

## CHLORIDE SPINELS: A NEW GROUP OF SOLID LITHIUM ELECTROLYTES

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**Abstract**—The chloride spinels  $\text{Li}_2\text{MCl}_4$  with  $\text{M} = \text{Mg, Mn, Fe and Cd}$  show very high lithium ionic conductivity in the solid state. The ionic conductivity in the compounds under investigation was established with the help of emf measurements. The specific conductivities measured by both frequency response analysis and the four probe ac method are  $1.3 \Omega^{-1} \cdot \text{cm}^{-1}$  for  $\text{Li}_2\text{CdCl}_4$ , and about  $0.9 \Omega^{-1} \cdot \text{cm}^{-1}$  for  $\text{Li}_2\text{MnCl}_4$ ,  $\text{Li}_2\text{MgCl}_4$ , and  $\text{Li}_2\text{FeCl}_4$  at 773 K. There are several indications that the ternary chlorides become highly disordered at elevated temperatures. Thus the Arrhenius plots, i.e.  $\ln \sigma \cdot T$  vs  $1/T$ -curves, exhibit significant bends, the slopes below the transition temperature being considerably higher than those above.

### INTRODUCTION

Since there are many potential applications of solid lithium electrolytes in the field of storing electric energy, a great deal of work has been done in recent years towards finding new materials suited for these purposes. As Pizzini[1] demonstrated in 1971, the spinel structure should be a suitable structure for compounds which are possibly good lithium conductors. In 1975, van Loon and de Jong[2] reported on four ternary chlorides  $\text{Li}_2\text{MCl}_4$  ( $\text{M} = \text{Mn, Cd, Mg, Fe(II)}$ ), which have an inverse spinel structure at room temperature. As we reported elsewhere[3], most of these compounds show an order-disorder phase transition. In order to confirm our interpretation of the observed phase transition as disordering of the cation sublattices, we have begun measurements of the electric properties of the chloride spinels. Since the inverse spinel structure has a high degree of intrinsic disorder, high ionic conductivity can be expected. With the intention of proving whether the electric conductivity is ionic or electronic in nature, we have determined the emf of a solid state galvanic cell with the compound serving as an electrolyte[4].

### 2. EXPERIMENTAL METHODS

The compounds were prepared according to van Loon and de Jong[2] by fusing the anhydrous binary chlorides in ampoules made from Duran glass at temperatures above the melting point on a vacuum line of  $10^{-7}$  bar. The ampoules were sealed under vacuum and the contents fused again, with subsequent slow cooling to room temperature at a rate of 5 K/hr. The anhydrous binary chlorides can be prepared by heating the hydrates in a stream of dry HCl-gas slowly up to at least 600 K. Cadmium chloride and manganese chloride are also commercially available with sufficient purity. Monocrystals of the chloride spinels can be obtained with the Bridgman-Stockbarger technique and the following conditions: furnace temperature 10 K above the melting point of the compound, pulling speed 3 mm/hr, ampoule diameter 10 mm.

The electrical conductivity of the compounds was measured by two methods: (i) by inspection of the com-

plex admittance in the frequency range from 5 Hz to 500 kHz and (ii) by a four-probe a.c. method. For both methods the same cell, made from Duran glass, was used, since this material is only slowly affected by the molten substances. The electrodes were made from platinum wire 2 mm in diameter. They showed only very little corrosion after several runs in the space of a few months. The cell was filled with powdered sample under a dry, inert atmosphere. After introducing the platinum electrodes and the thermocouple, the sample was melted and slowly cooled to form one large crystal, which made good contact with the electrodes. The cell constant was obtained by calibration with an aqueous NaCl solution of  $100 \text{ mol} \cdot \text{m}^{-3}$ .

For measurement of the complex impedance (or the complex admittance) a vector impedance meter (Hewlett-Packard model hp 4800 A) was used. The four-probe measurements were made using a LCR-meter (Hewlett-Packard 4261 A). The thermocouple voltage and the resistance were recorded automatically. The temperature of the furnace was controlled by a programmable temperature regulator. The emf. of the cell  $\text{Li}_{(1)}/\text{Li}_2\text{CdCl}_{4(s)}/\text{Cl}_{2(g, 1 \text{ bar})}$  was measured by the Pogendorf compensation method. The experimental design of this cell is shown in Fig. 1.

### RESULTS AND DISCUSSION

The results found for the frequency dependence of the complex admittance are presented in Fig. 2. Analysis of the semi-circles obtained in the complex admittance plane results in equivalent circuit representations of the types shown in Fig. 3 (for the method of analysis see Bauerle[5]).

The series capacitor  $C$  represents the double layer of the "blocking type" electrodes, and the ohmic resistor  $R$  is to be interpreted as that of the solid electrolyte. At low temperatures and hence low conductivity, the cell capacity  $C_c$  and the insulation resistance  $R_i$  contribute to the frequency dependence of the complex admittance; whereas at high temperatures and hence high conductivity of the sample, the complex admittance is determined only by  $R$  and  $C$ . The conductivity of the sample

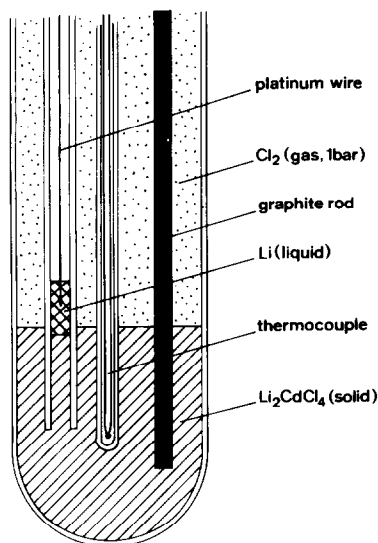


Fig. 1. Schematic sketch of the cell used for determination of the emf.

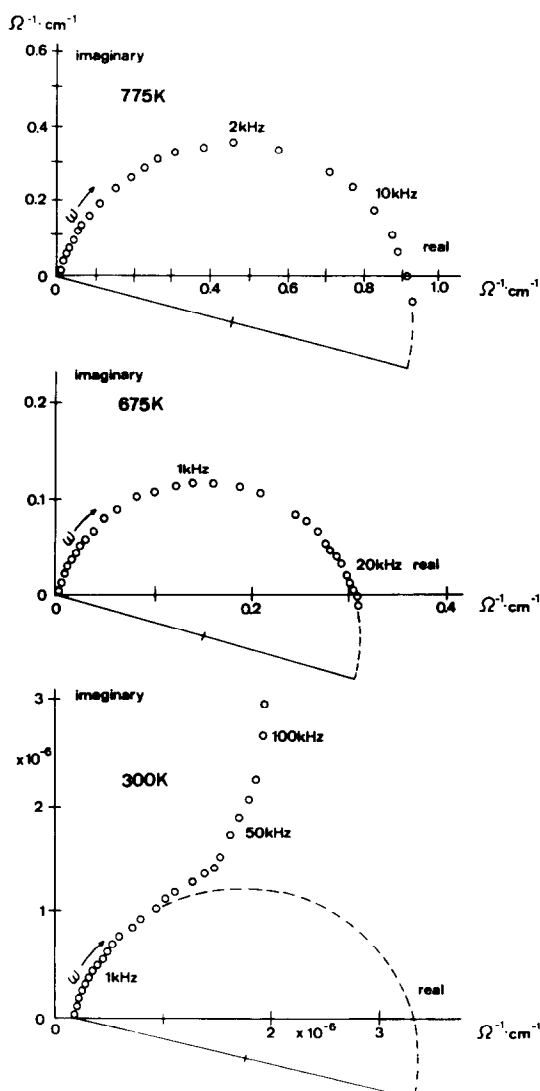


Fig. 2. Frequency dependence of the complex admittance of  $\text{Li}_2\text{MnCl}_4$  at 273, 573, and 675 K. Frequencies are in kHz.

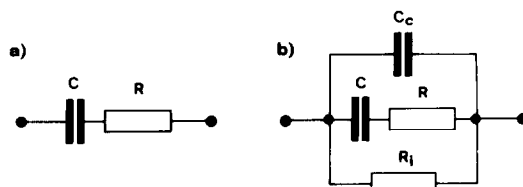


Fig. 3. Equivalent circuits for admittance diagrams of Fig. 2, (a) high temperature case, (b) low temperature case.

( $1/R$ ) can be obtained from the extrapolated intersection of the semi-circle with the real-part ( $G$ )-axis (see Fig. 2 and Table 2).

The semi-circles obtained are somewhat skewed in the complex admittance plane, with the diameter having a slope below the real axis (see Fig. 2). These slopes are found to be  $-0.25 \pm 0.02$  for all measurements, and they are obviously independent of temperature and do not deviate significantly for all four compounds under investigation. An explanation of such non-ideal behaviour has been given by Jonscher[6]. His concept of "Non-Debye dielectrics" predicts a slope  $1/a$  for the diameter of the semi-circles in the complex admittance plane for solid electrolytes, due to the discontinuous movement of the migrating ions and to screening effects.

On the other hand, we also found some experimental points in the complex admittance plane below the real part axis at frequencies above 50 kHz, which means some kind of inductive behaviour. Such phenomena have recently been reported by Grant *et al.*[7] for other solid electrolytes.

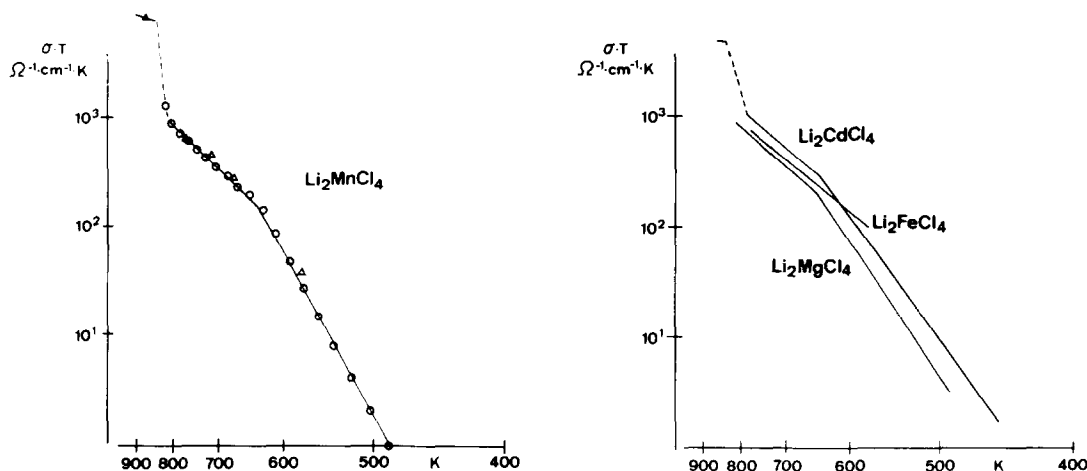
The temperature dependence of the electrical conductivity of the chloride spinels is shown in Fig. 4. There is no detectable deviation of the  $\ln \sigma \cdot T$  vs  $1/T$  curves (Arrhenius plots) from linearity, but at certain temperatures  $T_B$ , significant bends in the plots are observed, especially for  $\text{Li}_2\text{CdCl}_4$ ,  $\text{Li}_2\text{MnCl}_4$ , and  $\text{Li}_2\text{MgCl}_4$ . Below these temperatures the slopes of the lines are considerably higher than those above. According to Geller *et al.*[8, 9] such behaviour for the Arrhenius plots is related to phase transitions of order-disorder type. The conductivity of the melt is only twice as high as that of the solid sample just below the melting point. Data obtained during heating or cooling periods are in good agreement.

From the different slopes of the lines in the Arrhenius plots the energy terms  $\epsilon_A : \ln \sigma \cdot T \approx \exp \epsilon_A/kT$  have been calculated (see Table 2). The  $\epsilon_A$  terms can be interpreted as the activation energies for ionic transport. There is usually no straightforward relation of these energies to the lattice energy parameters[10]. However, from the calculated values it can be concluded that the mobility of the Li ions is much higher above the transition temperature  $T_B$  than below.

The emf of the cell  $\text{Li}_{(l)}/\text{Li}_2\text{CdCl}_{4(s)}/\text{Cl}_{2(g, 1 \text{ bar})}$  was determined to be  $3.25 \pm 0.08$  V at 650 K with very small temperature dependence. From this emf the Gibbs' enthalpy of the cell reaction  $\text{Li}_{(l)} + 1/2\text{Cl}_{2(g)} \rightarrow \text{LiCl}_{(s)}$  has been calculated to be  $-320$  kJ/mol. Values calculated from tabulated thermodynamic data[11] are of the order of 260 kJ/mol. The difference from the experimental value

Table 1. Specific conductivities of chloride spinels and series capacitor  $C$  of the double layer of the "blocking type" electrodes

	$\sigma [\Omega^{-1}\text{cm}^{-1}]$			$C [10^{-4}\text{F}]$
	773 K	673 K	573 K	773 K
$\text{Li}_2\text{CdCl}_4$	$1.3 \pm 0.1$	$0.62 \pm 0.03$	$0.12 \pm 0.03$	$8.0 \pm 1.0$
$\text{Li}_2\text{MnCl}_4$	$0.9 \pm 0.2$	$0.33 \pm 0.07$	$0.05 \pm 0.02$	$2.8 \pm 0.5$
$\text{Li}_2\text{MgCl}_4$	$0.8 \pm 0.1$	$0.33 \pm 0.04$	$0.05 \pm 0.01$	$2.3 \pm 0.5$
$\text{Li}_2\text{FeCl}_4$	$0.9 \pm 0.2$	$0.43 \pm 0.05$	—	$1.2 \pm 0.3$

Fig. 4. Temperature dependence of the electrical conductivity of the chloride spinels, O: four-probe a.c. method,  $\Delta$ : frequency response analysis.Table 2. Transition temperatures  $T_B$  and activation energies  $\epsilon_A$  of chloride spinels

	$T_B [\text{K}]$	$\epsilon_A [\text{kJ/mol}]$	
		above $T_B$	below $T_B$
$\text{Li}_2\text{CdCl}_4$	$620 \pm 10$	$36 \pm 3$	$75 \pm 5$
$\text{Li}_2\text{MnCl}_4$	$630 \pm 20$	$43 \pm 3$	$77 \pm 5$
$\text{Li}_2\text{MgCl}_4$	$630 \pm 20$	$44 \pm 4$	$75 \pm 8$
$\text{Li}_2\text{FeCl}_4$	—	$36 \pm 4$	—

may be due to the mixing enthalpy of  $\text{LiCl}$  and  $\text{CdCl}_2$ , which has been neglected.

However, from these experiments it can be concluded that  $\text{Li}_2\text{CdCl}_4$  is a purely ionic conductor having no measurable electronic conductivity. This should be true also for  $\text{Li}_2\text{MnCl}_4$  and  $\text{Li}_2\text{MgCl}_4$ . Since our samples of  $\text{Li}_2\text{FeCl}_4$  always contained traces of trivalent iron, electronic conductivity might be possible in this case.

The results of our investigation show that there is a very high conductivity for lithium ions in the chloride

spinel  $\text{Li}_2\text{MCl}_4$  ( $M = \text{Mg}, \text{Mn}, \text{Fe}$  and  $\text{Cd}$ ). The compounds are among the best solid lithium electrolytes known so far [10].

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