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IMPROVED SYNTHETIC ROUTES TO LAYERED Na, CoO₂ OXIDES

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ABSTRACT

Improved synthetic routes to four Na_xCoO_2 (0.52 $\leq x \leq 1$) oxides of varying compositions and structures are presented. A combination of ceramic techniques and oxidative deintercalation reactions were used to access this series. Comparisons are made to previously reported preparative methods and differences in unit cell parameters discussed.

INTRODUCTION

The high mobility of Na⁺ ions in layered Na_xCoO₂ ($0.5 \le x \le 1$) oxides¹ makes these compounds excellent candidates for ion exchange reactions, yielding such interesting layered materials as Ca_xCoO₂,² Ag_xCoO₂³ and Li_xCoO₂.⁴ Many of the previously described methods of preparing Na_xCoO₂ oxides, however, result in products that contain Co₃O₄ or other impurities. Furthermore, the unit cells of at least one of the Na_xCoO₂ oxides

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has been incorrectly reported. Here, we detail modified synthetic routes as well as unit cell parameters for a series of four Na_xCoO₂ oxides.

The structures of the series of Na_xCoO₂ oxides are varied. NaCoO₂ assumes the layered *O3* structure (O = octahedral coordination of the alkali; 3 = number of layers in the repeat unit).⁵ The structure consists of ∞ [CoO₂]_n layers of edge-sharing CoO₆ octahedra with oxygen atoms staggered in an ABCABC packing sequence along the *c*-axis of the cell.⁶ Near x = 0.7, Na_xCoO₂ will assume either the *O'3* structure (' denotes a monoclinic distortion of the unit cell) or the high temperature *P2* structure (*P* = trigonal prismatic coordination of the alkali) depending on reaction conditions, with the latter assuming an ABBA packing arrangement.^{5,7} Na_xCoO₂ oxides with lower sodium content (*i.e.*, Na_{0.5}CoO₂) may be prepared by oxidatively deintercalating sodium from NaCoO₂ or Na_{0.7}CoO₂, resulting in compounds with a layer shift (*P'3*) or an isostructural configuration (*P2*), respectively.^{8,9}

EXPERIMENTAL

Preparation of the Sodium Cobalt Oxides

NaCoO₂ (*O3*), Na_{0.75}CoO₂ (*O 3*) and Na_{0.7}CoO₂ (*P2*) were prepared by direct reaction of cobalt metal (Aldrich, 99.8%, $< 2 \mu m$) and sodium hydroxide (Aldrich, 99.99%). The sodium hydroxide should be analyzed for sodium content if a certificate of analysis is not provided by the manufacturer. Also, it should be noted that the small particle size for the cobalt metal greatly improves the reactivity of this reagent.

$$\text{Co} + \text{x} \text{ NaOH} + (1 - \frac{x}{4}) \text{ O}_2 \rightarrow \text{Na}_x \text{CoO}_2 + \frac{x}{2} \text{ H}_2 \text{O}$$

In a typical reaction 3.0 g (51 mmol) of cobalt metal is combined with stoichiometric amounts of sodium hydroxide (2.0 g, 51 mmol). In the case of x = 1, a slight excess of NaOH (0.1 mole %) is used to ensure complete reaction. The reactants were mixed and ground thoroughly with an agate mortar and pestle in an argon-filled dry box. The mixture was loaded into a 10 mL alumina boat (Coors Ceramics) and heated at either 500° C (x = 1, 0.75) or 700° C (x = 0.7) for five days in a tube furnace under flowing O₂. The reactants were reground daily. Prior to removal from the furnace, samples were allowed to cool to room temperature over a two-hour period under flowing O₂. All products were stored and handled in an argon-filled dry box. It should be noted that extended heating times, beyond those reported here, result in lower sodium contents in the products presumably due to the loss of volatile Na₂O.

 $Na_{0.5}CoO_2$ (*P* 3) and $Na_{0.5}CoO_2$ (*P*2) were prepared by oxidatively deintercalating sodium from $NaCoO_2$ and $Na_{0.7}CoO_2$, respectively.^{8,9}

$$Na_{x}CoO_{2} + (x-0.5)/2 I_{2} \rightarrow Na_{0.5}CoO_{2} + (x-0.5) NaI$$

Typically, 3.0 g (26 mmol) of NaCoO₂ (*O3*) or Na_{0.7}CoO₂(*P2*) precursor were placed in a round-bottom flask with at least a 100% molar excess of I₂ (14.7 g, 58 mmol, Baker, 99%) dissolved in acetonitrile (E. M. Scientific, reagent grade) and stirred at room temperature for two days under a blanket of nitrogen gas. The products were collected by vacuum filtration and washed with anhydrous methanol with minimal air exposure. After heating at 300° C under flowing O₂ for one day to remove any moisture and/or iodine, the products were stored and handled in an argon-filled dry box. All of the Na_xCoO_2 oxides are moisture sensitive.

Characterization

All reaction products were characterized by powder X-ray diffraction (XRD) and inductively coupled plasma (ICP) emission spectrometry. XRD was performed on a Philips X'Pert system using Cu- $K\alpha$ radiation ($\lambda = 1.5418$ Å) and a curved graphite monochromator. Powdered tungsten (Alfa, 99.999%) was used as an internal standard. Due to moisture sensitivity, samples were covered with polypropylenc film (Chemplex, 0.25 mil). Peak locations and intensities were refined with the program *ProFit*.¹⁰ Unit cell data were refined with the program *POLSQ*.¹¹ Quantitative metal analyses, performed on a Perkin Elmer Plasma 40 ICP spectrometer, used a standard addition method. Samples for ICP were digested in concentrated HCl. Metal compositions were always within 2% of the expected values of x in Na_xCoO₂.

RESULTS AND DISCUSSION

Many of the Na_xCoO₂ materials reported here can be prepared over a range of compositions within a given structure type: $O3 (0.80 \le x \le 1)$,¹² $O'3 (0.75 \le x \le 0.77)$,^{5,7} $P'3 (0.53 \le x \le 0.65)$,^{5,8,12} and $P2 (0.50 \le x \le 0.74)$.^{7,13} In NaCoO₂, for instance, which assumes the O3 structure, the sodium content can be as low as x = 0.80 without disruption to the structure.¹² The unit cell parameters, however, are sensitive to changes in composition over this range. The *a*-parameter of hexagonal unit cells, which represents the Co—Co distance within a ∞ [CoO₂]_n layer, will contract as sodium content decreases. Conversely, the *c*-parameter, the length in the hexagonal cell along [001], will expand due to the increased repulsion between ∞ [CoO₂]_n layers as their relative charge increases. A stated unit cell, therefore, is particular to a specific composition. It should be noted that the literature contains widely varying accounts of Na_xCoO₂ compositions. The sodium content of Na_{0.7}CoO₂ (*P2*), for example, reportedly can be reversibly cycled between 0.46 $\leq x \leq 0.83$ while maintaining the *P2* structure if the intercalation/deintercalation reactions are performed electrochemically.¹⁴ The compositions reported here refer to compounds which have been prepared chemically.

Most of the XRD results of the Na_xCoO₂ oxides summarized in Table I are in good agreement with previously published results. Na_{0.75}CoO₂ (O'3), Na_{0.7}CoO₂ (P2), Na_{0.5}CoO₂ (P2), however, are notable exceptions. For $Na_{0.75}CoO_2$ (O'3), we were unable to prepare a product free of Co_3O_4 , though others have reportedly done so.^{5,7} In the case of the P2 material, we find that the sodium content range accessible by direct reaction $(0.64 \le x \le 0.71)$ is in reasonable agreement with that reported by Delmas et al.;7 they, however, only report a single set of unit cell parameters for this composition range, whereas we see the appropriate variation in values as a function of x. For $Na_{0.5}CoO_2$ (P2), differences in composition do not appear to account for the discrepancies between the experimental and literature unit cell parameters.¹³ The preparation of this material in the literature involves the direct reaction of Na2O2 and Co3O4. We were unable to reproduce this synthesis without the product containing sizeable concentrations of Co₃O₄. Furthermore, the unit cell calculated by Jansen and Hoppe for Na05CoO2 corresponds very well to the unit cell of Na_{0.7}CoO₂ (P2), which may reveal

| Compound ^{a,b} | Unit cell | Literature unit cells | |
|---|---|---|--|
| NaCoO ₂ (<i>O3</i>) | Hexagonal a = 2.8894(2) Å c = 15.603(1) | Hexagonal ⁷ a = 2.880(3) Å c = 15.58(5) | |
| Na _{0.75} CoO ₂ (O '3) | Monoclinic ^c a = 4.930(5) b = 2.856(2) c = 5.846(6) $\beta = 110.6(1)^{\circ}$ | Monoclinic ⁷ a = 4.890(5) b = 2.866(3) c = 5.770(5) $\beta = 111.28^{\circ}$ | Monoclinic ⁵ a = 4.880 b = 2.866 c = 5.77 $\beta = 111.3^{\circ}$ |
| Na _{0.71} CoO ₂ (<i>P2</i>) | Hexagonal a = 2.834(1) c = 10.88(3) | Hexagonal ⁷ a = 2.833(3) c = 10.82(3) | |
| Na _{0.64} CoO ₂ (<i>P2</i>) | Hexagonal a = 2.832(1) c = 10.925(3) | | |
| Na _{0 53} CoO ₂ (<i>P2</i>) | Hexagonal a = 2.8155(5) c = 11.134(1) | Hexagonal ¹³ a = 2.84(3) c = 10.81(1) | |
| Na _{0.52} CoO ₂ (<i>P</i> '3) | Monoclinic a = 4.881(1) b = 2.817(1) c = 5.764(1) $\beta = 105.61(2)^{\circ}$ | Monoclinic ⁷ a = 4.839 b = 2.831 c = 5.71 $\beta = 106.3^{\circ}$ | Monoclinic ¹⁶ a = 4.899 b = 2.829 c = 16.53 $\beta = 90.58^{\circ}$ |

Table I. Composition and Unit Cells for Sodium Cobalt Oxides.

"Compositions from ICP data. ^{*b*}Structure type shown parenthetically." Sample contains Co_3O_4 impurity.

a problem with the authors' quantitative analysis. We have found that $Na_{0.5}CoO_2$ is best prepared by oxidative deintercalation.

The XRD results of $Na_{0.5}CoO_2$ (*P* '3) have been previously indexed on an inappropriately large unit cell. The nearly orthorhombic cells of Fouassier *et al.*,^{5,15} and Miyazaki *et al.*^{9,12} are essentially distorted *O3* cells, a few of which are listed in Table I. This has been a source of some confusion, for despite one group of authors later reindexing their XRD results,⁷ the incorrect unit cells were still being reported as late as 1986¹⁶ and have been subsequently reiterated in at least one book.¹⁷ Miyazaki *et al.* also reported a composition of $Na_{0.58}CoO_2$, which is a slightly higher sodium content than the material reported here. This may, however, reflect slight differences in the preparative methods, as their reaction time for the oxidative deintercalation was only one day, whereas ours was two days.

Conclusions

The Na_xCoO_2 oxides, diverse in structural chemistry and important as intermediates to other layered cobaltates, have proven to be synthetically challenging. Variable composition coupled with the structural intricacies has made their monophasic preparation quite complicated, leading to some confusion in the literature. Though further refinement of their syntheses may be expected and welcomed, the preparative methods presented here clarify many of the ambiguities and inaccuracies previously reported in the literature.

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