POTENTIAL RELAXATION AS A MEASUREMENT PROCEDURE FOR BIOSENSORS

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1. Introduction

We present a discontinuously working procedure for long-term measurement of the concentration of an analyte in a solution with an enzyme electrode.

As compared with this method the well-known amperometric procedure works continuously: The working electrode is permanently forced to a certain voltage, and a current results, the magnitude of which is a measure of the concentration of the analyte. The disadvantage may arise that the function of the working electrode can be affected by products of interfering reactions and succeeding reactions (e.g. polymerization). In in-vivo-application the permanently applied voltage at such electrodes can also cause electrochemical conversion of physiological substances into toxic ones and stimulate immune reactions leading to encapsulating of the sensor.

The presented relaxation procedure uses the same biosensor arrangement as the amperometric one. The respective voltages, however, are applied only for a short time (about one second) and the interruptions are long (in the range of minutes).

2. Principle of Measurement (see Fig. 1)

With no external current flowing the working electrode establishes the rest voltage V_{rest}. Then a control voltage, V_{contr}, is applied to the working electrode for the time t_1 with the aid of a timer-controlled potentiostat. This represents a disturbance of the rest condition: Electrons are "pumped" from (anodical) or to (cathodical) the working electrode depending on the sign of $(V_{contr} - V_{rest})$. The latter expression determines the new electron energy level of the working electrode. The voltage V_{contr} should be adjusted to a value where (if possible, only) the reaction to be measured at the working electrode takes place. The time t_1 determines how far the disturbance will proceed into the environment of the working electrode.

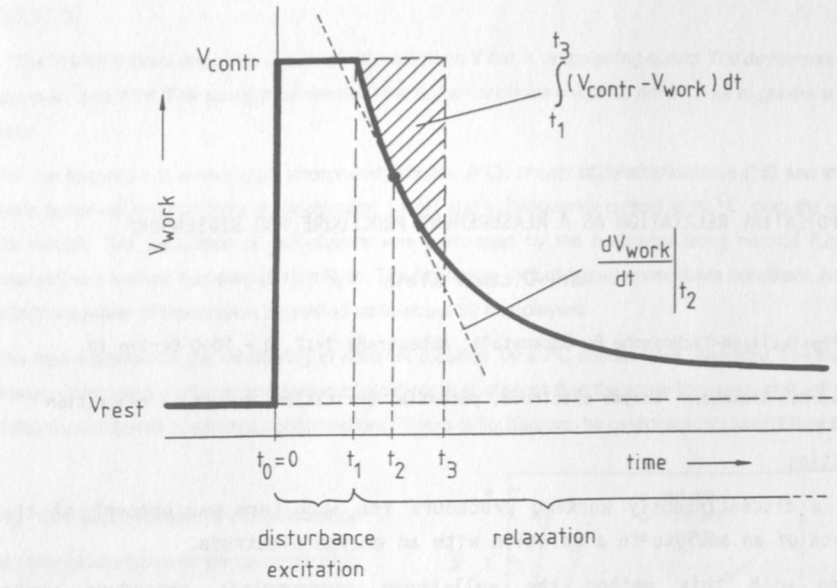

Fig. 1

Schematic diagram of a potential relaxation curve and its evaluation by a differential or integral

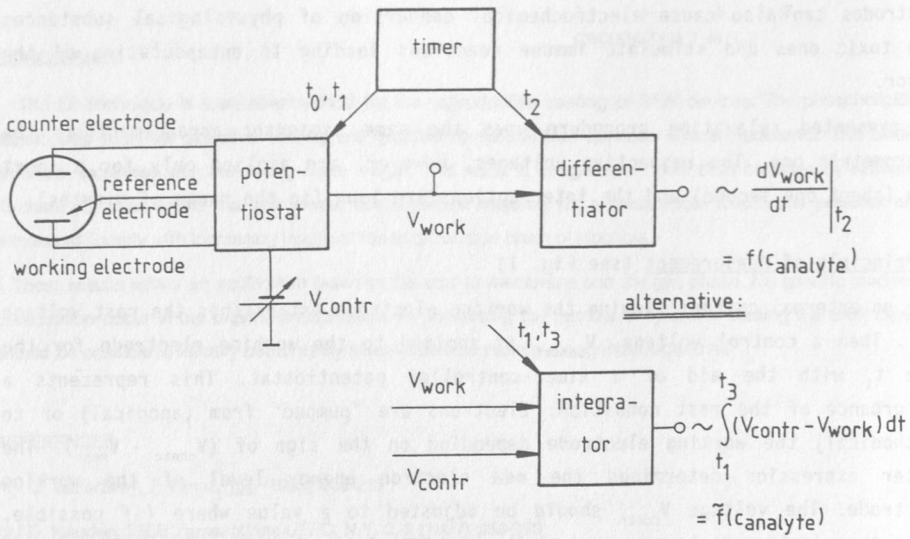

Fig. 2

Apparatus for measuring and evaluating potential relaxation curves

After the disturbance the voltage of the working electrode tends to return to V_{rest}. The rate of this process increases with increasing ability of the surrounding species to deliver the lacking electrons or accept the excessive electrons, respectively. Accordingly, the velocity of the voltage change after the disturbance is a measure of the concentration of these electron-delivering or -accepting substances or of a preceding enzyme reaction.

3. Realization of Measurement (see Figs.1 and 2)

The voltage of the working electrode is measured potentiometrically, and the value of the time differential at time t_2 is correlated to the analyte concentration.

Alternatively, the voltage of the working electrode can be integrated between times t_1 and t_3; the value of the integral is also correlated to the concentration to be determined.

After the working electrode has returned to the rest condition another measurement can be started.

By periodical variation of the control voltage the concentrations of more than one analyte may be measured with the same working electrode. An example may be the measurement of an electron-delivering and an electron-accepting reaction.

It is possible to combine the counter and reference electrodes to one electrode.

4.Applications

a) Measurement of H_2O_2 concentration by anodic oxidation (Figs.3 and 4):

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$

b) Measurement of glucose concentration by anodic oxidation of H_2O_2:

$$\text{glucose} + O_2 \xrightarrow{GOD} \text{gluconolactone} + H_2O_2$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$

c) Measurement of glucose concentration by anodic oxidation of a mediator A:

$$\text{glucose} + A_{ox} \xrightarrow{GOD} \text{gluconolactone} + A_{red} + 2H^+$$

$$A_{red} \rightarrow A_{ox} + 2e^-$$

d) Measurement of glucose concentration by cathodic reduction of oxygen:

$$\text{glucose} + O_2 \xrightarrow{GOD} \text{gluconolactone} + H_2O_2$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

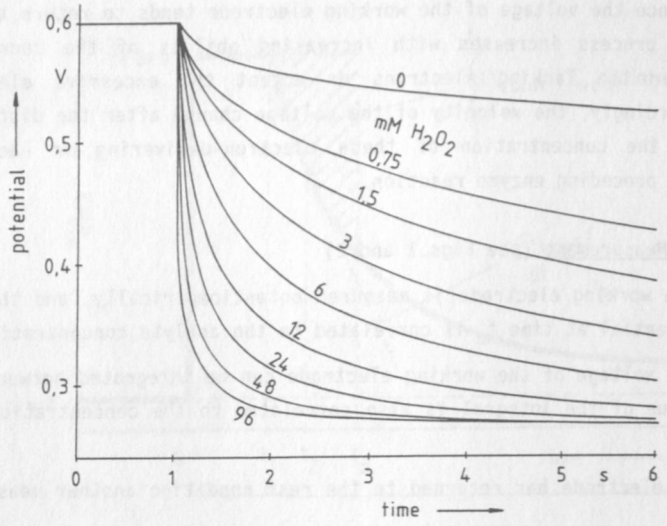

Fig. 3

Potential relaxation curves for measurement of H_2O_2 concentrations. Pt electrode covered with a cellulose membrane. Phosphate buffer 0,1 M; pH = 7. 37 °C. Excitation: + 0,6 V; 1 s. Ag/AgCl reference electrode

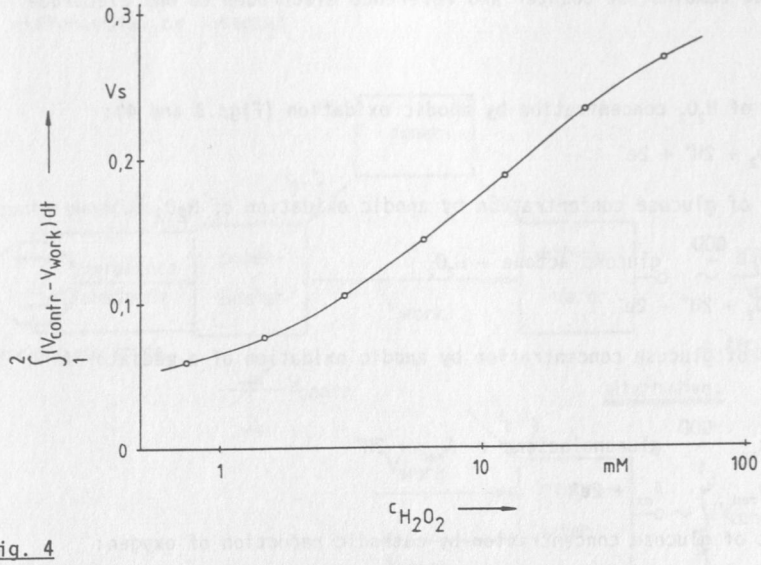

Fig. 4

Integral evaluation of the curves shown in Fig. 3