Short communication

# A novel flow battery—A lead-acid battery based on an electrolyte with soluble lead(II)
# Part VI. Studies of the lead dioxide positive electrode

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## ARTICLE INFO

## ABSTRACT

The structure of thick lead dioxide deposits (approximately 1 mm) formed in conditions likely to be met at the positive electrode during the charge/discharge cycling of a soluble lead-acid flow battery is examined. Compact and well adherent layers are possible with current densities >100 mA cm$^{-2}$ in electrolytes containing 0.1–1.5 M lead(II) and methanesulfonic acid concentrations in the range 0–2.4 M; the solutions also contained 5 mM hexadecyltrimethylammonium cation, $C_{16}H_{33}(CH_3)_3N^+$. From the viewpoint of the layer properties, the limitation is stress within the deposit leading to cracking and lifting away from the substrate; the stress appears highest at high acid concentration and high current density. There are, however, other factors limiting the maximum current density for lead dioxide deposition, namely oxygen evolution and the overpotential associated with the deposition of lead dioxide. A strategy for operating the soluble lead-acid flow battery is proposed.

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## 1. Introduction

The soluble lead battery with a methanesulfonic acid electrolyte is designed to be a flow battery without a membrane or separator. The overall cell reaction is:

$$2Pb^{2+} + 2H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Pb + PbO_2 + 4H^+ \qquad (1)$$
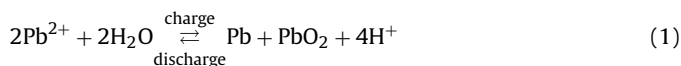
During charge, the decrease in lead(II) concentration is accompanied by an increase in acid concentration and these changes are reversed during discharge. In consequence, the two electrode reactions during charging, namely lead and lead dioxide deposition, must lead to thick layers (approximately 1 mm) with acceptable deposit qualities over a wide range of current density as well as electrolyte compositions. The actual range of electrolyte composition depends on both the solution composition initially introduced into the battery and the extent of charge/discharge. In early battery cycling experiments, it became apparent that, with respect to deposit quality, the major problems were associated with the negative electrode and the lead electrodeposit. Consequently, the initial effort sought an additive which allowed the deposition of good quality lead layers at the negative electrode over a wide range

of electrolyte compositions likely to be met during charge and discharge of the battery; the hexadecyltrimethylammonium cation at a concentration of 5 mM was selected as an appropriate additive [1].

In this paper, attention focused on the positive electrode reaction. We report a study of lead dioxide deposition, in solutions containing $Pb(CH_3SO_3)_2 + CH_3SO_3H + 5$ mM $C_{16}H_{33}(CH_3)_3N^+$ with the objective of defining the range of current density, deposit thickness and electrolyte composition where good battery performance is to be expected at the positive electrode. As in the previous paper [1], the experiments utilised cells with a low ratio of electrode area to solution volume so that, even with the deposition of thick layers, the electrolyte composition was little changed. Hence, the electrolyte composition studied should be regarded as 'snapshots' of the compositions to be encountered during charge/discharge of a flow battery.

While there is an extensive literature on lead dioxide deposition [2–5 and references therein], it generally focuses on the fabrication of stable, thin coatings on carbon or titanium for applications as anodes in electrolysis. This generally leads to optimised conditions with particular electrolytes, low current densities and low charge densities which are very different to the conditions in the battery.

## 2. Experimental details

The preparation of the electrolytes, the three electrolytic cells, the control equipment and the electron microscopy

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**Table 1**
Current density where oxygen gas evolution can be observed at the anode during lead dioxide deposition as a function of electrolyte composition

| [CH$_3$SO$_3$H] M | Current density at which O$_2$ evolution commenced (mA cm$^{-2}$) | |
| --- | --- | --- |
| | 0.3 M Pb$^{2+}$ | 0.5 M Pb$^{2+}$ |
| 1.2 | 90 | 110 |
| 1.6 | 70 | 100 |
| 2.0 | 60 | 80 |
| 2.4 | 50 | 70 |

Beaker cell stirred with magnetic bar (400 rpm).

conditions have all been described in the previous paper [1].

## 3. Results and discussion

Voltammograms recorded at a smooth vitreous carbon disc electrode in the solutions containing Pb(CH$_3$SO$_3$)$_2$ + CH$_3$SO$_3$H + 5 mM C$_{16}$H$_{33}$(CH$_3$)$_3$N$^+$ showed that, with some variation with the exact composition of the electrolyte, deposition of lead dioxide commences close to +1.60 V *vs.* SCE and the currents then increased rapidly to over 300 mA cm$^{-2}$. There were no features that allowed the separation of the currents for lead dioxide deposition and oxygen evolution and, inevitably, the responses were distorted by uncompensated IR drop. Hence, a series of current densities were applied to a PbO$_2$-coated carbon/polymer electrode and they were observed for gas evolution. The current densities when the first O$_2$ bubbles were seen are reported for two series of solutions where the methanesulfonic acid concentration was varied between 1.2 M and 2.4 M in Table 1. It can be seen that high current efficiencies for lead dioxide deposition can be expected with most electrolyte compositions but the maximum current density was found to decrease with decreasing lead(II) concentration and increasing acid concentration. A similar experiment was carried out with a solution containing 0.4 M Pb(CH$_3$SO$_3$)$_2$ + 1 M CH$_3$SO$_3$H + 1.4 M CH$_3$SO$_3$Na + 5 mM C$_{16}$H$_{33}$(CH$_3$)$_3$N$^+$ and then oxygen bubbles were not observed until a current density of 120 mA cm$^{-2}$ (cf. 70 mA cm$^{-2}$ with the electrolyte containing 2.4 M CH$_3$SO$_3$H). This confirms that it is the acid level rather than the methanesulfonate ion concentration that leads to oxygen evolution at lower current densities. The observation that oxygen evolution increased with higher acid concentration is surprising since thermodynamic considerations would predict the contrary. The experimental trend was, however, observed in several later experiments.

Cyclic voltammograms for all studied electrolyte compositions showed a stripping peak for the reduction of the lead dioxide back to Pb(II) on the reverse potential scan and these voltammograms also indicated that there were substantial overpotentials associated with lead dioxide deposition and reduction [6]. The overpotentials are, however, better estimated in a steady state experiment. Fig. 1 shows the potentials (measured *vs.* a SCE reference electrode) of both positive and negative electrodes as a function of current density during both charge and discharge; the measurements are made in the beaker cell with 1 M Pb(CH$_3$SO$_3$)$_2$ + 1.2 M CH$_3$SO$_3$H + 5 mM C$_{16}$H$_{33}$(CH$_3$)$_3$N$^+$ as the electrolyte. It can be seen that the potential of the negative electrode during charge and discharge are similar confirming that the kinetics of the Pb/Pb$^{2+}$ couple are rapid.
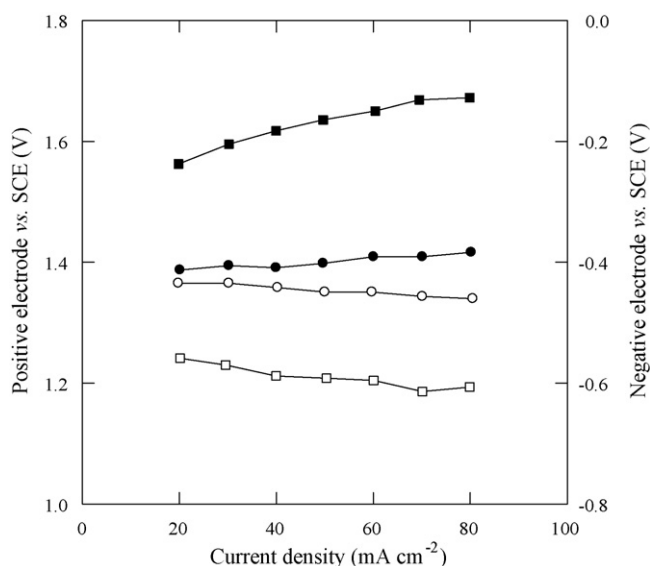


**Fig. 1.** Steady state potential of negative and positive electrodes (*vs.* SCE) as a function of current density. Beaker cell with carbon/polymer composite electrodes. Electrolyte: 1 M Pb(CH$_3$SO$_3$)$_2$ + 1.2 M CH$_3$SO$_3$H + 5 mM C$_{16}$H$_{33}$(CH$_3$)$_3$N$^+$. Magnetic stirrer bar, 500 rpm. Ambient temperature. (■) Positive electrode, charge; (□) positive electrode, discharge; (●) negative electrode, charge; (○) negative electrode, discharge.
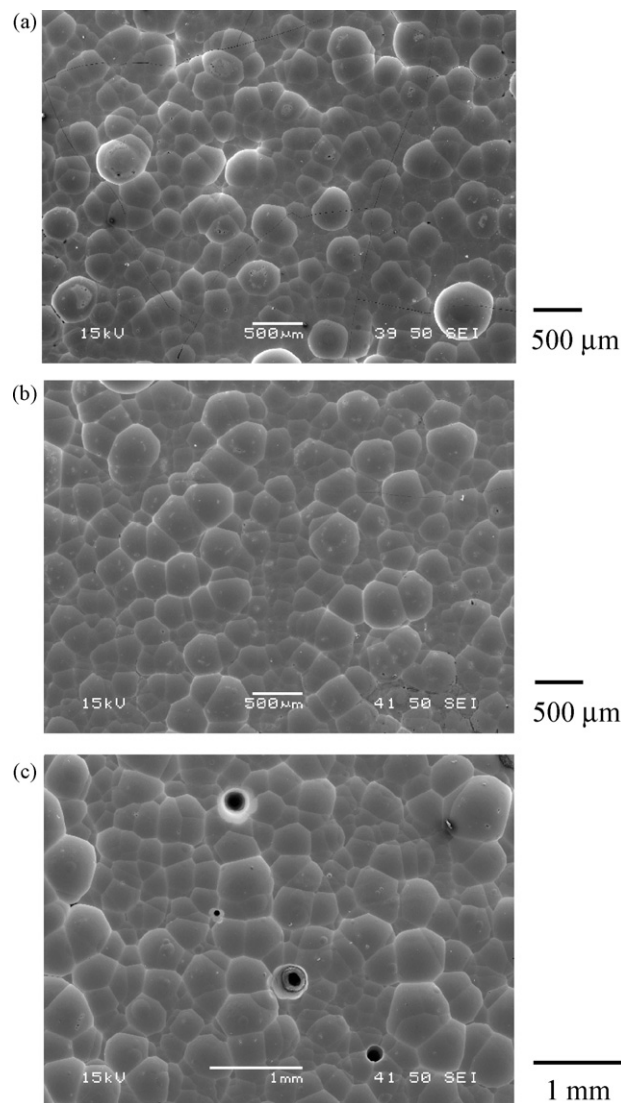


**Fig. 2.** SEM images of the lead dioxide deposits as a function of current density: (a) 50 mA cm$^{-2}$, (b) 80 mA cm$^{-2}$ and (c) 150 mA cm$^{-2}$. Deposition time: 2 h. Electrolyte: 0.5 M Pb(CH$_3$SO$_3$)$_2$ + 0.3 M CH$_3$SO$_3$H + 5 mM C$_{16}$H$_{33}$(CH$_3$)$_3$N$^+$. Beaker cell with carbon/polymer composite electrodes. Magnetic stirrer bar, 500 rpm. Ambient temperature.
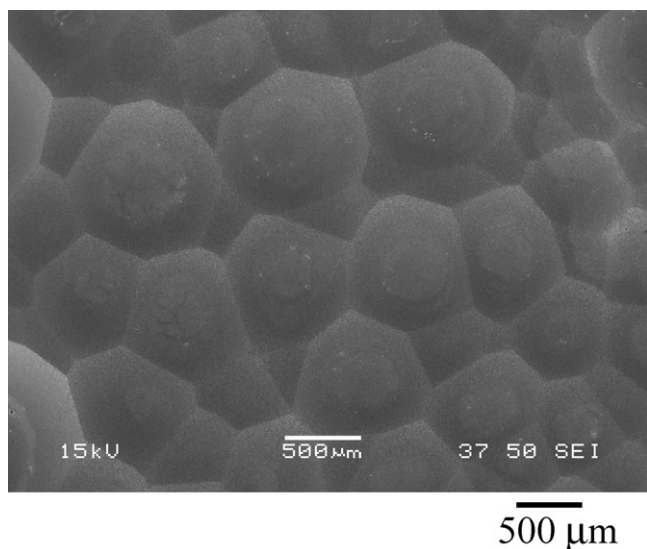
**Fig. 3.** Surface morphology of a lead dioxide deposit formed by 6 cycles, each cycle consisting of $100\,\text{mA}\,\text{cm}^{-2}$ for 30 min followed by $20\,\text{mA}\,\text{cm}^{-2}$ for 2 h. Electrolyte: $0.5\,\text{M}$ $Pb(CH_3SO_3)_2 + 0.3\,\text{M}$ $CH_3SO_3H + 5\,\text{mM}$ $C_{16}H_{33}(CH_3)_3N^+$. Beaker cell with carbon/polymer composite electrodes. Magnetic stirrer bar, 500 rpm. Ambient temperature.

In contrast, the potential of the positive electrode during charge and discharge is quite different and the overpotential increases significantly with current density especially during charge. The potential difference between charge and discharge is >400 mV and this is the major energy loss during a battery charge/discharge cycle.

Deposition of lead dioxide was carried out in the 'beaker' cell with carbon/polymer composite electrodes and containing an electrolyte, $0.5\,\text{M}$ $Pb(CH_3SO_3)_2 + 0.3\,\text{M}$ $CH_3SO_3H + 5\,\text{mM}$ $C_{16}H_{33}(CH_3)_3N^+$. First, the depositions were carried out at current densities between $50\,\text{mA}\,\text{cm}^{-2}$ and $150\,\text{mA}\,\text{cm}^{-2}$. All deposits were dense, uniform, black and reflective with an almost 'ceramic' appearance. The adhesion of the layers was also excellent. Fig. 2 shows SEM images of the surface morphologies and it can be seen that there is relatively little change with current density. With the deposit formed at $150\,\text{mA}\,\text{cm}^{-2}$, a small number of circular holes can be seen and these are presumably the result of gas bubble damage. In fact, however, the damage is minor considering the liberal co-evolution of oxygen gas in these conditions. In order to demonstrate that thick deposits were possible and that the current density could be varied during an extended deposition, an experiment was carried out where the current density was varied periodically between $20\,\text{mA}\,\text{cm}^{-2}$ and $100\,\text{mA}\,\text{cm}^{-2}$ over a 15 h period. The visual appearance was similar to the thinner deposits and the adhesion remained excellent. The SEM image of the surface, Fig. 3, revealed a very similar surface morphology to the thinner deposits shown in Fig. 2.

Figs. 4 and 5 show SEM images of cross-sections of lead dioxide deposits. The deposit in Fig. 4 was formed using a current density of $80\,\text{mA}\,\text{cm}^{-2}$ for 2 h. The layer can be seen to be compact and uniform and the excellent adhesion with the carbon/polymer composite substrate is readily understood. Although some structure may have been lost during the sectioning of the deposit, it can be seen that the deposit is made up of growth features having a large dimension, some with diameters of several hundred microns; these that lead to the surface morphologies seen in Figs. 2 and 3. It is clearly incorrect to interpret the surface morphologies as overlapping hemispheres. This is even more clearly seen in the SEM image of the deposit formed over a longer time period and using the programmed current density, as seen in Fig. 5. This SEM image is the
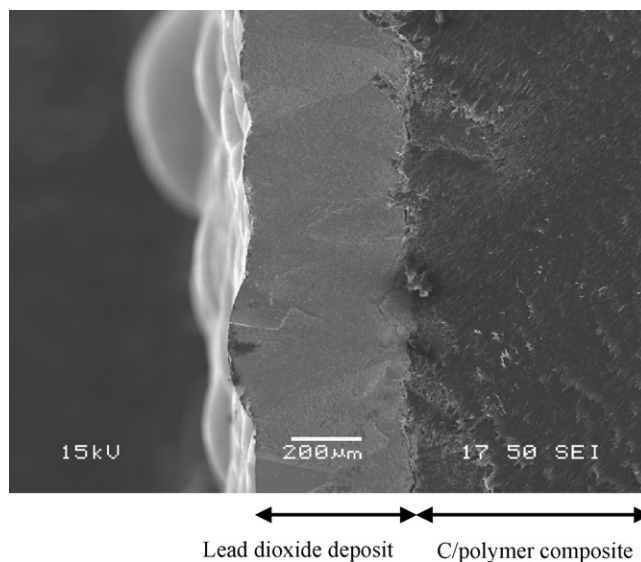


**Fig. 4.** Cross-sectional image of a lead dioxide deposit formed at $80\,\text{mA}\,\text{cm}^{-2}$ for 2 h. Electrolyte: $0.5\,\text{M}$ $Pb(CH_3SO_3)_2 + 0.3\,\text{M}$ $CH_3SO_3H + 5\,\text{mM}$ $C_{16}H_{33}(CH_3)_3N^+$. Beaker cell with carbon/polymer composite electrodes. Magnetic stirrer bar, 500 rpm. Ambient temperature.

cross-section of a fragment of the $PbO_2$ broken away from the substrate and this allows the interfaces at both the substrate and the solution to be seen. The lead dioxide crystallites have diameters of around 1 mm but lead to the same surface morphology (see Fig. 3). The fracture at the substrate/lead dioxide boundary shows that the deposit 'keys' well into the rough substrate surface and this leads to the excellent adhesion. The image shows another important feature of the deposit; the lead dioxide layers formed at $100\,\text{mA}\,\text{cm}^{-2}$ are significantly more compact than that deposited at $20\,\text{mA}\,\text{cm}^{-2}$.

Further experiments employed the Hull cell with carbon/polymer composite electrodes to define the influence of acid concentration and current density on the lead dioxide deposition reaction. The cell current was 1 A, giving a local current density range of $5$–$100\,\text{mA}\,\text{cm}^{-2}$ over the positive electrode plate,
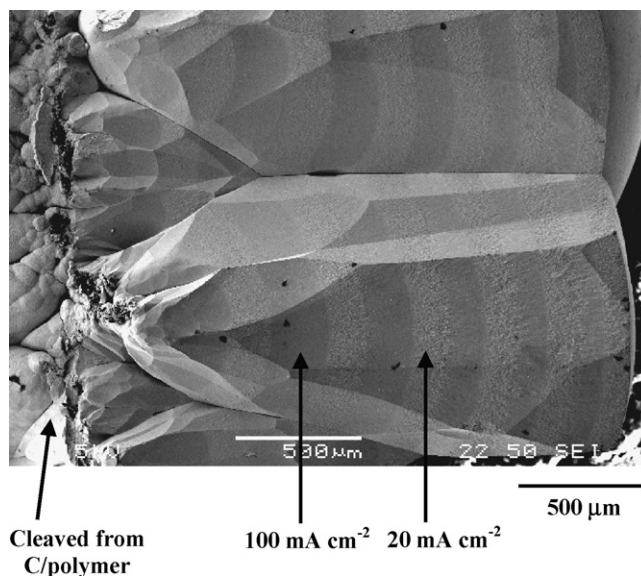


**Fig. 5.** Cross-sectional image of the lead dioxide deposit formed by 6 cycles, each cycle consisting of $100\,\text{mA}\,\text{cm}^{-2}$ for 30 min followed by $20\,\text{mA}\,\text{cm}^{-2}$ for 2 h. Electrolyte: $0.5\,\text{M}$ $Pb(CH_3SO_3)_2 + 0.3\,\text{M}$ $CH_3SO_3H + 5\,\text{mM}$ $C_{16}H_{33}(CH_3)_3N^+$. Beaker cell with carbon/polymer composite electrodes. Magnetic stirrer 500 rpm. Ambient temperature.
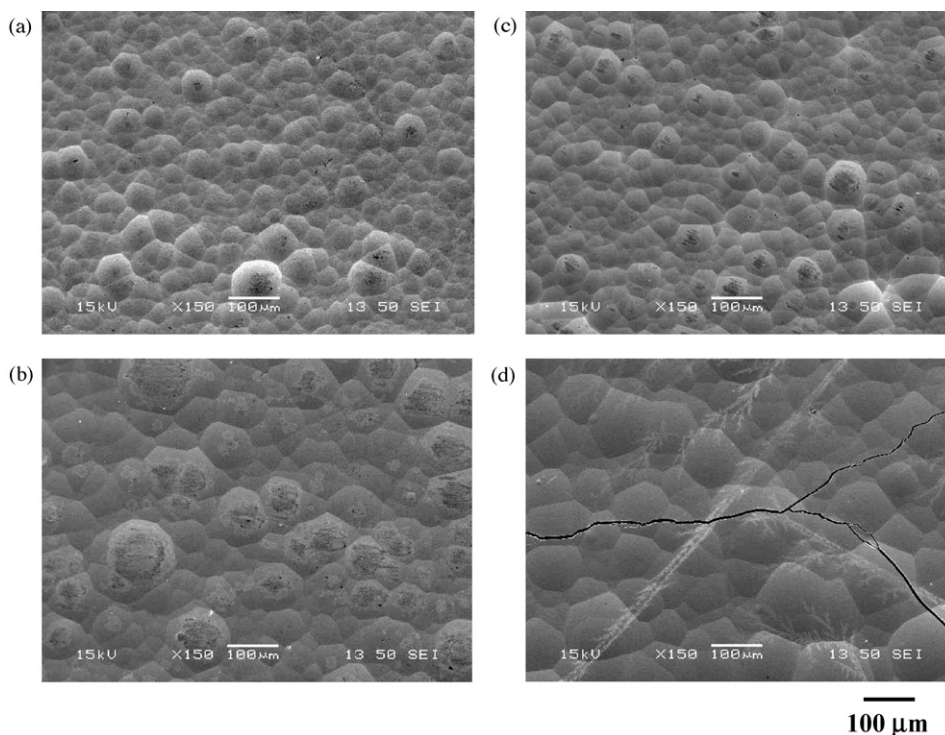
**Fig. 6.** SEM images of the lead dioxide deposits formed in the Hull cell with carbon/polymer composite electrodes at positions corresponding to current densities of (a), (c) 20 mA cm$^{-2}$ and (b), (d) 50 mA cm$^{-2}$. Deposition time: 2 h. Electrolytes (a), (b) 1.5 M Pb(CH$_3$SO$_3$)$_2$ + 0.15 M CH$_3$SO$_3$H + 5 mM C$_{16}$H$_{33}$(CH$_3$)$_3$N$^+$; (c), (d) 1.5 M Pb(CH$_3$SO$_3$)$_2$ + 1.5 M CH$_3$SO$_3$H + 5 mM C$_{16}$H$_{33}$(CH$_3$)$_3$N$^+$. Ambient temperature.

and the deposition time was 2 h. The first experiment employed 1.5 M Pb(CH$_3$SO$_3$)$_2$ + 0.15 M CH$_3$SO$_3$H + 5 mM C$_{16}$H$_{33}$(CH$_3$)$_3$N$^+$ as the electrolyte. By eye, the deposits were uniform, shiny and high quality over all the plate. In addition, the adhesion of the lead dioxide to the substrate was excellent over the whole plate. Fig. 6(a) and (b) reports SEM images of the PbO$_2$ deposit at the positions on the plate where the current densities were 20 mA cm$^{-2}$ and 50 mA cm$^{-2}$; the morphology did not change much with current density and the deposit can be seen to be uniform and the surface has the morphology disclosed in Figs. 2 and 3. When the experiment was repeated with the electrolyte, 1.5 M Pb(CH$_3$SO$_3$)$_2$ + 1.5 M CH$_3$SO$_3$H + 5 mM C$_{16}$H$_{33}$(CH$_3$)$_3$N$^+$, i.e. a 10-fold increase in acid concentration, the quality of the deposit was again good and, in most respects, the morphology was similar (see Fig. 6(c) and (d)). The SEM image of the deposit formed at 50 mA cm$^{-2}$, however, showed some small cracks. At positions on the plate corresponding to higher current densities, the cracks broaden and can be seen by eye and at the highest current densities, some of the deposit was lifting away from the substrate. It is clear that with the 1.5 M acid and at higher current densities, the lead dioxide layer was stressed. As long as these conditions were avoided, however, the deposits could all be regarded as satisfactory for battery operation.

The possibility of using nickel positive electrodes was investigated due to the perceived benefits from having all metal electrodes (current collectors) in large batteries. Depositions were carried out from electrolytes with several lead(II) and methanesulfonic acid concentrations. In all conditions, it was possible to electrodeposit thick layers. Also there were no immediate signs of nickel corrosion despite the very positive potential for the deposition. In contrast to the carbon/polymer substrates, however, the adhesion of the lead dioxide to the nickel was poor and the lead dioxide layer was less compact. In consequence, during experiments in the flow cell, much of the lead dioxide was eventually dislodged into the electrolyte and

the charge efficiency for a charge/discharge cycle rapidly declined to an unacceptable value.

## 4. Conclusions

1. Very compact and uniform, thick layers of lead dioxide, well adherent to the carbon/polymer composite, can be deposited from electrolytes containing a wide range of methanesulfonic acid and lead(II) concentrations and using a good range of current densities up to 100 mA cm$^{-2}$. The SEM images show that the surface morphology to be insensitive to the deposition conditions and satisfactory layers >1 mm can be deposited. The limitation to the deposition conditions appears to be stress within the layer leading to cracking of the PbO$_2$ layer and even lifting of the layer away from the substrate surface. The stress is greatest with concentrated acid and at high current density.

2. While high stress within the lead dioxide layer would limit the conditions satisfactory for battery operation, in practice other factors determine the maximum current density for lead dioxide deposition in the battery:

   (a) *oxygen evolution*: this does not necessarily damage the deposit to the extent that it would be unsatisfactory in a battery, but it does decrease the current efficiency for PbO$_2$ deposition and hence leads to loss in energy efficiency and to a chemical imbalance at the two electrodes (excess lead builds up on the negative electrode). Oxygen evolution on the lead dioxide surface increases with the concentration of methanesulfonic acid. Since the concentration of the acid increases during charge, this limits the extent to which a battery can be charged although this limiting current density is also a function of the current density.

   (b) *overpotential*: there is a significant loss in energy efficiency with increasing current density and this is largely associated with the overpotential at the PbO$_2$/Pb$^{2+}$ electrode.

3. All the electrolytes used in this work contained 5 mM $C_{16}H_{33}(CH_3)_3N^+$. This additive was present in the electrolyte to improve the uniformity of lead deposition at the negative electrode. It was found that the additive did not adversely affect the performance of the positive electrode; there was no evidence that it decomposed with time and it had a tendency to slightly improve the quality of the lead dioxide deposits.

4. In the previous paper [1], it was concluded that, from the viewpoint of the negative electrode in a flow battery, a possible electrolyte for newly installed batteries would be 1.2 M $Pb(II) + 5$ mM $C_{16}H_{33}(CH_3)_3N^+$ without added acid; it might then be cycled between 0.2 M $Pb(II) + 2$ M $CH_3SO_3H$ at top of charge to and 1.15 M $Pb(II) + 0.1$ M $CH_3SO_3H$ at bottom of charge. Also the current density could be up in the range of 20–80 mA cm$^{-2}$. The results in this paper imply that these would be suitable conditions for the positive electrode. This strategy will be examined in larger cells with electrode area to electrolyte volume ratios that allow large swings in electrolyte compositions; such cells are under construction.

## Acknowledgement

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