Electrodeposition of actinide compounds from an aqueous ammonium acetate matrix: Experimental development and optimization ☆

M.N. Torrico *, R.A. Boll, M. Matos

Nuclear Security and Isotope Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

ABSTRACT

Electrodeposition is a technique routinely employed in nuclear research for the preparation of thin solid films of actinide materials used in accelerator beam bombardments, irradiation studies, or as radioactive sources. This study investigates the deposition of both lanthanides and actinides from an aqueous ammonium acetate electrolyte matrix. Electrodepositions were performed primarily on stainless steel disks, with yield analysis evaluated using γ-spectroscopy. Experimental parameters (run time, current density, voltage, electrolyte concentration, and initial analyte mass) were studied and modified to optimize the uniformity and adherence of the deposition while maximizing yield. The procedure utilized samarium as the plating material, both with and without a radioactive tracer. Surface characterization studies were performed by scanning electron microscopy, electron microprobe analysis, radiographic imaging, and x-ray diffraction.

1. Introduction

Electrodeposition is a technique that has been used in radio-chemistry as a means to prepare thin solid films of actinide elements with applications ranging from source preparation for α-spectrometry to target fabrication for accelerator bombardments. Here a technique is described by which quantitative deposition of lanthanide and actinide elements onto a stainless steel cathode can be accomplished from an aqueous solution of ammonium acetate at low (10–20 V) applied voltages. Historically, electrochemical deposition has been performed from both aqueous and organic matrices. The technique is also referred to as "molecular plating" for its tendency to deposit the molecular form of the element, rather than the metallic. Electrochemical deposition from both organic matrices (e.g., isopropanol and isobutanol [1]) and aqueous solutions (e.g., ammonium sulfate or ammonium acetate (AmmAc)) requires meticulous purification of the analyte fractions before electrodeposition, as trace amounts of organic or metal contaminants can limit the yield [2]. Contaminants in the deposition can lead to unwanted spectral shifts and peak

broadening when producing a radiation source, particularly an α-source. Ion-exchange chromatography is often used to achieve the necessary purity of the materials. It is also important that the cathode, anode, and deposition cell be thoroughly cleaned with acid and/or alcohol to remove remaining contaminants. High-purity reagents must also be used throughout the electrodeposition process. The use of ammonium acetate as an electrolyte provides a neutral-pH buffer as well as an inexpensive matrix that requires low voltage (10–20 V) to achieve quantitative depositions. Organic matrices are unique in their resistance to decomposition and/or bubbling during electrolysis. However, organics can require voltages in excess of ∼100 V for successful deposition [3]. These high voltages can require the addition of a cooling system to the electrodeposition cell to maintain a lower operating temperature. Cells with AmmAc as the electrolyte do not require cooling or high-voltage shielding, simplifying handling and unit fabrication.

The use of AmmAc as a matrix for electrodeposition has received very little attention in the literature. Roman [4] explored the electrodeposition behavior of Ra, Th, U, and Po from 0.35 M AmmAc solutions onto stainless steel and found the plating behavior of the actinide fractions to be strongly dependent on pH. In this study, small amounts of HCl were used to dissolve the analyte as well as for pH control, while maintaining an operating pH between 3 and 5.

A surrogate material for Cf was used to allow experimentation outside a glove box or hot cell. The redox solution chemistry of Sm^{3+} and Cf^{3+} ions should be similar, as indicated by standard reduction potentials to the ground state of -2.3 V and -1.94 V, respectively (although it should not be assumed that the

* Corresponding author.
  E-mail address: illuminedmachine@gmail.com (M.N. Torrico).

lanthanide/actinide elements can be as easily electrodeposited as ground-state metals) [5]. Even though Dy is the electronic homolog to Cf, and Gd is closer to Cf in cationic radius, it has been suggested that Sm, like Cf, has a (transient) divalent state in acid solution between the trivalent and ground states [6,7]. It has also been shown via co-precipitation studies in various solvents that the reduction behavior of Cf will closely follow Sm [8]. This reduction behavior is an important aspect in electrodepositions.

Various analytical techniques were used to study and characterize the physicochemical properties of the deposit, including the spatial distribution of activity (radiographic imaging), basic microstructure and thickness (scanning electron microscopy), crystallinity (XRD), and the chemical composition of the plated material (wavelength-dispersive spectroscopy). Gamma spectroscopy was performed to quantify the ^{153}Sm and ^{140}La radioactive tracers ($t_{1/2} = 1.946$ d, $E_\gamma = 103$ keV for ^{153}Sm and $t_{1/2} = 1.678$ d, $E_\gamma = 487$ keV for ^{140}La) to determine electrodeposition yields [9].

2. Experimental

2.1. Reagents and materials

The following reagents were used.

(1) 0.35 M, 0.7 M, 0.175 M ammonium acetate (NH$_4$CH$_3$COO) solution(s) at neutral pH, prepared by dissolving anhydrous ammonium acetate solid (certified ACS reagent-grade NH$_4$CH$_3$COO purchased from Fischer Chemical) into deionized water.
(2) 0.1 M Sm^{3+} solution, prepared by dissolving Sm(NO$_3$)$_3 \cdot$6H$_2$O into 0.1 M HNO$_3$ (trace, purchased from Fischer Chemical) to give 0.1 M Sm^{3+} solution in 0.1 M HNO$_3$.
(3) Concentrated acids and bases: concentrated, reagent-grade (12.1 M) HCl purchased from EMD Chemicals®. Concentrated (14.5 M) NH$_4$OH certified ACS reagent purchased from Sigma-Aldrich.
(4) ^{153}Sm tracer ($t_{1/2} = 1.95$ d) obtained from irradiation of 99.2 wt% ^{152}Sm$_2$O$_3$ in the High Flux Isotope Reactor (HFIR) at an unperturbed thermal neutron flux of 4.05×10^{14} neutrons/cm^2/s. Between 1 and 10 µCi radioactivity was used per electrodeposition experiment.
(5) ^{140}La tracer ($t_{1/2} = 1.6780$ d) obtained as the daughter of ^{140}Ba ($t_{1/2} = 12.746$ d). Separation of daughter La(III) from parent Ba (II) was achieved using cation exchange chromatography with a disposable column of 1.0 mL bed volume and BioRad® AG-50 × 4 analytical-grade cation exchange resin.

2.2. Electrodeposition unit design

Many electrodeposition cell designs explored in the literature have been based on the "chimney" style with the cathode placed at the bottom of the well [2,3]. The unit fabricated for this study is more comparable to an "aquarium" with the plating cathode fastened to the side of the chamber (Fig. 1). The basic design involves the machining of a Teflon block with external dimensions 3.00 in. × 2.00 in. × 1.50 in. (length × width × height). The electrodeposition well is a 1.71 in. × 0.50 in. × 1.60 in. (length × width × depth) rectangular opening cut into the Teflon block, into which the electrolyte solution was transferred. The well contains a circular, 1.5 in. (3.81 cm), outer-diameter hole for securing the stainless steel cathode and a 0.50 in. (1.27 cm) cavity within this hole that serves as the active deposition area. The entire Teflon block is fastened to a stainless steel base, and electrical current is directed into a copper piece that screws onto the surface of the cathode to keep it firmly attached to the unit. A small Teflon piece separates the copper piece from the grounded stainless
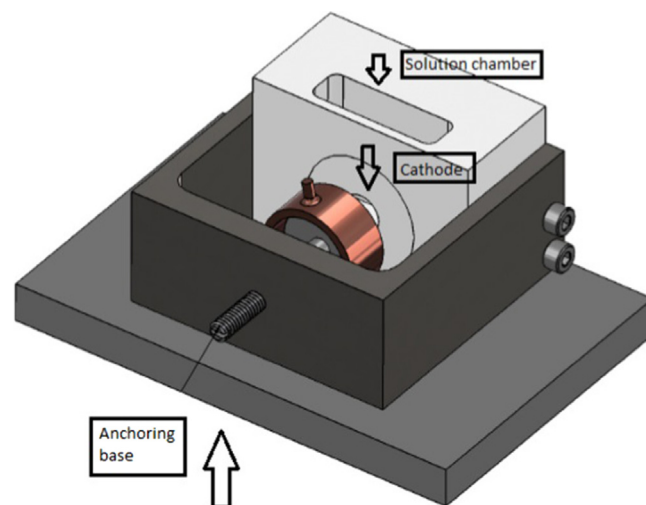

Fig. 1. Schematic diagram of the electrodeposition unit.

steel base, and a silicone rubber gasket seals the solution chamber from leaking around the cathode window. A flat round platinum disk, anode, was suspended in the aquarium ~0.25 in. (~0.64 cm) from the cathode, once the unit was assembled.

2.3. Experimental procedure

Experimental variables including run time, AmmAc concentration, solution pH, voltage/current, and mass of Sm dissolved were varied independently while keeping other variables constant. This allowed for testing of the system's response to adjustment of one variable at a time. The experimental procedure below attempts to optimize and maximize deposition yield. One 1.5 in. (3.81 cm) unabraded stainless steel disk with a 0.197 in^2 (1.27 cm^2) active deposition area was first wiped down with ethanol and a lint-free cloth to remove any trace oils. The disk was then rinsed thoroughly using deionized (DI) water and placed into the electrodeposition cell as the cathode. The unit was assembled, sealed, treated with weak HNO$_3$ solution, and washed with DI water. The electrodeposition unit was then "conditioned" with the electrolyte solution before adding the feed solution. The conditioning step involved filling the assembled unit with AmmAc solution for 1–5 min and then discarding the conditioning solution, with the electrodes in place. Although optional, the conditioning step is thought to leach contaminants out of the unit that would otherwise be mobile during the deposition process.

Once the electrodeposition unit was assembled, cleaned, and conditioned, the deposition material was prepared. Samarium masses of 300, 600, and 900 µg were used as they reflect the low concentrations of radioisotopes often encountered during radiochemical operations. A radioactive tracer (^{153}Sm or ^{140}La) was combined with the Sm material and dried. The dried combination was then dissolved in 0.25 mL of concentrated HCl, and the resulting solution was transferred into the well with four 3.5 mL rinse aliquots of AmmAc, bringing the total solution volume to approximately 14.25 mL. The "serial rinses" minimize loss of the radionuclide tracer during transfer.

The power was turned on and increased gradually during the first 5 min and then set at the desired constant current or constant voltage for a total of 4 h. Fig. 2 shows a deposition cell in use, and Fig. 3 shows a close-up view of the post-deposition cathode plate. No post-experimental conditioning or surface treatment was performed beyond a water wash. Electrodeposited samples were stored in sealed plastic petri dishes. Post-deposition characterization was performed using x-ray diffraction, radiographic