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The defect chemistry of $UO_{2\pm x}$ from atomistic simulations

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Abstract

Control of the defect chemistry in $UO_{2\pm x}$ is important for manipulating nuclear fuel properties and fuel performance. For example, the uranium vacancy concentration is critical for fission gas release and sintering, while all oxygen and uranium defects are known to strongly influence thermal conductivity. Here the point defect concentrations in thermal equilibrium are predicted using defect energies from density functional theory (DFT) and vibrational entropies calculated using empirical potentials. Electrons and holes have been treated in a similar fashion to other charged defects allowing for structural relaxation around the localized electronic defects. Predictions are made for the defect concentrations and non-stoichiometry of $UO_{2\pm x}$ as a function of oxygen partial pressure and temperature. If vibrational entropy is omitted, oxygen interstitials are predicted to be the dominant mechanism of excess oxygen accommodation over only a small temperature range (1265 K to 1350 K), in contrast to experimental observation. Conversely, if vibrational entropy is included oxygen interstitials dominate from 1165 K to 1680 K (Busker potential) or from 1275 K to 1630 K (CRG potential). Below these temperature ranges excess oxygen is predicted to be accommodated by uranium vacancies, while above them the system is hypo-stoichiometric with oxygen deficiency accommodated by oxygen vacancies. Our results are discussed in the context of oxygen clustering, formation of U_4O_9, and issues for fuel behavior. In particular, the variation of the uranium vacancy concentrations as a function of temperature and oxygen partial pressure will underpin future studies into fission gas diffusivity and broaden the understanding of $UO_{2\pm x}$ sintering.

1. Introduction

Due to its radiation tolerance, high melting point, and chemical stability UO_2 has been widely deployed as a nuclear reactor fuel. Particularly important is its ability to accommodate significant compositional changes without altering its crystal structure. This enables it to incorporate large concentrations of soluble fission products and radiation damage without the detrimental volume changes associated with phase transitions. The way in which large deviations in non-stoichiometry of $UO_{2\pm x}$ are accommodated can be understood in terms of its defect chemistry as function of oxygen partial pressure and temperature. Furthermore, defining the populations of uranium and oxygen defects for a given set of conditions is of great importance for understanding thermophysical and thermomechanical properties, mass transport during sintering, and fission gas release [1–4].

Uranium has a number of f and d electrons in its ground state of [Rn] 5f3 6d1 7s2, which enables it to access several valence states that are similar in energy. For example, uranium is nominally U^{4+} in UO_2 but can readily oxidize to U^{5+} creating a low energy $U_U^{\bullet}$ charge compensation mechanism for the negatively charged hyper-stoichiometric defects $V_U^{''''}$ and O_i'' (represented using Kröger-Vink notation [5]). As evidenced by the phase diagram (see Figure 1), UO_2 can be oxidized to UO_{2+x} or U_4O_9 [6, 7], and even up to UO_3 through further oxidation to U^{6+} [8]. The reduction of UO_2 to UO_{2-x} is also possible but only at high temperatures (above 1700 K), highlighting the reluctance of U^{4+} to be reduced to U^{3+} compared to its tendency for oxidation. By fitting to a large set of experimental data [9–23] Guéneau *et al.* [24] modelled the O/U ratio of $UO_{2\pm x}$ for different oxygen partial pressures and temperatures. Due

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