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THE ELECTROCHEMISTRY OF REDOX PROTEINS

Over the past few years, it has been possible to devise electrodes at which the electron transfer reactions of representatives of the major classes of redox proteins proceed rapidly and reversible. The guiding hypothesis is that the surface provided by the electrode should resemble that offered to the given redox protein by others with which it interacts *in vivo*. Thus in both instances, we are concerned with the nature of interfaces. Most current models of protein-protein complexes emphasize the electrostatic nature of the binding and pay particular attention to short-range interactions. Some proteins require no extensive electrode modification *e.g.*, *Pseudomonas aeruginosa* azurin or some cytochromes c_3. However most require the modification of the electrode surface, or at least the electrode-solution interface, before rapid heterogeneous electron transfer rates are observed. We have been concerned principally with three types of electrode: metal (especially) gold surfaces upon which are adsorbed bi- or poly-functional molecules; oxidized pyrolytic graphite surfaces with, or without, poly-valent cations; conducting metal oxide surfaces, especially RuO_2.

The most intensive investigations have been carried out on horse heart cytochrome *c*. This highly basic protein appears to have the following requirements: a negatively-charged surface, or at least one in which any adsorbate molecules have the negative end of the dipole disposed towards the solution; a hydrophilic surface; a surface upon which adsorption of the protein is reversible; the absence of competing poly-valent cations. These conditions are met by gold upon which is adsorbed molecules of the type, X~Y where X is a group which adsorbs on to the gold and Y is a negatively-charged group (or exposes the negative end of a dipole). 4,4'-Bipyridyl is the archetype of this class of adsorbate but there are now twenty or so compounds that act, when adsorbed on gold, as effective *promotors* of the electrochemistry of horse heart cytochrome *c*. Pyrolytic graphite, when carefully oxidized, also functions well as does the metallic oxide, ruthenium dioxide.

Acidic proteins require a different surface. There are a few compounds which, when adsorbed on gold, present a positive surface to the solution. The most straightforward method of promoting the electrochemistry of proteins such as plastocyanin is to have present in solution polyvalent cations such as magnesium(II) or hexamminochromium(III). Two effects appearing to be operating: a general effect on the electrode-solution interface and a specific effect which involves binding of the cation to the protein surface. Evidence for the latter comes from NMR spectroscopy. Recently compounds have been discovered that, when adsorbed on gold, allow the electrochemistry of *either* acidic *or* basic proteins to proceed.

Having gained rapid electrode reactions of redox proteins, what use can be made of them? Examples will be given of coupling of these reactions to enzyme-catalysed reactions and their use in synthesis and sensors.