Effect of UV Irradiation on Electrochemical Behavior of Zirconium Oxide at High Temperature Water Conditions

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1. Introduction

It has been reported that photon (gamma) irradiation may have a significant effect on zirconium alloy corrosion kinetics [1], and there are various photon sources with a wide energy spectrum in the core of a nuclear power plant, from ultraviolet (UV) light, generated by decelerating electrons in water (Cerenkov effect), to gamma from nuclear decays and γ emission. This photon irradiation can influence the corrosion of zirconium alloys by two different mechanisms, one is emergence of photocurrent generated by electron-hole pairs in the oxide itself, and the other is change of corrosion potential due to water radiolysis [2–4], and also it has been reported that the average photon energy from the Cerenkov effect is enough to generate photoelectrons in ZrO_2 (n-type with band gap between 2 and 5 eV) [5]. The differences between predicted weight gain vs measured weight gain from out-of-reactor data is much larger than in-reactor data, supporting the idea that photon (gamma) flux influences the corrosion rate of zirconium alloy. Furthermore, several literatures have been focused on the effect of UV effect on corrosion of zirconium alloy under BWR condition [2,6,7], but the effect of UV irradiation on zirconium alloy under PWR condition is not fully investigated. Therefore, in this study, to investigate the how UV influences on corrosion of zirconium alloy and the photocurrent mechanism, UV irradiation on Zircaloy-4 is used with a dedicated in-situ electrochemical system working at high-temperature and -pressure conditions.

2. Experimental

An advanced design concept has been developed for the in-situ UV irradiation EIS cell, and it is displayed in Figure 1. The cell design consist of 3 different parts, the first is the adaptor to the sapphire window, which is engineered on the wall of the 5 L autoclave, the second part is Pt disk with 1 mm thickness, and the last part is the Zircaloy-4 (Zr-4) disk supplied from Westinghouse with 0.9 mm thickness. Thanks to the adaptor, the cell geometry is maintained together with Magnesia-stabilized zirconia rods and washers, and the distance between the two disks can be set at 3 mm. Figure 2 shows the actual cell design with the adaptor, Pt disk, and Zircaloy-4 disk. The right figure in Figure 2 is the adaptor installed on the autoclave sapphire window. Corrosion experiment has been conducted at 320 ℃ DI water condition with circulation loop for maintaining water chemistry, dissolved oxygen below 100 ppb and dissolved hydrogen condition as 30 cm^3/kg for 12 d with UV irradiation. Open circuit potential (OCP) was measured at two different conditions; 1) In-situ OCP at 320 ℃ DI water with circulation loop at 12 d, and 2) UV-irradiated pre-corroded Zr-4 at 320 ℃ DI water with loop for 12 days in 0.01 M Na_2SO_4 solution. Also In-situ Mott-Schottky data of UV-irradiated and non-UV irradiated samples is compared to investigate the effect of UV on minority carrier concentration in the oxide layer.

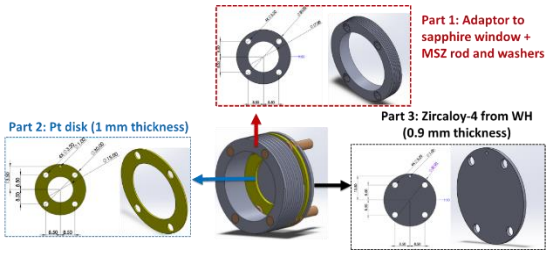

Figure 1. Advanced in-situ EIS cell design for sapphire engineered autoclave

Figure 2. The compromised cell (Pt and Zircaloy-4 disk, adaptor for the autoclave)

3. Results and Discussion

Figure 3 is the optical image of 12 d UV-irradiated Zircaloy-4 disk. Compared to non-irradiated region, the color of UV-irradiated region is much brighter than non-irradiated region, and the diameter of it is exactly same as the middle hole in the Pt disk, 15 mm, for penetrating UV from UV guide. OCP was measured at various condition for investigating the effect of UV irradiation on zirconium oxide. Figure 4 and 5 show the OCP reaction of 12 d corroded Zircaloy-4 with UV irradiation at 320 ℃ DI water and 0.01 M Na_2SO_4 solution. Both

results reveal that *n*-type behavior of oxide, decreased OCP when UV is on, but the value of OCP change is higher at room temperature experiment. It is likely due to the noise at high temperature experiment as well as different electrolyte condition.

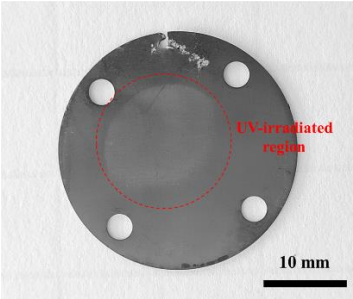

Figure 3. An optical image of UV-irradiated Zircaloy-4 for 12 d at 320 ℃ DI water

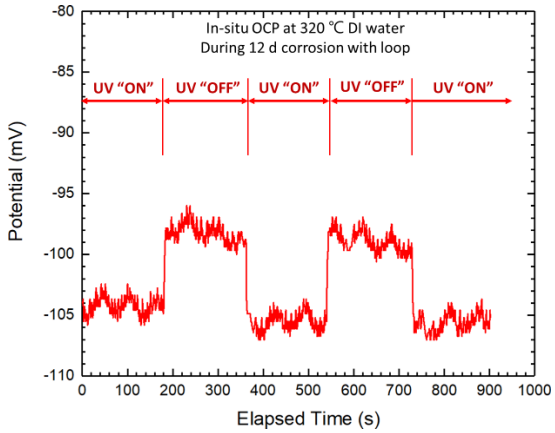

Figure 4. In-situ OCP change Zircaloy-4 with UV irradiation at 320 ℃ DI water

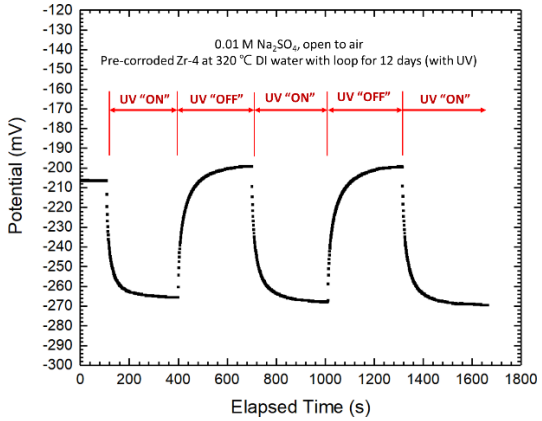

Figure 5. OCP change of 12 d UV-irradiated Zircaloy-4 at 0.01 M Na_2SO_4 solution

In-situ Mott-Schottky data is illustrated in Figure 6. The slope of Mott-Schottky graph of non-UV 45 d corroded Zircaloy-4 is steeper than that of UV irradiated 12 d corroded Zircaloy-4. It means that flat band potential of UV-irradiated sample is lower than that of non-UV irradiated sample. The donor density of UV-irradiated sample is higher than non-UV irradiated sample, and the value is $1.72 \cdot 10^{18}$ / cm^3, $7.91 \cdot 10^{17}$ / cm^3, respectively.

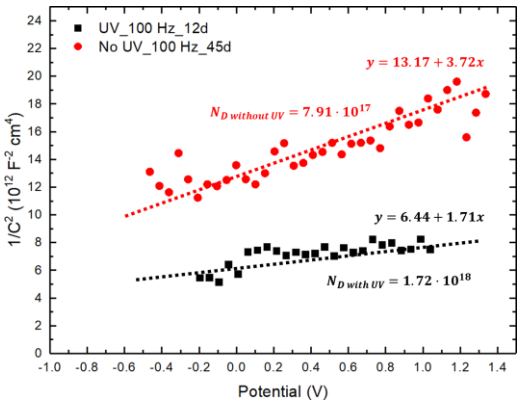

Figure 6. In-situ Mott-Schottky data at 320 ℃ DI water

4. Conclusions

The effect of UV irradiation on Zircaloy-4 at 320 ℃ DI water has been investigated in this study. As reported previously, microstructural characterizations show that magnetite crystals nucleate and grow on top of zirconium oxide under UV irradiation OCP change due to UV irradiation shows the *n*-type behavior of zirconium oxide. Mott-Schottky analysis shows that the flat band potential decreases -0.2 V with UV irradiation on the oxide and that the donor density at the oxide surface increases twice under UV.

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