

Electrochemical Pump for Handling Small Quantities of Liquid based on the Water Electrolysis Process

M. R. Milici, L. D. Milici, D. Cernomazu

Department of Electrotechnics, Faculty of Electrical Engineering and Computer Science, University of Suceava, University str. 13, 720229 Suceava, Romania, phone: +40 230 524801, e-mail: mami@eed.usv.ro

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Introduction

During the history there are many interests concerning the electrochemical pumps. The electrochemical pumps with liquid can find their application in various areas, especially in the biomedical engineering. In order to use small amounts of liquids, in technique there are met certain solutions known as electrochemical micropumps, a solution [1] consisting of a single body cavity inside of which there are introduced two immiscible liquids with different specific weights, one representing the circulated liquid and other the activ liquid that, under the action of electrolysis and Joule-Lenz effect, decomposes into gases, the excess pressure created in the cavity causing the evacuation of circulated fluid outside the pump. The described solution has the disadvantage that the two liquids are not physically separated from them, which may involve not only physical contact and chemical reaction between the two liquids.

The following are presented:

- description of a proposed electrochemical pump, pump with fuel cell working in electrolyzer mode,
- mathematical modeling of the proposed pump operation,
- some performance characteristics of the proposed pump, obtained from experimental measurements.

Proposal for an electrochemical pump for handling small quantities of liquid

One way to achieve an electrochemical pump for handling small quantities of liquid, which removes the disadvantages mentioned in foreword, was the object of patent application no. A/00911 dated 28.09.2010 and submitted to the State Office for Inventions and Trademarks (OSIM), Bucharest, Romania [2].

The invention relates to a pump with two liquids and a fuel cell working as electrolyzer, used for handling small quantities of liquid.

The proposed electrochemical pump removes the mentioned disadvantages by that the two liquids used in its operation are separated both physically and chemically.

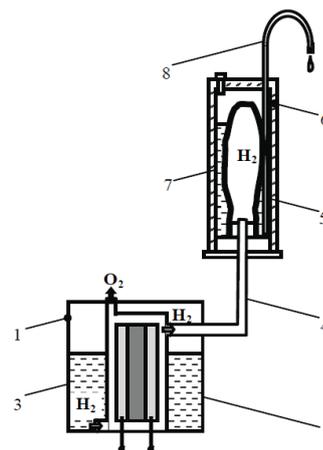


Fig. 1. Schematic diagram of the proposed electrochemical pump

The proposed electrochemical pump (Fig. 1) consists of a recipient (1), in which water (2) is introduced, as a liquid asset, and which is provided with a fuel cell (3) operating as electrolyzer and supplied from a constant voltage source not represented in the figure. The recipient (1) communicates through a conduit (4) with an elastic and deformable container (5), for example a rubber balloon, placed inside a transparent cylindrical tank (6) in which the circulated liquid (7) is introduced. The tank (6) communicates with the outside through a tubular pipe (8).

The fuel cell in the electrolyzer mode (3) decomposes the liquid asset (water) (2) into hydrogen and oxygen; oxygen is released to the atmosphere while the hydrogen is directed through the pipe (4), inside of the elastic and deformable container (5) which, by accumulating hydrogen expands, acting on the circulated liquid (7), pushing it off the tank (6) through the pipe (8).

The proposed electrochemical pump has the following advantages: design simplicity and reliability.

Described electrochemical pump can be reproduced with the same performance and features whenever necessary, which is an argument in favor of compliance with industrial applicability.

Mathematical modeling of the proposed pump operation

Modeling of voltage-current curve [3]. The voltage-current curve results from the combination of all the following physicochemical phenomena: thermodynamic phenomena, activation phenomena, diffusion phenomena and ohmic losses. The static curve can be modelled by the following equation

$$U_{cell} = U_{rev} + U_{act} + U_{\Omega} + U_{diff}, \quad (1)$$

where

$$U_{\Omega} = R_{\Omega} \cdot I, \quad (2)$$

$$U_{diff} = R_{diff} \cdot I, \quad (3)$$

U_{rev} is the reversible potential and is theoretically equal to 1.23 V, U_{act} – models the activation losses due to the kinetic phenomena

$$U_{act} = \frac{R \cdot T}{2 \cdot \alpha \cdot F} \cdot \ln \frac{I}{I_0}, \quad (4)$$

where R_{Ω} – models the ohmic losses (ionic conduction in the electrolyte, electronic conduction, and contact resistance), R_{diff} – models the linear behaviour of diffusion losses in this current density range.

Hydrogen production rate. According to the first law of electrolysis, the mass Δm of hydrogen dissociated through electrolysis is proportional to the electric charge Δq crossing the cell, therefore the flow rate of hydrogen released Q is proportional to the current intensity I

$$\Delta m = k \cdot \Delta q \rightarrow \frac{\Delta m}{\Delta t} = k \cdot \frac{\Delta q}{\Delta t} \rightarrow Q = k \cdot I. \quad (5)$$

Circulated liquid flow rate. Considering the gas (hydrogen) being ideal, using the thermal equation of state, for a certain intensity (density) of electric current, at two different moments of time $t_1, t_2 = t_1 + \Delta t > t_1$, inside the balloon having the volume V_1 respectively $V_2 = V_1 + \Delta V > V_1$, the accumulated mass of hydrogen are m_1 respectively $m_2 = m_1 + \Delta m > m_1$, and for the hydrogen inside the balloon we can write the relations

$$p_k \cdot V_k = \frac{m_k}{M_{H_2}} \cdot R \cdot T_k \rightarrow \frac{R}{M_{H_2}} = \frac{p_k \cdot V_k}{m_k \cdot T_k}, \quad (6)$$

where $k = 1, 2$; p is gas pressure (hydrogen pressure in the balloon), [Pa]; V – gas volume (volume of hydrogen in the balloon), [m^3]; m – mass of the substance in the system (mass of the hydrogen in the closed system cell-balloon), [kg]; M – molar mass of the gas (hydrogen), [kg/kmol]; R – ideal gas constant; T – absolute temperature (hydrogen temperature in the balloon), [K].

From the (6) results

$$\frac{m_2 \cdot T_2}{p_2 \cdot V_2} = \frac{m_1 \cdot T_1}{p_1 \cdot V_1}, \quad (7)$$

where from, taking into account that $m_2 = m_1 + \Delta m$ and $V_2 = V_1 + \Delta V$, the balloon volume variation can be expressed depending on the mass of the hydrogen released:

$$\Delta V = A \cdot \Delta m + B, \quad (8)$$

$$\frac{\Delta V}{\Delta t} = A \cdot \frac{\Delta m}{\Delta t} + \frac{B}{\Delta t}, \quad (9)$$

where $A = \frac{p_1 \cdot T_2 \cdot V_1}{p_2 \cdot T_1 \cdot m_1}$ and $B = \left(\frac{p_1 \cdot T_2}{p_2 \cdot T_1} - 1 \right)$.

Lets analyze (8). For $\Delta m = 0$ results $\Delta V_0 = B$, and for $\Delta m_0 = -\frac{B}{A}$ results $\Delta V = 0$. A graphical representation, of mathematical point of view, which corresponds to the function $\Delta V(\Delta m)$ is shown in Fig. 2. Since $\Delta m > 0$ and $\Delta V = 0$, we will not focus attention on parts of the graph represented by dashed lines, but only those represented by continuous lines. Depending on the sign of B there are three cases. Lets analyze them one at a time, taking into account the change in volume is the effect of accumulation of hydrogen in the balloon and not vice versa.

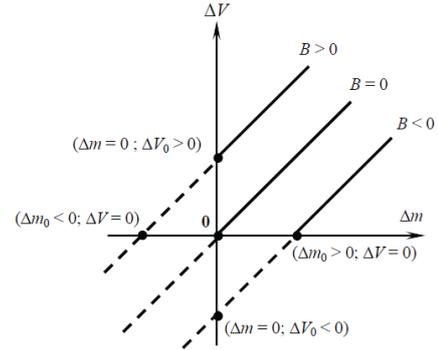


Fig. 2. Graphical representation of function $\Delta V(\Delta m)$

If $B > 0$, for $\Delta m = 0$ results $\Delta V_0 > 0$, which would mean that the balloon expands even without releasing hydrogen, which is false. Therefore the case $B > 0$ does not match reality.

If $B < 0$, for $\Delta V = 0$ results $\Delta m_0 > 0$, which means that the balloon begins to expand its volume after the accumulated mass of hydrogen exceeds the value Δm_0 , which can be explained by the fact that in the balloon must accumulate so mass of hydrogen as its pressure overcomes the pressure exerted by circulated liquid on the balloon, fact which was found in the experimental measurements, when only after a certain time of supplying the cell the balloon began to increase its volume. Therefore the case $B < 0$ can exist in reality.

If $B = 0$, $\Delta m = 0$ results $\Delta V = 0$, which corresponds to the case in which even starting with the cell powering and hydrogen accumulation in the balloon, it changes its volume, this being a particular situation which can occur if,

at the initial moment, the pressure inside the balloon is equal to that exerted by circulated liquid on it.

From the (8) and (9) we observe that the variation and the speed of variation of the balloon volume are proportional to the variation respectively speed of variation

of the mass of hydrogen released if the term $B = \frac{p_1 \cdot T_2}{p_2 \cdot T_1} - 1$

is neglected, so $\frac{p_1}{p_2} = \frac{T_1}{T_2}$.

In this case $\Delta V = A \cdot \Delta m$ and $\frac{\Delta V}{\Delta t} = A \cdot \frac{\Delta m}{\Delta t}$.

Taking into account the (5), and (9) could be written as

$$\frac{\Delta V}{\Delta t} = A \cdot Q + B = k \cdot A \cdot I + B \quad (10)$$

and for $B = \frac{p_1 \cdot T_2}{p_2 \cdot T_1} - 1 = 0$.

$$\frac{\Delta V}{\Delta t} = A \cdot Q = k \cdot A \cdot I, \quad (11)$$

which means that the balloon rate of volume changing is proportional with the hydrogen flow rate, respectively with the current.

Because in the time interval Δt , the volume of liquid removed is equal to the volume variation of balloon, (8) and (10) also represent the liquid removed, respectively its flow rate.

Analyzing (10) we can observe that the flow rate of liquid removed within time interval Δt depends on the initial state of the balloon (through p_1 , V_1 , T_1 and m_1), specifically through the mass of hydrogen already existing in the balloon. The ratio V_1/m_1 is lower, so the initial concentration of hydrogen in the balloon is higher, the lower liquid flow rate in time interval Δt .

Some performance characteristics of the proposed pump, obtained from experimental measurements

The pump was made using a commercial reversible fuel cell.

Electrolyzer module parameters used in pump construction are given in Table 1.

Table 1. Electrolyzer module parameters

Input voltage [V _{cc}]	Input current [A]	α	I_0 [mA]	R_Ω [m Ω]	R_{diff} [m Ω]	Hydrogen production rate [ml/min]
1,8-3	0,7	0,74	2,51	96,6	93,4	7 at 1 A

The experimental set-up is shown in Fig. 3.

Equivalent Resistance. Based on a series of measurements, dividing the direct voltage to the direct current the equivalent resistance of the cell can be calculated

$$R_{ecm} = \frac{U_m}{I_m}. \quad (12)$$

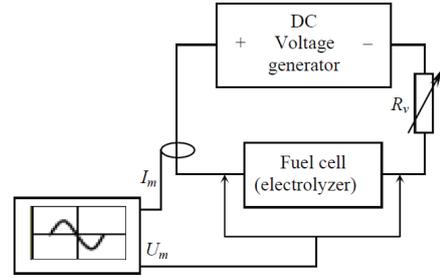


Fig. 3. Experimental set-up

Representing graphically (Fig. 4) the equivalent resistance according to the current, we can obtain an approximation curve, expressed by

$$R_e = 1336,7 \cdot I^{-0,97} \quad (13)$$

function that *very closely* approximates the equivalent resistance variation.

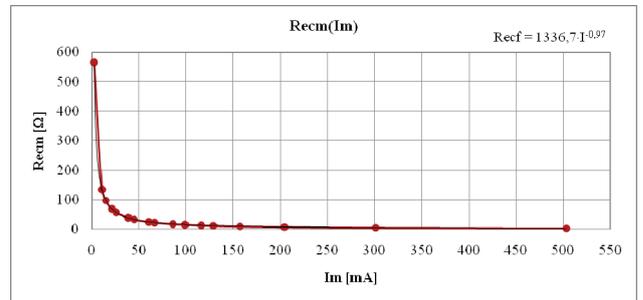


Fig. 4. Equivalent resistance calculated based on the measured values of voltage and its approximation function

Thus, the *equivalent* resistance can be *calculated* using *formula* (13), and obtaining the R_{ecf} .

Cell Power Consumption. For the same values of voltage and current the cell power consumption was calculated using the relationships respectively obtaining similar values:

$$P_{vc} = U_m \cdot I_m, \quad (14)$$

$$P_{rc} = R_{ecf} \cdot I_m^2, \quad (15)$$

From graphical representation of P_{vc} (Fig. 5) we can deduce a linear approximation function, having for the used cell, the next form

$$P_a = 0,0016 \cdot I_m. \quad (16)$$

So, even if the voltage is a strongly nonlinear function according to the current, the power consumed by cell is linear.

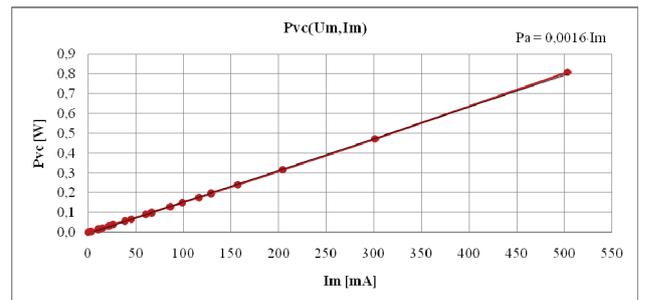


Fig. 5. Cell power consumption

Pump Flow rate. To determine the pump feature we done so: for some values of current intensity it was measured the necessary time interval to release 100 drops of circulated liquid, and it was calculated the dripping frequency and the pump flow rate.

Fig. 6 shows the flow-current curve.

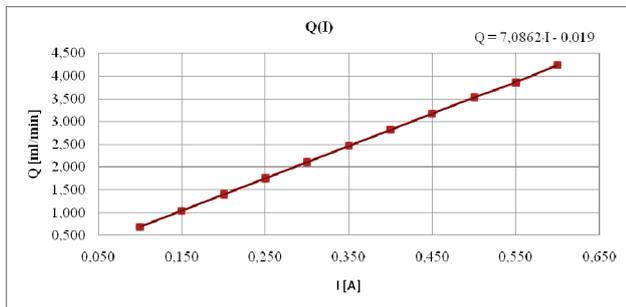


Fig. 6. Flow-current curve

As shown in Fig. 6, the characteristic is linear and is approximated by the function

$$Q = 7,0862 \cdot I - 0,019. \quad (17)$$

(17) has the same aspect as the (10), where

$$k \cdot A = 7,0862 \quad (18)$$

and

$$B = -0,019 < 0, \quad (19)$$

so, being verified the negative value of B .

We obtain $Q = 0$ for $I_0 = \frac{0,019}{7,0861} = 0,002681268 \text{ A}$,

a value very close to that of the cell data sheet ($I_0 = 2,51 \text{ mA}$).

Using the approximation function, the value of flow rate which would have been obtained for a current of 1 A is 7.067 ml/min, a value very close to 7 ml/min at 1 A as indicated in the data sheet, the errors being due to

measurement errors, modeling errors and the errors of approximation functions.

Conclusions

Pump flow rate is linear in relation to current intensity, which means that for a certain type of construction of pump, knowing the flow-current characteristic it may be prescribed a certain flow rate by current adjustment. A fine adjustment of current determines a fine adjustment of flow rate (number of liquid drops released by the pump during a given time interval). Such a pump could be used in biomedicine, for example.

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The field of electrochemical pumps is old, and during the history there are many interests concerning the electrochemical pumps. The electrochemical pumps with liquid can find their application in various areas, especially in the biomedical engineering. In order to use small amounts of liquids, in technique there are met certain solutions known as electrochemical micropumps, which have different disadvantages. The present paper propose a way to achieve an electrochemical pump for handling small quantities of liquid, pump based on the electrolysis process and also a modeling of its operating. The experimental data demonstrate that the pump flow rate is linear in relation to current intensity, which means that for a certain type of construction of pump, knowing the flow-current characteristic it may be prescribed a certain flow rate by current adjustment. A fine adjustment of current determines a fine adjustment of flow rate (number of liquid drops released by the pump during a given time interval). Such a pump could be used in biomedicine, for example. Ill. 6, bibl. 3, tabl. 1 (in English; abstracts in English and Lithuanian).

M. R. Milici, L. D. Milici, D. Cernomazu. Vandens elektrolizės principu veikianti elektrocheminė pompa mažiems skysčio kiekiams valdyti // Elektronika ir elektrotechnika. – Kaunas: Technologija, 2012. – Nr. 3(119). – P. 11–14.

Elektrocheminės pompos gali būti pritaikytos įvairiose srityse. Ypač plačiai jos naudojamos biomedicininėje inžinerijoje mažiems skysčio kiekiams valdyti. Tačiau jos turi daug trūkumų. Straipsnyje pateikiamas būdas, kaip elektrochemine pompa valdyti mažus skysčio kiekius naudojant elektrolizės procesą, bei veikimo modeliavimas. Eksperimento duomenys rodo, kad pompos srautas tiesiogiai priklauso nuo srovės intensyvumo, todėl, žinant šią priklausomybę ir pompos konstrukciją, galima nustatyti konkretų srautą. Tokia pompa gali būti naudojama biomedicinoje. Il. 6, bibl. 3, lent. 1 (anglų kalba; santraukos anglų ir lietuvių k.).