is coated with a layer of iridium oxide by sputtering. This electrode can be used in solutions where conventional pH electrodes tend to dissolve—such as a solution of hydrofluoric acid.

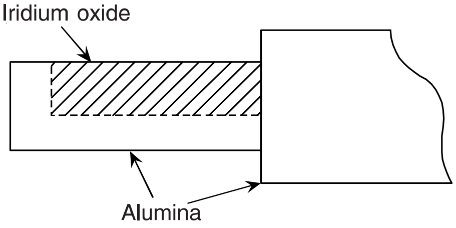

Fig. 6.13 The solid state electrode.

Molecular selective electrodes

Molecular selective electrodes have been developed for sensing concentration of certain molecular constituents in samples such as HCN, CO_2, glucose, urea, and so on. The two types of molecular selective electrodes are now briefly described.

Gas sensing electrodes: Gas sensing electrode is basically a measuring cell in which there is a reference electrode immersed in an internal solution which is held by a thin gas-permeable membrane and also there is a standard (Ag/AgCl usually) reference electrode as shown in Fig. 6.14.

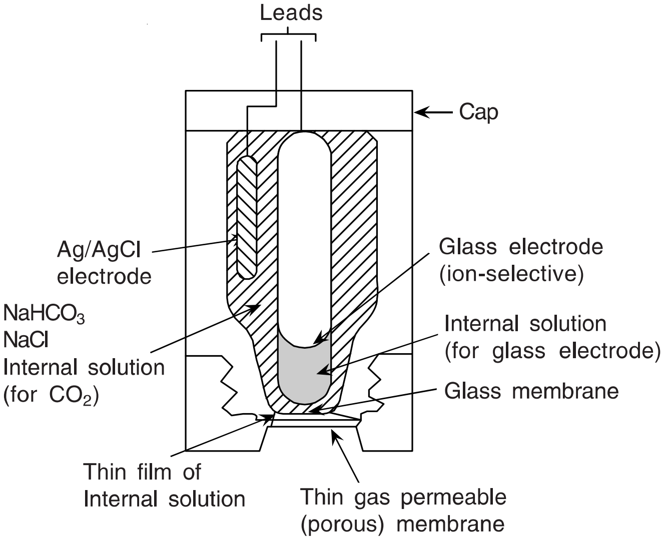

Fig. 6.14 Gas-sensing electrode.

A thin gas-permeable membrane separates the analyte solution from an internal solution; for CO_2 sensing, this is $NaHCO_3$ and NaCl. A pH-sensitive glass electrode is arranged so that a thin film of the internal solution is held between the gas-permeable membrane and the glass membrane. The reference electrode of Ag/AgCl is also placed in the internal solution. The pH of the film of liquid adjacent to glass electrode can be used to measure the gas content of the analyte. The gas passes on to the thin film of the internal solution and acts reversibly with it to form an ion to which the ion-selective electrode (the glass electrode here) responds. The activity of the ion in the thin film is proportional to the gas dissolved in the analyte and hence, the electrode response is directly related to the activity of the gas in the sample.

The gases, that are detected usually, are CO_2, SO_2, NH_3, and are detected by gas sensing electrodes based on the pH adjustment of the internal solution for equilibrium. The relevant equations are

$$NH_3 + H_2O = NH_4^+ + OH^- \tag{6.36a}$$

$$SO_2 + H_2O = HSO_3^- + H^+ \tag{6.36b}$$

$$CO_2 + H_2O = HCO_3^- + H^+ \tag{6.36c}$$

The pH indicated becomes a measure of the gas concentration.

The internal solution for SO_2 would be sodium hydrogen sulphite; for NH_3, it would be ammonium chloride solution. The stage-wise transfer, before the reactions given by Eqs. (6.36), is represented as

$$\underset{\text{analyte}}{CO_2(aq)} \rightleftharpoons \underset{\text{membrane pores}}{CO_2(g)}$$

$$\underset{\text{membrane pores}}{CO_2(g)} \rightleftharpoons \underset{\text{internal solution}}{CO_2(aq)} \tag{6.37}$$

The equilibrium constant K_e for the reaction Eq. (6.36c) is given by

$$K_e = \frac{[H^+][HCO_3^-]}{[CO_2(aq)]_{\text{analyte}}} \tag{6.38}$$

When concentration of HCO_3^- in the internal solution is high enough to be affected by the CO_2 from the sample, then one can write

$$K_n = \frac{K_e}{[HCO_3^-]}\,\frac{[H^+]}{[CO_2(aq)]_{\text{analyte}}} \tag{6.39a}$$

giving the hydrogen ion concentration in the internal solution due to CO_2 permeance in it as

$$[H^+] = K_n[CO_2(aq)]_{\text{analyte}} \tag{6.39b}$$

Hence, the voltage measured by the cell is

$$\begin{aligned} E &= E^0 - 0.0591\ \log\{K_n[CO_2(aq)]_{\text{analyte}}\} \\ &= E_0' - 0.0591\ \log\{[CO_2(aq)]_{\text{analyte}}\} \end{aligned} \tag{6.40}$$

There are two types of membrane materials—microporous and homogeneous. The former is made from hydrophobic polymers such as polypropylene or polytetrafluorethylene with 70% porosity, each pore having a diameter of about 10^{-6} m and thickness 0.1 mm. Gases pass through these membranes by the process of effusion. In homogeneous membranes, the analyte gas dissolves, then diffuses through and finally desolvates in the internal solution. A common membrane material of this category is silicone rubber. Its thickness is required to be less for the whole process of gas transfer to be faster. A thickness of 0.01–0.03 mm is quite common.

Different sensing electrodes, other than pH are used for different gases. Their selectivity would depend on the internal ion-sensing electrode (ISE), the internal solution, and the type of membrane. The other gases that can be assayed are H_2S, HCN, HF, NO_2, Cl and so on with ISE's made of Ag_2S, Ag_2S–LaF_3, immobilized ion exchange type, Ag_2S–AgCl respectively.

Biomembrane or enzyme electrodes: Enzymes are highly selective biochemical substances often used as catalysts. Enzyme is selective in the sense that it catalyzes only a small number of reactions. An electrode that has a membrane coated with an enzyme containing acrylamide gel can act as an ion-selective electrode. The enzyme catalyzed reaction of the analyte with this electrode is monitored by another internal ion-selective electrode. Thus, a couple of ion-selective electrodes, as stated, can make the electrode sensing system highly selective and free from interferences.

The gel and enzyme are held on the membrane surface by an inert physical support, even cellophane or nylon-gauge may be used for the purpose. Immobilization can also be done by other means such as physical absorption in a porous inorganic support like alumina, covalent bonding of the enzyme to glass beads or polymers or copolymerization of the enzyme with a monomer. These electrodes are often termed as *enzyme reactor electrodes.*

A case of enzyme electrode can be explained with urea-selective electrode. The membrane, that is, an ammonia-sensitive glass electrode is coated with acrylamide gel and urease (enzyme). The electrode when dipped in a solution containing urea, produces a reaction

$$\underset{\text{urea}}{CO(NH_2)_2} + H_2O \xrightarrow{\text{urease}} 2NH_4^+ + CO_2 \tag{6.41}$$

NH_4^+-selective electrode measures NH_4^+. Prior calibration of the electrode system is, however, necessary.

Biological electrode is a sort of enzyme electrode that uses living bacteria which excrete the enzymes in use. They can be replenished by proper nutritional treatment so that the bacteria may live on.

The ion-selective principle can be adopted in field-effect transistors to make ion-selective FET, ISFET which forms a class of ion-selective electrode. It is made by coating or depositing the ion-selective membrane on the gate of the FET. The membrane may be AgBr or a neutral carrier in PVC matrix. Prior to coating, a polyimide mesh is placed over the gate for retention of the matrix.

The analyte in contact with the membrane partially determines the potential of the membrane because of the activity of the analyte. This potential, as usual, determines the drain current in FET's. An ion-selective membrane adapted in an FET, that is, an ISFET is depicted in Fig. 6.15.

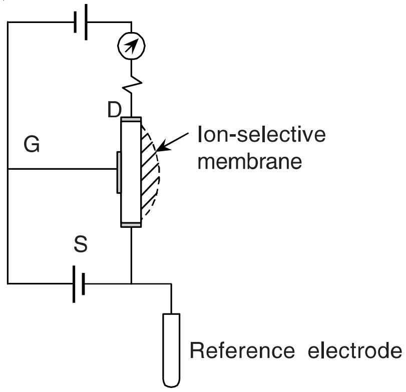

Fig. 6.15 The ion-selective membrane adapted in an FET.

6.8.3 Temperature Sensing Electrodes

The cell potential or electrode potential is highly dependent on temperature. Nernst equation includes the *T* and the value 0.0591 as in Eq. (6.12) is obtained for a temperature 25°C. This only prompts one to think that temperature could be measured using Eq. (6.8) when $E_c \propto T$.

In fact, in recent times a technique has been suggested for measurement of temperature using an internal reference electrode made of commercial variety of iron that consists of Mn(0.68), C(0.5), Si(0.19), Cr(0.18), Cu(0.13), Ni(0.07), P(0.024), and S(0.003). The internal reference solution is a solution of 0.5 M HPO_3, 0.1 M H_2O_2. The electrode is rod-shaped, the tip being kept open, the rest covered with a teflon sleeve. The scheme of sensing is shown in Fig. 6.16. The output voltage V_o shows a self-oscillating phenomenon with magnitude and period varying with temperature as shown in Fig. 6.17. This existence of oscillation is interpreted as a potential change associated with growth and dissolution of the passive film formed during anodic and cathodic reactions given respectively by

$$\text{Fe} \rightarrow \text{Fe}^{++} + 2\text{e} \tag{6.42a}$$

and

$$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O \tag{6.42b}$$

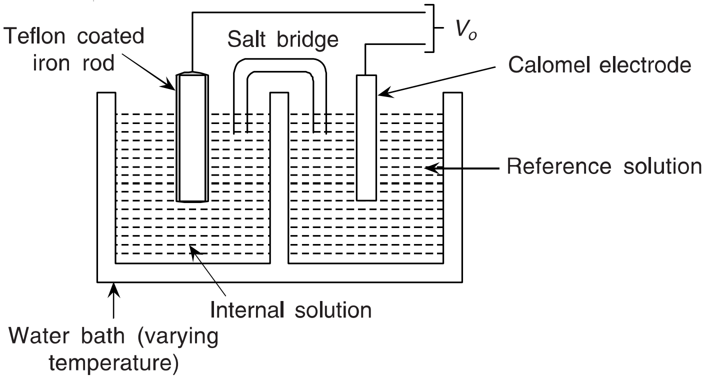

Fig. 6.16 Scheme of a cell for temperature sensing.

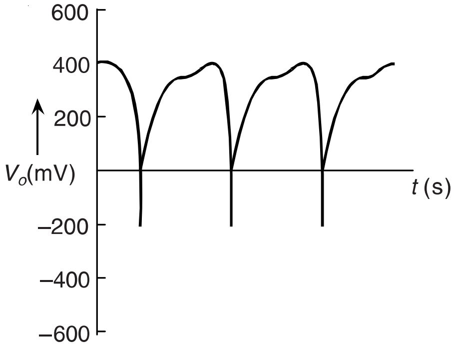

Fig. 6.17 Output waveform of the cell of Fig. 6.16.