COMPARISON OF $LiCoO_2$ AND $LiMn_2O_4$ AS CATHODE MATERIALS IN LARGE-SCALE LI-ION BATTERY DEVELOPMENT FOR ELECTRIC VEHICLE APPLICATIONS

Mo-Hua Yang, Jui-Chin Fang, Sheng-Fa Yeh, Jai-Hsin Tsai, Hung-Chun Wu

Materials Research Laboratories, Industrial Technology Research Institute, Taiwan

Introduction

Thanks to the blooming in portable electronic devices for past three decades, the technologies of rechargeable battery are advancing rapidly. It is known that Li-ion battery is the dominant power source for these applications due to its superior energy density and long cycle life. In addition, the development of large-scale Li-ion batteries in recently years for applying to electric vehicle (EV) system is process by many companies and laboratories. Safety problems due to abuse operation have become a large concern for the increasing capacity of this large-scale Li-ion battery development[1]. The safety of Li-ion cells is related mainly to the thermal reactivity of the materials in the cell. Therefore, the thermal stability of the material appears inside the cell system can be a critical issue for improving the safety performance.

In this study, the 10Ah scale power-type Li-ion batteries have developed especially for full power light EV use. In order to improve the safety and increase high current discharge capability of the cell, two kinds of cathode material, $LiCoO_2$ and $LiMn_2O_4$, were used in this study as well as the design of electrode and material system for reducing the internal resistance of cell.

Experimental

The cylindrical power-type Li-ion cells were developing by using $LiMn_2O_4$ and $LiCoO_2$ as cathode material and MCMB as anode material. All cells were aging for few days after assembly and then charge with small current, namely cell formation, before test. The specific power, rate capability and cycle life were characterized for the cell. For the specific power characterization, the cell was discharged to the desired SOC (State of charge), and then discharged with 30 s pulse current of 3 A, 15 A, and 45 A. Cycle life test at 60 - 80% SOC were carried out by charging and discharging test cell at the 1 C rate at ambient temperature and 55 ^{o}C, respectively. The safety tests include nail penetration, crush, overcharge and external short circuit. All cells were charge to 4.2 V before the safety test.
7 cells are connected in series equipped with independent management system to match nominal 24 V battery system for electric bike test. The module was fully charged and then discharged under 1C current and a preset driven pattern called “Lafree Think” (Lafree Think is the name of an electric bike from Giant, Taiwan) discharge power pattern which was to simulate an electric bike under heavy road loading. The total discharge time can be

Corresponding author:
Mo-Hua Yang
Institute for Chemical Technology of Inorganic Materials, Graz University of Technology, Austria;
Fax: +43-316-8738282, Fax: +43-316-8738272, e-mail: mhyang@itri.org.tw

counted to driving distance. The same test was held on 10Ah module of the cells which used $LiCoO_2$ as cathode material, the cell dimensions and battery management system was the same as the cells by using $LiMn_2O_4$ as cathode material, excepting upper voltage limit was set lower at 4.15 V.

Results and Discussion

Figure 1 shows the cylindrical lithium-ion cell and module developed in this work.

Fig. 1 *Lithium-ion Cell and module*

The comparison of the specification of cell by using $LiCoO_2$ and $LiMn_2O_4$ are shown in Table 1, respectively. The capacity and the specific energy of the $LiCoO_2$ cell are higher than that of $LiMn_2O_4$ cell. In the other hand, the specific power for $LiMn_2O_4$ cell is high than that of $LiCoO_2$ cell.

Table 1 *The specification of $LiCoO_2$ and $LiMn_2O_4$ cells*

	$LiCoO_2$	$LiMn_2O_4$
capacity	10 Ah	7 Ah
dimension	Φ40×113 mm	Φ40×113 mm
specific energy	102 $Wh.kg^{-1}$	95 $Wh.kg^{-1}$
specific power (80% SOC)	700 $Wh.kg^{-1}$	1200 $Wh.kg^{-1}$
cycle life (80% capacity retention)	> 500 cycles	> 500 cycles

Fig. 2 shows the discharge characteristics of $LiCoO_2$ and $LiMn_2O_4$ cells at different discharge current. $LiCoO_2$ cell demonstrates a high capacity in around 10 Ah for 0.2 C to 3 C discharge rate, but the voltage drop very significantly at 3C discharge rate. Due to the sharp decrease in the voltage, the cell can not continually to deliver the power when the discharge current is large than 40 A. In the other hand, $LiMn_2O_4$ cell shows an excellent discharge capability. It can be found form Fig. 2 that $LiMn_2O_4$ cell can discharge at 7 C rate (near 50 A) with slightly capacity drop. The nominal voltage at high discharge C rate still above 3.5 V. Our results show that the discharge capacity ratio of 10 C / 1 C rate is over 90% in $LiMn_2O_4$ cell. It can be concluded that the $LiCoO_2$ cell is good in his energy (high capacity), and $LiMn_2O_4$ cell is excellent in his discharge capability (high power). From the results, we can find that the material (in this case is cathode) plays an important role to the cell performance. $LiCoO_2$ is appropriate for the high energy cell design and $LiMn_2O_4$ will be a good candidate for the power cell design.

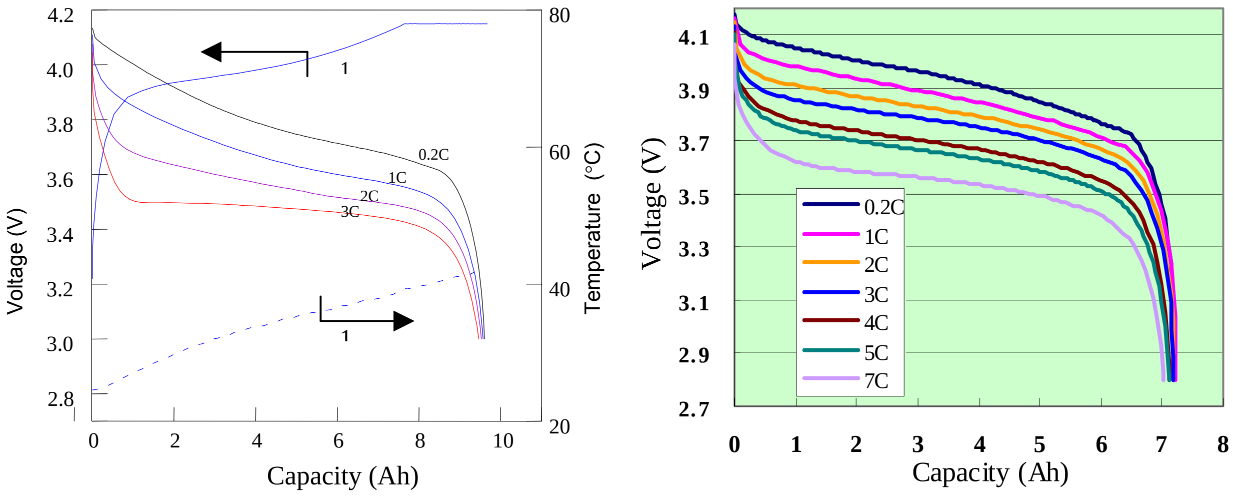

Fig. 2 *The discharge characteristics of $LiCoO_2$ and $LiMn_2O_4$ cells (at 1C charged rate).*

The test condition and result of safety tests are summarized in Table 2. For nail penetration, crush and overcharge tests, the safety vent opened promptly when the heat was increased to the temperature around 120 ^{o}C. All the safety test results show no fire and explosion.

The safety test shows no fire and no explosion for both energy and power type cells. It is know that $LiMn_2O_4$ has good safety property due to its higher decomposition temperature and lower heat generation when comparing to $LiCoO_2$ and $LiNiO_2$ (layer structure compounds) materials. Due to the advantage of thermal stability of $LiMn_2O_4$, we also found from our safety test results that the maxima temperature detected during all safety tests for the $LiMn_2O_4$ cell was about 150 ^{o}C but the temperature can be rise to 300 ^{o}C for the same test in $LiCoO_2$ cell. For the overcharge test, the $LiMn_2O_4$ cell can pass the test at 12V and $LiCoO_2$ can only pass the overcharge test at 5V.

Table 2 *Safety test condition and their results*

Test item	Conditions	Test result
crush	Force a plate to 17.2 MPa by a Φ 20 mm cylinder then release to form a 13 KN force to crush the cell	no fire, no explosion
nail	Penetrate a Φ 6mm nail into the centre part of the cell	no fire, no explosion
overcharge	Constant current (1 C rate) charge to 5 V for $LiCoO_2$ cell and 12 V for $LiMn_2O_4$ cell, then use constant voltage (5 V for $LiCoO_2$ cell and 12 V for $LiMn_2O_4$ cell) to charge the cells until current less than 0.01 C or 2.5 hr for the charging time.	no fire, no explosion
short circuit	Connecting positive and negative terminal with a low resistance wire until cell temperature down to RT.	no fire, no explosion

To have the electric bike test, seven cells were assembled in series to form a battery module with a battery management system. Table 3 showed the comparison of discharge data of two modules which are assembled by $LiCoO_2$ cells (10Ah module) and $LiMn_2O_4$ cells (7 Ah module). The 7 Ah $LiMn_2O_4$ module delivered 6.74 Ah capacity showed no specialty when compared with 10 Ah $LiCoO_2$ module which delivered 9.65 Ah under 1 C current discharge. Nevertheless, under driven pattern discharge, the 7 Ah module can deliver more energy when compared to the constant current discharge condition. Although the capacity for the $LiMn_2O_4$ cell was 30% less than $LiCoO_2$ cell, the 7 Ah module only shows 15% of energy less than the 10Ah module at driven pattern discharge condition. This is due to the low voltage drop at high current discharge for the module with $LiMn_2O_4$ cells.

Table 3 *The comparison of discharge characteristic of 10 Ah and 7 Ah modules*

	1 C discharge		Pattern discharge	
	Ah	Wh	Ah	Wh
10Ah module	9.65	241.4	5.38	133.8
7Ah module	6.74	181	4.23	113.2
7Ah/10Ah	69.8%	75%	78.6%	84.6%

Conclusions

In this study, a energy-type 10 Ah Li-ion cell by using $LiCoO_2$ as cathode material and a power-type Li-ion cell by using $LiMn_2O_4$ as cathode material were development. It was found that the $LiMn_2O_4$ material not only provides a good performance in safety but also provide an excellent high power capability. The safety test shows no fire and no explosion for both energy and power type cells. The maxima temperature detected during all safety tests for the $LiMn_2O_4$ cell was lower than $LiCoO_2$ cell. The $LiMn_2O_4$ cell can pass the overcharge test at 12 V and $LiCoO_2$ can only pass the overcharge test at 5 V. The further work will continue to improve the battery module performance by developing an advance battery management system for electric bike application, and plan to commercialize the Li-ion cell for electric bike application.

Acknowledgements

This project was supported by the Energy Commission of the Taiwan Ministry of Economic Affairs.

References

1. R. Spotniz, J. Franklin: J. Power Sources **113** (2003) 81-100.
2. S-I. Tobishima, K. Takei, Y. Sakurai, J-I Yamaki: J. Power Sources **90** (2000) 188-195.
3. Mo-Hua Yang, Jui-Chin Fang, Huikang Wu and Ching-Yih Yao: Proceeding of *The 19th international electric vehicles symposium*, Busan, Korea, October 2002.