

Temperature characterization analysis of LiFePO₄/C power battery during charging and discharging

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Abstract In order to study the surface temperature change and distribution during charging and discharging and in the simulation working condition of LiFePO₄/C power battery at normal temperature, the surface temperature is tested by placing the battery in the incubator and fixing 10 temperature probes on the battery surface. Results show that the temperature of the upper part is higher, and the temperature at the bottom is the lowest, while around the positive electrode is the highest during charging and discharging. The maximum temperature rising rate is reached at the moment of constant current charging transforming to the constant voltage charging during charging, and at the end moment during discharging. During charging in a certain range and discharging, the relations between the maximum temperature, the average temperature rising rate, and the maximum temperature difference of all the measurement points at the same time and the current are approximately linear, respectively. In the simulation working condition, the moment of the maximum temperature is consistent with the large current discharging instantaneous in each stage.

Keywords LiFePO₄/C battery · Temperature characteristic · Surface temperature · Temperature rising rate

Introduction

The demand for a secondary battery with high-specific power increases with the advancement of electronic devices. Accordingly, the research and development of secondary lithium battery has been intensified. At present, LiCoO₂ is used as the cathode material in commercial Li-ion batteries. However, it still suffers from some disadvantages such as high cost, toxicity, and limited sources of cobalt ore [1]. Among the candidates for the cathode, one of the most attractive materials to replace LiCoO₂ is LiFePO₄, which is the most promising candidate for lithium-ion battery in large-size and high-rate applications, such as power tools and hybrid electric vehicles [2, 3]. As volume and mass in a vehicle are rather limited, the battery system has to be smaller to take up less space [4]. Thus, thermal effect becomes more outstanding when developing the high power battery. The chemical reactions in the battery will release heat and induce battery temperature rising which intensifies the reactions further and releases more heat [5]. The heat generation rate rises as an exponential function of temperature, while heat transmission rate shows linear increase with the increment of temperature [6]. Hysteresis of the heat transmission will induce the heat accumulation inside the battery, which not only affects charging process and lowers battery longevity but also leads to thermal runaway and even the safety problem, such as burning and explosion when heat accumulates to some degree.

Therefore, temperature affects battery performance and cycle life remarkably due to the nature of heat generation of the battery itself. Reliable predictions of battery temperature and heat generation rate are required for the battery design and thermal management system [7].

The surface temperature characteristic is an important indication for battery safety. Accordingly, the surface

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temperature analysis during charging and discharging is essential for the development and design of the lithium-ion battery. Much has been reported about heat effect of battery [8–10] and modification of LiFePO_4/C battery by various methods [11, 12], but little has been reported on such temperature characteristic analysis of LiFePO_4/C battery. Working from this report, the author focuses on LiFePO_4/C battery, with the goal of studying the surface temperature change and distribution and the effect of the rate on the battery temperature during charging and discharging and in the simulation working condition. And, the regulation of the surface temperature change and distribution at different charge and discharge rates at ambient temperature 25°C is investigated.

Experimental

Battery and equipment

The LF-268092S lithium-ion battery ($80 \times 26 \times 92$ mm), rating capacity of 8 Ah and nominal voltage of 3.2 V is used as the test sample. The battery is fabricated with the electrodes, separator, and electrolyte. The positive electrode contains 82% carbon-coated LiFePO_4 , 8% conducting carbon, and 10% PVDF binder. The NMP (*N*-methyl pyrrolidinone) slurries are cast onto an aluminum current collector. The negative electrode is prepared from SL20 natural graphite (Superior Graphite) with 10% PVDF binder, and the mixture is coated onto a copper current collector. The battery uses Celgard 2300 as the separator and 1 mol/L LiPF_6 in EC + EMC + DMC (1:1:1 in volume) as the electrolyte. And steel is used as battery shell. Internal structure of the battery is shown in Fig. 1A battery management system with 10 temperature probes is used for

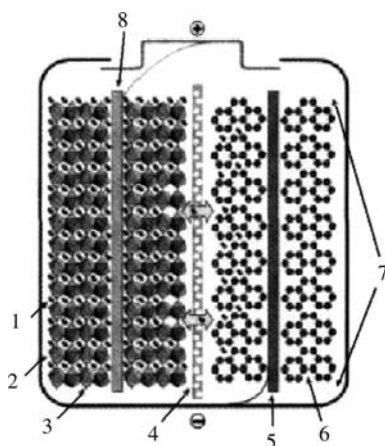


Fig. 1 Internal structure of LiFePO_4/C battery [13]. 1—Li-ion; 2— FeO_4 (ion); 3— PO_4 (phosphide); 4—separator; 5—anode; 6—C (graphite); 7—electrolyte; 8—cathode

testing the battery surface temperature. An Arbin Battery Testing Instrument is used to charge and discharge the battery. An incubator is used to make the test battery under the constant condition of 25°C .

Charging and discharging method

The test battery is charged in the method of constant current charging at a certain rate to 3.6 V and then constant voltage charging of 3.6 V until the current fall to 10% of the start current. And, it is discharged at a constant current from the fully charged state to the cut-off voltage 2.5 V.

The simulation working condition

According to 2005 Test standard used by high power lithium-ion battery in HEV of China, the simulation working condition is operated in the following method: (1) discharged at 1 C and the cut-off voltage is 2.5 V; (2) charged at 0.5 C to 3.6 V and at a constant voltage until the current lows to 10% of the start current; (3) rest 1 h; (4) discharging at 1 C for 3 min and pulse discharging at 60 A for 1 min is taken for the first stage; discharging at 1 C for 3 min and pulse discharging at 120 A for 30 s is taken for the second stage; the third stage is the same to the first stage and the fourth stage is the same to the second stage; there is 1 h rest time between stages. Discharging will be stopped if the voltage lows to 2.5 V in the four pulse stages; and (5) discharged at 1 C until the depth of discharge (DOD) reaches 100%.

Experimental process

In this study, at a constant temperature of 25°C , the surface temperature of the LiFePO_4/C battery is measured at different charging and discharging rates (1, 3, 5, 10, 15, 20, and 25 C) and in the simulation working condition. There is enough rest time after charging and discharging to make the temperature of 10 probes reach 25°C . According to Fig. 2, 10 temperature probes of the battery management

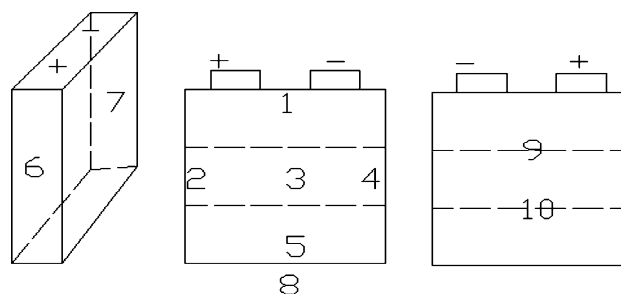


Fig. 2 The fixing method of temperature probes on battery surface

system are fixed on the battery surface, and the test battery is put in the incubator.

Results and discussion

Temperature distribution on the surface

Table 1 is the temperature sequencing of 10 probes when the maximum temperature appears on the surface at different charging and discharging rates. According to Table 1, the temperature distribution on the battery surface is almost consistent at different rates. The surface temperature change is caused by its internal heating. The uneven surface temperature distribution reflects a more uneven internal temperature. In all, the surface temperature of the upper part is higher, and the temperature at the bottom is the lowest, while around the positive electrode is the highest. The upper part of the battery is the connection of tab and post of the positive electrode and negative electrode, with contact resistance, which causes a higher temperature than the lower part at the same current. Moreover, the uneven heat generation and dispersion are caused by internal contact resistance and different thickness uniformity of the coating layer on electrodes. The higher the current, the larger the difference between 10 probes. Such as the temperature of probe 9, 10, 3, 7 and 4, 6, 8 are the same at 1 C.

In the following analysis, the temperature tested by the 3rd probe is used as the average temperature of the battery.

The behavior of 10 C is measured and the results are shown in Figs. 3 and 4. And, the straight line in the figure represents the end of the process. At the beginning, the temperature rises slowly and the difference between probes is small, then the temperature rises more quickly with the reaction carried through. The charging process ends at 6.3 min, and the temperature reaches the maximum 33.9 °C at 7.7 min; the discharging process ends at 4.5 min, and the temperature reaches the maximum 35.9 °C at 6.0 min. Therefore, the maximum temperature is reached after charging and discharging, which is caused

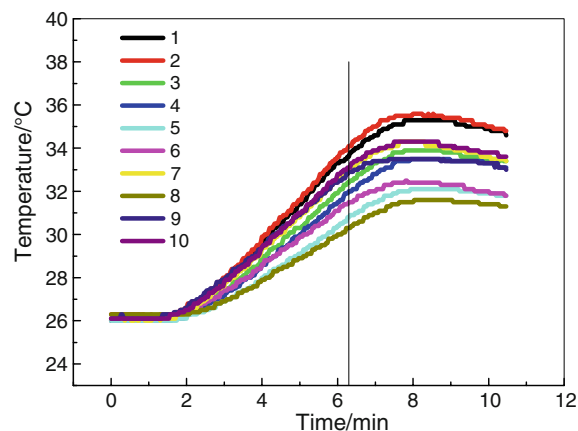


Fig. 3 Temperature curves during charging at 10 C

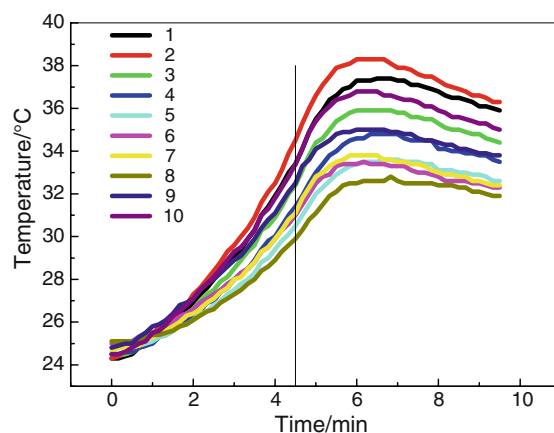


Fig. 4 Temperature curves during discharging at 10 C

by the unbalance between heat dissipation and heat generation. Amount of heat is accumulated in the battery and spreads gradually to the surrounding environment. The maximum temperature appears beside the positive tab first, and the temperature always keeps the highest during charging and discharging. It indicates that the materials around the positive tab, including active material and electrolyte, generate more heat than in other positions.

Table 1 The temperature sequencing of different probes at different rates

Rate	Charging	Discharging
1 C	2 > 1 > 9 = 10 > 3 = 7 > 4 = 6 = 8 > 5	2 = 1 > 10 > 3 = 4 = 9 > 5 = 7 > 8 > 6
3 C	2 > 1 > 10 > 4 > 3 > 9 > 7 > 5 > 8 > 6	2 > 1 > 10 > 3 > 4 = 9 > 7 > 6 > 5 = 8
5 C	2 > 1 > 10 > 3 > 9 > 4 > 5 > 6 = 7 > 8	2 > 1 > 10 > 3 > 9 = 4 > 6 > 5 = 7 > 8
10 C	2 > 1 > 10 > 7 > 3 > 9 = 4 > 6 > 5 > 8	2 > 1 > 10 > 3 > 9 > 4 > 7 > 5 > 6 > 8
15 C	2 > 1 > 10 > 7 > 3 > 9 > 4 > 6 > 5 > 8	2 > 1 > 10 > 3 > 4 > 9 > 6 > 7 > 5 > 8
20 C	2 > 1 > 10 > 3 > 9 > 4 > 5 = 7 > 6 > 8	2 > 1 > 3 > 10 > 7 > 9 > 4 > 6 > 5 > 8
25 C	2 > 1 > 10 > 3 > 9 > 7 > 4 > 6 > 5 > 8	2 > 1 > 10 > 3 > 7 > 4 > 9 > 6 > 5 > 8

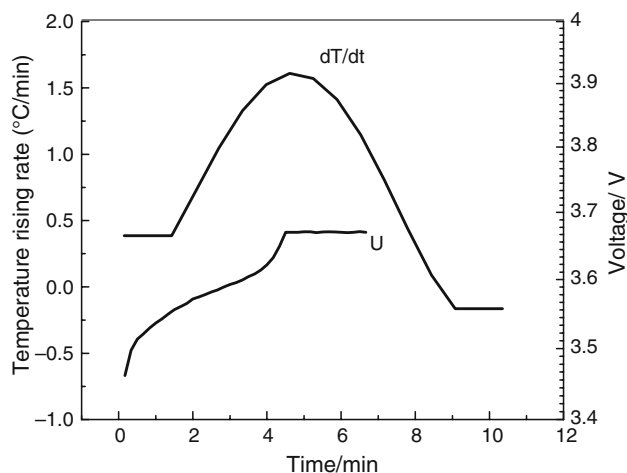


Fig. 5 The curves of temperature rising rate and voltage during charging at 10 C

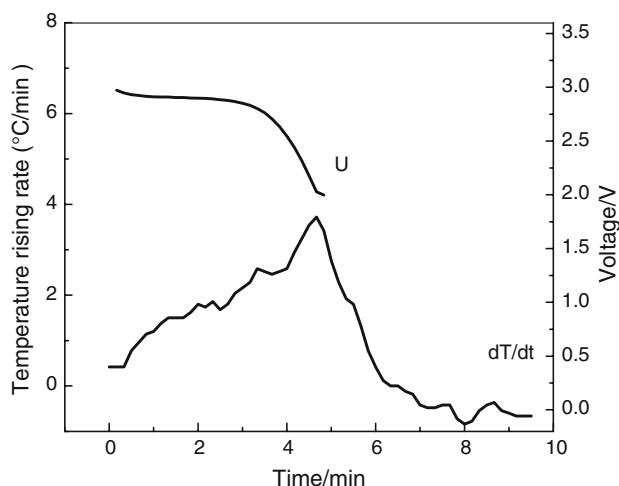


Fig. 6 The curves of temperature rising rate and voltage during discharging at 10 C

The temperature rising rate during charging and discharging

The process of 10 C charging and discharging is still taken, for example, the curves of temperature rising rate and voltage are shown in Figs. 5 and 6.

During charging and discharging, the temperature rising rate (dT/dt) almost increases linearly with time. The maximum dT/dt is 1.6 °C/min during charging and 3.68 °C/min during discharging. It also can be seen from Figs. 5 and 6 that the maximum dT/dt is reached at the moment of constant current charging transforming to the constant voltage charging during charging and at the end moment during discharging.

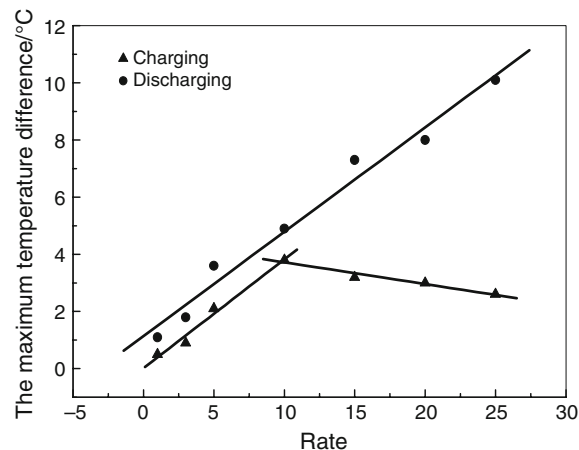


Fig. 7 The relationship between the maximum temperature difference and rate

The maximum temperature difference of measurement points at the same time

In order to analyze the uniformity of the surface temperature field at different rates, it is necessary to compare the temperature difference of measurement points in the process of measurement. In the whole process, the temperature of each measurement point is different from others at the same time, and the difference (ΔT) between the maximum and the minimum changes with the time. At first, the temperature of all measurement points is 25 °C. When the battery temperature reaches the maximum, the uniformity of the temperature field is the worst, and ΔT also reaches the maximum, namely ΔT_{\max} . The relationship between ΔT_{\max} and rate is shown in Fig. 7.

During discharging, the relation of ΔT_{\max} and current is approximately linear: $y = 0.365x + 1.136$. In the process of 1–10 C charging, ΔT_{\max} increases continually with increasing current, while ΔT_{\max} decreases continually with increasing current in the process of 15–25 C charging, which is caused by the difference between the charging process of 1 C, 3 C, 5 C, 10 C and 15 C, 20 C, 25 C. At the beginning of large current charging (15 C, 20 C, 25 C), the voltage is higher than 3.6 V due to the increasing polarization resistance, and then the current begins to decrease. Therefore, the actual charging process is constant current charging at about 56 A to 3.6 V and then 3.6 V charging until the current lows to 10% of the start current. Therefore, when charging at 15, 20, and 25 C, the maximum temperature difference of measurement points at the same time, temperature rising rate and the maximum temperature have a different change regulation with 1, 3, 5, and 10 C.

The temperature of all measurement points is almost the same at the beginning, which shows that the internal temperature field is relatively uniform. However, during

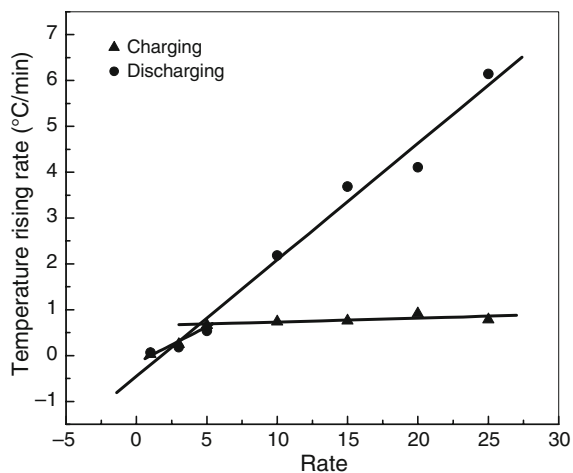


Fig. 8 The relationship between the average temperature rising rate and rate

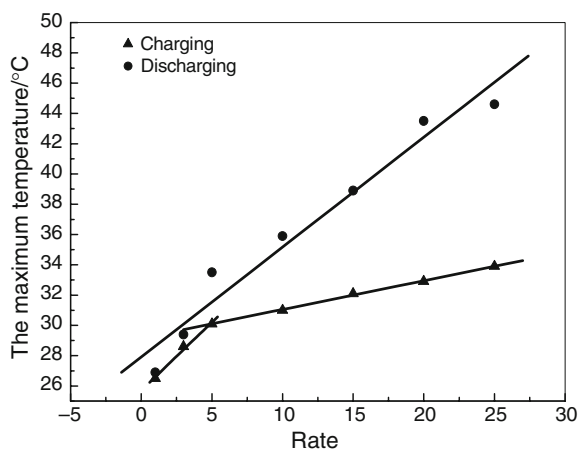


Fig. 9 The relationship between the maximum temperature and rate

charging and discharging, the difference gradually increases. The higher the rate, the larger the temperature difference. When the battery is discharged at 25 C, the maximum temperature reaches 10.1 °C unexpectedly, which shows that the internal temperature field is extremely uneven. Meanwhile, the temperature difference during discharging is larger than during charging and appears a more uneven temperature field.

The average temperature rising rate and the maximum temperature at different charge and discharge rates

The average temperature rising rate and the maximum temperature (T_{max}) at different rates are shown in Figs. 8 and 9. The differential curve of temperature with respect to time is made first, and the value at the half time of the actual charging and discharging process represents the average temperature rising rate in the whole process. The

temperature rising becomes faster with increasing discharging rate. And, the temperature rising rate is not high at 1 C: 0.062 °C/min during discharging and 0.030 °C/min during charging. However, average temperature rising rate rises to 6.145 °C/min and temperature rising reaches 19.6 °C at 25 C discharging. Therefore, battery management system with strong temperature regulation ability is necessary to carry out heat dissipation in the working environment with a high current.

The relation between the average dT/dt and current during discharging is approximately linear: $y = 0.254x - 0.455$, and T_{max} also increases linearity with discharging rate: $y = 0.268x + 27.704$. Accordingly, the average dT/dt and T_{max} at other rates (between 1 and 25 C) discharging can be predicted. During charging, the average dT/dt increases linearly with the increasing rate between 1 and 5 C, and it is almost unchanged with the increasing rate when it is larger than 10 C. T_{max} increases linearly with increasing rate when the rate is between 1 and 5 C and between 5 and 25 C, respectively. However, a gentle temperature gradient is maintained when the rate is higher than 5 C, while a steep temperature gradient is maintained when the rate is lower than 5 C. The reason is that the temperature have a different change regulation when charged at 15, 20, and 25 C, because these currents are not worthy of their name.

With the discharging rate increasing, the possible reason for the temperature rising becoming faster is that the thickness of the solid electrolyte interface film (SEI film) will increase continuously with the surface and internal temperature rising, which leads to internal resistance increasing and then generates more heat. Subsequently, the rate of generating heat will become higher due to more joule heat. In the mean time, too high temperature can change the crystalline form of cathode material and intensify heat releasing in the reaction between cathode and electrolyte, leading to possible thermal runaway of lithium-ion battery ultimately, and even causing security problems [14].

The larger the rate, the higher the maximum temperature on the surface and the worse the uniformity of the temperature filed. The main reason is: increasing current causes increasing polarization and then generates more joule heat and polarization heat, moreover, the time for dissipating heat will become short for increasing charging and discharging rate and then it is difficult to spread the heat quickly.

Measurement in simulation working condition

In order to study the surface temperature change of LiFePO₄/C power battery in the practical application of electric vehicles, the battery is tested in the simulation working

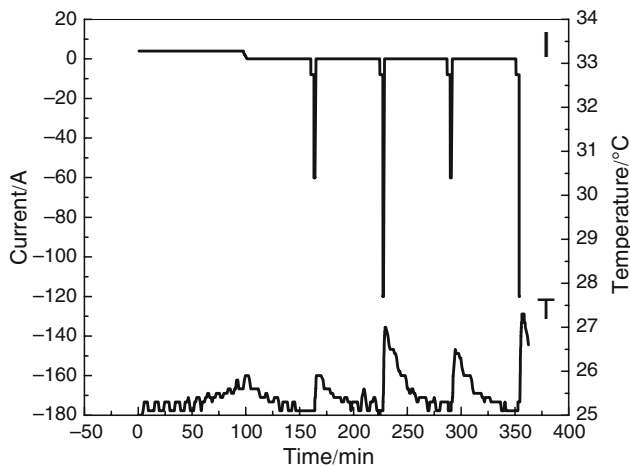


Fig. 10 The curves of temperature and current in the simulation working condition

condition. Figure 10 shows the curves of surface temperature and current with the time. It also reveals that the temperature rises rapidly when discharging at a high current, and the time of maximum temperature is consistent with the large current discharging instantaneous in each stage. The temperature tested by the 3rd probe is still used to be the average temperature of the battery. The temperature rises 0.9 °C when charging at the rate of 0.5 C. The temperature rises 0.8 °C and 1.4 °C, respectively in the first and third stage of pulse discharging at 60 A for 1 min, and the temperature rises 2.0 °C and 2.2 °C, respectively in the second and fourth stage of pulse discharging at 120 A for 30 s. Therefore, the temperature raises more during the second discharging stage at the same current. One reason is that the internal heat has not spread out wholly yet because the interval time is only 1 h, despite of the battery surface temperature having decreased to 25 °C before the next stage. Furthermore, compared with the temperature rising of 14.9 °C and 8.5 °C separately during discharging at 15 C (120 A) and 5 C (40 A), the temperature raising in the stage of instantaneous large current discharging is lower. However, if there is not a good heat dissipation system, the temperature rising will become larger, thus affects the performance and security of battery.

In order to analyze the uniformity of temperature field on the surface in simulation working condition, and to determine whether the temperature distribution in simulation working condition is the same with the process of charging and discharging at a certain current, the curves about the relationship between the temperature of each measurement point and test time are made, as shown in Fig. 11. The temperature of the 2nd probe is the maximum, and the temperature of the 5th probe is the minimum in all stages when the battery's temperature reaches the maximum, which is different from the process of charging and

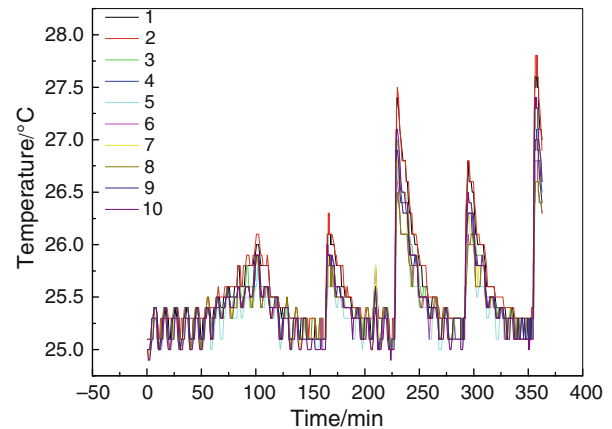


Fig. 11 The relationship between temperature of measurement points and test time

discharging at a certain current (the 2nd probe's temperature is the maximum and the 8th probe's temperature is the minimum), but the difference is not so large in the whole. Furthermore, comparing with the maximum temperature difference (ΔT_{\max}) of 7.3 °C and 3.6 °C separately during discharging at 15 and 5 C, it is concluded that the temperature field in stage of instantaneous large current discharging is more uniform.

Conclusions

During charging and discharging, the battery surface temperature of the upper part is higher than the lower part, and the temperature at the bottom is the lowest, while the temperature around the positive is the highest. The maximum temperature rising rate is reached at the moment of constant current charging transforming to the constant voltage charging during charging, and is reached at the end moment during discharging. During discharging and charging at 1–10 C, the relations of the maximum temperature, the average temperature rising rate and the maximum temperature difference between measurement points and current are approximately linear, therefore these values at other currents of the battery can be predicted. During discharging, the temperature rising is faster and the uniformity of the temperature field is worse than during charging. In the simulation working condition at 25 °C, the temperature rises rapidly when discharging at a high current and the time of maximum temperature is consistent with the instantaneous large current discharging in each stage. In the mean time, the temperature rising in the stage of instantaneous high current discharging is lower and the temperature field is more uniform.

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