Lifetime Analyses of Lithium-Ion EV Batteries

Peter Keil, Simon F. Schuster,
Christian von Lüders, Holger Hesse
Institute for Electrical Energy Storage Technology
Technical University of Munich (TUM)
Arcisstr. 21, 80333 Munich, Germany

Raghavendra Arunachala, Andreas Jossen
TUM CREATE Limited,
1 CREATE Way, Singapore 138602

***Abstract*—Most electric vehicles use lithium-ion batteries as energy storage system. As this battery technology shows degradation during service life, lifetime analyses are of interest to understand aging phenomena and to optimize batteries and their operation. For these analyses, we have carried out laboratory aging tests. Test conditions were defined according to the three main operation types: inactivity, driving and charging periods. The results show that battery lifetime depends on many operation parameters and, for different types of operation, different aging characteristics are observed. One of our findings is that real battery aging in the field is similar to calendar aging. Calendar aging has a substantial impact on battery life due to the prevailing inactivity periods. Charging of the batteries also has a strong influence on the achievable lifetime. Especially for high charging rates and low temperatures, the severe aging mechanism lithium plating is known to emerge as a result from increased anode over-potentials. The phenomenon of nonlinear aging, which describes an accelerated aging rate at residual capacities of approximately 80%, is closely related to lithium plating. A reduction of the charging current can postpone or even avoid nonlinear aging. We propose a new charging method that keeps the charging time short and simultaneously avoids accelerated aging. The adaptation of the charging current is correlated to the aging state of the battery.**

***Index Terms*—Lithium-ion battery, lifetime, charging method, calendar aging**

I. *Introduction*

Lithium-ion batteries (LIB) are the battery technology most commonly used as energy storage system in electric vehicles (EV) and plug-in hybrid EV. High energy density, reasonable specific power and fast cost reduction within the last few years are the reasons for the usage of LIB in EV applications. However, costs of EV batteries are still high and have a strong impact on the overall vehicle costs. Thus, further cost reductions are necessary and the lifetime of the battery should be as high as the expected vehicle lifetime. As a LIB is an electrochemical system, side reactions occur inevitably, which lead to capacity fade over time.

Even when the vehicle is not used (i.e. is parked), traction batteries suffer from aging. Many investigations have been performed regarding calendar aging. For standard lithium-ion cell technologies, such as lithium-cobalt-oxide (LCO), the relations between state of charge (SoC) and aging rate are well known. In state-of-the-art EV batteries, blended active materials, such as nickel-manganese-cobalt (NMC) and nickel-cobalt-aluminum (NCA) oxide, are used, resulting in different relations between SoC and aging rate.

Additional aging is caused by driving operation and EV battery charging, which are, in turn, largely determined by the user's way of operating the vehicle. Table 1 shows the average travel distance and the number of trips per day and person for selected European countries [1]. Within the same report, the average driving duration per car and day is reported to be about 1 h. For these cars, the driving duration is about 4-5% of a day and the daily cycle depth is in the range from 6% to 31%. In the following, 20 h per day of battery inactivity, 1 h of driving operation and 3 h of charging are assumed to represent an average usage scenario.

Table 1: Average number of trips and average travel distance per person and day in Europe [1]

Country	Average number of trips/person/day	Average travel distance in km/person/day
BE	3.0	--
DK	2,3	30.1
DE	3,5	38.5
ES	1,9	--
FR	2,9	35.3
LV	1,9	8.7
NL	3,4	33.6
AT	3,0	28.1
FI	2,9	45.8
SE	2,8	44.2
UK	2,8	29.9
NO	3.1	37.0
CH	3.6	47.6

For a better understanding of battery aging in EV, a concise review of battery aging behavior and mechanisms is given in the next section. In the subsequent section, the results of our investigations on battery aging are presented for the three operation modes (driving, charging and inactivity). Finally, a new charging method derived from the findings of the conducted charging experiments is presented.

II. *Review of Lithium-Ion Battery Aging*

As already mentioned, LIB suffer from calendar and cyclic aging. Consequences of aging are, basically, a loss of capacity and power capability with the latter originating from an increase of impedance. The reasons for aging can be divided into three groups, namely the loss of active materials, loss of usable lithium and deteriorated ionic kinetics [2]. The latter mainly results from passive layer growth, which in turn originates from electrolyte decomposition.

The evolution of passive layers, i.e. the solid electrolyte interphase (SEI) at the anode and the solid permeable interphase (SPI) at the cathode, takes on a key role regarding the aging of lithium-ion cells [3]. As the thickening and reconstruction of these layers occurs under the consumption of active lithium, there is a direct correlation to capacity fade and impedance increase [4, 5].

To understand the aging of lithium-ion cells is complex with regard to the quantity of distinct, partially interacting, aging mechanisms. Besides of the evolution of the aforementioned passive layers, the most relevant mechanisms are: irreversible structural changes in the cathode active material; loss of particle-to-particle or particle-to-collector bonds as a result from intercalation induced volumetric changes in the active materials; lithium plating. For an in-detail explanation of these mechanisms, the reader is hereby referred to [4-6].

As large cells show a stronger inhomogeneity in temperature and current distribution, the cell size and cell design have an impact on lifetime [7].

III. *LIFETIME ANALYSES*

To analyze the lifetime of lithium-ion EV batteries, two types of cells were investigated in independent laboratory tests. In addition, two traction battery packs were examined which had been used for approximately three years in the field. Thus, cells aged in laboratory tests could be compared to those aged in practical usage. The investigated EV cells were of the same type as cells used for the laboratory charging experiment.

A. Investigated Lithium-Ion Cells

For the laboratory tests, we selected two different types of cells, which comprise either NMC//graphite or NCA//graphite as active materials. Today, these two chemistries are most commonly used in EV applications. Table 2 lists required specifications of the investigated cells.

Table 2: Specifications of investigated cells

	NMC//graphite	**NCA//graphite**
Form factor	18650	18650
U_N	3.7 V	3.6 V
C_N	1.95 Ah	2.8 Ah
$I_{charge,max}$	1C	0.5C
Weight	43 g	45 g
Specific energy	170 Wh/kg	220 Wh/kg

B. Calendar Aging

As inactivity periods dominate during the EV service life, calendar aging is of high importance for the lifetime of an EV traction battery. Calendar aging strongly depends on temperature and SoC. In most standards, calendar aging is simply measured at full SoC and only a single defined temperature, e.g. 40 °C. In practical operation, the temperature can vary in a wide range; the SoC is a parameter that is influenced by the operation and the charging regime.

In our laboratory tests, we investigated the calendar aging of the NCA//graphite cells at different SoC and at 10 °C, 25 °C and 40 °C. At controlled temperature conditions of 25 °C, the capacity was measured periodically during the storage experiment. During the storage periods, the cells were in open circuit condition.

Figure 1 shows the results after 18 months of storage for eight different SoC. Especially temperatures above 25 °C accelerate calendar aging. At 40 °C, the calendar aging shows approximately a doubling compared to 25 °C for the entire SoC range. Moreover, the SoC influences the calendar aging in a nonlinear characteristic: SoC values of 60% and above have caused much higher capacity fades than SoC values below 50%. Moreover, the rate of calendar aging decreased with time. Hence, the aging rate in subsequent storage periods is lower than in the initial storage period. The averaged aging rate for the first 18 months of storage was up to 0.55%/month for 40 °C and up to 0.3%/month for 25 °C. For the cell type examined, a calendar life of more than ten years is expected.

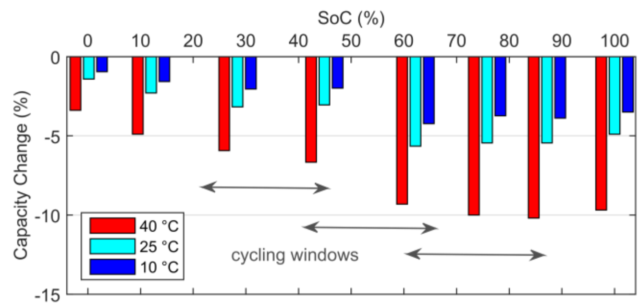

Figure 1: SoC-dependent capacity fade after 18 months of storage for the investigated NCA//graphite cell. The double arrows illustrate the three operating windows at low, medium and high SoC (see section *Aging by Driving Operation*).

C. Aging by Driving Operation

In addition to calendar aging, the traction battery of an EV is stressed by the driving operation. To investigate the aging effects that are caused by the driving operation, the NCA//graphite cells were examined with a dynamic load profile which was derived from the US06 highway drive cycle. The dynamic load profile was computed using a vehicle simulation model [7]. In our laboratory tests, this load profile was repeated two times before the cells were recharged again to their initial SoC. This led to 20 min of discharging and a cycle depth of 25%. The charging of the cells was performed with 0.25C, which is a moderate charging rate resulting in a charging duration of approximately 1 hour. As the calendar aging tests revealed a strong impact of the SoC on aging, we conducted the cycling tests at a low, a medium, and a high SoC range. The SoC ranges were defined by the charging voltage of the constant current charging procedure, as illustrated in Figure 2. The repetitive cycling procedure was performed with different cells at 10 °C, 25 °C and 40 °C to identify the impact of temperature on aging during EV driving operation.

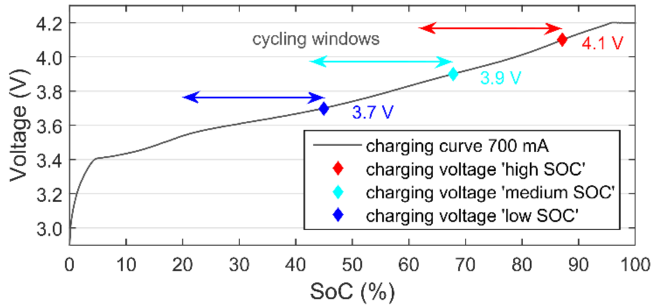

Figure 2: Cycling windows for the investigation of aging caused by the driving operation. [8]

Every 400 test cycles (about every 28 days), the cycling procedure was interrupted for a capacity test. As each discharging and charging cycle had a cycle depth of 25%, the test intervals between two capacity tests corresponded to 100 equivalent full cycles (EFC). Based on the assumed vehicle parameters and battery sizing, this represents a driven distance of about 10,000 km [8]. Figure 3 shows the capacity development for the different SoC ranges and temperatures.

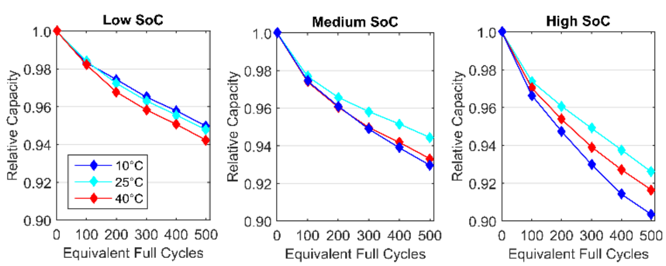

Figure 3: Aging caused by vehicle operation depending on SoC and temperature. [8]

After 500 EFC, representing a driven distance of about 50,000 km, the cells exhibit a capacity fade between 5% and 10%. The capacity fade increases with higher SoC, which is similar to the findings for calendar aging. At low SoC, the lowest capacity fade is observed for all temperatures. The influence of temperature depends notably on the SoC range. An increase of the temperature results in accelerated aging at low SoC. At medium SoC, the degradation at 10 °C is comparable to 40 °C; both capacity curves lie below the capacity curve of 25 °C. At high SoC, 25 °C provides again the best cycle life and the capacity degradation at 10°C is even faster than at 40 °C. Hence, low operating temperatures become more critical with increasing SoC.

To optimize the lifetime of a lithium-ion traction battery, it is beneficial to operate the battery at low and medium SoC. A full charging of the battery should only be performed, when the maximum driving range is really required. Charging the battery right before driving can also help to reduce the times of high SoC, in which increased calendar aging leads to an accelerated capacity fade. At higher SoC, it is advantageous to keep the battery temperature close to 25 °C during operation, as higher and lower temperatures led to accelerated battery aging. These results agree well with the findings in [9].

D. Aging by Charging

Regarding the third operation mode, i.e. battery charging, the aging mechanism lithium plating must be avoided by all means, as its occurrence may even lead to reduced battery safety [10]. Generally, the occurrence of lithium plating is provoked by low temperature and high charging rates, as these parameters both lead to increased overpotentials at the anode. If the anode potential drops below the critical value of 0 V vs. Li/Li^+, the lithium ions partially cannot be intercalated but metallic lithium is plated instead at the anode's surface [11]. Thus, in contrast to inactivity periods, where mainly calendar life limits reachable battery service life, low temperature is critical during EV operation. The menace of lithium plating can effectively be reduced by battery temperature conditioning or optimized charging strategies like boost charging (reduction of current rate at high SoC) [12-14].

However, lithium plating could be identified as the main cause of the phenomenon of nonlinear battery aging, which is often observed at residual capacities of approximately 80% [6]. For a combination of charging rate and temperature which is yet suitable for new cells, this implies the possibility of sudden occurrence of lithium plating at a certain state of aging. Figure 4 depicts the effects of the charging rate on the occurrence of the phenomenon of nonlinear aging for the investigated NMC//graphite cell. For the cell charged with the maximum rate of 1C, nonlinear aging seems to start already from the beginning, whereas for the minimum rate of 0.2C, the phenomenon is not observed at all within the experiment duration. Reducing the charging rate from 1C to 0.5C, the occurrence of nonlinear aging can be delayed for approximately 500 EFC.

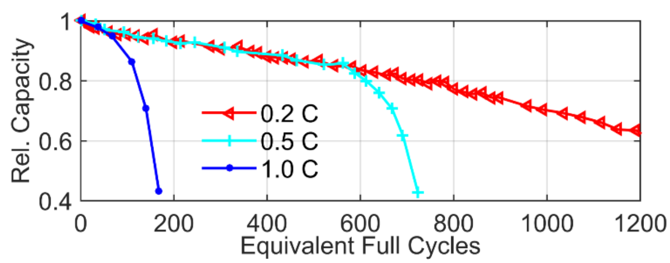

Figure 4: Capacity development vs. equivalent full cycles depending on the charging rate of investigated NMC//graphite cells. [18]

Common explanations for in-the-field aging of EV batteries are calendar aging for rest periods and (linear) cyclic aging for operation periods (both for discharging and charging). Additionally, for low current rate operation, time-controlled aging mechanisms and thus calendar aging are assumed to prevail [15]. Measurements of two traction batteries of the same EV model revealed a slightly advanced aging progress for a car with a higher mean temperature (stress factor of calendar aging) as well as a higher mileage (stress factor of cyclic aging) [16]. However, if a capacity fade of 2% is assumed per year of EV operation, the aforementioned residual capacity of 80% (for which nonlinear aging is observed to occur) is reached after 10 years which also corresponds to a generally expected EV lifetime. Thus, with regard to the expected traction battery life, nonlinear aging characteristics might rather be an issue for reuse concepts of EV traction batteries than for EV application itself [17]. Additionally, nonlinear aging is unlikely in practical EV as e.g. the battery management system (BMS) limits the cells' end of charging voltage [6]. In the next section, an improved charging method is proposed to retard or even avoid nonlinear aging characteristics.

IV. *Improved Charging Method*

Battery charging is commonly conducted using a two phase charging method, as is depicted in Figure 5: During the initial constant current (CC) phase, the battery is charged with the current I_{ch}. Voltage will follow the battery's open circuit voltage (OCV) curve superimposed by overpotentials. At time t_1, when the end of charging voltage is reached (U_{ch}), the BMS switches to a constant voltage (CV) charging phase, where U_{ch} is held constant, while the charging current is continuously reduced. The second phase is aborted at time t_2, when the threshold current I_{end} is reached.

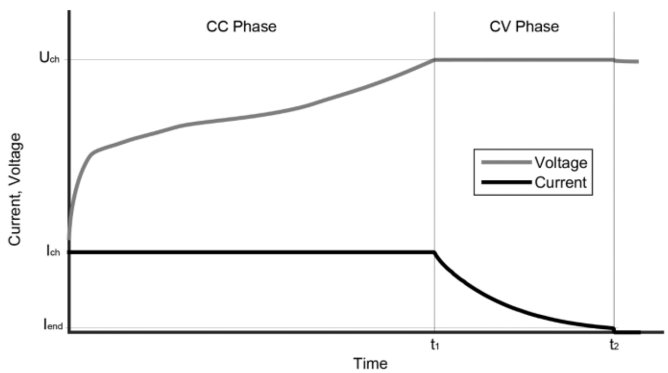

Figure 5: CC-CV standard charging procedure for Li-ion batteries. [18]

As the CC-CV charged cells which were shown in Figure 4 suggest the possibility of retarding nonlinear aging by CC-reduction, a two-step charging current adaptation method has been examined. **Fehler! Verweisquelle konnte nicht gefunden werden.** a) and b) show the capacity and charging rate developments of CC charged cells. The charging current I_{ch} depicted in red (in contrast to the cyan curve) is reduced from 0.5C to 0.2C shortly before the occurrence of nonlinear aging. Hence, nonlinear aging has been avoided by this two-step charging current adaption. However, to do so, perfect foresight of capacity development is required, which is usually not possible in the field. In the field, the proposed method is relevant for reuse concepts of aged traction batteries (in so called second life applications) [17,18].

To further refine the proposed charging method, the charging current I_{ch} is continuously adapted with regard to the battery's current state of aging:

$$I(Q)=I_{charge,max}\cdot(1-\delta\cdot C_{loss}(Q)/C_0\ )$$

Therein, C_0 denotes the initial capacity, C_{loss} the capacity loss observed for the cell after a certain amount of charge throughput and δ a cell-specific adaptation factor, which is varied hereafter with δ=1,2,4.

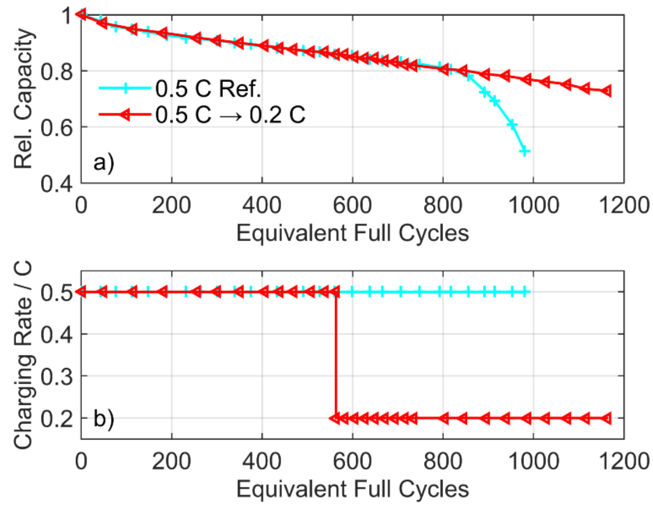

Figure 6: a) Capacity development and b) respective charging rates vs. equivalent full cycles for the proposed "Two Step Charging Current Adaptation" method and its reference test case. [18]

As can be seen in Figure 7 a), the reference case of high CC charging (green curve) provokes nonlinear aging after only about 100 EFC. Whereas the effect of nonlinear aging can only be attenuated by the test cases of δ=1 and δ=2, an adaptation factor of δ=4 effectively suppresses the critical aging phenomenon within the experiment duration.

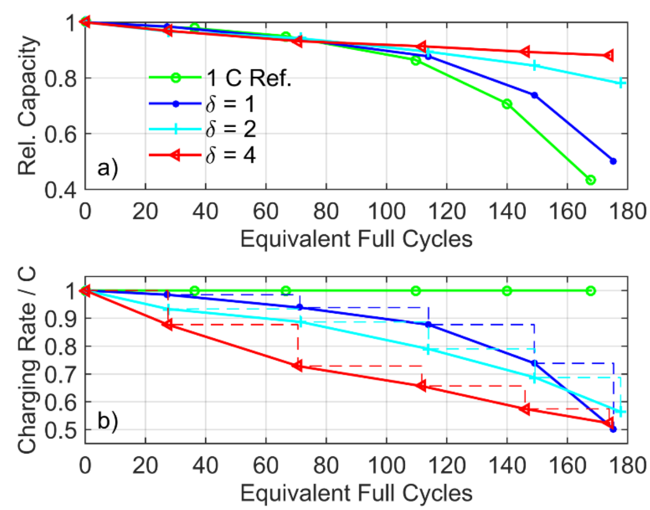

Figure 7: a) Capacity development and b) respective charging rates vs. equivalent full cycles for the proposed "Continuous Charging Current Adaptation" method and its reference test case. [18]

Interestingly, regarding the test case with the highest adaption factor δ=4 in Figure 7 a) and b), it does not only result in the best capacity retention, but – in the long-term - will also allow to keep charging times shorter when compared to the other adaptive charging approaches presented herein: After approximately 10% capacity fade (at 170 EFC), the charging rate has been reduced to 0.6C meeting with the rates of distinct test cases, which, however, already suffer from pronounced capacity fade. An extrapolation based on the assumption of continued linear aging would lead to an estimated charging rate of 0.4C at a residual capacity of 85%.

V. CONCLUSION

Aging of li-ion batteries in EV applications is caused during the three operation modes driving, charging and resting. During resting periods aging is accelerated with high temperatures and high SoC. While driving the SoC has the similar influence, however low temperatures result also in an increased battery aging. Especially driving at high SOC in combination with low temperatures is not recommended. A temperature of 25 °C results in highest lifetimes during driving.

The charging current of the CC-CV charge method has a strong impact on the battery lifetime, too. Higher charge currents result in shorter lifetime. A charge currents above a certain limit cause li-plating at the anode resulting in a fast and nonlinear capacity degradation. We present a novel charging method that uses an aging related adaptation of the charging current. This method allows keeping the charging time short – especially for cells in mint condition - and avoids nonlinear and accelerated aging processes to set in.

A continuation of this study will allow to prove that non-linear aging can be fully avoided using the adaptive method presented herein. It is worth mentioning, that the results shown have been obtianed with a specific cell rather prone to non-linear aging. This facilitates charge procedure optimization within reasonable measurement times. Nevertheless, physical mechanisms of nonlinear aging are found similar for other graphite-anode contianing lithium ion cells.

At optimum driving temperature of 25 °C in combination with a moderate or adaptive charging method, the calendar aging has the major impact on overall battery aging. Advanced charge and control systems, avoiding long resting periods at high SoC and high temperatures are beneficial for further battery lifetime extension.

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