Spin deposition of MoS_x thin films

J. Pütz, M.A. Aegerter[*]

Department of Coating Technology, Institut für Neue Materialien - INM, Im Stadtwald, Geb. 43, D-66123 Saarbrücken, Germany

Abstract

Thin films of MoS_2 and amorphous MoS_3 have been prepared on various glass and stainless steel substrates by thermolysis of spin cast solutions of $(NH_4)_2MoS_4$ in an organic diamine (ethylenediamine and 1,2-diaminopropane). After deposition the resulting single-source precursor film $[(H_3NC_nH_{2n}NH_3)MoS_4]$ was dried at 250°C in air and subsequently heat treated at temperatures between 300 and 800°C under inert nitrogen (N_2) atmosphere yielding films of MoS_x ($2 \leq x \leq 3$) with carbon impurities. The resulting films with thicknesses up to 160 nm (800°C) and 250 nm (300°C) are highly homogeneous with a metallic lustre and appear brown in transmission. While the films are amorphous to X-ray diffraction up to temperatures of 400°C, the crystallinity increases for higher temperatures due to the formation of MoS_2 micro-crystallites. Furthermore, the composition and the microstructure strongly depend on the used diamine solvent. Both X-ray and electron diffraction reveal a partially preferred orientation of the crystallites with their basal planes parallel to the substrate ($\perp$ c, type II). After heat treatment at 800°C under N_2 the MoS_2 layer stacks consist of three to four layers with a length of 5–8 nm. The optical characterisation of the thin films shows a strong absorption in the visible part of the spectrum characteristic of MoS_2 with an absorption coefficient α_{550} of 2×10^5 cm^{-1}. Tribological measurements up to 5000 cycles against steel reveal the highest wear-life with a friction coefficient $\mu < 0.1$ for coatings heat treated at 500°C. The highest capacity for reversible electrochemical Li intercalation of 30 mC/cm^2 was found in amorphous MoS_x coatings (400°C heat treatment). A weak electrochromic effect with a change in transmission of $\Delta T \approx 0.08$ around 800 nm was observed after Li intercalation.

Keywords: MoS_2; Thin films; Structural properties; Optical properties; Tribology; Electrochemistry

1. Introduction

Molybdenum sulphides have a wide range of potential applications including the use as photoactive materials in solar energy conversion [1], cathodes in secondary lithium batteries [2], lubricants [3], and hydrodesulfurisation (HDS) catalysts [4]. A variety of deposition techniques and routes has been used for the preparation of such films, including physical vapour deposition (PVD) [3] and chemical vapour deposition (CVD) methods [2], chemical bath deposition (CBD) [5], and electrodeposition (ED) [6]. However, wet chemical processes allowing for simple and inexpensive spin-, dip-, or spray-coating of the MoS_2 thin films have not been investigated so far. First results for the deposition of sulphides from organic solutions using the spin coating technique have been reported for amorphous As_2S_3 [7–11] and As_2Se_3 [12,13]. Similar attempts for the preparation of Sb_2S_3 and GeS_x thin films have not been successful due to the low solubility of the corresponding sulphides [9].

MoS_2 has a layer-type structure with S-Mo-S sandwiches held together by relatively weak Van der Waals-type forces. In the hexagonal polytype ($2H$-MoS_2) two such layers form a unit cell. In contrast, MoS_3 exists only in an amorphous form with short-range order [14–16]. By thermolysis of tetrathiomolybdate compounds molybdenum sulphides MoS_x with sulphur contents ranging from $2 \leq x \leq 3$ can be obtained depending on temperature and atmosphere of the decomposition [17].

This paper reports on the preparation of molybdenum sulphide thin films from tetrathiomolybdates by the spin coating method and on the properties of the resulting coatings. In particular, the differences arising from the use of different precursor solutions are described.

2. Experimental

Thin films of MoS_x have been prepared on AF45 glass (DESAG), fused silica, stainless steel (1.4301), and ITO coated borosilicate glass substrates (ASAHI) by the spin coating technique. Thiomolybdate solutions (0.5 M) have been prepared by dissolving $(NH_4)_2MoS_4$ [18] in ethylenediamine or 1,2-diaminopropane, respectively. During the preparation, part of the formed NH_3 is released vigorously

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[*] Corresponding author. Tel.: +49-681-9300-317; fax: +49-681-9300-249.

E-mail address: aegerter@inm-gmbh.de (M.A. Aegerter)

leading to a deep red solution of the corresponding diammonium compound ([$H_3NC_nH_{2n}NH_3$]MoS$_4$). The remaining dissolved NH$_3$ was removed from the solutions by a vacuum treatment (100 mbar) at ambient temperature during 15 min. Alternatively, these solutions can be prepared directly from the respective diammonium thiomolybdates ([$H_3NC_nH_{2n}NH_3$]MoS$_4$).

Because of the relatively high boiling points of the diamine solvents (118–120°C) the substrates were spun for 1 min at 2000 rev./min to pre-dry the precursor films. Subsequently the samples were dried in a convection furnace for 15 min at 250°C in air. The thermolysis of the thiomolybdates was completed under inert nitrogen atmosphere at temperatures between 300 and 800°C during 1h.

The coatings have been characterised by X-ray diffraction (XRD) with Cu K$_\alpha$ radiation on a Siemens D500 diffractometer under grazing incidence of 2.0°. Structure images of the films were obtained by high resolution transmission electron microscopy (HRTEM) with a Philips CM200FEG instrument after detachment of the coating with aqueous HF solution. The film fragments were taken up by copper grids and then viewed perpendicular to the film surface. For the optical characterisation, transmission and reflection (near normal incidence at 7.0°) spectra were taken in the range between 200 and 3000 nm using a Cary 5E spectrophotometer (Varian). A corrected transmission T_{corr} of the films was calculated from the measured transmission spectra T by correction for the reflection ($T_{corr} = T/(1 - R)$). The absorption coefficient α was determined from the absorption $A_{corr} = 1 - T_{corr}$ according to the law of Bouger–Lambert. From the plots of α^2 and $\alpha^{0.5}$ versus the energy the direct and indirect band gap, respectively, were obtained by straight line extrapolation towards zero absorption [19,20].

Friction tests were performed on 1,2-diaminopropane based films on steel substrates (1.4301) in a pin-on-disk tribometer (CSEM) in air at ambient conditions with a 1.0 N load and a speed of 0.1 m/s during 5000 cycles. A 100Cr6 steel ball with a diameter of 2.0 mm acted as the static partner.

Electrochemical properties were measured using an EG&G PAR 273A potentiostat in a three electrode cell with a liquid electrolyte of 1M LiClO$_4$ in propylene carbonate (PC). A 1 cm^2 Pt foil counter electrode and a Ag/AgClO$_4$/1M LiClO$_4$ in PC reference electrode were used. Thin films deposited on ITO borosilicate glasses (ASAHI) were used as working electrodes. Chronoamperometric cycles (CA) were recorded at a potential of −2.0 V (charging) and +0.2 V (discharging) during 300 s.

3. Results and discussion

The colour of the spin cast precursor films changes from orange to deeply brown on drying at 250°C. In order to avoid crystallisation of the diammonium thiomolybdate film, the temperature of drying has to be reached in approximately less than 1 min to partially decompose the precursor and thus to reach an amorphous intermediate stage. This fast decomposition is especially important in case of the ethylenediammonium salt which has a distinct tendency to crystallise. On the other hand, propylenediammonium thiomolybdate has not been observed to form crystals under these conditions. On further heating in inert atmosphere (N$_2$) at temperatures between 300 and 800°C the films become purple with a bright metallic lustre which can be attributed to a loss of sulphur and the formation of MoS$_x$ phases with a reduced sulphur content ($x \approx 2$). The films are highly homogeneous with thicknesses ranging from 90 nm (800°C) to 160 nm (300°C) for ethylenediamine and from 140 nm (800°C) to 250 nm (300°C) for 1,2-diaminopropane based films.

3.1. Structural properties

The diffraction patterns of ethylenediamine and 1,2-diaminopropane based films after heat treatment at temperatures of 600 and 800°C are shown in Fig. 1a,b, respectively. The broad diffraction peak between 15 and 30° is assigned to the silica substrate. The ethylenediamine based films (Fig. 1a) show a single distinct peak at $2\Theta \approx 14°$ corresponding to the (002) plane in 2H-MoS$_2$ (JCPDS 37-1492) or 3R-MoS$_2$ (JCPDS 17-744) whereas ($hk0$) and higher ($00l$) peaks are missing. The peak width decreases with increasing temperature and its position shifts from 13.3 to 14.0°, corresponding to a decrease in the interlayer distance from 0.67 to 0.63 nm. The interlayer distance of 0.615 nm (14.4°) that is found in natural 2H-MoS$_2$ is not obtained under these conditions. According to the calculations of Liang et al. [21], the average number of basal planes contributing to the diffraction pattern can be determined for poorly crystalline MoS$_2$ from the shift and the width of the (002) peak. The thus calculated number of planes per crystallite is 2.7 at 600°C and circa 4 at a temperature of 800°C. Due to the lack of corresponding ($hk0$) peaks, the size of the planes themselves could not be determined by this method.

Different diffraction patterns are found for 1,2-diaminopropane based films (Fig. 1b). After heat treatment at 600°C one does not observe a peak at $2\Theta = 14.4°$ but a broad scattering at low angles, which can be explained by the presence of small, finite crystallites [21,22]. This scattering peak shifts to 10.5° ($d = 0.84$ nm) after heat treatment at 800°C and a second peak at 13.5° ($d = 0.66$ nm) appears. A similar observation of an anomalous low scattering peak for MoS$_2$ has been described by Dunn et al. [23] for films prepared by ion beam assisted deposition (IBAD). The appearance of the low 2Θ peak and the (002) peak shift towards lower angles were explained by the occurrence of fork and dislocation defects by insertion of additional layers resulting in an increased spacing between the basal planes. In the case of the spin deposited films, another possible explanation could be the intercalation of foreign species such as carbon between the basal planes leading to a distinct
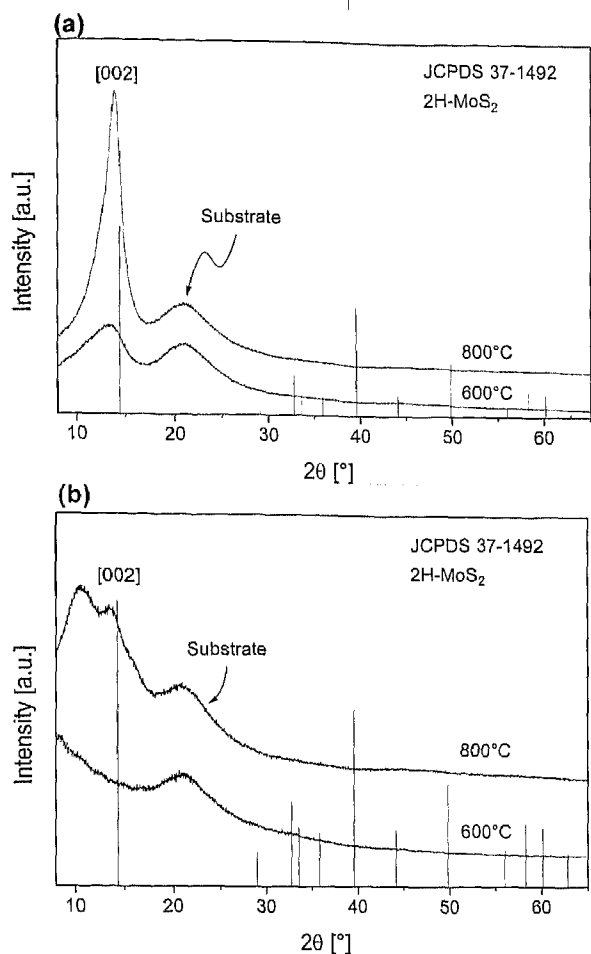
Fig. 1. X-ray diffraction patterns of (a) ethylenediamine and (b) 1,2-diaminopropane based films after heat treatment under N_2 at 600 and 800°C for 1 h, respectively.

spacing and hence the uprising of an additional peak. These carbon impurities would also explain the low crystallinity of the heat treated films. The calculation of the average number of basal planes per crystallite [21] for a film heat treated at 800°C leads to a value of approximately three which is significantly lower than the value obtained for the ethylenediamine based coating with an average of four planes per stack under the same conditions. The differences in microstructure arising from the counter ion might be attributed to the different crystallisation behaviour of the precursors. The ethylenediammonium salt films presumably consist of small ordered areas, whereas the propylenediammonium salt gives an amorphous network with a higher content of residual solvent included and consequently with a higher carbon content after decomposition.

The absence of the (hk0) peaks in both cases does not necessarily indicate a preferred orientation with the c-axis perpendicular to the substrate ($\perp$ c), as the crystallites are very small and the diffraction peaks of the (hk0) planes are small anyway. Another evidence for a film texture comes however from the electron diffraction diagram (Fig. 2). For the interpretation of this pattern one should keep in mind

that the electron beam is directed perpendicular to the film surface whereas in grazing incidence XRD the scattering planes have to be nearly parallel to the substrate. The sharp (100) ring together with the diffuse (002) halo indicate a parallel orientation of the MoS_2 planes relative to the substrate. The weak rings at larger angles belong to the (103), (105), and (110) plane, respectively.

The size of the crystallites is confirmed by the top view HRTEM images in Fig. 3a,b which show small packages of 2–4 basal planes with a length of circa 5–8 nm. In the case of the 1,2-diaminopropane based film (Fig. 3b) several stacks with an increased interlayer spacing or with an opening at one end of the stack can be observed which might explain the anomalous low scattering peak seen in the diffraction patter. In contrast, the planes in the ethylenediamine based film (Fig. 3a) seem to have a constant distance with less deviations from the parallel structure.

3.2. Optical characterisation

Fig. 4 shows the measured optical spectra of films prepared from solutions of $(NH_4)_2MoS_4$ in ethylenediamine and 1,2-diaminopropane after heat treatment at a temperature of 600°C for 1 h. The films are brown in transmission with a reflection between 30 and 45% in the visible range of the spectrum. The absorption coefficient at 550 nm is $\alpha_{550} = 2 \times 10^5$ cm^{-1} according to the relation $T = (1 - R) \cdot \exp(\alpha t)$. From a plot of α^2 and $\alpha^{0.5}$ versus the energy the direct and indirect band gap are determined as 1.8 and 1.2 eV, respectively. In the range from 450 to 620 nm two series of excitons can be found, which are characteristic of MoS_2 [24]. The strong absorption peak at 2.7 μm and the weaker absorptions at 2.2 and 1.4 μm are due to SiOH vibrational modes and related overtones in the silica substrate.
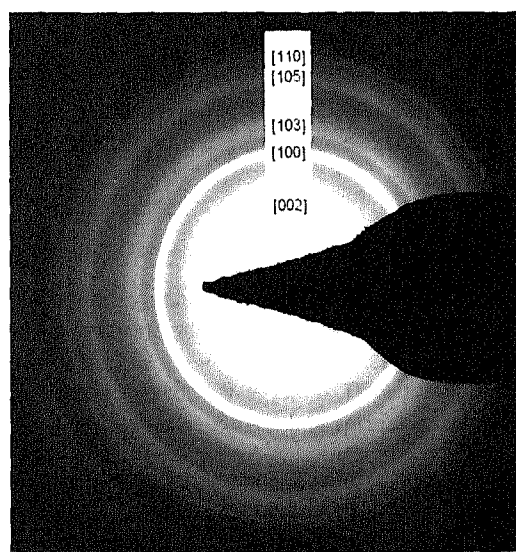

Fig. 2. Electron diffraction pattern of a MoS_x film prepared from a 0.5 M solution of $(NH_4)_2MoS_4$ in ethylenediamine, after heat treatment at a temperature of 600°C for 1 h.
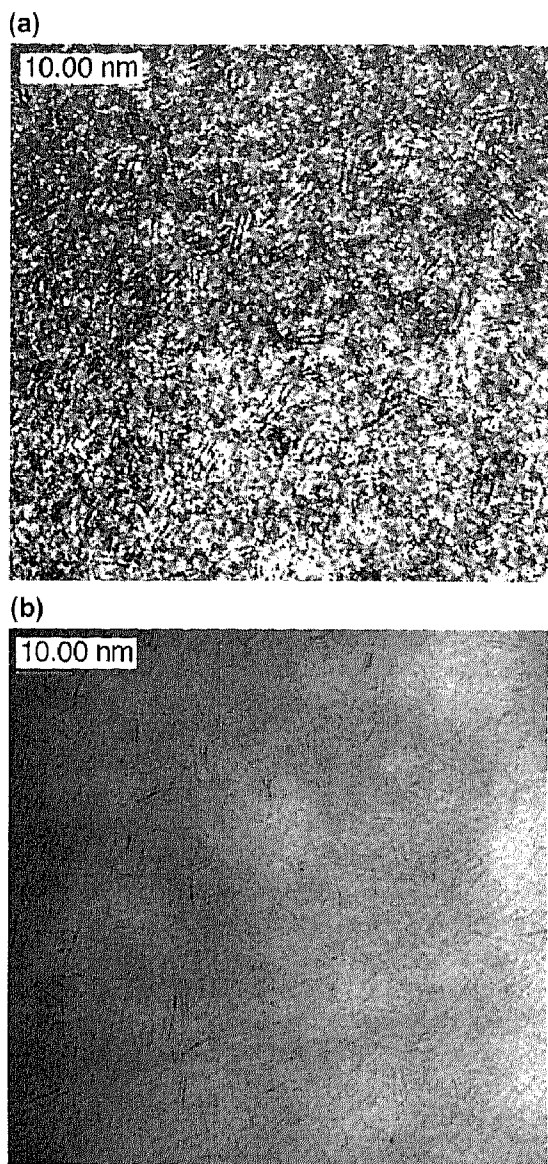
(a)

(b)

Fig. 3. HRTEM structure image of molybdenum sulphide films prepared from (a) ethylenediamine and (b) 1,2-diaminopropane solution of $(NH_4)_2MoS_4$ after heat treatment under N_2 at a temperature of 600°C for 1 h.

3.3. Tribological properties

The tribological properties of 1,2-diaminopropane based coatings are strongly dependent on the temperature of heat treatment (Table 1). After drying in air at 250°C and after heat treatment at 300°C under N_2 the coefficient of friction μ is 0.5 up to 600 cycles and then decreases to 0.1, possibly due to the formation of MoS_2 under sliding. Then μ increases slowly to a value of 0.3–0.4 for the dried films and to 0.8 for the 300°C heat treated sample, which is the value for sliding between the steel ball and the stainless steel substrate. Increasing the temperature of heat treatment to 400 and 500°C results in an improvement with initial values of $\mu = 0.08$ to 0.10. After heat treatment at 400°C the coef-

ficient of friction is constant up to circa 1700 cycles, whereas the coefficient of friction of the 500°C heat treated sample slowly increases and takes values of 0.10 to 0.14 during at least 5000 cycles. After 3000 cycles a partial failure of the film can be observed. Heat treatment at 600°C leads to blueing effects resulting in a rough surface and a poor frictional behaviour. During heat treatment at temperatures above 400°C a sulphidic interface layer is formed.

3.4. Electrochemical properties

Chronoamperometric measurements have been performed to investigate the Li intercalation in MoS_x coatings in dependence of the temperature of heat treatment and consequently of the composition (Fig. 5). It can be seen that the intercalation is not fully reversible in the first cycles at neither of the temperatures investigated (400–600°C). In these initial cycles, only about half of the Li that was charged in the 400 and 500°C heat treated samples is discharged subsequently. At a higher number of cycles (100 cycles) however the Li intercalation becomes reversible and saturation is reached within 300 s.

The capacity of the MoS_x coatings in regard to Li intercalation decreases with the temperature of heat treatment. A sample heat treated at 400°C for 1 h shows the highest capacity of the investigated coatings with values of 37 mC/cm^2 in the first cycle and circa 30 mC/cm^2 reversibly exchanged in subsequent cycles. A heat treatment at 500°C results in films with a capacity of 30 mC/cm^2 in the first cycle and 18 mC/cm^2 after 100 cycles whereas a heat treatment at 600°C gives films with poor intercalation characteristics. The capacity in the latter case is below 3 to 5 mC/cm^2.

These effects cannot be explained by a decrease in film thickness under heat treatment only, but is rather attributed to the microstructure and the chemical composition of the coatings. Amorphous coatings with a composition close to MoS_3 accordingly possess higher intercalation capacities compared with the microcrystalline MoS_2 containing film that is formed at 600°C.

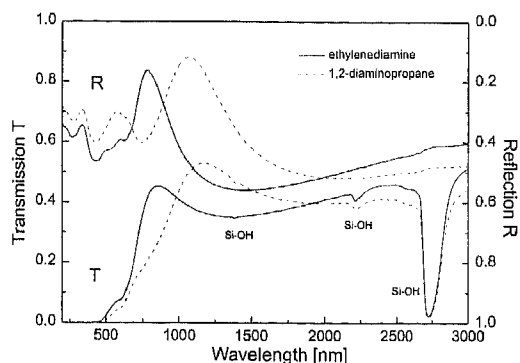Another observation that can be made under electroche-

Fig. 4. Measured transmission and reflection spectra of MoS_x films prepared from ethylenediamine (——) and 1,2-diaminopropane (- - -) based solutions after heat treatment under N_2 at 600°C for 1 h. The thickness of the films is 97 and 155 nm, respectively.

Table 1

Tribological properties of 1,2-diaminopropane based films on stainless steel substrates (1.4301) after heat treatment at different temperatures in air for 15 min (250°C) only or in addition in N_2 for 1 h (300–600°C)

Temperature (°C)	Coefficient of friction	Number of cycles	Remarks
250	0.5 ± 0.1	600	Minimum after 600 cycles at 0.1 ± 0.02 and subsequent increase to 0.3–0.4 ± 0.05
300	0.3 ± 0.1	700	Minimum after 700 cycles at 0.1 ± 0.05 and subsequent increase to 0.8 ± 0.1
400	0.08–0.1 ± 0.02	1700	Increase to 0.8 ± 0.1 after 1700 cycles
500	0.08–0.14 ± 0.02	> 5000	After 3000 cycles beginning destruction
600	–	–	Steel substrate blued initial value of 0.3 ± 0.1

mical Li intercalation is a reversible change in transmission of $\Delta T \approx 0.08$ with a maximum at about 800 nm (500°C heat treatment) or 850 nm (600°C heat treatment), respectively. The corresponding transmission spectra of a coating after heat treatment at 500°C is shown in Fig. 6 for the 3rd cycle. A slow decomposition of the coatings occurs at a higher number of cycles, visible as a slightly increased transmission compared to initial cycles.

4. Conclusions

Homogeneous thin films of MoS_x with varying sulphur content have been prepared with thicknesses between 90 and 250 nm by thermolysis of spin cast diammonium tetrathiomolybdates. The single-source precursors undergo decomposition to amorphous MoS_3 and further to microcrystalline MoS_2 containing impurities of carbon. Depending on the diammonium counter ion, the films show different compositions and structural properties. The interlayer distance in ethylenediamine based films is slightly increased compared to that found in $2H-MoS_2$, whereas in 1,2-diaminopropane based films a larger deviation and an additional

peak in XRD at low 2Θ can be observed that might be attributed to the intercalation of carbon. The MoS_2 films show a high absorption and reflection in the visible with an absorption coefficient of 2×10^5 cm^{-1} at 550 nm. Tribological measurements reveal the highest wear-life with $\mu \approx 0.1$ for films heat treated at 500°C. In Li intercalation experiments the highest capacity was obtained with amorphous phases (400°C), whereas microcrystalline MoS_2 shows only a low tendency to intercalate Li ions. In addition, Li intercalation results in a reversible change in transmission $\Delta T \approx 0.08$ in coatings heat treated at 500 and 600°C. However, this weak electrochromic effect is only observed in the microcrystalline MoS_2 phases.
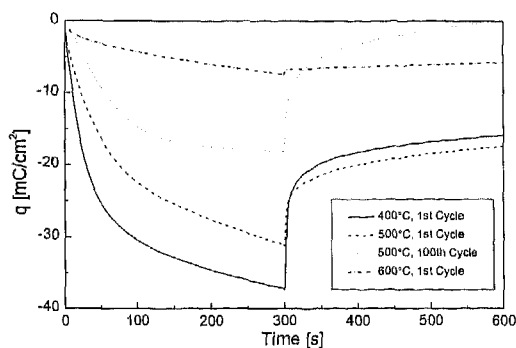
Fig. 5. Chronoamperometric measurements for ethylenediamine based films after heat treatment under N_2 at temperatures between 400 and 600°C. (electrolyte: 1 M $LiClO_4$ in propylene carbonate; charging: 2.2 V (300 s), discharging: + 0.2 V (300 s) versus Ag/AgClO$_4$).
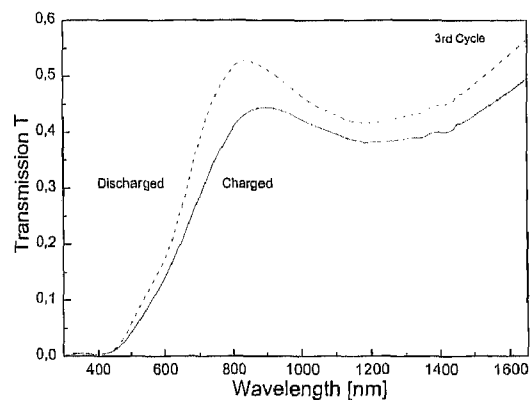

Fig. 6. Transmission spectra of an MoS_x sample heat treated at 500°C for 1 h after chronoamperometric cycling (3rd Cycle; electrolyte: 1 M $LiClO_4$ in propylene carbonate; charging: 2.2 V (300 s), discharging: + 0.2 V (300 s) versus Ag/AgClO$_4$).

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