



INTERDISCIPLINARY CENTRE FOR  
ADVANCED MATERIALS SIMULATION

The ICAMS Seminar presents

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## **Intermediates of the Electrochemical Oxygen Reduction in Aqueous Media**

The electrochemical oxygen reduction reaction (ORR) is a fundamental electrochemical process. At metal surfaces the ORR is the cathodic partial reaction and driving force for many corrosion processes including cathodic delamination. On the other hand, the electrocatalysis of the ORR in fuel cells is intensely studied with the aim of improving the kinetics and reducing the overpotential that limits the energy efficiency. The ORR has a complex multi-step mechanism with multiple reactive intermediates, which strongly varies with pH and electrochemical potential. In spite of many fundamental studies, the reaction mechanism is controversial. In this theoretical study, the reaction mechanism of the electrochemical oxygen reduction in aqueous solution is analyzed, based on the assumption that the elemental reaction steps correspond to either single electron transfers or single proton transfers. For this purpose, all intermediates that may be generated starting from oxygen by sequentially adding electrons and protons in arbitrary order are considered. Species with charges up to  $\pm 2$  are included. For a realistic description of electrochemical reactions, an adequate treatment of solvent stabilization effects is essential. Results from two complementary approaches will be presented. In a cluster approach a first hydration shell by explicit water molecules is used to capture specific interactions (e.g., hydrogen bonds) and supplemented by a self-consistent reaction field approach to cover long-range electrostatic effects. Alternatively, the intermediates are surrounded by a large number of water molecules using a supercell approach with periodic boundaries. The analysis of the comprehensive set of potential intermediates gives a detailed picture of the minimum energy reaction path, decomposed into elemental steps of electron or proton transfers. The relative stability of several intermediates changes with pH and electrode potential, indicating that the sequence of reactions along the minimum energy pathway and the rate determining steps change with reaction conditions.