Journal of International Scientific Publications: Materials, Methods and Technologies

Volume 8, ISSN 1314-7269 (Online), Published at: http://www.scientific-publications.net

RECENT ADVANCES IN HYDROGEN GENERATION BY CONTACT GLOW DISCHARGE ELECTROLYSIS: REVIEW

Sergii Bespalko

Department of Mechanical Engineering, Cherkasy State Technological University

460 Shevchenko Boulevard, Cherkasy, Ukraine 18006

Abstract

A review of investigations concerning special process called plasma electrolysis or contact glow discharge electrolysis (CGDE) is presented in the article. It is described physicochemical mechanisms leading to full glow discharge and phenomena occurring in the vicinity of a glow discharge electrode during the CGDE. Comparison of the CGDE as a hydrogen generating method with other methods of hydrogen production notably methanol steam reforming, conventional water and water vapor electrolysis is carried out as well. It is shown that the CGDE can be considered as a perspective technology for hydrogen generation in the future which is based on the non-Faradaic law phenomenon.

Key words: *liquid solution, electrode, high voltage, plasma electrolysis.*

1. INTRODUCTION

The sun and wind are the two largest sustainable sources of carbon-free power, but to utilize their potential a key hurdle posed by their intermittent nature must be overcome. Unlike other forms of renewable energy, such as hydropower and geothermal energy, the energy generated by the wind and by photovoltaics fluctuates. This fluctuation poses a sizable challenge to the power grid integration and widespread adoption as the mainstream power sources. (Pieper & Rubel 2010)

While there are several possible answers to the intermittency challenge, one of the more viable solutions is a credible form of electricity storage. Power storage can improve the efficiency and reliability of an electric utility system by reducing spinning reserve requirements to meet peak power demands. This makes better use of efficient base load generation and allows a greater use of intermittent renewable energy technologies. (Pieper & Rubel 2010, Steward et al. 2009)

Currently, hydrogen is regarded as one of the most suitable ways to store renewable electricity, because of its high energy density and hence high energy capacity. Combined with fuel cell technology, this makes hydrogen storage most appropriate for compensation of long-term fluctuations. (Steward et al. 2009)

Conventional electrolysis is the most common method used to produce 99% pure renewable hydrogen. But the current water electrolysis systems' capital cost, along with the high cost of electricity, limit widespread adoption of electrolysis technology for renewable hydrogen production. Water electrolysis capital cost reduction and efficiency improvement are required, along with designing utility-scale electrolyzers for grid integration that are compatible with low-cost, near-zero emission electricity sources.

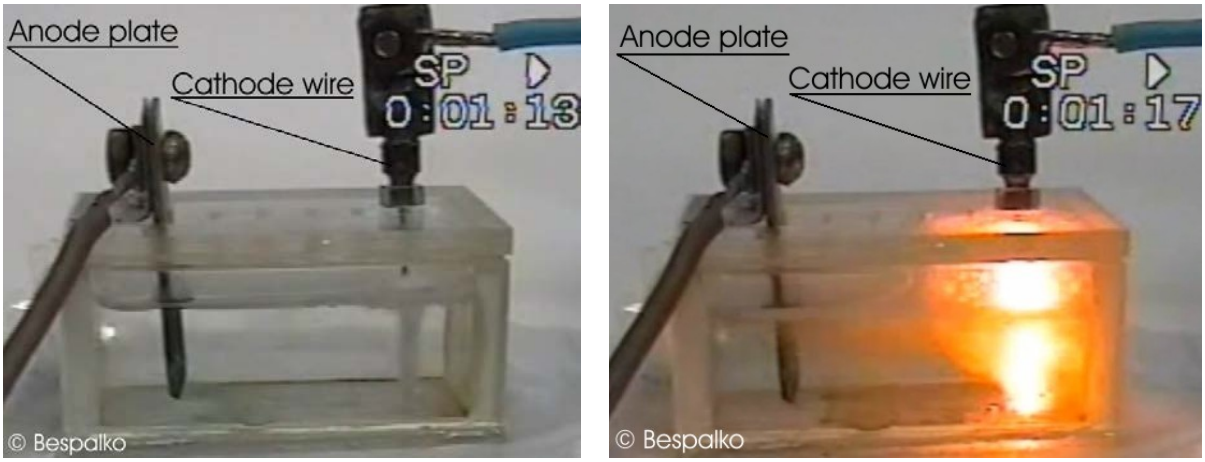
Recently much attention has been given to a special kind of electrolysis which is called plasma electrolysis or contact glow discharge electrolysis (CGDE). Studying this method, Japanese scientists found the anomalous hydrogen production by the plasma electrolysis process sometimes is 80 times higher than normal Faradic gas generation. The plasma is formed on the cathodic surface in a liquid solution when the immersed metal electrodes undergo high-voltage electrolysis. (Mizuno, Ohmori & Akimoto 2004, Mizuno, Akimoto & Ohmori 2002, Mizuno et al. 2005)

High efficiency and improved plasma electrolysis process output could overcome the drawbacks of renewable hydrogen production as a way of electricity storage.

Volume 8, ISSN 1314-7269 (Online), Published at: http://www.scientific-publications.net

2. PHYSICOCHEMICAL MECHANISMS LEADING TO FULL GLOW DISCHARGE AND PHENOMENA OCCURRING IN THE VICINITY OF THE GLOW DISCHARGE ELECTRODE

The contact glow discharge electrolysis is a novel kind of electrochemical process in which plasma is sustained by direct current or a direct current pulsed glow discharge between the electrode and the surface of the surrounding electrolyte. Conventional normal electrolysis is transformed into the contact glow discharge electrolysis when the applied voltage is sufficiently high in the aqueous media (Figure 1). A remarkable feature of the plasma electrolysis process is a strong deviation of the chemical yields in the vicinity of the glow discharge electrode, than there is in a conventional electrolysis predicted by Faraday's law. The chemical yields obtained near the glow discharge electrode are several times higher than the faradic value, and the chemical products are new for conventional electrolysis. (Yan, Chen & Wang 2006, Mills et al. 2002)



a) b)

Fig. 1 Transformation of the electrolysis process from conventional mode to the glow discharge mode with the applied voltage (Bespalko & Kachymov 2013):

a) conventional mode of the electrolysis process, b) full glow discharge mode.

Critical investigations (Sengupta & Singh 1994, Sengupta, Srivastava & Singh 1997, Sengupta, Singh & Srivastava 1998, Gangal, Srivastava & Sengupta 2009) of the contact glow discharge electrolysis growth in an aqueous media showed that the sequence of events leading to full CGDE involves: normal electrolysis, solvent vaporization near an electrode by Joule heating, the onset of hydrodynamic instabilities with vapour sheathing the electrode, ionization of the vapour sheath and finally glow discharges across the vapour sheath. Furthermore, electrode (anode or cathode) at which the conditions allow easier the onset of hydrodynamic instabilities is found to be the location of CGDE.

The critical voltage for the onset of full glow discharge at an electrode, called the mid-point voltage, is characteristically invariant to external variables. However, the mid-point voltage and the nature of the glow discharges at an anode are quite different from those at a cathode. (Jin et al. 2010)

Sengupta and coauthors (Sengupta & Singh 1994, Sengupta, Srivastava & Singh 1997, Sengupta, Singh & Srivastava 1998, Gangal, Srivastava & Sengupta 2009) studied the onset, location and chemical effects of contact glow discharge electrolysis. According to their comprehensive investigations, the mid-point voltage depends on the polarity of the CGDE: 420 V for the anodic CGDE and 160 V for cathodic CGDE in aqueous inert-type electrolyte of K_2SO_4 with 0.05 M concentration.

The study showed that non-faradaic yields of anodic CGDE originate in two different reaction zones (Figure 2): (1) the plasma around the anode and (2) the liquid phase near the plasma-anolyte interface.

(1) In the reaction zone within the plasma around the anode H_2O vapor molecules dissociate into H_2 and O_2 to a degree depending on the magnitude of the power dissipated there. Therefore, the reactions within the plasma appear to follow a mechanism observed for water vapor decomposition in electrical discharges (A. von Engel 1965):

$$H_2O \rightarrow H^{\bullet} + OH^{\bullet},$$

$$H^{\bullet} + H^{\bullet} \rightarrow H_2,$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O + \frac{1}{2}O_2,$$

$$OH^{\bullet} + H^{\bullet} \rightarrow H_2O.$$

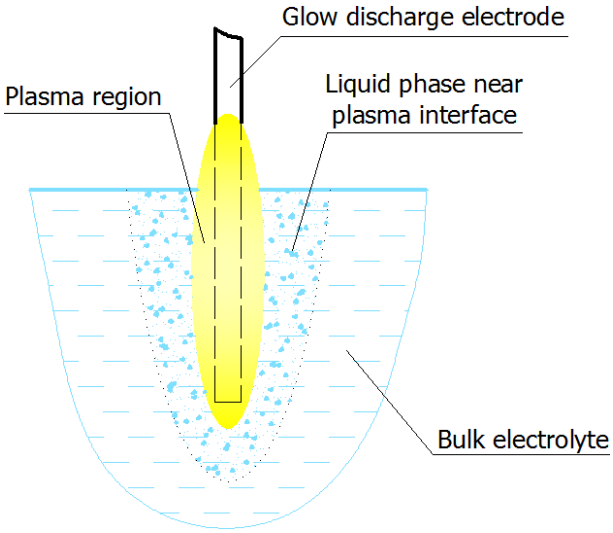


Fig. 2 Illustration of the reaction zones at the glow discharge electrode.

According to the research of Paulmier, Bell & Fredericks 2007, the water vapor molecules within the plasma discharge can be dissociated by four different processes:

- the photodissociation,
- the electron impact dissociation,
- the ion impact dissociation,
- and the thermal impact dissociation.

It was assumed that the thermal dissociative process can play a significant role. The temperature of neutral and ionized species is relatively high (approximately 500 K or higher) due to the high energy exchange by collision between the electrons, and the molecules and ions of the gas. The degree of ionization caused by the generated electrons remains relatively low making the electron impact dissociation process negligible in regard of the thermal one. Submitted to the high plasma temperature, the surface of the cathode is strongly heated and vaporized, the electrolyte is then thermally dissociated at the surface of the cathode. (Paulmier, Bell & Fredericks 2007)

(2) In the liquid-phase reaction zone near the plasma-anolyte interface, liquid H_2O molecules break up into H_2 and H_2O_2 plus O_2 by the Hickling's radiolytic mechanism. (Sengupta & Singh 1994, Sengupta, Srivastava & Singh 1997, Sengupta, Singh & Srivastava 1998)

According to the Hickling's radiolytic mechanism (Hickling & Ingram 1964), each $H_2O^+_{gas}$ ion, after acceleration in the steep cathode fall near the plasma-anolyte interface, is driven into the anolyte solution with energies sufficient to break up several liquid water molecules into $H^{\bullet}$ and $OH^{\bullet}$ radicals by ionization and activation, in addition to the breakup of one water molecule by normal electrolytic charge transfer to produce one $OH^{\bullet}$ radical. The radicals diffuse into the bulk anolyte and undergo several reactions which are known to

occur at high velocities from pulse radiolysis.

The relative importance of the two mechanisms, occurred in the plasma region and liquid-phase reaction zone, depends on the magnitude of the voltage applied. Around the mid-point voltage of 420 V, the mechanism occured is principally the liquid phase Hickling's radiolytic mechanism accounting for 90% of the yield. However, with a further rise in voltage, the gas phase mechanism becomes increasingly important and at 500 V accounts for 75% of the yield. (Sengupta & Singh 1994)

The total yield of anodic CGDE for the passage of electricity includes: faradaic yields, non-faradaic yields from the plasma reaction region and non-faradaic yields from the liquid-phase reaction zone near the plasma-anolyte interface. (Sengupta, Singh & Srivastava 1998)

During cathodic CGDE, most of the applied voltage drops in the vicinity of the cathode wire-plasma interface. Hence, the field near the plasma-catholyte interface in cathodic CGDE will be less than near the plasma-anolyte interface during anodic CGDE, and relative to authors' point of view, insufficient to rich the breakup of liquid water molecules in the catholyte. Therefore the entire yield of H_2 and O_2 seems to originate by dissociation of gaseous water molecules within the plasma at the cathode, following the mechanism of water vapour decomposition in electrical discharges. (Sengupta & Singh 1994)

Presumably, the insufficient field near the plasma-catholyte interface is linked with low applied voltage of 240 V only in cathodic CGDE comparatively with 500 V of applied voltage in anodic CGDE.

3. HYDROGEN GENERATION BY THE CONTACT GLOW DISCHARGE ELECTROLYSIS

Liu et al. 2012, investigated light emissions and radicals formed by plasma of anodic contact glow discharge electrolysis. In their study, the plasma was generated by glow discharges at the tip of Pt anode wire in contact with 0.015 M sulfuric acid solution. Emissions of H atoms and OH radicals were observed when the applied voltage was above 430 V. When the applied voltage increased to 450 V, emission of O atoms was additionally detected. The emission intensities of these radicals and atoms increased with the increasing applied voltage. When the applied voltage exceeded 460 V, thermal radiation from the Pt anode was apparent in the visible and infrared region. The emission spectrums defined in the study are quite similar to those in high frequency microwave discharge (Nguyen, Foster & Gallimore 2009), although the type of discharge is completely different.

Electron temperature of the plasma increased with the applied voltage from 10×10^3 K to 15×10^3 K by comparison of the intensities of H_α and H_β lines corresponding to 0.862 eV and 1.29 eV of electron energy respectively. The mean electron density was estimated to be 7.4×10^{17} cm^{-3}, at applied voltages from 440 to 500 V.

Mizuno T. and coauthors (Mizuno, Ohmori & Akimoto 2004, Mizuno, Akimoto & Ohmori 2002, Mizuno et al. 2005) studied hydrogen gas generation during cathodic plasma electrolysis. In the experimental work, the light K_2CO_3 water solution with a 0.2 M concentration was used as an electrolyte. The hydrogen generation, which exceeded Faraday's law, was continuously observed when temperature, current density, input voltage, and the electrode surface area met certain conditions. A minimum input voltage, required to induce the plasma state, was estimated as 120 V. The lowest electrolyte temperature at which plasma formed was 75 °C. The anode surface area was three times larger than the cathode surface area.

In conventional electrolysis, the hydrogen amount is proportional only to the input current. Current efficiency is defined as the ratio of the hydrogen amount predicted from input electric charge based on Faraday's law. Its value is unity in normal electrolysis.

However, when the input voltage was increased, current efficiency exceeded the unity in plasma electrolysis. Current efficiency was greater than ten when plasma electrolysis occurred at 300 V. It increased 80 times within a few seconds. However, it was an extremely unstable phenomenon.

Using the experimental results, Japanese scientists concluded that hydrogen excess in glow discharge electrolysis was generated presumably by thermolysis. Electrical power efficiency increased with an input voltage but it only reached 10% at 325 V.

Chaffin et al. 2006, showed that in plasma electrolysis, metallic electrodes do not have to be immersed in water to produce hydrogen and oxygen, as happened in traditional electrolysis. Instead, the electrodes can interact with water at atmospheric pressure, when plasma is located between the electrode tips and the water surface.

Experiments, and a spectral analysis of the plasma produced light, as well as a spectroscopic testing of gases from a region near the negative electrode, clearly indicated that the plasma associated with the negative electrode brought out hydrogen from the water. This method showed that high velocity hydrogen transport, through the gas phase plasma-bounding regions, might replace the low-speed diffusion through the liquid phase, which is currently used in conventional electrolysis.

Yan Zong-Cheng and coauthors (Yan, Chen & Wang 2006), studying the chemical yields and energy consumption in cathodic CGDE, determined that the volume of gas liberating from the cathode, after condensation of water vapour, was in substantial excess of the Faraday's law value. Cathodic output increased with the discharge voltage. The cathode gas contained considerable percentage of H_2, e.g. the cathodic liberating gas mixture contained 86.7% of H_2 and 13.3% of O_2 (volume concentration) at the condition of 400 V voltage across the circuit with Na_2CO_3 solution. When the voltage across the circuit was equal to 550 V, the volume of cathodic gas with Na_2CO_3 solution was 16.97 times greater than the Faraday's law value.

Carbon monoxide and carbon dioxide also were detected in the cathode liberating gas due to decomposition of CO_3^{2-} at the interface of plasma phase and liquid phase by the activation of active radicals produced in the plasma sheath presumably. The percentage of CO and CO_2 detected were 1.5% and 0.75% (volume consentration) respectively.

However, much power was depleted on the water vaporization over the cathode in this hydrogen generation process. It was estimated that at 650 V the total energy consumption was approximately 300×10^3 kJ per cubic meter of cathode liberating gas. The total energy consumption consisted of the energy consumption spent for water vaporization (approximately 290.87×10^3 kJ/m^3) and 9.13×10^3 kJ/m^3 (or 204.5 kJ/mol), named the net energy consumption, was spent to produce cathodic gas only. It is a matter of fact that value of the net energy consumption is less than the corresponding theoretic value of the conventional water electrolysis method (10.58×10^3 kJ/m^3).

The study also showed that methanol molecules are more active than water molecules. Thus, when the methanol electrolyte concentration equaled 5% (volume concentration), the cathodic output was 14.45 times higher than with a solution using water as the solvent only. The energy consumption per cubic meter of hydrogen was 10.381×10^3 kJ/m^3 when the methanol concentration was 5% (volume concentration). This value is less than the corresponding theoretic value of the conventional water electrolysis method (10.58×10^3 kJ/m^3). When the methanol concentration in water solution equaled 50% (volume concentration) the energy consumption was 3.496×10^3 kJ/m^3 (78.35 kJ/mol). (Yan, Chen & Wang 2006)

The hydrogen concentration was more than 95% and the oxygen concentration was less than 0.5% (volume concentration) if the volume concentration of methanol was greater than 15% (volume concentration). One thing that should be pointed out is that the concentration of CO_2 in liberating gas was very low, e.g. when the mass methanol concentration of the solution was 50% (volume concentration), the CO_2 concentration of the liberating gas was 1.4% (volume concentration). That is to say, to produce 1 hydrogen mole just 0.015 moles of CO_2 is released. Based on this, hydrogen production by methanol decomposition with cathodic CGDE can be regarded as a green technology.

Another study (Yan, Li & Lin 2009), performed by Yan Zong-Cheng and coauthors, showed that in plasma electrolysis of methanol solutions discharged polarity has important influence on hydrogen yield. The H_2 yield of cathodic CGDE was 9.13 and 10.57 times higher than H_2 yield of anodic CGDE at the same conductivity of the methanol solutions using NaOH and H_2SO_4 as the supporting electrolytes respectively.

In addition, the experimental results indicated that high energy electrons are the most important species to initiate methanol decomposition.

Moreover comparing different plasma-assisted hydrogen producing technologies notably dielectric barrier discharge (DBD) plasma, corona discharge and the CGDE, the study of Yan Zong-Cheng and coauthors (Yan, Li & Lin 2009) also showed that the CGDE displays better performances in accord with the energy consumption, hydrogen concentration and the CO_2 released per hydrogen volume at methanol decomposition.

Therefore, according to the review performed, it can be concluded that the CGDE can be considered as a feasible technology for hydrogen generation based on the non-Faradaic law phenomenon.

4. APPROPRIATENESS OF THE CONTACT GLOW DISCHARGE ELECTROLYSIS FOR HYDROGEN GENERATION

In order to define reasonability of hydrogen production by the plasma electrolysis process it is necessary to make comparison of the plasma way with other methods of hydrogen generation, notably:

- methanol steam reforming because as was noted before the methanol-water mixture was used as a liquid solution for highly effective hydrogen generation in some experiments,
- conventional water electrolysis because of its simplicity and widespread use,
- water vapor electrolysis because water vapor exists in the vicinity of the glow discharge electrode and breaks up into hydrogen and oxygen during plasma electrolysis.

4.1 Comparison of the contact glow discharge electrolysis as a hydrogen generating method with methanol steam reforming

The methanol steam reforming is a process used in chemical engineering, especially in the area of fuel cell technology, which utilizes methanol-water mixture as a hydrogen carrier to produce pure hydrogen gas and carbon dioxide. The favour for methanol as the chemical carrier for hydrogen generation is mainly due to its ready availability, high energy density, easy storage and transportation. (Lwin et al. 2000)

In the process, a liquid water-methanol mixture with a molar concentration ratio (water/methanol) equaled 1.0 ÷ 2.0 and in presence of catalyst is heated, vaporized and superheated to a temperature of approximately 200 ÷ 300 °C. (Suh et al. 2009)

The methanol steam reforming is described by the following thermo-chemical equation (Gulari & Brown 2002):

$$\underset{gas}{CH_3OH} + \underset{gas}{H_2O} \rightarrow 3\underset{gas}{H_2} + \underset{gas}{CO_2}, \quad \Delta H^0_{R,298} = +49.4\,\frac{kJ}{mol}.$$

The reaction is extremely endothermic, thus heat must be provided to sustain the process. At standard ambient temperature and pressure, a change of the standard reaction enthalpy is $\Delta H^0_{R,298}$=+49.4 *kJ/mol*.

Theoretically, the conversion efficiency of methanol is equaled to 100% but practically it is lower. According to the experimental research of Gulari & Brown 2002, in methanol steam reforming the maximum conversion efficiency and hydrogen yield depend on the amount of water. At molar feed ratio of 1.0, the maximum conversion was only 75% and hydrogen yield was 2.21 moles per mole of methanol whereas at 1.5 the maximum conversion was 92% and hydrogen yield was 2.71 moles. The highest methanol conversion efficiency was 95% and the hydrogen yield was 2.8 moles per mole of methanol at water/methanol molar feed ration of 2.0 corresponding to 47.1% of methanol mass concentration in water-methanol mixture.

Thus the methanol conversion and hydrogen production rate increase with increasing water/methanol molar ratio. But hydrogen yield cannot be raised above the theoretical limit of 3 moles per mole of methanol. (Lwin et al. 2000)

In the study, the methanol steam reforming occurred in presence of $Pt/CeO_2/Al_2O_3$ catalyst mixture. The highest methanol conversion efficiency of 95% was obtained at 1 atm. pressure and reaction temperature of 285 °C.

Taking into account heating, vaporization and superheating of the water-methanol mixture to the reaction temperature of 285 °C, in this case the overall energy consumption is 72.57 kJ per mole of hydrogen produced in methanol steam reforming.

As was shown before in the research of Yan Zong-Cheng and coauthors (Yan, Chen & Wang 2006), the energy consumption for hydrogen production was determined in plasma electrolysis of water-methanol mixture. In their study when the methanol concentration in the solution equaled 44.3% of methanol mass concentration, the energy consumption was 78.35 kJ per mole of hydrogen gas. Neglecting the small difference between methanol mass concentrations in observed investigations, the energy consumption in plasma electrolysis is approximately 1.08 times larger comparatively with the energy consumption estimated for methanol steam reforming.

In the case of consideration the difference between methanol mass concentrations we can assume the same energy consumption. Furthermore, as was shown above (Yan, Li & Lin 2009), in plasma electrolysis of water methanol mixture very small amount of CO_2 as a product of reaction (only 0.015 moles per 1 mole of hydrogen) is released. This quantity is approximately 22 times less than in conventional methanol steam reforming.

Relative to this fact, the plasma electrolysis of methanol solutions can be regarded as a CO_2 free technique.

But a main disadvantage of the plasma electrolysis process is that energy must be supplied in the form of electricity to induce the plasma versus the methanol steam reforming where energy is supplied in the form of heat.

4.2 Comparison of the contact glow discharge electrolysis with conventional and water vapor electrolysis

Electrolysis is the breakup of water into molecular hydrogen and oxygen through the introduction of electrical energy. The traditional principle involves the passage of direct current through water between two electrodes – cathode and anode. (Chaffin et al. 2006)

Essentially, through the electrolysis process, one mole of water produces 1 mole of hydrogen and 0.5 moles of oxygen gases. The overall reaction of the water electrolysis is (Laguna-Bercero 2012):

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2, \quad \Delta H^0_{R,298} = 285.83 \frac{kJ}{mol}.$$

The minimum electric energy supply required for the electrolysis process is equal to the change in the Gibbs free energy (ΔG) (Chaffin et al. 2006):

$$\Delta G = \Delta H - T\Delta S,$$

where ΔH is the enthalpy change (the total energy need), T is the operation temperature in Kelvin, ΔS is the entropy change.

Assuming that the process is implemented at 298 K and 1 atm. of pressure (ideal case of low temperature electrolysis), the total energy demand (ΔH) is equaled to 285.83 *kJ/mol*. Within the total energy needed to electrolyze water, only ΔG equaled 273.1 *kJ/mol* must be supplied in the form of electricity because TΔS in the quantity of 48.7 *kJ/mol* can be delivered from the environmental temperature. (Chaffin et al. 2006)

Although ΔG is the energy to be applied in the electrolysis to release hydrogen, the techniques and process factors for supplying the ΔG needed is fraught with losses in efficiency and energy. Furthermore, one of the key constraints is the problem of bubbles and slow diffusion rates of produced hydrogen in liquids. These constraints are minimized and possibly absent in the plasma electrolysis technology. (Chaffin et al. 2006)

Nowadays industrial applications of low temperature electrolyzers have energy efficiency of about 70-75%. (Laguna-Bercero 2012, Mazloomi, Sulaiman & Moayebi 2012)

Although low temperature electrolysis is a mature technology, high temperature steam electrolysis presents a greater potential. The required electrical power is reduced at higher temperatures if the unavoidable joule heat of an electrolysis cell is used in the H_2O splitting process. Another advantage of the high temperature electrolysis is the reduction of electrode overpotentials which cause power losses in the electrolytic cell. (Laguna-Bercero 2012)

Even though total energy demand is increased, the decrease in electrical energy demand is more noticeable, as over two thirds of the cost of electrolytic hydrogen arises from the use of electricity. Operating at higher temperature can therefore decrease the cost of the hydrogen produced, especially if the increase in heat energy demand can be fulfilled by an external heat source, such as nuclear power, renewable energy or waste heat from high-temperature industrial processes. (Laguna-Bercero 2012)

As was shown above in the research of Yan-Zong Cheng and coauthors (Yan, Chen & Wang 2006), the estimation of energy consumption per cubic meter of cathode liberating gas was carried out in plasma electrolysis. The results clearly showed that much energy approximately 290.87×10^3 *kJ/m*^{3} was spent on water vaporization and only 9.13×10^3 *kJ/m*^{3}, named the net energy consumption, was spent to produce cathodic gas.

According to the Chinese experimental results, the net energy consumption is less than the theoretic value of normal water electrolysis method of 10.58×10^3 *kJ/m*^{3} at 298 K and even the energy consumption of modern water vapour electrolyzers of $9.252 \times 10^3 \div 10.8 \times 10^3$ *kJ/m*^{3} at 1023 K (Laguna-Bercero 2012, Dönitz & Erdle 1985). This fact makes plasma electrolysis process attractive and perspective for hydrogen generation in the future.

But performed analysis clearly shows that the total energy consumption is fraught by energy consumption for water vaporization. Due to these losses, the power efficiency of hydrogen production is very small, only 3.5% in

accord with results of Chinese experiments (Yan, Chen & Wang 2006). In some experiments (Mizuno, Ohmori & Akimoto 2004) carried out by Japanese scientists, 10% of power efficiency was achieved. Thus, according to these data, the plasma electrolysis as a hydrogen generating process needs development with aim to increase power efficiency.

5. CONCLUSIONS

Thus, summing up the performed analysis following conclusions can be drawn:

1. The CGDE can be considered as a feasible technology for hydrogen generation which is based on the non-Faradaic law phenomenon.
2. The CGDE of water-methanol mixture can be regarded as a CO_2 free technique because of very low level of CO_2 emission, e.g. to produce 1 hydrogen mole just 0.015 moles of CO_2 is released. This quantity is approximately 22 times less than theoretic level of CO_2 emission in conventional methanol steam reforming at the same energy consumption.
3. In the CGDE the net energy consumption (energy spent to produce cathodic gas only) is less than the theoretic value of normal water electrolysis method of 10.58×103 kJ/m^3 at 298 K and even the energy consumption of modern water vapor electrolyzers of $9.252\times10^3 \div 10.8\times10^3$ kJ/m^3 at 1023 *K*. This fact makes plasma electrolysis process attractive and perspective for hydrogen generation in the future.
4. Currently power efficiency of hydrogen production by the CGDE of aqueous solutions is low. The greatest power efficiency of the process reached by Japanese scientists is only 10%. Thus, the plasma electrolysis as a hydrogen generating process needs development to overcome this main drawback.

REFERENCES

A. von Engel 1965, Ionized Gases, 2nd edition, Clarendon Press, Oxford.

Bespalko, S & Kachymov, A 2013, 'Contact Glow Discharge Electrolysis: Observation of the Full Glow Discharge at an Electrode', Proceedings of the IInd International Science-Technical Conference "Modern Issues in Physics, Chemistry and Biology", Sevastopol National Technical University, Sevastopol, pp. 62-64.

Chaffin, J, Bobbio, S, Inyang, H & Kaanagbara, L 2006, 'Hydrogen Production by Plasma Electrolysis', Journal of Energy Engineering, vol. 132, pp. 104-108.

Dönitz, W & Erdle, E 1985, 'High-temperature electrolysis of water vapor – status of development and perspectives for application', International Journal of Hydrogen Energy, vol. 10, pp. 291–295.

Gangal, U, Srivastava, M & Sengupta, S 2009, 'Mechanism of the Breakdown of Normal Electrolysis and the Transition to Contact Glow Discharge Electrolysis', Journal of the Electrochemical Society, vol. 156, pp. F131−F136.

Gulari, E & Brown, J 2002, 'Catalytic production of hydrogen gas by methanol reforming', Fuel Chemistry Division Preprints, vol. 47, pp. 727-728.

Hickling, A & Ingram, M 1964, 'Contact Glow Discharge Electrolysis', Transactions of the Faraday Society, vol. 60, pp. 783-793.

Jin, X, Wang, X, Yue, J & Zhang, H 2010, 'The effect of electrolyte constituents on contact glow discharge electrolysis', Electrochimica Acta, vol. 56, pp. 925-928.

Jin, X, Wang, X, Zhang, ., Xia, Q, Wie, D & Yue, J 2010, 'Influence of Solution Conductivity on Contact Glow Discharge Electrolysis', Plasma Chemistry and Plasma Processing, vol. 30, pp. 429-436.

Laguna-Bercero, M 2012, 'Recent advances in high temperature electrolysis using solid oxide fuel cells: A review', Journal of Power Sources, vol. 203, pp. 4-16.

Liu, Y, Sun, B, Wang, L & Wang, D 2012, 'Characteristics of Light Emission and Radicals Formed by Contact Glow Discharge Electrolysis of an Aqueous Solution', Plasma Chemistry and Plasma Processing, vol. 32, pp. 359-368.

Lwin, Y, Wan Ramli, Wan Daud, Mohamad, A & Yaakob, Z 2000, 'Hydrogen production from steam-methanol

reforming: thermodynamic analysis', International Journal of Hydrogen Energy, vol. 25, pp. 47-53.

Mazloomi, K, Sulaiman, N & Moayebi, H 2012, 'Electrical Efficiency of Electrolytic Hydrogen Production: Review', International Journal of Electrochemical Science, vol. 7, pp. 3314-3326.

Mills, R, Dayalan, E, Ray, P, Dhandapani, B & He, J 2002, 'Highly stable novel inorganic hydrides from aqueous electrolysis and plasma electrolysis', Electrochimica Acta, vol. 47, pp. 3909-3926.

Mizuno, T, Akimoto, T & Ohmori, T 2002, 'Confirmation of anomalous hydrogen generation by plasma electrolysis', Proceedings of the 4th Meeting of Japan CF Research Society, Iwate University, Japan, pp. 27-31.

Mizuno, T, Ohmori, T & Akimoto, T 2004, 'Generation of Heat and Products during Plasma Electrolysis', Proceedings of the 11th International Conference on Cold Fusion, Marseilles, France, pp. 161-177.

Mizuno, T, Akimoto, T, Azumi, K, Ohmory, T, Aoki, Y & Takahashi, A 2005, 'Hydrogen Evolution by Plasma Electrolysis in Aqueous Solution', Japanese Journal of Applied Physics, vol. 44, pp. 396–401.

Nguyen, S, Foster, J & Gallimore, A 2009, 'Operating a radio-frequency plasma source on water vapor', Review of Scientific Instruments, vol. 80, 083503.

Paulmier, T, Bell, J & Fredericks, P 2007, 'Development of a novel cathodic plasma/electrolytic deposition technique: Part 2: Physico-chemical analysis of the plasma discharge', Surface and Coatings Technology, vol. 201, pp. 8771-8781.

Pieper, C & Rubel, H 2010, Electricity Storage: Making Large-Scale Adoption of Wind and Solar Energies a Reality: Technical Report, the Boston Consulting Group, Inc.

Sengupta, S & Singh, O 1994, 'Contact glow discharge electrolysis: a study of its chemical yields in aqueous inert-type electrolytes', Journal of Electrochemical Chemistry, vol. 369, pp. 113-120.

Sengupta, S, Srivastava, A & Singh, R 1997, 'Contact glow discharge electrolysis: a study on its origin in the light of the theory of hydrodynamic instabilities in local solvent vaporisation by Joule heating during electrolysis', Journal of Electrochemical Chemistry, vol. 427, pp. 23-27.

Sengupta, S, Singh, R & Srivastava, A 1998, 'A Study on the Origin of Non-faradaic Behavior of Anodic Contact Glow Discharge Electrolysis: The Relationship between Power Dissipated in Glow Discharges and Nonfaraic Yield', Journal of the Electrochemical Society, vol. 145, pp. 2209−2213.

Steward, D, Saur, G, Penev, M & Ramsden T 2009, Lifecycle Cost Analysis of Hydrogen Versus Other Technologies for Electrical Energy Storage: Technical Report, National Renewable Energy Laboratory / TP-560-46719.

Suh, J, Lee, M, Greif, R & Grigoropoulos, C 2009, 'Transport phenomena in a steam-methanol reforming microreactor with internal heating', International Journal of Hydrogen Energy, vol. 34, pp. 314-322.

Yan, Z, Chen, L & Wang, H 2006, 'Experimental Study of Plasma Under-Liquid Electrolysis in Hydrogen Generation', The Chinese Journal of Process Engineering, vol. 6, pp. 396-401.

Yan, Z, Li, C & Lin, W 2009, 'Hydrogen generation by glow discharge plasma electrolysis of methanol solutions', International Journal of Hydrogen Energy, vol. 34, pp. 48-55.