

Nickel phosphorus trisulfide: an electroactive material for medium-temperature lithium batteries

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Abstract

In the present work the electrochemical behaviour of the layered NiPS₃ compound with reference to lithium has been studied at 200 °C in a cell which included an Li₃Sn counter electrode and a molten LiSCN–KSCN eutectic mixture as the electrolyte. It has been found that electroreduction of nickel phosphorus trisulfide (NiPS₃) proceeds in several stages at potentials from 2.7 to 1.8 V up to nearly a Li/Ni ratio of 7.5, then the products formed catalyse the electrolyte decomposition. It has been shown that the reversible behaviour of the NiPS₃ electrode of a lithium battery is possible in carrying out charge/discharge cycles within the $0 \leq \text{Li/Ni} \leq 3$ range, which considerably exceeds the region of the existence of the intercalation phase Li_xNiPS₃ ($0 \leq x \leq 1.5$).

Keywords: Lithium batteries; Nickel phosphorus trisulfide; Cathodes

1. Introduction

Nickel phosphorus trisulfide is closely similar in structure to TiS₂ and other layered transition metal dichalcogenides, widely studied as active cathodic substances in lithium batteries [1,2]. Its lattice involves a face-centred cubic packing of chalcogen atoms, where octahedral holes are layer-by-layer either unfilled completely, forming the van der Waals gap, or filled completely: two-thirds are filled with metal atoms and one-third with pairs of phosphorus atoms. Thus, 1.5 octahedral centres in the van der Waals gap, energetically favourable and approachable for reversible filling up with lithium, falls at the NiPS₃ formula unit. The intercalation process shows high values of free energy [1–4]. This is why NiPS₃ is considered as a promising active cathodic material in lithium batteries. However, up to now the basic attention has been focused on the study of the Li/NiPS₃ system with organic electrolytes, where the discharge-current density does not exceed 2 mA/cm².

As it is known, higher current densities can be realized in molten electrolyte systems, and a considerable in-

crease in the rate of electrochemical reactions for solid electrode active materials is to be expected even in the temperature range from 150 to 300 °C. In addition, this temperature range is worth considering with reference to transition metal phosphorus trisulfide cathodes because it is necessary to take into account that the thermal stability of the formed intercalation phases with lithium should be kept. For instance, according to Ref. [5], a NiPS₃ cathode in molten LiCl–KCl electrolyte at 400 °C showed unsatisfactory characteristics.

Analysis of the data reported in Refs. [6–9] has shown that the molten eutectic mixture of lithium and potassium thiocyanates (55.5 mol% LiSCN, $t_m = 146$ °C) should be a rather suitable electrolyte for studying the peculiarities of the electroreduction of transition metal phosphorus trisulfide cathodes in the medium-temperature range. The melt possesses the required region of electrochemical stability (from approximately 0.2 to 4.4 V relative to the lithium reference electrode) and is compatible with the anode of lithium-containing alloys. This work is devoted to the study of the electrochemical interaction between nickel phosphorus trisulfide and lithium in the molten thiocyanate electrolyte.

2. Experimental

2.1. Experimental cell

The electrochemical cell was a three-electrode system placed in a quartz glass. Its tight design provided anaerobic conditions. The cathodic material was tested at the bulk-type electrodes frequently used in such cases [5,7,10]. The cathode was prepared as a porous titanium crucible with a working surface area of 0.5 cm². The powder of the substance studied was put into the crucible, which was then screwed on a titanium current collector. It has been previously found that titanium is an optimum construction material for the electrolyte selected [7]. Alloyed Li₃Sn was used as the auxiliary electrode. The reference electrode was a silver one in a melt containing silver ions (0.1 M AgCl solution in KSCN); this electrode was placed in a quartz tube terminated in an asbestos diaphragm.

2.2. Reactants

Potassium thiocyanate (chemically pure) was recrystallized and dehydrated in air at 110 to 130 °C and then under vacuum at 150 °C for about 24 h with the use of a liquid nitrogen trap. Anhydrous lithium thiocyanate was synthesized by the technique described in Ref. [11]. The electrolyte was prepared by melting the eutectic mixture of components in a dry argon atmosphere and filtering the melt through a porous glass filter. After cooling it was prepacked into sealed ampoules. The test cathodic material was powdered NiPS₃ with 10 wt.% carbon black added to increase the electron conductivity. The weight of test samples was 0.01–0.02 g. (The NiPS₃ preparation method will be described in a next paper published in this journal.)

2.3. Techniques

The electrochemical cell was mounted in a dry box, then the cell was placed into a furnace. Before measuring, the electrodes were kept in vacuum for 15 min over the electrolyte melt at 160 to 180 °C and then immersed into the electrolyte without changing the cell pressure. Measurements were carried out at 200 °C in a dry argon atmosphere using a PI-50-1 potentiostat with automatically compensated *IR* drop in the reference electrode circuit. The values of the cathode potential obtained experimentally with respect to the AgCl reference electrode were converted to potentials relative to the lithium reference electrode. Discharge and charge curves obtained under galvanostatic conditions were plotted against *x*, the number of lithium gram-atom involved in the interaction with the gram-molecule of NiPS₃.

The potential of the NiPS₃ cathode under initial conditions (in the absence of current) at 200 °C ranges from 2.7 to 2.8 V for various samples of the material. This value is lower than that fixed at room temperature for the systems with an organic electrolyte (3.0–3.5 V) [3,12].

3. Results and discussion

The curve of the electrode currentless potential (or open-circuit voltage) against *x* plays an important role in the analysis of electroreduction processes [3,12]. Unfortunately, we could not study such a curve in detail because of the long duration of the experiment. Instead, a galvanostatic discharge curve has been obtained at a current density of 2 mA/cm², a relatively low discharge current for molten salts, whereas currentless potentials have been obtained for *x* values (in Li_{*x*}NiPS₃) equal to 0, 0.5, 0.75, 1.1 and 1.5. The data are presented in Fig. 1. The experimental points for potential in absence of the current appeared to be close to the kinetic curve. Thus, the process of NiPS₃ electroreduction at the above current density can be considered, to a known extent of assumption, as a quasi-equilibrium one.

Comparing our findings with those of other authors [3,7] it is interesting to note the following (see Fig. 1). On the one hand, an evident difference in the behaviour of NiPS₃ at room temperature (with an organic electrolyte) and at 200 °C (with a molten salt) is observed. In the latter case, the well-pronounced peculiarity of the compound consisting in the step-by-step filling up of two types of octahedral sites in the van der Waals gap (regions 0 ≤ *x* ≤ 0.5 and 0.5 ≤ *x* ≤ 1.5) with lithium ions disappears. It is seen from a monotonous decrease in a quasi-equilibrium potential to *x* ≈ 1.5–2.0. This may be due to more intensive heat motion of atoms in the host-material structure, which eliminates the effect of different coordinations of holes 2(d) and 4(h) with the second neighbours. At 200 °C the *E* = *f*(*x*) curve, as a whole, lies in the region of lower potentials than that for those at room temperature. However, on the other hand, the electroreduction of NiPS₃ shows higher potential values in comparison with that of titanium and iron disulfides studied under similar conditions. So, for TiS₂ the curve is 0.3–0.4 V lower and for FeS₂ 0.5–0.9 V lower than that for NiPS₃.

In the 2 ≤ *x* ≤ 5 range, a plateau with an average potential value of 1.95 V appears for NiPS₃. Then, the curve decreases smoothly and, at *x* ≈ 7, goes into another plateau, stabilized at 1.8 V and, which is remarkable, extending far beyond the limits corresponding to the maximum permissible quantity of lithium, e.g., by the reaction:



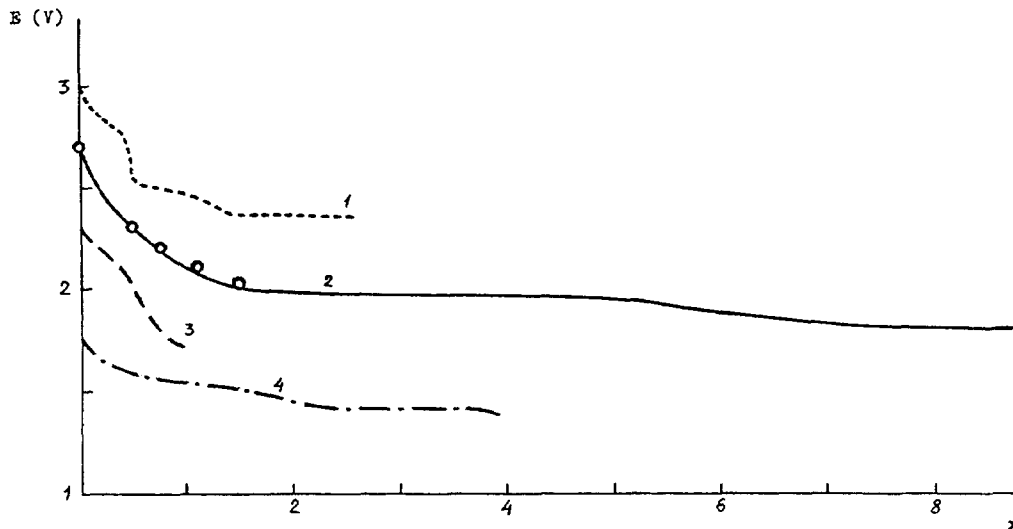
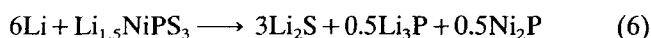
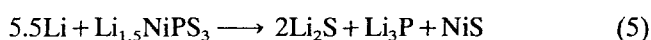
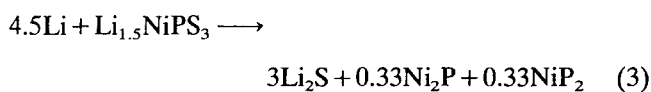
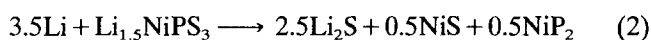


Fig. 1. Quasi-equilibrium potential of discharge (relative to the lithium reference electrode) for the $\text{Li}_3\text{Sn}/\text{melt Li, K|SCN|NiPS}_3$ system at $200\text{ }^\circ\text{C}$ in comparison with the open-circuit voltage curves for other systems: (1) $\text{Li}|1\text{ M solution of LiClO}_4\text{ in propylene carbonate|NiPS}_3$ at a room temperature [12]; (2) the present work: current density 2 mA/cm^2 , currentless potential values are marked with circles; (3) $\text{LiAl}/\text{melt Li, K|SCN|TiS}_2$ at $250\text{ }^\circ\text{C}$ [7], and (4) $\text{LiAl}/\text{melt Li, K|SCN|FeS}_2$ at $250\text{ }^\circ\text{C}$ [7].

The latter may be only due to a current-generating reaction associated with the electrolyte (thiocyanate ion) decomposition at the cathode which is catalyzed by the products of the NiPS_3 electroreduction. Such a phenomenon has been previously observed for FeS_2 discharge in the Li, K|SCN melt [7]. It is known from Refs. [7,13,14] that the reduction of FeS_2 in organic and molten halide electrolytes proceeds in two stages: at first, the ternary compound Li_2FeS_2 is formed in the $0 \leq x \leq 2$ range, then, in the $2 \leq x \leq 4$ range, it is reduced to free iron and lithium sulfide. However, in the presence of the Li, K|SCN melt the interaction at the second stage should become of a more complicated character, because, according to Ref. [15], iron subgroup metals are chemically incompatible with a thiocyanate melt and react with this melt to give sulfides. In other words, decomposition of thiocyanate ion begins in the case when electroreduction of the cathode material leads to the appearance of free metal in this material. These facts as an addition to the analysis of the NiPS_3 behaviour allow one to assume that after the formation of $\text{Li}_{1.5}\text{NiPS}_3$ intercalation compound its further electroreduction, at least up to $x = 6-7$, should be associated with reactions making the formation of metallic nickel impossible, for example:



These reactions fall into the interval of the x value (up to $x = 7.5$) preceding the observed beginning of the electrolyte reaction. It is not clear yet, however, which processes take place in fact.

Values of the theoretical specific energy of the NiPS_3 cathode calculated for various depths-of-discharge on the basis of the quasi-equilibrium curve given in Fig. 1 amounted to 508 Wh/kg ($0 \leq x \leq 1.5$ at the average potential $E_{\text{ave}} = 2.35\text{ V}$), 1520 Wh/kg ($0 \leq x \leq 5.0$; potential plateau at $E_{\text{ave}} = 1.95\text{ V}$) and 2194 Wh/kg (for the $0 \leq x \leq 7.5$ range corresponding to nearly the complete treatment of the active material which does not touch the electrolyte yet). For comparison, the theoretical value of the specific energy of TiS_2 and FeS_2 cathodes in the systems with molten thiocyanate electrolyte appeared to be equal to 466 Wh/kg ($0 \leq x \leq 1$; $E_{\text{ave}} = 1.95\text{ V}$) and 724 Wh/kg ($0 \leq x \leq 2$; $E_{\text{ave}} = 1.62\text{ V}$), respectively [7].

Fig. 2 illustrates the effect of a load on the behaviour of the discharge curves of NiPS_3 in the $0 \leq x \leq 1.5$ range. At a load of 50 mA/cm^2 , the discharge potential varies from 2.6 to 1.65 V , i.e. polarization does not exceed 0.45 V . In comparison with batteries with an organic electrolyte [3], in the given case, not only a considerable current density (two orders of magnitude greater) can be realized, but also a higher discharge voltage.

Discharge and charge carried out repeatedly under galvanostatic conditions have shown that NiPS_3 is able to undergo a reversible interaction with lithium in the thiocyanate electrolyte at $200\text{ }^\circ\text{C}$. In the experiments performed, the depth of cycling and the load current for various samples of the material were varied.

Fig. 3 shows curves for 20 charge/discharge cycles carried out in the $0 \leq x \leq 1.5$ range at 25 mA/cm^2 . As it is seen, as cycling proceeds the cathode material

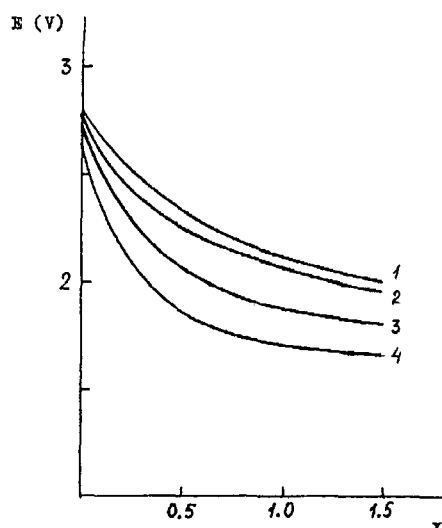


Fig. 2. The effect of current load on the discharge curves of NiPS₃ in the thiocyanate melt. Current density (mA/cm²): (1) 2; (2) 10; (3) 25 and (4) 50.

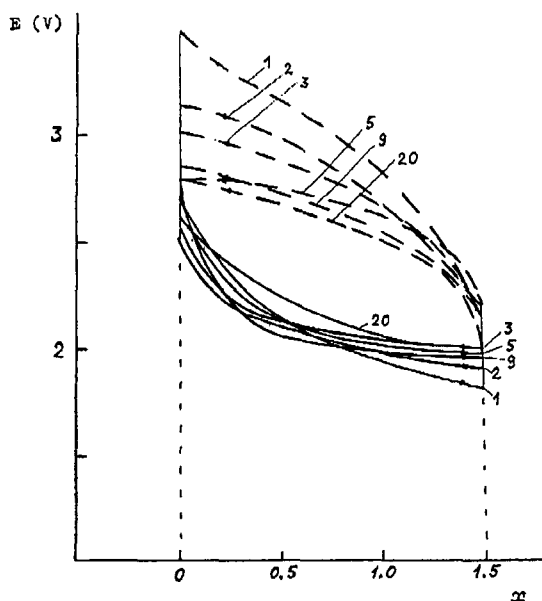


Fig. 3. Cycling curves for the NiPS₃ cathode in the $0 \leq x \leq 1.5$ range at a current density of 25 mA/cm². Figures denote the cycle numbers.

'formation' takes place, which manifests itself in a stabilization of the parameters after 4 to 5 cycles: charge proceeds up to a potential of 2.80 to 2.85 V, whereas discharge proceeds to 1.95–2.0 V.

In the next experiment, after the preliminary thrice repeated cycling of NiPS₃ in the $0 \leq x \leq 1.5$ range at a current density of 25 mA/cm², the depth of cycling has been increased up to $x=1.8$ (from the 4th to 7th cycles). The data given in Fig. 4 shows that, under these conditions, the cathode behaviour is also reversible. It is interesting to note that after the increase in the depth of cycling during the 4th cycle, the charge curve becomes closer to a straight line. The 5th cycle shows a steeper decrease in the discharge potential (2.77

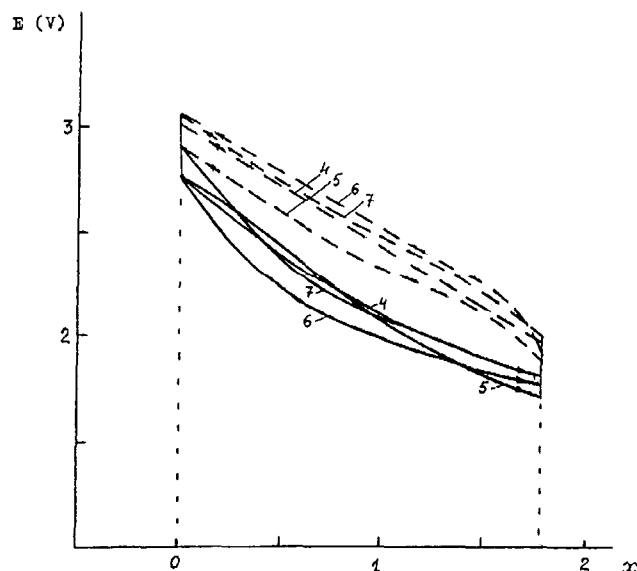


Fig. 4. Cycling curves for the NiPS₃ cathode in the $0 \leq x \leq 1.8$ range. Figures denote the cycle numbers. Current density: 25 mA/cm² for cycles 1 to 5 and 50 mA/cm² for cycles 6 and 7.

V → 1.71 V in comparison with 2.77 V → 1.8 V during the previous discharge) and the appearance of a concave section in the charge curve. Only in passing from cycle 6 to cycle 7 the trend towards restoration of the former shapes of the curves is observed. Some 'settling' of potential in the 6th discharge curve is due to the fact that the current density, starting from the 6th cycle, was increased up to 50 mA/cm².

Then, for the same sample of the material, a number of discharge/charge cycles (from cycles 8 to 13) has been carried out at a current density of 50 mA/cm², the cycling depth corresponding to $x=2.6-3.3$. It is seen in Fig. 5 that the behaviour of NiPS₃ in this case appeared to be a rather peculiar one. The discharge curves show mostly monotonous dependence on x with the potential varying from about 2.8 to 1.7 V. At the same time all the charge curves have a specific bend, where the concave section falls practically at the same value $x=1.5$.

Here, at least two regions ($x \leq 1.5$ and $x \geq 1.5$) with different mechanisms of the proceeding electrochemical reactions seem to exist. The first stage involves a reversible intercalation of lithium into the matrix of NiPS₃ without distortion of the structure of the latter. As to the second stage, the reactions of reduction and oxidation of the material proceed by no mechanism other than substitution to form products of different chemical compositions (probably, Eqs. (2) to (6)). It is unusual, however, that these further conversions in the multiphase region are also reversible. A possible explanation of such a fact is that the thiocyanate melt is a suitable medium for a fast exchange with sulfur atoms between the oxidized and reduced forms of the cathode material, for instance:

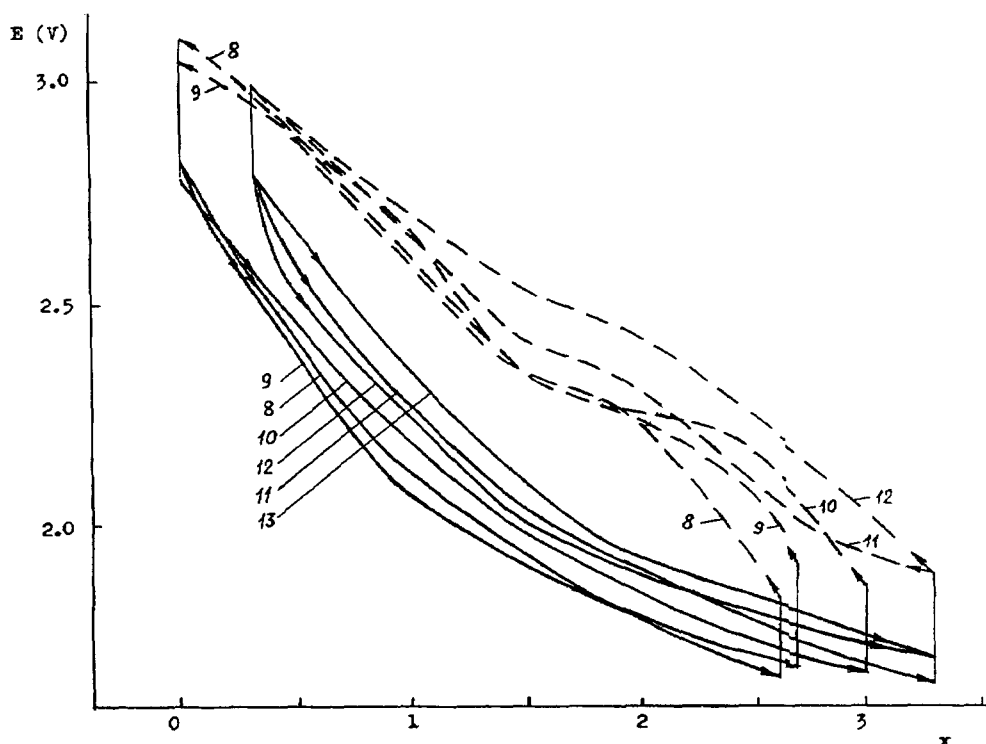
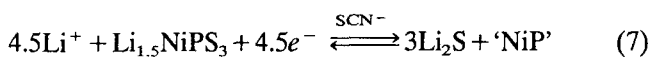


Fig. 5. Electrochemical behaviour of the NiPS₃ cathode on deep cycling. Current density = 50 mA/cm². Figures denote the cycle numbers.



In conclusion, our attention should be focused on the following fact. According to findings reported in Refs. [1,16-18], lithium intercalation into the layered structure of MPS₃ (M=Fe, Ni) is accompanied with an electron transfer to d-levels of M²⁺ cations, which causes the appearance of microdomains with reduced M^p atoms in the matrix. However, since, owing to the structure keeping intact, the domains remain surrounded with a coordination shell of sulfur atoms; this accounts for why catalytic reactions involving thiocyanate ions do not occur at the very initial stage of the lithium intercalation into the cathode material. Further electroreduction accompanied with degradation of the matrix structure seems to be due to the electron transfer to the orbitals of phosphorus atoms. As a result, new bonds are formed, in particular, between neighbouring atoms of phosphorus and metal (Ni), which makes a participation of the latter in the reactions with the electrolyte impossible.

4. Conclusions

It has been found that electroreduction of NiPS₃ proceeds in several stages at potentials from 2.7 to 1.8 V up to a Li/Ni ratio of ~7.5, then the products formed catalyze the electrolyte decomposition. It has

been shown that the reversible behaviour of the NiPS₃ electrode in the lithium battery is possible in carrying out charge/discharge cycles within the $0 \leq x \leq 3$ range, which considerably exceeds the region of the existence of the intercalation phase Li_xNiPS₃ ($0 \leq x \leq 1.5$).

Returning to the data given in Fig. 5, we should note that the practical specific energy of NiPS₃ calculated from these data for one cycle at the depth $0 \leq x \leq 3.0$ and a current density of 50 mA/cm² approximates to 900 Wh/kg, whereas the specific power reaches to 2550 W/kg. Thus, the above findings allow the system with a transition metal phosphorus trisulfide cathode and a molten thiocyanate electrolyte to be considered as a possible variant for the realization of power-intensive medium-temperature lithium primary and secondary cells.

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