

A fresh look at the Negative Active Material: three types of electrochemical reaction occurring simultaneously in the same location

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- **NAM Surface Capacitance** (charge/discharge) **PHYSICAL** Reaction Helmholtz Double Layer (solid/liquid interface) cf. e.g. [P14], [P15], Tiedemann, Newman J. Electrochem. Soc. <u>122</u> (1975) 70
- Oxidation of organics and carbon

pasting paper, additives (fibres, expander components, ...)

CHEMICAL Reactions

cf. Appendix for References to previous Conference Presentations [P1 - P16], further [References], Tables









Motivation for *"Fresh Look"* at NAM Narratives around (textbooks, papers) not coping with experiments **NAM** self discharge ! [11] a) H₂ evolution at NAM only upon overcharge [1] underpressure in VRLA upon stand ! [12] [P9,P10] O₂ reduction at NAM only upon overcharge [2] b) O₂ cycle with flooded known since ~1960 [13] [P1,P5,P12] O₂ reduction at NAM only with VRLA [3] C) applies for SEALED Ni/Cd, excess NAM capacity in VRLA, for PAM to go into overcharge first [4] d) but NOT for VRLA [14] "thin liquid film layer" on geometric surface of NAM [5] in VRLAe) fine **NAM** pores completely filled with e'lyte; "liquid film" in wide NAM pores "forced O₂ gas feed to NAM pores" - pressure-injected, as an **f**) NO pre-requisite for O₂ reduction enabler for O₂ reduction through "thin liquid film layer" [6] AGM partial pressure of O_2 in **AGM** separator << capillary pressure in fine **NAM** pores Electrolyte film ~0.01 µm ~0.1 um **e** $D_{0_{0}} = 9 \times 10^{-6} \text{ cm}^2 \text{ s}^2$ $= 9 \times 10^{-6} \text{ cm}^2 \text{ s}^3$ At fine-jet flow (Fig. 1 (II, II')), the gas has its excessive pressure $\Delta P \ge 4\sigma/D_2$ ($D_2 \gg D_1$), and gas ionization occurs in the electrode Positive electrode pores. Such a type of flow is characteristic of very fine-porous, soft from: Encyclopedia of Electrochemical NAM Power Sources, Elsevier, 1st Ed., 2009 from: SECONDARY BATTERIES -JPS 209 (2012) 289-294 ≈ LEAD–ACID SYSTEMS - Overview Elektrokhimiya 19 (1983) 200-2 Π

gure 6 Conceptual view of internal oxygen cycle in a valve-regulated lead-acid cell. Reproduced from Nelson (1999).

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Motivation for "Fresh Look" at NAM: narratives contradicting physical basics



-1:.

negativ	ve active mater	al					
NAM:	'Sponge Lead (+ additives, PbSO	,)	 porous metallic structure open micro- and meso-pores cf. [P4] NAM much wider pores than PAM high internal surface area high electrical conductivity 				
		Fig. frc J. Pow	<i>⇒</i> a perfe for elec om: Pavlov et.al., rer Sources <u>7</u> (1981) 153	<i>lace!</i> pore size dist	free of e'lyte with VRLA: ribution		
Tab.1:	NAM characteristics	symbol	typ. values (est'd)		0.10 - Fi	g. 10.19(a); p.466	(a)
Pb spec	. density	ρ (Pb)	11.3 g/ml		 م. 0.08 -		
NAM ap	parent density	<u>ρ (NAM)</u>	~ 4 g/ml		0.06 -	NAM	pores
NAM p	orosity	р	~ 60 vol%		ung 0.04 -	0.1	1.10μm
NAM p NAM tor	ore radius tuosity factor	R τ	~0.1 1 ~10 μm ~ 1.6	-i	Peo 0.02 - Fig. 11.12; p.493	PAM pores .02 <mark>0.1</mark> 1μm	
NAM sp	ec. pore volume	V _{por}	~ 0.15 ml/g		0.001 0.002 0.005 0.01 0.02	0.05 0 1 0.2 0.5	1 2 5 7 10
NAM sp	ec. pore surface area	A _{por}	~ 0.3 m²/g		Fig. from [P4], after D. Pavi	ov, Lead-Acid Batterie	əs, Elsevier 2011
5 Eberha	o mass utilization (@nom.cap.) ard Meissner — 19 ELBC 2024, 16-19 Sept	m.u.(Pb) ember 2024, Milan	~ 8 g Pb/Ah _{nom}		PAM Fig. 10. 19(a), p. 466, orig NAM data included, converted Fig. 11. 12, p. 493, origin	ginally from [JEcS 133 I from data taken from ally from [JEcS 121 (<i>ו (1986) 241]</i> ז 1974) 854]

Reactions at NAM: Pb/PbSO₄; PbO₂/PbSO₄; H_2^{\uparrow} ; O_2^{\uparrow} ; O_2^{\downarrow}



[II] H_2^{\uparrow} evolution at NAM possible whenever $\Phi^{-} < 0.0V$ [III] O_2^{\downarrow} reduction at NAM possible whenever $\Phi^{-} < +1.23V$

O₂↓ when reaching **NAM**

 \Rightarrow NO electrical overcharge required for [II] and [III]

i.e. **always**,

(reactions may proceed also during rest and discharge periods)

cf. [P5]

cf. D.Berndt, Maintenance-Free Batteries; 2nd ed., Wiley New York 1997; Chap.4 D.Berndt and U.Teutsch, J. Electrochem. Soc. 143 (1996) 790-798

as Pb/PbSO₄ potential < ≈ -0.3 V

(a))

 (\mathbf{b})



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3) Gas Interaction in NAM ? Oxygen Reduction $O_2 \downarrow$ Hydrogen Evolution _H₂↑ n^{headspace} ≈1bar $[III] (O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O)$ [II] $2 \operatorname{H}^+ + 2 \operatorname{e}^- \rightarrow (\operatorname{H}_2)$ (VRLA≈1.1bar) eʻlvte sep. where ? when ? how much ? H, gas, O, gas. Sink for O₂ Source of O **O**₂ generated inside **PAM** pores (@ fluctuating rate) $c(O_2) \rightarrow 0$ $C(O_2) < C_2$ NAM released to e'lyte p(headspace) =1bar / 1.1bar \Rightarrow always $p(O_2) \leq 1$ bar; $c(O_2) \leq c_{sat}(O_2)$ \mathbf{O}_2 [16] PAM O₂ TRANSPORT LIMITATION to NAM cf. [P5] $\Rightarrow p(O_2) < 1$ bar; $c(O_2) < c_{sat}(O_2)$ intermediate O₂ storage [P1,P5,P9,P12], [10] H₂ excess 0, ⇒ smoothed diffusion supply to NAM surface 0. **penetrating NAM**: " $O_2 \downarrow$ reduction is fast" [16] storage \Rightarrow O₂ cannot persist \Rightarrow $c(O_2) \rightarrow 0$ at NAM O_2 sink throttle tank O_2 source **Current Density** $C(O_2)$ cf. [P10,P12] \Rightarrow O₂ low penetration depth X into NAM ground resistor capacitor current <10⁻³ mol/L \Rightarrow $c(O_2) \approx 0$ in deeper layers of NAM cf. [P10,P12] poredepth of penetration R ≈ 0.1 mm ر**€(O**2) cf. [P5,P9] Profile of $c(O_2)$ E'lvte $C_{sat}(O_2)$ $C_{sat}(O_2)$ NAM TRANSPORT $C(O_2)$ LIMITATION PAM

NAM

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3) Gas Interaction in NAM ?



Capillary Pressure increasing gas pressure in bubbles



gas in <u>submersed bubble</u> experiences increased pressure vs. <u>free gas</u> ! $p^{G}_{bubble} = p^{G}_{free} + p^{hyd} + p^{cap} > p^{G}_{free}$

- > hydraulic pressure $p^{hyd} = h \cdot \rho (e'lyte) \cdot g$ $\rho (e'lyte) \approx 1.28 \text{ g/ml}; g = 9.81 \text{ m/sec}^2$
- > capillary pressure $p^{cap} = 2 \cdot \sigma (e'lyte) / R$ surface tension $\sigma (e'lyte) \approx 0.075 \text{ N/m}$
- cf. [P8] curvature of bubble 1/R, R = bubble radius
 - ⇒ higher gas solubility near small bubbles !
 - ⇒ small gas bubbles (small R) may not be stable

Table 2: cap. pressure + conc. of dissolved gas $c^{L}(G) = f(R)$

NAM pore size	R≈	p ^{cap} ≈	c(H₂) ≈	e.g.	$\mathbf{G}=\boldsymbol{H}_2$
free bubble	150 μm	0.01 bar	1.01·c _{sa}	t = 0.44	·10 ⁻³ mol/L
wide pore	15 μm	0.1 bar	1.1.c _{sat}	= 0.47	·10 ⁻³ mol/L
medium pore	1.5 μm	1.0 bar	2·c _{sat}	= 0.86	·10 ⁻³ mol/L
fine pore	0.15 μm	10 bar	11∙c _{sat}	= 4.8	·10 ⁻³ mol/L
typ. range of NAM pol cf. Tab.1	res,	'	cf. Tab.3	for mater	ial properties (backup)

Transport of H₂ in NAM pore structure

- when H_2 bubble is constricted in a NAM pore: $p^G(H_2) > p^{headspace} \approx 1 bar!$
- H_2 bubbles with small R (high $p^G(H_2)$) not stable, unless conc. $c^L(H_2)$ of dissolved H_2 is high
- 1. temporary H_2 bubbles in small pores **dissolve**
- 2. dissolved H₂ diffuses to wider pores and ... cf. OSTWALD Ripening of fine crystals !
- 3. ... finally reaches **NAM** outer surface (free electrolyte)
- 4. **ONLY IF** $c^{L}(H_{2}) > c^{L}_{sat}$ at **NAM** outer surface, $p^{G}(H_{2}) > 1$ bar - non-constricted H_{2} bubbles (*typ.* $R > \approx 150 \mu m$) may form - may **detach** from surface and rise to headspace
- 5. ONLY THEN, H₂ formed inside NAM may leave the cell



cf. electrodes in <u>Electrolyzer</u> [9]: $2 H_2O \rightarrow 2 H_2 + O_2$ H_2 diffusion in porous H_2 -evolving electrodes; transport rate strongly enhanced by steep $c^L(H_2)$ gradient due to high $p^G(H_2)$ in electrode interior little H₂ evolution needed to establish high H₂ conc. gradient: <u>Rough Estimation:</u> NAM pore volume ≈1.2 ml/Ah *) - dissolved H₂ reaches saturation c^L(H₂) already from 0,052 As/Ah *) electrolysis - theoretically, NAM pores filled with H₂ gas from 10 As/Ah *) *) cf. material properties, Tables 1, 2, 3, 4 (backup)

Transport of O₂ in NAM pore structure



cf. **Tab.3** for material properties (backup)



H₂ bubbles in NAM pore system may facilitate O₂↓ reduction !

effect expected to be especially **beneficial in dynamic and PSoC** battery duties: low DoD, short REC phases when H₂↑ and O₂↑ evolution are not steady and synchroneous, but dynamic, alternating, short period ⇒ O₂↓ reduction of stored O₂↓ [P1,P5,P9,P12], [10] continues upon Rest and DIScharge phases

VRLA: what makes the difference ?



<u>ALSO with VRLA</u>, e'lyte-filled fine NAM pore network impedes diffusion of dissolved O₂ to 'dry voids' in NAM: diffusion distance >> ≈100nm, far more than just through a "thin liquid film layer" [3,5,6] !

'dry voids' a) facilitate O₂↓ transport ⇒ when O₂ evolves at PAM (RECharge), c^L(O₂) may increase at NAM surface in AGM
 b) additional O₂ storage capability [Mol O₂/L], cf. [10], Tab.3: O₂ reduction also upon Rest and DIScharge ⇒ VRLA effect especially beneficial in dynamic and PSoC battery duties [P1,P5,P9,P12]

- NAM Main Reaction: [I] charge/discharge Side Reactions: [II] H₂↑ evolution [III] O₂↓ reduction independent: ONLY actual NAM potential Φ⁻ defines about currents iⁱ of main and side reactions
 Kirchhoff's Law i^{cell} = i^{neg} = i(main) + i(H₂↑) + i(O₂↓) ⇒ defines Φ⁻ Mixed Potential; NO CONTROL from external electrical current i^{cell}
- \succ ⇒ H_2^{\uparrow} evolution and O_2^{\downarrow} reduction <u>at any time</u>, incl. Rest and DIScharge → stored O_2^{\downarrow} can be reduced !
- Capillary Pressure in constricted bubbles (NAM pore, AGM pore): p^G(bubble) > p^G(cell headspace) + p^{cap}(R) prevents e'lyte-filled fine NAM pores from being displaced by gas pressure from outside, also with VRLA
- > VRLA 'dry voids': no vacuum, but gas phase (H_2 or mixed H_2 / O_2 bubbles, depending on operating phase)
- $\begin{array}{c} & O_2 \downarrow \text{ reduction is fast at NAM} \\ \text{ sparse (diffusion-controlled) } O_2 \text{ supply} \end{array} \begin{array}{c} \Rightarrow & \text{low conc. } c(O_2) < c_s(O_2) \\ \Rightarrow & "O_2 \text{ gas bubbles" cannot persist at NAM surface} \\ \Rightarrow & NO "pressure-forced O_2 \text{ bubbles" penetrating liquid-filled NAM pore structure / "electrolyte film"} \end{array}$
- \succ 'dry voids' (VRLA) and H₂ bubbles (flooded) in NAM pore system may facilitate O₂ \downarrow reduction
- > $O_2 \downarrow$ storage → more time for $O_2 \downarrow$ in dynamic operation, when $H_2 \uparrow$ and $O_2 \uparrow$ evolution not steady / synchroneous, but *alternating*: long-term PSoC duty, short REC periods, cf. [P1,P5,P6,P10,P12] → rate of $O_2 \downarrow$ reduction less critical !
- > additional O₂ storage in VRLA 'dry voids' [10]: further benefit of VRLA in dynamic applications, reducing water loss

- > many narratives about LAB are based on historic views and interpretations often outdated [8]
 - related to **old cell designs** e.g. with old PbSb alloys: $i(H_2^{\uparrow}) >> i(O_2^{\downarrow})$ in flooded design
 - valid only for **float duty** @ **SoC**→**100%** (*long-term constant-voltage*)
 - conclusions from experiments at unrealistic conditions, e.g. excessive overcharge rates ...>0.1 A/Ah [3a,b]
 - VRLA: naive (incorrect) carry-over from gas-tight Ni/Cd cells (= truly sealed, H_2O stable, no $H_2\uparrow$)
 - VRLA: improper target definition, e.g. capability for high O₂ transport upon overcharge seen as primary target
- > assumptions / simplifications made, some explicitly, many implicitly
 - **stationary** operating duty ($U^{cell} = const$, $i^{cell} = const$), "long enough time $t \rightarrow \infty$ "
 - transients ignored internal reactions instantaneously equilibrated after change of external conditions
 - fully charged: SoC→100%; assuming same SoC of PAM and NAM but cf. [P5]
 - assuming gassing to be stoichiometric (H_2^{\uparrow} : O_2^{\uparrow} = 2:1 vol) and simultaneous at PAM and NAM but cf. [P9]

BUT

- > with modern cell designs ('maintenance-free', VRLA), ratio of parasitic reactions has shifted
- with modern battery applications and duties (dynamic, PSoC), former times' simplifications no longer apply
 conclusions made decades ago may misdirect today !
- > Lead-Acid chemistry and physics have not changed but WE have changed a lot in design and application

it's OUR responsibility to be sceptical: check for plausibility and consistency of statements and conclusions ! consider views / background of authors & state of knowledge at time of publication !

NAM material characteristics

Tab 2: Material Properties



Pore radius, um

	Tab.5. Material Froperties	J		Value		
	spec.density Pb _{met}	$ ho (Pb_{met})$		11.3 g/ml		
	Molar gas volume (25°C, ideal gas)		\mathbf{V}_{mol}	24'790 ml/mol		
	Faraday constant		F	96'485 As/mol		
	Surface tension of e'lyte		σ	0.075 N/m		
	Solubility of H ₂ in e'lyte (p=1bar)		$c^{L}(H_2)$	0.43 ·10 ⁻³ mol/L	4	
O ₂ :	Solubility of O ₂ in e'lyte (p=1bar)		$c^{L}(O_2)$	0.65 ·10 ⁻³ mol/L	H ₂ : x100	
x63	Conc (all, ideal) gasses (gas phase)		c ^G (gas)	41 ·10 ⁻³ mol/L	◄	
	Diffusivity of dissolved H ₂ in e'lyte		$\mathcal{D}^{L}(H_2)$	3·10 ⁻⁵ cm ² /sec		
	Diffusivity of dissolved O ₂ in e'lyte		$\mathcal{D}^{L}(O_2)$	0.8 ·10 ⁻⁵ cm ² /sec		
	Diffusivity of H_2 in gas		$\mathcal{D}^{G}(H_2)$	1.6 cm ² /sec		
	Inter-Diffusivity of H ₂ +O ₂ gasses	\mathcal{D}^{G}	$(H_2 \leftrightarrow O_2)$	0.74 cm ² /sec		
	Diffusivity of O ₂ in gas		$\mathcal{D}^{\mathbf{G}}(O_2)$	0.18 cm ² /sec		
	TAFEL slope of H ₂ evolution			≈ -120mV/dek		
	TAFEL slope of O ₂ evolution			≈ +80mV/dek		
	Data at T \approx 25°C; e'lyte = sulfuric acid, $c \approx$ 4 mol/L					

Symbol

Valuo

Ratio of gas conc. [mol/L] in gas phase vs. dissolved in e'lyte: **O**₂: x63 **H**₂: x100



Tab.4: derived Material Properties	calculation	calculated Value
NAM pore volume / Ah _{nom}	V _{por} * m.u.(Pb)	≈1.2 ml/Ah _{nom}
NAM pore surface area / Ah _{nom}	A _{por} * m.u.(Pb)	≈2.4 m²/Ah _{nom}
NAM apparent volume utilization V.U.(NAM)	m.u.(Pb) / $ ho$ (NAM)	≈2.5 ml/Ah _{nom}
NAM Pb volume utilization V.U.(Pb)	m.u.(Pb) / $ ho$ (Pb)	≈0.88 ml Pb/Ah _{nom}
H ₂ gas evolution: vol. per charge equivalent	\mathbf{V}_{mol} /2 $m{\mathcal{F}}$	≈462 mL H ₂ /Ah
Charge of H_2 gas [Ah] possibly stored in NAM pores /Ah _{nom} (p=1bar)	≈0.26% DoD	≈9.5 As/Ah _{nom} ≈2.6 mAh/Ah _{nom}
Charge of diss. H ₂ [Ah] in e'lyte (p=1bar)	$c^{L}(H_2)$ * 2 \mathcal{F}	≈43 As/L ≈12 mAh/L
Charge of diss. H ₂ [Ah] possibly stored in NAM pore e'lyte (p=1bar)	≈0.0015% DoD	≈0.052 As/Ah _{nom} ≈0.015 mAh/Ah _{nom}
O ₂ gas evolution vol. per charge equivalent	\mathbf{V}_{mol} /4 $m{\mathcal{F}}$	≈231 mL O ₂ /Ah
Charge of diss. O ₂ [Ah] in e'lyte (p=1bar)	$c^{L}(O_2)$ * 4 \mathcal{F}	≈62 As/L≈17 mAh/L
O ₂ gas evolution vol. per charge equivalent	\mathbf{V}_{mol} /4 $m{\mathcal{F}}$	≈231 mL O ₂ /Ah
Charge of diss. O ₂ [Ah] possibly stored in total cell e'lyte [10]	≈0.07 - 0.1% DoD	≈0.7 - 1 mAh/Ah _{nom}

Data at $T \approx 25^{\circ}C$; e'lyte = sulfuric acid, $c \approx 4$ Mol/L



- [P1] E.Meissner @ Workshops "High-Temperature Durability Tests for Advanced Lead–Acid 12-V Batteries"
 - Kloster Eberbach, Gerrnany, 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 O₂ 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 PbSO₄ 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 PbSO₄ in NAM; Modelling of NAM Recharge;
 - Recommendation to design a fine pore structure for NAM, to give no room for growth of coarse PbSO₄ 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 , PbO₂ 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: O₂ Intermediate Storage Acting as a Charge Buffer", presented at AABC Europe, Wiesbaden Jan. 2020 - dynamic battery operation: i_{O2-red}@NAM **NOT** synchronous to i_{O2} @PAM; O₂ recombined at NAM generated MUCH EARLIER at PAM & stored intermediately
 - *) Full Title of series of **EFB Workshops**: "DCA and Heat": Testing Charge Acceptance and High Temperature Durability for Advanced Lead 12 V Batteries; organized by CENELEC and Consortium of Battery Innovation, Jan. 2017 (Eberbach), May 2018 (Alcala), May 2019 (Bruges), May + Nov 2020 (virtual), June 2022 (Bergamo)



*) 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) "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 O₂ Reduction Reaction at NAM", presented 12AABC Europe, Mainz June 2022 - charge acceptance of NAM degraded by O₂ recombination at NAM in PSoC duty (O₂ reduction during non-charge phases enhances Ostwald Ripening of PbSO₄)

- [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, O₂ Reduction Reaction, Ostwald, SoC imbalance
- [P12] E.Meissner, "Oxygen Reduction Reaction promoting Ostwald Ripening of PbSO₄ Crystals at NAM Electrode Surface", presented at 18ELBC, Lyon, Sept. 2022
 - O₂ reduction preferably at NAM geometrical surface; local discharge promotes PbSO₄ Ostwald Ripening and imbalance SoC(Pb) < SoC(H₂SO₄) < SoC(PbO₂)
- [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

Many aspects from [P1-P16] are addressed in

- [10] E.Meissner, "Valve-regulated batteries: Oxygen Cycle", Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, Elsevier, 2023, ISBN 9780124095472, <u>https://doi.org/10.1016/B978-0-323-96022-9.00067-0</u>. (https://www.sciencedirect.com/science/article/pii/B9780323960229000670)
- cf. E.Meissner, "Lead-Acid Systems Valve-regulated batteries: Oxygen Cycle" in: J.Garche et.al. (eds.), Encyclopedia of Electrochemical Power Sources, 2.ed., Elsevier, 2024, ISBN: 9780323960229 / 9780323958226

Further References

 Moseley, High rate partial-state-of-charge operation of VRLA batteries, J. Power Sources <u>127</u> (2004) 27 (TABLE 2) Moseley, Rand, Changes in the demands on automotive batteries require changes in battery design, J. Power Sources <u>133</u> (2004) 104 (TABLE 3)



- [2] see [1]
- [3] Nelson, Basic Chemistry of Gas Recombination in Lead-Acid Batteries, JOM <u>53,1</u> (2001) 28-33 (Journal of The Minerals, Metals & Materials Society) Moseley, Rand, Changes in the demands on automotive batteries require changes in battery design, J. Power Sources <u>133</u> (2004) 104 (TABLE 3)
 [3a] Kirchev et al., Gas-diffusion approach to the kinetics of oxygen recombination in lead-acid batteries, J. Power Sources <u>113</u> (2003) 245
 [3b] Pavlov et.al., Mechanism of the oxygen cycle reactions proceeding at the negative plates of VRLA batteries, J. Power Sources <u>144</u> (2005) 521
 Kazarinov, Burashnikova, Khomskaya, Kadnikova, A universal way for gas–liquid flow control in the design of hermetical lead-acid batteries, J. Power Sources <u>209</u> (2012) 289-294
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Further References

