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Extending lifespan of soluble lead flow batteries with sodium acetate additive

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TITLE:

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

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Lead Dioxide, Soluble Lead Flow Battery, Sodium Acetate, Methanesulfonic Acid, Electroplating,
Throwing Index, Electrolyte Additive, Energy Storage

SUMMARY:

A protocol for the construction of a soluble lead flow battery with an extended lifespan, in which sodium acetate is supplied in the methanesulfonic electrolyte as an additive, is presented.

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 PbO₂ 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 PbO₂ 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.

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.*¹⁻⁵. 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 PbO₂ 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 conditions⁶⁻¹⁰.

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 cycles¹¹, 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 electrolyte¹¹.

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.

1.1. Preparation of lead methanesulfonate (1 L, 1 M as an example)

1.1.1. 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.

1.1.2. 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.

1.1.3. Filter through the Büchner funnel with 70 mm cellulose filter paper to separate any undissolved lead oxide.

1.1.4. Repeat this procedure for 3 times. Add DI water to reach 1 L in total volume.

1.2. Preparation of electrolyte without additive (300 mL)

1.2.1. Add 20.595 g of MSA (70%) to a beaker. Add 150 mL of prepared 1 M lead methanesulfonate to the same beaker.

1.2.2. 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.

1.3. Preparation of electrolyte with sodium acetate (300 mL)

1.3.1. Add 20.595 g of MSA (70%) to a beaker. Add 150 mL of prepared 1 M lead methanesulfonate to the same beaker.

1.3.2. Add 1.23 g of NaOAc (98%) to the beaker as an additive agent.

1.3.3. 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.

1.4. Pretreatment of the positive and negative electrodes

1.4.1. 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.

128

129 1.4.2. Add 20.83 g of hydrogen chloride (35%) in 200 mL DI water and stir the solution until
130 all of the hydrogen chloride is dissolved.

131

132 1.4.3. Immerse the entire positive electrode in the prepared 1 M hydrogen chloride solution
133 overnight to remove impurities at the electrode surface.

134

135 1.4.4. Rinse the positive electrode thoroughly with DI water and dry the electrode with
136 delicate task wipers. Tape one side of each electrode using polytetrafluoroethylene (PTFE) tape
137 while exposing the other side of the electrodes.

138

139 1.4.5. Prepare another solution with 3.03 g of potassium nitrate (99%) and 300 mL DI water,
140 which results in a solution of 0.1 M potassium nitrate.

141

142 1.4.6. Immerse the positive and negative electrodes in 0.1 M potassium nitrate with the
143 exposed surface facing each electrode.

144

145 1.4.7. Apply a potential of 1.80 V vs. Ag/AgCl to the positive electrode for 5 min.
146 Subsequently, apply a potential of -1.0 V vs. Ag/AgCl to the positive electrode for 2 min.

147

148 1.5. Assemble the SLFB beaker cell

149

150 1.5.1. Attach the pretreated positive and negative electrodes to a home-made electrode
151 positioning board for a fixed electrode distance. Place the positioning board together with
152 electrodes in a beaker as schematically illustrated in **Figure 1** and add electrolyte to the beaker
153 until the designated level of immersion.

154

155 1.5.2. Place a magnetic stirrer into the beaker, position the beaker on a hot plate and
156 control the rotating rate of the stirrer. Connect the battery tester to the electrodes and cover
157 the beaker cell with plastic wrap to prevent evaporation.

158

159 1.6. Calculate the battery efficiency

1.6.1. After galvanostatic charge and discharge, calculate the efficiency of the battery as the following:

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

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

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**.

2.1. Measurement

2.1.1. Weigh and record two positive electrodes respectively before the experiments.

2.1.2. 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**).

2.1.3. 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.

2.1.4. 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).

2.1.5. After plating, rinse the two positive electrodes with DI water and dry them at room temperature overnight.

2.1.6. Weigh and record two positive electrodes again respectively and calculate the metal distribution ratio (MDR) according to the equation listed below.

2.1.7. 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).

2.2. Calculation

2.2.1. 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:

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

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

3. SEM Sample Preparation

3.1. Rinse the graphite electrode with DI water and dry at room temperature after electroplating.

3.2. 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 mm silicon carbide sand papers, subsequently.

3.3. Further polish the samples with 1 mm diamond suspension and 0.05 mm 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 range¹¹.

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 steeper 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 PbO₂ electrodeposit is observed in **Figure 5a** in an electrolyte with the NaOAc additive, compared to the more fractured PbO₂ surface plated without NaOAc as shown in **Figure 5b**. This morphological observation of PbO₂ 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.

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.

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 Ref¹¹ with permission.

Figure 4. A comparison of the metal distribution ratio to linear distance ratio measured by throwing index experiments (a) PbO₂ deposition at the positive electrodes; (b) Pb deposition at the negative electrodes. This figure has been modified from Ref¹¹ with permission.

Figure 5. SEM images of electroplated PbO₂ at the positive electrode by electrolyte (a) without additive; (b) with 50 mM NaOAc additive. The magnification is of 20,000X.

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 unignorablely. 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 PbO₂ 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 PbO₂ 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 PbO₂ electrodeposit observed in SEM images shown in **Figure 5a**. The extended cycle life of SLFBs is thus achieved by the plating of more integrated PbO₂ 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.

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DISCLOSURE:

We have nothing to disclose.

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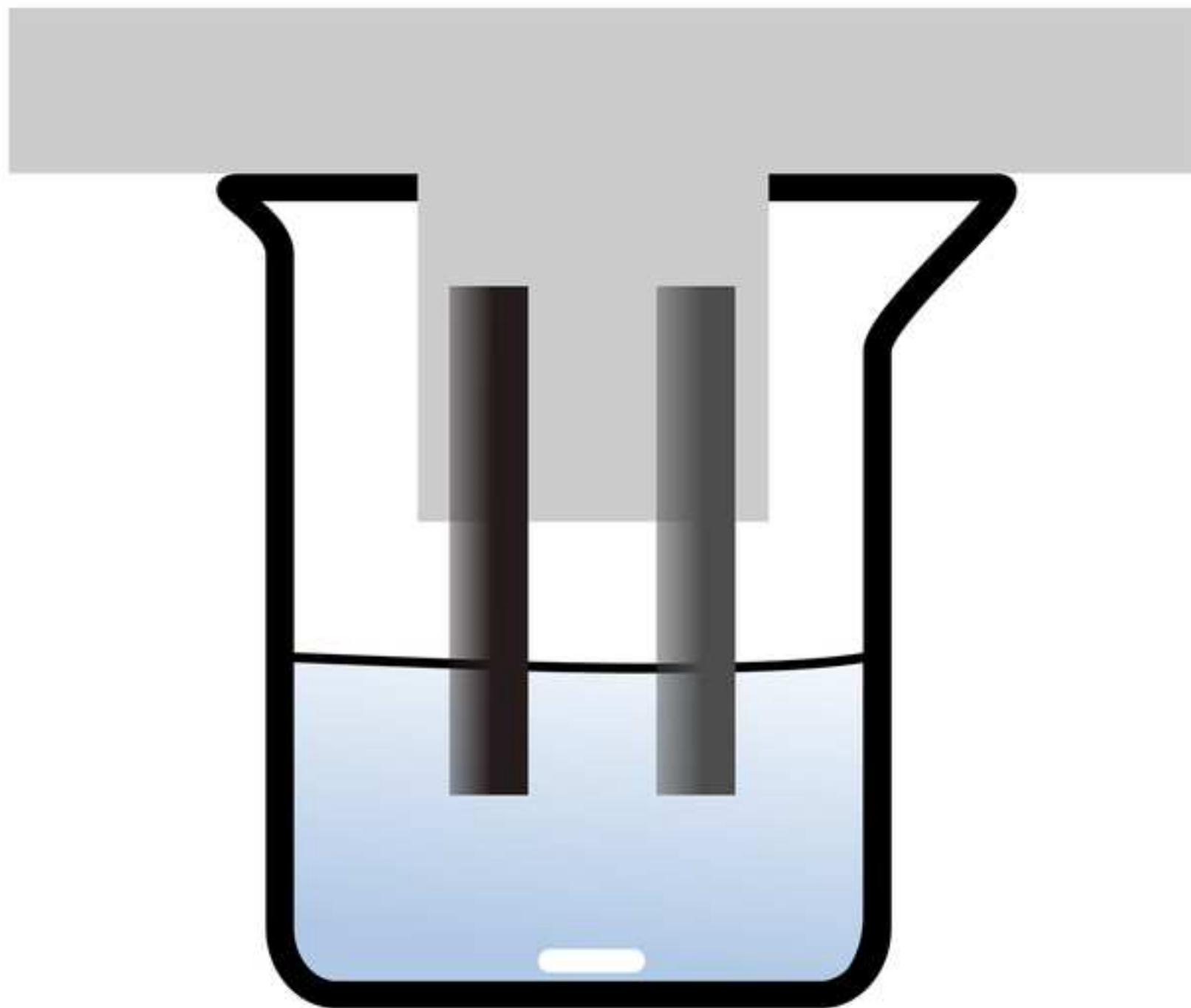
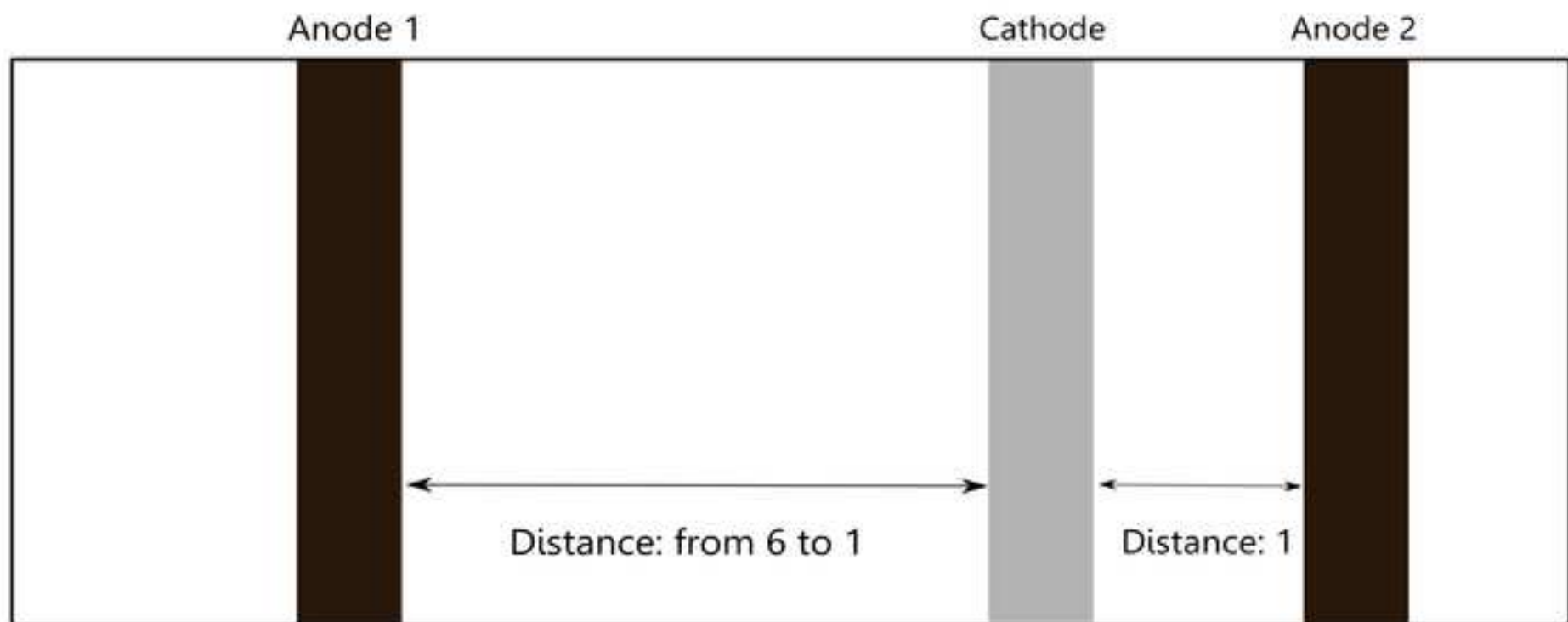


Figure 2



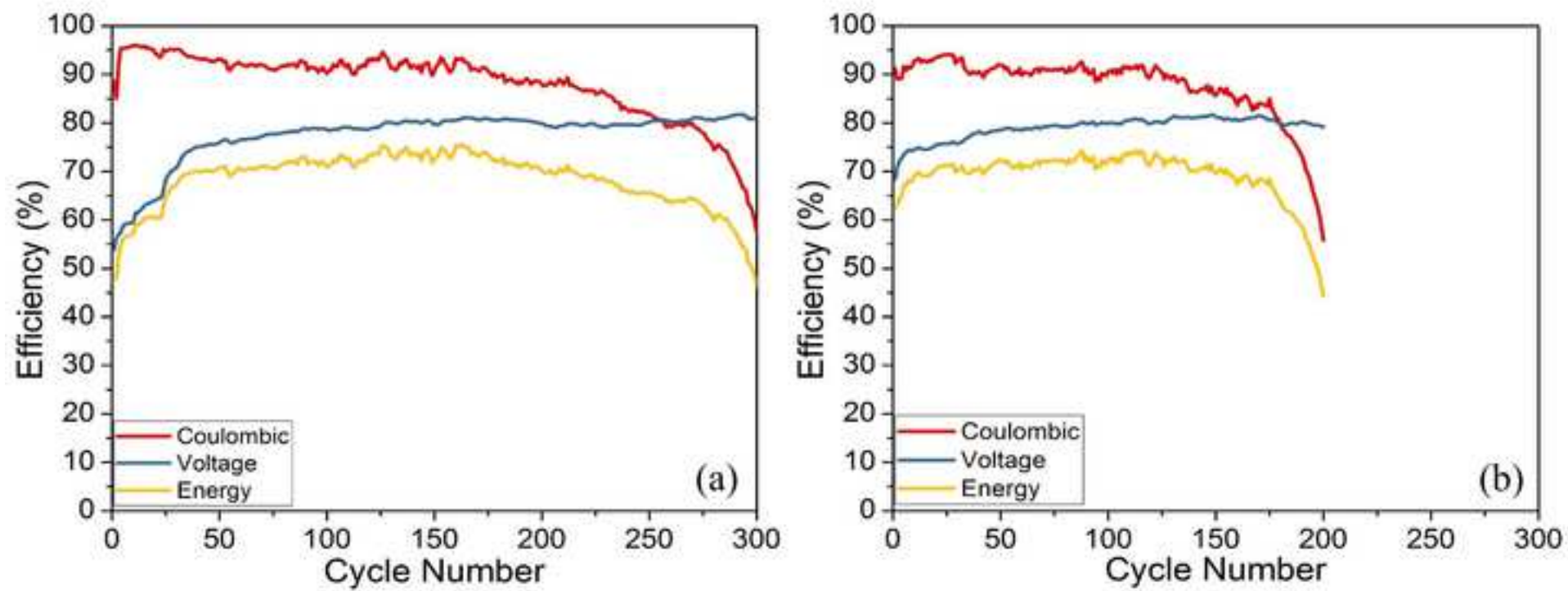


Figure 4

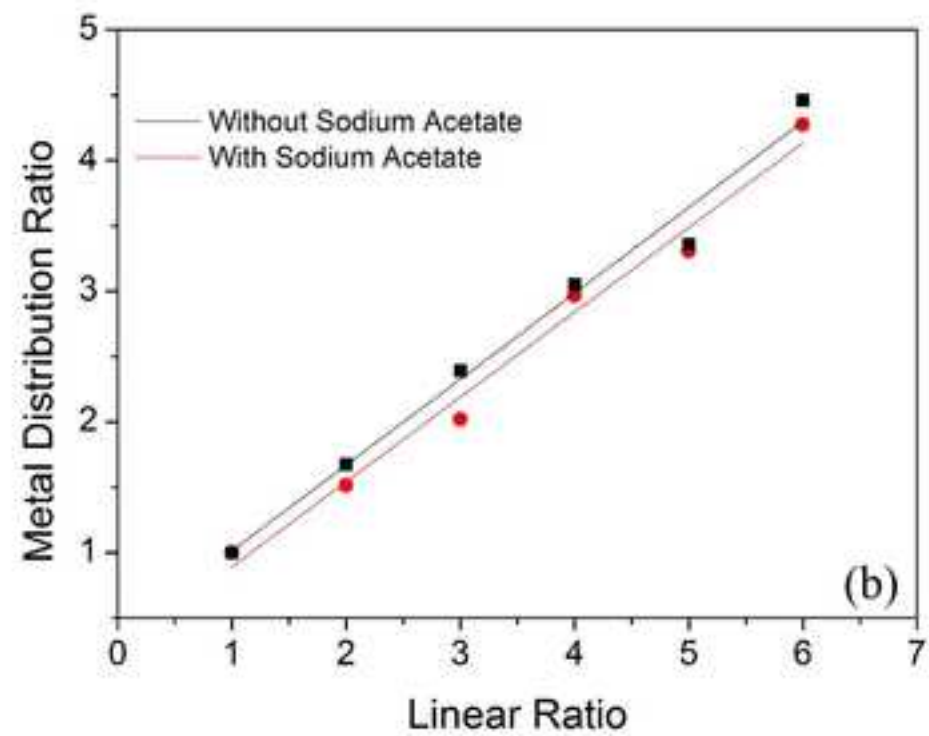
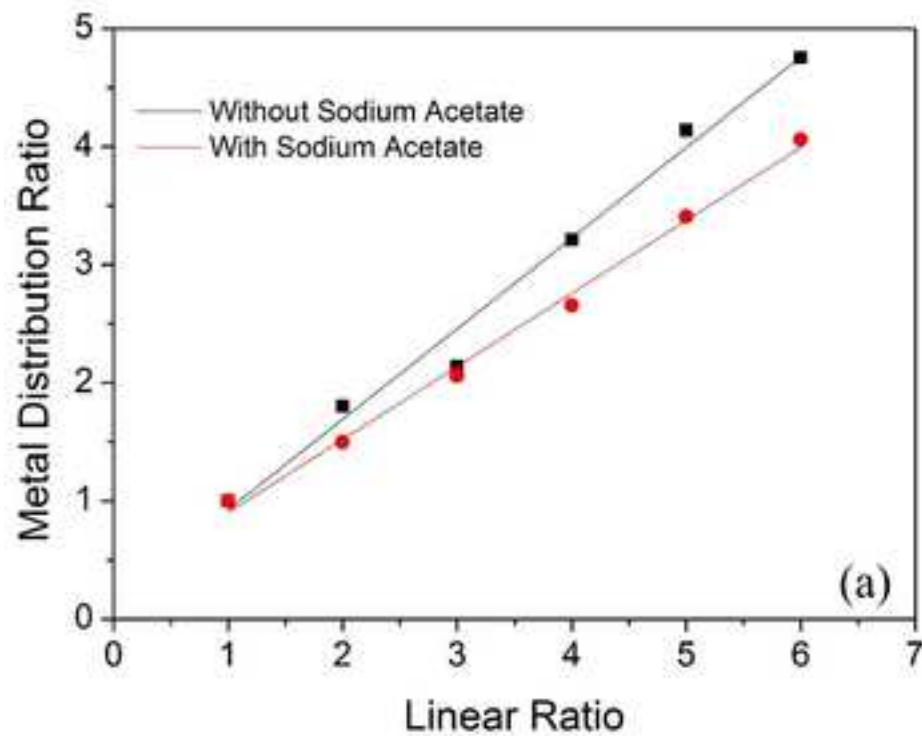
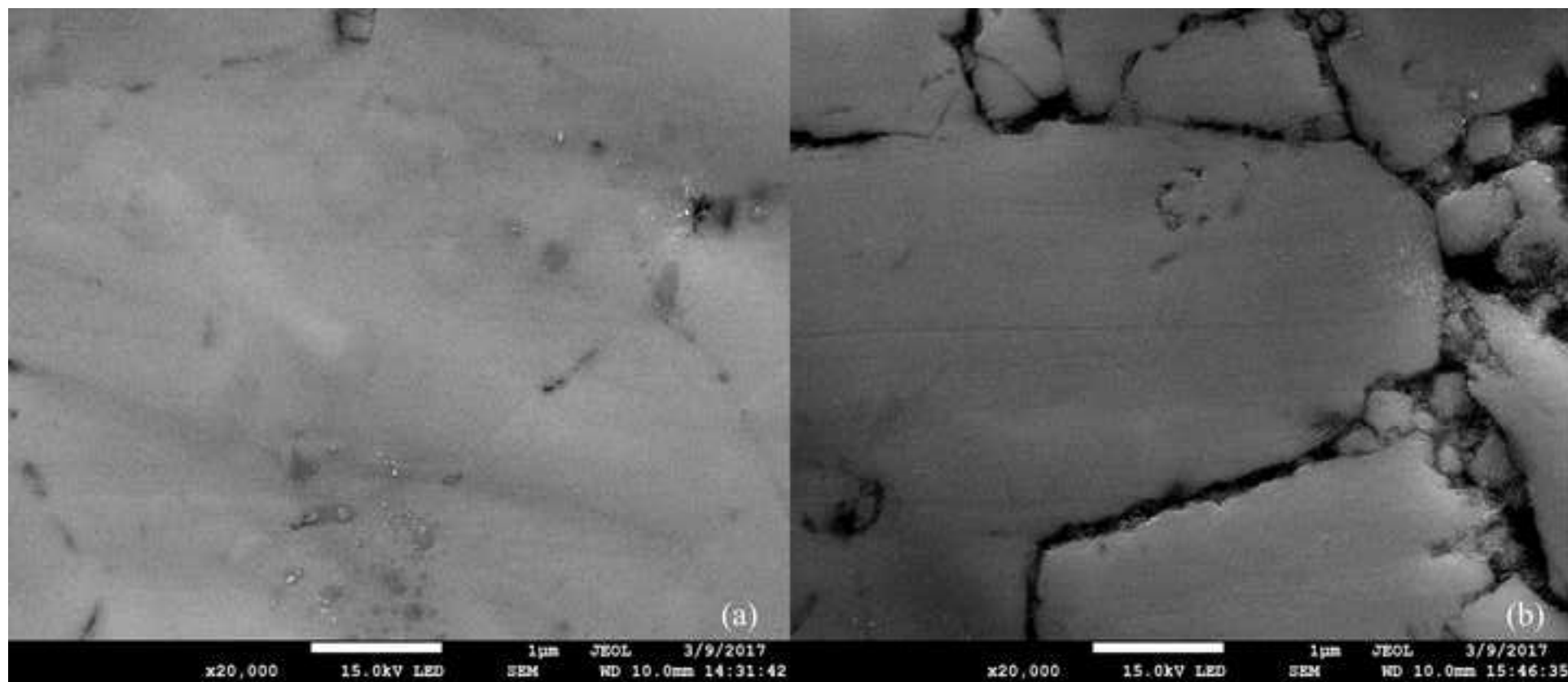


Figure 5



Name of Material/ Equipment	Company	Catalog Number	Comments/Description
70 mm cellulose filter paper	Advance		
Autolab	Metrohm	PGSTA302N	
BT-Lab	BioLogic	BCS-810	
commercial carbon composite electrode	Homy Tech,Taiwan		Density 1.75 g cm ⁻³ , and electrical conductivity 330 S cm ⁻¹
Diamond saw	Buehler		
Hydrochloric Acid	SHOWA	0812-0150-000-69SW	35%
Lead (II) Oxide	SHOWA	1209-0250-000-23SW	98%
Lutropur MSA	BASF	50707525	70%
nickel plate	Lien Hung Alloy Trading Co., LTD., Taiwan,		99%
Potassium Nitrate	Scharlab	28703-95	99%
Scanning electron microscopy	JEOL	JSM-7800F	at accelerating voltage of 15 kV
Sodium Acetate	SHOWA	1922-5250-000-23SW	98%
water purification system	Barnstead MicroPure		18.2 MΩ· cm



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Extending lifespan of soluble lead flow batteries with sodium acetate additive

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Ans: We have tried our best to proofread the manuscript to avoid spelling or grammar errors.

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Ans: We have uploaded the acquired copyright permission document, and denote the citation as suggested.

3. Please combine all panels of one figure into a single image file.

Ans: The figures are combined as suggested.

4. Figure 1: If possible, please use the same x-axis scale for both panels to facilitate comparison.

Ans: The figures are modified as suggested.

5. Figure 2: Please use the same y-axis scale for both panels to facilitate comparison.

Ans: The figures are modified as suggested.

6. Keywords: Please provide at least 6 keywords or phrases.

Ans: We have added more keywords as suggested.

7. Please rephrase the Introduction to include a clear statement of the overall goal of this method.

Ans: We have rewritten the last paragraph of the Introduction to state more clearly

the overall goal of this protocol.

8. Please use SI abbreviations for all units: L, mL, μ L, h, min, s, etc.

Ans: The units are modified to follow SI abbreviations as suggested.

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Ans: The commercial languages are removed from the manuscript, and the Table of Materials and Reagents are modified as suggested.

10. 1.4: Is lead oxide added to methanesulfonic acid? Please specify the liquid.

Ans: Yes, we have modified and rearranged this protocol section to make it more readable and less confusing.

11. 1.4-1.5: Are these steps conducted in the fume hood?

Ans: Yes, and this protocol section is rearranged to make it more readable and less confusing.

12. Please revise the protocol (lines 119-124, etc.) to contain only action items that direct the reader to do something (e.g., “Do this,” “Ensure that,” etc.). The actions should be described in the imperative tense in complete sentences wherever possible. Avoid usage of phrases such as “could be,” “should be,” and “would be” throughout the Protocol. Any text that cannot be written in the imperative tense may be added as a “Note.” Please include all safety procedures and use of hoods, etc. Please move the discussion about the protocol to the Discussion.

Ans: This protocol section is rewritten and rephrased as suggested.

13. 4.1: How to confirm the electrode is adequately polished?

Ans: The purpose of electrode polishing is to remove impurities left behind from commercial fabrication. We have modified the protocol section accordingly and added further explanation in the first paragraph in Discussion.

14. Please include single-line spaces between all paragraphs, headings, steps, etc.

Ans: We have included single-line spaces between all paragraphs as suggested.

15. Representative Results presented cycling performance, throwing index experiments and SEM images, but how to obtain such data are not mentioned in the protocol. Please consider including how to evaluate cycling performance, how to conduct throwing index experiments, and how to acquire SEM images in the protocol.

Ans: We have included the protocols and calculations in the Protocol section as suggested.

16. Please revise to explain the Representative Results in the context of the technique you have described, e.g., how do these results show the technique, suggestions about how to analyze the outcome, etc. The paragraph text should refer to all of the figures. However for figures showing the experimental set-up, please reference them in the Protocol. Data from both successful and sub-optimal experiments can be included.

Ans: We have modified the Representative Results section to better explain the additive effects in terms of galvanostatic charge/discharge, TI measurement, and SEM results.

17. As we are a methods journal, please revise the Discussion to explicitly cover the following in detail in 3-6 paragraphs with citations:

- a) Critical steps within the protocol*
- b) Any modifications and troubleshooting of the technique*
- c) Any limitations of the technique*
- d) The significance with respect to existing methods*
- e) Any future applications of the technique*

Ans: We have modified the Discussion section to better cover the points suggested by the editor.

18. References: Please do not abbreviate journal titles. Please include volume and issue numbers for all references.

Ans: We have followed the Reference style as suggested.

19. Please revise the table of the essential supplies, reagents, and equipment. The table should include the name, company, and catalog number of all relevant materials in separate columns in an xls/xlsx file.

Ans: We have revised the table of essential supplies, reagents and equipment as suggested.

Reviewers' comments:

Reviewer #1:

Manuscript Summary:

The author reported extending lifespan of soluble lead flow batteries with sodium acetate additive. It is an interesting and effective work, but following issues are needed to address:

1. The comparison of Figure 1a and Figure 1b should be merged into one graph. What is the calculation formula of efficiency of coulombic, voltage and energy? The exact point of cycle number should be marked.

Ans: We thank the reviewer for the comment. We have merged Figure 1a and 1b into one graph, and supplied the calculation formula of coulombic, voltage and energy efficiencies in Protocol 1.

We have also explained the meaning of cycle number in the first paragraph of Representative Results.

2. The relationship of MDR to LR in Figure 2 needs to be expounded in more detail.

Ans: We have elaborated on the meaning of MDR to LR in our TI measurement in the second paragraph of Representative Results as suggested by the reviewer.

3. The SEM results have been well explained. What is the experimental equipment? Model and experimental condition.

Ans: We have included the experimental condition for the acquired SEM sample in the third paragraph of Representative Results, and listed the experimental equipment model in the table of essential supplies, reagents and equipment.

Reviewer #2:**Manuscript Summary:**

This work purportedly attempts to demonstrate the effect of an additive on the deposition morphology of PO₂ in soluble lead flow batteries. However, it is very clear to me that this is a sub-standard manuscript. The authors had put the very minimal effort in producing it, hoping to get just one more citation. The experiments are described in an unacceptably vague manner. Basic experimental data is missing. Discussion is almost inexistent. This work is mis-guided and, unfortunately, its results cannot be used to draw any meaningful conclusions. See detailed reasons below. Unfortunately, I have to recommend the authors to familiarize themselves with electrochemistry, battery and flow battery technology by reaching to basic textbooks before attempting any further activities in the field. I recommend outright rejection. I am aware that the authors might have a video on this, and that the manuscript is a sort of a support for it. But my objection remains valid to any work performed in such conditions and reported in such manner.

Major Concerns:

-The first two references have been cited already too much and does not describe the "high efficiency and long cycle life" of the vanadium battery. This reveals the inexperience of the authors in this field. There are several, up to date reviews with the actual performance of modern systems, including vanadium, and the advantages of flow batteries. The authors failed at finding well-known recent publications on soluble lead flow batteries.

Ans: We have replaced reference 1 and 2 with two more recent reviews on redox flow batteries to make more appropriate. We also include a review on the SLFB published this year as reference 10.

-Can the authors explain what is the purpose of pre-treating the electrodes in potassium nitrate? This is not a usual procedure; therefore, its purpose should be stated.

Ans: The purpose of the electrochemical pretreatment with potassium nitrate is to remove impurities that may induce redox reactions between the potentials of 0 to 1.8 V vs. Ag/AgCl. We have included such a description in the first paragraph of the Discussion section.

-Regarding the results in Fig. 1. Temperature of the experiment is not even

mentioned, for neither of the plots. The volumetric flow rate and average flow speed of the electrolyte at the electrode compartments is not mentioned in the author's work, an unacceptable omission in a paper about flow batteries. Without this information, the authors work simply can't be related to the results by Lin et al., the comparison is invalid. Increased number of cycles in this manuscript might well be result of the reaction environment and not of the presence of the additive. Do the results in Fig. 1b have an ethanoate additive? This should be mentioned.

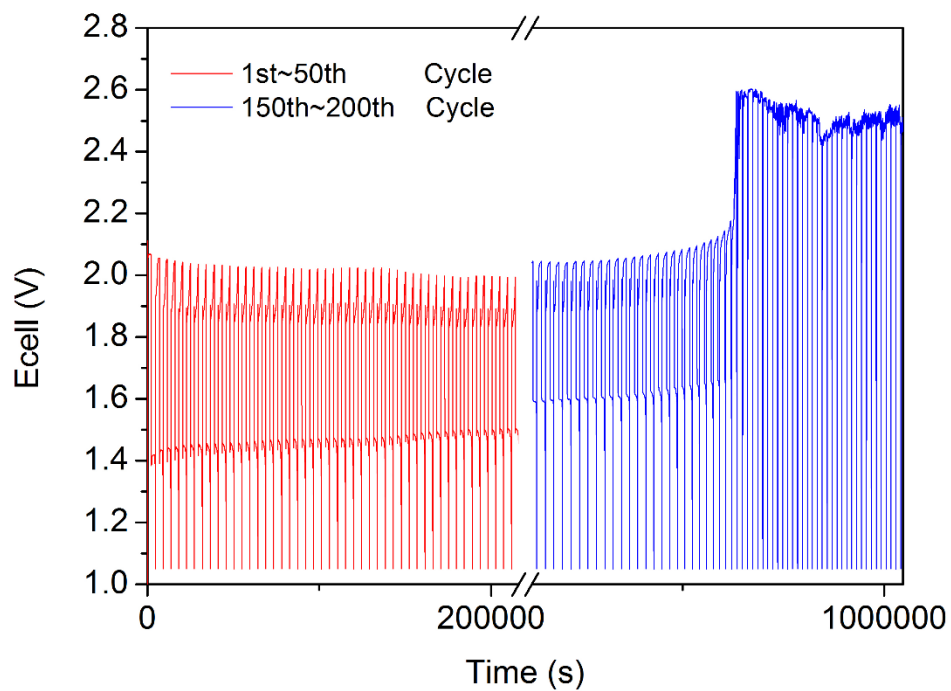
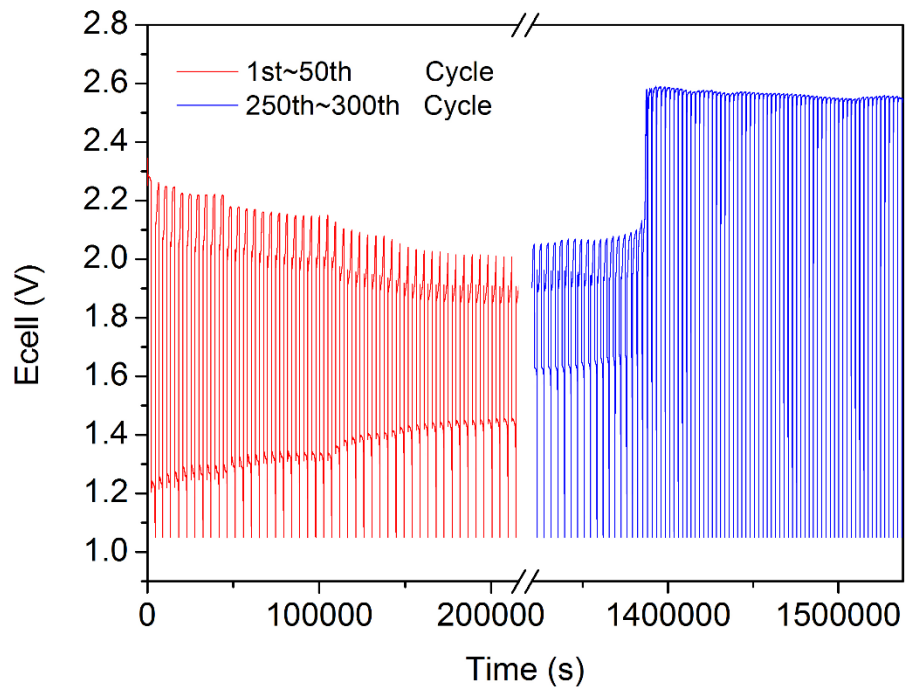
Ans: We have discussed these experimental conditions in the second paragraph in Discussion section, and they are stated as the following:

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 sever agitation. The temperature of beaker cells is not controlled in our experiments, which leaves it close to the atmospheric temperature in our lab (25 ± 5 °C). While temperature variation may affect the deposition quality and battery performance, the two compared experiments are conducted in parallel to avoid the temperature perturbation interference.

Also, Figure 1 (now Figure 3 in revised version) is plotted based on data published in our previous work, Ref. 11, with permission.

-Other omissions by the authors: the thickness of the electrode compartment is not reported, the presence or absence of a membrane, the actual electrode potential and cell potential of the battery is not given in a plot (without this, the reported efficiency % is not backed by any evidence.)

Ans: Since a beaker cell is used in our experiment, we have reported the electrode distance of 18 mm and the electrolyte volume of 260 mL instead. We don't find it necessary to provide cell potential figures in the manuscript, but attached here per the reviewer's request (The one up to 300 cycles is with NaOAc while the one up to 200 cycles is without NaOAc)



-It is not described how did the authors measured the throwing index. The 'throwing index experiments' mentioned in the caption for Fig. 2 must be carefully described. Can they provide an equation for this? Simply referring to the work by Lin et al. is not

acceptable, the authors should describe their own experiments. Not even a reference is suggested to the reader. Moreover, and critically, the state of charge for the SEM of the deposits is not reported. The morphology of these will be different depending of the state of charge, number of cycles, temperature, thickness of deposit, flow rate, etc.

Ans: We have added Protocol 2 in the manuscript on throwing index measurements and calculations, as well as a schematic diagram (Figure 2) describing the Haring-Blum cell. The PbO₂ electrodeposit for SEM is acquired after full 50-cycle charge/discharge, and we have added the information in the third paragraph of Representative Results section.

-Not surprisingly, the caption for Fig 3. is a single sentence. No parameter or further experimental condition is even mentioned. Figure 3b. seems to be out of focus. The nucleation of lead or the morphology of the deposit was not observed or discussed by the authors. Usually, it is rather easy to see the effect of an additive on the PbO₂ morphology using SEM, but this is not the case.

Ans: We have added Protocol 3 on SEM sample preparation, and the ordinary morphology of PbO₂ is polished off. But the excess defects in the electrodeposit plated without NaOAc is easily observed. We have also described the experimental information of the SEM sample in the third paragraph of Representative Results section.

-In the discussion, the authors say that reduced PbO₂ is observed in the 'beaker cell'. Does this mean that the experiments were not carried out in an actual flow cell? This is rather disappointing, as the title of this paper refers to "soluble lead flow batteries". Again, the experimental set-up is never described. Was it a beaker or a flow cell? Stirred or not? Which volume of electrolyte was used? Again, what was its temperature? Not a diagram or photo is supplied.

Ans: We have added a schematic diagram of the beaker cell setup (Figure 1) in the revised manuscript. 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.

Reviewer #3:**Manuscript Summary:**

The manuscript titled "Extending lifespan of soluble lead flow batteries with sodium acetate additive" submitted to JoVE has been critically reviewed. The authors have addressed a very interesting problem to stabilize the active material dissolution in SLFBs to enhance life of the systems. It is a very important necessity since redox flow batteries do serve as a potential alternative for large scale grid storage and large cycle life is essential for economic use of the batteries for desired application. The authors have identified pH fluctuations causing active materials loss as the degradation mechanism and have suggested additives approach as a method to stabilize pH resulting in enhanced cycle life. The approach is motivating because of the ease of the solution and they have demonstrated significant cycle life enhancement.

Minor Concerns:

I would like to suggest some minor changes before the manuscript can be considered for publication.

1. What are the other types of electrolytes used for SLFBs and how do they perform? A comparison needs to be discussed and why do other electrolytes cannot offer pH control?

Ans: We thank the reviewer for the comments. We have seen perchloric acid and fluoroboric acid employed for soluble lead flow batteries, as listed Ref. 1 and 2 below. However, in this work we focused on methanesulfonate electrolyte system. Whether the strategy of NaOAc additive will work or not in those other systems requires further examination and is beyond the scope of this work.

Reference

1. LIU, Dong-Yang, Jie CHENG, Jun-Qing PAN, Yue-Hua WEN, Gao-Ping CAO, and Yu-Sheng YANG. "All-Lead Redox Flow Battery in a Fluoroboric Acid Electrolyte." *Acta Physico-Chimica Sinica* 27, no. 11 (2011): 2571-2576.
2. Sun, Yanzhi, Shicheng Guo, Yu Wang, Junqing Pan, and Pingyu Wan. "A new lead single flow battery in a composite perchloric acid system with high specific surface capacity for large-scale energy storage." *Journal of Solid State Electrochemistry* 21, no. 12 (2017): 3533-3543.

2. The relevance of an electrolyte additive needs to be mentioned. How does this specific additive control the pH fluctuations?

Ans: In our previous work (Ref. 11, Fig 2), we have shown that a buffer effect of NaOAc will lead to levelled-off pH curves along with charge/discharge cycle. However, we believe NaOAc additive induces other effects on electrodeposition that is more important than pH buffering in SLFBs such as what we illustrated in TI and SEM results. Thus, we didn't include the pH data in this manuscript.

3. An image or a schematic of the cell setup is helpful to understand the half- cell reactions in the textual manuscript.

Ans: We have added a schematic diagram of the beaker cell setup as Figure 1 as suggested by the reviewer.

Reviewer #4:

I am pleased to review the paper titled "Extending lifespan of soluble lead flow batteries with sodium acetate additive". The paper provided a method for the construction of a soluble lead flow battery with extended cycle life by using sodium acetate additive. This presents interesting results. I think the paper can be accepted with minor revision. The comments are as following.

1. Spelling mistakes should be corrected carefully. Line 66, the abbreviation "SLFB" should be followed by its full name. line 137, "1 M potassium nitrate" should be "0.1 M potassium nitrate".

Ans: We thank the reviewer for the suggestions and we have made modifications accordingly.

2. It is suggested that how to conduct throwing index experiments and electrochemical experiments should be given. In addition, the experiment parameters for the SEM images should be given.

Ans: We have included the protocols in the Protocol section for TI experiment and electrochemical experiments as suggested. We also have included the experimental conditions for the acquired SEM sample in the third paragraph of Representative Results, and listed the experimental equipment model in the table of essential supplies, reagents and equipment.

3. Will sodium acetate additive be consumed by oxidation? The authors should give some comments or additional results and discussion.

Ans: In our previous work (Ref. 11, Fig 1), we have performed comprehensive cyclic voltammetry study on the methanesulfonate electrolyte with and without sodium acetate, and no additional redox reaction is observed in the potential range of SLFB operation. We have added an additional comment in the end of the first paragraph of Representative Results to clarify this concern.

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