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WE HAVE HYDROGEN AND WHAT NEXT[1]?

MAMY WODÓR I CO DALEJ[1]?

***Summary**: Hydrogen atom is the simplest atomic construction. When looking at abundance of the elements, we may state that hydrogen is the element, occurring in the Universe in the greatest quantities. Its structure is composed of one proton and molecular cloud, the particles of which surround its centre. It is so simple... Hydrogen on the Earth is entrapped in a form of H_2O, ammonia NH_3 and hydrocarbons. Its high quantities appear in a form of methane CH_4, especially, in methane hydrates[2] [25]. It is a very interesting source of hydrogen but the question arises: shall we be successful? Whether the humanity – a new Skłodowska-Curie or a new Maxwell[3] – when discovering the successive "obviousness" – will point out to the new horizons?*

Graphene[4] revolution has been hidden in laboratories. The "Azoty" Group (Poland) decided to develop independently the idea of production and popularization of this unusual material. Are we sure that we know and utilize fully a potential of the discussed material? If so, how can it help us to introduce the pre-hydrogen trend?

***Keywords**: hydrogen, graphene, pre-hydrogen trend*

***Streszczenie**: Atom wodoru jest najprostszą konstrukcją atomową. Patrząc na abundancję pierwiastków – wodór jest pierwiastkiem występującym we Wszechświecie w największej ilości. Na jego strukturalną budowę składa się jeden proton i obłok cząstek materii, które otaczają jego centrum. Takie to proste… Wodór na Ziemi jest uwięziony w postaci wody H_2O, amoniaku NH_3 oraz węglowodorów. Dużo go w postaci metanu CH_4, a szczególnie w hydratach metanu[2] [25]. Bo to bardzo ciekawe źródło wodoru, tylko czy się nam uda? Czy ludzkość – nowa Skłodowska-Curie czy nowy Maxwell[3] – odkrywający kolejne „oczywistości" wskażą nam nowe horyzonty?*

Grafenowa[4] rewolucja zaszyła się w zaciszach laboratoriów. Grupa Azoty postanowiła dalej samodzielnie rozwijać ideę wytwarzania i rozpowszechniania tego niezwykłego materiału. Czy na pewno znamy i wykorzystujemy w pełni potencjał tego materiału? A jeśli tak, w jaki sposób może nam pomóc we wdrażaniu trendu pro-wodór?

***Słowa kluczowe**: wodór, grafen, trend pro-wodór*

Future lies in hydrogen

The European energetic-climatic policy forces us to seek for the alternative solutions and sources of cheap electric energy. The introduction of RES policy and the resulting legal regulations run effectively whereas owing to the recent political decisions the hydrogen revolution (although being still ineffective) has a chance to develop dynamically, including also stabilization of the situation in respect of energy storage (*inter alia*, in Poland) and to make the pre-ecological activities[5] real. Constantly increasing participation of hydrogen in energetic sector, especially in global aspect, makes that the leading producers of electric energy increase the additional financing of the mentioned research areas.

The most intensive studies on the properties of hydrogen are implemented, first of all, in the United States, Germany and France. Poland has also the achievements in this field with its project by PKN Orlen and Lotos group, PGE, GAZ-SYSTEM SA, in cooperation with higher education schools, *inter alia*, AGH Unoiversity of Science and Technology in Cracow, Łódź Technical University and Warsaw University of Technology and Silesian University of Technology. A wide popularization of

[1] The paper has been changed and amended; primarily, it was published as: Klima K., Sikora A., "Universal everywhere. We have hydrogen and what next...? Energetyka Cieplna i Zawodowa 2/2016 (628) p. 48-49. ISSN 1734-7823; and "Entrapped in hydrogen. We have hydrogen and what next?" part 2 Energetyka Cieplna i Zawodowa 3/2016 (634) p. 108-113. ISSN 1734-7823

[2] Sikora A., „Trapped molecule"/ Andrzej Paweł SIKORA // Energetyka Cieplna i Zawodowa; ISSN 1734-7823. – The other titles of journal: Branżowy Magazyn Przemysłowy. Energetyka Cieplna i zawodowa; BMP Energetyka Cieplna i Zawodowa - 2014, no 4, p. 56 – 57. Bibliogr. P. 57. – Affiliation: AGH Technical University of Cracow

[3] He proved that electricity and magnetism are two types of the same phenomenon – electromagnetism; that electric and magnetic fields are dispersed in vacuum with the light velocity in a form of waves, i.e. that the light is the electromagnetic wave

[4] It is a flat strcture of carbon atoms – in 2010, Andriej Gejm and Konstantin Nowosiolov received Nobel Prize in the domain of physics for the studies on graphene, University in Manchester

[5] Cf. For example: https://www.gov.pl/web/klimat/rozpoczely-sie-konsultacje-publiczne-projektu-polskiej-strategii-wodorowej; https://eur-lex.europa.eu/legal-content/PL/TXT/?uri=CELEX%3A52020DCO102&qid=1610462287586; COMMUNICATION FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE COUNCIL , THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS. A hydrogen strategy for a climate-neutral Europe COM/2020/301 final https://eur-lex.europa.eu/legal-content?EN/TXT/?qid=1596807561238&uri=CELEX:52020DCO301; COMMUNICATION FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS on an EU strategy to reduce methane emissions; https://ec. europa.eu/energy/sites/energy/files/eu_methane_strategy.pdf; htpps://eur/lex.europa.eu/legal-content/PL/TXT/?uri=CELEX%3A52020DCO299&qid=1610462203898;

the discussed element in the Cosmos and the simple, though very expensive methods for its obtaining, have resulted in the development of energetics and rendering it a name of ecological (organic) fuel. Why, therefore, the process of replacing the universally employed petroleum or ground gas by hydrogen is inhibited? The so-far existing costs of hydrogen production have been lower than the energy obtained from its combustion what decided on the unprofitability of the process. Let's pay attention, therefore, to the advantages, speaking for the increase of hydrogen participation in the global and national production of electric energy. Its ecological nature, connected with the production of water (water vapour) in the combustion process should be confronted with sulphur dioxide and carbon dioxide, being the by-products of fossil fuel combustion. Moreover, hydrogen has a low ignition temperature and relatively very high combustion temperature in relation to the mass of the discussed element. The cars, driven by hydrogen, are becoming more and more popular; their performance and the application of "clean fuel" convince the users to bear higher expenses and overcome the difficulties connected with the lack of fuelling stations[6].

Aspects of storage and transfer of hydrogen in the industrial scale and the optimization of the mentioned process of its production seem to be a priority.

What may be a role of graphene in the "hydrogen revolution"?

Graphene is a flat structure consisting of carbon atoms; its form resembles a thin (thickness is only one atom) plaster of wax foundation. One of its main features includes heat conductivity (thermal conductivity is equal to 4840–5300 W/mK) which is intensively employed in different industrial branches. Being a very resistant material (100 times harder than steel), it is subjected to elongation even by 25%. Graphene may play a function of a very sensitive gas detector and it is connected with its sorption properties, in which the total surface of material participates. The possibilities of applying it as insulation/dam for the smallest atoms, *inter alia*, of helium or hydrogen, is the essence of the energy storage process and its chemical neutrality to water effect allows implement the idea of catalysis of water hydrolysis process. Graphene is susceptible to modifications and to affecting its physico-chemical properties (creation of materials for construction of organic electrodes, photovoltaic cells or construction of layers of solar collectors).

Some words about sorption capabilities...

Carbon-based materials may absorb well the particles of, *inter alia*, H_2. The results of physical sorption, conducted with graphene, have indicated its very high affinity to absorption of the hydrogen molecules and, what is most important (in storage aspect) owing to the mechanical tensions, the control of gas release from graphene is possible[7] [2]. When looking at the mentioned problems, it seems to be an ideal material, increasing the possibilities of energy storing in a form of hydrogen, isn't it so?

The above fact was considered, inter alia, by the research team of the University of Technology of Łódź , developing the graphene tank which allowed driving about 800 km without the necessity of refuelling the car (hydrogen as a fuel[8]) [3]. The process of absorption and recovery of the particles was carried out on the principle of temperature changes with the consideration of the earlier mentioned feature of graphene in control of sorption-desorption cycles. "As compared to the graphene, as produced now by the available methods, the graphene produced at the Technical University of Łódź has a higher durability and repeatability of physico-chemical properties in variable conditions of pressure and temperature[9]". Based upon the discussed graphene, nanocomposite for the reversible storage of hydrogen was produced; it is found under the development within the frames of the project implemented by the University of Technology of Łódź and company Seco Warwick S.A., entitled: "Graphene nanocomposites for a reversible storage of hydrogen – GraphRoll". The searches for the methodology and materials for the development and improvement of the currently obtained results in respect of the quantity as well as quality of hydrogen in the reversible gas storehouses are a priority in the hydrogen-promoting policy.

Whether to increase the effectiveness of hydrogen production?

Hydrogen is one of two gas products, generated during water hydrolysis process. Electric energy breaks the relatively strong links between oxygen and hydrogen atoms in water molecule, transforming both elements in a gas form. The excess of electric energy, resulting from RES is the first stage of the process of "entrapping the energy in hydrogen molecule". The period of demand on electric current during the year or even 24h varies and therefore, the storage of energy is necessary to make a buffer and ensure the energetic stabilization of the network in

[6] „Institute of Car Transport (ITS) has developed the plan of the project for construction of a network of several stations in Poland where it would be possible to fuel the vehicles (buses and personal cars) powered by fuel links, with hydrogen. ITS is one of the institutions, implementing the European Project Hit-2-Corridors, the aim of which is to create and later on, integrate with the European infrastructural network, serving for utilization of hydrogen as a fuel in road transport" Wojciech Gis explains. One of the effects of the work in the discussed project includes the plan of building the stations in Poland, mainly in the courses of the European transport corridors TEN-T. The answer to the question: "When it will be possible?" is not easy. The Institute assumes the construction of 9 such objects up to 2030, depending on the interest. "https://www.pb.pl/4365094,94750,polska-bedzie-miala-stacjewodorowe?utm_source=copyPaste&utm_medium=referral&utm_campaign=Firefox(access 2015/12/03) and 2021/01/22

[7] The document „Graphene is a new material on the basis of carbon", developed by Agnieszka Jędrzejczak, Multi-personal post for foreign economic cooperation and entrepreneurship, as placed in portal http://www.mazovia.pl, presenting the possibilities for graphene applications in aspect of its physical and chemical properties. Separation of functions of hydrogen and aspect of its storage

[8] Vision of Prof. Piotr Kula, Director of the Material Engineering Institute of University of Technology of Łódź, based upon the so-far obtained results of the studies on the application of graphene in the motorization revolution. The interview by Jacek Krywko for wyborcza.pl

[9] https://www.p.lodz.pl/pl/grafen-politechniki-lodzkiej

a given country. During the process of hydrolysis, platinum is a catalyst of reactions on anode (where hydrogen is released); it is cheap and rare in nature. The scientists have found also here the application for graphene. The catalyst based upon the mentioned materials is derived from Texas. It reaches not only a high efficiency but also is a cheap material in comparison to platinum. Signed Co-NH complex is cobalt, distributed in graphene matrix with the participation of gas ammonia[10] [4]. The obvious aim is to lower the cost of hydrolysis and, consequently, to lower the price of the obtained hydrogen.

When speaking about electrolysis, we cannot forget about PEM (Polymer Electrolyte Membrane) method that is the alternative to less effective but cheaper method (Alkaline Water Electrolysis). The only one but deciding disadvantage of PEM is its high cost. We might try to lower the costs of the mentioned method by replacement of platinum by graphene as catalyst.

Fuel cells are known all over the world. Their power generating capabilities place them higher than the traditional primary cells. How to utilize graphene, also in this aspect? It would allow lowering the production costs and improve durability and quality of the cells. Owing to the studies, conducted in the USA, the idea of the application of graphene catalyst in fuel cells has been positively considered[11] [5]. The research program was born from the same need as in the case of water hydrolysis. There are the attempts to replace the currently used catalyst, platinum, by the cheaper but equally effective material. Graphene is ideal for this purpose. A special attention should be paid to the studies of 2013, where the so-called "graphene nanoplatelets"[12] [6] in combination with one of the elements from 17.group – halogens. Synthesis with iodine occurred to be the most durable combination; it allowed generating by 33% more electric energy more in comparison to platinum-catalyst cells[13] [20]. A series of the so-far conducted studies on the application of graphene, carbon nanomaterials in power-generating processes seems to be optimistic.

In friendship with Renewable Energy Sources (RES)

One of the applications of the discussed above element includes graphene as a building material of the outer layer of solar collectors. A flat structure of carbon atoms is a very durable, flexible material with a low specific gravity. In respect of RES, and, more precisely, voltaic cells, it conducts the electric current by 50 times better than the earlier employed silicon. When considering its physical properties i.e. transparency, possibility to work at each light wave length and a perfect conductivity, we may state that graphene may be utilized both in the systems of energy conversion and in the processes of energy storage. The present work is focused on the construction of supercapacitors, being able to carry out the cycles of charging and discharging quickly and effectively; it could have the effect on the process efficiency. The mentioned studies include improvement of LFP cell (Lithium-Phosphorus-Ferrum), using a reduced graphene oxide[14], increasing its capacity and durability [7]. The researchers form University of California paid their attention on graphene layers with manganese dioxide[15], owing to which a high energy density was obtained (by 42 Wh/l) with the consideration of a very short time of charging (16 seconds) in comparison to lithium-ionic capacitors [8]. We should also mention an innovating discovery of the scholars, working under the guidance of Prof. Dan Li at Monash University in Australia in 2013. They employed the so-called graphene gel[16] with the aim to construct a supercapacitor with capacity of 60 Wh/l. Owing to such applications, the time of charging cycle of capacitor may be not only abbreviated but also a high electric capacity may be maintained; it is the essence of the application of cells/capacitors in aspect of motorization and renewable energy [9]. As far as sector of Renewable Energy Sources (RES) is concerned, we should mention that according to the opinion of scientists from MIT, the application of graphene cells may double value of maximum solar energy conversion in photovoltaic cells . The higher efficiency of the process means a higher production of electric energy which may be stored in a form of hydrogen; graphene will be the element, consolidating the mentioned processes.

If not graphene and carbon materials, so what then?

The answer to this question may come from the successive complex compounds, belonging to a group which generates molecular sieves, that is, **zeolites**. These unusual compounds,, characterized by a porous structure, possess very good sorption possibilities. We may distinguish natural and synthetic zeolites. A question arises: whether their sorption properties could be utilized in storage of hydrogen? Such studies were conducted at Latvian University[18] [22]. Pure zeolite does not possess high sorption possibilities (Fig. 1); however, the modification of the discussed material and the appropriate conditions may improve its physico-sorption possibilities. A group of the researchers[19]

[10]) Paper by Ewa Buczyńska „Graphene may lower the costs of hydrogen obtaining from RES for FCEVs" published in swiatoze.pl http://swiatoze.pl/aktualnosci/grafen-moze-obnizyc-koszty-pozyskiwania-wodoru-z-oze-dla-fcevs _385.html

[11]) Article by James Maynard : „New catalyst for fuel cells made from graphene could help boost renewable energy, e-cars", published in portal http://www.otechpost.com. http://www.itechpost.com/articles/10154/20130604/new-catalyst-fuel-cells=made-graphene-help-boost-renewable-energy.html

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Fig. 1. A diagram, representing value of adsorption for the particular zeolites and carbon materials[21] [Source 18]

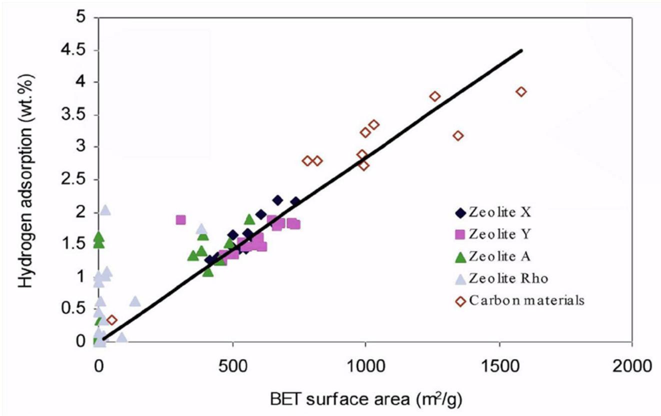


Fig. 2. A diagram, illustrating the process of Zeolite adsorption after ionic exchange Mg^{2+} and zeolite, washed with distilled water (pure zeolite, weight percentage of water content at time[22] [22]

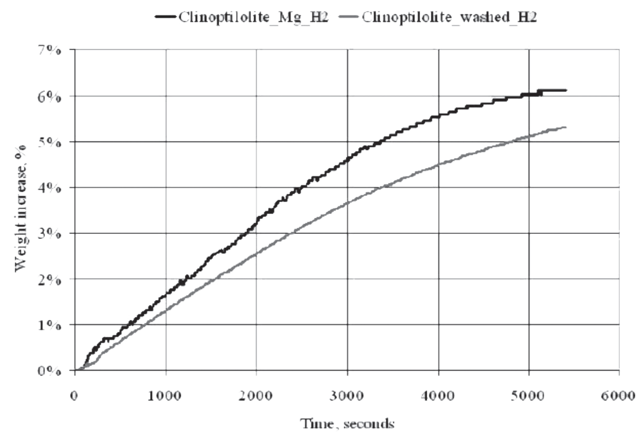
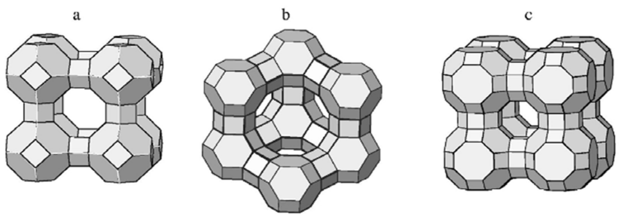


Fig. 3. Zeolite of type: 1/A; 2/X and Y; 3/RHO[24] [23]

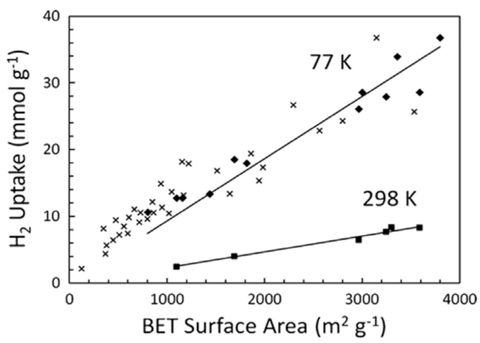


utilized naturally occurring zeolite material, klinoptylolite and the process of ion exchange with the used magnesium ions Mg^{2+} at temperature of 77 K what increased the sorption abilities of hydrogen. Ionic exchange in total improves adsorption-desorption properties of zeolite material; on the grounds of the results of the studies of Latvian scientists, the complex: zeolite-magnesium seems to be promising as compared to other sorbents[20].The obtained result – 6.2% by weight of adsorbed hydrogen for zeolite with Mg ionic exchange and 7% for pure zeolite, heated in nitrogen atmosphere allows optimistically looking at a wide spectrum of zeolite applications (Fig. 2); however, with the consideration of cryogenic conditions [22].

In 2003, a group of the scientists at Birmingham University worked upon a similar problem, i.e. sorption of hydrogen on synthetic zeolites A, X, Y and RHO[23] [23].

The conducted studies revealed[25] the best sorption properties of sodium zeolites NaA, NaX and NaY in relation to the complexes based upon the cadmium atoms [23]. Temperature was also a variable factor. The results, showing the highest value after adsorption-desorption cycles at temperature of 77K, that is, in cryogenic conditions, were unfavourable for the development of hydrogen technology (Fig. 4). In this aspect, we should pay attention to the necessity of increasing the costs connected with the maintaining the system in isothermal conditions. The successive disadvantage of the discussed application includes a low value of sorption (maximum 1.81% for NaY zeolite) at temperature of 77 K. The discussed technology has undoubtedly a potential but it requires many modifications. It should be mentioned that the present numerous studies and the trials to optimize mass production of zeolites from volatile ashes run in a very dynamic way. The utilization of by-product of combustion of coal and lignite in production of sorbent and later on, its use in storage and transfer of hydrogen affects a vision of environment-friendly future.

Fig. 4. A diagram, representing sorption H_2 on zeolite matrix at temperature of 77 K and 298K[26] [26]



[19] Source: footnote [15]

[20] Source: footnote [15]

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[24] Source: footnote [20]

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Over the states, there is a supreme-state [....] until I am going! [27] [24]

We know what hydrogen is, we know its properties, we are able to accumulate it and transform into electric energy. The ideas of its storage are dynamically developing. We hope that after the lecture of this paper, the Reader will have a question: when the "outburst of the hydrogen era" will take place. In our opinion, the mentioned period was commenced in the second decade of the 21st century. Hundreds of articles concerning the possibilities of utilizing hydrogen-driven mechanical vehicles, planned hydrogen refuelling stations, or construction of underground storehouses for H_2 in salt caverns are the premise of this trend. Perhaps it is enough that some would lie down under the apple tree or enter the tub with water and cry: "*Eureka*"!! (The motto for today is: to introduce graphene revolution and RES into the era of hydrogen!).

Economic aspects in such approach include optimization of manufacturing processes, storage and transmission of hydrogen in the industrial scale. The key may be the so-called wax foundation – the "leaven" of chemical honey plaster – Graphene. And perhaps the future belongs to sorbents with a high capacity! Michio Kaku wrote: "*In this century, we will harness the power of the stars, a source of the energy of Gods. In a short perspective, it will be the introduction of era of solar-hydrogen energy, which would replace fossil fuels; and in a longer time perspective –control of nuclear synthesis and even solar energy from the outer space*"[28] [21].

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