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State of charge influence on thermal reactions and abuse tests in commercial lithium-ion cells

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HIGHLIGHTS

- Accelerating Rate Calorimetry tests using $LiFePO_4$ and Li_x $(Ni_{0.80}Co_{0.1}5Al_{0.05})O_2$ cathodes.
- The cell were tested at different state of charge: 0%, 50% and 100%.
- State of charge correlation with self-heating and maximum cell temperature.

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ABSTRACT

Cycling stability and thermal runaway characteristics of four commercially available cylindrical cells based on Li_xFePO_4 (LFP) and Li_x $(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$ (NCA) cathode materials were investigated. The cells with different formats were cycled to three states of charge (SOC): 0, 50 and 100%, before adiabatic thermal analysis using an accelerating rate calorimeter (ARC). The charged cells experienced thermal runaway; the first rise in temperature due to the exothermic reaction and maximum cell temperature are discussed in detail for the different cells. Abuse testing (crush and nail penetration tests) was also performed at 100% SOC; the videos of the tests are available online as supplementary data. The LFP cathode exhibited superior cycling and thermal stability compared to NCA.

1. Introduction

Rechargeable lithium-ion batteries are widely used in portable electronic devices, electrical vehicles (EV) and stationary energy storage systems. The demand for lithium-ion batteries exceeded 25 GW h in 2016 due to increased EV production in China [1]. The safety of commercial Li-ion cells used in electrical vehicles and stationary energy storage is a key parameter. Exothermic reactions due to short circuit by dendrites, thermal abuse conditions (exposure to high temperatures) or mechanical stress [2] lead to thermal runaway where high temperatures are reached and toxic gases are released, as reported by Doughty et al. [3]. Feng et al. reported on accidents involving lithium-ion batteries in the last ten years [1]. In order to overcome the safety problems with Li-ion batteries, several devices such as positive temperature coefficient (PTC), safety vent and current interrupt device (CID) were utilized [4]. In addition, some flame retardants containing phosphorus additive (eg. phosphate and phosphazene) in liquid electrolytes were recently tested [5]. Different organizations such as the International Organization for Standardization (ISO) and Society of Automotive Engineers (SAE) have promoted battery standardization to enhance battery use in EVs and minimize the probability of accidents [6–10]. These standards describe several *ex-situ* destruction tests such as nail penetration and crush tests. *In-situ* diagnostic tests are very useful to understand the failure mechanism of Li-ion cells using X-ray micro computed tomography (X-ray micro-CT) were reported by Zhu et al. [2].

Co-based cathode materials, such as $LiCoO_2$ (LCO), $LiMnO_2$ (LMO), Li_x $[Ni_{0.80}Co_{0.15}Al_{0.05}]O_2$ (NCA) and Li $[Ni_xCo_yMn_z]O_2$ (NCM) with high energy density, are commonly used in electronic products and electric vehicles, however these materials are susceptible to thermal runaway. Numerous reports indicated that lithium iron phosphate-

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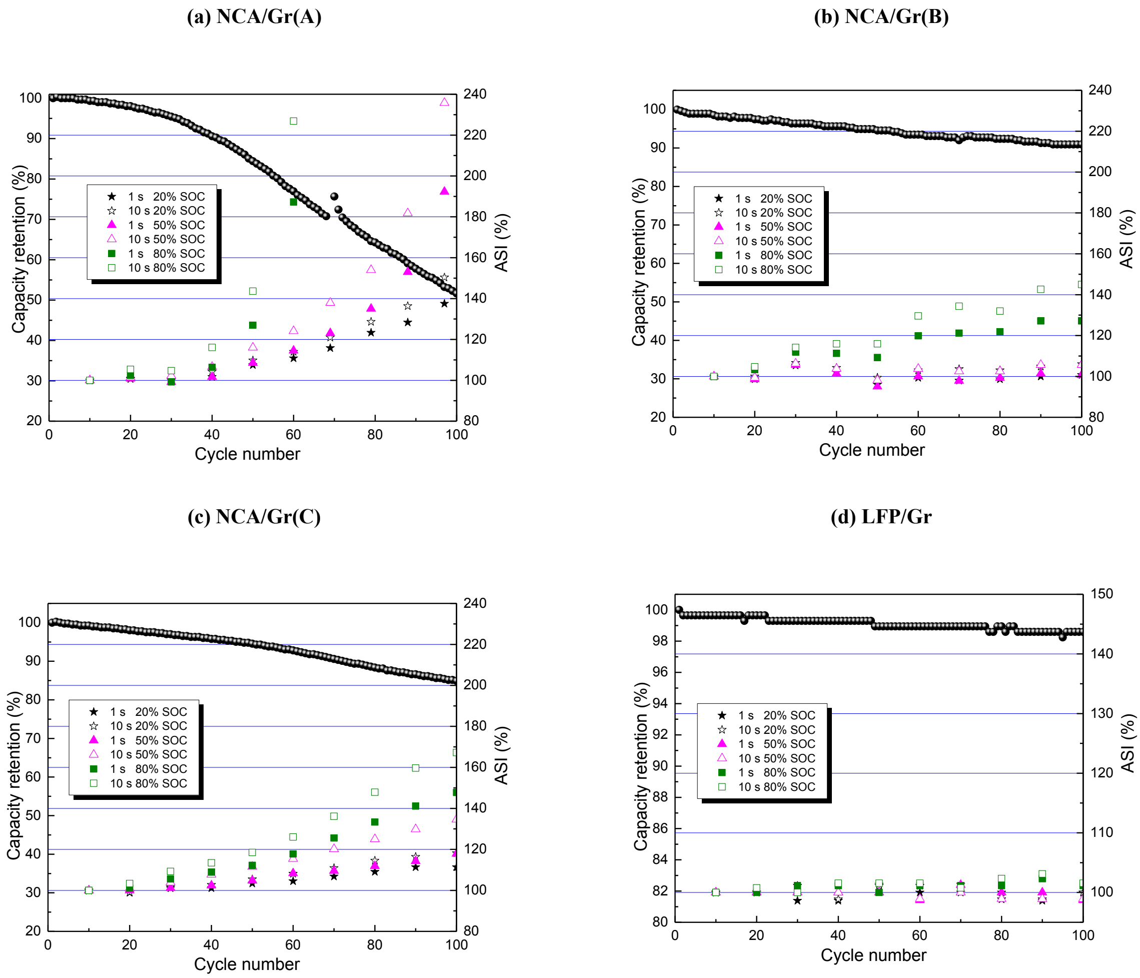

Fig. 1. Capacity and ASI retention of NCA/Gr and LFP/Gr batteries at 1C rate.

based batteries ($LiFePO_4$ batteries) are more stable and safer than other batteries due to the stable olivine structure of LFP [11–13]. Lei et al. reported an extensive experimental analysis of thermal runaway in 18650 cells comparing LFP, LMO and NCM [14]. The authors reported poor temperature tolerance for NCM at high temperatures and gas production at 90 °C for LMO, while LFP exhibited good thermal stability. Jhu et al. [15] reported that LCO is even more hazardous than NCM due to strong exothermic reactions. Börner et al. [16] investigated the aging effect on a commercial 18650 cell containing $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode and graphite anode in ARC under quasi adiabatic conditions: the authors observed the influence of anode degradation on capacity fading and the presence of mossy lithium metal plating on the graphite anode when the battery is cycled at low temperature with 1C rate, which is in agreement with the study by Friesen et al. [16].

In this paper, we report a new detailed *ex-situ* investigation of the thermal behavior and cycling stability of four different commercial cylindrical cells with different cathode chemistries: $LiFePO_4$ and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$. The thermal behavior of the cells is investigated under adiabatic condition with an accelerating rate calorimeter (ARC) at three states of charge. The influence of thermal stability under adiabatic conditions for LFP and NCA at different SOCs was compared to the state-of-the-art technology that was reported earlier [17]. Abuse testing was also performed at 100% SOC in accordance to the USABC standard procedure. These tests are conducted to simulate the deformation or perforation of a battery pack during collision of a vehicle. The videos from these tests are available online. Finally, the cycling stability of these cells at room temperature is shown with the ASI.

2. Experimental

2.1. Thermal characterizations

An accelerating rate calorimeter (ARC, Thermal Hazard Technology) was operated in a heat-wait-search (HWS) mode until an exothermic reaction was detected, and adiabatic conditions were maintained as long as the exothermic reactions were completed. The model of the ARC was the standard ARC calorimeter with 3 zones heating ARC™ design principle and operation. The maximum heating temperature was 300 °C, the temperature sensitivity was 0.01 °C and the maximum exotherm rate was 20 °C/min. The diameter of the calorimeter was 10 cm and the depth was 10 cm. In a typical ARC test, the cylindrical cell in the adiabatic calorimeter is heated to 50 °C, followed by a 15 min rest step to stabilize the cell temperature. During the rest step the calorimeter records the self-heating process with a sensitivity threshold of 0.02 °C/min. If no exothermic reaction is detected, the calorimeter is heated with a 5 °C step and the sequence is repeated. If an exothermic reaction is detected that is greater than the sensitivity threshold, the calorimeter switches to the adiabatic mode to follow the cell surface temperature changes.

Nail penetration and crush tests were performed at 100% SOC with all the cylindrical cells [10] using a laboratory-built hydraulic press setup. The nail-penetration test utilized a 3-mm diameter stainless steel rod and a penetration rate estimated to be 0.5 cm/s. The plate used for the crush test is composed of a semicircular bar. The cell voltage and cell surface temperature were monitored by a data logger. A type K thermocouple on the cell surface measured the cell temperature at the