



Buffer Effects of Electrolyte Additives on Soluble Lead-Acid Flow Batteries

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Introduction

The soluble lead-acid flow battery (SLFB) is a promising solution for economic energy storage; however, its long term cycling performance is impaired in part by PH fluctuation in operation. Addition of the appropriate amount and type of buffer solutions may be able to extend the cycle life of SLFBs, by mitigating pH perturbations. First, two kinds of buffer solutions are tested on methanesulfonic acid based system: sodium acetate and sodium tetraborate. Their PH variations and efficiencies are investigated over multiple operation cycles. Then, an electrolyte based on pure buffer solution, including lead (II) acetate, sodium acetate and acetic acid, is also examined.

Experimental

A solvent casted graphite electrode and a nickel plate is utilized as the positive and negative electrode, respectively, in all experiments. The positive electrode is comprised of the PVDF binder and graphite powder, and NMP is used as the solvent for casting. The nickel electrode is purchased with purity of above 99.5 wt%. In addition, four different kind of electrolytes are prepared for cyclic voltammetry and charge/discharge experiments; three of them are based on methanesulfonic acid (A1–A3) and another is based on lead acetate trihydrate system (B). The specific compositions are listed as follows:

A1. Methanesulfonic acid 0.5M, lead methane sulfonate 0.5M.

A2. Methanesulfonic acid 0.5M, lead methane sulfonate 0.5M and Sodium Acetate 0.05M

A3. Methanesulfonic acid 0.5M, lead methane sulfonate 0.5M and Sodium Tetraborate 0.05M

B. Lead (II) acetate trihydrate 0.2M, sodium acetate 1M and Acetic acid titrate solution to pH4.5

Results and Discussion

Cyclic Voltammetry Analysis

The effects of buffer additives in methanesulfonic acid system are examined with cyclic voltammetry experiments. First, different concentrations (0.5M, 0.05M, 0.01M) of sodium acetate (NaAc) are added to the A1 system to identify the appropriate addition amount. We find that addition of 0.05M NaAc leads to a higher and sharper reduction voltage peak in comparison to other concentration, as shown in Fig. 2. This result indicates that there are less side reactions occur during the reduction process with 0.05M NaAc addition. Then, 0.05M sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) is also added to A1 system for comparison. A broader reduction peak is observed in this system in comparison to the NaAc one via CV analysis. Thus, 0.05M NaAc is a better buffer additive to A1 system based on CV results.

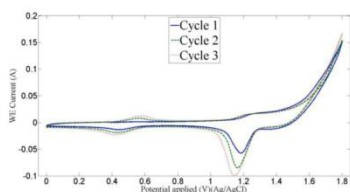


Fig. 1 A voltammogram of 0.01M NaAc additive to A1 system. The upper potential is 1.8V, scan Rate: 20 mV/s

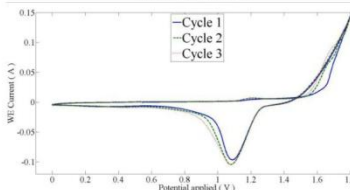


Fig. 2 A voltammogram of 0.05M NaAc additive to A1 system. The upper potential is 1.8V, scan Rate: 20 mV/s

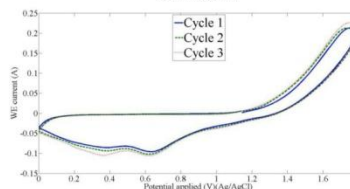
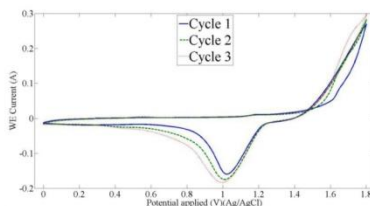


Fig. 3 A voltammogram of 0.5M NaAc additive to A1 system. The upper potential is 1.8V, scan Rate: 20 mV/s

Fig. 4 A voltammogram of 0.05M $\text{Na}_2\text{B}_4\text{O}_7$ additive to A1 system. The upper potential is 1.8V, scan Rate: 20 mV/s



pH variation during charge/discharge

Following the CV results of buffer additives, the pH and voltage variation are examined with charge/discharge experiments. We found 0.05M NaAc additive leads to a smaller pH variation in comparison to 0.05M $\text{Na}_2\text{B}_4\text{O}_7$, as shown in Fig. 5. Also, the energy efficiency of the 0.05M NaAc system is found to be more steady than the other. Yet the pH variation of the $\text{Na}_2\text{B}_4\text{O}_7$ system is still more stable compared to A1 system. Therefore, the result indicates that buffer additives in methanesulfonic system mitigate pH variation.

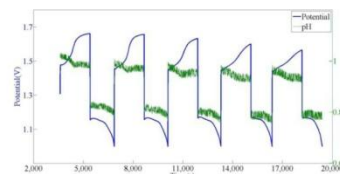


Fig. 5 A pH and voltage variations of 0.05M NaAc additive to A1 system by charge/discharge experiment. The current density is 20 mA/cm².

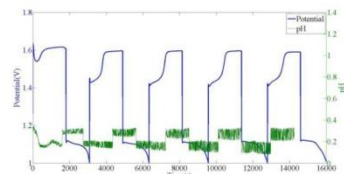


Fig. 6 A pH and voltage variations of 0.05M $\text{Na}_2\text{B}_4\text{O}_7$ additive to A1 system by charge/discharge experiment. The current density is 20 mA/cm².

The methanesulfonic acid system is investigated by charge/discharge experiment. Coulomb efficiency, voltage efficiency and energy efficiency are shown in Fig. 7. The result indicates that coulomb efficiency is around 80% for almost 80 cycle. Note that a dramatic decrease of voltage efficiency at around 15 cycle is caused by an artificial error.

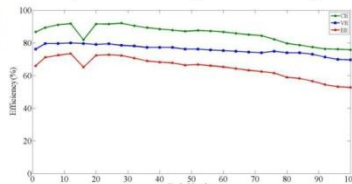


Fig. 7 Efficiency of A1 system by charge/discharge experiment. The current density is 20mA/cm², cut off potential: 0.01V.

Full buffer system - Acetic acid based electrolyte

The acetic acid system (HAc) is examined with charge/discharge experiment. A peculiar phenomenon that a sudden efficiency decrease at second cycle is observed. This efficiency dip is gradually recovered in subsequent cycles, but the system is practically unusable for energy storage. We thus further examined the pH variation during charge/discharge cycles.

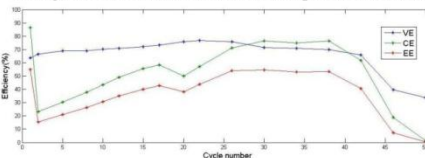


Fig. 8 Efficiency of acetic acid system. The current density is 20mA/cm², cut off potential: 0.01V.

pH variation during charge/discharge

The system is more acidic when charging in the first three cycles, while more basic when discharging in the subsequent cycles. The dramatic efficiency drop at the second charge/discharge cycle is highly related to this trend of pH variation. Literatures show that hydroxyl ions may react with lead through sophisticated processes in the system. More research need to be done to understand the underlying mechanisms so as to enhance the performance.

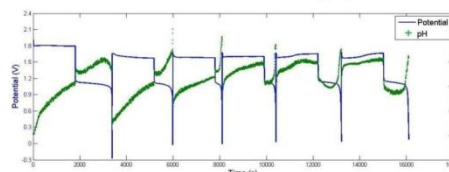


Fig. 9 pH and voltage variations of acetic acid system during charge/discharge experiment. The current density is 20mA/cm².

Conclusion

We add different buffer solutions to study their effects on SLFB systems with methanesulfonic acid. A pure buffer solution based on acetic acid is also examined. An optimal concentration of NaAc additive is demonstrated with CV experiments. Smaller pH variations are found in all buffered SLFB systems in comparison to the unbuffered. But the charge/discharge performance still awaits improvement. Further studies on the effects of hydroxyl ions reacting with lead need to be done to clarify the performance decay in buffered SLFB systems.

Acknowledge

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National Taiwan University

On Acetate Based Lead Acid Redox Flow Battery
Systems

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Advisor: Hsun-Yi Chen, Ph.D.

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Abstract

The state-of-the-art lead acid redox flow battery faces the issue that the acidity of electrolyte increases along with its operation and in turn leads to its degradation. Under high concentration of protons, Oury suggests that a passivation layer of PbO_x , which is insoluble and insulative, will form and eventually shorten the lifetime of the flow battery system. To alleviate fluctuation of acidity during charging/discharging of the system, a buffer solution based electrolyte may be a promising solution.

In order to create buffer effects in lead-acid RFBs, we titrated the electrolyte containing sodium acetate and lead(II) acetate with acetic acid to achieve the desired PH values. Our experimental results show that buffering electrolyte does work to contain pH variations within 0.1 in individual charging/discharging process. The pH variations of all experiments range from pH4.35 to pH4.6, when the initial pH value is titrated to 4.5.

Given the success of buffer effects led by acetate electrolyte, limited cycle life, serious dendrite growth and shed lead dioxide particles are hampering the usage of such a system. Thus, leveling agents including hexadecyl- trimethylammonium hydroxide hydrate and a mixture recipe of phenol, ethyl alcohol, gelatine are tested. Although the lead deposition appeared smoother and the lifetime of the system was improved slightly, the highest columbic efficiency that we can acquire is less than 50% in the additive modified system.

Further study of the concentration of additives in the electrolyte is needed to efficiently solve shedding of lead dioxide on the positive electrode. It is also important to understand underlying interaction mechanisms of acetic acid and lead oxide, which we believe is the key factor that results in all the aforementioned problems of acetate based lead acid RFB systems.

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List of acronyms

| Acronym | Definition |
|---------|---------------------|
| CE | Columbic efficiency |
| VE | Voltage efficiency |
| EE | Energy efficiency |
| s | Second |
| A | Ampere |
| RFB | Redox flow battery |
| + | Positive electrode |
| - | Negative electrode |
| V | Potential |

1. Introduction

Because we are using energy faster than ever, for example billions of smart phone applications are consuming more electricity than before, we need to find new and clean energy sources to sustain our economy activities. Future economy is expected to function without much fossil fuel, but relies on renewable energy to maintain the harmony between human beings and the environment. However, renewable energy is inherently intermittent and energy storage will play an important role in future power grids.

Smart grids incorporating solar and wind power depends heavily on large scale energy storage to smooth out the energy demands and supply. Electrochemical energy storage including various batteries is most flexible in applications within cities where space is limited. However, most of those batteries are too expensive to meet the market penetration requirement when scale up.

Among those batteries, the redox flow battery (RFB) is distinguished in that its overall capacity depends on how much electrolyte is pumped into the battery and how much density is the electrolyte. Since we can store the electrolyte in an external tank and then pump the electrolyte into the RFB while charging and discharging, the energy stored is not limited by the size of the battery itself.

The RFB has been studied for over forty years and still in the process of improving its efficiency. Most of the previous studies focused on improving its electrode and electrolyte. Although some RFB technology such as the all-vanadium system has already reached the performance for grid usage, its steep cost is preventing it from commercialization. On the other hand, lead acid redox flow batteries are based

on lead chemistry and are suitable for commercialization in terms of its cost. Thus, this research aims to develop lead acid RFB system and to make this system reach higher efficiency.

2. Research purpose

Lead acid RFB is still on the process toward the goal of large scale storage. Most of the research is based on methanesulfonic acid system, and the system is able to cycle more than three hundred times while the energy efficiency can reach 70%.

However, the end of the system of methanesulfonic acid is due to the system is rife of H^+ , causing the efficiency decrease gradually. In order to address the problem, we need a proper solution to dilute proton, which make the efficiency low. Buffer solution is maybe a good way to solve this problem because buffer solution is served to tilt pH in a range which may maintain the efficiency in RFB.

My research is based on the system design by Pletcher . I replace electrolyte methanesulfonic acid with acetic acid, sodium acetate and lead(II) acetate trihydrate. All experiments are designed to gain insight into working conditions of the acetic acid system.

3. Literature

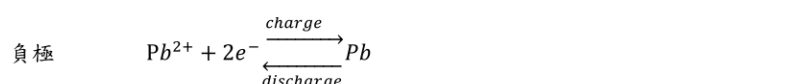
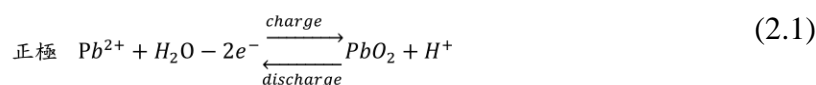
3.1 Redox flow battery development & character

The redox flow battery (RFB) is recently devised by NASA scientist in 1970s for large scale power storage in the space. Capacity of RFB system is depend on how much electrolyte you can store in the tank rather than on the scale of the battery which is different from other storage devices. In other word, the energy capacity of RFB is irrelevant to scale of battery. Power is depends on electrode area.

The following is character of RFB system

- i. Large scale: Capacity of RFB range from KW to MW so that customer can different kind of size depends on their usage.
- ii. Rate of reaction: RFB is quite sensitive to receiving electron to transfer electricity to chemical energy, not only sensitive to rapid current or to minute current. It makes RFB a brilliant candidate of storage for wind power plant and solar power plant which supply power unstably.
- iii. Energy density: Power of RFB depends on electrolyte volume and density.

Working mechanism of lead redox flow battery is Eq 2.1 、2.2². Both negative electrode and positive electrode reaction involve lead ions accompany with phase change from liquid state to solid state. Solid state of production will attach on electrode in that preventing self-redox reaction.



Device of RFB system is quite simple that all we need is pumping electrolyte into the battery. The structure of RFB system is as Fig. 1:

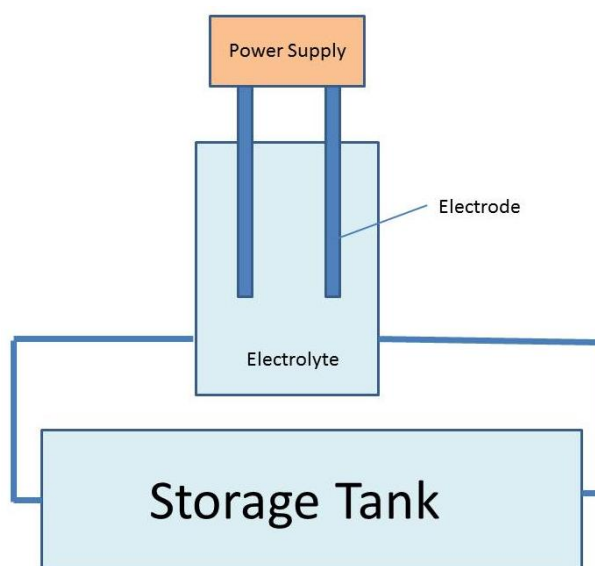


Fig. 1 Structure of RFB system

3.2 Redox flow battery material character

RFB is similar to lead storage battery in that positive electrode and negative electrode deposit element are lead dioxide and lead separately which is the same as RFB system. However we use different electrolyte rather than in lead storage battery, so we don't generate insoluble lead(II) sulfate but soluble lead(II) ions, the mechanism is as Fig. 2. Due to phase change during charging and discharging on electrode in RFB system which is irreversible, there are residual on both electrode while the end of discharging. After long period of charging-discharging cycle, some lead dioxide will drop off from positive electrode and also some insoluble lead oxide will form during cycle. There is lead dendrite on the brink of negative electrode after long period cycle, increasing the chance of short circuit.

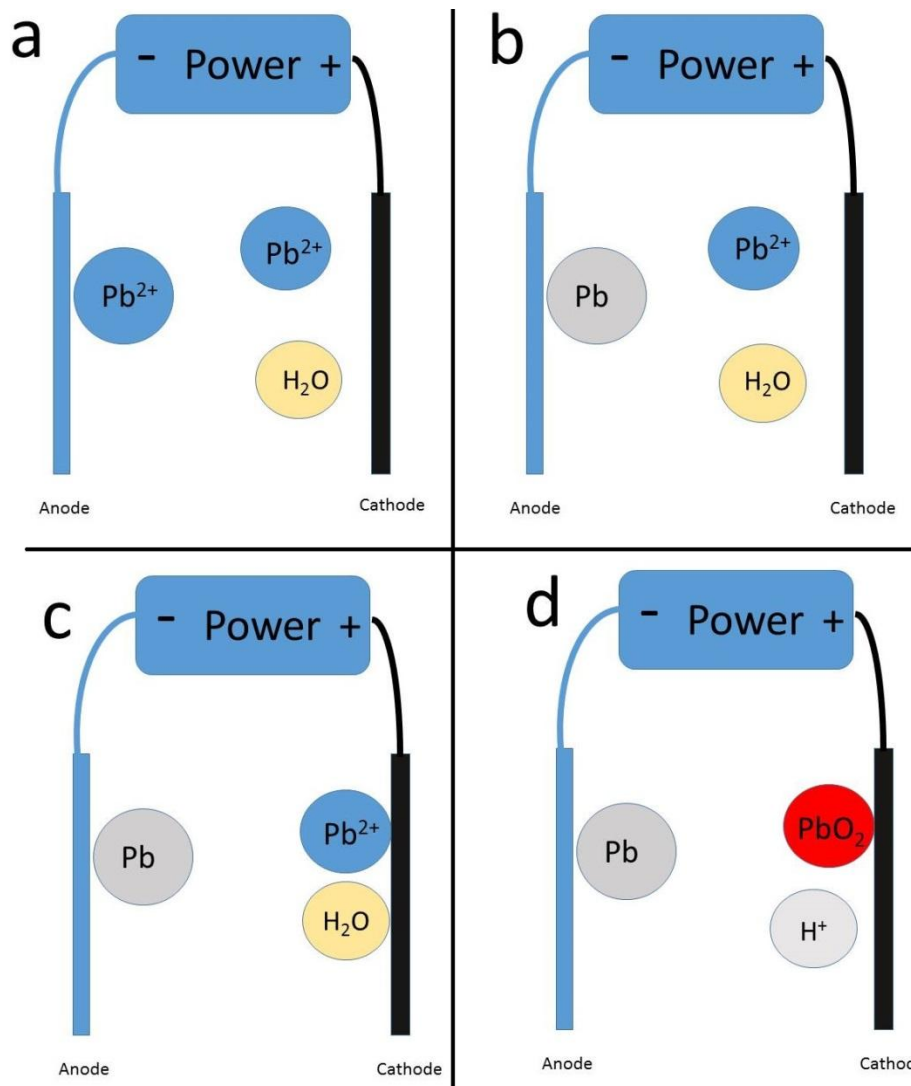


Fig. 2 Mechanism of charging in RFB

- a. Lead ions reduce to lead on negative electrode. b. Lead deposit on negative electrode. c. lead ions is oxidized to lead dioxide on positive electrode. d. Lead dioxide deposit on positive electrode accompany with protons.

3.3 Influence of pH in redox flow battery

Lead RFB system is working under condition of acid electrolytes, however, according to professor Oury, pH of electrolyte has a great impact on cycle ability. They conducted experiment of RFB under different pH conditions, find that when electrolyte is rife with H^+ will make efficiency decrease dramatically because of formation of $Pb(OH)_2$ during reduction of lead dioxide to lead(II) ions while discharging. If the proton density is too low, on the contrary, will cause the scant

element to react, leading to over potential⁴. $\text{Pb}(\text{OH})_2$ will transform to lead oxide hydrate and make the surface of lead dioxide tear apart and drop off, leading to decrease of efficiency.

3.4 Optimize lead dendrite on the negative electrode

Lead dendrite occurs seriously on the negative electrode during long period charging/discharging cycle. Dendrite will cause electron nonuniformly distribution on the electrode and lead to unstable potential while discharging.

Dendrite will decrease the distance between negative electrode and positive electrode. Lead preferably grows on the tip of dendrite. Lead will cause not only unstable potential but also short circuit which makes the device break down.

According to professor Edward Ghali's paper in 1985, he improve the deposition of lead on the negative electrode¹. The experiment conducted by electrolyte $\text{CH}_3\text{COONH}_4$, CH_3COOH , PbCl_2 under room temperature and unstirred condition. He infer a passive layer was formed which can prevent Cl and other impurity substance from negative electrode during charging. He smoothly deposit lead on negative electrode under charge density of 25 mA/cm^2 which is much larger than my experiment of acetate RFB's 5 mA/cm^2 . Fig. 3 is the picture of smoothly deposit lead on negative electrode without lead dendrite.

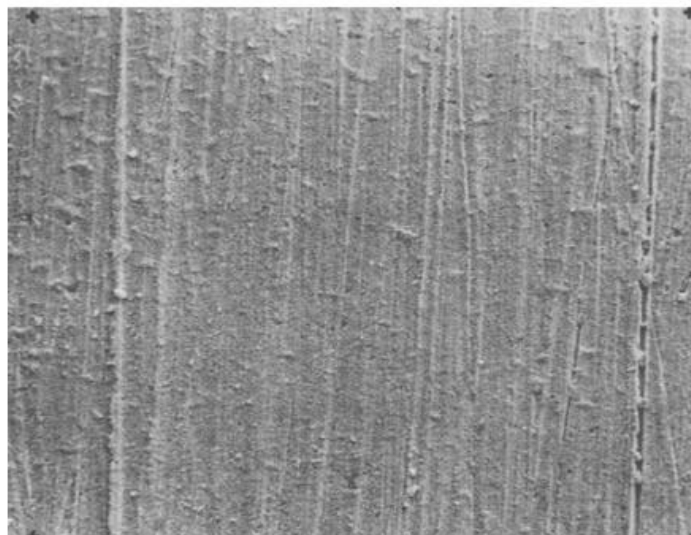


Fig. 3 SEM of lead deposit on Cu electrode

Professor Plether do research on different kind of leveling agent to suppress the dendrite⁵. Leveling agent is composed of surfactant. Take into account of toxicity, efficiency and influence on lead dioxide of leveling agents, I use hexadecyl-trimethylammonium hydroxide hydrate as leveling agent in my acetate RFB.

Hexadecyltrimethylammonium hydroxide hydrate successfully impedes the growth rate of lead dendrite on the negative electrode. Such leveling agent will increase the potential on the negative electrode surface and make the dendrite accumulation proportion to current density. On the contrary, growth rate of dendrite will increase rapidly without leveling agent.

3.5 Interaction between lead and acetic acid

Lead oxide compounds such as litharge can be found on the lead surface. Under the condition with water and acetic acid, lead oxide would interact with acetate ions and form lead acetate oxide hydrate³. The insoluble form of lead acetate oxide hydrate would interact with carbonates to form plumbonacrite and release acetate ions back to continue corrosion process. The reaction mechanism⁶ is shown by Taylor and Lopata as follow:



4. Experimental

In order to maintain pH in electrolyte, we add acetic acid and sodium acetate as buffer solution in Lead(II) acetate trihydrate solution. We expect the pH change slightly in the electrolyte. All the experiments are designed to research and to optimize the system by different way such as additives.

4.1 Experiment process

4.1.1 Electrolyte

a. RFB basic system

Lead(II) acetate trihydrate: 0.2M

Sodium acetate: 1M

Acetic acid titrate solution to pH4.5

b. Additives

1. Hexadecyltrimethylammonium hydroxide hydrate 0.5mM

2. Phenol, ethyl alcohol, gelatine

4.1.2 Electrode

Positive electrode (Solvent casted carbon electrode)

| Material | Description |
|-------------------------|----------------------------|
| Carbon | Diameter: 10 μ m |
| Polyvinylidene fluoride | PVDF, Supply by Alfa Aesar |
| N-Methyl-2-pyrrolidone | NMP, Supply by ECHO |

Material ratio is PVDF : C : NMP = 1:14:12

Step1: PVDF+NMP stirred for 1hr.

Step2: Add Carbon and stirred for 30min.

Step3: Pour the liquid in model on the surface of stainless steel.

Step4: Put the electrode in oven under 45 °C for 15hr.

Negative electrode

| Material | Description |
|----------|---------------|
| Nickle | Purity: 99.7% |

4.1.3 Installing

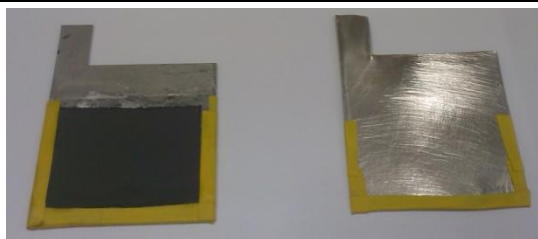


Fig. 4 Positive/Negative electrode

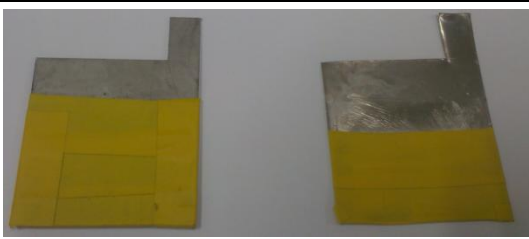


Fig. 5 Reverse side of electrode



Fig. 6 Device overview

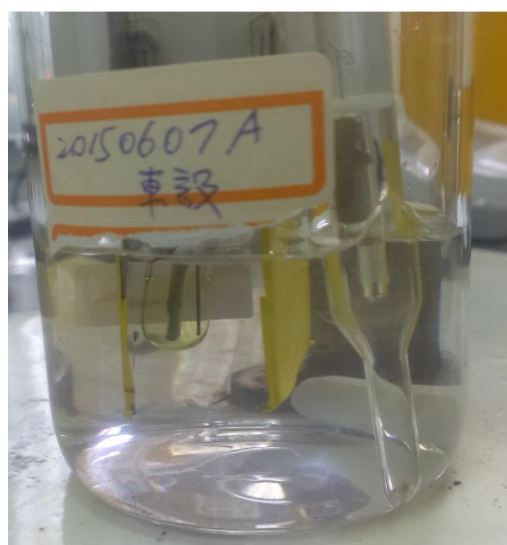


Fig. 7 pH meter 、Reference electrode

Fig. 4 The left is solvent casted carbon electrode and the right is nickel plate. The brink is covered by yellow insulating tape

Fig. 5 The yellow insulating tape is applied to cover the back side of stainless steel to prevent steel reacting with electrolyte.

Fig. 6 Both electrodes are placed as picture show. The beaker is filled with electrolyte.

Fig. 7 The pH meter is placed near positive electrode.

4.2 Control group

Lead(II) acetate trihydrate: 0.2M

Sodium acetate: 1M

Nitric acid titrate solution to pH4.5

Positive electrode: Solvent casted carbon electrode

Negative electrode: Nickel plate

4.3 Analysis equipment

4.3.1 AUTOLAB -PGSTAT302

Fig. 8 is the overview of AUTOLAB. We use it to conduct electrochemistry experiments. AUTOLAB's accuracy can reach 10^{-8} A. The main functions we use in the experiments are as follow:

- i. Constant ampere charging/discharging: To measure efficiency of system.
- ii. Cyclic voltammetry potentiostatic: To measure reaction redox potential of element on electrode
- iii. FRA impedance potentiostatic: To measure the resistance of system.
- iv. pH meter: To measure pH of system instantly while charging/discharging.



Fig. 8 AUTOLAB -PGSTAT302

4.3.2 Multiple Channels Battery Tester

We use the constant ampere charging/discharging function to measure the efficiency of our experiment.

4.3.3 EDS (JSM-6510LV SEM, quantitative analysis)

Energy Dispersive Spectrometer is used to analysis certain sample by emitting X-ray on it. When inner electron is stimulated by energy, it will transmit to higher energy level and generate electron holes. Electron from outer shell will then fills the holes and release energy which may stimulate electrons in other shells. Different element possess different pattern of stimulation and cause different peak distribution. Thus, we can distinguish different element in our sample.

5. Results and discussion

5.1 pH of electrolyte

The basic solution composed of Lead(II) acetate trihydrate 0.2M and Sodium acetate 1M. In order to determined which pH condition to apply on our following experiment. We titrate solution to pH5 and pH4.5 by acetic acid and do the cyclic voltammetry potentiostatic test (CV) to measure reaction redox potential of system. The CV plot is as Fig. 9 and Fig. 10. The pH5 solution's reduction potential peak is about 0.6V while the pH4 solution's reduction potential peak is about 0.7~0.8V. The reason why we choose pH4.5 is that higher reduction potential will make higher voltage efficiency. Also, the pKa of acetic acid is 4.76, which is closed to the pH we choose.

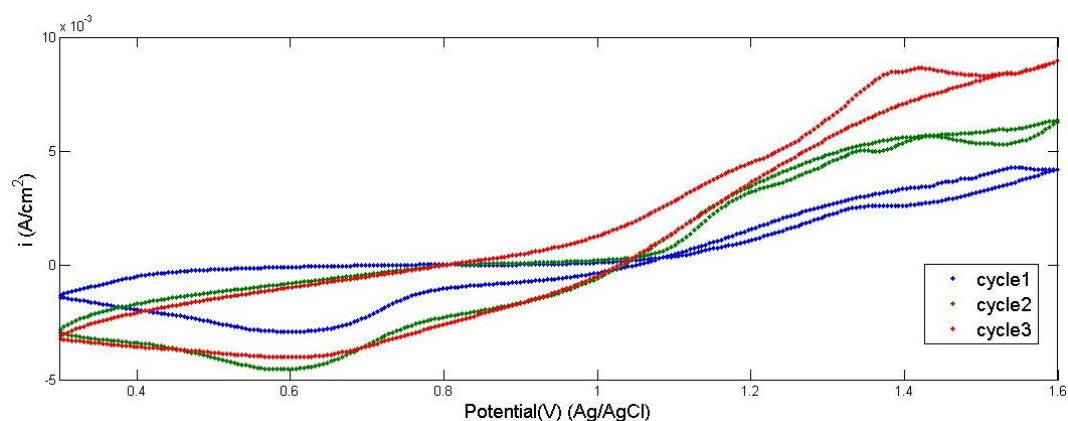


Fig. 9 CV of electrolyte under pH5

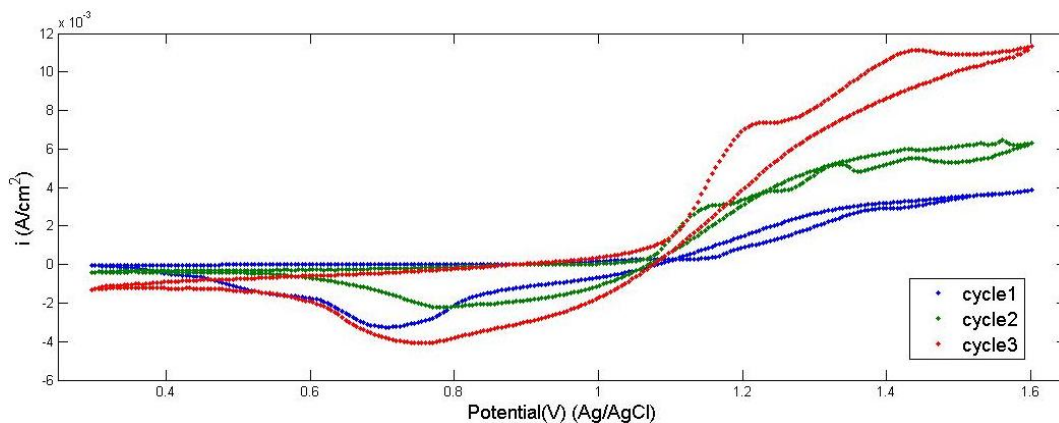


Fig. 10 CV of electrolyte under pH4.5

5.2 Negative electrode

After we fix the pH 4.5 of electrolyte, we are testing which kind of material will be the candidate of negative electrode. We use Titanium as positive electrode which is high electric conductivity and great resistance to corrosion. High-electric-conductivity carbon plate, stainless steel, nickel plates are tested as negative electrode and the CV plot is as follow separately Fig. 11, Fig. 12, Fig. 13.

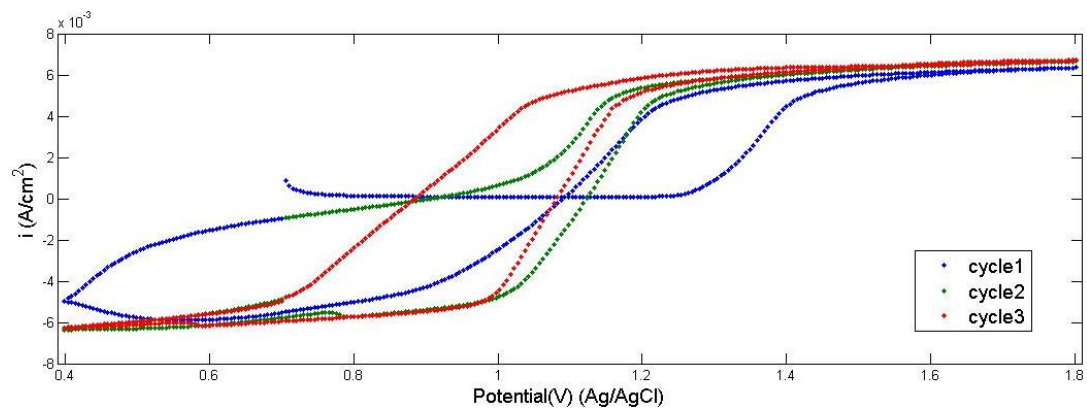


Fig. 11 CV of +Titanium, - high-electric-conductivity carbon plate

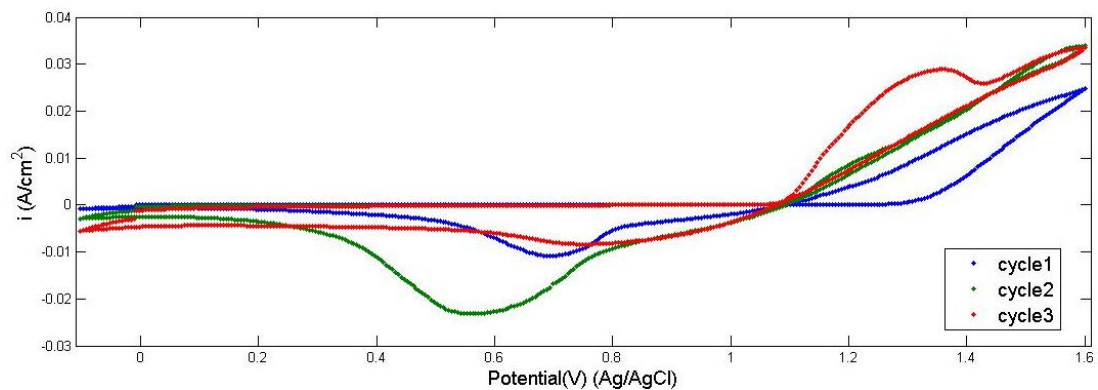


Fig. 12 CV of +Titanium, - stainless steel

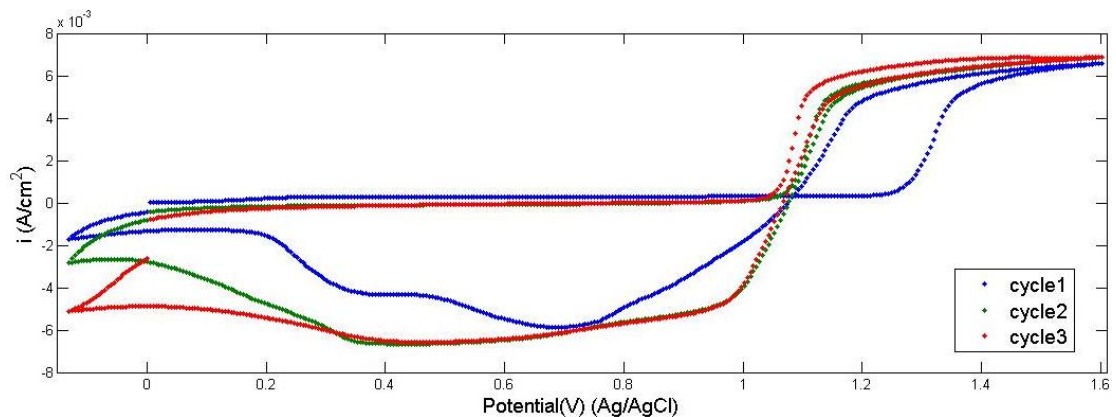


Fig. 13 CV of +Titanium, -nickel

According to Fig. 11, High-electric-conductivity carbon plate is not an ideal material, because there is no any reduction peak. It means that lead dioxide cannot reduction to lead(II) ions on positive electrode while discharging. According to Fig. 12, stainless steel seems at first glance a good negative electrode because of two cycle of CV shows obvious reduction peak, however, closed scrutiny of third cycle of CV show slight reduction peak which may indicate undesirable reaction happens after two cycle of CV process so that only a few lead dioxide transfer to lead ions during discharging and render it an unsatisfactory negative electrode. Fig. 13 manifests nickel plate a proper negative electrode. There is an obvious reduction peak on 0.8V. A plausible reason why the decrease of reduction peak of subsequent cycle of CV is because accumulating residual of lead dioxide from previous cycle and thus require higher negative potential to deplete lead dioxide on positive electrode. Nickel is an appropriate material as negative electrode compare to high-electric-conductivity carbon plate and stainless steel.

5.3 Positive electrode

After choosing certain pH condition and negative electrode, we need to find an ideal material as positive electrode. We fix nickel plate as negative electrode and test the material for positive electrode as follow: Solvent casted carbon electrode, fuel-cell electrode and titanium and CV plot according separately to Fig. 14, Fig. 15, Fig. 16 .

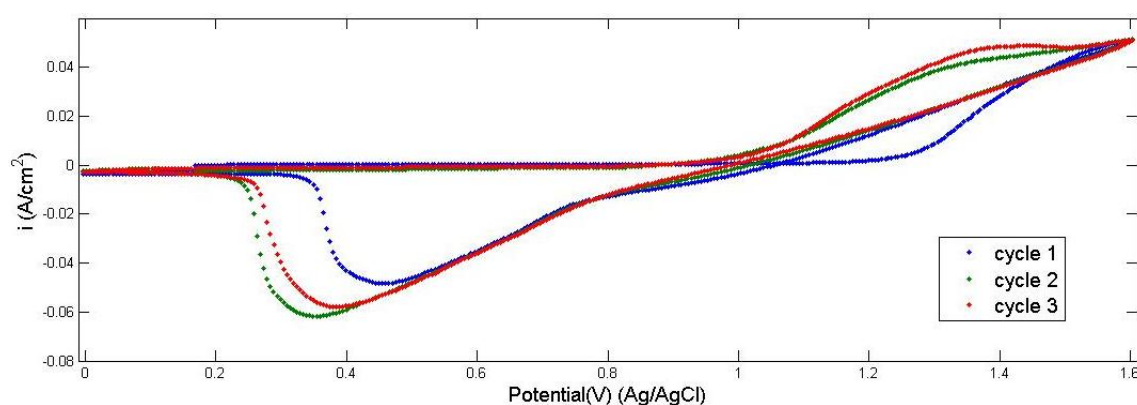


Fig. 14 CV of +Solvent casted carbonelectrod/-nickel

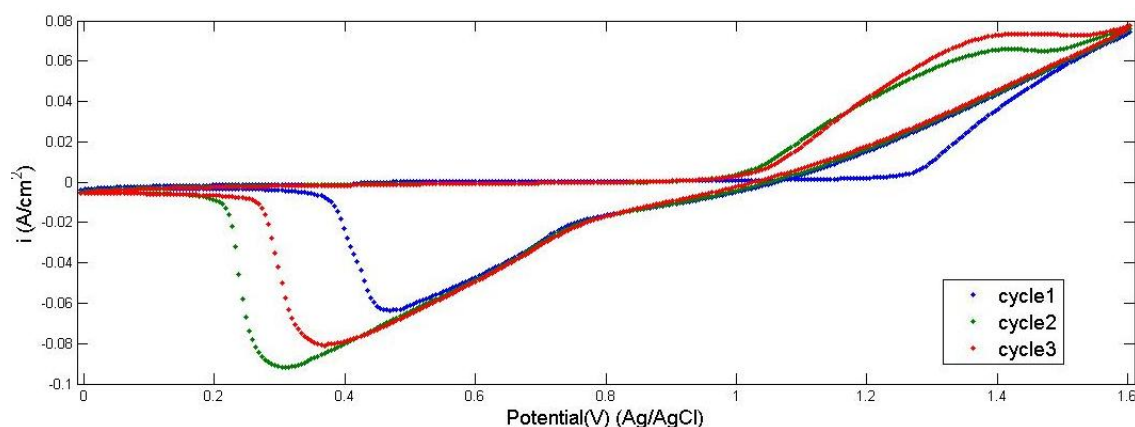


Fig. 15 CV of + fuel-cell electrode/-nickel

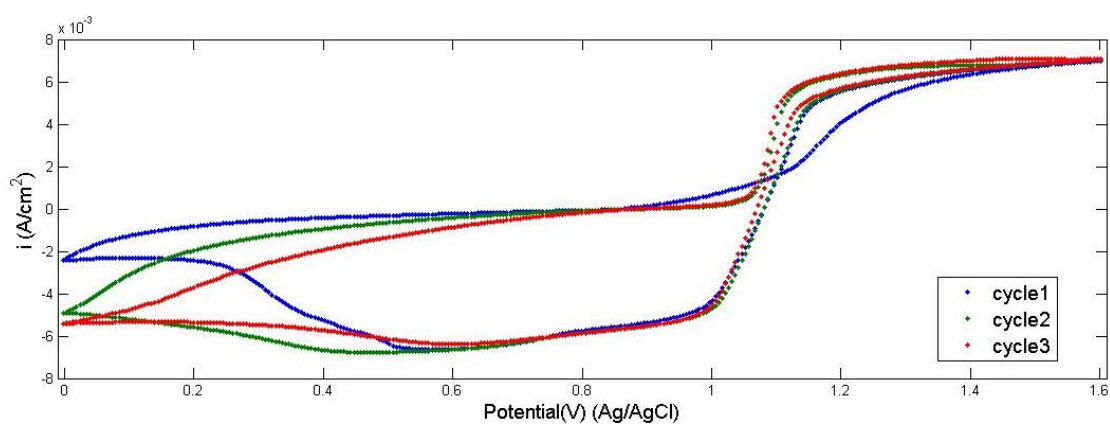


Fig. 16 CV of + Titanium/-nickel

Both solvent casted carbon electrode and fuel-cell electrode show clear reduction peak which indicate that lead dioxide transfer to lead ions efficiently as Fig. 14 and Fig. 15. Furthermore, relatively narrow range of reduction peak manifest solvent casted carbon electrode a stable power supply electrode. For titanium like Fig. 16, the first cycle of CV appear an obvious reduction peak while ensuing cycle don't. A reasonable explanation is that less adherent site for lead dioxide on the surface of titanium, so that a modicum lead dioxide can transfer to lead ions while discharging.

5.4 Long period charging/discharging of RFB

The experiment is conducted several times under nickel plate, solvent casted carbon electrode and electrolyte with pH4.5 condition. The charging potential is about 1.6V and discharging is about 1V. Fig. 17 is the V-t plot for long period charging/discharging (current density 5 mA/cm², charging 30 minute, cut off current while discharging potential under 0.1V, no rest between cycle.)

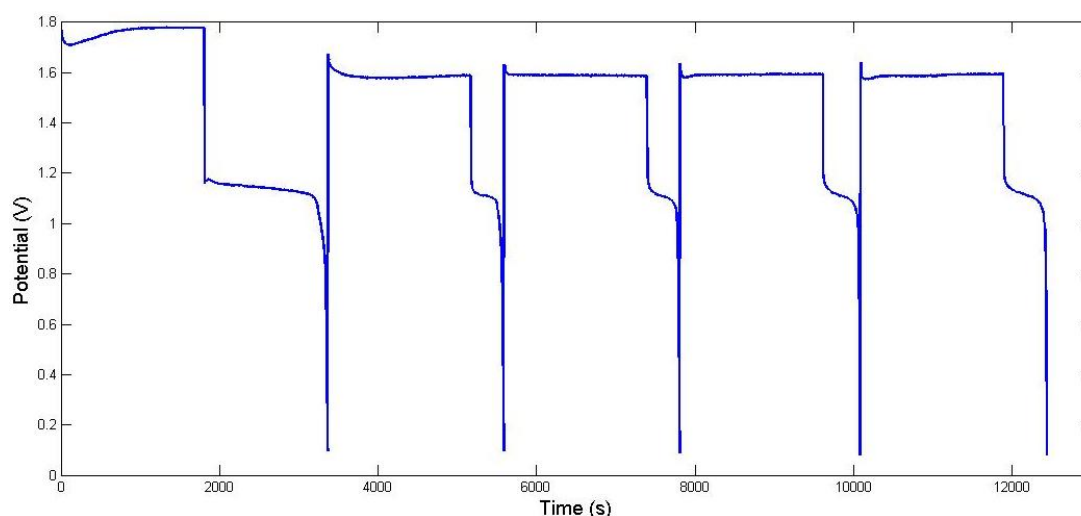


Fig. 17 Constant current (5 mA/cm²) Charging/Discharging, +Solvent casted carbon/-nickel

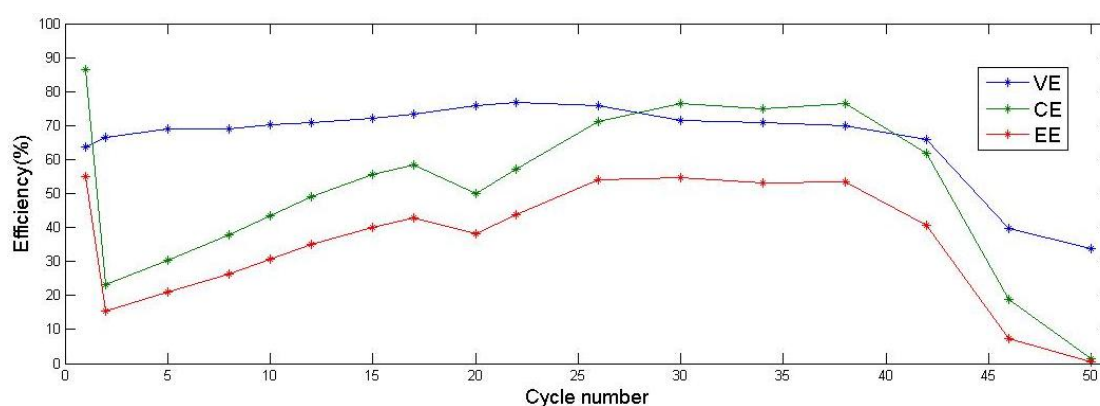


Fig. 18 Efficiency of system, +Solvent casted carbon/-nickel

Several similar experiments show that the system lifetime is about 43 cycles (Coulomb efficiency higher than 50%) as Fig. 18. The system would break down in 3 cycles and no longer charging and discharging. There is a peculiar phenomenon that while second cycle of charging/discharging, a strike decrease of efficiency to about

25% appear in every similar experiment. The efficiency increases gradually in the subsequent cycle but no more than the first high efficient cycle.

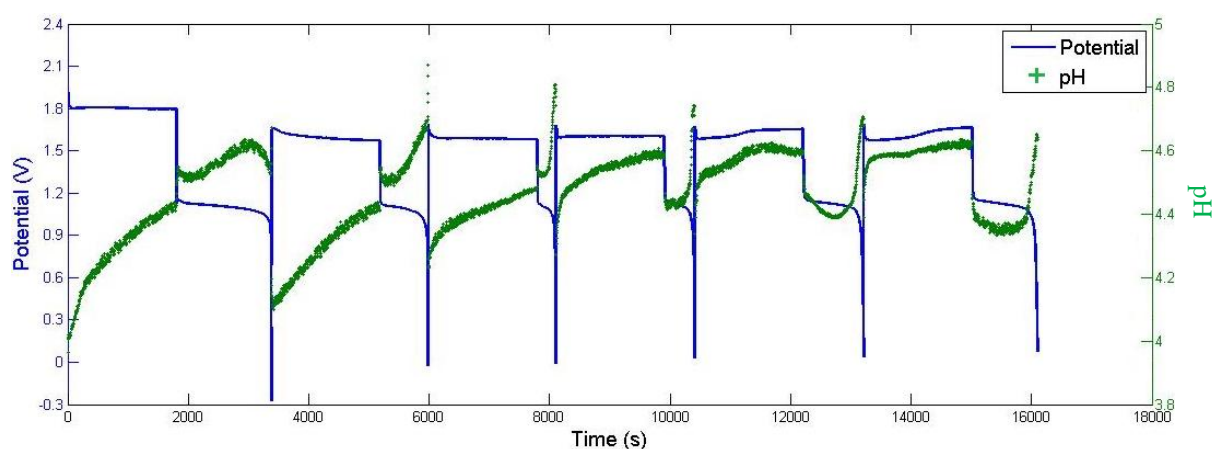


Fig. 19 pH variance of the system, +Solvent casted carbon/-nickel

We do monitoring pH while charging/discharging as Fig. 19. The pH values of charging in first three cycles are more acid while discharging are more acid in the following cycles. The pH of charging is less than 4.5 and pH of discharging is more than 4.5 in first three cycles. The buffer solution does work because the pH ranges from 4.0 to 4.8.

The overall view of the experiment is as Fig. 20 and Fig. 21. We can see serious growth of lead dendrite on the negative electrode as Fig. 20. Lead dioxide cannot attach tightly on the surface of solvent casted carbon electrode and cause the electrolyte dirty as Fig. 21, so the system can only work under unstirred condition which maybe lead to nonuniform proton and lead ions distribution.

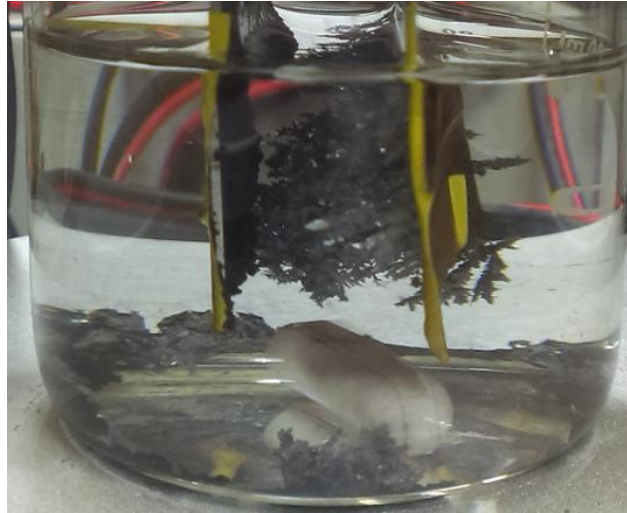


Fig. 20 Operation of system, +Solvent casted carbon/-nickel

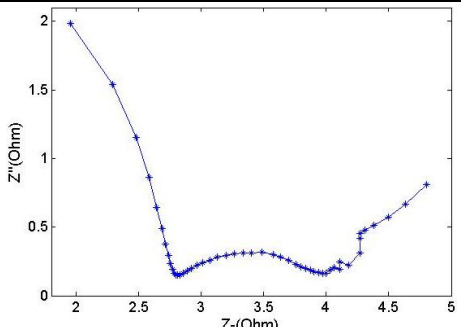
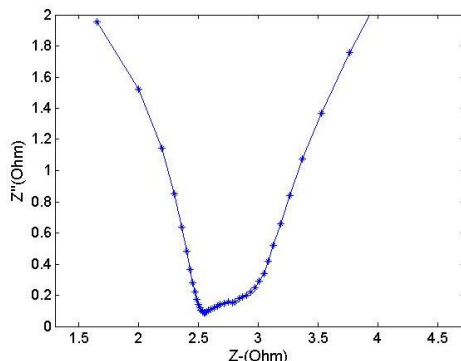
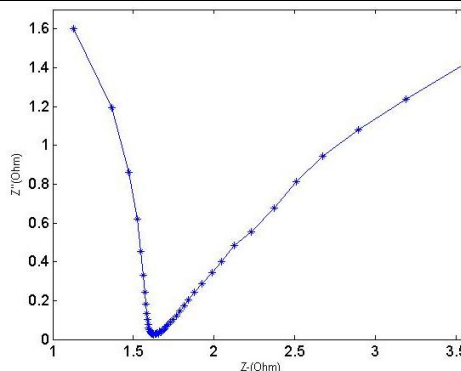
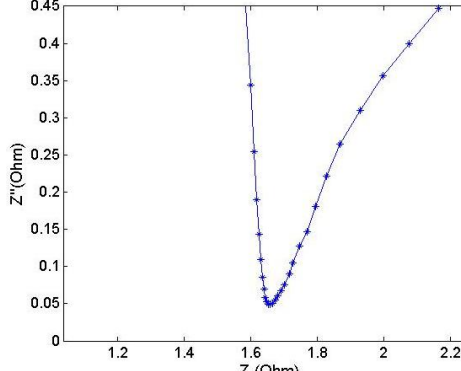


Fig. 21 Electrolyte full of Lead dendrite and lead dioxide

5.5 Impedance

In order to clarify what is happen in 2nd cycle which is extremely low efficiency during long period charging/discharging (current density 5 mA/cm², charging 30 minute, cut off current while discharging potential under 0.1V), we measure the impedance of the battery in each step of charging/discharging as Table 1.

Table 1 Impedance of each step of charging/discharging process

| Step | Impedance | description |
|---------------------------|---|--------------------------|
| 1 st Charge |  <p>Fig. 22 Impedance of system, 1st charging, +Solvent casted carbon/-nickel</p> | |
| 1 st Discharge |  <p>Fig. 23 Impedance of system, 1st discharging, +Solvent casted carbon/-nickel</p> | Zoom in plot CE83.3% |
| 2 nd Charge |  <p>Fig. 24 Impedance of system, 2nd charging, +Solvent casted carbon/-nickel</p> | Zoom in plot |
| 2 nd Discharge |  <p>Fig. 25 Impedance of system, 2nd discharging, +Solvent casted carbon/-nickel</p> | Zoom in plot CE 32.8% |

First charging system impedance is as Fig. 22. It shows apparent reaction resistance and mass transfer resistance. First discharging system impedance is as Fig. 23. It shows only mass transfer resistance because the first cycle has relatively high coulomb efficiency up to 80% which indicate that most of deposit is consumed. However, the second charging system impedance shows only mass transfer in Fig. 24 just like second discharging system impedance as Fig. 25 and lead to relatively low efficiency about 30%.

High efficiency cycle all shows obvious reaction resistance after charging in the battery and mass transfer resistance after discharging. A reasonable explanation for low efficiency in 2nd cycle is the insoluble and high resistance of lead oxide film (PbO_x) deposited on negative electrode while the charging/discharging process.

5.6 Optimize lead deposit on negative electrode

5.6.1 Leveling agent: Hexadecyltrimethylammonium hydroxide hydrate

In order to impede the serious growth of lead dendrite on the negative electrode which leads to low efficiency and short circuit, we add leveling agent Hexadecyltrimethylammonium hydroxide hydrate 0.5mM in electrolyte. The CV measurement is as Fig. 26. There is an obvious reduction peak on 0.5V during 3rd cycle of CV. The leveling agent would impede the deposit rate of lead on the negative electrode, so a few lead was deposited during previous two cycles. Compare CV to system without leveling agent as Fig. 14, the reduction peak is closed to system with leveling agent and lead to a little different voltage efficiency. The lifetime of the system is about 57 cycles (Coulomb efficiency higher than 50%) as Fig. 27 which is fourteen times more than system without leveling agent as Fig. 18.

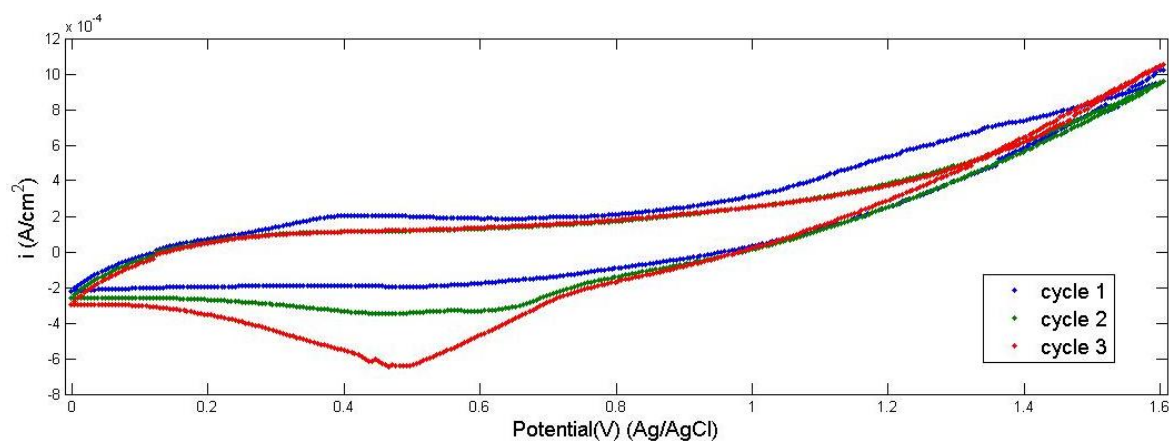


Fig. 26 CV of electrolyte with Hexadecyltrimethylammonium hydroxide hydrate

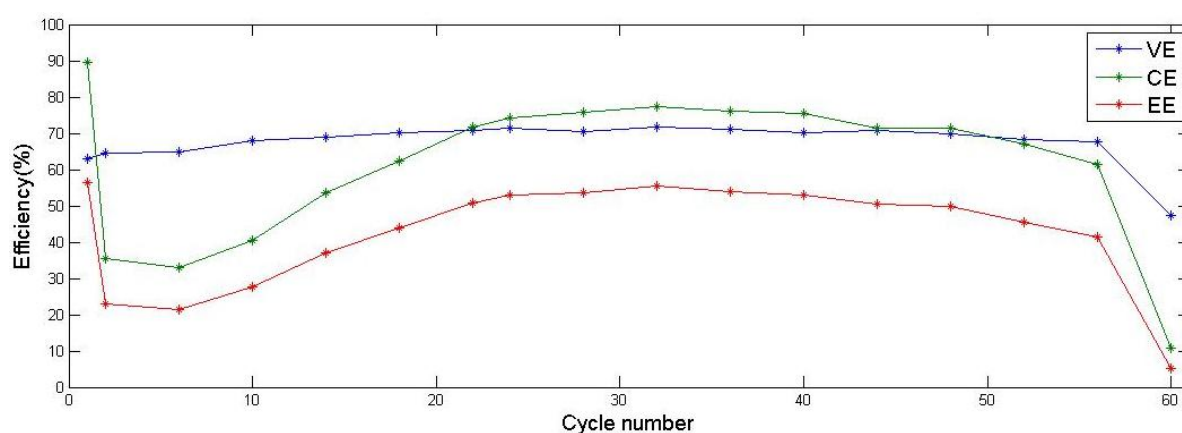


Fig. 27 Efficiency of system with leveling agent

Finish of the system is as Fig. 28 and Fig. 29. The leveling agent does improve the lead dendrite on the negative electrode. The dendrite is smoothly grows and lead to different morphology from dendrite without leveling agent. There is no particular difference of lead dioxide on positive electrode by naked eye. However, lead dioxide would drop off the electrode seriously as well as system without leveling agent.

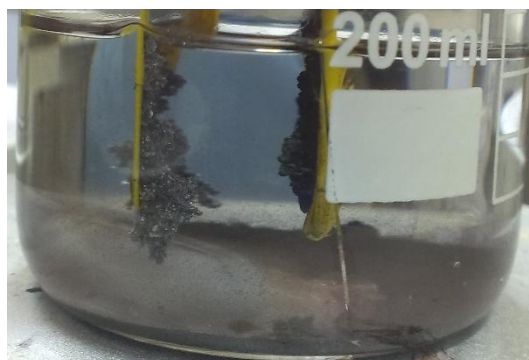


Fig. 28 Operation of system with leveling agent



Fig. 29 Operation of electrolyte full of lead dendrite and lead dioxide

5.6.2 Additives: Phenol, Ethyl alcohol, Gelatine

According to professor, Edward Ghali, he successfully deposited lead smoothly on copper negative electrode under high current density up to $25\text{mA}/\text{cm}^2$. I use copper as negative electrode and solvent casted carbon as positive electrode. Additives phenol $2.5\text{mL}/\text{L}$, ethyl alcohol $5\text{mL}/\text{L}$ and gelatin $0.05\text{g}/\text{L}$ was applied in the electrolyte. The CV measurement is as Fig. 30 and OCP value is 0.19V . There are two slight oxidation peak and one obvious oxidation peak on 0.8V which belongs to three additives.

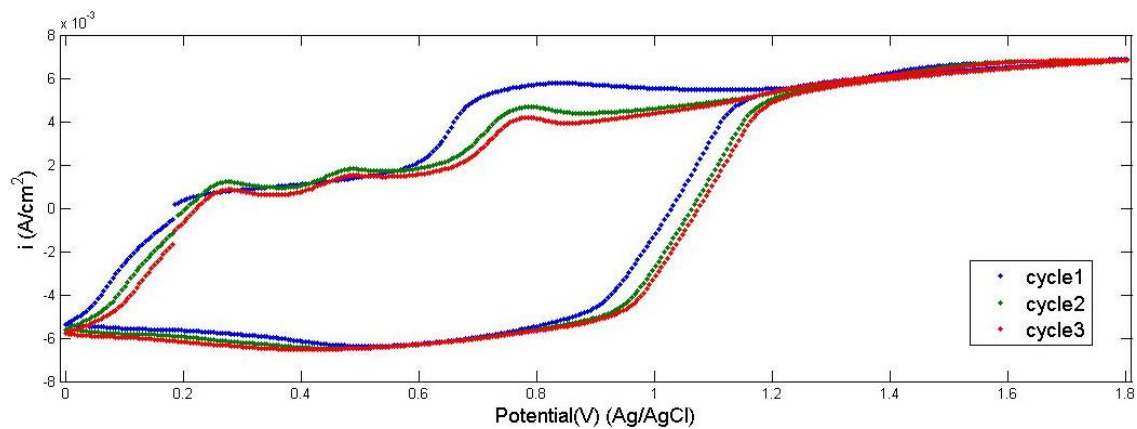


Fig. 30 CV of electrolyte with phenol, ethyl alcohol, gelatine

However, there is no apparent reduction peak. A plausible explanation is that additives is still generating passive layer on negative electrode which is irreversible during three CV cycles and impede lead and lead dioxide attach to electrode surface which lead to coulomb efficiency no more than 50%. The system operating picture is as Fig. 31. There is clear lead dendrite which morphology is disparate to dendrite form in electrolyte with leveling agent or in electrolyte without leveling agent. When we remove dendrite from the negative electrode, we find an extremely smooth and compact lead on electrode. There is some lead dendrite shed off the electrode while no any lead dioxide shed off the electrode in electrolyte which is different from Fig. 21 and Fig. 29. The additives concentration need further research to solve the problem of lead dioxide shedding off electrode.

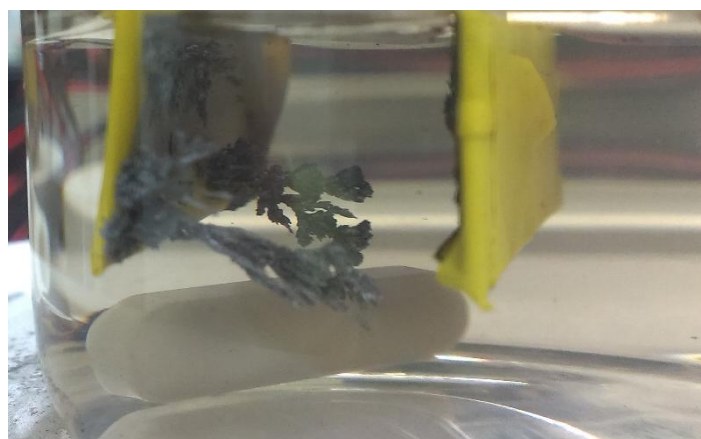


Fig. 31 Lead dendrite grow on negative electrode

5.6.3 Phenol, ethyl alcohol and gelatin with leveling agent

Under the idea of applying leveling agent, phenol, ethyl alcohol and gelatin together in the electrolyte, using both advantages with little coulomb efficiency decrease as compensate. Under the condition of copper as negative electrode and solvent casted carbon as positive electrode, CV measurement is as Fig. 32.

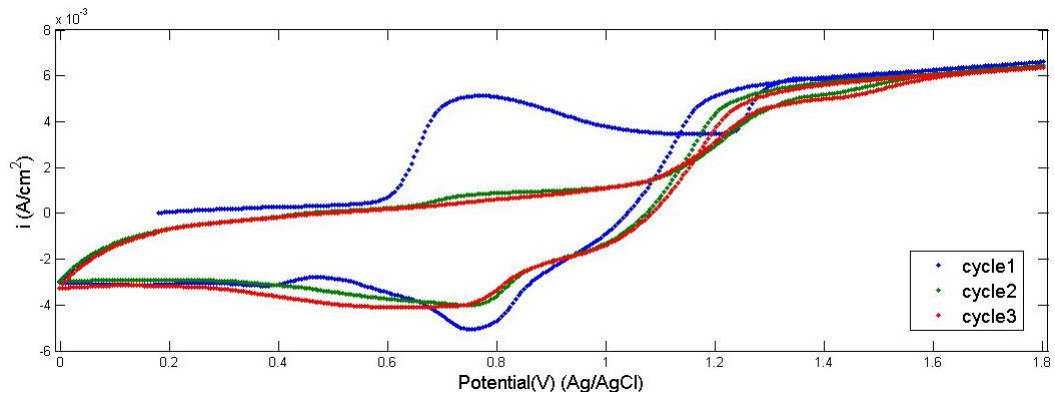


Fig. 32 CV of electrolyte with additives and leveling agent

The obvious oxidation peak on first CV cycle is refer to phenol, ethyl alcohol and gelatin, however, the reduction peak on 0.75V is quite strange because barely leveling agent in electrolyte with reduction beak is 0.5V while additives in electrolyte without reduction beak. The system operating picture is as Fig. 33, Fig. 34 and Fig. 35.

The dendrite grew on electrode is smooth, soft and compact as Fig. 33. The lead dioxide formed in grain style as Fig. 34 which is strikingly different from system without any additives and leveling agent. Only lead dendrite shed off electrode in electrolyte without any lead dioxide, and coulomb efficiency can reach 70% as Fig. 36.

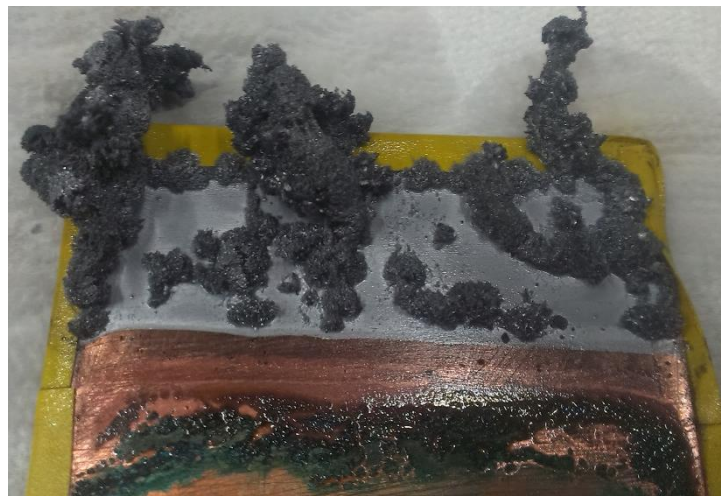


Fig. 33 Lead dendrite grow on negative electrode under electrolyte with additives and leveling agent

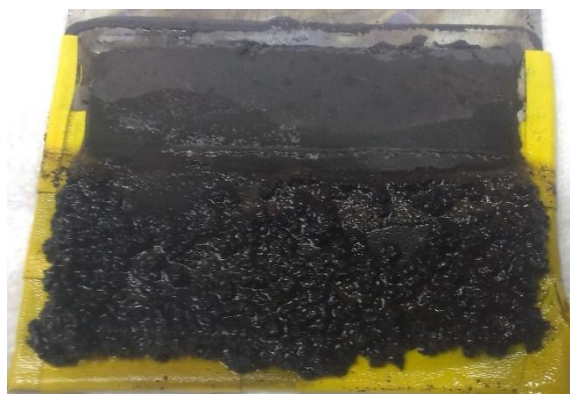


Fig. 34 Lead dioxide deposit on positive electrode under electrolyte with additives and leveling agent

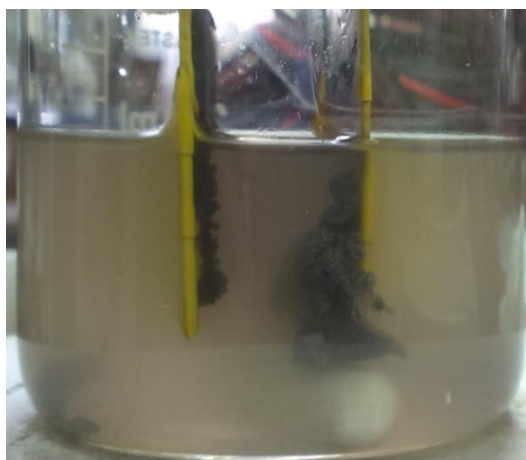


Fig. 35 Operation of system under electrolyte with additives and leveling agent

The efficiency of system is as Fig. 36. The coulomb efficiency increases gradually to 74% in the 49th cycle. A reasonable explanation is that it takes few cycles to consume phenol, ethyl alcohol and gelatin. The lifetime of system is 49 cycles (Coulomb efficiency higher than 50%) and breaking down immediately in the ensuing cycle.

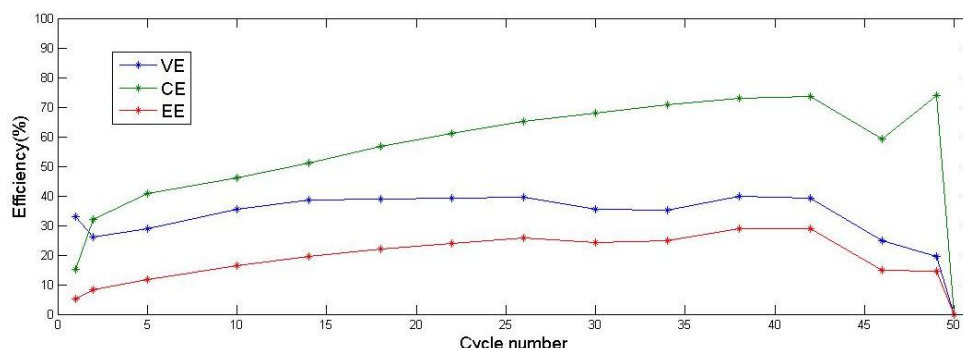
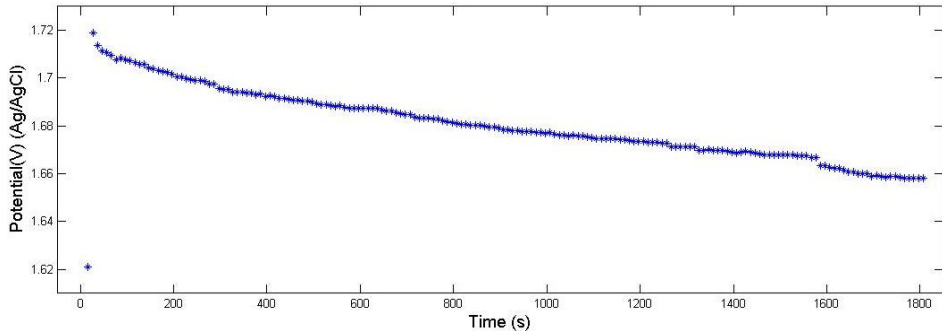
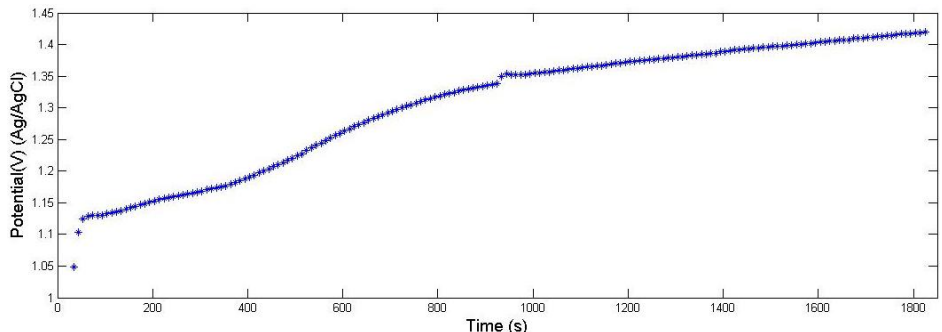
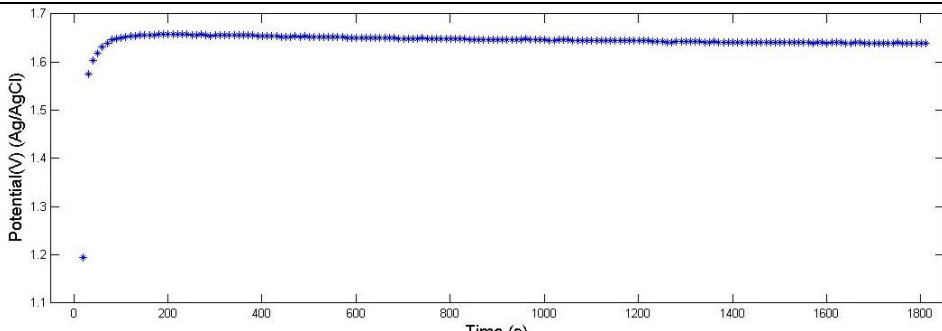


Fig. 36 Efficiency of the system under electrolyte with additives and leveling agent

5.7 Influence of electrode during charging/discharging

To understand which factor causes the decreasing efficiency of the system, we measure charging potential as Table 2 after replacing positive or negative electrode.

Table 2 Charging potential after changing electrode

| Replace electrode | Charging potential |
|-------------------|---|
| Replace positive |  <p>Fig. 37 Charging potential after replacing positive electrode</p> |
| Replace negative |  <p>Fig. 38 Charging potential after replacing negative electrode</p> |
| Replace both |  <p>Fig. 39 Charging potential after replacing both negative/positive electrode</p> |

We find that positive electrode is the critical factor of over potential during charging process. However, the efficiency isn't improved after replacing positive electrode. Thus, the degradation of electrolyte is the key factor of breaking down.

5.8 Rests between charging/discharging

During the time of measurement of impedance will lead to difference result of the system. According to Fig. 40, five cycle charging/discharging with rest time 15 minute while measuring impedance of system, there is no dramatically drop of coulomb efficiency in the 2nd cycle. According to Fig. 41, we find that the average pH of charging is lower than the average pH of discharging, which means more acid while charging.

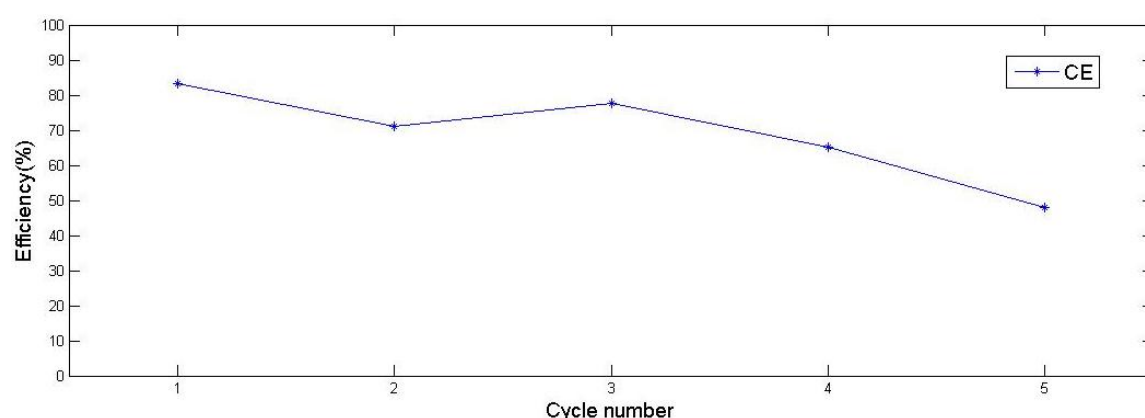


Fig. 40 Efficiency of system which rest 15 min during charging/discharging

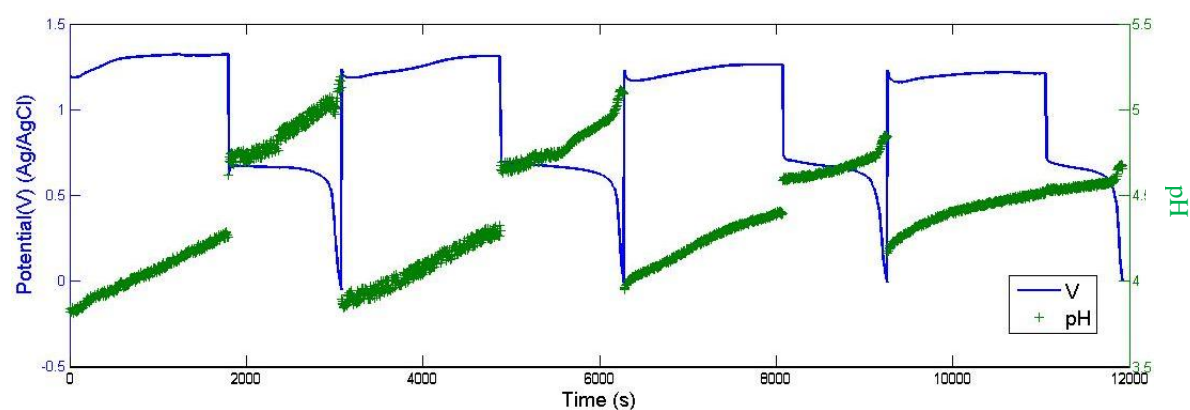


Fig. 41 pH and constant current charging/discharging with 15 min rest of system

However, 15 minutes rest time without impedance measurement will cause different results. The pH value and efficiency is as Fig.42 and Fig.43.

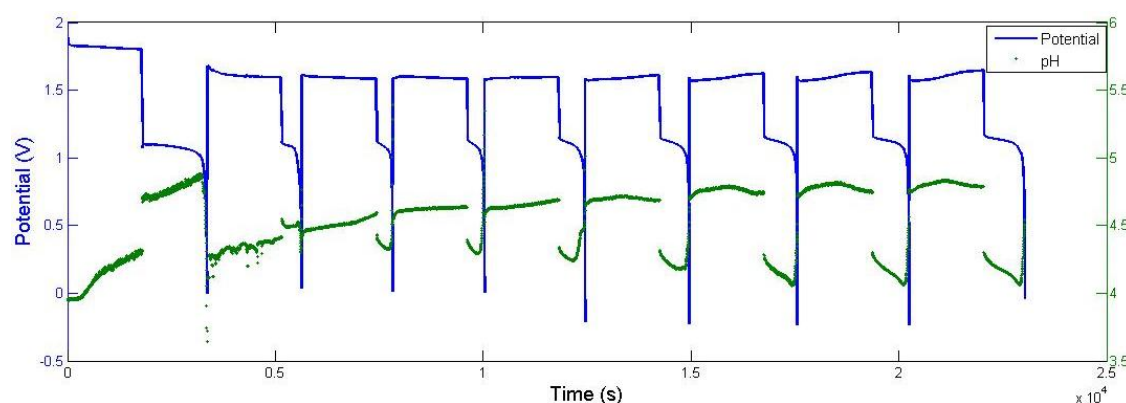


Fig. 42 pH variance of the system resting 15min, +Solvent casted carbon/-nickel

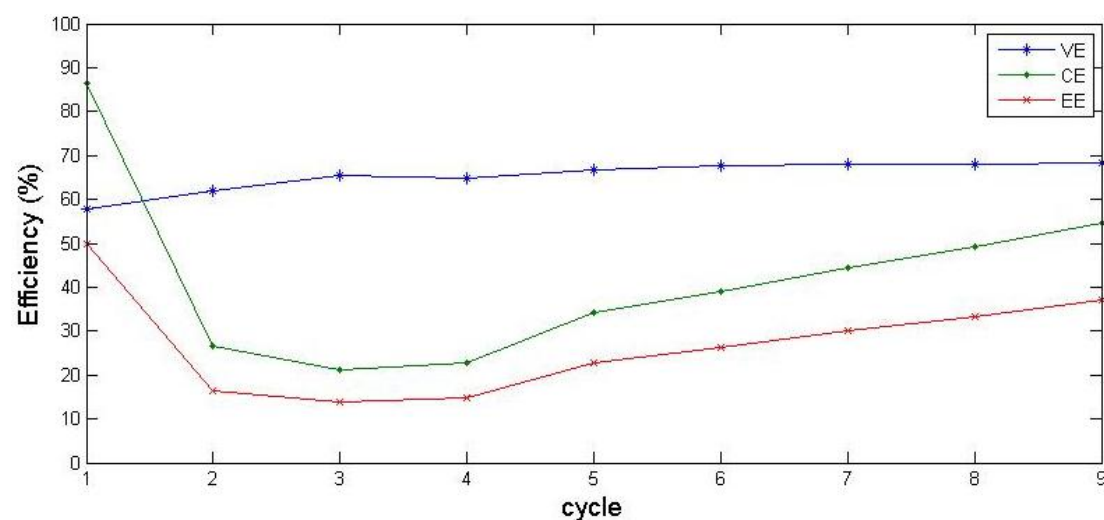


Fig. 43 Efficiency of system with 15min rest

The tendency of pH value and efficiency likes Fig. 19 and Fig. 18 respectively. The result indicates that impedance measurement does infect the system.

5.9 Titanium as positive electrode

In order to eliminate the factor of reaction between solvent casted carbon electrode which may cause pH difference and dramatically drop of efficiency, so we test Titanium electrode which is high electric conductivity and great resistance to corrosion as positive and nickel plate as negative electrode. The efficiency of long period charging/discharging process is as Fig. 44. Coulomb efficiency in the 1st cycle is

75% which is lower than solvent casted carbon electrode's 85%. The life time of this system is 23 cycles (Coulomb efficiency higher than 50%) which is less than solvent casted carbon electrode's 43 cycles. System with titanium meets the very same problem as system of solvent casted carbon electrode such as dramatically efficiency drop in the 2nd cycle and system break out rapidly. The variation of pH during charging/discharging is as Fig. 45, which indicates that the average pH of charging is higher than the average pH of discharging, which means more acid while discharging.

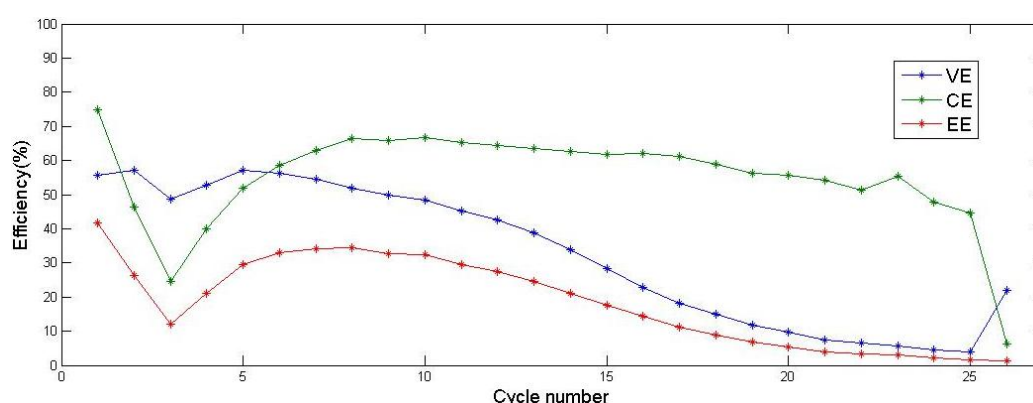


Fig. 44 Efficiency of system, +Titanium/-nickel

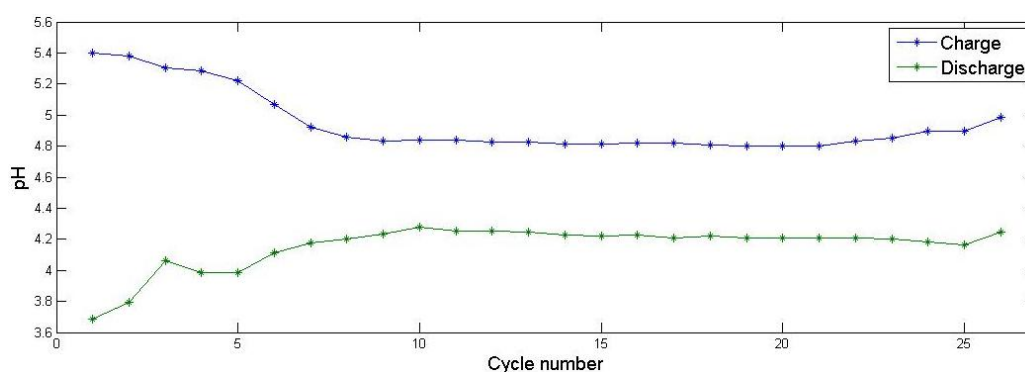


Fig. 45 Average pH during constant charging/discharging, +Titanium/-nickel

Thus, titanium is not an idea positive electrode regardless its high electric conductivity and great resistance to corrosion. A reasonable explanation is that less adherent site for lead dioxide on the surface of titanium, so that numerous lead dioxide precipitate in the electrolyte and an unknown film float on electrolyte as Fig. 46.



Fig. 46 Operation of electrolyte, +Titanium/-nickel

5.10 Control group – System titrate by nitric acid

In order to validate that every step conducting in acetic acid system is correct, I conduct an experiment which every step is the same as acetic acid system but only replace acetic acid as nitric acid. The measurement of CV is as Fig. 47. There is an obvious reduction peak at 0.39V in 1st cycle of CV which is closed to acetic acid system as Fig. 14, while no peak in subsequent cycles. The efficiency of long period charging/discharging process is as Fig. 48. The life time of this system is more than 90 cycles (Coulomb efficiency higher than 50%). There is no dramatically drop of efficiency in the 2nd cycle. The efficiency start to decrease at 9th cycle which may indicate that nitric acid can delay some undesirable reaction happens. The variation of pH during charging/discharging is as Fig.49 which the trend is same as acetic acid system as Fig. 19. The average pH of charging is higher than the average pH of discharging, which means more acid while discharging. The operation of system is as Fig. 50. There is only a few lead dendrite grows on the negative electrode without any lead dioxide drop off the positive electrode.

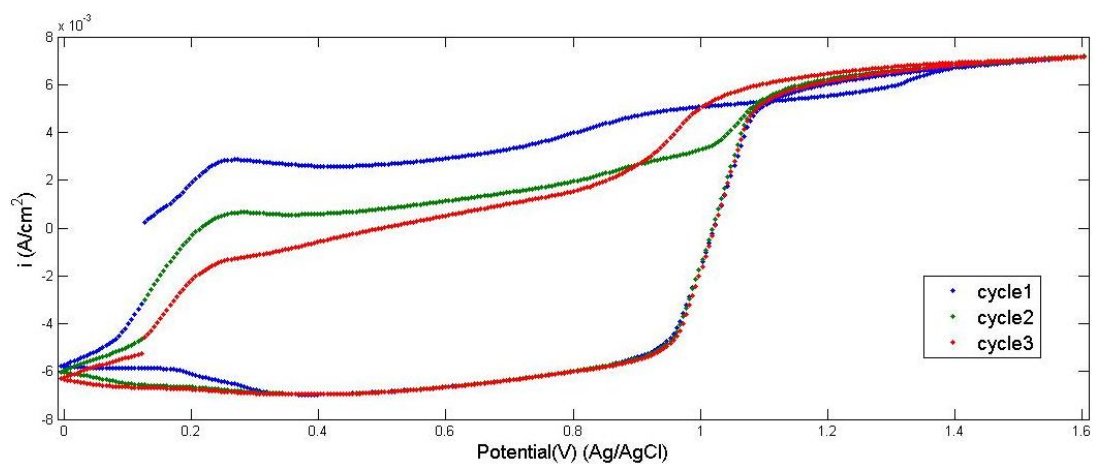


Fig. 47 CV of electrolyte with nitric acid

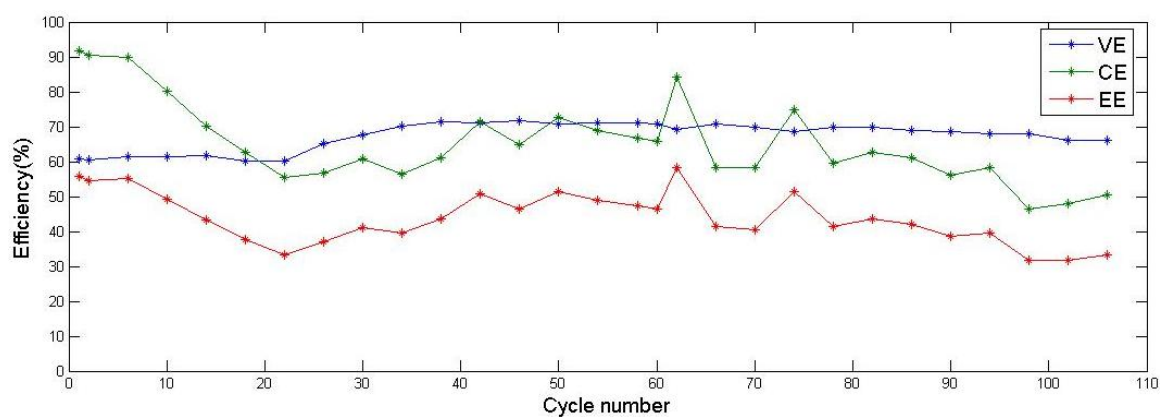


Fig. 48 Efficiency of system with nitric acid

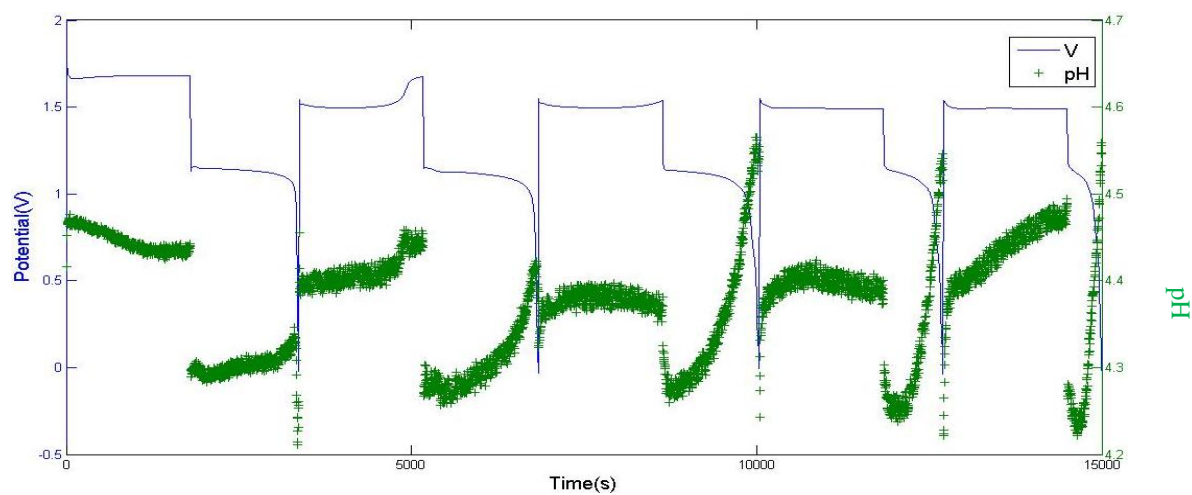


Fig.49 Variation of pH and constant charging/discharging potential of system

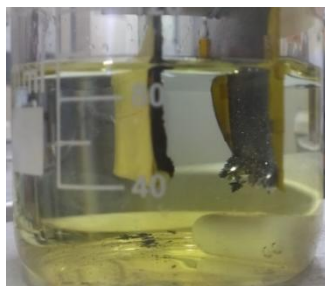


Fig. 50 Operation of system with nitric acid

The coulomb efficiency of different acidity of electrolyte with nitric acid under pH4.2 and pH4.5 is as Fig. 51. The result may indicate that electrolyte with more nitric acid will defer the decreasing of coulomb efficiency. In other word, electrolyte with more acetic acid would accelerate the corrosion of lead which may be the reason that caused the coulomb efficiency low.

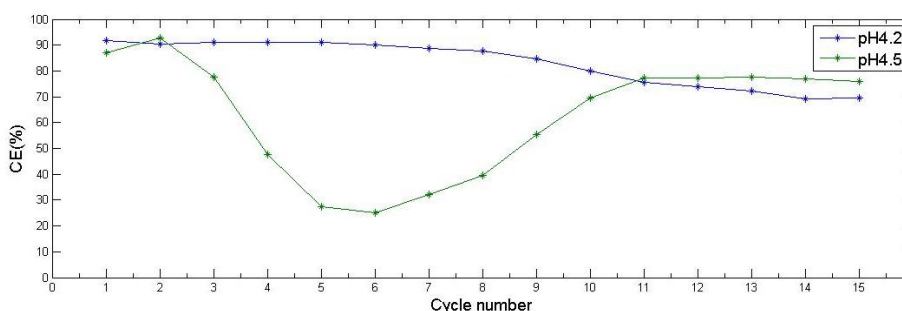


Fig. 51 Coulomb efficiency of electrolyte with nitric acid under pH4.2 and pH4.5

5.11 Effectiveness of buffer solution

In order to solve the problem of low efficiency due to high concentration of proton at the end of cycle in the system of methanesulfonic acid, we applied buffer solution in the electrolyte. Electrolyte of lead methanesulfonate is an irreversible reaction during charging/ discharging process and lead to accumulating of proton which render the efficiency drop gradually. The variation of pH during charging/discharging is as Fig. 52. The range of pH while charging and discharging is 0.15. The average pH of charging is lower than the average pH of discharging, which means that more acid while charging.

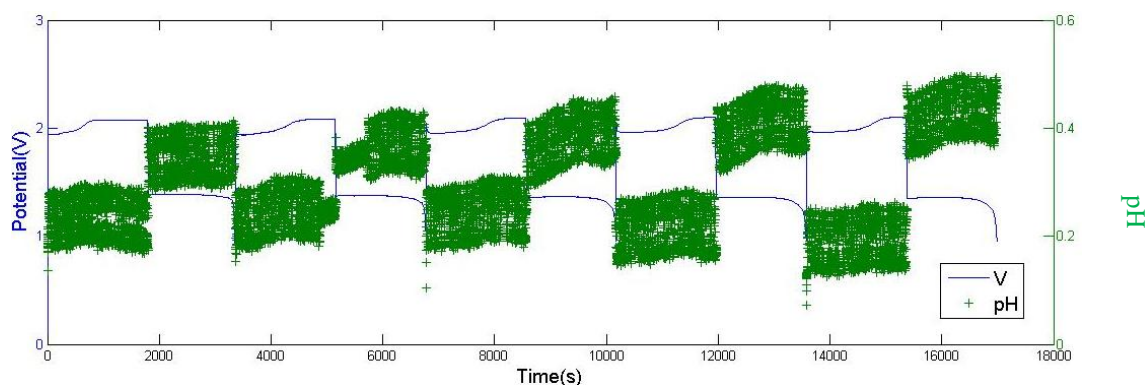


Fig. 52 Variation of pH and constant charging/discharging potential of system in methanesulfonic acid

The range of pH during charging is 0.05 while discharging is 0.1 in acetic acid RFB.

The range of pH during charging is 0.05 to 0.1 while discharging is 0.06 to 0.3 in nitric acid RFB. It is clear that acetic acid RFB work well as buffer solution which shows minimum pH range in the charging/discharging process.

5.12 Lead corrosion

In order to find out what certain molecule is generated during the second cycle while charging/discharging process which the coulomb efficiency was extremely low, we analyze the deposition of lead through EDS (JSM-6510LV SEM, quantitative analysis) after 2nd charging step and wash it by deionized water to remove the electrolyte. The area being analyzing of lead deposition is as Fig. 53. The quantitative analysis is as Table 3. Oxygen, carbon and lead are detected which may refer to undesirable corrosion of lead and generate lead acetate oxide hydrate $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot \text{PbO} \cdot \text{H}_2\text{O}$ or plumbonacrite $\text{Pb}_{10}\text{O}(\text{OH})_6(\text{CO}_3)_6$. This undesirable corrosion may lead to serious problem of dendrite and also dramatic decreasing of coulomb efficiency in 2nd cycle of charging/discharging process.

Relatively high coulomb efficiency in 1st cycle may be explain by fresh lead not yet been corrosion to lead oxide and able to be oxidize to lead ions effectively. Residual lead would oxidize to lead oxide and form a passive layer on the negative electrode which might prevent lead from attaching to electrode during charging in 2nd cycle, that was inferring by impedance measurement while no reaction resistance after charging in 2nd cycle and lead to extremely low efficiency. The passive layer would dissolve partly in acetic acid and few lead dendrites could grow on the electrode where passive layer has been dissolved. As cycle number increasing, more and more passive material on electrode surface has been dissolved and lead to increasing dendrite growth on electrode rather than on passive layer. The passive layer on dendrite provide a good structure for dendrite to grow firmly which maybe the reason why the dendrite grow seriously in acetic acid RFB. The passive layer wrap on dendrite surface would protect lead from further corrosion, also the passive layer would dissolve partly and pure lead would fill the sight immediately while charging. Pure lead on dendrite would transfer electron through lead dendrite which is high electricity conductivity to electrode and lead to increasing efficiency. There are many invisible dendrite reach positive electrode and cause self-redox reaction which lead to the end of system.

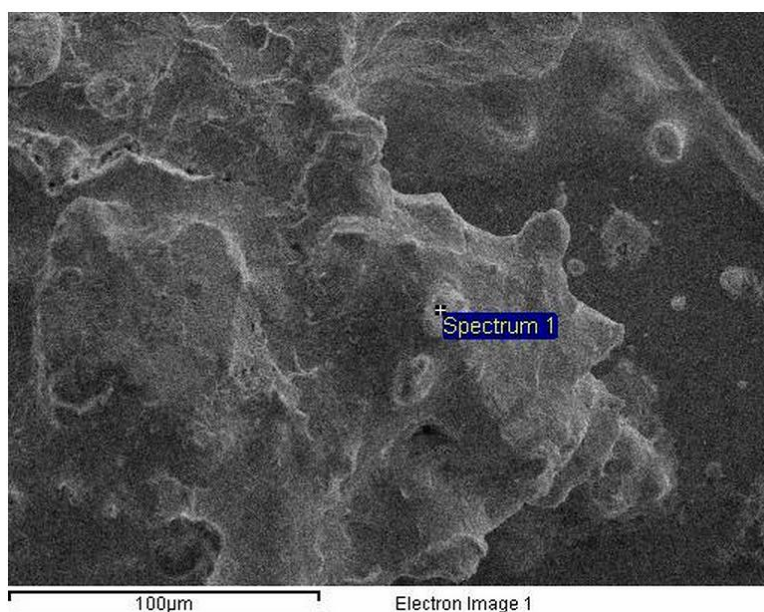


Fig. 53 The area being analysis of lead deposition by SEM

Table 3. Quantitative analysis of lead deposit on negative electrode by EDS

| Element | Weight% | Atomic% |
|---------|---------|---------|
| C | 14.19 | 53.68 |
| O | 10.50 | 29.81 |
| Pb | 75.32 | 16.52 |
| Total | 100.00 | |

6. Conclusion

Acetate based lead acid RFBs do show smaller pH fluctuation during cycling in comparison to methanesulfonic based system. However, the acetate based battery cannot operate under current densities higher than $5\text{mA}/\text{cm}^2$, because when it does serious lead dendrite will appear and numerous lead dioxide may shed off the positive electrode.

After testing various materials comprising the positive and the negative electrode, we find that with the experimental design of solvent casted carbon as the positive electrode and nickel plate as the negative will lead to relatively longer cycle life of up to 43 cycles. The CV tests show that electrolytes titrated by acetate acid to pH4.5 performs better the one titrated to pH 5.

Despite tens of cycles can be achieved, a sudden coulomb efficiency decrease in the 2nd charging/discharging cycle of our long term operation experiments, which may indicate undesired, irreversible chemical reactions of lead corrosion occur during very first cycle.

To improve the cyclability, we alleviate lead dendrite growth and improve cycle life of the battery up to 57 cycles by adding leveling agent of Hexadecyl-trimethylammonium hydroxide hydrate, though this additive cannot completely prevent dendrite formation and the abrupt efficiency decline. Alternatively, by adding phenol, ethyl alcohol, gelatin, the problem of lead dioxide shedding off the positive electrode is solved, and it also mitigates lead dendrite growth on the negative electrode; however, the coulomb efficiency of this system is relatively low. Further research is required to optimize the additive concentration in acetate based lead acid RFBs to solve the problem of lead dioxide shedding.

To gain insight into the sudden decay of coulomb efficiency after the first cycle, EDS (JSM-6510LV SEM, quantitative analysis) and impedance analyses are conducted. Oxygen, carbon and lead are detected on the negative electrode after first cycle, which may indicate undesirable corrosion of lead and the generation of lead acetate oxide hydrate $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot \text{PbO} \cdot \text{H}_2\text{O}$ or plumbonacrite $\text{Pb}_{10}\text{O}(\text{OH})_6(\text{CO}_3)_6$. This undesirable corrosion may lead to dramatic decrease of coulomb efficiency in the 2nd cycle.

To improve the acetate based lead acid RFB, further studies of reaction mechanisms in this system are needed so that additives can be applied to impede undesirable reactions in the battery.

7. Reference

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