

Chemical and electrochemical lithium insertion into ternary transition metal sulfides MMo_2S_4 (M: V, Cr, Fe)

S. Maffi and L. Peraldo Bicelli

Department of Applied Physical Chemistry of the Milan Polytechnic, Research Centre on Electrode Processes of the CNR, Piazza Leonardo da Vinci 32, 20133 Milan (Italy)

C. Barriga, P. Lavela, J. Morales and J. L. Tirado

Departamento de Química Inorgánica e Ingeniería Química, Facultad de Ciencias, Universidad de Córdoba, San Alberto Magno, s/n. 14004 Córdoba (Spain)

(Received January 23, 1992; in revised form March 26, 1992)

Abstract

The effects of lithium insertion in MMo_2S_4 (M: V, Cr, Fe) have been studied by means of chemical and electrochemical insertion methods. The reaction has a topotactic character and a higher degree of lithium insertion was found for the compound FeMo_2S_4 which has a greater unit cell volume. For this compound the changes in lattice parameters with lithium content are also more pronounced. The voltage composition curves show a smooth voltage decrease with a quasi-plateau located at around 1.3 V. For discharge at lithium content higher than 0.8, the voltage decreases quickly followed by an extended plateau below 1 V, a region where electrolyte decomposition may occur. The X-ray powder diffraction patterns of the electrochemical lithiated compounds show that the original monoclinic structure is maintained up to $0.8 e^-$ per mole, but with a significant change in the intensity of the peaks, indicative of an alteration of cation distribution for this degree of insertion. For high lithium content, such disorder promotes the collapse of the structure, resulting in the loss of long-range order of the material.

Introduction

Solid-state batteries have received an increasing attention during the last years due to their interest as power sources in different fields, such as those related with electronic devices [1]. In particular, lithium battery research and development is an area of significant activity, in which the search of compounds of potential applicability as cathodic materials constitutes an important aspect of this activity [2]. In this context, great efforts have been undertaken to increase the energy density of primary and secondary batteries by exploring new types of electrode materials. Much of this interest has been centered on transition metal-layered dichalcogenides, because the van der Waals gaps between the layers provide vacant lattice sites for the intercalation of guest ions [3]. However, three-dimensional framework host lattices may have significant advantages compared to two-dimensional layered compounds, such as three-dimensional electronic and ionic conductivity, and the elimination of electrolyte solvent co-intercalation with the lithium ions, a problem observed in some layered compounds [4].

Recent investigations have revealed that some sulfospinel behave as adequate cathode materials operating topochemically through Li insertion into vacant octahedral and tetrahedral interstitial sites [5]. In fact, it has been reported that performance characteristics of thiospinel-Li cells can be matched with that of TiS_2 cells [6]. Moreover, promising perspectives from an electrochemical point of view have been also found for the binary Chevrel phase Mo_6S_8 and related compounds [7-9].

Ternary sulfocompounds with an MMo_2S_4 (M: V, Cr, Fe) stoichiometry have a monoclinic type structure due to a strong intermetallic bonding between Mo trivalent ions [10, 11]. The structure consists of octahedral chains $(\text{MoS}_6)_n$ and $(\text{MS}_6)_n$ extending along the a and b directions. The structure can also be described as a MoS_2 -type layer structure. According to this model, the sulfur atoms have a deformed hexagonal close packing and metal ions occupy the octahedral positions. This leads to a ...-M-S-Mo-S-M-S-Mo-S-... layer-stacking sequence of atomic positions. Molybdenum ions occupy all octahedral sites between two sulfur layers while first transition row metals M occupy only half of the octahedral positions. Thus, these compounds have one vacant octahedral site per formula unit that could be occupied by Li^+ ions through a topochemical reaction mechanism.

In this paper we present measurements of the electrochemical Li insertion properties of these ternary chalcogenides. We also detail their reaction with *n*-butyllithium, and a comparative study is performed of the results obtained by using electrochemical and chemical intercalation methods.

Experimental

The ternary sulfides MMo_2S_4 (M: V, Cr, Fe) were prepared by direct combination of the constituent elements. All reagents were supplied by Strem Chemicals, except sulfur, supplied by Merck. All reactions were carried out in sealed silica tubes. Samples in pellet form were heated at 900 °C for 10 h and then cooled down slowly, reground and heated again at 1100 °C for 3 days.

The chemical lithiation reactions were done in a dry argon atmosphere (M. Braun glove box). The *n*-butyllithium was obtained from Strem Chemicals as 1.6 M solution in hexane. The reagent was diluted with dry hexane prior to use. A solution, which was 10:1 excess in *n*-butyllithium, was added to a known amount of each sample. After several days of reaction at room temperature, the solid was filtered, washed with hexane and dried. Lithium content was determined by atomic absorption spectrometry.

The electrochemical measurements were performed at room temperature using a standard equipment with two-electrode button-type laboratory cells assembled in a dry box under argon atmosphere. The cells, with an electrode surface of 1.13 cm², consisted of a cathode pellet (60 to 80 mg of ternary sulfide powder pressed at 200 MPa) supported on a copper substrate (99% reduced copper, Carlo Erba), of porous glasspaper discs soaked with the electrolyte and of a lithium disc anode (more than 99% lithium, Alfa Ventron). The electrolyte was 1 M LiClO_4 in a binary 1:1 mixture of propylene carbonate (PC) and 1,2-dimethoxyethane (DME). The computer-assisted galvanostatic discharge measurements were carried out at different current densities.

X-ray powder diffraction (XPD) data were alternatively obtained with a Philips PW1710 and a Siemens D500 diffractometer equipped with $\text{Cu K}\alpha$ radiation and graphite monochromator.

Results and discussion

Materials characterization and chemical insertion

The as-prepared ternary sulfide samples of nominal composition MMo_2S_4 (M: V, Cr, Fe) had a silvery aspect and their XPD patterns showed the presence of a single phase with a high degree of crystallinity.

After consecutive 10-day periods of reaction with *n*-butyllithium, the atomic absorption spectrometry measurements evidenced the progressive insertion of Li in the sulfide samples, as shown in Fig. 1. The colour of the lithiated samples changes to black and they lose metallic luster. From Fig. 1 it is worth noting that the degree of Li insertion increases in the sequence $\text{Fe} > \text{Cr} > \text{V}$ for a same lithiation time. In addition, Li content reaches values higher than unity for Fe. As reported earlier on the basis of magnetic measurements, Mo atoms have a formal oxidation state +3 in pristine MMo_2S_4 (M: V, Cr, Fe) [12]. The compositions of the lithiated sample imply the reduction of Mo to a mixed oxidation state between +2 and +3 and thus a theoretical composition up to $\text{Li}_2\text{MMo}_2\text{S}_4$ could be expected. However, the structure of these compounds consists of a limited number of distorted octahedral sites that may be adequate sites for Li^+ occupancy. The number of sites of this type coincides with the number of M ions. Thus, compositions with Li contents close to or higher than LiMMo_2S_4 may induce additional structural changes or the occupancy of other lower-coordination sites. The distortions of the structure for high Li contents are discussed below in the light of the electrochemical behaviour.

The unit-cell parameters of the pristine and lithiated samples lead to the unit-cell volumes which are shown in Table 1. From these data, a complex behaviour is observed. However, the clearest tendency is observed for Fe and Cr phases, in which most lithiated samples have a higher unit-cell volume than pristine samples. However,

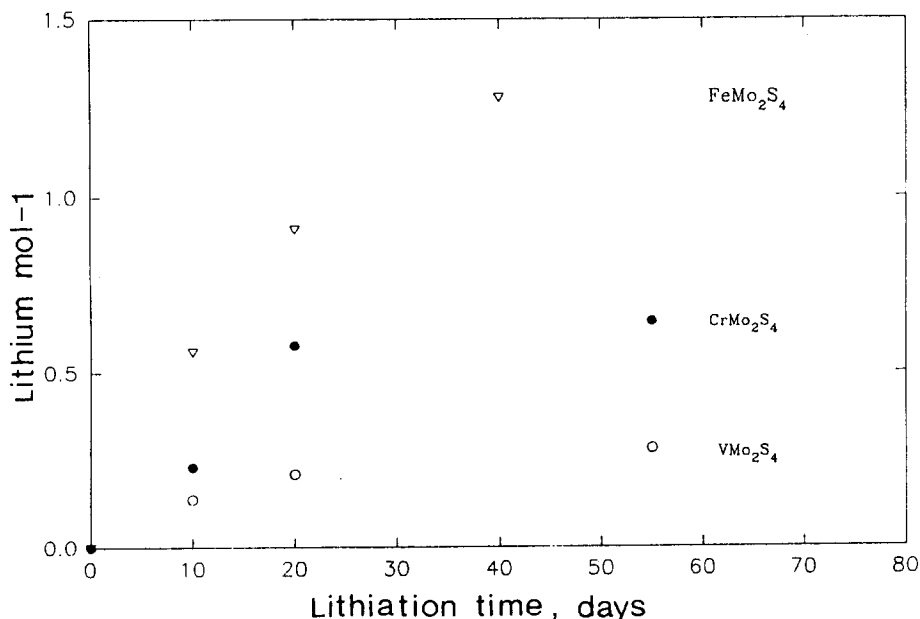


Fig. 1. Plot of lithium content vs reaction time with *n*-butyllithium of chemically-lithiated samples.

TABLE 1

Evolution of unit-cell volumes of MMo_2S_4 (M: V, Cr, Fe) during chemical and electrochemical lithiation

System	Chemical		Electrochemical	
	x	V (esd) ^a (\AA^3)	x	V (esd) ^a (\AA^3)
$\text{Li}_x\text{VMo}_2\text{S}_4$	0.00	901(3)	0.00	901(3)
	0.14	899(3)	0.10	903(5)
	0.21	899(3)	0.20	902(5)
	0.28	899(3)	0.50	900(4)
$\text{Li}_x\text{CrMo}_2\text{S}_4$	0.00	904(3)	0.00	904(3)
	0.23	907(3)	0.10	910(3)
	0.58	912(3)	0.30	911(3)
	0.65	901(3)	0.50	911(3)
			0.80	903(3)
$\text{Li}_x\text{FeMo}_2\text{S}_4$	0.00	924(5)	0.00	924(5)
	0.56	926(6)	0.10	929(6)
	0.91	928(6)	0.20	931(6)
	1.28	924(6)	0.50	927(6)
			0.75	926(7)

^aesd: estimated standard deviation.

the extent of these changes is low and this fact may be related to the rigidity of the three-dimensional network that acts as a host for Li ions [13]. In addition, it should be noted that Li insertion may induce two opposite effects on the size of the host lattice. First, it induces electrostatic attraction between the sulfide ions coordinating the initially empty octahedral sites and the incoming Li^+ cations. Second, lowering the formal oxidation state of the Mo layers it reduces the electrostatic attraction between these ions and sulfide anions. Both effects have opposite consequences on the unit-cell volume, thus partially cancelling each other. Further comments on this behaviour are discussed below, by including the data provided by electrochemically-lithiated samples.

Electrochemical results

Figure 2 shows the typical discharge curves of $\text{Li}/\text{CrMo}_2\text{S}_4$ cells at several current densities also showing the part below 1 V for sake of completeness. The curves exhibit an initial decrease with several slope changes followed by a quasi-plateau around 1.3 V and by an extended plateau in a region where electrolyte decomposition may also occur. The latter plateau was observed up to a discharge value of 5 F mol^{-1} , at a current density of 0.3 mA cm^{-2} . For higher values the curve went rapidly to zero. Moreover, pellets discharged at this voltage plateau increasingly reacted with water producing a strong hydrogen evolution. It is worth underlining that no hydrogen bubbles were formed by pellets discharged in the first part of the curve, i.e. above 0.5 to 0.6 V (at 0.3 mA cm^{-2}).

The influence of the current density on the discharged curves was regular. 10% addition of a binder polytetrafluoroethylene (PTFE) or of graphite to the pellets in order to improve the electrolyte permeability and the electrode conductivity, respectively, did practically not modify the experimental results. A similar behaviour, also as far

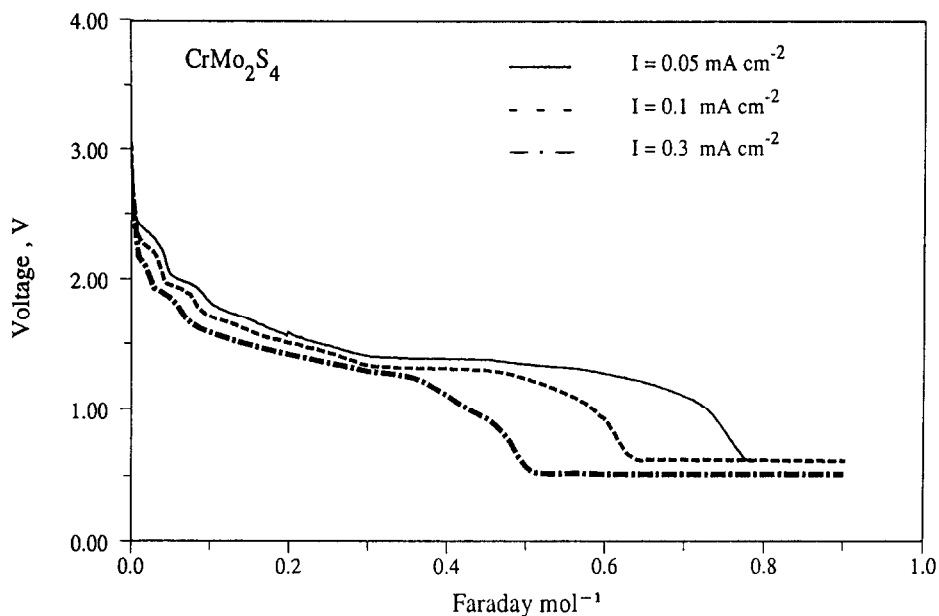


Fig. 2. Discharge curves of CrMo_2S_4 in 1 M LiClO_4 -PC+DME lithium cells at various current densities.

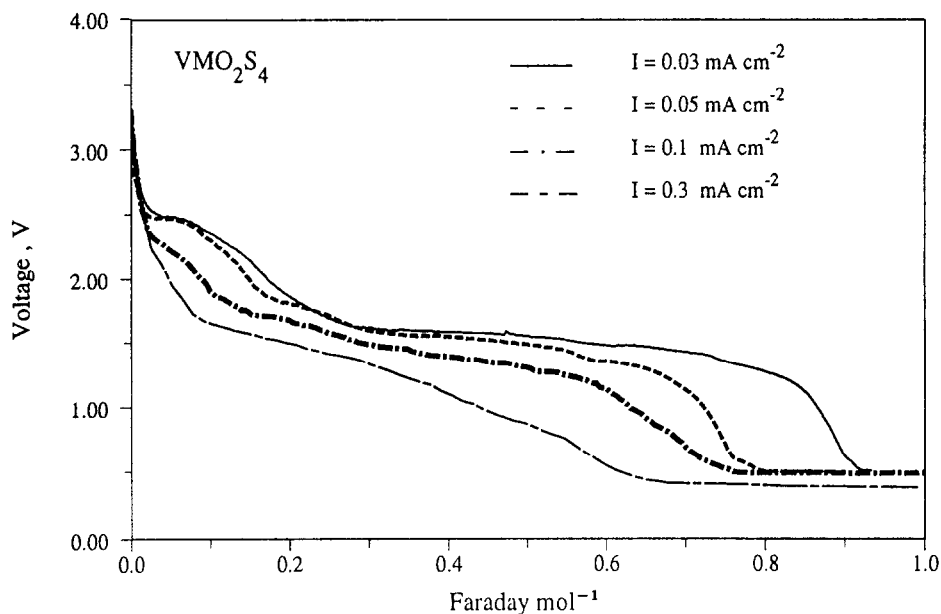


Fig. 3. Discharge curves of VMO_2S_4 in 1 M LiClO_4 -PC+DME lithium cells at various current densities.

as the pellet reactivity with water is concerned, was also found for VMo_2S_4 (Fig. 3) and for FeMo_2S_4 (Fig. 4). Although the Fe compound has an electrical resistivity at room temperature which is about 10 times higher than that of the other two sulfides [12], its discharge curve was also practically not influenced by the addition of graphite to the pellet.

Table 2 summarizes the performance up to a cutoff voltage of 1 V of the MMo_2S_4 (M: V, Cr, Fe) compounds in Li cells operating at different current densities. In particular, the average cell voltage and the depth-of-discharge as well as the gravimetric and volumetric capacity and energy are reported. The results evidence the moderate behaviour of these materials notwithstanding their structure (see below). In fact, based on the electrochemical stoichiometry, the volume energy density calculated for the system of potential applicability such as Li/TiS_2 is 1.2 W h cm^{-3} [8]. Table 2 also shows that at the lower current densities the discharged Li quantity up to a cutoff voltage of 1 V increases by passing the Fe to the Cr or V compound. These results seem to be in contrast with those obtained during chemical lithiation and reported in Fig. 1. From this plot, it turns out that the amount of the chemically-inserted Li quantity increases according to the sequence $\text{V} < \text{Cr} < \text{Fe}$, that is, in the order of increasing unit-cell volume, as expected. Indeed, during chemical lithiation of these same compounds, the powder was dispersed into the solution (*n*-butyllithium in hexane) and stirred for at least 20 days, so that its grain decreases in size. Therefore, the Li quantity inserted under these conditions depended in nearly the same way on the morphology of the three sulfides and followed the theoretical predictions. This was not the case during electrochemical lithiation since a different morphology of the three powders was observed. As evidenced by the scanning electron microscopy (SEM) pictures reported in Figs. 5(a), 6(a) and 7(a), the grain size of the Fe compound was

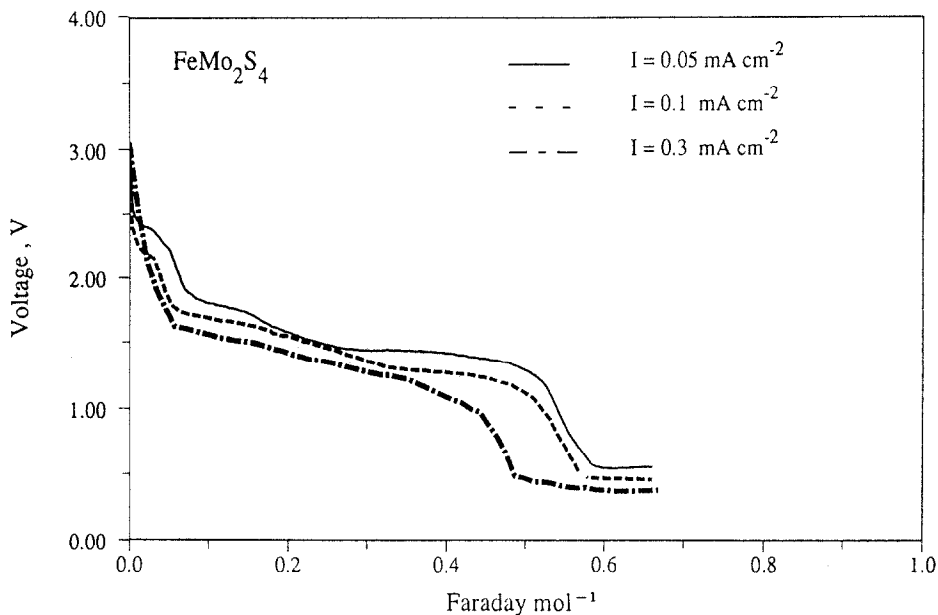


Fig. 4. Discharge curves of FeMo_2S_4 in 1 M LiClO_4 -PC+DME lithium cells at various current densities.

TABLE 2

Performance of CrMo_2S_4 , VMo_2S_4 and FeMo_2S_4 (original and ground) in 1 M LiClO_4 -PC+DME lithium cells at several current densities (cutoff voltage: 1 V)

	Current density (mA cm^{-2})	Average voltage (V)	Depth-of-discharge (F mol^{-1})	Gravimetric capacity (A h g^{-1})	Volumetric capacity ($\text{A h cm}^{-3\text{a}}$)	Gravimetric energy (W h g^{-1})	Volumetric energy ($\text{W h cm}^{-3\text{a}}$)
VMo_2S_4	0.03	1.70	0.87	0.06	0.33	0.11	0.60
	0.05	1.69	0.72	0.05	0.27	0.09	0.49
	0.1	1.58	0.63	0.04	0.22	0.07	0.38
	0.3	1.48	0.44	0.03	0.16	0.05	0.27
CrMo_2S_4	0.05	1.49	0.73	0.05	0.27	0.08	0.44
	0.1	1.47	0.59	0.04	0.22	0.06	0.33
	0.3	1.43	0.43	0.03	0.16	0.04	0.22
FeMo_2S_4	0.05	1.60	0.54	0.04	0.22	0.06	0.33
	0.05 ^b	1.83	0.78	0.06	0.33	0.10	0.55
	0.1	1.49	0.52	0.04	0.22	0.05	0.27
	0.3	1.41	0.44	0.03	0.16	0.04	0.22

^aAssuming a theoretical density of 5.5 g cm^{-3} for the three compounds [12].

^bThese data refer to the ground material.

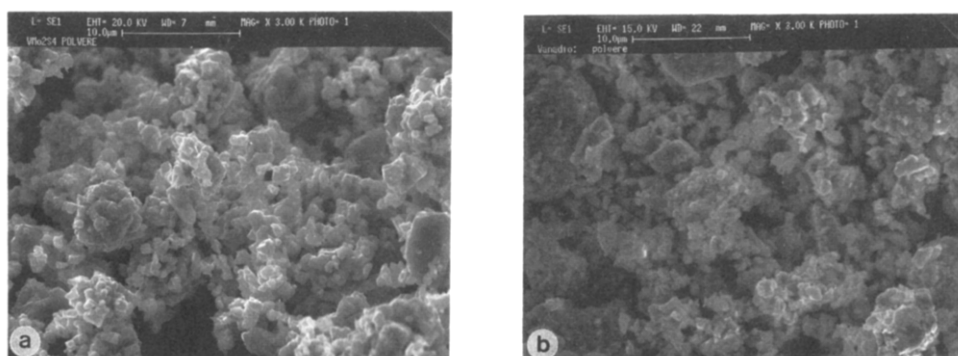


Fig. 5. Scanning electron microscopy pictures (a) of the original VMo_2S_4 powder and (b) of the same powder after the treatment in hexane.

very large, while that of the other two compounds was much smaller and followed the order: Cr slightly greater than V. By thoroughly grinding the FeMo_2S_4 preparing the pellet, its grain size decreased, and the related discharge curve improved as depicted in Fig. 8 which compares the electrochemical behaviour of the original and of the ground compound. Moreover, the Li quantity discharged up to 1 V and, in general, its behaviour (also shown in Table 2) was even greater than that observed for the V compound.

To confirm this point, we carried out the following experiment. The original powders were stirred in pure hexane in the same conditions as during chemical lithiation and subsequently observed under the electron microscope. As shown in Figs. 5(b), 6(b) and 7(b), the grain size strongly diminished after this treatment and the surface

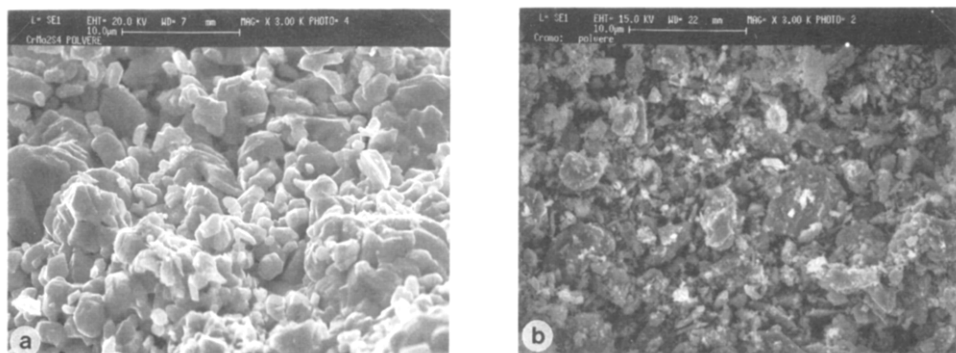


Fig. 6. Scanning electron microscopy pictures (a) of the original CrMo₂S₄ powder and (b) of the same powder after the treatment in hexane.

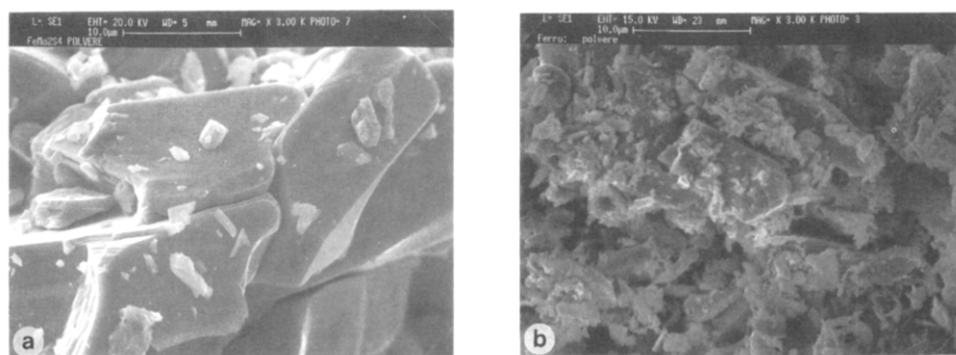


Fig. 7. Scanning electron microscopy pictures (a) of the original FeMo₂S₄ powder and (b) of the same powder after the treatment in hexane.

area increased, more especially in the case of the Fe compound. Now, the three sulfides had a very similar morphology. Unfortunately, owing to the relatively small quantity of material available, it was not possible to verify these results also through BET surface area determination. Finally, we prepared a pellet for electrochemical lithiation with the powder of the Fe compound treated as previously described. Better results were obtained, similar to those found for the ground material.

At the end of this discussion, it is worth noting that usually more Li could be inserted during electrochemical than chemical lithiation of sulfides powders of nearly the same particle size. This may be explained on the basis of the higher driving force in the former case where the electric field forces the Li ions into the cathode material.

The evolution of the unit-cell volume in electrochemically-lithiated samples was studied and Table 1 also includes these data. It is noteworthy that the electrochemical procedure allows the preparation of samples with lower Li contents than the chemically-prepared ones. The discharge curve can be halted at the desired compositions while using an excess of *n*-butyllithium does not allow to select the exact composition. Considering both chemically- and electrochemically-inserted samples, the values in Table 1 show an initial enhancement of the unit-cell volume which is especially evident for the FeMo₂S₄ system, which in turn has the highest value of this parameter in the

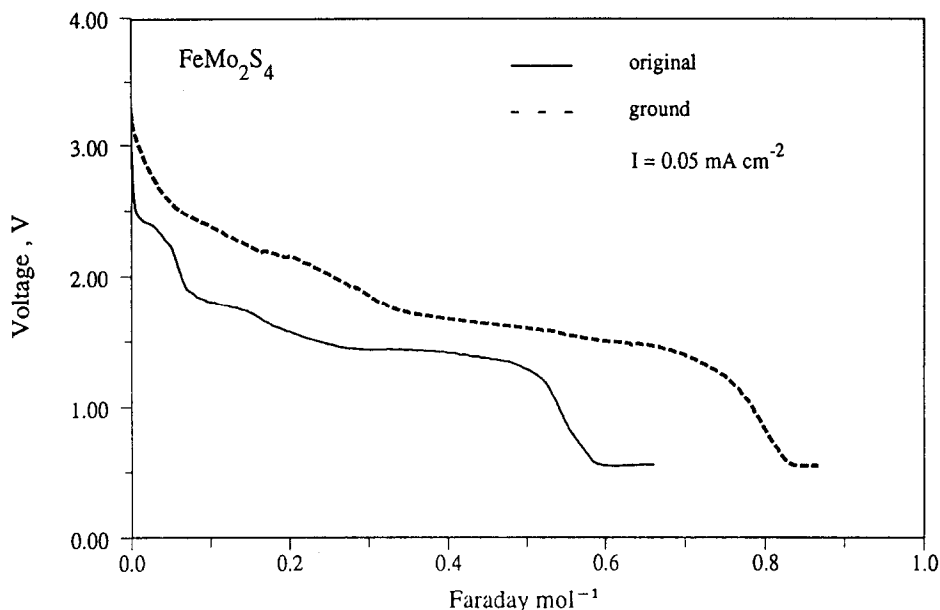


Fig. 8. Discharge curves of FeMo_2S_4 in 1 M $\text{LiClO}_4\text{-PC+DME}$ lithium cells at the current density of 0.05 mA cm^{-2} . The pellet was prepared with the original (—) and ground (---) powder.

pristine sample. For Li contents higher than 0.8 a decrease in volume occurs, which is accompanied by other changes in the XPD patterns of the samples. Thus, a decrease in the intensity of the 002 line relative to the 008 line is observed, as shown in Figs. 9 and 10. For the Fe case, the intensity ratio I_{002}/I_{008} takes values lower than unity for Li contents ≥ 0.75 . The XPD patterns of these compounds do not allow a detailed refinement of the complete structure due to the low scattering factor of Li and the low symmetry of the phases. However, the structural implications of these intensity changes were studied by simulating the XPD patterns of the original phase, according to the crystallographic data in ref. 10, before and after introducing controlled changes in atom positions and/or site occupancies. In this way, it was found that the ratio I_{002}/I_{008} is dramatically affected by the differences in scattering power of the metal atoms placed in alternate layers of the structure. This implies a possible cation redistribution as a result of the migration of Mo ions to part of the initially-empty octahedral sites neighbour to Fe ions, while Li may be inserted in the octahedral sites of both consecutive layers. However, this disorder leads to a deterioration of the structure which may collapse resulting in the loss of long-range ordering of the solid. In fact, the XPD patterns of the discharged products had enhanced background level and broadening of the reflections.

Discharge mechanism

From XPD analysis it seems that no structural changes occur during the Li discharge process up to the region where the cell voltage steeply decreases to form the extended plateau at about 0.5 to 0.6 V, whereas at a very deep discharge (e.g. 5 F mol^{-1}) electrochemical reactions took place forming products which could not

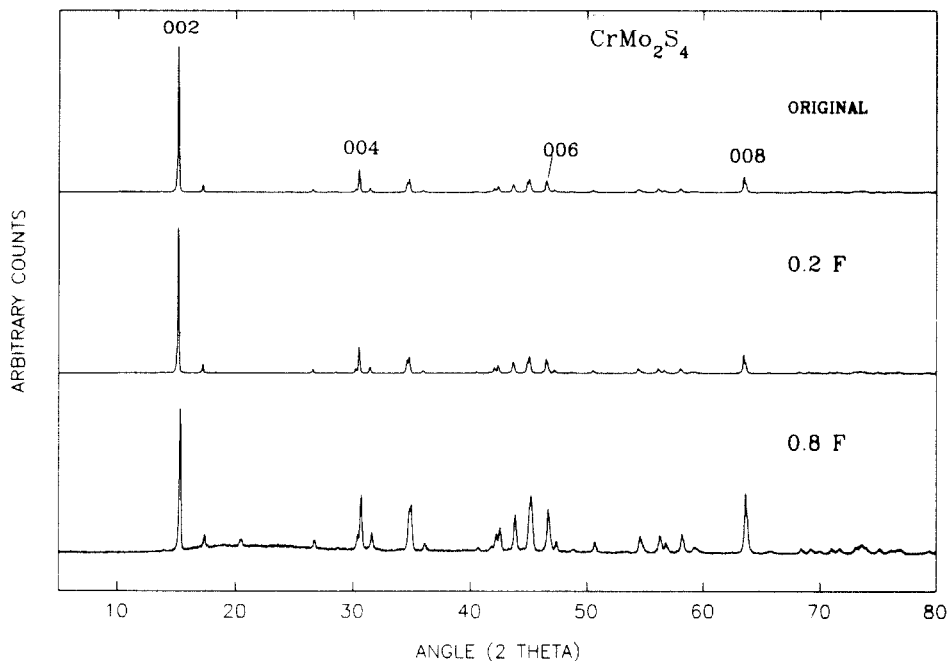


Fig. 9. Evolution of X-ray powder diffraction patterns of electrochemically-lithiated CrMo_2S_4 .

be recognized by X-ray investigation, possibly owing to their small quantity. In between these two regions the materials lose the long-range ordering. In the Fe compound discharged at the beginning of the plateau, LiOH was recognized when the pellet was not protected from air contamination by a polymeric thin film (domopack) during X-ray measurements (and only in this case), an indication that the reduced phases were reactive with air moisture, particularly in the presence of oxygen. However, this process was not ended since the same pellet was still reactive with water — in fact hydrogen bubbles formation was observed as for all the other pellets discharged in this region.

According to Chevrel *et al.* [12] the considered MMo_2S_4 compounds are characterized by one vacant octahedral site per formula unit in the plane containing the M atoms, so that their structures are formed by layers of the type $\text{M}\square\text{Mo}_2\text{S}_4$. The sulfur atoms give rise to a deformed close-packed hexagonal lattice while the elements M and Mo occupy octahedral sites. We therefore expect that Li ions, discharged in the homogeneous single-phase region, occupy such vacant octahedral sites and that the simultaneously-introduced electrons enter the semiconductor conduction band, i.e. reduce the trivalent Mo ions to the divalent state. Such Li intercalation process may be described as:



According to this mechanism, which utilizes M-ion vacancies, up to one Li atom could theoretically be intercalated per mole of the sulfide. However, a second Li atom per mole could be inserted with simultaneous reduction of the residual trivalent Mo ions. The experimental results show that the total discharged Li quantity up to a cut-off voltage of 1 V (the region of practical interest) is much smaller than two Li atoms per mole.

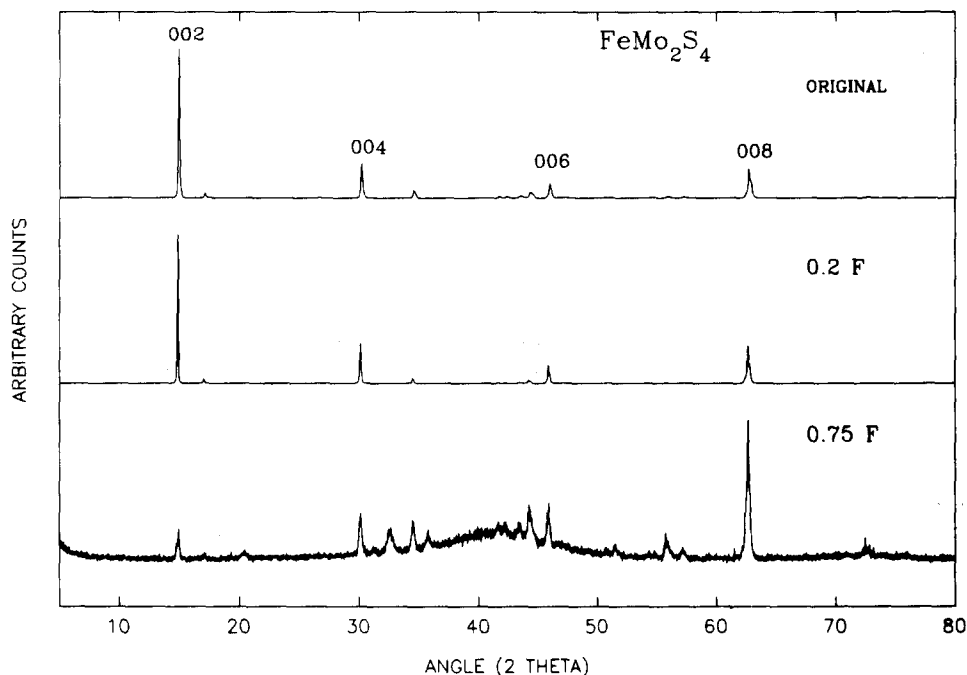


Fig. 10. Evolution of the X-ray powder diffraction patterns of electrochemically-lithiated FeMo_2S_4 .

TABLE 3

Standard enthalpy and Gibbs free energy of formation of several sulfides and related thermodynamic quantities

Compound	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	Ref.
FeMo_2S_4	(-464)		see text
Li_2S	-441.4		[14]
FeS	-100	-100.4	[14]
Fe_7S_8	-736.4	-748.5	[14]
FeS_2	-178.2	-166.9	[14]
MoS	(-129)		see text
Mo_2S_3	-364		[14]
MoS_2	-235.1	-225.9	[14]

Thermodynamic calculations

At the lower cell voltage, in addition to possible electrolyte decomposition, compound decomposition takes place. A multiphase system is obtained and, according to the Gibbs phase rule, a typical discharge plateau is observed. In this case, thermodynamic calculations are of primary interest. As shown in Table 3, thermodynamic data (taken from ref. 14) are lacking for the compounds of our interest. In particular, no data

are available for the V and Cr sulfides. Moreover, only the values of the standard enthalpy of formation, ΔH_f° are known for Li_2S and Mo_2S_3 , so, we are forced to use these quantities instead of the standard Gibbs free energy values, ΔG_f° , in calculating the decomposition cell voltage. In doing so, we expect to introduce a not too great error in our calculations since all the elements, from which our compounds are formed, are in the solid state in standard conditions. Where available also the standard Gibbs free energies were reported in Table 3, the two values differing by not more than 10 kJ mol^{-1} which is only a little higher than the usual approximation in this type of calculations. The enthalpy value of MoS was calculated from the values of the known Mo-S compounds that is of Mo_2S_3 and MoS_2 , simulating the trend of the Fe-S compounds.

As often occurs, no experimental thermodynamic values are known for the ternary compounds. In the absence of these data, we estimated the value of the enthalpy of formation of FeMo_2S_4 by summing those of the corresponding binaries as usually done [15]. This approximation implies that the reaction between the two binaries to form the ternary compound takes place without any enthalpy change. The decomposition reactions of FeMo_2S_4 possibly occurring during Li discharge are presented in Table 4, together with their standard enthalpy changes. From these quantities, we calculated the standard cell voltage, E° , from the relationship strictly valid, as already stated, for the reaction free enthalpy:

$$E^\circ \approx -\Delta H^\circ / zF \quad (2)$$

where z is the number of charges transferred during the reaction and F the Faraday constant. Taking into account that the enthalpy of formation of FeMo_2S_4 has a smaller value than that reported in Table 3, it turns out that the actual ΔH° and E° values of the decomposition reactions are greater and smaller, respectively, than those collected in Table 4.

From the data of Table 4 it results that all the decomposition reactions occur nearly at the same decomposition potential, although Fe seems to be slightly more reducible than Mo, particularly in comparison to when Mo^{III} reduces to Mo^0 . Moreover, these reactions occur, in equilibrium conditions, at a voltage which is much higher than that of the observed plateaus, so, they are thermodynamically possible in our experimental conditions even in the region of the quasi-plateau. In Table 4 reaction (f) is also reported. Indeed, Li insertion into the ternary sulfide reduces some of the trivalent Mo ions to the divalent state, and therefore the possible Mo^{II} reduction reaction must also be taken into account. Since we have no information on the

TABLE 4

Possible decomposition reactions of FeMo_2S_4 during lithium discharge and related thermodynamic quantities

Reactions	ΔH° (kJ)	E° (V)
(a) $\text{FeMo}_2\text{S}_4 + 2\text{Li} \rightarrow \text{Fe} + \text{Mo}_2\text{S}_3 + \text{Li}_2\text{S}$	-341.4	1.77
(b) $\text{FeMo}_2\text{S}_4 + 4\text{Li} \rightarrow \text{Fe} + 2\text{MoS} + 2\text{Li}_2\text{S}$	-676.8	1.75
(c) $\text{FeMo}_2\text{S}_4 + 2\text{Li} \rightarrow \text{FeS} + 2\text{MoS} + \text{Li}_2\text{S}$	-335.4	1.74
(d) $\text{FeMo}_2\text{S}_4 + 6\text{Li} \rightarrow \text{FeS} + 2\text{Mo} + 3\text{Li}_2\text{S}$	-960.2	1.66
(e) $\text{FeMo}_2\text{S}_4 + \text{Li} \rightarrow \text{Fe} + 2\text{Mo} + 4\text{Li}_2\text{S}$	-1301.6	1.69
(f) $\text{MoS} + 2\text{Li} \rightarrow \text{Mo} + \text{Li}_2\text{S}$	-312.4	1.62

composition of the lithiated compound, we preferred to consider MoS as the starting material. In any case, recalling our method of estimation of the multinary thermodynamic data from the binary ones, the thermodynamic contributions we calculated for reaction (f) are the same as those for the corresponding reaction involving the more complex Li-containing FeMo_2S_4 compound. By the way, FeS reduction to Fe and Mo_2S_3 reduction to MoS or Mo similarly occur at the same cell voltages as those reported in Table 4 for reactions (a), (c) or (d), respectively. As previously stated, compound decomposition was observed at the low voltage plateau but the decomposition products could not be identified by X-ray determinations, also owing to the worsening of the spectra quality with lithiation. So, other techniques (i.e., X-ray photoelectron spectroscopy analysis) must be employed in order to identify the Fe, Mo and S species in the discharged pellet and so to find out the actual decomposition mechanism. In addition, the reaction with water of the deeply-discharged compound with gas bubbles formation seems to be explainable by assuming that the reduced species decompose water by releasing hydrogen and forming LiOH. The X-ray detected presence of LiOH in the discharged pellet, not protected from air humidity, seems to agree with this hypothesis.

Conclusions

Lithium insertion reactions in MMo_2S_4 (M: V, Cr, Fe) have a topotactic character for low degrees of lithiation. Lithium contents of chemically-prepared samples are higher for FeMo_2S_4 and the variation in unit-cell volume is more marked for this compound.

In the electrochemical experiments, the voltage versus composition curves show a smooth voltage decrease with a quasi-plateau located at around 1.3 V and a fast voltage diminution for contents higher than 0.8 F mol^{-1} . The examined sulfides present an unsatisfactory performance. Nevertheless, owing to their structures, it would be interesting to investigate the reversibility of the Li discharge process and research in this direction is now in due course.

The original monoclinic structure is maintained up to a Li content of 0.8 per mole, but an alteration of cation distribution is observed for this degree of insertion, especially for the Fe case. For higher Li content, such disorder promotes the collapse of the structure, resulting in the loss of long-range ordering of the material.

Decomposition of the sulfides was finally observed (although the products could not be recognized) and thermodynamic calculations allow to indicate the possible decomposition routes.

Acknowledgements

The authors are indebted to the Italian and Spanish Ministry of Education for a Concerted Action (1991-13A) and the Spanish group is also indebted to CICYT (MAT88-0708).

References

- 1 C. Julien, *Mater. Sci. Eng.*, B6 (1990) 9.
- 2 K. M. Abraham and B. B. Owens (eds.), *Materials and Processes for Lithium Batteries*, The Electrochemical Society, Inc., Pennington, NJ, 1989.

- 3 M. S. Whittingham and A. J. Jacobson (eds.), *Intercalation Chemistry*, Academic Press, New York/London, 1982.
- 4 R. Schöllhorn, in J. L. Atwood, I. E. D. Davies and D. D. McNicol (eds.), *Inclusion Compounds*, Academic Press, New York/London, 1984.
- 5 A. C. W. P. James, B. Ellis and J. B. Goodenough, *Solid State Ionics*, 27 (1988) 45.
- 6 M. Eisenberg, *Electrochim. Acta*, 26 (1981) 955.
- 7 P. J. Mulhein and R. R. Flaering, *Can. J. Phys.*, 62 (1984) 527.
- 8 J. M. Tarascon, *J. Electrochem. Soc.*, 132 (1985) 2089.
- 9 T. Uchida, Y. Tanjo, M. Wakihara and M. Taniguchi, *J. Electrochem. Soc.*, 137 (1990) 7.
- 10 P. J. Guillevic, J. Le Marquille and D. Grandgean, *Acta Crystallogr.*, B30 (1974) 111.
- 11 J. M. van der Berg, *Inorg. Chim. Acta*, 2 (1968) 216.
- 12 R. Chevrel, M. Sergent, J. L. Meury, Dang Tran Quan and Y. Colin, *J. Solid State Chem.*, 10 (1974) 260.
- 13 R. Schöllhorn, *Pure Appl. Chem.*, 56 (1984) 1739.
- 14 D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, *J. Phys. Chem. Ref. Data., Suppl. 11* (1982).
- 15 D. Cahen and Y. Mirovsky, *J. Phys. Chem.*, 89 (1985) 2818.