Recycled Lead Acid Battery Paste for Soluble Lead Flow Batteries

Assessing the performance of various electrolytes

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Abstract

A significant challenge of modern energy storage, especially as reliance on variable generation rate renewable energy sources increases, is creating a stable electricity network for long-term energy storage [1]. Traditional lead-acid batteries (LABs) are unable to decouple power and energy, opening a window for Redox Flow Battery (RFB) technology. The aim of this project was to begin to assess the feasibility of making Soluble Lead Flow Battery (SLFB) electrolyte from recycled LABs, focusing on the effect of sulfate ions (SO_4^{2-}) leftover from processed LAB battery paste [2].

How do Soluble Lead Flow Batteries work?

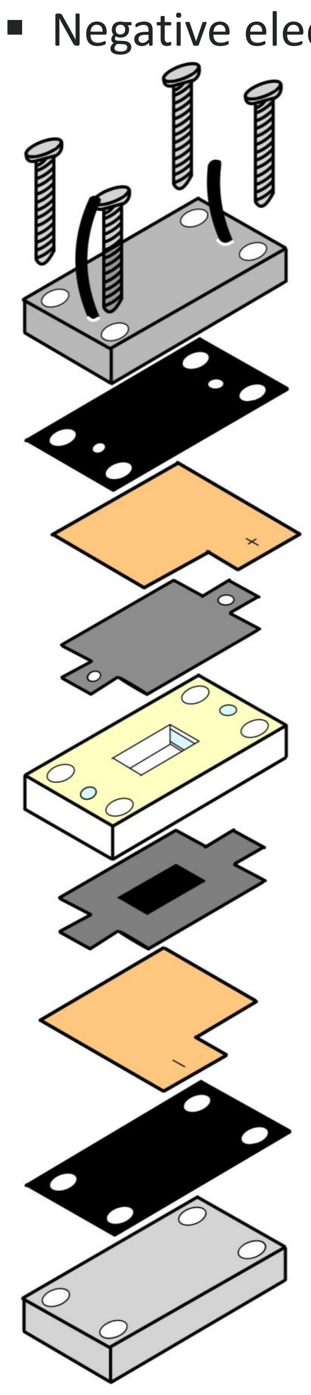
SLFBs make use of a pump to drive an electrolyte around a closed flow circuit. The electrolyte contains aqueous Pb^{2+} ions which oxidise and reduce to form solid lead-based deposits on the electrodes during charge. During discharge, the deposits electrochemically redissolve into the electrolyte.

- Positive electrode: Pb^{2+} is oxidised during charge to form PbO_2

$$Pb^{2+}_{(aq)} + 2H_2O_{(l)} \rightleftharpoons PbO_{2(s)} + 4H^+_{(aq)} + 2e^-$$

- Negative electrode: Pb^{2+} is reduced during charge to form Pb

$$Pb^{2+}_{(aq)} + 2e^- \rightleftharpoons Pb_{(s)}$$



The flow cell is assembled in a 'sandwich' structure. Electrolyte flows from the reservoir and passes the 10 cm² window in the flow plane, where the deposits are formed on the electrodes.

- Steel back-plate
- Rubber insulating gasket
- Copper current collector
- Pb15 electrode
- Foam compression gasket
- Acrylic flow plane
- Electrolyte

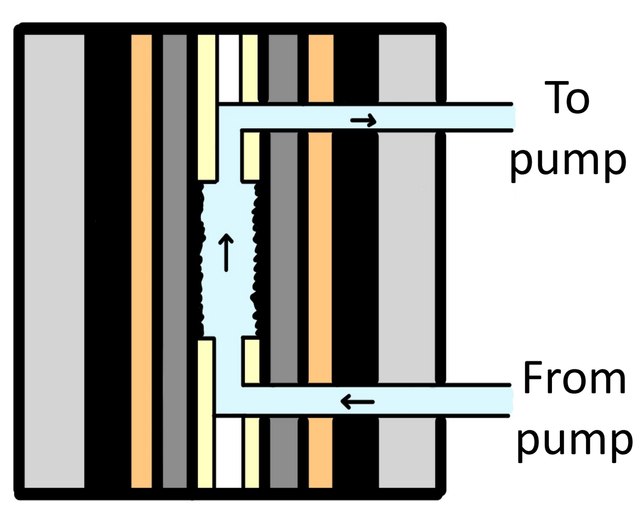


Fig 1: Exploded (left) and cross-sectional (above) view of flow cell.

SLFBs also have a distinct charge-discharge profile:

- Two-step charge – partial reduction of PbO_2 to PbO_x ($x < 2$) during discharge on positive electrode, instead of full reduction to Pb^{2+} [3].
- Constant-current charge and discharge (compared to LAB constant-voltage charge) – high current charging creates poor quality deposits in SLFBs.

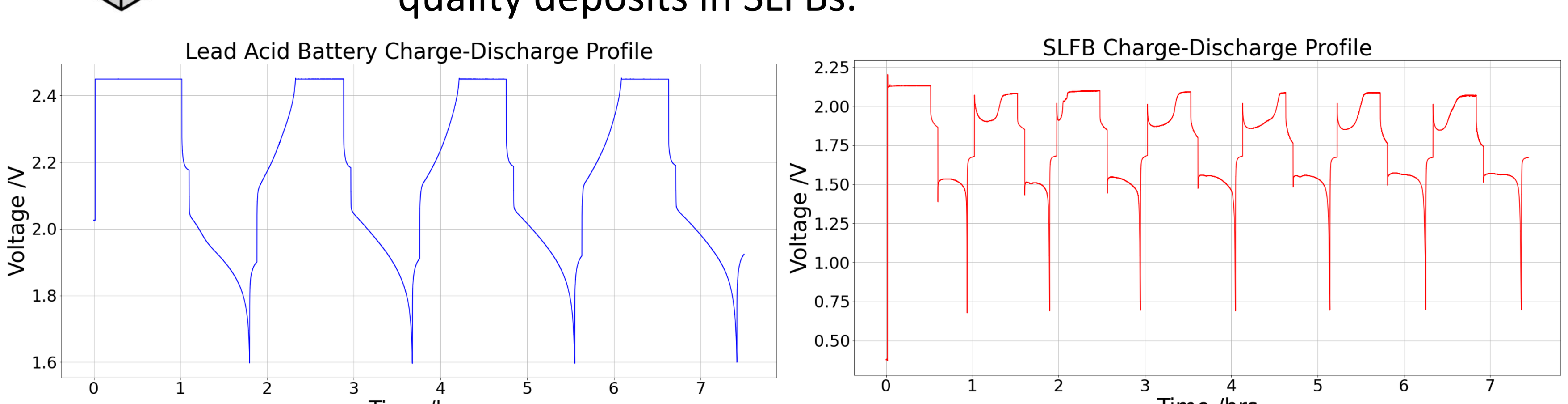
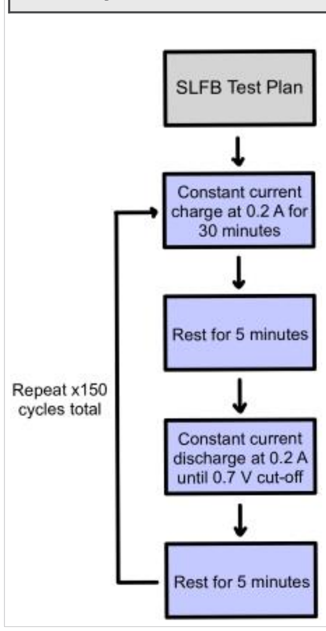


Fig 2: Comparison of LAB (left) and SLFB (right) charge-discharge profiles.

Methods

The experiment was run 5 times, each with 100 cm³ of electrolyte for 150 cycles over roughly 6 days. To introduce SO_4^{2-} ions, sulfuric acid was added. The SO_4^{2-} reacted with the aqueous Pb^{2+} ions to form an insoluble $PbSO_4$ precipitate.

Electrolyte	Contents
Standard	1 M MSA, 0.75 M Pb^{2+}
Filtered	1 M MSA, 0.75 M Pb^{2+}, 0.2 M H_2SO_4 precipitate filtered out
Unfiltered	1 M MSA, 0.75 M Pb^{2+}, 0.2 M H_2SO_4 precipitate in solution
Mimicked	1.4 M MSA, 0.55 M Pb^{2+}
Recycled Paste	2.5 M MSA, 0.75 M Pb^{2+} from 100 g paste



The experimental results were collected using an MTI BST8-3 battery analyser.

The supply chain for lead is already established via LABs, so the electrolyte would be produced at a much lower environmental and economical cost.

Fig 3 (left): SLFB test plan.

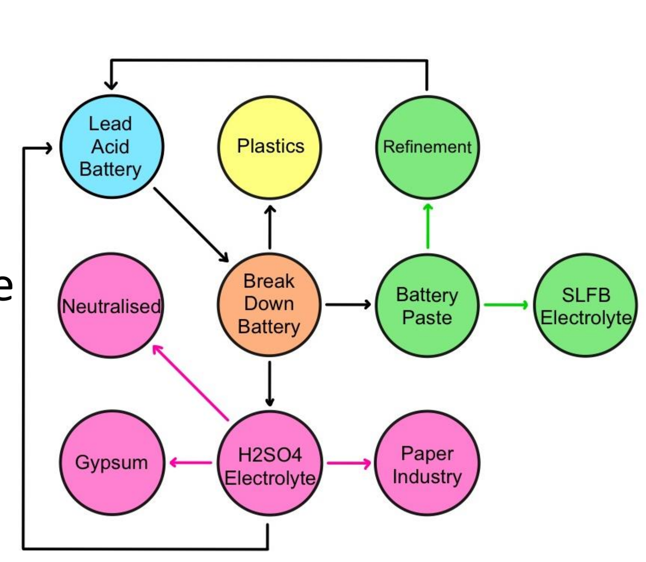


Fig 4 (right): LAB recycling procedure.

Results

The performance of the batteries was calculated using the coulombic efficiency of each cycle over the complete 150 cycle test plan. The coulombic efficiency relates the amount of charge (Q) put into the battery to the amount of charge that the battery returns upon discharge.

$$Coulombic\ Efficiency = \frac{Q\ Discharge}{Q\ Charge} * 100$$

Reasons for loss of efficiency include:

- Deposits fall off electrodes – Pb solids cannot be recovered to Pb^{2+} on discharge.
- Deposits cannot be stripped from electrodes – e.g. phases of PbO_2 on deposit formation affect mechanical stability and electrical conductivity [4].
- Gas evolution – H_2 and O_2 formed via water electrolysis at electrodes.

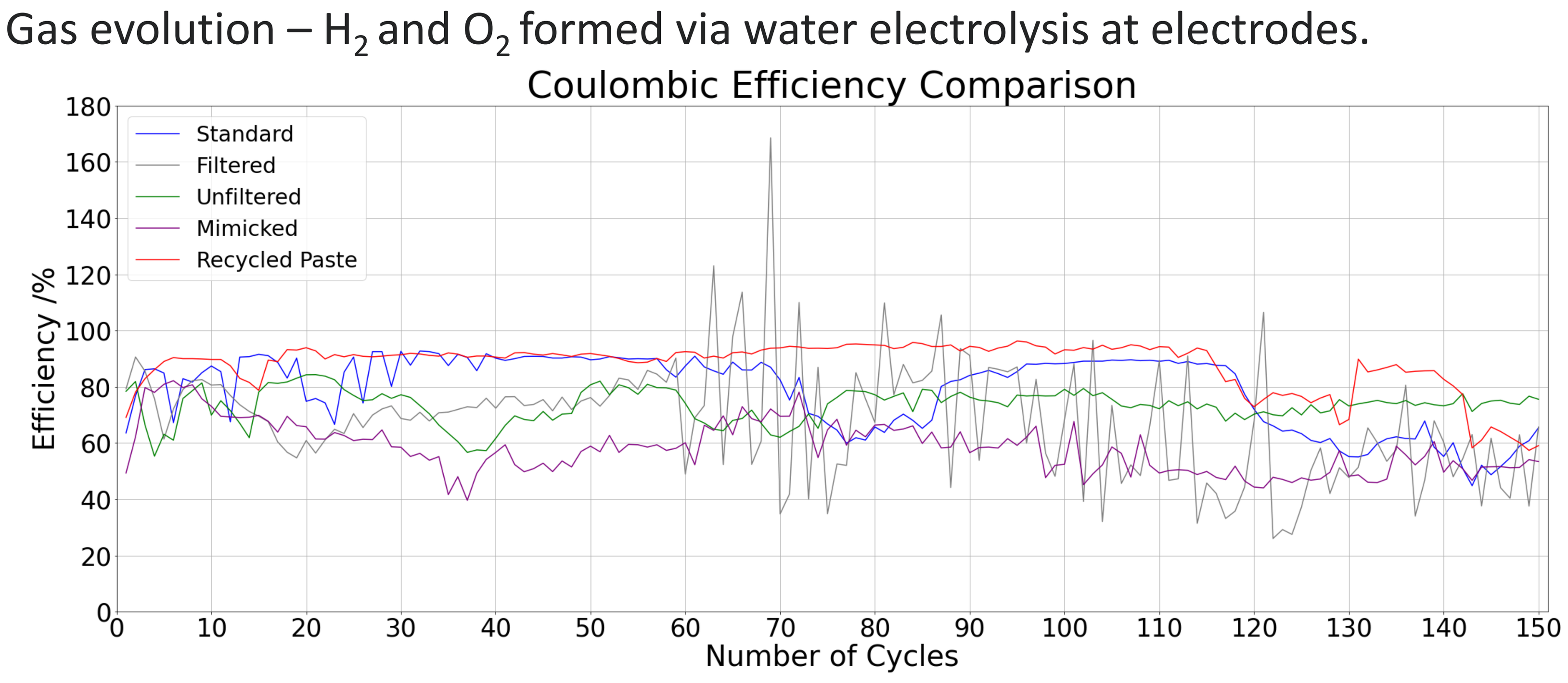


Fig 5: Coulombic Efficiency comparison.

Key findings:

- Filtered and unfiltered had similar early performance, however there is a clear divergence after approximately 100 cycles – unclear if caused by presence of $PbSO_4$ precipitate or anomalies in the filtered experiment.
- Recycled battery paste had very high and consistent efficiency of >90% until roughly cycle 115 – most likely due to stabilising additives present in the paste.
- Rapid spiking in standard filtered – probably caused by a section of the lead deposit on the negative electrode becoming partially dethatched, allowing it to short the circuit periodically as it moves in the flow.
- Mimicked chemistry experiment is theoretically identical to the filtered – difference in cycle efficiency could be caused by residual $PbSO_4$ precipitate after filtering. The poor-quality deposits and dendritic growth also reduce efficiency.

Fig 6 (left): Pb deposit from filtered experiment (top) vs. typical coherent Pb deposit (bottom).

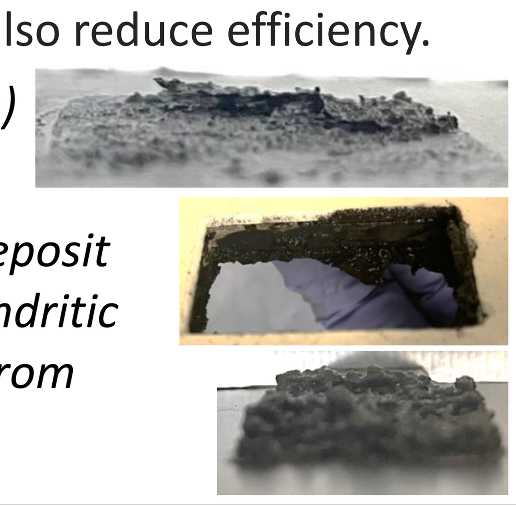


Fig 7 (right): lifting layer of PbO_2 deposit (top), deposit growth across flow plane (middle), significant dendritic growth on lead electrode (bottom) – all taken from mimicked chemistry experiment.

Conclusions

- Recycled battery paste has very high and sustained performance – could be a viable option for SLFB electrolyte.
- Results suggest some effect due to the presence of $PbSO_4$ – further testing required to determine repeatability.

Next steps

- Repeat filtered experiment using centrifuge to remove all $PbSO_4$ precipitate.
- Isolate effects of recycled battery paste additives and other non-lead substances present to determine what causes the increase in efficiency.

References

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- [2] Tan S. et al. (2019) 'Developments in electrochemical processes for recycling lead-acid batteries', *Current Opinion in Electrochemistry,* 16 83-89
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Intern bio

Jessica is a 3rd year mechanical engineering student at the University of Southampton. She has a particular interest in renewable technology and innovation for a more sustainable future.

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