Uranium Electrodeposition for Irradiation Targets

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Direct irradiation on targets inside nuclear research or multiple purpose reactors is a common route to produce ^{99}Mo-^{99m}Tc radioisotopes. The electroplating of low enriched uranium over nickel substrate might be a potential alternative to produce targets of ^{235}U. This work makes use of pulse electroplating either to create a nickel substrate or also to electrodeposit $UO_2(NO_3)_2$ solution diluted in isopropyl alcohol with final concentration of 10 mol/L [U]. The pulse electroplating employed 1 to 3 repetitions of 15 kilocycles, with duty cycle of 80% at 17 Hz at room temperature. The deposit presented an amorphous consistency. The amount of deposited uranium, measured by means of α-counting, was equivalent to around 2000 μg/cm^2 after 2700s of pulse electrodeposition. MEV/EDS technique and alpha-spectroscopy revealed that U-deposited material was natural uranium grade substance entrapped inside nickel substrate.

Introduction

Tecnecium-99 metastable (^{99m}Tc), as radiopharmaceutical, is used as the main radioisotope in cancer diagnostics, including thyroid, bones and breast. It is formed by decay of Molibdenum-99 (^{99}Mo), a subproduct of ^{235}U fission. This radioisotope is distributed weekly to hospitals inside generators that contain ^{99}Mo, which decay to its daughter ^{99m}Tc with a half-life of 66 hours. The ^{99m}Tc isotope has a convenient half-life of 6 hours is the radiopharmaceutical injected in the patients for radiodiagnosis. As many isotopes, the ^{99}Mo is usually produced by neutron irradiation of ^{235}U in a nuclear reactor [1]. For this, the enriched uranium nuclear material is shielding in a proper case and placed inside the reactor pool, for a relatively small period of 7 days to promote the maximum concentration of ^{99}Mo for later extraction. In most cases, the uranium target is still made with HEU (Highly Enriched Uranium, having more than 20%wt of ^{235}U) [2]. As HEU is used today for production of ^{99}Mo, it may also produce nuclear weapons. So, there is a concern about the possibility of fabricating nuclear explosive device using this material. The critical limit for safe use of uranium is up to 20 wt% enrichment of ^{235}U, called LEU (low enriched uranium). Due to these issues of possible use of HEU for military purposes, it has been developed the RERTR program of the U.S. Department of Energy, since 1978, aiming at reducing the enrichment of uranium

to LEU for use in nuclear fuel and irradiation targets for production of [99]Mo. However, presently, about 40 to 50 kg of highly enriched uranium is used annually for the production of medical isotopes. Currently, there is a lot of effort to develop LEU targets in accordance with the RERTR program [3, 4].

RERTR proposed a target using thin foil target U-Ni made by electrodeposition using molten salt electrolyte [5]. This method evolved significantly over the last decade since it has been first developed by Cintichem firm. It was modified and patented in 90´s by Argonne. Conceptually, in Chilean project, this target is a thin foil of uranium of 60mm x 100 mm x 135μm wrapped inside a 15μm nickel foil, which is placed in a sealed aluminum tube for irradiation [6]. This irradiation target holds around 250-300 mgU/cm^2.

A route based on electrodeposition is proposed in this work for preparing uranium targets for radiopharmaceutical production. For this purpose, the use of an aqueous electrolyte is not feasible, due the fact that uranium shows high oxidation potential in water. Considerable amounts of uranium can be electrodeposited using molten salts [7]. In acidic solutions, the ion containing uranium, such as UO_2^{+2}, has lower reduction potential than the H_3O^+. It seems possible to electrodeposit uranium in ionic solutions, since cyclic voltammetry indicates two peaks of cathodic reduction, suggesting uranium reduction in 2 steps – U(VI) to U(IV) and then precipitates as hydroxyl substances [8, 9]. Therefore, it seems feasible to use non-aqueous (aprotic) solvents for uranium electrodeposition. There are several possibilities of aprotic organic solvents which may be used [10-15].

Experimental and Results

Electroplating solution – The UO_2 solution, natural uranium grade, used in the electroplating, was prepared based on nitric lixivium process with nitric acid on calcined metallic uranium slags represented by the following reaction:

$$U_3O_8 \text{ (s)} + 8 \text{ HNO}_3 \text{ (l)} \rightarrow 3UO_2(NO_3)_2 \text{ (l)} + 2NO_2(g) + 4H_2O \text{ (l)} \quad [1]$$

The adopted process had the following parameters: (a) calcination of metallic uranium slag at 600ºC during 3h; sieving and segmentation of calcined slag in the range of 100-200 mesh; adding to 1molL^{-1}; temperature 40-50ºC; agitation of 300 rpm inside turbine stem type (45º inclination). The full lixivium took 9 hours. This lixivium produced uranyl nitrate solution, which was purified by solvent extraction method, using diluted n-tributhylphosphate. The purified uranium product was then precipitated as ammonium diuranate (ADU) at 60ºC, by injecting ammonium gas diluted with air, which was finally calcined and produced the used nuclear pure U_3O_8 dissolved in the same way by nitric lixivium, as described above [16]. The uranyl nitric solution (10 ml of nitric uranyl concentrate) was diluted in isopropyl alcohol to complete 1L, giving a final concentration of 10 mmol.L^{-1} [U]. The final pH of this solution was 1.75.This was the ionic solution used for electrodeposition of uranium.

Electroplating arrangement – It was used an electrochemical cell made with a vertical quartz tube containing the electrolyte solution housed inside a polypropylene structure, the working electrode, as cathode, was placed at the bottom of the cell. It was sealed by a rubber o-ring exposing an area of 2.641 cm^2 to the electrolyte interface. The used reference electrode was Ag/AgCl. The counter electrode for nickel electroplating was

electrolytic pure nickel bars with an immersed area at least twice bigger than cathode area. The arrangement for nickel plating is presented in Figure 1. The same arrangement was used for uranium electrodeposition without removing the nickel-plated substrate at the cathode. The system was rinsed with isopropyl alcohol before receiving the ionic solution containing 10 mmolL^{-1}[U]. The working electrode for U-deposition was platinum wire, with a sufficient area for not to impede the development of galvanostatic current.

Aluminum substrate – It was used coupons of cold rolled AA6061 with the dimensions of 22 x 22 x 2.25 mm. They were used as the substrate for nickel electrodeposition, before being submitted to uranium plating.

Nickel Electrodeposition – All samples of Al-substrate, before being submitted to U-plating, received a layer of nickel by pulsed

Figure 1 – Electroplating arrangement for nickel and uranium electrodeposition.

electrodeposition, using a square sign, using Watt's bath (0.85 mol.L^{-1} NiSO$_4$.6H$_2$O +0.15 mol.L^{-1} NiCl$_2$ + 36g.L^{-1} H$_3$PO$_4$) having pH = 3.7 [17]. The process was made with 1 repetition of 15 pulsing kilocycles with duty cycle of 80% under frequency of 17Hz, promoting an average galvanostatic current around -100 mA/cm^2.
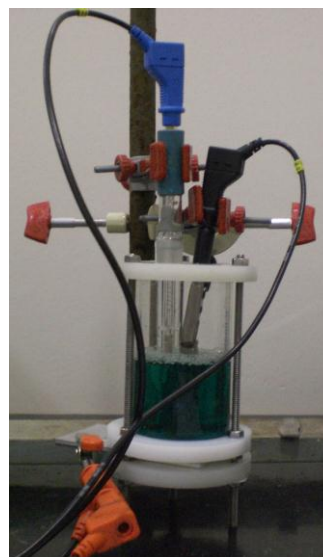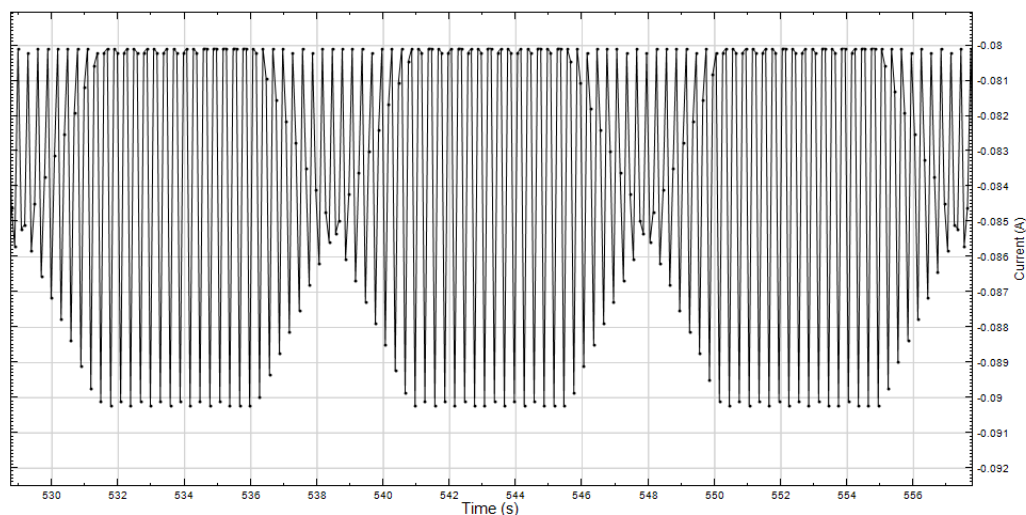

Figure 2 – Sample of current pulse during typical galvanostatic U-deposition with duty cycle of 80% under frequency of 17Hz.

Uranium electrodeposition – There was 2 types of uranium electrodeposition: (a) a DC potenciostatic (-3V) for 5 hours using the described ionic solution; (b) after lining the Al-substrate with nickel pulse plating, the sample was submitted to the uranium electrodeposition process. It was used a pulsing electrodeposition varying the number of kilocycles, so the total time of uranium depositing; the experiments used the following parameters: 1 to 3 repetitions of 15 kilocycles (1, 2 and 3); duty cycle of 80% under

frequency of 17Hz, which produced an average galvanostatic current between -80 to -90 mA over the whole area. A typical sample of pulsed current for U-deposition is presented in Figure 2.

Used equipment: For potenciometry measurements: Metrohm Autolab PGStat 302N equipped with FRA2, Buster BSTR20A, D.VOLT. MULT, ADC10M.X and SCAN250.X. For Scanning microscopy and microanalysis SEM/EDS, it was used a JEOL-6061 LA. Emission counter Ludlum dual scaler model 2929.

Results and Discussion

The first experiment was to test uranium electrodeposition using direct current with cathodic polarization. The used potential was -12V, made directly over aluminum substrate coupon, during 5 hours. It resulted in a deposition of an amorphous structure emitting very low average α-radiation counting. By indirect calibration of α-emission it is able to find the uranium content. Average mass was estimated to be deposited around 260 µg/cm^2 [U].

The pulse electrodeposition experiments were carried out over a previously Ni-electroplated layer made on aluminum substrate. The experiment consisted in increasing the number of pulsing cycles to promote electrodeposition over the Ni-layer using the same uranyl isopropyl ionic solution (50m.mol.L^{-1}[U]; pH=1.75). The imposed cyclic pulsing was galvanostatic (mean at -32 mA/cm^2) having 15 kilocycles with 5.10^{-2}s "on" followed by 1.10^{-2}s "off", with duty period varying up to 2000s . Figure 3 shows the coupons of the 2 experiments, with DC and pulsing galvanostatic electrodeposition. Micrographic images are shown these results in Figure 3.
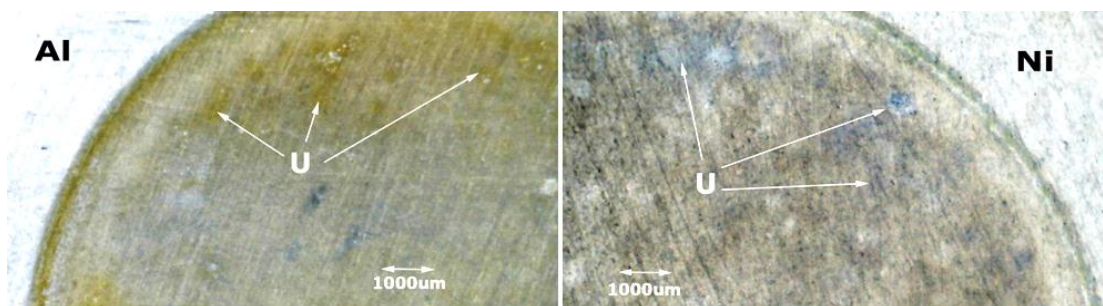

Figure 3 – (Left) Uranium electrodeposited over Al by cathodic polarization DC at -12V during 5 hours in 50 mmol.L^{-1} U isopropyl ionic solution; (Right) Pulsed electrodeposition of uranium of 15 kilocycles, using the same solution for 5.10^{-2}s "on" followed by 1.10^{-2}s "off".
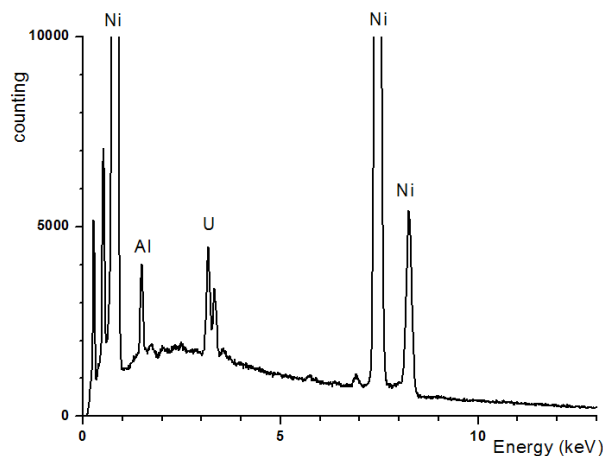
Figure 4 – EDS counting for uranium pulse electrodeposited in 15 kilocycles, using the uranyl isopropyl ionic solution with 10 mmol.L^{-1} [U].

SEM/EDS microanalysis revealed, qualitatively, a significant presence of uranium at electrodeposited samples, as shown in Figure 4. Alfa-emission of this sample had a counting of 53 cpm, which was far above the background (~4 cpm). Comparing the 2 experiments, it is possible to see that the pulsed method showed higher amounts (darker regions), since it covered a wider area of deposited uranium than the DC cathodic polarized method. A better comparison was made by SEM microstructures, as shown in Figure 5. Nevertheless, the darker areas of uranium deposition complex could not be properly seen, at the level of 1-10μm magnification. It appears as being an amorphous substance without any identifiable structure. Studies using IFIR and Raman showed a tendency to be hydroxide uranyl compounds.
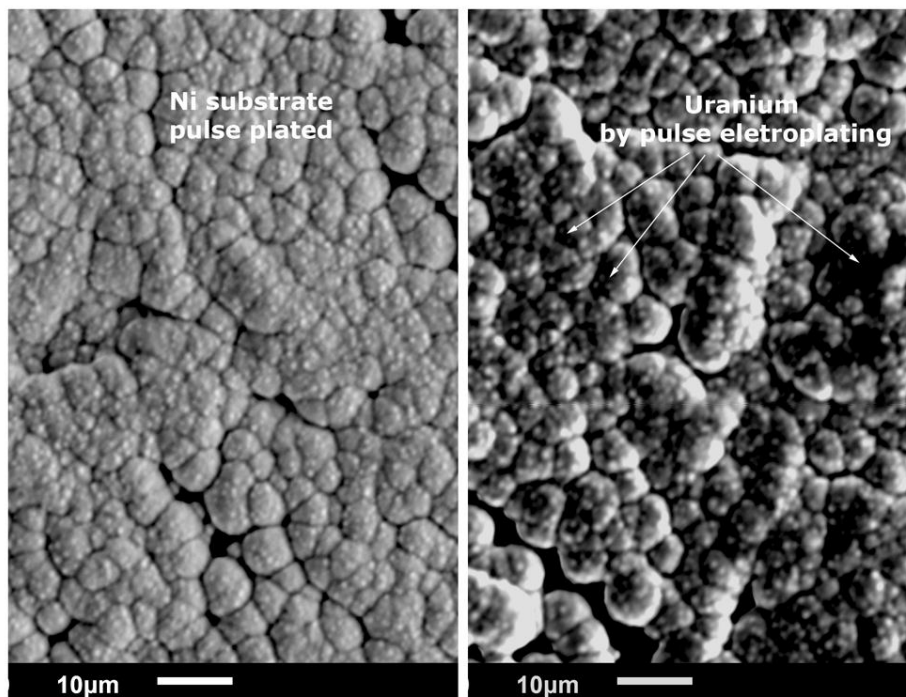

Figure 5 – SEM micrographs showing the nickel substrate (left) in contrast to the pulse electrodeposited uranium one after 15 kilocycles, using ionic uranyl solution with concentration 50 mmol.l^{-1}[U] for 5.10^{-2}s "on" followed by 5.10^{-2}s "off" (right).

To guarantee the presence of uranium, it was utilized alpha-spectroscopy, which generated a particle energy graph for α-emissions, as displayed in Figure 6. The measurement channels of the α-particles were duly converted to particle energy, in a direct proportion way, considering the energies of peaks of ^{238}U and ^{234}U. The level of energy due to ^{235}U, not introduced in the previous adjustment, confirmed the reliability of the interpolation, since it coincided precisely with the most typical ^{235}U α-emission (4.40 MeV).
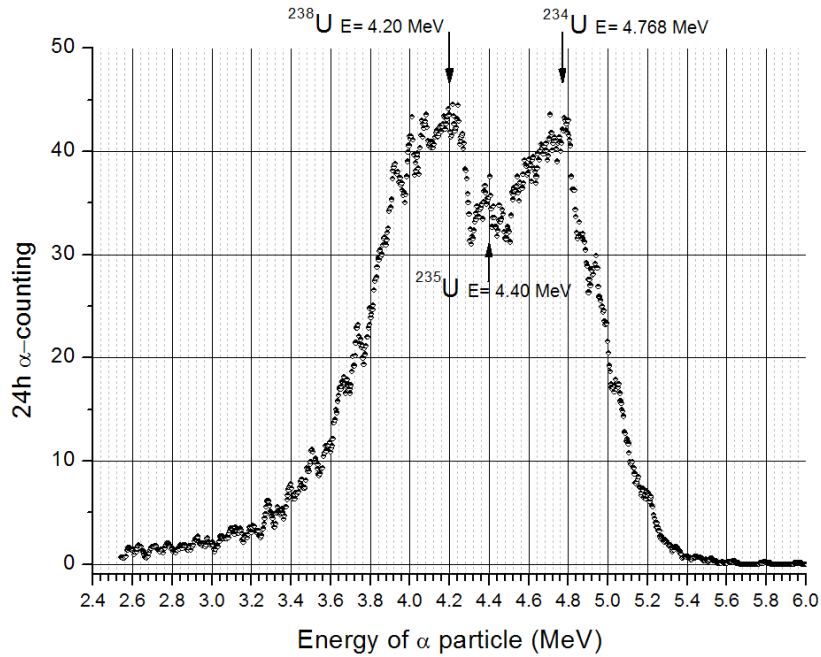

Figure 6 – Alpha-spectroscopy during 24h of an electrodeposited sample made by electropulse using 15 kilocycles, using $UO_2(NO_3)_2$ isopropyl solution with 50 mmol.l^{-1}[U] for 5.10^{-2}s "on" followed by 5.10^{-2}s "off" (right).

As could be seen in this graph, the α-particle spectrogram shows the peaks of the several uranium isotopes, with no major peaks heights alteration, than natural uranium. It reflects that the deposit was regular and it assures the presence of natural uranium (0.0054% ^{234}U; 0.72% ^{235}U and 99.275% ^{238}U) as the major radiation α-emitters.

It is possible to calibrate the mass of deposited uranium by using alpha emission counts per minute (cpm) compared with a precise uranium concentration in the prior solution before plating. The α-counting results for each electrodeposited sample may be calibrated as uranium mass deposited considering the 20μl of the prior planting solution had $2.38.10^{-3}$g of equivalent metallic uranium giving an average of α-counting of 65.99 ± 12.35 cpm. Based on this calibration, Figure 7 presents a graph of uranium mass electrodeposited against time. The used pulse electrodeposition experiments varied from 10 to 40 kilocycles, using $UO_2(NO_3)_2$ isopropyl solution with 50 mmol.l-1[U] for 5.10^{-2}s "on" followed by 1 to 5.10^{-2}s "off".

So, the average uranium mass deposition may be quantified with time, using statistical minimum square adjustment (R^2=0,6986) giving the following equation:

$$U\ deposit\ (\mu g.cm^{-2}) = 0.3573 + 855.88.t(s) \qquad [2]$$

This amount is relatively high if compared to potenciostatic DC cathodic electrodeposition at the same level of acidity. In this way, pulse electrodeposition seems to be more effective and productive. Technologically, it might be a latent route to produce irradiation [99]Mo-targets with LEU uranyl ionic solution, since the carried out experiments provided subsidies to develop an expanded study about optimization of electrodeposition for higher content of uranyl ions, longer electrodeposition time, under more intense voltage applied to larger areas. So, this field is still open in order to reach a useful amount to build commercial irradiation targets to produce the [99]Mo-^{99m}Tc radionuclides.

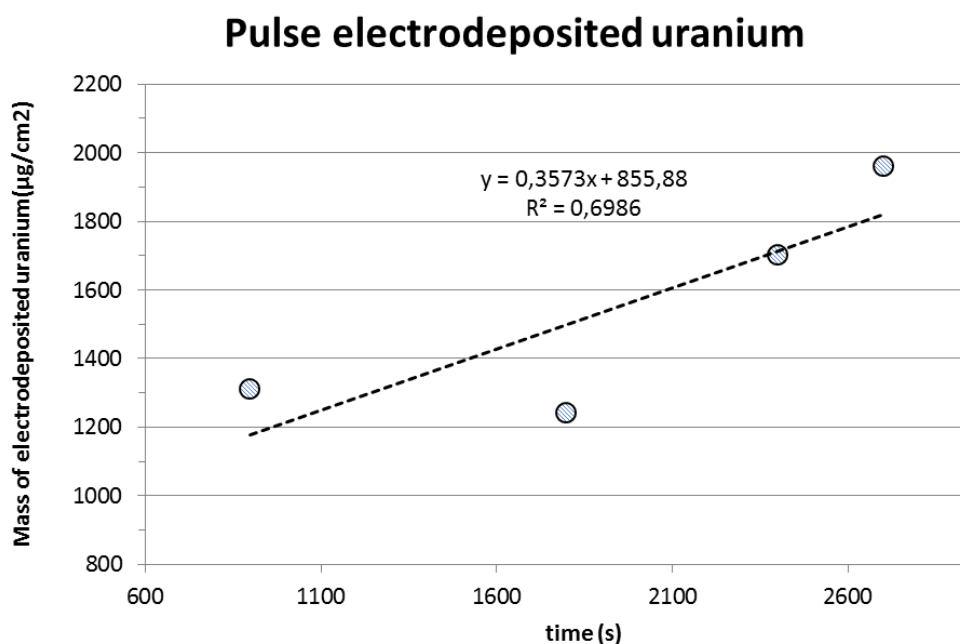## Pulse electrodeposited uranium

$y = 0,3573x + 855,88$
$R^2 = 0,6986$

Figure 7 – Evolution of uranium mass with time, using pulse electrodeposition one after from 15 to 45 kilocycles, using $UO_2(NO_3)_2$ isopropyl solution with 10 mmol.L^{-1}[U] for 5.10^{-2}s "on" followed by 1.10^{-2}s "off" (right).

Conclusions

In this work, pulse electrodeposition succeeded to deposit enough uranium substance entrapped in nickel substrate, using uranyl nitric solution diluted in isopropyl alcohol with uranium concentration of 50 mmolL^{-1} with duty time between 1 to 5. Natural uranium deposition was confirmed by SEM/EDS micrographs and microanalyses. By alpha emission counting it was possible to calibrate the amount of deposited uranium, giving a reliable equation of uranium deposition mass against time. The equation followed a logarithm scale, indicating that deposited material is not fully conductive, indicating as being a hydroxyl complex with unknown structure. The uranium mass electrodeposition reached an amount around 2000 μg/cm^2 just above 2700s using the suggested pulsing process. SEM/EDS technique and alpha-spectroscopy guaranteed that U-deposited material was natural uranium grade substance entrapped inside nickel substrate.

Acknowledgements

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