Abstract

An arising challenge is the large-scale production of sustainable energy. To tackle this problem, excess energy produced during peak production time is used to split water into oxygen and a CO2-neutral fuel: hydrogen gas. This method is based on two half-reactions: the rate-determining oxygen evolution reaction (OER) that splits water via four successive Proton-Coupled Electron Transfers (PCET's), followed by hydrogen evolution reaction (HER). A new generation of OER-catalysts are metal-oxides of which RuO2 has proven experimentally to be the most active. However, recent research revealed that theoretical calculations predict lower activities of RuO2 than experimentally proven, additionally the scientific community has not reached a consensus on pinpointing the rate determining PCET and therefore the origin of the overpotential. By combining Ab Initio Molecular Dynamic simulations and the implementation of explicit solvation effects these issues were addressed. Using an external potential to regulate the reaction coordinate of the first two PCET's, their activation barriers could be computed. The results showed that the neither of the first two PCET's is likely to be the rate-determining step, however, the trajectories revealed that these steps possibly commence via an alternative mechanism where through an intramolecular proton transfer the second active site, the bridging oxygen, is temporarily protonated. Furthermore, it was revealed that the coupled electron transfer is not barrier-less as was previously stated and might raise the reaction barrier. At last, it was shown that the surface is very dynamic and capable of containing different intermediates. Our results suggest that the catalytic activity of RuO2 is dependent on this coverage diversity, however in what way remains unknown.