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Quantitative validation of calendar aging models for lithium-ion batteries

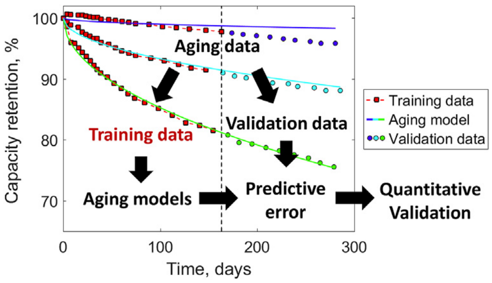
Severin Lukas Hahn[a,*], Mathias Storch[a], Ramanathan Swaminathan[a], Björn Obry[a], Jochen Bandlow[a], Kai Peter Birke[b]

[a] Daimler AG, Research & Development, Neue Strasse 95, 73230 Kirchheim u.T., Germany
[b] Chair for Electrical Energy Storage Systems, Institute for Photovoltaics, University of Stuttgart, Pfaffenwaldring 47, 70569 Stuttgart, Germany

EDITOR HIGHLIGHTS

- Extensive calendar aging study of automotive grade commercial pouch cells.
- Novel aging model considering an initial surface layer due to cell formation.
- Initial lithium loss due to formation is quantified by two matching methods.
- A quantitative validation technique splitting data into training and validation data.
- The derived model shows higher predictive capability than literature models.

GRAPHICAL ABSTRACT



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ABSTRACT

Calendar aging prediction is a key technique to develop durable and robust electric vehicles. Automotive grade pouch cells based on $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ and graphite are tested in an extensive accelerated calendar aging matrix and analyzed for capacity loss and evolved gas volume. This study derives an extended semi-empirical calendar aging model considering an initial solid electrolyte interface layer grown during the formation process. The extent of the thus lost active lithium is derived by open circuit voltage curve fitting as well as by inductive coupled plasma experiments. For this analysis the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ first cycle inefficiency is considered. Additionally, a validation technique based on the split of aging data into training and validation data is introduced with which it is possible to quantify the predictive capability of aging models. Using this technique the developed calendar aging model of this study is compared with competing aging models in literature. The derived global aging model is quantitatively shown to exceed other models in terms of their predictive ability, especially when little data is provided to the model.

1. Introduction

Lithium-ion batteries have been widely employed in portable consumer electronics requiring only a few years of lifetime. Electric vehicles, however, are expected to retain a large part of the initial battery capacity for up to 200–300'000 km and 10–15 years operating in various climatic conditions. Despite being exhaustive it is possible to test the entire estimated energy throughput and the corresponding cyclic aging. Testing for calendar aging over lifetime, however, is infeasible. Thus, various calendar aging models [1–8] have been developed to predict battery lifetime. Their accuracy is highly important to the automotive and other industries due to quality assurance, warranty

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[*] Corresponding author.
E-mail address: severin.hahn@daimler.com (S.L. Hahn).

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considerations and even regulatory requirements.

Cells degrade during storage because commonly used solvents such as ethylene carbonate are reduced at anode potentials below 0.8–1.2 V vs. Li/Li^+ which is inevitable when using graphite [9,10]. The solvent reduction products react with abundant Li^+ to form solid electrolyte interface (SEI) on the surface of anode particles [11,12]. These electrochemical side reactions consume both one lithium ion and a corresponding electron. Thus, the anode is delithiated while the cathode remains unaffected which is generally referred to as a purely *anodic side reaction* [12,13]. In fact, SEI growth takes place in absence of a cathode [14]. This anodic shift in relation to the cathode is equivalent to *loss of active lithium* [12,15]. In consequence the cycling window narrows which is the main cause for calendaric capacity loss in most lithium-ion batteries [3,12,13,16].

Observed capacity losses are passivated over time and strongly depend on temperature and charging state of the cell. The charging state may be defined by either cell voltage or empirically by state of charge (SOC). Several calendar aging models based on physical considerations have been presented in literature aiming to explain the observed behavior. Broussely et al. [1] assume a limiting electrical conductivity of the growing SEI attenuating further reduction which results in the well-known $t^{0.5}$ relationship for capacity loss where t is the aging time. However, inorganic SEI components such as LiF, Li_2CO_3 and Li_2O are known to be electrically insulating [17] indicating the model to be non-physical despite good results [1]. Further, the model assumes the immediate reaction upon electron transfer through the SEI. Consequently, (electro-)chemical kinetic effects such as an Arrhenius and exponential voltage dependency should not be observed. Still, corresponding temperature and voltage dependencies are found [7]. Ploehn et al. [2] then showed that a model considering limited solvent diffusion through the existing SEI with reduction on the anode surface yields the same $t^{0.5}$ relationship. Similar to Broussely et al. [1], an immediate reaction is assumed on the surface of the graphite denying a kinetic explanation for temperature and voltage dependence. It is important to realize that an Arrhenius dependency may be introduced assuming solid state diffusion of solvent molecules in SEI. The solid state diffusion coefficient D can be expressed as

$$D(T) = D_0 \cdot e^{\left(\frac{-E_a}{R \cdot T}\right)} \tag{1}$$

where D_0 is a frequency factor, E_a is the activation energy, R is the gas constant and T is the temperature. This expands the model of Ploehn et al. [2].

$$Q_{loss}(t) \propto \sqrt{D_0 \cdot t} \tag{2}$$

where Q_{loss} is the lithium lost due to solvent reduction and t is the aging time to a result

$$Q_{loss}(t, T) \propto \sqrt{D_0 \cdot e^{\left(\frac{-E_a}{R \cdot T}\right)} \cdot t} \propto e^{\left(\frac{-E_a}{2 \cdot R \cdot T}\right)} \cdot \sqrt{t} \propto e^{\left(\frac{C}{T}\right)} \cdot \sqrt{t} \tag{3}$$

where C is constant. A voltage dependency is not predicted. This model, however, is also disputed as the SEI has been shown to consist of a compact inner inorganic layer and a porous organic outer layer [2,18]. It is argued that solvent may not diffuse through this dense inner SEI layer composed of LiF, Li_2CO_3 and Li_2O [3,17]. Instead, Li et al. [3] suggest that electrons pass the inner SEI by tunneling. This results in a temporal behavior according to

$$Q_{loss}(t, x) = C_1(x) \cdot \ln(1 + C_2(x) \cdot t) \tag{4}$$

where C_1 and C_2 are factors that depend on the degree of lithiation x of the graphite anode [3]. While these parameters might be temperature dependent a clear exponential temperature dependency is not shown. Furthermore, Tang et al. [19] reject a tunneling effect based on their experimental results. In summary, theoretical considerations reveal strong modeling approaches but cannot encompass all aspects yet.

Due to the lack of a consistent theoretical model, many studies in literature successfully employ semi-empirical models to predict calendar aging [4–7,20–22]. These are often based on the discussed theoretical models. Even by the theorists [1,3] themselves the models are extended, adjusted or altered in order to describe the observed aging behavior lacking a clear physical explanation. Variable parameters are defined which are then fitted to the experimental data. In the following, fit parameters are denominated ***pi*** with the index i numerating parameters of a respective model. Ecker et al. [7] use the following exemplary aging model for the capacity retention $Q(t)/Q_0$ with both an Arrhenius term and a term similar to the Tafel equation

$$\frac{Q(t)}{Q_0} = 1 - \underbrace{p_1 \cdot e^{\frac{-p_2}{T}}}_{\substack{\text{Arrhenius}\\ \text{dependency}}} \cdot \underbrace{{p_3}^{p_4 \cdot (U_{cell} - U_0)}}_{\substack{\text{Voltage}\\ \text{dependency}}} \cdot \underbrace{t^{0.5}}_{\substack{\text{Time}\\ \text{dependency}}} \tag{5}$$

where T, U_{cell} and U_0 are the storage temperature, the cell voltage and a chosen equilibrium potential, respectively. Over the last years, researchers fitted different time dependencies than $p_1 \cdot t^{0.5}$ such as $p_1 \cdot t^{0.75}$ [5], the aforementioned $p_1 \cdot \ln(1 + p_2 \cdot t)$ [3], the superposition $p_1 \cdot t + p_2 \cdot t^{0.5}$ [5–7] or even fitted the time exponent itself with $p_1 \cdot t^{p_2}$ [4]. Also, different charging state dependencies such as the linear $p_3 \cdot U_{cell} + p_4$ [5], SOC^{p_3} [20,21] or $e^{p_3 \cdot SOC}$ [23] were investigated. These so-called *global* aging models like Eq. (5) may then be fitted in one step [22] to all aging conditions from an accelerated aging matrix. This is in contrast to models where parameters are fitted separately in a multi-step procedure or where only single aging conditions are fitted. When fit parameters p_i are thus determined by a global fit they may predict capacity loss due to storage for any timeframe at any charging state and temperature [7]. This paper will derive a novel semi-empirical global aging model based on theoretical considerations about the initial SEI layer grown during formation. For this, the extent of the initial SEI is investigated experimentally and used as a parameter of the aging model.

As the preceding discussion of various aging models suggests, it would be highly desirable to quantitatively rank lifetime prediction models in terms of their accuracy. In literature such aging models have been compared by their coefficient of determination R^2 to accelerated aging data [4–8,20,22]. This method, however, may critically favor overfitting models with many degrees of freedom. Overfitting describes the behavior of models which leads to a good fit to the given data but poor results compared with validation data. In fact, the predictive capability of aging models is not at all considered by R^2 analysis. Also, time dependencies are sometimes validated by R^2 analysis for select single curves [5,24] and not entire aging sets [7]. Only rarely, separate aging conditions are experimentally produced to validate the predictive capability, but only at select aging points [23]. Quantitative validation techniques for the predictive properties of lithium-ion battery aging models using the entire data set have not been discussed in literature to the best of our knowledge.

In response this paper aims to I) present a novel extended global aging model incorporating measured initial SEI growth due to formation, II) introduce a quantitative validation technique inspired by machine learning for aging models and III) compare the predictive capability of the extended model to existing models in literature. The comparison of these models is performed with data from an extensive calendar aging matrix of 54 automotive grade high-energy pouch cells which is discussed in detail. The derived aging model is parametrized with an experimentally determined initial lithium loss due to formation. After choosing common temperature and voltage dependencies for all considered aging models they are characterized for overfitting behavior and quantitatively ranked in terms of their predictive capability.

2. Experimental

The cell used for the aging experiment was the HEA50 pouch cell by Litec Battery GmbH with a nominal capacity of 50.8 Ah. These cells