

Modeling Oxidation States of Ce within Cerium Oxide using DFT+*U* and Hybrid-DFT : Choosing an Appropriate *U*

Natasha M. Galea and Graeme W. Watson
School of Chemistry, Trinity College Dublin, Ireland

Abstract

Cerium oxide has generated substantial research interest with regard to a wide range of catalytic applications. Current industrial operations focus, most significantly, on catalytic pollution abatement. However, considerable research has been carried out on cerium oxides's relatively new role in the emerging field of Solid Oxide Fuel Cells (SOFCs). Ceria (CeO_2 , containing Ce^{4+} ions) can be employed via its ability to store and release oxygen, known as the oxygen storage capacity (OSC), while utilizing the stability of both Ce^{4+} and Ce^{3+} ions within the material. Complete reduction of CeO_2 produces reduced cerium oxide (Ce_2O_3) exclusively containing Ce^{3+} ions.

To correctly model electron localization within DFT, compounds containing cerium require the addition of the Hubbard *U* term, which in turn will also accurately establish an insulating species. Discussion still occurs within the literature over the 'correct' *U* value for cerium, for both CeO_2 and Ce_2O_3 . This inconsistency in choosing the cerium Hubbard *U* term is a considerable obstacle when considering the complete reduction reaction of CeO_2 to Ce_2O_3 in its entirety. Theoretically modeling multiple cerium oxidation states using DFT+*U* must require the use of an identical *U* value throughout all corresponding calculations, in order to evaluate comparable data.

Our research will center on modeling the electronic structure, bonding and ground-state properties of bulk CeO_2 , Ce_2O_3 and the intermediate cerium oxide structure of $\text{Ce}_2\text{O}_3\text{-O}_{\text{interstitial}}$. $\text{Ce}_2\text{O}_3\text{-O}_{\text{interstitial}}$ is comprised of predominantly Ce^{3+} ions, however, the inclusion of an oxygen interstitial site should result in the oxidation of individual cerium ions to Ce^{4+} . By varying the *U* value within GGA+*U* calculations on these cerium-based structures, we hope to demonstrate the effects of altering the Hubbard *U* term on the properties of the system. Subsequent GGA+*U* results, determined for CeO_2 and Ce_2O_3 structures incorporating an identical *U* value for the multiple cerium oxidation states, will be directly compared with experimental and hybrid-DFT calculations in order to consider the overall reduction reaction process (reducing CeO_2 to Ce_2O_3). Furthermore, using different values of *U*, comparison will be made of the various ground-state properties of $\text{Ce}_2\text{O}_3\text{-O}_{\text{interstitial}}$. This will be a first of its kind study on $\text{Ce}^{3+}/\text{Ce}^{4+}$ cerium oxide intermediate structures containing predominantly Ce^{3+} ions, thus from a partially oxidized Ce_2O_3 point of view.