

Developments in soluble lead flow batteries and remaining challenges: An illustrated review



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ABSTRACT

The soluble-lead flow battery (SLFB) utilises methanesulfonic acid, an electrolyte in which Pb(II) ions are highly soluble. During charge, solid lead and lead dioxide layers are electrodeposited at the negative and positive electrodes respectively. During discharge, the deposits are electrochemically dissolved back into the recirculating electrolyte. The cell is normally undivided, which greatly reduces design complexity and cost, whilst also reducing the flow pumping requirements. Typical SLFB electrolytes offer up to 40 Wh kg⁻¹ of storage, with performance on the 100 cm² electrode scale reaching 90% charge and 80% voltage efficiencies across 100 cycles; however, the SLFB has also been tested on the 1000 cm² electrode, four-cell stack scale. This review considers the SLFB, highlighting important developments and discussing remaining problems. In particular, methods to achieve effective stripping of lead dioxide at the positive electrode and to prevent lead dendrites at the negative electrode in order to prevent contact between the deposits, and thus shorting, are explored. A detailed understanding of the effect of Pb(II) and methanesulfonic acid concentration on the physical electrolyte properties is presented, and possible improvements to the electrodes and electrolyte composition in terms of additives are discussed in order to improve cell efficiency and longevity. Also, the importance of cell design in preventing the failure mechanisms and therefore achieving a high performance is highlighted. Studies on mathematical modelling and cycling simulation are also reviewed. Continuing research needs are listed and a forward look to future developments is taken.

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Contents

1. Introduction	70
1.1. The scope of this review	70
1.2. The soluble lead redox flow battery	70
1.3. Constraints on the system	71
1.4. Brief history of lead-based batteries	71
2. Thermodynamics and storage capacity	73
3. Deposit and electrolyte properties	74
3.1. Lead	74
3.2. Lead dioxide	74
3.3. Methanesulfonic acid	74
3.4. Electrolyte density and viscosity	74
3.5. Electrolyte conductivity	75
4. Electrode kinetics	75
4.1. Negative redox couple	75
4.2. Positive redox couple	75
5. Operating conditions	77

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5.1.	Negative electrode	77
5.2.	Positive electrode	78
5.3.	Further discussion on the structure of lead dioxide	80
5.4.	Potential–time plots	80
5.5.	Discharge at the positive electrode	80
5.6.	Further observations at the positive electrode	82
5.7.	Flow rate	82
6.	Additives	82
6.1.	Negative electrode	82
6.2.	Positive electrode	82
7.	Electrode materials	83
8.	Electrolyte composition	83
8.1.	Conventional electrolyte	83
8.2.	Recycled electrolyte	84
9.	Performance	84
9.1.	Flow cells	84
9.2.	Flow battery	85
10.	Flow cell engineering	85
10.1.	Cell design	85
10.2.	Cell maintenance	87
11.	Modelling and simulation	87
12.	Conclusions and future work	88
	Acknowledgements	89
	References	89

1. Introduction

1.1. The scope of this review

With the growing global energy demand, energy storage will become a key component in maintaining a dependable energy supply whilst integrating renewables into electricity networks. Energy storage devices, by electrochemical or mechanical means, have been reviewed extensively, including those by Chen et al. [1] and Akhil et al. at the Sandia National Laboratories [2].

Redox flow batteries have been growing in popularity since modern research began in the 1970s [3]. A multitude of battery chemistries exists today, with the vanadium redox flow battery (VRFB) being the most advanced. These have also been reviewed in detail, including their operational principles and remaining technical challenges [4–7]. Furthermore, reviews focusing on the engineering aspects of flow batteries have been published by Arenas et al. [8] and Chalamala et al. [9]. The largest operational flow battery installation is the HEPSCO-SEI 15 MW/60 MWh VRFB used for renewables capacity firming at the Minami Hayakita substation in Hokkaido, Japan [10]. Flow batteries are readily scalable, and the VRFB has been shown to offer efficiencies of >90%, lifetimes of 20 years, low initial costs (the cost per kW decreases with greater storage capacity), robust construction, low maintenance and flexible operation. Safety is another key feature of flow batteries, which typically operate at ambient temperature.

A flow battery consists of several cells connected electrically in series, usually as a bipolar stack. In the general design, a flow cell is divided into two half-cells via a separator. The positive electrolyte and negative electrolyte are housed separately in external tanks and two flow networks circulate the electrolytes through the respective half-cells. The cell electrodes are connected externally to a power source/load. When power is supplied, the cell charges: electrochemical reactions occurring at the electrode surfaces cause a change in the oxidation states of the reactant species in the electrolyte. Energy is stored as these new, 'charged' species. On discharge, the reactions are reversed and the stored energy is released.

Research continues today to improve performance whilst reducing costs, and one such chemistry that has shown much promise is the soluble lead system. This review will focus solely on

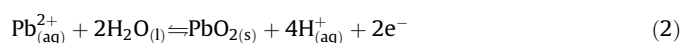
the soluble lead redox flow battery (SLFB). The concept of a SLFB and its differences with conventional static lead-acid batteries are discussed. A thermodynamic perspective of the chemical processes will be presented along with theoretical cell voltages. The review will critically assess the problems that hinder the SLFB's progression to a commercialisation stage and the work that has been done to mitigate these problems. Further aspects requiring development and recent improvements will also be discussed including summary data from voltammetry and several galvanostatic charge/discharge experiments. The task of optimising electrolyte concentrations and charge regimes will be discussed following a comprehensive analysis of each electrode reaction. Where relevant, experience from the coatings industry and other forms of flow batteries are also discussed in relation to the SLFB.

1.2. The soluble lead redox flow battery

The SLFB makes use of the variable oxidation states of lead, namely Pb, Pb(II) and Pb(IV). Electrolytes are formulated either from lead oxide, lead carbonate or aqueous lead methanesulfonate, $\text{Pb}(\text{CH}_3\text{SO}_3\text{H})_2$, and methanesulfonic acid (MSA), $\text{CH}_3\text{SO}_3\text{H}$. In the simplest SLFB design, Pb^{2+} ions are dissolved in an aqueous MSA electrolyte and this is then pumped through an undivided electrochemical cell. During charge, at the positive electrode, Pb^{2+} is oxidised and a phase change occurs, leading to the deposition of lead dioxide on the electrode. At the negative electrode Pb^{2+} is reduced, with an associated phase change resulting in metallic lead deposition onto the electrode. During discharge, the electrodeposits dissolve back into the electrolyte [11]. This is described by the following equations:



$$E_{-\text{ve}}^0 = -0.130 \text{ V vs. SHE}$$



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