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Formation of $LiNi_xCo_{1-x}O_2$ by decarbonization of organic gel precursors through treatment with nitric acid and hydrogen peroxide

A. Deptuła [a,*], W. Łada [a], T. Olczak [a], D. Wawszczak [a], B. Sartowska [a], K.C. Goretta [b,1]

[a] *Institute of Nuclear Chemistry and Technology, 03-195 Warsaw, Poland*
[b] *Argonne National Laboratory, Argonne, IL 60439-4838, USA*

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Abstract

We have used a complex sol–gel process to synthesize a family of compounds $LiNi_xCo_{1-x}O_2$ ($x = 0, 0.25, 0.5, 0.75, 1$). These compounds are candidates for electrode materials in high-energy-density batteries. Starting sols were prepared from $x\mathrm{Ni}^{2+} + (1-x)\,\mathrm{Co}^{2+}$ acetates/ascorbic acid aqueous solutions by alkalizing with LiOH and NH_3. With thermal treatment in air, nickel carbonates formed in quantities roughly proportional to Ni concentration. The carbonate impurities could not be fully removed by heating in air to high temperatures. Because formation of pure layered oxides was inhibited by the presence of the carbonates, we developed a new way to remove them from just-formed precursors by treating the intermediate phases (those formed after calcination at 750 °C) with concentrated HNO_3 and H_2O_2. All resulting powders were phase pure by X-ray diffraction and were easily friable. Various electrochemical properties of compacts prepared from these powders were measured.

Keywords: Oxides; Sol–gel chemistry; Thermogravimetric analysis; X-ray diffraction; Electrochemical properties

1. Introduction

Layered oxides have received considerable attention as electrode materials in high-energy-density Li-based batteries. $LiNiO_2$ and $LiCoO_2$ and their solid solutions have been extensively studied, as they, along with the $LiMn_2O_4$ spinels, are the only known positive-electrode materials capable of intercalating reversibly lithium ions at high cell voltage (3.5–4 V). Solid solutions, such as $LiNi_xCo_{1-x}O_2$, exhibit promise as alternative cathodes to the $LiCoO_2$ now found in commercial rechargeable Li-ion batteries. The new materials are comparable in performances to $LiCoO_2$, but cost substantially less [1]. The solid-state reaction routes commonly utilized to synthesize these types of materials have the drawback of requiring firing at high temperatures. Tarascon et al. [2,3] have produced by chemical synthesis fine particles of $LiNiO_2$ and $LiCoO_2$, which could be fired successfully at relatively low temperatures, and which led to higher cell capacities. Wet processing, especially various sol–gel methods, is capable of yielding fine particles, and it has been applied to mixed $LiNi_xCo_{1-x}O_2$ layered oxides [4–10].

In previous publications [4,10,11], we reported synthesis by our complex sol–gel process (CSGP) of a family of mixed oxides $LiNi_xCo_{1-x}O_2$, in which x ranged from 0 to 1. The salient feature of this process is addition of a very strong complexing agent, ascorbic acid (ASC), in preparation of the sols. For all samples prepared with ASC, we observed that thermal treatment of the resulting gels involved foaming, self-ignition, and, to varying degrees, formation of carbonates. Presence of carbonate impurities is not surprising in samples prepared from organic precursors, but by using similar techniques we have synthesized carbonate-free $LiCoO_2$ [11] and $Li_xMn_2O_{4\pm x}$ [12] that exhibited good electrochemical properties. The comparatively poor electrochemical properties that were obtained for our $LiNi_xCo_{1-x}O_2$ [11] were attributed to presence of carbonates in the final compounds. It is clear that Ni-containing layered oxides retain carbon more than their Co- or Mn-containing analogues. It has also been reported that carbonates hinder the formation and performance

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* Corresponding author.
E-mail addresses: adeptula@ichtj.waw.pl (A. Deptuła), ken.goretta@aoard.af.mil (K.C. Goretta).

[1] Present address: Asian Office of Aerospace Research and Development, 7-23-17 Roppongi, Minato-ku, Tokyo 106-0032, Japan. Tel.: +81 3 5410 4409; fax: +81 3 5410 4407.

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of high-temperature cuprate superconductors, which are also layered oxides [13].

We previously developed a proprietary processing procedure [13–15] for removal of carbonates from ceramics by low-temperature treatment with HNO_3. We believe that this processing approach can be effectively adapted to the other oxide systems. In this study, we have applied the CSGP method coupled with addition of oxidizing agents for synthesis of the layered oxides $LiNi_xCo_{1-x}O_2$.

2. Experimental details

The basic CSGP method used to prepare $LiNi_xCo_{1-x}O_2$ ($x = 0$, 0.25, 0.5, 0.75, 1) has been described [11]. Briefly, starting sols were prepared from xNi^{2+} + $(1 - x)$Co^{2+}/acetate–ASC aqueous solutions by alkalizing with LiOH and NH_3. The resulting gels were heated in air as in Ref. [11], with final treatment at 750 °C for 24 h. The heated samples, generally 20 g each, were milled and then placed in a Buchi RE 121 Rotavapor baker. HNO_3 was carefully added (≈1 mL/min) to achieve pH 1. Concentrated H_2O_2 was then introduced in a similar way. After drying under reduced pressure at 80 °C, samples were transferred to a furnace and further dried in air for 24 h at 200 °C. They were then heated at a rate of 3 °C/min to 750 °C and soaked for 1 or 24 h. A programmable Carbolite furnace (Type CSF 1200) was used for these thermal treatments.

X-ray diffraction (XRD) measurements were taken with Cu Kα radiation on a Philips Diffraction System and scanning electron microscopy (SEM) observations were made with a Zeiss DSM 942. A Perkin-Elmer Model 983 spectrometer and the potassium bromide pellet technique were used for infrared (IR) measurements. Carbonate concentrations were determined by internal standardization [16]; sodium nitride and ν_2 carbonate bands at 875 cm^{-1} were used. This method, to our knowledge not previously applied to $LiNi_xCo_{1-x}O_2$, is highly specific and accurate for carbonate determination. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were conducted with a Hungarian MOM Derivatograph.

3. Results and discussion

Carbonate content and sample characterization are shown in Table 1. The data and observations supported our previous contention [10,11] that, in materials containing Ni, very hard shards form owing to sintering, presumably with participation of a liquid lithium carbonate phase. The pure $LiCoO_2$ sample, in which lithium carbonate was not present, was a free-flowing powder.

Table 1
Characterization of $LiNi_xCo_{1-x}O_2$ compounds after heating for 24 h at 750 °C

Sample	CO_3 (wt.%)	Characterization
$LiNiO_2$	15	Very hard shard
$LiNi_{0.75}Co_{0.25}O_2$	14	Hard shard
$LiNi_{0.5}Co_{0.5}O_2$	3	Hard shard
$LiNi_{0.25}Co_{0.75}O_2$	1	Shard
$LiCoO_2$	0	Powder

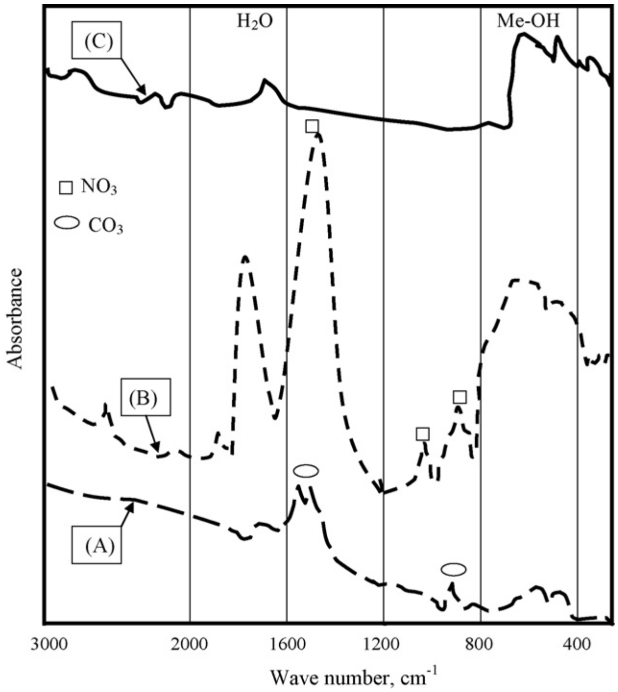

Fig. 1. Infrared spectra of precursors for $LiNi_{0.75}Co_{0.25}O_2$ synthesis in various stages of processing. (A) Sample before treatment, see Table 1; (B) sample A after treatment with HNO_3 + H_2O_2 and drying at 200 °C for 24 h; (C) sample B after final heating 750 °C for 1 h.

For the decarbonization studies, we selected from Table 1 the two compositions with the highest carbon concentrations. Addition of approximately 1 mL of HNO_3 per 1 g of sample was sufficient to attain pH 1. This concentration of acid, plus H_2O_2, completely eliminated the carbonates (Fig. 1, curve B). With reduced acidity, e.g., pH 5, the decomposition of strongly bonded carbonates was incomplete. XRD patterns of the $LiNi_{0.75}Co_{0.25}O_2$ gel dried at 200 °C are shown in Fig. 2. The IR and XRD data also revealed that significant quantities of nitrates were present in the gels.

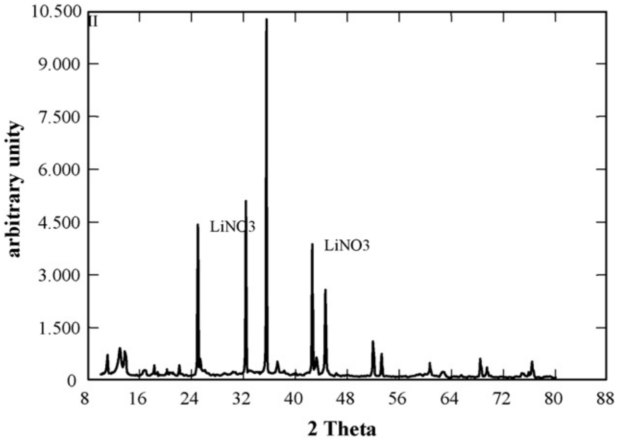

Fig. 2. XRD pattern of $LiNi_{0.75}Co_{0.25}O_2$ gel dried at 200 °C.

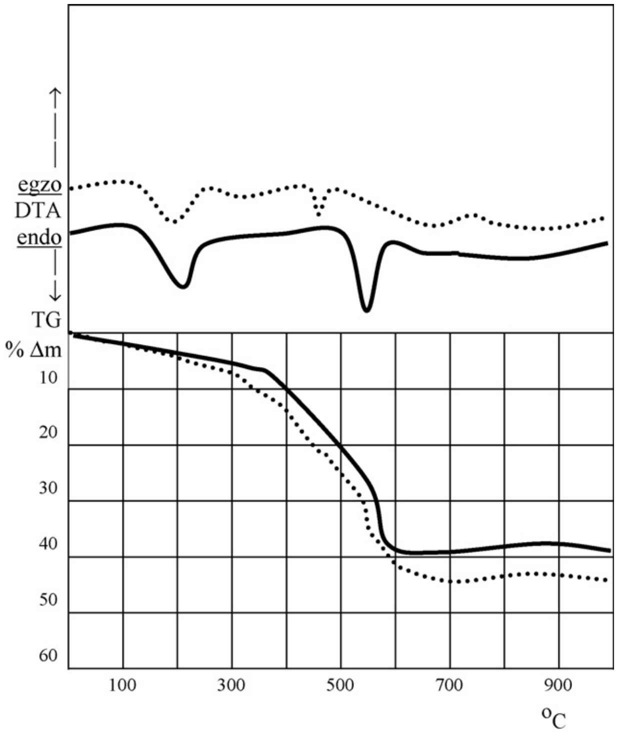

Fig. 3. TG and DTA traces of decarbonized gels after drying for 24 h at 200 °C: $LiNi_{0.75}Co_{0.25}O_2$ (solid line) and $LiNiO_2$ (dashed line).

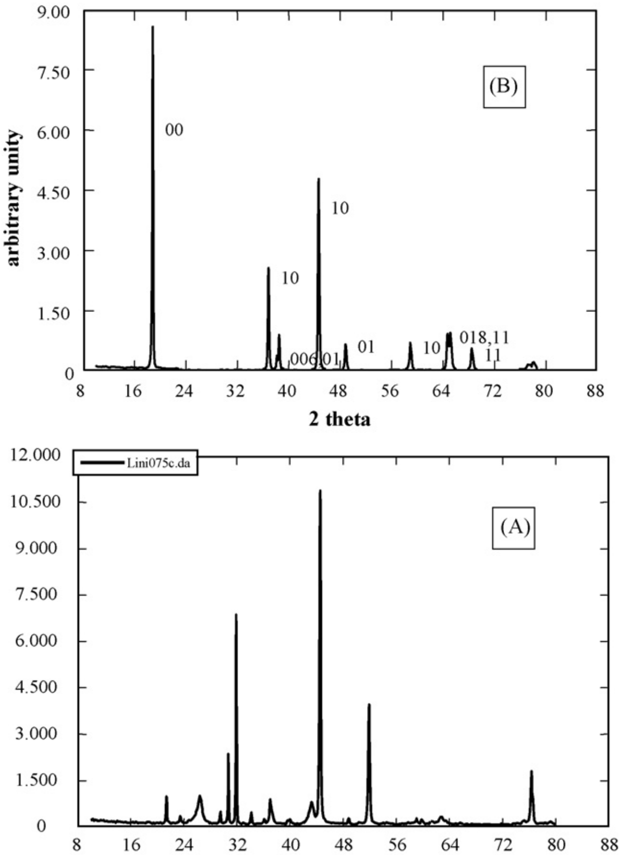

Fig. 4. XRD patterns of $LiNi_{0.75}Co_{0.25}O_2$ samples (A) before and (B) after decarbonization.

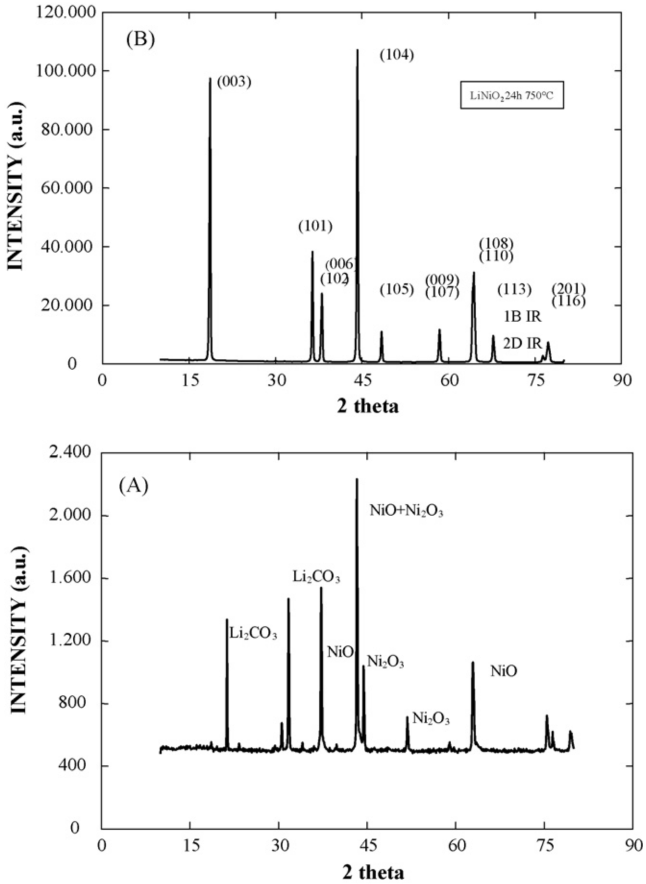

Fig. 5. XRD patterns of $LiNiO_2$ samples (A) before and (B) after decarbonization.

Thermal decomposition data from the dried gels and $LiNiO_2$ are shown in Fig. 3. The first endotherms corresponded roughly to melting. With further heating, intensive decompositions with evolution of gas from the liquid were observed, followed by solidification at ≈500 °C. After final thermal treatment at 750 °C, soft black cakes formed. IR spectra (Fig. 1C) indicated complete absence of carbonates, and XRD patterns (Fig. 4B) indicated formation of pure spinel phase. Before thermal processing, many phases, e.g., Li_2CO_3, NiO, and Ni_2O_3, were present.

As shown in Fig. 5, XRD patterns of a $LiNiO_2$ sample synthesized by CSGP (curve A) and after full processing (curve B) confirmed the efficiency of the decarbonization process. Pure Ni-containing spinel is extremely difficult to synthesize without imposing an atmosphere of pure O_2. Our process allowed it to form in air at relatively low temperatures. SEM photomicrographs of representative samples are shown in Fig. 6. Without chemical treatment, the products consisted of large grains, despite long-term milling. With chemical treatment, fine powders were obtained.

Kim et al. have reported that washing $Li(Co,Ni,Mn)O_2$ electrodes in HNO_3 improved their electrochemical performance [17]. $Li(Co,Ni,Mn)O_2$ ceramics do not retain significant carbon after heat treatment, and the measured improvement was ascribed to change in oxygen stoichiometry induced by the strongly oxidizing acid. The effects that we observed were, in contrast, attributable to elimination of carbonates.

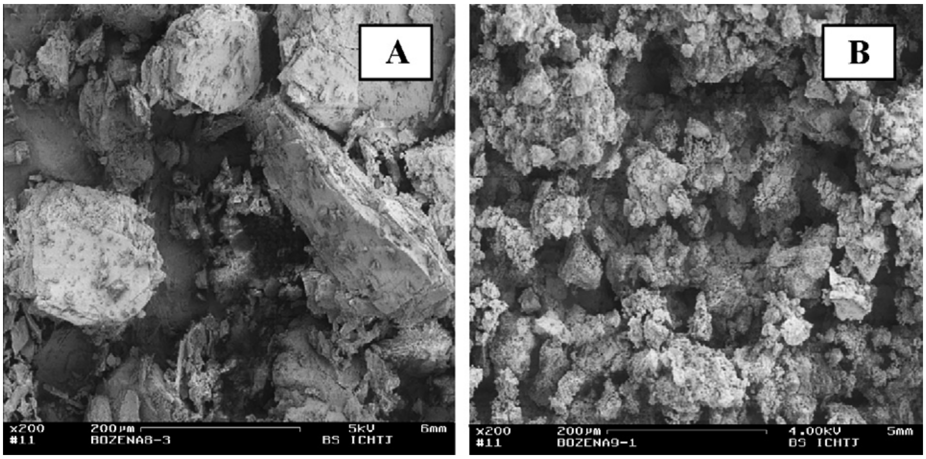

Fig. 6. SEM photomicrographs of $LiNiO_2$ samples (A) before and (B) after decarbonization.

Table 2
Discharge comparison at the 70th cycle at 1 mA/cm^2 at 25 °C

Property	$LiCoO_2$	$LiNi_{0.75}Co_{0.25}O_2$		$LiNiO_2$	
		Before	After	Before	After
mAh/g	125.4	≈70	122	≈60	120
Mid voltage	3.66	3.80	3.90	3.90	3.85
mWh/g	459.0	270	475	200	462

Electrochemical properties important for Li-battery applications were measured for our specimens; results are presented in Table 2. It was found that the values for decarbonized samples were comparable to the values that have been reported in literature for layered oxides of similar composition [4–10]. In contrast, samples without treatment with HNO_3 and H_2O_2 exhibited very poor properties. The stark differences between specimens were due primarily to carbon contents.

4. Conclusions

In $LiNi_xCo_{1-x}O_2$ prepared by a complex sol–gel process, during which ascorbic acid was added, carbonates were present in the resulting compounds. Treatment with HNO_3 and H_2O_2 prior to final heating in air was highly effective in removing the carbonates. Heating the decarbonized samples to 750 °C produced fine powders of layered oxides that exhibited nearly perfect XRD patterns. The electrochemical properties of the decarbonized samples were far superior to those of the carbonate-containing samples. The processing techniques that were followed should be effective in removing carbonates from other complex oxides.

Acknowledgments

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