## **Origin of the DCA Memory Effect**

The Role of the Pb<sup>2+</sup>/Organic Buffering Theory



### When We Last Spoke...

- We defined the concept of "DCA Memory"
  - DCA magnitude is inextricably linked to the process which came before  $\rightarrow$  the battery "remembers" what it just did
  - Measuring DCA post-discharge (ex.  $I_D$ ) typically provide a 3-5X higher value than measuring post-charge (ex.  $I_C$ )
- We suggested 3 theories to explain "DCA memory:
  - 1. Local Electrolyte Effect
    - Transient perturbations in SG following DCH (low SG) or CHR (high SG) provide a basis for hi/lo conductivity/current
  - 2. Lead Sulfate Ripening

- Continued in #515
- A subset of lead sulfate crystals reach a critical surface tension/energy which stabilizes them against dissolution, leads to gradually decreasing supply of Pb<sup>2+</sup>, and decreases charge current, particularly in Run-In
- 3. A Perturbation of Pb<sup>2+</sup> Diffusion Kinetics
  - [Pb<sup>2+</sup>] availability defines charge rate, but polymer-dynamicsdefined release of Pb<sup>2+</sup> from battery organics at high acid/salt (high SoC, or CHR-1<sup>st</sup> protocols) or low acid/salt (low SoC, or DCH-1<sup>st</sup> protocols) concentrations could explain the enhanced availability of Pb<sup>2+</sup> following DCH

One again, which process do you believe accounts for DCA memory in lead batteries?



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## Perturbation of Pb<sup>2+</sup> Diffusion as Memory Driver

#### THEORY

SO<sub>4</sub>

Pb

Transiently high SG

Morganic ● Pb<sup>2+</sup>

Pb<sup>2+</sup> supersaturation, locally driven by low SG/high Pb<sup>2+</sup> solubility, may be extended by interaction with organic expander following discharge (locally low SG, high Pb<sup>2+</sup> solubility = organic adsorption) not following charge (locally high SG, lower Pb<sup>2+</sup> solubility = no organic adsorption)



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## **Theoretical Calculations of Feasibility**

- ~52.0 μmol of Pb<sup>2+</sup> should be consumed in a single DCA event (10 s CHR at 1A/Ah), per Ah of rated capacity
  - 10 s pulse of 1 A/Ah = 10 As/Ah = 2.8 mAh/Ah of charge
  - Pb<sup>2+</sup> delivers 53.2 Ah/mol
  - 2.8 mAh/Ah / 53.2 Ah/mol = 52.0  $\mu$ mol of Pb<sup>2+</sup> /Ah
- ~7.5 nmol of Pb<sup>2+</sup> are available in NAM electrolyte due to solubility, per Ah of rated capacity
  - Equilibrated  $PbSO_4$  solubility in a pore electrolyte is ~0.005 mM
  - A high-porous NAM may have pore volume of ~0.15 ml/g, or ~1.5 ml/Ah
  - Amount of  $Pb^{2+}$  in pore electrolyte is therefore 1.5 mL/Ah \* 0.005 mmol/L = 7.5 nmol of  $Pb^{2+}/Ah$
- ~0.01% of needed Pb<sup>2+</sup> is available instantly, 99.99% from dissolution, oversaturation, or organic liberation
- 50 wt% of "Pb<sup>2+</sup> Buffer Capacity" must be provided by the organic to enable this theory
  - ~51.99 µmol Pb<sup>2+</sup> are missing \* 207.2 g/mol Pb/Ah = 10.77 mg Pb<sup>2+</sup>, per Ah of rated capacity
  - $~\sim 20$  mg of organic are deployed in the NAM, per Ah of rated capacity

# KEY QUESTION: How much Pb<sup>2+</sup> does the organic need to support to enable this theory of action?

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Ref. + Thanks to Drs Eckhard Karden, Eberhard Meissner (LABAT'20, to be published)

### 514-1: This theory is :

False

**Logically Sound** 

Novel

Substantiated by my Experience

**Worth Further Exploration** 

Going to Change the Way We Formulate Expander

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### 514-1: This theory is :

Logically Sound
Novel
Substantiated by my Experience
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Going to Change the Way We Formulate Expander

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True

True

Mentimeter

## **For Discussion**

- Round table discussion of the theory's logic
- Sharing of personal experience with organics and chemistries
- Experimental suggestions to disprove the hypothesis that organics are incapable of harboring DCA-supporting Pb<sup>2+</sup> reservoirs for fast implementation only following a discharge
- Open questions:
  - Is there an "optimal" Pb<sup>2+</sup> absorption?
  - Is the question less about total  $Pb^{2+}$  absorption, and more about rates of release/capture?
  - How to measure Pb<sup>2+</sup> reservoirs in situ?
  - How to promote  $Pb^{2+}$  storage and liberation following a charge step (improve  $I_c$ )?
  - Can organic chemistries be used to control open/closed dynamics and make them less dependent on battery SoC/[salt]?

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## Perturbation of Pb<sup>2+</sup> Diffusion as Memory Driver



- Under what condition do Pb<sup>2+</sup> absorb/desorb?
- Kinetics of release (k<sub>on</sub>/k<sub>off</sub>)?
- Vary by different organic?

