Electrical conductivity of MoS$_2$ based organic–inorganic nanocomposites

E. Benavente[1], **M. A. Santa Ana**[2], and **G. González**[*,2]

[1] Departamento de Química, Universidad Tecnológica Metropolitana, Avda. José Pedro Alessandri 1242, Santiago de Chile, Chile

[2] Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago de Chile, Chile

The electrical conductivities of a series of MoS$_2$-organic layer nanocomposites prepared by the intercalation of donors like poly(ethylene oxide) and secondary amines are compared. Although for intercalated MoS$_2$ species a metallic behavior is expected, the products behave as semiconductors probably because of their layered nature. Observed conductivities at room temperature depend on the host-guest charge transfer reflected in both the amount of residual lithium and the donor intercalation degree, as well as on the nature of the donor.

1 Introduction

In recent years interest in inorganic-organic nanocomposites has increased significantly [1, 2]. Among the reasons for the fast development of this chemistry is the possibility of changing positively the properties of many-layered inorganic species, for instance by increasing their electrical conductivities [3–7] or by improving the diffusion rates of electroactive intercalated species, like the lithium ion [7, 8].

Intercalation compounds arising from the insertion of different kinds of guests into a rigid inorganic layered matrix may be considered as nanocomposites in which two phases co-exist maintaining interphases extended at least in the nanometer scale. Although the intercalation reaction may be considered in a first instance as a topotactic process in which changes in the lamellar host are restricted to changes in the interlaminar distance, often there are host-guest interactions which alter to some extent the properties of the components.

In this paper we compare the electrical conductivity of a series of MoS$_2$-organic nanocomposites with the purpose of investigating the factors that determine the degree of charge transfer and thus the electronic conductivity of the products.

2 Experimental

2.1 Sample preparation

Li$_x$MoS$_2$(donor)$_y$ nanocomposites are obtained as reported elsewhere [9] by treating a suspension of LiMoS$_2$ in n-hexane with a solution of the donor in pure, double-distilled, carefully degassed water under vigorous stirring during 24 h. After neutralizing with diluted acid, the product is filtered, washed with water and n-hexane, and finally dried under vacuum at 50 °C for several hours.
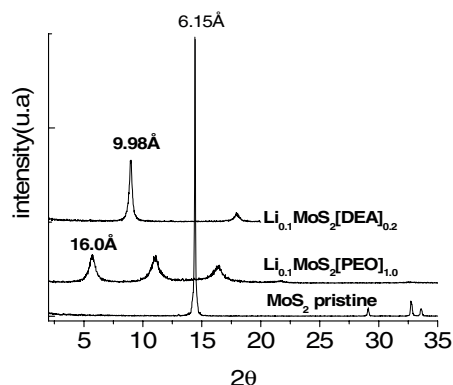
[*] Corresponding author: e-mail: ggonzale@uchile.cl

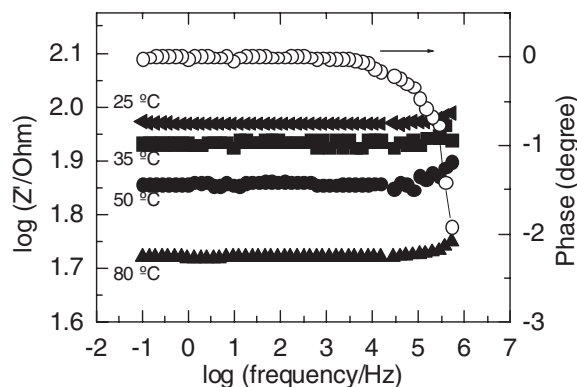**Fig. 1** Powder X-ray diffractograms of MoS$_2$-Donor nanocomposites.

Fig. 2 Bode plots of Li$_{0.1}$MoS$_2$(PEO)$_{1.4}$ at different temperatures.

The products are in general characterized by elemental analysis, differential scanning calorimetry (DSC), and powder X-ray diffraction analysis (Siemens D-5000, CuK radiation). Lithium analysis is performed by atomic emission spectroscopy. Differential scanning calorimetry measurements assure that neither the donor phase in the interlayer space nor the MoS$_2$ undergo any phase transition in the temperature interval used in this work. X-ray diffraction patterns guarantee that the products are always pure phases, also allowing the determination of the interlaminar distances in the intercalated products. A typical diffractogram is shown in Fig. 1.

2.2 Electrical conductivity measurements

Electrical conductivity was determined by impedance spectroscopy. Samples were prepared by pressing the polycrystalline powder (particle size $<2\,\mu$m in a die to obtain parallelepipedal pellets of about $5 \times 5 \times 1$ mm. The applied pressure was about 7 MPa. Samples were then sandwiched between gold electrodes and measured using frequencies in the 0.1 Hz to 1 MHz range. A typical result is that shown in Fig. 2. Both log Z′ and phase remain practically constant in the 0.1 Hz–10 kHz frequency range. Resistance decreases with increasing temperature.

3 Results and discussion

From the impedance spectroscopy measurements described above it is apparent that there is a total absence of polarization elements detectable in the measured frequency range. Therefore, classical interphases arising from grain boundaries or any other junction may be disregarded; i.e. our systems behave as simple electric conductors. Theoretically, the enhanced electron charge in the matrix leads to structural changes consisting of a rearrangement of the positions occupied by the metal between two sulfur layers, transforming the pristine trigonal prismatic coordination of the molybdenum into an octahedral one. A consequence of this phase change is the transformation of the pristine semiconductor into a solid with a metal-like band structure [10]. That should occur however only along the layers. In a perpendicular direction, i.e. across the van der Waals gap, either semiconducting or insulating behavior is expected. Given the intrinsic anisotropy of the particles together with the microcrystallinity of the sample, the resistance of the pressed powder could be reduced, in a first approach, to the sum of the resistance of the particles oriented with their laminar planes parallel and perpendicular to the current direction:

$$R = R_{\parallel} + R_{\perp}.$$

Although neither the number of particles oriented in a given direction nor the intrinsic resistance along or across the lamellae are known, it can be assumed that, like in graphite, the electrical resistance in the

Table 1 Electrical conductivity of MoS_2-donor nanocomposites.

compound	electrical conductivity $\sigma(298\ K)\ (S\ cm^{-1})$	interlaminar distance (Å)
$Li_{0.1}MoS_2(POE)_{0.5}$	4.80×10^{-4}	11.60
$Li_{0.1}MoS_2(POE)_{1.0}$	6.60×10^{-3}	16.30
$Li_{0.1}MoS_2(POE)_{1.4}$	1.04×10^{-2}	15.50
$Li_{0.2}MoS_2(DEA)_{0.42}$	2.51×10^{-1}	9.89
$Li_{0.2}MoS_2(DBA)_{0.19}$	1.97×10^{-1}	10.05
$Li_{0.1}MoS_2(DCHA)_{0.07}$	3.80×10^{-2}	10.60
MoS_2	2.09×10^{-6}	6.15

particles along the laminae is about 10^3 times lower than across the particles through the interlaminar spaces [11]. Conductivity will be therefore mainly determined by $R_\perp$, in agreement with the observed dependence of conductivity on temperature (Fig. 2).

Table 1 shows the electrical conductivities for a series of MoS_2-Donor nanocomposites at room temperature Although the range of values is rather wide, all of them are significantly higher than that of the pristine MoS_2 [3]. Besides the electron band structure of the host and the guest-host charge transfer mentioned above, factors like the interlaminar distances and the nature of the interlaminar phase also appear to be important for the conductivity in these solids.

The charge transferred from the guest to the laminar host should be directly related to the residual negative charge in the matrix which, in turn, could be seen from the analytical amount of lithium in the solid. However, there are reasons why such estimation may be not very significant, among them the change in the number of defects in the host, which may vary significantly with the treatment of the samples, and the real oxidation state of lithium in the interlaminar spaces, which depending on the donor ability of the guest may be lower than one [9]. Analysis of the data displayed in Table 1 shows that a rough correlation between conductivity and the nature of the donor may be established. The conductivities of the amine intercalates are clearly larger than those of the PEO intercalates.

If we consider now the products of the intercalation of poly(ethylene oxide) (PEO), where there are three pure phases containing different amounts of polymer, we can see that the electric conductivity of the composites, as shown in Fig. 3a, varies near linearly with the degree of intercalation.

Since in these compounds the interlaminar distances also increase with the degree of PEO intercalation, the tendency observed in Fig. 3a clearly does not reflect the behavior expected for the electronic conductivity across the interlaminar spaces analyzed above. We therefore think that such a tendency is mainly governed by guest-host charge transfer, increasing with the intercalation degree by a process occurring directly or through the increment of the activity of the lithium ion. Although the conductivity behaviour detected for the intercalates with amines is essentially similar to that of the polyethers (Fig. 3b), there are some peculiarities reflecting a distinctive feature of these nanocomposites. Indeed, in
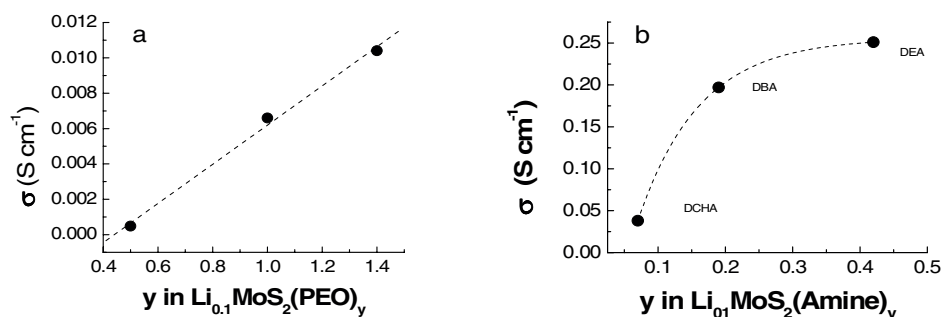

Fig. 3 Influence of the intercalated polymer amount on the electrical conductivity of (a) $Li_{0.1}MoS_2(PEO)_y$ and (b) $Li_xMoS_2(amine)_y$ nanocomposites.

the case of the DEA and the DBA, in contrast to the PEO intercalates, where lithium is homogeneously distributed in the interlaminar spaces, the alkaline species is found forming three- or four-atom clusters [10]. Indeed, the second magnetic moments M_2 (^{7}Li$-^7$Li) at low temperature observed for the PEO [13] and DEA [14] intercalates, which are 0.014 and 1.1 G^2, respectively, describe well such a difference.

4 Conclusions

In the light of the experiments discussed above it can be concluded that the intercalation of donors into MoS$_2$ modifies significantly the electronic structure of the host, increasing the electric conductivity of the products. The magnitude of this effect depends, however, on both the amount and the nature of the intercalated guest. Among the different factors which produce a conductivity increase, the variation of the lithium ion activity in the interlaminar space induced by the presence of the donors appears to be the most relevant. However, peculiarities arising from the nature of the donor and the self-organization of the latter in the interlaminar phase must also be considered.

References

[1] R. A. Vaia and E. P. Giannelis, MRS Bull. **26**, 394 (2001).
[2] G. A. Ozin, Adv. Mater. **4**, 612 (1992).
[3] M. G. Kanatzidis, R. Bissessur, D. C. DeGroot, J. L. Schinder, and C. R. Kannewurf, Chem. Mater. **5**, 595 (1993).
[4] R. Bissessur, M. G. Kanatzidis, J. L. Schinder, and C. R. Kannewurf, J. Chem. Soc., Chem. Commun. 1582 (1993).
[5] J. P. Lemmon and M. M. Lerner, Solid State Commun. **94**, 533 (1995).
[6] J. P. Lemmon and M. M. Lerner, Chem. Mater. **6**, 207 (1994).
[7] V. Sánchez, E. Benavente, M. A. Santa Ana, and G. González, Chem. Mater. **11**, 2296 (1999).
[8] E. Benavente, M. A. Santa Ana, F. Mendizábal, and G. González, Coord. Chem Rev. **224**, 87 (2002).
[9] E. Benavente and G. González, Bol. Soc. Chil. Quím. **42**, 555 (1997).
[10] M. A. Py and R. R. Haering, Can. J. Phys. **61**, 76 (1983).
[11] A. M. Hermann, R. B. Somoano, V. Hadek, and A. Rembaum, Solid State Commun. **13**, 1065 (1973).
[12] G. González and H. Binder, Bol. Soc. Chil. Quím. **41**, 127 (1996).
[13] A. C. Bloise, J. P. Donoso, C. J. Magon, J. Schneider, H. Panepucci, E. Benavente, M. A. Santa Ana, and G. González, J. Phys. Chem. B **106**, 11698 (2002).
[14] E. Benavente, M. A. Santa Ana, G. González, F. Becker-Guedes, N. C. Mello, H. C. Panepucci, T. J. Bonagamba, and J. P. Donoso, Electrochim. Acta **48**, 1997 (2003).