

## About the Efficiency of Charging and Discharging Processes in Lithium-Ion Accumulators

Investigations with the Coin Cell Module of the MMC 274 Nexus®

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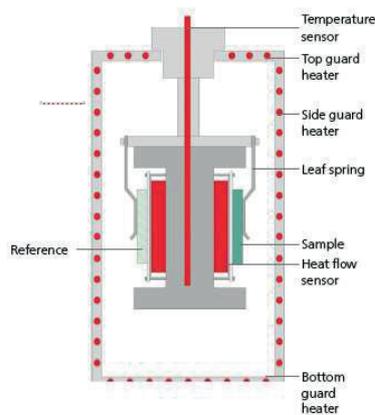


1 NETZSCH MMC 274 Nexus®

### Introduction

The NETZSCH Multiple Module Calorimeter (MMC) 274 Nexus® (figure 1) offers three different measurement modules. The ARC Module can be used for so-called heat-wait-search (HWS) tests or thermal runaway tests [1][2]; the Scanning Module is suited for such applications as the evaluation of endothermic or exothermic phase transitions as well as thermal hazard screening [3][4]; and the Coin Cell Module is specialized for the

investigation of batteries [5]. An external battery cycling unit can easily be connected to the Coin Cell Module via a LEMO connector. Signals for voltage and current can be transferred to the NETZSCH Proteus® evaluation software. The resulting power signal is automatically determined and can be independently quantified for charging and discharging. By detecting the heat loss during charging and discharging, it is possible to evaluate the efficiency of cycling a battery. To this end, the twin sample carrier offers a DSC-like differential setup (figure 2).



2 Schematic drawing of the Coin Cell Module; picture of the sample holder (left), four-wire technique (middle) and diagram of the differential set-up (right)

Since most of the non-destructive isothermal charging and discharging studies on batteries are carried out within a very small temperature range near ambient temperature, it is essential to have the calorimeter calibrated accordingly. For temperature and sensitivity calibration, metals are usually used as reference materials [6].

### Determination of the Battery Status

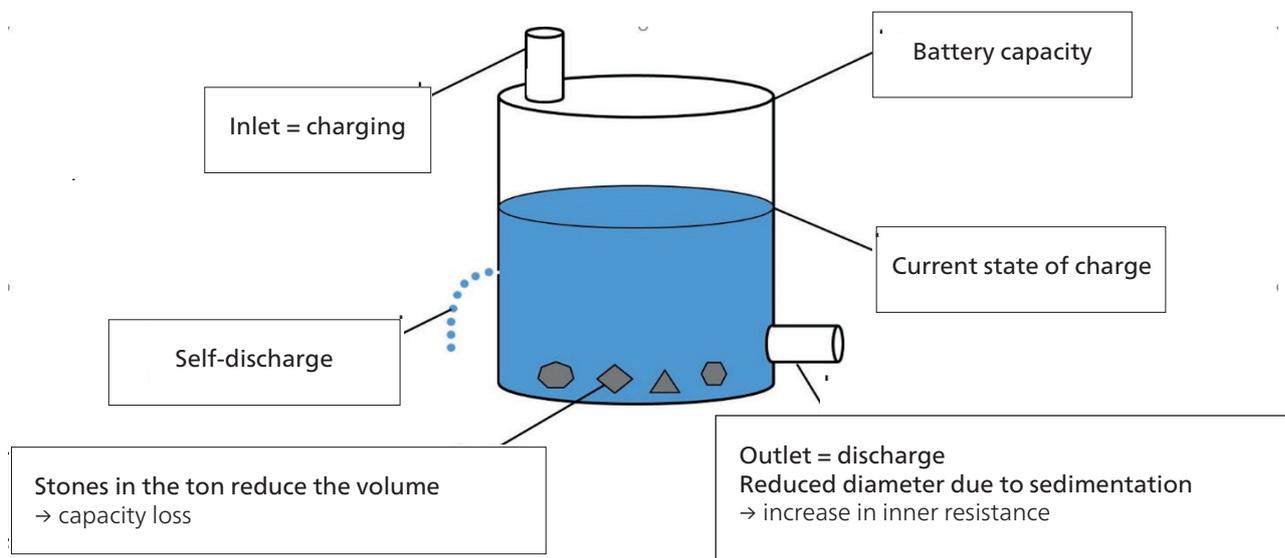
When it comes to using an energy storage system, its current “fill level” is always of interest – be it for evaluating the remaining runtime of a cell phone or a laptop, or with regard to the range of an electric vehicle. If the charging time of a cell phone or a laptop plays a rather minor role, it can be of particular importance in the context of electromobility.

#### Ton Model

Describing the current state of an energy storage system well can be more difficult than it first appears. According to [7], the barrel model serves to illustrate well, as it does a good job of visually describing the most important influential factors during use and, in particular, those

due to aging processes (fig. 3). The model compares the energy storage system with a rain barrel, where the level of the liquid in the barrel represents the current state of charge. The total volume in the new state corresponds to the maximum capacity of 100%. At the bottom of the barrel is an outlet for “discharging” and at the top an inlet for “charging”. The limited diameters of the inlet and outlet illustrate that there is a limit to the speed at which the barrels can be charged or discharged. This limitation corresponds to the internal resistance in the accumulator. Even when the inlet and outlet are closed, the barrel loses fluid over time because it has small holes and is therefore not perfectly tight. These losses represent the self-discharge of an accumulator. Aging of the accumulator is further described by the formation of “stones”. They reduce the usable volume of the barrel and thus the capacity of the energy storage system. Also, the barrel rusts over time, increasing the number of small holes and thus the losses due to “self-discharge”.

With this model, shown in figure 3, the most important processes in the operation of an accumulator can be described. The current state of an energy storage system is also referred to as the “state-of-health”.



**3** Barrel model for illustration of the battery status according to [7]

NGB · Application Note 231 · EN · 1121 · Technical specifications are subject to change.

### Losses During Charging and Discharging

Regardless of the battery status, energetic losses also occur during each charging and discharging process. We all know from our own experience that cell phones or laptops heat up during intensive operation and also during charging. These heat developments represent energetic losses, because the quantities of heat released in this way are not available for actual use through the energy storage system.

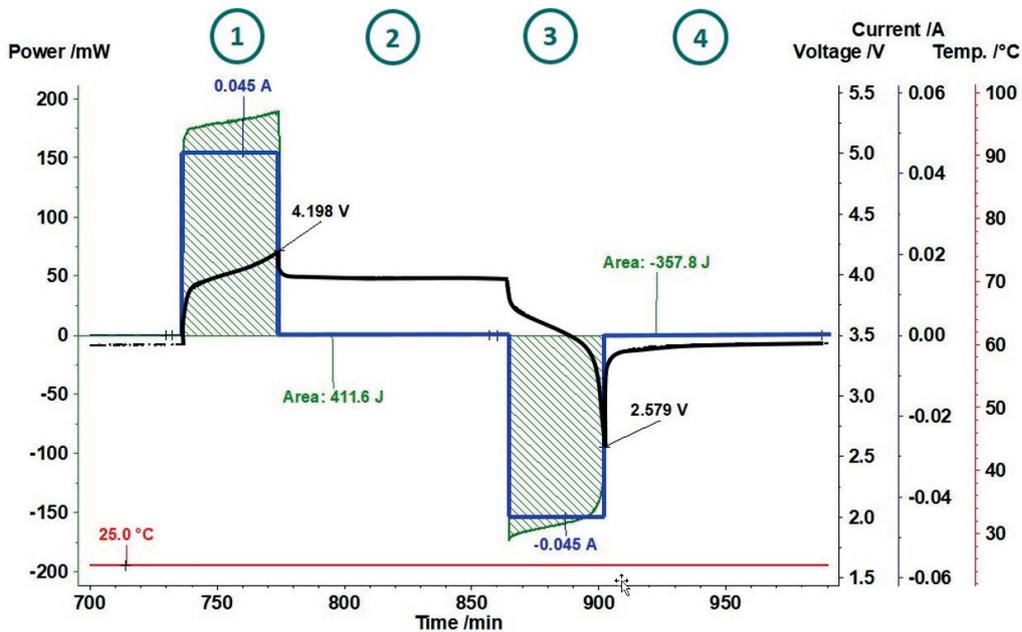
With the help of the sensor in the Coin Cell Module of the MMC (figure 2), these heat losses can be detected and quantified.

### Control of Charging and Discharging Cycles

Lithium-ion batteries are very sensitive with regard to overcharging, as this can easily lead to decomposition of the electrolytes. Therefore, common charging methods usually limit the maximum charging voltage to 4.2 V [7].

Also in this work, the charging and discharging cycles of a lithium-ion cell (LiR 2032) were limited using a cutoff voltage of 4.2 V for charging and 2.5 V for discharging. This results in the cycle shown as an example in figure 4. After a precharge cycle (not shown here), the coin cell is charged at 25°C with a constant current of 45 mA up to a cutoff voltage of 4.2 V ①. In the subsequent relaxation phase ②, the coin cell and the sensor return to thermal equilibrium. The discharging phase ③ is limited by the cutoff voltage of 2.5 V and is again followed by a relaxation phase ④.

The current and voltage signals are transferred from the cycling unit to the NETZSCH Proteus® evaluation software where a power signal is automatically calculated. For determination of the losses during charging and discharging, the invested power and the heat released can thus be determined independently for each partial cycle. This way, it is possible to indicate what proportion of invested energy was released as heat.

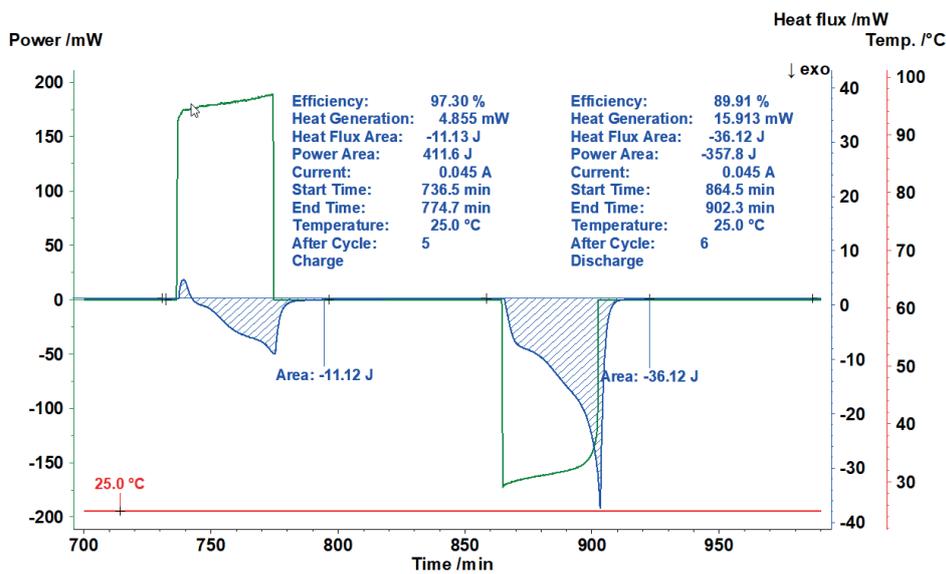


**4** Charging and discharging cycle of a lithium-ion cell (LiR 2032) in the MMC Coin Cell Module at 25°C; temperature (red), current (blue), voltage (black) and power (green)

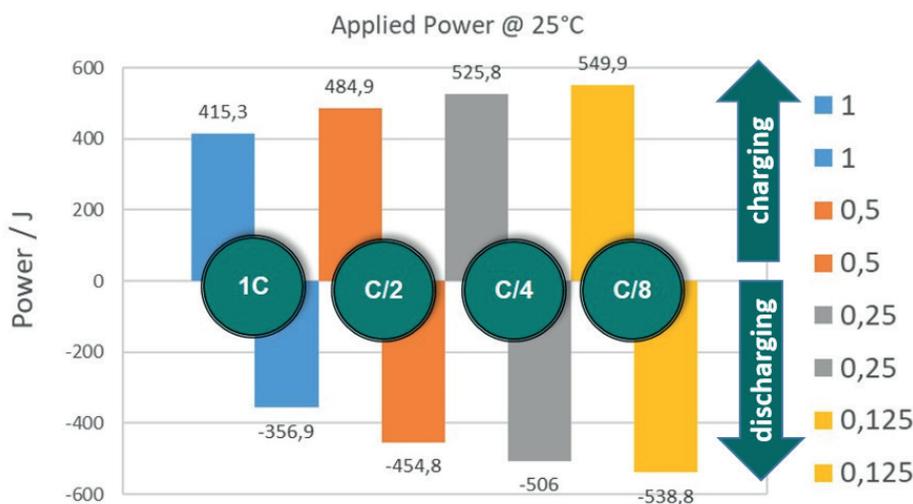
Figure 5 shows how the area evaluation of the heat-flux signal of the charging process automatically calculates the energy invested (here 411.6 J) and puts it into proportion with the heat-flux signal measured (here 11.12 J). This results in an efficiency of 97.3%. For the subsequent discharging, the efficiency amounts to only 89.9% due to the significantly higher heat generation.

### Different Charging and Discharging Rates

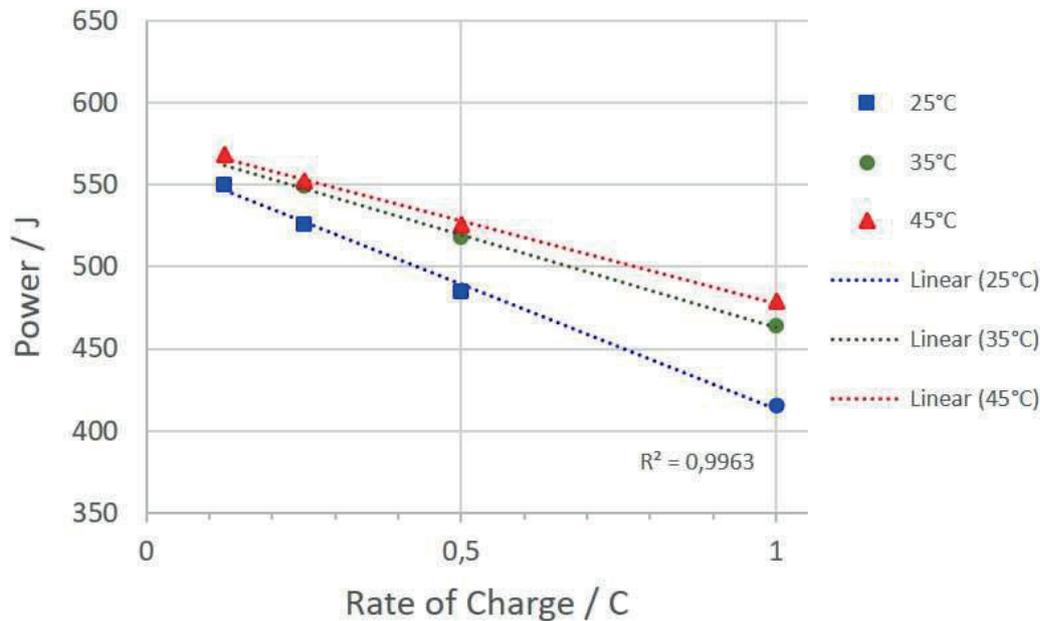
If charging and discharging cycles are carried out at different rates according to the aforementioned shutoff criteria, it can be seen that the energy absorbed by the energy storage system, and thus, of course, the amount of energy available during discharging, depends very strongly on the respective rate (figure 6). If the identical cell (LiR 2032) is charged at 45 mA (C/1), 415 J are absorbed, whereas at a charging rate of C/8 (5.6 mA), almost 550 J are absorbed.



5 Efficiency of a charging and discharging cycle; lithium-ion cell (LiR 2032) in the MMC Coin Cell Module



6 Variation of the charging and discharging rates (1C @ 45mA) (C/2 @ 22.5 mA) (C/4 @ 11.25 mA) (C/8 @ 5.6 mA)



7 Amount of energy in the charging cycles at 25°C, 35°C and 45°C

The temperature at which the accumulator is cycled also has an influence on the amount of energy absorbed and the charging and discharging efficiency. Figure 7 depicts the absorbed energies of the charging cycles at different temperatures.

### Summary

The MMC Coin Cell Module 274 Nexus® was used to investigate a rechargeable LiR 2032 coin cell at different temperatures and different charging rates with regard to the heat thereby occurring. For the charging cycles, an upper and lower cutoff voltage of 4.2 V and 2.5 V were used. The power delivered to the accumulator by the cycling unit during charging can be quantified from the current and voltage signals of the cycling unit. The heat released during this process is directly measured by the sensor of the Coin Cell Module. The ratio of the power transferred to the accumulator and the amount of heat released allows the efficiency for the charging and discharging processes to be determined independently. It has been shown that both the power absorbed and the respective charging and discharging efficiency are strongly dependent on the charging rates and temperature.

### Literature

- [1] Application Note 131, E. Füglein, "Hazard Potential of Decomposition Reactions Using the Example of Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>)"
- [2] Application Note 134, E. Füglein, "VariPhi® – The Patented Immersion Heater for Variation of the  $\phi$ -Factor in Thermal Runaway Tests"
- [3] Application Note 130, E. Füglein, S. Schmölzer, "Epoxy Curing Investigated by Means of the DSC 214 Polyma and MMC 274 Nexus®"
- [4] Application Note 132, E. Füglein, "Screening of Hydrogen Peroxide Solutions by Means of Scanning und ARC Tests"
- [5] Application Note 040, J.-F. Mauger, P. Ralbovsky, G. Widawski, P. Ye, "Coin Cell Cycling in a Novel DSC-Like System"
- [6] Application Note 216, E. Füglein, "About the Calibration of the Coin Cell Module of the MMC 274 Nexus®"
- [7] A. Jossen, W. Weydanz, „Moderne Akkumulatoren richtig einsetzen“, Inge Reichardt Verlag, Untermeitingen, 2006