

# A micropump driven by electrochemically produced short-lived bubbles

I V Uvarov<sup>1</sup>, S S Lemekhov<sup>1</sup>, A E Melenev<sup>1</sup> and V B Svetovoy<sup>1,2</sup>

<sup>1</sup>Yaroslavl Branch of the Institute of Physics and Technology RAS, 150007, Universitetskaya 21, Yaroslavl, Russia

<sup>2</sup>MESA+ Institute for Nanotechnology, University of Twente, PO 217, Enschede 7500 AE, The Netherlands

i.v.uvarov@bk.ru

**Abstract.** A new working principle for electrochemical micropump with the gas termination time as short as 100 microseconds is presented. It is based on water electrolysis with a fast change of voltage polarity. A simple electrochemical micropump is designed to demonstrate this pumping principle. The device consists of a working chamber with metallic electrodes, inlet and outlet diffusers, and channels for liquid. The chamber and the channels are filled with the electrolyte that plays a role of the pumped liquid. The pump was tested in different regimes. One of these regimes related to formation and termination of short-lived microbubbles is especially promising. Long time stability of the electrodes is demonstrated.

## 1. Introduction

Microfluidic devices are widely used in chemical, biological and medical applications including microreactors, implantable drug delivery systems, micro total analysis systems ( $\mu$ TAS), lab-on-a-chip [1]. Micropump is an essential component of these devices responsible for generation of the fluid movement. Several actuation mechanisms are known: pneumatic, piezoelectric, electromagnetic, and others [2]. Electrochemical actuation is based on the reversible electrochemical reactions that enable gas bubble expansion and contraction by electrolysis in the aqueous electrolyte solution. In comparison with the other mechanisms, the electrochemical actuation provides large driving force, accurate flow control, low power consumption, low heat generation and compliance with the lab-on-a-chip technology. The main drawback is a long response time due to slow recombination of the gas inside of the working chamber [3]. Recently a short-time electrolysis using alternating polarity voltage pulses was demonstrated, which allows fast generation and termination of the gas in the chamber [4]. Here we describe operation of a simple electrochemical micropump in the new pumping regime based on a short-time electrolysis of alternating polarity.

## 2. Design, operation principle, and fabrication of the micropump

Design of the pump is schematically shown in figure 1. The pump contains a chamber with a diameter of 500  $\mu$ m and metallic electrodes at its bottom. Inlet and outlet diffusers are connected to the chamber. The length of each diffuser is 200  $\mu$ m, the neck width is 20  $\mu$ m, and the diffuser angle is 9.5°. Channels connected to the diffusers having a width of 250  $\mu$ m. The pump has a planar configuration, all its elements have a rectangular cross-section with the same height of 6  $\mu$ m. Since the

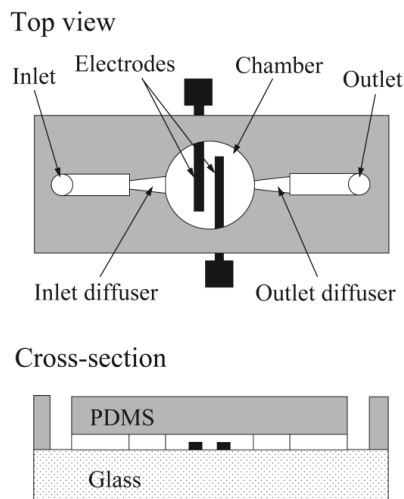


pump is used only for demonstration purpose the working fluid of the pump is the electrolyte, which is 1 M solution of  $\text{Na}_2\text{SO}_4$  in distilled water.

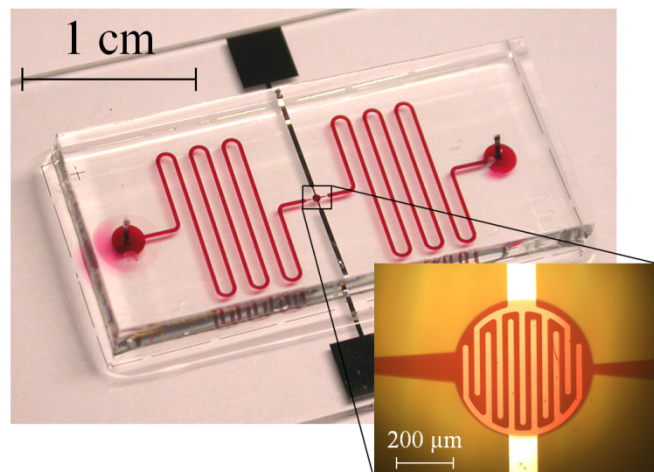
The pump operates in a cyclic mode. Each cycle consists of pumping and supplying phases. In the pumping phase a series of short ( $\sim 10\ \mu\text{s}$ ) voltage pulses of alternating polarity is applied to the electrodes. These pulses produce hydrogen and oxygen due to water electrolysis but all the gas is collected in nanobubbles [4]. The pressure increases in the chamber and pushes the fluid through the diffusers. More liquid is going via the outlet diffuser because it has smaller flow resistance. In the supplying phase the pulses are switched off and the gas in nanobubbles recombine into water in  $100\ \mu\text{s}$  or so releasing the pressure. This time more liquid is going via the inlet diffuser. Thus, the liquid is pumped from the inlet to the outlet. Then the cycle is repeated. The pump has no movable parts such as passive check valves. Flow direction is determined by the geometrical design of the diffusers.

The pump was constructed from two parts: the glass substrate with deposited metallic electrodes, and the polydimethylsiloxane (PDMS) structure containing channels for electrolyte. These parts were fabricated separately and then bonded together. Electrodes were deposited on the glass substrate by magnetron sputtering. Two types of electrodes were used: one is 100 nm thick Pt layer with an adhesion layer (Ti, 10 nm thick) and the other one is Ti/Al layers with a thickness of 100/500 nm on the same adhesion layer. PDMS structure was fabricated by pouring the liquid PDMS pre-polymer onto the silicon mold, degassing in vacuum and curing at the elevated temperature. To achieve a strong bond between the glass substrate and the PDMS structure, oxygen plasma treatment was used. Exposed surfaces were brought into contact immediately after the treatment. The electrodes and the chamber were aligned manually.

The fabricated pump with close-up view of the working chamber is shown in figure 2. For clarity channels are filled with water colored by food dye. The electrodes have interdigitated structure to increase the efficiency of the electrolytic bubble generation and pumping. The diameter of the overall electrode area is  $450\ \mu\text{m}$  which is close to the diameter of the working chamber. This is done in order to saturate the entire volume of the chamber evenly with the gas bubbles.



**Figure 1.** Design of the micropump.



**Figure 2.** Fabricated micropump.

### 3. Testing of the device

#### 3.1. Single polarity mode

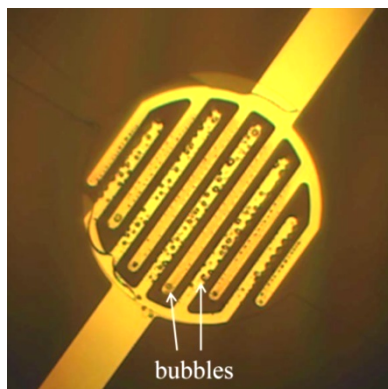
Standard operation mode of the electrochemical pump is the single polarity mode. In the pumping phase a voltage pulse is applied to one of the electrodes while the other electrode is grounded. Hydrogen is produced above the negative electrode and oxygen is produced above the positive one. The hydrogen and oxygen bubbles are spatially separated. The gases do not mix and have no chance to

react. In the supplying phase the voltage is removed and the bubbles recombine into water during a rather long time.

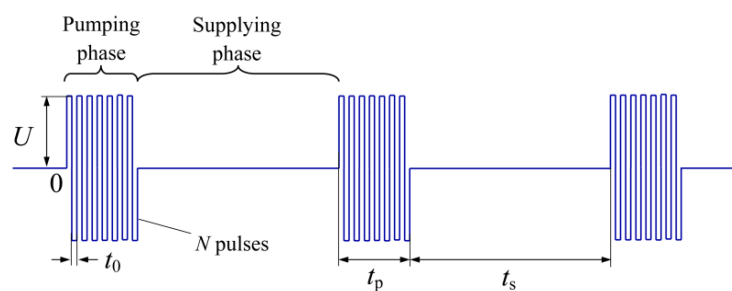
The micropump with platinum electrodes was tested in the single polarity mode. In the pumping phase the voltage pulse with an amplitude of 5 V and duration of 1 ms was applied to the sample. The pulses were generated by Keysight 33512B waveform generator and amplified 5 times using a homemade amplifier. A picture of the working chamber made in the moment  $t = 200$  ms is shown in figure 3. The gas bubbles are clear visible in the chamber. The bubbles disappear completely in about 5 s restricting the duration of the supplying phase. Gas termination restricts the operation frequency of the pump by a value of 0.2 Hz.

### 3.2. Alternating polarity mode

Recently a short-time electrolysis by alternating polarity voltage pulses was demonstrated, which allows fast generation and termination of the gas in the chamber [4]. This regime can be used for fast pumping of liquids. The voltage applied to the working electrode (the other one is grounded) is shown in figure 4. In the pumping phase it is a series of  $N$  rectangular pulses of alternating polarity with duration  $t_0$  and amplitude  $U$ . These pulses produce hydrogen and oxygen above the same electrode. For short pulses ( $t_0 \sim 10$   $\mu$ s) all the gas is collected in nanobubbles, which are invisible because they do not scatter light [4]. Due to gas production the pressure increases in the chamber and pushes the fluid through the diffusers. In the supplying phase the pulses are switched off. Unlike the single polarity mode, hydrogen and oxygen molecules are not spatially separated and form not only  $H_2$  and  $O_2$  bubbles, but also bubbles containing mixtures of  $H_2$  and  $O_2$  [5]. The latter disappear in the reaction, which is ignited in nanobubbles spontaneously. The mechanism of the reaction is still not completely clear but the reaction happens with the assistance of the gas-liquid interface [5]. When the pulses are switched off the pressure is reduced in about 100  $\mu$ s. Short recombination time makes it possible to reduce significantly the duration of the supplying phase.



**Figure 3.** Working chamber in the single polarity mode.



**Figure 4.** Voltage applied to the electrode in the alternating polarity mode.

The pump with platinum electrodes was tested in the alternating polarity mode. A series of  $N = 6000$  pulses was applied to the electrodes. The pulses were repeated with a frequency of  $f = 100$  kHz ( $t_0 = 5$   $\mu$ s) at the amplitude  $U = 12.5$  V. Duration of the pumping phase was  $t_p = Nt_0 = 30$  ms. For this test duration of the supplying phase was chosen to be  $t_s = 220$  ms to make the process observable with the naked eye but much shorter  $t_s$  can be used. Total duration of the pumping cycle was  $t_p + t_s = 250$  ms.

The expected flow rate produced by the micropump can be estimated as follows. Total number of gas molecules  $M$  produced during the pumping phase is

$$M = \frac{3I_F t_p}{4e} \approx 1.4 \times 10^{15},$$

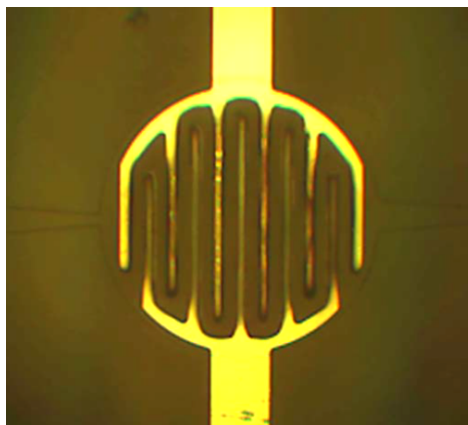
where  $e$  is the absolute value of the electron charge and  $I_F \approx 10$  mA is the amplitude of the Faraday current. All these molecules are densely packed in nanobubbles with a size of  $2r \sim 100$  nm. Pressure in these bubbles is dominated by a high Laplace pressure,  $P \approx 2\gamma/r \approx 28$  bar, where  $\gamma \approx 0.072$  J/m<sup>2</sup> is the surface tension of water. Significant part of the produced molecules recombines back into water without producing a useful work. As a conservative estimate one can take that only 10% of gas molecules [5] takes part in the pumping. Assuming also that the design of the diffusers provides a medium level of rectification  $\varepsilon = 0.1$  [7] we come to the estimate of the flow rate

$$R \sim 0.1\varepsilon f_p \frac{MkT}{P} \approx 5 \text{ nl/min},$$

where  $f_p = (t_p + t_s)^{-1} = 4$  Hz is the frequency of pumping and the thermal energy  $kT$  originates from the equation of state. This value is three orders of magnitude smaller than the flow rate  $R \sim 10$   $\mu$ l/min in micropumps with much larger volume of the chamber [3, 8, 9]. The pump described in this paper allows much higher pumping frequency of about 1 kHz or, probably, even more. The use of higher  $f_p$  can compensate for the low pumping rate.

The flow rate was determined experimentally observing the movement of the meniscus in the channel. The result  $R_{\text{exp}} \approx 0.15$  nl/min is significantly smaller than was predicted. It happens because PDMS is a very soft material with Young's modulus as low as  $E = 1.3$  MPa. Since the meniscus is moving the overpressure in liquid  $P_1$  is estimated somewhat larger than the Laplace pressure produced by the meniscus  $P_1 \geq \gamma/h = 12$  kPa, where  $h = 6$   $\mu$ m is the height of the channel. FEM modelling of the pump has shown that for this pressure the maximal deflection of the upper wall will be of  $d_0 = 2.2$   $\mu$ m. With this deflection the increment of the chamber volume  $\Delta V \approx 0.14$  nl is close to the volume of gas produced in one cycle  $\delta V = 0.1MkT/P \approx 0.21$  nl. Therefore, instead of pumping a significant part of the produced gas is used to inflate the chamber. It is clear that such a soft material cannot be used for fabrication of the chamber and channels. It is planned to use glass instead of PDMS to make the chamber stiff.

An important feature of the alternating polarity mode is a gradual wear of the electrodes. The working chamber after several hundred cycles is shown in figure 5. A strong damage of Pt electrodes was observed, fingers were thinned and blackened. To all appearance the damage was caused by a significant energy release in the close proximity of the electrode surface as the result of the combustion reaction between hydrogen and oxygen in nanobubbles [6]. Damage of the electrodes was accompanied by the decrease in the Faraday current and the decrease in the flow rate. Therefore, the choice of electrode material is essential to ensure the reliability of the pump. Almost no damage was observed for the aluminum electrodes covered by 100 nm of titanium. These electrodes provided smaller Faraday current than the platinum electrodes due to formation of titanium oxide on the surface during the electrochemical process. The pump with Ti/Al electrodes needed higher voltage amplitude or longer series of pulses in order to obtain the same flow rate as the pump with Pt electrodes.



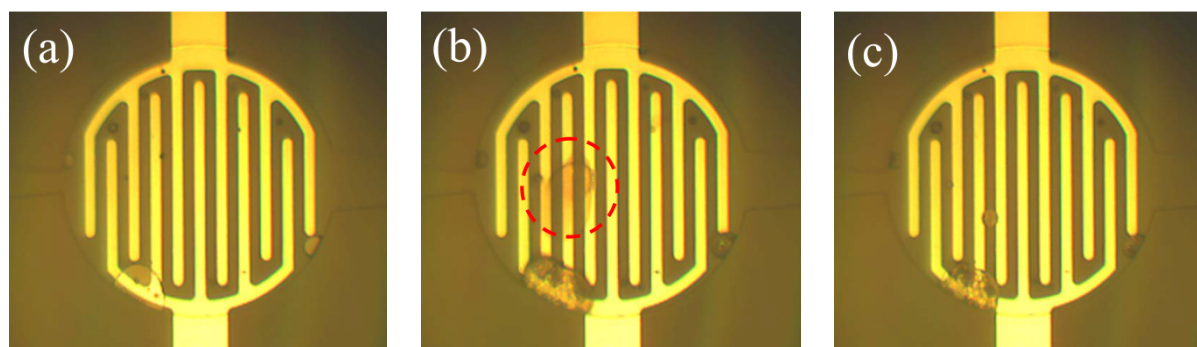
**Figure 5.** Working chamber in the alternating polarity mode.



### 3.3. Alternating polarity mode: long pumping phase

Extreme phenomena were observed when a relatively long series of pulses was applied to the device. The number of pulses was increased to  $N = 20000$  so that the duration of the pumping phase was  $t_p = 100$  ms. Duration of the supplying phase was chosen to be  $t_s = 900$  ms, and the total duration of the cycle was  $t_p + t_s = 1$  s. The driving pulses have the same parameters:  $U = 12.5$  V,  $f = 100$  kHz. The experiment has been done for the device with Ti/Al electrodes.

The chamber at the beginning of the pumping phase is shown in figure 6(a). Several bubbles are visible inside of the chamber, which appear during the filling of the device with the electrolyte and are not related to the electrochemical process. The end of the pumping phase is shown in figure 6(b). A bubble of about  $100\ \mu\text{m}$  in diameter emerges in the middle of the chamber, it is marked by the red circle. This bubble is not visible in the frame before and in the frame after. Since its image is not sharp we can conclude that the bubble exists much less than 40 ms (video was made at 25 fps). At the end of the pumping phase the liquid is sharply pushed out of the chamber through the diffusers. The chamber returns to its initial state in less than 40 ms as figure 6(c) shows.



**Figure 6.** Chamber of the micropump. (a) The beginning of the pumping phase. (b) The end of the pumping phase. (c) 40 ms after the frame (b).

The observations can be explained as follows. A relatively long series of the voltage pulses provides a high concentration of the  $\text{H}_2$  and  $\text{O}_2$  nanobubbles inside of the chamber. When the concentration is high enough, nanobubbles merge into a microscopic bubble, which can be vaguely seen in the optical microscope. The combustion reaction ignites spontaneously in this microbubble producing a significant pressure jump that pumps the liquid.

Appearance of short-lived microbubbles produced by short voltage pulses of alternating polarity was demonstrated by our group previously. Bubbles with a typical size of  $10\ \mu\text{m}$  were observed in a closed microchamber with dimensions of  $100 \times 100 \times 5\ \mu\text{m}^3$  [10]. They lived just a few microseconds and were accompanied by pressure jumps of 0.1-1 bar. The time scale of the events was too short to observe visually the dynamics of the bubbles. To all appearance similar processes happen in the chamber of the micropump. High concentration of  $\text{H}_2$  and  $\text{O}_2$  nanobubbles is produced by the electrochemical process; these bubbles merge and form a microbubble containing stoichiometric mixture of gases; the reaction in the microbubbles is ignited spontaneously releasing significant energy that drives the pump. The process was shot by an ordinary video camera with a frame rate of 25 fps and the images were not synchronized with the driving signal. The time resolution of the camera is 40 ms but the time scale of the processes in the chamber is expected to be on the time scale from micro- to milliseconds. To follow the dynamics of the bubbles we plan to use a fast video camera.

The alternating polarity mode using the long pumping phase allows to achieve a relatively high flow rate. The meniscus in the channel is moving at least  $100\ \mu\text{m}$  per cycle. For the pumping frequency  $f_p = 1$  Hz we obtain a flow rate of  $R = 9$  nl/min, which is almost two orders of magnitude higher than the flow rate observed in the regime without formation of the short-lived bubbles. More detailed investigation needed for the pumping regime with short-lived bubbles.

#### 4. Conclusions

A new pumping principle based on water electrolysis with a fast change of voltage polarity was demonstrated using a simplest valveless micropump. In comparison with normal single polarity mode, the alternating polarity mode allowed to achieve higher operation frequency of the pump due to a very short gas termination time. The observed flow rate in this regime was lower than expected. This is because the chamber of the micropump was made of PDMS, which is deformed during pumping leading to increase of the chamber volume. To obtain the maximum flow rate the chamber of the micropump has to be fabricated from a more stiff material. Fast degradation of the platinum electrodes was also observed. In contrast, almost no damage was observed for the aluminum electrodes covered by a titanium layer. At some parameters of the driving pulses short-lived microbubbles flicker in the chamber. This pumping regime is accompanied by a significant increase in the pumping rate even for the chamber made of PDMS and worth of more detailed investigation.

#### Acknowledgments

This work is supported by the Russian Science Foundation (Grant No. 15-19-20003).

#### References

- [1] Whitesides G M 2006 *Nature* **442** 368-73
- [2] Au A K, Lai H, Utela B R and Folch A 2011 *Micromachines* **2** 179-220
- [3] Yi Y, Buttner U, Carreno A A A, Conchouso D and Foulds I G 2015 *J. Micromech. Microeng.* **25** 105011
- [4] Svetovoy V B, Sanders R G P, Ma K and Elwenspoek M C 2014 *Sci. Rep.* **4** 4296
- [5] Svetovoy V, Postnikov A, Uvarov I, Sanders R and Krijnen G 2016 *Energies* **9** 94
- [6] Svetovoy V B, Sanders R G P, Lammerink T S J and Elwenspoek M C 2011 *Phys. Rev. E* **84** 035302(R)
- [7] Singhal V, Garimella S V and Murthy J Y 2004 *Sens. Actuators A* **113** 226-35
- [8] Lui C, Stelick S, Cady N and Batt C 2010 *Lab Chip* **10** 74-9
- [9] Li P-Y, Sheybani R, Gutierrez C A, Kuo J T W and Meng E 2010 *J. Microelectromech. Syst.* **19** 215-28
- [10] Postnikov A V, Uvarov I V, Prokaznikov A V and Svetovoy V B 2016 *Appl. Phys. Lett.* **108** 121604