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THE THERMAL STABILITIES OF LI-ION BATTERIES WITH NICKEL-RICH CATHODE: EFFECTS OF CATHODE MORPHOLOGY AND STATE OF HEALTH

Hungjen Hsu[1], Xiang Liu[2], Dongsheng Ren[1], Yu Wang[1], Xuning Feng[1,3], Languang Lu[1], Xiangming He[3], Minggao Ouyang[1*]

1 State Key Laboratory of Automotive Safety and Energy, Tsinghua University, Beijing 100084, China

2 Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA

3 Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China

ABSTRACT

The safety issues of lithium-ion batteries, i.e. thermal runaway, have attracted abroad attention and become more critical with the increase of battery energy density. In this study, the thermal runaway behaviors of high-energy-density lithium-ion batteries with nickel-rich cathode are investigated considering the effects of cathode morphology and state of health. The results show that the safety behaviors of batteries with single crystal cathode is almost same as that with the poly crystal cathode. However, after cycling, the battery with single crystal showed worsen thermal stability after cycling at 45°C, as the onset temperature of thermal runaway decrease, while the battery with poly crystal cathode exhibited opposite changes.

Keywords: lithium-ion battery, nickel cathode, battery safety, thermal runaway

NONMENCLATURE

Abbreviations	
ARC	Accelerating Rate Calorimetry
DSC	Differential Scanning Calorimetry
FIB	Focus ion beam
PC	Poly crystal
SC	Single crystal
SOH	State of health

1. INTRODUCTION

Electric vehicle is a promising solution to slow down the growth trend of CO2 and relief the pressure of global warming. Lithium-ion batteries are the most widely used power sources for electric vehicles, considering their high energy density and long cycle life. However, lithium ion batteries still suffer from safety problems, which will lead to safety accidents of electric vehicles and hinder the application of electric vehicles.

In most cases of the electric vehicle accidents, the battery exploded, which is called thermal runaway (TR), due to several reasons. Feng et al. categorized the causes of thermal runaway into three main kinds of abuse, i.e. electric abuse, thermal abuse and mechanical abuse. During the thermal runaway process, three important temperatures, (T1, T2 and T3) were proposed to evaluate the safety behaviors of lithium-ion batteries. Higher T1 and T2 indicate that batteries has better thermal stability, and a lower T3 reveals less energy release and a less possibility of thermal runaway propagation in the battery module [1].

To reduce the cost and increase battery energy density, nickel-rich cathode (such as NCM532, NCM622, and NCM811) is applied to lithium-ion batteries. However, with the increasing amount of Ni, the cathode material will become more unstable with lower oxygen release temperature [2] [3]. Several methods have been proposed to suppress or postpone the oxygen release [4-6]. Single crystal cathode material is one of the promised method due to lower surface area[7].

In this research, the thermal runaway behaviors of lithium-ion batteries with a nickel-rich cathode is $Ni_{0.83}Co_{0.11}Mn_{0.06}$ are studied, and the effects of different morphology (i.e. single crystal and poly crystal) and different state of health (SOH) on battery safety behaviors are compared.

2. EXPERIMENTS

2.1 Sample preparation

The capacity of the batteries is a lab scale pouch cell with the capacity of 600mAh. The cathode is $Ni_{0.83}Co_{0.11}Mn_{0.06}$ with different morphology. The anode material is all graphite

The aging batteries are cycled in 45°C with 1C/1C charge-discharge. The end-up conditions are decided by state-of-health 80% with Neware Battery Test System.

2.2 Morphology observation

The batteries with different operating conditions are charged to 100 SOC and disassembled in glove box to prevent from oxygen and water. Then the surfaces are observed by scanning electron microscope (SEM, ZEISS Merlin) and the cross sections of the cathode materials are cut by focused ion beam (FIB, ZEISS Crossbeam 550). The materials are collected from the electrode and stored in the glove box.

2.3 Material stability

The thermal stability of the electrode materials are tested by the differential scanning calorimetry (DSC, NETZSCH DSC214 polyma). The sample was prepared in the glove box with specific proportion same as the materials weight percentage in the full cell then put in the aluminum pan. DSC provides the results of heat flow detection with different combination of the materials and the heating profile is 10°C/min to 600°C. The gas analysis is carried out by simultaneous thermal analysis-mass spectrometer (STA-MS, NETZSCH STA449F5 and QMS403) with the same test condition as DSC.

2.4 Battery thermal runaway test

The thermal runaway test is operated in the Accelerating Rate Calorimetry (ARC) manufactured by Thermal Hazard Technology (THT). The schematic diagram of thermal runaway is shown in Fig 1. There are three important parameters of the thermal runaway including onset temperature of self-heating temperature, onset temperature of thermal runaway temperature and the maximum temperature, which are simplified as T_1, T_2 and T_3, respectively. The detailed definition of T_1 and T_2 are the heating rate reach 0.02 °C/sec and 1 °C/min, respectively.

The principle of the ARC is followed by heat-wait-seek method. After the battery is heat over self-heating temperature, T_1, the chamber stops heating and ensures the chamber temperature is same as the battery surface. Therefore, there is no heat exchange between the battery and the chamber after self-heating happen.

3. RESULT AND DISCUSSION

3.1 Materials in Microscope

Fig 2 a, b, f, and g are the SEM images of the fresh single crystal cathode (f-SCC), fresh poly crystal cathode(f-PCC), aging single crystal cathode (a-SCC) and aging poly crystal cathode (a-PCC), respectively. In Fig 2a and 2b, after cycling to specific state-of-health, though the SCC will crack and show the layer structure, it still remains the whole particle. Fig 2f and 2g compare the f-PCC and the a-PCC, the a-PCC can barely see the initial structure after several cycles. Fig 2c and 2h are the cross-sections of the a-SCC and a-PCC observed by FIB. According to Fig 2c, the cracks are found from both inside and outside the crystal. In Fig 2f, the crack of a-PCC is from the inside to the outside. To study the attenuation mechanism of the whole battery, we also find the discrepancy between fresh and aging anode. Fig 2d and 2e are the anode from f-SCC and f-PCC, and are more clear for the particle on the surface compare to Fig 2i and 2j, which are the cycled anode from a-SCC and a-PCC. The aging anode is covered by thick deposit layer and can be observed the porosity reduction due to better solid electrolyte interface formation[8].

3.2 Thermal behaviors of the cells

Table 1 is the result of thermal runaway characteristic temperature including T_1, T_2 and T_3. There is no obvious difference of the thermal runaway behaviors between single crystal battery and poly crystal battery. This might result from the only difference is the morphology instead of the composition of the cathode.

Both single crystal and poly crystal battery show the higher T_1 after high temperature cycling. It results from cycling under high temperature will help formatting relatively stable SEI and the T_1 is usually related to the decomposition of SEI. The different trends between T_2 and T_3 among the SC and PC batteries with fresh and aging operating condition indicate there are various thermal runaway mechanism.

	T_1	T_2	T_3
SC_fresh	85.44	204	529.7
SC_aging	104.83	192	471
PC_fresh	90.58	196.8	506.6
PC_aging	99.81	202	517.3

Table 1 The ARC results of the four batteries in this research

Fig 3 demonstrates the temperature heating rate during thermal runaway process. Though the fresh SC has lower T_1, the heating rate becomes lower than the aging one after 145°C and leads to lower T_2. There is almost no difference between the fresh PC and aging PC.

3.3 Thermal stability of the materials

Fig 4a compares different cathode with electrolyte tested by DSC. SC+ele appears early peak in low temperature range from 50 to 150°C. In the range of 180 to 200°C also shows a reaction peak. This phenomenon can describe the T_1 difference between fresh SC and PC. Fig 4b is the O_2 signal from MS. The results show that different from the other three, the oxygen signal of a-PCC release more O_2 after the main peak. The reason is result from the severe collapse of the poly crystal cathode shown in Fig 2g which the surface area increases dramatically.

4. CONCLUSION

The SEM, FIB, DSC, STA-MS and ARC analysis of the nickel-rich cathode full batteries with different crystal morphology are carried out in this paper. There is slightly difference between the fresh single crystal and poly crystal batteries is due to the nickel-rich content leads to unstable materials. After cycling, the single crystal will show some cracks on the surface and also inside the inner part. However, severe collapse will happen to the poly crystal cathode. And the battery safety evaluated by ARC shows that after high temperature cycling, the stable SEI will postpone the thermal runaway temperature effectively.

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FIGURE CAPTION

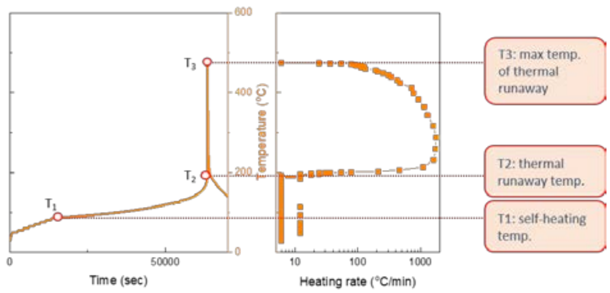

Fig 1 Introduction of thermal runaway and the important parameters T_1, T_2 and T_3

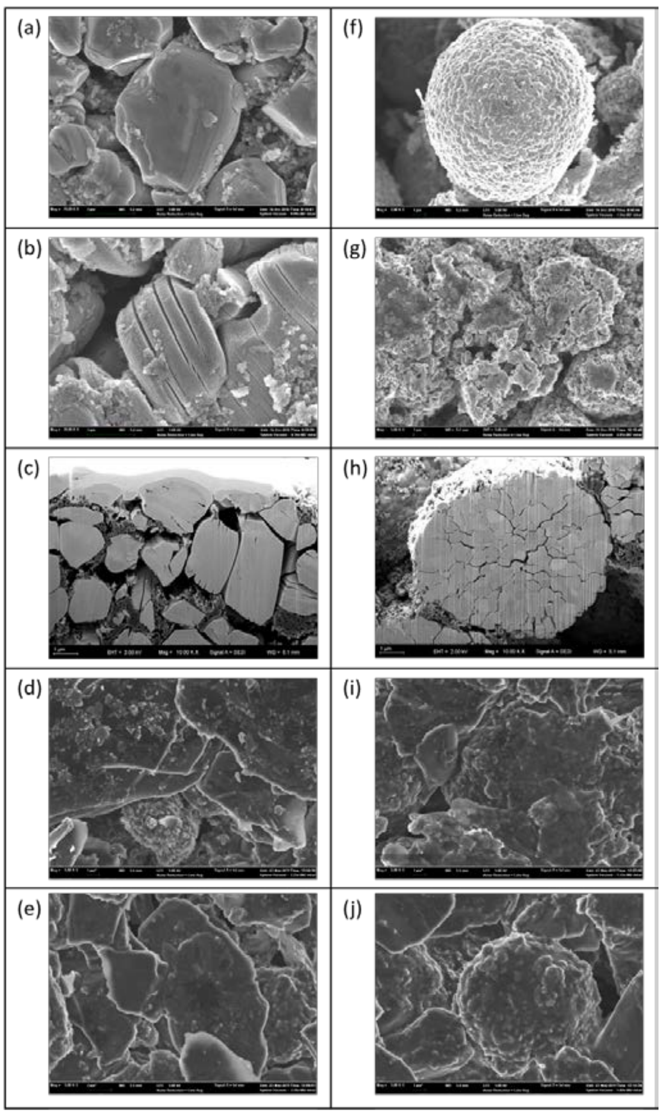

Fig 2 SEM images of (a) fresh single crystal cathode, (b) aging single crystal cathode, (c) cross-section of aging crystal cathode, (d) fresh anode of single crystal anode, (e) fresh anode of poly crystal anode, (f) fresh poly crystal cathode, (b) aging poly crystal cathode, (c) cross-section of aging poly cathode, (d) aging anode of single crystal anode, (e) aging anode of poly crystal anode,

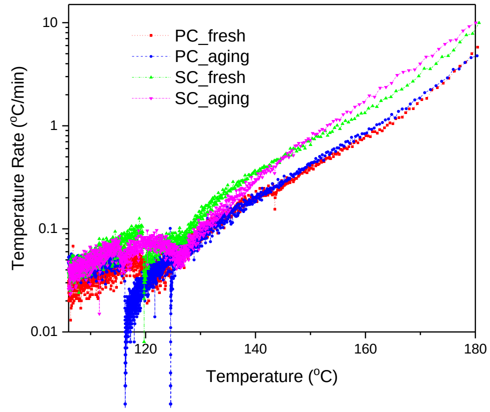

Fig 3 The temperature heating rate of the batteries in this study

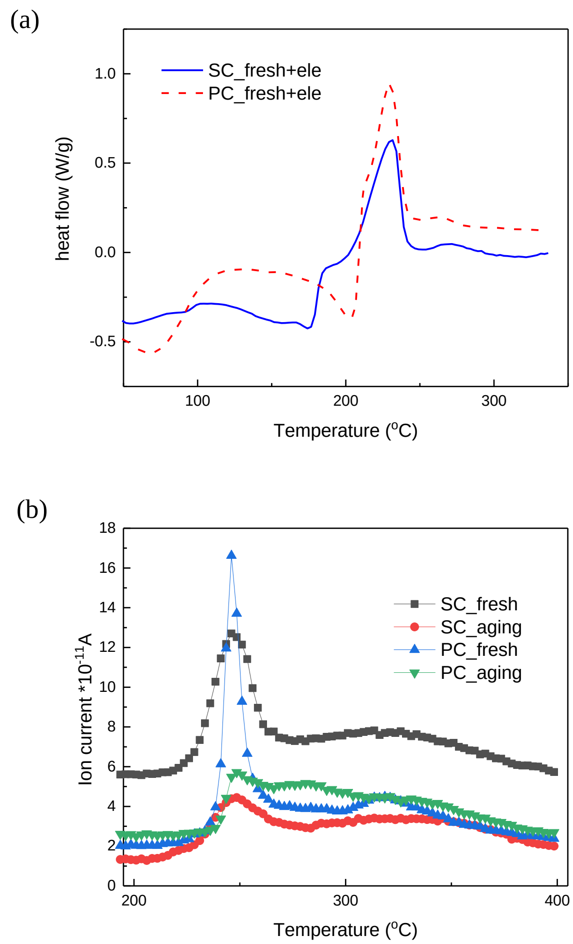

Fig 4 (a) The DSC result of the different cathode with electrolyte adding (b) the O_2 ion current from MS detection