Comparison of different electrode materials—Energy requirements in the electrolytic hydrogen evolution process

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Abstract

Hydrogen is one of the most widely produced commodities in the world economy. The basic technologies for producing hydrogen via the electrolysis of water have long been known. However, there are disadvantages when using this process. Two-thirds of the operation costs of the electrolyzers are electricity costs. The challenge, addressed by numerous companies and researchers in the last few years, is the cost cutting by increasing efficiency of the process.

The aim of this work was the attempt to optimize the electrolytic hydrogen production from alkaline solution, through the variation of cathode materials and use of ionic activators.

The part of our results shows the better electrocatalytic activity of intermetallic phases and the energy consumption is decreased when compared with the industrial data ($4.5–5\ kWh\ m^{-3}\ H_2$). The role of ionic activator used is also very significant. These results give the opportunity for further research of cumulative effect of the intermetallic electrodes and ionic activators on industrial level.
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1. Introduction

Development of new methods and improvement of conventional technology, for the electrolytic production of hydrogen, is getting in a center of scientific researches, as a part of the renewable energy cycle for truly sustainable systems. A principal focus of modern research in electrocatalysis is to discover electrode materials that exhibit desirable electrochemical stability and to show improved electroactivity toward typical electrochemical reactions. It is also preferable that these materials are not expensive and are abundantly available. Electrocatalytic hydrogen evolution on various electrode materials and from various electrolyte solutions is one of the most frequently studied electrode reactions [1].

Electrolytic water splitting has gained importance in recent years because of its promise of economic production without adverse environmental impact. For water electrolysis to become a more competitive and efficient process energy loss has to be minimized and the equipment cost has to be lowered. Therefore, the practical cell voltage should be reduced as far as possible in order to elevate the cost benefit of electric energy, since this is the main component of the hydrogen production cost.

Considering this fact, in this work different electrode materials were investigated, either pure metals, like iron and nickel, or different intermetallic phases, for the electrolytic hydrogen production. A significant upgrade of the electrolytic efficiency using intermetallics in aqueous KOH solution, as standard electrolyte, was achieved in comparison with conventional cathode materials (Fe and Ni), often used in the alkaline electrolysis. Nickel and iron were found to be a good electrocatalyst for the hydrogen evolution reaction (HER) in alkaline media and mostly 20–30 wt.% KOH aqueous solutions were used because of their optimum conductivity [2].

Also, we have found that some combinations of activating compounds (ionic activators added directly into the electrolyte, assuming in situ activation) could reduce energy needs per mass

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unit of hydrogen produced, for more than 10% in some cases, compared to those of non-activated standard electrolyte [3].

Here we will illustrate with few examples how it affects the energy consumption when different intermetallic phases are used as cathodes, activated and/or non-activated through typical electrochemical parameters, such as exchange current density, Tafel slopes and the energy of activation. It will with exactness show how good these activators and materials are.

The data were collected in a wide temperature range from about −20 to about +80 °C, and arranged to show dependence of energy consumption on the current density and temperature.

The results for the energy consumption are shown through dependence of energy consumption (kJ mol^{-1} or kWh m^{-3} of evolved H$_2$).

Such investigations offer a possibility to optimize the electrolytic process, based on a significant upgrade of the efficiency of some of the used intermetallic compositions, in regard to the need for the hydrogen production.

1.1. Theoretical consideration

The hydrogen evolution reaction is a heterogeneous catalytic reaction where an electrode material acts as catalyst. The electrocatalytic activity for various metals and intermetallic for the HER is a function of outer electron shell configuration. Different metals show different affinities toward hydrogen. Some metals form an alloy with hydrogen, some metals form a volatile hydrogen molecule and others are rather inert, only allowing an adsorption or not at all. It has been qualitatively noted that the catalytic activity shows periodic variation [4]. This should be understood with electronic structure of the metal. Because of the electronic configuration of outer shells of metals in their ground states, the catalytic activity first increases with the increase of the d-electrons, reaches its maximum at nearly filled d-orbital (at about d^8-electrons), sharply decreases after its completion with one or two electrons in the s-orbital and then increases again with successive additions of electrons to the p- and subsequent d-orbitals. Transition metals, with the increase of the number of d-electrons in the transition series along the Periodic Table, obey characteristic Gschneider type volcano plots [5], that reflect the periodicity of various physico-chemical features along the Periodic Table [4,6,7]. Since d-orbital participates in both the lattice bonding and the chemisorptive bond with various intermediates involved in both heterogeneous chemical and electrochemical reactions, the electrocatalytic features obey the same volcanic curves with a maximum at about d^8-electrons [4,8,9]. This optimal d^8-electronic configuration (in both transition metals and their intermetallic phases) agrees with the Balandin theory based on the well-known Sabatier principle [10] in heterogeneous catalysis.

Brewer's high temperature thermodynamics [11–13] suggests that the intermetallic phases with very strong bonds were made by bonding hypo- with the hyper-d-electronic transition metals where, in accordance with generalized Lewis acid–base reaction, there is a transfer of electrons from the orbitals with paired d-electrons onto the empty or half-filled d-orbitals. It has been shown [14,15] that more exposed d-orbitals in the

region from 3d to 5d correspond to the stronger cohesive and therefore weaker adsorptive bonding, resulting in higher electrocatalytic activity for the HER. The bond strengths (enthalpies of formation) then exhibit typical volcanic plots with a maximum at about d^8-electrons obtained for the following, most symmetric Laves phases: TiNi$_3$ [16], ZrNi$_3$, MoNi$_3$ [9], HfPd$_3$ [17] and MoPt$_3$ [18]. All intermetallics mentioned above exhibit synergism in electrocatalytic features [19] that means optimal electronic structure for electrocatalysis in the HER.

It has been shown that there is synergism in the catalytic activity for the HER in the combination of two or more d-metals from different parts of transition series, one from the left and the other from the right half of them. Besides synergetic effect, proper codeposition of such d-metals (from two branches of Balandin's volcano curve) improves and even exceeds the electrocatalytic activity of the platinum group of metals and provides a large surface area of active centers [19–22]. In other words, certain ionic activators when applied in situ can provide a very large surface area of active center for the HER. From our previous work tris(ethylenediamine)Co(III) chloride complex gave the best effect in combination with Na-molybdate, in this context. It is also shown that this Co–Mo combination of those two d-metals, from the two branches of Balandin's volcano curve [23], has created a remarkable electrocatalytic effect for the HER. Cobalt both in the metallic lattice and in its individual cationic and complex forms appears as a good proton transferring species, while molybdenum has been widely used both for hydrogenation and even dehydrogenation catalysis. This is very simple method for increasing efficiency of the electrolytic process that does not require high technology.

Recent requirements for the energy savings have stimulated numerous papers dealing with the electrocatalysis for the HER. Part of this paper is dedicated to intermetallic forms with close to optimal d-configuration, used as electrocatalytic materials for the HER. They show much less energy consumption for the HER, in comparison to nickel that is used in commercial alkaline water electrolyzers.

2. Experimental

Experiments considering energy consumption have been carried out in a Plexiglas-made electrolytic cell [24] with an interelectrode distance of 10 mm. The cathode was attached on one side, and the anode (Ni) on the other. The latter was a round shaped electrode of 29.5 mm in diameter ($P = 683.5$ mm^2).

The used cathodes were nickel and compact, homogeneous intermetallics, prepared in radio frequency induction furnace and glossy polished before use. The cathode surface areas of these intermetallics were determined by scanning all electrodes with a high resolution scanner along with a grid of precisely defined dimensions (for instance, 1 mm × 1 mm) for comparison. The picture was then magnified certain number of times (e.g. 1:100) in a graphic program (CorelDraw), and another fine grid of predefined dimensions put over it. Now, the number of these squares within the electrode contour was counted either manually or automatically, and the cathode area calculated from

the magnification factor. In both ways perfect agreement was achieved.

The amount of cathodically evolved hydrogen during certain time was determined using a water filled U-tube manometer. Time (t) of evolution of certain volume of hydrogen, along with overall voltage through the cell (U), were recorded for specified overall current through the cell (I) and temperature, in order to calculate corresponding energy consumption.

All these investigations were performed in a wide temperature range (253–323 K) and current density domain from 20 to 400 mA cm^{-2}. The following combination of compounds: 1×10^{-3} mol dm^{-3} of [Co(en)$_3$]Cl$_3$ complex and 1×10^{-2} mol dm^{-3} of Na-molybdate, in the standard electrolyte was used as ionic activator. The experiments were maintained by thermostat/cryostat, power supply and measuring electronics (computer controlled galvanostat) as was described elsewhere [1].

Other part of this paper refers to measurements of linear potential sweep voltammograms. Obtained kinetic parameters, e.g. Tafel slopes and exchange current densities from this experiment, on above-mentioned materials, are taken as an explicit measure of the catalytic activity for the HER [25]. The experiments were carried out in an unpressurized, three-electrode cylindrical electrochemical cell with double wall mantle to provide thermostatic temperature control. The electrochemical measurements were performed by PAR 174 potentioscan equipment coupled to a X–Y recorder (Hewlett Packard, 7015B). Working electrode was placed in vertical position, centered and situated to be surrounded by Winkler platinum gauze counter electrode and an Hg/HgO 30 wt.% KOH reference electrode equipped with the Luggin capillary in order to reduce *IR* potential drop. The Luggin capillary tip was set at approximately 1–2 mm above the working electrode surface. The electrolyte was 30 wt.% KOH aqueous solution as standard electrolyte or this standard electrolyte with above-mentioned ionic activators. The temperature of the solution in the electrochemical cell was varied within the temperature range between 298 and 333 K by means of thermostat. Before electrochemical measurements the electrolyte solution in the cell was saturated with purified N$_2$ by continuously bubbling at 1 bar pressure through the solution. Exposed surface of the electrodes was highly polished with 0.05 µm alumina prior to use. Cyclic voltammetric, *I–E* curves, were obtained by the usual method at a constant cathodic to anodic potential, ranging from −1.40 to −0.30 V, varying the potential at a rate of 1 and 5 mV s^{-1} in the cathodic direction. Exchange current densities were determined by extrapolation of linear parts of Tafel plots to the reversible potentials. Tafel plots were obtained for various temperatures ranging from 298 to 333 K. Temperatures were maintained constant by means of a thermostatic bath.

3. Results and discussion

3.1. Energy consumption

In the hydrogen electrode reaction, the electrode material acts as the catalyst. Its activity is closely related to the elec-

tronic configuration of these materials. Energy requirement for the electrolytic hydrogen evolution process is a measure of the electrocatalytic activity of electrode materials and is calculated using relation:

$$Q = I \times U \times t$$

where the specified properties are defined in Section 2.

Stable intermetallic phases along the Mo–Pt phase diagram (Table 1) have been investigated as cathode materials for hydrogen production from alkaline solutions to be compared with several cathode materials used earlier [26].

The results obtained for the room temperature are presented in Table 1 for all investigated electrodes. One important conclusion can be taken from the above data: the Pt$_2$Mo phase along with its activation with ionic activators looks like the best system of all investigated in this work. It proved once again the importance of activation, found earlier in our investigations [24]. The energy consumption of the system with Pt$_2$Mo phase as cathode material is shown in the 3D diagram (Fig. 1).

The energy requirement decreases with increasing temperature, as expected. Further, the ionic activator used demonstrates the electrocatalytic effect not only with this intermetallic but in all investigated systems.

On the basis of similar experimental results, the functional dependence of energy consumption on the intermetallic composition, for different current densities applied (40, 100 and 200 mA cm^{-2}) and at temperature of 298 K, together with enthalpies of formation in standard and activated electrolytes is presented in Fig. 2.

Next to Pt$_2$Mo cathode, in Table 1, sort by efficiency for the HER energy savings, are Hf based intermetallic. Polycrystalline compounds, Hf$_2$Fe and Hf$_2$Co, are Pauli paramagnetics with the same type structure. Hf$_2$Fe and Hf$_2$Co crystallize in the cubic Ti$_2$Ni type structure with 96 atoms per unit cell. The 32 Fe (Co) atoms are in positions 32e, the 64 Hf atoms are distributed on the two positions, 16c (Hf1) and 48f (Hf2). The unit cell constants
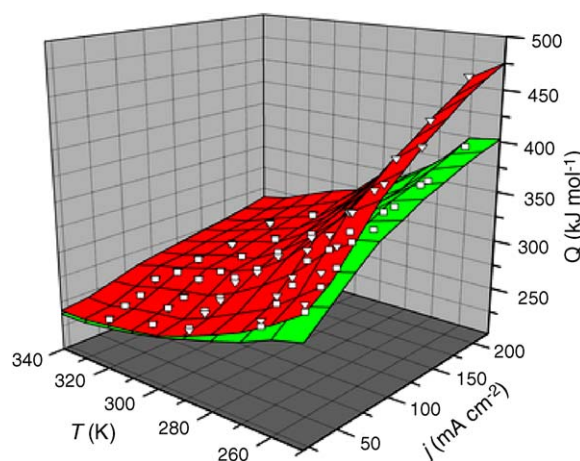

Fig. 1. 3D diagram: energy consumption per 1 mol of hydrogen evolved, as a function of current density at different temperatures for Pt$_2$Mo phase; upper surface—standard electrolyte; lower surface—activated electrolyte; rectangle dots—experimental data for standard electrolyte; circle dots—experimental data for activated electrolyte.

Table 1
Energy consumption per 1 mol of hydrogen evolved for different cathode materials

Cathode	Pt$_2$Mo	Hf$_2$Fe	Hf$_2$Co	PtMo$_2$	PtMo$_3$	PtMo$_4$	PtMo	TiPt	Fe	Ni[*]
Q (kWh m^{-3} H$_2$)										
Standard electrolyte	3.06	3.18	3.5	3.52	3.68	3.94	4.01	4.01	4.93	4.94
Activated electrolyte	2.93	–	3.48	3.5	3.63	3.73	3.75	3.8	4.01	4.54

Alkaline electrolyzer (T = 323 K; anode: Ni, Fe[*]; j = 40 mA cm^{-2}; electrode distance = 10 mm).

[*] In all investigated systems Ni was used as anode, except for Ni* where Fe anode was applied.
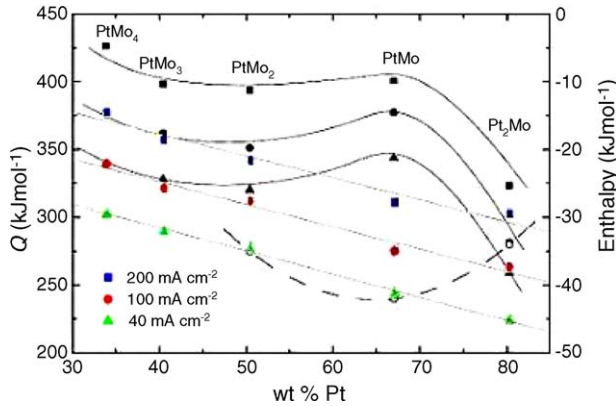
Fig. 2. Dependence of the energy consumption on the intermetallic composition, for different current densities applied at temperature of 298 K in standard electrolyte—curved line, activated electrolyte—straight line, and predicted enthalpies of formation for Pt–Mo phases calculated by Miedema et al. [27]—dashed curve.

are for Hf$_2$Fe: a = 12.033 Å and for Hf$_2$Co: a = 12.084 Å, both non-annealed.

These intermetallics belong to the group of binary systems formed between hypo-d-transition (Ti, Zr and Hf) and hyper-d-transition metals (Fe, Co, Pd and Pt). Among other reasons, they have been investigated as systems interesting for hydrogen storage, since they are able to form hydrides in hydrogen–metal atom ratios H/M ≥ 1 at rather high temperatures (T ≈ 3000 °C) and high pressures (>1 kPa) [28].

The results obtained, showing energy consumption for the HER, are presented in Fig. 3 in the three-dimensional graph for explicit insight.
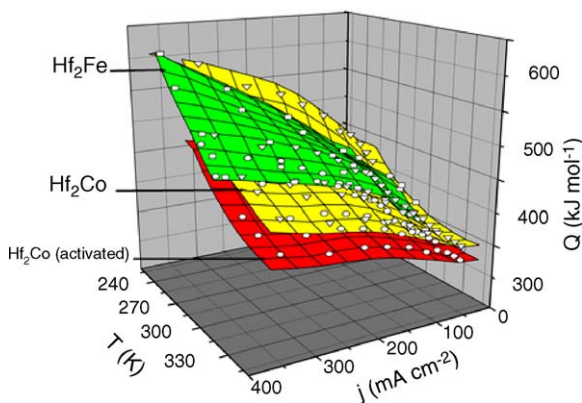

Fig. 3. 3D diagram: energy consumption per 1 mol of hydrogen evolved, as a function of current density at different temperatures. Cathodes: Hf$_2$Fe and Hf$_2$Co; anode: nickel; white dots: experimental data.
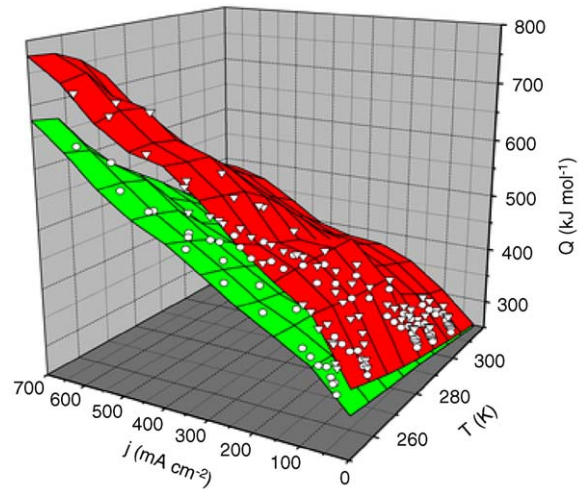

Fig. 4. Energy consumption per 1 mol of hydrogen evolved as a function of the current density at different temperatures: upper surface—standard electrolyte; lower surface—activated electrolyte. Cathode—Ti–Pt intermetallic; anode—nickel; white dots—experimental data.

It shows an expected type of dependence, increase of the energy consumption with the increase of the current density and an inverse temperature influence. The effect of ionic activator is also significant.

Same behaviour was exhibited and TiPt intermetallic phase was used as cathode material for the HER. Obtained results for this system are also shown in 3D diagram in Fig. 4.

Our previous investigations on nickel [24] are also shown on 3D diagram in Fig. 5. Energy consumption per 1 mol of hydrogen evolved, as a function of current density at different temperatures for nickel electrode, exhibits same type of dependence for energy consumption as for all investigated systems.

Comparison between the investigated intermetallic cathodes and conventional cathodes Ni and Fe brings the following order of these materials according to their electrocatalytic activity (the energy requirement for the HER is in the inverse order):

$$Pt_2Mo > Hf_2Fe > Hf_2Co > PtMo_2 > PtMo_3$$

$$> PtMo_4 > PtMo > TiPt > Fe > Ni$$

Additionally, use of ionic activators added in situ is very important. This procedure gives a possibility of producing fine metal powders as by products. These powders are dropping from the surface into the electrolyte after long-term electrolysis, which is confirmed in our previous experiments [24].

Possible reaction mechanism through which ionic activators increase electrolytic efficiency is very complex. It includes dif-
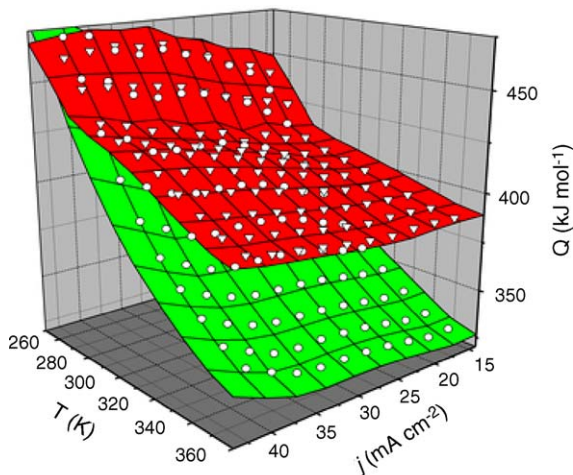
Fig. 5. Energy consumption per 1 mol of hydrogen evolved as a function of the current density at different temperatures: upper surface—standard electrolyte; lower surface—the activated electrolyte. Cathode—nickel; anode—nickel; white dots—experimental data.
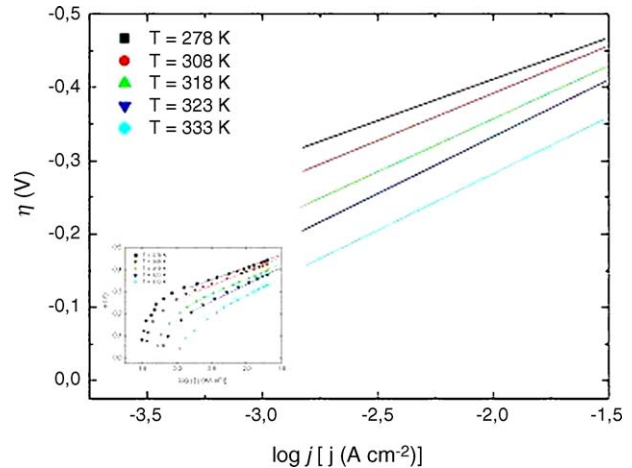

Fig. 6. Tafel plots: overvoltage as a function of the current density for the HER on a nickel electrode in the standard electrolyte at different temperatures: 278, 308, 318, 323 and 333 K. Inset: experimental data on polarization curves in the same system in an extended region of potential. Data are fit linear in the area of the cathodic hydrogen evolution.

ferent effects, with their specific contributions. One of them could be the electrocatalytic effect of metal(s) deposited on the electrode surface, providing very large surface area of active centers. However, the catalytic effects of ethylenediamine ligands, which are present in the electrolyte after decomposition of the corresponding complex and deposition of metals on the surface, have their own role in that mechanism. Therefore, there arises a kind of double electrocatalytic effect caused by metals and the complex ligands. That role is similar to the effect of EDTA (Rowland's effect [29,30]). It cleans the surface by destroying and removing the oxide film from the cathode surface, preparing it for deposition of metals. As a consequence, the active electrode surface becomes more developed. Further, hydrogen atoms are transported to the metal via an exchange with the electrolyte, and this will also have the effect of decreasing the activation energy and hence the overvoltage. In accordance with the *transition state theory*, it was suggested [30] that the transition complex acts as a "bridge" for hydrogen transfer from the electrolyte to the metal surface.

3.2. Electrokinetic parametars for the HER at selected cathode materials

The electrochemical activity for the HER of a nickel, TiPt and Pt_2Mo cathode was studied potentiodynamically versus Hg/HgO 30 wt.% KOH. Voltammograms for a nickel electrode in 30 wt.% KOH at various temperatures are shown in Figs. 6 and 7, in Tafel coordinates:

$$\eta = a + b \log j$$

for example, dependence of overvoltage η, on current density j, where a and b are constants. Constant b is called Tafel slope.

From these diagrams it was possible to obtain kinetic parameters, e.g. Tafel slopes b and exchange current densities j_o as an explicit measure of the catalytic activity for the HER. Tafel slopes are determined from the linear part of the curves

in Figs. 6 and 7. That presents the area of cathodically evolved hydrogen. The value of Tafel slopes may reflect how active the electrode metal is. The lower the Tafel slop is, the material is more active. From the other side, the exchange current density represents the unidirectional rate of the reaction at equilibrium and is estimated by the extrapolation of the Tafel line to $\eta = 0$, and it can also be used as a measure of the activity. With increasing the j_o, material is more active for HER. Also, j_o values also increase with increasing temperature. From a practical point of view the results mean that, apart from other contributing factors, the performance of the electrode improves with increasing temperature.

As it is shown in Table 2, Tafel slopes decrease with increasing temperature and with use of ionic activator. Also, j_o shows expected type of dependence.
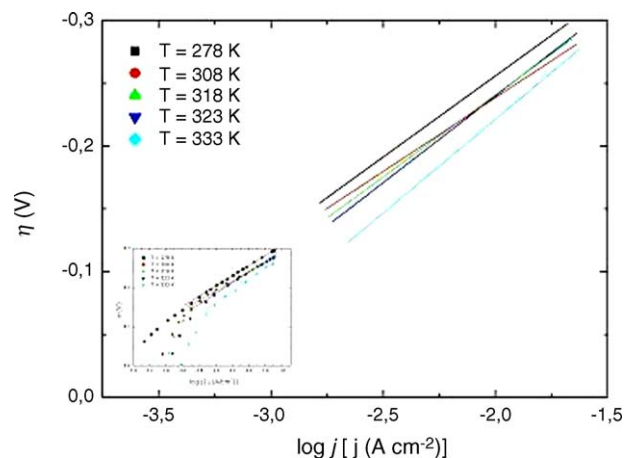

Fig. 7. Tafel plots: overvoltage as a function of the current density for the HER on a nickel electrode in the activated electrolyte at different temperatures: 278, 308, 318, 323 and 333 K. Inset: experimental data on polarization curves in the same system in an extended region of potential. Data were linearly fitted in the area of the cathodic hydrogen evolution.

Table 2
Tafel parameters for the HER on a nickel electrode at temperatures ranging from 298 to 333 K in standard and activated electrolytes

	T (K)				
	298	308	318	323	333
$-b$ (V)					
Standard electrolyte	0.109	0.127	0.143	0.152	0.157
Activated electrolyte	0.143	0.123	0.129	0.137	0.152
j_o (A cm^{-2})					
Standard electrolyte	1.7×10^{-6}	8.2×10^{-6}	3.2×10^{-5}	6.3×10^{-5}	1.3×10^{-4}
Activated electrolyte	1.05×10^{-4}	1.1×10^{-4}	1.3×10^{-4}	1.9×10^{-4}	3.0×10^{-4}

$\eta = a + b \log j$.

Furthermore, a complete picture of electrocatalytic performances of electrode for the HER and the influence of activator can be obtained from the apparent energy of activation (E_a) for this process.

In order to obtain E_a for the HER on Ni electrode in 30% KOH aqueous solution with and without activator from the cathodic polarization η–$\log j$ curves at various temperatures were used. When j_o values from η–$\log j$ curves for HER on nickel electrode were calculated, it was possible to obtain energy of activation from the slope of the Arrhenius diagram using the equation [31]:

$$\log j_o = \log A_i - \frac{E_a}{2.3RT}$$

where j_o is exchange current density (A cm^{-2}), A_i the Arrhenius pre-exponential factor (cm s^{-1}), E_a the energy of activation (kJ mol^{-1}), R the gas constant (8.314 J mol^{-1} K^{-1}) and T is temperature. From the Arrhenius plot for Ni in Fig. 8, it was possible to calculate apparent energy of activation.

An Arrhenius plot, i.e. $\log j$ versus T^{-1}, is shown in Fig. 8. The apparent energy of activations was calculated from this plot. The values of E_a are equal to 42.3 kJ mol^{-1} for standard electrolyte and 10.5 kJ mol^{-1} for activated electrolyte. With the same procedure on TiPt and Pt$_2$Mo for the HER in the standard and activated electrolytes, the following Tafel plots are obtained, and presented for comparison on Tafel diagram at room temperature
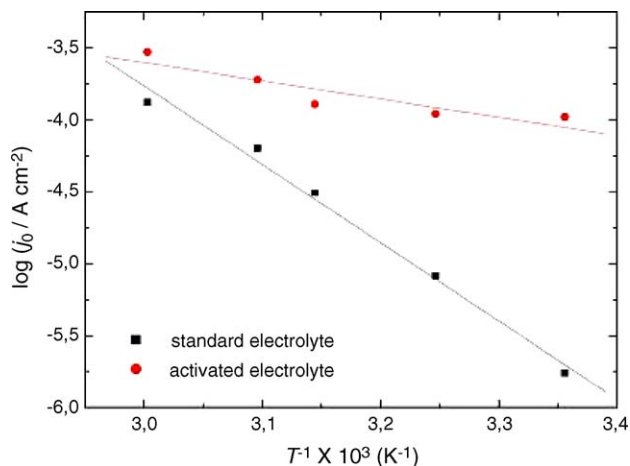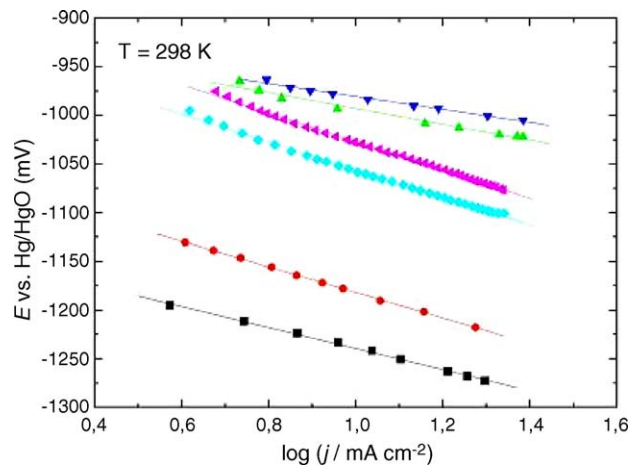

Fig. 9. Tafel diagram at room temperature: electrocatalytic effect of ionic activator in the standard electrolyte on nickel, TiPt and Pt$_2$Mo cathode for the HER. (■) Cathode Ni standard electrolyte, (●) cathode Ni activated electrolyte, (♦) cathode TiPt standard electrolyte, (◄) cathode TiPt activated electrolyte, (▲) cathode Pt$_2$Mo standard electrolyte and (▼) cathode Pt$_2$Mo activated electrolyte.

in Fig. 9. Corresponding values of E_a for the HER with or without activator for Ni, TiPt and Pt$_2$Mo are summarized in Table 3.

Corresponding values of E_a for the HER with or without activator for Ni, TiPt and Pt$_2$Mo are summarized in Table 3.

Obtained results for apparent energy of activation suggest that electrocatalytic properties of Pt$_2$Mo are significantly better than those for the Ni or TiPt which is in good agreement with above-presented energy consumption. Also, kinetic investigation of the activator effects on the hydrogen evolution reaction

Fig. 8. Arrhenius plots: current density as a function of temperature of nickel cathode in standard and activated electrolytes.

Table 3
Energy of activation for the systems: Ni, TiPt and Pt$_2$Mo used as cathodes for the HER in standard and activated electrolytes

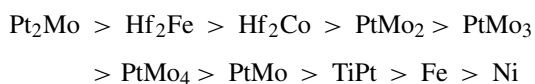| Cathode	E_a (kJ mol^{-1})
Ni	
Standard electrolyte	42.3
Activated electrolyte	10.5
TiPt	
Standard electrolyte	40.7
Activated electrolyte	35.1
Pt$_2$Mo	
Standard electrolyte	30.2
Activated electrolyte	10

on Ni, TiPt and Pt$_2$Mo electrode proved positive influence of both, intermetallic electrode materials and ionic activator added in situ, on the electrocatalytic activity.

4. Conclusion

Several intermetallic combinations of transition metals, like Hf$_2$Fe, Hf$_2$Co, Pt–Mo systems, TiPt and conventional materials like Fe and Ni, were used as cathode materials in the electrolytic evolution of hydrogen from alkaline aqueous solutions. In comparison with the conventional cathodes used commercially (Ni or Fe), an upgrade of the electrolytic effect using mentioned intermetallics has been achieved.

These intermetallics have shown significant electrocatalytic effects. According to their efficiency they could be ordered as follows:

$$\text{Pt}_2\text{Mo} > \text{Hf}_2\text{Fe} > \text{Hf}_2\text{Co} > \text{PtMo}_2 > \text{PtMo}_3$$

$$> \text{PtMo}_4 > \text{PtMo} > \text{TiPt} > \text{Fe} > \text{Ni}$$

The activation of the process by using ionic activators in situ exhibits an additional effect.

The pronounced electrocatalytic effects of these intermetallics were discussed in the context of the mutual interaction of their d-orbitals. Generally, all those effects connected with the electrocatalytic activity are in close correlation with d-electronic configuration of single transition metals and/or their mutual combinations.

However, complete picture of electrocatalytic performances of an electrode and the influence of activator was obtained from electrochemical parameters that are direct measure of the electrode activity for the HER. Electrokinetic measurements have shown that the most efficient electrode material of all investigated is Pt$_2$Mo. But, considering the price and availability of all investigated intermetallics, from one side, and very good effect of ionic activator added in situ on nickel as cathode material, from the other, lead to a conclusion that Ni is still the most appropriate material to be used in alkaline water electrolyzers. As our previous investigations showed [24], the Co–Mo deposit formed on Ni during hydrogen evolution appears extremely active and very stable in time which is relevant for the possible use of this method on a large scale.

Acknowledgement

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