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Combined cycling and calendar capacity fade modeling of a Nickel-Manganese-Cobalt Oxide Cell with real-life profile validation

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HIGHLIGHTS

- A semi-empirical mathematical lifetime model is presented for NMC-based cells.
- The model estimates influences of DOD, Mid-SOC, Temperature and storage conditions.
- The results of a large test-campaign containing 146 cells are presented.
- Highly dynamic validation tests based on WLTC profiles are conducted.
- The model showed a maximum error of 5% RMSE after 18 months of validation.

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ABSTRACT

This paper presents the development of a semi-empirical combined lifetime model for a Nickel Manganese Cobalt Oxide (NMC) cathode and a graphite anode based cell, considered as one of the most promising candidates for the automotive industry. The development of this model was based on a thorough understanding of the degradation behavior of a 20-A h NMC cell, based on the analysis of the results of an extensive test-matrix using 146 cells. This test-matrix was designed around four impact factors: temperature (25–45 °C), Depth-of-Discharge (100–20% DoD), middle State-of-Charge (80–20% Mid-SoC) and current rates (C/3 to 2C). Gathering sufficient data for a mathematical model requires a huge time-investment, and the measurements gathered over the course of 2.5 years offer a unique insight in the aging behavior of the NMC cells used in this study. Experimental results for cycling aging indicated that the capacity loss was strongly affected by the Depth-of-Discharge and temperature. For calendar aging, an initial increase in capacity was observed when stored at low State-of-Charges, due to electrochemical milling, while the deterioration of the capacity was affected most by high storage State-Of-Charges and storage temperatures. The developed combined lifetime model showed an error of less than 5% RMS compared to the measurement results after a Worldwide harmonized Light vehicles Test (WLTC) was applied for 18 months.

1. Introduction

Lithium-Ion Batteries (LiB) have been widely adopted in the automotive and space industry due to their power and energy capabilities [1]. More recently, LiB's have also emerged in off-grid renewable energy storage solutions [2–4]. Due to their electrochemical nature, LiBs suffer from degradation and lifetime losses which can be detrimental for commercial applications. Therefore, knowing the cells aging rate or remaining useful life, when submitted to a set of operating conditions is a significant asset. For example, this knowledge aids greatly while designing and sizing a battery module [5,6], optimizing the control strategies of the Battery Management System (BMS) [7], researching use cases of second-life battery modules [8] (for example off-grid applications [9,10]), impacting decision making during real-world electrification projects [11,12], etc. For battery or hybrid electric vehicles (BEV/HEV), this knowledge enables predicting the total expected lifetime of a battery module, and the durability of the cell.

Over the past few years, different approaches have been used for developing models and understanding cell aging behavior. These provide insight into various electrochemical phenomena

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accountable for capacity decline such as parasitic side reactions [13–15], Solid Electrolyte Interface (SEI) formation [15–19], and lithium plating [16,18,20–23].

However, due to the fast pace of LiB technology development, it is very difficult to study the degradation in real operation conditions, due to the large time-investment needed. That is why accelerated degradation testing is normally used by most of the researchers in order to characterize cell performance over a range of stress conditions [14,24–26]. Accelerating aging tests can be achieved for example by increasing the current rates [13,27,28], using high or low operating temperatures [14,29], large Depth-Of-Discharges [25,30] and the application of load profiles corresponding to drive profiles for EV's and HEV's [31–33]. Often, the main goal of such testing is to predict cell life subjected to real operating conditions by developing a lifetime model.

Over the years, a myriad of different methodologies have been developed with the goal of developing a model predicting the total expected lifetime of a particular cell chemistry, with limited accuracy. Analytical models describe the influence of load conditions using mathematical equations, not necessarily directly related to physical processes occurring in the cell. The mathematical equations can be expressed as Equivalent Circuit Models [34,35] or traditional sets of equations [36–38].

Electrochemical models typically rely on solving a set of partial differential equations, describing electrochemical kinetics and transport phenomena of the investigated chemistry. This can be done using simple single-particle models [39,40], porous electrode models [41], mechanistic approaches [42] etc. These models typically require many parameters, a large computational effort, and need large experimental dataset, thus these are not very interesting for the automotive industry requiring fast results. Also, pure electrochemical models are often not useful for predicting the total expected lifetime of a cell or battery module. These models are primarily used for expanding the knowledge of the electrochemical processes [42–44].

Data-driven approaches have gained traction in the recent past, using methods as neural-networks [45], Bayesian networks [46,47] and Vector machines [48,49] etc. These techniques require easily obtainable inputs (voltage, discharge current, discharged capacity, etc.) and are usually computationally very fast after the initial training phase, but they again are not able to extrapolate the aging prediction outside the area covered with the measurement points, and need a very large data-set for the learning mechanism to work reliably [50–52].

To provide the required data needed for any modeling approach, a significant amount of testing is required to develop an accurate lifetime model. So far a few groups have tried to formulate a lifetime model using such a large test matrix [30,35,53,54]. In addition, there are numerous studies about accelerated calendar [14,24,55,56] and cycle life [24,27,29] testing. Although calendar life is relatively well established and understood, cycle life still remains a more complex topic. Therefore, more research is needed in this field. Moreover, most of the research focuses either on the calendar life or cycle life and few of them, to the authors best knowledge, attempt to combine them into a single lifetime model [33].

Furthermore, the NMC based lithium-ion cell has been advised as one of most promising chemistries for large scale applications in the EV/HEV industries because of its high specific energy [29,57–60]. Nonetheless, capacity fade behavior and cycle life modeling for this cell has not been well analyzed or reported. A NMC lifetime model based on a large cycle test matrix at different constant stress conditions such as temperature, current rate and Depth-of-Discharge is presented in [38]. However, this model was based on 18,650 cells with a low nominal capacity (rated at 2.15 A h), while this paper considers pouch-cell type NMC cells, with a rated capacity of 20 A h.

In this paper, the applied validation methodology offered the possibility to quantify the effect of dynamic stress conditions on the lifetime of the cell with the application of a highly dynamic load-profile. Standardized driving cycles are commonly used to study the emissions and energy consumption of a vehicle under specific driving conditions. The drive cycle applied to the vehicle varies according to the region and type of vehicle. There are several standardized driving cycles, for instance the New European Driving Cycle (NEDC) [61], the Urban Dynamometer Driving Schedule (UDDS) [62] or the Worldwide harmonized Light vehicles Test Procedure (WLTC) [63]. In this paper, two WLTC profiles were chosen as validation profiles, along with more traditional validation tests. As cells used in automotive applications are never used in static conditions, there is an excellent motivation to study the validity of the model using highly dynamic load profiles. In fact, to the authors' knowledge, there is very few literature reporting dynamic validation tests showing the accuracy of lifetime models [33,54].

All of the aforementioned modeling methodologies have their advantages as mentioned. However, some models are based on a limited amount of input data [27,64,65], are only capable of modeling the influence of a limited amount of stress conditions [36,44,66–68]. Some lifetime models are based around specific operating conditions [69–71].

Therefore, considering all above-mentioned observations, the goal of this work was to develop an empirical model based on a large aging test matrix, with many different stress factors being considered: Temperature, storage State-of-Charge (SoC) level and storage time for calendar aging. The stress factors for cycling aging are Depth-of-Discharge (DOD), Middle-SoC (Mid-SoC), cycle number and operating temperature. These results were used as input data of the empirical lifetime model developed in this work.

The novelty presented here is the huge database of aging test results gathered over the course of 2.5 years using large format cells used in the automotive industry. The separation of the models presented for cycling and calendaring aging is unique when applied to NMC-cells. Also, the dynamic nature of the developed model, as it is able to accurately predict the evolution of the capacity fade in function of a wide range of impact factors. Lastly, two highly dynamic WLTC load profiles were chosen as validation profiles together with more traditional constant and simple dynamic load profiles.

The paper is structured as follows: Section 2 presents the aging test matrix and introduces the NMC cell. Section 3 explains the experimental setup with the aging tests results. Section 4 describes the lifetime model and used methodology. Section 5 discusses the validation of the model with the dynamic-validation profiles. Finally, conclusions are given in Section 6 followed by the future work. Fig. 1 shows the schematic overview of this paper.

2. Test matrix

2.1. General layout of the test campaign

The aim of a lifetime model is to estimate the evolution of the capacity fade during the lifetime of the cell. The capacity fade evolution is straightforward: it describes the total available charge or discharge capacity while the cell is subjected to various operating conditions (stress conditions), and thus degradation.

To parameterize the capacity fade model, aging tests are necessary. Generally, cell capacity fade (or degradation) happens both during operation (cycling aging) and during idle time periods (calendar aging), when no current is flowing through the cell. These are two separate factors in the degradation of the cell, and must