

Surface Hole Polarons in the Oxygen Evolution Reaction on Rutile Titanium Dioxide

Patrick Gono, Julia Wiktor, Alfredo Pasquarello

The exact mechanism of the oxygen evolution reaction (OER) on titanium dioxide is still a heavily discussed topic. Localised surface hole states are hypothesised to play a critical role in driving this reaction. As a possible mechanism of charge localization, polarons have been widely studied in both rutile and anatase. We investigate surface hole polarons that are formed in rutile as a consequence of strongly electronegative reaction intermediates adsorbed on the surface. The stability of these polarons at the interface with vacuum is studied using first-principles hybrid density functional calculations. We find that the the creation of a surface polaron can stabilise the intermediates by more than 1.5 eV. Furthermore, we use the blue moon approach to estimate the free energy barrier for polaron formation in an aqueous environment via constrained hybrid functional MD simulations. We find a relatively low barrier of 0.2 eV, which would allow for facile thermal generation of such polarons at room temperature. Taking into account the stability of these polarons we obtain the energetics of the oxygen evolution reaction using the computational hydrogen electrode method. We show that the occurrence of polarons is crucial to reconcile hybrid functional results for overpotentials with experimental data. This highlights the role of surface hole polarons in facilitating the oxygen evolution reaction and prompts their consideration in the search for novel catalysts.