

Electrodeposition of uranium dioxide films

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(Received February 26, 2004)

Uranium dioxide films in a hydrated form are electrodeposited onto nickel plates starting with a uranyl nitrate solution in ammonium sulfate. The process is incidental to water splitting which is the dominant electrochemical pathway and as a consequence, the uranium deposition is highly dependent on experimental parameters that require close control such as the pH and concentration of the supporting electrolyte as well as current density, and the cell design.

Introduction

The need arose to deposit uranium-containing films, about one micron thick, in the course of developing a miniature, scintillation-based, in-core, self-powered flux and temperature probe for HTGRs. The uranium is required as a neutron absorber which, upon fission, releases energy that is converted into light through the intervention of an overlying layer of an appropriate phosphor. The simplest approach to deposit a uranium film appeared to be the utilization of well established techniques for the bioassay of actinides based on electrodeposition.¹ The amounts of actinides present in samples of those materials are very small so that invisible deposits are produced which allow for high resolution alpha spectrometric analysis. The electrodeposition of actinides has been conducted in either alkaline or acid media but the latter has been developed and employed longest after finding a set of reliable conditions² that involve the use of ammonium sulfate as electrolyte in a simple electrochemical cell with a detachable plate as the cathode. The plate is used directly for counting and alpha-spectrometry. The present study was conducted to determine whether the electrochemical procedure used for bioassay could be adapted for the deposition of larger amounts of uranium and to clarify mechanistic aspects of film formation and composition.

Experimental

Aliquots of a solution containing natural uranium as uranyl nitrate in 2M nitric acid were introduced into a single compartment electrochemical cell. The uranium was derived from a stock solution with a known uranium content provided as a natural uranium standard by the National Bureau of Standards (predecessor of NIST). The cell is a plastic tube 19 mm ID that is threaded in

one end where a metal ring retains the plate used as cathode. The other end holds a metal cap through which the anode, a platinum wire, is introduced and ends in a loop a few millimeters from the cathode. Initial tests were conducted in an electrolyte 0.2M (NH₄)₂SO₄ adjusted to pH 2.2. The cell was connected to a model 173, Princeton Applied Research (PAR), potentiostat/galvanostat and Model 175, PAR, programmer. Uranium content of the films was established by radiochemical means; the plates were counted in a TC256, Tennelec, alpha spectrometer and weighed in a microbalance, when appropriate. A film was subjected to photo electron analysis (XPS) in a PHI ESCA 5600 spectrometer using Al K α radiation to establish the oxidation state of the uranium. Additional tests were conducted on a few samples by means of Raman spectroscopy in an effort to identify the oxidation state of the uranium. The Raman spectra were collected with a Dilor XY800 Raman microprobe and a Coherent Innova 308C argon ion laser operating at 100 mW to excite the sample.

Results

A few exploratory tests quickly demonstrated that the deposition of uranium by electrochemical means as described in Reference 2 is electrochemically inefficient although quite effective if conducted within certain critical experimental bounds. A distinction should be made between deposition efficiency and current efficiency; the former refers to the proportion of the initial amount of uranium introduced that is deposited on the cathode while the latter refers to the proportion of the current that is utilized in uranium deposition. Use of current is inefficient for uranium deposition because a considerable proportion is passed in the course of a run and all but a miniscule fraction goes into splitting water. A series of exploratory experiments were conducted initially to establish the main parameters that have a

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marked effect on the deposition efficiency. It became clear that the cell design and cathode material are very important. Poor uranium recoveries were observed when the cathode material was zirconium, that is probably related to poor film adherence. It is much better with plain steel disks, which are commonly used in the routine bioassay or with nickel which is acceptable because of its thermal and mechanical properties for the purposes of this project. Nickel will activate in the neutron environment of a reactor but its contribution would be much lower than that of the uranium film that it is holding.

The state of the nickel surface was found to affect the deposition efficiency. A highly polished surface promotes uranium deposition while a surface with scratches gives poor recoveries, presumably because it favors the water splitting pathway by providing nucleation sites for gas evolution.

The cell design was found to be important, initially the cathode was held at the bottom of the cell with an "O" ring and a clamp. The tube, close to the end, had a slight constriction, and evidently interfered with the fluid and gas flow so that the deposition was worse than that using a tube with a straight bore. That straight Lucite tube has an outside thread used to fasten a retaining metallic cap that holds the cathode plate. In this set-up the cathode plate is the only metal in contact with the electrolyte.

Other exploratory experiments demonstrated that subtle differences in pH or electrolyte concentration had a marked effect in the efficiency of the uranium deposition. This is illustrated in Fig. 1 which shows uranium deposition as a function of pH and electrolyte concentration. The pH window for efficient deposition is relatively narrow and seems to be most efficient at values close to pH 2.5. Most detrimental, apparently because of film dissolution, are the lower pH values. The deposition efficiency is affected by the electrolyte concentration through what appears a complex set of conditions. It appears that at lower electrolyte concentrations and hence higher resistivity in the medium, the electrolysis takes place at relatively higher temperatures while higher electrolyte concentrations improve conductivity and thus favor the water splitting pathway. The current density is also involved in these interrelated parameters and is maintained at about 0.6 A/cm². The effect of cell resistivity on uranium recovery is illustrated in Fig. 2. The same effect is evident also in Fig. 1, which shows a decrease in efficiency as the electrolyte molarity increases. It is interesting to note that the middle pH value is more tolerant of the increased electrolyte concentration. TALVITIE² also noted an improvement on plutonium deposition as the temperature of the electrolyte increased.

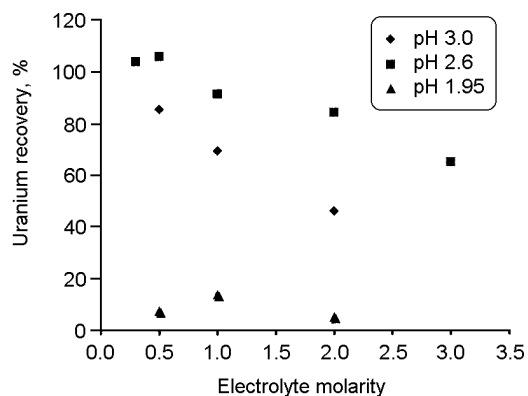


Fig. 1. Uranium deposition as a function of pH and electrolyte concentration

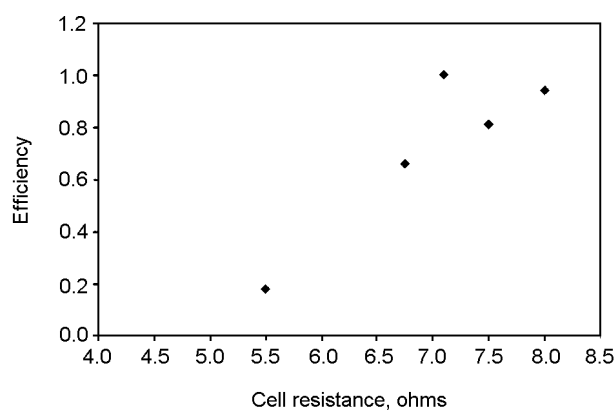


Fig. 2. Uranium deposition as a function of cell resistance. Data obtained through variation of current density/applied voltage and electrolyte concentration

A film deposited with 100% efficiency as established by counting, was shown to contain 71 wt.% uranium as found from weighing the cathode in a microbalance. This film was examined by XPS and found to be pure UO₂. The oxidation state of the uranium is based on the stoichiometry as derived from the integration of the signals and the appropriate sensitivity factors. The oxidation state of the uranium is also based on the binding energies for both uranium and oxygen although there was a small discrepancy on the binding energy for the uranium signal for U4f_{7/2} at 380.5 eV which is reported³ at 380.1. The film was definitely black which also agrees with the assignment. The discrepancy between the uranium content observed and the theoretical of 88.1 wt.% for UO₂ can be explained as due to moisture loss in the high vacuum environment of the spectrometer. TALVITIE² described the electrochemical deposits as hydrated oxides which supports the observations in the current study. Weighing of other films showed variable uranium contents that were about 50 wt.% in some cases. These observations

are reasonable in view of the “wet” route used to obtain these materials in contrast with sputtered films or those formed by direct oxidation of the pure metal. Another interesting aspect of the XPS analysis is that no elements other than uranium and oxygen were detected, (carbon is ubiquitous but the signal is eliminated with sputtering prior to analysis). There was no nitrogen or sulfur which could be retained as residues from the electrolyte but evidently once the film is formed and rinsed with a small amount of water no electrolyte is retained.

An attempt was made to obtain Raman spectra of different samples generated in the course of this study. It was hoped to identify the oxidation state of the uranium as an additional confirmation of the XPS result using published spectra,⁴ however, the films proved to be too thin, giving rise to weak spectra with broad bands. One of the samples produced a relatively more intense spectrum (Fig. 3), but because of broad bands at 420 and 750 cm^{-1} it suggested the presence of U_3O_8 which apparently formed as a result of oxidation while being exposed to the argon ion laser. Those bands appear to envelop the well resolved peaks in the published data with one set at 343, 412 and 474 cm^{-1} and another at 740 and 811 cm^{-1} . Bands not reported previously were observed at 131 and 240 cm^{-1} .

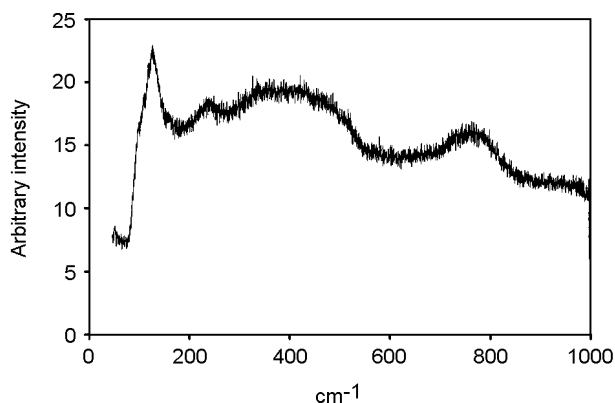


Fig. 3. Raman spectrum of uranium oxide film electrodeposited on a nickel plate

Alternate uranium electrodeposition media have been explored⁵ such as isopropyl alcohol, but deposition efficiencies are low and require multiple steps that incorporate annealing cycles between deposition runs.

Conclusions

Relatively thick, about one micron, adherent films of uranium oxide can be deposited on nickel cathode plates following procedures similar to those used in bioassay for trace amounts of actinides. Uranium electrodeposition results from the reduction of a starting uranyl salt to a hydrated form of uranium dioxide. The deposition is incidental to water splitting and as such is highly dependent on experimental parameters such as the pH and concentration of the supporting electrolyte as well as the nature of the cathode surface both in terms of the material used and its roughness.

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This work was funded by the U.S. Department of Energy through its Nuclear Energy Research Initiative. MJL sponsored by the Division of Materials Sciences and Engineering, U.S. Department of Energy, under Contract DE-AC05-00OR22725 with UT-Battelle, LLC.

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