Cycle performance of LiCo$_x$Ni$_{1-x}$O$_2$/graphite–coke hybrid carbon systems for long-life lithium secondary batteries

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Abstract

In our previous work, we found that the LiCoO$_2$/graphite–coke hybrid carbon system had less initial discharge capacity but better cycle performance than the LiCoO$_2$/pure graphite system, which is the most commonly used lithium secondary battery system.

In this report, we examine the effects of a better graphite–coke hybrid carbon mixing ratio for long-life use. We have found that the feature of the curve of the carbon negative electrode material influences the feature of the discharge curve of the battery, and graphite–coke hybrid carbons with a mixing ratio of 4/1 enable better cycle performance. We compared the initial discharge characteristics and cycle performance of batteries with LiCo$_x$Ni$_{1-x}$O$_2$/graphite–coke hybrid carbon systems with those of a LiCo$_x$Ni$_{1-x}$O$_2$/pure graphite system for $x = 0.3$ and 0.7. Moreover, we examined the cycle performance of 10-Wh class cells using some of these systems under load-levelling imitation conditions.
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1. Introduction

Lithium secondary batteries are widely used as rechargeable batteries providing the main power supply of portable devices. The LiCoO$_2$/graphite system is a typical combination of positive and negative electrode materials which is used in almost all lithium secondary batteries because it provides a large energy density and good cycle performance.

Recently, the development of lithium secondary batteries for dispersed energy storage systems, such as home-use load-levelling systems, has also focused on environmental protection. In such applications, batteries will need to have a much longer cycle life of perhaps 3500 cycles, which would allow about 10 years of use with daily charge/discharge cycles [1–3]. To achieve such a high level of cycle performance, we need to carefully select the positive and negative electrode materials and apply the best possible combination of them.

Various types of materials have been targeted as possible positive electrode materials for lithium secondary batteries. For instance, lithium transition metal oxides have been extensively studied; LiCoO$_2$, LiNiO$_2$ and, LiMn$_2$O$_4$ in particular have been focused on and developed [4–8], and batteries using these as positive electrode materials have been commercialized.

Lithium containing a cobalt nickel composite oxide, LiCo$_x$Ni$_{1-x}$O$_2$, has been the focus of our research on positive electrode materials for long-life lithium secondary batteries, because this material has a large discharge capacity and exhibits good cycle performance [9–12]. The discharge capacity and cycle performance of LiCo$_x$Ni$_{1-x}$O$_2$ ($x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8,$ and 0.9) have been reported [12]. In that study, LiCo$_{0.3}$Ni$_{0.7}$O$_2$ showed the largest discharge capacity and smallest deterioration ratio in the charge/discharge cycle test, and LiCo$_{0.7}$Ni$_{0.3}$O$_2$ had the second largest energy density.

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For the negative electrode, carbons, especially graphite, are also widely used in consumer lithium secondary batteries because carbon negative electrodes have superior cycle performance compared to lithium metal and lithium alloy negative electrodes [13–18]. However, the cycle performance of the graphite electrodes currently used in consumer products is insufficient for achieving the target of long-life use in energy storage systems.

To reach this target, we have looked for new carbon materials more suitable for a longer cycle life. We earlier reported that graphite–coke hybrid carbon, where coke was mixed with graphite, has a longer cycle performance than pure graphite or pure coke when $LiCoO_2$ is used as the positive electrode material [19,20].

In those reports, we analyzed the negative electrode using ^7Li NMR spectroscopy and reported that the amount of electrochemically inactive lithium on the negative electrode increased after the charge/discharge cycle test. The inactive lithium largely increased in the lower voltage region in a battery system using pure graphite as a negative electrode material, and largely increased in the higher voltage region in a system using pure coke. When we used a graphite–coke hybrid carbon, the addition of coke to the graphite reduced the production of inactive lithium, especially in the lower voltage region. A feature of the charge/discharge curves was that the graphite–coke hybrid carbons had slow potential changes in the higher potential region (in the lower voltage region of a battery). We considered the possibility that batteries using the graphite–coke hybrid carbon showed better cycle performance because the slow potential changes lead to fewer side reactions, such as electrolyte decomposition, and fewer unequal reactions. We also considered whether the effect of the fewer unequal reactions would be especially important in large-scale lithium secondary batteries, which have positive and negative electrodes with larger electrode areas.

Through this previous work, we found that the feature of the negative electrode's charge/discharge curve in the higher potential region (in the lower voltage region) is important, but the effect of the graphite–coke hybrid's mixing ratio on the cycle performance needed further investigation. Moreover, the cycle performance of a battery with a combination of $LiCo_xNi_{1-x}O_2$ and graphite–coke hybrid carbon had not yet been reported.

In the current report, we examine the graphite-and-coke mixing ratio, and discuss the cycle performance of a battery using $LiCo_xNi_{1-x}O_2$ and graphite–coke hybrid carbon. Moreover, we report on the charge/discharge cycle performance of the batteries under load-levelling imitation conditions.

2. Experimental

$LiCoO_2$, $LiCo_{0.7}Ni_{0.3}O_2$, and $LiCo_{0.3}Ni_{0.7}O_2$ were prepared from a stoichiometric mixture of lithium hydroxide (LiOH), cobalt hydroxide ($Co(OH)_2$), and nickel hydroxide ($Ni(OH)_2$) by heat-treating at 850 °C for 20 h. After milling of $LiCo_xNi_{1-x}O_2$ ($x = 1.0$, 0.7 or 0.3), an average particle diameter of 4.7, 4.4, or 4.3 μm, respectively, was obtained. We measured the average particle diameter with a laser-diffraction particle size analyzer. The graphite–coke (4/1 or 3/2) hybrid carbons were prepared by mixing graphite and coke at a weight ratio of 4:1 or 3:2. Table 1 lists the properties of the carbon materials used in this study. We calculated the lattice parameters of the materials from patterns measured by powder X-ray diffraction, and measured the average particle diameter in the same way as for the positive electrode materials.

We fabricated 2-Wh class cells and examined their initial discharge characteristics and cycle performance. The 2-Wh class cells were the 14500 type (diameter: 14 mm, height: 50 mm), and we used $LiCo_xNi_{1-x}O_2$ ($x = 1.0$, 0.7, and 0.3) with pure graphite or graphite–coke (4/1 and 3/2) hybrid carbons. The electrolyte solution was ethylene carbonate/diethyl carbonate (1:1, v/v) containing $1.0\,mol\,dm^{-3}$ of lithium hexafluorophosphate ($LiPF_6$). We examined their initial discharge characteristics and the cycle performance of the 2-Wh class cells under constant current charge and discharge at 200 mA in a range of 2.7–4.1 V.

To examine the cycle performance under load-levelling imitation conditions, we also fabricated 10-Wh class cells and examined their cycle performance under special conditions which imitated load-levelling use. The cells were the 30650 type (diameter: 30 mm, height: 65 mm) using $LiCo_xNi_{1-x}O_2$ ($x = 1.0$ and 0.3) and the graphite–coke (4/1) hybrid carbon. The composition of the electrolyte solution was the same as for the 2-Wh class cells. For battery systems A and F (conditions for system F are given in parenthesis), the specific energy of the 10-Wh class cells was fixed to $100\,Wh\,kg^{-1}$ and the calculated rated capacity was 2900 mAh (2980 mAh) because the constant discharge capacity—equal to 70% of the rated capacity—had to be taken out through the entire cycle test since we were targeting energy storage system applications.

In the cycle tests, the cells were charged to 2030 mAh (2086 mAh), which is equivalent to a 70% state of charge (SOC), at a constant current of 405 mA (415 mA). The cells were then discharged at a constant current of 405 mA (415 mA) until the voltage reached 2.7 V. To measure the entire capacity every 50 cycles, we charged the cells to

Table 1
Properties of the graphite and coke used in this study

	Purity (%)	Real density (g cm^{-3})	Particle size (μm)	Interlayer spacing (d_{002}, nm)	Crystallite size along the c-axis (L_c, nm)
Graphite	99.6	2.25	9	0.335	>100
Coke	99.9	1.96	16	0.344	3.2

2900 mAh (2980 mAh) or 4.2 V at a constant current of 405 mA (415 mA), and then discharged them at a constant current of 360 mA (370 mA) until the voltage reached 2.7 V.

3. Results and discussion

3.1. Mixing ratio of graphite–coke hybrid carbon

We previously reported that the discharge curves of pure graphite, pure coke, and graphite–coke hybrid carbons showed different features (Fig. 1), and that the cycle performance of a battery using graphite–coke (4/1) hybrid carbon as a negative electrode material was better than that of a battery using pure graphite when both batteries had a $LiCoO_2$ positive electrode [19].

To find better carbon materials for long-life use, we have investigated the mixing ratio of graphite–coke hybrid carbons. The graphite–coke (4/1 and 3/2) hybrid carbons were selected for further study, because graphite–coke (where 60% or more of the mixture is coke) hybrid carbons showed so little discharge capacity that batteries using them as a negative electrode material did not show a large enough discharge capacity (Fig. 1). We fabricated and investigated 2-Wh class cells with various combinations of carbon negative electrode and $LiCoO_2$ positive electrode. We used $LiCoO_2$ because it is the most commonly used positive electrode material in consumer lithium secondary batteries (battery systems A and B in Table 2).

The discharge curve features of the negative electrode materials (Fig. 1) significantly influenced the features of the ini-
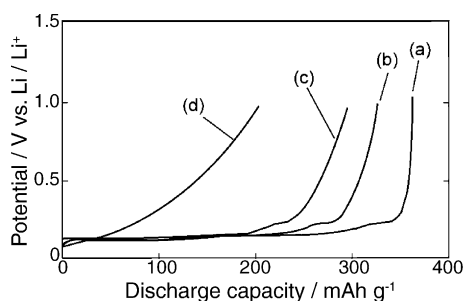

Fig. 1. Discharge curves of (a) pure graphite, (b) graphite–coke (4/1) hybrid carbon, (c) graphite–coke (3/2) hybrid carbon, and (d) pure coke in a three-electrode test cell at a constant current density of 0.25 mA cm^{-2} [19].

Table 2
Combinations of graphite–coke hybrid carbons and $LiCo_xNi_{1-x}O_2$

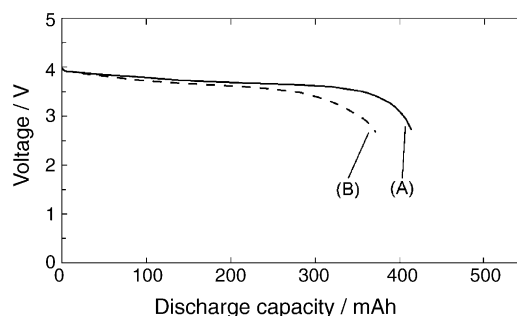| System	Negative electrode material	Positive electrode material
A	Graphite–coke (4/1) hybrid carbon	$LiCoO_2$
B	Graphite–coke (3/2) hybrid carbon	$LiCoO_2$
C	Graphite	$LiCo_{0.7}Ni_{0.3}O_2$
D	Graphite–coke (4/1) hybrid carbon	$LiCo_{0.7}Ni_{0.3}O_2$
E	Graphite	$LiCo_{0.3}Ni_{0.7}O_2$
F	Graphite–coke (4/1) hybrid carbon	$LiCo_{0.3}Ni_{0.7}O_2$

Fig. 2. Initial discharge curves of battery systems A and B in a 2-Wh class cylindrical cell at a constant current of 200 mA in a range of 2.7–4.1 V.

tial discharge curves of these batteries (Fig. 2). The battery using a graphite–coke (4/1) hybrid carbon showed a large discharge capacity of 413 mAh. As more coke was mixed with the graphite, the discharge capacity of the batteries decreased and the voltage change of the batteries became smaller in the lower voltage region.

In the cycle test, these batteries showed very good cycle performance of over 200 cycles (Fig. 3). Table 3 shows the deterioration ratios of battery systems A and B. We calculated the ratio through x charge/discharge cycles as

$$\text{deterioration ratio}\,(\%/\text{cycle}) = (D_1 - D_x)/D_1(x - 1),$$

where D_1 is the initial discharge capacity and D_x the discharge capacity after x cycles. The battery using the graphite–coke (4/1) hybrid carbon had a lower deterioration ratio of 0.07%/cycle, while the battery using the graphite–coke (3/2) hybrid carbon had a larger deterioration ratio of 0.09%/cycle.

We now consider the reason for the battery using the graphite–coke (4/1) hybrid carbon having better cycle performance. Using ^{7}Li NMR spectroscopy, we previously found that the amount of electrochemically inactive lithium on the negative electrode increased during a charge/discharge cycle test [20]. Specifically, in a battery system using pure graphite as a negative electrode material, the amount of inactive lithium largely increased in the lower voltage region. When pure coke was used as the negative electrode material,
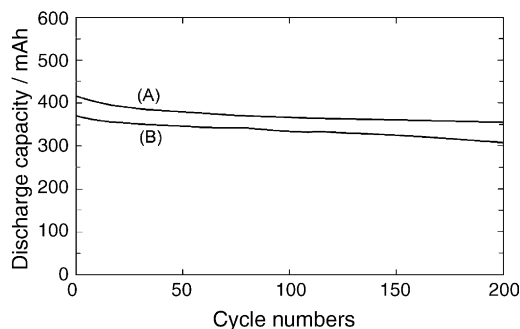

Fig. 3. Charge/discharge cycle performance of battery systems A and B in a 2-Wh class cylindrical cell at a constant current of 200 mA in a range of 2.7–4.1 V.

Table 3
Discharge capacity and deterioration ratio in the charge/discharge cycle test[a]

System	x in $LiCo_xNi_{1-x}O_2$	Mixture ratio of coke to graphite (%)	Discharge capacity (mAh)	Deterioration ratio (%/cycle)
A	1.0	20	413	0.07
B	1.0	40	370	0.09
C	0.7	0	473	0.15
D	0.7	20	413	0.11
E	0.3	0	550	0.10
F	0.3	20	486	0.07

[a] The test was done under constant current charge and discharge at 200 mA in a range of 2.7–4.1 V.

the amount of inactive lithium largely increased in the higher voltage region.

Thus, the production of electrochemically inactive lithium in the lower voltage region, caused by the presence of graphite, should be reduced by adding coke to the graphite. If the mixing ratio of coke is too large, though, there will be increased production of electrochemically inactive lithium in the higher voltage region, caused by the presence of coke. Our current research comparing graphite–coke (4/1 and 3/2) hybrid carbons indicates that a mixing ratio of 40% coke is too large and 20% coke is preferable.

3.2. Performance of a 2-Wh class cell using $LiCo_xNi_{1-x}O_2$

To study the cycle performance of a battery using $LiCo_xNi_{1-x}O_2$ and a graphite–coke hybrid carbon, we used $LiCo_{0.3}Ni_{0.7}O_2$ and $LiCo_{0.7}Ni_{0.3}O_2$ as positive electrode materials. We selected these materials because $LiCo_{0.3}Ni_{0.7}O_2$ showed the largest discharge capacity and smallest deterioration ratio in the charge/discharge cycle test, and $LiCo_{0.7}Ni_{0.3}O_2$ had the second largest energy density (Fig. 4) [12]. We used the graphite–coke (4/1) hybrid carbon because of its superior cycle performance when we used a $LiCoO_2$ positive electrode. We also examined batteries using pure graphite (which is often used in lithium secondary batteries and enables a large discharge capacity) as the negative electrode material because a battery with a large initial discharge capacity may still have a relatively large discharge capacity
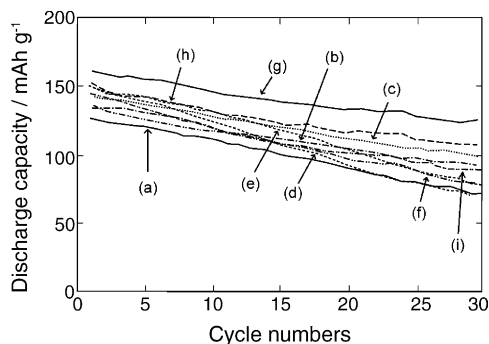
after a charge/discharge cycle test even if the cycle performance deterioration ratio is quite high.

The initial discharge characteristics of these batteries are shown in Fig. 5 as well as Table 3. The discharge capacities of battery systems D and F, which used the graphite–coke (4/1) hybrid carbon, were smaller, respectively, than those of systems C and E, which used pure graphite. In addition, the discharge capacities of battery systems E and F, which used $LiCo_{0.3}Ni_{0.7}O_2$, were larger, respectively, than those of systems C and D, which used $LiCo_{0.7}Ni_{0.3}O_2$. These results are easily understood with regard to the discharge capacities of the respective positive and negative electrode materials.

Next, we compared the cycle performance of these batteries. As shown by the charge/discharge cycle performance values in Fig. 6 and Table 3, battery sys-
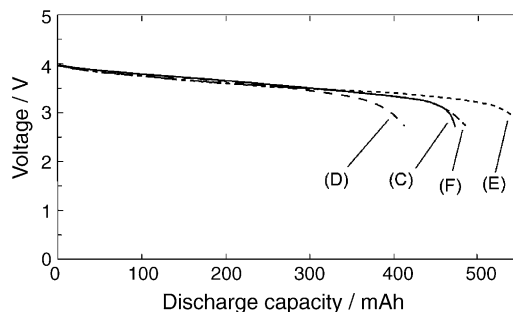

Fig. 5. Initial discharge curves of battery systems C–F in a 2-Wh class cylindrical cell at a constant current of 200 mA in a range of 2.7–4.1 V.

Fig. 4. Cycle performance of $x = 0.9$ (a), 0.8 (b), 0.7 (c), 0.6 (d), 0.5 (e), 0.4 (f), 0.3 (g), 0.2 (h), and 0.1 (i) in $LiCo_xNi_{1-x}O_2$ in a three-electrode test cell at a constant current density of $0.25\,mA\,cm^{-2}$ [12].
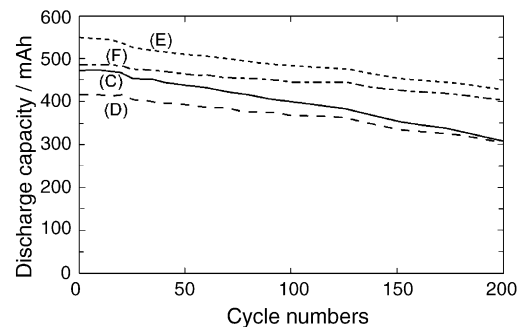

Fig. 6. Charge/discharge cycle performance of battery systems C–F in a 2-Wh class cylindrical cell at a constant current of 200 mA in a range of 2.7–4.1 V.
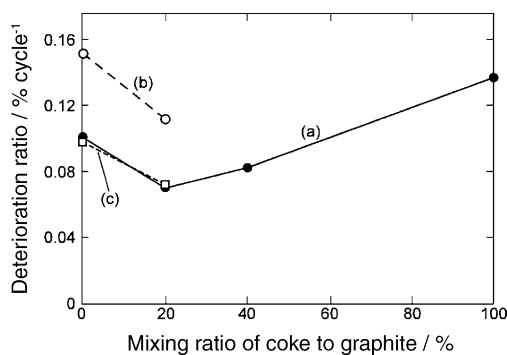
Fig. 7. Relationship between the coke-to-graphite mixing ratio and the deterioration ratio (a) $LiCoO_2$, (b) $LiCo_{0.7}Ni_{0.3}O_2$, and (c) $LiCo_{0.3}Ni_{0.7}O_2$. Some data is from [19].

tems E and F using $LiCo_{0.3}Ni_{0.7}O_2$ had lower deterioration ratios than battery systems C and D using $LiCo_{0.7}Ni_{0.3}O_2$. The superior cycle performance of the $LiCo_{0.3}Ni_{0.7}O_2$ positive electrode material compared to that of $LiCo_{0.7}Ni_{0.3}O_2$ has been reported elsewhere [12]. A structural difference in the positive electrode materials probably accounts for this difference. It is well known that $LiCo_xNi_{1−x}O_2$ has a completely ordered α-NaFeO$_2$ type structure and that the unit lattice volume of $LiCo_{0.3}Ni_{0.7}O_2$ is almost constant during charge and discharge [9,10].

Moreover, in batteries using either $LiCo_{0.7}Ni_{0.3}O_2$ or $LiCo_{0.3}Ni_{0.7}O_2$, we have confirmed that battery systems using a graphite–coke (4/1) hybrid carbon (systems D and F) show better cycle performance than battery systems using pure graphite (systems C and E). This trend can be understood in light of the results for the batteries using the $LiCoO_2$ positive electrode regarding the voltage change in the lower voltage region [19].

The relationship between the coke-to-graphite mixing ratio and the deterioration ratio is shown in Fig. 7. As the 20% mixture of coke to graphite enabled good cycle performance, we selected the graphite–coke (4/1) hybrid carbon as a negative electrode material for long-life use. The 4/1 mixing ratio is attractive because it suppresses the increase in electrochemically inactive lithium caused by graphite in the lower voltage region and caused by coke in the higher voltage region.

Thus, we decided that battery system F offered the best combination of positive and negative electrode materials for long-life use. Note that system F provided the same cycle performance as system A. In our charge/discharge cycle tests, we applied the same charge and discharge current (200 mA) to all batteries. It is disadvantage for cycle performance of the batteries with smaller discharge capacity in a point of charge/discharge current rate. However, the effect of the combination of positive and negative electrode is largely influenced their cycle performance than their disadvantage for the difference in discharge capacity.
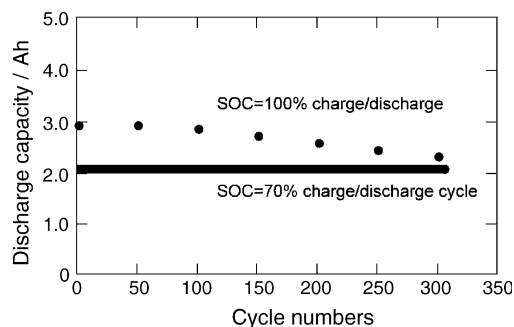

Fig. 8. Charge/discharge cycle performance of battery system A (graphite–coke (4/1) hybrid/$LiCoO_2$) in a 10-Wh class cylindrical cell under load-levelling imitation conditions.

3.3. Cycle performance of a 10-Wh class cell under load-levelling use

A battery with a larger discharge capacity is preferable for comparing the cycle performance, because the final target of this research is to develop a large-scale battery module for long-life use [1–3]. In this research, we used 10-Wh class cells, which were 30650 types (cylindrical cell, 30 mm in diameter, 65 mm in height) and had a much larger discharge capacity than batteries for consumer use in products such as cellular phones or portable PCs. We examined the cycle performance of $LiCoO_2$/graphite–coke (4/1) hybrid carbon (system A) and $LiCo_{0.3}Ni_{0.7}O_2$/graphite–coke (4/1) hybrid carbon (system F) battery systems using 10-Wh class cells under load-levelling imitation conditions. The cycle performance of each system under the load-levelling conditions is shown in Figs. 8 and 9.

Under these conditions, we repeatedly charged and discharged each battery to an SOC equal to 70% of the rated capacity. Both batteries showed good cycle performance and kept a discharge capacity of 70% of their rated capacity over more than 300 cycles. However, system F showed a larger discharge capacity after 300 cycles in the 100% SOC charge/discharge capacity, which we measured every 50 cycles to check the entire discharge capacity. Battery system F, with $LiCo_{0.3}Ni_{0.7}O_2$ and the graphite–coke (4/1) hybrid
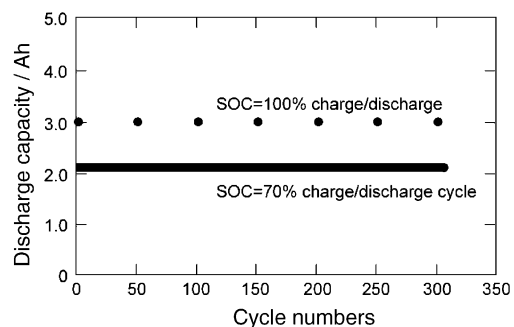

Fig. 9. Charge/discharge cycle performance of battery system F (graphite–coke (4/1) hybrid/$LiCo_{0.3}Ni_{0.7}O_2$) in a 10-Wh class cylindrical cell under load-levelling imitation conditions.

carbon, was clearly the better battery system according to the charge/discharge cycle test to imitate load-levelling use.

To develop a lithium secondary battery for long-life use, the right combination of a good positive electrode material and a good negative electrode material is critical. The selection of materials with a large discharge capacity is important, but the influence of each material's cycle performance and their combination is even more important.

4. Conclusions

To elucidate which system offers the best combination of a $LiCo_xNi_{1-x}O_2$ positive electrode and a graphite–coke hybrid carbon negative electrode for a lithium secondary battery for load-levelling use, we fabricated various battery systems and compared their characteristics. When using $LiCoO_2$, we found the best mixing ratio of coke to graphite was 20%. We then looked at the initial discharge capacity and charge/discharge cycle performance using $LiCo_{0.7}Ni_{0.3}O_2$, and $LiCo_{0.3}Ni_{0.7}O_2$ as positive electrode materials and pure graphite or graphite–coke (4/1) hybrid carbon as negative electrode materials. The battery system using the graphite–coke (4/1) hybrid carbon and $LiCo_{0.3}Ni_{0.7}O_2$ showed the best cycle performance among these systems. Clearly, careful selection of positive and negative electrode materials to enable good cycle performance and optimal combination of these materials are important to the development of a lithium secondary battery for long-life use.

Acknowledgment

References

[1] T. Hazama, M. Miyabayashi, H. Ando, R. Ishikawa, S. Furuta, H. Ishihara, J. Shonaka, J. Power Sources 54 (1995) 306.
[2] J. Aragane, K. Matsui, H. Andoh, S. Suzuki, H. Fukuda, H. Ikeda, K. Kitaba, R. Ishikawa, J. Power Sources 68 (1997) 13.
[3] T. Iwahori, I. Mitsuishi, S. Shiraga, N. Nakajima, H. Momose, Y. Ozaki, S. Taniguchi, H. Awata, T. Ono, K. Takeuchi, Electrochim. Acta 45 (2000) 1509.
[4] K. Mizushima, P.C. Jones, P.C. Wiseman, J.B. Goodenough, Mater. Res. Bull. 15 (1980) 783.
[5] J.R. Dahn, U. von Sacken, C.A. Michel, Solid State Ionics 44 (1990) 87.
[6] T. Ohzuku, A. Ueda, M. Nagayama, J. Electrochem. Soc. 140 (1993) 1862.
[7] T. Nohma, H. Kurokawa, M. Uehara, M. Takahashi, K. Nishio, T. Saito, J. Power Sources 54 (1995) 522.
[8] R.J. Gummow, A. de Kock, M.M. Thackeray, Solid State Ionics 69 (1994) 59.
[9] C. Delmas, I. Saadoune, Solid State Ionics 53–56 (1992) 370.
[10] C. Delmas, I. Saadoune, A. Rougier, J. Power Sources 43/44 (1993) 595.
[11] A. Ueda, T. Ohzuku, J. Electrochem. Soc. 141 (1994) 2010.
[12] A. Kinoshita, K. Yanagida, A. Yanai, Y. Kida, A. Funahashi, T. Nohma, I. Yonezu, J. Power Sources 102 (2001) 283.
[13] J.R. Dahn, R. Fong, M.J. Spoon, Phys. Rev. B 42 (1990) 6424.
[14] R. Kanno, Y. Takeda, T. Ichikawa, K. Nakanishi, O. Yamamoto, J. Power Sources 26 (1989) 535.
[15] M. Mohri, N. Yanagisawa, Y. Tajima, H. Tanaka, T. Mizuki, H. Wada, J. Power Sources 26 (1989) 545.
[16] J.R. Dahn, Phys. Rev. B 44 (1991) 9170.
[17] T. Ohzuku, Y. Iwakoshi, K. Sawai, J. Electrochem. Soc. 140 (1993) 2490.
[18] M. Fujimoto, K. Ueno, T. Nohma, M. Takahashi, K. Nishio, T. Saito, Proceedings of the Symposium on New Sealed Rechargeable Batteries and Supercapacitors, 1993, p. 280.
[19] Y. Kida, K. Yanagida, A. Funahashi, T. Nohma, I. Yonezu, J. Power Sources 94 (2001) 74.
[20] Y. Kida, K. Yanagida, A. Funahashi, T. Nohma, I. Yonezu, Electrochemistry 70 (2002) 26.