

A simple electrochemical micropump: Design and fabrication

I V Uvarov¹, S S Lemekhov¹, A E Melenev¹, V V Naumov¹, O M Koroleva¹,
M O Izyumov¹ and V B Svetovoy^{1,2}

¹Yaroslavl Branch of the Institute of Physics and Technology RAS, 150007,
Universitetskaya Street 21, Yaroslavl, Russia

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

Abstract. A micropump based on water electrolysis with a fast change of voltage polarity is presented. It is designed to demonstrate a new pumping principle with the gas termination time as short as 100 microseconds. 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, which is the pumped liquid. The pump is fabricated on a glass substrate with the deposited metallic electrodes. The substrate is bonded with a polydimethylsiloxane structure containing the channels and the chamber. Design, fabrication procedure and preliminary testing of the device are described.

1. Introduction

Microfluidic devices are widely used in chemical, biological and medical applications including microreactors, implantable drug delivery systems, micro total analysis systems (μ TAS), lab-on-a-chip [1]. Micropump is an essential component of microfluidic devices, it is responsible for generation of the fluid movement. Several actuation mechanisms of the micropump are known: pneumatic, piezoelectric, electromagnetic, and others [2]. Electrochemical actuation is based on reversible electrochemical reactions that enable gas bubble expansion and reduction 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 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 design and fabrication of a simplest micropump, which will be able to demonstrate the new pumping principle.

2. Design of the micropump and operation principle

Design of the pump is schematically shown in figure 1. The pump consists of a chamber with metallic electrodes inside it, inlet and outlet diffusers, and channels for liquid. The pump has a planar configuration, all its elements have a rectangular cross-section with the same height. Working fluid of the pump is the electrolyte that is molar solution of Na_2SO_4 in distilled water.

Operation principle of the pump is schematically shown in figure 2. 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 μs 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. Instead of a working fluid the device is pumping the electrolyte. This simplified design is used only for the purpose of demonstration.

Valveless design of microfluidic pumps is well known [5-7]. It has a number of advantages in comparison with the design including check valves: high reliability due to absence of mechanical fatigue, low sensitivity to contamination, fabrication simplicity. Performance of the pump is determined by the dimensions of the diffusers. It has been shown that the optimal performance is achieved when the diffuser angle is about 10° and the ratio between the diffuser length and the neck width is about 10 [6]. The dimensions of diffusers were selected using these considerations. The main geometrical parameters of the pump are demonstrated in figure 3. Channels and chamber of the pump have a height of 6 μm .

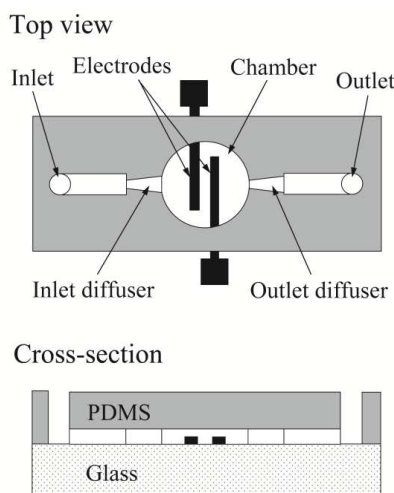


Figure 1. Design of the micropump.

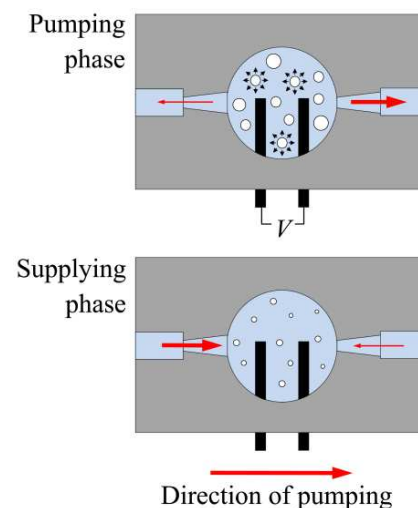


Figure 2. Operation principle of the pump.

3. Fabrication

The pump was constructed from two parts: one is a glass substrate ($76 \times 26 \times 1 \text{ mm}^3$) with deposited metallic electrodes and the other one is a polydimethylsiloxane (PDMS) structure containing channels for the electrolyte. These parts were fabricated separately and then were bonded together.

The main steps of the glass substrate fabrication are shown in figure 4. At the first step the substrate was covered by the positive photoresist layer (Shipley S1813) and the UV contact photolithography was performed. Then an adhesion layer (Ti, 10 nm) and 100 nm thick Pt layer were deposited by magnetron sputtering. At the final step the lift-off process was performed. Photograph of the glass substrate with close-up view of platinum electrodes is shown in figure 5. Electrodes have interdigitated structure to increase the efficiency of the electrolytic bubble generation and pumping. Each finger have a width of 20 μm , the spacing between fingers is also 20 μm . The diameter of the overall electrode area is 450 μm 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.

PDMS structure was fabricated by soft lithography technique [8]. Fabrication steps are shown in figure 6. First, a silicon mold containing the chamber, diffusers and channels was fabricated using deep reactive ion etching. SEM image of the mold is shown in figure 7. The height of the mold

features was $6\ \mu\text{m}$. Then liquid PDMS pre-polymer (Sylgard 184, a mixture of a base and a curing agent at 10:1 ratio) was poured onto the mold, degassed in vacuum and cured at the temperature of $100\ ^\circ\text{C}$ during 45 min. After the curing PDMS replica was peeled off from the mold. At the last step the inlet and outlet holes with a diameter of $0.5\ \text{mm}$ were made in the PDMS structure by a biopsy puncher.

Glass substrate with the metallic electrodes and PDMS structure were assembled together using irreversible bonding of PDMS to glass. To achieve this both structures were exposed to an oxygen plasma with the pressure of $0.5\ \text{mbar}$ and $300\ \text{W}$ power during 5 s. Exposed surfaces were brought into contact quickly after the plasma treatment aligning the electrodes and the chamber manually. After 15 min samples were ready for filling with the electrolyte and testing. Cross-section of the assembled micropump is schematically shown in figure 1. Photograph of the fabricated pump with close-up view of the working chamber is shown in figure 8. For clarity channels were filled with water colored by food dye.

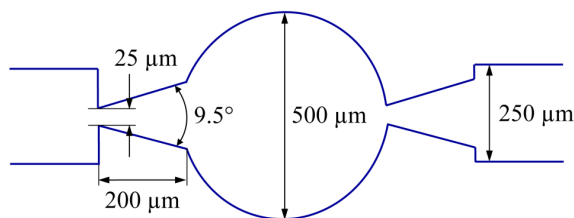


Figure 3. Dimensions of the main structural elements of the pump.

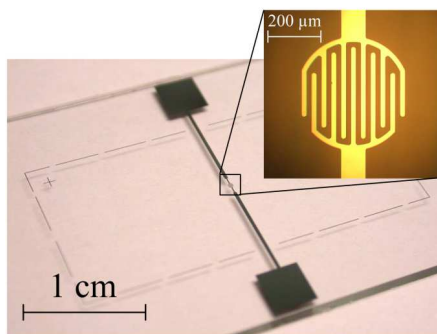


Figure 5. Glass substrate with metallic electrodes.

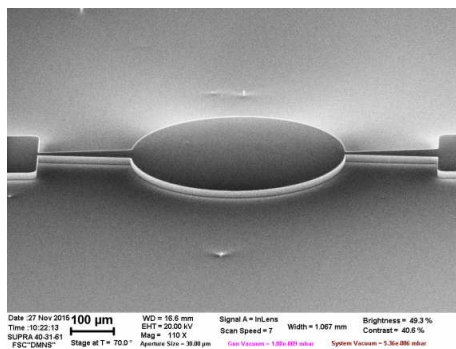


Figure 7. Silicon mold.

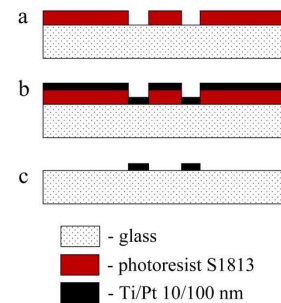


Figure 4. Preparation of the glass substrate.

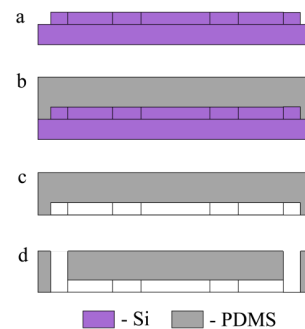


Figure 6. Preparation of the PDMS structure.

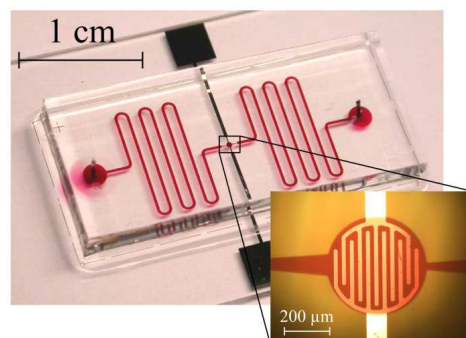


Figure 8. Fabricated micropump.

4. Preliminary testing of the pump

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 (figure 9). The hydrogen and oxygen bubbles are spatially separated. H_2 and O_2 gases do not mix and have no opportunity to react. In the supplying phase the voltage is removed and the bubbles recombine into water during a relatively long time.

Fabricated micropump was tested in the single polarity mode. In the pumping phase the voltage pulse with the amplitude of 5 V and duration of 1 ms was applied to the sample. Gas bubbles were produced above the electrodes. Photograph of the working chamber made at 200 ms after the pumping phase is shown in figure 10. Gas bubbles are clear visible in the chamber. The time of complete disappearance of bubbles, and therefore, the duration of the supplying phase, was about 5 s. Such a long duration did not allow to achieve a high pumping speed, operation frequency of the pump was less than 0.2 Hz.

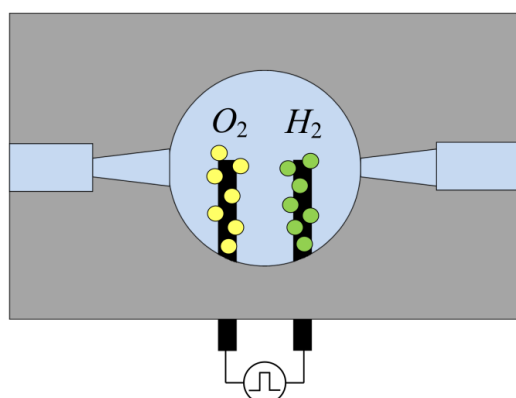


Figure 9. Gas production in the single polarity mode.

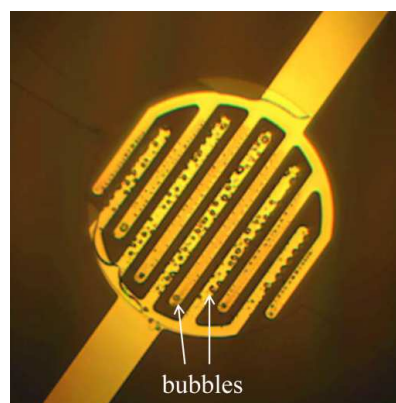


Figure 10. Working chamber in the single polarity mode.

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. Voltage applied to the working electrode (the other one is grounded) is shown in figure 11. 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 each electrode (figure 12). 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 spatially not separated and form not only H_2 and O_2 bubbles, but also bubbles containing mixtures of H_2 and O_2 [9]. 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 [9]. When the pulses are switched off the pressure is reduced in about $100 \mu s$. Short recombination time makes it possible to significantly reduce the duration of the supplying phase.

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

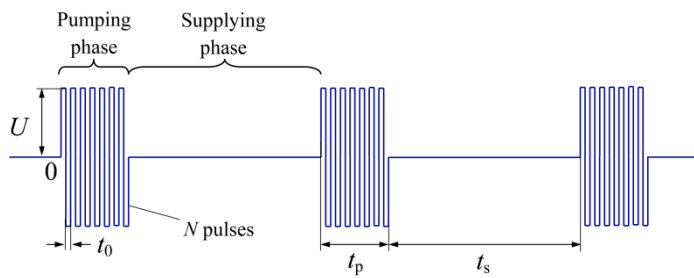


Figure 11. Signal applied to the electrode in the alternating polarity mode.

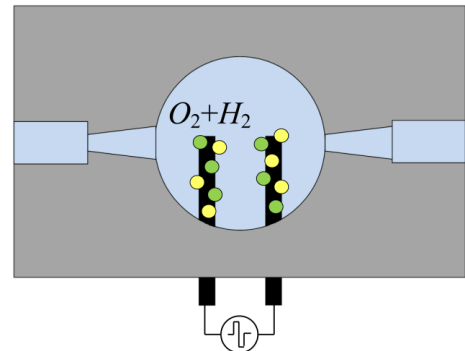


Figure 12. Gas production in the alternating polarity mode.

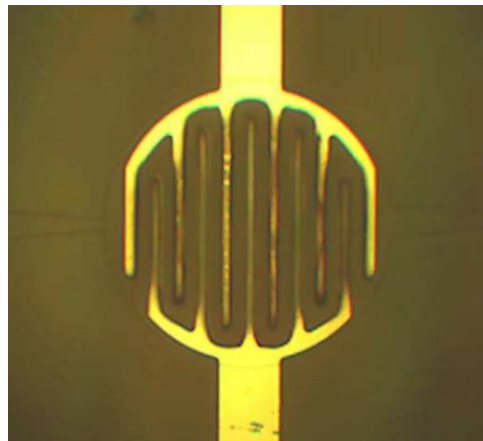


Figure 13. Working chamber in the alternating polarity mode.

Photograph of the working chamber at the pumping phase made after several hundreds of cycles is shown in figure 13. There were no visible bubbles inside the chamber because the gas was collected in nanobubbles with the size ~ 100 nm. A strong damage of Pt electrodes was observed. To all appearance the damage was caused by the significant energy release in the close proximity of the electrode surface as a result of combustion reaction between hydrogen and oxygen in nanobubbles [10].

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/m² is the surface tension of water. Significant part of the produced molecules recombines back to water without producing a useful work. As a conservative estimate one can take that only 10% of gas molecules [9] takes part in the pumping. Assuming also that the design of the diffusers provides a medium level of rectification $\varepsilon = 0.1$ 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 $R \sim 10$ μ l/min in

micropumps with much larger volume of the chamber [3,12,13]. 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 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 $h = 6$ μm is the height of the channel. FEM modelling of the pump using COMSOL Multiphysics has shown that for this pressure the maximal deflection of the upper wall will be about $d_0 = 2.2$ μm . 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 chamber and channels. One has to use instead more stiff material such as SU-8, PMMA, glass, or Si.

5. Conclusions

An electrochemical valveless micropump was presented. It was designed to demonstrate a new pumping principle based on water electrolysis with a fast change of voltage polarity. The device consisted of the glass substrate with metallic electrodes and PDMS structure with the chamber and channels for liquid. Preliminary testing of the micropump in the standard single polarity mode and recently proposed alternating polarity mode was performed. Alternating polarity mode allowed to achieve sufficiently higher operation frequency of the pump due to very short gas termination time. However, the flow rate in this regime was lower than expected. Two main problems were encountered. One is that PDMS is too soft material for the chamber, which increases its volume during pumping. The chamber of the micropump has to be fabricated from a more stiff material. The second problem is the fast degradation of the electrodes in the alternating polarity regime. An additional work has to be done to choose an appropriate material for the electrodes.

Acknowledgments

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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] Stemme E and Stemme G 1993 *Sens. Actuators A* **39** 159-67
- [6] Cui Q, Liu C and Zha X F 2008 *Int. J. Adv. Manuf. Technol.* **36** 516-24
- [7] Komatsuzaki H, Suzuki K, Liu Y, Kosugi T, Ikoma R, Youn S-W, Takahashi M, Maeda R and Nishioka Y 2011 *Jpn. J. Appl. Phys.* **50** 06GM09
- [8] McDonald J C and Whitesides G M 2002 *Acc. Chem. Res.* **35** 491-9
- [9] Svetovoy V, Postnikov A, Uvarov I, Sanders R and Krijnen G 2016 *Energies* **9** 94
- [10] Svetovoy V B, Sanders R G P, Lammerink T S J and Elwenspoek M C 2011 *Phys. Rev. E* **84** 035302(R)
- [11] Singhal V, Garimella S V and Murthy J Y 2004 *Sens. Actuators A* **113** 226-35
- [12] Lui C, Stelick S, Cady N and Batt C 2010 *Lab Chip* **10** 74-9
- [13] Li P-Y, Sheybani R, Gutierrez C A, Kuo J T W and Meng E 2010 *J. Microelectromech. Syst.* **19** 215-28