

A Surface Science Approach to Understanding the Key Steps of the Oxygen Reduction Reaction in Fuel Cells

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Fuel cells have a bright future as emission free sources of energy. A fundamental understanding of the fuel cell catalysis process is required to target existing manufacturing challenges. While the oxidation of pure hydrogen is not considered a technical hurdle in fuel cells, the power loss at the cathode during the electroreduction of oxygen is found to be significant. Pt has been the only metal which offers a good compromise in terms of performance and durability, but catalyst costs are high. Therefore it is essential to carefully examine the mechanistic pathway of the oxygen reduction reaction (ORR) and to identify a catalyst with improved performance for the electroreduction of oxygen in order to improve fuel cell efficiency and to reduce manufacturing costs.

A management of appropriate humidity level is necessary for the fuel cell to operate. The ORR reaction occurs at the triple phase boundary where gas, electrolyte containing water and catalytic metal particle contact forms humid and dry region on the surface of the catalyst. We have demonstrated active site poisoning by water, where the activation of oxygen to the adsorbed atomic phase occurs rapidly in the dry region, but not in the humid region. On the contrary, there is a promoter effect of water on the reduction of adsorbed atomic oxygen in the formation of a water-hydroxyl surface complex.

Hydrogen peroxide is formed as a by-product during the fuel cell operation and initiates the degradation of the ion exchange membrane. The hydrogen peroxide formation becomes prominent by hydrogen underpotential deposition on the catalyst. We have searched for a potential pathway of peroxide formation on the catalyst surface using surface science experiments and found that adsorbed hydrogen plays an important role. The presence of hydrogen stimulates an orientation transition of molecular oxygen from flat-lying to tilted-up with respect to the surface plane. We propose that the peroxide formation reaction channel is stimulated by this orientation transition of oxygen on the surface. Our preliminary studies further indicate that the tilted-up geometry sterically hinders the activation of oxygen for dissociation.

We have also found evidence that adsorbed water molecules behave as both promoters and retardants to the reaction. While adsorbed water molecules block the activation site to dissociate molecular oxygen, it is also found that the reduction of atomic oxygen to OH is promoted by water.

Using X-ray spectroscopic techniques including XPS and XAS we have focused on the oxygen reduction reaction on Pt.