

Direct mass analysis of water absorption onto ceria thin films

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ABSTRACT

Plutonium oxide (PuO₂) is one of the most highly radioactive components of nuclear fuel waste streams and its storage poses particular challenges due to the high temperatures produced by its decay and the production of gases (particularly H₂ and steam). Its high radiotoxicity necessitates the use of analogues, such as CeO₂, to allow the comprehensive study of its interaction with water under storage conditions.

We have developed a method which enables direct gravimetric measurement of water adsorption onto CeO₂ thin films with masses in the microgram region. Porous CeO₂ films were fabricated from a surfactant based precursor solution. The absorption of water onto the CeO₂ coating at different relative humidities was studied in a closed reactor. Quartz Crystal Microbalance (QCM) gravimetry was used as a signal transducer, as changes in crystal resonant frequency due to absorbed mass are directly and linearly related to mass changes occurring at the crystal surface. Using this method, we have determined the enthalpy of absorption of water onto CeO₂ to be -50.7 kJmol⁻¹ at 75°C, 12 kJmol⁻¹ greater than the enthalpy of evaporation. This enthalpy is within the range predicted for the absorption of water onto PuO₂, indicating this method allows for investigation of water absorption using microgram samples.

INTRODUCTION

Plutonium oxide (PuO₂) is one of the most highly radioactive components of nuclear fuel waste streams. This poses particular challenges in storing large amounts for reuse as mixed oxide fuel for the next generation of fast reactors or for eventual deposition into long-term geological storage, which has been proposed at a number of sites worldwide. Interim storage is typically within a series of nested steel canisters under a partially inert atmosphere. These canisters develop high internal temperatures due to the PuO₂ decay heat and have been observed to become pressurised due to the evolution of hydrogen gas and steam. A greater understanding of PuO₂ interaction with water is therefore imperative to allow the design of safe long-term storage facilities.[1-3].

Ceria (CeO₂) is widely employed as a model substrate for radioactive metal oxides such as plutonium oxide, due to the metals similar ionic radii and the oxides similar fluorite structure.[4] Ceria polycrystals exhibit a significant absorption of water vapour at high temperatures [5, 6], and previous studies have indicated this to be true of plutonium oxide. The absorption of water results in numerous physio- and chemi-absorbed layers, but the subsequent fate of this water under elevated temperatures and pressures and in the presence of highly radioactive material is unknown. Water adsorption on PuO₂ has previously been investigated by measuring headspace pressure, as a function of temperature within a closed system containing a fixed quantity of PuO₂ in the presence of varying amounts of deliberately added water [7, 8].

This involves making a number of assumptions relating to the PVT behaviour of the headspace of the closed system, usually based on the behaviour of an ideal gas, in order to estimate the mass of water adsorbed at the PuO₂ surface.[9, 10]

We have developed a method which enables direct gravimetric measurement of water adsorption onto CeO₂ thin films. We have previously reported the use of Quartz Crystal Microbalance (QCM) gravimetry as a signal transducer,[11] as changes in crystal resonant frequency are directly related to mass changes occurring at the crystal surface at ambient temperatures[13]. In this work, ortho-gallium phosphate (*o*-GaPO₄) crystals were used instead of quartz due to the linear dependence of their resonant frequency on as well as their higher piezoelectric limiting temperature,[8] allowing the absorption of water to be analysed under the high temperature conditions that develop in typical PuO₂ storage conditions. Herein, we describe preliminary experiments in the coating of *o*-GaPO₄ crystal electrodes with nano-scale crystalline CeO₂ films and measurements of their absorption of water.

EXPERIMENT

Materials and Reagents

All reagents used are AnalaR grade or higher, and purchased from Sigma Aldrich (Gillingham, Dorset, UK). All water used is Ultrapure doubly de-ionised water from a Direct-Q 3 UV Millipore water purification system (Millipore (U.K.) Limited, Watford, UK) to a resistivity of 18.2 M_Ω.cm. Nitrogen Whitespot grade (moisture content 3 ppm) is provided by BOC Ltd., Guildford, Surrey, UK. All *o*-GaPO₄ crystals used were 6 MHz with platinum electrodes and a piezoelectrically active area of 0.342 cm², purchased from Piezocyst GmbH, Austria. The heater, vessel and controller were purchased from Scientific and Medical Products, Cheadle, UK and had a system accuracy of ±1°C.

Methods

A CeO₂ film was deposited on *o*-GaPO₄ crystals using an adapted version of the Lundberg method for generating thin films of crystalline CeO₂[11]. A stock solution of 0.01 moles of CeNO₃ and 5% of triton-X (a non-ionic polxamer surfactant) dissolved in 10 mL of 1:1 water-methanol was created. A second solution was produced by 10-fold dilution of the stock solution. 10 µl of the diluted solutions were drop-coated onto one electrode surface of *o*-GaPO₄ crystal and allowed to evaporate in air, then calcined in air at 650°C for 5 h, resulting in formation of an iridescent layers adhered to the platinum piezoelectrode surface.

The formation of crystalline CeO₂ was confirmed by Raman spectroscopy and by XRD analysis of the layers. The morphology of the layers was investigated using a Phenom™ scanning electron microscope (Lambda Photometrics, Herfordshire). CeO₂-coated crystal electrodes were mounted into commercially available crystal holders (Colnatec, US) constructed of steel and ceramic leaving only the coated crystal face accessible. The crystal mount is suspended within a steel reaction vessel (vol = 1L, fig. 1) such that it is not in contact with any internal surface. A stream of dry nitrogen is passed into an inlet port on the reaction vessel and allowed to escape from an exhaust port while the vessel is heated in a furnace to ~400°C. This procedure is continued for 6+ hours, or until the observed frequency of the crystal remains steady. The system is then sealed and allowed to return to RT and the baseline frequency

recorded. A defined amount of water is added by microsyringe and the system is then re-sealed and the frequency and temperature recorded every second. As the water added to the system evaporated and redeposits onto the crystal surface, the frequency (inversely proportional to mass) is predicted to drop. Once a steady frequency is reached, the system is temperature cycled from RT to $\sim 350^{\circ}\text{C}$ with continuous recording of the temperature and corresponding frequency. Once at RT again, the gas inlet is re-attached and a slow stream of nitrogen passed through the system until the frequency stabilises. The above procedure is then repeated (from the initial heat cycling) with a different amount of water added.

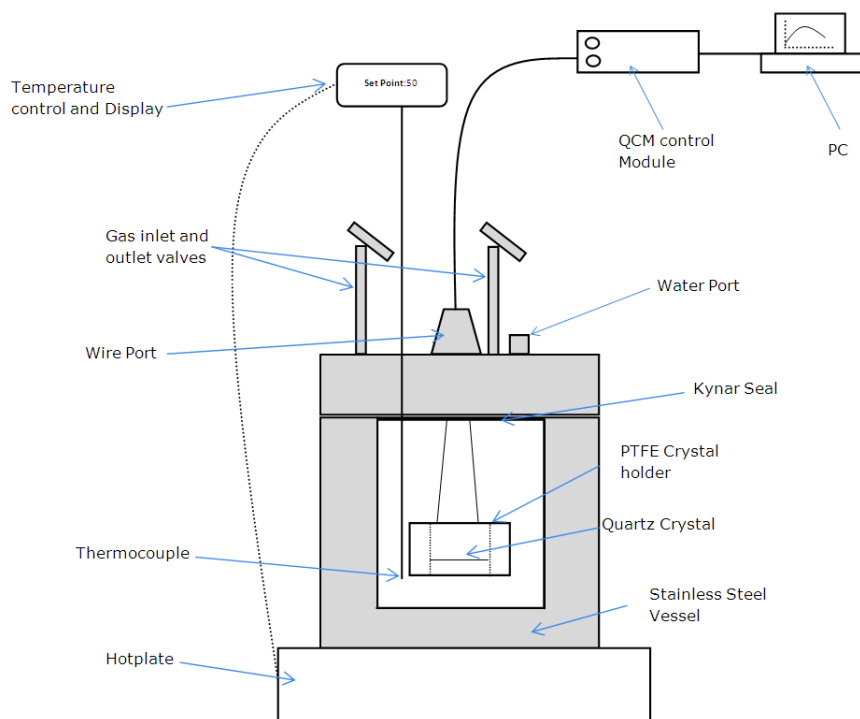


Figure 1. Schematic diagram of experimental setup.

RESULTS & DISCUSSION

The layers formed by drop-coating and calcination were found to be strongly adhered to the platinum electrode surface, being resistant to manual abrasion. Raman spectroscopy (785 nm excitation) showed a characteristic CeO_2 peak at 464 nm (fig. 2).[12] XRD measurements of a powder CeO_2 sample produced under the same conditions as the crystal coatings indicated the samples were crystalline CeO_2 (fig.3)[13].

Deposition of the CeO_2 layers resulted in a resonant frequency drop of 7450 Hz, equating to a 42 μg increase in mass. This is below the 2% threshold at which the Sauerbrey equation becomes unreliable to describe mass changes occurring at the composite resonator surface. Using the area of the crystal electrode coated and the density of bulk ceria (7.65 g/cm^3) [13], the layers were estimated to be 125 nm thick, assuming a homogenous non-porous coating with ideal geometry.

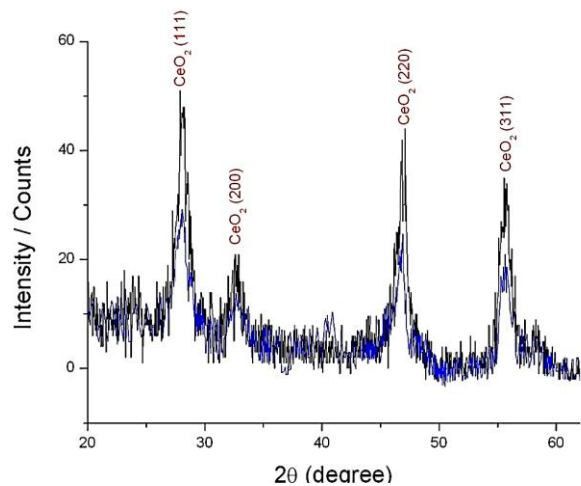


Figure 2. Powder XRD showing characteristic peaks for crystalline ceria, produced by evaporation calcination of the stock at 650°C.

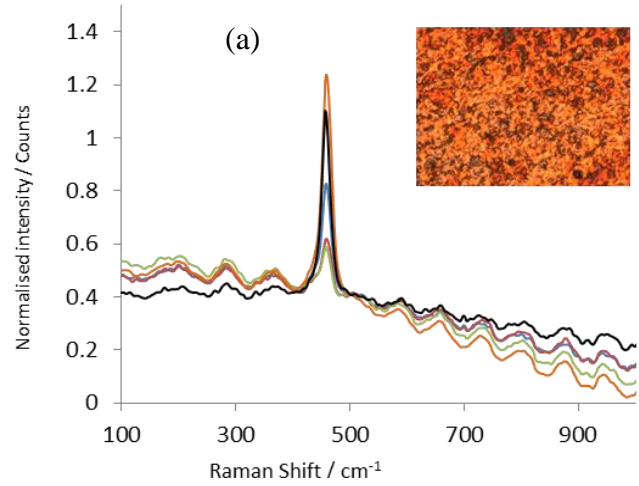


Figure 3. (a) Raman spectra of CeO₂ layer measured at five points, with characteristic peak at 464 cm⁻¹ (b) inset showing microscope image at 50 x magnification.

SEM imaging shows the layer to be comprised of a densely packed CeO₂ network with voids and pores present (Figure 4). The thickness of the films was also measured by XRF in a 36 point grid, giving an average thickness of 261 nm, ± 29 nm (figure 5). This gives a piezoactive volume of 8.9 x 10⁻⁶ cm³ and therefore a porosity of 54%.

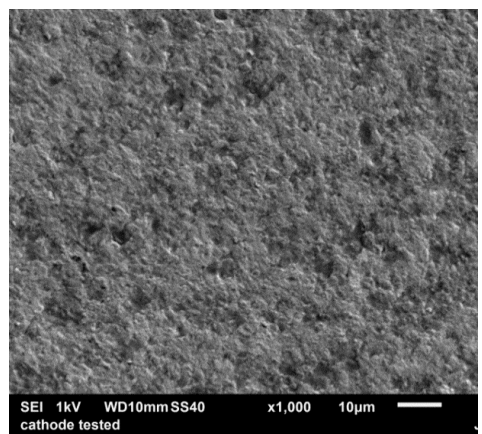


Figure 4. SEM image of a CeO₂ film on a platinum / o-GaPO₄ piezoelectrode.

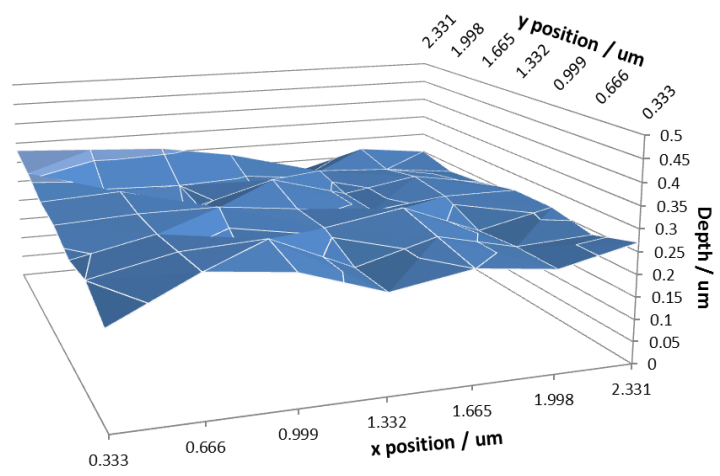


Figure 5. XRF map of CeO₂ film thickness at 36 different points. Average thickness, 261 nm.

Initial microbalance experiments with the coated crystals at were conducted at 75°C. It was found that the resonant frequency of the coated crystals reduced in response to the addition of water to the system, corresponding to a 2.4 µg mass increase per coated crystal (approximately 90 mg of water absorbed per gram CeO₂ layer) at 100% relative humidity. The relative humidity was varied by changing the amount of water added to the system and maintaining the temperature at a constant 75°C. It was found the amount of water absorbed onto the ceria coating increased with increasing partial pressure of water. A plot of this change in

frequency or mass against the partial pressure resulted in a graph typical of a type II adsorption isotherm (fig. 7(a)). Addition of further water to the already saturated system resulted in a linear increase in the mass of water detected on the crystal due to simple physical deposition. The BET equation (Eq. 1) can be used to calculate the enthalpy of adsorption (ΔH_{ads}) and the volume of a monolayer of molecular water adsorbed onto a surface:

$$1/\left[V_a \left(\frac{P_0}{P} - 1\right)\right] = \left(\frac{C-1}{V_M C}\right) \left(\frac{P}{P_0}\right) + \frac{1}{V_M C} \quad - \text{Eq. 1}$$

where V_m is the volume of an adsorbed monolayer and $C = \exp(\Delta H_{\text{ads}} - \Delta H_{\text{liq}}/RT)$. A plot of $P/V_a(P_0-P)$ versus P/P_0 yields a straight line, the slope of which is $(C-1)/(V_M C)$ and intercept is $1/V_M C$. The BET plot for H₂O adsorption produces a straight line, with R² values of 0.995 (fig. 7).

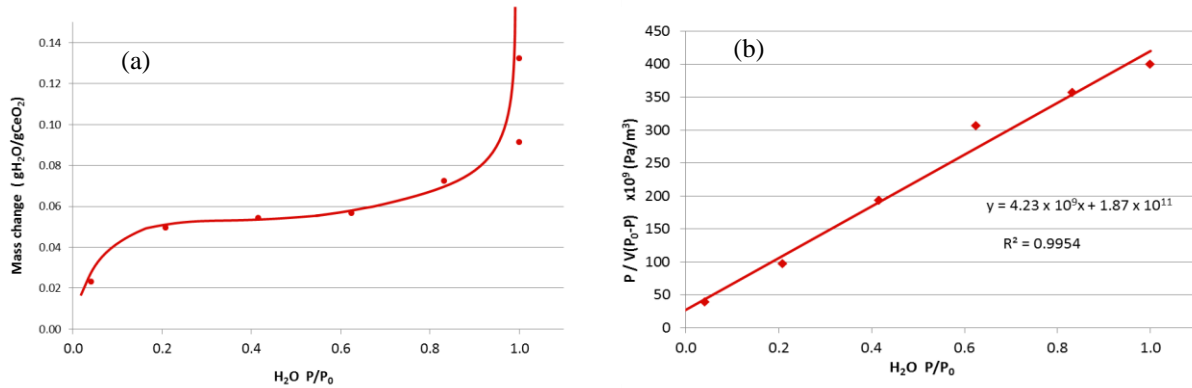


Figure 7. Graphs showing the a) change in mass of water with increasing partial pressure and b) the corresponding BET plot, with intercept $3.92 \times 10^{-9} \text{ Pa}\cdot\text{m}^{-3}$ and gradient $1.87 \times 10^{11} \text{ Pa}\cdot\text{m}^{-3}$.

The volume of an adsorbed monolayer of water on the CeO₂ films was calculated to be $2.43 \times 10^{-13} \text{ m}^3$ ($1.35 \times 10^{-8} \text{ m}^3\cdot\text{g}^{-1} \text{ CeO}_2$). Using an estimate for the footprint of a molecule of water of $1.60 \times 10^{-19} \text{ m}^2$, this corresponds to an accessible surface area of $1.30 \times 10^{-3} \text{ m}^2$ ($72 \text{ m}^2\cdot\text{g}^{-1} \text{ CeO}_2$). The mass of water absorbed at saturated humidity at 75°C corresponds to 7 monolayers of water. The ΔH_{ads} for water adsorption can also be calculated: Taking the ΔH_{liq} of water at 75°C to be 38.5 kJmol^{-1} , ΔH_{ads} for H₂O on CeO₂ was calculated to be -50.7 kJmol^{-1} . This value is within the range proposed by Paffett *et al.* for H₂O adsorption on PuO₂ of between -43 and -51 kJmol^{-1} [9], which suggests that molecular water adsorbed on CeO₂ is bound by a similar mechanism as on PuO₂.

CONCLUSIONS

We have developed a QCM based method for measuring water adsorption on CeO₂, in closed conditions. In our system, an *o*-GaPO₄ crystal is coated on one face with a voided CeO₂ film. Water adsorption on CeO₂ was measured by introducing various amounts of water into the vessel at 75°C, resulting in a range of humidities up to the saturation vapour pressure. It was found that up to 2.4 mg of H₂O adsorbs on the CeO₂ film at 75°C and 100% relative humidity, equivalent to 7 monolayers of water adsorbed over the top surface of the CeO₂ layer. This is within the range of monolayers of water reported to adsorb on PuO₂ powders [10, 14], suggesting a similar mechanism for CeO₂ binding of water. We have determined the enthalpy of

absorption of water onto CeO₂ to be -50.7 kJmol⁻¹ at 75°C, 12 kJmol⁻¹ greater than the enthalpy of evaporation. This enthalpy is within the range predicted for the absorption of water onto PuO₂, indicating this method allows for investigation of water absorption using microgram samples. Work continues to study the absorption of water onto CeO₂ at higher temperatures to discover the point at which all water is desorbed. Plans are also currently underway to apply this method directly to PuO₂ waste samples.

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