MICRO OXYGEN SENSOR WITH REDOX CYCLING

Jian Wu and Willy Sansen
K.U. Leuven, ESAT-MICAS
Kasteelpark Arenberg 10, B-3001
Leuven-Heverlee, Belgium
Fax : +32 16 32 19 75
email: jian.wu@esat.kuleuven.ac.be

In this communication, a micro oxygen sensor with enhanced sensitivity due to redox cycling between the closely spaced working electrode and counter electrode is proposed and implemented.

The concept of redox cycling between two closely spaced microelectrodes was first demonstrated by Bard *et al* in 1986 [1]. In this case, the electrochemical cell consists of four electrodes: working electrode (generator), collector, counter electrode, and reference electrode (Fig. 1). The working electrode(generator) and collector are closely spaced (in the range of µm). During operation, one electrode is held at potential to drive the reduction ,while the other electrode is held at potential to drive the oxidation. Species produced at one electrode diffuse back to the other electrode, where they are converted back to their original form, creating a process called redox cycling [2]. Up to now, according to our knowledge, all electrochemical sensors with redox cycling are based on the four-electrode setup. Meanwhile, in most cases, the cycling takes place in redox couples with fast reaction kinetics, such as $Ru(NH_3)_6^{2+}$/$Ru(NH_3)_6^{3+}$ or $Fe(CN)_6^{4-}$/$Fe(CN)_6^{3-}$.

Dissolved oxygen measurement is a key issue in blood gas analysis and many other biomedical applications. Lambrechts *et al* implemented a micro Clark cell in three-electrode configuration [3]. The electrochemical cell consists of a Au working electrode, a Pt counter electrode and a Ag/AgCl reference electrode. During operation, oxygen is reduced at the working electrode:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (1)$$

It is a common practice to suppose that what happens at the counter electrode does not influence the responses of the sensor. In macro electrochemical sensors, due to the large distance between the working electrode and the counter electrode, this assumption is normally held. However, this assumption is not always true in the micro electrochemical sensors. In the Clark cell with three-electrode setup, water is oxidized and oxygen is released at the counter electrode:

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \qquad (3)$$

If the distance between the working electrode and the counter electrode is small enough, redox cycling can take place.

In this communication, the proposed micro oxygen sensor with redox cycling is implemented and measurement results are presented. According to our knowledge, there is no such report in the literature up to now.

The sensor was fabricated by standard microelectronic processes. Fig. 2 is a SEM picture of the patterned electrodes. Fig. 3 shows the cyclic voltammogram of micro oxygen sensors in air saturated phosphate buffer solution. For curve (a), the counter electrode is the on-chip interdigitated counter electrode. The distance between the fingers of interdigitated working and counter electrodes is 20 µm. For curve (b), an external Ingold Au counter electrode is used. The current is larger in curve (a) than in current (b). This proves the proposed redox cycling effect. Similar results are also obtained in amperometric measurements.

References:
[1] A. J. Bard, *et. al.*, Anal. Chem., 58, 2321.
[2] A. Cohen, and R. Kunz, Sensors & Actuators B62, 23.
[3] M. Lambrechts, *et. al.*, Proc. 2nd International Meeting on Chemical Sensors, Bordeaux, 1986, pp572.

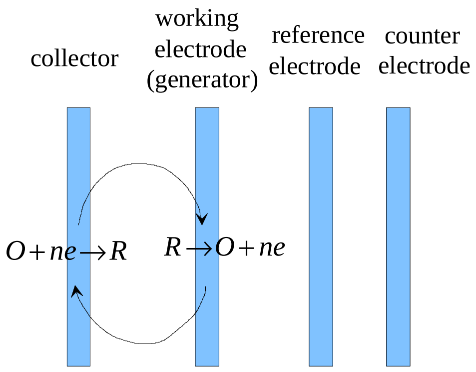

Fig.1 The redox cycling in the four-electrode setup.

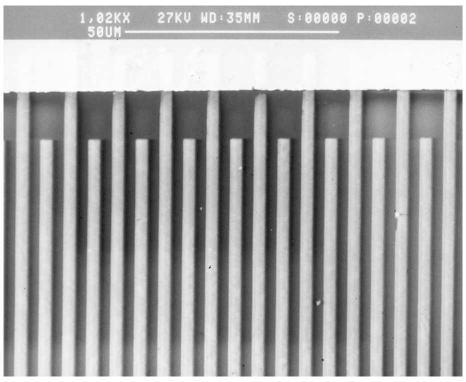

Fig. 2 The SEM picture of the interdigitated micro electrodes.

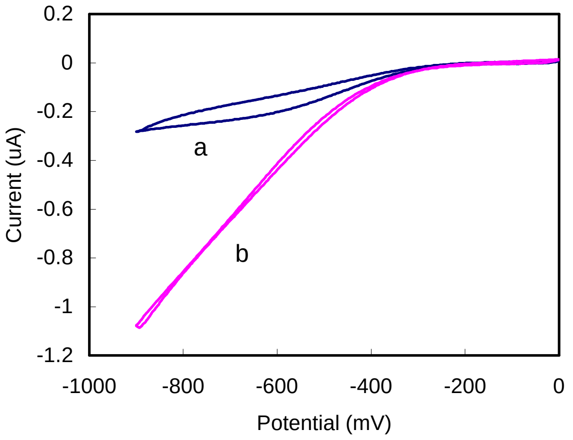

Fig. 3 The cyclic voltammograms of the oxygen sensor in air-saturated PBS solution