DEVELOPMENT OF LITHIUM IRON PHOSPHATE / GRAPHITE SYSTEM LITHIUM-ION CELLS FOR TELECOM APPLICATIONS

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ABSTRACT

Lithium iron phosphate ($LiFePO_{4)}$ is a very attractive positive active material because of features such as large discharge capacity of 160 mAh/g and has demonstrated long life even at high temperatures The current $LiFePO_4$ chemistries, however, have shown to have poor high rate discharge capability. Therefore, in order to improve this chemistry, prototype lithium-ion cells with an improved $LiFePO_4$/Gr electrode system have been developed. We made and evaluated 4Ah cells and 50Ah cells. The cells showed superior discharge performance with a flat voltage profile and maintain capacity retention of 98% even at high currents of 10CA. Furthermore, even after long term cycling at high ambient temperature of 45^{o}C, the cells retain a much higher capacity than conventional $LiMn_2O_4$/Gr chemistry. We compared the new chemistry with identically sized conventional $LiMn_2O_4$/Gr system cells (same cell case and terminals). The new cells have almost the same charge/discharge energy (Wh) and power capability (W). However, the $LiFePO_4$ cells showed much better life performance, especially at high temperature condition.

1. INTRODUCTION

Currently, lead-acid batteries are primarily used as a backup power source for telecommunication applications. Lead-acid batteries are a very mature technology and have a long history of use in the industry, and as such, its operating and life parameters are fairly well understood. However, they have relatively low specific energy and energy density compared with other newer batteries. Lithium-ion batteries have recently been evaluated as potential candidates for deployment in telecommunication networks. Its much higher specific energy and energy density enable up to a 70% reduction of weight and volume compared with lead-acid batteries. Additionally, lithium-ion batteries that have $LiFePO_4$ as positive active material demonstrate high capacity and longer life even at high temperature. In this study, we tried to improve the poor high rate discharge capability of $LiFePO_4$ lithium-ion cell due to low electron conductivity by optimizing the electrode design. 4Ah and 50Ah cells are manufactured and evaluated. [1)] [2)] We will discuss the electrical performance and life performance compared with conventional industrial lithium-ion batteries, which have $LiMn_2O_4$ positive active material. [3)]

2. EXPERIMENTAL

2-1 Small Cells

Manufacturing Process

Positive electrodes are made by a paste coating process on aluminum foil. The paste was prepared with $LiFePO_4$, carbon powder (as an electron conducting material), plastic binder, and organic solvent. Negative electrodes are made by a paste coating process on copper foil. The paste was prepared with graphite, plastic binder and organic solvent. These electrodes are pressed, dried in vacuum chamber, wound with plastic separators, and inserted into laminated film pouch case. The pouch cell was sealed after electrolyte filling. Using the small cell design, we made two different types of $LiFePO_4$ cells. One type has regular $LiFePO_4$ particles and the other type has carbon-loaded $LiFePO_4$ particles to improve the high rate discharge capability.[2] Hereafter, the cell with regular $LiFePO_4$ particles is called "Regular Fe Small Cell" and the cell with carbon-loaded $LiFePO_4$ particles is called "Improved Fe Small Cell." And also we prepared another cell, which has conventional $LiMn_2O_4$ positive material. The manufacturing processes are the same, except the positive active material. Hereafter, it is called "Conventional Mn Small Cell." These three cells will allow a comparison of the new $LiFePO_4$ cell chemistry with the standard $LiFePO_4$ chemistry along with a comparison to the existing $LiMn_2O_4$ chemistry currently in use.

Dimensions and Mass

The small cell dimensions are W65mm x L115mm x T11.3mm. The mass is 132g.
The internal structure and picture of the cell is shown in Fig. 1 and Fig. 2.

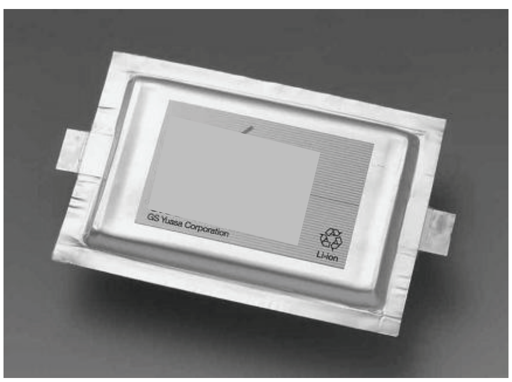

Fig. 1 Picture of the Small Cell

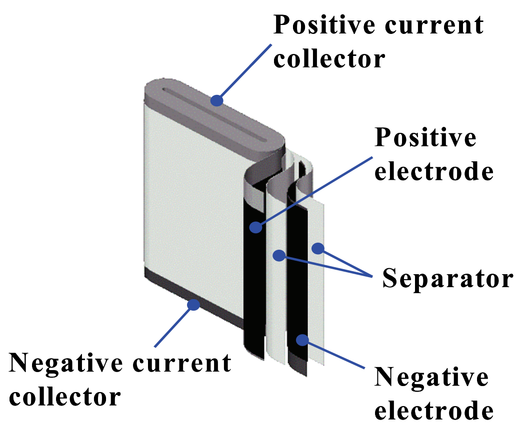

Fig. 2 Structure of the Small Cell

2-2 Large Cells

Manufacturing Process

The larger cells use the same case, cover and terminal hardware as our existing industrial LIM cells which use lithium manganese Spinel ($LiMn_2O_4$) /graphite system. [3)] Positive electrodes are made by a paste coating process on aluminum foil. The paste was prepared with $LiFePO_4$ carbon powder (as an electron conducting material), plastic binder, and organic solvent. Negative electrodes are made by a paste coating process on copper foil. The paste was prepared with graphite, plastic binder and organic solvent. These electrodes are pressed, dried in vacuum chamber, wound with plastic separators, attached current collectors and terminals, and inserted into stainless-steel metal case. After electrolyte filling, the stainless steel case was sealed. We made two versions of the large cell with the carbon-loaded $LiFePO_4$ particles and also our standard $LiMn_2O_4$. Hereafter, they are called “Improved Fe Large Cell” and “Conventional Mn Large Cell,” respectively. We can directly compare the large experimental cells with the existing $LiMn_2O_4$ cells to demonstrate the performance improvements.

Dimensions and Mass

The large cell dimensions are W 170mm x L 115mm x T 47mm. The mass is 2.1kg.
The picture of the cell is shown in Fig. 3.

Fig. 3 Picture of the Large Cell

3. TEST RESULTS AND DISCUSSIONS

3-1 Small Cells Experimental Results

Comparison between the Regular Fe Small Cell and the Improved Fe Small Cell

Discharging voltage profiles are shown in Fig. 4. The Regular Fe Small Cell provided 3.3Ah with condition of 1C (4A) constant current and 2.0V cut off. Comparatively, the Improved Fe Small Cell provided 4.1Ah under the same condition, that is, the Improved Cell achieved 25% capacity increase. From Fig. 4 it can also be shown that the Improved Fe Small Cell has a flat discharge curve over its capacity range, which will allow it to provide stable power (watts) during discharge.

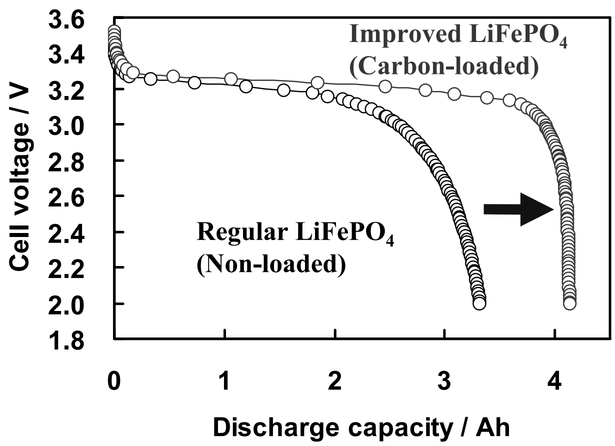

Fig. 4 Discharge Voltage Profiles of Regular Fe Small Cell and Improved Fe Small Cell

Charge: 4 A to 3.6 V followed by constant voltage until cutoff current of 0.04 A at 25^{o}C.

Discharge: 4 A to 2.0 V at 25^{o}C.

High Rate Discharge Test Results of the Improved Fe Small Cell

Fig. 5 shows discharge voltage profiles at various discharge rates. At a discharge rate of 10CA (40A), the cell showed 98% capacity vs. its 1C (4A) capacity, and at 20CA (80A), it provided 95% capacity of its 1C (4A) discharge rate. Fig. 5 also shows a relatively flat voltage profile, even at the very high discharge rates of 10C and 20C.

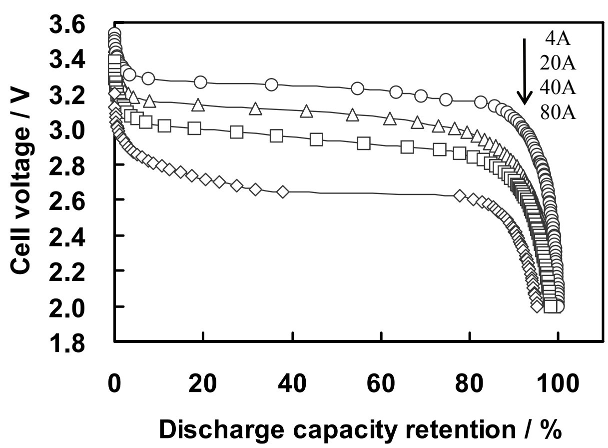

Fig. 5 Discharge Voltage Profiles of Improved Fe Small Cell at Various Discharge Rates

Charge: 4 A to 3.6 V followed by constant voltage until cutoff current of 0.04 A at 25 ^{o}C.

Discharge: 4, 20, 40, and 80A to 2.0 V at 25 ^{o}C.

Discharge Performance at Various Temperature of the Improved Fe Small Cell

Fig. 6 shows discharge voltage profiles at various temperatures. There is a temperature dependence of capacity with the Lithium Iron Phosphate system. For example, discharge capacity at –10°C was 73% of room temperature (25°C). This behavior is different from other lithium ion batteries that have $LiCoO_2$ or $LiMn_2O_4$ as a positive active material, which shows almost the same capacity even at low temperature such as –10°C. [3) 4)]

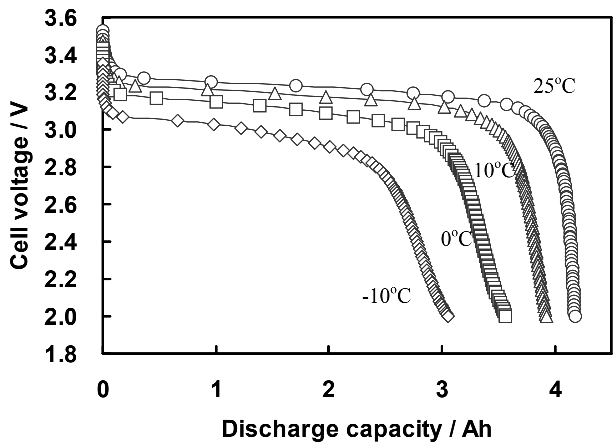

Fig. 6 Discharge Voltage Profiles of Improved Fe Small Cell at Various Temperatures

Charge: 4 A to 3.6 V followed by constant voltage until cutoff current of 0.04 A at 25 °C.
Discharge: 4A to 2.0 V at 25, 10, 0, and -10 °C.

Cycle Life Test Results

Cycling tests were performed on the Improved Fe Small Cell and Conventional Mn Small Cell to demonstrate improved cycle life performance. The test conditions are shown below.

Improved Fe Small Cell:

Charge: 1C (4A) constant current followed by 3.6V constant voltage until cutoff of 0.04A at 45°C
Discharge: 1C (4A) constant current until cutoff of 2.0V at 45°C

Conventional Mn Small Cell:

Charge: 1C (4A) constant current followed by 4.15V constant voltage for 3 hours at 45°C
Discharge: 1C (4A) constant current until cutoff of 2.5V at 45°C.

Fig. 7 shows cycle life test results. The Conventional Mn Small Cell shows 73% capacity retention after 500 cycles in this condition. This relatively large capacity loss is caused by the high temperature condition. [3)] However, the Improved Fe Small Cell shows 94% capacity retention after 500 cycles with the same condition.

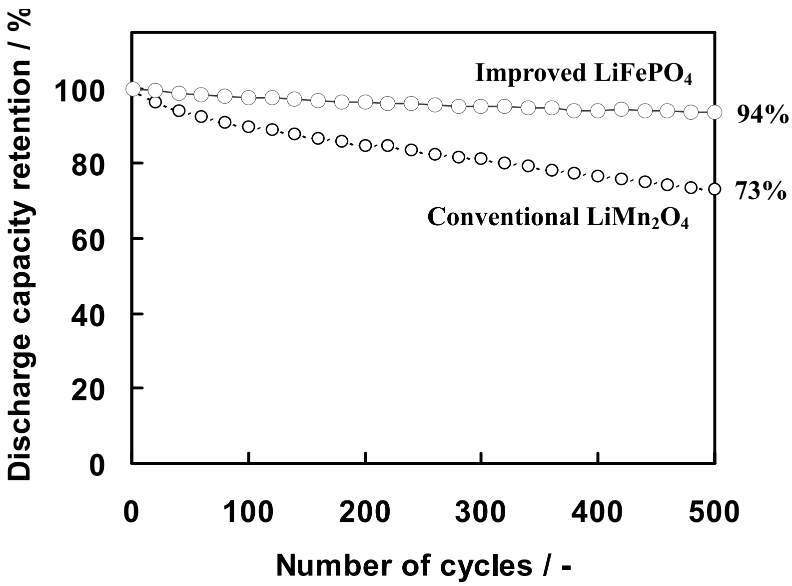

Fig. 7 Cycle Life Test Results of the Improved Fe Small Cell and the Conventional Mn Small Cell at 45 ^{o}C

Improved Fe Small Cell:
Charge: 1C (4A) constant current followed by 3.6V constant voltage until cutoff of 0.04A at 45 ^{o}C
Discharge: 1C (4A) constant current until cutoff of 2.0V at 45 ^{o}C

Conventional Mn Small Cell:
Charge: 1C (4A) constant current followed by 4.15V constant voltage for 3 hours at 45 ^{o}C
Discharge: 1C (4A) constant current until cutoff of 2.5V at 45 ^{o}C

The Outside Plant (OSP) environment requires a battery that can handle extreme temperature conditions. The life data at 45°C shows that the improved Fe cells can work well in this high heat environment. At the lower temperatures there is a temperature effect that is not as pronounced as in the currently deployed VRLA technologies so, even here, $LiFePO_4$ is an improvement.

3-2 Large Cells

Comparison between the Conventional Mn Large Cell and the Improved Fe Large Cell

Discharging voltage profiles are shown in Fig. 8. In terms of capacity delivered, the Conventional Mn Large Cell provided 45Ah with condition of 40A constant current discharge at 25^{o}C. Comparatively, the Improved Fe Large Cell shows 52Ah under the same condition. The cell voltage for $LiFePO_4$ chemistry is lower than other lithium ion chemistries (lithium cobalt, lithium nickel, lithium manganese spinel) this is a fundamental property of the $LiFePO_4$ chemistry. As shown in Fig. 5, the average discharge voltage of Improved Fe Large Cell was 3.3V as compared to 3.8V for the Conventional Mn Large Cell. But, because of higher discharge capacity, the energy delivered (Wh) of Improved Fe Large Cell discharge was 172Wh, and that of Conventional Mn Large Cell discharge was 171Wh. So, even with the reduced cell voltage, the energy delivered is the same between the Improved Fe Large Cell and the Conventional Mn Large Cell.

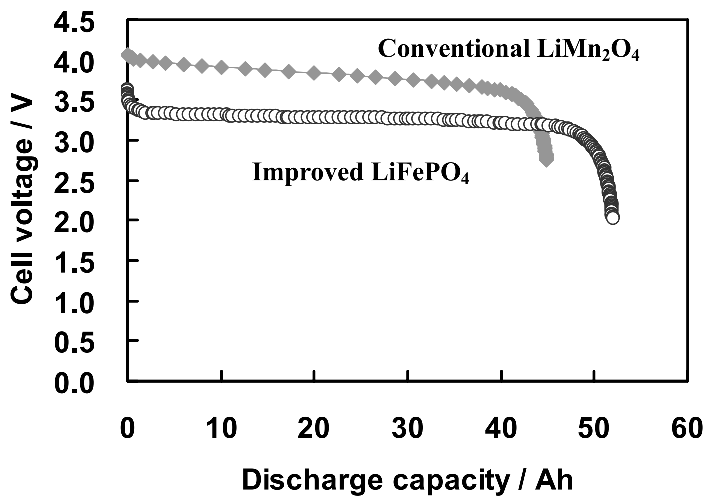

Fig. 8 Discharge Voltage Profiles of Improved Fe Large Cell and Conventional Mn Large Cell

Improved Fe Large Cell:
Charge: 40A constant current followed by 3.6V constant voltage until cutoff of 0.4A at 25 ^{o}C
Discharge: 40A constant current until cutoff of 2.0V at 25 ^{o}C

Conventional Mn Large Cell:
Charge: 40A constant current followed by 4.1V constant voltage for 3 hours at 25 ^{o}C
Discharge: 40A constant current until cutoff of 2.75V at 25 ^{o}C

High rate discharge test results of the Improved Fe Large Cell

The cell was discharged at 40A, 200A, and 400A constant current with a 2.0V cut off. The discharge capacity at 400A was 51.4Ah and corresponds to 99% of the capacity at 40A. The voltage profiles are shown in Fig.9. So, high range discharge does not appreciably reduce the capacity of the cell, even up to 10C for the larger cell.

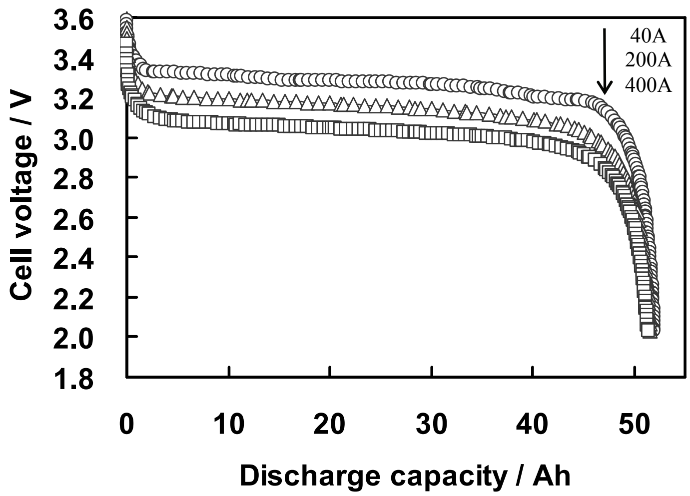

Fig. 9 Discharge Voltage Profiles of Improved Fe Large Cell at Various Discharge Rates

Charge: 40 A to 3.6 V followed by constant voltage until cutoff current of 0.04 A at 25 ^{o}C.
Discharge: 40, 200, and 400A to 2.0 V at 25 ^{o}C**.**

CONCLUSIONS

The cells that have carbon-loaded $LiFePO_4$ as a positive active material with 4Ah size pouch cell case demonstrated 25% larger capacity than the cell with regular $LiFePO_4$ at 1C discharge condition. High-rate 10C capacity retention was 98% and 20C capacity retention was 95% compared with 1C rate. However, it showed lower capacity at lower temperature; for example, capacity at –10^{o}C was 73% of one at 25°C at 1C rate. This behavior is different from other lithium ion batteries that have $LiCoO_2$ or $LiMn_2O_4$ as a positive active material, which show almost the same capacity even at low temperatures of around –10^{o}C. The cells that have carbon-loaded $LiFePO_4$ as a positive active material exhibited 94% capacity retention after 500 cycles at 45°C, compared with 73% capacity retention for same dimension $LiMn_2O_4$ cell. In the larger cell, 40Ah sizes, configuration study, the cell which has carbon-loaded $LiFePO_4$ shows 52Ah capacity, 3.3V average voltage, and 172Wh energy at 40A constant current discharge condition at 25°C. This compares with values of 45Ah, 3.8V, and 171Wh, respectively, for the conventional $LiMn_2O_4$ material cell tested under the same conditions. Even though the large Fe cell has a lower per-cell voltage, the energy delivered is the same between the Fe cell and the Mn cell. However, we think the capacity of $LiFePO_4$ cell can be further improved to increase the Wh delivered and maintaining the excellent long life performance at high temperature, the future of $LiFePO_4$ is very promising.

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