Influence of Trivalent- and Tetravalent-dopants on the Surface Structural and Electrochemical Properties of Uranium Dioxide

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ABSTRACT*: Gd- and Th-doped UO_2 with various doping levels were studied as simulated spent nuclear fuel. Those simulated fuels were investigated through X-ray diffraction, Raman spectroscopy, scanning electron microscopy, and electrochemical experiments to understand their surface structure and electrochemical properties. Surface structure studies showed the existence of oxygen vacancy in Gd-doped UO_2 and the grain structure on the surface of Gd- and Th-doped UO_2 depending on the doping level and stoichiometry. In an electrochemical experiment, it was concluded that both the doping level and oxygen-to-metal ratio affected the oxidation behavior.*

KEYWORDS*: Uranium dioxide, Doping, Surface structure, Spectroscopy, Oxidation*

I. Introduction

Spent PWR nuclear fuel considered as $(U,FP)O2_{\pm x}$ (FP, fission products) or a stoichiometric form is produced depending on the conditions of the nuclear reactor.[1,2] To understand the structure and characteristics of spent fuel, simulated spent fuel such as FP-doped $UO_{2\pm x}$ have been studied.[3-7] The structural changes from the doping effect have a significant influence on not only the relevant fuel performance but also on the kinetics of the fuel oxidation. In this study, Gd^{3+} and Th^{4+} are chosen as trivalent- and tetravalent-dopants in simulated spent nuclear fuel, respectively

II. Experiment Procedure

Gd- and Th-doped UO_2 sample pellets with various doping levels were prepared through a solid-state reaction. UO_2 and Gd_2O_3 (or ThO_2) powders were blended using an agate mortar. The powder mixtures were compressed into a pellet form. The pressed pellets were sintered at 1700 ℃ for 18 h in a hydrogen atmosphere. To make a hyper-stoichiometric form of Gd- and Th-doped UO2, sintered pellets were further heated at a specific temperature under a CO/CO_2 atmosphere. X-ray diffraction (XRD) data of each sample were obtained by using Bruker D8 Advance at room temperature. Scanning electron microscopy (SEM) images were also obtained, and the Raman spectra of each pellet were acquired using an ANDOR Shamrock SR500i spectrometer with a 633-nm wavelength He-Ne laser. For the electrochemical experiments, a standard three-electrode system was employed in carbonate solutions. The working electrode was a Gd - or Th-doped UO_2 pellet assembled on a rotating disk electrode.

III. Results and Discussion

It was confirmed that the dopant is uniformly dissolved in a UO_2 matrix as a solid solution when there is a linear relationship with a specific slope between the lattice parameter and the doping level. For Gd-doped UO_2, the lattice parameter

decreased linearly as the Gd doping level is increased. However, it is opposite for Th-doped UO_2. Our results showed similar features with previous studies.[5-7] Raman spectra of Gd-doped UO_2 showed the defect structure owing to the oxygen deficiency (Fig. 1). However, there is no defective structure in those of Th-doped UO_2 because the replacement from U^{4+} to Th^{4+} cannot produce an oxygen deficiency.[6]

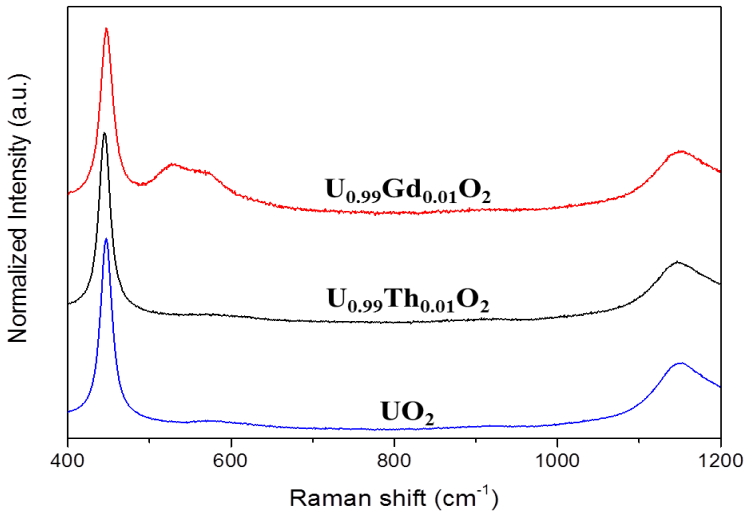

Fig. 1. Raman spectra of UO_2, $U_{0.99}Th_{0.01}O_2$ and $U_{0.99}Gd_{0.01}O_2$.

SEM images for Gd-doped UO_2 show that the grain size decreased with an increase in the Gd doping level and decreasing oxygen-to-metal ratio (Fig. 2). These features are strongly related to the oxygen vacancy and interstitial oxygen. However, there is a relatively small change for the grain size in those of Th-doped UO_2 with under the same conditions.

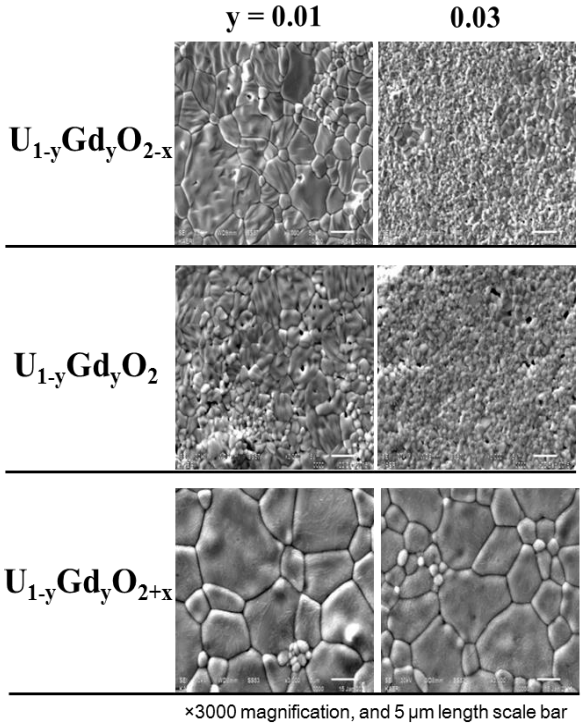

Fig. 2. SEM images of surface of $U_{1-y}Gd_yO_2$ and $U_{1-y}Gd_yO_{2\pm x}$ solid solutions with increasing Gd contents

Cyclic voltammetry experiments for sample pellets were conducted to determine the susceptibility to anodic oxidation. The Gd-doping effect shows the suppression of both stages of surface oxidation and its further oxidation (Fig. 3). Not only the doping level but also the oxygen-to-metal ratio affects the kinetics of the oxidation.

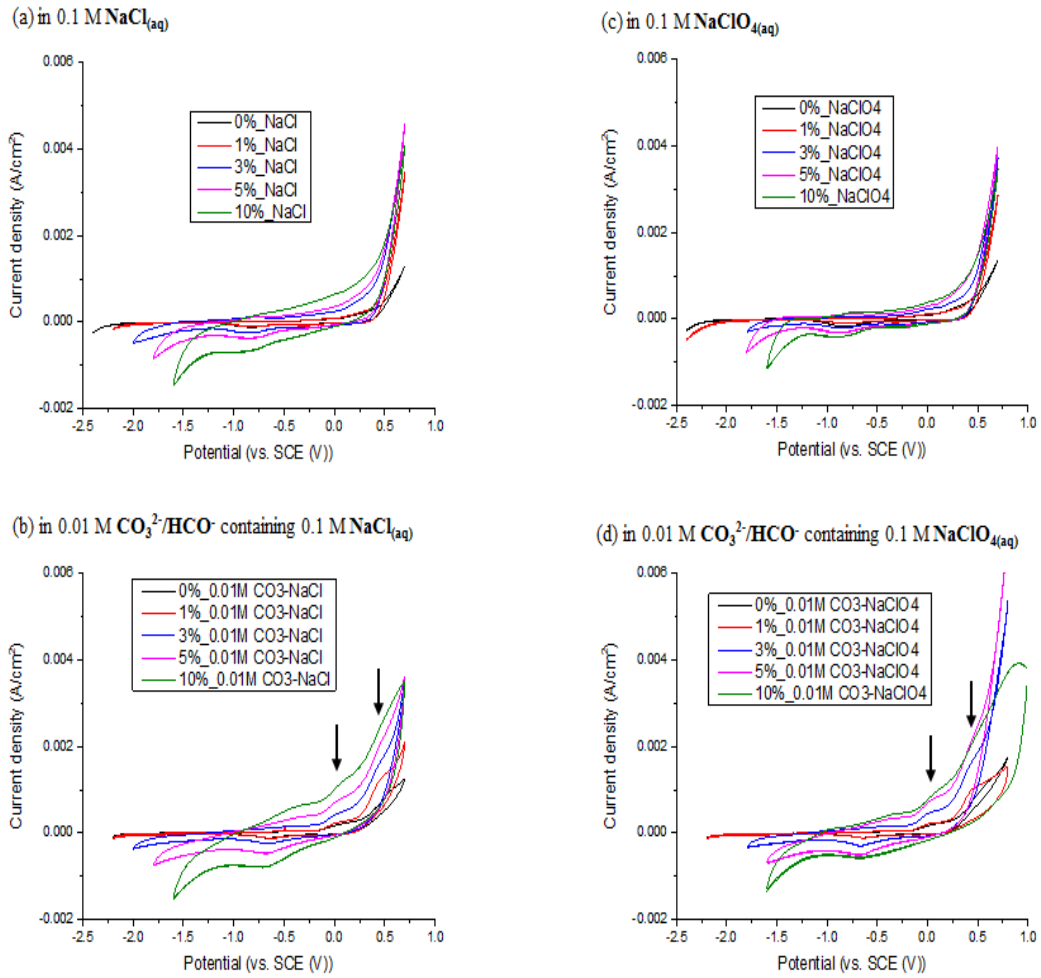

Fig. 3. Cyclic voltammograms of hypo-stoichiometric UO_2 and $(U,Gd)O_{2-x}$ (a) in 0.1 M $NaCl_{(aq)}$ solution, (b) in 0.01 M CO_3^{2-} /HCO^- containing 0.1 M $NaCl_{(aq)}$ solution, (c) in 0.1 M $NaClO_{4(aq)}$ solution, (d) in 0.01 M CO_3^{2-}/HCO^- containing 0.1 M $NaClO_{4(aq)}$ solution, at pH 9.0. Scan rate is 0.05 V/sec. % represents mol% of Gd in $(U,Gd)O_{2-x}$.

IV. Conclusions

Gd- and Th-doped UO_2 with various doping levels were investigated through XRD, Raman spectroscopy, SEM, and electrochemical experiments to understand their surface structure and electrochemical properties. Raman spectra showed the existence of oxygen vacancy in Gd-doped UO_2. SEM images showed the grain structure on the surface of Gd- and Th-doped UO_2 depending on the doping level and stoichiometry. In an electrochemical experiment, it was concluded that both the doping level and oxygen-to-metal ratio affected the oxidation behavior. These results provide fundamental data to improve our understanding of spent fuel.

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ACKNOWLEDGMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant(2017M2A8A5014754) funded by the Korea government (Ministry of Science, ICT and Future Planning, MSIP)

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