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RESEARCH ARTICLE

Erosion Behavior of Nickel Diffusion Membranes in Conditions of Water Electrolysis

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ABSTRACT

Preliminary studies of the erosion resistance of Ni diffusion membranes under the conditions of water electrolysis in various modes were carried out. Particular attention was paid to the time dependencies of the current, voltage and the electrolyte temperature during the process. Both electrodes, anode and cathode, were in the form of tubes of Ni-99.5% wt. The electrolyte was pure drinking water after the filter with mineralization (ppm) 14, as well as water with the addition of sodium bicarbonate (mineralization 140-160 ppm). It is demonstrated that after several hours of operation cathodes showed no signs of erosion or other damages. The degree of erosion was assessed by weighing, and the state (morphology) of the surface was visually examined using an optical microscope. As for the anode, even when electrolyzing sufficiently pure water (ppm=14), there is noticeable erosion and surface damage. To elucidate the reasons for such behavior of Ni electrodes, further studies are planned, in particular, using some other materials as an anode.

Keywords: Ni; diffusion membranes; water electrolysis

Introduction

The major volumes of technical hydrogen in the world are produced by gasification of solid, liquid or gaseous hydrocarbons, that is a serious source of air pollution. "The ultimate goals of a hydrogen-based economy include the production of hydrogen while generating minimal greenhouse gases" [1]. From this point of view, the most suitable method is the electrolysis of water. Indeed, during electrolysis one can produce hydrogen and oxygen from water (reaction equation $2H_2O=2H_2+O_2$), and then, when hydrogen is burned as a fuel, to get water again. In the technological process of hydrogen production, in addition to the actual electrolysis, i.e. decomposition of water molecules into hydrogen and oxygen, it is necessary to separate these gases and purify the resulting hydrogen from impurities (oxygen and water). The cost of hydrogen is largely determined by the degree of its purification. The cheapest is technical hydrogen with a purity of up to 99.95% vol. However, its cost is about two times higher than that of hydrogen obtained by gasification. Note, that it is possible not to separate the mixture of gases obtained during electrolysis (explosive gas), but directly use it as a fuel, which will be much cheaper. Note that in this case oxygen for the combustion reaction will not be absorbed from the atmosphere. In addition, since such gas is an explosive, this technology has a dual application.

The most expensive (except for spectrally pure) is ultra-pure hydrogen with a purity higher than 99.99% vol. Note that high-purity hydrogen is extremely necessary in the chemical and electronic industries, thermonuclear researches, etc. Fuel cells in the future also look like a wide area of high-purity hydrogen consumption. However, the expansion of the scale of production and use of pure hydrogen is limited by its high cost due to the need to use low-performance and expensive technologies for purifying cheaper technical hydrogen. Therefore, the development of new methods for obtaining high purity hydrogen is an urgent scientific and technical task of improving the technological process of its production.

There are numerous methods and devices for the electrolytic decomposition of water or water vapor [2-4]. However, to receive highly pure hydrogen (purity higher than 99.999% vol.) from the technical one obtained as a result of water electrolysis, it is necessary to use additional purification systems, using purification with intermetallic compounds [2], cryosorption methods [4] and others, including membrane technologies. This leads to a significant increase in the cost of high-purity hydrogen. In addition, the purity of the resulting hydrogen usually does not exceed 99.99% by volume.

On the other hand, a particularly clean (super-cleaned, with purity is better than 99.999 % vol.) hydrogen can be produced from hydrocarbons using membrane technologies [5-8]. It is used that through metal membranes from nickel, palladium (its alloys) at a temperature of 400-800°C only hydrogen penetrates, due to its very high diffusion coefficient in these metals. The raw materials for the production of particularly pure hydrogen are usually used by gas-shaped or liquid hydrocarbons, for example, methane, alcohol, gasoline, etc., therefore, the disadvantage of these methods is environmental unsafe, since emission of CO and CO_2 during the process. In addition, it is possible to poison the surface of membranes with carbon ($CO+H_2 = H_2O+C$), which leads to instability and a decrease in process productivity.

Unlike known methods, it is proposed to use special cathode structures when electrolysis of water, instead of usually used. This can be, for example, membranes in the form of nickel tubes (other metals with high hydrogen permeability can be used, for example, palladium and its alloys). One end of the cathode (diffusion-catalytic membrane) is hermetically sealed with argon-arc welding, and the other joins through the valve to the vacuum volume, or to the hydrogen accumulator [8]. Such a device would allow us to obtain ultra –pure hydrogen (with a purity of more than 99.999%) during the process of technical hydrogen or combustible mixture production, which will significantly reduce its cost.

But, in order to realize this, it is necessary to examine in detail the processes on the surface of diffusion-catalytic membranes (sorption and dissociation of hydrogen), dissolution, diffusion and permeability of hydrogen through the volume of metal, study the resistance of cathodes in conditions of prolonged exposure to various electrolytes in different modes, and create a working model of the pure hydrogen generator built into the technological process of water electrolysis. It is necessary to create new, more persistent materials for membranes, including coatings using plasma technologies. After that, it will be possible to integrate this method into the existing factory technologies of water electrolysis.

In this work, preliminary studies of the resistance of diffusion Ni-membranes in conditions of water electrolysis were carried out.

Experimental Fasility and Results

The diagram of the stand for experimentation is shown in Figure 1. The electrolyzer case served the glass container 1. Anode 3 and cathode 4, made of a nickel tube (Ni-99.5%) in size 120x5.4x0.2 mm, were installed on the lid 2, through which an electronic temperature meter JR-1 (T) was introduced, too. Since the "explosive gas" (mixture $2H_2+O_2$) is formed in the process, holes are provided in the lid for gas output. The power supply 5 is a rectifier on two V200 diodes connected to the autotransformer through limiting resistance. As an electrolyte, ordinary filtered water was used (mineralization measured using the TDS Meter 3 device was 14 ppm) and a 0.5% sodium bicarbonate (soda) solution in water (mineralization 157 ppm).

Figures 2-4 show the dependences of the current and voltage on the time of electrolysis of water in various modes. The monotonous current growth over time is most likely due to the slow increase in the temperature of the electro-lyte (Figure 4). Moreover, in the case of pure water, such growth is not observed. Apparently, this is due to the change and stabilization of the composition of the electrolyte, in that soda $NaHCO_3$ can be decomposed into Na_2CO_3, water and CO_2.

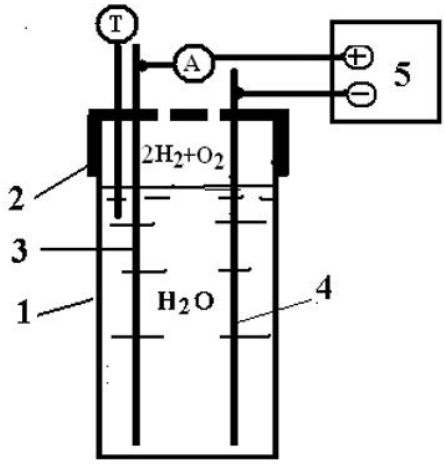

Figure 1: Experiment diagram: 1- electrolyzer case, 2- lid, 3- Ni anode, 4- Ni cathode, 5- power supply (0-200V, up to 200A), A-current meter, T- temperature meter.

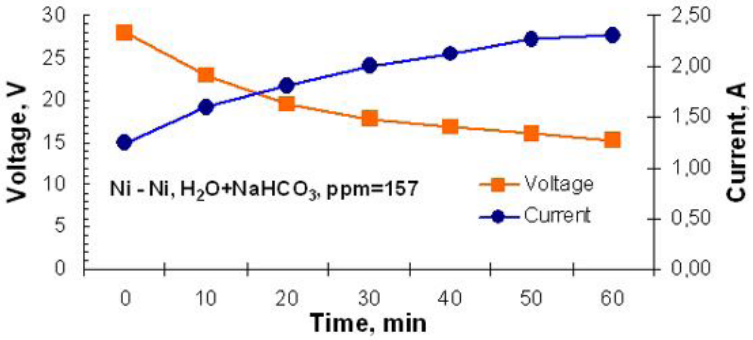

Figure 2: Time dependencies of voltage and current during electrolysis in a solution of soda in water. Both electrodes are nickel tubes.

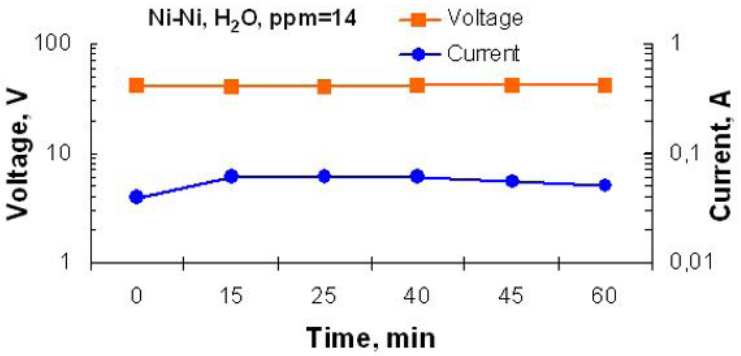

Figure 3: Time dependencies of voltage and current during water electrolysis, ppm = 14. Both electrodes are Ni tubes.

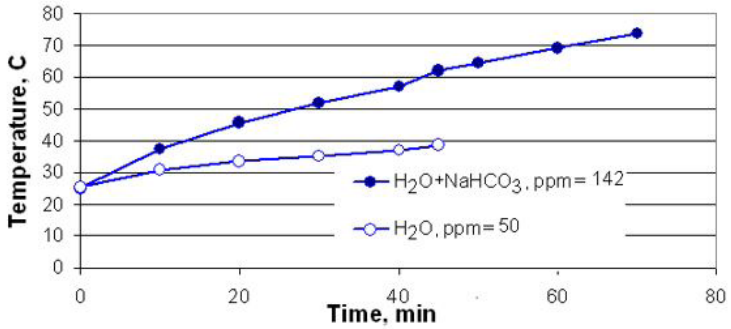

Figure 4: Evolution of the electrolyte temperature with electrolysis time in various modes.

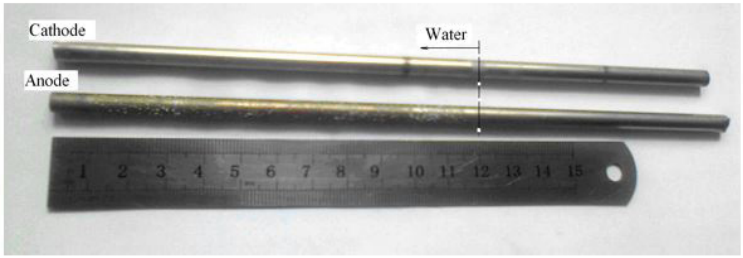

Figure 5: Ni electrodes after one hour of operation in the water electrolysis mode.

Damage of the electrodes surface was estimated by weight loss method using the VLR-200 weights and visually the MBS-9 microscope. After several hours of work, no signs of erosion or other damages were found on the cathodes surfaces (Figure 5). So they potentially could be used as diffusion membranes-cathodes in long time electrolysis process.

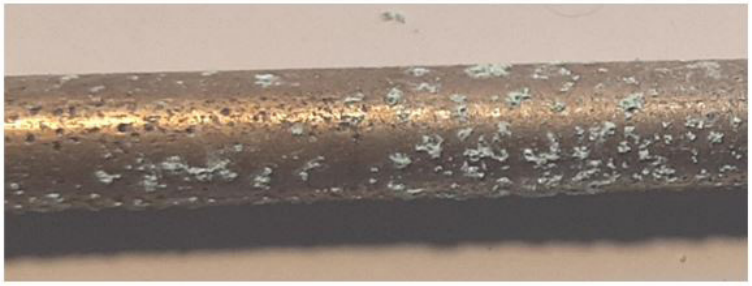

Figure 6: Damages on the surface of Ni-anode (5.4 mm in diameter) after one hour of operation in the water electrolysis mode.

As for the anode, even with electrolysis of quite clean water (14 ppm), noticeable erosion and surface damage are observed (Figure 6). Damages are point in nature and have the form of a micro cavities and light blue color interspersed (Figure 6). To clarify the nature of such damages, further studies of the resistance of the anodes are necessary, including using other materials.

Conclusion

Preliminary studies of the resistance of diffusion membranes from Ni in conditions of water electrolysis in various modes were carried out. It had been shown that the membrane cathodes after several hours of work did not manifested any signs of erosion, or other damage. Therefore, they have good potential to be used as diffusion membranes-cathodes in long time electrolysis process.

As for the anode, even with electrolysis of clean water (14 ppm), noticeable erosion and surface damage are observed. To clarify the reasons of such behavior of the Ni electrodes it is planned to carry out further research, in particular, using other materials as an anode.

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