Optimization of electrodes for the fast electrochemical actuator

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Abstract. Electrochemical membrane actuator based on water electrolysis of alternating
polarity (AP) was demonstrated recently. It operates several orders of magnitude faster than the
devices working on conventional DC electrolysis. However, extremely high current density of
the AP process leads to the fast degradation of the electrodes. Titanium electrodes demonstrate
the best durability, but they oxidize during operation that reduces the gas production. Proper
design can increase the efficiency of the electrodes and slow the degradation down. In this
work, four typical layouts are fabricated and tested in the AP electrolysis. Current flowing
through the cell, threshold voltage for the explosive operation and wear of the electrodes are
analyzed and compared.

1. Introduction

Electrochemical actuators are widely used in various microfluidic systems such as drug delivery
devices and laboratories on a chip [1, 2]. A main part of the actuator is a working chamber filled with
an aqueous electrolyte solution and containing two metallic electrodes inside. Voltage applied to the
electrodes causes the electrochemical decomposition of water. Hydrogen and oxygen bubbles
generated in the chamber push the flexible membrane up. Using a series of microsecond AP voltage
pulses instead of one single polarity pulse increases the operation frequency of the actuator by several
orders of magnitude [3]. However, the electrodes are quickly destroyed in the AP electrolysis due to a
high current density ~100 A/cm² [4]. It was empirically found that titanium electrodes are the most
durable, but they oxidize during operation [5]. As a result, the Faraday current and the gas production
decrease, and performance of the actuator deteriorates.

The amount of the generated gas can be increased by optimizing the electrode layout. Increasing
the surface area maximizes the contact of the electrode with the electrolyte, thereby reducing the
resistance of the electrochemical cell and increasing the current. In addition, the shape determines the
distribution of the current density and, therefore, the preferred location and rate of the degradation.
The distance between the electrodes is also important. In this work, we test typical layouts of the
electrodes in the AP process and choose the shape that ensures the highest gas generation efficiency
and the lowest wear.
2. Materials and methods

The electrodes are fabricated on a thermally oxidized silicon wafer with a 0.9 µm thick SiO₂ layer. They have a three-layer structure. First, a titanium adhesion film with the thickness of 10 nm is deposited by magnetron sputtering. Next, a 500 nm thick aluminum layer and a 500 nm thick titanium layer are deposited. The intermediate Al layer reduces the resistance of the contact lines, while Ti is a working material. Then the wafer is covered by the photoresist Shipley S1813 and the UV contact photolithography is performed followed by the wet etching of Ti/Al/Ti film through the photoresistive mask. After the patterning, a chamber with a diameter of 500 µm is formed around the electrodes in a 8 µm thick layer of the photoresist SU-8. This layer protects the connecting lines from the electrolyte. The size of the chamber is similar to that used in the fast electrochemical actuator [3], but the chamber is not covered by a membrane. The wafer is diced on separate samples with sizes of 8×20 mm². The fabricated electrodes are presented in figure 1. Figure 2 illustrates a schematic cross-section of the sample.

![Figure 1](image1.png)

Figure 1. Optical images of the electrodes of four typical layouts: (a) circular; (b) interdigitated; (c) rectangular; (d) triangular.

![Figure 2](image2.png)

Figure 2. A schematic cross-section of the sample with the indication of the materials.

The sample is placed in a Petri dish filled with the electrolyte, which is a molar solution of Na₂SO₄ in distilled water. The thickness of the electrolyte layer above the sample is about 2 mm. Square voltage pulses of alternating polarity are applied to the electrodes. One electrode is grounded while the other one is at a positive or negative potential with respect to the ground. The voltage is provided by a waveform generator Keysight 33500B and amplified 10 times using a homemade amplifier [5]. The electrodes are tested in two regimes. In the first one, the pulses are applied continuously during 180 s. The frequency of pulses is \( f = 200 \) kHz and the amplitude is \( U = 6 \) V. The amplitude is not large enough to cause explosions of the microbubbles [3]. Current flowing through the electrodes is recorded every 10 s by a PicoScope 5000 and the average absolute value is calculated. In the second regime, a series of \( N = 10^5 \) pulses is applied to the sample every 2 s. The amplitude is adjusted to the threshold level \( U_{th} \), at which the concentration of nanobubbles in the electrolyte reaches a critical value. They merge into a microbubble that explodes with a distinctive clicking sound [6]. This sound was recorded using a microphone to a digital file. The experiment lasts until the electrodes are destroyed or \( U_{th} \) exceeds 19 V that is the maximal output voltage of the amplifier. Three samples of each type are tested in each regime. The results below are averaged over these samples.
3. Results and discussion

3.1. Continuous regime

Time dependence of the average current $I_{av}$ is shown in figure 3. In general, $I_{av}$ decreases during the first 100 s of the electrochemical process due to the oxidation of titanium. A slight increase of the current is observed at the circular and interdigitated electrodes in the first 10 s of the test. The probable reason is the increase of the electrolyte temperature. At the beginning of the process the circular and interdigitated structures demonstrate the highest $I_{av}$ of 38-40 mA, while the rectangular and triangular electrodes conduct significantly smaller current of 22 and 16 mA, respectively. The electrochemical cell containing the electrodes and the chamber covered by the electrolyte is simulated by the finite element method (FEM) using the validated software. The calculated conductivity of the cells is given in figure 4. The higher the conductivity, the larger the starting current. The current reaches a steady state in about 100 s. At the end of test (180 s) the highest $I_{av}$ of 10 mA is observed at the interdigitated and rectangular electrodes. Triangular design exhibits the worst result of 7 mA. The drop of the current is reversible. One can return $I_{av}$ to the initial value by increasing the amplitude of pulses to $U \approx U_{th}$. The original current ratio between the layouts is also restored.

![Figure 3](image3.png)

**Figure 3.** Time dependence of the average current flowing through the electrodes of several types.

![Figure 4](image4.png)

**Figure 4.** Relative conductivity of the electrochemical cells with the electrodes of several types.

3.2. Explosive regime

The circular and interdigitated electrodes begin to generate explosions at the lowest value of the threshold voltage $U_{th} = 10$ V (see table 1). Triangular structure has the largest starting $U_{th}$ of 13 V. The threshold amplitude increases with time due to the oxidation of titanium. For triangular and interdigitated electrodes it grows rapidly and reaches 19 V just in 4 min. Rectangular structure begins to generate explosions at $U_{th} = 12$ V. This design demonstrates the lowest increase rate of $U_{th}$ (table 1), which allows the longest operation during 22 min.

The electrodes after the explosive test are shown in figure 5a. The darkening and partial removal of the material from the substrate are observed. The change of color is caused by a growth of titanium oxide on the electrode surface [7, 8], and the destruction is due to a high current density. The triangular structure demonstrates the less degradation, while the interdigitated layout suffers the most. The upper Ti layer is partially removed from the “fingers”, making the Al layer visible. The distribution of the current over the electrodes is simulated using the FEM software. The sites with the highest current density are indicated in figure 5b. They are located at the edges and corners of the electrodes and match with the experimentally observed places of the strongest wear.
Table 1. Characteristics of the electrodes in the explosive regime.

| Layout       | Initial $U_{th}$ V | Increase rate of $U_{th}$ V/min | Relative volume of the explosion sound |
|--------------|--------------------|---------------------------------|----------------------------------------|
| Circular     | 10                 | 1                               | 0.7                                    |
| Interdigitated| 10                 | 3                               | 0.4                                    |
| Rectangular  | 12                 | 0.32                            | 0.9                                    |
| Triangular   | 13                 | 1.5                             | 1                                      |

Figure 5. (a) Optical images of the electrodes after the explosive test. (b) A schematic illustration of the electrodes. The red color indicates the areas of the highest current density predicted by the FEM simulation.

The rectangular electrodes are able to generate explosions despite the strong degradation. One of the samples withstood 50 min of operation, and the threshold voltage maintained below 18 V. The test was stopped when the repeating explosions broke the SU-8 layer and made a pit in the substrate, see figure 6. The explosion happens when the concentration of nanobubbles in the electrolyte reaches a critical value and densely packed nanobubbles merge into a single microbubble. To all appearance, the rectangular electrodes provide better localization of nanobubbles than the other layouts and, therefore, generate the explosions at the lower amplitude of pulses.

The power of the explosions is estimated by the volume of the clicking sound. The loudest clicks are produced by the rectangular and triangular electrodes (table 1). The interdigitated structure creates the quietest sound, since the areas with the high current density, where the gas is produced more intensively, are narrow and located far from each other. As a result, several preferred places of the explosion are created, but a microbubble is formed by a small number of nanobubbles. However, in a closed chamber of the actuator the produced gas accumulates, and it is easier to reach the critical concentration. Probably, in the real application the interdigitated electrodes will operate more efficiently.
Figure 6. The rectangular electrodes after 50 min of operation in the explosive regime: (a) the optical image, top view; (b) the SEM image at the angle of 20° with respect to the substrate; (c) close-up view of the pit made in the substrate by the explosions.

4. Conclusions
The electrodes of four typical layouts were tested in the electrolysis of water performed by microsecond voltage pulses of alternating polarity. In the continuous operation regime, the circular and interdigitated structures provide the highest current at the beginning of the electrochemical process. During the first 100 s of the test the current drops due to the oxidation of titanium, but then the decrease stops. The circular, interdigitated and rectangular electrodes conduct approximately the same current in the steady state, while the triangular structure provides the significantly less current. In the explosive mode, the rectangular electrodes demonstrate the best result. They generate explosions for a relatively long time despite the strong wear. This feature is determined by the high localization of the nanobubbles. The triangular electrodes show weak degradation, but the amplitude of voltage pulses required for the explosion quickly reaches the limit value. The interdigitated layout demonstrates the strongest wear. The degradation is observed in the areas with high current density, predicted by the finite element simulation. The circular electrodes show the intermediate result on the degradation and the threshold voltage. Thus, the circular and rectangular structures are considered most suitable for the fast electrochemical actuator. However, the final choice of the layout will be made after testing in a chamber sealed by an elastic membrane.

Acknowledgments
This work is supported by the Russian Science Foundation, Grant No. 18-79-10038, and performed using the equipment of Facilities Sharing Centre “Diagnostics of Micro- and Nanostructures”.

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