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Complementary analyses of aging in a commercial $LiFePO_4$/graphite 26650 cell

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ABSTRACT

In this work we investigate the electrode degradation mechanisms in a commercial 2.5 Ah $LiFePO_4$/graphite 26650 cylindrical cell. Aged and fresh electrode samples were prepared by cycling two cells respectively five and 22 k times. Subsequently the cells were disassembled in a glovebox and the electrode samples were prepared for electrochemical testing in a 3-electrode setup, and for characterization with XRD, XPS and low-kV FIB/SEM tomography. A 1 μm thick CEI (cathode electrolyte interface) layer was observed at the electrode/electrolyte interface of the aged $LiFePO_4$ electrode. Relative to the fresh $LiFePO_4$ electrode, the aged electrode exhibited a larger series resistance which indicates the observed degradation layer increases the ionic resistance. In addition, micron-sized agglomerates, probably a mixture of carbonaceous material and decomposition products from the electrolyte, were observed at the electrode/electrolyte interface of the aged graphite electrode. These layers may contribute significantly to the loss of lithium inventory (LLI) in the cell, and to the loss of active material (LAM) in the graphite electrode. Low-voltage FIB/SEM tomography was used to detect local charging effects of graphite particles in the carbon electrode, an effect of poor dissipation of the electric charge to the ground after the sample interaction with the electron beam. The charging effects were primarily observed in the aged electrode and most of the locally charged particles were found to be close to the electrode/electrolyte interface, indicating a poorly percolating graphite network near this interface.

1. Introduction

Lithium ion batteries (LIBs) span a broad range of applications from portable devices to electric vehicles (EVs) [1,2]. However, limited lifetime is still a challenge for several LIB materials and the relation between degradation mechanisms and loss of performance is still not fully understood.

Despite its poor ionic and electronic conductivity $LiFePO_4$ (LFP) is one of the more interesting cathode materials for lithium-ion batteries due to its relatively high cyclability and safety [3,4]. To increase electron percolation in the electrode, the LFP is usually mixed with a carbonaceous additive such as carbon black. Graphite (Gr) is one of the early anode materials for commercial LIBs and it is still one of the most used anode materials [5]. Gr has a layered structure and is able to intercalate lithium ions between the graphitic layers. A solid electrolyte interphase (SEI) layer, with a thickness in the range of 10–100 nm, needs to be formed on the anode/electrolyte interface to protect the anode from solvent intercalation, resulting in exfoliation of the graphite, and to protect the electrolyte from decomposition [6–10]. An analogous less studied layer, called cathode electrolyte interface (CEI) layer, is also formed on the positive electrode surface and is usually thinner (~5 nm for $LiFePO_4$) than the SEI layer on the negative electrode [11–14].

Several studies have, in lab scale, examined the degradation mechanisms of LFP [15–18] and Gr electrodes [19–21], and various models have been presented to predict performance and lifetime of

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commercial $LiFePO_4$/graphite cells [22–25]. Loss of lithium inventory (LLI), loss of active material (LAM), loading mismatching between electrodes and decrease of the active electrode surface area are among the most common degradation processes responsible for the performance loss of Li-ion batteries [26]. However, strong links between several of the observed degradation mechanisms and the operation of the battery are still not fully established. It is therefore important to enhance these links by relating the morphological changes in the battery electrodes with the battery use. Very few studies are instead found on the evolution of the CEI layer on the positive electrode surface and they all include the use of surface sensitive techniques which only permit to analyze the layer within few nanometers of depth [11–14]. Even fewer investigations of the CEI layer after long-term battery cycling have been reported, and refer to solid state [27] and high voltage batteries [28].

This paper presents a comparative study of a fresh and a cycling-aged commercial $LiFePO_4$/graphite 26650 cylindrical cell. The morphology changes in the electrodes due to cycling are characterized by a palette of complementary analysis techniques such as X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Impedance spectroscopy and low-kV FIB/SEM tomography. The latter technique was developed to observe the electron percolation in SOFC anode Ni-networks [29] and has later been used to study the electron percolation in a laboratory $LiFePO_4$/CB electrode [17,30]. Here we use it to examine the electron percolation in the commercial graphite electrodes, in order to identify disconnected particles in the aged anode. Conventional FIB/SEM tomography is used to study morphological degradation and the evolution of the electrode/electrolyte interface in both the LFP and Gr electrodes.

2. Experimental

2.1. Battery cycling

Two commercial $LiFePO_4$/graphite 26650 cylindrical cells with a nominal capacity of 2.5 Ah were tested and characterized. The first battery was used as reference and labeled “F26650”. It was cycled five times between 0% and 100% state-of-charge at room temperature at a constant C-rate of 0.1 (250 mA). The second battery labeled “A26650”, was cycled 22000 times between 25% and 75% SOC at room temperature but at a constant C-rate of 4 (10 A). The 4C charge-discharge (25–75%) protocol was chosen because provides a very low degradation per kWh stored and represents relevant operation conditions without compromising the possibility for analysis and relating the observed degradation mechanisms with the test conditions. The test conditions are outlined in Table 1 and described in further detail below.

2.2. Battery disassembly

X-ray computed tomography (X-ray CT) was conducted on the batteries in part to prepare a suitable opening procedure. Further, before disassembling the fresh and aged battery, they were characterized with galvanostatic cycling with potentiostatic limitation (GCPL) and electrochemical impedance spectroscopy (EIS). The characterization methods are described in detail below. After X-ray CT, GCPL and EIS the two cylindrical cells were discharged to 2.8 V at 250 mA.

The two batteries were disassembled in an argon filled glovebox and the positive and negative electrodes were unrolled. The cylindrical cells consist of a 1.5 m $LiFePO_4$/carbonaceous additive positive electrode cast on both sides of an aluminum foil, a 1.5 m graphite (Gr) negative electrode cast on both sides of a copper foil and 2 polymeric separators soaked with liquid electrolyte. The total area of each of the battery electrodes and separators was 1950 cm^2. The battery configuration is schematically presented in Fig. 1. The carbonaceous additive in the positive electrode is unknown. In order to distinguish the additive from the graphite in the negative electrode we refer to the additive with “CB” and to the graphite in the negative electrode with “Gr”.

For the fresh battery, F26650, neither the anode nor the cathode foil showed any visible color difference between the various parts of the electrode; the part near the core of the battery and the part of the electrode near the skin of the battery as well as the edge and center parts looked the same. In contrast, a color difference was observed between the skin and the core part of the anode foil from A26650. As seen in the photos in the bottom part of Fig. 1, the anode foil is characterized by a blue shadowed region in the part of the foil close to the skin of the battery and a red region close to the core. In the presented photos the color saturation is increased to improve the visibility of the blue and the red region. The color covers almost completely the anode foil, with the exception of the sides of the electrode, where the original dark gray color of graphite is observed. Furthermore the edges appeared drier than the center regions, barely wetted by the electrolyte.

2.3. Sample set preparation

From each cylindrical cell the two electrode foils were rinsed with diethyl carbonate and vacuum dried at 120 °C for 2 h in order to remove the liquid electrolyte. From the four foils ten sample sets were cut. Each sample set consisted of several samples cut from proximately the same place in the foil. From F26650 two sample set were cut. One set from the cathode foil (labeled LFP_F) and one set from the anode foil (labeled Gr_F). From A26650 four sample sets were cut from the anode and four from the cathode. The sample sets were cut from the skin and core at the edge and center, respectively. The sample sets are labeled with respect to their original position in the foil: E.g. “_CE” refer to “Core, Edge” whereas “_SC” refer to “Skin, Center”. An overview of the sample sets is given in the lower part of Table 1. The positioning of skin, center, core and edge are indicated in Fig. 1. Samples from each sample set were prepared for microscopy, XRD, XPS analysis, lithium dendrite tests and electrochemical testing.

2.4. Characterization methods

2.4.1. X-ray computed tomography (X-ray CT)

The fresh and aged batteries were characterized using x-ray

Table 1
Test conditions for the examined samples.

Battery name	**F26650**		**A26650**							
Cycle number	5		22000							
C-rate	0.1		4							
SOC range	0–100%		25–75%							
Comment	Before disassembling, F26650 and A26650 were discharged to 2.8 V at 250 mA. Samples were cut from the washed and dried electrode rolls. For A26650 the samples were cut at the skin and core at the edge and center, respectively (Fig. 1)									
Sample set	**LFP_F**	**Gr_F**	**LFP_SE**	**LFP_CE**	**LFP_SC**	**LFP_CC**	**Gr_SE**	**Gr_CE**	**Gr_SC**	**Gr_CC**