

CONTROLLED HYDROGEN GENERATOR AND ADDITIONAL SOURCE OF ELECTRICAL CURRENT FOR INDEPENDENT OXYGEN-HYDROGEN POWER PLANTS

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Abstract

The objective of this work is to develop a safe and environmentally clean hydrogen storage system and at the same time a controlled hydrogen generator. We researched the question of controlled hydrogen generation in a hydronic chemical current source (CCS) with the aluminum anode for the subsequent use of the produced hydrogen in oxygen-hydrogen fuel cells (O₂/H₂ FC).

This work shows that based on the hydronic CCS with an aluminium anode it is possible to create a safe, environmentally clean and energy efficient hydrogen generator with a wide range of hydrogen discharge speed. And the “hydronic CCS + O₂/H₂ FC” system presents an effective and safe solution to the problem of hydrogen storage for independent power plants based on O₂/H₂ FC.

Acknowledgment

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1. Introduction

The unique physical & chemical properties of hydrogen and its virtually limitless amount in global water reserves allow us to count on hydrogen energy systems in further energy development. The use of hydrogen as a source of energy is also promising due to the fact that it is one of the few environmentally clean fuels,

which is especially important now when atmospheric pollution is constantly increasing. At present, there are two main directions of the hydrogen economy development: industrial hydrogen economy and hydrogen economy for special aims.

Currently, effective oxygen-hydrogen fuel cells (O₂/H₂ FC) with ion-exchange electrolytes are being developed under the second direction. Their price is relatively low and it is possible to use them even in household appliances.

It should be noted that the O₂/H₂ FC is a power plant (PP) which converts the chemical energy by means of an oxygen-hydrogen reaction directly into electrical power. Oxygen-hydrogen fuel cell is the most energy efficient one among independent hydrogen-based power plants. High density of energy output (119.0 MJ/kg or 33.1 kWh/kg) and thermodynamic efficiency of the oxygen-hydrogen reaction is increasingly attracting the attention of developers in various fields such as automobile industry and transport, portable applications, radio, aviation and space engineering, etc.

In other words, O₂/H₂ FC can be used in a wide range of applications such as household appliances and electronics as well as automobile transport or spacecraft.

In case of land usage, atmospheric oxygen for O₂/H₂ FC comes from air. But in an oxygen-free environment, for example, in space oxygen needs to be stored.

However, even in space the problem of oxygen storage is not that crucial as the problem of hydrogen storage.

Thus, the problem of hydrogen storage for O₂/H₂ FC is of top priority for today.

2. Hydrogen storage options evaluations

There are several hydrogen storage options which include compressed gas tank, cryogenic and combined hydrogen storage.

The gas tank storage approach (when hydrogen in a gaseous form is stored at high pressures) substantially reduces the overall energy efficiency and gravimetric capacities of a PP.

The cryogenic method to store hydrogen in a liquid state is very expensive due to the high cost of cryogenic systems. Besides, liquid hydrogen storage implies certain technological constraints, which also presents an obstacle in the use of hydrogen. Furthermore, cryogenic storage imposes certain restrictions on the application of O₂/H₂ FC-based PP in living conditions.

Both compressed gas tank and cryogenic hydrogen storage possibilities are highly inflammable and explosive due to pure hydrogen, which is very likely to produce a hazardous oxy-hydrogen gas in case of even a minor storage or transportation defect, thereby substantially increasing the possibility of an explosion.

However, there are hydrogen generation methods which create the possibility to produce hydrogen directly where it is needed – the so-called independent hydrogen generation systems. There are a lot of such hydrogen generators which can discharge hydrogen from different matters or solutions. Such systems can be divided into two main types – generators requiring energy and generators without energy consumption (power inputs). The first type of generators is also called electrolyzers, since they can discharge hydrogen from different solutions (mostly water solutions) only with the help of electrical power. The second type of generators produces hydrogen due to the nature of chemical elements inside. In the latter case, no energy consumption is required to produce hydrogen.

For instance, hydrogen can be discharged by means of reaction with some metals or other matters which discharge hydrogen rather

actively when reacting with water solutions. This method, the so-called “combined hydrogen storage”, is the safest today-known storage solution since pure hydrogen enters the system only as needed and is consumed at once in the O₂/H₂ FC. Prior to entering the system, hydrogen is tightly bound in water molecules. Such storage system resolves the problem of low temperatures, required by cryogenic systems, accuracy of manufacturing, and high reliability since water (as well as saline and alkaline solutions) is not explosive in case of leakage. In addition, this approach is more applicable for household usage than the previous two methods.

However, the major drawback of this method is that the speed (and therefore the amount) of hydrogen discharge is practically impossible to regulate. Aluminium is one of the most promising metals suitable for hydrogen generation owing to its relatively low cost (particularly, technical grades), widespread industrial production, and amphoteric properties which allow Al to extract hydrogen out of water (under certain conditions) as well as aqueous solutions of acids, alkalis, or salts.

The evaluation of hydrogen generation methods (1M or 2g of hydrogen) using the reaction of metals and hydrides with water per component mass unit is presented in Table 1.

Table 1. Evaluation of hydrogen generation methods using the reaction of metals and hydrides with water

Reaction	Specific Consumption g/(mole of hydrogen)
Hydride-Water Reaction	
$2\text{LiH} + 2\text{H}_2\text{O} \rightarrow 2\text{LiOH} + 2\text{H}_2\uparrow$	26
$\text{MgH}_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2\downarrow + 2\text{H}_2\uparrow$	31.15
$2\text{AlH}_3 + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3\downarrow + 6\text{H}_2\uparrow$	28
Metal-Water Reaction	
$2\text{Li} + 2\text{H}_2\text{O} \rightarrow 2\text{LiOH} + \text{H}_2\uparrow$	50
$2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2\uparrow$	82
$\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2\downarrow + \text{H}_2\uparrow$	60.3
$2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3\downarrow + 3\text{H}_2\uparrow$	54

In terms of hydrogen evolution from water, the “aluminium-water” system is the most efficient means of generating hydrogen per component mass unit and it trails only “lithium hydride-water” and “lithium-water” systems. The advantage of aluminium over the other systems and metals lies in the fact that it is a cheap and easily accessible material, an environmentally friendly, non-toxic agent, and the most abundant metallic element in the Earth’s crust (8% by weight).

Hydrogen required for an independent O₂/H₂ FC-based PP can be produced by simply dissolving aluminium in water. Such reaction can be conducted by using, for instance, Kipp’s apparatus, but in this case it is difficult to control the speed of hydrogen reduction.

However, our research shows that the speed of hydrogen discharge from water solution can be controlled electrochemically by means of a hydronic chemical current source (CCS) with an aluminium anode. Such CCS is called “hydronic” because it is composed by a metal-water electrochemical system. Moreover, the electrochemical reaction in hydronic CCS produces not only hydrogen but also electrical power due to a partial thermal-to-electrical energy conversion, whereas heat energy is lost if aluminium is directly dissolved in water.

A comparative energy efficiency analysis of the two hydrogen generation methods mentioned above and the principal electrochemical processes occurring are shown in Table 2.

Table 2. Comparative energy efficiency analysis of the methods using Al as an energy carrier

Chemical aluminium dissolution in water followed by hydrogen oxidation in O₂/H₂ FC		
4 Al + 12 H ₂ O → 4Al(OH) ₃ ↓ + 6 H ₂ ↑ + ΔH ₂₉₈	ΔH ₂₉₈ = -1830.04 kJ	
η _F = 0.0	m _{H₂} = 0.112 (g H ₂ /g Al)	
6H ₂ +3O ₂ → 6 H ₂ O + ΔG ₂₉₈	ΔG ₂₉₈ = -1423.44 kJ	
η _F =1.0	E ₂₉₈ =1.23 B	E _{spec} = -13.19kJ/(gAl)
	U = 1.0 B	E _{spec} = -10.72kJ/(gAl)

Electrochemical aluminium dissolution in water by hydronic CCS followed by hydrogen oxidation in O₂/H₂ FC		
4Al + 12H ₂ O → 4Al(OH) ₃ ↓ + 6 H ₂ ↑ + ΔG ₂₉₈	Δ G ₂₉₈ = -1781.12 kJ	
η _F = 1.0	m _{H₂} = 0.112 (gH ₂ /gAl)	
	E ₂₉₈ = 1.538 B	E _{spec} = -16.50kJ/(gAl)
	U = 0.5 B	E _{spec} = - 5.36kJ/(gAl)
6 H ₂ + 3 O ₂ → 6 H ₂ O + ΔG ₂₉₈	Δ G ₂₉₈ = -1423.44 kJ	
η _F = 1.0	E ₂₉₈ = 1.23 B	E _{spec} = -13.19kJ/(gAl)
	U = 1.0 B	E _{spec} = -10.72kJ/(gAl)

where:

ΔH₂₉₈ is reaction enthalpy at 298 K;

ΔG₂₉₈ is Gibbs energy at 298 K;

η_F is electrochemical reaction efficiency;

m_{H₂} is grams of hydrogen emitted as a result of dissolving 1g Al;

E₂₉₈ is theoretical electromotive force of the power source at 298 K;

U is actual terminal potential including all losses;

E_{spec} is specific energy obtained from 1g Al.

Unfortunately, inert cathodes usually used for hydronic CCS have a rather high overvoltage of the hydrogen evolution reaction. Due to the irreversibility of the processes and the overvoltage of hydrogen reduction on inert cathodes, the energy efficiency of hydronic CCS is about three times lower than the one presented in theory. Nonetheless, hydronic CCS can help create a combined hydrogen storage system where hydrogen generation can be controlled. In addition, hydronic CCS provides a source of electrical energy.

The final byproduct of aluminium oxidation in water is an aluminium hydroxide which is environmentally absolutely safe. Since an aluminium hydroxide is an intermediate product obtained during the manufacturing of metallic aluminium by the Bayer process, it can easily be regenerated into metallic aluminium using the current industrial method. In addition, it is commercially attractive in itself since it is widely used in various industries such as construction or medicine.

Thus, aluminium is virtually an energy carrier, which makes it possible to speak about

building a “hydrogen-aluminium economy” in order to ensure power supply of independent or stand-alone units.

3. Hydronic chemical current source

Hydronic CCS in essence is an electrochemical cell in which aluminium acts as the anode and an inert material like nickel or molybdenum acts as the cathode; space between these electrodes is filled with an electrolytic solution. Aluminium (the aluminium anode) and water are the consumable materials, whereas hydrogen, aluminium hydroxide $Al(OH)_3$, and electrical power are the by-products of the reaction.

Figure 1 is a basic diagram showing hydronic CCS with an alkaline solution and the principal physical & chemical processes occurring.

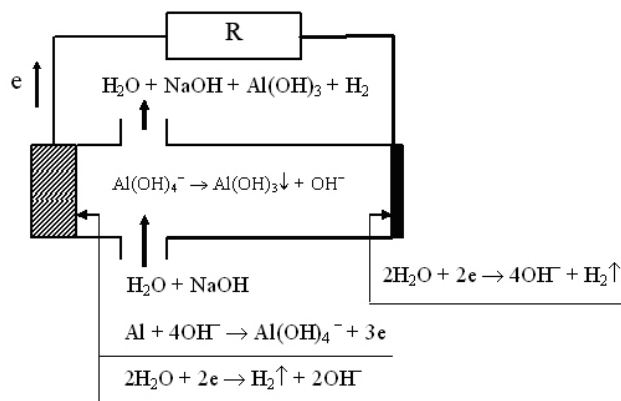
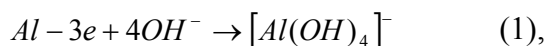
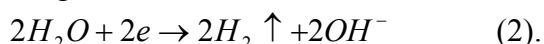


Fig. 1 Basic diagram showing hydronic CCS with an aluminium anode and an alkaline solution

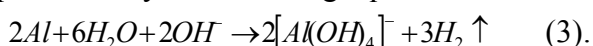
The following equation represents an anodic current-forming reaction arising during the work of hydronic CCS with an aluminium anode in an alkaline solution:



whereas hydrogen is regenerated from water on inert cathode according to the following reaction:



The total current-forming reaction in hydronic CCS with an alkaline solution is presented by the following equation:



Since the ‘aluminium-water’ system has a thermodynamic instability, the anode is consumed in the corrosion reaction apart from the current-forming reaction, which is expressed by the same overall equation (3). The only difference is that in this case hydrogen is emitted on the cathode area of corrosive aluminium.

The alkaline dissolution of aluminium forms an aluminate solution which is extremely disposed to supersaturation. However, after reaching a particular point of supersaturation such solution is decomposed with the release of solid aluminium hydroxide crystallizing in the form of gibbsite:



In a neutral saline electrolyte the current-forming reaction and the corrosion reaction can be described by the following equation:



As it follows from the (4) and (5) equations, the processes in both alkaline and neutral saline electrolytes give the same reaction by-products, i.e. $Al(OH)_3$ and H_2 . However, in a neutral electrolyte the aluminium hydroxide precipitates in the gel.

Therefore, for hydronic CCS aluminium and water refer to consumable matters, whereas hydrogen, aluminium hydroxide $Al(OH)_3$, and electric power belong to reaction products. The reaction products in hydronic CCS like aluminium hydroxide, remaining water and alkali (NaOH) are environmentally friendly and suitable for recovery, recycling or reuse.

3.1 Some experimental data of the hydronic chemical current source with aluminium anode

In the earlier research papers [1, 2] we presented a detailed description of the working processes in hydronic CCS and the results of the research carried out for different compositions of working materials (anode – electrolyte – cathode) in hydronic CCS. This paper includes some of the results in short.

The diagrams presented on fig. 2-7 show some experimental data referring to the polarization characteristics of anodic materials (i.e. a protective aluminum alloy AP4N (АП4Н) industrially made in Russia, an alloy of A99 aluminum and 0.6 wt% indium experimentally developed in MAI and further referred to as the Al-In alloy, and an industrially made A99 aluminum alloy) and cathodic materials (i.e. nickel, molybdenum, titanium, industrially made Russian steel alloys Ch18N10T (X18H10T), and steel St3 (Ст.3)) in the alkaline solution (4M NaOH with an inhibitive additive of sodium stannate 0.06M Na₂SnO₃ [3]) and in the saline solution (4M NaCl). Also, the diagrams show the corrosion characteristics of the investigated anodic materials and the characteristics of the total hydrogen discharge speed in hydronic CCS.

During the research of the electrochemical characteristics of hydronic CCS the voltamperometry method was used with the linear current density and the potential of the electrodes registered. The electrochemical tests were aimed at obtaining the polarization and corrosion characteristics of the anodic alloys and the cathodic processes.

The presented polarization characteristics of the electrodes were measured in relation to the saturated Ag/AgCl reference electrode with the Luggin capillary. The shown data were obtained from no less than 2 samples of the same material and no less than three measurements of each sample were made. The results were statistically calculated and approximated.

The use of the alkaline solution in hydronic CCS with the aluminum anode is possible if we use some additives to inhibit the corrosion of the aluminum anode. For instance, sodium stannate 0.06M Na₂SnO₃ [3] may serve as an additive. This type of electrolyte was especially developed by MAI researchers for aluminum-oxygen CCS with the Al-In anode. This anode-electrolyte pair shows that the electric current density increases while the corrosion current density decreases. It should be noted that all researched cathodes have a high hydrogen evolution overvoltage, which

significantly decreases the efficiency of hydronic CCS.

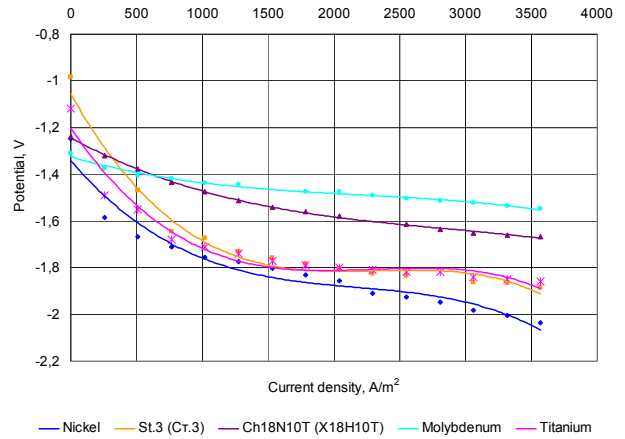


Fig. 2. Polarization characteristics of the cathodes in 4M NaOH + 0.06M Na₂SnO₃ solution, where T = 333K

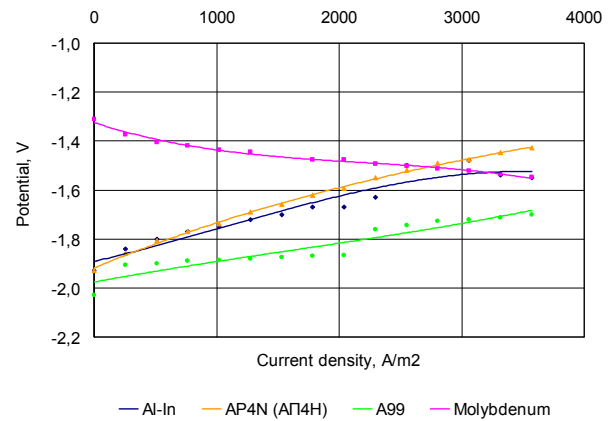


Fig. 3. Polarization characteristics of the aluminum anodes and the molybdenum cathode in 4M NaOH + 0.06M Na₂SnO₃ solution, where T = 333K

The hydrogen purity requirement for the O₂/H₂ FC is often very high depending on the type of a membrane used in the O₂/H₂ FC. In particular, no alkali is allowed to be present in hydrogen entering the O₂/H₂ FC, which may occur if hydrogen is produced in a hydrogen generator with an alkaline electrolyte. In this connection, we conducted an additional research of hydronic CCS with an aluminum anode in a neutral saline electrolyte, i.e. 4M NaCl.

For this type of electrolyte, the polarization characteristics of the cathodes and the anodes are shown on figure 4 and figure 5 respectively.

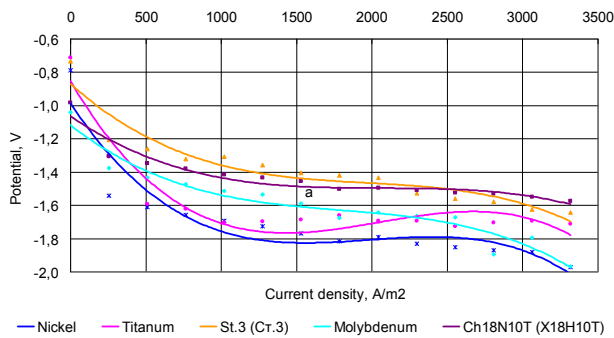


Fig. 4. Polarization characteristics of the cathodes in 4M NaCl, where T = 333K

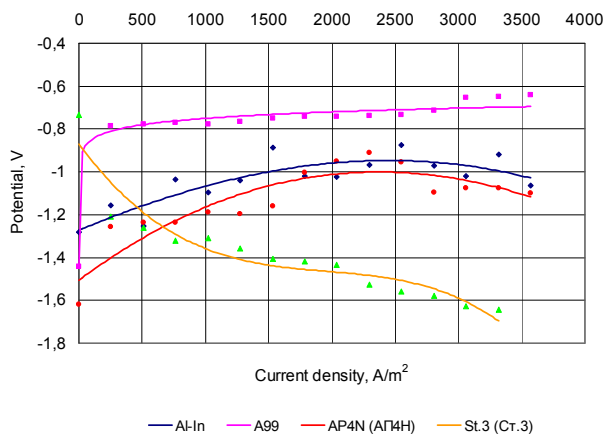


Fig. 5. Polarization characteristics of the anodes and the cathode from St3 in 4M NaCl, where T = 333K

The efficiency of hydronic CCS as a hydrogen generator for the O₂/H₂ FC can be evaluated by the hydrogen discharge speed as a result of the two reactions, i.e. an aluminum anode corrosion (3), and an electrochemical hydrogen evolution from water on the inert cathode (2). The relation between the hydrogen discharge speed and the current density in hydronic CCS is shown on fig. 6-7.

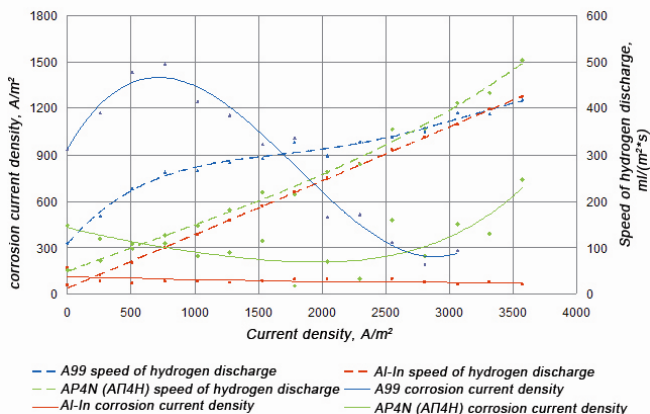


Fig. 6. Hydrogen discharge speed in hydronic CCS in 4M NaOH + 0.06M Na₂SnO₃, where T = 333K

In an alkaline-stannic solution (fig. 6), the relation between the corrosion current density and the electric current density has a maximum rate for the AP4N (AΠ4H) alloy, and both maximum and minimum rates for the A99 alloy, which makes it impossible to create a controlled hydrogen generator based on the said alloys. The Al-In alloy has an almost constant corrosion rate with a wide range of current density, which gives a better opportunity to control the hydrogen discharge speed.

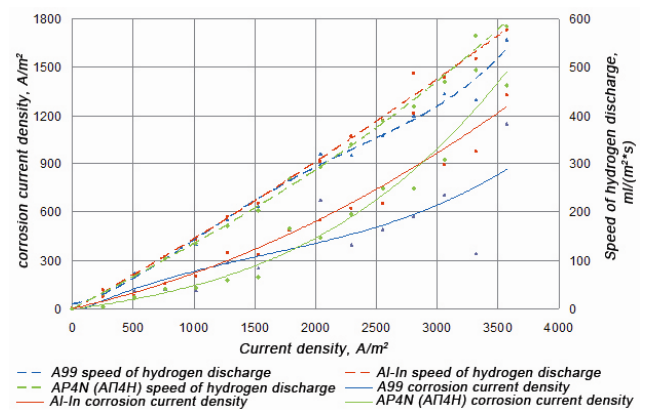


Fig. 7. Hydrogen discharge speed in hydronic CCS in 4M NaCl, where T = 333K

In a saline electrolyte (fig.7), the corrosion current density of the researched aluminum alloys and the total hydrogen discharge speed in hydronic CCS have an almost linear relation and increase in an almost linear way with the increasing of the current density. It should be noted that no corrosion occurs in this type of electrolyte with no electrical current.

From figures 3 and 5 it can be understood that the energy characteristics of hydronic CCS with an alkaline electrolyte are significantly higher than those of hydronic CCS with a saline electrolyte.

The results of the evaluation of the polarization and corrosion characteristics of the researched anodic and cathodic materials shows that the most efficient components for hydronic CCS with an alkaline solution (4M NaOH + 0.06 M Na₂SnO₃) are the Al-In alloy (developed in MAI) acting as the anode and molybdenum acting as the cathode. These components widen the range of current density

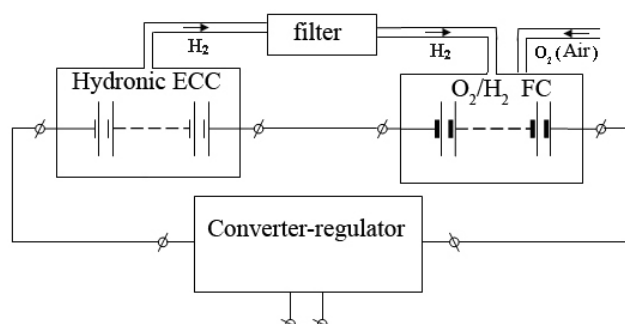


Fig. 9. Basic diagram of a combined power plant, option 2, series connection of the sources.

This type of the electrical connection allows operating without a hydrogen discharge control system since it is controlled automatically by the common current running in both sources. And this is a doubtless advantage of this connection type.

The second advantage of this option is the possibility to widen the range of hydrogen generation over the short-circuit current in hydronic CCS. But in this case the hydronic CCS starts consuming the missing energy for hydrogen generation from the FC, thus becoming an additional resistance in the FC electrical chain.

5. Evaluation of the energy efficiency of a combined power plant

Based on the data in Section 3.1 and with the purpose of identifying the power characteristics of a combined PP, we developed a mathematical model of a combined PP which consists of a hydronic CCS battery we designed specifically for this purpose and a commercial sample of O_2/H_2 FC ($N_{rated} = 1$ kW) supplied by a third party manufacturer, which are connected as shown in option No. 2 (fig. 9).

We designed two modules of an electrochemically controlled hydrogen source based on hydronic CCS with the following working materials: Al-In alloy as the anode, molybdenum as the cathode and 4M NaOH + 0.06M Na_2SnO_3 as the electrolyte. Based on the mathematical model, research data and test results we estimated the current-voltage and power characteristics of a combined PP (hydronic CCS + 1 kW O_2/H_2 FC).

Figure 10 is a diagram showing the power characteristics of O_2/H_2 FC, hydronic CCS as well as their combined characteristics (i.e. the characteristics of a combined PP) at the start of PP operation.

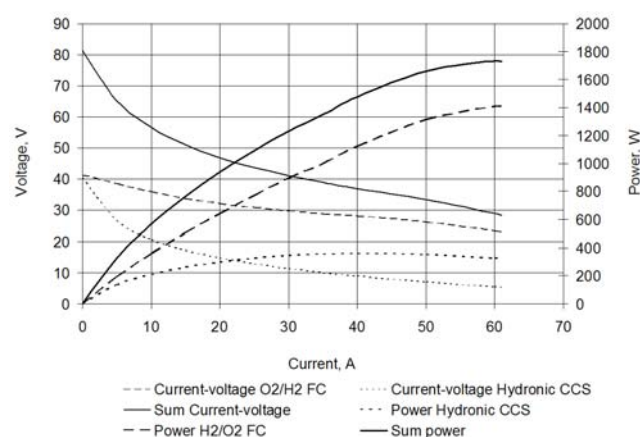


Fig. 10. Combined PP Power Characteristics showing the relationship between power/voltage of hydronic CCS, O_2/H_2 FC, the overall combined PP efficiency, and FC current. Alkaline-Stannate Solution. Combined PP Operation Start.

As we can see from the above diagram, at the start of operation the energy characteristics of O_2/H_2 FC are increased approximately by 35% by means of the energy from hydronic CCS. However, the energy characteristics of hydronic CCS deteriorate with a lapse of operating time due to a gradual increase in space between electrodes in a hydronic CCS FC. In other words, such deterioration is caused by reduction in an Al plate thickness (the anode is dissolved in the current-forming reaction and the corrosion reaction). Electrolyte water as well as aluminum plates are consumed during hydronic CCS operation, which necessitates the replacement of both electrolyte and anode plates in a hydronic CCS battery.

According to the obtained mathematical data, the proposed hydronic CCS can operate on the basis of one set of anodes for approximately 10 hours. The operating period of an electrolyte in the proposed hydronic CCS is 5 hours. Therefore, an electrolyte needs to be replaced every 5 hours and Al anode plates need to be replaced every 10 hours.

6. Research Results

The results of this research help to establish that the energy characteristics of hydronic CCS with an alkaline electrolyte are significantly higher than those of hydronic CCS with a saline electrolyte.

In the course of this research we designed two modules of an electrochemically controlled hydrogen source based on hydronic CCS with the following working materials: Al-In acting as the anode, molybdenum acting as the cathode, and 4M NaOH + 0.06M Na₂SnO₃ water solution acting as the electrolyte.

The energy efficiency of the entire combined PP consisting of the O₂/H₂ FC (N_{rated} = 1 kW) and the two designed modules of hydronic CCS have been estimated with the help of the developed mathematical model. This estimation shows that the proposed hydronic CCS is capable of providing the O₂/H₂ FC (N_{rated} = 1 kW) with hydrogen using one set of anodes in the course of minimum 10 hours. An electrolyte of hydronic CCS needs to be replaced only once after a 10-hour operation period. Besides, hydronic CCS increases the energy efficiency of the O₂/H₂ FC in the course of the entire operation time.

Additional research efforts are required to develop new and more efficient compositions of working materials (anode – electrolyte – cathode) in order to increase life cycle and energy efficiency of the proposed hydronic CCS and the entire combined PP.

It should also be noted that the size and weight dimensions of hydronic CCS can be optimized and a higher energy efficiency of hydronic CCS can be achieved during further research even with the same working materials.

7. Conclusions

This paper shows that based on the hydronic CCS with an aluminum anode it is possible to create an independent hydrogen generator with a wide range of hydrogen discharge speed.

Our research results illustrate that it is possible to create an independent combined power plant (PP) based on O₂/H₂ FC and hydronic CCS serving as a controlled hydrogen

generator, and such PP is characterized by high energy and weight efficiency values.

This paper also shows that a combined “hydronic CCS + O₂/H₂ FC” PP presents an effective and safe solution to the problem of hydrogen storage for an independent PP based on O₂/H₂ FC. The proposed solution is a brand new current source certified by the patents obtained in the course of research [4, 5].

The developed combined PP is efficient for land and household usage such as household and electronic appliances, independent power sources, or power plants in electric transport vehicles. The use of such PP is also promising for aviation and space industries since such PP can serve as the sources of electric power for small-size unmanned aircraft, reserve power sources, independent power plants for operation in open space, or power plants for satellites which require a long period after launch prior to starting operations.

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