

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

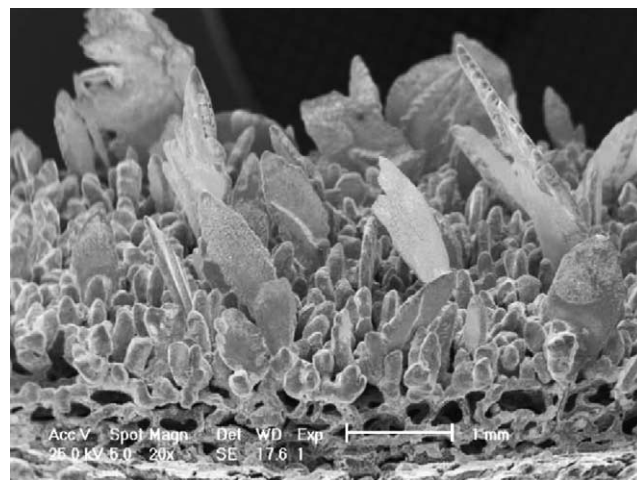


Fig. 1. Scanning electron micrograph of a type 2 (reticulated vitreous carbon) negative electrode after charging at 20 mA cm^{-2} for 3 h. Initial electrolyte: $1.5 \text{ M Pb}(\text{CH}_3\text{SO}_3)_2 + 0.9 \text{ M CH}_3\text{SO}_3\text{H}$ without any additive. Electrolyte flow rate: 10 cm s^{-1}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

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