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The influence of the solution of their amount on the process of water splitting by the electrolysis method

The article presents the results of an experimental study of the effect of the solution and their concentration on the process of splitting water by electrolysis under the action of a direct electric current using a Hoffman device. As solutions, we used sodium hydroxide, sodium phosphoric acid, sodium carbonate, sodium sulfate, sodium metaborate, sodium phosphoric acid 2 — substituted and potassium hydroxide. The number of salts in the solution varied from 0.2 mol to 0.8 mol. The study showed that the splitting water at constant current and voltage is influenced by both the nature of salts and their quantity. So, it was found that with the same amount of substances in the solution, the process of splitting water occurs faster in a solution containing potassium hydroxide. When using an aqueous KOH solution in an amount of 0.2 mol, the volume of hydrogen released was 15 ml, and at 0.8 mol, 19.5 ml. Using an aqueous solution of sodium metaborate with a similar concentration, the volume of hydrogen released was 2 ml and 4.5 ml, respectively. The obtained results allow to choose the solution and its amount during the process of photocatalytic splitting of water.

Keywords: water splitting, Hofmann apparatus, electrolysis, hydrogen, salt, solution, reactions, electrochemical process.

Introduction

Hydrogen is considered the ideal fuel of the future. Hydrogen fuel can be produced from clean and renewable energy sources, which will make it environmentally friendly. The sun and wind are the two main sources of renewable energy, as well as promising sources for the production of renewable hydrogen. Currently, the production of hydrogen by the above methods is not yet popular due to the high cost. Photovoltaic electrolysis of water can become more competitive, since the cost of hydrogen produced decreases with the development of technologies and materials used [1].

The photocatalytic splitting of water was first mentioned by Giacomo Ciamitian in the early 1900s [2]. Later, in 1970, Honda and Fujishima experimentally proved the possibility of splitting water by using a wide-band semiconductor and solar energy. Since then, revolutionary research by scientists on the photoelectrochemical decomposition of water has been published [3–9]. The works are mainly devoted to the study of the photocatalyst and its modification to improve the ability to split water [10–14]. However, it is necessary to take into account that even using a highly efficient photocatalyst, the splitting of distilled water is extremely difficult. Therefore, it becomes necessary to add sources of donor electrons to the purified water, which can serve as organic compounds methanol, ethanol and lactic acid, which significantly enhances the interaction of the electron/hole of the semiconductor and the solution used, leading to higher quantum efficiency [15, 16]. The addition of carbonate salts Na2CO3, HCO2–, C2O2- to water also increases the production of hydrogen and oxygen [17]. It can be concluded that the process of photo-splitting of water is affected not only by the high performance of the photocatalyst but also by the solution where the splitting of the water molecule into hydrogen and oxygen occurs, which makes this work relevant.

This paper presents the results of a study of the effect of the solution (sodium hydroxide, sodium phosphoric acid, sodium carbonate, sodium bicarbonate, sodium sulfate, sodium metaborate, sodium phosphoric acid 2 — substituted and potassium hydroxide) and their amounts on splitting water.

Experimental

To determine the effect of the solution on the water-splitting process, the following were used: sodium hydroxide (NaOH), sodium phosphoric acid 3 substituted (Na3PO4), sodium carbonate (Na2CO3), sodium bicarbonate (NaHCO3), sodium sulfate (Na2SO4), sodium metaborate (NaBO2), sodium phosphoric acid 2 substituted (Na2HPO4), potassium hydroxide (KOH). All the salts were dissolved in distilled water in a volume of 150 ml. The requirement for all samples was presented in the same way. The amount of the substance varied from 0.2 mol to 0.8 mol. The amount of hydrogen released at the cathode and oxygen at the anode was recorded every 5 minutes, with a total duration of 60 minutes.

All experimental work was carried out by electrolysis at constant voltage using the Hoffmann apparatus. The diagram of the working chamber of the Hoffmann apparatus is shown in Figure 1. The device consists of three vessels, each with a volume of 50 ml. Three vertical, glass communicating vessels, one of which is open and designed to inject an aqueous solution. Platinum electrodes are placed in the lower part of the vertical vessels. The electrodes are connected to the positive and negative poles of the current source. The electrolysis voltage is 3 V. When a voltage source is connected to the network, the electrolysis process takes place. The volume of hydrogen and oxygen released is recorded by the volume of the solution displaced by the gas. A universal power supply PHYWE with direct and alternating current was used as a voltage source.

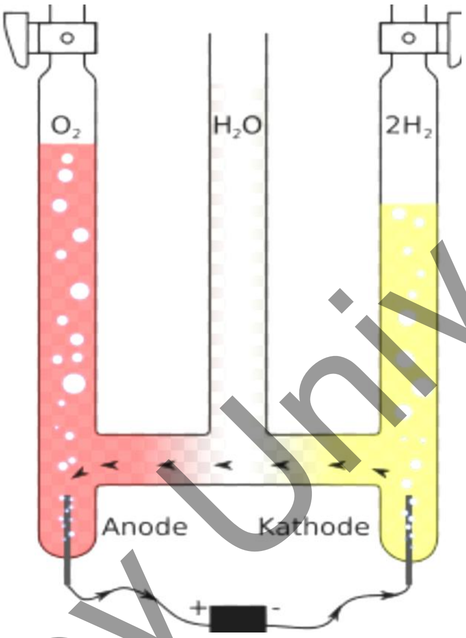
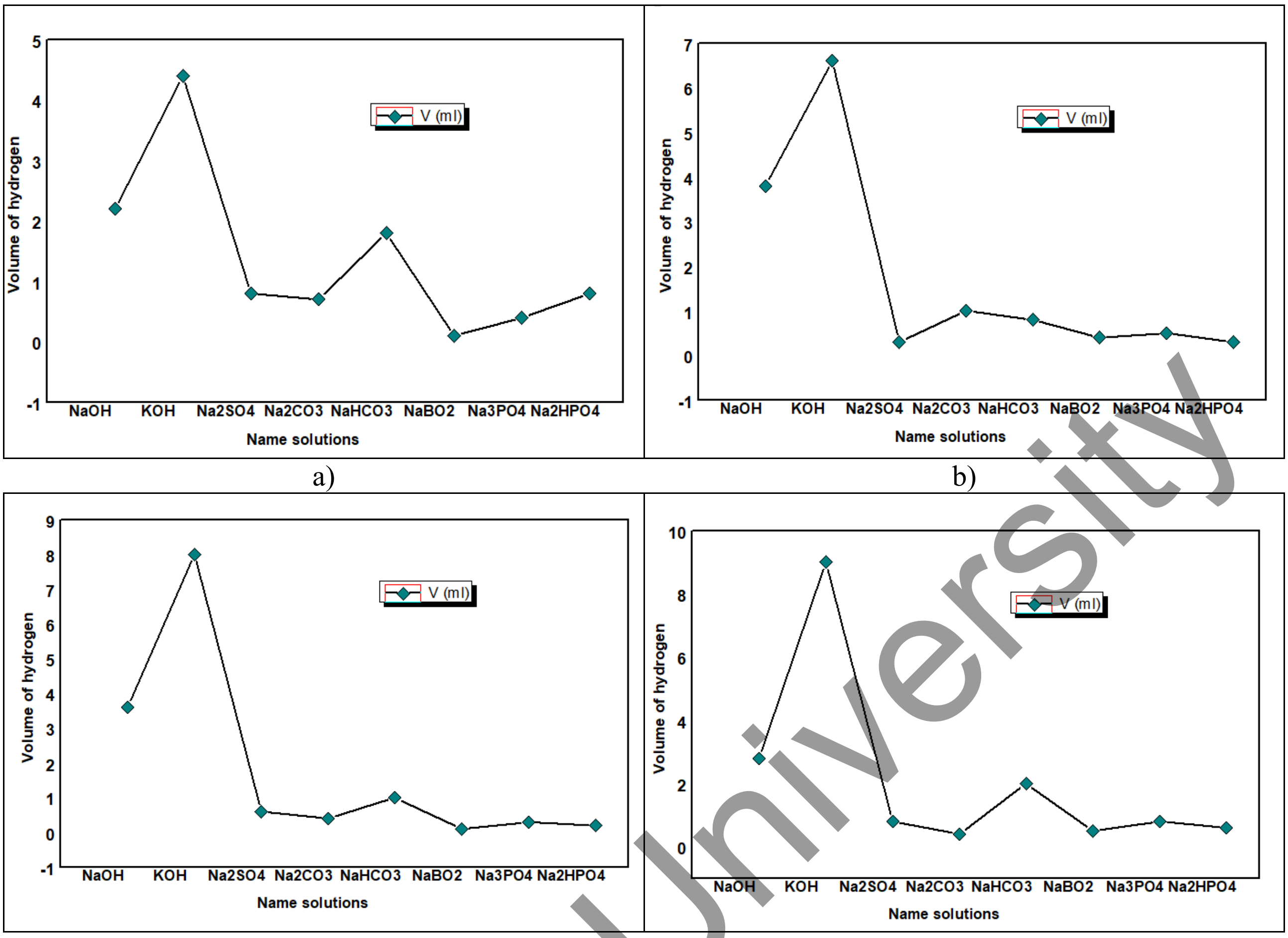


Figure 1. Scheme of the Hoffmann apparatus of three vessels

Sodium hydroxide NaOH is a solid substance, that dissolves well in water and emits a large amount of heat. Solubility in water 108.7 g per 100 ml temperature + 15 ^{0}C. KOH potassium hydroxide-solubility in water 107 g per 100 ml temperature +15 ^{0}C. Na2HPO4 sodium hydrophosphate-forms colorless crystals. It is well soluble in water. Solubility temperature +100 0C. Na2SO4 sodium sulphate g / 100ml at 0 °C -4.5 g, at 20 °C — 19.2 g, at 32.4 °C — 49.8 g at 100 °C — 42.3 g. Sodium acid Na2CO3 is insoluble in acetone and carbon disulfide, slightly soluble in ethanol, well soluble in glycerin and water. NaHCO3 has a low solubility of sodium bicarbonate in carbon dioxide water and increases slightly with increasing temperature: from 6.87 g per 100 g of water at 0 °C to 19.17 g per 100 g of water at 80 °C. Due to its low solubility, the density of saturated aqueous solutions of sodium bicarbonate differs little from the density of pure water. Sodium metabolate NaBO2 forms colorless hygroscopic crystals of trigonal syngony, dissolves well in water, easily forms saturated solutions. Na3PO4 sodium phosphate acid is highly soluble in water — 12.1 g / 100 ml. Together with water, a crystallohydrate with the general formula Na3PO4 ·12H2O is formed.

Results and Discussion

The effects of solutions of sodium hydroxide (NaOH), sodium phosphoric acid 3 substituted (Na3PO4), sodium carbonate (Na2CO3), sodium bicarbonate (NaHCO3), sodium sulfate (Na2SO4), sodium metaborate (NaBO2), sodium phosphoric acid 2 substituted (Na2HPO4), potassium hydroxide (KOH) at various amounts are illustrated in Figure 2.



a)

b)

c)

d)

a– (0,2 mol); b — (0,4 mol); c — (0,6 mol); d — (0,8 mol)

Figure 2. The effect of solutions on the process of splitting water by electric riveting.

Figure 2a demonstrates that when using hydroxide groups, carbonate salts and phosphates in the amount of 0.2 mol, the volume of hydrogen gas released is different. Moreover, when using a solution containing potassium hydroxide (KOH), the volume of hydrogen released is higher than with the other groups. For example, the volume of hydrogen released for him was 4.5 ml. The highest value of the released hydrogen belongs to a solution containing sodium metaborate NaBO2 (v= 0.2 mol) and is 0.2 ml. The remaining solutions occupy an intermediate value. Figure 2b represents that when the number of salts in the distilled water increased to 0.4 mol, the volume of hydrogen released increased 1.5 times for potassium hydroxide (KOH) and sodium hydroxide (NaOH), and when using Na3PO4, Na2CO3, NaHCO3, Na2SO4, NaBO2, Na2HPO4 remained practically unchanged and was in the range from 0 to 1 ml. A further increase in the number of salts in water to 0.6 mol showed (Figure 2c) that when using potassium hydroxide, the volume of hydrogen released increased by 2 times compared to 0.2 mol, while sodium hydroxide practically remained unchanged. An increase in the number of salts in the solution to 0.8 mol led to a decrease compared to 0.4 mol, and amounted to 2.8 ml (Figure 2 d). From the data obtained, it can be concluded that the best medium for splitting hydrogen is a solution containing 0.8 mol of potassium hydroxide, and the worst is sodium metaborate NaBO2. An increase in the amount of the substance in the water to 1 mol did not lead to an increase in the volume of hydrogen released.

Figure 3 shows the dependence of the volume of hydrogen released on the duration of electrolysis, with the amount of potassium hydroxide in the solution varying from 0.2 to 0.8 mol.

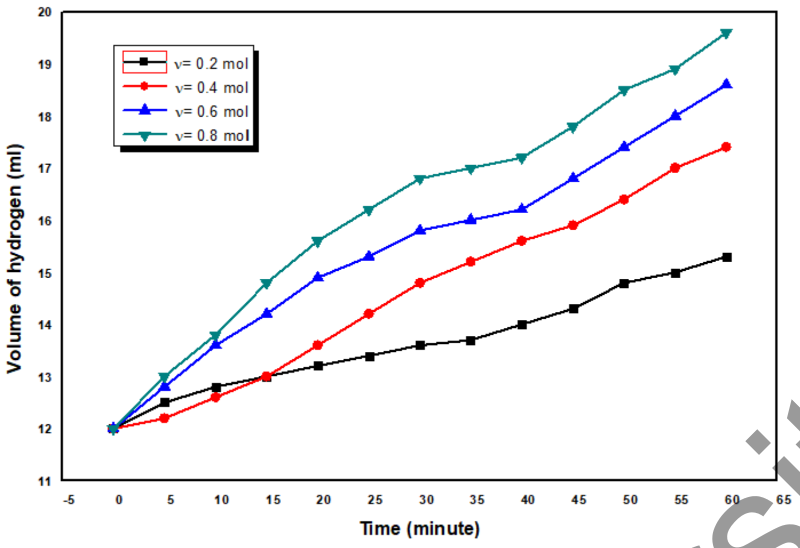


Figure 3. The effect of the amount of potassium hydroxide on the process of splitting water by electric riveting

One can see that during the electrolysis process lasting 60 minutes, the volume of hydrogen released increases with the amount of potassium hydroxide in water from 0.2 mol to 0.8 mol. So, at 0.2 mol, the volume of gas was 15 ml, and at 0.8 mol, 19.5 ml.

The solutions that we used in the experiment are called colloidal. Colloidal solutions are systems that comprise a solid dispersed phase distributed in a liquid or solid dispersion medium. Solutions are always single-phase, which are homogeneous gas, liquid or solid. This means that one of the substances is distributed in the mass of the other in the form of molecules, atoms, or ions.

Electrolysis of solutions is a complex process because, besides metal ions and acid residue, water molecules and H^+ and OH^- ions are present in the solution, which can also participate in the redox process during passaging electric current. To correctly determine the products formed in the electrodes during the electrolysis of hydrophytic solutions of electrolytes, it is necessary to adhere to the following important rules, which occur in the cathode and anode.

The passing process at the cathode depends on the position of the metal in the electrochemical series. Our solutions are part of the active metal activity: K, Ba, Ca, Na in which water is reduced to hydroxide ion to hydrogen, and only hydrogen is released at the cathode because of the reduction of water molecules.

$$2H_2O + 2\bar{e} = H_2 + 2OH^-$$

The strongest reducing agent is oxidized at the anode. During electrolysis of solutions of acid-containing salts oxygen is released on the anode O_2

$$2H_2O — 4\bar{e} = O_2 + 4H^+$$

Electrolysis Na_2So4.
(-) Cathode $\longleftarrow$ $2Na^+ + SO_4^{2-} \longrightarrow$ Anode (+)
Cathode: $2H_2O + 2e^- = \mathbf{H_2}\uparrow + 2OH^-$
Anode: $2H_2O — 4e^- = \mathbf{O_2}\uparrow + 4H^+$
Total: $2H_2O = 2H_2\uparrow + O_2\uparrow$

Conclusion: the electrolysis of this salt is reduced to the decomposition of water; salt is necessary to increase electrical conductivity, since pure water is a weak electrolyte.

Electrolysis KOH.

Cathode (-) $\longleftarrow$ $K^+ + OH^- \longrightarrow$ Anode (+)
Potassium cations will not be restored at the cathode since potassium is in the metal voltage range to the left of aluminum, instead, water molecules will be restored:
Cathode: (-) $2H_2O + 2e = H_2 + 2OH^-$
Anode: (+) $4OH^- — 4e = 2H_2O + O_2$
Total: $4H_2O + 4OH^- = 2H_2 + 4OH^- + 2H_2O + O_2$ $2H_2O = 2H_2 + O_2$
Electrolysis NaOH.

$4NaOH = 4Na + O_2 + 2H_2O$
Cathode: $2H_2O + 2e = H_2 + 2OH^-$
Anode: $4OH^- — 4e^- = O_2 + 2H_2O$
Water molecules are restored at the cathode. The growth of sodium hydroxide is reduced to the electrolysis of water.
Electrolysis Na_2CO_3.
Water electrolysis occurs:
$H_2O = H^+ + OH^-$
Cathode (K^-): $2H_2O + 2e^- = H_2 + 2OH^-$
Anode (A^+): $4OH^- — 4e^- = 2H_2O + O_2$
Total: $2H_2O = 2H_2 + O_2$
Sodium, as an alkaline metal, is not released at the cathode, and the $CO_3{}^{2-}$ ion is also not discharged, as an acidic residue of an oxygen-containing acid.
Electrolysis $NaHCO_3$.
Cathode (-) $H_2O+2e=H_2+2OH^-$
Anode (+) $2H_20–4e=O_2+4H^+$
The equation: $NaHCO_3+2H_2O = O_2+2H_2+NaHCO3$
In the equations of solution electrolysis $NaHCO_3$ there will be water electrolysis reactions, the oxidation of the bicarbonate ion does not occur.
Electrolysis Na_3PO_4.
Cathode: $2H^+ +2e= H_2$
Anode: $4OH^- — 4e= 2H_2O + O_2$
The equation: $Na_3PO_4 +5H_2O= 3NaOH +2H_2 + O_2 +H_3PO_4$

Hydrogen is released at the cathode and oxygen is released at the anode due to the electrolysis of water. Sodium cations are not reduced, since the electrode potential is lower than that of hydrogen. An excess of sodium hydroxide is formed in the near-cathode space. Hydroxide anions (water) are oxidized at the anode, oxygen is released. Phosphate anions are not oxidized, since their potential is higher. There is an excess of weak orthophosphoric acid in the near-anodyne space. In general, sodium orthophosphate salt is not subjected to electrolysis in this case.

The process at the cathode depends on the position of the metal in the electrochemical series. Our solutions belong to the range of activity of active metals: K Ba Ca Na, in which water is reduced to the hydroxide ion to hydrogen, and only hydrogen is released at the cathode due to the reduction of water molecules. It can be said that the electrolysis of salts is reduced to the decomposition of water, and salt is necessary to increase electrical conductivity since pure water is a weak electrolyte.

Conclusions

In the presence of substances in various amounts, such as sodium hydroxide, sodium phosphoric acid, sodium carbonate, sodium sulfate, sodium metaborate, sodium phosphoric acid 2 — substituted and potassium hydroxide, water electrolysis was carried out. At different time intervals, the volume of hydrogen released was recorded using the Hoffmann apparatus. The study designated that in the presence of potassium hydroxide, regardless of its amount, the electrolysis process occurs faster, as evidenced by the volume of gas released. Sodium hydroxide turned out to be less effective, as the remaining substances showed a low ability to generate hydrogen. In addition, the effect of the amount of substance per unit volume of water on the process of electrolysis of water was demonstrated, where the best result was recorded for a solution with an amount of 0.8 mol. Low efficiency is demonstrated by sodium metaborate NaBO2 at an amount of 0.2 mol.

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Суды электролиз әдісі арқылы ыдырату кезінде ерітіндінің және оның мөлшерінің әсері

Мақалада Гофман құрылғысын қолдана отырып, тұрақты электр тогының әсерінен электролиз арқылы судың бөліну процесіне ерітіндінің әсері мен оның концентрациясын эксперименттік зерттеу нәтижелері келтірілген. Ерітінді ретінде натрий гидроксиді, фосфорқышқылды натрий, көмірқышқыл натрийі, көмірқышқылды қышқыл натрий, күкіртқышқылды натрий, натрий метабораты, фосфорқышқылды натрий және 2— алмастырылған калий гидроксиді пайдаланылды. Ерітіндідегі тұздардың мөлшері 0,2 моль мен 0,8 моль аралығында болды. Зерттеу көрсеткендей, тұрақты ток пен кернеу кезінде судың ағу процесіне тұздардың табиғаты да, олардың мөлшері де әсер етеді. Сонымен, ерітіндідегі заттардың бірдей мөлшерімен судың ыдырау процесі калий гидроксиді бар ерітіндіде тезірек жүретіні анықталды. 0,2 моль мөлшерінде KOH ерітіндісін қолданған кезде бөлінетін сутектің көлемі 15 мл, ал 0,8 моль кезінде 19,5 мл болды. Осыған ұқсас концентрациясы бар натрий метаборатының сулы ерітіндісін пайдаланған кезде, бөлінген сутектің көлемі тиісінше 2 мл және 4,5 мл құрады. Алынған мәліметтер судың фотокаталитикалық ыдырауы кезінде ерітінді мен оның мөлшерін таңдауға мүмкіндік береді.

Кілт сөздер: суды ыдырату, Гофман аппараты, электролиз, сутегі, тұздар, ерітінді, реакциялар, электрохимиялық процесс.

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Влияние раствора и его количества на процесс расщепления воды методом электролиза

В статье приведены результаты экспериментального исследования влияния раствора и и его концентрации на процесс расщепления воды путем электролиза под действием постоянного электрического тока с применением устройства Гофмана. В качестве растворов нами были использованы гидроксид натрия, натрий фосфорнокислый, натрий углекислый, натрий углекислый

кислый, натрий сернокислый, метаборат натрия, натрий фосфорнокислый 2-замещенный и гидроксид калия. Количество солей в растворе варировалось от 0,2 до 0,8 моль. Результаты исследования показали, что на процесс ращепления воды при постоянном токе и напряжения влияет как природа солей, так и их количество. Так, было установлено, что при одинаковом количестве веществ в растворе, процесс расщепления воды происходит быстрее в растворе содержанием гидроксида калия. При использовании водного раствора KOH в количестве 0,2 моль, объем выделяемого водорода составил 15 мл, а при 0,8 моль — 19,5 мл. При использовании водного раствора метабората натрия с аналогичной концентрацией, объем выделенного водорода составил 2,0 и 4,5 мл соответственно. Полученные данные позволяют сделать выбор раствора и его количества при процессе фотокаталитического расщепления воды.

Ключевые слова: расщепление воды, аппарат Гофмана, электролиз, водород, соль, раствор, реакция, электрохимический процесс.