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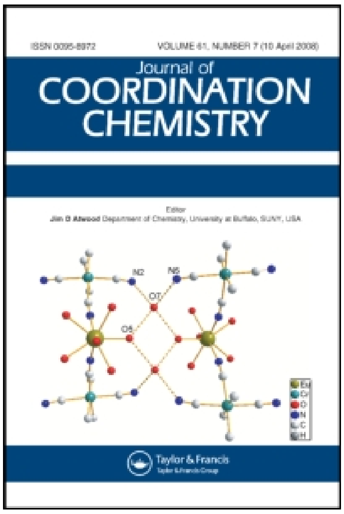

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REDOX POTENTIALS AND DIFFUSION OF LITHIUM IN LAMELLAR COMPOUNDS

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Thermodynamic and dynamic properties of intercalation products of lithium into MoS_2 are strongly determined by the coordination of lithium in the interlaminar spaces. Lithium redox potentials as well as lithium diffusion coefficients in MoS_2 pure, exfoliated, as well as in compounds where lithium is co-intercalated with the polymeric electron pair donors, poly(ethylene oxide) and poly-acrylonitrile, and discrete species, OH^- ions and secondary amines, were analyzed comparatively. Reduction potentials in pure or exfoliated MoS_2 are always much lower than those observed in lithium-donor co-intercalates. Thus, donors appear to effectively stabilize higher lithium oxidation states. The donors also influence lithium migration properties, with lithium diffusion coefficients in general higher than in pure MoS_2. Lithium diffusion activation energy in pure MoS_2 is constant in a relatively large lithium concentration range, while for co-intercalates it often depends on lithium intercalation degree. These more complex diffusion mechanisms probably arise from changes in the donor conformation in the interlaminar spaces, which affect the lithium first coordination sphere.

Keywords: Lithium; Intercalation compounds; Molybdenum disulfide; Organic-inorganic nanocomposites

INTRODUCTION

New fast ionic conductors are often host-guest compounds based on the intercalation of lithium in lamellar solids [1]. These systems may be considered

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as two phase nanocomposites; one phase, the matrix or host, is a rigid phase with the properties of a conventional solid; the other, where electroactive lithium species are found, is a high mobile phase, the guest, located in the matrix interlayer spaces [2, 3]. Materials in which the host is intrinsically an isolator, *i.e.*, with a large energy gap between valence and conduction bands, are pure ionic conductors. In these materials, the electrical conductivity is totally determined by the mobility of lithium in the interlaminar spaces. However, in the host often there are conduction bands of relatively low energy, with a small or nonexistent energy gap as it occurs in the case of conductors and semiconductors. These materials are more complex, behaving as mixed conductors. That is the case of the conductors based on the intercalation of lithium in transition metal chalcogenides. In these compounds the electromotive force leading to the intercalation as well as the electronic and ionic transport properties are strongly influenced by the lithium-host charge transfer [4, 5]. Since the energy associated to this process is determined by the chemical potential of the electron in both host and guest, it is the chemical environment of the guest – in the case of metal ions, their coordination sphere – that essentially determines the transport properties of the products. In this work we describe a series of systems involving the intercalation of lithium in pure and modified molybdenum disulfide, in which the coordination sites of lithium are defined solely by the matrix and modified by the presence of co-intercalated electron pair donors, respectively.

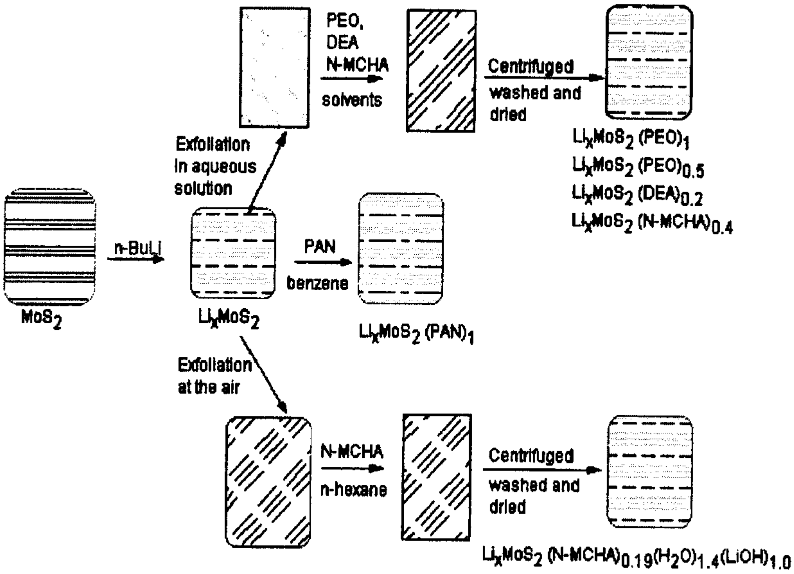
EXPERIMENTAL

Synthesis Work

Routes used for obtaining studied compounds are illustrated in Scheme 1.

Li_xMoS_2. MoS_2 was treated with 1.6 M n-butyl lithium in n-hexane for 48 h at room temperature. Products with variable lithium concentration but at least $x = 1.0$ are obtained [6]. Product was washed with n-hexane, dried under vacuum and stored in a dry box under an argon atmosphere. Alternatively, the compound may be obtained by microwave activation [7] where shorter reaction times, on the order of minutes, are needed; yield is, however, relatively lower.

$Li_{0.1}MoS_2$(guest), general procedure. The rapid hydrolysis of Li_xMoS_2 in de-ionized, deaerated water leads to a suspension of exfoliated MoS_2. Products are obtained by adding a stoichiometric amount of the guest dissolved or suspended in an appropriated medium – poly(ethylene oxide) (PEO) in water, dicyclohexylamine (DCHA) and N-methylcyclohexylamine



SCHEME 1 Synthesis routes for obtaining MoS_2-based intercalation compounds.

(N-MCHA) in n-hexane – and stirring for 24 h at room temperature. Products were washed with appropriate solvent, dried under vacuum and stored under argon.

$Li_xMoS_2(PAN)_y$. Li_xMoS_2 was treated with a stoichiometric amount of poly-acrylonitrile (PAN) in benzene.

$Li_xMoS_2(N\text{-}MCHA)_y(H_2O)_u(LiOH)_v$. Dry, exfoliated Li_xMoS_2 is hydrolyzed at the air, and then treated with stoichiometric amount of amine in n-hexane during 24 h.

All solvents and chemical precursors were carefully dried and distilled. Manipulations were performed in a dry-box under an argon atmosphere.

Analytical Results

Calcd. for $Li_{0.8}MoS_2(PAN)_1$: C, 18.0; H, 1.5; N, 7.0; Li, 2.5. Found: C, 18.4; H, 2.2; N, 7.01; Li, 2.1.

Calcd. for $Li_{0.1}MoS_2(PEO)_{0.5}$: C, 5.64; H, 0.94; Li, 0.66. Found: C, 5.75; H, 1.02; Li, 0.63.

Calcd. for $Li_{0.1}MoS_2(PEO)_1$: C, 12.4; H, 2.06; Li, 0.74. Found: C, 13.2; H, 2.22; Li, 0.73.

Calcd. for $Li_{0.1}MoS_2(DEA)_{0.2}$: C, 5.85; H, 1.34; N, 1.70; Li, 0.39. Found: C, 5.57; H, 1.33; N, 1.99; Li, 0.41.

Calcd. for $Li_{0.1}MoS_2(N\text{-}MCHA)_{0.4}$: C, 9.15; H, 1.63; N, 1.52; Li, 0.33. Found: C, 9.16; H, 1.64; N, 1.53; Li, 0.30.

Calcd. for $Li_{0.1}MoS_2(N\text{-}MCHA)_{0.19}(H_2O)_{1.4}(LiOH)_{1.0}$: C, 6.63; H, 1.18; N, 1.1; Li, 3.6. Found: C, 6.79; H, 1.38; N, 1.1; Li, 3.9.

Primary Characterization

Stoichiometry was determined by elemental combustion analysis (SISONS Model EA-1108) and lithium atomic absorption spectrometry (UNICAM 929). The content of organic components was confirmed by simultaneous TG-DTA thermal analysis (Netzsch STA 409C). Further characterization was performed by electron microscopy (Phillip M300) and Powder x-ray diffraction analysis (Siemens D-5000, Cu-K radiation).

Electrochemical Studies

Compounds with different lithium concentrations were obtained electrochemically by step-wise galvanostatic reduction, in a cell Li/0.5 M $LiClO_4$ in ethylene carbonate-propylene carbonate 1 : 1/Intercalation compound, at a current density of 150 μA cm^{-2} (PARC Model 175) [8]. Lithium concentration was determined coulombmetrically (PARC Model 179). *Quasi*-equilibrium potentials were obtained by the same experimental arrangement. Lithium diffusion coefficients were determined in the same cell by galvanostatic pulse-relaxation techniques [9] at variable temperatures and different lithium intercalation degrees.

RESULTS AND DISCUSSION

Thermodynamic Effects

Intercalation of Lithium in Pure Molybdenum Disulfide

Crystallographic as well electrochemical studies indicate that the insertion of lithium into MoS_2 induces a phase change from prismatic trigonal, $2H_b$, in pristine MoS_2 to a distorted octahedral 1T-MoS_2 modification with the molybdenum coordinated octahedrically [10] which, as recently established by electron crystallography [11], corresponds more properly to a WTe_2 type structure. By analogy with TaS_2, 1T-MoS_2 is expected to be an electronic conductor with a low-lying conduction band with an important dz^2 contribution [10].

Theoretical calculations in TiS_2 [12, 13] as well as in MoS_2 itself [14] lead to the conclusion that the intercalation process is associated to a guest-host electron transfer followed by a partial back-donation process in which, some of the originally charge transferred to the host, returns to the guest [12]. The final electronic configuration of the system is, in the case of MoS_2, strongly determined by the coordination of lithium to six sulfur atoms in the interlaminar spaces. Thus, fractional oxidation states for intercalated lithium are possible. ESCA experiments show indeed that intercalated lithium in $Li_{0.8}MoS_2$ has a rather low oxidation state [15].

The importance of the coordination sphere around lithium in determining the electronic configuration and therefore its actual oxidation state, may be better visualized by comparing the average potential values of the electrochemical intercalation of lithium into the systems MoS_2 and MoO_3. For the latter, the mean discharge potential is 2.5 V, significantly higher than that of MoS_2 (1.6 V) [16]. The most plausible explanation for such a different behavior is the large difference between the polarizabilities of the ligands, sulfur and oxygen, respectively.

Co-intercalation of Donors and Lithium into MoS_2

There is experimental evidence [17] of the effect of the donor strength of media on the redox potential of lithium. As observed in data reproduced in Table I, Lewis basicity of the solvent determines the stability of the lithium ion.

The coordination sphere around lithium in the interlaminar spaces may be efficiently altered by the co-intercalation of electron pair donor species. Thus, the effect of this new lithium environment should be reflected in the properties of the intercalates. Thermodynamically, the formation enthalpy

TABLE I Dependence of the half wave potential of the pair Li/Li^+ on the Lewis basicity of the solvent expressed as the donor number [18]

Solvent	*Donor Number (DN)*	$E_{1/2}$ Li^+/Li *V vs. BBCr*(I)*
Benzonitrile	11.9	−1.13
Acetonitrile	14.1	−1.20
Propylene carbonate	15.1	−1.25
Acetone	17	−1.38
Methanol	19	−1.48
N-Dimethyl acetamide	27.8	−1.70
Dimethyl sulfoxide	29.8	−1.72
N-Diethyl formamide	30.9	−1.77

*$E_{1/2}$ in volts using bis-biphenyl chromium(I) as internal reference.

of lithium ion in the intercalated state – taking the lithium intercalates in MoS_2 as a reference – should change with the ligand field strength characteristic of any particular arrangement.

Li_xMoS_2(donor species) intercalation compounds discussed in this work are described in Table II. All of them correspond to pure phases, which may be clearly identified by elemental analyses, powder x-ray diffraction analyses, and thermal analyses. Stoichiometries and interlayer distances in these compounds, are also in Table II. As apparent there, lithium may be co-intercalated in a wide concentration range but not the donor. In most cases, there is only one stable phase with a characteristic MoS_2 : donor ratio. Only for PEO, were two clearly identifiable stoichiometries found. Compounds obtained from water suspensions normally contain about 0.1 mol lithium per mol MoS_2. In the compounds obtained from a water-free procedure or by controlled hydrolysis with moisture, the amount of lithium in the product is about $x = 0.7-1.0$. In Table II, the ranges of lithium concentration corresponding to species obtained electrochemically by plating lithium from non-aqueous electrolytes are also considered.

The variations with lithium concentration of the open circuit potential under *quasi*-equilibrium conditions for the studied compounds are reproduced in Figure 1. In many cases there are variations of the reduction potential which could be indicative of phase changes. However there is always a mean value (see Tab. III) which expresses fairly well the relative stability of lithium in each medium.

As expected, hard ligands – as the oxygen environment in the intercalates containing POE or OH^--ions or nitrogen environments as in the amine derivatives – induce much higher reduction potentials than the pristine soft

TABLE II Composition and interlaminar distances of studied intercalation compounds obtained by chemical synthesis and modified by electrochemical lithium intercalation

	Stoichiometry ranges Mol Li per mol MoS_2		
Compound *	*Chemical synthesis*	*Electrochemical lithium intercalation*	*Interlaminar distance (Å)*
Li_xMoS_2	0.1–1.0	0.0–0.7	6.15
Li_xMoS_2(Exfoliated)	0.1	0.1–0.66	11.5
$Li_xMoS_2(PEO)_{1.0}$	0.1	0.1–0.8	16
$Li_xMoS_2(PEO)_{0.5}$	0.1	0.1–0.6	11
$Li_xMoS_2(PAN)_{1.0}$	0.7–1.0	0.0–0.76	11.5
$Li_xMoS_2(DEA)_{0.2}$	0.1	0.1–0.85	9.8
$Li_xMoS_2(N\text{-}MCHA)_{0.4}$	0.7–1.0	0.1–0.80	10.5
$Li_xMoS_2(N\text{-}MCHA)_{0.19}(H_2O)_{1.4}(LiOH)_{1.0}$	0.7–1.0	0.1–0.95	10.4

* Abbreviations: PEO = poly(ethylene-oxide); PAN = poly-acrylonitrile; DCHA = di-cyclohexylamine; N-MCHA: N-methylcyclohexylamine; DEA = diethylamine.

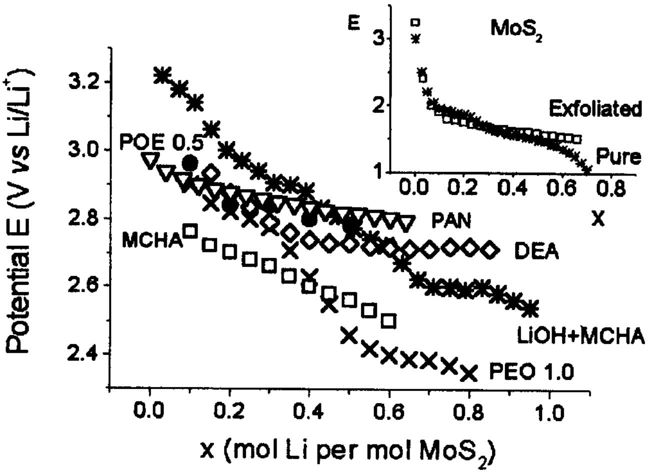


FIGURE 1 Variation of the reduction potential with lithium content along the intercalation of lithium into MoS_2 pure and modified by the co-intercalation of donors.

TABLE III Average open circuit potential under quasi-equilibrium conditions for the intercalation of lithium into MoS_2 pure, exfoliated, and modified by co-intercalation of electron pair donors

Compound *	*Average potential volts vs. Li/Li$^+$*	*Lithium concentration range mol Li per mol MoS$_2$(x)*
MoS_2(Pure)	1.60	0.2–0.6
MoS_2(Exfoliated)	1.64	0.2–0.6
$Li_xMoS_2(POE)_1$	2.61	0.2–0.6
$Li_xMoS_2(POE)_{0.5}$	2.78	0.2–0.6
$Li_xMoS_2(PAN)_{1.0}$	2.84	0.2–0.6
$Li_xMoS_2(DEA)_{0.2}$	2.80	0.2–0.6
$Li_xMoS_2(N\text{-}MCHA)_{0.4}$	2.60	0.2–0.6
$Li_xMoS_2(N\text{-}MCHA)_{0.19}(H_2O)_{1.4}(LiOH)_{1.0}$	2.80	0.2–0.6

*For abbreviation see Table II.

sulfur medium in Li_xMoS_2. Surprisingly, PAN with a donor group of relatively modest donicity [18] also induces potential values which are comparable to those of the amine derivatives. Thus, in all these cases, the actual oxidation state of lithium appears to be rather higher than in MoS_2.

Dynamic Effects

Molybdenum Disulfide

The diffusion of lithium across the solid is also strongly influenced by the coordination sphere of the lithium ion. Theoretical studies based on a quantum chemical model considering the variation of the electron chemical potential indicate that, in the case of intercalation of lithium into 1T-MoS_2, the diffusion of lithium in the interlaminar spaces occurs by ion hopping between octahedral sites [16]. In such a mechanism the tetrahedral sites, which are also present in the same space, would correspond to intermediate sites. Activation energy, E_a, obtained experimentally from the dependence of the diffusion coefficient on the temperature has a unique value of 0.31 eV, which does not depend on the lithium concentration in the range $x = 0.1 - 0.5$ [19]. This behavior is expected for a rigid matrix which does not change with lithium intercalation degree. Any significant change in E_a is indeed indicative of changes in lithium coordination environment in both ground state and activated complex which are, in turn, probably induced by a phase change in the matrix. That appears to occur in the case of Li_xMoO_3 for which diffusion coefficients lead to activation energies between 0.6 and 0.28 eV in the lithium concentration range $x = 0.1 - 0.4$ [16].

Co-intercalation of Donors

The influence of the coordination of lithium ion on the dynamics of the system is more complex. As observed in Table IV, the diffusion coefficients of lithium are, in general, enhanced by the co-intercalation of donors by at least in one order of magnitude. However, there is not enough information available for interpreting the relatively small difference between the features observed for the different compounds. Surely, the mechanisms are often governed by conditions determined by the particular nature and conformation of the donors in the interlaminar spaces. Such a conformation

TABLE IV Chemical diffusion coefficients of lithium intercalated in MoS_2 and MoS_2 modified by co-intercalation of electron pair donors at 25°C

	Chemical diffusion coefficient D *$cm^2\ s^{-1} \cdot 10^{14}$*		
	Lithium intercalation degree (mol Li per mol MoS_2)$\cdot 10^{14}$		
Compound *	$X = 0.2$	$X = 0.4$	$X = 0.5$
Li_xMoS_2(Pristine)	14	4.2	1.41
Li_xMoS_2(Exfoliated)	31	4.6	1.54
$Li_xMoS_2(PEO)_{1.0}$	200	45	26
$Li_xMoS_2(PEO)_{0.5}$	3000	100	8.5
$Li_xMoS_2(PAN)_{1.0}$	4300	580	23**
$Li_xMoS_2(N\text{-}MCHA)_{0.4}$	200	142	56**
$Li_xMoS_2(DEA)_{0.2}$	1480	170	–

*Abbreviations, see Table II.
**$x = 0.6$.

essentially determines the distance between the sites with the lowest energy and the nature of the intermediate states between these sites, affecting both the energy barriers and the diffusion rate of lithium. Furthermore, the conservation of such a mechanism though a wide lithium intercalation degree, as occurs in pure MoS_2 lithium intercalates, is not observed in cointercalates with complex molecular structures (see Tab. V). It is therefore possible that the arrangement and the conformation of the organic guest vary with the amount of intercalated lithium and the changes induced in the host by charge transfer from lithium. That appears to be general for practically all studied co-intercalates.

However, the system MoS_2-PEO is a special case. As observed in Table V, there is a large difference between the dynamic behavior of the compounds with low and high PEO content. The dependence of the activation energy on lithium content, $\Delta E_a/\Delta x$ – which, as commented above, is practically non-existent for pure MoS_2 – has a finite but relatively modest value for the compound $Li_xMoS_2(PEO)_{1.0}$ of about 0.2 eV per molar fraction unit, while for $Li_xMoS_2(PEO)_{0.5}$ the much higher value of about 1.6 is obtained. Such a difference is explained by the conformation of PEO in the interlayer spaces schematized in Figure 2. In the case of compounds with the stoichiometry $MoS_2:PEO = 1:1$, the observed interlayer distance (see Tab. II) indicates the existence of a bilayer arrangement of the polymer. The movement of lithium in this compound would be similar to that in pure PEO but in a bi-dimensional space. According to data in Table IV, increasing amount of co-intercalated lithium affects the diffusion rate; however, the mechanism reflected in the activation energies does not change very much (see Tab. V). The latter is probably due to both the limited space available for

TABLE V Activation energies for diffusion of lithium in MoS_2 pure and modified by co-intercalation of electron pair donors

	Activation energy eV		
	Lithium intercalation degree (mol Li per mol MoS_2)		
Compound *	$X = 0.2$	$X = 0.4$	$X = 0.5$
Li_xMoS_2(Pure)	0.31	0.31	0.31
$Li_xMoS_2(PEO)_{1.0}$	0.39	0.48	0.46
$Li_xMoS_2(PEO)_{0.5}$	0.52	0.74	1.01
$Li_xMoS_2(PAN)_{1.0}$	0.21	0.23	0.70**
$Li_xMoS_2(NMCHA)_{0.4}$	0.52	0.32	0.26**
$Li_xMoS_2(DEA)_{0.2}$	0.21	0.36	–

*Abbreviations, see Table II.
**$x = 0.6$.

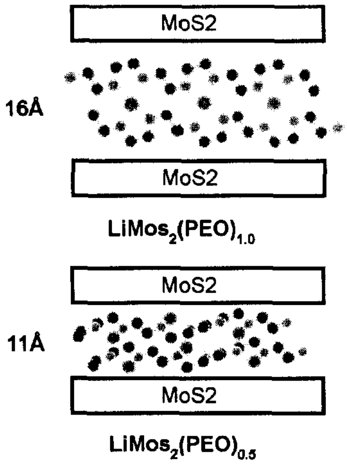


FIGURE 2 Schematic representation of the conformation of poly(ethylene oxide) in the MoS_2 interlaminar spaces of $Li_xMoS_2(PEO)_{1.0}$ and $Li_xMoS_2(PEO)_{0.5}$.

conformation changes in the organic donor and the screening effect from the influence of the polarization changes of sulfur atoms produced by the polymer. In the compound with 0.5 mole PEO per mole MoS_2 with a rather smaller interlaminar distance, the environment of lithium would be mixed coordination of both PEO oxygen and matrix sulfur ligands. In this case the increase of the concentration of lithium would induce changes in the diffusion mechanism as suggested by the strong dependence of E_a on the lithium intercalation degree. Such a change may be easily understood by considering how exposed lithium is to changes in both the polymer conformation and the polarization of sulfur atoms with lithium concentration. The activation energy for the diffusion of lithium also changes significantly with lithium content in the intercalation of PAN. A clearly non-linear relationship is observed, so that two different slopes ($\Delta E_a/\Delta x$), *e.g.*, 0.085 and 0.05 eV for the extreme low and high lithium concentration, respectively, are obtained. Drastic changes in the conformation of lithium sites in the interlaminar spaces, which could be related to the softness and high electron delocalization of PAN may be therefore inferred. Related studies concerning MoS_2-amine compounds are in progress.

CONCLUSIONS

The thermodynamic as well as the dynamic properties of the products of the intercalation of lithium into molybdenum disulfide are strongly influenced by the coordination sphere of lithium in the interlaminar spaces. The soft environment of lithium when it is coordinated solely by sulfur atoms results in poor stabilization of the cation, so the redox behavior of the system is similar to that of metallic lithium. However, when the sulfur environment is changed such that the first coordination sphere of lithium contains stronger and relatively harder ligands, a clear stabilization of the lithium cation is reached. Although the latter do not have reduction potentials as high as those observed for the oxygen environment in transition metal oxides such as NiO_2 and CoO_2 [20–22], relatively high mean values on the order of magnitude to MoO_3, are achieved. According to that, such a redox potential would correspond to the maximal potential possible for this system, whose limit would be determined mainly by the nature of the host.

The influence of the coordination environment of lithium on the dynamic properties of the system appears to be more complex; however it is clear that, in general, better conditions for lithium diffusion are reached by the presence of donor ligands. From the results discussed above it is also apparent that in many cases it is possible to observe fairly low activation energies.

The examples analyzed here indicate that varying the coordination of lithium in the interlayer spaces, it is possible to regulate the redox and transport properties for this kind of intercalation compounds.

Acknowledgments

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References

[1] J. L. Atwood, J. E. D. Davis and D. D. Macnicol, Eds., *Inclusion Compounds* (Academic Press, New York, 1994).

[2] D. O'Hare, *Inorganic Materials* D. W. Bruce and D. O'Hare, Eds. (Wiley and Sons, London, 1982).

[3] G. A. Ozin, *Adv. Mater.* **4**, 612 (1992).

[4] M. S. Whittingham, *Prog. Solid St. Chem.* **86**, 463 (1982).

[5] A. D. Yoffe, *Solid State Ionics* **39**, 1 (1990).

[6] M. B. Dines, *Mater. Res. Bull.* **10**, 287 (1975).

[7] E. Benavente and G. González, *Mater. Res. Bull.* **32**, 709 (1997).

[8] G. González, M. A. Santa Ana and E. Benavente, *J. Phys. Chem. Solids* **58**, 1457 (1997).

[9] S. Basu and W. L. Worrel, *Fast Ion Transport in Solids* P. Vashista, J. N. Mundy and G. K. Sheny, Eds. (North Holland, Amsterdam, 1979).

[10] M. A. Py and R. R. Hearing, *Can. J. Phys.* **61**, 76 (1983).

[11] J. Heising and M. G. Kanatzidis, *J. Am. Chem. Soc.* **121**, 638 (1999).

[12] C. Umrigar, D. Ellis, D. Wang, H. Krakauer and M. Posternak, *Phys. Rev. B* **26**, 4935 (1982).
[13] F. Mendizábal, R. Contreras and A. Aizman, *J. Phys.: Condens. Matter*. **9**, 3011 (1997).
[14] F. Mendizábal, M. A. Santa Ana, E. Benavente and G. González, unpublished results.
[15] G. González and H. Binder, *Bol. Soc. Chil. Quím.* **41**, 121 (1996).
[16] M. A. Santa Ana, E. Benavente, J. Páez and G. González, *Bol. Soc. Chil. Quim.* **45**, 491 (2000).
[17] O. Duscheck and V. Gutmann, *Mh. Chem.* **104**, 1259 (1973).
[18] V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions* (Plenum Press, New York, 1978).
[19] M. A. Santa Ana, V. Sánchez and G. González, *Electrochim. Acta* **40**, 1773 (1995).
[20] S. A. Campbell, C. Bows and R. S. McMillan, *J. Electroanal. Chem.* **284**, 195 (1990).
[21] K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, *Mater. Res. Bull.* **15**, 783 (1980).
[22] M. Winter, J. O. Besenhard, M. E. Spahr and P. Novák, *Adv. Mater.* **10**, 725 (1998).