ENZYMES AS ALTERNATIVE ELECTROCATALYSTS FOR HYDROGEN FUEL ELECTRODES

Arkady A. Karyakin, Sergey V. Morozov, Elena E. Karyakina, Sergey D. Varfolomeyev
Faculty of Chemistry, M.V.Lomonosov Moscow State University, 119992, Moscow, Russia

Molecular hydrogen is considered nowadays as the most promising chemical fuel, in particular for fuel cells. Fuel electrodes use platinum (or platinum metals) as electrocatalysts. There are, however, crucial problems, which make impossible wide applications of fuel cells in future.

First, it is the problem with the *cost* and *availability*. Platinum-based fuel cells producing one kilowatt of energy will cost from $ 200 to $ 2000. Thus, the 100 kW engine will cost from $ 20 000 to $ 200 000, exceeding the cost of the whole car. Moreover, to equip 57.5 millions of cars available already in 2000 with the 100 kW fuel cells 11500 tons of Pt are required. It is much higher than the annual production (180 tons) and even comparative with the assured Pt resources (100000 tons).

Second, it is the *poisoning problem*. The cheapest hydrogen produced as reforming gas usually contains 1 ÷ 2.5 % of carbon monoxide (CO). However, even in the presence of 0.1 % CO the activity of platinum electrodes decreases irreversibly 100 times in 10 minutes. The only possibility to recover catalytic activity of platinum is to oxidize the absorbed CO at high electrode potential. However, in conventional fuel cell this requires the regime, which is closed to the short circuit. The latter obviously destroys the electrodes after a few cycles.

We propose biocatalysis as a valuable alternative to the catalysis by noble metals in respect to development of fuel electrodes. Certain enzymes being immobilized on electrode materials are able to deliver electrons between their active site and the electrode material, the phenomenon is called direct bioelectrocatalysis (fig. 1).

In particular the hydrogen activating enzyme (hydrogenase) being immobilized onto carbon filament materials specially designed for fuel electrodes, serves as electrocatalyst for H_2 oxidation (fig. 2). After immersion of the enzyme electrode in neutral buffer solution saturated with molecular hydrogen, the equilibrium hydrogen potential is achieved. The enzyme electrode is characterized by high values of positive current in 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.*

Fig. 3 shows, that hydrogen enzyme electrodes operated in neutral solutions are able to achieve electrocatalytic activities similar to that of platinum-based fuel electrodes in sulfuric acid. In neutral media electrocatalytic activity of platinum electrodes is decreased in average 100 times, which makes them incomparably less active.

Hydrogenase enzyme electrode tested under different H_2 – CO mixtures showed no recognizable inhibition up to CO content of 0.1%. Only under 1% of CO the rate of hydrogen oxidation was decreased by approximately 10%. However, even after exposing to pure CO the hydrogenase electrode recovers 100% of its activity as soon as the atmosphere is changed back to hydrogen.

We conclude, that biocatalysis is a valuable alternative to the catalysis by noble metals in respect to development of fuel cells. The enzyme electrodes operated in neutral solutions are able to achieve electrocatalytic activities similar to that of platinum-based fuel electrodes in sulfuric acid. With the use of the enzymes instead of noble metals it is possible to avoid of crucial problems, which make impossible wide applications of fuel cells in future: (i) cost problem, (ii) poisoning by fuel impurities, (iii) lack of selectivity.

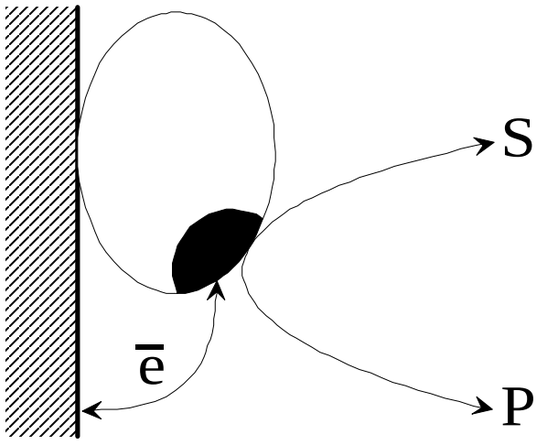

Figure 1. Principle scheme of bioelectrocatalysis; S and P are the enzyme substrate and product, respectively.

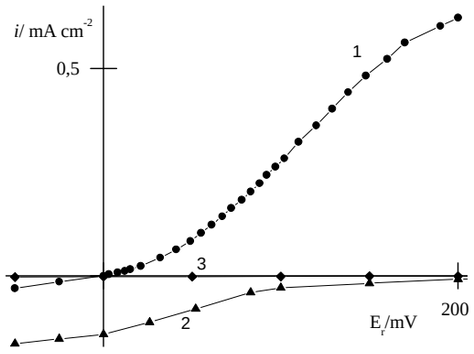

Figure 2. Electrode with hydrogenase from Th. roseopersicina (type I) in H_2 (1), Ar (2) and blank electrode (3). Phosphate buffer pH=7.0, 30°C. Reference: H_2/Pt electrode in the same solution.

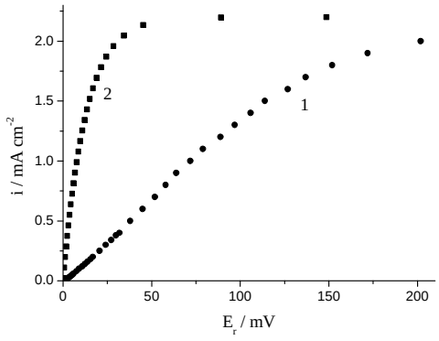

Figure 3. H_2 oxidation at 60°C (1) on hydrogenase electrode in phosphate buffer pH=7.0; (2) on a 7 μg_{Pt} cm^{-2} Pt/Vulcan rotating disk electrode in 0.5 M H_2SO_4 900 rpm.