

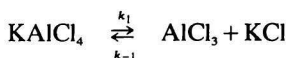
# Chronopotentiometric study of the molten system NaCl—KCl—AlCl<sub>3</sub>

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Received 8 June 1982

Cathodic process in molten electrolyte NaCl—KCl—AlCl<sub>3</sub> was studied by means of the chronopotentiometric method. It was found that kinetics of the process is controlled mainly by diffusion. The electrochemical reaction is, however, preceded by a chemical reaction. We suggest that this reaction corresponds to the decomposition of the complex ion AlCl<sub>4</sub><sup>-</sup>. Since the compound KAlCl<sub>4</sub> is more stable than NaAlCl<sub>4</sub>, we suggest that kinetics of the process is controlled by the chemical reaction according to the scheme

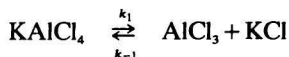


At the temperature  $T = 1000 \text{ K}$

$$D = (5.5 \pm 0.5) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}; \quad \frac{\pi^{1/2}}{2K(k_1 + k_{-1})^{1/2}} = + (0.3 \pm 0.04) \text{ s}^{1/2}$$

We found that after depletion of the electroactive species which is formed by the chemical reaction the direct reduction of aluminium from the complex AlCl<sub>4</sub><sup>-</sup> starts. This process proceeds at the potential about 130 mV more negative compared to that of reduction of aluminium from AlCl<sub>3</sub>.

С помощью хронопотенциометрического метода изучен катодный процесс в расплавленном электролите NaCl—KCl—AlCl<sub>3</sub>. Обнаружено, что кинетика этого процесса определяется, главным образом, диффузией. Электрохимической реакции, однако, предшествует химическая. Мы полагаем, что эта реакция отвечает распаду комплексного иона AlCl<sub>4</sub><sup>-</sup>. Поскольку соединение KAlCl<sub>4</sub> более устойчиво, чем NaAlCl<sub>4</sub>, мы полагаем, что кинетика процесса определяется химической реакцией, в соответствии со схемой



При температуре  $T = 1000 \text{ K}$

$$D = (5,5 \pm 0,5) \cdot 10^{-5} \text{ cm}^2 \text{ c}^{-1}; \quad \frac{\pi^{1/2}}{2K(k_1 + k_{-1})^{1/2}} = + (0,3 \pm 0,04) \text{ c}^{1/2}$$

Обнаружено, что после исчерпания электроактивного соединения, которое образуется путем химической реакции, начинается прямое восстановление алюминия из комплекса  $\text{AlCl}_4$ . Этот процесс протекает при потенциале, приблизительно 130 мВ более отрицательном, чем потенциал восстановления алюминия из  $\text{AlCl}_3$ .

Interest in the study of kinetics of electrode processes in the melts containing aluminium chloride has arisen after employing these systems for electrowinning of aluminium [1, 2].

In paper [3] results of the chronopotentiometric study of the cathodic process in equimolar molten mixture  $\text{NaCl} + \text{KCl}$  with the addition of  $\text{AlCl}_3$  are reported. According to that paper the electrode process is controlled only by diffusion. It was found that the diffusion coefficient depends on concentration. In papers [4, 5] sweep voltammetric technique has been used for investigation of the kinetics of the electrode processes. Using this method it is reported that the cathodic process is controlled only by diffusion. Rate constant of the electrode reaction has been determined to be  $k_s = 0.2 \text{ cm s}^{-1}$  [5]. None of the cited authors assumes the possibility of an electrochemical reaction which is preceded by a chemical reaction.

In this work we used for the study of the cathodic process in the system  $\text{NaCl} - \text{KCl} - \text{AlCl}_3$  the chronopotentiometric method [6—9]. This technique is experimentally simple and it is suitable for study of the electrode processes controlled by diffusion of electroactive species or by a combination of diffusion and chemical reaction which precedes the charge-transfer reaction. These cases are met quite often in molten electrolytes and therefore, we assumed that the method could be suitable for investigation of the electrode processes in the system in question. Moreover, transition time is insensible to the kinetics of charge transfer and to the change in activity of the deposited metal, which may be also considered an advantage.

## Experimental

### Chemicals

$\text{NaCl}$  and  $\text{KCl}$  of anal. grade were dried at  $600^\circ\text{C}$ ;  $\text{AlCl}_3$  of anal. grade (Fluka) was used. The electrolyte was prepared in a dry box. In some experiments  $\text{NaAlCl}_4$  was used instead of  $\text{AlCl}_3$ .  $\text{NaAlCl}_4$  was prepared from equimolar mixture of  $\text{NaCl}$  and  $\text{AlCl}_3$ , which was heated at  $200^\circ\text{C}$  in a flask with ground joint. After solidification the product was pulverized in the dry box and analyzed. We found, however, that it is very important to make analysis after each electrochemical experiment as well. The content of aluminium in samples was determined by gravimetric analysis and/or by a titration method. In the former case aluminium was precipitated by solution of hydroxyquinoline acetate and the precipitate of

$\text{Al}(\text{C}_6\text{H}_5\text{ON})_3$  was weighed [10]. The direct titration by complexon II on indicator 1-(2-pyridylazo)-2-naphthol (PAN) with addition of small amounts of copper complexonate acquitted well [11].

### Apparatus

The electrolytic cell was formed by a sintered-corundum crucible which was placed in closed silica glass tube. The tube was placed in a resistance furnace. Bottom of the silica glass tube was sealed and its upper part was closed by a cooled metal flange. The PtRh10—Pt thermocouple, electrodes, and the inlet of argon led through this flange and they were sealed with O-ring fittings. Temperature was kept constant  $\pm 1$  K. Several types of working electrodes were tested: tungsten, tantalum or platinum wire ( $\varnothing$  1 mm) were sealed in glass. Surface of the working electrode was about 30 mm<sup>2</sup>. Platinum spiral was used as the counter electrode. Potential was measured against the silver/silver chloride reference electrode [12] with  $6 \times 10^{-2}$  mole % of AgCl in the eutectic mixture NaCl—KCl. As a source of constant current the potentiostat Ple-60 (VPZ-SVUOM) working in galvanostatic regime was used. Voltage response was recorded on the X-Y plotter HP 7004 B or on the Storage oscilloscope Tektonix 434.

### Results and discussion

As we have mentioned we used tungsten, platinum or tantalum electrodes. We tested also the molybdenum electrode but we found that it is not suitable for measurement in this melt. The best reproducibility of experimental results was achieved with the tungsten electrode. Therefore all the data presented here are those obtained with this electrode. The measurements were carried out at the temperature 1000 K. Concentration of aluminium chloride in the melt changed in the range from  $1.5 \times 10^{-4}$  mol cm<sup>-3</sup> to  $1 \times 10^{-3}$  mol cm<sup>-3</sup>. Cathodic current density ranged from 0.16 A cm<sup>-2</sup> to 2.6 A cm<sup>-2</sup> and corresponding transition time changed from 0.1 to 2.2 s.

As a diagnostic criterion for evaluation of experimental data we used the dependence of the product  $j\tau^{1/2}$  on current density ( $j$  is the current density and  $\tau$  is the transition time). If kinetics of the electrode process is controlled only by diffusion of electroactive species towards the electrode, this term is always constant. If, however, a chemical reaction precedes the electrochemical step, the value of the product  $j\tau^{1/2}$  changes with current density. The experimentally obtained dependences of this product vs.  $j$  for five different concentrations of aluminium chloride are presented in Fig. 1. It follows that in the studied range of current densities and concentrations the value of the product  $j\tau^{1/2}$  decreases with increasing current density. We suggest that this fact can be explained by the theory developed in [6].

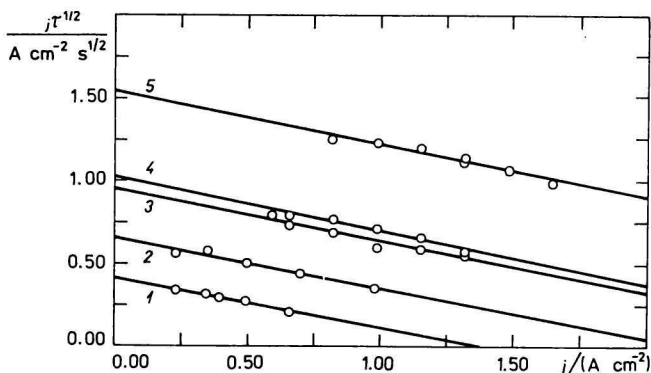
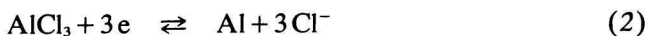


Fig. 1. Dependence of the product  $j\tau^{1/2}$  on  $j$  for different concentrations ( $c/\text{mol cm}^{-3}$ ) of aluminium chloride in the melt.

1.  $2.1412 \times 10^{-4}$ ; 2.  $3.3640 \times 10^{-4}$ ; 3.  $3.7376 \times 10^{-4}$ ; 4.  $5.8421 \times 10^{-4}$ ; 5.  $7.6352 \times 10^{-4}$ .

Let us assume that the complex in  $\text{AlCl}_4^-$  is reduced according to the following schemes



Because the nature of the cations can influence numerical values of the equilibrium and rate constants, it is better to write eqn (1) in the form



where M stands for an alkali metal.

Thermodynamic behaviour of the binary systems  $\text{MCl}-\text{AlCl}_3$  has been studied in [13] on the basis of vapour pressure measurements. According to the paper [13] dependence of the equilibrium constant of the reaction (3) on temperature can be described by the relationship

$$K = \exp \left[ -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \right] \quad (4)$$

The quantities  $\Delta H^0$  and  $\Delta S^0$  acquire the following values

$$\text{NaCl}-\text{AlCl}_3: \Delta H^0/\text{kJ mol}^{-1} = 85.1 \quad \Delta S^0/\text{J K}^{-1} \text{ mol}^{-1} = 26.2$$

$$\text{KCl}-\text{AlCl}_3: \Delta H^0/\text{kJ mol}^{-1} = 105.2 \quad \Delta S^0/\text{J K}^{-1} \text{ mol}^{-1} = 28.7$$

At the temperature 1000 K the thermodynamic equilibrium constant for the system NaCl—AlCl<sub>3</sub> equals  $8.38 \times 10^{-4}$  while in the system KCl—AlCl<sub>3</sub> its value is  $1.01 \times 10^{-4}$ . It is seen that the equilibrium of the reaction (3) is shifted strongly to the left hand side. It also follows from the data that the complex AlCl<sub>4</sub><sup>-</sup> is stronger in the system KCl—AlCl<sub>3</sub> than in the system NaCl—AlCl<sub>3</sub>.

If we assume that transport of the electroactive species as well as of M<sup>+</sup> · AlCl<sub>4</sub><sup>-</sup> is only due to diffusion and that the chemical reaction is formally of the first order (this is fulfilled when  $c(\text{KCl}) \gg c(\text{KAlCl}_4)$ ), then we can describe transport and chemical processes in the system by a set of partial differential equations. Solution of this set of equations for boundary conditions given by the chronopotentiometric technique yields the following relationship between the transition time  $\tau$  and current density  $j$  [6, 7]

$$j\tau^{1/2} = \frac{\pi^{1/2}}{2} n F c^0 D^{1/2} - \frac{\pi^{1/2}}{2} j \frac{1}{K(k_1 + k_{-1})^{1/2}} \operatorname{erf} [(k_1 + k_{-1})^{1/2} \tau^{1/2}] \quad (5)$$

where  $n$  is the number of transferred electrons,  $F$  is the Faraday constant, and  $c^0$  corresponds to the initial concentration of Al(III) species determined analytically. The equilibrium constant  $K$  is given by the ratio  $k_1/k_{-1}$  and it may be numerically different from the thermodynamic equilibrium constant. The relationship (5) has been derived under the assumption that diffusion coefficients of KAlCl<sub>4</sub> and AlCl<sub>3</sub> are equal.

Application of the relationship (5) to our experimental data (for easy survey only a part of these data is presented in Fig. 1) yielded the following set of kinetic parameters

$$D = (5.5 \pm 0.5) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}; \quad \frac{\pi^{1/2}}{2K(k_1 + k_{-1})^{1/2}} = + (0.3 \pm 0.04) \text{ s}^{1/2}$$

In the range of used concentrations and current densities the value of the function  $\operatorname{erf}(x)$  in eqn (5) is very close to one. Thus this function has no influence on the term  $j\tau^{1/2}$ . Limits of validity of eqn (5) for the case of a chemical reaction of the second order preceding the reduction step are discussed in paper [6].

At certain conditions (analytical concentration of AlCl<sub>3</sub> greater than 1.5 mass % and  $j > 1 \text{ A cm}^{-2}$ ) we observed two waves on the chronopotentiometric curves (plot of the potential vs. time). In agreement with the proposed mechanism of the cathodic process we assume that the second wave corresponds to a direct reduction of aluminium from the complex ion AlCl<sub>4</sub><sup>-</sup>. This reduction proceeds at the potential about 130 mV more negative compared with the potential of reduction of AlCl<sub>3</sub>. Quantitative evaluation of the transition time of the direct reduction of complex ions is under study.

## References

1. Grjotheim, K., Krohn, C., Malinovský, M., Matiašovský, K., and Thonstad, J., *Aluminium Electrolysis*. Aluminium-Verlag GmbH, Düsseldorf, 1977.
2. Silný, A. and Fellner, P., *Hutn. Listy* 37, 489 (1982).
3. Safnikov, V. I., Butorov, V. P., Meľnikov, B. V., Lebedev, V. A., and Nichkov, I. F., *Elektrokhimiya* 7, 1199 (1974).
4. Goldshtein, S. L., Raspopin, C. P., and Fedorov, V. A., *Elektrokhimiya* 13, 1791 (1977).
5. Ødegård, R., Bjørgum, A., Sterten, Å., Thonstad, J., and Tunold, R., *Electrochim. Acta* 27, 1595 (1982).
6. Delahay, P. and Berzins, T., *J. Amer. Chem. Soc.* 75, 2486 (1953).
7. Delahay, P., *New Instrumental Methods in Electrochemistry*. Interscience, New York, 1954.
8. Thirsk, H. R. and Harrison, J. A., *A Guide to the Study of Electrode Kinetics*. Academic Press, London, 1972.
9. Donald, D. D., *Transient Techniques in Electrochemistry*. Plenum Press, New York, 1977.
10. Tomiček, O., *Kvantitativní analýsa*. (Quantitative Analysis.) Státní zdravotnické nakladatelství. (State Publishing House of Health.) Prague, 1958.
11. Tikhonov, V. N., *Analiticheskaya khimiya alyuminiya*. Nauka, Moscow, 1971.
12. Littlewood, R., *Electrochim. Acta* 3, 270 (1961).
13. Linga, H., Motzfeldt, K., and Øye, H., *Ber. Bunsenges. Phys. Chem.* 82, 568 (1978).

Translated by P. Fellner