

CONSIDERATION OF LITHIUM NITRIDE HALIDES AS SOLID ELECTROLYTES IN PRACTICAL GALVANIC CELL APPLICATIONS

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Summary

The lithium nitride halides are fast, solid lithium ion conductors. Their potential use in practical battery type applications is discussed with emphasis on the kinetic, thermodynamic, and structural properties of lithium nitride chloride, $\text{Li}_9\text{N}_2\text{Cl}_3$. The general requirements of high decomposition voltage, absence of metallic dendrite formation during charge and discharge, low electronic transference number, and stability against reaction with lithium are fulfilled, in addition to fast ion transport and easy preparation and handling. The application of thin film solid electrolytes, *e.g.*, in integrated circuits, is proposed.

Introduction

Solid ion conductors are presently of particular interest for various practical applications. These, among others, include high energy and power density batteries, fuel cells, electrochromic displays, sensors or timers. Of predominant importance are lithium conductors, due to the low atomic weight of this element and to the high Gibbs free energies of formation of many of its compounds. This advantage has resulted in the discovery of a large number of fast, solid lithium ion conductors during the past decade. Some of the more important materials are: Li- β -alumina [1], Li_3N [2 - 4], Li_4SiO_4 - Li_3PO_4 solid solutions [5], LiAlCl_4 [6] and $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ (Lisicon) [7]. However, except for the long known LiI [8 - 10], which is commercially used in pacemaker batteries, none has shown a major breakthrough until now. The major difficulty which occurs is simultaneously matching a large variety of requirements necessary for successful long term operation of the solid electrolyte. It is likely that in some cases more time will be necessary for development.

The present paper presents our kinetic and thermodynamic results obtained for the ternary compounds in the systems lithium-nitrogen-chlorine, bromine and iodine. Special emphasis is placed on discussing the properties of these materials in the light of their technological use. Some proposals will be made with regard to cell designs and other factors influencing performance.

General considerations

Any galvanic cell consists of at least three phases which are in physical contact with each other: cathode, anode, and electrolyte. They have to co-exist in all discharge states of the electrodes without reacting with each other (not considering special systems which include this type of reaction in the overall electrochemical reaction). Even the formation of very thin reaction layers can result in serious problems, since the voltage is related to the difference in the chemical potential of the electroactive component at the transitions from ionic to electronic conduction, independent of the thicknesses of the phases present at these locations. On the other hand, it is expected that fast kinetic processes occur within the electrodes. Fast equilibration is required when the composition is locally changed by the transport of electroactive ions through the electrolyte. In addition, good "soft" contacts at the interfaces between the three phases are generally necessary in order to avoid large ionic transfer resistances. Because of the above mentioned reasons, the thermodynamic properties must be considered as important parameters having a large influence on the performance of the galvanic cell.

Since anodes and cathodes will be required which have large differences in the lithium activities, in the case of battery type application, high thermodynamic decomposition voltages of the electrolyte will be necessary. In addition, the lithium activity range ("stability window" [11]) has to include the activities of both electrodes. Generally, it is advantageous if the electrolyte exists in thermodynamic equilibrium with pure lithium, which is often considered as a convenient anode material. Slightly lower lithium activities may be sufficient in some cases when various lithium compounds or alloys, *e. g.*, Li-Al or Li-Si, are employed. This results, however, in a decrease of the energy density because of the lower lithium activity and the higher weight.

Though thermodynamic considerations are especially emphasized in this paper, kinetic requirements may not be disregarded. The partial electronic conductivity has to be orders of magnitude smaller than the ionic conductivity in order to avoid energy loss by self discharge of the galvanic cell. The ionic resistance has to be low enough to keep the ohmic polarization loss small compared with the e.m.f. of the cell. The situation may be generally improved by decreasing the thickness of the solid electrolyte, *e.g.*, by employing very thin sputtered or evaporated layers. It is obvious that thermodynamic stability of the electrolyte is most important in this case. The formation of small amounts of chemical reaction products may already cause a breakdown of the cell. Furthermore, the growth of short-circuiting metallic dendrites across the electrolyte is considered to be less severe in the case of isotropic crystal structures, in contrast to 2- or 1-dimensional ionic conductors.

In addition, several other factors must be considered for large scale fabrication. First of all, it should be easy and inexpensive to prepare the electrolyte, preferably in the shape of thin layers. It should be easy to handle the material without inconvenient precautions. It will be required that impurities do not change dramatically the thermodynamic and kinetic behaviour

of the electrolyte. Eventually, it will be advantageous to use polycrystalline pellets instead of single crystals without changing the characteristics of the electrolytic material.

Kinetic and thermodynamic properties of the lithium nitride halides

Lithium nitride, Li_3N , has shown high ionic conductivity along layers perpendicular to the crystallographic c axis [2, 3]. The material is, in addition, stable against reaction with elemental lithium. Some disadvantages are, however, the very low thermodynamic decomposition voltage of 0.44 V at room temperature [12, 13], the highly anisotropic structure, the large influence of impurities, and the sensitivity to air. This has led to the investigation of a series of related ternary compounds which may eliminate these limitations.

It is a common approach to alter the properties of solid cation conductors by partial substitution of the mobile component with other cations which often have a different valence. The purpose is to increase the disorder or to form new structures which show higher conductivities. This method turned out to be very successful, notably in the case of silver and copper conductors. The stability against pure silver or copper electrodes was generally unchanged for the mixture. A different situation holds in the case of lithium salts which are, in many cases, thermodynamically extremely stable (which is an important reason to consider lithium systems for energy storage). The dopant or added second salt (different cation, same anion) is typically less stable. Contact with elemental lithium will result in a reaction which displaces the dopant cation by lithium or a more complex reaction.

The approach employed in the present research was to substitute the anion (N) of the binary lithium salt (Li_3N) by other anions (Cl, Br, I). This does not change the stability against pure lithium since, in all cases, both binary salts (Li_3N and LiCl or LiBr or LiI) may exist in equilibrium with lithium, and no other ternary compounds of higher lithium content exist other than those along the quasi-binary cut Li_3N - LiCl , LiBr , LiI . In addition, the added lithium salts all have a much higher thermodynamic decomposition voltage than Li_3N . The room temperature (298 K) values are 3.98 V, 3.53 V and 2.80 V for LiCl , LiBr and LiI , respectively. The ternary lithium nitride halides will have decomposition voltages which are in between those of lithium nitride and the lithium halides. Accordingly, the use of the lithium halides will improve the thermodynamic properties compared with Li_3N . The precise values of the decomposition voltages of the ternary compounds are found experimentally, as reported later in this paper. The technologically most interesting salts allow cell voltages well above 2 V.

Previous investigations [14 - 16] have indicated the existence of two ternary compounds on the quasi-binary cuts Li_3N - LiCl , LiI , and three intermediate compounds in the case of Li_3N - LiBr . The compositions of all compounds are listed in Table 1. No other ternary compounds in the ternary

TABLE 1

Compilation of the compositions of all existing ternary phases in the systems $\text{Li}_3\text{N}-\text{LiX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)

System	Ternary phases		
$\text{Li}_3\text{N}-\text{LiCl}$	$\text{Li}_{11}\text{N}_3\text{Cl}_2$		$\text{Li}_9\text{N}_2\text{Cl}_3$
$\text{Li}_3\text{N}-\text{LiBr}$	$\text{Li}_{13}\text{N}_4\text{Br}$	$\text{Li}_9\text{N}_2\text{Br}_3$	Li_6NBr_3
$\text{Li}_3\text{N}-\text{LiI}$	$\text{Li}_{3x+1}\text{N}_x\text{I}$ ($1.89 < x < 2.76$)		Li_5NI_2

Gibbs triangles $\text{Li}-\text{N}-\text{Cl}$, Br , I have been observed. The most interesting lithium nitride halide of all is, for several reasons, lithium nitride chloride, $\text{Li}_{1.8}\text{N}_{0.4}\text{Cl}_{0.6}$ ($\text{Li}_9\text{N}_2\text{Cl}_3$). Therefore, most of this paper will be devoted to this compound. Detailed information on the other compounds may be found elsewhere [17 - 19]. Most arguments presented here are generally valid for the lithium nitride halides.

Lithium nitride chloride, $\text{Li}_{1.8}\text{N}_{0.4}\text{Cl}_{0.6}$, has a defect anti-fluorite structure with 10% vacancies in the partial lithium lattice. This fact is indicated by choosing the stoichiometric numbers of the compounds as indicated. The structural aspects are analogous to several well known oxygen and fluorine ion conductors, *e.g.* ZrO_2 doped with CaO :

Co-ordination

cubic	tetrahedral	
$\text{Zr}_{0.8}\text{Ca}_{0.2}$	$\text{O}_{1.8} \square 0.2$	fluorite structure O^{2-} conductor
$\text{N}_{0.4}\text{Cl}_{0.6}$	$\text{Li}_{1.8} \square 0.2$	anti-fluorite structure Li^+ conductor

The mobile ions are assumed to move along tetrahedral sites by a vacancy mechanism. The anti-fluorite and fluorite structures of the compounds do not exist in either case at ideal stoichiometric compositions when all the vacancies would be numerically filled. The stoichiometric width, Δx , of $\text{Li}_{1.8+x}\text{N}_{0.4+y}\text{Cl}_{0.6x-3y}$ is very small compared with $\text{Zr}_{0.2+y}\text{Ca}_{0.2+x-2y}\text{O}_{1.8+x}$.

Lithium nitride chloride solid electrolytes may be readily prepared by compressing intimate mixtures of commercially available Li_3N (*e.g.*, from Cerac) and LiCl powders (*e.g.*, from Fluka, Alfa Ventron, Cerac or Merck) in the molar ratio 2:3 into a pellet and sintering the pellet for about 24 h at approximately 430 °C. Alternatively, specimens may be prepared by melting a mixture of Li_3N and LiCl powder at 800 °C for about 30 min. under a nitrogen atmosphere or by passing a nitrogen gas stream with a chlorine partial pressure of the order of 10^{-7} atm at 330 °C over Li_3N powder. Another procedure consists of reacting lithium, suspended in mineral oil, with a mixture of nitrogen and chlorine gas bubbled through the liquid. It was observed that

the lithium nitride halides may be handled in dry air for extended periods of time without any noticeable reactions occurring.

The ionic conductivity, σ , of lithium nitride chloride, as determined by a.c. impedance techniques [20, 21], is shown in Fig. 1, together with results from measurements on the other lithium nitride halides. First order phase transitions are indicated by the dashed lines. A large dependence of the ionic conductivity upon the stoichiometry is seen for the two stoichiometries $\text{Li}_{9.11}\text{N}_{2.70}\text{I}$ and $\text{Li}_{6.67}\text{N}_{1.89}\text{I}$ of the same phase. The activation enthalpy of 0.49 eV for the product of the ionic conductivity and the absolute temperature, *i.e.*, the sum of the activation enthalpies of the diffusion coefficient and the concentration of the mobile ionic species, is among the lowest for $\text{Li}_{1.8}\text{N}_{0.4}\text{Cl}_{0.6}$, compared with the other lithium nitride halides. The straight lines tend to intersect the conductivity axis roughly at about the same value. This indicates about the same attempt frequencies for the jumps of the mobile ionic species or defects, independent of compositional and structural parameters.

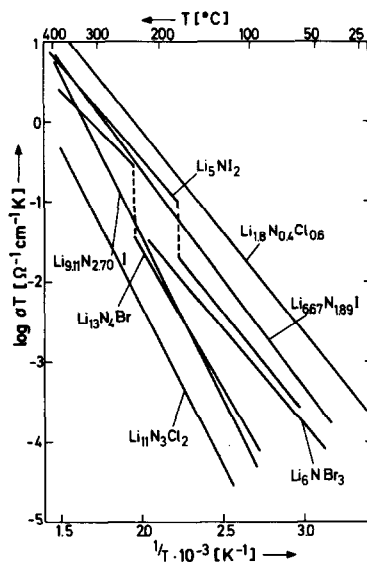


Fig. 1. Semilogarithmic representation of the product of the ionic conductivity, σ , and the absolute temperature, T , as a function of the reciprocal absolute temperature for all lithium nitride chlorides, - bromides and - iodides. The dashed lines indicate first order phase transformations. The compositions $\text{Li}_{9.11}\text{N}_{2.70}\text{I}$ and $\text{Li}_{6.67}\text{N}_{1.89}\text{I}$ indicate compounds that belong to the same nonstoichiometric phase.

The mobile ionic species were determined to be lithium ions by transference and e.m.f. measurements. Elemental lithium was pasted on one side of a lithium nitride chloride pellet of about 1 cm in diameter and 0.2 cm in thickness. A molybdenum sheet was provided at the opposite site as an electronic lead. Passing an electric current of $10 \mu\text{A}/\text{cm}^2$ to $10 \text{mA}/\text{cm}^2$ through

this galvanic cell has resulted in the quantitative deposition of lithium in the space between the sample and the molybdenum sheet according to the charge flux. Lithium has filled up the available cavities at the interface, but no dendrites or other signs of short circuiting the lithium nitride chloride have been detected after several weeks. The applied potential was kept below about 1 V in order to avoid decomposition of the sample. The e.m.f. experiment has made use of TiS_2 pellets instead of the molybdenum sheet in an otherwise identical cell arrangement. The observed potential agrees with the value reported by other authors who have used liquid organic electrolytes instead of $\text{Li}_{1.8}\text{N}_{0.4}\text{Cl}_{0.6}$ [22].

The partial electronic conductivity was measured by the Hebb–Wagner polarization technique [23 - 25] with the same experimental galvanic cell arrangement as in the lithium transference experiment. A reverse polarity of the applied potential was employed, however, to allow only the electrons and holes to be transferred under steady state conditions. It was found that the electronic transference number of the samples employed was always smaller than 10^{-4} at unity lithium activity over the entire temperature range investigated.

The thermodynamic properties related to the formation of $\text{Li}_{1.8}\text{N}_{0.4}\text{Cl}_{0.6}$ have been determined from the current–voltage relation obtained with the same cell configuration as in the Hebb–Wagner polarization experiment, by extending the range of applied cell potentials to values higher than the decomposition voltage. A linear ohmic increase of the current with the voltage was observed eventually. The charge carriers in this range are predominantly lithium ions instead of electrons. The straight line intersects the voltage axis at, e.g., 2.52 V at 100 °C and 2.21 V at 330 °C. Approximately the same values have been observed as cell potentials after switching off the external circuit. These decomposition voltages relate to the minimum lithium activities, according to Nernst's equation, at which the lithium nitride chloride may be thermodynamically stable corresponding to the 3-phase equilibrium $\text{Li}_{1.8}\text{N}_{0.4}\text{Cl}_{0.6}$ – LiCl – N_2 in the Gibbs triangle of the system Li – N – Cl , as shown in Fig. 2. With knowledge of the thermodynamic properties of LiCl , the Gibbs energy

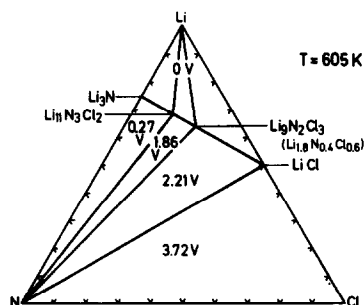


Fig. 2. Ternary phase diagram (Gibbs triangle) of the system Li – N – Cl . Numbers in the triangles of 3-phase equilibrium indicate the voltage of a galvanic cell with a lithium electrolyte using the corresponding 3-phase mixture as an electrode and an elemental lithium reference electrode.

of formation of lithium nitride chloride may be calculated, and a wide variety of thermodynamic data derived from the temperature dependence. Some selected results obtained in this manner are listed in Table 2. It is seen from Fig. 2 that lithium nitride chloride may be in thermodynamic equilibrium with elemental lithium without another phase or together with LiCl or $\text{Li}_{11}\text{N}_3\text{Cl}_2$. The stability with lithium was, in addition, checked experimentally by immersing lithium nitride chloride pellets in molten lithium. No visible reaction product or change of the X-ray powder pattern of the sample have been observed.

TABLE 2

Compilation of some important thermodynamic properties of the ternary lithium nitride halides

$a_{\text{Li}}^{\text{min}}$: minimum lithium activity; $p_{\text{Hal}_2}^{\text{min,max}}$: minimum, maximum equilibrium partial pressures of the halides at which the phase is thermodynamically stable; ΔG_f° : Gibbs free energy of formation from the elements under standard conditions. LT: low temperature phase; HT: high temperature phase

Compound	$\log a_{\text{Li}}^{\text{min}}$	$\log p_{\text{Hal}_2}^{\text{min}}$ (atm)	$\log p_{\text{Hal}_2}^{\text{max}}$ (atm)	ΔG_f° (kJ/g at.)	T (°C)
$\text{Li}_9\text{N}_2\text{Cl}_3$	-18.5	- 18.6	- 6.3	-185	332
$\text{Li}_{11}\text{N}_3\text{Cl}_2$	-15.5	-109	-10.7	-154	332
Li_6NBr_3	-11.8	- 16.8	- 8.7	-135	300
$\text{Li}_9\text{N}_2\text{Br}_3$	- 9.1	- 19.3	-11.4	-118	300
$\text{Li}_{13}\text{N}_4\text{Br}$ (LT)	-15.9				146
$\text{Li}_{13}\text{N}_4\text{Br}$ (HT)	- 5.8	- 49.0	-17.4	- 66	300
Li_5NI_2 (LT)	-26.6			-138	98
Li_5NI_2 (HT)	-14.7	- 16.6	- 4.7	-124	287
$\text{Li}_{3x} + {}_1\text{N}_x\text{I}$ (1.89 < x < 2.76)	- 7.9	- 50.0	-12.7	- 90	300

Discussion

Fast, predominantly ionic conduction in the solid state, in conjunction with a wide thermodynamic stability range with regard to lithium, *i.e.*, the high decomposition voltage of substantially more than 2 V, are essential fundamental features for the potential practical application of lithium nitride chloride in energy storage devices. In addition, several other properties support this prospect. The extremely small electronic conductivity at all lithium activities will allow extremely long shelf lives compared with most presently available systems. Tendencies for internal short-circuits of the electrolyte by metallic dendrite formation are small due to the isotropy of the structure. The material is easy to prepare and handle. Elemental lithium may be used as anode material, which is obviously matchless with regard to weight, activity of the electroactive component, and softness. Several poten-

tial cathode materials may be drawn from the present state of the art reported in the literature. TiS_2 has been employed tentatively in the course of our investigation. No chemical reaction with $\text{Li}_{1.8}\text{N}_{0.4}\text{Cl}_{0.6}$ was observed over a period of several days. A disadvantage of TiS_2 may be seen, however, in the very low chemical diffusion coefficient in this material.

Only the lithium ion conduction of Li_3N [2 - 4] and of $\text{Li-}\beta\text{-alumina}$ [1] are markedly higher than for $\text{Li}_{1.8}\text{N}_{0.4}\text{Cl}_{0.6}$ in the lower range of temperatures investigated. However, both are layered compounds, the thermodynamic stability range of Li_3N is very low (0.445 V at 25 °C), and $\text{Li-}\beta\text{-alumina}$ reacts with elemental lithium and is not thermodynamically stable. If an application of these materials is possible at all, specimens have to be used which are thick enough to retain an electrolytic separation of the electrodes. By contrast, lithium nitride chloride may be employed as a thin layer which will remain unchanged due to its thermodynamic stability. The relevant electrical resistance of the electrolyte will be sufficiently low, even at room temperature, because of this geometrical reason. It should be possible to sputter or evaporate lithium nitride chloride onto an anode or cathode substrate because the material melts congruently at 710 °C. In addition, several other techniques may be taken into consideration, especially because of known ranges of nitrogen and chlorine equilibrium partial pressures of the compound. It appears feasible to produce galvanic cells containing lithium nitride chloride solid electrolytes as integrated components in modern electric circuits.

In addition, it is attractive to consider lithium nitride chloride for application at medium temperatures when the ionic conductivity is higher than in the cases of Li_3N and $\text{Li-}\beta\text{-alumina}$. The melting point (710 °C) is sufficiently high for this purpose.

Several other types of application of lithium nitride chloride solid electrolytes may be taken into account beside primary and secondary batteries, e.g., electrochromic displays, long term stable memory elements or timers. Some of the requirements valid for battery applications, as described above and fulfilled in the case of $\text{Li}_{1.8}\text{N}_{0.4}\text{Cl}_{0.6}$, will be less severe in these cases.

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