

An Oxygen Sensor Composed of Tightly Stacked
Membrane/Electrode/Electrolyte

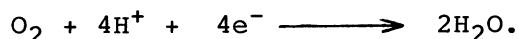
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A new type amperometric oxygen sensor operating at room temperature is constructed using Nafion, porous platinum cathode directly deposited on Nafion, and a polyethylene film covering the cathode surface directly. An oxygen reduction current is limited by oxygen diffusion rate through the diffusion-limiting polyethylene film and it changes in proportion to oxygen concentration of gases up to 100%.

Recently, many different types of electrochemical oxygen sensors, such as solid electrolyte type ones and Clark type ones, have been developed. YSZ and CSZ, which exhibit fairly high oxygen-ion conductivity at the elevated temperature, are utilized for the electrolytes of solid state oxygen sensors. However, these oxygen sensors are limited to the use only at the temperature higher than ca. 400°C^{1,2)} except for a few sensors which are lately reported to be able to operate at room temperature.^{3,4)} Oxygen dissolved in aqueous solutions and gaseous oxygen at room temperature are usually determined by Clark type oxygen sensors. Clark type and modified Clark type oxygen sensors are used also as a component of bio-sensors; Different kinds of enzyme are, for example, immobilized on the diffusion-limiting membrane of the Clark type oxygen sensor. Further more, applications of the Clark type oxygen sensor become increasing more and more. The Clark type oxygen sensor, however, has some weak points; e.g. difficulties in miniaturization and stabilities under conditions where the pressure may change. These difficulties originate from its principle that the sensor contains a liquid layer between a cathode and a polymer film through which

the gas to be detected permeates. Previously, we reported that oxygen was reduced on SPE (Solid Polymer Electrolyte) composite electrode which was prepared by electroless deposition of porous platinum electrode on Nafion, (Pt-Nafion) via a 4 electron process.⁵⁾



In this communication we propose a new type amperometric oxygen sensor operating at room temperature which is composed of SPE composite electrodes. The structural model of this new type sensor is schematically described in Fig.1. An oxygen permeable polymer film covers on the porous cathode (sensing electrode) which is bound on the surface of the Nafion. Nafion behaves as both an electrolyte and a support for the sensing electrode.

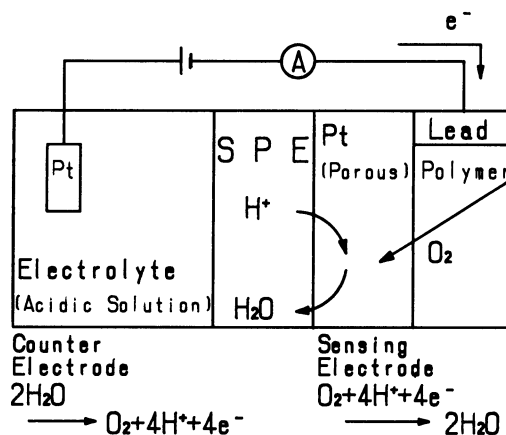


Fig.1. A Principle of the oxygen sensor structured with tightly stacked film/electrode/electrolyte.

A counter electrode is set either on the Nafion (not shown) or in the electrolyte solution contacting the Nafion (Fig.1). In the latter case, the above reaction can be forced to proceed potentiostatically. In this communication, the latter case was investigated. Oxygen in test fluids permeates through the polymer layer and reaches the sensing electrode bound on the Nafion which is set at the potential at which oxygen is reduced rapidly following the above equation. If the oxygen is reduced under diffusion limiting conditions through the polymer layer as in the case of Clark type sensors, the current will be proportional to the oxygen content in the test fluid. In comparison with a Clark type sensor, no solution is required to exist between a sensing electrode and a gas-permeable membrane. This structure enhances the stability and reliability of

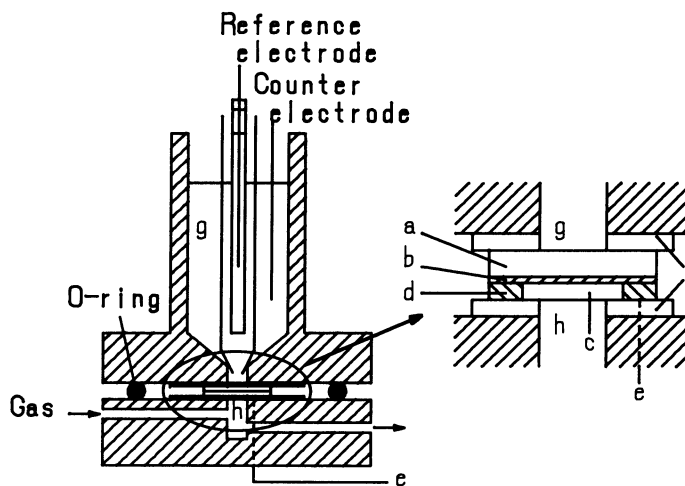


Fig.2. A schematic diagram of an oxygen sensor.
a) SPE b) Sensing electrode c) PE-film
d) Au-ring e) Au lead f) Packing
g) Electrolyte h) Gas compartment

the sensor⁶⁾ and enable its miniaturization.

In the present work, a sensor having 3 electrodes were prepared (Fig.2). Perfluorosulfonate cation-exchange membrane, Nafion 117, was used as an SPE material. A porous platinum sensing electrode was deposited directly on the Nafion surface (Pt-Nafion) by the method previously reported.⁷⁾ Polyethylene(PE) film (10 μm thick) was chosen as an oxygen permeable membrane and it was directly bound on the sensing electrode by hot-pressing (PE-Pt-Nafion).

A Scanning Electron Micrograph of Fig.3 shows that the PE film covers and contacts well with the rough surface of the porous cathode and that its thickness is fairly uniform. An outer surface of the PE-film is smooth and no pinhole is observed. The thickness of the polymer layer was controlled by changing the numbers of PE-films. A PE-Pt-Nafion was mounted in the cell. The bare Nafion surface of this composite electrode faced against a liquid electrolyte in which a counter electrode (platinum wire) and a reference electrode Ag/AgCl were immersed. As 1mol dm^{-3} sulfuric acid was used as an electrolyte, oxidation of water proceeds on the counter electrode. Test gases containing oxygen were introduced into a gas compartment of the cell at $1.7\text{ cm}^3\text{ s}^{-1}$. For comparison, Pt-Nafion which was not covered with PE on its electrode surface was also examined. Polarization curves were obtained by a cyclic voltammetry method at the scanning rate of 5 mV s^{-1} both on PE-Pt-Nafion and on Pt-Nafion using the cell of Fig.2.

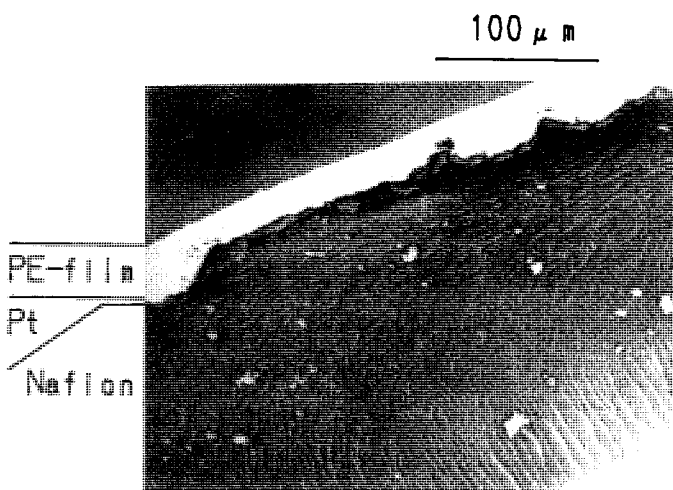


Fig.3. SEM photograph of the cross-section of the oxygen sensor.

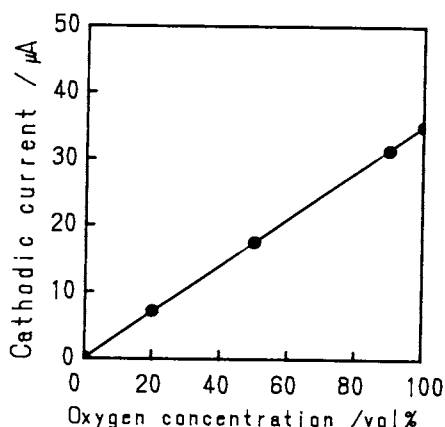


Fig.4. Linear relationship between cathodic current and oxygen concentration. (200 mV vs. Ag/AgCl)

It was revealed that the oxygen reaching the porous Pt electrode is reduced at the potential ranging from 0 to 250 mV under mass transfer limiting conditions on PE-Pt-Nafion.

The thickness of coating PE layer was changed between 10 and 50 μm . On the other hand, on Pt-Nafion any clear limiting current was not observed. These facts mean that the PE layer on the porous platinum electrode behaves as a diffusion-limiting layer. The dependency of the oxygen reduction current density on the oxygen content was examined changing the content from 0 to 100%. As shown in Fig.4, the current increased proportionally to the oxygen concentration in the whole examined range where the potential of the sensing electrode was set at 200 mV. The background current measured in argon was less than 2% of the current at 100% oxygen concentration. The response time was preliminary examined by changing stepwise the gas composition from argon to 100% oxygen. A 90% transient time for PE layer of 40 μm thickness was ca. 20 s and for 20 μm thickness was ca. 5 s. These values were in agreement with the theoretical value estimated from the PE layer thickness and the reported value of diffusion coefficient of oxygen through polyethylene.⁸⁾

From the above results it is concluded that PE-Pt-Nafion behaves as an amperometric type oxygen sensor and the current is in proportion to the oxygen content. This types of the sensor is expected to be miniaturized and to be used as a base component of many types of enzyme sensors.

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