A Preliminary Study on H_2O_2 Reactions on SIMFUEL with Different Doping Elements

L.Wu and D.W.Shoesmith
University of Western Ontario, London, ON, Canada, N6A 5B7 (lwu59@uwo.ca)

Abstract

Using electrochemical measurements, we have studied the effect of different doping elements on H_2O_2 reactions on simulated spent nuclear fuels. It is observed that H_2O_2 decomposition is significantly accelerated by the doped noble metal particles. Raman spectroscopy is used to analyze the surface lattice structure, and the rare earth elements doping is found to induce defects in the sublattice structure.

1. Introduction

The recommended approach for the long term disposal of used nuclear fuel in Canada is adaptive phased management including the isolation of the used fuel in centralized containment in a deep geological repository. Although it is not expected, in the event of container failure fuel corrosion and release of radionuclides would occur within the groundwater flooded container. The corrosion performance of spent nuclear fuel is highly influenced by the fission products from in-reactor burnup. Simulated spent nuclear fuel (SIMFUEL) replicates the chemical states and microstructure of irradiated fuel so that detailed experiments on corrosion behaviour, fission-gas release and thermal conductivity can be undertaken in the laboratory [1-2]. The fission-product composition of irradiated UO_2 is determined by its starting enrichment and irradiation history. Previous investigations on high bumup UO_2 fuels indicate two major categories of fission products, noble metal particles and rare earth elements. Noble metal elements (Mo, Ru, Rh, Pd, etc.) tend to segregate to grain boundaries to form uniformly distributed spherical precipitates referred to as ε-particles. Rare earth elements (La, Ce, Nd, Y, etc.) remain as substitutional ions within the fuel matrix. These fission products cause significant changes in fuel properties and dissolution rate [3].

Hydrogen peroxide produced from water radiolysis on fuel surface is expected to be the major oxidant of spent fuel under disposal conditions, and a major effort has gone into the research of H_2O_2 reactions on UO_2 and simulated spent fuel [4]. H_2O_2 drives the dissolution of UO_2 electrochemically, and can also decompose to O_2 and H_2O. To obtain an understanding of the kinetics and mechanism for H_2O_2 reduction on UO_2, the electrochemical reduction of H_2O_2 has been investigated on different electrodes under various conditions [5-8], using a series of SIMFUEL specimens containing different amounts of simulated fission products. Goldik et al. [6] have performed steady-state polarization measurements and cyclic voltammetric experiments followed by XPS analyses under diffusion-compensated conditions. It has been shown that the cathodic reduction of H_2O_2 is catalyzed by the formation of a thin surface layer of mixed oxidation states (U^{IV}/U^{V}), but kinetically blocked once U^{VI} species start to form. The H_2O_2 reduction rate is independent of pH between pH 10-12, but is suppressed at more alkaline values. The reduction of H_2O_2 proceeds with a weak dependence on applied potential and a fractional reaction order with respect to H_2O_2. It is also found that at low overpotentials, this process proceeds significantly faster on the noble metal particles than on the UO_{2+x} lattice [8].

However, the effect of doping elements on the kinetics of H_2O_2 oxidation and reduction is still not totally understood. The objective of this study is to improve understanding of different doping elements on the electrochemistry and lattice structure of uranium dioxide.

2. Experimental

2.1. Basic properties of SIMFUEL

SIMFUEL pellets contains stable elements added to simulate the composition of UO_2 fuels at 3% burn-up were supplied by Chalk River Laboratories. The pellets were sintered at 1650°C to achieve the atomic scale mixing and secondary phase development characteristics of high temperature fuels [2]. The electrodes are doped with either, or both, noble metal particles and rare earth (RE) elements. Ru, Mo, Rh and Pd segregate to form ε-particles, and the elements La, Ce, Nd, Y, Sr, Zr and Ba substitute for U^{IV} in the fuel matrix. Split SIMFUEL contains one or other of these two groups.

2.2. Equipment and procedure

A standard three-compartment cell is used in all experiments with a Solartron 1287 potentiostat providing IR compensation. All solutions used were made with MilliQ millipore water (18.2 MΩcm), and pH is adjusted with NaOH solution. Ar-purging is applied through all experiments.

The electrode is polished (wet) with 1200 grit polishing paper and rinsed with distilled deionized water. Before electrochemical experiments, the electrode is ultrasonically cleaned with distilled deionized water for 5 min to remove any polishing particles from the surface. SIMFUEL electrodes were cathodically cleaned at a potential of -1.2 V for 1~2 min prior to use. Raman and ToF-SIMS analyses were performed on freshly polished electrodes. In H_2O_2 decomposition experiments, uranium concentration is analyzed by ICP-AES, and H_2O_2 concentration by UV-vis spectroscopy based on the reaction of I^- and H_2O_2 that results in a UV absorbing species, I_3^-.

3. Results

3.1. Electrochemistry of split SIMFUEL

The corrosion potential (E_{CORR}) was measured on 3at.% SIMFUEL with different doping elements in Ar-purged 0.1M NaCl solution. After 20 hours, a stable potential of ~ -200mV is achieved. The E_{CORR} of electrodes doped with all 11 elements or with only rare earth were slightly higher than that of the electrode with noble metal particles.

The cyclic voltammogram for each electrode is shown in Fig. 1. The H_2O reduction currents are higher on the electrodes with ε-particles (black and red) is due to the catalytic effect of the ε-particles. A lower anodic current is observed on the electrodes with rare earth doping (black and blue). This is attributed to the suppression of the UO_2 oxidation process by rare-earth doping.

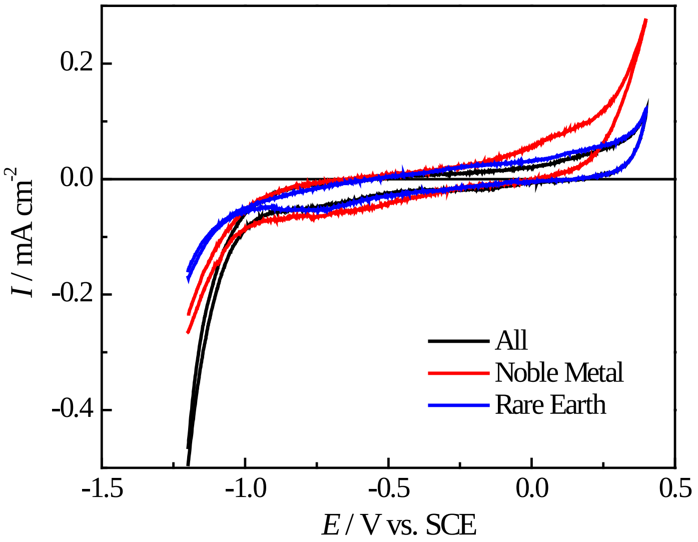

Fig. 1. Cyclic voltammogram recorded on 3at.% SIMFUEL with different doping in an Ar-purged 0.1mol/L NaCl solution at pH 9.5. Scan rate=5mV/s, and the rotation rate=0Hz.

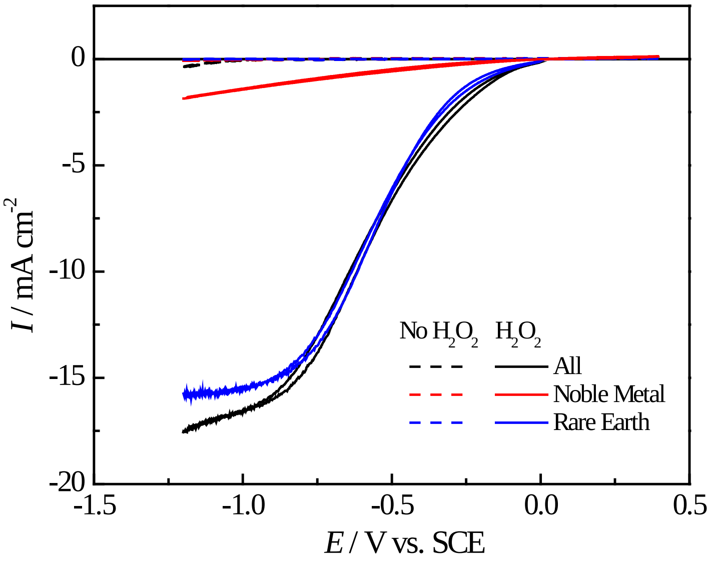

Fig. 2. Cyclic voltammogram recorded on 3at.% SIMFUEL with different doping in an Ar-purged 0.1mol/L NaCl solution with H_2O_2=0.01M at pH 9.5. Scan rate=15mV/s, and the rotation rate=16.7 Hz.

CVs in H_2O_2 solution show a significant difference between the electrode doped with noble metal particles and the other two in Fig. 2. The reduction currents on the rare earth doped electrode is close to that recorded on the electrode containing all 11 elements. However, for electrode with only noble metal particles the H_2O_2 reduction current is significantly lower. The steady-state reduction currents were also measured and a similar trend is observed. Presently, the reason for this low current is not understood.

3.2. The effect of ε-particle on H_2O_2 decomposition

Experiments on H_2O_2 decomposition were conducted in a solution containing 0.001M of H_2O_2 and 0.05M of Na_2CO_3. After the electrodes were held potentiostatically at +0.2 V for 4.3 hours (pH=11.0), amounts of H_2O_2 consumed (n_{H2O2}) and U dissolved (n_{UO2}) were determined by solution analysis, and the total anodic charge is calculated from current integration. Fig. 3 shows that the decrease of $[H_2O_2]$ (blue) is considerably higher in the presence of ε-particles, and much higher than the total charge consumed electrochemically, indicating that decomposition is the major cause of $[H_2O_2]$ consumption in the presence of ε-particles.

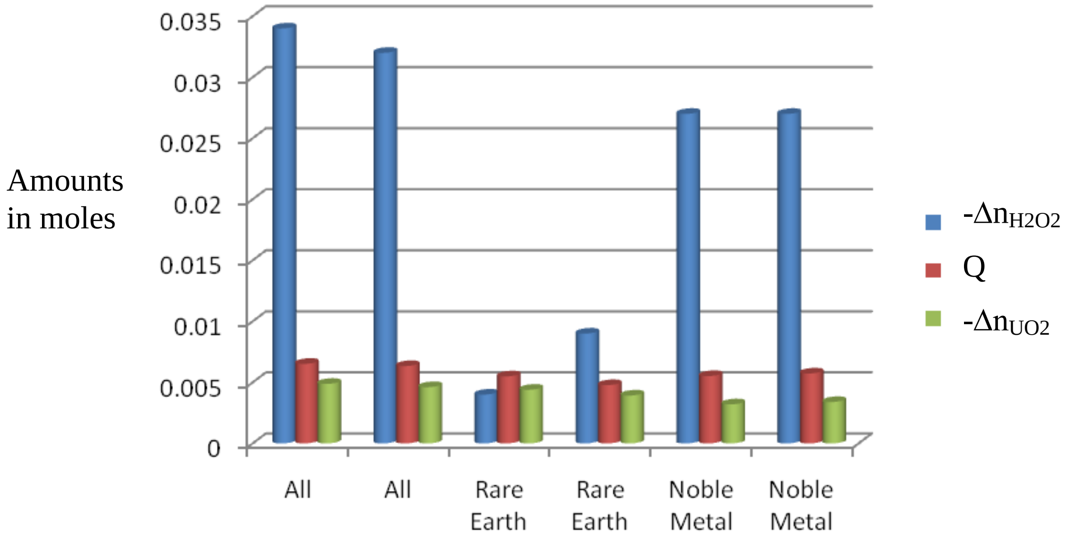

Fig. 3. The changes in H_2O_2 consumed (Δn_{H2O2}), the total electrochemical charge consumed anodically (Q converted to moles) and the amount of U dissolved ($\Delta n(UO_2)$, as UO_2^{2+}) in 0.001 M $[H_2O_2]$.

3.3. Raman

Raman microspectroscopy was used to research the influence of doping on defect structure. The spectra obtained on SIMFUEL doped with only noble metal particles possessed the single fundamental vibrational stretch of the fluorite structure at 445 cm^{-1}, and a broad band near 1150 cm^{-1} [9]. The bands are sharp and intense, and the T_{2g} band possesses only a single component, indicating a well-ordered fluorite structure. In contrast, the spectra obtained on the rare earth doped electrode have broader peaks, attributable to structural distortions within the anion sublattice, accompanied by an increased relative importance of the broad band associated with oxygen sublattice damage (630 cm^{-1}). Thus the surface lattice remains fine in the case of noble metal doping only, while rare earth doping will induce defects in the structure.

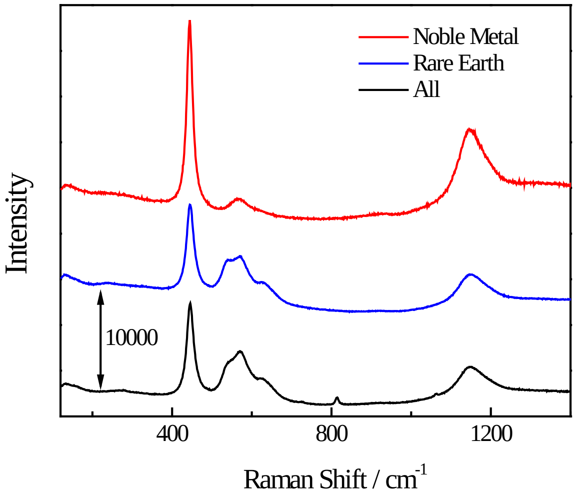

Fig. 6. Raman spectra obtained at different SIMFUEL electrode (freshly polished).

4. Conclusion

The effect of different dopings on electrochemical properties of SIMFUEL has been studied. It is found that H_2O_2 decomposition is significantly accelerated on noble metal particles. Thus fuel corrosion can be suppressed in the presence of noble metal particles. The doped rare earth elements are found to induce defects in the sublattice structure.

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