Choosing the electrode material for the fast electrochemical actuator

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Abstract. Electrochemical actuators are promising candidates for implementation in various microfluidic systems, but they suffer from a very long response time due to slow gas recombination. Water electrolysis performed by short voltage pulses of alternating polarity (AP) reduces the response time by several orders of magnitude. This process, however, results in a fast degradation of electrodes. It is important to find a material, which is able to withstand the AP operation without significant degradation. In this work the electrodes made of six metals are fabricated and tested. The current flowing through the cell, the threshold voltage for the explosive operation, and the wear of the electrodes are analyzed and compared.

1. Introduction
Microfluidic systems such as labs-on-a-chip and drug delivery devices are widely used in biology, chemistry and medicine [1, 2]. These systems require a compact, energy-efficient and microtechnology-compatible actuator to pump the fluid through the channels. Electrochemical actuators [3-6] meet these criteria. In these devices, H₂ and O₂ bubbles are generated in the working chamber during electrochemical decomposition of water and push a flexible membrane up. Conventional actuators based on the DC electrolysis suffer from a long response time due to slow recombination of the produced gas. Using microsecond AP voltage pulses instead of a constant voltage solves the problem. The gas disappears in milliseconds due to spontaneous combustion of hydrogen and oxygen in nanobubbles [7]. However, the electrodes in such an actuator degenerate fast. Firstly, the current density ~100 A/cm² is extremely high. Secondly, in contrast with the DC process, each electrode alternately serves as the cathode and anode. A proper selection of the electrode material will increase the durability, but behavior of the materials under these conditions is poorly investigated. In this work we test several metals and choose one that ensures the highest performance and the longest lifetime of the electrodes.

2. Materials and methods
Thin-film electrodes of Ti, Ta, Cu, Ni, Pt and Au are fabricated on an oxidized silicon wafer with a 0.9 µm thick SiO₂ layer. The metals are deposited by the magnetron sputtering. The layers of Ti, Ta, Pt and Au have a thickness of 100 nm and are deposited onto a 500 nm thick Al layer, which provides low electrical resistance of the signal lines. The layers of Ni and Cu have a thickness of 500 nm. The layered...
structure of the electrodes is given in table 1. The electrodes have a concentric shape with the outer diameter of 350 µm (figure 1). The signal lines are covered by 8 µm thick SU-8 insulating layer.

### Table 1. Layers of the electrodes with various working metals (from the bottom to top).

| Working metal | Layers with the thickness (nm) |
|---------------|--------------------------------|
| Ti            | Ti/Al/Ti 10/500/100            |
| Ta            | Ti/Al/Ta 10/500/100            |
| Cu            | Ti/Cu 10/500                   |
| Ni            | Ni 500                         |
| Pt            | Ti/Al/Pt 10/500/100            |
| Au            | Ti/Al/Ti/Au 10/500/10/100      |

Figure 1. Optical image of the electrodes, top view.

A chip with the electrodes is placed in a Petri dish filled with the electrolyte, which is a molar solution of Na₂SO₄ in distilled water. Rectangular AP voltage pulses are applied to the inner electrode, while the outer one is grounded. The signal is provided by a waveform generator Keysight 33500B and amplified 10 times using a homemade amplifier [8]. It was shown that the degradation of the electrodes slows down as the frequency of pulses $f$ increases [9]. Here we use $f = 500$ kHz that is the upper limit of our amplifier.

The samples are tested in two regimes. In the first one, the pulses of the fixed amplitude $U = 8$ V are applied continuously during 30 min. The current flowing through the electrodes is recorded every 10 s by a PicoScope 5000 and the absolute value of the current $I_{av}$ averaged over a period is calculated. In the second regime, a series of $N = 2.5 \times 10^5$ pulses are 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. The nanobubbles merge to form a microbubble, which explodes with a clicking sound [10]. The experiment is continued until the electrodes are destructed or until $U_{th}$ exceeds 17 V that is the highest output voltage of the amplifier. Three samples of each type are tested in both regimes. The results are averaged over these samples.
3. Results and discussion

3.1. Continuous regime
The time dependence of the average current is shown in figure 2. For all the structures $I_{av}$ decreases with time but then is stabilized. At the beginning of the test platinum, gold and copper electrodes demonstrate the highest current of 50-65 mA. For Ti structures $I_{av}$ starts with 43 mA. Pt and Cu electrodes exhibit lower decrease rate of the current in comparison with Ti and Au. However, Pt and Cu are susceptible to strong damage, which appears as blackening of the electrodes. Photographs of the samples after 30 min. of the continuous operation are shown in figure 3. This damage significantly reduces the performance of the samples. As a result, by the end of the test the largest current of 20 mA is supported by Au electrodes, which demonstrate smaller but still noticeable wear. The next is Ti with $I_{av} = 18$ mA. Only a slight color change due to the oxidation [11] is observed for these structures, as well as for Ta electrodes. However, Ta coating provides significantly lower current $I_{av} < 12$ mA. To all appearance, the reason is low conductivity of tantalum oxide. Titanium oxide is an n-type semiconductor [12] that allows the current flowing through the oxidized surface. The data for Ni electrodes are not shown in figure 2, since they are almost destroyed in 5 s of the electrochemical process. These structures produce visible bubbles due to a high rate of oxygen evolution [13]. This is unacceptable for the actuator, because the bubbles may fill the working chamber and block the electrodes from the electrolyte, thereby disrupting proper operation of the device. It is worth noting that the inner electrode usually suffers more than the outer one, because its area is almost two times smaller and, therefore, the current density is higher.

![Figure 2. Time dependence of the average current flowing through the electrodes made of different metals.](image1)

![Figure 3. Optical images of the electrodes after the continuous test.](image2)

3.2. Explosive regime
The electrodes of copper, titanium, platinum and gold, which provide the highest current during continuous operation, are chosen for the explosive test. For all the samples, the threshold voltage increases with time due to the degradation of the working layer. The Cu and Au structures begin to generate explosions at the lowest value of $U_{th} = 9.5$ V, see table 2. The electrodes coated with Ti require the largest starting voltage of 11.6 V. However, they demonstrate the highest durability. Ti structures produce explosions during 12 min, until the amplitude of pulses reaches 17 V. The damage is insignificant in comparison with the other samples, as one can see in figure 4. To all appearance titanium oxide protects the electrodes. The Cu structures generate explosions for 3.5 min, but then the operation stops due to the oxidation. The coatings of Pt and Au are removed from the electrodes by the explosions. The gold structures degrade slower than the platinum ones and operate longer (10.5 min for Au vs 1 min for Pt).
Table 2. Working characteristics of the electrodes in the explosive regime.

| Working metal | Cu  | Ti  | Pt  | Au  |
|---------------|-----|-----|-----|-----|
| $U_{th}$ initial, V | 9.5 | 11.6| 11  | 9.5 |
| $U_{th}$ maximal, V  | 12.5| 17 | 11  | 11.6|
| $U_{th}$ increase rate, V/min | 0.9 | 0.45 | 0  | 0.2 |

3.3. Oxidation resistant titanium electrodes

Some titanium samples demonstrate increased resistivity to oxidation. In the continuous regime, they provide much slower drop of the current compared to the standard electrodes, as shown in figure 5. In the explosive regime, their $U_{th}$ grows slower. As a result, these samples produce explosions for several tens of minutes without significant degradation. Energy dispersive X-ray analysis has shown that the standard and oxidation-resistant electrodes have identical chemical composition. As a rule, the durable samples are located in the middle of the wafer. Probably, the high resistivity to oxidation is related to the microstructure of the metal film. This phenomenon requires a separate investigation, because it is important for development of highly durable electrodes for the fast electrochemical actuator.

4. Conclusions

The electrodes of six different metals were fabricated and tested in the AP electrochemical process. In the continuous regime all the samples demonstrate decrease of the current with time. Platinum and copper structures provide the largest current at the beginning of the test, but the strong damage of the electrodes significantly reduces their performance. After several minutes gold and titanium electrodes ensure the largest current. Moreover, titanium shows the weakest degradation. Nickel structures are
completely destroyed in a few seconds of operation, while tantalum electrodes conduct a very small current due to oxidation. In the explosive regime titanium structures also exhibit the weakest wear. They are able to support explosions significantly longer than the electrodes made of other metals. The growth of the oxide film on the electrode surface reduces the gas production with time, but some samples demonstrate increased resistivity to the oxidation. Probably, this phenomenon is determined by the microstructure of titanium film, but a separate study is required to confirm this suggestion. Thus, among the investigated metals, titanium is a preferable material to use in the fast electrochemical actuator.

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References
[1] Temiz Y, Lovchik R D, Kaigala G V and Delamarche E 2015 Microelectron. Eng. 132 156
[2] Cobo A, Sheybani R and Meng E 2015 Adv. Healthcare Mater. 4 969
[3] Kim H, Hwang H, Baek S and Kim D 2018 Sens. Actuators A 277 73
[4] Yi Y, Buttner U, Carreno A A A, Conchouso D and Foulds I G 2015 J. Micromech. Microeng. 25 105011
[5] Lui C, Stelick S, Cady N and Batt C 2010 Lab Chip 10 74
[6] Lee D E, Soper S and Wang W 2008 Microsyst. Technol. 14 1751
[7] Uvarov I V, Lokhanin M V, Postnikov A V, Melenev A E and Svetovoy V B 2018 Sens. Actuators B 260 12
[8] Uvarov I V, Lemekhov S S, Melenev A E and Svetovoy V B 2017 J. Micromech. Microeng. 27 105009
[9] Shlepakov P S, Uvarov I V, Naumov V V, Mazaletskiy L A and Svetovoy V B 2019 Int. J. Electrochem. Sci. 14 5211
[10] Svetovoy V B, Prokaznikov A V, Postnikov A V, Uvarov I V and Palasantzas G 2020 Energies 13 20
[11] Van Gils S, Mast P, Stijns E and Terryn H 2004 Surf. Coat. Technol. 185 303
[12] Fujii T, Sakata N, Takada J, Miura Y, Daitoh Y and Takano M 1994 J. Mater. Res. 9 1468
[13] Lyons M E and Brandon M P 2010 J. Electroanal. Chem. 641 119