TRANSPORT PROBLEMS 2018 Volume 13 Issue 3
PROBLEMY TRANSPORTU DOI: 10.20858/tp.2018.13.3.7

Keywords: waste energy; efficiency; exhaust gases

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ELECTROCHEMICAL CYCLE FOR THE CONVERSION OF THE WASTE HEAT INTO ELECTRICAL ENERGY: THE POSSIBILITY OF USING IN WATER TRANSPORT

Summary. We developed a concept and calculated an efficiency of the electrochemical cycle of converting low-grade heat (temperature difference 10-80°C) into electricity. The cycle could be divided into two stages: creating a concentration difference by a solution distilled in a temperature gradient and electricity generation in concentration galvanic cell. The calculation shows that the efficiency of converting heat into electricity could reach 40-55% of Carnot efficiency in a temperature range of 0-100°C in the case of use of a multi-cascade distiller. The calculations show that ratio power/mass of the device is too low to be used in automobile or air transport, but it could be used in water transport.

1. INTRODUCTION

The aim of this work is to develop a simple device that can directly convert the heat energy into electrical energy using a small temperature gap, and make a conclusion about the possibility of using the device in transport for converting the heat of waste gases into electrical power.

Traditionally, electrochemical devices for converting heat into electricity have a construction of thermogalvanic cells. At the temperature range of 0-100°C, Seebeck coefficients of aqueous and nonaqueous thermogalvanic cells are higher than in solid thermoelectric [1-10].

Also, one approach to the problem of low-grade heat conversion into electricity is the thermally regenerative electrochemical cycle, which uses the dependence of electrode potential on temperature. By varying the temperature, an electrochemical cell is charged at a lower voltage than discharged; thus, thermal energy is converted into electricity [11-13].

In the previous paper, we described the electrochemical convertor, on which work is based on reaction of sulfuric acid salvation [14]. This reaction is reversible. We use direct reaction for the generation of electricity and heat energy to perform the reversal reaction. The processes of sulfuric acid distilling and energy generation were separated from each other at time and space. The external resistance R was much higher than internal resistance of the battery. In this case, we reduce the power of the cell, but increase its efficiency. The calculation shows that the efficiency of this way of heat converting into electricity could be 30-37% of Carnot efficiency in the temperature range 0-40°C.

In paper [16], we describe the concept and basic principles of work of the hybrid of thermogalvanic and concentration galvanic cells. We simplified the construction of the convertor, described in paper [14] and use an alkali electrolyte instead of an acidic one. In spite of the previous device, it was direct heat contact between the vessels with temperatures T_1 and T_2. Calculations show that in the temperature range of 20-80°C, the hybrid thermogalvanic cell with an alkaline electrolyte shows 8-11% of Carnot efficiency.

Independently, the group of Italian scientists shows that the theoretical efficiency of the cycle based on $ZnCl_2$ solutions distilling in two cascade distillers and further converting the concentration difference into electrical power in electrochemical cells can reach 80% of Carnot efficiency [16]. It is necessary to add that in paper [15], the calculations were made in suggestion that the work of concentration galvanic cell will be stopped only when the concentration in both half-cells will be equal. In practice, it requires too much time for the fulfillment of this condition.

So, the cycle based on solutions distilling and further electricity generation in concentration galvanic cell seems to be more rather promising if the processes of electricity generation and solution distilling are separated from each other in space and time and the multi-cascade distiller is used.

In this work, we made calculations for the electrochemical cycle with an acid electrolyte for a multi-cascade distiller and calculated the ratio power/mass of the device to make conclusions about the possibility of using the suggested device in the transport.

2. ANALYTICAL METHOD

To evaluate the possibility of distillation, it is necessary to have information about the numerical values of the vapor pressure above the sulfuric acid solutions of different concentrations at different temperatures. These data are presented in Table 1 [17, 19].

Table 1

The numerical values of the vapor pressure above the H_2SO_4 solutions with different concentrations

Concentration of sulfuric acid, %	Vapor pressure at temperature T, [mm Hg]										
	T=10 °C	T=20 °C	T=30 °C	T=40 °C	T=50 °C	T=60 °C	T=70 °C	T=80 °C	T=90 °C	T=100 °C	T=110 °C
10	8,80	16,6	30,0	52,9	88,5	143	223	337	498	720	
20	8,05	15,4	27,8	48,6	82,2	133	207	314	468	678	
25	7,46	14,3	26,0	45,6	76,7	124	195	295	437	637	
30	6,91	13,2	23,8	41,7	71,3	116	180	273	404	590	
35	6,23	11,8	21,2	37,3	63,0	102	159	244	369	540	768
40	5,22	9,95	18,0	31,8	53,9	87,3	138	211	319	474	679
45	4,19	8,10	14,7	26,0	44,7	73,0	116	179	271	405	580
50	3,19	6,20	11,3	20,3	35,2	58,0	92,5	143	217	326	471
55	2,26	4,43	8,29	14,8	26,0	43,0	69,6	108	167	253	367

As we can see from Table 1, the vapor pressure above the 50% solution of H_2SO_4 at 40°C is higher, than above 10% solution at 20°C. It means that if the temperature of the hot contact T_1 is 313 K (40°C), and the temperature of the cold contact T_2 is 297 K (20°C), we can perform the distillation of sulfuric acid solution from 10% to 50%.

Similarly, if T_1=333 K (50°C) and T_2=323 K (40°C), it is possible to perform the distillation of H_2SO_4 solution from 10% to 40% and etc.

The potential of $Pb/PbSO_4$ or $PbSO_4/PbO_2$ electrode in the sulfuric acid solution depends on the acid concentration.

In the traditional concentration, galvanic cells, the potential difference depends on the $\log c_1/c_2$ (c_1 is the concentration of the electrolyte within a vessel and c_2 is the concentration of the electrolyte in another vessel). In sulfuric acid solutions, it is correct only in solutions with pH>1.

If pH<1, we have practically linear dependence of EMF on the concentration.

We have this effect because a galvanic cell uses the exothermic reaction of the hydroxide dissolving in the water.

As it was shown in ref. [15], lead cell could work as concentration galvanic cell.

For the $Pb/PbSO_4$ electrode, the electrode process at the vessel with a high concentration of H_2SO_4:

$$Pb+SO42—2e→PbSO4 \quad (1)$$

The electrode process at the vessel with a low concentration of H_2SO_4:

$$PbSO_4+2e→Pb+SO_4^{2-} \quad (2)$$

For the $PbO_2/PbSO_4$ electrode, the process at the electrode at the vessel with high concentration of H_2SO_4:

$$PbO2+4H++SO42-+2e→PbSO4+2H2O \quad (3)$$

The process at the electrode at the vessel with low concentration of H_2SO_4:

$$PbSO4+2H2O-2e→PbO2+SO42-+4H+ \quad (4)$$

Similarly, in a vessel with a lower concentration of sulfuric acid, we have not only the release of sulfate ions but also absorption of water.

The efficiency of our method of conversion can be calculated as

$$\eta = \frac{A_1}{Q} \quad (5)$$

where A_1 is useful energy, which could be obtained on the external resistance and Q is heat, consumed in the cycle.

Heat consumed by the device cell can be calculated as

$$Q = nL + (q_2 - q_1) + c(T_1 - T_2) \quad (6)$$

where "L" is the molar evaporation heat of water; "n" is number of water moles that is necessary to evaporate to obtain a solution, which contains one mole of sulfuric acid with concentration c_1 from solution with concentration c_2; "c" is a heat capacity of the acid solution with concentration c_2 which contains one mole of sulfuric acid.

For example, to obtain 52% solution of sulfuric acid (empirical formula $H_2SO_4*5H_2O$) from 35% solution (empirical formula $H_2SO_4*10H_2O$) it is necessary to evaporate 5 moles of water.

Numerical values of the molar heat of vaporization of water were obtained in ref. [17].

Full energy which could be obtained at the cell is

$$A \approx q_1 - q_2 \quad (7)$$

where q_1 is the heat of sulfuric acid dissolving to the concentration c_1 and q_2 is the heat of the acid dissolving to the concentration c_2. The electromotive force of the cell

$$\varepsilon = \frac{A}{zF} \quad (8)$$

where "z" is the number of the electrons, participating in the reaction, and "F" is a Faraday constant.

Useful energy could be calculated as

$$A_1 = A\frac{R}{R+r} \quad (9)$$

"R" is external resistance, and "r" is internal resistance.

The numerical values of the molar heat of sulfuric acid dissolving [18,19] are presented in Table 2.

In the case of a multi-cascade distiller, the total efficiency was calculated as

$$\eta = \eta_1 + \eta_2(1-\eta_1) + ... \quad (10)$$

where η_1 is the efficiency in the first cascade, η_2 is the efficiency of the second cascade, and so on.

Power was calculated as

$$P = \frac{\varepsilon^2}{(r+R)^2}R \quad (11)$$

Internal resistance was calculated as

$$r = \rho_1 \frac{l}{S} + \rho_2 \frac{l}{S} \tag{12}$$

where ρ_1 and ρ_2 are the resistivity of sulfuric acid solutions with concentrations c_1 and c_2, l is the distance between the electrodes, and S is the square of the electrodes.

Table 2

The molar heat of the sulfuric acid dissolving in the water

Moles of H_2O per one mole of the acid	Concentration of the sulfuric acid, [%]	Heat of sulfuric acid dissolving, [kJ/mol]
1	84.4	28
2	73	42
3	64.5	49
4	57.6	54
5	52	58
6	47.6	61
8	40.5	67
10	35.3	70.2
15	26.6	71.5
20	21.4	72.7
30	15.4	73.1
40	12	73.4
50	9.8	73.7

The mass was calculated as

$$M = M_{electrodes} + M_{electrolyte} \tag{13}$$

The mass of the electrodes was calculated as

$$M_{electrodes} = 2S\Delta x\rho \tag{14}$$

where ρ is the density of the electrode and Δx is the thickness of the electrodes.

The mass of the electrolyte was calculated as 20% of the mass of the electrodes [19]. In all our calculations, l=0.01 m and Δx=0.005 m.

3. RESULTS AND DISCUSSION

Thus, we see that the efficiency of the device depends not only on the temperature difference, but also on the initial and final acid concentration.

The maximum efficiency of the electrochemical method is presented in Table 3.

As we can see from Table 2, single-cascade devices can give satisfactory efficiency only if the temperature difference is in the range of 20-30 °C. If the temperature difference is 50-70, two or three cascade distillers are necessary. Also, we can conclude that low values of c_2 decrease the efficiency of the device. We have this effect because of two factors: decreasing of the electrical conductivity of the solution and increasing of the water mass, which is necessary to evaporate. When ratio R/r=1, we could obtain the maximum value of the ratio power/mass, but with rather low efficiency. So the mode of work when R/r=2 seems more suitable to us.

The ratio power/mass is rather low, so it is impossible to use a suggested device neither in air transport where ratio power/mass is 100-500 W/kg nor in automobile transport where the minimum value of ratio power/mass is about 12 W/kg.

But in water transport, the suggested electrochemical convertor seems to be suitable. For example, the weight of a supertanker «Knock Nevis» was 657018 tons and power of turbines about 50000 horsepower which corresponds to 37 MW [21]. So the ratio power/mass was about 0,056 W/kg.

Thus, we can make a conclusion that only in water transport, using the proposed device will increase the total efficiency of converting the chemical energy of the fuel into mechanical or electrical energy without decreasing the ratio power/mass.

Table 3

The efficiency of heat converting at different temperatures

T_1, [°C]	T_2, [°C]	C_1, [%]	C_2, [%]	Number of the cascades	R/r	η, [%]	η_r, [%]	Power/mass, [W/kg]
50	30	52	20	1	1	1.1	17.7	0.089
50	30	52	35	1	1	2.6	42	0.065
50	30	52	35	1	2	3.4	55	0.058
60	30	55	20	1	1	1.3	14	0.091
60	30	55	30	1	2	3	33	0.06
80	30	52	35	2	1	5.1	36	0.065
80	30	52	35	2	2	6.6	46.6	0.058
100	30	52	35	3	2	9.8	52	0.058

4. CONCLUSIONS

1. The efficiency of the electrochemical cycle based on acid solutions distilling at a temperature gradient and electricity generation in the concentration galvanic cell could reach 55% of Carnot efficiency at the temperature range 30-100°C.
2. The calculations show that the ratio power/mass of the suggested device is about 0.058-0.089 W per kg.
3. The ratio power/mass of the existing model is too high for using in air or automobile transport, but it could be used in water transport.

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Received 05.05.2016; accepted in revised form 04.09.2018