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Influence of temperature on aging of lithium-ion batteries

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ABSTRACT

The influence of temperature on the lifetime of lithium batteries (LIBs) is significant, so it is important to fully understand the role of temperature in the aging of LIBs to extend the battery life. Although there are many reviews on the factors influencing the aging of LIBs, there is no systematic analysis of the effect of temperature on the aging mechanism of LIBs. This paper summarized the impact of temperature on aging mechanism. For anode, high temperature would accelerate the growth of SEI; while low temperature mainly results in lithium plating. For cathode, high temperature leaded to electrolyte oxidation and metal oxide decomposition; and low temperature leads to passive layer growth and phase change on the cathode surface, resulting in an increase in impedance. It should be note that, little research was conducted on low temperature. In addition, for electrolyte, the temperature mainly affects its impedance and its stability, and therefore, leading to the capacity degradation.

Keywords: Lithium-ion battery, temperature, aging mechanism, temperature related properties

1. INTRODUCTION

Lithium batteries are expected to be the main energy storage method due to their high energy density, power density, and low self-discharge rate. However, the performance degradation in hot or cold environments also limits its development, in which the temperature shows significant impact [1].

Therefore, the understanding about the aging of battery is necessary, including the mechanism, predicting model. For example, Kabir et al. [2] reviewed the classification of battery aging mechanisms and summarized the impact of key factors on battery ageing. Santhanagopalan et al. [3] reviewed models for predicting the cycling performance of batteries. Barré et al. [4] summarized the different aging mechanisms and the techniques, models, and algorithms for battery aging assessment.

Although the above reviews described battery aging from different aspects, the impact of internal temperature on battery ageing is not clear. To bridge the knowledge gap, this paper investigated the impact of temperature on the ageing of anode, cathode, and electrolyte. The results found in this paper could help better understanding on battery aging.

2. AGING MECHANISM

Battery aging could result in capacity degradation and power degradation, which can be affected by charge/discharge rate, temperature, SOC, overcharge and over discharge, high depth of discharge (DOD), and moisture. Among them, the temperature is a key factor. The impact of temperature (both high and low temperature) on anode, cathode, and electrolyte is reviewed in detail.

2.1 The effect of temperature on anode aging

Anode materials include graphite (C), $Li_4Ti_5O_{12}$ (LTO) and some alloy anode materials such as Si. Its aging is largely depended on the operating temperature, which limits the application of LIBs in sub-zero and high-temperature environments. The aging mechanism of the anode material with temperature is shown in Fig. 1.

2.1.1 <u>High temperature</u>

High temperature directly leaded to the electrolyte decomposition and the formation of graphite intercalation compound (GIC) [6].

The electrolyte decomposition resulted in the formation of solid electrolyte interface (SEI) film between the anode and the electrolyte, which continuously occurred throughout the life of cell. At high temperature, the growth of SEI film would be accelerated [7]. With the increase of thickness, the internal resistance of battery increased, the lithium ions cannot be permeated through SEI, leading to the decrease of recoverable lithium ions, resulting in the capacity fade and power degradation [8]. Besides, it could change the chemical composition of SEI film,

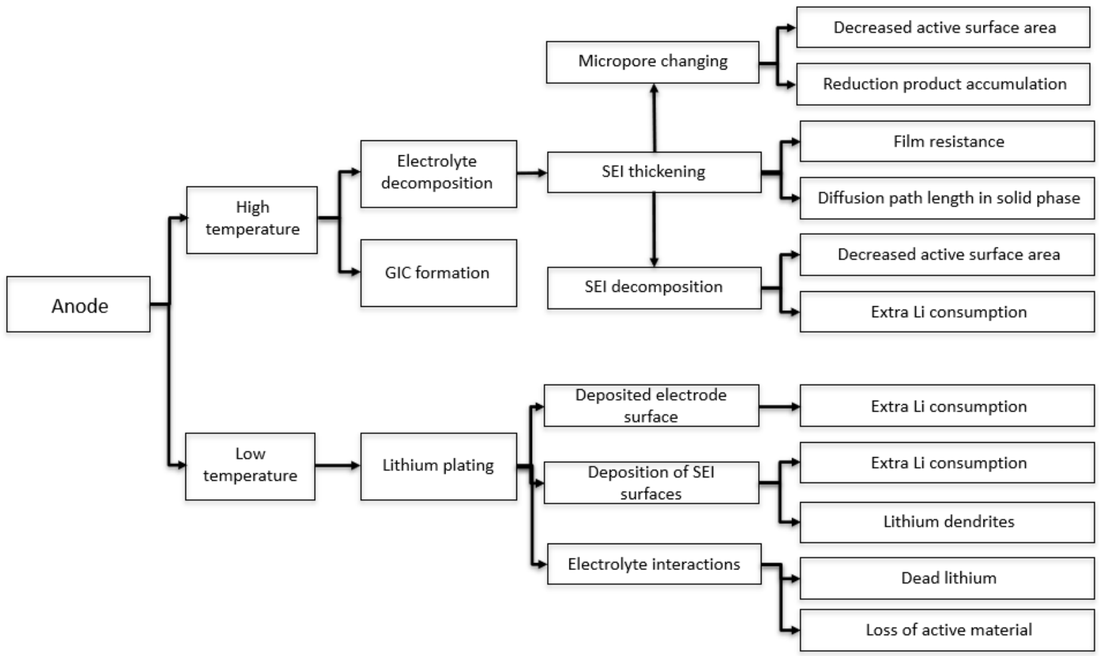

Fig. 1 Temperature dependent degradation process of anode

leading to cell capacity fade and impedance increase. In addition, SEI films are thermally unstable and high temperatures can lead to their decomposition. The decomposition products occupy the electrode surface space, the available surface area of the active material is reduced, and the formation of new SEI layers consumes additional Li [9]. High temperatures also cause changes in the pore structure, creating many defective spots in the SEI film. This produces an accumulation of species at these defective spots, which increases the amount of reduction products constituting the SEI film and consumes additional Li [10].

Another impact of high temperature would lead to the GIC formation. which in turn leaded to irreversible capacity fade. Leng et al. [11] investigated the effect of temperature on the aging rate of LCO electrode, graphite electrode, and electrolyte. Result showed high temperature leaded to a rapid increase in SEI and GIC, which in turn accelerated the aging of the cell.

2.1.2 Low temperature

At low temperatures, lithium plating dominated in terms of capacity decay, in which the side reactions were suppressed [12]. When the anode potential exceeded the threshold of 0 V (relative to Li/Li^+), lithium would be precipitated on the surface of anode [13]. It may occur in several ways: Firstly, lithium was deposited on the electrode surface, leading to the depletion of active lithium. In addition, local volume expansion occurs due to the active material being covered by the lithium plating layer, leading to increased mechanical stress [14]. During cycling, the increased mechanical stress can lead to cracking of the active material, which results in the loss of active material; Secondly, lithium plating can react directly with the electrolyte, which leads to partial loss of lithium [15]; Finally, lithium plating can also damage the SEI film, causing it to regrow, consume additional lithium ions, and increase its thickness [16]. In addition, lithium plating can also deposit on the surface of the SEI film and react with the electrolyte to form a second SEI film on the surface of the deposited lithium. When the SEI film covers the lithium plating completely, "dead lithium" is formed [13, 16].

Table 1 illustrates the aging mechanisms at different temperatures. When the temperature is higher than 25°C, aging is proportional to temperature. When it is lower than 25°C, aging is inversely proportional to temperature.

2.2 The effect of temperature on cathode aging

Fig. 2 shows the effect of temperature on cathode aging. Normally, high temperature would lead to metal oxide decomposition and electrolyte oxidation. And low temperature could increase impedance and loss of active material.

2.2.1 High temperature

At high temperature, two processes would occur (electrolyte oxidation and metal oxide dissolution),

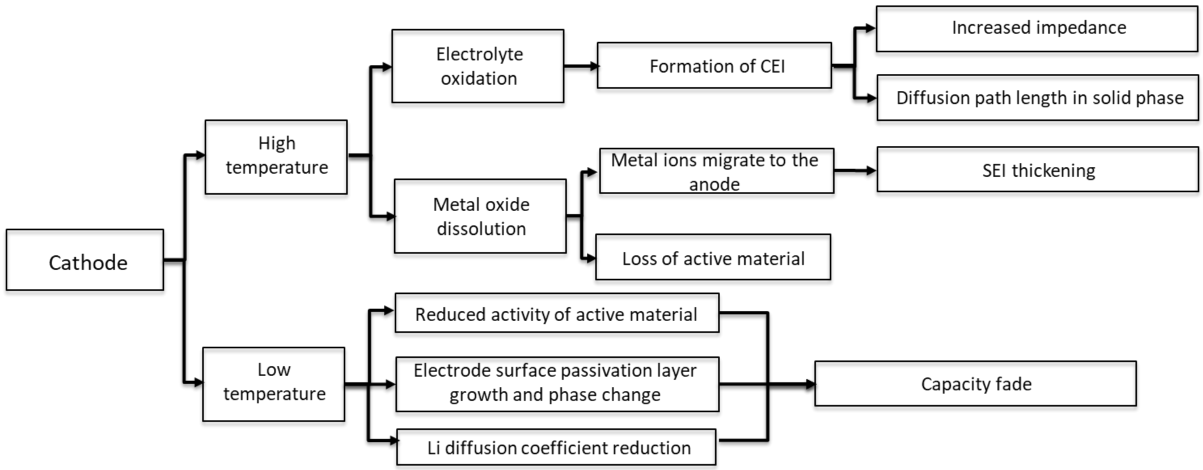

Fig. 2 Temperature dependent degradation process of cathode

which leaded to the aging of the battery. For the first one, it meant electrolyte oxidation, in which the formation of cathode electrolyte interface (CEI) happened [27]. Edstrom [28] investigated the effect of different cathode chemistries ($LiMn_2O_4$, $LiCoO_2$/$LiNi_{0.8}Co_{0.2}O_2$ and carbon cladding $LiFePO_4$) on the temperature of the CEI. Results showed that, the composition of the CEI layer is depended on the chemical composition of the cathode material. However, in all cases, the thickness of the CEI layer on the cathode increased with the increase of temperature. Leng [11] investigated the effect of temperature on the degradation of LCO ($LiCoO_2$) cathodes. They found that an increase of temperature leaded to a thickening of the CEI film on the LCO electrode and a change in the structure of the electrode.

***Table 1** Aging mechanism of anodes at different temperatures*

Thermal effect	Reaction Temperature	Aging Mechanisms	Author
High temperature	45°C	SEI film growth	Liu [17]
	60°C 、85°C、120°C	Chemical composition change	Bodine [18]
	55°C	SEI decomposition	Zane [19]
	25-55°C	GICs formation	Leng [11]
Low temperature	-22°C	Lithium plating	Petzl [20]
	-10°C	Lithium plating	Wu [21]

For the second process, it meant metal oxide dissolution, which leaded to loss of active material. On the one hand, the dissolution of manganese leads to the loss of active material [25]; On the other hand, the manganese ions dissolved in the electrolyte migrate to the anode and deposit on the anode surface or form a new surface film with the SEI film [26]. In addition, the dissolution of manganese increases the impedance of the anode [25].

Both mechanisms limit the reaction rate and charge transfer rate of lithium ion embedding/de-embedding. Moreover, the effect of these mechanisms on the degradation of LCO electrodes increases with increasing temperature [32].

2.2.2 Low temperature

Researchers have demonstrated that the performance of LIBs at low temperatures is more negatively affected by graphite anodes than cathodes. Currently, there are very limited studies on it. The capacity fade of cathodes at low temperatures is mainly caused by: (1) the decrease of the activation of the active material in the cathode. It in turn leaded to a decrease in capacity, in addition to a more difficult intercalation of Li^+, resulting in a greater loss of discharge capacity. (2) The increase of electrochemical impedance. It decreased the kinetics of the electrochemical reaction and increased the resistance to charge transfer. Wu et al. [33] applied a nondestructive aging assay to LIBs and found that low temperatures leaded to passive layer growth and phase changes on the cathode surface and increase the charge transfer resistance at the electrode-electrolyte interface. More work can be found in Table 2.

Table 2 *Mechanism of cathode aging at different temperatures.*

Thermal effect	Cathode Material	Aging Mechanisms	Remark	Author
High temperature	$LiCoO_2$ 25-45°C	The CEI film generated	CEI film formation affects the performance of lithium cobaltate cathodes. The CEI film becomes thicker at high temperatures, leading to a decrease in the chemical diffusion coefficient and an increase in lithium-ion polarization.	Guan [29]
	$LiNiCoO_2$ and $LiMn_2O_4$ 40°C	Manganese based battery active material dissolution; Nickel-cobalt battery impedance increase	High temperature accelerates the increase of impedance of Li-Ni-Co batteries; high temperature promotes the dissolution of manganese into the electrolyte.	Wohlfahrt-Mehrens [30]
Low Temperature	$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ -15°C-5°C	Resistance increases, Active LI loss	The performance loss of the cell at low temperatures is caused by the slow kinetics of the lithiation and desulfurization reactions.	Zhou [31]

2.3 The electrolyte

The impact of temperature on electrolyte could mainly conclude with electrolyte decomposition and increased impedance. For high temperature, it will decompose and oxidize. For example, Yang [35] and R. Genieser[36] demonstrated that LiPF6 dissociates at high temperatures to form LiF and PF5. Anderson et al. [7]showed that the LiF content on the graphite surface increased with increasing temperature, which was mainly due to the decomposition of electrolyte salts. Electrolyte salts decompose with increasing temperature. the formation of LiF leads to complete degradation of graphite electrodes in LiBF4-based cells at 60°C [8]. For low Temperature, it meant that the migration rate of Li+ in the positive and negative electrodes decreased, the impedance of the electrolyte/electrode interface increased and the viscosity of the electrolyte increased, and the Li^+ conductivity decreased, which leaded to a decrease in relative capacity. For example, Zhang et al. [37] showed that the decrease in relative capacity at low temperatures is mainly due to the increase in charge transfer resistance R_{ct}.

3. CONCLUSION

For LIBs, capacity degradation occurred if the temperature was outside of the optimal temperature. This paper summarized the impact of temperature on aging mechanism. For anode, high temperature would accelerate the growth of SEI; while low temperature mainly results in lithium plating. For cathode, high temperature leaded to electrolyte oxidation and metal oxide decomposition; and low temperature leaded to loss of active substance and rise of impedance. It should be note that, little research was conducted on low temperature. In addition, for electrolyte, the temperature mainly affects its impedance and its stability, and therefore, leading to the capacity degradation.

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