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A STUDY ON THE BEHAVIORS OF INTERNAL SHORT CIRCUIT IN LITHIUM-ION BATTERIES

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ABSTRACT

Internal short circuit (ISC) plays an important role in lithium-ion battery safety accidents. However, the mechanism of how ISC triggers thermal runaway is still unclear yet. We implant the shape memory alloy device into jelly-roll to trigger ISC and analyze the thermal and electrical behaviors under different ISC types and SOC variance conditions. The ISC resistance is identified by using the no-salt battery based on the electrochemical impedance spectroscopy tests. The proposed resistance identification method benefits further ISC mechanism and modelling research.

Keywords: Lithium-ion battery, internal short circuit, safety, energy storage

NONMENCLATURE

Abbreviations

ISC	Internal Short Circuit
TR	Thermal Runaway
EIS	Electrochemical Impedance Spectroscopy
EEC	Electrochemical Equivalent Circuit
WDE	Warburg Diffusion Element

1. INTRODUCTION

Recently, the safety accidents of lithium-ion batteries fire and explosion occurred frequently, with the large-scale application of lithium-ion batteries in electronics, electric vehicle and energy storage. The internal short circuit is the potential 'cancer' of battery safety[1]. The series accidents of Samsung Galaxy Note7 were finally confirmed that the high welding burrs on the positive electrode penetrated the insulation tape and separator inducing ISC, then the heat generation from ISC triggered the chain reactions of thermal runaway (TR)[2].

Several methods are proposed to reveal the mechanism of ISC, including 1) using mechanical load[3,4]; 2) using electrical abuse[5]; 3) introducing devices controlled by temperature, such as phase change

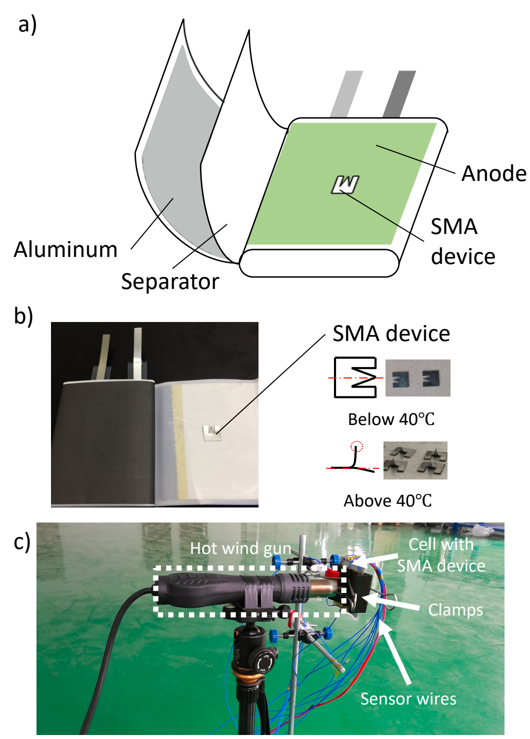

Fig 1 ISC triggering tests
a) Schematic diagram of ISC triggering method (Al-An type ISC as the example); b) Structure of SMA device;
c) Experimental bench.

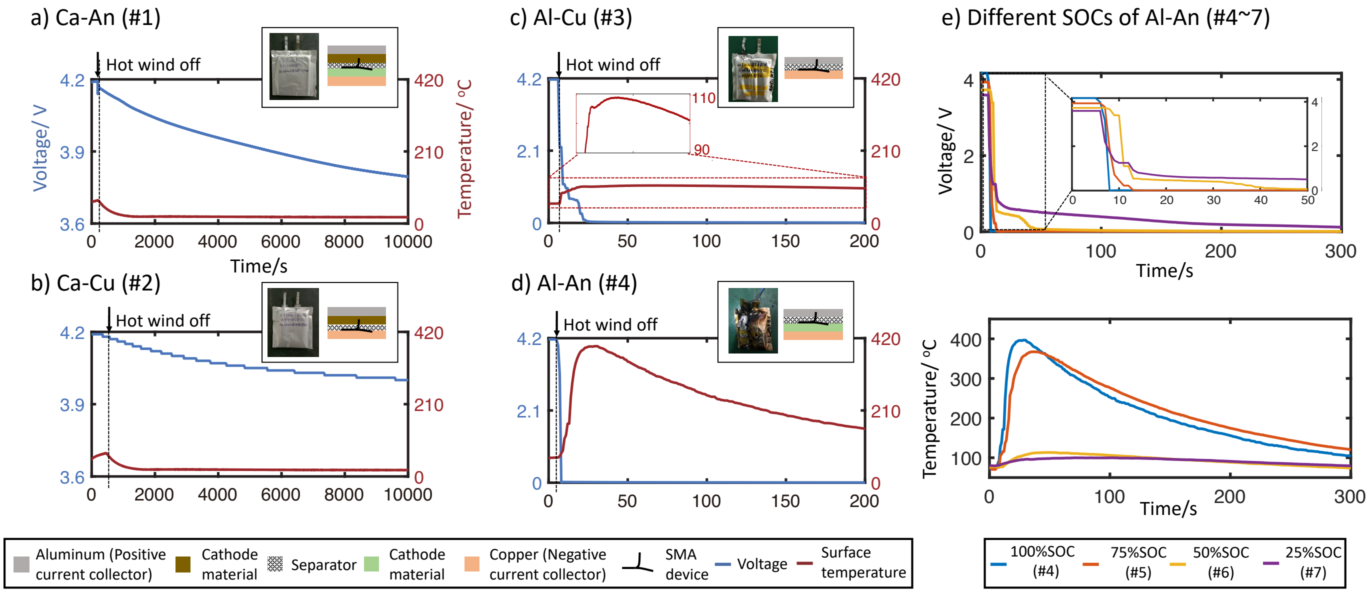

Fig 2 Voltage and temperature results of ISC tirggering tests
a) #1 Ca-An type ISC at 100% SOC; b) #2 Ca-Cu type ISC at 100% SOC; c) #3 Al-Cu type ISC at 100% SOC;
d) #4 Al-An type ISC at 100% SOC; e) Comprasion results of #4~#7 at 100%, 75%, 50%, and 25% SOCs of Al-An type ISC.

materials[6], low melting point alloy[7], shape memory alloy (SMA)[8]; 4) triggering ISC by metal contaminants during cycling[9].

In this work, we used the SMA ISC triggering method to study the thermal and electrical features of ISC under SOC variance and different ISC type conditions. Moreover, electrochemical impedance spectroscopy (EIS) of no-salt batteries was used to analyze the resistance of ISC based on the electrochemical equivalent circuit (EEC).

2. EXPERIMENTAL

2.1 ISC triggering tests with SMA devices

The thermal and electrical behaviors of ISC is studied on 1Ah pouch batteries with cathode material of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and anode material of graphite by introducing SMA devices. The SMA devices made by Ni-Ti alloy were implanted into jelly-rolls. The tip of the SMA device bent up and penetrated the separator to make a contact between cathode and anode when the temperature raised above 40°C, as shown in Fig 1. A hot wind gun was used to heat the battery to the triggering temperature. There are four types of ISC[10]: 1) Cathode material-anode material (Ca-An), 2) Cathode material-negative current collector copper (Ca-Cu), 3) Positive current collector aluminium-copper (Al-Cu), 4) aluminium-anode material (Al-An). In this work, batteries #1~#4 were triggered ISCs of different types at 100% SOC, whereas #4~#7 were triggered ISCs at different SOCs with the same type ISC Al-An. The voltage and central temperature of the battery surface were recorded with an interval of 1s.

2.2 No-salt batteries EIS tests with ISC

The 1:1:1 EC:DMC:EMC electrolyte without $LiPF_6$ replaced the normal electrolyte 1M $LiPF_6$ in 1:1:1 EC:DMC:EMC used in 2.1 to fabricate no-salt batteries. Batteries #8~#10 were the no-salt batteries without SMA devices, whereas the #11~#13 were the no-salt batteries with SMA devices made by the same jelly-roll from 2.1.

There's no ISC current and heat generation of no-salt batteries theoretically after triggering ISC so that EIS tests could be conducted with safety. EIS was investigated with an electrochemical workstation from Shanghai Chenhua. The frequency range was 100 kHz to 10 mHz with an excitation voltage of 5 mV at ambient temperature 25°C.

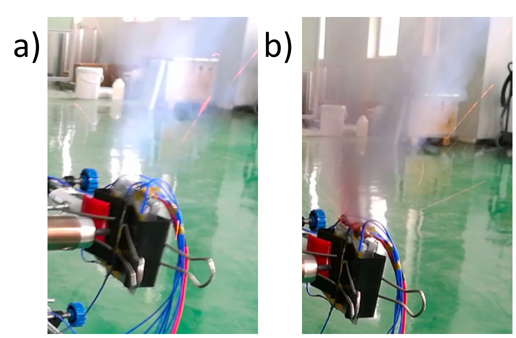

Fig 3 Thermal runaway with eruption of Al-An #4
a) White smoke and sparks; b) Black smoke and sparks.

3. RESULTS AND DISCUSSIONS

3.1 ISC triggering tests with SMA device

Fig 2 illustrates the results of ISC triggering tests. Ca-An #1 and Ca-Cu #2 were safe that the temperature decreased immediately after closing the hot wind. For these two types, the slow decline of voltage indicated the large ISC resistance and low heat generation. For Al-Cu #3, the voltage dropped down to 0V, whereas the maximum surface temperature is 105.7°C both appearing in 18s after ISC. Battery #3 swelled up but didn't erupt after ISC, thereby no fire or explosion. Conversely, Al-An 4# triggered TR with severe explosion after ISC as shown in Fig 3. The voltage of 4# dropped down to 0V in 3s after ISC and the maximum temperature 396.7°C appeared in 26s. As the consequence, Al-An type ISC is the most dangerous that must be inhibited during life cycle; Al-Cu type ISC has better thermal conductivity than Al-An mitigating the risk of TR, but the severity is influenced by the thermal stability of electrode materials. Ca-An and Ca-Cu type ISCs have poor electrical conductivity resulting in large resistance. Hence, how to identify these two type ISCs during practical application is necessary.

ISC behaviors of the most dangerous type Al-An under SOC variance are shown in Fig 2 e). The common feature is that the voltage dropped down sharply to 0V expect #7 to 0.12V at 25% SOC, indicating the resistance was equivalent. Conversely, the maximum surface temperatures of #4~#7 were 396.7°C, 367.4 °C, 113.3 °C and 99.9 °C obvious nonlinear relationship. #4 and #5 (group A) triggered severe TR, but the phenomenon of #6 and #7 (group B) was similar to Al-Cu #3 only gas generation, not eruption. The Joule heat of ISC relates to ISC resistance and the electric energy of battery, whereas the ISC resistance and heat dissipation conditions are similar for group A and B. If the local materials are heated to the temperature of TR chain reactions, there will be severe TR like group A. On the contrary, the heat accumulation of ISC doesn't trigger TR at low SOCs, resulting in low temperature and higher safety.

The ISC behavior for a specific type battery is the result of a comprehensive effect of ISC resistance (energy release rate), ISC type (heat dissipation rate) and SOC (total power energy). ISC location also influences the behaviors and will be investigated in future work.

3.2 No-salt batteries EIS tests with ISC

Table 1 EIS fitting results of no-salt batteries

	R_{ohm}/Ω	WoR/Ω	WoT/F	WoP	R_{ISC}/Ω
#8	0.82	3.18	0.41	0.43	∞
#9	0.81	3.09	0.41	0.43	∞
#10	0.76	3.21	0.41	0.43	∞
#	0.80	3.16	0.41	0.43	∞
#11	0.80	3.21	0.42	0.44	57.39
#12	0.81	3.12	0.42	0.43	40.69
#13	0.81	3.22	0.40	0.42	6.75

Remark: # is the average results of #8 ~ #10.

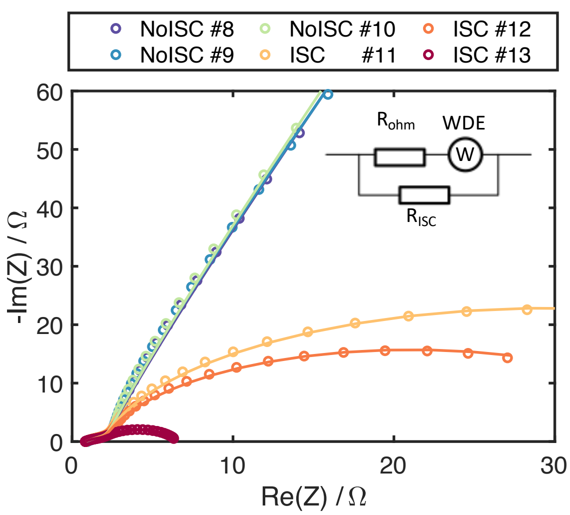

Fig 4 Impedance spectra results of no-salt batteries: symbols represent measured data, the solid line represents the fit.

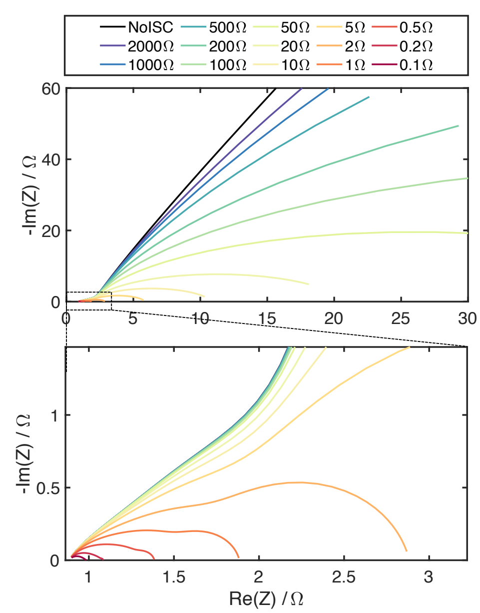

Fig 5 impedance spectra under different value of R_{ISC}.

Fig 4 and Table 1 shows the measured and fitting results. The electrode reaction is controlled by the diffusion process using the no-salt electrolyte. Hence, the EEC is the series circuit of the ohmic resistance (R_{ohm}) and the Warburg diffusion element (WDE), where the ISC resistance R_{ISC} is infinite when there's no ISC of #8~#10. The spectra are linear and achieve high repeatability, at low frequency.

When the ISC is triggered, there is an electronic channel inside the battery, described by the parallel circuit of ISC resistance of #11~#13. According to Table 1, the parameter variance of R_{ohm} and WDE is limited in ±10%. As a consequence, this EEC could be used to describe the physical process of the battery without $LiFP_6$ and ISC process and helps distinguish the ISC resistance.

The impedance spectra under the different value of R_{ISC} using the average parameters of #8~#10 are studied as shown in Fig 5. The resistance is higher, the spectra are more linear at low frequency, indicating that the main control process is the diffusion. As the internal resistance decreases, the spectra gradually bend downward.

The resistance of ISC has a great influence on the ISC electrical and thermal characteristics. This method helps to identify the specific resistance value of different ISC, benefiting to ISC modelling.

4. CONCLUSION

We implant the shape memory alloy device into jelly-roll to trigger ISC and analyze the thermal and electrical behaviors of ISC under different ISC types and SOC variance conditions. Al-An type ISC is the most dangerous ISC, whereas Ca-An and Ca-Cu type ISCs with high resistance inducing slow voltage decline are the potential threats of battery safety. We reveal that the ISC behavior for a specific type battery is the result of a comprehensive effect of ISC resistance, ISC type, ISC location and SOC. The boundary condition of ISC triggering TR by experimental and modelling need further research.

The ISC resistance is identified by using the no-salt battery based on the electrochemical impedance spectroscopy tests. This proposed method benefits further ISC modelling research and has the potential to ISC diagnosis.

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