Battery aging and the Kinetic Battery Model

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Abstract

Batteries are omnipresent, and with the uprise of the electrical vehicles will their use will grow even more. However, the batteries can deliver their required power for a limited time span. They slowly degrade with every charge-discharge cycle. This degradation needs to be taken into account when considering the battery in long lasting applications. Some detailed battery models that describe the degradation exist. However, these are complex models that require detailed knowledge. These models are in general computationally intensive, which does not make them well suited to be used in a wider context. A model better suited for this is the Kinetic Battery Model. In this paper, we this model would change due to battery degradation, by the results of our experimental degradation analysis. In our analysis we see that the degradation takes place in two phases. After the first phase of slow degradation, the battery suddenly starts to degrade rapidly.

Keywords: battery modeling, battery measurement, battery degradation

1. Introduction

Batteries-powered devices are everywhere; smart-phones, laptops, wireless sensors, electric cars and many more. The batteries provide portable power to these devices. However, the batteries have a limited life span. Obviously non-rechargeable batteries can be discharged only once before they need to be replaced. But, even rechargeable batteries will not be usable after some time.

How long a battery can be used depends on many factors, such as battery type, discharge and charge current, depth of discharge and temperature. It is hard to predict the lifetime of a battery for any given workload pattern. Electro-chemical and electrical circuit models, that require detailed knowledge of the used batteries, are available in literature, see for example [1, 2]. In recent work, Wognsen et al. [3] propose an approach to compare the impact of workload patterns have on the battery life through the Fourier Transform of the workload.

Although some theoretical work exists, little practical work is available in the scientific literature on measuring the battery degradation over time. In this report we present the results of our measurements on battery cells used in nano-satellite batteries.

These results are analyzed in the context of a widely used battery model, the Kinetic Battery Model. The analysis gives insight on how the degradation of the battery impacts the model parameters, and on how to possibly extend this model to cope with the effects of degradation.
The rest of this report is structured as follows. Section 2 gives a brief overview of related work on battery degradation modeling. Section 3 introduces the Kinetic Battery Model. In Section 4 the experimental set-up and the performed experiments are described. The results of the experiments are given in Section 5. We end with a discussion of the results in Section 6.

2. Related work

There are several types of battery models available in the scientific literature. [4] provides an overview of the most used models, such as electro-chemical models, electrical circuit models and analytical models. In [4] the focus is on predicting the duration of a single discharge cycle. These types of models are also used to describe the long term effects of battery degradation.

In [1], capacity fading is modeled with a electro-chemical battery model of a lithium ion battery. This type of model requires a very detailed knowledge of the battery, and are in general very computationally intensive.

In [2] an electrical circuit model is made that models capacity fading due to cycling, as well as the increase of the internal resistance due to cycling. The model should be configured with data from the battery data sheets. However, as also the authors mention, in general, it is very hard to obtain all required information.

High level analytical models, such as the the Kinetic Battery Model (KiBaM) [5], require much less knowledge of the battery, and can be easily combined with other models. For example, in [6] the KiBaM is extended to a random KiBaM and combined with a Markov Task Process that models the battery load. With the combined model, one can compute the probability the battery is depleted due to the defined load pattern. The KiBaM does not take into account the how the battery degrades; it is not known how the parameters are effected.

In this paper, we investigate the how the KiBaM-parameters change when the battery is repeatedly discharged. We take an experimental approach. We wear the battery by applying a relatively heavy load to the battery. This gives us the practical insight in how the battery degrades over time.

3. KiBaM theory

The Kinetic battery model is a compact battery model that includes the most important features of the battery, like the rate-capacity effect and recovery effect. The model has been developed by Manwell and McGowan in 1993 [5]. Originally, the model was aimed at lead-acid batteries, but analysis has shown it could also be used in battery discharge modeling for other battery types [7].

In the model, the battery charge is distributed over two wells: the available-charge well and the bound-charge well (cf. Figure 1). A fraction $c$ of the total capacity is put in the available-charge well (denoted $y_1(t)$), and a fraction $1 - c$ in the bound-charge well (denoted $y_2(t)$). The available-charge well supplies electrons directly to the load ($i(t)$), whereas the
Figure 1: The two well model of the Kinetic Battery Model.

bound-charge well supplies electrons only to the available-charge well. The charge flows from the bound-charge well to the available-charge well through a “valve” with fixed conductance, $k$. The parameter $k$ has the dimension $1/time$ and limits the rate at which the charge can flow between the two charge wells. Next to this parameter, the rate at which charge flows between the wells depends on the height difference between the two wells. The heights of the two wells are given by:

$$h_1(t) = \frac{y_1(t)}{c}$$

and

$$h_2(t) = \frac{y_2(t)}{1-c} - \frac{y_1(t)}{c}.$$ 

The change of the charge in both wells is given by the following system of differential equations:

$$
\begin{align*}
\frac{d y_1}{dt} &= -i(t) + k(h_2 - h_1), \\
\frac{d y_2}{dt} &= -k(h_2 - h_1),
\end{align*}
$$

(1)

with initial conditions $y_1(0) = c \cdot C$ and $y_2(0) = (1 - c) \cdot C$, where $C$ is the total battery capacity. The battery is considered empty when it is observed that there is no charge left in the available-charge well.

As shown in [7], we can transform the equations to

$$
\begin{align*}
\frac{d \gamma}{dt} &= -i(t), \\
\frac{d \delta}{dt} &= \frac{i(t)}{c} - k'\delta,
\end{align*}
$$

(2)

where $k' = k/(c(1-c))$, $\gamma = y_1 + y_2$ and $\delta = y_2/(1-c) - y_1/c$. We can interpret $\gamma$ as the total charge remaining in the battery, and $\delta$ as the height difference between the charge levels of the two wells. The initial conditions transform into $\gamma(0) = C$ and $\delta(0) = 0$. The battery is empty when $\gamma(t) = (1-c)\delta(t)$. 

3.1. *KiBaM* constant current discharge

When we consider a constant current discharge, i.e., $i(t) = I_d$, the differential equations are easily solved. The solution is:

\[
\begin{aligned}
\gamma(t) &= C - I_d t, \\
\delta(t) &= \frac{I_d}{ck'} \left( 1 - e^{-k't} \right).
\end{aligned}
\] (3)

The battery lifetime $L$, i.e., the time to empty the available charge well, for a constant current discharge is given by:

\[
L = \frac{C}{I_d} - \frac{1}{k'} \left( \frac{1 - c}{c} + W \left( \frac{1 - c}{c} e^{\frac{1 - c}{c} - \frac{c k'}{k}} \right) \right),
\] (4)

where $W(.)$ is the so-called Lambert $W$ function [8]. The Lambert $W$ function is the inverse function of $f(x) = xe^x$.

By measuring the the battery lifetime, and the delivered energy, as a function of the discharge current, we can determine the *KiBaM* parameters, $k$, $c$ and $C$ by fitting Equation 4 to the data.

3.2. *KiBaM* charging

Battery charging normally is performed in two phases. First, the battery is charged at a constant current. In this phase the voltage slowly rises. When the voltage reaches the maximum level, $V_{max}$, the second phase starts. During this phase the voltage is kept constant at $V_{max}$, and the charging current will drop.

We discuss the two charging phases in the context of the *KiBaM* model in the following sections.

3.2.1. *KiBaM* constant current charging

In the *KiBaM*, the charging with a constant current is very similar to discharging with a constant current. For a constant charging current $I_{ch}$ the *KiBaM* equations are:

\[
\begin{aligned}
\frac{dy_1}{dt} &= I_{ch} - k \left( \frac{y_1}{c} - \frac{y_2}{1 - c} \right), \\
\frac{dy_2}{dt} &= k \left( \frac{y_1}{c} - \frac{y_2}{1 - c} \right).
\end{aligned}
\] (5)

When we consider the battery fully empty at the start of the charging, the initial conditions are $y_1(0) = 0$ and $y_2(0) = 0$. The constant current charging phase ends when the available charge well is filled, thus $y_1 = cC$. In terms of $\delta_{ch} = \frac{y_1}{c} - \frac{y_2}{1 - c}$ ($\delta_{ch} = -\delta$) and $\gamma = y_1 + y_2$, the equations are:

\[
\begin{aligned}
\frac{d\gamma}{dt} &= I_{ch}, \\
\frac{d\delta_{ch}}{dt} &= \frac{I_{ch}}{c} - k'\delta_{ch},
\end{aligned}
\] (6)
The initial conditions transform into $\delta_{ch}(0) = 0$ and $\gamma(0) = 0$. The condition for the end of the constant current charging phase is $\gamma(t_{lin}) + (1 - c)\delta_{ch}(t_{lin}) = C$. This condition can be interpreted as follows, at time $t = t_{lin}$, the amount of energy put into the battery is $\gamma(t_{lin})$ and still $(1 - c)\delta_{ch}(t_{lin})$ needs to be charged.

The solutions for $\gamma$ and $\delta_{ch}$ are again easily obtained:

$$\begin{cases} 
\gamma(t) = I_{ch}t, \\
\delta_{ch}(t) = \frac{I_{ch}}{ck'}(1 - e^{-k't}), 
\end{cases} \tag{7}$$

where we see that the equation for $\delta$ is the same as for discharging, cf. (3).

Under the described conditions, the time it takes to fill the available charge well, $t_{lin}$, is the similar to the discharging lifetime, cf. (4):

$$t_{lin} = \frac{C}{I_{ch}} - \frac{1}{k'} \left( \frac{1 - c}{c} + W \left( \frac{1 - c}{c} e^{\frac{1 - c - W}{c/k'}} \right) \right). \tag{8}$$

So, under the assumption that the battery is completely empty, we expect that, when the battery parameters are the same for charging an the linear charging phase takes as long as the discharging lifetime.

### 3.2.2. KiBaM non-linear charging

After the linear charging phase, the battery is charged with a constant voltage and a decreasing current. In the KiBaM we can interpret this as follows. The constant voltage keeps the level of the available charge well at its maximum. The rate at which the battery can accept additional charge is limited by the flow between the two charge wells. This rate depends on the height difference between the two wells, and thus will decrease when the battery is further charged.

The available charge does not change, hence, $\frac{dy}{dt} = 0$. From the KiBaM equations we obtain:

$$i(t) = k \left( \frac{y_1}{c} - \frac{y_2}{1 - c} \right). \tag{9}$$

In terms of $\delta_{ch} = \frac{y_1}{c} - \frac{y_2}{1 - c}$ this yields:

$$i(t) = k\delta_{ch} = k'c(1 - c)\delta_{ch} \tag{10}$$

The KiBaM equations in terms of $\delta_{ch}$ and $\gamma$ now are:

$$\begin{cases} 
\frac{d\gamma}{dt} = i(t) = k'c(1 - c)\delta_{ch}, \\
\frac{d\delta_{ch}}{dt} = \frac{i(t)}{c} - k'\delta_{ch} = -k'c\delta_{ch}, 
\end{cases} \tag{11}$$

From these equations it follows that

$$\delta = \delta_0 e^{-ck't}, \tag{12}$$
Table 1: Parameters of the GomSpace batteries [9]

<table>
<thead>
<tr>
<th>name</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>nominal capacity</td>
<td>2600 mAh</td>
</tr>
<tr>
<td>maximum charge voltage</td>
<td>4.2 V</td>
</tr>
<tr>
<td>end of discharge voltage</td>
<td>3.0 V</td>
</tr>
<tr>
<td>maximum discharge current</td>
<td>3.75 A</td>
</tr>
<tr>
<td>maximum charge current</td>
<td>2.5 A</td>
</tr>
<tr>
<td>end of charge current</td>
<td>1.3 A</td>
</tr>
<tr>
<td>charge temperature range</td>
<td>-5 — 45 °C</td>
</tr>
<tr>
<td>discharge temperature range</td>
<td>-20 — 60 °C</td>
</tr>
</tbody>
</table>

where $\delta_0$ is the height difference between the two wells at the start of the non-linear charging phase ($I_{lin}$). $\delta_0$ depends on the charging current in the linear phase. From equations (7) and (8) it follows that

$$\delta_0 = \frac{I_{lin}}{ck'} \left(1 - e^{-ck't_{lin}}\right).$$

If $k't_{lin}$ is large, that is, if the height difference has approached its maximum value during the linear charging phase, we obtain

$$\delta_0 = \frac{I_{lin}}{ck'}.$$  

The height difference decreases exponentially, and thus the charging current should decrease exponentially. By fitting an exponential function to the measured current we can estimate the factor $ck'$. This gives additional information on how the KiBaM performs for charging the battery.

4. Experimental set-up

In the experiments we analyze 4 Li-ion battery cells with a capacity of 2600 mAh, obtained from GomSpace. The nano satelite battery packs consist of 4 to 8 of these battery cells. Table 1 gives an overview of the key parameters, as provided in the datasheets.

The measurements are done with the Cadex C8000 battery testing system. The tester is programmed to discharge and charge the cells in a controlled fashion according to a user-defined load profile, while measuring the voltage, current and temperature. This data is logged each second, and is used for the analysis of the battery properties. The system has four connections to test four batteries simultaneously. Figure 2 shows the set-up with the batteries and the Cadex system.

The experiments consist of multiple phases. In the first phase, KiBaM estimation measurements, the cells are discharged and charged at various constant rates. The charge rates vary from 0.1C to 0.9C, while the discharge rates vary from 0.1C to 1.4C. Table 2 gives an overview of the discharge and charge currents of the individual measurement cycles.
Figure 2: Experimental set-up with the Cadex C8000 battery tester.

Table 2: Discharge and charge currents for the KiBaM parameter estimation measurements.

<table>
<thead>
<tr>
<th>test</th>
<th>discharge current</th>
<th>charge current</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1C = 0.26 A</td>
<td>0.1C = 0.26 A</td>
</tr>
<tr>
<td>2</td>
<td>0.2C = 0.52 A</td>
<td>0.2C = 0.52 A</td>
</tr>
<tr>
<td>3</td>
<td>0.3C = 0.78 A</td>
<td>0.3C = 0.78 A</td>
</tr>
<tr>
<td>4</td>
<td>0.4C = 1.04 A</td>
<td>0.4C = 1.04 A</td>
</tr>
<tr>
<td>5</td>
<td>0.5C = 1.3 A</td>
<td>0.5C = 1.3 A</td>
</tr>
<tr>
<td>6</td>
<td>0.6C = 1.56 A</td>
<td>0.6C = 1.56 A</td>
</tr>
<tr>
<td>7</td>
<td>0.7C = 1.82 A</td>
<td>0.7C = 1.82 A</td>
</tr>
<tr>
<td>8</td>
<td>0.8C = 2.08 A</td>
<td>0.8C = 2.08 A</td>
</tr>
<tr>
<td>9</td>
<td>0.9C = 2.34 A</td>
<td>0.9C = 2.34 A</td>
</tr>
<tr>
<td>10</td>
<td>1.0C = 2.60 A</td>
<td>0.6C = 1.56 A</td>
</tr>
<tr>
<td>11</td>
<td>1.2C = 2.86 A</td>
<td>0.7C = 1.82 A</td>
</tr>
<tr>
<td>12</td>
<td>1.4C = 3.64 A</td>
<td>0.9C = 2.34 A</td>
</tr>
</tbody>
</table>
The data from these measurements will be used to estimate the parameters for the Kinetic Battery Model.

In the second phase, the degradation measurements, the cells are repeatedly fully discharged at 1C and charged at 0.5C. This high load will result in a relative fast degradation of the cells. After 50 discharge-charge cycles, the cycles of the first phase are repeated, in order to see whether and how the battery parameters have changed. The measurements of 50 discharge-charge cycles, and determining the battery parameters will be repeated until the cell capacity has dropped below 80% of its initial value. The results of these experiments give an indication on how the cells degrade over time.

5. Results

In this section we discuss the results of the performed measurements. First, we analyze the battery degradation due to the degradation measurements in Section 5.1. Then, we analyze the change of the KiBaM parameters for discharging and charging in Sections 5.2 and 5.3, respectively.

5.1. Degradation measurements

Figure 3 shows how the discharge capacity decreases as a function of the discharge cycle number. In the first discharge cycle, on average, the batteries deliver 92.8% of the nominal capacity (2600 Ah). In the subsequent cycles the discharge capacity slowly drops. The decrease in capacity is more or less linear. We fit a linear function, $y = \alpha \cdot \text{cycle} + \beta$ to the first 100 measurements. The fit yields $\alpha = -0.057 \pm 0.0025$ and $\beta = 92.8 \pm 0.14$. This means that the capacity, on average, drops 0.057 percentage point with every discharge-charge cycle.

After approximately 140 cycles the capacity decreases more rapidly. Battery 3 now degrades clearly faster than the other 3 batteries. We fit another line, $\text{Cap} = \alpha \cdot \text{cycle} + \beta$,
to the last 50 measurements, cycle 151 to 200. This yields, $\alpha = -0.41 \pm 0.027$ and $\beta = 144.2 \pm 4.8$. This means that the degradation is more than a factor 7 faster than at the start, with an average of 0.41 percent point per cycle.

Next to the capacity we investigate how the efficiency evolves when the battery is used. The efficiency is determined by: $E_{\text{dis},n} / E_{\text{ch},n-1}$, where $E_{\text{dis},n} \times 100$ is the delivered energy in cycle $n$, and $E_{\text{ch},n-1}$ is the charging energy of cycle $n-1$.

The results are shown in Figure 4. As for the capacity, we see that the efficiency also degrades in two phases. Again we fit two lines to the data. The first line is fit to the first 100 cycles. The efficiency starts at $89.3\% \pm 0.17$. The efficiency degrades linearly with a rate of $0.020 \pm 0.0028$ percent point per cycle.

The second line is fit to the last 50 cycles. Here we see that the efficiency degrades at a rate of $0.061 \pm 0.022$ percent point per cycle. This means that the efficiency degrades 3 times faster at the end of the battery life than at the beginning. Furthermore, we see that the variance in efficiency is much larger at the end of the battery lifetime.

Finally, we investigate the non-linear charge phase of the degradation measurements. According to the KiBaM theory the charge current should drop exponentially during the non-linear charge phase, cf. (12). We fit a negative exponential curve to the measured current. In Figure 5 the exponent, which corresponds to $k'c$, is plotted as a function of the cycle number. We see that the exponent decreases as the number of discharge-charge cycles increases. We have fitted a linear curve, $y = \alpha \cdot x + \beta$ to the data. This fit yields $\alpha = -1.71 \cdot 10^{-6} \pm 0.05 \cdot 10^{-6}$ and $\beta = 1.03 \cdot 10^{-3} \pm 0.005 \cdot 10^{-3}$. In the KiBaM, the decrease of the exponent $k'c$ is either caused by a decrease in $k$, i.e., the conductance between the available and bound charge well, or by a decrease in $c$, i.e., the size of the available charge well.

However, the KiBaM does not include the efficiency of the charging process. As we have seen earlier, the efficiency of the battery drops as the battery ages. This drop in efficiency
can also result in the slower exponential drop of the charging current during the non-linear charging phase.

5.2. Discharge KiBaM parameter estimation

We start the battery degradation analysis with a series of measurements for determining the KiBaM parameters. In these measurements the batteries are discharged and charged at various constant currents, cf. Table 2. These measurements have been repeated after every 50 cycles in the degradation measurements. Figure 6(a) shows the measured discharge capacity of the four batteries for the different discharge currents of the first series.

The measurements at 0.9C = 2.34 A discharging current have been performed twice. The first run, which was the first experiment that was performed, resulted for all batteries in a discharge capacity that was higher than expected. The second run resulted in a capacity that was in line with the other experiments. The reason for these results remains unclear.

For battery 3, we see a relative low capacity at the low discharge currents. We expect that this is some internal damage or lower quality of the battery. Battery 3 has a slightly lower performance throughout the experiments, as we will see in the later results.

The measured delivered capacity ($C_{\text{del}}$) in As as a function of the discharge current ($I_d$) is fitted to the function (cf. 4):

$$C_{\text{del}} = C_{\text{nom}} - \frac{I_d}{k'} \left( \frac{1 - c}{c} + W \left( \frac{1 - c}{c} e^{\frac{1 - c}{c} - \frac{C_{\text{nom}} k'}{I_d}} \right) \right)$$

(15)

In the fitting procedure we use the parameter $\kappa = 1/k'$ instead of $k'$, since the fitting algorithm was not stable when $k$ was used directly. In the fit we ignored the outliers of the first measurement and battery 3. The result is included in Figure 6(a). From the fit we obtained $C = 9.67 \cdot 10^3 \text{ As} \pm 220 \text{ As}$, which is higher than the nominal capacity of 2600 mAh = 9360 As. The other parameters are: $c = 0.90 \pm 0.015$ and $\kappa = 9.36 \cdot 10^3 \text{s} \pm 9.12 \cdot 10^3 \text{s}$. The
parameter $\kappa$ has a very large confidence interval, thus we cannot draw any strong conclusions on the actual value of this parameter, or the parameter $k = 1/\kappa$.

After every 50 discharge-charge cycles another series of measurements is done to determine the KiBaM parameters. The results are given in Figures 6(b) - 6(e). In these figures we see that, like in the degradation measurements, the capacity first drops slowly in Figures 6(b) to 6(d), and then drops dramatically in Figure 6(e). In all these measurement series, as in the results of the first series, battery 3 has a lower capacity for the low discharge currents. At high discharge currents, greater than 2.5 A, all batteries perform less than expected. When we include these measurements in the fitting procedure the results for the parameters $c$ and $\kappa$ are nearly meaningless, with extremely large confidence intervals. The degradation of the battery seems to have a larger impact when high discharge currents are applied. When we discard the high current measurements in the fitting procedure, the results are more in line with the analysis of the first measurement series. The values of the fitted parameters and their confidence intervals are given in Table 3. We see a decrease in the capacity of the battery, as expected. Also, the parameter $c$ slowly decreases, as the battery ages. This means that the decrease in capacity affects the available more than the bound charge. For the parameter $\kappa$ it is impossible to tell whether the battery degradation has any real impact, due to the large confidence intervals.

5.3. KiBaM charging

Next to the KiBaM parameters for discharging, we fit the KiBaM to the charging measurements. Figure 7 shows the energy put into the battery during the linear charge phase of the five series. In all five figures we notice some deviating measurements. These measurements coincide with the deviations in the discharge results. Battery 3, again deviates at low currents. However, the linear charge capacity is larger than for the other batteries at low currents, whereas the discharge capacity was lower.

The outliers are again discarded in the fitting procedure. The fitted curves are given in Figure 7, and the parameters are given in 4. Again, we can see that the capacity decreases. The estimated capacity is, however, smaller than for discharging. The parameter $c$ is much smaller during charging than during discharging. This implies that the available charge well is much smaller when the battery is charged.

For the parameter $\kappa$ it is again hard to draw firm conclusions. The estimated values for $\kappa$ are lower for charging than for discharging. This would suggest that the flow between bound and available charge is faster during charging than during discharging.

<table>
<thead>
<tr>
<th>experiment</th>
<th>$C(10^8 \text{ As})$</th>
<th>$c$</th>
<th>$\kappa (10^3 \text{s})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>series 1</td>
<td>9.67 ±0.22</td>
<td>0.90 ±0.015</td>
<td>9.36 ±9.12</td>
</tr>
<tr>
<td>series 2</td>
<td>9.25 ±0.10</td>
<td>0.90 ±0.019</td>
<td>4.37 ±2.66</td>
</tr>
<tr>
<td>series 3</td>
<td>9.23 ±0.08</td>
<td>0.86 ±0.019</td>
<td>3.76 ±1.56</td>
</tr>
<tr>
<td>series 4</td>
<td>9.26 ±0.15</td>
<td>0.83 ±0.027</td>
<td>4.43 ±2.24</td>
</tr>
<tr>
<td>series 5</td>
<td>8.67 ±0.26</td>
<td>0.70 ±0.080</td>
<td>2.85 ±2.05</td>
</tr>
</tbody>
</table>
Figure 6: KiBaM discharge fits
Table 4: parameters charge

<table>
<thead>
<tr>
<th>experiment</th>
<th>$C (10^3 \text{ As})$</th>
<th>$c$</th>
<th>$\kappa (10^3 \text{s})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>series 1</td>
<td>9.38 ±0.12</td>
<td>0.579 ±0.076</td>
<td>1.74 ±0.73</td>
</tr>
<tr>
<td>series 2</td>
<td>9.22 ±0.09</td>
<td>0.646 ±0.031</td>
<td>2.57 ±0.59</td>
</tr>
<tr>
<td>series 3</td>
<td>9.18 ±0.12</td>
<td>0.599 ±0.045</td>
<td>2.37 ±0.70</td>
</tr>
<tr>
<td>series 4</td>
<td>9.09 ±0.15</td>
<td>0.548 ±0.057</td>
<td>2.22 ±0.78</td>
</tr>
<tr>
<td>series 5</td>
<td>8.57 ±0.27</td>
<td>0.504 ±0.071</td>
<td>2.62 ±1.21</td>
</tr>
</tbody>
</table>

It is not clear how to interpret the differences between the KiBaM parameters for discharging and charging within the context of the battery processes. However, this does show that when the KiBaM model is used, we cannot just reverse the flow of the current and keep the parameters the same when we switch from discharging to charging.

6. Discussion

The degradation measurements clearly show the degradation of the battery during its cycle life. We see a linear drop in the capacity until approximately 140 cycles. After this point the capacity starts to degrade at a much higher rate. This point, 140 cycles, could be taken as the effective cycle life of the battery. Of course, we should add the 37 cycles of the KiBaM parameter estimation measurements to this to get a proper estimation of the cycle life of the batteries. This gives us a cycle life of approximately 180 cycles. This is much lower than the 350 cycles at 1C discharge rate that are given in the data sheets. This difference might be caused by temperature effects. During the discharge periods the battery temperature typically rose to 34°C, while dropping to 25°C during charging. Whereas the cycle life in the data sheet assumes a constant temperature of 25°C.

Next to the capacity loss, we see a decrease in the efficiency of the battery. The efficiency drops from approximately 90% at the start of the experiments to approximately 86% at the end of the cycle life of the batteries. We do not see a charge in the rate at which the efficiency decreases after the cycle life has been reached.

The analysis of the non-linear charge phase shows us that the exponential decay of the charging current becomes slower as the battery ages. Although this might indicate a change in the KiBaM parameters $c$ and $k$, this also might be caused by the decreasing efficiency.

The measurements for estimating the KiBaM parameters as well show the drop in the capacity for the aging battery. The fraction of available charge, parameter $c$, shows a decrease as well in the discharging measurements. In the charging measurements this decay is not so clear. However we do see that the parameter $c$ is different for discharging and charging. The analysis gives no conclusive results for how the parameter $k$ evolves for the aging batteries.

The experiments put forward a couple of limitations of the KiBaM. Although the decay of the capacity and the drop of the efficiency of the battery might be easily included into a more evolved KiBaM, the asymmetry between discharging and charging in the parameter $c$ may not be incorporated so easily. Changing $c$ when the battery changes from discharging...
Figure 7: KiBaM charge fits
to charging, might involve a redistribution of the available and bound charge as well. More
analysis, and possibly more measurements, are needed to see how we should adapt the
KiBaM to incorporate the observed phenomena.

references

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