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On-board capacity estimation of lithium iron phosphate batteries by means of half-cell curves

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HIGHLIGHTS

- A novel approach for total capacity estimation of LFP cells in EVs is presented.
- The method is based on the estimation of some degradation modes during lifetime.
- The algorithm allows estimating the total capacity with an error of approx. 1%.
- The obtained results allow the recalibration of a hysteresis model of the OCV.

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ABSTRACT

This paper presents a novel methodology for the on-board estimation of the actual battery capacity of lithium iron phosphate batteries. The approach is based on the detection of the actual degradation mechanisms by collecting plateau information. The tracked degradation modes are employed to change the characteristics of the fresh electrode voltage curves (mutual position and dimension), to reconstruct the full voltage curve and therefore to obtain the total capacity. The work presents a model which describes the relation between the single degradation modes and the electrode voltage curves characteristics. The model is then implemented in a novel battery management system structure for aging tracking and on-board capacity estimation. The working principle of the new algorithm is validated with data obtained from lithium iron phosphate cells aged in different operating conditions. The results show that both during charge and discharge the algorithm is able to correctly track the actual battery capacity with an error of approx. 1%. The use of the obtained results for the recalibration of a hysteresis model present in the battery management system is eventually presented, demonstrating the benefit of the tracked aging information for additional scopes.

1. Introduction

The on-board estimation of the actual battery capacity in electric (EV) and hybrid electric (HEV) vehicles is a challenging task for a battery management system (BMS). The capacity has to be calculated without the need to discharge the battery completely starting from a fully charged state. Moreover, the discharge process is often carried out in a dynamic condition under variable temperature. As introduced from Farman et al. [1], the on-board estimation of the total battery capacity for lithium-ion batteries can be carried out mainly in four different ways. Often the selected approach calculates the total battery capacity according to equation (1) (Coulomb counting method):

$$Q_{\mathrm{actual}} = \frac{\int_{t_0}^{t_1} i(t)\cdot dt}{SoC_{t_1} - SoC_{t_0}}\cdot 100 \tag{1}$$

Once the value of the Ah-throughput between two state-of-charge (SoC) values is tracked, the actual capacity can be calculated estimating the value of the SoC within the same time period

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independently from the capacity itself. One of the ways to achieve this is using open circuit voltage (OCV), from the knowledge of the relation "OCV − SoC". Two conditions are required: i) this relation has to be known and monotonous, and ii) it has to remain unchanged during the battery lifetime (or at least its changes have to be tracked). This methodology is presented in the literature published to date by Einhorn et al. [2] and by Plett [3] with satisfactory results, even though the issue regarding the change of the OCV curve due to aging is not handled by the authors. The use of the OCV-SoC relation of equation (1) for capacity estimation becomes more complicated or not feasible in case of lithium iron phosphate (LFP) cells. In fact, the flatness of the OCV curve and its remarkable hysteresis behavior make the diagnostic of this cell particularly difficult. Moreover, the aging mechanisms have an evident impact on the OCV curve, changing its characteristics in an impressive manner [4]. Thus, such easy methodology cannot be used for LFP cells and a new approach is needed. Some of the authors in the studies presented by date attempt to estimate the battery capacity by means of filter approaches applied for the parametrization of equivalent battery circuit models. Waag [5] presents a method for the estimation of the electromotive force during battery voltage relaxation and uses this to estimate the SoC and the battery's capacity according to equation (1). However the method is not feasible for LFP cells, due to the mentioned features. Methods based on filtering approaches [6–8] generally present promising results, although they can be hardly implemented in cheap microcontrollers. In another approach, the researchers concentrated on the observation of the so called quasi-OCV curves, studying their characteristics by a differential analysis. The differential analysis is a tool which allows following clearly the change of voltage characteristics during the battery lifetime, and it can therefore deliver information related to the actual battery capacity. The incremental capacity analysis (ICA) is carried out by the differentiation of the incremental capacity in respect to the battery voltage [9,10]. The trend obtained presents peaks in correspondence to the so called "two-phase transitions" (the meaning will be clarified later on). On the other hand, by the differential voltage analysis (DVA), the derivation of the voltage curve in respect to the capacity presents peaks in correspondence to single phase regions (stages) [11–12]. Some authors attempt to use those methods onboard for capacity estimation [13–15]. Unfortunately the derivative operation in signals with superimposed noise can lead to the amplification of this noise, and, in some cases, to the misinterpretation of the processed information. Using the ICA and DVA as offline tools, Dubarry et al. [16,17] and Groot [18] analyze the behavior of the quasi-OCV curve during battery lifetime and model by simple equations the relation among the aging mechanisms (or so called degradation modes) and the characteristics of the electrode voltage curves. A similar approach is also used by Han et al. [19] for different lithium-ion chemistries, and by Wang in Ref. [20] for LFP cells. This method represents a promising approach which can be used as a baseline for the development of algorithms for on-board capacity estimation for LFP cells. Schmidt et al. [21] use this approach for the offline analysis of the open circuit potential with the goal of identifying the composition of blended cathodes and their degradation modes. In Ref. [22] the authors present an algorithm for capacity estimation based on half-cell curves. However, this method is applied on nickel manganese cobalt cells and is based on the assumption that the electrode characteristics do not change during battery lifetime, an assumption which cannot be made for LFP cells [17].

Based on these research lines we propose a novel algorithm for battery capacity estimation in LFP cells. The algorithm is based on the online estimation of the single degradation modes and on the determination of the characteristics of the electrode curves. This process is carried out based on the information in terms of plateau lengths present in the full voltage curves. Knowing the width of the plateaus, the corresponding degradation modes can be estimated in order to find the correct position and dimension of the single electrode voltage curve. Therefore, the full cell curve can be reconstructed and the total battery capacity can be calculated.

The work is structured as follows: Section 2 introduces the characteristics of the voltage curves of LFP cells and the impact of aging on its shape, with the introduction of a model which describes these phenomena. Section 3 introduces a new BMS structure with the implemented algorithm for capacity estimation. Section 4 discusses the obtained results. A conclusion and outlook are given in Section 5.

2. Degradation of LFP cells

In this section a description of the main degradation mechanisms which can occur during the lifetime of an LFP cell are described. Moreover, a model to describe their effects on the electrode voltage curves and on the full cell voltage curve is presented.

2.1. Degradation mechanisms

The description of the impact of the so called degradation modes on the characteristic of the full voltage curve of an LFP cell is reported by Dubarry et al. in Ref. [17,23]. These effects are again proposed and reproduced in this work in Fig. 1. Fig. 1a) shows the trend of the cell's full voltage curve. This is obtained subtracting the anode from the cathode voltage curve. The cathode presents a flat voltage characteristic, or a so called plateau, for the entire SoC range. This flat region is indicated with the letter A. The physical phenomenon behind this effect is known and reported since long in the literature with the name of "two-phase transition" [24–26]. It involves the co-existence of two distinct phases, with constant concentration but varying size, which produces the typical constant voltage phase. In case the anode is composed of graphite, the anode voltage profile presents three flat regions indicated as I, II and V, representing also in this case two-phase transition phenomena [12,19,27]. Accordingly, the full voltage curve of an LFP cell with graphite electrode is characterized by three plateaus, which are indicated in the small box in Fig. 1a) as IA, IIA and VA. As it can be observed, the lengths of the cathode and anode curves (amount of Ah which can be delivered under the same current per surface unit) are not equal, since generally the anode is slightly oversized to avoid lithium plating [23]. Moreover, in the fresh state, the starting point of the anode and cathode curves are slightly shifted by an offset, which means that during the operation of the cell the two electrodes are not used entirely.

The characteristics of the single plateaus in terms of length and position change during the lifetime affected by the single aging mechanisms. In the literature different degradation modes are reported [17,28–30]. The loss of lithium inventory (LLI) involves mainly the loss of lithium in the formation of the solid electrolyte interface (SEI) which cannot take part anymore in the main reaction. The LLI is also one of the causes of the initial offset between cathode and anode curve, as shown in Fig. 1a). Additionally, so called lithium plating also leads to LLI and thus to a subsequent capacity fade in case of significantly high charging current rates or in case of low ambient temperatures. In extreme cases it can lead to dendrite formation and therefore to an internal short. The effect of the LLI on the full voltage curve is depicted in Fig. 1b), and can be represented by a left shift of the cathode curve in respect to the anode curve [17]. As a consequence, the length of plateau IA is reduced together with a decrease of the battery capacity. Another degradation mechanism is the loss of active material (LAM). This