

Electrochemical sensors

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Electrochemical sensors developed in the context of India's fast breeder reactor technology programme include sensors for hydrogen, oxygen and carbon, which must operate in liquid sodium at high temperatures, as well as gas-phase sensors. There are also applications in basic research.

AN intelligent processing industry requires sensors to monitor changes in process streams, or in the environment, to effect modifications to the process in a timely manner with a view to increasing efficiency, minimizing wastage, improving product quality and controlling the discharge of pollutants into the environment^{1,2}. For example, in steel making, optimum deoxidation control can be effected, while the steel is still in the molten state, on the basis of feedback from oxygen measurement using a sensor inserted into the converter. This results in improved quality and lower rejection rate. Similar deoxidation control is possible in aluminium making and copper refining. In general, oxygen sensors would be invaluable to most pyrometallurgical processes in which a metal is refined from its ores by selective oxidation and reduction. Exact control of both temperature and oxygen potential is important in such processes. On-line oxygen analysis in waste gases of boilers can be used for controlling the feeding rate of oil and air for optimal combustion. Similarly, air/fuel ratio in gasoline engines can be controlled to minimize NO_x emission and maximize the efficiency of fuel utilization, on the basis of feedback from an oxygen sensor in the exhaust gas line. In a heat treatment furnace the oxygen level has to be monitored to avoid oxidation of the metal. Semiconductor industry also demands oxygen control through continuous monitoring. Sensors are also required to monitor the levels of pollutants such as H₂S, SO_x and NO_x in the atmosphere. While control instrumentation is well developed and commercially available, sensor development has been lagging behind. Recent trends, however, suggest that the scientific community is paying increasing attention to sensor technology.

In the context of the fast breeder reactor development programme, which is the *raison d'être* of the Indira Gandhi Centre for Atomic Research (IGCAR), sensors are required to continuously monitor impurities such as hydrogen, carbon and oxygen in liquid sodium which is used as the heat-transport medium. In a fast breeder reactor, the nuclear heat which is generated in the reactor core is transported by liquid sodium to the intermediate heat exchanger in a closed loop that is referred to as the primary sodium loop. The sodium in

the secondary loop transports the heat from the intermediate heat exchanger to the steam generator where steam is raised for driving the turbine. In the steam generator liquid sodium at a few bar pressure is separated from water or steam at a pressure of more than 150 bar by the walls of the steam generator tubes. In the event of a leak developing in these tubes, water (or steam) at high pressure gets injected into sodium, leading to the formation of sodium hydride (and sodium oxide) or sodium hydroxide depending upon the prevailing temperature. Sensors are required to detect this steam ingress into liquid sodium at the very inception of the leak, so that corrective action can be taken before the leak develops further. Ingress of air or moisture into the sodium circuits would result in an increase of oxygen concentration and this can be measured by an appropriate oxygen sensor. Similarly, a carbon sensor would be useful in monitoring the carbon activity in molten sodium. This is important from the point of view of carbon transport through the medium of liquid sodium. As the solubility of carbon in sodium depends strongly on temperature, carbon activity is also highly temperature-dependent. This results in low carbon activity in sodium in the high temperature regions of the sodium circuit, where the structural material can lose carbon and high carbon activity in sodium in the low temperature region, where the structural material takes up carbon from sodium. As both carburization and decarburization are harmful to the material, it is essential to maintain the carbon activity at an appropriate level. This demands an on-line monitoring system.

All sodium systems, including the fast breeder reactor, have a blanket of cover gas which is usually argon. By monitoring the cover gas one learns a good deal about the sodium system. For this purpose, gas phase sensors are required.

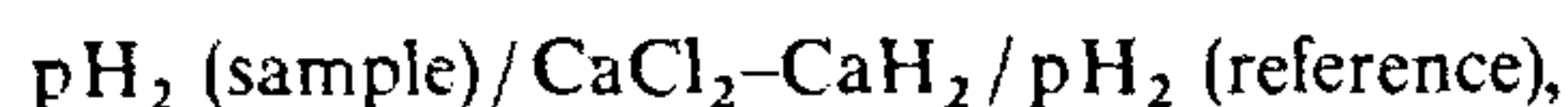
In this article, I summarize the work done in our laboratory on the development of sensors for use in liquid sodium as well as the cover gas, and bring out some of the applications of these devices in basic studies in thermochemistry. In this article, the term sensor refers to the sensing device while the term meter includes the measuring system as well. Occasionally, however, these terms may be interchangeably used for convenience.

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Sensors for use in liquid alkali metals

Hydrogen sensor

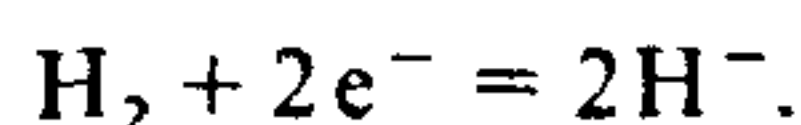
The electrochemical hydrogen sensor developed in our laboratory consists of a hydrogen concentration cell wherein two electrode compartments are separated by a hydride-ion conducting solid electrolyte. Sodium containing dissolved hydrogen constitutes one electrode of the concentration cell while the other (reference) electrode establishes a well-defined hydrogen partial pressure. The cell can be represented as



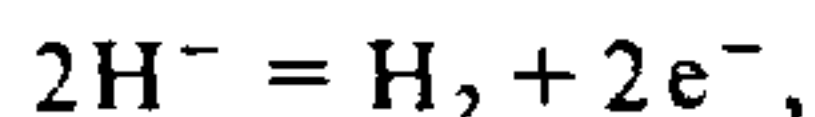
where pH_2 represents the hydrogen partial pressure.

When $pH_2 \text{ (reference)} > pH_2 \text{ (sample)}$, the electrode reaction can be written as

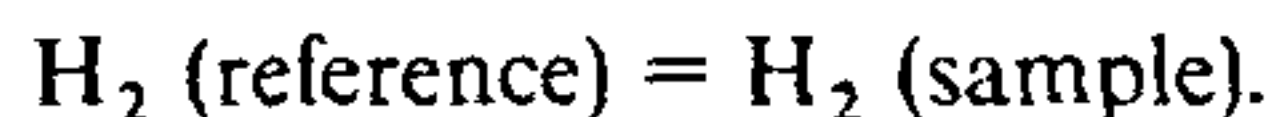
At the reference electrode



At the sample electrode



and the net reaction as



Solid CaCl_2 containing 5–7.5 mol% CaH_2 was chosen as the electrolyte based on the observation of Smith³ that it conducts by hydride ions and is suitable for use in sodium systems.

The $\text{CaCl}_2\text{--CaH}_2$ electrolyte must be contained in a thin-walled iron membrane, usually in the form of a cup, for the following reasons: (i) The electrolyte would be attacked by liquid sodium at the operating temperatures, leading to the formation of NaCl and free calcium metal. (ii) The mechanical properties of the electrolyte material do not allow its fabrication and use in the form of a tube.

Li/LiH mixture is chosen as the reference electrode as it has the right hydrogen potential. This is also contained in a thin-walled iron cup which dips into the electrolyte. The outer membrane, containing the electrolyte, is immersed in liquid sodium which is the sample electrode. Thus the inner membrane attains the equilibrium hydrogen potential of the reference electrode and the outer membrane that of liquid sodium at the temperature of operation. The electromotive force (EMF) of such a cell can be given as

$$E = (RT/nF) \ln [pH_2 \text{ (ref)}/pH_2 \text{ (sample)}],$$

where E is EMF in volts, R the gas constant, F the Faraday constant, T the temperature (K), and $n=2$.

Hydrogen concentration in sodium, $[H]_{\text{Na}}$ is related to the equilibrium hydrogen pressure $[pH_2]$ by

Sievert's Law

$$[H]_{\text{Na}} = K pH_2^{1/2},$$

where K is the Sievert's constant [$\text{ppm} \cdot \text{Pa}^{-1/2}$] when pH_2 is in pascals (Pa) and $[H]_{\text{Na}}$ is in parts per million. Thus the hydrogen concentration in sodium can be obtained from the measured EMF

$$E = (RT/2F) [\ln pH_2 \text{ (ref)} - 2 \ln [H]_{\text{Na}} + 2 \ln K].$$

A schematic diagram of electrochemical hydrogen sensor is shown in Figure 1. The details of construction and assembling the various constituents of the sensor are described elsewhere⁴. EMF is measured using a high impedance millivolt meter. These hydrogen sensors were tested in small laboratory-scale sodium loops to evaluate their performance. A typical bench-top sodium loop of this type is shown in Figure 2. It has a vertical limb consisting of two sodium pots, and a cold trap, and a side limb which enables the continuous circulation of sodium. The upper sodium pot is provided with a knife-edged flange outside the insulated zone, so that the sensor can be inserted into the sodium and sealed with a copper gasket at the flange. The side limb is provided with a DC electromagnetic pump based on a permanent magnet, which pushes the sodium up and ensures its flow through the system in the clockwise

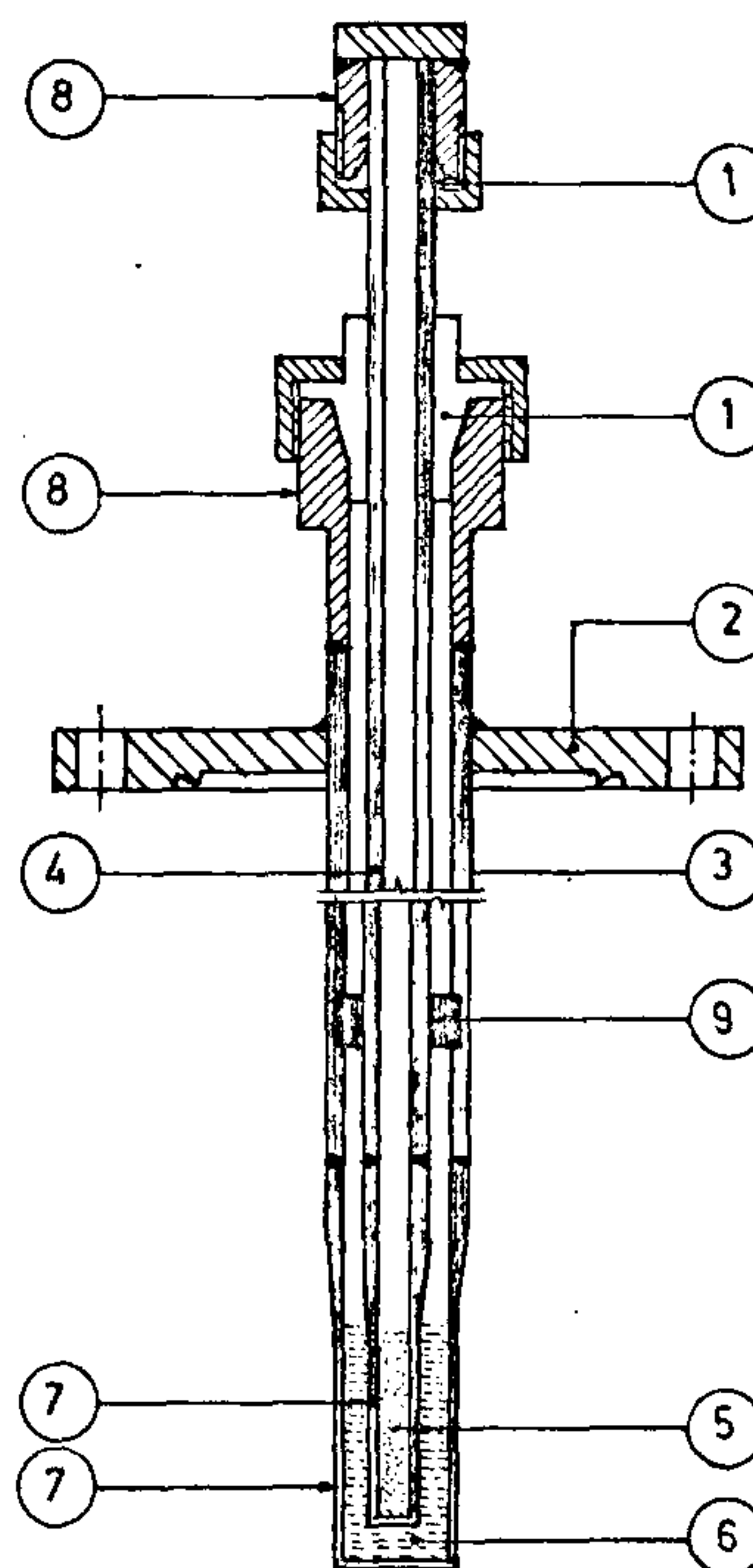


Figure 1. Electrochemical hydrogen sensor with $\text{CaCl}_2\text{--CaH}_2$ solid electrolyte. 1, Teflon ferrules; 2, knife-edged flange; 3, outer stainless steel tube; 4, inner stainless steel tube; 5, reference Li-LiH electrode; 6, $\text{CaCl}_2\text{--CaH}_2$ solid electrolyte; 7, thin-walled iron cups; 8, swagelok fittings.

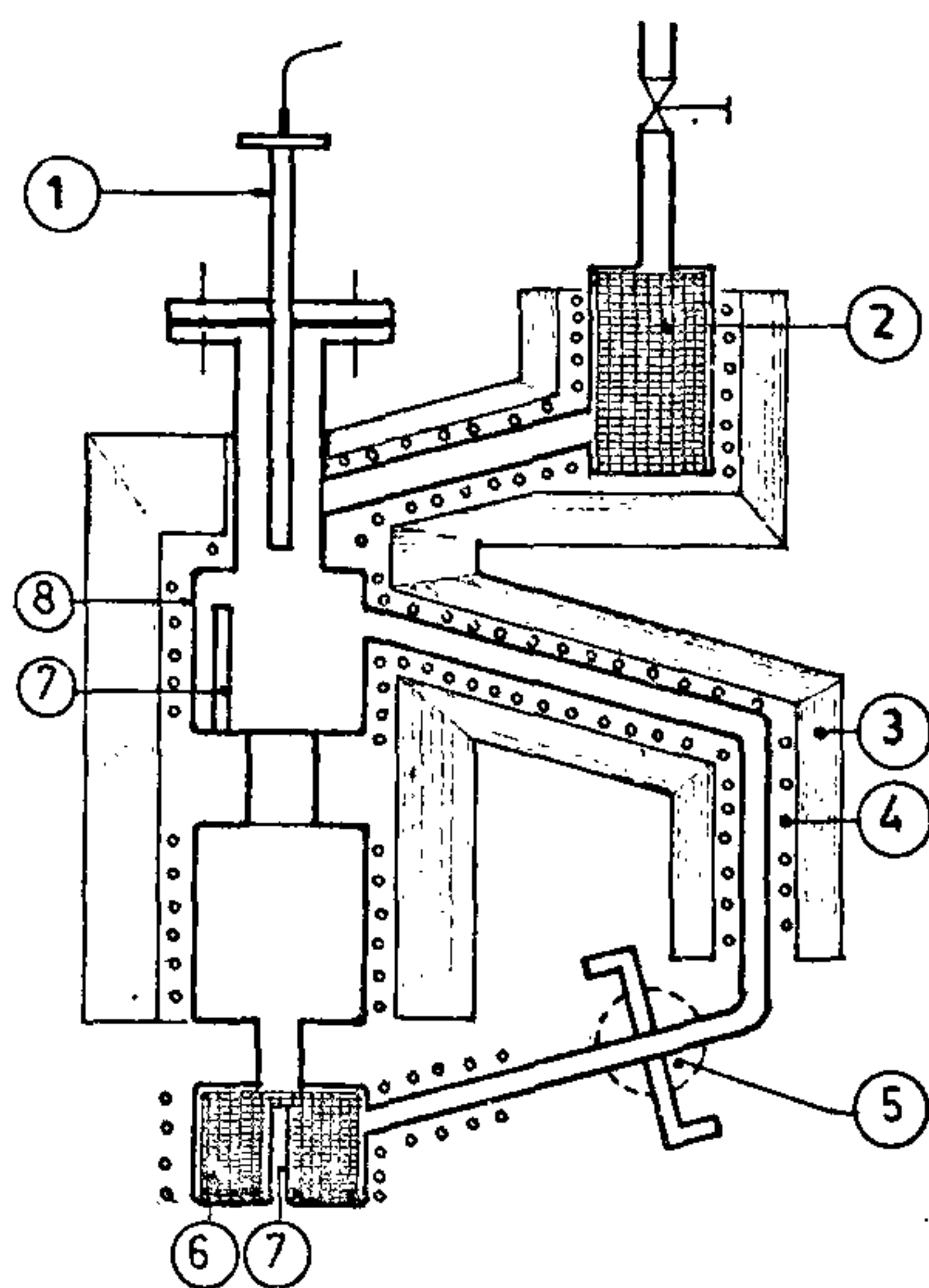


Figure 2. Schematic diagram of the bench-top sodium loop used for testing electrochemical hydrogen sensor. 1, Electrochemical hydrogen sensor; 2, stainless steel mesh packed vapour trap; 3, insulation material; 4, metal-sheathed heater; 5, permanent magnet with DC pump for circulation of sodium; 6, stainless steel mesh packed cold trap; 7, thermowells; 8, meter port.

direction. The cold trap (CT) fixes the hydrogen concentration in sodium to the saturation solubility at the cold point. Thus by varying the CT temperature the hydrogen concentration in sodium can be varied. The whole loop contains about 500 ml of sodium and operates continuously for long periods, thus making it possible to test the electrochemical sensors. The sodium temperature in the meter pot and in the cold trap is controlled independently to within ± 1 K.

Each sensor was tested in such loops for long periods. The sensor temperature was usually fixed at 723 K and the CT temperature was varied from 388 to 523 K, simulating the range of hydrogen concentrations likely to be encountered in the reactor. The lowest hydrogen level achieved was dictated by the characteristics of the loop. The response of a typical sensor is shown in Figure 3.

The hydrogen levels in sodium employed to test the sensors ranged from 47.5 ppb to 1.7 ppm. These values were deduced from the cold-trap temperatures in the loop using the solubility data for hydrogen in sodium as reported by Funada *et al.*⁵ The ± 1 K variation in sensor temperature would give rise to a variation of EMF equal to 1.41 mV if the hydrogen level is 100 ppb, whereas a variation of 10 ppb of hydrogen over the background level of 100 ppb would give rise to a 14.35 mV change in the sensor signal. At a background level of 50 ppb of hydrogen, a variation of 10 ppb would give rise to a 28.7 mV change in the sensor signal. These values are derived from theoretically

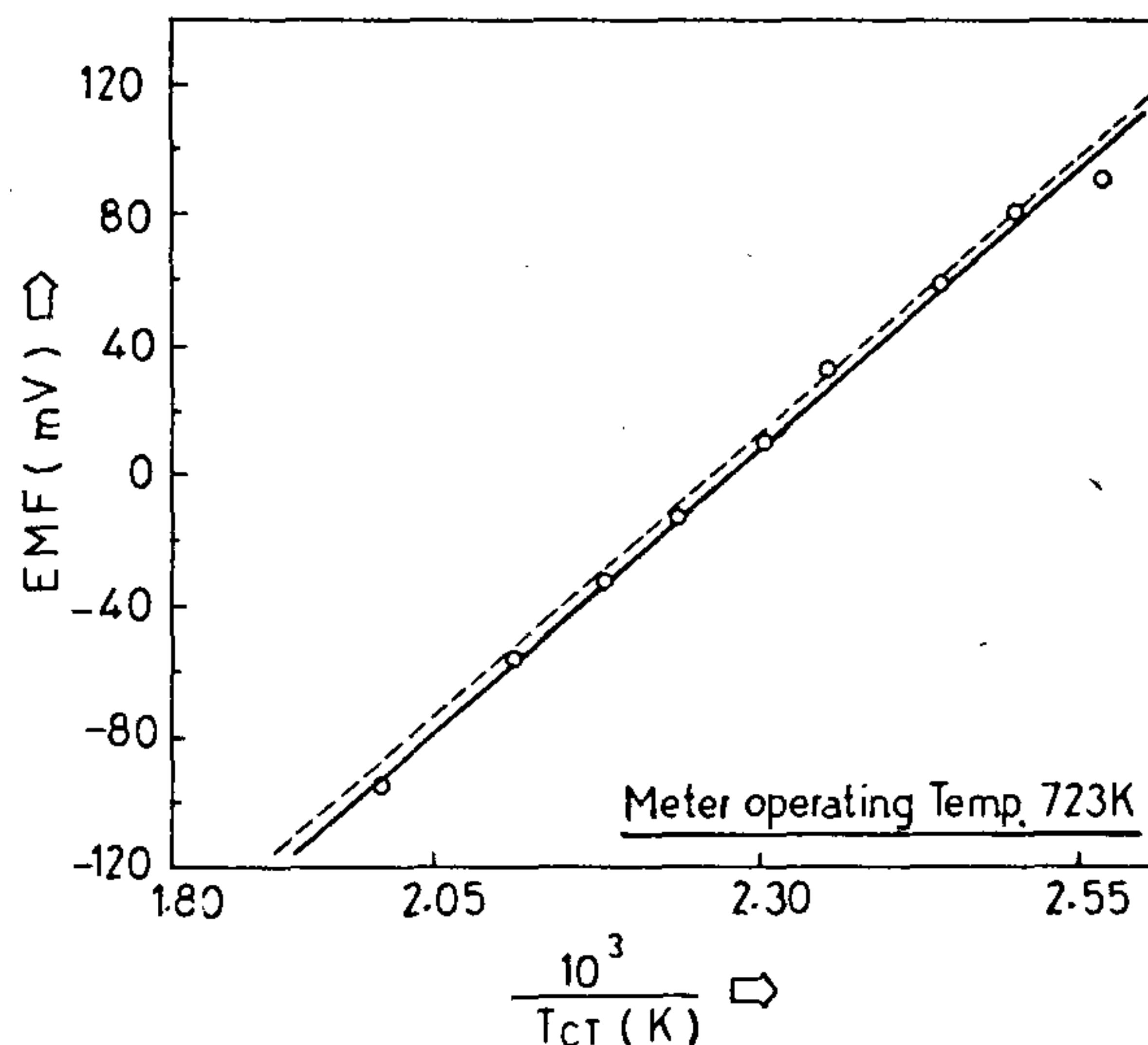


Figure 3. EMF from a typical electrochemical hydrogen sensor as a function of the cold trap temperature in the loop.

expected values calculated using the thermodynamic data on the Li-H system^{5a} and the Na-H system⁵. This sensitivity level is adequate for use in the sodium circuits of a liquid metal fast breeder reactor. For a given change in hydrogen concentration, the EMF changes more at lower values of hydrogen concentration, as is unique with electrochemical sensors. It is also seen from the experimental results that variation of the CaH_2 concentration in the electrolyte from 5 to 7.5 mol% does not lead to any change in the performance of the sensor. These electrochemical hydrogen sensors have been incorporated into the secondary loops of fast breeder test reactor (FBTR), where their performance has been found to be very good, and superior to the diffusion-type meters (originally provided on the basis of French knowhow). The new meters are also simpler, more reliable and much less expensive than the diffusion-type meter and, above all, totally indigenous.

Electrochemical carbon sensor

Since carbon can exist in liquid sodium in both dissolved and undissolved forms, the total carbon content does not represent the carburizing potential of sodium. Since the driving force for carburization is the chemical potential, it is important to measure the carbon potential of sodium. On-line measurement is preferred as the process of sampling itself can alter the carbon chemistry in sodium. Prior to the present work the only device that was developed to a level of testing in reactor circuits was the Harwell carbon meter⁶. The probe in the meter is a helically wound thin-walled iron

tube (6 mm diameter, 0.25 mm wall thickness) oxidized on the inside surface. The probe is kept immersed in sodium, and high purity argon gas is allowed to flow through the inside of the coil. Carbon diffusing through the iron tube from liquid sodium reacts with iron oxide on the inside surface, forming the oxides of carbon. These oxides of carbon are carried by the argon gas, converted into methane over a catalyst and estimated by a flame-ionization detector. The concentration of carbon in the carrier gas is related to the flux across the probe wall and the carbon activity (with which it is in equilibrium). The actual value is obtained by calibration. The detection and measuring systems are fairly complex.

As electrochemical sensors are much simpler to operate, efforts were made in our laboratory to develop electrochemical sensors. Here again, the principle is that of an electrode concentration cell which can be represented as

Reference electrode/electrolyte/sample electrode.

If a_C^R and a_C^{Na} represent the carbon activities of the reference and sodium (sample) electrodes respectively, then the EMF developed is given by

$$E = (RT/nF) \ln (a_C^R/a_C^{Na}),$$

The main problems relate to the choice of the electrolyte and the design of the reference electrode. Salzano *et al.*⁷ and Hobdell *et al.*^{7a} showed that a eutectic mixture of Na_2CO_3 and Li_2CO_3 in the molten state was a good electrolyte. Their carbon sensor, however, had a very short life on account of problems with the reference electrode. The sensor that was developed at IGCAR is also based on the molten carbonate electrolyte but has a long life and gives good performance for years⁸.

The details of the experimental assembly used in these studies are shown in Figure 4. It consists of a stainless steel vessel (50 mm diameter, 350 mm long) in which the sodium container is placed. The electrolyte is contained in an armco iron cup machined from a defect-free rod. The iron cup is welded to a 12-mm-diameter stainless steel tube. The reference electrode is positioned at the centre of the electrolyte and the two electrodes are coupled through a Conax fitting. A quartz tube is positioned in the annular space between the two electrodes to prevent direct contact between them. EMF is measured by a high impedance millivoltmeter connecting the two electrodes. The system is first heated to the required temperature using a resistance furnace controlled to ± 1 K. A stainless steel-sheathed chromel-alumel thermocouple is introduced into the system through a sliding seal. The thermocouple can be dipped into sodium to measure the temperature whenever required. This procedure is adopted to minimize the effect of the stainless steel sheath on the chemistry of

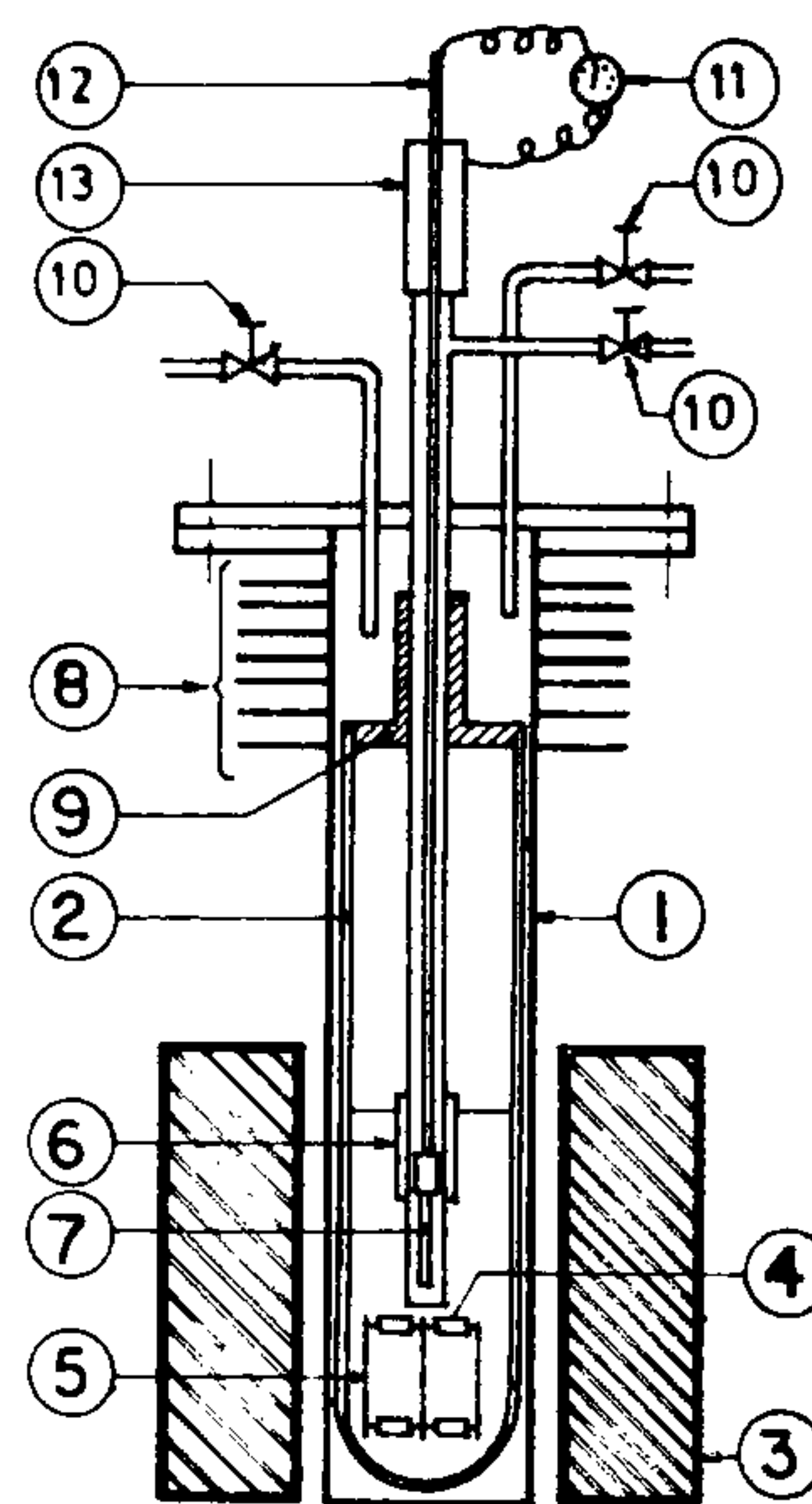


Figure 4. Schematic diagram of the electrochemical carbon sensor. 1, Metal vessel ss: 316; 2, alumina container; 3, furnace; 4, alumina bead spacer; 5, ss: 304 foil; 6, armco iron capsule; 7, nickel capsule containing graphite; 8, cooling fins; 9, sodium vapour trap; 10, diaphragm valve; 11, millivolt meter; 12, reference electrode; 13, Conax fitting. Item 5 is used in carbon potential measurements (ref. 20).

carbon in sodium. The reference electrode is a nickel capsule (3 mm dia, 50 mm long and 0.4 mm thick) filled with graphite powder. The capsule is equilibrated under inert atmosphere at 1173 K and then connected to a 3-mm-diameter stainless steel rod before positioning it in the centre of the iron cup containing the electrolyte.

Several such sensors have been built and tested in liquid sodium in static pots. The sodium used for this purpose was prepared by distillation to avoid undissolved carbon. The sensor was found to give Nernstian response. It was also tested by measuring the carbon activity of sodium which was simultaneously equilibrated with nickel foils. By retrieving the nickel foil and determining its carbon content, its carbon activity which should be the same as that of the sodium, is obtained. This agreed very well with the carbon activity measured by the sensor in its temperature range of operation [820 to 960 K].

Oxygen sensor

Since oxygen present in sodium enhances corrosion and activity transport in the sodium circuits of the reactor, it is important to control its level by on-line purification and continuous monitoring. Electrochemical sensors have been developed for this purpose based on the oxide-ion conducting solid electrolyte, yttria-

doped thoria (YDT)⁹. In/In₂O₃ is the preferred reference electrode while sodium containing dissolved oxygen forms the sample electrode. Thus the cell can be represented as



The cell output is dependent on the oxygen concentration in sodium according to the following equation

$$E/mV = A + BT + C \log [C_{\text{Na}}/C_{\text{Na}}^0],$$

where A, B and C are constants, C_{Na} is the concentration of oxygen in sodium, and the superscript 0 refers to saturation solubility at a temperature T . The sensor assembly is shown in Figure 5. The electrolyte is in the form of a high density tube. This is fitted to the sensor assembly using viton O rings. The cooling fins ensure that sodium remains frozen in this section and that the O-ring is at a low enough temperature. The 'Conoseal' joint makes a leak-tight connection to the sodium system such that the probe dips into sodium. The reference electrode is taken inside the YDT tube.

The choice of YDT as the electrolyte is based on its low lower electrolyte domain boundary (LEDB) which ensures that YDT remains an ionic conductor even at the very low oxygen potentials encountered in nuclear-grade sodium. However, these probes suffer from problems, viz. (i) sodium attack on electrolytes at high oxygen levels, (ii) high cost arising from difficulties in manufacture and (iii) unpredictable life ranging from a few hours to a few thousand hours.

In order to overcome the problems associated with YDT, particularly its non-availability, we reinvestigated the other commonly used oxide-ion conducting solid

electrolyte, viz. zirconia for use in these sensors. Calcia-stabilized zirconia (CSZ) was tried earlier by Steinmetz⁹ in 1965 but was given up owing to its electronic conductivity and susceptibility for sodium attack at the operating temperatures (~ 673 K) and even at low oxygen levels in sodium. When the electrolytic domain boundary of CSZ was remeasured in our laboratory, it was found that at low temperatures CSZ had better LEDB properties adequate for use with sodium. Moreover, the attack by sodium is expected to be less at low temperatures. Since the cell resistance would be high at low temperatures, a new low impedance reference electrode was designed and the cell thus developed can be represented as



The operating temperature of this sensor was optimized to get good cell resistance and minimum sodium attack. Figure 6 gives the construction of the cell. When this cell was tested in a sodium loop, the output was found to have a theoretical slope in the plot of EMF versus inverse cold trap temperature, indicating good performance of the electrolyte. The lifetimes achieved were about 3 to 6 months. However, these sensors showed an asymmetric potential arising out of the possible albeit slow reaction between sodium and zirconia. Since this varies from cell to cell, the meters requires independent calibration. In order to overcome this reaction, a strategy of stabilizing the electrolyte surface against sodium attack was resorted to by reacting the surface with calcia and converting it into calcium zirconate, which is stabler than the product of sodium attack, namely sodium zirconate. Since calcium zirconate is a line compound with good anionic mobility arising out of its perovskite structure it will not hinder potential

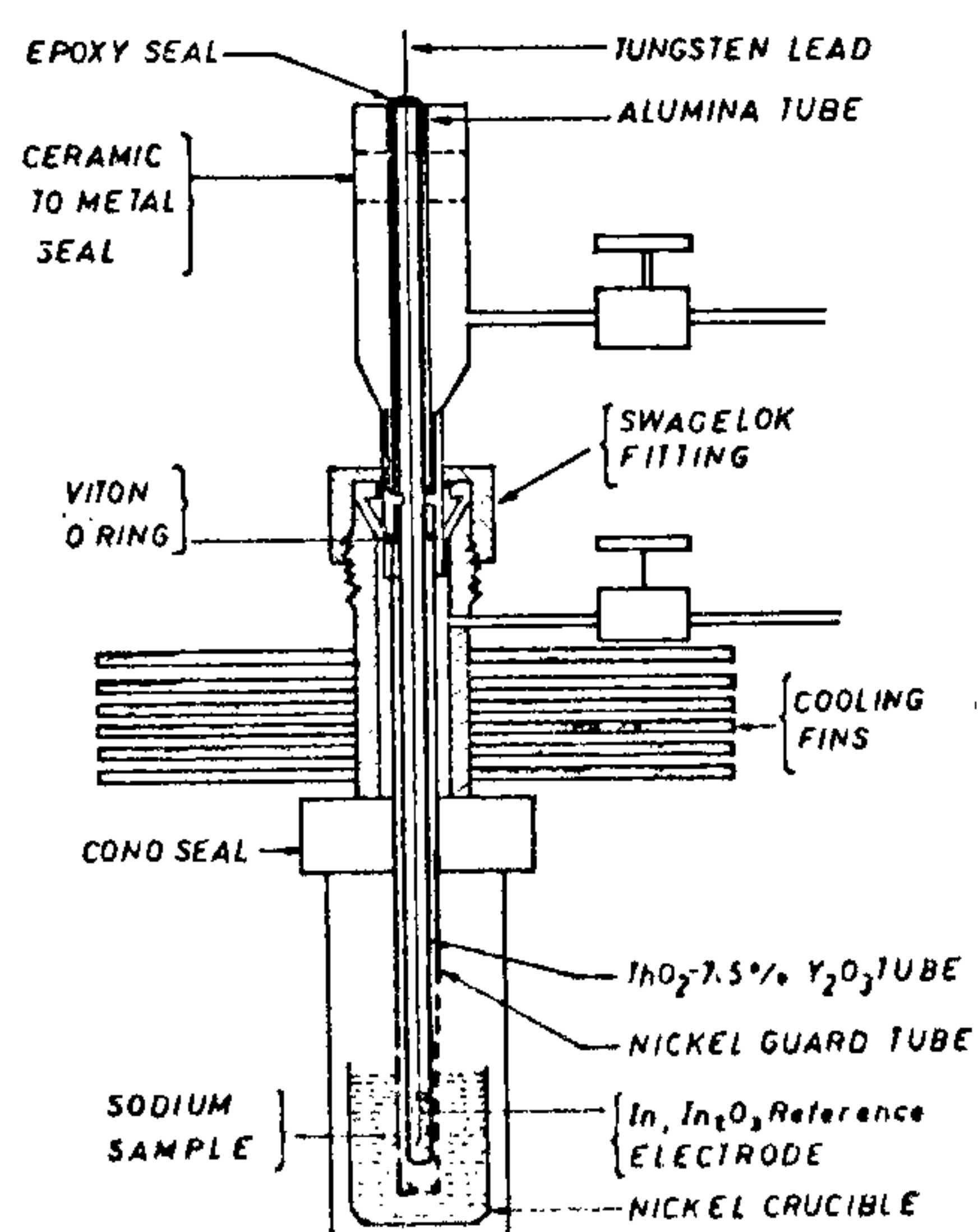


Figure 5. Schematic diagram of the electrochemical oxygen sensor with YDT as the solid electrolyte.

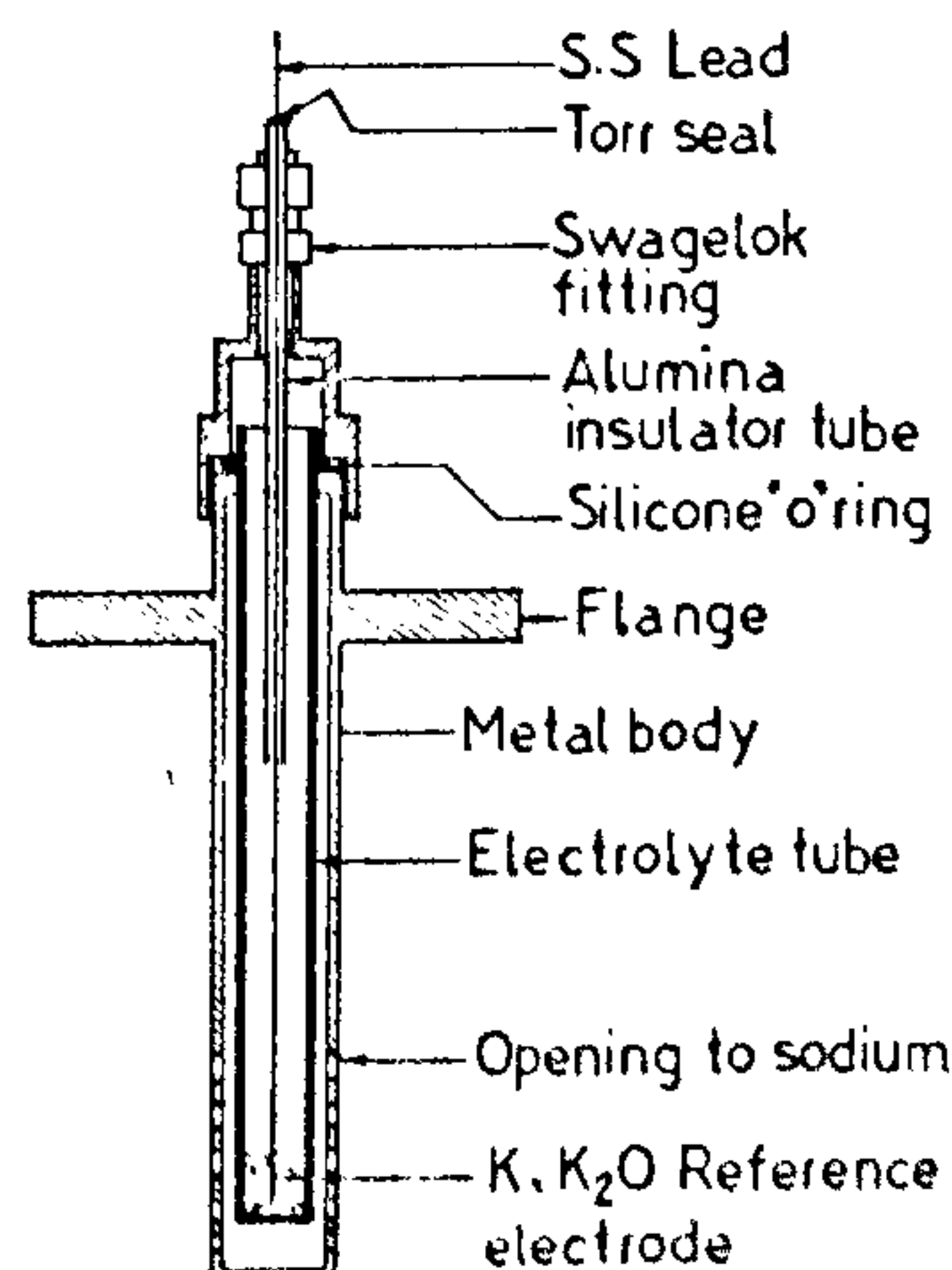


Figure 6. Electrochemical oxygen sensor with CSZ electrolyte and K, K₂O reference electrode.

development. Sensors constructed using this coated electrolyte, when tested, gave much better performance in terms of EMF scatter and electrolyte lifetime as evidenced in Figure 7. Thus a new inexpensive oxygen sensor has been developed for use in sodium circuits¹⁰.

Sensors for gases

Sensors for hydrogen in gases

The need of monitoring hydrogen in gas streams exists in various industrial processes. For instance, hydrogen evolution during electroplating can affect the quality of plating because of hydrogen entrainment in the metal substrate. Cathodic protection of structural steels employed in corrosive environment could lead to hydrogen evolution and result in hydrogen embrittlement of steel components. Sensors for hydrogen in gas streams capable of operating at ambient temperatures can be put to use for the control of process parameters in these processes. Electrochemical sensors using a new class of proton conductors such as hydrogen uranyl phosphate, $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ [HUP] and $\text{PVA-H}_3\text{PO}_4$ (ref. 11) are being developed in this regard.

In our laboratory we have constructed HUP-based sensors to measure hydrogen partial pressures in argon-gas streams of a diffusion-type hydrogen meter employed in sodium systems¹². A schematic diagram of the meter is shown in Figure 8. HUP-based sensors require both the reference and sample gas to be rich in moisture content. Dry gas streams would lead to the breakdown of the electrolyte and subsequent sensor failure. Need of moisture content has been overcome by encapsulating the electrolyte in a palladium membrane with a solid phase reference electrode¹³. These sensors have been shown to yield theoretical EMF down to

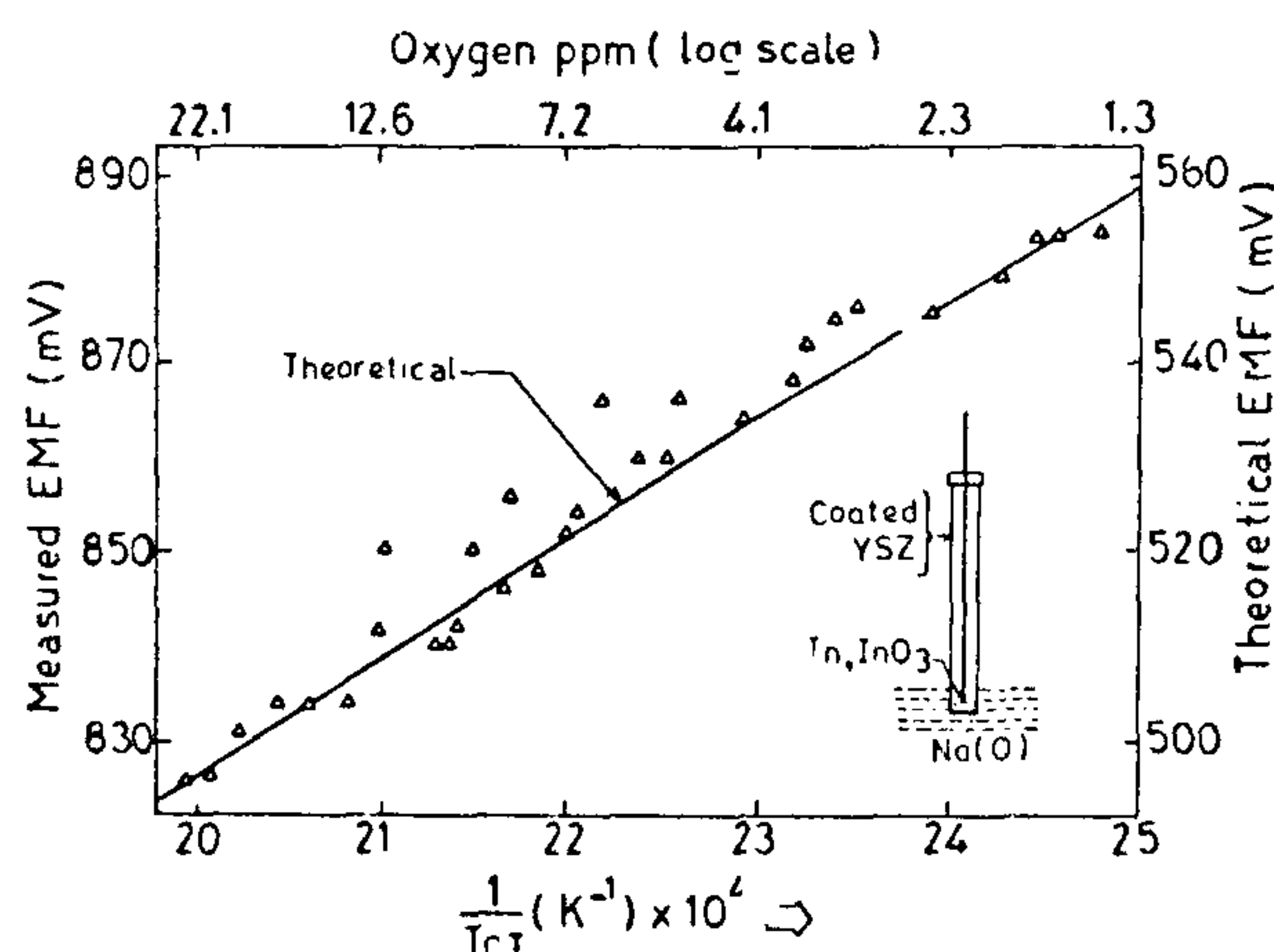


Figure 7. EMF output of electrochemical oxygen sensor with coated YSZ electrolyte.

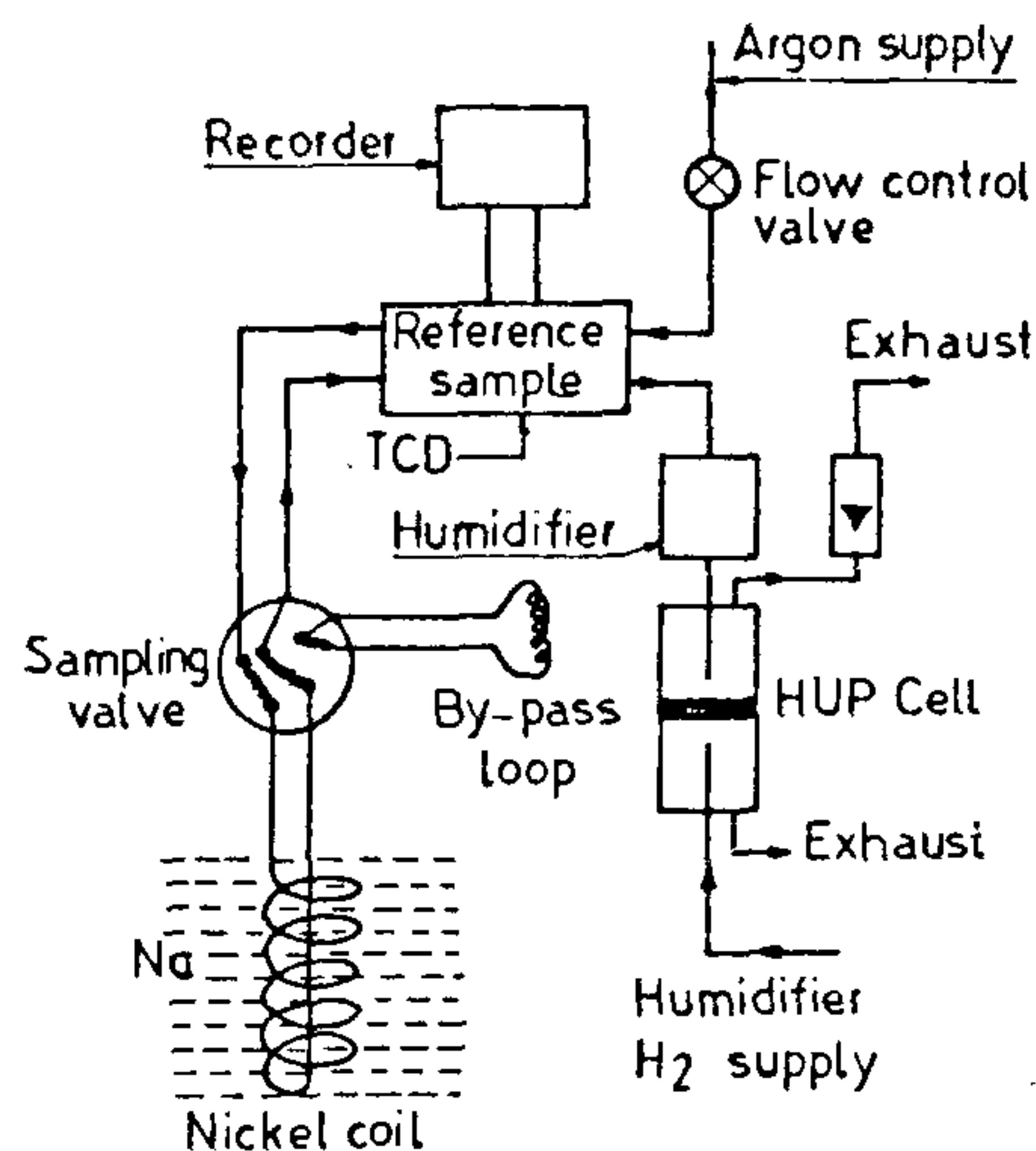


Figure 8. Schematic diagram of on-line hydrogen monitor with HUP-based hydrogen sensor.

0.6 ppm of hydrogen in sample gas streams. $\text{PVA-H}_3\text{PO}_4$ electrolyte supports proton conduction down to 233K and cells with this electrolyte were found to be capable of measuring hydrogen pressures in the range of 10^{-4} to 1 atmosphere. These cells were found to have fast response time, ~ 6 sec. Presence of CO (in greater than 1% concentration) as well as oxygen in gas streams has been found to affect the cell behaviour adversely.

Sensors for oxygen in gases

The most important industrial application of zirconia solid electrolytes is their use as oxygen sensors in gases. The EMF developed across the cell when the oxygen pressures are different on both sides of the electrolyte is given by the equation

$$E = (RT/4F) \ln (P_1/P_2),$$

where P_1 and P_2 are the oxygen pressures on sample and the reference compartments respectively. The most commonly used reference electrode is air for reasons of simplicity and temperature coefficient. Platinum is the most widely used electrode material. The cell can be represented as



The electrolyte can be in the form of a long tube or a pellet fused to a silica tube. In this sensor the cell potential gives the activity of oxygen adsorbed on the surface of the metal electrode which is in equilibrium with the gas phase immediately adjacent to the electrode. Electrode polarization becomes important at oxygen pressures less than 10^{-7} atmospheres and/or at temperatures below 773 K and this can introduce

deviations from theoretical outputs. This has limited the range of its use from 1 atmosphere to 10^{-7} atmospheres when the sample gas is not a buffered one.

The main application of this sensor is in combustion control in boiler and internal combustion engines. Since the oxygen potential of the exhaust or flue gas varies rapidly with air/fuel ratio, monitoring of the oxygen potential in this gas can be used for controlling air/fuel ratio and improving combustion. These oxygen sensors are also useful in the control of air/fuel ratio in lean-burn engines for automobiles where the air/fuel ratio is kept high (> 18) to get better efficiency of fuel usage and reduced emission of nitrogen oxides¹⁴. The typical design evolved for this purpose is shown in Figure 9. These sensors are quick in response (few seconds) and give good accuracy ($\pm 5\%$) for oxygen measurement in gases.

Since platinum has a tendency to form compounds with or chemisorb oxygen below 773 K and thus increase the electrode/electrolyte interfacial impedance, the above sensors have to be necessarily operated above 823 K. At such high temperatures the electrolyte gets aged after some period. The electrodes get sintered, leading to sluggish response. There are many advantages to be gained by reducing the operating temperature. Apart from smaller size owing to reduced heating requirements, low temperature sensors may also be used safely with explosive gases.

The electrode/electrolyte interfacial impedance increases significantly at low temperatures, leading to high cell resistance, thus limiting the temperature of operation. Use of low impedance electrodes will overcome this problem and make it possible to operate the cell at low temperatures. A new low impedance electrode, viz. RuO_2 was developed in our laboratory. Oxygen gauges were constructed using this as electrode

material and were tested for their performance by Nernst's law tests and Faraday's law tests. These tests showed that this sensor operates very well down to 483 K and this is the lowest temperature achieved with zirconia gauges so far. Techniques such as impedance spectroscopy and overpotential measurements were used to measure the interfacial impedance. From the activation energy for the cell resistance, the charge transfer step was identified as the rate-limiting step, unlike in the Pt electrode where surface diffusion to the triple-phase boundary is the rate-limiting step¹⁵. This RuO_2 /air electrode could also be used for thermodynamic measurements with liquid metals at low temperatures.

Sodium sensors

Sodium sensors based on β -alumina can be used to measure sodium in the liquid as well as the vapour phase. The former finds application in the aluminium industry where sodium content of aluminium has to be controlled for producing high-quality metal for structural and power transmission purposes. These sensors can also be used to measure the thermodynamic activity of sodium in alloys, thus providing important basic information in alloy thermodynamics. Measurement of sodium partial pressure in the vapour phase also has similar applications.

β -alumina is a complex sodium aluminate with an approximate formula $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$. It is a highly defective, non-stoichiometric compound that contains a large excess of sodium compared to its ideal formula. β -alumina is built up of spinel structure blocks with the formula $\text{Al}_{11}\text{O}_{16}$, which are separated by layers containing sodium ions. β -alumina is a closely related compound with the approximate formula $\text{Na}_2\text{O} \cdot 5.33\text{Al}_2\text{O}_3$ and it is even a better conductor of sodium ions. The layers between spinel blocks act as two-dimensional conducting planes for sodium ions. β -alumina has the higher ionic conductivity because the cation vacancies in its spinel blocks are compensated by extra sodium ions in the conduction plane.

The sodium sensors set up in our laboratory are based on β -alumina tubes made at the National Physical Laboratory, New Delhi. These tubes are sealed to α -alumina tubes using a glass seal. The reference electrode, taken in the electrolyte tube, is liquid sodium at low temperatures and sodium-silver or sodium-gold alloy at high temperatures.

Application of electrochemical sensors in basic studies

Basic information on chemical potentials and free energies of formation can be obtained from measure-

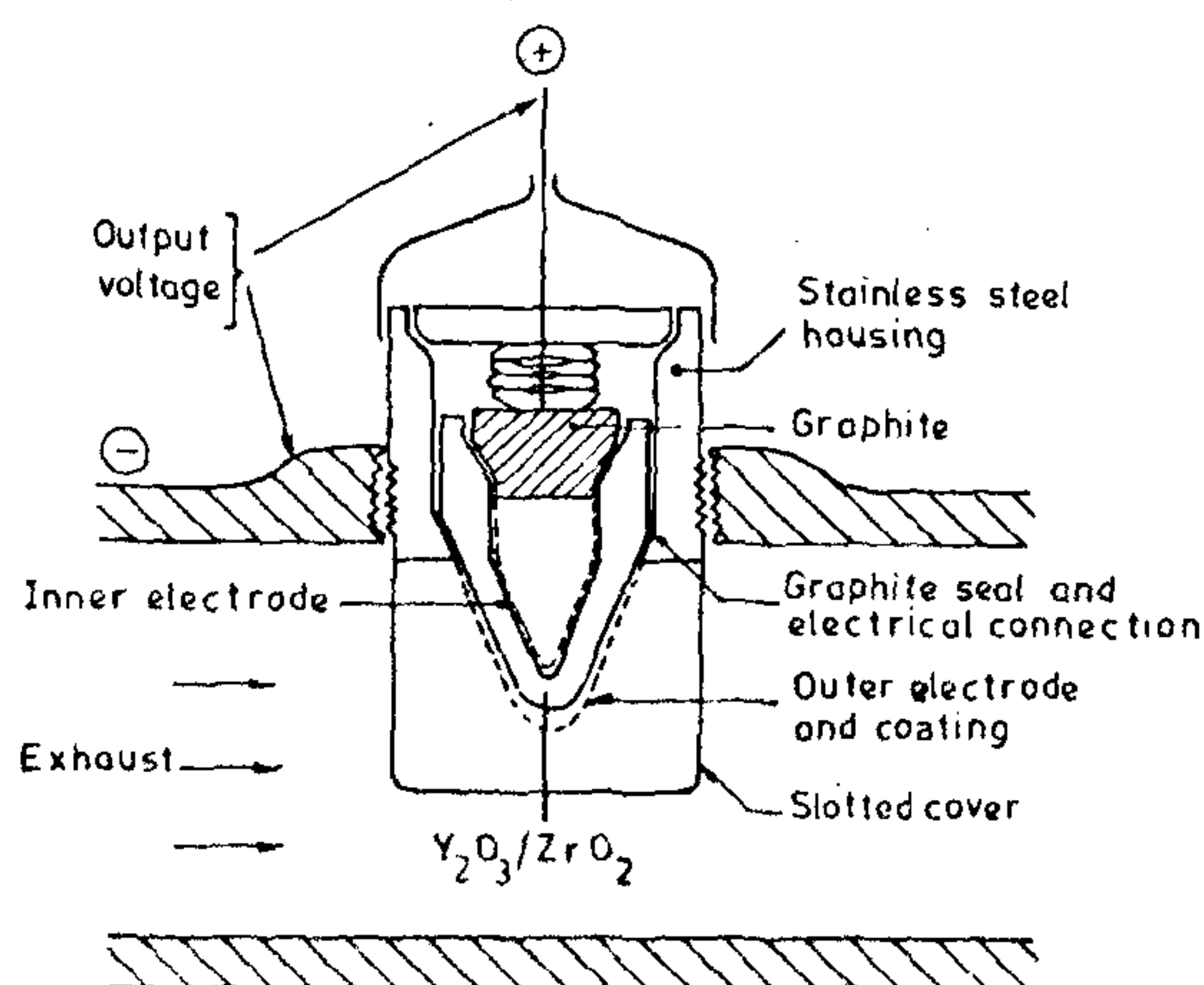


Figure 9. Schematic diagram of the electrochemical oxygen sensor for use in vehicle exhaust manifold.

ments using electrochemical sensors. They are also valuable tools in establishing phase equilibria and in locating temperatures of phase transitions. In this section I briefly touch upon a few examples of these applications drawn from the work carried out in our laboratory.

One of our major areas of study has been the basic science underlying corrosion effects in sodium-steel system. Oxygen plays a key role in this corrosion process and hence the ternary systems of sodium, oxygen and the constituents of stainless steels are of interest. We have investigated many such ternary systems. Here electrochemical oxygen probes have been very useful. As oxygen level increases it is usually the ternary oxide that gets formed. In a sodium-stainless steel system, the first ternary oxide that gets formed, when oxygen level is increased from zero, is sodium chromite. The reaction can be written as



where the rectangular brackets denote solution and the subscript represents the matrix. It is, therefore, of interest to find out the threshold oxygen concentration above which this reaction will take place. This is related to the oxygen potential of the ternary phase field Na-NaCrO₂-[Cr]_{ss}. One can calculate this from the free energy of formation of NaCrO₂ which we measured using different techniques, for example, high temperature mass spectrometry. This approach led to a very low oxygen level (1–2 ppm) which is difficult to maintain in a practical system. However, a direct measurement of the oxygen potential using an electrochemical oxygen sensor based on YDT gave a value higher by an order of magnitude. A detailed study showed that it is the carbides on the surface of stainless steel that actually participate in the reaction and thus raise the threshold oxygen level¹⁶. Similar measurements established the oxygen potential necessary for the formation of Na₃UO₄ when sodium comes in contact with UO₂ (ref. 17). In studying the Na-Mo-O system, a change of phase field from Na-Mo-Na₂O to Na-Mo-Na₄MoO₅ was observed at a temperature of 681 K (ref. 18). Thermodynamic measurements were taken to much lower temperatures than hitherto possible using a low-temperature oxygen sensor described above. Thus free-energies of formation of indium oxide could be studied at temperatures as low as 473 K (ref. 19). Non-Henrian behaviour of oxygen dissolved in sodium was observed when oxygen potential in sodium was measured using oxygen sensors based on coated CSZ (ref. 10).

The electrochemical carbon sensor is at the heart of a new method that we have developed to measure carbon potentials of metal carbides. The method involves the equilibration of the sample, usually a metal/metal carbide mixture, with liquid sodium with the simultaneous measurement of the carbon potential of sodium

using the carbon sensor. The new method overcomes many problems associated with the gas equilibration method that is usually employed and makes it possible to carry out these studies at lower temperatures (600°C) than before. This new method has been used in studying the carbon potentials UC, (U, Pu)C (which is the fuel used in FBTR) and different varieties of stainless steels^{20,21}. A model for carbide equilibria in stainless steels has emerged from these studies. Other interesting studies include the decomposition behaviour of carbide phases in ferritic steels²² and of sodium carbonate in liquid sodium²³.

The electrochemical hydrogen sensor was employed to study the reaction rate of liquid sodium: (i) with rust formed on ferritic steel components and (ii) with hydrocarbon coolant oil used to lubricate the shafts of centrifugal sodium pumps²⁴.

Electrochemical cells based on β -alumina have been constructed and used to measure the thermodynamic properties of Bi-Na binary alloys, with a view to understand the chemical bonding in this and similar quasi-ionic alloys²⁵. Studies are also underway on ternary alloys of sodium, indium and lead.

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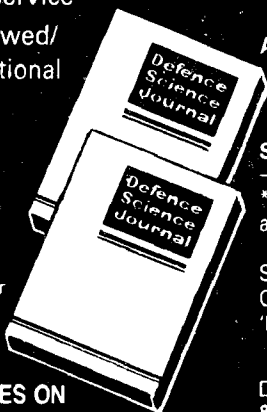
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