Positive and Negative Aspects of Electrode Reactions of Hydrogen Evolution and the Influence of a Constant Magnetic Field

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Abstract

Nowadays, the application of electrode reactions, including those concerning hydrogen evolutions, attracts great attention in industry and in power engineering worldwide. Thus, new ways of increasing the efficiency of electrode processes are of particular interest. One of them may involve a Constant Magnetic Field (CMF). The magnetic field influences both electrons and ionized atoms leading to dynamic effects (e.g. electrolyte movement in the layer adjacent to the electrode resulting from the Lorentz force). Investigations carried out with the CV method (Cyclic Voltammetry) proved that the reaction rate constant of hydrogen production increases under the influence of CMF. Alloys well adsorbing hydrogen such as Co-Mo, Co-W, Co-Mo-W (their composition was selected by the EDX method – Energy Dispersive X-ray Analysis) and alloys well absorbing hydrogen such as Co-Pd was obtained. CMF catalyzed the increase of the reaction rate of hydrogen generation, hydrogen probably being the main ecological energy source of the future. This finding was confirmed by SEM (Scanning Electron Microscopy). The influence of CMF on so-called hydrogen corrosion of metals was also established.

Keywords: Hydrogen; Alloys; Constant magnetic field; Lorentz force

Introduction

Reactions of hydrogen formation may be beneficial for the natural environment and for industrial applications. However, they may also lead to some undesirable results. It is common knowledge that hydrogen is supposed to become a basic fuel by the end of the twenty first century. Nowadays, the source of hydrogen production is first and foremost petroleum (50%), natural gas (30%), and coal (15%). Only 0.5% of hydrogen is obtained from water electrolysis even though water belongs to renewable energy sources, along with the wind, solar radiation and thermal water [1].

Hydrogen can also be evolved by electrolysis through adsorption of its atoms on metal surface [2]:

$$2H_2O + 2e^- = H_2 + 2OH^- \text{ (cathode)} \quad (1)$$

$$2OH^- = H_2O + \frac{1}{2}O_2 + 2e^- \text{ (anode)} \quad (2)$$

$$H_2O = H_2 + \frac{1}{2}O_2 \quad (3)$$

High - temperature water electrolysis increases the process efficiency by decreasing the value of Gibbs free energy ($\Delta G$), increasing the rate and number of reactions proceeding on the electrodes. It allows applying a higher current density, decreasing heat demand (by the amount of evaporation heat, as water vapor does no longer evaporate).

Hydrogen is an ecological fuel (the combustion product is water) and is easily ignited, contributing to more effective combustion. Hydrogen is easier and cheaper to store than electric energy. Its resources are unlimited. At present, its only drawback is the fact that it diffuses through metals, though this may also be turned into an advantage and used for storage.

Hydrogen can also be evolved by electrolysis through adsorption of its atoms on metal surface [2]:

$$H^+ + M + e^- \rightarrow MH_{ads} \text{ (acidic solutions)} \quad (4)$$

$$H_2O + M + e^- \rightarrow MH_{ads} + OH^- \text{ (neutral and alkaline solutions)} \quad (5)$$

Figure 1: Hydrogen adsorption on metal surface and hydrogen absorption inside metal.

where: $M$ - metal atom, $H_{ads}$ - adsorbed hydrogen atoms.

The majority of adsorbed hydrogen atoms are subjected to electrochemical desorption, and the generated molecules of $H_2$ dissolve in the solution or are removed from it in the form of gas bubbles. However, part of the adsorbed hydrogen atoms may permeate to the metal and become absorbed (Figure 1) [2]:

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\[ MH_{ads} \rightarrow MH_{abs} \]  \hspace{1cm} (6)

where: \( MH_{ads} \) - hydrogen atom absorbed inside metal.

Hydrogen may originate from the gaseous phase as well. Molecules of \( H_2, H_2S \) and others are capable of so-called dissociative chemisorption. Forces of chemisorption interaction of molecules (\( H_2, H_2S \)) with transition metal surface (Fe, Cr, Ni, Mo, W) overcome the mutual attraction of atoms in molecules, resulting in dehydrogenation and adsorption of hydrogen atoms on metal surface as follows:

\[ H_2 + 2M \rightarrow 2MH_{ads} \]  \hspace{1cm} (7)

\[ M_nX + 2M \rightarrow MH_{(n-1)}X + MH_{ads} \]  \hspace{1cm} (8)

where: \( X \) - anion

It was established that effective metal thickness involved in the process of adsorption is composed of several atomic layers [3,4]. Furthermore, a reaction according to Equation (6) may proceed.

Metallic systems capable of hydrogen absorption have found various applications in the synthesis of many transition metal combinations and alloys as catalysts in hydrogenation reactions, as membranes serving for hydrogen separation from other gases through diffusion, and for hydrogen isotope separation (the source of high purity hydrogen obtained through thermal decomposition of hydrides) [5-9]. Metallic hydrides are an object of common interest as they are used in hydrogen storage. A metal that easily absorbs hydrogen both from the gaseous phase and electrochemically from solutions is palladium (it may dissolve a hydrogen volume 850 times greater than its own volume) [10-13]. Hydrogen may be present in palladium in two phases, preserving the crystalline structure of the pure metal but characterized by an increased value of the lattice constant. At small hydrogen concentrations, a solid hydrogen solution in palladium, called the \( \alpha \)-phase, is generated. When the quantity of absorbed hydrogen increases, phase \( \beta \), which is a non-stoichiometric palladium hydride, commences to form. A particular role in the process of absorption is played by hydrogen located directly under the surface of palladium (a thickness of several hundred atomic layers), displaying properties different from those of the absorbed hydrogen. In this layer, the concentration of hydrogen exceeds its concentration in phases \( \alpha \) and \( \beta \) [14].

Compared to pure palladium, its alloys display slightly different properties in the process of hydrogen absorption. This may be explained by electron effects (changes in the electron structure after alloy formation) or by geometrical effects (changes in crystalline network parameters) [15]. Based on the electrochemical properties connected with hydrogen absorption such as the potential of absorbed hydrogen oxidation peak and the potential of \( \alpha-\beta \) phase transition, it is possible to determine the volumetric composition of palladium alloys by electrochemical method [16]. The catalytic activity of metals in the reaction of hydrogen formation may be determined from the value of exchange current density (\( \eta \)). The higher the energy of the bond \( M - H \), the more a given metal (\( M \)) is involved in the process of hydrogen generation catalysis and the smaller is the overpotential of its production. There is a relationship between the overpotential of hydrogen formation (\( \eta \)) and free enthalpy of hydrogen adsorption (\( H_{ads} \)) on various metals. The greater the enthalpy, the lower the overpotential of hydrogen formation is noticed for a given metal. The relationship between the overpotential of hydrogen formation (\( \eta \)) and current density (\( j \)) may be defined with an equation connected to exchange current density (\( j_0 \)):

\[ \eta = \left[ \left( R \cdot T \right) / \left( \alpha \cdot n \cdot F \right) \right] \log \left( j / j_0 \right) \]  \hspace{1cm} (9)

where: \( R \) - gas constant \( \left( 8.314 \right) /\left( \text{K-mol} \right) \), \( j \) - limiting current density \( \left( \text{A/cm}^2 \right) \), \( j_0 \) - exchange current density \( \left( \text{A/cm}^2 \right) \), \( T \) - temperature \( \left( \text{K} \right) \), \( \alpha \) - transfer coefficient [-], \( n \) - number ofelectrons participating in the reaction, \( F \) - Faraday constant \( \left( 96485 \text{C/mol} \right) \).

Exchange current density (\( j_0 \)) is a measure of hydrogen formation rate on metal (a metal electrode). The relationship between exchange current density logarithm (\( \log j_0 \)) in the process of hydrogen formation and free enthalpy of hydrogen adsorption on electrode surface (\( H_{ads} \)), i.e. the force of the metal-hydrogen bond made it possible to plot a so-called volcanic curve (Figure 2).

Depending on the type of metal, the stability of \( M-H \) bonds varies. This is demonstrated in the values of free enthalpy of hydrogen atom adsorption. Hence, it is concluded that the kinetics and mechanism of hydrogen formation on metallic electrodes is influenced by the type of metal. At the top of the curve, there are noble metals (Pt, Pd), being the most active in the process of hydrogen formation. Hydrogen is strongly adsorbed on the surface of such metals, which are characterized by the low overpotential of hydrogen formation (<0.2 V). Apart from the \( H - H \) interactions, hydrogen bonds with metal are formed. Transition metals are on the ascending part of the curve (Co, Ni, Fe) they form weak metal-hydrogen bonds, whereas metals strongly adsorbing hydrogen and being difficult to melt (Mo, W, Ti) are on the descending part of the curve. Those metals are characterized by average values of hydrogen formation overpotential (0.2–0.6 V) and by average values of exchange current of hydrogen formation reaction on those metals. There is no pure metal which would completely fulfill the electrocatalytic requirements. Thus, it is essential to search for alloy materials that would have more beneficial properties than noble metals. Metals and alloys adsorbing a lot of hydrogen (Co-Mo, Ni-Mo, Co-W, Ni-W) are characterized by high electrocatalytic activity in the process of hydrogen formation [17]. The adsorbed hydrogen considerably alters the electron structure of the electrode material [18]. According to the Brewery and Engel valence bond theory, catalytic activity in the process of hydrogen formation increases linearly as a function of metal-hydrogen bond force for alloys formed from transition metals. Furthermore, another theory of hydrogen formation on transition metal alloys is based on the electron structure of alloys in terms of the
direction of electron transfer between atoms located in the alloy [19].
The combination of various d metals in an alloy may surpass platinum
in respect of catalytic activity in the process of hydrogen production.
Co-Mo, Ni-Mo, Co-W, and Ni-W alloys, where the pairing up effect
provides a greater number of available d orbitals and ensures better
proton adsorption, surface adherence and surface transport. It was
proved that the highest electrocatalytic activity is displayed by alloy
combinations of metals from the dgroup characterized by minimal
entropy and easier overlapping of d orbitals, which are formed in
intermetallic compounds of the highest symmetry (e.g. MoCo, WCo,
MoNi, WNi).

While striving for the generation of the greatest quantity of
hydrogen possible through various reactions and its safe storage, and
despite the fact that it is regarded as the ecological energy source of the
future, it needs to be remembered that hydrogen production may be
noxious as well.

Both atomic and molecular hydrogen has a harmful influence
on all metals and alloys. Several atomic parts of hydrogen per
million parts of metal or alloy increase its embrittlement. The metal
microstructure decreases and the value of stresses increase under the
influence of hydrogen. So-called hydrogen embrittlement is ascribed
to atomic hydrogen diffusion in a metal or alloy and its accumulation
in spaces or internal surfaces, where molecular hydrogen in the
form of gas is produced. The higher the hydrogen concentration, the
greater the pressure of gaseous molecular hydrogen, contributing to
void expansion and cracking. Atomic hydrogen evolving on metal or
alloy surfaces is adsorbed. Diffusing adsorbed hydrogen may evolve as
molecular hydrogen in internal voids or on the boundary ‘inclusions –
matrix’. In the case of high hydrogen penetration rate, the pressure
generated by molecular hydrogen may cause the formation of bubbles
(so-called hydrogen cracks).

The influence of a constant magnetic field on alloy electrodeposition
was investigated earlier [20-22]. The impact of the Magneto-
Hydrodynamic Force (MHD) on the convection of the solution in a
three-electrode layer during metal and alloy deposition was established
as well [23,24]. Furthermore, the influence of a constant magnetic field
on hydrogen desorption on the surface of metallic electrodes was also
examined [25,26]. In this case, the hydrogen desorption rate increased
whereas the size of hydrogen bubbles decreased. The study presented
concerned the influence of a constant magnetic field on the kinetics of
electrodeposition reaction of two-component alloys (Co-Mo, Co-W,
Co-Pd) and three-component alloys (Co-Mo-W) and the concurrent
processes of hydrogen formation [20,27,28].

Experimental

Cyclic Voltammetry (CV), Scanning Electron Microscopy (SEM)
and Energy Dispersive X-ray Analysis (EDX) were used. A three-
electrode system was used consisting of the following components:
a working (gold, disk) electrode of 0.1 cm² surface area, an auxiliary
platinum mesh electrode of much larger area and a saturated calomel
electrode as a reference electrode. The measuring system was located
between the pole pieces of an N–S pole electromagnet (Figure 3).

The Constant Magnetic Field (CMF) applied for investigation of
magnetic induction B was from 0 to 1.2 T. Vector B was parallel to the
surface of the working chamber. The electrolyte applied (galvanic
bath) (depending on the alloy) was composed of: 0.27 mol/dm³ CoSO₄;
7H₂O; 0.07 mol/dm³ Na₂MoO₄; 2H₂O; 0.06 mol/dm³ Na₂WO₄; 2H₂O;
0.06 mol/dm³(NH₄)₂PdCl₄; 0.6 mol/dm³ sodium citrate (Na₃C₆H₅O₇ ∙
2H₂O); 0.05 mol/dm³ H₃BO₃; 0.025 mol/dm³ EDTA (C₂O₄H₂N₂Na₂ ∙
2H₂O) and 0.1 mol/dm³H₂SO₄ (Table 1).

The alloys were deposited for 3500s. Investigations by the CV
method were performed on an apparatus composed of the ER-2505
laboratory electromagnet with pole piece N and S, measurement vessel
with a three-electrode electrochemical system, a device controlling
the electromagnet PZP – 80, an SZP stable electromagnet current
source, a hallotron sensor of constant magnetic field, a TH-26
hallotronemeslometer, a CMR-02 digital temperature regulator, a set
for electrochemical measurements ATLAS (9933 Electrochemical
Interface, 9923 Frequency Response Analyzer) and a computer (with
POL-99 and IMP-99). SEM investigations were carried out using an
electron scanning microscope Vega 5135 MM produced by Tescan.
In the EDX method, an X-ray micro-analyzer EDX Link 300 ISIS,
produced by Oxford Instruments, was used to investigate the chemical
composition of the alloy (in terms of quality and quantity).

Table 1: The chemical compounds used for alloys electrochemical preparing.

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>Molar mass (g/mol)</th>
<th>Producer</th>
<th>Concentration in solution (mol/dm³)</th>
<th>Alloys Co-Mo</th>
<th>Co-W</th>
<th>Co-Mo-W</th>
<th>Co-Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSO₄ • 7H₂O</td>
<td>281.12</td>
<td>Fluka (Germany)</td>
<td>0.27</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na₂MoO₄ • 2H₂O</td>
<td>241.98</td>
<td>POCH S.A., Glawa (Poland)</td>
<td>0.07</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na₂WO₄ • 2H₂O</td>
<td>329.86</td>
<td>BHD Chemicals Ltd (England)</td>
<td>0.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(NH₄)₂PdCl₄</td>
<td>284.22</td>
<td>POCH S.A., Glawa (Poland)</td>
<td>0.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₂O₄H₂N₂Na₂ ∙ 2H₂O</td>
<td>294.12</td>
<td>POCH S.A., Glawa (Poland)</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₂O₄H₂N₂Na₂ ∙ 2H₂O (EDTA)</td>
<td>372.24</td>
<td>ZOCH Lublin (Poland)</td>
<td>0.025</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>81.64</td>
<td>POCH S.A., Glawa (Poland)</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂SO₄ (95%, d=1.84 g/cm3)</td>
<td>98.08</td>
<td>&quot;Chempur&quot;, Piekary Slaskie (Poland)</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 3: Scheme of the measuring system.
Results and Discussion

Studying the kinetics of electrochemical redox processes exposed to CMF, it was observed that a constant magnetic field may be an additional parameter controlling electrochemical processes. Currently, scientists are also interesting in investigating the processes of electrochemical hydrogen production. It was found that CMF increased the hydrogen production rate at a temperature of T=298 K. Figure 4 shows the influence of CMF on the hydrogen production rate on alloys deposited on golden electrodes (B) from 0 to 1200 mT. The constant of hydrogen formation reaction rate (k) was calculated, and the function was plotted (Figure 4).

Increased magnetic induction (B) led to higher constants of the hydrogen formation reaction rate (k). CMF affected both electrons and ionized atoms. Dynamic effects occurred, one of which was volumetric movement of the medium (movement of the electrolyte). Movement of the electrolyte in a diffusion layer under the influence of the Lorentz force (F) defined with the general equation:

\[ F = j \times B \]

where: \( j \) - limiting current density vector; \( B \) — magnetic induction vector,

as well as other MagnetoHydrodynamic Effects (MHD) more frequently activated the surface of the electrode by removing hydrogen bubbles (H\(_2\)) more rapidly. Therefore, hydrogen bubbles were smaller and new hydrogen ions (H\(^+\)) could discharge more promptly on the surface of the electrode. Both natural and MHD convections macroscopically stir the bulk electrolyte, whereas growth and detachment of gas bubbles induce microscopic convections on the electrode surface. In addition to macroscopic MHD forced convection, micro-MHD convection among gas bubbles might be induced by the sophisticated electric field. When the gas bubbles are produced very actively at more than 50 mA/cm\(^2\), the mass transfer process can be significantly enhanced by the superimposition of magnetic field (the conditions of the experiment of 200mT). The unique convection induced adjacent to the bubble nucleation and growth site probably helps agitating the electrolyte near the electrode to drastically decrease the supersolubility of dissolved H\(_2\) gas in a magnetic field. As mentioned in the Introduction, alloys (e.g. cobalt with molybdenum or tungsten) work better as electrodes in the processes of hydrogen formation than single metals. Molybdenum and tungsten are metals that strongly adsorb hydrogen, and moreover they are mechanically stable. Two-component alloys of Co-Mo and Co-W, which are characterized by a low overpotential of hydrogen formation (\( \eta \)), displayed high activity in these processes. The three-component alloy of Co-Mo-W, characterized by an even lower overpotential of hydrogen formation than two-component alloys, was obtained at the potential of -1.17 VSHE. With the EDX method, it was established that in the obtained alloy of Co-Mo-W there was 84.65% w/w of cobalt, 11.90% w/w of molybdenum and 3.45% w/w of tungsten. The process was carried out without a magnetic field. When electrodes covered with such alloys were transferred to CMF and subjected to the processes of hydrogen formation by the CV method, the relationship of current density (\( j \)) and magnetic induction (B) was established (Figure 5). The increase in the alloy of component, resulting in lower overpotential of hydrogen formation (\( \eta \)) (e.g. Pd, W, Mo), causes an increase the hydrogen evolution. Reduction overpotential of hydrogen formation (\( \eta \)), is a consequence higher energy of metal-hydrogen bond (e.g. W-H), which catalyzes the process of evolution of hydrogen [higher values the exchange current density (\( j_l \)].

Equation (12) defining this relationship is as follows: [20]:

\[ j \approx 0.63 \pi^{1/6} \cdot A^{-1/6} \cdot \rho^{-1/3} \cdot D^{5/9} \cdot \nu^{-2/9} \cdot \left( n \cdot Fc \right)^{4/3} \cdot B^{1/3} \]

where: \( j \) - current density [mA/cm\(^2\)], \( n \) — number of electrons participating in the reaction, \( A \) - area of the working electrode [m\(^2\) or cm\(^2\)], \( D \) — diffusion coefficient [cm\(^2\)/s], \( \nu \) — kinematic viscosity [m\(^2\)/s], \( c \) — concentration of electroactive ions in the electrolyte [mol/dm\(^3\)], B — magnetic induction [T or mT], \( \rho \) — electrolyte density [g/cm\(^3\)], \( F \) — Faraday constant [96485 C/mol].

The influence of CMF was also displayed by the decreasing thickness of a diffusion layer (SD) which may be defined by the following equation (13) [20]:

\[ \delta_D \approx 1,59 \left( \rho \cdot r \cdot \nu^{2/3} \cdot D^{1/3} \right)^{1/3} \cdot \left( n \cdot F \cdot c \cdot B \right)^{-1/3} \]

where: \( r \) - radius of the working disc electrode [mm].

Subsequently, an alloy of Co-Pd was obtained electrochemically. One of its components, namely palladium, located at the top of the volcano curve (Figure 2), is a noble metal of a low overpotential of hydrogen evolution, and is very active in the process.

The Co-Pd alloy was obtained at a temperature of T=298 K, at the potential of U=-1.05VSHE. Based on the EDX method it was established that after a redox reaction and without a magnetic field, a
solution with 0.27 mol/dm$^3$ of Co$^{2+}$ and 0.06 mol/dm$^3$ of Pd$^{2+}$ yielded an alloy of Co-Pd composed of 75.2% w/w of cobalt and 24.8% w/w of palladium. Apart from adsorbing hydrogen, the alloy displayed the capability of hydrogen absorption which could be a perfect method of its storage. Based on the peak of absorbed hydrogen oxidation, the quantity of this element could be determined in the alloy of Co-Pd using the CV method. Furthermore, the energy of adsorption changed with the potential applied. Thus, it may be concluded that controlling the electrode potential, the alloy may be coated with hydrogen up to a defined extent, or its total desorption may be achieved. SEM observations (at magnification x100) proved that CMF contributed to an increase in stresses in the structure when the alloy Co-Pd was formed, and some change in the surface microstructure occurred (Figure 6).

As previously mentioned, the increase of absorbed hydrogen in the Co-Pd alloy resulted in a higher alloy embrittlement (decreasing its mechanical strength). Faster hydrogen penetration into the alloy increased its internal pressure resulting in the formation of bubbles and cracks. This occurred most intensively in the palladium subsurface layer, where hydrogen concentration was even higher than in phases α and β, in which most of the hydrogen is adsorbed. For better visualization of CMF influence on hydrogen formation reactions in the Co-Pd alloy, Co-Pd alloy electrodeposition was performed at a potential of $U = -1.05$ V$_{\text{sh}}$, with magnetic inductions of $B = 0$, $B = 600$ mT and $B = 1200$ mT, but at a temperature of $T = 323$ K. Photographs were taken using a SEM at a magnification of X500 (Figure 7).

It may be observed that both the temperature and CMF accelerated the reaction of hydrogen formation. Obviously, this had a negative impact on the surface of the material (so-called hydrogen corrosion), but the advantage of the applied conditions was the increase of the hydrogen volume evolution. As hydrogen is intended to be the main ecological energy source of the future, every possibility of increasing its storage certainly represents a positive aspect of the actions undertaken.

Conclusions

A constant magnetic field (CMF) may be a parameter increasing the reaction rate constant (k) under the influence of CMF as determined with the CV method. Appropriately selected compositions of galvanic solutions and alloys well adsorbing hydrogen (Co-Mo, Co-W, Co-Mo-W), and additionally absorbing hydrogen (Co-Pd), determined with the EDX method, resulted in an increased reaction rate of hydrogen formation under the influence of CMF. While conducting investigations at two different temperatures, SEM imaging proved that, either temperature or CMF increase the reaction rate of hydrogen formation. This was observed the formation of bubbles and cracks of various sizes on the surface of the alloys.

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References