초청강연7

Metalloprotein Electrochemistry at Functional Electrodes and Its Applications

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In the present paper, electrochemistry of cytochrome c (Cyt. C), azurin (Az), ferredoxin (Fd) and myoglobin (Mb) will be at first summarized to understand their electron transfer reactions at various functional electrodes.

To understand more precisely the functions of modified electrodes, using STM and surface-enhanced IR absorption spectroscopy (SEIRAS), potential and pH dependencies of adsorbed species of various promoter molecules on single crystal electrodes were examined. For example, the 4-PySH modified electrode showed the rectangular unit cell of $p(5 \times \sqrt{3}R-30^\circ)$ structure with an interaction of two neighboring 4-PySH at the Au(111) surface. The STM images of other surface modifier molecules were also obtained. One of important findings in the present study is that the STM image obtained in an acid solution at a positive potential was not due to the structure of protonated species but due to exactly that of unprotonated species of the modifier adsorbed on the electrode at which surfaces the electron transfer reactions of metalloproteins such as Cyt. C and Az took place. By the surface structures of various modifier molecules evidenced in the present study, the enhanced and poor electrochemical responses of metalloproteins on these modified electrodes were clearly explained.

By using a functional electrode, electron transfer kinetics of metalloproteins were carried out. Electrochemical method has an advantage to obtain the kinetics without any variation of the driving force independent of the redox potentials of metalloproteins of interest. Mb and its modified molecules were examined to understand factors which control the electron transfer kinetics and effects of heme structures on biological functions of myoglobin. Effects of heme vinyl groups, for example, on the biological functions of Mb were clearly shown.

Also, on the basis of electrochemical responses of Fd and its mutated molecules, biological functions of some amino acid residues have been clarified. Bioelectrocatalytic reactions were also demonstrated.

In summary, on the basis of the developing functionally modified electrodes

electrochemical techniques have become very useful to study metalloproteins for both basic and applied aspects.

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