ELECTROCATALYTIC PROPERTIES OF NICKEL – BASED ALLOYS FOR HYDROGEN EVOLUTION IN ALKALINE WATER ELECTROLYSIS

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Rezumat

Această lucrare sintetizează ultimele cercetări referitoare la dezvoltarea de noi electrozi eficienţi pe bază de nichel, folosiţi pentru generarea hidrogenului prin electroliza apei. Principala problemă în obţinerea hidrogenului pe cale electrolitică constă în costul ridicat, astfel încât se fac eforturi pentru reducerea acestui cost. S-a demonstrat că, costul hidrogenului este direct proporţional cu tensiunea de electroliză. O cale de reducere a tensiunii de electroliză constă în descoperirea unor materiale cu o bună activitatea catalitică, ce vor prezenta supratensiuni mici de descărcare a hidrogenului şi oxigenului. Scopul acestei lucrări este analizarea efectelor catalitice a aliajelor pe bază de nichel asupra reacţiei de descărcare a hidrogenului.

Abriss

Dieses Werk synthetisiert die letzten Forschungen in der Entwicklung neuen Nickelelektroden, die man für die Wasserstoffgewinnung durch Elektrolyse gebraucht. Das Hauptproblem der Wasserstoffgewinnung durch Elektrolyse besteht in die hohen Kosten so das es werden zahlreiche Bemühungen durchgeführt um diese Kosten zu reduzieren. Es wurde festgesetzt dass der Preis dem Wasserstoff ist direkt verhältnisgleich mit der Elektrolysespannung. Ein Weg für die Reduzierung dieser Spannung besteht in der Entdeckung von Materialien mit einer guten katalytischen Tätigkeit, die kleinen Aufladeüberspannungen des Wasserstoffes und Sauerstoffes haben. Das Werk analysiert die katalytischen Effekten der Nickelegierungen über dem Wasserstoffaufladeprozess.

Résume

Cette œuvre synthétise les dernières recherches concernant le développement de nouveaux électrodes efficientes de nickel, utilises pour la génération de l'hydrogène par l'électrolyse de l'eau. Le problème principal dans l'obtention de l'hydrogène sur voie électrolytique consiste dans le coût élevé ainsi qu'on fait des grands efforts pou en diminuer. On a démontre que le coût de l'hydrogène est directement proportionnel avec la tension de l'électrolyse. Un moyeu pou diminuer la tension d'électrolyse est constitue par la découverte des matériaux a bonne activité catalytique, qui ont des petites surtensions de décharge de l'hydrogène et oxygène. Le but de cette œuvre est l'analyse des effets catalytiques des alliages de nickel dans la réaction de décharge de l'hydrogène.

Introduction

The hydrogen evolution reaction (HER) is one of the most important processes in electrochemistry. Fundamental studies that go back to the beginning of the century have helped considerably to establish the foundations of modern electrochemical dynamics. In industrial electrochemistry, the HER is particularly important in commercial water electrolysis, chlor-alkali electrolysis and other important processes.

The production of hydrogen by water electrolysis is of particular interest because of the many industrial applications that require pure hydrogen, like the food industry, the refining of metals, etc. More recently, a growing concern with environmental protection has seen good possibilities in the use of hydrogen in suitable energy converters like fuel cells. Combined with electrolytic hydrogen this allows the establishment of a totally clean and efficient energy cycle.

The main problem with electrolytic hydrogen is the higher cost when compared with hydrogen produced by vapor reforming of fossil fuels (but here the long-term cost of using fossil fuels for this purpose is not considered). Thus, efforts are being devoted to reduce the cost of electrolytic hydrogen. It has been demonstrated that, apart from the cost of electricity, which is a political issue, the cost of hydrogen is directly proportional to the voltage of operation of the electrolyser [Bo'85]. Traditional unipolar electrolysers operate with mild steel cathodes and nickel plated anodes in 28-30% KOH solution at about 80^0C. In bipolar electrolysers nickel is used for both anode and cathode. Under these conditions the overvoltages for HER and for the oxygen evolution reaction (OER) may be as high as 400 mV under operating conditions [We'98].

Thus, these overvoltages account for more than one third of the operational voltage of the electrolyser. From this consideration it becomes apparent that one way of reducing the operational voltage is to find materials with good electrocatalytic activity that will present lower overpotentials for the HER and OER.

It has been found a relation between the catalytic activity for the hydrogen recombination reaction and the overpotential for the HER (Bonhoffer, 1924):

Increase of the catalytic activity ⟶

Pb, Sn, Zn, Cu, Ag, Fe, Ni, W, Pd, Pt

⟵ Increase the overpotential for the HER

As can be seen, they are many precious metals with high electrocatalytic activity, like Pt, Pd, W. But in the search for electrocatalysts it must be taken into account that the cost of the material has to be consistent with the cost of the technology being proposed. This practically rules out the use of precious metals in ordinary alkaline electrolysis. Several materials have been studied as electrocatalysts for the HER, and significant reductions of the overpotential have been achieved with electrodeposited nickel alloys with transition metals[Tr'92]. Another approach has been to produce high active area materials by electrodepositing nickel with a suitable metal like zinc and then leaching the zinc in an alkaline solution [Gi'94]. One of the materials that were found to have a good electrocatalytic activity for the HER is electrodeposited NiFe [Ar'90] This is achieved through an activation process, which consists of a partial oxidation of the electrode in acid solution.

Discussion

Enhancement of cathodic activity of nickel for electrolytic hydrogen evolution has been carried out by the formation of nickel alloys such as Ni-S [Va'84], Raney Ni [En'87], Ni-Mo [Ka'98], Ni-Sn [Ya'99], Ni-Mo-O [Ka'99], Ni-Fe-Zn [Gi'00]. Recently, it has been found that Ni-Mo-O cathodes prepared by arc ion plating have excellent catalytic activity and durability for hydrogen evolution in the electrolysis of hot concentrated NaOH solutions [Ka'99]. Detailed examination by some of the present authors in comparing Ni-Mo and Ni-Mo-O alloys for hydrogen evolution revealed that the high activity is attributable to the enhancement of the rate-determining electrochemical desorbtion of absorbed hydrogen due to the modification of the electronic state of electrode metals by interaction with oxygen contained in the form of solid solution [Ka'99].

In this manner, the catalytic activity for hydrogen evolution can be enhanced by modification of the electronic state of electrode metals by alloying. Since electrodeposited various electrodes such as Ni-Mo and Ni-S have considerably high activity for hydrogen evolution, electrodeposition of nickel alloys will be a potential method for production of effective cathode materials.

The overpotential for the hydrogen evolution reaction can be obtained from Tafel relation:

$$\eta = a + b \lg i \qquad (1)$$

where η is the overpotential and i the current density

a and b are characteristic constants of the electrode system. A plot of electrode potential versus the logarithm of the current density is called the "Tafel plot" and the resulting straight line the "Tafel line". b is the "Tafel slope" that provides information about the mechanism of the reaction and *a* provides information about the rate constant (and the exchange current density) of the reaction.

Figure 1 [Me'00] summarizes the change in cathodic polarization curves with alloying additions. As can be seen, binary Ni-Fe alloys show higher activities for hydrogen evolution than those of nickel and iron metals. The Tafel slope of nickel, iron and Ni-Fe alloys is almost the same as each other, with $b = 0{,}15$ V, that is:

$$\partial E / \partial(\log i) = 2RT / F \tag{2}$$

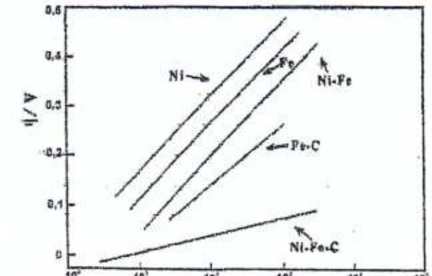
Assuming the surface coverage of adsorbed hydrogen is close to zero and the transfer coefficient is 0,5, the proton discharge seems to be the rate-determining step (rds) for hydrogen evolution [Tr'92]. Accordingly, if nickel and iron atoms are present on the electrode surface, the proton discharge occurs preferentially on more active iron atoms. The charge transfer occurs from nickel to iron. This act suggests that the rate-determining proton discharge receiving electrons from surface iron atoms is accelerated by the charge transfer from nickel to iron. Therefore, the higher activity of Ni-Fe alloys than nickel and iron metals for hydrogen evolution is attributable to the acceleration of the proton discharge as a result of charge transfer from nickel to iron by alloying.

When carbon is added to Ni-Fe alloys the hydrogen evolution is remarkably accelerated, changing the mechanism of the hydrogen evolution. The Tafel slope (*b*) becomes about 0,033 V. If we assume that the surface coverage of adsorbed hydrogen is close to zero and that the transfer coefficient is 0,5, when the desorbtion of adsorbed hydrogen by recombination is the rds:

$$\partial E / \partial(\log i) = RT / 2F \tag{3}$$

that is, 0,036 V. This suggests that the carbon addition significantly accelerates the proton discharge on iron so that the rds is no longer proton discharge but is desorbtion of adsorbed hydrogen. It has been shown [Mo'00] that the addition of carbon into Ni-Fe alloys considerably enhance the charge transfer from nickel to iron. Accordingly, the charge transfer from iron to proton for the proton discharge seems much easier by alloying with carbon.

Figure 1. Comparison of cathodic curves of Ni, Ni-Fe, Ni-C and Ni-Fe-C electrodeposits for hydrogen evolution in 8 M NaOH at 90^{0}C.



In conclusion, the formation of ternary Ni-Fe-C alloys leads to a significant charge transfer from nickel to iron, to accelerated electron transfer from iron to proton, and to accelerated proton discharge, with a consequent remarkable acceleration of the hydrogen evolution.

These cathodes maintain the high activity for hydrogen evolution in chlor-alkali electrolysis for more than 2 years and the high activity is not degraded by shutdown of electrolysis [Su'99]. Furthermore, after construction of industrial electrolysis cells using expanded-nickel cathodes for chlori-alkali electrolysis, the Ni-Fe-C alloy cathodes have been successfully prepared by electrodeposition on the nickel cathodes.

Figure 2 shows the polarization curves for nickel and nickel-zinc alloys with different nickel content. The progressive increase in the surface area up to 50% nickel results in lower overvoltage for hydrogen evolution reaction, which is reflected in the Tafel parameters, derived from the polarization studies, given in figure 2 and table 1 [Sh'02].

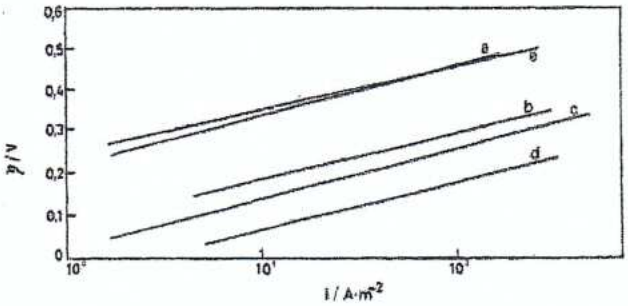
In conclusion, zinc – nickel alloy electrodes containing 50% nickel are effective in producing high surface area cathodes for use in alkaline water electrolysis and alloys having still higher nickel contents are not so useful.

Table 1

Effect of nickel content on the Tafel parameters

Electrode	a	b (V)	η_{H_2} (V)	i_0 (A cm^{-2})
Ni	0,57	0,54	0,105	$8,9615 \times 10^{-6}$
Zn – 75% Ni	0,54	0,56	0,110	$8,1113 \times 10^{-5}$
Zn – 50% Ni	0,60	0,28	0,100	$1,5848 \times 10^{-3}$
Zn – 25% Ni	0,60	0,36	0,100	$2,5212 \times 10^{-4}$
Zn – 15% Ni	0,63	0,33	0,095	$2,9764 \times 10^{-4}$

Figure 2. Polarization curves for nickel and different Ni-Zn alloys: a) Ni; b) 15% Ni; c) 25% Ni; d) 50% Ni; e) 75% Ni.



Of all nickel-based alloys, much attention has been concentrated on the Ni-S and Ni-S-Co alloys. In the course of Ni-S-Co electrodeposition, two reactions are involved. The first one is the direct depositions of Ni^{2+} and Co^{2+} ions, while another reaction is the decompositions of the complex ions formed by Ni^{2+} and Co^{2+} ions with $CS(NH_2)_2$, respectively, which competes with the first reaction. The cathodic polarization of such complex ions increases with the current density, therefore the contents of nickel and cobalt increase since the deposition of Ni^{2+}, Co^{2+} ions becomes stronger.

Table 2

Electrochemical parameters of various electrodes

Electrode	b (V)	η_{150} (V)	i_0 (mA cm^{-2})
Fe	0,119	0,39	$0,2 \times 10^{-2}$
Ni-S	0,0809	0,09	4,6
Ni-S-Co	0,0617	0,07	6,2

Figure 3 indicates the polarization curves of mild steel, amorphous Ni-S and amorphous Ni-S-Co electrodes in 28% NaOH solution at 80°C with corresponding electrochemical parameters listed in table 2. The HER activity of amorphous Ni-S-Co alloy is higher than that of the other two electrodes. The HER overpotential of amorphous Ni-S-Co alloy is 0,3 V, lower than the mild steel electrode and 0,02 V lower than that of amorphous Ni-S alloy current density of 150 mA.cm^{-2}. Its exchange current density is about two magnitudes higher than that of the mild steel electrode[Ha'03].

Figure 3. Polarization curves of mild steel, amorphous Ni-S and amorphous Ni-S-Co electrodes at 80^{0}C: 1) mild steel; 2) Ni-S; 3) Ni-S-Co.

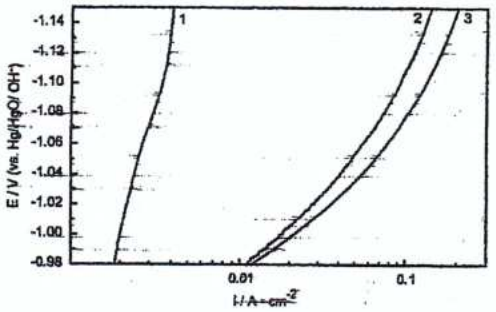
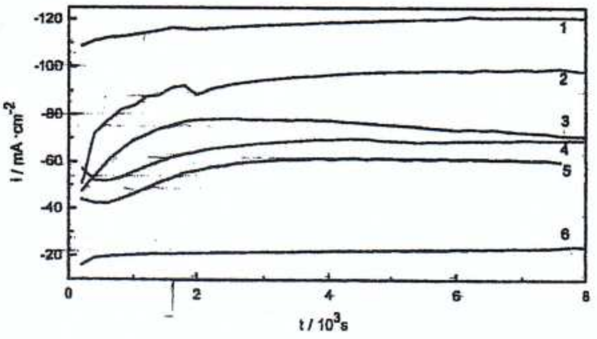


Figure 4 shows potentiostatic curves of several cathodes at – 1,2 V (vs. Hg/HgO/OH$^-$) in NaOH solution at 35^{0}C. As can be seen, the activities of all nickel-based alloys are much higher than that of the mild steel electrode. From the highest to the lowest, the order of their HER activities is: amorphous Ni-S-Co > amorphous Ni-S > amorphous Ni-Mo-Fe > Ni-Mo > Ni-P > mild steel. The HER current density of amorphous Ni-S-Co alloy is about 6 times higher than that of the mild steel electrode.

Figure 4. Potentiostatic curves of several cathodes at – 1,2 V (vs. Hg/HgO/OH$^-$): 1) amorphous Ni-S-Co; 2) amorphous Ni-S; 3) amorphous Ni-Mo-Fe; 4) Ni-Mo; 5) Ni-P; 6) mild steel.



1. Conclusions

1. The activity of iron for hydrogen evolution is naturally higher than that of nickel.
2. Formation of Ni-Fe alloys results in significant enhancement of hydrogen evolution and the activity of the Ni-Fe alloys for hydrogen evolution is higher than iron and nickel metals.
3. Electrodeposited Ni-Fe-C alloys are more active than that of Ni-Fe alloys for hydrogen evolution.
4. The Ni-Fe-Zn alloy shows promising results when examined as a cathode in alkaline water electrolysis. The overpotential for the HER is significantly lower than that observed on the traditional materials (mild steel, Ni) and the deposit presents good stability.

5. Very high electrochemical activity for HER is observed on amorphous Ni-S-Co electrode. The activity of amorphous Ni-S-Co alloy is about 6 times higher than that of the mild steel.

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