

## Poor cycling performance of C-LiFePO<sub>4</sub>/graphite Li-ion cells at high temperature

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### 1. Introduction

Recently, LiFePO<sub>4</sub> with an olivine-type structure has attracted significant interest as a cathode material for Li-ion batteries because it is proposed to be a low cost material with excellent safety characteristics and because it has the potential of providing a long cycle- and calendar life [1]. However, LiFePO<sub>4</sub> is an insulating material, which seriously limits its rate capability [2]. Recently, extensive work has been conducted to enhance the electronic conductivity of LiFePO<sub>4</sub> by coating it with carbon using a sugar process [2]. To date, most of the efforts to improve the rate capability of LiFePO<sub>4</sub> have focused on carbon-coated LiFePO<sub>4</sub> (C-LiFePO<sub>4</sub>) in cells with metallic lithium counter electrodes. Few studies have been made on the stability of C-LiFePO<sub>4</sub> in a Li-ion cell. In this paper, we report results of high-temperature cycling of C-LiFePO<sub>4</sub>/graphite Li-ion cells.

### 2. Experimental, results and discussion

LiFePO<sub>4</sub> was prepared at 700°C from a mixture of iron(II) oxalate, ammonium di-hydrogen phosphate and lithium carbonate under N<sub>2</sub> gas. The resulting gray powder was coated with carbon layers using a preheated flow of N<sub>2</sub>/C<sub>3</sub>H<sub>6</sub> in a gas-phase process. This new technique consists of feeding a pre-heated reactor furnace containing LiFePO<sub>4</sub> with a mixture of N<sub>2</sub> and propylene C<sub>3</sub>H<sub>6</sub> as the carbon source gas. The temperature where C<sub>3</sub>H<sub>6</sub> gas was decomposed is set at 700 °C. The carbon content in the olivine was determined by thermogravimetric techniques to be around 3.5 wt%. X-ray diffraction confirms that C-LiFePO<sub>4</sub> is a pure phase. High-temperature (37°C and 55 °C) electrochemical tests were carried out on laser-sealed 110-mAh prismatic cells. Figure 1 shows the cycling data of the C- LiFePO<sub>4</sub> / MCMB graphite cells. In this case, the prismatic cells were cycled between 2.7 V and 3.8 V at room temperature, 37°C and 55°C using LiPF<sub>6</sub>/EC:DEC (3:7) as electrolyte at the C/3 rate. At 25°C, the cell cycles extremely well with no capacity fade up to 100 cycles. However, when increasing the temperature to 37°C and 55°C, the cells show significant capacity loss after 100 cycles especially at 55°C. Similar capacity fade was also reported when storing the cells at 3.8V for 4 weeks at 55°C. These results show that the olivine system has a major issue with high-temperature cycling that is similar to that reported in the manganese spinel system. To understand the reason behind the significant capacity fade at 55°C of the olivine system, the stability of C-LiFePO<sub>4</sub> in the presence of electrolyte was investigated. An appropriate amount of C-LiFePO<sub>4</sub> powder was immersed in a 1.2 M LiPF<sub>6</sub> in EC:DEC (3:7) electrolyte; the powder/electrolyte solution was kept at 55°C for one week. The solution was then filtered and analyzed by the inductively coupled plasma (ICP) technique to quantify traces of iron ions that may have dissolved in the electrolyte. At the end of this aging process, about 535 ppm of Fe-ions was detected in the C-LiFePO<sub>4</sub> electrolyte solution. This amount is significantly higher than the 90 ppm of Mn<sup>2+</sup> ions dissolution obtained in the case of the stabilized manganese spinel (Li<sub>1.06</sub>Mn<sub>1.94</sub>O<sub>4</sub>) after 4 weeks of aging at 55°C [3].

To investigate the origin of the significant capacity fade of the C-LiFePO<sub>4</sub>/graphite cells during cycling at 37°C and 55°C, the AC impedance of cells during cycling at 55°C was measured using a specially designed Li-Sn reference electrode. The results are shown in Figures 2 and 3. The AC impedance was measured after one formation cycle at room temperature (Fig. 2) and after 50 cycles at 55°C (Fig. 3). At the initial stages of cycling, the impedances of the negative

electrode and positive electrode were very similar. However, after 50 cycles at 55°C, the impedance of the negative electrode increased significantly and accounted for almost 90% of the total cell impedance. It is thought that the dissolved Fe<sup>2+</sup> was reduced to active metallic Fe at the graphite surface, whose potential is ca. 0.06~0.1V vs. Li<sup>0</sup>, and that the iron metal played a catalytic role in the formation and growth of an interfacial film at the graphite surface, leading to the huge rise of the interfacial impedance of the negative electrode. Energy Dispersive X-ray Spectroscopy (EDXS) carried out on graphite anode confirm the existence of metallic-Fe at the surface. The performance of C-LiFePO<sub>4</sub> was improved significantly by selecting high voltage anode (1.5V) such as Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> spinel anode where Fe-ions couldn't be reduced to its metallic state or by changing to an HF free electrolyte such as lithium oxalateborate (LiBoB)

### 3. References

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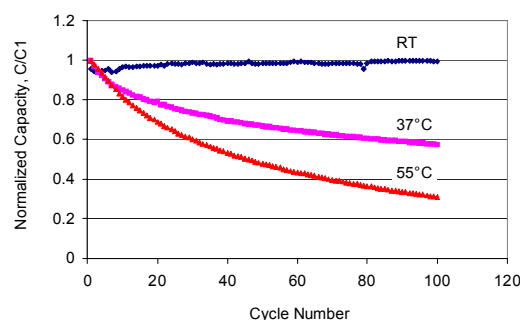


Fig. 1. Normalized discharge capacity with cycled number of C-LiFePO<sub>4</sub>/MCMB at 25°C, 37°C and 55°C

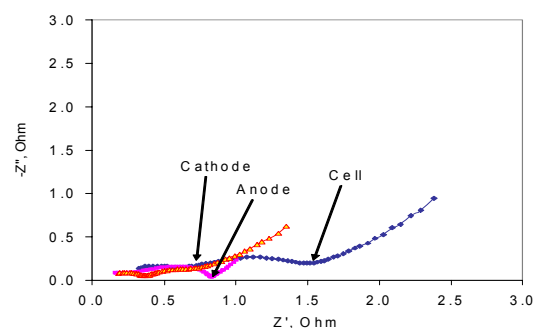


Fig. 2. AC impedance of positive, negative and full C-LiFePO<sub>4</sub>/graphite cell after 1 cycle at 25°C using Li-Sn alloy reference electrode

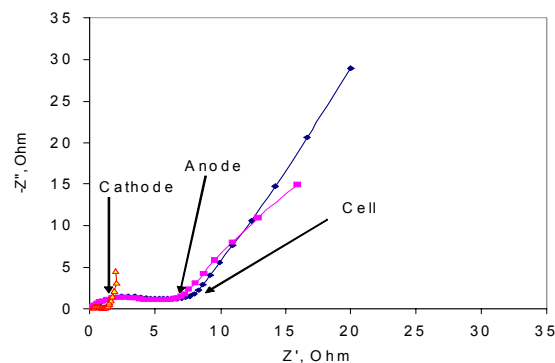


Fig. 3. AC impedance of positive, negative and full C-LiFePO<sub>4</sub>/graphite cell after 50 cycles at 55°C using Li-Sn alloy reference electrode