$LiFePO_4$ -blended cathode as a potential electrode for EV application

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Abstract

$LiFePO_4$- $Li[NiCoMn]O_2$ composite cathodes were investigated as an approach to increase the energy density and mitigate the relatively low operation voltage of $LiFePO_4$ -based batteries. The specific capacity and energy density of batteries could be improved by addition of $Li[NiCoMn]O_2$ to the $LiFePO_4$ electrodes and the reduced impedance of the composite cathodes contributed to enhance the power capability of the resulting batteries.

Keywords: lithium-ion battery, electric vehicle, energy, power, cycle life, safety

1 Introduction

Lithium-ion batteries are considered to be the most promising power solution for electric vehicles, particularly for the vehicles with extended electric driving range that need high energy capacity. As the requirements for battery performances are much more complicated and challenging for vehicle applications than for typical IT devices, diverse alternative chemistries are being explored to overcome the technical barriers of current lithium battery technology. Among these, $LiFePO_4$ has been drawing much attention as a cathode material for large format lithium-ion batteries that can be suitably used in the transportation applications due to its structural stability, inherent safety, and its reasonably high specific capacity. The natural abundance of the raw material also benefits its cost competitiveness in volume production projections. Ever since the practical opportunity of $LiFePO_4$ was proposed [1], much research has been dedicated to improve its low electronic conductivity and limited power capability [2-4]. Recent studies revealed that extremely high power can be achieved with $LiFePO_4$ by controlling the particle size and surface chemistry of the material [5] and now it is accepted that the power capability of $LiFePO_4$ is no more obstacle to its commercialization. In this study, we investigated $LiFePO_4$- $Li[NiCoMn]O_2$ composite cathodes to further enhance the energy density and the performances of $LiFePO_4$-based batteries.

2 Performances of $LiFePO_4$ -based batteries

It has been demonstrated that well balanced performance between output power and energy capacity can be achieved using $LiFePO_4$ as a cathode material. Table 1 shows the characteristics of $LiFePO_4$- based battery that was developed by EIG Ltd.

Table 1. Specification of $LiFePO_4$- based battery developed by EIG

Items		Unit	Specification
Capacity		Ah	14
Nominal Voltage		V	3.2
Dimension	T	mm	7.0
	W	mm	130
	L	mm	216
Weight		kg	0.38
Internal Resistance		mΩ	< 3
Specific Energy		Wh/kg	120
Energy Density		Wh/l	230
Specific Power (10sec, DOD50)		W/kg	2,300
Power Density (10sec, DOD50)		W/l	3,400

The rate capability of the developed battery is shown in figure 1. Owing to the low internal resistance, high power output of 15C continuous discharge was permitted without severe heat generation and loss of capacity. Figure 2 shows the pulse power capability measured at different depth of discharge (DOD). In the figure, it can be seen that the power capability of this battery is not so sensitive to the variation of DOD indicating that wide range of DOD can be utilized providing required power in deep charging/discharging mode.

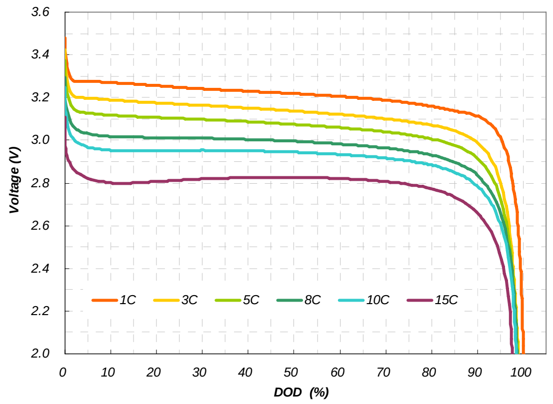

Figure 1. C-rate capability of the LiFePO$_4$-based battery measure at 25℃.

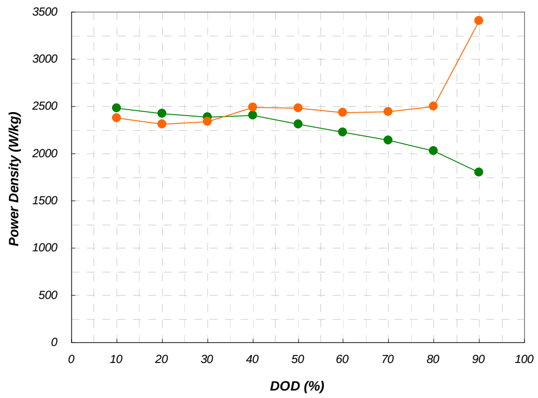

Figure 2. Pulse (10 sec) power capability calculated from HPPC test procedure [6].

The power capability inevitably decreases at low temperature due to the slowdown of reaction kinetics inside the battery. The temperature dependence of LiFePO$_4$-based battery is illustrated in figure 3. Although the power output slows down in lower temperatures, the remaining power is acceptable to initiate the operation of the vehicle even at the extremely low temperature

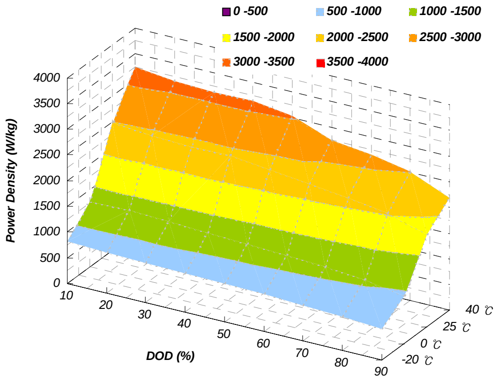

Figure 3. Discharge pulse (10 sec) power at various temperatures.

3 Performances of LiFePO$_4$-Li[NiCoMn]O$_2$ composite batteries

Figure 4 shows the comparative discharge profiles of LiFePO$_4$, Li[NiCoMn]O$_2$, and the 50:50 blends of the two materials. The voltage profile of the LiFePO$_4$-Li[NiCoMn]O$_2$ composite cathodes reflected well for each material, showing the clear separation point in the middle of discharge profile. Due to the contribution of Li[NiCoMn]O$_2$, the average discharge voltage was increased to 3.4V from 3.2V of LiFePO$_4$ and the resultant energy density of the battery was improved by 16% in gravimetric and 18% in volumetric respectively.

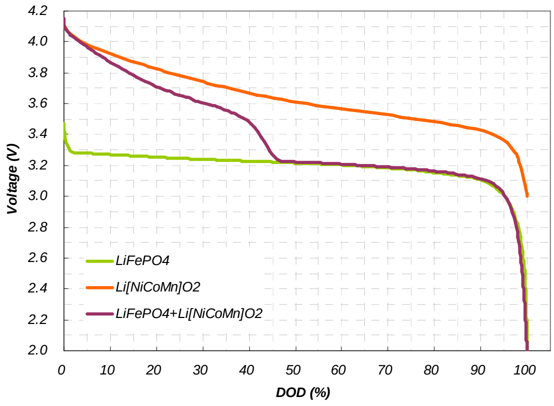

Figure 4. Discharge profiles of the batteries with Li[NiCoMn]O$_2$, LiFePO$_4$ and LiFePO$_4$-Li[NiCoMn]O$_2$ composite cathodes

Figure 5 shows the rate capability of the battery made from LiFePO$_4$-Li[NiCoMn]O$_2$ composite cathodes. It was found that the tendency of the voltage drop is more significant at the

$Li[NiCoMn]O_2$ region with increasing c-rate while the rate capability of the $LiFePO_4$ region is enhanced by the presence of $Li[NiCoMn]O_2$.

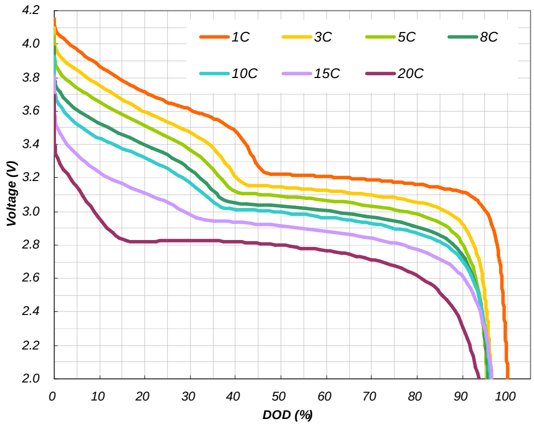

Figure 5. Rate capability of $LiFePO_4$-$Li[NiCoMn]O_2$ composite cathodes

The electrochemical impedance spectroscopy was carried out to analyze the enhanced power capability of $LiFePO_4$-$Li[NiCoMn]O_2$ composite cathodes. As can be seen in figure 6, the resistance of the $LiFePO_4$ electrode is reduced in the presence of $Li[NiCoMn]O_2$ resulting in the lower impedance of the blended composite electrode.

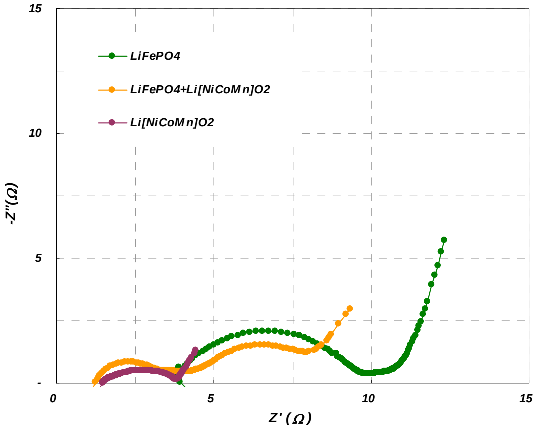

Figure 6. Impedance spectra of the batteries with $Li[NiCoMn]O_2$, $LiFePO_4$ and $LiFePO_4$-$Li[NiCoMn]O_2$ composite cathodes

The cycle characteristics of $LiFePO_4$ and $LiFePO_4$-$Li[NiCoMn]O_2$ composite cathodes are comparatively presented in figure 7(a). The structural stability of $LiFePO_4$ enables the extended cycle life even in deep charging/discharge condition. The $LiFePO_4$-$Li[NiCoMn]O_2$ composite batteries exhibited similarly stable cycle characteristics as can be seen in the figure. Figure 7(b) shows the variation of discharge profiles of $LiFePO_4$-$Li[NiCoMn]O_2$ composites while the cycling test was performed. In the figure, it is found that the capacity decay is mainly originated from the $Li[NiCoMn]O_2$ region accompanying the power loss in the region.

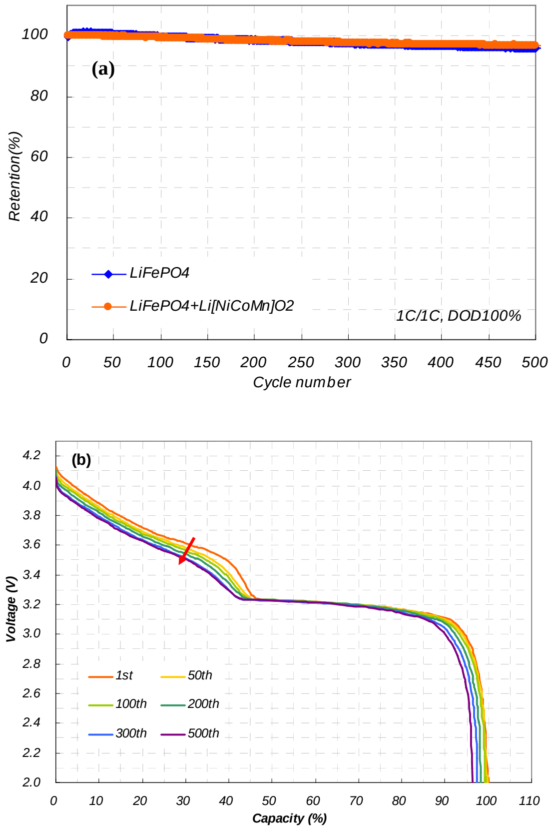

Figure 7. (a) Cycle life of $LiFePO_4$ and $LiFePO_4$-$Li[NiCoMn]O_2$ (b) voltage profile of $LiFePO_4$-$Li[NiCoMn]O_2$

It has been shown that the blending with $Li[NiCoMn]O_2$ increases the energy density and power capability of the $LiFePO_4$ electrodes but the safety performance of the $LiFePO_4$ chemistry can be diluted by addition of less stable cathode material. Especially, as $Li[NiCoMn]O_2$ has excess lithium in its fully charged state, uncontrolled abnormal reaction can proceed under the overcharging condition. Figure 8 shows the overcharging behavior of the $LiFePO_4$-$Li[NiCoMn]O_2$ composites in comparison with the pristine $LiFePO_4$ and $Li[NiCoMn]O_2$. In the figure, it can be seen that the addition of $Li[NiCoMn]O_2$ extends the time to reach limit voltage but the heat generation during the overcharging reaction is only slightly increased in the $LiFePO_4$-$Li[NiCoMn]O_2$ combined system.

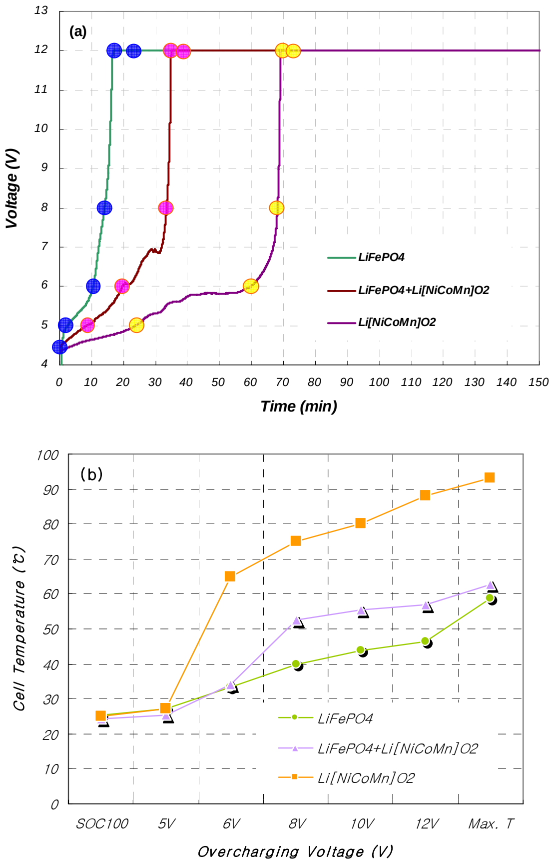

Figure 8. Overcharging behavior of $Li[NiCoMn]O_2$, $LiFePO_4$ and $LiFePO_4$-$Li[NiCoMn]O_2$ composites; (a) voltage profile and (b) temperature evolution. The temperature measurement points of the figure (b) were indicated in the figure (a).

4 Conclusion

The $LiFePO_4$-$Li[NiCoMn]O_2$ composite cathodes showed enhanced energy density and power capability maintaining stable cycle performance of $LiFePO_4$. It is concluded that the hybridization with a higher voltage cathode material could be a promising solution to mitigate the low operation voltage of $LiFePO_4$ as long as its safety benefits remain effective.

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