Thin-Layer Electrodeposition of Thorium Metal from Molten LiCl-KCl

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A new analytical technique for determining actinides in molten salts is proposed, which combines information from electrodeposition with the output of an alpha particle detector. This technique requires a thin actinide layer to be deposited on a metal substrate. Electrodeposition of a thin thorium layer from molten LiCl-KCl onto stainless steel and nickel plates is reported in this paper using chronoamperometry, chronopotentiometry, and repeating chronoamperometry. Repeating chronoamperometry was demonstrated as the most effective method for depositing approximately a 1 μm thick thorium metal layer on substrates. The effect of thorium concentration on deposition time was also determined. Re-usability of the detectors was shown via demonstrating the anodic stripping of the deposit verified by surface analysis (SEM-EDS).

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A three electrode setup was employed, with polished stainless steel or nickel coupons being the working electrode (total area of 4 cm²), a zirconium rod (1.27 cm diameter) being the (reactive) counter electrode, and a silver wire contacted with pure silver chloride [Ag/AgCl(100%)] enclosed in a mullite tube being the reference electrode. A schematic of the setup is depicted in Figure 2. Metrohm Autolab potentiostat PGSTAT302N was used, controlled by NOVA software package.

Three modes of electrodeposition were examined – chronamperometry (CA), chronopotentiometry (CP) and repeating chronamperometry (RCA). Cyclic voltammetry (CV) served as a diagnostic tool to determine regions of interest and to verify the reference electrode’s long-term stability.

A salt rinse of the metal coupon was performed after each run, consisting of dipping the coupon into ultra-pure water with mild agitation from a magnetic stirrer until all salt appeared removed (∼1 minute). Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS – Hitachi S-4800, Oxford EDS) was then performed on the coupon shortly afterwards before excessive oxidation of the surfaces had time to occur. A duplicate coupon was also sent to the partner lab for alpha spectroscopy investigation.

Salt samples were dissolved in 10 vol% HCl and analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES) to give reliable analyte concentration in the salt.

Analysis Approach

Half-cell reactions.—A reactive counter-electrode was sought in order to prevent Cl₂ formation during the electrodeposition of the actinides onto target substrates. Zirconium was selected based on its:

- Close standard reduction potential compared to thorium and uranium.
- Chemical compatibility (ZrCl₄ is soluble in salt).
- Expected presence in a real electrorefiner (Zr is a common fission product).

We aimed to avoid excessive zirconium co-deposition, as it would interfere with the alpha particle counting. Complete elimination of zirconium co-deposition is, however, unavoidable, due to its electrochemical properties (Zr redox potential more anodic than Th). Some small amount of zirconium always exists in the salt due to the oxidation counter-reaction at the anode. By design, the half-cell reactions are as follows.

At cathode: \( \text{ThCl}_4 + 4e^- \rightarrow \text{Th} + 4\text{Cl}^- \) \[1\]

At anode: \( \text{Zr} + 4\text{Cl}^- \rightarrow \text{ZrCl}_4 + 4e^- \) \[2\]

Proposed analytical method.—The deposition rate as measured by current \( i \) is in general a function of applied potential \( E \), salt concentration \( C \), and time \( t \).

\[ i = f (E, C, t) \] \[3\]

In order to establish proportionality between the deposited amount of analyte and its concentration in the salt, we need to eliminate the dependence on applied potential. This is done by conducting the deposition under the mass-transfer (diffusion) limited regime. There is no agitation (except natural convection) in our setup, thus by applying sufficiently negative potential we achieve diffusion limited current \( i_k \). Under these conditions the deposition rate is only a function of analyte concentration in the salt and time.

For a two-analyte system, the total deposited amount \( Q_{\text{TOT}} \) and time \( t \) are easily accessible from the electrochemical deposition run, but we need yet another piece of information to be able to determine the individual concentrations. Such information is for example the molar ratio of the two metals in the deposit \( X_1/X_2 \), which can be obtained from the alpha spectroscopy measurement of the deposit. It is important to state again that each of the two analytical techniques alone can give only a partial answer to the problem. It is their combination (hyphenation) that provides enough information about our system, enabling us to arrive at the correlation between the deposited amount and concentration in the salt, represented by Equations 4 and 5.

\[ Q_1 = f_0^i i_{1,d} dt = f_0^i f (C_1) dt \] \[4\]

\[ Q_2 = f_0^i i_{2,d} dt = f_0^i g (C_2) dt \] \[5\]

The task is to determine the relationship between deposition rate (current) and concentration for single analyte salts and then apply this relationship for two-analyte system, taking advantage of the additivity of currents (more precisely, charges).

\[ i_{\text{TOT}} = i_{1,d} + i_{2,d} \] \[6\]

\[ Q_{\text{TOT}} = Q_1 + Q_2 \] \[7\]

Deposition objectives.—Analysis using SRIM (Stopping and Range of Ions in Matter)\(^{11}\) was used to determine optimum deposit thickness for alpha spectroscopy measurements, a compromise between spectral broadening (worsens with deposit thickness) and signal intensity (improves with deposit thickness). The optimum thickness was found to be about 1 μm (see Table I), which became the target thickness for metal deposition. For 1 μm the spectral broadening is around 250 keV. This amount of broadening would still permit the resolution of major thorium, uranium and plutonium peaks, since differences in their energies are around those magnitudes or larger.

| Thickness | Spectral Broadening [keV] | Activity [Bq] |
|-----------|--------------------------|--------------|
| 50 nm     | 8.0E + 00                | 1.38E-01     |
| 500 nm    | 1.0E + 02                | 1.38E + 00   |
| 1 μm      | 2.5E + 02                | 2.77E + 00   |
| 5 μm      | 1.7E + 03                | 1.38E + 01   |
Assuming uniform coverage and theoretical density, by using Faraday's law the required amount of charge to reach this target is about 7 C for Th and 9 C for U.

Uranium is well known to form dendrites on cathodes when electrorefined in molten salt. Thus, one of our objectives was to develop an electrodeposition process that minimizes dendritic formation and achieves a uniform layer. This is because dendritic formation would potentially interfere with the alpha particle counting (it can shield alpha particles from reaching the detector, thus reducing the signal output and broadening the spectrum for the same amount of material deposited in comparison to a uniform layer).

The analysis' requirement to be near real-time puts some constraint on the total time needed for deposition. The deposition should be reasonably fast (not more than several minutes).

The detector should also be reusable, which translates into the necessity of stripping the deposit off once the measurement is finished. The stripping should not appreciably alter the detector surface (thousands of stripping cycles would be performed during the detector lifetime) and should be quantitative. The formation of alloys between analyte and substrate might complicate/prolong this step.

**Coupon material.**—Initially, stainless steel was used as a coupon material due to it being readily available, cheap, and easily machinable. Reduction potentials for its major components (Fe, Ni, Cr) are also sufficiently noble so as to not be electrochemically active in the potential range needed for deposition of actinides. Other materials like tungsten or molybdenum (which have even more noble reduction potential) were eliminated from consideration because of difficulty in machining. However, the final Schottky contact of the semi-conductor detector is not going to be stainless steel. It was later decided by Ohio State University researchers that it will likely be nickel. For this reason, nickel coupons are more appropriate for developing the actual deposition process. The most recent set of deposition runs were all done on nickel (low carbon alloy Ni-201) which was polished to remove the surface oxide layer prior to the experiments.

It should be noted that both thorium and uranium form alloys with nickel. The investigation therefore needs to focus not only on the deposition, but also on the stripping, as discussed in the previous section.

**Results and Discussion**

**Cyclic voltammetry (CV).**—The reduction/oxidation behavior of thorium was investigated on both stainless steel and nickel plates (coupons). Accordingly to literature, the reduction should be a one-step, four electron transfer [Th⁺⁴⁺/Th]. The cyclic voltammogram for both materials is displayed in Figure 3.

The thorium reduction peak on stainless steel is close to −2.4 V vs [Ag/100%AgCl], and the anodic limit is the onset of iron oxidation around −1.5 V. Single prominent reduction and oxidation peaks occur on stainless steel with some indication of minor overlapping peaks.

On the other hand, the nickel substrate shows some alloying tendencies. The thorium reduction peak is shifted anodically to about −2.3 V, and there are two major peaks during the oxidation part of the cycle. The Ni/Th binary phase diagram confirms the possibility of intermetallic formation between thorium and nickel.

The anodic limit is the onset of nickel oxidation at about −0.9 V. This increase in electrochemical range is useful to ensure that all deposited thorium can be anodically stripped prior to starting a new deposition cycle.

The cyclic voltammogram testing also serves as a diagnostic tool used prior to deposition to evaluate several issues. It is used to test the reference electrode stability (invariance of peak potential with time). It is used to verify the immersion depth of coupons (peak current in the expected range). It is used to test whether electrochemical equilibrium is reached (stable response between cycles). And it is used to guide selection of parameters for deposition (see below).

**Chronoamperometry (CA).**—Initial deposition runs were conducted using standard CA, i.e. constant potential deposition. Results from these runs are summarized in Table II. After using CV to identify the on-set potential for deposition (around −2.20 V), a range of constant overpotentials between −2.28 V and −2.70 V was investigated to determine optimum deposition conditions with analysis of deposits using SEM-EDS.

Samples generated from large overpotentials (E < −2.40 V) showed excessive dendritic formations and/or poor adherence of the deposit to the coupon surface. A composite two-step deposition with smaller overpotentials (initially E = −2.28 V, then E = −2.33 V) was attempted to diminish the amount of dendrites in the deposit and to shorten the time versus using only the initial overpotential (E = −2.28 V). Dendrite growth was suppressed; however they still existed (see Figure 4). Except from run 8 (see Table II), the samples took prohibitively long to collect the required amount of material, effectively rendering the method too slow for real-time analysis (deposition is only half of the process, the collection of alpha spectra requires some time too). Nevertheless, the suppression of dendrites and generally good surface coverage with similar-sized interconnected globules yielded somewhat satisfactory results in the later runs.

Figure 5 displays SEM image of one such run that shows no dendrites. Globular brighter formations 1–2 μm large (often

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**Table II. Results of chronoamperometry runs on stainless steel.**

| Run # | Applied potential [V] | Comment |
|-------|-----------------------|---------|
| 1     | −2.40                 | Deposit flaked off during rinsing |
| 2     | −2.70                 | Deposit flaked off during rinsing |
| 3     | −2.70                 | Current spikes during deposition, deposit flaked off during rinsing. |
| 4     | −2.28                 | Deposit located in scarce regions, deposition time ~10 min |
| 5     | −2.28, −2.32          | Deposit covers most of surface, deposition time ~20 min |
| 7     | −2.28, −2.33          | Deposit covers most of surface, deposition time ~23 min |
| 8     | −2.28, −2.32          | Deposit covers most of surface, deposition time ~7 min |
interconnected) are thorium deposits, whereas a darker bare spot on the right side reveals the iron substrate – rendering thorium distribution non-uniform with multiple regions bare of thorium content. This trend is evidenced on a different SEM image from the same run displayed in Figure 6. It shows EDS map overlay with individual elemental maps. Figure 7 contains approximate elemental composition of that image. It should be noted that each image was selected to contain some contrasting information (bare spot, dendrite, another abnormality), while most of the surface was covered without distinct abnormalities.

Zirconium content was nearing detection limit based on SEM-EDS in the layered regions of the deposit; however it was highly localized to regions of higher current density (dendritic structures) where it accounted for about 12 at%. These regions were scarce, so the overall zirconium content of the deposit is only a few at% at most. ZrCl₄ content in the salt (from the counter electrode oxidation) was below detection limit as measured with ICP-AES.

**Chronopotentiometry (CP).**—The constant current deposition regime was investigated due to the allure of shorter duration of the deposition. Very poor deposits were obtained with this method, however. Thorium was concentrated into scarce regions (less than 20% of surface), and the deposit was composed of different-sized clumps instead of similar-sized globules like in CA. By using CP the diffusion-limited regime could also not be ensured, so the technique was discontinued.

**Repeating chronoamperometry (RCA).**—Repeating chronoamperometry (RCA) – also known as bipolar current-pulse or potentiostatic pulsed deposition – alternates between two set potentials with rapid succession. The first potential is very cathodic and has a short duration (pulse period or on time, $E_{\text{pulse}}$), while the second potential is set to open-circuit potential or slightly anodic (dissolution takes place) and the duration is longer (relaxation period or off time, $E_{\text{relax}}$). These segments are repeated many times over. In theory, this ensures that only the very stable deposit remains in place, since the less stable portion (like dendritic formation) is dissolved during the relaxation period.
The validity of using RCA depends on the nucleation mode. During our experiments, we were not able to produce the characteristic three-region nucleation response using CA method which would enable us to distinguish between progressive and instantaneous nucleation mode. Many different overpotentials were selected along with two different cathode materials (2 mm diameter nickel or tungsten rods), however the result was always a simple cottrellian decay of current with no maximum. The only relevant literature available is the work of Cassayre, which determined progressive nucleation of thorium on tungsten. However, tungsten is inert as opposed to the reactive nickel electrode which is used here. Furthermore, the concentration of thorium was very small (0.2 wt% ThCl₄) whereas our concentration is at minimum 1.5 wt% ThCl₄. The validity of this reference is therefore very limited.

Based on CV results, the cathodic potential was selected to be at least the peak potential of the analyte, while the anodic potential was selected around the onset of analyte reduction current. This assures the deposition is diffusion-limited, and considerable fraction of deposit (optimum was found around 40%) is dissolved in each step (i.e. dendrite formation is suppressed).

A representative current transient for the nickel coupon is shown in Figure 8, and the typical evolution of charge over time is depicted in Figure 9. The transient for stainless steel would be of same shape, with different pulse and relaxation potentials.

SEM images of deposits created with this method demonstrated excellent uniformity and minimal dendritic formations. For the stainless steel coupon, a run with the following parameters is presented: \( E_{\text{pulse}} = -2.38 \text{ V}, \ E_{\text{relax}} = -2.28 \text{ V}, \ T = 773 \text{ K}, \ c(\text{ThCl}_4) = 1.5 \text{ wt%} \).

Figure 10 shows the SEM image, Figure 11 shows the EDS overlay map of the same image, and Figure 12 gives the elemental composition (averaged over the area) measured via EDS. The SEM image displays completely interconnected rows of globules (thorium deposit, as confirmed by the EDS map) about 1–2 μm thick. The underlying...
iron substrate is only scarcely seen, as well as dendritic formations (not present at all in this particular SEM image).

For the nickel coupon, Figure 13 displays typical SEM image obtained from a run of the following parameters: \(E_{\text{pulse}} = -2.24\) V, \(E_{\text{relax}} = -2.10\) V, \(T = 773\) K, \(c(\text{ThCl}_4) = 1.5\) wt%. Interconnected globules of thorium covering most of the surface are seen, with the substrate only in between the connected structures (similar to the case of stainless steel). Figure 14 shows another image from the same run with EDS map overlay suggesting an alloy formation between thorium and nickel (thorium signal not exclusively restricted to globular formations) in addition to pure thorium-deposit regions. Figure 15 shows the approximate elemental composition of the image measured via EDS.

Due to concerns about the reactive nature of nickel substrate, stripping of the deposit was performed to investigate possible difficulties with surface renewals (dealloying). The surface should not be altered during stripping, while all deposit must be stripped off to establish accuracy of subsequent alpha particle measurements. Stripping was done under CA conditions (initially at \(-1.00\) V, then \(-0.88\) V, then \(-0.78\) V) until equivalent amount of charge was passed to cancel the previously deposited amount (7 C). SEM-EDS analysis of the stripped coupon found no appreciable surface alterations, as shown in Figure 16 – the most prominent features are parallel ridges which are the characteristic result of initial polishing (prior to deposition). Their presence indicates that no significant surface alteration occurred as a result of the stripping procedure. The EDS elemental composition did not detect any thorium (or zirconium) residue.

Of interest is also the fact that the deposition time was significantly shortened compared to the other techniques – it takes less than 2 minutes to deposit the required amount of material. This might seem counterintuitive, since RCA alternates between cathodic and anodic currents while CA maintains cathodic current all the time. However, it is the effective current density which stays about the same during each bipolar segment of RCA. In CA the current density rapidly decays with...
used to prevent chlorine gas generation in our glove boxes. In a large hot cell that would be used for pyroprocessing, such a small amount of chlorine gas would be negligible. Thus, the system would most likely use an inert anode such as tungsten.

**Summary**

A hyphenated analytical technique combining electrochemical deposition and semi-conductor based alpha spectroscopy for safeguard-grade concentration monitoring of actinides has been proposed. For optimum performance, a thin layer (about 1 μm) of actinide elements needs to be deposited directly onto alpha particle detector metal contact.

This study investigated thorium deposition on stainless steel and nickel using three different electrochemical deposition methods (chronoamperometry, chronopotentiometry, and repeating chronoamperometry) to achieve a thin, uniform deposition while avoiding dendritic formations. Nickel surface was found to form alloys with thorium.

Uniform deposition of thorium on both stainless steel and nickel surfaces was achieved by electrodeposition under chronopotentiometry and repeating chronoamperometry conditions while using cyclic voltammetry as guidance for selecting deposition potentials.

Repeating chronoamperometry method resulted in better morphology of the deposit (analyzed by SEM-EDS), as well as in shorter deposition time (due to larger effective current density) in comparison to chronopotentiometry. The deposition time was found to decrease with increasing analyte concentration in the salt, which will ultimately be a key variable for calculating concentration of the actinides in the molten salt phase.

Deposition followed by stripping was performed on nickel with subsequent SEM-EDS analysis of the surface. No appreciable surface alterations were found, as well as no residue of thorium, confirming the possibility of detector reusability.

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