Electrodeposition of Uranium and Thorium onto Small Platinum Electrodes

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Abstract

Preparation of thin U- and Th-coated 0.3 mm diameter Pt working electrodes by the cyclic potential sweep method is described. Uranyl- and thorium hydroxide layers were electrodeposited from ethanol solutions containing 0.02 M natural uranyl and 0.02 M natural thorium nitrate, each with 3.6 M ammonium nitrate. The cell for electrodeposition was specially developed in order to accommodate the small working electrodes for this research by including a working electrode probe, 3-D translation stage, and microscope. The source material deposition was analyzed using digital microscopy and scanning electron microscopy, and confirmed using x-ray fluorescence measurements. The appropriate potential range for electrodeposition was determined to be -0.62 V to -0.64 V for a 0.3 mm diameter Pt working electrode placed 1 cm from the counter electrode. Smooth, uniform deposition was observed near the central region of the working electrode, while surface cracking and crystalline formations were found near the edge of the working electrode. The final procedure for sample substrate preparation, electrolytic solution preparation and electrodeposition are described.

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1 offered a very uniform layer, but often suffered from poor reproducibility [5]. Electrodeposition
2 methods are commonly optimized from the viewpoint of the maximum efficiency of the
3 electrodeposition, but depend heavily on electrochemical cell design [4, 5]. Still other methods
4 have been developed for rapid preparation of source material for nuclear waste analysis [3]. Both
5 of the previous methods call for working electrodes on the order of several square centimeters.
6 However, the objective of the present work is to deposit precise amounts of U and Th on very
7 small electrodes ($< 1 \text{ mm}^2$) for use as MPFD substrates. Although much of the chemistry from
8 previous methods can be used to aid in the development of MPFD substrates, the
9 electrodeposition method is being applied with a different objective. In contrast to many other
10 methods which strive for high electrodeposition efficiency, high precision and reproducibility is
11 important for the development and testing of MPFDs. The neutron-reactive coating for MPFDs
12 must be precisely deposited in order properly balance U and Th content to maximize device
13 lifetime [6].

14 Here, uranyl and thorium hydroxide layers were electrodeposited onto small Pt disk electrodes
15 using the cyclic potential sweep method [7]. The hydroxide layers were deposited by taking
16 advantage of an increase in pH at the vicinity of the electrodes as a result of the reduction of
17 nitrate [8]. The cyclic potential sweep method provides a more controlled means for such
18 electrochemically assisted deposition as compared to the more commonly used potential-step
19 method for the following two reasons. First, this method facilitates applying a potential required
20 for nitrate reduction for the shorter period of time by adjusting potential sweep rate. The longer
21 application of the cathodic potential using the potential-step method generates large gas bubbles
22 on the electrodes due to side reactions such as the reduction of water, preventing the deposition
23 of uniform hydroxide layers. The cyclic potential sweep permits the repetitive application of the

cathodic potential for the shorter period of time to induce a sufficient pH increase with minimum formation of large gas bubbles. Second, the deposition of the hydroxide layers can be monitored from the cathodic current recorded during the repetitive potential sweep. The deposition of insulating hydroxide layers leads to a decrease in the cathodic current due to the reduced exposure of the active Pt electrode area. After determining the appropriate potential sweep range, the number of potential segments can be adjusted to deposit a precise amount of U or Th material onto the Pt electrode. The present work developed an electrochemical cell appropriate for work with very small working electrodes and determined the effectiveness of the cyclic potential sweep method for the fabrication of MPFD substrate materials.

2 Experimental Method

The production of sample MPFD substrates with thin U and Th coatings consisted of three primary steps: electrode fabrication, solution preparation, and electrodeposition.

2.1 Electrode Fabrication

Electron beam evaporation was used to deposit metal contacts onto insulating substrates for electrodeposition testing. Shadow masks were used to create samples with circular electrodes as depicted in Fig. 1. Custom nickel shadow masks were manufactured at the Kansas State University Multiphase Microfluidics Laboratory using a Minitech Mini-Mill 3 micro-milling machine. The present work used 0.3 mm diameter, circular electrodes evaporated onto silicon dioxide substrates. Silicon dioxide was chosen for its smooth surface and ease in processing post-evaporation.

Prior to evaporation, each 3-inch silicon wafer was cleaned using a 5-minute bath in each of acetone and isopropyl alcohol, followed by a 1-minute buffered oxide etch and 5-minute de-

ionized water bath. The wafer was then dried using pressurized nitrogen gas. The custom shadow mask was fixed to the surface of silicon wafer just before insertion into the evaporation chamber. A 50 Å Ti evaporation was used to aid in the adhesion of the Pt layer. Afterwards, a 500 Å Pt layer was evaporated as the primary electrode material. Platinum was used due to its high melting point, resistance to corrosion, and low neutron-absorption cross-section [9]. Samples which did not utilize a thin Ti adhesion layer suffered from complete electrode material loss during the wafer dicing process. Wafer processing and evaporation was conducted in the class-100 cleanroom facility at the Kansas State University S.M.A.R.T. Laboratory. Following electrode evaporation, the wafers were diced into 5 mm x 5 mm square samples for electrodeposition testing. The samples were visually inspected for surface quality using a Hitachi S-3400N scanning electron microscope, as depicted in Fig. 1.

FIGURE 1 HERE

2.2 Solution Preparation

Uranyl nitrate hexahydrate (99.9%) and thorium nitrate hydrate (99.8%) were used as the respective sources of U and Th for each electrodeposition. The composition of the solutions used for U and Th deposition differed only in the quantities of uranyl nitrate and thorium nitrate. Prior to solution preparation, all of the glassware was cleaned using HNO₃, acetone, isopropyl alcohol, and a de-ionized water bath. The U/Th nitrate and ammonium nitrate were weighed using an Ohaus AR0640 scale, combined into a 250 mL beaker, and de-ionized water was added to bring the solution to 100 mL. A 25 mL ethanol/de-ionized water solution was then prepared and added to the U/Th nitrate and ammonium nitrate solution. The solution was placed on a magnetic stirring plate on a low (3 of 10) stirring setting. The final solution was then topped off to 150 mL with de-ionized water and a pH measurement was taken using a calibrated Thermo Scientific

Orion 3-Star pH monitor. The amount of each material used for the solution preparation and measured pH are shown in Table 1. The U solution possessed a slight yellow tint, while the Th solution was clear as depicted in Fig. 2. Precipitation of the U solution was observed after several days. Thus, fresh electrolytic solution was prepared for each electrodeposition batch, and the electrodeposition was conducted immediately after solution preparation.

TABLE 1 HERE

FIGURE 2 HERE

2.3 Electrodeposition via the Cyclic Potential Sweep Method

Samples were rinsed with isopropyl alcohol prior to electrodeposition. The CH Instruments CHI600E potentiostat used for the present work utilized an electrochemical cell with three electrodes. The electrochemical cell which was developed to accommodate the small electrode design included a 3-dimensional translation stage, counter/reference electrode assembly, working electrode probe, and Leica DMS300 microscope. The counter/reference electrode assembly was constructed using an Ag/AgCl reference electrode submerged in 3.0 M KCl inside a glass vial. The counter electrode (0.013 inch diameter 99.95% Pt wire) was then wrapped around the reference electrode glass vial as shown in Fig. 3. The 5 mm x 5 mm silicon sample with evaporated Pt working electrode and the counter electrode/reference electrode assembly were placed into a glass petri dish. Electrolytic solution was added to submerge both the silicon sample and the counter electrode. The stainless steel working electrode probe was insulated with exception of the tip to enable electrical contact with the working electrode, visible in Fig. 4. The 3-D stage was then adjusted to establish contact between the Pt electrode on the silicon sample and the working electrode probe, also depicted in Fig. 4. After electrical contact was established, U/Th was deposited onto the working electrode surface.

FIGURE 3 HERE

FIGURE 4 HERE

Determination of the optimal parameters required numerous trials, however a potential sweep from -0.62 V to -0.64 V was determined to yield the most consistent surface deposition using a 0.01 Vs⁻¹ sweep rate. Voltages beyond -0.64 V produced severe bubble generation and yielded more unwanted crystalline deposits on the surface of the working electrode. Additionally, no electrodeposition was observed from 0 V to -0.62 V. The present work tested the effectiveness of electrodeposition with 500 potential sweep segments. The electrodeposition was performed at room temperature (typically below 28 °C). The cyclic potential sweep process yielded current-voltage plots (cyclic voltammograms) representative of those depicted in Fig. 5 for uranyl-nitrate and thorium-nitrate solutions. All samples were rinsed with isopropyl alcohol after electrodeposition and allowed to dry before storage in individual sealed plastic bags.

FIGURE 5 HERE

3 Results and Surface Analysis

During each potential sweep segment, a small amount of insulating U/Th hydroxide was deposited onto the working electrode surface. As additional material was deposited, the electrochemically active surface area of the working electrode decreased to give a smaller cathodic current, as shown in Fig. 5. Small bubbles occasionally formed at the contact point of the working electrode probe and working electrode surface but quickly detached. The deposited material was clearly visible as the Pt surface changed in color from silver to yellow (U) and white (Th). A plated Th sample just after electrodeposition is shown in Fig. 6. Digital

1 microscopy, scanning electron microscopy (SEM), and x-ray fluorescence (XRF) analysis were
2 all used to determine the effectiveness of the electrodeposition process.

3 FIGURE 6 HERE

4 A Leica DVM 2500 microscope was used to visually inspect each sample. The color of the
5 samples indicated areas where U- or Th-hydroxides were deposited. Uranium samples had
6 golden-colored electrode surfaces while Th samples had white-colored electrode surfaces.
7 Special notes were taken of any regions where the electrode surface appeared absent of deposited
8 material. Some samples exhibited crystalline depositions around the perimeter of the electrode
9 surface as shown in Fig. 7.

10 FIGURE 7 HERE

11 The SEM was used to examine the surface features of the samples after electrodeposition,
12 showing three distinct regions depicted in Fig. 8. The first region was a smooth, conformally
13 coated region located in the center of the sample and extending radially as depicted in Fig. 8(A).
14 Near the edges of the samples, a cracked layer was observed, shown in Fig. 8(B). The crystalline
15 formations depicted in Fig. 7 were also observed in the same region as the surface cracking. The
16 crystalline depositions were observed to detach easily by coming in contact with the plastic
17 container in which the samples were stored. The cracked region was preferentially observed on
18 the side closest to the counter electrode. XRF analysis of the cracked region suggested larger
19 amount of U/Th in the cracked region. Finally, regions were observed on each sample where
20 little or no deposition had taken place shown in Fig. 8(C). These regions varied in size and shape
21 but are possibly due to surface contamination (dust particles for example), probe contact, or
22 detachment of a hydroxide layer.

23 FIGURE 8 HERE

X-ray fluorescence measurements were used as a qualitative assessment of the amount of U or Th deposited on each sample. Measurements were conducted for each of the regions of interest for each sample. The relative abundance of each sample material was calculated based on the XRF measurement results. Silicon, oxygen, and platinum were also included in the surface composition estimate due to the penetrating ability of the SEM electron beam and subsequent characteristic x-rays. Clear peaks were present in the XRF spectra depicted in Fig. 9 for U and Th. Results of XRF analysis for each region for a characteristic sample are summarized in Table 2. The XRF results clearly indicate deposition of both U and Th onto the electrode surface, but also suggest that thicker deposition occurs near the perimeter of the working electrode.

FIGURE 9 HERE

FIGURE 11 HERE

TABLE 2 HERE

4 Conclusions

Uranium and thorium hydroxides were successfully deposited on 0.3 mm diameter circular Pt electrodes on a silicon dioxide substrate using the cyclic potential sweep method. Digital microscopy, SEM, and XRF have all been used to analyze the surface of the Pt electrodes after electrodeposition. The exact composition of the surface deposition is unknown at this time, but is likely to be uranyl and thorium hydroxide considering the mechanism of the electrodeposition. Crystalline formations of higher U and Th content were found near the perimeter of the electrode surfaces, likely due to the higher electric field strength and enhanced diffusion of ions near the edge of the metal electrode. This effect was observed to be even more prominent on the side of the electrode which was closest to the counter electrode. The effectiveness of electrodeposition will depend heavily upon the electrode size and shape. The central region of the Pt electrodes

exhibited a conformal coating of U/Th compounds as verified by XRF analysis. Mass measurements of U and Th coated samples are currently under investigation. The number of sweep segments will also likely affect the amount of U/Th which is deposited on the working electrode and is currently being characterized.

Acknowledgements

Portions of this work have been supported by the US Department of Energy Office of Nuclear Energy under DOE-NE Idaho Operations Office Contract DE-AC07 05ID14517 & US Department of Energy Office of Nuclear Energy under DE-NE0008305. The authors would like to thank Dr. Amy Betz and the Kansas State University Multiphase Microfluidics Laboratory for use of equipment and assistance in machining shadow masks for this work.

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Tables & Figures

Table 1 Compositions of solutions used for electrodeposition of uranyl and thorium hydroxide layer on Pt electrodes.

Table 2 XRF results representing the relative abundance of four elements on U-deposited and Th- deposited Pt electrodes ($\sim 150 \mu\text{m} \times 150 \mu\text{m}$ for each region).

Fig. 1. SEM image of a circular Pt electrode prior to electrodeposition. The size and shape of each sample was verified after evaporation.

Fig. 2. Prepared solutions of 0.02 M $\text{UO}_2(\text{NO}_3)_2$ (left) and 0.02 M $\text{Th}(\text{NO}_3)_4$ (right).

Fig. 3. Schematic illustration of the electrochemical cell consisting of a reference electrode, count electrode, and working electrode.

Fig. 4. An optical microscope image of a Pt electrode with the working electrode probe prior to electrodeposition. Proper alignment of the working electrode probe and Pt electrode was necessary before electrodeposition was possible.

Fig. 5. Current vs potential plots measured at the sweep rate of 0.01 Vs^{-1} in (A) 0.02 M $\text{UO}_2(\text{NO}_3)_2$ and (B) 0.02 M $\text{Th}(\text{NO}_3)_4$. The cathodic current gradually decreased as a result of the repetitive potential sweep due to the deposition of a (A) $\text{UO}_2(\text{OH})_2$ (A) and (B) $\text{Th}(\text{OH})_4$ layer on the Pt electrode surface.

Fig. 6. Optical microscopy image of a Pt electrode after electrodeposition of the Th hydroxide. The electrode surface slowly changed color during the electrodeposition from silver (Pt) to white (Th).

1 Fig. 7. Optical microscopy image of a Pt electrode after U electrodeposition. Surface cracking
2 and crystalline formation is visible near the perimeter of the electrode.

3
4 Fig. 8 SEM image of a U-deposited Pt electrode showing three distinct regions: (A) a uniformly
5 deposited region, (B) a region with thick deposition layers, and (C) an undeposited region.

6
7 Fig. 9. XRF spectrum measured at the surface of a (A) U- and (B) Th-deposited Pt electrode.
8 Numerous U characteristic x-ray peaks were clearly present. Peaks for Pt, Si, and O are also
9 present due to the penetration of x-rays from the substrate through the thin electrodeposited
10 layer.

Figure1

Figure2

Figure3

Figure4

Figure5

Figure6

Figure7

Figure8

Figure9

Table1

Compon ent	0.02 M $\text{UO}_2(\text{NO}_3)_2$		0.02 M $\text{Th}(\text{NO}_3)_4$	
Uranyl or Thorium Nitrate	410	mg	480	mg
Ammoni um Nitrate	14,410	mg	14,410	mg
190 Proof Ethanol	5.78	mL	5.78	mL
Measure d Solution pH	3.4		3	

Table2

Sample and Region	Si Concentration	Pt Concentration	O Concentration	U / Th Concentration
U Central Region	64 wt. %	6 wt. %	21 wt. %	9 wt. %
U Cracked Region	61wt %	11 wt. %	15 wt. %	13 wt. %
Th Central Region	78 wt. %	10 wt. %	11 wt. %	1 wt. %
Th Cracked Region	53 wt. %	9 wt. %	16 wt. %	22 wt. %