

Electrochemical study of the anodic reactions on SIMFUEL (UO₂) in hydrogen peroxide solution

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Abstract

The recommended approach for the long-term management of spent nuclear fuel in Canada is adaptive phased management that includes centralized containment and the isolation of the spent fuel in a deep geological repository. A key barrier is the corrosion-resistant container that is expected to isolate the spent fuel for a very long time. However, it is judicious to examine the consequences of container failure and the exposure of spent fuel bundles to groundwater. In the anoxic conditions anticipated in a deep geological repository, water radiolysis will be the only source of oxidants resulting from the radiation fields associated with fuel. One of the alpha radiolysis products, H₂O₂, is demonstrated to be the primary driving force for fuel corrosion. Oxidation of fuel (U^{IV}) will produce the oxidized form (U^{VI}) with a considerably higher solubility leading to the release of radionuclides.

In addition to causing UO₂ dissolution, H₂O₂ oxidation can couple with its reduction resulting in its overall decomposition to H₂O and O₂. Thus, competition between these two anodic reactions can occur and the rate of fuel corrosion will depend on their relative kinetics.

These two anodic reactions have been studied on SIMFUEL in H₂O₂ solutions (pH=9.7) using voltammetric and potentiostatic techniques and electrochemical impedance spectroscopy. At low potentials (<0.2V vs. SCE), the oxidation process from UO₂ to UO_{2+x} is rate determining. For potentials 0.2 to 0.3 V, the chemical dissolution of the surface oxidized layer becomes the rate-controlling step and the current is independent of potential. At high potential (0.4 V), H₂O₂ oxidation becomes dominant and independent of the total carbonate concentration. The proposed mechanism is verified by EIS data. The surface/solution analyses including scanning electron microscopy, UV-vis spectroscopy and inductively coupled plasma atomic emission spectroscopy are undergoing.

Keywords

Uranium dioxide; Hydrogen peroxide; Anodic corrosion; Nuclear waste disposal.

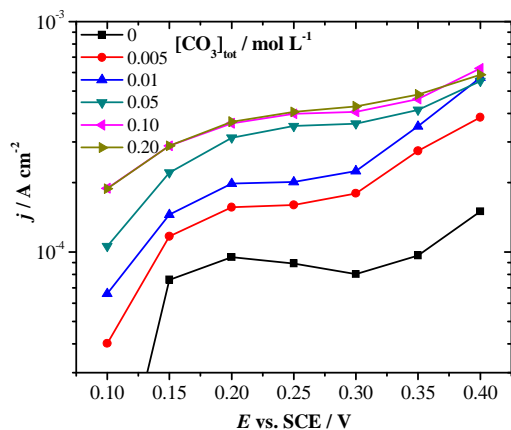


Fig. 1. Tafel plots for the oxidation/dissolution of 3 at.% SIMFUEL in 0.1 mol.L⁻¹ NaCl + 0.02 mol.L⁻¹ H₂O₂ with different carbonate concentrations at pH 9.7, $\omega=16.7\text{Hz}$.

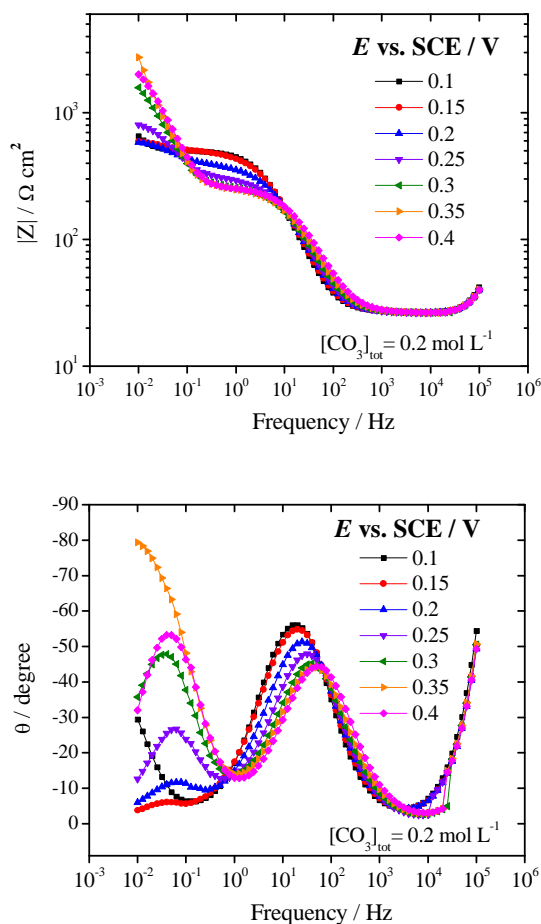


Fig. 2. Bode plots of EIS data obtained on 3 at.% SIMFUEL electrode at different anodic potentials in 0.1 mol.L⁻¹ NaCl + 0.02 mol.L⁻¹ H₂O₂ + 0.2 mol.L⁻¹ CO₃²⁻ / HCO₃⁻ at pH 9.7, $\omega=16.7\text{Hz}$.