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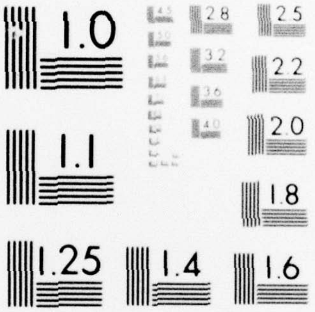

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The photoelectrolytic behavior of WO_{3-x} and $WO_{3-x}F_x$ has been investigated and both the magnitude of the photocurrents and the relative stability of the two compounds were determined. It was found that WO_{3-x} gives a much higher photocurrent than stoichiometric WO_3. The substitution of fluorine for oxygen, rather than the creation of oxygen defects, increases the stability of the electrode. There is an optimum amount of substituted fluorine which results in a maximum photocurrent.

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TECHNICAL REPORT NO. 1

TUNGSTEN OXYFLUORIDE PHOTOANODES

by

C. E. Derrington, C. A. Castro, W. Godek, R. L. Sanchez, and A. Wold

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TUNGSTEN OXYFLUORIDE PHOTOANODES

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ABSTRACT

The photoelectrolytic behavior of WO_{3-x} and $WO_{3-x}F_x$ has been investigated and both the magnitude of the photocurrents and the relative stability of the two compounds were determined. It was found that WO_{3-x} gives a much higher photocurrent than stoichiometric WO_3. The substitution of fluorine for oxygen, rather than the creation of oxygen defects, increases the stability of the electrode. There is an optimum amount of substituted fluorine which results in a maximum photocurrent.

INTRODUCTION

The use of WO_3 as a stable electrode in photoelectrolysis has been reported by several investigators. Butler, Nasby, and Quinn (1) have indicated that WO_3 is an n-type semiconductor with a band gap of 2.7 eV. Experiments performed with single crystals indicated that whereas there is an increase in the utilizable solar energy compared to TiO_2, WO_3 required an applied potential of several tenths of a volt in solution of pH < 7 in order to obtain a measurable photocurrent. In a 1M sodium acetate solution (pH = 8.7), a photocurrent was observed at zero bias. All potential measurements were taken vs a standard calomel electrode. Hodes, et al. (2) prepared polycrystalline anodes of WO_3 by either the decomposition of ammonium tungstate or oxidation of tungsten metal films. The results of this study were consistent with those reported on single crystal samples.

Hardee and Bard (3) have prepared WO_3 by three different methods. Unfortunately, their electrode surfaces were deep blue rather than yellow or yellow-green. This difference in coloration is indicative of the existence of either defect compounds of the type WO_{3-x} or hydrogen bronzes, H_xWO_3. Therefore, there seems to be some question as to the composition of the materials they studied.

It was therefore desirable to examine more closely the photoelectrolytic behavior of WO_{3-x}. It was also of interest to determine the effect on stability of substituting fluorine for oxygen in WO_3 rather than the creation of defects. There appears to be some question as to the long-term stability of defect oxides under strongly oxidizing conditions.

System WO_{3-x}. Samples of WO_3 films were prepared by heating tungsten foils in a stream of oxygen at 1000°C for 24 hours. Under these conditions foils of .010" thickness were completely oxidized. Defect compounds were obtained by heating the WO_3 films in evacuated sealed silica tubes in the presence of titanium turnings. The titanium was not in direct contact with the films. This technique is described by D. Schleich, et al. (4). When oxygen is removed from WO_3 films the color of these films changes from yellow to dark green and eventually to black. The resistivity of these films decreases as a function of defect concentration. When the resistivity is of the order of 300 Ωcm, the WO_{3-x} films can be used as anodes and the photocurrents observed by Hardee and Bard are consistent with the values obtained from samples with the composition WO_{3-x}. The magnitude of the photocurrents from such samples is much higher than those obtained for stoichiometric WO_3 anodes.

It is interesting to note that even if the compounds reported by Hardee and Bard were hydrogen bronzes (as indicated by their blue color) the photocurrents would be expected to be much higher than those obtained from stoichiometric WO_3 because the resistivity of the bronzes would be much reduced. The properties of WO_3 samples obtained by various investigators are summarized in Table 1. Using a Cahn electrobalance and standard T.G.A. techniques the value of x was determined to be less than 0.01.

$\underline{WO_{3-x}F_x}$. Samples of $WO_{3-x}F_x$ were prepared by placing a WO_3 film on a clean tungsten strip which was in a tungsten boat. The boat was then introduced into an inconel tube which was heated at 650°C and a stream of HF was passed over the sample. The HF was obtained by the thermal decomposition of bifluoride salts. The preparative details will be published elsewhere. Table 2 summarizes the preparative conditions, and the properties of the oxyfluorides obtained. The structural properties as a function of fluorine content are given in Table 3. It can be seen that an increase in the fluorine content results in a change from a monoclinic to an orthorhombic structure. These results are consistent with previous studies by Sleight (5) and Reynolds and Wold (6). The fluorine content was determined by a specific ion sensitive electrode and is summarized in Table 4.

The cell used for the photocurrent measurements is shown in Figure 1. It is essential that constant stirring of the electrolyte around both electrodes be maintained in order to assure stable photocurrent measurements. The light source was a 150 Watt high pressure xenon lamp (XBO-150). In Figure 2 a comparison is made of the photocurrents obtained for electrodes containing varying amounts of fluorine. The measurements were made in a 0.2M sodium acetate solution (pH = 7.8). It can be seen that there is an optimum value of fluorine substitution (x = .0079) and that higher values of x results in a decrease in the photocurrent obtained. Figure 3 compares the photocurrents obtained from samples of stoichiometric WO_3, WO_{3-x}, and $WO_{3-x}F_x$.

Finally, stability was ascertained for both the WO_{3-x} and $WO_{3-x}F_x$ electrodes by two methods. The electrodes were heated at 100°C/hour from room temperature to 1000°C and the weight change was monitored during this period. Figure 4 compares the results obtained for WO_3, WO_{3-x} ($x < 0.01$), $WO_{2.97}$ and $WO_{3-x}F_x$ ($x = 0.01$). There appears to be a marked difference in the stability of $WO_{3-x}F_x$ electrodes compared to those with a composition of WO_{3-x}.

In order to determine if this increased stability could be observed under the operating conditions of the cell, the various fluorinated electrodes were operated for periods up to 46 hours at currents of $1 mA/cm^2$ and weight measurements were made to determine the extent of solution of the electrode. There was no significant weight change of the electrodes, the photocurrent remained stable and there was no visible change in the electrode surface when viewed with a light microscope.

CONCLUSIONS

The photoelectrolytic behavior of WO_{3-x} and $WO_{3-x}F_x$ has been investigated and the relative stability of the two compounds was determined. It was found that WO_{3-x} ($x < 0.01$) gives a much higher photocurrent than stoichiometric WO_3. The substitution of fluorine for oxygen rather than creating oxygen defects increases the stability of the electrode. It can be seen from the data of Figure 3, that there is an optimum amount of substituted fluorine ($x = 0.0079$) which results in a maximum in photocurrent. Increasing the fluorine content beyond this value results in a decrease in the photocurrent.

ACKNOWLEDGEMENTS

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6. T. G. Reynolds and A. Wold, J. Solid State Chem., 6, 565 (1973).

TABLE 1

Properties of WO_3

Investigators	Preparation	Color	ρ (Ω cm)
Butler et. al.	Single crystals (CVT)	Green	~ 170
Hodes et. al.	Oxidation of metal decomposition of ammonium tungstate	Yellow	-
Hardee and Bard	Oxidation of metal chemical vapor decomposition solution evaporation	Deep Blue	-
This work	Oxidation of metal at [illegible]°C for 24 hrs. under flowing O_2	Yellow	10^6
This work	WO_{3-x} prepared by heating WO_3 film in sealed silica tube in presence of Ti turnings.	Dark Green	300

TABLE 2

Preparation of $WO_{3-x}F_x$

Sample	T,°C Fluorinating Agent	T,°C, WO_3	ρ	Color
#214	350°C	650°C	55 Ωcm	Light Green
#215	400°C	650°C	32 Ωcm	Green
#216	450°C	650°C	25 Ωcm	Dark Green
#216B	500°C	650°C	6 Ωcm	Blue-Black

TABLE 3

Structural Properties

Sample	a_o	b_o	c_o	α	β	γ
WO_3	7.285	7.517	3.835	90°	90.90°	90°
#214		MIXED PHASES				
#216	7.311	7.540	3.851	90°	90.88°	90°
#216B	7.369	7.403	3.848	90°	90°	90°

TABLE 4

ANALYTICAL DATA

SAMPLE	%F
#214	0.79%
#215	0.82%
#216	1.77%
#216B	6.63%

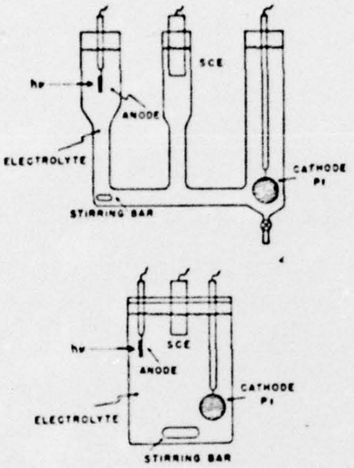

FIGURE 1

Photocell arrangement used to measure Photocurrents of WO_3, WO_{3-x}, and $WO_{3-x}F_x$. Both cells were constructed with quartz.

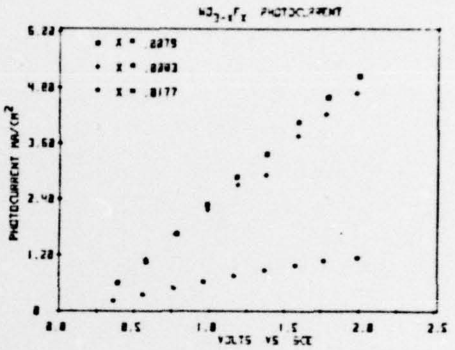

FIGURE 2

Photocurrent vs Applied Bias of Electrodes of $WO_{3-x}F_x$ containing various amounts of fluorine in 0.2 M Sodium Acetate (pH=7.8).

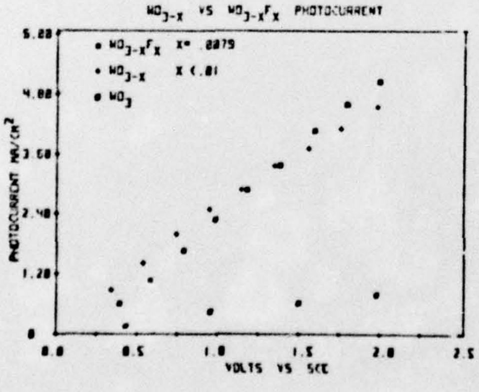

FIGURE 3

Photocurrent vs Applied Bias of WO_3, WO_{3-x}, and $WO_{3-x}F_x$ in 0.2 M Sodium Acetate (pH=7.8).

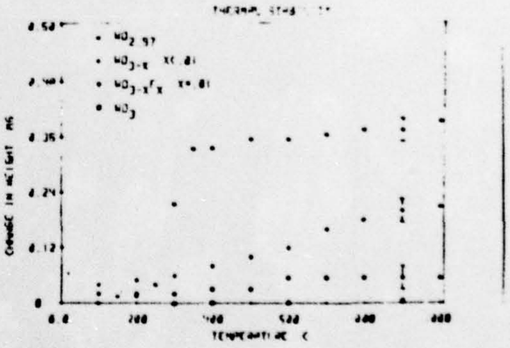

FIGURE 4

Relative Thermal Stability of $WO_{2.97}$, WO_{3-x}, $WO_{3-x}F_x$, and WO_3 in flowing O_2.

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