

A novel flow battery—A lead acid battery based on an electrolyte with soluble lead(II)

IV. The influence of additives

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Abstract

During development of an undivided flow battery based on the Pb(II)/Pb and PbO₂/Pb(II) couples in aqueous methanesulfonic acid, it was noted that battery performance might be improved by additives that (i) decrease the roughness of the lead deposit at the negative electrode and (ii) enhance the kinetics of the Pb(II)/PbO₂ couple at the positive electrode. This paper reports the study of sodium ligninsulfonate and polyethylene glycol as potential levelling agents for lead and of three inorganic ions as possible catalysts for the Pb(II)/PbO₂ couple. The addition of 1 g dm⁻³ ligninsulfonate leads to uniform deposits without the tendency to form dendrites but leads to a slight decrease in both charge and energy efficiency for the battery. Only nickel(II) reduced the overpotential for PbO₂ deposition but again it has an adverse influence on the energy efficiency.

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1. Introduction

In recent papers [1–3], a novel flow battery has been reported. The battery is based on the electrode reactions of lead(II) in methanesulfonic acid (see Eqs. (1)–(3) in the previous paper [3]). The reactions differ from those in the traditional lead acid battery [4,5] because lead(II) is highly soluble in methanesulfonic acid [6].

During these earlier studies, two potential roles for additives were identified. Firstly, it was found that although deposits of PbO₂ at the positive electrode always appeared to have the essential uniformity, under some conditions the lead deposit at the negative electrode became very uneven and there was the possibility of the metal growing across the interelectrode gap, hence shorting of the battery. Secondly, it was noted that the poor kinetics of the PbO₂/Pb²⁺ couple

led to overpotentials during both charge and discharge that were large compared to those at the negative electrode and the IR drop through the electrolyte. The overpotentials at the positive electrode were therefore the major cause of loss in energy efficiency during battery cycling. Hence, both levelling agents for lead at the negative electrode and catalysts for the positive electrode reaction were of interest. Clearly, any additive must be soluble and stable in the very acidic electrolyte. Moreover, in addition to achieving their objective, successful additives must also not influence adversely the behaviour of the other electrode since this battery is intended to operate without a separator. For example, additives designed to smooth the lead deposit must also be stable to oxidation at a PbO₂ anode.

A number of additives have been reported for levelling of lead electroplates from acid electrolytes [7–9], although these have been used only for the deposition of relatively thin electroplates in quite different conditions from those in a flow battery. Because of their solubility and stability in acidic media, sodium ligninsulfonate and polyethylene glycol were

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selected for study. A number of inorganic ions (e.g. Sb(V), Bi(III), Fe(III), Ni(II) and Ag(I)) are known to influence the conductivity and electrocatalytic properties of PbO_2 ([10–12] and references therein [13,14]). Moreover, Cu(II) is a common additive in recipes for the electroplating of PbO_2 layers [15–17], although its role is not clear and alloying elements in lead positive electrode current collectors in lead acid batteries are known to improve battery performance [4,5,16]. Hence, the influence of three such metals ions (Ni(II), Fe(III) and Bi(III)) in the electrolyte on the battery performance was also investigated.

2. Experimental

All solutions were prepared with water from a Whatman Analyst Purifier, methanesulfonic acid (Aldrich) and lead carbonate (BDH) and where appropriate sodium ligninsulfonate (Aldrich), polyethylene glycol, molecular weight 200 (Lancaster Synthesis), nickel carbonate (BDH), ferric nitrate (Hogg Laboratory Supplies) and bismuth nitrate (BDH). All solutions were thoroughly deoxygenated with a rapid stream of nitrogen bubbles prior to experiments.

Voltammetry was carried out in a two compartment, glass cell with a volume of $\sim 20 \text{ cm}^3$ and it was immersed in a Camlab W14 water thermostat at a temperature of 298 K. The vitreous carbon rotating disc electrode (area 0.08 cm^2) or rotating nickel disc (0.32 cm^2) working electrodes and the Pt wire counter electrode were in the same compartment but the saturated calomel reference electrode (SCE) was separated from the working electrode by a Luggin capillary. The cell was designed with a fine glass frit to allow efficient entry of gases to the solutions. Before each experiment, the rotating disc electrodes were polished with alumina powder ($1 \mu\text{m}$, then 0.3 and $0.05 \mu\text{m}$) on a moist polishing cloth (Beuhler), wiped on a clean piece of polishing cloth and rinsed well with deionized water after each polish.

The charge/discharge experiments were carried out in a small undivided flow cell with two electrodes, geometric areas 2 cm^2 and interelectrode gap either 4 or 16 mm [2]. The electrodes consisted of a carbon powder/high density polyethylene composite back plate (core), thickness 3.2 mm, with an active layer (tile) on the surface produced by heat bonding under pressure. Three types of electrodes with different active layers were used:

- (i) Type 1 electrodes were fabricated by pressing a piece of 40 ppi nickel foam, initial thickness 1.8 mm into the plate with a pressure of 6 kg cm^{-2} at 433 K.
- (ii) Type 2 electrodes were fabricated by pressing a piece of 70 ppi reticulated vitreous carbon, initial thickness 1.5 mm into the plate in the same conditions.
- (iii) Type 3 electrodes were prepared from type 2 by scraping away the reticulated carbon layer with a knife. This leaves a rough surface with many vitreous carbon particles.

Scanning electron microscope (SEM) photographs of these structures have previously been reported [2]. The electrolyte temperature was controlled at 298 K.

Electrochemical experiments were carried out using one of three sets of equipment: (i) a laboratory constructed potentiostat controlled by a PC with a National Instruments LabVIEW™ 5.1 interface card and in-house written software, (ii) a laboratory constructed galvanostat controlled by the PC with a Measurement Computing CIO-DAS-08/JR 12-bit interface card, (iii) a model 263A EG & G potentiostat/galvanostat coupled to a PC via a National Instruments MC-GPIB interface card; the system was controlled and data recorded using the EG & G M270 software package. The rotation rate of the disc electrodes (RDEs) was controlled with an EG & G Model 616 RDE unit. Deposits on the electrodes were examined employing a Phillips ESEM environmental scanning electron microscope including elemental analysis by EDAX. Deposit thicknesses were estimated using the facility to tilt the sample within the ESEM chamber in order to examine the edge. They were also estimated using Faraday's law and assuming 100% current efficiency for the deposition.

3. Results and discussion

3.1. Additives for lead electrodeposition

Fig. 1 shows an SEM of a type 2 (reticulated vitreous carbon) negative electrode after extensive charging in the flow cell with an electrolyte initially containing $1.5 \text{ M Pb}(\text{CH}_3\text{SO}_3)_2 + 0.9 \text{ M CH}_3\text{SO}_3\text{H}$. In fact, the cell with an interelectrode gap of 4 mm had shorted after 3 h when a charge of 216 C cm^{-2} had passed and it had been dismantled for examination. Some deposition of lead had occurred throughout the carbon foam but there was an accumulation at the

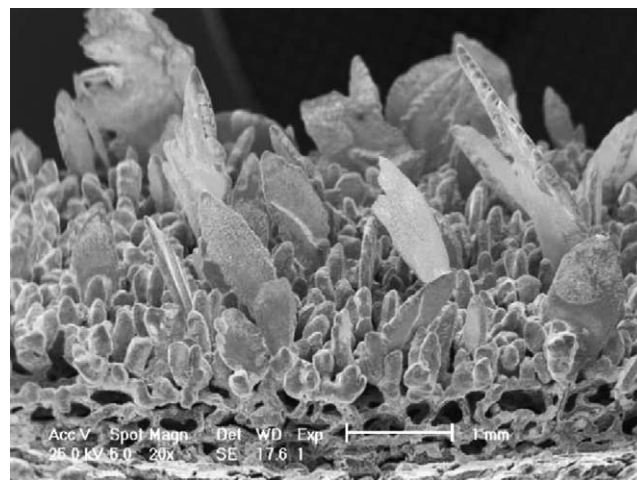


Fig. 1. Scanning electron micrograph of a type 2 (reticulated vitreous carbon) negative electrode after charging at 20 mA cm^{-2} for 3 h. Initial electrolyte: $1.5 \text{ M Pb}(\text{CH}_3\text{SO}_3)_2 + 0.9 \text{ M CH}_3\text{SO}_3\text{H}$ without any additive. Electrolyte flow rate: 10 cm s^{-1} .

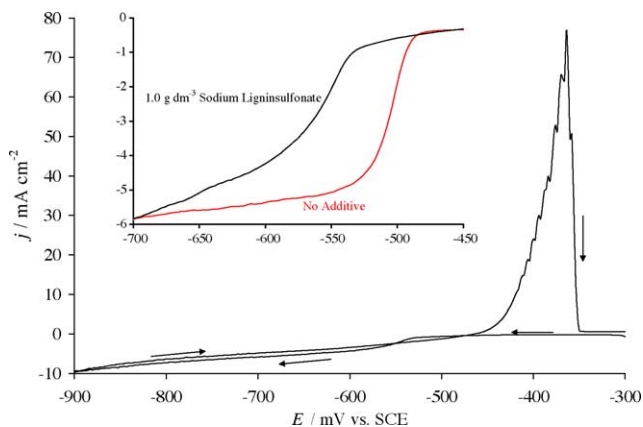


Fig. 2. Cyclic voltammogram at a Ni RDE (1600 rpm) in a solution of 4 mM $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 2 \text{ M CH}_3\text{SO}_3\text{H} + 1 \text{ g dm}^{-3}$ sodium ligninsulfonate. Potential scan rate: 50 mV s^{-1} . The inset shows a comparison on a more sensitive current scale of the forward scans for electrolytes with and without ligninsulfonate.

surface closest to the counter electrode. Moreover, an extensive network of dendrites can be seen growing from the front face of the reticulated vitreous carbon. Clearly, a levelling agent would be advantageous. The quality of the lead deposit depends on a number of experimental parameter, especially the deposition charge, current density, the form of the electrode, and whether the electrode has previously been charge/discharge cycled. For example, the deposits reported as Figs. 4 and 5 in [2] are much superior. The sample shown as Fig. 1 was deliberately selected to illustrate the possible need for an additive.

3.1.1. Sodium ligninsulfonate

A series of cyclic voltammograms were recorded at a Ni RDE (1600 rpm) in a solution of 4 mM $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 2 \text{ M CH}_3\text{SO}_3\text{H} + 1 \text{ g dm}^{-3}$ sodium ligninsulfonate. Fig. 2 illustrates the typical response for a voltammogram run over the potential range where lead deposition and re-dissolution is to be expected. The inset compares the forward scans for solutions with and without additive on a more sensitive current scale. While both solutions show waves for the reduction of $\text{Pb}(\text{II})$ to Pb on the scan towards more negative potentials, the presence of the ligninsulfonate clearly causes some increase in the nucleation overpotential for the deposition of lead (in fact from ~ 35 to $\sim 60 \text{ mV}$) and the reduction wave to become significantly more drawn out along the potential axis. The half wave potential is shifted negative by the addition of ligninsulfonate but at sufficiently negative potential, the limiting currents are the same and proportional to the square root of the rotation rate of the disc, confirming mass transport control. In both solutions, a 'nucleation loop' is clearly seen and the potential where the current is zero on the back scan (a reasonable estimate of the formal potential for the Pb^{2+}/Pb couple in the two solutions) is close to -470 mV , both with and without additive. On the other hand, the slope of the voltammogram through the formal potential is much lower with ligninsulfonate present reflecting the slower kinet-

ics of electron transfer when the additive is in the solution. Both solutions give a sharp lead dissolution peak positive to the formal potential and the ratio of charges associated with the dissolution and deposition of lead are very close to one. Pulsed current experiments confirmed that the overpotentials for the deposition and dissolution of lead are increased by the presence of ligninsulfonate but the magnitudes of the overpotentials remain very small compared with the other voltage losses in the battery. We would also note the ratio of ligninsulfonate to $\text{Pb}(\text{II})$ is much higher in the voltammetric experiments than in the battery electrolyte.

Using solutions containing $0.3 \text{ M Pb}(\text{CH}_3\text{SO}_3)_2 + 2.0 \text{ M CH}_3\text{SO}_3\text{H}$ with and without 1 g dm^{-3} sodium ligninsulfonate, lead layers were plated onto the Ni RDE (900 rpm) at a series of current densities and the deposits were examined by electron microscopy. At low current densities, the deposits were relatively smooth even without additive. At high current densities, the levelling action of the ligninsulfonate becomes apparent. Fig. 3 compares the deposits at two current densities; these pictures are all taken with the sample at an angle so that the thickness of the deposit and the quality of the edge can be assessed. With a current density of 50 mA cm^{-2} , the ligninsulfonate changes the deposit from one made up of large boulders of lead to a relatively smooth deposit. Even at 375 mA cm^{-2} , the influence of ligninsulfonate remains strong and the deposit changes from an uneven, angular and dendritic structure to a uniform 'cauliflower' form likely to be quite acceptable in battery operation.

Therefore, it can be concluded that ligninsulfonate is a levelling agent for lead in the battery electrolyte. The next stage was to examine whether it affects the positive electrode chemistry. Voltammograms were recorded with a vitreous carbon disc electrode over the range 0 to $+1900 \text{ mV}$ with a scan rate of 50 mV using solutions containing $1.5 \text{ M Pb}(\text{CH}_3\text{SO}_3)_2 + 0.9 \text{ M CH}_3\text{SO}_3\text{H}$ and with various additions of sodium ligninsulfonate. The cyclic voltammograms all had the general features for the deposition and dissolution of PbO_2 as reported previously [1]. On the other hand, additions of ligninsulfonate led to a progressive increase in the overpotentials associated with both nucleation and deposition of lead dioxide as well as a slight decrease in charge balance in the deposition and reduction cycle. For example, in experiments containing 1 g dm^{-3} ligninsulfonate the overpotential associated with PbO_2 deposition was 157 mV at 5 mA cm^{-2} (cf. 120 mV in the absence of ligninsulfonate) and the charge efficiency was 78% (cf. 88%). At least in part, the decrease in charge efficiency may be due to the oxygen evolution current during PbO_2 deposition becoming relatively more important as the PbO_2 deposition current density decreases. Scanning electron micrographs showed that the form and quality of PbO_2 layers on vitreous carbon was unaffected by the presence of sodium ligninsulfonate and deposits were almost structureless when viewed on a $10 \mu\text{m}$ scale.

The influence of sodium ligninsulfonate on the structure of the lead and lead dioxide deposits was also studied in a

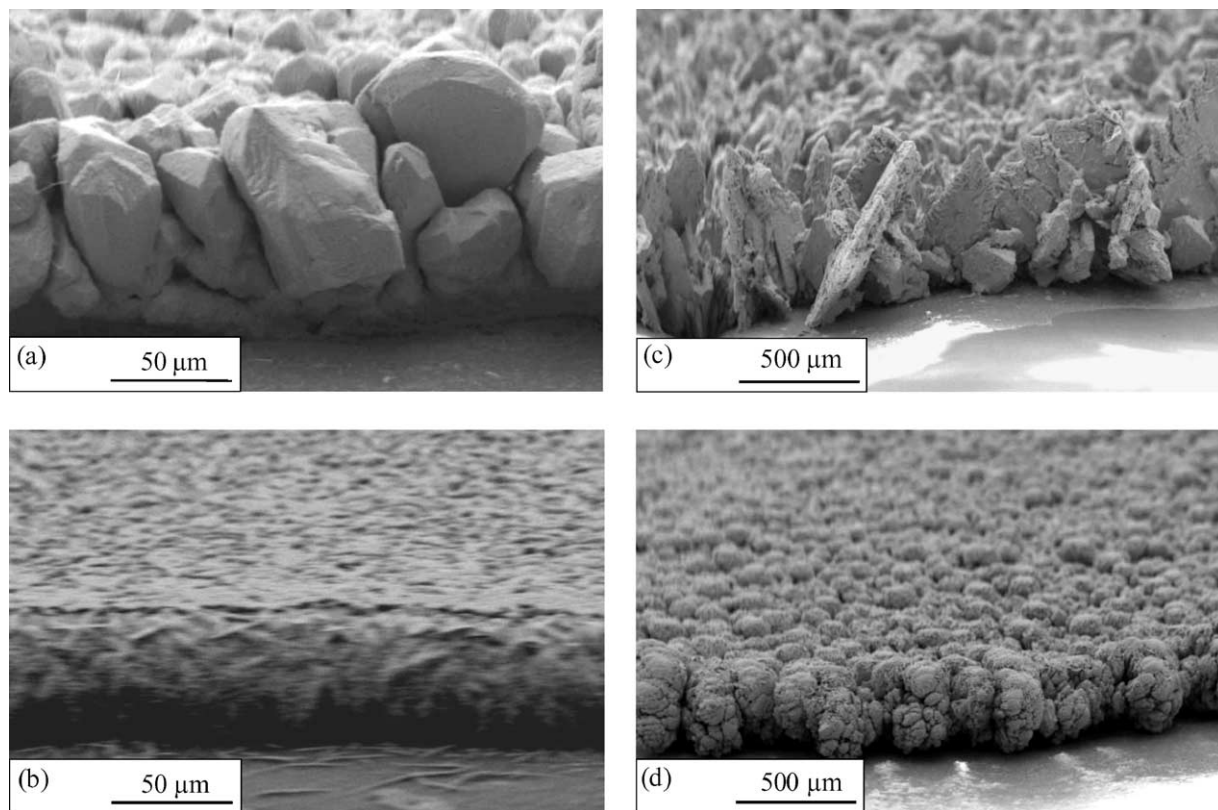


Fig. 3. SEM pictures of the edges (tilted at 70°) of Pb deposits onto a Ni RDE (900 rpm) from baths containing $0.3 \text{ M Pb}(\text{CH}_3\text{SO}_3)_2 + 2 \text{ M CH}_3\text{SO}_3\text{H}$ with (b and d) and without (a and c) 1 g dm^{-3} sodium ligninsulfonate. Current densities: 50 mA cm^{-2} (a and b) and 375 mA cm^{-2} (c and d). Deposition time: 600 s.

small flow cell [2], in these experiments fitted with two carbon powder/high density polyethylene composite plate electrodes (i.e. core without an active layer) with smooth surfaces. Fig. 4 shows SEM images of Pb layers plated during charging of the cell at 20 mA cm^{-2} for 1 h with an electrolyte containing $1.5 \text{ M Pb}(\text{CH}_3\text{SO}_3)_2 + 0.9 \text{ M CH}_3\text{SO}_3\text{H}$ and various concentrations of sodium ligninsulfonate. Without additive, the deposit can be seen to be made up of large individual grains that are not totally merged and there are also some deposit features growing out from the layer. With increasing additive concentration, the deposit becomes more continuous and compact and the grains less angular. Also, even with the lowest ligninsulfonate concentration, there is no sign of lead growing outside this layer towards the counter electrode. The positive influence of sodium lignin sulfonate is even clearer when the edges of these deposits are examined by obtaining images with the sample tilted at 70° , see Fig. 5. In the absence of additive, the individual grains are clearly visible and some dendritic growth is seen but with 1 g dm^{-3} lignin sulfonate, the deposit is smoother and more compact. Fig. 6 illustrates the PbO_2 deposits formed in the same conditions and with low concentrations of the additive; both surfaces are almost featureless on the $10 \mu\text{m}$ scale and the additive can be seen to have relatively little effect. With 5 g dm^{-3} ligninsulfonate, the de-

posit showed a number of hemispherical craters that were likely to result from oxygen bubbles damaging the deposit; this observation supports the postulate above that O_2 evolution consumes a larger fraction of the charge when deposition occurs from an electrolyte with high ligninsulfonate concentrations.

Further experiments examined the deposits on foam electrodes, nickel negative electrodes and reticulated vitreous carbon positive electrodes. The battery was charged at 20 mA cm^{-2} for 1 h with an electrolyte containing $1.5 \text{ M Pb}(\text{CH}_3\text{SO}_3)_2 + 0.9 \text{ M CH}_3\text{SO}_3\text{H}$, without and with 1 g dm^{-3} sodium ligninsulfonate. Fig. 7 shows SEM images of the Ni foam substrate and of the lead deposited onto the foam from solutions with and without 1 g dm^{-3} ligninsulfonate. Without additive, some nodular growth is apparent particularly on the surface facing the positive electrode. With the additive, the deposition is uniform throughout the foam structure. Fig. 8 reports the SEM images of the lead dioxide on the positive electrode after a 6 h charge with the electrolyte containing sodium ligninsulfonate. It can be seen that the deposition is uniform throughout the structure, forming over all exposed carbon surface and there is no sign of dendritic growth. In fact, the deposition is largely uniform in the absence of the additive but the uniformity is further improved by the addition of 1 g dm^{-3} to the electrolyte.

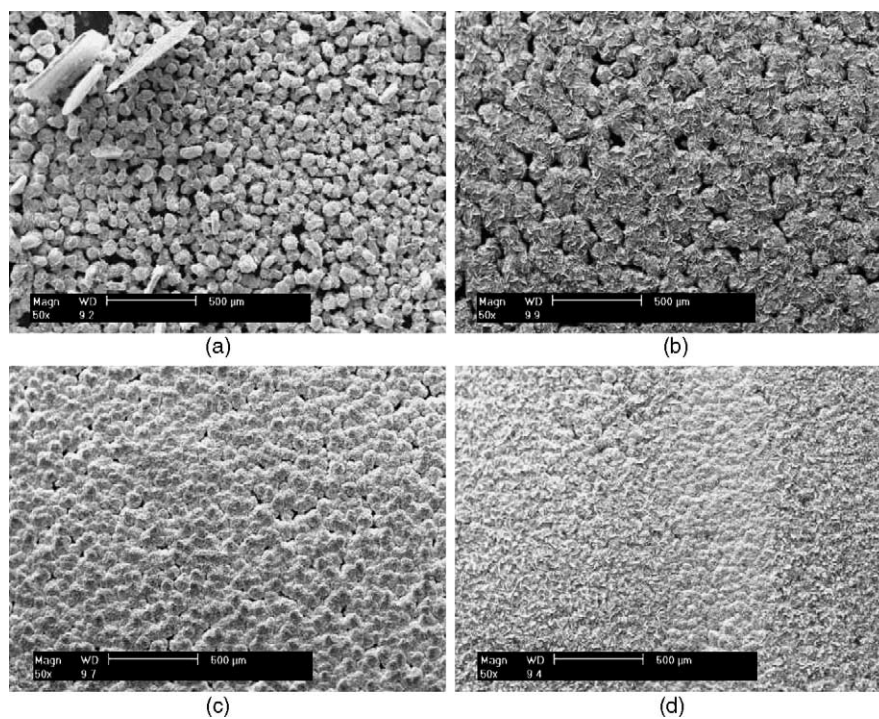


Fig. 4. SEM images of Pb layers plated onto a carbon powder/high density polyethylene composite plate (core without an active layer) from an electrolyte containing 1.5 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2$ + 0.9 M $\text{CH}_3\text{SO}_3\text{H}$ and sodium ligninsulfonate: (a) 0 g dm^{-3} , (b) 0.2 g dm^{-3} , (c) 1 g dm^{-3} and (d) 5 g dm^{-3} . Flow cell [2], mean linear flow rate: 2.5 cm s^{-1} . One hour deposition at: 20 mA cm^{-2} .

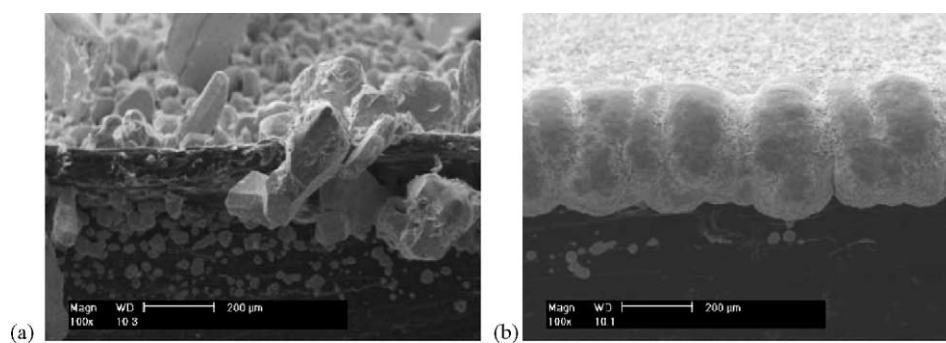


Fig. 5. SEM images of the edges of the electrodes with sample tilted at 70° : (a) 0 g dm^{-3} and (b) 1 g dm^{-3} sodium ligninsulfonate. Other conditions as in Fig. 5.

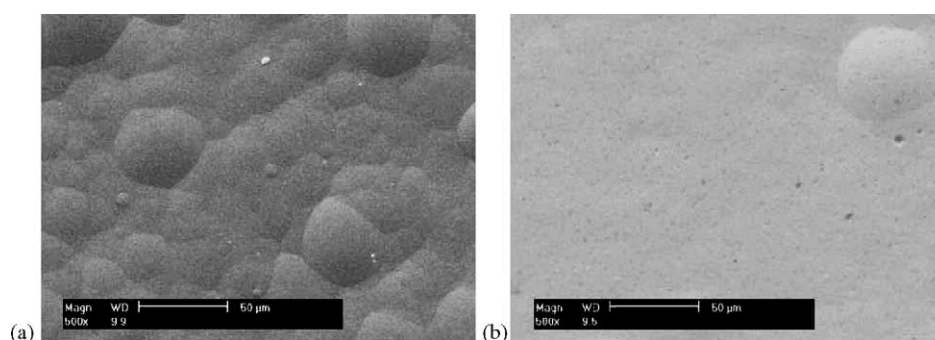
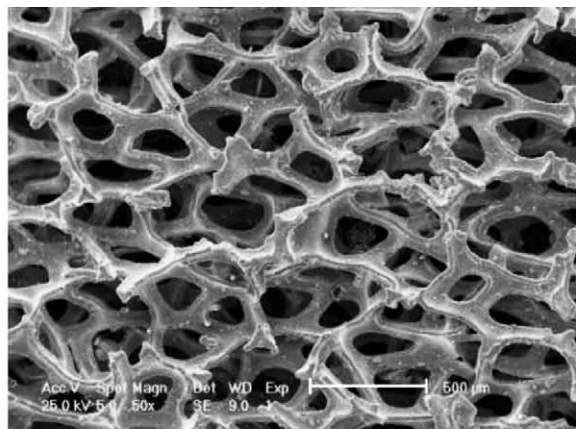
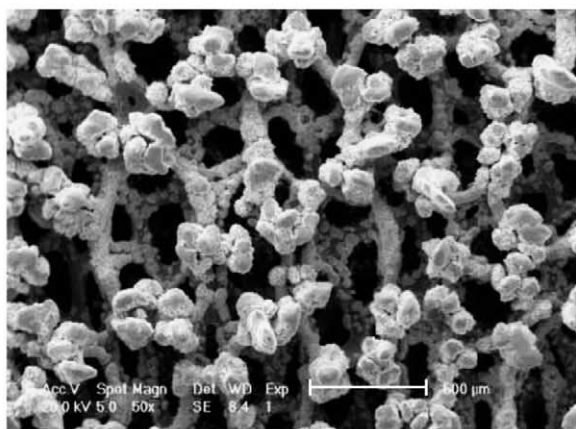


Fig. 6. SEM images of PbO_2 deposits formed at the positive electrode during the experiments of Fig. 5: (a) 0 g dm^{-3} and (b) 1 g dm^{-3} sodium ligninsulfonate.



(a) Ni electrode



(b) No additive

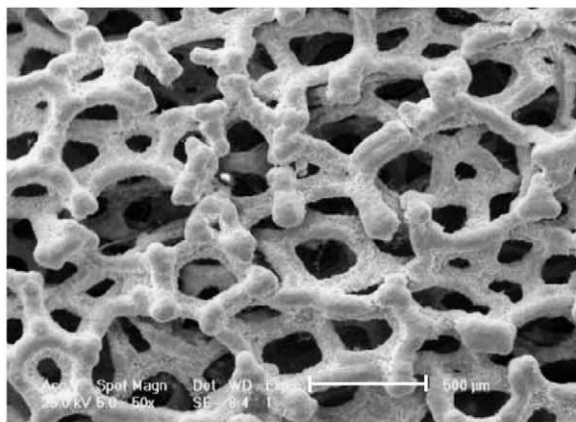
(c) 1 g dm⁻³ sodium ligninsulfonate

Fig. 7. SEM of Pb on Ni foam. Deposit formed by 1 h deposition at 20 mA cm⁻² from 1.5 M Pb(CH₃SO₃)₂ + 0.9 M CH₃SO₃H and sodium ligninsulfonate: (a) 0 g dm⁻³ and (b) 1 g dm⁻³. Electrolyte mean linear flow rate: 2.5 cm s⁻¹.

The conclusion is clear—sodium ligninsulfonate improves the quality and uniformity of the lead deposited on the negative electrode during charging without detrimental effects on the lead dioxide formed at the positive electrode. Several series of charge/discharge experiments were then car-

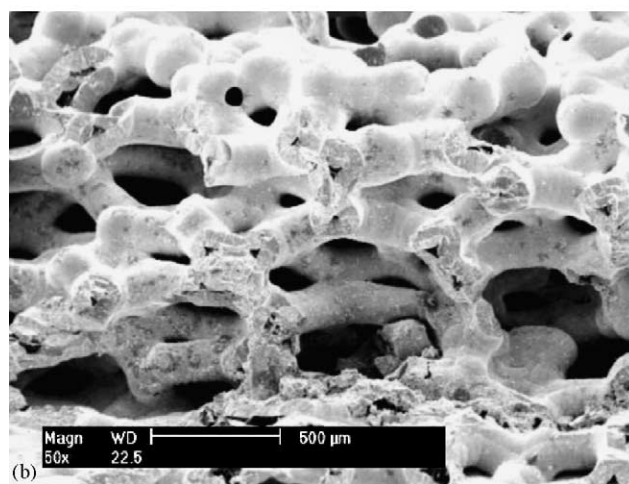
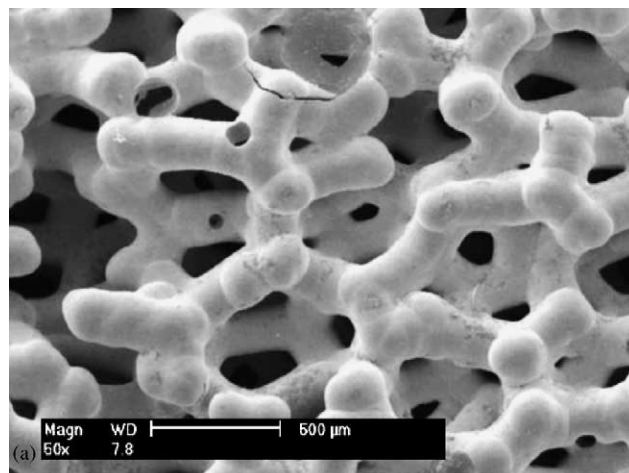


Fig. 8. SEM image of PbO₂ formed on reticulated vitreous carbon positive electrode during a 6 h charge from 20 mA cm⁻² from 1.5 M Pb(CH₃SO₃)₂ + 0.9 M CH₃SO₃H and 1 g dm⁻³ sodium ligninsulfonate: (a) surface facing negative electrode and (b) side view.

ried out without and with the additive using the electrolyte, 1.5 M Pb(CH₃SO₃)₂ + 0.9 M CH₃SO₃H.

Cells were constructed with two type 2 (reticulated vitreous carbon) electrodes and an interelectrode gap of 4 mm. The first was filled with electrolyte without sodium ligninsulfonate and the intention was to charge at 20 mA cm⁻² for 4 h but after about 3 h, shorting of the electrodes occurred; the negative electrode was examined by electron microscopy and as shown in Fig. 1, dendrites were observed on the negative electrode. Further experiments were then carried out with electrolyte containing 1 g dm⁻³ sodium ligninsulfonate using charge/discharge current densities of both 20 and 40 mA cm⁻². No shorting occurred. The voltage/time responses, see Fig. 9, show an almost constant voltage during charge (after an initial short period with a slightly lower value) and a voltage that decays only slowly during the discharge. As expected, the overpotentials are slightly higher with the larger charge/discharge current densities. The charge and energy efficiencies for these experiments are re-

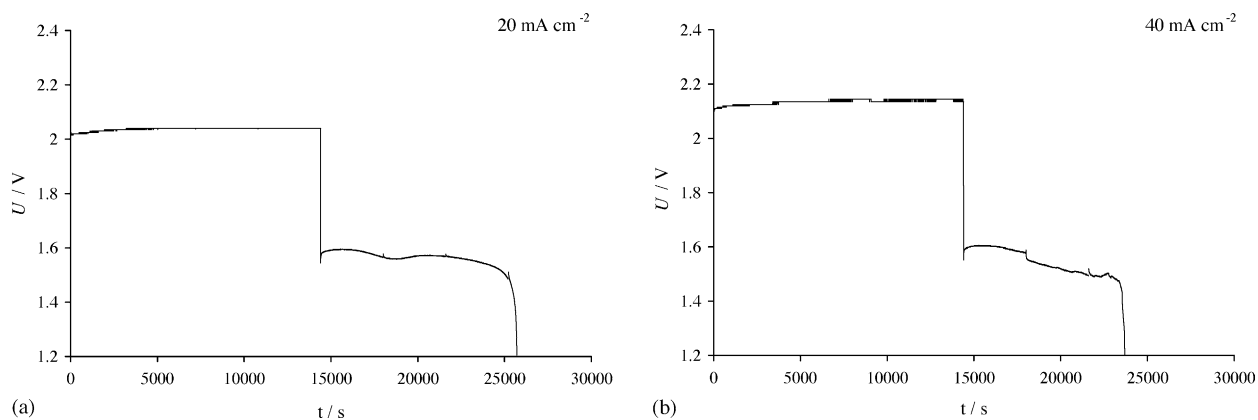


Fig. 9. Cell voltage vs. time responses for cell with two type 2 (reticulated vitreous carbon electrodes) and 4 mm interelectrode gap. Electrolyte: 1.5 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.9 \text{ M CH}_3\text{SO}_3\text{H} + 1 \text{ g dm}^{-3}$ sodium ligninsulfonate + 1 g dm^{-3} Ni(II). Mean linear flow rate: 10 cm s^{-1} . Current densities: (a) 20 mA cm^{-2} and (b) 40 mA cm^{-2} .

Table 1
The influence of ligninsulfonate on battery performance during 4 h charge/discharge experiments

| Ligninsulfonate concentration (g dm^{-3}) | Current density (mA cm^{-2}) | Charge efficiency (%) | Energy efficiency (%) |
|--|---|-----------------------|------------------------|
| 0 | 20 | | Cell shorted after 3 h |
| 1 | 20 | 79 | 60 |
| 1 | 40 | 65 | 47 |

Cell with two type 2 (reticulated vitreous carbon electrodes) and 4 mm interelectrode gap. Initial electrolyte: 1.5 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.9 \text{ M CH}_3\text{SO}_3\text{H}$. Mean linear flow rate: 10 cm s^{-1} .

ported in Table 1. It should be noted that at the higher current density, the charge passed is 576 C cm^{-2} corresponding to a lead deposit equivalent to a uniform layer $\sim 0.5 \text{ mm}$ thick.

Another set of cells with two type 2 electrodes were subjected to multiple, 1 h charge/discharge cycles at a current density of 20 mA cm^{-2} with electrolytes containing different concentrations of ligninsulfonate. Table 2 reports the performance of the cells during the third cycle and it can be seen that the additive has little effect at a 1 g dm^{-3} level but the higher concentration degraded performance significantly due to both a decrease in charge efficiency and an increase in overpotentials.

Experiments involving 84, 15 min charge/discharge cycles at 20 mA cm^{-2} were carried out in a cell with a type 1 (nickel foam) negative electrode and a type 3 (scraped reticulated vitreous carbon) positive electrode in electrolytes

Table 2
The influence of ligninsulfonate on battery performance during 1 h charge/discharge experiments at 20 mA cm^{-2}

| Ligninsulfonate concentration (g dm^{-3}) | Charge efficiency (%) | Energy efficiency (%) |
|--|-----------------------|-----------------------|
| 0 | 77 | 53 |
| 1 | 75 | 49 |
| 5 | 46 | 29 |

Cell with two type 2 (reticulated vitreous carbon electrodes) and 16 mm interelectrode gap. Initial electrolyte: 1.5 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.9 \text{ M CH}_3\text{SO}_3\text{H}$. Mean linear flow rate: 2.5 cm s^{-1} .

with 0 and 1 g dm^{-3} sodium lignin sulfonate. Fig. 10 reports the voltage during the 1st–6th and 79th–84th cycles for the electrolyte containing additive and the early cycles may be compared with those reported previously for the electrolyte without additive (Fig. 8 in [2]). The additive has little influence on the overall form of the responses. The presence of 1 g dm^{-3} ligninsulfonate does cause a small decrease in the charge efficiency, see Table 3, and the charge efficiency also declines very slightly with cycling. The energy efficiency depends on the overpotentials as well as the charge efficiency and with these short cycles, the energy efficiency actually increases with cycling. This results from the period of low overpotential at the beginning of the charge period that eventually extends throughout the 15 min charge. Unfortunately, on longer charges, this overpotential period does not last; an

Table 3
The influence of ligninsulfonate and Ni(II) on battery performance during 900 s charge/discharge experiments at 20 mA cm^{-2}

| Ligninsulfonate concentration (g dm^{-3}) | Charge efficiency (%) | Energy efficiency (%) |
|--|-----------------------|-----------------------|
| 0 | 93 → 92 | 76 → 78 |
| 1 | 85 → 83 | 68 → 70 |
| 0 + Ni(II) ^a | 80 → 80 | 65 → 75 |
| 1 + Ni(II) ^a | 80 → 77 | 67 → 70 |

The data are reported for 6th and 84th cycles. Cell with two type 2 (reticulated vitreous carbon electrodes) and 16 mm interelectrode gap. Initial electrolyte: 1.5 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.9 \text{ M CH}_3\text{SO}_3\text{H}$. Mean linear flow rate: 2.5 cm s^{-1} .

^a Ni(II) added at a level of 1 g dm^{-3} .

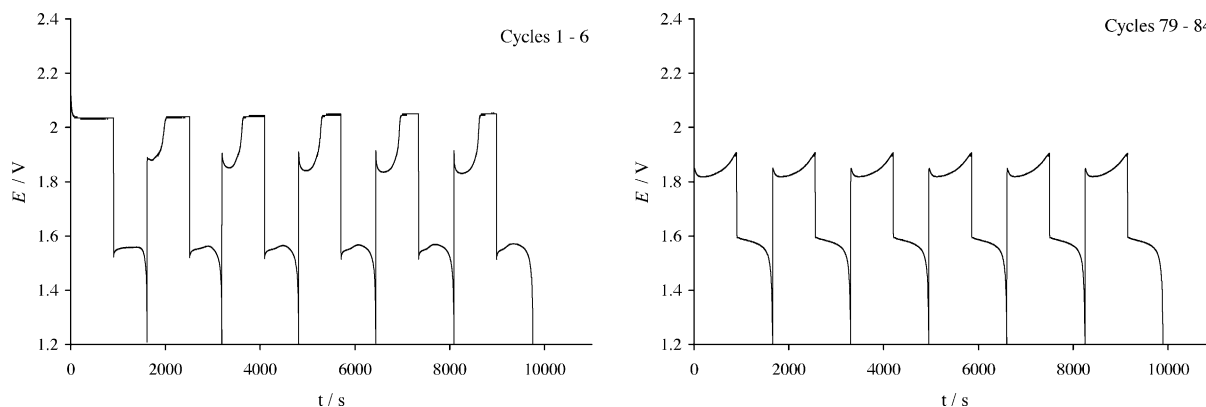


Fig. 10. Voltage during the 1st–6th and 79th–84th charge/discharge cycles of a cell with a type 1 (nickel foam) negative electrode and a type 2 (reticulated vitreous carbon) positive electrode and interelectrode gap 4 mm. Fifteen minutes charge/discharge cycles at 20 mA cm^{-2} . Electrolyte: $1.5 \text{ M Pb}(\text{CH}_3\text{SO}_3)_2 + 0.9 \text{ M CH}_3\text{SO}_3\text{H} + 1 \text{ g dm}^{-3}$ sodium ligninsulfonate + 1 g dm^{-3} Ni(II). Mean linear flow rate: 10 cm s^{-1} .

increase in overpotential is clearly seen in the responses early in the cycling. This behaviour has been explained [1–3] by the formation of some insoluble Pb(II) species remaining on the positive electrode surface during the reduction of the PbO_2 and this residue being easier to oxidize back to PbO_2 than Pb^{2+} in solution.

3.1.2. Polyethylene glycol

Polyethylene glycol has also been recommended as an additive for levelling lead deposits [7–9] and some preliminary experiments were carried out with a low molecular weight polyethylene glycol (200). It was found, however, that additions of up to 50 g dm^{-3} polyethylene glycol had little influence on the cyclic voltammetry for the deposition of either lead or lead dioxide (except for lower current densities resulting from the higher viscosity of the medium). Moreover, SEM images of the lead deposits showed little change with even large additions of polyethylene glycol. It was clear that polyethylene glycol is not an effective levelling agent during depositions from the methanesulfonic acid, battery electrolyte.

3.2. Additives for lead dioxide deposition/dissolution

On the basis of a literature that implies that the chemistry of PbO_2 may be changed by the incorporation of inorganic ions [10–14], Fe(III), Ni(II) and Bi(III) were selected for study with the target of enhancing the ki-

netics of the $\text{PbO}_2/\text{Pb}(\text{II})$ couple. Cyclic voltammograms were recorded at a vitreous carbon disc electrode in $1.5 \text{ M Pb}(\text{CH}_3\text{SO}_3)_2 + 0.9 \text{ M CH}_3\text{SO}_3\text{H}$ with additions of the metal ions in the range $0.1\text{--}10 \text{ g dm}^{-3}$. These experiments showed that the addition of Fe(III) and Bi(III) did not change the voltammetry significantly but the addition of Ni(II) led to a decrease in nucleation overpotential for the deposition of PbO_2 by up to 60 mV although the charge balance for the deposition/dissolution got worse. Hence, it was considered worthwhile to carry out further experiments in the flow cell in order to define the influence of Ni(II) on battery performance.

In the first experiments, cells with type 1 (Ni foam) negative electrode and type 3 (scraped reticulated vitreous carbon) positive electrode and an electrolyte with various Ni(II) additions were subjected to 900 s charge/discharge cycles at 20 mA cm^{-2} . Data taken from the 6th cycle is reported in Table 4. It can be seen that even the lowest Ni(II) addition leads to a lower cell voltage during charge but little change to the discharge voltage. Unfortunately, a loss in charge efficiency counter balances the lower charge voltage when the energy efficiency is calculated. When the experiment with 1 g dm^{-3} Ni(II) was extended to 84 cycles the same conclusion results; the addition of the Ni(II) lowers the charge voltage but there is a decrease in the charge efficiency leading to a very similar energy efficiency.

Four hours charge/discharge experiments with an electrolyte containing both 1 g dm^{-3} Ni(II) and 1 g dm^{-3} sodium

Table 4

The influence of Ni(II) on battery performance during 900 s charge/discharge experiments at 20 mA cm^{-2}

| NiCO ₃ (g dm^{-3}) | Average charge voltage (V) | Average discharge voltage (V) | Charge efficiency (%) | Energy efficiency (%) |
|--|----------------------------|-------------------------------|-----------------------|-----------------------|
| 0 | 1.93 | 1.54 | 91 | 73 |
| 0.1 | 1.88 | 1.55 | 80 | 66 |
| 1 | 1.88 | 1.55 | 80 | 66 |
| 5 | 1.88 | 1.55 | 86 | 71 |
| 10 | 1.86 | 1.53 | 74 | 61 |

The data are reported for 6th cycles. Cell with type 1 (Ni foam) negative electrode and type 3 (scraped reticulated vitreous carbon) positive electrodes and 4 mm interelectrode gap. Initial electrolyte: $1.5 \text{ M Pb}(\text{CH}_3\text{SO}_3)_2 + 0.9 \text{ M CH}_3\text{SO}_3\text{H}$. Mean linear flow rate: 10 cm s^{-1} .

ligninsulfonate were carried out at both 20 and 40 mA cm⁻². The cell voltage versus time responses shown in Fig. 9 are very similar to those in the absence of Ni(II). The same solution was also used for an extended number of short cycles. The 1st–6th and 79th–84th cycles are shown in Fig. 10 and data from the experiments shown in Table 3. Again, in longer timescale experiments, the advantage of adding Ni(II) is no longer apparent.

4. Conclusions

Sodium ligninsulfonate at a level of $\leq 1 \text{ g dm}^{-3}$ is an effective levelling agent for lead in methanesulfonic acid media even when thick layers are deposited at relatively high rates. The need for levelling of the electroplated lead appears to be greater with carbon as the substrate than when nickel is used and, indeed, this is the reason that reticulated vitreous carbon was used for many of the experiments in this paper focusing on the quality of the deposit. While leading to more compact and dendrite free deposits, the ligninsulfonate does adversely influence both the charge efficiency and the overpotentials at both negative and positive electrodes to a small extent, resulting in a slight decline in energy efficiency during battery cycling. In contrast, polyethylene glycol was found to be ineffective as a levelling agent in battery conditions.

The attempts to use inorganic ions as catalysts for the PbO₂/Pb²⁺ couple were not fully successful. While Ni(II) does reduce the overpotential for charging the positive electrode, at least on a short timescale, there is a parallel decrease in charge efficiency that largely negates any improvement in energy efficiency. Catalysis of the PbO₂/Pb²⁺ couple remains a target worthy of further attention.

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