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Characterization of large format lithium ion battery exposed to extremely high temperature

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HIGHLIGHTS

- Fading mechanisms for large Li-ion battery during a thermal runaway were studied.
- EV-ARC test was terminated before thermal runaway to study the fading mechanism.
- The separator melting point dictates the reusability of the battery after heating.
- Cycled after heating, the lost capacity of the battery may be recovered partially.
- Capacity loss was analyzed using ICA and discussed using a mechanistic model.

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ABSTRACT

This paper provides a study on the characterizations of large format lithium ion battery cells exposed to extreme high temperature but without thermal runaway. A unique test is set up: an extended volume-accelerating rate calorimetry (EV-ARC) test is terminated at a specific temperature before thermal runaway happens in the battery. The battery was cooled down after an EV-ARC test with early termination. The performances of the battery before and after the EV-ARC test are investigated in detail. The results show that (a) the melting point of the separator dictates the reusability of the 25 Ah NCM battery after a near-runaway event. The battery cannot be reused after being heated to 140 °C or higher because of the exponential rise in ohmic resistance; (b) a battery can lose up to 20% of its capacity after being heated to 120 °C just one time; (c) if a battery is cycled after a thermal event, its lost capacity may be recovered partially. Furthermore, the fading and recovery mechanisms are analyzed by incremental capacity analysis (ICA) and a prognostic/mechanistic model. Model analysis confirms that the capacity loss at extremely high temperature is caused by the increase of the resistance, the loss of lithium ion (LLI) at the anode and the loss of active material (LAM) at the cathode.

1. Introduction

Lithium ion batteries are the prevailing choices to power today's electric vehicles (EV), because of its high energy/power density and long cycle life compared with other choices. However, incidents such as battery fires after crashes have attracted much attention [1–3] and given rise to public concerns about the safety of the lithium ion batteries. Thermal runaway behavior is an important research topic which has been at the center of safety events.

Large format battery is of particular interest because of their increasing popularity in production of electric vehicles. Large format batteries have the advantages of reduced cell number and pack complexity [4], which lead to the improved reliability of a battery pack [5]. However, a large format battery is more vulnerable to thermal runaway because it contains more stored energy. Cooling is less effective because of its lower surface/volume ratio, which leads to higher non-uniformity of temperature distribution within the cell [5].

Batteries with $LiNi_xCo_yMn_zO_2$ (NCM) cathode are promising for EV applications. NCM cathode material demonstrates higher

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capacity, lower cost and less toxicity within the family of Li-ion batteries [6,7]. In thermal runaway tests, batteries with NCM cathode perform better than those with $LiCoO_2$ (LCO) and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) do, but worse than those with $LiMn_2O_4$ (LMO) and $LiFePO_4$ (LFP) [8]. Nevertheless, the NCM cathode shows better high temperature durability and higher specific capacity than LMO and higher energy density than LFP [8].

We have reported the thermal runaway features of large format prismatic lithium ion battery with NCM cathode using extended volume accelerating rate calorimetry (EV-ARC) in Ref. [9]. The thermal runaway process for the specific NCM large format battery has been divided into 6 stages based on the general knowledge from those reviews [10–14] of Li-ion battery safety. In Stage I, the capacity fades at high temperature (>50 °C). In Stage II, the solid electrolyte interface (SEI) decomposition starts and releases detectable heat if the reaction continues [15–21]. And it should be noted that the SEI decomposition will continue to a temperature as high as 250 °C (ends at Stage IV) [20,21]. Losing its protection layer, the lithium intercalated in anode starts to react with the electrolyte [15,17,20–22]. In Stage III, the separator melting causes a decrease in temperature rise rate as the temperature goes higher (120 °C–140 °C). In Stage IV (140 °C–240 °C), some cathode materials start to react with the electrolyte and release heat [5,23–25], while the NCM cathode seems to be strong enough not to react until the temperature reaches 240 °C or higher [26–31].

Besides thermal runaway, batteries may experience “near” thermal runaway conditions where they are exposed to extreme temperature beyond the limit set by a battery management system. To understand the safety features of the battery and to characterize the impact of the high temperature exposure on the battery performance, we investigate the status of the battery at different specific high temperature near thermal runaway point. We try to “freeze” the battery during a thermal runaway test like P. Roeder et al. did in Ref. [32] using an interrupted ARC test to see what the behavior of a large format battery is after being exposed to extreme high temperature before thermal runaway. It is indicated that high temperature capacity fading will happen as reported in Refs. [33–37]. Therefore, we can exploit previous mechanistic/prognostic methods to analyze and quantify the capacity degradation of a battery exposed to extremely high temperature.

Capacity degradation for lithium ion battery is mainly caused by the loss of cyclable lithium inventory (LLI) and the loss of active material (LAM) [38–44]. As shown in Refs. [42], the LLI at anode happens first, followed by the LAM at cathode as temperature rises. The LLI is mainly caused by the SEI decomposition and the anode reaction with electrolyte, while the LAM is mainly caused by the cathode decomposition. To analyze LLI and LAM, a parameterized prognostic and mechanistic model presented in Refs. [38,39,43–50] can be used, whose parameters are linked directly to certain capacity fading mechanisms. In such a prognostic and mechanistic model, the capacity loss can be quantified in simulation by selecting proper stoichiometric coefficient x and y in Li_xC_6 and $Li_yNi_aCo_bMn_cO_2$, respectively [39,43]. Moreover, incremental capacity analysis (ICA) has been used to analyze battery aging data and interpret the capacity fading mechanisms in many publications [51–59].

In this paper, we have investigated the characterization of large format lithium ion battery after suffering a short period of high temperature exposure. The battery was heated to an extremely high temperature using EV-ARC then cooled down before it runs into thermal runaway. The voltage drop and internal resistance rise during heating were quantified. The reusability of the 25 Ah NCM battery was evaluated by its discharge capacity. Scanning electron microscope (SEM) was employed to find the influence of the melting point of the separator on the reusability of the 25 Ah NCM battery. The capacity fading mechanisms were analyzed using ICA, and discussed using a prognostic/mechanistic model.

2. Experiment

2.1. An EV-ARC test with early termination

This work is a follow-up work of [9]. The battery was heated by an EV-ARC (Fig. 1), manufactured by Thermal Hazard Technology®. The functions of the EV-ARC are essentially the same as those pervasively used ARC. A common EV-ARC test also follows the heat-wait-seek method. The difference is that the calorimeter of the EV-ARC is much larger than that of the standard ARC. The selected EV-ARC can hold a large format battery with a capacity of 25 Ah investigated in this paper.

The 25 Ah battery employed for the EV-ARC test is a rechargeable $LiNi_xCo_yMn_zO_2$ polymer battery manufactured by AE Energy Co. Ltd. It has $LiNi_xCo_yMn_zO_2$ as its cathode and graphite as its anode. The separator is polyethylene (PE) based with ceramic coating. We have reported differential scanning calorimetry test result on the separator in our previous research in Ref. [9]. The detailed material composition of the battery is shown in Fig. 2.

Fig. 3 shows the locations of the thermal couples as reported in Ref. [9]. Table 1 summarizes the setup of all the EV-ARC tests. Battery No. 1 and No. 2 were installed with a thermal-couple TC_1 inserted inside the battery, as in Ref. [9]. Note that our previous research has established that for the EV-ARC test following the heat-wait-seek approach, the maximum temperature difference within the battery does not exceed 1 °C for 97% of the time during a thermal runaway test [9]. Therefore, no thermal couple is used for internal temperature measurement in most of our tests. Temperature data measured by thermal couple No. 2 (TC_2), which is representative of the internal temperature of the battery under the uniform temperature distribution condition, is used for thermal analysis in the following sections.

A unique test, which is called EV-ARC test with early termination, is set up to study the fading mechanisms for lithium ion battery exposed to extreme high temperature and “near” runaway conditions. In the EV-ARC test with early termination, the heating process was stopped once the temperature reaches a pre-defined value. The battery was pulled out of the chamber and a fan was

Fig. 1. Picture of the EV-ARC used for this research.