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Concept of Aluminum Hydrogen Energy Industry

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Abstract—The ecological consequences of atmospheric emissions of carbon dioxide and nitrogen and sulfur oxides, associated with the depletion of hydrocarbon fuels, induce demand for new low-cost and ecologically safe energy carriers. Hydrogen is presently considered to hold the greatest promise in this respect. The advantages of hydrogen include the availability of ecologically clean methods of its production and the possibility of direct conversion of its oxidation energy to electric and heat energy with a fairly high efficiency.

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At the same time, the use of hydrogen as an energy carrier is associated with a number of serious problems. Hydrogen is explosive, has a low density at normal pressure, and, as a consequence, a low volumetric energy capacity. The high cost of hydrogen, problems with developing infrastructure for its transportation and distribution, and high cost and low resource of air–hydrogen electrochemical generators retard development of hydrogen energy industry.

A radical solution of the above problems is provided by the use of aluminum for producing a steam–hydrogen mixture. Like hydrogen, aluminum is produced from natural raw materials, and, therewith, the total cost of its production is mostly contributed by power inputs (75–85%).

The aluminum content of the Earth™s crust is fairly high (8.8 wt%), and aluminum ranks first among metals and third among chemical elements (after oxygen and silicon) in abundance. This metal is inert in normal conditions, since it is covered by a thin oxide film due to reaction with oxygen. Its storage and transportation and safe and require no special infrastructure.

Let us briefly outline common features of the “aluminum” and hydrogen energetics. Hydrogen energy industry commonly perceived as the production of hydrogen from water and hydrocarbons and its accumulation and delivery to consumption sites. Hydrogen combustion and use as a fuel in electrochemical generators (ECGs) can be fairly efficient and involve minimal losses of stored energy and almost no hazardous emissions.

Storage of hydrogen as an energy carrier allows energy “storage.” It is known that the principal disadvantage of electric energy consists in that it is impossible to store effectively in condensers and accumulators.

Hydrogen forms no other products than water on combustion and can be used for creating a global and an ecologically clean power production system. Obviously, in terms of the minimal adverse environmental impact, hydrogen is best produced be means of nuclear power stations and from renewable, ecologically clean energy sources, specifically solar, wind, water, geothermal, etc. The modern concept of hydrogen energy does not also exclude hydrogen production from fossil fuels. However, this approach is obviously palliative and can only be realized during a time-limited transition period from the traditional to hydrogen energy industry.

The above-mentioned two principal postulates of hydrogen energetics are quite close to our proposed concept of “aluminum energetics” in that hydrogen is generated by the oxidation of aluminum with water. However, there are some differences that need to be discussed. Firstly, traditional fuels are hardly probable to replace by hydrogen in the foreseeable future. Secondly, it will be remembered that aluminum and hydrogen appreciably differ in energetic value and much differ in physical and chemical properties. Hydrogen has an extremely low density and is inflammable and explosive.

When comparing the “hydrogen” and “aluminum” concepts one should bear in mind one more quite an important circumstance. An essential advantage of hydrogen as an energy carrier consists in that the raw material for its production is almost exhaustless. In this connection, comparing hydrogen and aluminum, one should note that, provided aluminum oxidation products are returned in the production cycle, the output of bauxites and other aluminum-containing ores need not be expanded considerable, at least under conditions of stable consumption of aluminum as an energy carrier.

Provided the electrolytic production of aluminum makes use of renewable energy sources (hydroelectric, solar, wind, etc.), the "aluminum energy industry" should not contribute into the detrimental environmental effect. Finally, wide use of power devices fueled by hydrogen generated by the reaction of water with aluminum and its alloys will allow an energetically efficient solution of the problem of utilization of secondary aluminum.

Strange as it may seem, the potential of aluminum of a universal energy carrier has scarcely been considered up to now. The best developed devices that make use of aluminum in this role are air–aluminum fuel cells with aqueous electrolytes (AATCs). Attempts to develop power devices that realize the principle of the oxidation of aluminum and its alloys in water are known. The principal element of such constructions is a generator of a stem–hydrogen mixture that can be further used as a working body in traditional heat machines. The efficiency of known devices is always lower than theoretically predicted but compares to that of working examples of air–hydrogen fuel cells.

COST–PERFORMANCE ASSESSMENT OF FUEL CELLS ON THE BASIS OF ALUMINUM AND HYDROGEN

Cost–performance assessment was performed for several types of combined systems. The resulting data were compared with those for air–hydrogen proton-exchange membrane fuel cells (PEMFCs) and traditional air–aluminum fuel cells (AATCs) with an alkaline electrolyte and an Al–In alloy anode. A combined system comprising an AATC with a technical aluminum alloy anode and a built-over PEMFC. The other combined system comprising a hydrogen generator (HGen) based on the oxidation of aluminum in water, combined with a steam microturbine and an electrochemical generator (ECG) on the basis of stacks of solid polymer electrolyte fuel cells.

The parameters of the cost–performance assessment were the fuel energy efficiency (EE) and fuel component of produced energy (FComp). The energy efficiency is defined as the ratio of the energy produced from a specific energy carrier in a specific energy device to the energy consumed for production of this energy carrier. The fuel component is defined by the cost of the fuel or energy carrier to the quantity of energy produced from it.

PROTON-EXCHANGE MEMBRANE FUEL CELLS

The predicted cost of hydrogen at large-scale energy consumption is \$4–30/kg [1, 2]. The lower limit (\$4/kg) relates to hydrogen produced by steam methane reforming, and \$14/kg relates to hydrogen produced by water electrolysis in consumption sites with use of renewable sources. Taking account of the attained efficiency of PEMFCs of 40% [3], the FComp can be estimated at \$0.24–1.0/kW h. The EE of steam reforming is 70%. Then EE = E = 28%. At present (2005) in the USA to produce 1 kg of hydrogen by electrolysis takes no less than 11 kW h [5]. In this case, EE = 12%.

AIR–ALUMINUM FUEL CELLS WITH AN ALKALINE ELECTROLYTE AND AN AL–IN ALLOY ANODE

It is suggested that if the special Al–In anode alloy will be commercially produces, its market price will be no more than \$10/kg. The best attained efficiency of alkaline electrolyte Al–air systems is 55% [4]. The theoretical power density in the Al–air system is 8.1 kW h/kg. Then the FComp for this system is \$2.41/kW h. Electrochemical dissolution of 1 kg of Al gives 3 kg of $Al(OH)_3$. The market price of the hydroxide as the raw material for aluminum production is \$0.1/kg [4, 6]. In view of the fact that $Al(OH)_3$ is recycled, FComp = \$2.11/kW h.

To produce 1 kg of Al of A995 brand, 18 kW h is consumed. The production of the special alloy contributes 49% to the power inputs. Then the EE proves to be ca. 16%, which is higher than the EE of hydrogen.

COMBINED SYSTEM

The combined system comprises an AATC with a technical aluminum alloy anode and an air–hydrogen PEMFC (AATC–PEMFC). The combined system generates hydrogen due to the stray current corrosion of the anode alloy. The hydrogen produced is directed to the PEMFC for power generation. In such systems, the anode material can be technical aluminum or some of its commercial alloys which are much cheaper than special anode alloys. The following estimates are

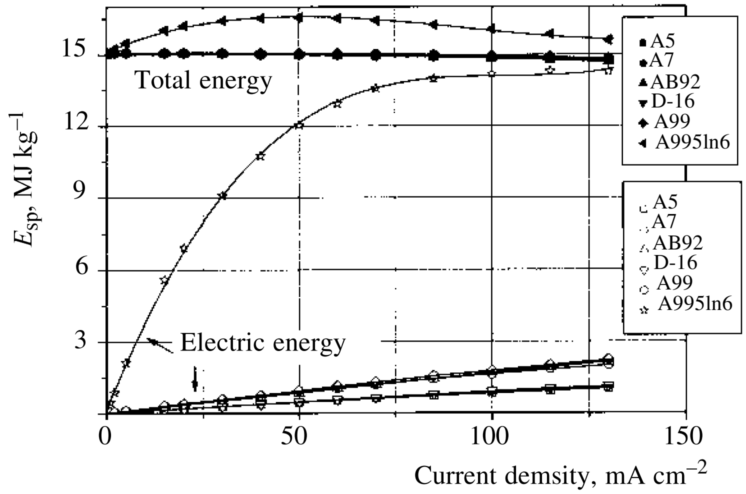

Fig. 1. Total specific energy of the hydrogen–aluminm electrochemical generator and its electric component at hydrogen utilization with an efficiency of 95%.

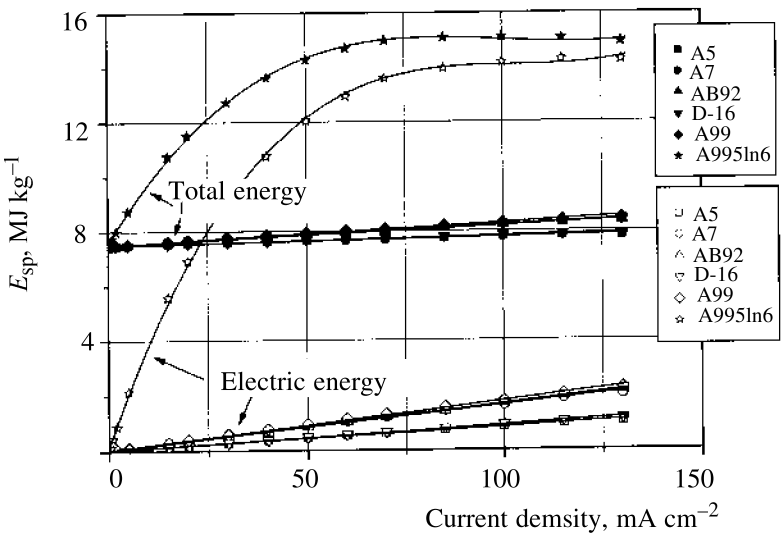

Fig. 2. Total specific energy of the hydrogen–aluminm electrochemical generator and its electric component at hydrogen utilization with an efficiency of 50%.

based on the results of the experiments described in detail in [8].

Figure 1 shows the plots of specific power vs. current density for an AATC with the anode made of technical aluminum alloys commercially produced in Russia. The light symbols relate to the quantity of electric power produced directly in the AATC. As seen, the specific electric power generated by AATC with commercial Al alloys is much lower (by almost an order of magnitude) than that of AATC with special Al–In alloys. The shaded symbols relate to the total energy produced as electricity and stored in the released hydrogen.

Figure 1 shows that, provided hydrogen is utilized with an efficiency of about 95%, for example, by burning in a water boiler, the energy efficiency of the combined devices on the basis of commercial aluminum is close to that of traditional AATCs with special activated alloys, such as Al–In.

Figure 2 shows the estimates for the case when hydrogen is utilized with an efficiency of 50%. Hydrogen is delivered into an air–hydrogen ECG , say, with a PEMFC. In this case, the total specific power of AATC+PEMFC is half that of the AATC with a special Al–In alloy anode.

Fuel components and fuel energy efficiencies

Device	Fuel component, \$/kW h	Fuel energy efficiency, %
Air–hydrogen ECG. Hydrogen production by methane reforming or by electrolysis	0.24–0.1	12–28
Air–aluminum ECG with special alloy anodes	2.11	16
Combined device: air–aluminum ECG with technical alloy anodes + air–hydogen ECG	0.50	15
Hydrogen generator + heat engine + ECG	0.08	22

The fuel component of the power production using commercial aluminum alloys will be estimated based on the metal price of \$1.1–1.2/kg.

The estimation should take account of the fact that the metal can be regenerated by returning the reaction product, $Al(OH)_3$, in the aluminum production cycle. Dissolution of 1 kg of aluminum gives 3 kg of $Al(OH)_3$. With its market price of \$0.1/kg [4, 6], we get for the power production from hydrogen with an efficiency of 50%:

$$\mathrm{FComp}_{50} = (1.2 - 0.3)\$/\mathrm{kg}:\ 8\ \mathrm{MJ\,kg^{-1}} = 0.11\$/\mathrm{MJ} = 0.50\$/\mathrm{kW\,h}. \quad (1)$$

For a 95% efficiency:

$$\mathrm{FComp}_{95} = (1.2 - 0.3)\$/\mathrm{kg}:\ 15\ \mathrm{MJ\,kg^{-1}} = 0.06\$/\mathrm{MJ} = 0.22\$/\mathrm{kW\,h}. \quad (2)$$

The power inputs for the production of 1 kg of aluminum are 15 kW h [4]. Based on the experimental data presented in Fig. 2 and the efficiency of the air–hydrogen ECG of 50%, we obtain EE = 15%.

HYDROGEN GENERATOR COMBINED WITH A STEAM MICROTURBINE AND ECG

The power device (Fig. 3) comprises a hydrogen generator (HGen) whose operation principle is based on the oxidation of aluminum with water, combined with a steam microturbine and an ECG with solid polymer electrolyte fuel cells. The stem–hydrogen mixture is formed by the steam oxidation of aluminum at high temperatures (200–1000°C) and pressures in generator *1*.

The operation principle of the device is as follows. The reaction ECG in reactor *1* forms bemit (AlOOH) and a mixture of hydrogen and water. This mixture passes to steam microturbine *2* hyphenated with a power generator. The exhaust mixture passes through separator *3* where, at a temperature of below 100°C and atmospheric pressure, it is separated into water and hydrogen. Hydrogen further passes to ECG. Consumer gets electric power produced by the steam turbine generator and ECG.

At present the Research and Engineering Center for Power-Saving Processes and Devices of UIHT RAS successfully produces nanocrystalline bemit using a steam–hydrogen generator with the following characteristics:

– ASD aluminum powder consumption 3.3 kg h^{-1};
– hydrogen yield 0.363 kg h^{-1} (4 $m^3\,h^{-1}$);
– steam yield 16–23 kg h^{-1};
– quantity of heat liberated with the steam–hydrogen mixture 56.1 MJ.

Let us now estimate the fuel component of the cost of the electric power generated by the device with the above characteristics. The efficiency of the steam turbine generator is taken to be 30% and that of ECG at 50%. The quantity of electric power produced by ECG is given by the product of the weight of hydrogen by the specific enthalpy of its oxidation reaction and ECG efficiency: $0.363\ \mathrm{kg} \times 120\ \mathrm{MJ\,kg^{-1}} \times 0.5 = 21.8\ \mathrm{MJ}$.

The total quantity of electric power is ECG.

The Russian market price of an ASD high-purity aluminum powder is \$10/kg. As mentioned above, aluminum hydroxides and oxides can be returned to the aluminum production cycle. In this case, they are marketed by the price of the raw material for alu-

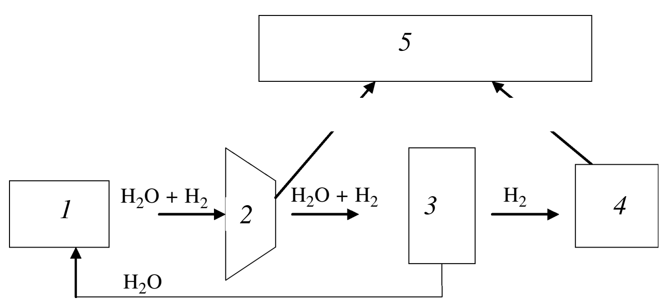

Fig. 3. Block scheme of a device on the basis of a steam hydrogen generator.

minum production, i.e. ~\$0.1/kg for aluminum hydroxide and ~\$0.3/kg for Al_2O_3. If the starting material is a highpurity fine Al powder, such as the abovementioned ASD, the reaction gives high-purity aluminum oxide or hydroxide powders (depending on the oxidation temperature). These compounds are widely used in the chemical and pharmaceutical industries, and power metallurgy. Their international market price can attain \$80/kg [9].

Let us use in the estimation the Russia market price of bemit (~\$10/kg). Taking into account the abovelisted parameters of the hydrogen generator, we obtain the following estimate for the fuel component per unit power output: (\$33 – \$60)/39 MJ, i.e. a negative value. In other words, in terms of the fuel component and actual bemit prices, this technology turns to be overprofitable.

The EE in this situation is EE = 22%.

Let us consider the situation, when bemit is not used as an independent product but is recycled. In this case, a high-purity aluminum powder is unnecessary, and a cheaper aluminum powder. It is produced on a large scale, and its Russian market price is ~\$3.5/kg. The price of bemit as a raw material for aluminum production is ~\$0.1/kg. Then the fuel component is estimated at EE: (11.5 – 0.6)\$/39 MJ = 0.28 \$/MJ or 0.08 \$/kW h^{-1}.

The calculation results are summarized in the table. Our estimates show that the technical and economic performance of the approach based on the use of aluminum for hydrogen production compares with that characteristic of traditional approaches to hydrogen storage, transportation, and use in power devices. Therewith, safety problems are successfully used, and the principle of the ecological safety of power production is fulfilled. Combined systems on the basis of hydrogen generators and a heat engine with a builtover ECG holds the greatest promise from the economic viewpoint. Such devices can work both as autonomous stationary low- and medium-power sources of electric and heat energy, as well as auxiliary or emergency devices.

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