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Glucose Sensor Based on a Solid Electrolyte Cell Using Sodium Ion Conductor

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A glucose sensor was developed based on a solid electrolyte cell as a transducer. The sensor element uses a sodium ion conductor (NASICON) as a solid electrolyte and a Pt-layer with immobilized GOD as a sensing electrode. EMF of the sensor varies logarithmically with glucose concentration from 5×10^{-5} to 5×10^{-3} M, following Nernst's equation (-53 mV/dec). The sensing mechanism as well as the interface of potential formation were investigated.

The use of all-solid-state transducers seems to be a successful approach for miniaturizing enzyme sensors.$^{1-3)}$ Solid electrolyte cells, which are inexpensive and simple in structure, provide the additional advantage of an incorporated solid-state reference electrode. Therefore a compact sensor, which is easy to handle, can be obtained. In our previous works this kind of transducers were introduced into enzymatic glucose sensors.$^{4-8)}$ F^- and H^+ conductors (LaF_3, $Sb_2O_5 \cdot nH_2O$) were used as solid electrolytes.

Based on these results applicability of a sodium ion conductor (NASICON) was tested for this kind of potentiometric enzyme sensor and the sensing mechanism of the sensor elements prepared was investigated. NASICON was used here because of its chemical stability, its easy preparation and its relatively high ionic conductivity at room temperature.

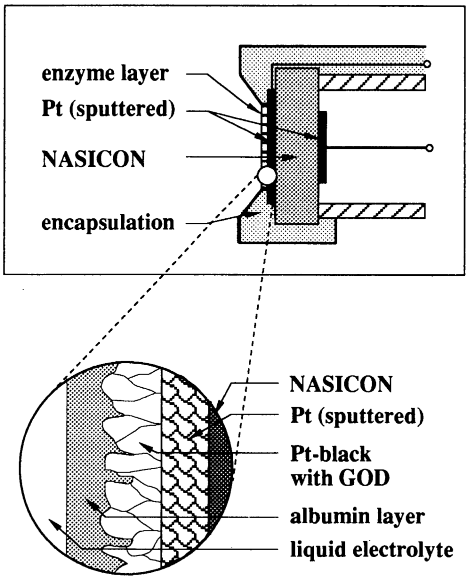

Fig. 1. Schematical cross-view of the glucose sensor.

NASICON ($Na_3Zr_2Si_2PO_{12}$) was synthesized from Na_3PO_4 and $ZrSiO_4$ by sintering at 1100 °C. Discs (Ø 8 mm × 1 mm) were prepared by pressing the obtained NASICON-powder and a second sintering process at 1200 °C. After polishing and treating the discs with distilled water, platinum (or gold) was deposited on the surface by using rf sputtering technique. On top of the sputtered layer Pt (or Au)-black was electrochemically formed by applying -0.3 V vs. Ag/AgCl in 1% solution of the respective hydrogen chlorometalate. The enzyme (glucose oxidase - GOD, supplied by SIGMA - from Aspergillus niger -) was immobilized into the metal-black layer by a direct adsorption technique: The sensor elements were dipped into the following phosphate buffer solutions in series for 15 min each: GOD-sol. (20 mg/ml, 150 U/mg)), albumin-sol. (5%), glutaraldehyde-sol. (2%) and albumin-sol. (5%) again. The internal reference electrode was prepared by sputtering Pt on the back side of the NASICON-disc. EMF-response of the sensors was measured at 30 °C in phosphate buffer (pH 6.9).

The sensor elements prepared in this way can be described by the following electrochemical scheme: air, Pt / NASICON / Pt, enzyme layer (GOD). A schematical view of the sensor is given in Fig. 1. The sensor was found to be sensitive to glucose for concentrations from 5x10^{-5} to 5x10^{-3} M, following Nernst's equation with a slope of -53 mV/dec. A typical sensitivity curve is shown in Fig. 2.

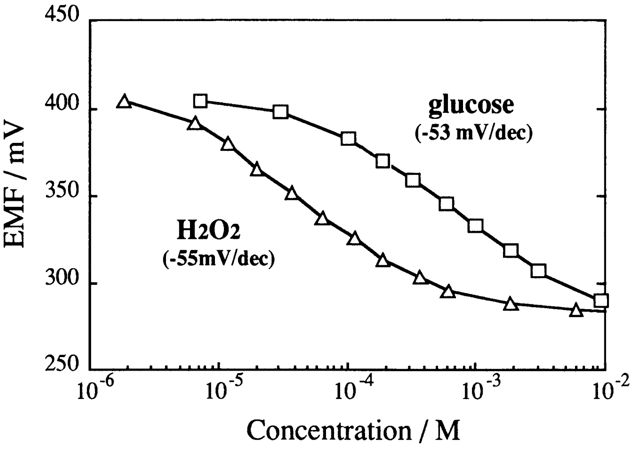

Fig. 2. Response characteristics of the NASICON-based sensor for glucose and H_2O_2 (sensing electrode: platinum, 30 °C).

The response rate of the sensor is dependent on the glucose concentration: The 90% response time for a concentration change from 4.00x10^{-5} to 7.45x10^{-5} M was 2 min, while that from 9.84x10^{-4} to 1.76x10^{-3} M was only 30 s (see Fig. 3). The lifetime obtained for the sensor until now is about 8 days in permanent liquid electrolyte contact.

The glucose sensor was also found to be sensitive to hydrogen peroxide with a slope of the EMF - concentration dependence of -55 mV/dec. The close similarities in sensing behavior (response rates, sensitivity) indicate that the glucose sensitivity can be ascribed to the H_2O_2 produced by the enzymatic reaction:

$$\text{glucose} + O_2 \xrightarrow{\text{GOD}} \text{gluconolactone} + H_2O_2 \qquad (1)$$

In relation to the H_2O_2-sensitivity curve, the glucose curve is shifted toward higher concentrations (see Fig. 2). This can be explained by the different conditions of both measurements: For the H_2O_2-detection the equilibrium concentration within the Pt-black layer corresponds to the H_2O_2-concentration in the bulk solution, while during glucose detection this concentration is determined by the rates of H_2O_2-production (enzymatic reaction, diffusion of O_2 and glucose into the Pt-black) and its diffusion out of the metal-black into the solution. The main reason for the lower steady state H_2O_2-concentration at the Pt-surface, compared to the glucose concentration in solution, can be seen in the faster diffusion of the produced H_2O_2 through the Pt-black and albumin layer in relation to glucose. Anyhow, the response time of the sensor seems to be determined by the H_2O_2-response of the sensing electrode. This can be concluded from the very similar response behavior to H_2O_2 and glucose at comparable sensor potentials.

The Pt-sensing electrode of the sensor can be replaced by an Au-electrode. In this case a very different response behavior was observed: The sensor responded to H_2O_2 as well as glucose but with an oppo-

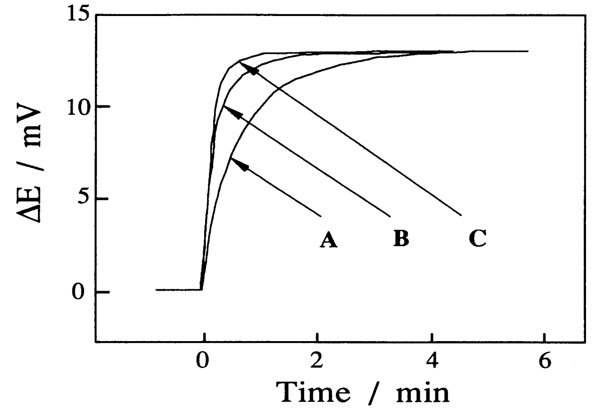

Fig. 3. Response transients of the glucose sensor.
A : 4.00x10^{-5} —> 7.45x10^{-5} M,
B : 1.86x10^{-4} —> 3.25x10^{-4} M,
C : 9.84x10^{-4} —> 1.76x10^{-3} M,
(ΔE = change in EMF).

site slope of the sensitivity curve (see Fig. 4). Response rates were found to be lower compared to the Pt-sensor, but with a similar concentration dependence. The detection range was shifted to higher concentrations.

In consideration of these results we tried to clarify the sensing mechanism of this solid electrolyte based structure. Two interfaces should be taken into account as potential determining sites: The metal/NASICON interface, which should be in contact with the liquid electrolyte to form a sensitive three-phase region and the liquid electrolyte/metal interface, which may be responsible for the H_2O_2-dependent potential (see also Fig. 1).

NASICON itself is an appropriate sensor material showing a reversible sodium ion exchange in electrolyte contact. Therefore sodium ion sensitivity of the glucose sensor vs. an external reference electrode was measured to clarify whether the liquid electrolyte can reach the solid electrolyte through the covering metal layer. The clear response to sodium ions for concentrations above 10^{-3} M, as shown in Fig. 5, can be seen as a proof for the ion exchange as well as the direct contact of solid and liquid electrolyte within the sensor structure.

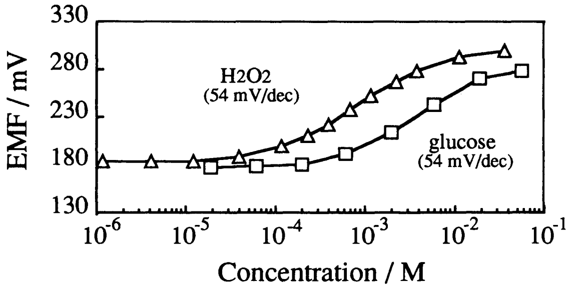

Fig. 4. Response characteristics of the glucose sensor using gold as sensing electrode.

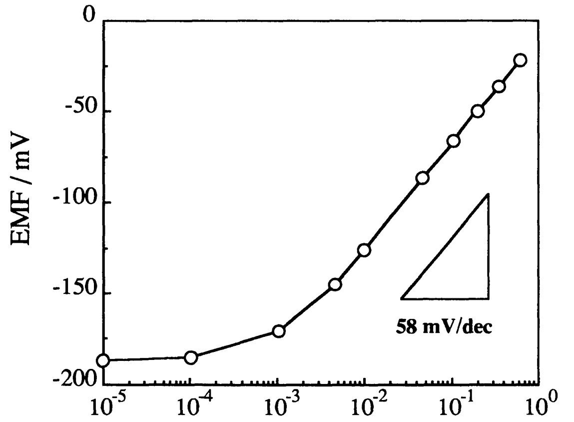

Fig. 5. Sodium ion response of the glucose sensor (potential difference between internal Pt/air and external Ag/AgCl-electrode).

Because of the different sensing behavior of the platinum- and the gold-attached sensor, both metals were examined to their H_2O_2-response by using an external reference electrode. The metals were investigated as sputtered films (on alumina substrates) as well as metal wires. No essential difference was found in the sensing characteristics. For the metal wires the results are shown in Fig. 6. The close similarities in sensing characteristics between the metal and the glucose sensors indicate that the metal determines response and direction of electron transfer.

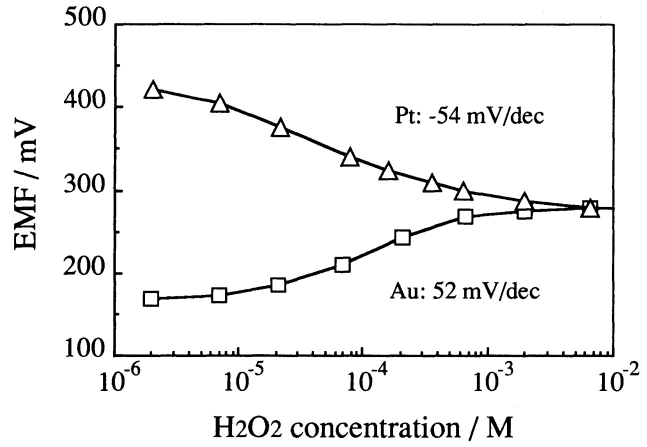

Fig. 6. Response of a Pt- and Au-wire (with metal-black) to hydrogen peroxide (potential vs. ext. Ag/AgCl-electrode).

An additional argument can be obtained by comparing the H_2O_2-response of the NASICON based sensor prepared with and without Pt-black on top of the sputtered Pt-layer. The result of this experiment is given in Fig. 7. Because platinizing changes only the metal surface and a different response was obtained after this process, the liquid electrolyte/metal interface seems to be the potential determining site. To support this point of view a sensor with a double metal layer as sensing electrode was fabricated: air,Pt/NASICON/Au/Pt,Pt-black.

With this sensor the typical response behavior of a sensor using only platinum (Pt/Pt-black) was obtained. Therefore the metal/NASICON interface appears less probable to be the potential determining place. In addition it was found that no measurable response was obtained when NASICON-discs were exposed to H_2O_2.

From these results it can be concluded that the metal/liquid electrolyte interface determines the H_2O_2 dependent potential of the sensing electrode. The established potential at the metal surface is, according to Hoare,[9] a mixed potential including a complicated interaction of O_2 and H_2O_2 with the metal surface. The slopes of the sensitivity curves obtained suggest a one electron oxidation/reduction of H_2O_2, which we want to describe by the following equations:

Pt-electrode: $H_2O_2 \Longleftrightarrow (HO_2)_{ads} + H^+ + e^-$ (2)

Au-electrode: $H_2O_2 + e^- \Longleftrightarrow (H_2O_2)^-_{ads}$ (3)

Despite of the similarities of the bare metal and the NASICON-based sensor, stability of the sensor signal (lifetime) seems to be influenced by the interaction of the solid electrolyte with the metal layer as well as the stability of the solid electrolyte to the electrolyte solution (e.g., solubility). This suggests that the solid electrolyte (NASICON), acting as an internal electrolyte to contact the reference electrode, can influence the state of the metal allowing stable measurement in solution. To verify this, further investigations are necessary.

Based on such a sensor concept the similarities among the different solid electrolyte based sensors so far reported can be well explained.

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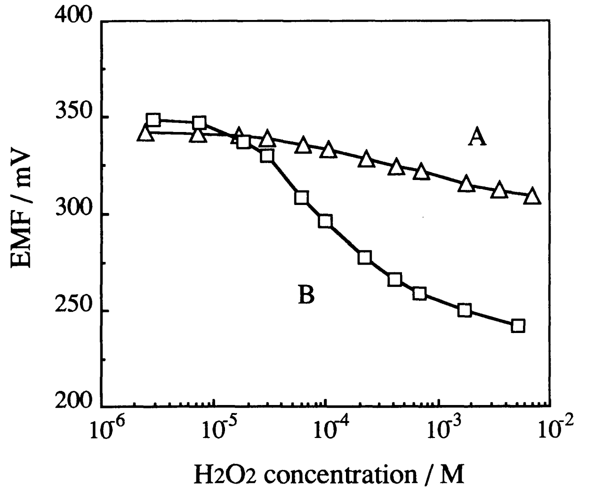

Fig. 7. Response of the NASICON-based sensor to hydrogen peroxide.
Sensing electrode: A - sputtered Pt only, B - Pt(sputtered)/Pt-black.

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