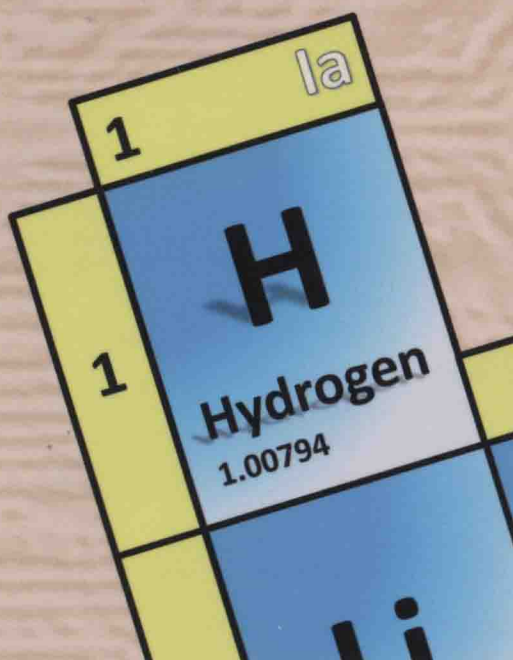
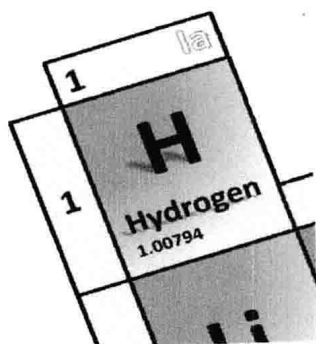


Electrocatalysts for Hydrogen Energy

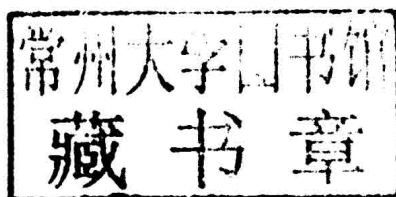


Edited by
Bożena Łosiewicz

Electrocatalysts for Hydrogen Energy



Special topic volume with invited peer reviewed papers only



Edited by

Bożena Łosiewicz

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Trans Tech Publications Ltd
Churerstrasse 20
CH-8808 Pfaffikon
Switzerland
<http://www.ttp.net>

Volume 228 of
Solid State Phenomena
ISSN print 1012-0394
ISSN cd 1662-9787
ISSN web 1662-9779

(Pt. B of Diffusion and Defect Data - Solid State Data (ISSN 0377-6883))

Full text available online at <http://www.scientific.net>

Distributed worldwide by

Trans Tech Publications Ltd
Churerstrasse 20
CH-8808 Pfaffikon
Switzerland

Fax: +41 (44) 922 10 33
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and in the Americas by

Trans Tech Publications Inc.
PO Box 699, May Street
Enfield, NH 03748
USA

Phone: +1 (603) 632-7377
Fax: +1 (603) 632-5611
e-mail: sales-usa@ttp.net

printed in Germany

Electrocatalysts for Hydrogen Energy

Edited by
Bożena Łosiewicz

Preface

The hydrogen energy covers all aspects of the production, transportation, storage, and end use of hydrogen. Hydrogen is not in and of itself an energy source, because it is not naturally occurring as a fuel. It is, however, widely regarded as an ideal energy carrier or energy storage medium, due to the ease with which electric power can convert water into its hydrogen and oxygen components through electrolysis. Hydrogen can be produced on a large scale through raw materials and processes which are economically profitable. Water electrolysis is one of the most utilizable industrial processes for hydrogen production today, and is expected to become even more important in the future. Although water electrolysis is not the least expensive method of hydrogen production, it supplies hydrogen of a very high purity and is nonpolluting. The best electrocatalysts for hydrogen evolution are noble metals, however, they cannot be used directly as solid metals for industrial processes because of their high cost. Hence, a principal focus of modern electrochemistry in hydrogen production by electrolysis is to develop novel electrode materials which should possess long-time stability, be capable of electrocatalytically reducing the energy barrier of the hydrogen evolution reaction, and be immune to the current interruptions and short circuit i.e., exposition in the solution under the open circuit conditions. Industrial hydrogen evolution was initially carried out on mild steel and nickel electrodes. Newer active electrode materials have been gradually developed and introduced, however, lack of proper scale-up practice is one of the primary drawbacks of the present hydrogen technologies.

This special topic volume deals with the development of novel solid state electrocatalysts of a high performance to enhance the rates of the hydrogen or oxygen evolution. It contains a description of various types of metals, alloys and composites which have been obtained using electrodeposition in aqueous solutions that has been identified to be a technologically feasible and economically superior technique for the production of the porous electrodes. Two ways for improvement of the electrode performance have been reported: use of electrode materials characterized by higher intrinsic activity i.e., higher exchange current density, and use of electrode materials characterized by large real surface area. Among electrodeposited composite electrocatalysts of particular importance were coatings containing oxides or metal powders of micron or nanometer size, which cannot be directly codeposited in a metallic form from aqueous solutions. Such multicomponent and multiphase composite electrocatalysts with modified structure become more popular as they exhibit higher electrochemical activity in comparison with pure metals. In the presented papers, composite electrocoatings belonging to the specific type of modified electrode materials consisted of a crystalline or amorphous matrix and the other solid

phase dispersed within it, have been investigated. It was found that the kind of a metallic matrix used (Ni, Ni-P, Ni-Mo, Ni-W, Ni-Co) and the type of embedded solid particles (Mo, Co, Cr, W, Ti, Al, NiAl, MoO₂, TiO₂, NiO, Cr₂O₃, MoS₂, Si, PTFE) determined the properties of the obtained composite materials. Due to the interaction between the matrix and dispersed substance a complex with properties different from the component's features is created. This is a reason for the occurrence of synergetic effect of the substrate in the course of hydrogen or oxygen electroevolution. The mechanism of H₂ and O₂ evolution on these electrodes was studied in alkaline solutions, and the kinetic parameters were determined using steady-state polarization and electrochemical impedance spectroscopy methods. Scanning probe electrochemistry techniques were used as a highly sensitive tool for studies of metal-hydrogen interactions and localized corrosion research of the electrocatalysts. These techniques are of central importance to nanoscience and nanotechnology. They allow characterization of the local structure and properties of surfaces and interfaces as well as corrosion and localized electrochemical events on the micro- to subnanometer scale, opening up the possibility to perform physical and chemical experiments on individual nanoscale objects.

The goal was to produce papers that would be useful to both the novice and the expert in hydrogen technologies. This volume is intended to be useful to the materials scientist or electrochemist, student or professional, who is planning studies of solid state electrocatalysts and who may have had little previous experience with electrochemical measurements. Such a reader will find an outline of basic theory and a discussion of experimental techniques and data analysis, with examples and appropriate references. It is hoped that the more advanced reader will also find this volume valuable as a review and summary of the literature up to the time of writing, with a discussion of current theoretical and experimental issues of research activity in the field of hydrogen energy.

This volume is dedicated to Professor Andrzej Lasia (Université de Sherbrooke, Québec, Canada) on the occasion of his retirement with warm thanks from the Institute of Materials Science (University of Silesia, Poland) for multiannual and valuable cooperation in the field of electrochemistry in the areas of new materials for water electrolysis and the studies of the mechanism and kinetics of hydrogen adsorption, absorption and evolution using electrochemical impedance spectroscopy techniques.

Bożena Łosiewicz

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I. Conventional and Novel Electrode Materials

Electrode Materials

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Keywords: Electrocatalysts, electrode materials, hydrogen/oxygen electroevolution.

Abstract. This review work was focused on conventional and modern electrodes which play an important role in electrochemical systems. Among many types of existing electrode materials, some of the most prominent materials from the conventional (metals and their alloys, graphite and mixed metal oxides) and the modern (amorphous, modified and composite) electrodes, have been outlined. What is also discussed is the recent intensive usability of nanocrystalline electrodes of better properties than their microcrystalline equivalents, and development trend of electrode materials.

Introduction

There are many reasons why hydrogen and oxygen are the gases more and more often listed as the most important components of the green fuel of the future [1-6]. With regard to the electrolytic way in which they are obtained, it must be, however, clearly stated that this method is still very expensive and requires further and very intensive research into the electrode materials. The research in this field is centered around the following issues: (i) learning about the actual nature of the reaction of the electron transfer during the electrolytic evolution of hydrogen or oxygen, (ii) determining the effects of the type of material, morphology of the electrode surface, the parameters of the structure and the chemical composition, and (iii) determining the electrochemical processing of the activation of the electrode material on the electrode reaction. The result of this study shall be proposing new electrode materials characterized by the catalytic effect of the hydrogen electroevolution reaction (HER) or oxygen electroevolution reaction (OER).

The most important tailored properties of electrode materials are catalytic properties, conductivity, corrosion resistance, hardness, current load, form, and size. Many of these are determined by inherent characteristics of the material. Toxicity is another feature which is particularly important when the material is operating in exposed or open environments.

During the electrolytic evolution of hydrogen there occurs simultaneous evolution of oxygen from the same electrolyte. Hence, it seems justified to join the research effort into finding the electrode materials that could meet the requirements of both the cathodic and anodic electrode materials [4]. The main aim of this work is to review the present condition and development trend of electrode materials used in electrochemical processes.

Conventional group of electrode materials

The conventional group of electrode materials consists of metals, graphite and metal oxides [4-6]. Recently, the attempts to improve their electrocatalytic activity with surface treatment and the use of composite electrodes have been made.

Metals and their alloys

Metals and their alloys are electrode materials of key importance. For several decades and still to a certain degree the most popular material for theoretical electrochemical studies has been mercury electrode because of the readily renewable surface. On an industrial scale the mercury electrode is often utilized in brine electrolysis, but there is the general tendency to replace it by solid metal electrodes due to the environmental harmfulness of mercury [5].

The catalytic activity of metals in the HER can be inferred from the value of the exchange current density [6]. The higher the binding energy of Me-H, the smaller the overpotential of its evolution. Having in mind the ability of the catalytic effect on the process of the HER, metals can be divided into three groups: (i) metals with low overpotential values of hydrogen evolution ($\eta < 0.2$ V), including: Pt, platinum metals, Ni, Au, Re, (ii) metals with average overpotential values of hydrogen evolution ($\eta = 0.2-0.6$ V), including: Cu, Ag, Fe, Al, Ti, Cr, Mo, W, Bi and the nickel chromium steel, and (iii) metals with average overpotential values of hydrogen evolution (η about 1.0 V), including: Hg, Pd, Cd, Sn, Zn, Tl, graphite, tin-lead alloys and zinc-cadmium alloys. The overpotential and mechanism of the HER strongly depend on the electrode material. Plotting the overpotential versus the decadic logarithm of the absolute value of the current density yields the Tafel plot [5]. This empirical relationship for the HER is given by the well-known Tafel equation:

$$\eta = a + b \log |j| \quad (1)$$

The electrocatalytic character of the HER follows from the marked dependence of the a and b constants of the Tafel equation for the cathodic process on the kind of the electrode material (Tab. 1). The quantity a can also be dependent on the activity of the hydrogen ion and the composition of the electrolyte.

Table 1. Constants a and b of the Tafel equation and the probable mechanism of the HER at various electrodes with H_3O^+ as electroactive species ($a_{\text{H}_3\text{O}^+} \approx 1$), where I - the Volmer mechanism, II - the Tafel mechanism, III - the Herovský mechanism, (s) - the slowest step of the overall process [7].

Cathode material	$-a$ [V]	b [V dec ⁻¹]	Mechanism of HER
Pb	1.52-1.56	0.11-0.12	I(s), III
Tl	1.55	0.14	I(s), III
Hg	1.415	0.116	I(s), III
Cd	1.40-1.45	0.12-0.13	I(s), III
In	1.33-1.36	0.12-0.14	I(s), III
Sn	1.25	0.12	I(s), III
Zn	1.24	1.12	I(s), III
Bi	1.1	0.11	I(s), III
Ga (I)	1.05	0.11	I(s), III
(s)	0.90	0.10	I(s), III
Ag	0.95	0.12	I(s), III
Au	0.65-0.71	0.10-0.14	I(s), III
Cu	0.77-0.82	0.10-0.12	I(s), III
Fe	0.66-0.72	0.12-0.13	I(s), III
Co	0.67	0.15	I(s), III
Ni	0.55-0.72	0.10-0.14	I(s), III
Pt (anodically activated)	0.05-0.10	0.03	I, II(s)
(large j)	0.25-0.35	0.10-0.14	I, III(s)
(poisoned)	0.47-0.72	0.12-0.13	I(s), ?
Rh (anodically activated)	0.05-0.10	0.03	I, II(s)
Ir (anodically activated)	0.05-0.10	0.03	I, II(s)
Re	0.15-0.21	0.03-0.04	I, II(s)
W	0.58-0.70	0.10-0.12	I, III(s)
Mo	0.58-0.68	0.10	I, III(s)
Nb (unsaturated with H)	0.92	0.11	I, III(s)
(saturated with H)	0.78	0.11	I, III(s)
Ta (unsaturated with H)	1.2	0.19	I, III(s)
(saturated with H)	1.04	0.15	I, III(s)
Ti	0.82-1.01	0.12-0.018	I, III(s)

During cathodic polarization metals are exposed to changes in the structure of the surface as a result of the hydrogenation or surface formation of an alloy with the metals of the base electrolyte. P - and sp -electron structure metals do not dissolve hydrogen very well, whereas the d -electron

structure metals are characterized by high affinity with hydrogen and absorb it during cathodic polarization [4,8,9].

Most widely used electrode materials are metals such as iron and its alloys, nickel, cobalt and copper. All of them are stable enough during cathodic polarization in neutral and alkaline environments. In acidic solutions they may be digested, especially when AC-polarization techniques are applied. During cathodic polarization iron, nickel, cobalt and copper also interact with hydrogen that is being released, forming solid solutions. Therefore, after long-term polarization of the electrode their surface morphology is greatly changed. Blisters and cracks appear and the profile of the surface of the metal is changed. Steel cathodes are generally used in the electrosynthesis of inorganic chlorine, oxygen, hypochlorites, chlorates, chloric acid and perborates. To reduce the overpotential of the HER on metals such as cobalt or nickel, special surface activation methods consisting in developing a real surface of the cathode are used, which leads to the reduction in current density. It is common practice that the surface is activated with metals and metal alloys with low overpotential of hydrogen evolution [3,4,6]. Especially electrodeposition is the appropriate method for surface modification of the metallic electrodes. Fig. 1 summarizes most of the metal pairs that have been codeposited electrochemically, either commercially or in laboratory studies [10].

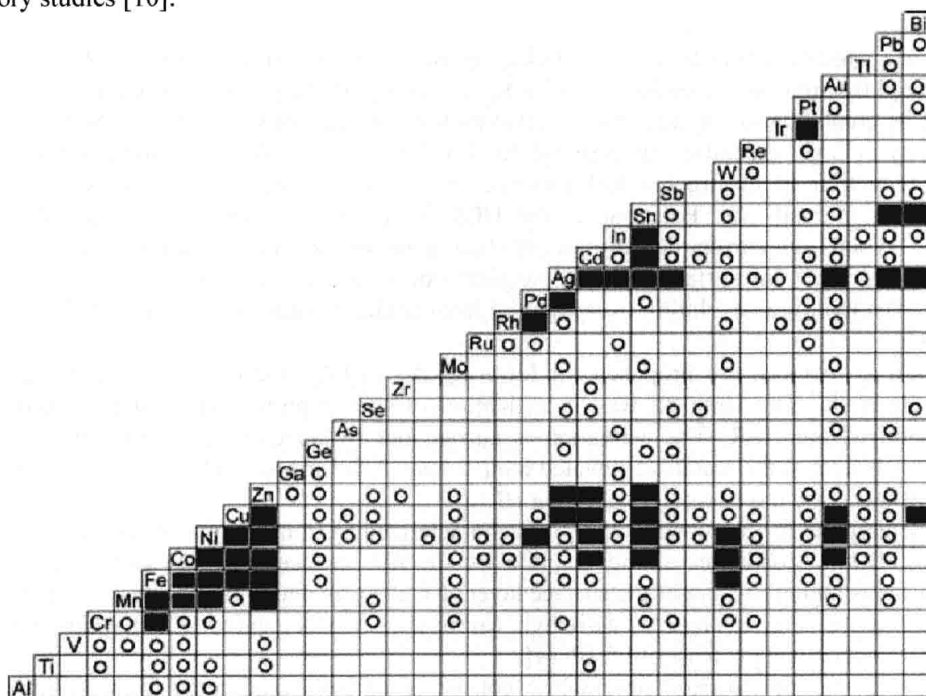


Fig. 1. Metal pairs that have been codeposited electrochemically: (○) demonstrated in laboratory studies and/or small-scale applications, and (■) technically interesting, widely employed alloys [10].

Due to the nature of the electrochemical process, anodic electrode materials are exposed to surface oxidation. The oxide coating which is formed as a result of high ohmic resistance can significantly prevent the process from taking place. There are cases, however, which show that the oxide coatings that are formed participate in the electrochemical reaction of transition, having a catalytic effect on its course [4]. The oxide layer of this kind can be often found on metallic substrates and of course on oxide electrodes. In other cases, due to the impact the oxygen has on electrode materials, these materials might be destroyed or gaseous oxidation products might be produced.

Two types of material are used as the anode electrode material: digestible and non-digestible ones. It turns out that it is not easy to offer a completely non-digestible anode material. The material

should preserve its initial electrochemical properties over a long period of time of anodic polarization of the electrode and should be also resistant to the aggressive environment in high temperatures. The oxygen emitted during the anodic electrode polarization oxidizes the surface of the anode material, slightly changing the electrochemical parameters. The oxide film on metals protects some of them from further oxidation and preserves stable electrochemical parameters in the process of electrolysis, which allows them to be used as the anode material. However, this is rarely the case since only platinum metals, nickel and some kinds of steel satisfy this condition.

Yet, there are various kinds of anode materials. This is thanks to the use of metals and their alloys, graphite and carbon-like materials, semi-conductive metal oxides and other semiconductors with a relatively high conductivity, characterized by a significant chemical resistance in aggressive environments [4].

Nickel is unstable during anodic polarization. Taking into consideration the low costs of this material and its alloys, the research that is being made is aimed at reducing the overpotential of oxygen evolution. Tests were carried out on powder coatings, Raney nickel and materials obtained by electrodeposition [4,11].

Graphite

Graphite is a cathodic material which is widely applied in industrial electrochemical methods. It is characterized by high overpotential of the HER, depending on the graphite production method and degree of its graphitization. It was observed that higher ordered structure of the graphite, its electric conductivity is larger (specific conductivity: $10^2 - 10^4 \text{ S cm}^{-1}$) [4]. At low current densities during cathodic reduction in electrochemical process, the whole surface of an electrode participates including the internal one. Potential of the HER in this case is lower than on solid smooth electrodes. When high current densities are applied, pores of the electrode are blocked by evolved hydrogen, and the total surface area of the electrode is decreased and current density quickly increases. The hydrogen evolution overpotential from acidic or alkaline environments is then equal 0.16-0.24 V.

Various methods are proposed for lowering the hydrogen evolution overpotential on the graphite electrode. The simplest way is activation of the graphite surface with metals of low overpotential of the HER. The activation is carried out by adequate treatment of the graphite saturated with salts of the metals at elevated temperature. The formed oxides of the metals (e.g. iron or titanium) decrease the overpotential of the HER.

The graphite is a porous material. It is characterized by considerable ability to absorb many substances. During oxidation of the graphite its specific surface area increases and adsorption ability becomes higher. Nature of the surface layer also changes due to formation on it characteristic functional groups, e.g. hydroxide, carbonyl, carboxyl, peroxide, quinone, activating selectively chosen electrochemical processes [4,5,12-14].

The crystalline structure of graphite consisting of hexagonal rings forming thin parallel plates (graphenes) is shown in Fig. 2 [13]. Each atom of carbon is covalently bonded to three other atoms in the plate where the angle between two bonds is 120° . One can observe that the outermost electron shell of a carbon atom has four valence electrons, where three of which are used by the covalent bonds. In covalent bonds the forth valence electron does not take part and it may be easily displaced from the electron shell by an electric field. These electrons provide electrical conductivity of graphite. The graphenes are bonded to each other by Van der Waals forces which are weak. The layered structure of graphite allows sliding movement of the parallel graphene plates. Weak bonding between the plates determines softness and self-lubricating properties of graphite. Graphite is rarely found as monocrystals. Most of graphite is present in form of flakes or lumps. Graphite possesses fine-grained structure and sometimes it is named amorphous graphite, however it is not really amorphous but microcrystalline material.