CONDUCTIVITY OF LiAlCl$_4$ SOLUTIONS IN NITROMETHANE CONTAINING SO$_2$

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Summary

The concentration and temperature (−30 to +25 °C) dependence on the conductivity of LiAlCl$_4$ solutions in nitromethane containing 25 and 50 wt.% SO$_2$ is studied in view of the possible use of these solutions in Li/SO$_2$ cells. The conductivity of the 1.2 molal LiAlCl$_4$ solution in nitromethane with 50 wt.% SO$_2$ in the whole temperature range is similar to that of 1M LiBr solution in acetonitrile with 70 wt.% SO$_2$, currently used in Li/SO$_2$ cells.

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1. Introduction

The excellent power performance of Li/SO$_2$ cells over a wide range of temperatures is mainly due to the high conductivity of the electrolyte solution containing 1M LiBr dissolved in a mixture of acetonitrile and sulphur dioxide in a weight ratio of 1:3 [1, 2]. This electrolyte solution, however, has exhibited some drawbacks which have resulted in a search for suitable substitutes [3 - 7]. The principle disadvantage of the presently used electrolyte composition is the strong reactivity between Li and acetonitrile (AN) when the SO$_2$ concentration is very low at the end of a cell discharge [8 - 10]. Methane is thought to be one of the reaction products, which may cause venting or, in extreme cases, explosion and fire [10]. Shah [9] showed that the system was unstable, the electrolyte, even at moderate temperatures (40 - 50 °C), becoming darker and depositing sediments of various colours. Fortunately, in the case of the Li/SO$_2$ cell, this process is inhibited in the presence of Li.

It has also been shown by Dey *et al.* that the conductivity of the AN electrolyte solution decreases when it is aged at 70 °C, and even at room temperature [6]. Another important drawback is that discharged D-size Li/SO$_2$ cells may contain up to 22 mg of CN$^-$ ions [11], which aggravates the problem of disposal of discharged cells.

The problem is that there are very few aprotic solutions of Li salts with a conductivity approaching that of LiBr + AN + SO_2 which are free from similar disadvantages. From the 17 candidate electrolytes containing 1M LiBr and 70 wt.% SO_2 in various organic solvents and their mixtures considered by Dey [7], only 8 exhibited higher or equal specific conductivity (κ) to that of the "standard" solution containing 23 wt.% AN. All 8, however, contained from 11 to 20 wt.% AN, implying that the problems concerning safety, reliability, and toxicity would not be completely resolved. A partial solution is the use of the AN solvent with the expensive and highly toxic $LiAsF_6$, which, however, has a lower specific conductivity [9].

A review of the literature on nonaqueous electrolytes with Li salts revealed that solutions of $LiAlCl_4$ in nitromethane have comparatively high conductivities. According to Timofeeva *et al.* [12] the specific conductivity of 2.2M $LiAlCl_4$ in nitromethane (NM) is 33 mho/cm at 25 °C. A similar solution was used in the reserve $Li/CuCl_2$ cells [13] where a current density of 100 mA/cm² was reached. The salt, $LiAlCl_4$, is available, nontoxic, and is successfully employed in $Li/SOCl_2$ primary cells. As seen in Table 1 most of the physicochemical properties of NM are close to those of AN [14].

Preliminary experiments revealed that NM is miscible with SO_2 at all ratios and that solutions with 50 wt.% SO_2 are in equilibrium at room temperature and at atmospheric pressure. Recent work by Bakhvalov *et al.* has shown that there is evidence of decomposition yielding HCl, LiCl, and some complex ions at 50 °C [15]. These results mean that the kinetics of the decomposition reaction must be studied further and that some inhibitor must be found. The effect the decomposition products have on the performance of Li/SO_2 cells filled with solutions of $LiAlCl_4$ in NM with SO_2 will also need to be investigated. It was not, however, considered necessary to delay the publication of the results presented below.

The aim of the work described in this paper was to study the temperature and concentration dependences of the conductivity of $LiAlCl_4$ in NM + SO_2 solutions as a first step towards assessing their applicability in Li/SO_2 cells. No studies were made of the explosion hazards of NM strongly diluted by SO_2, however, and these would have to be considered prior to the use of this solvent in a lithium cell.

TABLE 1

Physicochemical properties of acetonitrile and nitromethane

	Mol. weight	d_{25} (g cm^{-3})	M.P. (°C)	B.P. (°C)	n_d^{20}	Visc. (cP)	Diel. const.	Flash point (°C)	MAK (mg/m³)
AN	41.05	0.787	−45.2	80.06	1.3423	0.341	37.5	2	70
NM	61.0	1.131	−28.5	101.2	1.3819	0.610	35.9	40	250

2. Experimental

2.1. Materials

These were prepared as given below:

NM (Fluka) was dried with molecular sieves to a water content of less than 50 ppm.

LiCl (Merck) was vacuum dried at 380 °C to a water content of less than 25 ppm.

$AlCl_3$ (Fluka) was twice sublimed at 200 °C in a train of dry Ar.

$LiAlCl_4$ was obtained by melting equimolar amounts of the dried, simple salts at 180 °C for 2 h in an evacuated, sealed ampoule.

SO_2 was liquified under pressure for more than 48 h in a stainless steel vessel containing molecular sieves. It was then distilled in a similar vessel with molecular sieves and after 24 h its water content was reduced below 25 ppm.

The water content of all of the electrolyte solutions studied was less than 80 ppm.

2.2. Measurements

Conductivities were measured in a jacketed glass cell with smooth Pt electrodes and a constant of 2.04 cm^{-1} using a Wayne Kerr autobalance bridge at 1592 Hz.

The cell temperature was maintained with an accuracy of better than ±0.1 °C using a methanol filled cryostat.

3. Results and discussion

Initially it was found that at 25 °C mixtures of NM with 25 and 50 wt.% SO_2 can dissolve as much as 3.5 m of $LiAlCl_4$ and that the conductivity of $LiAlCl_4$ in NM + 50 wt.% SO_2 is approximately twice that of $LiAlCl_4$ in pure NM over its whole concentration range, as shown in Fig. 1. This higher specific conductivity could be assigned either to changes in the viscosity and the dielectric constant of the solvent or to a decrease in the association constant of the salt resulting from the dipole–ion interaction.

The conductivity of $LiAlCl_4$ in mixtures of NM + SO_2 was studied in the concentration range from 0.2 to 2.0 m (molal concentration) at temperatures from −35 to 25 °C. Only two concentrations of SO_2 were used: 25 and 50 wt.% since, at room temperature, solutions with the highest practically used concentration of SO_2 (70 wt.%) are only stable at pressures above 3 atmospheres.

The conductivity as a function of temperature for several concentrations of $LiAlCl_4$ solutions in NM with 25 wt.% SO_2 is presented in Fig. 2. The plots are almost linear with a slope increasing with the salt concentration. Figure 3 shows the effect of concentration on the specific conductivity, with temperature as a parameter. These plots have broad maxima with the
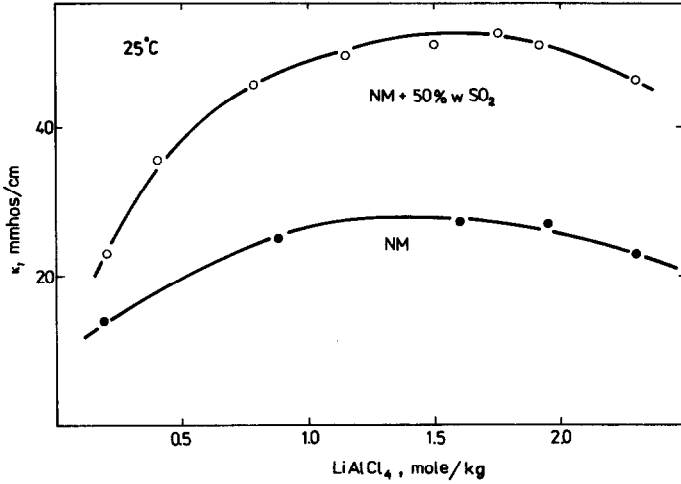
Fig. 1. Concentration dependences of the specific conductivity (κ) of LiAlCl$_4$ solutions in NM and NM with 50 wt.% SO$_2$.
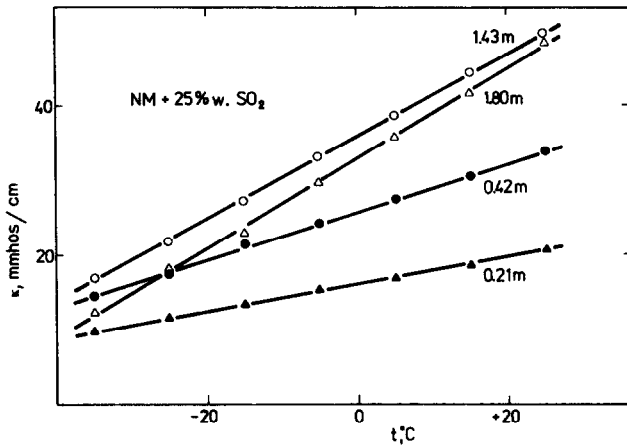

Fig. 2. Temperature dependences of the specific conductivity, κ, of LiAlCl$_4$ solutions at different molar concentrations in NM with 25 wt.% SO$_2$.

maximum specific conductivity (C_m) and the concentration at which it occurs increasing with temperature (indicated by the dotted line).

Similar temperature and concentration dependencies were plotted for a series of LiAlCl$_4$ solutions in NM with 50 wt.% SO$_2$, as Figs. 4 and 5 show. The results are quite similar. The increase in the SO$_2$ concentration from 25 to 50 wt.% causes only a 2 - 5% increase in the maximum specific conductivity. Hence, it is probable that increasing the SO$_2$ concentration to 70 wt.% will not appreciably affect the specific conductivity of the LiAlCl$_4$ solutions.
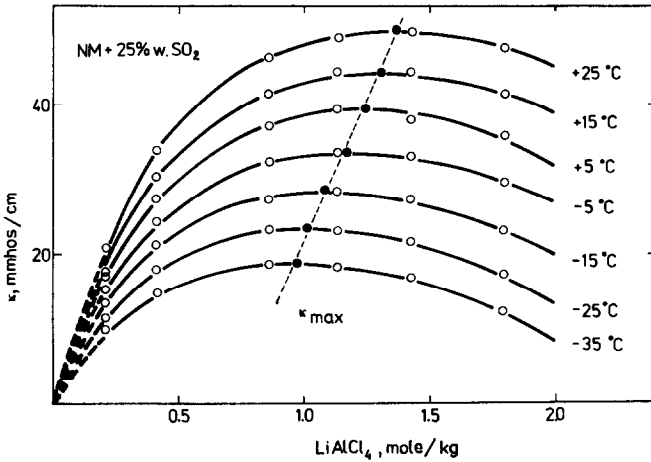
Fig. 3. Concentration dependences of the specific conductivity (κ) of LiAlCl$_4$ solutions in NM with 25 wt.% SO$_2$ at different temperatures.
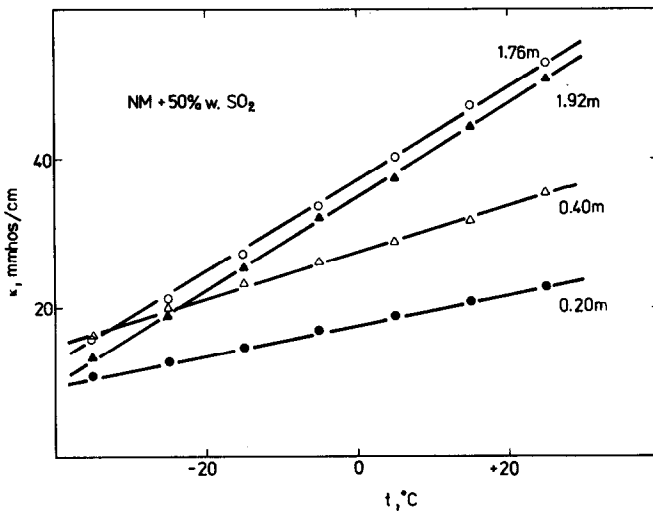

Fig. 4. Temperature dependences of the specific conductivity, κ, of LiAlCl$_4$ solutions in NM with 50 wt.% SO$_2$ at different concentrations.

The small effect which the SO$_2$ concentration has on the conductivity in the range 25 - 50 wt.% SO$_2$ implies that the ohmic voltage losses in a cell during discharge will not increase significantly.

From Figs. 3 and 5 the optimum LiAlCl$_4$ concentration needed to ensure a fast ion transport over the temperature range studied can be shown to be an ~1.2 molal LiAlCl$_4$ solution, as this deviates least from the maximum specific conductivity value between −35 and +25 °C.
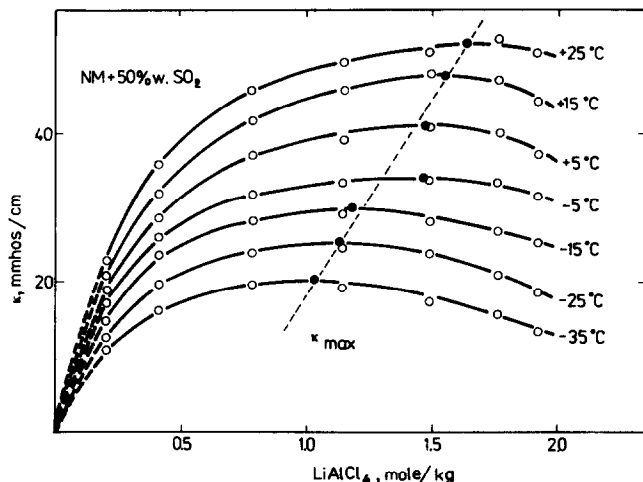
Fig. 5. Concentration dependences of the specific conductivity, κ, of LiAlCl$_4$ solutions in NM with 50 wt.% SO$_2$ at different temperatures.

The specific conductivity of the 1M LiAlCl$_4$ solution in NM with 50 wt.% SO$_2$ in the temperature range -35 to $+25$ °C is compared with that of the "standard" electrolyte, 0.73M LiBr in AN with 70 wt.% SO$_2$ [6], and with that of a 1M LiBr solution in AN with 50 wt.% SO$_2$ in Fig. 6. There is no significant difference in the conductivities of the solutions with 50 wt.% SO$_2$ despite the solvent and the solute differences. Compared with the 0.73M LiBr in AN with 70 wt.% SO$_2$, however, the 1M LiAlCl$_4$ in NM with 50 wt.% SO$_2$ has a slightly higher specific conductivity at 25 °C and is slightly lower at -35 °C.
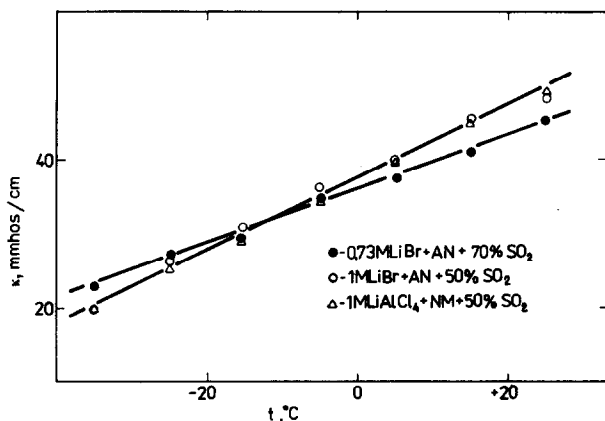

Fig. 6. Temperature dependences of the specific conductivity, κ, of: ●, 0.73M LiBr in AN with 70 wt.% SO$_2$; ○, 1M LiBr in AN with 50 wt.% SO$_2$; △, 1M LiAlCl$_4$ in NM with 50 wt.% SO$_2$.

The high conductivity of $LiAlCl_4$ in NM with SO_2 seems to justify further investigation of its stability, safety, and electrochemical parameters as an electrolyte in practical Li/SO_2 cells. Preliminary experiments have revealed that Li forms a thin, passivating film in this solution and a very thick, and highly resistive film in $LiAlCl_4$ solutions in NM without SO_2. This suggests that the Li anode will not react with the electrolyte at the end of the discharge as in the case of the LiBr + AN system.

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