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Effect of Temperature on Electrochemical Catalytic Decomposition of H_2O_2 on UO_2

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1. Introduction

Spent nuclear fuel is safely and permanently disposed of in deep geological environments. However, various safety scenarios are reviewed to ensure its safe management. Dissolution of spent nuclear fuel in groundwater exposure is a critical consideration from the perspective of radioactive material dispersal. Uranium oxide (UO_2) is oxidized by H_2O_2, a radiolysis product of water. When uranium (IV) oxide oxidized to U(V) or U(VI) oxides, uranium readily dissolves in groundwater through the formation of carbonate/bicarbonate complexes. [1].

However, unlike UO_2, spent nuclear fuel possesses oxygen vacancies due to lanthanide doping, and a small grain size. The oxidation of spent nuclear fuel by H_2O_2 is significantly suppressed. Furthermore, H_2O_2 decomposition is promoted by ε-particles (noble metal inclusions), so oxidation rarely occurs. The underlying mechanism for this oxidation inhibition is the decomposition of H_2O_2 on the UO_2 surface. In other words, the redox reaction between UO_2 and UO_{2+x} is understood to act as a catalyst for H_2O_2 decomposition [2].

The decomposition of H_2O_2 is influenced by various factors such as temperature, H_2O_2 concentration, and catalytic surface properties [3]. In this study, the effect of temperature on the electrochemical catalytic behavior of UO_2 was investigated. After confirming that UO_2 can act as a catalyst for H_2O_2 decomposition at room temperature based on redox potential analysis, its catalytic feasibility up to 100°C was evaluated by comparing temperature-dependent reduction potentials.

2. Methods and Results

2.1 Analysis Condition

The oxidation reaction of UO_2, which acts as a catalyst in groundwater, should be considered as oxidation to UO_{2+x} ($0 < x < 0.33$), but since it is difficult to obtain thermodynamic data for the corresponding compound, UO_{2+x} was conservatively approximated by assuming $x = 1$ for the purpose of potential estimation. In addition, the pH was assumed to be pH 9 considering the groundwater conditions. The pH at high temperatures should be calculated by considering the high-temperature dissociation and decomposition of carbonates. However, for simplicity, the high-temperature pH was estimated by applying a constant offset to the neutral pH of water at each temperature.

2.2 Analysis Methods

For the reduction potentials of H_2O_2 to H_2O and O_2 to H_2O_2 at 25°C, commonly known values were used. The potentials for the onset of reduction and oxidation of H_2O_2 at high temperatures were calculated by applying the chemical potential values at room temperature and the temperature-dependent heat capacity (C_p) values to the Linear Ionic Heat Capacity Approximation (LIHCA) method [3]. The chemical potential and heat capacity data of the compounds involved in the analysis were used from reported data [4]. Since the oxidation and reduction reactions of H_2O_2 and the redox reactions of UO_2/UO_{2+x} ($x = 1$ assumption), which are the considered reactions, have the same potential shift according to pH change at each temperature, the potential comparison was made based on pH 0 at each temperature.

2.3 Potential shift comparison for temperature change

For UO_2 to act as an electrochemical catalyst for the H_2O_2 decomposition reaction, both the oxidation of UO_2 and the reduction of UO_{2+x} by H_2O_2 must occur. As mentioned earlier, due to the lack of thermodynamic data, the analysis temporarily used data for UO_{2+1} by assuming $x = 1$. While the data was used conservatively, it should be noted that in real systems, once UO_2 is oxidized to UO_{2+1}, it is not reduced back to UO_2 by a reducing agent.

For the continuous oxidation of UO_2 and the reduction of UO_{2+x} by H_2O_2 to UO_{2+x} must occur spontaneously, and the reduction of UO_{2+x} to UO_2 must also occur spontaneously. Therefore, the redox potential of UO_2/UO_{2+x} must be lower than the reduction potential of H_2O_2 and higher than the oxidation potential of H_2O_2.

Figure 1 shows the reduction potential of H_2O_2, the oxidation potential of H_2O_2, the starting potential of H_2O_2 oxidation, and the redox potential of UO_2/UO_{2+1} over the temperature range of 25°C to 100°C. Each potential value was calculated for the pH = 0 condition. Since the pH at 25°C was set to 9, pH corrections at each temperature were necessary. However, since the potential shift due to pH change is constant at (2.303•RT/F)•ΔpH for all three reactions at a constant temperature, the potentials at pH 0 for the corresponding temperatures were compared with each other.

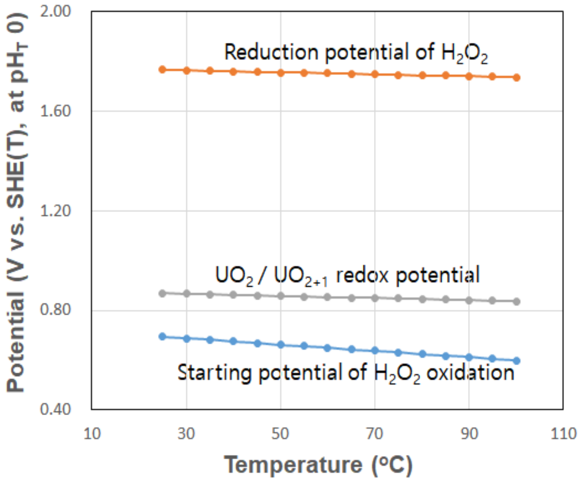

Fig. 1. Changes in reduction potential (vs. SHE(T)) with temperature. Reduction potential of H_2O_2 (orange), reduction potential of UO_{2+1} (to UO_2) (grey), reduction potential of O_2 (to H_2O_2) (blue).

As temperature increases, the redox potential of UO_2/UO_{2+x} (x = 1) decreases slightly, but remains consistently between the potentials at which H_2O_2 reduction and oxidation reactions begin in the temperature range of 25°C to 100°C. This suggests that the UO_2 surface can act as an electrochemical catalyst for H_2O_2 decomposition within this temperature range.

Meanwhile, the temperature-dependent potential slope for the H_2O_2 oxidation reaction was evaluated to decrease slightly more steeply with increasing temperature than the other two reactions. This reaction ($H_2O_2 \rightarrow O_2 + 2H^+ + 2e$) is different from other reactions in that it generates gas (O_2). This behavior can be attributed to the additional entropy contribution associated with O_2 gas formation, which affects the temperature dependence of the Gibbs free energy of the reaction.

3. Conclusions

Thermodynamic comparison of temperature-dependent reduction and oxidation potentials indicates that the UO_2 surface can function as an electrochemical catalyst for H_2O_2 decomposition in the temperature range of 25°–100°C. The slightly steeper temperature dependence observed for the H_2O_2 oxidation reaction is attributed to the positive entropy contribution associated with O_2 gas formation.

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