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Fig. 1. Electrolytic cell.

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Abstract

Full Text

PHYSICAL CHEMISTRY

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PRODUCTION OF HIGHLY DISPERSED ELECTROLYTIC DEPOSITS OF CERIUM CRYSTALLINE OXIDE UNDER THE ACTION OF IRRADIATION

(Presented by Academician V. I. Spitsyn, July 18, 1964)

Usually any change in the electrolyte is accompanied by corresponding disturbances in the kinetics or mechanism of growth of the electrolytic deposit. The latter, ultimately, leads to the appearance of various types of deposit structure (^{1}).

In the present work an attempt has been made to establish the degree of influence of ionizing radiation on the structure of electrolytic deposits. The final forms of Ce_2O_3 crystals,* deposited on the cathode during the electrolysis of a $CeCl_3$ solution ($^{2-4}$), were investigated. In the experiments an electrolytic cell was used with two electrodes placed in it and made in the form of plates, one of which (Pt—anode, area 1.5 cm^2) rotated at a speed of $\sim$ 120 rpm. The cathode was made of stainless steel ($\sim$ 2 cm^2) and was fixed immovably (Fig. 1).

The design of the cell made it possible to thermostat the solution. The pH value was monitored by means of a glass electrode and an LP-5 potentiometer. A direct-current generator served as the power source. The voltage in the circuit could be regulated from 0 to 24 V. The electrical circuit made it possible to monitor the current strength and the voltage at the electrodes during electrolysis (Fig. 2).

Fig. 1. Electrolytic cell. 1—rotating platinum anode; 2—stainless-steel cathode; 3—glass electrode for measuring the pH of the solution; 4—LP-5 tube potentiometer; 5—body of the electrolytic cell; 6—jacket for thermostatting.

Into the cell were poured 50 ml of a $CeCl_3$ solution with a concentration of 0.02 mg Ce^{3+} per 1 ml. Electrolysis was carried out at a current density of 70 mA/cm^2, voltage 12 V, pH 2.5, and temperature 55°. The entire process lasted 1 hour. Under these experimental conditions cerium crystalline oxide was schematic diagram of the cell power supply

Figure 2: schematic diagram of the cell power supply

deposited on the cathode, which is confirmed by the results of X-ray structural determinations (^{3}). In all cases the amount of deposit formed on the cathode was 0.8 ± 0.05 mg, or $80 \pm 5\%$ of the Ce^{3+} ions of the total cerium content in the solution (Table 1). After completion of the electrolysis the cathode was carefully removed from the solution and dried to constant weight in order to determine the amount of deposited crystalline oxide. Then, using an MIM-7 microscope (magnification 400×), the crystals were photographed (Fig. 3a). It should be noted that at the very edges of the cathode the deposit was usually coarse-crystalline.

As is evident from Fig. 3a, the electrolytic deposit consists of separate large crystals and of aggregates of crystalline blocks situated separately from one another. This type of deposit was obtained in all photographs when the experiments were repeated up to 10 times.

The next series of deposits was obtained with strict observance of the electrolysis-process conditions described earlier, but with the addition to the electrolyte of various amounts of $\mathrm{Ce^*Cl_3}$. The isotope Ce^{144} without carrier* was used, with a specific activity of 19.3 mCi/ml, $E_{\beta(\max)} = 0.3$ MeV, $E_{\gamma(\max)} = 0.1$ MeV, $T_{1/2} = 284$ days. The amount of impurities Sr^{2+}, Ba^{2+}, Ca^{2+}, Al^{3+}, Fe^{3+}, Mg^{2+} in the radiocerium solution was ~ 0.3 mg/ml. At the same time, Pr^{144}, present with it in radioactive equilibrium, was present in the solution: $E_{\beta(\max)} = 2.3$ MeV, $E_{\gamma(\max)} = 1.5$ MeV, $T_{1/2} \simeq 17.5$ min.

Fig. 2. Principal electrical circuit diagram of the cell power supply

Microphotographs of the deposits (Fig. 2b, c, d) correspond respectively to electrolytes containing 0.2; 2.0 and 20.0 mCi Ce^{144}–Pr^{144} in the total volume of solution. As may be concluded from these figures, with an increase in the amount of radioactive isotope in the liquid phase, the deposit formed regularly becomes more and more fine-crystalline. Strictly speaking, for an electrolyte with an activity of 20 mCi/50 ml, at a magnification of 400× it is already impossible to distinguish individual crystals; the electrolytic deposit uniformly covers the entire electrode as a crust. It must be noted that in this case the character of the deposit does not change over the entire area of the cathode.

The observed regularities cannot be attributed to the influence of chemical impurities introduced into the electrolyte together with the radioactive isotope. We carried out special experiments which showed that the addition to the solution

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* It should be noted that deposition of a mixture of oxides of Ce^{IV} and Ce^{III} on the cathode is equally probable.

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Fig. 3. Microphotographs of cerium deposits.

Figure 3: Fig. 3. Microphotographs of cerium deposits.

of ions Sr^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+} in amounts many times exceeding their content in the electrolyte with the highest radioactivity does not affect the structure of the cerium oxide deposit. Thus, the only factor affecting the structure of the electrolytic cerium deposit (and the only quantity changing in the course of the experiments) is the ionizing radiation of the radioactive isotope.

Since the primary action of ionizing radiation is evidently associated with radiation-chemical processes in the solution and at the electrodes, external irradiation of the electrolyte should also influence the electrolysis process. Experiments with irradiation of the entire cell were carried out using a Co^{60} source (40,000 g-eq Ra), with a nonradioactive electrolyte, all other experimental conditions being kept unchanged. Table 1 shows the absorbed radiation doses. Dosimetry was performed using ferrous sulfate.

As is evident from the data of Table 1, the number of crystals deposited remains constant and does not depend on irradiation of the solution. Only the structure of the electrolytic deposit changes (Fig. 3d, e, f). Characteristically, the structure of the deposit obtained with external irradiation is analogous to the deposit obtained earlier upon introduction of radioactive isotopes into the electrolyte solution (Fig. 3b, c, d). It should be noted that at equal absorbed— at equal doses the action of radiation from a radioactive isotope is more effective than external irradiation (Fig. 3g, d, e).

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Fig. 3. Microphotographs of cerium deposits.
a –nonradioactive electrolyte. Initial solutions containing Ce144 (in μ Cu): *b* –0.2; *v* –2.0; *g* –20.0. Deposits formed under irradiation (in ev/ml): *d* $-1.5 \cdot 10^{15}$; *e* $-1.0 \cdot 10^{16}$; *zh* $-2.0 \cdot 10^{17}$; *z* $-0.9 \cdot 10^{17}$ (with a closed cathode).

Thus, with an increase in the absorbed dose of ionizing radiation at the cathode during electrolysis, a finely dispersed precipitate of cerium oxide is deposited.

Table 1

Absorbed radiation doses and weight of the electrolytic precipitate

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* Since Ce^{144} was used in the experiments without carrier, the concentration of Ce^{3+} in the initial solution was constant.

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Radioactive electrolyte	Radioactive electrolyte	Radioactive electrolyte	Irradiation with Co^{60}	Irradiation with Co^{60}
radioactivity, mCu	absorbed dose, eV/ml	precipitate weight, mg (as Ce^{3+})	absorbed dose, eV/ml	precipitate weight, mg (as Ce^{3+})
0.0	0.0	0.85	$1.5 \cdot 10^{15}$	0.78
0.2	$1 \cdot 10^{13}$	0.82	$1.0 \cdot 10^{16}$	0.84
2.0	$2 \cdot 10^{14}$	0.75	–	–
20.0	$2 \cdot 10^{15}$	0.80	$2.0 \cdot 10^{17}$	0.73
–	–	–	$0.9 \cdot 10^{17}$	0.77

ceria. Evidently, this method for obtaining a homogeneous fine-crystalline precipitate should also be applicable to other systems.

The action of radiation reduces to the processes of radiolysis of the electrolyte and radiation-chemical changes at the cathode, both of these factors playing an equally important role. Indeed, at a dose of $0.5 \cdot 10^{17}$ eV/ml with electrodes protected by a layer of lead from the γ-rays of Co^{60}, the electrolytic precipitate obtained was, although fine-crystalline, nevertheless composed of larger crystals than in the case of an unshielded cathode (Fig. 3 ,).

The decisive importance for the mechanism of formation of the electrolytic precipitate is apparently the adsorption and interaction of radiolysis products with the cathode, as well as direct irradiation of the electrodes. It is known that irradiation of platinum and stainless steel by Co^{60} γ-quanta increases the adsorption capacity of both metals with respect to Ce^{3+} and Cs^{+} ions in aqueous solutions ([5]). Thus, the number of active sites on the electrodes increases, on which the growth of individual crystals is possible. From this point of view the reason is clear for the considerably greater influence on the structure of the electrolytic precipitate of radiation from Ce^{144} (at equal absorbed doses per 1 ml of solution) as compared with external irradiation from Co^{60} (Fig. 3e, d, e). Indeed, the absorbed dose (in eV per 1 cm^2 of cathode) will be several times greater for radioactive cerium than in the case of irradiation from Co^{60}, although the volume doses may be equal. With the cathode shielded from radiation (Fig. 3z), the active sites of the electrodes are apparently adsorbed products of water radiolysis or sites of interaction of H and OH radicals with the metal surface.

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