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Short communication

A novel flow battery: A lead acid battery based on an electrolyte with soluble lead(II). Part IX: Electrode and electrolyte conditioning with hydrogen peroxide

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ABSTRACT

Extended cycling of a soluble lead acid battery can lead to problems due to an imbalance in the coulombic efficiency leading to deposits of Pb and PbO2 on the electrodes. Periodic addition of hydrogen peroxide to the electrolyte of the soluble lead acid flow battery largely overcomes several operational problems seen during extended cycling, using a 10 cm × 10 cm parallel plate flow cell. It is shown that this treatment greatly extends the number of cycles that can be achieved with a reasonable energy-, voltage-, and charge efficiency of 54–66%, 71%, and 77–91%.

1. Introduction

The soluble lead acid flow battery [1–9] has been developed on the laboratory scale with a view to large scale energy storage. It differs from the traditional lead acid battery in that it employs a methanesulfonic acid electrolyte in which lead(II) is highly soluble so that the overall cell reaction is:

$$2Pb^{2+} + 2H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Pb + PbO_2 + 4H^+ \quad (1)$$

A previous paper in this series [8] has described charge cycling of the battery. Under certain conditions, a unit cell can be operated through more than 50 charge/discharge cycles. In general, however, the charge efficiency never exceeds 90% and this charge imbalance leads to a progressive build-up of solid deposits on both electrodes, namely lead on the negative electrode and lead dioxide on the positive electrode. After a number of cycles, this build-up of solids could lead to shorting and certainly to a drop in lead(II) concentration in solution. Consequently changes can occur in the structure of the deposits (the lead becomes more dendritic and the lead dioxide changes from α-PbO_2 to β-PbO_2) together with particulate lead dioxide from the positive electrode into solution. It has been shown [7] that the charge inefficiency during battery cycling results from incomplete reduction of the lead dioxide; it has been proposed that this is a consequence of acid starvation within the lead dioxide layer.

It has become clear that a procedure that restores both the electrodes and the electrolyte to their initial condition could be essential to the indefinite operation of the soluble lead acid flow battery. This paper describes such a procedure that involves periodic addition of hydrogen peroxide to the electrolyte when the battery is in a discharged state.

2. Experimental details

The experimental procedures, the flow cell and the control and data logging instrumentation have all been described in detail previously [8]. For the data reported here, the positive and negative electrodes were carbon polyvinyl-ester composite (Entegris) and nickel plate (Goodman Alloys Ltd.), respectively. Copper plates (10 cm × 10 cm × 0.3 cm) were used as current collectors. The electrodes were secured to the current collectors using polypropylene frame (TM Plastics Ltd.) and then masked using insulating tape to protect the copper from corrosion, giving the exposed electrode area 10 cm × 10 cm for both positive and negative electrodes. The inter-electrode gap of 1.2 cm was established using polypropylene frame and elastomeric EPDM gaskets (Klinger) which are put between frames to seal the cell.

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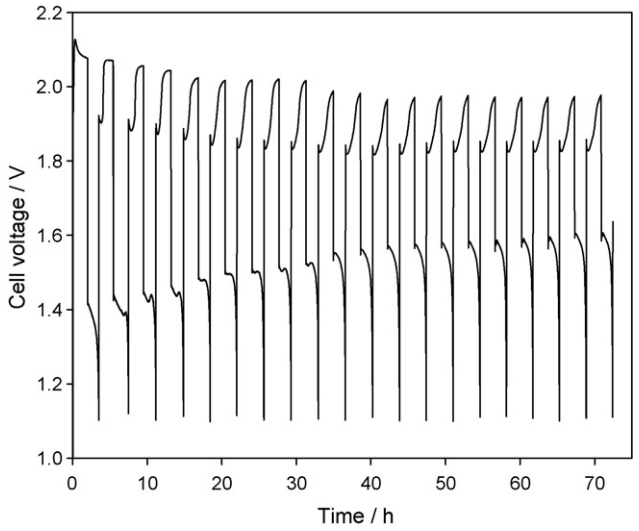

Fig. 1. Cell voltage *vs*. time responses for initial 20 charge/discharge cycles of a soluble lead acid flow cell. The cell was charged at a current density of 20 mA cm^{-2} for 2 h and then discharged at the same current density until the voltage dropped to 1.1 V. Inter-electrode gap: 1.2 cm. Flow rate: 2.3 cm s^{-1}. Temperature: 298 K.

The electrolyte comprised 0.5 M $Pb(CH_3SO_3)_2$ + 0.5 M CH_3SO_3H containing the additive, 5 mM $C_{16}H_{33}(CH_3)_3N^+$ added as the hydroxide, and had a volume of 1500 cm^3, which was stored in a 2-l cylindrical reservoir and circulated through the system via a pump (Totton Pumps, type T113095) with a mean linear flow velocity of 2.3 cm s^{-1} past the electrode surfaces. The charge/discharge cycling experiment was carried out using an in-house developed, computer controlled charge–discharge and automated logging system. Constant currents were applied and drawn using a dc power supply and load (Thurlby Thandar Instruments, UK). The cell voltage was measured directly using a National Instruments data acquisition system. The lead(II) concentrations in the electrolyte were determined using a vitreous carbon rotating disc electrode (RDE). The electrolyte was diluted 100-fold with 1 M $NaNO_3$ and voltammograms for the Pb^{2+}/Pb reaction were recorded. The slopes of limiting current *vs*. square root of the rotation rate plots were then compared with such plots for standard solutions prepared from crystalline lead nitrate.

After 15–20 cycles of charge–discharge at 20 mA cm^{-2} for 2 h duration, the electrolyte were treated with 0.86 mol of hydrogen peroxide (a 50% excess based on the Pb and PbO_2 estimated to be in the system). This was added as 30% H_2O_2 in 5 aliquots at ≈15 min intervals to the cell electrolyte with the cell on open circuit while the electrolyte continued to circulate through the cell.

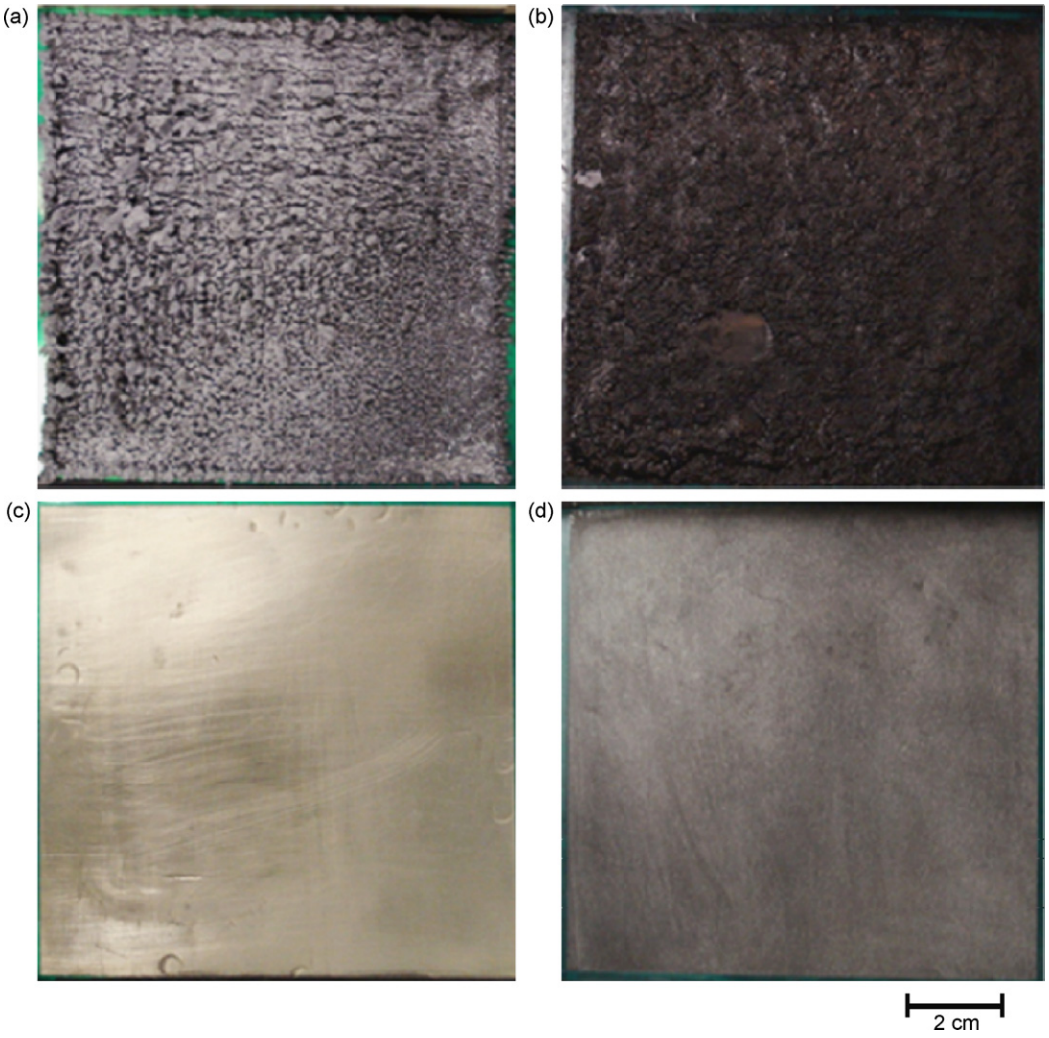

Fig. 2. Photographs of electrode surface morphologies before (a and b) and after (c and d) cleaning with H_2O_2: (a) Pb deposit on nickel negative electrode plate and (b) PbO_2 deposit on carbon positive electrode plate at the end of the discharge from the 20th cycle; (c) nickel negative electrode plate and (d) carbon positive electrode plate after cleaning with H_2O_2 by adding 30% H_2O_2 to the extent of a 50% excess over the quantity required to remove all the Pb and PbO_2 remaining in the cell and electrolyte after the 20th charge/discharge cycle.

3. Results

As reported in the previous paper [8], a series of charge/discharge cycling experiments were carried under the following conditions:

- undivided, parallel plate flow cell with no inlet/outlet distributors and 10 cm × 10 cm electrodes and 1.2 cm inter-electrode gap.
- Entegris carbon composite positive electrode and nickel negative electrode.
- Electrolyte: 0.5 M $Pb(CH_3SO_3)_2$ + 0.5 M CH_3SO_3H + 5 mM $C_{16}H_{33}(CH_3)_3N^+$, volume 1500 cm^3 and flow rate 2.3 cm s^{-1}.
- A charge at 20 mA cm^{-2} for 2 h followed by a discharge at 20 mA cm^{-2} until the cell voltage dropped to 1.1 V.

While it was possible to achieve extended cycling, it was noted that deposits built up on both electrodes, lead on the negative electrode and lead dioxide on the positive electrode, and shedding of material to give a blackened electrolyte was also observed. Clearly, some remedial treatment was essential.

A cell was subjected to 20 charge/discharge cycles under the above conditions (see Fig. 1). The cell voltage *vs.* time record shows no symptoms to indicate a problem; there is, in fact a slight improvement in voltage efficiency balanced by a slight drop in charge efficiency to give an almost constant energy efficiency of 60–65%. During, the 16th cycle, however, the electrolyte rather quickly changed from a clear solution to one containing fine, black particulate material and some black solid started to collect around the flow circuit in places where there was poor convection. After 20 cycles and at the end of discharge, the cell was opened and photographs were taken of the two electrodes (see Fig. 2). Fig. 2(a) shows the negative electrode and a lead deposit is clearly visible; the deposit is reasonably uniform although the deposit is heavier at the edges of the electrode. Fig. 2(b) shows the positive electrode surface and there is a significant black deposit. X-ray diffraction confirms that the deposit is largely PbO_2 [7]. The lead(II) remaining in the electrolyte at the end of the 20 cycles was determined using the RDE technique and found to be 0.14 M; the drop in electrolyte lead concentration from 0.5 M is consistent with the ≈15% loss in charge efficiency on each cycle being due to Pb and PbO_2 not being active during the discharge period and remaining on the electrode surfaces. In similar experiments, this material was scraped off, dried and weighed and the amount of PbO_2 was also consistent with a 10–15% loss in current efficiency in each charge/discharge cycle.

Hydrogen peroxide is an unusual reagent which is capable of both oxidation and reduction and its products from these reactions are only the innocuous species, O_2 and H_2O. Hence, hydrogen peroxide was selected as a reagent capable of reacting with both Pb and PbO_2 in the reactions:

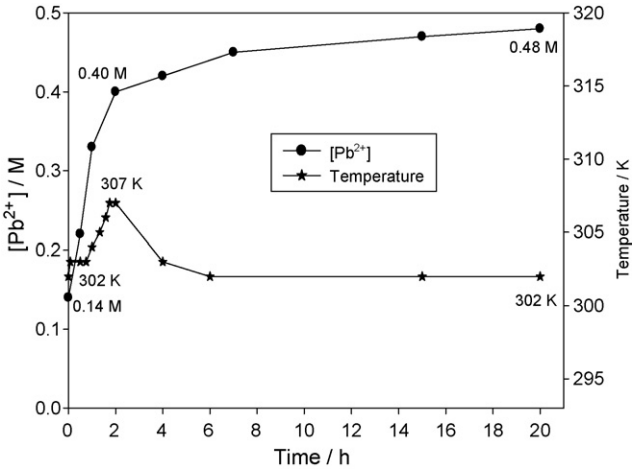

Fig. 3. Concentration of Pb^{2+} in the electrolyte and temperature of electrolyte *vs.* time following the addition of 30% H_2O_2 to the extent of a 50% excess over the quantity required to remove all the Pb and PbO_2 remaining in the cell and electrolyte after the 20th charge/discharge cycle at a current density of 20 mA cm^{-2} at 298 K for 2 h charge duration with a flow rate of 2.3 cm s^{-1}.

$$Pb + H_2O_2 + 2H^+ \rightarrow Pb^{2+} + 2H_2O \quad (2)$$

$$PbO_2 + H_2O_2 + 2H^+ \rightarrow Pb^{2+} + O_2 + 2H_2O \quad (3)$$

and therefore returning the cell and electrolyte to their initial conditions [10–12]. With the cell on open circuit, the electrolyte after 20 cycles was treated with 0.86 moles of hydrogen peroxide. Initially, the electrolyte foamed as a gaseous product was formed and the black particulate material in the electrolyte disappeared within minutes and the open circuit potential dropped from +1.64 to below +1.0 V rather quickly. A small temperature rise of 5 K from the initial value of 302 K, occurred initially before the temperature slowly declined back to 302 K. The lead(II) concentration was monitored, again using the RDE method and the value as a function of time from the first addition of the hydrogen peroxide is reported in Fig. 3. The lead(II) concentration has reached 0.4 M within 2 h; thereafter, the increase is somewhat slower, approaching the initial lead(II) concentration after 20 h. At the end of this period, the cell was opened and there was little deposit on either electrode as shown in Fig. 2(c) and (d). It would appear that the reaction of the hydrogen peroxide with the lead dioxide is rapid and all the lead dioxide is consumed by the time the addition of hydrogen peroxide is complete. The reaction with the lead is, unfortunately, slower but all of the lead does eventually redissolve.

Table 1
Data from an extended cycling of the soluble lead acid flow cell with periodic treatments of the cell and electrolyte by addition of hydrogen peroxide.

Action sequence	% Average charge efficiency	% Average voltage efficiency	% Average energy efficiency
Fresh electrolyte Cycles 1–18	91	72	66
H_2O_2 treatment Cycles 19–33	83	72	60
H_2O_2 treatment Cycles 34–49	80	72	58
H_2O_2 treatment Cycles 50–64	77	71	55
H_2O_2 treatment Cycles 65–80	77	70	54

The hydrogen peroxide remediation procedure was then tested during extended cycling; Table 1 reports such an experiment. Throughout, the battery cycling was continued until there was some build up of black deposit in the circulating electrolyte and/or there was evidence of oxygen evolution during charging. The latter led to excursions of the cell voltage to unusually high values and subsequent voltage oscillations and might be expected as the lead(II) concentration in the electrolyte drops below a critical value. Indeed, analysis of the lead(II) in the electrolyte indicated that before each remedial treatment, it had dropped to below half the initial value. It can be seen that the addition of hydrogen peroxide does not influence the voltage efficiency but does lead to a small decrease in the charge efficiency and hence energy efficiency. This may result from the addition of excess hydrogen peroxide. A total of 80 cycles was completed before the experiment was terminated and at the end the cell seemed to perform reasonably. Certainly, the electrolyte and cell components had a similar appearance to that at the start of the experiment and the procedure seems to offer a route to continuous, extended operation of the cells.

4. Discussion

It has been shown that a periodic treatment with hydrogen peroxide prevents the electrode deposits building up to an unacceptable thickness and probably also unwanted roughness of the deposits (and eventually cell shorting and massive shedding from the positive electrode), as observed in long term experiments without such treatments. In consequence, the periodic remediation procedure offers the possibility of very much extended battery cycling.

The need for a remediation treatment has, however, several drawbacks. It would lead to the requirement of a bigger cell house within the energy storage unit since, at any time, a fraction of the cells would be out of commission for the treatment; a faster treatment would minimise the fraction of cells out of commission and it should be noted that complete removal of the lead each treatment may not be essential. The treatment would also lead to additional plant units to handle the hydrogen peroxide. Finally, the hydrogen peroxide would have a significant cost and the energy used in its production should also be considered in the energy efficiency of the energy storage concept based on the soluble lead acid flow cell. For these reasons, the priority in the further development of the soluble lead acid flow cell remains the identification of modifications that lead to the reduction or elimination of the charge inefficiency on each cycle as well as the overpotential at the positive electrode.

5. Conclusions

A simple chemical approach to removing the Pb and PbO_2 from the electrodes and restoring the optimum electrolyte composition has been reported. The procedure involves the periodic addition of hydrogen peroxide to the electrolyte while the cell is in the discharged state. Such a procedure can restore both the electrodes and electrolytes to their initial conditions and would be a promising approach to long term operation of the soluble lead acid flow battery.

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