MODELING AND ANALYSIS OF LEAD-ACID BATTERIES WITH HYBRID LEAD AND CARBON NEGATIVE ELECTRODES

A Dissertation in
Mechanical Engineering

by

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Doctor of Philosophy

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ABSTRACT

Valve-regulated lead acid (VRLA) batteries used for hybrid electric vehicle (HEV) applications experience frequent high-rate partial state of charge (HRPSOC) cycling. The failure mode of VRLA batteries under HRPSOC cycling is accumulative sulfation in the negative electrodes. New HEV batteries, such as PbC batteries and UltraBatteries, based on the technologies combining conventional lead acid batteries and super capacitors have emerged in the last decade. PbC batteries replace the negative lead plate with an activated carbon (AC) plate, completely removing the sulfation in the negative electrode. UltraBatteries use a hybrid negative plate consisting of lead and AC materials and relieve the high-rate loads on the lead-acid cells and extend their lifetime. However, since the AC electrode material in PbC batteries and UltraBatteries lowers the battery energy density and increases gassing rate during charge, a model is useful to quickly optimize battery design and analyze gassing phenomena with different AC materials before physical prototypes. Further, the interactions between the battery and capacitor materials in an UltraBattery need in-depth understanding and the current partitioning between the two components needs to be predicted and evaluated.

To date, both lead acid battery models and electrochemical capacitor models are available, but were developed separately. No models have been developed to understand the hybrid battery with presence of both battery and capacitive electrodes. In this work, a mathematical model for PbC batteries was firstly developed to predict performance under various operating conditions. This model couples the electrochemical, mass transport and thermal processes and also accounts for the gassing behaviors at electrodes during charge. With the feature of capacity and gassing rate predictions the model can serve as a design
tool to compare and select desirable carbon candidates for specified applications of PbC batteries. The PbC battery model is applied to simulate and analyze the gassing and thermal behaviors during both galvanostatic charging and cycling processes. The galvanostatic charging processes with different gassing kinetics are investigated. Hydrogen gassing rate and charge efficiencies are focused on for cycling simulation and the effect of operational factors are demonstrated. The temperature rise due to gassing processes is compared among different electrode specifications.

In addition, a fundamental model for UltraBatteries with lead-acid cells and capacitor cells was developed. Dynamic behaviors of internal parameters such as electrolyte potential and current density across the cells during cycling are revealed. One important parameter is introduced as a design ratio, namely the volume fraction of the lead electrode portion in the cell. The effect of design ratio on energy and power performance, such as capacity, current partitioning between cells and electrode utilization efficiency are studied through cycling simulations. Operational factors are evaluated as well, including the effects of duty ratio of a cycle, $\frac{t_{\text{load}}}{t_{\text{total}}}$, starting SOC, cycling frequency and cycling current on current partitioning. This model unveiled the internal dynamics of current partition inside UltraBatteries through simulation results and offered guidelines for improving the design of batteries with hybrid electrodes and optimizing the operating strategies to reduce the peak discharge load on lead electrodes and thus prolong battery lifetime.
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**NOMENCLATURE**

- $a$: specific surface area (m$^2$)
- $AC$: activated carbon
- $CFD$: computational fluid dynamics
- $C$: capacity (Ah)
- $C_{dl}$: capacitance
- $c^i$: concentration of species $i$ in a phase (mol cm$^{-3}$)
- $c_p$: specific heat capacity (J kg$^{-1}$ K$^{-1}$)
- $D^i$: diffusion coefficient of species $i$ (m$^2$ s$^{-1}$)
- $EUC$: electrode utilization coefficient defined as the ratio of discharged to the maximum charge capacity
- $EV$: electric vehicle
- $F$: Faraday constant
- $H^i$: Henry constant
- $HER$: hydrogen evolution reaction
- $HRPSOC$: high-rate partial state of charge
- $h$: heat transfer coefficient
- $I$: current
- $i_{nj}$: transfer current density of reaction $j$ (A/cm$^2$)
- $i_{nj,ref}$: exchange current density
- $J_{\alpha_{eg}}$: interfacial mass transfer coefficient of oxygen
- $K$: interfacial mass transfer coefficient at the electrolyte/gas interface (cm/s)
- $L$: cell length (cm)
- $m$: mass (kg)
- $M$: molar weight
- $N$: cell number
- $n$: charge transfer number
ORR  oxygen reduction reaction

$q$  volumetric heat generation rate ($J/cm^3 s$)

$Q$  volumetric heat dissipation rate ($J/cm^3 s$)

$p$  pressure (atm)

$R$  gas constant

$S$  source term

SHE  standard hydrogen electrode

SLI  starting, lighting and ignition

SOC  state of charge

$T$  temperature

$t$  time

$t_0^+$  transference number of hydrogen ions

$U_j$  equilibrium potential of electrode reaction $j$ (V)

$V$  voltage (V)

VRLA  valve-regulated lead-acid

$V_c$  cell volume (cm$^3$)

$\widehat{V}_c$  partial molar volume of H$_2$SO$_4$ (cm$^3$/mol)

$\widehat{V}_0$  partial molar volume of H$_2$O (cm$^3$/mol)

$V_-$  negative electrode volume (cm$^3$)

$W$  weight (lb)

$w$  electrode width (cm)

Greek letters

$\alpha$  design ratio

$\alpha_d, \alpha_c$  charge transfer coefficient

$\beta$  duty ratio

$\epsilon$  porosity

$\phi$  potential (V)
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<td>$\gamma$</td>
<td>exponent for acid concentration dependence</td>
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<tr>
<td>$\eta$</td>
<td>overpotential (V)</td>
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<tr>
<td>$\kappa$</td>
<td>conductivity (1$\Omega^{-1}$ cm$^{-1}$)</td>
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<tr>
<td>$\lambda_c$</td>
<td>thermal conductivity of the case material</td>
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<tr>
<td>$\rho$</td>
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\( ref \) reference value
\( s \) solid phase
\( u \) utilization
\( 0 \) initial value
\(+\) positive
\(-\) negative
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Chapter 1

Introduction

New hybrid batteries based on the technologies of conventional lead acid batteries and super capacitors have emerged in the recent decade. They combine the advantages from these two energy storage systems and have achieved better performance and longer cycle lives, advantages which lead to a promising prospect for use of such hybrid batteries in transportation applications.

1.1 Background

Lead-acid batteries have been widely used as an electric power supply or storage system for almost 150 years. So far, the matured technology of battery manufacture has been able to provide customers with low-cost, reliable and versatile products. In recent years, the lead acid battery has been perceived as one of the best near-term power sources for transportation use. The requirements of these applications, however, are quite demanding for battery systems because the batteries would not be operated in shallow charge/discharge cycles such as Starting, Lighting and Ignition (SLI) batteries, or floating conditions like stand-by power systems. Instead, these batteries must survive in working conditions which are more severe such as the cycling with deep discharge or HRPSOC cycling [1-3]. Therefore, the cycle lives of batteries used for power traction become much shorter than those for stationary applications. Atlung [4] concluded that the failure of recombinant VRLA batteries during cycling was attributed to the negative electrode and
the major failure mechanism is sulfation due to insufficient recharge because the gassing reactions take a large percentage of charging current. Nakamura et al. [5] revealed the failure mode of VRLA batteries for HEV applications, working under HRPSOC cycling and charged by large currents and irregularly, is the accumulation of lead sulfate in the negative plates. Moseley[2] reviewed the HRPSOC applications of VRLA batteries and summarized the negative progressive sulfation as the major failure mode of batteries under HRPSOC operations. Lam et al. [1] conducted the HRPSOC cycling testing of VRLA batteries and destructive examinations of the electrodes. The results showed the VRLA battery fails prematurely due to the progressive accumulation of lead sulfate mainly on the surfaces of the negative plates.

From all the above studies, it can be confirmed that the failure mode of VRLA batteries under HRPSOC cycling is accumulative sulfation in the negative electrodes. This is due to two aspects. First, the batteries working under PSOC always have some portion of lead sulfate standby that could re-crystallize into hard sulfation and be difficult to recover[6]. Second, high-rate discharge produces a thin layer of lead sulfate that hinders further discharge[1]. This layer will grow progressively and thus lead to hard sulfation. Third, high-rate charge increases the mass transport overpotential of the primary reactions, and then result in higher potential for the positive electrode and lower potential for the negative potential, which favors both oxygen and hydrogen gassing processes. The gassing parasitic currents share the total charging current, so the battery will be left insufficiently charged. The factor that emphasizes the effect of HRPSOC cycling on the negative electrode other than the positive electrode is primarily the different specific surface area of both electrodes. The lead electrode usually has
substantially less surface area than the lead dioxide electrode, so to draw the same current from the two electrodes, the negative electrode must have a higher overpotential. At lower or mediate rates, this does not make much difference in charging the electrodes. But with higher rates the mass transport limitation is high, the difference in overpotential will be exaggerated and thus the negative overpotential grows faster than that in the positive electrode. The gassing side reactions in the negative electrode become severe first and prevent effective charging.

To improve the cycle life of VRLA batteries, effort has been undertaken over many years and the literature can be divided into two categories: controlling strategies and negative additives. Studies [7-13] focused on cycling algorithms and charging algorithms have been conducted to optimize the controlling strategies and extend battery cycle life. Nelson et al. [8] found that using high finishing currents in an alternating charge–rest algorithm results in proper recharge of the negative plate without creating unacceptable temperature increases. This has resulted in deep-discharge lifetimes of 800 to 1000 cycles, particularly when using a charging algorithm employing only partial recharges with 97–100% return interspersed with full conditioning recharges every 10th cycle. Petcova and Pavlov [9] investigated the effect of a three-step charge mode on capacity and cycle life and it was found that the current-voltage-current charging mode decreases the ohmic resistance and ensures complete charge of the negative electrode. Wong et al. [13] summarized the typical charge regimes such as constant current (CC), constant voltage (CV), CC and CV, CC-CV-CV. New regimes like intermittent charge regime and interrupted charge control (ICC) regime were included. The ICC can charge the battery to 100% SOC with only a small amount of overcharging. Carbon additives
have been added into negative electrodes of VRLA batteries to improve the cycle life under HRPSOC operations [14-18]. Shiomi et al. [14] reported that increasing amounts of carbon in negative electrodes of VRLA batteries reduces the PbSO₄ accumulation and extends the life performance in the cycle-life test using the operational pattern of HEVs. Saez et al. [15] and Boden et al. [18] investigated several different carbon additive candidates and carbon black was showed to work most effectively [15]. The mechanism by which carbon additives can help extend cycle life was explained in the work [16,17]. First, the carbon particles constitute an electric conductive network that improves the conductivity of negative electrodes. Second, carbon particles provide the nucleus on which the lead sulfate can land on so that the lead sulfate particles will be smaller and easy to recover. Third, the carbon additives in the electrode may form electric double layers (DLs) that support the high rate charge/discharge events and relieve high rate reactions for the lead electrode.

Although carbon additives can extend the cycle life of VRLA batteries to some degree, the improvement is very limited and still cannot meet the target requirement. A new PbO₂-Carbon hybrid design of battery was brought into market by a lead-acid battery manufacturer in recent years. This battery replaces the negative lead electrode with an AC electrode, so the sulfation ageing in negative electrode is completely removed. According to the statement of the manufacturer, all the necessary components are designed around the standard lead acid batteries and assembled with the same practices as lead acid batteries. Therefore, the cost is claimed to be close to that of conventional lead acid batteries. It was also stated that PbC batteries can achieve 1500 100% depth of discharge cycles, as opposed to 200~300 cycles for conventional batteries. In our labs,
the PbC batteries are also under testing, and have so far demonstrated 2~3 times the cycle life of other VRLA batteries. This hybrid battery design showed good cycle life performance because it completely removes the ageing mechanism of lead sulfation. However, the AC electrode adopted in the new hybrid battery has a lower overpotential of hydrogen evolution especially in acidic electrolyte, so the hydrogen gassing would be the most challenging issue for developing a hybrid PbC battery. This is also the focus of the modeling work in this thesis.

Due to the fact that the negative electrode is purely an AC capacitor electrode, the PbC batteries inherit partially the energy density characteristics of super capacitors. The available energy density is about 20Wh/kg~30Wh/kg, lower than conventional VRLA batteries. Also, the AC electrode has a higher self-discharge rate as it works in super capacitors. UltraBatteries [19-22] use a half-carbon half-lead hybrid negative plate and seem to overcome those drawbacks. As mentioned above, a high-rate charge or discharge generates high overpotential at the negative electrode, so the severe gassing process occurring at the negative electrode reduces the charging efficiency and leaves the electrode insufficiently charged. UltraBatteries are designed to effectively reduce the high currents applied on the negative lead electrodes because the half-carbon capacitor plates are connected in parallel with the lead plates and able to share the high input currents. Therefore, during HRPSOC cycling of an UltraBattery, part of the high load current is actually absorbed and released by the carbon capacitor electrode during every discharge or charge pulse, which effectively protects the lead electrode from sulfation and extends the cycle life of the UltraBattery. It was reported [19,20] that the cycle life of UltraBatteries is much longer than that of conventional batteries. The initial performance
characteristics of prototype UltraBatteries, such as capacity, power, cold cranking and self-discharge have been evaluated based upon the US FreedomCAR Battery Test Manual (DOE/ID-11069, October 2003). Results show that the UltraBatteries meet or exceed respective targets of power, available energy, cold cranking and self-discharge set for both minimum and maximum power-assist HEVs[20]. Three different cycling profiles have been tested and the cycling performance was compared between UltraBatteries and Ni-MH batteries. The results showed the cycle life of UltraBatteries to be at least four times longer than that of lead acid batteries and comparable with that of Ni-MH batteries. Because of the hybrid design features of PbC batteries and UltraBatteries, in this thesis both of them are termed as hybrid batteries.

1.2 State of the Art of Carbon Electrodes for Hybrid Batteries

The PbC battery replaces a conventional Pb/PbSO₄ negative electrode in a lead-acid battery with an AC capacitor electrode and the UltraBattery only changes the previous lead electrode into a lead and carbon hybrid one. It is clear that the key technology for the hybrid batteries is the performance of the carbon electrode and its compatibility with the previous working environment. The carbon capacitor electrode is not a new technology and has been widely employed in super-capacitor applications. However, this doesn’t make it any easier to install a carbon capacitor electrode in a lead-acid battery because the new hybrid battery has to meet the previous energy requirement. Even more challenging is the necessity that the capacitor electrode accommodate the previous acidic environment and working potential window. Thus the top two targets for
optimization of carbon electrodes in hybrid batteries can be summarized as: 1) to make hybrid batteries achieve comparable or higher capacity compared to that of conventional lead acid batteries; and 2) to suppress gassing processes within the desirable electrode potential window. The objective of this section is to provide a literature review of studies and approaches conducted to improve those two aspects of performance. The first section describes the capacitance performance of two carbon candidates that have been mostly employed in super capacitor: AC and carbon nanotube (CNT). The second part summarizes the methods to suppress hydrogen evolution reaction (HER) and promote oxygen reduction reaction (ORR) at carbon electrodes. The previous related modeling work on lead acid batteries and super-capacitors will be reviewed in the first part of the following chapters.

### 1.2.1 The Capacity of Carbon Capacitor Electrodes

Carbons with super specific area (SSA), such as ACs or CNTs, are widely considered as candidate electrode materials for energy storage devices with capacitor electrodes, namely super-capacitors or hybrid batteries. The capacity of such an electrode, if working potential window is assumed to be fixed, will depend on capacitance of the fabricated carbon electrode. Therefore, specific capacitance is one of the most important parameters to be considered when carbon materials are selected for capacitor electrodes. In general, the capacitance of carbon increases with surface area [23], so those two factors were usually evaluated in most studies of carbon electrodes.

*Activated Carbon*
More than 20 years ago [24], experimental carbon electrodes were made by AC fiber cloth and assembled into a super-capacitor. At that time the specific capacitance and specific energy of the capacitor were very low, 36.5F/g and 6~13 Wh/kg. The specific area was estimated as 1500-2500 m$^2$/g. Later, different precursor materials and electrode preparation methods were employed to improve the specific capacitance and area. Usually, AC is prepared from carbon-rich organic precursor as follows, by a thermal method (dry distillation) to form carbonized organic precursors, which can be activated to increase pore volume either thermally or chemically [25]:

1. Thermal method: Treatment at 700–1000°C in the presence of oxidizing gases such as steam, CO$_2$, steam/CO$_2$ mixtures, or air.

2. Chemical method: Treatment at 500–800°C in the presence of dehydrating substances such as ZnCl$_2$, H$_3$PO$_4$, or KOH, which are leached out afterwards.

AC material samples produced by steam originated from coconut shell, phenolic resin or coal exhibited a specific surface area of 1860-2120 m$^2$/g depending on the activation time [26]. Wang et al. [27] achieved 160F/g and 1180 m$^2$/g by using petroleum coke, and KOH and vapor etching and FeCl$_3$ catalysis. Wu et al. [28] prepared AC by placing firewood in a sealed oven at a temperature of 500°C in oxygen deficient environment. Specific capacitance up to 120F/g was obtained. Qiao et al. [29] used petroleum coke for porous carbon preparation by KOH activation, which led to a specific area of 400-2900 m$^2$/g, but the specific capacitance was limited to 44F/g. In Kierzek, et al. [30], various coal and pitch derived carbonaceous materials were activated for 5h at a temperature of 800C. A specific area in a range of 1900-3200 m$^2$/g and specific capacitance 200-320F/g was obtained. Radforda et al. [31] shows the effect of drying of
carbon electrode on specific capacitance. The reason could be reduced weight and improved accessible carbon surface occupied by moisture. Jung et al. [32] shows the effect of fluorination on AC performance. After this treatment, the specific capacitance was increased 375 and 145 F/g to 491 and 212 F/g with the scan rates of 2 and 50mV/s, respectively. Surface area and pore volume were likewise increased. Table 1-1 and Table 1-2 show the comparison before and after the treatment. F37MSP had a decreased specific capacity due to the increased surface resistance as the paper explained. Treatment of the exposed surface of AC materials with surfactant sodium oblate resulted in significant improvement of the specific capacitance[33-35]. This is attributable to improvement in wettability at the exposed pore surface resulting in higher usable surface area. AC nanofiber web in Ref. [36] manifested specific surface area in the range 500–1220m²/g. The specific capacitance was found in the range of 35–202 F/g depending on the steam activation temperature. AC produced by leaching metals from TiC and ZrC, [37,38] with highly tailorable specific capacitance and area at different synthesized temperature was reported. Specific capacitance and specific area can be adjusted in the range of 80-180F/g and 800-2000m²/g, respectively. To summarize, the data available so far for specific area and capacitance collected in other studies mostly falls into the range of 400-3000m²/g and 30F/g~300F/g. Shi [23] characterized 34 kinds of commercial AC microbeads and fibers, as showed in Table 1-3. The measuring data showed a great variety, based on which, the correlation between pore structure and electrochemical capacitance was investigated. It was reported the highest specific capacitance and area of electrodes reported were up to 413F/g and 2571m²/g, respectively.
Table 1-1: The specific capacitance for untreated and fluorinated AC based electrodes at different scan rate. RMSP-before; F19MSP, F28MSP, F37MSP-after.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific capacitance at different scan rates (F/g)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2mv/s</td>
<td>50mv/s</td>
<td></td>
</tr>
<tr>
<td>E-RMSP</td>
<td>375 ± 8</td>
<td>145 ± 12</td>
<td></td>
</tr>
<tr>
<td>E-F19MSP</td>
<td>422 ± 6</td>
<td>152 ± 7</td>
<td></td>
</tr>
<tr>
<td>E-F28MSP</td>
<td>491 ± 5</td>
<td>212 ± 9</td>
<td></td>
</tr>
<tr>
<td>E-F37MSP</td>
<td>255 ± 6</td>
<td>107 ± 15</td>
<td></td>
</tr>
</tbody>
</table>

Table 1-2: Textural properties of untreated and fluorinated AC. RMSP-before; F19MSP, F28MSP, F37MSP-after.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area (m²/g)</th>
<th>Total pore volume (cc/g)</th>
<th>t-plot micropore volume (cc/g)</th>
<th>Mesopore volume (cc/g)</th>
<th>Mesopore volume/total pore volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMSP</td>
<td>1875</td>
<td>0.8</td>
<td>0.72</td>
<td>0.08</td>
<td>10</td>
</tr>
<tr>
<td>F19MSP</td>
<td>2036</td>
<td>0.94</td>
<td>0.74</td>
<td>0.20</td>
<td>21</td>
</tr>
<tr>
<td>F28MSP</td>
<td>2338</td>
<td>1.27</td>
<td>0.97</td>
<td>0.30</td>
<td>24</td>
</tr>
<tr>
<td>F37MSP</td>
<td>2286</td>
<td>0.97</td>
<td>0.75</td>
<td>0.22</td>
<td>23</td>
</tr>
</tbody>
</table>
From the above review, it has been clear that precursor materials and preparation methods are two important determinant factors in specific capacitance and specific area of carbon electrodes. Besides, some other factors could also affect the electrode performance. In Ref. [39, 40], various ACs and AC fibers with specific area of 86-3000 m²/g were investigated. The results showed the capacitance was affected by the electrolyte and the relationship between pore size and the electrolyte ion diameter. Pyun et al. [41] showed that electrodes with smaller pores exhibit higher retardation in the ion penetration into pores during charging and discharging in comparison with electrodes.
with larger pores. The fact that the specific capacitance can be affected by loading current also indicated this effect. In Ref.[42], carbon electrodes were made from polyacrylonitrile fabrics by optimization of the carbonization temperature prior to CO₂ activation. A specific capacitance of 208F/g was found at low current load. At 10A/g a decrease to 129F/g takes place. An optimization [43] of the pore distribution in the AC material can lead to higher capacitor performance. Bigger pores provide good transport of ions though out the porous carbon layer whereas the smaller pores generate a larger interfacial area. In Ref. [44], it is shown that the specific capacitance of mesoporous AC is lower than or almost the same as that for microporous AC. However, at high discharge current, the specific capacitance of mesoporous carbon remains much higher than that of microporous AC, as Figure 1-1 shows. Raymundo-Pinero et al. [45] conducted analysis for different electrolytes and indicated that an adequate pore size is more important than a high surface area to obtain high capacitance. High power applications of AC electrodes were studied in Ref. [46], and results further confirmed that AC with larger percentage of bigger pores are more suitable for high-power capacitor, as Figure 1-2 shows.

Figure 1-1: Pore size distributions of ACs (L) and discharge capacitances of ACs in 1 M Et₄NBF₄/propylene carbonate (open symbol) and acetonitrile (closed symbol) solutions as a function of current density (R) [44].
Considering ion transport resistance, there would be no direct proportionality between specific surface area and specific capacitance. Significant increase in specific area does not provide corresponding specific capacitance increase. This conclusion was proved in Ref. [47] by one example where one of the samples with 700m²/g demonstrated a comparable specific capacitance with the values measured for ACFs and ACs with surface area higher than 2000m²/g. Spherical AC of 500m²/g and 3000m²/g exhibited specific capacitances of 35F/g and 40F/g in Ref [48].

Working conditions also impact the performance of capacitor electrodes. Beside the load current, as mentioned above, load changing frequency also affects the specific capacitance [49]. Composite electrodes by addition of metal oxide into AC can

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**Figure 1-2:** The relationship between discharge capacity and discharge current density of a super capacitor made of M-30 (avg-pore: 14.95Å°) and M-20 (avg-pore: 14.73Å°) [45]
significantly improve the specific capacitance, but this usually is limited to positive electrode application due to the gassing that may be caused by composite electrodes.

**Carbon Nanotubes**

A lot research has been done on carbon nanotubes as super-capacitor electrodes. For multiwalled carbon nanotubes (MWCNTs), specific capacitance in a range of 4-135F/g was found in Refs [50,51]. For singlewalled carbon nanotubes (SWCNT), a maximum specific capacitance of 180F/g in KOH electrolyte was reported in Ref.[51]. The enhancement of specific capacitance of CNTs has been achieved by addition of conducting polypyrrole [52,53] (170F/g) and electrochemical oxidation in Refs [54,55] (335F/g). Also, The wettability of CNTs also has a large impact on specific capacitance of CNTs. In Refs.[56,57], the introduction of surface carboxyl groups created a 3.2 times larger capacitance due to the increased hydrophilicity of MWCNTs in an aqueous electrolyte. In contrast, the introduction of alkyl groups resulted in very low capacitance. Complete disappearance of capacitance for samples functionalized with longer alkyl groups than octyl indicated perfect blocking of proton access to the CNTs surfaces by extreme hydrophobicity. In Ref. [58], activated CNTs were obtained by using KOH as activating agent. An increase in the specific surface area and specific capacitance takes place. Honda et al. [59] reported that vertically aligned MWCNTs can provide a discharge capacity of 10-15F/g even at an extremely high current density of 200A/g, which is said to be impossible for AC. This feature could be very useful for high-power application. Also, electrodes prepared from CNTs/ruthenium oxide composite exhibited higher specific capacitance due to pseudo-capacitance originated from the RuO₂.
nanoparticles [60-64]. However, Ref. [65] revealed that AC material exhibited higher capacitance than CNTs through a comparative investigation between AC and CNTs.

Addition of CNTs to AC instead of acetylene black or graphite powder for electrodes resulted in higher specific capacitance [66,67]. Liu et al. [68] proved this by showing an increase of specific capacitance from 130 to 180 F/g. Fernandez et al. [69] studied the amount percentage of SWCNT on specific capacitance and hydrogen evolution. Results indicated that although SWCNT increase specific capacitance, at the same time it increases hydrogen reaction exchange current density, and promotes hydrogen gassing.

1.2.2 Gas Evolution on Carbon Electrodes

Carbon electrodes in energy storage devices with aqueous electrolyte can easily cause gassing evolution if the working potential window is inappropriate. For electrochemical super-capacitors, the allowed working potential windows of electrodes, within which no gassing or negligible gas production can be observed, are usually characterized first to determine the achievable cell voltage. For hybrid batteries, however, the potential window of negative carbon electrode is limited due to the fact that the potentials of a positive electrode PbO₂/PbSO₄ and the voltage of the whole cell, which is usually around 1.7V vs Standard Hydrogen Electrode (SHE) and 2V, have to be accommodated. Therefore, suitable material candidates and proper preparation methods for carbon electrodes in hybrid batteries need to be thoroughly studied, aiming at
suppressing hydrogen evolution and promoting oxygen reduction in the specified potential window.

The gassing rate is impacted by two properties of an electrode: surface area and surface activity. In terms of surface area, the effort must be to lower the specific area without sacrificing too much capacitance. As mentioned above in Ref.[23], the relationship between specific capacitance and specific area was investigated for activated microbead carbon and AC fiber, with all the testing conditions such as electrolyte and load current the same. Eq. 1.1 shows the linear empirical relationship between capacitance and specific area, \( C_{\text{ext}}^{\text{di}} \) and \( C_{\text{mi}}^{\text{di}} \) are capacitance per unit area for external pores and micro pores; \( S_{\text{ext}} \), \( S_{\text{mi}} \) are the surface area contributed by external pores and micro pores. For microbeads, \( C_{\text{ext}}^{\text{di}} = 74 \pm 20 \mu F/cm^2 \), \( C_{\text{mi}}^{\text{di}} = 19.5 \pm 7 \mu F/cm^2 \); while for carbon fiber, \( C_{\text{ext}}^{\text{di}} = 7.5 \pm 1 \mu F/cm^2 \), \( C_{\text{mi}}^{\text{di}} = 14.5 \pm 5 \mu F/cm^2 \). From these empirical parameters, it can be seen that for the same surface area, \( C_{\text{ext}}^{\text{di}} \) and \( C_{\text{mi}}^{\text{di}} \), the carbon microbeads have larger capacitance, and it is also easier for carbon microbead to improve specific capacitance by shifting surface area between micropores and external pores with total surface area remaining the same. Therefore, the AC microbeads are more suitable for carbon electrodes than AC fiber considering large capacity and smaller gassing rate.

\[
C = C_{\text{ext}}^{\text{di}} \times S_{\text{ext}} + C_{\text{mi}}^{\text{di}} \times S_{\text{mi}}
\]  

1.1

The surface activity is usually referred to as kinetic parameters, such as exchange current density of HER or overpotential at the occurrence of significant hydrogen evolution in negative electrodes. Prosinia et al. [70] shows that CNTs easily produces
hydrogen in 1M sulfuric acid. Brennan and Brown [71] compares pyrolytic graphite with two orientations and vitreous carbon in promoting hydrogen evolution. The activities are different: pyrolytic edge ≈ vitreous carbon > pyrolytic face. Also, a deactivation process was preceded the test. The electrodes were cathodically charged with Hydrogen in a molar solution of perchloric acid at 0.2A. The activities in promoting hydrogen evolution are shown in Table 1-4. The reason was speculated, but insufficient evidence has been provided to explain the de-activation of surface. The exchange current density of HER for all carbon electrodes in acid electrolyte was suggested as 6.3e-8A/cm² in Ref. [72] due to the lack of reported data.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>( i_0 ) (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolytic Edge</td>
<td></td>
</tr>
<tr>
<td>New</td>
<td>8.8e-7</td>
</tr>
<tr>
<td>Pretreated</td>
<td>4.7e-8</td>
</tr>
<tr>
<td>Vitreous Carbon</td>
<td></td>
</tr>
<tr>
<td>New</td>
<td>6.8e-7</td>
</tr>
<tr>
<td>Pretreated</td>
<td>6.4e-7</td>
</tr>
<tr>
<td>Pyrolytic Face</td>
<td></td>
</tr>
<tr>
<td>New</td>
<td>5.8e-8</td>
</tr>
<tr>
<td>Pretreat</td>
<td>4.9e-9</td>
</tr>
</tbody>
</table>

An MWCNT electrode was compared with a graphite electrode through I-V characteristics in water electrolysis, as Figure 1-3 shows [73]. The MWNT electrode used as both anode and cathode has higher current densities. Therefore when the cathodic potential is applied, the MWNT electrode produces more hydrogen than graphite electrode. The work confirmed that MWCNT has higher surface area, and the activation energy barrier of oxygen reaction was lowered when it was used as anode due to the
absorption of OH⁻ in carbon nanotubes. Therefore, by the same mechanism, more absorption of H⁺ makes hydrogen evolution easier, and may also apply when it is used as cathode since the same trend was observed in this plot.

Wei et al. [74] reported a surfactant, namely, hexadecyltrimethylammonium bromide (HTMAB) that inhibited HER but promoted OER at Teflon treated carbon cloth (TCC) electrodes. The influence of HTMAB on H₂ and O₂ evolution rates was investigated by determining the chronopotentiometry of the TCC electrode at current density of 1mA/cm² under different concentrations of HTMAB, as Figure 1-4 shows; the HTMAB had the opposite effect on HER in comparison with OER. The overpotential of HER at 1mA/cm² was negatively increased and HER was inhibited.

Two nano-textured carbons with different content of surface functionalities were compared both in electrochemical capacity and gassing behaviors in Ref. [75]. These two carbons were obtained from the same seaweed carbon and pyrolyzed at different temperature: 600°C and 750°C, which were named LN600 and LN750. The cyclic voltammogram was conducted with 1M H₂SO₄ electrolyte at two different potential scan windows to study the capacitive and gassing behaviors, as Figure 1-5 shows. From the left figure, the capacitive response includes charging of the electrical double-layer (EDL) and the pseudo-faradic contribution of the surface functionality. Due to the richer content of surface functionality in LN600, the humps due to redox reactions both during anodic and cathodic scans can be observed and led to a larger capacitance. Meanwhile, in the right figure, the cathodic heap due to hydrogen evolution was shifted to a larger overpotential for LN600 which contains a larger amount of oxygenated functionalities.
This study shed some light on effective methods of preparation of carbon electrodes with wider working potential windows for capacitor applications.

Figure 1-3: Current density vs applied potential on electrodes [73]
Figure 1-4: Chronopotentiometry of electrode TCC at current density of 1mA cm$^{-2}$ for H$_2$ and O$_2$ evolution, respectively, in 0.5M H$_2$SO$_4$ with different concentrations of HTMAB [74]

Figure 1-5: Cyclic voltammograms (2mV/s) of LN600 and LN750 recorded in three-electrode cells with 1M H$_2$SO$_4$ [75]
It was reported [76] that the addition of a small quantity (10 μM) of the Cu(II) complex of 1,10-phenanthroline in the phosphate solution enhanced the electrocatalytic activity to four-electron transfer for O₂ reduction and inhibited the hydrogen evolution during oxygen reduction at a glassy carbon electrode. Figure 1-6 compares the cathodic currents from [Cu(phen)₂]²⁺/[Cu(phen)₂]⁺ and ORR. It can be seen the background current from Cu redox couple is small in comparison with ORR. Figure 1-7 shows the effect of different [Cu(phen)₂]²⁺ concentration in phosphate electrolyte on ORR. It is clear the higher [Cu(phen)₂]²⁺ concentration promotes ORR. The evidence of inhibition of HER was also provided in Ref.[76], but the effect was not very significant.

Two sulfides K₂S and FeS were employed as additives into electrolyte and electrode, respectively, to suppress hydrogen evolution in Fe/C air batteries in Ref. [77]. The results showed that both K₂S and FeS significantly suppressed hydrogen evolution in Fe/C electrode during cathodic charging. Figure 1-8 and Figure 1-9 shows the hydrogen currents at Fe/C electrode under -1.2V Hg/HgO and different concentrations of additives. From these two figures, it can be seen that both additives reduced the hydrogen evolutions by large gratitude once they were added no matter what kind of carbon was used in Fe/C electrodes.
Figure 1-6: Cyclic voltammogram of a glassy carbon electrode in 0.1M phosphate solution at pH = 5.3 containing $5 \times 10^{-4}$ M $\text{[Cu(phen)$_2$]}^{2+}$ with a scan rate of 100mVs$^{-1}$ with bubbling N$_2$ (1) and O$_2$ (2). Potential vs Ag/AgCl [76]
Figure 1-7: Voltammetric curves for the reduction of oxygen on a glassy carbon electrode in 0.1M phosphate solution at pH = 5.3 with a scan rate of 100mVs$^{-1}$ and bubbling O$_2$ at 25°C in various [Cu(phen)$_2$]$^{2+}$ concentrations: (1) without, (2) 1×10$^{-5}$ M, (3) 5×10$^{-5}$ M, (4) 5×10$^{-4}$ M. Potential vs Ag/AgCl [76]
Figure 1-8: Variation of the hydrogen evolution current of Fe/C electrodes on K$_2$S concentration (M) in additive-containing electrolyte at $-1.2\text{V}$ vs Hg/HgO. AB: acetylene black; VGCF: Vapor-grown carbon fibers; CNF: carbon fiber [77].
To make hybrid batteries like PbC or UltraBatteries competitive with conventional lead-acid batteries, higher specific energy must be achieved. The specific capacitance of carbon capacitor electrodes largely determines the specific energy of the super-capacitors or hybrid batteries in which the electrodes are assembled in. AC is selected due to its low cost and large specific capacitance. Up to 491 F/g (electrode) was reported, although in practice the number usually accomplished is much lower. CNT can reach up to 180F/g (electrode) as reported. However, CNTs have higher conductivities,

Figure 1-9: Variation of hydrogen evolution current of Fe/C electrodes with FeS additive on FeS concentration (wt%) at −1.2 V vs Hg/HgO. AB: acetylene black; VGCF: Vapor-grown carbon fibers; CNF: carbon fiber [77]
which is beneficial for designing electrodes with high specific power. So adding some
CNT into AC seems to be a good way to enhance the specific capacitance.

Because both AC and CNT have super specific area that promotes HER during charging, carbon electrodes have to be properly prepared to suppress HER at negative side. Potential approaches were summarized in this section, such as electrochemically deactivation, additives and impurities mixed into electrode or electrolyte.

1.3 Research Objectives

The objective of this work is to develop first-principle models of new hybrid batteries and provide fundamental understanding of internal physics during various operations through simulation results. The models account for electrochemical, mass transport and thermal processes and allow optimizations of structural design and operational strategies. The specific objectives are as following:

1) Development of a mathematical PbC battery model to understand the new features of internal physical processes and external performance behaviors.

2) Comparison of AC materials to display the influences of carbon material properties on capacity as well as gassing processes and the trade-off in carbon selection.

3) Investigation of gassing phenomena or evolution under galvanostatic or cycling operations to show the effect of gassing on electrochemical performance and thermal behaviors of PbC batteries.
4) Analysis of the impact of design parameters and cycling algorithms on gassing processes in PbC batteries to identify the approaches suppressing gassing behaviors and improving charge efficiencies.

5) Development of a mathematical model for UltraBatteries to understand the internal dynamics of current partition during cycling, which effectively prevents hard sulfation on the lead negative plate and leads to a longer cycle life of an UltraBattery than that of a conventional lead acid battery.

6) Evaluation of the influences of negative plate design and operational factors on both power and energy performance to maximize the current shared by the capacitor cells of hybrid batteries under high-rate cycling and to further extend the cycle life of batteries.
Chapter 2
MATHEMATICAL MODELING OF PbO₂-CARBON (PbC) BATTERIES

2.1 Introduction

PbC batteries combine the technologies of conventional lead-acid batteries and electrochemical capacitors by using PbO₂/PbSO₄ as positive electrodes and AC capacitor electrodes as negative electrodes. As the lead negative electrode is completely replaced by a carbon electrode, the negative sulfation ageing is removed and the lifetime of batteries can be extended. Moreover, the carbon capacitor electrode leads to a wider working voltage range, good charge acceptance and power performance of a PbC battery. The 6-cell battery can be discharged down to 3.6V and the capacitor electrode can release and store charge quickly, a desirable feature for HEV applications. All these features of such PbC batteries are new and distinct from those of conventional batteries, and bring a promising prospect for PbC batteries in HEV applications. However, so far no models have been brought up for such a hybrid battery. The related knowledge or understandings engineers and researchers in this area can obtain from the literature solely relies on the modeling work on conventional lead acid batteries or electrochemical capacitors.

Mathematical models [78-88] have been developed in one or two dimensions for flooded or VRLA batteries in order to understand the fundamentals inside the cells and capture voltage behaviors under different operating conditions. These models were developed physically from the basic conservation laws of mass, momentum, species,
charge and energy, and solved numerically. Thus the internal phenomena can be demonstrated as well as the voltage prediction. Newman and Tiedemann [78] first developed a porous electrode theory and applied it to model the discharge behavior of a lead-acid battery. Gu et al. [79] extended the models to predict cell behavior during discharge, rest, and charge cycles. Since the models mentioned above were solved in one dimension-across the thickness of cell, the acid stratification phenomenon along the height of cell in flooded battery was not accounted for. Bernadi [80] predicted acid concentration and current density distribution along height through a 2D model; however, they failed to study the effect of stratification on performance. Gu and Wang [86] coupled the electrochemical and transport processes and developed a comprehensive cell model for flooded batteries on the basis of porous electrode theory. This model was solved in two-dimensional and capable of predicting the transients of acid stratification and the ensuing effect on performance during charge and discharge processes. The internal information about the evolutions of porosity, state of charge during charge/discharge could also be demonstrated. Gu and Wang [87] used the previous model to simulate EV applications and showed the internal information such as concentration and electrode utilization distribution. The modeling works in Ref.[81-85,88] included the gassing cycle that is a unique feature of VRLA batteries and showed the effect of gassing processes on voltage behaviors during charge. These modeling works on gassing processes will be reviewed in detail in Chapter 3.

AC electrodes have been widely used in electrochemical capacitors, so the modeling work on electrochemical capacitors can be insightful for studying the performance of AC electrodes in PbC batteries. Models developed for electrochemical
capacitors can be categorized into two types: 1) equivalent circuit model; and 2) fundamental model based on porous electrode theory. As the equivalent model is usually used for system simulations and is not helpful in improving design and analyzing the internal parameters’ effects on performance, here only the fundamental models are reviewed. Posey and Morozumi [89] presented macroscopic equations to describe the charging of DL at constant current and constant potential and later those equations were used by other researchers to analyze the DL charging phenomena [90-93]. Pillay and Newman [72] studied the cycling of electrochemical capacitors to analyze the effect of the oxygen and hydrogen evolution reactions on charge efficiencies. Srinivasan and Weidner [94] used the porous electrode theory to develop a mathematical model for capacitors to simulate the electrochemical impedance. However, this model put emphases on energy and power performance without gassing accounted for. Lin et al. [95] developed a mathematical model of an electrochemical capacitor with hydrous ruthenium oxide (RuO$_2$,$x$H$_2$O) electrodes including both double-layer and surface faradic processes to predict the behavior of the capacitor under conditions of galvanostatic charge and discharge. The effect of RuO$_2$-xH$_2$O particle size was studied and showed that the smaller the particles the better the performance because of the increased surface area per unit volume or mass. Sikha et al. [96] developed a one-dimensional model for a battery-capacitor system to study the current share between two power systems without gassing included. From the above review of fundamental models of electrochemical capacitors, it is clear that a porous-electrode based model is necessary to characterize the internal features and properly design the AC electrodes in capacitors.
In conclusion, in present both lead acid battery models and electrochemical capacitor models are available at present, but were developed separately. Each of them has its distinct physical properties and working principles. No models have been developed to understand the hybrid battery with electrodes coming from these two different devices. The goal of this chapter is to develop a fundamental model combining the physics of a lead acid battery and a symmetric AC super-capacitor, solving the interaction between a PbO$_2$/PbSO$_4$ electrode and a carbon capacitor electrode inside one battery and providing guidelines for good design of PbC batteries.

### 2.2 Mathematical Model Development

The cell of the hybrid battery with a PbO$_2$ positive electrode and a AC negative electrode is schematically shown in Figure 2-1. As the figure shows, charge can be absorbed at the interface between solid and electrolyte phases. Eq. 2.2 and Eq. 2.1 give the primary reactions taking place at each electrode during discharge. When the cell is discharged, the positive electrode has the exact same reaction as the one occurring in a lead acid battery; whereas there is no electrochemical reaction at the negative electrode. The previously stored charge is released: electrons flow through external circuit to the positive side and protons are transported through the electrolyte phase. The AC electrode usually has a high specific area and specific capacitance, which ensures sufficient charge storage.
Figure 2-2 shows the open circuit voltage (OCV) vs state of charge (SOC) for the PbC battery. This figure displays the OCV changes linearly with SOC. The acid concentration of a lead acid battery at full charge usually falls into the range of between 4M and 6M. Here for the PbC battery, it is assumed to be 4.5M. With all the reasonable parameter values collected from the previous modeling experience of lead acid batteries, as shown in the Table 2-1 for the following model validation, it can be estimated that the average acid concentration at SOC=10% for a 60Ah PbC battery should be around 3.1M. However, as we know the equilibrium potential of the PbO₂/PbSO₄ reaction barely changes when the acid concentration varies in the range between 3.1M and 4.5M. Here.

\[ PbO_2 + 3H^+ + HSO_4^- + 2e^- = PbSO_4 + 2H_2O \] \hspace{1cm} (2.1)

\[ C_{6}^{x-}(H^+) = C_{6}^{(x-2)^-}(H^+_{(x-2)}) + 2H^+ + 2e^- \] \hspace{1cm} (2.2)
for simplicity, a constant equilibrium potential of 1.72V vs SHE is assumed to analyze the evolution of electrode potentials, as in Figure 2-3 by the red line shows. The green line in Figure 2-3 denotes the negative potential, and the slope is dependent on the AC electrode capacitance. To achieve the OCV of 2.07V at full charge as Figure 2-2 shows, the potential of the negative here should be around -0.35V vs SHE. Similarly, when the battery is discharged to 10%, the negative potential should be around 0.95V vs SHE. In Figure 2-3, the negative potential can evolve in the region surrounded by the dash lines during discharge. The starting point determines the cell voltage at full charge, and the electrode capacitance determines the slope. The starting value of negative potential, in other words, the initial negative potential at full charge can be adjusted by changing the weight ratio between two electrodes. When the AC electrode weight is fixed and the weight ratio changes the positive electrode weight and the whole cell capacity change. Therefore, the potential window of the AC electrode $\Delta \phi = \frac{Q_{\text{cell}}}{C_{\text{AC}}}$ will change accordingly, and finally the potential of the AC electrode at full charge will be adjusted. From this figure, three new features of PbC batteries can be concluded: 1) the negative potential changes linearly during charge or discharge due to its capacitive characteristic; 2) the capacitive electrode must use a much wider potential range to achieve sufficient discharge capacity; and 3) the variation of cell voltage is dominated by the change of negative potential.
Figure 2-2: Open circuit voltage vs State of charge for a PbC battery (Source from the manufacturer white paper)
This model also integrates the gassing side reactions as the previous models of lead acid batteries. Eq. 2.3 and Eq. 2.4 show oxygen evolution and hydrogen recombination at the positive electrode; Eq. 2.5 and Eq. 2.6 shows ORR and HER at the negative electrode.

\[
2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad 2.3 \\
H_2 \rightarrow 2H^+ + 2e^- \quad 2.4 \\
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad 2.5 \\
2H^+ + 2e^- \rightarrow H_2 \quad 2.6
\]

The above reactions constitute the internal oxygen and hydrogen cycles in the cell. In the presence of the side reactions, a PbC cell is a three-phase system consisting of
solid matrix, liquid electrolyte and gas phase. During charging and overcharging, oxygen is generated at the PbO\textsubscript{2}/electrolyte interface and may evolve into the gas phase after exceeding its solubility limit in the electrolyte. The oxygen can then be transported, via the liquid and gas phases, from the positive to negative electrode where the oxygen gas may dissolve back in the electrolyte and be reduced at the carbon/electrolyte interface. This process forms an internal oxygen cycle in the cells. Hydrogen is generated following Eq. 2.6 at the negative electrode when the electrode potential goes too low. Hydrogen recombination occurring at the positive electrode as described by Eq. 2.4 is negligible because of its poor kinetics [83]. Accumulation of oxygen and hydrogen in the gas phase contributes to the cell pressure build-up and venting may take place.

**2.2.1 Model Assumption**

1. A continuous gas-pore network exists in the cell for gas transport and there is a head space right above the cell with a constant volume to store excess gas. The gas obeys the ideal gas law.
2. The solid phase is completely covered by the electrolyte film. In other words, no mass transfer occurs at the active materials/gas interface.
3. Gas convection is neglected due to a small gas volume fraction inside the cell, leaving the gaseous oxygen transport by diffusion only.
4. With the exception of the dissolved oxygen species, interfacial chemical and electrical equilibrium exists in the electrolyte phase due to large values of the mass diffusivity and ionic conductivity.
5. Hydrogen recombination at the positive electrode is neglected due to its poor kinetics.
2.2.2 Governing Equations

All the governing equations can be found in Gu et al.’s work[88]. The new terms that solve the physics brought into model due to the AC electrode will be detailed with each equation.

Kinetic Rate Equations

The transfer current density for various electrochemical reactions can be calculated by Butler-Volmer equation. Eq. 2.7 gives the transfer current density for the primary reaction at the positive electrode. \( j = 1 \) denotes the reaction in Eq. 2.1.

\[
i_{ij} = i_{ij,ref} \left( \frac{c_{H}^{j}}{c_{ref}^{H}} \right)^{n_{ij}} \left[ \exp \left( \frac{\alpha_{ij} F}{RT} \eta_{j} \right) - \exp \left( - \frac{\alpha_{ij} F}{RT} \eta_{j} \right) \right] \quad j = 1
\]

Eq. 2.8 shows the equation for the oxygen reactions at both electrodes.

\[
i_{ij} = i_{ij,ref} \left( \frac{c_{H}^{j}}{c_{ref}^{H}} \right)^{n_{ij}} \left[ \exp \left( \frac{\alpha_{ij} F}{RT} \eta_{j} \right) - \left( \frac{c_{e}^{O}}{c_{ref}^{O}} \right)^{\delta_{ij}} \exp \left( - \frac{\alpha_{ij} F}{RT} \eta_{j} \right) \right] \quad j = 3, 5
\]

The hydrogen generation follows Tafel kinetics [83,85], as Eq. 2.9 shows.

\[
i_{ij} = -i_{ij,ref} \left( \frac{c_{H}^{j}}{c_{ref}^{H}} \right)^{n_{ij}} \exp \left( - \frac{\alpha_{ij} F}{RT} \eta_{j} \right) \quad j = 6
\]

The hydrogen recombination has been neglected in this work. In the above rate equations, \( F \) is Faraday’s constant, \( R \) the universal gas constant, \( T \) the cell temperature, and \( c \) the concentration of chemical species. The subscript \( j \) refers to reactions 2.1 through 2.6, respectively. The exchange current density is represented by \( i_{ij} \), with \( \alpha_{ij} \) and \( \alpha_{ij} \) being the anodic and cathodic transfer coefficients. The surface overpotential, \( \eta_{j} \), for reaction \( j \) is defined as Eq. 2.10 shows.
where $\phi_s$ and $\phi_e$ are the potentials of the solid electrode and electrolyte, respectively, and $U_j$ is the open circuit potential of reaction $j$. The following model equations are derived from the micro- and macro-scopic coupled description of porous electrodes and mass transport theory in Ref.[86,88], also the DL effect source term is derived from the DL modeling in Ref.[97].

Conservation of Charge Equations

Eq. 2.11 shows the conservation equation in solid phase which includes two source terms; one is from the electrochemical reaction and the other is from the DL effect.

DL can be formed at both electrodes; however, the AC electrode has much higher capacitance and surface area than the PbO₂ electrode. This is the new issue that the PbC battery model needs to resolve.

\[
\nabla \cdot (\sigma^{\text{eff}} \nabla \phi_s) = S^c_s + aC_{dl} \frac{\partial(\phi_s - \phi_e)}{\partial t} \tag{2.11}
\]

Eq. 2.12 shows the equation for electrolyte phase.

\[
\nabla \cdot (\kappa^{\text{eff}} \nabla \phi_e) + \nabla \cdot [\kappa^{\text{eff}} \nabla \left( \ln c_l \right)] = -S^c_e - aC_{dl} \frac{\partial(\phi_s - \phi_e)}{\partial t} \tag{2.12}
\]

Where

\[
\kappa^{\text{eff}}_D = \frac{RT \kappa^{\text{eff}}}{F}(2t^0 - 1) \tag{2.13}
\]

with $a$ and $C_{dl}$ being the electrode specific area and the capacitance per volume of the AC electrode, $\kappa^{\text{eff}}$ being the effective ionic conductivity of the electrolyte and $\kappa^{\text{eff}}_D$ the diffusional conductivity to account for the current flow resulting from diffusion of ionic...
species under a concentration gradient. Eq. 2.12 is used to determine the electric potential distribution in the electrolyte phase, $\phi_e$. The source term $S^e_e$ is given in Eq. 2.14. $S^e_e = 0$ in the carbon electrode represents there is no electrochemical reaction, which is the new feature of modeling PbC batteries.

\[
S^e_e = \begin{cases} 
ai_{n,1} & \text{in the PbO}_2 \text{ electrode} \\
0 & \text{in the separator} \\
0 & \text{in the carbon electrode}
\end{cases} \tag{2.14}
\]

\textit{Conservation of Species in Electrolyte}

Concentrated solution theory is used to describe the species transport in the electrolyte solution. There are two species in the electrolyte that participate in charge-transfer reactions: an ionic species $H^+$ and a neutral species $O_2$ (dissolved). Eq. 2.15 gives the conservation equations for the hydrogen ion concentration. Eq. 2.16 shows the source terms. In the carbon electrode, no electrochemical reaction takes place, but the DL formed at the interface of AC electrode and electrolyte also release and absorb hydrogen ions, which impacts the evolution of acid concentration. This term is related to the DL current generated in the carbon electrode.

\[
\frac{\partial (c^e_e \mathcal{E}^H)}{\partial t} + \nabla \cdot (\mathbf{v} c^e_e \mathcal{E}^H) = \nabla \cdot (D^H \nabla c^e_e \mathcal{E}^H) + S^H \tag{2.15}
\]

\begin{align*}
S^H &= \begin{cases} 
\frac{3 - 2t_e^0}{2F} ai_{n,1} & \text{in the PbO}_2 \text{ electrode} \\
0 & \text{in the separator} \\
1 - t_e^0 aC_{\text{dl}} \frac{\partial (\phi_e - \phi_x)}{\partial t} & \text{in the carbon electrode}
\end{cases} \tag{2.16}
\end{align*}
where $c^H$ is the concentration of hydrogen ion, $D_{\text{eff}}^H$ the effective diffusion coefficient in the electrolyte with the effects of porosity and tortuosity taken into account via Bruggeman correction, and $t^+_w$ the transference number of $H^+$ ions with respect to the velocity of the solvent.

Eq. 2.17 shows the conservation equations for oxygen in electrolyte. Eq. 2.18 gives the source terms. There is no difference between the AC electrode and the previous lead electrode in terms of ORR. However, the higher surface area of AC electrode makes ORR much easier than at the lead electrode.

$$\frac{\partial (\varepsilon c^O_e)}{\partial t} + \nabla \cdot (\nu c^O_e) = \nabla \cdot [D_{\text{eff}}^O_e \nabla (c^O_e)] + S^O_e$$ \hspace{1cm} 2.17

$$S^O_e = \begin{cases} \frac{1}{4F} a_{i_{\text{al}}} - J^O_{eg} & \text{in the PbO}_2 \text{ electrode} \\ -J^O_{eg} & \text{in the separator} \\ \frac{1}{4F} a_{i_{\text{as}}} - J^O_{eg} & \text{in the carbon electrode} \end{cases}$$ \hspace{1cm} 2.18

where $c^O_e$ is the concentration of $O_2$ dissolved in the electrolyte and $D_{\text{eff}}^O_e$ is its diffusion coefficient. The interfacial evaporation rate of oxygen from liquid to gas, $J^O_{eg}$, appearing in the source term can be determined by Eq. 2.19.

$$J^O_{eg} = K(c^O_{eg} - H' c^O_{g})$$ \hspace{1cm} 2.19

$K$ is the interfacial mass transfer coefficient of the dissolved oxygen on the electrolyte side and $H'$ the Henry constant. The detailed explanation about this term is available in Ref.[88]

*Conservation of Oxygen in Gas Phase*
Gaseous oxygen originates from evaporation of the dissolved oxygen in the electrolyte once its concentration exceeds the solubility limit. The conservation of gaseous oxygen concentration is expressed by Eq. 2.20.

\[
\frac{\partial (\varepsilon_g c_g^{O_2})}{\partial t} = \nabla \cdot (D_{g,eff}^{O_2} \nabla c_g^{O_2}) + J_{eg}^{O_2}
\]

Here, the gas volume fraction is assumed to be sufficiently small that gas convection is negligible. The diffusion coefficient in Eq. 2.20 is a critical parameter as it strongly depends on the liquid saturation level (i.e., \( s = \varepsilon_e / (\varepsilon_e + \varepsilon_g) \)) in the separator region. The detailed discussion about the relationship between the gas diffusion coefficient and the liquid saturation of separator has been elaborated in Gu et al.’s work[88].

From Eq. 2.20, the gaseous oxygen concentration can be calculated; accordingly the cell pressure can be further calculated by the ideal gas law in Eq. 2.21[88].

\[
p_{g,avg} = p_o + (c_{g,avg}^{O_2} - c_{g,o}^{O_2})RT + \Delta p^{H_2}
\]

With the average oxygen concentration in the gas phase and the pressure increase due to hydrogen evolution evaluated by Eq. 2.22 and Eq. 2.23 [88]

\[
c_{g,avg}^{O_2} = \frac{\int_{V_c} \varepsilon_g c_g^{O_2} dV}{\int_{V_c} \varepsilon_g dV}
\]

\[
\Delta p^{H_2} = \frac{RT \int_{V_c} a_i dV}{2F \int_{V_c} \varepsilon_g dV}
\]

where \( p_o \) is the initial (reference) pressure, \( V_c \) is the entire cell volume including that of the head space, and \( V_- \) is the volume of negative carbon electrode. It can be seen from
Eq. 2.21 that an increase in amount of oxygen and hydrogen gases will increase the pressure inside the battery.

Conservation of mass

Eq. 2.24 and Eq. 2.25 show the mass conservation in solid and electrolyte phase.

\[
\frac{\partial \varepsilon_s}{\partial t} = S_s^e
\]  
\[2.24\]

\[
\frac{\partial \varepsilon_e}{\partial t} + \nabla \cdot \nu_e = S_e^e
\]  
\[2.25\]

Eq. 2.26 and Eq. 2.27 give the source term details of mass conservation and electrolyte conservation, respectively. The term \(S_e^e\) implies that electrolyte displacement during battery operation results from the change in the partial molar volume between the reactants and products. Apparently, the charge absorption and release do not change the solid mass and the morphology of the electrode, but it does affect the mass and volume of the liquid phase, so here for the carbon electrode \(S_s^e = 0\) and \(S_e^e \neq 0\).
To solve for the electrolyte flow field in multiple spatial dimensions, conservation of momentum is necessary. The governing equations for solving the capillary flow and the derivations have been provided in Ref. [88] and will not be detailed here.

Conservation Equation of Thermal Energy

The thermal model for the PbC battery is also developed based on the lumped method as before. Some corresponding physical properties for an AC electrode are identified from literature to make the thermal prediction accurate. Eq. 2.28 shows the thermal energy conservation equation.

\[
\frac{d(\rho c_p T)}{dt} = q - Q
\]
q is the heat generation rate per unit volume and Q is the heat dissipation rate per unit volume. Assuming the phase transition heat is negligible, so q can be expressed in Eq. 2.29. The first term represents the heat from electrochemical reactions, and the second term represents the joule heating in electrolytic and solid phase. From this equation, it can be seen that the heat generated at the negative electrode of a PbC battery only comes from the electronic and electrolytic joule heating during discharge.

$$q = \frac{1}{V_c} \int_V \sum_j a_{ij} \left( \eta_j - T \frac{\partial U_j}{\partial T} \right) dV + \frac{1}{V_c} \int_V \left[ \kappa^{\text{eff}} \nabla \phi_e \cdot \nabla \phi_e + \sigma^{\text{eff}} \nabla \phi_s \cdot \nabla \phi_s \right] dV$$  \hspace{1cm} 2.29

### 2.2.3 Supplemental Relations

Input parameters and property correlations are described in the following equations. The local electrode utilization coefficient (EUC) is defined by Eq. 2.30 and Eq. 2.32. At the positive electrode, the local EUC represents how much active material has been used locally, which impacts the active surface area for further electrochemical reactions; whereas the charged status of a capacitor electrode does not affect the rate of further releasing or storing charge at all, so that EUC can be considered as constant for the negative electrode.
\[
\frac{\partial (EUC)}{\partial t} = S_u
\]

\[
S_u = \left\{ \begin{array}{ll}
\frac{-ai_{ai}}{Q_{max^+}} & \text{in the PbO}_2 \text{ electrode} \\
0 & \text{in the separator} \\
0 & \text{in the carbon electrode}
\end{array} \right.
\]

\[Q_{max^+}\] is the maximum theoretical charge capacity of the positive electrode active material. The initial \(EUC\) is set as 0 and the local \(EUC\) is used to update the specific area as Eq. 2.32 shows. The specific area is one important parameter determining the electrochemical reaction rate, which depends upon the properties of the electrode, such as porosity, particle size and local state of charge, or local \(EUC\). The value of specific area for charge applies to the oxygen generation at the positive electrode. These equations describe the amount of active area during discharge or charge, and the exponent \(\xi\) is a morphology factor describing the rate of change in the specific area. Obviously, an AC electrode does not have any change in specific area during charge or discharge, so the specific area for all electrochemical reactions at the negative electrode is always a constant, which is a property of the AC electrode.

\[
a = a_{max} (1 - EUC^\xi) \quad \text{for discharge}
\]

\[
a = a_{max} EUC^\xi \quad \text{for charge}
\]

The temperature dependence of physicochemical properties, such as the diffusivity and the ionic conductivity of the electrolyte are the essence of coupling the thermal model with the electrochemical and mass transport model to accomplish a comprehensive PbC battery model. The same thermal-electrochemical coupling approach
as that in Ref. [88] can be also employed here for the PbC battery model. However, some issues related to the thermal behaviors of the negative electrode are different between a lead acid battery and a PbC battery. Specifically, in this model it is assumed that the charge releasing and absorbing processes in the capacitor electrode are neither exothermal nor endothermal, so there is only joule heating and gassing heat generation in the carbon electrode. It also is assumed that there is no temperature impact in the rate of charge releasing and absorbing, so for the AC electrode the temperature only affects the rate of gassing reaction. The dependence correlation is based on Arrhenius' equation, which is showed in Eq. 2.33.

\[ \Phi = \Phi_{\text{ref}} \exp \left( \frac{E_{\text{act},\Phi}}{R} \left( \frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right) \]  

where \( \Phi \) is a general symbol representing the diffusion coefficient of a species, conductivity of the electrolyte, exchange current density of an electrode reaction, etc., with subscript ref denoting the value at a reference temperature. \( E_{\text{act},\Phi} \) is the activation energy of the evolution process of \( \Phi \). Its magnitude determines the relative sensitivity of cell behaviors to temperature. The greater its activation energy is the more sensitive the parameter to temperature.

Also, the open-circuit potential of electrode reaction \( j \), \( U_j \), is usually approximated as a linear function of temperature, and the correlation is showed in Eq. 2.34. Apparently, this does not apply to the negative electrode during discharge as there is no electrochemical reaction.

\[ U_j = U_{j,\text{ref}} + (T - T_{\text{ref}}) \frac{\partial U_j}{\partial T} \]
With the temperature-dependent properties, the electrochemical and thermal models of the PbC battery can be strongly coupled. The heat generation rate due to electrochemical reactions and Joule heating will be calculated locally via the detailed electrochemical model, and subsequently be used in the energy conservation equation to calculate the temperature evolution. This temperature information is, in turn, fed back to update the electrochemical calculations through temperature-dependent physicochemical properties. Figure 2-4 shows the relationship between two sub-models.

**2.2.4 Initial and Boundary Conditions**

The potentials in the solid and electrolyte phases are governed by Poisson equation without time derivatives; hence, their initial conditions are not necessary. Eq. 2.35 and Eq. 2.36 give the boundary conditions for $\phi_e$ equation. $L$ is the total length of a cell.

---

**Figure 2-4:** The thermal-electrochemical coupled model[88]
Eq. 2.37 and Eq. 2.38 give the boundary conditions for $\phi$ equation.

$$-\sigma_{\text{eff}} \frac{\partial \phi}{\partial n} = I, \text{ at } x = 0$$

$$\phi = 0, -\sigma_{\text{eff}} \frac{\partial \phi}{\partial n} = I, \text{ at } x = L$$

Eq. 2.37 and Eq. 2.38 show the boundary conditions and initial conditions for species equations.

$$\kappa_{\text{eff}} \frac{\partial \phi}{\partial x} = 0, \text{ at } x = 0$$

$$\kappa_{\text{eff}} \frac{\partial \phi}{\partial x} = 0, \text{ at } x = L$$

Eq. 2.39 and Eq. 2.40 show the boundary conditions and initial conditions for species equations.

$$\frac{\partial c^i}{\partial n} = 0 \quad i = H^+ \text{ and } O_2$$

$$c^i = c^i_0$$

Eq. 2.41 and Eq. 2.42 show the initial condition and boundary condition of the energy equation.

$$T = T_a \text{ at } t = 0$$

$$-\lambda_c \frac{\partial T}{\partial x} = h(T - T_a) \text{ at the outer surface of the battery case}$$

where $\lambda_c$ is the thermal conductivity of the case material, and $h$ the overall convective heat coefficient that may include the effects of other heat transfer modes. $T_a$ is the ambient temperature. The pressure initial condition is given by Eq. 2.43

$$p = p_0 = 1.01 \text{ atm}$$

The treatment of a venting event for the PbC battery model still use the strategy for a VRLA battery in Ref[88]. Whenever the internal gas pressure becomes greater than the valve preset opening pressure, $P_o$, gas is released into the ambient until the internal
pressure drops below the valve preset closing pressure, $P_c$. Assuming that the time of gas relief at pressures higher than the opening pressure of the valve is negligible, a single venting event can be simply modeled by the following procedure:

if $p_g < P_o$ (open valve), then $n_g = n_g$ and $p_g = p_g$

if $p_g > P_c$ (closed valve), then $n_g = n_g P_c/p_g$ and $p_g = P_c$

where $n_g$ is the number of moles in gas and $p_g$ the gas pressure calculated from the model.

The loss of water vapor in this process can also be calculated accordingly.

\[ 2.2.5 \text{ Numerical Procedure} \]

To numerically solve the foregoing model equations, the general computational fluid dynamics (CFD) methodology is adopted. The key to a successful application of CFD techniques is that all the equations in the present battery model can be cast into a general form of convection-diffusion type, as Eq. 2.44 shows,

\[
\frac{\partial (\rho \Phi)}{\partial t} + \nabla \cdot (\rho \mathbf{v} \Phi) = \nabla \cdot (\Gamma_\Phi \nabla \Phi) + S_\Phi
\]

accumulation convection diffusion source

where $\Phi$ is a general variable to be solved, $\Gamma_\Phi$ a diffusion coefficient, and $S$ a source term which includes all terms that cannot be included in the previous terms.

The general differential equation is then discretized by the control volume-based finite difference method of Patankar (1980) and the resulting set of algebraic equations is iteratively solved. The details of the numerical method can be found in Ref[88]. The grid number for all the simulation in this work is 30 across one cell.
2.3 Model Validation and Illustrative Results

2.3.1 Validation against Experimental Data

A 60Ah PbC battery is discharged to 3.6V and then charged to 13.8V at I=C/3 and I=C/15 in the testing. Data was recorded and used to validate the mathematical model, as shown Figure 2-5 and 2-6 show. The parameters used in the model are shown in Table 2-1. It can be seen that the AC electrode has a much higher specific surface area than the lead-dioxide electrode. The value in the table corresponds to a specific area of 1500m²/g. The mass of the carbon electrode doesn’t change during charge and discharge as there are no electrochemical reactions, thus no morphology factor is needed and the porosity remains the same. Also, the activation energy used for temperature corrections of exchange current density of electrochemical reactions doesn’t apply to the carbon electrode. The exchange current density of HER is an important parameter because the negative AC electrode can easily cause hydrogen gassing during charge processes. Here the value of the HER exchange current density is taken from Ref.[71].
### Specification

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity (Ah)</td>
<td>60</td>
</tr>
<tr>
<td>Number of cells in series</td>
<td>6</td>
</tr>
<tr>
<td>Number of cells in parallel</td>
<td>8</td>
</tr>
<tr>
<td>width of electrode plate (cm)</td>
<td>19.5</td>
</tr>
<tr>
<td>Height of electrode plate (cm)</td>
<td>16</td>
</tr>
<tr>
<td>Thickness of PbO$_2$ electrode (cm)</td>
<td>0.159</td>
</tr>
<tr>
<td>Thickness of separator (cm)</td>
<td>0.159</td>
</tr>
<tr>
<td>Thickness of carbon electrode (cm)</td>
<td>0.159</td>
</tr>
<tr>
<td>Porosity of PbO$_2$ electrode at fully-charged state</td>
<td>0.6</td>
</tr>
<tr>
<td>Porosity of separator</td>
<td>0.92</td>
</tr>
<tr>
<td>Porosity of carbon electrode</td>
<td>0.6</td>
</tr>
<tr>
<td>DL capacitance of PbO$_2$ electrode (F/cm$^2$)</td>
<td>15e-6</td>
</tr>
<tr>
<td>DL capacitance of carbon electrode (F/cm$^2$)</td>
<td>15e-6</td>
</tr>
<tr>
<td>Specific interfacial area of PbO$_2$ electrode ($\text{cm}^2$/cm$^3$)</td>
<td>2.3e5</td>
</tr>
<tr>
<td>Specific interfacial area of carbon electrode ($\text{cm}^2$/cm$^3$)</td>
<td>2.7e7</td>
</tr>
<tr>
<td>Morphology correction index for PbO$_2$ electrode</td>
<td>1</td>
</tr>
<tr>
<td>Concentration of acid (H$_2$SO$_4$) at fully charged state (mol/cm$^3$)</td>
<td>4.5e-3</td>
</tr>
<tr>
<td>Initial battery pressure (atm)</td>
<td>1.01</td>
</tr>
<tr>
<td>Valve opening pressure (atm)</td>
<td>1.170</td>
</tr>
<tr>
<td>Valve closing pressure (atm)</td>
<td>1.102</td>
</tr>
<tr>
<td>Saturation level of PbO$_2$ electrode at fully charged state (%)</td>
<td>85</td>
</tr>
<tr>
<td>Saturation level of separator at fully charged state (%)</td>
<td>93</td>
</tr>
<tr>
<td>Saturation level of carbon electrode at fully charged state (%)</td>
<td>85</td>
</tr>
</tbody>
</table>

### Kinetics

<table>
<thead>
<tr>
<th>Kinetics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference temperature (K)</td>
<td>298.15</td>
</tr>
<tr>
<td>Reference acid concentration (mol/cm$^3$)</td>
<td>4.9e-3</td>
</tr>
<tr>
<td>Reference concentration of O$_2$ in the electrolyte (mol/cm$^3$)</td>
<td>1e-3</td>
</tr>
<tr>
<td>Exchange current density of PbO$_2$/PbSO$_4$ rxn (A/cm$^2$)</td>
<td>4.19e-7</td>
</tr>
<tr>
<td>Activation energy of PbO$_2$/PbSO$_4$ rxn (J/mol)</td>
<td>4.1e-3</td>
</tr>
<tr>
<td>Anodic transfer coefficient of PbO$_2$/PbSO$_4$ rxn</td>
<td>1.15</td>
</tr>
<tr>
<td>Cathodic transfer coefficient of PbO$_2$/PbSO$_4$ rxn</td>
<td>0.85</td>
</tr>
<tr>
<td>Exchange current density of O$_2$ generation (A/cm$^2$)</td>
<td>1.5e-27</td>
</tr>
<tr>
<td>Anodic transfer coefficient for O$_2$ generation</td>
<td>2</td>
</tr>
<tr>
<td>Cathodic transfer coefficient for O$_2$ generation</td>
<td>2</td>
</tr>
<tr>
<td>Exchange current density of O$_2$ recombination (A/cm$^2$)</td>
<td>2.5e-36</td>
</tr>
<tr>
<td>Anodic transfer coefficient for O$_2$ recombination</td>
<td>2</td>
</tr>
<tr>
<td>Cathodic transfer coefficient for O$_2$ recombination</td>
<td>2</td>
</tr>
<tr>
<td>Open-circuit potential vs. carbon electrode for O$_2$ rxns at reference conditions</td>
<td>1.56</td>
</tr>
<tr>
<td>Activation energy of O$_2$ rxns (J/mol)</td>
<td>70e3</td>
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<tr>
<td>Exchange current density of H$_2$ evolution at carbon electrode (A/cm$^2$)</td>
<td>4.9e-9</td>
</tr>
<tr>
<td>Open-circuit potential vs. carbon electrode for H$_2$ rxn at reference conditions</td>
<td>0.33</td>
</tr>
<tr>
<td>Activation energy of H$_2$ rxn (J/mol)</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 2-5: Comparison between modeling and experimental at I=C/3
From those two figures, it can be seen that good agreements has been achieved between modeling results and experimental observations. During discharge, the voltage curve is mostly linear because the variation of the cell voltage during charge or discharge largely depends on the change of the negative electrode potential, as Figure 2-3 shows. The capacitor electrode potential keeps increasing as long as the battery is discharged. While approaching the end of charge, the increase in the voltage slows. This is because as the cell is being charged the bulk acid concentration rises, which raises the ionic conductivity and lowers the electrolyte potential gradient between the positive and negative sides. Finally the positive electrode potential cannot keep track of the linear

Figure 2-6: Comparison between modeling and experimental at I=C/15
growth of the negative electrode potential and slows down somewhat. This effect should be also influenced by the porous structures of layers and varies with different batteries.

2.3.2 Evolution of Acid Concentration

Figure 2-7 and Figure 2-8 reveal the evolution detail of the internal acid concentration distribution inside one cell. During discharge, hydrogen ions are consumed at the positive side and produced at the negative side; the opposite case takes place during charge. Comparing these two figures, one can find that a higher rate of charge or discharge results in a higher gradient of acid concentration due to the higher consumption rate and production rate of hydrogen ions at the two electrodes.

![Figure 2-7: The evolution of acid concentration distribution at I=C/3](image-url)
Figure 2-8: The evolution of acid concentration distribution at $I=C/15$

2.3.3 Distinct Features Separating PbC and Pb-Acid batteries

Figure 2-9 indicates the difference in the consumption of acid during the same capacity discharge between a conventional lead acid battery and a PbC battery. From the figure, it is assumed that the initial acid distribution is uniform. At the end of discharge, the acid concentration in the hybrid battery is higher than that in the lead acid battery. This is due to the fact that during discharge acid is consumed at both electrodes in the lead acid battery, whereas in the hybrid battery the positive electrode consumes acid and the negative electrode releases hydrogen ions during discharge. This figure is insightful
for designing the electrolyte concentration for a PbC hybrid battery. Since the total consumption range of acid concentration is narrow, the working range can be shifted to a lower level to decrease hydrogen gassing reaction equilibrium potential and further suppress gassing processes.

### 2.4 Parametric Study and Discussion

To design a PbC battery, there are two major performance criteria. One is to reach the energy density comparable to that of a conventional lead acid battery; the other one is to ensure the battery can function properly under the same cell voltage as that of the lead acid cell without serious gassing. The energy density of a PbC battery decreases from that
of a conventional lead acid battery because the AC electrode stores less energy per unit volume than the lead electrode, therefore the key approach to increase the energy storage in a PbC hybrid battery is to raise the charge storage in the capacitor electrode. Provided that the dimensions of the electrode and the potential window are fixed, the specific capacitance of the AC selected is the critical parameter determining the energy density. This section is designed to simulate and compare the performance of PbC batteries with a variety of AC materials. Also, discharge-charge simulations that involve the gassing process with the AC material candidates are conducted to demonstrate the trade-off in selecting carbon materials. More detailed gassing analysis will be presented in Chapter 3.

2.4.1 Effect of Specific Capacitance

Seven different AC materials are selected for simulation and comparison here. All the other parameters are set as fixed values, such as the weight ratio between positive and negative electrodes and cell dimensions. Table 2-2 shows the seven candidates selected from Ref.[23]. M-series are AC micro beads and all of the rest are AC fibers. It can be seen that even for one class of carbon, a higher surface area does not guarantee a higher specific capacitance.
Table 2-2: Specific capacitance and BET surface area for seven ACs

<table>
<thead>
<tr>
<th>ACs</th>
<th>M10</th>
<th>M20B</th>
<th>M30</th>
<th>FU2A</th>
<th>FU11C</th>
<th>FD1</th>
<th>SACF25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacitance (F/g)</td>
<td>224</td>
<td>413</td>
<td>272</td>
<td>154</td>
<td>249</td>
<td>135</td>
<td>207</td>
</tr>
<tr>
<td>BET (m²/g)</td>
<td>1370</td>
<td>1911</td>
<td>2571</td>
<td>1294</td>
<td>2015</td>
<td>1851</td>
<td>2371</td>
</tr>
</tbody>
</table>

Figure 2-10 compares the voltage behaviors of the AC candidates under a galvanostatic discharge at I=20A. It can be seen that the battery capacity increases with the capacitance of negative carbon electrode. M20B and FU11C almost have the same BET (m²/g), but the capacity behaves differently due to the different specific capacitance. This indicates that the capacity-determinant parameter for a PbC battery is the specific capacitance other than the surface area of the AC electrode.
Figure 2-10: Galvanostatic discharge process for batteries with different negative carbon materials

Figure 2-11 shows the acid concentration distribution in the end of discharge for batteries with different AC materials. The electrode with M20B in negative has the lowest acid concentration due to the largest depth of discharge.
Figure 2-12 compares the energy and power performance for the batteries with different AC capacitor electrodes. It can be seen that M10 with a higher specific capacitance yields good performance. Thus by using this model, one can quickly predict the performance curve on Ragone plot for any kind of carbon electrode employed in a PbC battery, and easily identify the desirable carbons of specified designs.
2.4.2 Carbon Material Selection

As stated above, to design a PbC battery, there are two major requirements. One is to reach the same energy density as a conventional lead acid battery; the other requirement is to ensure the battery can work properly under the same cell voltage as that of a conventional lead acid battery without serious gassing. The simulation above shows that specific capacitance of the carbon electrode is the dominant factor determining the consequential energy density. However, under an electrode potential of -0.3V vs SHE the AC electrode can easily produce hydrogen in aqueous acidic electrolytes during charge. Therefore, inhibiting HER at the AC electrode during charge is another important issue in
the design of PbC batteries. In this section, discharge-charge simulations including
gassing processes with the selected AC materials are conducted to investigate the coupled
effect of the carbon electrode specific capacitance, specific surface area and the exchange
current density of HER on battery performance, and also exhibit how to select the
optimal material candidate for the AC electrode via simulation results.

Figure 2-13 describes a process wherein the battery is discharged at I=20A to
6V/battery, then charged at I=20A. During charging, hydrogen gas is produced.
\[ i_{0,H_2} = 6.3e^{-8} \text{A/cm}^2 \] for all carbons suggested by Pillay and Newman[72]. The solid line is
the voltage and the dashed line is the gassing current. Each color is for one AC material.

![Figure 2-13: Cell voltage and H\textsubscript{2} gassing current during a discharge-charge process with seven different AC electrodes](image-url)
To compare the gassing rate, the hydrogen current at 1.75V for different carbon materials is showed in Table 2-3. By interpreting the above figure, one can quantitatively compare the capacities and gassing rates of cells with different carbon materials, and thus the trade-off in carbon selection can be determined. Here M20B leads to a larger capacity, but its gassing rate is higher. Comparing M10, M30 and FU11C, one finds M10 is a little lower in capacity and M30 has a higher gassing rate, so FU11C falls in between and may be the best selection.

Brennan and Brown[71] presented that for AC electrodes that have been cathodically polarized, $i_{\text{corr}} = 4.9e^{-9} \text{A/cm}^2$. Figure 2-14 shows the comparison between the cases with the AC electrode pretreated and untreated.

<table>
<thead>
<tr>
<th>Carbon Material</th>
<th>Hydrogen Current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M10</td>
<td>-1.25</td>
</tr>
<tr>
<td>M20B</td>
<td>-5</td>
</tr>
<tr>
<td>M30</td>
<td>-4</td>
</tr>
<tr>
<td>FU2A</td>
<td>-1</td>
</tr>
<tr>
<td>FU11C</td>
<td>-2.75</td>
</tr>
<tr>
<td>FD1</td>
<td>-0.8</td>
</tr>
<tr>
<td>SACF25</td>
<td>-2</td>
</tr>
</tbody>
</table>
From this figure, the voltage rising rate for the curve with $i_{0,H_2} = 6.3\text{e}{-8}\text{A/cm}^2$ slows down as the potential goes higher. This is due to the fact that the hydrogen gassing current shares the total input current, so the actual charging current is reduced. It can be seen that $I_{H_2} = -2.5\text{A}$ (the green dot) when $V_{cell} = 1.94\text{V}$ for the green curve, while $I_{H_2} = -18\text{A}$ (the blue dot) when $V_{cell} = 1.94\text{V}$ for the blue curve. So the gassing rate is reduced by 85% or more at this voltage due to the de-activation of the electrode.
Hydrogen evolution needs to be inhibited during charge. These results show it is more effective to suppress hydrogen production by decreasing $i_{0,H_2}$ (for example changing electrode composition or some de-activation procedures) than reducing the surface areas of carbon electrodes. The surface area usually can be changed in 2~5 times, but $i_{0,H_2}$ can vary in orders of magnitude. This model featuring both capacity and gassing predictions will be able to serve as a good tool for optimization of the material selection and carbon electrode composition during PbC battery design.

2.5 Conclusion

A mathematical model for PbC batteries was firstly developed to predict the performance behaviors under various operating conditions. This model features coupling of electrochemical, mass transport and thermal physics and also covers the gassing behaviors at electrodes during charge. The model was validated against testing data and showed good agreement. The internal physics were revealed through modeling results, such as the evolution of acid concentration during discharge and charge. The results showed that the wider range of a PbC battery voltage is a consequence of the large potential variation of the AC capacitor electrode and that the acid concentration gradient across the cell is larger when the applied current is larger. The difference between a PbC battery and a lead acid battery was illustrated by modeling results. It was indicated that the total acid consumption in the PbC battery is lower than that in the lead acid battery, and therefore the working range of acid concentration can be shifted to a lower level to
accommodate the electrode potential requirement and possibly to further suppress gassing processes.

Simulations for PbC batteries with a variety of AC materials have been conducted to investigate the effects of the specific capacitance and specific surface area of an AC electrode and the exchange current density of HER on discharge/charge performance. The results showed that the cell capacity largely depends on the specific capacitance rather than the specific surface area of an AC electrode. A typical discharge and charge process that involves the gassing process was simulated for the batteries with various AC electrodes to demonstrate the trade-off in selecting carbon materials. The demonstrated results showing the voltage and hydrogen gassing current behaviors provide a clear comparison among the material candidates in terms of capacity and gassing rate. The effect of the hydrogen gassing exchange current density was studied and the result indicated that it is more effective to suppress hydrogen production by decreasing \( i_{\text{h,H}_2} \) (for example by changing electrode composition or some de-activation procedures) than reducing the surface areas of carbon electrodes. The model developed here is based on first principle theories and promotes understanding of the internal physics of new PbC hybrid batteries. By incorporating capacity and gassing process predictions the model can serve as a design tool to compare and select the desirable carbon candidates for specified design of PbC batteries.
Chapter 3

ANALYSIS OF GASSING PROCESS AND ITS IMPACTS IN PbO$_2$-CARBON (PbC) BATTERIES

3.1 Introduction

Integrating an AC electrode with a battery electrode is not straightforward. As Lam and Louey [19] pointed out, the carbon capacitor electrode is usually used in a different working potential range from that of the negative lead electrode. For most super capacitor applications, AC electrodes are usually well tested via the cyclic voltammetry method to obtain a safe potential range within which neither hydrogen or oxygen would be produced[98]. The lower the carbon electrode potential, the more likely hydrogen would be produced; also the higher the potential of carbon electrode, the more likely oxygen would evolve. In most supercapacitors the AC electrodes work above the equilibrium potential of hydrogen evolution 0V vs SHE and below that of oxygen evolution 1.23V vs SHE under standard state. If salt or alkaline electrolyte is used instead[75], the potential will be shifted towards more negative range. For PbC battery applications, oxygen evolution would not be a problem as the AC electrode is applied on the negative side and the working potential rarely reaches as high as 1.2V vs SHE, that is, around the equilibrium potential for oxygen evolution under standard state. Thus the only gassing problem at the negative electrodes for PbC batteries is hydrogen gassing. To maintain the same open circuit voltage of cells-2V as lead acid batteries, the negative potential of PbC cells must drop to around -0.3V vs SHE below the equilibrium potential
in acidic electrolyte for HER. This would cause a severe hydrogen gassing problem, depending on the carbon electrode and operational conditions.

Much effort has been made to study the gassing process of lead acid batteries in the past [81-85,88,99]. Bernardi and Carpenter [82] added oxygen gassing reaction and recombination into lead acid battery model for the first time. The oxygen evolution and reduction were modeled and both the voltage and pressure behaviors during charge were predicted. Pavlov [99] showed the large impact of oxygen gassing circle on thermal rise during charge process. Later on, in the work [85] hydrogen evolution and recombination were included to describe the complete gassing behavior in lead acid batteries. Overcharge process was simulated through a complete gassing model in the work [88], where the effect of electrode design parameters and transport properties on voltage and pressure during overcharge process were all investigated. All the previous models were developed for batteries with lead negative electrodes, so for the PbC batteries with AC electrodes, the gassing behaviors will be different due to the inherent properties of AC electrodes.

A common application for AC electrodes is the electrochemical capacitor. However very few gassing studies for electrochemical capacitors are available. The reason is that the potential range of electrodes for capacitors is not limited to a precise window. The gassing process on AC electrodes of electrochemical capacitors has not been of interest and well studied. The only condition under which gassing evolves is in capacitors with acidic electrolyte. Pillay and Newman [72] investigated the effects of gassing reactions on the charging and cycling of electrochemical capacitors with sulfuric acid electrolyte through a porous electrode model. This model considered oxygen and
hydrogen generation as the dominant gassing reactions and presented the effect of
gassing on energy losses of electrochemical capacitors during cycling. However, this
model was design for a capacitor, so there were no any other electrochemical reactions
except gassing reactions, covering insufficient physics to model PbC batteries. Also, this
model was developed based on isothermal assumption that did not predict thermal
behaviors during gassing processes.

This chapter employs the fundamental non-isothermal model developed in
Chapter 2 to provide a profound understanding of the severe gassing problem that may take
place in PbC batteries, analyze the impacting factors on gassing and display the
resultant consequences of performance under various design and operational conditions.
Here the battery simulated is still a 60Ah PbC battery and all battery parameters listed in
Table 2-1 remain the same. In order to clearly show the effect of gassing on voltage
behavior during charge, a smaller Bruggeman correction factor[88] of acid conductivity is
used here, and thus the effect of increased acid conductivity on voltage during charge is
weakened.

3.2 Simulation of Gassing Process in Galvanostatic Charge

The first case to be considered is the gassing process that would occur during
galvanostatic charge. In most lab testing, the battery is discharged and charged at
constant current, and also different voltage limits are applied to let the battery reach full
charge as much as possible.
3.2.1 Effect of Gassing Process

Figure 3-1 shows that the 60Ah PbC battery is discharged at C/3 and then charged at C/3 to 13.8V as a cut-off voltage under different gassing kinetics. It is indicated from this figure that the voltage curve is only affected by the gassing process when the voltage goes beyond 12.0V. When no gassing is considered, the overpotential of positive electrode increases rapidly as the available charging surface area decreases in the end of charge, so the battery voltage quickly reaches the voltage limit; when hydrogen gassing is added, the rising rate of voltage becomes a little slower after passing 12.0V than that without any gassing. This is because the hydrogen gassing shares the entire charging current and the rate of carbon electrode potential decrease slows during charge. However, the voltage can still reach the limit quickly in the end. The most severe condition is with both oxygen and hydrogen evolutions. In this case, firstly only hydrogen is produced at the negative electrode, so the voltage curve is overlapped by the second case; after the voltage rise to a higher level, oxygen starts to evolve and part of the generated oxygen is transported to negative side and recombined there. This shows that a large percentage of charging current is shared by oxygen gassing reaction and the voltage curve enters a plateau. This is one severe condition during charge which occurs because the voltage is temporarily stabilized, and thus does not reach the voltage limit. The charging current keeps electrolyzing the water, which results in much water loss and heat build-up.
Figure 3-1: A 60Ah PbC battery discharge and charge curve at C/3 under different gassing kinetics

Figure 3-2 exhibits the electrolyte potential and actual charging current at the negative carbon electrode. As the blue curves indicate in the figure, without any gassing process the electrolyte potential of the negative capacitor electrode is linearly increasing during charge because the linear change of capacitor electrode potential dominates the variation of cell voltage. The actual charging current equals the input current and the capacitor electrode is consistently charged. When hydrogen evolves at the negative electrode, the actual charging current is significantly reduced due to the fact that hydrogen begins to share a large percentage of input current, so the charging rate, in other word, the rising rate of electrolyte potential is slowed down as the green potential curve
indicates. The red curve shows the simulation result with both oxygen and hydrogen gassing. At first the charging current is the same as that with only hydrogen gassing. When the positive potential increases beyond a certain value, oxygen evolves at the positive electrode and at the same time reduced at negative side. It can be seen from the figure that the charging current continues to drop as more and more current is shared by gassing processes due to the rising voltage. When the whole current is completely taken over by gassing processes or the gassing current is even larger than the whole input current, the voltage will decrease a little bit and finally reaches the balance between charging current and gassing current.

Figure 3-2: Electrolyte potential and charging current evolution during galvanostatic charge under different gassing kinetics
Figure 3-3 shows the pressure and gassing current for these three cases. When no gassing occurs, all the gassing current is 0 and the pressure stays constant. When only hydrogen gassing occurs in the end of charging, the current from HER quickly increases to -14A taking 70% of the whole input current. It can be seen from the figure hydrogen gassing alone is enough to accumulate sufficient gas pressure to open the valve, as the green solid curve indicates. Opening pressure of the valve is 1.17 atm and closing pressure is 1.10 atm. The battery is vented three or four times before the voltage reaches the limit. As predicted above, when oxygen generation and recombination is added in the end of charge the hydrogen current first increases and then decreases as oxygen starts to evolve and be recombined at the negative. The reduction current of oxygen at the negative becomes so large, as more and more oxygen produced at the positive side and transported to negative side, that it forces the hydrogen current to decrease. Due to the large amount of gas produced and the stable voltage the battery has reached during gassing, the battery keeps being vented frequently, which leads to much water loss and degradation.
3.2.2 Effect of Carbon Electrode Thickness on Capacity and Gassing during Galvanostatic Discharge and Charge

With the width and height of a cell fixed, the electrode thickness affects cell capacity. However, it is apparent that a thicker electrode provides more surface area for gassing, so proper selection of electrode thickness is important during design. This section is to quantitatively study the effect of electrode thickness on capacity and gassing rate within a common range of electrode thickness.

In order to compare the effects of oxygen and hydrogen gassing process, a larger value of oxygen exchange current density has been used corresponding to certain
electrode ingredient designs. In practice, a PbC battery uses the same positive electrode as an AGM lead acid battery and it is usually accepted that the positive electrode produces little oxygen when the voltage is below 13.8V for most brands of batteries. The work of this chapter therefore focuses mainly on hydrogen gassing in PbC batteries, but takes oxygen gassing into account in some simulation cases for completeness.

Figure 3-4 shows the discharge and charge voltage curve for different electrode thickness designs. Here all three layers of one cell are assumed to be the same thickness. It can be seen that with increasing electrode thickness the discharged capacity of battery increases. This is due to both the increased mass of the positive electrode and the increased capacitance of the negative AC electrode. For PbC batteries, the wide potential window largely depends on the capacitance of the AC capacitor electrode. The larger the capacitance, the less steep the discharge curve and the more capacity the battery can discharge.
Figure 3-5 demonstrates the effect of electrode thickness on hydrogen gassing current. It can be seen that once the battery voltage reaches a certain kick-off value of gassing, the hydrogen gassing current increases rapidly with even small increase of battery voltage. With the electrode thickness increasing the largest hydrogen current increases accordingly. This is due to the increased active surface area in AC electrodes which provides more reaction sites for gassing. Comparing those two figures, one can find that when the thickness is enlarged from 0.10cm to 0.18cm, or say 80% increase of electrode thickness leads to around 60% increase of capacity; however, the largest hydrogen current increases from -11A to -13.5 A, 20% increase of gassing current. It can
thus be concluded that thickening the electrodes is worthwhile in the trade-off between increased capacity and lower gassing current.

![Diagram](image)

Figure 3-5: The effect of electrode thickness on hydrogen current during charge process

### 3.2.3 Effect of Initial Carbon Electrode Potential

For conventional lead acid batteries, the primary reactions on both electrodes are as Eq. 3.1 and Eq. 3.2 show. The equilibrium potential on the electrode is 1.685V and -0.356V vs SHE, so the cell OCV is around 2V. For PbC batteries, the positive electrode is still the same as Eq. 3.1 shows, but the negative is an AC capacitor electrode.
Figure 3-6 shows the relationship between acid concentration and equilibrium potential of the positive electrode. It is clear that the variation of acid concentration does not cause much difference in equilibrium potential, as shown in Chapter 2. The potential is around 1.71V–1.72V vs SHE when the acid concentration varies from 3M to 5M. This indicates that the large voltage window of a PbC cell-[0.6V, 2V] is mainly contributed by the AC capacitor electrode. To maintain the same OCV-2V that has been widely accepted, the initial potential of AC electrode must be around -0.3V vs SHE, and with discharging the electrode potential increases so that the cell voltage decreases. In this section, the effect of the initial potential of negative capacitor electrode on the performance and gassing behaviors is studied. The initial potential of the AC electrode is designed and realized by adjusting the PbO₂: AC weight ratio, as explained in Chapter 2, which actually adjusts the working potential window of the AC electrode.

\[ PbO_2 + 2H_2SO_4 + 2H^+ + 2e^- \rightleftharpoons PbSO_4 + 2H_2O \ 1.685V \text{ vs SHE} \]  
\[ Pb + H_2SO_4 \rightleftharpoons PbSO_4 + 2H^+ + 2e^- -0.356V \text{ vs SHE} \]
Figure 3-7 displays the voltage and hydrogen gassing current with three different initial negative potentials. The cell is discharged at I=20A for 20 minutes and then charged at I=20A to the voltage limit. From this figure, it can be seen that the cell OCV linearly increases with the initial negative capacitor electrode potential. Also, the hydrogen gassing is almost nothing when a higher initial potential- -0.1V vs SHE is applied. The gassing current keeps increasing with the initial negative electrode potential decrease. When the potential is reduced to -0.4V vs SHE, the gassing current jumps to 15A in the end of charge. This is because the lower the initial negative electrode is, the
lower the overpotential of hydrogen gassing reaction will be, as Eq. 3.3 shows, and the larger the absolute gassing current will occur.

![Graph showing effect of initial negative electrode potential on cell voltage and hydrogen gassing current](image)

**Figure 3-7**: The effect of initial negative electrode potential on cell voltage and hydrogen gassing current

\[ \eta_{H2} = (\phi_a - \phi_{neg})_{U_{H2}} < 0 \] during charge \hspace{1cm} 3.3

Figure 3-8 summaries the effect of initial negative electrode potential on cell voltage and peak hydrogen current during the charge process described above. It can be seen that the cell voltage linearly increases with the initial negative electrode potential decrease and the peak hydrogen current increases exponentially with the initial negative potential decrease. This figure indicates that on one hand starting from the normal value -
0.3V vs SHE, raising the initial negative potential causes less hydrogen production during charge at the cost of linear decrease of cell voltage. One can observe that after -0.2V vs SHE, the decrease of hydrogen current slows greatly, so it is not worthwhile using a higher negative potentials or reducing the cell voltage. On the other hand, lowering initial negative potential linearly raises the cell voltage; however, the peak hydrogen gassing current become very sensitive to the negative electrode potential in this range and grows more rapidly with the initial negative potential drop, so the initial potential should be designed very carefully when adopting lower initial negative potentials for the carbon capacitor electrodes.

Figure 3-8: Summary of the effect of initial negative potential on cell voltage and peak hydrogen current during charge
Figure 3-9 shows the effect of initial negative potential on battery capacity and energy density. The energy density is calculated based on a discharge process at I=C/3 starting from SOC=1 to 3.6V and Eq. 3.4. \( N \) denotes the number of cells, \( t_d \) is the discharge time, \( V_{batt} \) is the total volume of the battery calculated from the overall dimensions.

\[
E = \frac{N}{V_{batt}} \int_0^{t_d} V dt
\]  

3.4

It can be seen from the figure that employing lower initial negative potentials definitely provides batteries with higher voltages, higher capacities and energy densities. However, considering hydrogen current suppression during charge, the optimal range of initial negative potential should be identified. Higher initial negative potentials assures small hydrogen gassing current, but weakens the capacity and energy performance; oppositely lower initial negative potentials lead to good energy performance, but favor gassing reactions. Based on the results of these two figures, the range of [-0.33V, -0.25V] vs SHE seems to be a good compromise between energy performance and gassing process.
Cycling operations are much more frequently encountered in practice than galvanostatic or potentiostatic charge/discharge. Most lifetimes of batteries for EV or HEV applications are spent on cycling, so it is of great importance to understand how the gassing process evolves in PbC batteries and how it impacts the performance during cycling since such batteries are designed for HEV operation. The objective of this section is to demonstrate the gassing process of PbC batteries, including both internal physics and external performance behaviors during cycling. The effect of some design factors and operational parameters on gassing process and cycling performance will be investigated.

Figure 3-9: The effect of initial negative potential on capacity and energy density

3.3 Simulation of Gassing Process during Cycling

Cycling operations are much more frequently encountered in practice than galvanostatic or potentiostatic charge/discharge. Most lifetimes of batteries for EV or HEV applications are spent on cycling, so it is of great importance to understand how the gassing process evolves in PbC batteries and how it impacts the performance during cycling since such batteries are designed for HEV operation. The objective of this section is to demonstrate the gassing process of PbC batteries, including both internal physics and external performance behaviors during cycling. The effect of some design factors and operational parameters on gassing process and cycling performance will be investigated.
3.3.1 Electrolyte Potential Evolution at the AC Electrode with Cycling

The simulation case here is that the battery is discharged for 20 minutes at I=C/3, then starts cycling. The cycle profile is I=C/3 discharge followed by I=C/3 charge, and both discharge and charge last 5 minutes.

In the simulation, the solid phase potential of negative electrode is always set as $\phi_{s,-} = 0$, and usually the electrolyte phase potential is assumed to be 0 when it is open circuit and fully charged, so the initial potential of carbon electrode at fully charged is set as $\phi_{s,-} - \phi_{e,-} = 0$. During discharge or charge, the only potential that changes at the AC electrode in this simulation is $\phi_{e,-}$, which actually reflects the variation of negative electrode potential. Figure 3-10 compares the electrolyte potential $\phi_{e,-}$ evolution during cycling with and without gassing. From this figure, it can be observed that the capacitor electrode can recover the equal amount of charge released during discharge part of each cycle without any loss, so every time it is charged the potential of the negative capacitor electrode can reach the same potential as the previous cycle. When the gassing is considered, $\phi_{e,-}$ keeps decreasing with cycling, which means the potential of capacitor electrode keeps rising. This is because during cycling gassing current shares the total input charge current, which reduces the actual charge current that contributes to the potential variation of the capacitor electrode. At every charge of each cycle, the capacitor electrode is unable to recover the same amount of charge released during the last discharge, which drags the potential down slightly in each cycle.
3.3.2 Electrode Potentials and Cell Voltage Development with/without Gassing

Figure 3-11 shows the development of negative electrolyte phase potential, positive equilibrium potential and cell voltage as cycling. All the curves denote the corresponding values at the end of charge in each cycle. Eq. 3.5 gives the relation among the three curves in this figure, in which $\eta$, and $(\phi_{e^+} - \phi_{e^-})$ can be considered as constant due to the constant current charge. After a few initial cycles the battery reaches steady state for the cycling conditions. It can be seen that the positive equilibrium potential
keeps constant with cycling. Also, due to the fact that the capacitor electrode can completely recover the charge released during discharge without gassing parasitic reactions, the electrolyte potential reflecting the capacitor electrode potential remains the same as cycling.

\[
V_{\text{cell}} = \phi_{a,+} - \phi_{a,-} \\
= (\phi_{a,+} - \phi_{c,+} - \eta_{a}) - (\phi_{a,-} - \phi_{c,-}) + (\phi_{c,+} - \phi_{c,-}) + \eta_{c} \\
= U_{eq,+} + \phi_{c,-} + \eta_{a} + (\phi_{c,+} - \phi_{c,-})
\]

3.5

Figure 3-11: The development of potentials during cycling without gassing

Figure 3-12 shows the development of negative electrolyte potential, positive equilibrium potential and cell voltage during cycling with gassing. As displayed in
Figure 3-10, the negative electrolyte potential at the end of charge of each cycle keeps decreasing due to the insufficient charge of the capacitor electrode caused by gassing current. Therefore, the cell voltage drops because the gassing current shares the total input current and causes insufficient charge of capacitor electrode.

![Graph showing potential development during cycling with gassing](image)

**Figure 3-12**: The development of potentials during cycling with gassing

### 3.3.3 Peak Hydrogen Current and Charge Efficiencies Evolutions during Cycling

The coulombic efficiency is defined as the ratio of the charge put into a battery and the charge released in the subsequent discharge. This is due to incomplete conversion of the charging current into utilizable reaction products. Eq. 3.6 and Eq. 3.7 give the equation for coulombic efficiency and energy efficiency calculations.
In this simulation, the battery is discharged for 20 minutes at \( I = C/3 \), which drains the battery to around 90% SOC. The battery is then charged for 5 minutes at the same current and subsequently discharged to the same SOC as that before the charge process. The above two equations are applied to calculate the coulombic efficiency and energy efficiency of this discharge-charge process. After the efficiencies were calculated, the battery continued discharge to complete the 5-minute discharge part of one cycle. Here 38 cycles have been simulated.

Figure 3-13 shows the development of peak hydrogen current, coulombic efficiency and energy efficiency during cycling. Here the peak hydrogen current corresponds to the value at the end of charge. It can be seen that the peak hydrogen current decreases with cycling and the decreasing rate becomes slower and slower with cycling. This is because the current depends on the overpotential of hydrogen gassing reaction, which actually relies on the negative electrode potential \( \phi_{e^-} \), as Eq. 3.8 indicates. A lower overpotential with a larger absolute value produces a larger gassing current. As presented in the above results, \( \phi_{e^-} \) at negative side raises higher and higher with cycling due to the fact that the electrolyte phase potential \( \phi_{e^-} \) at negative drops lower and lower, so \( \eta_{H_2} \) rises and \( i_{H_2} \) keeps dropping with cycling.
Coulombic efficiency and energy efficiency show the same trend as hydrogen current because the gassing current is the only factor that results in incomplete conversion of charge into utilizable reaction products. Energy efficiency is always lower than coulombic efficiency because the charging average voltage is always higher than that of the discharge due to kinetic, ohmic and mass transport overpotentials.

Figure 3-13: Peak hydrogen current and efficiency development during cycling

\[ i_{\text{H}_2} = a_i i_{\text{O, H}_2} \left[ \exp\left(\frac{\alpha_i F \eta_{\text{H}_2}}{RT}\right) - \exp\left(\frac{-\alpha_i F \eta_{\text{H}_2}}{RT}\right) \right] \]

\[ \eta_{\text{H}_2} = (\phi_{\text{H}_2} - \phi_{\text{H}_2}) - U_{\text{eq, H}_2} \]

To demonstrate the transient behavior of hydrogen current during the cycling charge time, Figure 3-14 selects three different time points during the whole cycling
simulation: the first cycle, the 20th cycle and the last cycle. It can be seen that during the
charging in each cycle, the hydrogen gassing current keeps increasing with the negative
electrode potential decrease. It is interesting to note that, as also indicated in last figure,
the hydrogen current is reduced significantly in the first 20 cycles. Specifically the
hydrogen current decreases from the starting peak value -4.5A to -1.3A, whereas in the
following 18 cycles the hydrogen current only falls by around 0.4A. It can be concluded
that the primary drop of hydrogen gassing current during cycling, being consistent with
the variation of negative electrode potential, occurs in the initial stage of cycling.

Figure 3-14: Hydrogen current transients during the charge part of cycles
Figure 3-15 presents the hydrogen current distribution in the end of discharge at different cycles. It can be seen that the current density distribution is almost uniform except that it is a little higher towards the interface between separator and negative electrode. This is because the electrolyte potential at the interface is a little higher during charge, as Figure 3-16 shows. So the electrode potential at the interface is lower, and the gassing current is larger, as Eq. 3.8 explained above. It is also noted that the potential difference across the cell is very small, which explains why the current density distribution is mostly uniform through the AC layer.

![Figure 3-15: Hydrogen current density distribution in the end of charge at different cycles](image-url)
3.3.4 Effect of Cycling Current on Charge Efficiencies

Cycling current here is referred to as the discharge and charge current during cycling. It usually depends on the loading requirements of practical applications, and also impacts the charge efficiency during cycling. Figure 3-17 shows the effect of cycling current on charge efficiencies. Here the efficiencies are all calculated at the first cycle of charge-discharge. It can be seen that larger cycling current can lead to higher charge efficiencies. However, when the cycling current falls below I=20A (C/3) for this battery, the efficiencies quickly drop; and also the efficiencies barely grow after the current is
increased beyond 30A. This result actually reflects the ratio between the hydrogen gassing current and the total input current. In the end of charge the voltage under different charging current barely differs, therefore the gassing current almost remains the same. When the entire current is very low, the major percentage is taken by the parasitic gassing current and the charge efficiencies are low. On the contrary, when the total current becomes very large, the gassing current will no longer greatly impact the efficiency.

Figure 3-17: The effect of cycling current on charge efficiencies
### 3.3.5 Effect of SOC on charge efficiencies

HEV applications usually require batteries running under partial SOC. Here the effect of running SOC on charge efficiencies is studied. Figure 3-18 shows the effect of initial SOC before cycling on the charge efficiencies. The simulated cycle is 10-min charge and discharge, and the efficiencies are calculated at the first cycle. From this figure, it is apparent that for this hybrid battery the SOC range between 0.8 and 0.9 is critical to the charge efficiencies. The coulombic efficiency drops from 0.98 to 0.72 when the starting SOC changes from 0.8 to 0.9. This is due to the fact that the onset of hydrogen gassing process falls into the SOC range between 0.8 and 0.9, and once the gassing process is triggered, it grows exponentially as the SOC increases. This is why the coulombic efficiency can quickly decrease with even a little increase of SOC. After the SOC passes 0.9, the hydrogen gassing process is even more severe, and the coulombic efficiency would go much lower. Energy efficiency, as expected, parallels the trend of coulombic efficiency and stays at a lower level than coulombic efficiency due to the difference between charge voltage and discharge voltage.
3.3.6 Effect of Cycling Pulse Width on Charge Efficiencies

Selecting an appropriate pulse width for a cycle profile is important to effective and efficient battery performance. Figure 3-19 shows the effect of pulse width of one cycle on coulombic and energy efficiencies for PbC batteries. The cycling current and initial SOC remain at 20A and 0.9, respectively. The cycling pulse width varies from 2.5 minutes to 12.5 minutes. It can be seen that the charge efficiencies decrease with the increased cycling pulse width. This is because during the charging pulse the hydrogen current is not constant, as stated above, and increases rapidly especially when SOC is
relatively high, as in the case of SOC=0.9 here. Thus the ratio between the gassing current and total current increases with the pulse width prolonged, and the coulombic efficiency drops accordingly.

3.3.7 Effect of Carbon Electrode Thickness on Charge Efficiencies during Cycling

Electrode thickness is always one critical design parameter when the battery design is customized for some specified applications as it determines the overall capacity, power performance and gassing behaviors. For HEVs, power performance is important, so a higher specific active area is desired; whereas for EVs deep discharge operations
expect batteries to have thick electrodes. In the above sections, the effect of electrode thickness on galvanostatic charge has been studied, while in this section the effect of thickness during cycling will be demonstrated.

Here the charge efficiencies are also calculated through a simulation of 5-min charge/discharge process with an initial SOC of 0.9. Figure 3-20 shows the effect of electrode thickness on battery capacity, coulombic efficiency and energy efficiency. As expected, the capacity increases linearly with electrode thickness, and the increase rate is 17Ah/0.08cm. The efficiencies decrease with electrode thickness increase. This is due to the fact that thicker electrodes have larger active surface areas that facilitate the hydrogen gassing reaction, so the efficiencies decrease. It can be noted that thinning the electrode by 0.04cm can improve the charge efficiency by 10%.
Figure 3-21 shows the details of hydrogen current evolution during the charging pulse of the first cycle. It can be seen that as mentioned above a larger electrode thickness leads to a higher hydrogen gassing current. Also the gassing current rises roughly linearly with the electrode thickness. Once again, this figure shows the gassing current evolution within the charge pulse. As explained above, the current increases rapidly with charging, so prolonging the pulse width will allow the gassing current to grow and result in lower charge efficiencies.
Battery thermal management is of great importance as it affects the performance, lifetime and stability of batteries. Batteries working under very low temperatures deliver poor performance and shorter cycle life; whereas batteries operated at very high temperature become unstable and may also show premature capacity loss. All of these phenomena are due to the fact that the physical properties of battery are closely related to temperature, for example kinetic parameter-exchange current density, or transport
parameter-ion diffusivity and conductivity. Therefore a proper temperature range is essential for a battery to achieve optimum performance and extend lifetime.

For VRLA batteries, the most outstanding thermal rise comes from the gassing process. When a VRLA battery is overcharged or reaches high voltages, the oxygen generation-recombination cycle starts, which releases a lot of heat and causes significant temperature rise. When the temperature is raised higher and the physical properties are increased by the high temperature and favor the side reactions, the battery is likely to enter a self-accelerating heat build-up, which is usually called thermal runaway.

The methods to investigate this thermal behavior for VRLA batteries can be experimental or modeling. Giess [100] and Haering and Giess [101] used a thermal video imaging system to investigate the thermal process. Pesaran and co-workers investigated the thermal problems arising in EV and HEV batteries using coupled calorimetric electrochemical device and proposed a battery thermal management system [102-104]. The work [105] studied the effect of separator on thermal runaway by testing different separators. Li et al.[106] studied the influence of temperature and state of charge (SOC) on the rate of recombination of H₂O. The thermal runaway during oxygen gassing cycle was investigated under constant voltage charging at different levels of voltage [107]. Gu and Wang [108] proposed a general form of thermal energy equation for a battery system. The thermal-electrochemical coupled model was used to predict both electrochemical and thermal behaviors of batteries.

In this thesis, an electrochemical and thermal coupled model has been developed for PbC batteries in Chapter 2. The effect of temperature rise on all physical properties has been integrated to reach a comprehensive prediction of hybrid battery performance.
The similarity between VRLAs and PbC batteries is that both of them would have gassing problems if not operated properly, and this would cause intense heat build-up inside the batteries. The difference is that less oxygen gassing should occur due to the lower cut-off voltage, 13.8V; whereas much more hydrogen gassing is expected in the end of charge process due to the lower electrode potential and the larger H$_2$ exchange current density at AC electrodes. This section is designed to focus on the battery thermal behaviors during the gassing process and their effects on performance.

3.4.1 Thermal Model Validation

The modeling prediction of temperature is validated against the testing data of a full discharge at I=C/3 followed by a charge process to a cut-off voltage of 13.8V at I=C/3. The modeling result of voltage has been compared with testing data during the mode validation in Chapter 2, so here only the temperature is compared to validate the thermal model. Figure 3-22 shows the comparison between modeling result and testing data. It can be seen that the modeling results mostly captured the trend of temperature rise in testing. The temperature consistently increases in discharge and charge processes. The fluctuation of the testing data is probably due to the environmental condition change during testing.
3.4.2 Temperature Rise during Gassing Processes

As mentioned in previous sections, massive oxygen generation at positive electrodes below the battery voltage of 13.8V is usually not expected for most brands of lead acid batteries. However, lower potentials at the AC electrodes in the end of charge may cause severe hydrogen gassing, so in this section efforts are focused on the hydrogen gassing process and the resultant effect on temperature rise. Two parameters are critical to determine hydrogen production rate; one is the HER exchange current density $i_{o,H_2}$, which
is affected by electrode material, electrolyte and additives; the other is the electrode specific surface area, which is an inherent property of a certain type of AC.

Figure 3-23 shows the effect of HER exchange current density on hydrogen current during charge. The value of $i_{0, H_2} = 4.9 \times 10^{-9} \text{A/cm}^2$ comes from Ref. [71], where the HER on pyrolytic graphite and vitreous carbon in acid solutions were studied. The value of $i_{0, H_2} = 4.9 \times 10^{-15} \text{A/cm}^2$ is the same as the one used in conventional lead acid batteries. Here it is just used as a very low value to suppress HER and study the effect of $i_{0, H_2}$. So from this figure it is clear if $i_{0, H_2}$ can be reduced to this order by any approach such as additives or surface treatment, the hydrogen current can be suppressed as low as that in the conventional lead acid batteries.
Figure 3-24 gives the corresponding voltage response to different $i_{0,\text{H}_2}$. It can be seen that during charge the two voltage curves overlaps before hydrogen gassing occurs. Once hydrogen starts to be generated, the voltage with higher hydrogen current becomes lower than that without hydrogen current. As explained before, the hydrogen current shares a percentage of total current, so the charge rate of the negative slows.
Similarly, before gassing the temperature curves are the same for two cases; after hydrogen gassing takes place, the rate of temperature rise is larger for $i_{0,H_2} = 4.9 \times 10^{-15}$ A/cm$^2$. This is because the irreversible heat generated for one electrochemical reaction is as Eq. 3.9 shows, then the gassing heat at the negative electrode can be calculated accordingly; however, the releasing and restoring charge of the capacitor electrode are assumed not to produce any reaction heat, so the gassing reaction leads to a quicker rise of battery temperature.

Figure 3-24: The effect of HER exchange current density on voltage during charge

Figure 3-25 shows the corresponding temperature rise with different $i_{0,H_2}$. 

![Graph showing the effect of HER exchange current density on voltage during charge](image)
Figure 3-25: The effect of HER exchange current density on temperature rise during charge

\[ q = i \eta = i(\phi_s - \phi_e - U) \]  

3.9

Figure 3-26, Figure 3-27 and Figure 3-28 study the effect of electrode specific surface area on gassing process and temperature rise. For AC electrodes, the specific capacitance usually increases with the specific surface area, but this is not always the case. Figure 3-26 shows the effect of AC electrode specific area on hydrogen current during charging processes. As the figure indicates, the blue curve is the base case; and the orange and purple curves denote the cases with changed specific surface areas but the same capacitances; the red and green curves represent the cases where the capacitance changes proportionally with the specific surface area. It can be seen from the figure that
with a larger capacitance, the varying rate of voltage is slower, so the charging time is longer. In the meantime, the peak hydrogen gassing current increases with the specific surface area of the AC electrode, and is not affected by the specific capacitance.

Figure 3-26: The effect of specific surface area at carbon electrodes on hydrogen current during charging

Figure 3-27 gives the voltage behaviors of the above simulation. As expected, a larger capacitance of the AC electrode leads to a slower rise of voltage and greater charge capacity. The capacity is almost linearly proportional to the capacitance of the AC electrode, which once again verifies the change in battery voltage is mostly dependent on the variation of the negative capacitor electrode. For the three curves in the middle of this figure, the larger hydrogen current slows down the rising of voltage to the limit in the end of charging.
Figure 3-27: The effect of specific surface area at carbon electrodes on voltage during charging

Figure 3-28 shows the temperature rise with different specific surface areas of AC electrodes during charging processes. It can be seen that the hydrogen current and temperature rise depend on the negative electrode surface area, provided that the capacitance of the AC electrode is fixed. A larger surface area results in higher hydrogen current and higher temperature rise accordingly. It can also be concluded from this figure that the capacitance impacts the temperature rise during charging processes as well. This is because a larger capacitance of the AC electrode allows the battery to discharge longer before reaching the cut-off voltage, so the battery or specifically the positive electrode can discharge more. The same explanation applies to the charging process, so longer charging processes produce more heat and higher temperature rise, as the figure indicates.
3.4.3 Possible Thermal Runaway involving Oxygen Gassing Cycle

From the above simulation results, it can be concluded that with the values of HER exchange current and possible surface area that are currently available in literature, the parasitic hydrogen current is significant. However, the battery voltage can still safely reach the voltage limit without any thermal runaway. This is due to the fact that even though at the negative electrode the input current is largely taken by the HER and the potential of negative electrode does not grow much while close to the end of charging,
the overpotential at the positive electrode can still increase rapidly, which causes the total battery voltage quickly reach the voltage limit and then the battery is shut down safely.

To cover all the possible cases for the hybrid battery operations, it is necessary to study the batteries assembled with PbO₂/PbSO₄ electrodes that have higher kinetic activities of oxygen evolution. In this way, the possible thermal runaway for PbC batteries can be predicted, evaluated and avoided during design processes or operations. This section is to adopt higher kinetics of oxygen generation, investigate the coupled effect of both oxygen gassing cycle and HER on temperature rise and predict the possible thermal runaway of PbC batteries.

Figure 3-29 summarizes the current, voltage and temperature variation during a discharge-charge process as a base case. The battery is discharge to 6V, and then charged to a cut-off voltage of 13.8V. The battery temperature increases by around 6°C.
Figure 3-30 shows the battery voltage and current partition in the negative electrode. Being consistent with the above results, the hydrogen current rapidly increases and the actual charging current for the capacitor electrode decreases accordingly. It can be seen that the oxygen gassing has not be initiated due to the lower kinetic parameter, $i_{0,o_2}$. 
Figure 3-30: Negative electrode current partition during a discharge-charge process with $i_{0, H_2} = 4.9 \times 10^{-9} \text{A/cm}^2$ and $i_{0, O_2} = 1.5 \times 10^{-27} \text{A/cm}^2$

Figure 3-31 shows the corresponding current, voltage and temperature curves when a higher $i_{0, O_2}$ is applied. As the figure shows, the voltage enters into a plateau at the end of charging before reaching the shut-down voltage limit, and also the temperature keeps rising during this phase of charging. This is a case of thermal runaway. The oxygen generation starts before the battery reaches the voltage limit. The large oxygen current takes over the largest percentage of total input current, so the positive electrode is barely being charged while the voltage remains the same. The massive oxygen production generates more heat due to the lower equilibrium potential than the primary charging reaction, so the temperature increases much more quickly than before. Also, the rising
temperature facilitates the oxygen reaction and leads to more heat production, which causes the battery to run under a self-accelerating temperature rise.

Figure 3-31: Current, voltage and temperature variation during a discharge-charge process with $i_{b,H_2} = 4.9 \times 10^{-9}$ A/cm$^2$ and $i_{b,O_2} = 1.5 \times 10^{-2}$ A/cm$^2$.

Figure 3-32 shows the internal details of current partition at the AC electrode and oxygen generation current at the positive electrode. It can be seen that for AC electrodes the onset of hydrogen gassing reaction is earlier than that of oxygen generation reaction. The hydrogen current quickly grows and reduces the actual capacitor charging current. Initially, there is no oxygen reduction current at the negative electrode, so the voltage and hydrogen current increase without any limitation. While it is close to the end of charging, the voltage increases rapidly, which leads to a quick jump of oxygen reaction
current at the positive electrode. The oxygen produced at the positive electrode is transported to the negative side and reduced there. The purple line denotes the reduction current of oxygen. As the oxygen gas is massively produced and transported to the negative side, the reduction current gradually dominates the entire input current. However, the hydrogen current is closely related to carbon electrode potential or cell voltage, so as the reduction current grows the cell voltage has to decrease to reduce hydrogen current. This is realized by a short reverse of charging current that makes the negative electrode potential increase slightly (cell voltage decrease). After the adjustment of current partition, the current partition reaches steady state.

![Graph showing current and voltage over time](image)

Figure 3-32: Negative electrode current partition during a discharge-charge process with $i_{0,H_2} = 4.9e^{-9}/cm^2$ and $i_{0,O_2} = 1.5e^{-25}/cm^2$
All the above cases use the specific area of \( a_+ = 2.3e5 \text{cm}^2/\text{cm}^3 \) and \( a_- = 2.7e7 \text{cm}^2/\text{cm}^3 \). Figure 3-33 shows the study of the effect of positive electrode surface area with \( a_+ = 1.1e5 \text{cm}^2/\text{cm}^3 \). It can be seen that there is not significant change from the above case. Figure 3-34 further studies a case with much a lower surface area of positive electrode \( a_+ = 2.3e4 \text{cm}^2/\text{cm}^3 \). This figure shows when the positive surface area is too low, the overpotential increases greatly and the battery reaches the voltage limit with a small temperature rise. From this figure, it can be verified that the increased heat generated due to higher positive overpotential does not contribute to the temperature rise as much as the gassing processes do.
Figure 3-33: Current, voltage and temperature variation during a discharge-charge process with $a_v = 1.1e5\text{cm}^2/\text{cm}^3$
Figure 3-35 and Figure 3-36 show the corresponding current partitions at the negative electrode for the above two simulated cases. The voltage curve with $a_v = 1.1e5\text{cm}^2/\text{cm}^3$ is a little higher than the one with $a_v = 2.3e5\text{cm}^2/\text{cm}^3$ in the plateau range due to the increased overpotential in the positive electrode, but this does not help prevent thermal runaway. Apparently, when $a_v = 2.3e4\text{cm}^2/\text{cm}^3$, the charging process ends earlier than the time when the massive oxygen reaction is about to start, so there is only the hydrogen current to share the total current with the actual charging current.
Figure 3-35: Negative electrode current partition during a discharge-charge process with $\alpha_r = 1.1e5 cm^2/cm^1$
The following two figures show the effect of negative electrode surface area on gassing processes and thermal behaviors. Figure 3-37 shows the simulation result with $a_+ = 1.3e7 \text{cm}^2/\text{cm}^3$, but the capacitance of the carbon electrode remaining the same. It can be seen that even though the voltage also reaches a plateau in the end of charging, the voltage finally safely reaches the voltage limit without a thermal runaway process. Comparing Figure 3-33, this figure demonstrates the bigger impact of negative surface area on charging voltage than that of the positive electrode. This is due to the fact that the voltage variation largely depends on the negative AC electrode.

Figure 3-36: Negative electrode current partition during a discharge-charge process with $a_- = 2.3e4 \text{cm}^2/\text{cm}^3$
Figure 3-38 shows the negative current partition with $a_\perp = 1.3e7 \text{cm}^2/\text{cm}^3$ and unchanged capacitance. The small plateau of voltage in the end of charging can be explained from this figure. It is also caused by the onset of positive oxygen generation. Comparing this figure with Figure 3-32, one can see that at the instant of the onset of oxygen reaction or fast jump of voltage the hydrogen current for this case is smaller, about 9A; whereas in Figure 3-32, the corresponding hydrogen current is about 14A. This is clearly due to the lower surface area of the negative AC electrode. Consequently
this case has a larger charging current for the capacitor electrode and the voltage rises faster. This is why the plateau becomes much smaller than that in Figure 3-35.

Figure 3-38: Negative electrode current partition during a discharge-charge process with \( a_c = 1.3e7\text{cm}^2/\text{cm}^3 \); capacitance unchanged

Figure 3-39 shows the simulation result with \( a_c = 1.3e7\text{cm}^2/\text{cm}^3 \) and the capacitance of the carbon electrode changes proportionally with the surface area. The decrease of capacitance leads to shorter discharge and charge time. Also, the temperature rise is reduced accordingly.
Figure 3-40 shows the negative current partition with $a_\neq=1.3e7cm^2/cm^3$ and changed capacitance. The smaller capacitance of the AC electrode leads to a higher decrease of negative potential during charge, so the resulting rise of positive potential is smaller than before and oxygen production is inhibited. Apparently, the reduced gassing current allows the capacitor to be charged more efficiently and the battery voltage quickly reaches the limit. This figure actually also displays the effect of the capacitance of an AC electrode on controlling temperature rise for a PbC battery. It can be concluded from all the results with variations of the AC electrode capacitance that the lower the
capacitance, the faster the battery voltage changes and reaches the voltage limit, effectively protecting batteries from large temperature rise.

Figure 3-40: Negative electrode current partition during a discharge-charge process with \( a_e = 1.3 \times 10^7 \text{cm}^2/\text{cm}^3 \); capacitance changed

3.5 Conclusion

In this chapter, the fundamental electrochemical-thermal coupled model developed in Chapter 2 was applied to simulate and analyze the gassing and thermal behaviors of PbC batteries during both galvanostatic charging and cycling processes. The results revealed that in the end of galvanostatic charging the hydrogen gassing reaction
shares the total input current and slows the decreasing rate of the negative electrode potential that represents the charging process of the AC electrode, which is reflected by the decreased voltage rising rate. However, the voltage can still reach the voltage limit very quickly before a severe gassing process occurs. The most severe condition is both oxygen and hydrogen production. In this case, at first the charging current is the same as that with only hydrogen gassing, so the voltage curve is overlapped by the case with only hydrogen gassing. After the voltage rises to a certain value, oxygen starts to evolve and part of the generated oxygen is transported to negative side and recombined there. Thus with the voltage increasing a large percentage of charging current is shared by the oxygen gassing reaction and the voltage curve enters a plateau. This condition is severe because the voltage is temporarily stabilized, thus does not reach the voltage limit and the charging current goes into the oxygen cycle, resulting in considerable heat build-up. Also, due to the large amount of gas produced and the stable voltage the battery has reached during gassing, the battery keeps being vented frequently, which leads to much water loss and degradation. The simulation of the electrode thickness effect indicates that a larger electrode thickness leads to a larger battery capacity, but the peak hydrogen current during charging increases with the electrode thickness due to the fact that a thicker electrode provides more reaction surface area for gassing. After the trade-off analysis, it is concluded that thickening the electrodes within the range between 0.10cm and 0.18cm is worthwhile as it achieves a higher capacity with a smaller rise of gassing. The cell voltage, capacity and energy density linearly increase with the initial negative electrode potential decrease. In the meantime, however, the peak hydrogen current increases exponentially with initial negative potential drop. Particularly below -0.35V vs SHE the
peak hydrogen gassing current become very sensitive to the initial negative electrode potential and grows more rapidly with the initial potential drop.

Cycling simulations were conducted to demonstrate the evolution of gassing processes with cycling, including both internal physics and external performance behaviors. The results showed that without gassing the capacitor electrode can recover the equal amount of charge released during the discharge part of each cycle without any loss, so that after the initial effect fades out the whole voltage will flatten off. In contrast, when the gassing is considered, the electrolyte potential keeps decreasing as cycling due to the gassing parasitic current. Therefore during the cycling the voltage firstly increases due to the initial effect of acid concentration distribution and then decreases because of gassing. The peak hydrogen current decreases with cycling and the decreasing rate becomes slower and slower with cycling. Coulombic efficiency and energy efficiency increase with cycling and energy efficiency is always lower than coulombic efficiency. Larger cycling current can lead to higher charge efficiencies. Specifically, the efficiencies quickly fall when the cycling current is below 20A and barely grow after the current is increased beyond 30A. The SOC and cycling pulse effect studies showed for this PbC battery the SOC range of [0.8, 0.9] is critical to the charge efficiencies and a narrow cycling pulse width raises the charge efficiencies. The thicker electrode can improve the battery capacity, however, during cycling the charge efficiencies decrease with electrode thickness increase due to the larger surface area for gassing reactions.

The thermal model proposed in last chapter was used to predict the thermal behaviors of PbC batteries during gassing processes. Simulation results showed the exchange current density of HER and the electrode specific area are two critical
parameters to determine the gassing process and temperature rise. The exchange current density usually varies in orders, which makes huge difference in the gassing process. A higher specific area leads to higher gassing current and a higher temperature rise. The specific capacitance of the AC electrode also plays a role in thermal behaviors because larger capacitance results in more capacity discharged from positive electrodes, which produces more heat and higher temperature rises. With only hydrogen gassing, the thermal runaway does not occur because at the end of charging the overpotential of positive electrode can quickly rise making the battery voltage reach the voltage limit. However, with both oxygen and hydrogen gassing the battery thermal runaway takes place after the onset of oxygen cycle and entering the voltage plateau. In terms of preventing from the thermal runaway, the specific area of positive electrodes does not have much effect unless it is reduced to a very low value that makes the battery reach the voltage limit fast with a small temperature rise. The specific area and specific capacitance of the negative carbon electrode have noticeable impacts on lowering temperature rise. A smaller specific area of the negative electrode can significantly reduce the hydrogen current and improve charging current, so the voltage can quickly reach the voltage limit with a small temperature rise.

This chapter conducted the analyses of gassing processes under various operational conditions through simulation results, and provides guidelines for better design and better controlling of PbC batteries in terms of gassing suppression and thermal management.
Chapter 4  
MODELING OF BATTERIES WITH HYBRID LEAD AND CARBON NEGATIVE ELECTRODES

4.1 Introduction

Electric vehicles are considered to be the most promising alternative to vehicles powered by fossil fuel and attract much attention from industry and academics. As a transition phase technology, hybrid vehicles seems to be more feasible for commercialization as they still employ the old IC engine technology and use other electrochemical power sources as assisting systems, thereby realizing low cost and high fuel efficiency simultaneously. Current commercial HEVs, such as the Toyota Prius and Honda Insight, usually combine the IC engine and battery back-up power system. The battery assists and makes the IC engine work under an efficient rpm so that the whole power system can reach the intended goal of fuel economy. Presently hybrid vehicles can be categorized into three types according to the power supply from battery systems. The first type, micro hybrid vehicles, which automatically shut down and restart the internal combustion engine to reduce the amount of time the engine spends idling, thereby reducing fuel consumption and emissions; the second type, mild hybrids, are essentially conventional IC engine powered with a large electric system including a motor and a generator. The mild hybrid allows the engine to be turned off when the car is coasting, braking and idling. The electric motor power can be up to 20kw. The third type is the full hybrid and this type also allows vehicle operation under most conditions with engine off,
with the electric motor power reaching up to 60kw. Another type has emerged recently, namely the plug-in hybrid vehicle, which relies on a battery powered system to drive a limited mileage range. After the battery is drained completely, the small IC engine takes over. In this way the drivable range of vehicles is improved. The Chevy volt is one model of plug-in hybrid car, and can drive around 300miles solely powered by batteries.

All the hybrid vehicle propulsion systems involve frequent dynamic operating scenarios, such as cranking, accelerating or braking. Those working conditions involve the energy storage system-batteries in operational scenarios of predominantly HRPSOC cycling. When high-rate discharge happens during engine cranking, as in micro hybrid vehicles, the engine will be cranked after every stop at traffic lights. High-rate charge describes the regenerative braking process. As present there are several candidates for the energy storage system of hybrid vehicles: valve-regulated lead-acid batteries, nickel-metal hydride, lithium-ion batteries and super-capacitors. As we know, each of those energy storage alternatives has their own pros and cons, as Table 4-1 shows. Apparently, the lithium-ion battery has the ideal performance and lifetime, but the cost and safety issues are still to be resolved. Super-capacitors as used especially for the power-assist application involve energy density far too low to meet the long drivable-range requirements. VRLA batteries have many advantages over the above two choices, such as very low initial capital cost, well established manufacturing lines, distribution network and high recycling efficiency over the other competitive batteries. However, shorter cycle life of lead-acid batteries keeps the operating cost high. For HEV applications, the state of charge of VRLA batteries must be maintained between 30%~70% to achieve a balance between sufficient cranking power output and good charge acceptance. This feature is
distinct from conventional SLI batteries, which run above 90% SOC during most of lifetime. Maintaining lead-acid batteries at higher SOCs is beneficial to extend their lifetimes, as has been well proved, thus HEV batteries usually have shorter cycle lives. As reviewed in Chapter 1, it is well documented that VRLA batteries operating at HRPSOCs tend to fail quickly due to the negative electrode sulfation[1,10]. The cause of hard sulfation was proposed[6,109] as re-crystallization of lead sulfate with cycling and several groups[110,111] have found experimental evidence to support the proposed explanation. Under partial state of charge, lead sulfate particles produced during discharge at negative electrodes are dissolved slowly and re-precipitated on the surface of fresh lead particles, preventing further discharge reactions for lead particles. Moreover, re-crystallization of lead sulfate particles is a chemical process and occurs much more slowly than an electrochemical process, so the resultant of re-crystallization has a flatter surface with lower activity than those electrochemically formed during discharge. The lead sulfate chemically formed in this way is “hard” lead sulfate or sulfation, the accumulation of which during cycling leads to the negative electrode and resulting battery failure. It has been pointed out[1,10] that under HRPSOC duty VRLA batteries fail prematurely due to the progressive accumulation of lead sulfate mainly on the surfaces of the negative plates. This is because the lead sulfate cannot be converted efficiently back to sponge lead during charging either from the engine or from regenerative braking due to the re-crystallization mechanism explained above. Eventually, the layer of lead sulfate develops to such extent that the effective surface area of the plate is reduced markedly and the plate can no longer deliver the high cranking-current demanded by the automobile. The key cause of this failure is high-rate discharge as a
mechanistic analysis of battery operation during HRPSOC duty, as has been shown [1,10], such that a compact lead sulfate layer can be formed on the negative plate that prevents further discharge reaction during high-rate discharge. Also it is easily understood that HER can be easily caused by the increased charging voltage during high-rate charge, thus resulting in significant water loss and insufficient charged of batteries.

<table>
<thead>
<tr>
<th>Candidate</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead-Acid Battery</td>
<td>Low initial cost; Reliable; Tolerant to over charge; Less self discharge; Highly recycled</td>
<td>Short cycle life; high cost per kwh per cycle; low energy density and power density; toxic material</td>
</tr>
<tr>
<td>Nickel-Metal Hydride Battery</td>
<td>Higher energy density; no toxic material</td>
<td>Severe self-discharge</td>
</tr>
<tr>
<td>Lithium Ion Battery</td>
<td>Highest energy density; much longer lifetime</td>
<td>High cost; low thermal stability</td>
</tr>
<tr>
<td>Super-capacitor</td>
<td>High power density</td>
<td>Low energy density and severe self discharge</td>
</tr>
</tbody>
</table>

The effective approach to protect batteries from high-rate charge and discharge for HEV applications is to connect batteries with super capacitors in parallel. Under such configuration, the high power requirement from cranking, acceleration and regenerative braking can be met by super capacitors that are able to release and absorb electric energy in very short instants. As a result of power shared by super capacitors, the load current applied on batteries can be significantly reduced and the lifetime can be extended. In actual electric power network, some electronic controlling devices have to be employed to regulate the current flow between two power devices. This auxiliary controlling device usually increases the cost of whole power system to a large degree and brings more complexity into system. UltraBatteries introduced in Ref. [19-22] realize the combination
of VRLA and super capacitor inside one battery without any extra electronic devices. The basic idea of the UltraBattery is the parallel connection of VRLA and super capacitor; however, it is not straightforward to combine two power devices due to the different allowable working potential ranges of different negative electrodes. Carbon electrodes without any additives working under the same potential range as conventional lead electrodes in VRLAs lead to the electrolysis of water in electrolyte and inability to deliver battery power as required. To accommodate the desired working potential range, some additives were included in carbon electrodes in UltraBatteries that successfully made carbon and lead electrodes compatible. It was reported that the UltraBattery was subject to a variety of tests and exhibited excellent cycling performance. To date, results show that the discharge and charge power of the UltraBattery is close to 50% higher than those of conventional lead-acid batteries and its cycle-life is at least four times longer than that of the conventional lead-acid counterpart.

This chapter aims to develop a fundamental model of hybrid batteries with lead-acid and capacitor cells for the first time. The model will help to establish in-depth understanding of the physics in this type of battery, provide a useful tool for better design and optimize controlling strategies of batteries in HEV applications, specifically in HRPSOC operation. Finally the results will provide insightful suggestions to improve battery performance in HEV and extend battery lifetime.
4.2 Model Development and Validation

4.2.1 UltraBattery configuration

The basic idea of the UltraBattery is to combine a conventional lead-acid battery with an asymmetric capacitor in one cell without any auxiliary electronic controlling devices. The motivation of this novel design is to remove sulfation from the lead plate and also use capacitor to share sharp dynamic load current during HRPSOC cycling. The schematic structure of an UltraBattery is shown in Figure 4-1. The lead acid cell consists of a lead dioxide positive plate and a lead sponge negative plate. The asymmetric super capacitor is composed of the same positive electrode as a lead-acid battery and a carbon electrode that is usually made of AC. The UltraBattery conceptually integrates the conventional negative lead plate (battery electrode) with AC plate (capacitive electrode) within one cell. Two plates are connected in parallel, share the same positive electrode and together provide input/output current. The current drawn from the lead plate comes from electrochemical reaction of lead and sulfuric acid, while the current from the AC plate is generated from the DL under varying electrode potential. In the real product design, it is possible to connect one lead acid battery cell and one asymmetric capacitor in parallel to construct a hybrid system because of the ease of manufacture and assembly. This is also the modeling assumption for this chapter. Figure 4-2 shows the structure for an UltraBattery treated as a hybrid system composed of two sub-cells: one is the lead acid component of UltraBattery named as battery cell and the other one is the asymmetric
capacitor termed as capacitor cell in this chapter. As the figure indicates, both cells have the same voltage and share the current due to the parallel connection.

Figure 4-1: Schematic Configuration of UltraBattery [19]
4.2.2 UltraBattery Fundamentals

4.2.2.1 Primary and Side Electrochemical Reactions

Negative electrode:
Eq. 4.1, describes the electrode reaction that occurs on a conventional lead electrode; Eq. 4.2, shows the charge absorption and release on a capacitor electrode; Eq. 4.3 and Eq. 4.4 show all the side reactions that would occur on the negative plates of both cells.

\[ Pb + H_2SO_4 \rightleftharpoons PbSO_4 + 2H^+ + 2e^- \]  
\[ C_6^{x-}(H^+)_{x} \rightleftharpoons C_6^{(x-2)}(H^+)_{(x-2)} + 2H^+ + 2e^- \]
\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (O_2 \text{ recombination}) \]
\[ 2H^+ + 2e^- \rightarrow H_2 \quad (H_2 \text{ generation}) \]

Eq. 4.5, shows the reaction that occurs on the positive electrode. This reaction is the same for both cells. Eq. 4.6 and Eq. 4.7 show all the side reactions that would occur on the positive plates.

\[ PbO_2 + 2H_2SO_4 + 2H^+ + 2e^- \rightleftharpoons PbSO_4 + 2H_2O \]
\[ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (O_2 \text{ generation}) \]
\[ H_2 \rightarrow 2H^+ + 2e^- \quad (H_2 \text{ recombination}) \]

4.2.2.2 Working Principles

During discharge, the lead dioxide positive electrode, lead negative electrode and electrolyte are consumed by electrochemical reaction. The capacitor electrode releases storage charge, protons and electrons, to electrolyte and then transferred to positive side. So for the battery cell part, the electrolyte or acid solution is consumed on both sides, however, with regard to capacitor cell, protons are consumed at positive side but produced at negative side. This feature makes the acid consumption for capacitor
electrode less than that of battery cell. During charge, lead dioxide is formed on the positive side and sponge lead is formed on the lead grid of negative electrode; at this time, protons are transferred from positive side to negative side and absorbed by AC capacitor electrode. So during charge, acid is produced on both sides of battery cell, but consumed on the AC electrode of the capacitor cell.

4.2.3 Model Assumptions

- A continuous gas-pore network exists in the cell for gas transport and there is a head space right above the cell with a constant volume to store excess gas.
- No mass transfer occurs at the active materials/gas interface.
- Gaseous oxygen transport is through diffusion only.
- Interfacial chemical and electrical equilibrium exists in the electrolyte phase due to large values of the mass diffusivity and ionic conductivity.
- Hydrogen recombination is neglected due to its poor kinetics

4.2.4 Governing Equations

Kinetic Rate Equations

The transfer current densities for the various electrochemical reactions listed above can be found using the general Butler-Volmer equation. Eq. 4.8 is for primary electrode reactions. Eq. 4.9 is for oxygen reaction and Eq. 4.10 is for hydrogen reaction.
Conservation of charge

Conservation of charge law is applied to both electrolyte and solid phase in electrodes. Eq. 4.11 is for electrolyte phase charge conservation, and Eq. 4.12 is for solid phase charge conservation. Here one more source term is added to the right side of charge conservation equation due to the DL capacitance effect formed at the interface between AC electrodes and electrolyte. \( a_{dl} \) and \( C_{dl} \) are specific area and specific capacitance of AC electrodes, respectively.

\[
i_{ij} = i_{ij,ref} \left( \frac{C_{H}^{ref}}{C_{H}^{ref}} \right)^{1/2} \left[ \exp \left( \frac{\alpha_{u} F}{RT} \eta_{j} \right) - \exp \left( - \frac{\alpha_{l} F}{RT} \eta_{j} \right) \right] \tag{4.8}
\]

\[
i_{ij} = i_{ij,ref} \left( \frac{C_{H}^{ref}}{C_{H}^{ref}} \right)^{1/2} \left[ \exp \left( \frac{\alpha_{u} F}{RT} \eta_{j} \right) - \frac{e_{i,i}}{e_{ref,i}} e_{i,ref} \right] \exp \left( - \frac{\alpha_{l} F}{RT} \eta_{j} \right) \tag{4.9}
\]

\[
i_{ij} = -i_{ij,ref} \left( \frac{C_{H}^{ref}}{C_{H}^{ref}} \right)^{1/2} \exp \left( - \frac{\alpha_{l} F}{RT} \eta_{j} \right) \tag{4.10}
\]

Conservation of mass

Conservation of mass law solves the mass transfer from reactant to product through reactions, so it accounts for the electrolyte and solid phase volumetric fraction change in electrodes that affects the mass transfer and reaction rates. Eq. 4.13 is for mass conservation in electrolyte phase and Eq. 4.14 is for solid phase.
Conservation of species

Species concentrations in electrolyte and gas phase also need to be solved as they are related to the electrochemical and thermal behaviors of cells, such as concentrations of acid, oxygen and hydrogen. Eq. 4.15 and Eq. 4.16 are proton and oxygen conservations in electrolyte phase; Eq. 4.17 is for oxygen conservation in gas phase.

\[
\frac{\partial (e_e c_e^H)}{\partial t} + \nabla \cdot (v_e c_e^H) = \nabla \cdot (D_e^H \nabla c_e^H) + S_e^H \tag{4.15}
\]

\[
\frac{\partial (e_e c_e^{O_2})}{\partial t} + \nabla \cdot (v_e c_e^{O_2}) = \nabla \cdot [D_{e,eff}^{O_2} \nabla (c_e^{O_2})] + S_e^{O_2} \tag{4.16}
\]

\[
\frac{\partial (e_g c_g^{O_2})}{\partial t} = \nabla \cdot [D_{g,eff}^{O_2} \nabla (c_g^{O_2})] + J_{e_g}^{O_2} \tag{4.17}
\]

Conservation of energy

Temperature is solved by a lumped thermal model based on conservation of energy law. It is assumed that the heat conductivity of the whole battery is large enough to reach a uniform temperature change without any spatial distribution. Eq. 4.18 shows the heat balance between heat generation and heat dissipation.

\[
\frac{d(\rho c_p T)}{dt} = q - Q \tag{4.18}
\]

All the source terms related to positive electrode, separator and lead negative electrode have been explained in details in Chapter 2, so here all source terms for the conservation equations are summarized in Table 4-2 below. All the above governing equations and source terms for the battery cell can be found in detail in Gu et al.’s
work[86-88], so here only the source terms for carbon electrode is highlighted and will be explained because this is the novel work in this thesis. As there is no electrochemical reaction in carbon electrode except for charge release or storage of capacitor, the first term is 0; the effect of proton release and absorption on acid concentration is accounted for by Eq. 4.19. Also, the electrolyte phase volume change due to charge transfer of capacitor and gassing reactions are considered by Eq. 4.20.

$$S^H = \frac{1-t^0_c}{F} aC_{dl} \frac{\partial(\phi_s - \phi_e)}{\partial t}$$  \hspace{1cm} 4.19

$$S^C_e = V_e \frac{1-t^0_c}{F} aC_{dl} \frac{\partial(\phi_s - \phi_e)}{\partial t} + \left[ \hat{V}_c(2-2t^0_e) - \hat{V}_o \right] \frac{a_i}{2F} + \left[ \hat{V}_c(2-2t^0_e) \right] \frac{a_i}{2F}$$  \hspace{1cm} 4.20

<table>
<thead>
<tr>
<th>Terms</th>
<th>Positive</th>
<th>Separator</th>
<th>Neg-lead</th>
<th>Neg-calcium</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^C_e$</td>
<td>$a(i_s + i_b)$</td>
<td>0</td>
<td>$a(i_s + i_b)$</td>
<td>$a(i_s + i_b)$</td>
</tr>
<tr>
<td>$S^H$</td>
<td>$a\left(\frac{3-2t^0_c}{2F} i_s + \frac{1-t^0_c}{2F} i_b\right)$</td>
<td>0</td>
<td>$\frac{1-2t^0_c}{2F} a_i + \frac{1-t^0_c}{2F} a_s(i_s + i_b)$</td>
<td>$\frac{1-t^0_c}{2F} aC_{dl} \frac{\partial(\phi_s - \phi_e)}{\partial t} + \frac{1-t^0_c}{2F} a_s(i_s + i_b)$</td>
</tr>
<tr>
<td>$S^{\alpha_2}_{e}$</td>
<td>$\frac{1}{4F} a_i - \hat{J}^{\alpha_2}_{eg}$</td>
<td>$-\hat{J}^{\alpha_2}_{eg}$</td>
<td>$\frac{1}{4F} a_i - \hat{J}^{\alpha_2}_{eg}$</td>
<td>$\frac{1}{4F} a_i - \hat{J}^{\alpha_2}_{eg}$</td>
</tr>
<tr>
<td>$J^{\alpha_2}_{eg}$</td>
<td>$k(c^{\alpha_2}<em>{e} - H^{\alpha_2}</em>{e} c^{\alpha_2}_{g})$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S^V_{e}$</td>
<td>$\left[ \hat{V}_c(3-2t^0_c) - 2\hat{V}_o \right] \frac{a_i}{2F}$</td>
<td>0</td>
<td>$\hat{V}_c(1-2t^0_c) \frac{a_i}{2F} + \left[ \hat{V}_c(2-2t^0_c) - \hat{V}_o \right] \frac{a_i}{2F} + \hat{V}_c(2-2t^0_c) \frac{a_i}{2F}$</td>
<td>$\hat{V}_c(1-2t^0_c) \frac{a_i}{2F} + \left[ \hat{V}_c(2-2t^0_c) - \hat{V}_o \right] \frac{a_i}{2F}$</td>
</tr>
<tr>
<td>$S^V_{s}$</td>
<td>$\left( \frac{M_{PbSO_4}}{PbSO_2} - \frac{M_{PbSO_4}}{PbSO_4} \right) \frac{a_i}{2F}$</td>
<td>0</td>
<td>$\left( \frac{M_{PbSO_4}}{PbSO_4} - \frac{M_{Pb}}{Pb} \right) \frac{a_i}{2F}$</td>
<td>0</td>
</tr>
<tr>
<td>$q$</td>
<td>$- \frac{1}{V_c} \int_{V_c} a_s \sum_j \left( U_j - T \frac{\partial U_j}{\partial T} \right) dV + \frac{1}{V_c} \int_{V_c} a_s \sum_j i_m(\phi_s - \phi_j) dV + \frac{1}{V_c} \int_{V_c} \left[ \kappa^{\text{eff}} \nabla \phi_e \cdot \nabla \phi_e + \sigma^{\text{eff}} \nabla \phi_s \cdot \nabla \phi_s \right] dV$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The models of the battery cell and the capacitor cell are both solved based on the above governing equations, and the difference lies in the source terms, as compared in Table 4-2. The integration between two cells is the parallel connection, so the cell voltages equal to each other, as Eq. 4.21 shows.

\[ V_{cell,batt} = V_{cell,cap} \]  \hspace{1cm} 4.21

Under this condition, the currents of the two cells \( I_{cell,batt} \) and \( I_{cell,cap} \) at every time instant can be predicted from the two sub models, respectively. So the current partition inside the UltraBattery under various operations can be demonstrated accordingly.

The governing equations were then solved using computational fluid dynamic technique. All the equations were discretized using the same finite volume technique introduced by Pantakar as before. The algebraic equations were solved iteratively and convergence is considered to be achieved when the relative error between iteration is less than \( 10^{-6} \). This method has been elaborated in Ref.[88]. The grid used in this chapter is 14 across the cell.

### 4.2.5 Model Validation

As Figure 4-1 showed, the two negative electrodes are connected in parallel. Here in order to specify the dimensions of two cells, one parameter is defined; design ratio, \( \alpha = \frac{V_{pb}}{V_{carbon} + V_{pb}} \). To simplify the study, the heights and the thicknesses of cells are assumed to be the same, so the design ratio actually is \( \alpha = \frac{width_{pb}}{width_{carbon} + width_{pb}} \). The
design ratio of the UltraBattery is a proprietary design parameter, so in this work it has to be roughly estimated. As Table 4-3 shows, this is done by comparing the UltraBattery with a conventional VRLA battery product with a few assumptions:

1) All the plates have the same height and thickness;
2) The weight of the carbon plate is negligible compared to the Pb and plates due to its low density; the weight of Pb plate and PbO2 plate are the same;
3) During galvanostatic discharge, the discharged capacity dominantly comes from the battery cell.

With all these assumptions, one can set $W_1, w, C_1$ as the weight, width and capacity of the conventional lead acid cell; set $W_2, C_2$ as the weight and capacity of the hybrid cell of an UltraBattery. So $\frac{C_2}{C_1}$ is the width of the lead acid part in UltraBattery cell and $\frac{W_2}{W_1} - \frac{C_2}{C_1}$ is half the width of the capacitor cell because the carbon electrode weight has been neglected. Now one can estimate the volumetric faction of the lead plate by capacity: $\alpha = \frac{\frac{C_2}{C_1} w}{\frac{C_2}{C_1} w + \left( \frac{W_2}{W_1} - \frac{C_2}{C_1} w \right) \times 2}$. For here after plugging in the values in the following table, $\alpha = 0.71$. In this work, the total width is assumed to be 27.5cm, so the width of the lead plate: $width_{\text{Pb}} = \alpha \times 27.5cm$ and $width_{\text{Carbon}} = (1 - \alpha) \times 27.5cm$. 
The model is validated against testing data of one UltraBattery of 75 Ah. The battery was subject to constant current (CC) (C/4) discharge completely, then charged to 13.8V using CC charging, and then hold for 3 hours to reach a fully charge. After a 24-hour rest, the battery was discharged at C/4 to 10.2V, and then charge to 13.8V at C/4. The discharge-charge curve was recorded and used to validate the modeling results.

Table 4-3: Comparison between Two Batteries

<table>
<thead>
<tr>
<th>Model</th>
<th>Capacity (Ah)</th>
<th>Weight (lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional VRLA</td>
<td>$C_1=90@C/4$</td>
<td>$W_1=75$</td>
</tr>
<tr>
<td>UltraBattery</td>
<td>$C_2=75@C/4$</td>
<td>$W_2=75$</td>
</tr>
</tbody>
</table>

Table 4-3, Table 4-5, Table 4-6 and Table 4-7 give all the input parameters for validation. Figure 4-3 shows the comparison between modeling result and experimental observation. It can be seen the modeling result captured the experimental behavior of the UltraBattery. From this figure, the model captured the transient voltage recover from discharge to rest time, and also the large voltage jump from rest to charge that indicates the high overpotential of this battery during charging process.
Table 4-4: Input Specification Parameters of the Battery Cell for Validation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity (Ah)</td>
<td>75</td>
</tr>
<tr>
<td>Number of cells in series</td>
<td>6</td>
</tr>
<tr>
<td>Number of cells in parallel</td>
<td>8</td>
</tr>
<tr>
<td>Width of electrode plate (cm)</td>
<td>19.5</td>
</tr>
<tr>
<td>Height of electrode plate (cm)</td>
<td>16</td>
</tr>
<tr>
<td>Thickness of PbO$_2$ electrode (cm)</td>
<td>0.159</td>
</tr>
<tr>
<td>Thickness of separator (cm)</td>
<td>0.159</td>
</tr>
<tr>
<td>Thickness of Pb electrode (cm)</td>
<td>0.159</td>
</tr>
<tr>
<td>Porosity of PbO$_2$ electrode at fully-charged state</td>
<td>0.6</td>
</tr>
<tr>
<td>Porosity of separator</td>
<td>0.92</td>
</tr>
<tr>
<td>Porosity of Pb electrode at fully-charged state</td>
<td>0.6</td>
</tr>
<tr>
<td>DL capacitance of PbO$_2$ electrode (F/cm$^2$)</td>
<td>15e-6</td>
</tr>
<tr>
<td>DL capacitance of Pb electrode (F/cm$^2$)</td>
<td>15e-6</td>
</tr>
<tr>
<td>Specific interfacial area of PbO$_2$ electrode (cm$^2$/cm$^3$)</td>
<td>2.3e5</td>
</tr>
<tr>
<td>Specific interfacial area of Pb electrode (cm$^2$/cm$^3$)</td>
<td>2.3e4</td>
</tr>
<tr>
<td>Morphology correction index for PbO$_2$ electrode</td>
<td>1</td>
</tr>
<tr>
<td>Morphology correction index for Pb electrode</td>
<td>1</td>
</tr>
<tr>
<td>Concentration of acid (H$_2$SO$_4$) at fully charged state (mol/cm$^3$)</td>
<td>4.5e-3</td>
</tr>
<tr>
<td>Initial battery pressure (atm)</td>
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<tr>
<td>Valve opening pressure (atm)</td>
<td>1.170</td>
</tr>
<tr>
<td>Valve closing pressure (atm)</td>
<td>1.102</td>
</tr>
<tr>
<td>Saturation level of PbO$_2$ electrode at fully charged state (%)</td>
<td>85</td>
</tr>
<tr>
<td>Saturation level of separator at fully charged state (%)</td>
<td>93</td>
</tr>
<tr>
<td>Saturation level of Pb electrode at fully charged state (%)</td>
<td>85</td>
</tr>
</tbody>
</table>
Table 4-5: Input Kinetic Parameters of the Battery Cell for Validation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference temperature (K)</td>
<td>298.15</td>
</tr>
<tr>
<td>Reference acid concentration (mol/cm³)</td>
<td>4.9e-3</td>
</tr>
<tr>
<td>Reference concentration of O₂ in the electrolyte (mol/cm³)</td>
<td>1e-3</td>
</tr>
<tr>
<td>Exchange current density of PbO₂/PbSO₄ rxn (A/cm²)</td>
<td>4.19e-7</td>
</tr>
<tr>
<td>Exchange current density of Pb/PbSO₄ rxn (A/cm²)</td>
<td>4.96e-6</td>
</tr>
<tr>
<td>Activation energy of PbO₂/PbSO₄ rxn (J/mol)</td>
<td>4.1e-3</td>
</tr>
<tr>
<td>Activation energy of Pb/PbSO₄ rxn (J/mol)</td>
<td>4.1e-3</td>
</tr>
<tr>
<td>Anodic transfer coefficient of PbO₂/PbSO₄ rxn</td>
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</tr>
<tr>
<td>Cathodic transfer coefficient of PbO₂/PbSO₄ rxn</td>
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</tr>
<tr>
<td>Anodic transfer coefficient of PbO₂/PbSO₄ rxn</td>
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</tr>
<tr>
<td>Cathodic transfer coefficient of PbO₂/PbSO₄ rxn</td>
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<tr>
<td>Exchange current density of O₂ generation (A/cm²)</td>
<td>1.5e-27</td>
</tr>
<tr>
<td>Anodic transfer coefficient for O₂ generation</td>
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</tr>
<tr>
<td>Cathodic transfer coefficient for O₂ generation</td>
<td>2</td>
</tr>
<tr>
<td>Exchange current density of O₂ recombination (A/cm²)</td>
<td>2.5e-36</td>
</tr>
<tr>
<td>Anodic transfer coefficient for O₂ recombination</td>
<td>2</td>
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<tr>
<td>Cathodic transfer coefficient for O₂ recombination</td>
<td>2</td>
</tr>
<tr>
<td>Open-circuit potential vs. Pb electrode for O₂ rxns at reference conditions</td>
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<tr>
<td>Activation energy of O₂ rxns (J/mol)</td>
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</tr>
<tr>
<td>Exchange current density of H₂ evolution at Pb electrode (A/cm²)</td>
<td>4.9e-9</td>
</tr>
<tr>
<td>Open-circuit potential vs. Pb electrode for H₂ rxn at reference conditions</td>
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<tr>
<td>Activation energy of H₂ rxn (J/mol)</td>
<td>0</td>
</tr>
</tbody>
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Table 4-6: Input Specification Parameters of the Capacitor Cell for Validation

<table>
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<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Capacity (Ah)</td>
<td>24</td>
</tr>
<tr>
<td>Number of cells in series</td>
<td>6</td>
</tr>
<tr>
<td>Number of cells in parallel</td>
<td>8</td>
</tr>
<tr>
<td>Width of electrode plate (cm)</td>
<td>8</td>
</tr>
<tr>
<td>Height of electrode plate (cm)</td>
<td>16</td>
</tr>
<tr>
<td>Thickness of PbO₂ electrode (cm)</td>
<td>0.159</td>
</tr>
<tr>
<td>Thickness of separator (cm)</td>
<td>0.159</td>
</tr>
<tr>
<td>Thickness of carbon electrode (cm)</td>
<td>0.159</td>
</tr>
<tr>
<td>Porosity of PbO₂ electrode at fully-charged state</td>
<td>0.6</td>
</tr>
<tr>
<td>Porosity of separator</td>
<td>0.92</td>
</tr>
<tr>
<td>Porosity of carbon electrode</td>
<td>0.6</td>
</tr>
<tr>
<td>DL capacitance of PbO₂ electrode (F/cm²)</td>
<td>15e-6</td>
</tr>
<tr>
<td>DL capacitance of carbon electrode (F/cm²)</td>
<td>15e-6</td>
</tr>
<tr>
<td>Specific interfacial area of PbO₂ electrode (cm²/cm³)</td>
<td>2.3e5</td>
</tr>
<tr>
<td>Specific interfacial area of carbon electrode (cm²/cm³)</td>
<td>2.7e7</td>
</tr>
<tr>
<td>Morphology correction index for PbO₂ electrode</td>
<td>1</td>
</tr>
<tr>
<td>Morphology correction index for Pb electrode</td>
<td>1</td>
</tr>
<tr>
<td>Concentration of acid (H₂SO₄) at fully charged state (mol/cm³)</td>
<td>4.5e-3</td>
</tr>
<tr>
<td>Initial battery pressure (atm)</td>
<td>1.01</td>
</tr>
<tr>
<td>Valve opening pressure (atm)</td>
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<tr>
<td>Saturation level of PbO₂ electrode at fully charged state (%)</td>
<td>85</td>
</tr>
<tr>
<td>Saturation level of separator at fully charged state (%)</td>
<td>93</td>
</tr>
<tr>
<td>Saturation level of carbon electrode at fully charged state (%)</td>
<td>85</td>
</tr>
</tbody>
</table>
Table 4-7: Input Kinetic Parameters of the Capacitor Cell for Validation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference temperature (K)</td>
<td>298.15</td>
</tr>
<tr>
<td>Reference acid concentration (mol/cm³)</td>
<td>4.9e-3</td>
</tr>
<tr>
<td>Reference concentration of O₂ in the electrolyte (mol/cm³)</td>
<td>1e-3</td>
</tr>
<tr>
<td>Exchange current density of PbO₂/PbSO₄ rxn (A/cm²)</td>
<td>4.19e-7</td>
</tr>
<tr>
<td>Activation energy of PbO₂/PbSO₄ rxn (J/mol)</td>
<td>4.1e-3</td>
</tr>
<tr>
<td>Anodic transfer coefficient of PbO₂/PbSO₄ rxn</td>
<td>1.15</td>
</tr>
<tr>
<td>Cathodic transfer coefficient of PbO₂/PbSO₄ rxn</td>
<td>0.85</td>
</tr>
<tr>
<td>Exchange current density of O₂ generation (A/cm²)</td>
<td>1.5e-27</td>
</tr>
<tr>
<td>Anodic transfer coefficient for O₂ generation</td>
<td>2</td>
</tr>
<tr>
<td>Cathodic transfer coefficient for O₂ generation</td>
<td>2</td>
</tr>
<tr>
<td>Exchange current density of O₂ recombination (A/cm²)</td>
<td>2.5e-36</td>
</tr>
<tr>
<td>Anodic transfer coefficient for O₂ recombination</td>
<td>2</td>
</tr>
<tr>
<td>Cathodic transfer coefficient for O₂ recombination</td>
<td>2</td>
</tr>
<tr>
<td>Open-circuit potential vs. carbon electrode for O₂ rxns at reference conditions</td>
<td>1.56</td>
</tr>
<tr>
<td>Activation energy of O₂ rxns (J/mol)</td>
<td>70e3</td>
</tr>
<tr>
<td>Exchange current density of H₂ evolution at carbon electrode (A/cm²)</td>
<td>4.9e-9</td>
</tr>
<tr>
<td>Open-circuit potential vs. carbon electrode for H₂ rxn at reference conditions</td>
<td>0.33</td>
</tr>
<tr>
<td>Activation energy of H₂ rxn (J/mol)</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 4-4 shows the current partition between the battery cell and the capacitor cell inside the UltraBattery during discharge. From this figure, at the initial stage of discharge, current shared by the capacitor cell almost reaches one third of the total discharge current, and then the capacitor current decreases gradually and levels off to a small value. The time the capacitor lasts depends on the capacitance of the asymmetric capacitor. This behavior reflects the effect of the asymmetric capacitor on the performance of whole ultra-battery during transient working conditions. While approaching the end of discharge, capacitor current increases again because most of the battery cell capacity has been drained and can not deliver the same current as before. Therefore at this time, the capacitor cell resumes to discharge again. From this result, it
can be concluded that the capacitor cell assists power supply effectively during the transient operations when the electrode potentials have significant variations, for example, in this case only at the two ends of discharge, the capacitor cell delivers large percentage of the entire discharge current.

Figure 4-4: Current partition between the battery cell and capacitor cell inside one UltraBattery during constant current discharge

Figure 4-5 indicates the corresponding capacity discharged from the battery cell and capacitor cell, respectively. As the discharge of the capacitor cell requires large potential variations, during the steady constant current discharge interval, the capacitor cell is barely discharged. Only at the two ends of discharge process would the capacitor
cell discharge significantly. Therefore, the primary discharged capacity of the whole battery comes from the battery cell whose state of charge almost reaches 0 in the end.

**Figure 4-5**: SOC variation of the battery cell and capacitor cell during constant current discharge. Blue: the battery cell; Green: the capacitor cell

### 4.2.6 Internal physics during simple cycling

In this section, the internal physics of UltraBattery during typical cycling operations will be displayed in details through cycling simulations. This is an important issue because this new type of battery is designated to be applied in hybrid vehicle application where it would experience frequent high-rate partial state of charge cycling.
The feature of current sharing between the battery cell and the capacitor cell in the UltraBattery relieves it from heavy sulfation on the lead negative electrodes during cycling that occurs in conventional lead-acid batteries. Less sulfation during cycling due to the addition of carbon electrode for UltraBatteries extends their cycle lives about 2~3 times, so it is important to provide a profound fundamental understanding of the internal physics of the new feature in this section.

The simulation load cycle is as shown in Figure 4-6 is 100A discharge and charge cycle. The time interval between rest and loading is 18s. The UltraBattery is firstly discharged to SOC=0.5 at constant current 20A, and then conducted the cycling simulation. Figure 4-7 shows the battery voltage response and current partition between the battery cell and capacitor cell inside. It can be seen that at the very beginning the battery is recovering from the constant current discharge. The voltage of the whole battery is gradually increasing to a steady level, during which the capacitor current is positive due the fact that the electrode potential is increasing. Also at this time the battery cell current is negative to compensate the capacitor current and maintain the whole loading current at 0. At every instant of step change of loading current, the capacitor cell is able to share up to one third of the entire current, which significantly lowers the peak loading current applied to the battery cell. As Ref.[1] mentioned above, during cycling especially high-rate current cycling the negative lead electrodes of lead-acid batteries tend to form a thin and hard layer that prevents further diffusion and mass transport into porous electrodes and further reactions. This layer will grow with cycling and finally lead to battery failure. For UltraBatteries, the capacitor cell assembled inside greatly reduces
the loading current on lead negative electrodes under transient conditions, which definitely prevents sulfation formation and leads to longer battery cycle life.

Figure 4-6: Cycling loading profile for simulation
It must be mentioned that even in the battery cell, there still exists an electrical DL effect, whose capacitance is much smaller compared with that of the asymmetric capacitor cell in the UltraBattery. Figure 4-8 displays the effect of the electrical DL effect on the current partition between electrochemical reaction current and DL current inside the battery cell itself. As the figure indicates the DL current keeps consistent with the change of electrode potentials. When the electrode potential decreases from rest to discharge or from charge to rest, the DL current is positive, trying to reduce the decreasing rate of electrode potentials and making the reaction current change gradually. Comparing Figure 4-7 and Figure 4-8, one can find that the time constant for DL
transient in the battery cell is less than 10 seconds, while the transient time constant caused by asymmetric capacitor is much larger.

The following figures will show the transient distribution of electrolyte potential and current density across the battery cell and the capacitor cell. They provide an understanding of how the dynamic loading affects the internal potential and its distribution, which are consequently reflected by the voltage dynamic behavior. Figure 4-9 gives the transients of electrolyte potential distribution during a step change of loading from rest to discharge. It can be seen that after loading up, the electrolyte potential changes immediately. At t=18s, even though the cell is idling, the electrochemical reaction with small magnitude of current is still going on because the
battery just recovered from the CC discharge to 50% state of charge. Thus the electrolyte potential distribution is not exactly uniform. The positive electrode has a higher surface area and capacitance, so the electrolyte potential distribution in the positive electrode is less uniform due to the larger DL current and larger compensate reaction current. In the capacitor cell this effect is not significant due to the larger acid concentration and ionic conductivity. At t=19s, the battery is loading up and the electrolyte potential shows non-uniform distribution to transfer the ion from negative to positive side.

Figure 4-9: Transient response of electrolyte potential distribution during step change from idling to discharge

Figure 4-10 shows the transient response of electrolyte potential distribution at the instant of unloading. At t=37s, the DL current in the battery cell takes place and tries to reduce the variation rate of potentials, so the distribution of electrolyte potential still follows the previous trend somewhat. This distribution will fade out and become uniform as the DL effect diminishes. The capacitor cell has opposite current to compensate the current from the battery cell, so the electrolyte potential shows a different distribution.
During discharge (at $t=36s$), the difference of charge stored at location A and B is $Q^{AB} = C\phi^{AB}$, where $C, \phi$ are capacitance and electrolyte potential. After unloading the DL capacitor at the location A absorbs more positive charge due to its lower potential than that of B. At this point, if the capacitance is small the whole AC electrode (both A and B) will all absorb positive charge till the potential distribution becomes uniform; however, if the capacitance is large the charge status difference is large. When the current from the positive electrode can not meet the absorption of the DL capacitor at the location A, which is the case here, the DL capacitor at B will supply positive charge to location A as well till the potential reach uniform, so the potential of B goes down accordingly.

![Figure 4-10](image1.png)

**Figure 4-10**: Transient response of electrolyte potential distribution during step change from discharge to idling

Figure 4-11 gives the transient response of electrolyte potential during charging load up. At the instant of applying charge current, the potential increases immediately. At this point, the battery cell and the capacitor share compatible current, as the Figure 4-7...
shows above, and the capacitor cell has a much larger capacitance than that of the DL effect in the battery cell, therefore the potential variation in the capacitor cell is much smaller. Figure 4-12 provides the transients during charge unloading. The DL current takes place and diminishes gradually, so the electrolyte potential distribution still follows the trend as before at t=73s. Similarly with the case after discharge unloading, after charge unloading the capacitor cell current is small, as Figure 4-7 indicated above, so within the AC electrode, the charge needs to be balanced out such that the electrolyte potential decreases at one end of the AC electrode and increases at the other.

Figure 4-11: Transient response of electrolyte potential distribution during step change from idling to charge
Figure 4-13 displays the transient current density distribution across the cell during a step change of loading from rest to discharge. The spatial distributions of both reaction current density and DL current density are shown. The DL current in the AC electrode comes from the capacitor formed at the interface between carbon surface and electrolyte. At the loading instant of discharge, both reaction current and DL current respond quickly. From the figure, it can be seen that in the battery cell the positive electrode has a higher capacitance and the DL current shares a higher percentage of total load current, almost at the same magnitude as the reaction current. The DL current can barely be seen in the negative electrode. In the capacitor cell, the AC electrode only has DL current, so it takes whole input current and is larger than the DL current of the positive side.
Figure 4-14 gives the current density distribution transients when the battery experiences a step change from discharge to idling. Before unloading at $t=36s$, all the output current in the battery cell comes from reaction current and there is no DL current because the battery cell has reached steady state of discharge. In the mean time, in the capacitor cell the AC electrode draws current from DL effect and the positive electrode has the reaction current. At the instant of unloading $t=37s$, the positive DL current takes place in positive electrode due to the rising electrode potential, so the discharge current is maintained at some level, as the blue curve indicates. It has to be noted that at this instant the total current from the battery cell is not 0 due to the fact that the capacitor cell also is providing current. This can also be verified from the current density of the capacitor cell. Obviously, the positive electrode of the battery cell has a higher surface area and capacitance than the negative, which leads to a higher DL current during the step change of unloading. It can be seen in the AC electrode after unloading the potential change.
invokes opposite large DL current at two ends of the AC electrode, which will gradually balance out each other, and finally vanish.

Figure 4-15: Transient response of current density distribution during step change from discharge to idling

Figure 4-14: Transient response of current density distribution during charge load up process. Similarly, before loading the battery cell reaches its steady state with a very low discharge current as the purple curve shows in this figure. At the instant of loading up, the current density increases immediately. Once again, at the positive electrode of the battery cell, DL current shares a larger percentage of the total current, which is even larger than reaction current; while in the negative electrode, the reaction current is larger than the DL current due to its lower surface area and capacitance. It can be seen that in the capacitor cell the DL current at the AC electrode is much larger due to the large capacitance.
Figure 4-15: Transient response of current density distribution during step change from idling to charge

Figure 4-16 shows the current distribution transients when the battery is unloaded from charging process. It is clear from this figure that in the battery cell before unloading the reaction current already takes over the output current completely and there is no DL current. Also, the capacitor cell enters steady state. At the unloading instant \( t=73 \text{s} \), in the battery cell DL effect produces the inverse current compared to the reaction current, reducing the potential step change and making the battery cell maintain the charge current at some magnitude, as the blue curve indicates. In the mean time, the same mechanism also applied to the capacitor positive electrode other than the negative AC electrode, where the spatial charge distribution is being redistributed. Once again, the charge inside the AC electrode is being balanced out after unloading due to the different changing rate of electrolyte potential change within the electrode, as showed in Figure 4-12.
4.3 Parametric Study- Design Ratio

UltraBatteries with hybrid cells change the conventional concept of lead-acid batteries and bring in new designs to remove negative sulfation as much as possible. With the new concept—the hybrid cell, the design process would involve new issues, such as the percentage of each cell. Therefore, a robust and reliable fundamental model for such batteries is indispensable for design purpose. The model should be able to predict the effects of all the design parameters on performance and provide a profound investigation of one certain parameter before practical prototyping. At present the design of UltraBatteries is still proprietary technology of the company that introduced the product. Therefore, this section is designed for three purposes: first, to show the functional capability of this new model in design procedure; second, to investigate the effects of all

Figure 4-16: Transient response of current density distribution during step change from charge to idling
design parameters on performance behaviors of such types of batteries; and third, to explore new designs that may improve battery energy and power performance.

4.3.1 Design Ratio of Battery cell to Capacitor Cell-Energy Performance

Figure 4-17 shows the discharge performance of batteries with different design ratios. With a cutting off voltage of 10.2V, as the figure indicates, the discharge capacity greatly depends on the lead part of the negative electrode; it can also be explained that the capacity of the whole battery depends on the battery cell (Pb-acid cell) rather than the capacitor cell. The blue curve corresponds to the discharge performance of UltraBattery, and it is almost proportional between the mass of lead electrode and the available capacity for the whole battery.
Figure 4-18 shows the evolution of load current shared by the battery cell and the capacitor cell during galvanostatic discharge. At the very beginning of discharge, the capacitor shares a large percentage of total current due to the sudden potential change, which greatly reduces the peak current imposed on the battery cell within the load pulse and is favorable for less degradation. With the discharge getting into the steady state, the capacitor current decreases gradually and the battery cell takes over. During the steady discharge, as the figure indicates, all the current comes from the battery cell, so there is no difference from discharging a lead-acid battery at this point. While approaching the end of discharge, the battery cell is almost completely drained and the capacitor cell supports the discharge current again. It can be observed from the figure that for a higher
design ratio $\alpha = 0.87$, the stable current shared by the capacitor cell is almost 0; while for a lower design ratio, such as $\alpha = 0.5$, the average current shared by the capacitor cell is enhanced, with beneficial effect on battery cell lifetime.

To be more specific, the effect of design ratio on the current partition at the initial stage of discharge process is shown in Figure 4-19. These curves in the two figures demonstrate the function of the capacitor cell to relieve high current load applied on the battery cell during the sudden load change. As Figure 4-19 shows, the smaller the design ratio, the larger the capacitor will be and the greater percentage of current will be shared by the capacitor cell. It can be seen that the battery with lower design ratio $\alpha = 0.1$, the largest capacitor cell here, can have capacitor cell share of more than 70% of the entire load current at the instant of discharge loading up.
Figure 4-20 gives the effect of design ratio on electrode utilization in the battery cell during galvanostatic discharge. These profiles of simulation results are consistent with those in Ref[87]. The active material utilization here is defined by the utilized percentage of the maximum charge capacity as determined by comparing the amount of active material participating in the electrode reaction to the initial amount. It can be seen that the active material utilization distribution is severely non-uniform at the positive electrode at the end of discharge, with the active material near the interface between the positive electrode and the separator being used most. The utilization of active material at the negative electrode generally remains low, indicating that a large amount of active material at the negative electrode is unused. From the figure, it can be seen that higher design ratios represent more mass percentage of lead-acid cell, which leads to larger discharge capacities and more utilization of the electrodes. This figure can therefore be used to guide the active mass loading design of electrodes to utilize electrodes as much as
possible when batteries are designated for different applications that require different design ratios. For the capacitor cell, the electrode utilization coefficients for different design ratios are almost the same due to the small discharged capacity, so it is not showed here.

Figure 4-20: Electrode utilization coefficient of the battery cell in batteries with different design ratios at the end of discharge

Figure 4-21 shows the concentration distribution in batteries with different design ratios at the end of discharge. It can be seen that in the battery cell the positive electrode is starved of acid in the end, so the acid diffusivity is low and there is large concentration gradient at the interface between the positive electrode and the separator.
4.3.2 Design Ratio of Battery cell to Capacitor Cell-Power Performance

Batteries with hybrid cells are designed to work for HEV or EV application, where the batteries mostly experience high-rate partial state of charge cycling. Batteries under such conditions must maintain their SOC in the range of 30%~70% to assure the abilities of acceleration-quick discharge and regeneration-charge acceptance. However, leaving batteries at partial state of charge easily causes negative sulfation that leads to battery failure, so hybrid cell design removes part of the lead electrode and negative sulfation to extend battery lifetime. In the mean time and more importantly, the added capacitor
electrode relieves peak current applied to the lead electrode, which prevents hard sulfation layer from occurring during dynamic loading, reported in Ref[1,19] to be one primary reason for HEV battery failures. Therefore one of the most important requirements for batteries with hybrid cells is power performance under dynamic loading conditions that represent acceleration and regeneration. For this section, the power performance of batteries with different design ratios is studied through simulation of one 8C-12s pulse discharge process.

Figure 4-22 shows the effect of battery design ratios on voltage responses. The battery is discharged at initial SOC=1, I=-640A, t_{discharge}=12s. This case simulates battery behaviors under large power requirements, such as cranking or accelerating. At the instant of discharge, the battery voltages drop rapidly and then reach a steady decrease rate. It is indicated from this figure that the higher design ratios, or larger percentage of the battery cell maintains higher voltages during pulse discharge process. This is because battery cells rely on electrochemical reaction to extract current, while carbon capacitors rely on potential change to draw large current, so voltages for battery cells do not drop as much as capacitor cells. Also, when the discharge current is unloaded, the voltage of batteries with lower design ratios recovers more slowly due to the large capacitances from the capacitor cells. To conclude, the higher the percentage of carbon capacitor is designed, the lower voltage corresponds to the pulse discharge.
Figure 4-23 gives the battery cell current transients for the above simulation. From this figure, it can be seen that a lower design ratio means more mass percentage of the capacitor cell, such that the current shared by the battery cell during the discharge pulse is smaller. For the case $\alpha = 0.1$, the current load on the battery is reduced to less than half. This is very valuable for micro-hybrid vehicle application where batteries experience frequent cranking processes similar to the case simulated here. Relieving large current loads on battery cells by adding large capacitor cells can effectively prevent hard sulfation layer formation that hinders mass transport and further reaction during pulse discharge process and thus can improve power performance.
Figure 4-24 provides the corresponding current shared by the capacitor cell. As explained above, the lower the design ratio is, the more current the capacitor can share during the pulse discharging. It is also noted that the current shared by the capacitor cell is almost inversely linearly proportional to the design ratios selected. This is because the design ratio determines the mass percentage of capacitor cell and the total capacitance of capacitor cell. After unloading, the current shared by the capacitor cell changes to positive that is inverse to the current produced by the battery cell, so the total output current is balanced to 0.
4.4 Effect of Operational Condition on Battery Performance

Operational condition is one critical controlling factor impacting both the performance and cycle lives of batteries in practical applications. The performance of lead-acid batteries, especially the cycling performance, largely depends on how the batteries are operated under real working conditions. Studies on cycling algorithms and charging algorithms have been conducted to optimize the controlling strategies and extend battery cycle life[7-13]. For instance, cycling batteries at higher SOCs can reduce the chance of hard sulfation, or reducing the standing time at lower SOCs or parasitic discharging time can prevent sulfation formation, or in contrast cycling at high SOC...
range may cause more positive corrosion. All those effects of operational parameters need to be studied thoroughly to generate a specific optimal running algorithm and charging algorithm for one certain battery design and one certain real application. Otherwise, batteries can easily be abused and damaged in some inappropriate operations that lead to premature failure. For example, batteries for SLI purposes usually stay under floating charge and higher SOC is maintained to crank the engine. Deep discharge or cycling must be avoided to prevent damage to batteries. Batteries for HEV or EV application, however, must maintain partial SOC to have both enough power for cranking or accelerating and sufficient charge acceptance to absorb regenerative power. For such batteries full charge process is necessary after a number of cycles to recover the product sulfate completely.

Batteries with hybrid cells are a new design for lead-acid products, and most recently they have been used for HEV applications [19-22]. So far, while some testing cycle protocols have been cast to verify the longer cycle life of UltraBatteries compared to conventional batteries, but the optimization study of operational strategies has not been conducted in terms of better utilizing and achieving optimal performance and cycle life. This section studies the effects of possible operational parameters of cycling for HEV applications, including the cycle profile, frequency, SOC and cycling current.

### 4.4.1 Effect of Duty Ratio

Duty ratio here is defined as the ratio between load time and cycle time \( \beta = \frac{t_{\text{load}}}{t_{\text{total}}} \).

This parameter evaluates the effect of loading time percentage on battery performance.
during cycling. For this section, the total simulated cycle time is $t_{\text{total}}=120s$ and the discharge load current is $1C=80A$. So when the duty ratio $\beta$ changes the whole battery shows different current partition between the battery cell and the capacitor cell.

Figure 4-25 gives four cycles of $1C$ discharge with $\alpha = 0.5$ and $\beta = 0.25, 0.5, 0.75$. The figure shows that in the first cycle, the currents from the battery cells for three cases are the same and the only difference lies in the fact that the loading time is different, while in the following cycles the situations are different. Lower duty ratios lead to smaller battery cell currents. This is because with a lower duty ratio the capacitor is discharged less in the first cycle, so in the following cycles the capacitor shares more current and the battery cell current is lower. However, this trend is not very significant and will diminish with cycling. This is due to the fact the design ratio $\alpha = 0.5$ and the capacitor cell is relatively small, so after each cycle both the battery cell and the capacitor cell have enough time to reach steady state. As explained before, under steady state the capacitor cell can barely take effective, so almost all the current would come from the battery cell. This is why with cycling the battery cell current during all discharge pulses come close to the total discharge current-80A.
Figure 4-25: The current shared by the battery cell during four cycles with design ratio $\alpha = 0.5$ and duty ratio $\beta = 0.25, 0.5, 0.75$.

Figure 4-26 gives four cycles of 1C discharge with $\alpha = 0.1$ and $\beta = 0.25, 0.5, 0.75$. This simulation result is designed to display the interactive effect between design ratio and duty ratio. The same cycle is simulated. As the figure indicates, in the first cycle all the batteries have not reached steady state after discharge before next cycle, which is one important feature for the case $\alpha = 0.1$. The lower design ratio leads to a larger capacitor cell that has a larger time constant. Obviously after each cycle there is not enough time for the battery to reach steady state before going to next cycle. So the transient potentials of electrodes can be maintained during cycling and the currents shared by capacitors mostly remain the same, which is around 35% of the total current.
for \( \beta = 0.25 \). From this figure, it can be seen under a smaller design ratio, the effect of duty ratio on cycling performance is more significant. Employing a lower duty ratio can produce a larger current shared by the capacitor cell, which is beneficial for extending cycle life.

Figure 4-26: The current shared by the battery cell during four cycles with design ratio \( \alpha = 0.1 \) and duty ratio \( \beta = 0.25, 0.5, 0.75 \)

Figure 4-27 shows the coupled effects of design ratio and duty ratio on electrode utilization coefficient (\( EUC \)) after four cycle simulation. From this figure, there is first of all one feature that the positive electrodes displays lower \( EUCs \), distinct from previous galvanostatic discharge simulation, in which higher \( EUCs \) in positive electrodes are usually predicted. This is because for dynamic conditions the battery cells are frequently
affected by the DL effect. Positive electrodes with higher surface area and higher capacitance generate much higher DL current than negative during cycling, so the electrochemical reaction current in positive electrodes decreases accordingly which leads to lower $EUC$s. The second piece of information from this figure is that lower design ratios magnify the effect of duty ratio on $EUC$. When design ratio $\alpha = 0.5$, it can be seen that a higher duty ratio results in higher $EUC$, but the magnitude of difference is small; while reducing design ratio to 0.1 really exaggerates the difference. This is due to the fact that at $\alpha = 0.1$, the battery cell and its corresponding capacity are small, so the electrodes can be fully used and the duty ratio easily impacts the $EUC$. Therefore, a conclusion can be reached that a lower design ratio can increase the $EUC$ of the battery cell, but it also exaggerates the effect of duty ratio on $EUC$. This should be kept in mind while composing the cycling profiles.
Figure 4-28 shows the effect of duty ratio on current partition inside the battery during cycling. The battery is cycled to reach the cut-off voltage. $t_{\text{total}}=120\text{s}$ and the discharge current $I=-40\text{A}$. From this figure, it can first of all be seen that a lower duty ratio leads to more cycles due to the small discharge capacity for each cycle. Secondly, the current shared by the battery cell during discharge initially is lower, then increases and stays at some values, and finally gradually decreases while discharge approaches the end. This is consistent with the previous simulation results of galvanostatic discharge process. At the beginning of cycling, the current shared by the capacitor cell is large due to the sharp potential change, then the initial effect fades out with cycling and the current partition becomes stable. When the battery cell is mostly discharged and can not support
the cycling current at the previous magnitude, the capacitor cell takes over again and the current shared by the battery cell decreases. This phenomenon has been observed for all three duty ratios. At last, it is indicated that a lower duty ratio leads to more current shared by the capacitor cell during cycling, which can be up to 15% of the total discharge current when $\beta = 0.25$, relieving a significant percentage of load current on the battery cell. This result provides insights for better operation of UltraBatteries in terms of preventing sulfation formation during cycling and extending battery calendar life.

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![Graph](image.png)

**Figure 4-28**: The effect of duty ratio on current shared by the battery cell during cycling to cut-off voltage.
Figure 4-29 gives the effect of duty ratio on electrode utilization coefficient during cycling to cut-off voltage. It is interesting to mention that for cycling to cut-off voltage, the lower duty ratio results in higher $EUC$ and positive electrodes have larger $EUC$, while in previous four-cycle simulation, as described previously, the lower duty ratio leads to lower $EUC$. This is because at the initial phase of cycling the higher duty ratio has longer discharge time, so the battery can discharge more capacity for the same number of cycles. In this protocol, however, a larger duty ratio results in a quick voltage drop during cycling, so the electrode utilization is lower. In the first few cycles, the DL current contributes much to the total output current, so positive electrodes with larger capacitance cause larger DL currents in electrodes, and the $EUC$ is lower. On the other hand, for this protocol, the battery is cycled to cut-off voltage and reaches steady state after the initial few cycles, thus DL current is not able to dominate the output current and $EUC$ depends on the initial active mass loading, wherein stoichiometrically positive electrodes would consume more active mass than negative electrodes.
4.4.2 Effect of Cycling Frequency

Figure 4-30 and Figure 4-31 show the effect of cycling frequency on current partition. From these two figures, it can be seen that a lower cycling frequency can improve the current shared by the capacitor cell at the instant of loading, but this effect does not seem to be significant.
Figure 4-30: The effect of cycling frequency on current shared by the battery cell during initial four cycles
4.4.3 Effect of Initial SOC of Cycling

Figure 4-32 displays the current shared by the battery cell under cycling with different initial SOCs. It can be seen from the figure that when the initial SOC is lower, the capacitor shares more and more current with cycling. This is because when the starting SOC is lower, the battery cell capacity and the ability to deliver current are weaker, so the entire current load has to resort to the capacitor cell.
Figure 4-32: The effect of starting SOC on current shared by the battery cell during cycling to cut-off voltage

Figure 4-33 gives the current from the capacitor cell correspondingly. With cycling, the battery with a lower starting SOC draws more current from the capacitor cell than the one with higher starting SOC. This is because for the case SOC=0.5, the battery cell capacity approaches the end of discharge more quickly with cycling, so the current from the capacitor cell increases accordingly and earlier than the case SOC=1.
Figure 4-33: The effect of starting SOC on current shared by the capacitor cell during cycling to cut-off voltage

4.4.4 Effect of Cycling Current

Figure 4-34 provides the effect of cycling current on the percentage of current shared by the battery cell for a hybrid battery. From this figure, comparing I=-40A and I=-20A, one can find that increasing cycling current leads to a larger percentage of load current shared by the capacitor cell, and this effect becomes more and more significant with cycling, although when the current is too large such as I=-80A, the battery would not last for many cycles. This is due to that when the cycling current is higher the
The electrode potential change in each cycle is large enough to produce higher current from the capacitor cell, so the current share percentage is higher accordingly.

It is worth mentioning that in the above figure there is some undershoot of current at the instant of discharge in each cycle. This is caused by the DL effect of the battery cell itself, which is largest at the beginning of cycling and will become stable with cycling. Also, the effect is affected by the cycling current. A higher cycling current can make the battery reach the stable state more quickly than a lower cycling current. So here when I=-20A, even when the battery is close to the end of discharge, there still exists undershoot of current. Figure 4-35 shows how the DL current causes the current...
undershoot and Figure 4-36 gives the details. It can be seen from those two figures that at every edge of loading, the DL current is large, but diminishes very quickly due to its small time constant, and that as a result the entire current shows undershoots of current. As the whole loading current gets larger, the effect of DL current becomes smaller.

Figure 4-35: Current partition in the battery cell during cycling to cut-off voltage
A fundamental model for hybrid batteries with lead-acid and capacitor cells was developed. The model was validated against experimental data of full discharge and charge cycle and the comparison showed good agreement. The modeling results captured the discharge curve, the transient recover of voltage during rest and large overpotential during charge process. A simple discharge-charge cycle was simulated to present the illustrative results showing internal physics and transient behaviors of some important parameters, such as electrolyte potential distribution and current distribution inside the cell.

Figure 4-36: Current partition in the battery cell for one cycle

4.5 Conclusions

A fundamental model for hybrid batteries with lead-acid and capacitor cells was developed. The model was validated against experimental data of full discharge and charge cycle and the comparison showed good agreement. The modeling results captured the discharge curve, the transient recover of voltage during rest and large overpotential during charge process. A simple discharge-charge cycle was simulated to present the illustrative results showing internal physics and transient behaviors of some important parameters, such as electrolyte potential distribution and current distribution inside the cell.
battery cell. The results indicated that at the instant of load step change, electrolyte potential responds immediately and shows corresponding distribution across the cells. However, due to the DL effect of the battery cell itself the internal electrolyte potential is non-uniform even when the current of battery cell is 0 and this phenomenon is more apparent in positive electrodes. The DL effect also makes the electrolyte potential maintain the previous distribution trend at the instant of unloading. Also, simulation results provide understanding of transient current density distribution at the edges of loading, and show the interactive effect between electrochemical reaction current and DL current. It is indicated that in the battery cell positive electrodes are affected by DL effect more significantly than negative electrodes due to their larger surface area and capacitance; while in the capacitor cell the DL current at the carbon electrode is much larger than that of the positive electrode.

Through cycling simulations, the effect of design parameters on cycling performance was studied, including current partitioning between the battery cell and the capacitor cell during cycling and electrode utilization efficiency. Results indicated that higher specific capacitances for carbon electrodes in hybrid cells increase the current shared by the capacitor cell, which protects the battery cell from high-rate loading and sulfation formation and leads to longer cycle life of batteries. Higher specific capacitances for carbon electrodes also lead to longer time constants for dynamic responses, so prolonging the loading time in each cycle can make this effect even more significant in terms of extending battery cycle life. Design ratio was introduced as one important design parameter, and equals the ratio between the lead-acid cell volume and the total volume of two cells. Simulation results showed that discharged capacity is
almost linearly proportional to the design ratio. During galvanostatic discharge, the capacitor cell always initially shares a large percentage of total current, then becomes stable at some level and finally increases again due to the complete drain of the battery cell. A lower design ratio can produce a larger percentage of total current shared by the capacitor cell, which is beneficial for extending cycle life. Results showed a higher design ratio leads to a larger capacity and more utilization of electrode. For power performance, a higher design ratio or more volumetric percentage of the battery cell makes the battery maintain a higher voltage during pulse discharge because the battery cell, unlike the capacitor cell (relying on potential change to extract current from electrodes) relies on electrochemical reactions to draw current. However, higher design ratios means smaller capacitor cells, so the currents shared by capacitor cells must be lower during the pulse discharge.

Operational conditions were investigated through cycling simulations, including the effect of duty ratio of a cycle, \( \beta = \frac{t_{\text{load}}}{t_{\text{total}}} \), starting SOC, cycling frequency and cycling current. It was found that a lower duty ratio of a cycle can lead to more current shared by the capacitor cell and this effect is exaggerated when the design ratio decreases. In the first few cycles, the DL effect in the battery cell is significant and the larger DL current in the positive electrode of the battery cell causes lower electrode utilization than that in negative electrode. This is no longer true after the battery experiences many cycles and the DL effect diminishes with steady cycling, so after the cycling to cut-off voltage has finished higher electrode utilization in positive electrode is observed. A lower starting SOC leads to a higher current shared by the capacitor cell as the battery cell has lower
capacity and ability to deliver current. Cycling frequency does not seem to affect the current partition much. Increasing cycling current causes a larger percentage of load current shared by the capacitor cell due to the large potential change during loading current change, and this effect becomes increasingly significant with cycling. The model developed in this chapter demonstrated the internal dynamics of current partition in UltraBatteries under various working conditions and the simulation results offered insights for better design of batteries with hybrid cells and the operational optimization to prolong battery lifetime.
Chapter 5

CONCLUSION

This work focused on understanding new features of hybrid batteries-PbC and UltrBatteries and studying the influence of design and operational factors under various working conditions in terms of performance and lifetime. Five major contributions can be summarized as follows. First, a mathematical PbC battery model was developed for the first time and provided the understanding of internal physical processes and external performance behaviors of PbC batteries. Second, a design tool for comparing and selecting desirable carbon materials for PbC batteries was delivered. Third, the gassing phenomena under galvanostatic or cycling operations were intensively analyzed and the effect of gassing on electrochemical performance and thermal behaviors of PbC batteries was demonstrated, identifying the proper approaches to suppressing gassing behaviors and improving charge efficiencies. Fourth, a mathematical model for UltraBatteries was developed which provided the understanding of the internal dynamics of current partition during cycling. Finally, the influences of negative plate design and operational factors on both power and energy performance of UltraBatteries were evaluated and the results offered insights into maximizing the current shared by the capacitor cells of hybrid batteries under high-rate cycling in order to further extend the cycle life.
5.1 Summary

In Chapter 2, a mathematical model for PbC batteries was first developed to predict performance behaviors under various operations. This model featured coupling of the electrochemical, mass transport and thermal physics and also accounted for the gassing behaviors at electrodes during charge. The modeling results revealed the internal physics, such as the evolution of acid concentration during discharge and charge. An important difference between a PbC battery and a lead acid battery was illustrated in that the total acid consumption in the PbC battery is lower than that in the lead acid battery, such that the working range of acid concentration can be shifted to a lower level to accommodate the electrode potential requirement and possibly further suppress gassing processes. A typical discharge and charge process with gassing processes involved was simulated for the batteries with various AC electrodes to investigate the effects of the specific capacitance and specific surface area of the AC electrodes on discharge/charge performance and further demonstrate the trade-off in carbon material selection. With the capabilities of capacity and gassing process predictions this model can serve as a design tool to compare and select the optimal carbon candidates for specified designs of PbC batteries.

In Chapter 3, the fundamental electrochemical-thermal coupled model developed in Chapter 2 was employed to simulate and analyze the gassing and thermal behaviors of PbC batteries during both galvanostatic charging and cycling processes. The results revealed that during the late phase of galvanostatic charging a most severe condition can occur when both oxygen and hydrogen are produced after the oxygen cycle begins. When this happens, the charging current extends into the oxygen cycle, resulting in excess heat
build-up, and frequent battery venting with eventual large loss of water and battery degradation. The electrode thickness study indicates that a larger electrode thickness leads to higher hydrogen current as well as a larger battery capacity. A trade-off analysis showed that thickening the electrodes within the range between 0.10cm and 0.18cm is worthwhile as it achieves a higher capacity with a smaller rise of gassing.

Cycling simulations were conducted to demonstrate the evolution of gassing processes with cycling, including both internal phenomena and external performance behaviors. Without gassing the voltage recovers after each cycle without any loss; whereas with gassing, the voltage decreases because of gassing. The peak hydrogen current decreases with cycling and as a result, the charge efficiencies increase with cycling. Larger cycling current can lead to higher charge efficiencies. The SOC and cycling pulse effect studies showed for this PbC battery the SOC range of [0.8, 0.9] is critical to the charge efficiencies and a narrow cycling pulse width raises the charge efficiencies. The thicker electrode can improve battery capacity, but reduces the charge efficiencies due to the larger surface area for gassing reactions.

The thermal behaviors of PbC batteries during gassing processes were predicted. Simulation results showed the exchange current density of HER and the electrode specific area are two critical parameters to determine the gassing process and temperature rise. With hydrogen gassing alone, thermal runaway is unlikely to happen. However, with both oxygen and hydrogen gassing the battery thermal runaway occurs after the onset of oxygen cycle. The specific area and specific capacitance of the negative carbon electrode have more noticeable impacts on controlling thermal runaway than those of the positive electrode. The analyses of gassing processes through simulation results under various
operational conditions actually provided the guidelines for better design and better controlling of PbC batteries in terms of gassing suppression and thermal management.

In Chapter 4, a fundamental model for hybrid batteries with battery and capacitor cells was developed. The effects of design parameters on cycling performance, such as current partitioning between the battery cell and the capacitor cell and electrode utilization efficiency were studied through cycling simulations. Design ratio was introduced that equals the ratio between the lead electrode volume and the total volume of two negative electrodes. Simulation results showed that discharged capacity is almost linearly proportional to the design ratio; however, a lower design ratio can produce a larger percentage of total current shared by the capacitor cell, a finding that is beneficial for extending cycle life. A higher design ratio improves the power performance of the battery cell but reduces the current shared by capacitor cells during the pulse discharge. Operational factors were investigated through cycling simulations, including the effect of duty ratio of a cycle, \( \beta = \frac{t_{\text{load}}}{t_{\text{total}}} \), starting SOC, cycling frequency and cycling current. It was found that a lower duty ratio of a cycle can lead to more current shared by the capacitor cell and this effect is exaggerated when the design ratio decreases. A lower starting SOC and higher cycling current cause a larger percentage of load current shared by the capacitor cell. This model unveiled the internal dynamics of current partitioning inside UltraBatteries through simulation results and offered guidelines for improving the design of batteries with hybrid cells and optimizing the controlling algorithms in terms of prolonging battery lifetime.
5.2 Recommendations

The fundamental models developed in this work provide a design tool and performance predictor for the new hybrid batteries. Due to the addition of carbon electrodes into batteries, the more emphasis should be put on characteristics and performance of carbon capacitor electrodes. Future modeling work in this area is therefore proposed herein.

5.2.1 Self-discharge Process of carbon electrodes

The carbon capacitor electrodes in a charged super-capacitor or battery are in a state of high positive free-energy relative to the discharged or partially discharged state. Conway et al. [112] proposed three self-discharge mechanisms for electrochemical capacitors or batteries. They also presented the modeling equations for those three mechanisms: activation-controlled, diffusion-controlled and ohmic leakage. Niu et al. [113] compared the self-discharge profile through potential-decay and float current measurement methods by employing the mechanisms and model equations brought up by Conway et al. [112]. Black and Andreas experimentally studied the effect of charge redistribution on self-discharge profile and the results showed agreement with Conway’s theory and model[112].

Hybrid batteries with carbon capacitor electrodes have a high rate of self-discharge. As claimed from the manufacturer, the PbC battery has a voltage decay of 2V/battery in 10 days on shelf. Although under the HRPSOC operations for HEV or EV applications the self-discharge may not be significant enough to affect dynamic
performance, it will be one important issue if the hybrid batteries are used for stand-alone
or standby applications, during which the models developed in this thesis would be able
to capture voltage decay behaviors over time if the self-discharge physics were integrated.
The modeling equations of three self-discharge mechanisms [112] were developed based
on first-principle theory describing the electrochemical kinetic and diffusion processes,
therefore it should be compatible and feasible to integrate them into hybrid battery
models.

5.2.2 Ageing model for hybrid batteries

Conventional lead plates have been replaced by carbon capacitor electrodes in
hybrid batteries, which completely modify the dominant ageing mechanisms. In the past,
the empirical or semi-empirical ageing model encompassed a series of complex ageing
mechanisms, of which negative sulfation played an important part. Now for hybrid
batteries, the ageing model can be simplified and the primary focus can be exclusively
put on the ageing of positive electrodes, such as corrosion, and positive incomplete
charge caused by oxygen gassing. Those processes may possibly be modeled through the
fundamental approach[114,115], and the ageing model might be built on the basis of
performance models delivered by this thesis, effectively serving as a lifetime predictor of
hybrid batteries.
Bibliography


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