ANNALS of the ORADEA UNIVERSITY.

Fascicle of Management and Technological Engineering, Volume VI (XVI), 2007

HYDROGEN GENERATION BY ELECTROLYSIS OF SEAWATER

Gabriela Elena Badea*, Alina Caraban*, Petre Cret*, Ion Corbu**
*University of Oradea, gbadea@uoradea.ro;acaraban@uoradea.ro, pcret@uoradea.ro
**Setko Impex and Spiru Haret University, Bucureşti, vicobnoru@yahoo.fr

Key words: seawater , hydrogen, electrolysis cell

Abstract: The sea waves-generated power and its utilization in situ for the hydrogen generation by seawater electrolysis is a very interesting way. The seawater electrolysis is technically feasible and is a perspective procedure for an environmentally-clean commercial production of hydrogen and associate products The aim of this work is to examine the variation of the tension and energy consumption at electrolysis of natural seawater (Black Sea – Constanta, Romania) comparative with electrolysis of a solution of 15% NaOH, in the same conditions.

1.INTRODUCTION

In view of the rising costs of fossil fuels and growing environmental pollution, the hydrogen economy is seen as a practical solution to the above problems. In this context, water electrolysis acquires a particular strategic role [7].

It is possible to generate hydrogen by conventional DC water electrolysis, but this is undesirable for environmental reason if the electrical energy for the electrolysis is produced in thermal power stations from fossil fuel because of the generation of carbon dioxide. Fuel cells are promising and various systems are being studied worldwide. The generation of carbon dioxide during hydrogen generation through natural gas for fuel cells can be reduced compared with thermal power stations, but carbon dioxide is still generated. Hydrogen generation by photo-catalysis is preferable but process efficiency is still very low for practical applications.

Recently, water electrolysis has been reconsidered as a method for hydrogen generation since the cost of electricity is decreasing, mainly as a result of wind-generated power, hydroelectricity and nuclear power [9]. The sea waves-generated power and its utilization in situ for the hydrogen generation by seawater electrolysis is a very interesting way.

The seawater electrolysis is technically feasible and is a perspective procedure for an environmentally-clean commercial production of hydrogen and associate products [3].

The produce hydrogen from seawater as a target product, an electrolysis production procedure can take three main routes [10]:

- *electrolysis to give hydrogen, oxygen and alkalis;*
- *electrolysis to give hydrogen, oxygen, chlorine and alkalis;*
- *electrolysis to give hydrogen and sodium hypochlorite (NaClO*);

The second route of the seawater electrolysis seems to be the most real one. In this case the process can be conducted with reasonable rates giving a great amount of target products. However, in this case the chlorine shall be a by-product, which may be returned into the environment only in a safe form. This can be done, for instance, by converting the chlorine containing in anodic gases into hypochlorite. The hypochlorite is an antibacterial product widely used for disinfection of drinking or waste waters.

The seawater is a solution of salts nearly constant composition, dissolved in variable amounts of water. There are >70 elements dissolved in seawater but only 6 make up >99% of all the dissolved salts; all occur as ions – electrically charged atoms or groups of atoms:

Chloride (Cl^-)	55.04 wt%	Sodium (Na^+)	30.61 wt%
Sulphate (SO_4^{2-})	7.68 wt%	Magnesium (Mg^{2+})	3.69 wt%
Calcium (Ca^{2+})	1.16 wt%	Potassium (K^{+1})	1,10 wt%

Total dissolved solids (TDS) vary from as low as approximately 8000 ppm (mg/L) in the Baltic Sea to as high as 60,000 ppm in bay areas of the Arabian Gulf, due to the evaporation by tropical heat in the desert air [12]. The „nominal" dissolved solids, upon which formulae for artificial seawater are based, is about 34,500 ppm, of which about 25,000 ppm is taken to be sodium chloride [3].

While the deep ocean waters are usually under saturated with respect to carbonates, surface waters are usually saturated due to wave action and exposure to carbon dioxide in the atmosphere. This saturation will affect the deposition of calcium and magnesium salts in cathodic reactions during corrosion or in the application of cathodic protection and in electrolysis of the seawater.

The electrode processes at seawater electrolysis [8] are:

- *Hydrogen evolution at cathode, conform to the reaction:*

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{1}$$

- *Oxygen and/or chlorine evolution at anode*, conform to the reactions:

$$6H_2O \rightarrow O_2 + 4H_3O^+ + 4e^- \tag{2}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{3}$$

During seawater electrolysis, a thin film of calcareous deposits forms at the cathode surface, mainly consisting of $CaCO_3$ and $Mg(OH)_2$ [6]. As result of the local pH increase in the vicinity of the cathode surface, due to evolution hydrogen reaction, it takes places the precipitation of the Ca^{2+} and Mg^{2+}, according to the following equations:

$$Ca^{2+} + OH^- + HCO_3^- \rightarrow CaCO_3 + H_2O \tag{4}$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \tag{5}$$

If cathodically formed scale deposits are not removed, they continue to grow. The higher the water temperature, the greater the hardness of the water and the flow velocity, the greater is the growth rate. The increase in flow velocity improves the mass transfer of Ca^{2+} and Mg^{2+} ions to the cathodic surface. Eventually, this leads to a total blockage of the electrode stack, and the gaps between the electrodes become filled with scale [5].

The anodes for oxygen evolution by seawater electrolysis must not evolve toxic chlorine and must have high efficiency and long durability. It is well known, however, that most of the conventional anodes for seawater electrolysis have been tailored to produce chlorine. The existence of commercial seawater electrolysers which efficiently produce hypochlorite solution from anodically generated chlorine [11] confirms the predominance of the chlorine evolution. Only manganese oxide coated electrodes are known to produce oxygen with high efficiency in seawater electrolysis [4].

The aim of this work is to examine the variation of the tension and energy consumption at electrolysis of natural seawater (Black Sea – Casino Constanța, Romania) comparative with electrolysis of a solution of 15% NaOH, in the same conditions.

2.EXPERIMENTAL

Experiments were made in an electrolytic rectangular glass cell with an active volume of 100 cm^3 (Fig. 1); two perforated plates of graphite used as anodes and a cathode of stainless steel (18%Cr-10%Ni- 0.04% C- 0.33% Si and Fe) with active aria of 43 cm^2 was positioned centrally at constant distance of 15 mm from each anode; a constant current DC rectifier, type STCO75, used to provide the necessary power to the electrodes.

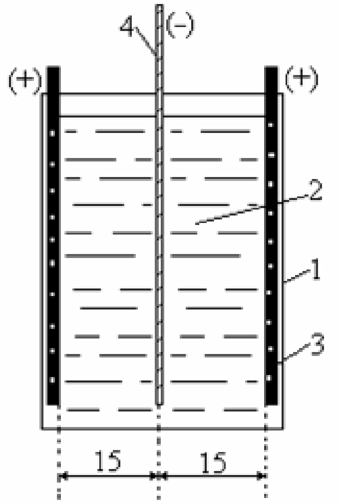

Figure1. Scheme of the electrolysis cell. 1- glass cell; 2 – electrolyte; 3 – perforated graphite anode; 4 – stainless steel cathode.

Stainless steel is generally considered corrosion resistant in sea water, and our studies confirmed that stainless steel 18Cr-10Ni shows good corrosion behavior in sea water both in open circuit when it became spontaneous passive[1], and as cathode when it is electrochemical protected.

The natural seawater (Casino-Constanța/Romania) and a solution 15% NaOH were used as electrolytes. The conductivity of the solutions was also measured as temperature function.

3.RESULTS AND DISCUSSION

Figure 2 shows the electric tension dependence on current density at seawater electrolysis comparative with electrolysis of a 15% NaOH solution.

A difference of about 1 V there is between electric tension measured at electrolysis of the seawater and that of the hydroxide solution. Also, it can be observed an increase more accentuated of the electric tension with current density in case of seawater electrolysis (curve 1 from fig. 2) comparative with hydroxide solution electrolysis (curve 2 from fig.2).

The difference of electrolysis electric tension between seawater and hydroxide solution is due in principal to the electric tension fall on electrical resistance of electrolytes, which varies inverse proportional with conductivity of the solutions, conform to the relation:

$$\Delta V_R = \frac{l}{\lambda} i \qquad (6)$$

were: ΔV_R – electric tension fall on electrical resistance of the solution, V; l – distance anod-cathod, cm; λ - solution conductivity, $\Omega^{-1}cm^{-1}$; i – current density, $A.cm^{-2}$

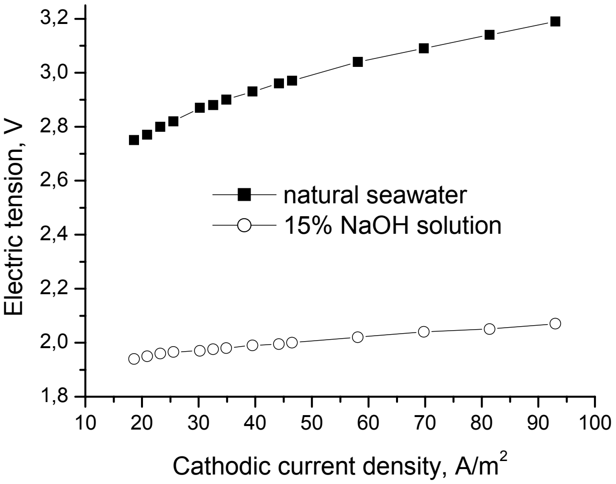

Figure 2. Electric tension dependence of cathodic current density at the electrolysis of the seawater and of a 15% NaOH solution at room temperature (25°C)

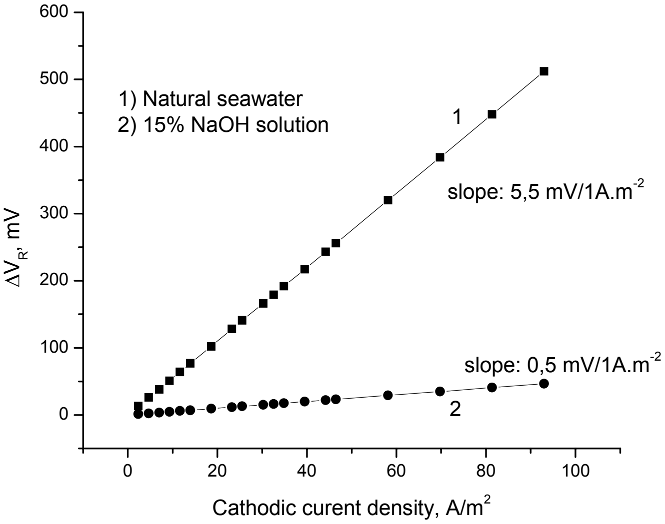

Figure 3. Variations of the electric tension fall on electrical resistance, ΔV_R, with cathodic current density

At 25°C the conductivity of the 15% NaOH (0.3 $\Omega^{-1}cm^{-1}$) is over 10 twice more then that of the natural seawater (0.027 $\Omega^{-1}cm^{-1}$). In fig. 2 are presented the variations of the electric tension fall on electrical resistance, ΔV_R, with current density for the two studied electrolytes.

The small conductivity of the natural seawater and the large electrolysis electric tension lead to the high energy consumption comparative with electrolysis of a classical solution of sodium hydroxide (Figure 4).

At high temperature (the working temperature of water electrolysis is about 80°C), due to increase of the water conductivity (Figure 4), the electric tension fall will be smaller and energy consumption will decrease in comparison with that of the room temperature.

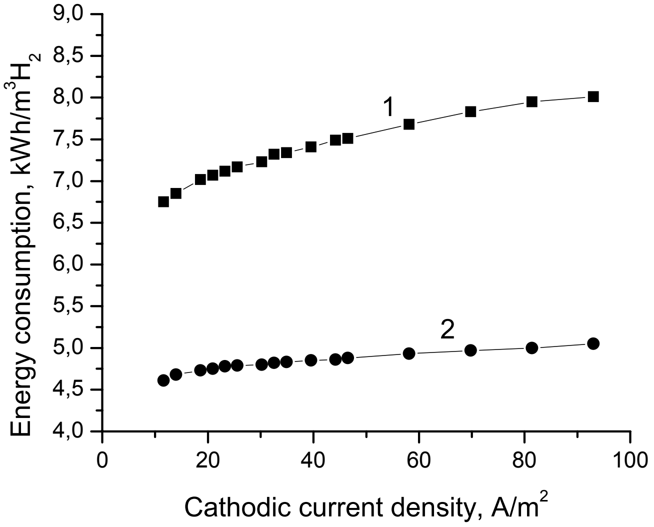

Figure 4. Energy consumption dependence of cathodic current density for hydrogen generation at electrolysis: 1 – natural seawater; 2 – 15% NaOH solution.

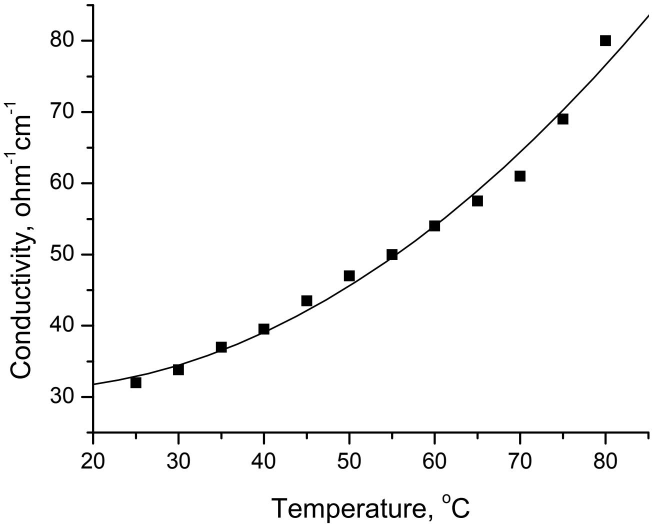

Figure 5. Temperature dependence of the natural seawater conductivity

4.CONCLUSIONS

The experimental studies indicated that the method of seawater electrolysis, in purpose to the hydrogen generation is a process reasonable with one condition: the electric energy have to be enough cheap to counterbalance the high consumption. The studies are a part of a project based on the invention "Ecological sea electro power station" which is protected by an international copyright © AMPI 205072 and for which was submitted an invention patent request A/00840/05.10.2004. This invention was presented as a functional model al the Invention Saloon from Geneva 2005, Eureka 2005 and Pittsburgh 2006 and it has received gold medals, cups and diplomas. In the energetic actual context the proposed model is oriented towards formulae considered prioritary both at EU and world level, respectively of renewable energies. The proposed model deals with capturing of a larger part from the sea waves chaotic energy, and its direct conversion in electrical energy, in mechanical and pneumatically energy and later into electrical energy and hydrogen. Such an electro power station may be executed in any ocean or sea, it is able to run continuously and can provide electrical energy and hydrogen with no additional fuel consumption[2].

5. BIBLIOGRAPHY

1. Cojocaru A., Badea G.E., Maior I. and Badea T., *Cor. Prot. Anticor.*, **II**, 2007**,** 40-44.
2. Corbu I., Electrocentrala Ecologica Marina, Cerere de brevet A00840/05.10.2004 si copyright ©AMPI 205072.
3. El-Manharawy S. and Hafez A., *Desalination*, **131**, 2000, 329-344.
4. Fujimura K., Izumya K., Kawashima A., Akiyama E., Habazaki H., Kumagai M. and Hashimoto K., *J.Appl Electrochem.,* **29**, 1999, 765-771.
5. Kraft A., Blaschke M., Kreysig D., Sandt B, Schröder F and Rennau J, *.J.Appl. Electrochem.,* **29** ,1999, 895-902.
6. Kraft A., Stadelman M., Blaschke M., Kreysig D., Sandt B, Schröder F and Rennau J., *J.Appl. Electrochem.,* **29** ,1999, 861-868.
7. Popa L., Guerrini E. and Trasatti S*, J. Appl. Electrochem*., **35**, 2005, 1213.-1223
8. Rotinian A.L., Tihonov K.I. şi Shoshina I.A., „Teoreticescaia electrohimia", Himia, Leningrad, 1981, p 364.
9. Shimizu N., Hotta S, Sekiya T. and Oda O., *J. Appl. Electrochem*., **36** ,2006, 419-423.
10. Temeev A.A., Belokopytov V.P.and Temeev S.A., *Renewable Energy*, **31**, 2006, 225-230.
11. ***http:/www.chlorine-eng.co.jp/eng/product/water/water3_1.html
12. ***http:/www.stanford.edu/grop/Urchin/seawater.html