Deposition of Ru-106 and I-125 on silver by internal electrolysis

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Abstract The application of internal electrolysis for the deposition of ruthenium-106 and iodine-125 on silver was examined. These investigations were aimed at the preparation of sealed radiation sources for brachytherapy. The current and voltage of a cell built of silver cathode and aluminium anode, immersed in electrolytes containing different concentrations of ruthenium were determined. The same parameters were measured for the cell consisting of silver anode and platinum cathode as a function of the concentrations of NaI and NaOH in the electrolyte. The changes of current and voltage of the cells as a function of duration of electrolysis were investigated. The influence of white light observed during the deposition of iodine indicates that photolysis of silver iodide formed on the anode affects the cell parameters. From the results obtained it follows that electrolysis performed without application of external electric tension is a simple and convenient method for fixing considerable amounts of both ruthenium-106 and iodine-125 on silver.

Key words electroless plating • internal electrolysis • iodine-125 • ruthenium-106 • sealed radiation sources

Introduction

Fixation of different radionuclides on metallic surfaces is important from the point of view of preparation of sealed radiation sources. Ruthenium-106 and iodine-125 are used in medical radiation sources for brachytherapy.

Electrodeposition of ruthenium for ornamental or protective purposes as well as radioruthenium for ophthalmic applications has been described in a series of papers [2, 3, 7, 8]. However, the methods described in the above papers do not ensure conditions necessary to obtain compact and adherent deposits when the ruthenium concentration is low, nor do they give conditions necessary for nearly complete removal of ruthenium from solution. Also operations connected with the preparation of stable electrolytes and elimination of the formation of volatile ruthenium tetraoxide at the anode are complex. Ruthenium nitrososalts in solutions exist in two forms, and equilibrium between them is attained slowly. One of these forms decomposes easily under the influence of current forming a metallic deposit on the cathode, whereas the second one is more stable. The platable form transforms into unplatable with ageing of the solution. In diluted solutions the unplatable form prevails [1, 3]. Efforts to apply electroanalytical methods [4] for the deposition of radioiodine have proved unsuitable.

The present paper presents a convenient method for electrodeposition of radioruthenium and radioiodine on silver by means of internal electrolysis [6]. This term indicates a procedure by which the electrolysis of a solution is

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obtained without the application of an external tension. Such a procedure is very simple, particularly as regards the experimental requirements, which is of importance when radioactive electrolytes are used.

From the point of view of preparation of radiation sources, an assumption was made that the deposition of both ruthenium and iodine should occur on silver. From among few metals examined as counter electrodes, aluminium for ruthenium plating and platinum for iodine deposition were chosen. Attempts with applying titanium, although more negative than aluminium, proved less suitable.

Experimental

Ruthenium deposition

Solutions of ruthenium nitrosyl-trichloride and ruthenium trichloride in sulphamic acid were electrolysed in a cell with silver cathode and aluminium anode. The cathode was separated from the anode by a separator made of polyethylene foil doped with silica (Cookson Eutec, England) with pores diameter of $2 \div 4$ μm. The ruthenium carrier concentration in the catholyte was $0.5 \div 2.0$ g/l in 4% wt. sulphamic acid, whereas the anolyte was a solution of 4% wt. sulphamic acid. For obtaining radioactive deposits, ^{106}Ru was added to this solution in the amount depending on the desired activity of a particular source prepared. Since the specific acticity of the radioisotope was about 100 Ci/g, the change in the concentration of the metal in the electrolyte was negligible. The volumes of both catholyte and anolyte were 10 ml each. The surface area of silver cathode was 3 cm^2 and that of the Al anode about 35 cm^2. The active surface area of the separator was about 2 cm^2 and the distance between the electrodes about 25 mm.

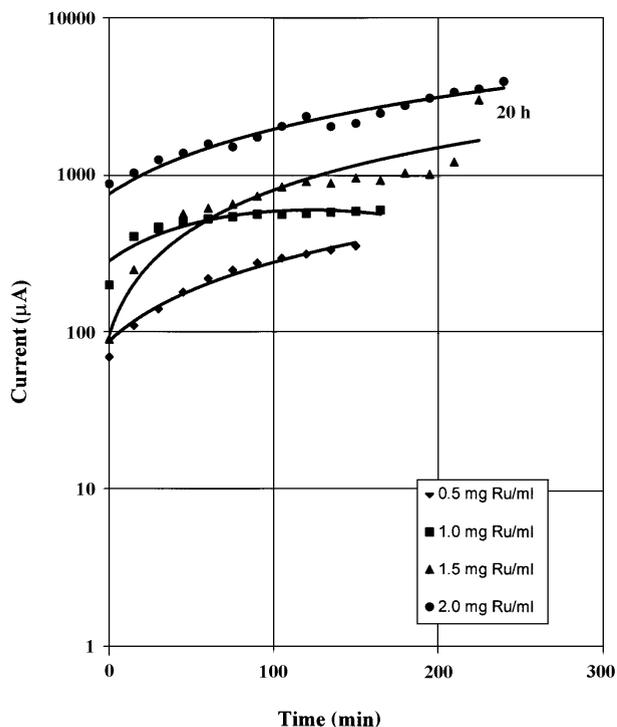Because ruthenium-106 is generally available in solutions of hydrochloric or nitric acid, the influence of acidification of the electrolyte with these acids was examined from the point of view of cell parameters and quality of deposits. The voltage of the cell at an elevated temperature was determined.

Iodine deposition

Alkaline solutions of sodium iodide were electrolyzed in a cell built of silver anode and platinum cathode. The concentrations of NaI and NaOH were from 1.6×10^{-4} M to 6.7×10^{-3} M and from 0.01 to 0.1 M, respectively. For the preparation of radioactive deposits, carrier-free iodine-125 was introduced to the electrolyte. The volume of the electrolyte was 30 ml and the surface area of the silver anode about 8 cm^2. Platinum gauze served as cathode. The distance between the electrodes was about 20 mm. A UV Mix Lamp (300 W) was used to determine the influence of light on the cell parameters. Current and voltage of the cell versus electrolyte concentration and time were measured. Cell voltage (V) and current (A) were measured by an electronic gauge type DT-300 Hi-Tec. The deposition of the desired radionuclides on silver electrode begins after short-circuiting of the electrodes.

Results and discussion

The measured current values of a cell with electrolyte containing different concentrations of ruthenium, as a function of time are plotted in Fig. 1. The results obtained show an increase of current with time although the electrodes of the cell were short-circuited between the measurements. Also higher current values were observed when the initial concentration of ruthenium in the electrolyte increased.
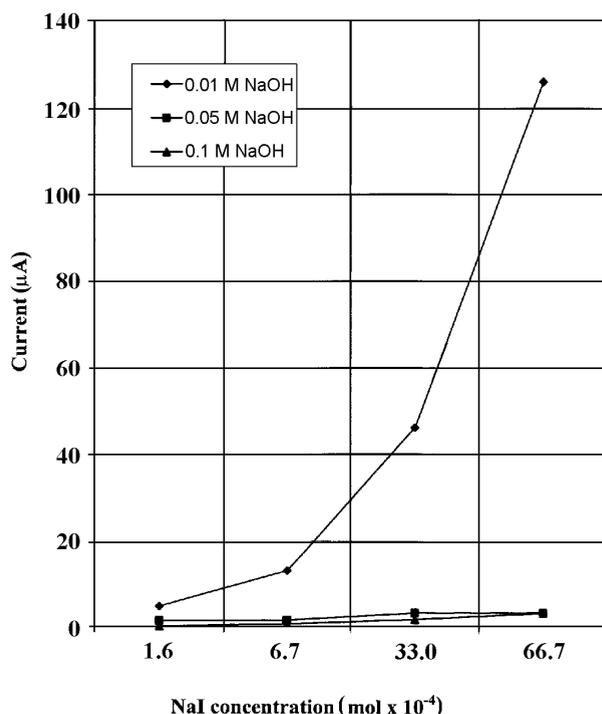

Fig. 1. Current of the cell $Al | H_2N \cdot SO_2 \cdot OH_{aq} | H_2N \cdot SO_2 \cdot OH_{aq}$, $Ru^{3+}_{aq} | Ag$ containing different concentrations of Ru in the electrolyte vs. time.

Fig. 2. Current of the cell $Ag | NaI_{aq}$, $NaOH_{aq} | Pt$ vs. concentrations of NaI and NaOH in the electrolyte.

The measured voltage was constant for all types of cells investigated and amounts to about 600 mV, irrespective of ruthenium concentration and time. During the internal electrolysis, dissolution of aluminium anode occurred. No precipitate formation in the anolyte was observed.

It is striking that although the concentration of ruthenium in the electrolyte decreases during the electrolysis, the current still increases. It can be caused by such phenomena as growth of the surface area of the aluminium anode due to dissolution or formation of diffusion layer on the electrodes. The process occurred without stirring. It has been observed that when the process, running in electrolyte containing 2 mg Ru/ml, was interrupted after some time and new electrodes immersed into the electrolyte, the current starts to increase from lower initial values. Further investigations should be performed to explain these phenomena. No effect was observed when ruthenium was added to the electrolyte in the form of $RuNOCl_3$ or $RuCl_3$.

Acidifying the electrolyte with inorganic acids (HCl, HNO_3) in the amounts corresponding to those which will be introduced with radioruthenium caused an insignificant decrease in the cell potential, slightly greater in case of HCl than HNO_3. A similar effect was observed with the rise of temperature up to about 70°C. Variation of sulphamic acid concentration between 2 and 5% wt. remained without influence.

After electrolysis, lasting for 24 h, 80% of ruthenium contained in the electrolyte solution was withdrawn and deposited on silver cathode. The deposits thus obtained were 2 μm thick, metallic and lustrous, adhering well to the underlying silver, showing no tendency to chipping or cracking.

The measured values of current and voltage of the cell used for deposition of iodine on silver anode are shown in Figs.
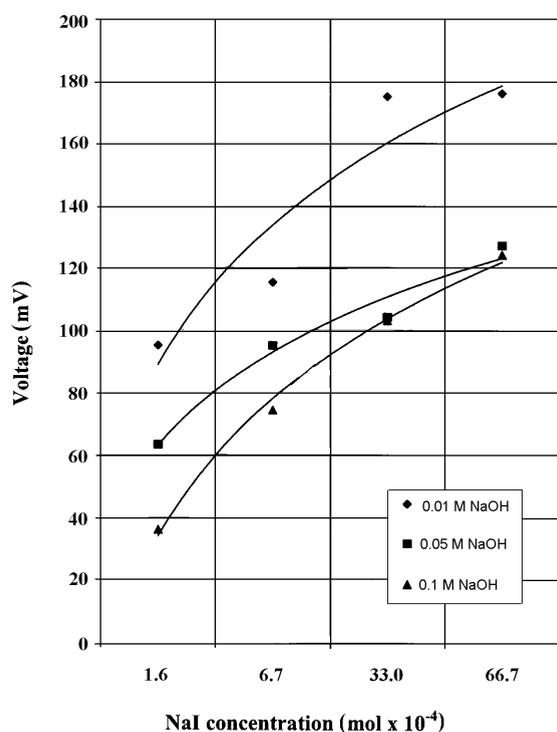
2 and 3, respectively. The plotted results indicate an increase of current with growth of the iodide concentration and a decrease of sodium hydroxide concentration in the electrolyte. It should be mentioned that the current values were measured immediately after the short-circuiting of the electrodes. They tend to decrease with time as it follows from the results plotted in Fig. 4. The cell voltage increased slightly with decreasing of NaOH concentration, remaining almost independent of the iodide concentration in the range between $3 \times 10^{-3} \div 7 \times 10^{-3}$ M. A decrease of iodine adsorption on silver with increasing of pH was observed earlier [5] due to the competition between I^- and OH^- ions. The current of the cell as a function of duration of the internal electrolysis are presented in Fig. 4. Between the measurements, electrodes of the cell were short-circuited.

From the results obtained it follows that the current decreases with working time of the cell during the first 8 days, irrespective of whether the cell remained under the influence of white light or not. In general, the cell protected from white light showed lower current values. Prolongation of the working time beyond 8 days caused negligible decrease of the current.

The potential of a cell exposed to the daylight decreases from initial 233 mV to 150 mV after 18 days. When the cell was protected against white light, slight decrease of voltage was observed, from 123 mV to 114 mV after 13 days. Short exposure of the cells to the light of a 300 W UV Mix Lamp caused increase of both current and voltage values. This may indicate that photolysis of silver iodide formed on the anode affects the cell parameters.

Conclusions

Internal electrolysis running without application of external electric tension proved suitable for fixing ruthenium-106 and iodine-125 on silver. Such a procedure, although long-
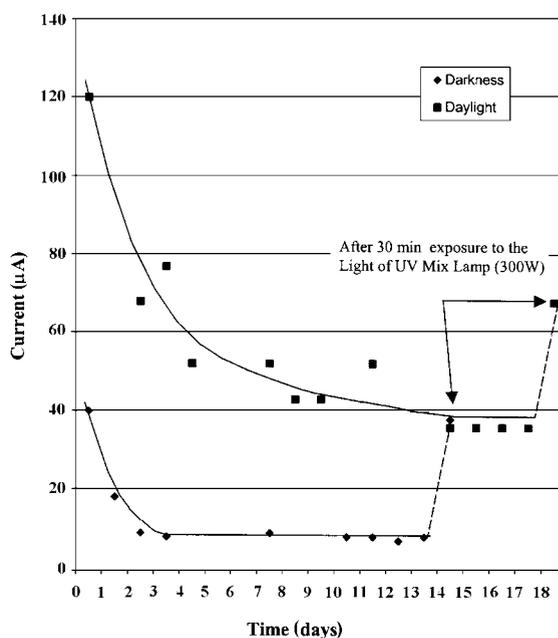

Fig. 3. Voltage of the cell Ag | NaI$_{aq}$, NaOH$_{aq}$ | Pt *vs.* concentrations of NaI and NaOH in the electrolyte.

Fig. 4. Current of the cell Ag | NaI$_{aq}$, NaOH$_{aq}$ | Pt *vs.* duration of the internal electrolysis.

-lasting, simplifies the experimental requirements which are important during operations with radioactive materials. The rate of withdrawal of the investigated radionuclides from the electrolyte solution is remarkable and amounts to 80% as concerns ruthenium and 98% in the case of iodine. One can expect that prolongation of ruthenium electrode-position will considerably increase this amount. Such expectation is plausible because further increase of the current was observed when duration of the electrolysis was prolonged up to 20 h (Fig. 1). It should be also emphasized that in practice higher concentrations than 2 mg/ml can be used.

Few ^{106}Ru ophthalmic applicators were manufactured using the described method and tested in accordance with PN-86-J-02000 eqv. ISO-2919. Maintaining a proper ratio between the carrier and tracer concentration in the electrolyte solution allows to control the activity of the metallic deposit. The activities of the applicators prepared were between 13 and 20 MBq depending on type, which assured the required surface dose rate of about 120 mGy/min. Fixing of 4.7 MBq of ^{125}I per square centimetre of the silver anode was achieved. This amount, although can be increased, is sufficient for practical purposes.

Irrespective of the importance of this method for fixing radionuclides on the surface of metals, it is also interesting from the point of view of applied electrochemistry. The current flow observed allows to consider the investigated cells as long-lasting current sources, although the electrodes remain short-circuited during a considerable period of time.

Discharge of the cell $\text{Al} \mid \text{H}_2\text{N·SO}_2\text{·OH}_{aq} \| \text{H}_2\text{N·SO}_2\text{·OH}_{aq}, \text{Ru}^{3+}_{aq} \mid \text{Ag}$ occurred after complete dissolution of the aluminium anode. Complete discharge of the cell $\text{Ag} \mid \text{NaI}_{aq}, \text{NaOH}_{aq} \mid \text{Pt}$ was not observed and, therefore, further investigations will be performed to explain the role of photolysis of silver iodide formed on the anode on the electric parameters of the cell.

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