

MOLYBDENUM TRISULFIDE THIN FILM CATHODES PREPARED BY CHEMICAL VAPOR DEPOSITION (EXTENDED ABSTRACT)

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Amorphous molybdenum trisulfide is a promising candidate as a host material in a lithium insertion battery. Initial studies of electrochemical discharge and chemical treatment with *n*-butyllithium indicated an exceptionally high lithium capacity of 4 lithium atoms per molybdenum atom [1]. Later studies of electrodes reported that cycling of molybdenum trisulfide was possible; however, the total number of lithium equivalents cycled and the number of cycles obtained were somewhat limited [2 - 4]. In all of these previous studies the electrode material was a pressed powder prepared by the thermal or chemical decomposition of ammonium tetrathiomolybdate. Recently, in order to determine if the fabrication method and subsequent morphology dramatically affected the electrochemical properties, we studied electrodes of MoS₃ prepared by a new, direct synthetic technique [5]. In this work we were still preparing electrodes from powders with binders added to improve conductivity.

We felt that the preparation of thin film electrodes would offer several advantages over powder electrodes. From a fundamental point of view, the thin films would allow for a study of pure MoS₃ without binders or other additives. The thin films should also exhibit mechanical integrity and continuous electrical contact, perhaps decreasing electrical resistance and increasing the capacity of the electrode. In addition, we felt that thin film cathodes offered a good possibility for achieving high discharge rates.

In order to prepare thin films of molybdenum trisulfide we chose to look at chemical vapor deposition as a viable route to the preparation of relatively large surface area films. In order to prepare MoS₃ thin films it is necessary that the substrate can be maintained at temperatures lower than the decomposition temperature, 275 °C. We had previously discovered [6] that it was possible to prepare MoS₃ even at sub-room temperatures using the reaction shown in eqn. (1):



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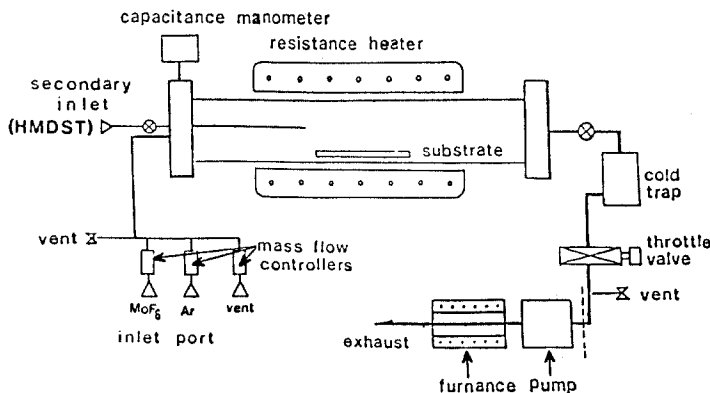


Fig. 1. Schematic diagram of hot-walled, low pressure reactor.

In this reaction the initial starting materials (hexamethyldisilthiane and molybdenum hexafluoride) both have high vapor pressure at room temperature and the only by-product (trimethylsilyl fluoride) is a gas at 18 °C. Since this reaction proceeds spontaneously at low temperature, it was necessary to experiment with several conditions in order to obtain films rather than powders. We elected to use a hot-walled, low pressure reactor (Vacronics Inc.) so that the maximum number of variables could be rapidly tested (Fig. 1).

We have been able to prepare films using the chemistry described by eqn. (1) throughout the temperature range 50 °C - 350 °C. As substrate material we have used silicon wafers, alumina wafers, silica, aluminum foil and nickel foil. The adherence of the film to the substrate is dependent on the substrate material, the temperature of deposition, and the rate of deposition. When either aluminum or nickel foil is the substrate material adhesion is excellent under almost any condition. In order to obtain good adhesion to the other substrates temperatures greater than 150 °C must be maintained and lower growth rates are preferred. For the electrochemical studies films were grown at 1000 Å min⁻¹. The growth rate is independent of temperature from 100 °C to 300 °C and varies with the partial pressure of active gas species. Since we always maintained excess hexamethyldisilthiane, the growth rate was dependent on the MoF₆ flow rate and pressure.

TABLE 1

Mo source	Substrate temperature (°C)	S/Mo ratio	Density (g cm ⁻³)
[(NH ₄) ₂ MoS ₄]	230	3	3.2
[MoF ₆]	230	3	3.2
[MoF ₆]	300	2.5	3.6
[MoF ₆]	180	3.5	3.3

In order to determine if the films prepared were pure MoS_3 we undertook chemical analysis, density, and spectroscopic analysis. The chemical analysis and density (Table 1) indicated that samples prepared at temperatures less than 200°C , or greater than 280°C , are probably not MoS_3 . The FTIR measurements confirm that the ideal growth temperature has a very narrow range.

We performed electrochemical measurements on samples grown on aluminum foil substrates. The cell configuration was an electrolyte-starved sandwich using a polypropylene membrane soaked with 1.0 M lithium perchlorate in propylene carbonate electrolyte. The cells were cycled at constant current between the voltage limits of 1.0 and 3.0 V. Even at moderate discharge rates (0.2 mA cm^{-2}) we observed very good cycling behavior of the electrode with very little loss after the first three cycles (Fig. 2).

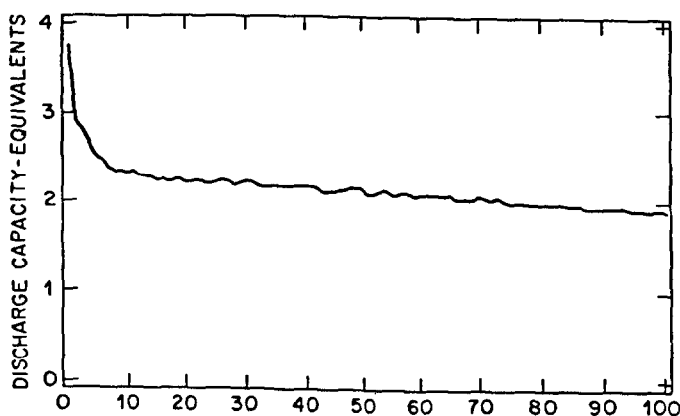


Fig. 2. Discharge capacity vs. cycle number.

The adherence and flexibility of these amorphous films is remarkable, and even after multiple cycling there is no visible degradation of the film continuity. The actual volumetric density of the film determined from the thickness is 2.1 g cm^{-3} relative to the measured density of 3.2 g cm^{-3} .

This particular CVD approach to preparing thin films of MoS_3 is quite effective and even in our small reactor it is easy to prepare electrodes with a substrate surface greater than 400 cm^2 . However, we are also exploring alternative low temperature sulfurization routes due to the cost and odor of hexamethyldisilthiane. We will discuss the advantages and disadvantages of similar organic mercaptans and sulfides in the preparation of thin film sulfides, specifically MoS_3 .

References

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