THE HYDROGEN PRODUCTION USING ELECTRICAL DISCHARGES OF COLD PLASMA TYPE

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The limited fossil fuel reserves available on Earth, rise more severely the issue of renewable energies (solar, wind, waves or tidal energy). As an important alternative for such renewable energy sources, we remind the use of hydrogen, which has to be produced by a method implying smaller prices and higher efficiency. Thus, the production of hydrogen becomes an important issue at the present time. This paper presents possibilities of using GlidArc type electrochemical reactors for hydrogen production, either starting from the hydrocarbons, either using pulverized water, exploiting the benefit of the pH growth effect, specific to the cold plasma compounds treatment.

Keywords: cold plasma, GlidArc, hydrogen.

1. Introduction

Identifying and using renewable energy sources has been a concern of the hour during the last decades, considering the fossil fuel exhaustion and the major pollution generated by their usage (in thermo-electrical plants and transports).

Considering this, the hydrogen production and usage represent an interesting alternative, if the major inconvenience related to the high energy consumption for such technologies, often exceeding the energy that can be produced by the obtained hydrogen, can be overrun. In addition, the environmental danger associated to producing and using hydrogen at a large scale, processes that generate H_2O and H_2O_2 with pollutant potential, possibly comparable to CO_2 emissions associated to fossil fuel burning, but with major reduction for potential effects, due to the short life time of free hydrogen (a few seconds compared to 100 years for CO_2). If we take into account the risk of self-detonation for concentration above 6% in air, we have a more accurate image of this alternative that concerns experts all over the world.

The main possibilities for hydrogen production refer to:

- catalytic processes
- water electrolysis processes
- chemical processes based on certain chemical reactions.

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Processes that use cold plasma type electrical discharges, processes that use hydrocarbons to obtain syngas, processes that use biogas or dissociation of H_2O by plasma processes in the pulsed corona discharge in water.

The main advantage of such methods, avoiding energy production by burning fossil fuels is to be remarked.

2. Cold Plasma Electrical Discharges. Electrochemical Reactors using Cold Plasma.

The electrical discharge has a stationary manifestation corresponding to intersection points between the **volt-ampere** dependence characteristic to electrical discharges, $\mathbf{U_d(i)}$, and the line **(U-Ri)**, called dynamic characteristic of the circuit, as can be observed in Fig. 1.

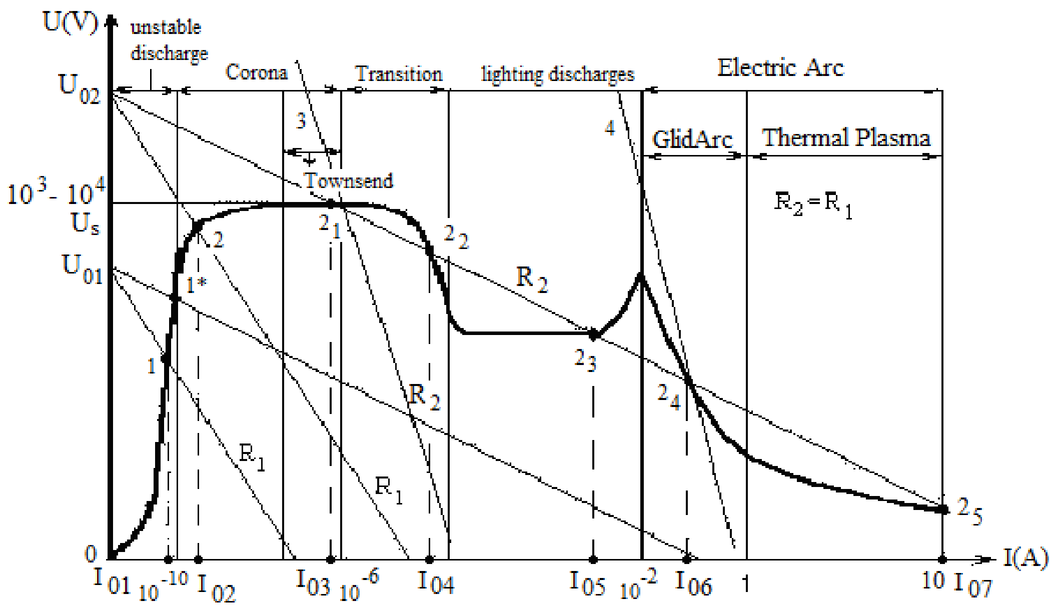

Fig. 1. Possibilities of obtaining cold plasma type electrical discharges.

The analysis of the working points for the electrical discharge behavior with respect to the $U_d(i)$ dependency defines five distinct areas:

- area (1), also called the cumulative area, characterized by very small values for the current through the discharge that increase with the voltage according to the very well known "3/2 law" in physics;
- area (2), called the multiplication area, where the number of charge carriers increases due to ionization phenomena, so that relatively small increases of the voltage with respect to the U_s voltage generate major increases for the

current through the discharge which can be Corona, dielectric barrier discharge (DBD) or pulsed type;

- area (3), where non-luminescent discharges occur, usually called Townsend area;
- area (4), corresponding to luminescent discharges, subnormal, normal or supernormal discharges, sometimes called "glow discharges";
- area (5) refers to discharges characterized by high values for the current towards electric arc.

The particularities regarding behavior for various types of electrical discharges as well as the conditions for obtaining these are suggested by the data in Table 1.

Table 1

Parameters for electrical discharges

Discharge type / Parameters	Corona	Pulsed DBD	Luminescent	GlidArc	**Electric Arc** Thermal plasma
U [kV]	> 10	100	5	1 - 20	30 V – 50 V
I [A]	$< 10^{-5}$	$< 10^{-3}$	0,1	1	$10 – 10^{3}$
p [atm]	<= 1	<= 1	<<= 1	1	1
T [K]	500	500	< 500	2000	> 10000
X	$< 10^{-6}$	$< 10^{-6}$	$< 10^{-4}$	$< 10^{-2}$	10^{-2} - 1
J [A/cm^2]	10^{-9}	10^{-5}	10^{-3}	$1-10^{2}$	$10^{2} - 10^{4}$

We specify the fact that "cold plasma" designates the electric discharge for which the absolute temperature is approximately 2000-3000 K but also are characterized by a notable difference between the electron's temperature, T_e and the ion's temperature, T_i, this being comparable with the gas temperature, T_g, as indicated by the curves in Fig. 2, thus, referring to a behavior outside thermodynamic equilibrium.

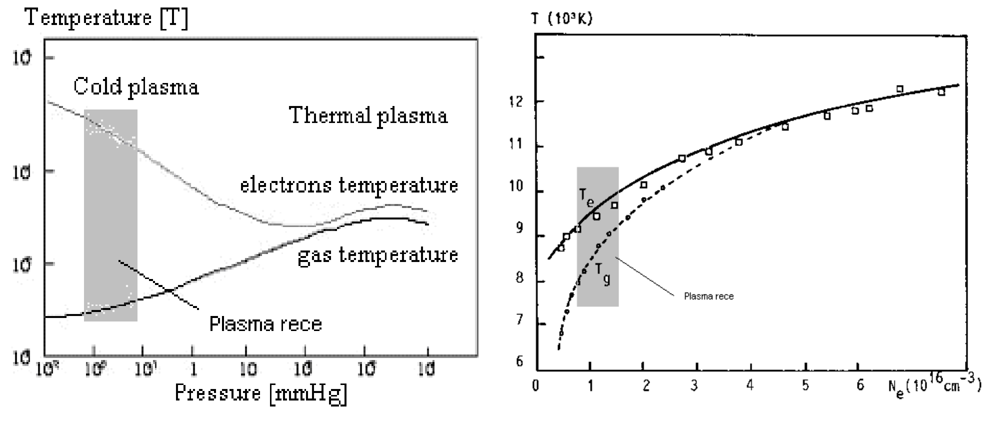

Fig. 2. Concerning cold plasma type electric discharges.

Cold plasma discharges are interesting, for example, from the point of view of electrochemical applications, since these generate active species (electrons, ions, excited particles, photons) having a very short life time, 10^{-5} s, but able to generate meta-stable radicals (for example OH^- and NO^+), with a much longer life time, of 10^{-4}-10^{-3} s, that can maintain useful electrochemical reactions, which does not occur for thermal plasma that eventually exploits thermal effects.

The operation of cold plasma electrochemical reactors is based on ensuring possibilities of igniting and burning of the useful electric discharge between two or more divergent metallic electrodes. The factors that influence the behavior of these electric discharges mainly refers to the plasmagen gas parameters, but the discharge's evolution has a highly depends on the electric circuit's parameters.

The ignition of electric discharges is critically influenced by the presence of free electrical charges in the space between the metallic electrodes, produced by cosmic radiation, X rays or UV radiation, of about 1000 electrons/cm^3, therefore the evolution of such phenomena and especially obtaining a certain type of discharge implies the simultaneous fulfillment of particular conditions for each factor of influence (pressure, temperature, gas nature, circuit's electric resistance, supply's voltage).

We announce the fact that there is a wide variety of cold plasma electrochemical reactors, using corona, DBD or gliding discharges, supplied with direct or alternative current, eventually with pulsed current, that have proven their usability in various areas such as air or compounds depollution, metallic or plastic surfaces treatments or bacterial bio-decontamination. Below, we will describe the GLIDARC type reactor, for which a particular reactive potential is announced, as indicated in Table 1.

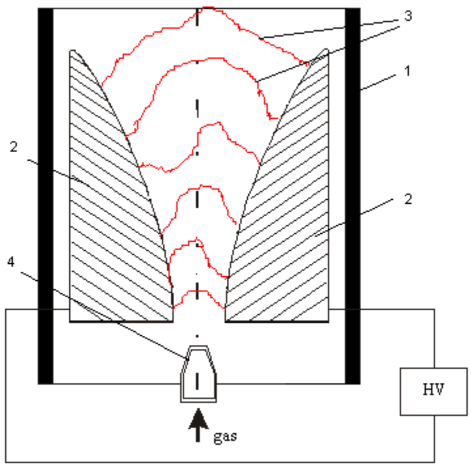

Fig. 3. GlidArc reactor. 1-enclosure; 2-main electrodes; 3-electric discharges; 4-calibrated nozzle

The principle configuration for a GlidArc reactor can be observed in fig. 3. Two main divergent electrodes (2), placed in the reactor's enclosure (1) are connected to a high voltage power supply (HV). A gas flow obtained using the calibrated nozzle (4) "washes" the discharges (3) that ignite between the main electrodes, maintaining the parameters at levels corresponding to cold plasma and ensuring the gliding of the discharges towards the upper part of the electrodes.

3. Methods for hydrogen production using cold plasma

Hydrogen production by GLIDARC type cold plasma usually appeals to hydrocarbons (fossil fuels, C_nH_{2n+2}), but can also employ using biogas. In particular temperature conditions, with a pre-heating up to (400-600) ºC, methane, for example, passed through a GLIDARC type reactor (other types of cold plasma can be used), along with the air that “washes” the useful discharge leads to syngas generation, according to the known reaction:

$$2CH_4 + O_2 \rightarrow 4H_2 + 2CO \quad (1)$$

After separating Co from this mixture hydrogen is obtained so that burning 1 Kg of methane that has as result obtaining 5000 KJ and CO_2 can be substituted with the non-pollutant burning of 250 g of hydrogen to obtain 30000 KJ, the non-pollutant residue being water.

Also bio-oils can be used for obtaining syngas, treated in cold plasma reactors, as indicated by research conducted at the University of Orléans, [6], where notable results were obtained using the previously suggested method.

Obtaining hydrogen is possible using a poor biogas, (35-50)% CH_4, in special conditions, using a GLIDARC electrochemical reactor, according to the reaction:

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \quad (2)$$

same result being possible if Glycerol (Glycerine), C3H5(OH3) is used.

Water dissociation for hydrogen production is an important challenge for experts, such preoccupations existing in laboratories world wide. The conductivity of the compound sprayed in the area where active species produced by the useful discharge are present has a major importance for using such methods, and obtaining hydrogen in quantities of over 5µMol/s using methanol or ethanol additions in water for a GLIDARC reactor operating with inert gas point to promising results for researches started in at the “Gh. Asachi” Technical University of Iaşi.

5. Conclusions

Hydrogen production using cold plasma type discharges is an interesting and promising alternative offered by current research, well situated in the competition with classic hydrogen production methods.

Such methods are based on using compounds like fossil hydrocarbons, biogas, bio-oils, but especially water that is highly accessible but also highly recoverable as residue in the process of exploiting hydrogen based energy.

Optimizing the operation of the electrochemical reactor and identifying the most convenient reaction conditions are directions to be followed for refining and imposing these methods.

Acknowledgements:

This work was supported in part by the Romanian National Authority for scientific research under a project PCE IDEI 977/19.09.2009

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