

Incorporation mechanism for doping of metal ions into a passivating film at the lithium/thionyl chloride interface

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Abstract

Effects of iron and titanium ions on corrosion processes of lithium in thionyl chloride electrolytes have been studied. Laws for the growth of the passivating film on the type and concentration of doped ions have been established, and equations for these are suggested. A stepwise mechanism of dopant incorporation into passivating film structure is presented.

Introduction

The presence of iron ions in thionyl chloride solutions is known to increase substantially the voltage drop of cells because of pronounced corrosion processes on lithium [1-3].

The presence of iron ions in solutions is due to corrosion of cell boxes and welds especially in acid solutions of thionyl chloride [2-4]. In spite of experimental evidence of excessive Li corrosion in solutions of this type, the quantitative relationship between corrosion concentration rate and the nature of the dopant have not been studied up till now. Besides, the mechanism of incorporation of metal ions into the structure of the passivating film was not studied either.

Experimental

Corrosion of Li was studied by gravimetry and by physicochemical methods of quantitative analysis of metal ions in the solutions of thionyl chloride and electrolyte.

Samples in disc form with an average size of 5 cm² were cut out from Li sheet with a thickness of 1 mm in the atmosphere of a glove box with moisture up to 50 ppm. After weighing the samples, 5 pieces each were placed into ampoules which were then filled with electrolyte, sealed off and stored under conditions of temperature control.

The initial electrolyte solution 1 M LiAlCl₄/SOCl₂ was prepared by the following procedures.

Commercial-grade 1 M LiAlCl₄/SOCl₂ was distilled three times over oleic acid till the elimination of impurities on IR spectra. Anhydrous AlCl₃ was obtained by

sublimation in vacuum. Lithium chloride was dried at a temperature of 140 to 160 °C in the course of three days. Excess of salts (5%) was used for complete neutralization of free AlCl_3 . The electrolyte was kept in a box for 24 h, then filtered and refluxed with metallic Li. The content of iron ions did not exceed 6 and 10 mg/l in the electrolyte of this type, respectively.

Increase of the doped ion concentration was achieved by the gradual incorporation into the initial solution of solutions with the concentration of iron and titanium ions of 4.0 g/l.

The quantity of iron, titanium, nickel and chromium ions was analysed by photocolometric analysis KFK-2 spectrometer after preliminary preparation of aliquots. The content of iron and titanium ions incorporated in the structure of a passivating film was determined by the same method. For this purpose the Li sample was dissolved in ethyl alcohol (70%) and then acidified by hydrochloric acid and the precipitate formed was dissolved and analysed as above.

Phase composition of the film was determined by the X-ray method using diffractometer 'DRON-3'. Data processing was carried out by the standard technique [5].

Results and discussion

Experimental studies of the dependence of sample weight changes on corrosion time show that maximum changes in corrosion rate take place during the first 360 to 720 h. It was established that great corrosion rates correspond to the higher concentrations of iron and titanium. This general trend holds in the temperature range of 25 to 50 °C (Fig. 1).

Processing of data plotted in Fig. 1, where, $\Delta p/s - \tau$, $\Delta p/s - \log \tau$, $\tau/(\Delta p/s) - \Delta p/s$, $\tau/(\Delta p/s) - \log \tau$, $\log(\Delta p/s - \log \tau)$ furnished the calculation of correlation coefficients. Maximum values allowed to state that the corrosion process obeys a specific law, e.g., the corrosion process in the initial electrolytes obeys the parabolic law as defined by:

$$\log(\Delta p/s) = -4.71 + 0.50 \log \tau \quad (1)$$

and,

$$\log(\Delta p/s) = -4.66 + 0.53 \log \tau \quad (2)$$

at 25 and 50 °C, respectively.

Deviation from the parabolic law to the logarithmic one occurs with increase of the concentration of doped ions in the electrolyte. The corrosion rate at 25 °C in electrolytes containing iron 100 mg/l or titanium 85 mg/l is explained by the following equations:

$$\Delta p/s = -1.56 \times 10^{-3} + 1.28 \times 10^{-3} \log \tau \quad (3)$$

and,

$$\Delta p/s = -1.97 \times 10^{-3} + 1.66 \times 10^{-3} \log \tau \quad (4)$$

The effect of ion concentration of iron and titanium on the change of corrosion mechanism is shown in Fig. 2.

The cross-over point of the straight lines is in agreement with a minimum concentration of dopant ions with the change of film growth law. With the elevation

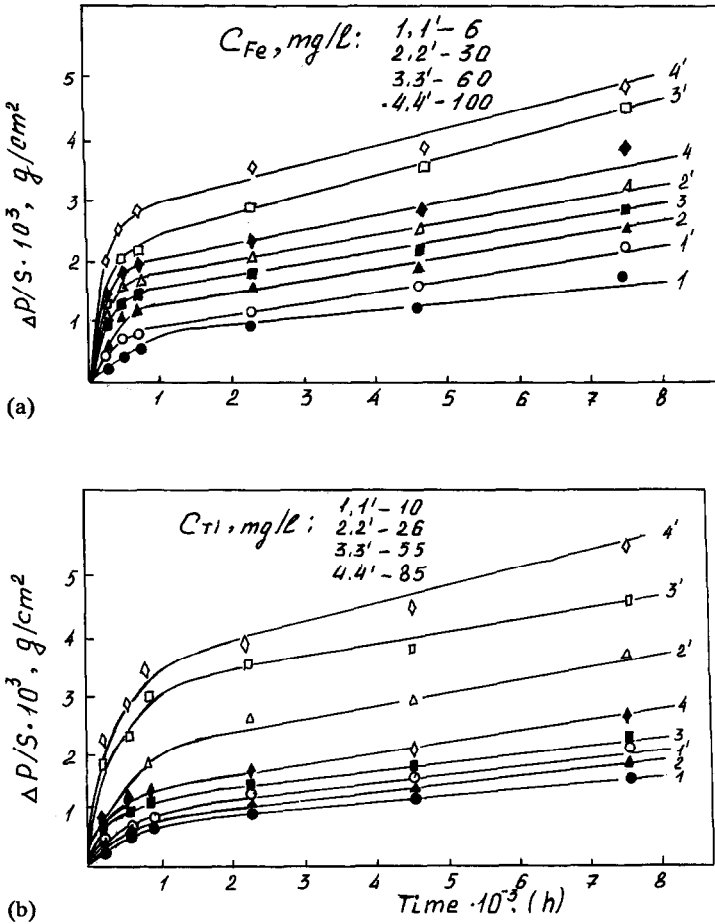


Fig. 1. Corrosion of lithium in thionyl chloride electrolyte with doped ions of (a) iron and (b) titanium; curves (1-4) at 25 °C, and curves (1'-4') at 50 °C.

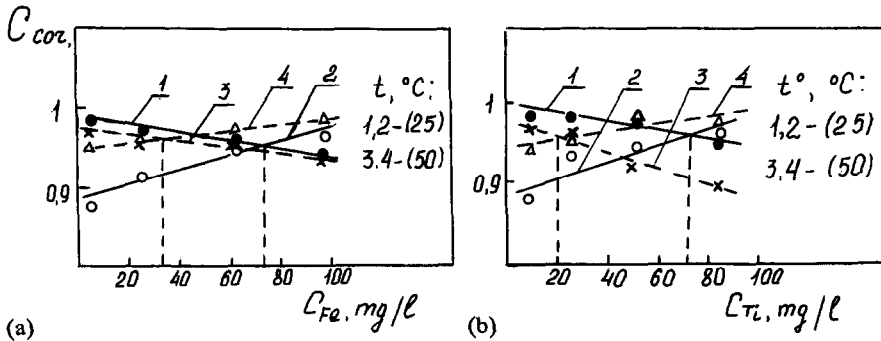
of temperature from 25 to 50 °C the transfer from the parabolic law to the logarithmic one takes place at lower concentrations of dopant ions.

Concentration in the solutions with iron ions reduced from 78 up to 36 mg/l, and that of titanium ions lowered from 76 up to 20 mg/l.

In solutions with the concentration of dopant ions which are in conformity with the change of mechanism and exceeding them there is an exponential growth of corrosion rate, e.g., for the solutions with the concentration from 20 to 1000 mg/l the change of weight corrosion rate index K_w^+ ($g\ cm^{-2}\ h^{-1}$) against the concentration of iron, C_{Fe} , at 50 °C in logarithmic coordinates is expressed by the following equation:

$$\log K_w^+ = -4.0 + 8.3 \times 10^{-4} C_{Fe} \quad (5)$$

The dependence of corrosion rate of Li on reciprocal temperature in the electrolytes with a fixed amount of dopant is shown in Fig. 3.



(a)

(b)

Fig. 2. Change of correlation coefficients of parabolic (eqns. (1), (3)) and logarithmic (eqns. (2), (4)) laws of film growth depending on the content of (a) iron ions and (b) titanium ions in a solution.

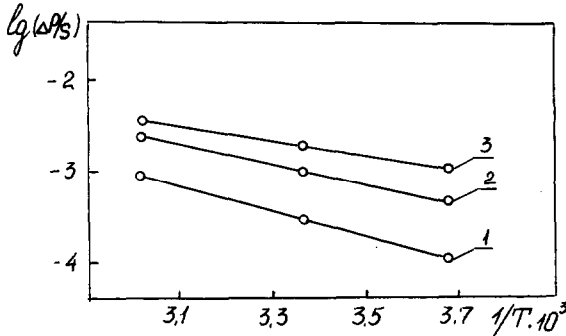


Fig. 3. Dependence of lithium corrosion on reciprocal temperature in thionyl chloride electrolyte. (1) without dopants, (2) $C_{Ti} = 55$ mg/l, (3) $C_{Fe} = 100$ mg/l). Corrosion time = 360 h.

Straight lines in coordinates $\lg(\Delta p/s) - 1/T$ allow to apply the Arrhenius equation for the calculation of activation energy.

For the corrosion time of 360 h, i.e., when formation of the initial film comes to an end, the values of activation energy of Li corrosion was found to be: 27.8 kJ/mol for electrolyte without dopants, 20.6 kJ/mol for the electrolyte with titanium ions (55 mg/l), and 12.4 kJ/mol for the electrolyte with iron ions (100 mg/l).

Regarding the magnitude of activation energy as one of the criteria for the determination of a limiting stage in a rate process, we draw the following conclusions: (i) charge transfer through the film is the limiting stage of film growth in a pure electrolyte, and (ii) according to Peleda [6], it depends on electron hole diffusion. In processes of this type corrosion rate follows the parabolic law.

Diffusion limitations in the transfer of Li cations through the passivating film occur in electrolytes with doped ions. Film growth obeys a logarithmic law.

Experimental data presented in Fig. 4 are indicative of the presence of iron and titanium ions in a passivating film during corrosion of Li in thionyl chloride electrolytes with doped ions.

Maximum ion accumulation of iron (Fig. 4(a)) and that of titanium (Fig. 4(b)) in a film takes place in the range of 160 to 360 h. This time corresponds to the formation and growth of the initial film. After 300 to 400 h the formation of a secondary

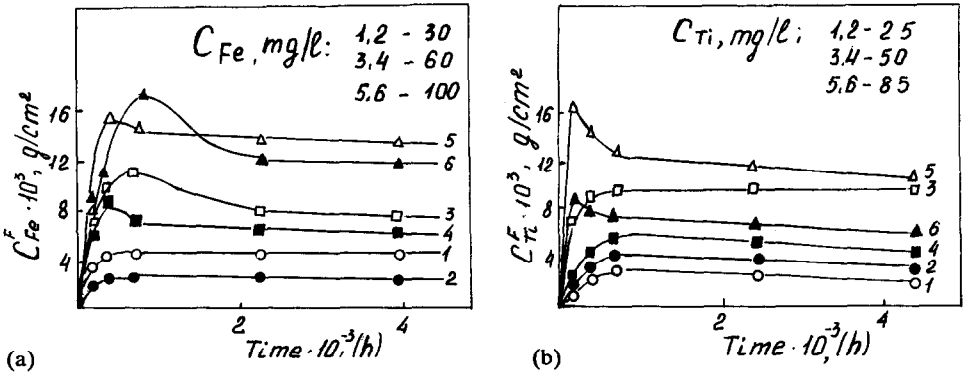


Fig. 4. Changes of the content of (a) iron ions, and (b) titanium ions in the passivating film depending on contact time of Li and the electrolyte: curves (1, 2, 5) at 25 °C, and curves (2, 4, 6) at 50 °C.

porous film begins by a multiple dissolution/precipitation mechanism of solid crystals of the initial film [7]. Doped ions first incorporated into the initial film transfer partially into the secondary one, and when dissolved they transfer into the solution. Thus, the content of doped ions in a passivating film is stabilized and even has a tendency to reduction as a result of partial dissolution of crystals in the secondary film within the long periods of contact of Li and electrolyte.

X-ray analysis of surface layers of Li which was in contact with thionyl chloride electrolyte containing iron ions within the period of 720 h demonstrated the presence of two substances: LiCl and LiFeO₂. These substances emerged from reactions on the boundary Li oxide/solution:



LiCl is the basis of a crystal lattice of the passivating film, and LiFeO₂ is a dopant in its structure.

According to [8], LiCl films have crystal lattice defects of Schottky type. Transfer of Li cations through the film volume occurs in conformity with vacancy mechanism. Electron hole-type conduction originates as a result of electron injection from the surface chlorine ions of a lattice to the thionyl chloride molecule.

Film defects increase with the incorporation of doped ions into its crystal structure. Figure 5 shows the dependence of electron defect concentration (C_e) in the initial film on the content of iron ions in it (C_{Fe}^F).

We calculated (C_e) with the help of Peleda equation [8] combining corrosion current (i_{corr}) and the concentration of film defects (C_e). Thus:

$$i_{corr} = \frac{FDC_e}{L} \quad (8)$$

where D is an electron diffusion coefficient in a solid phase of lithium chloride, ($cm^2 s^{-1}$), $D = 10^{-8} - 10^{-10} cm^2 s^{-1}$ – according to [9]. $D = 10^{-9} cm^2 s^{-1}$ – L is a film

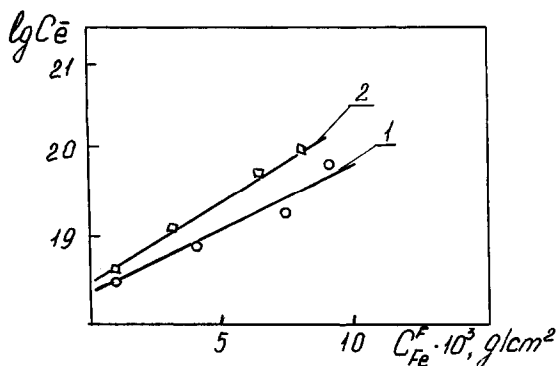


Fig. 5. Dependence of electron defect concentration in lithium chloride on the content of iron in the film; curve (1) corrosion temperature at 25 °C, and curve (2) corrosion temperature at 50 °C.

thickness, (cm). Corrosion current (i_{corr}), film thickness (L) and the content of iron in it (C_{Fe}^F) were calculated on the basis of gravimetric and photocolometric measurements of corrosion of Li samples during the formation of the initial film.

Data presented in Fig. 5 demonstrate that electron defect growth proceeds according to an exponential dependence on the concentration of iron ions in the film.

Electron conductivity of a film increases as a result of doped ions located in the forbidden band close by the bottom of the conduction band. The 3d sublevels of the electron layers remain unfilled. Doped iron ions have greater number of valent electrons than displaced Li cations, and thereby serve as electron donors into the conduction band. Thus, the corrosion rate increases.

As shown above, the following main stages of incorporation of dopant ions into the passivating film on a Li surface were proposed:

(i) Adherence of initial film with the formation of crystal centers of LiCl and LiFeO₂. Reaction (6) and (7) illustrate the processes within this stage.

(ii) Formation and growth of initial dense and mixed film. Transfer processes through the film are the basis of this stage. Li cation transfer is accomplished in accordance with the Peleda vacancy mechanism [6], and that of electrons obeys the conduction law of ion defect crystals after Chebotin's model [8].

(iii) The formation and growth of a secondary film was stated to occur during dissolution/precipitation of crystals according to the mechanism described by Moschtev [7].

Conclusions

From the results presented the following conclusions can be drawn:

(i) Quantitative correlation was established between the corrosion rate of Li and the concentration of Fe and Ti ions in thionyl chloride solutions. The kinetics of corrosion were established from the corresponding equations.

(ii) A change of film growth law was substantiated for the incorporation of doped ions into the solution.

(iii) A stepwise mechanism of incorporation of doped ions into the film, and formation and growth of the latter was proposed.

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