



Degradation Studies on Lithium Iron Phosphate - Graphite Cells. The Effect of Dissimilar Charging – Discharging Temperatures



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ABSTRACT

This work presents a systematic evaluation of the effect of dissimilar charging / discharging temperatures on the long-term performance of lithium iron phosphate / graphite based cells by using multi-factor analysis of variance. Specifically, the degradation of prototype pouch cells is presented in a range of charging and discharging temperatures from -20°C to $+30^{\circ}\text{C}$, counting a total of 10 temperature combinations. In this manner, not only the effect of charging and discharging temperatures was analyzed, but also the correlations between them.

Fitting of the data showed a quadratic relationship of degradation rate with charging temperature, a linear relationship with discharging temperature and a correlation between charging and discharging temperature. Cycling at the charge/discharge temperatures ($+30^{\circ}\text{C}$, -5°C) produced the highest degradation rate, whereas cycling in the range from -20°C to $+15^{\circ}\text{C}$, in various charge/discharge temperature combinations, created almost no degradation. It was also found that when $T_c \approx 15^{\circ}\text{C}$ the degradation rate is independent of T_d . When $T_c < +15^{\circ}\text{C}$, the higher degradation occurs at higher T_d and at $T_c > +15^{\circ}\text{C}$ lower degradation occurs at higher T_d .

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1. Introduction

In addition to performance, safety and cost, lithium ion battery (LIB) durability has become one of the main focal points of research [1–3]. While degradation is not a key issue for batteries in consumer electronics due to their limited lifetime (e.g. typically few years), degradation is critical and particularly challenging for automotive applications where significantly longer lifetime is required [4–6].

The initial performance (e.g. capacity, power, efficiency) of LIBs deteriorates over their lifetime due to both the effect of usage (i.e. electrochemical ageing) and due to the effect of time (i.e. calendar ageing). This deterioration may originate not from a single process but from various processes and their interactions [7,8]. Many factors, such as the cathode and anode material, the environmental conditions and the characteristics of the cycling profile (e.g. current loads, lower and upper cut-off voltages) can influence these processes and hence play an important role in the degradation of LIBs. From the literature, temperature is identified

as the main factor affecting the stability of battery electrode materials as well as the degree of side reactions between electrodes and electrolytes [9]. In general, exposure to elevated temperatures accelerates degradation [1,10,11], enhances solid electrolyte interface (SEI) growth [10,12,13], and promotes changes in SEI morphology and composition (e.g. cracking, dissolution and re-precipitation with further loss of cyclable lithium [10,12]). On the other hand, exposure to low temperatures results in different challenges. The intercalation potential of carbon materials is close to the reduction potential to metallic lithium, therefore lithium plating and dendrite growth (due to slow lithium ion diffusion into the carbon anode material and within the electrolyte) are prone to occur [7,14–16]. This metallic lithium may react further with the electrolyte, leading to reduced lifetime and safety [7,17]. Despite the enormous amount of work reported in the literature on battery durability at different cycling temperatures [1,10,11,18–20], the findings of these studies are only representative of the specific cells and testing methods used since extrapolation to other conditions, types of cells, even with the same chemistry, is not straightforward. This makes quantitative comparison an impossible task in most of the cases. Moreover, some aspects are given less attention, such as the differences in ageing that may arise from variations in the environmental temperature in the testing chamber, the

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temperature measured at the surface of the cell, the actual temperature inside the cell or the temperature gradients within the battery [21]. Typical battery ageing test methods reported in the literature use the same environmental temperature for charging and for discharging. One ageing study found in the literature using dissimilar temperatures for charge and discharge compared cycling at (+45 °C, +45 °C) with cycling at (+45 °C, +65 °C) [22]. Authors of this work reported a higher capacity fade at the higher temperature combination, attributed to SEI layer growth and lithium plating [22]. Similarly, relevant standards [23–27] and test method manuals [28–30] use the same environmental temperature for charging and for discharging. However, it can be anticipated that cycling at different charge and discharge temperatures may have an effect on the degradation of LIBs since many of the processes causing degradation are temperature dependent. Besides, this situation represents a more realistic scenario in some cases (e.g. e-bike battery being charged in a temperature controlled indoor environment, but e-bike being used at different outdoor temperature). In fact, automotive and many portable applications experience significant temperature variations during typical battery usage (e.g. seasonal and daily temperature fluctuations).

At constant temperature cycling, loss of cyclable lithium, degradation of active material, and increase in internal resistance have been identified as important manifestations of ageing [31,32]. Wang et al. [18] reported that the capacity fade followed a power law relationship with charge throughput in the temperature range between +15 °C and +60 °C. This was not the case at 0 °C, which suggests that different processes may be taking place depending on the temperature conditions. Several authors have reported a square-root of time relationship with capacity fade [20,34–38] which represents the irreversible capacity loss due to SEI growth which consumes active lithium and is often controlled by a diffusion process [34,35]. Capacity degradation also seems to have a portion of linear ageing, which was published in references [37–39]. Simulations of the capacity fade at different temperatures compared to experimental data showed an exponential behavior of ageing (e.g. capacity loss) on temperature [18,20].

In this paper, we present a systematic evaluation of the effect of dissimilar charging and discharging temperatures on the ageing performance/degradation of lithium iron phosphate (LFP) / graphite prototype pouch cells designed for sub-ambient temperature operation. The objective is to understand the influence temperature combinations can have on cell performance. The number of temperature combinations was minimized by using design of experiment (DOE) approach [40], which is a common method used in industrial process optimization, but less frequently used in battery ageing analysis. Forman et al. [41] applied this method to battery degradation modeling and analyzed its prediction's precision and time saving possibilities. The minimum and maximum cut-off voltages and the current rate (i.e. factors) were varied and the optimal combination of factors was calculated, which provided the minimum prediction error (D-Optimum). Alternatives to the DOE can also be found in the literature. Muenzel et al. [42] developed a multi-factor battery cycle life prediction model, without using DOE, by reusing data from the experimental work of Omar et al. [11]. They used a fitting procedure in the multi-factor space and calculated a degradation rate matrix (rather than a single number). Baumhöfer et al. [43] used a data mining algorithm to select the significant ageing factors. They identified 950 attributes from 48 identical cells (except manufacturing differences). However, detailed analysis of the top 10 attributes did not identify a clear influential one towards battery ageing.

In this work, the test matrix was designed by DOE and the results were fitted by non-linear least square fitting (polynomial) including first order interaction between the factors (charge and

discharge temperature). The coefficients and the degree of polynomial were evaluated by analysis of variance (ANOVA) to find out the most significant prediction model. The method helps to understand not only the effect of charging and discharging temperatures, but also the correlations between them. This information will be fundamental to define future fit for purpose / realistic usage protocols (e.g. for inclusion in standards).

2. Experimental

2.1. Pouch cell preparation and experimental set-up

Prototype lithium ion cells were prepared using artificial graphite (IMERYS[®], D50 about 6 μm) as anodic active material and lithium iron phosphate (LFP) (BASF[®], D50 about 11 μm) as cathodic active material. The electrodes were obtained by a comma bar roll coating over common commercial Cu (Schlenk[®], 16 μm thickness) and Al (Showa Denko[®], 20 μm thickness) metal foils. A 25 μm thick polypropylene membrane was used as separator (Celgard[®]). For each cell around 80 g of electrolyte (1 M LiPF₆ in ethylene carbonate: diethyl carbonate (2:3 w/w) + 1% vinylene carbonate liquid electrolyte) were used. The resultant pouch cells (B5 format, external dimension 250 mm x 164 mm, thickness around 4 mm) have an operational voltage between 2.50–3.70 V and 6 Ah rated capacity. After formation, cells were shipped at 30% SOC (~3.1 V).

For testing, cells were placed in custom-made Plexiglas[®] holders (15 mm thickness each of the two holder plates) which prevented the current collectors from being pulled apart or bended by the battery cyler cables. A Maccor Series 4000 battery cyler (Maccor, Tulsa, US) was used for cycling via a 4-wire connection (current and voltage accuracy: 0.025% and 0.02% of full scale, respectively). This cyler also controlled the BIA MTH 4.46 environmental temperature chambers (BIA, Conflans Saint Honorine, France) with a temperature deviation in the center of working space: ± 0.5 K and a temperature homogeneity in space relative to the set value: ± 1.5 K.

A thermocouple was placed in the center of one side of each cell to monitor surface temperature variations.

2.2. Electrochemical cycling

The electrochemical experiments performed can be classified in three types of cycling: **1**) cell conditioning, **2**) reference cycling and **3**) long-term ageing. A description of each type of cycling is presented in the following:

2.2.1. Cell conditioning

Prior to any electrochemical cycling, cells were placed in a temperature chamber at 25 °C for at least 12 h to ensure thermal equilibrium. Then, three full charge / discharge cycles were carried out, with CC-CV charging at 0.1C current (calculated from rated capacity) until 3.7 V (CV phase maintained until 0.01C or 1 h was reached), and CC discharge at 0.1 C until 2.7 V. A rest time of 30 min after each charging and discharging step was used. A reference cycle (please see 2.2.2 for details) was performed for initial capacity determination (C_i) (Table 1).

2.2.2. Reference cycling

To determine the irreversible degradation and to ensure comparable results for different cycling profiles, it is important to perform a standard control measurement cycle at periodic intervals. For this, a reference cycle was performed. This reference cycle, based on the test procedure described in IEC 62660-1:2011 [23], consisted in two constant current (CC) galvanostatic cycles at 0.3C at 25 °C environmental temperature. After each charging and

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