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SHORT COMMUNICATION

Electronic conductivity of salt-rich Li–LiCl melts

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1. Introduction

The latest review of the electrochemical properties of metal-molten salts solutions was given by Haarberg *et al.* [1]. Much work has been devoted to alkali metal–alkali halide mixtures, except for the case of lithium systems. In a recent paper [2] and thesis [3] we reported electrochemical determinations of the activity of lithium metal dissolved in molten LiCl. One of the features of the results was that dilute solutions of Li in LiCl exhibited surprisingly low values for the metal activity, even for lithium-saturated solutions, whereas, in the general case of molten alkali metal–alkali halide solutions, metal-saturated solutions exhibit unit metal activity. These results led us to suppose that the Li–LiCl phase diagram was significantly different from the simple diagrams with a miscibility gap described by Bredig [4] in the case of most metal-molten salt systems. Moreover, we had noticed in previous work [5] that the overall electrical conductivity increased very little when quantities up to 2 mol % lithium were added to molten lithium chloride. For these reasons we decided to measure the electronic conductivity of salt-rich Li–LiCl solutions in order to estimate the electrical mobility of the new species formed during the dissolution of lithium and to build a thermodynamic model for these solutions, based on the method recently described by Egan *et al.* [6].

2. Experimental details

LiCl (Prolabo Normapur) was pre-dried under vacuum at 250° C, then at 500° C and finally pre-electrolysed before each measurement [2, 3].

Lithium was freshly cut from Lithco ingots. Bismuth was Prolabo Rectapure. For electronic conductivity measurements, the method of Wagner [7], developed originally for solid electrolytes and adapted by Egan *et al.* [6, 8] to the case of molten salts, was used. The cell is shown in Fig. 1. The experimental setup was situated inside a transparent fused silica cylinder closed by a water-cooled brass cover. The conductivity cell was a cylindrical sapphire tube 3 cm long and of 1 mm inner bore. The cone-shaped upper part of this sapphire tube was tightly sealed by a carefully polished iron disc electrode which was pressed against the tube by a metallic spring. The tightness of this assembly was checked by applying vacuum inside the tube. The second electrode was a liquid Li–Bi alloy ($x_{\mathrm{Li}} = 0.2$) which maintained in the molten salt outside the sapphire tube a very small lithium activity of 4×10^{-5} at 660° C [9]. The reference electrode was an Armco wire situated inside a Li–Bi alloy ($x_{\mathrm{Li}} = 0.68$) contained in a boron nitride tube (Union Carbide HBN hot pressed). Both electrodes were immersed in molten lithium chloride. The sapphire tube was then filled in the following way. The sapphire tube being maintained over the melt, vacuum was applied inside the cell, then the sapphire tube was dipped into the melt and 1 atm argon pressure was let into the cell.

A cathodic potential step was applied to the iron upper electrode, with respect to the reference electrode, using a Par 273 potentiostat-galvanostat monitored by a Hewlett-Packard 300 microcomputer. The resulting current density-time curve was recorded (typical curves shown on Fig. 2). This current intensity reached a plateau I_l which was used for calculating the value of the electronic conductivity by the equation [6, 7, 8]:

$$\sigma_e = G \frac{dI_l}{dE}$$

where G = cell constant (357 cm^{-1}) and E = applied potential.

Before each determination, the value of the overall conductivity was checked using a Solartron 1250 frequency response analyser and a Solartron 1186 electrochemical interface.

3. Results

Figure 3 shows the variations in the limiting current I_l, as a function of the applied potential E at 650° C and 700° C. The vaules of I_l were not very reproducible (10 to 20%). From the slopes of these curves, the values of the electronic conductivity, σ_e, as a function of the activity of lithium was calculated. The results are presented in Fig. 4. The values of the electronic conductivity increased with metal activity and with temperature, but remained lower than $10^{-1}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. For the sake of comparison, the results obtained by Egan *et al.* [10] for the case of the Na–NaCl system at 900° C are also shown. For a given value of the metal activity the values of the electronic conductivity are comparable.

4. Discussion

Numerous tentative physical models have been applied to metal-molten salt solutions and have been reviewed by Warren [11, 12]. More recently, a chemical model

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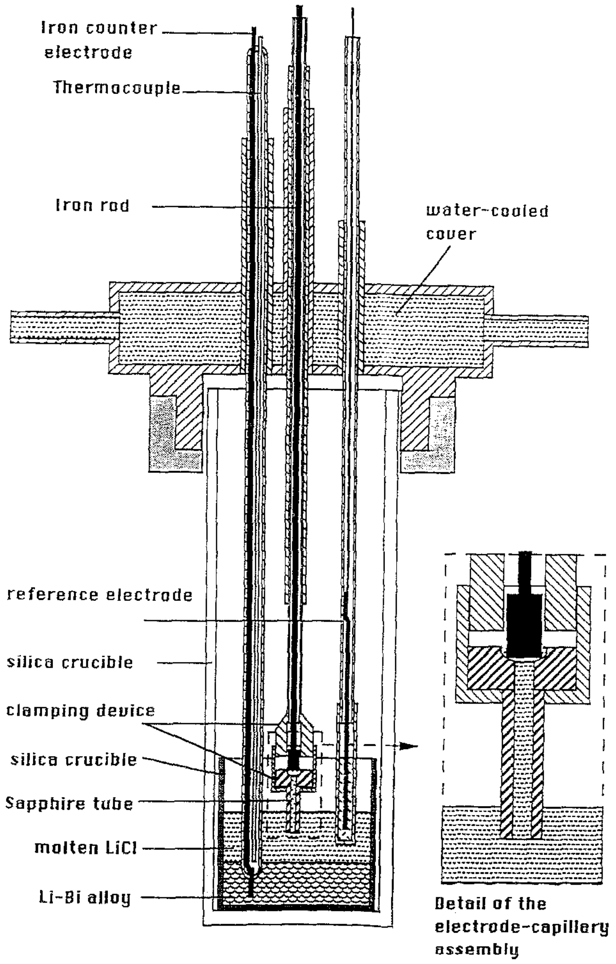

Fig. 1. Electronic conductivity cell.

based on the theory of ionic solids and defects in crystals has been applied with success [13] to salt-rich sodium-sodium halide solutions. We therefore applied such a model to the case of Li-LiCl solutions, in order to take into account both the thermodynamic and the electronic conductivity data.

The structure defects are:

V'_{Li}: Li vacancy

V^*_{Cl}: Cl vacancy

e′: free electron

h*: electron hole

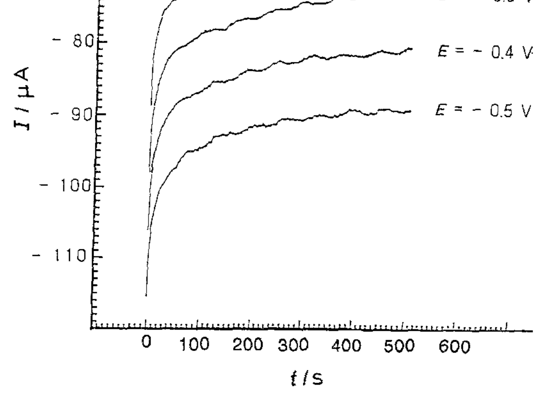

Fig. 2. Variations of the current intensity as a function of time for various values of the applied potential.

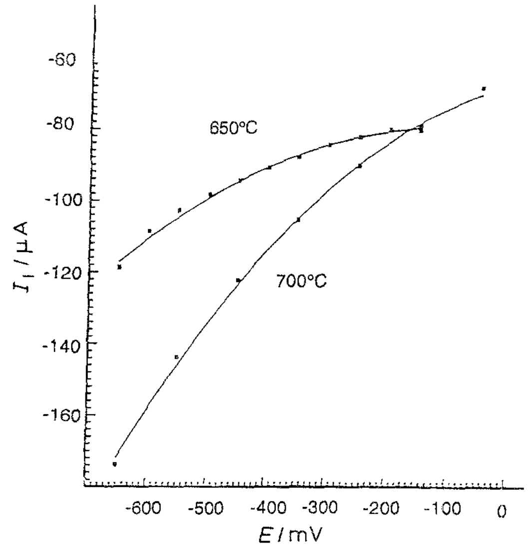

Fig. 3. Variations of the limiting current intensity as a function of the applied potential.

V^x_{Cl}: F centre (chlorine vacancy occupied by one electron)

$(V_{\mathrm{Cl}})^{x_2}$: a dimerized F centre

$(V_{\mathrm{Cl}})^*_2$: association between a F centre and a Cl vacancy

In pure lithium chloride,

$$[V^*_{\mathrm{Cl}}] = [V'_{\mathrm{Li}}]$$
$$[e'] = [h^*]$$

When lithium is added to the pure melt, Cl vacancies are created, electrons are injected into the system and the concentrations of electron holes and lithium vacancies are reduced. Therefore [h*] and $[V'_{\mathrm{Li}}]$ are neglected in the following.

The equilibrium equations for interactions between the defects are

$$\mathrm{Li} = \mathrm{Li}^x_{\mathrm{Li}} + e' + V^*_{\mathrm{Cl}} \qquad (1)$$

$$V^*_{\mathrm{Cl}} + e' = V^x_{\mathrm{Cl}} \qquad (2)$$

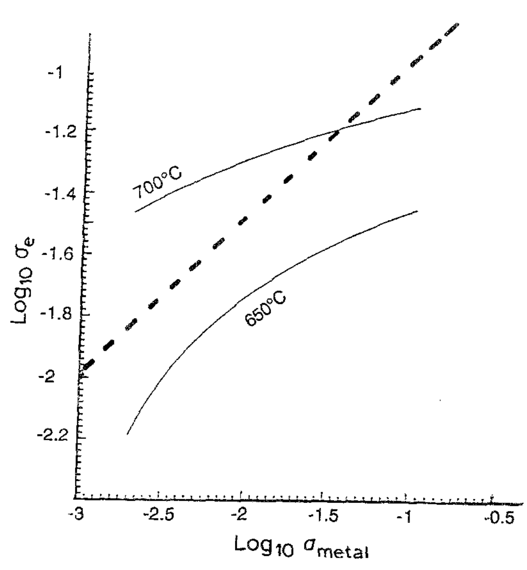

Fig. 4. Variations of the electronic conductivity of Li-LiCl solutions as a function of lithium activity. Comparison with Na-NaCl solutions, from [10]. (——) Li-LiCl solutions (this work); (- - -) Na-NaCl solutions at 900° C [10].

$$2V_{\mathrm{Cl}}^{x} = (V_{\mathrm{Cl}})_2^{x} \tag{3}$$

$$V_{\mathrm{Cl}}^{x} + V_{\mathrm{Cl}}^{*} = (V_{\mathrm{Cl}}^{*})_2 \tag{4}$$

The corresponding equilibrium constants are K_1, K_2, K_3 and K_4, respectively.

Electroneutrality demands that

$$[\mathrm{e}'] = [V_{\mathrm{Cl}}^{*}] + [(V_{\mathrm{Cl}}^{*})_2] \tag{5}$$

The excess metal concentration, δ, is equal to the sum of the concentrations of the various forms of electrons. Thus:

$$\delta = [\mathrm{e}'] + [V_{\mathrm{Cl}}^{x}] + 2[(V_{\mathrm{Cl}}^{x})_2] + [(V_{\mathrm{Cl}}^{*})_2] \tag{6}$$

Or, with Equation 5

$$\delta = [V_{\mathrm{Cl}}^{*}] + [V_{\mathrm{Cl}}^{x}] + 2[(V_{\mathrm{Cl}}^{x})_2] + 2[(V_{\mathrm{Cl}}^{*})_2] \tag{7}$$

Finally, combining Equations 5, 6, 7 and the expressions for the equilibrium constants lead to

$$\begin{aligned}[\mathrm{e}'] = {} & K_1K_2K_4a_{\mathrm{Li}}(K_1a_{\mathrm{Li}})^{1/2}(1 + K_1K_2K_4a_{\mathrm{Li}})^{-1/2} \\ & + (K_1a_{\mathrm{Li}})^{1/2}(1 + K_1K_2K_4a_{\mathrm{Li}})^{-1/2}\end{aligned} \tag{8}$$

$$\begin{aligned}[\delta] = {} & 2K_1K_2K_4a_{\mathrm{Li}}(K_1a_{\mathrm{Li}})^{1/2}(1 + K_1K_2K_4a_{\mathrm{Li}})^{-1/2} \\ & + K_1K_2a_{\mathrm{Li}} + (K_1a_{\mathrm{Li}})^{1/2}(1 + K_1K_2K_4a_{\mathrm{Li}})^{-1/2} \\ & + 2K_1^2K_2^2K_3a_{\mathrm{Li}}^2\end{aligned} \tag{9}$$

Since the lithium activity is small, the electron concentration is also small and we can consider that the mobility of these electrons is constant. Hence,

$$\sigma_{\mathrm{e}} = F[\mathrm{e}']\mu_{\mathrm{e}}/V_{\mathrm{M}} \tag{10}$$

where F is the Faraday, μ_{e} is the electron mobility and V_{M} is the molar volume of the liquid.

From a series of lithium activity – lithium excess δ data, and the value of the electronic conductivity, it was possible to calculate the four equilibrium constants and, from these values, the concentrations of the defects using a suitable mathematical method. As $\sigma = f(K_1, K_2, K_3, K_4)$ is not a linear relation, no analytical resolution of the system can be obtained, and the method of trust-region described by Pham Dinh *et al.* [14] was used. The following set of values at 700° C were obtained.

$$K_1 = [V_{\mathrm{Cl}}^{*}][\mathrm{e}']/a_{\mathrm{Li}} = 10^{-6}$$

$$K_2 = [V_{\mathrm{Cl}}^{x}]/[V_{\mathrm{Cl}}^{*}][\mathrm{e}'] = 9.912 \times 10^4$$

$$K_3 = [(V_{\mathrm{Cl}})_2^{x}]/[V_{\mathrm{Cl}}^{x}]^2 = 39.99$$

$$K_4 = [(V_{\mathrm{Cl}}^{*})_2]/[V_{\mathrm{Cl}}^{x}][V_{\mathrm{Cl}}^{*}] = 113.6$$

This set of values is not unique but the other possible values for the equilibrium constants were physically meaningless. The concentrations of the defects obtained are plotted on Fig. 5 as a function of the metal activity. This shows that the predominant defects are F centres or dimer F centres. The concentration of electrons is much smaller. This explains why the electronic conductivity is small. The calculated value of the electron mobility is: $\mu_{\mathrm{e}} = 0.26\,\mathrm{cm^2\,s^{-1}\,V^{-1}}$. This value is comparable to the values $0.25\,\mathrm{cm^2\,s^{-1}\,V^{-1}}$ obtained by Egan *et al.* [13] for Na–NaI or Na–NaBr systems, or with the value $0.1\,\mathrm{cm^2\,s^{-1}\,V^{-1}}$ published by Warren *et al.* [15] for the Cs–CsI system. In the case of sodium systems, the concentration of free electrons reaches much higher values. Consequently, the striking differences in electronic conductivity between sodium and lithium systems appear to arise from differences in the concentrations of free electrons.

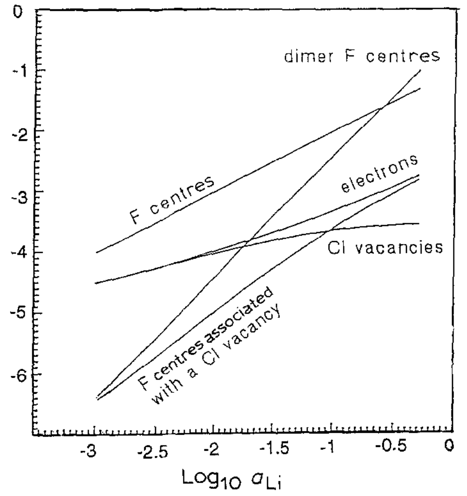

Fig. 5. Variations of the concentrations of different structural defects (in $\mathrm{mol\,cm^{-3}}$, log scale) as a function of Li activity in Li-LiCl solutions at 700° C.

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