

論文内容の要旨

論文題目 First principles study on electrocatalyst/water interfaces for
oxygen reduction/evolution reactions

(第一原理計算に基づく酸化還元/酸素生成反応の電極触媒/水界面に関する研究)

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The oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are the keys in the polymer electrolyte fuel cells (PEFC) and the photo(electro)catalytic (PEC) water-splitting. Reactions and structures at the interface between water and an electrocatalyst play an important role for electrocatalytic activities. To enable an atomic-scale analysis at the interface, density functional theory combined with electrochemical methods are applied. In this thesis, our goal is to overcome the challenges of revealing atomic-scale interfacial structures and reactions of electrocatalyst with the concept of modifying atomic-scale structures and bridging real electrode reactions and simulations.

In Chapter 1, background and motivation of the present research are described. The ORR is the cathode reaction of PERC and OER is the anode reaction of PEC water-splitting. To reduce the overpotential of ORR and OER, highly active electrocatalysts are strongly desired. In the search for ORR/OER electrocatalysts, theory for chemical reactions and thermodynamic guidelines have been developed. To go beyond the state-of-the-art, insights into effects of defects on electrocatalytic activity and an electron/hole transfer across the electrocatalyst/water interface should be addressed. Bridging the simulation model and experimental environment is also required to maximize the potential of materials.

In Chapter 2, density functional theory and its application for electrochemical system is introduced. Toward an 'in situ' atomic scale analysis by density functional theory, the methods that include the effect of electrode potential and pH are reviewed.

In Chapter 3, the mechanism for ORR on Ta_3N_5 (100) is examined as a Pt-free electrocatalyst. The purpose of the study is improving the activity on Ta_3N_5 by comparing the reactions on surfaces with and without impurities. Surface O_N impurities are introduced by substituting two O atoms for N atoms, notated as 'O2-substituted surface'. As a first elementary step of the reaction, oxygen adsorptions on clean and O2-substituted surfaces are examined. Based on the analysis of oxygen adsorption structure, the whole mechanism of the reaction is examined by calculating the energy diagrams. On clean surface, H_2O desorption is the rate-limiting step. Because of low reactivity to O_2 , almost all the active sites may be covered by H_2O and OH that decrease the catalytic activity. On the other hand, on O2-substituted surface, The oxygen molecule first adsorbs strongly and H_2O desorption is also the rate-determining step. Because the energy barrier for the water desorption is less than that on the clean surface, the O2-substituted surface has lower overpotential for ORR. From the comparison of electrocatalytic activities on clean and O2-substituted surfaces, it is shown that higher ORR activity can be achieved by controlling the energy level of the impurity state.

In Chapter 4, OER on Ta_3N_5 as a photoanode for PEC water-splitting is discussed. To lower the overpotential, in addition to lower the activation energy of the reaction itself, suppressing the recombination of excited charge carriers is of great importance. To examine a thermodynamics of hole transfer, an interfacial band diagram of n-type Ta_3N_5 /water in electrochemical condition is presented. Especially, whether band edge pinning or Fermi level pinning occurs is examined. First, band alignments of clean and n-type Ta_3N_5 with adsorbents in vacuum is examined to discuss how impurities and adsorbents affect the band positions and Fermi energies. O-substitution in bulk (bulk- O_N) is introduced with a composition of $\text{Ta}_3\text{N}_{4.75}\text{O}_{0.25}$ as n-type Ta_3N_5 . As a result, clean surface is an intrinsic semiconductor and the position of valence band (VB) maximum in bulk region almost match the redox potential of $\text{O}_2/\text{H}_2\text{O}$. On the other hand, bulk- O_N surface is n-type semiconductor and Fermi energy is locating in the conduction band (CB). Adsorptions of OH and O induce the down shift of band positions because negatively charged OH and O form dipole at the interface. By improving interface models to include the effect of electrode potential with explicit water molecules, the band diagrams of n-type Ta_3N_5 /water interfaces are obtained. From the calculations of the position of VB in bulk, position of VB at the surface, and semiconductor barrier height at given electrode potentials, it is clearly shown that the interface of n-type Ta_3N_5 /water shows the intermediate behavior between band edge pinning and Fermi level pinning. Consequently, the importance of surface modification is addressed from a view point of utilizing the Schottky barrier height to get a driving force for charge separation.

In Chapter 5, interfacial structures of RuO_2 /water under given electrode potential and pH are examined. Generally, the electrocatalytic activity depends on electrode potential and pH and an atomic-scale structure

in electrochemical environment is a first step toward the understanding of ‘in situ’ reactions. As models for interfacial structures, RuO₂(110) is selected and the formal valence of surface Ru atoms, and orientations of water molecules are varied for bridging sites (‘br’) and coordinatively unsaturated sites (‘cus’). Based on the calculations of interfacial Gibbs energy as functions of both pH and electrode potential, surface Pourbaix diagram is generated. As a result, a significant structural difference is found between pH values of 0 and 14 in the potential region of oxygen evolution reaction including overpotential (1.6 V vs. RHE at pH = 0 and 1.8 V vs. RHE at pH = 14). The surface structure at pH = 0 is O^{br}/O^{cus} with water layers, while the surface at pH = 14 is OH^{br}/O^{cus} with a water layer consisting of OH/H₂O; the water layer geometries and the surface Ru formal valence values are quite different. This variation of structures can result in the pH-dependent behaviour of the OER, either through a change in the mechanism or a variation in the most probable initial reactions.

In Chapter 6, the conclusions from Chapter 3-5 and future perspectives are summarized. Analysis on the atomic-scale interfacial structures and reactions of electrocatalysts can provide the guideline to improve the activities for ORR and OER.