

## CHEMICALLY DESODIATED THIOCHROMITES AS CATHODE MATERIALS IN SECONDARY LITHIUM CELLS

R. MOSHTEV\*, V. MANEV, A. NASSALEVSKA and A. GUSHEV

*Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Sciences, Sofia 1040 (Bulgaria)*

G. PISTOIA

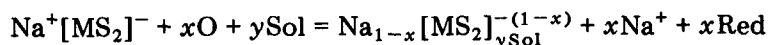
*Centro di Studio per la Chimica Fisica delle Interfasi, C.N.R., Via del Castro Laurenziano 7, Rome (Italy)*

### Summary

The chemical desodiation of non-doped and vanadium-doped sodium thiochromites has been studied. The changes in the chemical composition and X-ray diffraction patterns during desodiation of the stoichiometric compound reveal that the vanadium-doped thiochromite can be more effectively desodiated. The presence of vanadium in the disulfide layers enhances the covalency of the M-S bond; this probably facilitates a first order phase transition of the vanadium-doped material during deintercalation of both  $\text{Na}^+$  and  $\text{Li}^+$ . The electrochemical performance of cathodes prepared from the chemically desodiated, vanadium-doped thiochromite is assessed by cycling in a 1 M  $\text{LiClO}_4/\text{PC} + \text{DME}$  solution at a 3 h rate between 1.8 and 3.4 V. The volumetric energy density of the pressed cathodes is  $0.51 \text{ W h cm}^{-3}$  at the 100th cycle and drops to  $0.35 \text{ W h cm}^{-3}$  after 500 cycles.

### Introduction

In earlier studies we have shown that cathodes prepared from sodium thiochromite,  $\text{NaCrS}_2$ , and its vanadium-doped modification,  $\text{NaCr}_{0.85}\text{V}_{0.15}\text{S}_2$ , can be successfully cycled in  $\text{LiClO}_4\text{-PC} + \text{DME}$  solution versus a Li anode [1, 2]. In order to avoid the introduction to the electrolyte of  $\text{Na}^+$  ions, which are considered as detrimental to the cycling efficiency of the Li anode, it is necessary to remove them from the thiochromite (TC) prior to the preparation of the cathode mix. The desodiation of the ternary phase by chemical oxidation proceeds in aqueous [3] or in nonaqueous media [4] according to the general reaction:



\* Author to whom correspondence should be addressed.

where O is the oxidant, Red its reduced form, Sol is the solvent and  $MS_2$  the transition metal disulfide forming the layers in the host structure. The chemical oxidation results in an electron transfer from the transition metal to the oxidant.

Basically this is a topotactic reaction, wherein the crystal structure of the host does not change essentially during the deintercalation of the alkali ions. The deintercalation of  $Na^+$  from the layered host proceeds with the simultaneous oxidation of  $Cr^{3+}$  to  $Cr^{4+}$  and in the case of the V-doped compound, also of  $V^{3+}$  to  $V^{4+}$  and eventually to  $V^{5+}$ . In the more general case, the chemical desodiation reaction can be accompanied by solvent intercalation and by exchange of the  $Na^+$  ions with some ions in solution. Our preliminary experiments revealed that the degree of desodiation and the composition of the final product depend on a number of factors, the most important being:

- (i) the oxidation potential, concentration, and excess of the oxidant added;
- (ii) the type of solvent and the presence of other ions, *e.g.*, protons in the case of water;
- (iii) the dispersity of the thiochromite powder;
- (iv) the content of vanadium in the thiochromite;
- (v) temperature and time of treatment.

The proper choice of oxidant is determined basically by its standard oxidation potential, which, for a complete desodiation, should be by about 0.12 V more positive than that of the thiochromite. For aqueous solutions, the standard potential of the non-doped thiochromite, as estimated from the potential composition curve of the  $Na_{0.5}CrS_2/nhe$  couple and reported by Schöllhorn *et al.* [3], is *ca.* 0.0 V *versus* the *nhe*. For nonaqueous solutions, as a first approximation one can use for the potentials of the non-doped and V-doped thiochromites the values of 2.55 and 2.85 V *versus* the  $Li/Li^+$  reference electrode, determined from the potential-composition curves of the  $Li/Li_{0.5}Na_{0.2}CrS_2$  and the  $Li/Li_{0.5}Na_{0.1}Cr_{0.85}V_{0.15}S_2$  couples reported earlier [1, 2].

Table 1 presents the standard potentials,  $E_0$ , of a number of oxidants suitable for the chemical desodiation of thiochromites. It should be remembered that the standard potential of the  $Cr^{6+}/Cr^{3+}$  couple in aqueous solutions is 1.36 V, so that oxidants with potentials higher than this value should be avoided lest the thiochromite is decomposed into soluble dichromate.

The solvent should be chemically inactive towards both the oxidant and the thiochromite. It should also readily dissolve both the oxidant and the respective Na salt produced in the oxidation reaction. For example, acetonitrile (AN) is a suitable solvent for  $I_2$  as an oxidant because it dissolves both  $I_2$  and NaI satisfactorily. By contrast, AN cannot be used with  $Br_2$  as an oxidant since NaBr is practically insoluble in this solvent; the salt (NaBr) is incorporated within the desodiated thiochromite and it is almost impossible to remove.

TABLE 1

Standard electrode potentials ( $E_0$ ) of some redox couples

Couple	pH	Reference electrode	$E_0$ (V)
$O_2/H_2O$	7	nhe (aqueous solutions)	0.82
$O_2/H_3O^+$	0	nhe (aqueous solutions)	1.24
$H_2O_2/H_2O$	7	nhe (aqueous solutions)	1.35
$H_2O_2/H_3O^+$	0	nhe (aqueous solutions)	1.77
$I_2/I^-$	—	Li/Li <sup>+</sup> (CH <sub>3</sub> CN solutions)	3.30
$Br_2/Br^-$	—	Li/Li <sup>+</sup> (CH <sub>3</sub> CN solutions)	3.70

## Experimental

The stoichiometric thiocromites (non-doped and V-doped) were synthesized as described earlier [1, 2]. The host materials were in the form of fine-grained powders (BET surface area from 12 to 25 m<sup>2</sup> g<sup>-1</sup>). For the chemical desodiation (oxidation) the powdered samples were suspended in the oxidant solution. After 5 - 10 min of stirring the oxidized product was filtered, washed, and dried under vacuum. During the desodiation the dark-brown color of the V-doped thiocromite and the dark-orange color of the non-doped thiocromite both turned black, indicating an increase in the covalency of the bond of the disulfide layers.

Chemical analysis of the products was carried out by AAS for Na and V, and volumetrically for Cr and S. The crystal structures were studied by X-ray diffraction of the powdered samples.

## Results and discussion

### (i) Non-doped thiocromite

The desodiation of NaCrS<sub>2</sub> via oxidation with oxygen was first studied by Schöllhorn *et al.* [3], who found that in neutral aqueous solutions the final product is the hydrated phase Na<sub>0.4</sub>(H<sub>2</sub>O)<sub>y</sub>CrS<sub>2</sub>, with the same rhombohedral structure as the pristine phase, but strongly expanded along the *c* axis. As a result of water intercalation the distance between the layers increases from 6.49 to 11.47 Å. In strong acid solutions (1 N H<sub>2</sub>SO<sub>4</sub>) saturated with oxygen the product is H<sub>0.3</sub>CrS<sub>2</sub> [3]. It may be supposed that by virtue of the cation exchange properties of the hydrated phase the Na<sup>+</sup> ions are totally substituted by the protons in the solution. The structure of this phase is trigonal (1T) with an interlayer distance of 6.0 Å. This polymorphic transition from a rhombohedral to a trigonal setting (not observed in the Na<sup>+</sup>-containing phase) can be explained by the higher electric field of the proton overcoming the repulsion forces between the sulfide layers and allowing the width between the layers to decrease.

A deeper desodiation of  $\text{NaCrS}_2$  was achieved in aqueous solutions using  $\text{H}_2\text{O}_2$ , which is a stronger oxidant [5]. In order to avoid the oxidation of Cr to its sixth valence state the pH of the solution during the desodiation was maintained above 7. The final product in this case was  $\text{Na}_{0.2}(\text{H}_2\text{O})_y\text{CrS}_2$ . Its lattice parameters could not be assessed because of the low crystallinity, but it is reasonable to suppose that its interlayer distance has been increased by the intercalated water molecules. This assumption is in accord with the improved coulombic efficiency of cathodes prepared from the hydrated phase as compared with those prepared from electrochemically desodiated thiochromite [5].

The chemical desodiation of  $\text{NaCrS}_2$  by  $\text{I}_2$  in AN solutions is also incomplete. The final product is  $\text{Na}_{0.4}\text{CrS}_2$ , with exactly the same crystal lattice parameters as the stoichiometric phase. It should be remembered that the electrochemical desodiation of  $\text{NaCrS}_2$  to  $\text{Na}_{0.2}\text{CrS}_2$  in a nonaqueous solution (1 M  $\text{LiClO}_4$  in PC + DME) [6] leads only to an insignificant expansion along the  $c$  axis and no change along the  $a$  axis.

It is noteworthy that the attempts of Murphy *et al.* [4] to lithiate  $\text{LiCrS}_2$  by chemical desodiation with  $\text{I}_2$  only resulted in the formation of  $\text{Li}_{0.7}\text{CrS}_2$ , and the same phase was obtained by Whittingham [11] on electrochemical oxidation up to 3.5 V, at very low c.d., in a nonaqueous electrolyte solution. This difference in the behavior of  $\text{NaCrS}_2$  and  $\text{LiCrS}_2$  in respect of oxidation at similar potentials could be explained by their different crystal structures (R3M and 1T respectively).

#### (ii) Vanadium-doped thiochromite

Preliminary experiments revealed that in aqueous solutions containing oxygen the vanadium-doped thiochromite undergoes a destructive hydrolysis, even at pH close to 7, whereby part of the vanadium is evolved as a water soluble complex. This finding precluded further experiments with the V-doped compound in aqueous solutions.

It was found that  $\text{NaCr}_{0.85}\text{V}_{0.15}\text{S}_2$  can be readily desodiated by oxidation with  $\text{I}_2$  in AN solutions. The process takes some 5 - 15 min under continuous stirring, and the residual Na varies from 0.06 to 0.10 eq/mol. This residual amount could not be extracted, even after very long treatment with a large  $\text{I}_2$  excess. As reported by Murphy *et al.* [4] both  $\text{LiCr}_{0.75}\text{V}_{0.25}\text{S}_2$  and  $\text{Li}_{0.5}\text{V}_{0.5}\text{S}_2$  are completely delithiated by  $\text{I}_2$  in AN. It appears that the depth of oxidation depends on the content of  $\text{V}^{3+}$  in the phase. This can be explained by the fact that, in contrast to  $\text{Cr}^{3+}$ ,  $\text{V}^{3+}$  can be more readily oxidized to  $\text{V}^{4+}$  and even to  $\text{V}^{5+}$ . Thus  $\text{VS}_2$  and  $\text{V}_2\text{S}_5$  exist, while the Cr analogues of these compounds are unknown.

The X-ray diffraction data of the  $\text{Na}_{0.1}\text{Cr}_{0.85}\text{V}_{0.15}\text{S}_2$  phase, obtained by chemical desodiation of the stoichiometric compound by  $\text{I}_2$ , are presented in Table 2. As seen in this Table, they are similar to those of the  $\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$  phase, which was identified by Abraham *et al.* [8] as 1T structure. It is seen that contrary to the non-doped thiochromite, which upon desodiation preserves its R3M crystal structure, the vanadium-doped thiochromite

TABLE 2

X-ray diffraction data

$\text{Na}_{0.1}\text{Cr}_{0.85}\text{V}_{0.15}\text{S}_2$ (this paper)		$\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$ (ref. 8)		$\text{NaCr}_{0.85}\text{V}_{0.15}\text{S}_2$ (ref. 2)	
$d$ (Å)	$I/I_0$	$d$ (Å)	$I/I_0$	$d$ (Å)	$I/I_0$
5.63	100	5.71	40	6.44	30
2.81	12	2.78	5	2.57	100
2.48	69	2.49	100	2.05	15
1.97	41	2.01	65	1.90	31
1.59	21	1.61	30	1.76	40
1.56	10	1.57	25	1.64	9
1.54	14	1.55	20	1.53	11
				1.46	16

undergoes a polymorphic transition. More exactly, this is a polytypic transition, since the two polytypes are identical in the two directions lying in the plane of the layers and differ only in the direction perpendicular to the layers. The transition from the rhombohedral to the trigonal structure during the desodiation of the vanadium-doped thiochromite is accompanied by a considerable contraction along the  $c$  axis and a change in the stacking sequence. The X-ray data of the stoichiometric vanadium-doped phase are presented for comparison in the same Table.

The X-ray data of partially desodiated samples revealed that in the range  $0.6 > x > 0.1$ ,  $\text{Na}_x\text{Cr}_{0.85}\text{V}_{0.15}\text{S}_2$  contains both the R3M and the 1T phase, implying that the desodiation proceeds via a first order transition (coexistence of two phases). This is illustrated in Fig. 1, showing the change in the intensity of the 003 peak of the stoichiometric R3M structure and the

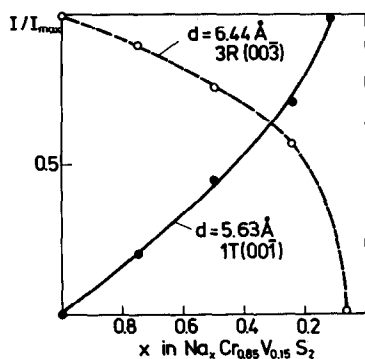


Fig. 1. Dependence of the relative intensity,  $I/I_0$ , of the peaks corresponding to the interlayer distances,  $d$ , in the 3R and 1T structures on the sodium content in the thiochromite phase.

00 $\bar{1}$  peak of the 1T structure pertaining to the Na-poor phase. The observed phase transition, accompanied by a decrease in the interlayer distance, can be assigned to the lower ionicity of the bond in the vanadium-doped disulfide layers. Using the structural approach of Hibma [9] it was estimated that the ionicities of the desodiated non-doped and V-doped thiochromites are 0.27 and 0.12, respectively. It might be supposed, then, that the weaker coulombic repulsion forces between the layers of the V-doped thiochromite can be overcome by the weak covalent bonds between the S atoms from neighboring layers [8] which, upon desodiation, can approach each other more closely.

The dependence of the interlayer distance of the non-doped and V-doped thiochromites on the ionic radius of the intercalated ions is shown in Fig. 2. The data for KCrS<sub>2</sub> are from the paper by Rüdorff *et al.* [10]. Similar linear relationships have been reported by Le Blanc *et al.* [11] in the case of ATiS<sub>2</sub> and ATaS<sub>2</sub>. Figure 2 shows also that the radius of the alkali ion has a small but positive effect on the *a* parameter. The value of *d* = 5.63 Å for the deeply-desodiated V-doped thiochromite (<0.1 eq Na/mol) is close to that of the other first row transition metal disulfides, which are also 1T phases (TiS<sub>2</sub>, 5.69 Å; VS<sub>2</sub>, 5.755 Å; Cr<sub>0.5</sub>V<sub>0.5</sub>S<sub>2</sub>, 5.71 Å, H<sub>0.4</sub>CrS<sub>2</sub>, 5.60 Å).

Samples of well desodiated V-doped thiochromite (Na<sub>0.1</sub>Cr<sub>0.85</sub>V<sub>0.15</sub>S<sub>2</sub>) were lithiated electrochemically at different levels by discharging cathodes *versus* a Li anode at a 20 h rate. After washing and drying, the Li<sub>*y*</sub>Na<sub>0.1</sub>Cr<sub>0.85</sub>V<sub>0.15</sub>S<sub>2</sub> samples were studied by X-ray diffraction. It was found that the Li-poor samples (*y* < 0.2) only exhibit the peaks of the 1T CdI<sub>2</sub>-type structure with *c* = 5.63 Å and *a* = 3.18 Å (see Table 2). The Li-rich samples (*y* > 0.8) only revealed the peaks of the 1T NiAs ordered-type structure with *c* = 5.90 Å and *a* = 3.46 Å, similar to those of the thermally synthesized LiCrS<sub>2</sub>, reported by Van Laar *et al.* [7]. In the intermediate region (0.2 < *y* < 0.8) peaks of both phases are observed. As the level of lithiation in the two-phase region grows the intensity of the 00 $\bar{1}$  peak of the Li-rich phase increases, while that of the Li-poor phase diminishes. The positions of both peaks remain practically constant. This situation is typical for a first order

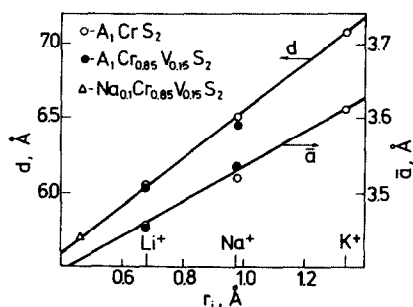


Fig. 2. Dependence of the interlayer distance, *d*, and the lattice parameter, *a*, on the radius of the alkali ion, *r<sub>i</sub>*.

phase transition. The present results correlate well with our previous data [2] for the shape of the OC potential-composition plot (Fig. 2 in ref. 2) of the  $\text{Li}/\text{Li}_y\text{Na}_{0.1}\text{Cr}_{0.85}\text{V}_{0.15}\text{S}_2$  cell, where the horizontal plateau in the  $0.1 < y < 0.6$  region implies the coexistence of two phases.

### (iii) Electrochemical performance

The performance of chemically-desodiated, non-doped TC in secondary Li cells has already been reported [1, 5]. The performance of the chemically-desodiated, V-doped TC was studied in a flooded cell with 1 M  $\text{LiClO}_4$  in PC + DME (1:1). The cathodes were prepared by pressing a blend of the active material with 30% Teflonized acetylene black on a Ni exmet. Typically, they were 0.4 mm thick, with a loading of  $0.8 \text{ g cm}^{-2}$  and an apparent density of  $1.8 - 2.0 \text{ g cm}^{-3}$ . They were cycled under galvanostatic conditions at a 2.5 h rate ( $i_d = i_c = 2 \text{ mA cm}^{-2}$ ) between 1.8 and 3.4 V. The good cycling performance is illustrated in Table 3, showing that some 500 useful cycles can be achieved before the cathode capacity drops to 50% of its initial value.

TABLE 3  
Electrochemical performance of cathodes

	Cycles					
	1	100	200	300	400	500
$Q$ ( $\text{A h g}^{-1}$ )	0.18	0.16	0.15	0.13	0.12	0.11
ED ( $\text{W h cm}^{-3}$ )	0.63	0.51	0.49	0.43	0.40	0.35
$U_d$ (V)	2.5	2.5	2.4	2.4	2.4	2.4

Note: The specific capacity,  $Q$ , is estimated *vs.* the weight of the active material, while the energy density, ED, is estimated *vs.* the volume of the pressed cathode.  $U_d$  is the mid-discharge voltage *vs.*  $\text{Li}/\text{Li}^+$  reference.

A lithium secondary cell with a cathode of vanadium-doped thiochromite is protected by Bulgarian Pat. No 39778/30.10.1984, and is patented in U.S.A., U.K., Canada, Japan, West Germany, and France.

### References

- 1 R. Moshtev, V. Manev, A. Nassalevska and G. Pistoia, *J. Electrochem. Soc.*, 128 (1981) 1399.
- 2 R. Moshtev, V. Manev, B. Pouresheva and G. Pistoia, *Solid State Ionics*, 20 (1986) 259.
- 3 R. Schöllhorn, R. Arndt and A. Kubny, *J. Solid State Chem.*, 29 (1979) 259.
- 4 D. Murphy, F. Di Salvo and J. Carides, *J. Solid State Chem.*, 29 (1979) 339.
- 5 V. Manev, R. Moshtev, A. Nassalevska and G. Pistoia, *Solid State Ionics*, 13 (1984) 181.

- 6 V. Manev, R. Moshtev, A. Nassalevska and G. Pistoia, *Ext. Abstr., 32nd ISE Meeting, Dubrovnik, 1981*, p. 885.
- 7 M. S. Whittingham, *Prog. Solid State Chem.*, 12 (1978) 41.
- 8 K. Abraham, P. Harris and D. Natwig, *J. Electrochem. Soc.*, 130 (1983) 2309.
- 9 T. Hibma, in *Intercalation Chemistry*, Academic Press, New York, 1982, p. 289.
- 10 W. Rüdorff and K. Stegemann, *Z. Anorg. Allgem. Chem.*, 251 (1943) 376.
- 11 A. le Blanc, M. Danot, L. Trichet and J. Rouxel, *Mater Res. Bull.*, 9 (1974) 191.