Application of SECM to the Investigation of the Local Corrosion Kinetics of UO$_{2+x}$

Heming He, Zack Qin, R. Zhu, P. Keech Z. Ding, and D. W. Shoesmith

The University of Western Ontario
London, Ontario, Canada

Nuclear Waste Disposal

Deep Geologic Repository

Geosphere

Stable Waste Form Buffer Backfill

Corrosion-Resistant Container

Copper Lid

Steel Lid

Fuel Bundles

Copper Shell

Fuel Basket

Used Fuel Container
Oxidants Produced by $\alpha$ Radiolysis

$\alpha$ radiolysis

$H_2O \xrightarrow{\alpha} H^+ + OH^-$

$2OH^+ \rightarrow H_2O_2$

Fuel corrosion

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

$2H_2O_2 + 2e^- \rightarrow H_2 + 2OH^-$

- The primary oxidant available to drive fuel corrosion will be hydrogen peroxide produced by the $\alpha$ radiolysis of water.
- Anodic $UO_2$ dissolution is mainly supported by cathodic $H_2O_2$ reduction.
Fuel Corrosion

- Anodic fuel dissolution supported by cathodic reduction of radiolytically produced $\text{H}_2\text{O}_2$.
- Failure of the container will lead to the interaction of two corrosion fronts with a large difference in $E_{\text{corr}}$. 

**Redox Gradient**

**Anodic Corrosion of the carbon steel liner**

**Radiolytic Corrosion of the uranium dioxide**
Hyperstoichiometric UO$_2$ (UO$_{2+x}$)

Extra O$^-$ ions incorporated into the UO$_2$ fluorite lattice at interstitial sites produces UO$_{2+x}$

Removal of an electron from the 5f Hubbard band converts insulating UO$_2$ to a UO$_{2+x}$ p-type semiconductor
Non-stoichiometry Variants

![Graphs and images related to non-stoichiometry variants.](image-url)
Sources of Non-stoichiometry

- Grain boundaries could be incompletely reduced during fuel fabrication.
- Produced during in-reactor irradiation since some fission products are only stable as metals.
- Air oxidation during storage prior to final disposal.
- Non-stoichiometric sites are unevenly distributed.
Will non-stoichiometric sites be more reactive?

The higher degree of non-stoichiometry, the higher anodic current density.
Effects of Hyperstoichiometry

Increase of conductivity by converting insulating UO$_2$ to a UO$_{2+x}$ p-type semiconductor.

Non-stoichiometric locations known to provide donor-acceptor (U$^{IV}$/U$^{V}$) sites which catalyze O$_2$ or H$_2$O$_2$ reduction.

Oxygen could diffuse more easily within a slightly distorted UO$_{2+x}$ lattice.

Dissolution of more reactive UO$_{2+x}$ inward along grain boundaries could cause grains to fall apart and increase the overall surface area.
Scanning Electrochemical Microscopy (SECM)

- SECM can be used to determine if this non-stoichiometry produces lateral variations in UO$_2$ reactivity.
- Feedback mode: redox couple as a mediator
- Positive feedback ($i_T > i_{T,\infty}$) - catalytic regions boost signal
- Negative feedback ($i_T < i_{T,\infty}$) - insulating regions diminish signal by restricting flow
The cathodic kinetics of Fc reduction on UO₂ are expected to be similar to those of H₂O₂, since the standard reduction potentials for the two are similar. The rate constant for reaction of UO₂ with Fc⁺ is much larger than that for reaction with O₂.
**UO₂ Corrosion**

- Fc oxidation and O₂ reduction are negligible under the open circuit condition used.
- Anodic UO₂ dissolution (iₐ) is primarily supported by cathodic Fc⁺ reduction (iₛ).
- At the corrosion potential, $E_{corr}$, $i_{corr} = i_A = -i_S$. 
SECM Model

Measured Fc tip oxidation rate $i_T$

SECM modeling and simulation

Fc$^+$ substrate reduction rate $i_S$

UO$_2$ substrate corrosion rate $i_{corr}$

\[
\frac{\partial^2 c(r, z)}{\partial r^2} + \frac{1}{r} \frac{\partial c(r, z)}{\partial r} + \frac{\partial^2 c(r, z)}{\partial z^2} = 0
\]

\[
I^*_T = \frac{2\pi}{I_{T,\infty}} \int_0^a i_T(r) r \, dr \quad \text{where} \quad i_T(r) = nFD \left[ \frac{\partial c(r, z)}{\partial z} \right]_{r \leq a, z = d}
\]

\[
k_f = k^0 \exp\left[ -\frac{\alpha nF}{RT} (E - E^0) \right] ; \quad k_b = k^0 \exp\left[ \frac{(1-\alpha)nF}{RT} (E - E^0) \right]
\]
Boundary Conditions

\[ D \left[ \frac{\partial c(r, z)}{\partial z} \right] = 0 \quad r = a, z = d \]

\[ c(r \leq a, z = d) = 0 \]

\[ D \left[ \frac{\partial c(r, z)}{\partial z} \right] = 0 \quad r = 0 \]

\[ c(r, z)_{outer} = c^o \]

\[ J(r \leq b, z = 0) = -D \left[ \frac{\partial c(r, z)}{\partial z} \right] = k_f [c^0 - c(r \leq b, z = 0)] - k_b c(r \leq b, z = 0) \]
Numerical solutions are needed for boundary valued PDE’s.

COMSOL is a modeling package based on the Finite Element Method.

FEM is based on the principle that the solution of PDE’s can be represented as a linear combination of unknown parameters and appropriately selected functions that satisfy the boundary conditions.
**COMSOL Simulations**

- $k^o \geq 10^{-2}$ m s$^{-1}$, reaction is fast and diffusion controlled.
- As $k^o$ is decreased, the extent of positive feedback decreases, and eventually switches to negative feedback for $k^o \leq 8 \times 10^{-6}$ m s$^{-1}$ as the reduction of Fc$^+$ becomes kinetically limited.
- $k^o < 10^{-7}$ m s$^{-1}$, the rate is too slow to support regeneration of Fc.


SECM and Simulation
SECM and Simulation

![Graphs and images showing SECM and simulation results for UO₂ and UO₂.1 with normalized current over distance and concentration]
Conclusions

✓ Non-stoichiometry is an important factor that could influence corrosion of nuclear fuel.
✓ A method, which involves fitting experimental approach curves to simulated curves determined by a COMSOL model, has been developed to determine cathodic kinetics and, ideally, to determine local corrosion kinetics of the UO$_{2+x}$ under natural corrosion conditions.
✓ The results quantitatively demonstrate that the corrosion kinetics vary over a broad range, and that this range is determined by the degree of non-stoichiometry and the diversity of structures on the UO$_{2+x}$ surface.
✓ SECM can be used to determine an uneven distribution of corrosion reactivity.
Electrochemical and Corrosion Studies at Western

http://publish.uwo.ca/~ecsweb/

Thank You

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