Interaction of water with plutonium oxide analogues

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The Technical Challenge

- ~250 tonnes of separated Pu currently stockpiled worldwide.

- ~50% in long-term storage in UK whilst the Government develops its options:
  1. Reuse as fuel in modern reactors.
  2. Prompt immobilisation for disposal.
  3. Continued long term storage (prior to disposition).

- Need to understand how the structure and properties of PuO_2 change with time under storage conditions (e.g. in the presence of H_2O).

- To understand the roles these processes play in gaseous product evolution from PuO_2 in storage.

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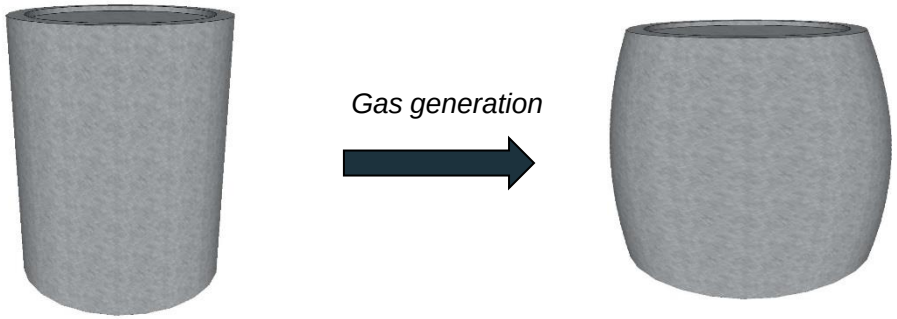
PuO_2 during Interim Storage

- Interim storage of PuO_2 involves sealing in inert steel containers.
- Under certain circumstances, these gas cans may pressurise; this must be avoided in practice.

*"worker performing general housekeeping and relocating storage cans in the interim storage vault noticed plutonium bearing storage can was **bulging on both ends*** " – Lawrence Livermore National Laboratory 1994



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Stored PuO_2 gas evolution

5 routes to gas production have been suggested:

- (i) Helium accumulation from α decay;
- (ii) Decomposition of polymeric packing material;
- (iii) H_2O desorption (steam) from hygroscopic PuO_2;
- (iv) Radiolysis of adsorbed water;
- (v) Generation of H_2 by chemical reaction of PuO_2 with H_2O, producing a postulated PuO_{2+x} phase.

The last 3 processes all involve PuO_2/H_2O interactions and are complex, inter-connected & poorly understood.

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Chemical interaction between PuO_2/H_2O

- Seems to be evidence for species that may be PuO_{2+x} or PuO_2OH
- Haschke has suggested a reaction: $PuO_2 + H_2O \rightarrow PuO_{2+x} + H_2$
  This has been disputed on thermodynamic grounds.
- Evidence for a chemical reaction may be obtained via:

  * Quantification of H_2O adsorption/desorption, e.g. by crystal microbalance.

  * Electrochemical studies analogous to those on UO_{2+x}

Quantification of H_2O adsorption/desorption

- Experimental methods have been employed to determine extent of H_2O adsorption, typically through measurement of pressure changes and use of the ideal gas equation to indirectly determine water adsorption at the plutonium oxide surface.
- At Lancaster we are seeking to directly measure water adsorption through use of Quartz Crystal Microbalance methodology. Initial work has focussed on the use of a Ceria model, in order to optimise and validate this approach.
- Current models suggest water is initially absorbed as a chemi-absorbed monolayer followed by multiple, physi-sorbed layers (with possible intermediate layers of differing binding energies).
- Knowing the surface area of the metal oxide layer and the mass of water absorbed allows the number of layers to be accurately calculated.
- The differences in temperature at which water absorption/desorption occurs allows the thermodynamics to be determined, indicating which layers are chemi- or physio-sorbed.

Quartz Crystal Microbalance

- The QCM measures in-situ mass changes at the surface of a piezoelectrode.

- Changes in mass, due to oxide formation or dissolution at the electrode surface or adsorption/desorption of gases, result in resonant frequency changes of the quartz crystal.

- Changes in frequency can be related to changes in mass through the Sauerbrey equation:

$$\Delta f = -C_f \Delta m$$

C_f = Calibration factor

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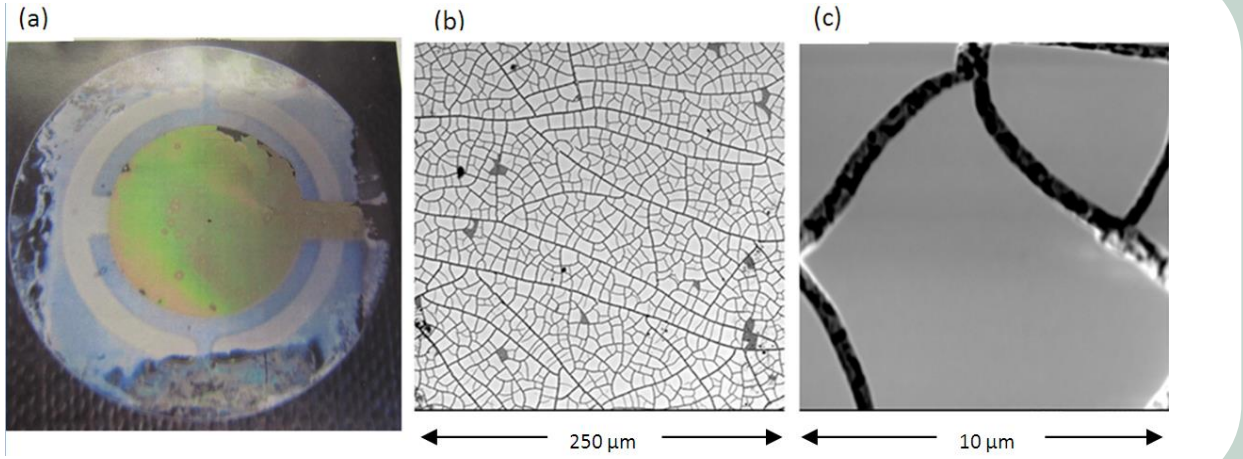
Ceria thin layer coating

Thin films of ceria were coated onto QCM crystals *via* spin-coating of a precursor solution followed by calcination at 300^{o}C.

Layers of differing depth and porosity could be produced by altering the spin-coating duration and precursor / surfactant concentration.



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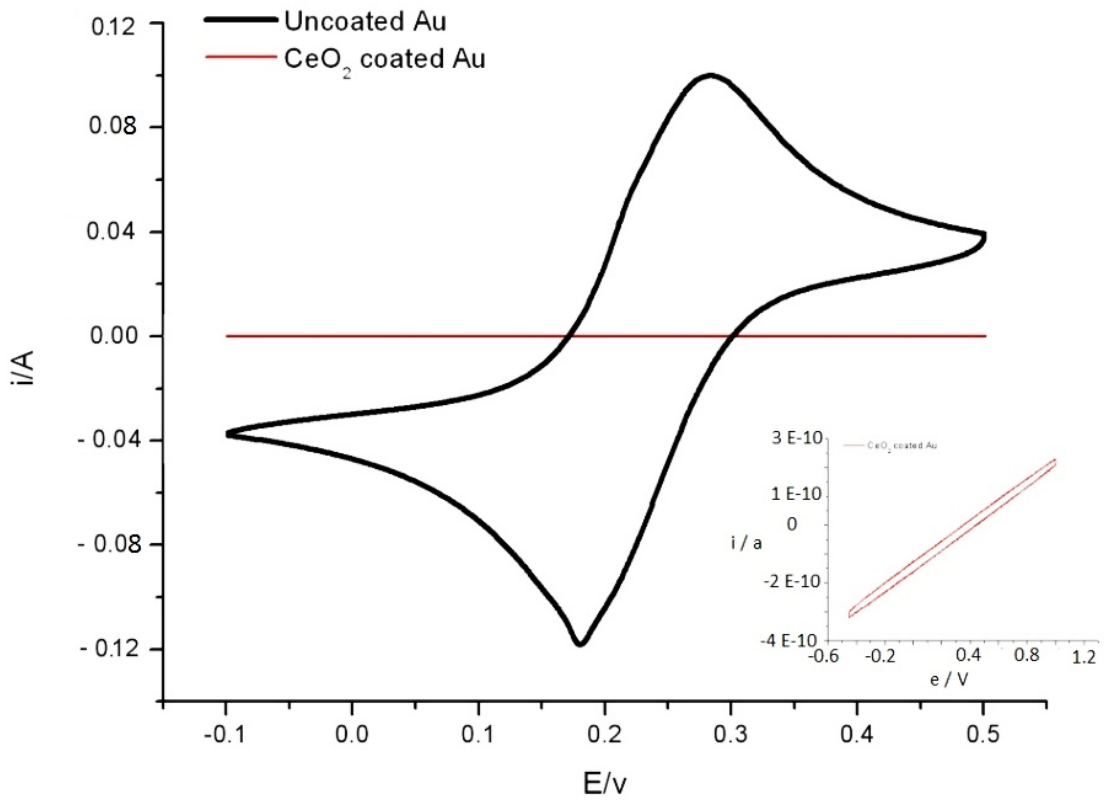
Coated crystal electrochemistry

- Crystal coated with Ceria were found to have none-conductive by cyclic voltametry, indicating complete coverage of the electrode surface.



Cycle Voltammograms of a QCM crystal employed as a working electrode in a 3 electrode cell in 0.005moles/L of ferricyanide, at a scan rate of 5mV/sec, before and after deposition of a 400nm – thick CeO2 layer.

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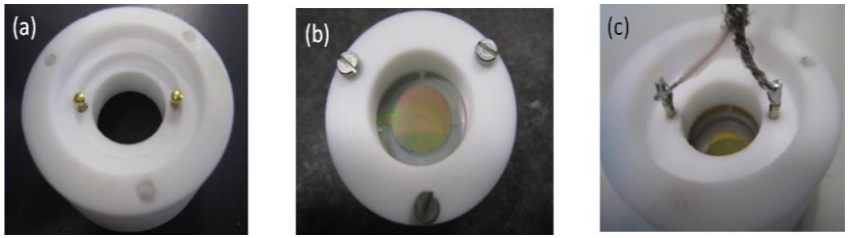
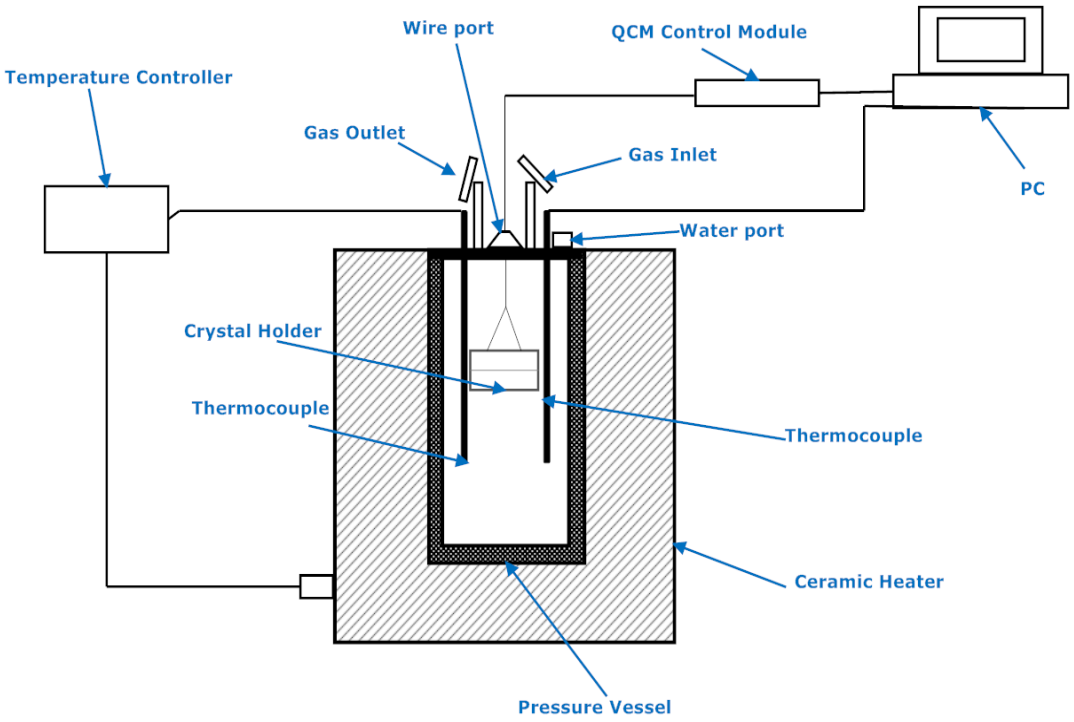
Experimental setup

The ceria-coated crystals were enclosed in a bespoke holder that allows for rapid swapping of crystals and measurement of voltage changes produced.



This assembly then sealed in a closed reactor system capable of monitoring and controlling temperature and pressure. The addition of aliquots of water allows the relative humidity to be controlled.



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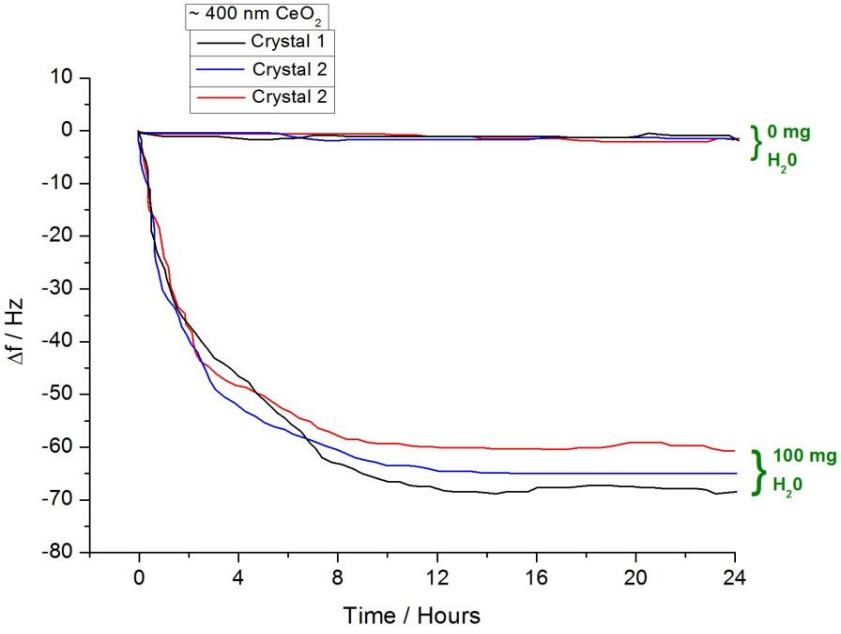
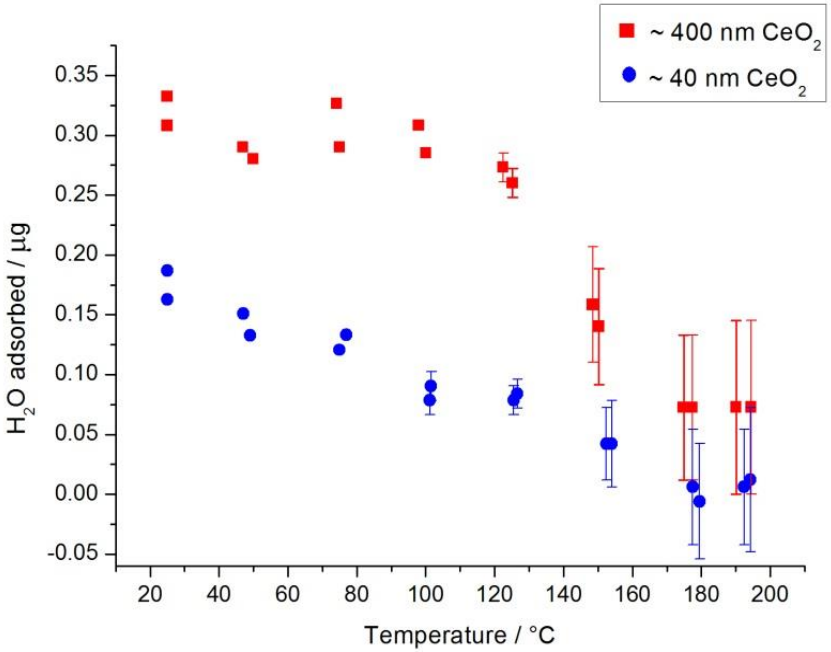
Lancaster results



Water adsorption on 40 nm thick CeO_2 coated quartz crystals at RT.



Temperature dependence of water adsorption on 40 nm and 400 nm thick CeO_2

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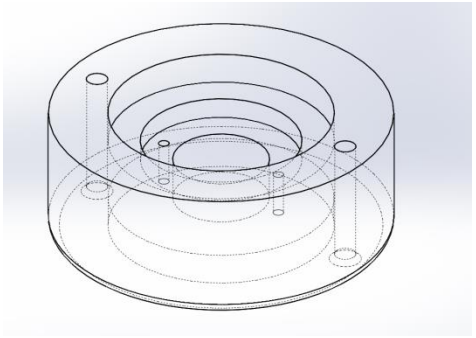
Challenge 1: Increasing accuracy up to >200°C.

- Use of $GaPO_4$ crystals (commercially available), which have a linear temperature-frequency dependence, making higher temperature measurements much more accurate

- Increase accuracy of temperature control in the vessel through positioning of sensing element near crystal surface.

- Use of a multi-crystal holder to allow concurrent measurements for direct comparison.



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Challenge 2: Increasing temperature to >500°C

- Use of $GaPO_4$ crystals, which have a higher piezoelectric limiting temperature, allowing for higher calcination temperatures of metal oxide coatings (up to ~900^{o}C).

- Increase accuracy of temperature control in the vessel through positioning of sensing element near crystal surface.

  -> Achieved through use of commercially available high temperature QCM probe (up to ~600°C).

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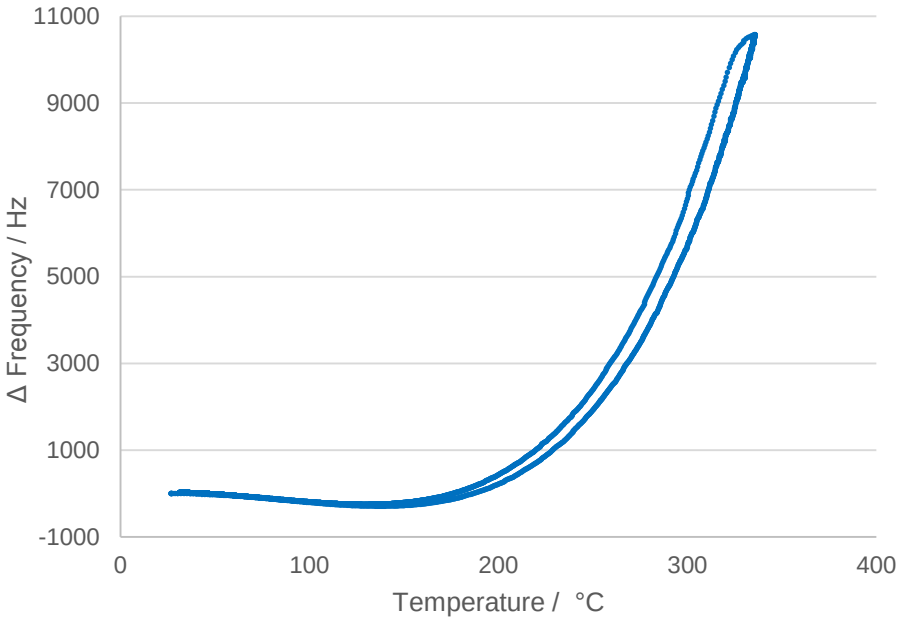
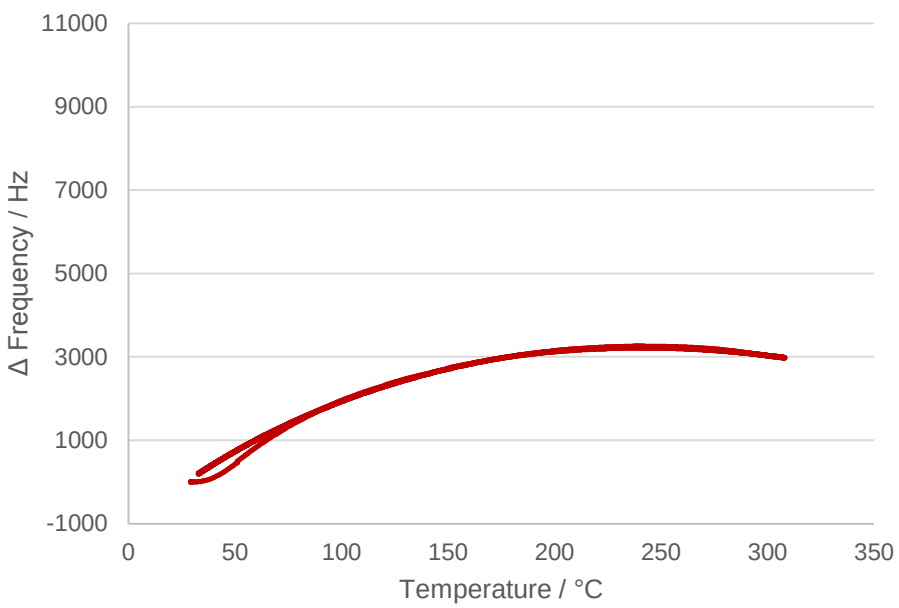
Crystal frequency temperature dependence

a)



b)



Temperature dependence of uncoated a) Quartz and b) Galium phosphate crystals, between 30 and 300°C, using high temperature QCM probe.

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Challenge 3: Doped thin films

- Pure PuO_2 is none conductive. Electrochemical studies accessible through use of doped PuO_2 samples.
- Use of UO_2 doped with Eu to mimic natural contamination of PuO_2 with Am.
- Thin layers of UO_2 and PuO_2 can be formed by oxidation and calcination of corresponding 3+ salts.
- **UTGARD Lab: U/T**h β-**G**amma **A**ctive **R**&**D** Lab
- +ve / -ve P glove boxes, SEM/EDX, γ spectroscopy, UV-vis, Raman microscopy, FT-IR/Raman, HPLC, IC, TGA, centrifugal contactors, electrochemical workstations

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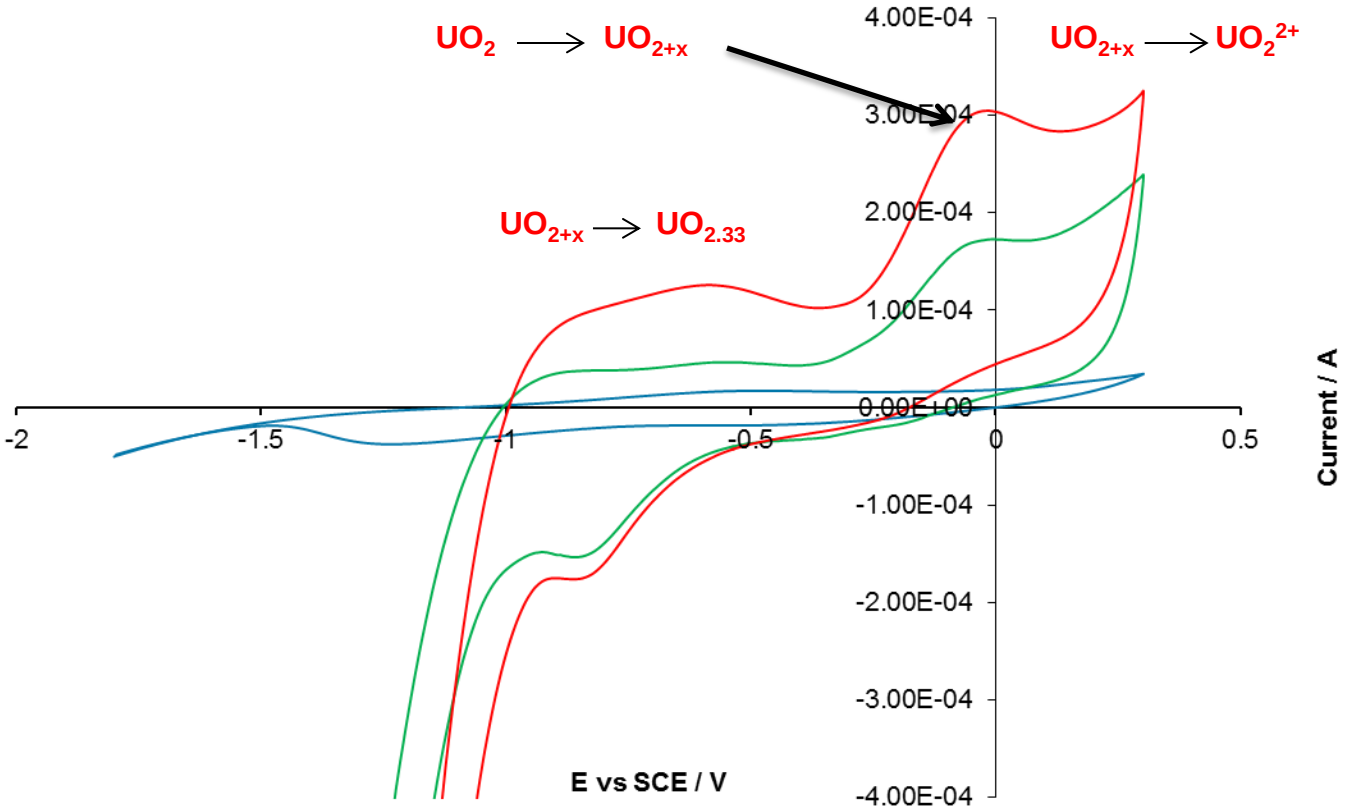
UO_2, 25 & 43 GWd/tU SIMFUEL CVs
Ar sparged 0.1 M Na_2SO_4



- Voltammetry reveals AGR SIMFUELs to be more susceptible to electrochemical oxidation than LWR;

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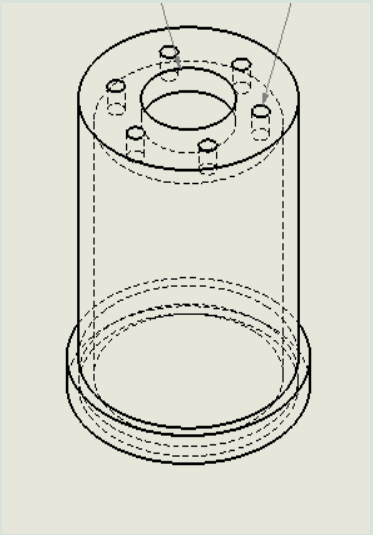
Next steps

- Have reaction vessel build to accommodate HT QCM sensor.
- Coat $GaPO_4$ crystals with cerium oxide containing different dopants (e.g. Eu).
- Temperature cycle ceria-coated quartz and $GaPO_4$ crystals.
- Electrochemical studies to probe oxide formation in doped cerium and uranium oxides.



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