

Short communication

## Use of low-cost aluminum in electric energy production

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### Abstract

Suppression of the parasitic corrosion while maintaining the electrochemical activity of the anode metal is one of the serious problems that affects the energy efficiency of aluminum-air batteries. The need to use high-purity aluminum or special aluminum-based alloys results in a significant increase in the cost of the anode, and thus an increase in the total cost of energy generated by the aluminum-air battery, which narrows the range of possible applications for this type of power source. This study considers the process of parasitic corrosion as a method for hydrogen production. Hydrogen produced in an aluminum-air battery by this way may be further employed in a hydrogen-air fuel cell (Hy-air FC) or in a heat engine, or it may be burnt to generate heat. Therefore, anode materials may be provided by commercially pure aluminum, commercially produced aluminum alloys, and secondary aluminum. These materials are much cheaper and more readily available than special anode alloys of aluminum and high-purity aluminum. The aim of present study is to obtain experimental data for comparison of energy and cost parameters of some commercially produced aluminum alloys, of high-purity aluminum, and of a special Al–In anode alloy in the context of using these materials as anodes for an Al-air battery and for combined production of electrical power and hydrogen.

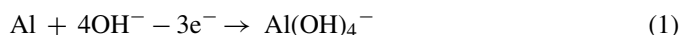
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*Keywords:* Aluminum anode; Corrosion; Aluminum-air electrochemical generator; Combined energy installation

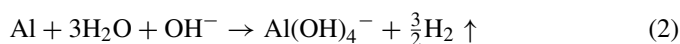
### 1. Introduction

Aluminum-air electrochemical generators with aqueous electrolytes (AIA ECG) hold certain promise for use as small-scale self-contained power plants, power units for vehicles, and facilities for emergency power supplies. In these applications, they may present a reasonable alternative to hydrogen-air fuel cell (Hy-air FC) due to the possibility of keeping AIA ECG in long-term storage before operation and to the simplicity and safety of the energy carrier.

In addition to the current-generating reaction



the reaction of parasitic corrosion



occurs at the anode during operation of an AIA ECG. This latter reaction causes an additional consumption of the material and release of hydrogen.

The need to suppress the parasitic corrosion while maintaining the electrochemical activity of the anode metal is one of the serious problems that affect the energy efficiency of AIA ECG. It has been demonstrated that this problem may be solved in part either by using aluminum of higher purity or by employing aluminum-based anode materials with minor additions of indium, gallium, zinc, magnesium, tin, and thallium [1]. In the latter option, it is expedient to introduce alkali stannate-based additions into the electrolyte, as well as organic acids, ethyl alcohol, or glycerin [1–5]. The need to use high-purity aluminum or special aluminum-based alloys results in a significant increase in the fuel factor (FF) of the cost of energy generated and in a significantly narrowed range of possible applications of AIA ECG.

An alternative approach to raising the efficiency of AIA ECG is based on treating the process of parasitic corrosion as a method for producing hydrogen, which may be further employed in a Hy-air FC or a heat engine, or it may be burnt

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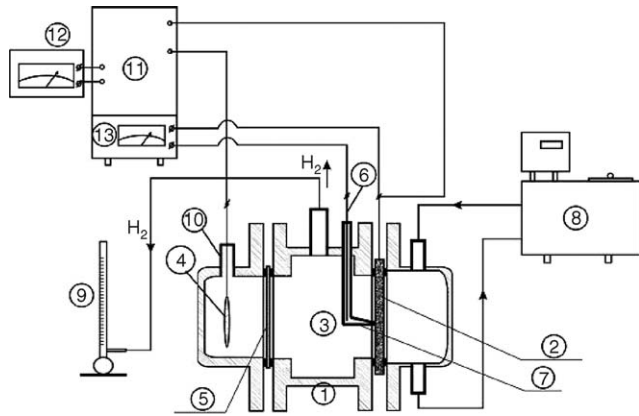


Fig. 1. Scheme of the experimental set-up.

to generate heat. Commercially pure aluminum, commercially produced aluminum alloys or secondary aluminium may serve as the anode. These materials are much cheaper and more readily available than special anode alloys of aluminum and high-purity aluminum.

The aim of this study is to obtain experimental data for comparison of the specific energy characteristics of some aluminum alloys produced in Russia, of high-purity aluminum, and of a special anode alloy in the context of using these materials as anodes in AIA ECG for combined production of electrical power and hydrogen.

The experiments involve the use of mass-produced (and therefore, most readily available) D16, A5, A7, AV92, and AV87 aluminum alloys, A99 (trade marks according to Russian standards) high-purity aluminum, and an anode alloy developed at the Moscow Aviation Institute (MAI) for use in an AIA ECG with an alkali electrolyte (hereinafter, referred to as A995In6 alloy). The chemical composition of the investigated alloys is given in Table 1.

## 2. Experimental

The anode polarization and the rate of hydrogen release as a function of the anode current density were determined. The experiments were performed over the temperature range 20–70 °C.

The experimental procedure is illustrated in Fig. 1. The equipment included an experimental cell 1 and electric, gas, and thermostatic-control circuits. The cell consisted of: an anode 2,

made of aluminum alloy; an electrolyte 3; an auxiliary electrode 4, made of nickel gauze and divided from the anode space by a diaphragm 5 that was used to separate the hydrogen released on the auxiliary electrode from that released on the anode as a result of its corrosion. The anode potential was measured with respect to a standard silver chloride reference electrode 6 via a Luggin capillary 7. A thermostat 8 was used to perform thermostatic control, with the temperature maintained within  $\pm 0.5$  °C.

The gas from the anode region was delivered to a circuit for measuring the gas flow rate. The rate of hydrogen release was determined by means of a burette 9 in which the gas volume was obtained by the displacement of the meniscus of a surfactant film. The error in the measurement of the rate of hydrogen release was  $\sim 3\%$ . The gas released on the auxiliary electrode was removed via tube 10.

The electric measuring circuit consisted of a potentiostat 11 for the galvanostatic measurements. The cell 1 and a milliammeter 12 (absolute error of measurement of 1.5 mA) were connected to the potentiostat. The high-resistance voltmeter 13 of the potentiostat was used to monitor the anode potential in relation to the reference electrode.

Polarization measurements were performed at four values of temperature, namely, 20, 40, 55, and 70 °C. The deviation of temperature from the pre-assigned value did not exceed 1 °C. Aluminum disks of 30 mm in diameter were used as experimental samples and were cut off from the same alloy sheet or ingot. Ten samples of each alloy were examined.

Prior to experiment, each sample was cleaned, after which it was washed with distilled water and placed in the cell. After experiment, the sample was once again washed with distilled water and the state of its surface was examined.

The electrolyte was a 4 M aqueous solution of NaOH prepared from analytically pure alkali. The concentration of electrolyte was checked and corrected by its density which was determined using a class 0.2 areometer. The electrolyte was replaced before each experiment. The polarization and corrosion characteristics of A995In6 alloy were determined using the electrolyte developed for that alloy [5], namely, 4N NaOH + 0.06 M  $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ .

The rate of hydrogen release was used to calculate the corrosion current density ( $\text{mA cm}^{-2}$ ), i.e.,

$$j_{\text{corr}} = \frac{n \cdot V \cdot F}{1000 \cdot \tau \cdot V_0 \cdot S} \quad (3)$$

Table 1  
Chemical composition of aluminum alloys

Type of alloy	Potential at 70 °C	Chemical composition (wt.%)									
		Al	In	Cu	Si	Zn	Fe	Ti	As	Mn	Mg
A99	−1.66	99.99	–	$2.3 \times 10^{-4}$	$12.3 \times 10^{-4}$	$4.4 \times 10^{-4}$	$18.7 \times 10^{-4}$	$1.2 \times 10^{-4}$	–	$0.21 \times 10^{-4}$	$0.7 \times 10^{-4}$
A7	−1.65	99.7	–	0.005	0.11	0.02	0.1	0.006	0.001	–	–
A5	−1.43	99.5	–	0.01	0.11	0.02	0.15	0.01	0.01	–	–
AB92	−1.558	94.61	–	0.79	0.99	0.74	0.43	0.04	–	–	2.4
AB87	−1.34	87.39	–	3.8	3.8	2.0	1.8	0.11	–	0.27	0.42
D16	−1.51	93.4	–	4.5	–	–	–	–	–	0.6	1.5
A995In6	−1.9	99.4	0.6	$1 \times 10^{-3}$	$1.5 \times 10^{-3}$	$1 \times 10^{-3}$	$1.5 \times 10^{-3}$	$1 \times 10^{-3}$	–	$1 \times 10^{-3}$	$1 \times 10^{-3}$

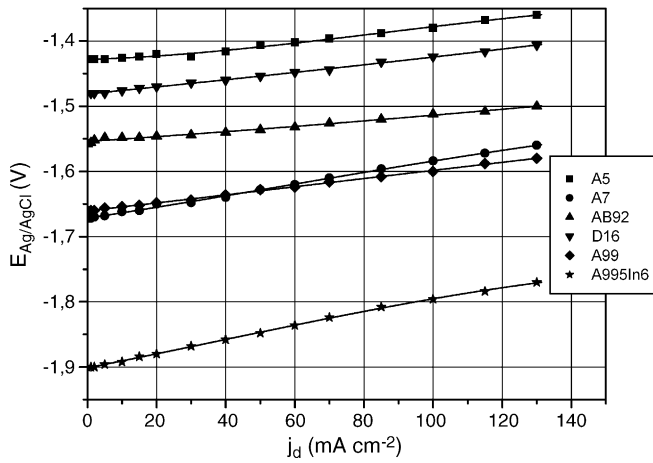


Fig. 2. Polarization curves of aluminum alloys at 70 °C.

where  $V$  is the volume of released hydrogen,  $L$ ;  $n = 2$  is the number of electrons involved in the reaction;  $F$  the Faraday constant,  $\text{As mol}^{-1}$ ;  $\tau$  the time during which the volume  $V$  was released,  $s$ ;  $V_0 = 22.4$  is the molar volume of gas,  $L$ ; and  $S$  is the electrode area,  $\text{cm}^2$ .

### 3. Results and discussion

A complete investigation was undertaken of the electrical and corrosion characteristics of A99, A5, A7, AV92, and D16 aluminum alloys, as well as for A995In6 alloy. The A87 alloy displays abnormal behaviour: it corrodes actively with the rapid formation of pits. This gives rise to appreciable fluctuations of the time dependence of current and voltage and that affect the accuracy of the current density calculation.

The anode potential of the alloys as a function of current density at 70 °C is plotted in Fig. 2. While the corrosion current as a function of polarization current at the same temperature is given in Fig. 3. The temperature dependence of polarization curves does not qualitatively differ for the tested alloys: the electrode potential shifts in a negative direction with increasing temper-

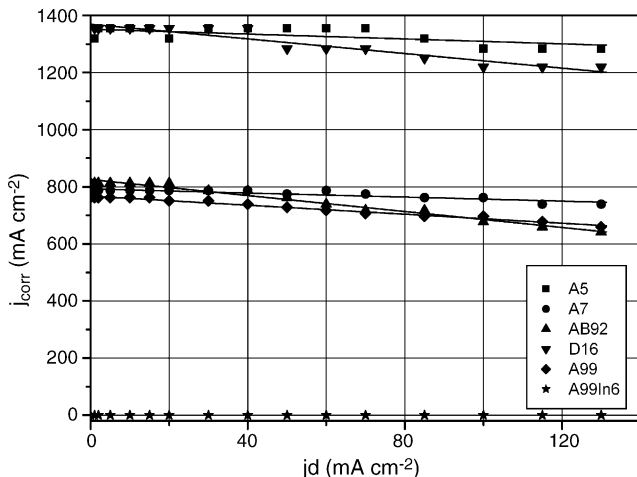


Fig. 3. Corrosion current as a function of anode current for aluminum alloys at 70 °C.

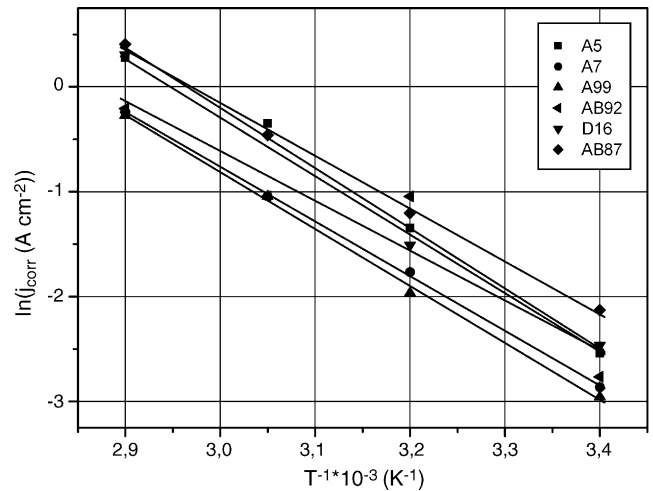


Fig. 4. Corrosion current as a function of temperature for aluminum alloys.

ature. The temperature increase is further accompanied by an increase in the electrochemical activity of aluminum and by an increase of the hydrogen yield (corrosion current). The hydrogen yield decreases with increasing anode current. At 40 °C, the increase in anode current to 100  $\text{mA cm}^{-2}$  causes a reduction in the corrosion current by a factor of two. At 70 °C, however, the corrosion current decreases by less than 5%.

The corrosion current as a function of temperature for the alloys is shown in Fig. 4. The linear dependence of the logarithm of corrosion current on the inverse of temperature indicates that the corrosion is a thermally activated process. The activation energy of the chemical corrosion of aluminum, calculated from the temperature dependence of the corrosion current (Fig. 4) is in the range from 46 to 53  $\text{kJ mol}^{-1}$ .

An increase in the impurity content of aluminum causes both the open-circuit potential and the potential under load to shift towards more positive values. This is accompanied by an increase in the non-uniformity of dissolution of aluminum and by a decrease in its Faraday efficiency and utilization factor. The exception is A5 aluminum which reports potentials that are more positive than the respective potentials of A7 aluminum of a similar composition. The effect is apparently associated with the high content of corrosion-active elements Fe, As, Cu. Another exception is a result of the influence of indium [2], in the case of A995In6 alloy. For this alloy, the voltage is  $-1.9$  and  $-1.6$  V at  $j_d = 0$  and  $130 \text{ mA cm}^{-2}$ , respectively.

The following analysis examines the economics of using commercially available aluminum alloys in a hybrid installation that consists of an AIA ECG and a topping unit for the production of hydrogen. For this purpose, an estimation is made of the amount of electrical power generated in an AIA ECG, as well as the energy stored in hydrogen released due to corrosion. This assumed that the released hydrogen is used to generate electrical power in a device with an efficiency of  $\sim 50\%$  (for example, in a Hy-air FC) or to generate heat with an efficiency of 95%.

The total specific energy generated using an AIA ECG is:

$$A = \frac{(A(\text{Al})_{\rightarrow \text{I}} + A(\text{Al})_{\rightarrow \text{H}_2})}{\nu(\text{Al})} \quad (4)$$

where  $A(\text{Al})_{\rightarrow I} = I_d U \Delta t$  (J) is the part of the energy produced in the form of electrical power, and  $A(\text{Al})_{\rightarrow \text{H}_2} = \eta \Delta_r H \nu(\text{H}_2)$  (J) is the part of the energy stored in hydrogen obtained in AIA ECG as a result of anode corrosion;  $\Delta_r H$  the enthalpy of water formation;  $\eta$  the efficiency of the hydrogen utilization device;  $I_d$  and  $U$  denote, respectively, the current and voltage of the AIA ECG;  $\Delta t$  the time; and  $\nu(\text{Al})$  is the number of moles of aluminum reacted during time  $\Delta t$ .

According to Faraday’s law, the amount of hydrogen released during time  $\Delta t$  is:

$$2F \frac{\nu(\text{H}_2)}{\Delta t} = I_{\text{corr}} \rightarrow \nu(\text{H}_2) = \frac{I_{\text{corr}}}{2F} \Delta t, \quad (5)$$

where  $F$  is the Faraday constant ( $\text{C mol}^{-1}$ ) and  $I_{\text{corr}}$  is the corrosion current. Therefore, the specific energy stored in hydrogen is:

$$A(\text{Al})_{\rightarrow \text{H}_2} = \eta \Delta_r H \frac{I_{\text{corr}}}{2F} \Delta t, \quad (6)$$

The respective amounts of aluminum used to generate electrical power and of aluminum which reacted in the corrosion reaction with the formation of hydrogen are:

$$\nu(\text{Al})_{\rightarrow I} = \frac{I_d}{3F} \Delta t \quad \text{and} \quad \nu(\text{Al})_{\rightarrow \text{H}_2} = \frac{I_{\text{corr}}}{2F} \Delta t \frac{1}{1.5} = \frac{I_{\text{corr}}}{3F} \Delta t \quad (7)$$

The total amount of aluminum spent during time  $\Delta t$  is:

$$\nu(\text{Al}) = \frac{\Delta t}{3F} (I_d + I_{\text{corr}}) \quad (8)$$

The resultant relations are substituted into formula (4) to derive the expression for the total specific energy, i.e.,

$$A = \frac{I_d U \Delta t + \eta \Delta_r H (I_{\text{corr}} / 2F) \Delta t}{(\Delta t / 3F) (I_d + I_{\text{corr}})} = 3FU \frac{I_d}{I_d + I_{\text{corr}}} + \frac{3}{2} \eta \Delta_r H \frac{I_{\text{corr}}}{I_d + I_{\text{corr}}}, \quad \text{J mol}^{-1}(\text{Al}) \quad (9)$$

In order to perform numerical calculations by formula (9), it is necessary to know the current–voltage characteristics of a model AIA ECG that employs different anode alloys. The current–voltage curve of the model AIA ECG  $U = f(I_d)$  was calculated as the difference between the polarization behaviour of anodes and a gas-diffusion cathode [6] (Fig. 5). Current–voltage characteristics obtained in this way were used to calculate the specific power generated by AIA ECG using aluminum alloys.

The specific energy as a function of the discharge current for the investigated aluminum alloys under conditions of utilization of hydrogen with an efficiency of 95 and 50% is given in Figs. 6 and 7, respectively. In the case of 95% efficiency (combustion to generate heat), the values of the total specific energy obtained with anodes of A995In6 and commercial-grade alloys are close to each other. The total specific energy is approximately  $15 \text{ MJ kg}^{-1}$ , with the discharge current density ranging from 50 to  $120 \text{ mA cm}^{-2}$ . For utilization of hydrogen at 50% efficiency (generation of electrical power in a Hy-air FC),  $\sim 8 \text{ MJ}$  of electrical energy may be produced per 1 kg of aluminum alloy.

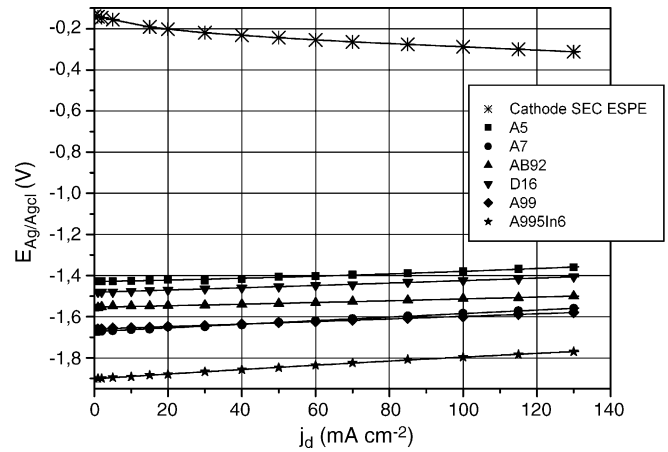


Fig. 5. Polarization curves of aluminum alloys and gas-diffusion cathode.

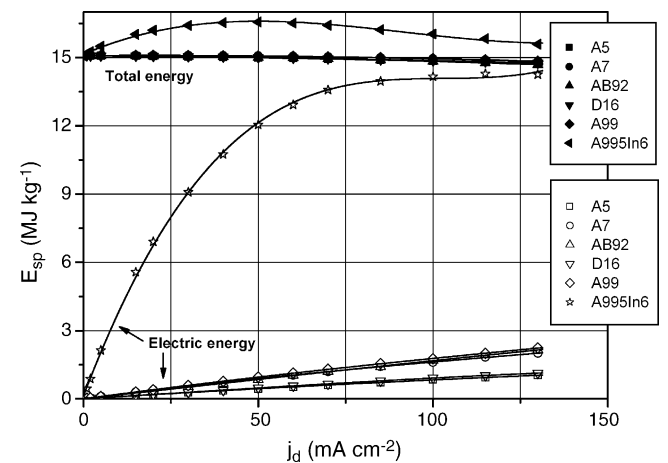


Fig. 6. Total specific energy of AIA ECG and its electric component (hydrogen utilized with efficiency of 95%).

In order to estimate the economic effect produced by substituting of a special-purpose anode alloy (such as A995In6 alloy) with a commercially available aluminum alloy, an estimation is made of the fuel factor (FF) of the cost of energy for both types of alloy. The fuel component is defined as the ratio of the cost

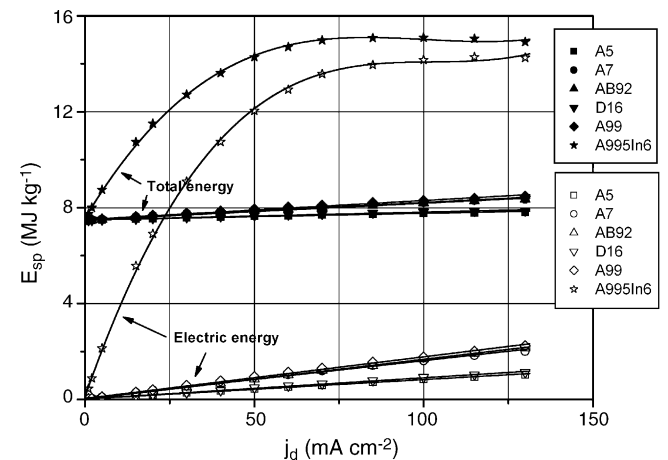


Fig. 7. Total specific energy of AIA ECG and its electric component (hydrogen utilized with efficiency of 50%).

Table 2  
Fuel factor of cost of energy for electrical power generation

Type of unit	Characteristic of unit and processes	FF (\$ kWh <sup>-1</sup> )
Hy-air FC	50% Efficiency	0.24–1.8
AA ECG	Special-purpose alloy	2.41
AA + AH ECG	AH ECG of 50% efficiency + regeneration	0.32–0.4
AA FE + hot-water boiler	95% combustion efficiency + regeneration	0.17–0.22

of fuel (Al alloy) to the amount of energy produced from this fuel. For comparison, the fuel component of the cost of energy produced by a Hy-air FC<sub>2</sub> is also estimated.

In accordance with known data [7,8] the proposed hydrogen cost lies in the range \$4–30 kg<sup>-1</sup>. The former cost corresponds to hydrogen production via the natural gas (NG)—steam conversion process as realized in a large plant (150 t day<sup>-1</sup>) [8]. It is necessary to emphasize that production of hydrogen from NG is accompanied by carbon dioxide emissions and that the resources of NG are limited. The \$30 kg<sup>-1</sup> cost relates to the production of hydrogen by electrolysis of water with the use of renewable energy sources.

The enthalpy of steam formation during the oxidation of hydrogen under normal conditions is 33 kWh kg<sup>-1</sup>. This quantity characterizes the amount of energy that may be produced from 1 kg of hydrogen in some hypothetical power-generating device of 100% efficiency. With the 50% efficiency of a Hy-air FC, 16.5 kWh of electric energy may be produced per 1 kg of hydrogen. This gives values of the energy cost (fuel factor, FF) in the range of \$0.24–1.8 kWh<sup>-1</sup>.

An estimation is also made of the FF of electrical power generated in an AIA ECG using A995In6 special-purpose anode alloy. The present-day cost of this material in the Russian market may be as high as \$200 kg<sup>-1</sup>. Nevertheless, there is reason to believe that, in the case of commercial production, the cost may be reduced to \$~10 kg<sup>-1</sup>. The corresponding FF is \$2.41 kWh<sup>-1</sup>.

In the case of power generation using commercially available aluminum alloys, the FF is derived using the cost of the metal given in [9,10], i.e., \$1.0–1.2 kg<sup>-1</sup>. Account is also taken of the regeneration of metal by recycling of the reaction product Al(OH)<sub>3</sub> [9]. The dissolution of 1 kg of aluminum results in the production of 3 kg of aluminum hydroxide. Given the market price of \$0.1 kg<sup>-1</sup> for the latter [9,11], the FF for electrical power generation from hydrogen with 50% efficiency is:

$$FF_{50} = \frac{\$(1.2 - 0.3) \text{ kg}^{-1}}{8 \text{ MJ kg}^{-1}} = \$0.11 \text{ MJ}^{-1} = \$0.4 \text{ kWh}^{-1} \quad (10)$$

Heat generation from hydrogen with 95% efficiency yields:

$$FF_{95} = \frac{\$(1.2 - 0.3) \text{ kg}^{-1}}{15 \text{ MJ kg}^{-1}} = \$0.06 \text{ MJ}^{-1} = \$0.22 \text{ kWh}^{-1} \quad (11)$$

The calculation results are summarized in Table 2.

The results of calculations based on our experimental and literature data demonstrate that the use of some commercially available aluminum alloys in an AIA ECG, instead of special-purpose alloys, makes it possible to reduce significantly the FF of the cost of generated energy, provided that hydrogen released in the process of corrosion will also be used to generate energy. In this case, the cost of energy turns out to be comparable (or lower) with that for Hy-air FC.

This concluded that commercially available aluminum alloys are appropriate for use as the anode material in self-contained installations that generate electrical power and heat. In such installations, an AIA ECG with a power of several kilowatts may be combined with a Hy-air FC and a hot-water boiler with an air-hydrogen burner. With low consumption of electrical power and hydrogen, released hydrogen may accumulate in a buffer reservoir. At peak electrical and heat loads, all three elements of the system are made operational, namely AIA ECG, Hy-air FC and hot-water boiler. Optimization of operation of the suggested combined power-generating system for the intermediate modes of energy consumption has not been attempted, but will be the subject of separate experimental and theoretical investigation.

#### 4. Conclusions

The main results obtained in this study are as follows:

1. The effect of discharge current on the polarization characteristics of the anode and on the corrosion current for A99 aluminum and six aluminum-based alloys has been investigated. The presence of impurities in an amount of 1–10 wt.% in aluminum causes a shift of the open-circuit potential in the positive direction by approximately 20% relative to pure aluminium, and also a shift of the voltage versus current curves. The corrosion current for alloys is 1.7 times higher than for A99 aluminum. The open-circuit potential of the A995In6 special alloy is –1.9 V, and its corrosion current is two orders of magnitude lower than that of A99 aluminum and aluminum alloys.
2. Experimental data are used to calculate the specific energy which may be obtained via the use of a combined installation with a AIA ECG using commercial grade alloys as the anode material. Calculations are carried out with respect to the energy stored in released hydrogen. If the enthalpy of combustion of hydrogen, is taken into account, the special anode alloy A995In6 and commercial grade aluminum alloys give similar values of energy density.
3. An estimation is made of the fuel component in the cost of produced energy for installations of different types, namely, Hy-air FC and AIA ECG, as well as AIA ECG which utilizes commercial aluminum alloys and is topped with an Hy-air FC and/or hydrogen fuel-fired hot-water boiler. Correction of the FF, which arises when the reaction products are recycled back to aluminium, is taken into account. Estimations demonstrate the principal possibility of economically justified utilization of commercially produced aluminum alloys as fuel in environmentally benign power sources that involve aluminum-air electrochemical generators.

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