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Electrochemical properties of the $LiCoO_2$ powder obtained by sol–gel method

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Abstract

Lithiated layered transitional metal oxide materials of the $LiMO_2$ type and especially $LiCoO_2$ presents interesting specific properties as high energy density, long life cycle, and constant discharging properties in a wide range of working conditions as well as a good safety. These properties made these materials excellent candidates as active compounds for high capacity cathode materials for rechargeable lithium batteries.

In the present work, $LiCoO_2$ powder was prepared by sol–gel method using inorganic precursors, $LiNO_3$ and $Co(NO_3)_2 \cdot 6H_2O$, and citric acid as chelating agent.

The prepared powders were studied by DTA/TG analysis. Based on the DTA/TG results, several thermal treatments between 300 and 700 °C were performed. IR spectroscopy, X-ray diffraction determinations were performed along with electrochemical measurements.

The correlation between the structure of the obtained powders, determined by the applied thermal treatment, and the electrochemical behavior was established.

Keywords: Sol–gel processes; X-ray methods; Electrical properties; Batteries

1. Introduction

Lithium-based layered transition metal oxides like $LiMO_2$ (where M is a 3d transition metal such as Ni, Co, Mn, Al, V) have attracted a worldwide great interest in the last period of time. Their specific properties such as high energy density, long cycle life, good safety, constant discharging properties and wide range of working temperatures made them excellent candidates as active compounds for high capacity cathode materials for rechargeable lithium batteries.

The usual structure of these materials is similar with sodium chloride lattice with the cations filling the octahedral interstices and oxygen atoms situated in close packed sites. In most of the cases in $LiMO_2$ oxides, the cations are arranged in an ordered structure that presents tunnels that permit the deintercalation and reintercalation of the lithium ions during the recharge process, promoting it by this.[1–4]

Among other compounds mentioned above, $LiCoO_2$ is the most used material for the commercial lithium batteries due to its excellent electrochemical stability after a long period of cycling. The excellent stability comes from the material structural stability, where the layered cation ordering is extremely well preserved even after a repeated process of insertion and removal of Li^+ ions.

Even though the technology is rather expensive and the material is highly toxic, lithium cobaltite is still the mostly used cathode material in lithium-based batteries.

New approaches for the preparation of $LiCoO_2$ with improved properties have been developed in the last period of time. The sol–gel method is a very widely spread technique for both powders and films preparation due to some well known advantages: an easy way to obtain homogenous distribution of precursors, the possibility to introduce controlled amounts of dopants, chemical methods of reaction control, viscosity advanced control as well as low processing temperatures.[5]

Several sol–gel routes were approached in order to prepare $LiCoO_2$. The sol–gel method starting with alkoxides was used by Fey et al.,[6] Quinlan et al.,[7] Szatvanyi et al.[8] The carboxylic route was experienced by Yazami et al.,[9] Yoon and Kim,[10] Shlyakhtin

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et al.[11] and Cho et al.[12] Some combined inorganic-carboxylic route were also taken into consideration by Zhecheva et al.,[13] Kang et al.,[14] Kushida and Kuriyama[15] and Uchihida et al.[16]

Using carboxylic route the bonding of the metallic ions in a chelating complex is assumed to lead to a highly homogeneous precursor gel and should diminish the particle size of the resulting oxides due to their formation in an organic matrix. In the same time during the thermal treatment the organic species evolved by matrix decomposition could be retained on the particle surface, hindering again the particle growth.[8]

In the present work we took into consideration an inorganic-carboxylic route starting with $Co(NO_3)_3 \cdot 6H_2O$, $LiNO_3$ and using citric acid as chelating agent for $LiCoO_2$ powder synthesis.

2. Experimental

2.1. Sample preparation

As starting compounds, the following materials were employed: $Co(NO_3)_3 \cdot 6H_2O$ and $LiNO_3$ as metal oxides sources, absolute alcohol p.a. reagent as solvent and citric acid as chelating agent. The precursors were introduced with the following molar ratio $Li:Co:C_6H_8O_7 \cdot H_2O = 1.1:1:2$. The solution pH was corrected to 5–5.5 by NH_3 addition. The solution was left for gelation in a dry oven at 80 °C and were subjected to differential thermal analysis and thermogravimetric analysis (DTA/TGA) in order to establish the thermal treatment schedule. Based on the obtained results, the gel was thermally treated with a heating rate of 1 °C/min up to desired temperature in the range 300–700 °C, where for 24-h plateau was maintained.

2.2. Structural characterization of the samples

The thermal behavior of $LiCoO_2$ powders was determined by differential thermal analysis and thermogravimetric analysis (DTA/TGA) using a MOM—Budapest (Hungary), OD—103 Derivatograph, up to 1000 °C.

The phase composition of the samples was determined by a X-ray analysis, using Philips APD 15 powder diffractometer with Cu Kα radiation, internal Si standard and computer data management.

The structural characterization of the gel was realized by IR spectroscopy, using a Specord M-80 spectrometer and KBr pellets.

2.3. Electrochemical characterization of the samples

The electrochemical characteristics were performed in a two type of traditional cells[17]:

- three-electrodes glass cell with lithium reference electrode in excess of electrolyte, and with a floating test electrode and
- in a three-electrode metal cell fully modeling coin cell CR2032 but with the advantage of reference electrode.

The electrolyte consisted of a solution of 1 M $LiPF_6$ (or $LiClO_4$) in a EC:PC:DMC (ethylene carbonate, propylene carbonate, dimethyl carbonate) in 1:1:2 ratio by volume mixture. The composite test electrode material was a mixture of the compounds studied with Teflonized Acetylene Black (TAB-2) at a 8:2 ratio by weight, pressed on 15 mm in diameter expanded nickel grid, covered on both sides. The weights of the test electrodes typically were 50 mg, without the nickel grid. The 0.2 C charge–discharge currents were applied in all of the electrochemical tests.

3. Results and discussions

In the experimental conditions presented above an amorphous violet gel was obtained.

3.1. DTG/TGA analysis

DTA/TG analysis of the obtained gel is presented in Fig. 1. The loss of weight starts at 70 °C with the alcohol and absorbed water evolution. At higher temperatures the complex Li–Co citrate gel formed in the experimental conditions mentioned above decomposes. The thermal effect at 260 °C is assigned to burning out organic residue resulted form the complex decomposition. The nitrate brought by the used precursors decomposes in the same temperature range. Some thermal effects at temperature higher than 500 °C can be attributed to the structural OH evolution and $LiCoO_2$ formation. The corresponding thermal effects and their assignment are summarized in Table 1.

3.2. IR analysis

The characteristic IR vibration bands corresponding to the starting precursors ($LiNO_3$, $Co(NO_3)_3 \cdot 6H_2O$ and citric acid) together with the vibration bands of the as-prepared gel are presented in Table 2.

The as-prepared gel presents a different IR spectrum, as compared to the reagents used for its preparation. The broad band

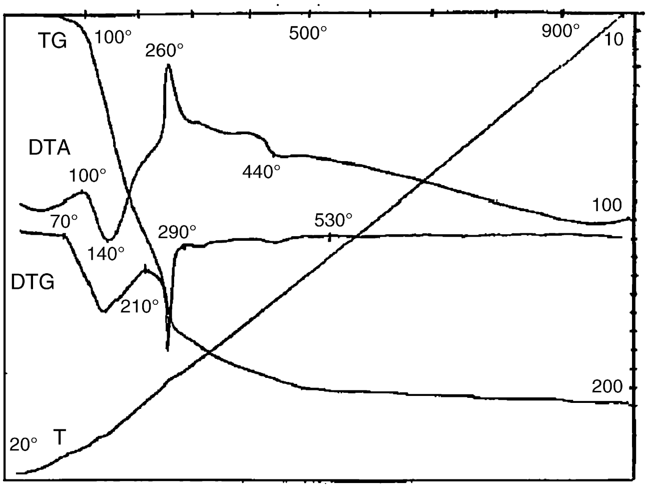

Fig. 1. DTG/TGA curves of $LiCoO_2$ starting precursor.

Table 1
DTA/TGA results of the $LiCoO_2$ precursor gel

Sample	Temperature range (°C)	Effects (°C)		Weight loss (%)	Assignment
		Endo	Exo		
$LiCoO_2$ from $LiNO_3$ and $Co(NO_3)_3 \cdot 6H_2O$ with $C_6H_8O_7 \cdot H_2O$	20–210	140	100	30.65	Adsorbed water and ROH evolution; Li–Co citrate complex decomposition
	210–290		260	6.88	Burning out organic residue and nitrates decomposition
	290–530	440	–	8.06	Structural OH evolution and
	530–1000	–	–	8.44	$LiCoO_2$ formation
Total loss				54.03	

Table 2
The IR frequencies for the starting precursors, of the $LiCoO_2$ precursor gel and thermally treated at 700 °C

ν (cm^{-1})					Assignment
$LiNO_3$	$Co(NO_3)_3 \cdot 6H_2O$	Citric acid	$LiCoO_2$ (gel)	$LiCoO_2$ (700 °C)	
500			480	440	LiO_4 tetrahedral
			500	490	
	530		520	530	CoO_6 octahedral
	620		590	590	
			620	710	
			700		
		880	800		ν –CH_2–
			1050		ν C–OH
		1180			ν –COOH
~1350	1330	1370	1370	~1410	ν –NO_3/adsorbed CO_2
~1650					Molecular water
2200–2400	2200–2400		2200–2400		CO_2 in gas phase
3000–3600	3000–3600	3200–3600	3000–3600		Structural OH groups

between 3500 and 3100 cm^{-1} corresponds to the structural OH groups vibration and the presence of this band in the IR spectrum is normally due to the wet chemical method of preparation used. In the same time the band at ~1620 cm^{-1} can be attributed to the bending mode of the molecular water. The band at ~2330 cm^{-1} can be assigned to the CO_2 in the gas phase physically adsorbed on the material surface. The bond at ~1380 cm^{-1} may correspond to the –NO_3 vibration and the presence of this band in the spectrum is due to the precursors employed. The small bands between 3000 and 1800 cm^{-1} and between 1300 and 800 cm^{-1} correspond to the –CH_2 and –CO groups introduced by the citric acid. These bands are shifted and have lower intensity as compared to the pure citric acid, due to its interaction with Co and Li ions. So, the formation of a complex Li–Co citrate can be supposed. The absorption bands at ~530 and 630 cm^{-1} represent the vibration of condensed octahedral CoO_6 while the vibrations at 480 and 500 cm^{-1} can be attributed to the tetrahedral LiO_4.[18]

The IR spectra of the $LiCoO_2$ as-prepared precursor gel and of the gel thermally treated at 700 °C are presented in Fig. 2.

In the spectrum of the material annealed at 700 °C, the vibration bands corresponding to the structural OH groups, molecular water and citric acid disappear and the vibration bands corresponding to CoO_6 octahedra, as well as, the band assigned to LiO_4 tetrahedral are better defined. The band at ~1410 cm^{-1} corresponds to the symmetric stretching vibration of the adsorbed CO_2.[18]

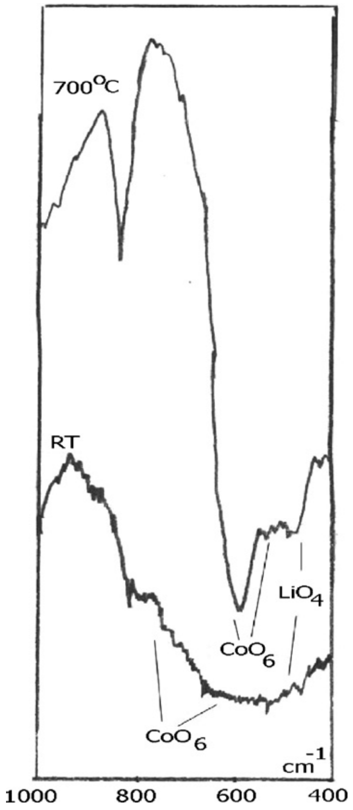

Fig. 2. The IR spectra of the $LiCoO_2$ as-prepared precursor gel and thermally treated at 700 °C.

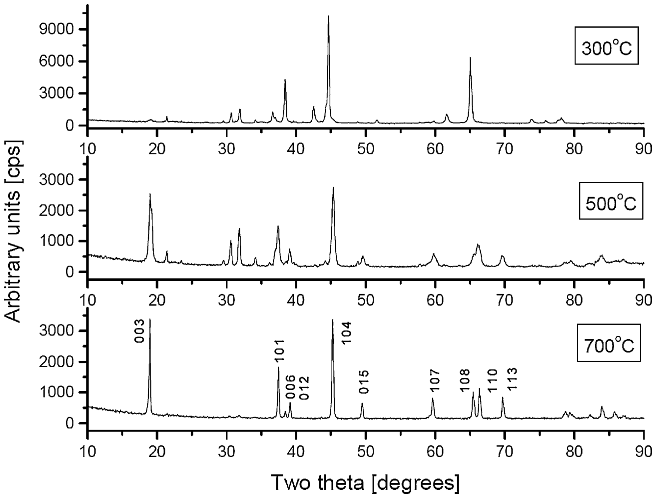

Fig. 3. The XRD patterns of $LiCoO_2$ thermally treated at 300, 500 and 700 °C.

3.3. XRD characterization

Based on the results of the DTG/TGA analysis that underlined that the main decomposition of the Li–Co citrate complex takes place under 300 °C and having in mind that by sol–gel process reactive nanodispersed powders are obtained, the subsequent thermal treatment was realized step-wise. Three temperatures of thermal treatment of the obtained gel were chosen: 300, 500 and 700 °C for 24 h. The XRD patterns of the thermally treated gels are shown in Fig. 3. From the picture it can be seen that the 300 °C thermal treatment did not lead to the formation of pure layered structure of the sample. Only one of the main peaks (at 104) assigned to $LiCoO_2$ appeared besides very low crystallized peaks attributed to the Li_2CO_3 formed by complex decomposition. At 500 °C the XR diagram shows that the process of $LiCoO_2$ crystallization is almost complete but some extra peaks are noticed that belong also to better crystallized Li_2CO_3. In this way a competition between reaction and crystallization of this compound could be noticed. The result indicates that the temperature of thermal treatment at 500 °C for 24 h was not sufficient for $LiCoO_2$ single phase formation. When thermal treatment of 24 h and 700 °C is applied the XRD patterns show that the sample becomes almost pure layered $LiCoO_2$ phase.

Starting from sol–gel process it was assumed to diminish the synthesis temperature of $LiCoO_2$ and to improve the crystallinity of the sample, because a higher crystallinity is very important for the good electrochemical behavior.[19] The impurities detected by the XRD even at the selected thermal treatment temperatures do not influence the electrochemistry of the sample but indicate that an additional annealing for 24 h at 800 °C is necessary to be checked.

3.4. SEM results

Previously obtained[20] SEM picture of the $LiCoO_2$ powder obtained in the experimental conditions presented above, thermally treated at 700 °C, is shown in Fig. 4. The sample consists of aggregates of about 200 nm formed of particles of much lower dimensions of nanometric size.

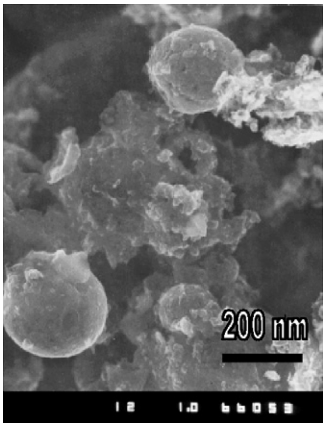

Fig. 4. Scanning electron micrograph of the obtained $LiCoO_2$ sample.

3.5. Electrochemical characterization

The electrochemical tests have been performed in a three-electrode glass cell with floating electrode or three-electrode metal cell. The advantages of both constructions are already discussed in the literature.[17,19] The electrochemical tests have been started with slow voltammetric measurements of $LiCoO_2$ prepared by the new method presented in Fig. 5. The first cycle shows delithiation peak at about 4.08 V and the lithiation peak is at about 3.86 V. The voltage values of the first delithiation and lithiation peaks are typical for this active material. It seems that the first delithiation peak is not a single peak. According to the literature[21] it consists of three different close to each other peaks. The fit analysis gave the peak values of 3.99, 4.07 and 4.15 V respectively. These values are similar to the ones reported by other authors.[21] The voltage values of the delithiation and lithiation peaks of the second cycle are 3.975 and 3.86 V, respectively. The voltage value of the second delithiation peak drops, comparing to that from the first cycle. This polarisation drop most probably is due to the re-ordering of the structure after first lithiation. This process continues during the second cycle because the voltage value of the third delithiation peak is 3.96 V while the value of the lithiation peak is really the same −3.86 V.

The calculated specific capacity of the lithium cobaltite during first delithiation is 155 mAh g^{-1} while the specific capacity during lithiation is 112 mAh g^{-1} for the same cycle. The difference between the specific capacities on the first cycle is 43 mAh g^{-1}, which is comparatively the same to that obtained at *C*/5 rate. The delithiation specific capacity is 113 mAh g^{-1} and the lithiation specific capacity is 105 mAh g^{-1} on the second cycle. The relatively low specific capacity and not so good reversibility could be explained by the rather low synthesis temperature (700 °C) that does not allow to obtain lithium cobaltite with well ordered structure.

Typical charge–discharge curves of the $LiCoO_2$ investigated samples are presented in Fig. 6. The charge and the discharge are effectuated with relatively high current rate of 0.2 C (5 h). In this case the charge–discharge capacity of the sample is illustrated in Fig. 4. It can be seen that the capacity at the first charge is 155 mAh g^{-1}, value very close to the capacity recorded on the slow voltammetric test (SVT). This result confirm that

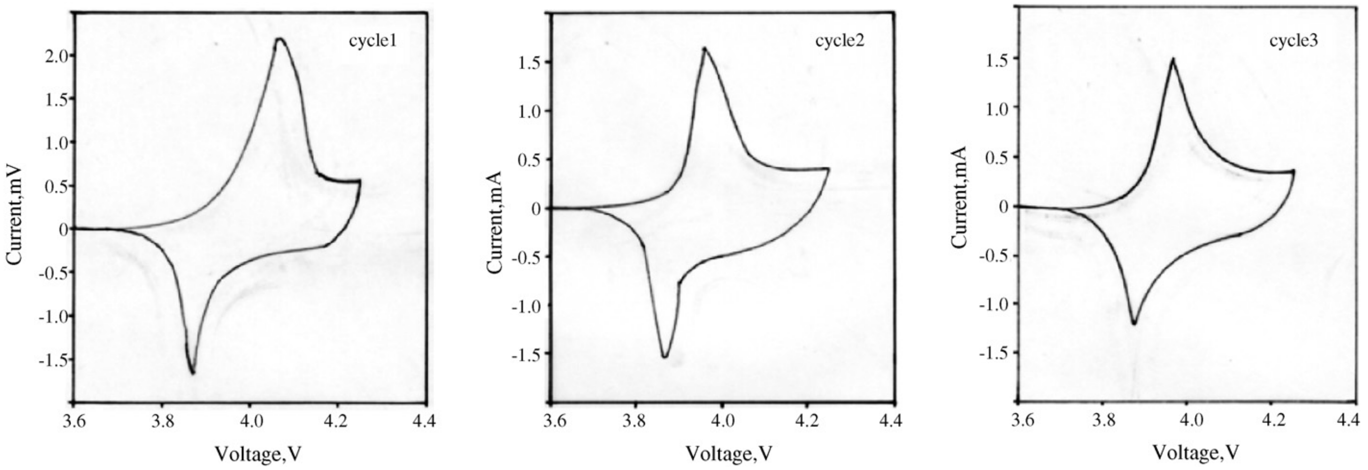

Fig. 5. Cyclic voltammograms of $LiCoO_2$ electrode at 30 μV s^{-1} scan rate.

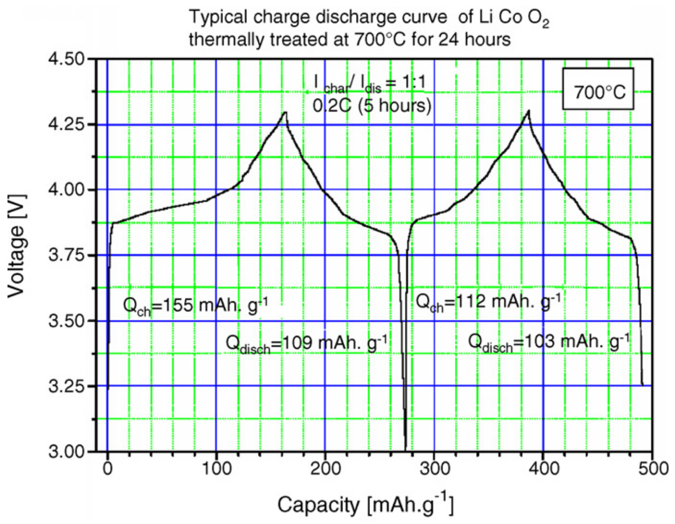

Fig. 6. The charge–discharge profile of lithium cobaltite with the charge and discharge capacities at the first and second cycle.

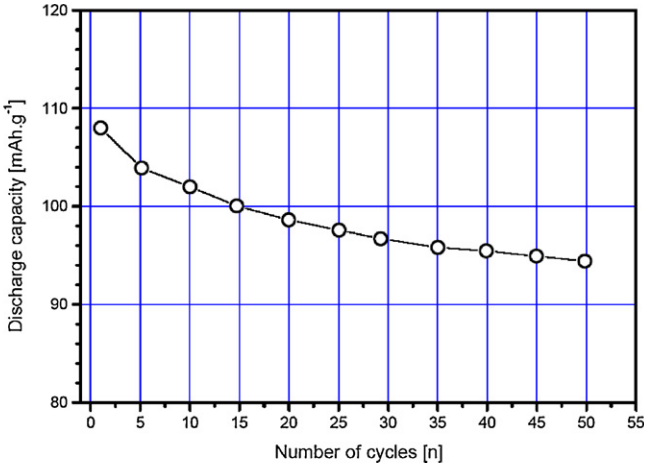

Fig. 7. Long term cycling of sol–gel $LiCoO_2$ sample tested in real coin cell CR2032.

the sample work without diffusion limitation. The displayed discharge capacity is relatively low only 109 mAh g^{-1}, but again very close to the data pointed out from the SVT. From the second charge discharge curves presented in Fig. 6 the displayed capacities are more reasonable 112 mAh g^{-1} for charge and 103 mAh g^{-1} for discharge. The obtained values are in some extent lower as compared with the results reported by other authors.[21]

The long term cycling of the $LiCoO_2$ sample is presented in Fig. 7 It can be seen from the picture that the test sample deliver the capacity of 109 mAh g^{-1} at the 1st cycle 102 mAh g^{-1} at the 10th cycle and more than 95 mAh g^{-1} at the 50th cycle. The results are satisfactory and show the potential for improvement.

4. Conclusions

The prepared lithium cobaltite according to the above described method exhibit interesting electrochemical properties.

Based on the developed in IPC-RAS method allow the formation of active electrode materials as thin films on an appropriate substrate.

Relatively good electrochemical performances of thus obtained active electrode material confirm that the $LiCoO_2$ thus obtained can be used as cathode in solid-state batteries.

Acknowledgments

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