

Computational investigation of the formation of hyperstoichiometric uranium dioxide  
( $\text{UO}_{2+x}$ )

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The stability of spent nuclear fuel as a waste form depends upon the oxidation behavior of uranium dioxide ( $\text{UO}_2$ ) under repository conditions. Because  $\text{U}^{6+}$  phases are more soluble than  $\text{U}^{4+}$  phases, understanding the formation of higher-oxidized  $\text{UO}_2$  phases is important. While a variety of diffraction and spectroscopic studies have been used to investigate the oxidation behavior of  $\text{UO}_2$  to  $\text{U}_4\text{O}_9$ , questions still remain as to the effect of interstitial oxygen on the oxidation state of uranium in hyperstoichiometric  $\text{UO}_2$ . In this study, computational techniques were used to investigate questions such as: Is the formation of  $\text{U}^{5+}$  or  $\text{U}^{6+}$  more energetically favorable upon the oxidation of  $\text{UO}_2$ ? And, how do calculated activation energies for the diffusion of interstitial oxygen in  $\text{UO}_2$  compare with experimental values?

A density functional theory (DFT) approach was used to investigate the structural location of interstitial oxygen, the energy associated with oxygen substitution into different interstitial sites, and the influence of interstitial oxygen on the redox chemistry of uranium dioxide. Two different quantum mechanical programs were used to perform these calculations, one based on planewaves (CASTEP) and another that uses atomic-like basis functions to describe the electronic structure of each atom (Dmol<sup>3</sup>). Preliminary results from planewave calculations suggest that the formation of one  $\text{U}^{6+}$  is favorable to

a more delocalized charge distribution resulting in the formation of two  $U^{5+}$  for every interstitial oxygen atom.

Experimental studies suggest that two symmetrically unique locations exist for the incorporation of interstitial oxygen in bulk  $UO_2$ . Excess oxygen is thought to be incorporated along the perpendicular bisectors or the body diagonals of the unoccupied cubic sites created by lattice oxygen atoms in the  $UO_2$  structure. Using a single unit cell starting model, quantum mechanical calculations allow us to compare the relative energies associated with placing oxygen on these incorporation sites. Activation energies for the diffusion of oxygen from one such local energy minimum site to another are also evaluated. Calculations are expanded to larger defect cluster formations within the computational limits of DFT methods.