

## LITHIUM ION CONDUCTIVITY OF $\text{LiPN}_2$ and $\text{Li}_7\text{PN}_4$

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Received 29 January 1990; accepted for publication 15 February 1990

Single phase lithium phosphorus nitrides  $\text{Li}_7\text{PN}_4$  and  $\text{LiPN}_2$  were prepared by reaction of the binary nitrides  $\text{P}_3\text{N}_5$  and  $\text{Li}_3\text{N}$  at 620 and 800°C, respectively. The compounds were identified by X-ray powder diffraction techniques. The lithium ion conductivity of both compounds was investigated by complex impedance spectroscopy in the temperature range between 50 and 350°C. The specific conductivity was found to be  $\sigma(400\text{ K}) = 1.7 \times 10^{-5}$  and  $6.9 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$  for  $\text{Li}_7\text{PN}_4$  and  $\text{LiPN}_2$ , respectively. The activation energy was 46.7 kJ/mol for  $\text{Li}_7\text{PN}_4$  and 58.9 kJ/mol for  $\text{LiPN}_2$ .

### 1. Introduction

Lithium solid electrolytes are of considerable interest for the production of solid state lithium batteries. Among the class of binary and ternary lithium nitrides  $\text{Li}_3\text{N}$  has the highest lithium ion conductivity of about  $10^{-3} \Omega^{-1} \text{ cm}^{-1}$  [1]. However, the decomposition voltage of  $\text{Li}_3\text{N}$  has rather a low value of 0.44 V at room temperature, and it decreases rapidly with increasing temperature [1]. Thus the possible application of binary lithium nitride as a solid state electrolyte at elevated temperatures is limited. In order to compensate for this disadvantage several ternary lithium nitrides have been investigated and their lithium ion conductivity has been measured [2–6]. Aiming at a practical use of the compounds, ternary lithium nitrides containing the main group elements boron, aluminum, and silicon have been of particular interest [2–4].

Recently we have developed a new synthetic route for binary  $\text{P}_3\text{N}_5$  [7]. We have started to investigate systematically the quasi-binary system  $\text{Li}_3\text{N}-\text{P}_3\text{N}_5$ . As a result pure ternary lithium phosphorus nitrides have become accessible on a preparative scale. Single phase  $\text{LiPN}_2$  and  $\text{Li}_7\text{PN}_4$  have been prepared. Using the Rietveld method applied on X-ray powder diffraction data we were able to refine the crystal structure of both compounds [8,9]. The atomic ar-

rangement in  $\text{Li}_7\text{PN}_4$  resembles an anti-fluorite type of structure. In the solid the compound contains “isolated”  $\text{PN}_4$ -tetrahedra framed by lithium cations [8]. In  $\text{LiPN}_2$  a three-dimensional net of corner-sharing  $\text{PN}_4$ -tetrahedra is formed analogously to  $\beta$ -cristobalite. However, compared to  $\beta$ -cristobalite all  $\text{PN}_4$ -tetrahedra are rotated about their  $\bar{4}$  axes. Lithium cations occupy the remaining holes resulting in a chalcopyrite analogous type of structure [9]. Structural features of both  $\text{LiPN}_2$  and  $\text{Li}_7\text{PN}_4$  suggest a considerable lithium ion conductivity of these ternary phosphorus nitrides.

The present paper deals with the preparation of  $\text{LiPN}_2$  and  $\text{Li}_7\text{PN}_4$ . The lithium ion conductivity of both compounds has been investigated by means of complex impedance spectroscopy, and the results have been compared to those of other ternary lithium nitrides.

### 2. Experimental

Pellets of polycrystalline lithium phosphorus nitrides were prepared by reaction of  $\text{Li}_3\text{N}$  and  $\text{P}_3\text{N}_5$  of molar ratio 1:1 ( $\text{LiPN}_2$ ) and 7:1 ( $\text{Li}_7\text{PN}_4$ ). Each mixture was finely pulverized in an agate-ball mill and filled into the cylinder (material: graphite) of a hot press. During the reaction period of one hour the compounds were sintered to pellets of 10 mm in diameter and 2–4 mm in thickness under a pressure of

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$3 \times 10^6$  Pa at a reaction temperature of  $900^\circ\text{C}$ . The pellets were then cooled to room temperature. Graphite adhering to the surface of the pellets was abraded. Due to the sensitivity of  $\text{Li}_3\text{N}$  and  $\text{Li}_7\text{PN}_4$  against moisture all operations had to be carried out under carefully controlled inert conditions (nitrogen atmosphere). In order to complete the reaction and to obtain single phase products the pellets were heated in a tungsten boat under pure nitrogen atmosphere at  $800$  and  $620^\circ\text{C}$  for  $\text{LiPN}_2$  and  $\text{Li}_7\text{PN}_4$  respectively (reaction time: 24 h). The final pellets exhibited a pale yellowish-brown color and were micro-crystalline.

For the determination of the ac conductivity as a function of temperature and frequency a computer-controlled measuring system based on an HP 4192A impedance analyzer was used. The signal frequency ranged from 5 Hz to 10 MHz. The signal amplitude was 500 mV. Two springs were used to maintain permanent contact between the tungsten electrodes and the pellets. Thin silver films were evaporated onto the pellet surfaces. The cell was placed under inert atmosphere in a furnace. A Pt/Rh thermocouple was placed next to the sample to monitor the sample temperature. A detailed description of the measuring cell is given in [10].

### 3. Results and discussion

X-ray powder diffraction patterns of the materials obtained agreed well with the previous results and all diffraction peaks were indexed [8,9].

The complex impedance diagrams (190 measurements between 5 Hz and 10 MHz) of  $\text{LiPN}_2$  and  $\text{Li}_7\text{PN}_4$  each consist of a semicircle and a straight line. The real part of the minimum of the complex impedance at lower frequencies was taken as the total resistance of the sample. The complex impedance spectra were recorded in the temperature range between  $50$  and  $350^\circ\text{C}$  ( $\Delta T = 2^\circ\text{C}$ ). The conductivity  $\sigma$  of  $\text{LiPN}_2$  and  $\text{Li}_7\text{PN}_4$  as a function of the absolute temperature  $T$  is shown in fig. 1. In accordance with an Arrhenius-type behaviour of the diffusion coefficient of the moving species a linear relation of  $\log(\sigma T)$  versus  $1/T$  was observed indicating an activation energy of  $58.9$  and  $46.7$  kJ/mol for  $\text{LiPN}_2$  and  $\text{Li}_7\text{PN}_4$ , respectively. dc experiments with ionically

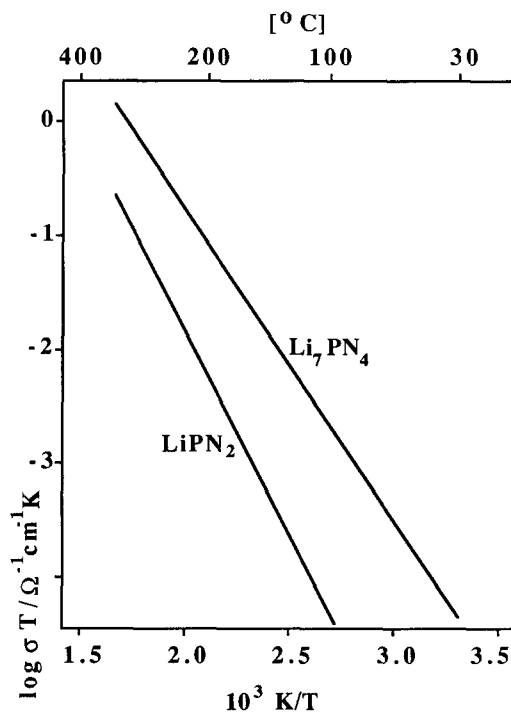


Fig. 1. Temperature dependences of ionic conductivity of  $\text{LiPN}_2$  and  $\text{Li}_7\text{PN}_4$ .

blocking, but electronically reversible, electrodes (tungsten) clearly indicated that the observed conductivity had to be attributed to a predominant transport of ionic species. In either case the electronic conductivity was less than 1% of the total conductivity.

$\text{Li}_7\text{PN}_4$  exhibits a lower activation energy and a higher ionic conductivity than  $\text{LiPN}_2$ . This marked difference should be discussed in relation to the respective crystal structure, the configuration around the lithium ions, and the number of charge carriers available. In both compounds the lithium cations are nearly tetrahedrally coordinated by nitrogen atoms with Li-N-distances of a similar size ( $\text{LiPN}_2$ : Li-N 209 pm;  $\text{Li}_7\text{PN}_4$ : Li-N 196-224 pm). According to its stoichiometry  $\text{Li}_7\text{PN}_4$  possesses a higher number of charge carriers available for ionic conduction than  $\text{LiPN}_2$ .  $\text{Li}_7\text{PN}_4$  resembles an anti-fluorite type of structure which can be formulated as a defect CsCl-type of structure. Thus a large number of interstitial sites can be occupied by the lithium cations. In con-

Table 1  
Lithium ion conductivity and activation energy of some ternary lithium nitrides

	$\sigma_{400\text{ K}}$ ( $\Omega^{-1}\text{ cm}^{-1}$ )	$E_a$ ( $\text{kJ mol}^{-1}$ )	Refs.
$\text{LiSi}_2\text{N}_3$	$1.9 \times 10^{-7}$	64	[4]
$\beta\text{-Li}_3\text{BN}_2$	$6.3 \times 10^{-7}$	64	[2]
$\text{LiPN}_2$	$6.9 \times 10^{-7}$	59	this work
$\text{Li}_3\text{AlN}_2$	$7.9 \times 10^{-6}$	52	[3]
$\text{Li}_7\text{PN}_4$	$1.7 \times 10^{-5}$	47	this work
$\text{Li}_8\text{SiN}_4$	$5.0 \times 10^{-4}$	46	[4]

trast, the closely packed atomic arrangement of  $\text{LiPN}_2$  has no interstitial positions comparable to those in  $\text{Li}_7\text{PN}_4$ . Therefore a higher ionic conductivity and a lower activation energy of  $\text{Li}_7\text{PN}_4$  seem to be quite reasonable.

In theory doping of  $\text{LiPN}_2$  with magnesium or oxygen according to the formulas  $\text{Li}_{(1-2x)}\text{Mg}_x(\text{V}_{\text{Li}})_x\text{PN}_2$  or  $\text{Li}_{(1-x)}(\text{V}_{\text{Li}})_x\text{PO}_x\text{N}_{(2-x)}$  ( $\text{V}_{\text{Li}}$  = vacancy in the cation lattice) should increase the conductivity of  $\text{LiPN}_2$ . At present appropriate experiments are being made.

As summarized in table 1 the ionic conductivity of  $\text{Li}_7\text{PN}_4$  is higher than that of  $\text{LiSi}_2\text{N}_3$ , and  $\text{Li}_3\text{AlN}_2$  while  $\text{Li}_8\text{SiN}_4$  has been reported to show the highest ionic conductivity of the ternary lithium nitrides mentioned above [4]. According to its stoichiometry  $\text{Li}_8\text{SiN}_4$  has the highest number of charge carriers. However, structural features of this compound cannot be discussed because  $\text{Li}_8\text{SiN}_4$  is only very poorly characterized. No structural data have been evaluated and so far only ambiguous diffraction patterns have been reported for this compound [4,11].

#### 4. Summary

Ternary lithium phosphorus nitrides  $\text{LiPN}_2$  and

$\text{Li}_7\text{PN}_4$  represent a new group of lithium ion conductors. The specific conductivity of  $\text{LiPN}_2$  ( $\sigma_{400\text{ K}} = 6.9 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$ ,  $E_a = 58.9 \text{ kJ/mol}$ ) and  $\text{Li}_7\text{PN}_4$  ( $\sigma_{400\text{ K}} = 1.7 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$ ,  $E_a = 46.7 \text{ kJ/mol}$ ) is comparable to that of other ternary lithium nitrides.

#### Acknowledgement

The authors would like to thank Prof. Dr. M. Jansen, University of Bonn, F.R.G., for his kind support as well as Prof. Dr. A. Rabenau and his staff at the Max-Planck-Institute for Solid State Research, Stuttgart, F.R.G., for technical assistance and also for the lithium nitride. This research was partly supported by the Fonds der Chemischen Industrie F.R.G. and by the Minister für Forschung und Wissenschaft – Nordrhein Westfalen (F.R.G.).

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