ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 4, pp. 657–659. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © Editorial Board, 2007, published in Russkii Khimicheskii Zhurnal, 2007, Vol. 50, No. 6, pp. 3–4.

# PREFACE

**DOI:** 10.1134/S1070363207040287

The main goal of the present issue of the "Russian Chemical Journal" consists in getting the readers interested in a real state-of-the-art of the global problem called "hydrogen energetics" familiar, as objectively as possible, with specific tasks that are being currently solved by world's researchers and tasks that are to be solved in the nearest and far future. We believe that this issue will be useful to young experts and post-graduate students, chemists and materials researchers, specializing in the field of unconventional energy sources. The latter undeniably include such an energy carrier as hydrogen.

Nowadays nonspecialists perceive the widely known term "hydrogen energetics" simply as the replacement by hydrogen of conventional energy carriers: liquid motor fuels, oil, coal, natural gas, nuclear energy, etc. The common vision is based on the mispresentation of the essence of the problem by some engaged experts which "prove" their positions both by horror stories about a depletion of energy resources and such beautiful words and terms as "ecological crisis," "greenhouse effect," "global warming," "alternative energy sources," "economic feasibility," and many other things. In periodic, popular scientific, or even scientific publications, these numerous authors substantiate the necessity of the civilization to pass to "hydrogen energetics" as fast as possible by that the resources of hydrocarbon fuels are already close to depletion, which should actually be taken into account, and that the hydrogen sources the World Ocean are limitless and infinite, which is also the real truth. Therewith, the fact that hydrogen is absent on the Earth in the pure state and does not form its own deposits is completely ignored. Unlike coal, oil, gas, and the situation on the Floodlight, hydrogen is no more that a carrier of energy from the Sun and secondary sources (oil, gas, coal, wind, and water) to a consumer.

From this it follows that for the very beautiful and tempting idea called "hydrogen energetics" to come true, one first should obtain hydrogen, i.e. spend energy. And, what is important, to obtain it by an economically justified method, i.e. the cost of the power equivalent of this energy carrier should be commensurable with the cost of traditional energy carriers and the energy carrier that has been used for hydrogen production. The irrepressible humanitarian "enthusiasm" of journalists which wish to convince the audience that the gain in energy due to the use of hydrogen will override the energy consumption for hydrogen production is obviously caused by blanks in school education.

*The first and the main task* of hydrogen energetics is to replace hydrocarbon raw materials, but the basic problem consists in that today there is no commonly accepted technology meeting all requirements of this global task. All presently known methods of hydrogen production are far from being perfect. First, they all are power-consuming. Second, hydrogen production is often accompanied by huge emissions of carbon dioxide and other toxic substances, especially characteristic of coal technologies. Today the contribution of $CO_2$ to increasing concentration of greenhouse gases in the atmosphere is still rather insignificant and causes no more than concern, but transition to hydrogen fuel produced, say, by methane reforming, will increase $CO_2$ emissions tens and hundreds times. Therewith, each calorie taken from hydrogen is 3–4 times more expensive than that obtained by gasoline combustion, and with hydrogen generated by water electrolysis this cost loss increases to 6–9 times. In this situation, speculations on the ecological cleanliness of hydrogen are only possible in the absence of systems thinking.

Among various approaches to this complicated problem, there are four that seem encouraging, but even they are still fairly fantastic. The first involves the use of thermonuclear energy which has not still been produced on the industrial scale, and its production and application safety has not still been substantiated. In this connection, the most grandiose and promising international project on thermonuclear synthesis deserves mentioning. The first stone in its realization has been laid in the form of the memorandum on the creation in France a Tokamak Experimental Reactor, signed in November 2006.

Advances in microbiology and biotechnology point to the possibility of developing effective hydrogen-generating microorganism strains, but, unfortunately, the latter still remain *terra incognita*, and nobody can guarantee that such strains will be developed and used in the foreseeable future.

The third way is the production of "clean" electric energy by semiconductor photocells powered from the primary energy source, the Sun, and further use of this energy for water electrolysis or for accumulation in high-temperature superconductor devices. Unfortunately, photocells are still quite expensive, and their quantum yield and durability are low.

And, finally, development of materials that split water under the action of sunlight. In particular, titanium dioxide nanotubes for hydrogen generation by photocatalytic water splitting have been reported. In spite of unclear perspectives, works on hydrogen production is being conducted in almost all directions, even such "ancient" as dissolution of metals in acids, alkalis, and water.

*Hydrogen transportation and storage* is the second, no less challenging problem to be solved in the framework of the hydrogen energy problem. Hundreds and even thousands kilograms of hydrogen, especially at stationary consumption, can be processes by means of available technologies, i.e. standard gas cylinders or cryogenic vessels. But the transition of economy to a new kind of energy carrier with annual demand for several ten million tons of hydrogen necessitates radically new technologies of hydrogen delivery and storage. Especially challenging is the problem of hydrogen application for powering various mobile power devices, from chargers in cell phones and portable computers with powers of several tens of milliwatts, up to vehicle power devices, first all automobile, with powers of several tens of kilowatts and above. A liquid hydrogen pipeline not only thousands kilometers but even hundreds meters long is hard to imagine, at least now. Nevertheless, mobile blocks for refuelling motor vehicles with liquid hydrogen produced with the use of cryotechnologies already exist. Unfortunately, they all are demonstration samples whose mission is to convince public and governments that hydrogen differs little from other energy carriers, such as methane, and the problem is possible and necessary to invest.

However, one should realize that conviction is not enough. The problem is much more complicated and expensive than seems at first glance, since each of the known methods of hydrogen storage and transportation possesses certain doubtless advantages but *fails to satisfy simultaneously* to all technology requirements. This is a stricly Gogol's situation: "...provided the lips of Nikanor Ivanovich, say, are put to Ivan Kuzmich's nose, and something is taken from Baltazar Baltazarovich's forwardness...". But nor Agaf'ya Tikhonovna nor we can come nearer to an ideal.

In our case, this "ideal" it contained in the U.S. Department of Energy's targets: *"The material should contain no less than 5.5 wt% of hydrogen at room temperature, the hydrogen sorption–desorption process should be reversible at temperatures not above the 120°C, the system should be safe and show stable performance over 5000 discharge–charge cycles."* Even though these requirements will undoubtedly change as one or another decision will be put in practice, it is important to be clear in one's mind that today a decision even close to meet these requirements is unavailable.

Sorbents whose capacity for hydrogen absorption is based on physical adsorption are incapable, by virtue of the nature of the phenomenon, to come nearer to these requirements, since sufficiently high adsorbate contents are achievable only at low temperatures. On the contrary, covalent or ionic hydrides with high weight hydrogen contents require very high temperatures to evolve or bind hydrogen. This not only complicates technical decisions at realization of the problem, but makes such systems much more dangerous in operation. From here it follows that an acceptable decision lays somewhere between physically sorbing materials and chemisorbing covalent hydrides. The future will show what is the nature of such a material and whether it exists at all. Coordination carcass compounds and composite materials on the basis of covalent hydrides of light metal seem to hold much promise. It is not excluded that research on these substances will disprove expectations after a while, as was the case with carbon sorbents or alanes.

And, finally, the third actual task which seemed solved quite recently—*the creation of a fuel cell* (FC). Even superficial glance on the design and operation of the "simplest" medium-temperature FC reveals to an objective reader some problems. The operation principle of FCs is transparent for understanding and known already more than 160 years (the pathbreaker is William Robert Grove, 1843). The designs of modern FCs, such as desired by their customers, hide serious problems. To prototype a FC for a toy electric car, is obviously not a big problem. But developing a model capable to stand resource tests in operating conditions within 1000 hours, raises questions of such a basic character that answers to them are searched all over the world for decades and not still found. Thus, a cheap and easily utilized material for bipolar plates, meeting on large-scale production requirements for chemical stability, high electrical and heat conductivities, strength, etc., has not yet chosen. How platinum or another catalyst should be applied to plate surface for not being washed off and remaining active while in service? What material the proton-exchange membrane should be fabricated of (now Nafion is actually the only one) to be durable in conditions when not only water, as is stated, but also a little hydrogen peroxide is formed in the system?

Apologists of this idea somehow forget that the oxidation of hydrogen with oxygen in the presence of platinum deposited on charcoal is the most advanced technology of hydrogen peroxide production. These components are all present is fuel cells, and the above side process undoubtedly occurs. There are questions but there are no adequate answers. Thus, FC is already not simple a task, this is a problem for experts in various sciences and, first of all, for materials scientists. Even though the decision of this problem and prototyping a FC are not a matter for near future, but its successful decision seems to be more probable than satisfactory decision of the above-mentioned tasks. The optimism is supported by the major global investments in the creation of a working FC, which presently approach several billion dollars.

The composers of this issue set themselves the task to outline, as comprehensively as possible, the range of technical and technological problems associated with the use of hydrogen. However, this task proved quite difficult to solve because of they poor compatibility of topics, objects, and relevant problems. However, we included in the list two articles, one of which shows the real use of hydrogen in the form of hydrides in commercial chemical current sources (accumulators), i.e. in high-tech technologies, and the other present technologies without which no hydrogen industry is imaginable, i.e. hydrogen sensors.

Unfortunately, hydrogen materials science and safety in their modern interpretation with reference to problems to be solved in the XXI century turned to be beyond the scope of this issue. It is quite clear that their solution will determine in many respects the viability of the whole construction which is very successfully and sonorously called "hydrogen energetics."

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