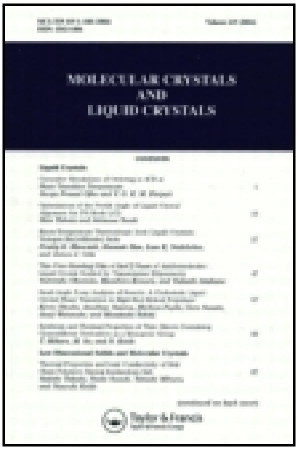

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Molybdenum Disulfide Intercalates with Special Transport Properties

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Chemical modification of molybdenum disulfide based either in the restacking of the layered solid or the intercalation of lithium or organic donors as poly(ethylene oxide) or dialkylamines leads to products with improved transport properties. The products are mixed electronic-ionic conductors. Electrical conductivity, which in pressure compacted samples shows a clear anisotropic behavior, depends on the nature of the intercalated phase. For some dialkylamines σ-values of about 10^{-2} S cm^{-1} are reached. Electrode potentials available from charge/discharge curves in lithium electrochemical cells are mainly determined by both the trigonal prismatic-octahedral phase equilibrium in the matrix and the capacity of the guest for stabilizing Li^+ ions in the interlaminar spaces. MoS_2 phase change during lithium intercalation is also detected in the analysis of the ^{7}Li-NMR linewidths of the Li_xMoS_2 intercalates. Lithium diffusion coefficient analysis indicates that the mass transport of modified MoS_2 is in general better than in the pristine compound.

Keywords: Intercalation compounds; molybdenum disulfide; transport properties

INTRODUCTION

In the context of the intercalation chemistry of transition metal disulfides, molybdenum disulfide has a peculiar behavior which certainly affects its potential for technical applications like the use in electrodes for rechargeable batteries. The properties of MoS_2 contrast with those of TiS_2, a compounds which has been often proposed as electrode material for rechargeable lithium batteries[1-3]. Indeed, TiS_2 is an electronic conductor which intercalates lithium and organic donors topotactically without any notorious phase change and that shows a relatively large lithium diffusion coefficients. Contrastingly MoS_2, which is a semiconductor with a structure that changes with lithium intercalation, shows a relatively poor lithium diffusion, and is rather inert to intercalation reactions. During the last several years we have studied this disulfide with the aim of improving its properties as mixed ionic-electronic conductor. In this paper, it is described how three important features in the use of MoS_2 as a material -- namely the anisotropic behavior, the phase changes during lithium intercalation and lithium diffusivity -- may be changed by chemical modifications so the transport properties of the pristine MoS_2 are much improved.

RESULTS AND DISCUSSION

Chemical Modification of MoS_2

MoS_2 may be modified by the topotactic intercalation of donor species (metals, discrete molecules, and polymers) in the interlaminar spaces. Intercalation of lithium is the most simple and versatile modification of MoS_2. Reaction of the disulfide with butyl lithium activated thermally[4] or by micro-wave irradiation[5] leads to species Li_xMoS_2 $(0<x\sim 1.0)$. This compound with x near or equal to 1 is the substrate for the preparation of intercalates based on the insertion of other donors[6]. Via an exfoliation process[7], the intercalation of donors as amines and polyethers has been achieved[8,9]. The intercalation process and the purity of the products may be normally followed by powder X-ray diffraction analysis, in which the reflection corresponding to the 00l planes may be clearly identified.

Anisotropic Electrical Conductivity

Molybdenum disulfide is a semiconductor with a band-gap of approximately 1.2 eV[10] and a relatively low electrical conductivity at room temperature. However, conductivity increases notoriously when lithium or an organic donor is intercalated (Table 1). Specially interesting are the nanocomposites obtained from the intercalation of dialkylamines.

TABLE 1. Electrical conductivities for MoS_2 and MoS_2-donors nanocomposites

Compound	σ (298 K) S cm^{-1}
MoS_2	2.1×10^{-7}
$Li_{0.1}MoS_2(PEO)_{0.5}$	4.8×10^{-4}
$Li_{0.1}MoS_2(PEO)_{1.0}$	6.6×10^{-3}
$Li_{0.1}MoS_2$(d-c-hexylamine)$_{0.21}$	3.8×10^{-2}
$Li_{0.1}MoS_2$(d-ethylamine)$_{0.42}$	2.5×10^{-1}

Because of its lamellar structure MoS_2 has anisotropic properties. The anisotropy factor $\sigma_{//}/\sigma_{\perp}$ for the electrical conductivity in a single crystal is of about 10^3[10] In polycrystalline powders, however, the conductivity depends on the preparation of the sample.

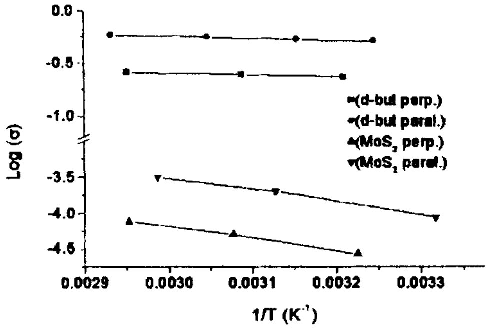

FIGURE 1. Anisotropic electrical conductivity in MoS_2 pure and modificated by the intercalation of an dialkylamine. Samples were prepared applying a pressure of 900MPa. Accumulated measurement errors are lower than mark sizes. Errors in the slopes are indicated in the E_a values given in the text.

As shown in Fig. 1, for compacted samples, different conductivities are observed in the parallel and perpendicular directions to applied pressure. The variation of the conductivity with the temperature for MoS_2 in both directions, parallel and perpendicular, corresponds to a semiconductor behavior with activation energies, obtained from plots log σ versus 1/T in Fig. 1 ($\log \sigma = C - 0.434 \cdot E_a / 2 \cdot RT$), of 0.68 ± 0.05 and 0.66 ± 0.05 eV respectively.

Interestingly, although the dependence of σ on applied pressure is rather complex, the determining rate in the electron transport mechanism appears to be approximately the same for all studied pressures The influence of the pressure should be then more related to the carrier concentration. Similar phenomena are observed for MoS_2-donor nanocomposites. Thus, for the case on the intercalation of amines a factor $\sigma_{//} / \sigma_{\perp} = 2.5$ is reached by applying a pressure of 900 MPa. Activation energies from Arrhenius plots in Fig. 1, accounting 0.077 ± 0.002 and 0.065 ± 0.002 eV for the parallel and perpendicular directions respectively, are however rather lower than for MoS_2.

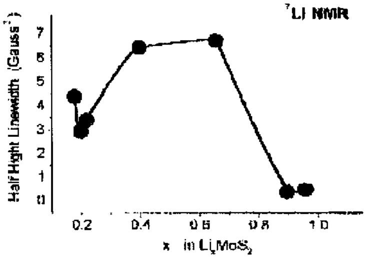

FIGURE 2. Half-high linewidths for Li_xMoS_2 samples.

Intercalation Induced Phase Change

The intercalation of lithium into MoS_2 by both chemical and electrochemical methods reveals the existence of a phase equilibrium which strongly depends on the amount of intercalated lithium. The pristine trigonal prismatic phase is stable only until $x \leq 0.2$. Further addition of lithium implies the change to an octahedral phase. As established by analyzing the shape of ^{7}Li NMR at different temperatures and lithium concentrations (Fig. 2), the sample corresponds to an heterogeneous mixture of crystallites[11].

In the intermediate lithium concentration range some of them correspond to the trigonal prismatic phase with lithium molar fraction of about 0.2 and the rest to microcrystals of the octahedral MoS_2 modification and with a lithium molar fraction near to one. Most transport properties as well as the inerticity toward direct intercalation are probable associated to such a phase change.

Phase change energetic is also visualized in the electrode potential of the material. Discharge curves (open circuit potential) for samples starting with of trigonal prismatic MoS_2 as well as with derivatives prepared by chemical modification of the former are compared in Fig. 3. Inclusive for the restacked MoS_2, obtained by an exfoliation process of the pristine MoS_2, the voltage curve is rather smoother than for trigonal prismatic MoS_2 showing that in the modified material only one phase of the matrix is present during the intercalation. Another interesting feature is that the mean potential of the electrode during the intercalation which depending on the nature of the co-intercalated donor is rather higher than in the pristine MoS_2. That could be very interesting from the point of view of the use of these materials as electrodes.

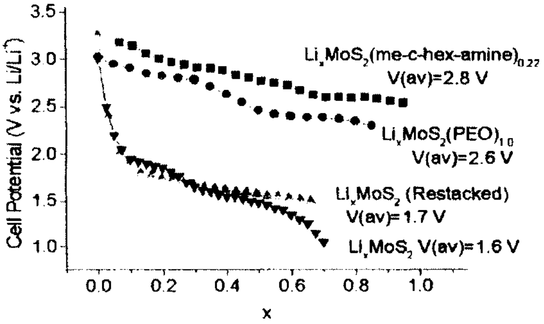

FIGURE 3. Discharge curves for pure and modified MoS_2 in a lithium electrochemical cell at room temperature.

Ion Transport Properties

Intercalated MoS_2 derivatives are mixed ionic-electronic conductors. The ionic resistivity contribution may be determined by polarization experiments like the example shown in Fig. 4. The total electrical conductivity, which determined by AC complex impedance measurements accounts $2{\cdot}10^{-1}$ S cm^{-1}, is thus mainly determined by the electronic conductivity. According to the rigid band model, lithium in the interlaminar spaces is found as a ionic species whose charge is compensated by the polyanionic matrix. Migration of lithium in such a bi-dimensional space is determined by both the thermodynamic stability of the site in which it is located and the energy barrier for jumping to a neighboring site, which in turn depends on both the electronic structure of the matrix and the nature of the sites in the interlaminar spaces.

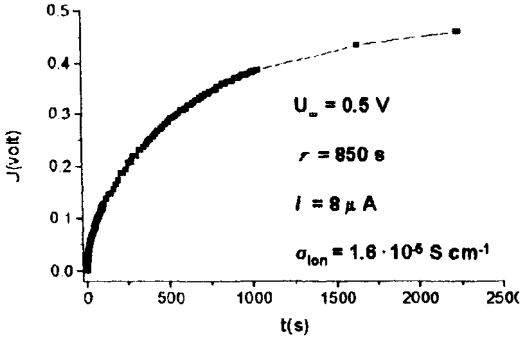

FIGURE 4. Galvanostatic polarization in the electron-blocked electrochemical cell $Li/LiClO_4(PC)/Li_{0.1}MoS_2(NHR_2)_{0.19}/LiClO_4(PC)/Li$ (R= n-butyl).

In Table 2 are compared the diffusion coefficients for the migration of lithium in different MoS_2 derivatives as well as with TiS_2. In general, the modification of the matrix leads to materials which, from the point of view of the mass transport, are rather better than the pristine disulfide.

TABLE 2 Lithium Chemical Diffusion Coefficients at 25°C

Compound	D ($cm^2 s^{-1}$)	Reference
Li_xMoS_2 x = 0.1 - 0.4	4.2×10^{-13} - 4.2×10^{-14}	12
$Li_xMoS_2(PEO)_{0.5}$ x = 0.1 - 0.4	1×10^{-10} - 1×10^{-12}	13
$Li_xMoS_2(PEO)_1$ x = 0.1 - 0.4	5×10^{-12} - 4.5×10^{-13}	13
Li_xMoS_2(me-c-hex-amine)$_{0.22}$ x = 0.6	$5.6\ 10^{-13}$	14
Li_xTiS_2 x = 0.05-0.36	1.4×10^{-10} – 1.6×10^{-14}	13

Conclusions

Chemical modification of MoS_2 leads to mixed ionic-electronic conducting materials which from the point of view of its potentiality as electrode materials are better than the pristine MoS_2. Modified materials appear to be in some aspects better than the TiS_2. The properties of the products depend on the kind of the modification, so the modulation of the properties for specific uses should be possible. Moreover, the typical anisotropy shown by these materials, which may be enhanced by physical methods, could be also useful for special electronic devices.

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