Synthesis and electrochemical properties of lithium cobalt oxides prepared by molten-salt synthesis using the eutectic mixture of LiCl–Li$_2$CO$_3$

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Abstract

Lithium cobalt oxide powders have been successfully prepared by a molten-salt synthesis (MSS) method using a eutectic mixture of LiCl and Li$_2$CO$_3$ salts. The physico-chemical properties of the lithium cobalt oxide powders are investigated by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), particle-size analysis and charge–discharge cycling. A lower temperature and a shorter time ($\sim$700°C and 1 h) in the Li:Co=7 system are sufficient to prepare single-phase HT-LiCoO$_2$ powders by the MSS method, compared with the solid-state reaction method. Charge–discharge tests show that the lithium cobalt oxide prepared at 800°C has an initial discharge capacity as high as 140 mA h g^{-1}, and 100 mA h g^{-1} after 40 cycles. The dependence of the synthetic conditions of HT-LiCoO$_2$ on the reaction temperature, time and amount of flux with respect to starting oxides is extensively investigated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Molten-salt synthesis; Lithium-ion battery; Lithium cobalt oxide

1. Introduction

Nowadays, one of the most promising power sources is the rechargeable lithium-ion battery. High-performance lithium-ion batteries are favoured in applications where low weight or small volume is desired, e.g. laptop computers, cellular phones and electric vehicles. A significant number of recent studies has focused on the synthesis, processing and/or electrochemical identification of cathode materials. Only three materials are usually identified as suitable for use as cathodes in 4 V lithium-ion batteries, namely, the spinel phase of LiMn$_2$O$_4$ and the layered LiCoO$_2$ and LiNiO$_2$ compounds [1].

In the most widely studied compound, LiCoO$_2$, high-temperature firing for many hours is required to obtain the α-NaFeO$_2$ type cation ordered material (so-called HT-LiCoO$_2$) when starting with physically mixed metal salts. Lower temperature firing has also been observed to result a low-temperature phase (LT-LiCoO$_2$) with inferior electrochemical performance [2]. In fact, high-temperature firing for an elongated period to obtain the HT-LiCoO$_2$ via a solid-state reaction method causes inhomogeneity, irregular morpho-

logy, and a broader particle-size distribution of powder. To overcome these disadvantages, several solution routes have been developed such as sol–gel [3,4], co-precipitation [5], Pechini process [6], and freeze-drying [7] methods. These methods require a large quantity of solvent and organic materials like citric acid, ethylene glycol, polyvinyl alcohol, and polyvinyl butyral [8].

A molten-salt synthesis (MSS) or flux growth synthesis method has been reported to be one of the simplest means to prepare pure and stoichiometric powders of multi-component oxides, in which the molten salts are utilised as solvent or reacting species, or sometimes both [9,10]. Since the diffusion rates of the components in molten salts are much higher than those in the solid-state reaction, the various powders, e.g. Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ and ferrites, can be prepared at significantly lower temperatures using molten-salt synthesis [11,12]. Yang et al. have investigated the preparation of lithium manganese oxides by molten-salt synthesis using γ-MnOOH as a manganese source and LiCl, LiNO$_3$, Li$_2$SO$_4$ or LiOH as flux [13]. As far as we know, however, a systematic study on the process parameters which are important for preparing LiCoO$_2$ has not reported.

In this paper, we have carried out the characterisation of HT-LiCoO$_2$ powders prepared by molten-salt synthesis using eutectic mixtures of LiCl and Li$_2$CO$_3$ molten salts, in order to understand the effects of process parameters,

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such as formation temperature, time and amount of flux. Emphasis is given to powders prepared in the flux ratio of Li:Co=7.

2. Experimental procedure

Reagent-grade chlorides (LiCl and $CoCl_2 \cdot 6H_2O$) and carbonate (Li_2CO_3) were used in the study. A $0.6LiCl$–$0.4Li_2CO_3$ flux was used as the eutectic composition with a melting point of 506°C. The amount of flux is defined here by the flux ratio F (=mole of total Li ion/mole of Co ion). Appropriate amounts of these chlorides and carbonate were ground with a mortar and pestle. After drying at 110°C for 24 h, the dried powders were placed in covered alumina crucibles and then heated in a muffle furnace at temperatures from 550 to 900°C. The heating rate was set at 200°C h^{-1} for all temperature settings. After heating, the resulting powders were cooled to ambient temperature and a residual flux was removed from the products by washing with distilled water and 1 M acetic acid solution for 20 min. The powders were finally dried at 120°C for 2 h.

The resulting powders were identified by X-ray diffraction (XRD) using a MAC science MXP3A-HF diffractometer which employed Cu Kα radiation. The structure was refined by the Rietveld method using the Fullprof program [14]. The peak shape is described by a pseudo-Voigt function and the background level is defined by a polynomial function. For each diffraction pattern, a scale factor, a counter zero point, the peak asymmetry and the unit-cell parameters were refined in addition to the atomic parameters. The morphology and microstructure of the powders were examined using a scanning electron microscope (SEM) (JEOL JSM-5310LV). Conducting samples were prepared by gold sputtering the powder specimens. The particle-size distribution was determined by a laser particle analyzer (Northrop Microtack II) with the dispersion of powders in water by ultrasonic vibration.

The electrochemical characteristics of the powders were checked using a two-electrode electrochemical cell. The positive electrode, which consisted of 16 mg of the powder (80 wt.%), acetylene black (15 wt.%) and PTFE (5 wt.%), was pressed and then vacuum dried at 120°C for 24 h. The lithium metal and polypropylene film were used as the negative electrode and the separator, respectively. The electrolyte was 1 M $LiPF_6$ in 1:1 EC/DMC solution. The entire cell was assembled in the argon-filled glove box. The cells were tested using a constant current of 0.3 mA cm^{-2} in the voltage range 4.2 and 2.8 V with an Arbin charge–discharge cycler.

3. Results

Before studying the effect of flux, the non-fluxed reaction was examined by XRD. The XRD profiles of the
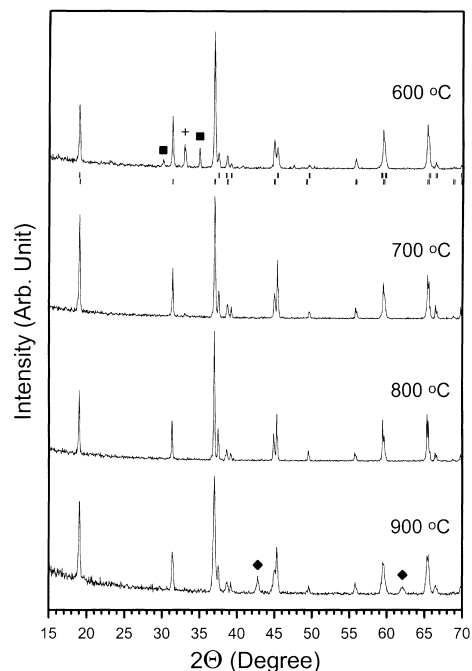

Fig. 1. X-ray diffraction patterns of powders prepared at various temperatures for 24 h in Li:Co=1 system. Upper tick: HT-$LiCoO_2$; lower tick: Co_3O_4; (◆): CoO; (■): LiCl and (+): unidentified.

powder prepared at temperatures from 600 to 900°C for 24 h in the F (Li:Co)=1 system are presented in Fig. 1. At 600 and 700°C, a spinel phase (lower tick) with a unit cell parameter $a \sim 8.08$ Å (space group $Fd3m$) was primary formed with a small amount of lithium cobalt oxide phase (space group $R-3m$, upper tick), unreacted LiCl (■, JCPDS No. 4-0664), and an unidentified phase (+). Upon firing at 800°C, the spinel peaks decrease, while the lithium cobalt oxide peaks are little increased. Rietveld refinement for the samples prepared at 600 to $\sim$800°C shows that the amount of HT-$LiCoO_2$ continuously increases from 21 to 53 wt.% as the reaction temperature increases. Heat-treatment at 900°C results in decomposition into a three-phase product of HT-$LiCoO_2$, Co_3O_4 and CoO (◆, JCPDS No. 43-1004). The weight percentage of each phase, the unit cell parameters and $c:a$ ratios are given in Table 1.

The effect of flux ratio, F, on the formation of HT-$LiCoO_2$ was studied by firing at 800°C for 24 h. Fig. 2 shows the XRD profiles of the powders prepared using different F values which range from 1 to 9. For the $F=3$ system, the spinel Co_3O_4 peak as well as the HT-$LiCoO_2$ phase is observed. The single-phase HT-$LiCoO_2$ powders were obtained under two conditions, $F=5$ and 7. Residual Li_2CO_3 is not observed for $F \le 7$. Since a molten salt phase makes the reaction path short, it seems that the presence of a large quantity of molten salt phase probably aids the formation of the HT-$LiCoO_2$ phase. Residual Li_2CO_3 peaks (◆, JCPDS No. 22-1141) were detected in $F=9$ system, however, even though the product was thoroughly washed in water and

Table 1
Phase composition and unit cell parameters of powders for the $F=1$ system

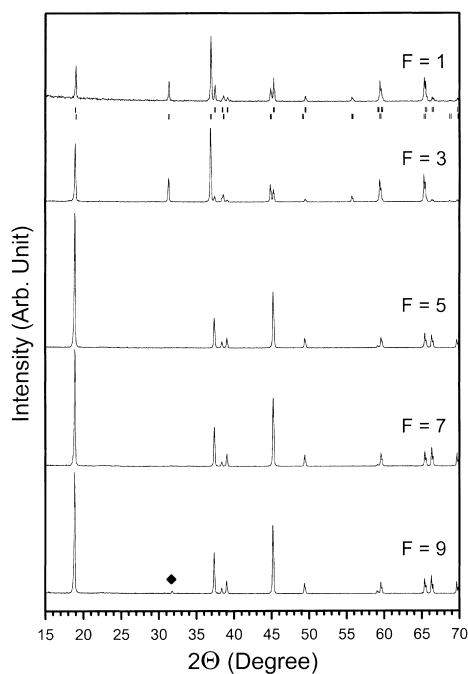| Reaction temperature (°C)	Percentage of phase (wt.%)			Unit cell parameter (Å)			
	Co_3O_4	HT-$LiCoO_2$	CoO	Co_3O_4	HT-$LiCoO_2$		
					a (Å)	c (Å)	$c{:}a$
600	79	21	–	8.0791(4)	2.8143(2)	14.051(3)	4.99
700	61	39	–	8.0801(2)	2.8151(7)	14.050(2)	4.99
800	47	53	–	8.0779(2)	2.8146(1)	14.044(4)	4.99
900	45	40	15	8.0739(3)	2.8138(2)	14.043(4)	4.99

Fig. 2. X-ray diffraction patterns of powders prepared at 800°C for 24 h in various Li:Co systems. Upper tick: HT-$LiCoO_2$; lower tick: Co_3O_4 and (◆): Li_2CO_3.

Fig. 3. X-ray diffraction patterns of powders prepared at various temperatures for 24 h in various Li:Co systems. Upper tick: HT-$LiCoO_2$ and lower tick: LT-$LiCoO_2$.

acetic acid solution. Therefore, further studies were conducted on the $F=7$ system. The relative amounts and unit cell parameters of HT-$LiCoO_2$ are listed in Table 2.

The XRD profiles of powders prepared at different temperatures for 24 h in the $F=7$ system are presented in Fig. 3. For the powder prepared at 550°C, a mixed phase of HT-
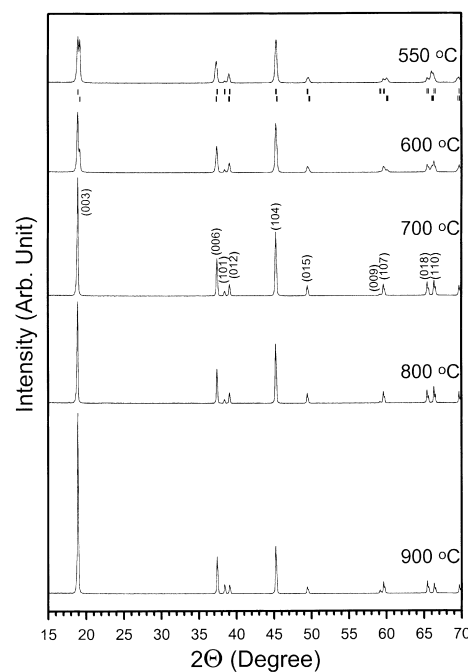
$LiCoO_2$ (upper tick) and LT-$LiCoO_2$ (lower tick) is observed. Upon firing at 600°C, the LT-$LiCoO_2$ peaks decrease from 53 to 26%, whereas the HT-$LiCoO_2$ peaks increase. The observed, calculated and difference XRD profiles of the sample prepared at 600°C are shown in Fig. 4a. The structural refinement of the mixed phase of

Table 2
Phase composition and unit cell parameter of powders with various F values

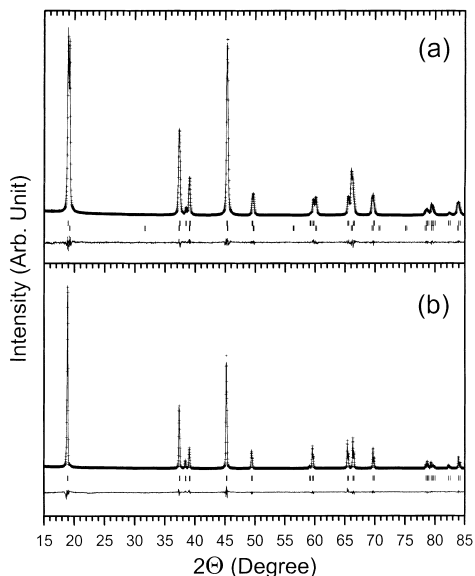| Li:Co ratio, F	Percentage of phase (wt.%)			Unit cell parameter (Å)			
	Co_3O_4	HT-$LiCoO_2$	Li_2CO_3	Co_3O_4	HT-$LiCoO_2$		
					a (Å)	c (Å)	$c{:}a$
1	47	53	–	8.0779(2)	2.8146(1)	14.044(4)	4.99
3	70	30	–	8.0789(2)	2.8147(2)	14.0469(8)	4.99
5	–	~100	–		2.8143(1)	14.0451(6)	4.99
7	–	~100	–		2.8149(1)	14.0483(6)	4.99
9	–	96	4		2.8145(1)	14.0456(6)	4.99

Fig. 4. Observed, calculated and difference powder X-ray diffraction profiles for powders prepared at 600°C (a) and 800°C (b) for Li:Co=7 system. Upper tick: HT-LiCoO$_2$ and lower tick: LT-LiCoO$_2$ in (a).

Fig. 5. X-ray diffraction patterns of powders prepared at 800°C with various duration times.

LT-LiCoO$_2$ (*Fd3m*) and HT-LiCoO$_2$ (*R-3m*) yield structural parameters that are in good agreement with those obtained by Gummow et al. [15]. The single-phase HT-LiCoO$_2$ can be obtained at 700 and 800°C. With increasing firing temperature, the LT-LiCoO$_2$ disappears while the HT-LiCoO$_2$ increases. The measured, calculated and difference profiles of the XRD patterns for the sample prepared at 800°C are shown in Fig. 4b. The good agreement between the measured pattern and the fitted pattern for HT-LiCoO$_2$ is indicative of a reliable refinement. The refined cell parameters of *a* and *c* are 2.8149(1) and 14.0483(6) Å, respectively, This correspond well with the values of 2.8161(5) and 14.0536(5) Å obtained from a single-crystal XRD study [16]. At 900°C, the peak intensities of (0 0 3), (0 0 6) and (0 0 9) are relatively stronger than the other peaks, as generally observed in the literature. It may be due to the preferred orientation which results from the growth of the particles as the reaction temperature increases. The phase composition, unit cell parameter and *c:a* ratio are listed in Table 3.

The XRD profiles for the samples heated at 800°C in the *F*=7 system for various lengths of duration time are presented in Fig. 5. At a time of 1 h, a small amount of CoO appeared at $2\theta=42.94°$. With further increase of duration time, single phase HT-LiCoO$_2$ was obtained. This result strongly suggests that molten-salt synthesis needs a lower calcination temperature and shorter time than the solid-state reaction method where the calcination temperature is almost 900°C and calcination time is longer than 24 h with intermediate grinding. That is, the duration time rarely affects the amount of HT-LiCoO$_2$ and a duration of at least 1 h is necessary to obtain single phase HT-LiCoO$_2$. The unit cell parameters and *c:a* ratio of HT-LiCoO$_2$ are listed in Table 4.

Scanning electron microphotographs of the powders obtained at different calcination temperatures and times for the *F*=7 system are given in Fig. 6. Clearly, the morphological changes as the synthetic temperature increases. Powders prepared at 600°C are loosely aggregated. As the

Table 3
Phase composition and unit cell parameter of powders for the *F*=7 system

Reaction temperature (°C)	Percentage of phase (%)		Unit cell parameter (Å)			
	LT-LiCoO$_2$	HT-LiCoO$_2$	LT-LiCoO$_2$	HT-LiCoO$_2$		
			a (Å)	*a* (Å)	*c* (Å)	*c:a*
550	53	47	7.9961(4)	2.8151(2)	14.0403(9)	4.99
600	26	74	7.9956(4)	2.8152(2)	14.0443(9)	4.99
700	–	~100		2.8146(1)	14.0467(5)	4.99
800	–	~100		2.8149(1)	14.0483(6)	4.99
900	–	~100		2.8150(2)	14.0467(6)	4.99

Table 4
Unit cell parameter of powders prepared at 800°C for various duration periods

Reaction time (h)	a (Å)	c (Å)	$c:a$
1	2.8142(3)	14.045(2)	4.99
12	2.8138(3)	14.053(2)	4.99
24	2.8149(2)	14.048(3)	4.99

synthetic temperature increases, crystallisation of the samples is observed. For a sample prepared at 800°C for 24 h, a well-crystallised hexagonal shape can be seen without agglomeration. Typical particle size distributions for the crystallites in these samples are given in Fig. 7. The average particle sizes of the samples prepared at 600, 700, 800 and 900°C are 10.95, 8.85, 7.51 and 14.41 μm, respectively, and the distribution of the particle size becomes narrow as the temperature increases up to 800°C. This decrease of particle size is due to the breaking of agglomerated powder with crystal growth as the calcination temperature increases. For a sample prepared at 900°C, crystallite growth is more prominent than the breaking of agglomerated powder. This results in an abrupt increase in particle size.
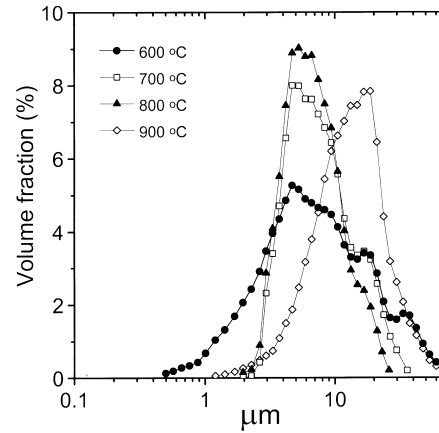

Fig. 7. Histogram of particle-size distribution in samples obtained at various temperatures for 24 h for the $F=7$ system.

Charge–discharge curves at a constant current density of 0.3 mA cm^{-2} for powders prepared at 600, 700, 800 and 900°C for the $F=7$ system are presented in Fig. 8. The evolution of the specific capacity as a function of cycle number is given in Fig. 9. A cell composed of the powder prepared at 600°C shows two discharge plateau at 3.9 and
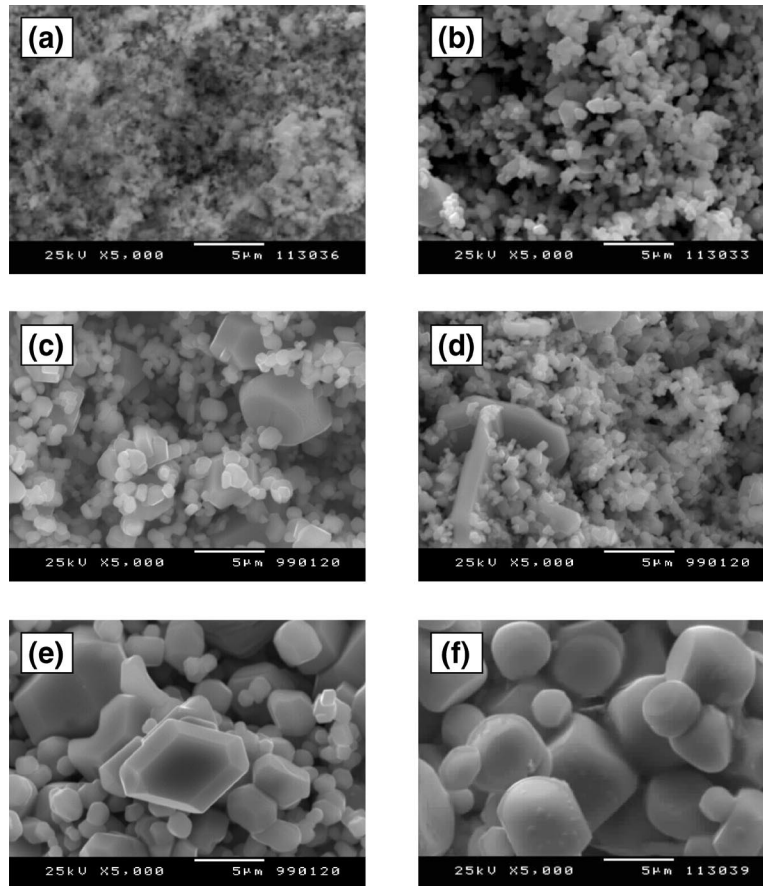

Fig. 6. Scanning electron microphotographs of powders prepared at: (a) 600°C for 24 h; (b) 700°C for 24 h; (c) 800°C for 1 h; (d) 800°C for 12 h; (e) 800°C for 24 h and (f) 900°C for 24 h.
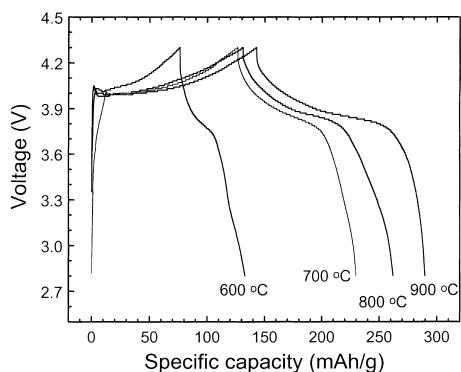
Fig. 8. Voltage profiles of first charge–discharge cycle of powders prepared at different temperatures for 24 h.
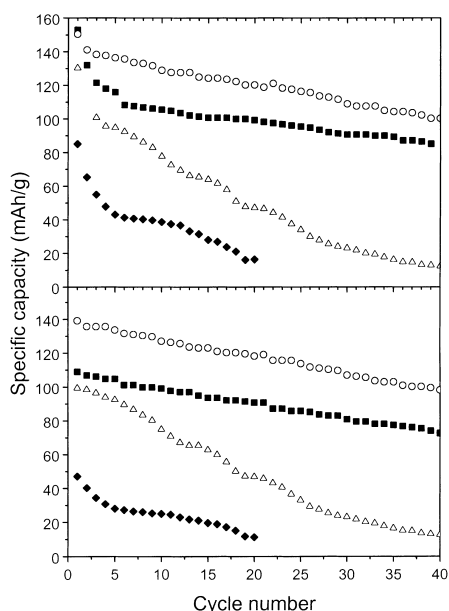

Fig. 9. Evolution of charge and discharge capacities with number of cycles of powders prepared at different temperatures for 24 h. (◆): 600°C, (△): 700°C, (■): 800°C and (○): 900°C.

3.3 V due to the mixed phase of HT-LiCoO$_2$ and LT-LiCoO$_2$, respectively, as confirmed by the XRD results. A cell composed of the powder prepared at 700°C displays a pronounced and continuous decrease in capacity with cycling from, at best, 100 to 15 mA h g^{-1} after 40 cycles. By contrast, cells composed of powders prepared at 800 and 900°C show good capacity retention and deliver, on average, approximately 100 and 120 mA h g^{-1} after 40 cycles.

4. Discussion

Spinel lithium cobalt oxides of the type Li$_x$Co$_{3-x}$O$_4$ are obtained by the solid-state reaction of lithium and cobalt salts in an oxygen atmosphere, where the cubic unit cell parameters vary from 8.080 (x=0) to 8.089 Å (x=0.4) [17].

By comparing the unit cell parameters with those of Li$_x$Co$_{3-x}$O$_4$, it can be demonstrated that the spinel phases in the F=1 and 3 systems are non-lithiated Co$_3$O$_4$. If the lithium cobalt oxides prepared at lower temperatures adopted an ideal layered structure with a c:a ratio of 4.90, it should be a non-lithiated LT-LiCoO$_2$ from the structural point of view. The data in Table 1 show, however, that the c:a ratio of 4.99 differs significantly from the value of 4.90 despite small variations in a and c values. This indicates that lithium cobalt oxides prepared in the F=1 and 3 systems are HT-LiCoO$_2$, even though the single-phase lithium cobalt oxide is not obtained. Meanwhile, lithium cobalt oxides prepared at lower temperatures in the F=7 system show a different XRD pattern compared with those obtained in the F=1 system. For powders prepared at 550 and 600°C, a mixed phase of LT-LiCoO$_2$ and HT-LiCoO$_2$ is observed instead of Co$_3$O$_4$ and HT-LiCoO$_2$ (Table 3). In contrast to the idealised structure of HT-LiCoO$_2$ in which the octahedral sites 3a and 3b are solely occupied by lithium and cobalt ions, respectively, the best fit for LT-LiCoO$_2$ yielded a spinel structure in which the 16c and 16d octahedral sites are occupied by both lithium and cobalt ions. Although the cation distribution in LT-LiCoO$_2$ is intermediate between the layered and spinel type structures, it can be concluded from electrochemical behaviour that LT-LiCoO$_2$ adopts the spinel phase [18]. Fitting was performed on the composition (Li$_{0.95}$Co$_{0.05}$)$_2$-[Co$_{0.95}$Li$_{0.05}$]$_2$O$_4$ [2]. Rietveld refinement for the powder prepared at 600°C shows the existence of 26 wt.% LT-LiCoO$_2$ and 74 wt.% HT-LiCoO$_2$. Single-phase HT-LiCoO$_2$ can be obtained above 700°C. HT-LiCoO$_2$ is distinguished by high intensity of the (0 0 3) line and clear splitting between the (0 0 6)/(0 1 2) and (0 1 8)/(1 1 0) lines. In Fig. 3, all these features are clearly evident in samples fired at 700°C and above.

According to the phase analysis of lithium cobalt oxides from the XRD data, there exist different reaction mechanisms between the solid-state reaction and molten-salt synthesis in the course of crystallisation of HT-LiCoO$_2$. In the solid-state reaction method, layered rock salt HT-LiCoO$_2$ is generally obtained through the reaction between lithium precursors and Co$_3$O$_4$ without the formation of lithium doped Co$_3$O$_4$, irrespective of the starting materials [15]. As mentioned above, Co$_3$O$_4$ obtained in the F=1 system is a non-lithiated Co$_3$O$_4$. Therefore, it can be demonstrated that HT-LiCoO$_2$ is formed through the restructuring of the starting materials and Co$_3$O$_4$ in the solid-state reaction, even though pure HT-LiCoO$_2$ is not formed in the F=1 system. With the F=7 system, however, LT-LiCoO$_2$ instead of Co$_3$O$_4$ is first formed near the melting point (506°C) of lithium salt mixture. Ordering of lithium and cobalt then results in HT-LiCoO$_2$ as the temperature increases.

A cell composed of the powder prepared at 600°C lost its capacity quickly and only delivered a capacity of 10 mA h g^{-1} after 20 cycles. This can be attributed to the significant reactivity of the oxidised LT-Li$_x$CoO$_2$ electrode, which results in the formation of passive layers, and a slow

transport of lithium into the oxides to repeat the extraction and insertion of lithium [19]. Cells composed of powders prepared at 800°C show good capacity retention after 40 cycles. This is the characteristic of HT-LiCoO$_2$. It seems that the highest capacity and best cycle life of the powder fired at 900°C is due to the larger particle size, as shown in Fig. 6.

5. Conclusion

HT-LiCoO$_2$ powders are simply prepared by molten-salt synthesis using a eutectic mixture of 0.6Li$_2$CO$_3$–0.4LiCl molten salt at temperature which ranges from 700 to 900°C. This finding strongly suggests that the synthesis requires a lower calcination temperature and shorter time to prepare an electrochemically active HT-LiCoO$_2$. This method may be useful for the preparation of other intercalation oxides. XRD observations show that different synthetic mechanisms exist for HT-LiCoO$_2$ according to the flux ratio F. For the F=7 system, LT-LiCoO$_2$ is first formed at temperatures 550–600°C, while Co$_3$O$_4$ is formed in the F=1 system.

Acknowledgements

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