Mechanism Analysis of Capacity Decline of LiFePO4 Cells During Aging and Abuse

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Abstract

In order to characterize the influence of different factors on battery capacity, it is necessary to analyze the mechanism of different aging factors and overcharge and over discharge behavior. By introducing the lithium intercalation rate-electrode voltage constraint, the side reaction mechanism in the charging and discharging process of different factors was analyzed, and the rules of battery capacity change caused by different factors were obtained. Design aging tests to verify theoretical analysis. In conclusion, the loss of lithium inventory and the loss of active material lead to a decrease in battery capacity. The overcharge behavior leads to an increase in battery capacity and the over-discharge behavior leads to a decrease.

Keywords: loss of lithium inventory, Loss of electrode active material, over charge, over discharge

1. Introduction

Studying the battery aging mechanism is the first step in the evaluation of the state of decommissioned lithium-ion batteries. There are two main purposes: one is to determine whether the battery is available, and the other is how to use it efficiently. Study battery aging mechanism Design battery physical model parameters to estimate battery health, and design battery model parameters to achieve consistent reorganization of decommissioned lithium-ion batteries.

The traditional battery health status is primarily indicated by the battery capacity value. However, considering the diversity of operating conditions before the decommissioning of lithium-ion batteries for electric vehicles, the article estimates the health status of battery capacity based on the battery physical model parameter values. The article estimates the battery capacity loss caused by two main aging modes: Loss of Lithium Inventory (LLI) and Loss of Active Material (LAM). Achieve multidimensional health state estimation of decommissioned lithium-ion batteries.

2. The reasons for capacity change

The battery is accompanied by a decline in battery performance during charging, discharging, and storage. The deterioration of battery performance is directly related to the side reaction inside the battery and the change in battery material characteristics. These changes will result in changes in characteristics such as a decline in battery capacity and an increase in internal resistance of the battery. There are two factors that cause battery capacity degradation: loss of recyclable lithium ions and loss of active materials. There are two factors that cause an increase in battery capacity: overcharge behavior and over-discharge behavior.

2.1 Loss of lithium inventory

The loss of lithium inventory (LLI) means that during the cycle of charge and discharge of the battery, a side reaction that consumes electrolyte to circulate lithium occurs, causing a decrease in the working range of the electrode. In lithium-ion batteries, the LLI usually occurs in the negative electrode region. There are mainly two mechanisms: one is to form a solid-liquid interface film (SEI), and the other is to deposit lithium on the surface of the negative active particle.

(1) Formation and thickening of SEI

Arora & White pointed out in 1998 that several decomposition reactions existed in electrolytes. Among them, ethylene carbonate (EC) in the electrolytic solution has a reduction reaction which is decomposed and generates an SEI film. The literature [1-3] gives two steps in the EC electrolyte decomposition reaction:

\[
\begin{align*}
EC + e^- & \longrightarrow EC^- \\
2EC^- + 2Li^+ & \longrightarrow CH_2OCO_2Li_2 + C_2H_4
\end{align*}
\]

In this chemical reaction, the main component of the produced SEI is (CH2OCO2Li)2. The SEI generation

...
process consumes lithium, and the generation and thickening of the SEI causes loss of recyclable lithium ions.

(2) Negative electrode precipitation of lithium
Electrode lithium deposition refers to a phenomenon in which lithium ions in an electrolyte solution are deposited on the surface of the electrode active particles. Generally, the lithium intercalation ability of the graphite negative electrode is weaker than that of the positive electrode. During the charging process of the battery, when the surface potential of the negative electrode active particles is lower than 0 V, a phenomenon of lithium plating occurs at the negative electrode. When the operating temperature of the battery is low, the charging current is too large, or overcharging occurs, a local potential region of the graphite electrode exhibits a potential of 0 V, causing lithium plating. When lithium plating occurs in the battery, the recyclable lithium ions in the electrolyte are consumed and the battery capacity is attenuated.

2.2 Electrode active material loss
The loss of the electrode active material (LAM) refers to a phenomenon in which the lithium electrode material cannot be embedded and ejected, and the function of storing the charge is lost. The loss of the electrode active material causes a decrease in the charge storage capacity.

(1) Electrode active particle cracking
During the charging and discharging of the battery, due to the insertion and extraction of lithium ions in the active particles of the electrode, the electrode particles have a non-negligible shrinkage and expansion. Under the action of current stress and internal pressure, the electrode active particles will be mechanically fatigued, causing cracks. This deactivates the electrode material and causes loss of the electrode active material.

(2) Electrolyte material dissolution
For some positive electrode chemicals, the active material has a phenomenon of dissolving into the electrolyte solvent. For LiFePO₄/graphite (LFP/GIC) batteries, when the internal temperature of the battery is high, the electrolyte purity is poor, or impurities are present inside the active material, the surface of the positive electrode material is corroded.

(3) Electrode particle agglomeration
Electrode particle agglomeration refers to the process by which smaller electrode particles combine to form larger average radius particles. The agglomerated electrode particles lose their activity due to detachment from the binder. Along with the change of the structure of the electrode particles, the internal stress of the battery becomes large, which makes the internal particles of the battery more susceptible to cracks, affecting the physical path of electron transfer, and causing the particles to lose activity.

(4) Collector corrosion
When the battery is severely over-discharged, the negative electrode potential of the battery is too high, and the negative current collector is prone to electrochemical reaction and corrosion. The fluid collector corrosion causes contact with the negative active material to deteriorate, resulting in the active material being isolated and losing activity.

3. Battery aging mode characterization
3.1 Loss of lithium inventory
For LFP/GIC batteries, the generation and thickening of SEI and lithium plating mainly occur on the graphite negative electrode. Assuming that the capacity loss due to LLI is \( q_{loss} \) during a charge, the effect of LLI on the open circuit potential and its operating range is illustrated in Figure 1.

![Figure 1 Schematic diagram of LLI](image)

The process of LLI is described as follows: During a charging process, the battery is charged from the fully discharged state to \( p_1 \). Then, a side reaction of consuming lithium ions occurs in the negative electrode, so that the negative electrode active particles cannot receive lithium ions. The state of charge of the negative electrode remains unchanged, while the positive electrode normally deducts lithium ions, and finally the terminal voltage of the battery reaches a high potential at \( p_1 \) as \( p_0 \). In this process, the phenomenon of potential dislocation between positive and negative electrode results in the loss of available capacity of the battery as \( q_{loss} \).

\[
Q_{cell1} = Q_{cell0} - q_{loss} \tag{2}
\]

Among them, \( Q_{cell0} \) is the initial capacity, and \( Q_{cell1} \) is the battery capacity after LLI occurs.

\( SOC_{n0} \) and \( SOC_{p0} \) indicate the initial SOC of positive and negative poles when the upper limit cut-off voltage is applied. When \( SOC_{n1} \) and \( SOC_{p1} \) indicate the lower cut-off voltage, the positive and negative poles terminate SOC.

\[
\begin{align*}
SOC_{n0}^{LLI} &= SOC_{n0} - (q_{loss} / Q_n) \\
SOC_{p1}^{LLI} &= SOC_{p1} - (q_{loss} / Q_p) \tag{3}
\end{align*}
\]
Here, $SOC_{n0}^{LLI}$ is the initial SOC of the negative electrode after LLI, $SOC_{p1}^{LLI}$ is the termination SOC of the positive electrode after LLI, and $Q_{s}$ is the negative electrode capacity.

3.2 Loss of electrode material

The electrode material loss includes four cases: the loss of lithium containing active materials of negative electrode ($LAM_{\text{LAM}}$), the loss of the lithium-free active materials of negative electrode ($LAM_{\text{defPE}}$), the loss of lithium containing active materials of positive electrode ($LAM_{\text{LAM}}$), and the loss of lithium-free active materials of the positive electrode ($LAM_{\text{defPE}}$). Experimental studies have found that even if the battery capacity is attenuated to 70% of the initial capacity, the positive electrode material of the LFP/GIC battery is still not significantly attenuated. In addition, the study found that the loss of LFP/GIC electrode material is mainly due to the loss of lithium-free material, and LAM_{defPE} has little effect on the OCV of the battery. Therefore, this article considers that the cathode material does not lose and the positive time capacity is constant. Figure 2 is a schematic view showing a loss process of a lithium-free material of a negative electrode.

The process of LAM_{defNE} can be abstracted as LAM_{defNE} occur after the battery is emptied. If the amount of material loss at this time is 10% $Q_{\text{cell}}$, it is represented by $q_{\text{loss}}$. The potential of the negative electrode shrinks; the positive potential curve does not change, and the open circuit voltage of the battery changes. In this process, the battery capacity does not change, and after LAM_{defNE} the capacity of the negative electrode $Q_{s1}^{LAM_{\text{defNE}}}$ is:

$$
\begin{cases}
Q_{\text{cell}} = Q_{n0} \\
Q_{s1}^{LAM_{\text{defNE}}} = Q_{s0} - q_{\text{loss}}
\end{cases}
(4)
$$

The initial SOC after LAM_{defNE} of the negative electrode can be expressed as:

$$
SOC_{s0}^{LAM_{\text{defNE}}} = SOC_{s0} - SOC_{s1} \frac{Q_{s0}}{Q_{s1}^{LAM_{\text{defNE}}}} + SOC_{s1}
(5)
$$

The loss process of LAM_{\text{LAM}} is shown in Figure 3, and this process can be abstractly expressed as LAM_{\text{LAM}} occur when the battery is fully charged. If the amount of material loss at this time is 10% $Q_{\text{cell}}$, the battery capacity loss and the negative electrode capacity loss are the same, and are expressed by $q_{\text{loss}}$. At this time, the capacity of the negative electrode is reduced from 100% $Q_{s0}$ to 90% $Q_{s0}$.

Figure 3 Schematic diagram of LAM_{\text{LAM}}

During this process, the battery capacity changes, and the working range of the negative electrode and the positive electrode changes. The changes of battery capacity and negative electrode capacity can be expressed as:

$$
\begin{align*}
Q_{\text{cell}} &= Q_{n0} - q_{\text{loss}} \\
Q_{s1}^{LAM_{\text{LAM}}} &= Q_{s0} - q_{\text{loss}}
\end{align*}
(6)
$$

Among them, $Q_{s1}^{LAM_{\text{LAM}}}$ is the negative electrode capacity after LAM_{defNE} occurs. At this point, the working range of the negative and positive electrodes changes:

$$
\begin{align*}
SOC_{s0}^{LAM_{\text{LAM}}} &= 1 - 1 - SOC_{s0} (Q_{s0} / Q_{s1}^{LAM_{\text{LAM}}}) \\
SOC_{p1}^{LAM_{\text{LAM}}} &= SOC_{p1} - (q_{\text{loss}} / Q_{p})
\end{align*}
(7)
$$

In electric vehicle applications, it can be considered that the battery is almost full and full, and the loss of LAM_{defNE} and the loss of LAM_{\text{LAM}} are equal. Therefore, in the aging mode of material loss, the initial SOC of the battery negative is unchanged:

$$
SOC_{s0}^{LAM} = SOC_{s0}
(8)
$$

The corresponding capacity loss in the process of material loss is:

$$
Q_{\text{loss}}^{LAM} = Q_{s0} - Q_{s1}^{LAM} / 2
(9)
$$

3.3 Battery overcharge behavior

The battery overcharge behavior (OC) process can be abstracted as the positive electrode continues to pull out excess lithium ions when the battery is fully charged. If the amount of lithium ions desorbed from the positive electrode at this time is $q_{\text{add}}$, part of the lithium ions participate in the excessive growth of the SEI at
the negative electrode, and the amount of lithium ions participating in the excessive growth of the SEI is \( q_{\text{add}}^{\text{SEI}} \). The battery capacity changes before and after overcharging is:

\[
\begin{align*}
Q_{\text{cell}} & = Q_{\text{cell}0} + q_{\text{add}} - q_{\text{loss}}^{\text{SEI}} \\
Q_{\text{p}} & = Q_{\text{p}0} + q_{\text{add}}
\end{align*}
\]

(10)

Among them, \( Q_{\text{cell}0} \) is the initial capacity, and \( Q_{\text{cell}1} \) is the battery capacity after overcharge.

It is mentioned in the literature [4-5] that overcharging of the battery leads to Fe deposition, which is mainly derived from Fe impurities in the positive electrode material. The positive electrode material did not cause decomposition, so the side reaction of Fe deposition did not cause loss of the positive electrode active material. During the overcharge process, more positive active material participates in the reaction to generate lithium ions. The amount of lithium ions desorbed from the positive electrode is greater than that involved in the excessive growth of the SEI, so the working range of the positive and negative electrodes is enlarged.

After the positive and negative working sections change, the initial SOC of the positive electrode and the SOC of the positive terminal will change accordingly. Using \( SOC_{\text{p}0}^{\text{OC}} \) and \( SOC_{\text{p}1}^{\text{OC}} \) indicate the initial SOC of the negative electrode and the SOC of the positive terminal after the loss of lithium inventory occurs:

\[
\begin{align*}
SOC_{\text{p}0}^{\text{OC}} &= SOC_{\text{p}0} + (q_{\text{add}}^{\text{SEI}} / Q_{\text{p}1}) \\
SOC_{\text{p}1}^{\text{OC}} &= 1 - (1 - SOC_{\text{p}1})(Q_{\text{p}} / Q_{\text{p}1}^{\text{OC}})
\end{align*}
\]

(11)

3.4 Battery over discharge behavior

The battery overcharge behavior (OD) process can be abstracted as follows. After the battery is emptied, continuous discharge increases the negative electrode potential to 4.5V, and the cathode potential drops to 3.16V. In the negative collector, Cu is oxidized to Cu\(^{2+}\), Cu\(^{2+}\) which diffuses to the positive electrode and deposited as metallic copper. After over discharge, a normal charge is made, and in the process, a new SEI is generated, consuming lithium ions in the electrolyte. In summary, the over discharge behavior consumes lithium ions in the battery, causing the corrosion of the collector and promoting the decomposition and reconstruction of SEI. The positive and negative pole materials did not lose during the whole process. Using \( SOC_{\text{n}0}^{\text{OD}} \) and \( SOC_{\text{p}1}^{\text{OD}} \) indicate the initial SOC of the negative electrode and the SOC of the positive terminal after over discharge.

\[
\begin{align*}
SOC_{\text{n}0}^{\text{OD}} &= SOC_{\text{n}0} - (q_{\text{loss}} / Q_{\text{n}}) \\
SOC_{\text{p}1}^{\text{OD}} &= SOC_{\text{p}1} - (q_{\text{loss}} / Q_{\text{p}})
\end{align*}
\]

(13)

4. Battery aging experiment

In order to analyze the relationship between battery health and battery usage, a multi-factor battery cycle aging experiment was designed in this section. Characteristic experiments and cycle aging experiments were performed on the subjects. LFP/GIC battery experiment system is shown in Figure 4.

![Battery test system](image)

Figure 4 LFP/GIC battery experiment system

The characteristic experiment is used to obtain the capacity health status and aging mode of the battery under normal temperature environment. Characteristic tests include: 1/2C constant current-constant voltage charge and discharge and 1/20C charge. There are two experimental conditions for battery cycle aging experiments: First: normal temperature 30 °C, 1C charging and discharge; Second: high temperature 60 °C, 1C charging and discharge. The battery experiment process is shown in Figure 5. 110%SOC overcharge test and 110%DOD overshoot test were designed respectively to verify the theoretical analysis.

![Battery aging experiment process](image)

Figure 5 Battery multi-factor aging experiment process
5. Results

Design the aging test separately: 30 degrees, full cycle; 60 degrees, full cycle; 30 degrees, half cycle. The fig. 6 shows the relationship between battery capacity, SOC, Q and battery aging.

As shown in Fig. 6(a), LLI, LAM\text{LINE} and LAM\text{deNE} occur in the case of conditional full cycle. LLI and LAM\text{LINE} lead to battery capacity decay, so the battery capacity decays with aging. Affected by temperature, the higher the temperature, the faster the cell capacity decays. In half cycle, only LLI and LAM\text{deNE} appear, so the cell capacity decays slowly with aging. In Fig. 6(b), inl half cycle, only LAM\text{deNE} appears, so SOC\text{r0} increases. Under condition full cycle, LAM\text{LINE} and LAM\text{deNE} appears in the negative electrode, so SOC decreases. When the SOC\text{r0} changes caused by LAM\text{LINE} and LAM\text{deNE} are close, SOC\text{r0} will remain unchanged, as shown in the blue curve platform in conditional halfcycle-30deg. In Fig. 6(c), the negative capacity of the battery is Q\text{n} in condition halfcycle-30deg, which decreases rapidly with aging and then remains unchanged. In conditional fullcycle-30deg, Q\text{n} slowly declines and then decreases rapidly.

![Figure 6](image1.png)

Figure 6 (a) The battery capacity (b) The SOC\text{r0} of negative electrode (c) Capacity normalized value with different experimental conditions, fullcycle-30deg, fullcycle-60deg, and halfcycle-30deg

An over charge experiment with 110% SOC was performed, and the experimental data is shown in Figure 7(a) and Figure 7(b). CC-CV fills the battery and then statically reduces the temperature to room temperature. Next, it uses a low magnification to overcharge. It can be seen that during the overcharging process, the voltage rapidly rushes from 4.5V to 5.2V, the voltage drops slightly.

![Figure 7](image2.png)

Figure 7 (a) Overcharge experiment (b) Temperature at overcharge (c) Result of overcharge

As shown in Figure 7 (c), overcharge increases the battery capacity and positive electrode. The \( q_{\text{add}} \) stretches the positive working area, so the battery is full of longer time.

Just like overcharge, the battery is kept in place until the battery temperature drops to room temperature before the discharge test with 110% DOD. As shown in Figure 8 (a), the discharge voltage will be reduced to -0.8V. Positive and negative electrode materials do not lose. SEI decomposition leads to an increase in battery capacity. The increase of internal resistance in the charging process reduces the charging efficiency.
6. Conclusion

The loss of lithium inventory attenuates the battery capacity and the positive and negative electrode capacities are also attenuated. Loss of the non-lithium-deposited negative active material leads to a decrease in the capacity of the negative electrode, but the battery capacity does not change. Loss of the lithium-incorporated negative active material causes simultaneous decay of the negative electrode and battery capacity. The overcharge behavior causes the positive electrode to continue to take out excess lithium ions, and part of the lithium ions participate in the excessive growth of the SEI, and finally this behavior leads to an increase in battery capacity. Over discharge causes fluid corrosion, SEI decomposition. Finally the behavior leads to a decrease in battery capacity.

7. Acknowledge

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Reference

[8] Zhang Q; White, R.E. Calendar life study of Li-ion pouch cells, 179 (2) 2008, 785-92