Anodic reactions occurring on simulated spent nuclear fuel (SIMFUEL) in hydrogen peroxide solutions containing bicarbonate/carbonate – The effect of fission products

Ziyan Zhu, Linda Wu, James J. Noël, David W. Shoesmith

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The anodic behaviour of simulated spent nuclear fuel (SIMFUEL) was studied in NaCl solutions containing H₂O₂ and various concentration of HCO₃⁻/CO₃²⁻ using electrochemical, surface and solution analytical techniques. The two main anodic reactions are the oxidative dissolution of UO₂ and H₂O₂ oxidation. The relative importance of both reactions is controlled by the presence or absence of noble metal (ε) particles dispersed throughout the UO₂ matrix, the applied potential and the HCO₃⁻/CO₃²⁻ concentration. Both reactions are suppressed by the formation of U⁴⁺ surface films. When the formation of these films is prevented at higher HCO₃⁻/CO₃²⁻ concentrations, both reactions occur readily on the sublayer of U⁴⁺, 2xU²⁺₂O₂⁻₂. When present, noble metal (ε) particles support H₂O₂ oxidation over the full potential range.

1. Introduction

The universally accepted concept for the disposal of high-level nuclear waste, in particular spent nuclear fuel, is based on multiple barriers, including the fuel waste form, durable metal containers, a clay buffer and seals around the container, and a deep geologic repository (DGR) [1]. While such a DGR can provide acceptable assurance for long term containment, it is necessary to consider the consequences of container failure, which could lead to exposure of the fuel to groundwater. Since the spent fuel contains the radioactive fission and activation products, its behaviour in contact with groundwater provides the critical radioactivity source in assessments of repository safety [2,3].

The chemistry/electrochemistry of UO₂ has been studied in a range of proposed repository conditions [4–11]. The redox condition of the groundwater contacting the fuel after container failure is the key factor likely to control the fuel corrosion rate, since the solubility of U is orders of magnitude higher for U⁴⁺ than for the reduced U⁴⁺ form [12]. If container failure occurs while significant radiation fields exist in the fuel, oxidizing conditions are expected to prevail near the fuel surface as a consequence of water radiolysis [9,13,14].

The radiation-induced dissolution of spent fuel has been investigated both experimentally and computationally [15–19], and the key oxidant has been shown to be H₂O₂ produced by the alpha radiolysis of the ground water [13,20,21]. The fate of H₂O₂ is either to be consumed where it is produced at the fuel surface, or to be transported away from the fuel surface and scavenged by available reducing species such as Fe²⁺ and H₂ produced by corrosion of the steel containment vessel. Fuel corrosion involves the coupling of UO₂ corrosion and H₂O₂ reduction [22,23].

H₂O₂ + 2e⁻ → 2OH⁻  

UO₂ → UO₂²⁺ + 2e⁻  

However, H₂O₂ can also undergo oxidation reaction 3, and the coupling of reaction 1 and 3 would lead to H₂O₂ decomposition to produce the alternative oxidant O₂.

H₂O₂ → O₂ + 2H⁺ + 2e⁻
While an oxidant, O₂, would react over two orders of magnitude more slowly with UO₂ than the radiolytically produced H₂O₂ [4]. As indicated in Fig. 1, the relative importance of the two anodic reactions will determine the stability of UO₂ in H₂O₂ solutions.

Attempts have been made to determine the mechanistic balance between UO₂ dissolution and H₂O₂ decomposition under open circuit (corrosion) conditions. At low [H₂O₂] (<10⁻⁴ mol L⁻¹), the corrosion potential (E₉₀₉₉) increased from −0.4 V to −0.1 V (vs. SCE) with increasing [H₂O₂], and recent studies showed that the value of the steady-state E₉₀₉₉ achieved was directly related to the extent of oxidation of the surface, as determined by X-ray photoelectron spectroscopy [24]. Over the intermediate [H₂O₂] range, 10⁻⁴ to 5 × 10⁻³ mol L⁻¹, E₉₀₉₉ rose rapidly to a final steady-state value (∼0.1 V), indicating that the first stage of oxidation of the surface from U⁰U₂ to U¹⁻₂xU²⁺₂xO₂⁻₂x was rapid. At potentials in this range, both oxidative dissolution as U²⁺ and H₂O₂ decomposition are possible. Based on the independence of E₉₀₉₉ from [H₂O₂], it was claimed that the corrosion of the surface and the decomposition of H₂O₂ on the U¹⁻₂xU²⁺₂xO₂⁻₂x layer were both limited by the slow dissolution of U¹⁻⁻species from a U⁰U₂ surface layer. XPS measurements confirmed the presence of U¹⁻ on the electrode in this potential range.

For [H₂O₂] ≥ 5 × 10⁻³ mol L⁻¹, E₉₀₉₉ increased approximately linearly with concentration, and coverage of the electrode by UVI species increased. Experiments in which the amount of dissolved U⁰ was measured showed that, at these higher [H₂O₂], dissolution was accelerated [25,26], and the rate became first order with respect to [H₂O₂]. The increase in dissolution rate coupled to an apparently greater coverage by oxidizing and potentially blocking surface UVI species was taken as an indication of enhanced dissolution at locally acidified sites on the electrode surface [27]. How these changes influenced the rate and mechanism of H₂O₂ decomposition was not investigated. A similar mechanism was proposed for the influence of x-radiolytically produced H₂O₂ on U⁰U₂ corrosion and H₂O₂ decomposition [13]. It has also been claimed that, in the presence of both H₂O₂ and HCO₃⁻/CO₃²⁻ at high concentrations, U⁰U₂ corrosion is accelerated by the formation of a soluble peroxy carbonate complex, U⁰U₂(O₂)₃[CO₃]₂⁻₂x⁻₂y [28,29].

While the cathodic reduction of H₂O₂ on UO₂ has been investigated [22,23,26,30,31], the kinetics of H₂O₂ oxidation and its relative importance when accompanied by the anodic dissolution of UO₂ has received minimal attention. Wu et al. [32] studied the anodic behaviour on a SIMFUEL electrode in HCO₃⁻/CO₃⁻ solutions containing various concentrations of H₂O₂. The rates of both anodic reactions were found to be at least partially controlled by the chemical release of U⁰⁰⁰⁰⁰ surface species as (U⁰⁰⁰⁰⁰)₃[CO₃]₂⁻₂x⁻⁻, and H₂O₂ oxidation appeared to be the dominant reaction, although a quantitative separation was not achieved. In addition, the role of the noble metal (ε) particles, known to exist in spent fuel and present in the SIMFUEL used [33,34], on these anodic reactions remains unknown.

In this study, the mechanisms of both the anodic reactions are investigated. The specific goals are the following: (i) to determine the mechanisms of both reactions; (ii) to determine their relative importance as a function of potential and carbonate concentration ([CO₃]ₙat); and (iii) to elucidate the role played by noble metal (ε) particles in determining the relative importance of anodic dissolution and H₂O₂ decomposition.

2. ii) Experimental

2.1. a. Electrode materials and preparation and solutions

SIMFUELS are UO₂ pellets doped with non-radioactive elements to replicate the chemical effects of in-reactor irradiation [35]. Two different SIMFUEL samples were used in this study: one doped with 11 elements (Sr, Y, Ce, Nd, La, Zr, Ba, Pd, Ru, Mo, Rh) to simulate a fuel with both a rare earth-doped lattice and noble metal (ε) particles, designated (RE + ε), and a second one not containing the noble metal elements (Pd, Ru, Rh, Mo) and hence free of ε-particles, designated RE. The SIMFUELS were fabricated and supplied by Atomic Energy of Canada Ltd. (Chalk River, Canada).

All solutions were prepared with Type-1 water (resistivity, ρ = 18.2 MΩ cm) purified using a Millipore milli-Q-plus unit to remove organic and inorganic impurities. Experiments were conducted in a 0.1 mol L⁻¹ NaCl solution containing 0.02 mol L⁻¹ H₂O₂ with the pH adjusted to 9.7 with NaOH. NaHCO₃ was added to a concentration ([CO₃]ₙat) in the range 0.01–0.1 mol L⁻¹. All chemicals were reagent grade and purchased from Fisher Scientific.

2.2. b. Electrochemical cell and equipment

Experiments were conducted using a three-compartment, three-electrode electrochemical cell. The reference electrode was a commercial saturated calomel electrode (SCE) (0.242 V vs. SHE) at 20 °C. The counter electrode was a Pt foil spot-welded to a Pt wire. The cell was placed in a Faraday cage to minimize interference from external noise. The rotation rate of the rotating disc electrode (RDE) was controlled using an analytical rotator from Pine Instruments (model ASR). All the electrochemical experiments were performed with a Solartron 1287 potentiotstat controlled by CorrWare Version 2.7 software. The electrode resistivity (ρ (RE) = 174 Ω cm; ρ (RE + ε) = 81 Ω cm) was compensated using the current interrupt procedure [36].

Fig. 1. Schematic illustration of the possible reactions of H₂O₂ on a UO₂ surface, showing that the H₂O₂ oxidation reaction can be catalyzed by a UO₂⁻ₓ surface or by noble metal (ε) particles.
2.3. c. Electrochemical Experiments

Before each experiment, the SIMFUEL electrode was wet polished with 1200 grit SiC paper and rinsed with Millipore water. The working electrode was then cathodically cleaned at a potential of $-1.2$ V for 2 min prior to each experiment. For potentiostatic experiments, the working electrodes were oxidized for 10 min at a potential in the range of $0.1$–$0.4$ V until a steady-state current was achieved. In dissolution experiments, the working electrode was held at each potential for 1 h.

In these experiments, the electrodes were oxidized for 1 h either at the corrosion potential ($E_{\text{CORR}}$) or at a positive applied potential ($E$) ($0.2$, $0.3$ or $0.4$ V). The amount of dissolved U in the solution was then measured and converted into an equivalent charge using Faraday’s Law:

$$m = \frac{Q M}{F n}$$

where $m$ is the mass reacted, $Q$ is the electrochemical charge equivalent to the amount of U dissolved, $F$ is Faraday’s constant ($96,485$ C mol$^{-1}$), and $n$ is the number of electrons involved in the dissolution reaction ($2$ for U$^{IV}$ $\rightarrow$ U$^{VI}$). After anodic oxidation for 1 h, the electrode was quickly transferred to a H$_2$O$_2$-free solution for cathodic stripping voltammetry (CSV) to estimate the amount of charge consumed in the production of surface oxidized layers.

2.4. d. Electrode surface and solution analyses

2.4.1. i. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

The concentration of U in the solution was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). These analyses were performed with a PerkinElmer Optima 3300 Dual 24 View ICP-AES located in the Biotron facility (Western University). The U emission was monitored at a wavelength of $419$ nm, with a detection limit of $0.01$ mg L$^{-1}$. Prior to injection into the spectrometer, samples were mixed with $2\%$ HNO$_3$ to prevent U precipitation. The calibration standards used were $0.5$, $1.0$, and $5.0$ mg L$^{-1}$ U solutions, and a $2\%$ HNO$_3$ solution was used as a blank sample.

2.4.2. ii. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

The surface morphology of the electrode was obtained using a Hitachi S-4500 field emission scanning electron microscope equipped with a Quartz XOne energy dispersive X-ray analyzer located at Surface Science Western (SSW). Immediately after an experiment, samples were rinsed with Millipore H$_2$O and dried in an Ar stream prior to being placed in the microscope. The electron beam potential was maintained at $5.0$–$15$ keV and the working distance was $10$ mm during image collection, resulting in a spatial resolution of $<2$ nm. Micrographs were recorded at various magnifications ($100$ $-$ $5000X$).

2.4.3. iii. Raman spectroscopy

Raman spectra were obtained using a Renishaw 2000 Laser Raman spectrometer (Renishaw PLC., UK) equipped with a Leica DMLM microscope. Spectra were excited using a He-Ne laser with a wavelength of $632.8$ nm. The laser beam was focused to $\sim 2\mu$m in diameter with a $50\times$ uncoated objective lens on to the electrode mounted on carbon tape attached to a glass slide. The power of the laser beam was kept at $50\%$ to avoid laser heating effects. The spectrometer was calibrated with a standard Si wafer, which has an intense Raman band at $520$ cm$^{-1}$.

The deconvolution of the broad band at $500$–$700$ cm$^{-1}$ has been described in detail elsewhere [37,38].

3. iii) Results and discussion

3.1. a. Cyclic voltammetry

Fig. 2 shows CVs recorded on the two electrodes in a $0.1$ mol L$^{-1}$ NaCl solution containing $0.02$ mol L$^{-1}$ of NaHCO$_3$ (pH $= 9.7$). In the absence of H$_2$O$_2$, Fig. 2 A, there was no significant difference between the two electrodes in the anodic region. However, the cathodic current increased significantly at $-0.8$ V on the RE$^+\epsilon$ electrode due to the catalysis of H$_2$O reduction on the noble metal ($\epsilon$) particles. When H$_2$O$_2$ was added to the solution, Fig. 2 B, the cathodic current was significantly enhanced and reached a maximum at $0.27$ V on the RE electrode with the decreases at positive potential indicating the formation of corrosion products on the UO$_2$ surface and the inhibition of one or both of the anodic oxidation
processes. On the RE + ε electrode, the current was further enhanced and no peak was observed at the positive potential limit of the scan. This enhancement suggested a role for the ε-particles in determining the anodic current over the full potential range shown.

3.2. Characterization of noble metal (ε) particles

3.2.1. SEM and EDX

Fig. 3 shows the surface morphology of the RE + ε and RE electrodes. The RE + ε electrode (Fig. 3 A) featured distinct particles mainly residing on grain boundaries and possessed a smaller grain size than the RE electrode. The EDX analyses, Fig. 4, showed that the distinct particles contained Ru, Pd, Rh and Mo, consistent with previous analyses [35]. A more extensive analysis of the composition of a number of ε-particles in the RE + ε electrode showed their composition to be Pd (40 ± 6%), Ru (29 ± 5%), Rh (14 ± 3%) and Mo (15 ± 4%) [39].

3.2.2. Raman analyses

Fig. 5 shows representative Raman spectra recorded on the RE and RE + ε electrode surfaces. These spectra exhibit a number of bands [37].

(i) The dominant peak at 445 cm\(^{-1}\) can be attributed to the fundamental U-O stretching mode of the fluorite lattice.

(ii) A band at 1150 cm\(^{-1}\) (not shown) has been assigned as an overtone (2L-O) of the first order L-O phonon observed at 570-575 cm\(^{-1}\) [40].

(iii) The broad band between 500 and 700 cm\(^{-1}\) can be attributed to UO\(_2^+\) lattice damage, due to the formation of defects caused by lattice doping.

The band in this last region was deconvoluted into three peaks at 540 cm\(^{-1}\), 570 cm\(^{-1}\) and 640 cm\(^{-1}\). The peak at 570 cm\(^{-1}\) was attributed to a first order phonon (as noted above) while the peak at 540 cm\(^{-1}\) was attributed to the creation of oxygen vacancies (OV) [41,42] in response to the need for charge compensation due to RE\(^{III}\) doping, a process which appears to involve the formation of RE\(^{III}\)-OV clusters.

A peak at 640 cm\(^{-1}\) has been commonly assigned to distortion of the anion sublattice associated with a vibrational mode involving clusters of interstitial O atoms in a non-stoichiometric UO\(_2^+\) lattice. Since the SIMFUELs used in these experiments were sintered and reduced they were expected to be stoichiometric, making this assignment of the peak at 640 cm\(^{-1}\) unlikely. It has been suggested [38] this peak can be attributed to a Zr-O\(_8\) complex since Zr\(^{IV}\) doping would cause a decrease in the UO\(_2^+\) lattice parameter, a feature that would be expected to lead to lattice stabilization against anodic oxidation.

Since the peak at 445 cm\(^{-1}\) is characteristic of the undisturbed fluorite lattice and the 540 cm\(^{-1}\) peak can be attributed to the creation of OV associated with RE\(^{III}\)-doping, the area ratio of these two peaks has commonly been used as a measure of the number of such vacancies [38]. Fig. 6 shows the peak areas normalized to the area of the peak at 445 cm\(^{-1}\). If it is accepted that the ratio of the 540 cm\(^{-1}\) and 445 cm\(^{-1}\) peak areas is a measure of the number of OV created by RE\(^{III}\) doping, then the RE electrode appeared to have a slightly higher density of OV than the RE + ε electrode.

3.3. Steady-state currents at various [CO\(_3\)]\(_{tot}\)

Fig. 7 shows the current densities recorded on both electrodes over a range of E in a 0.1 mol L\(^{-1}\) NaCl solution containing 0.1 mol L\(^{-1}\) of [CO\(_3\)]\(_{tot}\) and 0.02 mol L\(^{-1}\) of H\(_2\)O\(_2\). The current reached a steady-state value rapidly on both electrodes, but slightly
more rapidly on the RE electrode especially at the higher E.

Fig. 8 A and B show the steady-state currents plotted against E. On the RE electrode, the current exhibited the same dependence on E as observed voltammetrically, Fig. 7, increasing over the low potential range before decreasing again at higher E. The decrease in current beyond the peak became less marked as [CO$_3$]$_{tot}$ was increased. On the RE$^{+\varepsilon}$ electrode, the current showed a similar behaviour at low E, but any tendency to decrease at more positive E was overcome by a further current increase for E $>$ 0.3 V.

Fig. 8C shows the difference between the currents ($\Delta j$) recorded on the two electrodes,

$$\Delta j = j_{RE^{+\varepsilon}} - j_{RE}$$

Since the key difference between the two electrodes is the presence of noble metal ($\varepsilon$) particles in the RE$^{+\varepsilon}$ electrode, this suggested $\Delta j$ could be attributed to reactions occurring on these particles, not on the UO$_2$ surface. As will be demonstrated below, the second possibility, that the anodic reactivities of the two doped UO$_2$ matrices are different, can be ruled out. The enhanced currents on the RE$^{+\varepsilon}$, given by $\Delta j$, Fig. 8C, can be divided into two distinct
regions: (i) For sufficiently low E, \( \Delta j \) became independent of E, while clearly dependent on \([\text{CO}_3]_{\text{tot}}\); (ii) As E was increased, \( \Delta j \) increased steeply with E and became independent of \([\text{CO}_3]_{\text{tot}}\).

3.4. d. Anodic dissolution of UO\(_2\)

The currents recorded in the potentiostatic experiments, Figs. 7 and 8, contain contributions from both UO\(_2\) and H\(_2\)O\(_2\) oxidation. To separate these contributions, the electrodes were potentiostatically oxidized at different applied potentials for 1 h and the solutions then analyzed for dissolved U. In addition, the charge consumed by the formation of the oxidized surface layers, \( \text{U}^{IV}_{1-2x}\text{O}_2\text{O}_{2-x} \) and \( \text{U}^{IV}_{3}\text{O}_3\cdot\text{H}_2\text{O} \) and possibly studtite (\( \text{U}^{IV}_{0}\cdot\text{H}_2\text{O}_4 \)), which could form in the presence of H\(_2\)O\(_2\) [19,42–44] was determined by cathodic stripping voltammetry. This charge was found to be negligible compared to the total anodic charge consumed and was not, therefore, taken into consideration.

Fig. 9 shows that the amount of U dissolved was almost identical for both electrodes, irrespective of the \([\text{CO}_3]_{\text{tot}}\). Despite the differences in the total amount of charge consumed, obtained by integration of the current over the 1 h duration of the experiment, the data in Fig. 9 show that the extent of U dissolution was similar on the RE and RE + \( \varepsilon \) electrodes. This demonstrates that the extent of dissolution was uninfluenced by the presence of noble metal (\( \varepsilon \)) particles, and hence not responsible for the differences in anodic current, \( \Delta j \) (Fig. 8C). Also, this similarity in \( \text{U}^{VI} \) release rates confirmed that the slight differences in the number of \( \text{REE}^{III}-\text{O}^{IV} \) clusters indicated by the Raman analyses had minimal influence on the anodic reactivity of the UO\(_2\) matrix. This is consistent with previous observations on the influence of \( \text{REE}^{III} \) doping on the anodic reactivity [45].

SEM micrographs recorded on the RE + \( \varepsilon \) electrode, Fig. 10, showed some etching of the surface, possibly with some enhanced grain boundary dissolution. Although not shown, similar changes in surface morphology were observed on the RE electrode.

At \( E_{\text{CORR}} \), the amount of \( \text{U}^{VI} \) dissolved was effectively independent of \([\text{CO}_3]_{\text{tot}}\). Fig. 9, indicating that the slow step in the overall dissolution process was the anodic formation of the \( \text{U}^{VI} \) species from the preformed \( \text{U}^{IV}/\text{U}^{V} \) surface layer

\[
\text{U}^{IV}\text{O}_2 \rightarrow \text{U}^{IV}_{1-2x}\text{O}_2\text{O}_{2-x} \rightarrow (\text{U}^{VI})_{\text{surf}} \rightarrow \text{U}^{VI}\text{O}_2(\text{CO}_3)^{2-y}+ 
\]

At higher E and low \([\text{CO}_3]_{\text{tot}}\), only a marginal increase in \( \text{U}^{VI} \) release was observed prior to the inhibition of release at high E (0.3 V, 0.4 V), when the surface became covered with a \( \text{U}^{IV}\text{O}_3\cdot\text{H}_2\text{O} \) film, although the formation of studtite (\( \text{U}^{IV}_{0}\cdot\text{H}_2\text{O}_4 \)) was also possible in the presence of H\(_2\)O\(_2\) [19,42–44] This suppression of dissolution at high E on the RE electrode was consistent with the low currents observed at 0.3/0.4 V (Fig. 8A), which demonstrates that the anodic oxidation of H\(_2\)O\(_2\) was also suppressed at these potentials. By contrast, the suppression of \( \text{U}^{VI} \) dissolution on the RE + \( \varepsilon \) electrode under these conditions, Fig. 9, was not accompanied by a decrease in current, Fig. 8B, confirming that the higher currents at 0.3/0.4 V were due to an increase in the anodic oxidation of H\(_2\)O\(_2\) on the noble metal (\( \varepsilon \)) particles.

At higher \([\text{CO}_3]_{\text{tot}}\), the intermediate \( \text{U}^{IV}_{1-2x}\text{O}_2\text{O}_{2-x} \) layer was considerably thinner and anodic dissolution proceeded more rapidly through \( \text{U}^{IV}/\text{U}^{V} \) surface intermediates [46].

\[
\text{U}^{IV}\text{O}_2 + \text{HCO}_3^- \rightarrow \text{U}^{IV}\text{O}_2(\text{HCO}_3)_{\text{ads}} + e^- 
\]
At low E, the amount of UVI released increased with E indicating control of the dissolution reaction by reaction 8. For \( E > 0.3 \) V, the amount released became independent of E but exhibited a dependence on \( [CO_3]_{tot} \) consistent with a switch in rate control to the final chemical dissolution (reaction 9). It is possible that this dissolution reaction was accelerated by the formation of a soluble peroxycarbonate complex, \( \text{UVI}_2(\text{O}_2)x(\text{CO}_3)y^2-2x-2y \). The formation of such a species was shown to accelerate UO\(_2\) dissolution when \( \text{H}_2\text{O}_2 \) and \( \text{HCO}_3/\text{CO}_3^2- \) concentrations were higher than those employed in this study [28,29].

Based on these analyses, the total charge consumed by anodic dissolution (\( \text{QU}_\text{VI} \)) was calculated and compared to the total amount of anodic charge. The ratio of these charges is plotted in Fig. 11, which provides a measure of the relative importance of U\(^{VI}\) dissolution. On the RE electrode, the ratio (i.e., the importance of dissolution) increased with E for all \( [CO_3]_{tot} \), as indicated by the green arrow, Fig. 11, with dissolution becoming the dominant reaction at 0.4 V despite the overall decrease in current, Fig. 8A, and the suppression of U\(^{VI}\) release, Fig. 9, particularly at low \( [CO_3]_{tot} \).

These results confirmed that the formation of U\(^{VI}\) surface films strongly suppressed the anodic oxidation of \( \text{H}_2\text{O}_2 \). However, the dependence on \( [CO_3]_{tot} \) at both 0.3 V and 0.4 V, in particular the latter, peaked at intermediate \( [CO_3]_{tot} (0.02 \text{ mol L}^{-1}) \) before decreasing again at higher concentrations, as indicated by the red arrows in Fig. 11. This suggested two influences of \( \text{HCO}_3/\text{CO}_3^2- \): (i) at the two low \( [CO_3]_{tot} \) an increase leads to a significant promotion of the importance of anodic dissolution, confirming that the increased anodic current can be attributed to an acceleration in the rate of the electrochemical reaction 8; (ii) at the higher \( [CO_3]_{tot} (0.05 \text{ and } 0.1 \text{ mol L}^{-1}) \) the relative importance of the dissolution reaction was decreased; i.e., the relative importance the anodic oxidation of \( \text{H}_2\text{O}_2 \) increased, once the surface U\(^{VI}\) layer was rapidly dissolved and the conductive underlying U\(^{IV}_{1-2x}\)U\(^{V}_{2x}\)O\(_2\) layer exposed.

Significantly different behaviour was observed on the RE + ε electrode. At low \( [CO_3]_{tot} \) the ratio decreased to 3.5% as E was increased to 0.4 V, as indicated by the green arrow in Fig. 11. This decrease accompanied the overall decrease in U\(^{VI}\) release, Fig. 9, and the accompanying increase in anodic current, Fig. 8B and Fig. 8C, confirming the dominance of \( \text{H}_2\text{O}_2 \) oxidation under these conditions. Since the surface of the UO\(_2\) matrix remained protected by the U\(^{VI}\) surface film at low \( [CO_3]_{tot} \), these observations clearly...

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**Fig. 9.** The amount of U dissolved at \( E_{\text{CORR}} \) and various E values (1 h) for both RE and RE+e electrodes.

\[
\text{U}^{VI}_2(\text{HCO}_3)_{ads} + \text{OH}^- \rightarrow \text{U}^{VI}_2(\text{CO}_3)_{ads} + \text{H}_2\text{O} + e^- \tag{8}
\]

\[
\text{U}^{VI}_2(\text{CO}_3)_{ads} + \text{HCO}_3 \rightarrow \text{U}^{VI}_2(\text{CO}_3)_{2-} + \text{H}^+ \tag{9}
\]

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**Fig. 10.** SEM micrographs of the RE + ε electrode before and after anodic oxidation at \( E = 0.35 \text{ V} \) for 1 h in a solution of 0.1 mol L\(^{-1}\) NaCl, 0.02 mol L\(^{-1}\) \( \text{H}_2\text{O}_2 \) and 0.1 mol L\(^{-1}\) NaHCO\(_3\) with pH = 9.7: (a) and (b), the freshly polished electrode; (c) and (d) the surface of the electrode after anodic oxidation at 0.35 V for 1 h.

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demonstrated that the acceleration of H₂O₂ oxidation was supported on the noble metal (ε) particles. At higher [CO₃]tot the relative importance of UVI dissolution was revived as the UVI surface film dissolved, as indicated by the red arrow in Fig. 11B.

3.5. e. The anodic oxidation of H₂O₂

The importance of H₂O₂ oxidation, and the influence of [CO₃]tot and E on it, are demonstrated in Fig. 12, which shows the anodic charge due to H₂O₂ oxidation (QH₂O₂) calculated by subtracting the charge due to UO₂ dissolution (QUO₂) from the total electrochemical charge. At low E (0.2 V), QH₂O₂ increased with [CO₃]tot on both electrodes. This, and the observation that the current for H₂O₂ oxidation on noble metal (ε) particles was enhanced in this potential region 1 (Fig. 8C), demonstrated that HCO₃⁻/CO₃²⁻/CO₂⁻ in films influenced H₂O₂ oxidation in two ways: (i) as discussed above it accelerated UVI dissolution leading to the exposure of the conductive UIV₁₋₂x层 on which H₂O₂ oxidation could occur; (ii) it accelerated H₂O₂ oxidation on the noble metal (ε) particles in region 1 (Fig. 8C).

This dependence of the current and the charge for H₂O₂ oxidation on [CO₃]tot indicated that a carbonate-mediated oxidation of H₂O₂ was occurring on the noble metal (ε) particles in potential region 1 (Fig. 8C). The combination of H₂O₂ and HCO₃⁻/CO₃²⁻/CO₂⁻ is known to form a reactive peroxycarbonate species,

\[
2HCO₃⁻ + H₂O₂ → HCO₃⁻ + H₂O + 2HCO₃⁻
\]

a reaction which can catalyze H₂O₂ decomposition and is known to enhance its reactivity [47]. Once formed, its anodic oxidation to O₂ and the regeneration of HCO₃⁻ was rapid on the noble metal (ε) particles,

\[
2HCO₃⁻ → 2H₂CO₃ + O₂ + 2e^-
\]

On the RE electrode, the ability of HCO₃⁻/CO₃²⁻ to revive H₂O₂ oxidation by dissolving the insulating UVI layer to expose the underlying catalytic UIV₁₋₂x层 layer was clear, QH₂O₂ increasing with [CO₃]tot at all three potentials.

While the value of QH₂O₂ also increased with [CO₃]tot on the RE + ε electrode, the extent of H₂O₂ oxidation was much greater at 0.4 V than it was on the RE electrode, and the excess current, Δj, showed that the reaction was not dependent on [CO₃]tot, although it was occurring on the noble metal (ε) particles. This can be attributed to the direct oxidation of H₂O₂ on the noble metal (ε) particles, this reaction having been shown to be catalyzed by oxidized states on the surface of noble metals [48–52], e.g., Pd⁺ on Pd,
Pd + 2H₂O → Pd⁰(OH)₂ + H⁺ + 2e⁻  

Pd⁰(OH)₂ + H₂O₂ → PdII(OH)(H₂O₂)₂ads  

PdII(OH)(H₂O₂)₂ads → Pd + O₂ + 2H₂O  

4. iv) Summary

Fig. 13 shows a schematic summary of the reactions occurring on the various features and surface states on the UO₂/e-particle surface.

- At all potentials, including E_{CORR}, the surface was covered by a thin conductive UVI,1-2xU²V₂O₅.x layer able to support both anodic dissolution of the UO₂ matrix and anodic oxidation of H₂O₂.
- The balance between these anodic reactions varied with: (i) the presence or absence of noble metal (e) particles dispersed throughout the fission product-doped UO₂ matrix, (ii) the potential applied, and (iii) the [CO₃]tot.
- At low [CO₃]tot both anodic reactions were retarded by the dissolution of this thin UVI layer in solution to expose the underlying conductive UVI,1-2xU²V₂O₅.x layer.
- The dissolusion of this thin UVI layer was accelerated in the presence of HCO₃⁻/C¹⁵, leading to increases in the rate of both anodic reactions.
- The presence of noble metal (e) particles did not influence the anodic dissolution of the UO₂ matrix but offered an additional pathway for the anodic oxidation of H₂O₂.
- At low potentials, in the presence of HCO₃⁻/CO₃²⁻, a peroxycarbonate species, HCO₃⁻ was formed and rapidly oxidized to O₂ on the particles.
- At high potentials, H₂O₂ was directly oxidized on the noble metal (e) particles, which were rendered catalytic by their electrochemical oxidation (e.g., Pd → PdII).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.electacta.2019.07.057.