



ELSEVIER

Journal of Power Sources 97–98 (2001) 545–547

JOURNAL OF  
POWER  
SOURCES

www.elsevier.com/locate/jpowsour

# Promising thin films ( $\text{WO}_{1.05}\text{S}_2$ and $\text{WO}_{1.35}\text{S}_{2.2}$ ) as positive electrode materials in microbatteries

I. Martin-Litas<sup>a,\*</sup>, P. Vinatier<sup>a</sup>, A. Levasseur<sup>a</sup>, J.C. Dupin<sup>b</sup>, D. Gonbeau<sup>b</sup>

<sup>a</sup>Institut de Chimie de la Matière Condensée de Bordeaux, CNRS and Ecole Nationale Supérieure de Chimie et Physique de Bordeaux Avenue Pey Berland, BP 108, 33402 Talence Cedex, France

<sup>b</sup>Laboratoire de Physico — Chimie Moléculaire (UMR 5624), Université de Pau et des Pays de l'Adour, 2, Avenue du président Angot, 64053 Pau Cedex 9, France

Received 6 June 2000; received in revised form 17 January 2001; accepted 22 January 2001

## Abstract

Tungsten oxysulfide thin films ( $\text{WO}_y\text{S}_z$ ) have been prepared by reactive radio-frequency magnetron sputtering using a  $\text{WS}_2$  target and a mixture of argon and oxygen gas. The composition, the texture and the structure depend on the sputtering parameters, such as the oxygen partial pressure and the total pressure ( $\text{Ar} + \text{O}_2$ ). For a total pressure of 1 Pa, the range of the chemical composition is wide, from  $\text{WS}_2$  when no oxygen gas is introduced in the chamber, to  $\text{WO}_3\text{S}_{0.02}$  when the oxygen partial pressure is equal to  $10^{-2}$  Pa. Two amorphous thin films ( $\text{WO}_{1.05}\text{S}_2$  and  $\text{WO}_{1.35}\text{S}_{2.2}$ ) have given promising electrochemical performances as positive electrode in the cell:  $\text{Li}/\text{LiAsF}_6$ , 1 M  $\text{EMC}/\text{WO}_y\text{S}_z$  with a current density up to  $37 \mu\text{A}/\text{cm}^2$  between 1.6 and 3 V. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Reactive RF magnetron sputtering; Thin film cathodes; Lithium batteries; Tungsten oxysulfide

## 1. Introduction

Several studies on the cathode materials have been realised to improve the electrochemical performances of microbatteries for their use in the microelectronics devices. Some well-known materials used as positive electrode in lithium-ion batteries as  $\text{LiMn}_2\text{O}_4$  [1–3],  $\text{V}_2\text{O}_5$  [4,5],  $\text{LiCoO}_2$  [6–8] and  $\text{TiS}_2$  [9], have been prepared in the form of thin film by various deposition methods. In order to make possible their integration in electronic circuits, studies on the preparation of thin film cathodes at low temperature have been undertaken. Shokoohi et al. [10] have studied  $\text{LiMn}_2\text{O}_4$  thin films obtained by postdeposition annealing at temperatures below  $400^\circ\text{C}$ . In the same way, as-deposited thin film materials have been tested by Birke et al. [11].

Some of the authors of this paper have for a long time undertaken study of new thin films which can be used in microbatteries: titanium and molybdenum oxysulfide films ( $\text{TiO}_y\text{S}_z$  and  $\text{MoO}_y\text{S}_z$ ) [12–14]. These films have been deposited by reactive radio-frequency magnetron sputtering. The electrochemical behaviour of the cells tested with these

films depends on their oxygen content. Our interest has turned to the study of new tungsten oxysulfide thin films [15] elaborated on not heated substrates. The cells tested between 1.6 and 3 V could be used in microelectronics devices because it has been shown that many electronic components operate at lower voltage. In this paper, we will discuss the electrochemical performances of two thin films used as positive electrode ( $\text{WO}_{1.05}\text{S}_2$  and  $\text{WO}_{1.35}\text{S}_{2.2}$ ).

## 2. Experimental

The tungsten oxysulfide thin films have been prepared by reactive radio-frequency magnetron sputtering with a target made of a commercial powder of  $\text{WS}_2$  (Cerac-99.8%). The polycrystalline material has been pressed at 250 MPa to make a pellet of 5 cm in diameter and nearly 3 mm thick. Before beginning the sputtering deposition a vacuum of  $2 \times 10^{-5}$  Pa has been obtained in the chamber. Then the oxygen gas (99.5% pure) has been introduced. The discharge gas was a mixture of argon (99.995% pure) and oxygen and the total pressure was 1 Pa. The target-substrate distance and the power have been fixed at, respectively, 7 cm and 25 W. During the sputtering the substrates have not been heated. The films have been deposited during 1 h on stainless steel substrates of 1.3 cm in diameter. The substrates have been

\* Corresponding author. Tel.: +33-556-842726; fax: +33-556-846698.  
E-mail address: vinatier@icmcb.u-bordeaux.fr (I. Martin-Litas).

previously polished with four different sandpapers (from 800 to 4000). The cathode materials have been prepared with two oxygen partial pressures of  $10^{-3}$  and  $2 \times 10^{-3}$  Pa. To avoid a possible contamination of the films the sputtering machine is connected to a glove box with an argon atmosphere (99.95% pure).

Two different thin films have been obtained and tested (with a current density of  $37 \mu\text{A}/\text{cm}^2$ ) in a cell with a liquid electrolyte: Li/LiAsF<sub>6</sub>, EMC 1 M/WO<sub>y</sub>S<sub>z</sub>. The chemical composition of the films has been determined by Rutherford Backscattering Spectroscopy (RBS) using an incident beam of <sup>4</sup>He<sup>+</sup> ions (energy of 2 MeV). RBS analyses have been performed on films deposited on a vitreous carbon during 20 min.

The X-ray photoelectron spectroscopy (XPS) analyses have been performed using a Surface Sciences Instruments spectrometer (model 301) with a focused monochromatized Al K $\alpha$  radiation (1486.6 eV). The experimental curves were fitted with functions which are a combination of Gaussian (80%) and Lorentzian (20%).

### 3. Results and discussion

After 1 h of sputtering the films are 0.3  $\mu\text{m}$  thick. The RBS analysis results of the two films prepared with two different oxygen partial pressures ( $10^{-3}$  and  $2 \times 10^{-3}$  Pa) are given in Table 1. The compositions are, respectively, WO<sub>1.05</sub>S<sub>2</sub> and WO<sub>1.35</sub>S<sub>2.2</sub>. As expected when the oxygen partial pressure is higher, the oxygen content in the film increases. In order to be sure that the composition does not change through the film, an Auger electron spectroscopy (AES) analysis has been performed on the WO<sub>1.05</sub>S<sub>2</sub> film and has evidenced that the oxygen, the sulphur and the tungsten atomic ratios are constant in the whole film. X-ray diffraction and transmission electron microscopy studies have shown that the two tungsten oxysulfide thin films are amorphous as expected for deposition on not heated substrate. Furthermore up to now crystallised tungsten oxysulfide materials do not exist.

The films have been used as positive electrode materials in cells studied between 1.6 and 3 V with a current density of  $37 \mu\text{A}/\text{cm}^2$ . About 2 h of relaxation have been provided between each charge and discharge. Both cells have the same behaviour, so only the results of the battery made with the WO<sub>1.35</sub>S<sub>2.2</sub> film are presented.

Table 1

Composition determined by Rutherford Backscattering Spectroscopy (RBS) of two thin films deposited with two different oxygen partial pressures

Oxygen partial pressure (Pa)	Total pressure (Pa)	O/W	S/W	Film composition
$10^{-3}$	1	1.05	2.00	WO <sub>1.05</sub> S <sub>2</sub>
$2 \times 10^{-3}$	1	1.35	2.20	WO <sub>1.35</sub> S <sub>2.20</sub>

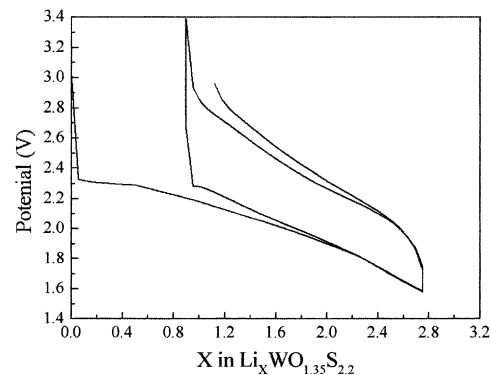


Fig. 1. Two first cycles for the cell Li/LiAsF<sub>6</sub>, EMC 1 M/WO<sub>1.35</sub>S<sub>2.2</sub>, with a current density of  $37 \mu\text{A}/\text{cm}^2$  between 1.6 and 3 V.

#### 3.1. Li/LiAsF<sub>6</sub>, EMC 1M/WO<sub>1.35</sub>S<sub>2.2</sub>

As shown in Fig. 1 the first cycle is not reversible for the WO<sub>1.35</sub>S<sub>2.2</sub> film: 2.75 lithium per tungsten are intercalated and 1.85 are de-intercalated. The initial discharge capacity is  $46 \mu\text{Ah}/\text{cm}^2$ . The evolution of the discharge capacity with the cycle number (Fig. 2a) shows that the capacity first decreases during 40 cycles then becomes constant and equal to  $13 \mu\text{Ah}/\text{cm}^2$  for the next ones. 0.8 lithium per tungsten can then be intercalated and de-intercalated reversibly. The reversibility of redox processes is good and the differential plot ( $-dx/dV$  versus V) confirms this behaviour. The derivative curve (Fig. 2b) between the cycle number 180 and 240 exhibits broad peaks at 1.9 and 2.4 V during, respectively, the discharge and the charge.

The cell with WO<sub>1.05</sub>S<sub>2</sub> as positive electrode exhibits the same behaviour as in the previous battery, the first cycle is not completely reversible but the next cycles are very well reversible, 0.6 lithium per tungsten can be reversibly intercalated and de-intercalated.

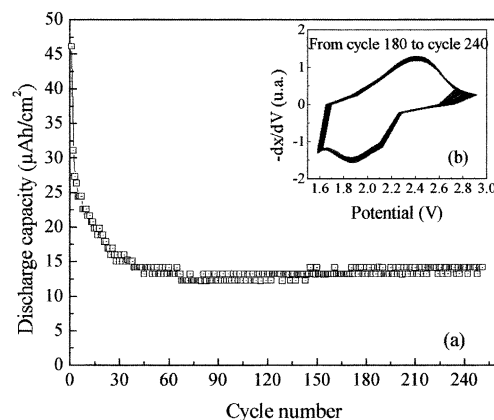


Fig. 2. WO<sub>1.35</sub>S<sub>2.2</sub> thin film used with a current density of  $37 \mu\text{A}/\text{cm}^2$  between 1.6 and 3 V: (a) variation of the discharge capacity ( $\mu\text{Ah}/\text{cm}^2$ ) vs the cycle number; (b) the derivative curve ( $-dx/dV$ ) vs the cell potential for the last cycles.

### 3.2. XPS (X-ray photoelectron spectroscopy) analysis

In order to understand the mechanisms involved during the discharge and the charge, an XPS study has been carried out. As previously reported for oxygen rich tungsten oxysulfide thin films [15], the tungsten atoms are characterised by three different formal oxidation states and three different environments:  $W^{4+}$  (doublet A) in a sulphur environment,  $W^{5+}$  (doublet B) in a mixed oxygen-sulphur environment ( $O^{2-}$ ,  $S_2^{2-}$  pairs and  $S^{2-}$ ) and  $W^{6+}$  (doublet C) in an oxygen environment.

Lithium intercalation and de-intercalation processes have been studied by XPS for the two thin films. As a more complete analysis has been carrying out for  $WO_{1.05}S_2$  thin films, this sole result is presented. The data obtained for intercalated ( $Li_1WO_{1.05}S_2$  and  $Li_{2.7}WO_{1.05}S_2$ ) and de-intercalated materials ( $Li_{1.6}WO_{1.05}S_2$ ) are reported in Fig. 3.

During the first stages of lithium intercalation ( $x = 1$ ), a small proportion of  $W^{6+}$  ions is reduced in  $W^{5+}$ ; simultaneously the  $S_2^{2-}$  pairs are partially reduced in  $S^{2-}$  ions. For a more intercalated material ( $Li_{2.7}WO_{1.05}S_2$ ), a new doublet noted G (31.9–34.0 eV) on the low energy side appears with the same binding energy as the one of metallic tungsten (31.5–33.7 eV), it is attributed to  $W^0$  species (tungsten with full d orbitals). The  $W^{6+}$ ,  $W^{5+}$  and  $W^{4+}$  ions are then partially reduced in  $W^0$  and the  $S_2^{2-}$  pairs are still partially reduced in  $S^{2-}$  ions. The lithiated films are very hygroscopic. In spite of great care, we have not been able to

prevent their hydrolysis which is revealed by the presence of a doublet attributed to  $WO_3$ ,  $2H_2O$ .

The analysis of a de-intercalated material ( $Li_{1.6}WO_{1.05}S_2$ ) has shown that the processes are reversible for the tungsten ions but not completely for the sulphur ones.

This study has revealed that the tungsten and the sulphur atoms are both affected during the redox processes. A similar role of the sulphur ions has been also evidenced previously by a XPS study of molybdenum oxysulfide thin films [16]. Furthermore an electron transfer on the sulphur ions has also been characterised by a XANES study on the sulphur K-edge in lithium intercalated titanium disulfides ( $Li_xTiS_2$ ) [17].

### 4. Conclusions

While  $WS_2$  is not a suitable material as cathode in lithium cells, the oxysulfide thin films are active materials as positive electrode in microbatteries and have shown interesting properties on the range (1.6–3.0 V) with a current density of  $37 \mu A/cm^2$ . The results obtained for  $WO_{1.05}S_2$  and  $WO_{1.35}S_{2.2}$  films are promising, 0.6 and 0.8 lithium, respectively, can be intercalated and de-intercalated reversibly. We currently, try to test these materials with a higher current density, and also to increase the thickness of the film in order to improve the discharge capacity.

### References

- [1] C.H. Chen, E.M. Kelder, J. Schoonman, J. Power Sources 68 (1997) 377.
- [2] N.J. Dudney, J.B. Bates, R.A. Zuhr, S. Young, J.D. Robertson, H.P. Jun, S.A. Hackney, J. Electrochem. Soc. 146 (7) (1999) 2455.
- [3] P. Liu, J.G. Zhang, J.A. Turner, C.E. Tracy, D.K. Benson, J. Electrochem. Soc. 146 (6) (1999) 2001.
- [4] J.B. Bates, N.J. Dudney, D.C. Lubben, G.R. Gruzalski, B.S. Kwak, X. Yu, R.A. Zuhr, J. Power Sources 54 (1995) 58.
- [5] P. Liu, J.G. Zhang, J.A. Turner, C.E. Tracy, D.K. Benson, R.N. Bhattacharya, Solid State Ionics 111 (1998) 145.
- [6] P. Fragnaud, T. Brousse, D.M. Schleich, J. Power Sources 63 (1996) 187.
- [7] B. Wang, J.B. Bates, F.X. Hart, B.C. Sales, R.A. Zuhr, J.D. Robertson, J. Electrochem. Soc. 143 (10) (1996) 3203.
- [8] J.D. Perkins, C.S. Bahn, P.A. Parilla, J.M. McGraw, M.L. Fu, M. Duncan, H. Yu, D.S. Ginley, J. Power Sources 81/82 (1999) 675.
- [9] S.D. Jones, J.R. Akridge, Solid State Ionics 86–88 (1996) 1291.
- [10] F.K. Shokoohi, J.M. Tarascon, B.J. Wilkens, D. Guyomard, C.C. Chnag, J. Electrochem. Soc. 139 (7) (1992) 1845.
- [11] P. Birke, W.F. Chu, W. Weppner, Solid State Ionics 93 (1997) 1.
- [12] G. Meunier, R. Dormoy, A. Levasseur, Mater. Sci. Eng. B3 (1989) 19.
- [13] E. Schmidt, G. Meunier, A. Levasseur, Solid State Ionics 76 (1995) 243.
- [14] E. Schmidt, C. Sourisseau, G. Meunier, A. Levasseur, Thin Solid Films 260 (1995) 21.
- [15] I. Martin, P. Vinatier, A. Levasseur, J.C. Dupin, D. Gonbeau, J. Power Sources 81/82 (1999) 306.
- [16] L. Benoist, D. Gonbeau, G. Pfister-Guillouzo, E. Schmidt, G. Meunier, A. Levasseur, Solid State Ionics 76 (1995) 81.
- [17] Z.Y. Wu, G. Ouvrard, S. Lemaux, P. Moreau, P. Gressier, F. Lemoigno, J. Rouxel, Phys. Rev. Lett. 77 (10) (1996) 2101.

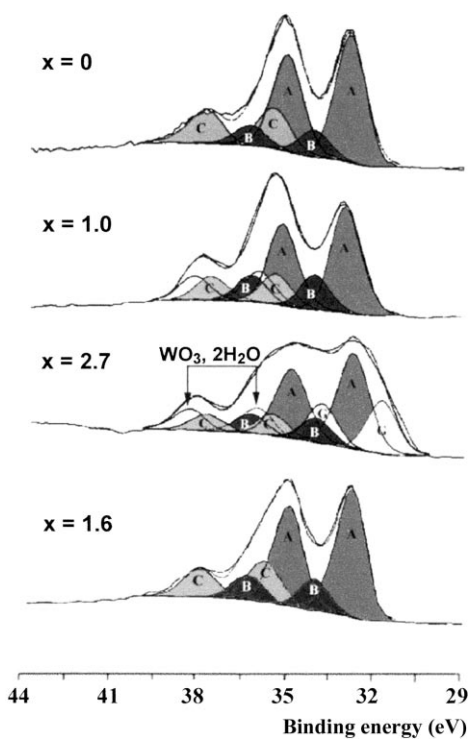


Fig. 3. XPS analysis: W 4f peak in intercalated ( $Li_1WO_{1.05}S_2$  and  $Li_{2.7}WO_{1.05}S_2$ ) and de-intercalated ( $Li_{1.6}WO_{1.05}S_2$ ) materials. Doublets: A ( $W^{4+}$  ions), B ( $W^{5+}$  ions) and C ( $W^{6+}$  ions).