Hydrogenase Enzyme Electrodes For Hydrogen Fuel Cells

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Molecular hydrogen is considered nowadays as the most promising chemical fuel, in particular for fuel cells. The hydrogenase enzyme electrode uses the catalytic properties of the hydrogenase enzyme, able to activate the hydrogen molecule, for energy inter-conversion between H₂ and electricity. The development of enzyme electrodes requires the successful coupling of the enzyme with the electrochemical reactions.

The most attractive coupling is a direct electron exchange between the electrode and the active site of the enzyme. This phenomenon is called direct bioelectrocatalysis [1]. However, the modification of electrode surfaces by redox mediators in order to establish an electrical communication with enzyme molecules remains an important problem in the field of enzyme electrodes.

For direct bioelectrocatalysis the hydrogenase from *Thioclaspas roseopersicina* was adsorbed onto pretreated carbon tissue from aqueous solution. After immersion of the enzyme electrodes in neutral buffer solution saturated with molecular hydrogen, the equilibrium hydrogen potential is achieved (fig. 1). The enzyme electrode was characterized by high values of positive current in the positive potential region. A comparison with blank experiments shows that the anodic current is due to hydrogen oxidation on hydrogenase electrode, and the standard potential observed is the hydrogen equilibrium potential. A correlation between the cathodic current generated by the hydrogenase electrodes in argon atmosphere and the rate of hydrogen production was demonstrated by mass-spectrometry [2].

Direct bioelectrocatalysis is extremely sensitive to both the morphology of the electrode support and its surface chemistry. Thus, enzymes from other sources were not active when adsorbed directly onto carbon tissue. To enlarge a number of electrode materials and enzymes suitable for development of biofuel electrodes we decided to design suitable surface artificially. For modification of electrodes we have chosen electropolymerization of substituted pyrrole. We believed, that by using artificial hydrogenase mediators (viologens), such as electropolymeterized pyrrole derivatives, it will be possible to wire the enzyme to the electrode surface. Hydrogen enzyme electrodes were made by adsorption of hydrogenases on carbon tissue electrode covered with viologen substituted poly(pyrrole). Hydrogenases from different sources have demonstrated efficient bioelectrocatalysis on poly(pyrrole) modified electrodes (fig. 2).

The most important problem of platinum-based hydrogen fuel electrodes is their poisoning by carbon monoxide and sulfur compounds. We have shown that hydrogen enzyme electrodes are insensitive to CO up to 1% [1]. The presence of 5mM of Na₂S does not affect the activity of hydrogenase electrode as well (fig. 3).

We conclude, that surface design is powerful method to provide bioelectrocatalysis by different hydrogenases. Hydrogenase enzyme electrodes preserve enzyme tolerance to CO and sulfide.


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