ELECTROCHEMICAL AND SURFACE ANALYSIS OF HYDROGEN EFFECTS ON URANIUM DIOXIDE

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ABSTRACT

Electrochemical and X-ray photoelectron spectroscopic (XPS) techniques were used to investigate the effect of hydrogen on the aqueous corrosion of SIMFUEL (UO_2) electrodes with different degrees of simulated burn-up under nuclear waste disposal conditions. Corrosion potential measurements (E_{CORR}) showed that as fuel burn-up increased, E_{CORR} in 5% H_2/95% Ar decreased. XPS, performed after E_{CORR} measurements, showed the surface film composition as a function of the purge gas used (Ar or 5% H_2/95% Ar). The uranium ($4f_{7/2}$) peak was resolved into contributions from U^{IV}, U^{V}, and U^{VI}. When purged with H_2, the film composition is mainly U^{IV}, meaning very little oxidation to U^{V} and/or U^{VI} has occurred. This suppression of oxidation can be attributed to the presence of ε-particles in the SIMFUEL since experiments on SIMFUEL samples with no ε-particles showed a lower percentage of U^{IV} and higher percentages of U^{V} and U^{VI}, due to more extensive surface oxidation. Consistent with this observation, E_{CORR} on the SIMFUEL containing no ε-particles was 150 mV more positive than values recorded on the SIMFUEL with ε-particles.

INTRODUCTION

The disposal of spent nuclear fuel is being proposed as a possible scenario for the management of high-level nuclear waste. The wasteform would be placed in canisters made of an outer layer of copper, and an inner layer of carbon-steel. The canisters would be buried 500 – 1000 m deep in the granitic rock of the Canadian Shield [1]. Each container will then be surrounded by compacted bentonite clay and crushed rock. In the unlikely case of container failure, water will come in contact with both the carbon steel inner liner and spent fuel. Since environmental oxidants will be rapidly consumed by waste container corrosion and mineral / biochemical oxidation processes [2], they will not exert any significant influence on fuel corrosion. By contrast, radiolytic oxidants will be produced directly in the environment immediately adjacent to the wetted fuel surface. It is sensible to analyze the effects of container failure, to better understand the possible consequences. A reasonable assumption is that the fuel will not be wetted while γ / β radiation fields are insignificant (i.e. the container will last a minimum of 1000 years) and that, consequently, only the effects of α-radiolysis need be considered.

The expected behaviour of a UO_2 surface as a function of surface redox condition (expressed as a corrosion potential, E_{CORR}) is summarized in Figure 1. The onset of observable oxidation occurs around -400 mV (vs SCE), the lowest potential for which an increase in U^{V} content of the fuel surface can be observed by XPS [3]. Over the potential range -400 mV to ~ 0 mV, the ratio of U^{V} / U^{IV} in the fuel surface increases due to the formation of a thin surface oxide layer, UO_{2+x} (2 – 8 nm). The region marked A in Figure 1 indicates the range of fuel E_{CORR} values predicted by a mixed potential model [4] from first contact with groundwater (neglecting any influence of β / γ radiolysis effects). Initial conditions will be more oxidizing, i.e., ~ + 50 mV, since there will be more radiolytic oxidants present, but will eventually achieve more reducing conditions, ~ -250 mV, as the available oxidants are consumed. A comparison to the threshold for oxidation / dissolution (corrosion) indicates that the surface redox condition of the fuel is predicted to always be in the range where corrosion is feasible. However, this prediction does not include consideration of the possible influence of hydrogen.

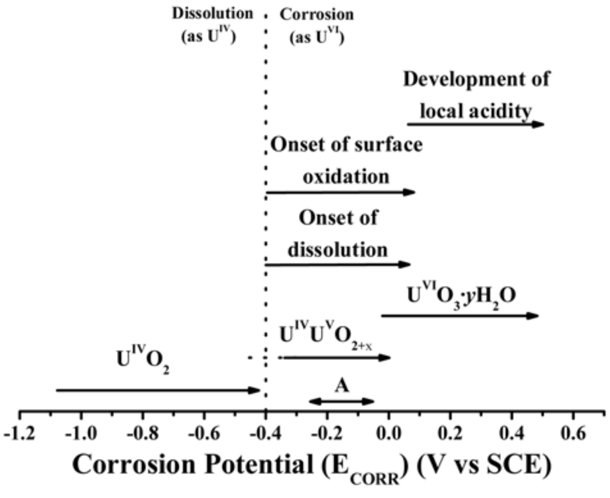


Figure 1: Composition and corrosion behaviour of UO_2 as a function of the UO_2 corrosion potential.

Using 1.5 at. % SIMFUEL, previous results [5] showed that E_{CORR} decreased to ~ -700 mV at a H_2 pressure of 0.01 MPA. At atmospheric pressures, E_{CORR} was ~ – 300 mV. This potential is more reducing than the anoxic conditions expected in the disposal vault, but still slightly positive of the oxidation / dissolution threshold of – 400 mV. E_{CORR} measured on 1.5 % SIMFUEL with no ε-particles in the presence of 5% H_2/95% Ar was ~ 150 mV more positive than on 1.5 % SIMFUEL with ε-particles. This value was almost identical to that achieved under anoxic conditions. It was concluded that hydrogen oxidation was catalyzed on the ε-particles present, and that galvanic coupling between these ε-particles and the UO_2 matrix resulted in a decrease in E_{CORR}.

This paper further studies the effects of hydrogen on SIMFUEL electrodes, with emphises on determining surface oxidation states on different SIMFUEL electrodes in a 5% H_2/95% Ar purged solution.

EXPERIMENTAL

Experiments were performed on SIMFUEL electrodes cut from pellets fabricated by Atomic Energy of Canada Limited (Chalk River, Ontario, Canada). SIMFUEL is an unirradiated analogue of used nuclear fuel, produced by doping natural UO_2 with a series of stable elements (Ba, Ce, La, Mo, Sr, Y, Rh, Pd, Ru, Nd, Zr) in proportions appropriate to replicate the chemical effects of CANDU reactor irradiation to various burn-ups [6, 7]. As a consequence of doping, holes are injected into the 5f band, due to the substitution of trivalent rare-earth species for U^{IV} in the UO_2 fluorite lattice, which leads to an increase in electrical conductivity. The noble, and other, metal elements (Mo, Ru, Rh, Pd), insoluble in the oxide lattice, congregate in metallic ε-particles. This phase consists of small, spherical precipitates (0.5 – 1.5 μm diameter) uniformly distributed in the UO_2 matrix [6]. The SIMFUEL used in these studies mimics UO_2 fuel irradiated to either 1.5, 3, or 6 at. % burn-up. As well, a SIMFUEL sample doped to 3.0 at. %, but containing no ε-particles was used.

Experiments were conducted using a three-electrode, three-compartment electrochemical cell. The reference electrode was a commercial saturated calomel electrode (SCE), with a reference potential of 216 mV (vs. SHE) at 60°C, while the counter electrode was a platinum foil with a surface area of 13 cm^2, spot-welded to a platinum wire.

Prior to the start of each experiment, the electrode was polished with 220 grit, and then 1200 grit SiC paper, and rinsed with deaerated water. All solutions were prepared with distilled deionized water (resistivity, $\rho = 18.2\ M\Omega\cdot cm$) purified by using a Millipore milli-Q-plus unit to remove organic and inorganic impurities, and subsequently passed through milli-Q-plus ion exchange columns. All experiments were performed at 60°C in 0.1 $mol\cdot L^{-1}$ KCl solution adjusted to pH 9.5, saturated with Ar or 5% H_2 / 95% Ar gas.

Within the glass cell, E_{CORR} measurements were recorded for various lengths of time, but generally until a steady-state value was achieved. XPS was performed on electrochemically oxidized specimens and after E_{CORR} measurements to determine the surface film composition as a function of electrode potential and purge gas (Ar, O_2 or Ar/H_2). An SSX-100 spectrometer was used to record all XPS spectra. Spectra were excited using AlK_{α}-radiation to bombard the surface with high energy monochromatic x-rays ($h\nu$ = 1486.6 eV). The position of the C (1s) line at 285.0 eV was recorded and used to correct for surface charging. The U ($4f_{7/2}$), satellites associated with this region, and the valence band regions of the UO_2 spectra were recorded. The uranium ($4f_{7/2}$) peak was resolved into contributions from U^{IV}, U^{V}, and U^{VI}. A more detailed description of the XPS procedures can be found in the literature [3].

RESULTS AND DISSCUSSION

Figure 2 shows E_{CORR} measurements on 1.5 at. %, 3.0 at. %, 6.0 at % SIMFUEL with ε-particles, and on 3.0 at. % SIMFUEL with no ε-particles in solutions purged with 5% H_2/95 % Ar. Obvious in this figure is a decrease in E_{CORR} with increased burn-up. This was expected since the number of ε-particles available to catalyze the H_2 oxidation / reduction reaction increases with degree of simulated burn-up. The final E_{CORR} for 6 at. % SIMFUEL was – 402 mV, which is on the threshold of measurable oxidation / dissolution of UO_2. This indicated that a galvanic coupling between the rare-earth doped UO_2 matrix and the ε-particles can suppress E_{CORR} sufficiently to prevent measurable oxidation/dissolution. On 3.0 at. % SIMFUEL with no ε-particles, E_{CORR} leveled off to a value of –165 mV, 235 mV more positive than the 6 at. % sample, and 140 mV more positive than the 1.5 at. % SIMFUEL. At 60°C and atmospheric pressure, a soluble concentration of 10^{-5} mol·L^{-1} H_2 would be present in solution. In solutions purged with argon, little difference in the E_{CORR} values was observed.

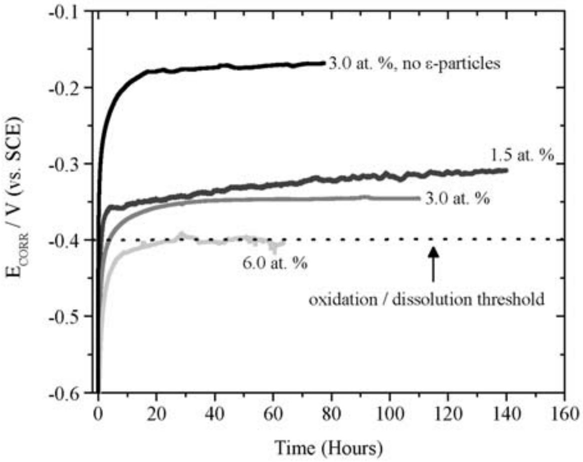


Figure 2: E_{CORR} measurements on 3.0 at. % SIMFUEL with no ε-particles, 1.5 at. %, 3.0 at. %, and 6.0 at. % SIMFUEL with ε-particles in solutions purged with 5% H_2/ 95% Ar at 60C.

E_{CORR} experiments were followed by XPS analyses to determine the surface composition. These results were compared to a calibration plot constructed by performing one-hour potentiostatic experiments at various potentials, followed by XPS. These electrochemical experiments show the evolution of surface composition as the oxidation potential is increased. At low potentials (-300 mV to -500 mV), the surface composition is predominantly U^{IV}, with small amounts of U^{V} and U^{VI}. This composition is almost identical to the composition at –1.2 V, where a fully reduced surface is expected. The U^{V} content of the surface can be attributed to the U^{V} present in the rare earth doped SIMFUEL matrix, while the U^{VI} signal is most likely due to surface oxidation in the time needed to transfer the electrode from the glass cell to the spectrometer. At 0 mV, all three oxidation states of uranium are seen, with U^{IV} being the lowest percentage. Further oxidation increases the U^{V}/U^{VI} content of the surface. For potentials greater than +250 mV, the decrease in U^{VI} and increase in U^{IV} has been attributed to the acidification of pores on the surface resulting in the dissolution of U^{VI} [3].

Figure 3 shows XPS data for E_{CORR} experiments performed on 1.5 at. % SIMFUEL with ε-particles. The lines show the surface composition determined electrochemically. The data for the experiment performed in 5% H_2/95% Ar fits the calibration curve very well. The surface is predominately U^{IV}, with little U^{V} and U^{VI}. In the Ar experiment, a decrease in the U^{IV} and an increase in U^{V} and U^{VI} content was observed.

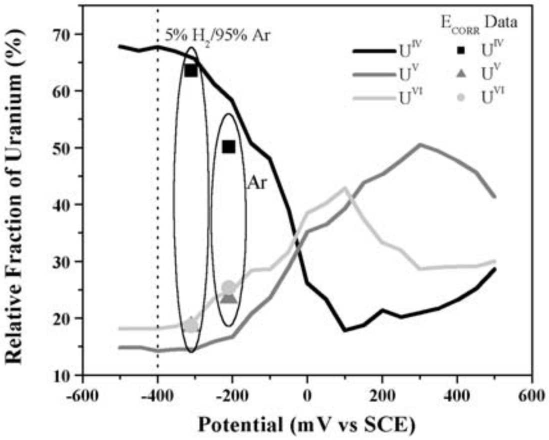
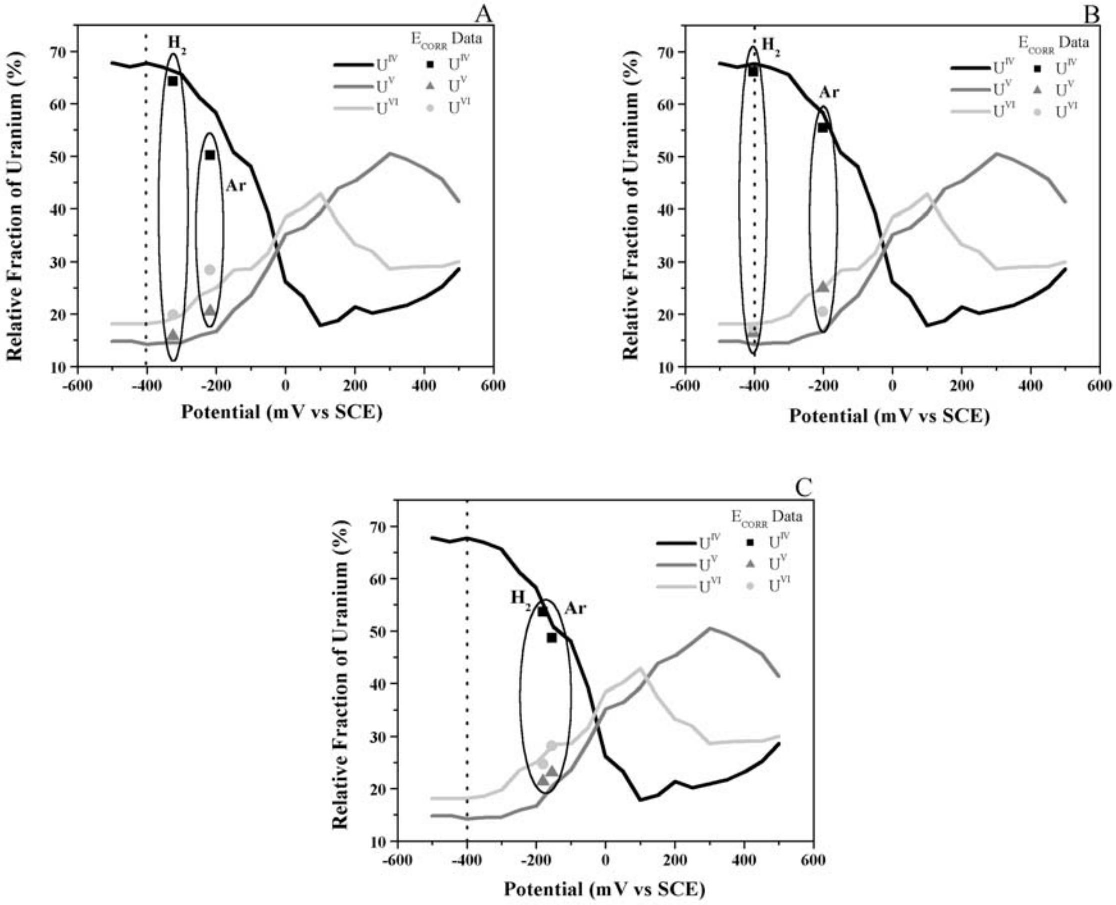


Figure 3: XPS results for 1.5 at. %. SIMFUEL with ε-particles plotted on an electrochemically determined calibration curve.

Figures 4A, B, and C show the XPS results for 3 at. % and 6 at. % SIMFUEL and for 3.0 at. % SIMFUEL without ε-particles. Fits for experiments performed in 5% H_2/95% Ar match the calibration plot well. The 6 at. % SIMFUEL sample shows the highest percentage of U^{IV} as expected for E_{CORR} at –403 mV, a value on the threshold for oxidation. For 3.0 at. % SIMFUEL without any ε-particles, the percentage of U^{IV} is significantly reduced, while the percentage of the other two uranium states has increased. The composition of the surface is very similar to that for the experiment performed in Ar.

These results demonstrate the role of ε-particles in suppressing oxidation of SIMFUEL, and show that, as the number of ε-particles is increased, E_{CORR} is restrained to the threshold for SIMFUEL oxidation. When no ε-particles are present E_{CORR} is significantly more positive, and accompanied by an increase in surface oxidation. The experiments performed in Ar all show a more extensive oxidation with E_{CORR} values all approximately the same. The observed similarities in composition are to be expected.



Figures 4A, B, and C: XPS results for (A) 3.0 at. % and (B) 6.0 at. %. SIMFUEL with ε-particles, and (C) 3.0 at. % SIMFUEL with no ε-particles on an electrochemically determined calibration curve.

SUMMARY AND CONCLUSIONS

The influence of H_2 on the corrosion of UO_2 has been studied using a range of SIMFUEL electrodes containing various amounts of noble metal ε-particles. E_{CORR} measured on these electrodes showed identical behaviour under anoxic conditions (Ar-purged) but in 5% H_2/95% Ar purged solutions E_{CORR} decreased as the number of ε-particles increased. When a large number of these particles were present E_{CORR} was suppressed to the electrochemically-determined threshold for UO_2 oxidation. XPS measurements confirmed that the decrease of E_{CORR} was accompanied by a suppression in the extent of oxidation of the surface. The observed compositions of the surface were consistent with those determined electrochemically. The observed behaviour was attributed to the galvanic coupling of ε-particles to the rare-earth doped SIMFUEL matrix. The potential established on these particles can be attributed to the H_2 oxidation/reduction reaction leading to a suppression of the potential on the UO_2 surface.

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