SURFACE ELECTROCHEMISTRY OF UO_2 IN DILUTE ACIDIC HYDROGEN PEROXIDE SOLUTIONS

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Introduction

A thorough understanding of corrosion and dissolution processes that spent nuclear fuel undergoes is central to its safe and effective long-term disposal. Containment using bentonite-clay-encased copper vessels in deep geological repositories, as per a current proposal in Canada, is forecast to exceed the period when nuclear radiation can produce oxidizing conditions. Nonetheless, it is prudent to assess a failure scenario in which some vessels allow groundwater to contact the fuel inside and initiate its corrosion and the dissolution of radionuclides. It is reasonable to assume the container lifetime will exceed the period of time when β/γ radiation fields persist (~300-1000 years), after which only α-radiolysis of water will affect corrosion[1].

Generally, the spent fuel system has been studied in neutral and slightly alkaline environments, consistent with the expected groundwater of the Canadian Shield. At $pH > 5$, surface oxidation results in incorporation of O^{2-} anions into octahedral holes in the UO_2 fluorite lattice[1]. This results in the generation of a U^V-containing surface layer of composition UO_{2+x} (eg. $UO_{2.25}$), which facilitates further O_2 or H_2O_2 reduction, and concurrent UO_2 oxidation, resulting in dissolution as UO_2^{2+}. However, it has been theorized that acidic conditions may prevail in localized regions within the surface of the fuel[2],[3]. Recent studies have shown that at pH values less than 3, the U^V-containing surface lattice layer observed in less acidic conditions becomes unstable and, instead, an adsorbed U^V-layer forms on the electrode surface[4],[5]. Much like the lattice layer, this adsorbed state can act as a catalyst for O_2 or H_2O_2 reduction and when coupled to UO_2 oxidation, can accelerate oxidation to U^{VI}. At low pH, the corrosion product deposit $UO_3 \cdot yH_2O$, which block dissolution in neutral solutions, becomes unstable and undergoes dissolution as the uranyl cation, UO_2^{2+} [2]. The exact conditions that favour the formation and stabilization of this adsorbed U^V layer and its stoichiometric chemical composition are still unknown[4].

Experimental

Electrochemical materials and preparation

Electrodes were prepared from SIMFUEL pellets fabricated by Atomic Energy of Canada Limited (Chalk River, Ontario, Canada). SIMFUEL is an unirradiated analogue of spent nuclear fuel, produced by doping UO_2 with stable elements (Ba, Ce, La, Mo, Sr, Y, Rh, Pd, Ru, Nd, Zr) in the proportions required to simulate fuels from in-reactor conditions. Electrodes approximately 2 mm thick and 1.2 cm in diameter were cut from pellets using a published procedure[5]. Electrodes were polished on wet 1200 SiC paper and rinsed with Millipore water ($\rho = 18.2 M\ \Omega \cdot cm$) before experimentation.

A standard three-electrode, three-compartment cell was used. All experiments used a saturated calomel reference electrode (SCE) and the counter electrode was a 5 cm^2 Pt sheet spot-welded to a Pt wire. A Solartron model 1287 potentiostat was used to control applied potentials and to record current responses. Corrware™ software (supplied by Scribner Associates) was used to control the instruments and to analyze the data. Air-formed oxides were reduced through application of the cathodic minimum potential for the experiment, which was either -1.6 V or -1.2 V vs. SCE, for up to 10 min at the beginning of each experiment. Solutions were prepared with Millipore water and deaerated with Ultra Pure grade argon prior to, and during, all experiments. Electrolytes were prepared with NaCl, and the pH was adjusted using HCl. Hydrogen peroxide (3%, w/v, supplied by Fisher Scientific) was added to the cell immediately prior to electrochemical experiments. The H_2O_2 concentration in the cell was determined by UV/Vis spectrophotometric techniques.

Scanning Electron Microscopy

Images were obtained using a Hitachi S-4500 Field emission scanning electron microscope. During image collection, electron beam potential was maintained at 10.0 kV and working distance was 10 mm.

Results and Discussion

Figure 1 shows a cyclic voltammogram recorded at a scan rate of 10 mV s^{-1}, and illustrates the reduction of hydrogen peroxide on the two surface layers. At this pH (2.6) H_2O_2 is being reduced on a UO_{2+x} surface layer between -1.2 and -0.7 V (SCE), and on an adsorbed U^V surface layer between -0.4 and -0.2 V.

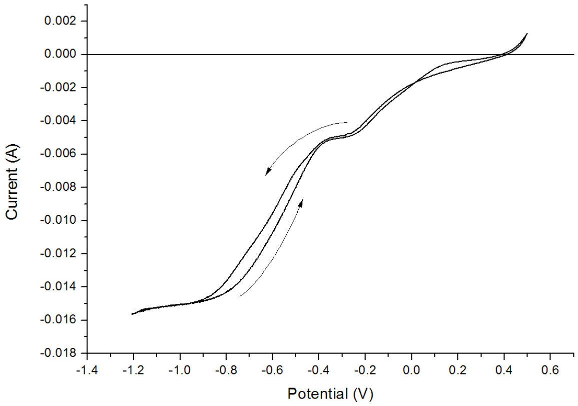


Figure 1 – Cyclic voltammogram recorded on 1.5 at.% SIMFUEL at 10 mV s^{-1} and an electrode rotation rate of 16.7 Hz in 0.1 mol/L NaCl (pH=2.6) containing 5 x 10^{-3} mol/L H_2O_2. The arrows indicate the scan direction.

This data is evidence that H_2O_2 reduction is sustained on both surfaces under some conditions. For comparison, a series of voltammetric scans performed over the pH range 3.0 to 1.0, **Figure 2** shows that H_2O_2 reduction on UO_{2+x} disappears for pH < 2.2. (The unrelated increase in current at highly negative potentials, as the pH is decreased, is attributed to H^+ reduction on the noble metal particles in the SIMFUEL electrode).

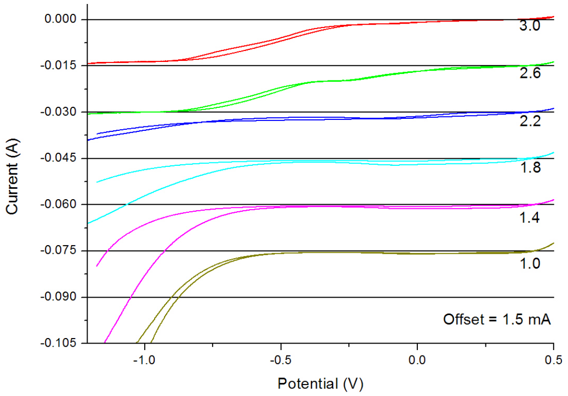
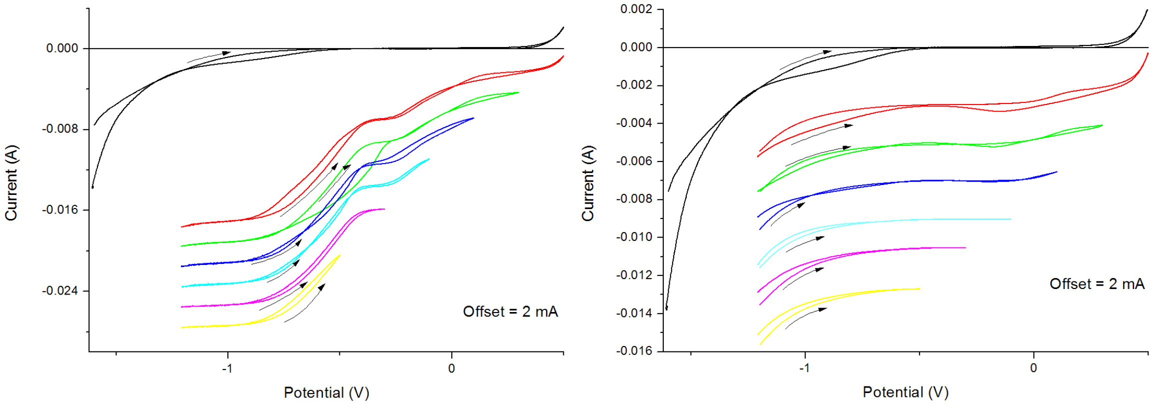


Figure 2 – Cyclic voltammogram recorded on 1.5 at.% SIMFUEL at 10 mV s^{-1} and an electrode rotation rate of 16.7 Hz in 0.1 mol/L NaCl containing 5 x 10^{-3} mol/L H_2O_2. The numbers below the curves show the pH for each scan.

These results confirm that the mechanism by which H_2O_2 reduction occurs is pH dependent. This is consistent with the published claim that the UO_{2+x} lattice surface layer is stabilized by hydroxide and suggests that an adsorbed oxidation layer is only stable under more acidic conditions. Based on thermodynamic information, the UO_{2+x} layer would be expected to disappear for pH ≤ 5.0[4],[6]. However, since H_2O_2 reduction produces OH^- ions at the fuel surface, it is possible that the pH varies from the set value for the bulk solution.

One possible method to mitigate localization of pH is to decrease the H_2O_2 concentration; thereby, decreasing the rate and extent of OH^- formation at the fuel surface. **Figure 3** (a-b) shows the effect of decreasing the H_2O_2 concentration at constant pH and electrode rotation rate. At higher concentrations (a) both peroxide reduction pathways can be sustained at this pH value, whereas at lower concentrations (b) reduction occurs only on the adsorbed layer.

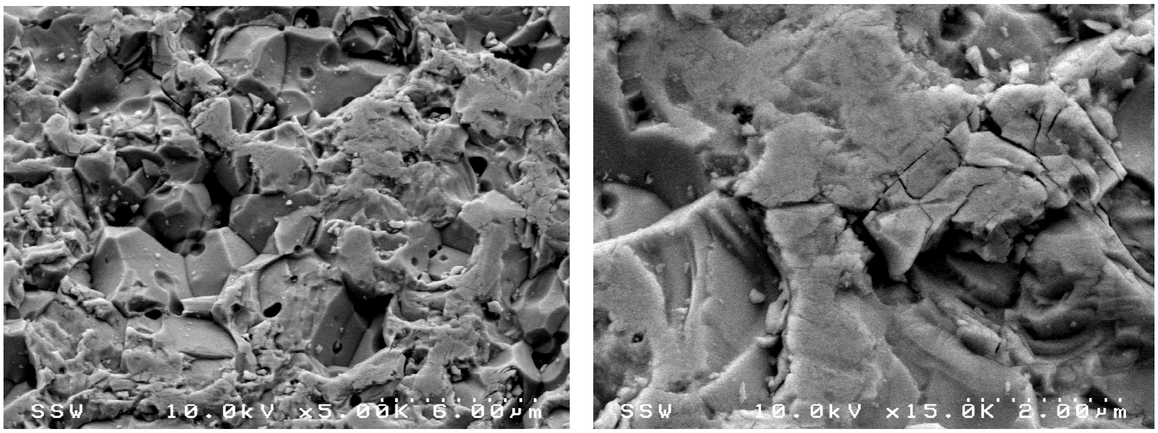


(a) (b)

Figure 3 – Cyclic voltammograms recorded on 1.5 at.% SIMFUEL at 10 mV s^{-1} and an electrode rotation rate of 16.7 Hz in 0.1 mol/L NaCl (pH=2.6). The arrows indicate the scan direction. (a) $[H_2O_2] = 5 \times 10^{-3}$ mol/L; (b) $[H_2O_2] = 1.5 \times 10^{-3}$ mol/L.

These results are consistent with the supposition that at high H_2O_2 concentrations the surface pH is significantly higher than the bulk solution and able to stabilize a UO_{2+x} surface lattice layer. Decreasing the concentration allows more effective buffering at the electrode surface which destabilizes the UO_{2+x} layer and stabilizes the adsorbed layer. Thus, only one reduction mechanism is observed in the cyclic voltammograms.

To understand how this pH variance might be localized at the fuel surface, scanning electron microscopy (SEM) was used to observe the microstructure of the surface. **Figure 4** (a-b) shows the rough, irregular surface structure of the polished electrode.



(a) (b)

Figure 4 – SEM images of 1.5 at.% SIMFUEL. Images were collected using a 10.0 kV electron beam and a working distance of 10 mm. Magnification and scale is indicated on the images.

The rough surface houses numerous cavities, pores, and locations of missing UO_2 grains, in which pH localization could readily occur. The depths of these cavities create mass-transfer conditions which are essentially independent of electrode rotation rate, and thus, diffusion control cannot be established within them. This prevents hydroxide removal from the electrode surface allowing stabilization of the UO_{2+x} layer at lower bulk pH values than would be expected.

Conclusions

It has been shown that in acidic solutions with pH < 2.6, hydrogen peroxide reduction catalyzed by an adsorbed U^V containing layer is the dominant reaction pathway, while at higher pH values (pH > 2.6), reduction catalyzed on a UO_{2+x} surface lattice layer dominates. At pH 2.6 with high hydrogen peroxide concentrations, reduction on both surfaces is sustainable. However, if hydrogen peroxide concentration is decreased, reduction on an adsorbed layer becomes the dominant pathway. Lowering hydrogen peroxide concentration increases the buffer capacity of the solution and prevents pH localization at the electrode surface. The resultant destabilization of the

UO_{2+x} surface lattice layer suppresses hydrogen peroxide reduction on such a surface layer.

Acknowledgements

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