Journal of Power Sources 305 (2016) 191–199

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Correlation between capacity and impedance of lithium-ion cells during calendar and cycle life

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HIGHLIGHTS

- Correlation behavior depends strongly on storage and operational conditions.
- Deviations in the development possibly linked to layered SEI structure.
- Correlation between capacity and impedance principally enables SoH quick tests.
- SoH quick test must be parameterized with aging data similar to practical use.
- SoH quick tests promote an economic implementation of 2nd-life application.

ARTICLE INFO

Article history:
Received 23 September 2015
Received in revised form
21 November 2015
Accepted 24 November 2015
Available online 10 December 2015

Keywords:
Correlation
State of health
Quick test
Aging
Second life
Impedance

ABSTRACT

Conventional capacity measurement techniques are time-consuming and thus expensive. But to know the capacity of battery units is necessary, e.g. to select most equal cells for battery pack assembly or to decide whether single units of an aged battery pack are worthy to be reused in a 2nd-life application. So, a quick and easy approach to refer to the actual capacity is of great technical and economic interest.

In this paper, the correlation between capacity and impedance of lithium-ion cells during calendar and cycle life is analyzed and assessed, whether it can serve as a base for capacity quick tests. Therefore, new cells, cells aged in the laboratory and those out of two identical electric vehicles are characterized to yield a broad set of data. Results of this work imply the feasibility of correlation based capacity quick tests. However, parameterization of needed functional dependencies between capacity and impedance must be done with laboratory aging data similar to the practical use as a strong dependency of the correlation behavior from the operational and storage conditions is observed. Especially high temperature leads to strong deviation which could be linked to the layered structure of the solid electrolyte interphase.

1. Introduction

Up to now, lithium-ion batteries are predominantly used in mobile devices like cell phones and laptops [1]. However, the demand for lithium-ion batteries will be increased by recent and future fields of application such as electromobility and stationary energy storage [2]. Although the increased demand for lithium-ion battery systems could generally lead to a price reduction, the costly large-size storages actually impede a broader market penetration of these new applications. Recycling of disused lithium-ion batteries is not economically feasible for now [3]. In contrast to that, reusing lithium-ion batteries exhausted upon battery electric vehicle (BEV) operation is actually a hotly debated topic. By helping provide disused BEV traction batteries to a 2nd-life, both the customers' acquisition costs of BEV and stationary energy storages could be reduced [4–10]. Thereby, a profound understanding and predictability of battery aging behavior is a prerequisite to assess overall system cost and economic benefit of battery reuse. Additionally, cell-to-cell variation caused by deviations in the production process is reported to increase during the progress of aging [11–15]. As a result of this, only a fraction of the units (cells, modules, etc.) of a BEV battery pack might be worthy to *refurbish for 2*nd*-life application* from an economic point of view. To decide whether a battery

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http://dx.doi.org/10.1016/j.jpowsour.2015.11.096
0378-7753/

unit should be reused or immediately recycled, the state of health (SoH) must be measured which is defined by its actual power capability or residual capacity.

Regarding energy-optimized application like BEV, the SoH is quantified by the ratio of the actual referred to the nominal or initial capacity [16,17]. However, capacity measurement with conventional strategies requires appropriate machinery, is highly time-consuming and thus expensive [18]. For example, capacity determination according to standards or manufacturer guidelines usually requires at least a complete charge and discharge cycle with a current less or equal than 1 C [19,20]. So, a quick and easy SoH test, without the need of costly machinery, might be of great use and could especially raise the economic feasibility of reusing aged batteries by reducing refurbishing costs.

To assess the actual power capability of a battery unit, the impedance can be determined either in the frequency or in the time domain [20–22]. Regarding the applicableness for *SoH quick tests*, the raised impedance part must be independent of the state of charge (SoC), as a prior adjustment of it would be nearly as time-consuming as capacity measurement itself. Alternatively, a SoC correction function is necessary. In the frequency domain, for lithium-ion cells made of different active materials, the complex impedance value at which the imaginary part is zero, i.e. the ohmic resistance, can approximately be regarded as independent of the SoC [18,23,24]. This part of impedance is also quickly to measure because of its occurrence at high frequencies in the magnitude of 1 kHz, as reported in Ref. [21] for lithium-ion cells comprising graphite on the negative and nickel, manganese and cobalt (NMC) on the positive electrode. Additionally, as the impedance spectrum of a lithium-ion cell is highly sensitive to temperature fluctuations, controlled temperature conditions are always mandatory to be able to compare results.

Various methods to estimate the actual SoC and SoH with battery management systems (BMS) have been described in Ref. [25]. Furthermore, in Refs. [18] and [26], approaches of reasoning the actual capacity from the corresponding impedance value are suggested. With an alleged correlation between capacity and impedance, the actual capacity of a battery unit could quickly be calculated by measuring the raised impedance value, e.g. the ohmic resistance. On the base of pairs of impedance parts and corresponding capacities, collected within a laboratory aging experiment, the main idea is to calculate a functional dependency from the variables e.g. by simple linear regression [18,26]. As a result, such a SoH quick test for high-energy application battery units, based on a substitution of capacity with the ohmic resistance under the assumption of correlation, could be of high economic interest for the implementation of 2nd-life application or lithium-ion cell classification in general. Thereby, a major difference of the own approach compared to [18] and [26] is the underlying of data sets comprising a variety of distinct operational conditions. When considering an alleged correlation between capacity and impedance as the base for SoH quick tests, it must be usable for battery units aged under a variety of different load profiles and ambient conditions, not only for cells cycled with one single specific load profile in the laboratory.

So, the main aim of this work is to investigate the correlation between capacity and impedance of lithium-ion cells during calendar and cycle life, and to assess, whether it can serve as a base for SoH quick tests for typical high-energy application like BEV. At the beginning of this work, electrochemical fundamentals and possible explanations on the interaction between capacity fade and impedance increase of lithium-ion cells are discussed. Furthermore, mathematical fundamentals of descriptive statistics to quantify the grade of correlation are given. For all performed tests presented in this work, cells of the same type, e.g. with the same product name, chemistry and manufacturer, were used. The investigated cells were aged in different operational conditions; that is to say laboratory aging experiments as well as three years of usage in two identical BEV. The laboratory aging tests can be subdivided in calendar and cycle life tests, which in turn consist of a variety of distinct test cases. In complete, 484 new cells and 954 aged cells, out of two BEV each (i.e. 1908 BEV cells in total), were characterized to yield a broad set of data regarding a concrete *state of aging*. In addition, the data of 83 cells during the *progress of aging* was collected within the aforementioned laboratory aging experiments. For each batch of cells, the grade of correlation is calculated and it is assessed, whether there is a functional dependency between capacity and ohmic resistance with sufficient precision for SoH quick tests. At the end of this work, the question shall be answered, if, during the progress of aging, correlation is increased by aging mechanisms of lithium-ion cells provoking capacity fade accompanied by impedance increase.

In the previous publication [15] of the authors, partially, identical sets of experimental data (new and BEV cells) were statistically analyzed. In contrast to this work, however, the distributions of *single variables* were investigated in terms of central tendency and dispersion. Instead of univariate analysis of descriptive statistics, bivariate analysis is carried out in this work to describe the relationship between *pairs of variables*. More specifically, the correlation between capacity and corresponding impedance part of lithium-ion cells during calendar and cycle life is analyzed and assessed, whether it can serve as a base for SoH quick tests.

2. Interaction between capacity fade and impedance increase

In general, the consequences of aging in lithium-ion cells are the loss of capacity and the reduction of power capability due to increased impedance [22]. The reasons for aging can basically be subdivided into three groups, which are the loss of active materials, the loss of cyclable lithium and the deterioration of ionic kinetics [27].

Theoretical background of raising the correlation between capacity and impedance as a base for SoH quick tests is a reported interaction between aging mechanisms leading both to capacity loss accompanied by impedance increase. The formation and evolution of passive layers in the interfaces of electrodes and the electrolyte is of major importance regarding the aging behavior of lithium-ion cells. Usually, the layer at the anode is referred to as the solid electrolyte interphase (SEI) and the one at the cathode as solid permeable interphase (SPI) [28]. The name of the SPI can be attributed to its feature of being only partly passivating, while the SEI ideally prevents any further decomposition of the electrolyte [29–31]. In general, electrolyte decomposition (by reduction at the anode or oxidation at the cathode) leads to an increase of the ohmic resistance. Both layers tend to thicken under high temperatures and SoC, or can even break due to volumetric changes of active materials caused by insertion and extraction of lithium cations, with the result of automatic reconstruction due to the electrodes' exposition to the electrolyte (accompanied by electrolyte decomposition) [32–36]. As the formation, thickening and reconstruction of both passive layers occur under the consumption of active lithium, these processes also come along with capacity fade [32,34,37–40]. In addition, the passive layers must be regarded as resistive obstacles through which the lithium cations have to penetrate when being inserted into or extracted from the electrodes [32,34,37–40]. This *interaction between capacity fade and impedance increase* caused by the formation, thickening and reconstruction of SEI and SPI can be interpreted as the theoretical background of using the correlation between those two variables for SoH quick tests. Besides, especially the evolution of the SEI is