2025 *)
- small amount of ‘freshly created’ PbO_2 has special properties, explains potential/plateau uplift + high spec. pseudo-cap/slope; quantification, mechanism $\Rightarrow$ **SoF**↑

some aspects from [P1-P18] are addressed in

E.Meissner, “Valve-regulated batteries: Oxygen Cycle”, Reference Module in Chemistry, Molecular Sciences and Chemical Engineering,

Elsevier, 2023, ISBN 9780124095472, <https://doi.org/10.1016/B978-0-323-96022-9.00067-0> <https://www.sciencedirect.com/science/article/pii/B9780323960229000670>

and in: J.Garche et.al. (eds.), Encyclopedia of Electrochemical Power Sources, 2.ed., Elsevier, 2024, ISBN: 9780323960229 / 9780323958226

<https://www.sciencedirect.com/referencework/9780323958226/encyclopedia-of-electrochemical-power-sources>