

## Sodium Intercalation into $\text{WO}_2\text{Cl}_2$

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Sodium has been intercalated into the layered host  $\text{WO}_2\text{Cl}_2$ . This has been achieved using a new chemical intercalating agent, the di-*t*-butylphenoxide,  $\text{Na-O-2,6-Bu}'_2\text{C}_6\text{H}_3$ , which is easily prepared and may be stored until required. Up to one sodium per formula unit has been inserted and two new phases identified. Possible structural models for the new phases are discussed. © 1990 Academic Press, Inc.

### Introduction

Sodium intercalation into inorganic hosts has received less attention than that of lithium. This is due to three main factors: first, the long-standing technological interest in developing new lithium intercalation compounds as cathodes for rechargeable batteries based on this metal; second, whereas the small  $\text{Li}^+$  ion may readily intercalate into many simple compounds with close-packed structures this is not the case for the larger  $\text{Na}^+$  ion; and third, the wide availability of the lithium intercalating reagent, *n*-butyl lithium, in contrast to the lack of equivalent and convenient sources for the chemical intercalation of sodium.

While intercalation of guest species into oxide and halide host structures has been extensively investigated (1-3), reports of intercalation into mixed-anion oxyhalide systems are relatively rare (4, 5). The oxyhalides which have received most attention to date are those based on trivalent transition metal cations,  $\text{MOCl}$  where  $M$  may be Ti, V, Cr, or Fe (4). These oxyhalides crystallize with a layered structure and intercalation occurs between adjacent sheets of van der Waals bonded chloride ions. More recently, it has been shown that lithium may be intercalated into another oxyhalide  $\text{WO}_2\text{Cl}_2$  (6). This compound also possesses a layered structure but the structure differs from that of the  $\text{MOCl}$  phases. Up to two lithiums may be inserted, yielding a compound  $\text{Li}_2\text{WO}_2\text{Cl}_2$ , which appears to retain the basic structure of the parent tungsten oxychloride.

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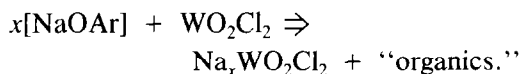
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In this paper we report on sodium intercalation into WO<sub>2</sub>Cl<sub>2</sub>, presenting both structural and electrochemical data on the intercalated materials. The insertion of sodium is achieved by a chemical route using a sodium phenoxide. As far as we are aware this is the first report of the use of such an intercalating agent.

### Experimental

Where necessary, all manipulations of air-sensitive materials were carried out in an argon-filled Mbraun glove box, the atmosphere being continuously cycled through columns of molecular sieves and oxygen catalysts. It is essential to maintain the lowest possible humidity when handling sodium metal as was necessary during the assembly of the electrochemical cells used in this work. Therefore the water and oxygen levels were constantly monitored and both maintained at less than 1 ppm.

Tungsten dioxidichloride (Alfa, 99%) was used as received. Na-O-2,6-Bu'<sub>2</sub>C<sub>6</sub>H<sub>3</sub> was prepared by treatment of HO-2,6-Bu'<sub>2</sub>C<sub>6</sub>H<sub>3</sub> with metallic sodium (7). Chemical intercalation was carried out using the sodium di-*t*-butylphenoxide [NaOAr] according to the following reaction



It is assumed that the Na-O bond cleaves heterolytically to yield a Na<sup>+</sup> ion and a di-*t*-butylphenoxide ion which, in the proximity of a WO<sub>2</sub>Cl<sub>2</sub> particle, donates its electron to the conduction band of the solid as the Na<sup>+</sup> ion simultaneously enters the structure. Evidence for the “organics” produced during the reaction is provided by <sup>1</sup>H NMR spectroscopy on the organic products. A 50:50 mixture of HO-2,6-Bu'<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and the biphenol is observed, suggesting that the 2,6-di-*t*-butylphenoxy radical is formed, which then undergoes para C-C coupling

followed by enolization of the resultant dimer to give the biphenol. Such rearrangements of phenoxy radicals are well documented (8). In practice, chemical intercalation at ambient temperature requires a solvent which is capable of dissolving the intercalating agent but not the host. Unfortunately, polar solvents suitable for dissolution of the phenoxide intercalate into the layered WO<sub>2</sub>Cl<sub>2</sub> and cleave the compound. In our studies toluene was found to act as a suitable medium for intercalation. The tungsten dioxidichloride appears to be insoluble in this solvent whereas sodium di-*t*-butylphenoxide exhibits at least partial solubility. The reaction therefore proceeds in the presence of solid Na-O-2,6-Bu'<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, a solution of this phenoxide in toluene and solid WO<sub>2</sub>Cl<sub>2</sub>. The toluene (BDH, Analar Grade) was rigorously dried over freshly activated molecular sieves prior to use. A mixture of approximately 40 ml of toluene, 0.3 g of WO<sub>2</sub>Cl<sub>2</sub>, and an appropriate amount of phenoxide was continuously and vigorously stirred for 4 days at room temperature under argon. On standing, the intercalated material settled out quickly, allowing the remaining suspension to be decanted off. The solid intercalate was then washed several times with anhydrous toluene and finally dried under vacuum. Analysis for C and H indicated the absence of organic material in the product and in particular that toluene is not present in any significant quantity within the Na<sub>x</sub>WO<sub>2</sub>Cl<sub>2</sub> particles.

The resulting solids were characterized by atomic absorption spectroscopy using a Pye-Unicam SP9 spectrometer. Na<sub>x</sub>WO<sub>2</sub>Cl<sub>2</sub> was dissolved in boiling concentrated H<sub>2</sub>SO<sub>4</sub>. A solid precipitated out on cooling which was dissolved by addition of a concentrated solution of NH<sub>4</sub>OH. X-ray diffraction was undertaken in sealed capillary tubes using a Stöe-Guinier camera and CuKα radiation. Ten different compositions were prepared and examined.

Electrochemical measurements were

carried out using two electrode cells. Because of the instability of the oxychlorides toward polar solvents, conventional non-aqueous electrolytes, such as  $\text{NaClO}_4$  in propylene carbonate, could not be used; instead, a solid polymer electrolyte  $[(\text{CH}_2-\text{CH}_2-\text{O})_n]:\text{NaClO}_4$  with an ether oxygen to sodium ratio of 20:1 was employed. The polymer, polyethylene oxide (BDH, m.wt = 5 million) was dried under vacuum at  $55^\circ\text{C}$  for 2 days. The salt,  $\text{NaClO}_4$ , (Aldrich, 99%) was dried by heating under vacuum at  $180^\circ\text{C}$  for approximately 7 hr. Both salt and polymer were then dissolved in dry acetonitrile (Aldrich, 99%, anhydrous, Gold Label) and films of the electrolyte cast in Teflon molds by slow evaporation of the acetonitrile from the mixture. Subsequently the films were heated under vacuum at  $80^\circ\text{C}$  for 2 days to ensure removal of any traces of acetonitrile. The intercalation cathode was prepared by pressing approximately 7 mg of  $\text{Na}_x\text{WO}_2\text{Cl}_2$  onto a stainless steel grid. The sodium anode was formed by rolling out a section of sodium metal cut from an ingot (Johnson-Matthey, 99.95%). Teflon-bodied cells with stainless steel electrode contacts were used; these have been described previously (9). The intercalation cathode and sodium anode were separated by two  $100\text{-}\mu\text{m}$  thick disks of the polymer electrolyte; this sandwich is then placed between the stainless steel contacts and pressure applied axially to ensure good contact between the electrodes and the electrolyte. The cell is mounted in a gas-tight stainless steel chamber fitted with electrical breakthroughs and a thermocouple; this permits the electrochemical measurements to be made with the cells removed from the glove box. The open circuit voltage measurements were carried out at  $80^\circ\text{C}$  to ensure a sufficiently high electrolyte conductivity. This was achieved by placing the cells in thermostated oil baths in which the temperature could be maintained within  $\pm 0.5^\circ\text{C}$ . Open

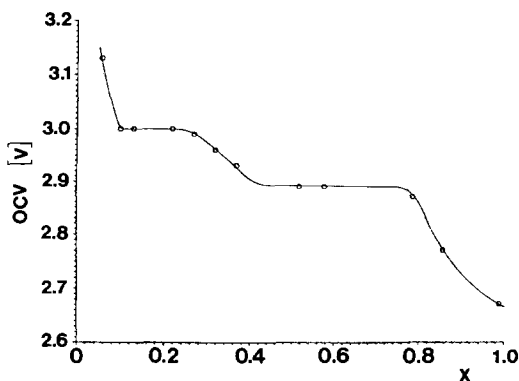


FIG. 1. Variation of the open circuit voltage, ocv, with sodium content  $x$  for  $\text{Na}_x\text{WO}_2\text{Cl}_2$  at  $80^\circ\text{C}$ . The voltages are measured with respect to a sodium electrode.

circuit voltages were measured by connecting cells to a Schlumberger 1286 electrochemical interface.

## Results and Discussion

The variation of open circuit voltage, ocv, with sodium content,  $x$ , is presented in Fig. 1. Considering the changes in ocv with increasing  $x$ , the following conclusions may be drawn. Up to a value of  $x = 0.1$  sodium appears to intercalate without disrupting the host  $\text{WO}_2\text{Cl}_2$  structure. Within the composition range  $0.1 < x < 0.25$  two phases coexist, one possesses the parent  $\text{WO}_2\text{Cl}_2$  structure whereas the other is a new phase, the ideal composition of which is believed to be  $\text{Na}_{0.25}\text{WO}_2\text{Cl}_2$ , as discussed below. The continuous decrease in voltage with increasing  $x$  in the range  $0.25 < x < 0.4$  suggests that this new phase has a narrow range of stoichiometry. At a higher sodium content a two-phase region is again obtained extending from  $x \approx 0.4$  to  $x \approx 0.8$  composed of a phase with the structure of the  $\text{Na}_{0.25}\text{WO}_2\text{Cl}_2$  compound and a second new, sodium rich phase. Above  $x = 0.8$  the continuous decrease in ocv indicates that the second phase

TABLE I

$\text{Na}_{0.25}\text{WO}_2\text{Cl}_2$  PRIMITIVE ORTHORHOMBIC CELL,  $a = 7.400$  (4) Å,  $b = 7.580$  (5) Å,  $c = 15.435$  (1) Å

$hkl$	$d_{\text{calc}}$ (Å)	$d_{\text{obs}}$ (Å)	$I$
002	7.717	7.714	vs
004	3.859	3.858	m
020	3.790	3.792	m
202	3.336	3.337	m
204	2.671	2.675	w
220	2.648	2.645	m
106	2.430	2.429	m
131	2.363	2.362	m
116	2.313	2.311	m
400	1.850	1.850	w
036	1.803	1.804	w

TABLE II

$\text{NaWO}_2\text{Cl}_2$  PRIMITIVE TETRAGONAL CELL,  $a = 3.799$  (1) Å,  $c = 15.726$  (1) Å

$hkl$	$d_{\text{calc}}$ (Å)	$d_{\text{obs}}$ (Å)	$I$
002	7.862	7.889	vs
004	3.931	3.946	s
010	3.799	3.793	vs
011	3.693	3.696	vs
012	3.421	3.415	s
013	3.076	3.077	m
111	2.648	2.650	vs
006	2.621	2.622	vs
115	2.043	2.043	s
008	1.966	1.967	s
020	1.900	1.899	s
022	1.847	1.845	m
0010	1.572	1.571	m

also exists over a range of compositions  $0.8 < x < 1.0$  but with an ideal composition  $\text{NaWO}_2\text{Cl}_2$ , as also discussed below.

Using the sodium di-*t*-butylphenoxide we have not succeeded in intercalating more than one sodium per  $\text{WO}_2\text{Cl}_2$ ; however, preliminary results using a more strongly reducing intercalating agent, *n*-butyl sodium (prepared following the procedure in Ref. (10)), indicate that up to two sodiums may be intercalated. Further work is required to characterize the composition range  $1 < x < 2$ .

Interpretation of the variation in open circuit voltage with composition is corroborated by our X-ray diffraction measurements. Reflections corresponding to two new phases may be identified. The  $d$ -spacings for each were extracted from the powder diffraction data and indexed using the program TREOR, and the lattice parameters were then refined using POWREF. The unit cell parameters obtained following this procedure are presented for each phase in Tables I and II, along with a list of the observed and calculated  $d$ -spacings for the most intense lines.

A structural model for the host compound  $\text{WO}_2\text{Cl}_2$  has been proposed on the basis of single crystal X-ray diffraction measure-

ments (11). The structure may be derived from that of tetragonal  $\text{SnF}_4$ , which itself consists of  $\text{SnF}_2$  layers between which are located layers of F atoms (12). In  $\text{WO}_2\text{Cl}_2$ , Fig. 2, the  $\text{SnF}_2$  layers are replaced by those of  $\text{WO}_2$ , and above and below these layers are located sheets of Cl atoms, thus forming a  $\text{Cl}(\text{WO}_2)\text{Cl}$  tri-layer block. Each tungsten

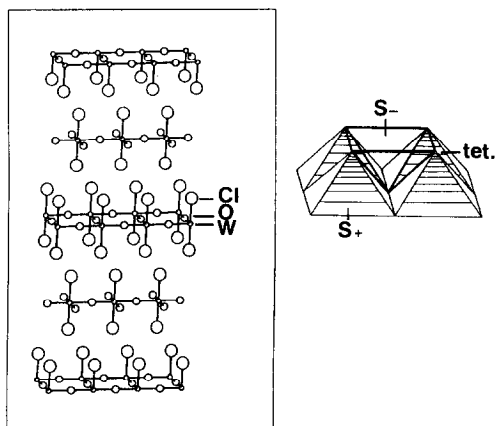


FIG. 2. An idealized model for the structure of  $\text{WO}_2\text{Cl}_2$ , derived from that of  $\text{SnF}_4$ . The cation sites available between each pair of adjacent chlorine layers are shown on the right of the diagram.

is coordinated by a square planar arrangement of oxygens within the  $\text{WO}_2$  layer, with each square being connected by sharing common corners. The octahedral coordination of tungsten is completed by one chlorine from each of the adjacent layers in the block. The blocks are stacked in the  $c$  direction, thus forming the overall three dimensional structure by van der Waals bonding between adjacent chlorine layers. According to Jarchow (11) the W, O, and Cl atoms are displaced from their ideal  $\text{SnF}_4$  positions and the tetragonal symmetry is lowered to that of monoclinic with space group  $Aa$ , and unit cell parameters  $a = 7.68 \text{ \AA}$ ,  $b = 3.89 \text{ \AA}$ ,  $c = 14.42 \text{ \AA}$ ,  $\beta = 105.4^\circ$ . An alternative body-centered orthorhombic unit cell has been reported to fit the  $d$ -spacings observed by powder X-ray diffraction (13). We have confirmed that both the monoclinic and smaller orthorhombic cells fit the  $d$ -spacings obtained from powder X-ray diffraction equally well. The orthorhombic cell ( $a = 3.847 \text{ \AA}$ ,  $b = 3.888 \text{ \AA}$ ,  $c = 13.885 \text{ \AA}$ ) is compatible with a somewhat less-distorted structure than that reported by Jarchow. The single crystal structure determination was complicated by the presence of polytypic twinning; it may be that the structure is in fact less distorted than they assume, alternatively the distortions may simply be difficult to detect in the powder X-ray pattern.

In the absence of further information we assume that the basic layered structure of  $\text{WO}_2\text{Cl}_2$  is correct, recognizing that the nature of the minor distortions may require further investigation. Comparison of the crystallographic data in Tables I and II with that for the host compound, particularly the orthorhombic cell for  $\text{WO}_2\text{Cl}_2$ , indicates that the layered structure is maintained on intercalation. The sodium ions intercalate between adjacent van der Waals bonded chlorine layers. For every  $\text{WO}_2\text{Cl}_2$  formula unit there are two tetrahedral and two square

pyramidal sites between the chlorine layers which are available for occupation by cations (Fig. 2). On the basis of Jarchow's structure, the distance from a vertex of a tetrahedral site to its center is approximately  $2.25 \text{ \AA}$ . For a square pyramidal site an average value of  $2.73 \text{ \AA}$  may be estimated for the distance between the center of the base and a basal vertex, and a value of  $2.45 \text{ \AA}$  for the height of the pyramid. Comparing these site sizes with the bond length in sodium chloride,  $2.82 \text{ \AA}$ , it is reasonable to suggest that sodium ions enter the larger square pyramidal sites. On intercalation the  $c$ -axis expands significantly, corresponding primarily to an increased separation between adjacent chloring layers and consequently an increase in the height of each pyramidal site, thus better accommodating the  $\text{Na}^+$  ion.

The square pyramidal sites located between adjacent chloride layers may be divided into two sets, each with their apices pointing in opposite direction perpendicular to the layers. We designate the two sets of sites as  $S_+$  and  $S_-$  respectively, Fig. 2. All the square pyramids of one set of sites are connected by sharing common edges belonging to the base of the pyramids only. In contrast, connection between  $S_+$  and  $S_-$  pyramids occurs via edges which link the base of each pyramid to its apex. The distances between the centers of neighbouring  $S_+$  or  $S_-$  sites is greater than that between a  $S_+$  and a neighboring  $S_-$  site. Full occupancy of either the  $S_+$  or the  $S_-$  sites between each pair of chloride layers would correspond to the composition  $\text{NaWO}_2\text{Cl}_2$ . Alternatively the same composition is obtained by fully occupying all the  $S_+$  and  $S_-$  square pyramidal sites between alternate pairs of chloride ion layers; this would correspond to a stage-two structure. The latter model would destroy the body centering whereas the occupancy of only  $S_+$  or  $S_-$  between pairs of chloride layers would not.

We tentatively suggest that the primitive tetragonal sodium rich phase is a stage-two structure with ideal composition  $\text{NaWO}_2\text{Cl}_2$ . Comparing the tetragonal lattice parameters of this phase with the orthorhombic parameters for  $\text{WO}_2\text{Cl}_2$  it may be noted that contraction occurs in the  $a$ - $b$  plane, whereas the insertion of  $\text{Na}^+$  between the Cl-layers causes expansion along the  $c$ -axis.

The more sodium-deficient phase possesses an orthorhombic structure with approximately double the  $a$  and  $b$  axes of the orthorhombic cell for  $\text{WO}_2\text{Cl}_2$ . This is consistent with an ideal composition for this phase of  $\text{Na}_{0.25}\text{WO}_2\text{Cl}_2$  corresponding to a 50% occupancy of one set of square pyramidal sites between alternate pairs of chlorine layers in an ordered fashion in the  $a$ - $b$  plane. Such ordering would ensure only corner sharing between occupied square pyramidal sites, which minimizes  $\text{Na}^+$  repulsions and leads to a doubling of the  $a$  and  $b$  axes. The  $c$  lattice parameter is slightly smaller than that of  $\text{NaWO}_2\text{Cl}_2$ . These structural interpretations of the X-ray data for the two new phases are at this stage tentative. It is possible only to show that certain plausible models are consistent with the data presently available. It is hoped that more detailed structural work using single crystal X-ray or powder neutron diffraction will be undertaken in the future to determine the location of sodium and its ordering in these new intercalation compounds.

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