Video Article

Extending the Lifespan of Soluble Lead Flow Batteries with a Sodium Acetate Additive

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Abstract

In this report, we present a method for the construction of a soluble lead flow battery (SLFB) with an extended cycle life. By supplying an adequate amount of sodium acetate (NaOAc) to the electrolyte, a cycle life extension of over 50% is demonstrated for SLFBs *via* long-term galvanostatic charge/discharge experiments. A higher quality of the PbO_2 electrodeposit at the positive electrode is quantitatively validated for NaOAc-added electrolyte by throwing index (TI) measurements. Images acquired by scanning electron microscopy (SEM) also exhibit more integrated PbO_2 surface morphology when the SLFB is operated with the NaOAc-added electrolyte. This work indicates that electrolyte modification can be a plausible route to economically enable SLFBs for large-scale energy storage.

Video Link

The video component of this article can be found at https://www.jove.com/video/58484/

Introduction

Renewable energy sources including solar and wind have been developed for decades, but their intermittent nature poses great challenges. For a future power grid with renewable energy sources incorporated, grid stabilization and load leveling are critical and can be achieved by integrating energy storage. Redox flow batteries (RFBs) are one of the promising options for grid-scale energy storage. Traditional RFBs contain ion-selective membranes separating anolyte and catholyte; for example, the all-vanadium RFB has shown to operate with high efficiency and a long cycle life[1,2]. However, their market share as energy storage is very limited in part due to the expensive comprising materials and ineffective ion-selective membranes. On the other hand, a single-flow soluble lead flow battery (SLFB) is presented by Plectcher *et al.*[1,2,3,4,5]. The SLFB is membrane-less because it has only one active species, Pb(II) ions. Pb(II) ions are electroplated at the positive electrode as PbO_2 and the negative electrode as Pb simultaneously during charging, and convert back to Pb(II) during discharging. A SLFB thus needs one circulation pump and one electrolyte storage tank only, which in turn can potentially lead to reduced capital and operational cost compared to conventional RFBs. The published cycle life of SLFBs, however, is so far limited to less than 200 cycles under normal flow conditions[6,7,8,9,10].

Factors leading to a short SLFB cycle life is preliminarily associated with deposition/dissolution of PbO_2 at the positive electrode. During charge/discharge processes, the electrolyte acidity is found to increase over deep or repeated cycles[11], and protons are suggested to induce the generation of a passivation layer of non-stoichiometric PbO_x[12,13]. The shedding of PbO_2 is another phenomenon related to SLFB degradation. Shed PbO_2 particles are irreversible and can no longer be utilized. The coulombic efficiency (CE) of SLFBs consequentially declines because of imbalanced electrochemical reactions as well as accumulated electrodeposits at both electrodes. To extend cycle life of SLFBs, stabilizing the pH fluctuation and electrodeposit structure are critical. A recent paper demonstrates an enhanced performance and extended cycle life of SLFBs with addition of sodium acetate (NaOAc) in methanesulfonic electrolyte[11].

Here, a detailed protocol for employing NaOAc as an additive to the methanesulfonic electrolyte in SLFBs is described. The SLFB performance is shown to be enhanced and the lifespan can be extended by over 50% in comparison to SLFBs without NaOAc additives. In addition, procedures for throwing index (TI) measurement are illustrated for the purpose of quantitative comparison of additive effects on electrodeposition. Finally, a scanning electron microscopy (SEM) sample preparation method for electrodeposit on SLFB electrodes is described and the additive impact on electrodeposit is manifested in acquired images.

Protocol

1. Construction of a SLFB Beaker Cell with a Sodium Acetate Additive

NOTE: This section describes the procedure to construct a SLFB beaker cell with an additive for long-term cycling experiment. The protocol includes the electrolyte preparation with and without additive, electrode pretreatment, cell assembly, and efficiency calculations.

1. **Preparation of lead methanesulfonate (1 L, 1 M as an example)**
    1. In the fume hood, add 274.6 g of methanesulfonic acid (MSA, 70%) to a beaker stirring with a stir bar. Dissolve the MSA with 300 mL of deionized (DI) water.
    2. Prepare 223.2 g of lead (II) oxide (98%) and add in increments to the aforementioned beaker until the prepared lead oxide is completely dissolved.
    3. Filter through the Büchner funnel with 70 mm cellulose filter paper to separate any undissolved lead oxide.
    4. Repeat this procedure for 3 times. Add DI water to reach 1 L in total volume.

2. **Preparation of electrolyte without additive (300 mL)**
    1. Add 20.595 g of MSA (70%) to a beaker. Add 150 mL of prepared 1 M lead methanesulfonate to the same beaker.
    2. Add DI water to reach 300 mL in total volume and stir the electrolyte until uniformly mixed, which results in a solution of 0.5 M lead methanesulfonate mixed with 0.5 M MSA.

3. **Preparation of electrolyte with sodium acetate (300 mL)**
    1. Add 20.595 g of MSA (70%) to a beaker. Add 150 mL of prepared 1 M lead methanesulfonate to the same beaker.
    2. Add 1.23 g of NaOAc (98%) to the beaker as an additive agent.
    3. Add DI water to reach 300 mL in total volume and stir the electrolyte until uniformly mixed, which results in a solution of 0.5 M lead methanesulfonate, 0.5 M methanesulfonic acid, and 50 mM sodium acetate.

4. **Pretreatment of the positive and negative electrodes**
    1. Repeatedly polish the positive (commercial carbon composite) and negative (nickel) electrodes with a sandpaper (aluminum oxide, P100) until no visible impurities are left and then rinse electrodes with DI water.
    2. Add 20.83 g of hydrogen chloride (35%) in 200 mL DI water and stir the solution until all of the hydrogen chloride is dissolved.
    3. Immerse the entire positive electrode in the prepared 1 M hydrogen chloride solution overnight to remove impurities at the electrode surface.
    4. Rinse the positive electrode thoroughly with DI water and dry the electrode with delicate task wipers. Tape one side of each electrode using polytetrafluoroethylene (PTFE) tape while exposing the other side of the electrodes.
    5. Prepare another solution with 3.03 g of potassium nitrate (99%) and 300 mL DI water, which results in a solution of 0.1 M potassium nitrate.
    6. Immerse the positive and negative electrodes in 0.1 M potassium nitrate with the exposed surface facing each electrode.
    7. Apply a potential of 1.80 V *vs.* Ag/AgCl to the positive electrode for 5 min. Subsequently, apply a potential of -1.0 V *vs.* Ag/AgCl to the positive electrode for 2 min.

5. **Assemble the SLFB beaker cell**
    1. Attach the pretreated positive and negative electrodes to a home-made electrode positioning board for a fixed electrode distance. Place the positioning board together with electrodes in a beaker as schematically illustrated in **Figure 1** and add electrolyte to the beaker until the designated level of immersion.
    2. Place a magnetic stirrer into the beaker, position the beaker on a hot plate and control the rotating rate of the stirrer. Connect the battery tester to the electrodes and cover the beaker cell with plastic wrap to prevent evaporation.

6. **Calculate the battery efficiency**
    1. After galvanostatic charge and discharge, calculate the efficiency of the battery as the following:

Coulombic efficiency:
$$CE = \frac{Q_{discharge}}{Q_{charge}}$$

Voltage efficiency:
$$VE = \frac{V_{discharge}}{V_{charge}}$$

$$\text{Energy efficiency: } EE = \frac{E_\text{discharge}}{E_\text{charge}}$$

Here, Q denotes coulombs of charged/discharged equivalent electrons, V the apply/output voltage, and E the total energy stored/consumed.

2. Throwing Index Measurement

NOTE: This section describes the procedure to measure throwing index (TI) of the electrodeposit at positive electrodes in SLFB cells. Reversing the role of positive and negative electrodes delivers the other set of TI results. Here, TI is investigated by using a home-made Haring-Blum cell as schematically depicted in **Figure 2**.

1. **Measurement**
    1. Weigh and record two positive electrodes respectively before the experiments.
    2. Place the negative electrode at the center of a Haring-Blum cell and one positive electrode at a distance ratio of 1 from the negative electrode. Place the second positive electrode at another distance ratio from the negative electrode (take 6 as an example in **Figure 2**).
    3. Immerse the two positive electrodes and one negative electrode with the same immersed surface area (2 cm^2 here) in the Haring-Blum cell with the electrolyte of interest.
    4. Apply a controlled current density (20 mA·cm^{-2} here) at the electrodes by using a battery tester. Carry out the galvanostatic charge for a certain duration (30 min here).
    5. After plating, rinse the two positive electrodes with DI water and dry them at room temperature overnight.
    6. Weigh and record two positive electrodes again respectively and calculate the metal distribution ratio (MDR) according to the equation listed below.
    7. Repeat the aforementioned experiments by placing the second positive electrode at various linear distance ratios (LR) to acquire the TI diagram (varied from 6 to 1 here).

2. **Calculation**
    1. As an example, consider the anode as the electrode of interest, and determine each data on the TI diagram by the measured MDR *versus* LR, which are calculated as the following:

$$MDR = \frac{\text{Weight of electrodeposit on the near anode}}{\text{Weight of electrodeposit on the far anode}}$$

$$LR = \frac{\text{Distnace from cathode to the far anode}}{\text{Distance from cathode to the near anode}}$$

3. SEM Sample Preparation

1. Rinse the graphite electrode with DI water and dry at room temperature after electroplating.
2. Slice graphite electrodes into the desired sample size by diamond saw with care. Cold mount the electrode sample and then mechanically polish it with 14, 8, and 3 μm silicon carbide sand papers, subsequently.
3. Further polish the samples with 1 μm diamond suspension and 0.05 μm Al_2O_3. Deposit the cold-mounted sample with platinum and attach it with copper tapes to ensure conductivity for SEM observation.

Representative Results

To extend cycle life of SLFBs, NaOAc is supplied as an electrolyte additive. Cycling performance of SLFBs with and without NaOAc additive are examined in parallel, and results are shown in **Figure 3**. For easier quantitative comparison of cycle life, we define the "death" of a SLFB as when its CE is lower than 80% under continuous galvanostatic charge/discharge. **Figure 3a** and **3b** show that approximately 50% cycle life extension of the SLFB is achieved when 50 mM NaOAc is added to the electrolyte of 0.5 M lead methanesulfonate and 0.5 M MSA, under 40-minute charge/discharge with a current density of 15 mA cm^{-2}. The cycle number we hence accounted for is a representation of the battery life under full depth of discharge. The positive effect of NaOAc additive on SLFB performance is even more pronounced when the depth of charge/discharge is increased, and no additional redox reaction is observed in the SLFB operational potential range[11].

Since SLFB is operated through electroplating/dissolution, TI experiments are conducted for the positive and negative electrodes of SLFBs, with and without NaOAc, to gain insight into the additive effect. TI measurements conducted for the positive electrodes employing an electrolyte with NaOAc demonstrate a shallower slope of the metal distribution ratio (MDR) to linear distance ratio (LR) than the one without additive in **Figure 4a**. The steeper slope of MDR to LR in TI measurement suggests that the electrodeposition is more affected by non-uniform current distribution, and a high-quality electrodeposit is harder to be plated. On the contrary, TI results for negative electrodes in **Figure 4b** show similar slopes of MDR to LR for both electrolytes. This result indicates that a better quality of PbO_2 deposition is achieved with NaOAc-added electrolyte at the positive electrode, while the Pb plating at the negative electrode is nearly unaffected by NaOAc additive.

In addition, SEM images are acquired for the PbO_2 electrodeposits as plated at the positive electrodes of SLFBs after 50-cycle galvanostatic charge/discharge experiments, under 60-minute charge/discharge with a current density of 15 mA cm^{-2}. A smoother surface with less defects of the PbO_2 electrodeposit is observed in **Figure 5a** in an electrolyte with the NaOAc additive, compared to the more fractured PbO_2 surface plated without NaOAc as shown in **Figure 5b**. This morphological observation of PbO_2 electrodeposit is in accordance with the TI measurement results, which indicates higher quality of electrodeposition with NaOAc additive.
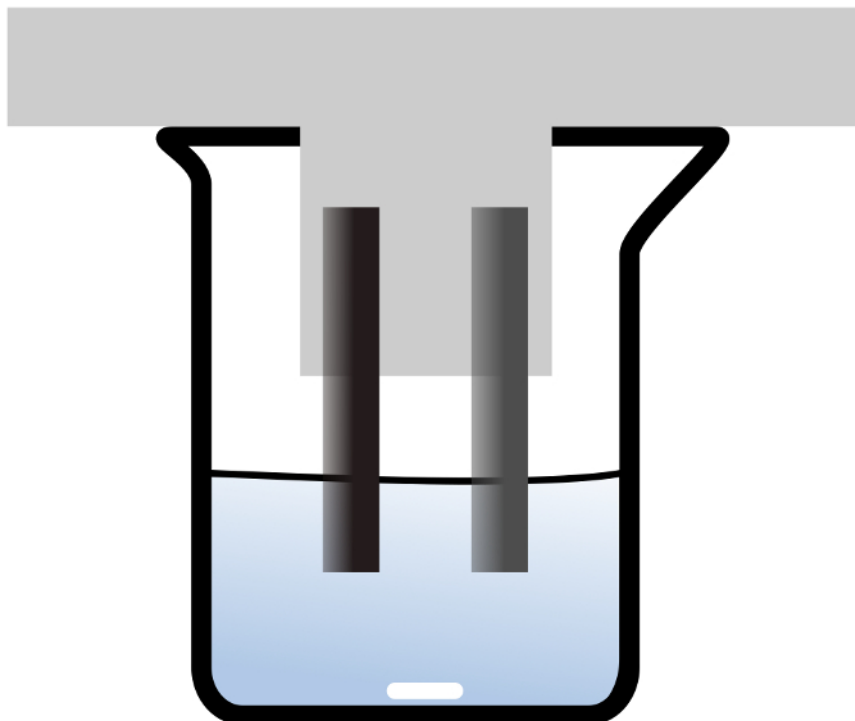

Figure 1. A schematic diagram of the beaker cell employed for SLFB galvanostatic charge/discharge experiment. A home-made electrode positioning board is used to fix the electrode distance (18 mm), and the electrolyte mixing is achieved by controlling the rotation rate of the magnetic stirrer. Please click here to view a larger version of this figure.
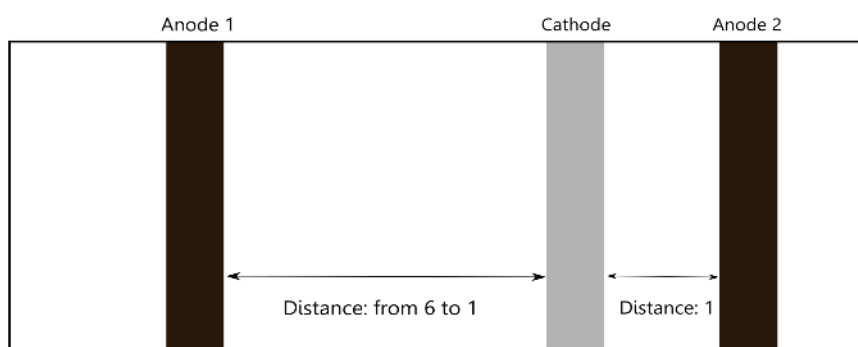

Figure 2. A schematic diagram of the Haring-Blum cell employed for TI measurements. In this diagram, the far to near anode distance ratio is set at 6 to 1. The complete set of TI results is acquired by varying the far to near electrode distance ratios with fresh electrodes in each individual measurement. Please click here to view a larger version of this figure.
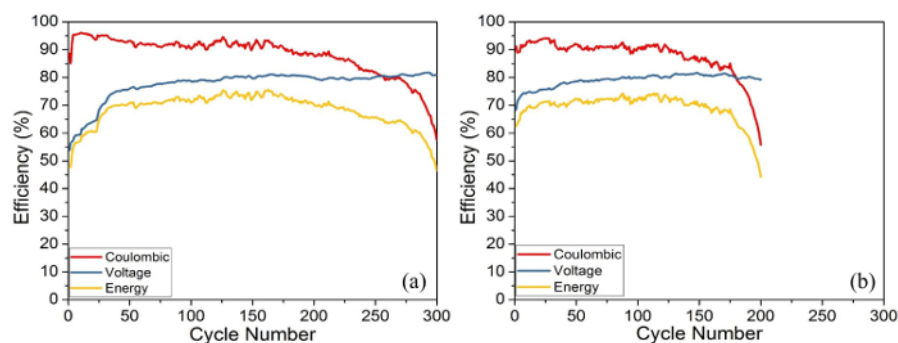
Figure 3. Galvanostatic charge/discharge cycle efficiencies of SLFBs with electrolyte (a) with; and (b) without 50 mM NaOAc additive; under 40-minute charge/discharge cycling and a current density of 15 mA·cm^{-2}. The cutoff potential is set at 1.05 V and the electrolyte volume is of 260 mL. This figure has been plotted based on data in Ref[11] with permission. Please click here to view a larger version of this figure.
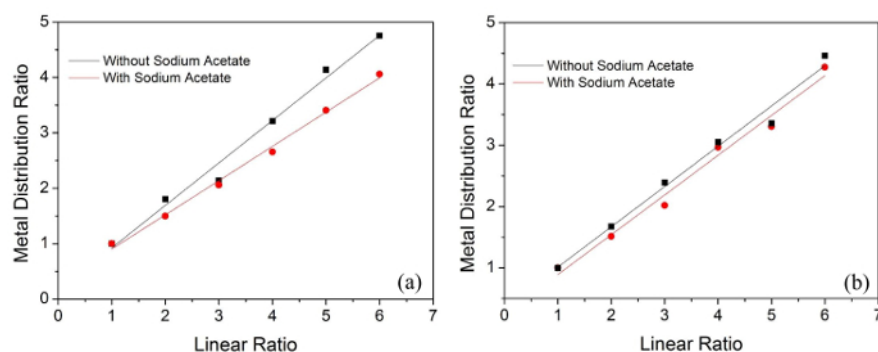
Figure 4. A comparison of the metal distribution ratio to linear distance ratio measured by throwing index experiments (a) PbO$_2$ deposition at the positive electrodes; (b) Pb deposition at the negative electrodes. This figure has been modified from Ref[11] with permission. Please click here to view a larger version of this figure.
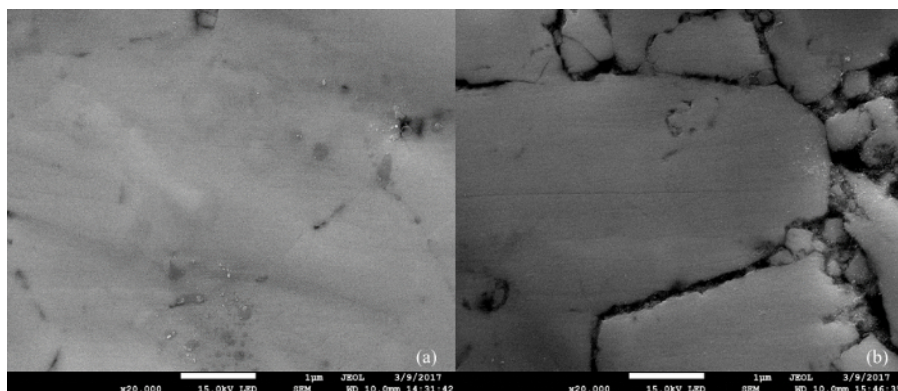
Figure 5. SEM images of electroplated PbO$_2$ at the positive electrode by electrolyte (a) with 50 mM NaOAc additive; (b) without additive. The magnification is of 20,000X. Please click here to view a larger version of this figure.

Discussion

This paper describes an economical method to extend the cycle life of SLFBs: by employing NaOAc agent as an electrolyte additive. A batch of fresh graphite electrodes and nickel plates are preprocessed as aforementioned in Step 1 before long-term cycling experiments. Because inconsistency among commercial carbon electrodes may cause performance deviation of the SLFBs, the physical/chemical pretreatment in Step 1.4 is critical to remove surface residues. The second part of Step 1.4 is employing electrochemical methods to remove impurities that may induce redox reactions between the potentials of 0 to 1.8 V *vs*. Ag/AgCl. As demonstrated in **Figure 3**, the cycle life of SLFBs is extended by approximately 50% when the NaOAc additive is supplied in 50 mM to the MSA based electrolyte, under a current density of 15 mA cm^{-2} and a charge/discharge duration of 40 min.

Since the focus of this study is on the electrolyte additive effects, we employed beaker cells rather than flow cells to minimize uncertainties derived from flow conditions. The beaker cell is magnetically stirred at a rotation rate of ~200 rpm to maintain a certain level of concentration

uniformity of the electrolyte without severe agitation. The temperature of beaker cells is not controlled in the experiments, which leaves it close to the atmospheric temperature (25 ± 5 °C). While temperature variation, if significant enough, may affect the deposition quality and battery performance, the two compared experiments are conducted in parallel to avoid the temperature perturbation interference. In addition, the long-term charge/discharge cycling of SLFBs can continue for several weeks during which the electrolyte in beaker cells will evaporate unignorably. It is thus also important to conceal the beaker cell to prevent excess evaporation. We find the aforementioned beaker cell experiment useful to simplify the analysis of electrolyte/electrode modification effects in single-flow RFBs.

Since the SLFB is a single-flow energy storage device operates through electroplating/stripping of PbO_2 and Pb at the positive and the negative electrode, respectively, during charge/discharge, the quality of electrodeposits is pivotal to the battery efficiency. TI measurement has been historically utilized to investigate the quality of electrodeposit and thus is employed here to assess the additive effect. A pivotal consideration for accurate TI measurement in Step 2 is to choose the appropriate plating duration. Since the weight of electrodeposit is proportional to the amount of charges supplied and the current density is chosen to be representable of the battery operation condition, the plating duration should be chosen to accumulate appropriate amount of electrodeposit for later measurements.

Another prominent phenomenon observed in NaOAc-assisted SLFBs is the significant decrease of PbO_2 shedding, which can be visually observed in the beaker cell. This reduced shedding in electrolyte with NaOAc additive is in accordance with the more congregated surface of the PbO_2 electrodeposit observed in SEM images shown in **Figure 5a**. The extended cycle life of SLFBs is thus achieved by the plating of more integrated PbO_2 deposits when NaOAc is added adequately to the electrolyte.

In this report, we present findings on a significant extension of SLFB lifespan by the NaOAc additive. Our work marks substantial improvement of SLFB technology and sheds lights on the failure mechanisms of SLFBs. In light of how high-quality electrodeposition can be assisted by NaOAc additive, our work opens up an exciting avenue to the advancement of batteries involving redox reactions associated with electrodeposition during cyclization.

Disclosures

We have nothing to disclose.

Acknowledgements

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