The influence of Gd_2O_3 doping on the electrochemical reactivity of uranium dioxide

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Abstract

The influence of a trivalent dopant, Gd^{3+} (6 weight %) on the structure, surface morphology and electrochemical reactivity of uranium dioxide was studied using Raman spectroscopy, Scanning Electron microscope (SEM)/Energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS) and Cyclic Voltammetry. The results show that the electrodes are uniformly doped and the redox behaviour demonstrates that doping to this level stabilizes the cubic fluorite structure of UO_2 against anodic oxidation/dissolution.

1. Introduction

One option Canada is considering for the management of spent nuclear fuel is its disposal in copper containers in a deep geological repository in the Canadian Shield [1]. The concept comprises a series of barriers such as a waste container, a clay buffer compacted around the container, repository sealing materials, and the geosphere. However, a safety assessment of this repository requires a detailed understanding of the corrosion mechanism of the spent fuel in the event of failure. Spent fuel consists mainly of UO_2 (>95%) with the remainder being radioactive fission isotopes produced by irradiation. UO_2 is often doped with gadolinium (Gd) which is used as a burnable poison in light water reactors (LWR), modern pressurized water reactors (PWR) and heavy water reactors (HWR) [2]. Due to its high neutron absorption cross section, it offers a better efficiency at the beginning of the burning cycle. In addition, its use increases the burn-up of the fuel which reduces the generation cost in reactors and increases power density [3]. It can also be considered a representative rare-earth dopant of the spent fuel to be disposed of.

Therefore, it is important to study its influence on fuel reactivity. Its effect on the air oxidation of UO_2 has been studied [4-6] and found to enhance the stability of the cubic fluorite structure (U_4O_9-type structure with respect to U_3O_8-type) to higher temperatures and higher O/M ratios as compared to undoped UO_2.

Park and Janeczek [2, 7], attempted to explain this increase in oxygen potential/stability of the cubic phase on oxidation of doped UO_2. It was proposed that oxygen interstitial sites are blocked by the dopant cations and are,therefore, inert to oxidation. The phase-relationships between lanthanide-oxides and uranium oxide suggest that the solubility of lanthanide elements in UO_{2+x} decreases with an increase in x and that these elements are insoluble in the U_3O_8 phase. However, a kinetically metastable state (rare earth doped U_3O_8 phase) is possible by oxidation of rare-earth doped UO_2 [8].

Based on the expectation that UO_2 stability will increase with increasing burn-up/doping content, we have investigated the effect of Gd-doping by electrochemical methods using 6 weight % Gd_2O_3 doped UO_2 electrodes. These electrodes were also characterized by Raman spectroscopy.

2. Experimental

2.1 Electrode material, Solution and Equipment

Experiments were performed on unirradiated 6 weight% Gd-doped UO_2 electrodes prepared by Cameco, Canada. Solutions were prepared using deionized water (ρ =18.2 MΩ cm) purified using a Millipore milli Q plus unit to remove organic and inorganic impurities. Electrolytes were prepared with NaCl (0.1 M), saturated with Ar-gas (Praxair). The solution pH was adjusted to the desired value using either HCl or NaOH. All chemicals used were analytical grade.

Experiments were performed in a standard three-electrode, three-compartment cell. A Pt sheet ~ 6 cm^2 spot-welded to a Pt wire was used as a counter electrode. A Solartron model 1287 potentiostat was used to control applied potentials and to record current responses. The current interrupt method was employed to compensate for potential drop due to the electrode and solution resistances. Corrware^{TM}, version 3.0, software was used to analyze the data. All the potential measurements were recorded against a saturated calomel electrode (SCE).

2.2 Experimental Procedure

In Cyclic Voltammetric (CV) experiments the electrode was cathodically reduced at -1.5 for 1 minute and then scanned twice from this potential to different anodic limits and back while recording the current. The CVs give a summary of the oxidation (anodic or forward scan) and reduction (cathodic or reverse scan) processes that can occur on the electrode surface within the potential range scanned. A Renishaw 1000 Confocal Raman Spectrometer (λ = 632.8 nm) was used to acquire Raman spectra.

3. Results

3.1 Electrochemistry of Gd_2O_3 doped UO_2

Gd_2O_3 doped UO_2 and 1.5 atom% SIMFUEL electrodes were electrochemically cleaned after emersion in Ar-purged electrolyte. Figure 1 (a, b) shows the CVs recorded in the potential range of -1.5V to +0.4V. No significant oxidation current was observed in the -0.8V to -0.2V region indicating the absence of non-stoichiometric grain boundaries in both the electrodes. However, the anodic currents for SIMFUEL were slightly higher than those for Gd-doped UO_2 in this region (Figure 1b inset).

A slight increase in anodic current appears beyond ~0 V on the Gd-doped electrode. This can be attributed to the general oxidation of the stoichiometric grains from UO_2 to UO_{2+x}, which occurs via the injection of O^{2-} ions into interstitial sites in the UO_2 fluorite lattice [9]. By contrast, Figure 1b (inset) shows that on SIMFUEL this oxidation process starts around ~ -0.2V which is lower than on the Gd-doped electrode. This indicates a decreased reactivity for the Gd-doped resulting in a delay of this first oxidation step.

The large increase in anodic currents in the region E ~ +0.4 V (Fig. 1(a and b)) is due to the oxidation of this UO_{2+x} layer to soluble uranyl species, UO_2^{2+} and the formation of a U^{VI} ($UO_3.\gamma H_2O$) deposit due to its limited solubility at this pH. On the reverse scan both the layers (UO_{2+x} and $UO_3.\gamma H_2O$) are reduced in the potential range -0.6 to -0.9 V. On the SIMFUEL electrode the large currents present at very negative potentials are due to H_2O reduction on noble metal particles present in the UO_2 matrix. UO_2 doped with Gd does not show the significant oxidation at positive potentials, and, moreover currents are inhibited throughout the redox region from -1.5V to +0.4V as compared to 1.5 atom% SIMFUEL (Fig. 1b). A possible explanation is that the fluorite structure is stabilized by the doping and according to the literature it has been explained that Gd^{3+} replaces U^{4+} sites in the fluorite lattice which leads to the co-existence of U^{4+} and U^{5+} $[U^{4+}_{1-2y}U^{5+}_{y}Gd^{3+}_{y}O^{2-}_{2}]_{fluorite}$ for the formal charge balance in the UO_2 lattice [10]. Therefore as Gd content is increased, the U^{IV} content would decrease leading to a lowering of the first oxidation step.

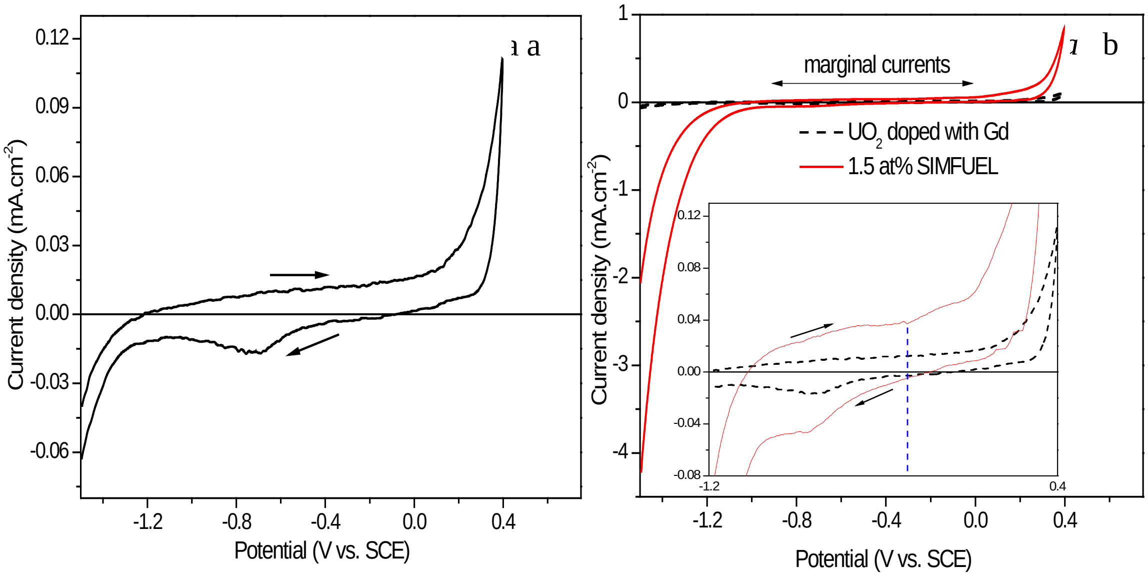

Figure 1 CVs recorded on a (a) 6 weight % Gd_2O_3 doped UO_2 (b) 1.5 atom% SIMFUEL electrode in Ar-purged 0.1M NaCl solution at pH=9.5. The scan rate=10 mV/s. The inset in Figure 1(b) shows a comparison of the currents measured on the two electrodes.

3.2 Surface Analysis by Raman Spectroscopy

Figure 2a shows the optical image of the Gd-doped electrode with two different areas and Fig. 2b shows the spectra collected at these two locations. Both spectra exhibit a band at 450 cm^{-1} which is assigned to the symmetric (O-U) stretching mode of the fluorite structure of UO_2 [11]. The very small kink around 1150 cm^{-1} is diagnostic band for the stoichiometric UO_2 [11]. The decreased intensity of this band has been attributed to increased doping levels and is accompanied by a corresponding increase in intensity of the broad peak in the 500-700 cm^{-1} region. The dominant presence of this broad band indicates a highly defective fluorite structure.

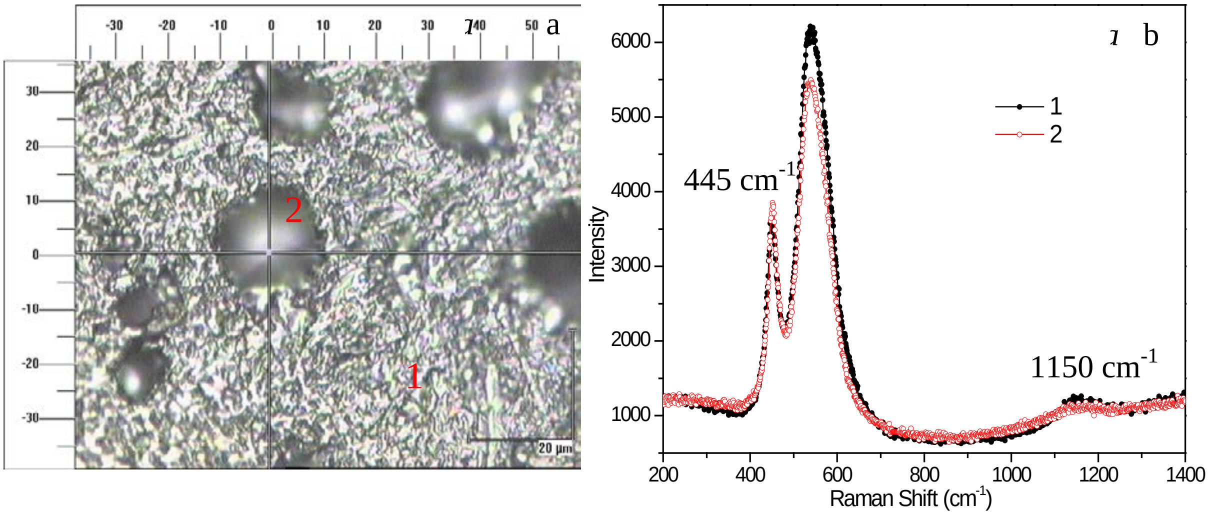

Figure 2 (a) Optical image of the surface of a 6 weight % Gd-doped UO_2 electrode at 50X showing two distinct areas 1 and 2 (b) Raman spectra obtained on the two locations shown in (a)

4. Conclusion

Electrochemical investigation shows that the Gd-doping has an inhibiting effect on the overall oxidation process of the fuel. A doping level of 6 weight % significantly stabilizes the cubic fluorite structure and delays the initial oxidation step, which is also supported (elsewhere) by our XPS analyses. However, to determine if the level of Gd-doping controls the redox process, more experiments on electrodes doped to different extents is required.

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