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**ELECTROCHEMICAL STUDIES ON ⁹⁹Mo TARGET MATERIALS:
ACIDIC DEPOSITION OF URANIUM COMPOUNDS**

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Abstract

The electrochemistry of uranium at low temperature might be important for an alternative route to produce ⁹⁹Mo irradiation LEU targets. Usually electrodeposition of uranium is made using ionic and aqueous solutions producing uranium oxide deposits. The performance of uranium electrodeposition is relatively low because there is a big competition in the window of electrochemical reduction potential with H₂ evolution. In the present study, it was used an ionic electrolyte based on isopropyl alcohol with addition of uranyl nitrate aliquot containing 50 mmol/L of natural uranium. The electrodeposition experimentation followed an experimental design for response surface, varying the direct cathodic polarization from -2 V to -4 V, with time varying from 1800 to 3600 seconds over a nickel pre-plated substrate. The optimum deposited mass rate was 0,53 µg/cm²s. As the solution was very acidic (pH<1), the deposited was partially corroded during the experimentation, losing mass. The SEM/EDS and IFIR inspection of electrodeposit microstructure revealed that the deposition of uranium compounds followed an electrochemical and chemical phenomenology of UO₂(OH)_{x=1,2} deposition displaying a floccular appearance, which happened preferentially at grain boundaries at nickel substrate.

1. Introduction

The nuclear Brazilian reactor RMB will process LEU irradiation targets to produce mainly the ^{99}Mo radioisotope for nuclear medicine. It is envisaged to follow a picture-frame route using the fissile material encased in AA6061 matrix. This target will pass through an alkaline dissolution route to dissolve the aluminum and the irradiated uranium content. Purification follows this dissolution process to finally separate the ^{99}Mo , which is one of desirable fission product to produce the generator of $^{99\text{m}}\text{Tc}$ used for medicine procedures [1].

This work based its studies on a hypothetical target core made with uranium electrodeposition in between nickel plating, encased in AA6061 matrix. This set would be rolled in dimensions of a mini-plate, following similar treatment and assembling as a nuclear fuel plate [2].

High temperature of uranium electrodeposition has already been studied, even patented, to produce irradiation targets [3, 4]. Usually low temperature electrodeposition of uranium is made using ionic and aqueous solutions producing uranium oxide deposits [5]. Nevertheless, the performance of uranium electrodeposition is relatively low because there is a big competition with the reduction of H_2 inside the potential window. The use of ionic solutions for low temperature is normally made by using supporting ionic solvents in order to improve the completion of deposits instead of H_2 evolution [5-11].

2. Experimental and Results

The uranium electrodeposition experiments were made using uranyl nitrate solution $\text{UO}_2(\text{NO}_3)_2$ as electrolyte. It was prepared by leaching U_3O_8 with nuclear purity with nitric acid. The nitrate solution was diluted with isopropyl alcohol to a concentration of $0.05 \text{ mol}\cdot\text{L}^{-1}$ of natural uranium ($\text{pH}=0.95$). The electrochemical cell was made with a vertical quartz tube containing the electrolyte solution inside. A polypropylene structure supported the cell body and the electrolyte, which makes contact with working electrode (cathode) at the cell bottom sealed with an O-ring rubber. The experimental device exposed an area of 2.641 cm^2 . The reference electrode used was Ag/AgCl . All electrodeposition experiments were carried out in a Metrohm Autolab 302SN.

Cyclic voltammetry of uranium redox reactions was made on screen printed electrode DS 110, composed by carbon working electrode with $\varnothing 4\text{mm}$ and carbon counter electrode and silver reference electrode) carried out in potentiostat 910 PStat Mini Metrohm. The electrolyte was aqueous and contained 2 mmol/L [U]. The dissolution was made using aqueous uranyl nitride concentrate, described above. The acidity of used solution drop was around $\text{pH}=3$. All experiments were made at room

temperature. The cyclic voltammetry was repeated for 20 cycles. The resulting curves are shown in Figure 1.

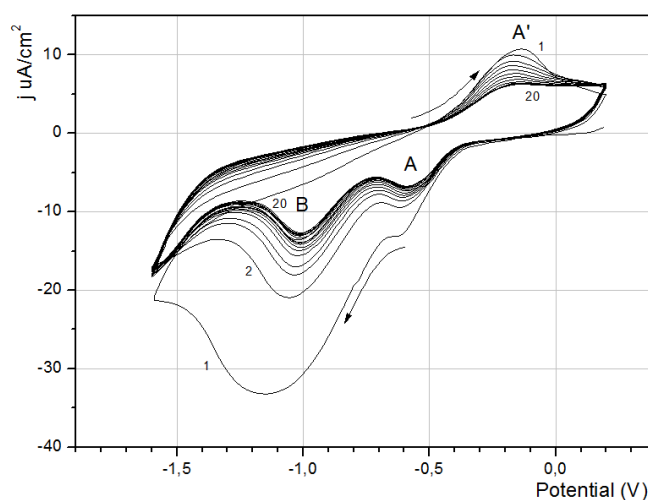
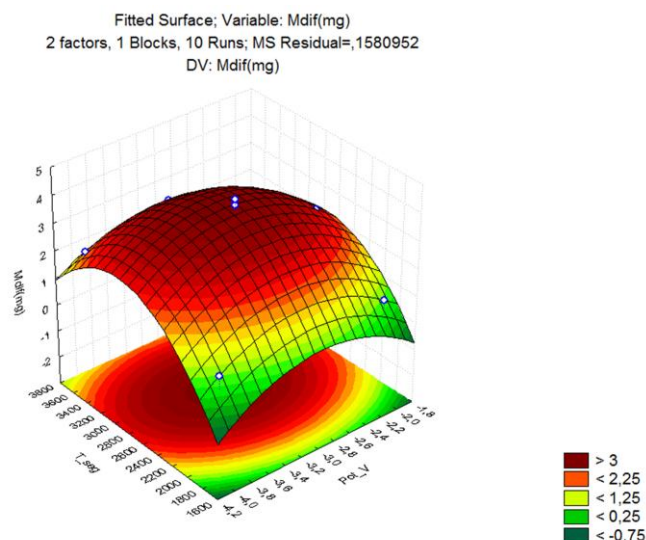


Figure 1 – Cyclic voltammetry curves of uranyl nitrate (aqueous solution at $2 \times 10^{-3} \text{ mol.L}^{-1}$) with a scan rate of 0.05 V/s. The reference electrode used was silver.

A response surface statistical design was planned to evaluate the amount of deposited mass. Table 1 shows the parameters and results. The level of statistical significance of this project was quite relevant as given by ANOVA, indicating that main factors governing this uranium electrodeposition were *quadratic time* (p-value <0.0028), *quadratic potential* (p-value <0.016), *linear time* (p-value <0.033) with MS residual <0.16.

Table 1 – Response surface experimental design and results using uranyl nitrate solution $\text{UO}_2(\text{NO}_3)_2$ diluted in isopropyl alcohol (50mmol/L [U]). Sample area: 2.614 cm^2

Exp	Pot ($\text{V}_{\text{Ag}/\text{AgCl}}$)	Time(s)	Sample	$\Delta\text{M}(\text{mg})$
1	-4	1800	104	0,85
2	-4	3600	105	2,05
3	-2	1800	108	0,75
4	-2	3600	109	1,15
5	-4	2700	107	2,55
6	-2	2700	102	2,55
7	-3	1800	110	1,15
8	-3	3600	103	2,65
9	-3	2700	111	3,95
10	-3	2700	106	4,15



	Lower limits	Critical values	Upper limits
Potential (V _{Ag/AgCl})	-4,000	<u>-3,095</u>	-2,000
Time (s)	1800,000	<u>2842,397</u>	3600,000

Figure 2 – Response surface and resulting optimum values for direct cathodic potential for uranium compound electrodeposition in potentials between -4 and -2 V_{Ag/AgCl}.

3. Results Analysis

This graph of Figure 1 shows that uranyl ion (UO₂²⁺) undergoes a process of electrochemical reduction (Peak A), which reflects a symmetrical peak of oxidation (Peak A'). The peak A is possibly explained by reduction of U(IV) to U(V) (UO₂²⁺ → UO₂⁺) and convoluted with to U(V) to U(VI) (→ UO²⁺) resembling a reversible process around the reduction potential -0.6 V_{Ag} and oxidation at -0.15 V_{Ag}. The reduction peak A, in cathodic direction, between -1,2 to -1,0 V_{Ag}, is followed by a second non-reversible reduction peak wave which is unrelated to a non-reversible electrochemical reaction, accounted to be the electrochemical UO₂ or U⁰ deposition phenomena. This second wave may be explained by the following events:

- 1) Reduction peak linked to the reaction: UO₂²⁺ + 4H⁺ + 6e⁻ → U⁰ + 2H₂O (E° = -0,910 V_{SHE}), leading to uranium metal reduction;
- 2) Hydrogen production, as indicated in the reaction: 2H₂O + 2e⁻ → H₂ + 2OH⁻ (E° = -0,827 V_{SHE}), producing H₂ and OH⁻ locally which is associated to UO²⁺ or UO₂⁺ partially produced in the first wave at peak A.

One observation that supports the occurrence of UO₂ electrodeposition is the reduction in the height of the waves (region B in Figure 1) during cyclic voltammetry repetition. It can be observed that the cycles at Peak B reduce in height. The same phenomenon occurs in the symmetrical peaks A-A'. This is supposed to be caused by

content reducing of uranyl ions in much diluted solution in a small drop over the printed mini-electrode, indicating a continuous deposition of uranyl hydroxide with consequent exhaustion of the solution.

The results in response surface experimentation showed that the highest electrodeposition mass obtained by electrodeposition was at direct cathodic polarization -3.095 V, during 2842 s (critical values). The maximum rate of uranium compound electrodeposition rate corresponded to $0.52 \mu\text{g}/\text{cm}^2\cdot\text{s}$. This mass deposition rate is very small to be considered technologically valid to produce targets.

As these experiments were carried out at low pHs (< 1), which are not normally appropriate to produce thicker layers of UO_2 electrodeposition, other relevant uranium electrodeposition experiments are being carried out. The on-going tests use higher pHs, potential pulse techniques and diverse ionic solutions, giving promising results. These experiments are presently being scrutinized, but they already revealed that more significant technological results are achievable, giving electrodeposition rates in the range of 20 times more than the present result being communicated in this work.

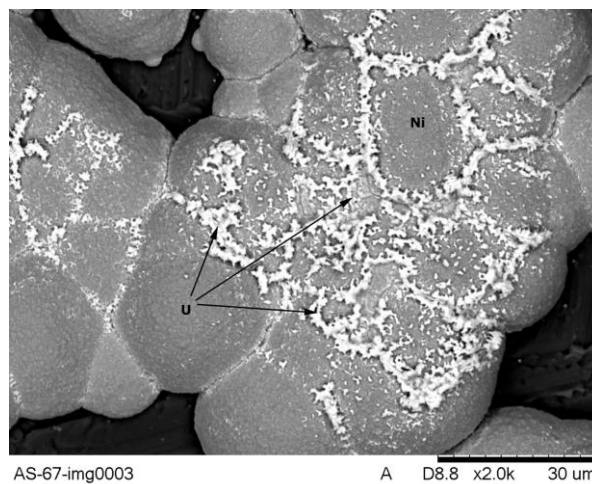


Figure 3 – SEM microstructure of electrodeposition of uranium over nickel substrate.

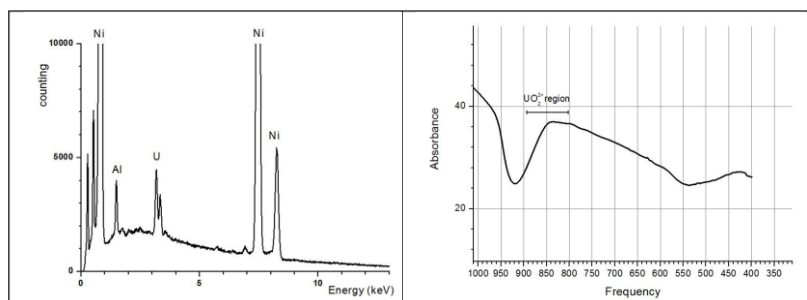


Figure 4 – Graphs: (left) EDS of the region and FTIR of scratch powder. Both show the presence of uranium and UO_2^{2+} compound.

As shown in Figure 3 and Figure 4, the SEM microstructure displays common view of uranium deposits in these experiments. It can be noted that during the electrodeposition process over nickel substrate, the uranium compounds deposited preferentially in regions of high energy as at nickel grain boundaries. The uranium deposits appear as a floccular arrangement, indicating the presence of hydroxide/oxide structure, which was confirmed by FTIR evaluation.

The hydroxide precipitation occurred in preferential areas, where water electrolysis might have been favored at the cathode surface, for instance at grain boundaries. At the cathode, in acidic media, the H^+ is consumed H_2 gas formation ($2H_2O + 2e^- \rightarrow H_2 + 2OH^-$) leaving the nearby region instantly alkaline. This phenomena is promoted by localized concentration of OH^- which allows precipitation of $UO_2(OH)_2$ at more active areas.

4. Conclusions

Uranium electrodeposition in form of $UO_2(OH)_2$ is feasible to be produced at acidic solution containing uranyl diluted in isopropyl alcohol (50 mmol/L [U]; pH=0.95). Surface response statistical design revealed an optimum rate of $0.53 \mu\text{g}/\text{cm}^2\text{s}$ with direct cathodic polarization at $-3.1 V_{\text{Ag}/\text{AgCl}}$ during 2842 s. The highly acidic solution did not allow full covering with floccule like uranium hydroxide. The preferential deposition at grain boundaries is explained as OH^- being an electrolysis product and chemically reacting with uranyl ion at electron favored flow (grain boundaries).

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