

# Development of a lithium ion battery using a new cathode material

T. Nukuda\*, T. Inamasu, A. Fujii, D. Endo, H. Nakagawa, S. Kozono, T. Iguchi,  
J. Kuratomi, K. Kohno, S. Izuchi, M. Oshitani

Corporate R&D Center, GS Yuasa Corporation, Nishinosho, Kisshoin, Minami-ku, Kyoto 601-8520, Japan

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## Abstract

LiMn<sub>2</sub>O<sub>4</sub> is used as the cathode material in large lithium ion batteries for industrial and other uses because of its low cost, excellent thermal stability, and other attributes. Nevertheless, LiMn<sub>2</sub>O<sub>4</sub> has weak points including severe capacity, deterioration at high temperatures, and low energy density. To overcome these points we conducted our research and development with a focus on LiCo<sub>x</sub>Ni<sub>y</sub>Mn<sub>z</sub>O<sub>2</sub> composite oxides (layered lithium manganese composite oxides). We developed an industrial synthesis technology for layered lithium manganese composite oxides, and employed them as the new cathode material for the EX25A, an industrial lithium ion battery. Compared with the lithium ion batteries that used LiMn<sub>2</sub>O<sub>4</sub> as their cathode material, the EX25A has double cycle life characteristics at high-temperature (according to our standards), and is capable of large 10 C discharges.

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## 1. Introduction

LiCoO<sub>2</sub> [1], proposed by Goodenough and coworkers as an active material of batteries for electric vehicles, is used in nearly all lithium ion batteries because of its good overall balanced characteristics. Meanwhile, LiMn<sub>2</sub>O<sub>4</sub> [2,3], proposed by Hunter, is used in large lithium ion batteries because of its excellent safety. Each of these represents development efforts: for LiCoO<sub>2</sub> they are cost and resources, while for LiMn<sub>2</sub>O<sub>4</sub> it is capacity retention at high temperature. Recently, Yabuuchi and Ohzuku reported on a novel insertion material consisting of LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>, [4] which has the superior characteristics of these two materials. This material was prepared from LiOH·H<sub>2</sub>O and a triple hydroxide of cobalt, nickel, and manganese, and then heated at 1000 °C in air.

We tried to use reactive crystallization to synthesize precursors with different ratios of these Co, Ni and Mn components, then heated them with lithium hydroxide to obtain layered lithium manganese composite oxides with various

LiCo<sub>x</sub>Ni<sub>y</sub>Mn<sub>z</sub>O<sub>2</sub> compositions. We then performed electrochemical measurements on them and measured their thermal stability. The layered lithium manganese composite oxides were further used to make a 25 Ah unit cell and a seven-cell module, whose cycle life characteristics and other characteristics were investigated.

## 2. Experimental

### 2.1. Synthesis of LiCo<sub>x</sub>Ni<sub>y</sub>Mn<sub>z</sub>O<sub>2</sub> composite oxides

We synthesized LiCo<sub>x</sub>Ni<sub>y</sub>Mn<sub>z</sub>O<sub>2</sub> composite oxides with LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> compositions using the following methods.

Solid-phase method: LiOH·H<sub>2</sub>O, Co(OH)<sub>2</sub>, Ni(OH)<sub>2</sub> and Mn<sub>2</sub>O<sub>3</sub> were put in a mortar so that the molar ratio of Li:Co:Ni:Mn would be 3:1:1:1, and then they were uniformly mixed. This mixed powder was formed into pellets, which were transferred to an alumina boat, and placed in an electric furnace in air (air flow: 0.5 l/min). The temperature was raised from room temperature to 1000 °C, held at that temperature, and then allowed to cool to room temperature naturally. Mea-

\* Corresponding author. Tel.: +81 465 32 2244; fax: +81 465 32 2241.  
E-mail address: [toshiyuki.nukuda@jp.gs-yuasa.com](mailto:toshiyuki.nukuda@jp.gs-yuasa.com) (T. Nukuda).

surement of the heated product by X-ray diffraction (XRD; RINT-2500V, Rigaku) revealed that the powder was single-phase with a layered rock salt structure. Inductively coupled plasma-atomic emission spectrometry (ICP; ICPS-1000IV, Shimadzu) confirmed the  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  composition.

**Reactive crystallization method:** An aqueous sodium hydroxide solution was put in a sealed reactor vessel with blades, and the solution was stirred while blowing in argon gas to remove dissolved oxygen. An external heater kept the solution in the reactor vessel at  $50^\circ\text{C}$ . Next we prepared an aqueous solution with  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$  so that the molar ratio of Co:Ni:Mn was 1:1:1. This solution was continuously dropped into the sealed reactor vessel, and an aqueous ammonium salt was dropped in synchrony with this to mix the two. After dropping began, the aqueous solution of sodium hydroxide was added whenever necessary to maintain the solution in the sealed reactor vessel at a constant pH. The solution was maintained at a constant temperature by the heater. Further, a flow pump took slurry outside the system to keep the amount of solution in the vessel constant, while we collected the slurry of the Co, Ni and Mn composite hydroxides, which were the reactive crystallization products. The slurry was washed with water, filtered, and dried overnight at  $110^\circ\text{C}$  to obtain the Co, Ni and Mn composite hydroxides. These hydroxides and  $\text{LiOH} \cdot \text{H}_2\text{O}$  were then weighed so that  $\text{Li}/(\text{Co} + \text{Ni} + \text{Mn}) = 1.0$  in molar ratio, and mixed using a planetary mixer. The obtained mixture was pressed into pellets, and put into an alumina pot, which was placed in an electric furnace. In a dry air flow the temperature was raised to  $1000^\circ\text{C}$  at a rate of  $100^\circ\text{C}/\text{h}$ , held at  $1000^\circ\text{C}$  for 15 h, lowered to  $200^\circ\text{C}$  at a rate of  $100^\circ\text{C}/\text{h}$ , then allowed to cool naturally, resulting in  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  compositions. We used the same method to synthesize layered lithium manganese composite oxides with other compositions, and confirmed their compositions with ICP.

## 2.2. Evaluation

We used the following procedure to determine the electrochemical characteristics of the layered lithium manganese composite oxides. The cathode consisted of the oxides, and we used acetylene black as the conductive agent and polyvinylidene fluoride (PVdF) as the binder. After kneading the materials, the product was made into a paste using *N*-methyl-2-pyrrolidone, and cast on an aluminum foil serving as the current collector. Drying and pressing yielded the cathode. The counter electrode was lithium foil pressed onto a nickel plate. The separator was polyethylene film with micropores. The electrolyte used was 1 M  $\text{LiPF}_6$  dissolved in ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate (1:1:1, v/v). We used this two-pole test cell to investigate the following electrochemical characteristics. Nominal capacity of these test cells was 10 mA. For the initial characteristics we charged the cell to 4.2 V at a current of 0.2 C at  $25^\circ\text{C}$ , then discharged it to 3.0 V at the same current. For

high-rate discharge characteristics we determined the discharge capacity ratio for 2.0 and 0.2 C. Investigating storage characteristics involved leaving the cell in a charged state for 1 week at  $50^\circ\text{C}$ , and then finding the recovery capacity at 0.2 C. To test cycle life characteristics we charged the cell to 4.2 V at  $25^\circ\text{C}$  and 0.5 C current, discharged it to 3.0 V at the same current, and repeated this cycle 100 times.

Differential scanning calorimetry (DSC; DSC200C, Seiko Instruments) was used to evaluate the thermal stability of the charged cathode with electrolyte. We clipped the charged cathode containing electrolyte to 2.5 mm in diameter, and sealed the electrode in a SUS container that was filled with argon for DSC measurements. Measurement conditions were in the temperature range of room temperature to  $500^\circ\text{C}$ , with temperature rising at a rate of  $5^\circ\text{C}/\text{min}$ . The temperature when the highest calorific value appeared on the DSC curve was considered the exothermic peak.

## 2.3. Lithium ion battery (EX25A)

We made an EX25A cell using layered lithium manganese composite oxides, and constructed a modular EX25A-7 by connecting seven EX25A cells in series. Table 1 presents its specifications.

In this paper, “rated capacity” is given as capacity at the end of life. The conventional battery testing methods were used to perform EX25A charging and discharging tests.

## 3. Results and discussion

### 3.1. Characteristics of layered lithium manganese composite oxides

We evaluated the layered lithium manganese composite oxides having the composition  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ , which were synthesized by the solid-state method and reactive crystallization method. XRD analysis yielded diffraction lines showing that the products of both methods have a layered rock salt structure. However, results of the initial characteristics evaluation found that the layered lithium manganese composite oxides made with the solid-phase method cannot provide sufficient capacity. We therefore raised charg-

Table 1  
Specifications of the lithium ion unit cell and the battery module

	EX25A (unit cell)	EX25A-7 (module)
Rated capacity (Ah)	25	25
Nominal voltage (V)	3.7	26
Dimensions		
Length (mm)	37	381
Width (mm)	145	155
Height (mm)	124	155
Weight (kg)	1.4	11.5 <sup>a</sup>

<sup>a</sup> Equipped with battery management unit (BMU).

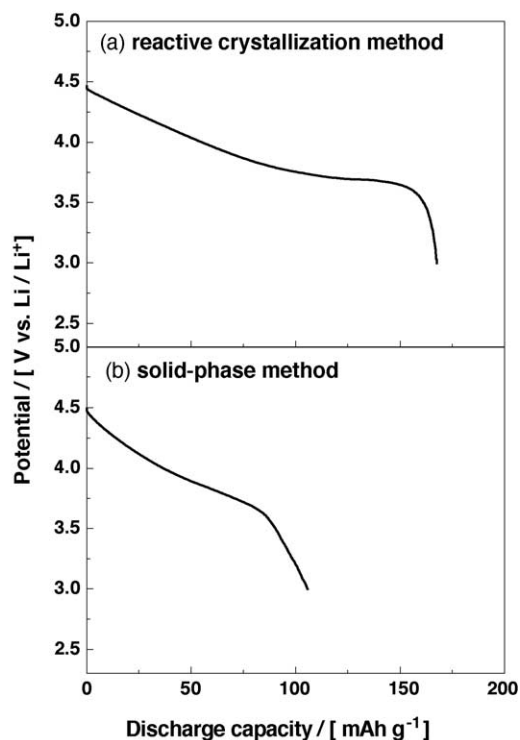


Fig. 1. Discharge curves of Li/LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> ((a) reactive crystallization method, (b) solid-phase method) cells at a rate of 0.24 mA/cm<sup>2</sup> at 20 °C after charging up to 4.5 V. The electrolyte was 1 M LiPF<sub>6</sub> dissolved in EC:DMC:EMC (1:1:1, v/v). The electrode consisted of 90 wt.% LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>, 5 wt.% acetylene black and 5 wt.% PVdF.

ing voltage to 4.5 V and discharged at 0.2 C. Results are in Fig. 1. Although capacity of about 170 mAh/g was obtained with the reactive crystallization method, the solid-phase method provided about 100 mAh/g capacity, which was insufficient for battery use. Fig. 2 shows the results of the DSC measurements for Li<sub>0.34</sub>Co<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (solid-phase method) and Li<sub>0.12</sub>Co<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (reactive crystallization method). The DSC samples were prepared by electrochemical constant-current charge at 0.2 C up to 4.5 V. As seen in Fig. 2, mainly exothermic spikes were observed at ca. 230 °C for the solid-phase method and a spike at ca. 270 °C for the reactive crystallization method. The thermal reaction of the reactive crystallization method starts later than that of the solid-phase method. This is probably due to a lower utilization rate that came about because of a heterogeneous composition of the three elements, suggesting that layered lithium manganese composite oxides made with the solid-phase method do not have a uniform composition.

We therefore elected the reactive crystallization method and used reactive crystallization to synthesize various hydroxides with different ratios of Co, Ni and Mn, which were heated with lithium hydroxide to synthesize various three-component compound active materials with the LiCo<sub>x</sub>Ni<sub>y</sub>Mn<sub>z</sub>O<sub>2</sub> (layered lithium manganese composite oxides). We evaluated their electrochemical characteristics and performed DSC measurements. Fig. 3 and Table 2 show

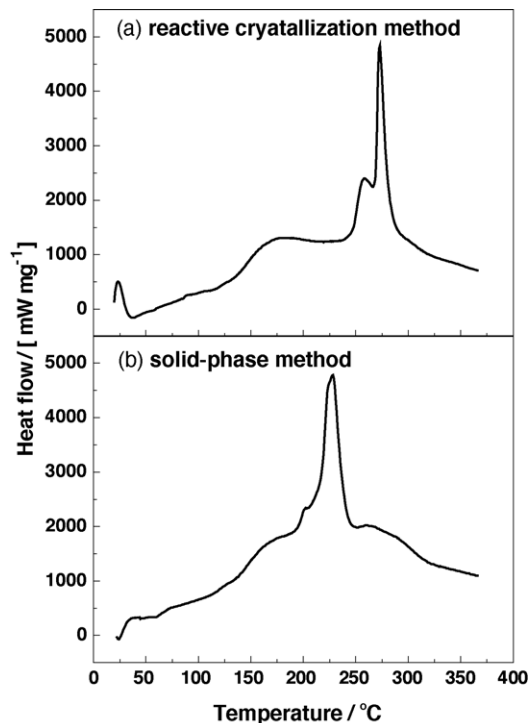


Fig. 2. DSC curves for (a) Li/LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (reactive crystallization method) and (b) Li/LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (solid-phase method) containing electrolyte (1 M LiPF<sub>6</sub> dissolved in EC:DMC:EMC (1:1:1, v/v)). Both samples were prepared by charging the LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> electrode. Scan rate was 5 °C/min.

the results. We found that Ni-rich compositions had high initial capacity, but low initial efficiency. Mn-rich compositions had excellent thermal stability, but unsatisfactory capacity. Co-rich compositions had long cycle life, but Co has cost and resources problems. Controlling these Co, Ni and Mn components made it possible to find compositions that can obtain the merits of each component.

Next we optimized layered lithium manganese composite oxides adapted to industrial use while taking these merits

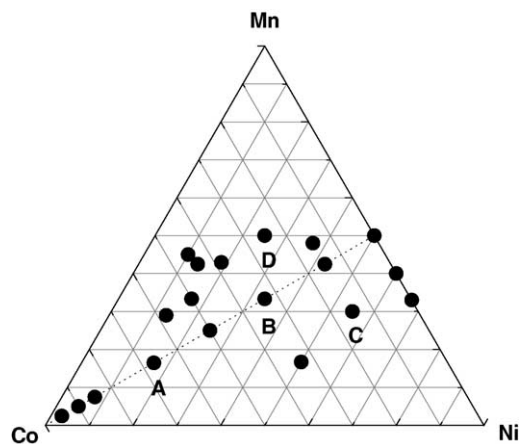


Fig. 3. Gibbs triangle showing the stoichiometry of many samples of LiCo<sub>x</sub>Ni<sub>y</sub>Mn<sub>z</sub>O<sub>2</sub>.

Table 2  
Summary of the samples

Sample	Capacity (mAh/g)	Initial efficiency (%)	Exothermic peak (°C)	Rate ratio (%)	Stored retention (%)	100 cycles retention (%)
A	156	93	298	91	96	98
B	156	88	310	87	98	96
C	163	84	282	84	99	95
D	130	88	312	85	96	96

into consideration. In attempting optimization we selected conditions such as the following for our experiment:

- Potential profile with a certain gradient.
- Excellent power characteristics.
- Long cycle life.
- High energy density.

The layered lithium manganese composite oxides selected on the basis of these conditions combine the advantages of  $\text{LiCoO}_2$ , which are high energy density and good power characteristics, with those of  $\text{LiMn}_2\text{O}_4$ , which are safety and low-cost, thereby yielding a new cathode material having an excellent overall balance.

Characteristics of the lithium ion battery using the new cathode material (EX25A).

Following are the characteristics of the industrial-use lithium ion battery (EX25A), which employs the new cathode material, and of the EX25A-7, which connects seven EX25A cells in series.

### 3.1.1. EX25A charging characteristics

Voltage was set to 4.1 V when charging the EX25A. Fig. 4 shows an example of charging characteristics when the cell was quick-charged (maximum current: 5 C). This cell excels at quick charging, and can be charged to about 80% in 15 min. Its temperature rises about 5 °C during the charge. The EX25A does not experience the rapid temperature increase near the end of charging that is observed in sealed lead-acid batteries or in alkaline batteries, which means that fine controls to avoid this heat increase are unnecessary.

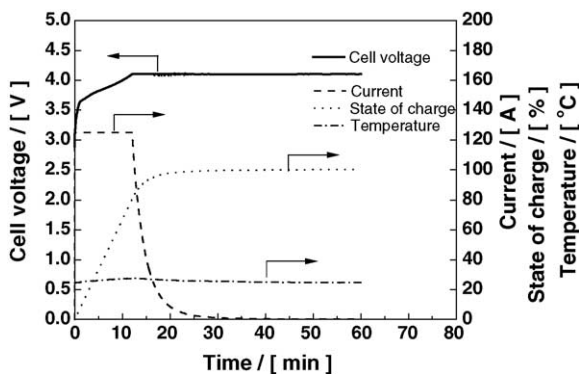


Fig. 4. Charge profiles in a quick-charging test of the EX25A. Charge was constant-current constant-voltage, conducted under the conditions of 5.0 C to 4.1 V at 25 °C.

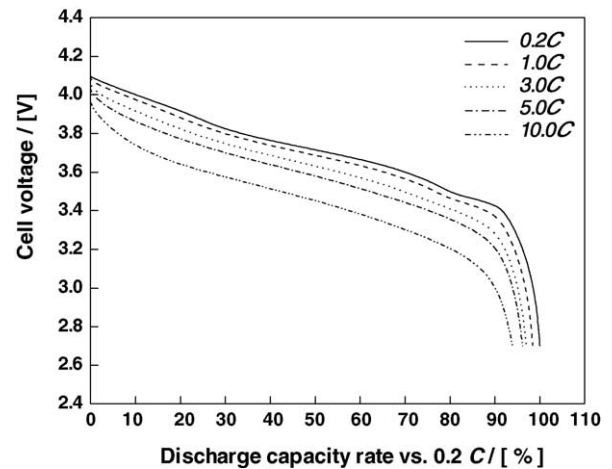


Fig. 5. Discharge characteristics of the EX25A at various rates. Discharge was constant-current at a temperature of 25 °C and a cut voltage of 2.7 V.

### 3.1.2. EX25A discharge characteristics

Fig. 5 shows discharge characteristics at various currents, and Fig. 6 shows discharge characteristics at various temperatures. EX25A discharge characteristics have a certain gradient slope, allowing the cell to maintain good performance to the end of discharging, and making it easy to monitor capacity and to use.

The EX25A has excellent super high-rate discharge characteristics; up to 5.0 C discharging provides more than 95% of 0.2 C discharging capacity. Even when discharging at 10 C, it provides at least 90% capacity at 0.2 C equivalence, making it suitable for applications requiring super high-rate discharge.

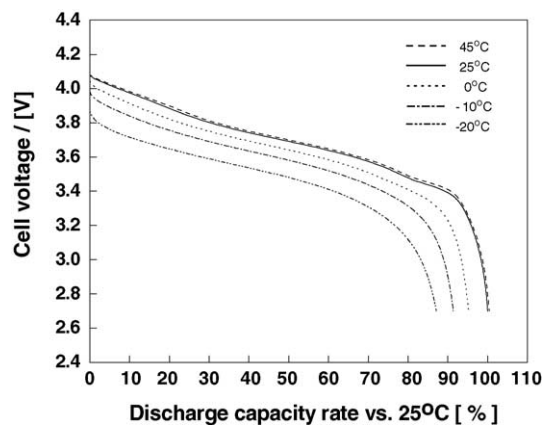


Fig. 6. Discharge characteristics of the EX25A at various temperatures. Discharge was constant-current at a current of 1.0 C and a cut voltage of 2.7 V.

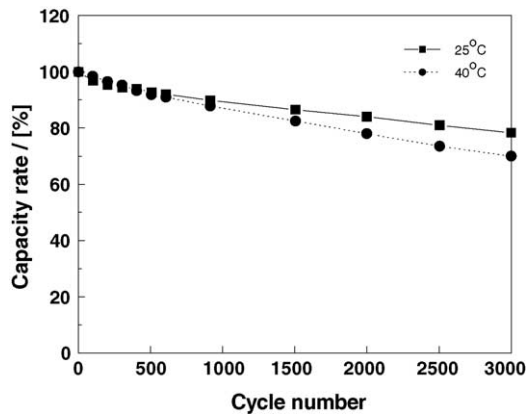


Fig. 7. Cycle life testing at various temperatures on the EX25A. Cycling was performed at charge rates of 1.0 C to 4.1 V, followed by a taper at 4.1 V to a current of 0.05 C. Discharging was at 1.0 C to 3 V.

Furthermore, even when discharging at 1 C in an ambient temperature of  $-20^{\circ}\text{C}$ , there was little drop in capacity and it provided at least 85% capacity at  $25^{\circ}\text{C}$  equivalence, demonstrating that low-temperature discharging is also excellent.

### 3.1.3. EX25A storage and cycle life characteristics

Fig. 7 shows the results of cycle life testing on the EX25A. The EX25A, which uses layered lithium manganese composite oxides as its new cathode material, has excellent cycle life performance, maintaining about 70% of its initial capacity even after 3000 cycles at  $40^{\circ}\text{C}$ . It has achieved long life over twice that of our  $\text{LiMn}_2\text{O}_4$ -type lithium ion batteries [5].

Fig. 8 shows the results of a storage test on various state of charge (SOC) at  $20^{\circ}\text{C}$ .

Plotting the square roots of storage periods on the x-axis produces a linear relationship and allows estimation of

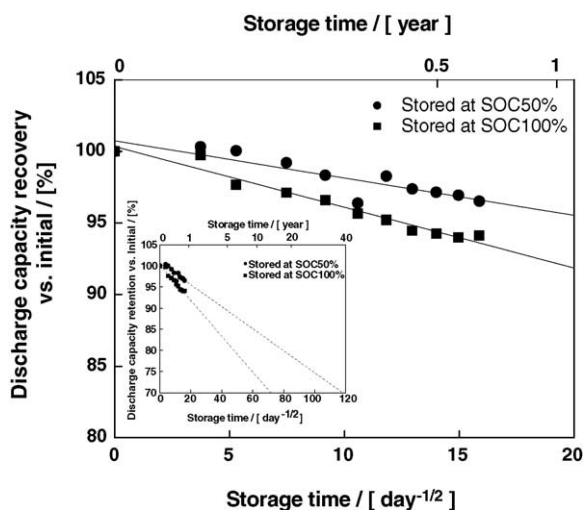


Fig. 8. Storage performance of the EX25A. Charge was constant-current at 1.0 C to 4.1 V (SOC 100%) and 3.75 V (SOC 50%). The cells were stored at  $20^{\circ}\text{C}$  for one month, and then the discharge capacity retention was measured. Results obtained by repetition of the procedure are plotted as the square roots of the storage periods on the x-axis.

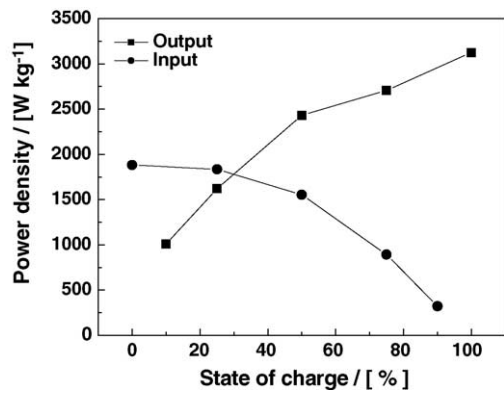


Fig. 9. Power characteristics in various charge states at  $25^{\circ}\text{C}$ . Output and input power for a cell was calculated by extrapolation of the  $I$ - $V$  curves for 10 s.

battery life. We were able to estimate that when stored at SOC 50% (3.75 V) it would take more than 20 years for the decline to 70% of initial capacity, and that even when stored at SOC 100% (4.1 V) it would take about 14 years. This satisfies the life performance requirement for industrial-use batteries.

### 3.1.4. EX25A power characteristics

Fig. 9 presents the power characteristics at  $25^{\circ}\text{C}$ . The EX25A attained 2000 W/kg output and 1300 W/kg input at SOC 50%, suggesting that it is adequate for use in hybrid electric vehicles.

### 3.1.5. EX25A-7 characteristics

The EX25A-7 is a standard battery module comprising seven EX25A cells connected in series, and integrated into a single unit with a battery management module (BMU), which is designed so that it can safely obtain the maximum capability from the battery. We therefore successfully created a module that does not impair any of the EX25A characteristics described above, such as those for charging, discharging, and storage/cycle life.

## 4. Conclusion

Using the reactive crystallization method, we succeeded in the synthesis of layered lithium manganese composite oxides that can satisfy the requirements of high output, high energy density, and long life. We further developed an industrial-use lithium ion battery called the EX25A, which employs this new cathode material.

The EX25A was designed to fulfill the requirements of large-current charging and discharging and long life which are demanded for industrial applications, and it has the following characteristics.

A. *Designed for large-current charging and discharging:* Commercialized small lithium ion batteries are designed

to use a maximum discharge rate of about 2.0 C, but the EX25A is capable of large-current continuous discharging of 250 A (10 C).

- B. *Long cycle life design*: Commercialized small lithium ion batteries have short service lives of only about 500 cycles, but the EX25A promises at least 3000 cycles. At high temperatures it has about twice the life of our batteries using  $\text{LiMn}_2\text{O}_4$  as the cathode material.
- C. *High energy density*: The EX25A is best for applications with limited installation space and for mobile applications because of its small size and light weight.

The EX25A lithium ion battery for industrial applications has a good overall balance in which high-load

characteristics, long life, high energy density and safety have been achieved on a high order.

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