ELECTRODE PROCESSES AT THE ELECTROLYSIS OF MOLTEN CALCIUM CHLORIDE


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ABSTRACT

The paper presents experimental data on the mechanisms and kinetics of the electrode processes taking place on the interacting and indifferent anodes and cathodes at the electrolysis of molten CaCl$_2$. The conclusions made are of great interest for the development of physical-chemical fundamentals of new technologies of the metals (especially calcium) and alloys production by the electrolysis of CaCl$_2$-based melts.

1. INTRODUCTION

Electrolysis of CaCl$_2$-based melts is used for production of copper-calcium alloy which can be further used in the steel industry or for the extracting of pure calcium by vacuum distillation (1, 2). A common disadvantage of the known methods of calcium production (2) is high energy costs and multistage process. Thereby it is interesting to study the physical-chemical fundamentals of copper-calcium alloy production and its subsequent separation to pure calcium in a single electrochemical reactor.

In addition we have found a lot of new papers about the “electro-deoxidation” of the oxides to metals and alloys at the electrolysis of CaCl$_2$-based melts (3-5). According to these papers, oxygen removed from the oxide cathode MeO$_n$ at the electrolysis of molten CaCl$_2$ by the reaction:

$$\text{MeO}_n + 2ne = \text{Me} + n\text{O}^{2-}$$

[1]

at the potential difference which is 0.1-0.5 V less than decomposition voltage of CaCl$_2$ (3.28 V at 1075 K). Formed O$^{2-}$ anions are moved to the melt and then transferred to the carbon anode, wherein they discharge to CO and CO$_2$. The CaCl$_2$-based melt serve as a medium, which can dissolve and transfer a large amount of O$^{2-}$ anions (in form of CaO) (6).

Presented papers (3-5) don’t take into account some important features of the CaCl$_2$-based melt nature that may influence the mechanisms of electrode and chemical processes at the electrolysis (7, 8). Depending on the design of the electrolytic cell and the electrode materials this influence can be significant (8). In our point of view, this is one of the reasons why the works did not find any practical development. Commonly the process of the metal and alloy production from oxides at the electrolysis of CaCl$_2$-based melts (FFC-Cambridge process) provokes scientific interest.

The above research areas suggest investigation of physical-chemical processes taking place at the electrolysis of CaCl$_2$-based melts. This work is devoted to the analysis of experimental data on the kinetics and mechanisms of electrode processes at the electrolysis of CaCl$_2$-based melts.
2. ANODE PROCESSES

2.1. Carbon anodes

The anode process on carbon in the chloride melts can be described by the following physical steps. Formation of the chlorine bubbles begin after the saturation of the layer near the carbon anode with dissolved chlorine at low current densities. The formation, growth and removal of the bubbles are observed mainly from the pores, hollows and cracks. With increasing current density the energy irregularity of the anode surface decreases, a number of chlorine bubble nucleation centers increases, and their distribution becomes more uniform.

The primary anode process on the carbon in molten CaCl2 is:

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e \]  

[2]

Today it is common to associate the anode overpotential with adsorption-desorption reactions at the electrode surface. In the chloride melts these are the chlorine atom adsorption [3], recombination [4] and electrochemical desorption [5]:

\[
\begin{align*}
\text{Cl}^- & \rightarrow \text{Cl}_{\text{ads}} + e \\
\text{Cl}_{\text{ads}} + \text{Cl}_{\text{ads}} & \rightarrow \text{Cl}_2 \\
\text{Cl}^- + \text{Cl}_{\text{ads}} & \rightarrow \text{Cl}_2 + e
\end{align*}
\]


Depending on the experimental conditions the rate of the common anode process [2] can be limited by steps [4] and/or [5]. After reaching the critical anode current density anode effect occurs, accompanied by an abrupt increasing of the electrode resistance, an increasing the cell voltage, and an abrupt current drop.

Studying the anode process is accompanied by the oxidation of Ca\(^+\) ions present in CaCl2-based melts (7, 8) to Ca\(^{2+}\) ions at the anode (up to 0.3-0.6 A cm\(^{-2}\)). Also the chemically oxidation of Ca\(^+\) ions occurs near the anode surface layer saturated with chlorine according to the reaction:

\[ \text{Ca}^+ + 1/2\text{Cl}_2 \rightarrow \text{Ca}^{2+} + \text{Cl}^- \]  

[6]

The anode process on carbon becomes more complicated at the addition of CaO in molten CaCl2. Two consequent electrochemical steps (9):

\[
\begin{align*}
\text{O}^2^- + x\text{C} & \rightarrow \text{C}_x\text{O}_{\text{ads}} + 2e, \\
\text{O}^2^- + \text{C}_x\text{O}_{\text{ads}} & \rightarrow \text{CO}_2 + (x-1)\text{C} + 2e
\end{align*}
\]

[7]  [8]

can be limited by the preceding formation of the oxide-chloride complexes during the CaO dissolution in molten CaCl2. Potentiostatic investigations of the carbon anode behavior in CaCl2-CaO melt (10) showed that anode process includes a number of steps, associated with the CO, CO2, Cl2 gases evolution, and also with the COCl2 gas evolution at high anode current densities.

Part of CO2 from the reaction [8] dissolves in the melt near the anode surface with the formation of CO3\(^2-\) anion, which may be discharged at the anode or transferred to the cathode by the melt flow, where it is discharged to form the dispersed carbon in the melt:

\[ \text{CO}_3^{2-} \rightarrow \text{C} + 3\text{O}^2^- - 4e \]  

[9]

A part of carbon from the reaction [9] can react with CO2 dissolved in an anolyte with the formation of CO which is removed from the cell together with the anode gases. However the interaction of carbon with Ca\(^+\) ions near the cathode is most likely:

\[ 2\text{Ca}^+ + 2\text{C} \rightarrow 2\text{Ca}^{2+} + \text{C}_2^{2-} \]  

[10]

It follows from the above that the using carbon anodes at the electrolysis of CaCl2-CaO melts in cells without separation of anolyte and catholyte leads to the changes in the physical -chemical properties of the melt and to decreasing of the values of anode and cathode current efficiencies, especially at low currents (3-5).
2.2. Oxygen-evolving anodes

Due to the high solubility of CaO in CaCl₂ melt (6) oxygen-evolved anodes can be studied at the electrolysis of CaCl₂-CaO melts. The solution of this problem will allow replacing anhydrous CaCl₂ by the cheaper CaO material and creating ecologically pure process with oxygen evolving at the anode. The behavior of oxide anodes of different composition in the CaCl₂-(5 wt.%)CaO melt were studied at 1075 K both under current load and without current load (11). Li₂O-doped NiO (resistivity 0.1-0.01 Ω·cm) was found to be the best material; for the following studies according to the values of electric conductivity and corrosion resistance at the electrolysis.

Fig.1 demonstrates polarization dependencies of the NiO-Li₂O anode on the CaO concentration in the melt and cell atmosphere. At high current densities chlorine evolves and the anode surface becomes covered by green NiO film. Under otherwise equal conditions the limiting current of O₂⁻ ion discharge is lower in the helium atmosphere than in the oxygen atmosphere. The slope of the polarization curve changes before the limiting current is applied. The slopes of initial parts of the curves match.

![Polarization curves obtained on NiO-Li₂O anode in molten CaCl₂-CaO at 1075 K with the CaO concentrations, mol. % (11): 1 – 9.4 (O₂); 2 – 9.4 (He); 3 – 3.9 (He); 4 – 1.9 (He); 5 – 0.8 (He). Chlorine reference electrode.](image)

Effect of helium can be explained by:

1 – its adsorption at the anode surface, which leads to the surface area decreasing, where O²⁻ ions are discharged and O₂ evolves. At low current densities helium adsorption does not influence on the overpotential value, as areas, which are not occupied by helium are sufficient for O²⁻ ion discharge;

2 – the processes at the three-phase boundary (gas-anode-melt). They can significantly influence the anode process current generation, because of the simplified
extrication of O$_2$ at the anode and oxide ions supply to the reaction area, which are formed at the gas-melt interface according to the exchange reaction:

$$2\text{Cl}^- + \frac{1}{2}\text{O}_2 \leftrightarrow \text{Cl}_2 + \text{O}^{2-}$$  \[11\]

At the analysis of the mechanism of the O$^{2-}$ ion discharge at the oxygen-evolving anode authors (12) divide the total reaction:

$$\text{O}^{2-} \rightarrow \frac{1}{2}\text{O}_2 - 2e$$  \[12\]

on the O$^{2-}$ ion diffusion from the melt bulk to the anode surface:

$$\text{O}^{2-}_{\text{bulk}} \rightarrow \text{O}^{2-}_{\text{s}}$$  \[13\]

the oxygen ion discharge with the adsorbed atom formation:

$$\text{O}^{2-}_{\text{s}} \rightarrow \text{O}_{\text{ads}} + 2e$$  \[14\]

recombination:

$$2\text{O}_{\text{ads}} \rightarrow \text{O}_2(\text{ads})$$  \[15\]

electrochemical desorption:

$$\text{O}^{2-} + \text{O}_{\text{ads}} \rightarrow \text{O}_2(\text{ads}) + 2e$$  \[16\]

and detachment of molecular oxygen:

$$\text{O}_2(\text{ads}) \rightarrow \text{O}_2(\text{g})$$  \[17\]

The model simulation of the anode process kinetics at the oxygen-evolving anode demonstrated that the polarization dependencies of the limited recombination [15] and electrochemical desorption [16] have qualitatively the same form. Moreover the calculated curve better coincides with the experimental one during the limited recombination (12).

The obtained experimental data and results of the theoretical calculations allow concluding that adsorption-desorption reactions at the anode surface are limiting ones. To clarify the studied process mechanism additional research using the non-stationary methods to study kinetics is required.

Corrosion of the oxide electrode is due to both chlorine ions discharge resulting in its direct chlorination and secondary reaction [11] (12, 13), which resulted in chlorine formation that can interact with the oxide anode. The rate of reaction [11] decreases as the CaO concentration in the melt increases and as CaF$_2$ and (3-6) mol.% CaO are added no chlorine is observed in oxygen in the output. The CaF$_2$ influence may appear because of complex formation. To specify the nature of the effect under study further research is necessary.

The actuality of the oxygen-evolving anode creation for the CaCl$_2$-CaO melt electrolysis is reported in the later works (14, 15). Basing on the preliminary studies within a number of metals (W, Mo, Ni, Fe, Au, Pt, Ag, Ru and other) and oxides, NiFe$_2$O$_4$ and CaRuO$_3$ spinels are suggested as the most perspective anode materials.

### 3. CATHODE PROCESSES

#### 3.1. Indifferent cathodes

At the CaCl$_2$-based melt electrolysis the near cathode layer acquires the properties of ion-electron liquid as the result of the Ca$^{2+}$ ion reduction and metal dissolution according to reaction (7, 8):

$$\text{Ca} + \text{Ca}^{2+} \leftrightarrow 2\text{Ca}^+$$  \[18\]

Due to the fact that such alloys have ionic and electronic conductivities, how it will influence the kinetics and mechanism of cathode processes.
Fig. 1 Polarization curves on Cu, W, Mo, and Fe cathodes in molten CaCl$_2$ at 1075 K (16). Chlorine reference electrode.

Fig. 2a demonstrated the stationary polarization curves obtained on the indifferent cathodes (W, Mo, Fe) at 1075 K in the CaCl$_2$ melt (16). Even in the thoroughly purified (especially from moisture) melt the mixture reduction currents are significant (to $10^{-2}$ A cm$^{-2}$). The polarization character of calcium-indifferent cathode made of different materials is the same. The linear area with a constant slope up to the calcium extraction potential ($\approx 3.28$ V at 1075 K), is described by Tafel equation $\eta = a + b \ln i$. The calculations demonstrated that the calcium cation discharge at this area proceeds with one electron. Increasing electrolysis temperature leads to the cathode potential shift to the positive area and discharge current growth, which can exceed 0.3 A cm$^{-2}$ at 1075 K (16). Thus, the cathode process at the CaCl$_2$ electrolysis takes place at diffusion regime. It can be represented in general form. At the initial moment at current load the calcium ion reduction process takes place according to reaction:

$$\text{Ca}^{2+} + e \rightarrow \text{Ca}^+$$ \[19\]

It will proceed until the Ca$^+$ ion concentration equal to its solubility is reached in the near cathode layer of the melt. Then two processes, which lead to calcium formation, take place at the cathode:

$$\text{Ca}^+ + e \rightarrow \text{Ca}$$ \[20\]
$$\text{Ca}^{2+} + 2e \rightarrow \text{Ca}$$ \[21\]

A fraction of each process in the cathode process is defined by kinetic factors. The potential of the indifferent cathode during reaction [19] acquires the value of the melt redox potential:

$$E = E_{\text{Ca}^{2+}/\text{Ca}^+}^* - RT / nF \ln \{[\text{Ca}^{2+}] / [\text{Ca}^+]\}$$ \[22\]

where [Ca$^{2+}$]$_s$ and [Ca$^+$]$_s$ are the molar concentrations of Ca$^{2+}$ and Ca$^+$ ions near the cathode surface (mol cm$^{-3}$), $n$ is the number of electrons taking place in the cathode reaction, $E_{\text{Ca}^{2+}/\text{Ca}^+}^*$ is the conventional standard potential (V).

Presence of the conductivity electron compound greatly influences the melt transport properties. The values of the $D$ diffusion coefficient of Ca$^+$ subions, which were assessed from the chronopotentiograms (17), at 1100-1275 K were $1.1-1.7 \times 10^{-3}$ cm$^2$
sec\(^{-1}\), which is twice orders higher than that of Ca\(^{2+}\) cations. The electron conductivity of Ca-CaCl\(_2\) is not influenced by the redox processes in the near cathode layer and at some distance from the electrode surface (17). It is one of the reasons of the current efficiency decrease during the calcium production by electrolysis. The Ca dissolution in CaCl\(_2\) (18) is accompanied with its dissociation on the Ca\(^{2+}\) subions, which interact with solvent ions, forming complex ionic groups and solvated electrons. The current efficiency can be assumed to be high at high current (5-10 A cm\(^{-2}\)) that will allow producing calcium by the CaCl\(_2\) electrolysis.

The molten CaCl\(_2\) and KCl mixtures with the liquidus temperature of 925 K appear to be interesting at calcium production as the potassium extraction potential is more negative than that of calcium. Main regularities of the cathode process are maintained considering the Ca\(^{2+}\) activity. Work (18) demonstrates that at KCl and CaCl\(_2\) additions the reaction [19] current decreased and the calcium extraction potential shifts to the negative area.

Voltammetric studies of the cathode process in the CaCl\(_2\)-based melts (3-5) also show the presence of the reaction (voltammogram peak) preliminary to the metal calcium extraction according to reaction [21]. However the authors of these works consider that this reaction is the “electro-deoxidation” of oxides [1] present in the CaCl\(_2\) melt contacting the indifferent cathode (current lead). To verify or argue against this point of view, it is necessary to perform a thorough study using different electrochemical methods.

3.2. Interacting cathodes

Calcium electroextraction at the calcium-interacting cathodes is accompanied by the significant depolarization, appearing due to the alloy formation and calcium activity decrease. The advantage of such cathodes is a significant decrease in reverse calcium dissolution, the alloys may be used independently for metallurgical application (1, 2).

The main characteristic of the calcium alloy production electrolysis is that the process rate depends not only on the melt transport properties, but also on the rate of calcium extraction from the surface to the alloy bulk. The processes can be influenced by the liquid-metal electrode surface tension dependence on the electrode potential value and electromagnetic melt mixing at high current loads.

Let us analyze the role of depolarization at calcium alloys production. The potential of calcium extraction according to reaction [21] on the indifferent cathode is equal to:

\[
E = E_0 + \frac{RT}{2F} \ln \alpha_{Ca^{2+}}.
\]

and on the interacting liquid-metal electrode it is:

\[
E_1 = E_0 + \frac{RT}{2F} \ln \left( \frac{[a_{Ca^{2+}}]}{[a_{Ca^{0}}]} \right)
\]

where \(E_0\) is the standard potential of calcium reduction (V); \(a_{Ca^{2+}}\) and \(a_{Ca^{0}}\) are the activities of Ca\(^{2+}\) ions in the melt and calcium metal in the alloy (mol cm\(^{-3}\)).

The difference between the \(E\) and \(E_1\) is equal to the depolarization value:

\[
\Delta E = -\frac{RT}{2F} \ln \alpha_{Ca^{0}}.
\]

Thus the depolarization value is determined by the alloy thermodynamics and composition on the interface with the melt. During the electrolysis process its value will decrease as \(a_{Ca^{0}}\) increases.

The polarization curves on the calcium-interacting cathodes in the CaCl\(_2\)-based melts have several characteristic areas of reduction of these metal cations, which appeared in the melt because of corrosion, at potentials from 1.7 V (especially Cu) by reaction
[19] and calcium extraction with depolarization (see Fig. 2b, curve for Cu (16)). Formation of solid intermetallic compounds at the surface of liquid melt can also influence the character of the polarization curves. Thus, the calcium-rich alloy, which concentration change is negligible due to the decelerated calcium extraction from the surface to the bulk of the melt, is formed near the calcium extraction potential on copper at the cathode surface. The values of depolarization of calcium extraction, for example, on the solid copper, hard zinc, and cadmium were 0.28 (16), 0.78 and 0.75 V (19), respectively.

The solubility of calcium from the alloy to the CaCl₂ melt remains high (20). Therefore, cathode processes, taking place at alloy production will be described by regularities common for calcium extraction at the indifferent electrode considering depolarization and diffusion difficulties, appearing at calcium extraction to the alloy bulk.

4. CONCLUSION

According to the analysis of the experimental data on kinetics and mechanisms of electrode processes taking place at CaCl₂-based melts the following conclusions can be made.

1. Usage of carbon anodes at the CaO-containing CaCl₂ melt electrolysis in the cells with undivided anode and cathode implies changes in physical-chemical properties of the melt, decrease in the current efficiency, especially at low current loads.

2. Research on specification of the nature of the cathode process step up to calcium extraction is of a primary interest for development of physical-chemical bases for new metal (especially Ca) production techniques.

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