

Electrochemical cycling behavior of LiCoO_2 cathode prepared by mechanical alloying of hydroxides

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Abstract

Well-ordered high-temperature LiCoO_2 (HT- LiCoO_2) is synthesized by mechanical alloying (MA) of $\text{LiOH}\cdot\text{H}_2\text{O}$ and Co(OH)_2 powders and subsequent firing. Its electrochemical properties are investigated. The maximum discharge capacity of a sample mechanically alloyed and fired at 600°C for 2 h is 152 mAh g^{-1} at the $C/40$ rate, which is comparable to that obtained from a sample made by conventional solid state reactions. The cycleability is inferior, however, due to a relatively low crystallinity. When the firing temperature is increased to 850°C , the first discharge capacity of 142 mAh g^{-1} at the $C/5$ rate is increased by more than 10%, and retains 93% of its maximum value after 30 cycles. These cycling properties are about the same, or slightly higher, than those synthesized by firing a sample mixture of the same starting materials at 600°C for 8 h and then at 850°C for 24 h. Consequently, given the lower firing temperature and/or reduced reaction time, MA could prove a promising synthetic process for cathode materials used in rechargeable lithium batteries. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: LiCoO_2 ; Mechanical alloying; Discharge capacity; Cycleability; Hydroxide

1. Introduction

Because of the easy synthesis, stable discharge capacity and good rate capability, layered LiCoO_2 is still the most widely used positive electrode material in commercial rechargeable lithium batteries, even though its raw materials are toxic and costly. Generally, well-ordered high-temperature LiCoO_2 (HT- LiCoO_2) is synthesized by a solid state reaction between Li carbonates or nitrates and Co oxides or carbonates at elevated temperature (above 800°C) for long times (above 24 h) to enhance the diffusion process and to obtain highly crystallized powders [1–3]. Owing to this high temperature and long period of reaction time, there are some disadvantages such as lithium volatilization, contamination, and higher processing cost. Furthermore, when lithium nitrate is employed as the raw material, NO_x gas is emitted in the final stage of the manufacturing process [4]. Thus, removal of this gas renders mass production more difficult.

Therefore, many researchers have studied alternative methods for synthesizing HT- LiCoO_2 at lower temperature in order to overcome the above disadvantages [5–7]. Recently, mechanical alloying (MA), which is also referred

to as high-energy ball milling, reactive milling, mechanochemical synthesis, etc. has been recommended [8–11] as a useful technique to synthesize transition metal oxides for lithium-ion batteries.

In an early study, Fernandez-Rodriguez et al. [8] reported that a phase structurally related to the layered LiCoO_2 was obtained by ball milling mixtures of lithium and cobalt hydroxide for 10 h in an agate jar. They showed that spinel Co_3O_4 appeared due to the enhanced lithium mobility by mechanical activation of the LiCoO_2 phase. Obrovac et al. [9] studied the effect of ball milling on LiCoO_2 and LiNiO_2 with a mixer mill, type SPEX 8000D. As the milling time was increased, the samples were converted from hexagonal to cubic which indicated transformation into a disordered rock-salt structure, and the lattice constants became larger. The effects were caused by loss of lithia (Li_2O) and oxygen to form $\text{Li}_x\text{M}_{1-x}\text{O}$ ($0.25 \leq x \leq 0.5$). The resulting materials were found to exhibit poor electrochemical performance. Kosova et al. [10,11] have shown that the mechanochemical milling technique is an efficient method to obtain LiMn_2O_4 spinel.

In our previous work [12], we reported that well-ordered HT- LiCoO_2 could be synthesized by MA of hydroxides ($\text{LiOH}\cdot\text{H}_2\text{O}$ and Co(OH)_2) and subsequent firing at a relative low temperature (600°C) and a reduced time (2 h). From

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analysis of TG-DSC plots and XRD patterns, this advantage of firing conditions for ball-milled precursors arose from the absence of Co_3O_4 , which was observed as an intermediate phase in the case of firing a simple mixture of same starting materials at $300\text{ }^\circ\text{C}$. This result was considerably different from that of an earlier study [8] which reported the occurrence of Co_3O_4 during milling. This discrepancy may be due to higher milling energy and less oxidative surroundings in our work.

In this study, we have evaluated the electrochemical cycling properties of LiCoO_2 powders, synthesized by MA and subsequent firing, in order to confirm the usefulness of MA as a synthetic process for cathode material for rechargeable lithium-ion batteries. These powders were compared with those of LiCoO_2 samples prepared by firing the simple mixture at 600 and $850\text{ }^\circ\text{C}$.

2. Experimental

By MA, the LiCoO_2 precursors were synthesized from starting materials of $\text{LiOH}\cdot\text{H}_2\text{O}$ (Aldrich) and $\text{Co}(\text{OH})_2$ (Aldrich) powders. As reported in previous work, the optimized conditions for MA were a ball-to-power weight ratio of 15:1, a ball size of 12.7 mm in diameter, a milling time of 6 h, and the use of shaker-type ball mill (SPEX 8000D) with a zirconia vial set. In this work, the same conditions were employed except for the vial set. The hardened steel vial set, which gave easier control of the atmosphere and a higher collision energy, was employed in order to use an oxygen atmosphere for comparison. The starting materials were charged under air into a hardened steel vial, in a molar ratio of $\text{Li}:\text{Co} = 1:1$ with two steel balls, and then milled for 6 h. Subsequent heat treatment was carried out in a tube-type furnace at $600\text{ }^\circ\text{C}$ for 2 h under air. The LiCoO_2 synthesized in this way will be referred to as MA600 for brevity. To investigate the effect of milling and subsequent firing conditions on electrochemical cycling behavior, sample powders were also synthesized under different conditions. Milling times of 2 and 4 h, an oxygen atmosphere during milling, and firing temperatures of $750\text{ }^\circ\text{C}$ (MA750) and $850\text{ }^\circ\text{C}$ (MA850), respectively, were employed. For comparison of electrochemical performance, LiCoO_2 was also synthesized by conventional solid state reaction of the same starting materials. The stoichiometric simple mixture of starting materials was mixed in an agate mortar and fired for 8 h at $600\text{ }^\circ\text{C}$ (will be referred to as SM600) and then for 24 h at $850\text{ }^\circ\text{C}$ (SM850) under air.

The crystal structures of prepared sample powders were characterized by X-ray diffractometry (Rigaku D-MAX 3000) using $\text{Cu K}\alpha$ radiation.

The electrochemical cycling properties were evaluated using a two-electrode cell with a lithium metal foil as the negative electrode and a microporous polyethylene separator. The cathodes were prepared by the following procedure. First, the prepared LiCoO_2 powders were mixed well with

12 wt.% carbon black in an agate mortar, then mixed with 8 wt.% polytetrafluoroethylene (PTFE) dispersed in distilled water at 300 g l^{-1} , and isopropyl alcohol added. The resulting dough-type film of 1 cm^2 was pressed on a stainless Exmet screen and vacuum dried for at least 12 h at $150\text{ }^\circ\text{C}$ before assembling the cells. The weight of active materials was 15–20 mg. The entire cell with an electrolyte of 1 M LiPF_6 in EC:DMC (1:1 v/v) mixture (Starlyte) was assembled in an argon-filled dry box with a moisture content below 1 ppm.

Electrochemical cycle tests were performed between 3.0 and 4.2 V at ambient temperature ($26 \pm 2\text{ }^\circ\text{C}$) using an automatic galvanostatic charge–discharge unit (Maccor series 4000) at various constant currents, C/x ($x = 2, 5, 10, 40$). The x value in the C/x current density corresponds to the time for removal of 1 M Li in LiCoO_2 in x number of hours (i.e. $1C = 274\text{ mAh g}^{-1}$).

3. Results and discussion

3.1. Structural analysis

The XRD patterns of prepared powders are shown in Fig. 1. For the samples prepared by MA, firing at relatively low temperature of $600\text{ }^\circ\text{C}$ for only 2 h (Fig. 1(a)) is

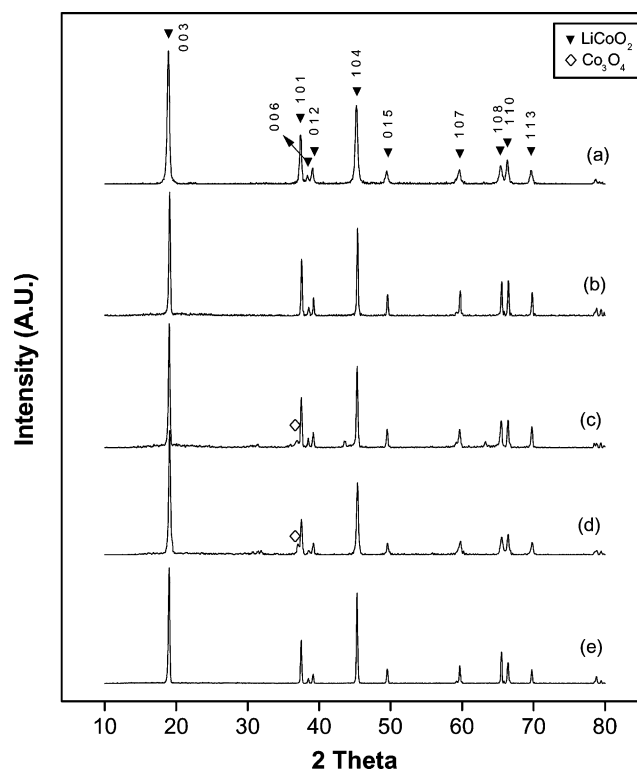


Fig. 1. XRD patterns of LiCoO_2 samples prepared with different firing conditions: (a) MA600 ($600\text{ }^\circ\text{C}$, 2 h); (b) MA850 ($850\text{ }^\circ\text{C}$, 2 h); (c) MA850 under O_2 ($850\text{ }^\circ\text{C}$, 2 h); (d) SM600 ($600\text{ }^\circ\text{C}$, 8 h); (e) SM850 ($600\text{ }^\circ\text{C}$, 8 h and then $850\text{ }^\circ\text{C}$, 24 h).

sufficient to obtain the well-ordered HT-LiCoO₂ phase which shows the high intensity of the (0 0 3) peak and clear splitting between the (0 0 6)/(0 1 2) and (1 0 8)/(1 1 0) peaks. With increasing the subsequent firing temperature to 850 °C (Fig. 1(b)), the peaks become sharper and the peak splittings clearer. This indicates an increase in crystallinity and an improvement in cation ordering. For MA under an oxygen atmosphere and firing at 850 °C (Fig. 1(c)), the Co₃O₄ phase formed during the milling does not disappear completely since, though the firing temperature was sufficiently high, the duration time of 2 h was too short for transformation to LiCoO₂. On the other hand, for the samples prepared by conventional solid state reaction of a simple mixture of starting materials, the peaks for the SM600 sample fired at 600 °C for 8 h (Fig. 1(d)) are analogous to those for MA600, but the peaks for the Co₃O₄ phase are still observed in spite of the longer time of firing. This is because of the difference in the reaction sequence between the two samples, as discussed earlier [12]. With further firing at 850 °C for 24 h (Fig. 1(e)), highly crystallized HT-LiCoO₂ without any minor phases was obtained. Nevertheless, the intensity ratio of the (0 0 3)/(1 0 4) peaks is reduced markedly. This suggests that some cation mixing originates from the loss of lithium content during the firing.

3.2. Electrochemical cycle test

A comparison of the typical first charge–discharge curves for (a) MA600, (b) SM600, and (c) SM850 is given in Fig. 2.

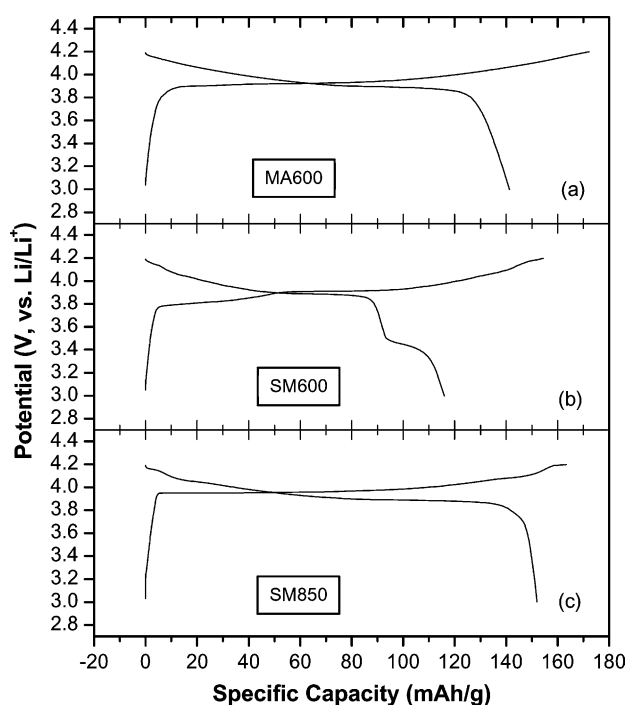


Fig. 2. Typical first charge–discharge curves for LiCoO₂ cycled at the C/10 rate: (a) MA600; (b) SM600; (c) SM850.

The samples were cycled between 3.0 and 4.2 V at a constant current density of C/10 rate (corresponding to 27.4 mA g⁻¹). The charge and discharge voltage plateaux for MA600 were 3.92 and 3.88 V versus Li/Li⁺, respectively. These are much the same as those for conventional HT-LiCoO₂. In spite of the shorter firing times at 600 °C, the maximum discharge capacity of MA600 (141.2 mAh g⁻¹) is much higher than that of SM600 (116.1 mAh g⁻¹). Besides, in the case of the SM600 sample, minor plateaux are observed in the discharge curves at 3.45 V, which may be due to the retained intermediate phase of Co₃O₄. Generally, due to the highly negative heat of formation of this oxide, high temperatures (above 850 °C) and long times (above 24 h) are required to form a well-ordered LiCoO₂ phase. In this respect, consequently, mechanically alloyed precursors have an advantage of requiring lower temperatures and shorter times at the same temperature because they have no oxides but are comprised of only some water and pulverized LiCoO₂ with lower crystallinity [12]. Moreover, only CoOOH appeared as an intermediate phase during MA. Therefore, mechanically alloyed LiCoO₂ (MA600) shows a slightly lower maximum capacity than the SM850 sample (145.2 mAh g⁻¹) prepared by firing a simple mixture at 600 °C for 8 h and then at 850 °C for 24 h, which is a highly crystallized and well-ordered phase. As shown in Fig. 3, however, the cyclic capacity decay of MA600 is faster than that of SM600 or SM850. After 30 cycles, the discharge capacity of MA600 is about 72% of its maximum capacity, whereas it is 95% for SM850 and 80% for SM600.

The differential capacity (dx/dV, where *x* is the number of moles of delivered Li ion) for the three samples is given in Fig. 4. The inset in Fig. 4 (expanded scale) shows the existence of two minor peaks between 4.0 and 4.2 V. The SM850 sample has one major peak at 3.9 V and two minor peaks at 4.05 and 4.16 V, whereas only one major peak at 3.88 V is observed for the MA600 sample. According to

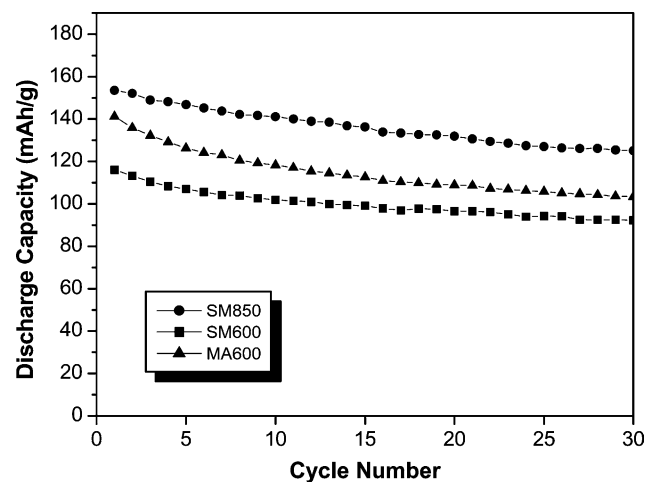


Fig. 3. Discharge capacity as function of cycle number for LiCoO₂ cycled between 3.0 and 4.2 V at the C/10 rate.

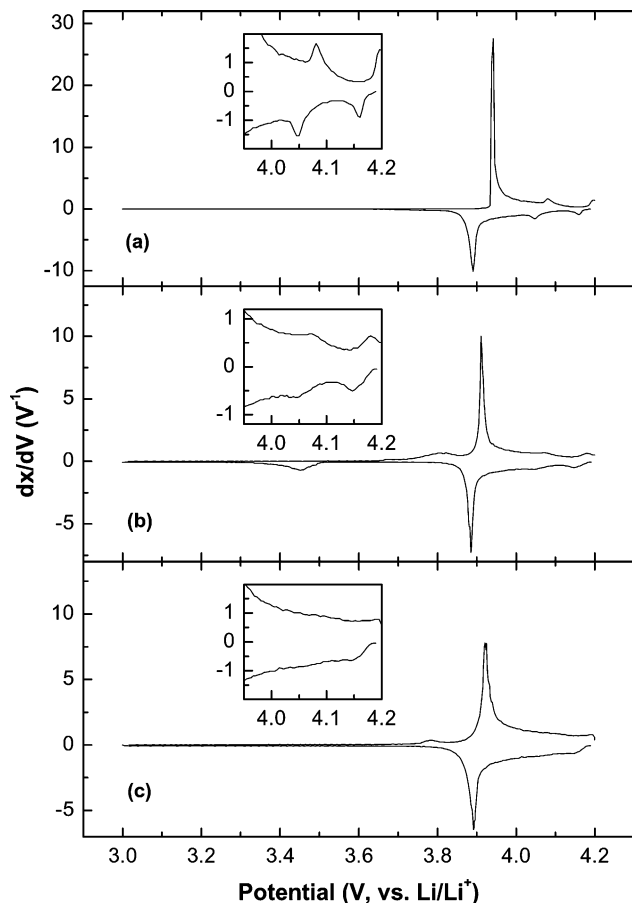


Fig. 4. Derivative dx/dV as function of cell potential for first charge-discharge at the $C/10$ rate: (a) SM850; (b) SM600; (c) MA600.

Reimers and Dahn [13], the major peak is associated with a first-order transition from LiCoO_2 to $\text{Li}_{0.8}\text{CoO}_2$ which also has a hexagonal lattice expanded in the c direction, and minor peaks represent a reversible order–disorder transition from hexagonal to monoclinic symmetry. The derivative dx/dV shows clearly this order–disorder transition [14]. Consequently, it is considered that there is no phase transition from hexagonal to monoclinic in mechanically alloyed LiCoO_2 (MA- LiCoO_2), which usually occurs at around $x = 0.5$ in Li_xCoO_2 . The reason for this feature is not clearly understood, nor whether it is a general characteristic of MA- LiCoO_2 . Contamination with iron from the balls and vial could be a possible cause.

The first discharge curves for MA600 at various discharge rates which indicate the rate capability of MA- LiCoO_2 are given in Fig. 5. The maximum first discharge capacity is 151.8 mAh g^{-1} at the $C/40$ rate. At the $C/5$ and $C/2$ rates, which are typical discharge rates in commercial products such as cellular phones and video cameras, the discharge capacity is 130 and 115 mAh g^{-1} , respectively. According to Koksang et al. [15], who reviewed the performance of cathode materials for lithium-ion batteries reported by many research groups, typical reversible capacities of LiCoO_2 cathodes prepared by various methods are in the range

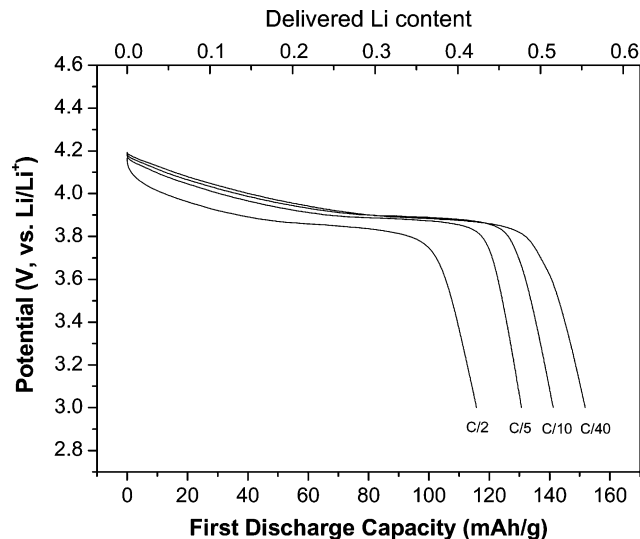


Fig. 5. First discharge curves at various C rates for sample mechanically alloyed and fired at 600°C for 2 h (MA600).

$120\text{--}140 \text{ mAh g}^{-1}$. Therefore, the electrochemical performance of LiCoO_2 synthesized by the MA is comparable to that obtained by other processes.

3.3. Effect of MA and subsequent firing conditions

In spite of its comparable initial capacity, the cycleability of MA600 is inferior to that of conventional HT- LiCoO_2 (SM850). Therefore, to obtain better electrochemical performance, the effects of MA and subsequent firing conditions on the cycling behavior of MA- LiCoO_2 were investigated.

The effect of milling time is shown in Fig. 6. With increasing time up to 6 h, followed by firing at 600°C for

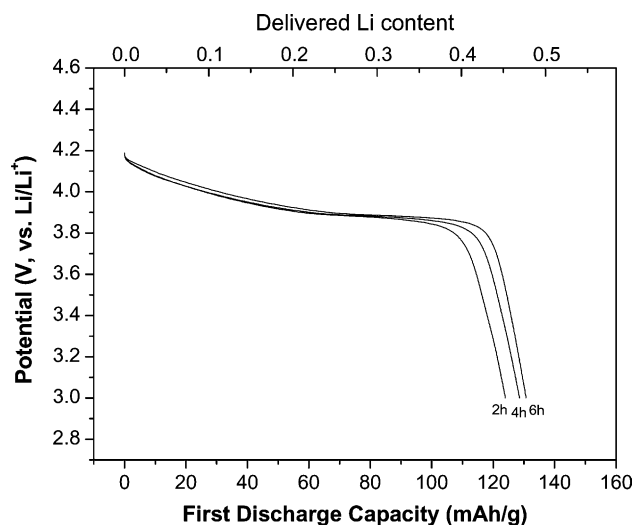


Fig. 6. First discharge curves at the $C/5$ rate for samples mechanically alloyed for different times and fired at 600°C for 2 h.

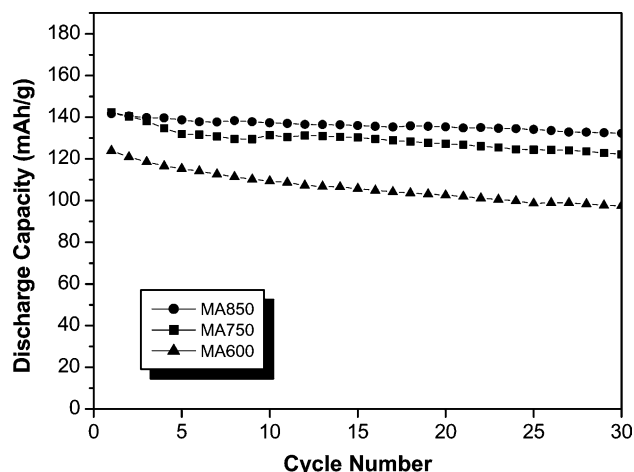


Fig. 7. Discharge capacity as function of cycle number for samples prepared by MA and firing at different temperature (cycled between 3.0 and 4.2 V at the $C/5$ rate).

2 h, the first discharge capacity increased slightly. Nevertheless, the cycle life (not shown) was virtually unaltered. Therefore, it is concluded that during MA, the powders become pulverized and more homogeneous, and only CoOOH appears as an intermediate phase. For these reasons, a firing temperature of 600°C for 2 h could be sufficient for transformation to LiCoO_2 phase in the case of only 2 h milling. The minor increase in discharge capacity may be ascribed to a more refined particle size.

The cycle life of MA- LiCoO_2 at the $C/5$ rate with increasing subsequent firing temperature is presented in Fig. 7. On increasing the temperature from 600 to 850°C , the discharge capacity increases from 124 to 142 mAh g^{-1} , and cycleability and charge–discharge efficiency (not shown) are improved markedly. From analysis of XRD patterns, these improvements are due to increases in the crystallinity and the degree of cation ordering. After 30 cycles, the discharge capacity for 600 , 750 and 850°C is 78, 86 and 93%, respectively. Although the firing condition is simple and more energy efficient, the cycling performance of MA850 (MA- LiCoO_2 fired at 850°C for 2 h) is about the same or slightly higher than that of SM850 (simple mixture fired at 600°C , 8 h and then at 850°C , 24 h) at the same discharge rate of $C/5$. After 100 cycles, the structure of MA850 still has highly ordered hexagonal symmetry and cation ordering; it shows a high $(003)/(104)$ intensity ratio of 4.6 and higher intensities for the (001) planes reflection (shown in Fig. 8).

The effect of oxygen atmosphere during the milling operation is presented in Fig. 9. The maximum discharge capacity for the sample prepared by MA under oxygen is much lower (102 mAh g^{-1} , $C/5$ rate) than that for the sample obtained under air. This is due to the retained Co_3O_4 phase, as shown in Fig. 1(c). Its cycleability, however, was as good as that of MA850 due to high crystallinity and high cation ordering. As a result, the use of an oxygen atmosphere during MA of hydroxides is not necessary, rather it should

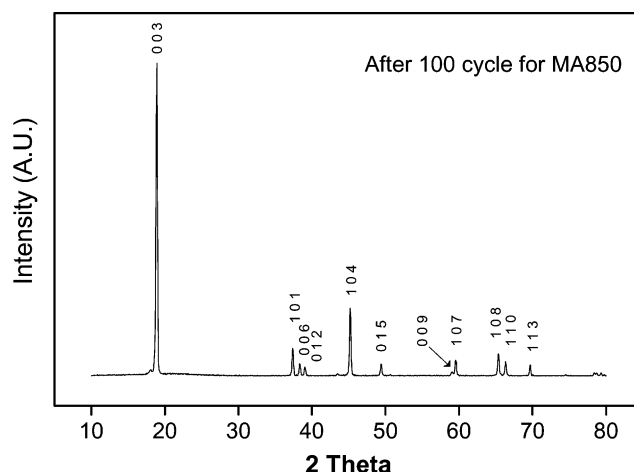


Fig. 8. XRD pattern for sample MA850 after 100 cycles between 3.0 and 4.2 V at the $C/5$ rate.

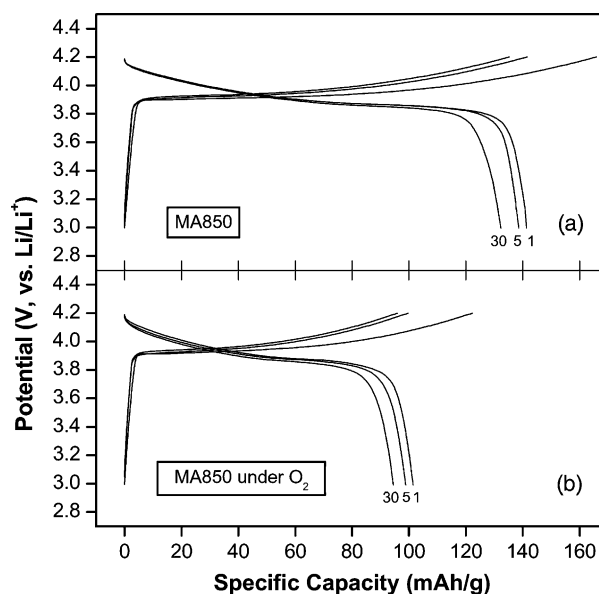


Fig. 9. Comparison of charge–discharge curves for samples mechanically alloyed under different atmospheres followed by firing at 850°C for 2 h: (a) ball-milled under air; (b) ball-milled under oxygen.

be forbidden in order to obtain a pure LiCoO_2 without any minor phases like cobalt oxides.

4. Conclusions

As a result of electrochemical cycling tests, it is confirmed that MA could be a promising synthetic process of cathode materials for rechargeable lithium batteries. Well-ordered HT- LiCoO_2 with a maximum discharge capacity of 152 mAh g^{-1} at the $C/40$ rate can be obtained by MA and reduced subsequent firing (600°C , 2 h) of $\text{LiOH}\cdot\text{H}_2\text{O}$ and $\text{Co}(\text{OH})_2$ powders as starting materials. In comparison with conventional solid state reactions, the firing condition is less expensive and saves energy. Although the discharge

capacity is comparable, the cycleability is about 72% of the maximum value after 30 cycles and is inferior to that of conventional processes due to relatively low crystallinity. In addition, the phase transition from hexagonal to monoclinic, which usually occurs at around $x = 0.5$ in Li_xCoO_2 , is not observed in MA-LiCoO₂.

When milling times are increased from 2 to 6 h in air, the maximum discharge capacity increases slightly, and the cycle life is about the same. The use of an oxygen atmosphere during milling operation causes formation of the Co_3O_4 phase and consequently, shows considerably reduced discharge capacity even though the subsequent firing temperature is increased to 850 °C. In an air atmosphere, however, increasing the subsequent firing temperature from 600 to 850 °C causes an increase in the maximum discharge capacity by more than 10% (142 mAh g⁻¹ at the C/5 rate), and the cycleability and charge–discharge efficiency are improved.

Acknowledgements

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References

- [1] K. Mizushima, P.C. Jones, P.J. Wiseman, J.B. Goodenough, *Mater. Res. Bull.* 15 (1980) 783.
- [2] T. Ohzuku, A. Ueda, *J. Electrochem. Soc.* 141 (1994) 2972.
- [3] J. Kim, P. Fulmer, A. Manthiram, *Mater. Res. Bull.* 34 (1999) 571.
- [4] K. Hasezaki, M. Kamada, *J. Jpn. Soc. Powder Powder Metall.* 46 (1999) 317.
- [5] G.G. Amatucci, J.M. Tarascon, D. Larcher, L.C. Klein, *Solid State Ionics* 84 (1996) 169.
- [6] Y.M. Chiang, Y.I. Jang, H. Wang, B. Huang, D.R. Sadoway, P. Ye, *J. Electrochem. Soc.* 145 (1998) 887.
- [7] P.N. Kumta, D. Gallet, A. Waghray, G.E. Blomgren, M.P. Setter, *J. Power Sources* 72 (1998) 91.
- [8] J.M. Fernandez-Rodriguez, J. Morales, J.L. Tirado, *Reactiv. Solids* 4 (1987) 163.
- [9] M.N. Obrovac, O. Mao, J.R. Dahn, *Solid State Ionics* 112 (1998) 9.
- [10] N.V. Kosova, I.P. Asanov, E.T. Devyatkina, E.G. Avvakumov, *J. Solid State Chem.* 146 (1999) 184.
- [11] N.V. Kosova, N.F. Uvarov, E.T. Devyatkina, E.G. Avvakumov, *Solid State Ionics* 135 (2000) 107.
- [12] W.T. Jeong, K.S. Lee, *J. Alloys Comp.* 322 (2001) 205.
- [13] J.N. Reimers, J.R. Dahn, *J. Electrochem. Soc.* 139 (1992) 2091.
- [14] J.N. Reimers, J.R. Dahn, U. Von Sacken, *J. Electrochem. Soc.* 140 (1993) 2752.
- [15] R. Koksang, J. Barker, H. Shi, M.Y. Saidi, *Solid State Ionics* 84 (1996) 1.