A hybrid of thermogalvanic and concentration galvanic cells as an effective device for converting low-potential heat energy into electricity

CrossMark

Sergei Vassel *, Natalia Vassel

Rostov Branch of Moscow State University of Technology and Management, Russian Federation

ABSTRACT

In this work we developed a concept and calculated the efficiency of a hybrid of thermogalvanic and concentration galvanic cells.

The proposed device consists of two vessels with the sodium hydroxide solution of various concentrations, Ag/Ag_2O or $Fe/Fe(OH)_2$ electrodes, chamber for water vapor transferring and the ion bridge or a porous partition.

Concentration difference is kept because of two factors: distillation of sodium hydroxide solution in temperature gradient and dependence of solubility of sodium hydroxide on temperature ($NaOH \cdot H_2O$ crystalline hydrates melting). Calculation shows that the efficiency of the hybrid cell may be about 10% of Carnot efficiency.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The aim of this work is to develop a simple device that can directly convert the heat energy into the electrical energy using a small temperature gap. This device may be suitable for solar, geothermal or waste heat using.

Thus, we developed an electrochemical way of converting heat energy into the electrical energy.

Traditionally, electrochemical devices for converting heat into electricity have a construction of thermogalvanic cells.

Seebeck coefficients of aqueous thermogalvanic cells is higher then in solid thermoelectrics [1–9]. For example, using ferricyanide/ferrocyanide redox couple and multi-walled carbon nanotube as electrodes it is possible to obtain 1.4% of Carnot efficiency [6].

A new approach to increase the efficiency and Seebeck coefficients of thermogalvanic cells is based on the use of complex ions, the equilibrium of which is shifted to the complexation at lower temperatures, while it is inverted at elevated temperatures [8,9]. Using triiodide ions in α-cyclodextrin it is possible to obtain Seebeck coefficient in 2 mV/K [9].

Non-aqueous thermo-galvanic cells show higher Seebeck coefficients (5 mV/K in [10]) than aqueous thermo-galvanic cells, but the resistance of non-aqueous solutions is rather high, so non-aqueous thermogalvanic cells can not show higher efficiency than ferricyanide/ferrocyanide cells.

In the previous paper we described the electrochemical convertor, which work is based on reaction of sulfuric acid salvation [11]. This reaction is reversible. We use direct reaction for the generation of electricity and we use 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 to electricity could be 4.5% (70% of Carnot efficiency) if $T_1 = 313$ K (40 °C) and $T_2 = 293$ K (20 °C).

In this paper we describe the concept and basic principles of work of electrochemical convertor with alkali electrolyte.

We simplified the construction of the convertor, described in paper [11] and use an alkali electrolyte instead of an acid one.

All calculations we did for R = r (the mode of maximum power generation by the cell) and R = 2r.

The construction of the device is shown in Fig. 1. As we can see it is a hybrid of a thermogalvanic cell and a concentration galvanic cell.

Where:

1. Ag/Ag_2O electrode or $Fe/Fe(OH)_2$ electrode
2. The vessel with a higher concentration of alkali
3. The vessel with a lower concentration of alkali
4. The chamber for water vapor transfer
5. Ion bridge with an alkali solution (instead of ion bridge porous partition may be used).

* Corresponding author.
  E-mail address: sergei-vassel@yandex.ru (S. Vassel).

Nomenclature

A	total electrical energy obtained from the galvanic cell [J]
A_1	useful electrical energy obtained from the galvanic cell [J]
C_1	concentration of electrolyte in a hot vessel [%]
C_2	concentration of electrolyte in a cold vessel [%]
F	Faraday constant
q	heat of reaction $NaOH + nH_2O \rightarrow NaOH \cdot nH_2O$
$q_{H2O} = q/n$	heat of reaction $NaOH + nH_2O \rightarrow NaOH \cdot nH_2O$ per one mole of water
Q	heat consumed by the device [J]
Q_{eV}	heat required for water evaporation [J]
Q_{hl}	lost heat [J]
L	molar heat of vaporization of the water [J]

R	external resistance [Ohm]
r	internal resistance of the cell [Ohm]
T_1	temperature of the hot contact [K]
T_2	temperature of the cold contact [K]
ΔT	temperature difference
z	the number of electrons involved in the reaction

Greek symbols

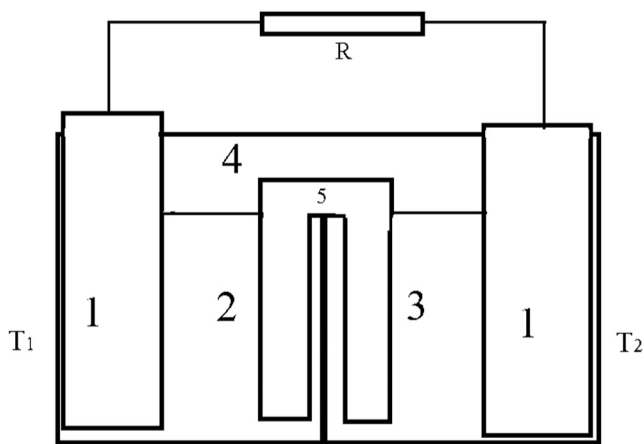|	
η	efficiency [%]
η_r	ratio η/η_{Carnot} [%]
ρ	the resistivity of sodium hydroxide solution [Ohm m]
χ	coefficient of thermal conductivity [W m^{-1} K^{-1}]
$\Delta\varphi$	is electrical potential difference

Fig. 1. Hybrid of thermogalvanic and concentration galvanic cell.

The work of proposed device can be divided in two stages: distillation of the alkali solution in the temperature gradient and generating the electrical energy in the galvanic cell. In Fig. 2 $T_1 > T_2$. The water evaporates from the solution in vessel 2, the vapor diffuses in the chamber 4 and finally condenses in the solution in vessel 3. This process keeps the concentration difference
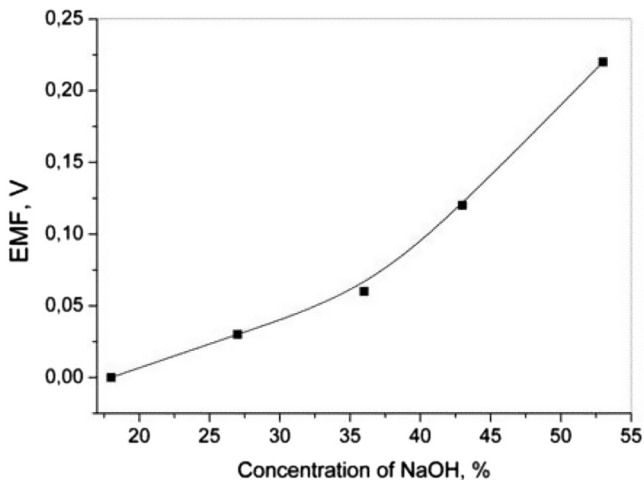

Fig. 2. The dependence of the EMF of the concentration galvanic cell on the concentration of sodium hydroxide concentration in reduction vessel (c_1). The concentration of sodium hydroxide in the oxidation vessel (c_2) is 18% at all points.

between the solutions in vessels 2 and 3. The generation mechanism of electricity is similar to the concentration galvanic cells.

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 alkali solutions of different concentrations at different temperatures. These data are presented in Table 1 [12,13].

As we can see from Table 1, the vapor pressure above the 45% solution of NaOH at 45 °C is higher, than above 25% solution at 20 °C. It means that if the temperature of the hot contact T_1 is 318 K (45 °C), and the temperature of the cold contact T_2 is 297 K (20 °C), we can perform the distillation of sodium hydroxide from 25% to 45% solution.

Similarly, if T_1 = 333 K (60 °C) and t_2 = 297 K (20 °C), it is possible to perform the distillation of NaOH solution from 10% to 50% and etc.

As we can see, in Table 1 there are no data about the vapor pressure above the solutions of more then 30% at the temperature of 20 °C. Also no information is provided about the vapor pressure above the solutions of more then 50% at the temperature of 45 °C. It means that it is impossible to prepare the solution of such concentration at these temperatures. The dependence of sodium hydroxide solubility on temperature is presented in Table 2.

As we can see, there is a gap of sodium hydroxide solubility at the temperature of 70 °C. The reason of this fact is the melting of NaOH·H$_2$O crystalline hydrates at the temperature about 64 °C.

So, there are two factors that keep the concentration difference in the vessels in Fig. 1. They are distillation of the solutions in temperature gradient and the dependence of sodium hydroxide solubility on temperature.
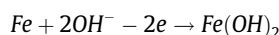
The potential of Fe/Fe(OH)$_2$ electrode in the alkaline solution depends on the concentration of hydroxide ions.

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 electrolyte in another vessel). In sodium hydroxide solutions it is correct only in solutions with pH < 13 [13].

If pH > 14 we have the dependence of EMF on the concentration, presented in Fig. 2.

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

Process on the electrode in the vessel with higher concentration of NaOH:

$$Fe + 2OH^- - 2e \rightarrow Fe(OH)_2$$