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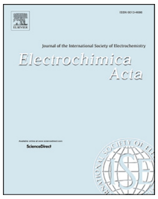

# Stabilizing the electrodeposit-electrolyte interphase in soluble lead flow batteries with ethanoate additive

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ABSTRACT

The soluble lead flow battery (SLFB) is a promising energy storage system. In comparison to conventional flow batteries, the membrane-less and single-flow design of SLFBs is potentially much more economical to scale up for utility-scale applications. However, SLFB lifespan reported so far is less than 200 cycles under normal flow conditions. This study reports a method for significantly extending the cycle life and expanding capacity of SLFBs. By adding an adequate amount of sodium ethanoate to the electrolyte, lead dioxide ($PbO_2$) deposition stability is materially improved and shed $PbO_2$ particles are substantially reduced. Lifespan of ethanoate-added SLFBs is shown to extend by over 50%, and under optimal condition exceeds 500 cycles at over 65% energy efficiency. This improvement in SLFB performance is primarily attributed to the stabilization of both the electroplated $PbO_2$ layers and proton activity at the electrodeposit-electrolyte interphase. We demonstrate a novel and economical approach for advancing performance of membrane-less flow batteries that involve redox reactions associated with acidity variation and operate through electrodeposition.

## 1. Introduction

Renewable energy sources including solar and wind are intermittent in nature and generation is often not in sync with demand. Load leveling and power system stabilization can be achieved by means of energy storage. One of the most flexible options for grid-scale energy storage is redox flow batteries (RFBs) because their power and capacity can be designed independently and the latter is easy to expand. RFBs typically contain ion-selective membranes separating anolyte from catholyte, and some systems such as the all-vanadium RFB have been shown to operate with high efficiency and long cycle life [1,2]. However, the market penetration of RFBs has been very limited primarily due to the high cost of comprising materials like noble metals or the membrane, and in part due to the inability of some membranes to completely prevent cross-contamination [3].

A soluble lead-acid flow battery (SLFB) that does not require an ion-selective membrane is presented a decade ago by Pletcher et al. [4–6] This design differs from conventional RFBs in that it has only one active species, lead, dissolved in aqueous methanesulfonic acid (MSA) electrolyte as Pb(II) ions prior to operation. Pb(II) ions are oxidized to $PbO_2$ and reduced to Pb at the positive and the negative electrode, respectively and simultaneously, during charging, while the deposited $PbO_2$ and Pb are dissolved back to Pb(II) ions in the electrolyte during discharging. A SLFB requires only one circulation pump and one electrolyte storage tank, and the active material, Pb, is of higher availability and lower cost compared with noble metals such as vanadium. The capital cost of SLFBs is thus potentially much lower than conventional RFBs, and a scaled-up system is also easier to design and build. While lead is toxic to human beings and can result in hazardous effects including neurological damage [7], state-of-the-art lead acid batteries are designed to avoid leakage and human exposure, and lead materials in spent batteries are highly recyclable [8]. In addition, the SLFB is more environmentally benign than conventional lead-acid batteries because MSA is a relatively green chemical in comparison to sulfuric acid [9]. Subsequent investigations, including using alternative electrode materials and electrolyte additives, have enhanced the battery performance and attained approximately 65% energy efficiency, but the cycle life of SLFBs is currently limited to less than 200 cycles

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[10–13]. One exception, a two-thousand-cycle run of SLFBs, is conducted under severe stirring condition and may not be viable in practical applications [14].

The electrochemical reactions involved in the operation of SLFBs are shown below:

$$\text{Negative}: \quad Pb^{2+} + 2e^{-} \rightarrow Pb \quad E^0 = -0.125\ V \tag{1}$$

$$\text{Positive}: \quad Pb^{2+} + 2H_2O - 2e^{-} \rightarrow PbO_2 + 4H^{+} \quad E^0 = 1.468\ V \tag{2}$$

$$\text{Overall}: \quad 2Pb^{2+} + 2H_2O \rightarrow Pb + PbO_2 + 4H^{+} \quad E^0 = 1.593\ V \tag{3}$$

The primary causes for short SLFB cycle life are associated with $PbO_2$ deposition/dissolution at the positive electrode. When the electrolyte acidity increases appreciably over long or deep charge/discharge cycles, protons are suggested to diffuse deeper into the deposited layer and a passivation layer of non-stoichiometric $PbO_x$ is deduced to form [15,16]. Accumulation of the passivation layer at the positive electrode in turn leads to higher overpotential and poor efficiency in the long run. Another salient phenomenon associated with SLFB degradation is the shedding of $PbO_2$. These disintegrated $PbO_2$ particles can no longer undergo reverse reduction in subsequent discharge processes, which induces incomplete oxidation of previously deposited $Pb_{(s)}$ at the negative electrode. The coulombic efficiency of SLFBs declines as a result of imbalanced electrochemical reactions and accumulated electrodeposits at both electrodes. $PbO_2$ deposits of poor adherence and low quality are found to occur when the electrolyte is low in lead ions and high in acidity [17]. In addition, undissolved $PbO_2$ is observed to form islands of micrometric-scale porous structures during stripping [16]. Lead ions tend to nucleate on top of those undissolved $PbO_2$, creating excess surface area that reduces overpotential in the early stages of electrodeposition. During stripping, however, these protruded porous structures of $PbO_2$ react with protons and are prone to detach from the bulk, leading to $PbO_2$ shedding.

Since the conductivity, morphology, and homogeneity of $PbO_2$ coatings are highly dependent upon proton activity, stabilizing pH fluctuation and electrodeposit structure can be critical in achieving extended cycle life of SLFBs. Sodium ethanoate (NaOAc), which can serve as a pH buffer agent, has previously been used as an electroplating medium for either lead or lead dioxide [18–21]. In this research, we apply NaOAc additives of various concentrations to the methanesulfonic electrolyte in SLFBs to mitigate pH variation and alleviate structural evolution during charge/discharge cycles. Lifespan of over 500 cycles under normal agitation is demonstrated in NaOAc-added SLFBs, and primary effects of the ethanoate additive on SLFBs are further elucidated.

## 2. Experimental

### 2.1. Materials

Electrolytes are prepared with analytical grade reagents and deionized water distilled using the Barnstead MicroPure water purification system (18 MΩcm). The electrolyte is synthesized through the chemical reaction of highly pure lead (II) oxide (SHOWA, 98%) in an MSA solution (BASF, 70%), which results in a solution of 0.5 M lead methanesulfonate ($Pb(SO_3CH_3)_2$) mixed with 0.5 M methanesulfonic acid (MSA, $HSO_3CH_3$). The sodium acetate (SHOWA, 98%) is employed as additive agent to the methanesulfonic electrolyte. The positive electrode employed is a commercial carbon composite fabricated by Homy Tech, Taiwan, which is hot-pressed with modified epoxy resin and graphite powder. These graphite plates are of density 1.75 g cm$^{-3}$, and of electrical conductivity 330 S cm$^{-1}$. Prior to each experiment, the carbon composite electrode is polished with 3 M sandpaper (aluminum oxide, P100) then immersed in 1 M hydrogen chloride (SHOWA, 35%) to remove impurities. Before use, the electrode is activated with electrochemical pretreatment via applying a potential of 1.80 V vs. Ag/AgCl to the pretreated electrode for 5 min followed by −1.0 V for 2 min in the electrolyte of 0.1 M potassium nitrate (Scharlab, 99%). The negative electrode used is a nickel plate of 99.5% purity supplied by Lien Hung Alloy Trading Co., LTD., Taiwan. All potentials mentioned reference the Ag/AgCl electrode (Metrohm).

### 2.2. Cyclic voltammetry

Cyclic voltammetry (CV) experiments are performed using Autolab PGSTAT302 N and monitored using the Nova companion software. The working electrode is a glassy carbon (GC) rotating disk electrode of 3 mm diameter, and the auxiliary is a stainless steel electrode with a larger surface area. The reference electrode is an Ag/AgCl electrode (Metrohm). The potential range of our CV investigations is between 1.80 V and 0 V. While the potential sweep is set at a scan rate of 20 mV s$^{-1}$, the GC disk electrode is controlled at a rotation rate of 1600 rpm.

### 2.3. In situ pH measurements

A Pyrex beaker cell comprised of a carbon-composite positive electrode, a nickel negative electrode, and the methanesulfonic electrolyte is utilized. The PX1000 module of Metrohm Autolab is employed for pH measurements during charge/discharge cycles, and the pH sensor is placed in between the positive and the negative electrodes with a spacing of 18 mm. The applied potentials are chosen to achieve similar depth of change and discharge in various electrolyte compositions, and the cut-off current is set at 0.5 mA. The electrode surface exposed to the electrolyte is 14 cm$^2$ in area. The MSA based electrolyte is magnetically stirred at 200 rpm.

### 2.4. Throwing index

Throwing index (TI) is defined as the reciprocal of the slope of the fitted curve of metal distribution ratio (MDR) versus linear distance ratio (LR), where MDR is the weight ratio of electrodeposits at the near electrode to the far electrode; LR is the distance ratio between the controlled electrode to the far electrode and that to the near electrode. TI is measured using a Haring-Blum rectangular cell (2.0 cm wide, 14.0 cm long, 2.0 cm solution depth) comprised of one cathode and two separate anodes for $PbO_2$ deposition, and the far to near linear distance ratio of the two anodes is controlled to vary from 6 to 1. TI measurement is conducted under the unstirred condition with a plating duration of 30 min. The current in this galvanostatic experiment is supplied by a battery test system, Bio-Logic BCS-810.

### 2.5. Galvanostatic cyclization

Charge/discharge experiments are carried out in the Pyrex beaker cell under stirring, with the positive and negative electrodes of 14 cm$^2$ immersed area respectively and 1.8 cm distance. The beaker is filled with 260 mL of electrolytes and the stirring rate is set at 200 rpm. Current density, if not specified, is of 15 mA cm$^{-2}$, and the cut-off potential for discharge is set at 1.05 V.