A pressure transducer based on liquid sodium

B. CLEAVER, S. P. KUMAR

Department of Chemistry, The University, Southampton SO9 5NH, UK

A transducer is described in which the e.m.f. of the electrochemical cell, Na(l, pressure $p°$)/beta"-alumina/Na(l, pressure p), is used to measure the pressure, p. In the cell, the left-hand electrode contains sodium under its saturated vapour pressure, $p°$; the right-hand electrode is exposed to the process pressure, p. For pressures of a few hundred bar, the output is linear and reversible, and the e.m.f. is related to the pressure by the equation $E = -pV_m/F$, where V_m is the molar volume of liquid sodium at the experimental temperature and F is the Faraday constant. An experimental device has been made and tested and is found to behave as predicted by this relation. Its output is 0.0259 mV bar^{-1} at 120° C.

1. Introduction

It is often convenient to measure hydrostatic pressure by means of an analogue device which has an output e.m.f. proportional to the pressure. This e.m.f. can be used to power a display to indicate the pressure, or to activate other equipment such as valves, pumps, etc. At room temperature, the most commonly used devices are those based on the change of electrical resistance of a wire under tension. Coils are wound around the outside of a hollow tube, to the inside of which the pressure is applied. The dilation of the tube strains the wire coils, which undergo a proportional change in resistance. By winding a pair of such coils around the tube and another similar pair around a solid rod, connecting the two pairs in opposite arms of a conventional Wheatstone bridge, it is possible to detect the applied pressure by the proportional out-of-balance current. Devices based on this principle are cheap, rugged and reliable when used within prescribed limits; however, pressurization beyond these limits causes permanent strain in the tube or wire, resulting in a zero shift and, possibly, also a change in the slope of the e.m.f. versus pressure curve.

Any physical property which changes with pressure could be made the basis of a transducer. Devices based on solids all suffer from the basic defect that the overstrain of the deformed member beyond its elastic limit will cause a permanent change in the response, so that such devices require periodic recalibration or repair.

There is a wide choice of materials available for bonded strain gauges at room temperature, but as the operating temperature is raised the choice becomes more restricted. The elastic limit of most materials falls with temperature, and there are also problems in finding suitable bonding and insulating materials. These considerations limit the temperature to which a given device may be used. These difficulties are avoided by cooling the sensitive parts of the transducer, but this may perturb the system under examination (for example, by causing local freezing of a hot liquid sample). A more logical and elegant approach is to design a transducer which can be kept at the process temperature, in which the transducing element is a liquid. Liquids are fundamentally incapable of undergoing permanent strain, and are free from all the drawbacks inherent in bonded strain gauges.

Many such devices could be envisaged. The change with pressure of the resistivity of a conducting liquid could be made the basis of a transducer: the liquid could be a metal such as mercury, or an electrolyte. The latter category can be subdivided into aqueous electrolyte solutions and molten salts. In each case the pressure would be transmitted to the liquid by a flexible diaphragm, and the liquid would be confined in a capillary tube made from a suitable insulating material. Electrical leads would be fed into the capsule through insulated terminals. The upper temperature limit to which such a device could be used would be set by problems of containment, corrosion and insulation. The change in conductivity of molten salts with pressure has been studied extensively at temperatures up to 1000° C [1], and many suitable substances exist which could be used to make such a transducer.

A second series of devices could be made which involve measuring the change with pressure of the e.m.f. of a reversible electrochemical cell. Again, application to high temperature environments would require that the cell components should withstand the temperature without suffering corrosion or permanent strain. For the reasons outlined above, it is logical to choose cells with liquid electroactive components, and it is convenient if the cell has zero e.m.f. when there is no applied pressure. This can be achieved by connecting two similar cells back to back, or, more elegantly, by choosing a cell with two electrodes made from the same material, but only one of which is subjected to pressure. Such a cell is:

Na(l, pressure $p°$)/beta"-alumina/Na(l, pressure p).

Two liquid sodium electrodes are separated by a partition of the solid sodium ion conductor beta″-alumina. One sodium electrode is evacuated, and so is under a pressure equal to the saturated vapour pressure of sodium, $p°$, at the prevailing temperature. The other electrode is exposed to the pressure to be measured, p. The spontaneous cell reaction is

sodium at pressure p ⟶ sodium at pressure $p°$,

and the free energy change corresponding to this reaction is the isothermal work of compression of the liquid metal from pressure $p°$ to p. If V_m is the molar volume of sodium, this free energy change is given by

$$\Delta\mu = \int_{p°}^{p} V_m \, dp \qquad (1)$$

For pressures of the order of a few hundred bar, V_m may be treated as independent of pressure, and thus (1) becomes

$$\Delta\mu = V_m (p - p°) \qquad (2)$$

Equating this with the electrical work on virtual passage of a charge F (Faraday constant), we have the following expression for the e.m.f.:

$$E = -V_m (p - p°)/F \qquad (3)$$

If $p°$ is small compared with p, this is well-approximated by

$$E = -V_m p/F \qquad (4)$$

In this régime, the e.m.f. of the cell is, therefore, a linear function of the applied pressure, p, and the calibration constant, V_m/F, is known. A device based on Equation (4) will, therefore, be capable of acting as a primary standard. For higher pressures, however, the variation of V_m with p must be taken into account, when (4) becomes

$$E = -\left(\frac{1}{F}\right) \int_{p°}^{p} V_m \, dp \qquad (5)$$

The integration in (5) must be carried out numerically, or can be based on a power series expression for V_m as a function of p. The necessary information is available in the literature, but the calibration of the device is then dependent on the pressure standard used in the original compressibility determination.

The minus sign in Equations (3), (4) and (5) indicates that the high pressure electrode is the negative pole of the cell, corresponding to the reaction

$$Na \longrightarrow Na^+ + e^-$$

The device can also be used to measure sodium vapour pressures less than the saturated vapour pressure of sodium [2], in which case the polarity of the cell is reversed.

Brennan first proposed the use of the sodium cell as a pressure transducer [3]. He also demonstrated a practical device, but was not equipped to measure the pressure directly; instead he deduced this from the hoop strain of a tube under internal pressure. We now report confirmatory experiments in which pressure
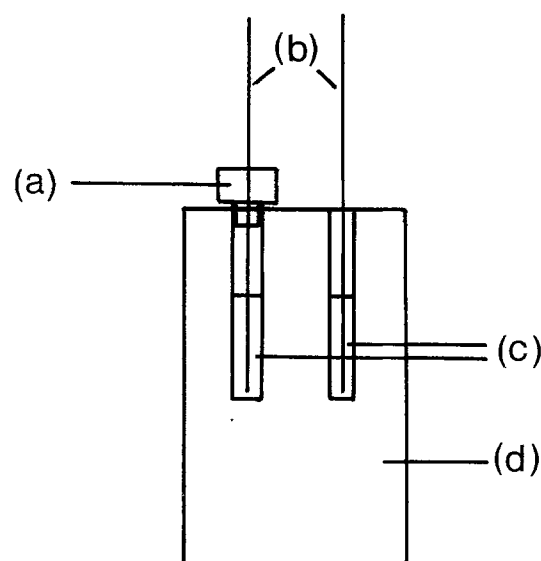

Fig. 1. The experimental sodium cell: (a) boron nitride plug, secured by Araldite resin; (b) nickel wires; (c) liquid sodium; (d) beta″-alumina cylinder.

was applied to the sodium electrode using an inert gas. Equation (4) was shown to be obeyed, within experimental error.

2. Experimental details

The experimental cell is illustrated in Fig. 1. It was made from a cylindrical block of beta″-alumina [4] of diameter 18 mm and length 29 mm. Two holes of 3 mm diameter were drilled into one circular end of the cylinder to a depth of about 14 mm, using diamond-tipped hollow drills. A plug of boron nitride was machined to fit into one hole; the plug had a central hole through which a nickel wire was inserted. The plug was sealed into the hole, and the wire through the plug, using Araldite resin. A nickel wire was placed into the open hole. The end of each wire touched the beta″-alumina at the bottom of the respective holes. The base of the beta″-alumina cylinder was then immersed in a shallow pool of liquid sodium, and a direct current was passed between this pool and each nickel wire in turn. The charges passed were calculated to cause each of the holes to become about half filled with liquid sodium by electrolysis. All these operations were carried out in an atmosphere of dry nitrogen.

The filled cell was then transferred to a heated pressure vessel, to which dry, oxygen free nitrogen could be admitted. The vessel and ancillary equipment have been described elsewhere [5]. The e.m.f. between the two nickel wires was measured, as a function of applied pressure, using a digital multimeter (Thurlby, model 1905a). The experiment was carried out at 120° C, above the melting point of sodium but below the softening point of the Araldite resin. There was a small asymmetry potential between the electrodes at zero applied pressure, which was discounted by using the 'null' key on the DVM. Pressure runs were carried out to 400 bar, and pressures were
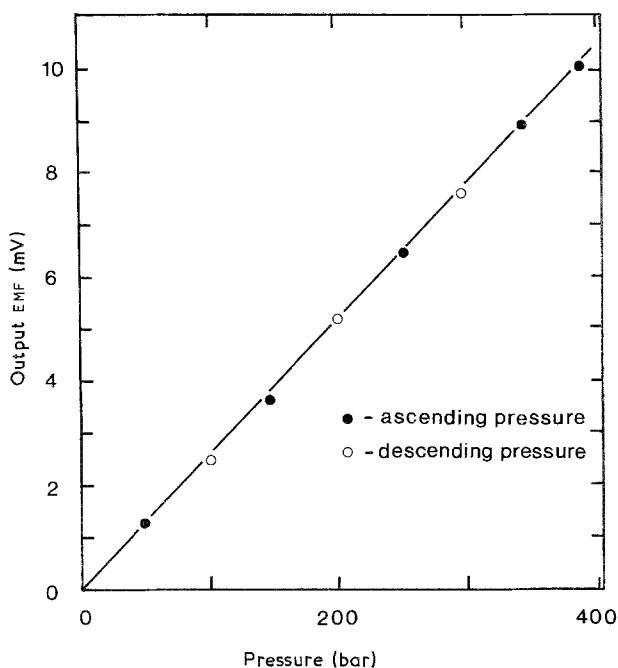
Fig. 2. Output e.m.f. against pressure for the sodium transducer, (●) ascending pressure, (○) descending pressure.

measured using a Bourdon gauge (Budenburg) calibrated against a dead weight tester. The precision of the pressure measurement was ±5 bar.

Five runs were carried out. In two of them, the pressure was allowed to remain steady for 4 minutes before readings were taken. In the third run the pressure was allowed to rise steadily by opening the pressure vessel directly to the compressor. In the fourth and fifth runs the pressure was changed in a stepwise manner in order to investigate the time response of the device. However, these last experiments were inconclusive in that the response of the sodium cell could not be distinguished from that of the rest of the apparatus. It was established that the response to a pressure step was essentially instantaneous, but it seems likely that rapid pressure changes would produce a transient temperature change in the pressurized sodium compartment which would contribute a small error term to the output e.m.f.. This error would disappear as the thermal gradient was dissipated. Thus, the ability of the device to measure correctly the size of a 'square' pressure step is open to doubt.

The maximum pressure used in these experiments was 540 bar, at which pressure there was some evidence of leakage of gas into the 'sealed' compartment. Whether this leakage was due to failure of the

Araldite seal or to porosity in the beta″-alumina is not known.

3. Results

Figure 2 shows e.m.f. against pressure for the first run. The result from the second run was essentially identical. The plots are linear, and show no hysteresis. Figure 3 shows the results from an experiment in which the output from the sodium transducer and the output from a strain gauge transducer (Intersonde, model XR17, rated to 2000 bar) were connected to the Y and X channels of an X-Y pen recorder, respectively. The pressure was allowed to rise continuously by opening the pressure vessel to the compressor. Because of the pipework arrangement, the Intersonde transducer experienced each incremental pressure rise fractionally earlier than the sodium transducer. This caused the pen to trace out a series of very close steps corresponding to the individual strokes of the compressor, and for this reason the upper part of the line shows some thickening. When the pressure was finally released, the pen retraced its path (but without the small steps); this trace falls within the thickness of the 'ascending pressure' line, which indicates the absence of hysteresis.

Table 1 shows the slopes of the e.m.f. against pressure curves in the first two runs, and also the response based on the calibration curve of the Intersonde transducer used for the experiment illustrated in Fig. 3. Finally, the table shows the slope calculated using Equation (4). The molar volume of sodium at this temperature is $24.95\,cm^3\,mol^{-1}$, based on the following equation for the density:

$$density(g\,cm^{-3}) = 0.927 - 0.238 \times 10^{-3}(t-100)$$

where t is the Celsius temperature [6]. The measured

Table 1. e.m.f. — Pressure response of the sodium transducer

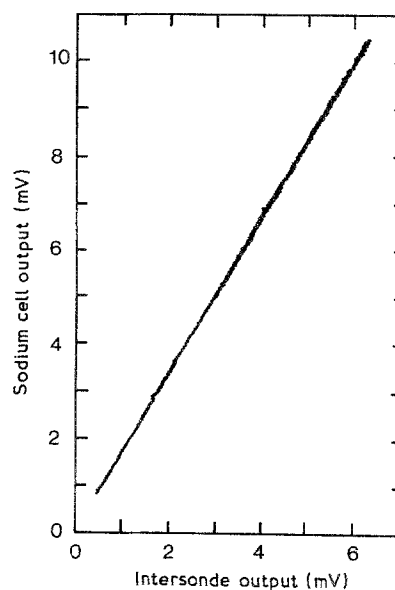| Experiment	Response $(mV\,bar^{-1})$
Run 1 (Fig. 2)	0.0261
Run 2	0.0259
Run 3 (Fig. 3)	0.0258
Eqn. (4)	0.0259

Fig. 3. X-Y recorder plot of sodium cell output against Intersonde transducer output, with pressure vessel open to the gas compressor. The line thickening in the upper part of the diagram corresponds to pen movement during individual strokes of the compressor (see text).
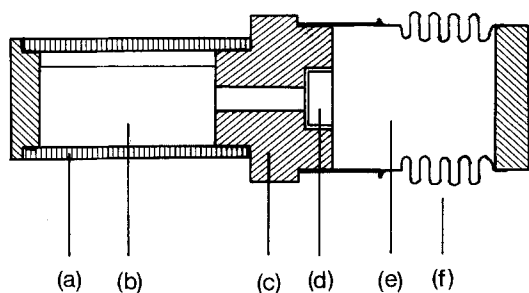
(a)   (b)   (c)   (d)   (e)   (f)

Fig. 4. The experimental sodium transducer: (a) rigid tube containing sodium under its own vapour pressure, p°; (b) sodium; (c) alpha alumina insulator; (d) beta″-alumina disc, sealed to alpha alumina by a glaze; (e) sodium subjected to process pressure, p; (f) stainless steel bellows.

values are in excellent agreement with the theoretical one (within 1%, which is the precision of the Bourdon gauge).

4. Discussion

The observed performance is in satisfactory agreement with theory at 120° C. The experimental cell used here could not be used at temperatures very much higher than this because the Araldite resin used to seal the closed electrode would soften. Extension of the temperature range would be possible if a glass was used to seal the beta″-alumina to an insulating material; alpha alumina might prove a more suitable insulator than boron nitride, as it can also be joined to metals such as stainless steel. The technology for making these joints already exists. In the sodium-sulphur battery, which can operate to 400° C, alpha alumina is joined to stainless steel. In the high pressure sodium lamp, which reaches 700° C, alpha alumina is joined to niobium end caps using a glaze. A device has been constructed according to the design shown in Fig. 4. This did not prove entirely satisfactory in practice as the glaze used to seal the small disc of beta″-alumina to the alpha alumina tended to run over the surface of the beta″-alumina and so blocked it for electrolytic action. Replacement of the beta″-alumina disc by a small tube of beta″-alumina might prove more satisfactory; this would also raise the pressure differential which the device could withstand.

The upper pressure limit to which the device could be used is determined by the mechanical strength of the beta″-alumina membrane, and the strength of the bond between it and the insulating collar in which it is mounted. Another consideration is that the device will work only if both sides of the membrane are in contact with the liquid sodium. Since the reference compartment is only partially filled, to ensure that the sodium is under its own vapour pressure, this means that the device must be inserted the right way up in order to function correctly. A wick might be used to assist wetting, and in this case the device might function in any attitude; again, the necessary technology is embodied in the design of the sodium-sulphur cell, in which a similar problem arises.

One application for which the sodium transducer would be ideal is the measurement of pressure in liquid sodium itself, for example in the heat exchange circuit of a sodium-cooled reactor. Here the bellows section of the cell shown in Fig. 4 would be dispensed with, and the beta″-alumina membrane would be presented directly to the process fluid. The device would indicate pressure continuously, and would respond rapidly to sudden changes in pressure such as would occur if a pinhole developed in the pipework, allowing sodium to escape or steam to enter the heat exchanger.

Acknowledgements

References

[1]   B. Cleaver, 'The Use of High Pressure in the Study of Molten Salts', in *Advances in Molten Salt Chemistry*, Vol. 4, (edited by G. Mamantov and J. Braunstein), Plenum, New York, (1981), Chapter 2.

[2]   O. Takikawa, A. Imai and M. Harata, *Solid State Ionics, 7* (1982) 101.

[3]   M. P. J. Brennan, *Electrochim. Acta,* **25** (1980) 629.

[4]   J. Sudworth and A. R. Tilley, 'The Sodium Sulphur Battery', Chapman & Hall, London, (1985), chapter 2.

[5]   B. Cleaver and S. I. Smedley, *Trans. Faraday Soc.* **67** (1971) 1115.

[6]   'International Critical Tables', Vol. 2, (1st edn.), (edited by E. W. Washburn), McGraw Hill, New York, (1927); p. 463.