ANODIC DISSOLUTION OF THORIUM IN SALT MELTS

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ANODIC DISSOLUTION OF THORIUM IN SALT MELTS

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There are no works in the literature devoted to the study of the processes of anodic dissolution of metals in salt melts, which are of interest for the theory and practice of the electrolysis of molten salts. The present communication gives the principal results of a study of the process of anodic dissolution of metallic thorium in a melt of alkali-metal chlorides.

The experiments were carried out in a cell whose design is shown schematically in Fig. 1. It consisted of a wide quartz test tube, hermetically sealed at the top. The electrolyte was a molten equimolar mixture of sodium and potassium chlorides. It was prepared by fusing pure salts in an atmosphere of dry hydrogen chloride, which was passed through the melt for some time. In order to remove dissolved gases, the salt melt was kept before the experiments under a reduced pressure of about 0.1 mm Hg, and all measurements were made under an atmosphere of pure argon. The thorium anode, whose geometric surface area was about 1 cm^2, was fastened to a molybdenum current lead. A molybdenum wire was used as the cathode, being placed in a quartz test tube in order to prevent penetration of the alkali metal to the anode. There was a small opening at the bottom of the test tube. The cell was situated in a massive metal block heated in an electric resistance furnace with automatic temperature control, which was maintained constant at the specified value within \$±\$1°.

The experiments consisted in measuring the thorium anode over a wide range of current densities (calculated for the geometric surface of the electrode), from $2 \cdot 10^{-3}$ to 8 A/cm^2 at 710 and 815°. At a specified current strength the anode was polarized for 3–4 sec. As preliminary experiments showed, this time was sufficient for establishing a stationary potential. The potentials of the thorium anode were measured relative to a chlorine electrode by means of a loop oscillograph at the moments when electrolysis was interrupted by a special time relay, which connected the oscillograph to the cell simultaneously with switching off the polarizing current. The chlorine reference electrode consisted of a tube of spectrally pure carbon, through which chlorine, obtained by electrolysis of molten lead chloride, was passed continuously (1). In order that chlorine could not reach the thorium anode, the chlorine electrode was placed in a quartz test tube with a small opening at the bottom, which was closed by an asbestos diaphragm.

Fig. 1 and Fig. 2: schematic cell and polarization curves

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Polarization measurements were begun after the thorium electrode in the initial molten equimolar mixture of sodium and potassium chlorides had acquired a constant potential, equal to −2.558 V at 710° and −2.524 V at 815°. The results of the measurements at the indicated temperatures are presented in Fig. 2 in a semilogarithmic coordinate system ($\lg i$—φ).

As can be seen, at $D_a < 0.05$ A/cm^2 the potential of the thorium anode changes little with current density and in magnitude is close to the potential of the thorium electrode in a melt of alkali-metal chlorides in the absence of polarization. Above this

0.05 A/cm^2 the anode potential increases linearly with the logarithm of the current density: $\varphi = a + b \lg i$. The slope of the polarization curves (the coefficient b before the logarithm of the current density), equal to 0.095 at 710° and 0.105 at 815°, is, within the possible errors of measurement, close to $2.3RT/2F$. This course of the polarization curves is observed up to approximately 1 A/cm^2. At higher current densities they deviate toward more positive potentials. When the current density exceeds 4 A/cm^2 at 710° and

Fig. 1. Cell. 1—thermocouple; 2—tube for introducing argon; 3—cathode; 4—chlorine reference electrode; 5—quartz test tube; 6—thorium anode.
Fig. 2. Polarization of a thorium anode in a melt of an equimolar mixture of potassium and sodium chlorides at 710 and 815°.

6 A/cm^2 at 815°, the potential of the thorium anode practically ceases to change with any further increase in the electrolysis current. In magnitude it approaches the value of the equilibrium potential of thorium in melts with a high concentration of $\mathrm{ThCl_2}$.

As in the case of cathodic polarization (^{2}), it may be assumed that the thorium anode is in equilibrium with the adjacent layer of the salt melt. In a melt of alkali-metal chlorides containing no thorium ions, the potential of the thorium electrode is established when equilibrium is reached between the surface layers of the metal and the electrolyte:

$$x\,\mathrm{Th}\,(\mathrm{s}) + 2\,\mathrm{Na}^{+}\,(\mathrm{melt}) \rightleftharpoons \mathrm{Na_2Th}_{x-1}\,(\mathrm{s}) + \mathrm{Th}^{2}\,(\mathrm{melt}),$$

$$\mathrm{Th}\,(\mathrm{s}) + 4\,\mathrm{Na}^{+}\,(\mathrm{melt}) \rightleftharpoons 2\,\mathrm{Na}_2^{+}\,(\mathrm{melt}) + \mathrm{Th}^{2+}\,(\mathrm{melt}),$$

$$2\,\mathrm{Th}^{2+}\,(\mathrm{melt}) \rightleftharpoons \mathrm{Th}\,(\mathrm{s}) + \mathrm{Th}^{4+}\,(\mathrm{melt}).$$

The surface layers of the electrode and electrolyte that are in contact with one another are not in equilibrium with the bulk layers of the corresponding phases. Therefore the ions formed, Th^{2+} and Na_2^+, diffuse into the bulk of the salt melt, while the alkali metal deposited diffuses into the interior of the electrode, where their concentrations are practically equal to zero. In the absence of electrolysis, the diffusion current of thorium ions is compensated by the discharge and recharge current of alkali-metal ions.

During electrolysis with anodic current densities below the magnitude of this diffusion current of Th^{2+} ions, what essentially occurs is the replacement of the discharge and recharge of alkali-metal ions by direct ionization of metallic thorium. The potential of the thorium anode then varies within the limits of the potential difference between the alloy Na_2Th_{x-1} and Th (approximately 0.058 V at 710° and 0.049 V at 815°).

Diffusion of thorium ions begins to affect the polarization of the anode at higher current densities ($D_a > 0.05$ A/cm^2), when the reaction of displacement and reduction of alkali-metal ions by metallic thorium is suppressed. In our previous work it was shown that melts containing an overwhelming amount of Th^{2+} ions may be in equilibrium with metallic thorium. If, in addition, one takes into account the circumstance that in chloride melts Th^{4+} ions form less mobile complex groupings with anions than do Th^{2+} ions, then it may be assumed that the thorium passing into the electrolyte diffuses into the bulk of the melt mainly in the form of divalent ions. This is supported, in particular, by the formation in the electrolyte of a fine suspension of metallic thorium, observed during electrolysis with a thorium anode in a closed electrolyzer that excludes access of atmospheric oxygen. The metal suspension is evidently formed as a result of a partially occurring disproportionation reaction (until the equilibrium concentration of Th^{4+} ions is reached):

$$2\mathrm{Th}^{2+}(\mathrm{melt}) \rightleftarrows \mathrm{Th}^{4+}(\mathrm{melt}) + \mathrm{Th}(\mathrm{s}).$$

Thus, the anodic current density can be expressed by the equation

$$i = \frac{2F}{\delta} D_{\mathrm{Th}^{2+}} [\mathrm{Th}^{2+}]_S,$$

where δ is the thickness of the diffusion layer, $D_{\mathrm{Th}^{2+}}$ is the diffusion coefficient of Th^{2+} ions in the salt melt, and $[\mathrm{Th}^{2+}]$ is the stationary mole-fraction concentration of these ions in the near-electrode layer of electrolyte, determining the magnitude of the anodic potential:

$$\varphi = E^{\circ}_{\mathrm{Th}/\mathrm{Th}^{2+}} + \frac{RT}{2F} \ln f_{\mathrm{Th}^{2+}} [\mathrm{Th}^{2+}]_S,$$

where $f_{\mathrm{Th}^{2+}}$ is the activity coefficient of Th^{2+} ions in the melt. As our studies have shown, the activity coefficient of thorium dichloride, and hence also of

Th^{2+} ions, in molten mixtures with alkali-metal chlorides changes little with concentration up to the pure salt. Therefore, without great error one may set

$$\varphi = E^{\circ}_{\mathrm{Th/Th^{2+}}} + \frac{RT}{2F}\ln[\mathrm{Th}^{2+}]_S.$$

Substituting here the expression for $[\mathrm{Th}^{2+}]_S$ through the diffusion current i, we obtain

$$\varphi = \mathrm{const} + \frac{2.3\,RT}{2F}\lg i,$$

where

$$\mathrm{const} = E^{0}_{\mathrm{Th0/Th^{2+}}} + \frac{2.3\,RT}{2F}\lg\frac{\delta}{2FD_{\mathrm{Th^{2+}}}}.$$

With increasing temperature, the polarization curves shift toward more positive potentials, since the quantity $E^0\mathrm{Th/Th}^{2+}$ entering into the constant has a large positive temperature coefficient ($\sim 1.0 \cdot 10^{-3}$ V/deg).

Above 1 A/cm^2 at 710° and above 1.5 A/cm^2 at 815°, the anodic potential, having reached, respectively, values of −2.375 V and −2.130 V, begins to increase with current density much more rapidly than would follow from the equation we derived, if one assumes that the thickness of the diffusion layer δ remains unchanged as the concentration of thorium ions in the near-anode layer of the electrolyte increases. In reality, as experiment shows, this assumption is justified only at relatively low concentrations, the upper limit of which can be estimated from the experimental data.

Previously we found the dependence of the equilibrium potential of a thorium electrode on a molybdenum current lead relative to a chlorine electrode (including the thermoelectromotive force between molybdenum and carbon) on temperature and on the mole-fraction concentration of Th^{2+} ions in a molten equimolar mixture of sodium and potassium chlorides. It is expressed by the equation:

$$E = -3.199 + 10.60 \cdot 10^{-4}T + 0.992 \cdot 10^{-4}T\lg[\mathrm{Th}^{2+}].$$

From this equation one can calculate the limiting mole-fraction concentration of thorium ions in the near-anode layer of the electrolyte at which the linear dependence of the potential on the logarithm of the current density is still observed. It is found to be $5.81 \cdot 10^{-3}$ at 710° and $3.59 \cdot 10^{-3}$ at 815°.

Apparently, in the region of higher concentrations the thickness of the diffusion layer ceases to be a constant quantity and begins to increase rapidly with current density; this, in turn, leads to a decrease in the diffusion rate, i.e., to an increase in the concentration of thorium ions in the near-electrode layer of the electrolyte and to a corresponding increase in the anodic potential.

When the concentration of thorium chloride in the near-anode layer of the melt approaches 100%, the anode potential reaches a value very close to the equilibrium potential of thorium in a melt of its chloride, equal to -2.204 V at 710° and -2.089 V at 815°.

Thus, during electrolysis of mixed chloride melts with a metallic thorium anode, practically only Th^{2+} ions pass into the electrolyte, even at relatively high current densities (on the order of 10 A/cm^2). Concentration polarization is observed in this case. A different picture is found in the electrolysis of molten thorium tetrachloride, which has predominantly anionic conductivity. Here, already at relatively small anodic current densities (~ 0.1 A/cm^2), the reduction reaction is suppressed:

$$\mathrm{Th} + \mathrm{ThCl_4}\ (\mathrm{melt}) \rightleftarrows 2\,\mathrm{ThCl_2}\ (\mathrm{melt})$$

and dissolution of the metal proceeds through the formation of Th^{4+} ions without noticeable polarization. This phenomenon was used by us in one of our works to determine the decomposition voltage of molten thorium tetrachloride (3).

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Note: Figure translations are in progress. See original paper for figures.