

Synthesis of Novel Molybdenum Chalcogenides

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Recently, there has been substantial interest in using molybdenum chalcogenides as active cathodes in lithium batteries. It has been observed that the structural make-up of the material (crystalline or amorphous) is often of critical importance in the ability of the compound to intercalate lithium. We have directly synthesized molybdenum chalcogenides with different molybdenum/chalcogen stoichiometries by reacting various molybdenum halides with hexamethyldisilthiane. The resulting sulfides have been intercalated by using *n*-butyl lithium, and show high lithium uptake. Initial electrochemical measurements show that 3Li/Mo may be reversibly discharged in our MoS₃. © 1986 Academic Press, Inc.

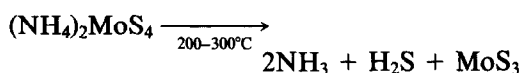
Introduction

Molybdenum chalcogenides have a wide range of possible applications including heterogeneous catalysts, superconductors, and active cathodes in lithium batteries. Within the binary molybdenum-sulfur system the compounds MoS₃, MoS₂, Mo₂S₃, and Mo₃S₄ are known (1, 2). In addition the hydrated compound Mo₂S₅ · 3H₂O can also be prepared (3). The techniques for preparing these compounds can in general be divided into two types: (1) Direct high-temperature synthesis and (2) Indirect or low-temperature synthesis.

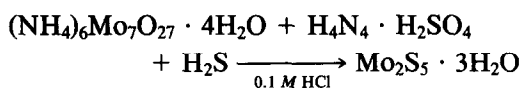
The direct high-temperature synthetic route is the classical one of mixing together the elements in the proper proportions and heating in evacuated sealed tubes at high temperature. The molybdenum sulfides MoS₂ and Mo₂S₃ can both be prepared by this approach.

The indirect or low-temperature routes for synthesis can be varied considerably and yield compounds that may be either crystalline or amorphous. It is via these in-

direct or low-temperature techniques that the other molybdenum sulfides are formed. In the case of Mo₃S₄, a crystalline compound is formed when *M*Mo₃S₄ (where *M* = Cu, Ni, Ca, Fe, Mn, Cr, Mg, Cd, Zn) is attacked by hydrochloric acid (2). The amorphous compounds MoS₃ can be prepared either by the thermal decomposition of ammonium thiomolybdate



or by the precipitation of molybdenum (6+) in acidic aqueous solutions saturated with hydrogen sulfide. There exists no report in the literature of a crystalline compound MoS₃. There have been attempts to synthesize the compound Mo₂S₅; however, the only well-characterized compound showing a sulfur-to-molybdenum ratio of 2.5 is the hydrated Mo₂S₅ · 3H₂O prepared by the precipitation of aqueous, acidic molybdenum(V) in solutions by hydrogen sulfide:



Chianelli and Dines prepared MoS₂ at room temperature by reacting molybdenum halides with lithium sulfide in polar organic solvents (4):



It was this work and the subsequent studies on this amorphous material as an active cathode in lithium batteries which initiated our interest in the synthesis of molybdenum sulfides. Although reports on crystalline MoS₂ showed that only 0.03Li/Mo could be electrochemically inserted during battery operation (5), using a cathode prepared from the low-temperature amorphous MoS₂, 1Li/Mo could be electrochemically cycled (6).

Subsequent work indicated that if crystalline MoS₂ were discharged under particular conditions to allow for a phase change, a much greater lithium capacity could be obtained (7). In the case of molybdenum disulfide it appeared as though the specific structure and morphology of the material strongly affected the applicability of MoS₂ as an active lithium cathode.

In the search for better lithium cathode materials for reversible Li batteries researchers also examined the chemical and electrochemical properties of amorphous MoS₃ prepared by both the thermal degradation and the chemical precipitation technique. The reaction of MoS₃ with *n*-butyl lithium resulted in Li/Mo ratios ranging between 3 and 4, and electrochemical discharges indicated that as many as 3.5Li/Mo could be discharged (8).

Unfortunately, although the theoretical energy densities for this cathode material are excellent (~1000 WHR/kg allowing only for the weight of the cathode in a lithium battery), the low rate characteristics and poor rechargeability prevented the use of this material as a cathode in a working lithium battery. However, since only the amorphous material prepared by the previ-

ously mentioned techniques has been used as cathode material, we felt it necessary to explore other synthetic routes to prepare molybdenum sulfides, particularly MoS₃. It was our further goal to monitor how these sulfides could function as active cathodes in nonaqueous lithium batteries.

Experimental

Synthesis of MoS_x (x = 2, 2.5, 3)

Molybdenum disulfide and dimolybdenum pentasulfide were synthesized by dissolving or dispersing the corresponding molybdenum halide in methylene chloride under dry argon. Hexamethyldisilthiane (HMDST) was then slowly injected with a 10% excess and the reaction allowed to proceed overnight while stirring.

Because of the extreme volatility and reactivity of molybdenum hexafluoride, extreme care had to be taken in introducing it into the methylene chloride. This was accomplished by trapping the fluoride with dry ice/actone under vacuum. Dry nitrogen or argon was then introduced, the system closed, and then upon warming the vapor was introduced into the methylene chloride, forming a yellow solution. HMDST was then very slowly injected while stirring.

All three reactions were exothermic but only the last required cooling. A black-brown precipitate was formed in all cases and this was separated by filtration followed by washing with tetrahydrofuran in a Soxhlet extractor. The samples were then heated at 100°C under vacuum to remove any remaining THF.

Lithium Intercalation

Lithium was chemically inserted by the *n*-butyl lithium technique. Under argon, 50 ml of hexanes was added to 0.5 g of the sulfide. Excess 1.6 *M* *n*-butyl lithium in hexanes was then added and the reaction vessel was sealed. An exothermic reaction

occurred in all cases and the reaction was allowed to proceed for at least 4 days. The sulfide was then filtered off and analyzed for lithium content.

Materials

The methylene chloride, hexanes, and 1.6 M *n*-butyl lithium in hexanes were anhydrous and used as obtained from Aldrich Chemical Company. Molybdenum salts were used as obtained from the following companies: ammonium molybdate(VI) tetrahydrate and molybdenum pentachloride from Aldrich, molybdenum tetrachloride from Noah Chemical Company, and molybdenum hexafluoride from Var-Lac-Oid Chemical Company. Hexamethyldisilthiane was obtained from various sources: Petrarch Systems, Inc., Lancaster Synthesis, and Fluka Chemical Corporation. The HMDST was fractionally distilled and material with a boiling range of 160–162°C was collected and used.

Elemental Analysis

Molybdenum. Molybdenum standards were prepared from molybdenum metal dissolved in aqua regia. Standards of 0, 10, 20, and 30 ppm were made. The molybdenum sulfides were likewise dissolved in aqua regia and diluted to approximately 20 ppm. Molybdenum concentrations were measured on a Perkin–Elmer Atomic Absorption Model 305.

Sulfur. The molybdenum sulfides were oxidized in a hot mixture of bromine, carbon tetrachloride, and nitric acid. The resulting precipitate was then dissolved by the addition of hydrochloric acid. When cooled, Ba(NO₃)₂ was added to precipitate BaSO₄. This was then filtered, dried, and weighed to determine sulfur content.

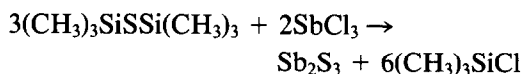
Lithium. Lithium standards were prepared from lithium carbonate and dissolved in acidic solution. Standards of 0.0 to 1.0 ppm were made. The intercalated compounds were dissolved in hot aqua regia

and diluted to concentrations of approximately 0.5 ppm. Lithium concentrations were measured on a Perkin–Elmer Atomic Absorption Model 305.

Chlorine. The samples were dissolved in a hot mixture of nitric acid and sulfuric acid. Silver nitrate was then added to precipitate silver chloride. This was then filtered off, washed with distilled water, dried, and weighed to determine chlorine content.

Results and Discussion

Chianelli and Dines (4) observed that the stable disulfide was obtained from the low-temperature solution technique, even when the transition metal halide had a formal oxidation state higher than 4+. As an example of this reduction phenomenon, they reported the formation of NbS₂ from the precursor NbCl₅. With this information we felt it was necessary, rather than the ionic route, to try a covalent metathesis reaction which might prevent oxidation reduction reactions. In the 1960's Abel and co-workers reported the formation of various organometallic sulfides and nontransition metal sulfides using various silyl sulfides (9). This series of publications indicated that under most conditions the reaction of hexamethyldisilthiane with metal halides would result in the cleaving of the two silicon–sulfur bonds and subsequently form silicon–halide and metal–sulfur bonds. When the proper stoichiometric ratio was employed all the halogens on the metal could be replaced by sulfur:



Some later work using the same reagent on TiCl₄ indicated that perhaps amorphous TiS₂ could be prepared by this technique, although no actual characterizations were performed on the solid obtained (10).

TABLE I
ELEMENTAL ANALYSIS OF MOLYBDENUM SULFIDES

Compound ^a	%Mo	%S	Corresponding formula
MoS ₂ Classical	61.3	41.8	MoS _{2.05}
Mo ₂ S ₅ · 3H ₂ O Classical	47.0	41.3	Mo ₂ S _{5.24} · 2.7H ₂ O
MoS ₃ Classical	50.0	50.8	MoS _{3.05}
MoS ₂ by HMDST	60.2	39.4	MoS _{1.96}
Mo ₂ S ₅ by HMDST	54.8	46.16	Mo ₂ S _{5.05}
MoS ₃ by HMDST	49.0	51.0	MoS _{3.10}

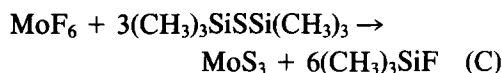
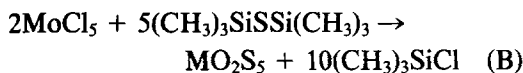
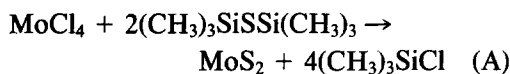
^a HMDST = Hexamethyldisilthiane.

The reaction of the molybdenum halides, MoCl₄, MoCl₅, and MoF₆ with hexamethyldisilthiane all occurred spontaneously at room temperature with the formation of a blackish brown precipitate. In all cases the reaction was exothermic; however, only in the case of MoF₆ was it necessary to cool the reaction vessel in order to avoid the boiling of the methylene chloride used as solvent. In the case of MoF₆ the reaction mixture froths from the release of volatile (CH₃)₃SiF, whereas the less volatile CH₃SiCl remains in the methylene chloride.

After filtering, washing with methylene chloride under dry nitrogen, and drying under vacuum, initial chemical analysis indicated a high chloride content for MoS₂ and Mo₂S₅. We felt that since these reactions were heterogeneous due to the poor solubility of the molybdenum salts in the methylene chloride, that trapped MoCl₄ and MoCl₅ probably remained in the sulfide. Subsequent washing of the compounds in a Soxhlet extractor with dry THF resulted in compounds which tested negative for chloride.

Chemical analysis (see Table I), indicated to us that the metathesis reaction of

the molybdenum halide with the hexamethyldisilthiane was complete at room temperature for the following reactions:



Although the chemical analyses indicated that the technique produced material having stoichiometries corresponding to the oxidation state of the initial molybdenum halide, characterization of the sample was necessary to indicate that oxidation-reduction and subsequent sulfur formation did not occur. X-Ray diffraction patterns only showed broad peaks indicative of noncrystalline character (see Fig. 1). We performed differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) to determine if sulfur was present (melting point ≈ 112 – 120°C) and to determine the thermal stability of our compounds (Figs. 2 and 3). In no case did we see an exotherm corresponding to the melting of sulfur. Also, we observed that in the case of Mo₂S₅ and MoS₃ a loss of weight corresponding to the transformation of these sulfur-rich com-

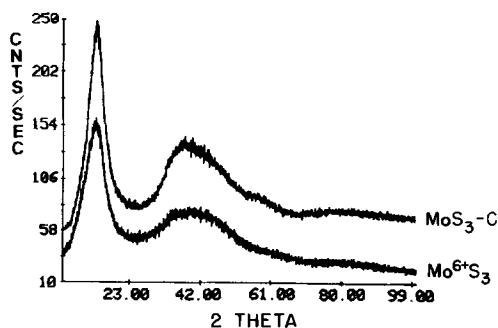


FIG. 1. X-Ray powder diffraction of molybdenum trisulfides. MoS₃-C was prepared by thermal degradation of ammonium thiomolybdate. Mo⁶⁺S₃ was prepared by reaction of MoF₆ and HMDST.

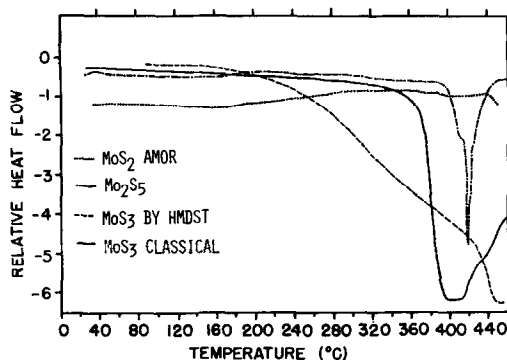


FIG. 2. Differential scanning calorimetry of molybdenum sulfides.

pounds to sulfur and molybdenum disulfide. In the case of molybdenum disulfide no weight loss was observed until after 450°C, at which temperature a sublimation of the fine powder was observed.

The magnetic susceptibility for all the compounds, measured on a Faraday balance, indicated that all the compounds were diamagnetic at room temperature with paramagnetic behavior at low temperatures corresponding to impurities of less than 1%, assuming one unpaired electron per paramagnetic impurity. For both MoS_2 and MoS_3 these results correspond to materials prepared by the previously described techniques. However, for Mo_2S_5 this indicates

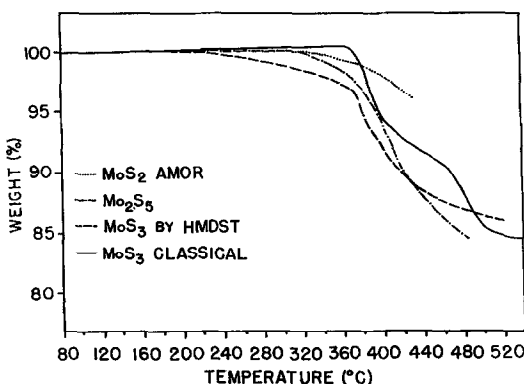


FIG. 3. Thermal gravimetric analysis of molybdenum sulfides.

TABLE II
AMOUNT OF LITHIUM CHEMICALLY INTERCALATED INTO MOLYBDENUM

Compound	%Li after reaction	Li/Mo ratio
MoS_2 Classical	5.36	1.3/1
MoS_2 by HMDST	13.1	3.5/1
Mo_2S_5 by HMDST	12.2	3.53/1
MoS_3 classical	11.6	3.63/1
MoS_3 by HMTST	13.07	4.25/1

the existence of very little residual MoCl_5 , a paramagnetic material. This also tells us that if we have a material with molybdenum in the (V) oxidation state, then we most probably have interaction between pairs of molybdenums resulting in a magnetic moment of zero. Initial measurements of the sulfur 2p and molybdenum 3d binding energies by electron spectroscopy for chemical analysis (ESCA) were performed. No second peak for sulfur other than the sulfide peak at 162 eV binding energy has been observed for all our samples. Further work is in progress to see if the oxidation state of the molybdenum in these compounds can be definitely established using this technique. Unfortunately this technique only probes the surface and may give misleading information about the bulk material.

In order to determine if these materials may offer interesting possibilities as cathodes in lithium batteries we reacted them with excess *n*-butyl lithium to determine chemical lithium uptake (see Table II). This technique usually determines maximum electrochemical lithium uptake and can be performed rapidly. It can be seen that our MoS_2 gives a chemical uptake substantially superior to that observed for amorphous MoS_2 prepared by Chianelli and Dines. The compounds Mo_2S_5 and MoS_5 also show very high lithium uptakes. It is the high capacity of these compounds which makes them of interest as possible cathodes in reversible lithium batteries. Further studies

of electrochemical reversibility are currently in progress and will be reported; however, initial work indicates that up to three lithiums may be reversibly cycled in our MoS_3 .

Conclusions

Although further work is certainly necessary, it appears that hexamethyldisilthiane may be used to prepare molybdenum sulfides with unusual stoichiometries. We have been able to prepare for the first time the anhydrous compound Mo_2S_5 (or $\text{MoS}_{2.5}$) and by a direct route an amorphous MoS_3 . At this time we are not able to say whether the structure of our amorphous MoS_3 is identical to that of the MoS_3 made by the thermal decomposition or aqueous precipitation technique. This direct procedure does allow us additional possibilities of forming a crystalline material by changing the reaction conditions. We are currently undertaking an EXAFS (extended X-ray absorption fine structure analysis) study of our materials in order to be better able to describe them structurally.

This organometallic technique is certainly not limited to molybdenum salts and we expect to study several different metathesis reactions between transition metal halides and hexamethyldisilthiane in order to prepare sulfides with unusual stoichiometries. It appears that the reaction is energetically limited to those compounds without very high binding energies between the transition metal and the halide. A reaction between MoCl_3 and hexamethyldi-

silthiane does not take place even at temperatures over 100°C .

Acknowledgments

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