Hydrogenase electrodes for fuel cells

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Abstract
Considering crucial problems that limit use of platinum-based fuel cells, i.e. cost and availability, poisoning by fuel impurities and low selectivity, we propose electrocatalysis by enzymes as a valuable alternative to noble metals. Hydrogenase electrodes in neutral media achieve hydrogen equilibrium potential (providing 100% energy conversion), and display high activity in H₂ electrooxidation, which is similar to that of Pt-based electrodes in sulphuric acid. In contrast with platinum, enzyme electrodes are highly selective for their substrates, and are not poisoned by fuel impurities. Hydrogenase electrodes are capable of consuming hydrogen directly from microbial media, which ensures their use as fuel electrodes in treatment of organic wastes.

Introduction
Among the most important problems of the modern human society is a search for alternative energy sources. Molecular hydrogen is considered nowadays as the most promising chemical fuel. Fuel cells, being the most progressive energy conversion devices, use platinum as an electrocatalyst. There are, however, crucial problems that make wide applications of such fuel cells impossible.

First, it is the problem with cost and availability. Platinum-based fuel cells producing 1 kW of energy will cost from $200 to $2000 [FY2003 Progress Report for Hydrogen, Fuel Cells, and Infrastructure Technologies Program, U.S. Department of Energy, Washington, D.C. (http://www.eere.energy.gov/hydrogenandfuelcells/annual_report03.html)]. Thus a 50 kW engine will cost from $10,000 to $100,000. Moreover, during the past 30 years, prices for platinum have increased more than five times [1,2].

Concerning Pt availability, one has to consider that every year more than 60 million cars are produced [The International Organization of Motor Vehicle Manufacturers Statistics Report (http://www.oica.net/htdocs/statistics/tableaux2003/worldprod_country2003.pdf)]. To equip all cars with 50 kW engines, 6000 tons of Pt would be required. However, the annual Pt production is just 195 tons [2], and world’s total Pt resources are just 50,000 tons [3]. The second issue is the poisoning problem. The cheapest hydrogen produced as reforming gas usually contains 1–2.5% of CO [4]. However, even in the presence of 0.1% CO, activity of platinum electrodes decreases irreversibly 100 times in 10 min [5]. Oxidation of CO at high potential proposed for electrode recovery [6] is not realizable in fuel cells. Poisoning of Pt by hydrogen sulphide (H₂S), necessarily present in biogas is even faster [7].

The third issue is the selectivity problem. Since Pt is active in both H₂ oxidation and O₂ reduction, contamination of a paired electrode compartment reduces the effectiveness of fuel cells from the theoretical value of 90–95% to 40–60%.

Bioelectrocatalysis
We propose biocatalysis as a valuable alternative to catalysis by noble metals for development of fuel electrodes. As we reported 20 years ago [8], hydrogenase from *Thiocapsa roseopersicina* immobilized on carbon black served as an efficient electrocatalyst for hydrogen oxidation–evolution. In hydrogen atmosphere, a hydrogenase electrode generates hydrogen equilibrium potential.

To elaborate the technology of fuel enzyme electrodes, we have chosen carbon filament materials as supports. These materials were specially designed for fuel electrodes. After sorption of hydrogenase, the corresponding enzyme electrodes were characterized by the attainment of a hydrogen equilibrium potential and a high current of hydrogen oxidation [9].

Surface design for direct bioelectrocatalysis
Direct bioelectrocatalysis is extremely sensitive to both morphology of the electrode support and its surface chemistry. To enlarge a number of electrode materials suitable for development of biofuel electrodes we decided to design artificially suitable surfaces. For the modification of electrodes, we have chosen electropolymerization of pyrrole substituted with artificial hydrogenase mediators (Viologens) [10,11].

Electrochemical kinetics of hydrogenase electrodes
Steady-state current–voltage curve for hydrogenase electrodes can be simulated in terms of two sequential electron transfer stages [8,10]. The corresponding current equation contains two fitting parameters. Exchange current (mainly the electrocatalyst’s characteristics) is a sum of the two fitting parameters.

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Surface design by a conductive polymer (polypyrrole) drastically improves electrocatalytic activity of the enzyme and even increases its concentration on the electrode surface. Exchange current for Desulfovibrio baculatum hydrogenase-based electrode per active centre of the electrocatalyst is three orders of magnitude higher than that for the Pt electrode in neutral solution.

Hydrogen fuel electrode based on hydrogenase

We propose biocatalysis as an alternative to the catalysis by noble metals. Figure 1 shows the current–voltage curve of the Pt-based fuel electrode in sulphuric acid [12] compared with a stationary hydrogenase electrode in a neutral solution and hydrogen gas was bubbled through the solution. We note that, in neutral media, electrocatalytic activity of platinum electrodes is decreased on average 100 times, which makes them incomparably less active than the enzyme electrodes.

Tolerance of hydrogen enzyme electrodes to fuel impurities (CO, H₂S)

As mentioned above, the most important problem of Pt-based hydrogen fuel electrodes is their poisoning by CO and H₂S. When hydrogenase enzyme electrode was tested under different H₂/CO mixtures, no recognizable inhibition was observed up to CO content of 0.1%. Only under 1% of CO the rate of hydrogen oxidation was decreased by approx. 10% [9]. Moreover, inhibition of hydrogen enzyme electrode by CO is completely reversible. Even after exposing to pure CO, the hydrogenase electrode recovers 100% of its initial activity as soon as the atmosphere is changing back to hydrogen [9].

Current–voltage curves of hydrogenase electrodes recorded in the absence and presence of 5 mM Na₂S were nearly identical. Thus hydrogen enzyme electrodes are not sensitive to sulphide presented even in such high concentrations.

We conclude that using the enzymes as electrocatalysts, one can solve the most important problem of the modern fuel cell technology: poisoning by fuel impurities.

Hydrogen consumption from microbial media

Treatment of organic wastes with energy output is one of the most important problems of current interest. Most methods involve hydrogen evolution at the first stage. However, the use of biogas in conventional fuel cells is limiting due to a presence of H₂S. Moreover, microbial digestion of organic compounds is shifted towards hydrogen evolution only for hydrocarbons. In cases of alcohols and, in particular, of organic acids, hydrogen evolution is not favourable. Thus hydrogen consumption directly from microbial medium is necessary, which is obviously impossible for Pt-based fuel electrodes.

We investigated hydrogen enzyme electrodes in microbial media. Figure 2 shows open circuit potential versus time dependence of hydrogenase electrodes with hydrogen evolving microorganisms immobilized on the top. In the presence of an organic substrate, after a certain time required for initiation of cell growth, a potential of the hydrogenase electrodes decreases. A potential value corresponds to it for hydrogen equilibrium potential (with deviation <10 mV), calculated considering both an amount of hydrogen in gas phase and solution pH.

Thus a hydrogenase electrode senses an appearance of dissolved hydrogen, which is produced by microorganisms. Moreover, current–voltage curves recorded in microbial cultural medium and in hydrogen saturated buffer are nearly identical, showing that hydrogenase electrodes are capable of consuming hydrogen directly from microbial media.

Conclusion

We conclude that electrocatalysis by enzymes is a valuable alternative to catalysis by noble metals in respect to development of fuel cells. Hydrogenase electrodes in neutral media achieve hydrogen equilibrium potential (providing 100% of energy conversion), and display high activity in H₂.
electrooxidation, which is similar to Pt-based electrodes in sulphuric acid. Enzyme electrodes are insensitive to fuel impurities poisoning Pt and noble metals. Moreover, the enzymes have a completely renewable source, and hence their cost will be comparatively less.

Although enzyme-based fuel cells are not developed enough for car engines, hydrogenase electrodes are ready to use for treatment of organic waste, giving energy output. The activity of hydrogenase electrodes is even greater than microbial hydrogen production rates.

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References

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