

THE M—O—X TRANSITION METAL OXYHALIDES: A NEW CLASS OF LAMELLAR CATHODE MATERIAL

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Summary

The transition metal oxyhalides MOX (M = Fe, Cr, V, Ti) possess a structure with bidimensional character and behave as a host structure for lithium intercalation. Both chemical (n-butyl lithium) and electrochemical means have been used to study the lithiation of the compounds to give Li_xMOCl derivatives. FeOCl in particular has been found to give reversible intercalation reactions, and thus is a very good candidate as cathode material for high energy density batteries, comparable in this respect to TiS_2 .

Introduction

The transition metal oxyhalides represent an example of the orthorhombic FeOCl type structure. The lattice can be described as bidimensional, built up from two layers of halide ions sandwiching a corrugated metal-oxygen plane (Fig. 1). The weak bonding between adjacent halide sheets allows them to be easily pulled apart through various molecular intercalation reactions [1, 2].

This work deals with lithium intercalation studied by both chemical and electrochemical means.

On this point the oxyhalides were expected to bear a close resemblance to the MY_2 transition metal dichalcogenides for which extensive work on alkali metal intercalation has been done [3 - 5].

Considerable interest has been raised by this class of compounds in the field of electrochemical energy storage, as possible cathode materials working via reversible intercalation reactions. Non-stoichiometric intercalates presenting both ionic and electronic conductivity have been defined as solid-solution electrodes [6], and, for example the feasibility of the Li/TiS_2 secondary battery has been recently demonstrated with stored energy densities in excess of 100 Wh/kg [7].

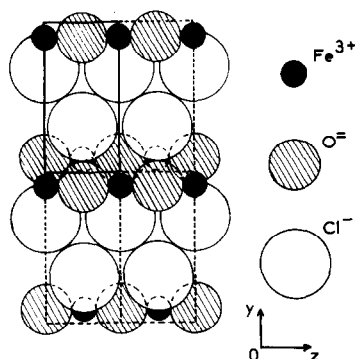


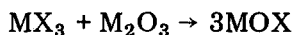
Fig. 1. The structure of FeOCl.

TABLE 1
MOX oxyhalide cell parameters

| Oxyhalide | Temperature of reaction (°C) | Parameters | | |
|-----------|------------------------------|--------------|--------------|--------------|
| | | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) |
| FeOCl | 460 | 3.181 (6) | 3.893 (8) | 3.293 (3) |
| VOCl | 480 | 3.770 (5) | 7.930 (6) | 3.290 (3) |
| VOBr | 400 | 3.775 (4) | 8.425 (7) | 3.380 (4) |
| CrOCl | 460 | 3.852 (3) | 7.755 (7) | 3.168 (2) |
| CrOBr | 380 | 3.86 (3) | 8.36 (9) | 3.23 (2) |

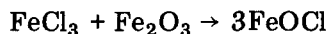
Preparation

The oxyhalides are usually prepared simply by addition of the halide to the corresponding oxide [8]:



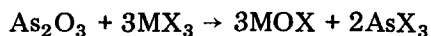
The reaction is carried out for a few days in a Pyrex tube sealed under vacuum.

This method is readily applicable to the preparation of the iron derivative at 460 °C:



Excess FeCl₃ is removed by either sublimation under vacuum or dissolution with absolute ethanol.

The other less volatile MX₃ halides usually lead to an incomplete reaction, even at 600 - 700 °C [9, 10]. In this case, the more convenient reaction between arsenic(III) oxide and the halide is preferred. As₂O₃ has a vapor pressure of 10 mmHg at 260 °C and leads to:



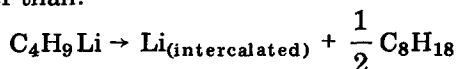
The molecular arsenic halide and excess As_2O_3 are easily removed by sublimation to leave the oxyhalide crystals.

CrOBr and VOBr were first prepared by Rouxel and co-workers by this type of reaction [11, 12]. The X-ray diffraction powder patterns of the compounds agree with the reported results (Table 1).

Part I: Chemical intercalation

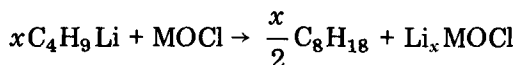
Experimental

Intercalation was accomplished by means of the n-butyl lithium technique first described by Armand in the case of the graphite compounds [13]. Chianelli and Dines [14] and Murphy [15] have transposed this method to the lamellar chalcogenides, and have shown that virtually no side reaction other than:



was observable.

Lithiation of the oxyhalides was done under dry N_2 atmosphere. n-Butyl lithium (1 M commercial solution in hexane) was diluted ten times and a known amount allowed to react on the solid. At 60 °C, reaction times ranged from 24 hours to 8 days, indicative of different intercalation rates. When a concentrated (1 M) solution was used, a fast reaction was observed, with evolution of heat (boiling of the solution). Reaction products were filtered, washed with hexane and dried. Lithium content was analyzed by atomic absorption spectroscopy. The upper limit of intercalation, according to the reaction:



corresponds to $x \leq 1$, even when a large excess of lithiating reagent is used. Dilution of the n-butyl lithium also does not affect the limit of intercalation.

X-ray powder spectra were taken, the samples being prepared in Lindemann glass capillaries under nitrogen. The resulting patterns are of poor definition with broad diffuse lines indicating some loss of order during the intercalation process.

Results and discussion

n-Butyl lithium reacts with all the oxyhalides. In every case, a distinct color change is noted, all intercalated samples being black.

FeOCl

All the compositions $0 < x < 1$ have been prepared. Up to $x = 0.5$, almost no change in cell parameters can be observed. Also, the definitions of the patterns decreases (turbostratic stacking of the FeOCl sheets).

It is very interesting to note that lithium can be washed out by water to yield the original structure, as for example in the case of TaS_2 . In this case, a redox process has to be involved to explain the conservation of the +3 valency for the iron ions; either water reduction or oxidation with O_2 can be evoked. This reaction, however, gives convincing evidence of the stability of the FeOCl host lattice.

The most probable positions of the lithium ions in the FeOCl lattice are the octahedral sites corresponding to the $2c$ Wyckoff positions (0, 0, 0.64) of the $Pm\bar{m}n$ space group of FeOCl . Lithium is surrounded by five chlorine ions at 2.53 Å (2.56 Å in LiCl) and one oxygen ion at 2.41 Å (2.3 Å in Li_2O). This relatively loose coordinating environment would tend to be favorable to a fast diffusion process of the lithium ions.

The poor quality of the X-ray spectra, however, made it impossible to confirm the position of the lithium ions. Structural investigations with the use of broad-line n.m.r. and site potential calculations are in progress.

Even though it has not been possible to obtain single crystals good enough for precise electrical conductivity measurements, it is clear that a sharp transition from the semi-conducting state of FeOCl to a metallic state takes place. This is to be related to the electron hopping mechanism between Fe^{2+} and Fe^{3+} ions at the percolation threshold in Li_xFeOCl .

VOCl

The vanadium compound is of special interest considering its anomalously high value of the b parameter compared to CrOCl (the remark being valid also for the oxybromides). This fact can be related to a strong Jahn-Teller effect due to the d_2 structure of the V^{2+} ion. Lithium intercalation corresponds to the reduction of V^{3+} to V^{2+} in an octahedral environment and should lead to the disappearance of the Jahn-Teller effect. In $\text{Li}_{0.8}\text{VOCl}$, the lattice parameters on the sharp X-ray patterns obtained have been found to be:

$$a = 4.07 \text{ \AA}; b = 7.68 \text{ \AA}; c = 3.31 \text{ \AA}$$

compared with $b = 7.93 \text{ \AA}$ for the pure host structure. This decrease in the interlayer space after intercalation thus corroborates the importance of the Jahn-Teller effect. A similar phenomenon has been observed in VSe_2 intercalates [4].

CrOCl

The chromium(III) halogen bonds have a highly covalent character thus reflected by the chemical inertness of CrCl_3 . However, in contrast to the iron derivative, Li_xCrOCl , as well as Li_xVOCl , are decomposed by water to give mainly lithium chloride and the transition metal oxides. Thus, no general rule allows to predict the stabilities of the lithium intercalates as a function of the coordinating transition element.

Part II: Electrochemical intercalation

For the purpose of studying electrochemically the intercalation reaction, we have adapted the voltametric technique to solid-state electrode processes.

Principle

The classical three-electrode apparatus has been used unmodified (Fig. 2).

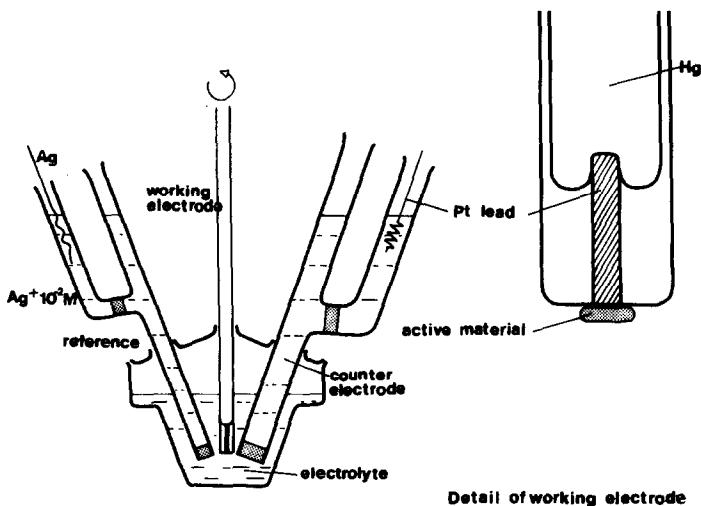


Fig. 2. Schematic drawing of the three-electrode apparatus used for the voltametric studies.

Acetonitrile has been chosen as the electrolyte base, because of its relative low ionicity (DN (donor number) = 14.1) [15], to favor the desolvation of the Li^+ ion before intercalation and avoid the problems of solvent co-intercalation. Lithium perchlorate (0.1 M) was dissolved in CH_3CN , purified and dried by known procedure [16].

The compound under investigation was deposited as a thin film ($10\ \mu m$) on the working electrode (platinum $1\ mm^2$) from a slurry in DMSO followed by drying. A binder (5% by weight) and carbon black ensure good adherence and electrical contact of the film.

Poly(vinylidene fluoride) was chosen as the macromolecular binder for its chemical and electrochemical inertness and its high dielectric constant ($\epsilon = 8.4$ at 60 Hz and $25\ ^\circ C$) making it compatible with the solvent used. This polymer is soluble in DMSO but only swells in acetonitrile. The reference electrode was $Ag/Ag^+ 10^{-2}\ M$ (at + 3.4 V versus Li/Li^+).

The electrochemical intercalation reaction, written as:



takes place when the potential is swept cathodically and corresponds to a current flow between the working and counter electrodes.

Application of Fermi Dirac statistics to the ions and electrons in the lattice [17] gives the potential-composition relationship as:

$$e = e_0 + \frac{2RT}{F} \ln \frac{x}{1-x}$$

When assuming that the rate-determining step is the transport of the Li^+ ions in the solid matrix, the differential equation for diffusion has been solved [17]. In this case, the current maximum corresponds to the potential at half saturation of the intercalation sites ($x = \frac{1}{2}$). The value e_0 can thus be taken as the standard potential for the intercalation process.

Results and discussion

FeOCl

The voltametric sweep (1000 mV/mn) between 0 and -0.5 V (Fig. 3), shows two well defined waves corresponding to the intercalation-de-intercalation process. The value of the potential at the cathodic current peak gives $e_{0 \text{ FeOCl}} = -270$ mV vs. Ag/Ag^+ and indicates the ease of reduction of the Fe^{3+} species via lithium diffusion. The re-oxidation wave at -80 mV corresponds to a one-cycle charge recuperation in excess of 80%. This finding corroborates the conclusion of the chemical study on the good reversibility.

Since the boundary conditions are not the same, only the reduction peak obtained with uncycled FeOCl is to be taken as e_0 . However, the small difference (<200 mV) between the anodic and cathodic peak potentials gives a qualitative clue of a fast electrochemical process (*i.e.* diffusion in the solid).

Comparison with titanium disulphide in the same conditions gave $e_{0 \text{ TiS}_2} = -1200$ mV and similar shifts in the two waves of the cyclic voltametric sweep.

One can then expect similar diffusion coefficients for these two layer compounds (D in $\text{Li}_x\text{TiS}_2 = 10^{-8}$ cm^2/s at room temperature [6]).

CrOCl-CrOBr

The two chromium oxyhalides are characterized by the stability of the +3 valence of the transition element. The chloride gives $e_{0 \text{ CrOCl}} = -1340$ mV and the bromide $e_{0 \text{ CrOBr}} = -940$ mV (Fig. 4). As can be predicted, the smaller Cl^- ion stabilizes the higher valency of chromium more effectively than the bulkier Br^- , as reflected by the more negative potential of reduction. In both cases, no re-oxidation peak was observed, indicating that the electrochemical process is irreversible in the solvent used.

VOCl

Again, we find here the relative stability of the V^{3+} state compared to divalent vanadium ($e_0 = -1460$ mV) (Fig. 4). As in the case of the Cr deriva-

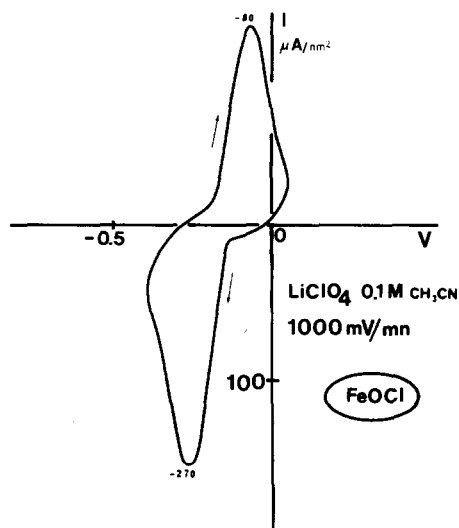


Fig. 3. Cyclic voltametric sweep for FeOCl. Sweep: 1000 mV/mn; acetonitrile-LiClO₄ (0.1 M).

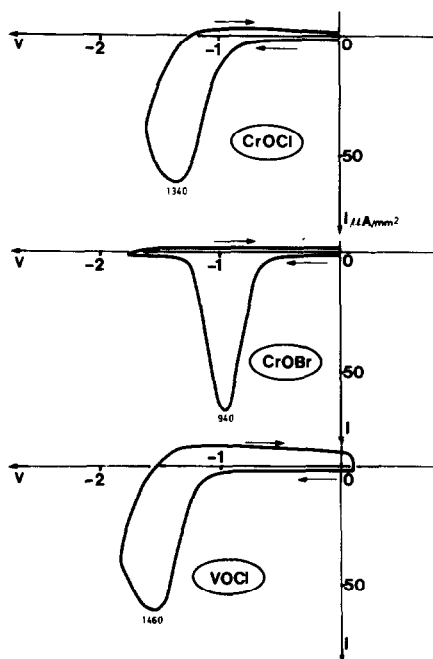


Fig. 4. Cyclic voltametric sweep for the chromium and vanadium oxyhalides.

tive, the irreversibility of the intercalation is apparent and again in agreement with the chemical part of this work. Considering the exceedingly small quantity (μg) of compound deposited on the working electrode, no morphological change or escape of soluble species could be observed in either case.

Conclusions

The parallelism drawn between the transition metal dichalcogenides and the oxyhalides is justified by the similarities of the lithium intercalation reactions observed by chemical or electrochemical means. FeOCl, with a reversible intercalation process thus bears a close resemblance to TiS₂. The irreversibility of the intercalation for the other oxyhalides tested can be explained in terms of the enhanced reactivity (reducing power) of the lithiated compounds leading to fast destructive reaction with the solvent or the impurities present (water, oxygen). In this respect, these compounds resemble MoS₂, this disulphide giving highly reductive lithium intercalates and disproportionation for the alkali metal rich derivative.

From the point of view of its practical use as a cathode material, FeOCl, in solid-state or organic solvent batteries might present the following advantages over TiS₂: (i) a more positive potential of the lithium intercalation,

leading to larger e.m.f. (3.2 V *vs.* Li/Li⁺ for FeOCl and 2.2 V for TiS₂), corresponding to higher theoretical energy densities (780 Wh/kg to 510); (ii) straightforward preparation of stoichiometric FeOCl in which no transition metal atom bridges the layers and hinders the diffusion of the lithium atoms, as shown in the case of the disulphide [6]; (iii) use of non-depletable elements (iron).

On the other hand, the low electrical conductivity of the starting material (before intercalation) raises a problem of current distribution and requires an inert conducting additive (carbon). This inconvenience could also be solved with appropriate doping of the compound by valence induction to increase the concentration of free electrons, as for FeO_{1-x}F_xCl in which the introduction of one fluorine ion corresponds to one Fe²⁺ in the lattice.

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