MoS_3 Thin Film Cathodes Prepared by Chemical Vapor Deposition

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ABSTRACT

Thin films of MoS_3 have been prepared by chemical vapor deposition from molybdenum hexafluoride (MoF_6) and hexamethyldisilthiane (HMDST). Continuous, adherent films were obtained at deposition temperatures in the range of 150° to 400°C on aluminum, nickel, silica, and alumina substrates. Infrared analyses indicate that deposition temperatures between 200° and 250°C produce the purest films. Growth rates in this temperature range are controlled by the reactant flow rates, and averaged 1000Å/min in this study. Four point resistivity measurements showed a minimum in film resistance (90 kΩ-cm) at a deposition temperature of 230°C. The MoS_3 films were studied electrochemically in nonaqueous, secondary lithium cells. The best electrochemical performance was achieved on films deposited in the range of 210°C to 240°C, which corresponded to those films analytically determined to be MoS_3. Four equivalents were discharged and three equivalents could be reversibly cycled at an average discharge voltage of 1.9V *vs.* lithium. Substantial capacity (≈2 equivalents) was maintained after 100 deep cycles (down to 1.0V *vs.* lithium) at a rate of 0.2 mA/cm^2.

Amorphous molybdenum trisulfide (MoS_3) is a promising candidate as a host material in a lithium insertion battery. Initial studies of electrochemical discharge and chemical treatment with n-butyl lithium indicated an exceptionally high lithium capacity of 4.2 lithiums per molybdenum atom (1). Later studies (2-4) of electrodes prepared by the thermal decomposition of $(NH_4)_2$ MoS_4 reported that cycling of MoS_3 was possible. However, the total number of lithiums cycled and the number of cycles obtained were somewhat limited. Recently, in order to determine if the fabrication method and subsequent morphology of the MoS_3 dramatically affected the electrochemical properties in a lithium battery, we studied electrodes of MoS_3 prepared by the thermal and chemical decomposition of ammonium thiomolybdate, as well as by a new direct synthetic technique (5). All electrode studies to date have been on bulk powdered materials compressed or bonded together to form the cathode. We had previously observed that the conductivity of our powders, independent of the preparation technique, was always low and remained low even after lithium insertion (5). This low conductivity limited the discharge rate in a lithium/MoS_3 battery and also added a substantial voltage drop to the system. Graphite or other conductive additives can be used to increase the bulk conductivity; however, these additives act to decrease the energy density of the electrode, and cannot assure that all of the cathode material will be in electrical contact.

We felt that the preparation of thin film MoS_3 electrodes would offer several advantages over the previous techniques. From a fundamental point of view, the thin films would allow for a study of the electrochemical behavior of pure MoS_3 without binders or other additives. The thin films should also exhibit mechanical integrity and continuous electrical contact, decreasing the overall electronic resistance and allowing for accurate determination of the capacity of the electrode. Finally, from an applied perspective, we felt that thin film cathodes offered a good possibility for achieving high discharge rates with large surface area batteries.

Previously we had shown that bulk MoS_3 could be prepared at low temperature from the reaction shown in Eq. [1]

$$MoF_6 + 3(CH_3)_3\,Si\text{-}S\text{-}Si\,(CH_3)_3 \rightarrow MoS_3 + 6\,(CH_3)_3SiF \quad [1]$$

Since this reaction proceeded at temperatures lower than the decomposition temperature of MoS_3 (250°C); the only by-product, trimethylsilylfluoride, is a gas at 18°C; and both reagents, MoF_6 and hexamethyldisilthiane (HMDST), have high vapor pressures, we decided that chemical vapor deposition (CVD) would be possible. We feel that CVD film techniques offer the capability of inexpensively preparing large surface area, thin films that could have industrial applications.

Experimental

Materials.—Molybdenum hexafluoride (Var-Lac-Oid Chemical Company) was used as obtained. HMDST (Fluka Chemical Corporation) was fractionally distilled, and material within a boiling range of 160°-162°C was collected and used. The argon (Linde, 99.9995%) diluent and carrier gas was used as obtained.

Reactor design.—A low pressure, hot-walled reactor was used to prepare the thin films (see Fig. 1). The flow of MoF_6 and argon was controlled by a standard mass flow control meter (Brooks 5850). The pressure inside the reactor was monitored with a capacitance manometer (Vacuum General CML-21), and controlled via a feedback loop (Vacuum General 80-6A) to a throttle valve system (Vacuum General MDV-015). The vacuum within the system was maintained by a mechanical pump (Alcatel 2008A). The exhaust gases were pyrolyzed under air in a high temperature furnace (1000°C) to control odor. The temperature within the reaction zone was maintained by controlling (Partlow MIC2000) a Kanthal wound furnace. The temperatures inside the furnace were measured with a Chromel/Alumel thermocouple standardized *vs.* ice and boiling water.

Analysis of films.—Resistivity and film thickness were determined on films deposited on alumina substrates. The thickness of the films was determined by measuring the profile of the surfaces which were scratched with a razor

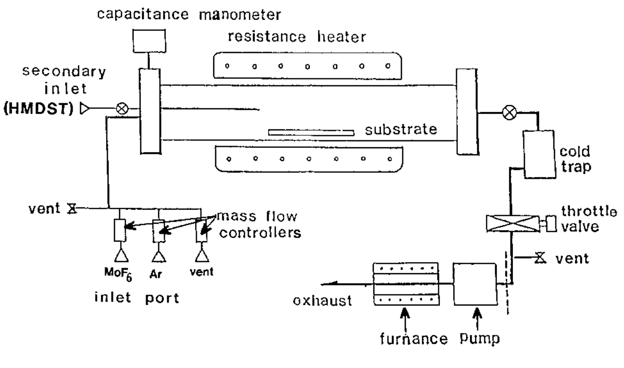

Fig. 1. Schematic representation of the CVD reactor

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blade, using a Dektak-1 Profilometer. For resistivity measurements, a four-point probe technique was used by applying varying voltages to the film to assure that true Ohm's law resistances were measured (Probex station, using a Keithley 230 Voltage Source and 619 Electrometer/Multimeter). The molybdenum content of the films on aluminum foil was determined by dissolving a known area of film in aqua regia. The resulting solutions were analyzed for Mo concentration using inductively coupled plasma emission spectrometry (Thermo Jarrell Ash, Plasma 200), with a 1000 ppm Mo standard (Fisher) as the reference solution. This molybdenum analysis, coupled with the electrochemical measurements, allowed for an accurate determination of the lithium concentration in the electrode films during the electrochemical experiments. Infrared (IR) measurements were performed on films deposited either on alumina, silica or silicon substrates. The MoS_3 film was scraped off the substrate and mixed with KBr or CsI. A 1 cm pellet was prepared by compressing the mixture to 3 metric tons. All spectra were run from 400 to 4000 cm^{-1} on a Digilab Ft-60 Fourier transform spectrometer. IR spectra from 150 to 450 cm^{-1} were obtained on a Mattson Cygnus 100 on CsI pellets. Density measurements were performed by the flotation technique using CCl_4 as the flotation liquid. The CCl_4 density was calibrated with single-crystal silicon immediately prior to use. The measured density was compared to the film density using samples of known thickness deposited on Al foil. X-ray powder diffraction, to verify that no crystalline phases were present, was performed on a Philips automated diffractometer (APD 3720) using CuK_α radiation. Energy dispersive x-ray analysis (EDAX) was performed using a Hitachi H-800, 200 kV scanning transmission electron microscope (STEM) with a Kevex Quantum detector.

Electrochemical.—All films used for electrochemical measurements were grown on aluminum foil substrates. Half-inch disks of the films were used as positive electrodes with a scraped lithium disk (Foote Chemical) negative electrode. The cell configuration was an electrolyte-starved sandwich of the positive and negative electrodes held within an insulating 1/2-inch Swagelok holder by a stainless steel spring and 1/2-inch stainless steel rods. The separators were one disk each of glass filter paper (Fisher, GF/A) and polypropylene membrane (Celgard, CG3402) soaked with 1.0*M* lithium perchlorate in propylene carbonate ($LiClO_4$/PC) electrolyte. Cells were assembled in a helium-filled glove box maintained at <1 ppm each of water and oxygen.

The electrochemical cells were discharged and charged at constant current between preset voltage limits. A microcomputer was used to control the experiments and record data, using either a current source and voltage meter (Keithley 220 or 224 and Keithley 192 and 195a) or a potentiostat/galvanostat (PAR 173 with Model 276 interface plug-in). All films were initially cycled at low rate (0.01 mA/cm^2), while a film deposited at 210°C was used to study higher rate capability (up to 0.2 mA/cm^2) and cycle life (up to 100 cycles).

Results and Discussion

In order to optimize the growth conditions for films of MoS_3, our reactor design allowed for rapid change in several parameters. A schematic representation of the reactor design is shown in Fig. 1. The total pressure within the reactor could be successfully monitored and controlled within the range of 1-100 torr. The flow rates available for the MoF_6 were 1-1000 standard cubic centimeters per minute (sccm). The MoF_6 could be readily diluted with argon within the mixing manifold, and therefore further reduce the partial pressure of MoF_6 within the reactor. The flow of HMDST was controlled by changing the temperature and hence the vapor pressure within the reservoir. The exact position of HMDST injection into the reactor could be changed by extending or reducing the length of the glass injection port. The temperature of the entire reaction zone could be set as desired, and since a temperature gradient normally existed within the furnace, several temperatures could be monitored during one reaction.

Initial experiments were performed at total pressures of 10 torr with the MoF_6 introduced at 20 sccm with no argon dilution. The HMDST was maintained at 50°C. Under these conditions a black powder rapidly formed throughout the reactor. In addition, these conditions led to extreme excesses of the sulfurizing agent, HMDST, which rapidly filled the dry ice/acetone trap.

After changing many of the conditions we found that good quality films could be regularly produced under the conditions shown in Table I. Although we were able to deposit films with no difficulties at temperatures as high as 400°C, we suspected that any films grown at temperatures greater than 300°C would probably contain phases other than MoS_3, because of thermal decomposition. Also, as the temperature of the reactor is increased above 200°C, the quartz vessel is readily attacked during the reaction. In order to prevent destruction of the reactor as well as reduce impurity incorporation into the films, we completely coated the exposed reactor components with nickel.

Several substrates were used during the deposition process. For electrochemical studies we selected aluminum and nickel foil. For determining thickness, conductivity, and IR characteristics we deposited the films onto single crystal wafers of silicon and alumina as well as quartz slides. The physical characteristics of the films depended substantially on the growth temperatures. At very low temperatures (50°C), adhesion on all substrates was poor and cracking and peeling occurred in all films. As the temperature increased to 100°C, the adhesion was markedly improved on the aluminum and nickel foils; however, cracking and flaking were still evident on the silicon, silica, or alumina substrates. At deposition temperatures equal to or greater than 150°C, adhesion and film quality was excellent on alumina, as well as aluminum and nickel foil. The adhesion quality on silicon and silica is only moderate, and some cracking occurs even at elevated deposition temperatures. The films deposited on metal foils have excellent adhesion and resistance to cracking. In fact, even after electrochemical cycling, the film remains intact and resistant to cracking.

Under the conditions previously described in Table I, the growth rate is independent of substrate temperature in the range from 150°-300°C. Therefore, the limiting step at these temperatures is the rate at which the active chemical species can arrive at the substrate, rather than a thermally activated decomposition process. In this temperature range, the films grew at 1000 ± 200 Å/min. At very low temperatures, *i.e.*, less than 100°C, the growth rate is temperature-dependent and slower than at higher temperatures.

Film characterization.—Although we had previously shown that bulk MoS_3 could be prepared by the metathesis reaction between HMDST and MoF_6 (5-6), we were unsure of the existence of the desired phase under chemical vapor deposition conditions. X-ray powder diffraction of this amorphous material can only indicate that no crystalline phases are present and cannot detect trapped impurities. Fourier transform infrared (FTIR) can rapidly determine if

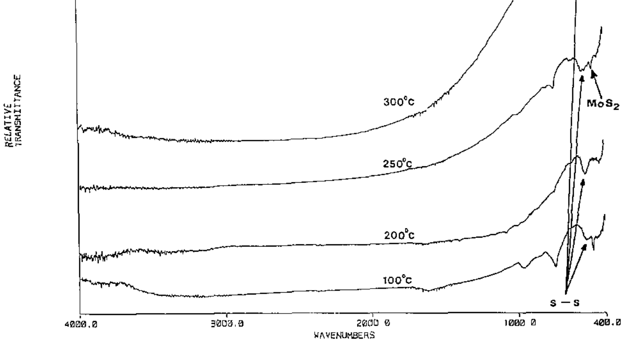

Fig. 2. FTIR spectra (4000-400 cm^{-1}) of MoS_3 films obtained by CVD

the amorphous material formed shows the necessary MoS_3 absorptions as well as if any anomalous absorptions are present. In Fig. 2 we show the FTIR transmission spectra for films grown on silicon substrates at various temperatures. The films prepared at 100°C show anomalous absorptions between 400-1000 cm^{-1} not expected for pure MoS_3 (7). The sharp peak observed at 741 cm^{-1} corresponds to a Mo-F fundamental vibration frequency for MoF_6 [v_1 ($a_{1}g$) = 741 cm^{-1}, $v_3(f_{1u})$ = 741 cm^{-1}] (8). In view of this absorption, and the hygroscopic nature of molybdenum fluoride, the peak observed at 950 cm^{-1} most likely corresponds to a molybdenum-oxygen bond. A strong absorption near 950 cm^{-1} is observed for molybdenum oxyfluorides and has been assigned to a molybdenum-oxygen double bond (9). An expansion of the scale on the 100°C film also indicates weak peaks at 1600 and 3500 cm^{-1} corresponding to water (10).

These results tend to prove that at 100°C the sulfurization of MoF_6 is not complete. As the deposition temperature is raised to 200°C, the anomalous peaks disappear. The only absorbances observed directly match those expected for MoS_3. Specifically, a very clear peak is evident at approximately 540 cm^{-1} which corresponds to a sulfur-sulfur stretch. The other, weaker absorption at a lower (431 cm^{-1}) frequency has been observed by Raman spectroscopy for MoS_3 (7). As the deposition temperature is raised to 250°C, the spectrum again changes. The intensity of the S-S stretch decreases and broadens. In addition, a small peak characteristic of MoS_2 appears. Films prepared at 300°C show almost no peak at 540 cm^{-1}, indicating that by this temperature little if any amorphous MoS_3 phase containing S-S bonds exists. The samples were examined in the low frequency range (150-500 cm^{-1}) to see if the sharp peak at 385 cm^{-1} corresponding to crystalline MoS_2 is visible (Fig. 3). The only peak observable is a broad peak at about 350 cm^{-1} as expected for classical MoS_3 (7). The sample prepared at 300°C does show a peak at ≈382 cm^{-1}, which is broader than that observed for crystalline MoS_2, but could very well correspond to poorly crystallized material.

Resistivity measurements.—Since the FTIR measurements indicated that pure MoS_3 films existed only within a narrow temperature range, we concentrated our resistivity measurements on several samples prepared at small temperature intervals close to 200°C. Table II contains the four probe resistivity values in Ω-cm for films prepared on alumina substrates. All the films showed relatively high resistivity values; however, since the films are thin, the total electrode resistance will be less than 1 kΩ. A minimum in the resistivity appears at a deposition temperature near 230°C. Since the FTIR indicates that films prepared at 250°C have noticeable decomposition, and that films prepared below 200°C contain impurities, this minimum may represent an optimum growth temperature for pure MoS_3 film electrodes.

Table I. General reaction parameters

MoF_6	2 sccm flow rate
Argon (diluent)	175 sccm flow rate
HMDST	25°C
Total pressure	1.5 torr
Reaction temperature	50°-400°C

Table II. Four-point resistivity and film thickness

Temperature (°C)	Resistivity (Ω-cm)	Thickness (μm)
180	750×10^3	8.8
210	260×10^3	3.5
230	90×10^3	5.5
240	480×10^3	4.5
250	350×10^3	3.4

Table III. Density of MoS_3 film

Growth temperature	Displacement density (g/cm^3)	Actual film density (g/cm^3)	Volumetric packing
(230°C HMDST)	3.20 ± 0.10	1.90	59.4%
230° [$(NH_3)_2MoS_4$]	3.20 ± 0.10		
300°C	3.63 ± 0.10		

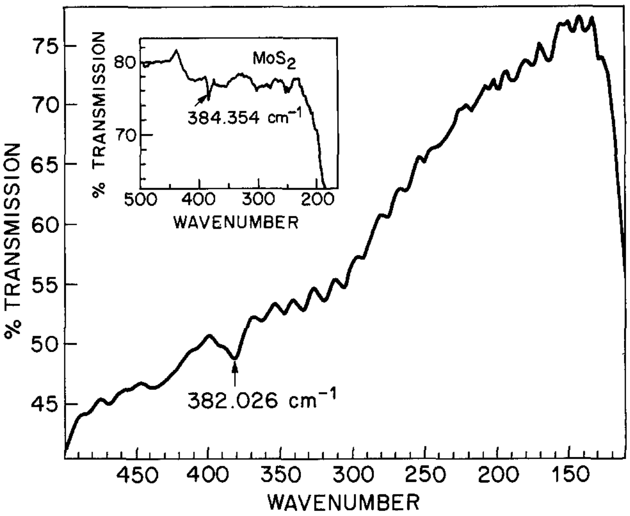

Fig. 3. FTIR spectra (500-150 cm^{-1}) of MoS_3 films obtained by CVD

Density measurements.—In order to continue our verification of film modifications as a function of temperature, we measured the flotation density of thin films scraped off silica glass slides. In Table III we see the measured densities as a function of growth temperature. The increase in density of films grown at temperatures greater than 230°C indicates that these films are probably richer in molybdenum than MoS_3. Within experimental error, the density of our thin films grown at 230°C is identical to that of MoS_3 powders prepared from thermal decomposition of $(NH_4)_2MoS_4$ at 230°C. The actual film density calculated from the measured film thickness and weight is about 60% of the density of the pure material for the optimum 230°C sample.

EDAX measurements.—Since we observed Mo-F vibrations in the films prepared to 100°C, we felt it was necessary to verify that no impurities could be detected in the 230°C film of primary interest. Using a low energy detector, we observed no fluorescence typical of either fluorine or silicon. The only observed peaks could be explained on the basis of molybdenum, sulfur, and aluminum from the substrate. Due to the extreme overlap between sulfur and molybdenum peaks, it is impossible to obtain an accurate stoichiometry relationship between molybdenum and sulfur.

Electrochemical measurements.—The electrochemical voltage curves for the MoS_3 films agree well with previously reported data for the powdered MoS_3 electrodes (5). Figure 4 shows the first cycles of a MoS_3/Li cell, cycled at 0.01 mA/cm^2 between the voltage limits of 1.0 and 3.0V. The electrode film in this cell was deposited at 210°C. As observed in the earlier work on MoS_3 powders, approximately four equivalents of lithium can be discharged on the first cycle, followed by reversible cycling of approximately 3 equivalents of lithium. This supports the hypothesis that the retention of lithium in the positive electrode after the first discharge is a characteristic of the active material, rather than a failure of the composite electrode fabrication technique. Approximately one equivalent of lithium appears to be retained within the host matrix, and cannot be removed electrochemically. Recent IR/Raman studies seem to indicate that at high insertion values, the S-S bond in MoS_3 is completely broken, and could explain the irreversibility (11). The average discharge voltage of the MoS_3/Li cell is approximately 1.9V, corresponding to a theoretical specific energy density of 796 Wh/kg, assuming 3 reversible equivalents.

The voltage curves for most of the films deposited within the temperature range of 200°-250°C were quite similar.

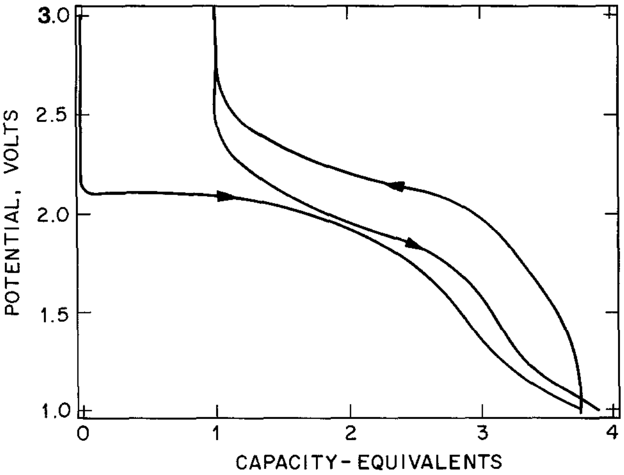

Fig. 4. Voltage curve for the first cycle of a MoS_3 film deposited at 210°C, cycled at 0.01 mA/cm^2 between 1.0 and 3.0V *vs.* lithium.

Small variations in the film capacity (±5%) can be attributed to the uncertainty of the molybdenum analysis and nonuniformity of the deposited films. Films deposited at low temperatures (≤200°C) generally showed a voltage delay during the initial segment of the hysteresis. Figure 5 shows the voltage curve for a MoS_3/Li cell (200°C deposition), cycled at 0.01 mA/cm^2 between the voltage limits of 1.0 and 3.0V. The inferior cell performance may be attributed to impurities incorporated in the film during deposition, causing irreversible reactions with lithium.

The long-term cycling capabilities were studied on a film deposited at 210°C. After some variable rate tests during the first six cycles, the cell was allowed to cycle up to 100 cycles at a rate of 0.2 mA/cm^2 between the voltage limits of 1.0 and 3.0V. This discharge capacity of the cell is shown in Fig. 6 as a function of cycle number. The cell maintained substantial capacity (≈2 equivalents of lithium) even after 100 deep cycles. Most of the capacity loss occurred during the first six cycles, as the cycling rate was increased. Only approximately 10% of the cycling capacity was lost during the last 94 cycles at a constant rate of 0.2 mA/cm^2. This cycling behavior represents a dramatic improvement over the cycling behavior reported for powdered MoS_3 composite electrodes (5). Under the same voltage conditions, the capacity of the composite electrodes dropped below 2 equivalents after 20 cycles, and reached ≈1 equivalent of discharge after 90 cycles. This improvement in cycle life can be largely attributed to the superior electrical and mechanical properties of the continuous film electrode. A composite electrode of powdered active material generally shows deterioration of structure with cycling, leading to loss of contact between particles and decline in capacity.

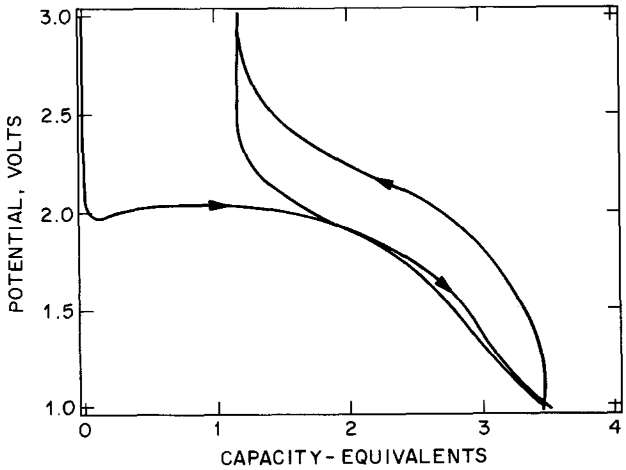

Fig. 5. Voltage curve for the first cycle of a MoS_3 film deposited at 200°C, cycled at 0.1 mA/cm^2 between 1.0 and 3.0V *vs.* lithium.

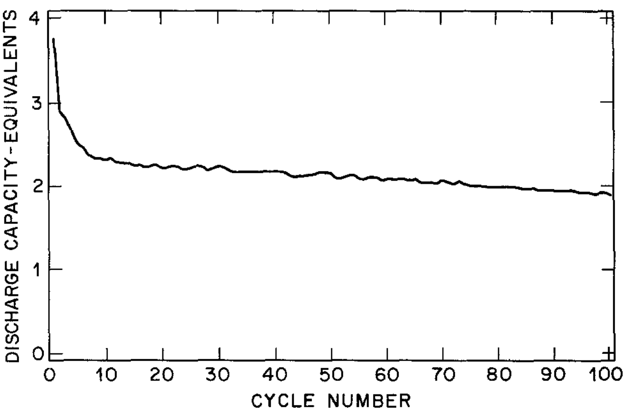

Fig. 6. Cycle life of a MoS_3/Li cell (film deposited at 210°C), cycled at low rates during first six cycles, followed by 0.2 mA/cm^2 to 100 cycles, between voltage limits of 1.0-3.0V *vs.* lithium.

Short-term cycling tests on films deposited at higher temperature showed inferior cycling behavior. For an electrode deposited at 300°C, the capacity began to deteriorate and the voltage hysteresis, especially at the end of charge, increased significantly after less than 10 cycles. On disassembly after cycling, the electrode film was brittle and could be removed from the aluminum substrate by rubbing. The film adhesion was noticeably worse compared to uncycled films. Films deposited at lower temperature (<250°C) were generally adherent to the substrate, even after cycling. This cracking or loss of mechanical stability may be caused by precipitates of MoS_2 within the MoS_3 film. Crystalline MoS_2 also undergoes electrochemical reduction under these conditions, with accompanying phase changes (8). Although the contribution from MoS_2 reduction and oxidation is not evident in the electrochemical measurements, this added phase may produce stress or defects in the film, causing loss of structural integrity.

The rate capability of these films was studied during the first few cycles of a MoS_3/Li cell made with a film deposited at 210°C. Figure 7 shows the discharge curves for this cell at rates of 0.01, 0.02, 0.1 and 0.2 mA/cm^2. As expected, the voltage and capacity are both lowered with increased rate. However, the more than tenfold increase in current density had a relatively small effect on total cell performance. The curves for 0.01 and 0.02 mA/cm^2 are nearly identical, while there is a more noticeable drop in voltage at the higher rates. The effect of higher rates is most apparent during the last equivalent of reduction, below about 1.5V *vs.* Li, suggesting that either the resistance of the film increases with lithium content or that this last insertion process is different than the preceding ones. While 0.2 mA/cm^2 may seem like a relatively low current, the electrode films are very thin, so high currents can be achieved with high surface area cell designs. For this particular cell, the electrode capacity was ≈0.172 mAh/lithium equivalent, so a full deep cycle (charge and discharge) at 0.2 mA/cm^2 took only 3h. In applications where further decline in ca-

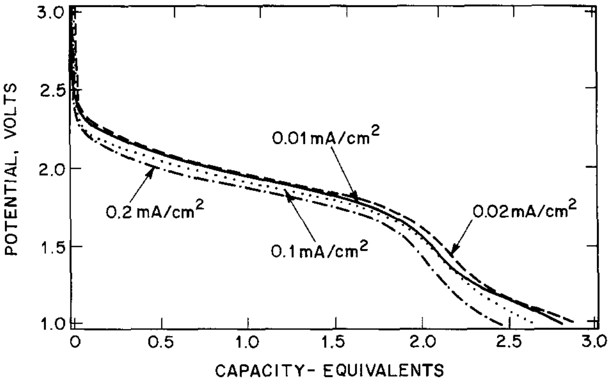

Fig. 7. Discharge curves for MoS_3/Li cell (film deposited at 210°C), at rates of 0.01, 0.02, 0.1, and 0.2 mA/cm^2.

pacity is acceptable, these films are capable of even higher discharge currents.

Conclusion

From these studies it appears that high-quality amorphous molybdenum sulfide films can be prepared by chemical vapor deposition. The density of films prepared close to 200°C corresponds well to the density of bulk MoS_3 prepared by classical techniques. As the temperature of film preparation is increased, there is a rapid increase in density, corresponding to a loss of sulfur, as expected. For both the bulk and thin film MoS_3, it seems impossible to be certain of the exact stoichiometry. However, the density and FTIR results support that the materials are the same. The films can be readily deposited on various substrates, including simple aluminum foil. The films are very flexible and, even when deposited on Al foil, the adherence is remarkably good. Under our deposition conditions we obtain packing densities of approximately 60%. The films can easily be prepared even in our small research reactor with surface areas of several hundred square centimeters. The growth rate has not been optimized, but the rates described in this work (1000 Å/min) are sufficient for most applications. If indeed one of the main problems of the application of MoS_3 as a cathode material is the intrinsic resistivity of the material, this problem has been diminished but not eliminated by thin film preparation. The careful control of temperature has allowed us to minimize the resistivity of the films, and the minimum occurs when the stoichiometry is close to MoS_3. We are continuing our work on thin films of MoS_3 to obtain resistivities substantially lower than the lowest observed, of 90 kΩ-cm. It is our feeling that the only possible method of lowering the resistance is to heavily dope the material.

The thin film work has allowed us to rapidly analyze several materials electrochemically and to observe the intrinsic limits of MoS_3 without binders or additives. The electrochemical behavior of thin films prepared in the temperature range of 200°-250°C closely parallels the results obtained for bulk MoS_3; however, superior long-term cycling behavior was demonstrated. Two-thirds of the original cycling capacity was maintained after 100 deep discharge cycles at a rate of 0.2 mA/cm^2, with almost all of this loss occurring during the first 6 cycles. In addition, increasing the current density by a factor of 20 caused only moderate change in the voltage characteristics. The electrochemical films show promising properties for use in high surface area, high rate batteries, and for solid electrolyte, thin film batteries.

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Electrodeposition of Silver under Direct and Pulsed Current

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ABSTRACT

Electrodeposition of Ag^+ ions on a vertical plane cathode immersed in stagnant 0.5*M* $AgNO_3$ and 0.5*M* $AgNO_3$-0.5*M* HNO_3 solutions was carried out under direct and pulsed current. The morphological variations with electrolytic conditions were examined by measuring the average diameters of the electrodeposits using the intercept method. The ratio of the particle diameter obtained in a $AgNO_3$-HNO_3 solution under pulsed electrolysis to that under direct current at the same average current density was minimum near 50-60 mA/cm^2. It was further enhanced with a decrease in the duty cycle when the pulse-on time and the charge density were maintained at 1 ms and 9 C/cm^2, respectively. The concentration profiles of Ag^+ ions in $AgNO_3$ solution were also measured by holographic interferometry. In these experiments, the duplex diffusion layer model proposed by Ibl (18) was found to adequately describe the phenomena provided that the pulse-on time was sufficiently long. Based on the concentration profile measurements, it was deduced that the appearance of the minimum ratio of particle diameter was closely related to the depletion of the surface concentration of Ag^+ ions during the pulse-on time, that is, to the concept of limiting current pulse.

It is well known that industrial silver electrorefining in nitrate solution has certain disadvantages such as the need for scrapers and a large distance between electrodes due to dendrite formation. A number of studies have been reported (1-4) on research to find ways to overcome these difficulties.

Many papers (5-11) have also been published on electrocrystallization. From the standpoint of technological importance, the studies on polycrystalline substrate (7, 10, 11) are noteworthy. Fisher observed that nitric acid had an inhibiting effect on the silver deposition (7, 10). Vereecken and Winand (11) studied the effect of electrolyte composition, temperature, current density, and duration on morphology. They qualitatively summarized the nature of the

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