JOURNAL OF Materials CHEMISTRY

Microwave-assisted solid-state synthesis of $LiCoO_2$ and its electrochemical properties as a cathode material for lithium batteries

V. Subramanian, C. L. Chen, H. S. Chou and G. T. K. Fey*

Department of Chemical Engineering, National Central University, Chung-Li, Taiwan 32054, ROC. E-mail: gfey@cc.ncu.edu.tw

Received 6th June 2001, Accepted 11th September 2001
First published as an Advance Article on the web 17th October 2001

Polycrystalline homogeneous lithium cobalt oxide powder was synthesized by a solid-state method using microwaves. The synthesis was carried out in a domestic microwave oven. $LiCoO_2$ was synthesized with a microwave irradiation time of 20 min. This process remarkably reduced synthesis time and $LiCoO_2$ was produced relatively quickly for the first time. The synthesized material showed reasonable electrochemical characteristics.

Introduction

$LiCoO_2$ is one of the best cathode materials being widely used in commercial lithium-ion batteries because of its high specific capacity and excellent cycle life.[1,2] Synthesis of $LiCoO_2$ is generally carried out *via* a conventional ceramic route that involves high temperatures and long times. Many solution-assisted methods such as sol–gel, hydrothermal, emulsion drying, *etc.*, have been reported.[3–5] Recently, synthesis of $LiCoO_2$ from a molten salt was reported.[6] Although solution-assisted methods offer a greater degree of homogeneity over a relatively shorter period of time, the processing requires careful manipulation. Also, the use of various organic acids as chelating or precipitating agents may increase the cost of production if quantities need to be scaled-up for commercial production. Furthermore, special heating arrangements would also have to be made in order to accommodate the exothermic reaction during the burning of the organic acids.

Microwave-assisted synthesis of materials has become more important in recent years. Various inorganic materials have been synthesized using microwave energy for different applications.[7–10] Rao *et al.* have reviewed this subject in detail.[11] $LiCoO_2$ was synthesized using microwaves with starting materials that were dissolved in water and precalcined at 400 °C. The calcination process was carried out using micro wave energy for 10 min.[12] Although the calcination time was very short, the total time involved in the precalcination processes of the above study was more than 50 h.[12] The X-ray diffractograms indicated that $LiCoO_2$ formed at 400 °C and only the crystallinity increased when microwave sintering was used.[12] Microwave-assisted synthesis of $LiMn_2O_4$ with good electrochemical properties has been reported.[13–15] Recently, the fundamentals of the microwave heating process were reported.[16]

Here, we report the one-step microwave-assisted solid-state synthesis of $LiCoO_2$ for the first time. The effect of varying microwave irradiation time on the structural and electrochemical properties of $LiCoO_2$ is discussed.

Experimental

Synthesis procedure

The synthesis of $LiCoO_2$ was carried out using Li_2CO_3 and Co_3O_4 as starting materials in a stoichiometric ratio of 1 : 1. The synthesis was carried out in a domestic microwave oven with a maximum power output of 900 W and a magnetron frequency of 2.45 GHz. The advantage of Co_3O_4 being a microwave susceptor was exploited to synthesize the oxide material within a shorter time. The stoichiometric amounts of Li_2CO_3 and Co_3O_4 were well mixed in a pestle and mortar and pelletized. The pellets were put in a clean quartz crucible and placed on a mullite refractory slab. The rotating glass turntable of the domestic microwave oven was removed and the mullite refractory slab was placed on glass wool. Everything was arranged carefully to enable rotation of the mullite slab. The pellets were exposed for different irradiation times ranging from 5 to 25 min. The reaction started after 30 s and the glow typically observed during the reaction is shown in Fig. 1. The experiment was performed based on the microwave exposure time because it is very difficult to measure the actual temperature during irradiation. Use of thermocouples without proper shielding may lead to serious problems and an IR-pyrometer may not measure the actual temperature.

Phase analysis and SEM studies

The structural properties of the materials synthesized with different microwave irradiation times were evaluated using X-ray diffraction studies (Siemens D-5000, Mac Science MXP 18). The diffraction patterns were recorded using nickel-filtered Cu-Kα radiation at room temperature between scattering angles of 5 to 80° in increments of 0.05°. The surface morphology of the particles of $LiCoO_2$ synthesized with different

Fig. 1 Glow typically observed inside the microwave oven during the reaction between Li_2CO_3 and Co_3O_4.

DOI: 10.1039/b105008g

microwave irradiation times were studied using scanning electron microscopy (SEM; Hitachi S-4700I).

Surface area and particle size analysis

The BET surface area measurement was performed by the N_2 adsorption–desorption method (Micromeritics ASAP 2010). The particle size analysis was performed using a laser scattering particle size distribution analyzer (Microtrac X100).

Electrochemical studies

Electrochemical properties of the materials prepared using microwaves were studied by assembling 2032 coin cells with lithium metal as an anode and 1 M $LiPF_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1 : 1 by volume) as an electrolyte. All the manipulations were made in an argon-filled glove box (VAC, MO 40-1) with oxygen and moisture content less than 2 ppm. The cathode for the coin cells was prepared by mixing 85 wt% active material with 10 wt% of conducting carbon black additive and 5 wt% polyvinylidene fluoride (PVdF) binder in *N*-methyl-2–pyrrolidone (NMP). The intensively mixed slurry was blade-coated onto aluminium foil and dried overnight at 120 °C in an oven. The circular electrodes were punched after roller-pressing the dried foil. The cells were cycled between 3.0 and 4.2 V in a multi-channel battery tester (Maccor series 4000).

A slow scan-rate cyclic voltammetry (SSCV) experiment was performed in a three-electrode glass cell placed inside a glove box. The cathode materials were prepared as described above and coated on both sides of an aluminium foil. The cells were assembled inside an argon-filled glove box with lithium metal foil as counter and reference electrodes. The cyclic voltammetry experiment was performed using a Solartron 1287 electrochemical interface at a scan rate of 25 $\mu V\ s^{-1}$ between 3.0 and 4.2 V. The same set-up was used to record the a.c. impedance spectra at different depths of charge and discharge. The impedance spectra were recorded using a Solartron 1250/1287 apparatus between a frequency of 65 kHz and 0.001 Hz. The impedance spectra were analyzed using Z-view software from Scribner Associates. The cells were galvanostatically charged and discharged to record the impedance spectra at various depths of intercalation and deintercalation.

Results and discussion

X-Ray diffraction studies

The X-ray diffractograms recorded for the materials synthesized with different microwave irradiation times are shown in Fig. 2. The materials heated for 5, 10 and 15 min show peaks corresponding to unreacted Li_2CO_3 and Co_3O_4 phases, indicating that the irradiation time was not sufficient to form a complete $LiCoO_2$ phase. The X-ray diffractograms for the materials heated for 18, 20, 22 and 25 min show all peaks indexable in the layered hexagonal lattice corresponding to a $LiCoO_2$ structure. However, there was evidence of a small amount of CoO in the XRD near the $2\theta = 42.9°$ peak for the materials heated for 18, 22 and 25 min.[6] The intensity of this peak was at a minimum for the material heated for 20 min. The reason for the presence of CoO was a slight decomposition of Co_3O_4 because of the heat absorbed in the microwave field. Similar observations were reported for the microwave-assisted synthesis of $La_{1-x}Sr_xCoO_3$.[16] All the X-ray diffractograms for the materials prepared with irradiation times of 15, 18, 20, 22 and 25 min show a clear splitting of the hexagonal characteristic peaks (006)/(102) and (108)/(110), which indicates that the formed compounds have layered characteristics.

It is clear from the X-ray diffraction studies that the materials are highly crystalline as evidenced by the I_{003}/I_{104} ratio. Also, the lattice parameters calculated for the $R\bar{3}m$ space group, assuming a hexagonal setting, show excellent agreement with those reported in the literature ($a = 2.8149$, $c = 14.0536$ Å).[17] The lattice parameters calculated for the materials prepared with different microwave irradiation times compared to those for a commercial sample and reported values are given in Table 1. The *c*/*a* ratio calculated indicates that the system was predominantly in the HT-$LiCoO_2$ phase, although the compounds were prepared within a short time. However, it is very difficult to identify the presence of minimal quantities of the spinel LT-$LiCoO_2$ phase co-existing with the HT-$LiCoO_2$ phase using X-ray diffraction methods.[18]

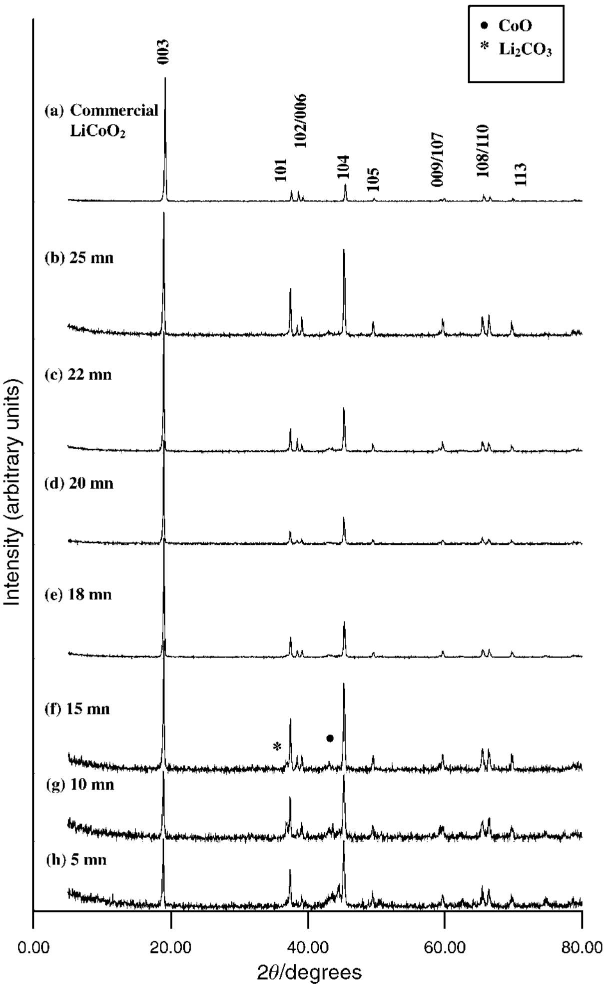

Fig. 2 X-Ray diffraction patterns of $LiCoO_2$ prepared with different microwave irradiation times: (a) commercial sample, (b) 25, (c) 22, (d) 20, (e) 18, (f) 15, (g) 10 and (h) 5 min.

Table 1 Lattice parameters of $LiCoO_2$ synthesized with different irradiation times

Irradiation time/min	d_{110}/Å	*a*/Å	d_{003}/Å	*c*/Å	*c*/*a*	I_{003}/I_{104}
15	1.4050	2.8100	4.6800	14.0400	4.99	1.47
18	1.4061	2.8122	4.6695	14.0080	4.98	3.26
20	1.4074	2.8148	4.6795	14.0386	4.99	4.19
22	1.4074	2.8148	4.6791	14.0373	4.99	2.73
25	1.4067	2.8134	4.6765	14.0295	4.99	1.39
JCPDS $LiCoO_2$	1.4067	2.8135	4.6670	14.0010	4.98	
Single crystal $LiCoO_2$[a]		2.8149		14.0536	4.99	
Commercial $LiCoO_2$	1.4072	2.8143	4.6764	14.0292	4.98	4.31

[a] Taken from ref. 17.

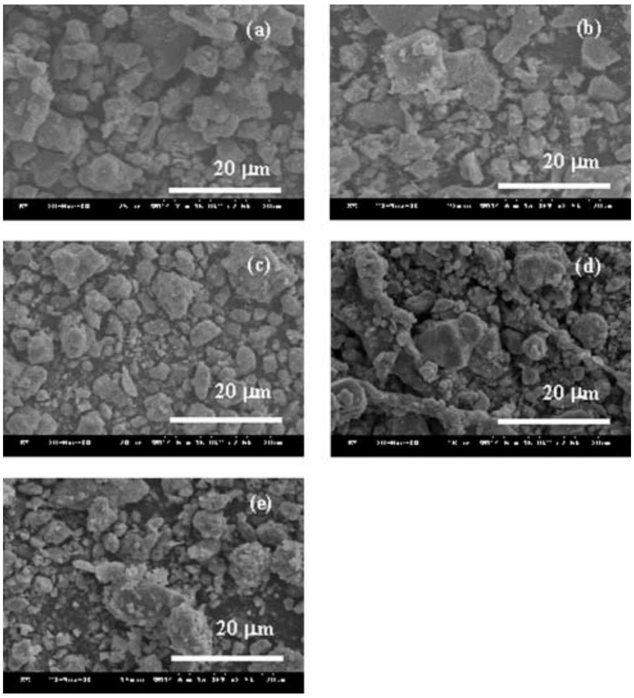

Fig. 3 SEM pictures of $LiCoO_2$ prepared with different microwave irradiation times: (a) 25, (b) 22, (c) 20, (d) 18 and (e) 15 min.

Surface morphology and surface area studies

The scanning electron micrographs of the materials synthesized with different microwave irradiation times are shown in Fig. 3. The microstructure, as evidenced by the SEM studies, shows no agglomeration of grains. The average grain size of the synthesized materials ranges from 4–8 μm. As the irradiation time was increased, there was an observed increase in grain size. However, the particle sizes, as determined by the particle size analysis of the compounds prepared with different irradiation times, were in the order of 20 μm, as summarized in Table 2. The BET surface area, pore volume and pore size of the synthesized compounds with different irradiation times are summarized in Table 2. It can be seen from the table that the surface area was greatest for the compound synthesized with an irradiation time of 20 min. The surface area of the electrode material always has a direct effect on the electrochemical performance of the system, as discussed below.

Electrochemical studies

Charge–discharge properties. The electrochemical cycling performance of $LiCoO_2$ synthesized with various irradiation times was examined over the range 3.0–4.2 V *vs.* Li/Li^+. The first discharge capacity of the material heated for 15 min was 105 mA h g^{-1} and the tenth was 100 mA h g^{-1}. When the irradiation time was increased to 18 min, there was an observed increase in the discharge capacities in both the first and tenth cycles to 111 and 104 mA h $^{-1}$g, respectively. An increase to 20 min showed a discharge capacity of 112 mA h g^{-1} for the first cycle and 103 mA h g^{-1} after 10 cycles. Typical charge–discharge curves for the material prepared with an irradiation time of 20 min are shown in Fig. 4. Further increasing the irradiation times to 22 and 25 min led to a decrease in capacity values, as summarized in Table 3.

Table 2 Average particle size, pore volume and BET surface area studies of $LiCoO_2$ synthesized using microwaves for selected irradiation times

Irradiation time/min	Av. particle size/μm	Pore size/ Å	Pore volume/ cm^3 g^{-1}	BET surface area/m^2 g^{-1}
15	19.75	143.79	0.003839	1.07
20	20.96	85.19	0.003388	1.59
25	21.00	88.09	0.002048	0.93

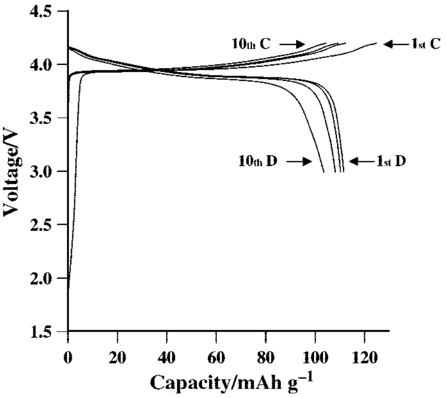

Fig. 4 Typical charge–discharge curves of $LiCoO_2$ synthesized using a microwave irradiation time of 20 min.

Table 3 Discharge capacity of $LiCoO_2$ synthesized with different microwave irradiation times

	Synthesis time/min				
	15	18	20	22	25
Cycle number	Discharge capacity/mA h g^{-1}				
1	105	111	112	100	96
2	104	110	110	99	95
3	104	110	110	98	94
4	103	109	109	97	92
5	103	109	108	96	91
6	102	108	107	95	90
7	101	107	106	93	89
8	101	106	105	92	87
9	100	105	105	90	86
10	100	104	103	89	84

Discharge capacity values were lower for the compounds prepared in this study compared to compounds reported in previous literature. $LiCoO_2$ usually exhibits discharge capacities ranging from 135 to 140 mA h g^{-1}, depending upon synthesis and cycling conditions. Although the present method requires a shorter synthesis time, it needs to be improved in order to achieve reasonable capacity values comparable to those already reported in other literature. Optimization of the synthesis procedure may yield a compound with better electrochemical properties. Similarly to our results, a new synthesis procedure, an emulsion process adopted for synthesizing $LiCoO_2$, produced a first discharge capacity of 96 mA h g^{-1} at a 0.33 C rate.[5]

The reason for the lower capacity may be the uneven heating of the sample during microwave irradiation. This is a problem that must be overcome if the capacity of the material is to be increased. The possibility that a coexisting LT-$LiCoO_2$ phase might also be responsible for the decrease in capacity was considered, but this was ruled out using cyclic voltammetry and a.c. impedance spectroscopy, as discussed below. The first discharge capacity initially increased with increasing irradiation time, but then decreased after a particular point. The main objective of increasing the irradiation time was to remove the small amount of the CoO phase that coexists with the $LiCoO_2$ phase. However, increasing the irradiation time resulted in an increase in CoO concentration, as evidenced by the greater intensity of the peak near $2\theta = 42.9°$ in the XRD

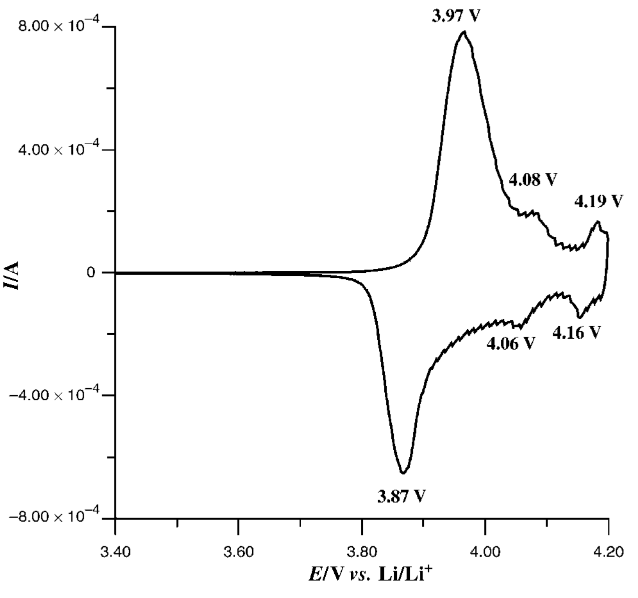

Fig. 5 Cyclic voltammogram of $LiCoO_2$ synthesized with 20 min of microwave irradiation at a scan rate of 25 μV s^{-1} between 3.00 and 4.20 V.

plot for the materials heated for 22 and 25 min. The reason that the intensity increased may be that more Co_3O_4 decomposed to CoO during heating in the microwave field.[16] Further efforts are in progress to synthesize the material without any additional phases and to optimize the synthesis procedure.

Cyclic voltammetry studies. Fig. 5 shows the cyclic voltammogram for the material synthesized using 20 min of microwave irradiation. The purpose of this study was to identify the possible reasons for the lower capacity values of materials synthesized using microwaves. There is a possibility that a second phase of LT-$LiCoO_2$ coexisting along with the HT-$LiCoO_2$ phase might have caused the reduction in capacity because of the lower capacity of the LT-$LiCoO_2$ phase. Cyclic voltammetry is an effective tool for identifying the coexisting electroactive phases from the oxidation and reduction potentials of the compound. It is very difficult to identify the HT and LT-$LiCoO_2$ phases using X-ray diffraction and XAS studies were employed to determine the structure of the HT and LT phases.[18]

Garcia *et al.*[19] have studied the LT and HT phases of $LiCoO_2$ synthesized at a range of temperatures from 400 to 800 °C using slow-scan cyclic voltammetry in order to identify the phase purity of the compounds formed. According to their study, the compound synthesized at 400 °C had broader oxidation and reduction peaks at 3.75 and 3.47 V, respectively.[19] For the materials synthesized at 800 °C, the above peaks were observed at 3.98 and 3.93 V; the separation of only 0.05 V indicates the high reversibility of the material.[19] On the other hand, for the material synthesized at 600 °C, two anodic peaks at 3.73 and 3.92 V were observed, with corresponding cathodic peaks at 3.90 and 3.49 V, respectively.[19] Cyclic voltammetry of the compound synthesized with 20 min of microwave irradiation showed only one anodic and one cathodic peak, observed at 3.97 and 3.87 V, respectively, with a difference of only 100 mV between them, which indicates the system is highly reversible. However, there are two reversible peaks at high voltage, *viz.* 4.08 and 4.06 V and the other at 4.19

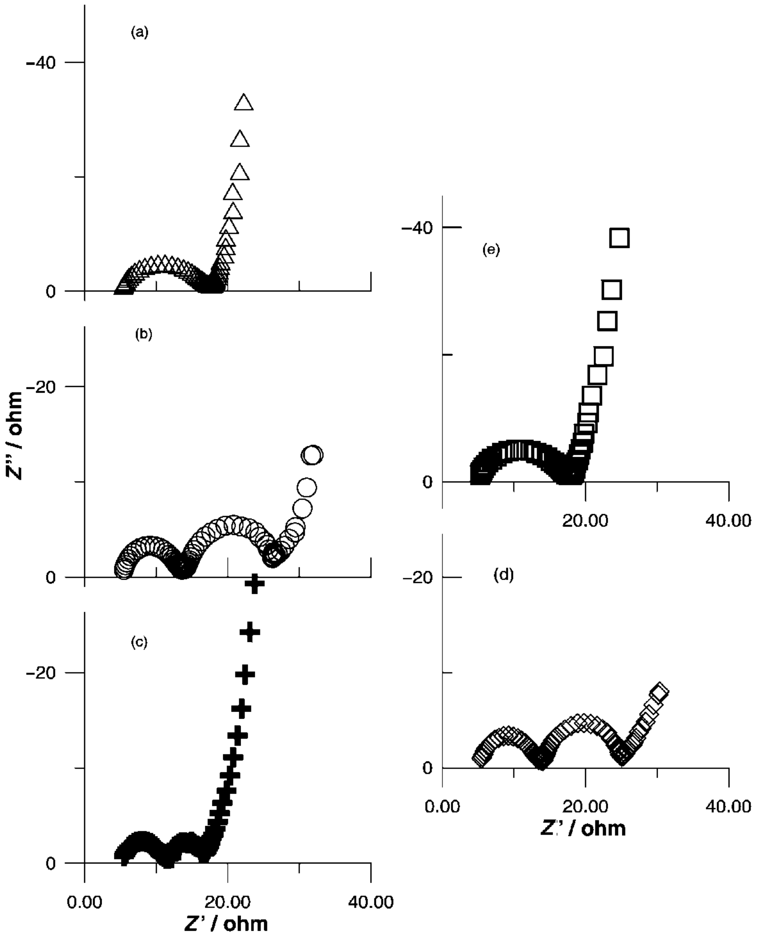

Fig. 6 Nyquist plots of $LiCoO_2$ synthesized with 20 min of microwave irradiation time at different depths of charge and discharge: (a) as-assembled cell, (b) charged to 3.90 V, (c) charged to 4.25 V, (d) discharged to 3.90 V, (e) fully discharged to 3.40 V.

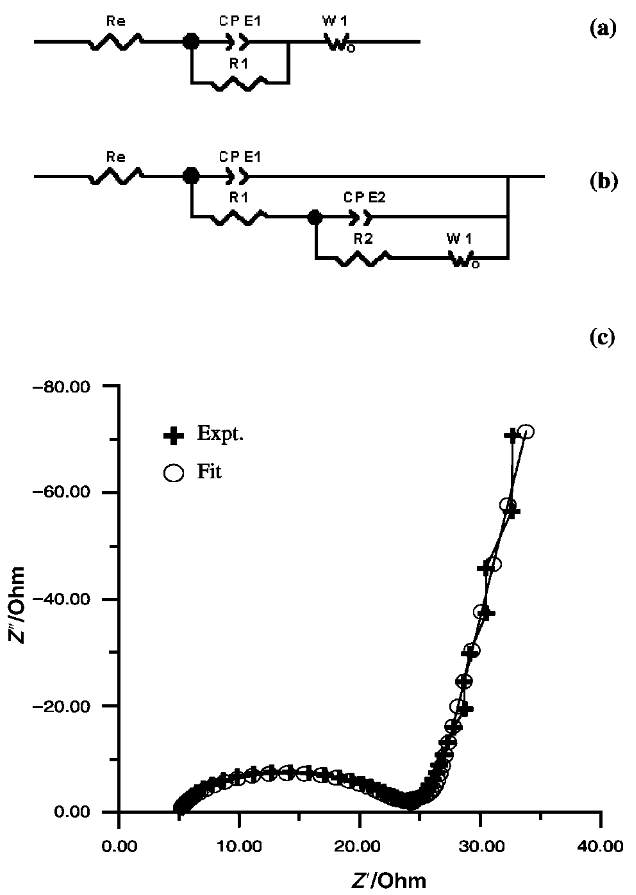

Fig. 7 Equivalent circuit models used to explain the impedance behavior at different intercalation and deintercalation levels of the microwave-synthesized $LiCoO_2$:[23] (a) Model 1; (b) Model 2. (c) Typical experimental and FIT plot for the impedance spectra of an as-assembled cell.

and 4.16 V. These peaks are mainly due to phase transitions occurring during the topotactic reactions because of the order-to-disorder transition of lithium ions in the CoO_2 framework.[20] Hence, this confirms that the formed compound has a complete HT-$LiCoO_2$ phase. The coexistence of an LT phase must have led to a situation similar to that for the compound synthesized at 600 °C, as discussed above. Hence, the reason for the decrease in capacity is not the presence of any LT-$LiCoO_2$ phase mixed in with the HT-$LiCoO_2$ phase. From this study, it can be concluded that the reason for the lower capacity values may be the trace amount of CoO phase coexisting with the HT-$LiCoO_2$, as evidenced by XRD.

Electrochemical impedance spectroscopic studies. The family of Nyquist plots recorded for the porous $LiCoO_2$ synthesized using 20 min of microwave irradiation at various charging and discharging voltages is shown in Fig. 6. For the assembled cell, the impedance spectra mainly show a high frequency semicircle and a low frequency spike, which indicate surface film formation over the oxide surface and the diffusion of lithium ions in the solid matrix, respectively. When lithium ions are removed (charging), a second semicircle is observed in the intermediate frequency range, as shown in Fig. 6(b). Also, with respect to the increase in charging voltage, as more lithium ions are deintercalated, the diameter of the second semicircle decreases. The appearance of the second semicircle is due to charge transfer phenomena at the oxide electrode–electrolyte interface. There is also a Warburg part, observed in all the impedance spectra, which is mainly due to the diffusion of lithium ions in the oxide electrode. The decrease in the charge transfer resistance with respect to the increased deintercalation of lithium ions is because of an insulator-to-metal transition.[21] Similar observations have been reported by many others studying $LiCoO_2$.[22,23]

The impedance study shows that the material synthesized with an irradiation time of 20 min in a domestic microwave oven is HT-$LiCoO_2$. Electrochemical impedance spectroscopy (EIS) was used as a tool to identify the phase formation of $LiCoO_2$ synthesized at two different temperatures, 400 and 800 °C. The impedance spectra recorded at different depths of charge and discharge for the material synthesized at 800 °C were similar to the behavior discussed above.[24] On the other hand, for the material synthesized at 400 °C, the intermediate frequency (second) semicircle was not observed.[24] According to the authors, its absence was due to the interaction between the constant phase angle of diffusion impedance and the charge transfer impedance.[24] The impedance results complement the results of cyclic voltammetry, corroborating that the compound synthesized with a microwave irradiation time of 20 min is indeed HT-$LiCoO_2$ and not a mixture of LT- and HT-$LiCoO_2$ phases.

The impedance plots were fitted using the equivalent circuit model proposed by Choi and Pyun,[23] as shown in Fig. 7(a) and (b). Model 1 describes a simple combination of solution resistance in series with the constant phase element associated with the interfacial resistance and Warburg impedance (Z_w).[23] The equivalent circuit shown in Model 2 describes two constant phase elements and a Warburg impedance (Z_w) associated with the charge transfer process and passivating film formation. The Warburg parts in both models are associated with the diffusion of lithium ions in the solid oxide matrix.[25,26] The impedance parameters are summarized in Table 4. A typical plot using the above model is shown in Fig. 7(c).

The diffusion coefficient was calculated using the formula:[26]

$$D_{Li}=(\pi f_T r^2)/1.94$$

where r is the radius of the oxide particles and f_T is the frequency at which the impedance spectrum shows a transition

Table 4 Various impedance parameters evaluated using the equivalent circuit model for $LiCoO_2$ synthesized using 20 min of microwave irradiation

Voltage	$R_e{}^a/\Omega$	$R_p{}^a/\Omega$	$R_{ct}{}^a/\Omega$	CPE-1 T^b/ 10^{-5} F	CPE-1 P^b/F	CPE-2 T^b/F	CPE-2 P^b/F	Z_w Warburg impedance/Ω W1-R^c	W1-T^c	W1-P^c
As-assembled (OCV 3.4 V)[d]	4.93	17.24	—	1.12	0.87	—	—	11.63	0.07	0.47
3.93 V (Charging)[e]	5.11	8.59	12.65	1.86	0.83	0.012	0.91	120.30	1850.00	0.73
4.2 V (Charging)[e]	5.20	5.81	4.25	1.57	0.86	0.013	0.78	8.63	28.42	0.43
3.9 V (Discharging)[e]	5.04	8.62	11.64	1.50	0.85	0.014	0.84	28.40	916.50	0.66
After full discharge (OCV 3.4 V)[d]	4.84	12.69	—	1.28	0.86	—	—	2163.00	52.75	0.85

[a] R_e is the electrolyte resistance; R_p is the oxide particle–particle resistance; R_{ct} is the charge transfer resistance. [b] Capacitances for CPE = constant phase element; T and P are the constant phase element parameters of the equation $Z=1/[T(I^*\omega)^P]$, used to fit the depressed semi-circle of the Nyquist plot, where * represents the complex conjugate, $I=\sqrt{-1}$, and ω is the angular frequency of the a.c. signal. [c] P, R and T are the Warburg (W) parameters of the equation $Z=R^*$ ctnh $([I^*T^*\omega]^P)/(I^*T^*\omega)^P$, used to fit the low frequency straight line of the Nyquist plot (*, I and ω as before). [d] Calculated using Model 1 [Fig. 7(a)]. [e] Calculated using Model 2 [Fig. 7(b)].

from semi-infinite diffusion behavior to a finite-length behavior. The diffusion coefficients calculated at different charging and discharging voltages were between 10^{-9}–10^{-11} cm^2 s^{-1}. Similar results from EIS studies have been reported for commercial grade $LiCoO_2$.[22]

Conclusions

In conclusion, microwave-assisted solid-state synthesis of $LiCoO_2$ has been carried out successfully in a domestic microwave oven and was found to be a very effective method. $LiCoO_2$ was synthesized within the short time of 15–20 min.

The X-ray diffraction studies showed the formation of a hexagonal layered $LiCoO_2$ system with lattice parameters that agree with those previously reported. Trace amounts of the CoO phase were identified as coexisting with $LiCoO_2$ and found to be at a minimum for the material synthesized with an irradiation time of 20 min. The discharge capacity of the compound heated for 20 min was 112 mA h g^{-1} for the first cycle and 103 mA h g^{-1} after 10 cycles. The reason for the lower capacity may be the CoO phase coexisting with the HT-$LiCoO_2$ phase, formed due to the slight decomposition of Co_3O_4 in the microwave field.

To further clarify the phase formation of $LiCoO_2$, slow scan cyclic voltammetry and electrochemical impedance spectroscopic studies were performed. The anodic and cathodic peaks in the cyclic voltammogram indicate that the phase formed after 20 min microwave irradiation is HT-$LiCoO_2$. Impedance studies complemented the above cyclic voltammetry studies.

Commercial production of $LiCoO_2$ by the microwave synthesis method would reduce the time required for synthesizing the material and be more economical.

Acknowledgements

Financial support by the National Science Council of the Republic of China is gratefully acknowledged (NSC-90-2214-E-008-003). V. S. thanks the National Science Council for the award of a post-doctoral position.

References

1 K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, *Mater. Res. Bull.*, 1980, **15**, 783.
2 T. Nagaura and K. Tazawa, *Prog. Batteries Sol. Cells*, 1990, **9**, 20.
3 G. T. K. Fey, K. S. Chen, B. J. Hwang and Y. L. Lin, *J. Power Sources*, 1997, **68**, 519.
4 M. Tabuchi, K. Ado, H. Kobayashi, H. Sakaebe, H. Kageyama, C. Masquelier, M. Yonemura, A. Hirano and R. Kanno, *J. Mater. Chem.*, 1999, **9**, 199.
5 C.-H. Lu and P.-Y. Yeh, *J. Mater. Chem.*, 2000, **10**, 599.
6 C.-H. Han, Y.-S. Hong, C. M. Park and K. Kim, *J. Power Sources*, 2001, **92**, 95.
7 B. Vaidyanathan, M. Ganguli and K. J. Rao, *Mater. Res. Bull.*, 1995, **30**, 1173.
8 D. R. Baghurst and D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1988, 829.
9 D. R. Baghurst, A. M. Chippindale and D. M. P. Mingos, *Nature (London)*, 1988, **332**, 311.
10 H. Zhang, S. Ouyang, H. Liu and Y. Li, *Mater. Res. Soc. Symp. Proc.*, 1996, **430**, 447.
11 K. J. Rao, B. Vaidyanathan, M. Ganguli and P. A. Ramakrishnan, *Chem. Mater.*, 1999, **11**, 882.
12 H. Yan, X. Huang, Z. Lu, H. Huang, R. Xue and L. Chen, *J. Power Sources*, 1997, **68**, 530.
13 H. Yan, X. Huang and L. Chen, *J. Power Sources*, 1999, **81–82**, 647.
14 M. Y. Saidi, *U.S. Pat.*, 5,770,018, 1998.
15 P. S. Whitfield and I. J. Davidson, *J. Electrochem. Soc.*, 2000, **147**, 4476.
16 Y. F. Liu, X. Q. Liu and G. Y. Meng, *Mater. Lett.*, 2001, **48**, 176.
17 J. Akimoto, Y. Gotoh and Y. Ososawa, *J. Solid State Chem.*, 1998, **141**, 298.
18 S. G. Kang, S. Y. Kang, K. S. Ryu and S. H. Chang, *Solid State Ionics*, 1999, **120**, 155.
19 B. Garcia, J. Farcy, J. P. Pereira-Ramos, J. Perichon and N. Baffier, *J. Power Sources*, 1995, **54**, 373.
20 K. Dokko, M. Mohamedi, Y. Fujita, T. Itoh, M. Nishizawa, M. Umeda and I. Uchida, *J. Electrochem. Soc.*, 2001, **148**, A422.
21 F. Corse, F. Nobili, A. Deptula, W. Lada, R. Tossici, A. D. Epifanio, B. Scrosati and R. Marassi, *Electrochem. Commun.*, 1999, **1**, 605.
22 M. D. Levi, G. Salitra, B. Markovsky, H. Teller, D. Aurbach, U. Heider and L. Haider, *J. Electrochem. Soc.*, 1999, **146**, 1279.
23 Y. M. Choi and S. I. Pyun, *Solid State Ionics*, 1997, **99**, 173.
24 C. Y. Yao, T. H. Kao, C. H. Cheng, J. M. Chen and W. M. Hurng, *J. Power Sources*, 1995, **54**, 491.
25 O. Yamada, M. Ishikawa and M. Morita, *Electrochim. Acta*, 1999, **44**, 1607.
26 B. E. Conway, *J. Electrochem. Soc.*, 1991, **138**, 1539.