Electrochemical studies of SIMFUELS

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Abstract

The properties of a standard UO_2 fuel and three SIMFUEL materials (unirradiated analogues of used nuclear fuels) have been characterized electrochemically and under natural corrosion conditions. The general oxidation and reduction behaviour was determined voltammetrically. The effect of substituents on the surface reactivity was determined by studying the electroreduction of O_2. Under natural corrosion conditions, SIMFUELs oxidize more rapidly than does UO_2, but then appear to dissolve at a similar rate.

1. Introduction

In our attempts to elucidate the factors that control the reactivity of used nuclear fuel under waste disposal conditions, we have been investigating the electrochemical properties of SIMFUELs. These materials provide a practical means to study the effect of the impurities created by fission in UO_2 fuel on the fuel's corrosion (oxidative dissolution) behaviour. SIMFUELs contain 11 stable elements in proportions appropriate to replicate the chemical effects caused by reactor irradiation of UO_2 to various degrees of burn-up [1].

Recently, we have developed an electrochemical model to predict the dissolution rate of UO_2 as a function of the redox conditions [2]. Here, we compare the electrochemical and open-circuit corrosion behaviours of three SIMFUELs with that of a standard specimen of unirradiated UO_2 fuel, which has been well characterized [3].

2. Experimental details

Our electrochemical and open-circuit corrosion procedures have been described in detail elsewhere [3, 4]. The SIMFUEL pellets from which electrodes were fabricated were prepared at the Chalk River Laboratories of AECL Research [1]. All the pellets were well-sintered ceramics with about 97% of theoretical density and compositions representative of 1.5, 3.0 and 6.0 at.% burn-up in a Canada Deuterium Uranium (CANDU) reactor.

3. Results and discussion

Figure 1 compares cyclic voltammograms recorded on all four electrodes in 0.1 mol l^{-1} $NaClO_4$ (pH 9.5).

The form of the voltammograms is similar in each case, demonstrating that the oxidation (positive sweep) and reduction (reverse sweep) processes are basically the same; however, important differences exist. In region A, distinct anodic peaks are observed only for the standard UO_2 specimen; it is thought that they may result from submonolayer oxidation of the surface, perhaps associated with hyperstoichiometric grain boundaries [5]. The absence of these peaks from the other voltammograms (Fig. 1) presumably reflects the heavy uniform doping of the SIMFUEL materials. The main surface-oxidation process (region B, prior to extensive oxidative dissolution at $E \geq 0.3$ V vs. SCE) appears to be the same on all the electrodes; it has been shown to be the oxidation of the UO_2 surface to approximately $UO_{2.33}$, which achieves a thickness of 5–8 nm at this pH [5, 6].

Process C results from the reduction of the $UO_{2.33}$ layer back to UO_{2+x} (near-stoichiometric UO_2 is never quite re-attained, as demonstrated by X-ray photoelectron spectroscopic measurements [5, 6]). A measure of the $UO_{2.33}$ film thickness is provided by the area of peak C; clearly, thinner films are formed on the SIMFUEL specimens than are formed on the UO_2 specimen, which is consistent with a smaller degree of oxidation occurring during the forward sweep.

The greatest difference between UO_2 and the SIMFUEL is the current in region D, which results from the reduction of water (with H_2 evolution). Pronounced enhancement of this reduction process (current shifts toward positive potentials by about 400 mV) is thought to arise from uniform doping of the SIMFUEL matrix with trivalent rare earth cations.

Measurement of the kinetics of O_2 reduction is an ideal method of investigating the surface properties of
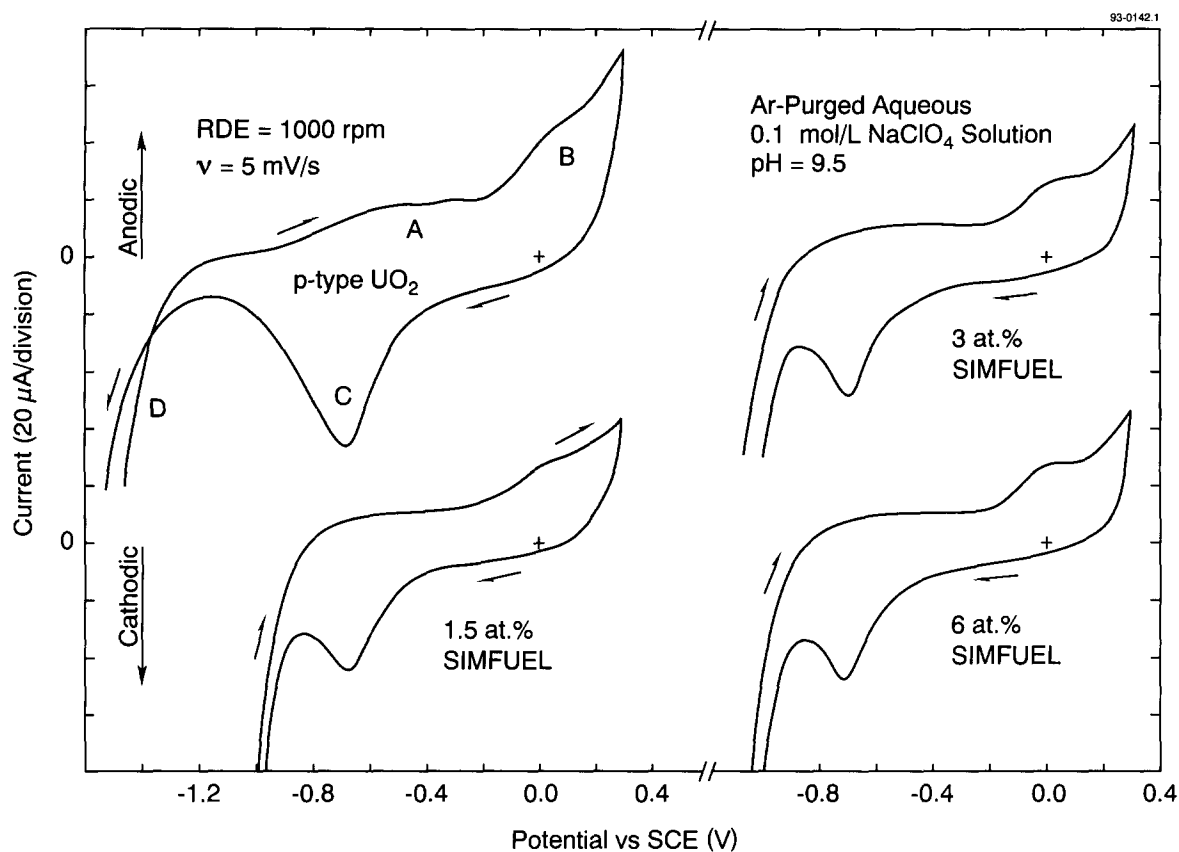
Fig. 1. Voltammetric response of standard (unirradiated) UO_2 fuel and three SIMFUELS with various simulated burn-ups.

conducting oxide materials. The electron-transfer reactions involved in O_2 reduction appear to occur exclusively at active surface sites formed by adjacent cations in different valence states [4, 7]. For UO_2, the valence states involved could be U^{6+} and U^{5+}, although other combinations are possible, with the higher oxidation state in the surface and the lower state directly beneath it. According to the theory of Presnov and Trunov [7], such active sites function as electron acceptors relative to the bulk of the oxide and as electron donors relative to O_2 molecules adsorbed on the surface. The rate-controlling step in O_2 reduction on UO_2 appears to be the first electron transfer, but the current–voltage relationship deviates from that predicted by electrochemical theory. This deviation has been attributed to the potential dependence of the concentration of donor–acceptor sites in the surface [4], with the number of sites decreasing because of the electrochemical reduction of U^{6+} species in the surface over the potential range -0.3 V to -1.0 V.

The current–voltage curves for O_2 reduction on the SIMFUELS are similar in form to that for standard UO_2. A first-order dependence of the cathodic current on the O_2 concentration has also been consistently found. These results indicate that O_2 reduction proceeds by the same basic mechanism on all the electrodes. For

a given potential in the range -0.1 V to -0.7 V, however, the current for O_2 reduction increases in the order $I(UO_2) < I(1.5$ at.% SIMFUEL$) < I(3.0$ at.% SIMFUEL$) < I(6.0$ at.% SIMFUEL$)$, which is consistent with an increase in the density of donor–acceptor sites in the electrode surface as the dopant concentration in the SIMFUEL increases. Substitution of trivalent ions (such as Y^{3+}, La^{3+} or Nd^{3+}) for U^{4+} in the uraninite structure leads to further ionization of the remaining uranium ions to U^{5+} or U^{6+} to maintain the overall charge balance. Thus, donor–acceptor sites for O_2 reduction are created, with their number density increasing as the concentration of trivalent dopant increases.

Figure 2 shows a series of curves of the corrosion potential as a function of the time of exposure to O_2-saturated solutions of 0.1 mol l^{-1} $NaClO_4$ (pH 9.5). Oxidation and dissolution of the electrode occur in two stages: (i) oxidation of the surface to approximately $UO_{2.33}$ over the potential range -400 mV to more than 0 V; (ii) steady-state oxidative dissolution of the $UO_{2.33}$ surface at potentials of around $+70$ mV. Clearly, the SIMFUEL electrodes oxidize more rapidly than does UO_2 under the conditions in Fig. 2.

For UO_2, the oxidation process ($UO_2 \rightarrow UO_{2.33}$) appears to be controlled by the cathodic half-reaction,
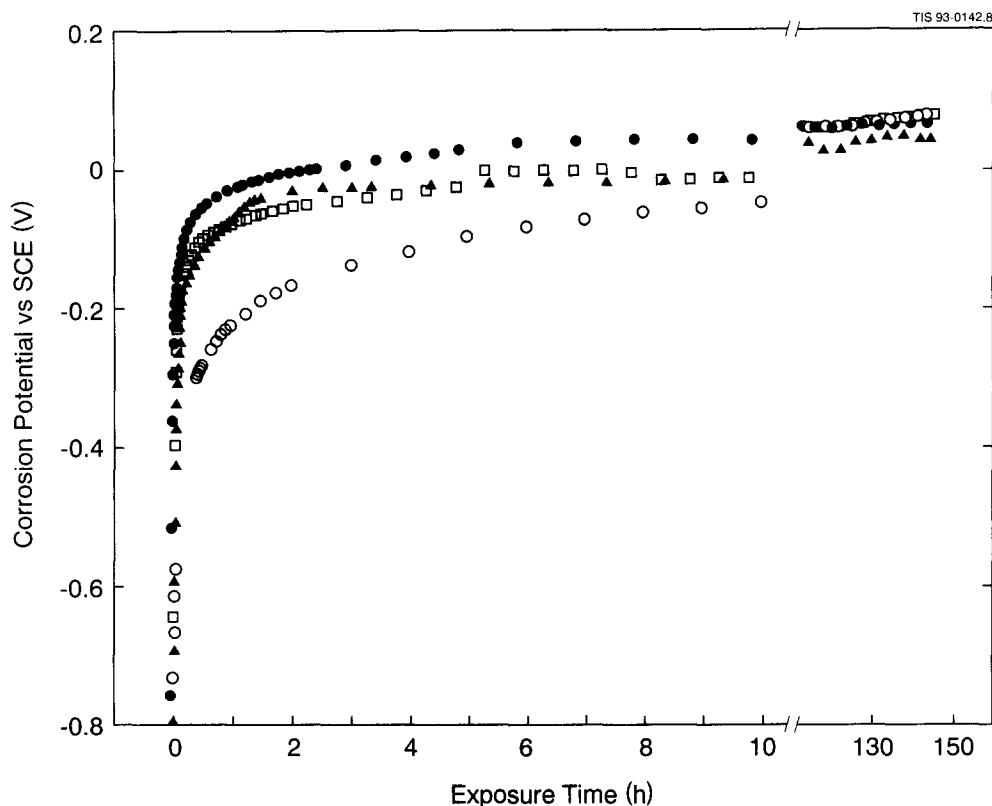
Fig. 2. Corrosion potentials for standard UO_2 fuel (O) and three SIMFUELS as a function of time of exposure to O_2-saturated aqueous solution of 0.1 mol l^{-1} $NaClO_4$ (pH 9.5): ●, 6 at.% SIMFUEL; ▲, 3 at.% SIMFUEL; □, 1.5 at.% SIMFUEL.

i.e. by the reduction of O_2 on the UO_2 surface. Our electrochemical studies have shown that the first electron-transfer step is rate determining for O_2 reduction, and is partially controlled by the number of donor–acceptor sites in the UO_2 surface. The faster rate of SIMFUEL oxidation can be attributed to the increase in the number of such sites and their catalysis of the O_2 reduction process; whether precious-metal particles also play a role remains to be determined [1, 4].

In contrast, all four electrodes achieve approximately the same final corrosion potential (Fig. 2), which dictates the steady-state oxidative–dissolution rate [2]. This coincidence suggests that the corrosion of UO_2 fuel is unaffected by the degree of doping (burn-up). Because the steady-state electrochemical characteristics of the SIMFUELS at positive potentials remain to be determined, such a conclusion must be considered as tentative. However, a common oxidative–dissolution rate would be consistent with a dissolution process controlled by the properties of the $UO_{2.33}$ layer, which is formed on the SIMFUELS as well as on UO_2. An equivalent surface composition as a function of the corrosion potential has been demonstrated (for all four electrodes) by X-ray photoelectron spectroscopy.

Acknowledgments

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