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THERMO EFFECT EXAMINATION OF THE LITHIUM-POLYMER BATTERIES DURING DISCHARGE

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Abstract

A significant focal point of the Research Centre of Vehicle Industry is on research into electric driven vehicles. Within this research field this study investigates the changing temperature during discharge of ultra-capacity lithium-polymer batteries applied in electric and hybrid vehicles.

The causes of temperature change during discharge effect depending on low voltage threshold and capacity are investigated. The applied measuring system with the relevant chemical background is also presented.

Key words: *Lithium polymer battery, battery testing, hybrid and electric vehicles, chemical structure of lithium-polymer batteries*

Introduction

In recent years lithium-based batteries have become widespread due to increasing demand, financial investments and technological advantages (better energy density, longer lifetime, easier handling, rechargeability). They are also becoming more available, economical and reliable.

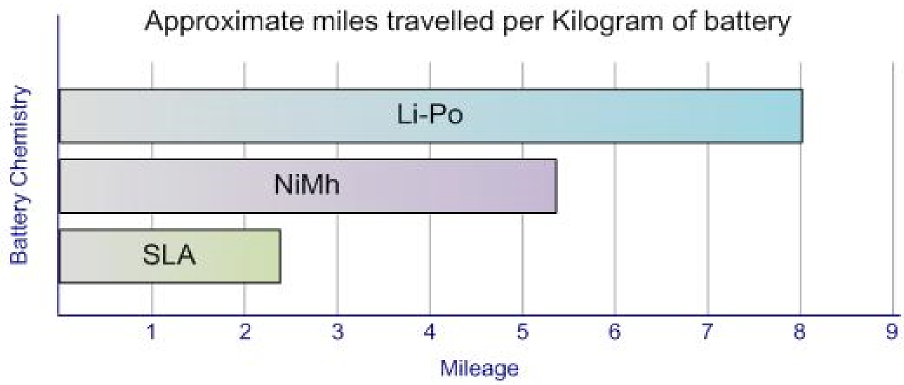

Fig. 1 Comparison of different batteries [14]

Several development and operational problems can arise during battery application. One of the main difficulties is wear with capacity loss in case of continuous operation.

Main causes of the above mentioned phenomena:

- Overcharging or charging more than the nominative voltage level
- Over discharging or discharging lower than the nominative voltage level
- Wear and ageing problems

These are influenced by the following factors:

- Battery type

- Manufacturing method
- Connection system
- Application mode

In Figure 2 the default ideal charging and discharging sections given by the manufacturers can be seen.

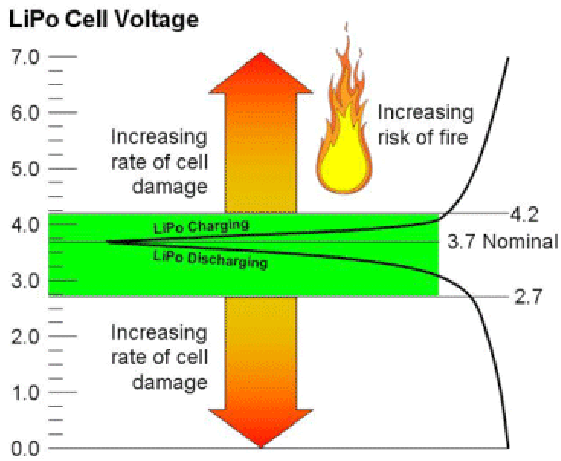

Fig. 2 Default charging and discharging values by the manufacturer [11] [13]

In case of overcharging the battery can catch fire:

Fig. 3 Overcharging [13] [11]

Over discharging can also significantly damage cells and result in considerable capacity loss; in some cases even the whole battery can be damaged. In order to have long-life battery cells and packs an optimal voltage interval is needed, which is the least destructive of cells. In the default lower discharge interval given by the manufacturer batteries can overheat and buckle. The goal is to select a voltage interval, which does not cause warming and full capacity is applicable.

The goal of this study is to define a voltage limit, which is optimal depending on capacity and lifetime. [10]

Chemical reactions of lithium-polymer batteries

Charging and discharging process of lithium-polymer batteries can be seen in Figure 4.

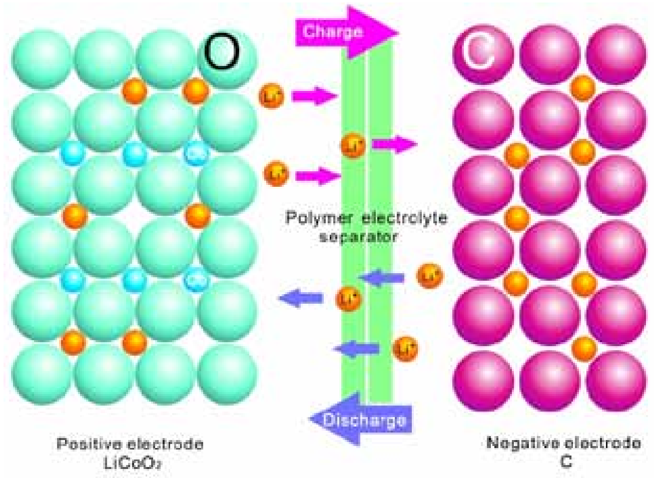

Fig. 4 Charging and discharging process of lithium-polymer batteries [9]

Currently there are two commercialized technologies, both lithium-ion-polymer (where polymer stands for polymer electrolyte/separator) cells. These are collectively referred to as; polymer electrolyte batteries.

The battery is constructed as:

- Cathode: $LiCoO_2$ or $LiMn_2O_4$
- Separator: Conducting polymer electrolyte
- Anode: Li or carbon-Li intercalation compound

Typical reaction:

- Anode: carbon–Lix → C + xLi+ + xe−
- Separator: Li+ conduction
- Cathode: Li_1−xCoO_2 + xLi+ + xe− → $LiCoO_2$

Polymer electrolytes/separators can be solid polymers (e.g., polyethyleneoxide, PEO) plus $LiPF_6$, or other conducting salts plus SiO_2, or other fillers for better mechanical properties (such systems are not yet available commercially).

Chemical Changes

Batteries are electrochemical devices which convert chemical energy into electrical energy or vice versa by means of controlled chemical reactions between a set of active chemicals. Unfortunately the desired chemical reactions on which the battery depends are usually accompanied by unwanted chemical reactions which consume some of the active chemicals or impede their reactions. Even if the cell‘s active chemicals remain unaffected over time, cells can fail because of unwanted chemical or physical changes to the seals keeping the electrolyte in place.

Lithium Battery Failures

Over-Voltage

If the charging voltage is increased beyond the recommended upper cell voltage, typically 4.2 volts, excessive current flows give rise to two problems.

Lithium Plating

With excessive currents the lithium ions cannot be accommodated quickly enough between the intercalation layers of the anode; subsequently lithium ions accumulate on the surface of the anode where they are deposited as metallic lithium. This is known as lithium plating. The consequence is an irreversible capacity loss and ultimately a short circuit between the electrodes.

Overheating

Excessive current also causes increased joule heating of the cell, accompanied by an increase in temperature

Under-voltage / Over-discharge

Rechargeable lithium cells suffer from under-voltage as well as over-voltage. Allowing the cell voltage to fall below about 2,7 volts by over discharging or storage for extended periods results in progressive breakdown of the electrode materials.

Anodes: First the anode copper current collector is dissolved into the electrolyte. This increases the self-discharge rate of the cell and can ultimately cause a short circuit between the electrodes.

Cathodes: Keeping the cells for prolonged periods at voltages below 2,7 volts results in the gradual breakdown of the cathode over many cycles with the release of oxygen by the lithium cobalt oxide and lithium manganese oxide cathodes and a consequent permanent capacity loss.

Equipment definition and unit connection for testing

Main devices for testing procedure:

- Power supply: Hameg HMP 4030
- Test load: EL-3000
- Data collector: NI Usb 6341
- Temperature sensors: NI Usb 6341
- Central computer for test with Labview software pack
- Battery: Turnigy nano-tech 5000 mAh
    - Maximum voltage: 4,2 V
    - Minimum voltage: 2,7 V
    - Capacity: 5 Ah

Both the power supply and test load can be connected to a computer via a USB port, at which the potential maximum baud rate is 115 k. Voltage and temperature values are collected by NI USB 5341 data collector card.

In Figure 5 the charging and discharging circuits with battery connection are structured.

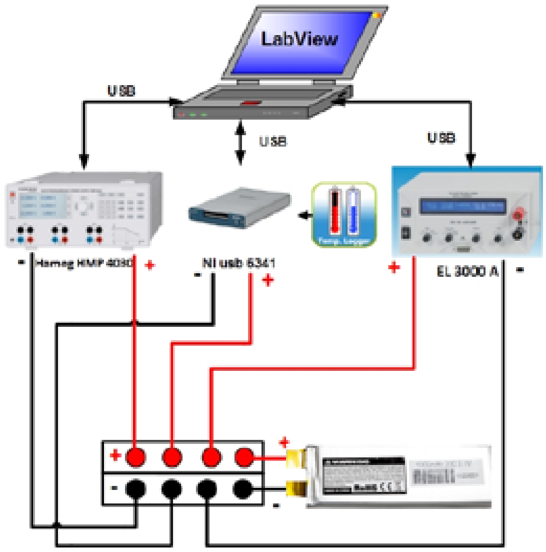

Fig. 5: Scheme of battery testing equipment

A cyclic charging and discharging LabView program has been developed for realizing charging and discharging cycles. Tests can be carried out at different parameter settings.

Main program parameters:

- cycle counter;
- at charging: supply current and upper voltage limit;
- at conditioning;
- at discharging: discharging current value and lower voltage limit.

The outside and battery pack temperature is monitored continuously. Beyond a certain temperature limit the test is stopped.

Block scheme of the testing procedure can be seen in the following figure (Figure 6):

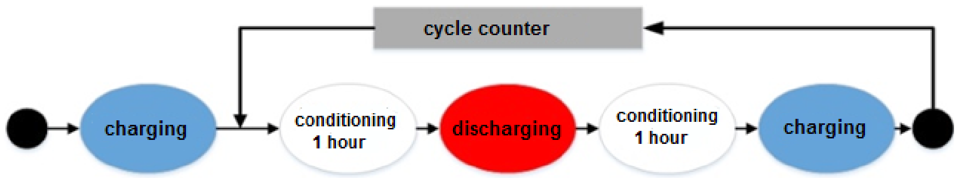

Fig. 6: Test cycle

Principles of test operation (order):

1. Battery charging by constant current till full charge and discharging till supply current falls under its limit
2. Charged battery conditioning for one hour
3. Discharging till threshold voltage falls under a certain limit
4. Conditioning for one hour
5. Start of second charging process

Temperature dependency

Chemical reactions internal to the battery are driven either by voltage or temperature. Heat is a major battery killer, either excess of it or lack of it, and lithium secondary cells need careful temperature control.

Low temperature operation

Chemical reaction rates decrease in line with temperature (Arrhenius Law). The effect of reducing the operating temperature is to reduce the rate at which the active chemicals in the cell are transformed. This translates to a reduction in the current carrying capacity of the cell both for charging and discharging. In other words its power handling capacity is reduced. Furthermore, at low temperatures, the reduced reaction rate (and perhaps contraction of the electrode materials) slows down, and makes more difficult, the insertion of the lithium ions into the intercalation spaces. As with overvoltage operation, when the electrodes cannot accommodate the current flow, the result is reduced power and anode plating with irreversible capacity loss.

High temperature operation

Operating at high temperatures brings a different set of problems, which can result in the destruction of the cell. In this case, the Arrhenius effect helps to get higher power out of the cell by increasing the reaction rate, but higher currents give rise to higher I^2R heat dissipation and thus even higher temperatures. This can be the start of positive temperature feedback and unless heat is removed faster than it is generated the result will be thermal runaway.

Thermal Runaway

The operating temperature, which is reached in a battery, is the result of the ambient temperature augmented by heat generated by the battery. If a battery is subject to excessive currents the possibility of thermal runaway arises resulting in catastrophic destruction of the battery. This occurs when the rate of heat generation within the battery exceeds its heat dissipation capacity. There are several conditions which can bring this about:

- During charging the charging current induces an exothermic chemical reaction of the chemicals in the cell which reinforces the heat generated by the charging current.
- During discharging the heat produced by the exothermic chemical action generating the current reinforces the resistive heating due to the current flow within the cell.
- The ambient temperature is excessive.
- Inadequate cooling

Own measurements

Two sensors are integrated for temperature effect tests:

1. One on the battery for battery pack heat measurement
2. One further from battery for outside temperature

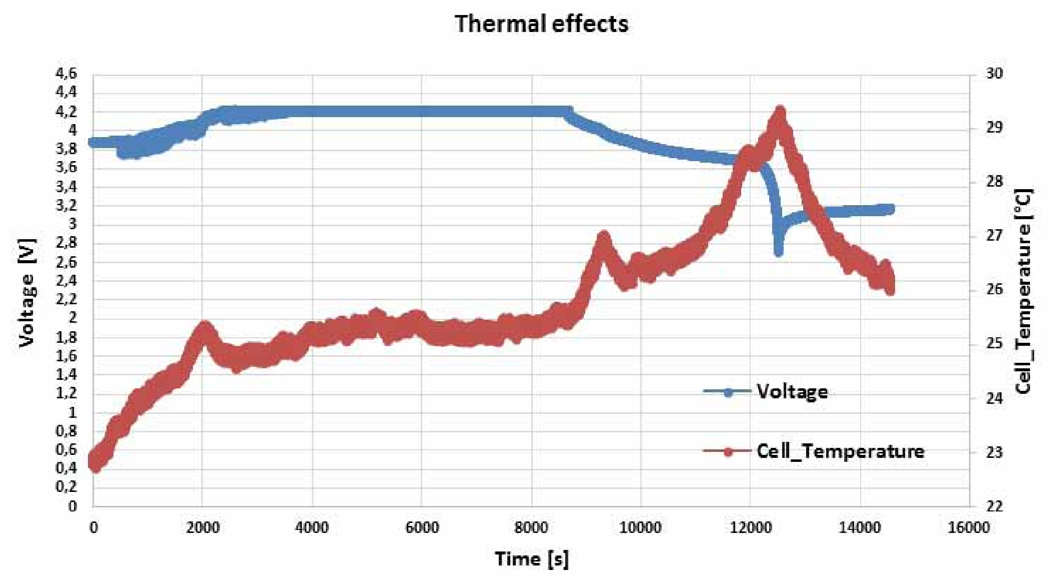

Fig. 7 Temperature change at lower voltage limit 2,7V

It can easily be seen that there is a large jump in temperature change at the end of the discharging process. The difference between outside and cell temperature change is presented in Figure 8.

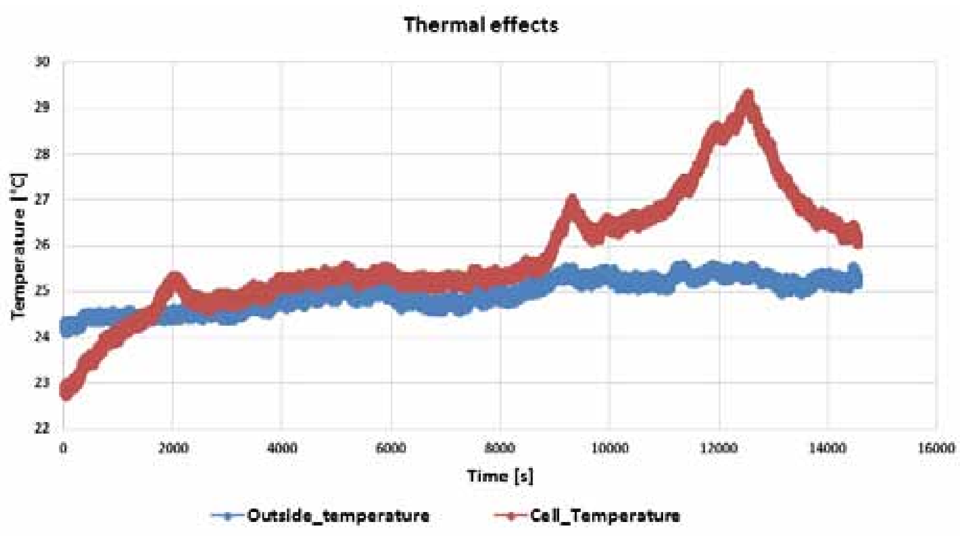

Fig. 8 Temperature change

In the test the expected battery capacity was 66.600J, 18,5Ah. Used capacity based on the former values 72.233J which is 20,06Wh meaning 108,46% deviation from 100% comes from the novel battery condition and constant 5A (1C) load.

In the following test the lower voltage limit was 3,0V and the discharging current was 5A. In Figure 9 heat increase and voltage change are shown.

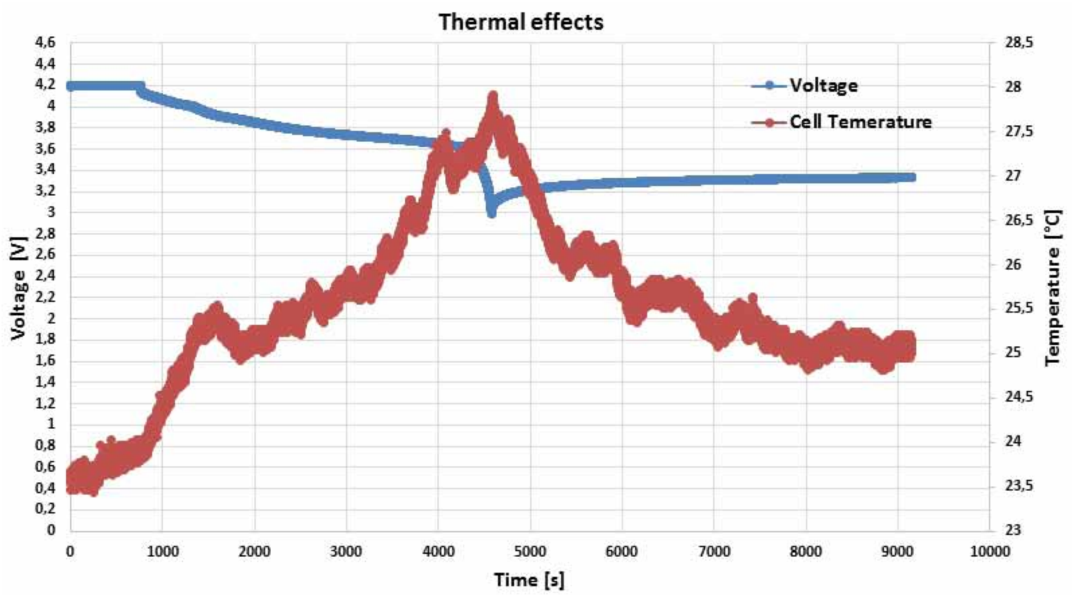

Fig. 9 Temperature change at lower voltage limit 3V

The difference between outside and cell temperature change is presented in Figure 10.

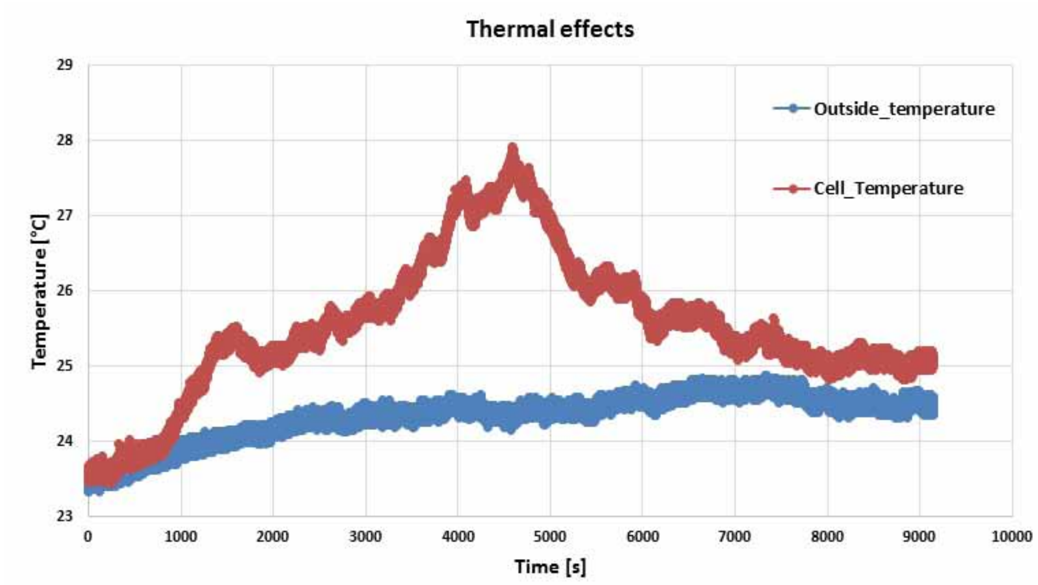

Fig. 10 Temperature change at lower voltage limit 3V

In the test the expected battery capacity was 66.600J, 18,5 Wh. Used capacity based on the former values 72.155J which is 20,04 Wh meaning 108,34%.

Summary

In temperature examination a substantial pack temperature increase was experienced during discharging. The reason for this is the acceleration of heat production at the end of discharging, since the difference in stationary voltage potential and voltage changes very fast. In order to avoid any difficulties the lower voltage value was increased, which resulted in decreased warming and hence used capacity approximately stayed the same. In the case of one cell there is also 1-1,5 °C less warming, which can mean a significant difference in cases of bigger packs.

Examination results show that the low voltage threshold between 2,7-3V is not necessarily ideal. It would be worth selecting a higher voltage threshold for a better temperature effect. In order to determine exact voltage levels whole low threshold voltage examinations and long-run tests are needed. These measurements are in progress and results will be published at a future date.

This is the method by which LiPo battery life time can be improved through determination of discharging cycles.

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