Performance of recovered and reagent grade electrolyte in a soluble lead redox cell

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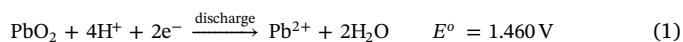*Energy Technology Group, University of Southampton, Southampton, SO17 IBJ, UK*

ABSTRACT

This paper presents the performance of 'recovered' electrolyte for the soluble lead flow battery, made by recycling conventional lead-acid battery electrodes, and compares it to reagent grade electrolyte for the same system. The two electrolyte compositions were cycled in static and flow cells and their charge, energy, and voltage efficiencies compared. The average charge, energy, and voltage efficiencies of static cells using $1.0\ mol\cdot dm^{-3}\ Pb^{2+}$ recovered electrolyte were 89%, 86%, and 96%, while cells using reagent grade electrolyte averaged 63%, 49%, and 78%, respectively. The average charge efficiency of flow cells with recovered electrolyte was consistently above 80% and within 10% of the average for cells with reagent grade electrolyte. The average energy and voltage efficiencies were 62% and 73%, respectively, diverting from averages for the reagent grade electrolyte cells by less than 15%. The highest average cycle life was for cells with recovered electrolyte at 187 cycles, while that of cells with reagent grade electrolyte peaked at 102. Trace elements in both electrolyte compositions were analysed and their presence in the recovered electrolyte appears to enhance performance of the soluble lead cells. The recovered electrolyte is an electrochemically viable substitute for the reagent grade electrolyte.
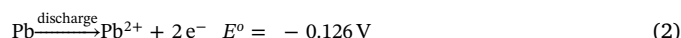
1. Introduction

It is anticipated that the utilisation of electrical energy storage systems will be critical for high penetration levels (i.e. > 50%) of renewable energy, as currently envisaged in many countries' energy plans [1]. Within the megawatt (MW +) electrical energy storage technology sector, redox flow batteries are emerging as a viable option for enabling renewable energy penetration [2] and are expected to become commercially competitive [3].

The soluble lead cell using methanesulfonic acid as electrolyte was introduced by [Pletcher et al. 4–9] using the redox couples PbO_2/Pb^{2+} and Pb/Pb^{2+}, on the positive and negative electrodes respectively. The electrolyte provides the Pb^{2+} ions, which are electrochemically converted to solid PbO_2 and Pb and deposited on the positive and negative electrodes respectively during charge, and stripped back into electrolyte as soluble ions during discharge. The reactions are as follows [4–10].
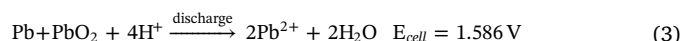
Positive electrode

$$PbO_2 + 4H^+ + 2e^- \xrightarrow{\text{discharge}} Pb^{2+} + 2H_2O \qquad E^o = 1.460\ V \qquad (1)$$

Negative electrode

$$Pb \xrightarrow{\text{discharge}} Pb^{2+} + 2e^- \quad E^o = -0.126\ V \qquad (2)$$

Overall

$$Pb + PbO_2 + 4H^+ \xrightarrow{\text{discharge}} 2Pb^{2+} + 2H_2O \quad E_{cell} = 1.586\ V \qquad (3)$$

The choice of acid for making electrolyte for the soluble lead flow battery (SLFB) is dependent on lead (II) ion solubility. Other factors include ionic conductivity needed to transfer ions between the electrolyte and the deposit, a low electrical conductivity that prevents electrical losses, stability at the operation voltages, and at operation temperature. Low toxicity, corrosiveness and volatility are also critical. Ideally, the chemicals used to make the electrolyte should also be low cost and easy to obtain. In practice it is difficult to find an electrolyte that possesses all these qualities. Therefore a compromise is often found.

In the Table 1 below methanesulfonic acid (MSA) compares favourably with other acids for making Pb^{2+} electrolyte. Solubility of Pb^{2+} is highest in methanesulfonate at $2.6\ mol\cdot dm^{-3}$ [11]. MSA costs the least (Sigma Aldrich prices as at 06/2018), and is the least corrosive. MSA is also stable at an acceptable range of temperatures and at the operation voltage of 0–2.0 V. Even though its ionic conductivity is

Table 1
Comparison of common acids used as electrolytes on lead solvation, ionic conductivity, corrosiveness and cost.

Acid	$[Pb^{2+}]$ / mol dm^{-3}	Ionic Conductivity in 1 N Acid / S cm^2 mol^{-1}	Corrosive	Stable at Temperature T / °C	Cost (S.Aldrich)	At purity (S.Aldrich)
MSA	2.600	299.60 [12]	No	17 – 167	£44.10/L	(70%)
Sulfuric acid	0.0001	444.88 [12]	Highly corrosive	10 – 300	£66.00/L	(95-98%)
Hydrochloric acid	0.034	346.11 [12]	Corrosive	−30 – 61	£372.00/L	(36.5-38%)
Nitric acid	1.803	370.00	Highly corrosive	−42 – 83	£239.00/L	(70%)

lower compared to the other three acids, it is still acceptably high.

1.1. Reagent grade soluble lead flow battery electrolyte

Reagent grade electrolyte (RGE) for the SLFB is made from high purity lead methanesulfonate (462667 Aldrich) and methanesulfonic acid (471348 Sigma Aldrich). Existing literature indicates that different concentrations of the Pb^{2+} ions and of the acid have been tested to determine effects on operation of the soluble lead cell [4–6]. Li et al. [12] found that low concentration of Pb^{2+} (0.1 mol·dm^{-3}) in electrolyte resulted in a powdery deposit on the positive electrode, which contributes to accumulation of solids on the positive electrode and consequently, on the negative electrode as well. Hazza et al. *ibid* [4] showed that the higher the concentration of acid, the higher the conductivity of the electrolyte, while at the same time recommending a maximum acid concentration of 2.0 mol·dm^{-3} to prevent reaching the solubility limit of Pb^{2+} in methanesulfonate. They also recommended the same acid concentration to prevent deposit cracking on the positive electrode [9]. A higher concentration of Pb^{2+} (0.7 mol·dm^{-3}) is recommended [13] in order to store practical amounts of energy and optimise electrochemical activity. Based on these considerations, electrolytes with a Pb^{2+} concentration of 0.9 mol·dm^{-3}, 1.0 mol·dm^{-3} MSA [8] and 0.7 mol·dm^{-3}, 1.0 mol·dm^{-3} MSA [13] have been recommended.

In this paper we present results comparing the reagent grade electrolyte (RGE) typically used for the SLFB with a recycled electrolyte (RE) prepared from discarded Starting, Lighting and Ignition (SLI) lead acid batteries. The use of such a recycling process, which was introduced by Orapeleng et al. [14], would provide an alternative materials source for further development of the SLFB.

2. Experimental

A comparison of RGE and RE based on several performance criteria have been carried out to asses efficacy of the RE. Comparison criteria focussed on performance evaluation of both electrolytes in a soluble lead static cell (SLSC) and a soluble lead flow cell (SLFC).

To assess performance in an electrochemical energy storage cell, criteria outlined by Ponce de Leon [2] was used. In these criteria, standard parameters suitable for evaluating different battery technologies were used. These are charge, energy, and voltage efficiencies. These help to normalise the performance of different technologies and different size cells, making it possible to compare dissimilar batteries:

Voltage efficiency, $\eta_V = \dfrac{V_{cc}(Discharge)}{V_{cc}(Charge)}$ (4)

Charge efficiency, $\eta_C = \dfrac{Q(Discharge)}{Q(Charge)}$ (5)
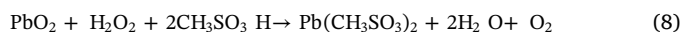
Energy efficiency, $\eta_e = \dfrac{E(Discharge)}{E(Charge)}$ (6)

Power efficiency, $\eta_P = \dfrac{IV_{cc}(Discharge)}{IV_{cc}(Charge)}$ (7)

To compare the above parameters, the electrolytes were galvanostatically cycled in a 5 cm x 5 cm SLSC and in a 4 cm x 2.5 cm SLFC. Battery cycle life, which is an important indicator of battery life and has

implications on lifetime costs of a storage system, was determined for both cell types.

2.1. Recovered soluble lead flow battery electrolyte

Recovered electrolyte (RE) was prepared using electrodes from an expended 7 Ah, 12 V Valve Regulated Lead Acid (VRLA), Yuasa NP7-12 L battery in methanesulfonic acid and hydrogen peroxide. The electrodes were crushed into solids of rough diameter 10^{-4} - 10^{-3} m and used as the solute in 2.5 mol·dm^{-3} methanesulfonic acid. To aid reduction of the PbO$_2$ and oxidation of Pb into Pb^{2+} ions, 0.1 mol·dm^{-3} hydrogen peroxide was added [15] (p600). The reactions are:

$$PbO_2 + H_2O_2 + 2CH_3SO_3\,H \rightarrow Pb(CH_3SO_3)_2 + 2H_2\,O + O_2 \quad (8)$$

$$Pb + H_2O_2 + 2CH_3SO_3H \rightarrow Pb(CH_3SO_3)_2 + 2H_2O \quad (9)$$

A full description of the method used to make recovered electrolyte is covered in [14].

The composition of the recovered electrolyte, analysed using Inductively Coupled Plasma Mass Spectroscopy, is given in Fig. 4.

2.2. Equipment

An eight channel battery analyser by MTI Corporation was used for galvanostatic cycling. The electrochemical battery analyser was connected to a laptop with software that allowed control of experiments as well as recording of the data as the experiment progressed. During flow cell electrochemical tests, a Watson Marlow 505S peristaltic pump was used to circulate electrolyte for the soluble flow cell.

2.3. Test cells

2.3.1. Static cell
A static cell was made of two 5 cm x 5 cm x 2 mm SIGRACELL graphite electrodes. The electrodes were separated by a silicone insulator, which created a 5 cm x 5 cm x 8 mm cell chamber in which electrolyte was collected. The silicone gaskets also provided insulation against electrolyte leaks. A 5 cm x 5 cm x 0.1 mm thick nickel foil was placed flush against the back of each electrode to act as a current collector. Silicone gaskets were used to insulate the cell's conductive parts from the clamps that held the cell together. The current collectors were connected to the battery analyser leads. The cell had an active area of 25 cm^2 on each electrode. The cell-gap was maintained at 8 mm. The cell is shown in Fig. 1.

2.3.2. Flow cell
The soluble lead flow cell, shown in Fig. 2, is made of a polyvinyl chloride (PVC) backing board which gives the cell structural support. Silicone rubber sheets isolate the functional parts of the cell. The cell had 5.0 cm x 4.0 cm x 2.0 mm thick carbon polymer electrodes. A 5.0 cm x 4.0 cm x 0.1 mm thick nickel foil was used to collect current from each electrode. Two acrylic cell chambers provided a 4.0 cm x 2.5 cm by 2 cm half-cell chamber either side of a VPX-20 anion exchange membrane. Each of the acrylic chambers had an inlet and an outlet through which electrolyte entered and left the cell. The electrolyte was circulated between the reservoir and the cell using Watson Marlow 505S peristaltic pumps and Masterflex Norprene tubes. An