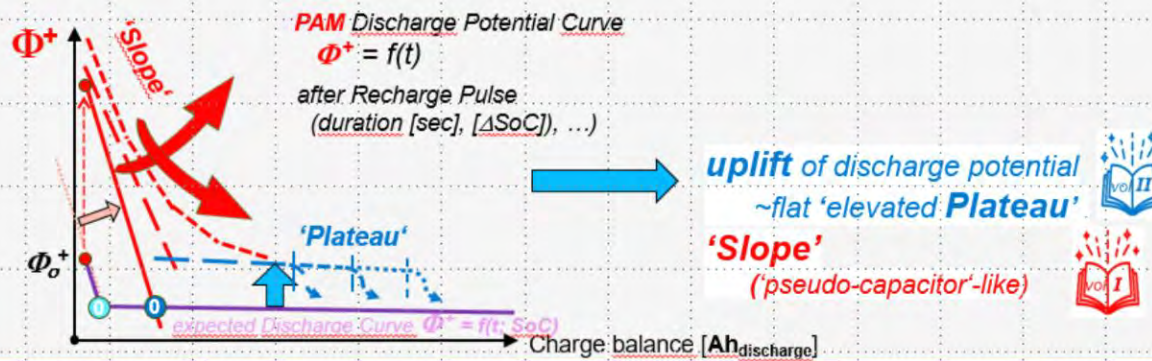




uplift of discharge potential
 ~flat 'elevated **Plateau**'
 'Slope'



CR11: Understanding PbO₂ structure: fast SoF recovery @ PSoC

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

after previous (partial) REcharge

Dr. Eberhard Meissner

– Battery Specialist –

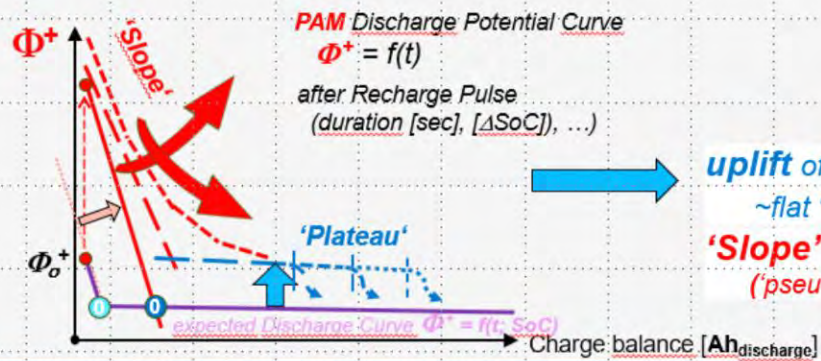
260507 'Plateau uplift': caused by 'fresh' PbO₂ with high surface en
 high REC polarization η^* essential for keep
 electro-chemical OSTWALD Ripening → f



'plateau'

bottom-up analysis and hyp

after



CR11: Understanding PbO₂ structure: fast SoF recovery @ PSoC

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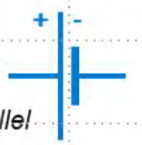
Dr. Eberhard Meissner

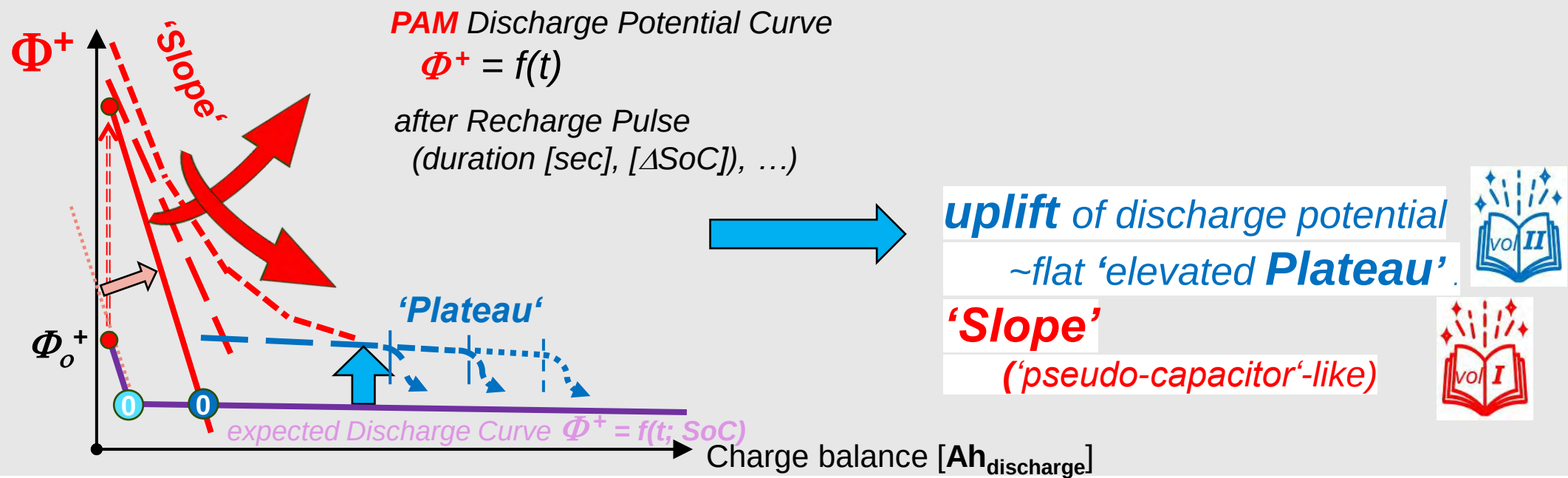
– Battery Specialist –

260507 'pseudo-capacitance': define and compare vs. 'Helmholtz' Cap and 'Battery Electrode';
 dimensions of storage mechanisms: **C** and **SoC**;
 equilibration currents and relaxing voltage, when Cap and Battery parallel
 case of @open circuit = 'pause'



'Slope' + 'pseudo-cap'





CR11: Understanding PbO_2 structure: fast SoF recovery @ PSoC

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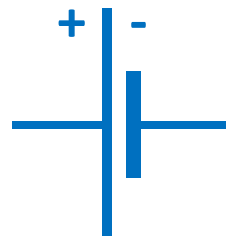
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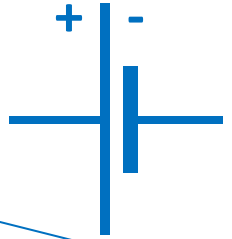


'plateau uplift'

260507 'Plateau uplift': caused by 'fresh' PbO_2 with high surface energy / particle curvature
 high REC polarization η^+ essential for keeping nuclei nano-sized
 electro-chemical OSTWALD Ripening → fading of potential @Rest



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



C.II Mechanisms behind ‘uplift of discharge Plateau’

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

cf [P18] E.Meissner, ALBA Torino 2025, CRM1
“PAM Structure and fast SoF Recovery:
Steps to understand those Characteristics”

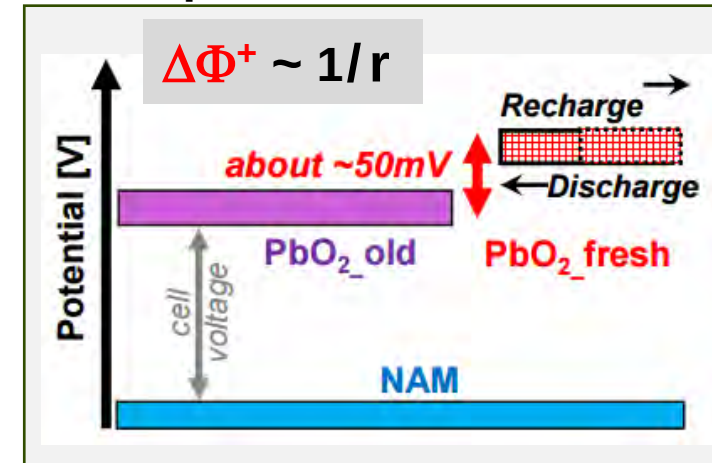
Lessons learned from ALBA2025 Torino (cf. presentation CRM1 E.Meissner [P18])

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

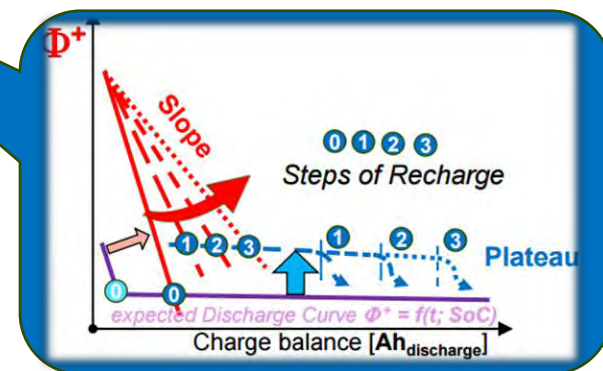
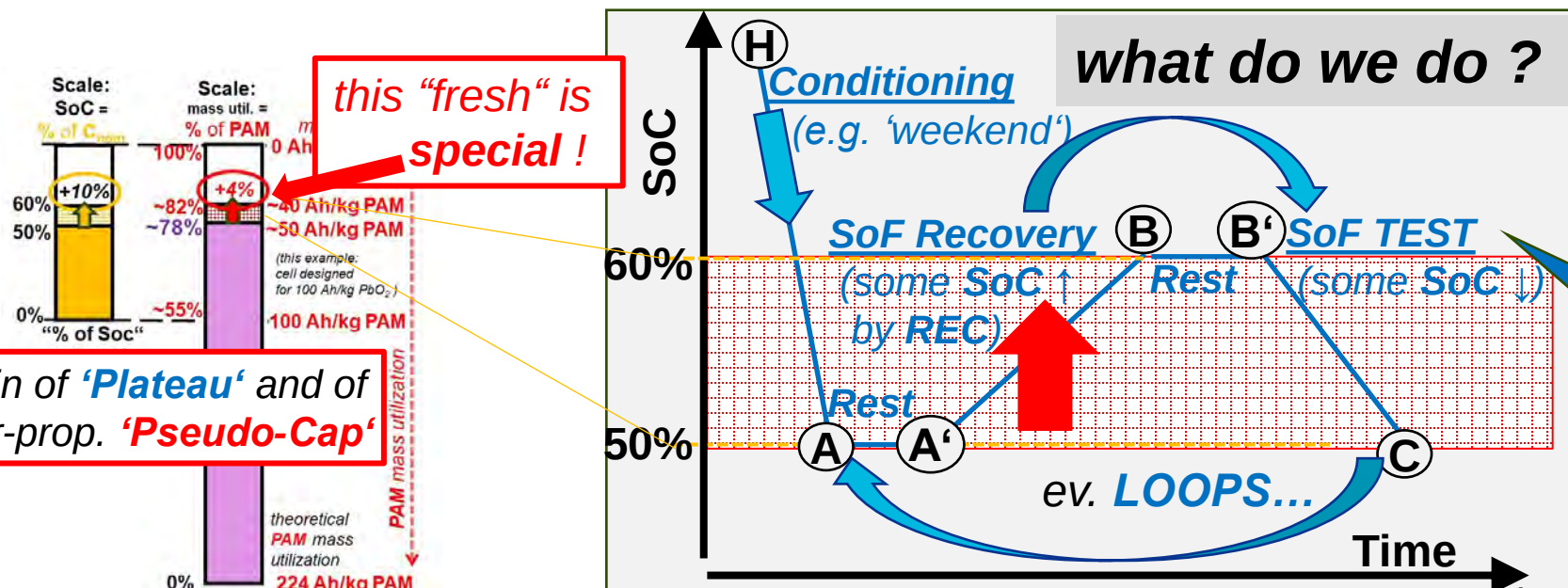
if “**freshly**” created PbO₂ particle surfaces @RECharge = electro-deposition !

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

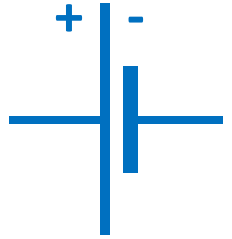
e.g. **fine** PbO₂ particles (nano << 20 nm; cf. electro-catalysts)



what do we do ?



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



C.II Mechanisms behind ‘uplift of discharge Plateau’

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

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

> amount of ‘fresh’ PbO₂ material [g] always = **4.1 g/Ah** of charge used for electro-deposition,
INDEPENDENT from CONDITIONS of RECharge, e.g. recharge current rate i [A], current profile $i(t)$,
polarization η^+ [V], temperature [°C], acid density, electrolyte additives, PAM recipe, PAM additives ...

> structure of ‘fresh’ PbO₂ material very SENSITIVE to CONDITIONS of RECharge

(a well-known effect from galvanizing industry ! electro-winning of metals, -plating, -structuring, nano-sizing ...)
esp. recharge current rate i [A], current profile $i(t)$, polarization η^+ [V], temperature [°C], ...

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

⇒ **more nuclei, finer** structure of deposit, **less regular** crystallinity

⇒ leading to (II.) ‘plateau uplift’ and

(I.) ‘increase of pseudo-capacitance’

i.e. high spec. current density
= current / deposition area [A/m²]
N.B.: a threshold to be exceeded
→ Pb²⁺ depletion
close to location of deposition (CNT) !

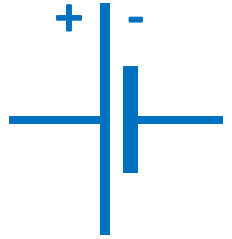
HOW to achieve OUR GOAL ? MAXIMIZE PAM potential @ recharge !

> maximize Recharge Voltage (within technical constrictions)

> ANY improvement of NAM Recharge kinetics helpful: fine PbSO₄, Carbon add., high poro ...

cf Summary Page of [P18]
E.Meissner, ALBA Torino 2025, CRM1
“PAM Structure and fast SoF Recovery:
Steps to understand those Characteristics”

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



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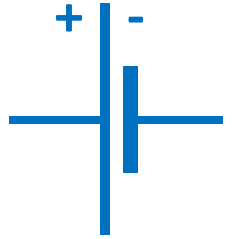
Questions: $\Rightarrow$ for ‘Plateau uplift’, how to control regime @RECharge ?

- i) how to **create** “fresh” PbO₂ particle surfaces with higher surface energy σ ? esp. “fine” / nano-sized
- ii) while RECharge continues: how to **mitigate / impede / limit further growth** of such fresh nuclei ?
- iii) after end of RECharge: “**survival**” of “fine” / nano-sized particles ? ... until we want to DIS them

Strategy: - generate **billions** of nuclei **simultaneously** by diffusion-controlled nucleation @REC
- run **REC** reaction at **high polarization η^+** of positive half cell

$\Rightarrow$ **let’s find the answers !**

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

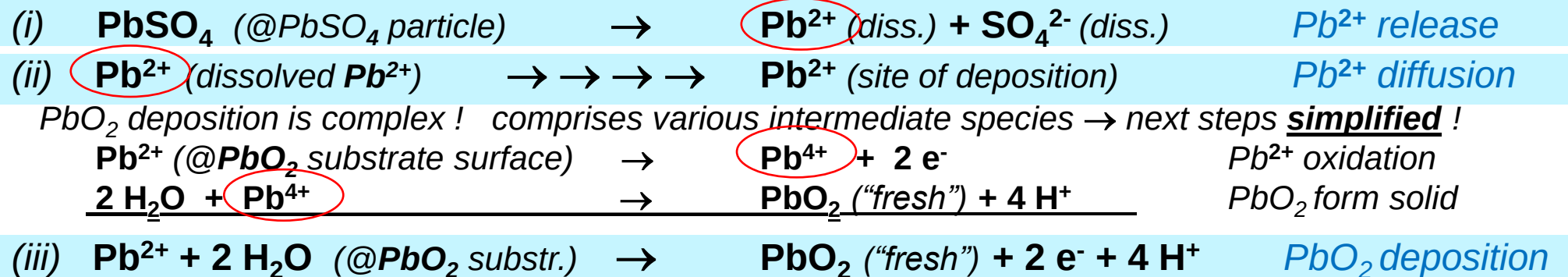


C.II Mechanisms behind ‘uplift of discharge Plateau’

a) origin of ‘uplift’ – basics from thermodynamics; surface energy *cf. [P18]*

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

PbO₂ deposition reaction



N.B.: dissolution of Pb²⁺ from solid PbSO₄ and diffusion to site of deposition is critical (Pb²⁺ sparsely soluble),
while transport of other species involved can be neglected due to their (rel.) abundance:
conc.(H₂O) ≈ 45 mol/L conc.(SO₄²⁻) several mol/L conc.(H⁺) several mol/L

2 Steps **SUPPLY / TRANSPORT of Pb²⁺** = (i) PbSO₄ dissolution + (ii) Pb²⁺ diffusion
 CHARGE TRANSFER → solid = (iii) electro-deposition of PbO₂

limiting Step decisive ⇒ **1) Rate of Reaction**

cf. Theory of Kinetics

2) Structure of Deposition

cf. Classical Nucleation Theory (CNT)

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

C.II Mechanisms behind 'uplift of discharge Plateau'

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

When Potential (polarization η^+) of substrate is increased

⇒ **Rate of PbO₂ electro-deposition** ...

- (i) increases further in case of **kinetic control**, but
- (ii) levels off when **diffusion control** starts limiting

PbO₂ deposition CANNOT EXCEED max. Pb²⁺ transport!
"Pb²⁺ supply chain"

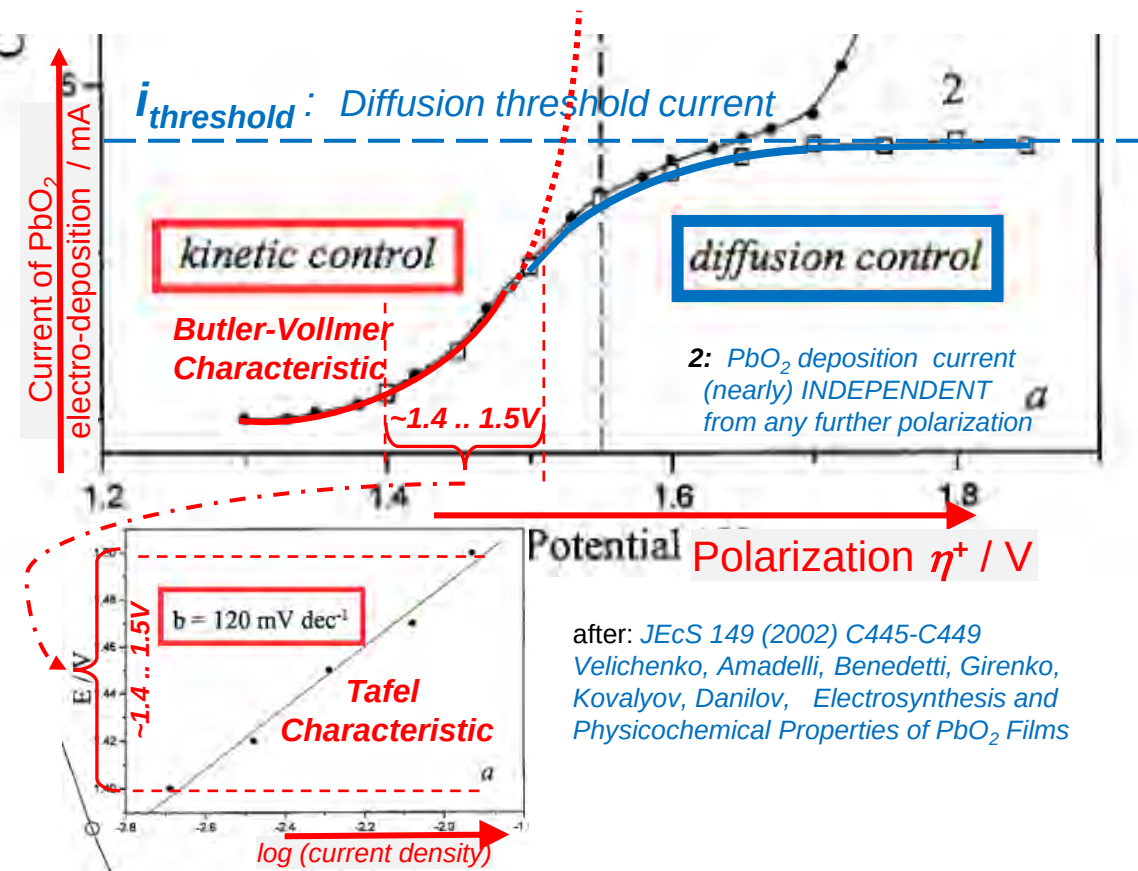
electro-deposition of **PbO₂** on **Pt**
from solution 0.1m Pb(NO₃)₂ in 0.1m HNO₃
at various polarization η^+

at sufficient **HIGH Polarization η^+** of substrate,

$i_{threshold}$ for Pb²⁺ ion transport is reached !

⇒ **conc.(Pb²⁺) → 0** at the sites of electro-deposition ("depletion zone")

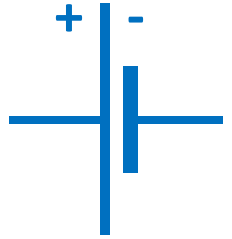
⇒ deposition **current** CANNOT be increased by even higher **Polarization η** !



after: JECs 149 (2002) C445-C449
Velichenko, Amadelli, Benedetti, Girenko,
Kovalyov, Danilov, Electrosynthesis and
Physicochemical Properties of PbO₂ Films

diffusion-control

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



C.II Mechanisms behind ‘uplift of discharge Plateau’

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

Rôle of High Polarization η^+

CNT: a fresh nucleus is stable ONLY when size > **Critical Radius** r_{crit} [m]

1) $\Rightarrow$ **small critical radius** r_{crit} :
small particles stable
(as long as potential is high ...)

CNT:

Critical Radius r_{crit} [m]
of a deposit

$$r_{crit} = \frac{2 \cdot \gamma \cdot V_m}{z \cdot F \cdot |\eta^+|}$$

$\gamma = \sigma$ = surface energy
 V_m = molar Volume
 z = # of electrons (=2)
 F = Faraday Const.

2) $\Rightarrow$ **high Nucleation Rate** J_{nuclei} :
very many particles
(separated individuals)

CNT:

Nucleation Rate J_{nuclei}
= Number N of fresh nuclei deposited
[/sec /area]

$$J_{nuclei} = K_1 \cdot \exp \left(-\frac{K_2}{(\eta^+)^2} \right)$$

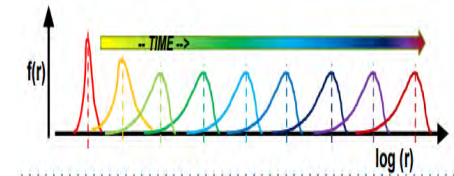
1)+2) $\Rightarrow$ **very many small particles**
(many separated individuals)

N.B. all available Pb²⁺ ions used up
(**depletion zone** around each nucleus),
before nuclei can grow much
and bigger particles be formed

(semi-empirical formula) :
average particle diameter d

$$d \approx k \cdot j^{-n}$$

$n \approx 0.1 \dots 0.5$



High Polarization η^+

$\Rightarrow$ i) create many “nano-sized” PbO₂ particles (high σ)



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

C.II Mechanisms behind ‘uplift of discharge Plateau’

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

“Depletion Zone”:

Radius $r_o = f(t)$ of diffusion layer around each deposition site

$$r_o(t) = \left[\frac{2DC^*Mt}{\rho} \right]^{1/2}$$

$$r_o(t) \sim \text{sqrt}(t)$$

Ec.Acta 47 2000 671–677 Liu, Favier, Ng, Zach, Penner Size-selective electrodeposition of meso-scale metal particles a general method

Consequence of formula:

particles **radii homogenize** over time, **if η^+ kept high**,
i.e. distribution curve (dispersion) of size narrows.

reducing **variety** in size $\Delta r / r$, “particles about **similar size**”

cf. **LSW Theory of OSTWALD Ripening** [P2, P3, P8] ALBA 2020 / 21

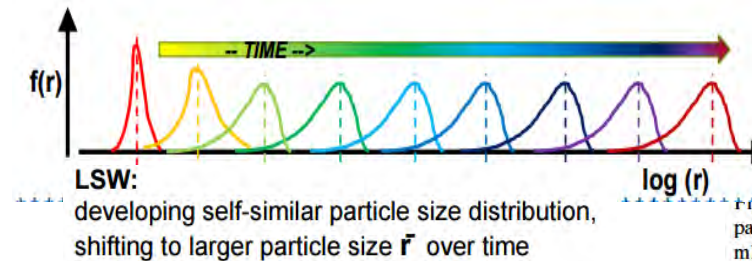
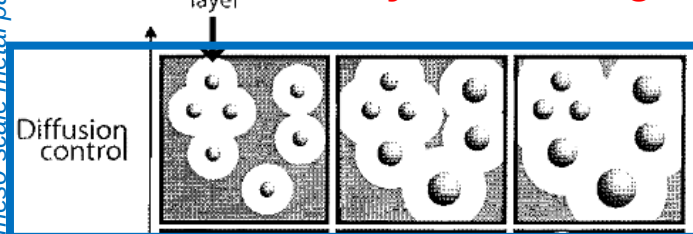
many nuclei

close together

⇒ their diffusion zones overlap

⇒ **many nuclei compete for Pb²⁺** (sparse in e⁻lyte)

depletion layer ⇒ **only moderate growth**



LSW: developing self-similar particle size distribution, shifting to larger particle size $\bar{r}$ over time

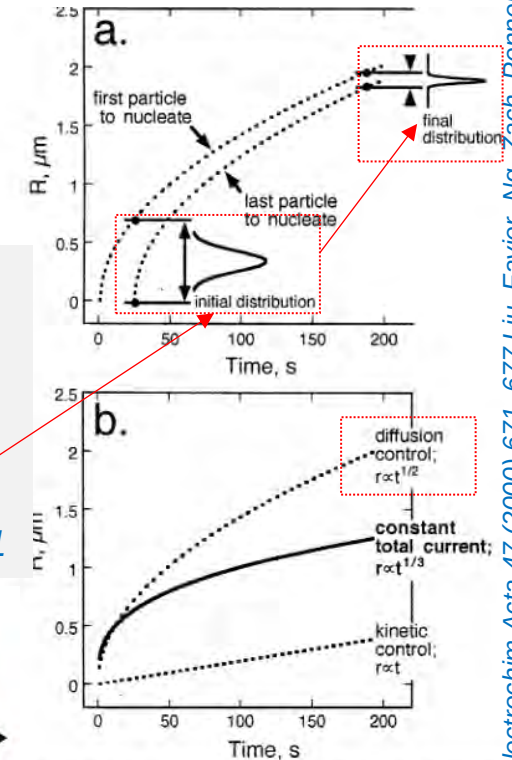


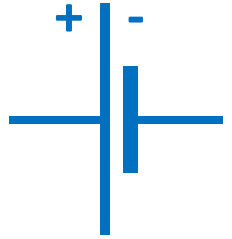
Fig. 1. (a) Calculation of the radius as a function of time for silver particles growing at diffusion control from a solution containing 1.0 mM silver ion. (b) Qualitative comparison of growth laws for constant total current and kinetic control with diffusion control.

High Polarization η^+

⇒ ii) while RECharge continues: **mitigate / impede further growth**



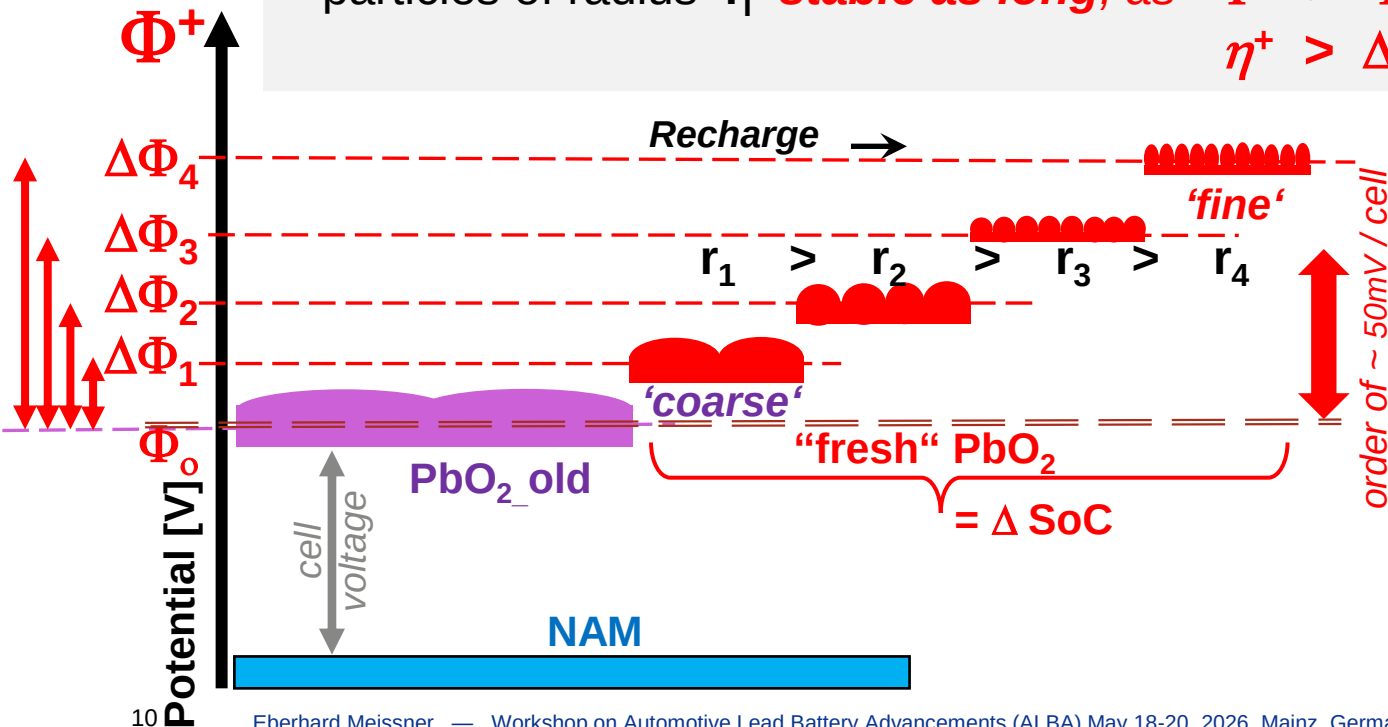
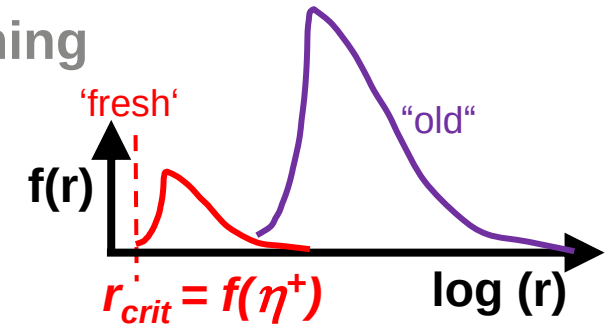
CR: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



C.II Mechanisms behind 'uplift of discharge Plateau'

- b) 'fine PbO₂ particles' generated by diffusion-controlled nucleation @REC
- c) conditions for '**survival**' of '**fine PbO₂ particles**'
- d) coarsening mechanism: **electro-chemical OSTWALD Ripening**

"fresh" PbO₂: a distribution of more or less '**fine**' particles
particles of radius r_i **stable as long, as** $\Phi^+ > \Phi_o + \Delta\Phi_i$
 $\eta^+ > \Delta\Phi_i$



Polarization η^+

- may be kept sufficiently high
- by **external power source** @REC
 - by the (internal) '**pseudo-capacitor**'
(if previously charged up sufficiently high)

otherwise ?

⇒ d) coarsening ...

electro-chemical OSTWALD Ripening

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



C.II Mechanisms behind 'uplift of discharge Plateau'

c) conditions for '**survival**' of '**fine PbO₂ particles**'

d) coarsening mechanism: **electro-chemical OSTWALD Ripening** [P18]

Requirements for electro-chemical OSTWALD Ripening:

- particles - **conductive** - **connected electronically**
- **nano-sized** (sufficient potential difference)

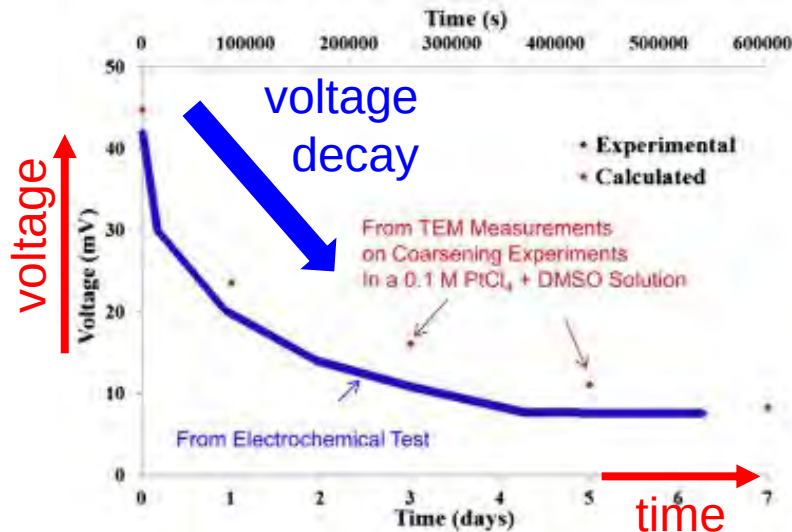


Fig. 5. Voltage vs. time plot of Pt-C catalysts measured with respect to bulk platinum in 0.1 M PtCl₄ + DMSO for ~7 days. The datapoints (diamonds) represent the voltage calculated assuming $\gamma = 0.5 \text{ J m}^{-2}$ using the corresponding particle sizes of Pt catalyst treated for various test durations – as-received, 1 day, 3 days, 5 days and 7 days in 0.1 M PtCl₄ + DMSO solution. The measured voltage appears segmented instead of a continuous curve due to a temporary issue with the recording software.

exp. evidence

- with metals
(Pt, Ag, Cu, Pd, ..)
- with alloys
(Pd-Rh, ...)

unwelcome

aging mechanism
with electro-catalysts

- **fuel cells**
- **electrolyzers**

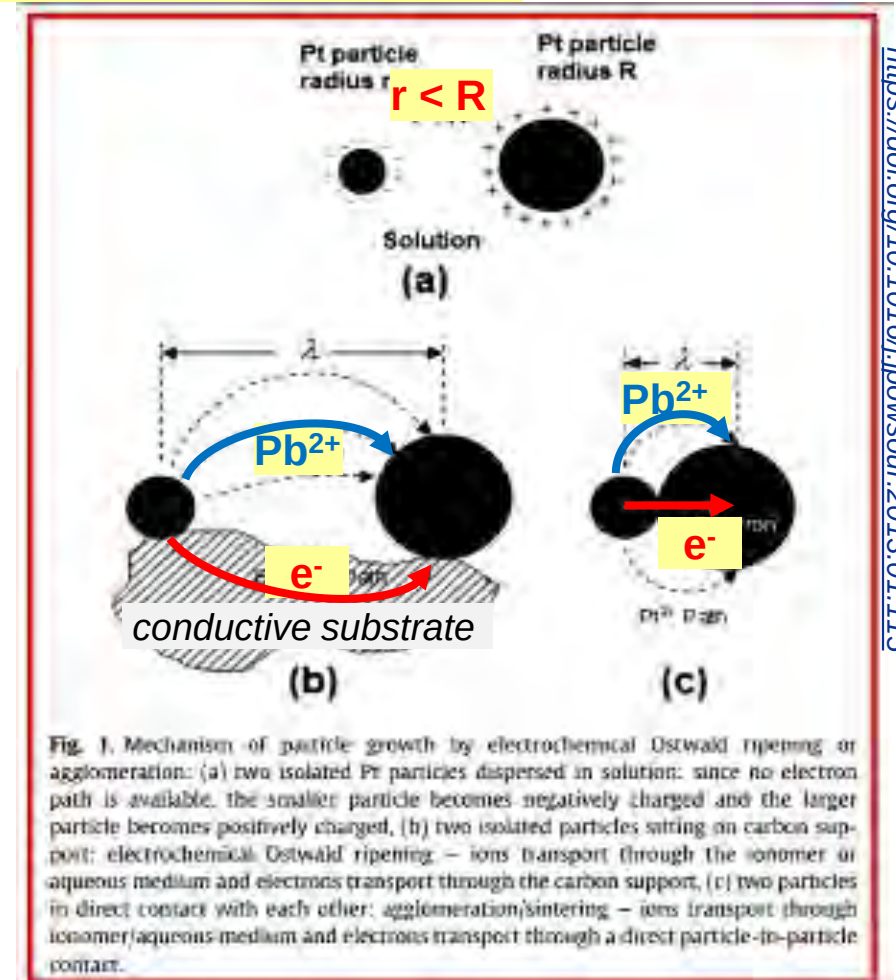


Fig. 1. Mechanism of particle growth by electrochemical Ostwald ripening or agglomeration: (a) two isolated Pt particles dispersed in solution: since no electron path is available, the smaller particle becomes negatively charged and the larger particle becomes positively charged, (b) two isolated particles sitting on carbon support: electrochemical Ostwald ripening – ions transport through the ionomer or aqueous medium and electrons transport through the carbon support, (c) two particles in direct contact with each other: agglomeration/sintering – ions transport through ionomer/aqueous medium and electrons transport through a direct particle-in-particle contact.

Preethy Parthasarathi et.al., J.Power Sources 234 (2013) 82-90
<https://doi.org/10.1016/j.jpowsour.2013.01.115>
Electrochemical Ostwald Ripening of Pt and Ag catalysts

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



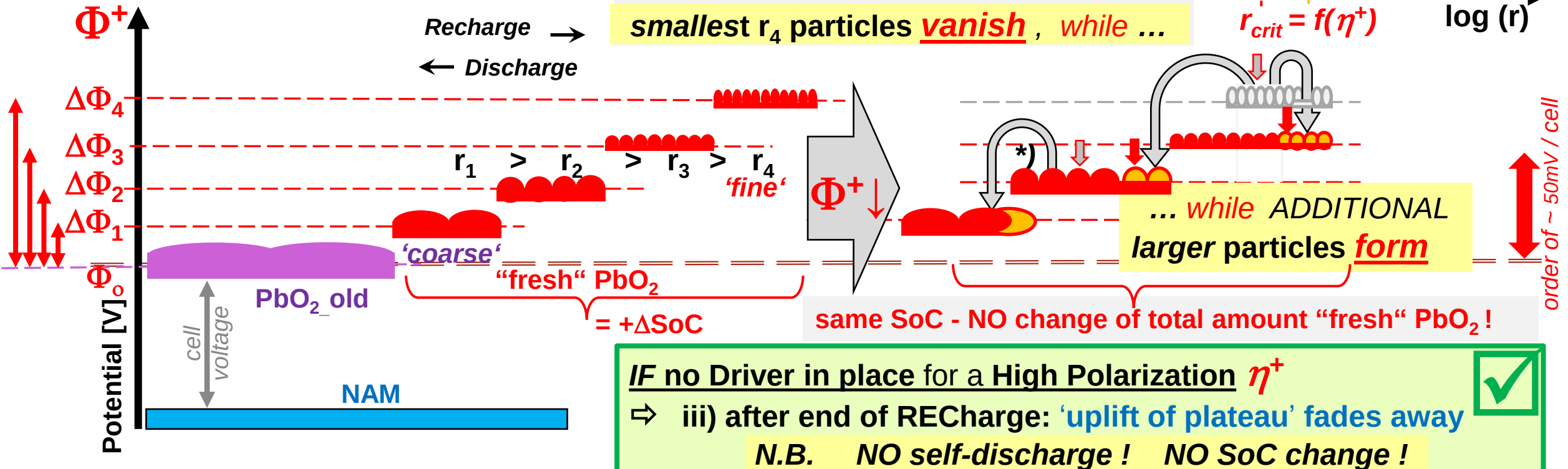
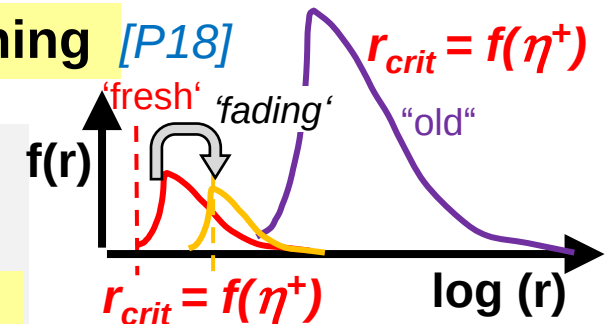
C.II Mechanisms behind 'uplift of discharge Plateau'

c) conditions for '**survival**' of '**fine PbO₂ particles**'

d) coarsening mechanism: **electro-chemical OSTWALD Ripening** [P18]
- fading of '**uplift**'

*IF Φ^+ decreases (for ANY reason),
e.g. case of $\Phi^+ \rightarrow \Phi_o + \Delta\Phi_3$ *)*

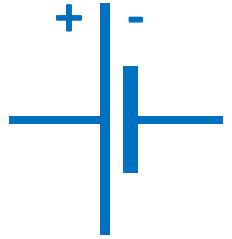
smallest r_4 particles vanish, while ...



IF no Driver in place for a High Polarization η^+
⇒ iii) after end of RECharge: '**uplift of plateau**' fades away
N.B. NO self-discharge! NO SoC change!

*) *IF Φ^+ decreases further (for ANY reason), step-wise all 'fine' particles will vanish*

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



C.II Mechanisms behind 'uplift of discharge Plateau'

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

... but what means '**High**' Polarization η^+ ?

Polarization $\eta^+ = \Phi^+ - \Phi^+_o$, when Electrode Potential $\Phi^+ \neq$ equilibrium $\Phi^+_o \Leftrightarrow$ **current flow i**

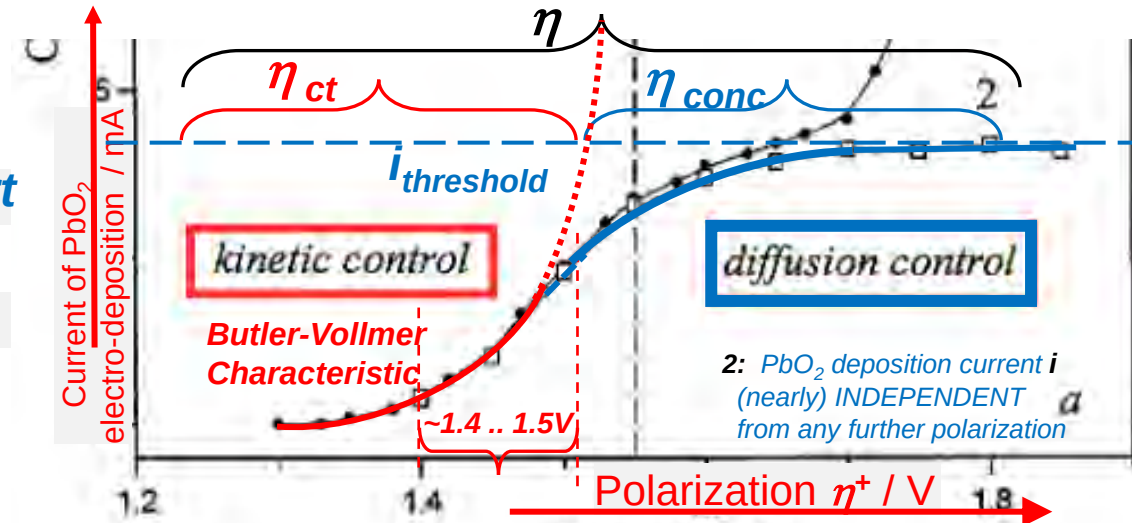
$\Rightarrow \eta^+ = \eta^+_{ct} + \eta^+_{conc} + i \cdot R$ **charge-transfer** + **Pb²⁺ depletion** + **ohmic** (case of PAM recharge)

- (i) charge-transfer polarization η_{ct} **kinetics**
(Butler-Vollmer) at e'lyte / AM particle surface
- (ii) concentration polarization η_{conc} **Pb²⁺ transport**
(Fick's Law) diffusion zone in e'lyte around particle
- (iii) ohmic losses $i \cdot R$ **resistivity**
(Ohm's and Kirchhoff's Law) AM, e'lyte, grid/top lead ...

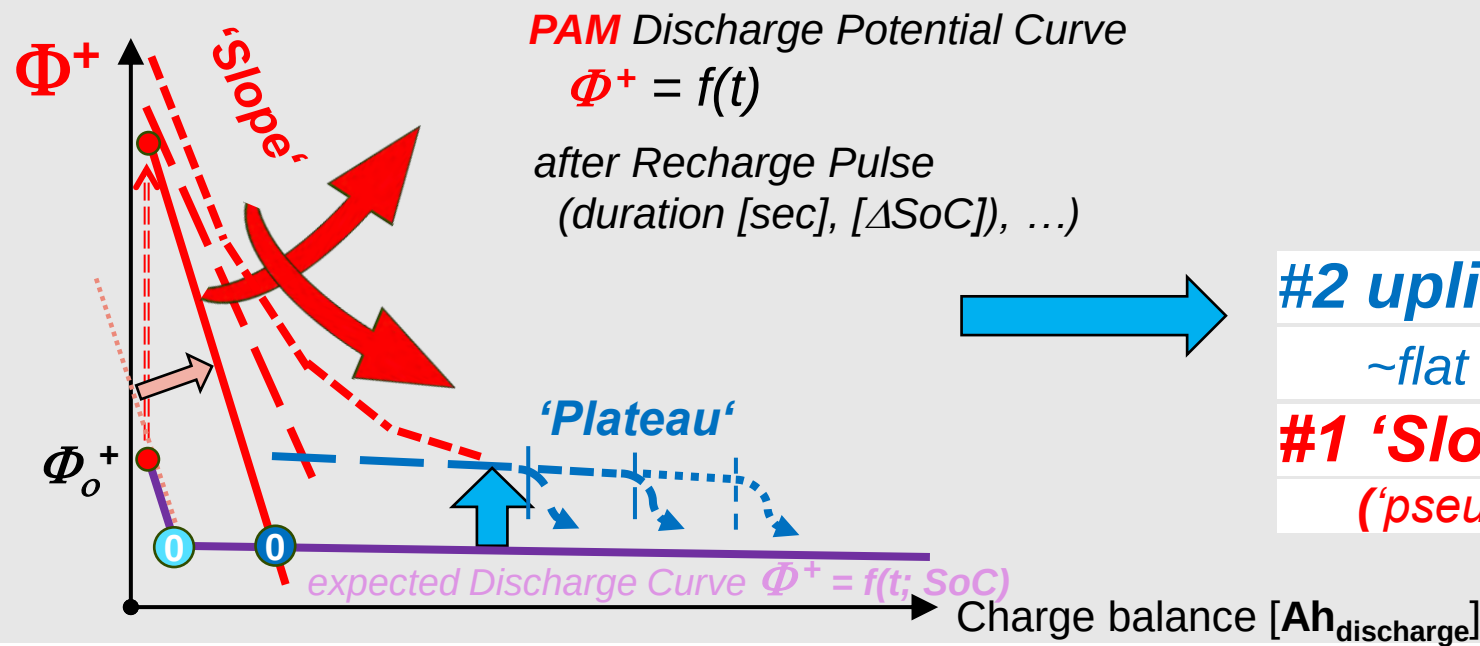
Diffusion threshold current $i_{threshold}$ of Pb²⁺ depends on

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

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



pos. Polarization η^+ (sufficiently) 'high', 
when η^+_{conc} is 'high' :
 i (nearly) INDEPENDENT from increasing η^+



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 –



'Slope' + 'pseudo-cap'

260507 'pseudo-capacitance': define and compare vs. 'Helmholtz' Cap and 'Battery Electrode';

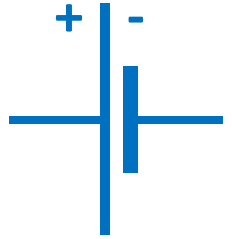
dimensions of storage mechanisms: **C** and **SoC**;

equilibration currents and relaxing voltage, when Cap and Battery parallel

case of @open circuit = 'pause'



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

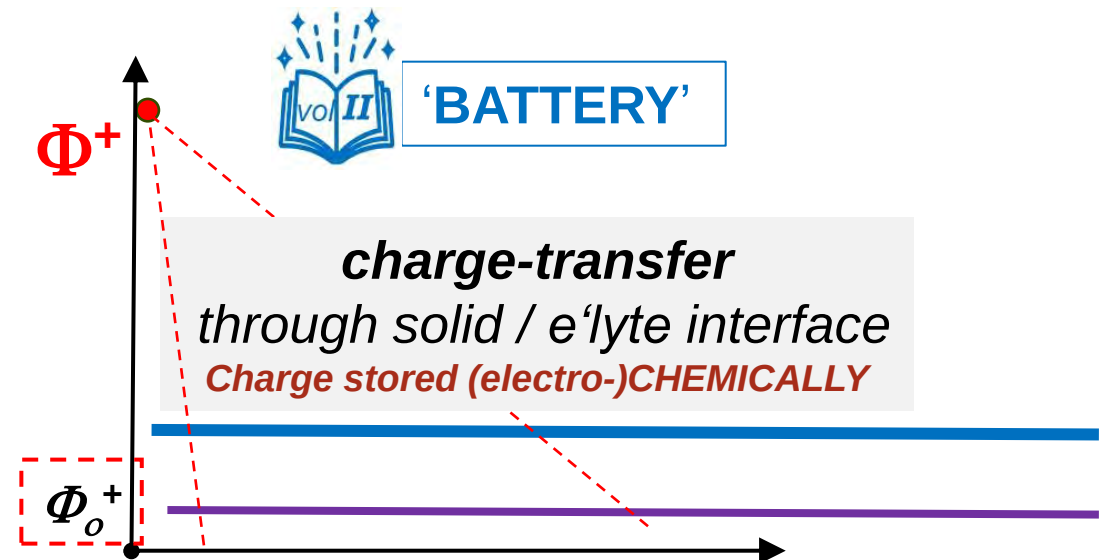
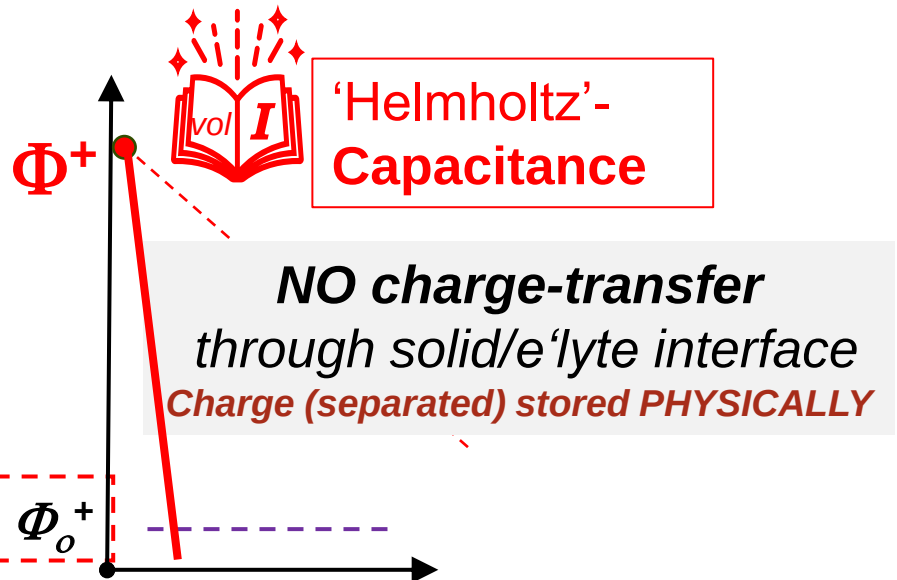
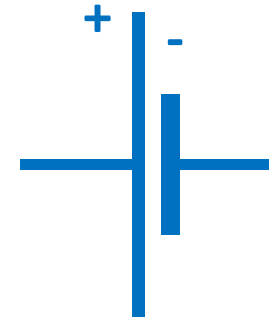
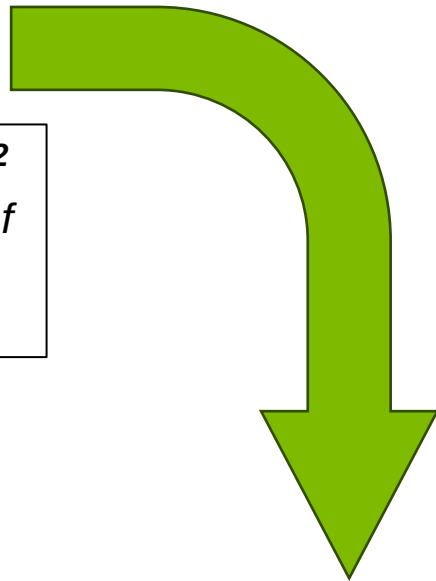


C.I Mechanisms behind 'pseudo-capacitance' Slope

a) WHAT is a PSEUDO-Capacitor ?



typ. value $\sim 10 \mu\text{F}/\text{cm}^2$
can explain only $\sim 10\%$ of
'slope' seen with PbO₂
cf. [P14, P15, P16, P18]



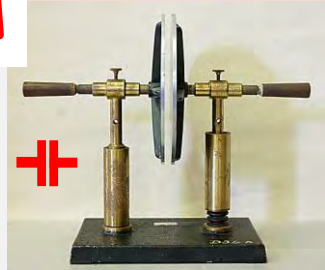
CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses

C.I Mechanisms behind 'pseudo-capacitance' Slope

a) WHAT is a 'Helmholtz' Capacitance ?

= *conductive electrode in an e'lyte*
⇒ a **SURFACE EFFECT**

"ideal Capacitor"



Charge stored
PHYSICALLY

Isolating
Diaphragm

NO charge
transfer

Charges separated by
Virtual Diaphragm !

with 'Helmholtz':
 A, d, ϵ_r may
depend on $\Phi, pH \dots$!

$$C = \epsilon_0 \epsilon_r \cdot \frac{A}{d}$$

$C = [As/V] = [F]$

ϵ_0 permittivity of vacuum
= $8.8 \cdot 10^{-12}$ As/Vm [F/m]
 ϵ_r rel. static permittivity
(=1 for vacuum)

U
[V]

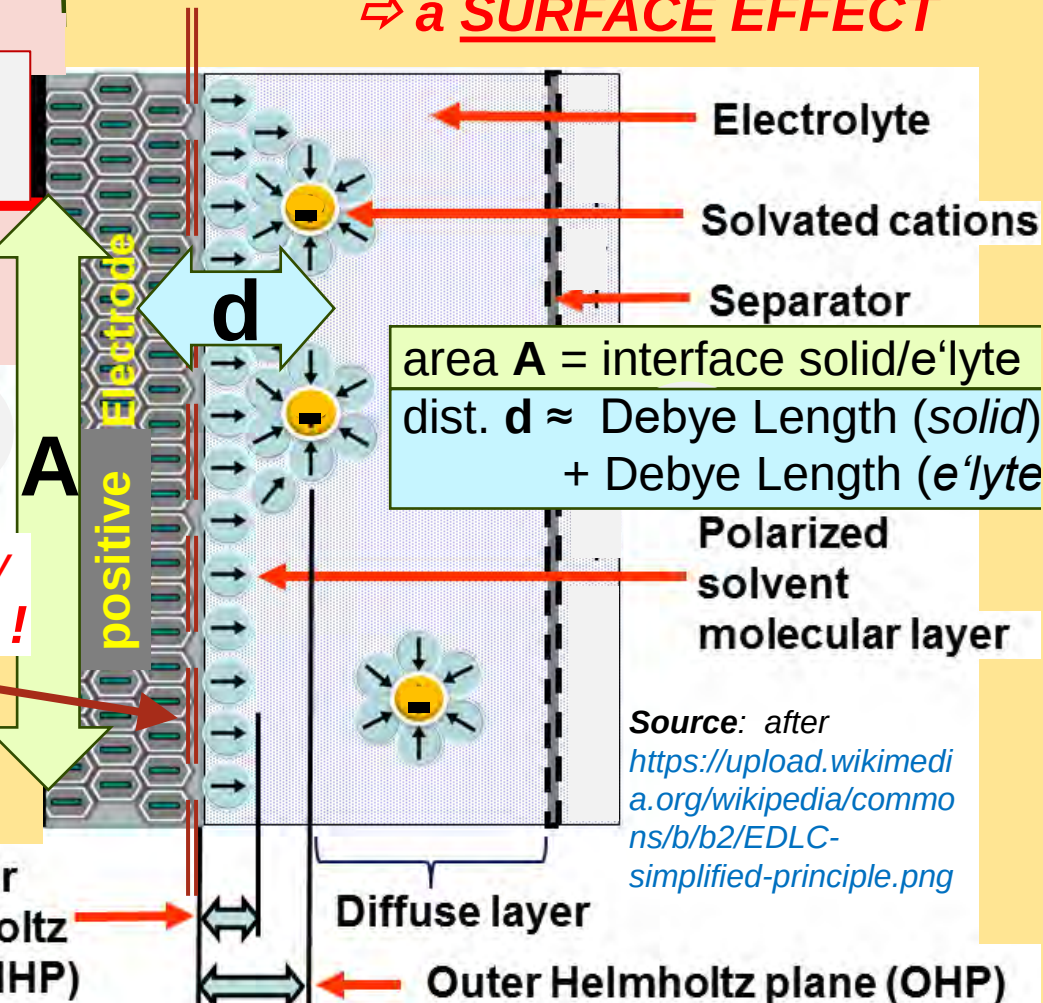
Characteristic $U = f(q)$
slope $dU/dq \sim 1/C$
constant **ONLY**,

IF $area\ A = const.$

$dist.\ d = const.$

$rel.\ \epsilon_r = const.$

dq [As]



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



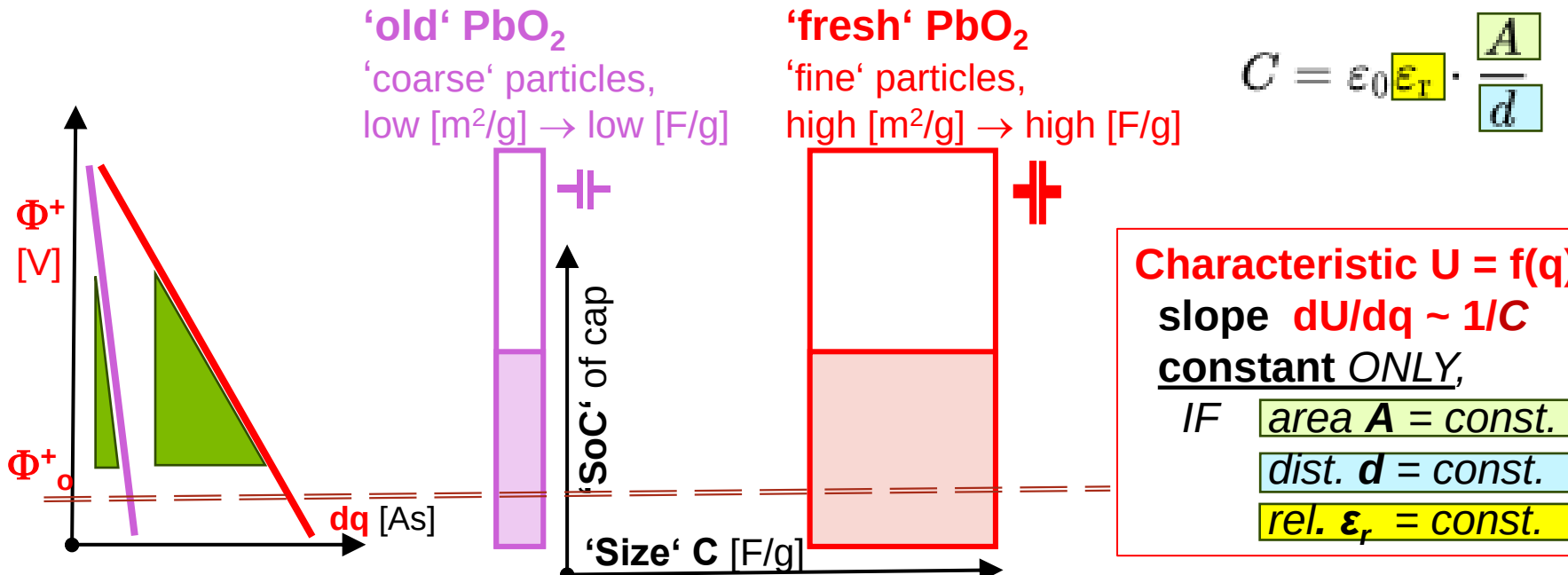
C.I Mechanisms behind 'pseudo-capacitance' Slope

a) WHAT is a 'Helmholtz' Capacitance ?

Case of PbO₂: charge storage in 'Helmholtz' Capacitance has two dimensions

- (i) "Size C" of capacitor [F], prop. to solid/e'lyte area $\sim A = \text{area/mass [m}^2/\text{g}] * \text{mass [g] of PbO}_2$
- (ii) "SoC" of capacitor [%], prop. to actual potential $\sim (\Phi^+ - \Phi^+_o)$

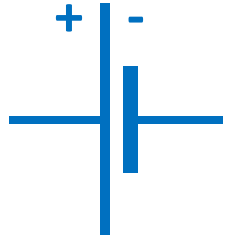
INDEPENDENT: "SoC" can change w/o changing "Size C" ! "Size C" depends on "battery"



Helmholtz $\approx 10 \mu\text{F}/\text{cm}^2$
can explain only $\sim 10\%$ of
'slope' seen with PbO₂
cf. [P14, P15, P16, P18]

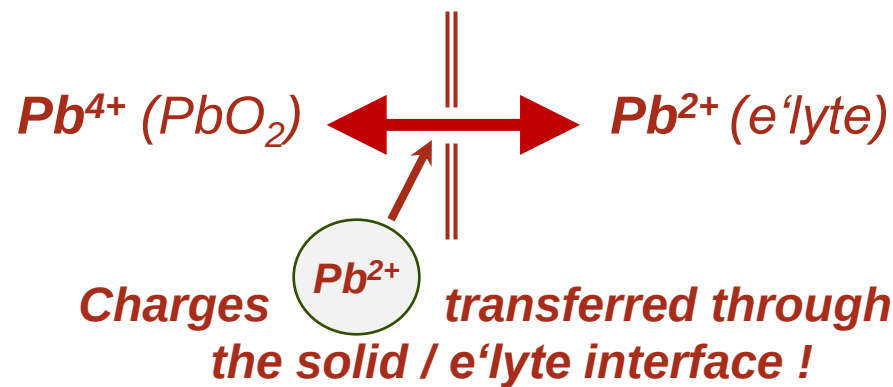
A, d, ϵ_r
may depend
on $\Phi, \text{pH} \dots$!

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



C.I Mechanisms behind 'pseudo-capacitance' Slope

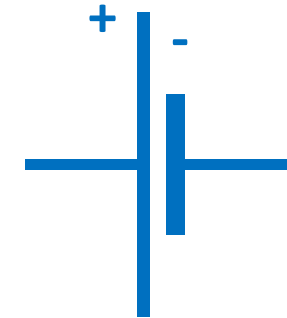
a) WHAT is a 'BATTERY' electrode ?



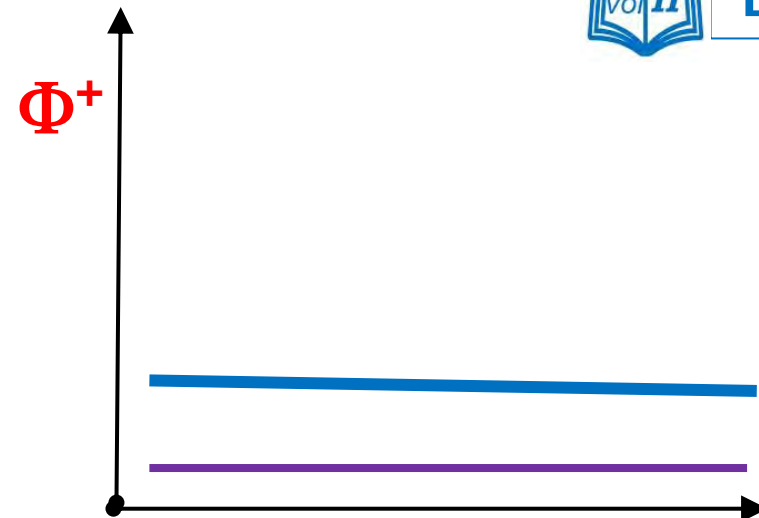
Charge stored (electro-)CHEMICALLY

electro-deposition

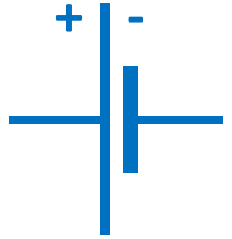
A BULK EFFECT



'BATTERY'



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



C.I Mechanisms behind 'pseudo-capacitance' Slope

a) WHAT is a 'BATTERY' electrode ?

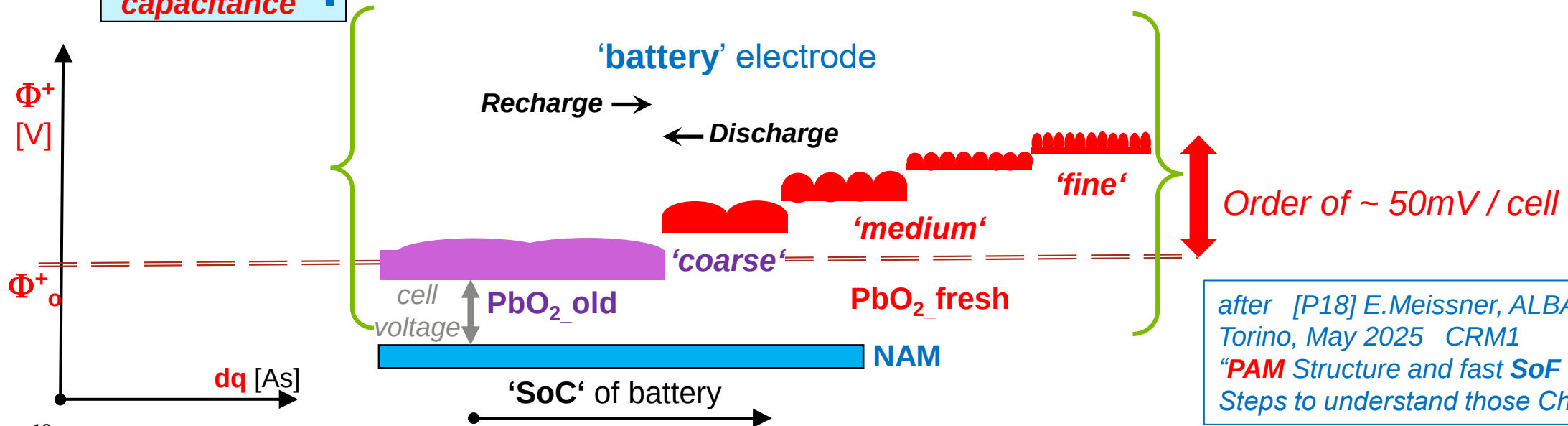


Case of PbO₂: charge storage in 'BATTERY' electrode has **two dimensions**

- (i) "SoC" of battery electrode [%], prop. to actual total mass m [g] of PbO₂ $\sim (m - m_o(\text{SoC}=0))$
- (ii) "Size & structure" of PbO₂ particles - a distribution, depending on operating history, may influence Φ^+ both at open circuit and under load

NOT INDEPENDENT: "SoC" change of "battery" always changes PbO₂ "Size & structure" thereby impacting also 'pseudo-capacitance' "Size C"

OTHER than 'capacitance' !



after [P18] E.Meissner, ALBA Workshop, Torino, May 2025 CRM1
"PAM Structure and fast SoF Recovery: Steps to understand those Characteristics"

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

C.I Mechanisms behind 'pseudo-capacitance' Slope

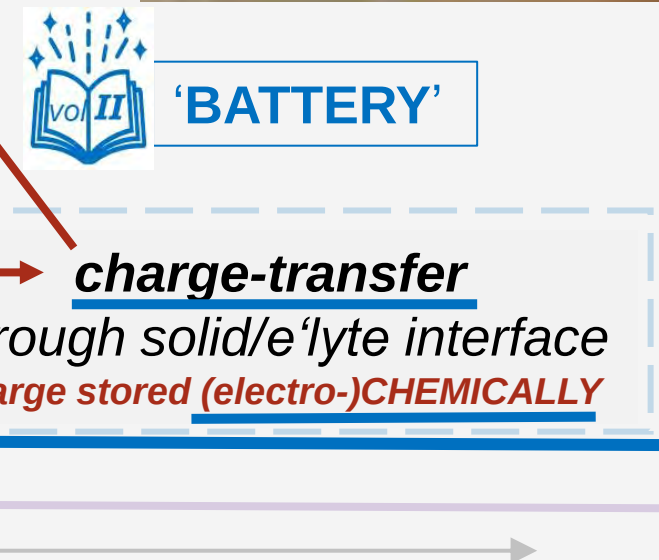
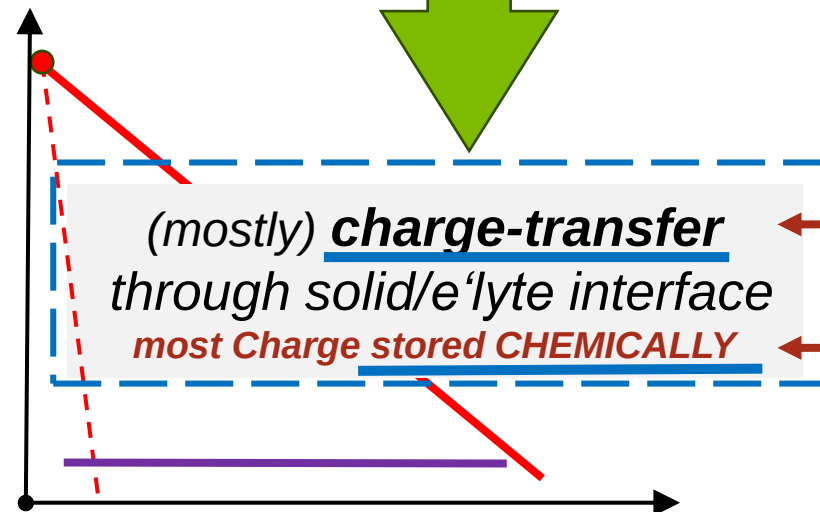
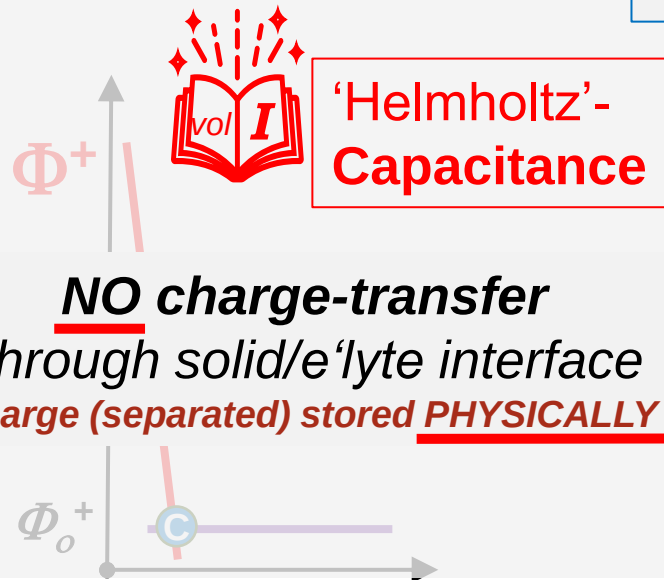
a) WHAT is a **PSEUDO**-Capacitor ?

"PSEUDO-" !

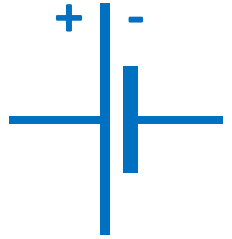
... just to please the
electrical engineers ...

a NAME given
to describe a
'capacitance-like'
electrical behaviour:
superposition of (several) reactions,
(mostly) **charge-transfer**

Mimicry !



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



C.I Mechanisms behind 'pseudo-capacitance' Slope

a) WHAT is a PSEUDO-Capacitor ?



(*superposition of several*)
(mostly) **charge-transfer reactions**,
(together) showing '**capacitance-like**'
electric behaviour
most Charge stored (electro-)CHEMICALLY

- not 'ideal'** - e.g. **C** may vary with actual Φ !
- e.g. Mechanisms with *limited range* of Φ only
 - e.g. **C** depends on frequency
low penetration depth at higher frequencies,
often near-surface AM bulk preferred
 - not limited to geometrical surface
 - some **charge transfer ('Faradic')** reactions

superposition - may comprise SEVERAL mechanisms

'ideal' (pure)
capacitor

Φ^+

'pseudo-capacitor'

'Helmholtz' is only
one among many

Φ^+_0

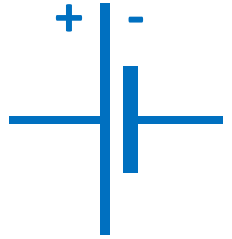
SEVERAL mechanisms

EXAMPLES for 'pseudo-capacitance'- type mechanisms:

A	Adsorption Pseudocapacitance	B	Redox Pseudocapacitance	C	Intercalation Pseudocapacitance
<i>Chem.Rev. 120 (2020) 6738–6782 Fleischmann REVIEW Pseudocapacitance: From Fundamental Understanding to High Power Energy Storage Materials</i>					

- A** **adsorption/attachment:** Anions (e.g. HSO_4^- , ...) to solid/e'lyte surface, often incl. some atom exchange
- B** **valence change** of metal ion in metal oxide / changing stoichiometry in metal oxides (e.g. $\text{PbO}_{2-\delta}$)
- C** **insertion reactions:** small Cations (e.g. H^+ , Li^+ , ...) into AM bulk (metal, metal oxide, carbon, ...)

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



C.I Mechanisms behind 'pseudo-capacitance' Slope

a) WHAT is a PSEUDO-Capacitor ?



(*superposition of several*)
(mostly) **charge-transfer reactions**
(together) showing '**capacitance-electric behaviour**'
most Charge stored (electro-)CHEMICALLY



Contribution to 'pseudo-capacitance'
from PbO₂ particles: nano-sized ' vs. 'coarse'

NOT just simple narrative: '*finer 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 ...**) depend on orientation
- surface energies $\sigma_{[h,k,l]}$ (Wulff's Law) → **local potential**
- **dangling bonds** → adsorption of species

'ideal' (pure)
capacitor

Φ^+

'pseudo-capacitor'

'Helmholtz' is only
one among many

Φ^+_0

SEVERAL mechanisms

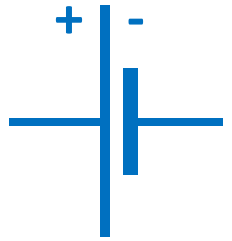
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*Chem.Rev. 120 (2020) 6738–6782 Fleischmann REVIEW Pseudocapacitance:
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CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



C.I Mechanisms behind 'pseudo-capacitance' Slope

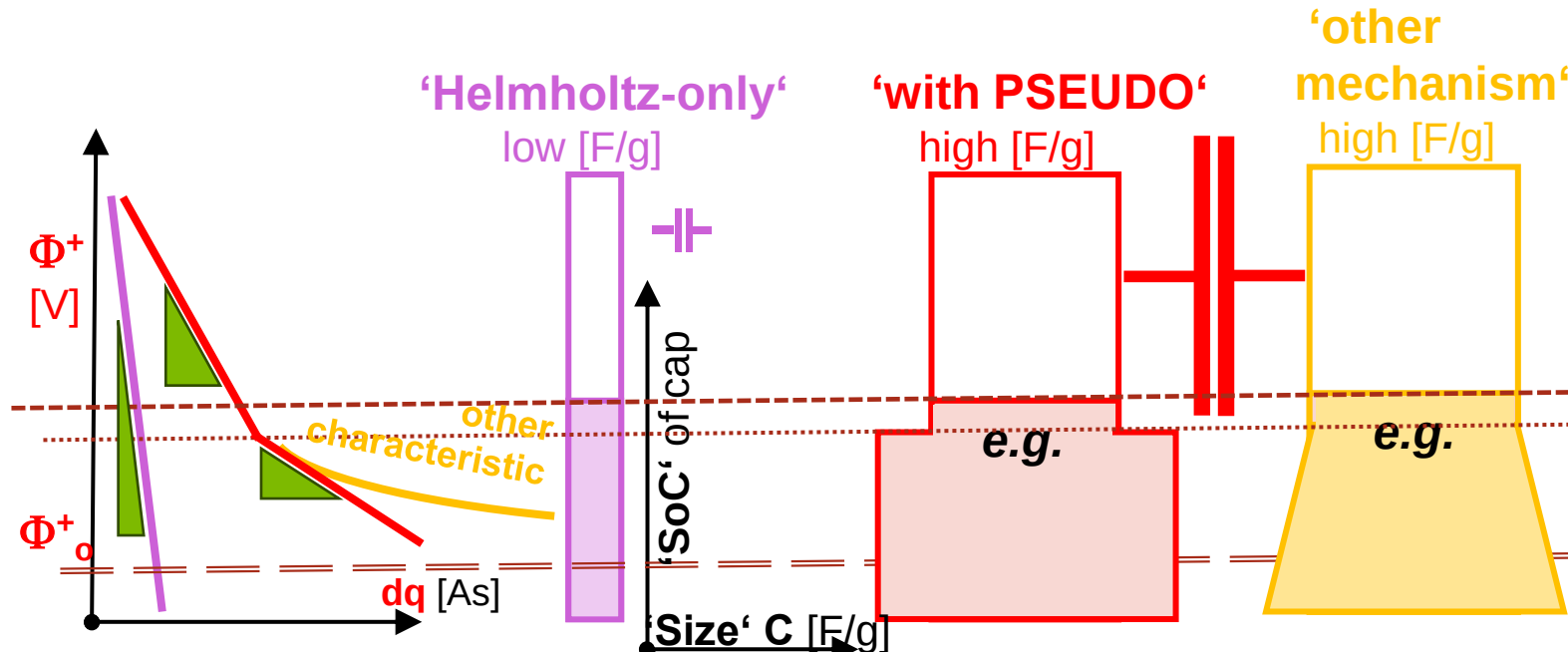
a) WHAT is a PSEUDO-Capacitor ?

Case of PbO₂: charge storage in '**pseudo-capacitance**' two dimensions

- (i) "**Size C**" of capacitor; depends on type of contributing mechanisms !
may depend on solid/e⁻lyte area, mass weight, facet of crystal, on potential Φ^+ , pH...
- (ii) "**SoC**" of capacitor [%], ~~prop.~~ related to actual potential $\sim (\Phi^+ - \Phi^+_o)$
INDEPENDENT: "**SoC**" can change w/o changing "**Size C**" !

N.B. similar to '**Helmholtz**'
but **INDIVIDUAL**
for **EACH** reaction
and mechanism

"**Size C**" depends on
properties of "**battery**"



$$C = \epsilon_0 \epsilon_r \cdot \frac{A}{d}$$

Characteristic $U = f(q)$
slope $dU/dq \sim 1/C$
constant ONLY,

IF $\begin{cases} \text{area } A = \text{const.} \\ \text{dist. } d = \text{const.} \\ \text{rel. } \epsilon_r = \text{const.} \end{cases}$

correct only
locally -
within small
ranges of Φ^+

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



C.I Mechanisms behind 'pseudo-capacitance' Slope

b) capacitance $C = \Delta Q / \Delta \Phi^+$ may depend on potential Φ^+ !

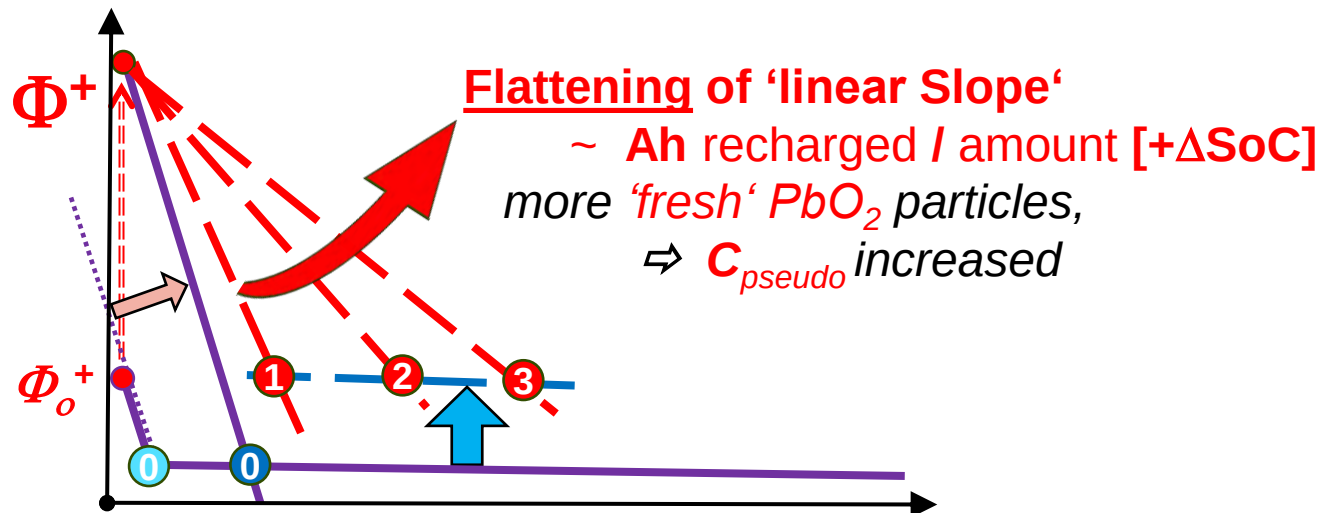
experimental findings: e.g. EXIDE's recent experiments, literature

'flattening' + 'curvature' of 'capacitance slope' pattern

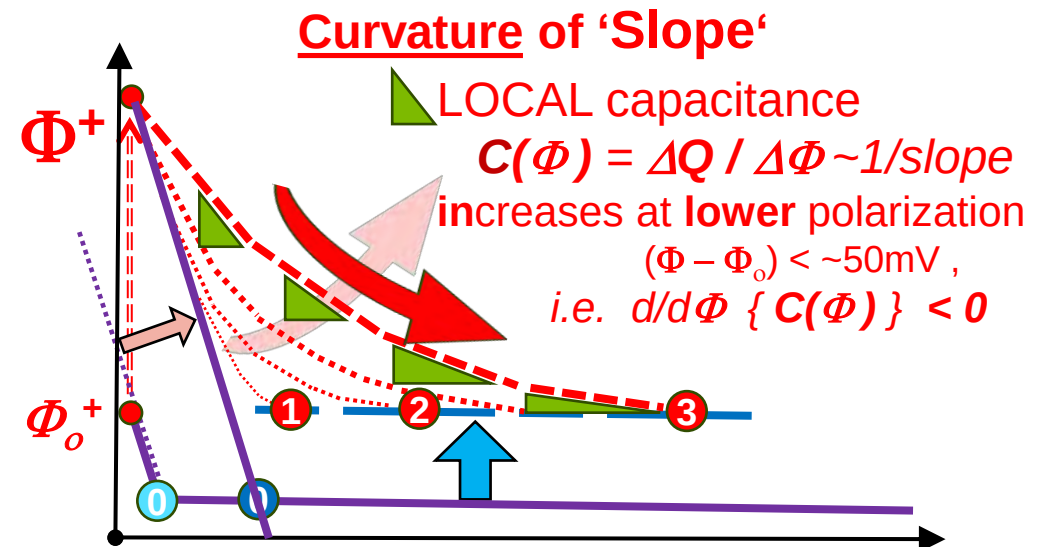
- ev. various TYPES of different 'pseudo-capacitance' mechanisms
- various RATE / KINETICS of same mechanism, non-linear (e.g. *log-type*) mechanism

... 'flattening' of 'capacitance' pattern might be simulated by some 'even higher plateau levels' ?

so far: **some Simplistic View !**



Observed Reality



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

BACKUP

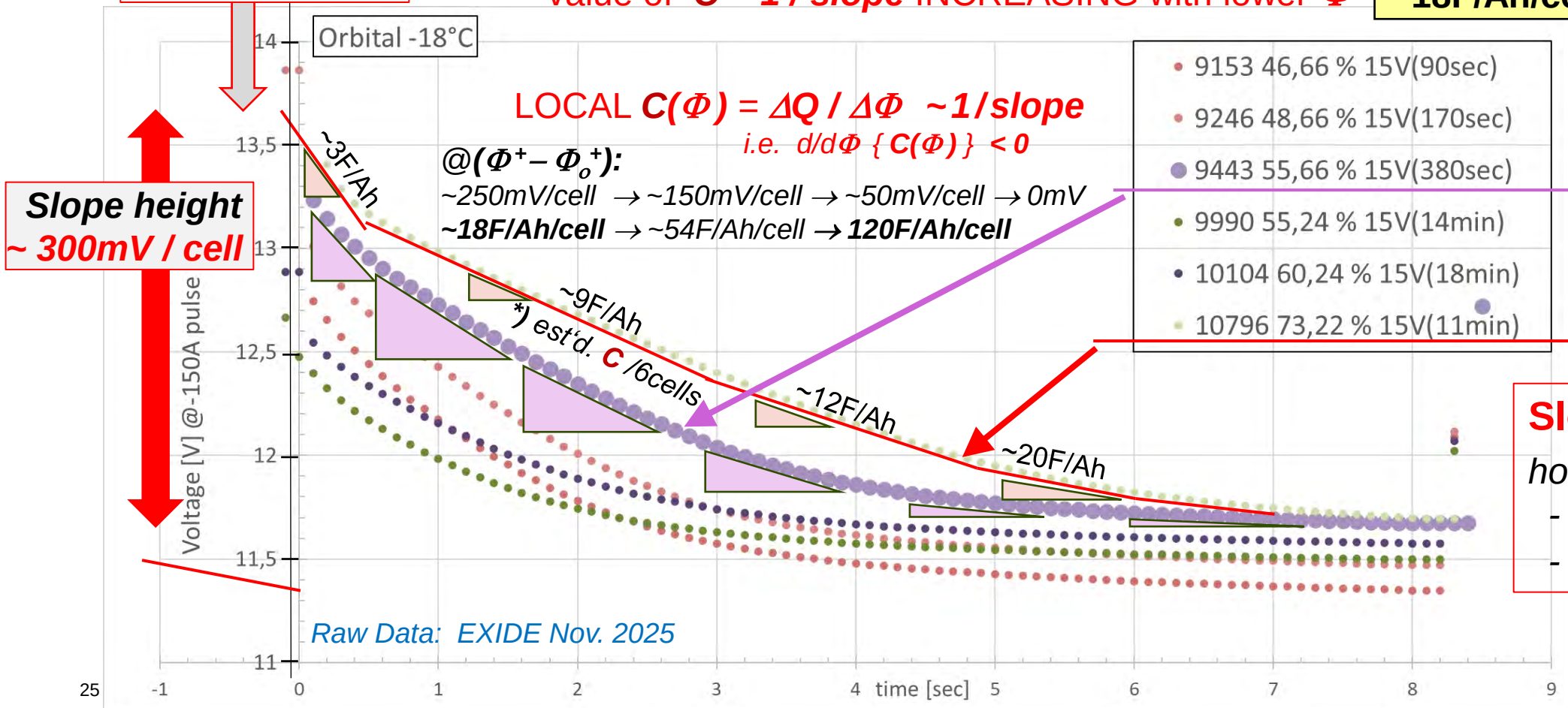


C.I Mechanisms behind 'pseudo-capacitance' Slope

b) capacitance $C = \Delta Q / \Delta \Phi^+$ may depend on potential Φ^+ !

- EXIDE exp. finding: *curved slope* $U(t)$ @ SoF-test load = 3 A/Ah_{nom} (const.) !

value of $C \sim 1 / \text{slope}$ INCREASING with lower Φ^+ **~18F/Ah/cell → ~120F/Ah/cell**



Slope changes

how / where

- to measure ?
- to compare ?

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



C.I Mechanisms behind 'pseudo-capacitance' Slope

a) WHAT is a **PSEUDO**-Capacitor ?

a BUZZ-Word !

Mimicry !



In context of 'pseudo-capacitance', lazy and fuzzy wording is common !

Journal Editors address improper terminology usage in submitted publications

ACS Nano 12 (2018) 2081–2083 Gogotsi, Penner *Energy Storage in Nanomaterials – Capacitive, Pseudocapacitive, or Battery-like*

ACS NANO

Energy Storage in Nanomaterials – Capacitive, Pseudocapacitive, or Battery-like?

EDITORIAL

The first question a researcher should ask when doing electrochemical data analyses on a new nanomaterial is whether the material is battery-like or capacitor-like.

The ability to decompose the total current into contributions from Faradaic pseudocapacitance and double-layer capacitance is critically important in terms of providing an understanding of the charge-storage mechanisms that are operating.

SCIENCE 343 (2014) 1210-1211

Simon, Gogotsi, Dunn

Where Do Batteries End

and Supercapacitors Begin

<http://dx.doi.org/10.1126/science.1249625>

VIDEO Where Do Batteries End

& Supercapacitors Begin

<https://www.youtube.com/watch?v=zqJ9TiSgY2M>

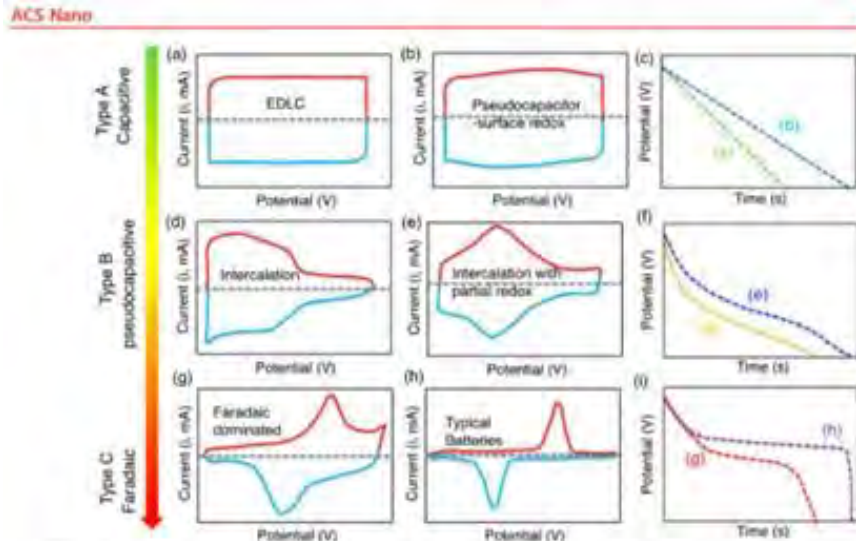


Figure 1. (a, b, d, e, g, h) Schematic cyclic voltammograms and (c, f, i) corresponding galvanostatic discharge curves for various kinds of energy-storage materials. A pseudocapacitive material will generally have the electrochemical characteristics of one, or a combination, of the following categories: (b) surface redox materials (e.g., MnO₂ in neutral, aqueous media), (d) intercalation-type materials (e.g., lithium insertion in Nb₂O₅ in organic electrolytes), or (e) intercalation-type materials showing broad but electrochemically reversible redox peaks (e.g., Ti₃C₂ in acidic, aqueous electrolytes). Electrochemical responses in (g–i) correspond to battery-like materials.

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



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a) WHAT is a **PSEUDO-Capacitor** ?

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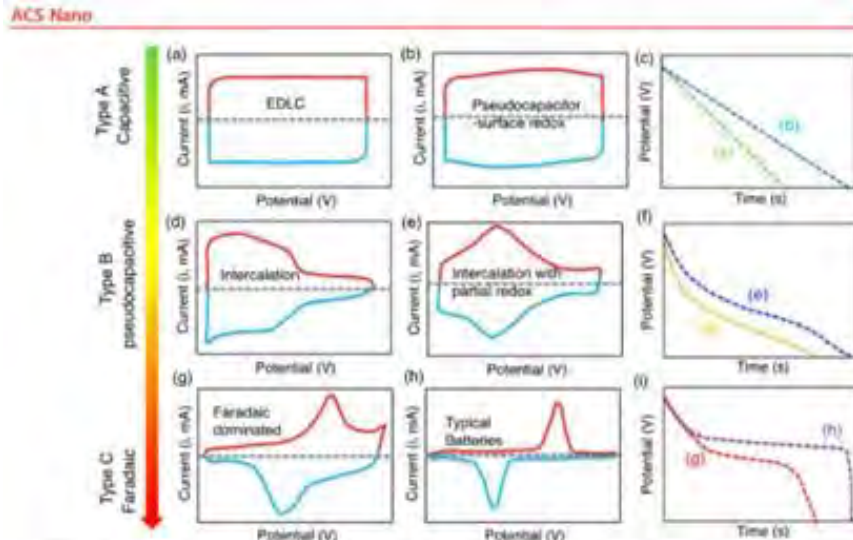
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– Capacitive, Pseudocapacitive, or Battery-like



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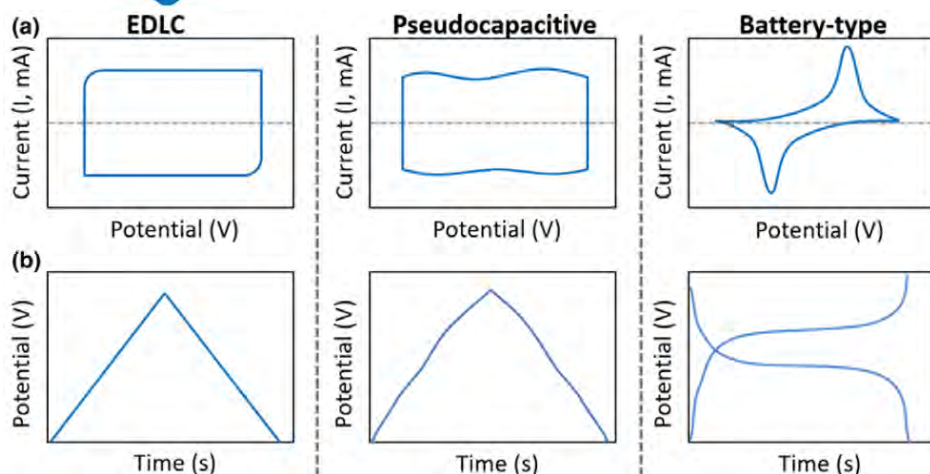
CR11: PbO₂ Structure and SoF Recovery: bottom-up analysis and hypotheses



C.I Mechanisms behind 'pseudo-capacitance' Slope

a) WHAT is a PSEUDO-Capacitor ?

further reading: 'pseudo-capacitance' vs. "Helmholtz Capacitor" and "Battery"



JECs 162 (2015) A5185-5189 Brousse ..

To Be or Not To Be Pseudocapacitive

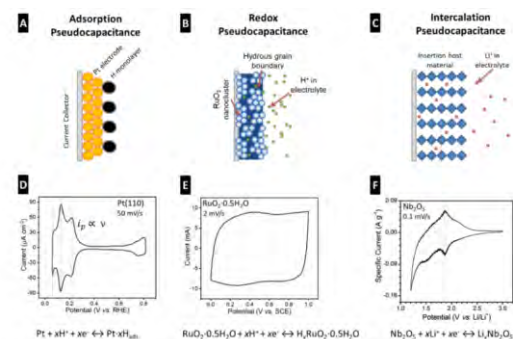
JECs 138 (1991) 1539 CONWAY

Transition from "Supercapacitor" to "Battery" Behavior in Electrochemical Energy Storage

Energy Environ. Mat 2 (2019) 30–37

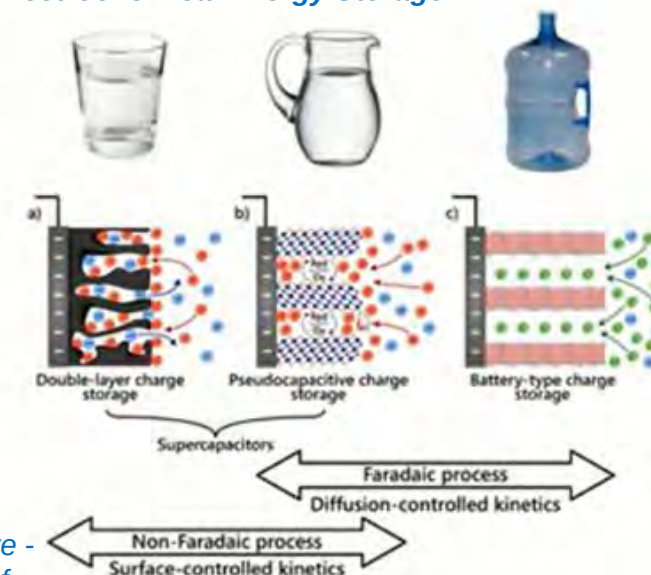
Y.Jiang, J. Liu

Definitions of Pseudocapacitive Materials A Brief REVIEW



Chem.Rev. 120 (2020) 6738–6782 Fleischmann REVIEW
Pseudocapacitance From Fundamental Understanding to High Power Energy Storage Materials
<https://doi.org/10.1021/acs.chemrev.0c00170>

Figure 4. (A–C) Illustration of the three types of mechanisms that give rise to pseudocapacitance as defined by Conway and (D–F) their corresponding cyclic voltammograms. (A) Adsorption pseudocapacitance, (B) redox pseudocapacitance, and (C) intercalation pseudocapacitance. Adapted from ref 25 with permission from The Royal Society of Chemistry. (D) Cyclic voltammogram of a Pt (110) surface in aqueous 0.1 M HClO₄ solution cycled at 50 mV/s. RHE stands for the reversible hydrogen electrode, *i_p* for peak current, and *v* for sweep rate. The dotted lines indicate the high reversibility of the Faradaic adsorption processes. Adapted from ref 15. Copyright 2004 American Chemical Society. (E) Cyclic voltammogram of a RuO₂·0.5H₂O electrode in aqueous 0.5 M H₂SO₄ solution cycled at 2 mV/s. SCE stands for the standard calomel electrode. Adapted with permission from ref 24. Copyright 1995 IOP Publishing. (F) Cyclic voltammogram of T-Nb₂O₅ nanocrystalline film in a nonaqueous Li⁺ electrolyte cycled at 0.1



Adv.Energy Mat 9 (2019) 1902007 Mathis ..

Energy Storage Data Reporting in Perspective - Guidelines for Interpreting the Performance of Electrochemical Energy Storage Systems

Lead Battery Advancements (ALBA) May 18-20, 2026, Mainz, Germany

Mathis et al. Advanced Energy Materials, 2019, 9 (39): 1902007c

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



C.I Mechanisms behind '**pseudo-capacitance**' Slope

c) WHAT DOES a PSEUDO-Capacitor upon no-load periods :

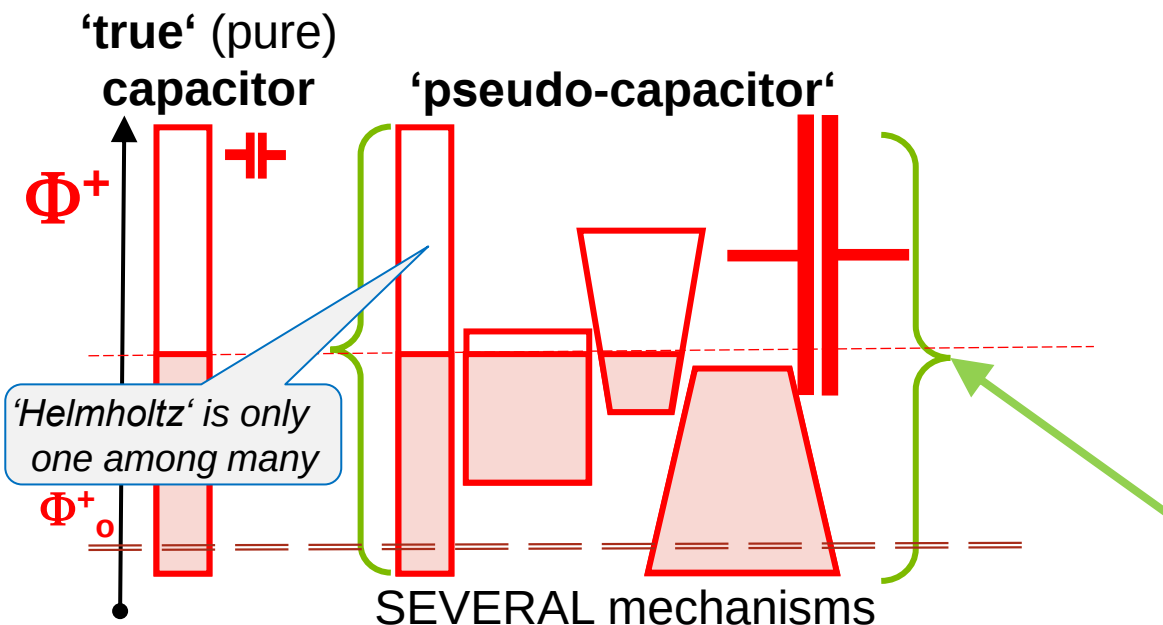


(superposition of several)
(mostly) **charge-transfer reactions**,
(together) showing '**capacitance-like**'
electric behaviour
most Charge stored (electro-)CHEMICALLY

several DIFFERENT mechanisms !

DIFFERENT kinetics / mechanisms contribute DIFFERENTLY
to electrical current during electrical load periods

(upon both DIScharge and RECharge),
→ may lead to temporarily DIFFERENT **SoCs** !



upon no-load periods:

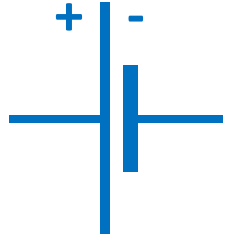
equilibration of potential

... among DIFFERENT storage mechanisms
within '**pseudo-cap**' (internal)

⇒ **equilibration #1:**

all '**pseudo-cap**' mechanisms to SAME **SoC**

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



C.I Mechanisms behind 'pseudo-capacitance' Slope

c) WHAT DOES a PSEUDO-Capacitor after End of Recharge ?

- EXIDE exp. finding: *curved slope* $U(t)$ @ SoF-test load = 1 A/Ah_{nom} (const.) ! $C(\Phi) \sim 1 / \text{slope}$ INCREASING

IMPORTANT: we need to distinguish various types of decline of pos. Potential Φ^+ after end of REC !

1) under external electrical $i(t)$
(e.g. SoF test, e.g. @ $i=\text{const}$)

DIS of "pseudo-cap" to external circuit

DIS current $i(t)$ is externally pre-defined / measurable

vs.

2) free (currentless) relaxation

DIS of "pseudo-cap" to internal (other, "sink") reaction

DIS current $i(t)$ is NOT pre-defined / NOT measurable

$|i(t)|$ is declining: $d/dt |i(t)| < 0$ N.B. $i(t) < 0$

discharge overvoltages of both "pseudo-cap" and "sink"
change (differently) in unknown manner,
while current $|i(t)|$ is decreasing

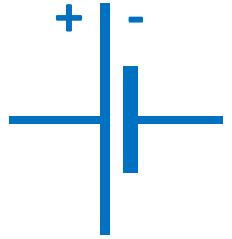
3) forced relaxation

forcing potential quickly to (known) final (equilib.) value, using a potentiostat

DIS current $i(t)$ can be measured and [Ah] integrated

cf. W.Borger, U.Hullmeine, H.Laig, E.Meissner, RELAXATION OF POTENTIAL RESISTANCE AND CAPACITY IN FLOW-THROUGH PbO₂ ELECTRODES
in: Keily & Baxter (eds.), Power Sources 12 (1988) 131-145, Proc. of 16th Int. Power Sources Conf., 1988, Bournemouth

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



C.I Mechanisms behind ‘pseudo-capacitance’ Slope

c) WHAT DOES a PSEUDO-Capacitor after End of Recharge ?

case of @open circuit = ‘**Pause**’: Equilibration Currents, Relaxing Voltage

“pseudo-cap” = superposition

- SEVERAL different pseudo-cap mechanisms with DIFFERENT kinetics (*all connected in parallel*), i.e. mechanisms may contribute DIFFERENTLY to electrical current during electrical load periods (upon both DIS and REC),
→ leading to temporarily ‘DIFFERENT SoCs’ !

SoC(1), SoC(2), SoC(3), ...



upon no-load period - equilibration #1:
... among various storage mechanisms within ‘pseudo-cap’

“battery” and “pseudo-cap”

- different mechanisms with DIFFERENT kinetics (*while connected in parallel*), i.e. mechanisms do contribute DIFFERENTLY to electrical current during electrical load periods (upon both DIS and REC),
→ leading to temporarily ‘DIFFERENT SoCs’ !

SoC(pseudo-cap -total), SoC(batt)



upon no-load periods - equilibration #2:
... among ‘pseudo-cap’ and ‘battery’

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

C.I Mechanisms behind 'pseudo-capacitance' Slope

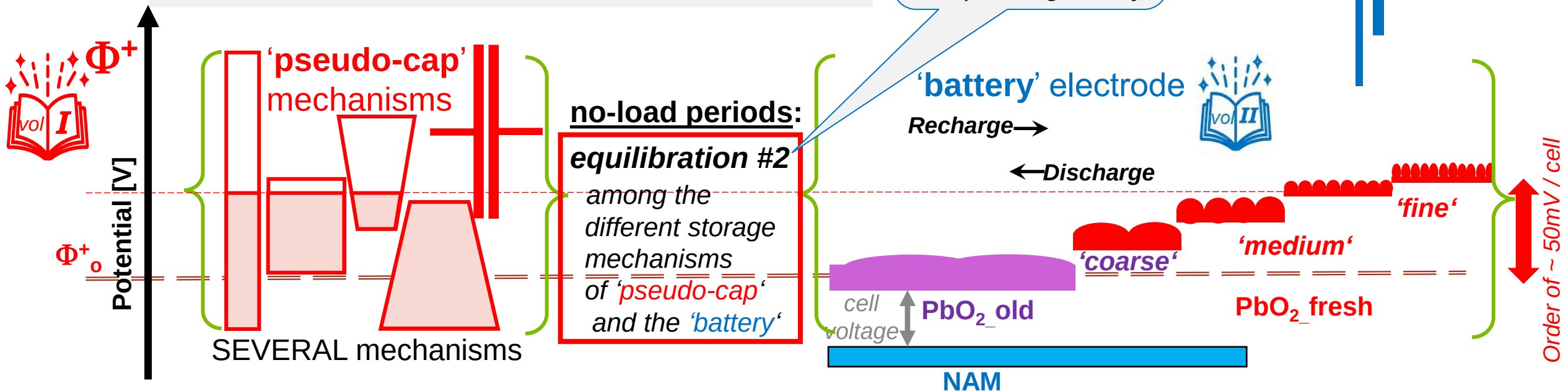
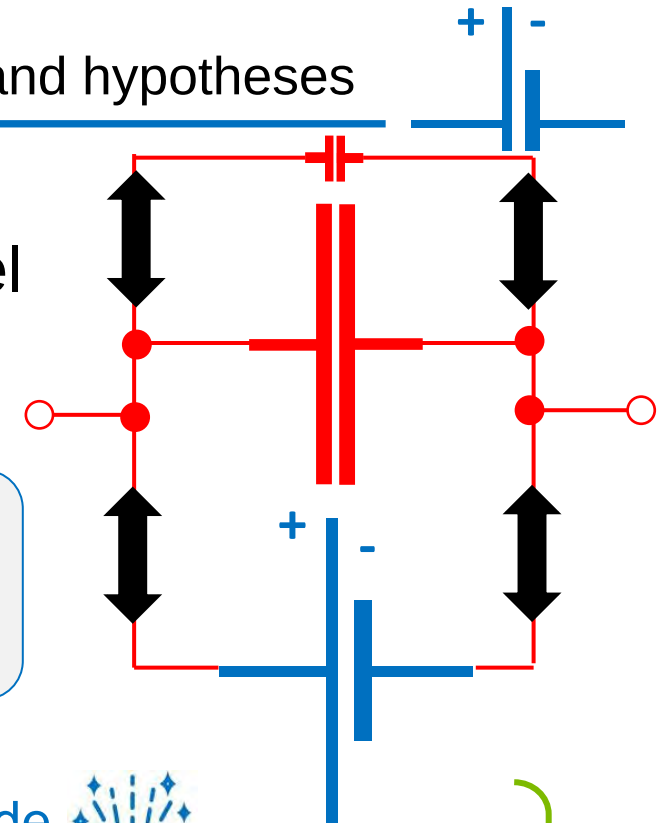
d) 'Helmholtz' ↔ 'pseudo-cap' ↔ 'Battery' in parallel

@open circuit = 'Pause': Equilibration, Voltage Relaxing

DIFFERENT kinetics of 'pseudo-cap' and 'Battery'

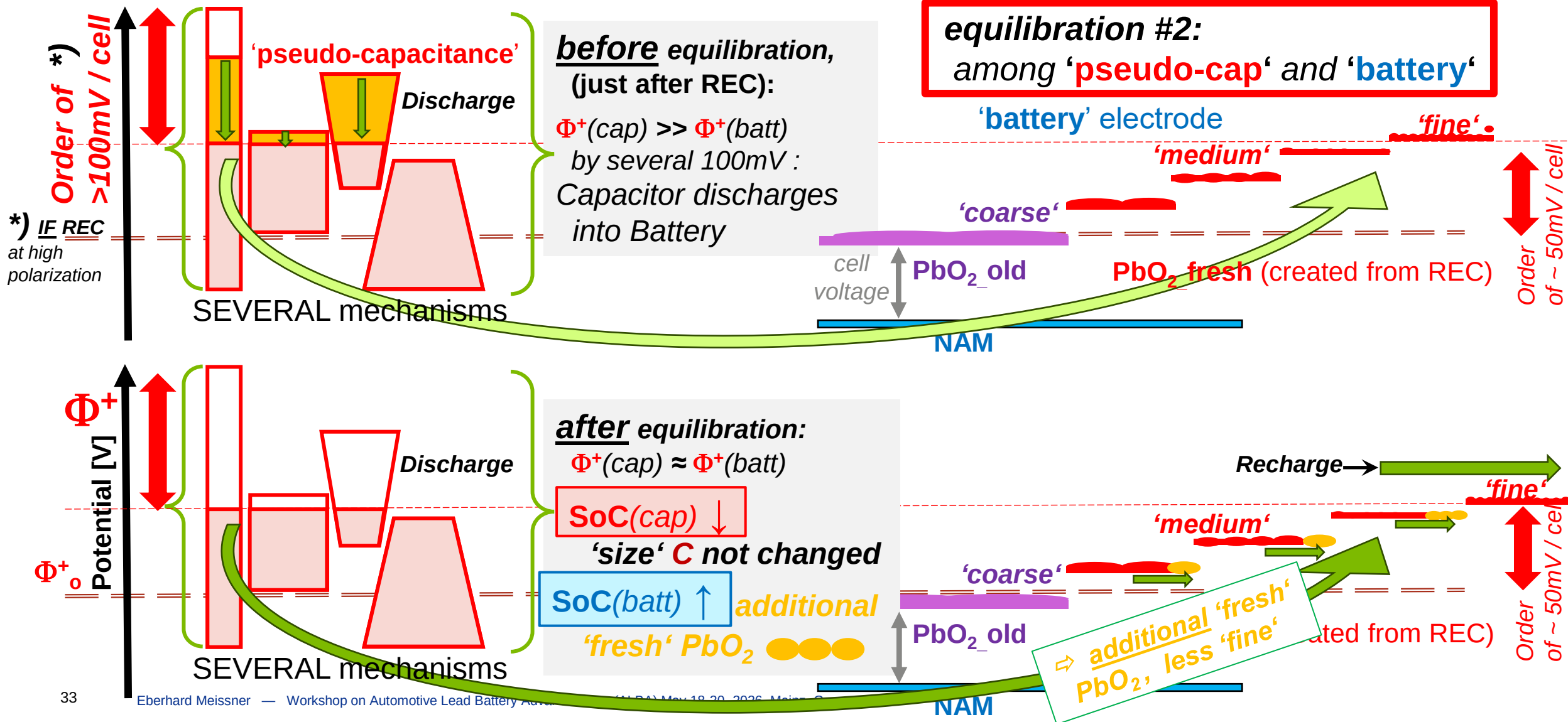
⇒ mechanisms contribute DIFFERENTLY
to electrical current during electrical load periods
(upon both DIScharge and RECharge),
→ leading to temporarily 'DIFFERENT SoCs' !

Direction of
equilibration currents
depend on kinetics
and operating history



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

Equilibration Currents and **Relaxing Voltage:** case of @open circuit = “**Pause**”



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

C.I Mechanisms behind 'pseudo-capacitance' Slope

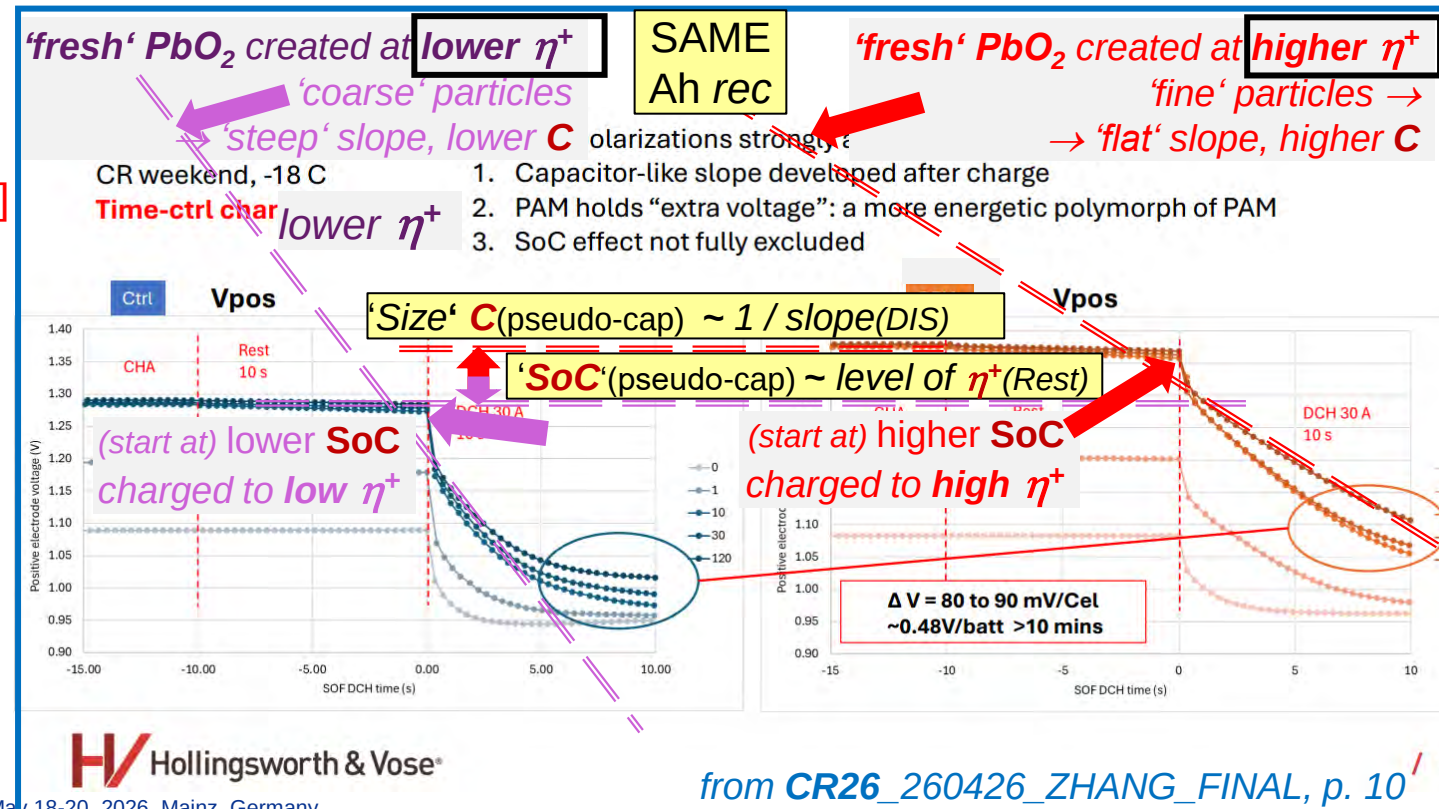
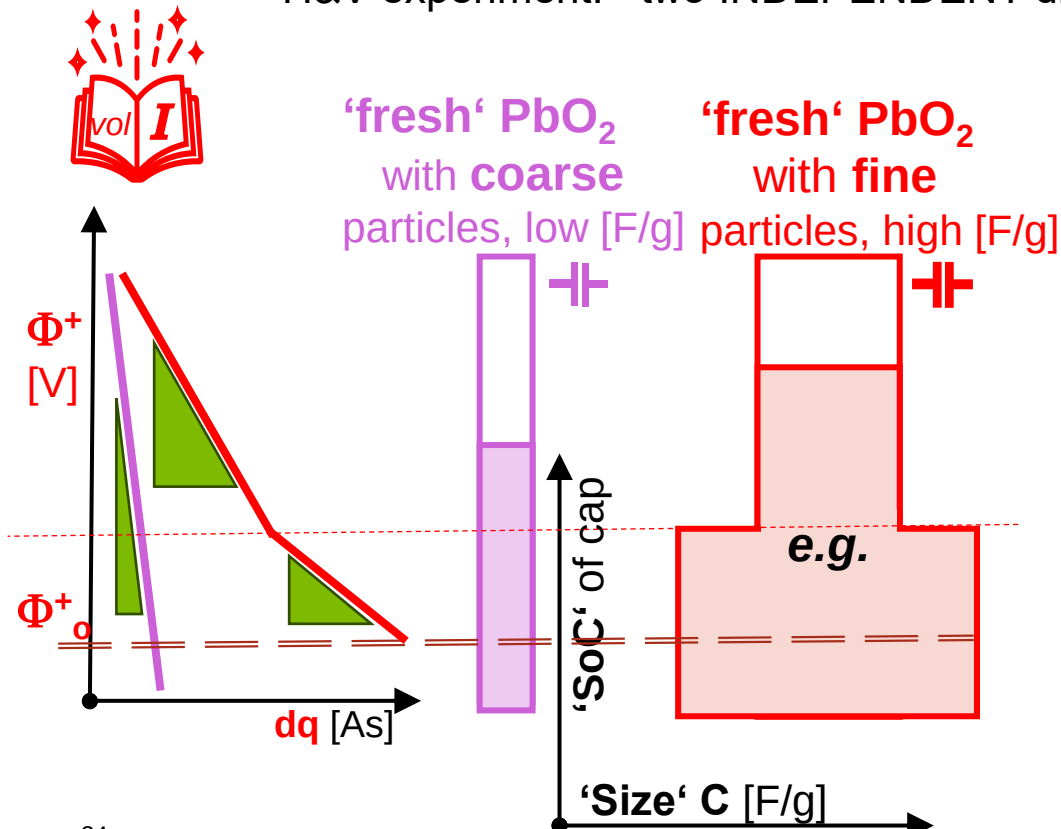
a) .. PSEUDO-Capacitor has two INDEPENDENT dimensions !

- (i) "Size **C**" of pseudo-cap [F], related to overall properties of all sizes of PbO₂ material particles ('fresh' dominating !)
- (ii) "SoC" of pseudo-cap [%], related to (not prop.to as with Helmholtz) actual potential ($\Phi^+ - \Phi^+_o$) = η^+

- H&V experiment: two INDEPENDENT dimensions of 'pseudo-cap': Capacitance **C** and **SoC**

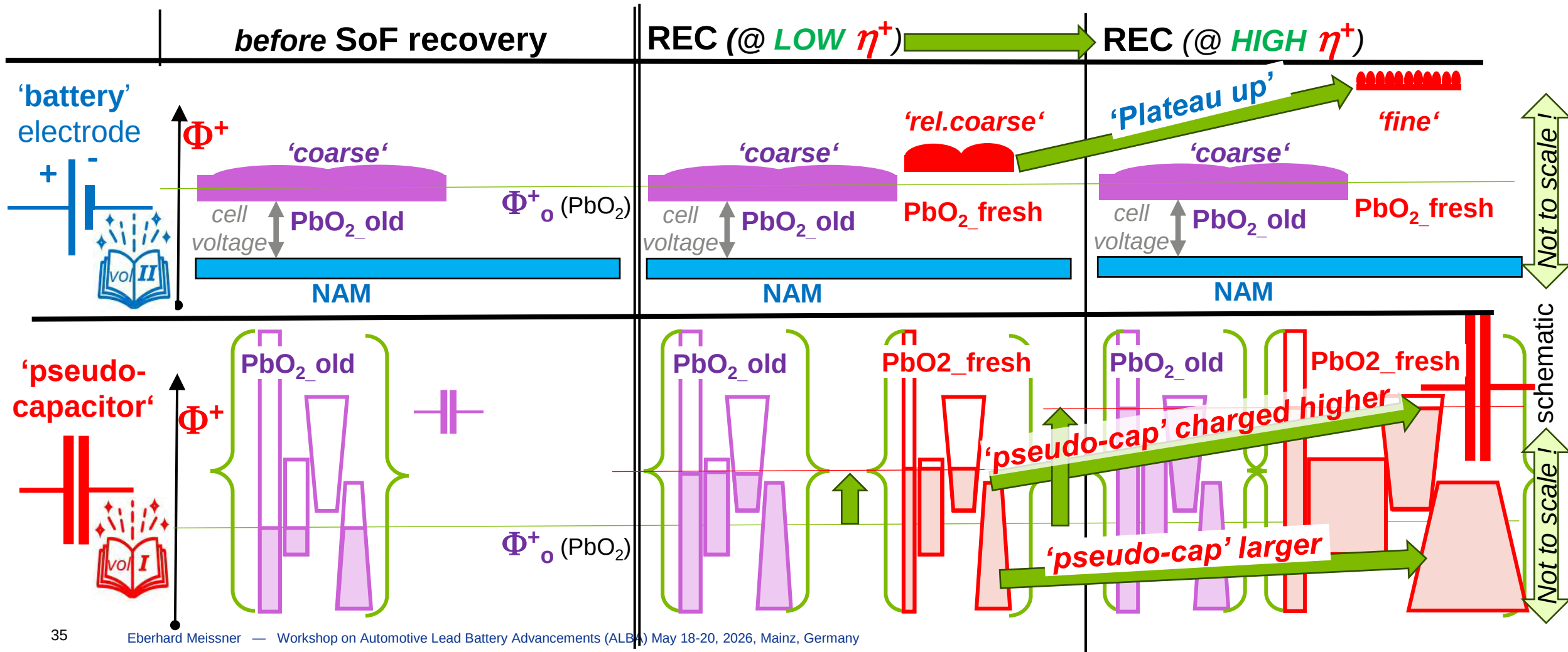
after SoF recovery:

this "fresh" is special !



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

C.I + C.II Mechanisms behind **'uplift of discharge Plateau'** + **'pseudo-capacitance' Slope**
 high positive polarization η^+ [V] is good for both **'Plateau uplift'** and **'Slope'**



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'*

SoC(pseudo-cap) $\downarrow \Rightarrow$ **SoC(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. **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) $\uparrow \uparrow \gg$ 100mV $\uparrow$

[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: SoC(pseudo-cap)** $\downarrow \Rightarrow$ **SoC(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')

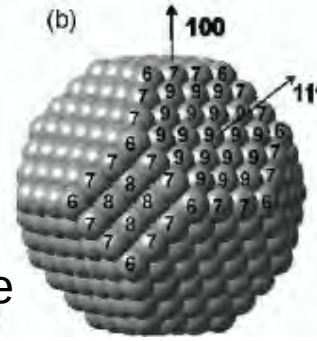


naive macro-homogeneous vision:

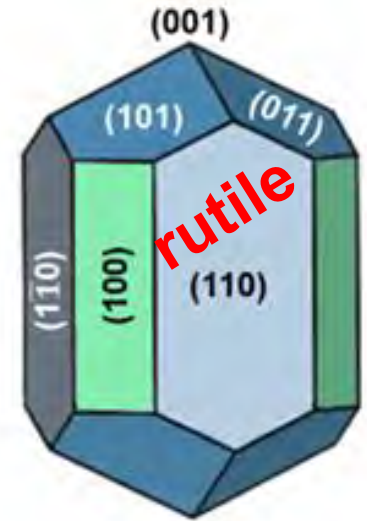
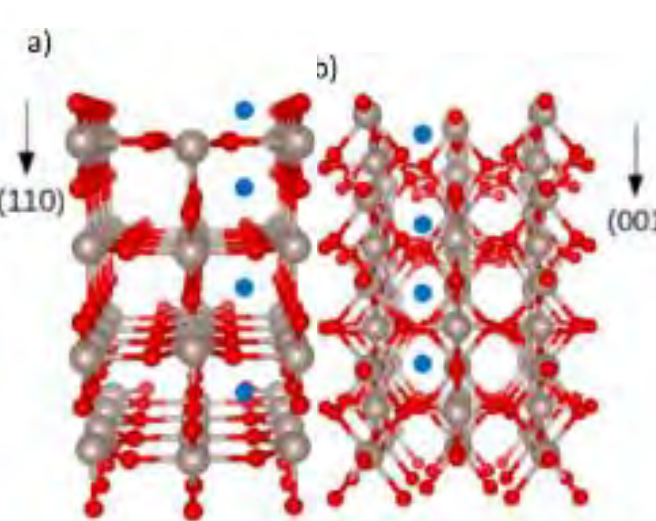
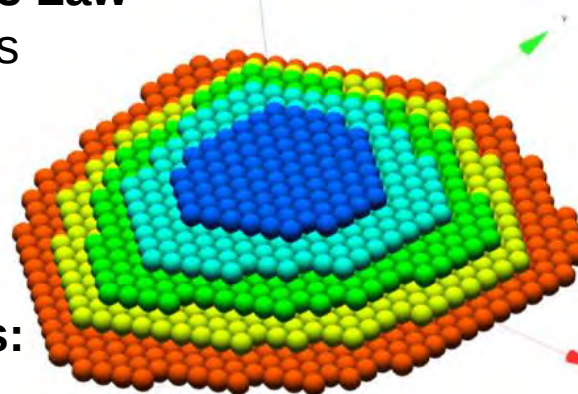
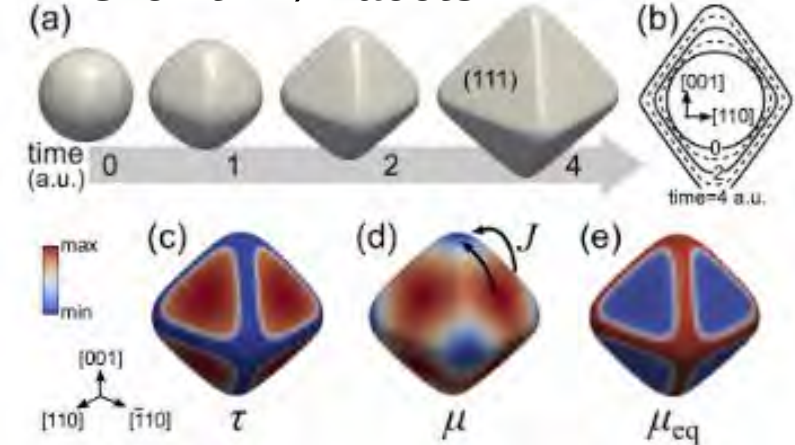
- small ball-shaped nuclei, smooth surface

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^- , $O \dots$) depends on orientation



Growth → Facets



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

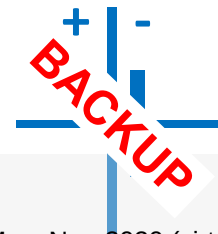
CR11: References to Conference Presentations addressing topics in this context & Key messages and caveats



- [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)

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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>