

Ionic Conductivity of Solid and Molten Lithiumthiocyanate and Its Hydrate

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Lithium ion conducting solids have potential uses as solid electrolytes in Li-batteries and in other electrochemical devices.¹ The monohydrates of lithium iodide, bromide and chloride have solid electrolyte properties, and have been studied by us^{2,3} and others in recent years.⁴⁻⁶ Surprisingly, no other of the alkali metal halides form stable monohydrates at ambient temperatures. However, the existence of $\text{LiSCN} \cdot \text{H}_2\text{O}$ has been reported,⁷ and it was found of interest to subject this compound as well as LiSCN to a conductivity study in the solid state.

Experimental. $\text{LiSCN} \cdot x\text{H}_2\text{O}$ (Ventron) was dried 48 h at 200 °C in vacuum. The material was thereafter transferred to an Ar-filled drybox. The samples with 50 and 66.7 mol % water of hydration were made by mixing the dried LiSCN with stoichiometric amounts of water in sealed pyrex ampoules. Conductivity measurements were made in sealed calibrated pyrex cells with tungsten electrodes.²

The measuring procedure was as follows: 1–2 g of powder was loaded into the cell, which in turn was flame-sealed under $\frac{1}{3}$ atm of pure argon. The cell was heated to above the melting point of the LiSCN -material. The cell was then allowed to cool, whereby the material generally solidified around the two W-wire electrodes (approx. 10 mm long, 1 mm diameter). Repeated heating and cooling experiments could be carried out with the same cell.

Ac-conductivities were determined by a Solartron 1174 frequency response analyser controlled by a PDP 11/23 computer system. The admittance was measured between 1 Hz and 1 MHz with an applied voltage of 50 mV.

The derived dc bulk conductivity was obtained by standard equivalent circuit analysis of the complex admittance data.

X-Ray data were obtained with a Philips PW 1050 diffractometer using Ni filtered $\text{CuK}\alpha$ radiation. The samples were contained in a tight container with a polyethylene window.

Results. X-Ray examination of materials. The powder patterns of anhydrous LiSCN and of $\text{LiSCN} \cdot 2\text{H}_2\text{O}$ are given in Table 1. The pattern of as-received material and of material with a nominal composition corresponding to the monohydrate phase were both simple superpositions of the patterns of the anhydrous and the dihydrate phase. Three different attempts were made in order to produce the monohydrate phase reported by Nikolaev:⁷

- (i) A $\text{LiSCN}-\text{H}_2\text{O}$ mixture (1:1) was slowly cooled from 200 to 25 °C.
- (ii) Some material was annealed at 40 °C for one week;
- (iii) Some 1:1 material was dissolved in ethanol and subsequently dried under vacuum at 35 °C.

None of these materials contained any new phases. We thus assume that the monohydrate phase was not present in the samples used for conductivity measurements.

The crystal structures of LiSCN and $\text{LiSCN} \cdot 2\text{H}_2\text{O}$ have never to our knowledge been reported. The complexity of the diffraction patterns indicates a low crystal symmetry of both compounds.

Conductivity measurements. LiSCN. The sealed conductivity cell was heated to above the melting point of the salt (found by a DSC-measurement to be approx. 277 °C). The conductivity of molten LiSCN was ~ 0.4 S/cm which is typical of molten salts. The conductivity of the solidified material dropped dramatically with decreasing temperature, cf. Fig. 1. Two conductivity regimes were observed with a "knee" temperature around 190 °C. The energy of activation for conduction obtained from a $\log \sigma$ versus $1/T$ fit was 0.8 eV between 100 and 150 °C and 1.8 eV for the region between 190 and 260 °C.

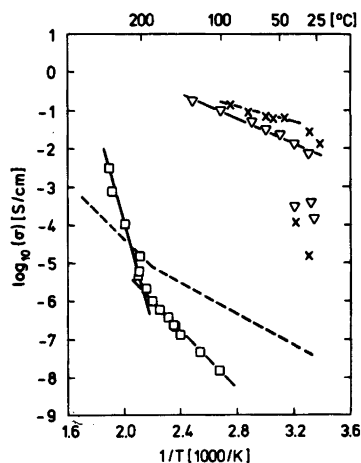


Fig. 1. Specific conductivity of LiSCN-H₂O samples from ac-measurements. (Key: □: LiSCN; ▽: LiSCN/H₂O=1; X: LiSCN·2H₂O. Dashed curve is for polycrystalline LiI.²

The conduction appeared to be ionic in nature since no dc-current could be passed at an applied voltage of 100 mV.

Conductivity data² for polycrystalline LiI, which is the best Li-ion conductor among the lithium halides,¹ are included in Fig. 1 (dashed curve). It can be seen that LiSCN has a higher activation energy for conduction both in the high and low temperature regions than LiI (and any of the remaining lithium halides).¹ Due to these high energies of activation

Table 1. X-ray powder diffraction data. CuK_α-radiation. Samples were kept in argon under a polyethylen window.

LiSCN		LiSCN·2H ₂ O	
<i>d</i> (Å)	<i>I</i> _{rel} (%)	<i>d</i> (Å)	<i>I</i> _{rel} (%)
4.79	14		
3.79	5	3.75	< 1
3.16	58	3.64	31
2.96	51	3.36	< 1
2.72	100	3.26	19
2.61	44	3.14	17
2.57	7	3.05	< 1
2.36	9	2.93	74
2.14	4	2.91	98
2.03	14	2.70	100
1.99	4	2.64	48
1.91	5	2.61	38
1.88	14	2.48	36
1.78	5	2.42	50
1.70	5	2.40	81
1.69	5	2.31	17
1.63	9	1.89	52
1.53	9	1.65	26
1.45	4	1.59	33
1.44	4	1.43	14
1.34	7		
1.23	9		

LiSCN turns out to have a higher conductivity between 200 °C and its melting point, *i.e.* $\sigma \sim 3 \cdot 10^{-3}$ S/cm at 250 °C, than found for any of the Li-halides. On the other hand, the extrapolated room temperature specific conductivity, σ_{25} of LiSCN, amounts to only $\sim 2.5 \cdot 10^{-11}$ S/cm (assuming a linear log (σ) vs. $1/T$ relationship to hold).

LiSCN-H₂O (1:1 and 1:2). Samples with a nominal composition corresponding to a mono- and di-hydrate, respectively, both show a strong tendency to supercool down to room temperature. A 1:1 sample has a solid appearance around room temperature due to precipitation of LiSCN. As can be seen from Fig. 1 very high conductivities, 10^{-2} – 10^{-1} S/cm, and low activation energies, 0.16–0.33 eV, are obtained above ~ 30 °C indicating that a liquid conductive phase, *i.e.* molten LiSCN-hydrate, must be present.

The high degree of scatter in the conductivity around 20–30 °C was due to this partial crystallisation of the samples. The incongruent melting point of LiSCN · 2H₂O is reported to be at 34 °C.⁷ Storing the samples at –20 °C for several days allowed the material to crystallise. It did not prove possible to establish an Arrhenius behaviour for either of the crystallised samples.

Conclusions. The monohydrate of LiSCN could not be prepared. The temperature variation of the conductivity of anhydrous LiSCN has some resemblance to the lithium halide family, irrespective of the fact that LiSCN has a different structure. The conductivity of LiSCN below the melting point of Li-metal (179 °C) is too low for the compound to be useful in solid electrolyte batteries. The X-ray powder diffraction patterns of LiSCN and LiSCN · 2H₂O are reported for the first time.

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