Study on the Heat Generation Characteristics of Lithium Ion Power Battery with NCM/Si-C Composite Anode Material

Chuncheng LIU[1], Jing Wang[3*], Yuefeng SU[3], Shi CHEN[3], Feng WU[3*]

School of Materials Science & Engineering
Beijing Institute of Technology
Beijing, China.
e-mail : wangjingbit98@bit.edu.cn,
wufeng863@bit.edu.cn

Shiqiang LIU[2], Chunjing LIN[4], Fang WANG[5*]
China Automobile Technology and Research Center
Tianjin, China
e-mail: Wangfang2011@catarc.ac.cn

Abstract—**Thermal characteristics of lithium ion batteries are particularly important for both the optimization of the battery cells and design of the thermal management system for battery packs. The Si-C composite applied in lithium ion battery could improve the battery's energy density. For a 3 Ah pouch lithium ion battery with NCM/Si-C composite material system, the thermal characteristics were analyzed during the charging and discharging processes using the Extended Volume-Accelerating Rate Calorimeter. Meanwhile a 3 Ah pouch lithium ion battery with NCM/graphite composite material system was used as the reference sample. The internal resistance has great influence on the thermal behavior of Li-ion batteries. Thus, internal resistances of the battery cell were measured using the electrochemical impedance spectroscopy (EIS) method. Experimental results showed that the battery cell with NCM/Si-C generated much more amount of heat during charging and discharging processes. Temperature rise and heat generation power of the batteries increased as the current rate rising during charging and discharging processes. In addition, the overall internal resistance obtained by EIS had a close relationship with the heat generation behavior.**

Keywords-lithium ion battery; Si-C composite; thermal characteristics; internal resistance; EIS

I   INTRODUCTION

Lithium ion batteries are widely applied in electric vehicles(EV), energy storage equipments and portable electronics with their favorable features of high energy density, high power density and long life etc., and have become a significant research topic[1][2][3]. During the processes of charging and discharging, lithium ion batteries generate large amount of heat due to the effects of ohm resistance, Li-ion migration and polarization phenomenon etc. For the lithium-ion cells with large capacities that are used in EVs, safe and long-time operations, that were affected by the ambient temperature and the internal temperature distribution inside the batteries[4], are necessary. With the development of electric vehicle, the development of high energy density battery is of the most urgent task. At present, graphite is the major anode material for lithium ion power battery. Silicon is the most promising alternative material as anode material in lithium-ion batteries to replace graphite for its higher gravimetric capacity, low average voltage and rational production cost [5][6].

In recent years, quantitative analysis on the thermal behavior of lithium-ion battery has been reported in several works. E. Schuster et al. [7] analyzed the thermal characteristics of a 40 Ah pouch lithium-ion cell at different charging/discharging currents from 0.0125C to 1C under both isoperibolic and adiabatic conditions. Akram Eddahech et al.[8] focused on the thermal behavior of high-power lithium-ion cells during charge-discharge at several current rates and the influence of the state-of-charge variation and the impact of charge-discharge current rate on battery heat generation. Veth et al. [9] analyzed the thermal characteristics of a 50 Ah large-format pouch lithium-ion cell under high current discharge conditions and the influence on the thermal behavior of lithium ion cells in charging and discharging process. Yoshiyasu Saito et al. [10] characterized the thermal behavior of 18650-type lithium-ion batteries which had degradation after long time storage during charging and discharging process using calorimetry. C. Lin et al. [11] studied the heat generation and energy efficiency of a prismatic 40 Ah LiFePO4/C battery and analyzed the influence of temperature on battery capacity during a mixed charge-discharge cycle. These works are basically based on battery cells with LFP or NCM/graphite material systems, and the thermal behavior of batteries with new material systems such as the NCM/Si-C should be studied. What's more, the battery internal resistance is the important factor that influence the heat generation in charging and discharging process. The ohmic and charge transfer resistances of the battery cell at different SOCs and temperatures could be studied using the electro-chemical impedance spectroscopy (EIS). Evaluations of the battery internal resistance by EIS are reported in the literature[12][13]. The thermal characteristics and internal resistance of large capacity lithium ion power batteries have always been concerned.

In this paper, the thermal characteristics of lithium ion battery cells were quantitatively analyzed during the charging and discharging processes using the Extended Volume-Accelerating Rate Calorimeter (EV+-ARC) in association with a battery electrochemical test system. A comparison of the thermal characteristics between the lithium ion battery with NMC/Si-C composite material system and NMC/graphite material system were studied. In addition, EIS was applied to analyze the internal resistance

of the battery cell at different state of charges (SOCs). Heat generation characteristic of the lithium ion cell were also compared with the obtained internal resistance. This work emphasized on the heat generation characteristics and the internal resistance of lithium ion batteries with NMC/Si-C composite material, which could be helpful for the optimization of high-energy power battery cells and the design of their thermal management systems.

II EXPERIMENT

A. Battery Cell

A pouch power battery with 126 mm in length, 100 mm in width and 3 mm in height was selected for use in this study. The Li (Ni0.5Co0.3Mn0.2) O2 with layered structure was used as the cathode material. The anode material consisted of a Silicon/Carbon composite that contained 90wt% of SiOx(x approximately equal to 1), 5wt% of graphite and 5wt% of binder and conductive agent. The charging and discharging termination voltage were 4.35 V and 2.75 V, respectively. And the capacity was 3 Ah and the mass was 62 g. The battery was named Battery 1# in this work for convenience. Battery 2# was taken as a reference sample, in which the graphite was used as the anode material and the other materials are the same.

B. Experimental Equipment

The EV+-ARC produced by Thermal Hazard Technology (THT) wass used for the measuring of specific heat capacity and heat generation. During the test of the battery thermal behavior, Arbin battery test system and the EV+-ARC were coupled in utilization during charging and discharging processes. The German Zahner-zennium electrochemical workstation was applied in the EIS analysis. Specific environment with constant temperature and humidity was provided by the Giant Force chamber.

C. Experimental Methods and Procedures

1) Electrochemical-thermal analysis of the battery

To evaluate the thermal performance under adiabatic working conditions, the battery was charged at a rate of 0.5 C and discharged at rates of 0.5C, 1C. The initial temperature of the battery cell and ARC chamber is 25±2 ℃. Charge of the Li-ion battery was performed in the constant current-constant voltage (CC-CV) mode and discharge of the battery was performed in the constant current mode in the 25±2℃ environment. The heat generation quantity and instantaneous heat generation power could be calculated using the Equation (1) and Equation (2), respectively.

$$Q = mC_p\Delta T \qquad (1)$$

$$P = mC_p \frac{dT}{dt} \qquad (2)$$

Where Q is the battery heat generation in J, m is cell mass in g, C_p is the cell specific heat capacity in J/(g K), Δ T is cell temperature rise in K, P is battery instantaneous heat

generation power in W, and dT/dt is temperature rise rate in K/s.

2) EIS test

By measuring the cell open-circuit voltage over time when applied with current excitation, electrochemical impedance spectra EIS test could differentiate the ohmic internal resistance, charge transfer resistance, of a Li-ion battery. The one-way scanning frequency of the small-amplitude sine wave was from 10 kHz to 10 MHz.

III RESULTS AND DISCUSSION

A. Analysis of the Electrochemical Impedance Spectra

The internal resistance of the Lithium ion battery was the key factor affecting the heat generation measured by EIS. The EIS technique is a method to analyze the internal resistance of battery. The Nyquist curve of Battery 1# could be obtained by the EIS test as depicted in Figure 1.
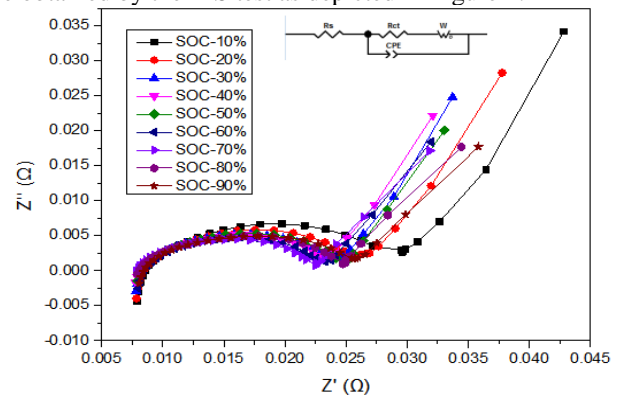

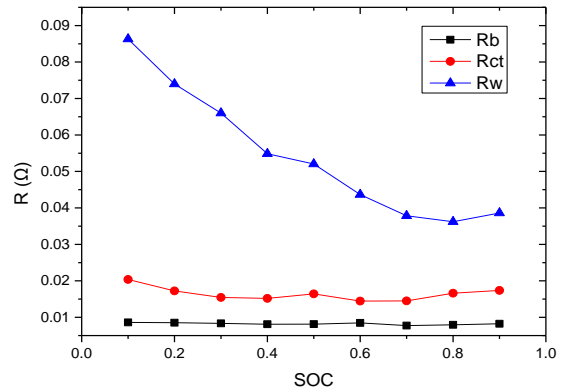Figure 1.   The Nyquist curve of the Li-ion battery cell at different SOCs of Battery 1#.

Figure 2.   Nyquist Analysis of Battery 1#.

It could be found that the Nyquist curves in the high frequency range showed no obvious changes with the SOC increasing from 10% to 90%. The diameters of the semicircles varied at different SOC, and the maximum of diameters appeared at SOC =10%. The equivalent electric circuit (EEC) was identified in order to reproduce the internal electric effects of the battery. And the ohm internal resistance Rb, the charge transfer resistance Rct and the diffusion resistance Rw could be analyzed by equivalent electric circuit, as shown in Figure 2.

TABLE I.   MEASUREMENT OF THE BATTERY HEAT GENERATION IN CHARGING PROCESS

Sample	Current Rate	Terminal temperature rise(℃)	Maximum Temperature Rise(℃)	Average Heat Generation Power(W)
Battery 1#	0.5C	6.312	6.567	0.0843
Battery 1#	1C	15.029	15.469	0.3289
Battery 2#	0.5C	2.094	2.209	0.0294

Performing fitting of the Nyquist curves in Figure 1, the ohmic resistance Rb and charge transfer internal resistance Rct of Battery 1# at different SOCs were obtained, as shown in Fig. 2. It could be seen that the fluctuation and value of charge transfer resistance with SOC were obviously higher than that of ohmic resistance. The ohmic resistance Rb, which is about 8.24 mΩ, appeared almost constant when SOC increasing from 10% to 90%. The charge transfer resistance Rct was relatively larger in high and low SOC section, that is much larger at SOC=10%. And the diffusion resistance Rw decreased with the increase of SOC with a greater change.

B. Electrochemical Calorimetric Analysis of Li-ion battery

Battery 2# served as a reference sample for the electrochemical thermal analysis of Battery 1#.

1) Specific heat capacity

The specific heat capacity is essential to calculate the heat generated of the battery. According to the literature [7], the specific heat capacity of a Li-ion battery was measured by using an ARC. The temperature data, mass and heating power were recorded in the test. The specific heat capacity of Battery 1# and Battery 2# were calculated from the Equation (3) to be 1.48 J kg-1 K-1, 1.59 J kg-1 K-1, respectively.

$$Cp = \frac{Pt}{m(T_2 - T_1)} \quad\quad (3)$$

Where Cp is the specific heat capacity of a Li-ion battery, P is the heating power, t is the heating time, m is the mass of battery, and T1 and T2 are initial temperature and termination temperature of the battery in the test.

2) Thermal characteristics of Li-ion cell

a) Charging process

The temperature rise and average heat generation power of the Li-ion battery cell during the charging processes were shown in Table 1. The terminal temperature rise was 6.312 ℃,15.029 ℃ and 2.094 ℃ of Battery 1#-0.5C, Battery 1#-1C and Battery 2#-0.5C, respectively. The average temperature rise rates were 0.055℃/min, 0.215 ℃/min and 0.017 ℃/min, respectively. It can be observed that the heat generation and power of Battery 1# were much higher than Battery 2# during 0.5C charging processes. When the current was 1C, the temperature rise increased as the charging current rate rising.

The heat generation power and current as a function of time during charging processes were shown in Figure. 3. It could be seen that the temperature rise rates of Battery 1# increased obviously when the charge current rate rose from 0.5C to 1C-rate, the temperature rise rates of Battery 2# was

lower than Battery 1# in 0.5C current rate in charging process. After that, the heat generation power decreased gradually with the charging in process. In the constant current charging period, the heat generation power fluctuated over time that was a little bit lower in the later period. During the constant voltage charging stage, the heat production power gradually reduced as current gradually dropping to 0.6 A, and the temperature could be a little bit lower.
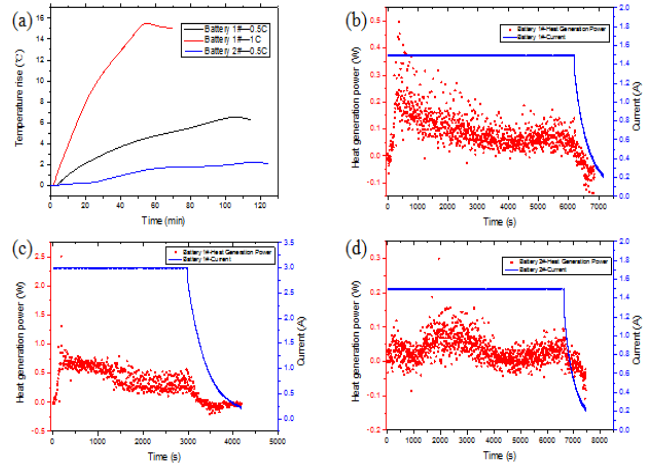

Figure 3.   The temperature rise, heat generation power and current as a function of time during charging processes (a) Temperature rise (b) Battery 1# -0.5C charging current rate (c) Battery 1# -1C charging current rate (d) Battery 2# -0.5C charging current rate.

b) Discharging process

The total temperature rise and the average heat generation power of the battery cell during the discharging process were shown in Table 2 and Figure 4. It could be seen that, the temperature rise and the heat generation power of Battery 1# were much higher than Battery 2# in 0.5C and 1C-rate discharging processes. In discharging process, the average temperature rise rates of Battery 1#-0.5C.Battery 1#-1C and Battery 2#-0.5C Battery 2#-1C were 0.076℃/min, 0.316℃/min and 0.032℃/min, 0.152℃/min, respectively. The average temperature rise rates of the cell during discharging process increased significantly with current rate rising. The heat generation powers of Battery 2#-0.5C were small during the majority of discharging time. It could be observed in Figure 4(b), that the heat generation power of the batteries increased obviously both in magnitude and fluctuation as the discharge rises. The heat generation power varied in a similar way in different current rate. Also, in the final stage of the discharge, heat generation power was increasing significantly. In addition, the heat generation powers of the cell were relatively higher during the initial and final periods, and relatively lower during the middle stage.

TABLE II.   MEASUREMENT OF THE BATTERY HEAT GENERATION IN DISCHARGING PROCESS

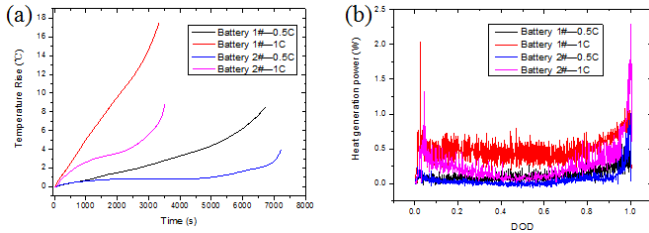| Sample	Current Rate	Terminal temperature rise(℃)	Average Heat Generation Power(W)
Battery 1#	0.5C	8.484	0.1156
Battery 1#	1C	17.531	0.4815
Battery 2#	0.5C	3.881	0.0565
Battery 2#	1C	8.839	0.2653

Figure 4.   The thermal behavior of Battery 1# and Battery 2# during discharging process,(a)temperature rise as functions of time (b)the instantaneous heat generation power as functions of DOD.

The heat generation power and voltage as a function of time during charging processes at different current rates were shown in Figure 5. For these discharge cases, the battery was discharged at a certain current rate to the same cutoff voltage of 2.75V. The voltage was dropping during discharging process. And for Battery 1#, the trend of voltage dropping was relatively stable. The voltage of Battery 2# dropped more rapidly in the later discharging period. In the initial and final stage of the discharge, the heat generation power increased quickly when the voltage dropped rapidly on the account of charge transfer internal resistance. The variation trend of heat generation power and voltage was relatively stable in the middle of the discharge process.
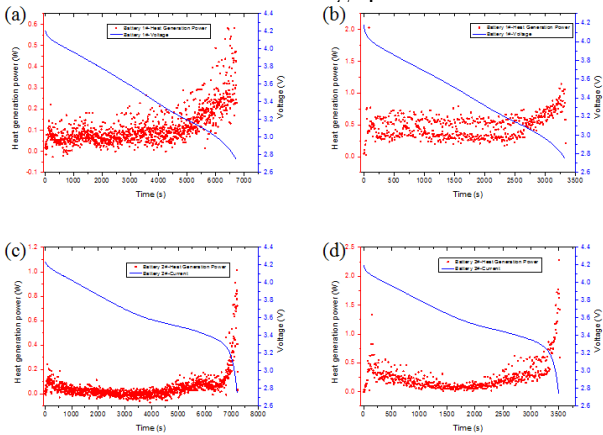

Figure 5.   The heat generation power and voltage as a function of time during discharging processes (a)Batter 1#-0.5C discharging current rate (b)Batter 1#-1C discharging current rate(c) Batter 2#-0.5C discharging current rate(d) Battery 2# -1C discharging current rate.

To further investigate the relationship between the internal resistance and the heat generation, the internal resistance calculated by heat generation powers obtained by the ARC test of Battery 1# were compared with the ones measured by the EIS test in Figure 6. It can be observed that the internal resistance obtained from these two methods were well fitted in trend. And the result from EIS was a little bit larger. The influence of the heat characteristics deserves further study, during battery discharging process from the irreversible ohmic heat, and the reversible reaction heat and the side reaction heat.
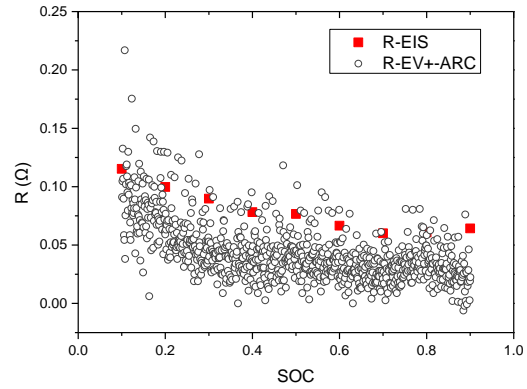

Figure 6.   The internal resistance obtained by the ARC test results in Battery 1# 0.5C-rate discharging process and total internal resistance from the EIS test.

IV   CONCLUSION

In this paper, the internal resistance was analyzed by the electrochemical impedance spectroscopy (EIS). The numerical and variation amplitude shows: Rb< Rct< Rw. The behavior of the heat generation between the lithium ion battery with different anode material during both charging and discharging processes were conducted. The temperature rise and heat generation power of the batteries increased as current rate rising in charging and discharging process. And the heat generation power curve shows symmetrical U-shaped characteristic during discharging processes. The lithium ion power battery with NCM/Si-C composite material could generated more amount of heat in charging and discharging process in comparison to that with NCM/graphite material. In charging process, the heat generation power became lower when the current dropped in the constant voltage stage. In the final stage of discharging process, the heat generation power rose as the voltage dropping. The heat generation power was relatively stable in the middle stage of charging and discharging process. What's more, the internal resistances calculated by the ARC measured were close to the EIS test results. Thus, the EIS test could provide some reasonable results for the estimation of the battery heat generation power.

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