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RESEARCH ARTICLE

IMPROVEMENT ELECTROLYSIS OF WATER EFFICIENCY FOR HYDROGEN PRODUCTION USING STAINLESS STEEL NANOPARTICLES SYNTHESIZED BY LASER TECHNIQUE

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ABSTRACT

Hydrogen generators offer the possibility of zero-emissions electricity generation. The current research involves improving the hydrogen generator performance of electrolysis of water by increasing electrolyte efficiency. Stainless steel nanoparticles (SSNPs) were prepared using Pulsed Laser Ablation in Liquid (PLAL) technique and then (0.004g) added to the electrolyte. For the purpose of comparison, the same generator was operated but using an electrolyte composed of a strong alkali (NaOH) dissolved in high purity water. The amount of hydrogen produced during the operating period was measured and the maximum product quantity was 230 ml within one minute. Nanoparticles were characterized by means of AFM test, PH measurement, and an Electrical Conductivity (EC) test of the nano solution.

KEYWORDS

Electrolysis, Hydrogen generators, Pulsed laser ablation technique, Stainless steel nanoparticles.

1. INTRODUCTION

Material properties and its behavior in nano scales show greatly differs when they compared to micro scales. In nano levels, the outstanding characterizations such as optical, electronic, and electrical of nanoparticles becomes differ from that of bulk material of which they are made [1]. Different methods have been used and available to reduce the particles size in order to get new properties for the manufacturing of nanomaterials.

One of the most important techniques for preparing metal nanoparticles is PLAL. It is a simple, effective, and flexible method compared with conventional chemical and physical methods. PLAL has advantages of purity, stability of the fabricated nanoparticle colloids, and do not require a vacuum chamber. In addition, controlling the size and the shape of the prepared particles could be achieved by optimization of laser parameters [2, 3]. In this technique, the solid target is immersed in high purity water and the laser beam is focused on it. The material particles absorb laser energy and evaporate into plasma. The plasma cloud then expands and this causes rapid cooling of the reaction zone, so the nucleation and growth occurs in the liquid and the nanoparticles are obtained. Solvent molecules in the surrounding solution act on solving nanoparticles clusters. The entire manufacturing process occurs in a few microseconds [4, 5]. The produced nanoparticles scatter or absorb the irradiation laser and thus prevent more ablation of the target. The energy of the laser pulses will be reached the target surface and will be smaller than that just after operating. To resolve this problem, appropriate liquid is used with smaller absorption coefficient to insure no laser radiation be absorbed by this liquid. However, liquid should be carefully selected because it has influence on the properties of ablated particles. [6].

Plumes are produced during the laser ablation process at the laser- target interaction zone, where both the target surface and the surrounding liquid are vaporized and formed micro-bubbles. The bubbles extend to reach a certain critical set of temperature and pressure before being then collapse [7, 8]. Temperatures of thousands of Kelvins and pressures in the range of kPa to several GPa could be reached inside the bubbles, producing novel materials [9].

With increasing international concern about the depletion of typical fossil fuels (gas, caol, crude oil) and the growing problem of environmental pollution with greenhouse gases. Several studies have been conducted on alternative fuels and sustainable renewable energy production. Numerous attempts have been made to employ nanotechnology - simple and inexpensive manufacturing methods and the choice of perfect nanomaterial - to find alternative sources of energy and to develop fuel cells. Efforts have expanded to include the search for natural sources of energy such as biomass, microbial cells, and hydrogen energy. Effective use of the renewable energies to their fullest demands efficient conversion and energy storage devices. These devices should be able to accommodate the fluctuation nature of renewable energies. A perfect solution is to convert renewably generated electricity into fuels, such as ethanol, methane, and hydrogen. Hydrogen is known as the ideal transporter of energy because it possesses many advantages such as; it has 122 kilojoules of energy per one gram which exceeds that of gasoline (40 kJ / g), an element available widely in nature or can be produced from raw materials as simple as water, completely renewable fuel and could be produced by biomass, could be efficiently produced and converted to electricity without producing any pollutants or greenhouse gases nor environmental harmful effect [10,11].

One way to produce hydrogen gas is to separate the water molecule into oxygen and hydrogen [12]. An electrolyzer consists of two electrodes connected through an external DC power supply and immersed in water is used to break the bonds between the oxygen and hydrogen atoms. To increase the conductivity of water, usually a strong acid or a strong alkali is dissolved in the water and the aqueous solutions create ionic electrolyte. The external current induces reduction reaction at one of the electrodes where H_2 gas is produced and at the other electrode, the electrons produced by the electrochemical reaction return to the positive terminal of the DC source. The minimum voltage required in this process is 1.23V, which is also known as the equilibrium voltage [13]. The reaction equation is [14]:

$$2H_2O \rightarrow 2H_2 + O_2 \qquad (1)$$

Some applications require materials with special and unique specifications. Stainless steel is one of these materials which are distinguished from other metals by its high: hardness, corrosion resistance, and electrical conductivity. These properties make it eligible for use in coatings, forming composite materials, and even can be used as a catalyst [7]. In the present proposal, stainless steel nanoparticles were prepared using PLAL technique and were added to a hydrogen generator, thus avoiding the corrosion problems of the electrode caused by ordinary acidic electrolytes. The effect of steel NPs on gas production compared with sodium hydroxide (NaOH) have been studied for different concentrations. The research aims to increase the gas evolution rate, reduce the electrochemical decomposition energy of water, and above all, reduction in operation and maintenance costs.

2. MATERIALS AND METHODS

There are two basic types of electrochemical cells: the first type, which is called the electrolyte cell, converts external electricity into chemical energy. It consists of two electrodes made of the same material (usually graphite or copper) and immersed in an electrolyte solution, not of the same material of the electrodes. The second type is called the Galvanic Cell in which the energy from spontaneous chemical processes is converted into electrical energy. One of its electrodes is made of copper and the other is zinc. Each electrode is immersed in an electrolyte solution containing the electrode salts. In the current work, a hybrid cell of the former two types was constructed. It is composed of stainless-steel electrodes (as in the first type) and immersed in an electrolyte, which is water and stainless steel nanopowder (as in the second type) that was manufactured by laser ablation.

2.1 Preparation of stainless-steel nanoparticles

The colloidal solution of stainless-steel nanoparticles (SSNPs) was prepared by PLAL technique. The stainless steel target was immersed in UPW (0.45μS/cm) and subjected to 850 mJ/pulse Nd:YAG laser (1064 nm, 5Hz , 6ns). Modulation has been made on the ablation system to ensure that the ablation site is continually changed. This modification includes the use of a stabilizer to fix the target inside the flask and then rotate the flask with its contents using a rotary motor. The ablation setup is shown schematically in Figure 1.

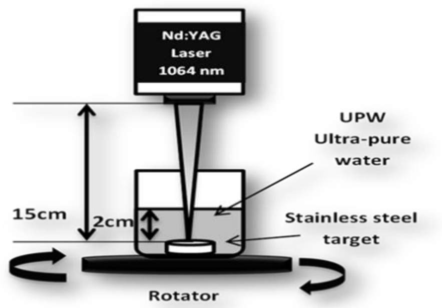

Figure 1: Scheme of the modified PLAL system

The target was weighed before and after ablation to estimate the quantity of the removed mass and the weights were 0.4249 g and 0.4209g respectively. The ablation process took 15 minutes then the product colloidal solutions placed in the ultrasonic cleaner to homogenize. The produced stainless-steel NPs were characterized by a number of tests including AFM, PH meter, and Electrical conductivity. Finally, the SSNPs have been used in the hydrogen generator as an electrolyte.

2.2 Hydrogen production

The new design of the hydrogen generator (production) consists of 10 stainless steel electrodes (cathode and anode) immersed in one liter of UPW. Each electrode of (8 × 10 × 0.1) cm dimensions and the generator was feed by DC power supply. 0.004g of the prepared SSNPs was added to the UPW and used as electrolyte (Enhanced electrolyte). The product hydrogen gas (H_2) was collimated in scaled volumetric container and the generator had been tested at ambient temperature and pressure. Apparatus set up is shown in Figure 2.

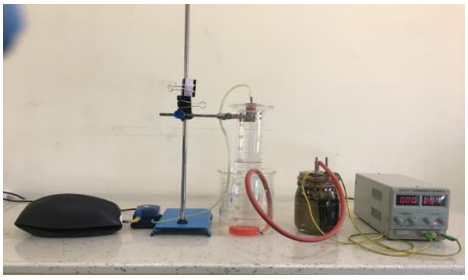

Figure 2: Hydrogen Generator

For the purpose of comparison, the same design was used but by replacing its electrolyte with another one commonly used, which consists of NaOH solved in UPW (Comparative electrolyte). The taken sodium hydroxide concentrations were: 0.1%, 0.5% and 1% respectively.

3. RESULTS AND DISCUSSION

3.1 Atomic force microscopy (AFM) analysis

A thin film of the prepared SSNPs has been made by deposition on a glass substrate. AFM measurement was made for evaluation of the surface morphology and roughness. The result is displayed in Figure 3.

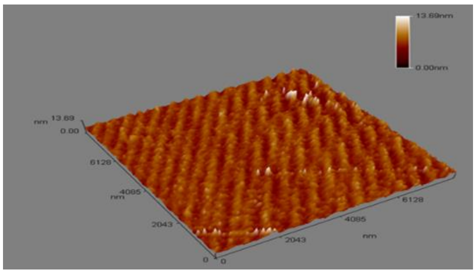

Figure 3: AFM micrograph of the prepared SSNPs

The 3D AFM image indicates a fine stricter with Small grain size of 13.69 nm. A widely used parameter in AFM analyzing is the Root Mean Square (RMS). In this work the, RMS was 0.845 nm which characterizes the surface roughness.

3.2 pH and EC measurements of nano-colloidal

The lack of water for abundant amounts of free ions leads to a weakening of its electrolysis ability. Therefore, the electrolyte of the hydrogen generator is usually treated with the addition of either strong acid such as sulfuric acid or strong alkalis such as sodium hydroxide. In the current research, the acidic index (PH) for both electrolytes (the enhanced and comparative) was measured and the evolution of pH values is illustrated in Figure 4.

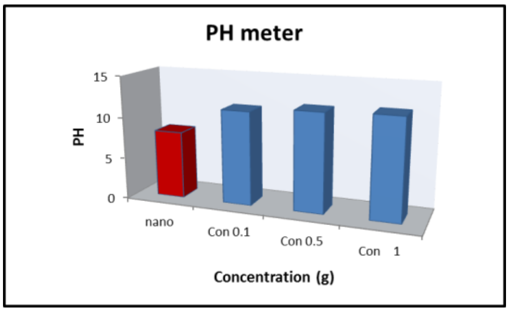

Figure 4: PH values of the electrolytes as a function of concentration

The starting pH value of the nanofluid was 8.11 with regard to the base fluid (Water), and then at higher Sodium hydroxide concentration, pH values became lower or even saturated at approximately 12 PH. The differences in pH value increases as the sodium hydroxide concentration increase.

The measured electrical conductivity of the UPW was 0.45μs/cm and it becomes 7.7ms/cm after the addition of the SSNPs. The main reason of this trend is that, the dispersion of nano particles in the base fluid leads to

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significant enhancement of the volume ratio of Water/ SSNPs. The later in its turn leads to formation of surface charges by polarization. At the comparative electrolyte, the EC increased in a linear behavior as the Sodium hydroxide concentration increased but it is still less than that of enhanced electrolyte as shown in Figure 5.

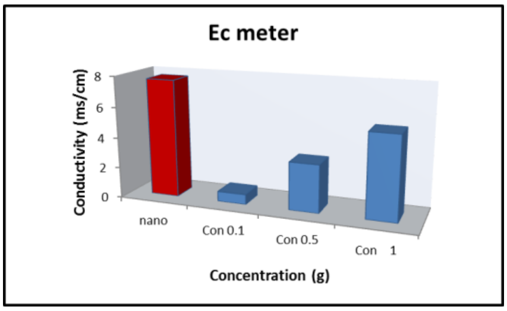

Figure 5: Electrical conductivity of the electrolytes as a function of concentration

3.3 Accumulated Gas Volume

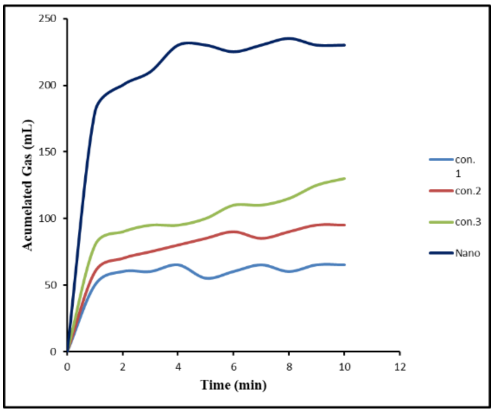

Figure 6: Accumulated gas volume as a function of time

Hydrogen generation process was carried out via electrochemical water splitting and accumulated gas was quantified using liquid displacement at room temperature. It can be observed from Figure 6 that the hydrogen evolution increased linearly with respect to Sodium hydroxide concentration in NaOH electrolyte. The higher rate of accumulated hydrogen generated is (230mL) for steel NPs with pH 8.11 and electrical conductivity 7.7ms/cm, compared to water and Sodium hydroxide. This can be attributed to its high electrical conductivity.

4. CONCLUSIONS

Nanotechnology has been employed to improve the performance of the electrochemical water separation cell. The main problem in acidic electrolytes is the erosion of electrodes and in the alkali electrolytes is the occurrence of side reactions that reduce the production of hydrogen gas. In the proposed design, these two problems were overcome by using the stainless steel nano powder. The high conductivity of this material increases the efficiency of the electrolyte. During operation, oxygen atoms are generated, which often cause electrode oxidation and thus decrease the performance of the electrolysis cell. In the current design, the choice of electrodes made of SSNP is the most successful procedure since this material is the only one that remains conductive to the electrically even after it is converted into oxides.

Based on the aforementioned results, it could be concluded that; Replacing strong acids or strong bases with SSN powder increased the electrolyte efficiency and overcame the problems of electrodes erosion and side reactions, thus increasing the amount of gas produced. At the same time, the exclusion of catalysts (acids and alkali) has contributed in reduction the manufacturing cost of hydrogen generator with a longer operating lifespan without the need for continuous maintenance.

Finally, the addition of 0.004g SSNPs served as a catalyst and significantly increased the efficiency of the electrolysis, which promotes the production of hydrogen in larger quantities than those produced by adding sodium hydroxide. Also reduced the amount of energy spent in water analysis. In the laser ablation system, the sample rotation ensures that the laser is not focused at the same location, thus increasing the regularity of the ablation process.

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