

Verifying the Defect Chemistry of PuO₂

R.T. Bedford¹, S.T. Murphy¹, H. Green², W.D. Neilson³, M.W.D Cooper³

¹School of Engineering, Lancaster University, Bailrigg, Lancaster, LA1 4YW

²Sellafield Ltd., Cumbria, CA20 1PG

³Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico

* Contact: r.t.bedford@lancaster.ac.uk

The UK possesses one of the largest civilian stockpiles of separated plutonium in the world, the majority of which is stored at the Sellafield site. The nature of the stored plutonium can vary, but in general, the plutonium is stored as an oxide powder within an inner breathable can that is then welded shut into an outer over-pack container. The defect chemistry of PuO₂ constantly evolves overtime in storage, as a result of the radioactive nature of plutonium, and the interactions of headspace gas species entrained inside the can. Therefore, ensuring safe long-term storage requires us to understand how the defect chemistry of the material changes as a function of time. In this work, we employ *ab initio* techniques in conjunction with thermodynamic models in the DefAP code [1] to predict the defect chemistry of PuO₂ in the conditions relevant to storage canisters.

Conventional DFT methods are unable to accurately describe PuO₂ due to self-interaction of the 5f-electrons of Pu. To address this, the DFT+*U* method is employed, where a correction parameter, *U*, is applied to the 5f-electrons of Pu. The experimental bandgap for PuO₂ ranges between 1.8 eV [2] and 4.1 eV [3], which can result in confusion around the ideal value for the *U* parameter. The work of Neilson *et al.* [4] fitted *U* = 7 eV to the bandgap of PuO₂, calculated using the hybrid functional HSE06, which has been shown to accurately reproduce experimental bandgaps of many materials. Whilst Neilson *et al.*'s [5] further work on the accommodation of Am in PuO₂ was in good agreement with experimental results, some may still question the choice of *U* = 7 eV given that it is much greater than values used for other actinide oxide studies [6][7]. Chen's [8] recent work recommended *U* = 4 eV for 3k longitudinal anti-ferromagnetic (3k AFM) PuO₂ in DFT.

In this work, we compare the defect chemistry of PuO₂ when *U* = 4 eV and *U* = 7 eV, observing how the oxygen potential as a function of stoichiometry aligns with values determined from experiment. The effect of calculating the standard chemical potential of oxygen using a non-DFT+*U* reference material against using PuO₂/Pu-metal is also included. Finally, we analyse how the *U* parameter affects the accommodation of uranium, a decay product of Pu, by tuning the *U* values for both plutonium and uranium.

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