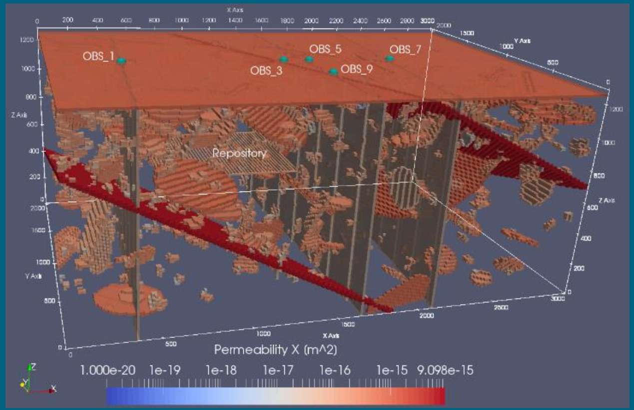

Electrochemical Corrosion Testing of SIMFUEL for FMDM Development

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Rationale for electrochemical model and testing

- The Fuel Matrix Degradation Model (FMDM) was developed as an electrochemical model because the dominant pathway for radionuclide release from the UO_2 matrix fraction of Commercial Spent Nuclear Fuel (CSNF) is an electrochemical process: the oxidation of $U^{IV}O_{2(s)}$ to much more soluble U(VI) species

$$UO_{2(s)} \rightarrow UO_2^{2+} + 2e^-$$

Experimental Objective: To quantify the sensitivity of simulated spent fuel (SIMFUEL) degradation kinetics to fuel composition (burnup) and environmental conditions (e.g., H_2, pH, CO_3^{2-}, Eh, Br^-, and temperature) using electrochemical test methods for FMDM development

- Controlled electrochemical experiments are designed to elucidate mechanisms (e.g., galvanic and catalytic effects of noble metal fission product particles embedded in the UO_2 matrix)

- Model predictions are validated and parameters calculated from short-term electrochemical measurements

Electrochemical testing using simulated spent fuel (SIMFUEL)

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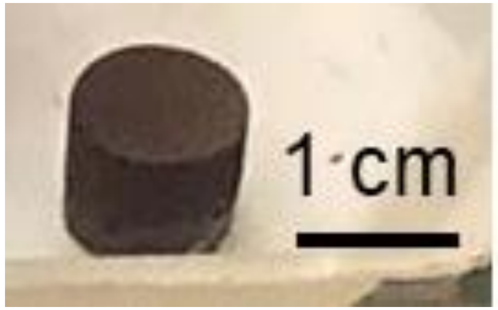
- Results from electrochemical tests quantify effect of single variables on measured electrochemical parameters to replace place holder values with empirical data for reaction rate constants
  - Noble metal content
  - Dissolved H_2 concentration
  - Total carbonate concentration
  - Temperature
- Results from electrochemical tests may indicate need to include additional parameters and processes not currently considered in FMDM
  - Noble metal alloy composition
  - Fuel composition and compositional changes over time
  - pH
  - Catalytic poisons (Br^-)
  - Galvanic coupling between UO_2 matrix and noble metals and UO_2 matrix and waste package alloys

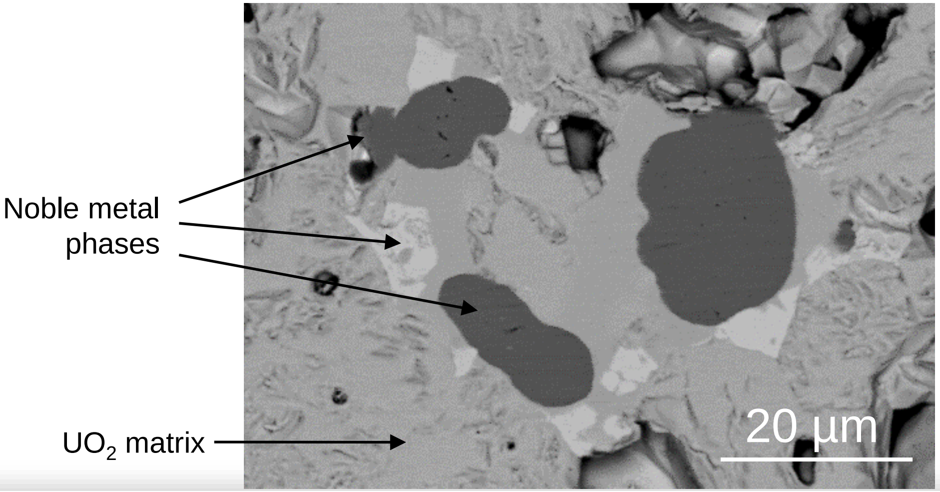
SIMFUEL synthesis and electrode fabrication

- SIMFUEL materials prepared by pressing mechanically mixed powders then sintering under vacuum
- SIMFUEL compositions include different amounts of lanthanide oxide and noble metal surrogate fission products that represent different fuel burnups[1]
  - None (UO_2-N), low (UO_2-L), medium (UO_2-M), and high (UO_2-H)

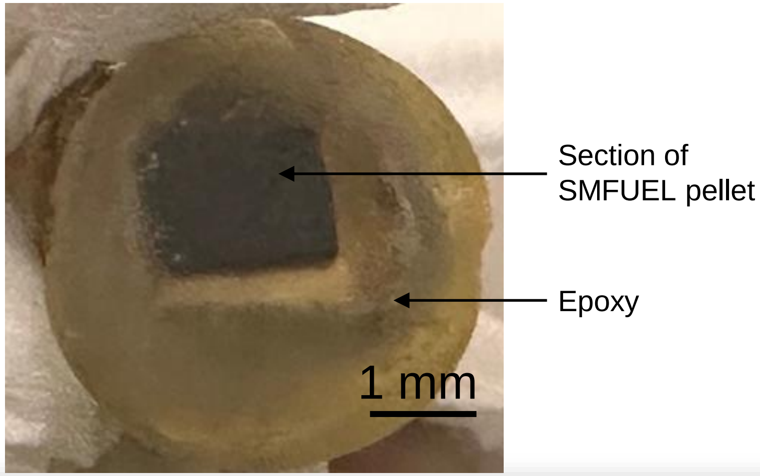
Sintered SIMFUEL pellet



Backscattered electron micrograph of polished UO_2-H surface



SIMFUEL electrode



[1] Based on Lucuta, P. G., Verall, R. A., Matzke, H., and Palmer, B. J. **1991**. “Microstructural Features of SIMFUEL - Simulated High-Burnup UO_2-Based Nuclear Fuel.” *Journal of Nuclear Materials* 178: 48–60.

Electrochemical parameters in FMDM

- FMDM considers 11 half reactions that occur on the fuel surface and calculates the corrosion potential (E_{CORR}) and current densities (i) of each half reaction such that at E_{CORR}, $\sum i_{anodic} + \sum i_{cathodic} = 0$
- UO_2 dissolution rate is directly calculated as the sum of current densities of 3 surface reactions
- Parameters to model rates of oxidation and reduction half reactions occurring at fuel surface can be determined from electrochemical measurements

Current density equation in FMDM for half reaction x

$$i_x = n_x F \sigma \boldsymbol{k_x} [C]^a e^{\left[\frac{\alpha_x F}{RT}(E_{CORR} - E_{0,x})\right]}$$

- Fraction of fuel surface area containing sites where reaction occurs (σ)
- Concentration of chemical reactant at fuel surface ($[C]$)
- Determined from electrochemical measurements (E_{CORR})
- Determined from electrochemical measurements (i_x)
- Rate constant parameter (k_x) (FMDM currently uses placeholder values for many reactions)

Electrochemical methods

- Electrochemical tests employ SIMFUEL as the working electrode in the standard three electrode method
- Method enables solution pH, chemistry, and temperature control
- Solutions purged with Ar/H_2 gas mixture to maintain dissolved H_2 concentration
- Determining the effect of one variable under known exposure conditions involves multiple measurements

Electrochemical measurements

- Open circuit potential (OCP) measurements
- Potentiodynamic (PD) scans
- Potentiostatic (PS) tests

SIMFUEL surface characterization

- Electrochemical impedance spectroscopy (EIS)
- Scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDS) analysis

Solution composition

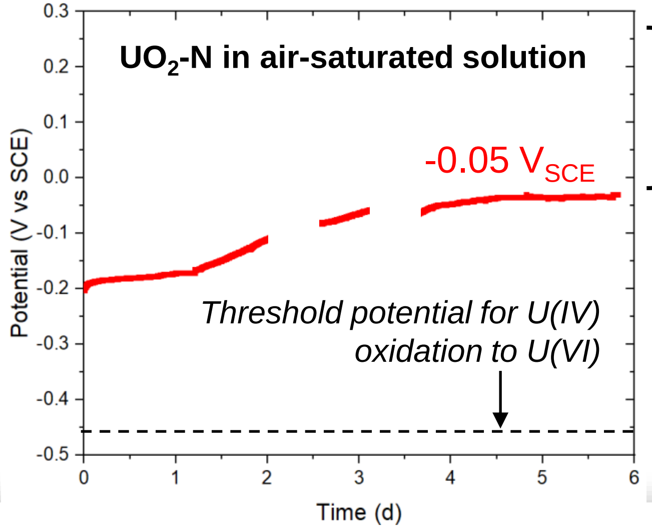
- Inductively coupled plasma mass spectrometry (ICP-MS) for dissolved metal concentration

Electrochemical methods and results

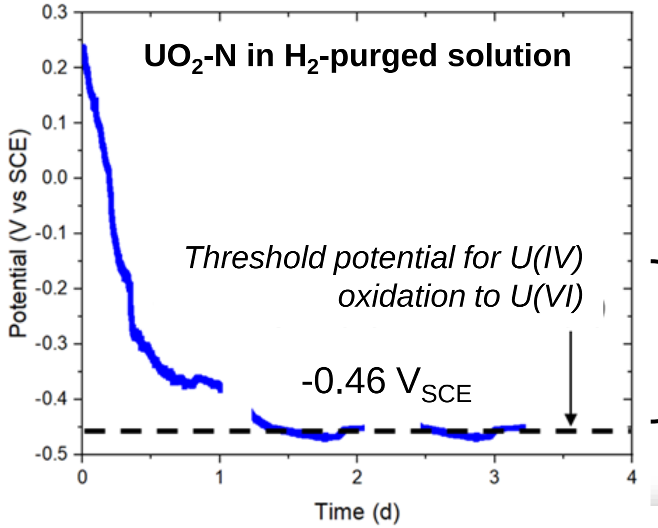
Open circuit potential (OCP) measurements:

- Provide insight into thermodynamic stability of SIMFUEL surface under known exposure conditions
- Are directly compared to FMDM parameter E_{CORR}
- Are used to select fixed surface potentials to apply during potentiostatic (PS) tests

Effect of dissolved H_2 on measured OCP



Select applied surface potentials above OCP for PS tests



Select applied surface potentials above OCP for PS tests

Summary

- Electrochemical experiments are designed to quantify the effect of individual variables on surface reaction kinetics by controlling:
  - SIMFUEL composition (noble metal content)
  - Solution chemistry and temperature
  - SIMFUEL surface potential
- Results are used to calculate rate constants for individual reactions already included in FMDM and identify other key mechanisms to include in FMDM

Effect of temperature

Effect of fuel composition (Noble metal particles)

Effect of solution composition ($[H_2]$, $[CO_3^{2-}]$)

Current density equation in FMDM for reaction x

$$i_x = n_x F \sigma \boldsymbol{k_x} [C]^a e^{\left[\frac{\alpha_x F}{RT}(E_{CORR} - E_{0,x})\right]}$$

Directly and indirectly determined from electrochemical measurements