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Capacity Decrease vs. Impedance Increase of Lithium Batteries. A comparative study.

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Abstract

In this article the performance of lithium-ion batteries (Li-Ion) over their lifetime is analyzed. Like all batteries Li-Ion are subjected to permanent ageing due to storage and cycling; both reducing their performance in terms of resistance and capacity. Electrochemical impedance spectroscopy (EIS), hybrid pulse power cycles (HPPC) and coulomb counting are used in this article to reveal those changes. It is shown that the systems impedance is rising and the capacity is fading with ongoing ageing. These changes are observed and analysed for trends. At several frequency regions an interdependency between the rise in impedance and the fade in capacity can be detected. Based on this interdependency, a method using impedance values to calculate the actual cell capacity is introduced and finally validated by measurements.

Keywords: Li-ion battery, ageing, impedance spectroscopy, battery management

Introduction

Lithium based batteries are predominantly employed in mobile applications nowadays but they also are the most propitious candidate for future use in automotive power supply [1]. Successful long-term operation of this new type of applications with their higher lifetime ($\geq$10 years) [2] will require precise knowledge of the current battery condition. As the operational range of an electric vehicle is among the major concerns of potential customers regarding electric vehicles [3], simple and reliable methods to predict the power capability and the remaining energy content of a battery pack have to be found. The method proposed in this work will help to simplify on-board performance analysis of Li-Ion as it allows to estimate the current cell capacity based on a sole impedance measurement or current pulse respectively.
In literature many publications e.g. [2, 4–6] can be found where an increase in impedance and a decrease in capacity of the cell are assigned to ageing. The progress of the slopes shown in [7–9] indicate a traceable correlation between these two performance values. A method using this dependency for monitoring of lead acid batteries was already developed in the middle of the 80s [10].
Hence, in this work the dependency between impedance and capacity is now investigated for Li-Ion chemistry too. First, the cells, the test equipment and the measurement procedure are introduced. Second, the results are presented and analyzed. Third, a discussion of the results with focus on the link between impedance and capacity is made. Finally, a conclusion and future perspectives are given.

Experimental Setup

The cells tested were six brand-new manganese spinel cells. Three cells of the type $LiMn_2O_4$ (LMO) and three cells of the type $LiCo_xNi_yMn_zO$ (NMC) were investigated; more detailed operating values can be seen in Table 1. Prior to the measurement the cells are preconditioned to ensure that forming processes are finalized or rather negligibly small; meaning if the capacity

Table 1: Operating values of investigated battery according to manufacturer.

	LMO	NMC
Nominal Capacity	5.2 Ah	37.8 Ah
Min. Voltage	2.8 V	2.7 V
Max. Voltage	4.2 V	4.1 V
Case	Pouch	Cylindrical

Table 2: Operation profiles for the investigated cells.

	LMO	NMC
SOC range	100-0%	95-20%
Profile	Full cycles	PHEV profile
Max. current	2 C	5 C
Test temp.	23 °C	45 °C

change is less than 3 % during conditioning the cells' chemistry is considered to be fully mature and the preconditioning is aborted. Minimum three to maximum five full cycles with a 1 C discharge and 1 C charge are applied to the cells. The average charge of the cells with the same chemistry withdrawn during the last cycle is taken as the nominal capacity of the cells. The profiles for cycling are adapted to these values.

After forming again a capacity measurement and an impedance measurement (LMO with EIS, NMC with current pulses) at several different state of charge (SOC) levels were taken using the new values for the nominal capacity. Then the LMO cells were operated with 200 ageing cycles according to Table 2 and the NMC cells were constantly cycled for a period of 2 weeks according to Table 2. After cycling the cells were characterized and the sequence started over again. The EIS measurement for LMO was done in galvanostatic mode with a current of 0.05 C to operate the cell in a quasi-stationary mode (for details cf. [11]). The investigated frequency range was from $f_{max} = 5\,\mathrm{kHz}$ down to $f_{min} = 5\,\mathrm{mHz}$. The current pulses for NMC were done with a current of 2 C and the values were taken after 1 s at SOC 50 %; the capacity was measured with a current of 1 C.

The PHEV profile was taken from [12, 13] and adapted to the average measured cell capacity during forming. The charging was first performed with a constant current and then with a constant voltage phase to the according end of charge voltage with a shut off current of 0.05 C.

The profile for the LMO cell exploits the whole usable voltage range considering the different ageing effects at different voltage levels and encouraging cell ageing [2, 6], while the profile for the NMC cells avoids regions of saturation or depletion where the ageing takes place rapidly. Further the LMO cells were cycled at 23 °C while the NMC cells were cycled at 45 °C. These different setups help to observe whether the strategy developed in this paper can be used for various operating scenarios.

Results

Fig. 1a illustrates the decreasing cell capacity development of the LMO cells with ongoing cycles. Fig. 1b depicts the impedance curves of the LMO cells at their begin of life (BOL) and end of life (EOL). The measurements were made for several SOC levels. To illustrate the changes in impedance during the ageing process a SOC level of 50 % was chosen; other SOC levels have been investigated and show similar behavior as well. The SOC level was adapted to the current cell capacity.

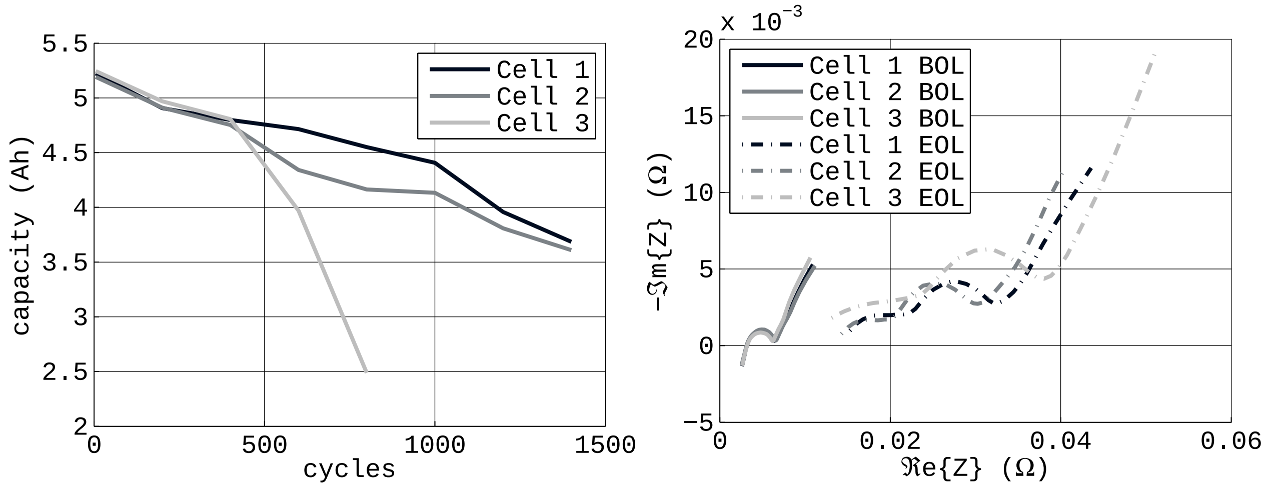
For the NMC cells the same trends can be observed but the results are not shown here for the reasons of brevity.

Discussion

In this section first the impedance and the capacity development are discussed and second the cell degradation is examined.

Impedance and Capacity Development

As mentioned before the impedance increases and the capacity decreases with ongoing cycles. Based on this observation the frequency points of the impedance slope on the different states of health (SOH) of the cells were checked to determine whether they could provide information about the available charge amount. A monotone increase in impedance which takes place over the whole SOC range for all frequencies was found. SOC levels in the middle range (between 20 and 80 %) show a moderate and predictable growth as no saturation or depletion effects are influencing the process. In Fig. 2a (top) the magnitude of the impedance is outlined dependent on the actual cell capacity at the according SOH for the LMO cells. Also a linear fit of all the three cells is indicated. Fig. 2a (bottom) shows the relative deviation between the original values and the fitted values. Even the slope of cell 3 where ageing takes place much faster the dependency between capacity and impedance is comparable to the other cells which show slower ageing. It can be seen that a maximum deviation



(a) (b)

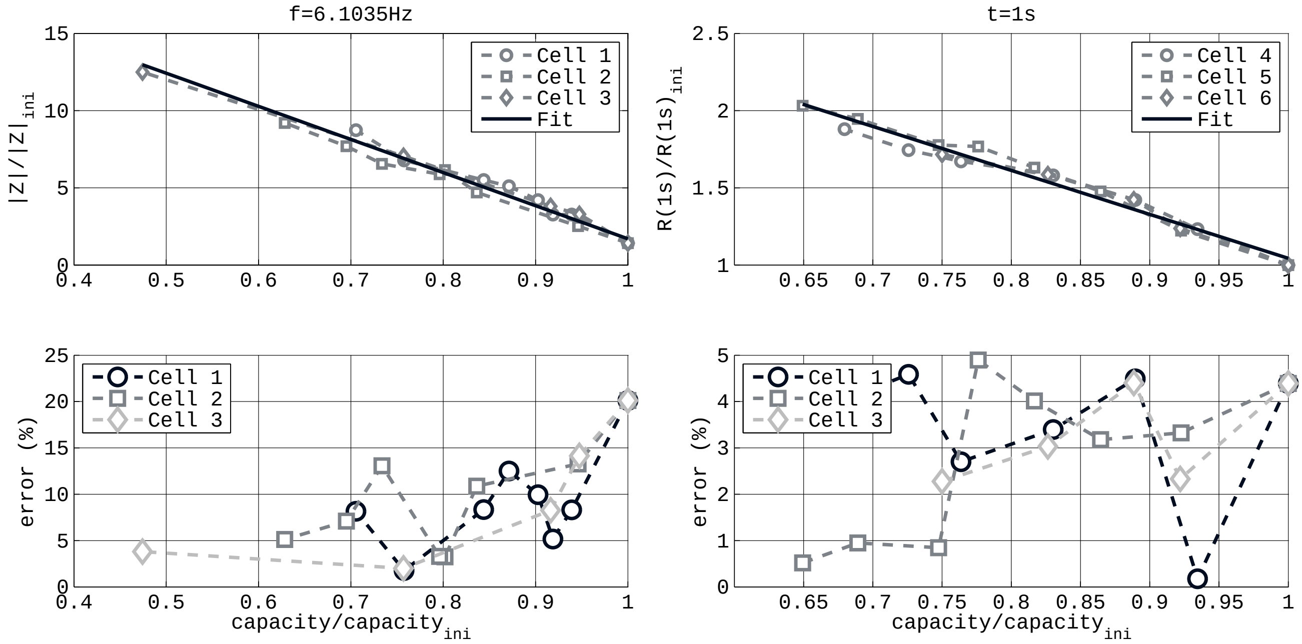
Figure 1: Capacity developement of the LMO cells with ongoing cycles (a). Impedance curves for LMO cells measured at BOL (solid) and EOL (dashed) at SOC 50 % (b).

of 20 % is produced at the beginning while the error decreases to $\leq$ 5 % for values with advanced ageing.

As expected there is an inverse proportional correlation between the decrease in capacity and the increase in impedance. This is valid for all the examined SOC levels. Thus a prediction of the actual capacity can be made by an impedance measurement, producing an error of maximum 20 % for measurements close to the cells' BOL. Near the cells' EOL where the estimation of the capacity becomes more important the error of the method is significantly decreased to $\leq$ 5 %.
This observations are supported by the results of the NMC cells. Fig. 2b (top) shows the resistance over the capacity measured for the NMC cells every two weeks. Also a linear fit of all the three cells is indicated. Fig. 2b (bottom) shows the relative deviation between the original values and the fitted values. Similar to the LMO cells a constant, almost linear relation between these two performance values can be found. For the NMC cells measured with current pulses an error $\leq$ 5 % is produced when the capacity is calculated by using the impedance value. This could be the result of the higher currents used for this measurement or because the temperature conditions during the measurement of the LMO cells were not as stable as they were for the NMC cells.
The linear behaviour of the slopes observed for both cell types are of interests, as the cells have been cycled in different SOC windows, with different current profiles and at different temperatures. Thus knowledge about the cell impedance at certain SOC levels allows to draw conclusions of the current capacity of the cell.
One advantage of this method is that the cell does not have to be fully discharged for the estimation. The cells' impedance to capacity change ratio can be measured at the outset in order to gain the necessary characteristics, and this data can thus be used for the application. The frequency investigated ($f = 6.1\,\mathrm{Hz}$) and also the measurement current ($i = 250\,\mathrm{mA}$) can be applied within a μC based battery management system (BMS). When the battery is idle the BMS can execute a measurement with relatively low energy consumption or can extract the required data even during normal operation of the vehicle [14]. The values for the current pulse method could be gained from the BMS during the acceleration of the electric vehicle. Using the impedance data, a SOC estimation can also be performed and the BMS strategy can be adapted to the current working conditions.

Cell Degradation

The LMO cells were cycled to their EOL ($C_{EOL} \leq 0.5\,C_{BOL}$, $|Z|_{EOL} \geq 12\,|Z|_{BOL}$). At these stages the cell degradation is in an advanced state. Fig. 3 shows a picture taken after removing the cell at the end of the test where a structured surface is clearly visible. All the three tested pouch cells show this phenomenon. This stained surface could be caused by dendrite or spinel growth, reducing active surface and consuming lithium both affecting the cell performance [6]. In contrast, the cell packing is still close-fitting, so no gases and no volumetric changes occurred. A post mortem analysis has to be performed to get more details.



(a) (b)

Figure 2: Dependency between capacity and impedance magnitude for LMO cells (a) and NMC cells (b) over cell life time (solid) with according linear fit (dashed) (top) and the deviation of the original curves to the linear fit (bottom).

The NMC cells are still under test, so no statement about possible cell degradation can be given at this time.

Conclusion and Outlook

The applications for Li-Ions' are increasing and thus is the number of operated cells. Ageing still plays a major role in the performance behavior of LiIo and an on-board prediction of this indicator helps to improve the BMS.

In this article EIS and current pulses were used as non-destructive methods to investigate encapsulated Li-Ion cells. Furthermore it was shown that the impedance behavior and the capacity are negatively effected with rising cycle number. A correlation between these two values was found and a method to use their dependence for a capacity determination through the observation of the impedance of a single frequency was found. Finally, how this method can be integrated in a modern BMS was presented.

In future work, cells using different electrode materials, electrolytes, etc. should be examined to expand the stated theory. In addition as a major part of the product-life of Li-Ion batteries in EV application is standstill time, also the impedance vs. capacity behavior of batteries during storage tests has to be investigated in more detail. The progress of the data shown in [8] suggests that the proposed method can be extended to this application as well.

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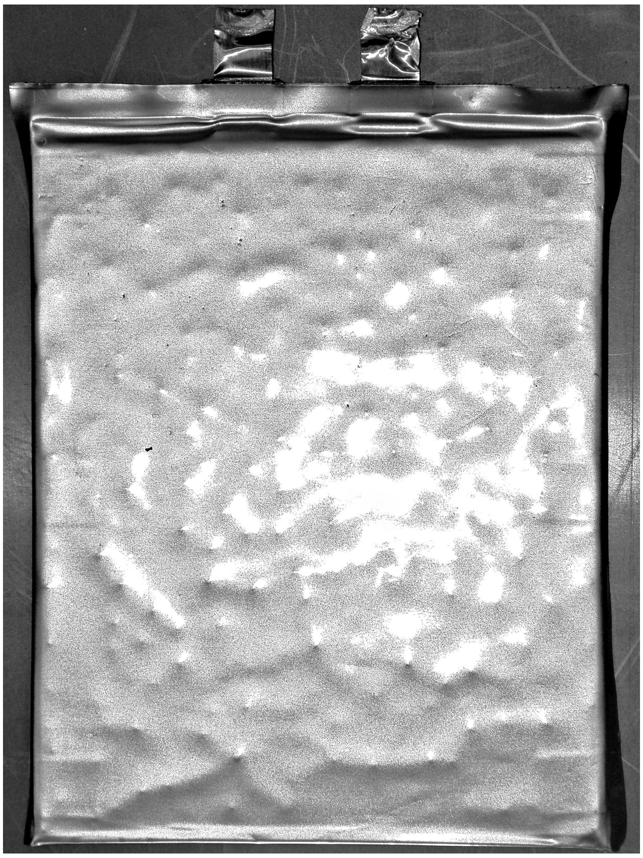

Figure 3: Pouch cell at EOL after the cycling test.

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