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Membrane divided soluble lead battery utilising a bismuth electrolyte additive

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HIGHLIGHTS

- We describe a membrane divided soluble lead battery.
- The positive influence of electrode specific additives is demonstrated.
- Modified reaction pathway and kinetics are observed for the positive electrode.
- Increased cycle life is achieved compared to equivalent non-divided cells.

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ABSTRACT

A soluble lead battery benefiting from the incorporation of an ion exchange membrane to separate the positive and negative electrolyte compartments has been described. A static cell, using an electrolyte volume of 7.5 ml, was configured with and without a membrane. The use of a membrane enables the selection of electrode specific additives. In this paper, a proof of concept cell is shown with the use of Bi^{3+}, which when added to the positive electrolyte compartment leads to a twenty-fold increase in cycle life of the cell. The bismuth ions cause a shift in the reaction mechanism and kinetics of lead dioxide dissolution during the discharge reaction.

1. Introduction

Recent literature has described the design, characterisation and chemistry of the soluble lead flow battery [1–3]. This battery utilises an electrolyte comprising Pb^{2+} ions solvated in aqueous methanesulfonic acid. During charge, solid lead and lead dioxide deposits are electroplated onto the negative and positive electrodes respectively. During discharge, the electrodeposits are electrochemically converted back to soluble Pb^{2+} ions. Unlike many flow batteries, no ion exchange membrane has been used in studies of this system as the same electrolyte is required for the positive and negative electrode reactions and the solid phases of the charged state prevents significant self-discharge of the cell. Flow batteries without an ion exchange membrane benefit significantly from reduced cell complexity and cost. As a consequence, the incorporation of a membrane into the soluble lead system would only be beneficial if; (1) the added cost of the membrane was offset by extended operational lifetime and (2) the increased cell resistance associated with the membrane was offset by improved efficiency or an increased cell potential (hence higher battery voltage and power). Currently, cycle life and efficiency limitations of the soluble lead battery are primarily associated with; (1) morphology of the electrode deposits (dendritic/spongy Pb and creeping PbO_2 formations) and (2) reversibility of the positive electrode reaction [1,4–6]. The use of electrolyte additives can be employed to improve the efficiency and reversibility of the electrode reactions. Numerous electrolyte additives have been selected and trialled, including fluorosurfactants, sulphates, ammines and metal ions [1,7,8]. None, however, have successfully addressed the issues with both electrode reactions. A motivation for the incorporation of a membrane is the possibility of using electrode specific electrolyte additives. Bi^{3+} ions are used as dopants for the positive active mass in conventional (sulphuric acid electrolyte, pasted electrodes) lead acid batteries. They are thought to increase the specific capacity of

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the positive active mass and accelerate oxygen transition reactions within the PbO_2 phases [9,10]. In this work it is shown that Bi^{3+} ions provide beneficial performance improvements for the positive electrode reactions (PbO_2 deposition and dissolution) but adversely affect the negative electrode performance. A unit cell is utilised to demonstrate the soluble lead battery operating with a Nafion® ion exchange membrane where Bi^{3+} is added to the positive electrolyte solution only to give enhanced charge efficiency and cycle life.

2. Experimental details

All solutions were prepared using water from a Purite Ondeo 15 purifier, methanesulfonic acid (CH_3SO_3H) from BASF, lead carbonate ($Pb(CO_3)_2$) from Sigma Aldrich and bismuth oxide (Bi2O3) from Sigma Aldrich. The preparation of the electrolyte solutions has previously been described [3]. Three stock electrolytes were used in these studies:

- Voltammetry of the negative electrode reactions used an electrolyte solution comprising 10 mmol dm^{-3} Pb^{2+} in aqueous CH_3SO_3H (1.0 mol dm^{-3}).
- Voltammetry of the positive electrode reactions used an electrolyte solution comprising 0.5 mol dm^{-3} Pb^{2+} in aqueous CH_3SO_3H (1.0 mol dm^{-3}).
- Unit cells were supplied with an electrolyte solution initially comprising 1.5 mol dm^{-3} Pb^{2+} in aqueous CH_3SO_3H (1.0 mol dm^{-3}).

Where stated, 10 mmol dm^{-3} of Bi^{3+} was added to these stock electrolytes.

Voltammetric studies of the Pb/Pb^{2+} and PbO_2/Pb^{2+} electrode couples utilised a standard two compartment, three-electrode glass electrochemical cell containing approximately 25 cm^3 of electrolyte and was setup as previously described [3]. The working electrode was a glassy carbon disc with area 0.07 cm^2 and the counter electrode was a Pt wire. The working electrode was rotated at 900 rpm in all voltammetric studies. Potentials were measured against a saturated calomel reference (SCE) electrode. The electrochemical cell was maintained at 293 K and controlled using an EG&G model 263A potentiostat operating with EG&G PowerSuite software.

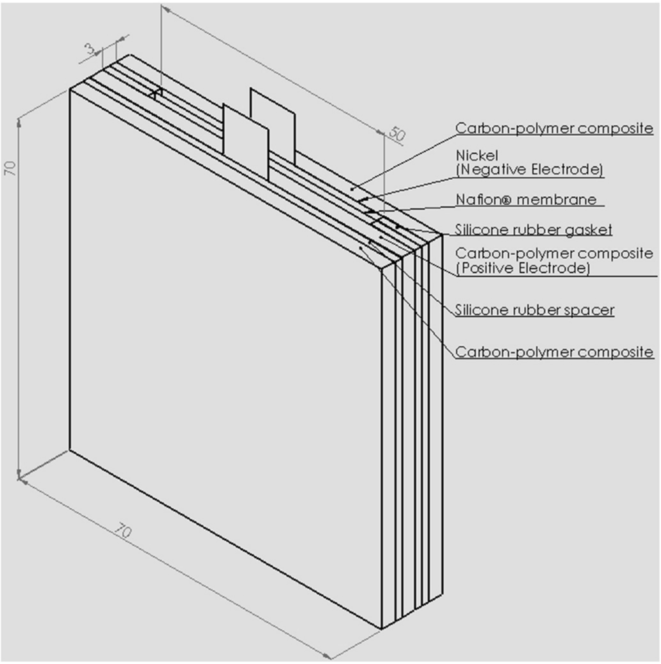

Fig. 1. Soluble lead acid cell diagram, showing component materials and dimensions.

Table 1
Cell configurations and nomenclature.

Cell identifier	Separator	Additives	
		Negative	Positive
Lead1	None	None	None
Lead2	Nafion®	None	None
Bismuth1	None	10 mM Bi^{3+}	10 mM Bi^{3+}
Bismuth2	Nafion®	10 mM Bi^{3+}	10 mM Bi^{3+}
Bismuth3	Nafion®	None	10 mM Bi^{3+}

A parallel plate unit cell was constructed using Entegris carbon-polymer composite for the positive electrode and nickel foil for the negative electrode. The cell wall was constructed from two silicone rubber gaskets (RS 506-3264). Both electrodes were planar with geometric active surface area of 25 cm^2. A schematic of the cell is presented in Fig. 1.

The electrolyte chamber is 50 × 60 × 3 mm, as each gasket is 1.5 mm in thickness. Between the gaskets was placed a Nafion® NF 115/H^+ membrane in three of the five cell configurations, which are shown in Table 1.

The unit cell was tested in five different configurations to assess the effects of using 1) Bi^{3+} as an electrolyte additive and 2) an ion exchange membrane to separate the positive and negative electrolyte chambers. Two cells, Lead1 and Bismuth1, were undivided (without a membrane) and three cells, Lead2, Bismuth2 and Bismuth3, were divided into separate electrode chambers using the Nafion® membrane. Bismuth2 had the additive added to both the positive and negative electrolyte chambers while Bismuth3 had the additive only added to the positive (lead dioxide) electrolyte chamber.

Charge/discharge cycling of the cell was controlled using an MTI battery analyser operating with MTI Battery Analyzer software. Constant current charge and discharge cycling at 150 mA (6 mA cm^{-2}) was used throughout, which corresponds to the C_1 charge rate for the volume of electrolyte contained within the cell. During cycling the battery was subjected to a series of 10 min charge periods followed by full discharge. During charging, an upper cut off voltage of was 3 V. Discharge periods were ended when a cut-off voltage of 1.4 V was reached. The charge passed

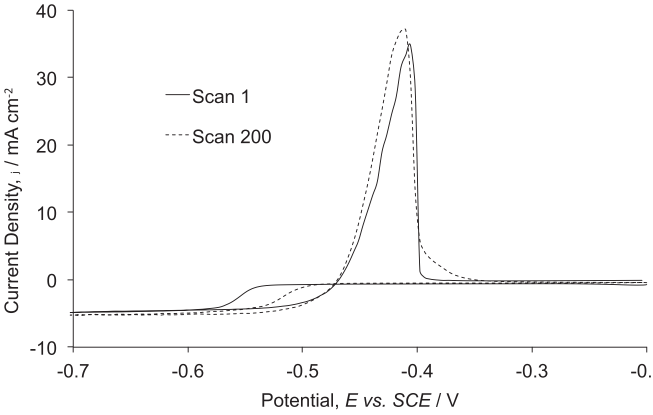

Fig. 2. Cyclic voltammograms for the Pb^{2+}/Pb electrode couple in methanesulphonic acid (1.5 mol dm^{-3}) at a glassy carbon rotating disc electrode. Voltammograms show the first and two hundredth consecutive cycle between −0.2 and −0.7 V *vs.* SCE. The electrolyte was maintained at 295 K and initially contained 10 mmol dm^{-3} Pb^{2+}.