

Research and Development
of
Long Life Lead Carbon Battery for Energy Storage
by
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Author's Declaration

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Abstract

This thesis is a summarization of a lead acid battery research and development work. The first four sections present briefly the lead acid battery (LAB) history, battery structure, fundamental theory, application in energy storage and a literature of latest research on carbon as an additive in advance lead acid battery system.

In the following main sections, the detailed research design, procedure, lab experiments, experiment result are discussed. The research goal is to highly improve the deep cycle life and rate performance of the conventional lead acid battery in a cost-efficient way. According to latest research using carbon material as additive in the negative electrode paste could be the direction. The practical way to experiment this Lead Carbon Battery (LCB) idea is presented. Then the experiment procedures and test methods, like negative paste preparation, quality control, single cell assembly and performance testing, are all detailed in text, tables and/or pictures. There after an optimized experiment procedure and test protocols is concluded. This would be the guidance to the high-performance lead acid battery industrial manufacturing. Finally, a comparison of LCB and conventional LAB in terms of 100% DOD (depth of discharge) cycle life and specific energy cost is discussed.

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List of Abbreviations

AC: activated carbon

AGM: adsorptive glass mat

Ah: ampere hors

C₂₀: 20 hours Capacity when discharging at a certain current to cut off voltage; mAh or Ah

nC₂₀: charge/discharge rate at current equals to "n" multiplied by C₂₀ in mAh /Ah; mA or A

CB: carbon black

CC-Chg: constant curent charge

CC-Dchg: constant curent discharge

CV-Chg: constant voltage charge

CL: cathodoluminescence

DI: deionized

DOD: depth of discharge

EMP: electron microprobe

HRPSOC: high rate partial state of charge

PSOC: partial state of charge

LAB: lead acid battery

LCB: lead carbon battery

NAM: negative active material

PV: photovoltaic

RGO: reduced graphene oxide

VRLA: valve regulated lead acid (battery)

1. History of Lead Acid Battery

The lead acid battery is about 160 years old. Since it was invented in middle of 19th century, the contributions made to improve the performance of the battery system has never stopped.

In Germany, 1801, Johann Wilhelm Ritter (1776 - 1810) became the first person to experiment using lead plates as electrodes in the so-called accumulator system. But the electrolyte he used was saline (H_2O and $NaCl$) instead of sulphuric acid [1]. The later experiments, performed by Kästner in 1810, Nobili in 1828, Schönbein in 1838 and Wheatstone in 1843 respectively, built the foundation of the lead acid accumulator system. In their experiments PbO_2 was formed on one of the electrodes as the electric current went through lead electrodes immersed in H_2SO_4 solution [1].

In 1854, Wilhelm Joseph Sinsteden (1803 - 1891), a German medical officer, invented the first lead acid battery system. The electrodes were made from lead, and the electrolyte was dilute H_2SO_4 . Sinsteden noticed the electrical storage capability of this system and thus discovered the working principle of the lead acid battery system. The cell delivered electric current and had a specific energy output of 0.1 Wh kg^{-1} for 15 minutes of discharge [1, 2].

In 1859, based on his fundamental research, Gaston Plante invented the first practical lead acid battery. The figure 1. Shows the lead acid battery he designed between 1859 and 1879. It should be noted that Gaston Plante's lead cell electrodes were built directly from thin lead plates.

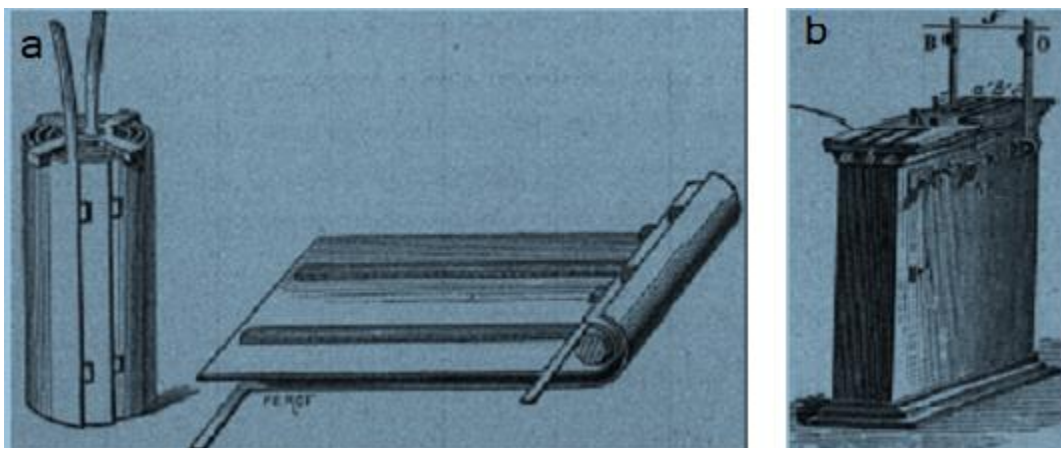


Figure 1. Drawings from [3] Recherches sur l'Électricité. (a) Lead coil cells with Lead plates separated by rubber strips. (b) Secondary cell with parallel lead plates.

From then on, many improvements were made to Plante's lead acid battery system. These great works dramatically improved the lead acid battery performance by using materials, novel structure designs on both electrodes, separators and electrolytes. Some major contributions are listed as follows:

In 1860, Wilhelm Siemens in Germany discovered a lead acid cell with carbon electrodes impregnated with lead salts and immersed in acid solution [4]. This was the earliest technology using carbon related materials in a lead acid battery system.

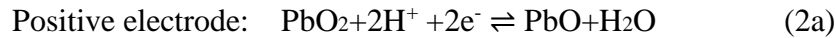
In 1881 Faure patented his technology of covering lead plates with porous active mass [5]. This patented technology raised the specific energy of the lead/acid cell to 8 Wh kg⁻¹ at the 10-h rate. In the same year Volckmar invented Grids in Paris [6]. This started the pasted electrodes era in the lead acid battery system.

In 1882 Aron [7] filed a patent adding cellulose as an additive to the active mass material. This technology showed the first time additives had an impact on the lead acid battery's performance.

In 1882 Müller [8] and Gardner in 1886 [9] patented using carbon as additives to the active mass to increase the electronic conductivity in electrodes.

2. Theory of the Lead Acid Battery

In 1882 Gladstone and Tribe published the first theory of the lead acid system [10]. They proposed that the following reactions occur:



It is noted that PbO was proposed as an intermediate product in the positive electrode. This is the so-called double sulfate theory of the reaction in a lead acid battery.

In 1935 Haring and Thomas demonstrated the experimental proof of the double sulfate theory [11].

During the discharge process, protons are produced at the negative plate and consumed at the positive plate. There is a net flux of protons from the negative to the positive plate during discharge. And the electrons travel around the external circuit.

3. Lead Acid Battery for Energy Storage Application

Due to global warming and climate change many calls are made for clean, renewable and sustainable energy that can meet the world's energy consumption. As a result, photovoltaic (PV) solar and wind power stations are becoming increasingly popular. The electricity generated by these technologies is growing steadily.

For these power generation systems to emerge the grid, an efficient and reliable electricity storage battery system is essential to store the generated electrical power since the PV and wind systems generate electricity intermittently by nature. Batteries in this field are stationary batteries that are designed to cycle rather than float.

The cycling stationary batteries can also be used to do load leveling and utility peak-power shaving, like in a smart grid system and distributed renewable energy storage system. In the highly resilient smart grids, a large-scale energy storage system with the ability to store energy for times of peak demand and in case of network outages is essential and critical.

A new market in residential energy storage in utility peak period and consuming at off-peak period is growing thanks to an almost doubled rate of electricity used during these two periods. Many governments are subsidizing this small scale distributed energy storage system in combination with green energy systems such as photovoltaic (PV) and wind power systems.

As discussed above, the renewable energy system, smart grid technology, and distributed energy storage system all need to be safety, reliable and have a long life electrical energy storage. The world market is quickly growing with unlimited potential. These combined factors have created a huge demand for energy storage stationary batteries.

The key performance requirement of energy storage battery is lifetime (cycles) at 80-100% DOD (Depth of Discharge) deep discharge and cost. A life cycle 1500-2000 cycles at 100% DOD is expected to meet the market requirement. The lead acid battery (LAB) is well known by its safety and low cost. It would be a promising candidate if it has an improvement in terms of cycle life at deep discharge cycling. The conventional LAB for deep discharge application can run 300-500 cycles before it failed, which is considered insufficient. Many efforts have been made to extend

the LAB cycle life. The main stream is to hinder passivation happening in the negative electrode by increasing carbon quilt a bit into the paste. The following literature view will present the new research and development in this field. This work will mainly focus on activated carbon but will also consider other carbon additives in the negative paste to improve the cell life performance.

4. Literature Review

As mentioned in the previous section, a lot of effort has been done to improve the lead acid battery cycle life performance to meet the growing requirement of wider applications. Using carbon as an additive in negative electrode paste to reach the goal has a long history despite the mechanism being not yet fully understood.

Not so long after the lead acid battery was invented, in 1882 Müller [8] and Gardner in 1886 [9] filed patents claiming using carbon as additives in the active mass increases the electronic conductivity in electrodes. From then on carbon material like carbon black became a basic additive to the active mass but was limited to 0.15-0.3% wt [12]. In 1995 K. Nakamura et al. [13] found that the addition of 3-10 times the conventional standard amount of carbon could recharge the lead sulphate more easily. This was done by building conducting bridges through carbon particles surrounding the sulfate crystals during the HRPSOC (high rate partial state of charge) cycling. Doing so slows down the capacity loss and contributes to a longer cycle life. In 2006 M. Calabek et al. [14] discovered that graphite in the large pores of the NAM (negative active material) could hinder the lead sulfate growth in a PSOC (partial state of charge). This leads to the cycle life performance improvement of the negative electrode. In recent years a lot of researchers have done many works in this area by selecting different forms of carbon to do the tests [15-21]. These carbon forms range from micrometer size to nanometer size carbon particles in carbon black, activated carbon, graphite, carbon nanotubes, nano-carbon fibers, rGO etc. The newest trend is the synthesized PbO and carbon composite as an additive in negative electrode paste [22-25]. These researches have discovered some beneficial effects of carbon material in the lead acid battery and developed a novel technology based on a 160 years old secondary battery system. This newly developed lead carbon battery (LCB) technology is crucial to keep the lead acid battery (LAB) competitive to the new generation energy storage system on the market.

4.1 Carbon Functions

Although there are many forms of carbon to be used in terms of physical properties, in order to boost LAB performance, their beneficial functions or effects can be summarized into two basic groups. One is the electric double layer capacitive energy storage, and the other one is carbon benefitting the electrochemical process of LCB.

4.1.1 Carbon Related Capacitive Energy Storage

This rapid capacitive charge-discharge process can be observed by cycling LCB with a discharge process at a high rate for a short period of a few seconds. A well-done observation has been carried out by D. Pavlov and collaborators [18]. They designed and experimented the HRPSOC cycling of LCB cells with activated carbon and carbon black as carbon additives in negative plates. The following figure presents schematically a summary of the experiment and types of tests and analyses performed within their study. TDA is the activated carbon with particle size $<44 \mu\text{m}$, BET surface $1615 \text{ m}^2 \text{ g}^{-1}$. AC3 is the Carbon black with particle size 12 nm , BET surface $1475 \text{ m}^2 \text{ g}^{-1}$.

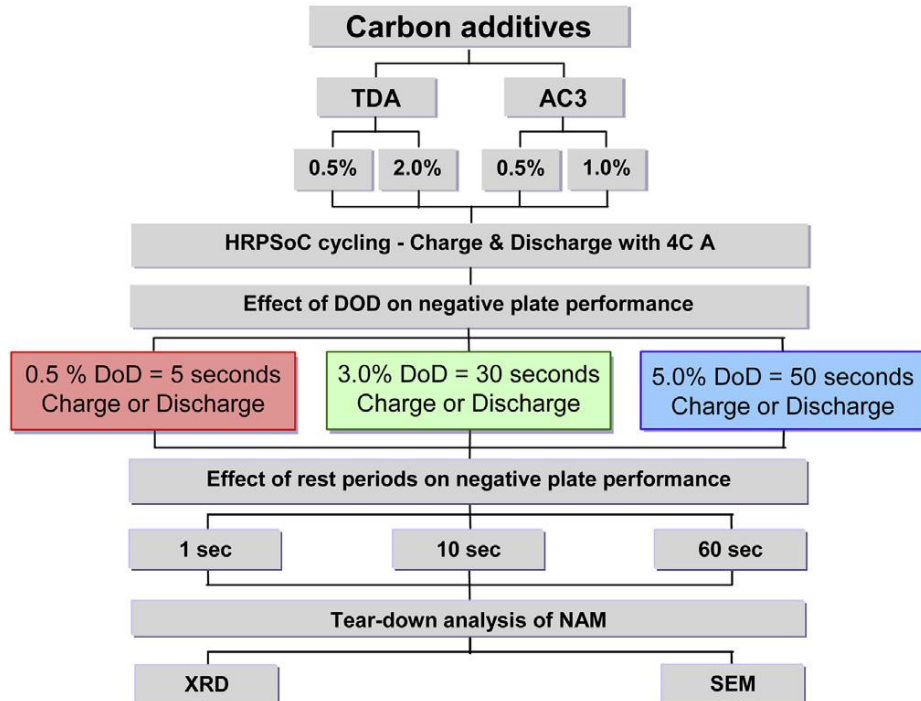


Figure 2. Summary of the negative plate variants used in this study and of the types of tests performed.

(Source: D. Pavlov, 382 P. Nikolov / Journal of Power Sources 242 (2013) 380-399)

The experiment successfully demonstrated the capacitive charge-discharge process by a 5 seconds pulse cycling process. The tested LCB cells presented similar high cycle ability (as much as 400,000 cycles from AC doped LCB cell) and reversibility as the electric capacitor. This is also proven by the cycle ability decreasing abruptly down to 10,000 cycles when the same cell cycled at a 30 seconds pulse. The experiment indicates that the capacitive cycling process takes place very quickly, in mere seconds and the energy storage is very limited, only 0.22% of the capacity of the tested 4.5Ah cell. It would indicate from the test that a capacitive charge/discharge step will happen at the very first seconds when the LCB cells are experiencing a charging or discharging process. As the article concludes, this step is from the electric double layer capacitor formed on the carbon/lead and electrolyte interface. Following this fast step, the relatively slow electrochemical charge/discharge process takes place to finish the rest of cycling. Normally in discharging or resting at this stage, small PbSO_4 particles will recrystallize into big PbSO_4 crystals and partial sulfation happens on the negative plates. These processes occur often in LAB cells and lead to capacity loss when the negative plates are not fully charged. In contrast the carbon particles in the LCB cell plates will hinder the growth of PbSO_4 crystals. This is one of the most promising proposed functions of carbon as an additive in LCB cells. These functions are discussed in following section.

4.1.2 Carbon Benefits to Electrochemical Process

There have been a few beneficial functions proposed for the additional carbon that can influence or improve the electrochemical process of the negative plate of LCB cells. Active researches are currently being carried out to discover which of these functions is (are) responsible for the enormous performance improvement of the negative plates of lead–acid batteries. Meanwhile the research work would be able to point out which form or forms of carbon or carbon combination have the most promising effects. The research can also help provide the optimum weight fraction of carbon to be used in terms of all kinds of LAB applications. The two most researched functions are briefly discussed in the following sections.

4.1.2.1 Electronic Conductivity Enhancing

Enhancing the electronic conductivity of the active material of negative electrodes was the earliest suggested mechanism for the carbon function. The electronic conductivity of carbon is not as good as metallic lead, but when the cell is discharged partially or fully, the locally occupied lead sulfate, which is an insulator, reduces the electrode conductivity dramatically. Well mixed carbon particles into the electrode paste might build an electron conducting pathway so to improve the conductivity of the electrode in discharged or partial discharged state. This would facilitate the recharge process.

D.P. Boden et al. [17] measured the resistivity of compact mixtures of pure dry lead sulfate powder (>99% purity and D50 ~5.6 μ m) a set of different doses of graphite, carbon black and activated carbon, and also the 2% wt of graphite, carbon black and activated carbon in the dry unformed pastes. The results are graphed in the following 3 figures.

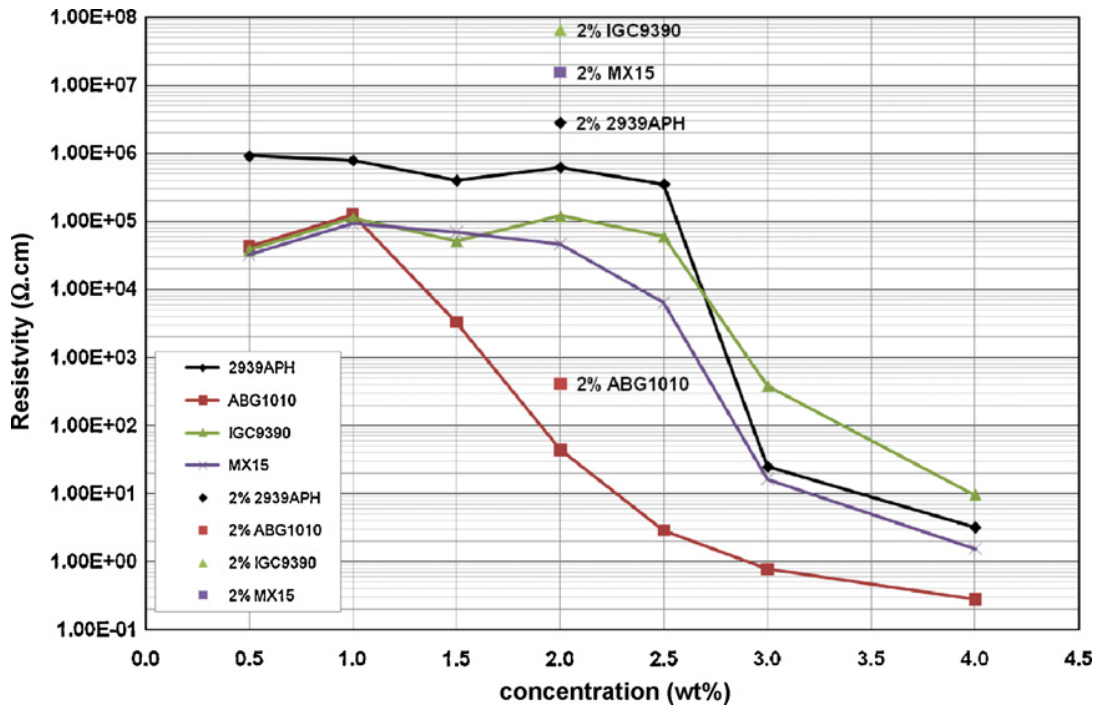


Figure 3. Resistivity of graphite materials in lead sulfate and at 2% loading in dry, unformed active material

(Source: D. P. Boden et al., *J. Power Sources*, 195(14), 4470–4493, 2010.)

Three of four types of graphite and PbSO₄ mixtures show a high conductivity over 3.0% graphite dosing. The expanded graphite and PbSO₄ mixture produces higher conductivity than others with a progressive increasing between 1% and 3% graphite dosing.

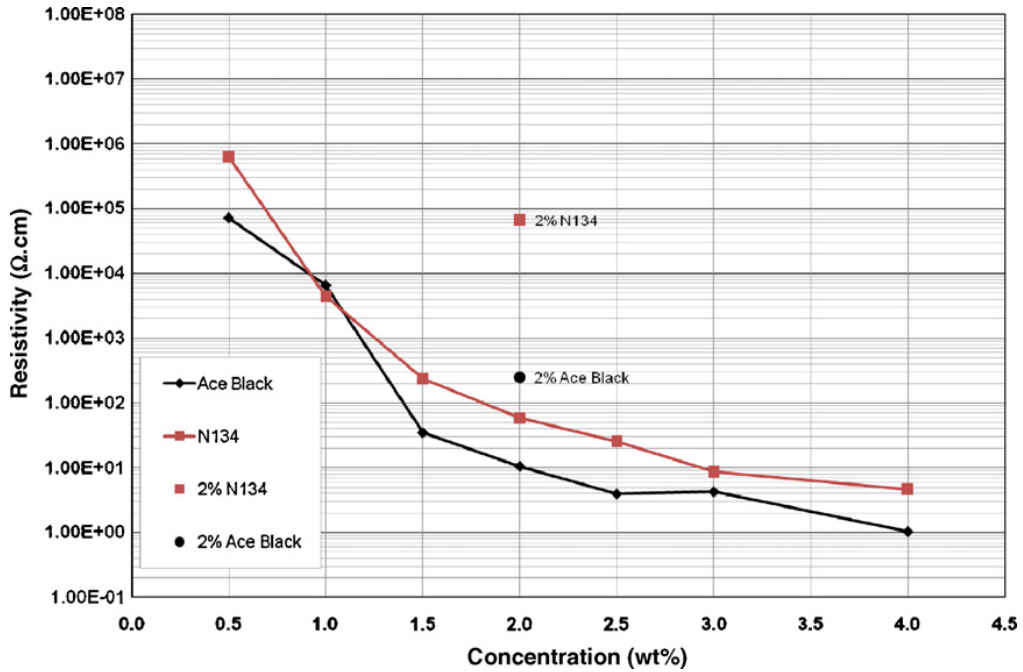


Figure 4. Resistivity of carbon blacks in lead sulfate and at 2% dry loading in dry, unformed active material.

(Source: D. P. Boden et al., *J. Power Sources*, 195(14), 4470–4493, 2010.)

This figure presents that the carbon blacks and PbSO₄ mixtures, similar to the expanded graphite one, has a gradual increase in conductivity with concentration. As well, the increasing conductivity slows down at a higher carbon black dosing, within the 2% to 4% range.

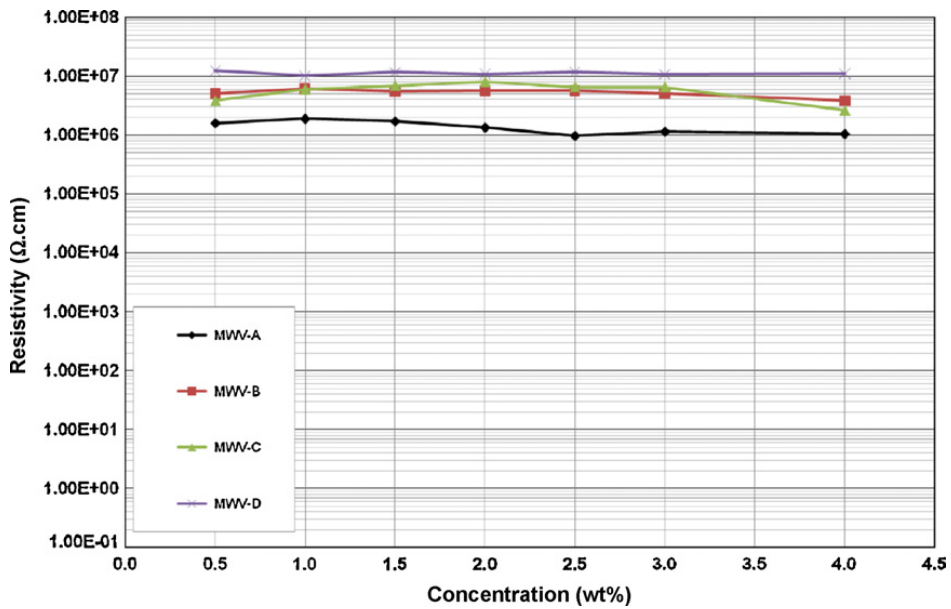


Figure 5. Resistivity of activated carbons in lead sulfate.

(Source: D. P. Boden et al., *J. Power Sources*, 195(14), 4470–4493, 2010.)

As shown in this figure the activated carbons have almost zero effect on the conductivity of lead sulfate over the 0.5% to 4% dosing range studied.

To obtain the measurement closer to the real negative paste material, D.P. Boden and collaborators fabricated some negative plates with different carbon and carbon combinations as additives. The plates were cured and then the paste was separated from the grid and ground for the resistivity measuring. This dry unformed material contains basic lead sulfates, lead oxide, lead particles, carbon, barium sulfate, lignosulfonate, etc. As expected, the conductivity of the cured paste is low for all that contained activated carbons. In contrast the paste that contained graphite, carbon black shows high conductivity with values depending on the composition of the additive.

From the other side, Masaaki Shiomi et al. [26] did an interesting experiment to relate the $PbSO_4$ residual amount to the different carbon amount by forming the lab made negative electrodes which had the paste made of $PbSO_4$ powder and 0, A%, 3A% amount of some type of carbon. "A" is the standard amount carbon but not disclosed. The form of carbon is not pointed out either. The experiment result demonstrated that the residual of $PbSO_4$ decreased considerably by adding carbon in the paste. It also showed the 3A% amount carbon negative electrode had less $PbSO_4$ residue than the A% one. The following figure presents the test result.

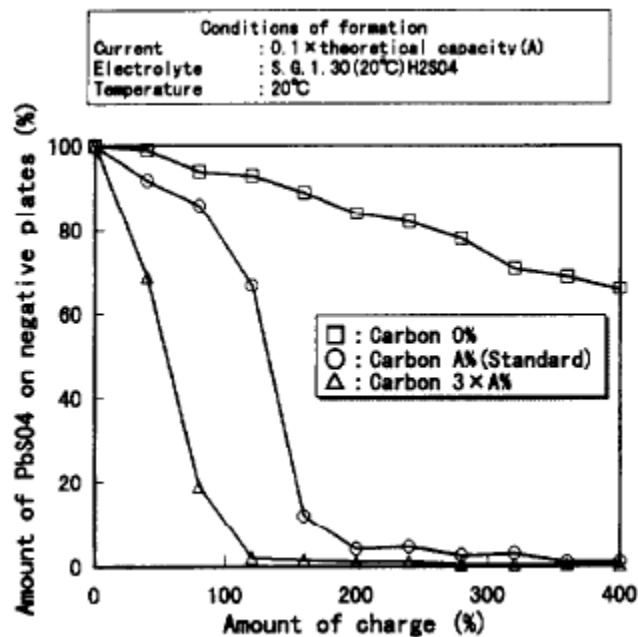


Figure 6. Changes of the amount of $PbSO_4$ on the negative plates during formation; thickness of the positive plates: 0.9 mm

(source: M. Shiomi et al. /Journal of Power Sources 64 (1997) 147-15.)

According to this discovery, the researchers suggested that the conductivity of the partially discharged negative active material must be enhanced thanks to a conductive network of carbon particles distributed between the crystals of lead sulfate. A proposed conductive network schematic is shown in the following figure.

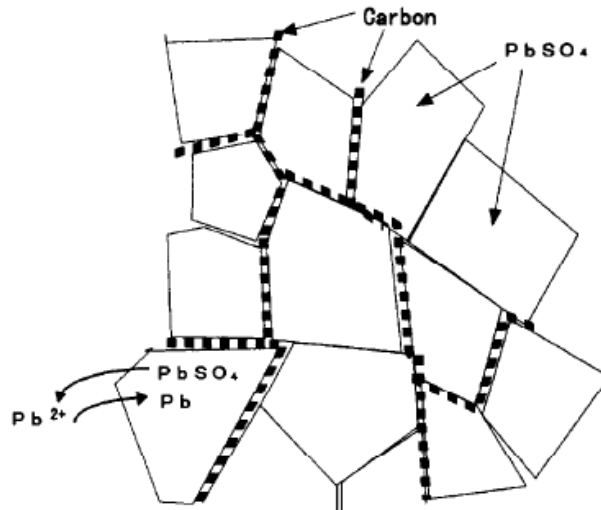


Figure 7. Carbon conductive network formed on the discharged negative plates.

(source: M. Shiomi et al. /Journal of Power Sources 64 (1997) 147-15.)

A conductive path (network) between/on PbSO₄ is built by the volumetric connection of carbon particles. Therefore, the rechargeability of PbSO₄ in the negative plates is improved substantially.

4.1.2.2 Suppressing PbSO₄ Crystal Accumulation and Uniform PbSO₄ Particles [17]

It is verified that a passive film of lead sulfate will form on the surface of the negative plates of VRLA batteries experiencing a partial-state-of-charge (PSOC) cycling application [29]. This dense film is very difficult to be reduced to lead by conventional recovery cycling. Therefore, this phenomenon will cause a permanent loss of capacity of batteries. As the batteries keep cycling the film becomes thicker and thicker. Finally, the progressive reduction of capacity leads to premature failure of batteries. Trying to find a way to suppress the PbSO₄ crystal accumulation on the surface of the negative plates D.P. Boden and collaborators [17] researched the effects of a few sets of graphite and carbon black mixtures in the negative plates of LAB in HRPSOC mode cycling. Their finding is that 2% wt graphite/2% wt carbon black mixture can eliminate the buildup of lead sulfate films on the negative plate surface. The electron microprobe (EMP) imaging and cathodoluminescence (CL) instrumentation used in the research provide demonstrable images of

the distribution of lead sulfate in a cross section of negative paste after 3596 HRPSOC cycles, showing below.

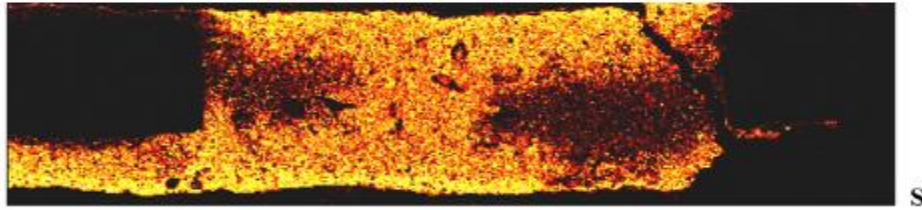


Figure 8. Composite EMP images of negative plate cross section after 3596 PSOC cycles.

(Source: D. P. Boden et al., J. Power Sources, 195(14), 4470–4493, 2010.)

This S(sulfur) image shows the distribution of sulfur. The yellow color indicates the high S concentration. Lower S concentrations are in a darker red coloration. The cross section of grids is showing as black rectangles (no sulfur). The top and bottom black edges are the epoxy holding the sample. It can be seen there is very little built up lead sulfate on the plate surface even after 3596 HRPSOC cycles and it has a uniform distribution through the cross section of the paste. This suggests that nucleation of PbSO_4 perhaps takes place on the implanted carbon particles. The work [27] has also shown similar findings. It has been confirmed by battery manufacturers [28] in full-sized batteries with cycle lives of up to 300,000 PSOC cycles.

5. Engineering Procedure and Materials of Negative Electrode of Lead Carbon Battery (LCB)

In general, the performance of a lead acid battery, in terms of energy efficiency, energy and power densities, and cycle life, is strongly dependent on the electrode material composition and morphology, electrode design and structure, and manufacturing procedure.

The fabrication **procedure and material** are two essential **parameters affecting the engineering research goal** in this research. Each of them has several sub parameters which also have next level sub parameters and so on, which according to the research, can go on necessarily. By evaluating the effect of the different parameters on the research goal the optimized parameters combination would be discovered to help reach the research goal. The goal of this LCB research is to dramatically improve the cycle life performance of the Lead Acid battery by modifying the paste formula of the negative electrode with carbon and /or other additives. In the following different sub parameters, whichever shows a considerable effect to the battery cycle life performance directly or indirectly, will be discussed experimentally.

5.1 Negative Electrode

The negative electrode is one of the key components in the lead acid battery. The negative electrode determines the cold-temperature performance. Like in the starting, lighting, and ignition (SLI) lead acid batteries, cranking ability is often limited by the negative plate at a lower temperature range (<5 °C). The composition, structure, morphology, and design of negative active material (NAM) can affect battery performance. The negative electrode consists of two parts: the electrical current collector/grid and NAM.

5.1.1 Negative Electrode Grid

The function of a battery grid is to support and hold the paste/active material. The battery grid also conducts electrons between the active material and the cell terminal. Battery grids are often made of a lead alloy which normally contains lead, calcium, tin, and aluminum.

Testing Grid (the right one) thickness: 1.0-1.1mm; 147mm wide and 128mm high

Control grid (the left one) thickness: 0.8mm

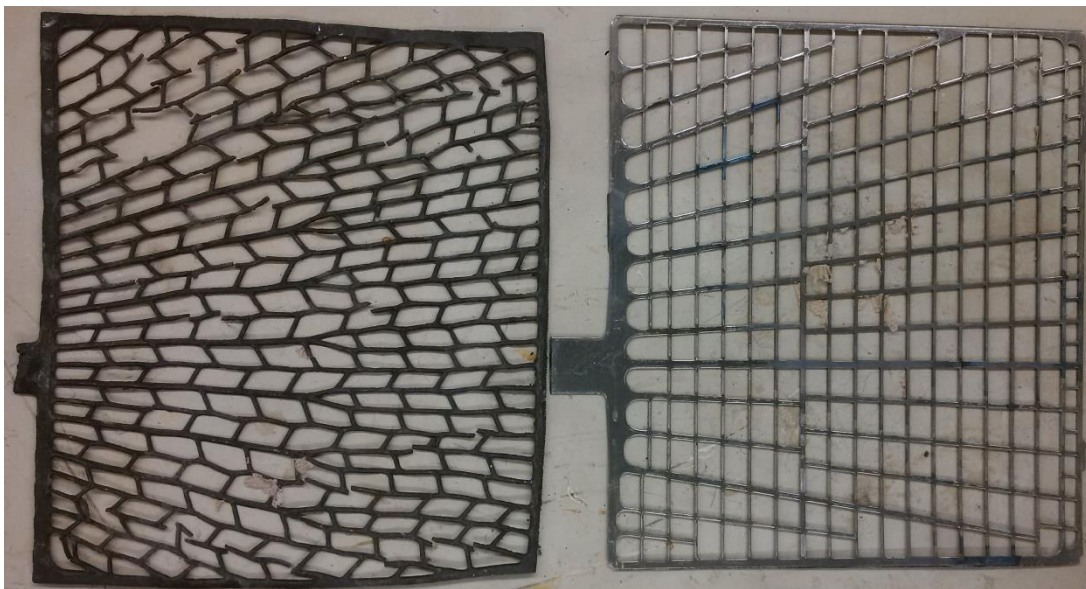


Figure 9. A grid from a deep cycle Lead Acid battery (left); the grid tested in this work (right)

5.1.2 Negative Electrode Paste Ingredients

Nowadays the most dominant method used to fabricate negative electrodes was patented by Faure in 1881. The core idea of Faure's invention is preparing electrode paste as the precursor of negative active material. The basic materials for the negative electrode paste are PbO, H₂SO₄, BaSO₄(barium sulfate), carbon black, sodium lignosulfonate, humic acid, and water. The type/application of the lead acid battery will decide the ratio between these components. Normally, SLI (starting, lighting, and ignition) batteries will have a low ratio of PbO: H₂SO₄, deep-cycle batteries design with a relative high ratio of PbO: H₂SO₄.

In this work, the starting materials and design ratio between the components is on Table 1:

Table 1. Experimental design - different AC: PbO ratio in negative electrode

Material	Unit	Amount	Standard	A-AC 1%	B-AC 4%	C-AC 8%
PbO	g	25	500	496.485	481.440	461.380
Activated carbon (AC)	g	0.075	1.50	5.015	20.060	40.120
H ₂ SO ₄	mL	1.50	30.00	30.00	30.00	30.00
DI water	g	3.65	73.00	73.00	133.00	133.00
Barium Sulfate (BaSO ₄)	g	0.20	4.00	4.00	4.00	4.00
Sodium lignosulfonate	g	0.04	0.80	0.80	0.80	0.80
Humid acid	g	0.15	3.00	3.00	3.00	3.00

A conventional negative active materials list is below. Additives such as lignosulfonates, BaSO₄, and carbon black are added to the negative paste. The finished Paste density is about 4 g/cm³.

PbO 25 kg

H₂SO₄ 1.5 L

Water 3.65 L

Barium sulfate (BaSO₄) 0.2 kg

Carbon black 0.075 kg

Sodium lignosulfonate 0.04 kg

Humic acid 0.15 kg

The difference is made with the additive of carbon. This work will use high surface area activated carbon instead of carbon black.

Table 2. Activated Carbon properties

Properties	Surface Area	Porosity	Ash	Fe	Conductivity	Intense Density	D50	Capacity
Units	m ² /g	ml/g	%	ppm	S/mm	g/ml	um	F/g
Datas	1500-1700	0.4-0.5	<0.5	<50	0.3-0.35	0.30-0.40	5.0-6.0	140

PbO

Industrial grade PbO powder is purchased as the main active material for the electrode paste. As presented in the following SEM picture, PbO particles are shale-like layers about 0.5x1—1.5x2 μm in size. The smaller round particles are probably the lead metal left over.

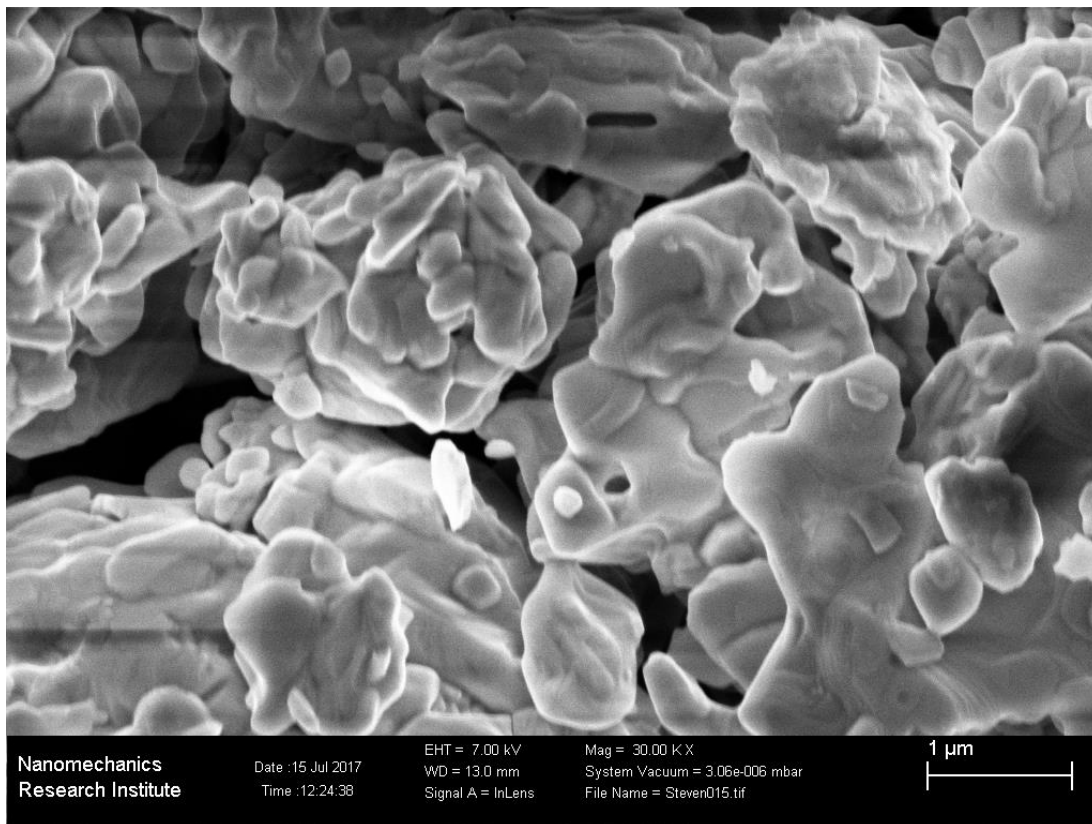


Figure 10. PbO powder SEM Magnification:3000KX

H₂SO₄ (from Sigma-Aldrich Meets ACS Requirements Current ACS Specification)

Properties

Grade	ACS reagent
Vapor Density	<0.3 (25 °C, vs air)
Vapor Pressure	1 mmHg (146 °C)
Description	Nominally 95-98% H ₂ SO ₄
Assay	95.0-98.0%
Appearance	Free from suspended or insoluble matter
Ign. Residue	≤5 ppm
Colour	APHA: ≤10
bp	~290 °C(lit.)
Density	1.840 g/mL at 25 °C(lit.)
Anion Traces	MnO ₄ ⁻ reducers: ≤2 ppm chloride (Cl ⁻): ≤0.2 ppm nitrate (NO ₃ ⁻): ≤0.5 ppm
Cation Traces	As: ≤0.01 ppm Fe: ≤0.2 ppm Hg: ≤5 ppb NH ₄ ⁺ : ≤2 ppm Heavy metals (as Pb): ≤1 ppm

Humid acid (Black Powder or Crystals)

Properties

Grade	Technical
Melting Point/Range	300 °C (572 °F)
Solubility	0.1G in 10ML water

Barium Sulfate (BaSO₄ in white powder form) from Sigma-Aldrich

Properties

Grade: Puriss., meets analytical specification of Ph. Eur., BP, 97.5-100.5%

Density: 4,400 g/cm³ at 20 °C (68 °F)

Molecular weight: 233.39 g/mol;

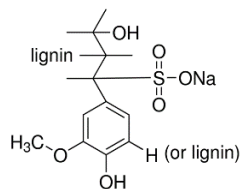
pH=7,

Melting point: 1,580 °C (2,876 °F);

Boiling point: 1,600 °C (2,912 °F) at 1,013 hPa (760 mmHg);

Water solubility: Insoluble; ≤0.3% soluble in acid

Sodium lignosulfonate (brown powder)



Properties

Mol wt average Mn ~7,000; average Mw ~52,000

Composition Na, 8 wt. %

Impurities 4 wt. %

Reducing Sugars 6 wt. %

Solubility H₂O: soluble

5.1.3 Negative Electrode Fabricating Procedure

In this section the fabrication process of negative electrodes of lead acid/carbon batteries will be discussed briefly.

5.1.3.1 Paste Formula—Modified Faure Formula with Carbon

Following Table 1, the experiment has different carbon to PbO ratio but keep the other components the same with a total weight of 500g per batch. Water may be added more to adjust the paste density due to more carbon added. The amount of carbon at different %wt is listed below for reference:

- 1) Activated Carbon by different weight ratio to the standard PbO 500g plus activated carbon AC 1.5g (see Table 1.1)
 - a) 1% wt Activated Carbon is 5.015g
 - b) 4% wt Activated Carbon is 20.06g
 - c) 8% wt Activated Carbon is 40.12g
- 2) Other Carbons
 - a) 2% wt Carbon fiber (10.03g) and 4% wt Activated Carbon (20.06g)
 - b) 2% wt Carbon Black 600JD (10.03g) and 2% wt Graphite (10.03g)
 - c) 2% wt Carbon Black 300J (10.03g) and 2% wt Graphite (10.03g)
 - d) 0.5% wt Super P (2.5g) and 3.5% Activated Carbon (17.56g)
 - e) Carbon less than 0.2% wt(1g) of PbO mass in conventional LAB

5.1.3.2 Ingredients Weighing

The experiment has 500 grams of PbO and 1.5 grams of carbon, a total weight of 501.5 grams as a standard batch weight with other additives and de-ionized water and sulfuric acid. The weight ratio of carbon to PbO for testing is changing between 1% to 8% in this experiment, with the DI water amount changing accordingly to adjust the paste density, while keeping the other component's amounts unchanged. To calculate the amount of carbon at a certain ratio, for example 1% wt of PbO, is done by multiplying 501.5 to 1%, which yields 5.015 grams of carbon. To test the 1% wt carbon paste 5.015g of carbon is weighed with a balance, Denver Instrument, MXX 2001, see Figure below. And 496.485g ($501.5 - 5.015 = 496.485$) of PbO powder is weighed too. Then weigh the rest of the solid ingredients following the recipe.

The liquid state components such as DI water and sulfuric acid are measured with measuring cylinders as needed.



Figure 11. Balance for weighting solids and solids Measuring in a cup

5.1.3.3 Dry powder ingredients Mixing

To maximize the additive function in the electrode paste, the homogenous mixing of these additives with the PbO powder is extremely important. This step will decide the electrode performance essentially. To get the homogenous mixing, the selection of a suitable mixing device is critical according to the materials to be mixed. Sometimes the specially designed mixing device is needed. The total mixing time is about 30 minutes for a 500g standard experimental batch.

The dry powder mixing method used in this work is basically mechanical mixing and blending through shearing operation. Mixing devices that have been used can be simple as the drill press mixing machine or an intensive laboratory mixer. They are shown in pictures below.



Figure 12. Drill press mixing machine and mixed dry powder

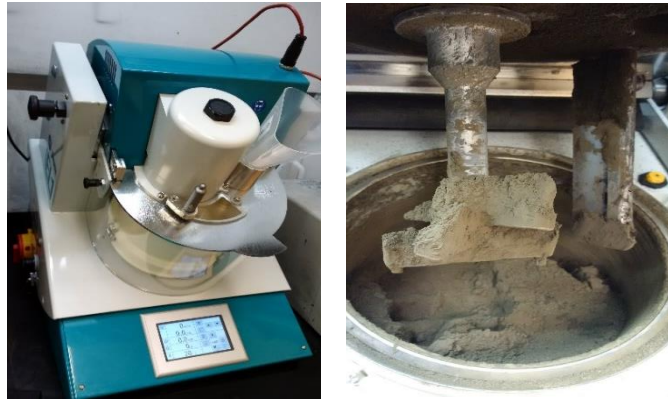


Figure 13. Intensive mixer ELI and mixed powder

5.1.3.4 DI water Addition

Following the dry powder mixing, the next step is DI water addition. This a simple operation performed with the mixer running and just pouring the amount of water needed. The amount of water is important to get the right paste density. From the experiment, too much water in the paste will cause the cracks on the electrode to surface during the curing process. If there is not enough water, the paste that comes out will be too dry to do the pasting process. Generally, a 5 ml offset to the desired amount of water for a 500g batch with 4% wt carbon is reasonable. As carbon is hydrophobic, the more carbon in the batch, the more water is needed to keep the mixture pasty. The following figure shows the state of the paste after the DI water is mixed with the 4% wt carbon powder.



Figure 14. A DI water and powder mixture of a 4%wt activated carbon batch

5.1.3.5 Sulfite Acid Addition

For every 500g experimental batch, 30 ml of 98% sulfuric acid addition is needed. During the addition and mixing, the reaction: $\text{PbO} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{PbSO}_4 + \text{H}_2\text{O}$ happens. This is an exothermic reaction. The acid addition speed is crucial to keep the mixture temperature not exceeding 65°C. For this experimental setting a speed of 0.5-0.75 ml/min is suitable. A thermal couple is used to measure the paste temperature during the addition. As well, a certain mixing speed is required to get a uniform dispersion of acid throughout the mixture. At the end of the acid addition, if the paste is too dry, an extra amount of DI water can be added. And vice versa, 1-2 ml more acid can be added too if it is too wet. The total process will take about 1 hour for a 500g batch. As the acid is added into the mixture, the paste will become stickier, so the adjustment of the mixer speed and power may be necessary. The following figure shows the nearly finished paste with the acid addition.



Figure 15. The paste in the mixing bowl after the sulfuric acid addition

5.1.3.6 PTFE emulsion Addition

PTFE emulsion is not added into the paste at the original formula. To solve the paste shedding off issue during the cell cycling, the PTFE emulsion was the first try and it works perfectly as an active material binder to keep the paste sticking to the grid. Since PTFE is electrical isolator the amount added in is small. 11ml of 60% wt PTFE emulsion (dispersion in water) per 500g batch has been tested. Although the PTFE emulsion is the last ingredient to be added in as designed, it is still necessary to adjust the paste density by adding extra DI water or sulfuric acid. The following figure shows the paste after the PTFE emulsion addition in the mixing bowl.



Figure 16. Finished paste with PTFE emulsion addition in a mixing bowl

5.1.3.7 Paste Density Measuring

A 38ml volume measuring cup is used to do the measurement. The first step consists of filling the cup with the finished paste and compacting the paste as much as the cup can hold. Then the cup filled with the paste is weighted on the balance, shown in the figure below. The density can then be calculated by the weight and volume from the previous measurement. For a 4% wt activated carbon 500g batch the finished paste density is 3.6g/cm^3 approximately. It is lower than the conventional negative paste in the lead acid battery, which has a density about 4.0g/cm^3 , due to the addition of a higher percentage of very low density activated carbon.



Figure 17. Paste density measurement

5.1.3.8 Grid pasting

Once the paste is ready the grid pasting process can start in order to make the negative electrode. The grid serves as a mechanical support for the paste at this moment. First the grid is cleaned and weighed. Then the grid is laid down over a piece of paper on the lab counter top and paste can be spread on top of the grid evenly, showing in the figure below. The following main process is pressing and pasting the paste evenly with a hand plastic scraper on the one side of the grid to fill all the holes and cover all the metal bars and edges. Then flip the half-pasted grid over and finish the other side of the grid with paste, again covering all the metal bars and edges. Try to make the finished electrode surface smooth and even and have a uniform thickness across the entire area. In the lead acid battery industry, the grid pasting machine can do this job more efficiently and with higher quality. Before pursuing the next step, the pasted electrode will be weighted and recorded for reference.

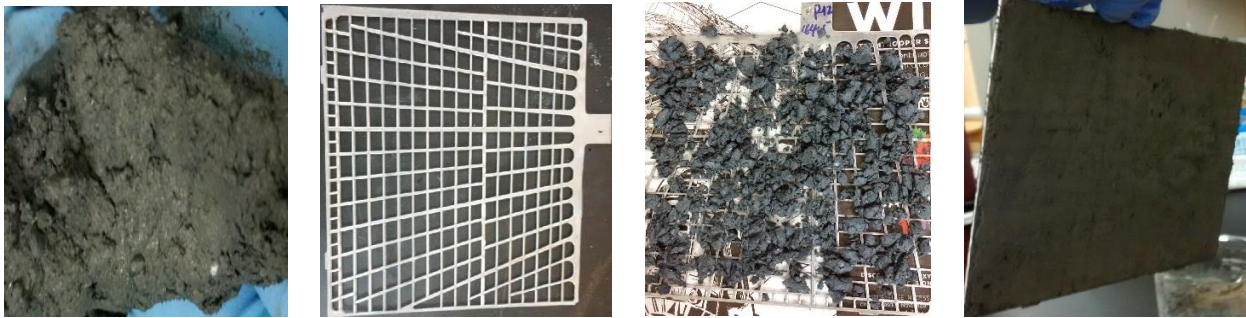
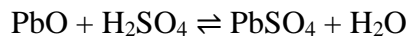


Figure 18. Grid pasting process in the Lab

5.1.3.9 Electrode Plate Curing

(1) Curing Chamber and Setup

As soon as the electrode is paste ready, it will start the curing process in a warm and humid chamber; one is showing in the following figure. The electrode will be hanging on the racks inside the chamber. The curing process, which converts wet active paste into dry porous material, will be going under a certain temperature and relative humidity during a certain time all decided by the electrode design and battery application. The temperature can range from 65°C to 95°C. The relative humidity could be set at 95% or over. The controlled high temperature and high humidity ensures the oxidization of free lead in the paste. Generally, the free lead content in the paste should be less than 2% after curing. In the curing process, the reaction:



also happens, and the paste can form a tetrabasic lead sulfate $4\text{PbO} \cdot \text{PbSO}_4$ (4BS) dominated crystal structure, or a tribasic lead sulfate $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ (3BS) dominated crystal structure. After curing in the chamber for a designed time, the negative electrodes will be taken out from the chamber with a visual check for any defects. They can then be stored for later testing.

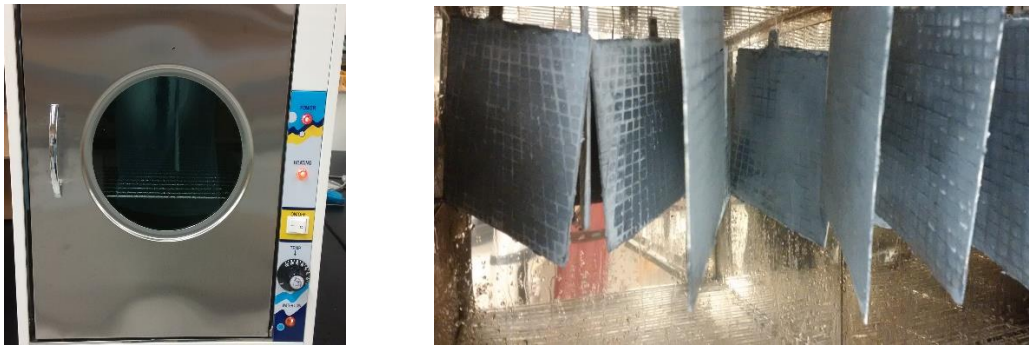


Figure 19. Curing chamber and the curing electrodes hanging inside the chamber

(2) Curing parameters: Temperature, Time effect

a) Temperature

First curing stage temperature is at 90 and 95°C. Q group cells Q-1,2,3,4,5,6 cured at 90°C at first stage.

So far from the formation result of Q-2,4 cells the 5-degree difference of curing temperature shows no difference on the battery's 20 hours discharge performance. Rate test 1 and 2 are ongoing.

Suggest doing more tests on lower curing temperatures in the first stage in the future to save curing energy consumption.

b) Curing time

Normal curing time is 48 hours 95°C plus 18 hours 50°C. P-1,2,3,4,5,6 cells cured only 17 hours at 95°C. P-7,8,9 cells cured at room condition and had very bad cracks due to the wet paste. P-10,11,12,13 cells cured for 13 hours. P-14,15,16 cells had a normal curing procedure and do not have any cracks on plates subject to very dry paste (drying out the wet P batch paste by spreading paste on a piece of paper in lab room environment.)

The two-testing group P-5,6 and P-14,15,16 from different curing times show similar formation and rate test 1 and 2 results at the same testing setup and battery tester machine. This indicates the curing time doesn't affect the battery performance at this test stage. In terms of cycle life effect, the real cycling test still needs to be done.

5.2 Positive Electrode

The plate positive electrode of a lead acid battery has the same fabrication procedure as the negative one. It uses the same or a similar grid and the paste mixing process is the same. As well, the curing process is similar. The paste for the positive electrode has the same components such as PbO, sulfuric acid, water, carbon as negative one. The difference is the positive paste will have Pb₃O₄ red lead as an additive instead of the expanders used in the negative paste.

This work is focused on improving the negative electrode performance for now so the market positive electrodes with the same grid as the negative grid will be using to assemble the testing cells. A picture of this positive electrode plate is showing in the below figure. The dimension of the positive electrode is 147x128x1.7mm. The total mass is 156-160g.



Figure 20. A market positive electrode used in the work

5.3 Electrolyte Preparation

The electrolyte of a lead-acid battery is H_2SO_4 , sulfuric acid in an aqueous solution. The impurities could cause high self-discharge, thus shortening the cycle life of the lead-acid battery. The sulfuric acid used should meet the purity requirement of the lead acid battery standard. The theoretical amount of H_2SO_4 that would yield 1 Ah of electricity is 3.659 g. The concentration and volume needed for a certain lead acid battery are dependent on the battery design and application. In this work, to maximize the negative electrode performance, the testing cells will be flooded with diluted sulfuric acid aqueous solution electrolytes. The concentration of sulfuric acid solution is 33% wt, $1.245\text{g}/\text{m}^3$ at 25°C , it is diluted from the 98% sulfuric acid from Sigma Aldrich, Canada, with lab DI water.

5.4 Separator

The battery separator is between the negative and positive electrodes in the cell to prevent electronic shorts. At first, to prevent shorting, the separators must act as an electronic insulator. And second, the separator must supply a pathway for ionic flow between the electrodes so that the electrochemical reactions can proceed.

To meet the above two requirements, separators are fabricated from electronic nonconducting materials that are in a porous manner that allows for ionic migration. And the separator materials must also be mechanically strong and stable enough in strong sulfuric acid for a long battery life. today these materials include the PE separator, AGM (Absorptive glass mat), rubber, cellulosic, and PVC.

5.4.1 AGM

To suit the deep cycle application in this research work, the AGM separators are chosen to be used in the testing cells. It has been found that AGM batteries demonstrate low or no water loss and have a lower chance of acid stratification. The AGM separators have a positive support to the positive active material, this will benefit active material keep bonding to the grid during the deep cycling. In these deep cycle applications, AGM separators shows a high heat resistance, which is important for the safety operation of the batteries. The following figure shows smooth and rough sides of an AGM separator being used in the cell. It matches the size of the electrodes.

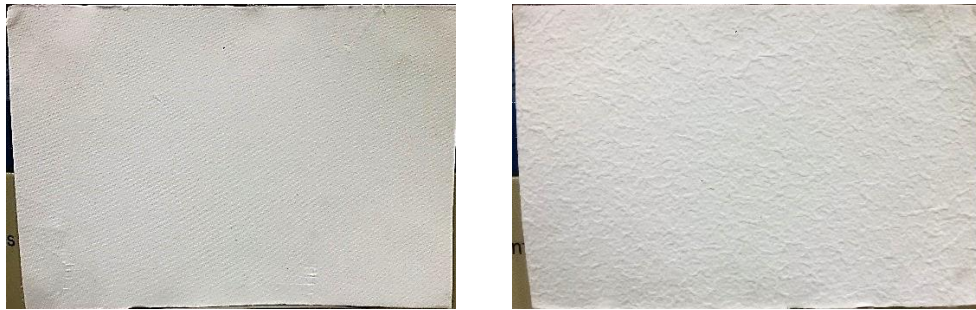


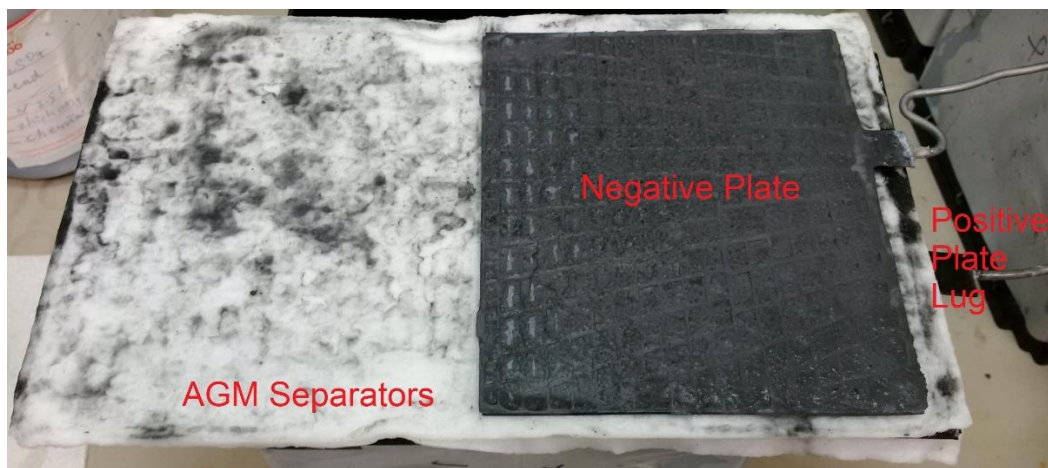
Figure 21. Two sides of an AGM separator used in the testing cell

5.5 Electrode Plate Electrochemical Test

5.5.1 Cell Assembly

The testing cell body is assembled with one negative plate and one or two positive plates. The one negative plate and two positive plates combination will have a cell performance limited by the negative electrode. The most cell performance tests will be done on these one or two combinations.

To do the assembly, first wrap a negative plate in the folded in half AGM separator with the smooth side of the AGM separator facing outside. Then stack a positive plate on one side of the AGM wrapped negative plate with the lug apart from the negative plate's lug. Wrap one more AGM separator to hold the plates together and rubber band two grid -sized, 1/8" thick PVC plates to press the electrode plates closely. See the figure a) and b) below. Figure c) shows the two positive plates assembly. It is assembled with one more positive plate on the other side of the negative plate. It is worth noting that when wrapping the electrode plates, make sure the AGM separator overlaps the edges of the plate. This can provide some protection against the electrical shorts during the cell operation life.



a)



b)



c)

Figure 22. Test cell assembly

Once finished with the cell assembly, it can be soaked into the sulfuric acid solution electrolyte for 1-2 hours in a partition of a battery box. See the following figure below. After soaking for 1-2 hours, all cell fabrication will be complete. The cell then can proceed to the electrochemical procedure, the formation charging step.



Figure 23. Soaking assembled cells in the battery box

5.5.2 Cell Formation

As the paste of negative and positive plates are made from lead monoxide PbO and aqueous sulfuric acid, even after curing the plates they are not functional electrodes yet. One more step, formation, is needed to complete the conversion. This electrically forming or charging process will convert the lead monoxide in the negative paste to a soft spongy gray lead. In this electrochemical process, on the negative electrode plates, the PbO on Pb/Pb-alloy grids are reduced to Pb in the H₂SO₄ aqueous solution; on the positive electrode plates, the PbO on the Pb/Pb-alloy grids are oxidised to PbO₂ in the H₂SO₄ aqueous solution. After the formation process, the cell electrodes are fully charged, and the cell is functional as a rechargeable cell for the future use. The formation is a necessary step during the lead acid battery manufacturing process.

In practice, the discharge-charge cycle step will be performed to define the ampere hour capacity of the cell. This step will be carried out to determine the 20 hours rate capacity C₂₀ or 10 hours rate capacity C₁₀ of the cell. Different charge-discharge profiles will be tested on the cells as well. The formation is carried out on the 5V20A Neware battery tester devices, shown in the following figure.

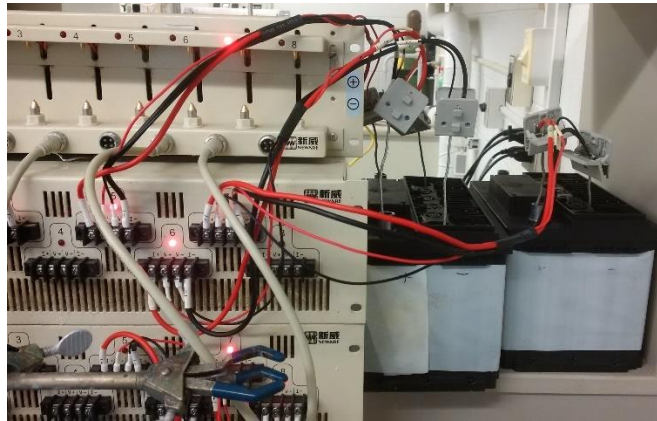


Figure 24. Lead acid cell on formation cycling

5.5.3 Performance Test of Negative Electrodes

The main performance tests of the negative electrode of a lead-acid battery includes the following tests: (1) capacity test, (2) rate capability test, (3) cycle life test, (4) charge rate acceptance test, etc. This work will only perform the first 3 types of tests.

5.5.3.1 Capacity Test

Normally the capacity test is finished following the cell formation. It defines the 10 hour-rate or 20-hour rate capacity of the test cell from the first 3-6 charge-discharge cycles which have steady capacities. Since the actual discharge time is not always an exact 10 or 20 hours, the capacity with the least discharge time in the range 10-10.5hours or 20-20.5 hours will be selected as the 10-hr or 20-hr rate capacity, named as C_{10} or C_{20} in mAh. This capacity will be related to the constant charge and discharge currents in the following rate capability tests.

5.5.3.2 Rate Capability Test 1

The rate capability test 1 is carried out on the new cell after the capacity test and 10-hour capacity C_{10} mAh or 20-hour capacity C_{20} mAh have been determined. This test is to diagnose the negative electrode discharge performance from the low discharge rate to a rate as high as the cell can discharge to the battery loads. The charge rate stays the same at every charge-discharge cycle. The charge or discharge current setup for the test is defined according to the test rate. for example, at $0.05C_{20}$ rate, the current will be $0.05 \times C_{20}$ in milli amperes. Let C_{20} equals 5000mAh, then $0.05C_{20}$ will be $0.05 \times 5000\text{mA}$, 250mA. The other higher discharge rate current will follow the same method to setup the current.

The test protocol is:

Step 1, Constant current charge (CCC) at $0.1C_{20}$ mA current to cut-off voltage of 2.30V;

Step 2, Constant voltage charge (CVC) at 2.30V to cut-off current of 110mA;

Step 3, Rest for 10 minutes;

Step 4, Constant current discharge (CCD) at $0.05C_{20}$ mA to cut-off voltage 1.75V;

Step 5, Rest for 10 minutes;

Repeat step 1 through step 5 with the different CCD currents: 0.1/0.2/0.5/1/2/3/4/5C₂₀ mA. A sample testing result is shown in the following figure.

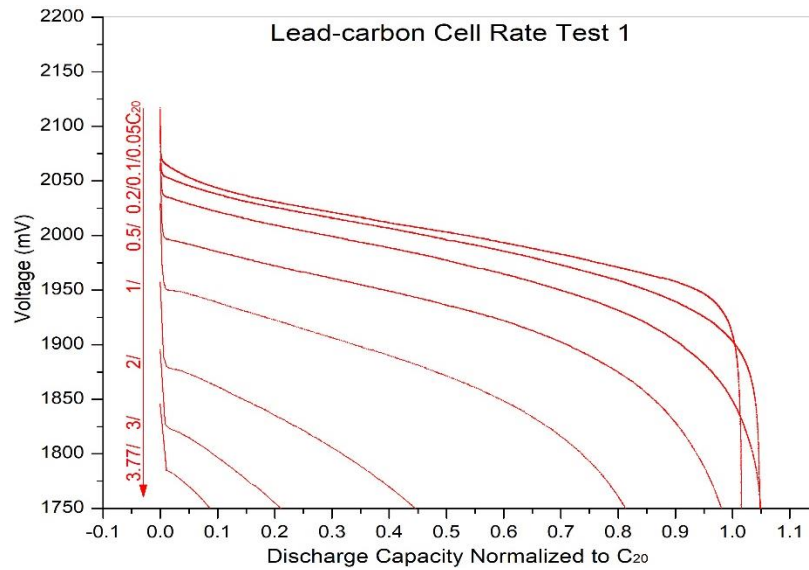


Figure 25. A sample rate test 1 result of a lead acid cell

5.5.3.3 Cell Rate Test 2

The rate capability test 2 is carried out on the new cell after the capacity test and 10-hour capacity C₁₀ mAh or 20-hour capacity C₂₀ mAh have been determined. This test is to diagnose the negative electrode's constant current charge (CCC) ability and constant current discharge (CCD) performance from the low rate to the high rate. The CCC or CCD currents are related to the C₁₀ or C₂₀. The charge and discharge currents are calculated in the same way as in rate test 1.

The test protocol is:

Step 1, Constant current charge (CCC) at 0.05C₂₀ mA current to cut-off voltage of 2.30V;

Step 2, Constant voltage charge (CVC) at 2.30V to cut-off current of 110mA;

Step 3, Rest for 10 minutes;

Step 4, Constant current discharge (CCD) at 0.05C₂₀ mA to cut-off voltage 1.75V;

Step 5, Rest for 10 minutes;

Repeat step 1 through step 5 but change the CCC and CCD currents to 0.1/0.1; 0.2/0.2; 0.5/0.5; 1/1; 2/2 C₂₀ mA respectively. A sample testing result is shown in the following figure.

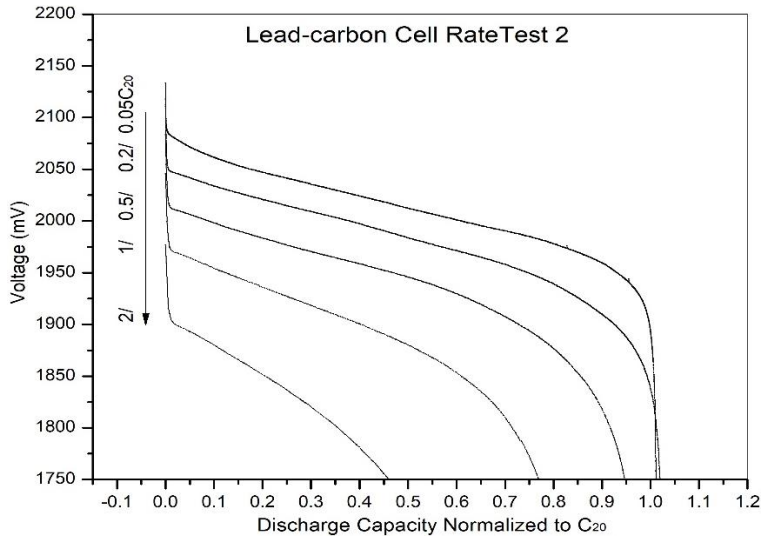


Figure 26. A sample rate test 2 result of a lead acid cell

5.5.3.4 Cell Cycle Life Test

The battery cycle life is the amount of charge-discharge cycles that can occur until capacity drops to 80% of its rated capacity. Normally, the lead acid battery capacity decreases with cycle number due to the increasing of internal resistance, active material reducing and water loss. Different applications will have different cycle life test protocol, depth of discharge and life ending criteria. A typical cycle life test from this work is showing in the following figure as an example:

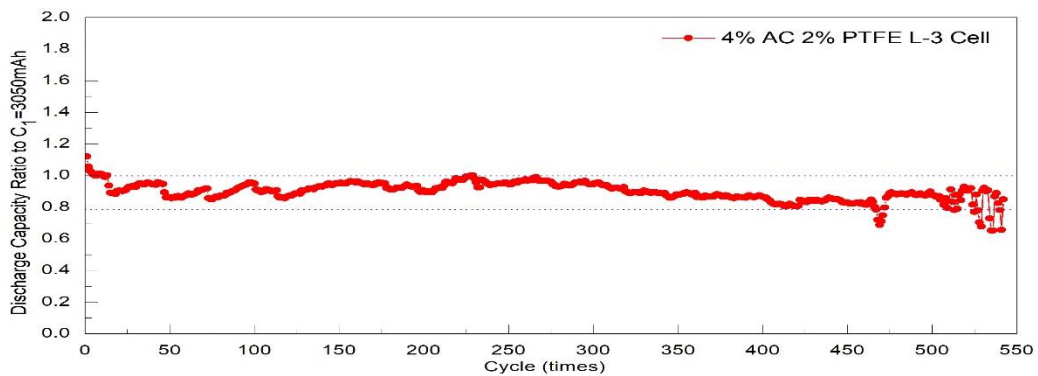


Figure 27. A sample of LAB cell cycle life test

6. Optimization and Result

6.1 Optimization of Fabrication Procedure of Negative Electrodes

6.1.1 Dry powder mixing

The Eirich EL1 intensive mixer overpasses the home assembled drill press mixer in terms of tested cell cycle life. The G cells, mixed with the drill press mixer, have a maximum cycle life of 588 cycles in one cell showing in figure below. On the contrast the L cells, mixed with Eirich EL1 intensive mixer, have a maximum cycle life 1090 cycles, see figure below.

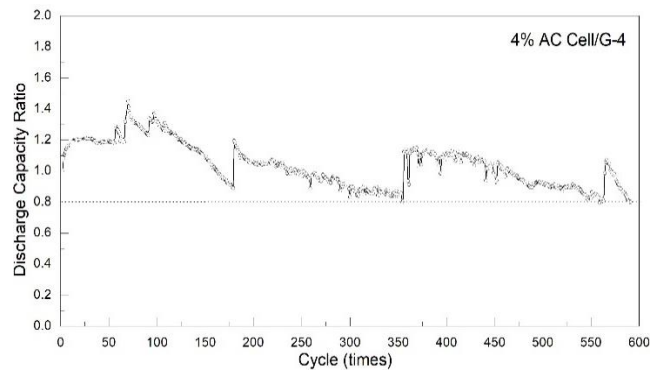


Figure 28. Drill press mixer mixing cells have 588 maximum cycles

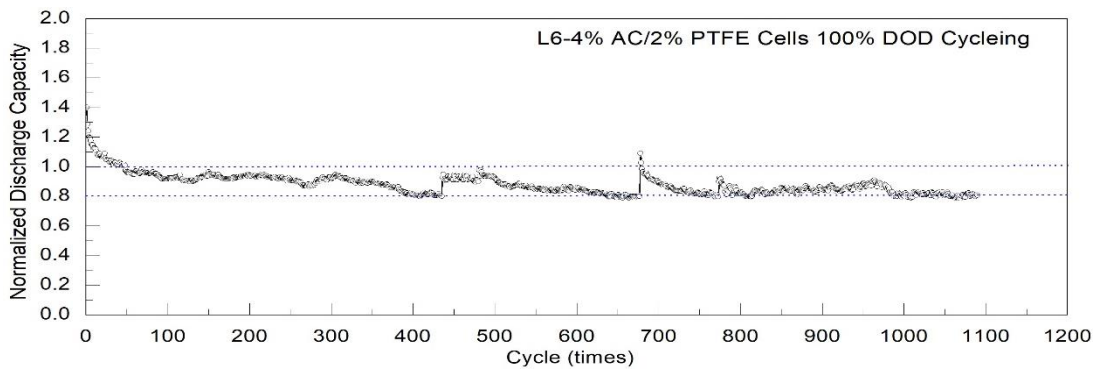


Figure 29. Eirich el1 mixer mixing cells have 1090 maximum cycles

The rotor speed of the Eirich EL1 mixer is set at 1920rpm, suggested by the manufacture according to the materials properties. It is worth noted that the sliding and ball milling like effect of the tilted mixing pan benefits the mixing process. This is outstanding compared to other mixers. Mixing time would be 20-30 minutes for one single standard batch. A quick visual check may be applied to give an idea of the bulk uniformity of the mixed powder.

To get the best mixing result in terms of cycle life, four times(4x) material(2000gram) of the standard batch (500gram) is suggested to mix at once thanks to the big volume of the mixing pan. The cycle life experimental data of negative electrodes made from the 500g and 2000g dry powder mixing is shown in the following figures. Both cells have good cycle life of up to 542 cycles and 782+ cycles respectively with first 2 counter positive plates. The 2000g one has 240+ cycles more and is still cycling over 80% initial capacity.

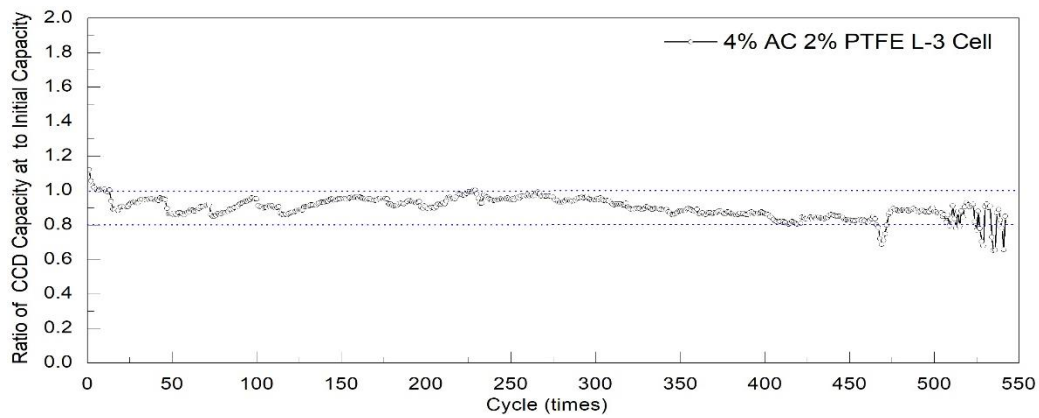


Figure 30. Cycle life of a 500g dry powder mixing cell

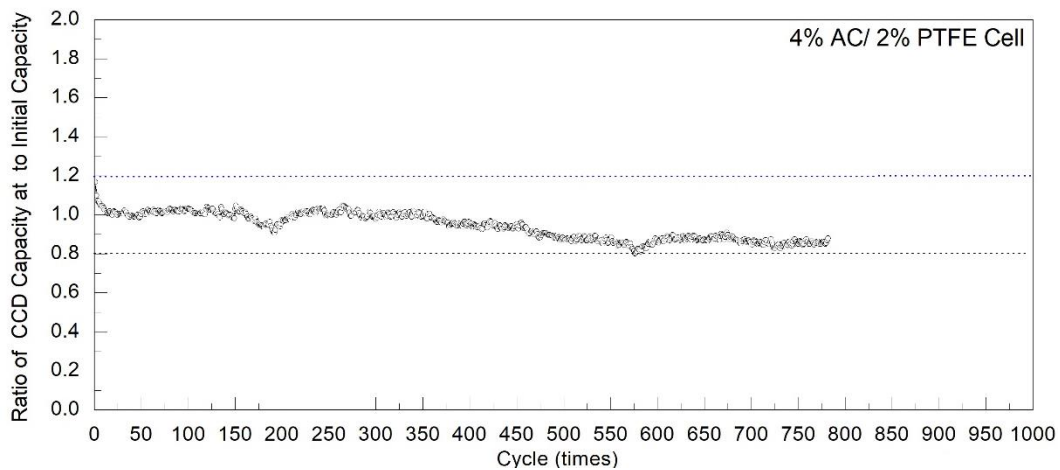


Figure 31. Cycle life of a 2000g dry powder mixing cell (cell still cycling)

6.1.2 Water Amount Optimization

The paste density is dependent on how much water is added into the paste when other components have a set weight/ratio. Therefore, it might be good idea to finish acid addition first and then adjust the paste density by adding water bit by bit. The conventional lead acid battery has 73 ml of water in the standard 500g paste recipe. More water is needed if more carbon in the paste to benefit grid pasting. A starting amount 130ml water is necessary for 4% AC carbon 500g paste after acid addition to sink the reaction heat and stable the mixing quickly. Then adding water in a small amount 5-10 ml once to adjust the density to the requirement. The paste density would be 3.5-4.0 g/ml. The wet paste is easy to do hand pasting but with big chance getting cracks along the grid bars during curing process. A picture shows the cracks on the electrodes after curing in following figure. Wrap the plates piece of paper to keep the moisture during curing process could prevent the cracking. Also note that too wet paste will not stick around the grid bars and the pasting would be fail. The higher paste density is drier, and it is hard to paste the grid manually. It is noted from the experiments that there is less chance cracking in curing process if putting acid into mixed dry powder before water.

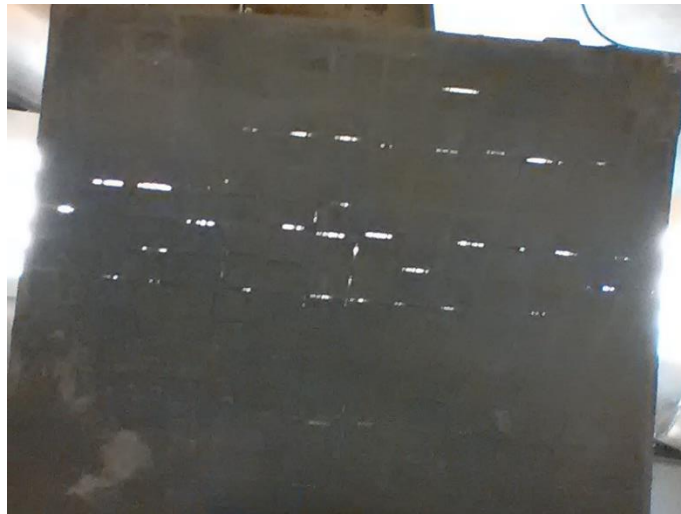


Figure 32. Through plate cracks on a cured negative electrode

6.1.3 Acid (98% H₂SO₄) adding Speed Optimization

Due to the reaction heat, 98% high concentration and, the small volume 30ml of sulfuric acid comparing to the dry powder volume of 320ml in a 500g standard batch, the acid addition speed could be optimized to even the dispersion of acid in the bulk powder and minimize the temperature rise of paste and the addition time. Acid spraying while mixing is a good practice in industrial manufacturing to get a uniform dispersion. In this work a spray droplet likewise dropping addition is applied. The paste temperature is measured by a thermo probe sticking inside the paste. The acid adding average speed ranges from 0.5 to 0.75 ml/min, which counting the paste cooling time. Some cell rate capability testing results are graphed in the following figures.

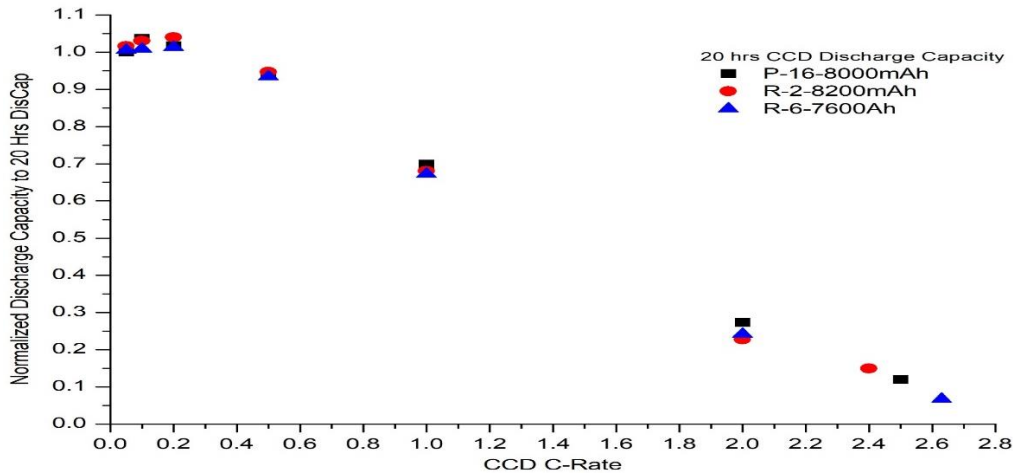


Figure 33. Cell rate capability comparison of 0.5ml/min (R cells) and 0.6ml/min (P cell) acid addition speed

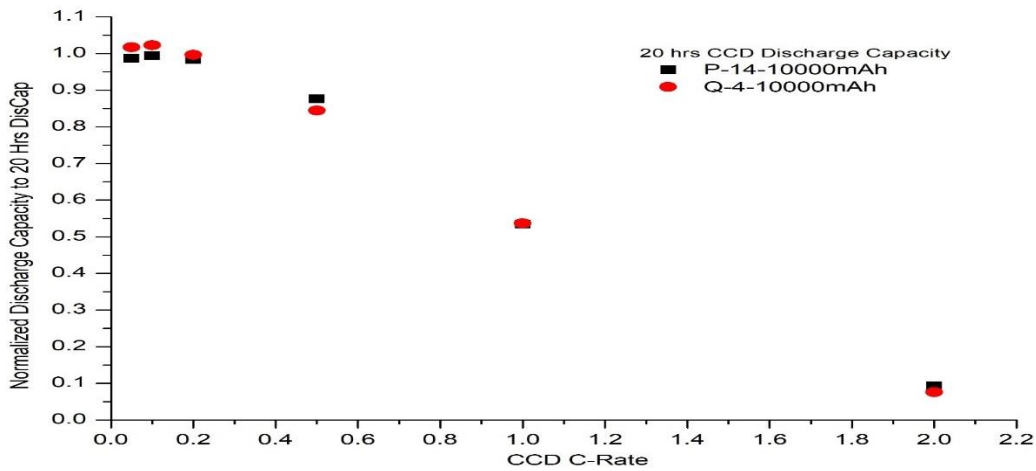


Figure 34. Cell rate capability comparison of 0.6ml/min (P cell) and 0.75ml/min (Q cell) acid addition speed

These two figures show the relation of the normalized capacity and discharge rate (discharge current) of cells at 0.05/0.1/0.2/0.5/1.0/2.0/2.6C₂₀ mA, C is the 20 hours capacity. It indicates for cells with similar C₂₀ capacity, such as P-16 and R-2,6, have very close normalized capacity despite that their difference on acid addition speed in paste preparation. So do cells P-14 and Q-4. This could suggest that for the time saving the acid addition speed can be as high as possible with good temperature rise control in paste mixing.

6.2 Optimization of Carbon Additive of Negative Electrodes

It is generally believed that carbon additive in negative paste can improve the electrode performance. In the lead acid battery manufacturing activated carbon, carbon black or graphite are one of the components of the paste expanders. The function of them is limited to give a little improvement of the paste conductivity. There are still a lot of work needed to be done to select the right type of carbon and find out the dose of the carbon in the paste for high performance and long cycle life application. This work will focus on the test on activated carbon as negative paste additive to extend negative electrode cycle life. Choosing activated carbon is because of its high surface area, good conductivity and low cost. The other carbon materials will be the substitutes working as either the essential or an extra additive.

The testing activated carbon (AC)'s characteristics reads in table 1.2. Following the designed experiment recipe showing in table 1.1, three different AC wt%: 1%, 4%, 8% will be tested with the whole procedure mentioned in before chapter. As the expectation the AC could function as /like an organic expander to set a uniform distribution of spongy lead during charging process and PbSO₄ in the discharging. Or AC can function as a supercapacitor- electric double layer energy storage place just like it works in supercapacitors. And it also could function as a Pb electrochemical redox reaction site/as a substrate: like the skeleton lead Pb on the Pb current collector but with extreme high surface area. All these functions indicate that the more AC into the paste the more benefits to the negative electrode performance. But in experimental practice the cell tested with paste including 8% wt of AC had very low discharge capacity, the active mass PbO utilization is less than 10% at the 1/3-7-hour rate, which is not usable in practice for energy storage.

In contrast the 1% and 4% wt of AC cells have the similar active mass utilization comparing to the conventional lead acid battery cells at all tested hour rates. Refer to the table below.

Table 3. PbO Utilization of 4%AC cells and Conventional cell

Tested Cells	C20 (mAh)	PbO Loaded(g)	PbO Utilization (%) at Different Discharge Rate				
			0.05C20	0.2C20	0.5C20	1C20	2C20
4% AC Cell 1	10000	74.84	57.2	52.9	41.6	25.2	5.8
4% AC Cell 2	12000	84.6	60.96	50	32.96	18.3	7
Conventional Cell	11000	88.38	54.29	50.4	39.2	27.2	Not tested

According to the discussion above, the 4% wt is chosen as the optimized amount of carbon including in the negative paste recipe. Any wt% between 4% to 8% will be considered as a substitute. A mixed 4%wt AC and 2%wt carbon fiber, 6% wt carbon additive in total, had tested in the negative paste. It demonstrated a promising rate capability and cycle life; especially the 100% DOD. Depth of Discharge cycle life has improved from 325 cycles without the carbon fiber to 852 cycles with the carbon fiber when tested in the cell with double positive electrodes. It seems the AC and carbon fiber combination additive has a very positive effect in terms of cycle life of negative electrodes.

Intending to improve the rate capability with the high conductivity carbon black 600JD and graphite, which are used in Lithium ion battery as a conductive agent, it had been mixed into the negative paste at the amount 2% wt each to do the test. The result is similar to the 8%wt AC including the paste coming out with less than 10% PbO utilization. It is not useful in practical energy storage. Then a combination of 2% wt AC and 2% wt 300J carbon black was mixed in the negative paste. The cells made from these negative electrodes with 2%wt carbon black and 2% wt AC had been tested. The capacity is very low at a low hour rate and the PbO utilization is as low as the 8%wt AC paste cells. Then another negative electrode fabricated from the paste including a carbon combination of 3.5%wt AC and 0.5%wt of Super P carbon black. The discharge test result says it has similar PbO utilization as 4%wt AC cells. Therefore, it seems that too much carbon black has a negative effect on the discharge capacity of the negative electrode. The 300/660 JD carbon black would be out of the negative paste recipe for this work.

All in one the optimized carbon additive would be the 4% wt AC and 2% carbon fiber combination to reach the best cycle life. To improve the internal electrical conductivity the 300/600 JD carbon black is not a good choice. The Super P carbon black could be added with an amount more than 0.5% wt. The effect of Super p carbon black and the graphite will be tested more in future work.

6.3 Binder Selection in Negative Paste

There is no binder agent used in the negative electrode of the conventional lead acid battery. It is cautioned against using a binder because of the extra cost and uncertain impact on the battery performance. Experimental practice makes it evident that a binding agent is necessary for the successful integrity of the paste and grid. A set of pictures took from experiment in the following figure shows the dramatical difference of testing negative electrodes with and without binders.



Figure 35. Negative electrode without binder (right) after 20 cycles and with PTFE as binder (left) after

This contrast in the pictures verifies that the PTFE binder is necessary and crucial in terms of negative electrodes with a high percentage of carbon additive to reach a long cycle life. It also indicates that large amounts of carbon decrease the adhesiveness of the paste. The carbon paste adheres to lead grids very poorly, which is one of the challenges of adding extra carbon into paste. The PTFE emulsion is first introduced, and it works perfectly to extend the cycle life of negative electrodes.

Different binders such as CMC/SBR combination was mixed into negative paste and tested as well. The result shows that it doesn't work as well as the PTFE emulsion. Some paste shed off the grid leading to a shorter cycle life than PTFE paste. This happens because CMC has a low stability

when immersed inside sulfuric solution for a long time. The pictures in the following figure illustrates the performance difference of the PTFE and CMC/SBR binding agent in negative paste. This suggests PTFE emulsion would be a better binder than CMC/SBR for negative electrodes of a lead acid battery system. For sure it will have more binders suitable for this application, but regarding the low cost and easy access of PTFE, it is the best choice at this point. With concern to the poor conductivity of PTFE material, the amount of usage in the paste were tested too. The weight percentage %wt has been lowered from 10.8% to 2%. But this change didn't affect cells rate capability significantly. Hence 2%-10.8% wt is a safety range for PTFE emulsion addition as a binder in negative electrode paste.

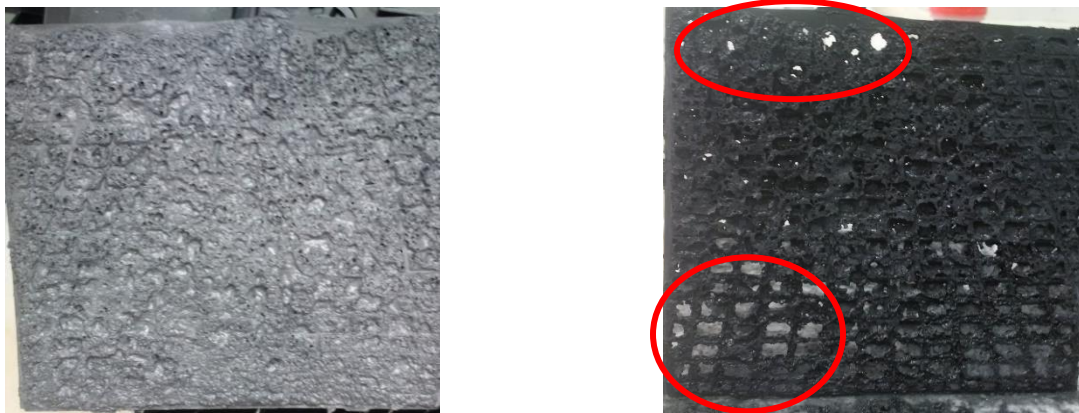


Figure 36. Negative electrode with PTFE after 1090 cycles (right), and with CMC/SBR after 100 cycles (left); red circle area showing the left holes due to paste shedding off

6.4 BaSO₄ Amount Affects Cycle Life

It is well known that the barium sulfate functions as a nucleating agent for lead sulfate crystal formation and growing in the negative electrode discharging process in a lead acid battery. The small sized barium sulfate particles, in the order of 1 μm or less, work like tiny seed crystals and are well distributed into the plate paste volume through powerful mixing processes. When the lead acid battery starts discharging, the lead sulfate produced will form crystals taking barium sulfate particles as nuclei and grow bigger thanks to the isomorphism between BaSO₄ and PbSO₄ crystals. Thus, the distribution of lead sulfate crystals will be as uniform as barium sulfate particles through the whole active material volume on the electrode. This homogeneous distribution of lead sulfate can be reduced to lead particles active material efficiently and contributes to the even distribution of lead particles during charging process. And vice versa this will benefit the next discharge-charge cycle leading to a long cycle life of lead acid batteries.

It is reasonable to believe that more barium sulfate in the negative electrode paste would benefit the electrode cycle life performance according to the barium sulfate nucleating effects. To check this out two negative plates with double doses of barium sulfate in the paste were tested out. The cycle life test result is presented in the following figure.

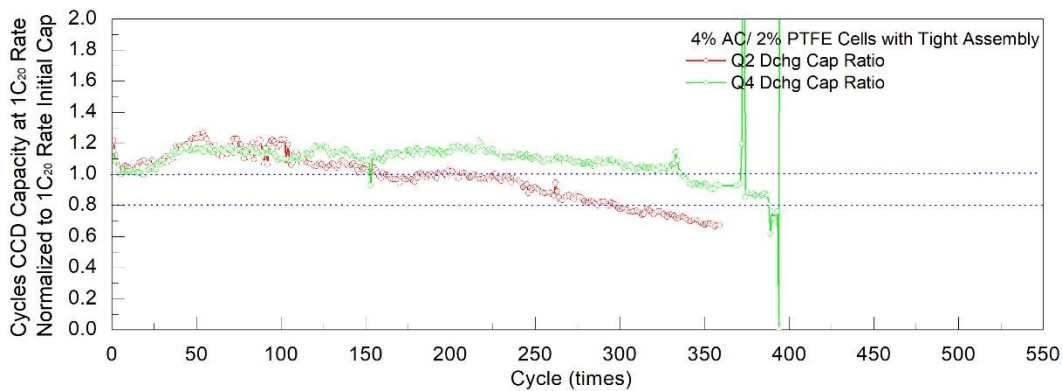


Figure 37. Cycle life of two cells with double dose of BaSO₄ in Negative plate on 100% deep cycling

As read from the above figure, these two cells have 298 and 379 cycles before capacity decreasing to 80% of the initial steady capacity respectively. On contrast, the other two cells were tested on same conditions except having only single dose of barium sulfate in the negative plate paste. Their cycle life are 453 and 507 cycles respectively, presented in following figure.

This comparing test suggests the cell with double dose barium sulfate has a 30% lower cycle life than the one with single dose barium sulfate. It reveals some information about the barium sulfate effect in terms of cell cycle life on deep cycling operation. Through it is too early to conclude that too much barium sulfate will be detrimental to the cell's cycle life, the standard single dose 0.8% wt of barium sulfate will be applied in future experiments.

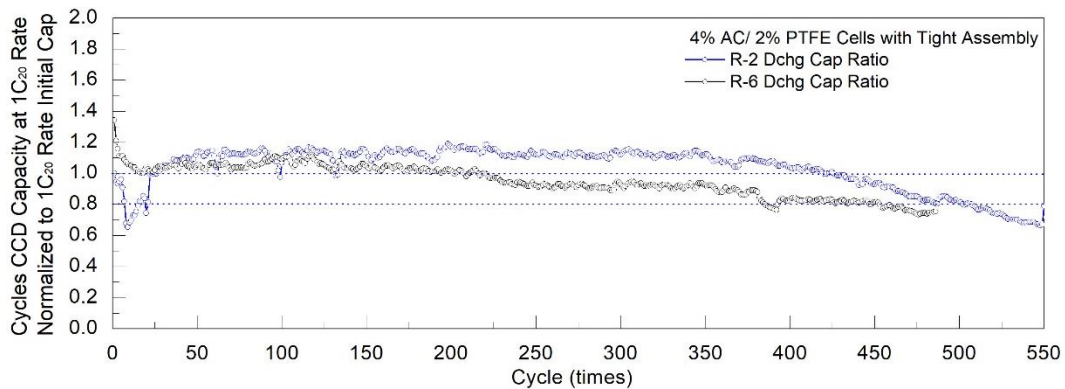


Figure 38. Cycle life of two cells with single dose of BaSO₄ in Negative plate on 100% deep cycling

6.5 Formation Protocol Optimization

As mentioned before the cured lead monoxide PbO paste plates needs a formation process to turn them into functional negative electrodes. The first step during formation is to electrically charge plates. The charge current will reduce the all Pb (II)-related materials electrochemically to metal Pb with a porous matrix structure in the paste. Then a discharge step may carry out and recharge the plates/cells back again. Sometimes it requires a few more cycles to verify the plates initial capacity and performance. The formation protocol is dependent on the battery applications and could be adjusted to find the most energy and time efficient way to do it.

Three formation protocols, presented in tables following, have been tested on 6 cells which have negative plate paste from the same preparation batch

Table 4. Formation protocol 1

Step Number	Step Process	Time (m:s:ms)	Cut off Vol(V)	Cur(mA), Capacity Depended
1	CC_Chg	300:00:00	2.75	300
2	CC_Chg	1440:00:00	2.75	500
3	CC_Chg	900:00:00	2.75	600
4	CC_Chg	600:00:00	2.75	500
5	CC-DChg	60000000:00	1.9	3000
6	CC_Chg	1200:00:00	2.75	600
7	CC_Chg	1200:00:00	2.75	300
8	CC-DChg	60000000:00	1.8	3000
9	CC_Chg	600:00:00	2.75	600
10	CC_Chg	900:00:00	2.75	300
11	Rest	30:00:00		
12	CC-Chg	120:00:00	2.65	300
13	Rest	60000:00		
14	Stop	CC: constant current; Chg: charge; DChg: Discharge		

Table 5. Formation protocol 2

Step Number	Step Process	Time (m:s:ms)	Vol(V)	Cur(mA), Capacity Depended
1	CC_Chg	1440:00:00	2.4 (cut off)	200
2	CV_Chg	900:00:00	2.4	50 (cut off)
3	CV_Chg	60:00:00	2.4	20 (cut off)
4	Rest	20:00		
5	CV_Chg	60:00:00	2.4	20 (cut off)
6	Rest	20:00:00		
7	CV-Chg	60:00:00	2.4	20 (cut off)
8	Rest	60:00:00		
9	CC-DChg	120:00:00	1.8 (cut off)	200
10	Rest	60000:00		
11	Stop	CC: constant current; CV: constant Voltage; Chg: charge; DChg: Discharge		

Table 6. Formation protocol 3

Step Number	Step Process	Time (m:s:ms)	Vol(V)	Cur(mA), Capacity Depended
1	CC_Chg	1440:00:00	2.4 (cut off)	200
2	CV_Chg	300:00:00	2.4	80 (cut off)
3	Rest	60:00:00		
4	CC-DChg	120:00:00	1.7 (cut off)	500
5	Rest	20:00		
6	Cycle	Start step 1; Cycles count 3		
7	Stop	CC: constant current; CV: constant Voltage; Chg: charge; DChg: Discharge		

The protocol 1 is used for the first 5 testing cell sets in this work. The water loss is severer than the cells during the formation with the other 2 protocols. The charging-discharging figure of one of the cells using formation protocol 1, shown below, presents that the high cut off voltage causes the cell to be charged in the gas evolution stage during constant current charge process. This gassing stage is the period of the cell voltage arising steeply and flattening at 2.5-2.6 V on the Voltage to Capacity curve.

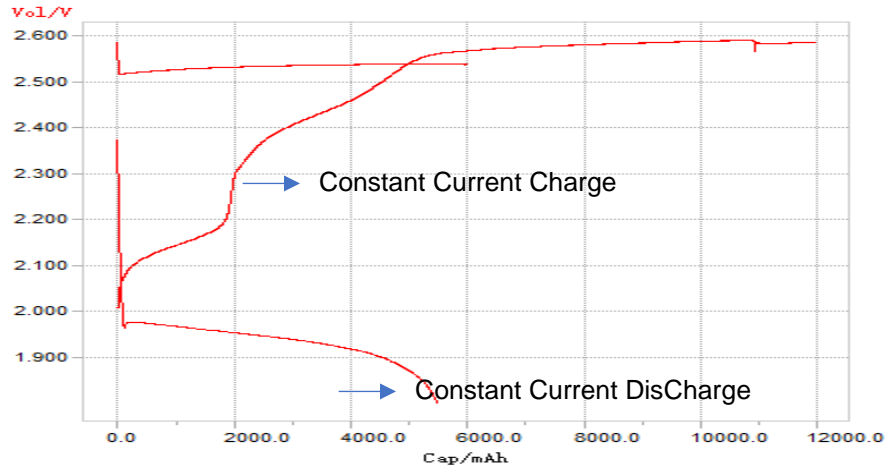


Figure 39. A cell voltage to capacity curve during formation cycle with protocol 1

To minimize the gas evolution during formation, protocol 2 and 3 with lower constant current charge cut off voltage, 2.4 V, were tested on 3 other cells from the same paste. The cell voltage to capacity curves are presented in the following figures. The two charge curves in these figures indicate that 2.3V cut off voltage during constant current charge could be the beginning of the gassing stage for these 4% AC paste plates. According to this observation the 2.3 V cut off voltage for constant current charge step of formation and cycling tests will be an optimized set voltage for all 4% AC paste plates. And it is also the cut off voltage for constant voltage charge step. The current setup in constant current charge step would be dependent on the load of paste on the plates.

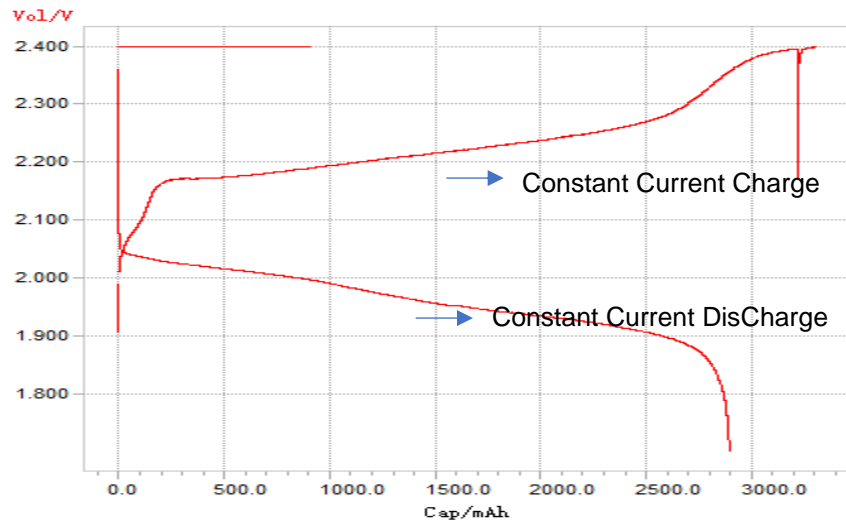


Figure 40. A cell voltage to capacity curve during formation cycle with protocol 2

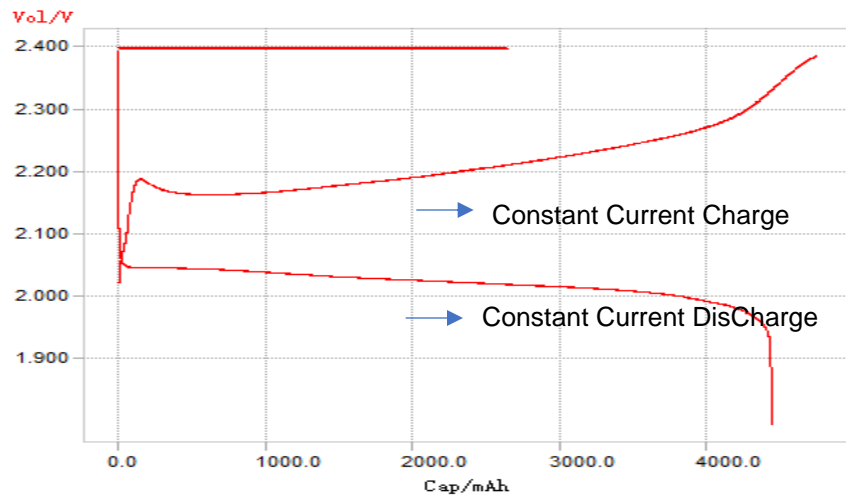


Figure 41. A cell voltage to capacity curve during formation cycle with protocol 3

6.6 Optimization Summary

Following the experimental procedure and the observations from the finished tests, a few optimizations can be made. First, regarding the negative plate paste recipe, 4% activated carbon plus 2% carbon fiber combination is more promising in terms of cycle life. The binding agent is necessary and PTFE emulsion is the best choice so far. Barium sulfate is essential but can not be overdosed.

Secondly, during paste preparation a powerful and efficient mixer to make a uniform dry powder is crucial, which is fundamental to have a promising performance. Enough material loading and mixing time are also important to maximize the mixing effect. Acid addition speed is mostly depended on the mixing paste volume and its temperature control. For a batch loading 1500g - 2000g a 0.5-0.75l/min speed is reasonable to limit the paste temperature below 65 °C with air draft cooling in the lab. Water amount is adjusted according to the finished paste density which is 3.5-4.0 g/cm³. A starting amount 130ml is needed for a 500g batch. Water can be added before or after acid. Adding acid first could contribute to easy paste density control and a crack-free paste on the plate surface.

Thirdly, the constant current charge cut off voltage would be set at 2.3V during the formation or performance test stage. This setting will hinder the gas evolution at the negative electrode side. Proposal formation and cycle test protocol are listed below.

Table 7 Proposal formation protocol

Step Number	Step Process	Time (m:s:ms)	Vol(V)	Cur(mA), Capacity Depended
1	CC_Chg	6000:00:00	2.30 (cut off)	20 hours rate
2	CV_Chg	300:00:00	2.3	100-130 (cut off)
3	Rest	30:00:00		
4	CC-DChg	120:00:00	1.75 (cut off)	20 hours rate
5	Rest	20:00		
6	Cycle		Start step 1; Cycles count 3	
7	Stop		CC: constant current; CV: constant Voltage; Chg: charge; DChg: Discharge	

Table 8 Proposal cycle test protocol

Step Number	Step Process	Time (m:s:ms)	Vol(V)	Cur(mA), Capacity depended
1	CC_Chg	6000:00:00	2.30 (cut off)	2 hours rate
2	CV_Chg	300:00:00	2.3	100-130 (cut off)
3	Rest	10:00:00		
4	CC-DChg	120:00:00	1.75 (cut off)	1-hour rate
5	Rest	10:00		
6	Cycle		Start step 1; Cycles count 2999	
7	Stop		CC: constant current; CV: constant Voltage; Chg: charge; DChg: Discharge	

7. Comparison to Conventional LAB Cell

7.1 Extended Cycle Life

The cells carry out cycling tests after formation to evaluate their life cycle performance. The test protocol is the one showing in the table presented above. In comparison, a cell from a conventional deep cycle battery carried out this cycle test too. It is well known that most lead-acid batteries designed for deep discharge applications can only survive 300 to 500 cycles under these 100% DOD (depth of discharge) operating conditions. This conventional cell cycled 473 cycles before failing. The experimental cell with 4% AC negative electrode and 2 conventional positive electrodes assembly is having 1090 cycles and is still cycling. The cycling comparison of these two cells is shown in the following figure. It indicates that the 4%AC cell has a significantly longer (2.3 times) cycle life in deep-discharge applications.

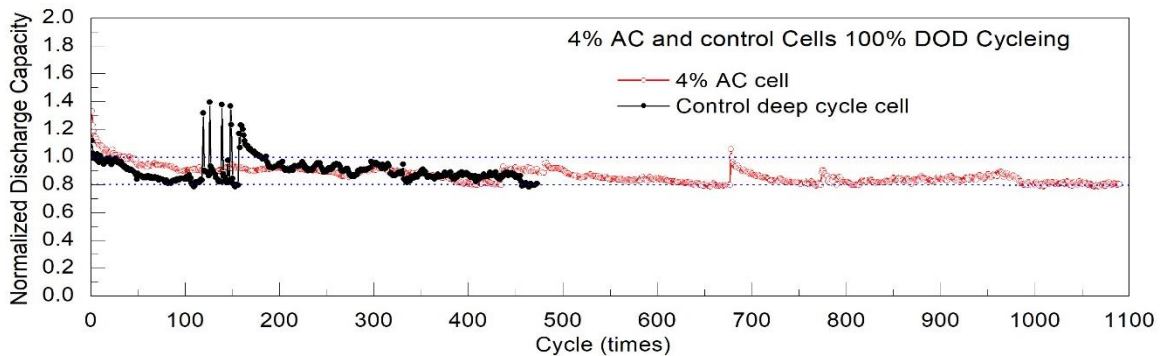


Figure 42. 4% AC cell and a conventional cell cycle life comparison

7.2 Competitive Low Cost

As well, the long cycle life of 4% AC negative electrodes has a competitive low manufacturing cost compared to the conventional one. Since both type of negative plates has a similar amount of lead in the forms of grids and PbO powder as the major material, and lead is the most expensive ingredient, the cost of the negative plates doesn't change much even with a little extra cost of a small amount AC and PTFE emulsion. The 4% AC lead carbon cell has the exact same positive electrodes and other components as the conventional one. The total cost of a cell with the same capacity will not rise by much. A figure below presents the 4% AC cell cost of materials for a 12wh cell (2VX6Ah@C20) is

LCB: 0.07907 us\$/wh, is only **0.93%** higher than **LAB: 0.07834 us\$/wh**. (Cost estimated on the material market in China and converted to US\$ at exchange rate 1:6.33 on April 30, 2018).

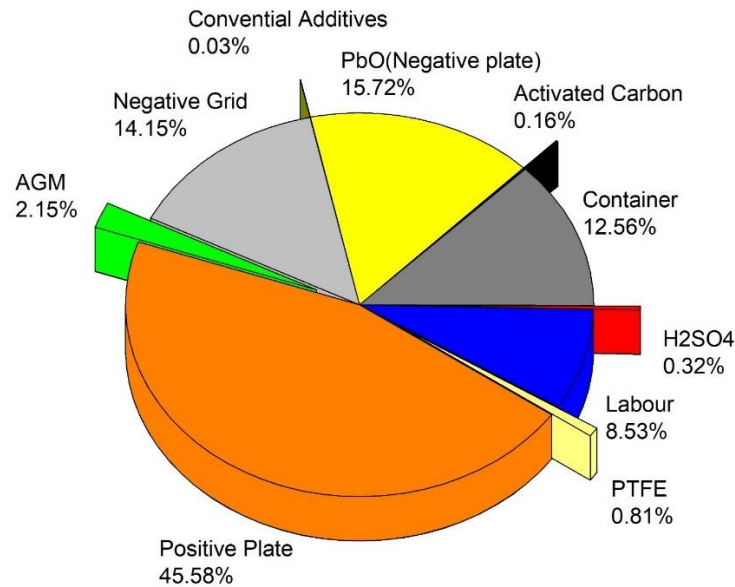


Figure 43. Detailed materials cost in a LCB cell

With the same manufacturing procedure and equipment as a conventional lead acid battery's the total cost will retain the same as the conventional one. The life cost of a lead carbon battery will be much lower than the conventional one thanks to the extended cycle life. This would set LCB, lead carbon battery, at a very competitive position on the energy storage market.

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