Fast electrochemical actuator

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Abstract. Lack of fast and strong microactuators is a well-recognized problem in MEMS community. Electrochemical actuators can develop high pressure but they are notoriously slow. Water electrolysis produced by short voltage pulses of alternating polarity can overcome the problem of slow gas termination. Here we demonstrate an actuation regime, for which the gas pressure is relaxed just for 10 µs or so. The actuator consists of a microchamber filled with the electrolyte and covered with a flexible membrane. The membrane bends outward when the pressure in the chamber increases. Fast termination of gas and high pressure developed in the chamber are related to a high density of nanobubbles in the chamber. The physical processes happening in the chamber are discussed so as problems that have to be resolved for practical applications of this actuation regime. The actuator can be used as a driving engine for microfluidics.

1. Introduction
The last decennium has witnessed an impressive trend to miniaturize systems of virtually any kind. This trend has many reasons: small systems are often cheaper to produce, they can have properties large systems have not, and they may facilitate use of large systems (cars, for example). An important and generic component in microsystems is the actuator. It plays role of a motor transforming electricity or other kind of energy into mechanical motion. In contrast with large scale systems, where effective engines are available (internal combustion or electromagnetic motors), microsystems suffer from lack of strong and fast actuators [1, 2]. Small electromagnetic motors cannot generate forces of useful magnitude but internal combustion engines [3] perform poorly due to increased heat losses via the volume boundary [4, 5] when the volume decreases.

Existing microactuators are using mostly two types of forces [1, 2, 6, 7]: electrostatic forces, which are weak, and those generated by thermal expansion, which are slow. Fast and strong piezoelectric elements are not compatible with microtechnology, need a high voltage for actuation, and have a small stroke. Electrochemical actuation was also discussed in many papers [8–14] but it is notoriously slow. One can produce a large amount of gas in a short time but it is impossible to get rid of this gas also fast.

Electrochemical decomposition of water is a well-known process but electrolysis performed in microsystems on a short-time scale brought unexpected surprises [15]. It was found that the local current density can be three orders of magnitude larger than that for the normal long-time (> 1 ms) electrolysis. The local relative supersaturations in the short-time regime (1 – 100 µs) was larger than 1000. In these conditions homogeneous nucleation of bubbles must happen and
was, indeed, observed [16]. Applying potential with the fast change of polarity (> 20 kHz) visible production of gas disappeared but the current via the electrolyte practically did not change. A whole number of effects indicated that the gas disappearance is related to the reaction between hydrogen and oxygen that happens spontaneously in nanobubbles with the size smaller than 200 nm.

The phenomenon of gas combustion in nanobubbles puzzled many researches (see, for example, [17]). It is not clear why the reaction is ignited. High Laplace pressure in the bubbles at room temperature is not sufficient to ignite the reaction. Fast microseconds dynamics can be important but taken along it can hardly explain the ignition of the reaction. For the ignition one has to overcome a high energy barrier that seemed not possible at room temperature. Moreover, in contrast with the standard combustion theory [18] the reaction happens without significant temperature increase in the bubbles [15] although deposition of a large amount of energy is well visible. Combustion reactions inside of a small volume is an additional mystery of nanobubbles. The other well-known problem is unexpectedly long stability of surface [19] and bulk [20] nanobubbles.

In spite of poor understanding of the reaction mechanism the discovered phenomenon can be used to build a fast and strong actuator [21]. This actuator consisted of a microchamber covered with a flexible membrane and filled with an electrolyte. The electrolyses was performed by short voltage pulses of alternating polarity. The pressure in the chamber increased and pushed the membrane but no visible bubbles were formed. This is because most of the gas was packed in nanobubbles, which did not scatter light. When the pulses were switched off the pressure relaxed for 100 µs or so. It can be compared with the usual electrochemical actuators, for which the time scale is minutes [8, 9].

In this paper we describe a new actuation regime, for which a high pressure can be reached but it is relaxed just for 10 µs.

2. Experimental

We did experiments with the devices (see Fig. 1) fabricated on Si wafers covered with a layer of silicon nitride (530 nm thick). Platinum electrodes were deposited on top of this layer. Underneath of the electrodes there is a heat sensor made of polysilicon. Within the chamber area the nitride was made free by etching the Si wafer from the back side so that nitride layer played the role of a membrane. The chamber and filling channels were isotropically etched in borofloat glass. The silicon and glass wafers were anodically bonded. Nominal dimensions of the chamber are 100 × 100 × 5 µm³. The details of the design and fabrication were reported earlier [21]. The chamber was filled via the channel with 1 M solution of Na₂SO₄ in deionized water. The in/outlet openings of the channel were sealed after the filling.

Square voltage pulses of alternating sign were applied to the electrodes at frequencies
Figure 2. (a) and (b) Stroboscopic snapshots of the chamber at $t = 400 \mu s$ for a frequency of driving pulses $f = 150$ and $200 \text{kHz}$, respectively. The arrow shows a pinned bubble, which existed before the process started. These images show the visible situation in the chamber during normal actuation. (c) and (d) The same parameters of driving pulses but the images were made at $t = 600 \mu s$. The arrow in (d) indicates a bubble that appears in the chamber for a very short time. Appearance of the short-lived bubbles is the signal of the new actuation regime.

$f \sim 100 \text{kHz}$. To get high currents we use the electrochemical cell in the ohmic regime applying voltage amplitudes above $5 \text{V}$ [21]. Gas formation in the chamber was observed with a homemade stroboscope [22] ($10 \mu\text{s}$ flashlight and a wavelength of $\lambda \approx 530 \text{nm}$).

Gas production in the chamber resulted in a pressure rise and a deflection of the membrane. Detailed information on the pressure was collected by observing deflection of the membrane nearby its center with a vibrometer (Polytec MSA-400). The laser beam ($\lambda = 633 \text{nm}$, size $1.5 \mu\text{m}$) was focused on an opaque spot on the back side of the membrane to prevent possible scattering by occasional microbubbles formed in the chamber. The current and movement of the membrane were recorded in separate channels of the instrument. The membrane deflection $d$ was calibrated by applying a static gas pressure, giving $\Delta P = 2.03d + 0.27d^3$ [21], where $\Delta P$ is the overpressure in bars and $d$ is in $\mu\text{m}$.

3. Results

Normal actuation of the device was described in Ref. [21]. It was demonstrated that the pressure in the chamber can be as high $P = 4.6 \text{bar}$ and the time for pressure relaxation can be as short as $100 \mu\text{s}$. The actuator works well at frequencies $f > 20 \text{kHz}$. At high frequencies very few gas is visible in the chamber as one can see in Fig. 2(a) and (b), which correspond to $f = 150$ and $200 \text{kHz}$, respectively. Both images were made at the time moment $t = 400 \mu\text{s}$ and the process run at the voltage amplitude $U = 8 \text{V}$. At lower frequencies the amount of visible gas increases and below $20\text{kHz}$ the chamber becomes completely filled with the gas and the actuation becomes impossible. A small amount of visible gas in the chamber exists in the form of small microbubbles located above the electrodes. New actuation regime manifests itself when the process run longer. In this case a faint contrast appears in between the electrodes. For example at $t = 600 \mu\text{s}$ it can be seen in Fig. 2(c) and (d), which also correspond to $f = 150$ and $200 \text{kHz}$, respectively. This contrast resembles rather large microbubbles ($10 - 20 \mu\text{m}$ in diameter), which appear out of focus due to motion blur. This conclusion is supported by the observation of the chamber with a fast camera (180 000 frames per second) described in [23], where these bubbles are well visible. They appear in the chamber just for a few microseconds and accompanied by significant pressure jumps in the chamber (see below).

Typical response of the membrane on the electrical pulses with the amplitude $U = 9 \text{V}$ at frequency $f = 100 \text{kHz}$ is shown in Fig. 3(a). Well visible oscillations are superimposed on the monotonous increase of the membrane deflection. These oscillations are in phase with the driving pulses. As was explained in [21] they are related to the reaction happening in
nanobubbles containing a stoichiometric mixture of $\text{H}_2$ and $\text{O}_2$ gases. The monotonous deflection of the membrane is due unburned gas. For example, if a bubble contain only hydrogen or only oxygen the reaction does not happen and such a bubble will contribute to the pressure increase in the chamber. This gas is also collected in nanobubbles, which do not scatter light and cannot be observed in visible light. Very few bubbles visible in the chamber (see Fig. 2) cannot be responsible for a significant pressure increase. When the driving pulses are switched off the pressure drops down even faster than it was build up. It is explained by merging of non-stoichiometric bubbles with the following reaction between gases. The process is very sensitive to the external or internal temperature increase. Particularly, change of the slope in the membrane deflection in Fig. 3(a) is explained by the heat produced by the reaction of water formation.

If the same process run at higher frequency, for example, at $f = 150 \text{ kHz}$ as in Fig. 3(b), the pressure increases slower but then it jumps high for a very short time. These pressure jumps mark transition to the new regime. As was already explained these jumps are related to the short-lived microbubbles appearing in the chamber. The jumps never appear immediately after switching on the current. There must be an incubation period before the jumps can appear. The incubation time decreases with the increase of the voltage amplitude and decreases strongly even with a small temperature rise ($\sim 10^\circ \text{C}$). We did not observe the pressure jumps at frequencies below 100 kHz. On the other hand, the amplitude of the jumps increases with the frequency above 100 kHz.

If the process run sufficiently long time, the pressure in the chamber reaches a saturation point on average but continues to fluctuate around this point. This situation is demonstrated in Fig. 4(a) for the amplitude $U = 8 \text{ V}$ and frequency $f = 300 \text{ kHz}$. A typical pressure jump is shown in Fig. 4(b). One can see that the jumps are very short and highly energetic events. The width of a separate peak is estimated as $3 \mu\text{s}$. The energy released in the pressure jump is $\delta E = \delta P V_{ch} \approx 3.5 \text{nJ}$, where $\delta P \approx 0.7 \text{bar}$ (as follows from Fig. 4(b)) is the amplitude of the jump and $V_{ch} = 5 \times 10^4 \mu\text{m}^3$ is the volume of the chamber. Since the jump is related to the appearance and termination of one short-lived bubble with a size $D \sim 10 \mu\text{m}$, the pressure change inside of this bubble can be estimated as $\Delta P_b = \delta E/V_b \sim 100 \text{ bar}$, where $V_b = \pi D^2 h/4$ is bubble volume and $h = 5 \mu\text{m}$ is the chamber height. The only process which is able to provide this energy scale

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{(a) Normal actuation regime. Membrane deflection as a function of time is presented as measured with the vibrometer. The frequency of the driving pulses is $f = 100 \text{ kHz}$. The inset shows a detailed view around the point of maximal deflection. (b) Transition to the new actuation regime at higher frequency $f = 150 \text{ kHz}$. High and short peaks are a characteristic feature of this regime.}
\end{figure}
is the combustion between hydrogen and oxygen inside of the short-lived bubbles. We expect that these bubbles appear in the chamber due to merging of non-stoichiometric nanobubbles when the density of nanobubbles becomes critical [23]. The formed microbubble contains the stoichiometric mixture of gases, which are able to react. The reason for the ignition of the reaction is still not known. However, there are no doubts that the reaction happens because a huge amount of gas produced by the Faraday current does not show up in the chamber.

The most prominent feature of the new actuation regime is the time for the pressure relaxation when the driving pulses are switched off. As one can see in Fig. 4(a) it happens extremely fast just for 10 μs or so. Actually the pressure rises much slower than it is going down. This is a very important property for the fast actuation. Figure 5 demonstrates actuation of the membrane by three series of pulses separated by 200 μs pauses. The first series is 400 μs long. It is longer than the other two series, which are 200 μs long each, because of the incubation period. This first example of actuation in the new regime already demonstrates significant achievements. For quite a stiff SiN membrane the stroke is around 0.5 μm and overpressure in the chamber is around 1 bar. Termination of the gas is not a problem for this actuation regime and the response time is limited by the production of gas.

4. Discussion
Long incubation period gives a restriction on the fast performance of the actuator. The physical reason for this delay time is that one has to produce a significant concentration of nanobubbles before they start to merge. This incubation time is very sensitive to the temperature and can be easily reduced a few times by increasing temperature on 10 – 20 °C. It can be done, for example, with a heating element, which keeps the actuator at elevated temperature.

Fluctuations of pressure in the chamber are not favorable for smooth actuation. This problem can be solved by the proper design of the electrodes. The size of the short-lived microbubbles is related to the distance between the electrodes. Making this distance smaller and distributing electrodes more homogeneously in the chamber we can smooth out the fluctuations. The choice of working frequency is also an important parameter in this respect.

Combustion of hydrogen and oxygen is a highly exothermic process. For this reason the
Figure 5. Actuation of the membrane by three series of pulses separated by 200 µs pauses. The first series is 400 µs long and the other two are 200 µs long. The driving pulses have the amplitude $U = 8$ V and frequency $f = 150$ kHz.

reaction between gases in nanobubbles, which are formed in close proximity to the electrodes, influences significantly on the electrodes resulting in their degradation with time. The effect is especially strong at relatively low frequencies $20 - 50$ kHz [15]. When the combustion happens in microbubbles one could expect faster degradation of the electrodes. However, we did not observe this effect in the new actuation regime. This is because most of the gas reacts in microbubbles located in between the electrodes. In this case highly energetic events of bubble termination do not harm the electrodes. Also, in this regime much higher frequencies are used to get a similar stroke of the membrane. The higher the frequency the smaller stoichiometric nanobubbles are formed resulting in a weaker influence on the electrodes. Nevertheless, a long-time stability of the electrodes was not analysed yet. Material for the electrodes is also an important issue. It was established that electrodes wear correlates with the material’s yield strength [15]. The weakest effect was observed for tungsten and the strongest one for gold. Up to now we tested the actuators only with platinum electrodes.

One of the most important actuation parameter is the stroke. Current version of the actuator uses rather stiff silicon nitride membrane. For this membrane with the size $100 \times 100$ µm$^2$ the stroke that has been reached is $\sim 1$ µm. It can be increased further using softer material for the membrane. A convenient material in this respect is SU8. It has Young’s modulus 100 times smaller than that for SiN and its thickness can be easily changed in a wide range to program a desired stroke. The stroke can be also increased due to higher pressure in the chamber. It is possible to do by increasing the Faraday current, which is related to the design of electrodes.

During operation of the actuator one or a few pinned bubbles often appear in the chamber as one can see in all four images in Fig.2. In most cases pinning happens at the edge of the chamber at structural inhomogeneities. Sometime a pinned bubble can grow during the operation. In this case it becomes a real problem, which prevents normal functioning of the device. For practical application of the actuator one has to understand the reasons for pinning to be able to control it.

Summarising, the fast electrochemical microactuator has a number of very attractive features. It has a large stroke in comparison with its size, it needs rather low actuation voltage, it has
a short response time and can develop a high pressure. Finally, the actuator is completely compatible with the standard microtechnological process. The main disadvantage is a low efficiency of the actuator. This is because the electrochemical process in general has the low efficiency. Then, only part of the gas produced electrochemically makes a useful work; a significant part of the gas is burned in stoichiometric nanobubbles without production of the mechanical work. In spite of this disadvantage the total power consumption is still below 100 mW.

5. Conclusions
We presented here a new actuation regime of the electrochemical actuator that is driven by short alternating polarity voltage pulses. Extremely short ($\sim 10 \mu s$) termination time of the produced gas can be reached in this regime. This fast termination of gas is possible due to a very high density of nanobubbles in the chamber of the actuator. The high density of nanobubbles is also responsible for the high pressure developed by the actuator. The response time is limited by the rate of the gas production but not by the gas termination time as one could expect for an electrochemical actuator. We discussed problems and possible ways to improve performance of the actuator.

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