

## PROPERTIES OF AMORPHOUS NICKEL HEXATHIODIPHOSPHATE, Ni<sub>2</sub>P<sub>2</sub>S<sub>6</sub>

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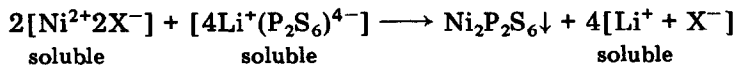
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### Summary

Transition metal thiophosphates can be prepared through "soft chemistry" reactions leading to amorphous phases. From nickel nitrate and lithium thiophosphate in aqueous solutions, a-NiPS<sub>3</sub> can be obtained. Because of its highly divided structure, this amorphous material readily reacts with atmospheric moisture, and it must be handled in neutral atmosphere. Open circuit voltage curves of the Li/a- and c-NiPS<sub>3</sub> have been studied. The amorphous phase shows a higher voltage and a lower polarization. A continuous decrease of the potential in the case of a-NiPS<sub>3</sub> is consistent with the absence of microdomains of reduced and unreduced nickel, as was shown to be the case for c-NiPS<sub>3</sub>.

### 1. Introduction

It has been shown recently [1, 2] that amorphous NiPS<sub>3</sub> (a-NiPS<sub>3</sub>) as opposed to crystallized NiPS<sub>3</sub> (c-NiPS<sub>3</sub>), and, more generally, most MPS<sub>3</sub>s, can be prepared either as gels (M = Ni and Fe) or amorphous precipitates (M = Mn, Cd) in aqueous solvent. Using, as precursors, a nickel salt, NiX<sub>2</sub>, and Li<sub>4</sub>P<sub>2</sub>S<sub>6</sub>, both ionic and soluble species, one obtains the following reaction:



Local structural characterization of the gel and the amorphous phase remains to be done, but the use of a-NiPS<sub>3</sub> as a positive electrode in lithium batteries was of interest. In particular, the reason for the difference in potential and polarization between a-NiPS<sub>3</sub> and c-NiPS<sub>3</sub> required study. Also, the possible improved cyclability of NiPS<sub>3</sub> in its new form could lead to renewed interest in this much studied cathodic material.

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## 2. Experimental

The procedure used was that described in refs. 1 and 2. Initially, aqueous solutions of nickel nitrate and lithium thiophosphate were mixed at room temperature under ultrasonic stirring. Half the  $\text{NiX}_2$  solution was added to the  $\text{Li}_2\text{P}_2\text{S}_6$  solution, and then, after complete reaction, the remainder was slowly added. The nickel salt was used in overstoichiometric proportions ( $n(\text{NiX}_2) = 1.2 - 1.5n(\text{Li}_2\text{PS}_3)$ ) in order to achieve complete reaction of all the thiophosphate anions. This was done because washing was carried out with acetone (see below), in which lithium thiophosphate is not very soluble. With concentrations of  $0.4 \text{ mole l}^{-1}$ , thick gels are obtained (below  $0.3 \text{ mole l}^{-1}$ , the reaction leads to a colloidal solution). A centrifugation of the gel is carried out to separate the solvent from the compound, which is then dried at  $50^\circ\text{C}$  under dynamic vacuum to remove the residual water, and give a powdery structure to the phase to aid filtration. At least three successive washings and filtrations with acetone were performed to remove the remnant salts ( $\text{Ni}(\text{NO}_3)_2$  and  $\text{LiNO}_3$ ); water was not used because of its tendency to dissolve the highly dispersed a- $\text{NiPS}_3$ . A final drying at  $150^\circ\text{C}$  under  $10^{-3} \text{ atm}$  for at least 10 h followed, allowing pure a- $\text{NiPS}_3$  to be obtained.

## 3. Elemental analysis results

Although great care was taken to wash thoroughly the amorphous product obtained from the above synthesis procedure, the analytical data showed a departure from the 100% total one would expect for a pure compound (see Table 1). However, the weight percentages readjusted to 100% yielded a satisfactory atomic ratio, and led to consideration of the impurities present in the compound. The correct (even slightly low) nickel content immediately excluded the presence of nickel nitrate, which was a possible element impurity because of the excess salt used in the reaction. Nor was it possible to contemplate the presence of lithium thiophosphate, since practically no lithium could be detected by flame spectroscopy, a sensitive method for alkali metals. The remaining possibility was the presence of water, despite the  $150^\circ\text{C}$  temperature and vacuum used in the drying process. This possibility, however, was difficult to accept. Assuming that the phase recovered after the final drying was pure a- $\text{NiPS}_3$ , we removed, under inert gas, a fraction of a just-prepared sample, and monitored the weight change in air. It appeared (see Fig. 1) that a- $\text{NiPS}_3$  takes up water (and/or oxygen) very rapidly (a 5% weight increase is recorded after 6 h), the final weight increase after one day being in the 12% range; that is, around one  $\text{H}_2\text{O}$  mole per a- $\text{NiPS}_3$ , if it is water which is fixed by the amorphous material.

Since no specific precautions were taken in sample handling and analysis, this provides a very good explanation of the discrepancy between experimental and theoretical data. Further analyses will have to be carried

TABLE 1

Element analysis of amorphous nickel thiophosphate prepared from  $\text{Li}_2\text{PS}_3$  and  $\text{Ni}(\text{NO}_3)_2$ 

		Ni (%)	P (%)	S (%)	Total (%)
Theoretical	(wt.%)	31.59	16.66	51.75	100
Crystallized sample	(wt.%)	31.29	15.59	52.79	99.7
(high temperature preparation)	(corrected wt.%)	31.39	15.64	52.96	100
	(mole ratio)	0.99	0.94	3.07	
Precursor	(wt.%)	28.43	14.88	48.08	91.4
nickel nitrate	(corrected wt.%)	31.1	16.28	52.61	100
mechanical stirring (1)	(mole ratio)	0.98	0.98	3.05	
Precursor	(wt.%)	28.95	15.03	48.75	92.7
nickel nitrate	(corrected wt.%)	31.22	16.21	52.57	100
ultra-sound stirring (2)	(mole ratio)	0.99	0.97	3.05	

Sample (1) was obtained using mechanical stirring; sample (2) was prepared using ultra-sound. The first line gives raw data, the second gives proportions calculated to 100%, followed by the corresponding molar proportions.

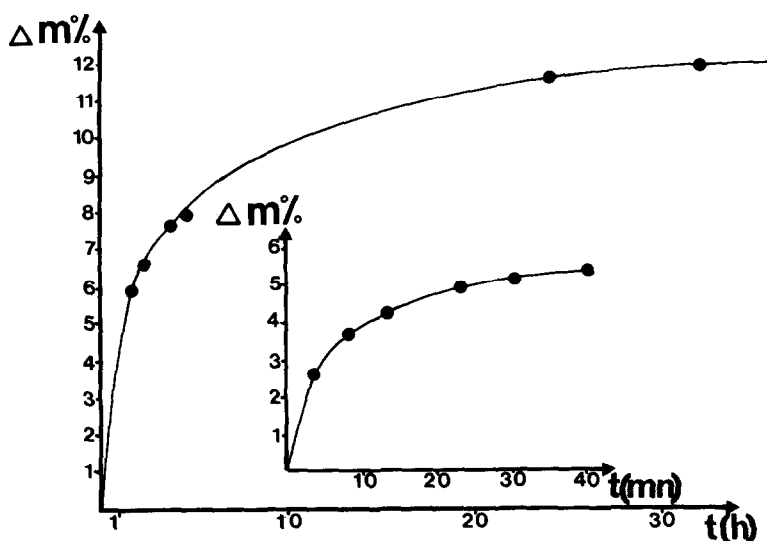


Fig. 1. Recording of the weight increase of a sample of a-NiPS<sub>3</sub> prepared by drying under vacuum at 150 °C (15 h), and left open to atmosphere. The reabsorption of water is very important and reaches around 12% after 24 h.

out under inert conditions to confirm the findings. Indeed, for all subsequent measurements and experiments, a-NiPS<sub>3</sub> was used in the presence of oxygen-free, dry gas.

#### 4. OCV study of lithium intercalation in a-NiPS<sub>3</sub> and c-NiPS<sub>3</sub>

This study was undertaken in order to compare the behaviors of the two allotropic phases and to determine the effect of disorder. These must be large differences because, on the one hand (c-NiPS<sub>3</sub>), well shaped and ordered two-dimensional pathways exist within the crystallites, while on the other hand (a-NiPS<sub>3</sub>), the presence of microcrystals and Van der Waals gaps, in the normally accepted sense of these words, may be questioned.

The electrochemical cells used were of the type described elsewhere [3], the electrolyte was 2 M LiClO<sub>4</sub> in dioxolane, the NiPS<sub>3</sub> materials were mixed with 15 wt.% carbon black, and the anode was lithium metal. The OCV curves recorded were obtained via the AUTEBAT system developed in our laboratory. Before starting the experiments, the stability of the amorphous nickel thiophosphate was determined by soaking it in the electrolyte at 70 °C for 24 h. Neither polymerization nor apparent destruction of the electrolyte was observed, neither was there any apparent solubility of a-NiPS<sub>3</sub>.

The OCV curves were obtained with a constant current of 30 μA cm<sup>-2</sup> delivered for 1 h, followed by a relaxation, the duration of which was determined from the slope of the potential variation *versus* time value (lower limit fixed at 10 mV h<sup>-1</sup>). The amount of the phase used was in the region of 30 mg.

The curves obtained for a- and c-NiPS<sub>3</sub> are compared in Fig. 2. The potential of the amorphous material remains higher than that of the crystallized material and decreases steadily, whereas, for c-NiPS<sub>3</sub>, a quasi-constant plateau at around 2.0 V is rapidly reached. The reason for the absence of a plateau for a-NiPS<sub>3</sub> may be explained, in part, by the structural disorder that makes the presence of reduced and unreduced microdomains in c-NiPS<sub>3</sub> (that gives two-phase or pseudo single phase [4] characteristics to the discharge

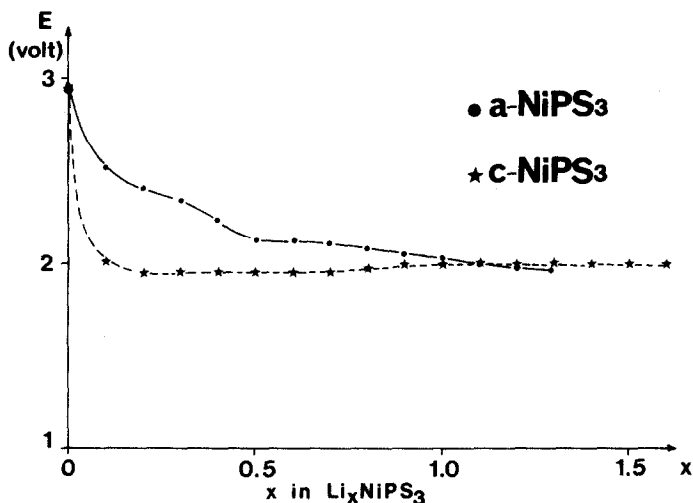


Fig. 2. Open circuit voltage (OCV) discharge curves of the Li/NiPS<sub>3</sub> system, the nickel thiophosphate being in its crystallized and amorphous forms.

curve of the Li/c-NiPS<sub>3</sub> system) unlikely. It will be seen that, after numerous cyclings, c-NiPS<sub>3</sub> becomes amorphous and tends to single phase behaviour upon discharge [5]. This is in line with theoretical considerations [6] that support the presence of microdomains spreading perpendicularly to the c-NiPS<sub>3</sub> layers. The amorphous state prevents such a possibility. Observations on Li<sub>x</sub>a-NiPS<sub>3</sub> phases similar to those by which microdomains were first revealed by <sup>31</sup>P NMR studies, should show a continuous shift of the <sup>31</sup>P resonance line with regard to *x*, rather than the existence of two distinct peaks attributed to two different (actually reduced and unreduced) domains [7].

The difference between the two curves is illustrated in Fig. 3, where the derivatives  $dQ/dE$  are plotted. This last function is equivalent to a volt-amprometry diagram undertaken at equilibrium. It will be seen that a small break at  $x = 0.5$  for the amorphous material is recorded. This was unexpected if, for c-NiPS<sub>3</sub>, one accepts the meaning of such a break, related to the successive filling of the two kinds of octahedral sites (*2d* and *4h*) in the crystalline state monoclinic cell. In effect, for a quasi-amorphous phase, such an explanation is invalid. Actually, the break, contrary to earlier reports on the Li/c-NiPS<sub>3</sub> discharge curve is not even recorded for c-NiPS<sub>3</sub>, and all these

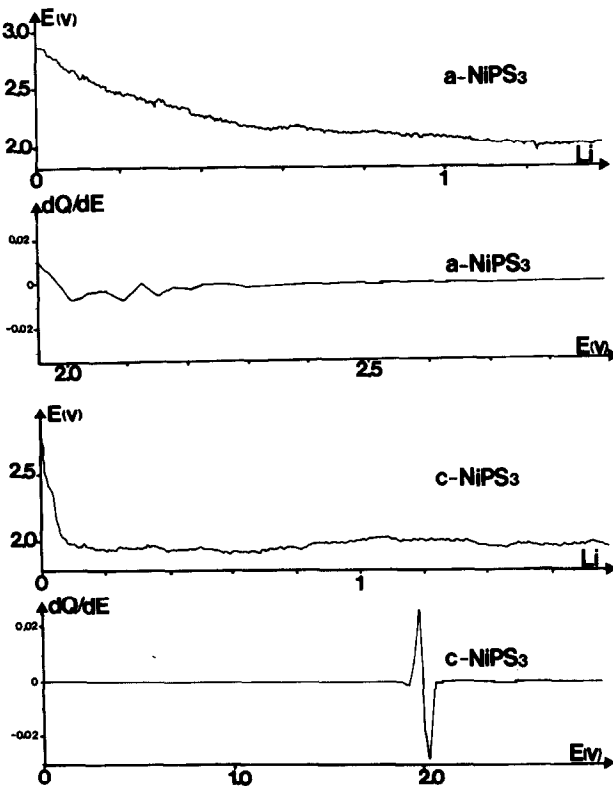


Fig. 3. OCV for a- and c-NiPS<sub>3</sub> and their derivative curves  $dQ/dE$  revealing the two different plateaux.

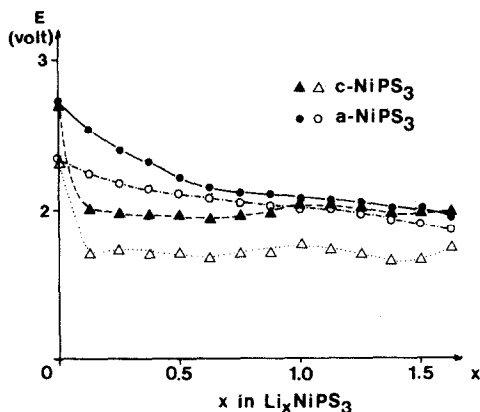


Fig. 4. Polarization behaviour of a- and c-NiPS<sub>3</sub> upon lithium intercalation (O.C.V. curves). Upper lines correspond to the potential at the end of relaxation, lower lines to the potential at the end of discharge.

data mean that previous experiments and explanations must be reconsidered, along with the reproducibility of the potential variation *versus* lithium content.

Finally, the polarization of the two cathodes, linked to the lithium diffusion and corresponding to the difference between potentials measured after the discharge and the end of the relaxation, may be studied. The differences between the compounds are obvious (see Fig. 4), since c-NiPS<sub>3</sub> presents a constant polarization of 250 mV over the whole concentration range, whereas a-NiPS<sub>3</sub>, with the same difference between potentials at the start of the discharge, sees its polarization decrease constantly to reach 50 mV for Li<sub>0.6</sub>NiPS<sub>3</sub>. Clearly, lithium diffusion is achieved more quickly in the disordered phase, showing an easy and fast breaking-in of the positive material. Extensive cycling experiments must be undertaken to assess the true characteristics of this NiPS<sub>3</sub> allotrope.

### Acknowledgements

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### References

- 1 E. Prouzet, G. Ouvrard, P. Seguineau and R. Brec, *Solid State Ionics*, 31 (1988) 79.
- 2 E. Prouzet, *Thesis*, Nantes, France, 1988.
- 3 A. Dugast, *Thesis*, Nantes, France, 1980.
- 4 G. Ouvrard, *Thesis*, Nantes, France, 1980.
- 5 R. Brec, G. Ouvrard, A. Louisy, A. Le Méhauté and J. Rouxel, *Solid State Ionics*, 6 (1982) 185.
- 6 E. Sandré, G. Ouvrard and R. Brec, *Mater. Res. Bull.* to be published, 1988.
- 7 C. Berthier, Y. Chabre, P. Segransan and G. Ouvrard, in P. Vashista, J. N. Mundy and G. K. Shenoy (eds.), *Fast Ion Transport in Solids*, Elsevier North-Holland, Amsterdam, 1979, p. 221.