Electrochemical oxidation of americium and its role in nuclear waste processing

Nuclear energy is a promising source of renewable energy, however, to facilitate its adoption and avoid nuclear proliferation, solutions to the handling, reprocessing, and disposal of nuclear waste must be addressed. In the United States, commercial reactors currently store their waste on site. It contains lanthanide and actinide elements, some of which are fissile and can be re-used in a reactor, while others are not. Americium accounts for the majority of the heat generated from the waste, and is severely radiotoxic. Allowing it to remain in a waste stream severely limits disposal options.

It is very difficult to selectively separate americium from the other minor actinides in the waste and from the lanthanides. They are similar in size, and exist in the same +3 oxidation state in the acidic solutions used for nuclear fuel dissolution and processing.

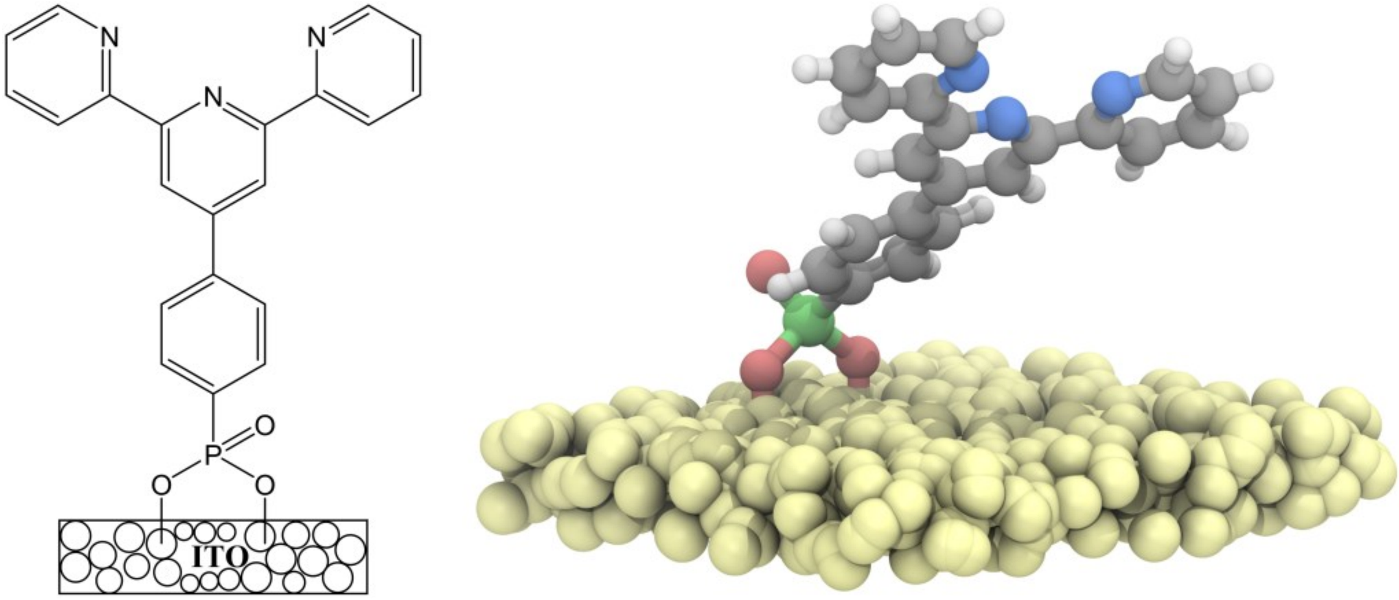

Fig. 1. Molecular structure of the terpyridine ligand on the surface of an tin-doped indium oxide (ITO) nanoparticle electrode.

In one avenue of research for separating americium, chemicals and materials are being investigated which take advantage of very small differences in properties to selectively remove americium. Understandably though, given the small differences, selectivity is difficult to achieve. An alternative is to take advantage of the oxidation chemistry of americium in acidic solutions, which is essentially non-existent for the other major elements present. When oxidized to Am(V) or Am(VI) from Am(III), it forms a di-oxo complex – either $[AmO_2]^+$, or $[AmO_2]^{2+}$. This change in oxidation state and structure dramatically alters its properties, making it different from the remaining elements in the waste stream, facilitating selective separation. The difficultly with this approach is in carrying out this oxidation without complicating the subsequent waste processing steps. The one-electron oxidation of Am(III) to Am(IV) is difficult, requiring a very high potential, more than twice that required for the oxidation of water to oxygen in 1-molar acid.. Potentials for the subsequent oxidations of Am(IV) to Am(V) and Am(VI) are less difficult.

Strategies exist to oxidize Am(III) to Am(VI) by using strong chemical oxidants. However, using them creates downfield waste processing complications. Electrochemistry is a promising cleaner method to oxidize Am(III). This method has been investigated in the past with varying degrees of success. These earlier approaches used highly concentrated acid solutions, or the addition of molecules which stabilize Am(IV), making it easier to generate. However, these earlier procedures also suffered from complications either from the additives, or, were not feasible for mass reprocessing.

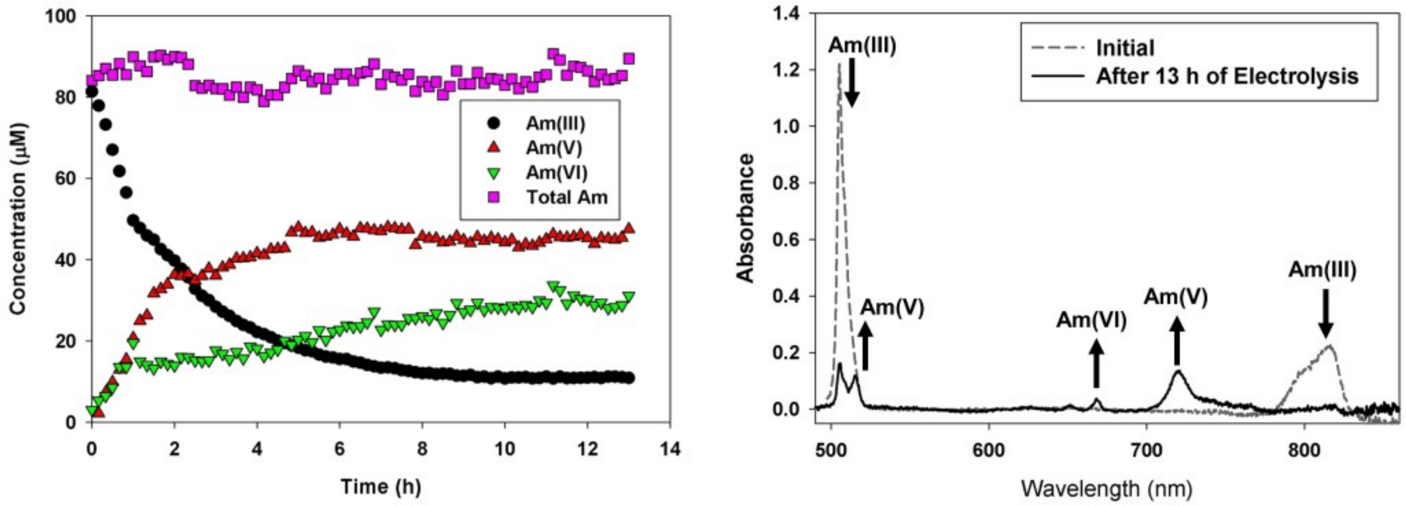

Fig. 2. Electrochemical oxidation of 84 uM Am(III) in 0.1 M nitric acid with 0.9 M sodium nitrate using a terpyridine–derivatized ITO electrode at an applied potential of 2.25 V versus SCE. (Left) Am speciation as measured by visible spectroscopy in a 50-cm waveguide. (Right) Visible spectra of species before controlled potential electrolysis and after 13 hours of electrolysis with highlighted speciation changes.

Recently, Dares et al. reported the use of a terpyridine derivatized oxide electrode capable of oxidizing americium in nitric acid solutions without the addition of chemicals to the waste stream (Fig. 1). In their approach, they use a conductive metal oxide electrode, and coated with a molecule that is able to bind Am(III), and release it upon oxidation to Am(VI) (Fig. 2). This compound is a terpyridine ligand which is known to bind to a variety of metals, including americium. In the present study, the authors took advantage of the solution-surface equilibrium for americium binding and oxidation, without relying on selective oxidation. Dares et al. also point out that at the voltages required to initiate americium oxidation, water oxidation to oxygen is a competitive reaction, but, coating the electrode with the terpyridine ligand slows down this process, and, allows for selective americium oxidation.

The experiments and results that Dares and co-workers describe show that electrochemical oxidation of Am(III) to Am(VI) is possible. These results could have a major impact on nuclear fuel cycle research, and provide a platform for fundamental chemistry studies of Am(VI), which, in the past, has been greatly limited by the absence of a convenient method of generation.

Christopher J. Dares, Thomas J. Meyer
The University of North Carolina at Chapel Hill

Publication

Electrochemical oxidation of $^{2?3}$Am(III) in nitric acid by a terpyridyl-derivatized electrode.
Dares CJ, Lapides AM, Mincher BJ, Meyer TJ
Science. 2015 Nov 6