

pH and Flow-Independent On-Line Measurement of Free Chlorine in Water

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A modified design of the Au-SenSys™ chlorine sensor is presented. A drastic reduction of the hydrodynamic effect on the sensitivity is achieved by a diminution of the microdisk diameter. The use of an auxiliary electrode for local pH control is demonstrated, thus making chlorine measurement pH independent.

The Au-SenSys™ microelectrode-array-sensor has been optimized for high reliability long term monitoring of various oxidizing agents, including in particular chlorine a major disinfecting agent for drinking and swimming pool water^[1]. While the existing chlorine sensor characteristics were found to be suitable for most applications, a further improvement of two characteristics of the sensor, hydrodynamic and pH dependences, was needed to increase the accuracy and to facilitate its implementation in specific applications.

Microelectrodes, defined as electrodes with a critical dimension smaller than the Nernst diffusion layer, have an intrinsic low dependence on hydrodynamic conditions. When microelectrodes are exposed to high flow rates the Nernst diffusion layer thickness decreases and smaller microelectrode dimensions are required. A new process has been set-up to efficiently fabricate microdisk arrays with smaller disk diameters. In the new architecture the microdisks are created in a cavity instead of on the top of the passivation layer as shown in Figure 1.

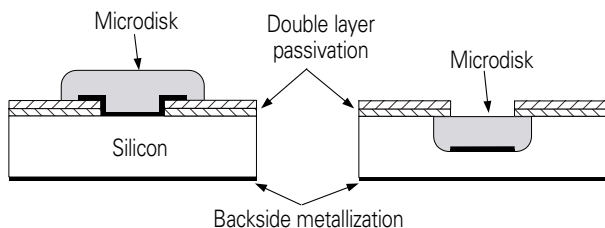


Figure 1: Schematic cross-section of previous (left image) and new (right image) microdisk array.

This new design brings the following advantages:

- A reduction of the disk diameter from 15 μm to 2 μm
- An improvement of the water corrosion resistance by the use of identical materials
- A simpler fabrication process based on a single photolithographic mask.

Figure 2 shows only a small dependence of the sensitivity on the flow speed, demonstrating that a major reduction of the hydrodynamic effect is obtained with the new design.

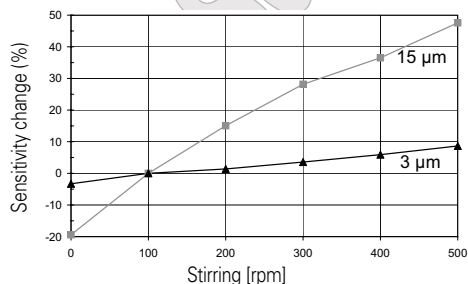


Figure 2: Reduction of the flow dependence of the sensor response by reducing the electrode disk diameter from 15 μm to 3 μm.

Chlorine is measured as "free" chlorine, i.e. the sum of the two species HOCl + OCl⁻. In the usual drinking-water pH

range, the ratio of the two species varies between 2% OCl⁻ at pH 6 and 98% at pH 9. As OCl⁻ and HOCl responses are slightly different on a gold microdisk array the pH effect is not negligible (ca. 25%).

An auxiliary electrode surrounding the microdisks^[2] is used to compensate the pH effect by taking advantage of the local acidification produced by an anodic current:



Boron doped diamond (BDD) has also been used as auxiliary electrode material as shown in Figure 3.

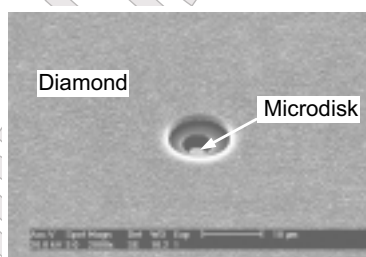


Figure 3: Gold microdisk surrounded by an auxiliary BDD electrode.

Local acidification to a value lower than 6 where chlorine is found only in the HOCl form will suppress pH dependence. Figure 4 shows that complete pH compensation could be obtained in drinking-water by applying a current density of 0.5 mA/cm² to the auxiliary electrode.

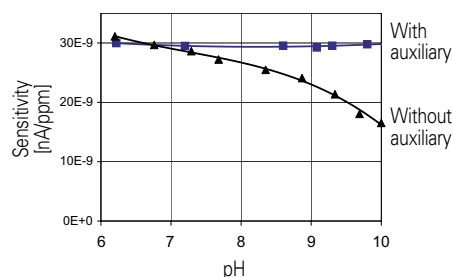


Figure 4: pH effect on chlorine measurement in drinking water, without and with auxiliary electrode.

Both metal and BDD auxiliary electrodes are fabricated in a simple high yield process based on the new microdisk design. Other applications taking advantage of the auxiliary electrode principle are under development.

The support of OFES is gratefully acknowledged.

^[1] J. Gobet, Ph. Rychen, F. Cardot, E. Santoli, "Microelectrode Array Sensor for Water Quality Monitoring", Water Sci. Techn. 47 (2003) 127

^[2] Electrode system for electrochemical sensor, CSEM Patent WO 02/095387