Reduction of H_2O_2 on SIMFUEL Electrodes in Dilute Alkaline Aqueous Solution

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INTRODUCTION

The assessment of geological disposal of used nuclear fuel requires a prediction of the radionuclide release rate as a function of disposal time. Since UO_2 is a solid for which the solubility increases substantially under oxidizing conditions, the dissolution rate will be a function of vault redox conditions. Although these conditions at the planned depth of the disposal vaults are expected to be initially reducing, it is possible that oxidizing conditions could eventually be encountered on exposure of the fuel to groundwater, due to the potential for oxidant production by the radiolysis of water. Data suggest that, in the long term, the corrosion process will be sustained predominantly by the reaction of UO_2 with the oxidants produced by the α-radiolysis of water. As the primary product of α-radiolysis, hydrogen peroxide is expected to play a key role in fuel corrosion. It is therefore necessary to elucidate, as far as possible, the mechanistic interaction of this oxidant with UO_2.

EXPERIMENTAL

The rotating-disc electrode technique was employed for all electrochemical experiments. Reduction currents were recorded as a function of electrode rotation rate at a series of applied potentials. The currents were corrected for: i) background currents due to water reduction; ii) transport effects using the Koutecký-Levich technique; iii) the internal resistance of the electrode using the current interrupt method. In open circuit experiments, H_2O_2 was added and E_{OC} measured over time as a function of peroxide concentration.

RESULTS AND DISCUSSION

Koutecký-Levich plots were constructed from the current versus rotation rate data, Figure 1. The measured slopes are in reasonable agreement with the theoretical value. Extrapolation to $\omega^{-1/2} = 0$ yields the kinetic-limiting currents, i_k, which can be plotted in a Tafel form, Figure 2. The Tafel slopes of 317-377 mV/decade are comparable to those obtained on normal p-type UO_2 (~ 350 mV/decade). The currents are over an order of magnitude higher than those seen for O_2 reduction on the same material, suggesting the H_2O_2 reduction is not limited by the availability of donor-acceptor reduction sites on the UO_2 surface.

The time required for the open circuit potential to reach a value of –100 mV vs. SCE, t_{-100}, is proportional to the rate of the oxidation process $UO_2 \rightarrow UO_{2+x}$, where $x < 0.01$. This process is quite rapid even in dilute peroxide solutions (t_{-100} is on the order of a few seconds). The steady state open circuit potentials (($E_{OC})_{SS}$) have almost no dependence on the concentration of H_2O_2, Figure 3, suggesting that the anodic dissolution of UO_2 may be accompanied by surface-catalyzed H_2O_2 decomposition to H_2O and O_2.

CONCLUSION

H_2O_2 rapidly oxidizes SIMFUEL surfaces, with corrosion likely driven by the decomposition product, O_2.

This condition of redox buffering suggests that the fuel dissolution rates under disposal conditions will be independent of the fuel's α-source strength.
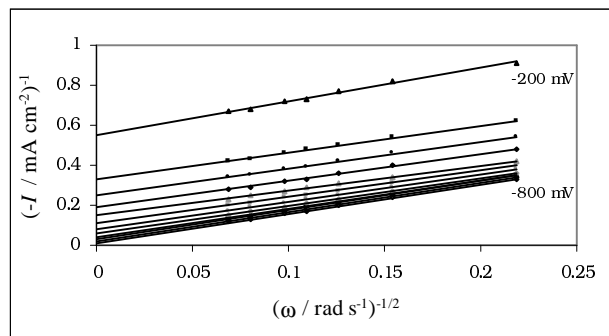
Fig. 1 Koutecký-Levich plots for H_2O_2 reduction on a SIMFUEL electrode.
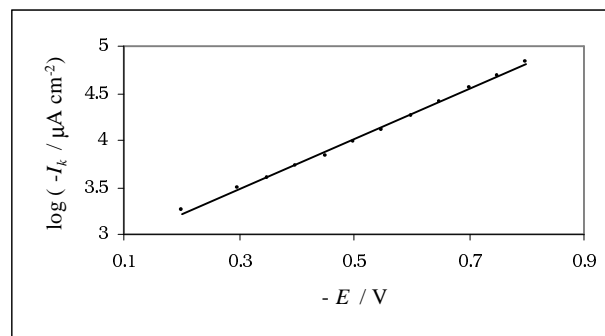

Fig. 2 Tafel plot for H_2O_2 reduction on a SIMFUEL electrode.
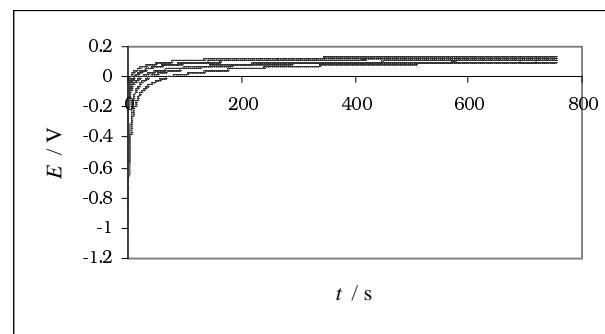

Fig. 3 Open circuit potentials over time for various H_2O_2 concentrations on a SIMFUEL electrode.