**Synthesis method and thermodynamic characteristics of anode material Li$_3$FeN$_2$ for application in lithium-ion batteries**

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**Abstract:** Li$_3$FeN$_2$ material was synthesized by two-step solid-state method from LiN (adiabatic camera) and FeN$_2$ (tube furnace) powders. Phase investigation of LiN, FeN$_2$, and Li$_3$FeN$_2$ were carried out. Discharge capacity of Li$_3$FeN$_2$ is 343 mAh g$^{-1}$, that is about 44.7% of theoretic capacity. The molar heat capacity of Li$_3$FeN$_2$: at constant pressure in the temperature range 298-900 K should be calculated as $C_p = 77,831 + 0,130 \times T - 6,289 \times T^2$. Thermodynamic characteristics of Li$_3$FeN$_2$ were determined as next: entropy $S_{298} = 116.2$ J mol$^{-1}$ K$^{-1}$, molar enthalpy of dissolution $\Delta H_{298} = -206,537 \pm 2,8$ kJ mol$^{-1}$, the standard entropy of formation $\Delta S_F = 116.2$ J mol$^{-1}$ K$^{-1}$ (W.Herz rule), the standard Gibbs free energy of formation $\Delta G_{298} = -767,7$ kJ mol$^{-1}$.

**Keywords:** lithium-ion battery; anode battery; lithium-ion thermodynamics; solid-state synthesis

1. Introduction

Increasing energy needs in modern society, the concern over the fossil energy crisis and the demand for environmental sustainability leads to the search for any possible energy resources, such as renewable energy.

Electrochemical energy storage methods play an increasingly important role in transport and stationary applications. The lithium ion battery (LIB) is one of the best decisions in the field of electrochemical energy storage as a technology and market of choice for portable electronics, backup power and vehicle electrification. To meet high standard requirements, such as high energy density, high power density, long service life, low cost, environmental friendliness and safety, a lot of effort was directed to the development of more advanced batteries, i.e. the attempt on nanostructural material for electrode materials [1-2], increasing the capacity and voltage of cathode materials [3], safety issues [4]. As a promising source of energy for the electric car revolution, LIB has proven its market position. There are a lot of anode materials that attracted attention due to their high theoretical specific capacities [5, 6].

Previous works shows good electrochemical properties of Li$_3$N-type anodes, e.g. Li$_3$Na$_3$N$_2$ and Li$_3$Na$_2$N$_2$ phases [7], LiBeN [8], Li$_3$N-Mg$_3$N$_2$ [9] and others.

Li$_3$FeN$_2$: first was obtained by Frankenburger et al. by reaction of lithium nitride (LiN) with elemental iron in nitrogen atmosphere [10]. After decades, Fromont investigated the reaction of LiN with iron using thermogravimetry [11]. These studies shows that Li$_3$FeN$_2$ was indexed by an orthorhombic cell with lattice parameters $a = 9.65$ Å, $b = 8.66$ Å and $c = 8.38$ Å.

In this article two-stage synthesis and properties of promising anode material Li$_3$FeN$_2$ is shown. Firstly, LiN synthesis was obtained at adiabatic chamber. Then, mixed with iron nanopowder, Li$_3$FeN$_2$ was obtained at tube furnace.
2. Materials and Methods

A 16 mm diameter and 0.6 mm lithium plate sliced and polished in argon glovebox, iron nanopowder, nitrogen and ammonia (NH₃) were used as starting components for Li₃N, Fe₂N and LiFeN₂ synthesis (Table 1). Lithium sliced plates were put into titanic autoclave nitrogen filled bomb of Netzsch APTAC 264 as shown on Figure 1. The Li₃N synthesis parameters are next: temperature is 170°C, heat rate 2°C/min, synthesis time 6h and nitrogen pressure is ~709.3 kPa (7 atm).

![Scheme (a) and photo (b) of Netzsch APTAC chamber.](image)

(a)  
(b)  

Iron nanopowder and nitrogen were used as source for Fe₂N. Ceramic crucible with initial powder was put into tube furnace (BTF-1700C). Tube was purged by ammonia (NH₃) for 30 min before synthesis. Synthesis was carried out in NH₃ atmosphere at 530°C for 6h with heat rate of 8°C/min. Mechanically mixed and powder was hot pressed for 2 hours at 1100°C. Received hot pressed sample was heated at N₂ atmosphere for 10 h at 700°C (heat rate was 5°C/min). After heat treatment, sample was mechanically grind into ivory colored powder.

XRD analysis was held with Bruker D8 Advance with a step of 0.02°. Structural parameters were refined by the Rietveld method using TOPAS5 software.
Table 1. Summary of chemicals descriptions.

| Name                  | Formula | Source                                      | Purity, %   |
|-----------------------|---------|---------------------------------------------|-------------|
| Iron nanopowder       | Fe      | Changsha Easchem Co., Ltd.                  | 99.9        |
| Lithium               | Li      | Xiamen Tmax Battery Equipments Ltd.         | 99.9        |
| Nitrogen              | N2      | Qingdao Guida Special Gas Co., Ltd.         | 99.9-99.999 |
| Ammonia               | NH3     | Wuhan Newradar Trade Company Ltd.           | 99.9        |
| Lithium nitride       | Li3N    | prepared here                               | 98.9        |
| Iron nitride          | Fe2N    | prepared here                               | 98.4        |
| Lithium iron nitride  | Li3FeN2 | prepared here                               | 99.1        |

1 Purity according to XRD analysis

Lithium plate, the same as described above, was used as a counter-electrode. 25 µm thickness Celgard 2400 was used as separator. Electrolyte solution was 1.1 M LiPF6 in diethyl carbonate: dimethyl carbonate: ethylene carbonate (DEC/DMC/EC) 1:1:1 by mass mixture. Mixture of 80% Li3FeN2 powder, 10% of conductive additive (Super P) and 10% of polyvinylidene fluoride, dissolved in N-methylpyrrolidon was used as experimental electrode.

The synthesized nitrides powders were examined by X-ray diffraction analysis (XRD). XRD was performed with Bruker D8 ADVANCE diffractometer with a vertical goniometer and Cu Kα-radiation. Diffraction angles (2θ) are 5-100º, 10-80º and 5-120º for Li3N, Fe2N and Li3FeN2, respectively.

Electrochemical tests were performed with battery test system BTS NEWARE CT-3008-5V10 mA (NEWARE, China).

Calorimetric measurements were performed using TAM IV Microcalorimeter at 298 K with the cell volume of 20 ml. Calorimetric cell was filled with aqueous solution of 1 mol dm-3 HCl (~ 5 ml) and the ampoule was placed inside the cell in a special holder. The ampoule was broken when thermal equilibrium was established, and nitride powder began to dissolve in HCl solution. Thermo-EMF vs. time was registered during the dissolution process providing the heat dissolution curve. Integration of this curve gave the value of dissolution enthalpy.
3. Results

Figure 2 shows XRD pattern of synthesized Li$_3$N (a) and Fe$_2$N (b) powders. All peaks are in good correlation with database one. Li$_3$N has $P6/mmm$ space group with lattice parameters $a=3.6711$ Å, $b=3.6711$ Å and $c=3.8770$ Å, which are in good correlation with [12] and PDF #30-0759. Fe$_2$N reflection peaks also are in good correlation with [13] and PDF #50-0978. Space group of Fe$_2$N is $P312$ with lattice parameters $a=4.7912$ Å, $b=4.7912$ Å and $c=4.416$ Å.

![XRD pattern of synthesized Li$_3$N and Fe$_2$N](image)

Figure 2. XRD pattern of synthesized (a) Li$_3$N at 170°C for 5 h at N$_2$ atmosphere (709 kPa) and (b) Fe$_2$N at 530°C for 5 h at NH$_3$ atmosphere.

Figure 3 shows XRD pattern of Li$_3$N, Fe$_2$N and Li$_3$FeN$_2$ after heat treatment at Netzsch APTAK chamber, tube furnace with ammonia atmosphere and tube furnace with nitrogen atmosphere, respectively. Parameters $a$ and $c$ calculated by the Rietveld method for Li$_3$FeN$_2$ are $a=4.872$ Å, $b=9.677$ Å and $c=4.792$ Å, respectively, $Ibam$ space group. XRD patterns of Li$_3$FeN$_2$ synthesized at different temperatures are shown on Figure 3. Sample synthesized at 850°C shows high purity of 97.2 % with Li$_2$O impurity. Other samples include such impurities as Li$_2$O (PDF #01-076-9237), Li$_5$FeO$_4$ (PDF #01-075-1253), LiFeO$_2$ (PDF #74-2284) and Li$_2$O$_{0.75}$N$_{0.25}$ (PDF #01-080-4542).

![XRD patterns of Li$_3$FeN$_2$](image)

Figure 3. XRD patterns of Li$_3$FeN$_2$ after heat treatment at 750, 800 and 850 °C for 10 h at N$_2$ atmosphere. The vertical lines in the bottom indicate diffraction positions of Li$_3$FeN$_2$ structure (PDF #01-080-0718).
Electrochemical performance of lithium-ion cell is shown on Figure 4. Charge and discharge capacity at beginning of life (BOL) is about 371 mAh g\(^{-1}\) and 343 mAh g\(^{-1}\), after 100 cycles are 357 mAh g\(^{-1}\) and 329 mAh g\(^{-1}\), respectively, are shown on Figure 4, a. Coulombic efficiency is 92.7% and 89.5% before cycling (BOL) and after 100 cycles.

The structure refinement defined that Li\(^+\) is in 4b and 8g, Fe\(^{3+}\) is in 4a and N\(^-3\) is in 8j sites. All calculations were carried out with using TOPAS 4 software by Bruker. The final structure parameters (including site occupancy) are listed in Table 2.

| Atom/void | Site | x    | y    | z       |
|-----------|------|------|------|---------|
| Li\(_1\)  | 8g   | 0.91 | 0.0  | 0.25745 |
| Li\(_2\)  | 4b   | 1    | 0.0  | 0.5     |
| Fe        | 4a   | 1    | 0.0  | 0.0     |
| N         | 8j   | 0.98 | 0.219979 | 0.113757 |

Figure 4. Cycling performance (a) and charge-discharge curve at constant current 0.1 C (b).

The theoretical capacity of Li\(_3\)FeN\(_2\) with whole lithium deintercalation using Faraday’s law is

\[ C_T = z \cdot \frac{F}{M} \]  

where \( z \) is lithium ions of compound stoichiometry, \( C_T \) is theoretical capacity in mAh g\(^{-1}\), \( F \) is Faraday constant and \( M \) is molar mass of Li\(_3\)FeN\(_2\) compound. Theoretical capacity is equal to \( C_T = 768 \) mAh g\(^{-1}\) by formula (1). Discharge capacity is 343 mAh g\(^{-1}\), that is about 44.7% of theoretic capacity \( (C_T) \).

4. Discussion

4.1. The standard enthalpy of formation

The enthalpy of Li\(_3\)FeN\(_2\) (LFN) formation from single nitrides is calculated according the following equation \((\Delta H_{\text{LFN}})\):

\[ \text{Li}_3\text{N} + 0.5\text{Fe}_2\text{N} + 0.25\text{N}_2 \rightarrow \text{Li}_3\text{FeN}_2 \]  

and single nitrides were synthesized by reactions, described in Experimental section:

\[ 6\text{Li} + \text{N}_2 \rightarrow 2\text{Li}_3\text{N} \]  

\[ 2\text{Fe} + 2\text{NH}_3 \rightarrow 2\text{FeN} + 3\text{H}_2 \]
For enthalpy calculation we used thermodynamic cycle with the following reactions, Figure 5:

\[
\text{Li}_3\text{FeN}_2 + 6\text{HCl}_{(aq)} \rightarrow 3\text{LiCl}_{(aq)} + \text{FeCl}_3_{(aq)} + \text{N}_2 + 3\text{H}_2, \quad (5)
\]

\[
\text{Li}_3\text{N} + 4\text{HCl}_{(aq)} \rightarrow 3\text{LiCl} + \text{NH}_4\text{Cl}, \quad (6)
\]

\[
2\text{Fe}_2\text{N} + 8\text{HCl}_{(aq)} \rightarrow 4\text{FeCl}_2 + 2\text{NH}_3 + \text{H}_2, \quad (7)
\]

\[
\text{N}_2 + 8\text{HCl}_{(aq)} \rightarrow 2\text{NH}_4\text{Cl} + 3\text{Cl}_2, \quad (8)
\]

where the subscript \((aq)\) means “aqueous”. The standard enthalpy of this reaction \(\Delta_d H_{LFN}\) has been measured directly in the calorimeter. The value obtained from calorimetry was equal to \(-1972.96 \pm 25 \text{ J g}^{-1}\), Table 3.

![Figure 5](image)

**Figure 5.** Thermochemical cycle scheme. Dissolution enthalpy connection of \(\text{Li}_3\text{FeN}_2\) with its formation enthalpies from single nitrides.

The resulting value of \(\Delta_{ox} H_{LFN}\) is obtained by next equation:

\[
\Delta_{ox} H_{LFN} = \Delta_d H_{Li3N} + 0.5\Delta_d H_{Fe2N} + 0.25\Delta_d H_{N2} - \Delta_d H_{LFN}, \quad (9)
\]

The values of \(\Delta_d H_{Li3N}, \Delta_d H_{Fe2N}\) and \(\Delta_d H_{N2}\) were also measured by calorimetry method. Measurement results are shown at Table 3. The value of \(\Delta_{ox} H_{LFN}\) by formula (9) is equal to \(-94.833 \text{ kJ mol}^{-1}\). This value is negative, it means that \(\text{Li}_3\text{FeN}_2\) is a stable phase and there is an energy benefit in the formation of \(\text{Li}_3\text{FeN}_2\) from single nitrides.

**Table 3.** Values of specific and molar enthalpies of dissolution in 1 mol dm\(^{-3}\) aqueous HCl at 298 K, \(p = 101 \text{ kPa}\).

| Compound     | Specific enthalpy, J g\(^{-1}\)       | Molar mass, g mol\(^{-1}\) | Molar enthalpy of dissolution, kJ mol\(^{-1}\) | Ref.        |
|--------------|---------------------------------------|----------------------------|-----------------------------------------------|-------------|
| \(\text{Li}_3\text{N}\) | -3 163.853 ± 30                        | 34.83                      | -110.197 ± 1.7                                | this work   |
| \(\text{Fe}_2\text{N}\) | -13.79 ± 1.5                           | 125.701                    | -1.734 ±0.04                                  | this work   |
| \(\text{N}_2\)     | -71.716 ± 10                           | 28.014                     | -2.56 ± 0.12                                  | this work   |
| \(\text{Li}_3\text{FeN}_2\) | -1 972.96 ± 25                        | 104.684                    | -206.537 ± 2.8                                | this work   |
| \(\text{Li}_3\text{Na}_3\text{N}_2\) | -2 285.96 ± 13.4                     | 117.807                    | -269.3018                                    | [9]         |

Finally, it is possible now to calculate the enthalpy of \(\text{Li}_3\text{FeN}_2\) formation from elements by formula:

\[
\Delta H_{LFN} = \Delta H_{Li3N} + 0.5\Delta H_{Fe2N} + 0.25\Delta H_{N2} + \Delta_{ox} H_{LFN}. \quad (10)
\]

Standard enthalpies for the calculation were taken from the handbooks [14, 15], Table 4.
The calculated value of the enthalpy of LiFeN₂ formation by formula (10) is \(-291.331 \pm 5.7 \text{ kJ mol}^{-1}\), Table 4. Enthalpy of formation \(\Delta H^0\) for LiFeN₂ has the same order as those for similar compounds, namely lithium metallonitrides (Table 4), that confirms correctness of the measurements. This value can be recommended to use in thermodynamic estimation and simulations of LiFeN₂ reactivity.

4.2. The isobaric heat capacity

The temperature dependence of the isobaric heat capacity of the LiFeN₂ is shown on Figure 6. According to XRD data (Figure 3), obtained powder material contains a certain amount of lithium oxide Li₂O. This amount must be taken in account for calculating the heat capacity of the LiFeN₂. This impurity could appear during synthesis process or contact with oxygen in air atmosphere. XRD quantitative methods have limitations, but the heat capacity of a two-phase system must be recalculated by additive consideration:

\[
mC_p = m(\text{LFN})C_p(\text{LFN}) + m(\text{Li}_2\text{O})C_p(\text{Li}_2\text{O}),
\]

where \(C_p\) is a specific heat capacity at constant pressure and \(m\) is a mass. The sample weight consists of synthesized compound (LiFeN₂) and impurity (Li₂O). So, the heat capacity of LiFeN₂ is expressed from eq. (11) as:

\[
C_p(\text{LFN}) = \frac{mC_p - m(\text{Li}_2\text{O})C_p(\text{Li}_2\text{O})}{m(\text{LFN})}
\]

The weight of the components can be found from the sample total mass, calculating through the mass fraction of lithium oxide, \(\omega(\text{Li}_2\text{O})\):

\[
m(\text{Li}_2\text{O}) = m\omega(\text{Li}_2\text{O})
\]

and

\[
m(\text{LFN}) = m[1 - \omega(\text{Li}_2\text{O})]
\]

According to eq. (13) and (14), eq. (12) can be written as follows:

\[
C_p(\text{LFN}) = \frac{C_p - C_p(\text{Li}_2\text{O})\omega(\text{Li}_2\text{O})}{1 - \omega(\text{Li}_2\text{O})}
\]

Thereby, the heat capacity of LFN can be calculated from the experimental data and heat capacity of lithium oxide impurity. For eq. (15) it is necessary to know temperature dependence of the lithium oxide specific heat capacity. For this, tabular data for the lithium oxide heat capacity at constant pressure [15] was used. For temperature range (300-900 K) the commonly used polynomial formula for the heat capacity:

\[
C_p = a + bT - cT^2
\]

where \(T\) is absolute temperature; \(a, b, c\) – empirical coefficients. The obtained coefficients for lithium oxide are: \(a = 76,666 \text{ J mol}^{-1} \text{ K}^{-1}, b = -13,63 \times 10^3 \text{ J mol}^{-1} \text{ K}^{-2}, c = -18,624 \times 10^5 \text{ J mol}^{-1} \text{ K}^{-3}\). The heat capacity of LiFeN₂ for 300-900 K temperature range was recalculated using
eq. (16) and (15) considering Li₂O impurity presence. According to XRD data (Figure 3) Li₃FeN₂ contains about 2.8±0.04 wt% Li₂O. Experimental and recalculated LFN heat capacity is shown on Figure 6 and Table 5. Empirical values for heat capacity were calculated by Neumann-Kopp rule. This rule prescribes to calculate the molar heat capacity of complex compound from the heat capacities of constituent elements by adding them in corresponding with compound stoichiometry. But this calculation method gives good results for room temperatures and rough results for high temperatures. For more accurate results binary compounds were used instead to single elements (especially if all the components are in the same aggregate state):

$$C_p(CN) = \sum n(BN)C_p(BN)$$  

where $C_p$ is molar heat capacity at constant pressure, $n$ is a stoichiometric coefficient, $CN$ and $BN$ are complex and binary nitride, correspondingly. For LFN, eq. (17) can be written as (according to eq. (2)):

$$C_p(LFN) = C_p(LiN) + 0.5C_p(FeN) + 0.25C_p(N_2)$$  

The temperature dependence of the heat capacity calculated from eq. (18) using tabular data [15] is also shown on Figure 6 and Table 5.

Table 5. The temperature dependence of experimental (exp.), recalculated by eq. (15) (rec.) and calculated by Neumann-Kopp (N-K) rule (eq. 18) heat capacities (Cp) of Li₃FeN₂(s).

| T, K | $C_p$(exp.), J K⁻¹ mol⁻¹ | $C_p$(rec.), J K⁻¹ mol⁻¹ | $C_p$(N-K), J K⁻¹ mol⁻¹ |
|------|-------------------------|--------------------------|-------------------------|
| 300  | 126,9                   | 124,1                    | 117,8                   |
| 400  | 134,1                   | 132,6                    | 130,7                   |
| 500  | 146,3                   | 144,3                    | 141,9                   |
| 600  | 160,5                   | 158,3                    | 152,8                   |
| 700  | 173,8                   | 171,9                    | 163,4                   |
| 800  | 183,3                   | 180,7                    | 173,6                   |
| 900  | 186,1                   | 178,8                    | 183,5                   |

Figure 6. Temperature dependences of the experimental, recalculated and Neumann-Kopp rule heat capacities of Li₃FeN₂. The line for Neuman-Kopp rule is given as an approximating allometric line.

The temperature dependence of the heat capacity determined from eq. (18) using tabular data [20] is shown on Figure 6 and Table 5. The temperature dependence of the heat capacity calculated by Neumann-Kopp rule is in good correlation with recalculated heat capacity (taking into account Li₂O impurity amount). However, XRD quantitative analysis gives rough results for small presence of compounds in material. For another quantitative methods the amount of impurities can be measured more accurately, for example thermogravimetry or volumetric methods.
4.3. Entropy

Entropy is another thermodynamic function that should be calculated. Planck’s postulate says that the entropy of an ideal crystal at 0 K is equal to zero. So, the absolute value of the entropy can be calculated from the formula:

$$S(T) = \int_0^T \frac{C_p(T)}{T} dT + \frac{\Delta H_1}{T_1} + \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT + \frac{\Delta H_2}{T_2} + \cdots + \int_{T_k}^T \frac{C_p(T)}{T} dT$$  \hspace{1cm} (19)

where $S$ is entropy, $\Delta H_k$ is enthalpy of the k-th phase transition, $T_i$ is temperature of the k-th phase transition ($0 < T_i < T$). Since the entropy can be calculated by Neumann-Kopp rule and if there are no phase transition till calculation temperature, entropy can be also calculated by Neumann-Kopp rule:

$$S(T) = \int_0^T \frac{\sum C_p(T, BN)}{T} dT = \sum \int_0^T \frac{C_p(T, BN)}{T} dT = \sum S(T, BN),$$  \hspace{1cm} (20)

where $BN$ is the binary nitride compound (see eq. (17)). According to eq. (17) and (18), eq. (20) can be written in the following way:

$$S_{\text{LFN}} = S(\text{LiN}) + 0.5S(\text{FeN})$$  \hspace{1cm} (21)

The entropy of Li$_3$FeN$_2$ at room temperature is 113.2 J mol$^{-1}$ K$^{-1}$ according to eq. (21) and tabular data [15, 20]. Additive rule for entropy calculation is suitable if the sum of the molar volumes of binary compounds differs a bit with the molar volume of the complex compound [21]. Thus, the molar volume for Li$_3$N is 27.2 cm$^3$ mol$^{-1}$ ($\rho$=1.28 g cm$^{-3}$ [21]), for Fe$_2$N is 19.8 cm$^3$ mol$^{-1}$ ($\rho$=6.35 g cm$^{-3}$ [21]) and for Li$_3$FeN$_2$ is 33.9 cm$^3$ mol$^{-1}$ ($\rho$=3.09 g cm$^{-3}$ [22]). The sum of the molar volumes of binary nitrides with their corresponding coefficients is 37.1 cm$^3$ mol$^{-1}$ and differs about 9% of the LFN molar volume, which allows usage of additive scheme.

Also, the LFN entropy can be calculated by W.Herz rule [23]:

$$S_{298}^0 = K_H (M/C_{p, 298})^{1/3} m,$$  \hspace{1cm} (22)

where $K_H$ is Herz constant ($K_H = 20.5$), $M$ is molar mass, $C_{p, 298}$ is isobaric heat capacity, $m$ is atoms per formula. According to eq. (22) and considering $C_{p, 298}$ from Table 5 the LFN entropy is 116.2 J mol$^{-1}$ K$^{-1}$. Thus, the LFN entropy calculated by Herz rule is in good correlation with Neumann-Kopp rule result.

4.4. The standard Gibbs free energy

The enthalpy of formation and entropy calculated above makes possible to calculate the standard Gibbs free energy of Li$_3$FeN$_2$ formation at room temperature:

$$\Delta_f G_{298}^0 = \Delta_f H_{298}^0 - 298 \Delta_f S_{298}^0.$$  \hspace{1cm} (23)

The resulting value of the Gibbs free energy for Li$_3$FeN$_2$ at room temperature is -276.7 kJ mol$^{-1}$.

The next reaction is suggested for determination of stability against metallic lithium with subsequent calculation of the Gibbs free energy at room temperature:

$$3\text{Li} + \text{Li}_3\text{FeN}_2 = 2\text{Li}_2\text{N} + \text{Fe}$$  \hspace{1cm} (24)

To determine the Gibbs free energy of reaction it is required to subtract from $\Delta_f G_{298}^0$ of the reaction products values of the Gibbs energy for initial reagents. The $\Delta_f G_{298}^0$ for single elements is equal to zero, for Li$_2$N and is -128.6 kJ mol$^{-1}$ [20]. The Li$_3$FeN$_2$ Gibbs free energy has been determined above. Thus, the Gibbs free energy for reaction (24) is 19.5 kJ mol$^{-1}$ and this reaction is thermodynamically impossible. Finally, Li$_3$FeN$_2$ is stable against metallic lithium at room temperature.
5. Conclusions

The thermodynamic characteristics were determined for LiFeN₂: anode material for lithium-ion battery. Two-step synthesis method allowed to produce highly pure compound with less than 3%wt. of Li₂O impurity according to XRD data. The enthalpy of LiFeN₂ formation from binary nitrides was calculated according to the measured enthalphy of dissolution of reagents and product of LiFeN₂ formation reaction. The obtained value is equal to -206.5 ± 2.8 kJ mol⁻¹. The LiFeN₂ standard enthalpy of formation from elements is equal -291.3 ± 5.7 kJ mol⁻¹. This value can be used in further thermodynamic modeling and determinations.

The heat capacity value was recalculated taking into account presence of Li₂O impurity. The temperature dependence of the heat capacity is in good correlation with calculated by Neumann-Kopp rule. Finally, the heat capacity can be described by formula Cₚ(T) = 78,997+0,132 × T + 4.654×1⁰⁻²×T⁻², where T is absolute temperature. The LFN entropy is equal to 113.2 J mol⁻¹ K⁻¹, the Gibbs free energy of LiFeN₂ formation is -276,7 kJ mol⁻¹. Calculations confirm that LiFeN₂ material is stable against metallic lithium. All thermodynamic values and functions can be used for modelling and further calculations.

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