Lead Battery Challenges for Energy Storage Systems

FRANCISCO TRINIDAD

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2.Challenges

- Investment Cost
- Charge Efficiency
- Cycle Life
- Sustainability

3.0pportunities

- Reduce material cost
- Fast Charge Recovery
- Cycle Optimized Designs
- Active Material Additives
- 4.Summary and Outlook

Introduction

Energy Storage Systems (ESS) are expected to be the fastest growing battery market in the next coming years.

Lead batteries are facing significant challenges to comply with customer expectations for ESS applications.

Charge efficiency and maintenance needs of industrial vented cells are not always fulfilling the application requirements.

Maintenance free valve-regulated designs (VRLA) improve charge efficiency and cycle life, but initial cost need to be reduced to compete with advanced electrochemical systems.

The most critical factor is to reduce the Total Cost of Energy Storage (TCOES), that includes:

- ✓ Initial investment
- Operation and maintenance
- Charge efficiency
- ✓ Cycle life

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Challenges

INVESTMENT COST

Lithium battery prices are falling, after a temporary increase in 2022 due raw materials availability.

ESS are mainly using low-cost cathode chemistries, like the lithium iron phosphate (LFP).

Initial cost of vented Lead batteries is competitive (in terms of €/kWh) but maintenance and operation costs are still high.

Valve Regulated (AGM or GEL) designs do not need regular maintenance, but investment costs need to be reduced.

Lead battery initial cost need to be reduced further to be competitive with low material cost Li-ion chemistries.

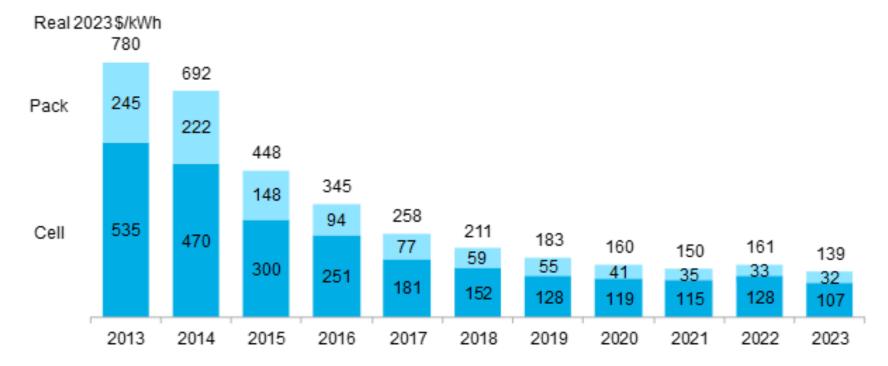


Figure 1: Volume-weighted average lithium-ion battery pack and cell price split, 2013-2023

Source: BloombergNEF. Historical prices have been updated to reflect real 2023 dollars. Weighted average survey value includes 303 data points from passenger cars, buses, commercial vehicles, and stationary storage.

Battery Industry News (8 July 2024)

Challenges

CHARGE EFFICIENCY

Lead sulfate crystals produced during the discharge tend to grow on the lead electrode surface, hindering the electrochemical charge reactions.

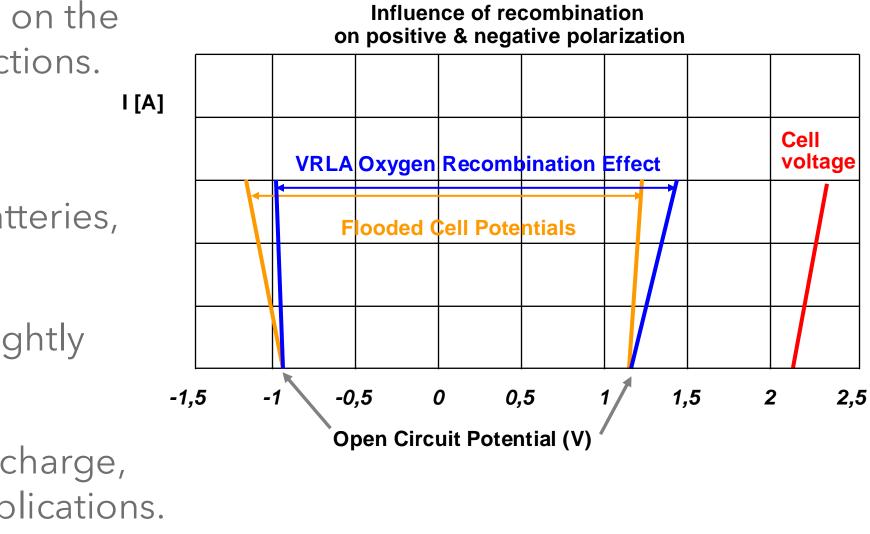
The negative plate is polarized, reducing the charge current.

Oxygen recombination depolarizes the negative plate of VRLA batteries, allowing higher charge potential of the positive plate.

Energy efficiency is improved, although coulombic efficiency is slightly reduced due to the energy lost in the recombination reaction.

Different technical approaches have been proposed to allow fast charge, but energy efficiency should be improved for ESS high-power applications.

Lead batteries need to be safely and efficiently recharged in minutes instead of hours.



Source: Exide Technologies

Challenges CYCLE LIFE

ESS applications require that the batteries can readily provide and receive energy from the grid.

Under Partial State of Charge (PSoC) conditions, there is a charge deficit in every cycle that produces early failure.

The root cause is high negative plate potential in charge, but the consequence is positive plate undercharge.

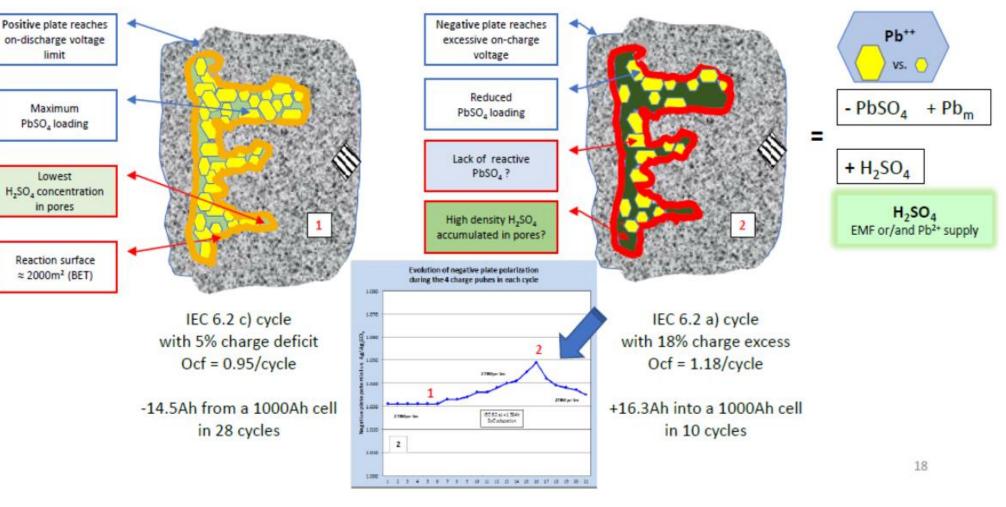
The PbSO4 accumulated inside the internal pores can be fully converted with adequate maintenance charging.

However, maintenance during operation is difficult to perform adequately for many ESS applications.

Cycle life under PSoC determine one of the key factors for energy storage applications (depreciation cost).

Maximum PbSO₄ loading Lowest H₂SO₄ concentration in pores

> Reaction surface ≈ 2000m² (BET)



H. Giess / 18th Asian Battery Conference, Denpasar-Bali, Indonesia (2019)

Challenges

SUSTAINABILITY

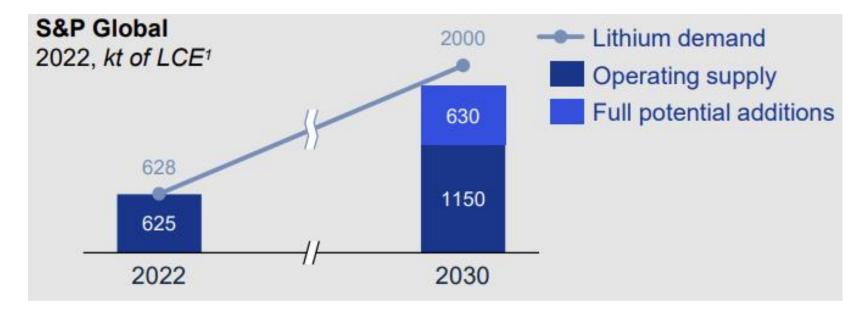
Lithium supply is expected to be at risk due to the increase in demand and possible delays in recycling or new mining projects.

There is an opportunity for Lead and other battery technologies to fulfill Industrial, EV fast charging and Residential applications.

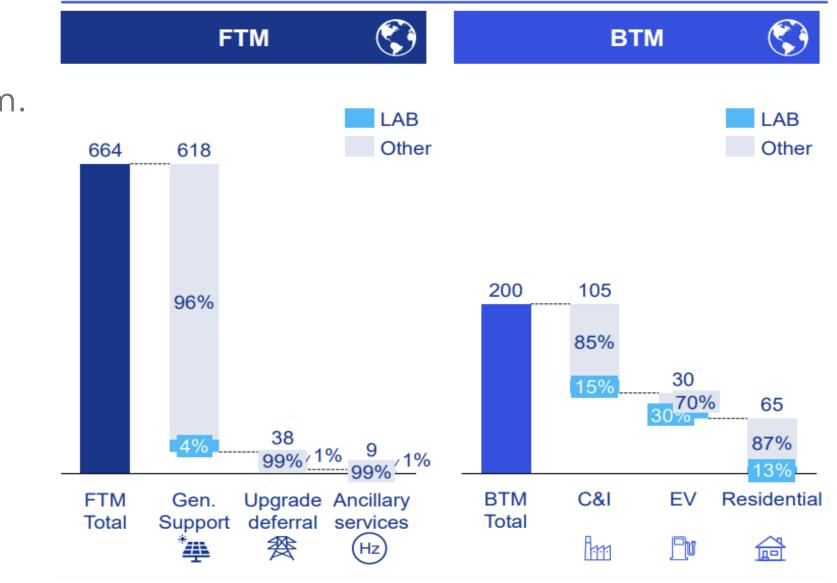
Sustainable material costs, process automation and cycle life improvements will contribute to keep lead as alternative to Lithium.

Other battery energy storage systems (Redox flow, Na-ion...) are also expected to play a role in ESS applications, but material cost and sustainability are questionable.

Lead batteries need to maintain fully recyclable and more sustainable materials than the other electrochemical systems.



Lead battery breakdown in 2035 - FTM & BTM [GWh]



A. Davidson / CBI EU Technical Workshop, Paris (FR), June 2024

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REDUCE MATERIAL COST

Several strategies have been considered to reduce material cost of non-active components (lead grids and intercell connectors).

Bipolar plate design is attractive because grid and top lead are eliminated, while reducing the electrolyte amount (absorbed).

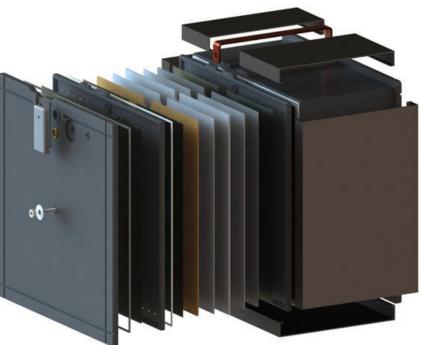
Improved active material efficiency and simplified assembly operations have the potential to reduce production costs.

Simulated ESS cycle life tests show promising results (energy efficiency >90% and projected calendar life>7 year).

Sustainability can also be maintained by using fully recyclable materials for all the battery components.

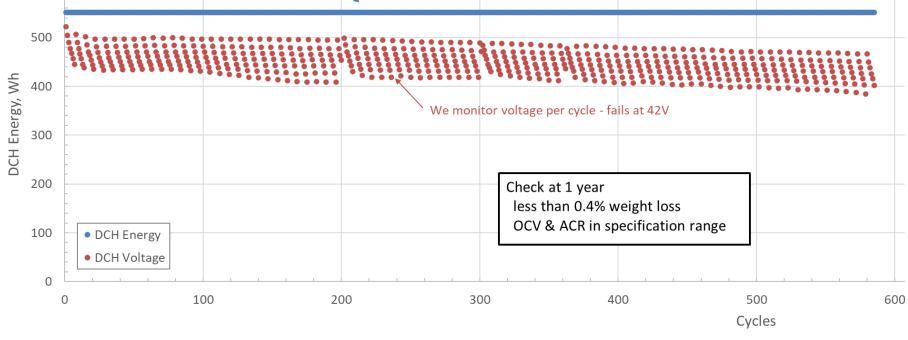
New bipolar designs can reduce material cost but need further development and tests in industrial relevant environments.

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BIPOLAR ESS 48V 2kWh Battery

7 Cycles 4H DCH/RCH Constant Power; +4h CV Charge on 7th Cycle, Customer sees constant energy per cycle



E. Shaffer / 20th Asian Battery Conference, Cambodia (September 2023)

FAST CHARGE RECOVERY

Lead batteries contains a powerful capacitor inside the Positive Active Material (PAM) due its high surface area and pseudo-capacitance of non-stoichiometric PbO_(2-x).

However, the Negative Active Material (NAM) is hindering charge acceptance due to its low surface area.

NAM charge acceptance can be significantly increased with high surface area Carbon Black (CB) and conductive Expanded Graphite (EG).

Charge current at PSoC (<60%) exceeds that of a parallel connection of the lead battery with a Super-capacitor.

current (A) Charge 150 100 50

350

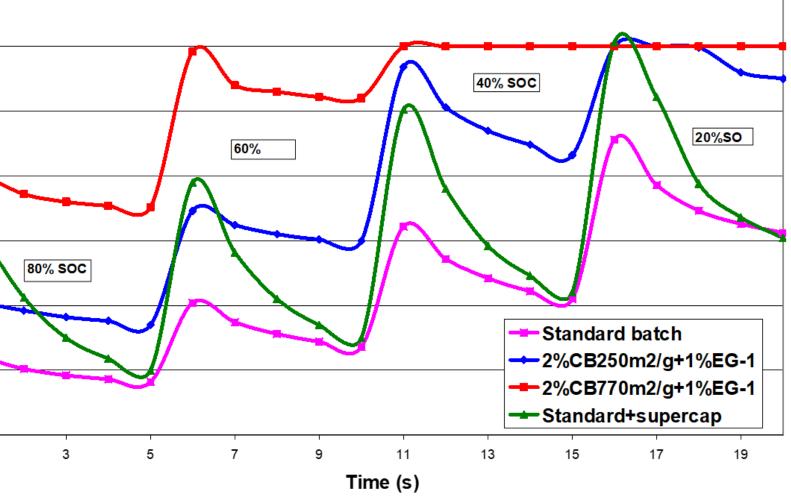
300

250

200

Fast charge recovery of Lead batteries looks feasible with additives that increase NAM surface area.

Charge Acceptance at 25°C **Effect of Carbon additives on Fast Charge recovery**



M. Fernández / Advanced Battery Development for Automotive and Utility Applications (Mainz 2010)

Opportunities CYCLE OPTIMIZED DESIGNS

GEL batteries are already used for long-life Industrial applications, due to its maintenance free and good cycle life performance.

PSoC cycle life (IEC 61427 – Solar) can be improved with suitable charge strategies and electrolyte additives (>2000 cycles at 40°C).

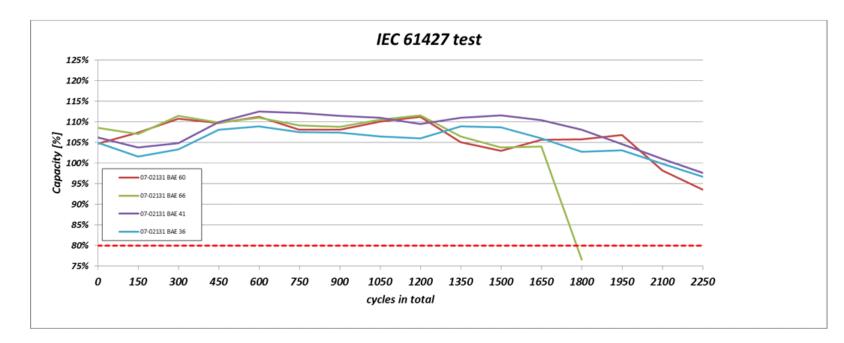
Carbon additives reduce the negative overpotential, allowing faster charge recovery of the positive plate.

Deep cycle life (100% DoD) can be significantly improved (up to 4x) with high surface area Carbon additives.

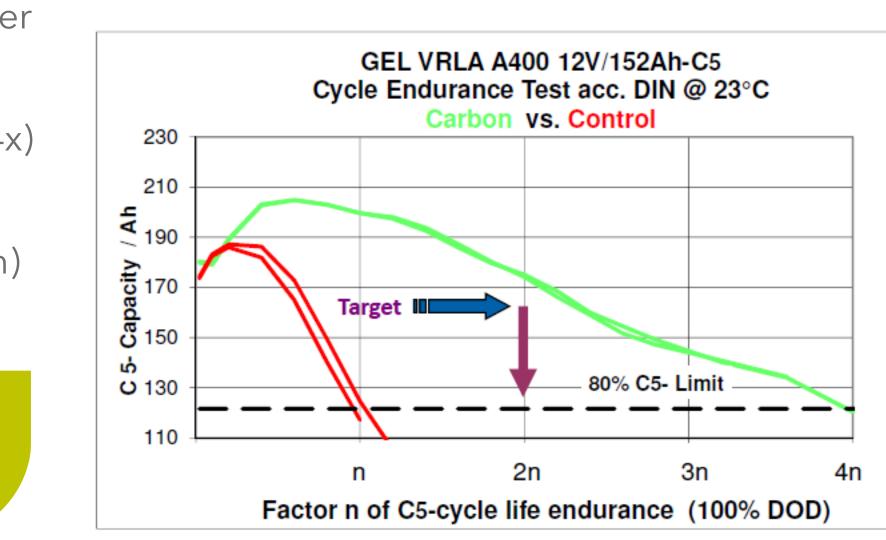
Potential harmful effects on gassing reactions (hydrogen evolution) are not critical in GEL batteries due to the excess of electrolyte.

Cycle optimized VRLA batteries can also be successfully applied to EV fast charge and Residential energy storage applications.





B. Monahov / ALABC Steering Committee Meeting (2013)



H. Nieprasch / ILAB Europe Conference - Würzburg , Germany (2015)

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ACTIVE MATERIAL ADDITIVES

BaSO₄ acts as the nuclei during discharge and assist in the formati PbSO₄ crystals in the curing process.

Crystal size formed after curing is affected by the $BaSO_4$ particles used as nucleation sites.

However, the increase in cured NAM surface area produced by Nano-BaSO₄ is lost after formation and initial cycling of the battery.

PSoC life test (IEC 61427-1) showed very small influence on capacity (but higher End of Discharge Voltage) with the Nanomaterial.

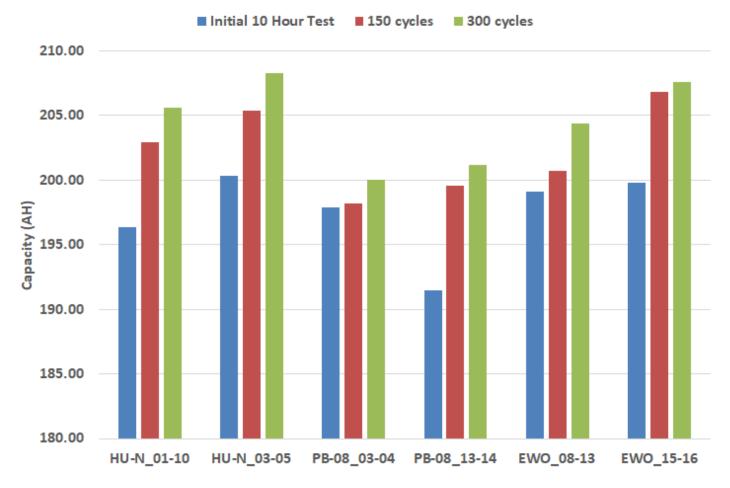
Failure mode in this test is positive plate degradation, that may explain why the capacity is not increased with the Nano-BaSO₄.

Optimizing barium sulfate particle size in the NAM may improve PSoC cycle performance of ESS batteries.

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BaSO₄ Sample	Particle size (µ)	Cured NAM Surface Area (m²/g)	Formed NAM Surface Area (m2/g)
EWO (Standard)	1.8	1.46	0.85
PB-08 (Submicron)	0.23	1.48	0.88
HU-N (Nano)	0.04	1.59	0.78

IEC-61427-1 10 Hour Capacity



T. Wojcinski, E. Gao, J. Miller, R. Fegely, M. Raiford / CBI Project # 2021-002

ACTIVE MATERIAL ADDITIVES

The expanders composition (Organics, BaSO₄ & Carbon) determine the NAM Charge Acceptance (CA) and Water Loss (WL) performances.

Blending two different organic materials (lignin or synthetic) optimize high-rate performance and reduce water loss at high temperature.

Submicron particle size BaSO4 increase NAM surface area.

NAM electrochemical behavior can also be affected by the carbon type and surface post-treatment:

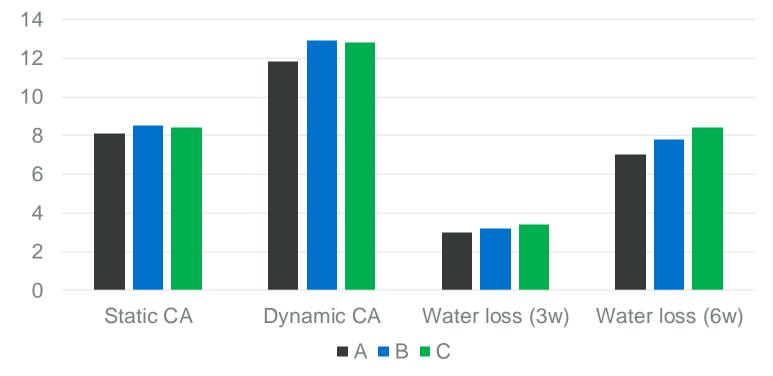
CA (0°C): Treated Carbon > Carbon Black > Acetylene Black

 \blacktriangleright WL (60°C) : Carbon Black > Treated Carbon > Acetylene Black

Blending different types of Expander components could be critical to obtain the desired performance for each ESS application.

Blend	Organic Materials	BaSO₄ Particle size	Carbon Types
Α	Lignin + Synthetic	Submicron	Acetylene Black + Graphite
В	Lignin + Synthetic	Submicron	Treated Carbon + Graphite
С	Lignin + Synthetic	Submicron	Carbon Black + Graphite

Charge Acceptance (0°C) vs Water Loss (60°C)



Source: Hammond International Group

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Summary and outlook

Lead battery challenges for ESS can be addressed with new developments, some of them successfully applied in automotive, but lacking sufficient maturity level for long life industrial applications:

- Reducing cost and weight of passive components (grids and intercell connectors)
- Increasing charge efficiency (oxygen) recombination and charging strategy).
- Optimizing cycle life of VRLA designs (high) surface area conductive Carbon)

containing:

- Lignin and Synthetic Organics ✓ Surface Treated Carbon and Graphite ✓ Submicron Barium Sulfate

There are also short-term opportunities that could be levered by new expander compositions



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francispoyatos.com

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