EVS24
Stavanger, Norway, May 13-16, 2009

High-Performance Electric Vehicle Battery with Lithium Iron Phosphate for Positive Active Material

Isao Suzuki, Tomotada Mochizuki, Takeshi Nakamoto, Yasushi Uebo, Koichi Nishiyama
Corporate R&D Center, GS Yuasa Corporation
1, Inobanba-cho, Nishinosho, Kisshoin, Minami-ku, Kyoto 601-8520, Japan
E-mail: isao.suzuki@jp.gs-yuasa.com

Abstract

$LiFePO_4$ is very attractive positive active material because of its features such as environmentally-friendly chemicals and high thermal stability. New prototype carbon-loaded $LiFePO_4$/graphite lithium-ion cells with large capacity of 25 Ah have been developed for electric vehicles (EVs) applications. The developed cells show remarkably high discharge performance with a flat voltage profile and high-rate capacity retention of 99% even at large current of 5 CA (125 A). The specific output power turned out to be high value over 600 W/kg at 50% SOC at 25 ^{o}C. The cells exhibit outstandingly good cycle life and calendar life performances even at high ambient temperature of 45 ^{o}C compared with the $LiMn_2O_4$/graphite system for EVs, automatic guided vehicles (AGVs), and so on. Furthermore, it was found that the cells showed the superior safety of EUCAR hazard level 3 from the result of crush and overcharge tests. The developed prototype carbon-loaded $LiFePO_4$/graphite lithium-ion cells will be suitable for EVs applications.

Keywords: Lithium battery, cycle life, battery calendar life, safety, EV

1 Introduction

It is very interested in EVs as environmentally-friendly transportation because it doesn't emit the greenhouse gases while running. The mileage per charge and useful life of EVs are greatly controlled by the energy density and life performance of the batteries of power source. Lithium-ion cells have contributed to the spread of the portable information device because the cells are high energy density. Our company is developing the large capacity lithium-ion cells such as LEV 50 [1] and LIM series [2] with long life and high-rate discharge capability for various applications of the EVs and AGVs, and so on.

$LiFePO_4$ is recently expected as new positive active material because of its features such as environmentally-friendly chemicals and high thermal stability [3], though these existing cells are applying the lithium manganese oxide to its material. $LiFePO_4$, however, had the major issue for large current discharge due to the low electric conductivity. It is reported that this issue is improved by carbon-loading on the surface of $LiFePO_4$ [4]. This paper describes the performances of new prototype carbon-loaded $LiFePO_4$/graphite lithium-ion cells with large capacity of 25 Ah.

2 Specifications of Cell and Battery Module

Newly developed lithium-ion cells are applying to carbon-loaded $LiFePO_4$ and graphite as positive and negative active material, respectively. The specification and appearance of the cells are showed in table 1 and Fig. 1.

Table 1 Specifications of 25 Ah prototype $LiFePO_4$/graphite lithium-ion cell.

Dimensions	**/ mm**	**H 100**
		W 171
		T 27
Volume	**/ l**	**0.46**
Mass	**/ kg**	**1.03**

Table 2 Specifications of 25 Ah prototype $LiFePO_4$/graphite lithium-ion battery module.

Number of cells		**4**
Dimensions	**/ mm**	**H 121**
		W 190
		L 125
Volume	**/ l**	**2.9**
Mass	**/ kg**	**4.6**

The winding assembly of a positive electrode, a negative electrode, and separators is inserted into a stainless-steel metal case as shown in Fig. 2. This cell is appropriate for the large current charge and discharge, because the edge of the electrodes is connected with current collector parts in the short distance.

The one example of specification and appearance of battery module consisting of four cells connected in series are shown in Table 2 and Fig. 3. The rectangular shape of a single cell achieves a compact module size, and results in the space-efficient module design.

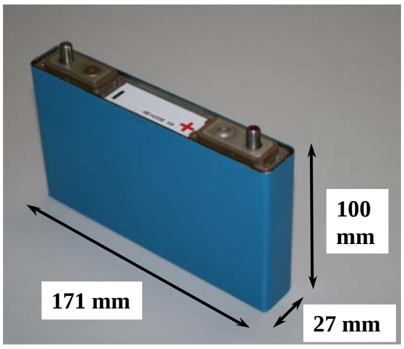

Fig. 1 Appearance of 25 Ah prototype $LiFePO_4$/graphite lithium-ion cell.

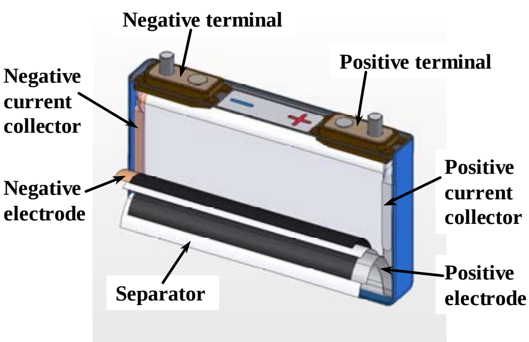

Fig. 2 Structure of 25 Ah prototype $LiFePO_4$/graphite lithium-ion cell.

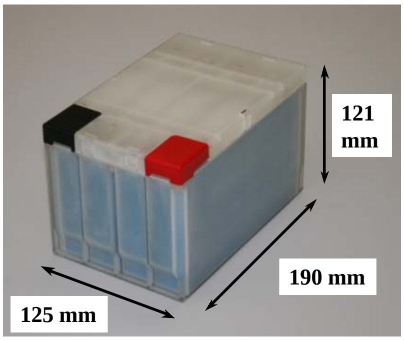

Fig. 3 Appearance of 25 Ah prototype $LiFePO_4$/graphite lithium-ion battery module.

3 Cell Performances

It introduces the charge and discharge results in various conditions as follows about the developed cells.

3.1 Charge and Discharge Performances

The change in the voltage, current, and state of charge during charge at 1 CA was investigated in order to evaluate the charge acceptance. The results are shown in Fig. 4. This cells exhibit the good charge acceptance that it is charged until 95% SOC by constant current and 98% SOC within one hour.

The discharge characteristics from 1 to 5 CA were confirmed for the grasp of the large current discharge performance. The results are shown in Fig. 5. The cells provide the discharge capacity of 26.4 Ah at 1 CA. The energy becomes 83.7 Wh resulting in energy density and specific energy of 182 Wh/l and 81.3 Wh/kg, respectively. Furthermore, the cells show remarkably high discharge performance with flat voltage profile and high-rate capacity retention of 99% even at large current of 5 CA. This findings indicate that the discharge performance of the cells become stable within the wide range of the current by carbon-loading of the $LiFePO_4$.

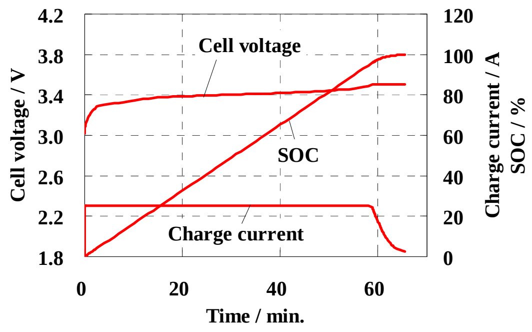

Fig. 4 Charge characteristics for 25 Ah prototype $LiFePO_4$/graphite lithium-ion cell. Charge: 1 CA to 3.5 V followed by constant voltage until cutoff current of 0.1 CA at 25 °C.

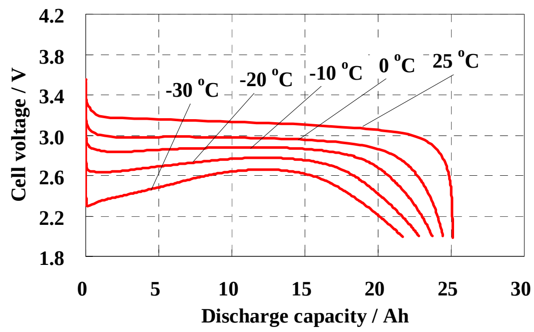

Fig. 6 High-rate discharge characteristics at various ambient temperatures for 25 Ah prototype $LiFePO_4$/graphite lithium-ion cell. Charge: 1 CA to 3.5 V followed by constant voltage until cutoff current of 0.1 CA at 25 °C; Discharge: 2 CA to 2.0 V at various ambient temperatures.

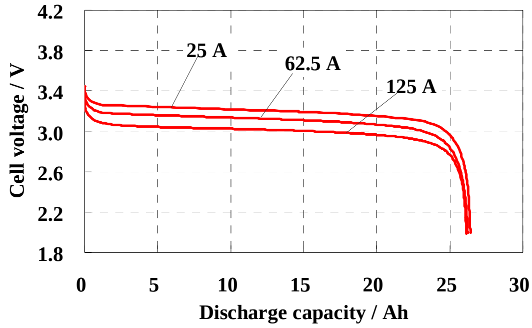

Fig. 5 Discharge characteristics at various currents for 25 Ah prototype $LiFePO_4$/graphite lithium-ion cell. Charge: 1 CA to 3.5 V followed by constant voltage until cutoff current of 0.1 CA at 25 °C; Discharge: Various currents to 2.0 V at 25 °C.

The discharge characteristics were investigated by changing the ambient temperature form -30 to 25 °C for the examination of the temperature influence at high-rate discharge. The results are shown in Fig. 6. It was found that the cells showed a flat voltage profile at high-rate discharge of 2 CA as well as the case of 25 °C under the low temperature environment of -10 °C. The discharge capacity, however, decreases with the decrease in ambient temperature. It seem that the behavior at low temperature is improved by the optimization of electrolyte though it is one of the issues of lithium-cells using $LiFePO_4$ as positive active material.

The specific output power at 50% SOC was examined by changing the ambient temperature from -20 to 45 °C in order to evaluate the effect of temperature on pulse discharge. The results are shown in Fig. 7. The specific output power turned out to be high value over 600 W/kg at 25 °C.

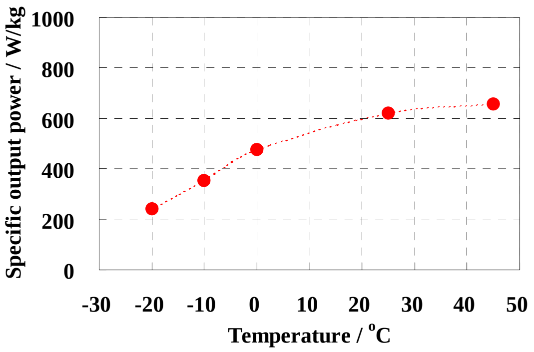

Fig. 7 Specific output power at 50% SOC at various ambient temperatures for 25 Ah prototype $LiFePO_4$/graphite lithium-ion cell. The power was calculated from V-I characteristics at 0.3, 1, and 2 CA for 10 seconds at various ambient temperatures. Maximum allowable current: 10 CA; Lower limited voltage: 2.0 V.

The output power depends at the ambient temperature. Its power at -20 °C decreases to 240 W/kg below the half of the value of room temperature.

3.2 Life Performances

The change in the discharge capacity and DC resistance (DCR) during cycling at 45 °C was investigated in order to evaluate the life performance under the condition of high ambient temperature. The results are shown in Fig. 8. The capacity retention at 1000th cycle is a remarkably high value of 90% compared with the $LiMn_2O_4$/graphite lithium-ion cells [1], [2].

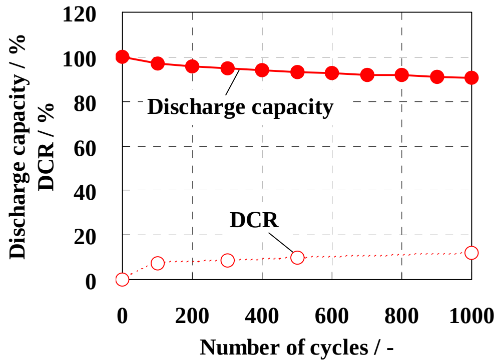

Fig. 8 Cycle life performance for 25 Ah prototype $LiFePO_4$/graphite lithium-ion cell at high ambient temperature of 45 °C. Charge and discharge conditions: 1 CA to 3.5 V followed by its voltage until cutoff current of 0.1 CA at 45 °C and 1 CA to 2.0 V at 45 °C. DCR at 50% SOC was calculated from V-I characteristics at 0.3, 1, and 2 CA for 10 seconds at 25 °C.

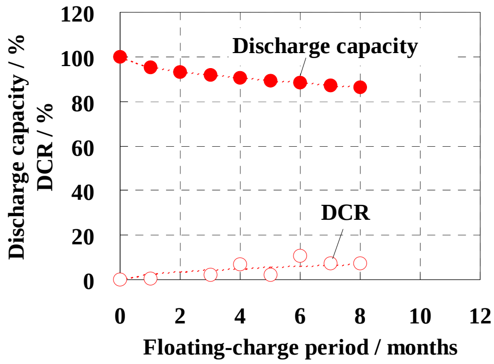

Fig. 9 Calendar life performance at constant voltage charge of 3.5 V for 25 Ah prototype $LiFePO_4$/graphite lithium-ion cell at high ambient temperature of 45 °C. Monthly capacity check conditions: 1 CA to 3.5 V followed by its voltage until cutoff current of 0.1 CA at 25 °C and 1 CA to 2.0 V at 25 °C. DCR at 50% SOC was calculated from V-I characteristics at 0.3, 1, and 2 CA for 10 seconds at 25 °C.

The $LiFePO_4$/graphite lithium-ion cells were found to exhibit outstandingly good cycle life performance even at high ambient temperature of 45 °C. It is suggested that the stable discharge performance is maintained for an extended period because the rise of DCR is very small during cycling.

The change in the discharge capacity and DCR during the floating charge at 45 °C was examined in order to confirm the performance loss caused by the storage at high ambient temperature of $LiFePO_4$/graphite lithium-ion cells. The results are shown in Fig. 9. As for the capacity retention at 8 months, 86% is maintained, and the storage performances of the cells turn out to be improved compared with the case of $LiMn_2O_4$ under such a high temperature environment. In addition, it was found that there was little DCR rise during the storage at high temperature, too.

The capacity loss during the floating charge is thought to be caused by the generation of the surface film on negative active material. The prediction theory is reported that the loss is proportional to the square root of time [5]. It is forecast to maintain the capacity over 60% after five years by applying this theory as shown in Fig.10. The performance loss in storage becomes small by applying $LiFePO_4$ to a positive active material compared with the case of $LiMn_2O_4$ [1], [2]. Therefore, $LiFePO_4$/graphite lithium-ion cells are suitable for long life applications because the cycle and calendar life of the cells is expected to become extremely long.

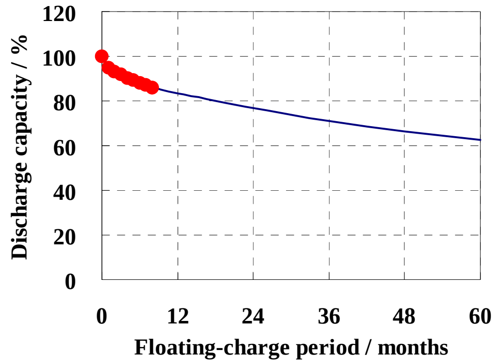

Fig. 10 Calendar life prediction for 25 Ah prototype $LiFePO_4$/graphite lithium-ion cell at constant voltage charge of 3.5 V and high ambient temperature of 45 °C. Monthly capacity check conditions: 1 CA to 3.5 V followed by its voltage until cutoff current of 0.1 CA at 25 °C and 1 CA to 2.0 V at 25 °C.

3.3 Abuse Tests

The crush test of fully charged cells was carried out by a 15.8 mm diameter bar in order to simulate the internal short circuit. The results of change in voltage and temperature during crush test and the appearance after its test are shown in Fig. 11 and 12. The cell voltage drops slowly until 0 V after crush. The cell temperature increases up to about 100 °C caused by internal short circuit. The fume of electrolyte is slightly observed from the rupture valve, and the EUCAR hazard level is 3 in this test.

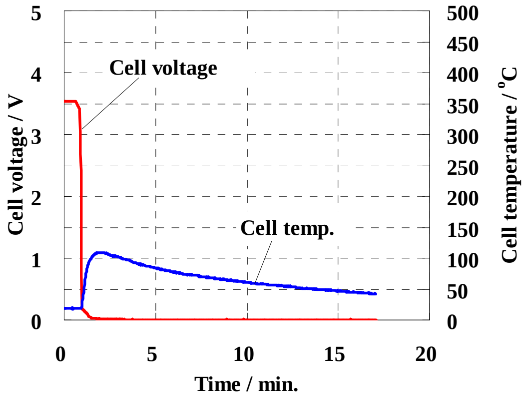

Fig. 11 Change in cell voltage and temperature during crush test for 25 Ah prototype $LiFePO_4$/graphite lithium-ion cell. The fully charged cells was crushed until 3/4 of its thickness by a 15.8 mm diameter bar.

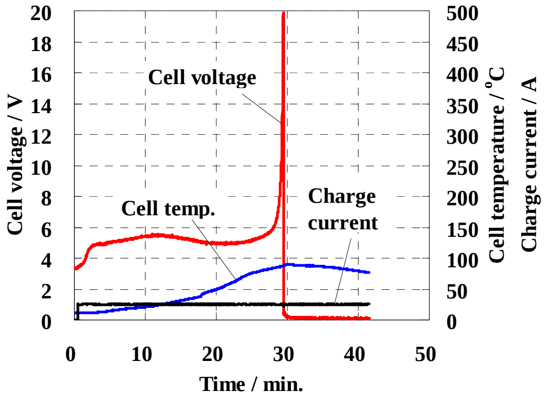

Fig. 13 Change in cell voltage, current, and temperature during overcharge test for 25 Ah prototype $LiFePO_4$/graphite lithium-ion cell. The fully charged cells was overcharged at 1 CA to 20 V followed by its voltage.

Fig. 12 Appearance of 25 Ah prototype $LiFePO_4$/graphite lithium-ion cell after crush test.

Fig. 14 Appearance of 25 Ah prototype $LiFePO_4$/graphite lithium-ion cell after overcharge test.

The overcharge test was performed by charging from the state of full charge to 20V at 1 CA in order to investigate the behavior at overcharge. The results of change in voltage, current and temperature during overcharge test and the appearance after its test are shown in Fig. 13 and 14. The cell voltage increases up to plateau around 5.5 V with the decomposition of electrolyte and then decreases a little to around 5.0 V caused by the rise of cell temperature. After that, the voltage achieves the upper limit of 20 V at about 30 minutes and the current keeps 1 CA owing to internal short circuit. The cell temperature increases up to about 90 °C. The fume of electrolyte is slightly observed from the rupture valve, and the EUCAR hazard level is 3 in this test.

It is demonstrated that new prototype carbon-loaded $LiFePO_4$/graphite lithium-ion cells show high safety from these results of crush and overcharge tests even at large capacity of 25 Ah.

4 Conclusions

New prototype carbon-loaded $LiFePO_4$/graphite lithium-ion cells show the superior performances such as high-rate discharge and long life. The cells are suitable for long life applications such as EVs because of high safety even at large capacity of 25 Ah. These conclusions demonstrate the great potential of carbon-loaded $LiFePO_4$/graphite lithium-ion cells. The cells will come into wider use after the further detailed investigation for a long term in addition to the improvement of various performances.

References

[1] S. Kitano, K. Nishiyama, J. Toriyama, and T. Sonoda, Development of Large-sized Lithium-ion Cell “LEV50” and Its Battery Module “LEV50-4” for Electric Vehicle, GS Yuasa Technical Report, 5-1(2008), 21

[2] I. Suzuki, T. Shizuki, and K. Nishiyama, *High Power and Long Life Lithium-ion Battery for Backup Power Source*, IEICE/IEEE INTELEC 2003 Proceedings, Yokohama, 2003, 317

[3] A. Yamada, S.C. Chung, and K. Hinokuma, *Optimized $LiFePO_4$ for Lithium Battery Cathodes*, J.Electrochem.Soc., 148(2001), A224

[4] I. Suzuki, T. Mochizuki, T. Inamasu, K. Nishiyama, and T. Sonoda, *Development of Long-life Lithium-ion Cells with $LiFePO_4$ for Positive Active Material*, GS Yuasa Technical Report, 5 -1(2008), 27

[5] T.Inoue, T.Sasaki, N.Imamura, H.Yoshida, M.Mizutani, and M.Goto, *Calendar and Cycle Life Prediction of 100 Ah Lithium-ion Cells for Space Applications*, NASA Aerospace Battery Workshop, Huntsville, AL, 2001

Authors

Isao Suzuki
Corporate R&D Center
GS Yuasa Corporation

Tomotada Mochizuki
Corporate R&D Center
GS Yuasa Corporation

Takeshi Nakamoto
Corporate R&D Center
GS Yuasa Corporation

Yasushi Uebo
Corporate R&D Center
GS Yuasa Corporation

Koichi Nishiyama
Corporate R&D Center
GS Yuasa Corporation