

Research Topic – Catalysis of Hydrogen Evolution on Mercury Electrodes*

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Keywords Cases of electrochemical hydrogen evolution catalysis often represent problems that electrode kineticists find difficult to solve. On the other hand, they offer chances of finding electrochemical methods for specific and sensitive studies of a variety of substances, notably those of biological importance.

hydrogen overpotential
mercury catalysis
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chronopotentiometry

INTRODUCTION

Catalytic evolution of hydrogen is one of the most commonly occurring electrochemical reactions because, with the exception of platinized platinum, the electroreduction of hydrogen ions on all materials proceeds with a certain overpotential which can be, and often is, lowered by a variety of catalysts. Such a catalyst is any species that causes hydrogen to evolve at electrode potentials less negative than in its absence. Since the overpotential of hydrogen electroreduction on mercury is the highest of all metals, the automatically renewable mercury electrodes – the dropping mercury electrode (DME) and the hanging mercury drop electrode (HMDE) – have become ideal tools for research and for applications of the catalysis of hydrogen evolution. The subject was opened already in the early years of polarography.¹

In the case of DME, the time factor of the catalytic reaction is strictly limited by the drop-time, usually a

few seconds, which makes that electrode a tool applicable for researching the mere basis of the catalytic process. A catalytic reaction involving a slow step need not be observable with DME at all. In the case of HMDE, on the other hand, there is no time limit for measurement, the rate of potential scan can be widely varied and, moreover, the individual catalytic reagents can be accumulated at the electrode surface. HMDE thus allows investigation of many details of the mechanism of catalytic evolution of hydrogen. In spite of decades of utilizing this kind of catalysis for practical purposes, in many cases its physicochemical background still remains insufficiently well interpreted. Considering the wide field of potential applicability of this common electrochemical process, especially in biology² and medicine,³ a systematic research of hydrogen evolution catalysis is nowadays an obviously needed and promising research topic.

* Dedicated to the memory of the late Professor Marko Branica.

CURRENT STATE OF KNOWLEDGE

»Presodium« Catalysis

Historically, the first discovered catalysts of hydrogen evolution on DME were the albumins of human blood serum.⁴ Their action was interpreted⁵ as the mediating transfer of protons from solution to the electrode, where they combine with hydrogen atoms bound to the mercury surface under overpotential, and subsequently get reduced. Catalytic evolution of hydrogen from blood serum occurred at potentials more positive than the electroreduction of sodium ions, and thus that kind of hydrogen catalysis became known as »presodium catalysis«. This term denotes catalytic action by a species, which unassisted initiates hydrogen evolution by placing protons at the mercury surface. The resulting catalytic current is within certain limits a linear function of the volume concentration of the catalyst. The catalytically active species is usually not redox active, which greatly increases the number of substances that can be followed by electrochemical methods. The key atom of the species, bearing a free electron pair by means of which it passes over the proton, from the stock of a proton donor in the solution to the surface of the electrode, is either nitrogen, oxygen, phosphorus or sulfur, suitably situated in the molecular structure of the catalyst. The critical point of the process is the contact of the protonized atom with the mercury surface, which can be favored by adsorption of the catalyst, but which can also occur as a mere rightly oriented collision in the course of thermal motion. Appropriate conformation of the catalyst near the electrode with respect to the electrode double layer is the decisive condition of the process.⁶ A hydrogen evolution catalyst of the »presodium« type is either a species stable in the solution or an intermediate in cathodic electrode reaction of a reducible substance, which catalyses hydrogen evolution in the course of its lifetime within a limited potential span.⁷

Metal Deposition Catalysis

Another type of hydrogen evolution catalyst was described soon after the »presodium catalyst« became known. It is a metal of hydrogen overpotential lower than mercury and of limited solubility in mercury, formed at the electrode by cathodic reduction of some of its compounds – islets of the metallic deposit become nuclei, at which hydrogen evolves on the electrode surface, at potentials less negative than on pure mercury. The first identified catalysts of this kind were the platinum metals.⁸ It was duly recognized^{9,10} that the electrochemical basis of this effect is common with that of »presodium catalysis«. Electroreduction of a cation can be accompanied by catalytic evolution of hydrogen even before the deposition stage has been reached, as exemplified by the hexaqua-cobaltous ion.¹¹

»Brdička« Catalysis

In the early nineteen-thirties, R. Brdička announced^{12–14} that a new type of catalytic evolution of hydrogen appears in the presence of cobalt ions in ammoniacal buffer solutions of cystine or cysteine, or of proteins or peptides containing these amino acids in their structure. This catalytic effect occurs at potentials considerably more positive than the »presodium« one, and in the case of proteins it is characterized by two clearly developed current maxima, the so-called »Brdička's double wave«. Its application in medical diagnostics made the relatively simple »Brdička reaction« or »Brdička test« widely known and used.^{15–22} Nickel ions produce similar effects, though much weaker, under the same conditions.^{23,24} Later on, it was repeatedly shown that cations of other metals,^{25,26} and in buffers other than ammoniacal,^{27,28} cause catalytic evolution of hydrogen in the presence of certain ligands.^{29,30} The Brdička type of catalysis represents a combination of the two above described cases – the presodium and the metal deposition cases. This combination provides several possibilities for the mechanism of catalysis – depending to the experimental conditions, there can be as many as three actual catalysts, active in different potential ranges: the catalyst alone, its complex with the metallic ion and the metal deposit. In the unlikely case that the catalyst does not interact with the metallic ion in the solution, hydrogen will start evolving on the metallic deposit, at a potential that might be affected by the catalyst. In the more common case where the metallic cation does form complexes with the catalyst, the resulting catalytic effect depends upon whether under the given conditions one or more complexes are formed, how fast is the kinetics of complex formation, and what the values of the corresponding complexity constants are. The electroreduction of the ultimate complex usually occurs via »ligand catalysis« based on the fact that electroreduction of certain transition metal complexes occurs at more positive potentials than that of the free solvated cations.³¹ Over years of research, many stable complexes were also found that yield catalytic evolution of hydrogen during their electroreduction.²⁰ The primary product of this reduction may be a catalytically active intermediate »zero-valent complex«,³² possibly in the adsorbed state, sufficiently stable to allow catalytic activation of hydrogen evolution within its lifetime. The final products of the metallic complex electroreduction are the metallic deposit and the liberated ligand; depending on the concentration ratio of the solution components and on the rates of their possible interactions, once electroreduction is completed, the catalyst can still cause hydrogen evolution on the surfaces of either the deposit or the mercury. The often observed decrease of the catalytic current at negative potentials has been often ascribed to desorption of the catalyst from the mercury surface;³³ another reason can be the tunneling of elec-

trons to a certain distance from the electrode, which increases with negative potential, so that the electroactive species accept electrons already in the solution, and the crucial contact of the protonated catalyst with the electrode surface, followed by electron transfer and evolution of H₂, cannot take place any more.

Experimental Approach

All instrumental voltammetric methods are useful for detailed research of hydrogen evolution catalysis: direct current –, cyclic –, normal pulse –, differential pulse –, square wave –, cathodic –, anodic –, adsorptive stripping – and adsorptive transfer stripping³⁴ voltammetries have been and can be applied for faradaic current measurements; impedance voltammetry or electrocapillary measurements are best suited for adsorption studies. Particularly convenient is the constant current derivative stripping chronopotentiometry, highly sensitive to hydrogen catalysis. In the $(dE/dt)^{-1}$ versus E plots, the method yields for hydrogen evolution catalysis a typical prominent signal denoted as »peak H«. In chronopotentiometry, polarization of the electrode by currents of the order of microamperes occurs by several orders of magnitude faster than in the currently used scanning rates in voltammetry, so that the peak H, in addition to increased faradaic part, contains also the component due to the fast change of electrode capacity accompanying the catalytic reaction. If higher polarizing currents are used, the electrode potential changes so fast that the relatively slow catalytic reaction does not show on the curve at all. Introduction of solid amalgam electrodes³⁶ allows studying the effect of the electrode material on the potential and the course of catalytic reaction, practically without losing the wide range of potentials attainable with mercury.

OUTLOOK

In general, as shown above, the process of catalytic evolution of hydrogen depends on many experimental factors, and the modern electrochemical instrumentation and techniques offer a chance not only to study its reaction mechanism in detail, but also to find optimal conditions for specific and sensitive methods of determination and study of various prospective catalysts, which include many biologically important compounds.

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SAŽETAK

Predmet istraživanja: kataliza razvijanja vodika na živinim elektrodama

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Procesi katalize elektrokemijskog razvijanja vodika često predstavljaju teško rješive probleme za istraživače kinetike elektrodnih reakcija. Oni se, međutim, mogu iskoristiti za razvoj jedinstvenih i osjetljivih elektrokemijskih metoda za proučavanje različitih tvari, posebice onih od biološke važnosti. U radu se opisuje povijest istraživanja kataliziranog razvijanja vodika na živinim elektrodama i navode se tri tipa katalizatora.