Journal of Power Sources 312 (2016) 55–59

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Influence of memory effect on the state-of-charge estimation of large-format Li-ion batteries based on $LiFePO_4$ cathode

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HIGHLIGHTS

- The memory effect in a $LiFePO_4$/graphite battery is more complex than in a half-cell.
- The memory effect is affected by the depth of discharge during the memory writing.
- The memory effect in large batteries is affected by parameter distribution.
- The memory effect needs to be considered in a battery management system.

ARTICLE INFO

Article history:
Received 9 October 2015
Received in revised form
4 January 2016
Accepted 11 February 2016
Available online 21 February 2016

Keywords:
$LiFePO_4$ battery
Memory effect
Partial charge
SOC
DOD

ABSTRACT

In this work, we systematically investigated the influence of the memory effect of $LiFePO_4$ cathodes in large-format full batteries. The electrochemical performance of the electrodes used in these batteries was also investigated separately in half-cells to reveal their intrinsic properties. We noticed that the memory effect of $LiFePO_4$/graphite cells depends not only on the maximum state of charge reached during the memory writing process, but is also affected by the depth of discharge reached during the memory writing process. In addition, the voltage deviation in a $LiFePO_4$/graphite full battery is more complex than in a $LiFePO_4$/Li half-cell, especially for a large-format battery, which exhibits a significant current variation in the region near its terminals. Therefore, the memory effect should be taken into account in advanced battery management systems to further extend the long-term cycling stabilities of Li-ion batteries using $LiFePO_4$ cathodes.

1. Introduction

The lithium (Li)-ion battery is one of the most promising energy storage systems used in large-scale energy storage applications such as pure electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs), as well as grid applications [1–5]. To extend the lifespan of Li-ion batteries, advanced battery management systems (BMSs) have been widely used, especially for high energy/power-density applications. However, the success of Li-ion systems strongly depends on accurate determination of the state of charge (SOC), which has a closed relationship with cell voltages and estimation of battery performances. During the last a few decades, many complicated methods have been proposed for the accurate determination of cell voltage and SOC. These methods include the extended Kalman filter [6–8], the dual Kalman filter [9–11], nonlinear observers [12,13], the sliding-mode observer [14], fuzzy neural networks [15–17], and the reduced-order electrochemical model [18]. Generally, equivalent circuit models, including the first-order, second-order, or electrochemical equivalent models [19,20], were used to simulate the open-circuit voltage and terminal voltage, where terminal voltage is cell voltage under load or during charge. To date, $LiFePO_4$ cathode material has been widely used in energy storage systems including EV and large-scale stationary applications because of its excellent cycling performance, low cost, and environmentally benign properties. However, the very flat

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http://dx.doi.org/10.1016/j.jpowsour.2016.02.041

voltage profile of $LiFePO_4$ makes it difficult to estimate the SOC with high accuracy. Although memory effect is one of the other factors that significantly affect estimation of the SOC in nickel cadmium batteries [21] and nickel metal hydride batteries [22], the absence of a memory effect has often been regarded as one of the advantages of Li-ion batteries.

Surprisingly, Sasaki et al. [23] reported recently that $LiFePO_4$ cathode material does exhibit a memory effect. After $LiFePO_4$ cathode was partially charged/fully discharged (so called “memory writing”) process, the voltage profile during subsequent charge (so called “memory release”) process exhibits positive deviation or a bump at the location corresponding to the SOC reached during the memory writing process. This deviation will lead to SOC estimation error. A multi-particle model based on the two-phase equilibrium (a Li-rich phase coexisting with a Li-poor phase) of the $LiFePO_4$ system was proposed by Sasaki et al. to explain the memory effect [23]. For a practical BMS, a slight voltage bump may not have significant effects on the SOC estimation of a cathode with a large voltage slope, but it will have remarkable effects on a cathode with a very flat voltage profile (such as $LiFePO_4$). Therefore, it is necessary to investigate how this newly discovered memory effect affects the management of full batteries used in practical applications.

In Sasaki's study [23], coin cells with a configuration of $LiFePO_4$/Li half-cells was used to study the memory effect in $LiFePO_4$. However, most commercial $LiFePO_4$ batteries used graphite as the anode. In this case, the influence of the memory effect of a $LiFePO_4$ cathode on the battery management becomes more complicated due to the multi-voltage plateau of graphite anodes (in contrast to the single voltage plateau of $Li_4Ti_5O_{12}$). Therefore, the primary challenge of determining the influence of the memory effect on commercial batteries is to distinguish the source of the voltage variation in $LiFePO_4$ batteries. The memory effect of $LiFePO_4$ was found to occur near the SOC value where the previous partial charge was terminated during the memory writing process. However, the values of voltage deviations vary significantly with the maximum SOC level reached during the memory writing process, thus increasing the uncertainty of SOC estimation in the next cycle.

In this work, we investigated the voltage fluctuation phenomenon at different SOCs and DODs using commercial $LiFePO_4$/graphite batteries. For clarity, we used SOC and depth of discharge (DOD) to represent the maximum SOC reached during the charge process and the maximum DOD reached during the discharge process of the memory writing step, respectively, unless specified otherwise. To improve the reliability of SOC estimation used in BMSs, the effect of the memory phenomena of $LiFePO_4$ cathode and the multi-stage voltage of graphite have been combined as the voltage bumps observed in the full batteries. The relationship between these voltage bumps and the amplitude of the voltage bumps in commercial $LiFePO_4$/graphite batteries was also identified.

2. Experimental

A 2 Ah battery (Model 26650, A123 Systems, LLC) with a $LiFePO_4$ cathode and a graphite anode was used to investigate the memory effect in a full battery. The battery was first fully charged/discharged between 2.5 V and 3.65 V using a battery testing system (Model BT-2000, Arbin Instruments), then partially charged/discharged to different SOC intervals. The $LiFePO_4$ cathode and graphite anode used in the $LiFePO_4$/Li and graphite/Li half-cell tests were obtained from a disassembled, as-received A123 battery. The dimensions of the electrode for the 26650 type A123 battery are 1.6 m (length) × 55 mm (width), and the dimensions of the tab are 10 mm (length) × 5 mm (width). The anode current collector (copper foil) is 7 μm thick, the cathode current collector (aluminum foil) is 13 μm thick, and the positive and negative electrodes each have four tabs. The 2032 coin-type half-cells were assembled in an argon filled glove box with oxygen and moisture levels of less than 1 ppm. Celgard 2045 was used as the separator and 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate solution (volume ratio = 1:2) was used as the electrolyte. The reassembled half-cell was initially charged/discharged at a rate of C/10 for five cycles until a stable capacity was reached. The memory-writing and memory-release procedures were the same as those reported by Sasaki et al. [23]. In this process, a memory writing cycle is a partial charge/discharge process; a memory release cycle is a full charge/discharge process after a memory writing cycle. The rest time after partial charge was set at 1 h, the rest time between memory writing (including partial charge and rest) and memory releasing was set at 10 min, and a C/2 rate was used in all the tests unless specified otherwise.

3. Results and discussion

3.1. Positive and negative electrode matching

To identify the loading ratio of battery and Li-ion insertion/extraction regions in both electrodes, the half-cell and full-cell capacities were tested at 1 mA with 2032 coin-type cells. In the power type $LiFePO_4$/graphite battery investigated in this work, ~10% more cathode material has been used. Fig. 1 shows the initial voltage profiles of reassembled coin-type half cells and full cell using positive electrode ($LiFePO_4$), the negative electrode (graphite) obtained from a disassembled A123 commercial battery. As shown in Fig. 1, the $LiFePO_4$ (LFP) cathode shows slightly higher capacity than the graphite anode. It indicates that the battery investigated in this work has an areal specific capacity ratio of 1.2:1.1:1 for LFP:graphite:battery.

3.2. Memory effects at different SOCs and DODs

Fig. 2 shows the memory-effect testing profiles and voltage curves at different SOC levels for a 2 Ah $LiFePO_4$/graphite battery when the DOD was fixed at 100%. As shown in Fig. 2a, the memory writing (a partial charge/full-discharge process) and memory release (a full-charge/full-discharge process after a memory writing process) processes were carried out at different SOC ranges between 30% and 80%. Fig. 2b shows voltage deviation curves derived by subtracting the standard charging voltage from the charging

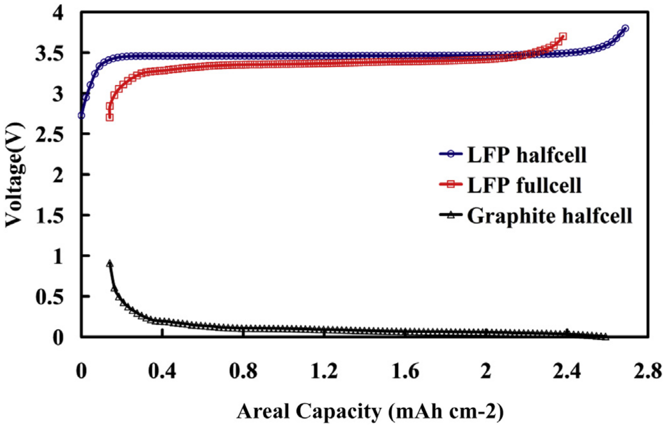

Fig. 1. Initial voltage curves of reassembled coin half-cells and full cell using electrodes [positive electrode ($LiFePO_4$), negative electrode (graphite)] from an A123 commercial battery.