The Influence of Composition and Structure on the Reactivity of UO_2

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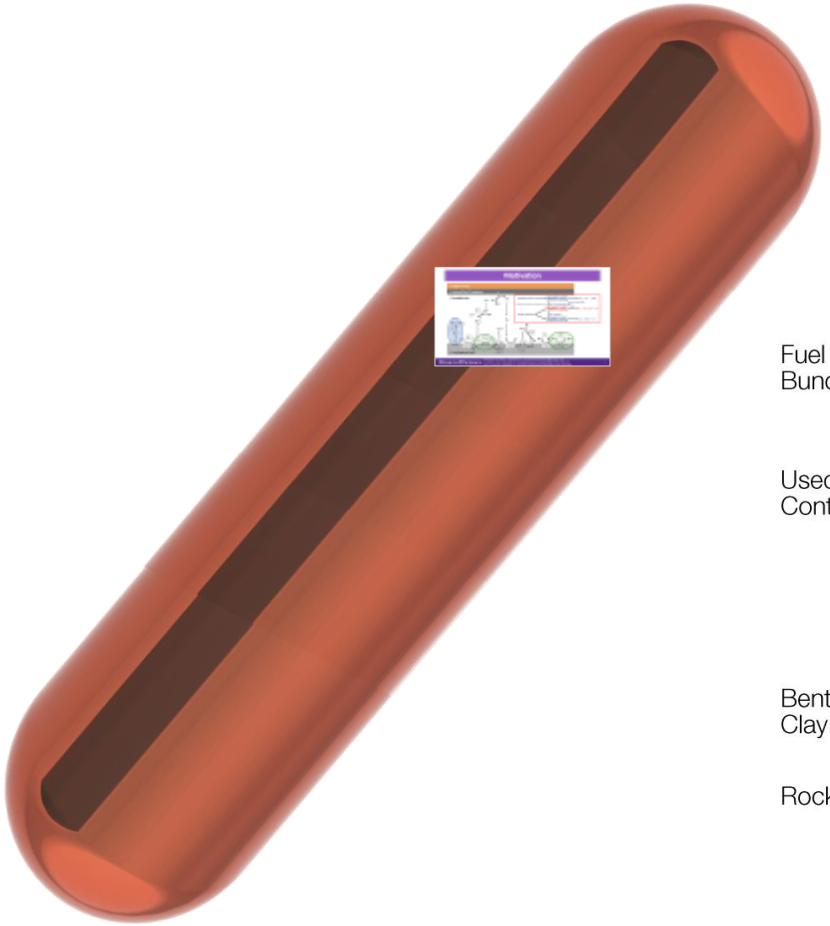
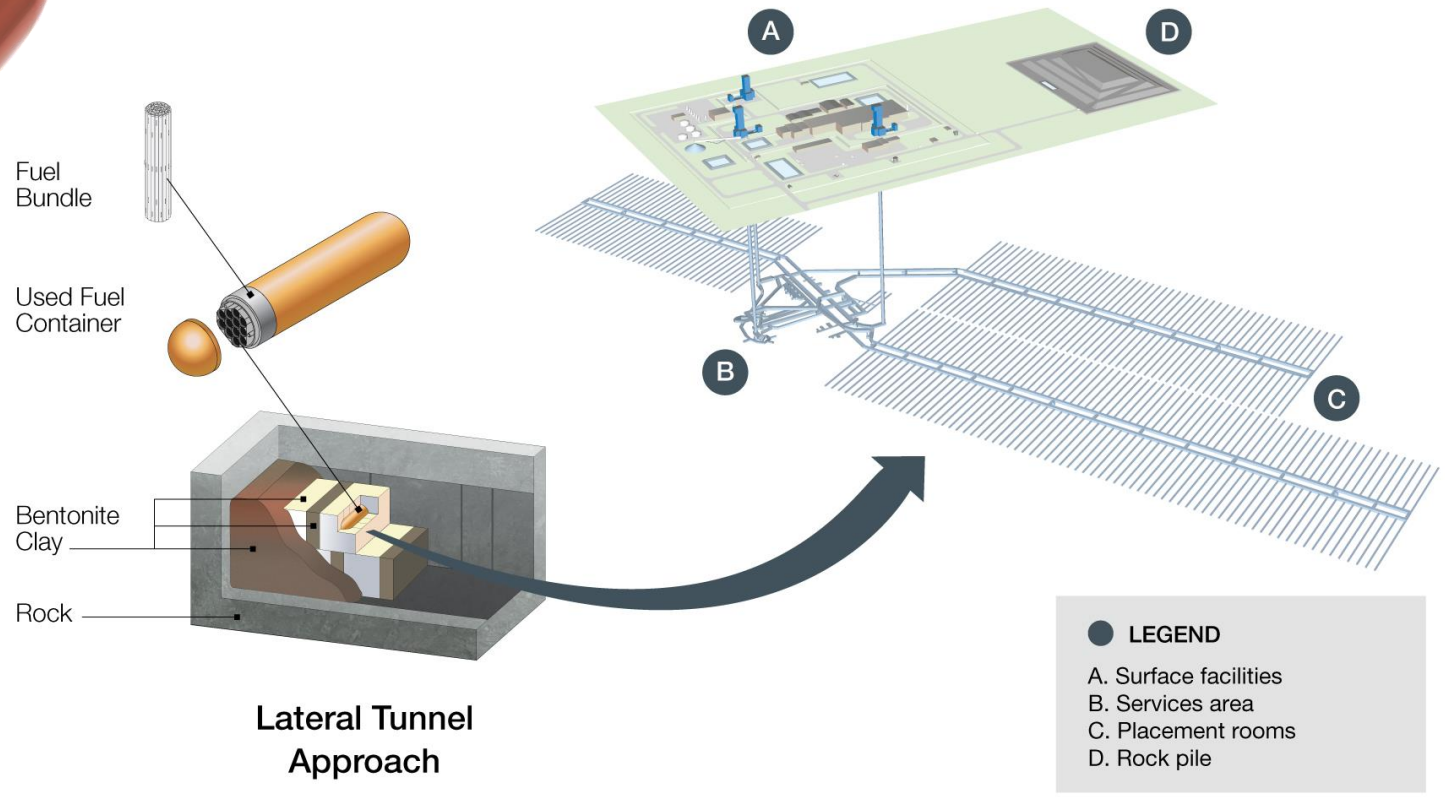
PREMIER LEAGUE
ELECTROCHEMISTRY & CORROSION SCIENCE

Canada's Plan for Used Nuclear Fuel



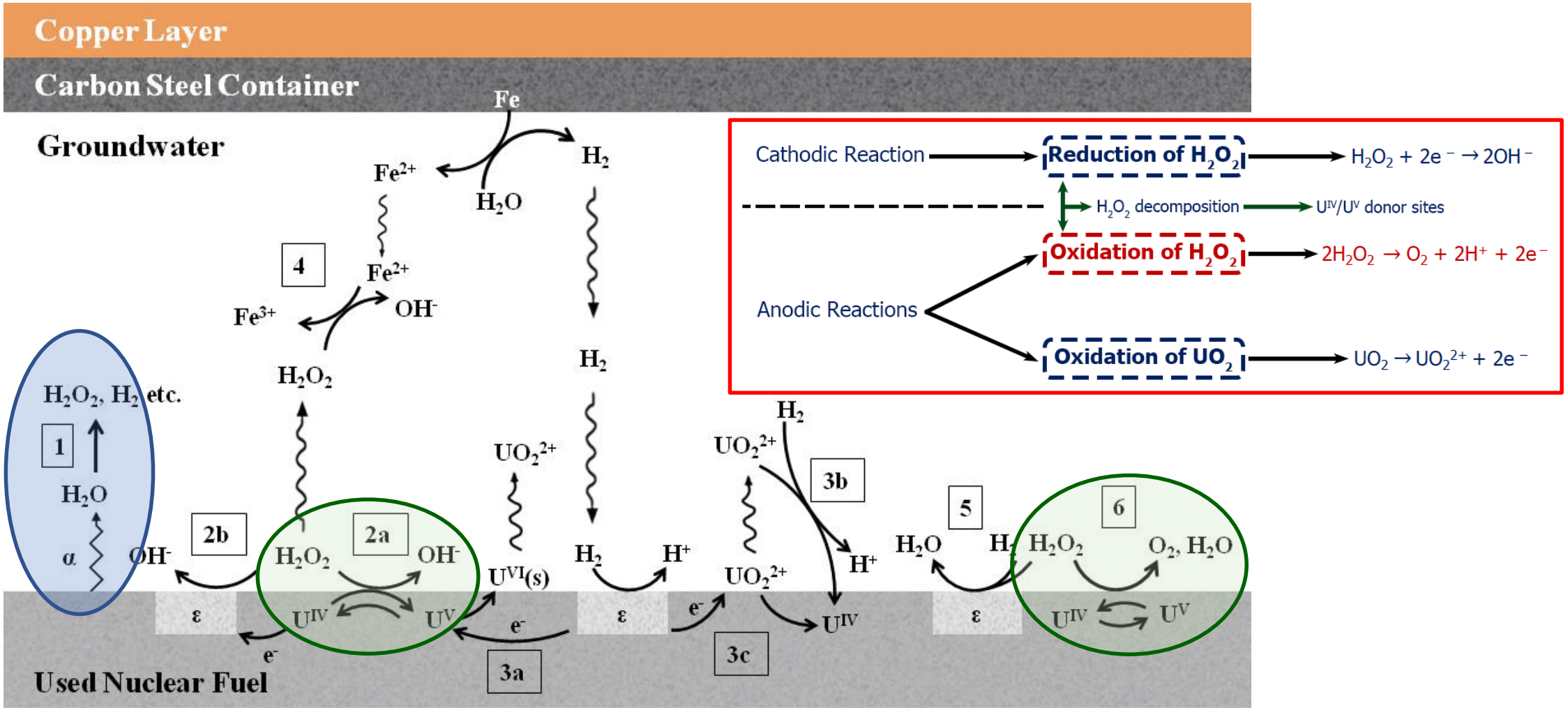
Deep Geological Repository (DGR)



Lateral Tunnel Approach

NWMO, Implementing Adaptive Phased Management 2016-2020, 2016.

Motivation



- Investigate the effect of radiolytically produced H_2O_2 on the reactivity of UO_2 specimens with variable properties

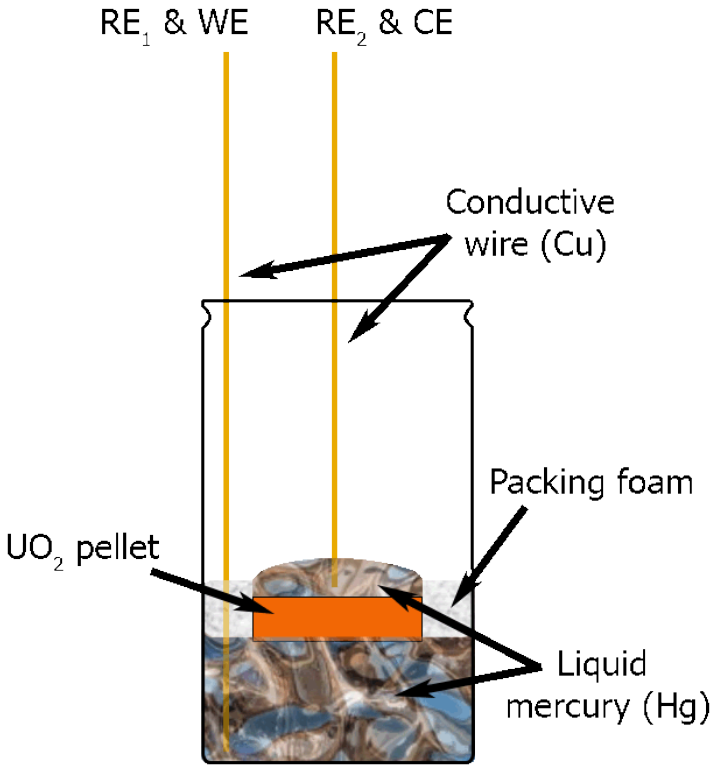
Broczkowski, M. E.; Noël, J. J.; Shoesmith, D. W., *Journal of Nuclear Materials* **2005,** *346* (1), 16-23.
Liu, N.; Wu, L.; Qin, Z.; Shoesmith, D. W., *Environmental Science & Technology* **2016,** *50* (22), 12348-12355.
Wu, L.; Liu, N.; Qin, Z.; Shoesmith, D. W., *Journal of The Electrochemical Society* **2014,** *161* (8), E3259-E3266.

Project Goals

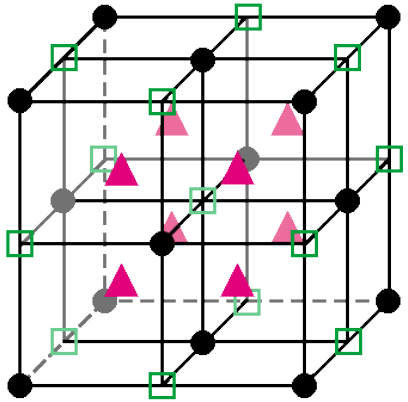
- Investigate matrix defect structures, their lateral distribution across the fuel surface, and how they influence corrosion
- Investigate possible correlations between defect structures, grain morphology, and reactivity
- Determine the variations in reactivity of fuel specimens manufactured over many years

Electrical Resistance Measurements of UO_2

- Sinusoidal input ± 10 mV
- Frequency range: 10^5 to 10^{-1} Hz
- 11 points per decade
- Sample thickness ~ 2-3 mm



The value of x in UO_{2+x} determines the conductivity

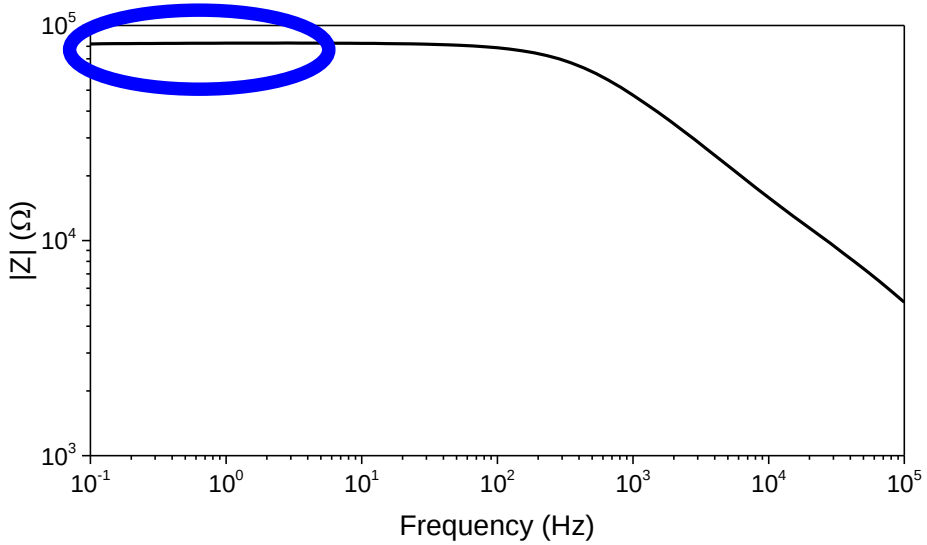


● – U
▲ – O
□ – Interstitial sites

$$\sigma = 3.8 \times 10^6 \left[\frac{(2x)(1-x)}{T}\right] \exp\left(\frac{-0.3}{kT}\right)$$

σ – conductivity (S•cm^{-1})
T – temperature (K)
k – Boltzmann constant
x – degree of hyperstoichiometry

As frequency → 0, the impedance measures the pellet resistance



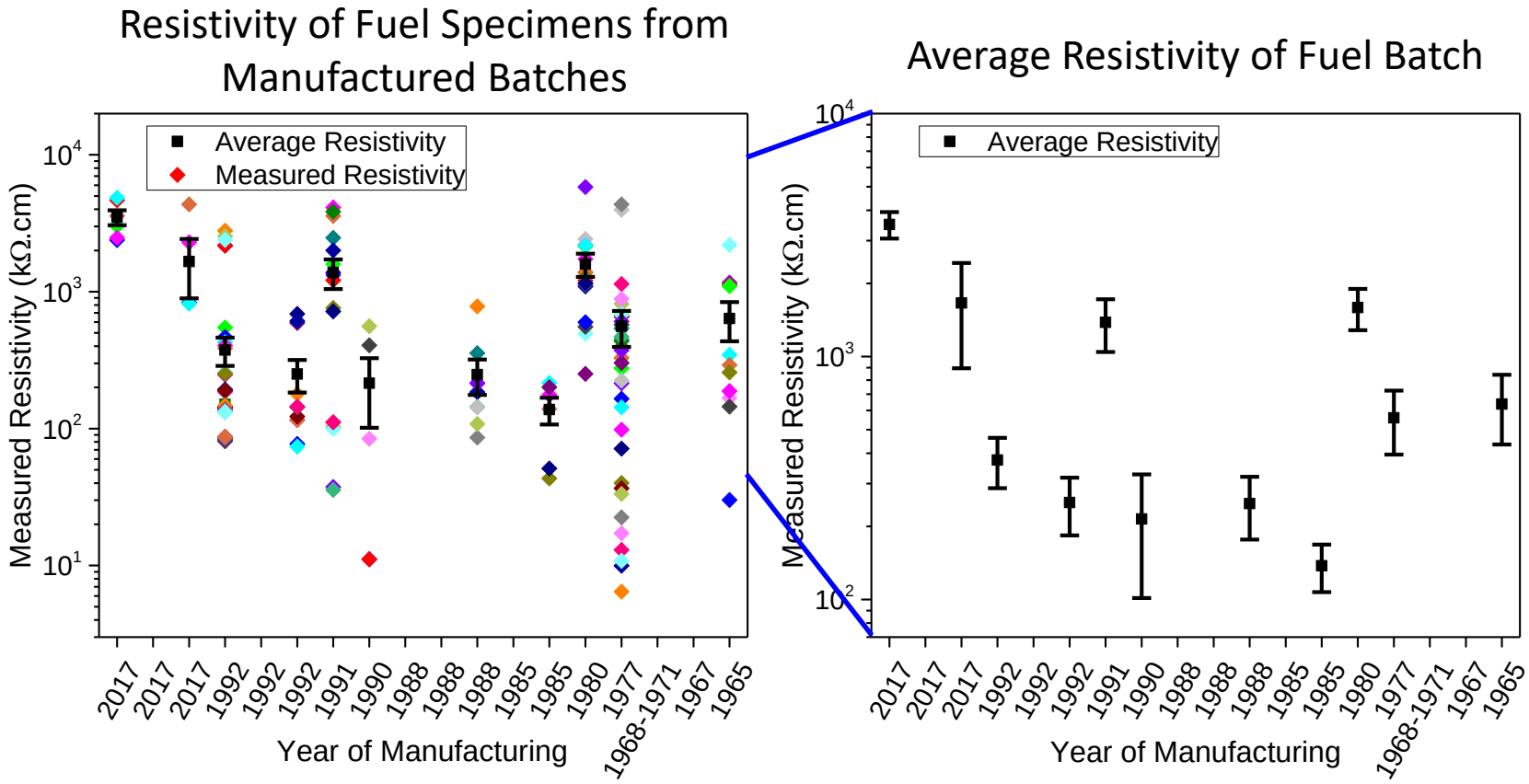
He, H.; Zhu, R. K.; Qin, Z.; Keech, P.; Ding, Z.; Shoesmith, D. W., *Journal of The Electrochemical Society* **2009,** *156* (3), C87-C94.

Resistance Measurements

Increases as the degree of hyperstoichiometry decreases

UO_2 pellet resistivity

Decreases as the degree of hyperstoichiometry increases

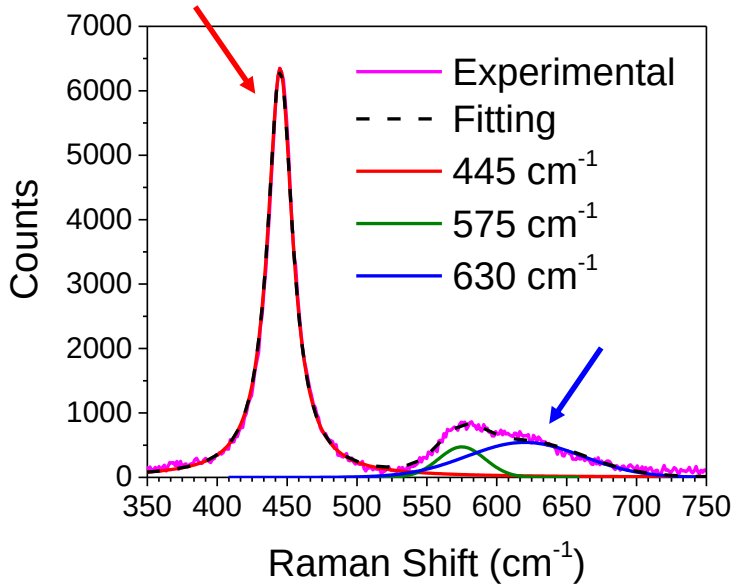


- The large range of resistivities within individual pellets could be due to incomplete reductive sintering
- Samples with low resistivities (~ 6 kΩ.cm), and others with extremely high resistivities (~ 5000 kΩ.cm)
- In general, resistivity measurements indicate a low degree of non-stoichiometry for all fuel specimens

Investigation of Lattice Defects

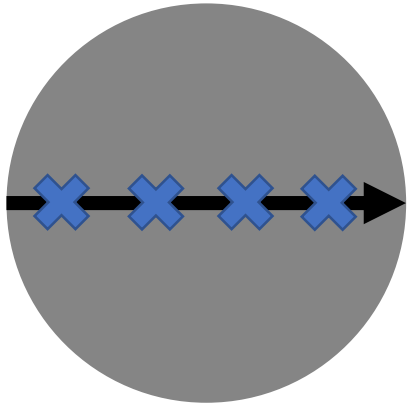
- Raman identifies material phases to identify lattice defects by probing vibrational states

- Raman peak assignments:
  1. 445 cm^{-1} → T_{2g}, fundamental U – O stretch → undisturbed UO_2 matrix
  2. 575 cm^{-1} → first order L – O phonon
  3. 630 cm^{-1} → A_{1g}, excess O^{2-} ions → lattice distortions due to increased O content



Raman Line Scan:
- Collect Raman spectra across sample surface at regular intervals

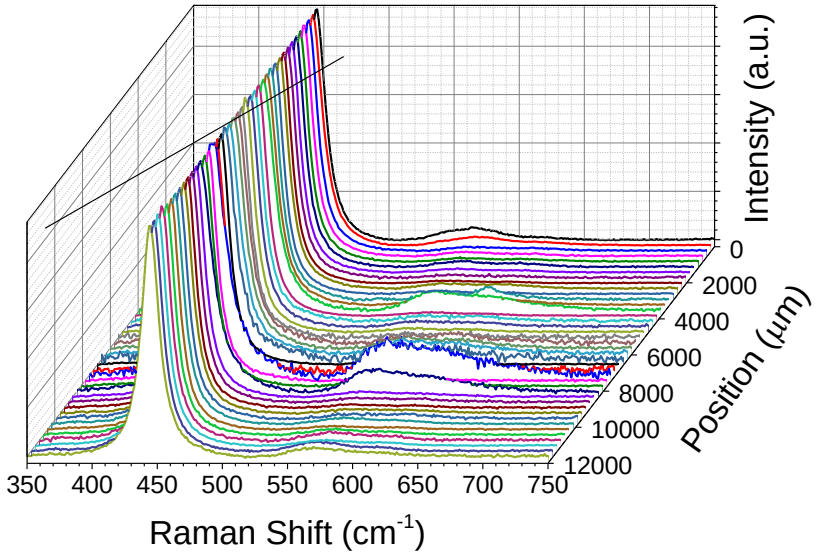
Raman Mapping:
- Map the surface to identify lattice distortion sites
- Identify lateral variations in non-stoichiometry

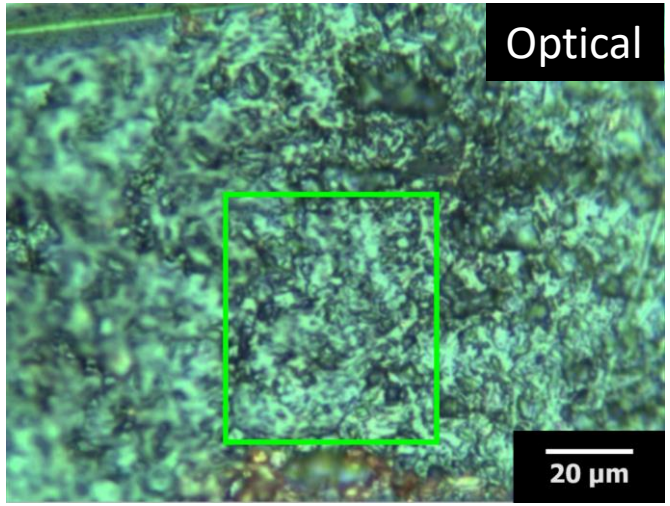


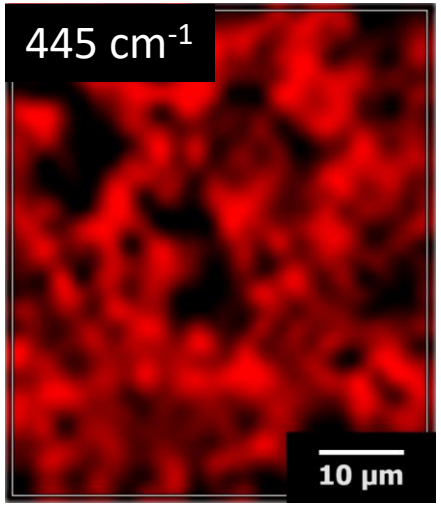
He, H.; Shoesmith, D. W., *Physical Chemistry Chemical Physics* **2010,** *12* (28), 8109-8118.

Determining Lattice Variations in Matrix Structure

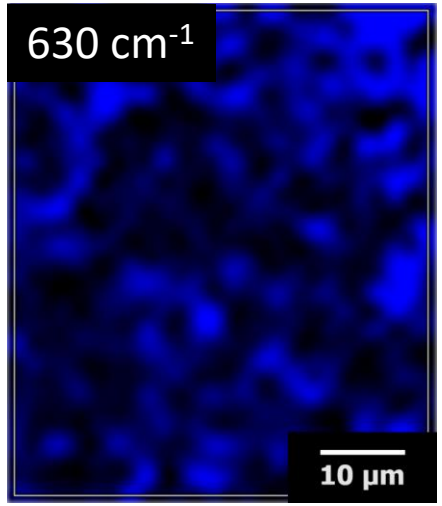
- Fuel specimen from 1990
  - Low resistivity (~ 11 kΩ.cm, thickness of 1.94 mm)
- Generally defect-free, with only a few defective locations
- Clear segregation between defect structure and undisturbed matrix







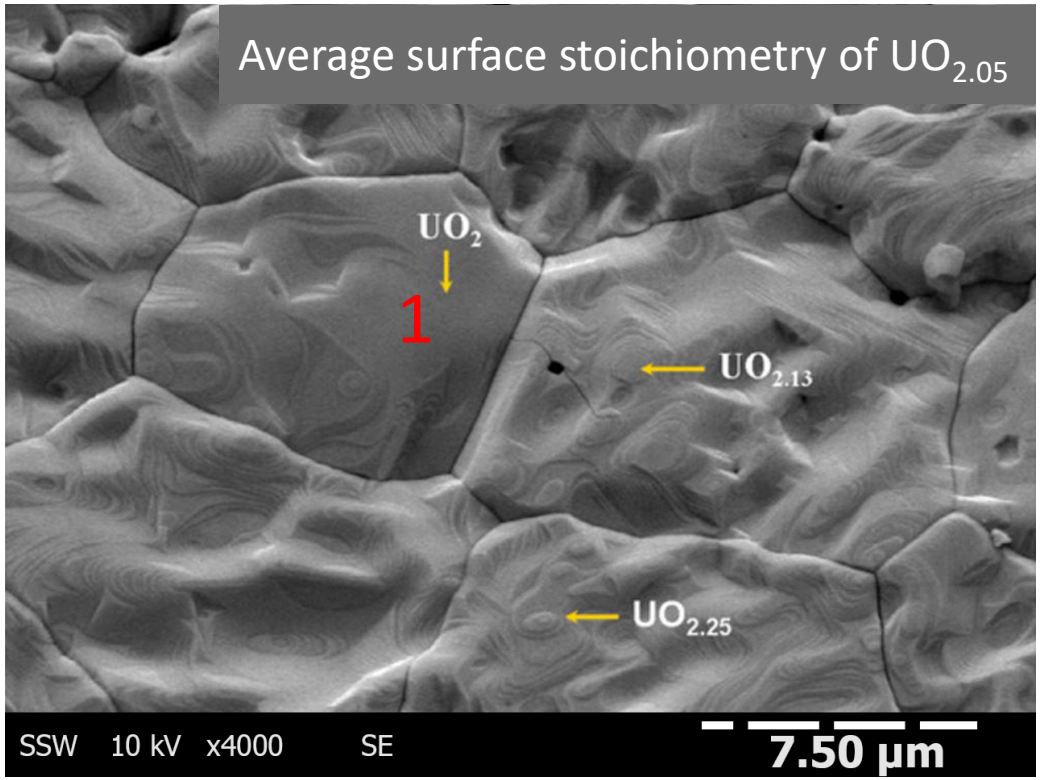
Undisturbed matrix

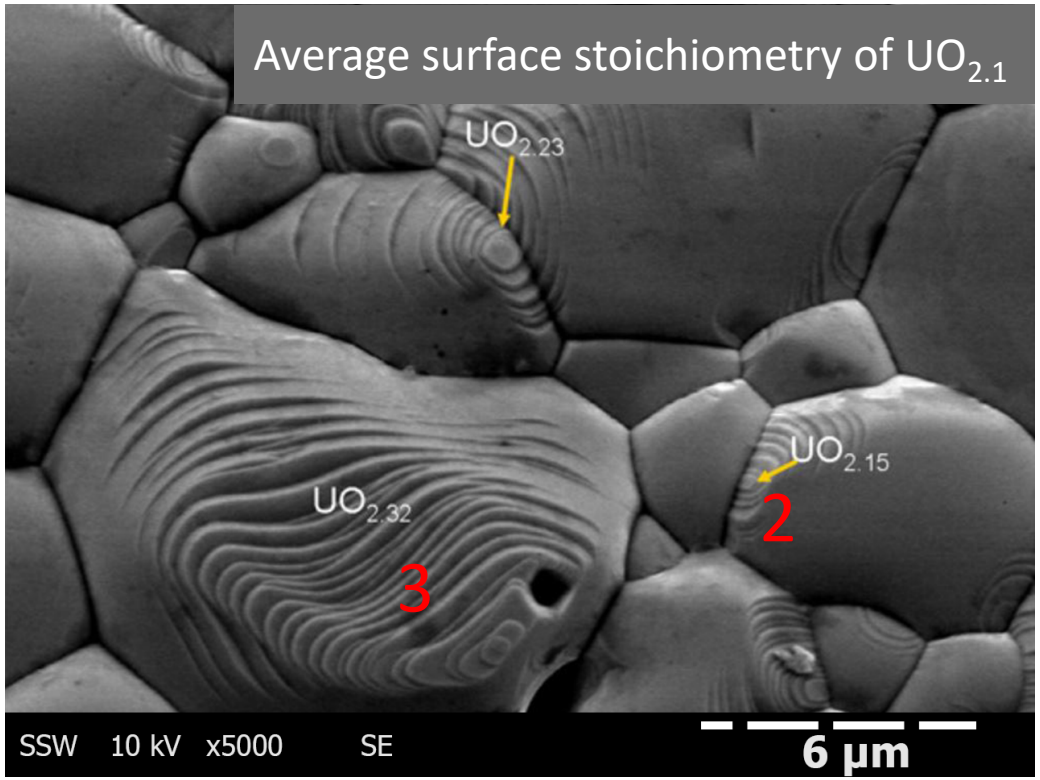


Lattice defects

Grain Morphology

UO_{2+x} pellets with nominal degrees of non-stoichiometry (from $UO_{2.05}$ to $UO_{2.1}$) show variations indicating composition and morphology may be related



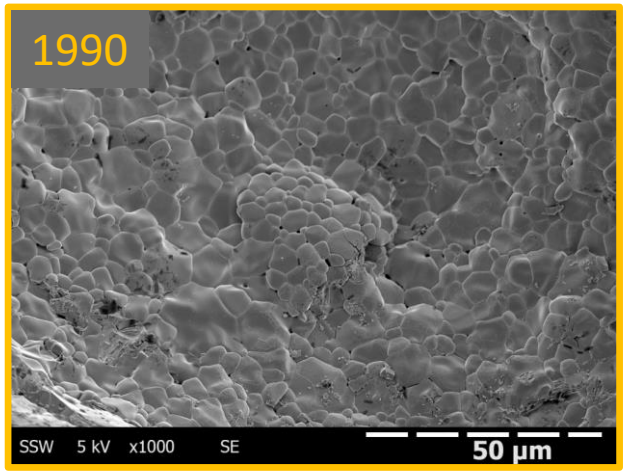


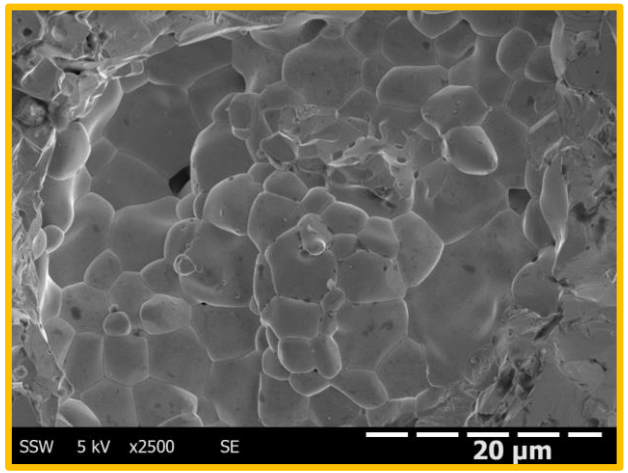
1. Smooth flat grain, approximately UO_2
2. Shallow stepped pattern, slightly hyper-stoichiometric composition of $UO_{2.15}$
3. Highly non-stoichiometric spiral-like grain with $UO_{2.32}$

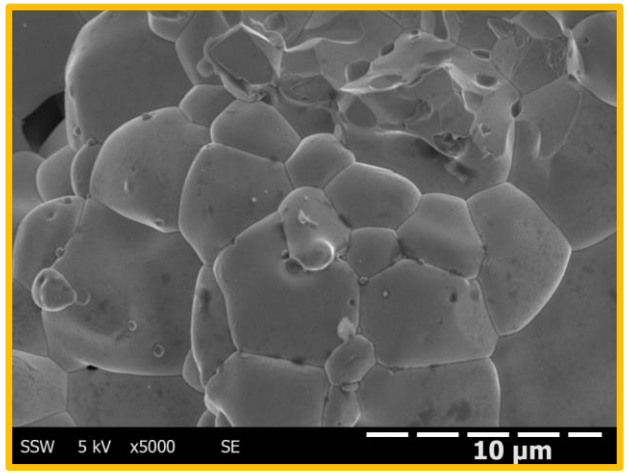
He, H.; Qin, Z.; Shoesmith, D. W., *Electrochim. Acta* **2010,** *56* (1), 53-60.

Grain Morphology

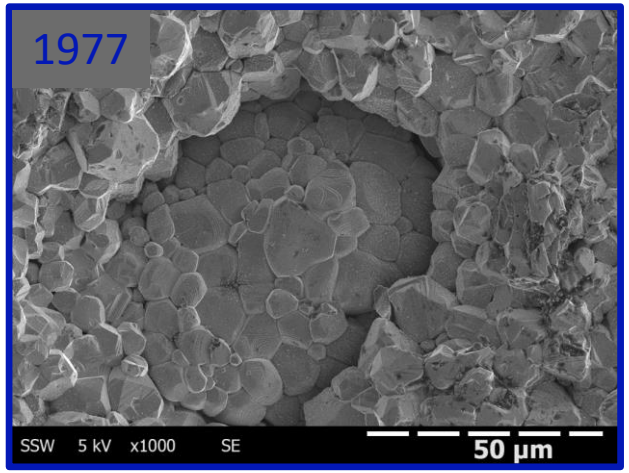
- Fuel specimen (1990) with a low resistivity (~ 11 kΩ.cm)
- Uniform grain structure observed

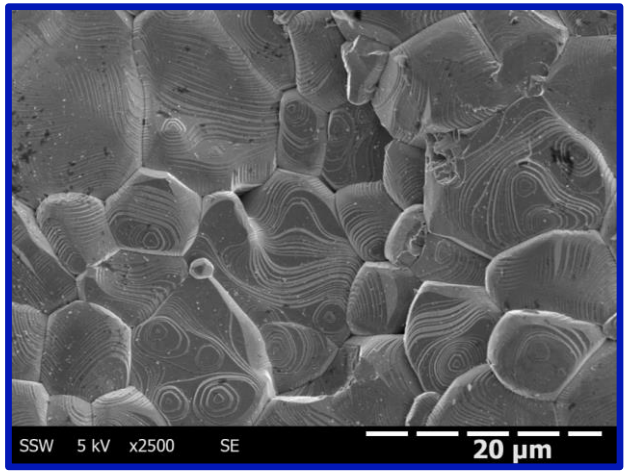


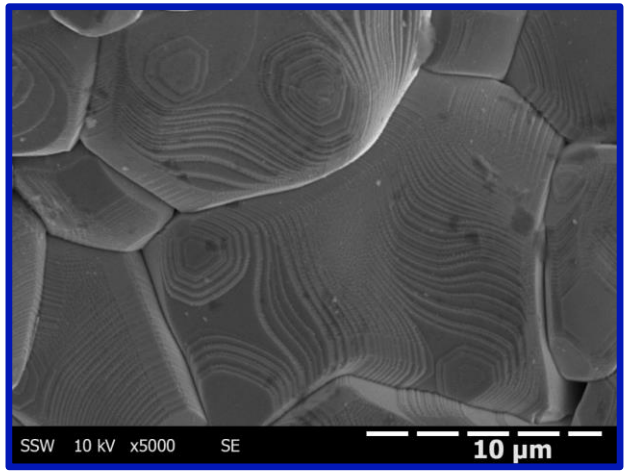




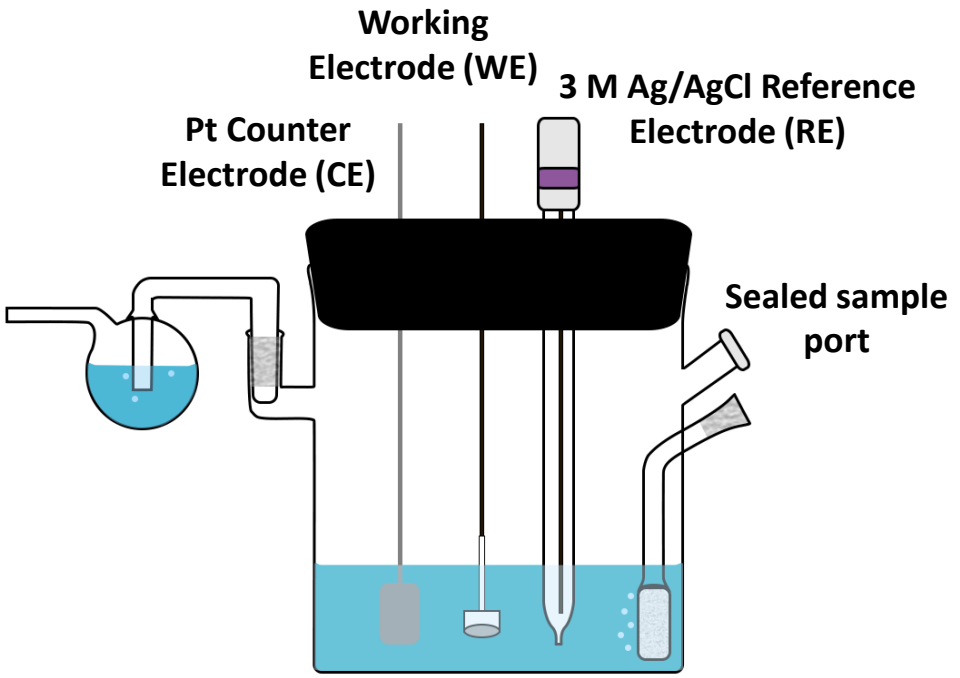
- Fuel specimen (1977) with a larger resistivity (~ 155 kΩ.cm)
- Spiral-like surface features observed







The Effect of $[H_2O_2]$



- Undoped, natural UO_2 fuel pellets
- Solution: [NaCl] = 100 mM, $[CO_3^{2-}]$ = 50 mM
  $[H_2O_2]$ = 0.5 – 20 mM
  pH: 9.5, Ar-sparged

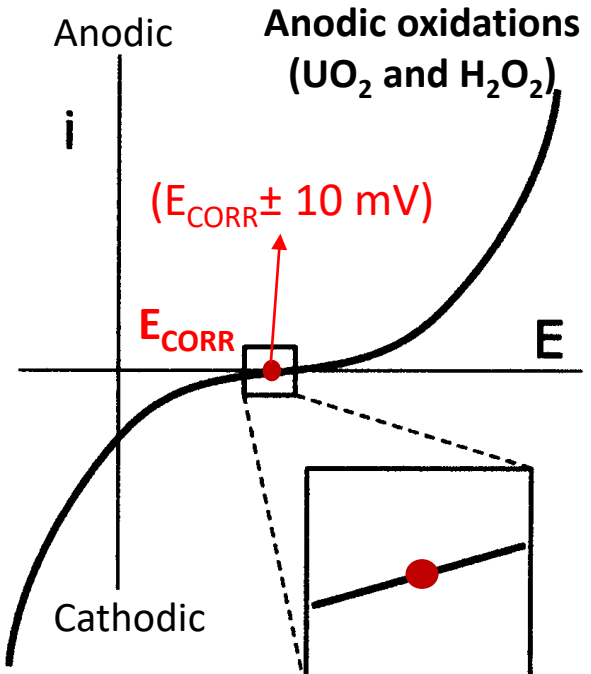
24 hour corrosion potential (E_{CORR}) measurement

Increases as conditions become more oxidizing

CORROSION POTENTIAL (E_{CORR})

Decreases as conditions become less oxidizing

Polarization Resistance (R_P) measurements every hour



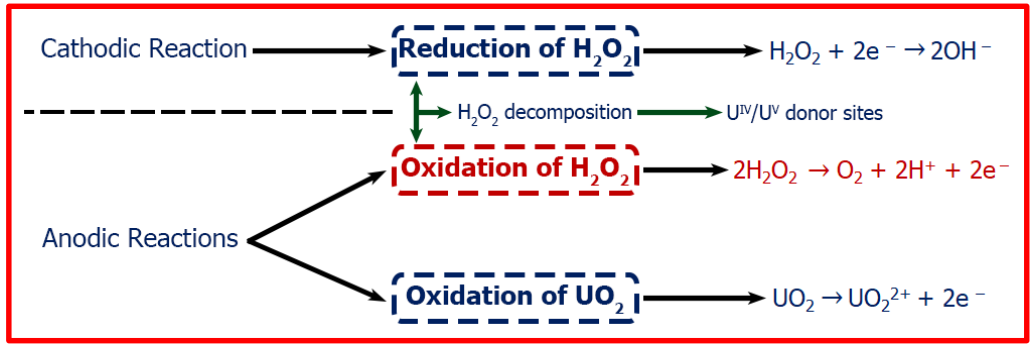
R_p^{-1} proportional to the total interfacial charge transfer rate

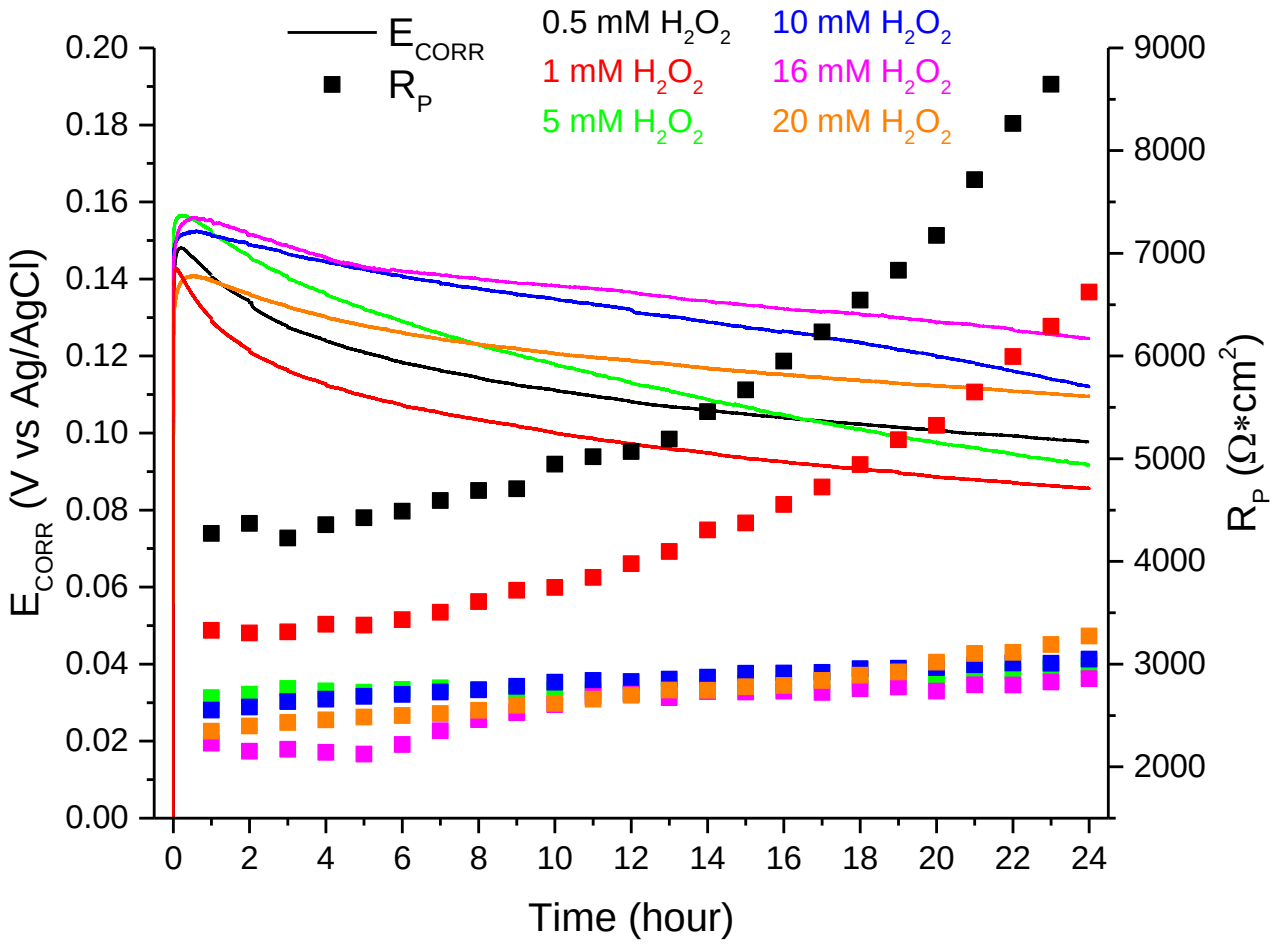
$$\mathbf{i_{UO_2} + i_{H_2O_2} = i_A + -i_C}$$

$$\frac{1}{R_P} = \left[\frac{\Delta i}{\Delta E}\right]_{\Delta E \to 0}$$

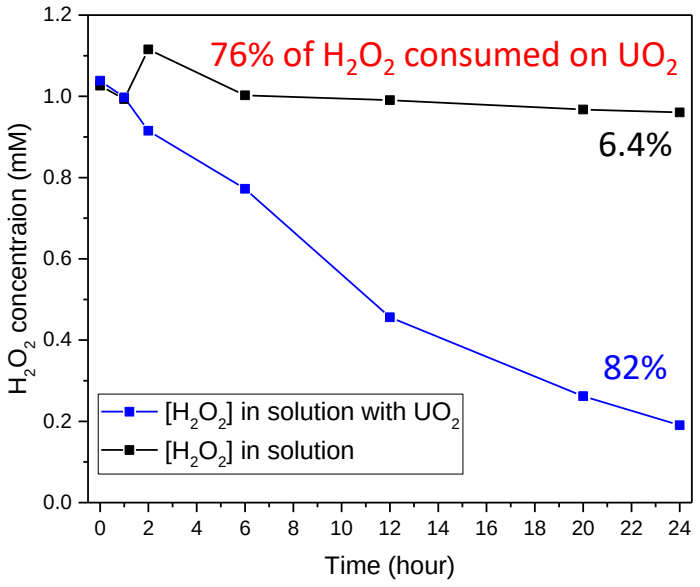
The Effect of $[H_2O_2]$

- E_{CORR} and R_P are more stable at higher $[H_2O_2]$
- Decrease in E_{CORR} with increasing R_P indicates suppression of the cathodic reaction
- At 0.5 mM and 1 mM H_2O_2 increased R_P may reflect H_2O_2 consumption leading to transport control

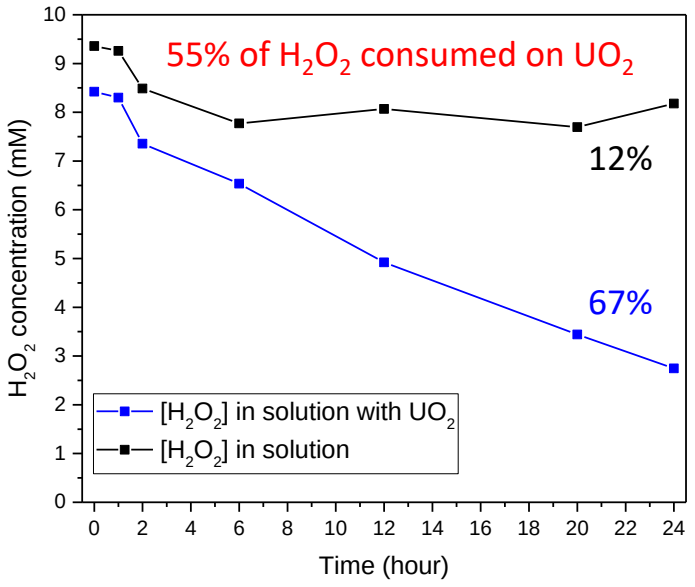




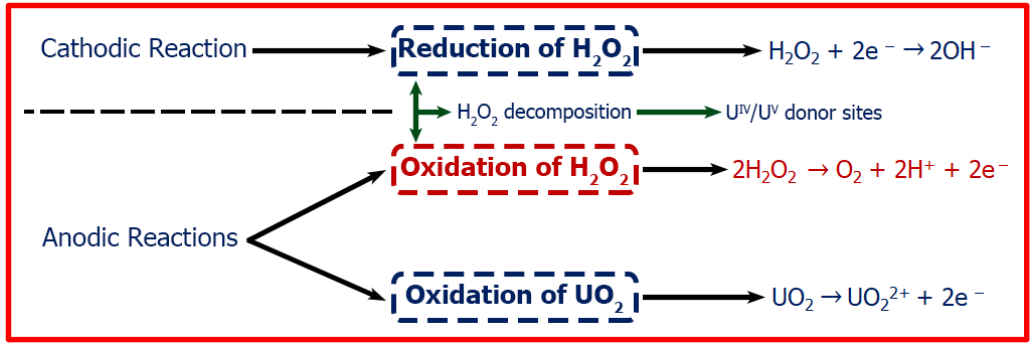
The Effect of $[H_2O_2]$



1 mM H_2O_2



10 mM H_2O_2

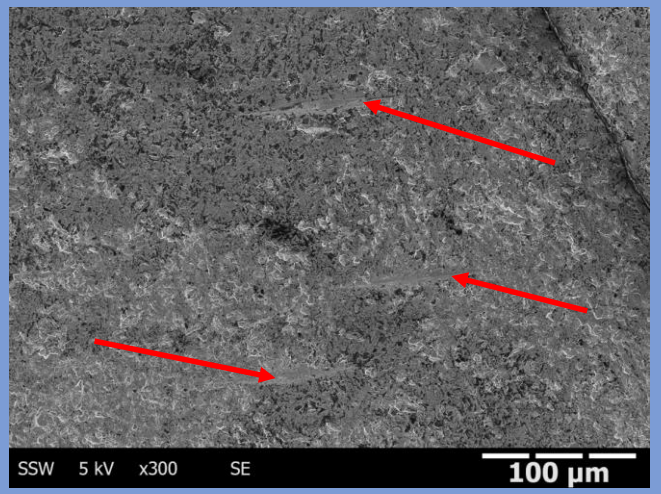


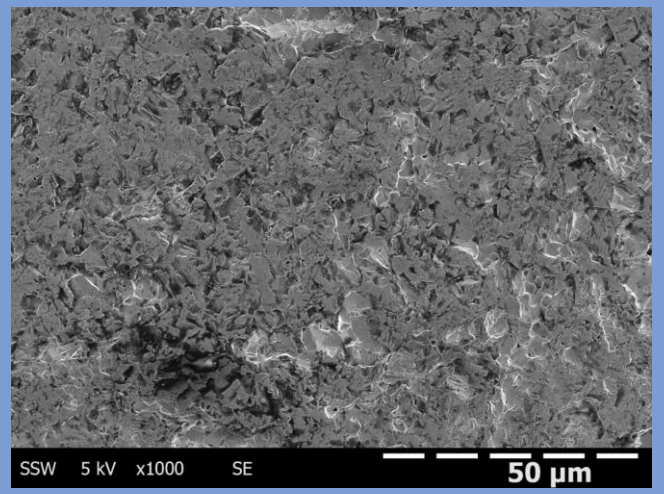
- Generally very little H_2O_2 decomposition in solution
- At low $[H_2O_2] < 1$ mM there is a higher consumption on the UO_2 surface, while at $[H_2O_2] > 5$ mM there is less H_2O_2 consumption
- This may reflect a higher extent of surface oxidation leading to a less catalytic surface
- Fraction of H_2O_2 consumed on UO_2 surface higher than observed on SIMFUELs

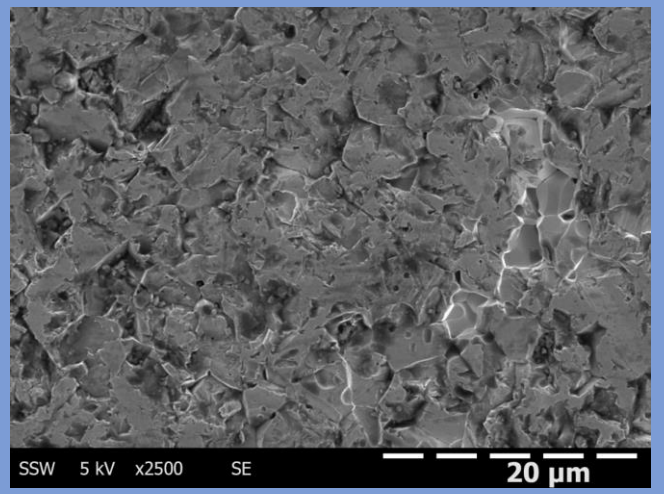
Nilsson, S.; Jonsson, M., *Journal of Nuclear Materials* **2011,** *410* (1), 89-93.

The Effect of $[H_2O_2]$

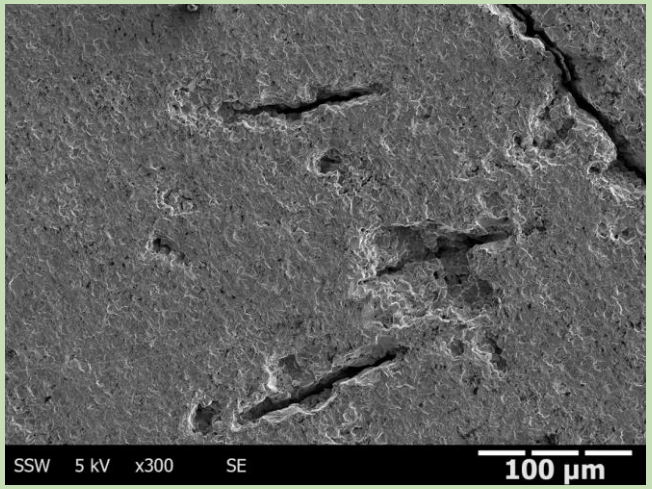
Before

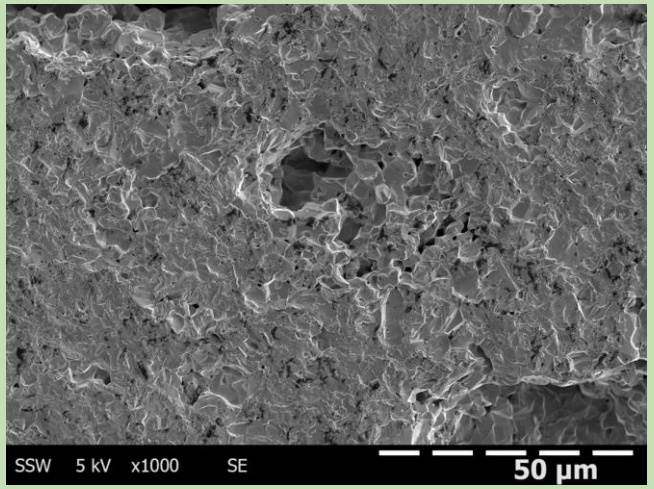


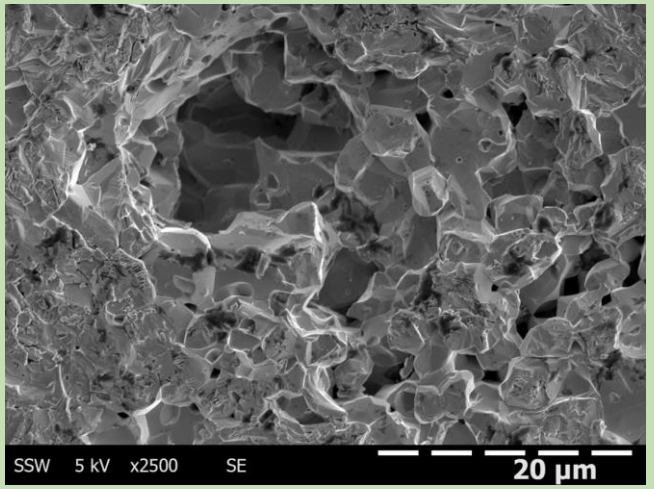




After







Conclusion

- Resistivity measurements indicate a low degree of non-stoichiometry for all fuel specimens
- Raman mapping suggests the presence of localized regions of non-stoichiometry, with differences between individual grains
- Grain morphologies suggest non-stoichiometric defect structures may be present in some older specimens, suggesting incomplete reductive sintering
- Initial electrochemical experiments show significant H_2O_2 decomposition at low H_2O_2 concentrations, with sustained UO_2 oxidation at high H_2O_2 concentrations
- H_2O_2 consumption is higher on natural UO_2 specimens than observed on SIMFUELs
- Using SEM, localized damage observed along surface fractures and sites of micro-indentation

Ongoing Work

- Perform ICP-MS to determine [U] in solution post immersion
  - Distinguish between H_2O_2 anodic dissolution vs anodic oxidation of UO_2 at fuel surface
- Repeat same experiment for samples displaying:
  1. Significantly higher resistivity measurement
  2. Grain morphologies suggesting a high degree of non-stoichiometry
- Perform potentiostatic experiments in 1 mM, 5 mM and 20 mM H_2O_2 followed by XPS to observe surface oxidation at varying potentials
- Investigate H_2 effect on H_2O_2 decomposition on undoped UO_2 samples

Thank You!

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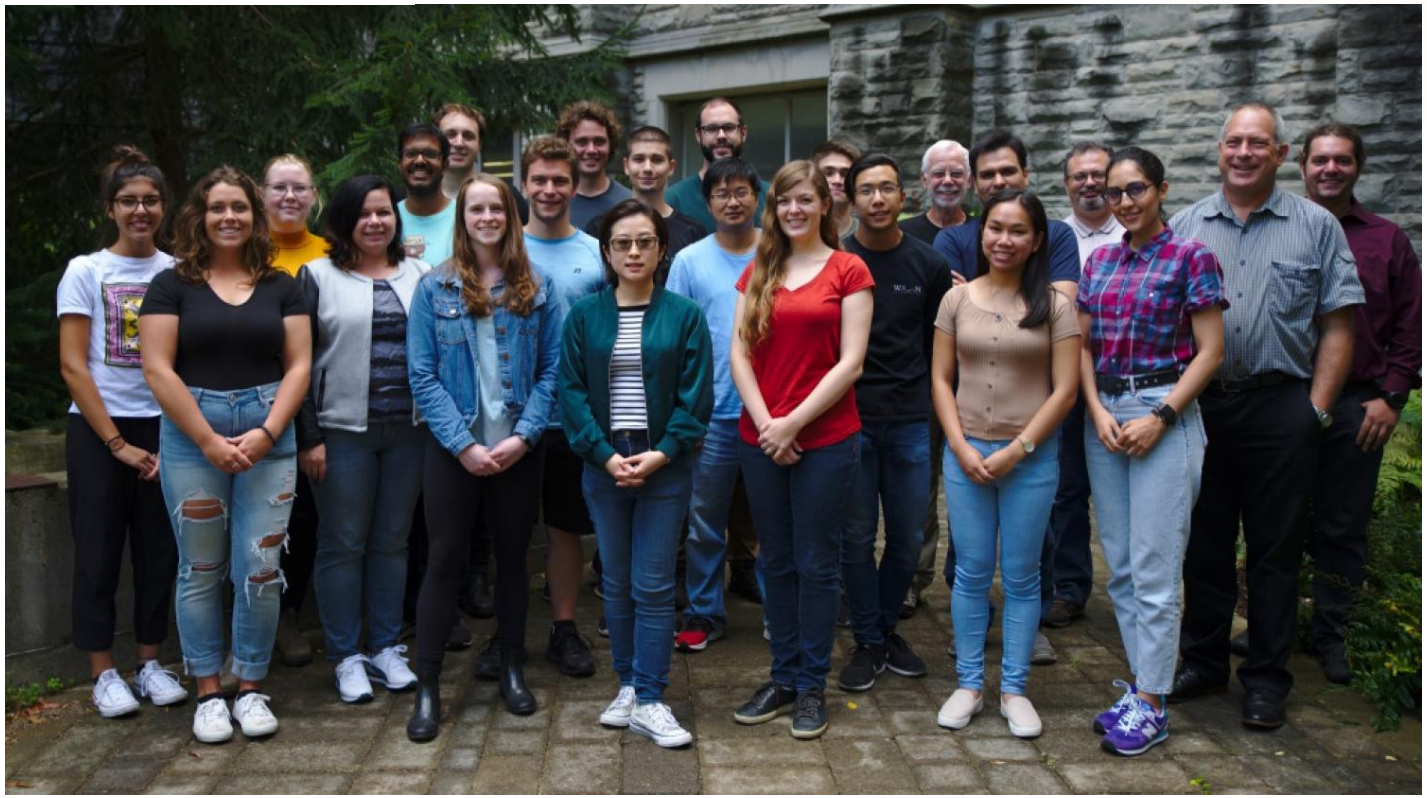

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