STUDIES ON HIGH-SURFACE ELECTRODE PRODUCTION FOR WATER ELECTROLYSIS

Maria Poroch-Seriţan, Violeta Vasilache, Alice Roşu, Amelia Buculei
"Ştefan cel Mare" Univresity of Suceava

Abstract

The paper focuses on present research to obtain nanostructures on metallic sublayer through electrochemical method and their testing in order to increase considerably the real surface of the electrodes as compared to the apparent surface.The possibility to obtain high area surfaces at economically low cost is being studied intensively, since these electrodes have to comply with conditions of chemical stability, corrosion resistence, mecanical resistence and non toxicity as well so that the impact of future technologies upon the environment should be minimised.

***Key words:** hydrogen, electrolysis, high-surface electrode.*

Introduction

Water electrolysis is a process known for a long time and uses energy to dissociate hydrogen from oxygen of water molecule:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \qquad E_0 = 1.229\ V$$

In principle this reaction may occur on any conductive surface (so, on any type of electrode). In reality, due to the decrease of discharge over voltage, some metals allow obtaining better efficiencies than others and also the high surface of electrodes allows higher efficiencies because it can be worked at lower current densities.

During the last decade, nano-crystalline materials have been developed due to their exceptional mechanic, magnetic properties etc. Since Erb' and his co-workers' pioneering work (Erb, 1993), research on nano-crystalline materials obtained through electroplating have advanced considerably.

In comparison with high-area evaluation of porous electro catalyst materials, an important "scaling" factor is the ratio (noted by$\Re$) between the real area and the apparent one of the cathode material. At a given operating current in a fuel-cell or electrolyser system, the polarisation and hence power consumption of the system is determined by the *real* current-density, taking into account the scaling factor $\Re$.

In the case of comparative evaluation of various porous electrode materials, especially for H_2 evolution electro catalysis, it is important to know what performances have been improved by intrinsic changes occurring within electro catalysis according to fine-particle structure (figure 1) and are simply due to increase of $\Re$ values. Procedures for real area evaluation are reviewed for the evaluation of effectiveness of cathodic H_2 evolution performance in the water electrolysis process (Impraga, 1998).

Fig. 1. Electrode Enlarged Surface

The reaction efficiency refers to the main factors determining hydrogen cost: *specific consumption of electric energy* $W_p = \frac{V \cdot I \cdot t}{n_{H_2}}$, $[Wh/mol]$ and *energy efficiency* $\eta_w = \eta_I \cdot \eta_V$. The working tension, V, of water electrolysis process has influence upon these factors, which equals with:

$$V = \varepsilon_{o_2} - \varepsilon_{H_2} + \eta_{O_2,e} + \eta_{O_2,c} - \eta_{H_2,e} - \eta_{H_2,c} + \sum RI$$

The following conclusions are drawn from the analysis of the terms composing the working tension:

1. The difference $\varepsilon_{O_2} - \varepsilon_{H_2}$, represents *the theoretical decomposing tension*, *E_0*, which value at 25C is of 1.23V and does not depend on the electrolyte nature (alkaline or acid solution). The reversible potentials at a given system temperature and some concentration of the water solution can be determined electrochemically by the electrode potential standard from the Nernst equation.

2. *The electrochemical polarizations of the hydrogen discharging,* $\eta_{H_2,e}$ *and oxygen* $\eta_{O_2,e}$ *and the concentration polarization,* $\eta_{O_2,c}$ *and* $\eta_{H_2,c}$ have a high degree importance in the tension balance and therefore it is

desirable for their values to be low. The electrodes over-potentials under the smallest density can be estimated by Butler-Volmer equation.

For a higher current density, the over-potential is dominated by the diffusion of molecules and ions from the solution. The reducing of the electrochemical polarizations of the hydrogen discharging, $\eta_{H_2,e}$ and oxygen $\eta_{O_2,e}$ can be realized by: increasing the temperature and the working pressure, decreasing the current density, researching and obtaining new materials for obtaining the electrodes.

Experimental

The electroplating is a relatively cheep and easy method in which the original size of the nucleus (crystallization germs) can be completely controlled by the over-potential applied and non-porous materials, dense are obtained, avoiding in this way the following density.

Results and discussions

Quantum Sphere Inc. (QSI) (Energy Research Laboratory, QuantumSphere Inc., Santa Ana, CA 92705, USA) has developed a disruptive technology to increase the efficiency of water electrolysis, using its capability to manufacture high surface area electrodes through the laying of nano-particles (of 3-50 m).

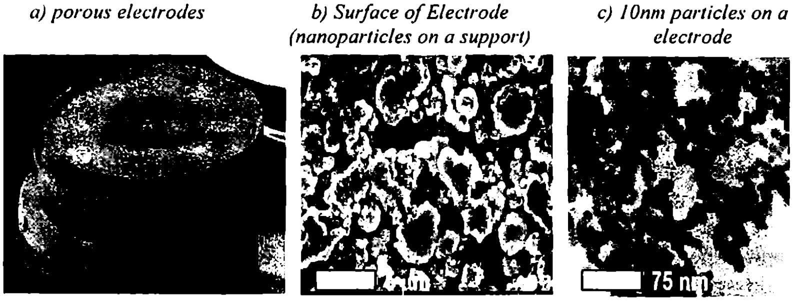
A unique electrode structure for alkaline water electrolysis has been developed on this purpose. These electrodes have high areas of water contact and also allow the evolution of the gaseous products of reaction. The gas bubbles leave the area where they were formed as soon as the liquid comes into contact with the electrode metal, the process being carried out in continuous flow.

The reference electrode is a zinc wire and the electrolyte is eutectic KOH (33% aqueous). This type of electrode allowed the growth of the hydrogen generation efficiency up to 75%. This fact also allows the elimination of the expensive platinum electrodes with a supplementary costs reduction. The precious metal platinum has shown great activity for water electrolysis, reaching over 50% efficiency, efficiency considered till recently quite good. The electrodes obtained by QSI and based on metallic nanostructures has achieved up to 80% efficiency at obtaining hydrogen at lower current flow rates (100 mA/cm2) and approximately 60% efficiency at higher rates (1000 mA/cm2).

Many researchers express the energy efficiency as a percentage calculated from the energy contained in the produced hydrogen divided by the energy used to obtain that hydrogen. This is a more directly comparable unit of electrolysis efficiency, since it is independent of assumptions regarding electricity price and delivery costs.

QSI uses high surface area metallic electrodes with nano-particles as liquid and gas diffusion electrodes for water electrolysis by compression and sintering into porous plates.

Figure 2 shows a scanning electron micrograph of a porous electrode (nano-particles on a metal particle substrate) and a transmission electron micrograph of the individual nano-particles.



a) porous electrodes

b) Surface of Electrode (nanoparticles on a support)

c) 10nm particles on a electrode

Fig. 2: a) Pictures of QSI porous electrode used in electrolysis b) SEM image of surface of electrode, and c) TEM image of 5 nm QSI nanoparticles.

On the table 1 are presented the data resulted after the measurements realized by the productive company, but also by an other company (DoppStein Enterprises [DSE] din Marietta, GA, USA, 2006). These data show the electrodes good performances (QuantumSphere, Energy Research Laboratory, 2006).

Table 1: Conversion efficiency for several electrodes. Electrodes prepared from high surface area nanometals demonstrate the best performance (QSI Nano I and II).

Electrode Type	Conversion Efficiency 0,1 A/cm^2	Conversion Efficiency 1 A/cm^2
Nickel Powder	46%	19%
Black Platinum	67%	42%
QSI Nano I	71%	49%
QSI Nano II	81%	58%
DoE2010 Target	75%	75%

Among other recent research on obtaining electrodes with high area surface from nanometals we mention:

Metikoš-Huković et al have obtained electrodes from amorphous Zr-Ni alloys. There were investigated $Zr_{100-y}Ni_y$ alloys, with y=33 to 60. An enhanced activity was observed along with the increasing of y in these alloys. This fact was associated with a rapid increase of electronic density of states at Fermi energy level, D (E_F) of the 3d Ni band with increasing Ni concentration in the alloy.

The formation of Ni-hydrides during hydrogen evolution was prevented and the high activity of the 3d Ni band for the h.e.r. (hydrogen evolution reaction) was preserved.

According to the researchers estimations the highest catalytic activity could be expected for y=65, when a maximum hybridization of 3d–4d orbitals (for Ni) and a rapid decrease of minimum density of 4d Zr states at the Fermi level was observed (Metikoš-Huković, 2000).

In other study, Suffredinie points out research on obtaining high surface electrodes using Ni and Ni–Co alloys as well as the deposition of a highly active Ni–Fe layer. It also describes the formation of $NiCo_2O_4$ layers on several substrates using the Sol-Gel method. High area Ni and multilayer Ni–Co alloy coatings have been obtained with a new electroplating methodology that allows the complete removal of Zn. There were generated highly porous surfaces with roughness factors of 2200 for Ni and 4400 for Ni–Co. The hydrogen over-potential measured for these coatings at 135 mA cm^{-2} and 70°C was 0.1V and 0.09V, respectively for Ni-Co. Rough Ni–Fe coatings having 40 at % of Ni were deposited from an acetate bath and were activated by anodic polarization in HCl. Analyses by SEM and dissolution voltammetry suggest that the activation removes a passivating layer on the surface, revealing an active Ni–Fe phase.

Polarization curves obtained at different temperatures presented Tafel slopes of 63–80 for 25–80°C and apparent activation energy of 55kJ mol^{-1}. Working with a solution 4M NaOH at 135 $mA\cdot cm^{-2}$ showed a hydrogen over-potential of 0.16V at 70°C, a value considerably lower than 0.35V found for smooth Ni or 0.49V for an equivalent Ni–Fe metallurgical alloy. Active anodes were prepared by the synthesis of $NiCo_2O_4$ using the Sol-Gel method on Ni and Ti substrates. The measurements showed oxygen over-potential of nearly 0.3V, approximately 0.6 V less than that obtained for pure Ni oxide anodes, under the same experimental conditions. These anode materials were tested in long term operations at 135 mA cm−2 and 70°C for periods up to 200 h. without any evidence of a decrease in their catalytic activity (Suffredini, 2000).

Another group of researchers (Kleinke, 1997) concentrated upon the study of different amorphous alloys because the microstructure of the electrode material influences the efficiency of the electrolysis process. Among those investigated there were amorphous Fe-Ni-Si-B which exhibit oxygen potential vs Hg/HgO of around 600 mV at 300mA/cm^2 in 30wt.% KOH at 60°C.

Polycrystalline Ni was less electro-active, indicating that the amorphous state is a better precursor for the formation of an active surface layer. In the alloys tested, metal-metalloid glasses are chemically unstable for high concentrations of iron and the electrode over-potential decreases with an increase of iron. Consequently, corrosion resistance and electrode performance were found to have opposite dependence on iron concentration.

Studies on nickel-cobalt-molybdenum electrodes in a 30 wt% KOH solution at temperatures from 298° to 353°K have been carried out. These electrodes which are ternary materials were fabricated by the electroplating on a stainless steel screen, initially at a current density of 0.5A cm^{-2} and subsequently at 2A cm^{-2}.

They showed good adhesion to the substrate, high surface roughness and they enhanced the HER in water electrolysis compared with nickel, cobalt, nickel-molybdenum and cobalt-molybdenum deposited electrodes. The HER enhancement on the ternary materials with respect to nickel-molybdenum and cobalt-molybdenum was attributable to their large surface area. On the ternary materials, two Tafel slopes were distinguished on the HER polarization in the low and high HER over-potential ranges.

However, no conventionally proposed relation between Tafel slope and temperature was found; the transfer coefficient increased with temperature under the experimental conditions (Chonglun Fan, 1994).

Raney-nickel cathodes (Pushpavanam, 1993) were prepared using different methods and they were applied in the two most important electrochemical technologies, chloralkali and water electrolysis. The effectiveness in enhancing the catalytic activity of nickel electrodes by employing three types of particulate materials, namely Raney-nickel, aluminium and alumina powders during the cathodic co-deposition of nickel has been investigated. The amount of co-deposited precursor depended on its specific gravity and the geometrical arrangement of the substrate (cathode). Composites produced by keeping the substrate horizontal during the deposition exhibited higher catalytic activity.

The Tafel parameters for hydrogen evolution have been compared for the above three types of electrodes with those of mild steel and nickel. Cyclic voltammograms indicated high tolerance to current reversals with electrodes prepared using an aluminium precursor. The catalytic activity was in the order of cathodes from Ni-Al > $Ni\text{-}Al_2O_3$ > Ni-Raney-Ni composites.

The new concept, named I.M.E. technology (inorganic membrane electrolyte) might be another solution to the problem (Vandenborre, 1985). With this technology it was produced hydrogen under pressure (0.5–4.0MPa) at current densities up to $12500Am^{-2}$ and temperatures not exceeding 120°C. Electro-catalysts based on non-noble metals were deposited on perforated Ni plates.

These electrodes are pressed against an inorganic ion-exchanger membrane based on polyantimonic acid. Circular cells (surface area up to $0.2m^2$) are then assembled in a filter-press type manner. The hydrogen production rate ranged from $2.5Nm^3h^{-1}$ to $25Nm^3h^{-1}$. Multicell performances (up to 60 unit cells) at 2000 Am^{-2} are 1.6 V at 90°C and even 1.5 V at 120°C.

At a 5 times higher current density (10000 Am^{-2}) cell voltages only increased with 0.3 V at 90°C and 0.2 V at 120°C. The electrical power consumption (at 2000 Am^{-2}) per normal cubic meter of hydrogen produced was 3.81 kWh at 90°C and 3.65 kWh at 120°C.

Conclusions

This concise review of research evolution on obtaining highly improved performance electrodes producing hydrogen leads to the conclusion that studies might focus on two directions:

1. Increase of real area of electrodes by electrochemical increase of nano-crystalls on sublayer;
2. To obtain new materials which electrodes are made of, taking into consideration the following factors as well: accessible cost, chemically and physically stable, to be widely produced in industry and to require a discharge tension as low as possible so as to obtain hydrogen by low energy consumption.

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