学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Studies on Electrocatalytic Activities of Boron Nitride of Various Structures towards Oxygen Reduction Reaction and Hydrogen Evolution Reaction

(種々の構造をもつ窒化ホウ素の酸素還元反応および水素生成反応に対する電極触媒活性に関する研究)

Fuel cells (FCs) are anticipated as one of the best possible energy conversion devices in future society due to their high energy density, high efficiency, and negligible emission of exhaust gases. The cathodic oxygen reduction reaction (ORR) has been extensively studied because it is the most crucial process in FCs. Although the thermodynamic potential of ORR is 1.23 V vs. SHE, currently there exsists a large overpotential even when Pt, which is the best electrocatalyst, is used.

Hydrogen is the cleanest fuel and is considered to be one of the most promising energy carriers. It is currently produced from fossil fuels but must be produced from water for hydrogen to be considered as a really clean fuel. Electrocatalysis of water is the most promising method to produce large amounts of hydrogen from water.

Although Pt has high electrocatalytic activity for ORR and hydrogen evolution reaction (HER), its scarcity and high cost inhibit large-scale applications. Hence, it is important to develop non-precious metal catalysts as efficient electrocatalysts for practical applications and many electrocatalysts have been developed to reduce the overpotential of ORR and the HER. One of the most interesting electrocatalysts is nitrogen- and/or boron-doped carbon. Boron nitride (BN) has a similar structure to graphite but is an insulator and, therefore, has not been considered as an electrocatalysts. Recent theoretical works suggests that BN can be a good ORR electrocatatlyst if defects are introduced and/or it is placed on a suitable substrate.

In the present thesis, I have proved that BN acts as good electrocatalysts for ORR and HER, opening a new possibility to design efficient Pt free catalysts for fuel cell technology and hydrogen production based on materials, which have never been considered as catalysts in the past.

The structure of present thesis is as follows:

In Chapter 1, the introduction of FCs, ORR and HER are given. The electrocatalytic activity of various catalysts such as precious metals, non-precious metals, and metal free catalyst for ORR and HER are briefly reviewed. The electron tunnelig properties and possible catalytic activities of traditionally inert materials are also reviewed.

In Chapter 2, the description of the experimental details such as materials, catalyst preparation methods, electrochemical measurements, and characterization techniques are given.

In Chapter 3, the electrocatalytic activities of various types of h-BN such as BN nanotube (BNNT), BN nanosheets (BNNS), and sputter deposited BN, coated on Au, glassy carbon (GC) and Pt electrodes, for ORR are examined. The overpotential for ORR at Au electrode is reduced by ca. 100, ca. 270, and ca.150 mV by coating with BNNT, BNNS, and sputter deposited BN, respectively, showing the enhancement of electrocatalytic activity. Rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) studies shows that O_2 is reduced to H_2O_2 by 2-electron reduction. On the other hand, ORR activity of GC electrode is not enhanced and that of Pt is reduced by the BNNS modification, suggesting that the BN-Au substrate interaction plays an important role for BN to become ORR active.

In Chapter 4, the electrocatalytic reactivity of BNNS decorated with Au nanoclusters (Au/BNNS) on Au for ORR is examined. The overpotential of ORR at Au electrode is significantly reduced by 300 mV by the modification of Au/BNNS. The enhanced catalytic activity of Au/BNNS is attributed to the electron transfer at the interface between Au and neighboring B- and/or N- atoms. The number of electrons involved in ORR determined from the slope of Koutecky-Levich plot is about 3 and RRDE measurements suggest the partial production of H_2O_2 by 2-electron reduction and H_2O by 4-electron reduction. This is in contrast to the results at the bare and BNNS modified Au electrodes, where only H_2O_2 is formed by 2-electron reduction. Electrocatalytic activity for ORR is enhanced even at the GC electrode when it is modified by Au/BNNS, confirming the importance of Au-BN interaction for the enhancement of electrocatalytic activity.

In Chapter 5, the electrocatalytic evolution of hydrogen at Au, GC and Pt modified by BNNS and BNNS decorated with Au- and Ni-NCs are investigated. HER at Au, GC and Pt electrodes are enhanced, not much changed, and reduced, respectively, by BNNS modification as for ORR. HER at Au, GC and Pt electrodes are all enhanced by the modification by BNNS decorated with Au-NCs (Au/BNNS). HER activity of Au electrode modified by Au/BNNS is very high with only ca. 50 mV more overpotential than Pt. Modification by BNNS decorated with Ni-NCs (Ni/BNNS) also showed enhanced HER activity but much less than by the Au/BNNS modification, showing the important role of Au-BN interaction for the enhancement of HER as well. Interestingly, hydrogen oxidation reaction (HOR), i.e., reverse reaction of HER, at Au electrode is not enhanced by BNNS and Au (or) Ni/BNNS modification, showing the unique feature of this catalyst.

In Chapter 6, the general conclusion of the present thesis and future prospects are given.