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Lithium-ion cell-to-cell variation during battery electric vehicle operation

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HIGHLIGHTS

- Strength of variation and amount of outliers increased with the progress of aging.
- Outliers mostly found on the side of higher degradation.
- Alteration from symmetrical normal to skewed Weibull distribution.
- Outliers random and inevitable due to non-existing link to BEV operational history.

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ABSTRACT

484 new and 1908 aged lithium-ion cells out of two identical battery electric vehicles (i.e. 954 cells each) were characterized by capacity and impedance measurements to yield a broad set of data for distribution fit analysis. Results prove alteration from normal to Weibull distribution for the parameters of lithium-ion cells with the progress of aging. Cells with abnormal characteristics in the aged state mostly exhibit lower capacities as compared to the distribution mode which is typical for the left-skewed Weibull shape. In addition, the strength of variation and the amount of outliers both are generally increased with the aging progress.

Obtained results are compared to vehicles' operational data to provide recommendations with the aim to minimize the increasing parameter spread. However, neither temperature gradients in the battery pack nor an insufficient balancing procedure were determined. As the appearance of cells with suspicious parameters could not be assigned to local weak spots of the battery pack, a random and inevitable type of origin is assumed. Hence, the battery management system must ensure to detect outliers in a reliable manner and to balance resulting drifts of cells' states of charge to guarantee a safe battery storage operation.

1. Introduction

The global wide launch of battery electric vehicles (BEV) accompanied by an increased share of regenerative energies in the grid is without any serious alternative regarding the reduction of greenhouse gases. Nevertheless, barely 2% of newly registered cars in Germany in 2013 were pure or hybrid electric [1]. Besides of the establishment of a suitable charging infrastructure still being in its very infancy, the reserved product acceptance of customers mainly originates from the high price of BEV which in turn is caused by the costly battery storage. Since the recycling of lithium in contrast to lead-acid batteries is not economically feasible for now, a potential reuse of disused BEV battery storages could broaden the value-added chain and thus reducing customers' acquisition costs [2]. Helping provide disused batteries to a *2nd-life* in the field of stationary energy storage, like buffering the intermittent supply of regenerative energies or to avoid grid-strengthening investments, promises high revenue potentials [3–9]. However, a profound understanding of battery aging behavior, and especially of the *life cycle distribution*, is a prerequisite to assess overall system cost and economic benefit of battery reuse. As initial *cell-to-cell variation* has

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been reported to increase with the progress of aging, only a fraction of the single units (cells, modules, etc.) of a BEV battery pack might be worthy to refurbish from an economic point of view [10–13].

For the pristine state, cell-to-cell and lot-to-lot variation must be attributed to deviations in the production process, such as changes in the weight fraction of active materials or the thickness of electrodes [14,15]. Reducing the mixing or thickness tolerance leads to excessive manufacturing costs at a comparably low improvement of the cells' performance [14]. Besides this intrinsic origin of cell parameter variation, there are extrinsic reasons which comprise temperature gradients in the battery pack, or deviations in the conductor resistances, cells' contact resistances and their type of interconnection [16]. For a parallel string, differences in the cells' resistances lead to an uneven current distribution, which in turn causes a drift of corresponding states of charge (SoC) [17]. Cells connected in series are loaded with the same current but within distinct voltage windows ΔV, as the weakest cell always determines the performance of the whole string [18]. In conclusion, intrinsic cell-to-cell variation leads to different loads for interconnected cells, which in turn results in different aging mechanisms and rates. As an example, for two $LiFePO_4$ (LFP) based cells connected in parallel, a 20% mismatch in the ohmic resistance led to a lifetime reduction by 40% when compared to a compound with optimally matched resistances [17]. As a consequence of a high parameter variation of a battery pack's single units, effective balancing algorithms must be implemented in the battery management system (BMS) to ensure a safe and efficient mode of operation.

Main aim of this publication is to compare the lithium-ion cell-to-cell parameter variation (capacities, impedance parts) in the new state to that after BEV operation by raising conventional statistical approaches like distribution fit analysis. Therefore, 484 new and 954 aged cells, each out of two identical BEV with different operational history, were characterized at first in order to yield a broad set of data. For the latter, variation and local deviations of lithium-ion cell parameters are compared to logged BEV operational data and tried to be assigned to weak spots of the battery pack. As a conclusion, inferences are drawn with the aim to minimize the increasing parameter spread by recommending actions addressing the operational mode of the BMS, the battery pack configuration and residual system components.

2. Statistical methods used to analyze the experimental data

The symmetric normal (or Gaussian) distribution is commonly used to describe the battery cell-to-cell parameter variation which is imposed by the production process and to evaluate the quality of it [19–22]. In the field, a total dispersion is mostly composed of multiple smaller dispersions. If these are normally distributed, same is obtained for their sum. Otherwise, if the distribution is unknown or abnormal, the central limit theorem helps stating that the sum of a sufficiently large number of stochastically independent dispersions can approximately be regarded as normally distributed [23]. In other words, if a distribution appears to be normal, only random errors underlie, which characterizes a high-quality production process without any systematic errors. The normal probability density function for the normal distribution is expressed as follows:

$$f(x,\mu,\sigma) = \frac{1}{\sqrt{2\pi}\cdot\sigma}\cdot e^{-\frac{(x-\mu)^2}{2\sigma^2}} \tag{1}$$

Thereby, the parameter μ is the arithmetic mean value of the distribution, σ its standard deviation and σ^2 the variance. To be able to compare different sets of data, the relative coefficient of variation $\kappa = \sigma/\mu$ is used. As an example, the distribution of capacity or internal resistance of 20,000 pristine LFP based lithium-ion cells was reported in Ref. [10] to correspond to a normal distribution with $\kappa = 1.3\%$ or 5.8%, respectively.

Another well-known parameter to characterize if a variation is normally distributed is the skewness s, which is calculated as follows with the expected value E:

$$s(x,\mu,\sigma) = \frac{E(x-\mu)^3}{\sigma^3} \tag{2}$$

The skewness describes the asymmetry of the data around the mean value. If $s < 0$ the distribution is left-skewed, which means that the data is more spread to the left, and for $s > 0$, distribution is right-skewed. For a symmetrical distribution (like normal distribution), s is equal to zero.

In contrast to the normal distribution, the Weibull distribution is typically used in materials engineering for reliability analysis, i.e. to describe probabilities of failure and make predictions of it within confidence bounds [23–29]. As such, there is a major distinction in the typical field of application of these two distributions: While the normal distribution is generally used to describe the dispersion of a parameter for a fixed period of application, the Weibull distribution is usually raised to characterize the *life cycle* or the spread of maximum periods of application before failure of an electronic device. As this publication aims to compare the lithium-ion cell-to-cell parameter variation in the new state to that after BEV operation, the normal distribution is used in its typical field. However, this suggests a new and alienated area of use for the Weibull distribution as cell-to-cell parameter variation at a fixed period of application is investigated. The Weibull probability density function in terms of a two-parameter distribution (β, η) is expressed as follows:

$$f(x,\beta,\eta) = \frac{\beta}{\eta}\cdot\left(\frac{x}{\eta}\right)^{\beta-1}\cdot e^{-\left(\frac{x}{\eta}\right)^{\beta}} \tag{3}$$

Thereby, β is the shape parameter which can be raised to refer to different types of failure in case of classical use of Weibull for lifetime analysis. According to [30], a $\beta < 1.0$ represents a defect in the initial step caused by manufacturing errors with a decreasing failure rate vs. time ($x = t$), a $\beta = 1.0$ a random failure with a constant failure rate and a $\beta > 1.0$ a failure caused by abrasion or aging and therefore an increasing failure rate vs. time. The scale parameter η quantifies the expected life of a device by giving the value for which 63.2% will have failed. In case of failures which definitely do not start at $t = 0$ days, years, cycles, etc., the three-parameter Weibull distribution should be used instead with the additional failure-free time, minimum life or location parameter γ [30]. Substitution of x in Eq. (3) by $x - \gamma$ transforms the two-to a three-parameter distribution which is expressed as follows:

$$f(x,\beta,\eta,\gamma) = \frac{\beta}{\eta}\cdot\left(\frac{x-\gamma}{\eta}\right)^{\beta-1}\cdot e^{-\left(\frac{x-\gamma}{\eta}\right)^{\beta}} \tag{4}$$

There is no definite rule which one of the two Weibull distributions is the better choice for a certain set of data of a product without known lifetime expectation. Decision has to be made based on engineering expertise and experience, and by assumptions about the expected lifetime of the investigated product. However, Eq. (4) is only valid if a finite failure-free time γ can absolutely be ensured.

It has to be considered that in classical reliability analysis the length of operation time until failure is investigated. In this publication, the parameter variation of aged BEV lithium-ion cells, all