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Characterization of Electrodeposited Technetium on Gold Foil

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The reduction and electrodeposition of TcO_4^- on a smooth gold foil electrode with an exposed area of 0.25 cm^2 was performed in 1 M H_2SO_4 supporting electrolyte using bulk electrolysis with a constant current density of 1.0 A/cm^2 at a potential of −2.0 V. Significant hydrogen evolution accompanied the formation of Tc deposits. Tc concentrations consisted of 0.01 M and 2 × 10^{-3} M and were electrodeposited over various times. Deposited fractions of Tc were characterized by powder x-ray diffraction, x-ray absorption fine structure spectroscopy, and scanning electron microscopy with the capability to measure semiquantitative elemental compositions by energy-dispersive x-ray emission spectroscopy. Results indicate the presence of Tc metal on all samples as the primary electrodeposited constituent for all deposition times and Tc concentrations. Thin films of Tc have been observed followed by the formation of beads that are removable by scratching. After 2000, the quantity of Tc removed from solution and deposited was 0.64 mg Tc per cm^2. The solution, after electrodeposition, showed characteristic absorbances near 500 nm corresponding to hydrolyzed Tc(IV) produced during deposition of Tc metal. No detectable Tc(IV) was deposited to the cathode.
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Technetium, element 43, has 34 radioactive isotopes that are known, with none being stable, from mass 85–118. The most common isotope, ^{99}Tc ($t_{1/2}$ = 2.14 × 10^5 y), is present in large quantities in spent nuclear fuel, where it constitutes approximately 6% of the fission yield.[1] With regard to nuclear waste management, Tc presents a threat to the biosphere because it is very stable and mobile as the anion pertechnetate. Two methods to reduce the potential long-term environmental hazards of Tc have been considered: transmutation of Tc metal targets by neutron capture in a reactor to produce stable isotopes of ruthenium or the incorporation of Tc into stable forms for long-term geological disposal (i.e., Tc alloys or oxide materials).[2,3] For this reason, the production of Tc metal for eventual use in a target or waste form represents a challenge for the management of nuclear wastes. Different methods to produce Tc metal have been reported.[4-8] A common route of reduction is to use H_2 gas or an Ar/H_2 mixture at 400–1100°C from NH_4TcO_4[4] and TcO_2[6].

Secondary techniques such as the electrodeposition of Tc from aqueous solutions have also been previously explored as an option for the recovery of Tc as the metal. With regard to Tc electrodeposition, technetium is unique. It is a very complex element to study electrochemically because of its large variety of chemical forms, oxidation states, and known disproportion reactions available to it in various aqueous systems that have the ability to hinder production of Tc metal on a cathode substrate.[9-12] The potential uses of the electrodeposition of TcO_4^- for the recovery of Tc metal from aqueous solutions has gained notoriety as a possible method for the isolation of this fission product prior to being introduced into a waste form. This technique potentially eases the recovery of Tc from spent nuclear fuel and reprocessing activities. This may be used as a possible precursory step in the production of Tc metal, Tc containing waste forms, or thin films of Tc metal for target preparation. Attempts to electrodeposit Tc metal are often hindered due to the formation of oxides.[13,14] Habitually, results are misleading or repeated experiments do not mimic results reported in literature. Because of this ambiguity, and because deposition products are not well structurally characterized, we have investigated the most simple system of TcO_4^- in H_2SO_4, electrodeposited onto gold. In the current study, we report the main electrodeposition product of TcO_4^- in the presence of 1 M H_2SO_4 onto a gold foil cathode at current densities of 1 A/cm^2 as hexagonal Tc metal.

Experimental

Chemicals.— The starting material NH_4TcO_4 was obtained from stocks at the Los Alamos National Laboratory originally purchased from the Oak Ridge Office of Isotope Sales. Prior to use, the NH_4TcO_4 was purified by dissolution into a dilute NH_4OH/H_2O_2 solution followed by evaporation to dryness. The solutions used for electrodeposition were prepared by dissolving the dry NH_4TcO_4 into deionized (DI) water. The final concentration of the stock Tc solution was quantified by LS counting. Concentrated sulfuric acid was purchased from J.T.Baker and used as received. Gold foil, 0.1 mm thick 99.99% was purchased as a 25 × 25 mm sheet and cut into individual electrodes. Samples to be electrodeposited consisted of 10 mL stock solutions containing $[H_2SO_4]$ = 1 M and $Tc[2 \times 10^{-3}]$ and $[1 \times 10^{-2}]$ M Tc representing 2 or 10 mg dissolved Tc. Additionally, solutions were not purged of oxygen, nor actively deaerated during deposition experiments. Crystalline TcO_2 was prepared by thermal decomposition of NH_4TcO_4 at 700°C under argon atmosphere whereupon the sample was collected for future use or was converted to Tc metal under 5% H_2/Ar atmosphere for an additional 24 h. Water was purified to >18 MΩ cm by a Milli-Q system. All other commercially available chemicals were used as received.

Experimental setup.— A three-electrode commercially available computer-controlled potentiostat (CH Instruments Electrochemical Workstation) was used for all Tc electrodeposition experiments. Solutions were rapidly stirred, without purging, at room temperature throughout the deposition with a constant current density of 1 A/cm^2. Depositions were monitored against a 3 M Cl^- Ag/AgCl reference electrode. A solid sheet of platinum metal was used as the counter electrode with an exposed surface area of 2 cm^2 separated by 3 cm from the gold foil cathode. The gold foil was cut into sheets with an exposed deposition area of 0.25 cm^2 where the Tc was deposited. Following Tc deposition, electrodes were washed with DI water and allowed to air dry. Electrodes were prepared for x-ray diffraction (XRD), extended x-ray absorption fine structure (EXAFS), and scanning electron microscopy/energy-dispersive x-ray emission spectroscopy (SEM/EDS) analysis. The quantity of Tc deposited onto the gold foil was quantified by liquid scintillation counting (LSC). Following electrodeposition, the solutions were analyzed by UV-visible spectroscopy (Cary 6000i).

X-ray diffraction.— Electrodeposited Tc was examined by placing the portion of the electrode containing a Tc deposit directly onto a silicon wafer and held in place with moldable clay underneath the electrode. The XRD patterns were obtained using a Philips Panalyti-

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cal X'Pert Pro, Cu Kα target with Ni filter and an X'elerator multiple Si-strip solid-state detector. The XRD patterns were quantified by Rietveld analysis using the TOPAS 3.0 software.[15]

X-ray absorption fine structure spectroscopy.— X-ray absorption fine structure (XAFS) measurements were completed at the Advanced Photon Source (APS) at the BESSRC-CAT 12 BM station at Argonne National Laboratory. Technetium compounds (NH_4TcO_4, TcO_2, Tc metal, and deposited Tc) were diluted (~1% Tc in mass) in boron nitride or directly taped to the aluminum sample holders with kapton. XAFS spectra were recorded at the Tc–K edge (21,044 eV) in fluorescence mode at room temperature using a 13-element germanium detector. A double crystal of Si [111] was used as a monochromator for the photon source. The energy was calibrated using steam-reformed Tc metal, decomposed from NH_4TcO_4, according to Ref. 16.

For each sample, four spectra were recorded in the k range (k = [0,17] Å^{-1}) and averaged. Background contribution was removed using ATHENA[17] software and data analysis was performed using WINXAS.[18] For the fitting procedure, amplitude and phase shift functions were calculated by FEFF8.2.[19] Input files were generated by Atoms[20] using crystallographic structures of technetium dioxide.[21] Adjustments of the k^3-weighted EXAFS spectra were performed under the constraints $S_0^2 = 0.9$. A single value of energy shift ($\blacksquare E_0$) was used for all scattering. The uncertainty determined by EXAFS on the coordination number (CN) was ±20% and ±0.02 Å on the reported atomic distances (R).

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Scanning electron microscopy and energy-dispersive X-ray emission spectroscopy.— SEM and EDS analysis were completed directly on the electrodeposited samples. The SEM images and EDS measurements were performed using a JEOL-5610 scanning electron microscope equipped with secondary electron and backscattered electron detectors with the capability to measure elemental analysis semiquantitatively by energy-dispersive x-ray emission spectroscopy.

Other techniques.— ^{99}Tc concentrations were evaluated by LS counting using a Packard 2500 scintillation analyzer. The scintillation cocktail used was Ultima Gold AB (Packard). The concentrations of solutions prior to and following electrodeposition were determined using calibration curves performed in solution with a composition similar to the experimental parameters. All recorded UV-visible spectra were collected at room temperature in a 1 cm quartz cell on a Cary 6000i double beam spectrometer with background subtraction.

Results

X-ray powder diffraction.— XRD patterns were recorded between 2θ = 20° and 2θ = 120° with a step rate of 1.16°/min using the Bragg-Brentano method. The fitted patterns presented in Fig. 1 confirm the formation of Tc metal with lattice parameters of a(Å) = 2.74354(15) and c(Å) = 4.39524(14) for 0.01 M Tc and a(Å) = 2.74427(94) and c(Å) = 4.4212(17) for 0.01 and 0.002 M Tc solutions electrodeposited for 500 s. These values are in agreement with literature.[22-25] Tc metal has two crystalline phases, hexagonal and cubic. The cubic phase is produced at temperatures above 800°C from the hexagonal phase. Lattice parameters are in agreement with the hexagonal phase; no other phases were detectable other than the gold foil that the deposit was adhering to. Though XRD is a useful tool to probe for the presence of Tc metal, the presence of amorphous, or other nondiffracting phases in a deposit cannot be completely distinguished from the diffracting metal deposits on the electrode. Therefore, the need to provide more structural information on the electrodeposited Tc was completed by XANES and XAFS spectroscopy.

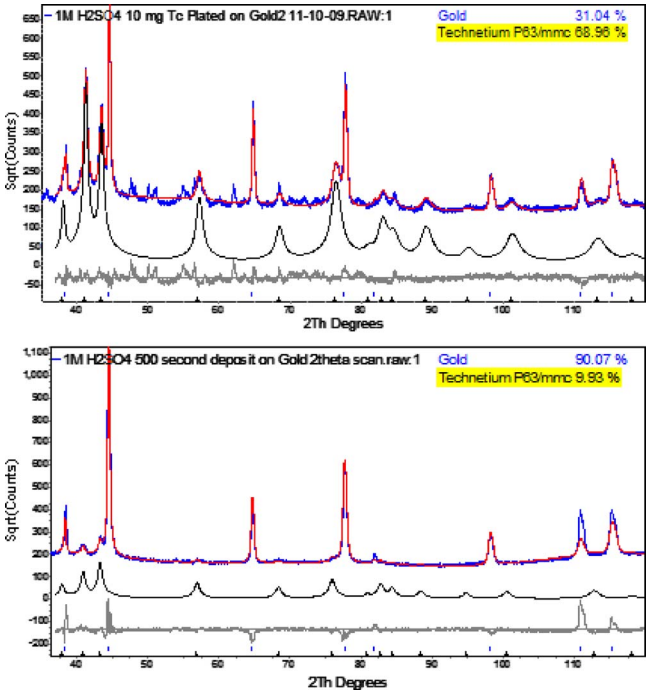

Figure 1. (Color online) XRD hexagonal Tc metal, [Tc] = 0.01 (top) and 2 × 10^{-3} M (bottom), [H_2SO_4] = 1 M, t = 500 s deposition.

XANES.— XANES provides local geometry of the electrodeposited sample. Three standards were used to provide spectra for Tc in the 0, IV, and VII oxidation states: Tc metal, TcO_2, and NH_4TcO_4. Figure 2 shows the absorption regions of each standard and one electrodeposited sample of Tc on the substrate from aqueous sulfuric acid solutions. All electrodeposited samples tested show similar results in the XANES region for the shift in energy. The electrodeposited sample is Tc metal with the sample's shift in energy corresponding to that of the Tc metal standard. Additionally, there is no pre-edge peak in the XANES spectra further indicating that the originating Tc(VII) species is no longer present on the cathode after electrodeposition.

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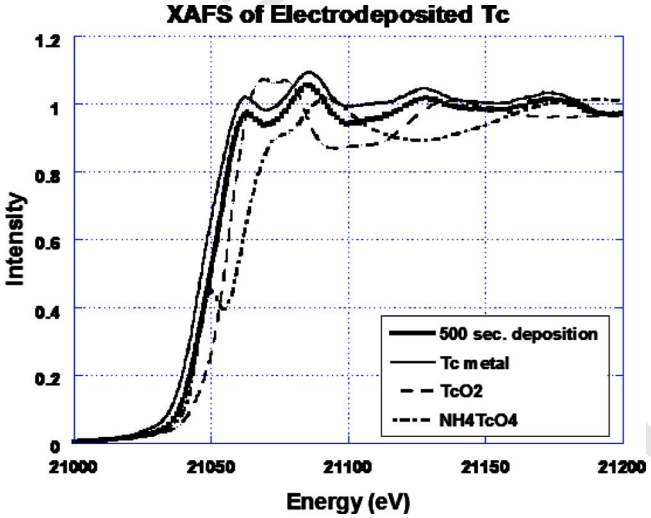

Figure 2. (Color online) XANES spectra of Tc_0, Tc(IV), and Tc(VII) and electrodeposited Tc, [Tc] = 0.01 M.

Table I. EXAFS structural parameters of electrodeposited Tc on gold; [Tc] = 0.002 M, [H_2SO_4] = 1 M, 500 s deposition, 1.0 A/cm^2. MS = multiscattering between the absorbing atom and neighboring Tc atom. CN = coordination number, *R* = radius, and σ2 = Debye-Waller factor.

Tc	Structural Parameters		
Scattering Atom	C.N	R (Å)	σ2 (Å2)
Tc0–Tc1	5(1)	2.71(2)	0.007
Tc0–Tc2	**5(1)**	**2.74(2)**	**0.006**
Tc0–Tc3	5(1)	3.88(4)	0.008
Tc0–Tc4	15(3)	4.76(5)	0.009
MS (Tc0 and Tc2)	24	5.38(5)	0.015
MS (Tc2 and Tc5)	12	5.42(5)	0.02
Tc0–Tc5	6	5.42(5)	0.02
Tc0–Tc6	12	6.11(6)	0.015

EXAFS.— In order to confirm the formation of Tc metal after electrodeposition, XAFS measurements were performed on various deposits of Tc. Results indicate that there is no Tc–O scattering and no oxygen contribution in the Fourier transform corresponding to a Tc–O peak. Table I shows the structural and scattering parameters for the electrodeposited Tc and coordination distances. From [Tc] = 0.01 M, the Tc_0–Tc_1 contribution has come from Tc–Tc, further indicating the formation of hexagonal Tc metal after electrodeposition.[26] Tc_0–Tc_2 scattering distance has been recorded as 2.74(2) Å, further indicating the formation of hexagonal Tc metal after electrodeposition from aqueous solution in 1 M H_2SO_4 (Fig. 3).

Scanning electron microscopy and electron dispersive spectroscopy.— The cathode deposit obtained from the ammonium pertechnetate, sulfuric acid solution appeared to be Tc metal. The deposit was not dissolved by concentrated HCl and could be removed from the cathode surface by scratching. The formation of a mirrored surface is visualized immediately following electrodeposition of Tc for all samples, across all deposition times and concentrations of Tc on gold. The mirrored deposit on the electrode surface is possibly due to the formation of a homogenous monolayer initially. This becomes more dull following longer deposition times when the order of the deposits becomes more randomized. The smooth, thin and lustrous layer of Tc (Fig. 4a) formed on the gold foil has little texture which forms layers of approximately 250–750 nm in thickness, as estimated from Fig. 4d. A longer electrodeposition time was required to form beads when deposited from less concentrated solutions. These beads varied in diameter from 1 to 10 μm, which formed on the smooth mirrored surface (Fig. 4b). SEM indicated that the estimated depth of the final layer is 1–3 μm in thickness (Figs. 4c and 4d), which does not significantly increase with longer deposition times. Indication of this effect is observed by quantifying the electrodeposited Tc from solution by LS counting before and after deposition of the 0.01 M Tc solution.

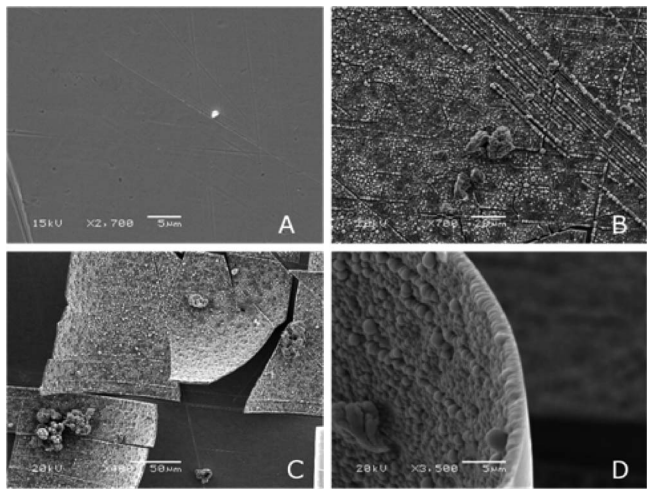

Figure 3. SEM micrographs for (A) formation of thin-layered Tc, *t* = 100 s deposition [Tc] = 2 × 10^{-3} M, [H_2SO_4] = 1 M; (B) formation of Tc beads, *t* = 500 s deposition, [Tc] = 0.01 M, [H_2SO_4] = 1 M; (C) mechanically stressed deposit layers of electrodeposited Tc (bright phase), gold foil underneath (dark phase), 500 s deposition with flake formation, [Tc] = 0.01 M, [H_2SO_4] = 1 M; and (D) initial Tc electrodeposited layer (250–750 nm) followed by bead formation and a new layer of Tc (1–3 μm).

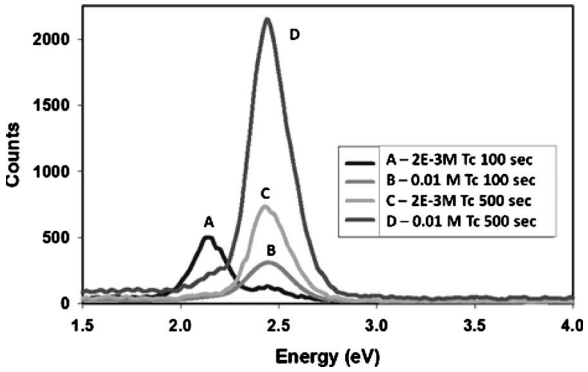

Figure 4. Electron dispersive spectra of electrodeposited Tc on gold, *t* = 100 and 500 s, [H_2SO4] = 1 M, [Tc] = 0.01 and 2 × 10^{-3} M.

The Tc absorption line corresponding to the Kα1 peak at 2.424 eV was monitored by EDS. EDS has shown the presence of Tc on the surface of the electrodeposited film from both 100 and 500 s deposition times in 1 M H_2SO_4 from solutions containing [Tc] = 0.01 and 2 × 10^{-3} M. The peaks corresponding to gold absorption lines at 2.123 eV were observed significantly for only one sample: the sample deposited from [Tc] = 2 × 10^{-3} M with a deposition time of 100 s. No significant peaks were observed for oxygen at 0.525 eV in any of the samples analyzed, though low energy oxygen x-rays are not readily detected by EDS. This helps further confirm the presence of Tc metal as the major constituent deposited in this electrodeposited series. The EDS Tc peak has also shown an increase in counts with an increase in deposition times and more concentrated.

LS counting.— LS counting was used to monitor the quantity of Tc remaining in solution after deposition. Quantities of deposit were estimated by this technique. For an electrodeposited sample initially containing 2 mg Tc in solution, after 2000 s of deposition, 0.167 mg of Tc metal was deposited with the highest rate of deposition occurring within the first 165 s (Fig. 5) with a final deposit of 0.64 mg Tc metal deposited per cm^2.

UV-visible (UV-vis) spectroscopy.— A slight change in the color of the solution was observed following deposition of Tc in all solutions. Following electrodeposition, both solutions with initial Tc concentrations of [Tc] = 0.01 and 0.002 M and constant sulfuric acid changed from translucent to slightly brown, as reported previously.[27] The [Tc] = 0.01 M solution, after electrodeposition, has a characteristic absorbance (Fig. 6) at 500 nm corresponding to a Tc(IV) species which formed during electrodeposition.[28]

Conclusion

The present study has shown the ability to electrodeposit Tc metal onto gold foil cathodes. Results indicate that the morphology of the electrodeposited Tc from 1 M sulfuric acid solutions with high current produces Tc metal. The final Tc deposits were con-

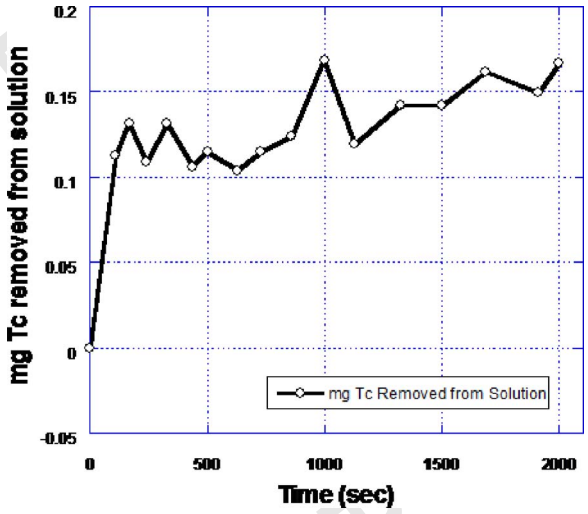

Figure 5. (Color online) LS counting of electrodeposited Tc onto gold foil; initially 2 mg Tc, 2000 s deposition, current density 1.0 A/cm^2, maximum Tc deposition 0.167 mg; 0.64 mg Tc/cm^2.

firmed as hexagonal Tc metal by powder XRD and XAFS with the latter indicating the absence of oxygen in the deposits. SEM/EDS has also confirmed the absence of oxygen in the deposits with a changing surface upon longer deposition times and higher concentrations of Tc present during electrodeposition. UV-vis has indicated that the formation of Tc metal is hindered due to the formation of Tc(IV) species during electrodeposition. Further investigation into a range of solution conditions, various initial forms of Tc, and different types of cathodes are of interest in regard to future studies to understand the range of conditions that Tc metal can be electrodeposited from. This work also presents an opportunity to use this as a recovery process for Tc metal prior to inclusion into a metallic waste form and an important possible option for management of Tc in nuclear waste streams.

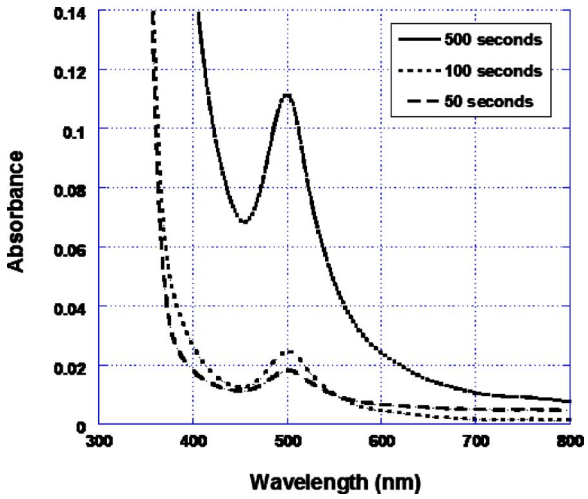

Figure 6. (Color online) UV-vis spectra of solution after electrodeposition, [Tc] = 0.01 M initially.

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