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NOTE

Li_xVO_2 ($0 < x \leq 1$): A New Series of Layered Oxides*

Introduction

Solid solutions based on layered transition metal chalcogenides such as Li_xTiS_2 have attracted considerable attention in view of their potential use as electrodes in secondary batteries (*1*). The importance of such systems is that the electropositive metal can be reversibly inserted into and extracted from the layered chalcogenide with minimum structural change (*2*). Recently Mizushima *et al.* (*3*) have shown that it is possible to remove lithium electrochemically from $LiCoO_2$ forming the Li_xCoO_2 series. We report here the formation of Li_xVO_2 ($0 < x \leq 1$) by chemical oxidation of $LiVO_2$ using Br_2 as the oxidant in $CHCl_3$.

Experimental

$LiVO_2$ was prepared by heating Li_2CO_3 and V_2O_5 in a 1 : 1 molar ratio in hydrogen atmosphere, first at 500°C for 4 hr, and then at 700°C for 10 hr. Chemical analysis of the sample carried out potentiometrically using Ce(IV) as oxidant (*4*) showed that the total vanadium content is 56.2% (calcd. for $LiVO_2$ is 56.67%) and the average oxidation state of vanadium is 3.02. An X-ray powder diffraction pattern of the sample (Fig. 1a) recorded using Ni-filtered CuK_α radiation could be indexed on a hexagonal cell with $a = 2.84$ and $c = 14.79$ Å. The values of a and c reported for $LiVO_2$ in the literature (*5*) are 2.85 and 14.70 Å, respectively.

We carried out preliminary experiments of oxidation of $LiVO_2$ using I_2 and Br_2 in CH_3CN medium, since the former is known to oxidize $LiVS_2$ to VS_2 (*6*). These experiments showed that, while there was no oxidation with I_2, Br_2 in CH_3CN did oxidize $LiVO_2$ to Li_xVO_2. However, there was considerable dissolution of the product as indicated by the green color of the solution. We found that the oxidation by Br_2 can be carried out neatly in $CHCl_3$ medium.

The following method was used for the preparation of Li_xVO_2 with different values of x. Known amounts of $LiVO_2$ (about 2 g), taken in stoppered bottles, were mixed with the required volumes of 0.05 *N* Br_2 in $CHCl_3$ to give Li_xVO_2 with $x = 0.75$, 0.50, 0.25, and 0.00. The bottles were kept in the dark with periodical stirring. The reactions yielding $Li_{0.75}VO_2$ and $Li_{0.5}VO_2$ were complete in 1 and 3 days, respectively (as indicated by the disappearance of bromine color). Products with smaller values of x required prolonged reaction. After the reaction, the solid products were filtered off, washed with CH_3CN (to remove LiBr), and vacuum-dried. Total vanadium content and its oxidation state in the samples were determined as before.

Results and Discussion

Chemical analysis of Li_xVO_2 (Table I) shows that delithiation of $LiVO_2$ occurs as expected, resulting in an increase of the oxidation state of vanadium. For preparations of Li_xVO_2 with $x = 0.75$ and 0.50, the oxidation state of vanadium is slightly more

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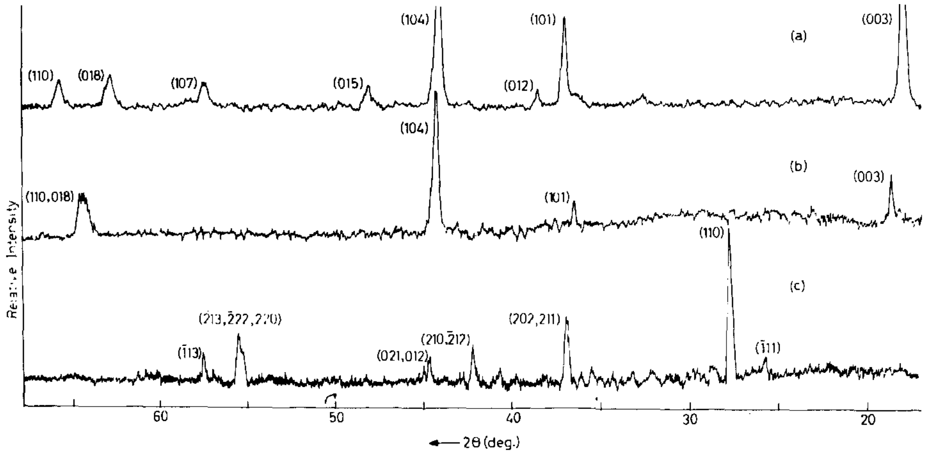

FIG. 1. X-Ray powder diffraction patterns of (a) $LiVO_2$, (b) $Li_{\sim 0.1}VO_2$, and (c) monoclinic VO_2.

than expected; with $x = 0$, the reaction is incomplete even after 20 days, and the composition of the product is $Li_{\sim 0.1}VO_2$.

The X-ray powder diffraction patterns (Fig. 1) of Li_xVO_2 for different values of x are similar to $LiVO_2$ and could be indexed on the hexagonal cell (Table I). This reveals that the delithiation

$$LiVO_2 + (1 - x)/2\ Br_2 \rightarrow Li_xVO_2 + (1 - x)\ LiBr$$

occurs topochemically, retaining the parent structure of $LiVO_2$. With decreasing value of x in Li_xVO_2, there is a marked decrease in the c axis, while the a axis increases slightly. Moreover, as delithiation proceeds, the diffraction patterns become poorer, showing the disappearance of weak lines. In addition, the intensity of the (003) line steadily decreases with decreasing lithium content.

Complete removal of lithium from $LiVO_2$ would result in a new modification of VO_2 having the $CdCl_2$ structure. We prepared a sample of VO_2 by treating $LiVO_2$ with excess Br_2 in $CHCl_3$ for 14 days. Chemical analysis indicated that the oxidation state of vanadium in this sample is close to 4+. This sample, is, however, found to be X-ray

TABLE I

CHEMICAL ANALYSIS AND LATTICE PARAMETERS OF Li_xVO_2

Composition expected	Total vanadium (%)	Oxidation state of vanadium	Composition obtained	Lattice parameter (Å)	
				a	c
$LiVO_2$	56.2	3.02	$LiVO_2$	2.84	14.79
$Li_{0.75}VO_2$	55.6	3.35	$Li_{0.65}VO_2$	2.84	14.80
$Li_{0.5}VO_2$	57.8	3.55	$Li_{0.45}VO_2$	2.86	14.54
$Li_{0.25}VO_2$	58.2	3.75	$Li_{0.25}VO_2$	2.89	14.31
VO_2	56.0	3.90	$Li_{\sim 0.1}VO_2$	2.89	14.24

amorphous and, on heating in an evacuated tube at 450°C for 4 days, transforms to monoclinic VO_2 (Fig. 1c).

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