JFE TECHNICAL REPORT
No. 6 (Oct. 2005)

A High Capacity and Safe Nickel-Based Cathode Material for Lithium-Ion Batteries†

1. Introduction

The batteries most commonly used in existing cellular phones, personal computers, and other electronic devices are lithium-ion secondary batteries, and lithium cobaltate is the main cathode material for these devices. As cellular phones become more functionally powerful, however, a cathode material offering larger capacity, longer service life, and higher safety is required. The nickel-based cathode material has long been known to have larger capacity than lithium cobaltate and lithium manganate[1,2]. Nevertheless, nickel-based cathode material has rarely been used commercially for safety reasons, because oxygen is liberated from cathode material crystals as the temperature rises during overcharging, which could induce ignition and explosion. To solve this safety problem, JFE Mineral has developed special nickel-based cathode material: cobalt, aluminum, and other elements are added as well as nickel, to form $LiNi_{0.78}Co_{0.19}Al_{0.03}M_xO_2$ (Product No. 503LP), using JFE Mineral's exclusive technology for synthesizing composite oxides and for controlling compositions and crystals. The new nickel-based cathode material also offers good cycle characteristics, indicating a longer service life than lithium manganate.

This report describes the characteristics of nickel-based cathode material 503LP. The 503LP has already been adopted for the cathode of lithium-ion batteries for electric motorcycles.

2. Characteristics of the Product

2.1 Powder Characteristics

The process of manufacturing 503LP includes the step of mixing and firing the raw materials to synthesize the product. The 503LP is spherical in shape, with particle sizes ranging from 10 to 20 μm, as shown in **Photo 1**. **Table 1** shows the powder characteristics of 503LP in terms of average particle size, specific surface area, tap density, and bulk density.

2.2 Electric Capacity

Figure 1 shows the charge/discharge characteristics indicating the electric capacity. The charge/discharge characteristics were measured under following conditions, such as charge voltage of 4.2 V-CC/CV (CV = 1.5 h), discharge cut voltage of 2.9 V, and current of 40 mA (0.2C). The evaluation cell was fabricated as 200 mAh class small size sheet battery, using mixture of 503LP, conductor, and binder as cathode; a carbon-based anode material as anode; and LiPF6/EC as the elec-

Table 1 Powder characteristic of 503LP

Chemical formula	$LiNi_{0.78}Co_{0.19}Al_{0.03}M_xO_2$ (x = 0.0005–0.01) M: Na, Sr, Ba, ····
Average particle size (μm)	12.2
Specific surface area (m^2/g)	0.38
Tap density (g/cm^3)	2.45
Bulk density (g/cm^3)	1.39

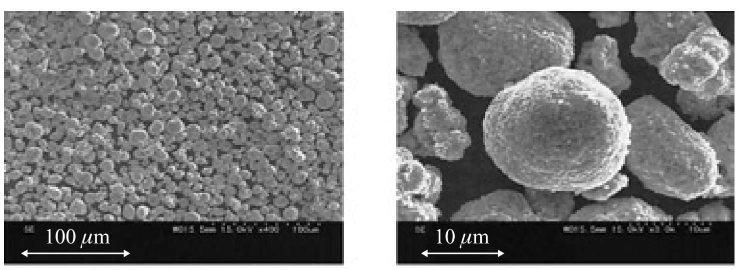


Photo 1 SEM images of 503LP

† Originally published in *JFE GIHO* No. 8 (June 2005), p. 60–62

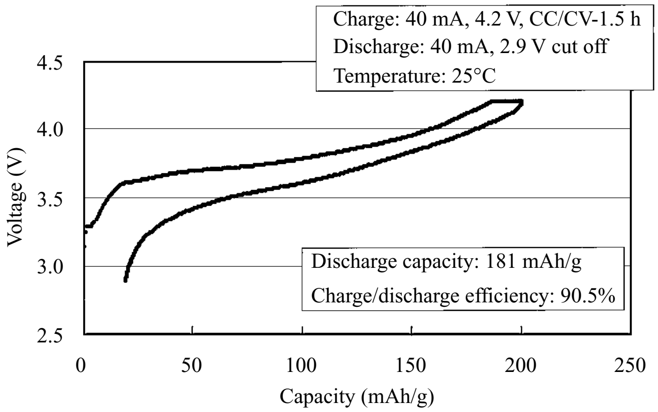


Fig. 1 Charge/discharge curve

trolyte. The measured discharge capacity was as high as 181 mAh/g, 20% higher than that of typical lithium cobaltate and 40% higher than that of lithium manganate.

2.3 Cycle Characteristics

The condition of measuring cycle characteristics were follows, such as charge voltage and condition of 4.2 V-CC/CV (CV = 1.5 h), discharge cut voltage of 3.0 V, and measuring current of 200 mA (1C). The same evaluation cell as for measuring the electric capacity was used.

As shown in **Fig. 2**, the discharge capacity ratio after 100 cycles was 97%, whereas that for lithium manganate after 100 cycles was not more than 90% under the same conditions. Thus, this result showed that the cathode material 503LP had good cycle characteristics.

2.4 Safety

A safety issue of general lithium nickelate is the possibility of smoke and ignition during overcharging. When a battery is overcharged, the temperature of the battery cell increases and induces an unstable state in which excess lithium ions leave from the lithium nickelate crystals. Together with the oxygen liberating reaction, the battery cell temperature rises further and the oxygen liberating reaction is accelerated. Ultimately, the liberated oxygen reacts with the organic solvent in the electrolyte to induce smoke and ignition, which may result in explosion. Therefore, it is important to minimize the generation of oxygen in a high-temperature state where the temperature of the battery cell increases.

Figure 3 shows the oxygen generation from overcharged nickel-based cathode materials. The battery was charged to 4.2 V, and the cathode material in it was picked out from the battery, rinsed, vacuum-dried, and measured the oxygen release by thermogravimethic/gas analysis system. As shown in Fig. 3, the conventional lithium nickelate started to release oxygen at 200°C, and oxygen release was rapidly increased at 230°C. Also, the lithium nickelate containing Co started to release oxygen at 200°C. In contrast, 503LP did not release oxygen even at 250°C. The reason is considered that both effect of additive Co, Al, Ba, Sr, Na, and other elements and the exclusive firing technology of JFE Mineral becomes the crystallity of lithium nickelate improved. Therefore it suppresses the liberation of oxygen at high temperature.

Safety tests were conducted on batteries using material of 503LP, lithium cobaltate, and lithium manganate. The nail penetration test was performed by penetrating a stainless steel nail (5 mm in diameter) through the battery after charging the battery to 4.4 V with constant current of 160 mA. The overcharge test was performed by charging the battery to 12 V with constant current of 2.4 A (3C). For the evaluation cell, aluminum-laminated battery, which has capacity of 800 mAh and the size of 83 × 49 × 3 mm (thick), was fabricated with using 503LP as cathode, carbon material as anode, LiPF6-EC/DEC system as electrolyte, and polyolefin micro-porous membrane (25 μm thick) as separator.

Table 2 shows the result of the evaluation tests. The nail penetration test showed no generation of smoke, rupture, or ignition from the battery using 503LP, whereas the battery using lithium cobaltate suffered

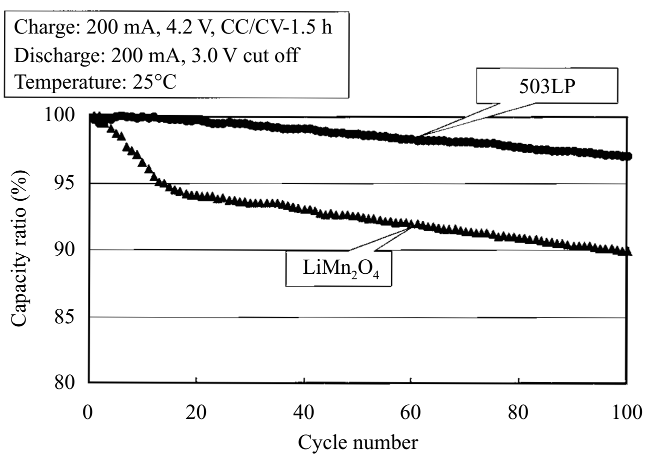


Fig. 2 Cycle performance of 503LP vs. $LiMn_2O_4$

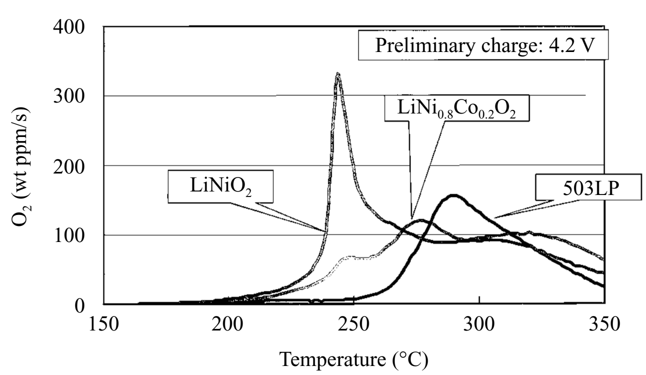


Fig. 3 Oxygen generation curve of cathode materials

Table 2 Safety test and nail penetration test

Cathode material	Nail penetration			Overcharge test	
	Cell temperature (°C)	Nail temperature (°C)	Evaluation	Cell temperature (°C)	Evaluation
503LP	52	48	Good	73	Good
$LiCoO_2$	–	134	Ignition	94	Good
$LiMn_2O_4$	59	50	Good	104	Good

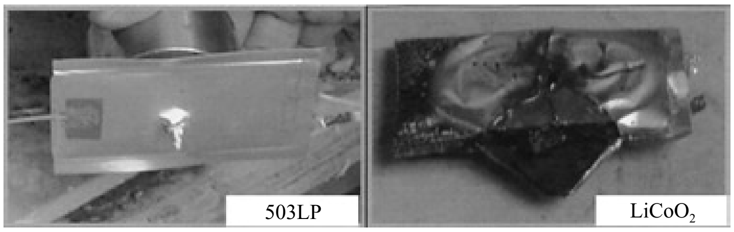


Photo 2 Safety test and nail penetration test

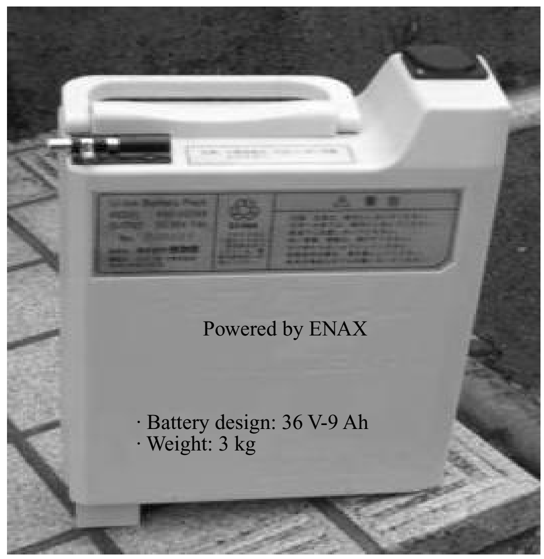
ignition and explosion. **Photo 2** shows the state after the nail penetration test. All the battery after the overcharge test showed no smoke, rupture or ignition. Nevertheless, compared with the lithium cobaltate and with the lithium manganate, the battery using 503LP showed a temperature increase by 73°C in the battery cell, which was the lowest among the three, proving its high safety.

3. Product Applications

Photo 3 shows a lithium-ion battery for electric motorcycles that 503LP is used as the cathode material. The use of 503LP makes the mileage per charge longer and the battery lighter.

4. Conclusions

JFE Mineral has developed a nickel-based cathode material, 503LP, having large capacity, high safety, and excellent cycle characteristics. Production of 503LP in the pilot plant scale of 5 t/month began in Dec. 2004, and has entered the supplying sample stage for mass production. Production capacity is scheduled to be increased to 50 t/m onth when starting commercial production.



Lithium ion battery

Photo 3 Example of application

References

1) Hamano, Y. et al. Abs. of the 45th Battery Symp. in Japan. 2004.
2) Hamano, Y. et al. Abs. 153, 12th Inter. Meeting on Lithium Batteries. 2004.

For Further Information, Please Contact to:

Advanced Materials Sales Dept.,
Advanced Materials Div.,
JFE Material
Phone: (81) 3-5288-6849 Fax: (81) 3-5288-6876