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Electrochemical Oxidation of Trivalent Americium Using a Dipyrazinylpyridine Modified ITO Electrode

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We present here the electrochemical oxidation of Am(III) to $Am^{V}O_2^{+}$ and $Am^{VI}O_2^{2+}$ in pH 1 nitric acid using a mesoporous tin-doped indium oxide electrode modified with a covalently attached dipyrazinylpyridine ligand. The applied potential affects the distribution of Am oxidation products. At potential 1.8 V, only Am(V) is observed, while increasing the potential to as much as 2.0 V, results in oxidation of Am(III) to Am(V) and subsequent oxidation of Am(V) to Am(VI). At applied potentials > 2.0 V, Am(III) is oxidized to Am(V), while Am(VI) is reduced to Am(V). The latter reduction reaction is likely due to the increased rate of hydrogen peroxide formation from the 2-electron oxidation of water at the electrode at these high potentials. The development of future ligand modified electrodes for actinide oxidations must consider how they facilitate An oxidations while disfavoring unwanted or competing reactions.

Nuclear energy is a viable option for global future energy needs given its relatively low carbon footprint, and large power production relative to its land usage. A problem with the expansion of nuclear energy however is the reprocessing of used nuclear fuel. There are reprocessing schemes in place to separate uranium and plutonium which can be subsequently reconstituted for re-use in nuclear reactors. Presently, the remaining used fuel components (fission products including tri-valent lanthanides, and neutron capture products including the minor actinides Am and Cm) are not appropriately dealt with. This is not ideal as Am is responsible for the long-term heat load associated with UNF. Many countries, including France and the United Kingdom have adopted processes which partially separate americium, in an effort to more fully recycle their fuel elements, and, to conserve space in their repositories.[1] In the United States however, this is not currently implemented. Americium is a challenge to separate from UNF due to its similar oxidation state (+3) and charge density compared to the lanthanides.[2] Through judicious ligand design, many have developed organo-soluble ligands that selectively bind to trivalent Am vs. Ln, which can subsequently be used to separate Am by solvent extraction.[3-4] Such separation schemes require multiple steps, and can cause more down-stream complications as ligands degrade in the strong radiation field and produce reactive species.[5]

There is therefore, a need to develop a simplified fuel cycle where Am is separated with U and Pu so that it can be more efficiently removed from the fission products, and used in a fast reactor. Our approach to this problem has involved investigating methods to generate Am(VI). In its hexavalent state, Am(VI) exists as $Am^{VI}O_2^{2+}$, and has a structure analogous to that of other hexavalent actinides (UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+}).[6] It is therefore anticipated that it will have similar binding characteristics to these similar high-valent species, which are substantially different from Am(III) or Ln(III). Nevertheless, this oxidation is not thermodynamically simple, given the high 1-electron Am(IV/III) couple at 2.6 V vs. SCE.[7] This severely limits the chemical oxidants available that are viable options from an industrial standpoint. There has been notable progress in developing new oxidants which are capable of generating Am(VI) which persists long enough to effect a solvent extraction.[8-9]

The subsequent Am(IV) generated via 1-electron oxidation of Am(III) is unstable and can either reduce back to Am(III), or be oxidized to $Am^{V}O_2^{+}$ ($E_{1/2}$ for Am(V/IV) is 0.84 V vs. SCE).[10] $Am^{V}O_2^{+}$ has a thermodynamic oxidation potential of 1.60 V to $Am^{VI}O_2^{2+}$, which reinforces the point that in most systems, the initial oxidation of Am(III) is the most challenging hurdle. Our efforts to oxidize Am(III) have involved a Ligand Modified Electrode (LME) strategy. We previously demonstrated that an electrode comprised of a terpyridine ligand covalently attached to the surface of a mesoporous film of tin-doped indium oxide (*nano*ITO|terpy) is capable of electrochemically generating Am(VI) at potentials as low as 1.8 V vs. SCE.[11] Paramount to the

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operation of these LMEs is the ability to coordinate Am(III) and decrease the potential required to generate Am(IV), and, to decrease the faradaic efficiency for unwanted reactions including the 2-electron oxidation of water to hydrogen peroxide, and nitrate to nitrous acid.[12] Attachment of a relatively non-polar organic ligand modifies the hydrophobicity of the surface, ultimately increasing the overpotential for water oxidation relative to a bare *nano*ITO electrode. In this work, we extend this LME strategy to a similar *nano*ITO electrode modified with a phenylphosphonic acid derivatized dipyrazinylpyridine (dpp); capable of oxidizing Am(III) to Am(V) and Am(VI) at similar potentials. The dpp ligands coordinate more strongly to Am(III) than their terpyridine analogues in acidic solutions,[13] suggesting that they may be better candidates for the electrochemical generation of Am(VI).

A detailed preparation of our *nano*ITO electrodes is described elsewhere.[11] The preparation of our dpp ligand is described using a modified procedure reported elsewhere, where acetylpyrazine was used in place of acetylpyridine.[14-15] Characterization by ^{1}H-NMR and ^{31}P-NMR (Figures S1, S2, S3) are consistent with literature, confirming the structure of our ligand. Further experimental details are provided in the supplementary information.

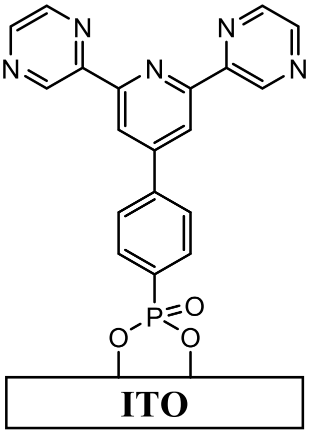

Figure 1. Molecular structure of a dpp ligand attached to a *nano*ITO electrode.

LMEs were prepared by soaking a *nano*ITO electrode in a 1 mM methanol solution of the dpp ligand (Figure 1). Surface coverage of dpp at *nano*ITO was determined by soaking the LME in a solution containing $Fe(ClO_4)_2$ and acquiring the associated cyclic voltammogram (Figure S6). The charge under the resultant Fe(III/II) oxidation wave associated with *nano*ITO|$Fe(dpp)_2^{2+}$ is related to the surface coverage using the equation $\Gamma = Q/nFA$, were Γ is the surface coverage in mol/cm^2, Q is the charge under the oxidation wave in Coulombs, n is the number of electrons involved in the redox process (1), F is Faraday's constant (96,485 C/mol), and A is the surface area of the electrode in cm^2 (typically 1.0 cm^2, though this was determined with a Vernier calliper in each case). The binding isotherm was determined by varying the concentration of the ligand loading solution (Figure S7), and corresponds to a Langmuir isotherm (Eqn. 1). The surface coverage of the dpp ligand on *nano*ITO—calculated using—Eqn. 1 is 29×10^{-9} mol/cm^2, which corresponds to a well packed monolayer.

In the absence of Am(III), no electrochemical redox events are observed with the *nano*ITO|pdpp electrode. Upon substitution of the solution for one with 0.81 mM Am(III), a minor quasi-reversible redox couple is observed at 1.55 V vs. SCE (Figure 2) ascribed to an Am(IV/III) couple. At potentials above 1.8 V vs. SCE catalytic oxidative current is observed, with new reduction peaks at 0.58 V and 0.43 V vs. SCE (Figure S8).

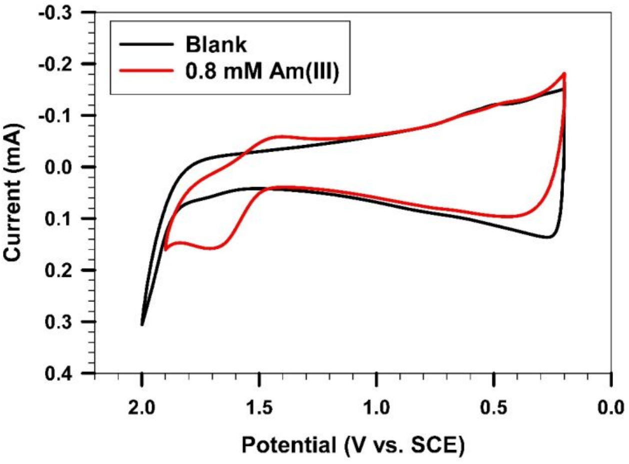

Figure 2. Cyclic voltammograms of a *nano*ITO|dpp electrode in 0.1 M HNO_3 in the absence (**Black**) and presence (**Red**) of 0.8 mM Am(III). Scan rate is 50 mV/s.

Controlled potential electrolysis with concurrent UV-visible measurement was performed with the same *nano*ITO|dpp electrodes in 0.1 M nitric acid solutions containing 0.81 mM Am(III). At an applied potential of 1.8 V vs. SCE, Am(III) was oxidized to Am(V), while no Am(VI) was observed. After 4 h of electrolysis at 1.8 V, the concentration of Am(V) reached 0.51 mM, while the concentration of Am(III) had dropped to 0.28 mM. The mechanism associated with this oxidation is analogous to what has been proposed for similar LMEs:[11] two sequential 1-electron oxidations of Am(III) to Am(IV) and then Am(IV) to Am(V). This first redox event requires an equilibrium coordination of Am(III) to the *nano*ITO|dpp electrode followed by the 1-electron oxidation to form Am(IV). Am(IV) is a stronger Lewis acid, and so will bind to the electrode more tightly than Am(III). The subsequent oxidation of Am(IV) to Am(V) is lower than that to oxidize Am(III) to Am(IV) (E(Am(V/IV) = 0.84 V vs. SCE). The oxidation of Am(IV) to Am(V) is proton-coupled and requires 2 molecules of water within the inner coordination sphere of Am(IV) to generate AmO_2^+.

$Am^{V}O_2^+$ is a weak Lewis acid (weaker than Am^{3+}), and is therefore expected to dissociate from the electrode. Given that the Am(V) is formed, Am(VI) should also be thermodynamically possible, however, Am(V) has less affinity for the surface thereby decreasing the rate of electron-transfer at the electrode surface from dpp sites likely occupied by excess Am^{3+}.

Am(III) + *n*ITO|dpp ⇌ *n*ITO|dpp-Am(III) (1)
*n*ITO|dpp-Am(III) → *n*ITO|dpp-Am(IV) + e^- (2)
*n*ITO|dpp-Am(IV) + $2H_2O$ → *n*ITO|dpp + AmO_2^+ + $4H^+$ + e^- (3)
$AmO_2^+ \rightarrow AmO_2^{2+} + e^-$ (5)

While Am(VI) may be electrochemically generated from Am(V) at 1.8 V, it is rapidly reduced by radiolytically produced reducing agents such as hydrogen peroxide or nitrous acid.[16] Increasing the applied potential from 1.8 V to 2.0 V does not appreciably change the rate of disappearance of Am(III), which can be approximated to a first order reaction with a rate constant of 8.1 × 10^{-5} s^{-1}. This indicates that Am(III) diffusion to the electrode limits the rate of Am(III) oxidation. At a 2.0 V applied potential, Am(V) now decreases in concentration, while Am(VI) starts to appear. After 2 hours of electrolysis at 2.0 V, the concentration of Am(V) has dropped by 0.12 mM (0.51 mM to 0.39 mM), while the concentration of Am(VI) increased to 0.31 mM. This indicates that at 2.0 V not only is Am(V) oxidized to Am(VI), but, Am(III) is also oxidized to Am(VI) before significantly diffusing from the electrode surface.

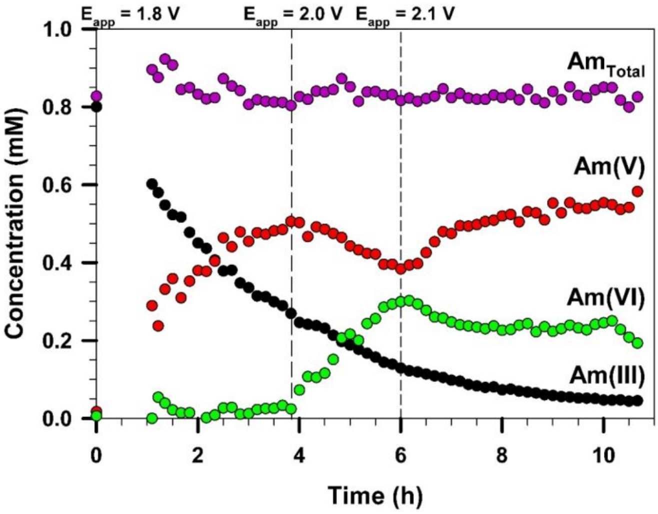

Figure 3. Am speciation derived from UV-visible spectroscopy during controlled potential electrolysis with a *nano*ITO|dpp electrode. Applied potentials are labelled in V vs. SCE.

At potentials above 2.0 V, the rate of disappearance of Am(III) is unchanged, however, Am(V) increases in concentration, concurrent with a decrease in Am(VI) concentration. This suggests Am(III) is being oxidized to Am(V) and Am(VI). However, unwanted electrochemical reactions are now more significant, and are producing reducing agents which act on Am(VI). One possible unwanted reaction at the electrode surface is the 2-electron oxidation of water to form hydrogen peroxide ($E_{1/2}$ = 1.8 V vs. SCE).[17] The overpotential associated with this reaction is likely large, and therefore requires > 2.0 V to become significant. Additional studies are currently underway to quantify these side reactions. A cyclic voltammogram of the Am solution after bulk electrolysis was acquired with a glassy carbon working electrode. There is a single ill-defined quasi-reversible redox couple centred at 1.61 V vs. SCE ascribed to the one-electron Am(VI/V) couple (Figure S9).

Comparison of the reactivity of the *nano*ITO|dpp to a *nano*ITO|terpy electrode (where terpy is 4′-phosphonyl-(4-phenyl)-2,2′:6′,2″-terpyridine) shows some similarities and differences.[11] Both electrodes are able to effect the electrochemical oxidation of Am(III) to yield a mixture of Am(V) and Am(VI), however, the product ratios as a function of applied potential are different. The *nano*ITO|dpp electrode presented here also selectively produces Am(V) at 1.8 V vs. SCE. At the same potential, this selectivity is not observed with *nano*ITO|terpy electrodes. Additionally, there is a narrow potential range where Am(VI) is generated with our *nano*ITO|dpp electrodes, which is not reported for the *nano*ITO|terpy electrodes. This is explained by the slightly faster electron transfer kinetics associated with the *nano*ITO|dpp electrodes compared to those of *nano*ITO|terpy. This qualitative statement is partially made based on the appearance of a well-defined Am(IV/III) couple (Figure 2), not observed with *nano*ITO|terpy. As the applied potential is increased, the driving-force for a redox event is increased according to the Nernst equation. This is true however not only for desired reactions (Am oxidation), but, also for unwanted reactions, including the 2-electron oxidation of water to hydrogen peroxide (which is energetically favourable at an applied potential greater than 1.8 V vs. SCE).

$$2H_2O \rightarrow H_2O_2 + 4H^+ + 2e^- \ (E_{1/2} = 1.78\ \text{V}) \qquad (6)$$

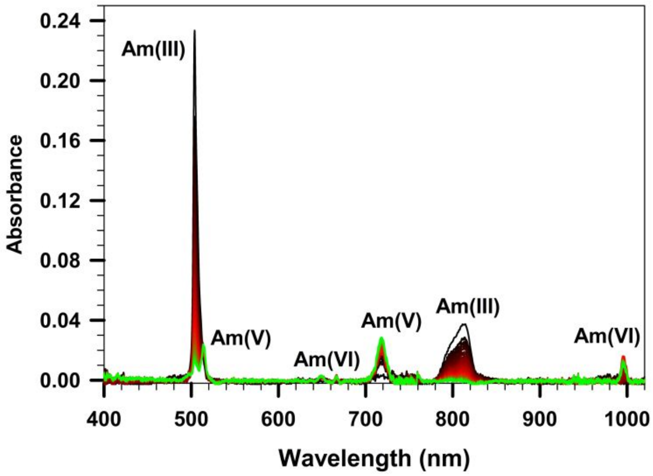

Figure 4. UV-vis spectra of initially 0.81 mM Am(III) in 0.1 M nitric acid over 11.5 h during bulk electrolysis using a *nano*ITO|dpp electrode at potentials between 1.8 and 2.1 V vs. SCE. Changes with time are highlighted by a change in spectra colour from black to red (0 to 5.7 h), and finally red to green (5.7 to 11.5 h).

At applied potentials above 2.0 V, electrochemical hydrogen peroxide generation appears to become significant, and is the likely culprit associated with the reduction of Am(VI) to Am(V) (Figure 3). With a *nano*ITO|terpy electrode, Am(VI) is generated at an applied potential upwards of 2.25 V vs. SCE in lower molar ratios, suggesting that even at potentials exceeding 2.2 V, the generation of hydrogen peroxide is not as significant. The oxidation of Am(V) to Am(VI) and oxidation of water to hydrogen peroxide at similar potentials therefore compete with one another. Ultimately, these competing reactions limit the utility of *nano*ITO|dpp electrodes, and mean the quantitative generation of Am(VI) will require precise control of the applied potential to disfavour hydrogen peroxide formation over Am(VI) generation from Am(III) and Am(V).

Conclusions

The low-potential electrochemical generation of $Am^{V}O_2^{+}$ and $Am^{VI}O_2^{2+}$ from Am(III) using a *nano*ITO|dpp LME is demonstrated. An Am(IV/III) redox couple at 1.60 V vs. SCE is observed in a 0.1 M nitric acid solution with 0.81 mM Am(III).

The 0.81 mM solution of Am(III) in 0.1 M HNO_3 is converted into 0.39 mM Am(V) (48 %), and 0.31 mM Am(VI) (38 %) after 6 h of electrolysis at 2.0 V. Increasing the applied potential above 2.0 V increases the rate of electrochemical oxidation of Am(III) and Am(V) to Am(VI), but also increases the rate of hydrogen peroxide generation which reacts with Am(VI) decreasing its mole fraction. It is therefore not enough to simply consider how to facilitate Am binding and oxidation when developing a LME for Am oxidation, but also to be cognizant, and design a LME that inhibits unwanted reactions that may poison the solution. The results in this work facilitate the development of a LME platform for this purpose, ultimately to develop an efficient LME to generate only Am(VI). As Am(VI), Am has the potential to be separated in a single step along with other hexavalent actinyl cations. Efforts must continually be made to increase the rate of wanted oxidation reactions (Am oxidation), and increase the overpotential for unwanted reactions such as the oxidation of water to hydrogen peroxide and the electrochemical deactivation of radiolytically produced reducing agents such as nitrous acid, both of which retard the generation of Am(VI).

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Conflicts of interest

There are no conflicts to declare.

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