Powerful Oxidizing Agents for the Oxidative Deintercalation of Lithium from Transition-Metal Oxides

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NO_2^+ and MoF_6 are shown to be powerful oxidizing agents for the deintercalation of lithium from $LiCoO_2$ and Li_2CuO_2. The oxidations, which usually were accompanied by some side reaction, yielded materials of composition Li_xMO_2 with $x \sim 0$ for $M =$ Co and $x \sim 1.5$ for $M =$ Cu. Both starting materials are insulating ($\rho > 10^3 \ \Omega$ cm), but the deintercalated products are much more conducting (by at least four orders of magnitude). © 1989 Academic Press, Inc.

Introduction

Previous studies of the intercalation chemistry of many transition metal chalcogenide systems have established that I_2 and Br_2 are effective reagents for the oxidative deintercalation of lithium from sulfide and selenide compounds (see, for example, (1)). A familar example of such a deintercalation is the reaction of iodine with $LiTiS_2$,

$$LiTiS_2 + 1/2 \ I_2 \xrightarrow{CH_3CN} TiS_2 + LiI,$$
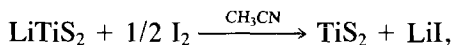
in which titanium is oxidized from 3+ to 4+. We have been interested in developing lithium deintercalation chemistry as a synthetic route to highly oxidized transition metal *oxides*. There are only a few reports in the literature of lithium deintercalation from oxides; these include both *chemical* oxidation (of $LiVO_2$ (2), $LiNbO_2$ (3), and $LiCoO_2$ (4), using bromine or iodine as oxidizing agent) and also *electrochemical* oxi-

dation (of $LiCoO_2$ (5) and $LiNiO_2$ (6)). In the reported chemical oxidations with bromine, the removal of lithium did not usually proceed to completion, and we expect that some oxides will require more powerful oxidants than bromine for any reaction to occur at all; thus we have been searching for such oxidants capable of deintercalating lithium from oxides.

Three potentially useful oxidizing agents are NO^+, NO_2^+, and MoF_6. Figure 1 shows the estimated redox potentials of the couples NO^+/NO (7), NO_2^+/NO_2,[1] and MoF_6/MoF_6^- (7) in acetonitrile solution, as well as an estimated value for PtF_6/PtF_6^-,[2] for comparison. All are at substantially higher potentials than the commonly used agents I_2 and Br_2. (Note that the PtF_6/PtF_6^- potential

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+4.4 —PtF$_6$/PtF$_6^-$

+2.4 —MoF$_6$/MoF$_6^-$
+2.1 —NO$_2^+$/NO$_2$
+1.7 —NO$^+$/NO
+1.1 —Br$_2$/Br$^-$

↑
INCREASING
OXIDIZING   +0.5 —I$_2$/I$^-$
POWER

0.0V vs. NHE—
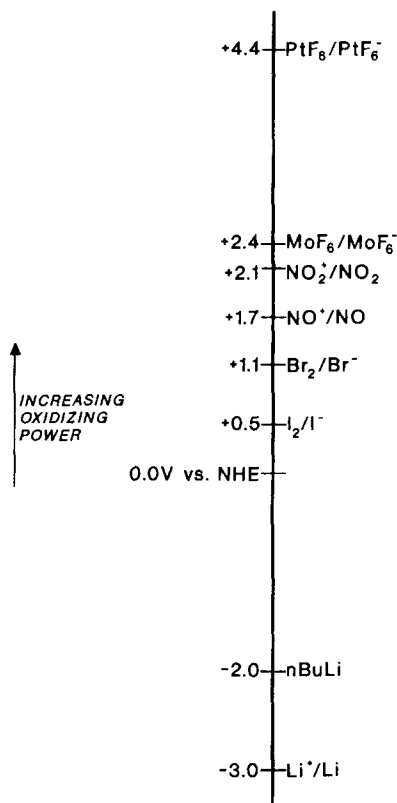
-2.0 —nBuLi

-3.0 —Li$^+$/Li

FIG. 1. *Estimated* redox potentials in acetonitrile. After a similar figure from Ref. (*1*).

is well beyond the oxidative decomposition limit of acetonitrile, which is at approximately +3 V versus NHE.) Our work has focused around two oxides, LiCoO$_2$ and Li$_2$CuO$_2$. LiCoO$_2$, which has an ordered rock-salt structure with alternating layers of lithium and cobalt, was chosen to allow comparison with previous deintercalation studies using Br$_2$ as the oxidant (*4*). The main structural feature of Li$_2$CuO$_2$ (*10*) is a one-dimensional chain of edge-sharing CuO$_4$ square-planar units, with lithium positioned in tetrahedral sites between the chains (see Fig. 2). In this previously unexamined case, removal of lithium would formally oxidize the copper from 2+ to 3+, possibly changing the insulating Cu^{2+} phase

into a metal or even a superconductor. While the square-planar CuO$_4$ units in Li$_2$CuO$_2$ are edge-sharing rather than corner-sharing to form chains or sheets as in the recently discovered high-T_c superconductors, the connection between structure and superconductivity in copper oxides has still not been elucidated and it may be useful to search for superconductivity in mixed Cu^{2+}/Cu^{3+} oxides with various structural features.

Experimental

LiCoO$_2$ was prepared as a black powder by heating Li$_2$CO$_3$ and cobalt metal in air to 900°C for 2 days. Li$_2$CuO$_2$ was prepared as
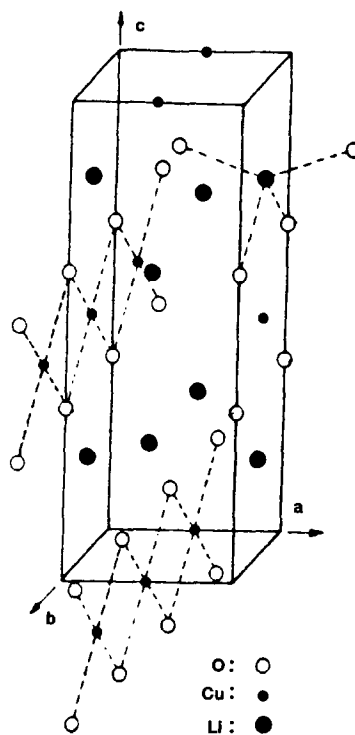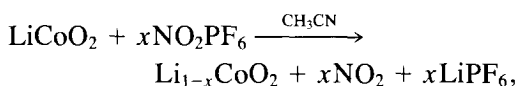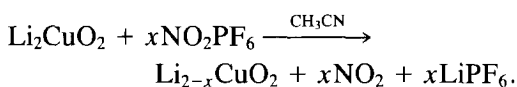

o: ○
Cu: •
LI: ●

FIG. 2. Li$_2$CuO$_2$ unit cell. Shows one-dimensional chains of edge-sharing CuO$_4$ units; Li$_2$CuO$_2$ crystallizes in the orthorhombic space group *Immm* with $Z =$ 2, $a = 3.66$, $b = 2.86$, and $c = 9.39$ (crystallographic data is from Ref. (*10*)).

a red-brown powder from Li_2O_2 and CuO in a platinum crucible under flowing oxygen at 500°C for 5 days.

The oxidations were carried out in acetonitrile under an argon atmosphere. The source of NO_2^+ was a soluble hexafluorophosphate salt, NO_2PF_6 (Morton Thiokol Alfa). The salt was heated to 100°C under vacuum to remove volatile impurities and was then reacted with the oxides:

$$LiCoO_2 + xNO_2PF_6 \xrightarrow{CH_3CN}$$
$$Li_{1-x}CoO_2 + xNO_2 + xLiPF_6,$$

or

$$Li_2CuO_2 + xNO_2PF_6 \xrightarrow{CH_3CN}$$
$$Li_{2-x}CuO_2 + xNO_2 + xLiPF_6.$$

(The $LiPF_6$ is soluble in acetonitrile, while the oxide product remains behind as the only solid phase.) The NO_2^+ oxidation of Li_2CuO_2 was especially vigorous.

Reactions with MoF_6 were carried out by condensing gaseous MoF_6 into acetonitrile containing the oxide:

$$LiCoO_2 + xMoF_6 \xrightarrow{CH_3CN}$$
$$Li_{1-x}CoO_2 + xLiMoF_6.$$
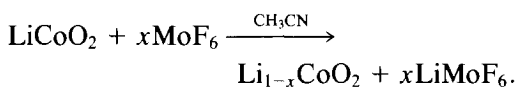
After filtration and drying *in vacuo*, the oxide powders were characterized by X-ray powder diffraction and atomic emission (Li) or absorption (Cu) spectroscopy.

Results and Discussion

Mizushima *et al.* (5) examined the X-ray diffraction pattern of $Li_{1-x}CoO_2$ as a function of lithium content. For $x < 0.5$ they were able to index all peaks on the hexagonal cell of $LiCoO_2$ and to observe gradual changes in the c lattice parameter by following the position of the (003) line in the diffraction pattern. (The (003) d-spacing gives the spacing between CoO_2 layers.) They noted that for $x > 0.67$ diffraction peaks became few and broad. Consistent

with their results, we observe from X-ray diffraction that the product $Li_{1-x}CoO_2$ with x near 1 is highly disordered. When $LiCoO_2$ is treated with half an equivalent of NO_2^+, the (003) and (104) peaks remain from the powder pattern of the starting material, with slightly shifted d-spacings; after reaction with a full equivalent of NO_2^+, only one peak is visible, in the approximate position of the (003) line of the starting material. Because this peak is consistently observed as the lithium content in $Li_{1-x}CoO_2$ is gradually varied, it seems reasonable to conclude from its presence that the CoO_2 layer structure is retained and to interpret its position as representing the spacing between CoO_2 layers. Note that since only a single line is visible in the diffraction pattern of $Li_{1-x}CoO_2$ for x near 1, the disorder in the structure cannot be just a simple stacking disorder (see, for example, (11)), but must also involve irregular spacing of the CoO_2 layers along the c axis.
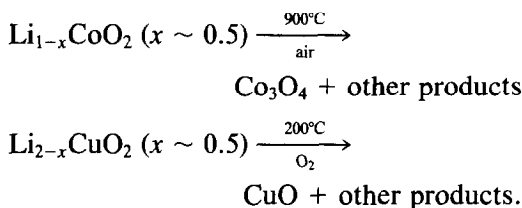
X-ray diffraction results for the copper compound indicate that the material of *nominal* composition $Li_{2-x}CuO_2$ ($0 < x < 1$) is actually a mixture of two phases: stoichiometric Li_2CuO_2 and a new second phase (of approximate composition $Li_{1.5}CuO_2$) characterized by seven broad diffraction peaks (see Table I).

TABLE I

X-Ray Powder Data for the Product of the Reaction of Li_2CuO_2 with One Equivalent of NO_2PF_6

d (Å)	Estimated intensity
4.84	100
3.58	30
2.87	50
2.78	25
2.47	25
2.13	40
1.95	50

Both the cobalt and copper products are unstable at high temperatures, decomposing as follows:

$$Li_{1-x}CoO_2 \ (x \sim 0.5) \xrightarrow[\text{air}]{900°C}$$

$$Co_3O_4 + \text{other products}$$

$$Li_{2-x}CuO_2 \ (x \sim 0.5) \xrightarrow[\text{O}_2]{200°C}$$

$$CuO + \text{other products.}$$

The oxidation of $LiCoO_2$ with MoF_6 appears to be close to 100% efficient. However, the oxidations with NO_2^+ of both $LiCoO_2$ and Li_2CuO_2 involve significant side reaction. During the reaction of NO_2^+ with Li_2CuO_2, 10% of the Li_2CuO_2 decomposes into solution, according to an atomic absorption measurement of the Cu concentration in the acetonitrile reaction solution. Also, elemental analysis of the product $Li_{2-x}CuO_2$ reveals a large difference between the *nominal* composition (based on the amount of NO_2^+ used) and the *actual* composition:

Nominal x in $Li_{2-x}CuO_2$	Actual value
0.50	0.25
0.75	0.42
1.00	0.49

Similarly, in the reaction of NO_2^+ with Li_2CoO_2, some cobalt ends up in solution, as evidenced by the cobalt oxide precipitate which forms on addition of aqueous base to the reaction solution; as with the copper compound, significantly less than one Li is removed for each NO_2^+ used. Unfortunately, direct elemental analysis of the product $Li_{1-x}CoO_2$ was not possible due to its poor solubility. Also, analysis of the reaction solution for lithium would not give a reliable estimate of the degree of deintercalation since some of the lithium in solution would be due to a destructive side reaction of $LiCoO_2$ rather than to deintercalation. In the absence of a direct chemical method for
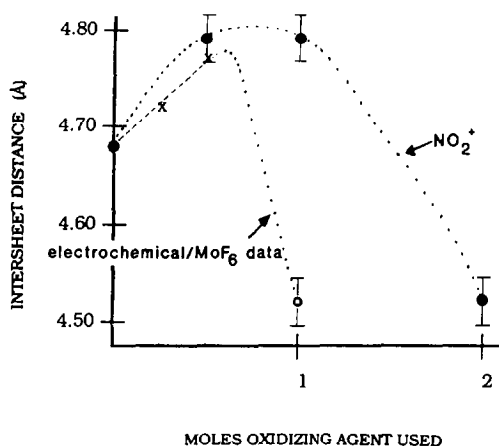

FIG. 3. X-ray diffraction results for $Li_{1-x}CoO_2$: intersheet distance versus amount of oxidant used. X, Electrochemical deintercalation data from Ref. (5); ●, NO_2^+ data; O = MoF_6 data.

determining the lithium content of the deintercalated samples, we have attempted to monitor the degree of deintercalation with X-ray diffraction by correlating the observed interlayer spacings with the amount of oxidizing agent used. This correlation is summarized in Fig. 3, a plot of interlayer spacing versus amount of oxidant used; here the "interlayer spacing" is an average value as measured by the position of the one visible diffraction peak. Data from electrochemical deintercalations by Mizushima *et al.* (5) have been included on the figure. Since NO_2^+ is not completely efficient at deintercalation, the NO_2^+ data points do not overlap the electrochemical or MoF_6 data; that is, two equivalents of NO_2^+ are required to achieve maximal deintercalation. The observed increase in the interlayer spacing with decreasing lithium content is somewhat unusual in that such spacings usually *decrease* on deintercalation. A similar increase was observed by Mendiboure *et al.* (4) in an electrochemical deintercalation of $LiCoO_2$.

Two-point resistance measurements were obtained on pressed powders in an ar-

gon-filled glove box. Calculated resistivities for the cobalt compounds are $5.4 \times 10^3 \ \Omega$ cm for $LiCoO_2$ and $0.6 \ \Omega$ cm after reaction with one equivalent of NO_2^+; in the copper system, the resistivity is greater than $10^6 \ \Omega$ cm for Li_2CuO_2 but drops to $71 \ \Omega$ cm upon reaction with one equivalent of NO_2^+. Both compounds show a drop in resistivity of four or more orders of magnitude upon oxidation. While such measurements cannot be trusted for quantitative comparison due to the importance of interparticle contact resistance, the large decrease in resistivity clearly indicates that the products are more conducting than the reactant solids. Magnetic susceptibility measurements by the Faraday method show that the product oxides are not superconducting down to 4 K.

In summary, we report here the use of the powerful oxidizing agents NO_2^+ and MoF_6 to deintercalate lithium from transition metal oxides. Although with some oxides side reaction can be significant, these and similar chemical oxidants may provide an effective low-temperature route to the synthesis of highly oxidized transition metal oxides.

Acknowledgments

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