초청강연1

DYNAMIC PROPERTIES OF ELECTRON TRANSFER PROTEINS AT ELECTRODE INTERFACES

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It has been shown that the electron transfer reaction of electron transfer proteins are strongly influenced by the surface structure of electrodes. The redox potential of cytochrome *c* is shifted about 500 mV more negative upon the adsorption at bare electrode surfaces. The shift of the redox potential is due to the reversible unfolding of the protein molecules at the electrode surface (1). 4,4-Bipyridine was proposed as a surface modifiers and was the first example to facilitate a reversible electron transfer reaction of cytochrome *c* at gold electrodes (2). Since then, numerous surface modifiers have been proposed to facilitate reversible electrode reactions of electron transfer proteins.

In the present paper, we report on the electrochemical behavior of cytochrome *c* at electrode interfaces in the absence and presence of surface modifiers studied by voltammetric and in situ spectroelectrochemical techniques.

1) Cytochrome *c* at bare gold and silver electrodes. Redox reaction of cytochrome *c* adsorbed on gold and silver electrodes was monitored by the potential modulated UV-vis electroreflectance technique and found that its redox potential (formal potential) is 380 mV (*vs.* NHE), which is 440 mV more negative that that of the native form (1, 3). Because of the large redox potential difference between cytochrome *c* in solution and that adsorbed on the electrode surface, the electron transfer between the electrode and cytochrome *c* in solution is inhibited. The spin state of the adsorbed cytochrome *c* was investigated by using SERS and is found to be 5cHS state in contrast the 6cLS state for the native form in the solution (4).

2) Cytochrome *c* at gold and silver electrode in the presence of 4,4-bipyridyl or iodine molecule at electrode surfaces.

It has been shown that cytochrome *c* in the solution phase exhibits a reversible voltammetric response at both 4,4-bipyridyl (2) and iodine modified

electrodes (5). It was shown by SERS studies that cytochrome *c* is coadsorbed with 4,4-bipyridyl and the redox potential of cytochrome *c* coadsorbed on gold electrodes depends on the concentration of 4,4-bipyridyl and varies from 380 mV (in the absence of 4,4-bipyridyl) to 165 mV (in 10 mM 4,4-bipyridyl solution). The spin state of cytochrome *c* at 4,4-bipyridyl and iodine modified electrodes is a mixture of both 5cHS and 6cLS states (6,7). That is, there are two forms of cytochrome *c* at the modified electrode surfaces. One is an unfolded form with the redox potential of 380 mV and 5cHS state and the other is the native form with the redox potential + 60 mV and 6cLS. The interchange between 5cHS and 6cLS states is so rapid that the redox potential of the mixed states measurable in the voltammetric time domain is given by an average between two states. The electrode reaction of cytochrome *c* in solution phase may take place through the adsorbed cytochrome c with the native form.

3) Cytochrome *c* immobilized on self-assembled monolayers. Mercapto-pyridine, mercaptobenzoic acid, dithiodipyridyl, and carboxylic acid-terminated alkanethiols form self-assembled monolayers (SAM) on gold electrode surfaces. Cytochrome *c* immobilized on these SAMs exhibits reversible voltammetric response and its spin state is 6cLS. Cytochrome *c* desorbs from the SAMs at higher concentrations of supporting electrolytes (e.g. higher than 100 mM phosphate buffer solution).

The electron transfer reaction rates from the gold electrode to cytochrome c through alkanethiol SAMs with different chain lengths were measured by the potential modulated UV-vis electroreflectance technique (8). The electron transfer rates through longer alkanethiol chains, which have more than eight methylene groups in the chain, follow the non-adiabatic electron transfer mechanism given by the following equation.

$$k\text{app} = k\text{o} \exp(-n)$$

Where represents the decay factor and is 1.09 0.02 per CH2 (0.86 0.016 -1) and *n* represents a number of CH2 groups in the alkyl chain. The electron transfer rates through shorter chain lengths, the electron transfer rates reach to a limiting value (8). We assume that the electron transfer rate is controlled by the reorganization of cytochrome *c* followed by the electron transfer reaction.

cytochrome *c* (Fe3+)(I) == cytochrome *c* (Fe3+)(II)

cytochrome *c* (Fe3+)(II) + e == cytochrome *c* (Fe2+)(II)

Cytochrome *c* (Fe3+)(II) represents the favorable conformation for the electron transfer reaction at the carboxylic acid-terminated alkanethiol SAMs. That is, cytochrome *c* (Fe3+) immobilized on carboxylic acid-terminated alkanethol SAMs exhibits a dynamic nature.

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