THE DEVELOPMENT OF LOW COST LiFePO$_4$-BASED
HIGH POWER LITHIUM-ION BATTERIES

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ABSTRACT

The cycling performance of low-cost LiFePO$_4$-based high-power lithium-ion cells was investigated and the components were analyzed after cycling to determine capacity fade mechanisms. Pouch type LiFePO$_4$/natural graphite cells were assembled and evaluated by constant C/2 cycling, pulse-power and impedance measurements. From post-test electrochemical analysis after cycling, active materials, LiFePO$_4$ and natural graphite, showed no degradation structurally or electrochemically. The main reasons for the capacity fade of cell were lithium inventory loss by side reaction and possible lithium deposition on the anode.

INTRODUCTION

Much research has been devoted to the study of rechargeable lithium batteries for application in hybrid electric vehicles (HEVs), where low price, long calendar life, safety and high power capability are required [1,2]. The active materials found in consumer-size lithium batteries, such as the synthetic graphite MCMB and LiCoO$_2$, will need to be replaced with lower cost materials such as natural graphite and cathode materials, such as those containing iron and manganese.

In the Batteries for Advanced Transportation Technologies (BATT) program sponsored by Department of Energy (DOE), we have been studying the LiFePO$_4$/natural graphite cell with a liquid electrolyte, as a low-cost baseline cell for application in EV, HEV or FCEV's. In previous work, we reported a limited cycle life for this cell system due to the consumption of the cycleable lithium at the anode by side reaction [3]. This was determined from post-test electrochemical analysis of the electrodes removed from the cycled cells [4]. In this work, we report on the addition of a carbon coating to the Al current collector which results in 2.5 times increased cell cycle life for 100% DOD cycling at C/2. In addition, the area specific impedance (ASI) of our pouch cells has dropped by an order of magnitude. This brings this technology into the realm of possibility for applications requiring high power as well as high-energy.

EXPERIMENTAL

The twelve-cm^2 pouch cells contained LiFePO4 cathodes and natural graphite anodes. The cathodes were prepared from 82% carbon-coated LiFePO$_4$ from the University of Montreal, 8% conducting carbon and 10% PVdF binder (Kureha). The NMP slurries of were cast onto either bare Al current collectors or carbon-coated Al (C/Al) current collectors. The C/Al were prepared in our lab with very thin coatings of Shawinigan

black and PVdF from the same type of slurry. These were dried extensively before preparing the cathodes. The anodes were prepared from SL20 natural graphite (Superior Graphite) and 10% PVdF binder (Kureha) on bare copper current collectors. The 10mAh pouch cells were assembled with Celgard 2500 and 1M $LiPF_6$+EC/DEC (1/1) electrolyte in an Ar-filled glovebox. Two formation cycles were carried out at C/25 to form a smooth SEI layer on the anode. Cycle-life testing was carried out with constant cycling (C/2) between 2.5 and 4.0V. A reference performance test (RPT) with high pulse of discharge 5C and charge 3.75C was carried out every 80 cycles to monitor the pulse power capability of the cell. More details of the manufacturing process and test protocol were described in previous work [5]. After cycling, the pouch cell was disassembled in the fully discharged state and each electrode was washed in DEC before electrochemical and other analysis in the glovebox. Electrochemical analysis of the electrode components before and after cycling was carried out in half-cells with Li reference and counter electrodes and the same electrolyte.

RESULTS AND DISCUSSION

The C/Al used in this work contained a layer less than 10 μm thick with a loading of about 0.1 mg/cm^2. The performance of $LiFePO_4$ cathodes prepared on C/Al and Al current collectors is compared in Fig. 1 which shows discharge voltage profiles for discharge rates from C/5 to 5C. The $LiFePO_4$ cathode on Al foil (left figure) shows large ohmic drops at high rates in the region of the flat plateau and a large decrease of specific capacity as rate is increased. The very thin carbon layer on the current collector (C/Al) appears to greatly reduce the contact resistance between electrode layer and current collector. Ohmic resistance of these cathodes, calculated from voltage increase at the end of discharge, decreased almost 80% (196Ω–cm^2 $\rightarrow$ ~40Ω–cm^2).

The cycle performance of $LiFePO_4$/natural graphite pouch cells prepared from these two types of cathode is compared in Fig. 2. Both cyclability and coulombic efficiency are significantly improved with the use of the C/Al in the cathode. Part of the improvement can be traced directly to the lower impedance of the cells with the C/Al. Fig. 3 shows the ASI (area specific impedance) of the pouch cells, which is calculated from RPT, before and after cycling. The ASI of cell with the C/Al in the $LiFePO_4$ cathode is significantly lower than cell with normal $LiFePO_4$ cathode, but more significantly, this low impedance is maintained during cycling. The ASI of the improved cell after 400 cycles is much lower than that of old cell after 80 cycles. However, the improved cell still has high capacity fade rate of about 0.1%/cycle. Our target for these pouch cells is 0.05%/cycle or a loss of 20% of the C/2 capacity loss after 400 cycles. In order to gain more insight into the capacity fade in these cells, they were taken apart as discussed above and the electrodes were examined in half-cells against lithium.

Electrochemical Diagnostics

Many different mechanisms have been invoked for the explanation of capacity fade occurring in lithium-ion cells, most concerning the stability of one or both of the electrodes. Our lab has examined several mechanisms for power and capacity fade observed in high-power lithium-ion cells containing Co-doped $LiNiO_2$ and graphite, such as 1) degradation of active material, 2) impedance rise of cell by formation of SEI layer,

3) lithium inventory loss by side reaction, 4) loss of carbon as conductive additive from cathode, etc. [6-10]. In our previous work with the $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cells, performance loss was found to be a combination of loss of lithium inventory and structural degradation of the cathode active material and impedance characteristics. In contrast, our early studies of $LiFePO_4$/natural graphite cells showed that lithium inventory loss and structural degradation of the anode were most important. The $LiFePO_4$ was found to be exceptional stable to long-term cycling [11,12].

The $LiFePO_4(C/Al)$/natural graphite cell was cycled 400 times and then fully discharged at C/25 before disassembly in the glovebox for electrochemical diagnostic analysis. The potential profiles during the C/25 cycling of the anode and cathode against lithium metal in excess electrolyte are compared with those from fresh electrodes in Fig. 4. The C/25 capacities of fresh and cycled electrodes indicate how much lithium can be cycled into and out of the active material without ohmic effects. This gives a measure of the structural stability and reversibility of active material. In Fig. 4, the C/25 capacities of cycled anode and cathode are almost same with fresh electrodes. The data show that these active materials are electrochemically stable during 400 cycles. This result for natural graphite is consistent with those from literature for other types of graphite [11-13]. The C/25 behavior of the $LiFePO_4(C/Al)$ cathode again shows excellent stability, in contrast to the structural degradation and phase segregation seen with the $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathodes [10].

The electrode samples were also measured at high rate to look at the changes in electrode impedance characteristics. The 5C profiles (Fig. 4) from the cycled cathodes also compare very well with those from the fresh $LiFePO_4(C/Al)$ cathodes, in contrast to previous results for cathodes with un-coated current collectors [12]. The carbon coating appears to ensure maintenance of a low contact resistance with the $LiFePO_4$ active material. This is a direct reflection of the stable cell impedance shown in Fig. 3. The cycled anodes also showed excellent capacity and no significant impedance rise with cycling when compared to the fresh anodes.

These analyses have eliminated all of the capacity/power fade mechanisms proposed above, except for the consumption of cycleable Li from the cell. The measure of lithium loss is demonstrated in Fig. 5. The first charge of the cycled cathode, in a half-cell against lithium, reveals how much cycleable lithium is remaining in the cell after cycling. We are fairly confident that since the cell was discharged at slow rate before disassembly and the anode samples tend to show voltages greater than 1.5V vs. Li, that there is no **cycleable** Li remaining in the anode. Comparison of this first charge capacity with the full capacity on the second cycle (shown in Fig 4 and 5) shows that the $LiFePO_4$ cathode contains only 55% of the original Li content after formation and cycling. Part of this, about 24%, was lost during the anode formation process and the balance of about 21% was lost during cycling. From results of Figs 4 and 5, we conclude that the main reason for the capacity fade in these $LiFePO_4$/natural graphite pouch cells is the loss of cycleable lithium. This type of loss is usually associated with the continual formation of the SEI, which is possibly preceded by the dissolution of the SEI. We did observe a significant amount of gassing in these pouch cells during cycling, suggesting the continual oxidation of the electrolyte solvent(s). The fact that the impedance of the anode was not compromised during this side-reaction also suggests that the SEI is maintaining a fairly steady thickness, or at least is maintaining a high conductivity.

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The cyclability curves in Fig. 2 show small but sharp drops in capacity at the 80 cycle intervals where the RPT tests are carried out, suggesting that the high current pulses in this measurement may be exacerbating the capacity loss in the cell. The high overpotentials developed during the 10-second 3.75C charge pulses at high SOC could lead to lithium deposition on a low conductivity anode. This is especially apparent for the cell without the C/Al in the cathode. To investigate the effect of the RPT measurements on the capacity maintenance in these cells, we replaced the RPT with a full-spectrum impedance measurement to keep track of the increases in cell resistances during cycling. The AC perturbation employed potential swings of only $\pm$ 10 mV and is not expected to lead to large overpotentials or Li deposition. However, as is shown in Fig. 6, the cyclability and coulombic efficiency are essentially the same whether subjected to the RPT pulses or not. Both of these cells contained the C/Al in the cathode. However, comparison of the impedance changes in Fig. 7 shows that impedance of the cell subjected to the RPT is much higher than the cell without RPT after 80 cycles, even though the impedances of fresh cells (small figure in Fig. 7) were quite similar. Further analysis of the anodes after cycling will be carried out to understand this added sources of degradation, which could be quite significant to the application of the $LiFePO_4$/natural graphite cell in a high-power pulse application such as the HEV..

CONCLUSIONS

The addition of a carbon-coated current collector to the cathode of the $LiFePO_4$/natural graphite cell lead to 2.5 times improvement in cyclability. In addition, the cell impedance was reduced by an order of magnitude and the impedance rise during cycling was only a few percent. Post-test electrochemical analysis of cycled electrodes showed that these electrodes did not lose their original capacity when provided a large source of Li, even after 400 cycles. However, it was revealed, in the half-cell studies of the cathode, that 21% of cycleable lithium was consumed during cycling. Cells cycled with and without periodic high-current-pulse RPT measurements showed similar cyclability but a faster rate of impedance rise during cycling for the cell subjected to the RPT. This could possibly result from lithium deposition during the charging pulses at high SOC. Spectroscopic analysis of the anode surfaces will be carried out to further understand the side-reactions going on in this cell.

ACKNOWLEDGEMENTS

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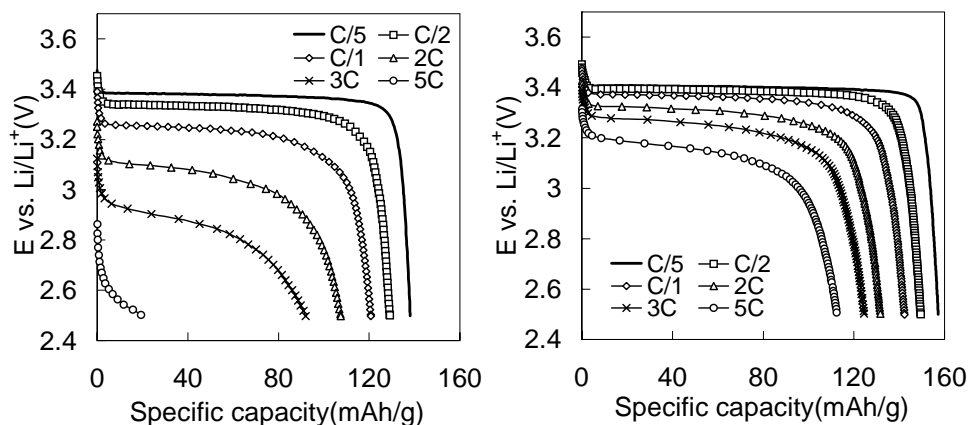
Fig. 1. Discharging voltage profiles of LiFePO$_4$ cathodes on only Al foil (left) and carbon-coated Al foil (right) for various C rates. Charging rate C/2.
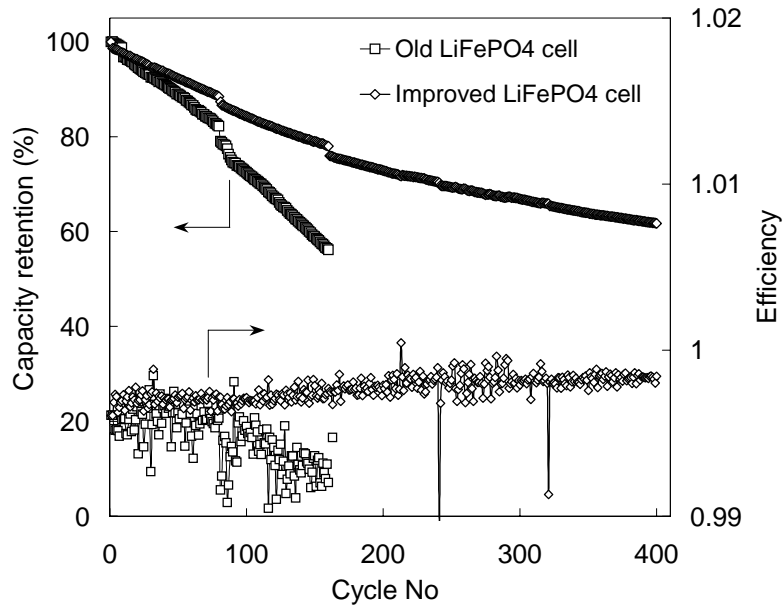
Fig. 2. Cyclability and efficiency of pouch lithium-ion cells for constant C/2 cycling
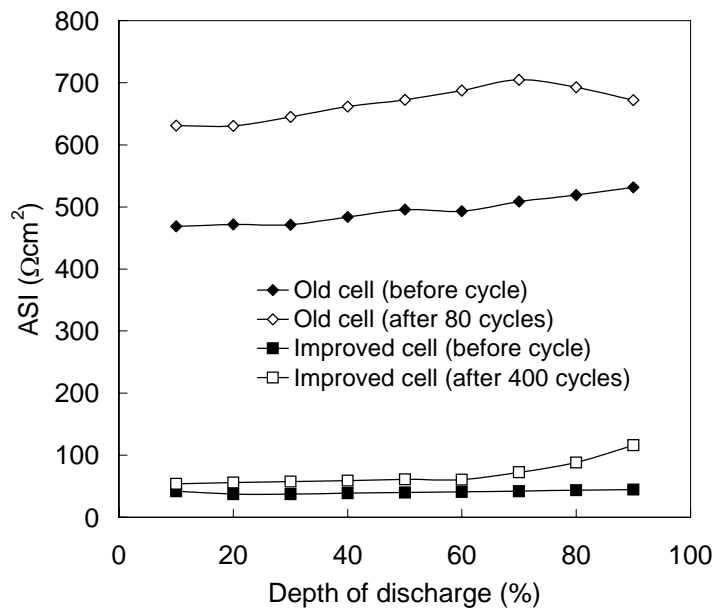

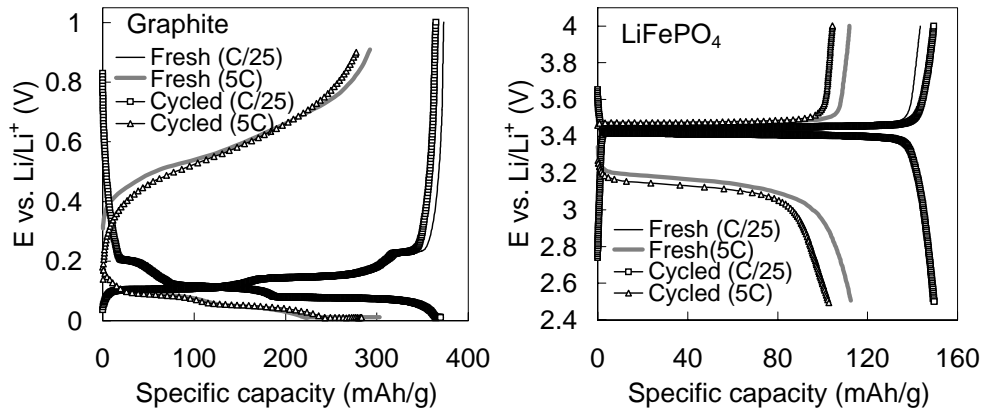Fig. 3. ASI (area specific impedance) of pouch cells, which was calculated from RPT

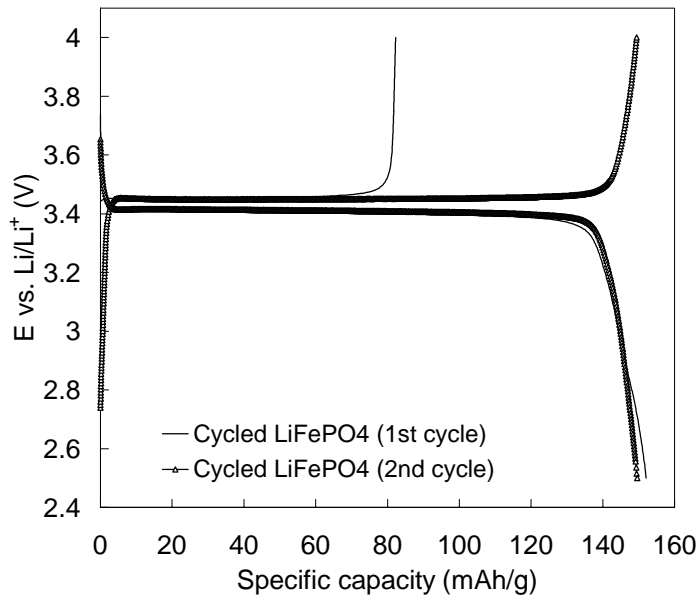Fig. 4. Post-electrochemical test of electrodes in half-cell against fresh Li metal

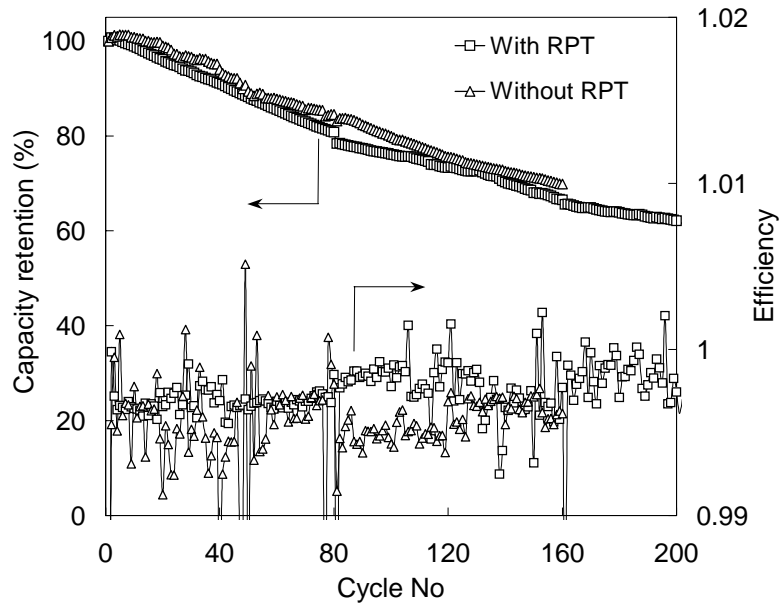Fig. 5. Voltage profile of cycled cathode at C/25 in half-cell against fresh Li metal

Fig. 6. Cyclability and efficiency of pouch cells with and without RPT for constant C/2 cycling
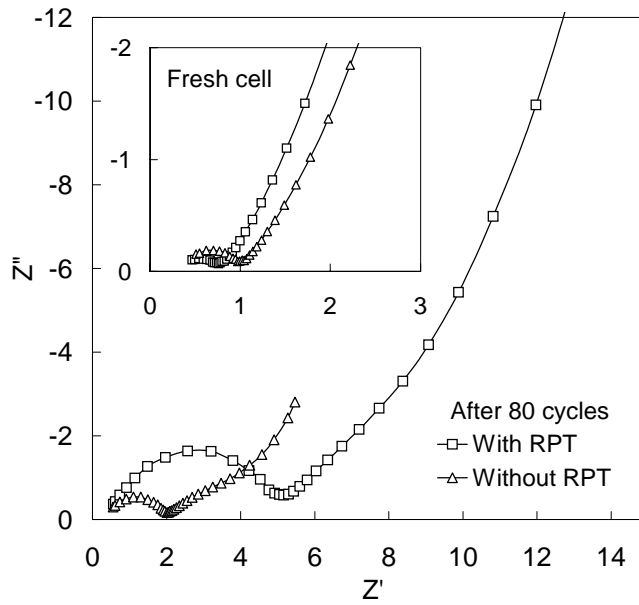

Fig. 7. Impedance plots of cells with and without RPT before and after cycling