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A short tutorial on uranium electropolishing

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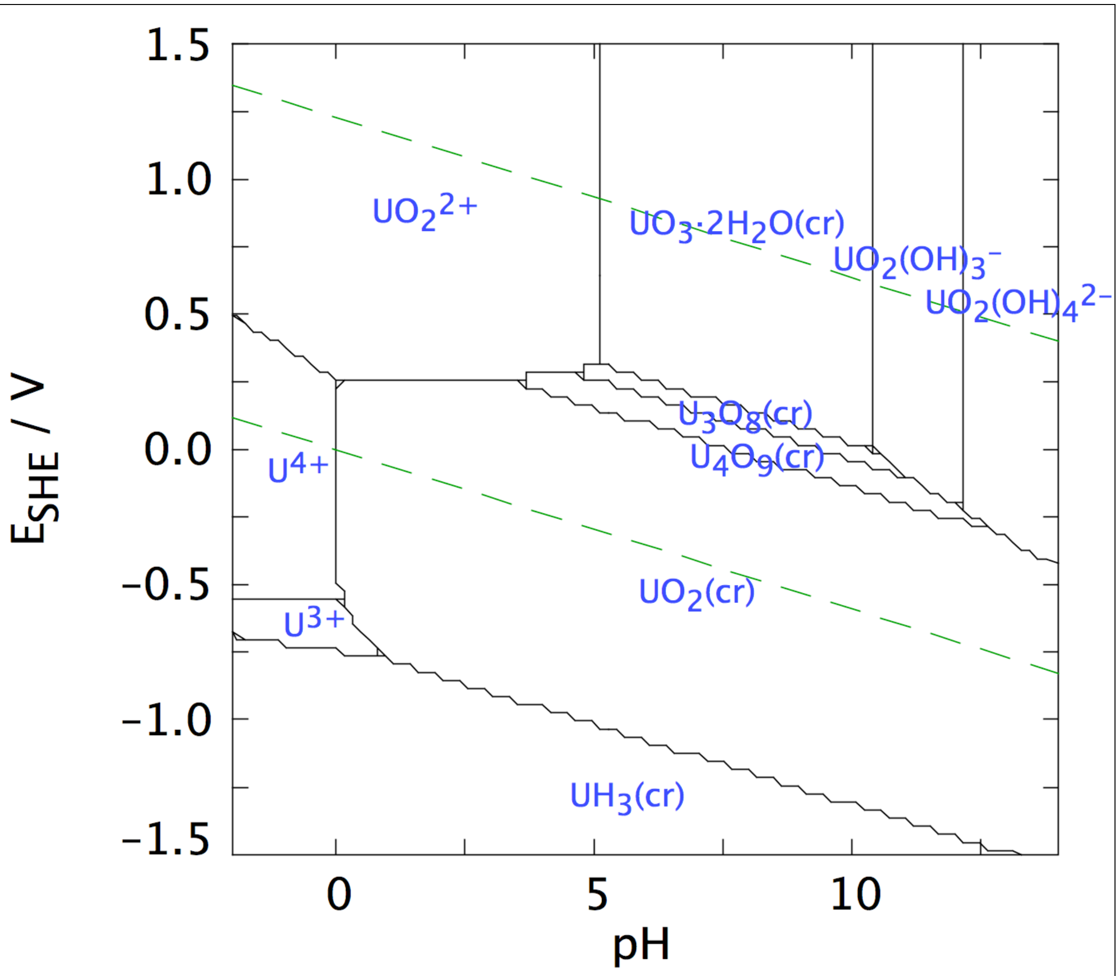
Summary

Electropolishing of uranium metal is best performed in a simple aqueous solution of phosphoric acid. With +3 to +10 volts of bias potential applied to the uranium (anode) relative to a Pt counter electrode (cathode). As summarized in a Pourbaix stability diagram, these conditions yield dissolution of the U surface as UO_X containing solution species without the possibility of injecting hydrogen into the metal surface. However, if the uranium is biased to negative potentials relative to the counter electrode then water may be reduced at the U surface and hydrogen gas becomes available for reaction with the U metal. The stability diagram may be modified if there are other complexing species present in solution and the potential scale shifted if a different metal is use for the counter electrode. These effects can be understood in a known way as long as solution and electrochemical cell conditions are recognized.

Questions answered

1. What are good parameters (chemical and electrochemical conditions) for effecting an electropolish of α-uranium metal through removal of the metal surface and resulting in a coherent passive oxide layer?
2. Under what conditions does the electropolish result in the possibility of H_2 gas formation at either the uranium surface or the counter electrode?
3. Under what conditions is there the possibility of injecting hydrogen into the near surface uranium metal during the electropolish process?
4. Can the amount of uranium metal removed in an electropolish operation be estimated or quantified?



Pourbaix diagram for U in aqueous solution (non-complexing = no other molecular solution reactions). At 25°C and $[U^{4+}]_{tot}$=10.0 μm. Dashed green lines indicate limits of water stability. At low E_H water is reduced to H_2 and at high E_H water is oxidized to O_2. Below the lower green line is the H_2 evolution region and above the upper green line water is oxidized to O_2. Water is stable between these two lines.

The figure shows a Pourbaix stability diagram for a uranium metal sample biased relative to a Pt electrode by the potential shown (E_{she} in units of volts) as a function of the pH of the aqueous solution. Regions of chemical stability are shown with the charged species existing as ionic species in solution and the species with designation (cr) existing as solids (at the surface of the U electrode).

The green dashed lines show the stability region of water. Between the lines, water is stable towards decomposition (electrolysis does not happen) to H_2 and O_2.
At potentials above the upper green line the water is oxidized by the reaction
$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+ + 4e^-$

with H+ necessary as counter ions in solution (not available to react with U) and $O_{2(g)}$ is available for surface reaction. At the counter electrode (Pt in this case) the water is reduced to form hydrogen gas. Note the large number of solvated UO_x ionic species for the positive potentials at the uranium electrode, showing exactly why this works as an electropolish etching method through solvation of U atoms.

At potentials below the bottom green line, the water is reduced by the reaction
$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-$
with H_2 now available to react with the U surface. At the counter electrode (Pt in this case) the water is oxidized to form oxygen gas. Note in fact that for larger negative potentials at the uranium electrode, the solid product UH_3 is thermodynamically favored.

Adjustments

If the solution contains high concentrations of other complexing species (such as CO_2 or carbonate for example), that might form other solution molecular species (or ions) then this Pourbaix stability diagram is modified, and can be represented in a known way.
Furthermore, if the counter electrode is not Pt (with standard hydrogen electrode conditions) then the potential scale on the ordinate of the plot is shifted by same amount up to a few volts depending upon the metal. This can also be understood and represented in a known way.

So the bottom line is

If the uranium metal sits at a positive potential (relative to a Pt counter electrode) of at least ~+0.25 V across the full range of pH, then the uranium surface is dissolved as UO_x aqueous species and a good electropolish takes place. However, if the U metal sits at a negative potential then the reduction of water may be favorable (forming H_2) and hydrogen may be dissolved into the near surface uranium metal and/or the stability of solid UH_3 may be favored.

The amount of uranium metal removed during the electropolish may be calculated by knowing the exposed area of the uranium sample, measuring the total coulombic charge passed in process (current and time).

For a pH < 5 and a U electrode potential of +10 V the following electrochemical reactions are active:
U anode
$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+ + 4e^-$
$U + O_2 \rightarrow UO_2^{2+} + 2e^-$
Pt counter electrode (cathode)
$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-$

The key reaction for the electropolish is $U + O_2 \rightarrow UO_2^{2+} + 2e^-$ $E^o=-0.45$ V for removal and solvation of U from the surface, and so 2 electrons are transferred per U atom removed from the surface. The reaction at the cathode is $2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-$

The amount of uranium removed from the sample can be related to the surface area of the sample, A, the current, I, and the time of electropolish, t. If we assume that removal is uniform across the full surface area of the sample then a uranium thickness, d, removed may be estimated:

Thickness $d = \frac{I \cdot t \cdot MW}{A \cdot \rho}$

For ^{238}U metal this is $d(nm) = 645.742 \times \frac{I \cdot t}{A}$

where

d = thickness of U metal removed in nm

I = current in amps

t = electropolish time in seconds

MW = molecular weight of 238 g/mol

ρ = density of 19.1 g/cm^3

A = sample area in cm^2

<u>In practice</u>

- For small uranium coupon samples, I prefer to use concentrated phosphoric acid (about 85% H_3PO_4) followed by a DI water cleaning. For the uranium anode I typically use +10 volts relative to a Pt counter electrode (and current limit dependent on the surface area of the sample), as this treatment gives a quick electropolish etch and leaves a thin coherent, very passive (towards further oxidation or hydriding), UO_2 oxide layer. The uranium sample is treated with some time length of current flow so that the darker pre-existing oxide is quickly removed to expose a shiny silver U metal surface which continues to be electro-dissolved into solution.

- A lower concentration H_3PO_4 solution also works. A 10% solution in water gives a pH of about 1.

- There are other solutions which are also used for U electropolishing. These include acetic acid/perchloric acid mixtures, perchloric acid/organic solvent mixtures, phosphoric acid/organic solvent mixtures, and other. (ASM Handbook, 1985, Volume 9 Metallography and Microstructures, section on Electrolytic Polishing). These tend to be problematic or hazardous to use since they contain perchloric acid (perchlorate former), organic acids, or organic solvents.