Journal of Advances in Science and Technology

Vol. VII, Issue No. XIV, August-2014, ISSN 2230-9659

AN ANALYSIS ON THE DIFFERENT PROCESSES OF WATER ELECTROLYSIS

AN INTERNATIONALLY INDEXED PEER REVIEWED & REFEREED JOURNAL

Journal of Advances in Science and Technology
Vol. VII, Issue No. XIV, August-2014, ISSN 2230-9659

An Analysis on the Different Processes of Water Electrolysis

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Abstract – Electrolysis is an electrochemical process in which electrical energy is the driving force of chemical reactions. Substances are decomposed, by passing a current through them. The first observation of this phenomenon was recorded in 1789. Nicholson and Carlisle were the first who developed this technique back in 1800 and by the beginning of the 20th century there were already 400 industrial water electrolysis units in use.

As mentioned before, water is decomposed to hydrogen and oxygen, by passing a current through it in the presence of suitable substances, called electrolytes. Electric current causes positively charged hydrogen ions to migrate to the negatively charged cathode, where a reduction takes place in order to form hydrogen atoms. The atoms formed then combine to form gaseous hydrogen molecules (H2). On the other hand, oxygen is formed at the other electrode (the positively charged anode). The stoichiometry of the reaction is two volumes of hydrogen to one volume of oxygen. The most important part of the construction of electrolysis units is to use adequate electrodes to avoid unwanted reactions, which produce impurities in the hydrogen gas. Another necessary component of such a unit is a separating membrane that allows the passage of ions, or electrons and not oxygen, or hydrogen atoms. This membrane allows the gases to be kept separate in order to avoid the risk of an explosive mixture being formed in the electrolysis unit.

In the initial discovery of electrolysis, an acidic water solution was used, but nowadays there is a trend towards alkaline electrolytes such as potassium hydroxide (KOH). This technology offers the advantages of materials which are cheaper and less susceptible to corrosion compared to those required to handle acids. Electrolysis plants with normal or slightly elevated pressure usually operate at electrolyte temperature of 70-90oC, cell voltage of 1.85-2.05 V and consume 4-5 KWh / m3 of hydrogen, which is obtained at a purity of 99.8% and more. Pressure electrolysis units run at 6-200 bar and there is no significant influence on the power consumption. Because of its high energy consumption and also of the quite substantial investment, water electrolysis is currently used for only 4% of world hydrogen production.

Nowadays research and development into high efficiency electrolysers is flourishing in many areas. A way of improving electrolysis units efficiency is by increasing the process temperature which lowers the voltage required to electrolyse the water, but also requires more expensive materials. Despite the fact that the total energy needed for the electrochemical decomposition of water decreases only slightly with increasing temperature, the reversible part of the energy requirement (ΔF), which is supplied as electrical energy, decreases considerably. Therefore an increasing amount of the total energy could be supplied as heat. At elevated temperatures (800-900oC) the electric power consumption is approximately only 3 kWh / m3 of hydrogen. It must be noted that this technology is still in the development stage.

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INTRODUCTION

Water electrolysis can be done under alkaline conditions with nickel electrodes and many commercial electrolysers utilize this method. Acidic water electrolysis is interesting for the development of PEM-based electrolysers. With a PEM system in connection with e.g., a windmill, it is possible to have a single unit forming hydrogen when the load is low and producing electricity when the load is high. Such a unitised regenerative fuel cell has for instance been used for space applications.[1]

Unfortunately acidic electrochemical water splitting is associated with substantial energy loss, mainly due to the high over-potentials at the oxygen-evolving anode. It is therefore important to find the optimal oxygen-evolving electro-catalyst in order to minimize the energy loss. In a previous researches we have investigated the origin of the over-potential for elemental metal electrodes applying density functional theory calculations. It was found that an oxygen layer has to be formed on the metal surface in order for oxygen evolution to occur. This oxygen layer demands a high potential to be stabilized.

Several experimental investigations have shown that oxide surfaces, particularly rutile-type oxides like RuO2, IrO2 are considerably better as oxygen-evolving electrodes than the elemental metals. In the present study we investigate the reason for this by calculating the stability of the intermediates in the reaction. We consider the most stable surface of three rutile-type oxides, RuO_2, IrO_2 and TiO_2, TiO_2 being included because it is an interesting catalyst for the photo-electrolysis of water and additive to stabilize active RuO_2 and/or IrO_2 anodes. The present work can be viewed as a first step towards a theoretical description of these complex systems. The aim is to determine volcano-type relations of the activity of the anode materials as a function of one single descriptor.[2]

The electrolysis of water is considered a well-known principle to produce oxygen and hydrogen gas. The core of an electrolysis unit is an electrochemical cell, which is filled with pure water and has two electrodes connected with an external power supply. At a certain voltage, which is called critical voltage, between both electrodes, the electrodes start to produce hydrogen gas at the negatively biased electrode and oxygen gas at the positively biased electrode. The amount of gases produced per unit time is directly related to the current that passes through the electrochemical cell.[3]

HISTORY

The history of water electrolysis started as early as the first industrial revolution, in the year 1800, when Nicholson and Carlisle were the first to discover the ability of electrolytical water decomposing. By 1902 more than 400 industrial water electrolysis units were in operation and in 1939 the first large water electrolysis plant with a capacity of 10,000 Nm3 H2/h went into operation. In 1948, the first pressurized industrial electrolyser was manufactured by Zdansky/Lonza. In 1966, the first solid polymer electrolyte system (SPE) was built by General Electric, and in 1972 the first solid oxide water electrolysis unit was developed. The first advanced alkaline systems started in 1978. The history ends up in our days with the development of proton exchange membranes, usable for water electrolysis units and fuel cells, by DuPont and other manufacturers, due to the developments in the field of high temperature solid oxide technology and by the optimization and reconstruction of alkaline water electrolysers [4].

ELECTROLYSIS OF WATER

Electrolysis is the driving of a non-spontaneous chemical reaction by passing a direct electric current through an electrolyte. In electrolysis, positive ions migrate to the cathode and negative ions to the anode. The reactions occurring depend on electron transfer at the electrodes and are therefore redox reactions.

At the anode (+) negative ions in solution may lose electrons to form neutral species. Alternatively, atoms of the anode can lose electrons and go into solution as positive ions. The process is oxidation. At the cathode (-) positive ions in solution can gain electrons to form neutral species. Cathode reactions are reduction reactions. Electrolyte: A liquid that conducts electricity as a result of the presence of positive and negative ions. Electrode: A conductor that emits or collects electrons in a cell. Usually an inert material such as platinum. In the school laboratory hydrogen and oxygen production via electrolysis is usually performed using a Hoffman Voltameter. This is an expensive piece of equipment due to the intricate shaped glassware and use of platinum electrodes.

In this article we will describe the preparation of a simple electrolysis cell that can be cheaply made and used year after year in the science classroom. Ordinary tap water can be used for the electrolysis of water. Water decomposes above 2.0 V into hydrogen and oxygen in a process known as electrolysis. More bubbles form on the negative (hydrogen) electrode than on the positive (oxygen) electrode.

At the anode (+) water decomposes to form oxygen and hydrogen ions:

$$2H_2O\,(l) \rightarrow O_2\,(g) + 4H^+\,(aq) + 4e^- \qquad E^0_{ox} = -1.23\ V \tag{1}$$

At the cathode (-) water decomposes into hydrogen and hydroxide ions:

$$2H_2O\,(l) + 2e^- \rightarrow H_2\,(g) + 2OH^-\,(aq) \qquad E^0_{red} = -0.83\ V \tag{2}$$

And the overall reaction:

$$2H_2O\,(l) \rightarrow 2H_2\,(g) + O_2\,(g) \qquad E^0_{cell} = -2.06\ V \tag{3}$$

The negative cell value (E^o_{cell}) indicates that the process will not proceed spontaneously and electrical energy has to be added.

Pure water conducts electricity very poorly so a water-soluble electrolyte has to be added to "close the circuit". This electrolyte dissociates into cations and anions that carry the charge through the liquid. Care must be taken not to select a salt with ions that are easier electrolyzed than water. Sodium (Na+) is safe as cation, as well as SO_{42}- or CO_{32}- as anions.

Usually sodium hydroxide, NaOH, sodium bicarbonate, $NaHCO_3$ or dilute sulphuric acid is used.

ELECTROLYSIS OF WATER ON OXIDE SURFACES

Direct electrochemical splitting of water is a non-polluting way of producing pure hydrogen. The products are free of carbon-mono-oxide, which is a strong poison in proton exchange membrane (PEM) fuel cells. If the energy needed to run the reaction is provided from sustainable sources, like wind, hydro or solar power, the hydrogen is a clean and CO2-free energy carrier.

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WATER ELECTROLYSIS WITH INDUCTIVE VOLTAGE PULSES

The main idea of Hydrogen Economy is to create a bridge between the energy resources, energy producers and consumers. If hydrogen is produced from renewable energy sources (wind, solar, hydro, biomass, etc.), and used for energy production in the catalytic combustion process, then the energy life cycle does not pollute nature longer. With transition to Hydrogen Economy the Society will live accordingly to the sustainable development model, defined in the 1987.

Hydrogen is not available on Earth in free form; therefore the production process is representing a major part of the final price of hydrogen (Hydrogen Pathway, 2011). This is the main reason while research for effective electrolysis methods is very urgent. On our Planet the hydrogen is mainly located in compounds such as hydrocarbons, water, etc. and appropriate energy is needed to release hydrogen from them. In principle the amount of consumed energy is always greater than that which can be extracted from the hydrogen, and in the real operating conditions, the cycle efficiency does not exceed 50%. The current problem is motivated to seek improvements to existing and discovering new technologies to produce hydrogen from the water – widely available and renewable resource on the Earth.[7]

Water electrolysis is known more than 130 years already, and different technologies are developed giving power consumption around 3.6 kWh/m^3 - high temperature electrolysis, and 4.1 kWh/m3 - room temperature alkaline electrolysers and proton exchange membrane electrolysers. Lower hydrogen production costs is for technologies using closed thermo-chemical cycles, but only in places where huge amount of waste heat is available (for example, nuclear power stations.

Nevertheless what will be the hydrogen price today, in future only hydrogen obtained from renewable resources using electricity from renewable energy sources will save the World, as it was stated in 2nd World's Hydrogen Congress in Turkey. For Latvia the hydrogen obtained in electrolysis using electricity from renewables (wind, Sun, water) also would be the best solution to move to Hydrogen Economics (Dimants et all, 2011). That is because all renewables available in Latvia's geographical situation are giving non- stable and interrupt power, for which the storage solutions are necessary. Usage of hydrogen as energy carrier to be produced from electricity generated by renewables, stored and after used in fuel cell stack to generate electricity is the best solution (Zoulias, 2002).

Efficient and stable electrolysers are required for such purposes. Smaller electrolysis units are necessary also for technical solutions were hydrogen is produced and used directly on demand, for example, hydrogen welding devices, hydrogen powered internal combustion cars.[8,9]

DC power typically is used for electrolysis, nevertheless pulse powering also is proposed. Using a mechanically interrupted DC power supply next interesting phenomena was noticed: immediately upon application of voltage to an electrochemical system, a high but short-lived current spike was observed. When the applied voltage was disconnect, significant current continues to flow for a short time. In 1984 Ghoroghchian and Bockris designed a homopolar generator to drive an electrolyser on pulsed DC voltage. They concluded that the rate of hydrogen production would be nearly twice as much as the rate for DC.

The Latvian Hydrogen Research Team is developing inductive pulse power circuits for water electrolysis cell (Vanags et all, 2011a, 2011b). The studies revealed a few significant differences compared to conventional DC electrolysis of water. New model is established and described, as well as the hypothesis is set that water molecule can split into hydrogen and oxygen on a single electrode (Vanags et all, 2011a). There has been found and explained the principle of high efficiency electrolysis. A new type of power supply scheme based on inductive voltage pulse generator is designed for water electrolysis. Gases released in electrolysis process from electrodes for the first time are analyzed quantitatively and qualitatively using microsensors (dissolved gases in electrolyte solution nearby electrode) and masspectrometer (in atmosphere evolved gases). The hypothesis of hydrogen and oxygen evolution on a cathode during the process of pulse electrolysis is original, as well as interpretation of the process with relaxation mechanisms of electrons emitted by cathode and solvated in electrolyte (Vanags, 2011b).[10,11]

CONCLUSION

Reactive short voltage pulse generator is designed to power water electrolysis cells of different constructions, both with spatially separated and with variable distance electrodes. Required value of electrolysis voltage in the primary circuit of power supply can be reduced by inserting the electrolysis cell in secondary circuit of power supply together with inductive element and reverse diode. For example, in this work electrolysis is provided with direct pulse amplitude 1 V, which induces a short high voltage pulse (tens, hundreds of volts, depending on the conductivity of electrolyte) in the secondary circuit. For studying the process of electrolysis the microelectrode sensors are used to measure concentration of dissolved hydrogen and oxygen gas in the direct vicinity of cathode for the first time.

Electrolysis drives a reaction that is not spontaneous and therefore requires the input of energy to occur. Have your older children research other electrolysis reactions and electroplating (a similar type of reaction) and their uses in industry.

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