

Electrochemical-calorimetric studies on different lithium-ion cells

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Abstract

The lithium-ion batteries used in current electric vehicles evidently have reserves. When the capacity in each cell was optimally utilized, more energy could be put in and delivered again. Thus, the driving range of electric vehicles could be significantly increased.

In this work, commercial lithium-ion pouch cells were cycled at varying C-rates under isoperibolic and adiabatic conditions in an accelerating rate calorimeter (ARC) with external battery cycler to investigate their performance and their thermal behavior. A thermal camera was also used to investigate the heat effects and the local temperature distribution during cycling in more details.

Different factors that have influence on the performance of energy storage such as temperature, charging/discharging current and state of charge (SOC) have been studied. The isoperibolic investigations were performed at specific temperatures in the range from 25 to 60 °C. The results show that the applied environmental temperature did not largely influence the battery thermal behavior. Both isoperibolic and adiabatic tests were performed at different charging/discharging rates in the range from C/4 to 3C. The results show a considerable temperature rise with increasing rate. Additionally, the heat capacities and the calorimeter constant were determined to calculate the total generated heat during cycling.

Electrochemical-calorimetric measurements

As kind of clean energy, lithium ion batteries used in electric vehicles are getting more and more attention. Therefore it is important to understand the heat generation and dissipation of single lithium ion cells and packs, respectively, since this is closely coupled to battery performance and safety issues.

Energy balance

The heat generation and heat dissipation in a single cell obey an energy balance [1]:

$$\dot{q}_{Tot} = \dot{q}_{enth} + \dot{q}_{diss} = m c_p \frac{dT_{cell}}{dt} - hA(T_{cell} - T_{env}) \quad (1)$$

where \dot{q}_{Tot} is the total heat generation rate, \dot{q}_{enth} the enthalpy accumulation rate, \dot{q}_{diss} the heat dissipation rate, m the mass of the cell, c_p the measured heat capacity of the cell, h heat transfer coefficient, A the battery area exposed to the environment, T_{cell} and T_{env} the cell surface and environment temperatures, respectively [1].

The heat effect of lithium-ion cells was measured using an Accelerating Rate Calorimeter (ARC) with a battery cycler (internal or external) as seen Figure 1.



Fig. 1: ES ARC, EV+ ARC and Digatron MCT Cell Tester

Isoperibolic and adiabatic studies

In this study, commercial 18650 lithium ion cells (1.6Ah) with LiMn_2O_4 cathodes as well as 20Ah pouch cells with LiFePO_4 cathodes were cycled under isoperibolic and adiabatic conditions in an Accelerating Rate Calorimeter (ARC, THT Company). Isoperibolic condition means that all the heat produced in the cell is dissipated out of the system, so that the environmental temperature is constant. Under adiabatic conditions there is no heat loss in the system and all the heat generated in the cell is used to heat up the cell. This is important because in reality the cell is surrounded with other cells in a battery pack. Figure 2 a) shows for example the experimental results for the cylindrical cell.

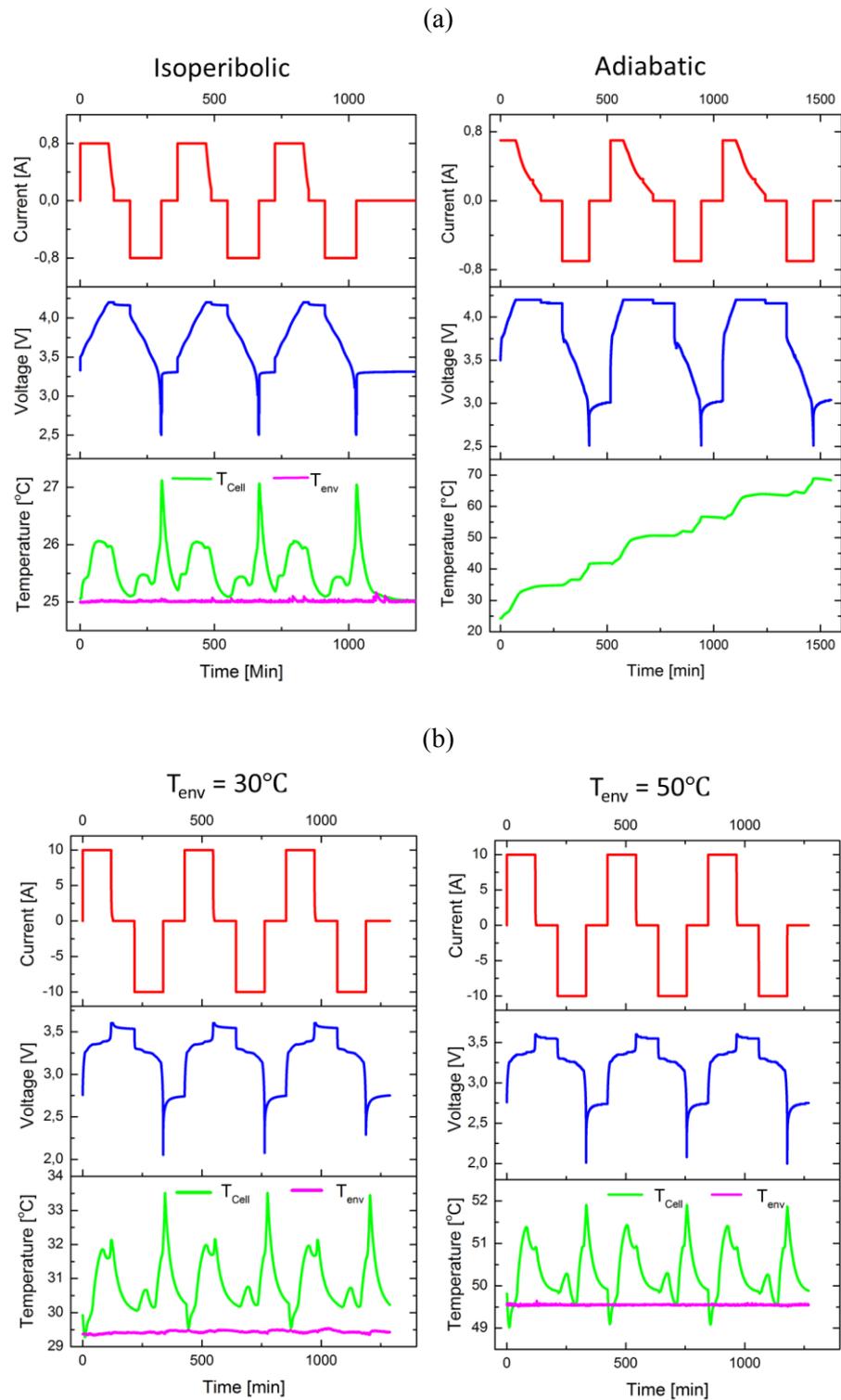


Fig. 2: a) Isoperibolic and adiabatic cycling of the cylindrical cell
 b) Isoperibolic cycling of the pouch cell

During isoperibolic cycling the temperature rise of cylindrical cell is only about 2 °C. Under adiabatic conditions the temperature rise of the cell after one cycle is about 18 °C. In Figure 2 b) under isoperibolic conditions the temperature rise of the pouch cell is about 3 °C at 30 °C and 2 °C at 50 °C. Obviously the environmental temperature did not largely influence the battery thermal behavior.

DC-impedance technique: CIT

In battery modeling the equivalent circuit model (ECM) is commonly used for two purposes: to predict battery performance and to provide state of charge (SOC) estimation in battery management systems [2]. Figure 3 shows a general equivalent circuit model. For the description of this ECM see [3] for more details.

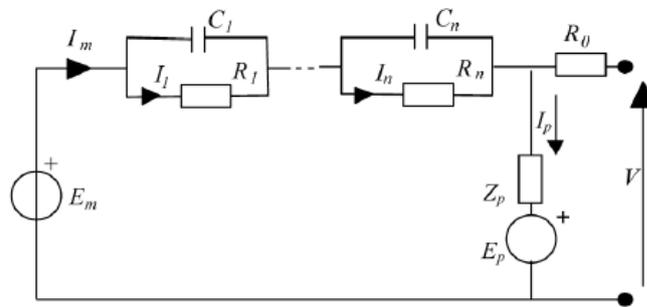


Fig. 3: General equivalent circuit model of an electrochemical cell [2]

The current interruption technique (CIT) is a frequently used tool to provide data for the different elements in the ECM. In the CIT the cell is charged and discharged stepwise by interrupting the current at a certain voltage or after a certain time followed by a defined relaxation time. Lookup-tables are used to model the nonlinear behavior of ECM to extract its system parameters. These lookup-tables can be measured via CIT as described in Figure 4. This pulse provided important information about the open-circuit voltage and the circuit dynamics at the given SOC [2].

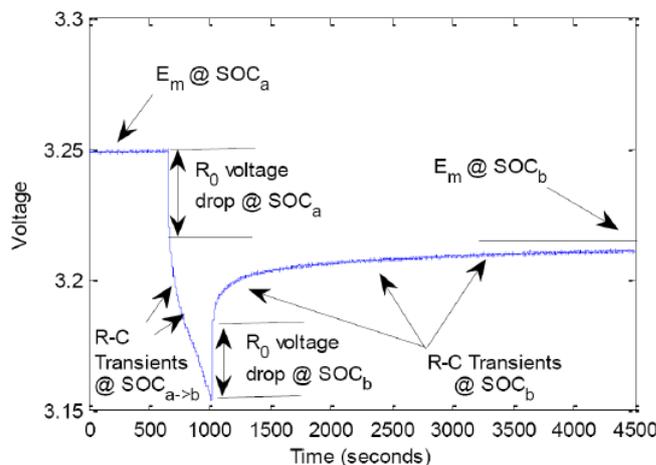


Fig. 4: Pulse discharge tests [2]

In this work the charge and discharge current was $I = 10 \text{ A}$ ($C/2$ rate) for the pouch (20 Ah) cell. After each current interruption, the cell was left to relax for 60 min at open circuit (see Figure 5). The instantaneous voltage drop (V_i) was measured after current interruption, and the cell voltage drop during relaxation (V_{rel}) was also recorded. The instantaneous voltage drop (V_i) is mainly due to the ohmic resistance of the cell and partially due to the concentration polarization. The relaxation voltage drop (V_{rel}) is due to concentration polarization in the liquid electrolyte and in the solid electrode materials. The instantaneous impedance (R_i) and the relaxation impedance (R_{rel}) were estimated using Eq. (2) [4].

$$R_i = \frac{V_i}{I} \quad R_{rel} = \frac{V_{rel}}{I} \quad (2)$$

In Figure 6 a closer look at a single pulse (Fig. 6a)) and at the cell impedance at different points of depth of discharge (DOD) (Fig. 6b)) are shown. The instantaneous impedance was almost identical at the beginning of discharge and a sudden increase was noticed at DOD 0.98, which means the ohmic resistance of the cell increases at the end of discharge. A slight increase with a slight decrease in the relaxation impedance was noticed at DOD 0.90-0.98. This may be due to a phase change in the cathode material or to structural transformation in the anode electrode [4]. There was also a sudden increase in the the relaxation impedance at DOD 0.98. This may be due to the concentration polarization, which usually increases significantly with DOD [4].

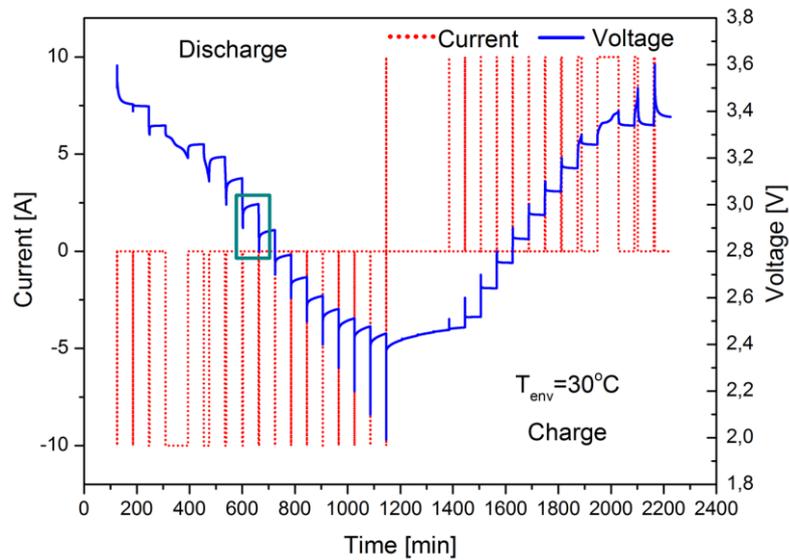


Fig. 5: Schematic of the DC-impedance (current interruption) technique

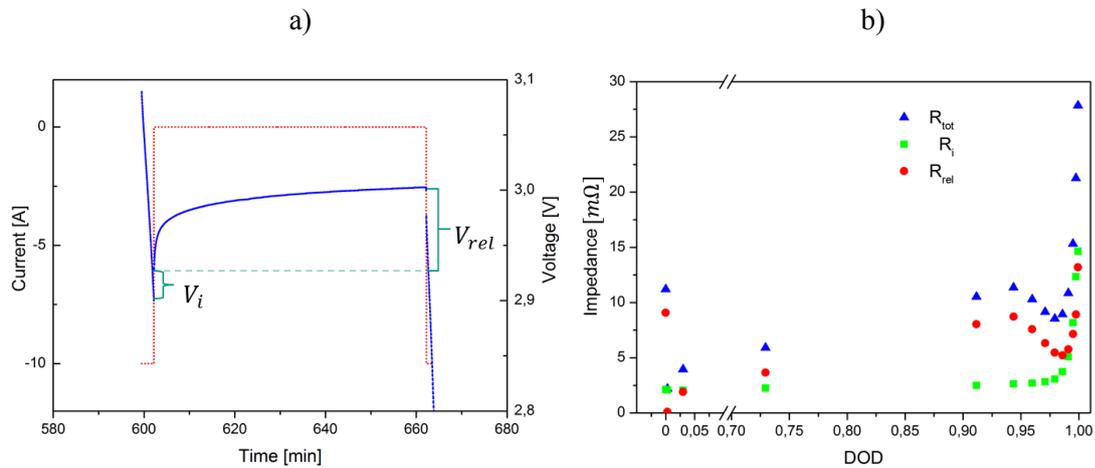


Fig. 6: a) One pulse from the test and b) impedance as a function of DOD

Thermography

Accelerating Rate Calorimeters are reliable and very useful for spot temperature measurement, but for scanning large areas or components, it is easy to miss critical effects. A thermal imaging camera can scan entire components at once – never missing any overheating hazards. In our work, a thermal camera (FLIR X6540 sc, France) was used to investigate the heat effects and the local temperature distribution during cycling in more details. The camera has 640 by 512 pixels and the wavelength range is 3.5 to 5 μm . The camera is connected to a computer to save the thermal imaging using software (FLIR Research IR, FLIR Systems, France). Figure 7 shows the thermal imaging setup for the lithium iron phosphate pouch cell in an environmental chamber (Vötsch, VT³ 4018-S, Germany). The cell was oriented in a vertical configuration and connected to the Digatron MCT Cell Tester. The aluminum packaging of the cells provides a too low emissivity ($\epsilon = 0.09$) for accurate IR imaging. Therefore, the surface of the cell was coated with graphite that has an emissivity of approximately 1.0 to ensure a uniform emissivity. A high emissivity surface effectively eliminates reflections from the object being imaged [5].



Fig. 7: Thermal imaging setup

The cell was thermally imaged at charge/discharge rate $C/2$ at room temperature. Figure 8 shows the thermal images taken at the beginning and the end of the discharge. The cell was fully discharged from 100 % to 0 % SOC. In Figure 8, a rectangle outlines a separate area (Ar1), where the cathode, separator, and anode are physically located. The thermal imaging was almost symmetrical with the maximum temperature at the center of the cell area (Ar1) and minimum temperature at corner. At the end of the discharge the cell has the temperature difference of $1.7\text{ }^{\circ}\text{C}$ ($T_{\max} = 27.8\text{ }^{\circ}\text{C}$, $T_{\min} = 26.1\text{ }^{\circ}\text{C}$), compared to the beginning of the discharge where it is $0.6\text{ }^{\circ}\text{C}$ ($T_{\max} = 21.4\text{ }^{\circ}\text{C}$, $T_{\min} = 20.8\text{ }^{\circ}\text{C}$). So the cell shows relative good temperature uniformity during discharge at discharge rate $C/2$.

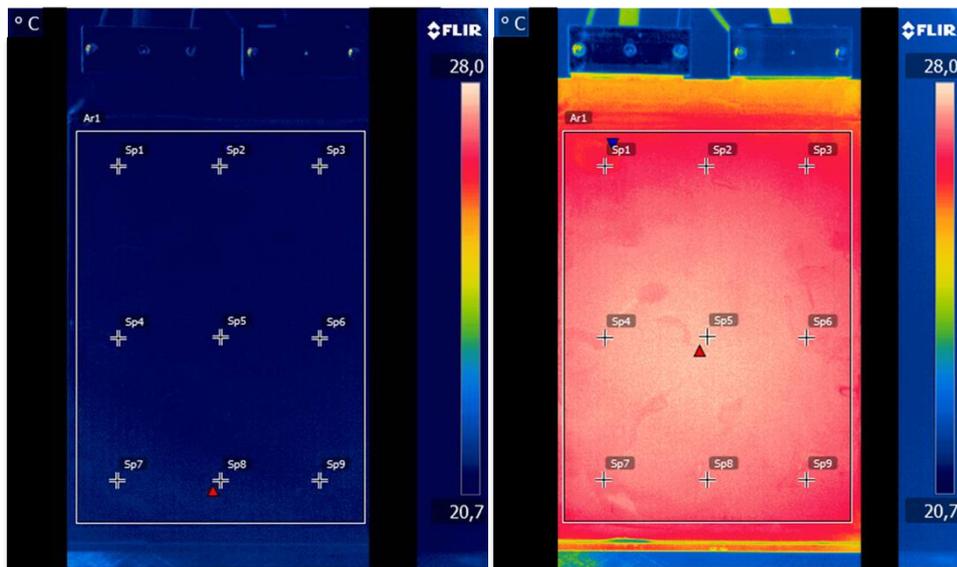


Fig. 8: Thermal imaging at the beginning and the end of discharge

Conclusion and outlook

Experimental results for isoporibolic and adiabatic cycling were presented. The measured data were then applied to the energy balance getting the total heat generated in the cell during cycling. An endothermic effect was noticed at the beginning of charge, followed with an exothermic effect. This is due to the deintercalation of Li ions from positive electrode at lower SOC and at higher SOC ohmic and polarization impedance increase significantly and is greater than the entropic heat effect. The total cell impedance during discharge was defined by using CIT. Its change is well matched with the heat effect of the cell at the end of the discharge. Results of two different methods (ARC and thermocamera) can be compared. In future research the measured temperature data can be transferred into heat data, which can then be used as input data for thermal modeling.

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