

DFT-Based Theoretical Insights into the Mechanism of the Oxygen Reduction Reaction on Pt(111)

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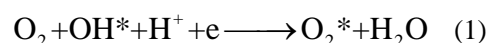
The mechanism and kinetics of the oxygen reduction reaction (ORR) on Pt are among the current research focuses in electrochemistry and fuel cells, due to the seemingly indispensable role of Pt in catalyzing the ORR in fuel cell cathodes and its relatively low activity and durability. Adsorption of various oxygenated species plays key roles in the ORR and the degradation-related oxidation of Pt. Despite extensive studies during the past years, there remain a few standing questions in the ORR mechanism, for instances, the rate determining step (rds), the exact nature of the volcano relation between the ORR activity and the binding to oxygenated species, the nature of the Tafel slope variation with potential, and so on.

In this study, the formation and evolution of the adsorption structures of oxygenated species on Pt(111) surface in O₂ free and saturated media respectively were considered based on DFT-calculated adsorption isotherms and the experimental voltammograms reported in the literature. It is concluded that at potentials above 0.7V (vs RHE), a globally ordered OH*/H₂O* co-adsorption network dominates the surface of Pt(111) surface, with the coverage of OH* rapidly increasing to 1/3 monolayer at ca. 0.8 V, which may be responsible for the “butterfly” peak on the blank voltammetry of Pt(111).

In O₂ free condition, the ordered co-adsorption phase is stable till the potential is close to 1.0 V, at which OH* starts to be de-protonated to the adsorbed oxygen atoms (O*). The de-protonation of OH* to O* is found to be a self-accelerated process due to that the presence of O* can destabilize the nearby OH*/H₂O* network. In results, the surface phase is rapidly transformed to an ordered $\sqrt{3} \times \sqrt{3}$ adsorption structure of O*.

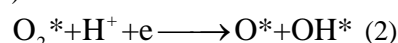
In O₂-saturated condition (i.e., ORR condition), the ordered OH*/H₂O* network phase becomes unstable as potential goes positive to ca. 0.85 V, above which the ordered O* adsorption phase and the ordered OH*/H₂O* network phase co-exist on the surface unless the potential is more positive than ca. 1.0 V.

The reaction free energies of various possible steps in the ORR are computed on Pt(111) surfaces with the ordered OH*/H₂O* co-adsorption structure and the ordered O* adsorption structure respectively. The results suggest that the first step, namely, the adsorption of O₂, might be the rds in the ORR, which is thermodynamically much more difficult to take place on the surface covered with the ordered O* adsorption structure than with the OH*/H₂O* co-adsorption structure. The most favourite reaction channel for O₂ adsorption on Pt(111) surface with the OH*/H₂O* co-adsorption phase structure is identified to be the reaction (1).



The O₂ molecule adsorbs on surface in a t-b-t configuration with one O atom occupying the central Pt atom inside the OH*/H₂O* hexagonal structure and the other one displaces an OH* in the hexagonal structure. The displaced OH* is simultaneously reduced to H₂O. This means that the rds in the ORR on Pt(111) bearing the OH*/H₂O* co-adsorption phase is a proton-coupled electron transfer process. However, the intermediate formed in this process might not be the usually believed end-on OOH.

The t-b-t adsorbed O₂* may dissociate through reaction (2).



As potentials go above 0.85V, the OH*/H₂O* co-adsorption structure becomes unstable and O* adsorption structure is gradually built up. This may be the reason of the rapid decline in the ORR activity of Pt at potentials positive to 0.85V. It might be also the origin of the Tafel slope change around 0.85V.

The present calculation results may also explain the predominant 4 electron pathway of ORR on Pt, and to unify the earlier propositions by Damjanovic et al. and Yeager et al for ORR mechanism.