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BRIEF COMMUNICATION

Electrochemistry in Molten Hydroxides: Synthesis of $NaCuO_2$

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An effort to produce highly oxidized copper oxides by electrodeposition in NaOH/KOH melts has resulted in the discovery of a new synthetic route to the Cu^{3+} compound $NaCuO_2$. Crystals were grown on a platinum-wire working electrode over a range of temperatures (200–300°C) and applied current (−2.0 to −15.0 mA). The products were pure and single phase as confirmed by powder X-ray diffraction and energy dispersive X-ray spectroscopy. The isolation of $NaCuO_2$ indicates that electrolysis in hydroxide melts is a useful method for the preparation of highly oxidized copper oxide materials.

INTRODUCTION

Hydroxide melts have been shown previously to be useful as solvents in the low temperature synthesis of the copper oxide superconductors $La_{2-x}M_xCuO_4$ (M = Na, K) (1) and $EuBa_2Cu_3O_7$ (2), as well as new highly oxidized cuprates (3). The utility of hydroxides as solvents is derived from the fact that the electrochemical-potential window is sufficiently large to stabilize metals and oxygen in various oxidation states. For example, highly oxidized species such as O_2^{-1} and O_2^{-2} (4), and Cu^{3+} (5) have been reported. In this communication, we present the results of a study of the electrolysis of NaOH/KOH melts of various compositions containing dissolved CuO at temperatures between 200 and 300°C, as well as the effects of adding La^{3+}, Ca^{2+}, or Ba^{2+} on the electrolysis product.

All of the products obtained thus far by air oxidation of Cu^{2+} in molten hydroxide are precipitated at temperatures above 300°C. For example, while air oxidation produces $La_{2-x}Na_xCuO_4$ at temperatures above ~320°C, no product is obtained at lower temperatures (1). We postulate that this is because $La_{2-x}M_xCuO_4$ dissolves in hydroxide melts that are H_2O rich (O^{2-} poor); higher temperatures are necessary to remove a sufficient quantity of water (6). However, since highly oxidized species are stabilized in the hydroxide melts, and can be produced by application of an oxidizing potential at any temperature, we felt that electrolysis would provide a low temperature synthetic route to highly oxidized compounds that are not precipitated by air oxidation in H_2O-rich melts.

Here, we report the synthesis of $NaCuO_2$, in which the formal copper oxidation state is +3. The product was obtained by electrodeposition in a NaOH/KOH flux at temperatures less than 300°C and over a period of several hours. This phase was originally prepared by Klemm *et al.* (7) by heating Na_2O_2 and CuO in flowing oxygen for several days, and has more recently been synthesized from a $NaOH/Na_2O_2$ melt (8).

EXPERIMENTAL

The hydroxide starting materials, NaOH (Alfa, ultrapure) and KOH (Alfa, ultrapure), were used without pretreatment; due to exposure to the atmosphere, they contain roughly 10–15 wt% water (4). In all experiments, the total weight of the hydroxide flux was kept constant at 20.0 g. However, the percentage of KOH in the hydroxide melt was varied from 25–100%, with the balance being NaOH. Although the melting point of pure KOH is 360°C, melts were obtained between 200 and 300°C, presumably due to the presence of a sufficient quantity of water which evaporated slowly; in contrast, pure NaOH melts (melting point = 318°C) were not obtained in this temperature range.

The hydroxides were heated to temperatures between 200 and 300°C in a Teflon crucible exposed to the atmosphere. In various experiments, from 0.05 to 0.36 g CuO (Aldrich, 99.99%) was added to the molten hydroxide, and the melt was stirred until a clear, dark-blue solution was obtained. Some experiments included the addition of La_2O_3 (Aldrich, 99.99%), $Ba(OH)_2 \cdot 8H_2O$ (Alfa, 98% min.), or CaO (Alfa, 99.95%) in a 1 : 1 molar ratio with CuO to study the effect of La^{3+}, Ca^{2+}, or Ba^{2+} on the product of electrodeposition.

Two platinum wires were used as electrodes, and a

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constant current from −2.0 to −20.0 mA was applied for melts held at constant temperatures between 200 and 300°C. After several hours, the current was stopped and the electrodes were removed from the flux. In cases where a product was obtained, washing of the working electrode with distilled water to remove the hydroxides revealed blue-grey to blue-black crystals in the shape of needles. After drying overnight, the crystals were scraped from the wire. The products were characterized by powder X-ray diffraction with Cu$K\alpha$ radiation and energy-dispersive X-ray spectroscopy (EDS).

RESULTS AND DISCUSSION

The product removed from the working electrode was in all cases found to be $NaCuO_2$; previously Eluard and Tremillon performed similar experiments and also claimed to have prepared a product containing Cu^{3+} which they tentatively identified as Cu_2O_3 (9). We have determined that electrodeposition of $NaCuO_2$ occurs over a range of temperatures, applied current, and melt compositions. Specifically, we isolated $NaCuO_2$ over the entire temperature range investigated (200–300°C) for a melt composition of 50 wt% NaOH to 50 wt% KOH containing varying amounts of CuO if the applied current was between −5.0 and −15.0 mA. At an applied current less negative than −5.0 mA, $NaCuO_2$ was not formed at the high end of the temperature range investigated. If a current more negative than −15.0 mA was applied, all Cu^{2+} ions in solution were reduced and deposited at the counter electrode; presumably, this could be avoided and higher currents could be used if another reducible metal cation were added to the melt.

Application of a current in melts with significantly less NaOH, as low as 30% by weight, also produced $NaCuO_2$ of comparable purity. However, at less than 30% NaOH, no product was deposited on the working electrode. It is notable that even in pure KOH, $KCuO_2$ was not obtained. The melts are H_2O rich below 300°C, and perhaps $KCuO_2$ is soluble under these conditions. If this is the case, it may be possible to prepare $KCuO_2$ if the experiments are performed at higher temperatures in melts with less water (more O^{2-}).

The presence of La^{3+}, Ca^{2+}, or Ba^{2+} in the melt did not affect the product. The absence of impurities in $NaCuO_2$ was confirmed by EDS measurements. We conclude that these cations do not alter the melt chemistry significantly, and do not substitute for Na^+ in $NaCuO_2$ under the conditions investigated. Furthermore, $La_{2-x}M_xCuO_4$ (M = Na, K) is not deposited; since this product is obtained by air oxidation of La_2O_3 and CuO dissolved in NaOH/KOH melts at temperatures above ~300°C (1), it appears that higher temperatures are required either to reduce the amount of water (increase the amount of O^{2-}) to exceed the solubility limit or to reduce the amount of dissolved O_2 to precipitate products with lower formal copper oxidation states (between Cu^{2+} and Cu^{3+}).

All the peaks in the powder X-ray diffraction pattern of the product can be indexed to a monoclinic unit cell with the lattice parameters a = 6.346(2) Å, b = 2.748(1) Å, c = 6.107(3) Å, and β = 120.78(3)°; these are in excellent agreement with those reported previously (8, 10). EDS measurements indicate that K^+ is not incorporated into the structure, even for products precipitated from KOH-rich melts. This is presumably due to the rigid structure of $NaCuO_2$, consisting of layers of edge-shared NaO_6 octahedra separated by chains of edge-shared CuO_4 squares (8, 10, 11). Although reported to be extremely hygroscopic and unstable in air (7, 8, 10, 12), $NaCuO_2$ is relatively stable when synthesized by electrodeposition. This result is most likely due to the increased purity and crystallinity of the electrodeposited product.

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