

Uranium Electrochemistry Applied to Mo-99 Irradiation Targets

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Introduction

Electrodeposition is a method commonly used in preparing samples for alpha spectroscopy [1,2]. Another potential area for uranium use is the manufacturing of irradiation targets to produce the radionuclides pair ^{99}Mo - $^{99\text{m}}\text{Tc}$ [3]. The metastable technetium-99 ($^{99\text{m}}\text{Tc}$) is formed by the decay of molybdenum-99 (^{99}Mo), a byproduct of ^{235}U fission. The challenge is to produce targets containing up to 20wt% of ^{235}U (LEU – Low Enriched Uranium) [4].

As summarized by Santos et al [5], the uranium electrodeposition in NH_4Cl medium produces films containing uranyl groups isolated or linked to other uranyl groups. They found that the reduction of H^+ ions was relevant during the process and the solution becomes more alkaline at very near the cathode. These results support the results published by Wheeler et al [6] suggesting that the electrodeposition can develop a polymerized structure under hydrolysis with increasing pH. The precipitation occurs when the polymerization reaches the solubility product of the species in solution. A UO_3 hydrate is then deposited from the electrolyte as a hydrated polymeric compound containing oxygen bridges in the chain.

In general, compounds of the actinide are dissolved in acid form in small volumes. The aqueous phase is then administered in an organic solvent. According to analysis of Crespo [2], deposit of actinides in an organic medium (e.g., isopropyl alcohol) is formed by insoluble compounds, generally hydroxides.

In the present study, we performed some experiments with potentiostatic polarization to promote uranium electrodeposition in order to examine the possibility of use this process for preparing irradiation targets. Techniques of cyclic voltammetry and electrochemical impedance spectroscopy were also employed to elucidate the steps involved during the uranium electrodeposition.

Experimental

The uranyl nitrate solution $\text{UO}_2(\text{NO}_3)_2$ was prepared by leaching nuclear purity U_3O_8 [7] with nitric acid. The nitrate solution was diluted with isopropyl alcohol to a concentration of 0.05 mol.L^{-1} of uranium (pH=0.95). This ionic solution was used for uranium electrodeposition. Cyclovoltametry with a less concentrated uranium aqueous solution ($2.10^{-3} \text{ mol.L}^{-1}$) was used to give a general idea of uranium of electrochemical behavior.

The electrochemical cell was made with a vertical quartz tube containing the electrolyte solution inside. A polypropylene structure supports the cell body and the electrolyte makes contact with working electrode (cathode in this case) at the bottom of the cell, which is sealed with a sealing rubber O-ring type. The experimental device exposes an area of 2.641 cm^2 as the interface with the electrolyte. The reference electrode used was Ag/AgCl . The same arrangement is used for both substrate preparation (nickel electrodeposition) and uranium electrodeposition. Aluminum coupons were used as a substrate for nickel electrodeposition, before being subjected to uranium electrodeposition. The process was carried out in a potentiostatic manner. Two levels of experiments were conducted, one at -3V and another at around -30V on the total area of 2.614 cm^2 .

Results and Discussion

The cyclovoltametry of the uranyl nitrate in diluted aqueous solution at $2 \times 10^{-3} \text{ mol.L}^{-1}$ resulted in a 20 cycles curve, as shown in Figure 1.

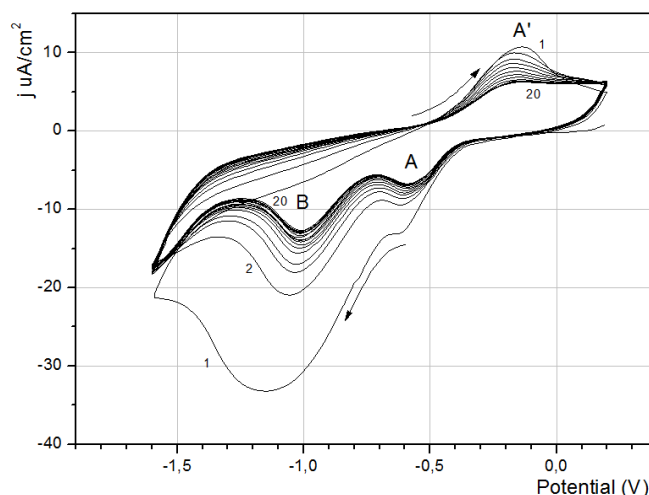


Figure 1 - Cyclovoltametric curve of uranyl nitrate (aqueous solution at $2 \times 10^{-3} \text{ mol.L}^{-1}$) with a scan rate of 0.05 V/s. The reference electrode used was Ag.

This graph shows that uranyl ion (UO_2^{2+}) undergoes a process of electrochemical reduction, which restores a symmetrical peak of oxidation (the A-A'). Possibly that is related to oxidation of U(VI) to U(V) ($\text{UO}_2^{2+} \rightarrow \text{UO}_2^+$) that is reversible, as shown in Figure 2 around the potential -0.6 VAg. This peak is followed by a second non-reversible wave related to a non-reversible electrochemical reaction, accounted as electrochemical deposit. This second wave can be explained to two factors: 1) reduction peak linked to the reaction: $\text{UO}_2^{2+} + 4\text{H}^+ + 6\text{e}^- \rightarrow \text{U}^0 + 2\text{H}_2\text{O}$ ($E^0 = -0,910 \text{ V}$), which leads to reduction to uranium metal or 2) hydrogen production, as indicated in the reaction: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ ($E^0 = -0,827 \text{ V}$), producing H_2 and OH^- locally which associates with the UO_2^{2+} or UO_2^+ maybe produced in the first wave. One observation that indicates the occurrence of this sequence is the reduction in height of the waves (region B in Figure 1) with the cycles repetition. A consequent reduction of uranyl ions in the very diluted solution occurs due to the continuous deposition of amorphous uranyl hydroxide.

The two levels of electrodeposition with polarization-3V and-30V for 3600 s are shown in the graphs of Figure 2.

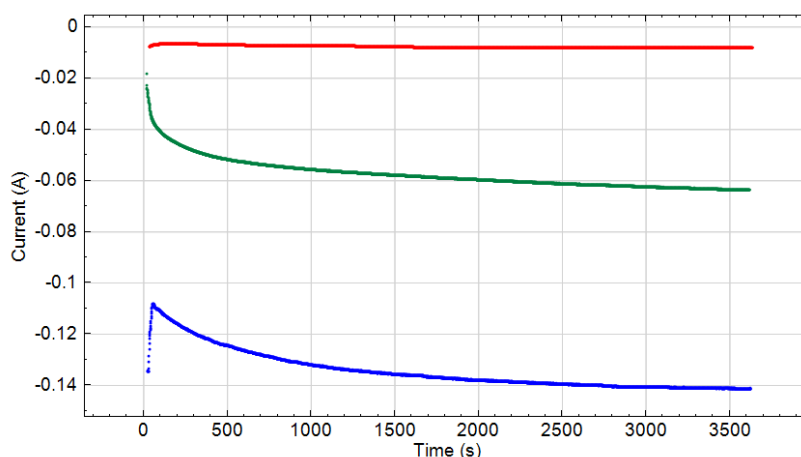


Figure 2 - Electrodeposition curves of uranyl nitrate ($0.05 \text{ mol.L}^{-1} \text{ U}$) during cathodic polarization with 3600 s over an area of about 2.6412 cm^2 : $P = -3\text{V}$ (upper curve); $P = -20\text{V}$ (middle) and $P = -30\text{V}$ (lower curve)

The mass coating rate of the experiments, in the most effective tests, reached around $10 \mu\text{g}/\text{cm}^2\text{s}$. However, this level is still under 10 times a production level rate necessity (around $100 \mu\text{g}/\text{cm}^2\text{s}$) required for construction of an irradiation target. The process with more polarization in the cathode promotes a marked increase in the H_2 production and also the OH^- production at the electrode surface, promoting the deposition.

Conclusions

Uranium electrochemistry and its various redox reactions promote a complex picture of potential reactions that are not fully consistent in the literature due to different organic electrolytes used to prepare the ionic solutions. Based on voltammogram of an aqueous uranium solution, it was concluded that there are two peaks in the cathodic electrodeposition process. The first is related to a redox reaction of $\text{UO}_2^{2+} \rightarrow \text{UO}_2^+$ which has its pair in the anodic field. The second peak with high intensity in the cathodic field promoted strong electrodeposition of uranyl ions, since the absolute heights of the peaks diminish substantially with cycling. Most likely the deposition is due to the H_2 production reaction, which produces large amount of hydroxyl ions near the cathode surface and promotes the deposition of UOOH compounds at the cathode surface. There is a significant increase in the resistance of the cathode, indicating that the level of conductivity lowered substantially after electrodeposition, which shows that the deposited product is not metal, indicating that the product could be UOOH , as reported in the literature.

The maximum level of uranium deposition rate by cathodic polarization for 3600 s was about $10 \mu\text{g}/\text{cm}^2\text{s}$. This level is less than 10 times the required rate for construction of an irradiation target for producing the pair ^{99}Mo - $^{99\text{m}}\text{Tc}$ by direct polarization.

Acknowledgements

The authors thank FAPESP through project 2010/01244-2, for assisting financially the implementation of this work. We are also grateful to CNPq for financial support through the Universal Project (476594/2010-3).

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