

Article

Intercalation of Oxyethylene Compounds (Crown-Ethers and PEO) into Molybdenum Disulfide

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Neste trabalho é reportada a obtenção de novos materiais nanocompósitos oriundos da intercalação de éteres-coroa (12-crown-4, 15-crown-5 e 18-crown-6) e óxido de polietileno, PEO, em MoS₂. Primeiramente, o sulfeto é tratado com butil-lítio, e posteriormente, com água, produzindo assim uma esfoliação que facilita a inserção de compostos oxietilênicos. À mistura reacional inicial são adicionados sais de metais alcalinos, objetivando a incorporação dos correspondentes complexos metal-ligante quando da etapa de reempilhamento, isto é, da reorganização das lamelas individuais do MoS₂. A lavagem com água dos materiais obtidos resulta na eliminação progressiva dos compostos intercalados, dando origem a sólidos de estequiometria variável. As condutividades elétricas são superiores à do MoS₂ não-intercalado, sendo melhor correlacionadas com a redução do retículo hospedeiro, ocasionada pela ação do butil-lítio, do que com a intercalação dos complexos íon metálico/espécie oxietilênica.

New nanocomposite materials based on the intercalation of some crown-ethers (12-crown-4, 15-crown-5 and 18-crown-6) and poly(ethylene oxide), PEO, into MoS₂ are reported here. The sulphide is firstly treated with butyllithium, followed by a treatment with water, producing a delamination which facilitates the insertion of the involved oxyethylene compounds. Alkali-metal salts are added to the starting reaction mixture with the aim to incorporating the corresponding metal-ligand complexes during the restacking step, *i.e.*, the reorganization of the MoS₂ single layers. Washing the resulting materials with water provokes the progressive elimination of the intercalated compounds, giving solids of variable stoichiometry. The electrical conductivity is enhanced with respect to pristine MoS₂, being related to the host lattice reduction by the butyllithium action, rather than to the oxyethylene/metal-ion complex intercalation.

Keywords: *intercalation, molybdenum disulfide, crown-ethers, PEO, electrical conductivity*

Introduction

The ability of oxyethylene species, such as the crown-ether macrocyclic compounds and the poly(ethylene oxide), PEO, to intercalate layered solids was first reported in processes involving phyllosilicates belonging to the smectite clay-mineral group¹⁻³. This class of solids contains exchangeable cations in their interlayer spaces able to form intracrystalline complexes with some macrocyclic compounds. Thus, the intercalated oxyethylene compounds remain associated with those interlayer cations, replacing their natural hydration shell. In these cases, the resulting

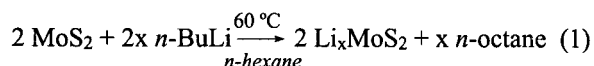
intercalation compounds provide the opportunity to design and prepare nanocomposite materials useful for either solid electrolytes or ion-selective membrane applications².

Crown-ethers can also be intercalated in other layered host solids, such as transition-metal phosphorous trichalcogenides⁴ (MPS₃, M = Mn, Cd, previously exchanged with alkali-metal ions such as Na⁺ and K⁺), and in vanadium pentoxide xerogel⁵. In the last case, the inherent proton mobility is modified according to the electrical conductivity changes observed after crown-ethers intercalation⁵. PEO also intercalates different inorganic layered solids of variable electrical behaviors, as was recently reviewed⁶.

It is well known that MoS₂ is a layered solid able to intercalate organic species, which occurs *via* intermediate Li_xMoS₂ compounds^{7,8}. Furthermore, it is generally accepted that this process takes place following an exfoliation produced by the reaction of Li_xMoS₂ with water, which gives MoS₂ single layers facilitating the insertion of organic materials in the subsequent restacking process⁹. Based on this procedure, poly(ethylene oxide), PEO, has been previously intercalated into MoS₂¹⁰⁻¹². In this context, we now report here that these methods are also useful for crown-ether compound intercalations into MoS₂. The MoS₂ host lattice was selected because of its semiconducting behavior, with the aim of trying a controlling modification of its electrical properties by the incorporation of both lithium and other alkali-metal ions, together with crown-ethers and PEO, which *a priori* could form stable metal-ligand complexes.

Experimental

Li_xMoS₂ was prepared (Eq. 1) by the reaction of MoS₂ (2H phase; Aldrich, 99% purity) with 1.6 M butyl lithium (*n*-BuLi) in a hexane solution (Aldrich) at 60°, operating under Ar in a dry-box (< 0.4 ppm of H₂O), and generally following Murphy's method¹³.

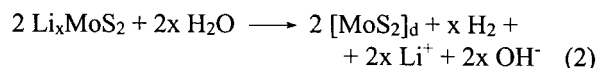


The oxyethylene compound intercalations were carried out in a second step, by the treatment of the Li_xMoS₂ phase (0.5 g) with a mixture composed of: i) 1 M water solution (5 mL) of oxyethylene compound (either PEO or one of the following macrocycles: 12-crown-4 (12C4), 15-crown-5 (15C5) or 18-crown-6 (18C6), Merck > 98% purity), and ii) a 1M water solution of a MCl metal salt (M=Li, Na, K, Rb, Cs, *p.a.* quality). The mixture was maintained under continuous and vigorous stirring for 24 h at 25 °C. Finally, the resulting products were recovered by filtration, water washed and vacuum dried at room temperature. The resulting intercalation materials were characterized by chemical analysis (CHN microanalysis, EDX, and atomic absorption) and the XRD technique (Philips PW 1710), working with samples in the form of oriented aggregates. The electrical conductivity was determined from measurements using a four-probe system (Van der Paw method^{14,15}) applied on pellets pressed at 4 000 kg/cm².

Results and Discussion

The intercalated lithium phase (Li_xMoS₂) obtained according to Eq. 1, was used in a second step for the oxyethylene compound intercalations in the presence of water, which is used simultaneously for the exfoliation process and as a solvent for the oxyethylene ligands. Thus, the Li_xMoS₂ phase gives a violent reaction with water,

generating hydrogen molecules (Eq. 2) which, according to Murphy *et al.*¹³, expand and separate the MoS₂ layers, forming *single layers* ([MoS₂]_d, *delaminated phase*). The subsequent restacking of these single layers allows the intercalation, or better the *incorporation*, of the oxyethylene compounds (Eq. 3).



In a first approach, the affinity of the crown-ethers (and also PEO, although to a lesser extent) to act as ligands (L) to form complexes towards the alkali-metal ions (M⁺) that are present in the reaction mixture has to be considered. These M⁺ cations are incorporated into the reaction by adding LiCl, NaCl, KCl, RbCl and CsCl aqueous solutions, as described in the Experimental section. Thus, the formation of [L/M⁺] intercalated species can be proposed as indicated in Eq. 3:



The XDR patterns of the resulting ([L/M⁺]_xMoS₂) materials, compared to those of the pristine MoS₂, reveal a loss of crystallinity, although some rational 00l orders are still observed. Figure 1 shows some representative diffractograms corresponding to several PEO and crown-ether MoS₂ intercalation materials. From the 00l reflections the interlayer distances are determined, *i.e.*, the *c* parameters. As such, taking into account the thickness of the MoS₂ layers (*c* = 6.2 Å), the increase in these distances (Δ*c*) represents the thickness of the intercalated organic species. Thus, the Δ*c* values range from 4 to 10.5 Å.

It should be pointed out that in samples exhaustively washed with water, progressive changes in the *c* parameter values are observed. These observations indicate the lack

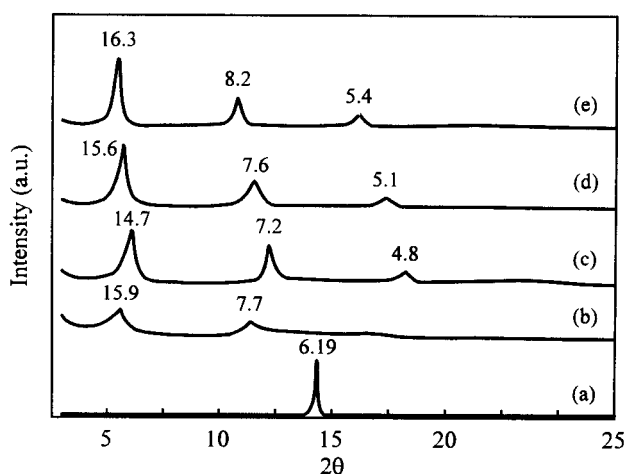


Figure 1. XRD patterns of (a) pristine 2H-MoS₂, and of the intercalation compounds obtained by treatments of intermediate Li_xMoS₂ phase with (b) 12C4, (c) 15C5, (d) 18C6 and (e) PEO.

of a tendency towards the formation of well-defined phases. As a general rule, water washing produces a decrease in the interlayer distances, although in the cases of [(PEO/LiCl)MoS₂], [(PEO/CsCl)MoS₂], [(18C6/LiCl)MoS₂], and [(12C4/NaCl)MoS₂] materials, an increase in the Δc values takes place. These behaviors suggest some rearrangement processes of the oxyethylene compounds into MoS₂ layers occurring under a soft experimental treatment such as the washing operation.

The amounts of oxyethylene compounds that remain associated with MoS₂ after restacking vary greatly, *i.e.* from 0.05 to 1.6 moles of oxyethylene units (OEU) per mole of MoS₂ (Table 1). It was found that the oxyethylene compounds are inserted without any dependence between the nature of the involved cations (M⁺) and the ligands (L), contrarily to the expected stoichiometry $L/M^+ = n$ ($n: 1, 2$)

relationship (Table 2). Thus, it appears that the complexes initially formed in the pristine mixture reaction undergo alterations during the entrapping in the restacking step of the MoS₂ single-layer dispersion. It should be noted that this image illustrates the mechanism predominating in the intercalation process of oxyethylene compounds into molybdenum disulfide.

As indicated above, a water washing treatment of the resulting materials produces a partial removal of both the organic compound and the alkali-metal salt associated with the MoS₂ framework. The EDX analyses of the samples indicate a complete elimination of Cl⁻ ions after washing, although some M⁺ cations remain associated with the intercalated compound. This fact could be explained assuming a partial reduction of the Mo(IV) by the BuLi, giving rise to (MoS₂)ⁿ⁻ electrically charged layers. Hence, a lattice

Table 1. Summary of the starting compounds involved in the initial reaction mixture to obtain the different oxyethylene compounds/MoS₂ materials: (a) the *c* parameters represent the interlayer distances which are deduced from the 001 rational reflections; (b) the Δc values correspond to the increase of interlayer distances calculated as $\Delta c = c - 6.2$; (c) this value corresponds to a bilayer of water molecules; (d) values in parentheses indicate the interlayer distances before water washing; (e) from elemental analysis; (f) OEU: oxyethylene units, *i.e.*, -CH₂-CH₂-O; (g) measured by the four probe method; (h) Li⁺ content before water washing; Li_{1.25}MoS₂·nH₂O is shortly expressed as "Li-MoS₂". See Experimental section for more details.

Sample	XRD results		Amounts of intercalated oxyethylene compounds		electrical conductivity (g) σ (S/cm)
	<i>c</i> [Å] ^(a)	Δc [Å] ^(b)	%C ^(e)	OEU ^(f) (moles)	
MoS ₂	6.2	—	—	—	5.7×10^{-6}
Li _{1.25} MoS ₂ ·nH ₂ O ^(h)	11.9	5.7 ^(c)	—	—	7.4×10^{-3}
12C4 + LiCl + Li-MoS ₂	6.2 (15.0) ^(d)	0 (8.8)	1.8	0.12	6.1×10^{-2}
12C4 + NaCl + Li-MoS ₂	15.4 (14.9)	9.3 (8.7)	3.3	0.24	0.11
12C4 + KCl + Li-MoS ₂	6.2 (15.5)	0 (9.3)	1.0	0.08	2.8×10^{-3}
12C4 + RbCl + Li-MoS ₂	7.5 (15.8)	0 (9.6)	2.4	0.16	7.5×10^{-2}
12C4 + CsCl + Li-MoS ₂	9.7 (16.6)	3.5 (10.4)	2.0	0.12	1.2×10^{-3}
15C5 + LiCl + Li-MoS ₂	10.0 (15.1)	3.8 (8.9)	2.3	0.15	1.9×10^{-3}
15C5 + NaCl + Li-MoS ₂	11.4 (14.3)	5.2 (8.1)	7.1	0.55	0.1
15C5 + KCl + Li-MoS ₂	11.7 (15.5)	5.5 (9.3)	14.4	1.30	0.1
15C5 + RbCl + Li-MoS ₂	9.7 (15.6)	3.5 (9.49)	0.9	0.05	0.1
15C5 + CsCl + Li-MoS ₂	9.7 (12.7)	3.5 (6.5)	1.0	0.05	7.4×10^{-2}
18C6 + LiCl + Li-MoS ₂	15.1 (15.9)	8.9 (9.7)	7.9	0.60	0.1
18C6 + NaCl + Li-MoS ₂	11.5 (15.9)	5.3 (9.7)	1.0	0.06	0.3
18C6 + KCl + Li-MoS ₂	16.2 (16.3)	10.0 (10.1)	1.5	0.12	0.1
18C6 + RbCl + Li-MoS ₂	9.5 (15.1)	3.3 (8.8)	1.3	0.06	0.2
18C6 + CsCl + Li-MoS ₂	9.6 (10.9)	3.4 (4.7)	0.8	0.06	4.8×10^{-2}
PEO + LiCl + Li-MoS ₂	16.2 (16.3)	10.0 (10.1)	16.7	1.61	6.1×10^{-2}
PEO + NaCl + Li-MoS ₂	12.6 (13.2)	6.4 (6.9)	9.9	0.80	1.1×10^{-3}
PEO + KCl + Li-MoS ₂	9.5 (15.3)	3.3 (3.5)	3.8	0.27	4.7×10^{-2}
PEO + RbCl + Li-MoS ₂	9.7 (9.7)	3.5 (3.9)	7.5	0.58	8.4×10^{-2}
PEO + CsCl + Li-MoS ₂	16.2 (10.2)	10.0 (9.6)	11.6	0.98	3.9×10^{-4}

Table 2. A selection of representative samples of oxyethylene compounds/MoS₂ where the alkali-metal contents are indicated. See footnote in Table 1 for symbol explanation.

Starting samples	XRD results c [Å]	oxyethylene compound OEU (moles)	electrical conductivity σ (S/cm)
MoS ₂	6.2	–	5.7×10^{-6}
Li _{1.25} MoS ₂ nH ₂ O	11.9	–	7.4×10^{-3}
Crown-ether samples	XRD results c [Å]	oxyethylene compound OEU (moles)	electrical conductivity σ (S/cm)
[12C4] _{0.03} Li _{0.21} MoS ₂	6.2	0.12	6.1×10^{-2}
[12C4] _{0.03} Na _{0.06} MoS ₂	15.4	0.24	0.1
[15C5] _{0.03} Na _{0.11} MoS ₂	11.4	0.55	0.1
[15C5] _{0.03} K _{0.26} MoS ₂	11.7	1.30	0.1
[18C6] _{0.03} Li _{0.10} MoS ₂	15.1	0.60	0.1
[18C6] _{0.03} K _{0.02} MoS ₂	16.2	0.12	0.1
PEO samples	XRD results c [Å]	oxyethylene compound OEU (moles)	electrical conductivity σ (S/cm)
[CH ₂ CH ₂ O] _{1.6} Li _{0.21} MoS ₂	16.2	1.61	6.1×10^{-2}
[CH ₂ CH ₂ O] _{0.8} Na _{0.13} MoS ₂	12.6	0.80	1.1×10^{-3}
[CH ₂ CH ₂ O] _{0.3} K _{0.22} MoS ₂	9.5	0.27	4.7×10^{-2}
[CH ₂ CH ₂ O] _{0.6} Rb _{0.17} MoS ₂	9.7	0.58	8.4×10^{-2}
[CH ₂ CH ₂ O] _{1.0} Cs _{0.45} MoS ₂	16.2	0.98	3.9×10^{-4}

reduction was reported by Scholhorn and Weiss for MoS₂ treated with alkali-metals in liquid ammonia⁷. As such, the remaining cations in the intercalation compounds under study must be compensating the electrical charge of the reduced MoS₂ lattice.

On the other hand, in some cases the crown-ether intercalated materials show interlayer distances that are compatible with an intracrystalline arrangement of the macrocycle with its molecular plane close to the perpendicular direction of the chalcogenide layer, *i.e.*, to the (ab) plane. This structural model is illustrated for the 15C5/MoS₂ compound (Fig. 2). The observed Δc values could be alternatively explained by supposing that the crown-ethers are arranged with their molecular plane lying parallel to the MoS₂ layers, acting as “pillars” between those layers. Other possible explanations which are also compatible with the Δc found values consist of the formation of interstratified materials. Further work is now in progress in order to ascertain the molecular disposition of these ligands in the interlayer region of the MoS₂ lattice.

In the case of the PEO incorporation into MoS₂, the resulting nanocomposite materials exhibit c parameter values between 9.5 and 16.2 Å (Table 2). The corresponding Δc values may be interpreted as oxyethylene chains intercalated into MoS₂ in a planar in a zigzag conformation disposed in either one (thickness: 3.5-4.0 Å) or two (thickness: 7-8 Å) polymer layers. Furthermore, more or less

distorted helical conformations, which are typical of PEO-salt complexes¹⁶ and PEO/layer silicate nanocomposites³, may be also considered. At present it is not possible to

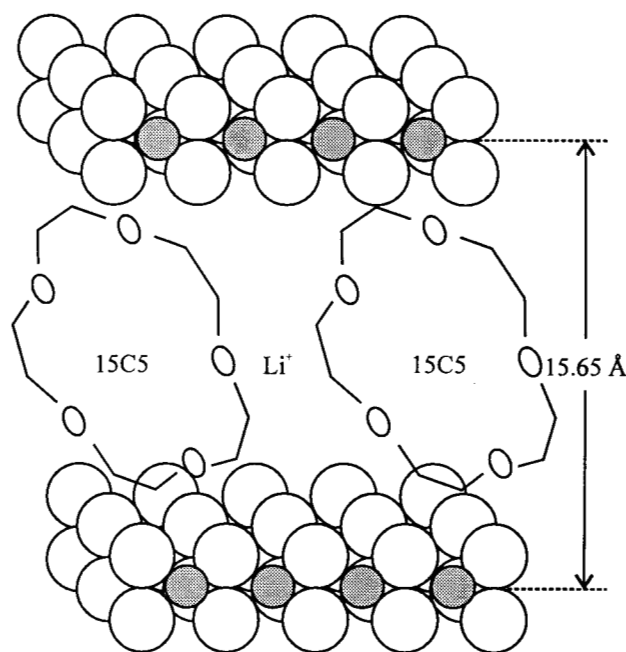


Figure 2. Schematic representation of nanocomposite materials based on a crown-ether (in this example, 15C5) intercalated into MoS₂.

determine what is the real interlayer arrangement of PEO in the intracrystalline region of molybdenum disulfide.

Concerning the electrical conductivity of the oxyethylene/MoS₂ resulting materials, an increase in the electrical conductivity values (four-probe dc measurements) from 5.7×10^{-6} S/cm in pristine MoS₂ to about 10^{-3} S/cm was observed in the intercalated oxyethylene compounds (Table 1). This significant increase in the electronic conductivity may be related to a partial reduction of Mo(IV) belonging to the host lattice, forming (MoS₂)ⁿ⁻ charged layers⁸. In addition, it is known that the reduction of the host lattice is accompanied by important structural modifications ($2H \rightarrow 1T$)^{17,18}. Thus, we can conclude that the BuLi treatment is the main cause determining the electrical properties of the resulting materials. Unfortunately, at this stage of our research we are not able to discriminate the ionic conductivity associated with the added metal salts capable of forming complexes with the crown-ethers and the PEO, oxyethylene compounds. In this way, the former idea using the presence of Li⁺ and other alkali-metal ions to prepare new ionic-electronic mixed conductors based on their association with crown-ethers or PEO intercalated into MoS₂, may still be suitable for controlling ion mobility. However, the relatively high electronic conductivity of the inorganic host overlaps the ionic contribution of these materials. It might still be interesting to prepare new promising cathode materials derived from these systems, such as oxyethylene/MoS₂ compounds combined with PEO/salt polymer electrolytes in order to increase the number of ion charge carriers.

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