Arrhenius-Equation Based Approach for Modelling Lithium-Ion Battery Aging Effects

Dominik DVORAK; Hartmut POPP; Thomas BÄUML; Dragan SIMIC; Hansjörg KAPELLER;
AIT Austrian Institute of Technology GmbH, Giefinggasse 2, A-1210 Vienna

-Kurzfassung-

Diese Arbeit beschäftigt sich mit der Entwicklung und Implementierung eines Alterungsmodells für Lithium-Ionen Batterien. Das Modell basiert auf der Arrhenius-Gleichung für die Alterung über der Zeit sowie auf einer Polynomfunktion welche die Alterung über den Zyklen abbildet und ermöglicht die Simulation des Alterungsverhaltens einer Batterie unter Berücksichtigung der Batterietemperatur und des Ladezustandes. Der entwickelte Alterungsalgorithmus kann für eine große Anzahl an Simulationsszenarien, in welchen das Alterungsverhalten von Lithium-Ionen Batterien unter Berücksichtigung der oben genannten Einflüsse berechnet werden soll, verwendet werden. Ein mögliches Anwendungsszenario ist die Bestimmung von Ladezustand- und Temperaturintervallen in welchen eine Lithium-Ion Batterie in automobilen Anwendungen betrieben werden muss um eine möglichst lange Lebensdauer zu erreichen.

-Abstract-

This contribution deals with modeling and implementing a temperature- and state of charge dependent aging prediction model for lithium-ion batteries in order to investigate the impact of both influences on the aging rate. Therefore an Arrhenius-equation based approach for the aging taking place over time as well as a polynomial function representing the aging during charge transfer is followed. The developed aging algorithm can be used for a large number of simulation scenarios in which the aging behavior of lithium-ion batteries needs to be calculated while considering battery state of charge and temperature during operation. One possible application scenario is to determine the state of charge and temperature intervals in which a lithium-ion battery must be operated in automotive applications in order to obtain the longest possible cycle life.

-Introduction-

In the automotive sector simulation models are commonly used to investigate the operating behavior of multiphysical systems and sub-systems in certain application scenarios. As they eliminate the need to analyze the system performance during protracted real-life tests, a lot of time and money can be saved.

Energy efficiency and sustainability are key issues in automotive applications. As the battery is the only power source in an electric vehicle, the performance of the battery is crucial for the performance of the entire vehicle. Testing and analyzing the aging effects on batteries takes a lot of time and hence costs a lot of money. As aging effects have a high impact on the battery performance they should not be neglected. By means of an appropriate aging model, extensive investigations of the aging behavior of a battery during certain application scenarios can be performed within only a fractional amount of time than would be necessary for real-life tests.

This paper deals with the modeling and implementation of a temperature- and state of charge (SOC) dependent aging prediction model for lithium-ion batteries in order to investigate the impact of both influences on the aging rate. Therefore an Arrhenius-equation based approach for the aging taking place over time, as well as a polynomial function representing the aging during charge transfer is followed.

-Arrhenius Equation-

The Arrhenius equation [1], [2] describes the dependence between the temperature and the reaction rate of a chemical process. This is also valid for side reactions leading to battery degradation like decomposition of active material or building passivation films, meaning that the higher the temperature the faster the battery ages. A similar approach can be applied for the SOC level. The side reaction rate gets higher when the SOC gets closer to saturation. As the degrading processes slow down over time, aging effects are in total also dependent on the square-root of time. All these influences can be summarized for simulation purpose in an extended Arrhenius equation [2].

The derived extended Arrhenius equation is shown in (1). The Arrhenius equation describes the aging rate proportional to $\sqrt{t}$. The factor A_0 scales the trend of the $\sqrt{t}$-function to the actual aging behavior of the respective battery cell at reference conditions SOC_0 and T_0. Using the Arrhenius equation, an exponential correlation between the aging rate and the deviation of the current state of charge SOC from the reference value SOC_0 is assumed. The same applies for the battery temperature. The deviations from the reference values are further scaled by the model parameters b for the SOC and c for the temperature, respectively.

$$T_{Age} = A_0 \cdot e^{\frac{SOC-SOC_0}{b}} \cdot e^{\frac{T-T_0}{c}} \cdot \sqrt{t} \tag{1}$$

-Battery Model and Aging Simulation-

For simulating the transient operating behavior of a lithium-ion battery either an equivalent circuit model or a chemical transport model can be used. As the traction battery of an electric vehicle usually consists of multiple (up to several hundred) cells, the simulation with a chemical transport model would be very time consuming. Therefore equivalent circuit models are a more convenient choice for automotive simulations.

The ElectricEnergyStorages (EES) library, which was developed by the AIT Austrian Institute of Technology GmbH, is based on the programming language Modelica [3]. Modelica is a modern, object-oriented modeling language which is based on algebraic and ordinary differential equations. It is specialized on modeling complex, multiphysical systems. The battery models which are included in the EES library provide several ready-to-use equivalent circuit battery models. Furthermore, the modular structure of the models allows the extension of the existing models with the new aging approach. Therefore this library was chosen for simulating the battery aging scenarios in this work.

Figure 1 depicts the implementation of the electric battery cell model in Modelica which is included in the EES library. The model can be connected to an electric load by using the positive and negative pins `pin_p` and `pin_n`. The thermal connector `heatPort` is used to forward the electric losses to the external thermal model in order to consider not only electric but also thermal aspects. The ideal voltage source `OCV` represents the open circuit voltage. The `cellImpedance` model consists of one serial resistance and up to two RC-parallel circuits. The serial resistance is used to consider the ohmic voltage drop whereas the two RC-parallel circuits are used to consider transient voltage drops with different time constants, like the short-term double-layer effect and the long term diffusion effect [4]. The `parameterAdaption` block is composed of two sub blocks. One sub block calculates values that cannot be measured directly such as the SOC and the number of charge-discharge cycles. The other sub block is used to consider reversible effects regarding the parameters of the electric equivalent circuit depending on the SOC and the battery temperature. The parameters are then forwarded to the respective electric components via connectors of data type real.

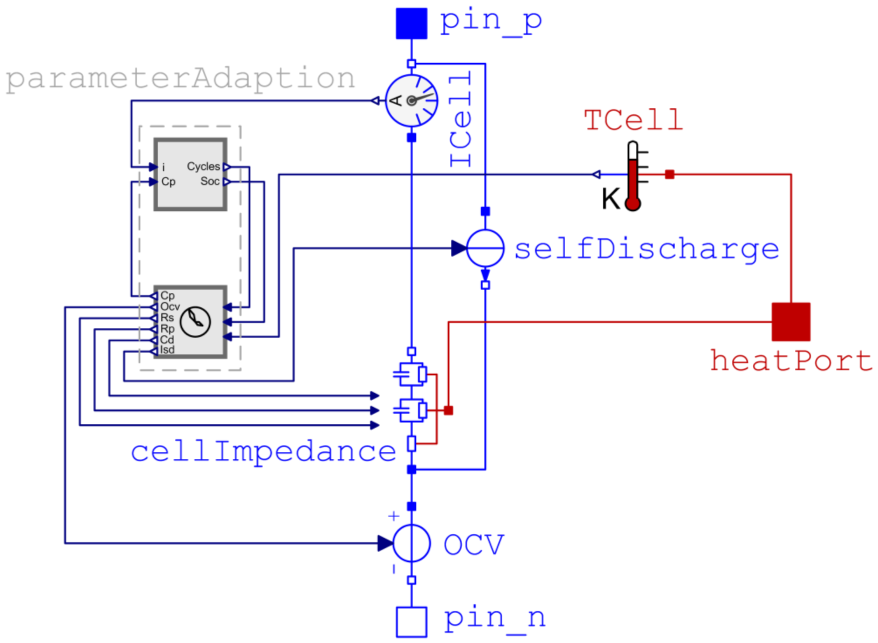

Figure 1: Implementation of the electric battery cell model in Modelica (EES library)

The aging block is used to consider irreversible aging effects such as:

- fade of the cell capacity and
- increase of the internal resistance.

Starting with the day of production lithium-ion batteries are subjected to permanent aging mechanisms even if being unused. One main aging factor is that the graphite anode is out of the stability window of the electrolyte. Thus a protective passivation layer, called solid electrolyte interface (SEI) is formed. This layer is continuously consuming lithium-ions to form and also to mature. Other reasons for the aging mechanisms are side reactions on both electrodes degrading the electrolyte and the electrodes and mechanical disintegration caused by volume changes due to lithiation and delithiation during cycling [5,6].

The aging block considers two causes respectively for the aforementioned aging effects:

- cyclic aging and
- calendaric aging.

Cyclic aging considers aging effects which are caused due to charge transfer. Calendaric aging means that the aging rate is proportional to the time and hence independent of whether the battery is cycled or not. The cyclic aging block calculates the aging effects based on the number of charge-discharge cycles, whereas the calendaric aging block considers the SOC and battery temperature for calculating the irreversible aging effects during operation. Both, the cyclic and the calendaric aging mechanisms mutually influence each other.

As the `parameterAdaption` block is used to modify the parameters of the electric equivalent circuit, the interfaces for considering the aging effects are already available. Therefore the aging algorithm is added to this block.

-Results-

This paper outlines the applicability of the Arrhenius equations for modeling the aging behavior of lithium-ion batteries with respect to the SOC and battery temperature. Therefore scenarios at different ambient conditions are tested. Furthermore the battery is operated at different SOC levels.

With the aging simulations performed in this paper, the worst case scenarios regarding battery temperature and SOC range, in which the battery is operated, can be determined. The identified worst case scenarios can then be avoided during operation in favor of longer battery lifetime.

Figure 2 depicts the measured and fitted aging factors of a Lithium-Iron-Phosphate (LFP) battery cell over time at different ambient temperatures. The fitted aging data at 23°C is taken as reference value to calculate A_0. The curves at 45°C and 60°C are used to calculate the temperature dependency factor c of the aging model. The SOC dependency factor b was identified following the same principle as for the temperature. Therefore a SOC of 0.8 was taken as a reference value. The calculated aging factor is directly proportional to the aging rate.

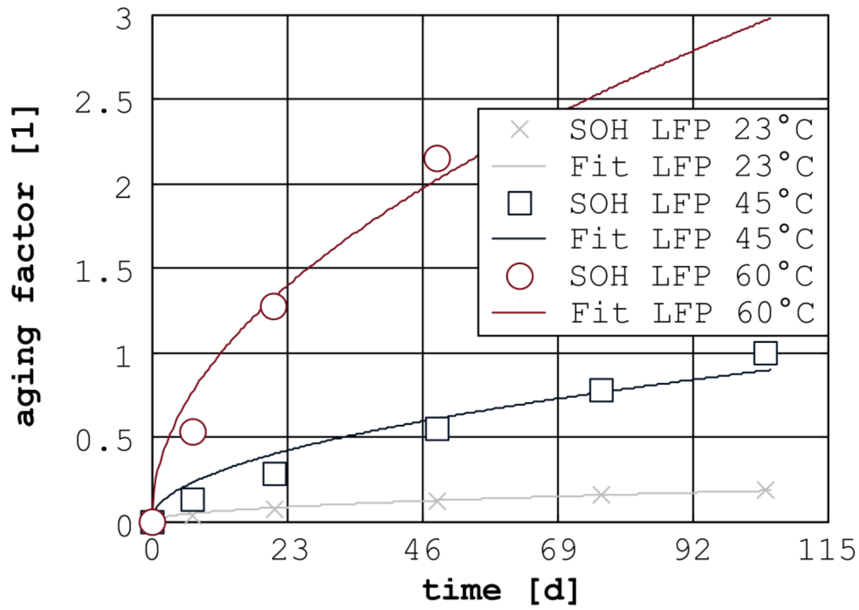

Figure 2: Measured and fitted aging factors of a LFP cell over time at different temperatures

The annual temperature profile which was used for predicting the aging behavior of the chosen battery cell is illustrated in Figure 3. The temperature trend represents the average daily temperatures of Linz (Austria) during an entire year [7]. Typically, the temperatures for central European regions are between -1 and 10°C for the first and last months, climbing to around 23°C in the middle of the year.

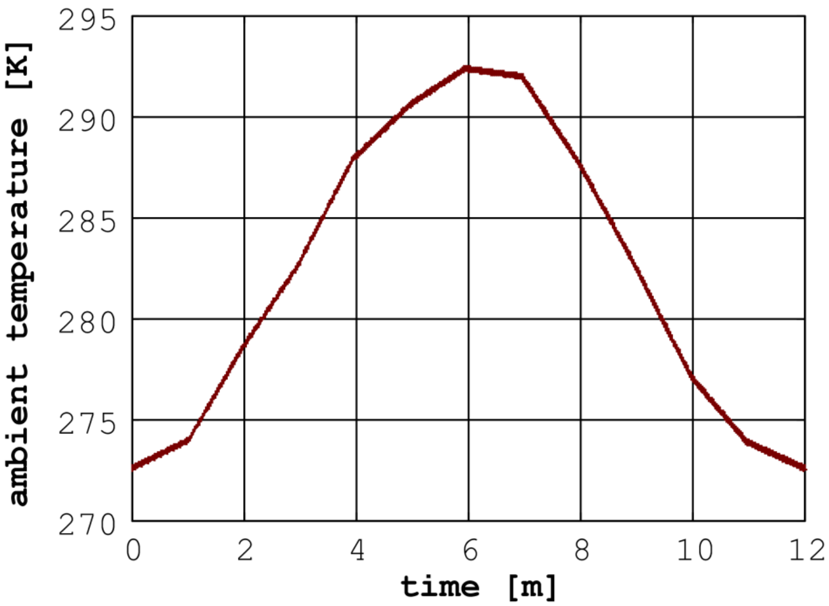

Figure 3: Annual average ambient temperature profile used for aging simulations

For the simulated battery pack, an energy content of 25.6 kWh with realistic cell configuration was assumed. Different scenarios were derived from real world applications. These scenarios include conventional usage and Vehicle to Grid (V2G) modes, which means that the vehicle supplies energy in high load phases to support the grid and gets charged in low load phases. Driving distances of 60 km per day and grid stabilization of 6 kWh were assumed as standard values leading to a 50% discharge of the pack in total. Short distance is 30 km per day and V2G peak load is 3 kWh with doubled power per day. Figure 4 shows the results of the aging simulation based on five different load cycles. The simulated scenarios are summarized in Table 1.

Table 1: Overview of the application scenarios used for simulation

Scenario	V2G	Driving distance per day [km]	Charging
Normal use	No	60	Whenever available
Controlled charge	No	60	When grid is ready
V2G	Yes	60	When grid is ready
V2G short distance	Yes	30	When grid is ready
V2G peak load	Yes	60	When grid is ready

Figure 4 shows the simulation results based on the scenarios shown in Table 1. The aging model was parameterized based on the measured aging effects during 105 days (see Figure 2) and with cycling data of 1800 full electric cycles. In the simulation the configured aging model is used to extrapolate the aging effects in different application scenarios to 10 years in order to analyze the capacity fade. The results show that the best-case scenario regarding battery aging is the controlled charge scenario. In this scenario, the battery will reach 80% of the initially available capacity after 4 years. Figure 4 also shows that the end of life is reached significantly earlier when the batteries are operated additionally in V2G mode. If V2G mode is used, the cells will reach 50% of the initial capacity more than 2 years earlier than without using V2G.

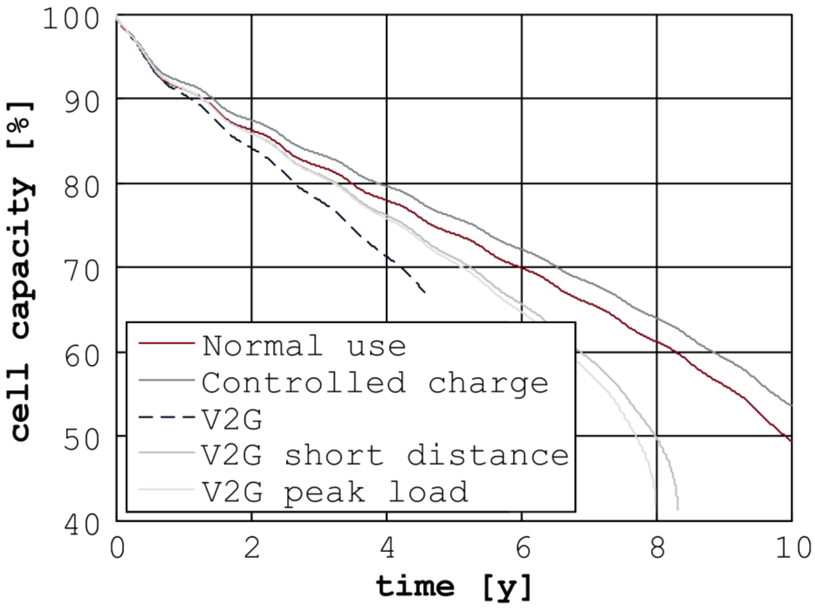

Figure 4: Predicted decrease in cell capacity of a LFP cell in different load scenarios

-Conclusion and Outlook-

In this contribution, a temperature- and SOC dependent aging prediction model for lithium-ion batteries was developed. The model can be used to investigate the impact of both influences on the aging rate. Therefore an Arrhenius-equation based approach for the aging taking place over time as well as a polynomial function representing the aging during charge transfer was followed.

The aging model which was developed in this contribution can be used to estimate the aging behavior of battery cells during different load cycles while considering varying ambient conditions. One practical use case for the model is to determine worst-case scenarios which can then be prevented with an appropriate operating strategy of the vehicle.

This paper proved the applicability of the Arrhenius equation for simulating the aging behavior of lithium-ion batteries. This approach is easy to parameterize and enables appropriate simulation times. Further work can deal with the validation of the predicted aging behavior of the battery cells during the five scenarios presented in this contribution.

-Literature-

[1] Liaw, B. Y.; Roth, E. P.; Jungst, R.; Nagasubramanian, G.; Case, H. L. & Doughty, D. H., “Correlation of Arrhenius behaviors in power and capacity fades with cell impedance and heat generation in cylindrical lithium-ion cells”, Journal of Power Sources 119-121, 874-886, 2003.

[2] Guenther, C.; Schott, B.; Hennings, W.; Woldowski, P. & Danzer, M. A., “Model-based investigation of electric vehicle battery aging by means of vehicle-to-grid scenario simulations”, Journal of Power Sources 239, 604-610, 2013.

[3] Modelica, “Modelica - A Unified Object-Oriented Language for Physical Systems Modeling”, 2012.

[4] A. Jossen and W. Weydanz, „Moderne Akkumulatoren richtig einsetzen“, Reichardt Verlag, 2006.

[5] J. Vetter, P. Novák, M. Wagner, C. Veit, K.-C. Möller, J. Besenhard, M. Winter, M. Wohlfahrt-Mehrens, C. Vogler, and A. Hammouche, „Ageing mechanisms in Lithium-ion batteries“, Journal of Power Sources, vol. 147, no. 1- 2, pp. 269 - 281, 2005.

[6] A. Barré, B. Deguilhem, S. Grolleau, M. Gérard, F. Suard, and D. Riu, “A review on lithium-ion battery ageing mechanisms and estimations for automotive applications”, Journal of Power Sources, vol. 241, no. 0, pp. 680 - 689, 2013.

[7] ZAMG - Zentralanstalt für Meteorologie und Geodynamik, „Klimadaten von Österreich 1971 – 2000“, 2014, [Accessed at: 28.08.2014]. Available: http://www.zamg.ac.at/fix/klima/oe71-00/klima2000/klimadaten_oesterreich_1971_frame1.htm