Interaction of water with plutonium oxide analogues

Dominic Laventine
Colin Boxall
Lancaster University

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Lancaster

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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).

- Under certain circumstances, these gas cans may pressurise; this must be avoided in practice.

- 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

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}

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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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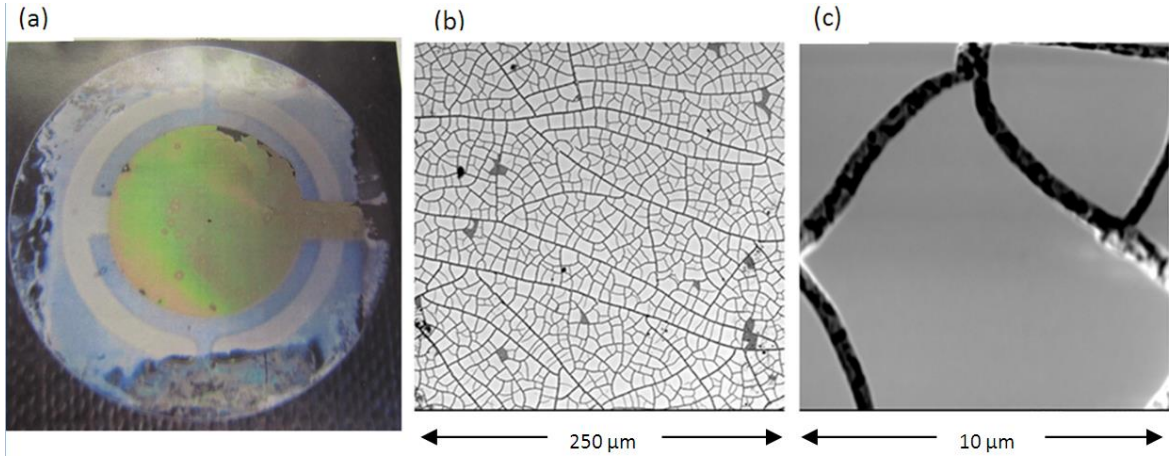
Ceria thin layer coating

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

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



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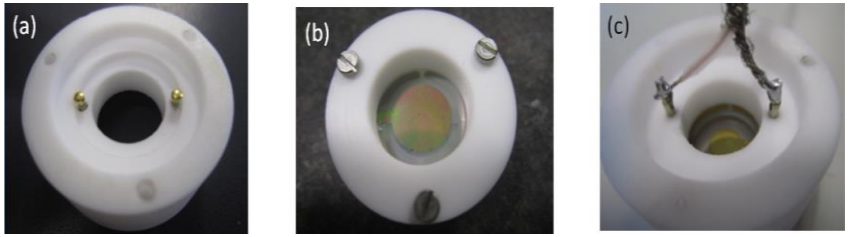
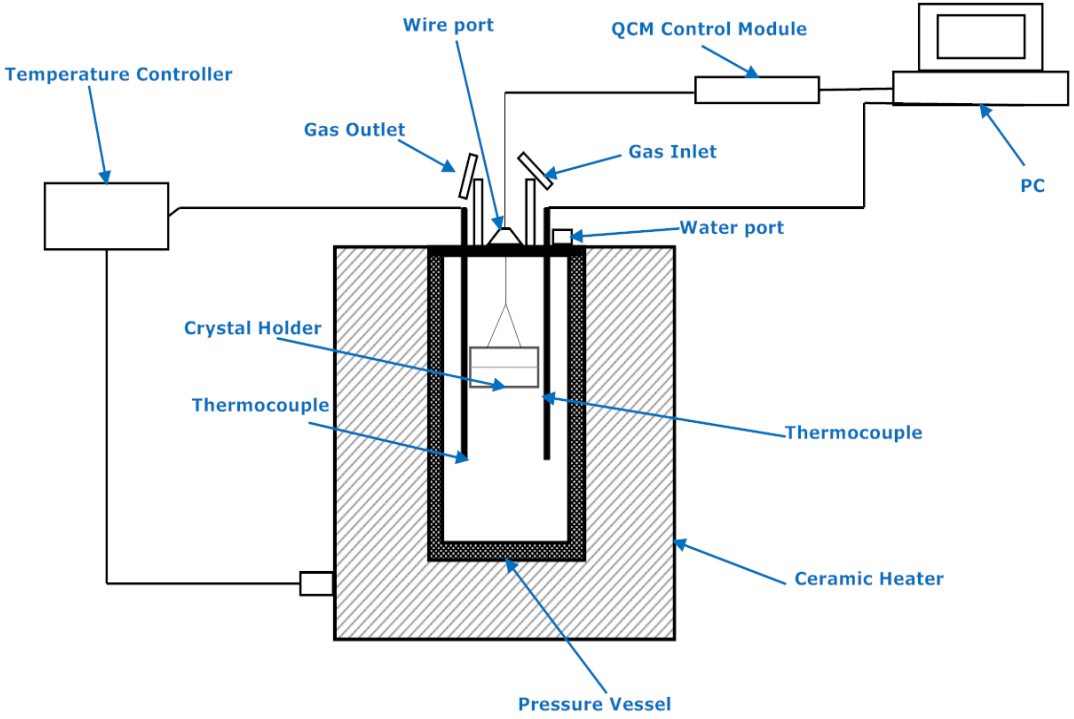
Experimental setup

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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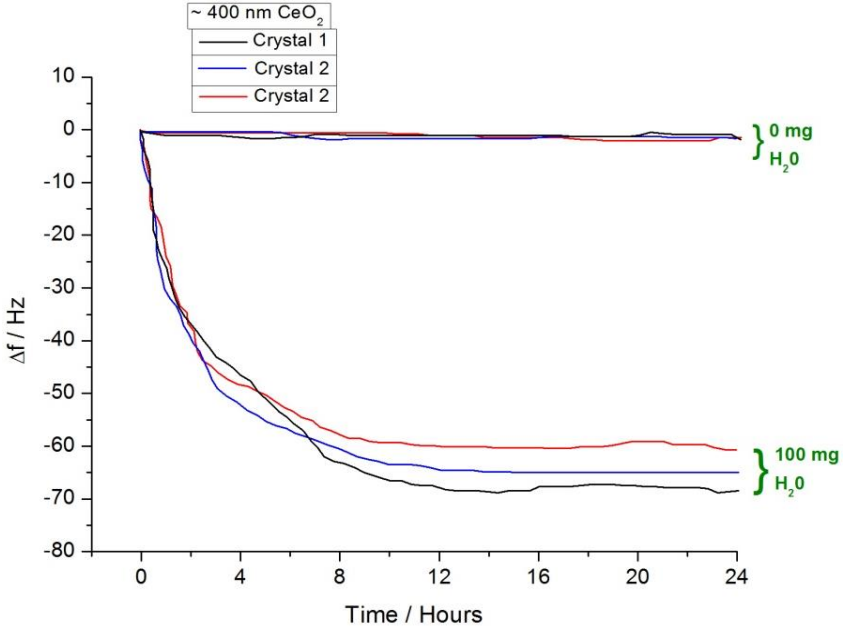
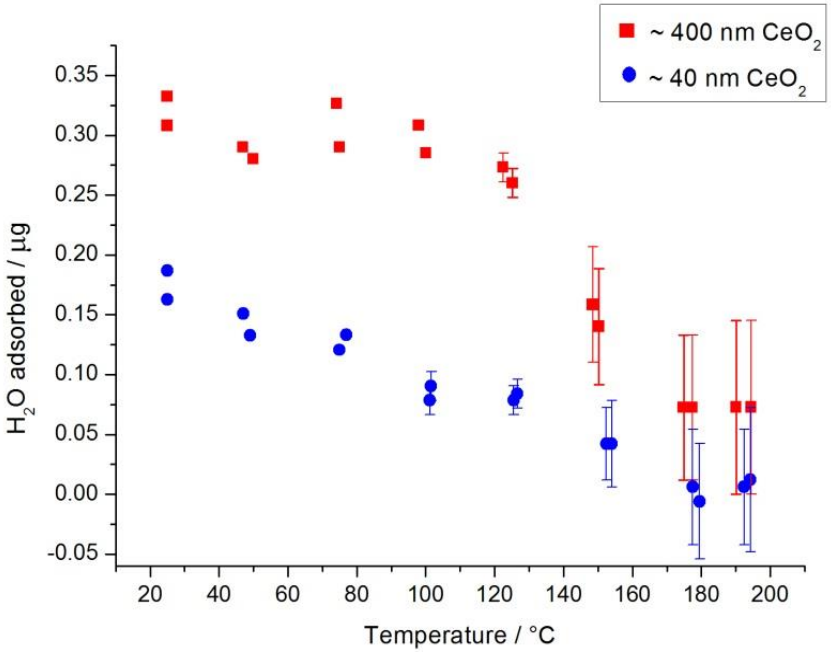
Lancaster results



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



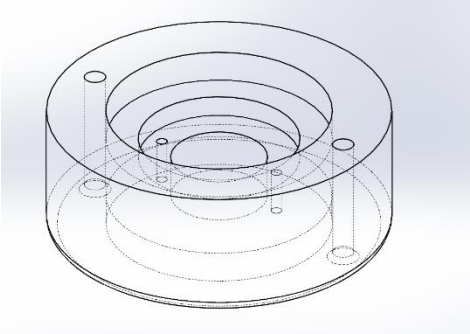
Temperature dependence of water adsorption on 40 nm and 400 nm thick CeO_2

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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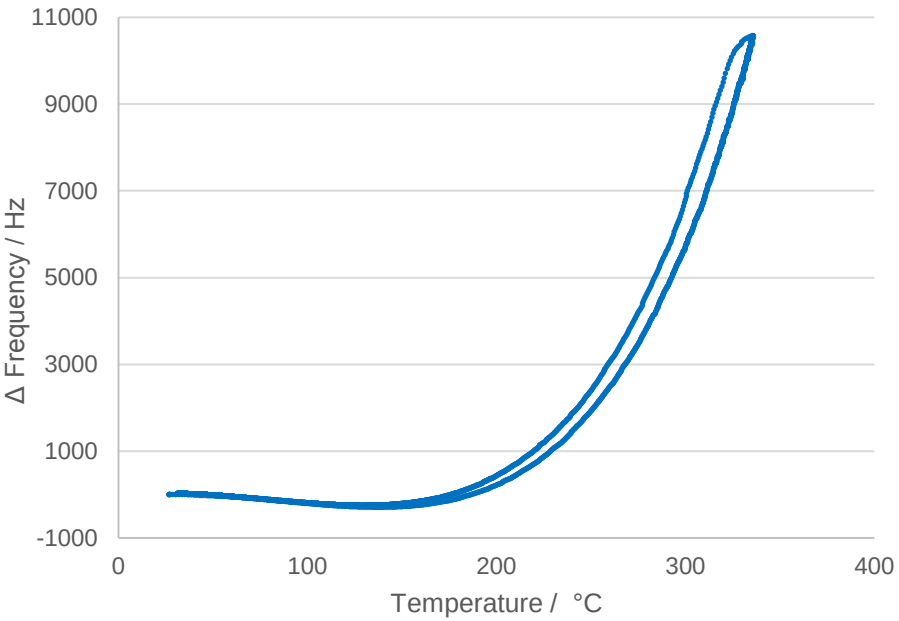
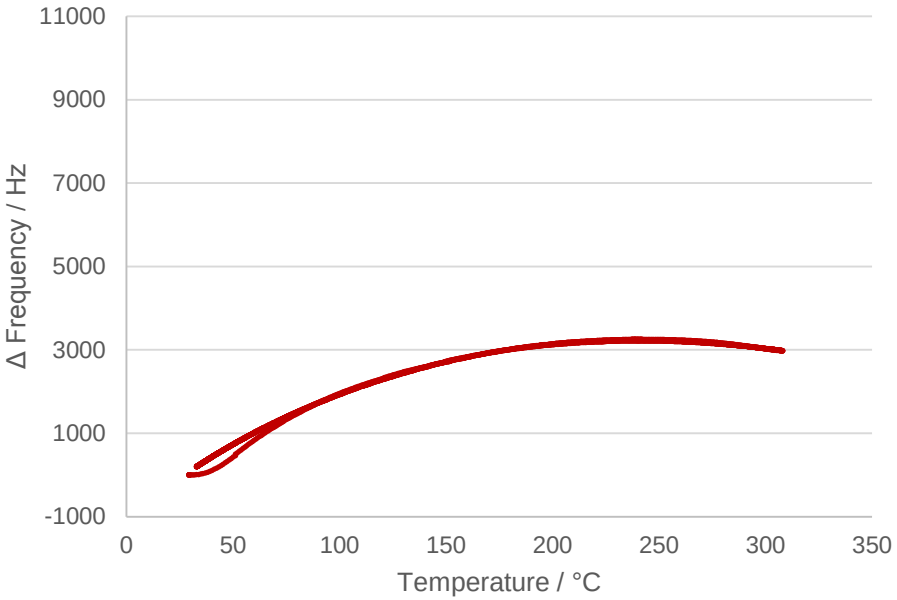
Crystal frequency temperature dependence

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 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°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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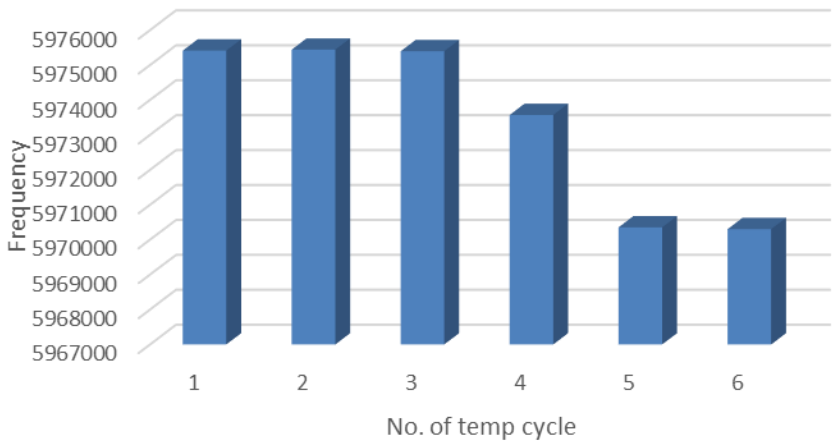
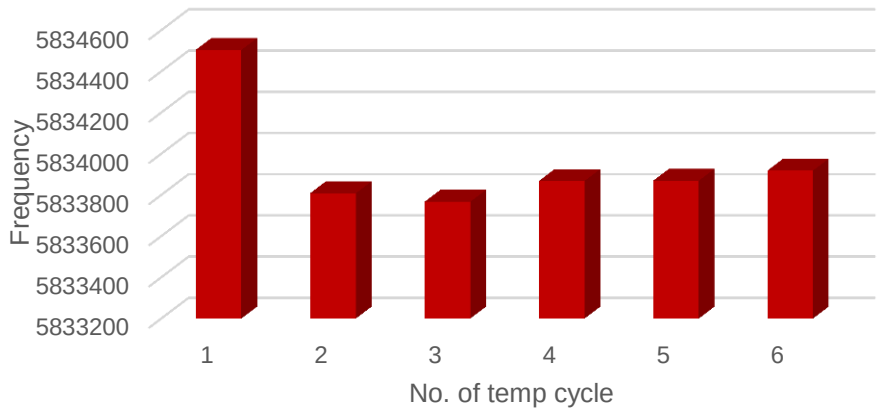
Crystal tolerance of high temperatures

a)



b)



Frequency of uncoated a) Quartz and b) Galium phosphate crystals at room temperature after repeated temperature cyclking to 550ºC.

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Ceria drop-coated $GaPO_4$ crystals

Uncoated crystal F_{25^oC} = 5833918 Hz
Coated crystal F_{25^oC} = 5826468 Hz

$$\Delta f = -\left(\frac{n f_0^{\,2}}{A\sqrt{\rho_q \mu_q}}\right)\Delta m$$

ΔF_{25^oC} = –7450 Hz
Δm = 65.5 μg

vol = 8.6 x 10^{-6} cm^3
Thickness = 250 nm

ρ_q = 3.570 $g.cm^{-1}$ n = 1
μ_q = 2.147 x 10^{11} $g.cm^{-1}s^{-2}$
Coated area = 1.54 cm^2
Active area = 0.342 cm^2
d_{CeO_2} = 7.65 $g.cm^{-3}$

$$A = N_A \frac{M}{m_r} \cdot \frac{\ln(2)}{t_{1/2}}$$

$A_{Pu^{239}}$ = 210 KBq
$A_{Pu^{240}}$ = 768 KBq
($A_{Pu^{241}}$ = 350 MBq)

$A_{Pu^{239\text{-}240(70:30)}}$ = 377 MBq

N_A = 6.022 x 10^{23} mol^{-1}
Pu^{239} $t_{1/2}$ = 24100 yrs = 760 x 10^9 s
Pu^{240} $t_{1/2}$ = 6560 yrs = 207 x 10^9 s
Pu^{241} $t_{1/2}$ = 14.4 yrs = 0.454 x 10^9 s

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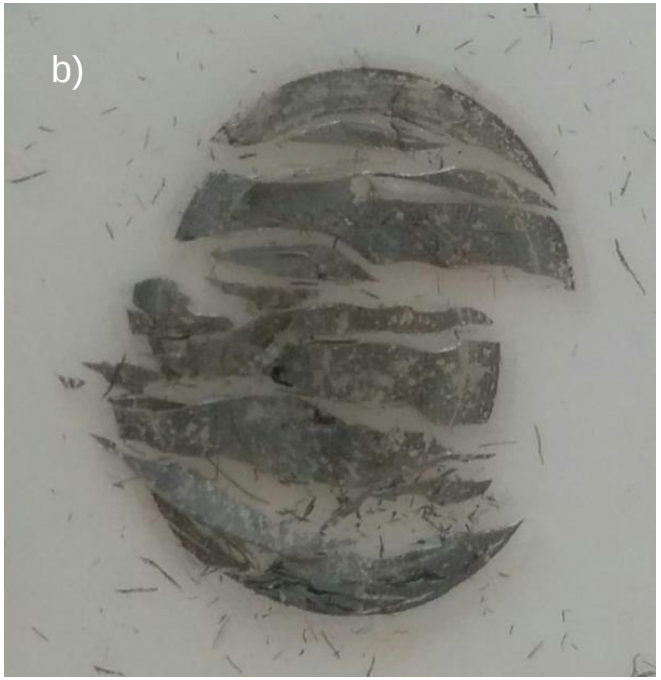
Eu-doped ceria coated crystals



a) $GaPO_4$, and b) quartz crystals, coated with 250 nm 5% Eu-doped CeO_2 coated $GaPO_4$ crystals, calcined at 950 °C

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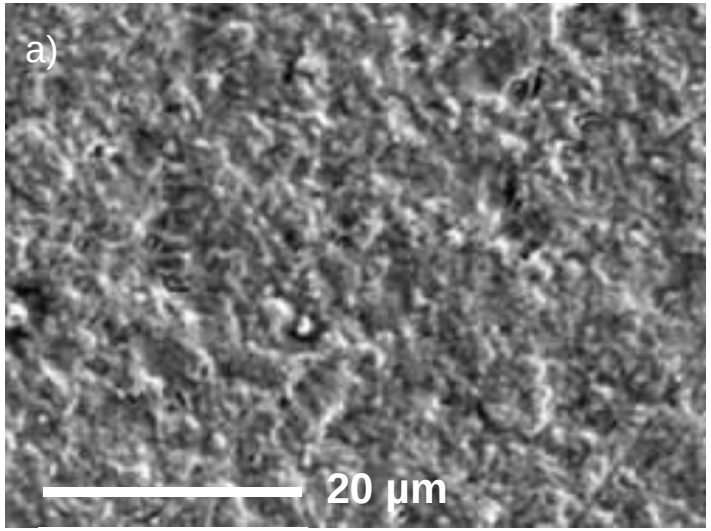
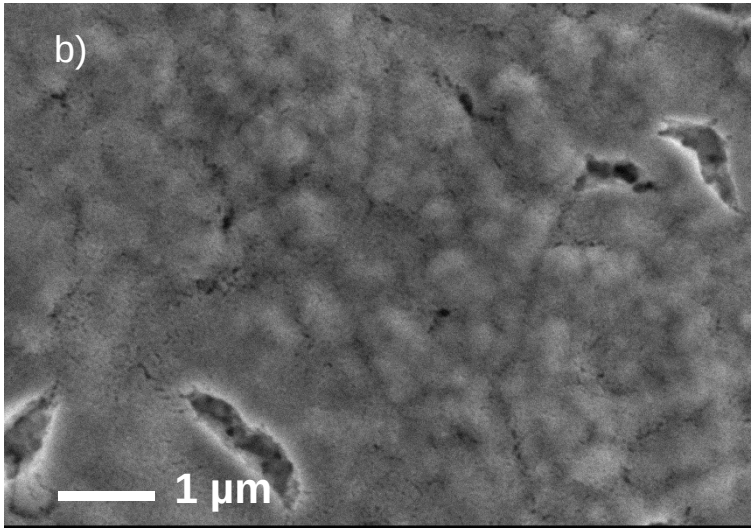
DISTINCTIVE

Eu-doped ceria coated crystals





SEM images of 250 nm coated 5% Eu-doped CeO_2 coated $GaPO_4$ crystals, calcined at 550 °C

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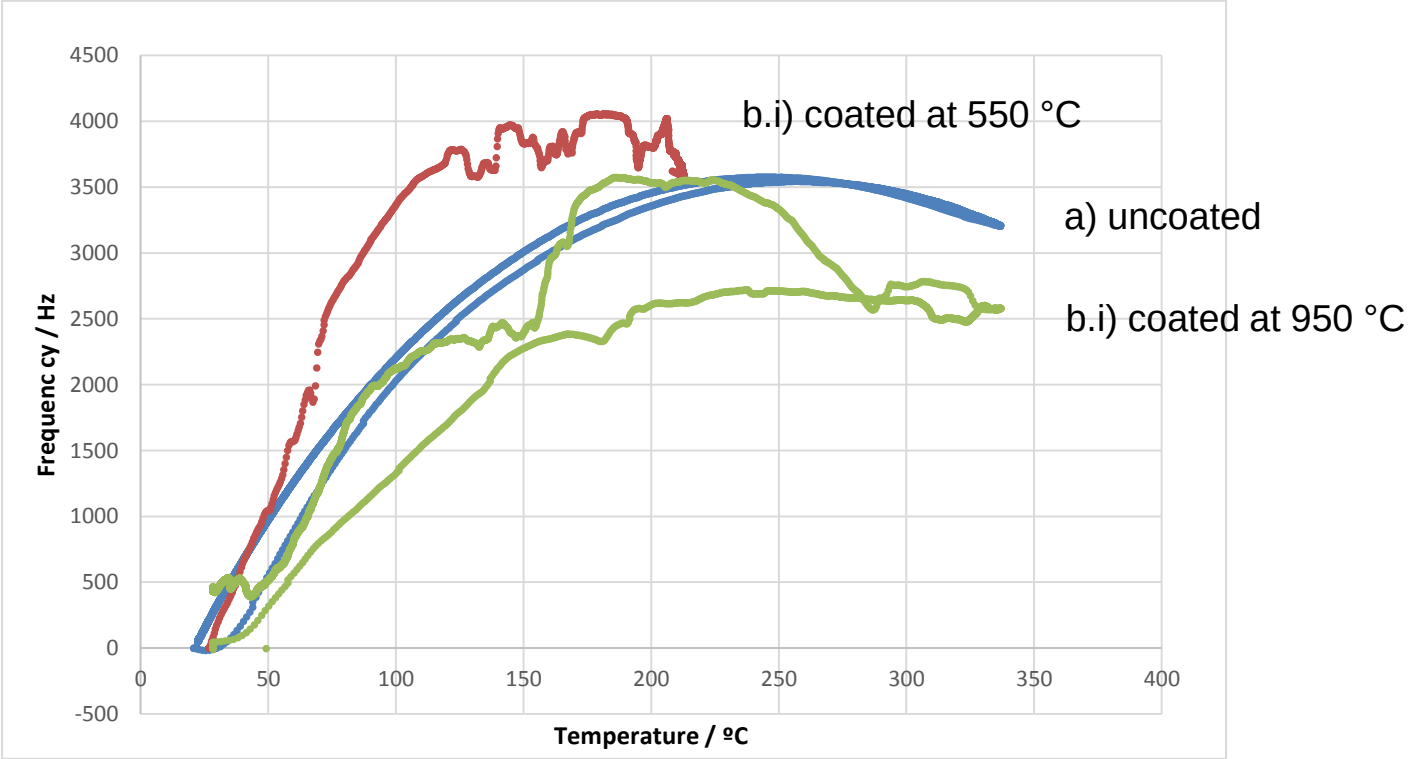
DISTINCTIVE

Eu-doped ceria coated $GaPO_4$ crystals



Frequency-Temperature dependence a) uncoated and b) 250 nm 5% Eu-doped CeO_2 coated $GaPO_4$ crystals, calcined at i) 550 and ii) 950 °C

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Ceria drop-coated $GaPO_4$ crystals

Uncoated crystal F_{25^oC} = 5975394 Hz
Coated crystal F_{25^oC} = 5974459 Hz

ΔF_{25^oC} = – 935 Hz
Δm = 7.7 μg

vol = 96.8 x 10^{-6} cm^3
Thickness = 29 nm

$$\Delta f = -\left(\frac{n f_0^{\,2}}{A\sqrt{\rho_q \mu_q}}\right)\Delta m$$

ρ_q = 3.570 $g.cm^{-1}$ n = 1
μ_q = 2.147 x 10^{11} $g.cm^{-1}s^{-2}$
Coated area = 1.54 cm^2
Active area = 0.342 cm^2
d_{CeO_2} = 7.65 $g.cm^{-3}$

A_{Pu239} = 20 KBq a
A_{Pu240} = 87 KBq a
A_{Pu241} = 40 MBq b
A_{Pu242} = 1.5 KBq a

$$A = N_A \frac{M}{m_r} \cdot \frac{\ln(2)}{t_{1/2}}$$

N_A = 6.022 x 10^{23} mol^{-1}
Pu^{239} $t_{1/2}$ = 24100 yrs = 760 x 10^9 s
Pu^{240} $t_{1/2}$ = 6560 yrs = 207 x 10^9 s
Pu^{241} $t_{1/2}$ = 14.4 yrs = 0.454 x 10^9 s
Pu^{242} $t_{1/2}$ = 373300 yrs = 11.8 x 10^{12} s

Magnox waste = $Pu^{239:240:241:242}$ 68.8 : 25.0 : 5.3 : 1.2
$A_{PuMagnox}$= 2.2 MBq

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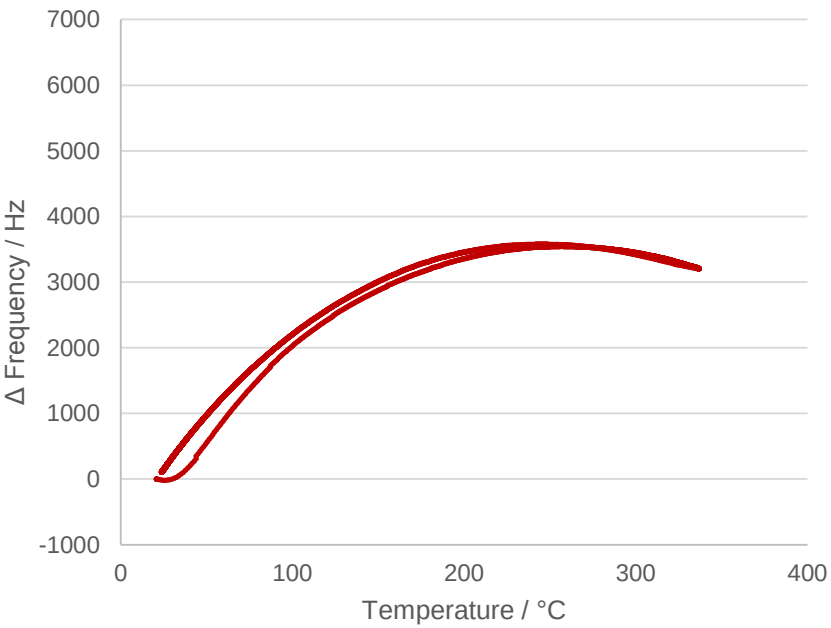
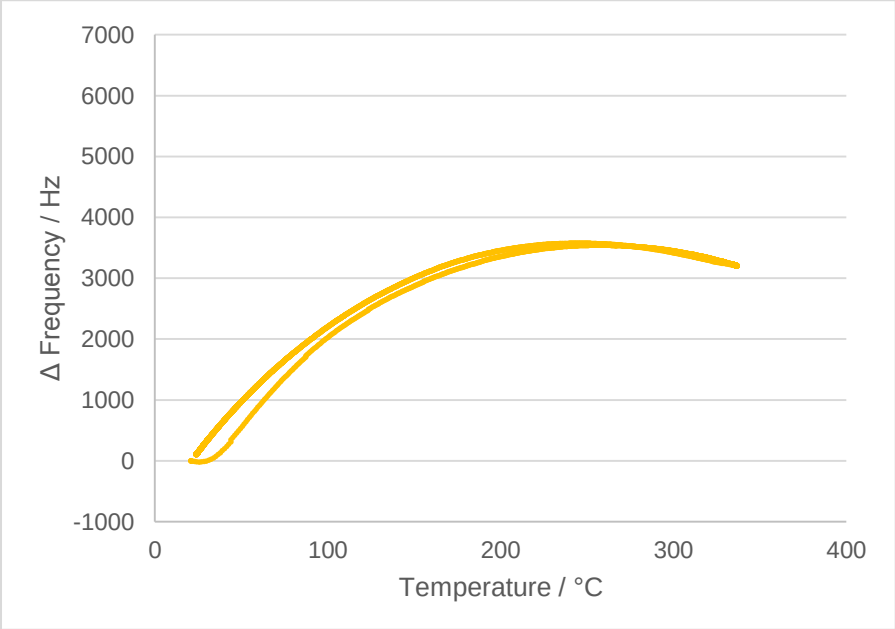
Ceria coated $GaPO_4$ crystals

a)



b)



Frequency-Temperature dependence a) uncoated and b) 28 nm 5% Eu-doped CeO_2 coated quartz crystals, between 30 and 350°C, using high temperature QCM probe.

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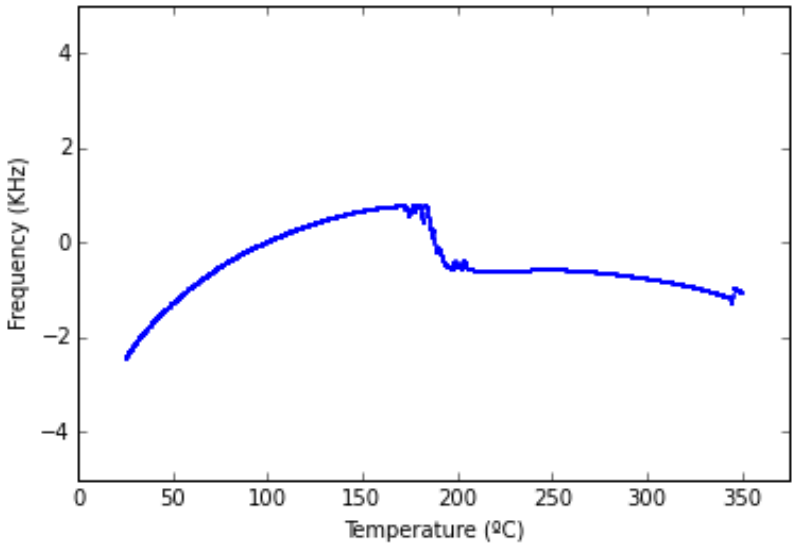
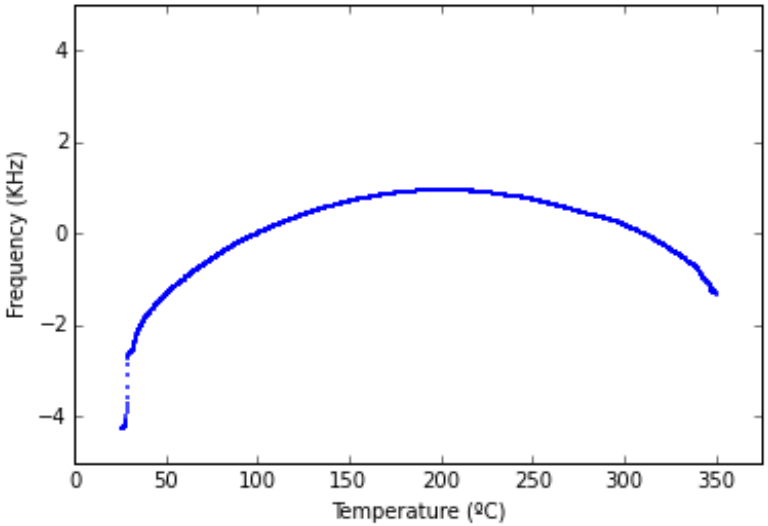
Water absorption 28 nm CeO_2 coated $GaPO_4$ crystals

a) Internal heating



b) External heating



Frequency-Temperature dependence 28 nm 5% Eu-doped CeO_2 coated GaO4 crystals, heated in a sealed vessel with internal heating with a) dry air and b) 300 µL water .

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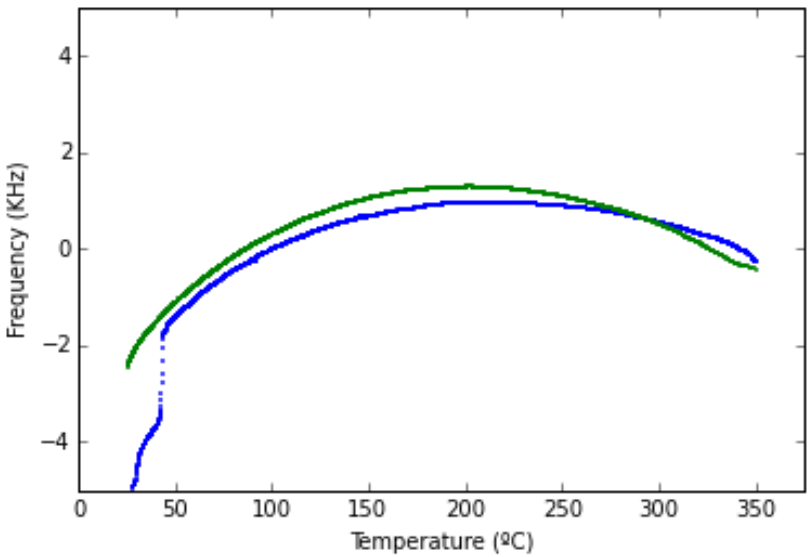
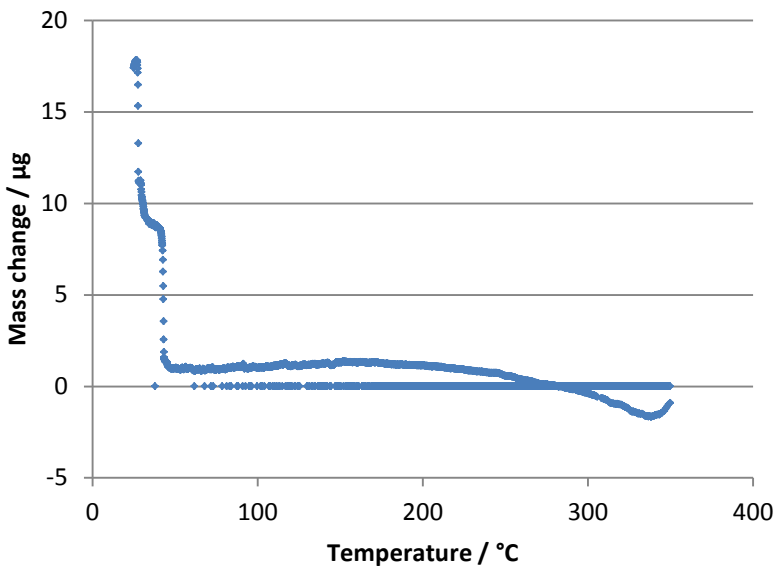
Water absorption 28 nm CeO_2 coated $GaPO_4$ crystals

a)



b)



a) Frequency-Temperature dependence, and b) calculated mass change for 29 nm 5% Eu-doped CeO_2 coated GaO4 crystals, heated in a sealed vessel with 300 µL water .

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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 with stopped-flow, Raman microscopy, FT-IR, HPLC, IC, TGA-DSC-MS, centrifugal contactors, electrochemical workstations

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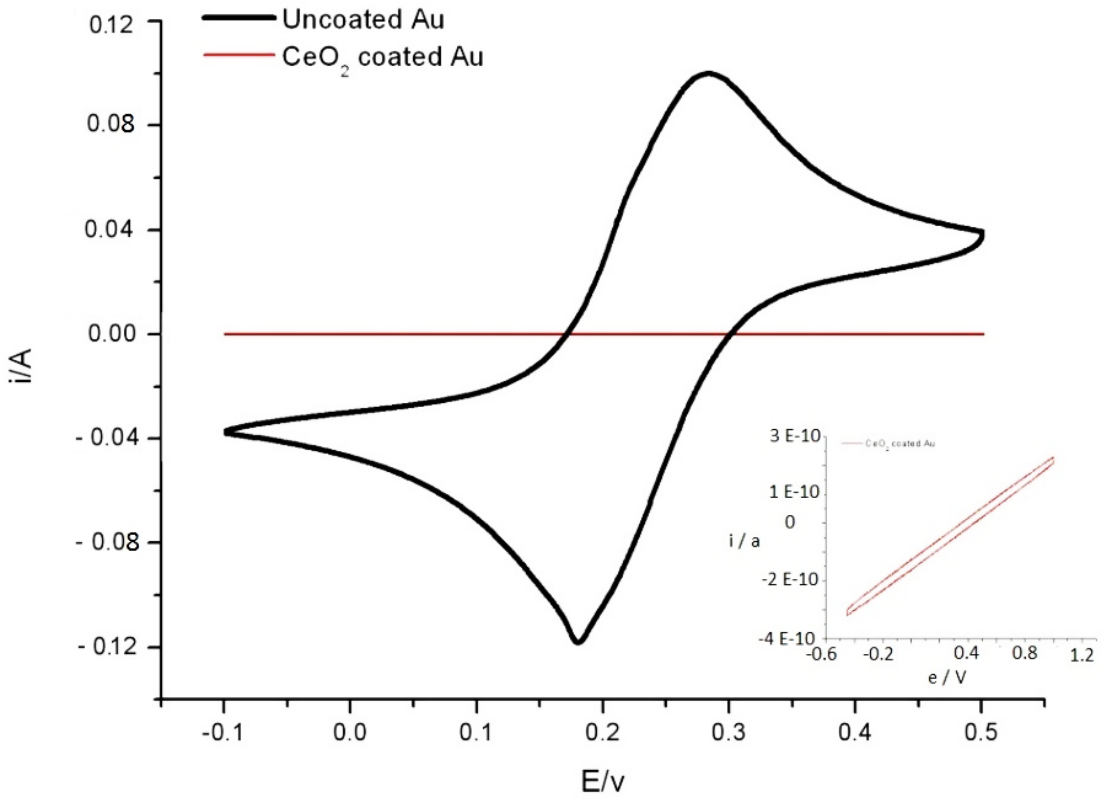
Coated crystal electrochemistry

- 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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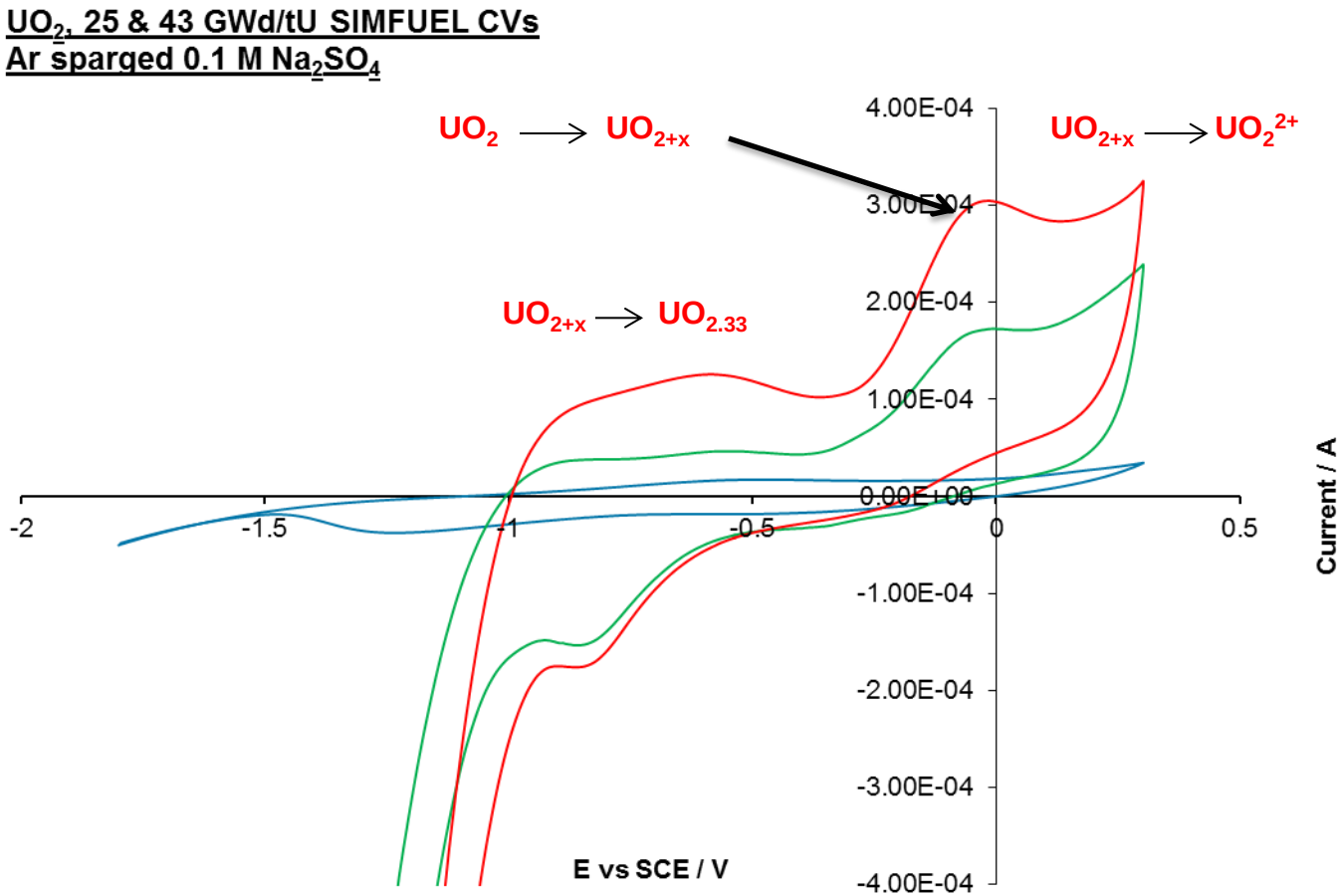
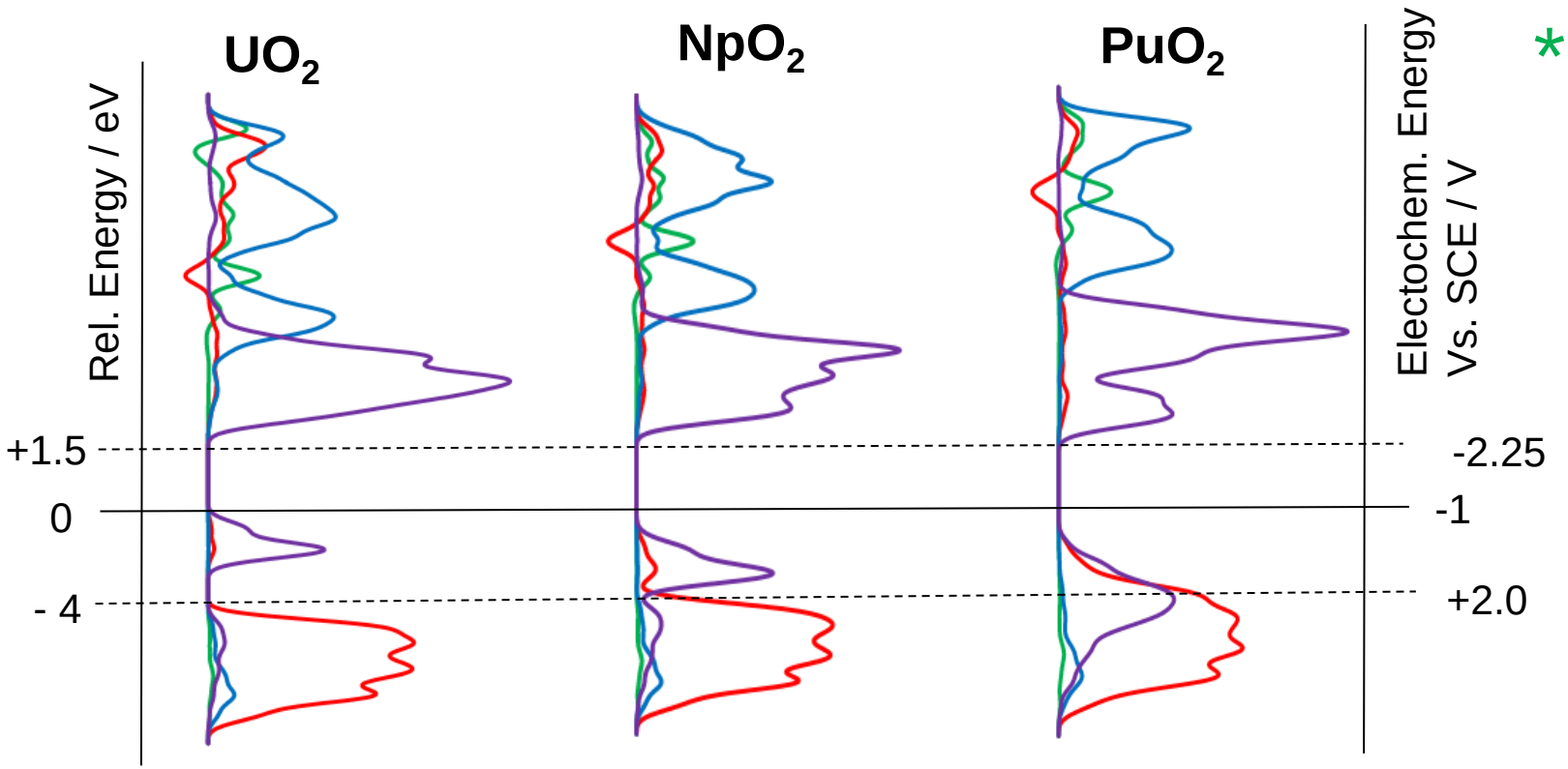


- Voltammetry reveals AGR SIMFUELs to be more susceptible to electrochemical oxidation than LWR;

Electronic Structure Calculations



- Electronic structure of bulk AnO_2 clusters calculated with PBE0 function.
- UO_2 and NpO_2 predicted to be Mott-Hubbard insulators, PuO_2 predicted to be a charge transfer insulator.
- PuO2 requires solvent with higher electrochemical limit e.g. butyrolactone

* Joseph Wellington, Nikolas Kaltsoyannis, Modelling Water Adsorption on Plutonium Oxide Surfaces, 2015

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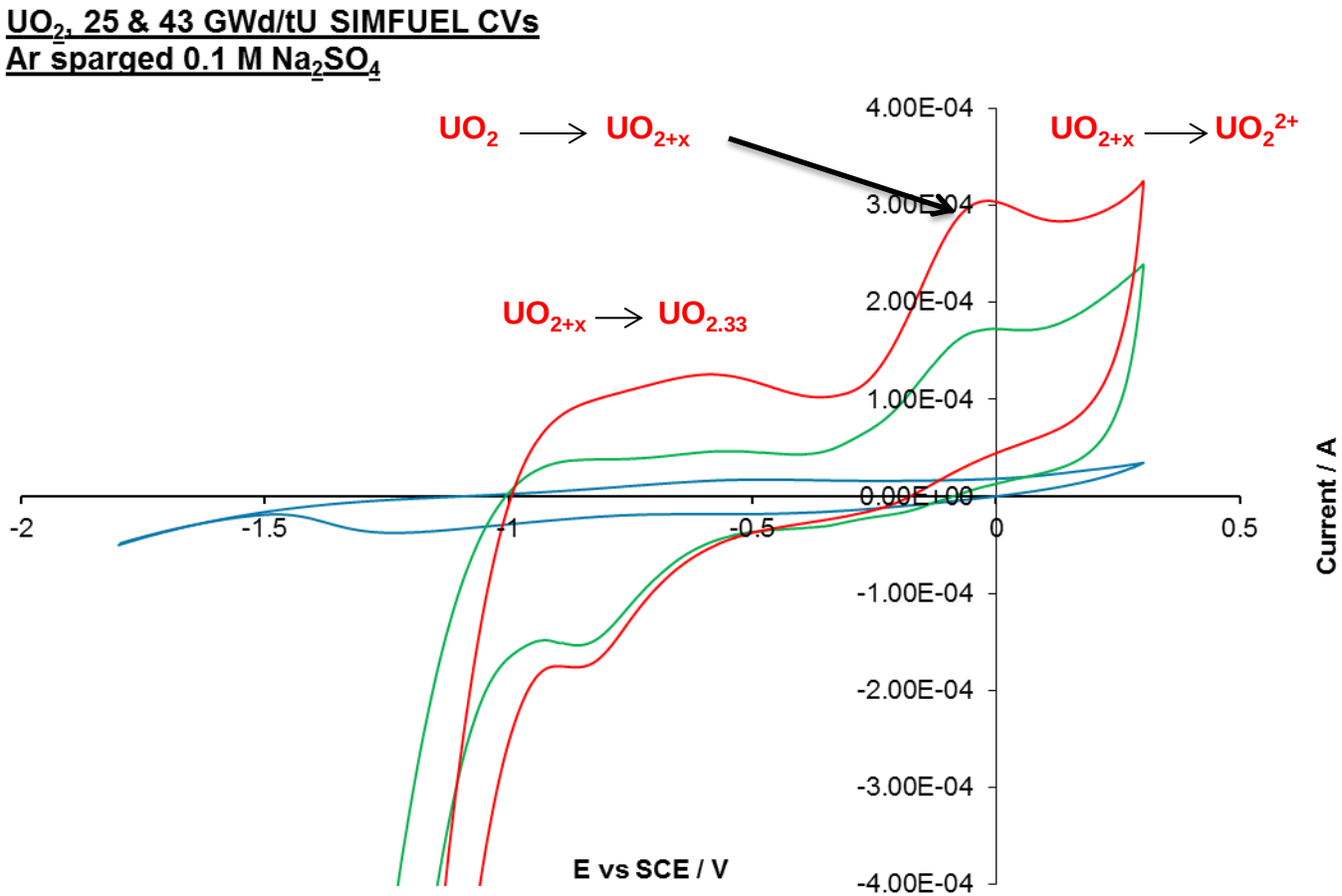


- Voltammetry reveals AGR SIMFUELs to be more susceptible to electrochemical oxidation than LWR;

Sol-Gel UO_2 & PuO_2 layers 1

$UO_2(NO_3)_2.6H_2O$

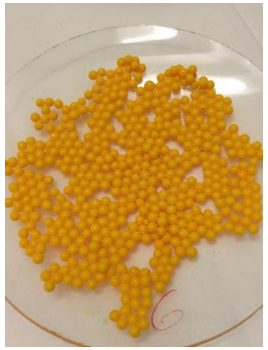
+ HMTA + Urea

$\xrightarrow[60^oC]{H_3O}$

U_xO_y (gel)

Air, 800ºC → U_3O_8

H_2, 1200ºC → UO_2



Studies on preparation of $(U_{0.47},Pu_{0.53})O_2$ microspheres by internal gelation process
A. Kumar, J. Radhakrishna, N. Kumar, Rajesh V. Pai, J.V. Dehadrai, A.C. Deb, S.K. Mukerjee.
Journal of Nuclear Materials (2013), 434, (1-3), 162-169.

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Sol-Gel UO_2 & PuO_2 layers 2

$$PuO_2(NO_3)_2.2H_2O + HMTA + Urea \xrightarrow[60\ ^oC]{H_3O} PuO_y\ (gel) \xrightarrow[1000\ ^oC]{Air} PuO_2$$

$$Pu(NO_3)_4 \xrightarrow[50^oC]{H_3O} Pu(C_2O_4)_2 \xrightarrow[450\text{-}1000\ ^oC]{Air} PuO_2$$

$$Pu(NO_3)_4 \xrightarrow{Air,\ 600\ ^oC} PuO_2$$

S. E. Bronisz and D. L. Douglass. Physica status solidi (b) 29(2), (1998) K95–K97
Grain Growth in Thin Films of ThO_2, NpO_2, and PuO_2

X. Machuron-Mandard, C. Madic. J. Alloys and Cmpds 235 (1996) 216-224
Plutonium dioxide particle properties as a function of calcination temperature

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Next steps

- Coat $GaPO_4$ crystals with cerium- and uranium oxide containing different dopants (e.g. Eu).
- Further optimisation of QCM studies (e.g. pre-drying system).
- Electrochemical studies to probe oxide formation in doped cerium and uranium oxides.
- Training for plutonium work at NNL
  - → Monitored worker training 2-9th December 2015
  - → Classified worker training 17-18th December 2015

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LU and NNL training

Examples of the types of variation in plutonium composition produced from different sources[1]

Reactor type	Mean fuel burn-up (MW d/t)	Percentage of Pu isotopes at discharge					Fissile content %
		Pu-238	Pu-239	Pu-240	Pu-241	Pu-242	
PWR	33000	1.3	56.6	23.2	13.9	4.7	70.5
	43000	2.0	52.5	24.1	14.7	6.2	67.2
	53000	2.7	50.4	24.1	15.2	7.1	65.6
BWR	27500	2.6	59.8	23.7	10.6	3.3	70.4
	30400	N/A	56.8	23.8	14.3	5.1	71.1
CANDU	7500	N/A	66.6	26.6	5.3	1.5	71.9
AGR	18000	0.6	53.7	30.8	9.9	5.0	63.6
Magnox	3000	0.1	80	16.9	2.7	0.3	82.7
	5000	N/A	68.5	25.0	5.3	1.2	73.8

1 http://www.world-nuclear.org/info/Nuclear-Fuel-Cycle/Fuel-Recycling/Plutonium/

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