



Comprehensive study of the influence of aging on the hysteresis behavior of a lithium iron phosphate cathode-based lithium ion battery – An experimental investigation of the hysteresis



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ABSTRACT

In this work a detailed investigation of the hysteresis behavior of the open circuit voltage (OCV) in a lithium iron phosphate (LiFePO₄) cathode-based lithium-ion cell is presented. For the first time the hysteresis behavior of the OCV in a LiFePO₄ cell is investigated in detail, taking the aging state of the cells into account as a fundamental factor. Tests were carried out in a time window of more than two years on cells in different aging states. The dependency of the major and minor loops of the OCV on temperature, current rate, short-term history and aging are shown and deeply discussed. The results show that the characteristics of the hysteresis of the OCV change completely during battery lifetime, not only concerning the major OCV boundaries but also regarding the single minor loops obtained through partial charge/discharge processes. The paper discusses the results considering different approaches presented in the literature published by date, and addresses the necessity of understanding the physic-chemical behavior of the cell in order to correctly determine the battery state in the application.

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1. Introduction

Lithium-ion cells invaded the market of electrochemical energy storage systems approximately 20 years ago. Since that time their usage has continuously grown, due to their excellent cell characteristics in terms of energy and lifetime [1,2]. Beyond mobile applications, such as computers and cell phones, the field of electric vehicles (EV) and plug-in hybrid electric vehicles (PHEV) seems to become the next objective. In this area, lithium iron phosphate (LiFePO₄) cathode-based lithium-ion cells have been individuated as one of the possible candidates in the automotive field, thanks to their long lifetime, excellent rate capability and intrinsic safety features [3]. On the other hand, among the limited drawbacks,

the flat behavior in an extended state-of-charge (SoC) range and the remarkable hysteresis characteristic of the open circuit voltage (OCV) make the online diagnostic of these cells complicated. Therefore, the complete knowledge and comprehension of the hysteresis behavior of this kind of cells during battery lifetime and their dependency on battery aging is of fundamental importance.

Hysteresis phenomena have already been identified in the past in several areas, such as mechanical [4] and magnetic fields [5]. In the area of electrochemical storage systems, the hysteresis of the OCV of nickel metal hydride (NiMH) cells is treated in several publications [6–8]. In [7] the authors state that the value of the voltage during the steady state, the so called open circuit potential (OCP), is a mix between the effect due to the intercalation reaction in the nickel hydroxide electrode and the effect due to the oxygen evolution side reaction. These two effects are unlikely separable, and they contribute concurrently to the hysteretic behavior of the OCV. In [9] Gerschler et al. give an overview of the hysteretic behavior that can be found in the world of lithium-ion batteries. They associate the hysteresis behavior of the OCV to the existence of a two-phase transition process. In this case the hysteresis is

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mainly due to the dissipation of energy in the crystal structure of the electrode during the two-phase transition. Examples of this can be found for both cathode and anode. In 1991, Sleight et al. [10] reported the existence of a hysteresis behavior in lithium batteries, studying the insertion processes in a manganese oxide (LiMnO₂) based electrode. Hysteresis is also studied in the intercalation/deintercalation process of a cobalt oxide (LiCoO₂) based electrode in [11] by Carlier et al. Small hysteretic phenomena are visible for each two-phase transition present in the OCV of the cell. In [12,13] traces of hysteretic behaviors in the potential of carbon and graphite electrodes are also reported. However, among all lithium-based batteries, the LiFePO₄ cathode-based cells are well known for their remarkable hysteresis behavior of the OCV, and its strong dependency on the short-term history. Several authors describe how the intercalation and deintercalation processes take place in the cathode's active material [14,15], namely the FePO₄, and under which processes the interaction among lithium ions and active material particles happens. These aspects represent fundamental factors in the explanation and comprehension of the hysteresis behavior of the OCV and its origin. Srinivasan et al. [16,17] debate this topic in detail by means of the introduction of the shrinking core theory. According to this, the two-phase transition in the cathode takes place through a first-order phase transition, i.e. the formation of a lithium-rich shell and a lithium-poor core region during intercalation, and of a lithium-poor shell and a lithium-rich core region during deintercalation. Between the two regions a phase barrier exists which moves toward the core of the particles or in the opposite direction, in a way that the concentration of lithium inside the region remains constant. As the value of the potential of a particle is directly correlated to the composition and ion concentration on the shell surface [18,19], a characteristic voltage plateau, i.e. a zone at two-phase transitions, is visible in the electrode potential curve. In [17] the authors use the shrinking core theory to investigate and explain the path dependency individuated in the LiFePO₄ electrode, namely the hysteresis. Different charge/discharge sequences are investigated in terms of electrode voltage trend. However, the authors highlight clearly that the individuated hysteresis does not have thermodynamic origin as for NiMH cells, but it is a rate-dependent phenomenon, which disappears with low current rate. The same shrinking core theory is employed in [20] for NiMH cells, and broadly used by Roscher [18,19,21] to study the power capability of a LiFePO₄ cell related to the path dependency. A huge contribution in this direc-

tion is given by Dreyer et al. [22,23], where the authors investigate the real thermodynamic origin of the hysteresis. The work clarifies that the battery as a system and its behavior during the achievement of the steady state condition cannot be represented as a single particle, but rather as a multi-particle combination, in which the interaction among the single elements (in form of exchange of lithium ions) cannot be neglected. According to this, for a defined battery SoC, depending on the recent past history, the value of the steady state voltage (equilibrium state) is strictly related to the equilibrium states that single particles in the electrode's active material reach through the interaction with each other. The same approach is employed by Sasaki et al. [24] to clarify a possible memory effect in lithium-ion batteries.

Summarizing, although the phenomena have been known for a long time and various authors have contributed with their studies and theories, there is not yet a clear explanation of the hysteresis of the OCV in lithium-ion batteries. Further and deeper investigations at cell and electrode levels could provide fundamental contributions. However, it is hard to find a complete investigation of the hysteresis phenomenon of the OCV in the literature where possible dependencies on short-term history, temperature, current rate and aging are considered. Table 1 shows a resume of a literature survey related to the hysteresis phenomena of the OCV in batteries. As it can be observed the mentioned factors are often only marginally discussed, while some of them (as the aging state) have never been considered.

At this point it becomes clear that a systematic investigation of the hysteresis phenomena, considering different fundamental parameter dependencies, is partially or completely missing. Therefore, the goal of this paper is to investigate in detail the dependency of the hysteresis of the OCV of a LiFePO₄-cathode based lithium-ion cell on different factors, and find out whether these dependencies can change with the battery state-of-health (SoH). The dependency of the hysteresis of the OCV on temperature, current rate and short-term history is investigated in LiFePO₄ cells in different aging states. The results are profoundly discussed, in order to clarify the origin of the found dependencies. The qualitative discussion has the goal to give a possible explanation of the impact of the SoH on the hysteresis, and to make aware that neglecting it can cause significant errors in the estimation of the battery state in the application. Therefore, the investigation of the impact of the aging state on the hysteresis behavior of several cells aged through different conditions and

Table 1
Resume of the literature review related to the investigation of the hysteresis behavior of the OCV in batteries. The symbols have the following meanings: ✕ - Phenomenon not investigated; ■□□ - Phenomenon only marginally discussed; ■■□ - Phenomenon partially investigated; ■■■ - Phenomenon fully investigated. The meaning of the different phenomenon considered is reported in Section 2.

Refer. no.	Description	Major loop	Minor loop	Minor loop path	Temperature	Current rate	Aging state
<i>Physico-chemical and electrical model</i>							
[25–27]	Modeling of the voltage behavior of NiMH cells	■■□	■■□	■□□	■■□	✕	✕
[9]	Investigation of the OCV of different lithium-ion batteries	■■■	■■□	■■□	■■□	✕	✕
[18,19,21,28]	Investigation of the physical and electrical behavior of the LiFePO ₄ OCV characteristics	■■□	■■□	■■□	■□□	■□□	✕
[29–31]	Electrical modeling of the LiFePO ₄ OCV behavior	■■□	■■□	✕	✕	✕	✕
[32,33]	Electro-thermal model and aging behavior of LiFePO ₄ cells	■■□	✕	✕	■□□	✕	✕
[34,35]	Modeling of OCV through Preisach's approach	■■□	■■□	✕	✕	✕	✕
<i>SoC estimation</i>							
[36–38]	SoC estimation by means of filters	■■□	✕	✕	■■□	✕	✕
[39–41]	SoC estimation using the OCV and the filtering approaches	■■□	■□□	✕	■■□	✕	✕
[42]	Balancing of LiFePO ₄ battery packs	■□□	✕	✕	✕	✕	✕
[43]	Electrical model for SoC estimation of LiFePO ₄ cells	■■□	■■□	✕	✕	✕	✕
<i>System simulation</i>							
[44]	Batteries for full EVs	■□□	✕	✕	✕	✕	✕
[45,46]	Batteries for V2G	■■□	■□□	✕	■□□	✕	✕

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