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On the complex ageing characteristics of high-power $LiFePO_4$/graphite battery cells cycled with high charge and discharge currents

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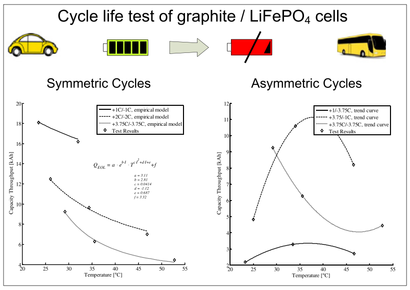
HIGHLIGHTS

- Cycle life test of cylindrical power optimised $LiFePO_4$/graphite cells; 1… 4C-rate, +23…+50 °C.
- Monotonously increasing ohmic resistance, correlated to time and capacity throughput.
- Non-monotonously increasing low-medium frequency impedance.
- Rest periods, decreased average current or lower average temperature may lead to shorter cycle life.

GRAPHICAL ABSTRACT



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ABSTRACT

Li-ion batteries are known to undergo complex ageing processes, where the operating conditions have a profound and non-linear effect on both calendar life and cycle life. This is especially a challenge for the automotive industry, where the requirements on product lifetime and reliability are demanding. The aim of the present work is to quantify the ageing in terms of capacity fade and impedance growth as a function of operating conditions typical to high-power automotive applications; high charge and discharge rate, elevated temperatures and wide state-of-charge windows. The cycle life of 34 power-optimised $LiFePO_4$/graphite cells was quantified by testing with charge and discharge rates between 1 and 4C-rate, temperatures between +23 °C and +53 °C, and a depth-of-discharge of either 100% or 60%. Although all cells show similar ageing pattern in general, the cycle life and the impedance growth is remarkably different for the tested cases. In addition, it is concluded that high charging rates, high temperatures or intensive cycling do not always lead to a shorter cycle life. One specifically interesting finding is that the combination of 1C-rate discharge in combination with 3.75C-rate charging was found to degrade the tested cells more rapidly than a symmetric cycle with 3.75C-rate in both directions.

1. Introduction

Li-ion batteries are widely used in the automotive industry, small electronics, aerospace applications and renewable energy storage systems. This battery technology plays an important role in the automotive sector due to various advantages over other

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batteries technologies such as high specific energy, high efficiency and relatively long lifetime.

Both hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs) have successfully been introduced into the market for commercial vehicles, at least in small series. Although the development of electrical energy storage systems is rapid, especially for Li-ion batteries, the battery cycle life and cost is still a barrier towards a wide market penetration, especially for full electric vehicles. Within the Li-ion battery family, the $LiFePO_4$/graphite type has been considered to be one of the most suitable technologies for high-power automotive applications due to an attractive combination of safety, cycle and calendar life and performance [1–3].

Energy storage systems used in HEVs are required to supply and store electric energy at comparably high power rates within a limited state-of-charge (SOC) range, typically 30–60%. In contrast, energy storage systems for PHEVs often usually utilize a larger ratio of the total energy (50–100%). In addition, the ability to accept fast charging is regarded as a key attribute to enable a wider usage, especially for heavy-duty commercial vehicles such as city buses, distribution trucks and off-road vehicles. Here, accurate control of the complete powertrain is essential to obtain stable vehicle performance, in turn requiring an accurate estimation of the battery performance and lifetime [4]; again especially for heavy-duty commercial vehicles where very high power is expected and with a very high usage rate of 10–20 h/day.

Unfortunately, all Li-ion batteries show performance degradation as a function of time (calendar ageing) and as a function of usage (cycle life) [5–7]. This degradation is caused by a multitude of reactions and processes occurring both at electrode/electrolyte interface and in the bulk material. Generally, the ageing can be categorised into three groups based on the symptoms: a) loss of active electrode material, b) loss of cyclable Li and c) loss of conductivity in electrodes or electrolyte. In most cases, the degradation rate for each ageing process is strongly related to certain operating conditions such as temperature, charge and discharge rate, depth-of-discharge (DOD) and SOC region [8–11]. Regrettably, factors accelerating certain ageing processes may decelerate other. Furthermore, large cells are likely to experience a wide distribution of thermal, electrical and mechanical stresses in different parts of the cell, in turn resulting in an uneven degradation, as shown by Refs. [10,12]. Consequently, the overall ageing is complex and has proved to be very difficult to predict [13].

Whereas the temperature in most cases can be controlled by a separate cooling system, the SOC range and the current rates for charge and discharge are directly linked to the overall powertrain efficiency. Thus, a reduction of current rates will lead to significantly reduced vehicle performance or the need for a larger battery system, in turn leading to higher powertrain cost. Hence, a precise knowledge about the influence of the current rate on the lifetime of Li-ion batteries can be used for optimization of the battery size of electric vehicle with respect to battery life, vehicle performance and total lifetime vehicle economy. This is especially important in applications where fast charging may enable a significantly smaller battery system such as electric city buses.

Most Li-ion cells show both capacity fade and impedance growth as they age, but the relation between these two degradation characteristics and their implications on a vehicle level varies; whereas a moderate impedance growth has little effect on a low-power EV battery, it may have a dramatic effect on a high power HEV battery. Consequently, both impedance growth and capacity fade must be characterised for each application to assess the actual battery performance over the vehicle lifetime.

1.1. Current rate influence on the degradation of the $LiFePO_4$/graphite battery cells

Often, battery cycle life tests are performed under accelerating conditions such as elevated temperatures, high DOD or high current rates. Although such tests undoubtedly provide valuable information for comparisons and material studies, they are more seldom applicable to actual vehicle usage where the battery is subjected to complex load profiles. That is, few applications are designed to keep the batteries at temperatures above +40 °C in average, or where the charging/discharging rate is constantly high. Moreover, it is of great interest to the automotive industry to quantify the ageing caused by either rapid but not frequent fast charging or rapid charging at partial SOC combined with relatively slow discharges.

Generally, higher charging and discharging current rates are accelerating cell degradation due to several different ageing mechanisms ranging from uneven distribution of current and temperature on a macroscopic level to material stress at microscopic level where the Li-ion intercalation and diffusion speed are the speed limiting factors. In turn, this can lead to uneven ageing, deposition of the metallic lithium and solid electrolyte interphase (SEI) growth [14].

Several research studies on the estimation of the battery cycle life have been made in the recent years, but very few addressed the influence of the current rate on the battery cycle life. For example, Omar *et al.* analyses a comparative study of three different battery cells, also including the $LiFePO_4$/graphite type, for use in PHEVs [15]. This comparative study included different ageing factors such as temperature and current rates (0.33C, 1C, 2C, 5C and 10C) for charging and discharging but did not treat impedance growth at all. Another extensive study by Wang *et al.* [16] included both cycle life testing and the development of a semi-empirical capacity fade model for $LiFePO_4$/graphite battery cells. Although this work included the current rate dependence and temperature, the charge current rate was limited to 4 A ($\approx$1.7 C-rate) and the impedance rise of the cells was not included.

Furthermore, the work performed by Ref. [17] indicated that charging and discharging the battery at 2C instead of 1C or 0.5C may reduce the cycle life to 50%. In contrast, Ref. [11] concluded that the current rate is the least important ageing factor compared to temperature and SOC region but did not consider impedance growth and the subsequent power fade. The average current was also treated as an ageing factor for $LiFePO_4$/graphite cells at standard operation temperature in Ref. [3] and for $LiFePO_4/Li_4T_5O_{12}$ cells in Ref. [18] but with no specific investigation of power fade or impedance growth.

A complex lifetime dependence on the current rate was also found in Ref. [8] but the difference in ageing rate between symmetric/non-symmetric cycles or load patterns with rest periods was not studied. Furthermore, both capacity fade and impedance rise of $LiFePO_4$/graphite battery cells during accelerated calendar and cycle ageing were studied in Ref. [9] but with no quantitative investigation of the current rate influence on the ageing rate. Likewise, a new fast-charging method for $LiFePO_4$/graphite, were presented in Ref. [19] together with a cycle life test results for a single specific case, and [20] investigated the lifetime of $LiFePO_4$/graphite battery cells for different levels of DOD in the specific application case vehicle-to-grid but with fixed charge/discharge patterns.

To sum up, although a substantial amount of research on degradation of $LiFePO_4$/graphite cells has been made only a few studies have included several levels of fast charging where both capacity fade and impedance growth have been analysed. Moreover, to the authors' best knowledge, none of the papers published