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New amorphous molybdenum oxysulfide thin films Their characterization and their electrochemical properties

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Abstract

New amorphous molybdenum oxysulfides have been obtained by r.f. sputtering using an MoS₂ target. Their chemical composition depends on the partial pressure of oxygen introduced in the plasma during the preparation. All the properties depend on their composition. By transmission electron microscopy some randomly oriented ordered domains were found and identified as a 2H-MoS₂-like phase in which a partial substitution of oxygen for sulfur has been evidenced. The low oxygen content thin films have the best electrical conductivity but can intercalate only 1.7 lithium per molybdenum. On the opposite, the high oxygen content ones are able to intercalate up to 3.5 lithium. Whatever the composition of the material, the intercalation of the first lithium is never reversible. By X-ray photoelectron spectroscopy it was found that this phenomenon corresponds to the reduction of Mo⁶⁺ to Mo⁵⁺ and Mo⁴⁺, the reversible part is mainly due to the further redox process of Mo⁵⁺ and Mo⁴⁺ and also of disulfide pairs S₂²⁻.

Keywords: Molybdenum oxysulfide

1. Introduction

It is well known that physical or chemical deposition methods allow to obtain new materials in form of thin films. In addition, the miniaturization of devices with their own power sources has led to a large growth in research on microbatteries. In a recent past, very attractive results have been obtained in these domains [1–3].

Starting from commercial TiS₂ and using r.f. sputtering, some of the authors of the present paper have previously obtained and characterized amorphous titanium oxysulfide thin films used as positive electrode materials in microbatteries [1,4,5]. With the same technology, and starting from MoS₂, new amorphous molybdenum oxysulfide thin films have been obtained and studied. A summary of these results is presented in this paper.

2. Experimental

The molybdenum oxysulfides were prepared at room temperature by r.f. magnetron sputtering. To avoid water contamination of both target and thin films, the system is set up in a dry argon glove box. The target (50 mm in diameter) was prepared from commercial 2H-MoS₂ powder.

The sputtering conditions were the following: a power density of 2.3 W cm⁻² at a frequency of 13.56 MHz, an argon pressure of 1 Pa and a target to substrate distance of approximately 70 mm. The average sputtering rate was about 130 Å min⁻¹. Before deposition, the chamber was evacuated to a pressure of 10⁻⁵ Pa.

In order to obtain a high oxygen content in the thin films pure oxygen was admitted into the chamber through a leak-valve, so that the partial pressure of oxygen in the argon was between 10⁻⁵ and 10⁻² Pa.

3. Chemical composition of sputtered MoO_xS_z films

The chemical composition was determined by Rutherford backscattering spectroscopy. The unavoidable

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presence of oxygen in the films was observed, due to traces of oxygen in argon in the dry box and in starting materials. As mentioned in Section 2, the introduction of oxygen in the sputtering chamber allows further the composition to be modified. For an easier presentation, in the following of this paper, the discussion will deal with formal oxydation numbers associated with entire charges, although in reality many gradations may exist.

Table 1 reports the values obtained for y and z .

The very large composition domain can be explained by the presence of three different oxidation states of molybdenum (Mo^{6+} , Mo^{5+} , Mo^{4+}) and two oxidation states of sulfur (S^{2-} , S_2^{2-}) as evidenced by X-ray photoelectron spectroscopy (XPS) studies [6]. By electronic microprobe, the chemical composition was found uniform at any point of a thin film [7]. Auger electron spectroscopy (AES) analysis gave information on the element distribution in the depth profile of the film. The films are homogeneous and no superficial hydrolysis was observed.

X-ray diffractograms of MoO_yS_z films were characteristic of an amorphous compound.

4. Characterization by transmission electron microscopy

For this TEM study, films of about 50 nm thick were deposited on copper grids coated with an amorphous carbon film as substrate. For annealed films, golden grids were used. The TEM micrographs and diffraction patterns were obtained at a 200 kV accelerating voltage. Some ordered domains, randomly oriented versus one other, were found; they were identified by electron diffraction as a 2H-MoS₂-like phase (Fig. 1). After annealing the films, starting from an amorphous or poorly crystallized phase, a crystalline one can be obtained. In this case, the identification of the different phases found is easier; the same kind of domains, but larger, are visible; in addition, large single crystals, identified as MoO₂, are present. X-ray diffraction analysis confirms the presence of MoO₂ and 2H-MoS₂-like phases. The position of the main diffraction lines of the 2H-MoS₂-like phase shifts when the composition of the thin films changes indicating a partial substitution of oxygen for sulfur [7]. Indeed, d_{002} increases from 6.31 Å (MoO_{0.4}S_{2.0}) to 6.42 Å (MoO_{1.5}S_{2.0}) and d_{100}

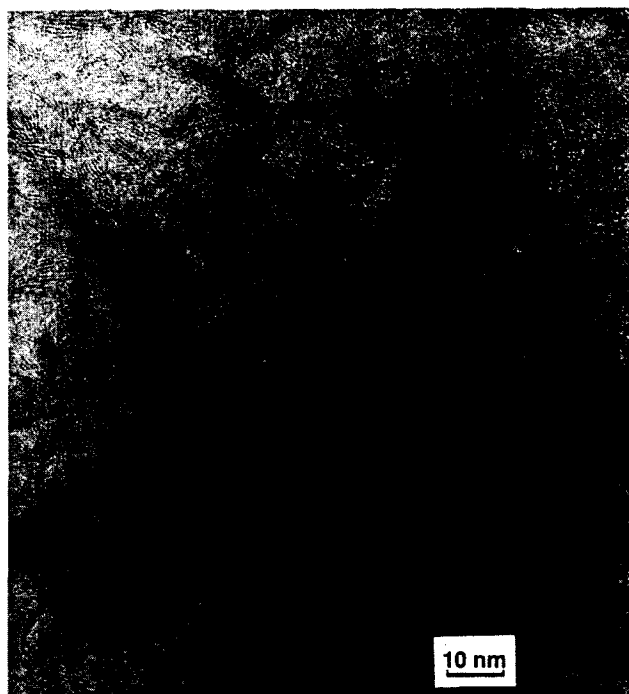


Fig. 1. TEM micrograph of an MoO_{0.2}S_{1.7} film.

decreases from 2.72 to 2.65 Å, respectively, for the same compounds. The contraction of the a -parameter and the expansion of the c -parameter can be explained by steric and electronic considerations [7,8].

5. Electrical conductivity

Single crystalline MoS₂ (Mo in a trigonal prismatic site) has a semi-conducting behaviour characterized by a gap of about 1 eV between the filled d_{z^2} band and the higher lying conduction bands ($d_{x^2-y^2}$, d_{xy}) [9].

Molybdenum oxysulfide thin films have also a semi-conducting behaviour and their electrical conductivity depends on their composition [10]. If one assumes that the band structure of MoO _{y} S _{z} is similar to that of MoS₂, the electrical conductivity of thin films can be easily related to their compositions. The best values of electrical conductivity have been obtained with a low oxygen content, ($y < 1$ and $z > 2$). In this case, the predominant species are Mo⁴⁺ (d^2) and Mo⁵⁺ (d^1) [6]. The d_{z^2} band is half filled or completely full; the electronic transitions become easy and the corresponding materials have a semi-conducting behaviour ($10^{-1} \Omega^{-1} \text{cm}^{-1}$ at 298 K) [10].

On the contrary, for high oxygen content films ($y > 1$ and $z < 2$), the predominant molybdenum species is Mo⁶⁺ (d^0) [6]; the d_{z^2} band is almost empty and the electronic transition to the conduction band is quite impossible; therefore the electronic conductivity is low ($10^{-5} \Omega^{-1} \text{cm}^{-1}$ at 298 K) [10].

Table 1
Chemical composition of MoO _{y} S _{z} thin films

	y	z
Without O ₂ introduction	0.3–0.5 ± 0.1	2.1–1.8 ± 0.1
With O ₂ introduction (10 ⁻⁵ to 10 ⁻² Pa)	0.6–3.1 ± 0.1	2.0–0.1 ± 0.1

6. Electrochemical behaviour

The electrochemical tests have been realized galvanostatically in an Li/liquid electrolyte/ $\text{Li}_x\text{MoO}_y\text{S}_z$ cell with a current density of $3 \mu\text{A cm}^{-2}$ between 3 and 1.6 V and 60 min of relaxation at the end of each charge and discharge. The behaviour of the batteries depends on the composition of the films used as positive electrode (Fig. 2). Up to 3.5 lithium can be intercalated in the films with high oxygen content ($\text{Li}_{3.5}\text{MoO}_{1.6}\text{S}_{1.8}$); 2.5 lithium can be de-intercalated during the first charge. The other cycles are similar to each other but different from the first one and 200 can be achieved easily, but 50% of the specific capacity is lost (with respect to the second cycle) after 100 cycles and a stabilization seems to be established afterwards [11]. 1.7 lithium only can be intercalated in a film with a low oxygen content $\text{MoO}_{0.4}\text{S}_{1.2}$; 0.6 lithium can be de-intercalated. In general, when $y < 1.5$, the amount of lithium intercalated during a given discharge is higher than the one de-intercalated during the preceding charge (Fig. 2(a)–(c)). For an unknown reason, oxidation seems to be more difficult than reduction. The thin films are

quickly saturated by lithium; only 50 discharge/charge cycles are possible in these cases [11].

The diffusion coefficient of lithium within the films were determined using the method developed by Honders et al. [12]. At the beginning of the discharge, for the high oxygen content films, the diffusion coefficient is rather low, about $3 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ [11] similar to the one found for MoS_2 in powder or in the form of thin films [13,14].

7. Characterization by X-ray photoelectron spectroscopy

The XPS analysis were performed with a Surface Science Instrument spectrometer using a focused monochromatized Al $K\alpha$ radiation (1486.6 eV) [6].

The reference compounds (MoO_2 , MoO_3 , MoS_2 and MoS_3) were first analysed [6].

For the MoO_yS_z thin films, three composition domains have been defined as a function of the Mo(3d) and S(2p) peaks shape.

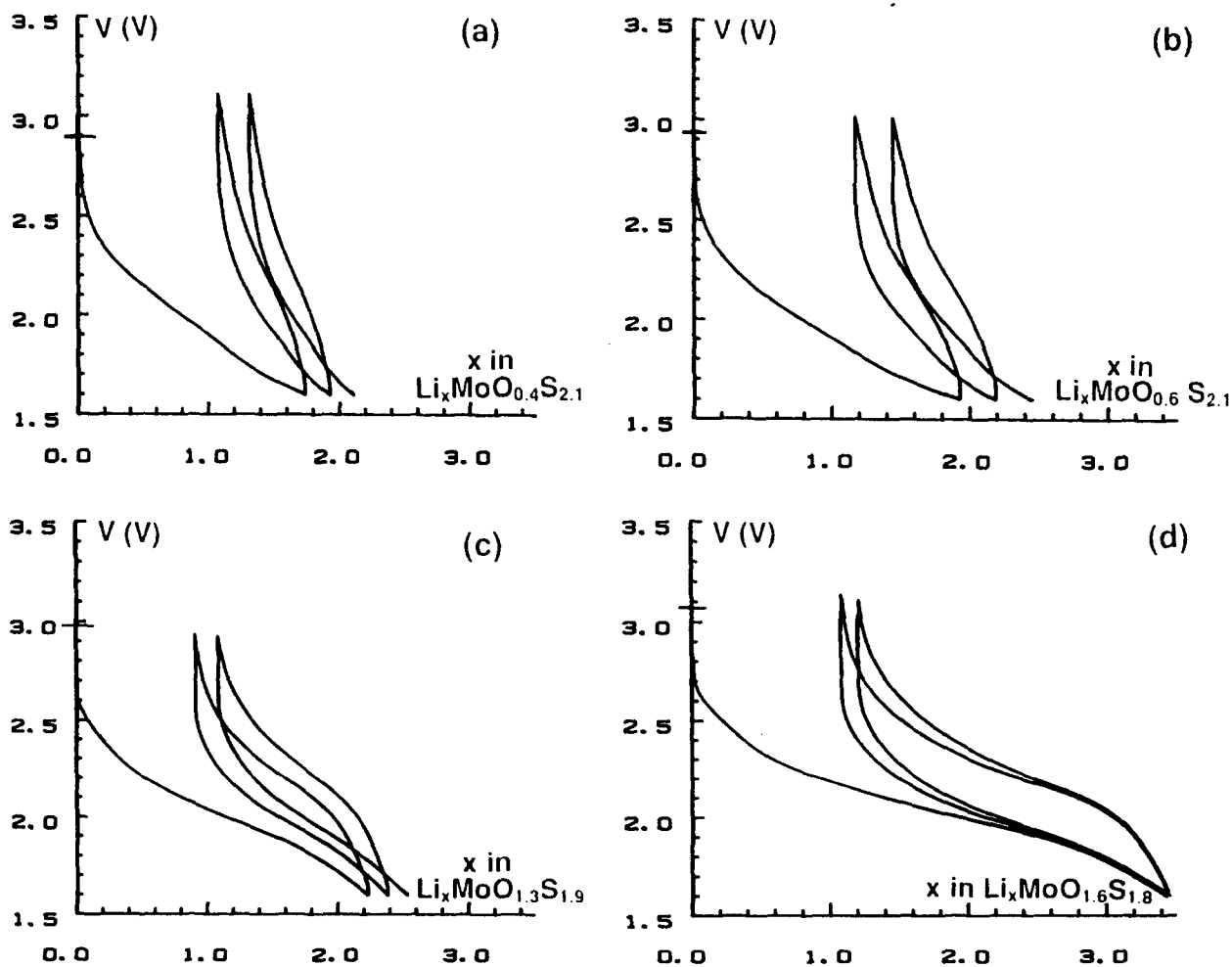


Fig. 2. Electrochemical behaviour of different composition thin films in Li/liquid electrolyte/ $\text{Li}_x\text{MoO}_y\text{S}_z$ batteries.

7.1. $y < 0.6$; $z > 2$

Molybdenum atoms are principally in a trigonal prismatic environment as in MoS_2 (Mo^{4+}); sulfur atoms are present as S^{2-} . In order to satisfy electrical neutrality, the hypothesis of one Mo^{5+} is suggested, but the S(2p) peak shape rules out the possibility of a high proportion of MoS_3 (Mo^{5+} and S_2^{2-}).

7.2. $y > 3$; $z < 1$

As in MoO_3 there is only a single Mo environment corresponding to Mo^{6+} in octahedral-sites [6].

7.3. $0.6 < y < 3$; $1 < z < 2$

In addition to the two main molybdenum species (Mo^{6+} and Mo^{4+}) a third one has been identified as Mo^{5+} having O^{2-} and S_2^{2-} as closest neighbours [6].

In connection with these results, an XPS study of the intercalation and de-intercalation of lithium in the films has been undertaken. Several thin films have been studied at various stages of their discharge or charge in microbatteries. The XPS data, in agreement with the cyclic voltammetry results allow a better understanding of the redox mechanisms especially for the film with a high oxygen content. As shown in the previous Section, the first part of the discharge is irreversible; this phenomenon corresponds to the reduction of Mo^{6+} to Mo^{5+} and Mo^{4+} and a partial reduction of disulfide pairs S_2^{2-} . The second part of the discharge is reversible and more significant when the oxygen content is high; the main species, then involved, are Mo^{5+} and Mo^{4+} being reduced up to the zero-oxidation state and the disulfide pairs (being reduced to S^{2-}) present in a particularly high proportion in the oxygen-rich thin films. The results obtained have clearly indicated the peculiar character of the MoO_yS_z thin films and the important contribution of the sulfur atoms as well as the transition element during the redox processes [6].

8. Conclusions

The properties of these new amorphous molybdenum oxysulfide thin films depend strongly on their chemical composition. Their characterization have shown that at least three molybdenum species have been identified with different surroundings. Their electrochemical behaviour involves the oxydo-reduction of both molybdenum and sulfur. These materials are good candidates as positive electrode materials for microbatteries.

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