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ELECTROCATALYSTS FOR WATER ELECTROLYSIS

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The review paper accumulates the latest information on the analysis of catalyst synthesis for the electrolysis of water in alkaline and partially in acidic media. Literature data on the production of electro-catalysts based on noble, refractory, transition and pure metals, as well as metals doped with molybdenum, phosphorus, and other elements, are presented. Given the different methods of synthesis of electro-catalyst, the advantage of the electrochemical method is emphasized as easy, accessible method enabling to regulate the composition of synthesized electrodes by changing the content of an electrolyte and the conditions of electrolysis, controlling the properties of synthesized materials.

Keywords: *synthesis, hydrogen, energy, water electrolysis.*

Introduction

Presently, there is a considerable shortage of fossil energy and resources; therefore the production of hydrogen as "a pure" energy carrier is particularly important, since it can be obtained directly from renewable energy sources by decomposition of water. The review article [1,2] retraces the entire prehistory development, crisis stages and subsequent significance, the past, present and prospects, as well as the future related to the production of hydrogen by electrolysis of water. It is well known that more active materials for hydrogen evolution include noble metals such as platinum, gold, silver, palladium and ruthenium [3]. This is explained as being due to the fact that the rate of adsorption of protons on their surfaces is almost equal to the rate of desorption or recombination accompanied by the formation of gaseous hydrogen. However, high costs for these metals make them no possible to be widely used in the production of hydrogen on a large Industrial scale. To ensure the economy with environmentally friendly and sustainable hydrogen energy, it is necessary to produce hydrogen at lower prices. For this to happen, it'd be appropriate to develop new electrode materials with increased electrocatalytic activity for the hydrogen evolution reaction. The ideal electro-catalyst should have a low overvoltage of hydrogen evolution at industrial current densities with a constant potential value that remains invariable in the course of time, has good chemical and electrochemical resistance, a long service life and does not emit harmful products during electrolysis, has good adhesion to the substrate, does not contain impurities that reduce the sensitivity of electrodes, is not be sensitive to short-circuit and voltage drops, safe from the environmental point of view and, finally, its production is easy at low costs [4-7].

Productivity of electro-catalysts can be improved either by increasing their real surface area, or by changing their electrochemical activity and the Tafel slope of polarization curves. The cost of electrodes can be reduced by alloying precise metals with other metals or through developing new electrode materials based on cheaper elements.

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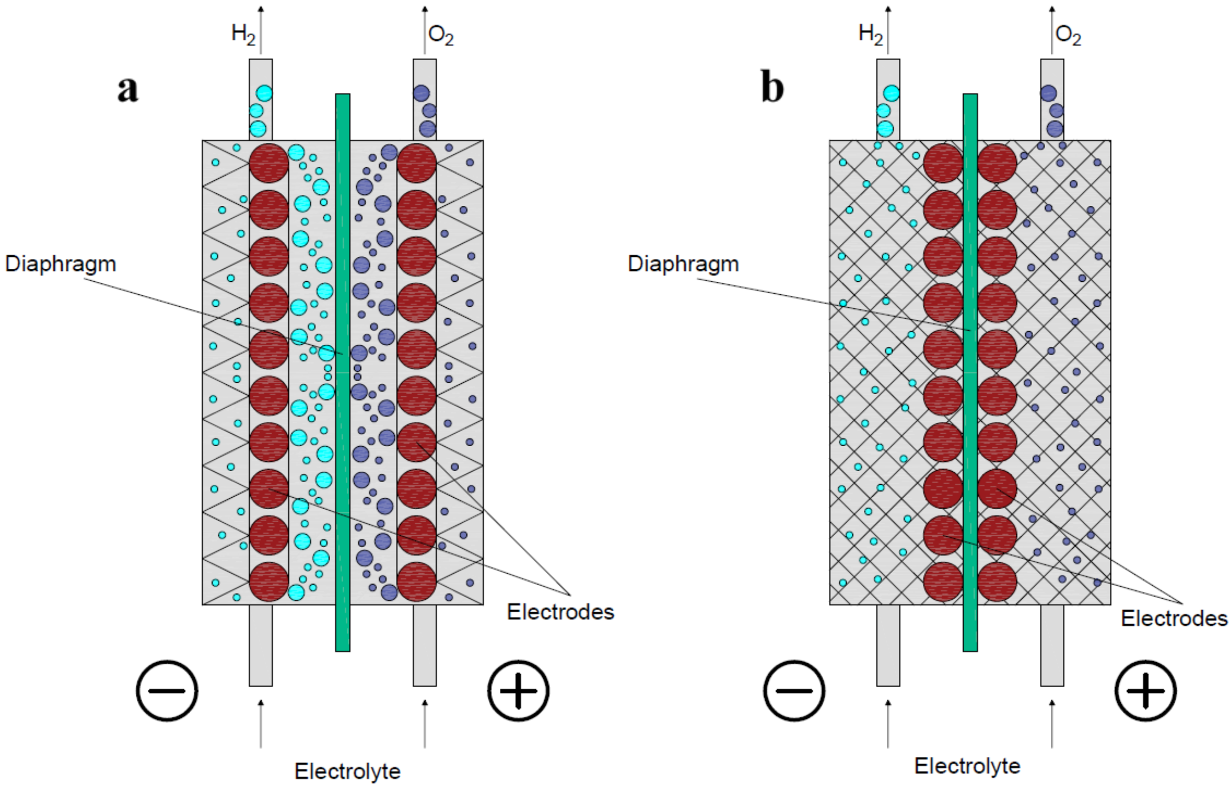

Fig. 1. Inter-electrode gap (a) and zero-gap (b) alkaline cell structures.

As for the alkaline electrolysis, a diaphragm (e.g., asbestos, potassium titanate, polypropylene) serves to separate anode and cathode compartments. This helps to avoid intermixing of anode and cathode solutions, as well as separate H_2 and O_2. The commonly used 30% KOH electrolyte is highly corrosive and sensitive to CO_2 in the ambient air (K_2CO_3 formation) [8]. The usual cell structure with an inter-electrode gap (Fig. 1a) is rather simple to remove reaction products; however, the diaphragm is relatively thick resulting in higher cell ohmic resistance [9].

Zero-gap design (Fig. 1b) has provoked a new approach to the design of the electrochemical cell. The most important advantage is the possibility of avoiding circulation in liquid electrolyte [10] and the significant reduction of the cell ohmic resistance due to the direct contact of electrodes with two membrane surfaces. This allows minimizing the voltage drop between the electrodes [11]. Moreover, the use an anion exchange membrane (AEM) in place of the electrolyte results in a compact system, similar to a PEM device, which is free of bubble effects, and has low resistance and high stability [12].

AEM and zero-gap technologies also offer the possibilities that catalyst layers can be produced from catalyst nanoparticles directly onto the membrane surfaces to give better adhesion, lower resistance [11] and produce membrane-electrode assemblies (MEAs) well-known in PEM fuel cell/electrolysis technology (catalyst coated membrane MEA fabrication [13]).

Raney nickel and skeletal nickel-based catalysts having a large surface area are often used in commercial alkaline water electrolyzes with Ni mesh support (Fig. 2). Also, the Ni foam [14] and Ni fiber paper [15] could be used as an electrode which is suitable to use in a zero-gap cell with or without AEM as it provides the porous media allowing effective gas removal. Moreover, both catalyst-coated membrane (without catalyst support) and catalyst-coated substrate (electrode or gas diffusion layer (GDL)) approaches could be used for MEA preparation.

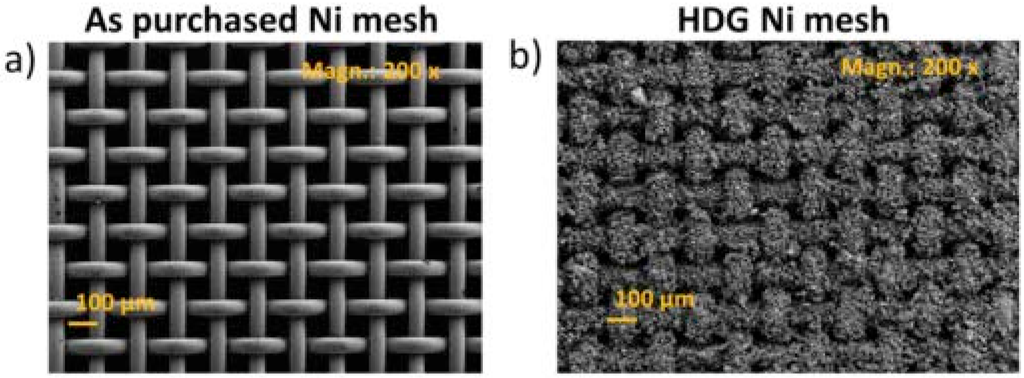

Fig. 2. SEM pictures of the **As-**purchased Ni mesh (a) and the Ni mesh coated through the use of hot-dip galvanization (b) [16].

1. Electrodes based on precious metals

In [17], there is reduction of oxygen on electro-catalysts from Pt-M/C (M = V, Cr, Co) and Ag-Pt/C alloys and on electrodes from various manganese oxides (MnO/C, Mn_3O_4/C, MnO_2/C) in a solution of KOH. Electrochemical measurements indicate an increased electro-catalytic activity of Pt alloys as compared to pure platinum which is associated with decline in the degree of adsorption of oxygen species caused by drop in the reactivity of Pt. Note that the increase in the activity of Ag atoms in Ag-Pt/C alloys as compared to pure Ag is due to the electronic effect caused by the presence of Pt, which leads to an increase in the degree of adsorption of Ag-O. In the case of Mn_yO_x/C materials, the results show a low electrochemical activity of MnO/C and a higher activity for MnO_2/C and Mn_3O_4/C compounds. This is explained as being due to the fact that the activity of the oxygen reduction in the reaction (ORR) of the electrode in the presence of large amount of MnO_2 is high due to the reduction of Mn (IV) to Mn (III) [17].

The Pt-Co alloy deposited on carbon and electro-activated with silicon-tungstic acid (STA) ions of $SiW_{12}O_{40}^{4-}$ and without it, was used as cathodes for the hydrogen evolution reaction (HER) in 3M KOH at 70°C. The characteristics of these electrodes were studied by neutron activation (NA) and electrochemical impedance spectroscopy (EIS) methods. The best HER results were observed on Pt-Co alloys, electro-activated by $SiW_{12}O_{40}^{4-}$ ions which was explained as being due not only to the change in the surface chemical composition of the electrode but also to the increase in its active surface [18].

In order to reduce energy consumption, the inter-metallic compounds $PtMo_4$, $PtMo_3$, $PtMo_2$, PtMo and Pt_2Mo both exposed and unexposed ionic activation were analyzed as cathode materials for hydrogen production through the electrolysis of aqueous solutions of KOH. When a combination of activating reagents in the form of tris-Co and sodium molybdate complexes is added to a standard electrolyte, electro-deposition of a fine-grained precipitate occurs on the cathode surface which leads to the increase of the real surface of the electrode by nearly 10 times. As a result, the overvoltage of the hydrogen evolution decreases, the catalytic activity of the electrodes increases, and the energy consumption decreases [19].

The discharge of hydrogen ions was carried out on three different electrodes from the inter-metallic Pt-RE alloys (where RE is Ce, Sm, Ho), namely Pt-Ce, Pt-Sm and Pt-Ho, all of them having equiatomic composition. The electrodes were tested in an aqueous solution of 8M KOH at 25°-85°C temperature intervals. The activation energy values for Pt, Pt-Ce, Sm-Pt and Pt-Ho electrodes were calculated. Obtained results show that the addition of RE improves the activity of the Pt electro-catalyst [20]. The Pt and Pt-Pd cathodes were analyzed by the voltammetry method in galvanostatic conditions. It was shown that the electrochemical activity of the Pt-Pd cathode in the hydrogen evolution in a 30% solution of KOH at a temperature of 90°C is twice as high as that of a purely platinum electrode [21].

In [22-25] analyzed the possibility of reducing the cost of precious metal catalysts for the HER, reducing their content in the composition of the electrodes. The possibility of significant reduction in the value of catalysts for the hydrogen evolution reaction, through the use of synthesized single-phase fine-grained carbide films as substrates was proposed [22]. WC, W_2C, Mo_2C were found to be excellent materials as a cathode carrier on whose surface mono-films (ML) were deposited from Pt, Pd and Au. These electrodes displayed activity in the HER as comparable to bulk Pt electrodes, while exhibiting stable activity during the chronopotentiometric measurements of HER. The results of the studies cited in the work indicate prospects for carbide materials, the use of which significantly reduces costs in the production of hydrogen by electrolysis of water, as stable low cost carriers for ML from precious metals [22].

In [24] Au nanoparticles were applied on active surface areas of the molybdenum disulfide (MoS_2) electrode to increase the catalytic activity of the electrode. At a room temperature, through the use of classical Hoffman cells operating at atmospheric pressure and at different cathode potentials there were tested electrodes prepared from platinum, nickel, stainless (SS) and low carbon (LCS) steels.

The electrodes were tested in a 10% aqueous solution of 1-n-butyl-3-methylimidazolium ($BMI.BF_4$) at a current density of i =10-42mA/cm^2, with a total hydrogen production efficiency of 82 to 98%. The highest values of i –current density obtained on the Pt, Ni, SS and LCS electrodes were 30, 12, 10 and 42mA/cm^2, respectively, and their efficiency was 85-99%.

These comparative results show that the LCS electro-catalyst is an attractive alternative for the industrial production of high purity hydrogen [23]. To produce hydrogen from alkaline electrolytes, the synthesized nanoparticles of Au precipitated on the macroporous Ni electrode were used as cathodes [25]. The alloying of macroporous Ni by the Au nanoparticles not only increased the surface area, but also improved the catalytic activity of the alloy. Fig.3. shows the polarization curves recorded in KOH 30 wt.% at 30^{0}C and 80^{0}C in the electro-catalysts examined: smooth Ni, macroporous Ni and macroporous Ni-Au NPs. The information obtained from the Tafel polarization data says that the macroporous electrodes are more active for HER to indicate the macroporous Ni-AuNP's the best performance.

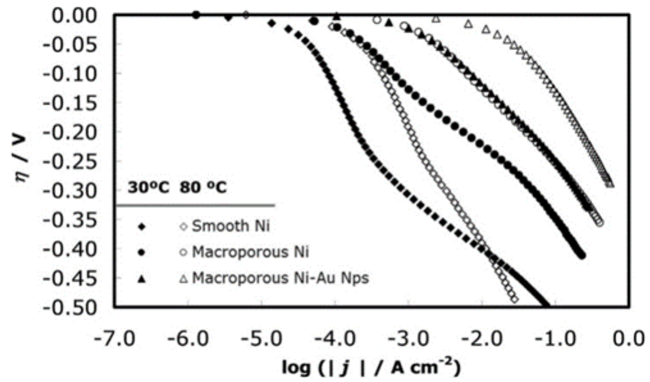

Fig.3. Linear Tafel polarization curves recorded on the analyzed electro-catalytic coatings in 30 wt.% KOH solution at 30^{0}C (filled dots) and 80^{0}C (empty dots).

The nanoplatinum (Pt) catalyst sustained by tungsten carbide (WC) was obtained by impregnation with a finished solution of WC and H_2PtCl_6 [26]. Powders of tungsten carbide were obtained by a gas-solid reaction in an atmosphere of CH_4/H_2 through the use of ammonium metatungstate (AMT) which was treated through drying as a precursor. The results of SEM and XRD show that the average particle diameter of Pt, well dispersed on the Pt/WC surface, is about 13.5 nm. The electro-catalytic properties and chemical stability of the Pt/WC powder microelectrode for the reaction of hydrogen evolution in an acidic solution were analyzed through the use of electrochemical methods: cyclic and linear voltammeter. The Pt/WC electrode exhibits high catalytic activity in the hydrogen evolution reaction. The current density of the exchange during the evolution of hydrogen is $4.42 \cdot 10^{-3} A/cm^2$, the activation energy is 26.20 kJ/mol with an overvoltage of 250mV [26]. Research into the structure and electro-catalytic activity in the reaction of the electroreduction of oxygen in the acid medium of nanostructured materials from Pt-Ag/C are described in [27]. It revealed that the films are characterized by uneven distribution of metals in the nanoparticles. The influence of various factors (synthesis temperature, electrolyte composition, pH of the environment, etc.) on the properties of synthesized electrodes was studied in the work.

The authors examined Pd-Au electrodes with different ratios of both metals obtained by electro-deposition on carbon used as electro-catalysts in the hydrogen evolution reaction in a neutral phosphate buffer solution. The amount of gaseous hydrogen obtained at different electrodes was estimated to comply with chronoamperometry data. The highest rate of hydrogen evolution was achieved on electrodes obtained from an electrolyte with an equal content of Pd and Au [28]. These studies inspired the authors [29] to synthesize electrodes from Pd-Ag. Cyclic voltammograms taken after annealing in 0.1M hydrofluoric and perchloric acid solutions on this electrode show that the Pd-Ag electrode has oxidation-reduction properties.

Cathode materials designed for application in the water decomposition reaction should have a minimum hydrogen overvoltage value, be stable without signs of corrosion, have a large surface area and have improved electro-catalytic activity. Properties like the large surface area are required to stimulate the catalytic interaction, high chemical stability and independent control of nanomaterial parameters. Note that all these properties depend on each component of the nanostructure. There are two ways to improve the performance of electrode materials: 1) use electrode materials characterized by a higher intrinsic activity, i.e. a higher value of the current density, 2) use electrodes characterized by a large surface area. Both methods are used in practice. In considering various materials of electrodes: smooth metals, alloys, inter-metallic compounds and composites, Raney type materials (Raney Ni, Zn, etc.), oxides, carbides, sulfides, borides, phosphides, amorphous and nanocrystalline materials, etc. it can be concluded that the most active materials are noble metals, then Raney alloys, alloys of IrO_2/Ru_2O, sulphides, borides and Ni/Mo based alloys. Unfortunately, precious metals are very expensive and easily poisoned, and their activity decreases with time. In spite of the fact that many materials can be improved and optimized for their use in HER, it is necessary to study a detailed mechanism and kinetics of HER in respect to these materials, as well as the relationship between morphology (surface roughness) and intrinsic electro-catalytic properties.

2. Electrodes based on nickel and molybdenum

Platinum is an electrode material with the highest catalytic activity for HER. However, its high cost and deficiency are the two main drawbacks for through the use of it in the industrial electrolysis of alkaline electrolytes. All these make it necessary to look for cheaper and more accessible materials with good catalytic activity. Electrodes synthesized on the basis of iron group metals with refractory metals are widely used as a material in the electrolysis of water. Interest in these studies is great, since it is hydrogen that is the fuel of the future [30, 31]. In recent years, lots of work was devoted to the synthesis of active electro-catalysts without the participation of noble metals [32], since it is more economical to use cheaper materials and at the same time, ecologically clean electrodes should be used from the ecological point of view [33,34].

Ni-based alloys are widely used cathodes for the electrolysis of alkaline waters due to the relatively high catalytic activity of Ni, and the synergism in the catalytic behavior of various components in the metal alloy. Alloys such as NiCo [35-41], NiFe [42-46], NiMo [43,47-59], NiW [47,60,61], NiCu [62,63], NiAl [6,64-68], NiZn [69-73], NiMoFe [56,74-77] were used by means of different methods. Materials based on nickel and molybdenum attract ever growing attention because of their activity for HER and sufficient corrosion resistance in low-cost alkaline solutions [43,48,49,78]. The synthesis of new nano-structured materials is very important for their application in the hydrogen energy. The electrochemical deposition method allows obtaining new nano-sized films with predetermined properties. Electro-deposition is considered to be a cost effective, convenient and intensive method of obtaining nanophase and nanocrystalline metallic materials with excellent reproducibility whose composition is easily regulated by changing the concentration of components in the electrolyte and the conditions of electrolysis [34,79].

It is known that electrolysis of water for the production of hydrogen is carried out in neutral, acidic and alkaline solutions, therefore, the review article will consider the most effective electrodes used in these electrolytes.

Electrochemical method was used to obtain thin films based on Ni from alkaline solutions on a substrate of stainless steel [42,74,80,81].

In [42] the electrocatalytic properties of electrodes based on copper and nicel were studied. Fig.4. shows the polarization curves of electrolysis of Cu/Ni, Cu/Fe, and Cu/NiFe electrodes in a 1M solution of KOH. The slopes of Tafel found from these curves show that the catalytic activity of NiFe coatings in the HER reaction is much higher than in copper electrodes coated with Ni and Fe.

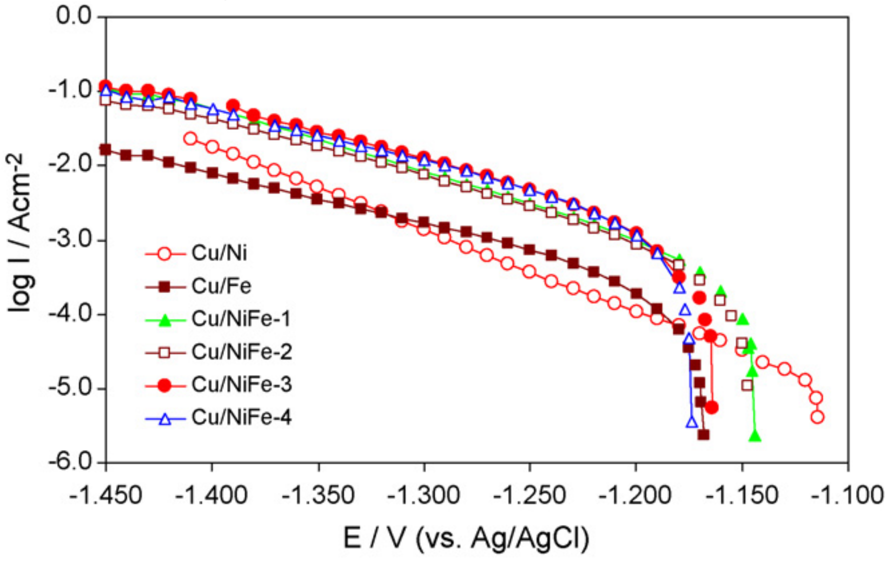

Fig. 4. Cathodic current–potential curves of working electrodes recorded in 1M KOH solution at 298 K.

The electrochemical behavior of Ni-Mo-Fe based coatings used as catalysts in the process of water electrolysis was studied. According to the authors, in a dilute alkaline medium (activity of the films was studied in a 1M KOH solution), these films proved to be a good catalyst for hydrogen evolution [74]. Note that Ni-Ce alloys also have electrocatalytic activity in the hydrogen evolution reaction [80,82]. It found that when the Ni-Ce alloy is electro-deposited on a steel substrate, an increase in the content of cerium sulfate in the bath still more reduces the value of the effective cathode current. The rate of the hydrogen evolution from the NaOH solution rises together with the cerium content increase in the alloy. Among the various Ni-Ce alloys, an alloy with a content of Ni-77% and Ce-23% showed maximum catalytic activity [80]. High-performance composite electrodes of Ni-Zn /CeO_2 were prepared in alkaline solutions through the use of the method of composite electro-deposition in a Ni-Zn bath containing suspended particles based on micro- or nano-particles of CeO_2. The addition of CeO_2 particles significantly influences the microstructure and electro-catalytic properties of Ni-Zn coatings upon hydrogen evolution [83]. Electrodes Ni-RE were also synthesized where RE is a rare-earth metal (La, Ce). These electrodes were obtained through the use of Ni as base, with the addition of metal acetylacetonates or metallic powders of acetylacetonates. The electrodes were synthesized at various temperatures (800°C, 900°C, 1000°C and 1200°C) for 3 hours, and then the comparative characteristics of the synthesized electrodes were compared.

It was established that Ni –RE electrode materials have a more uniform shape (hemispherical) and a smaller crystal size than the Ni powders and consequently exhibited greater electro-catalytic activity [84,85]. A study into the process of electrochemical Ni-La coating production shows that as cathode current density increases, the La content in the alloy increases as well. The results of the studies indicate that when the hydrogen is discharged into an alkaline solution, the exchange current density for a Ni-La electrode obtained by electro-deposition is larger than for a pure Ni electrode and its value rises as La content increases in the alloy. The effective electro-catalytic activity of the Ni-La alloy for HER is due to the synergism of the electronic structure of La and Ni [81].

The electro-deposited NiW film was used as cathode material for HER [47,60]. The electro-catalytic activity and stability of NiW films were specified in a 10% NaOH solution by (EIS) and in the removal of the Tafel curves. It found that the electro-catalytic activity of NiW films grows together with the rise in the gravity coefficient (G), with films exhibiting high stability [60]. NiW precipitations were subjected to electro-deposition under various conditions of gravity arising from alternating rotational speed of the centrifuge where the electrolysis cell was located. The morphology of NiW films was characterized by SEM. Owing to the removal of the Tafel curves and the use of electrochemical impedance spectroscopy (EIS) method, the electro-catalytic activity and stability of NiW films for HER in a 10% NaOH solution were determined. The results showed that NiW films electro-deposited under normal gravity consist of cell grains and micro-cracks. The electro-catalytic activity of NiW films for HER intensified as the gravitational coefficient (G) rose. Corrosion resistance of a NiW film deposited at a G=256 value was higher than that of a film obtained under normal gravity conditions.

Through the use of electro-deposition, macroporous electrodes of the Raney-Ni type were obtained on the Ni-Co surface deposited on AISI 304 stainless steel, suitable for the hydrogen evolution reaction. Hydrogen evolution on these electrodes was explored in the solutions of 30% KOH. The results showed that these electrodes operate more effectively than pure nickel electrodes while the energy consumption in the cell is reduced by about 25% [35]. Activated coatings from the nickel Raney alloy were used as an anode material in the electrolysis of water [46,86] while saving was about 100mV at 40A/dm^2 [86].

The Ni-Mo and Ni-Mo-Fe alloys obtained from alkaline-citrate bath on soft steel strips were explored as cathodes for HER in the alkaline medium. Their stability in open circuit conditions, resistance to electrochemical corrosion, electro-catalytic properties, stability, chemical composition and crystal structure of phases were established [34].

Ni-Mo-based electro-catalysts from organic electrolytes in the reaction of hydrogen and oxygen evolution in the alkaline medium were synthesized [48]. The obtained nanocrystalline $Ni_{0.006}$-Mo; $Ni_{0.1}$-Mo and NiMo powder materials were explored as electro-catalysts for hydrogen evolution. The best productivity for hydrogen evolution was obtained on $Ni_{0.1}$-Mo electrode, and NiMo electrode was effective in the oxygen evolution reaction.

The authors of [43] explored Ni-Mo alloy obtained by electrolysis from electrolytes of varied composition. This alloy showed high catalytic activity and stability with hydrogen evolution in 1M NaOH solutions at 25°C; however in a solution of 33% NaOH at 85°C (in industrial electrolysis) the electro-deposited Ni-Mo alloy along with high electro-catalytic activity showed a low stability as a result of the alloy deterioration[43].

Electrochemical methods were used to obtain powders of Ni-Mo alloys from solutions containing ammonium sulfate and ammonium chloride at various concentrations of Ni and Mo ions, and the polarization curves of their co-precipitation were taken. Morphology, chemical and phase compositions of electro-deposited powders of Ni-Mo alloy were examined through the use of DSC, TGA, SEM, EMF and XRD analysis. Analyzes showed that the composition of the powders depends on the ratio of the concentrations of Ni / Mo ions and on the conditions of electrolysis [87].

Glycine was used as a complexing agent during the electro-deposition of many binary metal alloys [49,70,88-90]. Electro-deposition of nano-crystalline Ni-Mo alloys was carried out through the use of two different molar ratios of Ni:Mo in a solution of sodium glycinate at pH 9.3 [49]. The corrosion resistance of Ni-Mo alloys in a 3.5% NaCl solution was studied through the use of potentiodynamic polarization and the electrochemical impedance method. The Ni-Mo alloy electro-deposited from a solution containing a molar ratio of$[MoO_4^{2-}]$ / $[Ni^{2+}]$ = 0.2 demonstrates a higher corrosion resistance than precipitates obtained from solutions with a molar ratio of 0.1 and pure Ni. The preparation and properties of new electro-catalysts from Ni and La were studied in [36,91]. Alloys $Ni_{3.6}$-$Co_{0.75}$-$Mn_{0.4}$-$Al_{0.27}$, La-$Ni_{4.9}$-$Si_{0.1}$,Ti_2Ni and Ni-Mo were tested as a cathode for the hydrogen evolution reaction. Their electro-catalytic activity in the hydrogen evolution process and stability were analyzed in a solution of 30% KOH at 700°C.The morphology of the surface and the chemical composition of these electrodes were examined before and after the electrolysis. The results show that the hydrogen evolution activity increases with increasing molybdenum content. These electro-catalysts not only have a low overvoltage with hydrogen evolution, but also maintain a high stability under continuous and discontinuous electrolysis [91].

The influence of different methods of processing Ni-P films on the properties of alloys was studied. The analysis was carried out through the use of X-ray diffraction and atomic force microscopy. The processing of alloys consisted of heating up to 400°C within 1 hour and electrochemical treatment (anodization at 0.5V followed by multi-cyclic polarization). Information about the performance characteristics of the deposit, treated and non-treated Ni-P coatings as anodes for the oxygen evolution reaction in alkaline media is derived from stationary state polarization curves and the corresponding Tafel slopes [92]. The effect of the composition and structure of electro-deposited nickel-phosphoric coatings on their catalytic properties in the hydrogen evolution reaction was also studied in [93]. It found that rise in the content of phosphorus in the alloy from 0.1 to 12.6% by weight leads to rise in the rate of hydrogen evolution. Coatings obtained in galvanostatic conditions exhibited a higher activity than those obtained in potentiodynamic conditions. It revealed that the rate of hydrogen evolution depends on the composition of the alloy: Ni-P alloys containing up to 6.5% by weight of phosphorus had a real catalytic activity, whereas phosphorus-enriched coatings contribute to the release of hydrogen due to a significant increase in their area. As a result of the research it was discovered that the main factors influencing the composition of Ni-P sediments are temperature, pH and concentration of $NaH_2PO_2{\cdot}H_2O$ in the electrolyte. The maximal electro-catalytic activity manifested itself in the precipitation with a phosphorus content of up to 7 at% [94, 95]. The influence of TiO_2 on the physicochemical and electro-catalytic properties of Ni-P electrodes was studied in [96, 97]. It found that the plates with optimum phosphorus content consist of a mixture of amorphous and crystalline phases. Doping of Ni-P plates with titanium oxide (TiO_2) increases the coefficient of electrode roughness, as well as the number of electroactive nodes and its ability to adsorb hydrogen. Reinforced TiO_2 plates from Ni-P exhibited high electrocatalytic activity during the HER [96].

A simple method to produce composite catalysts for the evolution of H_2, including the simultaneous reduction of a graphene oxide film and the electrochemical deposition of Ni on its surface is described in [98]. The resulting composites show enhanced electro-catalytic activity against HER in alkaline media as compared to pure electro-deposited Ni. The electro-catalytic characteristics of the hydrogen evolution on the composite metal alloys Co-Mo, Ni-Mo, Co-Mo-P-S, Ni-Mo-P-S, obtained from citrate electrolytes, were analyzed. It revealed that the activity of electro-catalysts is accounted for by the morphology of alloy surface and the content of metallic and nonmetallic activators. The consistent introduction of non-metallic elements P and S into the alloy increases the rate of hydrogen evolution [99,100].

NiFeZn coatings were obtained through the use of the electro-deposition method, followed by chemical leaching of them in a KOH solution [101]. A sulfate bath on a mild steel substrate was used for electro-deposition of NiFeZn alloys. The evaluation of this material as electro-catalyst for the hydrogen evolution reaction was carried out in alkaline solutions by taking stationary polarization curves. Studies revealed that at a current density of $135mA/cm^2$, the films exhibit good stability during 200 hours. A positive aspect of this cathode is that on the polarization curves, only one slope of Tafel appears in the 25-80°C temperature range. The working potential of NiFeZn in 28% KOH at 80°C is about 100mV which is much lower than that of mild steel (400 mV) [101].

The electrochemical behavior of the two modified Ni/Re_{87}-Co_7 and Ni/Re_{57}-Co_{37} electrodes (electrolytic Ni coated with a thin electrolyte layer of the Re-Co alloy) as electrodes for the hydrogen evolution in 6M KOH solution was studied. The obtained data were compared with a pure Ni electrode. Both modified electrodes exhibited significantly higher hydrogen evolution rates and exchange current densities than the nickel electrode. The hydrogen overvoltage on both electrodes is much lower than the value of the overvoltage on a pure Ni electrode. A Ni alloy with a low content of Re (Ni/Re_{57}-Co_{37}) exhibits better electro-catalytic properties [102]. Binary nickel-silver alloys of different composition having a higher activity than the pure nickel in the hydrogen evolution process were synthesized. Studies on a spinning disc electrode show that the hydrogen evolution activity in the $Ni_{0,75}Ag_{0,25}$ electrode is approximately as twice as that of pure nickel [103]. The electrochemical activity of these coatings was also studied during release of hydrogen in a 5M KOH solution through the use of the stationary polarization and (EIS) methods.

The Ni+Mo composite coating also exhibits enhanced activity as electro-catalyst during separation of hydrogen from the Ni-Mo alloy coating. The increase in the efficiency of the Ni+Mo electro-catalytic composite coating can be due to an increase in its actual surface area, as well as an increased catalytic activity at contact points of molybdenum with a nickel matrix. The increase in the number of molybdenum particles implanted in the matrix of Ni+Mo composite electrodes significantly raises their electro-catalytic activity [50,104]. Note that the electro-catalytic activity of the crystalline $Ni_{65}Co_{29}Y_6$ alloy in the HER was also studied. The microstructure of the alloy was analyzed by optical microscopy, scanning electron microscopy in combination with electronic sounding microanalysis and X-ray measurements. The kinetic parameters of the HER were estimated by electrochemical impedance spectroscopy and polarization curves in a 1M NaOH solution at room temperature. Obtained results were compared with the results of polycrystalline Ni. The increased electro-catalytic activity observed with HER on the analyzed alloy was attributed to the pronounced synergistic effect between the alloy components, i.e. the inter-metallic compounds $Ni_{63}Co_{37}$ and $(Ni, Co)_{17}Y_2$ [37].

The properties of the obtained Ni-Co layers were analyzed in a 30% KOH solution. The results of the studies show that these electrodes work in line with the Folmer-Geirovsky mechanism. Synthesized coatings had a higher catalytic activity than a smooth industrial Ni electrode. As the Co content in the bath increases, the roughness coefficient of the surface of the precipitated alloys decreases. Ni-Co alloys with a Co content up to 43% have the highest catalytic activity [38].A convenient electrochemical method for the production of three-dimensional (3D) nanosite structures of CoNiCu was reported and the possibility of through the use of them as an effective electrocatalyst for hydrogen evolution was demonstrated in [105]. These structures demonstrated good activity in the HER. Gold nanoparticles (Au-NP) were successfully synthesized and incorporated onto the surface of a macroporous Ni electrode made by galvanostatic electro-deposition at a high current density [106]. During addition of Au-NP to the macroporous surface of Ni, an improvement in the electrocatalytic properties was caused not only by an increase in the surface of the electro-catalyst but also by an improvement in the intrinsic catalytic activity of the alloy, as can be seen from the values of the exchange current density calculated from the actual surface area. Metal coatings of Ni and Ni-Mo were deposited galvanostatically on a substrate of stainless steel AISI 304. The evaluation of these electrodes was carried out in 30% KOH by taking stationary polarization curves and electron spectroscopy ohmic impedance at different temperatures. According to the results of the Tafel curves, it was concluded that NiMo electrodes have a higher catalytic activity than Ni [107].

The deposition of Ni, Co, Zn, Ni-Zn, Co-Zn and Ni-Co-Sn on a platinum electrode was studied by cyclic voltammetry. It is important to note that the electrochemical stability of the electrodes is observed in the presence of Sn^{2+} ions. (XRD) analysis showed only Ni phases, indicating that the other elements are inside the nickel matrix. Potentiodynamic polarization measurements have shown that the Ni-Co-Sn alloy has the highest exchange current, low overvoltage of hydrogen evolution, high corrosion resistance and is a better electro-catalyst than the other two binary alloys for the HER [39]. The comparative efficiency of the electrodes in a 1M solution of NaOH at 298K shows that doping the Ni-Co electrode with chromium, manganese and copper leads to an increase in its electrocatalytic activity in the process of oxygen evolution. High activity also possess electrodes $Ni_{60}Co_{30}Mn_{10}$ and $Ni_{60}Co_{30}Cr_{10}$ [40], the latter being the best electro-catalyst for the oxygen evolution reaction.

When studying the evolution of hydrogen from an alkaline electrolyte, the Ni-Co alloys were electrochemically activated by Mo ions by adding sodium molybdate to the electrolyte. The hydrogen overvoltage on Ni-Co alloys activated with/without molybdenum showed that the electro-catalytic properties of the Ni-Co electrode alloy are improved upon activation with molybdenum. The electrocatalytic properties of Ni-Co alloys are dependent on the amount of sodium molybdate in the electrolyte. The value of the exchange current density for Ni-Co alloys without Mo is about $4.1\cdot10^{-6}$A/cm^2, and with activation this value reaches about $3.5\cdot10^{-4}$A/ cm^2. Thus, the value of the current density of exchange is nearly a hundred times higher than molybdate ions available in the solution [108]. The catalytic activity of electrodes from electrochemically deposited Ni-Cu alloys in the hydrogen evolution reaction depends on its composition. Thus, electrodes with a low Ni content show higher electro-catalytic activity [62]. The hydrogen evolution was studied by cyclic voltammetry in 6M KOH solution at 298 K. When these alloys are doped with copper, the catalytic activity of these alloys increases significantly [62]. The composite NiCu coating obtained from electrochemical deposition on a copper electrode (Cu / NiCu) was analyzed as electro-catalyst for a hydrogen evolution reaction in the 1M KOH solution. It turned out that the coating has a compact and porous structure with satisfactory stability during the electrolysis for 120 hours, while the hydrogen evolution mechanism did not change. Corrosion tests showed that the resistance of the Cu/NiCu electrode varied to let the cathode current into the system [63].

Nanolayers based on Ni were electrodeposited on a substrate of low-alloyed carbon steel from an alkaline electrolyte at a current density of 20mA/cm^2 for 30 minutes. The influence of co-precipitated elements (Fe, Mo) on the morphology, mechanical and electrochemical properties of the sediment was analyzed. The Ni-Fe alloy consisted of 96% Ni, 3% Fe and 1% O, and the binary Ni-Mo alloy had the following composition: 65% Ni, 33% Mo, 2% O. The Ni-Mo-Fe ternary alloy contained 46% Ni, 49% Mo, 1% Fe, and 4% O [109]. The Ni-Mo-Fe ternary compound showed high corrosion resistance in seawater ($1.7 \cdot 10^{-3}$mm/year) and low overvoltage with hydrogen evolution (-850 V), which leads to rise in its release rate.

The intermetallic electrodes of Ni, Mo, and NiMo for the hydrogen evolution in 1M NaOH solution at 25°C were studied by measuring the AC impedance and taking the polarization curves. It found that the Ni-Mo alloy as an electrode in the electrolysis of water significantly reduces the overvoltage of hydrogen in case where it is isolated in comparison with the electrodes of Ni and Mo [110,111].

Ternary alloys possessing electrocatalytic activity in the electrolysis of water are also proposed: Ni-Mo-Cu [111], Cu-Co-Ni [112], and Fe-Co-Ni [113].

For hydrogen evolution is taken 3 composition- Cu-Co-Ni 1:1: 1, 1:2:1and 1:1:2. And we saw that the first electro-catalytic activity is the best highest (Fig5).

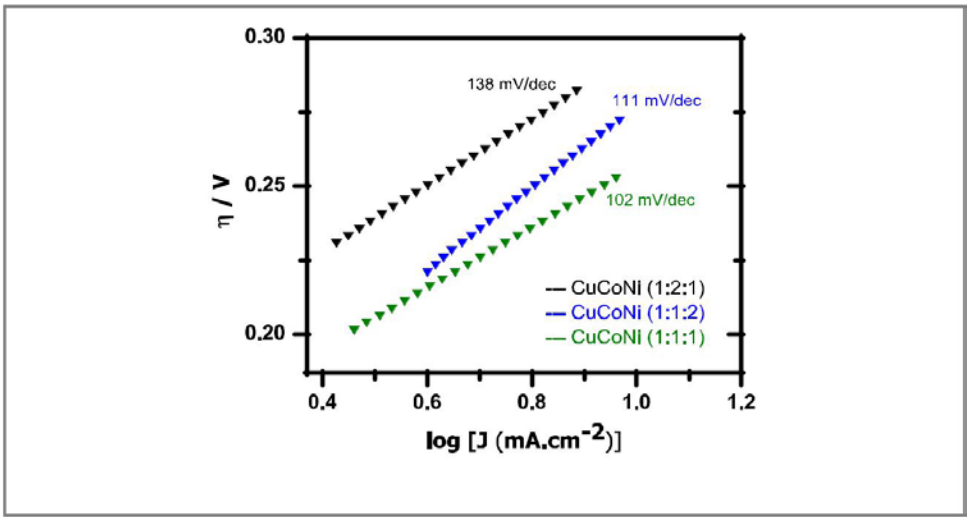

Fig.5. Tafel plot of the T1, T2 and T3 catalyst.

The results showed that the Ni-Mo-Cu coating on the Cu substrate is coarse, has a structure similar to cauliflower and is more active than the binary Ni-Mo electrode. A significant increase in catalytic activity is associated with higher surface area of the resulting alloy [111]. The authors of [114] electrochemically deposited onto the graphite surface the composite precipitates of NiMn (C/NiMn, C/NiMnZn, C/NiMnZn-PtRu and C/NiMnZn-PtPd) to use them as electrodes for hydrogen evolution. These coatings were etched in a concentrated alkaline solution (30% NaOH) to obtain a porous and electro-catalytic active surface.

After the leaching process, a small amount of PtRu or PtPd was deposited on the etched surface of NiMnZn deposits. The layer of $NiMoO_4$ powder was converted into one solid electrode and contained amorphous metal oxides Ni and Mo(IV).The distribution of the Ni and Mo components in this electrode can increase the interaction between them, which results in the growth of the electrocatalytic activity of the Ni-Mo electrode, the hydrogen overvoltage at a current density of 700mA/cm^{2}is 150 mV in 5M KOH at 70°C [51].

To contribute to the reaction of hydrogen and oxygen evolution in an alkaline medium, nickel-molybdenum catalysts in organic media were electrochemically synthesized [115]. Nano-crystalline powders of the composition $Ni_{0.006}Mo$, $Ni_{0.1}Mo$ and NiMo were obtained. Studies showed that materials with a stoichiometric ratio of 1:1 can be considered as a promising electro-catalyst for the oxygen evolution reaction. In [116], amorphous Ni-Sn electrodes were used to remove polarization curves from a solution of 1M NaOH at 25°C which showed that this electrode is electro-catalytically more active in the hydrogen evolution reaction than the mixed crystalline electrode. The high activity of the amorphous Ni-Sn electrode is explained as being due to the rapid charge transfer on it and the rate of electrochemical adsorption and desorption of hydrogen atoms compared to a mixed crystalline electrode of the same composition [116].

Modification of the leached ternary Ni-CoZn coating by depositing small amounts of Ag, Pd and Pt on its surface can further improve the electro-catalytic properties of this Raney electrode. The order of the activity of the analyzed catalysts for the hydrogen evolution reaction is as follows: Ni<NiCoZn<NiCoZn-Pd<NiCoZn-Ag<NiCoZn-Pt. Electrolysis analysis showed that the modified Pt electrode has greater stability during long-term operation than others [41].

Wu and et.al. reported that a porous Ni_3Al electrode with a smaller pore size has a high activity for HER in the6M KOH solution [6]. The cathodes showed long-term stability and retained high catalytic activity under industrial conditions. The instability of Raney Ni electrodes due to the dissolution of the active element during operation was the main factor to restrict its usage. However, the intermetallic compound Ni_3Al is still considered by researchers because of its high resistance to corrosion in an alkaline solution [64-67]. The high activity of this catalyst for HER in the 6M alkaline solution is explained as being due to the high porosity and large real surface of the Ni_3Al electrode [68].

Very active and stable nickel-aluminum and nickel-molybdenum Raney electrodes were proposed for the hydrogen evolution reaction in [52,117]. Two types of electrodes were tested as electro-catalysts for the hydrogen evolution process: pressed Ni or Al powders with NiMo, heated to 700°C and Ni-Al-Mo films deposited by vacuum plasma deposition. These materials were treated with an alkaline solution for leaching aluminum. The addition of molybdenum significantly improved the catalytic activity of the electrode [52].

The hydrogen evolution reaction was analyzed on electro-deposited coatings of base metals to replace expensive precious metal electrodes. These were composite coatings with the inclusion of MoO_2 particles, electro-deposited NiSn alloy coatings [118], and Ni-Sn alloys deposited at different current densities from a bath containing $0.1MSn^{2+}$ and $0.1MNi^{2+}$ ions in a solution of glycine pyrophosphate [119]. It was Ni-Sn coatings that manifested increased catalytic activity in 6M KOH solutions. The authors of [69] carried out a study of the catalytic properties of electro-deposited Ni/Zn and Ni-Co/Zn alloys for the hydrogen evolution reaction in an alkaline medium (30% KOH). The obtained electrodes at a temperature of 30°C were characterized by high electro-catalytic activity for HER and a very low hydrogen overvoltage at a current density of $250mA/cm^2$. The high activity of the electrodes is mainly due to the large surface area of the designed electrodes. In [120] through the use of the example of studying Zr-Ni alloys for suitability in the hydrogen evolution reaction, the authors concluded that the amount of absorbed hydrogen largely depends on the microstructure of the alloy and the value of the potential applied during the experiment. Therefore, the enhancement of the electro-catalytic properties of a nanocrystalline alloy can be explained only by its favorable microstructure (for example, a higher defect density) and a weak degree of hydrogen absorption in nanostructures.

Ternary Ni-Co-M (M = Cr, Mn, Cu) alloys were tested as electro-catalysts for the production of oxygen in the electrolysis of alkaline water in the 1M NaOHelectrolyte at 298K [121]. It was established that doping of Ni-CoCr alloys with manganese and copper increases their electro-catalytic activity. The best results for the separation of oxygen were obtained on the electrodes $Ni_{60}Co_{30}Mn_{10}$ and $Ni_{60}Co_{30}Cr_{10}$.

The electro-catalytic activity of the electro-deposited nanocrystallineCoNiFe alloy in the hydrogen evolution reaction was studied in a 1M NaOH solution. The results showed that the CoNiFe alloy has a higher specific activity than Ni [122]. The nickel-sulfur electrode was obtained in a bath with the addition of thiourea. The effect of thiourea concentration, current density, temperature and pH of the electrolyte on the sulfur content of the Ni-S alloy was studied. The results showed that the main factors affecting the sulfur content of Ni-S coatings are thiourea concentration and current density. Ni-S electrodes demonstrated significantly higher electrochemical activity in the hydrogen evolution reaction than mild steel or other nickel-based alloys [123]. The electro-catalytic behavior of Co-Mo and Co-Mo-C alloys, electro-deposited in a magnetic field, was also studied [124,125]. It found that the addition of molybdenum and carbon reduces the hydrogen overvoltage in comparison with pure cobalt. Tests were carried out in the 8 MNaOH at 90°C. Binary alloys with 30% Mo content show the greater activity in the process of hydrogen evolution. The addition of carbon to the electrolytic Co-Mo alloy improved the electrode's activity, and when the electrode was immersed in the solution at idle there was a slow dissolution of molybdenum, but no complete dissolution was achieved [125].

Iron molybdates with ratios of Mo:Fe of 1.0, 1.5, and 3.0 were obtained by co-precipitation as thin films on a Ni substrate. Studies show that this electrode is very active in the reaction of oxygen evolution from alkaline solutions, and its activity depends on the molar ratio of Mo and Fe in the oxide. Note that the oxide with a component ratio of Mo:Fe 1,0 has the greatest electro-catalytic activity [126].

Electro-catalysts based on NiFe for producing oxygen, methods for their synthesis, chemical properties and catalytic properties were analyzedin [44]. The advantages and disadvantages of each class of NiFe-based compounds are summarized.

The photocatalytic activity of $NiSn_xO_y/G$ electrodes used to produce hydrogen was evaluated by irradiation in the visible light region (λ>420nm) through the use of triethanolamine (TEOA) as a donor. Results obtained showed that $NiSn_xO_y$ adhering in large quantities to the surface of the graphene sheet, forms active regions, where hydrogen evolution is not visibly apparent. After irradiation, the $NiSn_xO_y/G$ electrode showed higher photocatalytic characteristics than the Ni/G electrode which is also subject to irradiation due to the higher photocatalytic activity of $NiSn_xO_y$ it self [127].

Cathodes produced by electro-deposition of NiMo on carbon fabric, exhibiting high electro-catalytic activity for hydrogen evolution in microbiological cells were developed [128]. Electro-deposition of Ni-Mo on carbon fabric occurs at a ratio of Mo:Ni in the electrolyte of 0.65, current density of $50mA/cm^2$ and the duration of electrolysis is 10 min. Obtained results can significantly reduce costs of manufacturing cathodes for electrolysis of water.

The possibility of the use of three-dimensional volumetric porous electrodes from carbon-fibrous and foamy metals, surface of which having been covered with a Ni-Re alloy was studied to produce hydrogen by electrolysis. Modification of the surface of the electrode makes it possible to obtain a high reactive surface with a low hydrogen overvoltage, gives a description of the developed compact electrochemical reactors for hydrogen energetics and suggests a method for separating the oxygen-hydrogen mixture in the process of water electrolysis [129].

The role of Zn in increasing the electro-catalytic properties and the optimal concentration of Zn in the NiMoZn alloy were established [130]. A low concentration of Zn facilitates the process of charge transfer, an increase of the Zn content in the alloy leads to a strong inhibition of the adsorption of protons on the electro-catalyst’s surface. The NiMoZn alloy with the 1-3 at. % Zn concentration shows extremely high electro-catalytic activity for HER as compared to most electro-catalysts of base metals.

Moreover, electrodes with 2 at. % Zn composition demonstrates high stability in acidic conditions, due to which alloy becomes a promising candidate for replacing electro-catalysts from noble metals with water addition [130]. The co-precipitation of MoO_3 with Ni on smooth and rough Ni substrates from electrolytes of various compositions was studied. Morphology and sediment composition were studied by cyclic voltammetry, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and energy dispersive X-ray spectroscopy. The activity of composite catalysts for the isolation of H_2 in alkaline solutions was determined by the removal of quasistationary polarization curves. It found that the activity of precipitation increases depending on the MoO_x content in the Ni layer. The composite catalysts Ni-MoO_x exhibit a high catalytic activity similar to the commercial Ni-RuO_2 catalyst. Stability tests showed that the Ni-MoO_x electrodes are stable under constant current conditions and at repeated electrolysis [131].

The electro-catalytic activity of the crystalline $Ni_{65}Co_{29}Y_6$ alloy was studied by electrolysis of water in the hydrogen evolution reaction [37]. The kinetic parameters of the compound were evaluated on the basis of the electrochemical impedance and the removal of stationary polarization curves in 1M NaOH solution. The enhancement of the electro-catalytic properties of the alloy is explained as being due to the pronounced synergistic effect between the alloying components.

3. Cobalt-based electrodes

The choice of cobalt for the synthesis of cathode materials is accounted for by the interesting properties of cobalt alloys and by the easy release of hydrogen into them; the most popular are Co-Mo [132,133], Co-Cu [88], Co-Zn [89]. Co-Mo deposits were used as test objects in the electrolysis of water [134-138]. An electrolyte for electro-deposition of the Co-Mo alloy from a bath with triammonium citrate is proposed. The optimum electrolyte composition for the Co-Mo alloy is $CoSO_4$-0.3M, $(NH_4)_2MoO_4$-0.25M, triammonium citrate -0.2 M, pH-8, current density i_k=4A/dm^2, electrolyte temperature 303K. The hardness of the precipitated alloy increases together with rise in molybdenum content to anneal it. An increase in the Mo content in the alloy favored an improvement in the electro-catalytic properties. The obtained Co-Mo alloys can be used as effective catalysts for hydrogen evolution reactions, being an alternative to platinum group metals [134]. Electro-catalytic layers of cobalt oxide were obtained on nickel substrates through the use of thermal decomposition methods and electrochemical deposition [139]. The activity of the obtained oxide layers when studying their suitability for the oxygen evolution in a 30% solution of KOH was higher than that of nickel.

The electro-catalytic activity of cobalt and Co-Mo alloys was analyzed in the reaction of hydrogen evolution in acidic, neutral and alkaline media. To apply coatings, a nontoxic citrate pyrophosphate electrolyte was used. It found that alloys having the same chemical composition, but differing in phase composition, can exhibit different activity. The best electrolyte for the production of catalytically active Co-Mo alloys is a solution with a ratio of Co:Mo= of 10:1. In this case, the reduction in overvoltage of hydrogen evolution in an alkaline solution is about 400mV at 30mA/cm^2 as compared to pure cobalt [135].

Co-Mo and Co-Mo-P alloys were precipitated from the citrate electrolyte at pH 4-6. Studies show that the value of hydrogen overvoltage on Co-Mo and Co-Mo-P is lower than of pure cobalt [140].

The electro-catalytic activity of binary alloys Co-W, $Co_{95}W_5$, $Co_{90}W_{10}$, $Co_{85}W_{15}$, $Co_{80}W_{20}$ and $Co_{70}W_{30}$ (atomic%) was studied on the basis of electrochemical data obtained in 1M NaOH solution at 298K. The results were compared with the ones obtained from polycrystalline Co. The values of the Tafel-slope (b), the density of the current exchange (i_0) and the overvoltage indicate a high electro-catalytic activity of Co-W electrodes. Alloys of composition $Co_{90}W_{10}$ possess the best productivity [141].

An electrochemical method for obtaining three-dimensional (3D) nanoscale structures was developed and the possibility of their utilization as effective electro-catalysts for hydrogen evolution was demonstrated [142]. It is reported that these 3D structures of CoNiCu exhibit higher electro-catalytic properties in the HER.

4. Thin films on different bases

Some electro-catalytic properties of crystalline alloys Fe-R (where R are rare-earth metals), $Fe_{90}Ce_{10}$, $Fe_{90}Sm_{10}$, $Fe_{90}Y_{10}$ and $Fe_{90}MM_{10}$ (where MM are lanthanides) for the hydrogen evolution in 1M NaOH solution at 298K are studied [126,143,144]. The results were compared with the amorphous G14 alloy ($Fe_{60}Co_{20}B_{10}Si_{10}$), which is a good catalyst for this reaction, and it was concluded that the catalytic activity of the $Fe_{90}Ce_{10}$ and $Fe_{90}MM_{10}$ electrodes was higher than that of the G14 electrode [143]. Electrodes of iron molybdate with the ratio [Mo]/[Fe] 1.0, 1.5, and 3.0 were obtained through the co-precipitation in the form of thin films on a Ni substrate. Studies show that new oxide has a higher activity in the oxygen evolution reaction in alkaline solutions and its activity apparently depends on the molar ratio of Mo and Fe in the oxide. The electrode with a component ratio [Mo]/[Fe] = 1.0 had the highest electro-catalytic activity [126].

Alloys from sulfamic acid electrolytes were electrochemically synthesized [145]. It revealed that the value of overvoltage of oxygen release on Fe-W alloy is 300 ÷ 400 mV, hydrogen on Fe-Co alloy is 150 ÷ 200 mV lesser than on steel and Fe-Ni alloy. The use of Fe-W and Fe-Co alloys in the electrolysis of water can reduce the energy costs for the release of oxygen and hydrogen.

The mechanism and kinetics of the hydrogen evolution reaction were analyzed in a 1M NaOH solution on the Fe-Mo electrode obtained by electro-deposition at a constant current density from the pyrophosphate electrolyte. A number of electrodes containing molybdenum from 34 to 59 at% were fabricated. The electrodes were porous in kind and their real surface area was specified by the electrochemical impedance spectroscopy method. As molybdenum content increased, the electrodes became more active and the real area of their surface expanded [144]. The kinetic parameters of the separation of oxygen and hydrogen on iron alloys with nickel, cobalt and vanadium were studied in Ref. [145].The lattice of nanoports of NiMo alloy on a titanium grid were synthesized by electro-deposition method [146]. This electrode is bifunctional, behaves in a solution of 1M KOH as a long-lasting effective anode for oxygen release at a current density of 10mA/cm^{2}and an overvoltage of 310mV combined with excellent catalytic characteristics for hydrogen evolution at the same current density and overvoltage of 92mV. Through the use of the bifunctional electrode, an alkaline electrolyzer was made at a current density of 10mA/cm^2 and cell voltage of 1.64V. Electro-deposition of copper-zinc intermetallic compounds (in particular, $CuZn_5$) was carried out on a steel substrate of AISI 1018 from an alkaline solution at room temperature [147]. The analysis of the obtained chrono-amperograms was used to understand the mechanism of nucleation and growth of these inter-metallic compounds. An electro-catalytic activity of the obtained inter-metallic compounds was analyzed for the hydrogen evolution reaction. In [148], polarization curves and electrochemical extraction were used to analyze the electro-catalytic activity of ternary Ti-V-Cr alloys. An optimal composition of the electro-catalyst which ensures the maximum possible desorption of hydrogen at a given temperature was chosen. Results obtained help to understand and optimize the process of electrochemical saturation of alloys with hydrogen.

Anodic electro-catalysts were made of Ir, Ru and their oxides, and a flow-through membrane cell with satisfactory performance and durability of the regenerative fuel cell (RFC) used in the system was developed. To study the performance and stability of these electro-catalysts, a repeated cyclic voltammetry of bound Nafion electrodes was performed. It showed that the electrodes of IrO_2 demonstrate a low productivity and instead a considerable high resistance than other electro-catalysts [149].

Zn-Ni alloys of different compositions were prepared by the electro-deposition method [150]. Alloys obtained on electroformed nickel films were etched for leaching and obtaining a porous electro-catalytic Raney surface suitable for hydrogen evolution. The electrodes were studied by polarization curves and the use of cyclic voltammetry. SEM method was used to study changes in surface properties during repeated cycling and X-ray diffraction - to specify the microstructure. It found that the catalytic activity, as well as the life of the electrode consisting of 50% of Zn, is higher than that of others [150]. It was reported in [151] that although copper and titanium were weaker catalysts for hydrogen evolution, a combination of these two components formed a unique hollow regions with hydrogen bond energy like platinum which led to an increase in the electro-catalytic activity of an electrode. The porosity of this copper-titanium catalyst provides a large surface area and improves mass transfer which also contributes to the rate of hydrogen evolution.

MoS_2 nanoparticles were first synthesized on Au in an ultrahigh vacuum [24], however MoS_2/carbon electro-catalysts with a carbon component were studied in [152]. The catalytic activity of these catalysts under hydrogen evolution was analyzed. Through varying the particle size and the coverage of the samples, accurate relationship was established between the structure and the catalytic activity of the MoS_2 nanoparticles.

The HER reaction was studied at room temperature through the use of a Hoffman cell on the molybdenum nickel, iron electrodes, containing chromium, manganese and nickel by through the use of aqueous solutions of ionic liquid (IL), such as 1-butyl-3methylimidazolium tetrafluoroborate. The efficiency of the system was very high - 97.0% - 99.2% conformably to all the tested electro-catalysts. Obtained results show that the production of hydrogen can be carried out through the use of cheap materials at room temperature, which makes this method economically attractive [153].

Amorphous films of cobalt selenide on flat titanium substrates were obtained through the use of electrochemical method from aqueous electrolyte in ordinary conditions. These films were used as electro-catalysts for the hydrogen evolution reaction. Electrolysis was carried out in a 0.5M H_2SO_4 solution and at a current density of $10mA/cm^2$, hydrogen overpressure on films of cobalt selenide was ~ 135 mV. Galvanostatic measurements showed the stability of these films during 16 hours of continuous operation. The ease of preparation and activity of cobalt selenide films suggest that electro-deposited metal chalcogenides are quite attractive to be used as electro-catalysts for the HER [154].

The kinetics and the mechanism of the hydrogen evolution reaction on tin electrodes in the0.1M H_2SO_4solution were studied through stationary polarization curves and electrochemical impedance spectroscopy. The rate constants of Volmer Geierovsky and the Tafel steps for this reaction were established. At high negative potentials where the hydrogen yield reaches its limiting value, the hydrogen evolution mechanism is described by the Volmer Geierovsky equation [155].

Composite electro-catalytic layers of iridium oxide, Nafion® and hydrophosphate of zirconium were made on the glass-carbon disk electrodes. Zirconium hydrophosphate was obtained by mixing zirconium oxychloride and phosphoric acid. The behavior of the electrodes was studied electrochemically in an oxygen evolution reaction from the 0.5M sulfuric electrolyte at a room temperature. The voltammogram of the behavior of the electrodes taken at low values of the linear expansion showed that the work of the electro-catalyst is of minor effect [156].

Automated systems for the electrochemical synthesis of photo-electrochemical materials were developed and used to prepare mixed-metal oxides based on tungsten, $W_nO_mM_x$ [M = Ni, Co, Cu, Zn, Pt, Ru, Rh, Pd and Ag] for the production of hydrogen by photoelectrolysis of water [157]. An automatic measurement of the photocurrent through the use of scanning photo-electrochemical cell showed that the mixed oxide of W-Ni had the largest value of the relative zero displacement of the photocurrent, especially at low Ni concentrations (5-10 atomic percent Ni).

5. Catalysts on graphene type carriers

Graphene, a two-dimensional sheet composed of sp2 bonded carbon atoms with one-atom-thick carbon arranged in hexagonal pattern (like a honeycomb) have higher surface area, superior conductivity with high chemical and thermal stability [158].This material offers high specific surface area, chemical and electrochemical stability, high conductivity, and low cost [159].

In [98,127,160] the facile preparation of highly porous Co-Ni-graphene (Co-Ni-G) composite electrodes was reported. The incorporation of graphene into the Co-Ni matrix enhances the catalyst's activity for the hydrogen evolution reaction (HER) in an alkaline solution.

In [161] the AEM electrolysis anode was a hybrid graphene oxide-coated and oxidized Ni electrode. The surface groups of graphene oxide adhered to the Ni electrode through electrostatic attraction of the groups forming a continuous film. The hybrid electrode had lower resistance and provided broader surface area for contact with the membrane to improve its electrochemical properties.

Liang et al. [162], reported a hybrid material constituting Co_3O_4 nanocrystals grown on reduced GO as a high-performance bifunctional catalyst for the both the ORR and the OER. Co_3O_4 or graphene oxide alone have little catalytic activity, their hybrid materials exhibit unexpected, surprisingly high ORR and OER activities in alkaline solutions, comparable to fresh commercial Pt/C catalyst but far exceeding Pt/C in stability and durability. All afore-mentioned examples show that graphene could significantly enhance the activity and stability of HER and OER catalysts in alkali media. Moreover, graphene also improves the properties of HER [163,164,165] and OER [166,167] catalysts in acid media, which could be successfully used in PEM water electrolyzers.

To sum up, it should be noted that hydrogen is the most promising contender for the clean fuel in the future. In this respect, a question of the synthesis of new cheap materials used as cathodes to replace expensive, made of precious metals ones, in the electrolysis of water and the production of chlorine, is relevant and interesting for researchers. The work has focused on the synthesis of new alloys with electro-catalytic properties, low overvoltage with hydrogen evolution, large real surface and corrosion resistance. In this aspect, amorphous alloys are preferable to crystalline alloys because of their high corrosion resistance and really extensive area under the electrodes. The most promising method among all the methods of synthesis of new alloys is the electrochemical method. It is possible to regulate the composition of alloys and, consequently their electro-catalytic properties by electrochemical method.

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В обзоре представлена последняя информация об исследованиях в области синтеза катализаторов для электролиза воды в щелочных и частично кислотных средах. Представлены литературные данные по изготовлению электрокатализаторов на основе благородных, рефрактерных, переходных и чистых металлов, а также металлов, легированных молибденом, фосфором и другими элементами. Принимая во внимание различные методы синтеза электрокатализаторов, подчеркнуто преимущество электрохимического метода как простого и доступного, позволяющего регулировать состав синтезированных электродов путем изменения состава электролита и условий электролиза, что в свою очередь позволяет контролировать свойства синтезированных материалов.

Ключевые слова: *синтез, водород, энергия, электролиз воды.*

SUYUN ELEKTROLİZİ ÜÇÜN ELEKTROKATALİZATORLAR

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Məqalədə qələvi və qismən turş mühitlərdə suyun elektrolizi üçün yüksək effektivliyə malik katalizatorların sintezinin araşdırılması haqqında ən son məlumatlar təqdim olunur. Müxtəlif metallar əsasında sintez edilmiş elektrokatalizatorların hazırlanmasına dair ədəbiyyat məlumatları, eləcə də molibden, fosfor və digər elementlərlə katalitik xassələri aşkarlanmış ərintilər təqdim olunmaqdadır. Elektrokatalizatorların sintezinin müxtəlif metodlarını nəzərə alaraq, elektrokimyəvi metodun üstünlüyü qeyd olunur. Bu metodla sintez edilmiş elektrodların tərkibini elektrolitin tərkibini və elektroliz şəraitini dəyişməklə tənzimləmək olur.

Açar sözlər*: sintez, hidrogen, enerji, suyun elektrolizi.*