The Electrodeposition of Ruthenium from a Ruthenium(III) and Ruthenium(IV) Solution and a Fission Products Solution

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Ruthenium in an aqueous solution may be present as a variety of chemical species, and its chemical behavior is affected by various factors. Thus the complete separation of ruthenium is one of the most difficult problems in the separation of fission products. In order to solve this problem, various separation methods, including solvent extraction,[1,2] ion exchange[3] and ruthenium-tetroxide distillation[4], have been proposed. Since ruthenium is one of the noble metals, the electrochemical method should be useful for the separation of ruthenium from fission products. Although some electrochemical studies of ruthenium have been reported (they will be described below), no electrochemical method has yet been applied successfully to the separation of ruthenium from fission products.

The electrochemical studies of ruthenium were carried out by Griess and Lietzke,[5,6] by Haissinsky and El Guebely[7,8] and by other investigators. Griess and Lietzke reported that the complete electrodeposition of ruthenium was possible from a ruthenium nitrosyl chloride solution at concentrations higher than 5×10^{-5} M, while an 80% deposition was obtained at concentrations of 5×10^{-6} M or less. Haissinsky and Guebely investigated the electrodeposition of ruthenium on the cathode and the anodic oxidation of ruthenium sulfate using a sulfuric acid solution.

In this study, we will attempt to find an electrochemical method of separating ruthenium from fission products. For this purpose, the electrodeposition will be investigated with sample solutions containing ^{106}Ru-labeled ruthenium in the form of ruthenium chloride and ruthenium nitrosyl chloride. Moreover, the electrodeposition method will be successully applied to the separation of ruthenium from fission products. The ruthenium deposited on a platinum electrode is easily recovered into a solution by anodic oxidation, using sodium hydroxide as the electrolyte.

Experimental

Cells for Electrolyses.—Cells of two types were used for the electrolyses: one of them was a Joliot cell[9] made of Plexiglass, while the other, shown in Fig. 1, was a cylindrical glass cell clamped on the cathode plate by a brass stand. The latter was used for the electrolyses at elevated temperatures and for the separation of ruthenium from fission products. Silver-coated copper (20×0.5 mm.) and platinum (20×0.05 mm.) plates were used as the cathode, and a platinum wire (0.50×100 mm.), as the anode. As the reference electrode, a saturated calomel electrode was used for the Joliot cell and a silver-silver chloride electrode for the cylindrical glass cell. The cathode potential was kept at a given potential against the reference electrode by a potential regulator.

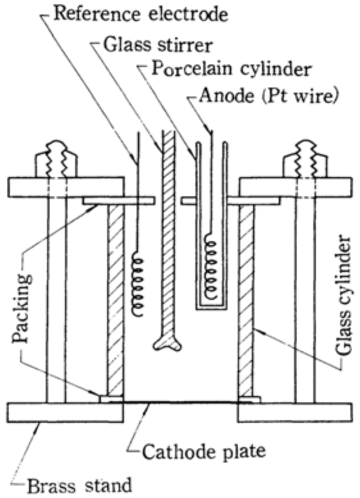

Fig. 1. Cylindrical glass cell.

The Preparation of a Ruthenium Sample Solution and the General Procedure.—Radioruthenium-106 (as ruthenium chloride) in a hydrochloric acid

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solution was imported from the Radiochemical Center, Amersham, England. A 1×10^{-7} M ruthenium chloride sample solution was prepared by evaporating the radioruthenium chloride and by dissolving the residue in 0.1 M hydrochloric acid. A 2×10^{-4} M ruthenium chloride solution was prepared by the following method. Radioruthenium was added to a ruthenium chloride solution of an appropriate concentration ($\sim10^{-3}$ M), and then ruthenium tetroxide was distilled. The distilled ruthenium tetroxide, containing radioruthenium, was absorbed in dilute hydrochloric acid containing a small amount of hydrogen peroxide. The solution was then evaporated to dryness, and the residue was dissolved in 0.1 M hydrochloric acid. The ruthenium concentration was determined by the colorimetric method with a ruthenium thiourea complex. Ruthenium nitrosyl chloride was prepared according to the method of Griess; the resulting ruthenium nitrosyl chloride was dissolved in 0.1 M hydrochloric acid.

Five milliliters of the sample solution was placed in a cell equipped with a silver-coated copper plate as the cathode, a platinum wire as the anode, and a motor-driven glass stirrer. The solution was then electrolyzed while being continuosly stirred for a given period of time. In some cases, a Geiger counter was placed close to the outside of the cathode plate, which constituted a part of the wall of the cell, in order to measure the radiation from the inside. The rate of increase in the counting rate was directly related to the rate of electrodeposition. The activity of the electrolyte solution was measured with a well-type NaI(Tl) scintillation counter, and the activity of the electrodeposited ruthenium on the cathode plate, with a Geiger counter.

The Electrolysis of the Fission Products.—The gross fission products in a nitric acid solution were imported from the Oak Ridge National Laboratory, U. S. A., and aged for about 3.5 years, until they consisted mainly of ^{144}Ce-^{144}Pr, ^{90}Sr-^{90}Y, ^{137}Cs, and ^{106}Ru-^{106}Rh. An aliquot of this sample was evaporated to dryness and dissolved in 0.1 M hydrochloric acid. Ten milliliters of the solution was electrolyzed in the cylindrical glass cell by the general procedure except that a platinum plate was used as the cathode and the cathode and anode electrolytes were separated.

The Determination of the Total Ruthenium Activity in the Fission Products.—Aliquots of the fission products solution before and after electrolysis were converted from a hydrochloric into a sulfuric acid solution and mixed with a ruthenium carrier (0.5 mg.) in a sulfuric acid solution. Then the solution was made alkaline with some sodium hydroxide solution, and antiformine (a commercial sodium hypochlorite solution) was added in order to oxidize the ruthenium to ruthenate or perruthenate. To this solution, carbon tetrachloride was then added, after which the solution was slightly acidified with sulfuric acid. After the solution had been shaken for about two minutes, the ruthenium was completely extracted with carbon tetrachloride as ruthenium tetroxide, while the other fission products remained in the aqueous phase. In this method, the activity of the ruthenium extracted in carbon tetrachloride was measured on the fission products solution before and after the electrolysis, and the percentage of ruthenium electrodeposited from fission products was calculated.

The Dissolution of the Ruthenium Deposited on a Platinum Plate.—In order to remove the ruthenium deposited on a platinum plate, anodic oxidation was performed by the following procedure. An electrolytic cell was equipped with the platinum plate carrying the ruthenium deposit as the anode (and a copper wire as the cathode). With 0.1 M hydrochloric acid as the electrolyte, electrolysis was carried out for ten minutes at room temperature. The anode potential was maintained at a given potential (each of the potentials presented in Fig. 8) against a silver - silver chloride electrode.

The anodic oxidation was also carried out with a 0.1 M sodium hydroxide solution without controlling the anode potential. In this case, the current was supplied by a six-volt storage battery and controlled to give a rapid evolution of oxygen gas at the anode. By this method, the deposited ruthenium was completely removed from the platinum in ten minutes; the cleaned platinum plate was thereafter used repeatedly.

Results

Ruthenium Chloride and Ruthenium Nitrosyl Chloride.—Figure 2 shows the results of the electrolysis of 1×10^{-7} M ruthenium chloride in 0.1 M hydrochloric acid for 90 min. There was no deposition of ruthenium at the cathode potential of −0.2 V. vs. SCE. The ruthenium deposition increased with the decrease in the cathode potential until it reached a maximum at −0.55 V. vs. SCE; it decreased with the further decrease in the cathode potential. The deposition curve for 2×10^{-4} M ruthenium

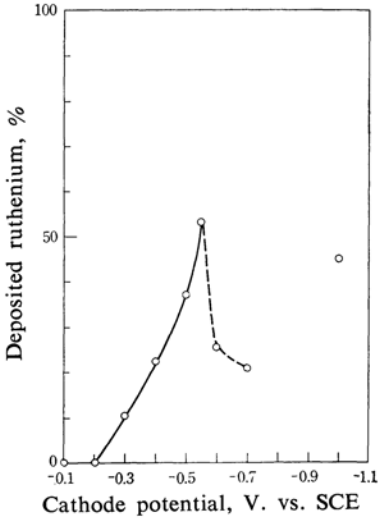

Fig. 2. Deposition curve of 1×10^{-7} M ruthenium chloride (0.1 M HCl, room temperature, 90 min.).

chloride is presented in Fig. 3. This curve is unlike the cuve for 1×10^{-7} M ruthenium chloride and has no maximum. In Figs. 4 and 5, the activity of the ruthenium deposited on the cathode plate is plotted against the loss of ruthenium activity from the electrolyte. The findings on 2×10^{-4} M ruthenium chloride at cathode potentials between −0.4 and −0.8 V. fell on a straight line, as would naturally be expected, but the findings on 1×10^{-7} M deviated from the linear relationship at cathode potentials lower than −0.6 V.

Figure 6 shows the results on electrolyses of 1×10^{-7} M ruthenium nitrosyl chloride in 0.1 M hydrochloric acid for 60 min. The deposition curve has a maximum at −0.6 V. vs. SCE. A comparison of Fig. 6 with Fig. 2 will indicate that ruthenium nitrosyl chloride more easily produces a metal deposit than does ruthenium

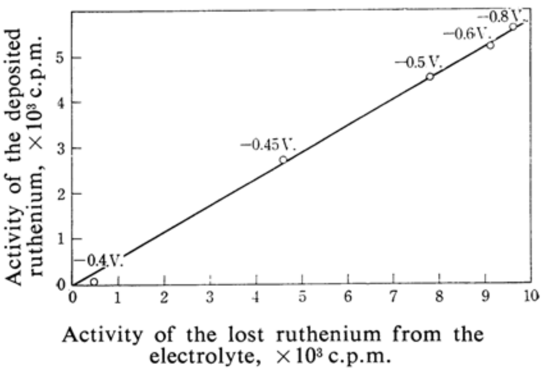

Fig. 5. Relationship between the deposited and the lost ruthenium from a 2×10^{-4} M ruthenium chloride electrolyte.

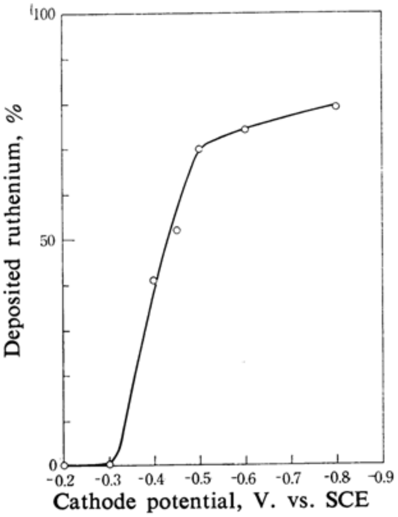

Fig. 3. Deposition curve of 2×10^{-4} M ruthenium chloride (0.1 M HCl, room temperature, 30 min.).

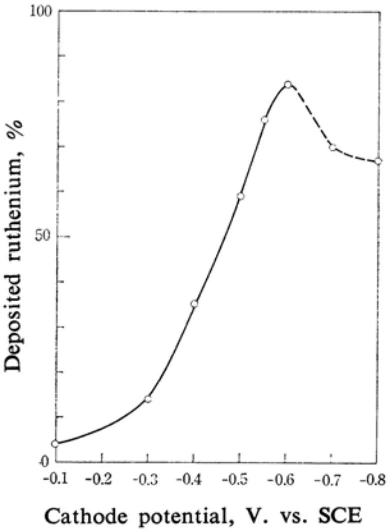

Fig. 6. Deposition curve of 1×10^{-7} M ruthenium nitrosyl chloride (0.1 M HCl, room temperature, 60 min.).

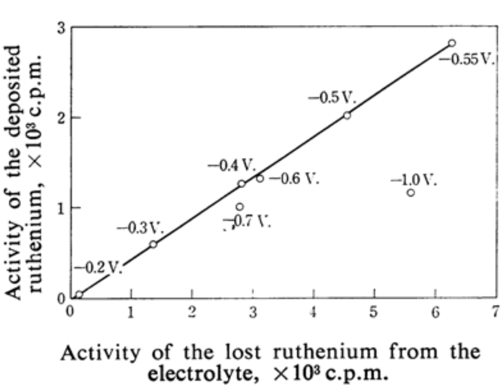

Fig. 4. Relation ship between the deposited and the lost ruthenium from a 1×10^{-7} M ruthenium chloride electrolyte.

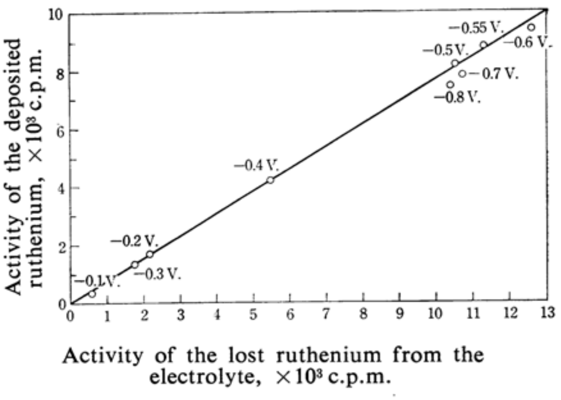

Fig. 7. Relationship between the deposited and the lost ruthenium from a 1×10^{-7} M ruthenium nitrosyl chloride electrolyte.

TABLE I. ELECTRODEPOSITION OF Ru FROM Ru NITROSYL NITRATE IN 0.1 M HNO_3
(one hour)

Cathode pot. vs. SCE	% Ru deposited
−0.3	15.8 (14.4)
−0.4	18.6 (36.4)
−0.5	36.3 (69.2)
−0.6	34.6 (84.0)
−0.7	21.1 (70.8)

Values in parentheses are data of Ru nitrosyl chloride in 0.1 M hydrochloric acid.

chloride. The relationship between the activity of the ruthenium deposit on the cathode plate and the loss of ruthenium activity from the electrolyte is presented in Fig. 7, which also shows deviation from a linear relationship at lower cathode potentials.

Experiments with a 0.1 M nitric acid solution were also carried out, since nitrosyl ruthenium normally occurs in a nitric acid solution. The results are given in Table I. The ruthenium depositions were not as good as those from a 0.1 M hydrochloric acid solution.

Since about six hours were required to obtain a 90% deposition of ruthenium from a 1×10^{-7} M ruthenium chloride solution at a cathode potential of −0.5 V. vs. SCE at room temperature, some experiments were attempted in an attempt to speed up the rate of ruthenium deposition. The results showed that a platinum plate was more useful as the cathode than a silver-coated copper plate; it gave an 85% deposition in two hours at 45°C. When 100 γ of hexachloroplatinic(IV) acid was added to the electrolyte as the carrier, 97% of the ruthenium was deposited in one hour at room temperature using a platinum plate as the cathode.

The Dissolution of the Deposited Ruthenium.—The results of the anodic oxidation are presented in Fig. 8. The ruthenium deposited on a platinum plate was completely removed from the plate in a 0.1 M hydrochloric acid solution in ten miutes at anode potentials higher than 1.2 V. vs. a silver - silver chloride electrode. At these potentials, oxygen gas evolved at the anode plate. The dissolution of the ruthenium deposited on a platinum plate was also complete within ten minutes when electrolysis without the anode potential control was carried out in 0.1 M sodium hydroxide with a current strong enough to produce a violent evolution of oxygen gas at the anode.

Fission Products.—On the basis of the experimental results described above, the separation of ruthenium from fission products was carried out under the following conditions: the cathode potential was −0.5 V. vs. a silver-silver chloride electrode, and the cathode electrolyte solution (fission products solution) and the anode electrolyte solution (0.1 M hydrochloric acid) were separated by a diaphragm in order to prevent the oxidation of ruthenium(III) or ruthenium(IV) to higher oxidation states. The results are presented in Table II. The nuclide separated by this method was identified as ruthenium-106 by gamma-spectrometry.

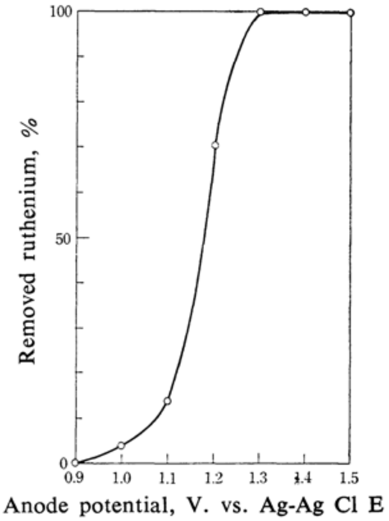

Fig. 8. Anodic oxidation of deposited ruthenium on platinum electrode (0.1 M HCl, room temperature, 10 min.).

TABLE II. ELECTRODEPOSITION OF Ru FROM FISSION PRODUCTS

Temperature	% Ru deposited
Room temp.	72.8
Room temp.	73.0
75°C	97.5
75°C	95.5
Room temp.	100 (Ru carrier; 0.5 mg.)

Discussion

Haissinsky and Guebely carried out experiments on the electrodeposition of ruthenium from solutions at the concentration of 5×10^{-9} g.equiv./l. in sulfuric acid without separating the cathode and the anode electrolyte; they found that the ruthenium deposited on the cathode decreased at lower cathode potentials. They thought that this decrease in the electrodeposition might be attributed to the rapid evolution of hydrogen gas at the cathode at lower potentials partially preventing the ruthenium deposition, although they also found, in their experiments on anodic oxidation, that the ruthenium oxide or hydroxide was deposited on the wall of the cell. On the other hand, Griess, who carried out electrolyses using a salt bridge to separate the cathode and the anode electrolyte, did not report any decrease in the ruthenium deposition on the cathode at lower potentials.

In the present study, the same tendency as had been reported by Haissinsky and Guebely was observed in experiments with a 1×10^{-7} M ruthenium solution, while a different tendency was observed at the concentration of 2×10^{-4} M.

If the decrease in ruthenium deposition had been effected mainly by the evolution of hydrogen gas at the cathode, the abnormal decrease should have been observed not only in the experiments at 1×10^{-7} M and in those by Haissinsky and Guebely, but also in the experiments at 2×10^{-4} M and in those by Griess, and a linear relationship would naturally exist between the activity of the deposited ruthenium and the activity of the ruthenium lost from the electrolyte, even at lower cathode potentials (-0.6 V.) Actually, however, no mention was made of any such abnormality by Griess, and a deviation from the linear relationship was observed in some of the present experiments (Fig. 4, 5 and 7).

From these facts, the abnormal phenomenon can be explained as follows. At lower cathode potentials, especially at -1.0 V., where gases rapidly evolved from the cathode and anode, an appreciable portion of the ruthenium in a 1×10^{-7} M solution disappeared from the electrolyte, probably due to oxidation to higher oxidation states, followed by deposition on the wall of the cell and the anode and/or by volatilization as ruthenium tetroxide. With a 2×10^{-4} M ruthenium solution, the portion of ruthenium oxidized was negligible as compared with the total, and a normal deposition curve resulted. Although no decisive conclusion could be derived from the present study, it seems very probable that the anodic oxidation of ruthenium, as well as the evolution of hydrogen gas at the cathode, is responsible for the abnormality in the deposition of ruthenium from the 1×10^{-7} M solution.

Griess and Lietzke reported the dissolution of the ruthenium deposited on a gold or platinum electrode. When they carried out electrolysis in a strong sodium cyanide solution using a gold or platinum electrode as the anode, the ruthenium deposited on the gold or platinum plate was completely removed from the plate by the electrochemical dissolution of the base gold or platinum metal. In the present study, however, our tentative conclusion is that the removal of the ruthenium that had been deposited on a platinum plate was effected by the anodic oxidation of the ruthenium, for an electrolytic solution (acidic or alkaline) took on an orange-yellow color when ruthenium in a macro amount was electrolytically removed from a platinum plate, whereas the solution was colorless with ruthenium in a micro amount.

It has been shown that this electrochemical method for the separation of ruthenium may be successfully applied to fission products. Unlike other methods, such as tetroxide distillation method and some solvent extraction methods, this method does not require the addition of an oxidizing, a reducing or a complexing agent and is free from trouble in the subsequent steps needed for the separation of other nuclides.

Summary

The electrodeposition of ruthenium from ruthenium chloride and ruthenium nitrosyl chloride solution has been studied and has been applied to the separation of the radioactive ruthenium contained in fission products. When the amount of the ruthenium deposited in a given time was plotted against the cathode potential, the curves for 1×10^{-7} M solutions of chloride and nitrosyl chloride showed a maximum. The decrease in the electrodeposition at lower cathode potentials may be due to the anodic oxidation of ruthenium as well as to the evolution of hydrogen gas at the cathode. The rate of electrodeposition was found to depend on the material used as the cathode, and to be increased by an increase in the temperature and by the addition of the carrier platinum or ruthenium. A complete separation of radio-ruthenium from fission products resulted when electrolysis was carried out with a 0.1 M hydrochloric acid solution of fission products containing carrier ruthenium under the appopriate conditions mentioned in the text. The ruthenium electrodeposited on the platinum electrode was completely recovered into the solution by anodic oxidation.

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