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A PROCEDURE FOR THE COMPLETE ELECTRODEPOSITION OF SMALL AMOUNTS OF RUTHENIUM

J.C. GRIESS, JR.

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Abstract

A study was made to determine the conditions necessary for complete removal of small amounts of ruthenium from solution by electrolysis. Complete deposition (> 99%) was possible when the ruthenium was present as the nitroso compound at low concentrations ($5x10^{-4}M$). Ruthenium metal was deposited in a smooth and adherent form on copper cathodes at cathode potentials more negative than -0.40V vs. the saturated calomel electrode. A procedure is given for the deposition of the radio-ruthenium produced at Oak Ridge National Laboratory.

Introduction

In order to use radioisotopes as a localized source of radiation for medical therapy, either the element or a compound of the element must be in a suitable form for the desired purpose. Perhaps the most suitable form is the elemental state, especially if the element in question is a metal. If the metal is a relatively noble one, it can usually be electrodeposited on any one of several different base metals of the desired shape and size. It is possible, therefore, to electroplate certain metals on needles for insertion into the body or on foils for direct contact with the skin or other parts of the body.

Ruthenium is a noble metal which can be easily plated from aqueous solutions and in addition has a radioisotope, Ru^{106}, of particular interest in radiotherapy. Fortunately, the predominant ruthenium isotope among the fission products after long decay periods is Ru^{106}, which has a half-life

of approximately one year and decays to Rh^{106} by the emission of a low energy beta particle. The decay scheme of Rh^{106} has been reported by Peacock[5] and will not be discussed here. It is sufficient to say that a large fraction of the radiation consists of very hard beta particles and a smaller fraction of gamma rays. Since Ru^{106} and Rh^{106} are in secular equilibrium, the half-life of the radiation can be considered to be one year. Hence, "Ru^{106}" has all the characteristics necessary for a high energy beta source.

The electrodeposition of ruthenium has been successfully carried out in two different concentration regions. Recently an analytical method[2] for the determination of trace concentrations of radio-ruthenium has been based on the complete electrodeposition of ruthenium from an aqueous solution. The supporting electrolyte contained both nitric acid and sodium nitrite. Further details of the process are not completely available.

The electrodeposition of ruthenium for protective and ornamental purposes has been well worked out. In a series of patents[6] issued to Baker and Company, Incorporated, numerous plating baths are described and in all of these baths the ruthenium is present either as the nitroso or as the nitrosoammino compound. The plating baths contain one to two grams of ruthenium per liter and can be operated at pH values from one to fourteen. However, the above-mentioned patents do not describe conditions necessary to obtain a good, adherent deposit when the initial ruthenium concentration is low nor do they give the conditions necessary for complete deposition from solution.

As previously stated, Ru^{106} is produced in the process of uranium

fission and is one of the isotopes offered for sale by the Isotopes Division of the Atomic Energy Commission. The separation of ruthenium from the other fission products ultimately depends on the volatility of the tetroxide. In the usual process of separation, inactive ruthenium is added and the total ruthenium content is distilled in an all glass apparatus. The distillate is collected in hydrochloric acid where the chloride ion reduces the ruthenium tetroxide to the quadrivalent state. The present stock of radio-ruthenium available at Oak Ridge National Laboratory is in the form of a solution of constant-boiling hydrochloric acid containing approximately fifty parts per million ruthenium. The activity of the solution is about one-half millicurie per milliliter.

In the present paper a method is described for the electrodeposition of the ruthenium mentioned in the preceding paragraph. It should be pointed out that only a satisfactory method was sought; no effort was made to investigate all possibilities. For the method to be suitable the following three requirements had to be met: 1) a compact and adherent deposit, 2) a minimum of operations in the preparation of the electrolyte, and 3) essentially complete removal of ruthenium from solution.

Experimental Details

Apparatus

All electrolyses were carried out in a cell of the type previously described[3]. In general, the cell assembly consisted of a brass stand on which a copper foil cathode rested. A glass cylinder with an outside ridge

$1\frac{1}{4}$ in. from the bottom rested on the cathode and was held in position by a brass collar bolted to the base. The area of the cathode exposed to the solution was 5 cm^2. Bridges were used to allow the anode and reference electrode to be placed outside the solution. The outside anode prevented the possible loss of ruthenium by volatilization of the tetroxide at the anode. The bridges were filled with 6N hydrochloric acid and a tight filter-paper plug was placed in the end of the bridge in contact with the electrolyte to minimize diffusion.

The potential of the cathode was controlled within $\pm$ 10 mv. by the use of a regulator designed in our laboratory. The regulator was similar to the one described by Lamphere and Rogers[4], but was capable of delivering currents up to 5 amps. and of supplying an anode-cathode potential of 100 Volts.

The voltage regulator and the described electrolysis cell were not essential to the successful completion of the problem but were used because of convenience. However, the use of the regulator did permit a determination of the minimum cathode potential necessary for complete deposition.

All radioactive samples were counted by means of a thin mica end-window Geiger-Mueller counter tube. The samples were maintained at a predetermined distance from the window by an aluminum support.

Preparation of Solutions

All ruthenium solutions were prepared from ruthenium chloride (J. Bishop and Co.). Sufficient ruthenium chloride was dissolved in water to form a 0.1M solution. All other solutions were prepared by suitable di-

lution of this solution.

In order to convert the normal ruthenium salt to the nitroso compound, the normal salt was evaporated to near dryness and then treated with 1 ml. of red-fuming nitric acid (Baker and Adamson, Technical Grade, sp. gr. = 1.59 - 1.60). The resulting solution was then taken to dryness and the residue treated with concentrated hydrochloric acid and again evaporated to dryness. The residue was then dissolved in the desired acid solution.

Ruthenium tracer was added to all solutions before conversion to the nitroso compound to facilitate analysis. The amount of tracer added did not affect the over-all ruthenium concentration.

The acid solutions were not standardized but were prepared by diluting the concentrated acid using the concentration given in the Handbook of Chemistry. Spot checks on some dilute solutions indicated that the concentrations were within $\pm$ 5% of the specified values.

All solutions used in the electrolyses were 5×10^{-4}M in ruthenium and 0.3N in acid. The ruthenium concentration was chosen at this value because the concentration of radio-ruthenium produced by the Operations Division, for whose use this process was developed, was of this order of magnitude. The choice of the acid concentration will be explained later.

General Procedure

A 20 ml. portion of solution was electrolyzed for a given period of time. During the electrolysis the electrolyte was stirred by means of a motor-driven, single-blade glass stirrer. All electrolyses were carried

out at room temperature (about 25°C) using a copper foil cathode.

In order to determine the amount of ruthenium remaining in solution at any given time, a 0.100 ml. aliquot was pipetted from the cell without interrupting the electrolysis. The aliquot was then evaporated to dryness and counted. At the completion of an electrolysis, the cathode was removed and counted.

The counting technique was identical to that described by Griess and Rogers[3]. All counts were corrected for coincidence, size of aliquot, difference in backscattering and counter geometry. Decay corrections were unnecessary since all counts were referred to a standard counted at the same time.

Results

Deposition Potential

In order to determine the potential necessary to obtain complete deposition of ruthenium from a 5×10^{-4}M solution, a series of electrolyses was run under the same conditions but at different cathode potentials. The ruthenium existed as the nitroso compound and the supporting electrolyte was 0.3N hydrochloric acid. At the completion of a four-hour electrolysis the cathode and an aliquot of the electrolyte were counted and a material balance obtained. The results of the material balances are shown in Table I and the data from the electrolyses are plotted in Figure 1. From the curve it is obvious that a minimum cathode potential of -0.40V vs. the saturated calomel electrode (S.C.E.) was necessary to obtain complete deposition in four hours. As a result, all future electrolyses were run at a cathode potential of

-0.60V vs. S.C.E. to insure complete deposition.

Rate and Completeness of Plating

The deposition rate of ruthenium was determined under constant conditions of stirring, electrode size and shape, and volume of solution. The solid line in Figure 2 represents the rate of ruthenium plating from a $5x10^{-4}$M ruthenium nitroso chloride solution in either 0.3N hydrochloric or 0.3N sulfuric acid. From the curve it is evident that 99% of the ruthenium was deposited in approximately three hours when the supporting electrolyte was either 0.3N sulfuric or hydrochloric acid. In some runs where the electrolysis was continued for five hours as much as 99.7% of the ruthenium was deposited from solution.

The broken line curve in Figure 2 shows the rate and completeness of ruthenium plating when 0.3N nitric acid was used instead of sulfuric or hydrochloric acid. It should be observed that the plating practically ceased after approximately 80% of the ruthenium had been deposited.

Electrolysis of a ruthenium chloride solution which had not been treated with red-fuming nitric acid showed that only about 80% of the ruthenium could be deposited in three hours. The plating rate curve in this case was very similar to the broken-line curve in Figure 2.

Complete deposition could not be obtained by electrolyzing solutions in which the ruthenium chloride had been previously evaporated to dryness with either concentrated nitric acid or aqua regia instead of red-fuming nitric acid. In both cases the rate and completeness of deposition were nearly identical to that described in the preceding paragraph.

Discussion

The method of preparing the nitroso compound of ruthenium proposed in one of the Baker and Company, Incorporated patents (Brit. 466, 126) depends upon the dissolving of hydrated ruthenium dioxide in aqua regia followed by evaporation to dryness. In the present problem the ruthenium was in solution and precipitation of the dioxide would have involved an added step which was highly undesirable in view of the activity of the ruthenium. Evaporation of a ruthenium chloride solution with aqua regia did not produce a compound from which complete plating could be obtained. In the same manner evaporation with concentrated nitric acid followed by solution in dilute acid did not produce a suitable electrolyte although it was reported by Deford[1] that the nitroso compound could be prepared in this manner.

Presumably the nitroso compound can be formed by treatment of a ruthenium compound with a mixture of sodium nitrite and nitric acid. Since the report[2] concerning the use of nitrous acid in the plating of ruthenium was not available at the time the experimental work was done, this method of forming the nitroso compound was not investigated. However, it appears that the presence of nitrate ion would prevent complete deposition of the ruthenium under the conditions used in the present investigation.

Evaporation of quadrivalent ruthenium chloride to dryness with red-fuming nitric acid formed a different compound than when the tetrachloride was treated with either aqua regia or nitric acid under the same conditions. This was shown by the fact that the residue obtained by evap-

oration to dryness with red-fuming nitric acid was a light tan color. The residue obtained by evaporation to dryness with either aqua regia or nitric acid was very nearly black. This difference in color was also apparent when the residues were dissolved in aliquots of the same solvent.

In the present study, the removal of the nitrate ion before electrolysis was necessary for complete deposition. The results obtained when nitric acid was used as supporting electrolyte are shown in Figure 2. The same type phenomenon occurred when the red-fuming nitric acid used to convert the ruthenium to the nitroso compound was not completely removed before electrolysis. The difficulty caused by the presence of nitrate was undoubtedly due to the reduction products of the nitrate ion. In the present investigation, however, no study of electrode reactions or electrolysis products was undertaken.

The deposits obtained from the nitroso compound of ruthenium in either sulfuric or hydrochloric acid were excellent for the intended purpose. The deposit was grey in color but had a highly polished appearance. The adherence was very good. It was possible to put a right angle bend in the cathode without a measurable loss of activity. Rubbing the cathode deposit with coarse filter paper did not remove any detectable amount of the ruthenium. In general, the cathode deposit was of such a nature that no difficulty should be encountered in depositing a thin film of some inactive metal over the ruthenium.

Deposits obtained from the ruthenium nitroso compound in 0.3N nitric acid were also good but the deposit did not seem to adhere quite as

well as when plated from hydrochloric or sulfuric acid solutions; however, the difference was very slight. When the normal ruthenium salt was used instead of the nitroso salt, the deposit was distinctly poorer. This was shown by the fact that an appreciable quantity of the ruthenium could be removed by rubbing the deposit with filter paper.

The acid concentration of the supporting electrolyte did not appear to be critical. Some experiments of a qualitative nature indicated that good deposits could be obtained at acid concentrations considerably higher than 0.3N. The choice of 0.3N acid was dictated by the electrode arrangement. As stated previously, the anode was in a separate vessel and connected to the electrolysis cell by a bridge which had a resistance of approximately 250 ohms. Hence, at hydrogen ion concentrations greater than approximately 0.3N, the current became excessive due to hydrogen evolution. When the current through the bridge became greater than 0.1 amp., the heat produced in the bridge caused bubbles to form which broke the circuit.

Under the conditions employed, a cathode potential of -0.40V vs. S.C.E. corresponded to a current density of 1.0 amp./dm^2 while a cathode potential of -0.60V vs. S.C.E. corresponded to approximately 3.0 amp./dm^2. As mentioned previously, the minimum potential necessary to obtain complete plating in four hours was -0.40V vs. S.C.E. and the maximum potential investigated was -0.60V vs. S.C.E. Hence, good deposits and complete plating were obtained at current densities between 1.0 and 3.0 amps./dm^2 and perhaps could be obtained at even greater current densities.

Procedure

The following is a procedure for the conversion of radio-ruthenium solutions available at Oak Ridge National Laboratory to a nitroso compound and the complete electroplating from a solution of this compound:

Evaporate to dryness under an infrared bulb an appropriate size aliquot of the ruthenium chloride solution. (The total ruthenium content should be 10 mg. or less). Dissolve the residue in a minimum of water and add 1 ml. of red-fuming nitric acid and again evaporate to dryness. To the residue add approximately 2 ml. of concentrated hydrochloric acid and evaporate to dryness for the third time. Dissolve the residue in sufficient 0.3N hydrochloric acid to form a solution 10^{-4} to 10^{-3}M with respect to the ruthenium concentration. Electrolyze the resulting solution at a current density of 1 to 3 amps/dm^2 (cathode potential of -0.40 to -0.60V vs. S.C.E.) using a copper cathode and a platinum anode. The anode may be placed directly in the electrolyte, but in order to avoid possible loss of ruthenium it is recommended that the anode be separated from the electrolyte by use of a bridge. To determine the completeness of plating at any given time a small sample of the electrolyte can be counted and compared with a similar size aliquot of the original solution.

Summary

It has been shown that essentially complete deposition of ruthenium from dilute solutions is possible when the ruthenium is present as the nitroso compound. Either sulfuric or hydrochloric acid is suitable as supporting electrolyte, but the presence of nitrate ion in the electrolyte prevents

complete deposition. The deposits obtained are adherent and have a highly polished appearance. A procedure is given for electroplating the ruthenium which is obtained from the fission products at Oak Ridge National Laboratory.

Table I

Effect of Potential on the Completeness of Plating of Ruthenium from a 5×10^{-4}M Ruthenium Nitrosochloride Solution in 0.3N Hydrochloric Acid

CATHODE POTENTIAL vs. S.C.E.	% RUTHENIUM IN SOLUTION	% RUTHENIUM ON CATHODE	% MATERIAL BALANCE
-0.40V	1.5	98	100
-0.30V	6.2	94	100
-0.25V	16	85	101
-0.23V	28	72	100
-0.20V	75	24	99
-0.15V	98	1.4	99

Fig. 1

Deposition curve for 5×10^{-4} M Ruthenium Nitrosochloride in 0.3 N HCl. (Each point represents a four hour electrolysis at the given potential.)

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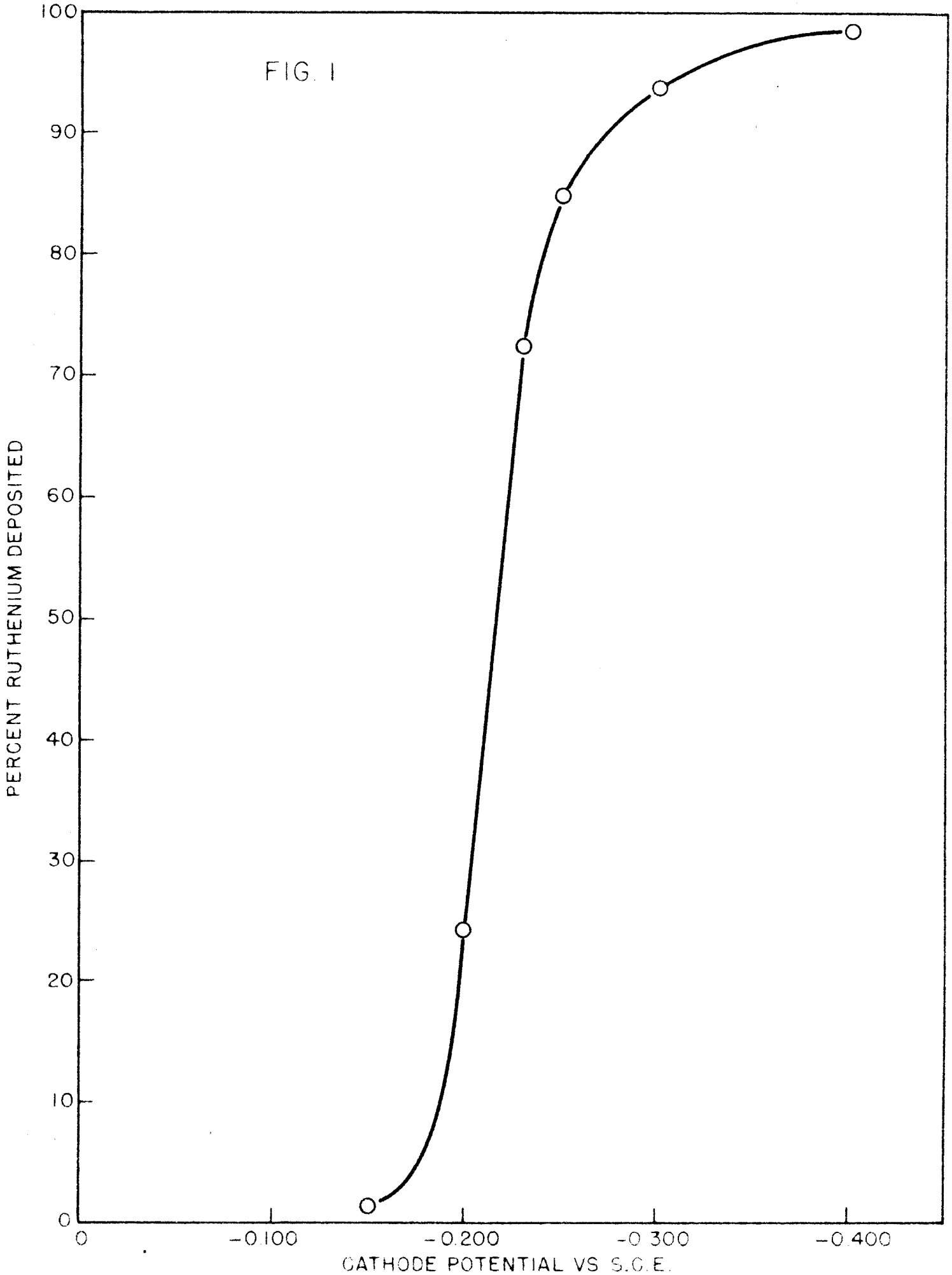

Fig. 2

Rate of Deposition of 5×10^{-4} M Ruthenium Nitrosochloride at -0.60 V vs. S.C.E.

O - 0.3N HCl Supporting Electrolyte

Δ - 0.3N H_2SO_4 Supporting Electrolyte

● - 0.3 N HNO_3 Supporting Electrolyte

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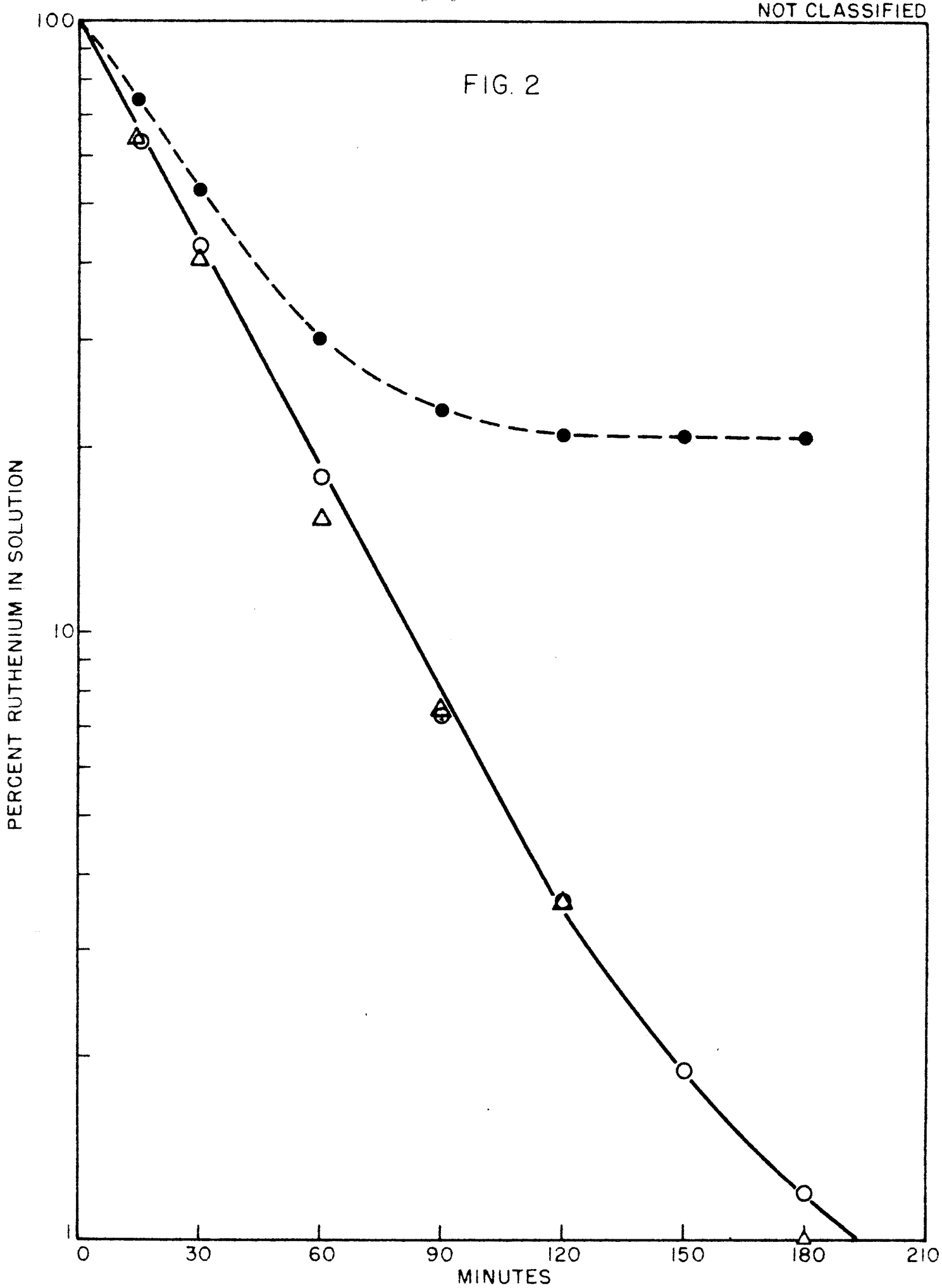

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