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A thesis submitted in partial satisfaction
of the requirements for the degree
Master of Science in Chemical Engineering

by

Wendi Li

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ABSTRACT OF THE THESIS

Model Prediction for Lead-acid Batteries with Super-capacitor Anodes

by

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Master of Science in Chemical Engineering
University of California, Los Angeles, 2016
Professor Yunfeng Lu, Chair

The existing prediction models used in Battery Management Systems for lead-acid batteries have difficulty in applying to lead-acid batteries with changed structure or materials. Four different lifetime prediction models of lead-acid batteries to be mainly used as energy storage for PV systems, EV, and hybrid EV are examined. Equivalent full cycles to failure, “Rain flow” cycles were counting, the Schiffer weighted Ah-throughput model and recurrent Neural Network-based Model are discussed for the accessibility and availability of the lead-acid batteries with the supercapacitor anode (hybrid batteries). By examining the mechanism, “Rain flow” cycles counting, the Schiffer weighted Ah-throughput model and recurrent Neural Network-based Model were three models could be used in hybrid batteries. By comparing the accuracy of these models in photovoltaic systems, the Schiffer weighted Ah-throughput model and recurrent Neural Network-based Model were selected to be the promising solutions. A modification of the Schiffer weighted Ah-throughput model is discussed based on the chemical mechanism. All possible effects are taking into account in the modified model based on the detailed analysis. Further estimations can be simply conducted through the factory data sheet of hybrid batteries.

The thesis of Wendi Li is approved.

Selim M. Senkan

Robert F. Hicks

Yunfeng Lu, Committee Chair

University of California, Los Angeles,

2016

DEDICATION

First of all, my deepest gratitude goes first and foremost to Prof. Yunfeng Lu, my supervisor, for his constant encouragement and guidance. He has walked me through all the stages of this thesis. Without his consistent and illuminating instruction, this thesis would not have reached its present form. He gave me a fantastic chance for pursuing my master degree in UCLA and provided everything I needed in doing research in these two years.

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Above all, I also own my sincere gratitude to my friends and my classmates who offer me their help and times in listening to me and helping me work out my problems during the challenging course of the thesis.

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Thank you to you all!

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Chapter 1
Introduction

1.1 Model prediction for batteries in Battery management systems

Batteries are one of the largest energy storage devices that fulfill the daily demand of energy consumptions from human beings. To make batteries work more efficient and safe, the concept of Battery Management Systems (BMS) is introduced by scientists [1-5]. The standard definition of BMS is:

“The primary task of a Battery Management System (BMS) is to ensure that optimum use is made of the energy inside the battery powering the portable product and that the risk of damage inflicted upon the cell is minimized. This is achieved by monitoring and controlling the battery’s charging and discharging process.” [3]

Dating back to 1990s, BMS varied in performance and applications. Although BMS are much more complex in designing, we can directly address BMS into three categories: Distributed, Centralized and Modular. Distributed BMS need a board to install to each cell being the only communicator between cell and controller. Centralized BMS connect to whole cells by multiple wires while modular BMS contains a few controllers connecting to a particular number of cells [3].

- In an individual application, the function of BMS can be divided into eight parts:
- Data Management: Data is analyzed by BMS to improve performance by controllers.
- Communication: Communication between BMS and each cell connected.

- Charge Management: Control the charge-discharge process in applications.
- Protection: Shut down part of systems when dangers are detected.
- Cell Balance Management: Control the temperature and pressure of different cells.
- SOH: State of Health: The lifetime of cells.
- SOC: State of Charge: The charge statues of cells.
- SOB: State of Backup: The backup statues of the system.

Although BMS always works a whole component, take electric vehicles as example (Fig. 1) we can improve the performance of systems by increase the efficiency in terms of these functions.

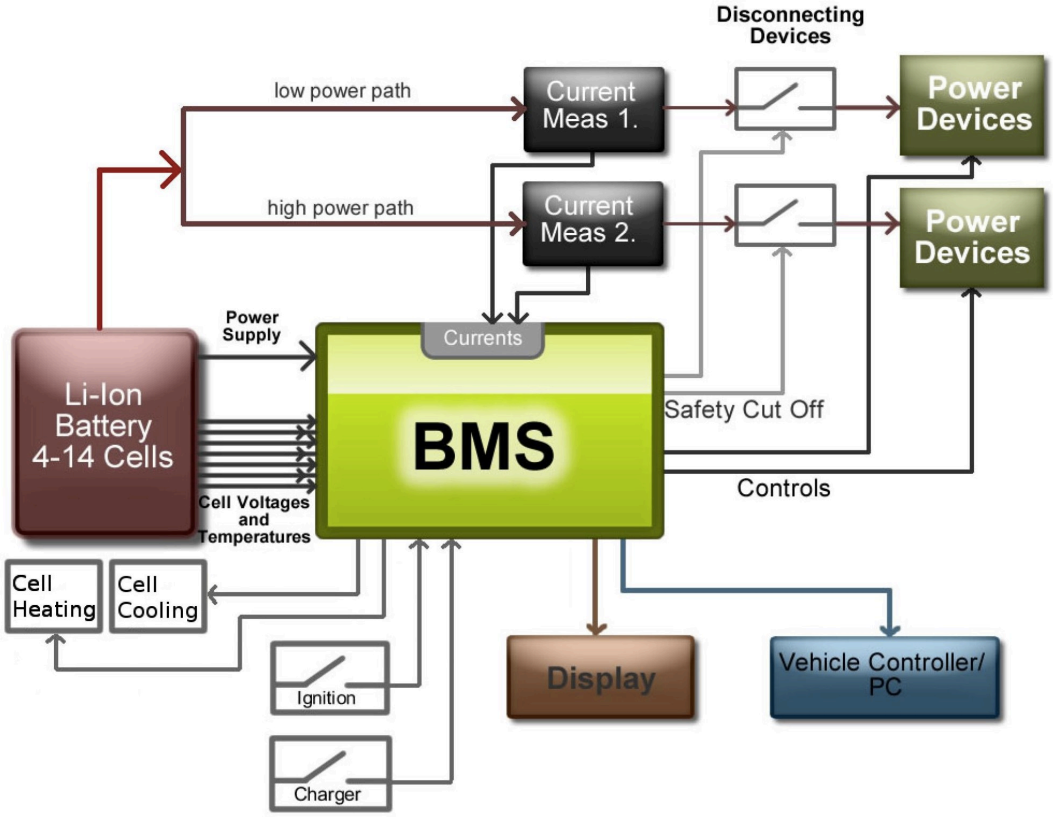

Fig. 1 A common circuit of electric vehicles

The SOH and SOC are two key factors related to the lifetime of batteries. Because it is costly and difficult to measure the batteries in operating, most of BMS use simulation approach in SOH and SOC part. Therefore, the model prediction is an important task in this area.

To develop a useful BMS, especially more accuracy SOH and SOC prediction, it is essential to clarify the types, the operating conditions and the potential dangers of batteries. Hence, lets move on to introduce lead-acid batteries.

1.2 Mechanisms of Lead-acid batteries and its applications

The history of lead-acid batteries dates back to 1860, the Frenchman Gaston Planté (1834–1889) invented the first rechargeable battery that using lead material. The principle of this kind of batteries is one of the well-known lead-acid chemistry: Half-cell reactions are described as following [5,6]:

For the positive plate:

$$PbO_2 + 3H^+ + HSO_4^- + 2e^- \xrightarrow{disch\arg e} PbSO_4 + 2H_2O$$

For the negative plate:

$$Pb + HSO_4^- \xrightarrow{disch\arg e} PbSO_4 + H^+ + 2e^-$$

The total cell reaction:

$$PbO_2 + Pb + 2H_2SO_4 \xrightarrow{disch\arg e} PbSO_4 + 2H_2O$$

And the reaction reverse when charging process.

In the discharge process, both sides of plates become $PbSO_4$ and the electrolyte (H_2SO_4) converts to the water. This process passes two electrons from negative plate to the positive plate through the external circuit.

In the charge process, the reaction reverse and the negative plate consists of Pb while positive plate consists of PbO_2. The electrolyte solution suffers dilution by the water. [7]

In total, a regular single lead-acid battery can provide 2.1V-2.3V. It is easy to use a clear sketch to show a full battery:

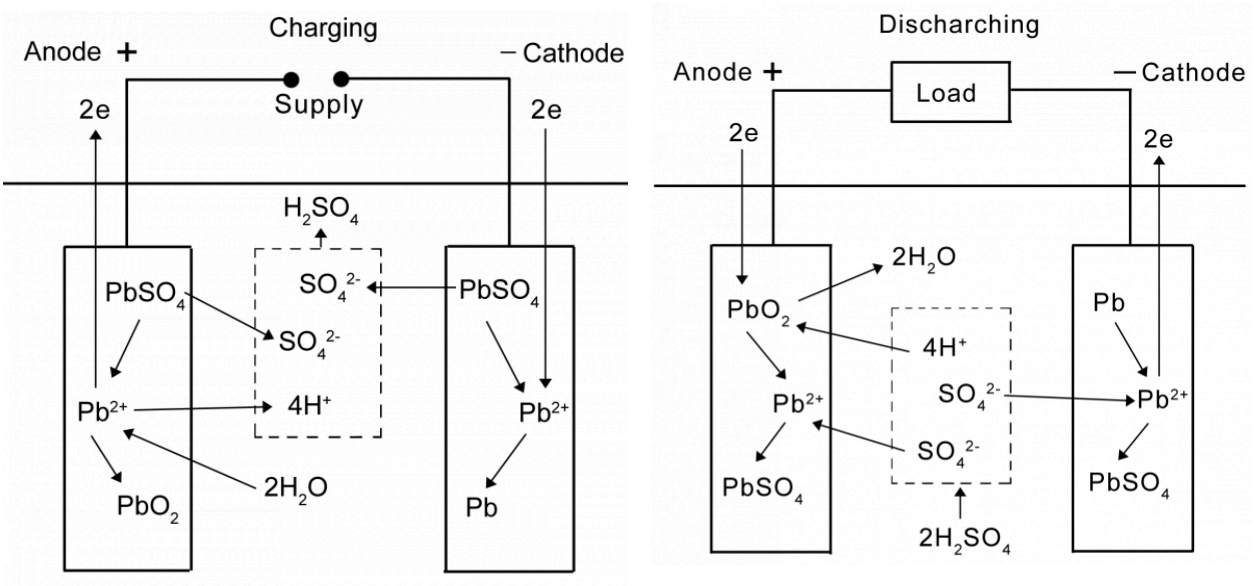

Fig. 2: Sketch of Charging and discharging process of lead-acid batteries.

Lead-acid batteries have become one of the world largest consumptions in recent years due to the rapid development in vehicle and photovoltaic systems. Comparing to other batteries, lead-acid batteries have the following features:

The advantages of lead-acid batteries	**The disadvantages of lead-acid batteries**
Low cost.	Very heavy and bulky.
Reliable. Over 140 years of development.	Danger of overheating during charging
Robust. Tolerant to abuse; Tolerant to overcharging.	Typical columbic charge efficiency only 70% (can be improved by special designs)
Indefinite shelf life if stored without electrolyte	Must be stored in a charged state once the electrolyte has been introduced

Low internal impedance.	Typical cycle life 300 to 500 cycles
Can deliver very high currents.	Not suitable for fast charging

Table 1. Features of lead-acid batteries

As sketch shown in Fig.2, the structure of batteries can be demonstrated using sheet lead plates for electrodes and dilute sulfuric acid as electrolyte. Although the chemical process and structure of lead-acid batteries are simple, modeling a full-cell is still hard due to the ageing process happened in every part of batteries. In the modeling, we should select essential features from the certain application of batteries. [10,11]

Lead-acid batteries have tremendous usage in our daily life ranging from load leveling by electrical companies to small batteries used in hand tools. Common applications are:

[a] Automotive and traction applications

[b] Standby/Back-up/Emergency power for electrical installations

[c] Submarines

[d] UPS (Uninterruptible Power Supplies)

[e] Lighting

[f] High current drain applications

[g] Sealed battery types available for use in portable equipment.

[h] Grid scale energy storage

A straightforward classification is “Deep” for that used for electric vehicles and “Float” for that used for emergency lighting applications. And a number of simulations are based on this rough classification. [11-14]

1.3 Motivation of the research – Lifetime issues of lead-acid batteries

With the usage of lead-acid batteries, it is important to know the potential problems. One key factor causes explosion or failure of batteries is ageing. The most direct way to evaluate batteries and avoid dangers is measurement by experiments that is obviously time-consuming and costly. However, we couldn’t measure batteries all the time when they under operating conditions. Therefore, precise and low cost evaluation methods are needed.

Thanks to the modern computing technologies, a promising way to avoid these potential dangers is modeling and simulation. With certain initial data or only a little measurement, one can predict the health of batteries by modeling. Note that the lifetime of batteries is a complicated result of working conditions that requires people to consider as much factors as possible to obtain the best prediction results. Hence we need to select the specific features happened within the battery carefully. [15,16]

Along with the large applications of lead-acid batteries, series research developed comprehensive models for each application. [17-20] And some scientists reported analytical models for manufacturer’s data[21-24] while others considered better designed circuits in BMS. A number of scientists considered specific chemical mechanism in their model. [26-33] According to Ref.[25], the existing battery models have drawbacks such as requiring intensive computation due to high complexity or not applicable for electrical circuit design and simulation. According to proposed models, among different applications, potential problems encountered in lead-acid batteries include:

Gassing: Gassing of the battery leads to safety problems and to water loss from the electrolyte. The water loss increases the maintenance requirements of the battery since the water must periodically be checked and replaced.

Electrode damage: The lead at the negative electrode is soft and easily damaged, particularly in applications in which the battery may experience continuous or vigorous movement.

Stratification: Sulfuric acid is a heavy, viscous liquid. As the battery discharges, the concentration of the sulfuric acid in the elecotrolyte is reduced, while during charging the sulfiric acid concentratin increases. This cyclicing of sulfuric acid concentration may lead to stratification of the electrolyte, where the heavier sulfuric acid remains at the bottom of the battery, while the less concentrated solution, water, remains near the top. The close proximity of the electrode plates within the battery means that physical shaking does not mix the sulfuric acid and water. However, controlled gassing of the electrolyte encourages water and sulfuric acid to mix, but must be carefully controlled to avoid problems of safety and water loss. Periodic but infrequent gassing of the battery to prevent or reverse electrolyte stratification is required in most lead acid batteries in a process referred to as "boost" charging.

Sulfation: At low states of charge, large lead sulfate crystals may grow on the lead electrode as opposed to the finely grained material which is normally produced on the electrodes. Lead sulphate is an insulating material.

Loss of active materials: The loss of active material from the electrodes can occur via several processes. One process that can cause a permanent loss of capacity is the flaking off of the active material due to volumetric changes between lead and lead sulphate. In addition, Improper charging conditions and gassing can cause shedding of active material from the electrodes, leading to a permanent loss in capacity.

Corrosion: . Corrosion means a conversion of the lead grid of the positive electrode into different lead oxides that form a layer with a complex structure on the grid.

Spillage of the sulfuric acid: If sulfuric acid leaks from the battery housing it poses a serious safety risk. Gelling or immobilizing the liquid sulfuric acid reduces the possibility of sulfuric acid spills.

Freezing: If the battery is at a low discharge level following the conversion of the whole electrolyte to water, then the freezing point of the electrolyte also drops.

Depending on which one or more of the above problems is of most concern for a particular application, appropriate assumptions should be made when using different models.

Most of these models are based on the simple traditional lead-acid batteries. Hence they are not suitable for the material or component change in the lead-acid batteries due to the internal and external features changes. Only Seldom focused on the state-of-art lead-acid batteries with improved structures or materials. [35,36]

Hence, in this thesis, four promising models are described and modified according to the negative material change of lead-acid batteries. Two models are traditional models for the rough estimation and two others are more complicated by modeling in chemical and non-chemical way respectively.

Chapter 2
Methods

2.1 Target system

As introduced in the above chapter, selecting specific target system is the first step of lifetime prediction. Conventional lead-acid batteries are studied well since the rapid development of vehicle industry. However, with increasing demand of safety and energy supply performance, new types of lead-acid batteries are developed within these years. Thanks to the state-of-art material engineering technology, scientists found that conventional anode or cathode material can be improved or replaced by other materials.

One of the promising ways is to replace or add negative electrode by a supercapacitor. [33-35] And other components remain the same. It is normally called hybrid batteries due to the combination of lead-acid batteries and supercapactiors. A few applications have been published such as Ultrabattery [34] shows:

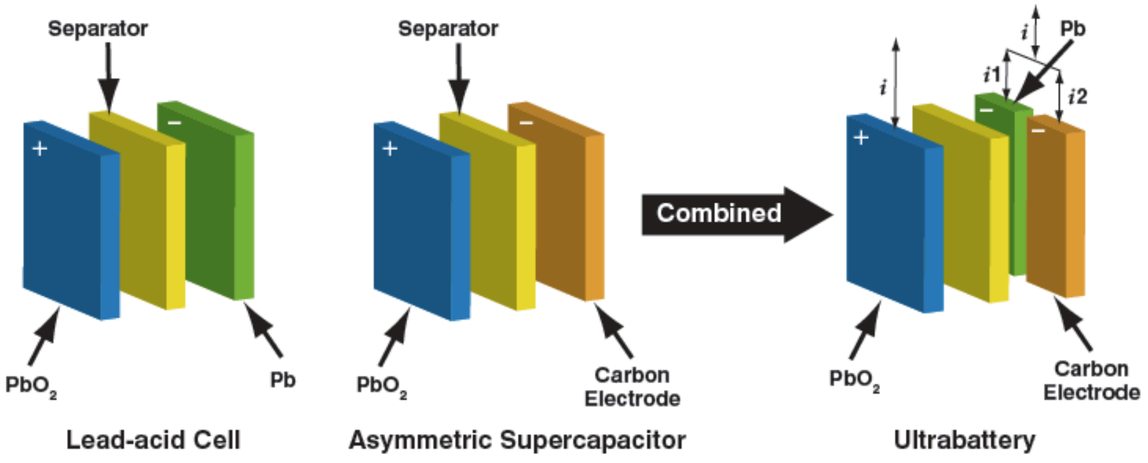

Fig.3 Scheme of the Ultrabattery [35]

The ultra-battery is a hybrid energy-storage device, which combines an asymmetric supercapacitor, and a lead-acid battery in one unit cell, taking the best from both technologies without the need for extra electronic controls. The capacitor will enhance the power and lifespan of the lead-acid battery as it acts as a buffer in discharging and charging. [35] Some research analyzed this hybrid battery in different ways [37-38]. Most the hybrid batteries been subjected to a variety of tests. Some of results show that the discharge and charge power of the ultra-battery is about 50% higher and its cycle-life is at least three times longer than that of the conventional lead-acid counterpart. [36] Obviously, the performance of hybrid batteries is considered to be much better than single lead-acid batteries. Therefore, models that are suitable and accurate in traditional lead-acid battery may not fit hybrid batteries well.

Although there are some proposed models for hybrid lead-acid systems. Most of them focus on the certain applications and operating modifications. It is essential to simplified this approach and find a general lifetime prediction model for this hybrid batteries. Therefore, a simple model are used in this thesis as figure 4 shows:

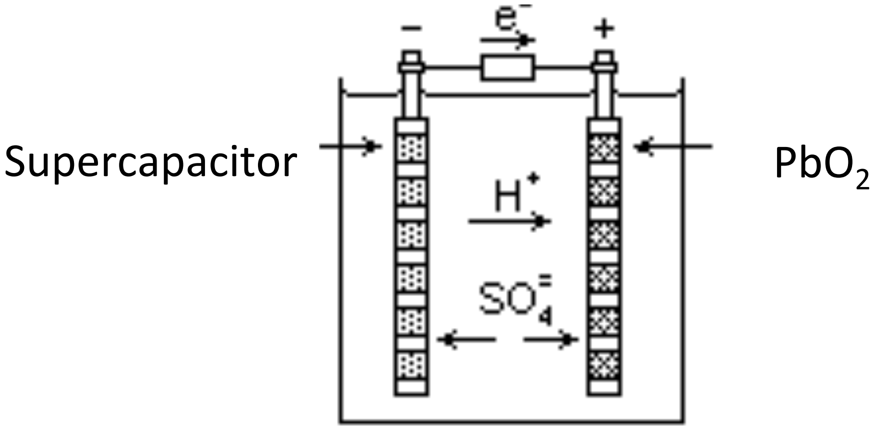

Fig. 4: New type of lead-acid batteries.

Comparing to conventional lead-acid batteries, we assume that this type of lead-acid batteries have the following features:

Flexible Voltage: Anode is a supercapacitor with voltage from -0.4V to 0.6V (vs SHE) while conventional one is about -0.36V.

High Capacity: New type of batteries has the capacity of 100 mAh/g while conventional one is about the half (~70 mAh/g).

Anti-Corrosion: Replace lead plate with anti-corrosion material can reduce the aging danger of batteries hence increase the lifetime.

Stable Material: The negative electrode is replaced by stable materials resulting in less sulfation process occurs. Hence the degradation process reduced in electrode.

Half-cell reaction: Only PbO_2 reaction happened:

$$PbO_2 + 3H^+ + HSO_4^- + 2e^- \xrightarrow{discharge} PbSO_4 + 2H_2O$$

None reaction happens in negative electrode with supercapacity function:

$$Supercapaciter \xrightarrow{discharge} 2e^-$$

Full cell reaction reduces to:

$$Supercapaciter + PbO_2 + H_2SO_4 \xrightarrow{discharge} PbSO_4 + 2H_2O$$

As mentioned at the end of last chapter, many models can be applied to traditional lead-acid batteries. However, few of them aim at a system with replaced electrode (for example: anode). This gives opportunities to us discover if we can predict the lifetime using conventional model. Even though only one component of batteries changed, features we used in the prediction may change a lot. Traditional models that fit lead-acid batteries well may not work anymore on this type of batteries.

In this thesis, we tried to model the new type of lead-acid batteries with modified conventional models, taking into account the changes on the anode (voltage, capacity, corrosion, structure etc.) Additionally, we gave suggestions to the future study on this type of batteries according to the preliminary prediction results.

We will discuss these differences and challenges in the 2.3 sections.

2.2 Methodology

The ageing mechanisms of lead-acid batteries have been published in some previous studies. Models vary with different assumptions and principles, specifically, vary with the definition of lifetime (we will discuss it in the next sections).

Most commonly, batteries lose their “life” because of the loss of capacity that caused by the ageing processes. The main aging processes can be described as five parts [46-48]:

1. Corrosion: Corrosion means a conversion of the lead grid of the positive electrode into different lead oxides that form a layer with a complex structure on the grid.
2. Acid stratification: Acid stratification builds up during charging and discharging and results in a gradient of the acid concentration. Acid stratification itself is not an ageing effect, but it accelerates ageing.
3. Gassing: Gassing is by far the most important side-reaction in lead- acid batteries. It occurs when the cell voltage is so high that hydrogen evolves at the negative electrode and oxygen at the positive electrode.
4. Sulfation: Lead sulfate ($PbSO_4$) is created during discharging at both the positive and the negative electrode. During charging, the crystals are converted back to the respective active material. Crystals that cannot be removed during standard charging cannot

contribute any longer to the capacity of the battery.

5. Degradation: Degradation is a general term for processes that result in a capacity loss due to changes in the active mass structure and composition.

Although all five effects happen since battery started to work, external parameters have great effects on these processes as following table shows:

	Gassing	Corrosion	Sulfation	Acid Stratification	Degradation
Temperature	X	X			X
Charge Method	X	X	X	X	X
DoD			X		X

Table 2: Relations between external and internal processes.

Hence, we should consider carefully when we taking all effects into account. Note that in some models one or more effects are ignored due to the modeling mechanism.

In the next section, we will discuss different modeling methods and its principles. Certain modification will be made according to our target systems.

2.3 Models for lifetime prediction

In this work, four different methods to estimate the lifetime of the batteries have been considered. They are explained in the following sections:

2.3.1 Equivalent full cycles to failure

This method is introduced as a good simulation and optimization tools in batteries (not only lead-acid batteries) [37]. Instead of conventional SOH lifetime, a new definition of the end of the battery lifetime is described. It uses specific number of cycles [38] replacing IEC standard one [39].

The lifetime consists of adding the charge cycling:

$$Z(t+\Delta t)=Z(t)+\frac{|I_{disch\arg e}(t)|\bullet\Delta t}{C}$$

Where the $I_{discharge}(t)$ is the absolute value of the discharge current,C is the nominal capacity of the single battery. The lifetime is the time when Z(t) reached Z_{IEC}.

This is the most straightforward way to estimate lifetime that only using discharge current data.

2.3.2 "Rain flow" cycles counting

This model is more complex than previous one. This algorism is introduced by Downing[40]. It also called "rain flow" because of the method of counting cycles. It was further developed in the later research [41].

This model uses the Depth of Discharge (DOD) as main factor to count charge/discharge cycles where Z_i corresponding to each range of the DOD for a year. One can set up intervals of DOD and obtain the number of cycles to failure (CF_i) by measurement. Then lifetime can be calculated as following:

$$Lifetime = \frac{1}{\sum_{i=1}^{m} \frac{Z_i}{CF_i}}$$

Take m=10 as example, we can got sample cycles to failure as following:

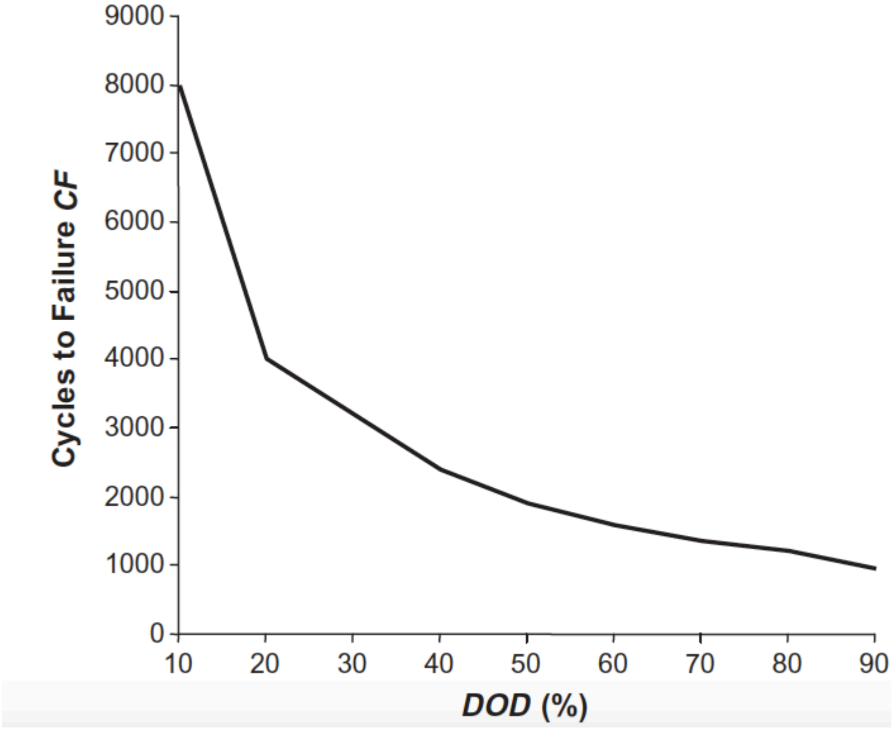

Fig. 5. The cycles to failure vs DOD. [41]

This model is more precise but still doesn’t take other factors into account except DOD.

2.3.3 The Schiffer weighted Ah-throughput model

This model is always called Ah-throughput approach due to its basing on the assumption that the working conditions are much more severe than testing conditions. Hence the actual Ah throughput is multiplied by a weight factor that reflects the operating conditions. In this way, not only this type of batteries but also any other batteries can be modeled by using different data sheet information. In this model lifetime is defined as following:

Lifetime is the time remained before a battery's available capacity reduced to 80%. Which is usually known as SOH in BMS.

SOH is defined as the percentage of nominal capacity. The commonly used method is given by

$$\mathrm{SOH} = \frac{\text{nominal capacity} - \text{loss of capacity}}{\text{nominal capacity}}.$$

Nominal capacity: It is the average capacity when batteries are discharged at 0.2C within one hour of being charged for 16 hours at 0.1C and 20± 5°C. Unit: Ah (Ampere Hours).

As mentioned in the previous section, this method considered all possible aging process from chemical-physics point of view. The loss of capacity is calculated by mining initial battery capacity C(0) by corrosion capacity $C_{corrosion}(t)$ and degradation capacity $C_{degradation}(t)$ as following shows [54]:

$$C_{remaining}(t) = C(0) - C_{corrosion}(t) - C_{\deg radation}(t)$$

Model algorism:

Note that the remaining capacity is defined as the capacity of the battery in the fully -charge state in a certain discharge current rate (typically 10h current).

A simplified flow diagram of the model is shown in the Figure 6.

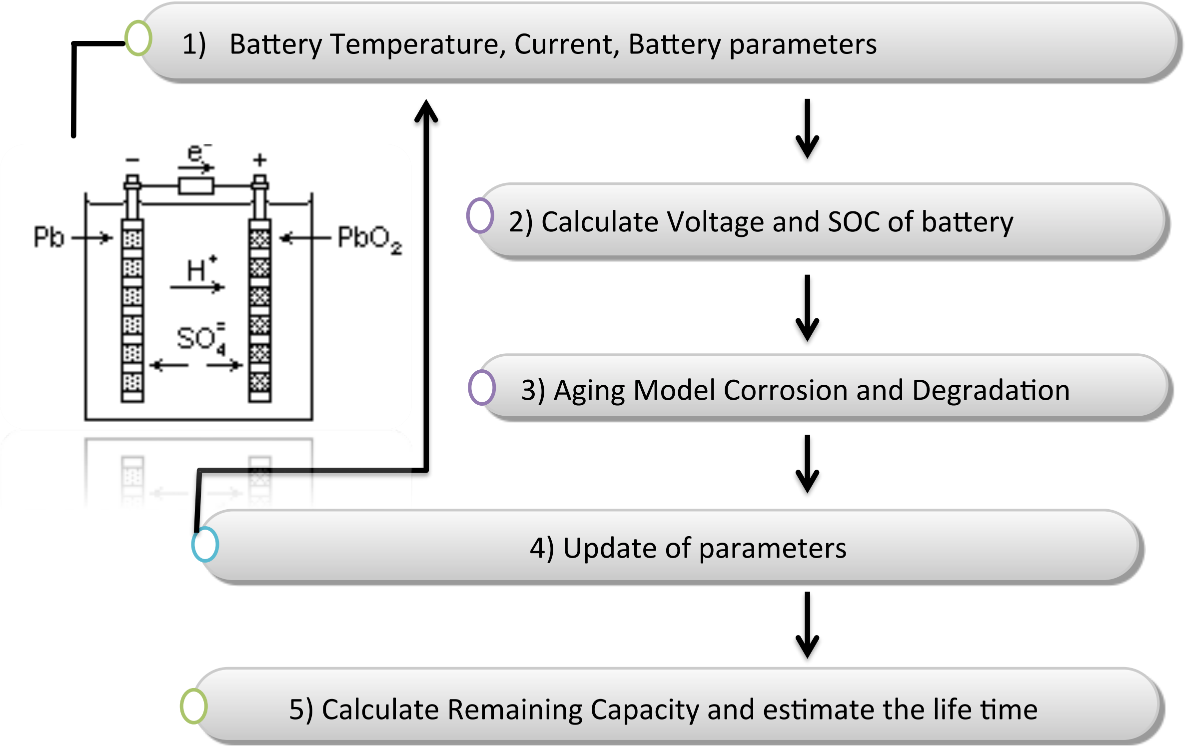

Fig. 6. Flow diagram

At the first simulation step, the voltage and SOC are calculated according to the input data. Based on the Shepherd equation, voltage can be calculated. And SOC is the difference between the total battery current and gassing current. [54] We can calculate gassing current by using Tafel approximation. Once we have voltage and SOC of a certain time, aging model of corrosion and degradation can be adopted. By obtaining the capacity of corrosion and degradation, the remaining can be calculated according to the above equation. Then the main output SOH can be calculated. Because the condition of batteries is changing along with time, the time related step should be calculated again and updated to determine the initial parameters.

Because most of the chemical-physical process is temperature related, we use the simplest approach that the battery temperature is equal to the ambient temperature in a certain time. As mentioned in the [54], the temperature effects become minor when the current integrated time by time in high average current.

In some equations, the functions are chosen to represent real physical or chemical processes. It is hard to explain the reason or determine the most accurate functions. Hence most choices are made according to the experience from related work and the data from the measurement.

This model is much more complicated than previous two because all possible aging effects are taking into account. It is import to know the mathematic relations between chemical or physical process and input data. Hence we talk about a brief introduction of the choice of aging model of degradation and corrosion. Detailed calculation process and modification of this model will be discussed in the next sections.

Degradation capacity:

As mentioned in the above sections, degradation is a common process happened in batteries resulting in a capacity loss. Because the structure and composition changes in batteries, the active material reduces or failures to react. Most possible causes of degradation are shedding (mechanical lose from gassing), sulfation (irreversible sulfate crystals) and softening (loss of electronic conductivity). According to the former research, the gassing process is the major reason of the mechanical stress changes hence the degradation of active material. This is the reason why battery lifetime always depended on the depth-of-discharge (DOD) during cycling. The Larger DOD leads to larger gassing, hence resulting in higher the mechanical stress. Based on these theories, the degradation capacity can be calculated as following with the IEC cycles that can be found in the factory data sheet.

$$C_{\deg radation}(t) = C_{\deg radation,\lim it} \bullet \exp[-C_z \bullet (1 - \frac{Z(t)}{1.6 \bullet Z_{IEC}})]$$

where $C_{\text{degradation,limit}}$ is the degradation limit (the capacity at the end of lifetime, we can take it as 80% of initial capacity) ,C_z is chosen as 5 when taking into account boundary conditions. Factor 1.6 is chosen because the weighted effective number of cycles of aging without corrosion is approximate $1.6Z_{IEC}$.

The Ah throughput is related to SOC, discharge current and the acid stratification. Hence the weighted number of cycles without corrosion Zw(t) is calculated as:

$$Z(t+\Delta t) = Z(t) + \frac{|I_{disch\arg e}(t)| \bullet f_{soc}(t) \bullet f_{acid}(t) \bullet \Delta t}{C}$$

where f_{soc} is SOC related factors and f_{acid} is acid stratification related factors. This is based on the Equivalent full cycles to failure model but taking into account influence of SOC and acid stratification.

Determination of f_{soc}:

Degradation increases with increasing DOD of batteries (with decreasing SOC of batteries). Both of the magnitude of the lowest SOC and the length of time when batteries under low SOC have impact on the lifetime. Hence SOC weighted factor can be calculated by the following equation:

$$f_{soc}(t) = 1 + (C_{soc,0} + C_{soc,\min} \bullet (1 - SOC_{\min}(t)|_{t_0}^{t})) \bullet f_I(I,n) \bullet (t - t_0))$$

where t_0 is the time of the last full charge, $SOC_{min}(t)$ is the minimum SOC since the last full charge, Csoc,0 represent the increase in f_{SOC} with time at SOC=0 and $f_I(I,n)$ is the current factor.

Because the small discharge currents will lead to larger lead sulfate crystals, the lead sulphate crystals will grow with each cycle and stay in the electrodes. This process depends mainly on the current at the beginning of the discharge after a full charge. A boundry factor of 0.9 is artificially setup to determine the number of bad charges. If the battery is charged to SOC that higher than 0.9 and lower than 1, it is counted as bad charge. The current factors hence calculated by the number of bad charges (n) as following shows:

$$f_I(I,n) = \sqrt{\frac{I_{10}}{I(t)}} \bullet \sqrt[3]{\exp(\frac{n(t)}{3.6})}$$

where I_{10} is defined as 10h current ($I_{10} = C_{10}/10$) in discharging.

When the SOC reaches about 1, the number of bad charges resets to 0. And when maximum SOC is still between 0.9 and 1, we can count n as follows [53]:

$$n(t+\Delta t) = n(t) + \Delta n = n(t) + \frac{0.0025 - (0.95 - SOC_{\max})^2}{0.0025}$$

Determination of f_{acid}:

The stratification increases with the increasing inhomogeneous led by low current. Although high current also affects stratification process, we ignore the influence of high current because its insignificant impact. Hence the acid stratification factor can be modeled by the increased or decrease factor (fplus and fminus) that calculated by SOC and gassing current (detailed can be found in the discussion sections).

$$f_{acid}(t) = 1 + f_{stratification}(t) \bullet \sqrt{\frac{I_{10}}{I(t)}}$$

and

$$f_{stratification}(t + \Delta t) = (f_{plus}(t) - f_{\min us}(t))\Delta t + f_{stratification}(t)$$

where fplus and fminus are an increase and a decrease of acid stratification, respectively.

With taking into account both factors, the capacity of degradation of active mass can be calculated. Note that this model based on the assumption that non-active materials cannot be converted resulting in reduction of the discharge capacity while all active materials are converted into the charged state during every charge (always fully charged).

Corrosion capacity:

Because the corrosion mostly affects the positive electrode, the influence of negative electrode can be ignored. By adopting the concept of a corrosion "layer" with lower conductivity (grows over the lifetime of batteries), the effect of corrosion can be calculated by counting an effective layer thickness, W , which is undated during each simulation steps. The effective layer is related to the loss of active materials that assumed to be lost from electrode. According to the Ref.[51] the corrosion processes vary with the potential of the batteries. Hence W can be obtained by

$$\Delta W(t) = \Delta W(t - \Delta t) + k_s \Delta t$$

where t is the duration of one time step and ks is the corrison speed parameter that changes with time. Further details will be discussed in the modification sections.

Then the capacity loss by corrosion is:

$$C_{corrosion}(t) = C_{corrosion,\lim it}(t) \bullet \frac{\Delta W(t)}{\Delta W_{\lim it}}$$

where $C_{corr,limit}$ is the limit of the loss of capacity by corrosion and W_{limit} is the corrosion layer thickness when battery reached the end of float lifetime (can be found in the battery datasheet).

Note that the calculation of $C_{corr,limit}$ is based on the assumption that 20% of the capacity decrease at the end of life is caused by corrosion and remaining 80% loss of the capacity is caused by active material loss. The assumption can be found in several studies [43] and proved to be successful in modeling [44,45].

2.3.4 Recurrent Neural Network-based Model

Unlike previous Ah-throughput approach focusing on the chemical or physical relations, recurrent Neural Network-based Model (RRNs) is based on the purpose of explain which and why some key parameters are dynamic and interdependent. Although simple electrical networks can roughly used to model lead-acid batteries, the large amount of battery data becomes costly and time consuming when computing the functions of State of charge (SOC), depth of discharge (DOD), and electrolyte temperature [47-49].

This method uses RNN model working with SOC observer to establish a suitable charge algorithm. According to Ref.[46], two steps are introduced to present a nonlinear mathematical prediction model. In this thesis, only the first step (a design of RNNs to predict terminal voltage and SOC) is discussed while second step (using RNNs results establish tuning procedure of the mathematical battery model parameters) is omitted. In this section, both the mathematical battery model and RNN-based modeling of battery will be briefly introduced.

Mathematical battery model:

As first reported in [50,51], the basic mathematical model equations of lead-acid battery are the following:

$$\frac{dq}{dt} = i, SOC = 1 - \frac{q}{C_0}$$
$$v = E(SOC) - R(SOC^*)i$$

where SOC* is a fictitious SOC that related to the effective SOC, DOD and current discharge rate. C_0 is the rated battery capacity (Ah).

Then

$$E(SOC) = E_0 + E_e \ln(SOC)$$
$$R(SOC^*) = R_0 + R_1 \ln(SOC^*)$$

The SOC* can be calculated:

$$SOC^* = \eta[\sigma(SOC)^2 - \eta \cdot DOD \cdot SOC \cdot (\frac{i}{I_n})^{\delta}]^{-1}$$

where E_0 and R_0 are constant, DOD = 1-SOC, while η, σ, δ, are empirical coefficients, and I_n is a reference current equal to a value representative of the typical usage of a given battery. It is about ten times the value of the rated discharge current. [50] In this way a SOC observer can be obtained as a function of η, σ, δ. Details can be found in Ref.[52]. The related equivalent network of lead-acid battery is shown in Figure 7.

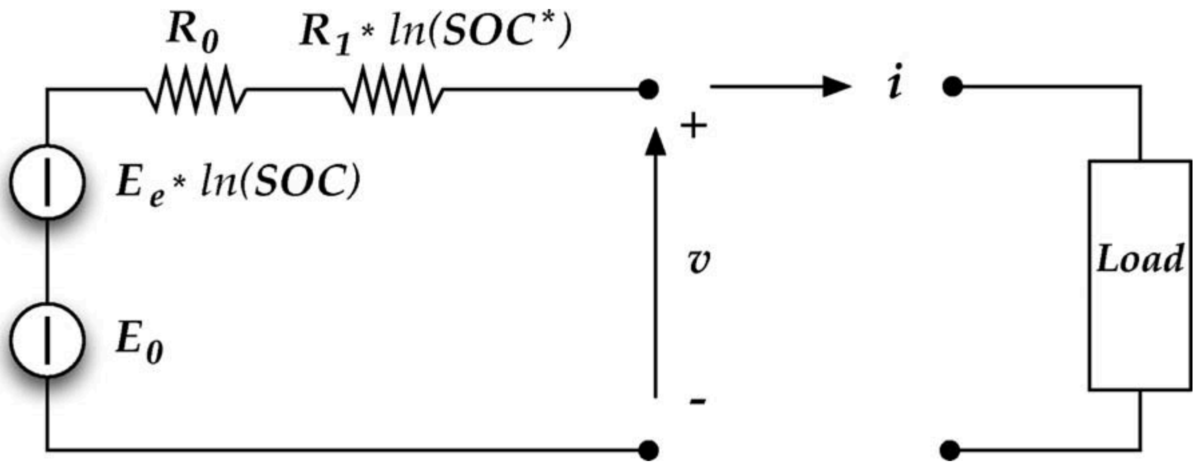

Fig. 7. Equivalent network of lead-acid battery.[47]

RNN-based modeling of battery:

RNNs Model is based on the basic elements of dynamic neural units (DNUs) receive not only external inputs but also the feedback signals from themselves and other neurons. With many interconnected DNUs, a neural network forms the layered configurations. As introduced by [52], an individual neuron aggregates its inputs and output a nonlinear activation function with a threshold. There are tree types of connections: intralayer, interlayer, and recurrent connections.

The intralayer connections: links between neurons in the same layer of the network.

The interlayer connections: links between neurons in different layers.

The recurrent connections: self-feedback links to the neurons.

In order to acquire dynamic learning, the stability of the equilibrium points with decaying transients is important. A scheme of RNN for battery model is shown as follows:

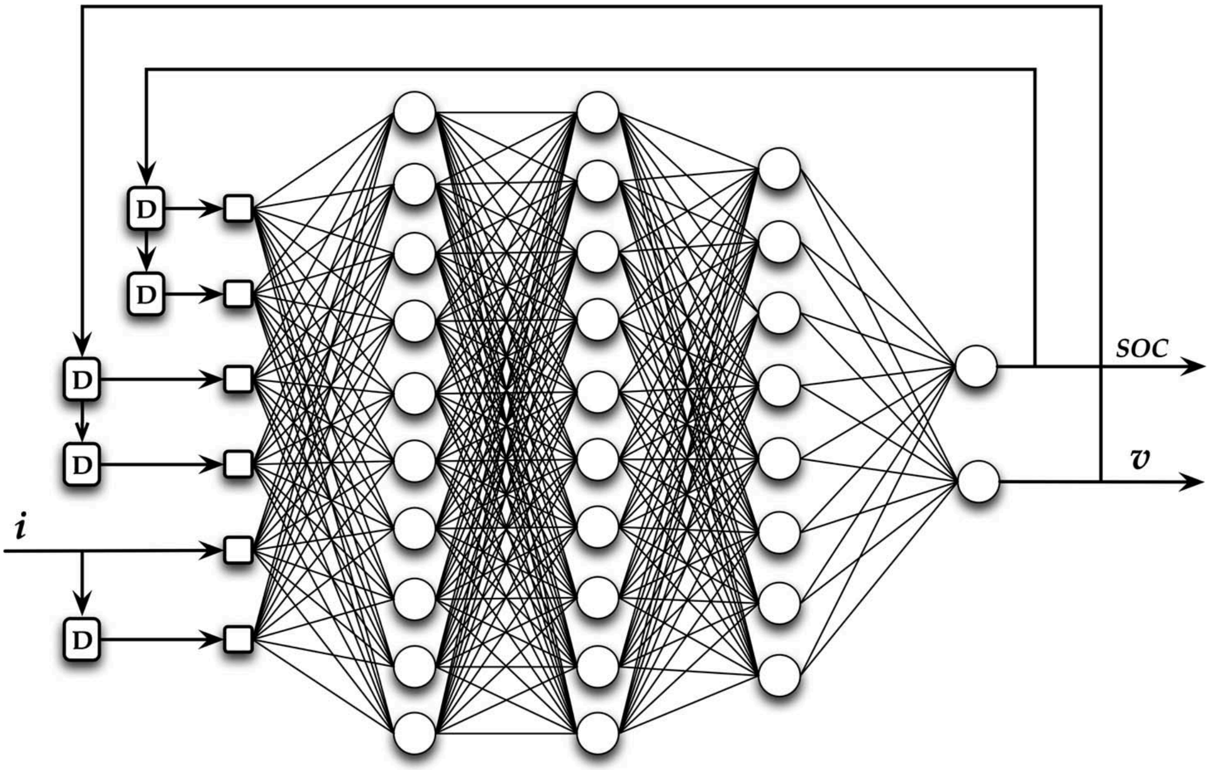

Fig. 8. A scheme of RNNs of lead-acid battery. [47]

The SOC evaluation can be calculated by:

$$SOC(k) = f(SOC(k-1), i(k-1), v(k-1))$$

and battery voltage output equations of RNN are given by:

$$v(k) = g(SOC(k-1), i(k-1), v(k-1))$$

where f and g are nonlinear functions.

RNN modeling is a suitable tool to consider the nonlinear modeling of lead-acid batteries where the charge-discharge processes are concerned. Detailed algorism can be found in the reference [18]. Note that this model is algorism-based which means no chemical process is considered in modeling. This feature let RNNs-based model reach high prediction accuracy only when empirical coefficients are chosen correctly and calculated based on large experiment data.

Chapter 3
Model modification and discussion

3.1 Model comparison and selection

Until now, not any model can be perfect fit all batteries due to the large amount of variables and the complexity of applications. Every model has it pros and cons, choosing the right model is hard but exciting work in the simulation and prediction. In this section, the advantages and disadvantages will be discussed to fit our target system.

3.1.1 Equivalent full cycles to failure

As the most “classic” lifetime prediction models, equivalent full cycles counting model is proved to do not work well in some systems (especially in photovoltaic systems [53]). There are several reasons:

(1) Because the pre-determined parameter is IEC cycles, it is not easy to keep IEC test condition when batteries in working. For example, in the PV systems, the battery’s bank capacity is usually high hence the IEC cycles is usually high, which leads to the IEC cycles in the testing condition is high.

(2) The working condition of batteries is always changing, State of charge, temperature and charging methods may change the charge and discharge currents a lot.

Hence, this model is not suitable in our further predictions.

3.1.2 “Rain flow” cycles counting

The “Rain flow” cycles counting model is more complex than previous model. It takes depth of discharge (DOD) as the main factor to predict lifetime of a battery. However, it is always hard to obtain an accurate DOD or SOC when batteries under working. The disadvantages of the model can be conclude as follows:

(1) The accuracy depends on intervals of DOD. The smaller the interval is, the higher accuracy will be. However, the money and time cost of testing will increase dramatically with the decreasing interval.

(2) In the prediction, only DOD or SOC is the input parameters, which lead to high possibility of wrong prediction due to the difficulty of obtaining SOC in working conditions.

Although it based on simple but powerful theory, a number of studies show the failure of this model [53]. The predict lifetime sometimes can be 10 times of the real lifetime if the systems have large temperature variation like PV systems. However, in other systems, they always have lower battery-bank capacity and there are always backup generators in the system to keep the batteries from staying in a long time in low charge states. Their operating conditions are therefore not so different than those in the standard IEC tests.

Hence this model may be used as a rough prediction in some applications that operating in the stable condition.

3.1.3 The Schiffer weighted Ah-throughput model

As described in reference [54], this model takes into account all effects based on a detailed analysis and understanding of ageing process in lead-acid batteries. In addition, according to [51-54], it works well in renewable energy systems, autonomous power-supply systems and photovoltaic systems.

A comparison between weighted Ah-throughput model and former models in household PV system are shown in the tables using the data of Ref.[53]:

Models	Lifetime prediction
Equivalent full cycles to failure	5.8
"Rain flow" cycles counting	19.1
The Schiffer weighted Ah-throughput model	17.6

Table 3. Battery lifetime prediction (years) for the household PV systems (real lifetime: 6.2 years)

A comparison between weighted Ah-throughput model and former models in alarm PV system are shown in the tables [53]:

Models	Lifetime prediction
Equivalent full cycles to failure	4.4
"Rain flow" cycles counting	16.1
The Schiffer weighted Ah-throughput model	16.1

Table 4. Battery lifetime prediction (years) for the alarm PV systems (real lifetime: 5.1 years)

It is clear to see that both average full equivalent model and "rain flow" cycle counting model failed to prediction the lifetime of lead-acid batteries in PV systems. Both of them have 2-3 times higher predict lifetime than the real one. However, weighted Ah-throughput model obtained better results, which shows much more stability and accessibility in the lifetime prediction of different lead-acid batteries.

3.1.4 Recurrent Neural Network-based Model

The RNN-based modeling of charge-discharge phenomena of the lead-acid battery is a new way to predict lifetime of batteries that used in PV systems, electric vehicles and hybrid electric vehicles. This method relies on the using of soft-computing technics and RNN to model the complex systems. Theoretically, the more parameters used in training RNNs, the more accuracy it will be. Reference [52] shows a successful calculation which results are in good agreement with the experimental data shown in Figure 8.

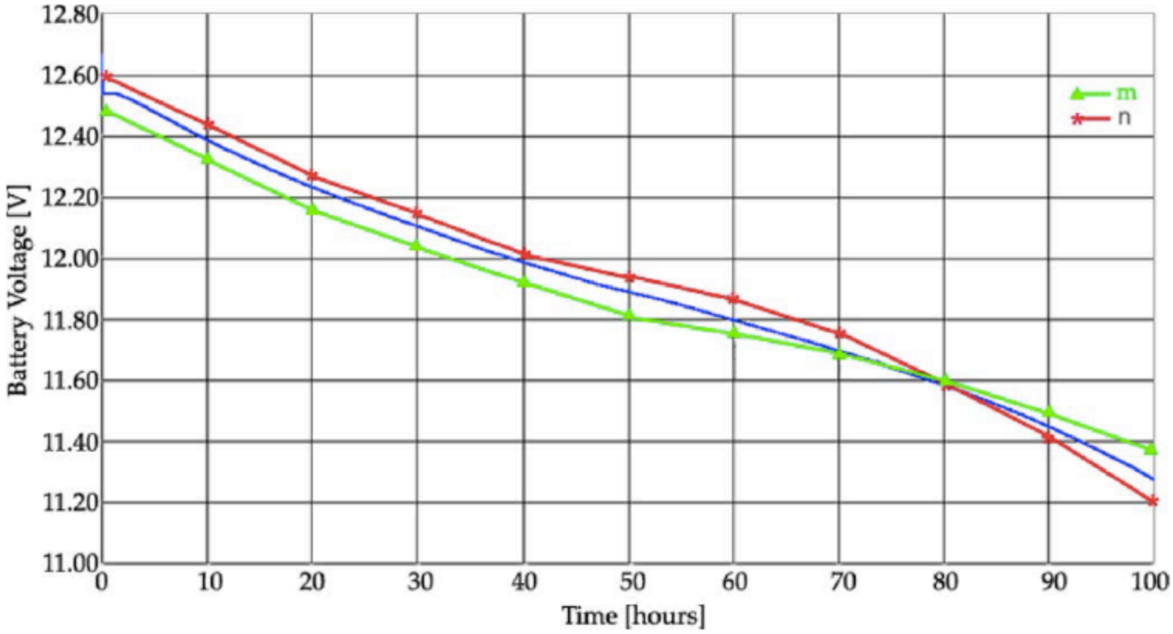

Fig. 8. Simulated curves(n,m) and experimental data at low discharge rate.[52]

And the reference proposed a tuning procedure of the empirical parameters by using selected RNN resulting in better fitting results.

However, it is always hard to select features to train RNNs in real applications. In our target systems, slight modification is needed.

To sum up, we briefly review four models and their accessibility in our target system. The result is conclude in the table：

Models	Target systems	Parameter Complexity	Accuracy	Computational Cost	Modification
Equivalent full cycles to failure	No	Easy	Low	Low	No
“Rain flow” cycles counting	Yes	Easy	Low	Low	No
The Schiffer weighted Ah-throughput model	Yes	Hard	High	Medium	Yes
Recurrent Neural Network-based Model	Yes	Medium	High	High	No

Table 5. Comparison of four Battery lifetime prediction models

Both Equivalent full cycles to failure and “Rain flow” cycles counting models are easy to use but lack of accuracy. “Rain flow” cycles counting could be chosen as a rough calculation in target system due to its low cost.

Both the Schiffer weighted Ah-throughput model and Recurrent Neural Network-based

Model have high accuracy. However, the parameter preparation and computational cost are relatively high in the Schiffer weighted Ah-throughput model. In order to fit this model well in our target systems, further modification are needed. The details will be introduced in the next section.

3.2 Model modification

3.2.1 Modification of The Schiffer weighted Ah-throughput model

Before modification, it is essential to know which part of weighted Ah-throughput model takes into account anode. In other words, we should clarify the relationships between anode and chemical or physical processes in lead-acid batteries. As explained in the section 2.2, five major processes affect the lifetime of batteries. Based on the basic algorism of weighted Ah-throughput model shown in Figure 6, gassing current, state of charge (SOC) and the voltage of cell, should be calculated at first. Then ageing process, corrosion and degradation should be considered. The following modification will follow this order.

Gassing current:

As the significant side-reaction in lead-acid batteries, the gassing process affects batteries' operating current hence the voltages. It reduces the columbic efficiency of batteries. The gassing current increases with increasing battery temperature (Arrhenius law) and with increasing cell voltage (Butler-Volmer process).

This process happens in no matter what electrodes are. Because both sides of electrodes in target system have the similar voltage to conventional one, the same quantitative equation can be employed to calculate gassing current. Specifically, gassing current is calculated by the Tafel approximation due to the high overpotentials:

$$I_{gas\sin g} = \frac{C_N}{100} I_{gas\sin g,0} \cdot \exp(c_u (U - U_{gas\sin g,0}) + c_T (T - T_{gas\sin g,0}))$$

where $I_{gassing,0}$ is the normalized gassing current (100 Ah nominal battery capacity at nominal voltage $U_{gas,sing,0}$) and nominal temperature $T_{gassing,0}$; U is the cell voltage; T is the battery temperature; C_u is the voltage coefficient and C_T is the temperature coefficient. Because most of the parameters in this equation are not relevant to time and temperature, the initial values of these parameters should be carefully considered.

State of Charge (SOC):

As the most important parameter in the calculation, State of Charge stands for the magnitude of charge/discharge state that how many sulfate crystals convert into positive or negative electrode.

Because in target system, the anode is replaced by supercapaciter, only positive plate reaction happens. SoC of 1 means the state where all sulfate crystals converted completely into PbO_2 in the cathode. Therefore, the SOC can be calculated by integrating the current minus the gassing current divided by the nominal capacity:

$$SOC(t) = SOC(0) + \int_0^t \frac{I(\theta) - I_{gas}(\theta)}{C_N} d\theta$$

Cell Voltage:

According to Ref.[54], The cell voltage is calculated by a modified shepherd equations. Four terms should be considered: Open-circuit voltage, open-circuit voltage changes that affected by SOC, voltage changes that affected by ohmic loss and overvoltage that affected by current and SOC. No transient effects are taken into account due to the long time-step evaluation algorism (always larger than 1min). Because no electrode reactions are considered in this calculation, reported equations can be directly employed in the target system. In the charging process, the cell voltage can be calculated as follows:

$$U(t) = U_0 - g(1 - SOC(t)) + \rho_c(t)\frac{I(t)}{C_N} + \rho_c(t)M_c\frac{I(t)}{C_N}\frac{SOC(t)}{C_c - SOC(t)}$$

where U is the terminal voltage of the cell; U_0 is the open-circuit equilibrium cell voltage at the fully-charged state; g is an electrolyte proportionality constant. SOC is state of charge (SOC=1 when fully charged, SOC=0 after discharge of the nominal capacity, SOC < 0 is also possible); I is applied current (I >0 when charge; I <0 when discharge); C_N is the nominal capacity; ϱ_c is effective internal resistance. Mc is the charge-transfer overvoltage coefficient; C_c is the normalized capacity. And for the discharging process, voltage can be calculated at the same way. Note that the parameter used in charges and discharges are different and should be considered respectively.

After obtaining gassing current, state of charge (SOC) and the voltage of cell, the ageing process (corrosion and degradation) can be calculated.

Corrosion:

Corrosion always happened in the positive electrode that lead grids convert into different lead oxides forming a layer with lower conductivity. Reported corrosion capacity calculation are based on the estimation of corrosion voltage from only positive electrode as following (detailed in 2.3.3 section)[55-57]:

$$\Delta W(t) = \Delta W(t-\Delta t) + k_s \Delta t$$

when corrosion voltage is high; And

$$\Delta W(t) = k_s [(\frac{\Delta W(t-\Delta t)}{k_s})^{\frac{1}{0.6}} + \Delta t]^{0.6}$$

when corrosion voltage is low; where W is the effective layer thickness.

Here, corrosion voltage can be determined by the same way as cell voltages:

$$U_{corrosion}(t) = U_{corrosion,0} - a \cdot g(1 - SOC(t)) + b \cdot \rho_c(t) \frac{I(t)}{C_N} + b \cdot \rho_c(t) M_c \frac{I(t)}{C_N} \frac{SOC(t)}{C_c - SOC(t)}$$

where the corrosion voltage $U_{corr,0}$ is a function of the acid concentration. Factor a and b are electrode contribution factor that determined by the experiment.

Not that the in the second term a is the SOC contribution to the electrode. According to [60,61], a can be assumed to be 10/13 because a typical change in OCV from fully charged to fully discharge is 130mV with 100mV from positive electrode and 30mV from negative electrode. And b can be set as 0.5 when considering the ohmic losses and charge factor are equally distributed between the positive and the negative electrode.

Because only positive electrode is considered in the model, there are no differences between conventional model and hybrid model. Therefore, as reported in Ref.[54], the corrosion capacity can be calculated:

$$C_{corrosion}(t) = C_{corrosion,\lim it}(t) \bullet \frac{\Delta W(t)}{\Delta W_{\lim it}}$$

Degradation of active material:

Degradation is a capacity loss process caused by cycling of batteries. Because the specific volume of lead sulfate formed in discharging and that of Pb in negative electrode (volume change factor = 2.4) or PbO_2 in positive electrode (volume change factor 1.96), the replacement of negative electrode (Pb) in hybrid batteries reduces this effect dramatically. This concept has been proved by experiment [62], and a comparison shows as following:

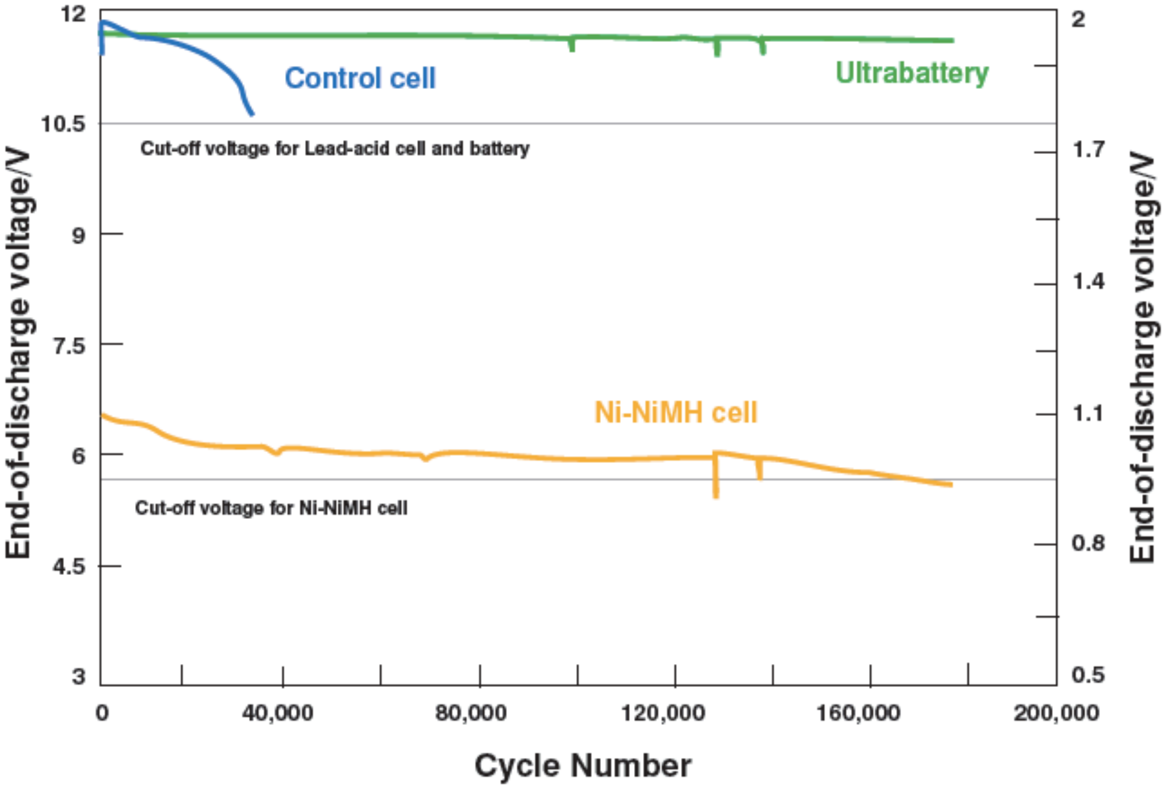

Fig. 7. Lifetime test between three types of battery (Green: lead-acid battery with added carbon capacity in negative electrode, blue: normal lead-acid battery, yellow： Ni-NiMH cell)

The Ultrabattery with replaced carbon capacity in negative electrode has nearly 5 times lifetime of the traditional lead-acid batteries while relatively longer lifetime than Ni-NiMH cell too. Therefore the difference in degradation process between hybrid batteries and normal lead-acid batteries should be carefully considered.

For calculation of capacity loss due to degradation, the weighted number of cycles Z is calculated with:

$$Z(t+\Delta t)=Z(t)+\frac{|I_{discharge}(t)|\bullet f_{soc}(t)\bullet f_{acid}(t)\bullet\Delta t}{C}$$

where f_{soc} is SOC related factors and f_{acid} is acid stratification related factors.

Then the capacity loss due to the degradation $C_{degradation}$ is calculated:

$$C_{\deg radation}(t)=C_{\deg radation,\lim it}\cdot\exp[-C_z\cdot(1-\frac{Z(t)}{k\cdot Z_{IEC}})]$$

The factor K can be estimated as the IEC cycle lifetime without corrosion due to the fact that the effective number of cycles (ZIEC) is the combination of corrosion and degradation. A reasonable choice of K is 1.6 according to Ref. [37].

The impact of SOC:

The degradation would occur whenever a lead-acid battery's 'state-of-charge' remained significantly below 100% for a sustained period. The lower SOC is, the higher is the impact on the battery lifetime. On the one hand, the capacity loss is due to the mechanical stress on the active material because of SOC. On the other hand, the capacity loss comes from the increasing size of the sulfate crystals. In the hybrid battery, the sulfation effects are largely reduced by the replacement of negative electrode. Therefore we can model the loss of capacity from mechanical stress only by omitting the current factor reported in Ref.[54]:

$$f_{soc}(t)=1+(C_{soc,0}+C_{soc,\min}\bullet(1-SOC_{\min}(t)|_{t_0}^{t}))\bullet(t-t_0))$$

where $C_{SoC,0}$ and $C_{SoC,min}$ represent the increase in f_{SoC} with time at S0C = 0 and the minimum SOC since the last full charge.

Note that this relationships are modeled by the factor $f_{SoC,}$ which is set to 1 at each full charge and which increases with the time since the last full charge, i.e.,tSoC = t–t_0, where t_0 is the time of the last full charge.

The impact of acid stratification:

Acid stratification itself is not an ageing effect, but it accelerates ageing. It is fully reversible at any time if sufficient gas evolves or if electrolyte agitation systems are used. Acid stratification builds up during charging and discharging and results in a gradient of the acid concentration. Diffusion and gassing bring a mixing of the electrolyte. Ageing as a result of acid stratification occurs because the differences in the acid concentration result in different electrochemical potentials at different levels in the battery. Therefore, the current distribution along the electrodes is inhomogeneous.

Charging is preferred in the upper parts of the electrode (lower density, lower potential), discharging is preferred in the lower part of the electrode (higher density, higher potential). Consequently, the state-of-charge in the lower part of the electrode is significantly lower compared with the upper part and therefore sulfation is accelerated. This has been confirmed by models [63] and measurements [64].

Therefore, the increase and decrease of stratification can be modeled:

$$f_{stratification}(t+\Delta t) = (f_{plus}(t) - f_{\min us}(t))\Delta t + f_{stratification}(t)$$

and

$$f_{acid}(t) = 1 + f_{stratification}(t) \bullet \sqrt{\frac{I_{10}}{I(t)}}$$

The increase of Acid stratification:

Acid stratification increases during cyclic operation. It is more distinct the lower the state-of-charge since the last time acid stratification is removed and the higher the discharge current. Removal of acid stratification is assumed to take place due to extensive gassing. Taking into account all the factors described above, the factor for the increase of acid stratification becomes:

$$f_{plus}(t) = c_{plus}(1 - SOC_{\min}|_{t_0}^{t})\exp(-3f_{stratification}(t))\frac{|I_{discharge}(t)|}{I_{reference}}$$

Note that there are no factors affected by the replacement of negative electrode. However, the reference current should use the data from hybrid batteries.

The decrease of Acid stratification:

Acid stratification is removed by diffusion and by gassing. Diffusion is slow, so it is typically only noticeable during long pauses (which is can be omitted in this model). And the gassing mechanism is based on the assumption that the mixing effect is directly proportional to the amount of gas generated in the cell. Gas generation increases exponentially with temperature and voltage.

Hence the decrease of stratification distributed in gassing can be modeled as:

$$f_{minus} = f_{minus,gassing} = \sqrt{\frac{100}{C_N}}\frac{I_{gassing,0}}{I_{gassing}} \cdot \exp(c_u(U - U_{gassing,0}) + c_T(T - T_{gassing,0}))$$

where U is the cell voltage. This factor is designed to be equal to $f_{minus} = 0.1$ if the cell voltage equals to the reference voltage and $T = T_{gas,0}$ for a 100 Ah battery. Acid stratification is harder to remove in large batteries than in small batteries, therefore $f_{minus,gassing}$ is weighted with the nominal battery capacity. $I_{gassing,0}(t)$ is the normalized gassing current taking into account the present state of ageing of the battery, and Igassing,0 is the initial normalized gassing current.

In the end, the total remaining capacity can be calculated by:

$$C_{remaining}(t) = C(0) - C_{corrosion}(t) - C_{degradation}(t)$$

Then, the lifetime can be predicted by comparing the remaining capacity with the factory data sheet.

So far, the weighted Ah-throughput model is fully modified according to the hybrid battery. Note that although this model is carefully discussed based on the electrode change, further calculation is needed to validate this model with experiment data. In the estimation of battery lifetime, a list of initial parameters should be carefully chosen. Some of the parameters can be calculated based on the factory data sheet and basic measurements. The descriptions and symbols are listed in following table:

Parameters	**Description**
$\mathbf{C_N}$	Nominal capacity
$\mathbf{Z_{IEC}}$	Number of cycles under standard conditions
$\mathbf{L}$	Float lifetime
$\mathbf{U_o}$	Full charge open-circuit voltage
$\mathbf{g}$	Gradient change in OCV with SOC
$\mathbf{M_c}$	Effective charge-transfer resistance
$\boldsymbol{\varrho_c}$	Effective internal resistance
$\mathbf{C_c}$	Normalized capacity of battery
$\mathbf{I_{ref}}$	Normalized reference current

$\mathbf{U_{corrosion,0}}$	Corrosion voltage of fully charged battery
$\mathbf{I_{gassing,0}}$	Normalized gassing current
$\mathbf{c_u}$	Voltage factor of gassing current
$\mathbf{C_T}$	Temperature factor of gassing current
$\mathbf{U_{gassing,0}}$	Nominal gassing voltage
$\mathbf{K_s}$	Corrosion speed coefficient
$\mathbf{T_{gassing,0}}$	Nominal temperature of gassing
$\mathbf{T_{corrosion,0}}$	Nominal temperature of corrosion
$\mathbf{SOC_{limit}}$	Minimum SOC for bad charges

Table 6. Parameter list (Those can be estimated and directly measured)

Chapter 4

Conclusion and suggestion

This thesis reviews four different lifetime modeling of lead-acid batteries to be mainly used as energy storage for PV systems, EV, and hybrid EV.

Equivalent full cycles to failure, “Rain flow” cycles counting, the Schiffer weighted Ah-throughput model and recurrent Neural Network-based Model are discussed for the accessibility and availability of the lead-acid batteries with the supercapacitor anode.

Equivalent full cycles to failure and “Rain flow” cycles counting are two traditional and easy-to-use model in lifetime prediction. However, These models only work when the operating condition are the same as IEC test conditions. In most estimation, these two models show a much longer estimated lifetime by underestimating the aging process in different operating conditions. Although they have restrictions in applications, they use only one parameter in prediction which is much more convenient and cheap in preliminary predictions.

The Schiffer weighted Ah-throughput model is one of the possible models for the lead-acid batteries with the supercapacitor anode (or hybrid batteries). Because the real lifetime of the battery can differ from the estimated lifetime by several years due to the severe operating conditions, a dynamic mathematical model based on rhe physical and chemical process of batteries is carefully developed. However, the model adopted in the traditional lead-acid batteries is not directly suitable for the hybrid batteries. We modified the model in detail according to the change of negative electrode material. Although further simulation should be conducted and be compared with experiment results, modified weighted

Ah-throughput model is the most promising one by taking into account all effects. Note that the key factor of successful prediction is the parameters choice (Table. 6) based on the experiment and empirical assumption.

Recurrent Neural Network-based (RNNs) Model is discussed as another possible model for hybrid battery. Several contributions are presented in the literature about the use of soft-computing techniques for the estimation of the battery voltage, but most of them utilize static neural networks to model nonlinear dynamic phenomena of the lead-acid battery as the charge–discharge phenomena. The strength of the use of the RNNs is that they provide a dynamic modeling of the voltage and SOC of the battery simultaneously. The selected RNN is designed starting from the dynamic equations that describe the charge–discharge phenomena of a lead-acid battery. Samples of main simulation results are reported by Ref.[24] and all are in good agreement with the experimental and model calculated data. The battery modeling and simulation is a critical task for electrical engineers that often use mathematical models and the relative electrical networks. This model can fit hybrid battery well due to its computing mechanism having no relevant to the chemical process.

To sum up, as one important part of BMS, lifetime prediction model should be carefully considered and selected based on the demand of applications. In general, the Schiffer weighted Ah-throughput model with modification and recurrent Neural Network-based (RNNs) Model are two promising models for the hybrid lead-acid batteries.

For the future work, it is essential to apply modified Schiffer weighted Ah-throughput model in the hybrid batteries in different operating conditions. Besides we will also use the RNNs model to compare the estimation results with former one. The model will be modified again, and features will be added or removed after compared to the measurement data. To increase the prediction accuracy, the combination of these two or other models is also a promising solution in the future.

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