Physicochemical Characteristics of Electrochemically Deposited Molybdenum Sulfide and Polypyrrole–Tetrathiomolybdate/Molybdenum Trisulfide Composite Electrodes

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Amorphous molybdenum sulfide and polypyrrole–tetrathiomolybdate/molybdenum sulfide thin films obtained by electrodeposition from aqueous solutions of ammonium tetrathiomolybdate and pyrrole + ammonium tetrathiomolybdate, respectively, have been characterized by elemental analysis, Auger electron spectroscopy, X-ray photoelectron spectroscopy, infrared spectroscopy, and X-ray absorption spectroscopy. Our data revealed that the structure of electrochemically and thermally produced molybdenum trisulfide are identical but that additional sulfur is also present in the electrodeposited material. On the other hand, polypyrrole films grown in the presence of tetrathiomolybdate as the counterion also contains molybdenum trisulfide. Elemental analysis and X-ray absorption spectroscopy of polypyrrole–tetrathiomolybdate/molybdenum trisulfide thin film suggest that 30% of molybdenum is under the MoS_4^{2-} form and 70% is present as MoS_3.

Introduction

Transition metal sulfides and oxides have been extensively investigated as cathode materials for secondary ambient temperature alkali metal batteries.[1] Much attention has been focused on low dimensional materials such as TiS_2 and MoS_2. The structure of these materials consists of superimposed sheets of metal ions sandwiched between two S^{2-} ion sheets. The interaction of the Li^+ ion with the layered transition metal dichalcogenides occurs via an intercalation mechanism where the lithium atom is inserted between the host dichalcogenide layers. Such a reaction mechanism leads to minimal structural changes upon Li incorporation (a small lattice expansion) and consequently these materials show good reversibility. The layered structure of the material assures also a good diffusivity of the Li atom in the electrode material.

In MoS_2, it was found that the capacity of Li uptake decreased continuously with increased crystallinity. This result points to the role of defect states in the chemistry of Li reaction with the MoS_2.[2] Amorphous molybdenum trisulfide prepared either by chemical or thermal decomposition of ammonium tetrathiomolybdate has therefore been investigated as a potentially interesting material to be used in ambient temperature Li batteries. It was found that MoS_3 reacts electrochemically with up to 3.8 Li per MoS_3 under constant current conditions above 1.40 V. On recharge at constant current, the system shows good reversibility.[3] The MoS_3 prepared by chemical and thermal decomposition is a powder and pressed pellets of this material (sometimes with additives such as Teflon and graphite) require several weeks to complete one cycle of charge/discharge.

Recently, thin films of molybdenum sulfide have been obtained by electrochemical oxidation of aqueous or methanolic ammonium tetrathiomolybdate solutions[4,5] and chemical vapor deposition from molybdenum hexafluoride and hexamethyldisilthiane.[6] Due to their limited thicknesses, these films require only several hours to complete a cycle of charge/discharge. However, the conductivity of molybdenum sulfide is known to be relatively low, $\sim 10^{-5}$ $S \cdot cm^{-1}$(ref 6) and a more efficient electrode should require a material with a higher conductivity. To circumvent this limitation, it was therefore proposed to incorporate the molybdenum sulfide in a conductive polymer such as polypyrrole. Accordingly, polypyrrole doped with tetrathiomolybdate anions/molybdenum trisulfide composite electrodes have been realized.[7]

Unlike other chalcogenides of transition metals of MX_3 stoichiometry (where M is the metal and X the chalcogenide), MoS_3 can only be prepared in the amorphous form. This peculiarity precludes the use of conventional X-ray diffraction analysis to elucidate the structure of that material. In the last decade, the structural charac-

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terization of amorphous molybdenum trisulfide (a-MoS_3) prepared by thermal decomposition of ammonium tetrathiomolybdate has therefore relied on the use of various spectroscopic techniques such as X-ray photoelectron spectroscopy, XPS,[2,8-11] X-ray radial distribution function,[2,10-12] and extended X-ray absorption fine structure, EXAFS.[2,11-14] On the other hand, electrochemically synthesized molybdenum trisulfide has only been investigated using Rutherford backscattering technique[5] and Raman spectroscopy.[4]

It is the purpose of this report to address the question of the structure and bonding of the electrochemically deposited molybdenum sulfide and polypyrrole–tetrathiomolybdate/molybdenum sulfide composite electrodes. This determination has been conducted with various techniques including elemental analysis, Auger electron spectroscopy, X-ray photoelectron spectroscopy, infrared spectroscopy, and X-ray absorption spectroscopy.

Experimental Section

Chemicals. Pyrrole (Aldrich) was freshly distilled before use. $(NH_4)_2MoS_4$ was prepared according to a published procedure.[15] All others standard chemicals were used as received.

Electrode Fabrication and Deposition of the Films. Tin oxide-coated glass (Swift Glass Co, 20–50 Ω/□) and platinum foil were used as electrode substrates. These were cleaned before electrodeposition by soaking in aqua regia and rinsing with distilled H_2O. Platinum disk electrodes were prepared by sealing a 1-mm diameter platinum wire in glass. The platinum disk electrode was polished with diamond polishing compound to the 1-μm level and then to the 0.5-μm level with an aqueous alumina slurry (Techmet, Canada). The auxilliary electrode was either a large platinum flag or a large tin oxide-coated glass plate and the reference electrode was a saturated calomel electrode, SCE.

Amorphous molybdenum sulfide thin films were prepared by oxidative electrodeposition at 0.3 V vs SCE from aqueous solutions containing either 40 mM $(NH_4)_2MoS_4$ + 1 M Na_2SO_4 or only 40 mM $(NH_4)_2MoS_4$. The polypyrrole–tetrathiomolybdate/molybdenum trisulfide, $[(PPy^{+\cdot})_{1/2}MoS_4^{2-})/MoS_3]$-coated electrode was prepared by anodic electrochemical deposition at 0.7 V from an aqueous solution containing 0.5 M pyrrole and 0.5 mM $(NH_4)_2MoS_4$.[7] Films of various thicknesses were produced by varying the deposition time. After film preparation, electrodes were removed from the preparation medium and washed with distilled water. Amorphous molybdenum trisulfide powder was prepared by thermal decomposition of ammonium tetrathiomolybdate under a pure nitrogen atmosphere at 300 °C.[3]

Electrochemical Equipment. Electrochemical experiments were performed by using either a PAR Model 273 potentiostat/galvanostat with a Houston Instruments Model RE 0091 recorder or a Pine Model RDE 4 bipotentiostat equipped with a Kipp and Zonen BD 91 x–y–y' recorder. All electrochemical experiments were carried out under N_2 in a conventional one-compartment cell.

Sample Characterization. Thicknesses of molybdenum sulfide and $[(PPy^{+\cdot})_{1/2}MoS_4^{2-})/MoS_3$ thin films were obtained with a Talysurf profilometer. A step across which the stylus of the surface profiler was drawn was produced by applying sticking tape to part of the electrode surface and removing it after film deposition. Elemental analyses on molybdenum sulfide and polypyrrole–tetrathiomolybdate/molybdenum sulfide films grown on tin oxide electrodes were performed by Galbraith Laboratories, Nashville, TN. However, since a large amount of material (~20 mg) is required for the elemental analysis, it was necessary to remove the deposit from the tin oxide substrate with a scalpel and repeat this procedure several times in order to obtain the required mass of material.

Infrared absorption spectra were obtained with either a Digilab, Model FTS-50 Fourier transform-infrared spectrometer, or a conventional Perkin-Elmer, Model 783 infrared spectrometer. The molybdenum sulfide powder was mixed with Nujol and placed between either CsI or KBr pellets for IR measurements.

Auger electron spectroscopy was performed on a Perkin-Elmer Model PHI 660 system. Depth profiling was performed by using a 3-kV beam from a differentially pumped Ar^+ ion gun while scanning the element peaks of interest. XPS measurements were carried out on a VG, Escalab MKII spectrometer equipped with an hemispherical analyzer and a twin anode (Mg and Al). The Mg anode (Kα X-rays at 1253.8 eV) was used in these experiments at 12–14 kV and 10–20 mA. X-ray absorption spectroscopy measurements at the Mo K edge were conducted at LURE-DCI (1.85 GeV, 250 mA). The synchrotron radiation was monochromatized by using a Si(331) channel-cut crystal. The thin film absorption spectra of electrochemically deposited MoS_3 were obtained by using the total electron yield technique at atmospheric pressure.[16] On the other hand, the absorption spectra of polypyrrole–tetrathiomiolybdate/molybdenum trisulfide electrodes were measured in the fluorescence mode by using a newly developed plastic scintillator detector.[17] The absorption spectra of powder reference samples were recorded in the classical transmission mode. It has already been established that all three detection modes convey the same information.

In the absorption spectra, the zero energy reference was set to 20 keV (Mo metal). The energy position of the absorption threshold was measured as the first inflection point in the abrupt rise of the absorption cross section. A complete description of the procedure involved in the analysis of the EXAFS signal is beyond the scope of this report and the interested readers are referred to the book of Teo[18] and references therein. In brief, the analysis of the EXAFS oscillations involves a background substraction. The radial structure function is obtained by performing a Fourier transformation of the EXAFS signal: the peaks occur at R values that differ by a phase shift from the real interatomic distances. By an inverse Fourier transformation in k space, the EXAFS oscillations corresponding to only one neighbor shell are sorted out. Comparison of the phase and amplitude of various model compounds with those of the sample by data fitting in k space yields the structural parameters (number and nature of atoms surrounding the absorber and their distances from it). $(NH_4)_2MoS_4$ has been used as a reference compound to determine the phase and amplitude functions of the Mo–S pair of atoms. The functions have been proved to yield the expected Mo–S distance by analyzing MoS_2.

Results

Electrodeposition of Molybdenum Sulfide and Polypyrrole–Tetrathiomolybdate/Molybdenum Sulfide Thin Films. Thin films of dark brown molybdenum sulfide were deposited on electrodes by oxidative electrodeposition from an aqueous solution containing ammonium tetrathiomolybdate. In an aqueous solution containing 40 mM $(NH_4)_2MoS_4$, a film is deposited as long as the potential is more positive than about 0.1 V vs SCE. A typical current–time transient for the deposition of molybdenum sulfide on a platinum electrode resulting from

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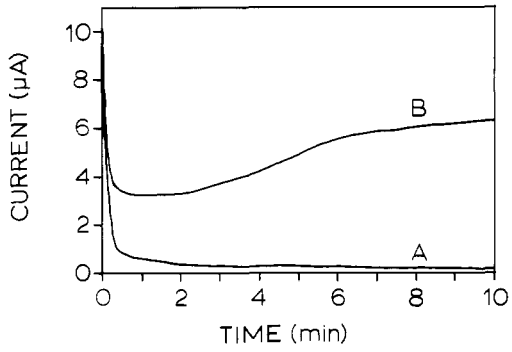

Figure 1. Current-time transients on a platinum electrode for (A) amorphous molybdenum sulfide electrodeposition from aqueous 40 mM $(NH_4)_2MoS_4$ at 0.3 V and (B) polypyrrole–tetrathiomolybdate/molybdenum sulfide electrodeposition from an aqueous solution containing 0.5 M pyrrole and 0.5 mM $(NH_4)_2MoS_4$ at 0.7 V. Area of the electrode = 0.007 85 cm^2.

a potential step from 0 to 0.3 V is shown in Figure 1, curve A. The constantly decreasing current is indicative of a poorly conductive layer.

On the other hand, electrodes immersed in an aqueous solution containing 0.5 M pyrrole and 0.5 mM $(NH_4)_2MoS_4$ were coated with a black deposit when the potential was set at 0.7 V vs SCE. A typical current vs time profile resulting from a potential step from 0 to 0.7 V (Figure 1, curve B) is characterized initially by a rapid decrease of the current and its subsequent rise as the film began to grow. The anodic current then remained fairly constant even for an electrosynthesis time of 60 min (not shown). This is to be contrasted with the current-time transient obtained for the electrodeposition of MoS_3 alone (Figure 1, curve A). These observations suggest that the conductivity of the composite film is higher than that of the electrodeposited MoS_3 layer. Indeed, conductivity measurements performed on 0.2-μm-thick films with the dual electrode/mercury pool method revealed that the conductivity of the polypyrrole–tetrathiomolybdate/molybdenum sulfide composite film is 2.6×10^{-2} S cm^{-1} and thus 2 orders of magnitude larger than the conductivity of an electrodeposited molybdenum trisulfide film for which the conductivity was reported to be 5.2×10^{-4} S cm^{-1}.[19]

Elemental Analysis. Elemental analysis of the electrodeposited molybdenum sulfide (grown in the absence of the Na_2SO_4 supporting electrolyte) gave 41 wt % molybdenum and 54 wt % sulfur. These values, which corresponds to a $MoS_{3.8}$ formula, are different from those expected on the basis of the MoS_3 chemical formula. On the other hand, the elemental analysis on molybdenum sulfide prepared by thermal decomposition of ammonium tetrathiomolybdate in an inert atmosphere at 300 °C yielded 45.6% molybdenum and 46.9% sulfur, which is in agreement with the expected stoichiometry of MoS_3.

The elemental analysis of the polypyrrole–tetrathiomolybdate/molybdenum sulfide film gave the following results: C 23.3%, H 1.9%, N 6.6%, Mo 24.8%, and S 27.9% and the formula $PPy(MoS_{3.3})_{0.55}$.[19] The Mo:N atomic ratio of 0.55 is much larger than the 0.25 dopant:N ratio found in the literature for other polypyrrole films.[20,21] This higher molybdenum content is presumably brought

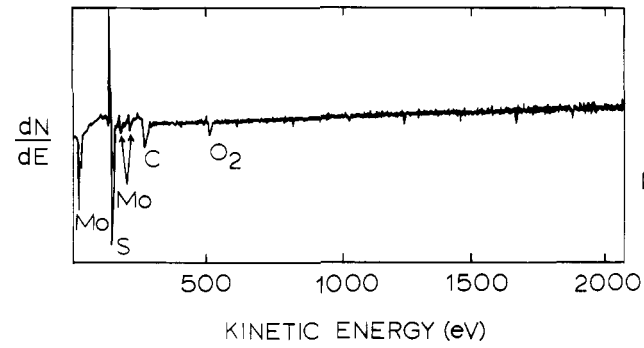

Figure 2. Auger spectrum of tin oxide/molybdenum sulfide surface. The thickness of the electrodeposited molybdenum sulfide thin film is 0.2 μm.

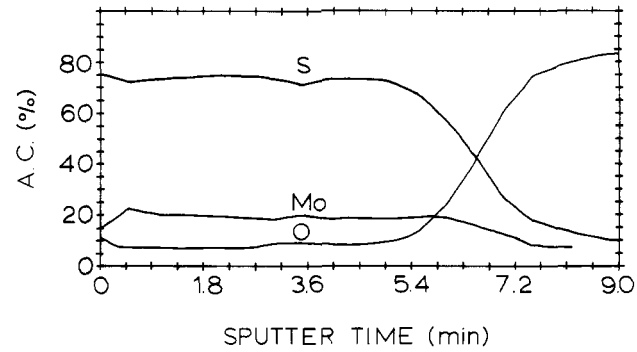

Figure 3. Auger depth profile produced by Ar^+ sputter of tin oxide/molybdenum sulfide.

about by the simultaneous formation of molybdenum sulfide in the polypyrrole matrix during the formation of polypyrrole–MoS_4^{2-} film. The elemental analysis of these materials showed that the sum of the given values does not account for 100%. Part of the missing material in both the electrodeposited molybdenum sulfide and the polypyrrole–tetrathiomolybdate/molybdenum sulfide may be due to oxygen present in the deposited films as water and also carbonyl oxygen in the case of the polypyrrole composite film.[22]

Auger Electron Spectroscopy. The electrodeposited MoS_3 films were studied by Auger spectroscopy to establish their composition and stoichiometry. The Auger spectra of the electrodes show signals for Mo, S, C, and O (Figure 2). The carbon peak can be eliminated by briefly sputtering the exposed surface with a beam of reactive Ar ions. On the other hand, oxygen is always present in our film (vide supra), even after sputtering of a thin layer of the surface. No additional signals are observed, and in particular we find little or no detectable signal for N (400 eV) from NH_4^+ of the $(NH_4)_2MoS_4$ salt.

A depth profile of the electrodeposited molybdenum sulfide film grown in the absence of Na_2SO_4 supporting electrolyte is shown in Figure 3. A similar profile is obtained when Na_2SO_4 is added as supporting electrolyte. The atomic composition in percentage is given as a function of the film depth. Note that oxygen is present in the whole depth of the film and that for long sputtering time, the increase of the oxygen signal is associated to the presence of the SnO_2 substrate. An average S:Mo ratio of (3.8 ± 0.5):1 can be evaluated from the depth profile data. This value is in agreement with our elemental analysis data

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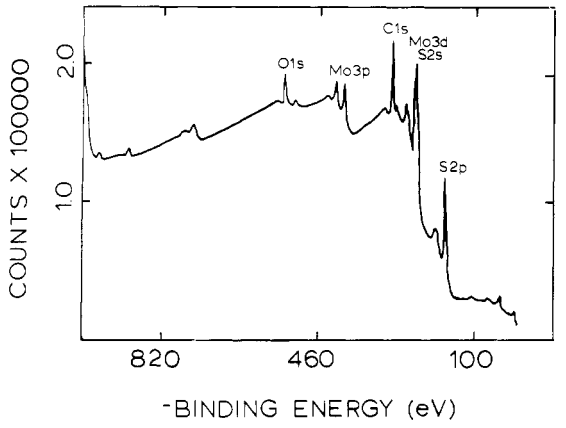

Figure 4. XPS survey spectrum for a molybdenum sulfide thin film electrodeposited onto a platinum foil.

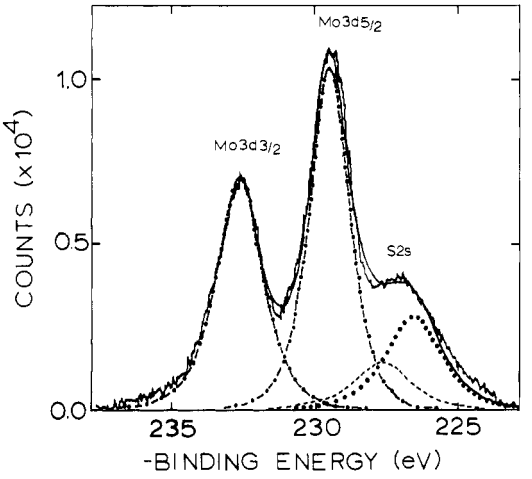

Figure 5. XPS Mo 3d and S 2s core level spectra of electrodeposited molybdenum sulfide. The S 2s core level peak is fitted with sulfide (···) and polysulfide (– – –) species.

(vide supra). Figure 3 also shows that the composition and the Mo:S ratio is fairly constant over all the thickness of the film. The exactness of the sensitivity factors used for Mo and S has been checked by carrying out Auger measurements with MoS_2 and a S:Mo ratio of 2.1 ± 0.3 has been found. Furthermore, a S:Mo ratio of (2.8 ± 0.3):1 has been obtained with molybdenum trisulfide powder prepared thermal decomposition of $(NH_4)_2MoS_4$ in inert atmosphere.

X-ray Photoelectron Spectroscopy. To get more precise information concerning the structure and chemical bonding in electrodeposited molybdenum sulfide, X-ray photoelectron spectroscopy measurements (XPS) were carried out. Figure 4 shows the XPS survey spectrum for an electrodeposited film with the Mo and S peaks at 230 and 162 eV, respectively. The survey spectrum exhibits only the characteristic Mo and S peaks with some carbon and oxygen coming from contamination of the surface and water molecules. Figure 5 and 6 show the Mo 3d and S 2p signals from the electrodeposited film respectively. The contribution of the S 2s, at a binding energy of 227.2 eV, is also clearly noticeable on the low binding energy side of the Mo 3d signal on Figure 5. Table I lists the observed binding energies for the Mo 3d and S 2p peaks. The Mo 3d signal shows the characteristic doublet of Mo $3d_{5/2}$ and Mo$3d_{3/2}$ at binding energies of 229.5 and 232.7 eV, respectively. The binding energies of the Mo atom in a thermally prepared sample of MoS_3 were identical to those

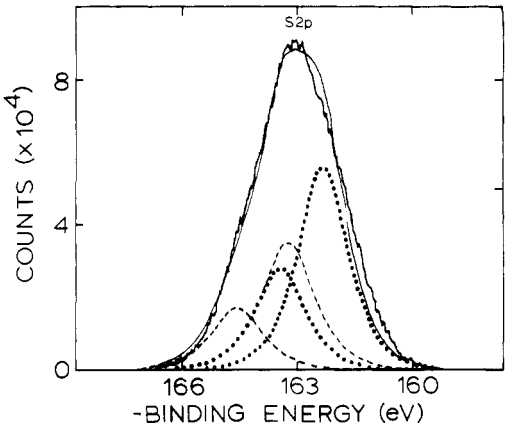

Figure 6. XPS S 2p core level spectra of electrodeposited molybdenum sulfide and curve fitting with sulfide (···) and polysulfide (– – –) species.

Table I. Binding Energies for Mo and S in Molybdenum Sulfide

		this work	Liang et al.[2,11]	Stevens and Edmonds[8]
Mo 3d $_{3/2}$		232.7		231.9
Mo 3d $_{5/2}$		229.5	229.4	228.7
S 2p $_{1/2}$	S^{2-}	163.4	162.2[a]	162.9
S 2p $_{3/2}$		162.4	161[a]	161
S 2p $_{1/2}$	S_2^{2-}	164.6	163.3[a]	164.4
S 2p $_{3/2}$		163.3	162[a]	163
S 2s	S^{2-}	226.6		
S 2s	S_2^{2-}	227.7		

[a] Evaluated from Figure 3 of ref 11.

obtained from the electrodeposited material. For reference, the values reported in the literature[2,11] for the thermally prepared molybdenum trisulfide are also reported in Table I.

For the electrodeposited material, a S:Mo ratio of (3.2 ± 0.4):1 can be estimated from these peaks. On the other hand, a S:Mo ratio of (2.7 ± 0.2):1 was found for thermally prepared molybdenum trisulfide. Thus it seems that by XPS one can not distinguish between thermally and electrochemically formed MoS_3. This result seems at odds with what was found by elemental analysis and Auger electron spectroscopy. This point will be further discussed below (see Discussion).

The S 2p ($2p_{3/2}$ and $2p_{1/2}$) signal originating from the electrodeposited MoS_3 consists unequivocally of more than one sulfur species. It resembles that of the product of decomposition of ammonium tetrathiomolybdate in vacuum[8,10] and to the S 2p signal measured on our in-lab thermally prepared MoS_3 sample. It can be fitted with two types of sulfur characterized with the S $2p_{3/2}$ peaks at 162.4 and 163.3 eV. One of these species is possibly the sulfur ions with E_b ($2p_{3/2}$) = 162 eV,[2,11,23] since XPS measurements on MoS_2 yielded a S $2p_{3/2}$ peak at 162.5 eV. The second one, with a higher binding energy, can be attributed to polysulfides species.[2,11,23] The ratio of the S^{2-}/S_2^{2-} components is 2. This is the ratio of the S^{2-}/S_2^{2-} components found with our in-lab thermally prepared MoS_3 and by Liang and co-workers on thermally prepared MoS_3.[2,11] The similarity of the Mo 3d and S 2p signals originating from the thermally prepared and electrodeposited MoS_3 samples constitutes therefore evidence that the chemical bonding of the Mo and S atoms is the same

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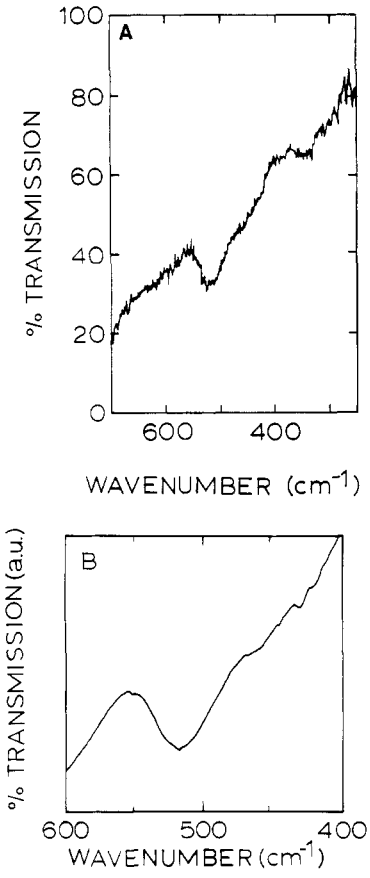

Figure 7. (A) Infrared spectrum of electrodeposited molybdenum sulfide. (B) An expanded view of the spectrum between 400 and 600 cm^{-1} for the electrodeposited material. The molybdenum sulfide powder was removed from the tin oxide electrode surface with a scalpel and mixed with Nujol. CsI (A) and KBr (B) pellets were used to record the spectra.

in both material. From the S 2p spectra shown in Figure 6 there is no evidence for the presence of elemental sulfur in the electrodeposited material.[2]

For the $[(PPy^{+\cdot}{}_{1/2}MoS_4^{2-})/MoS_3$ electrode it is not possible to discriminate between MoS_4^{2-} and MoS_3 species. This occurs most because MoS_4^{2-} anions decompose readily to MoS_3 in the ultra high vacuum conditions of the XPS analysis chamber.[10]

Infrared Spectroscopy. Transmission IR spectra of an electrodeposited molybdenum sulfide film are shown in Figure 7. The spectrum in Figure 7A from 200 to 800 cm^{-1} shows the characteristic features of thermally prepared amorphous molybdenum trisulfide with absorption bands at about 520 and 340 cm^{-1}, corresponding to S–S and Mo–S stretch respectively.[24] There is no clear evidence of absorption bands at 385 and 478 cm^{-1}. This suggests that the electrodeposited film would not consist of or contain MoS_2 or MoS_4^{2-}, respectively.[24] Moreover, a *very* weak absorption band, attributed to S_8,[24] can be seen at about 460 cm^{-1} on Figure 7B. The same absorption band at 460 cm^{-1} was also barely seen in the case of thermally prepared molybdenum trisulfide to which was added an amount of sulfur corresponding to 0.8 sulfur atom per MoS_3. The absence of absorption band corresponding to Mo–O stretch (ν = 950 cm^{-1}) rules out the possiblity that an oxysulfide compound may be produced by the electrodeposition process.

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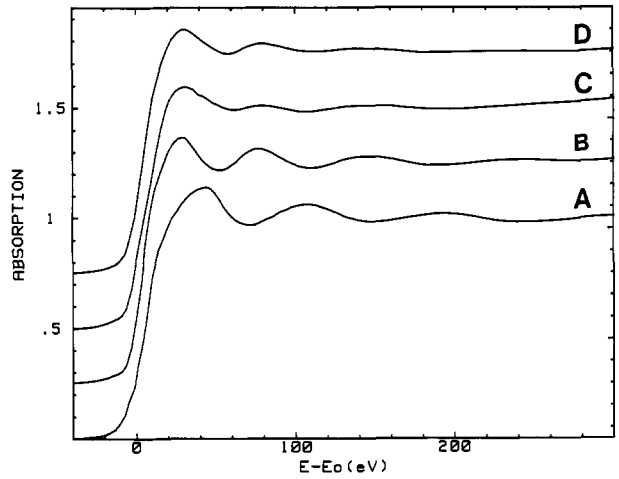

Figure 8. Mo K edge absorption spectrum of (A) $(NH_4)_2MoS_4$, (B) electrodeposited MoS_3 onto platinum (C) $Pt/[(PPy^{+\cdot}{}_{1/2}MoS_4^{2-})/MoS_3]$ composite electrode, and (D) a linear combination of $(NH_4)_2MoS_4$ and MoS_3 with a ponderation factor of 0.3 and 0.7, respectively. The zero energy reference is set at 20 keV.

The attempts to detect the presence of MoS_4^{2-} and/or MoS_3 within the polypyrrole by IR spectroscopy were unsuccessful presumably because the molybdenum concentration in the polymer was too low.

X-ray Absorption Spectroscopy. Figure 8 depicts the X-ray absorption near-edge structure (XANES) spectrum of $(NH_4)_2MoS_4$ powder (curve A) and of the electrodeposited MoS_3 thin film (curve B). Thin electrodeposited MoS_3 films were obtained by varying the deposition potential (0.2 and 0.8 V), the deposition time and the electrolytic solution (aqueous solution with and without 1 M Na_2SO_4). The XANES absorption spectra of all these samples have been recorded and are identical to each other. The XANES absorption spectrum of thermally prepared MoS_3 was also measured and could not be differentiated from that of the electrodeposited material.

Figure 8 (curve C) also shows the XANES absorption spectrum of a $[(PPy^{+\cdot}{}_{1/2}MoS_4^{2-})/MoS_3]$ composite electrode. This absorption spectrum is different from the preceding ones. In fact, curve D of Figure 8 shows that the XANES absorption spectrum of $[(PPy^{+\cdot}{}_{1/2}MoS_4^{2-})/MoS_3]$ composite electrode is a linear combination of the absorption spectrum of the $(NH_4)_2MoS_4$ powder (with a ponderation factor of 0.3) and of the electrodeposited MoS_3 (weighting factor of 0.7). This is a direct evidence that the $[(PPy^{+\cdot}{}_{1/2}MoS_4^{2-})/MoS_3]$ composite film contains both electrodeposited MoS_3 and MoS_4^{2-} anions.

Figure 9, curves A and B, shows the Fourier transform (FT), which represents the radial structure function of the atoms surrounding the molybdenum atom, of the extended X ray absorption fine structure region of the absorption spectrum of $(NH_4)_2MoS_4$ powder and of the electrodeposited MoS_3 thin film, respectively. As expected from the crystalline structure of $(NH_4)_2MoS_4$ (4 S atoms at a mean distance of 2.17 Å from the Mo), the radial structure function is symmetric and has its maximum intensity at a distance that differs from the bond length by a characteristic phase shift.

When compared to $(NH_4)_2MoS_4$, the maximum of the radial structure function of the electrodeposited MoS_3 is displaced toward the larger distance and is reduced in intensity. The major peak of the FT is also symmetric.

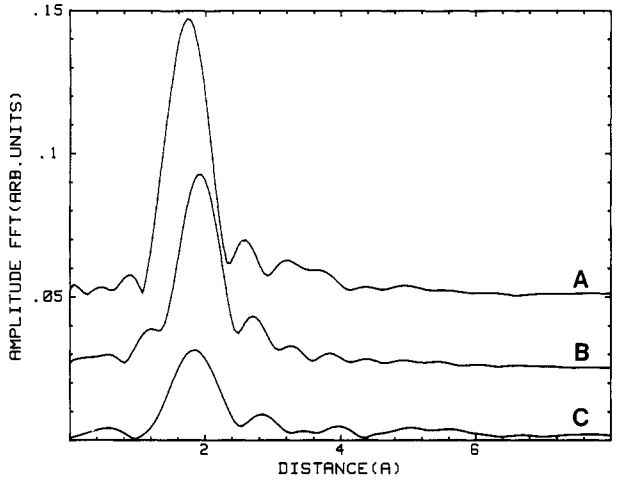

Figure 9. Radial structure function of the k^3-weighted EXAFS oscillations of (A) $(NH_4)_2MoS_4$ powder, (B) electrodeposited MoS_3 onto platinum, and (C) the Pt/[$(PPy^{+\cdot}{}_{1/2}MoS_4^{2-})/MoS_3$] composite electrode.

A two-shell model with only S atoms as backscatterers has been used to perform the fit on the EXAFS oscillations originating from that peak. The parameters of the shell are the following: $N(1) = 4.0$, $R(1) = 2.43$ Å, $\sigma^2(1) = -0.004$ Å^2, $N(2) = 2.0$, $R(2) = 2.61$ Å, $\sigma^2(2) = -0.003$ Å^2, where N stands for the coordination number, R, the distance between the Mo and the S atoms, σ^2, the square of the standard deviation of the distance, and the numbers 1 and 2 represents the first and second coordination subshells, respectively. The same Fourier transform curve is obtained if the deposition potential, the deposition time, or the composition of the electrolytic solution are varied. The radial structure function of thermally prepared MoS_3 was also measured and shown to be similar to that of the electrodeposited material. In particular, no evidence for a shoulder on the large distance side of the radial structure function was observed.[13]

Figure 9, curve C, shows the FT curve of the [$(PPy^{+\cdot}{}_{1/2}MoS_4^{2-})/MoS_3$] composite film. This radial structure function shows a marked diminution of intensity compared to that of curve B. Good fit of the inverse Fourier transform oscillations originating from that peak can be obtained by using a three shells model with only S atoms as backscatterers. The parameters and the proportion of the first two shells have been fixed to the characteristic values found for the electrodeposited MoS_3, while the Mo–S distance of the third shell was fixed at 2.18 Å (the Mo–S separation distance in $(NH_4)_2MoS_4$). Using this procedure, it was found that good fit can be obtained if $N(1) = 4.0$, $N(2)$, $= 2.0$ and $N(3) = 1.1$.

Discussion

The characterization of the material obtained by the electrochemical oxidation of an aqueous solution of ammonium tetrathiomolybdate has been performed by using various techniques and compared to the thermally formed amorphous molybdenum trisulfide. In the first place, elemental analysis and Auger electron spectroscopy have shown that the stoichiometry of the material obtained by electrodeposition is different from that formed by the thermal procedure. The electrodeposited material contains additional sulfur and this yields a S:Mo ratio higher than 3. A high S:Mo ratio suggests that the electrodeposited material consists of either a mixture of MoS_3 and MoS_4^{2-} and/or MoS_3 with elemental sulfur. At first glance, it seems that IR spectroscopy would be useful to determine which one of these two hypothesis is right. Indeed, MoS_4^{2-} (Mo–S stretch at 478 cm^{-1}) and S_8 (S–S stretch at 460 cm^{-1}) have characteristic absorption bands that can be used for their detection.[24] We have shown that the intensity of the S_8 band is very weak in both the electrodeposited material and a mixture of MoS_3 and S_8 for a S_8 concentration necessary to yield an overall stoichiometry of $MoS_{3.8}$. On the other hand, MoS_4^{2-}, which is easily detectable in a mixture of 80% MoS_4^{2-} and 20% MoS_3 that gives an average S:Mo ratio of 3.8, is clearly not present in the electrodeposited material. Therefore, the IR spectroscopy data suggest that the electrodeposited material is not a mixture of MoS_4^{2-} and MoS_3 and most likely consists of MoS_3 and elemental sulfur.

These observations have interesting consequence when the chemical processes involve in the electrochemical oxidation of MoS_4^{2-} to MoS_3 are questioned. It is known that the thermal decomposition of the $(NH_4)_2MoS_4$ involves the formation of NH_3 and H_2S besides MoS_3.[3] On the other hand, controlled potential electrolysis of an aqueous solution of $(NH_4)_2MoS_4$ required 2 e$^-$/mol of MoS_4^{2-} transformed in MoS_3.[30b] In addition, the pH of the electrolyte remained constant throughout the a 3-h electrodeposition of MoS_3. This observation suggests that sulfide species are not generated during the electrodeposition process because in this case the pH of the deposition solution should increase due to the sulfide/hydrogen sulfide equilibrium. The chemical processes involve in the electrochemical synthesis of molybdenum sulfide are therefore different from that occurring during the thermal procedure. Accordingly, we propose that molybdenum trisulfide deposition occurs via reaction 1.

$$MoS_4^{2-} \rightarrow MoS_3 + {}^1/_8S_8 + 2e^- \quad (1)$$

Presumably, this reaction first involves the oxidation of the sulfur ligands,[25] followed by an intramolecular electron transfer from the sulfur ligand to the central molybdenum metal and the loss of sulfur. The presence of additional sulfur atom in the electrodeposited material suggests that this elemental sulfur remains entrapped in the MoS_3 film during the electrodeposition process.

By XPS we were unable to find any evidence for the presence of elemental sulfur in the electrodeposited material. In addition, preliminary X-ray absorption spectroscopy experiments at the S K edge show that the electrochemical and thermal material cannot be distinguish by this technique as well. We have recently shown by thermogravimetric analysis that electrodeposited MoS_3 suffers a small loss of weight in the temperature range 100–225 °C which was attributed to the departure of the entrapped elemental sulfur. We therefore hypothesize that, owing to the ultrahigh-vacuum conditions of the analysis chamber, the elemental sulfur entrapped in the electrodeposited material was evaporated from the top layer (30–40 Å) of the film probed by XPS.

In the second place, the question of the Mo and S chemical bonding has been addressed by using IR and XPS measurements. Infrared spectroscopy measurements of the electrodeposited MoS_3 material yield the characteristic S–S and Mo–S stretch bands of the thermally prepared MoS_3. On the other hand, XPS measurements

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of the Mo 3d and S 2p levels, and in particular the proportion of the S^{2-}/S_2^{2-} components were shown to be similar in both the electrodeposited and thermally prepared MoS_3 samples. All these indications point to the fact that the chemical bonding of the Mo and S atoms in electrodeposited and thermally formed MoS_3 samples are identical. This is a first indication that both preparation methods should yield a compound with the same atomic structural arrangement.

The fact that electrochemically and thermally formed MoS_3 have the same chemical bonding is qualitatively confirmed by X-ray absorption spectroscopy. Since the Mo K edge XANES spectrum of an element is sensitive to the local environment of the absorbing atom, the similarity of the Mo K edge XANES spectrum of the electrodeposited and thermally prepared MoS_3 materials is therefore a direct evidence that the Mo atoms are in the same environment in both samples.

Quantitative structural informations are more easily obtained by analysing the EXAFS region of an X-ray absorption spectrum and the comparison of electrodeposited and thermally prepared a-MoS_3 has been conducted with this technique. Again the similarity of the radial structure function obtained in analysing both samples points to the fact that they are identical. Clearly, one cannot distinguish between a MoS_3 sample prepared by electrochemical oxidation of an aqueous solution of ammonium tetrathiomolybdate or thermal decomposition of the salt using either XANES or EXAFS spectroscopies.

Thermally produced MoS_3 has already been investigated by X-ray absorption spectroscopy at the Mo K edge.[2,13,14] The maximum intensity of the radial structure function was at about 2.0 Å and shoulders were visible on both sides of that peak. They found that the Mo atom was surrounded by six S atoms at a distance of 2.44 Å. They also claimed that the MoS_3 subunits were stacked on each other and that dimerization of the Mo atoms was occurring, leading to short Mo–Mo bonds along the chain. This dimerization process was thought to be the origin of the peak occurring at 2.75 Å in the FT curve.

We find no evidence of that dimerization process in both the thermally and electrodeposited materials. The FT curves obtained with both materials do not show any peak at 2.75 Å. Our results also show that the first coordination shell, made of sulfur atoms, is constituted of four atoms at 2.42 and two at 2.62 Å. Our results are consistent with the XPS analysis showing that two types of S atoms are involved in MoS_3. This result vary significantly from those found by the Exxon group. They claimed that the first coordination shell around the Mo atom was composed of six sulfur atoms at a unique distance of 2.44 Å,[13] although they found by XPS analysis two types of chemical bonding for the sulfur atoms (S_2^{2-} and S^{2-}).[2,11]

It is instructive to examine the structure and chemical bonding of other transition metal trichalcogenides. The structure of the parent crystalline compound $ZrSe_3$ is known and it was shown by XPS measurements at the Se 2p core levels that two types of selenium species exist in that compound (Se_2^{2-} and Se^{2-}).[26] This transition metal trichalcogenide is made of chains of MX_3 distorted trigonal prisms extending parallel to the *b* axis of the monoclinic cells. In $ZrSe_3$ the examination of the crystalline structure reveals that six Se atoms are found at a distance of 2.73 Å from the Zr atom while two other ones are at 2.88 Å. Of the six Se atoms at 2.73 Å, four are situated in the chain of the trigonal prism, while the other two belong to the adjacent chains. As expected, the difference in chemical bonding of the Se atoms lead to a difference in the Zr–Se bond length.

The first coordination shell of both thermally and electrochemically prepared MoS_3 also shows that two Mo–S bond lengths are involved in the chemical bonding. As already mentioned, this result is consistent with what was found by XPS analysis for the S 2p core levels. However, unlike the crystalline $ZrSe_3$ compound, only six sulfur atoms are involved in the first coordination shell of the Mo atom. These results can be accounted for if the structure of the MoS_3 is made of chains of trigonal prisms without any ordering of the chains. Recently, a model calculation study was conducted by Chien et al.[27] on MoS_3 to explain the results obtained by X-ray radial distribution function calculations. Although they still proposed a model involving a short Mo–Mo distance, they proposed a structure involving short (2.4 Å) and long (2.6 Å) Mo–S bonds for the S^{2-} and S_2^{2-} sulfur atoms, respectively.[27] On the basis of these results, the chemical structure of molybdenum sulfide is best described by Mo(V) ($2S^{2-} + {}^1/_2S^{2-}{}_2$).

In principle at least, one should be able to infer the oxidation state of a particular element from the position of its absorption edge. However, the Mo K hole has a natural width of 6 eV[28] which tends to blur the displacement of the absorption edge of the element following a modification of its oxidation state. A shift of only 6 eV is observed between the absorption edge of the metallic molybdenum (Mo^0) and that of (Mo^{+6}), while at the Cu K edge for example, a shift of 8 eV was observed between Cu^0 and Cu^{+2}.[29] In these conditions, the position of the Mo K edge can be hardly used to reveal change in the oxidation state expected between MoS_4^{2-} and Mo ($2S^{2-} + {}^1/_2S^{2-}{}_2$).

The elemental analysis and XANES and EXAFS data show unequivocally that both MoS_4^{2-} and MoS_3 are present in the [$(PPy^{+\cdot}{}^1/_2MoS_4^{2-})/MoS_3$] composite electrodes. At first glance, the deposition of both polypyrrole doped MoS_4^{2-} and MoS_3 may seem surprising since the electrodeposition of MoS_3 occurs at potential more positive than 0.2 V[30] while the formation of the polypyrrole doped with MoS_4^{2-} requires electrode potential more positive than 0.65 V.[31] At an electrode potential of 0.7 V, the formation of the MoS_3 should be strongly favored. However, by appropriately choosing the concentrations of pyrrole and MoS_4^{2-}, it is possible to grow composite electrode where the MoS_4^{2-} anions included in the polypyrrole assures the electroneutrality of the film while at the same time MoS_3 is formed within the film.[7,19] On the basis of an examination of the XANES results, it can be said that about 30% of the molybdenum atom include in the film are present as MoS_4^{2-} anions, the other 70% belonging to the MoS_3 phase.

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The $MoS_{3.3}$ stoichiometry deduced from the elemental analysis and XANES data for the $[(PPy^{+\cdot})_{1/2}MoS_4^{2-})/MoS_3]$ composite film electrode seems at odds with the $MoS_{3.8}$ stoichiometry of the electrodeposited molybdenum sulfide and the S:Mo ratio of 4:1 for MoS_4^{2-}. Indeed a S:Mo ratio between 3.8 and 4 is expected for the composite material. The $MoS_{3.3}$ stoichiometry suggest that the additional sulfur generated with MoS_3 during the electrodeposition of the $[(PPy^{+\cdot})_{1/2}MoS_4^{2-})/MoS_3]$ material is not entrapped within the polymer matrix or that MoS_3 is formed by another chemical route, as was recently proposed.[19] According to that scheme, MoS_3 would be formed by the acidic chemical decomposition of tetrathiomolybdate anions[33,34] owing to the fact that protons are released during the formation of polypyrrole and that the local pH in the polypyrrole film can be quite low. In this case hydrogen sulfide would be the sulfur containing species generated by the electrochemical/chemical process.

Conclusion

Amorphous molybdenum trisulfide obtained by electrochemical deposition from an aqueous solution containing ammonium tetrathiomolybdate and thermal decomposition of ammonium tetrathiomolybdate has been characterized by various techniques. Our data show that MoS_3 with the same structure is produced with both procedures but that additional sulfur is present in the electrodeposited material. The electrochemical process that yields MoS_3 involves the two electron oxidation of MoS_4^{2-} and the generation of elemental sulfur remaining entrapped in the MoS_3 matrix. Interestingly, the homogeneous two-electron oxidation of MoS_4^{2-} by organic disulfides has recently been reported in the literature.[32] This reaction led to the generation of reduced molybdenum to the +5 state, following an internal redox process involving the oxidation of the sulfur ligands. The electrochemical growth of polypyrrole in the presence of tetrathiomolybdate anions yields a material that contains both molybdenum trisulfide and MoS_4^{2-} in the ratio 70:30. In this case the molybdenum trisulfide is most likely generated within the polypyrrole matrix by acidic chemical decomposition of tetrathiomolybdate anions. Finally, it would be of interest to vary the concentrations of both the pyrrole monomer and the ammonium tetrathiomolybdate salt in order to prepare composite materials with various PPy/MoS_3 ratios and presumably materials with different properties.

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