

Iron and nickel phosphorus trisulfides as electroactive materials for primary lithium batteries

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Abstract

The theoretical specific capacities of a family of layered compounds MPX_3 ($M=Fe, Co, Ni$; $X=S, Se$) for current-producing reactions involving 1.5, 2, 6 and 9 lithium atoms per MPX_3 molecule have been estimated. These data show that $FePS_3$ and $NiPS_3$ are good electroactive materials for primary lithium cells. Conditions which allow one to shorten substantially the synthesis time of iron and nickel phosphorus trisulfides in ampoules are presented. According to conductivity measurements in the 293–673 K temperature range, $NiPS_3$ is an intrinsic and $FePS_3$ an extrinsic semiconductor. The discharge characteristics of Li/MPS_3 ($M=Fe, Ni$) cells with an organic electrolyte have been studied; they confirmed that the participation of nine electrons in the redox process is possible. For a primary button cell of the standard size 2325, with a $FePS_3$ cathode, the specific capacity and specific energy values obtained in a discharge 1.8–1.2 V range at load resistances of 3.0 to 30 k Ω were 500–1160 Ah/kg and 700–1770 Wh/kg (on a pure $FePS_3$ basis), respectively.

Keywords: Primary lithium batteries; Trisulfides: Nickel; Iron; Phosphorus

1. Introduction

Primary lithium cells with organic electrolyte and solid cathode, whose advantage is a high discharge voltage (nominal value: 3 V), are known to have usually a relatively low specific capacity [1]. Therefore, it seems to be justified to search for systems which would make it possible to get a considerable gain in specific capacity instead of conventional cells containing silver, mercury, cadmium, lead and bismuth compounds with a lower discharge voltage (nominal value: 1.5 V).

Great advances in developing lithium batteries were associated with the use of layered compounds, as positive electrodes, which can be reversibly intercalated with lithium [1–8]. So, the lamellar phases MPX_3 ($M=Fe, Co, Ni$; $X=S, Se$) demonstrated a high electrochemical efficiency [9–19]. These compounds are structurally close to layered transition metal dichalcogenides, but, in contrast to the latter, they have a rather broad van der Waals gap; therefore, lithium intercalation does not affect the unit cell parameters of the matrix [8, 17]. The number of octahedral sites in the van der Waals gap, which can be occupied by lithium atoms,

is 1.5 per MPX_3 molecule. This value was found [10–18] to determine the region of reversible intercalation where the non-stoichiometric phase Li_xMPX_3 ($0 < x < 1.5$) is formed.

Nevertheless, an analysis of these data shows that the reaction between the oxidant and reducing agent is not limited to the lithium intercalation stage and can continue with reasonable efficiency up to $x \approx 3$. It follows that the Li/MPX_3 system can form the basis for the development of a primary cell with a higher capacity than that of a rechargeable cell. However, one of the reasons restricting the practical use of the active cathodic materials MPX_3 is an inefficient and complicated procedure for their synthesis, which is conventionally carried out in sealed ampoules for a rather long time [19].

In this paper, we give the results of experimental studies concerning the preparation methods and the electrical conductivity of iron and nickel phosphorus trisulfides as well as the electrochemical behaviour of these compounds in primary lithium cells with organic electrolyte (with more emphasis on $FePS_3$, which is relatively poorly characterized [14,17,19]). The above

substances were chosen on the basis of a preliminary estimation of the specific capacity of MPX_3 phases in comparison with other known cathodic materials.

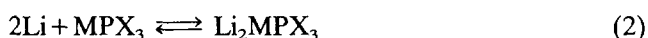
2. Theoretical specific capacity of MPX_3 phases

Let us consider the possible current-producing reactions in Li/MPX_3 systems and estimate for each case the theoretical specific capacity, which may be useful for a subsequent analysis of the experimental results. The specific capacity, Q , is known to be determined by the x coefficient value, i.e., by the number of lithium gram atoms involved in the interaction with one gram molecule of the oxidant.

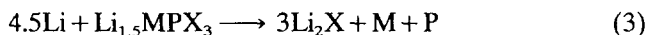
At the initial stage, Li/MPX_3 cells are discharged by a topochemical mechanism. If one proceeds from the condition that all the octahedral voids in the van der Waals gaps of the MPS_3 layered lattice are filled with lithium atoms, the maximum theoretical capacity for one discharge cycle is determined by the following stoichiometry [13,17,18]:



However, one should also bear in mind another possible situation where the reversible behaviour range of the cathode will be limited not by geometric factors but by the number of acceptor centres in the matrix for the electrons transferred from the intercalated species. It may be considered proved today [17,20] that the d-levels of M^{2+} cations are such acceptor centres; therefore, lithium intercalation is accompanied by a reduction of cations, $M^{2+} \rightarrow M^0$, in the MPX_3 structure. Then, the maximum theoretical capacity for lithium involved in the electrochemical intercalation process increases:



It seems to be possible to attain a higher discharge capacity, but the corresponding reactions will give rise to irreversible changes in the active cathodic material, e.g.:



These two reactions are interesting in terms of estimating the characteristics of primary batteries since Eqs. (1) and (3) result in the implication of six, and in view of Eq. (4), nine lithium atoms per one MPX_3 molecule in the interaction. It remains to be cleared up to what extent they are electrochemically efficient and how free energy varies in the orders $1.5 \leq x \leq 6$ and $6 \leq x \leq 9$.

Table 1 presents a comparison of the theoretical specific capacity values for iron subgroup metal phosphorus trichalcogenides which were found using Eqs.

(1) to (4); it also lists data for other known cathodic materials [1], which were calculated in terms of different possible stoichiometry of their reactions with lithium. These data and the above ones allow iron and nickel phosphorus trisulfides to be chosen (taking into account the ready availability and cost of the basic substances) as efficient materials not only for secondary ($x=1.5$ or 2) but also for primary batteries ($x > 2$).

3. Synthesis of the $FePS_3$ and $NiPS_3$ compounds

A commonly used and relatively simple method for the preparation of transition metal phosphorus trisulfides is the 'one-zone' heating at 973–1023 K of a stoichiometric mixture of suitable components in evacuated ampoules for five and more days followed by a very slow cooling [10,12,23].

The main shortcoming of this method and other ampoule methods [19] is the long duration of the synthesis, which is due to the slow heterogeneous reaction between the metal-containing solid phase and the gaseous phosphorus- and sulfur-containing reactants. If one starts from the stoichiometric charge, the MPS_3 formation kinetics is significantly slowed down at the final stage of the synthesis when the pressure of the gaseous reactants becomes low. The reaction does not practically proceed to completion due to the product equilibrium dissociation conditions being reached; this is the main barrier to accelerate the process through raising the temperature.

It was reasonable to assume that for the reaction:



to be accelerated and shifted towards the formation of products, the simultaneous action of two factors is needed: a higher temperature and an excess of the reactants that determine the pressure in the system (provided that the presence of these excesses does not lead to the formation of new compounds). Taking these considerations as a guide, we made a series of experiments, in which we varied the temperature and duration of the synthesis as well as the composition of the starting charge towards larger excess amounts of phosphorus and sulfur. The synthesis was carried out by both 'one-zone' and 'two-zone' methods.

Highly pure metal powders (Fe or Ni), red phosphorus and sulfur were used as the basic substances. The components were mixed in the required ratio and placed in quartz ampoules, which were then evacuated (with intermediate argon bleed-in) to a residual pressure of about 1 Pa, and sealed off. We used ampoules of two sizes: 9–10 mm in inner diameter and 100–180 mm in length (for several grams of charge), and 19–20 mm in inner diameter and 160–280 mm in length (for a few tens of grams of charge). The length of ampoules

Table 1

Theoretical specific discharge capacity values for some transition metal phosphorus trichalcogenides and other compounds as lithium battery oxidants^a

Oxidant formula	x	Q _w (Ah/kg)	Q _v (Ah/l)	Oxidant formula	x	Q _w (Ah/kg)	Q _v (Ah/l)
FePS ₃	1.5	220	681	NiPSe ₃	1.5	123	617
	2.0	293	908		2.0	164	822
	6.0	879	2724		6.0	492	2467
	9.0	1318	4086		9.0	739	3700
CoPS ₃	1.5	216	689	TiS ₂	1.0	239	770
	2.0	288	919		1.0	223	1124
	6.0	864	2756		2.0	447	2247
	9.0	1296	4134		4.0	894	4495
NiPS ₃	1.5	216	714	FeS	1.0	305	1433
	2.0	288	952		2.0	610	2867
	6.0	865	2856	CuS	1.0	280	1312
	9.0	1298	4284		2.0	561	2624
FePSe ₃	1.5	124	588	CuO	1.0	337	2173
	2.0	166	785		2.0	674	4347
	6.0	497	2354				
	9.0	745	3531				

^a The density data for the calculation of Q_v were taken from Refs. [21,22].

was determined by the heating conditions ('one-zone' or 'two-zone' method). Heating to the required temperature was performed in a horizontal furnace at a rate of about 5 K/min; the furnace cooled within about 10 h without control. As the run was finished, the ampoules were opened, and their contents were held under vacuum for about 0.5 h at 570 K to remove unreacted sulfur and its compounds with phosphorus.

The formation of FePS₃ and NiPS₃ was checked by X-ray phase analysis using interplanar spacing data that have been published for these compounds [23]. To identify other phases (if they were found in the diffractograms), we referred to the ASTM diffraction data card file. Chemical analyses were only used to determine quantitatively metal sulfides according to Refs. [24,25], since these substances predominated as impurities in the synthesis products.

In the case of the single-zone heating of the ampoules, the best results were obtained when the base mixture contained excesses of both phosphorus and sulfur, each being equal to about 15 wt.% of the stoichiometric amounts, and the reaction was carried out at 1073–1123 K. Under these conditions, the synthesis of FePS₃ and NiPS₃ practically terminates in 25 to 30 h; there is not more than 1 wt.% of metal sulfides impurities in products. Other ternary metal–phosphorus–sulfur compounds differing from MPS₃ were not detected.

For comparison, MPS₃ (M = Fe, Ni) was synthesized from a stoichiometric mixture of the M, P and S elements by the method reported in Ref. [10] (at 973 K for 140 h followed by cooling at a rate of 5 K/h). The product removed from the opened ampoule had a perceptible specific smell, which was due to the presence of unreacted phosphorus sulfides. The smell was not per-

ceived after heating the sample at 573 K under vacuum for 20 min. The purity of the compounds obtained turned out to be somewhat lower (they contained about 2 wt.% metal sulfides) compared with the compounds prepared under the above conditions.

When the 'two-zone' ampoule synthesis method was used, it was taken into consideration that the FePS₃ and NiPS₃ compounds, in a closed system, can be sublimated and transported at 953–973 K through the gas phase from the 'hot' zone (reaction zone) to the 'cold' zone (growth zone) [26]. This process, however, is accompanied by a partial decomposition of the compounds, which begins at lower temperatures (673–773 K) [12]. Therefore, it was assumed that the temperature of the reaction zone can be substantially increased in the presence of phosphorus and sulfur excesses, which suppresses the MPS₃ dissociation. A temperature gradient makes it possible to accelerate appreciably both the product formation reaction and the transport of the product to the growth zone.

During the experiments by the two-zone method, we have determined the conditions under which the synthesis of FePS₃ and NiPS₃ is completed actually in 15 h; the excess of phosphorus and sulfur in the charge is 3–7 wt.% of the stoichiometric amount each, and the temperature conditions are 1173–1223 K for the reaction zone, and 813–853 K for the growth zone. (The growth zone was preliminarily purified by holding a turned-over ampoule for 4 to 5 h at the same temperature gradient.)

The advantage of the 'two-zone' method consists in the sublimated MPS₃ compound being spatially separated from most impurities and unreacted substances. Therefore, the purity of the compounds is higher in

this case compared with the 'single-zone' method. This is confirmed by X-ray and chemical analyses data, i.e., no metal sulfide impurities are detected in the product. The course of the reaction is easily checked visually by the amount of the solid-phase residue in the reaction zone. The reasons of the temperature interval from 813 to 853 K being taken for the growth zone are that it should be somewhat higher than the boiling points of sulfur and sulfur-phosphorus compounds [22] but not exceed the sublimation temperature of MPS_3 . Under these conditions, a relatively low pressure in the ampoule and the possibility to raise safely the reaction zone temperature up to 1173–1223 K are provided. In some runs (with large ampoules) it was found that the gas-phase transport efficiency can reach values from 1.5 to 2.0 g/h.

Subsequent experiments described here were performed using FePS_3 and NiPS_3 samples prepared by the 'two-zone' method. The compounds obtained are agglomerates of intergrown large (up to 8 mm) and small very thin plate-like black crystals. The crystals are readily deformable and, therefore, lend themselves to be ground in a mortar or ball mill with difficulty. We have found that a laboratory vibrating mill provides a good and rapid grinding.

4. Electrical conductivity of the FePS_3 and NiPS_3 phases

To obtain additional information on the stoichiometry and purity of the compounds synthesized, the electrical conductivity of polycrystalline samples has been studied. The substances were ground to form a powder with a particle size of not more than 30 μm . Then the powder was pressed into tablets of 10 mm diameter and 2 to 3 mm thickness at 350 MPa, their density being 90–92% of the theoretical value. The tablets were rubbed with fine-powdered graphite on both sides and clamped between two graphite contacts. Conductivity versus temperature was measured in an argon atmosphere using an a.c. R-5021 bridge at a 10 kHz frequency.

At room temperature, polycrystalline samples have the following specific conductivity values (S/cm): 0.8×10^{-6} for FePS_3 and 1.4×10^{-7} for NiPS_3 according to our data; according to Ref. [12], they are 5×10^{-5} and 6.7×10^{-7} , respectively (experimental conditions are not given there). A very low conductivity value in the case of the NiPS_3 compound is believed to be due to the very small number of charge carriers [13,27] and, hence, to the very high degree of phase stoichiometry. The somewhat higher specific conductivity of the iron compound is attributed to the slight deviation from the stoichiometric composition, which is peculiar to it. Our results obtained do not contradict this conclusion. At the same time, they indicate lesser differences

in the conductivity values for both substances compared with the data of Ref. [12]; therefore, the synthesis of FePS_3 by our method may be assumed to result in a more stoichiometric product.

Fig. 1 shows the Arrhenius conductivity plots, $\ln \sigma$ versus T^{-1} , for FePS_3 and NiPS_3 . Both compounds exhibit an activation nature of charge transport with close values in the high-temperature region. In the case of NiPS_3 it is impossible to distinguish an extrinsic region, which allows one, in accordance with the conclusion made in Ref. [28], to regard the material as an intrinsic semiconductor. Above 500 K, the slope of the curve corresponds to the activation energy value ($E_\sigma = 1.6$ eV), which is comparable with the band gap ($E_g = 1.6$ eV) determined from optical spectra [29]. The FePS_3 compound, vice versa, exhibits clearly an extrinsic region (up to about 473 K) and an intrinsic region. The extrinsic conductivity increases linearly in the 303–393 K range with an activation energy of $E_\sigma = 0.45$ eV, and then the curve takes a sigmoid form. Such a type of dependence is observed [30] when all donor impurity electrons are in the conduction band (or the valence band electrons are on the acceptor levels) at a lower temperature, and the semiconductor enters the saturation region with approaching the sigmoid part of the curve. Above about 518 K, the conductivity is again given by a straight line, which corresponds with the intrinsic region. Thus, we obtained an additional corroboration of the fact that some non-stoichiometry is characteristic of iron phosphorus trisulfide, owing to which it is an extrinsic semiconductor at room temperature. The presence of a saturation zone, however, might indicate that non-stoichiometry is in this case not so pronounced as with the compound synthesized

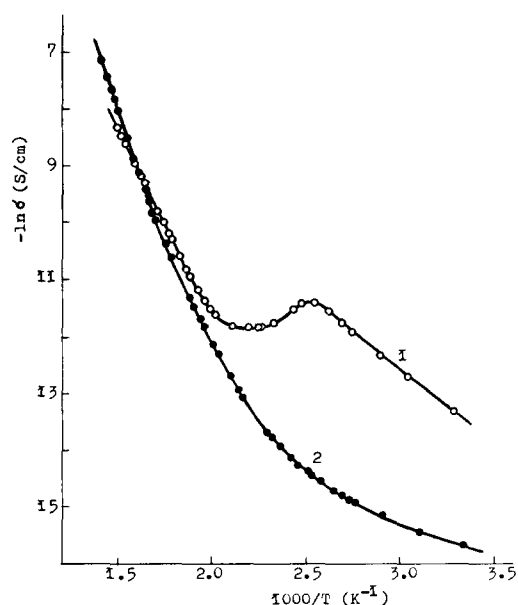


Fig. 1. Temperature dependence of the specific conductivity of pressed polycrystalline (1) FePS_3 and (2) NiPS_3 samples.

by the method of Refs. [10,12,23] since its conductance curve, which was studied in Ref. [28], exhibited no saturation zone. The iron derivative has a lower activation energy value in the intrinsic region ($E_{\sigma}=1.2$ eV) compared with the nickel derivative; it is in a bad agreement with the band gap of FePS_3 ($E_g=1.5$ eV) found from optical measurements [29]. It should be also noted that, judging by the reproducibility of the measurement results during heating and cooling, the compounds possess a fairly good thermal stability up to 673 K.

5. Behaviour of FePS_3 and NiPS_3 as cathodes of primary lithium batteries with organic electrolyte

When studying the electrochemical behaviour of FePS_3 and NiPS_3 , we used an experimental three-electrode cell and tested materials in button cells.

The cathodic material was prepared by mixing MPS_3 with carbon black, fine graphite powder and polytetrafluoroethylene (the amount of each additive was ~ 5 wt.%). The mixture obtained was pressed onto a nickel net with a current collector and dried under vacuum at 523 K. Two other nickel nets with pressed lithium were the auxiliary and the reference electrodes. All the electrodes together with separators made of porous polypropylene were placed in a sealed Teflon vessel which was filled with electrolyte. We used a 1 M solution of LiBF_4 in γ -butyrolactone (γ -BL) prepared according to the recommendations of Ref. [1] as the electrolyte. The electrochemical cell assembled in this way was evacuated and filled with argon. All manipulations were made in a dry box. The discharge curves were measured under galvanostatic conditions using a PI-50-1 potentiostat.

As we have seen, pure FePS_3 and NiPS_3 demonstrate a very high electrical resistance, which affects their electrochemical activity. Therefore, preliminary experiments were made to optimize the composition of the positive electrode containing an electronic conductor (EC) (namely a mixture of carbon black and fine graphite in an equal ratio). Fig. 2 illustrates the variation of the conductivity and specific capacity as a function of the composition of the FePS_3 -EC system. An especially sharp increase in σ and Q is observed at EC additions of 0–10 wt.%. Subsequent increase in the EC content causes a slight increase in conductivity and a simultaneous decrease in the specific capacity of the composite material. These experiments show that addition of 10 wt.% EC ensures apparently the optimum characteristics of the positive electrode.

Figs. 3 and 4 show galvanostatic discharge curves taken at different current densities ($i=0.1, 0.25$ and 0.5 mA/cm²) for FePS_3 and NiPS_3 cathodes. A fairly stable behaviour of the discharge potential, U_d , at least

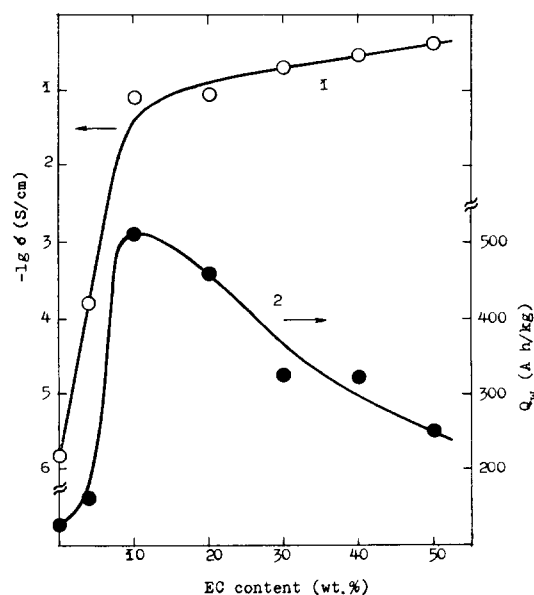


Fig. 2. The variation of the conductivity and specific capacity as a function of the composition of the FePS_3 -EC system.

in the range $0 \leq x \leq 2$, is noteworthy. An increase in the current load leads to its decrease, which is not very large, and to a narrowing of the initial region, where the main U_d drop takes place. In this case, the shape of discharge curves is not affected in any way at high current densities by the different natures of current-producing reactions up to $x \approx 2.5$ and by the presence of two stages of lithium intercalation into the cathode material (successive filling of octahedral voids of two types in the orders $0 \leq x \leq 0.5$ and $0.5 \leq x \leq 1.5$ [11,17,18]). The inflection of the curves at $x > 1.5$ observed for NiPS_3 is probably due to the transition from the region controlled by the topotactic intercalation reaction to the heterophase region, where a further cathode electroreduction takes place by another mechanism [10,11,18].

It is noteworthy that the system Li/FePS_3 is characterized by a discharge potential close to 1.5 V. Hence, there is a possibility to replace by the already existing 1.5 V cells, if it is possible to attain a reasonably high discharge capacity at the same weight and size. Nickel phosphorus trisulfide shows higher discharge potentials (~ 1.9 – 1.7 V at $0 \leq x \leq 1.6$) and has besides a transition region in the discharge curves ($1.6 \leq x \leq 2.3$), making it less suitable for the above purposes.

The practical characteristics of the FePS_3 cathode were studied using an industrial-type button lithium cell of the standard size 2325 (23 mm in diameter and 2.5 mm in height). (The cathode and electrolyte compositions were the same as mentioned above.) The measurements of voltage versus time (or versus x) were carried out at load resistances of 30, 12, 5.6 and 3.0 k Ω .

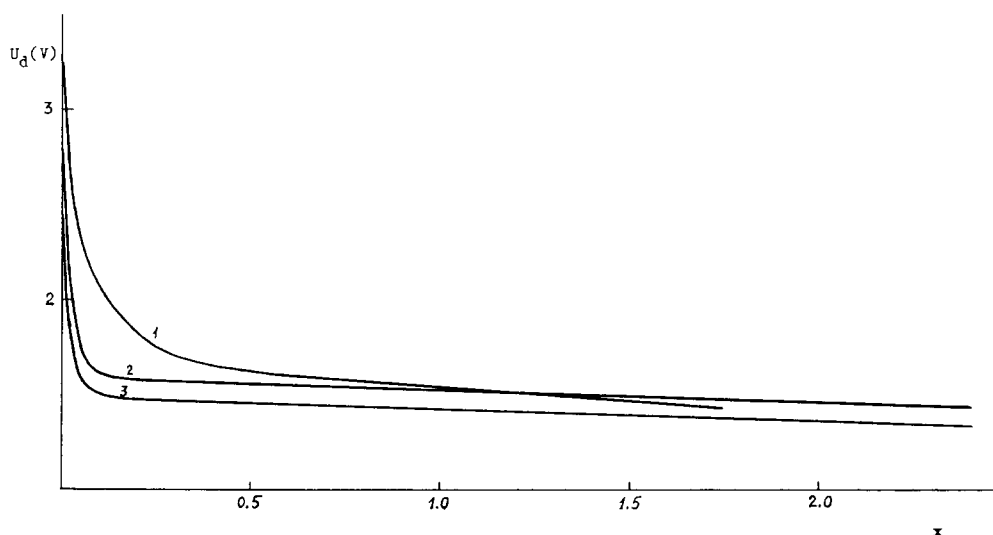


Fig. 3. Discharge potential vs. x in Li_xFePS_3 obtained in an experimental electrochemical cell at different current densities (mA/cm^2): (1) 0.1, (2) 0.25, and (3) 0.5.

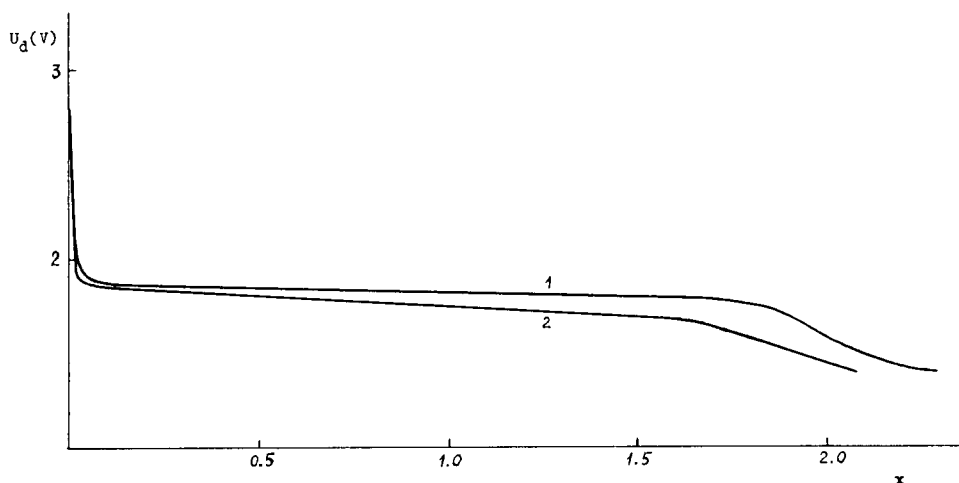


Fig. 4. Discharge potential vs. x in Li_xNiPS_3 obtained in an experimental electrochemical cell at different current densities (mA/cm^2): (1) 0.25 and (2) 0.5.

Discharge tests of the cell at the $30\text{ k}\Omega$ load, which lasted over 9000 h (Fig. 5), gave interesting information. At this load, the current density is fairly low ($\sim 20\ \mu\text{A}/\text{cm}^2$) and the discharge process can be considered to occur not far from the equilibrium conditions. Therefore, the discharge curve obtained is a good illustration of the peculiarities of FePS_3 electroreduction at various stages. The initial region, where the most abrupt voltage drop (from 3.4 to 2.0 V) is observed, may be attributed to the filling with lithium of octahedral voids of 2(d)-type in the layered FePS_3 structure ($0 \leq x \leq 0.5$) [17,18]. After that, lithium atoms begin to occupy the other 4(h)-type, octahedral voids of the van der Waals gap ($0.5 \leq x \leq 1.5$); this manifests itself as a slight but fairly distinct inflection in the discharge curve. Then, the curve has a long and fairly even region, where one

more slight change in its trend corresponds to the value $x \approx 5$, which may be treated as a change of electroreduction mechanism (passing from Eq. (3) with the range $1.5 \leq x \leq 6$ to Eq. (4) with the range $6 \leq x \leq 9$).

Two results, which are most important in our opinion, should be emphasized here. First, the presumption has been proved that a limiting case corresponding with the participation of nine electrons in the redox process (according to the sum of Eqs. (1), (3) and (4)) is possible in the Li/FePS_3 system. Second, the cell is discharged mostly at voltages in the vicinity of 1.5 V.

The total specific capacity of FePS_3 in the experiment in question (with $30\text{ k}\Omega$ load) at a final voltage of 1.0 V was actually the same as the theoretically attainable value ($Q_w = 1315\text{ Ah}/\text{kg}$, $Q_v = 4080\text{ Ah}/\text{l}$), and the specific energy, W , was $2090\text{ Wh}/\text{kg}$ ($6480\text{ Wh}/\text{l}$). It is

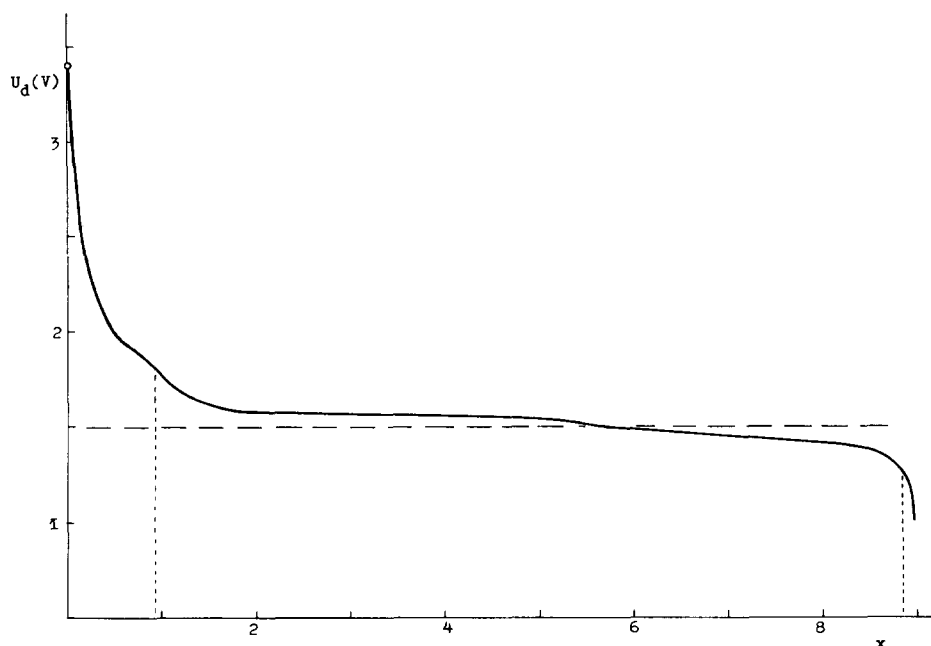


Fig. 5. Discharge curve for a button cell of the standard size 2325 for the Li/FePS₃ system at a resistance load of 30 kΩ. The vertical dashed lines bound the portion of the curve where the discharge voltage varies from 1.8 to 1.2 V.

known, however, that the operating voltage range for 1.5 V cells is limited by the values from 1.8 to 1.2 V. In the curve shown in Fig. 5, this region is between two vertical dashed lines ($0.94 < x < 8.85$); hence, the specific capacity and specific energy values found are 1160 Ah/kg (3595 Ah/l) and 1770 Wh/kg (5485 Wh/l), respectively.

As the load resistance decreases, the character of cell discharge undergoes regular changes (Fig. 6). For

instance, when passing from the 30 and 12 kΩ loads to the 5.6 and 3.0 kΩ loads, the initial region, corresponding with an abrupt voltage drop, becomes shorter and shorter, and the inflection in the curve disappears. The main plateau shifts somewhat below 1.5 V and becomes at the same time shorter, extending to $x \approx 4$.

Table 2 summarizes specific characteristics of FePS₃ cathodes for cell discharge up to a final voltage of

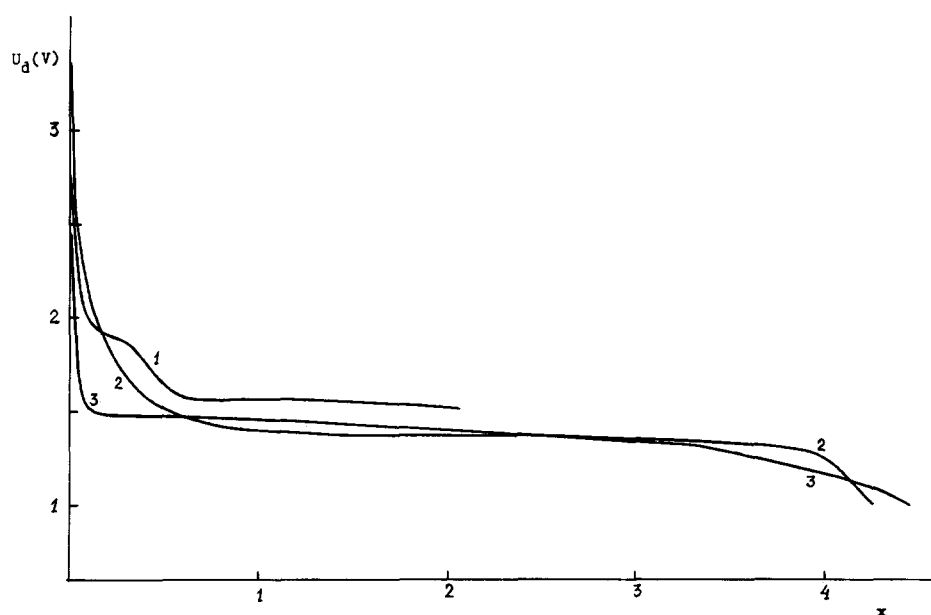


Fig. 6. Discharge curves for button cells of the standard size 2325 for the Li/FePS₃ system at load resistances of (1) 12 kΩ, (2) 5.6 kΩ and (3) 3.0 kΩ.

Table 2

Electric parameters of button cells of the standard size 2325 and specific characteristics of iron phosphorus trisulfide cathodes

Parameter	Load resistance	Load resistance
	5.6 k Ω , $U_f=1.2$ V	3.0 k Ω , $U_f=1.2$ V
\bar{U}_d (V)	1.43	1.39
\bar{i}_d (mA/cm ²)	0.09	0.16
x in Li _{x} FePS ₃	4.00	3.84
Q_w (Ah/kg)	586	562
W_w (Wh/kg)	838	781
Q_v (Ah/l)	1817	1742
W_v (Wh/l)	2598	2422

$U_f=1.2$ V at loads of 5.6 and 3.0 k Ω as well as average discharge current densities (\bar{i}_d) and voltages (\bar{U}_d).

The operating parameters obtained and their comparison with those for other systems [1,31] allow lithium batteries with an FePS₃ cathode to be considered suitable for giving energy to electronic circuits and devices, where a long service life at a relatively low power consumption is required.

6. Conclusions

Examination of possible current-producing reactions in Li/MPX₃ systems (M = Fe, Co, Ni; X = S, Se) allowed us to choose iron and nickel phosphorus trisulfides as materials with a potentially high specific capacity. Therefore, the main attention in the present study was given to some aspects of the preparative chemistry of these compounds and to their behaviour in primary lithium cells with organic electrolyte.

It has been found that the synthesis of FePS₃ and NiPS₃ in ampoules can be carried out considerably faster due to a higher reaction temperature, provided that the reaction is conducted in the presence of excess amounts of phosphorus and sulfur. This makes a strict proportioning of the charge components unnecessary. The data on electrical conductivity measured in the 293–673 K range show that both compounds have a high specific resistance, NiPS₃ being an intrinsic and FePS₃ an extrinsic semiconductor. The fact that the iron derivative has an extrinsic region is associated with a slight deviation from the stoichiometric composition, which is typical of it.

Electrochemical interaction in Li/MPS₃ systems can be represented as a process consisting of two main stages: at the first stage, an intercalation mechanism acts, and subsequently, at a ratio of Li/M > 1.5, various substitution reactions proceed, which lead to an irreversible breakdown of the original cathode structure. Our results confirm the high electrochemical activity of NiPS₃ in the intercalation region (0 < x < 1.5). However, FePS₃ appears, in our opinion, to be more attractive

as the cathode for primary cells since it demonstrates acceptable and stable characteristics (on a level of 1.5 V or somewhat lower) at a fairly large depth-of-discharge. The experimental corroboration of the possibility to realize in the Li/FePS₃ system a limiting case corresponding to the involvement of nine electrons in the redox process, according to the above current-producing reactions, is noteworthy in this connection. The specific capacity and specific energy of the active material FePS₃ tested in a button cell of the standard size 2325 at load resistances of 3.0 to 30 k Ω were 500–1160 Ah/kg and 700–1770 Wh/kg, respectively.

It seems to be expedient in the future to concentrate efforts on attaining higher discharge currents of such cells and on developing economically advantageous methods for producing transition metal phosphorus trisulfides.

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