Available online at www.sciencedirect.com
ScienceDirect
Electrochimica Acta 52 (2007) 7386–7395
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

The influence of temperature on the anodic oxidation/dissolution of uranium dioxide

M.E. Broczkowski *, J.J. Noël, D.W. Shoesmith **

Department of Chemistry, The University of Western Ontario, 1151 Richmond Street, London, Ontario N6A 5B7, Canada

Received 7 February 2007; received in revised form 11 June 2007; accepted 12 June 2007
Available online 17 June 2007

Abstract

The anodic dissolution of $U^{IV}O_2$ has been studied at 60 °C in 0.1 mol dm^{-3} KCl using a range of electrochemical methods and X-ray photoelectron spectroscopy (XPS). The results were compared to previous results obtained at 22 °C. This comparison shows that the threshold for the onset of anodic dissolution (−400 mV versus SCE) is not noticeably changed by this increase in temperature. However, both the oxidation of the surface (to $U^{IV/V}O_{2+x}$) and the rate of anodic dissolution (as $U^{VI}O_2^{2+}$) leading to the formation of a $U^{VI}O_3{\cdot}yH_2O$ deposit are accelerated at the higher temperature. The XPS analysis shows that the conversion of U^{V}–U^{VI} occurs at lower potentials at 60 °C. Consequently, once the surface becomes blocked by the presence of a $U^{VI}O_3{\cdot}yH_2O$ deposit, rapid dissolution coupled to uranyl ion hydrolysis causes the development of locally acidified sites within the fuel surface at lower potentials at the higher temperature.

Keywords: Electrochemistry; SIMFUEL; Temperature; X-ray photoelectron spectroscopy; Uranium dioxide

1. Introduction

Canada's Nuclear Waste Management Organization has recommended to the federal government an Adaptive Phased Management Approach for the long-term management of Canada's used nuclear fuel [1]. This approach includes centralized containment and isolation of the used fuel in a deep geologic repository, with the Canadian Shield being a potential site. In such a repository, the used fuel would be sealed in metallic containers surrounded by compacted bentonite clay, with excess space within the repository backfilled with a mixture of clay and crushed rock. Performance assessment calculations indicate that containers, fabricated with an outer shell of copper (for corrosion protection) and an inner liner of carbon steel (for mechanical strength), should not fail by corrosion [2,3], but it is judicious to assess the consequences if they did.

If failure were to occur, both the spent fuel wasteform and the carbon steel could be exposed to groundwater. This ground water is expected to be anoxic, since environmental oxidants (e.g., dissolved O_2) would be rapidly consumed by the corrosion of the copper liner and mineral/biological oxidation processes in the materials used to backfill the waste repository [4]. Consequently, the main source of oxidants to drive fuel corrosion within a failed waste container will be the radiolytic decomposition of water.

A realistic assumption is that containment will prevent wetting of the fuel until γ/β radiation fields have decayed to insignificant levels and only the effects of the α-radiolysis of water need be considered. Recently, we published a model, based on electrochemical mixed-potential principles, to predict fuel corrosion behaviour due to α-radiolysis inside a failed container [5]. Presently, an experimental research program is underway to develop a better understanding of the fuel corrosion/dissolution process, and to measure values of important parameters required to quantify the model. A key effect in the development of this model is the influence of temperature on fuel corrosion, since the fuel temperature will remain well above ambient for many years. Calculations of the thermal evolution within a waste container show that the fuel temperature will be in the range 80–40 °C for the majority of the assumed failure scenario [6].

The influence of temperature on UO_2 corrosion has been studied under a variety of conditions [7–20], and generally expressed as an activation energy. A recent review [7] found that the activation energy for the corrosion of UO_2 depended greatly on the

* Corresponding author.
** Corresponding author. Tel.: +1 519 661 2111; fax: +1 519 661 3022.
E-mail addresses: mbroczko@uwo.ca (M.E. Broczkowski), dwshoesm@uwo.ca (D.W. Shoesmith).

0013-4686/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2007.06.027

composition of the exposure environment with values ranging between 20 and 70 kJ mol^{-1} [7–12]. When measured in acidic solutions, with oxidants such as Fe^{III}, V^{V} and H_2O_2, values between 50 and 67 kJ mol^{-1} were observed, and in carbonate solutions for pH values between 8 and 10, activation energies were in the range 42–67 kJ mol^{-1}. However, in non-complexing neutral solutions, the measured values were significantly lower, at 29–34 kJ mol^{-1}. In one case, in granitic groundwater, a decrease in corrosion rate with increase in temperature was observed [10], and attributed to the formation of mineralized deposits. The formation of these secondary deposits at elevated temperatures suggests that the lower activation energies obtained in non-complexing neutral solutions can be explained as a partial suppression of dissolution by the accumulation of a corrosion product deposit [12–15]. This implies that the higher activation energies obtained in acid and carbonate solutions are more appropriate values since dissolution was occurring from a deposit-free surface.

Other studies have suggested additional ill-defined complexities. Matzke [16,17] showed by Rutherford backscattering that the oxidized surface layer formed on UO_2 varied from 5 to 8 nm in thickness at room temperature to 100–150 nm at temperatures between 150 and 200 °C. De Pablo et al. [18,19] showed that even in carbonate solutions, when surface films and deposits should be avoided (or, at least, minimized in thickness), a change in mechanism occurred over the temperature range 20–75 °C making any activation energy determined over this range only an apparent value.

Given these mechanistic issues and the large range of measured activation energy values, the present use of activation energies for individual reactions incorporated in our model [5] could lead to significant uncertainties in predicted fuel behaviour. In this paper we present a series of electrochemical and surface analytical (XPS) results on the anodic dissolution of UO_2 at 60 °C. This temperature was chosen as a representative value for fuel within a waste container.

2. Experimental

2.1. Electrode materials and preparation and solutions

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 irradiation of $U^{IV}O_2$ fuel in a CANDU reactor to various burn-ups [21,22]. As a consequence of this doping procedure, holes are injected into the 5f band, due to the substitution of trivalent rare-earth species (e.g., Nd^{III}, Y^{III}) for U^{IV} in the UO_2 fluorite lattice. This leads to an increase in electronic conductivity. The noble 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) randomly distributed in the UO_2 matrix [21]. The SIMFUEL used in these studies mimics UO_2 fuel irradiated to 1.5 at.% burn-up.

Slices approximately 3 mm thick and 12 mm in diameter were cut from the SIMFUEL pellets and the electrodes prepared as previously described [23]. 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, $\rho = 18.2\,M\Omega\,cm$) purified using a Millipore milli-Q-plus reverse osmosis unit to remove organic and inorganic impurities, and subsequently passed through milli-Q-plus ion exchange columns. All experiments were performed in Ar-saturated 0.1 mol L^{-1} KCl solution adjusted to pH 9.5. The temperature used was 60 °C.

2.2. Electrochemical cell and equipment

Experiments were conducted using a three-electrode, three-compartment electrochemical cell fitted with a jacket to allow control of the cell temperature using a Haacke circulating water bath. The reference electrode was a commercial saturated calomel electrode (SCE) (0.242 V versus SHE) at 20 °C, while the counter electrode was a platinum foil with a surface area of 13 cm^2, spot-welded to a platinum wire. The cell was housed in a grounded Faraday cage to minimize external noise. A Solartron model 1287 potentiostat was used to control applied potentials and to record current responses. Corrware/Corrview™ software (supplied by Scribner Associates) was used to control the instruments and to analyze the data.

2.3. Experimental procedure

In all experiments, the electrode was cathodically cleaned by polarizing to a potential of −1.5 V for 5 min and then to −1.0 V for another 5 min. Various electrochemical experiments were then performed. Potentiostatic oxidations were performed for 1 h at potentials in the range −0.5 to 0.5 V, and then followed by either cathodic stripping voltammetry (CSV) or X-ray photoelectron spectroscopy (XPS). CSVs were performed from the potentiostatic oxidation potential to −1.2 V at 2 mV s^{-1}. Cyclic voltammograms were recorded from −1.2 V to various more noble potentials and back, at 5 mV s^{-1}.

An SSX100 spectrometer was used to record all XPS spectra. Spectra were excited using Al Kα-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 O 2p and U ($4f_{7/2}$) peaks and associated satellites, and the valence band region 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}; the satellite structure in the vicinity of this peak and the behaviour in the valence band region were used to check the validity of the fit. A detailed description of our analytical and spectral fitting procedures has been published elsewhere [24].

3. Results and discussion

Fig. 1 shows a series of cyclic voltammograms recorded by scanning the potential from −1.2 V to various anodic poten-