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The mercury/mercuric oxide electrode in high temperature aqueous solutions

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The mercury/mercuric oxide electrode is examined for its applicability to high temperature alkaline solutions. It is found to be stable and reliable at temperatures up to 250°C in solutions of up to 5 M sodium hydroxide. It has been calibrated against the hydrogen electrode at temperatures up to 200°C. Loss of hydrogen from the autoclave prevented the calibration being extended to higher temperatures. Tests for the practicability of the electrode for use in high temperature polarization cells indicate that contamination of the solution in the working compartment results from slight dissolution of mercuric oxide. This contamination can be suppressed by isolating the reference electrode with a porous p.t.f.e. separator.

1. Introduction

Reference electrodes for high temperature aqueous solutions are necessary for electrochemical corrosion, fuel cell and solution thermodynamic investigations. Suitable electrodes must be reliable and stable and must not be sources of electroactive contaminants in the solution. Numerous electrodes have been studied in acid solutions; the literature has been recently reviewed by Jones and Masterson [1]. Many of the electrodes which behave suitably at room temperature fail at temperatures above 100°C. Lietzke and Stoughton [2] showed that the Ag/AgCl and Ag/Ag_2SO_4 electrodes may be used at high temperatures in acid solutions, but that the corresponding mercury salt electrodes underwent disproportionation and hydrolysis especially in the lower concentrations of acid. In hydrogen saturated solutions there was also evidence that the hydrogen electrode reaction became dominant on silver based electrodes [3, 4].

High temperature alkaline solutions are of particular interest for boiler corrosion and fuel cell studies. Such studies have relied upon cold reference electrodes with thermal junctions [1, 5] or upon the hydrogen electrode [1]. Mesmer, Baes and Sweeton [6] have demonstrated the thermodynamic reliability of the hydrogen electrode at 150°C. Indig and Groot [7] point out, however, that in corrosion studies the hydrogen electrode reaction can become dominant on the sample and can thus invalidate experiments. A more inert reference electrode for alkaline solutions would therefore be valuable.

The product of spontaneous disproportionation and hydrolysis of mercurous salts at higher temperatures is mercuric oxide [8] e.g.

$$Hg_2SO_4 + H_2O \rightarrow Hg + HgO + H_2SO_4 \quad (1)$$

Such reactions can be expected to proceed to completion rapidly in high temperature alkaline solutions. The mercury/mercuric oxide electrode is therefore a logical choice for use in such environments. Ives and Janz [9] describe it as 'uniquely well behaved' among metal/metal oxide electrodes at room temperature and Every and Banks [10] showed that it could be used at temperatures up to 100°C in 5M sodium hydroxide.

Calibration of the mercury/mercuric oxide electrode against the silver/silver oxide electrode (the standard potential of which is known to 275°C [3]) in mixed hydroxide/chloride solutions may not be practicable. Hydrolysis of the silver chloride to oxide at intermediate temperatures, and spontaneous decomposition of the silver oxide at higher temperatures is to be expected. Since, however, the hydrogen overvoltage on mercury is very large at room temperature, and still considerable at 200°C (Conning [11]) the electrode should not be affected by hydrogen dissolved in the solution. Calibration of it against the hydrogen electrode was therefore undertaken. This is described below together with a test for mutual consistency of the electrodes, and a diagnostic test for contamination effects in a high temperature polarization cell.

2. Experimental

2.1 *Cells and autoclaves*

Preliminary bias potential measurements on the mercury/mercuric oxide electrodes were performed in a small autoclave with C.E.R.L. seals as described by Jones and Masterson [1]. The electrodes were prepared in wells machined in a p.t.f.e. cell liner. For the measurement of the potentials of mercuric oxide electrodes relative to silver chloride or hydrogen electrodes a p.t.f.e. tube was used to separate the mercury electrodes from the solution. Contact was made via a solution-saturated porous p.t.f.e. plug in the side of the electrode compartment. Wetting of the membrane by the solution was facilitated by soaking the plug in acetone before inserting it into the electrode tube and immersing this in solution.

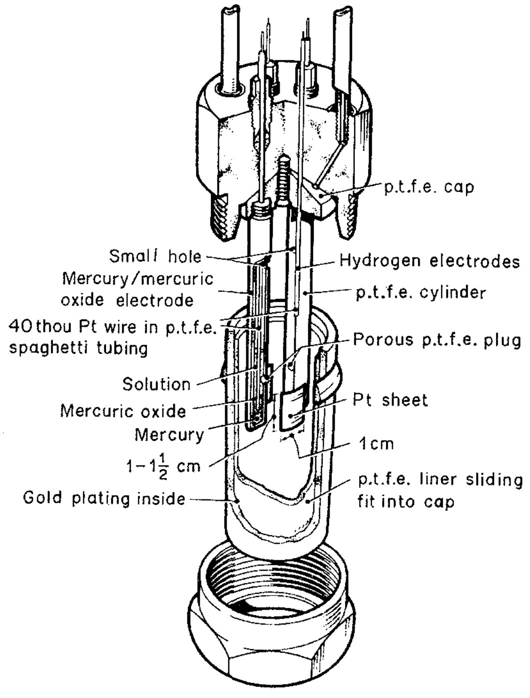

Fig. 1. High temperature calibration cell.

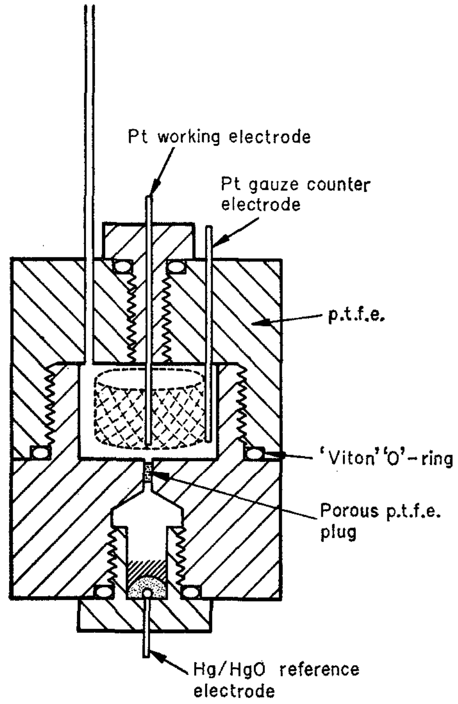

Fig. 2. High temperature polarization cell.

A modified autoclave illustrated in Fig. 1 was designed for use with hydrogen electrodes. It was provided with ports for de-gasing and flushing with hydrogen when assembled. The autoclave was gold plated internally to a thickness of 0·012 mm on the nimonic base and 0·025 mm on the stainless steel head. The cell was enclosed in a p.t.f.e. liner with a tightly fitting cap which was screwed to the autoclave head. In testing for contamination effects a mercury/mercuric oxide electrode was mounted in the lower compartment of the p.t.f.e. polarization cell shown in Fig. 2. This cell was contained in a mild steel autoclave and pressurized with argon to suppress evaporation. The upper compartment of the cell contained a 1 mm diameter platinum wire working electrode with a coaxially mounted platinum gauze counter electrode. The compartments were linked by a drilling into which a porous p.t.f.e. plug could be inserted.

2.2 *Electrodes*

Silver/silver chloride electrodes were of the thermal type prepared according to directions given by Ives and Janz [9]. Mercury/mercuric oxide electrodes were prepared from a small quantity of redistilled mercury on top of which was placed a little Analar red mercuric oxide powder which had been finely ground with a few drops of mercury. A 1 mm diameter platinum wire sheathed in p.t.f.e. spaghetti tubing in the cell in Fig. 1, and shrunk into the electrode holder in the cell in Fig. 2, made a metallic contact below the mercury surface. Hydrogen electrodes were fabricated from platinum sheets of approximately 10 mm^2, 0·25 mm thick, spot welded to 1 mm platinum wire. After cleaning in a chromic acid mixture, hydrogen was evolved at the electrodes for a few minutes in dilute sulphuric acid. A layer of platinum black was deposited on the electrodes from a solution of chloroplatinic acid (1 g Pt equivalent in 100 ml of solution), to which 80 mg of lead acetate trihydrate was added. This procedure took approximately 10 s at a current density of 1·5 mA mm^{-2}.

All solutions were prepared from Analar grade chemicals and doubly distilled water.

2.3 *Procedure*

Before commencing bias potential measurements on mercury oxide electrodes in the simple autoclave both the solution and autoclave were thoroughly de-aerated with 'white-spot' nitrogen in a glove box. The behaviour of the silver chloride/mercury oxide cell was studied in a very similar autoclave also deaerated with nitrogen. When using the mercuric oxide/hydrogen electrode system, hydrogen was bubbled through the solution in the assembled autoclave as illustrated in Fig. 1. The gas entered by way of a short length of p.t.f.e. spaghetti tubing (not shown in the diagram) which ended below the surface of the solution and was connected to a stainless steel capillary tube on the inlet port. After 30 min the valves were closed and the potential was observed for approximately an hour. This procedure was repeated until a stable potential was reached indicating that all the oxygen had been flushed from the system.

The autoclaves were heated in a Perkin Elmer precision oven, the temperatures in the air space being measured with chromel-alumel thermocouples driving a Kent millivolt recorder with scale expansion and zero suppression. Temperatures could be read to 0·5°C, were accurate to ±1°C and remained steady within these limits. Approximately 1 h was required for equilibration at each temperature. Potentials were measured for at least 30 min after this, using a Solartron digital volt meter Type LM 1420, before the temperature was changed.

The presence of mercuric oxide contamination in the polarization cell was monitored by cyclic sweep polarization of the platinum working electrode. This was performed using a potentiostat (Chemical Electronics TR 70/2A) programmed by a sweep generator (Servomex LF 51). The current was plotted against potential on an XY plotter (Bryans 26000 A4) which measured the potential drop across a 1 kΩ standard resistor. Experiments were performed to determine the effect of porous p.t.f.e. plugs between the working and reference electrodes.

3. Results

The potential of a nominal silver chloride

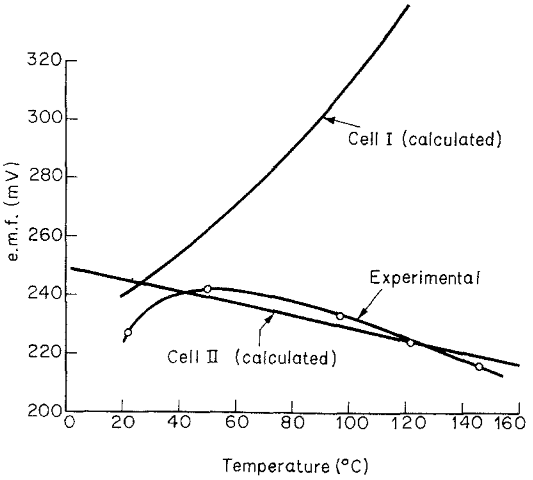

Fig. 3. Variation of potential with temperature of the nominal cell.
Ag | AgCl | NaCl (10^{-1} M) NaOH (10^{-1} M) | HgO | Hg

electrode against a mercury oxide electrode in a mixed chloride-hydroxide solution is shown in Fig. 3. The calculated lines refer to the e.m.f. values for the cell (I).

$$\mathrm{Ag}\,|\,\mathrm{AgCl}\,|\,\underset{10^{-3}\mathrm{M}}{\mathrm{NaCl}}\ ,\ \underset{10^{-1}\mathrm{M}}{\mathrm{NaOH}}\,|\,\mathrm{HgO}\,|\,\mathrm{Hg} \qquad \mathrm{(I)}$$

assuming that the silver electrode behaves reversibly to the chloride ion and that the mercury electrode is reversible to the hydroxyl ion, and for cell (II)

$$\mathrm{Ag}\,|\,\mathrm{AgO}\,|\,\underset{10^{-1}\mathrm{M}}{\mathrm{NaOH}}\,|\,\mathrm{HgO}\,|\,\mathrm{Hg} \qquad \mathrm{(II)}$$

assuming that both electrodes are reversible to the hydroxyl ion.

The measured temperature variation of the potential of the cell

$$\mathrm{Pt}\,|\,\mathrm{H_2}\,|\,\mathrm{NaOH}\,|\,\mathrm{HgO}\,|\,\mathrm{Hg}$$

is shown in Fig. 4. The values given are the mean of those for the two identical pairs of electrodes. Deviations of the e.m.f.'s from this mean were ±0·1 mV at 20°C ±0·4 mV at 187°C and ±1 mV at 200°C.

Fig. 5 illustrates the results of potential sweeps on a platinum electrode in a solution in contact with a mercury/mercuric oxide reference electrode in 1M sodium hydroxide solution at 210°C.

4. Discussion

Suspicion that not only mercurous halide electrodes but also silver halides would effectively revert to the corresponding oxides at moderate temperatures in alkaline solutions was confirmed by the observed behaviour of silver chloride electrodes in a mixed chloride-hydroxide solution. The anticipated e.m.f.s. assuming (*a*) that the silver electrode responds reversibly to choride ion. and (*b*) that it responds reversibly to hydroxyl ion were computed from standard potentials and electrode potential temperature cofficients quoted by Ives and Janz [9]. Values of K_w, the ionic product of water, which were used in the calculation, were abstracted from the conductance data of Bignold, Brewer and Hearn [12]. As shown in Fig. 3, above 50°C the potential variation of a cell containing a 'nominal' silver chloride electrode is very close to that calculated for the silver oxide/mercuric oxide cell.

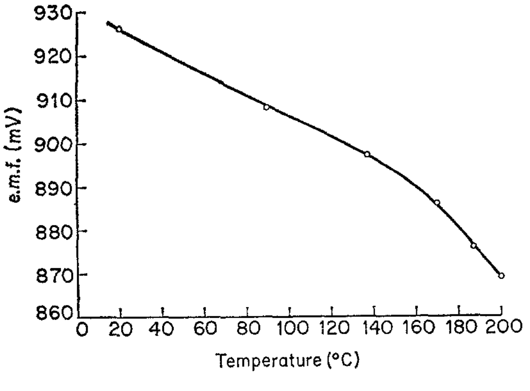

Fig. 4. Temperature variation of the potential of the cells. $\mathrm{Pt}\,|\,\underset{1\ \mathrm{atm}\ (25^{\circ}\mathrm{C})}{\mathrm{H_2}}\,|\,\mathrm{NaOH}\,|\,\mathrm{HgO}\,|\,\mathrm{Hg}$

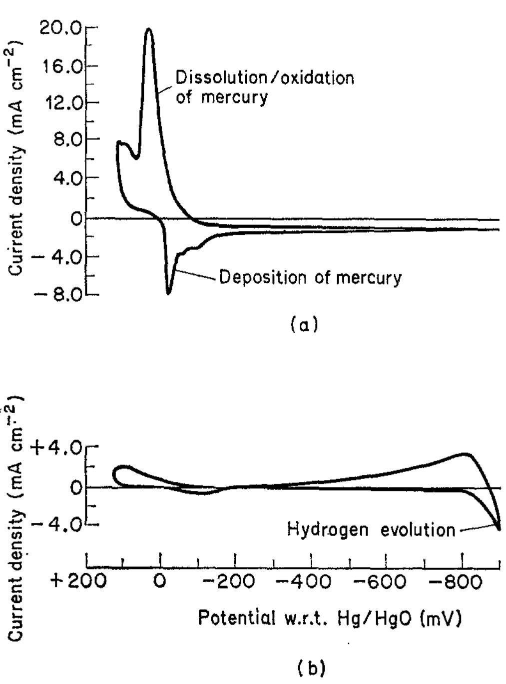

Fig. 5. Cyclic potential sweeps on platinum in 1 M NaOH at 210°C. Sweep rate 100mV s^{-1}.

(a) without porous plug isolating the reference compartment and

(b) with porous plug.

Although silver oxide electrodes behave reasonably well as reference electrodes up to about 160°C, above 180°C this oxide was observed to decompose spontaneously to silver. Mercuric oxide showed no evidence of decomposition when electrodes were heated in 0·1 M sodium hydroxide up to 280°C. Potentials between three identical electrodes were less than 0·2 mV up to 220°C and at 280°C they were within 1 mV of each other.

At 25°C the cell

$$\underset{p = 1\text{ atm (25°C)}}{\mathrm{Pt}\,|\,\mathrm{H_2}}\;|\,\mathrm{NaOH}\,|\,\mathrm{HgO}\,|\,\mathrm{Hg} \qquad \text{(III)}$$

attained a potential within 1 mV of the equilibrium value of +926 mV quoted by Ives and Janz [9] after bubbling hydrogen through the cell solution for between 30 min and 1 h. The correct reversible potential was also observed when the partial pressure of hydrogen in the cell was 3×10^{-2} atm, although the rate of attainment of equilibrium was slower.

Up to 200°C the e.m.f. values of cell III became steady in about an hour at temperature and remained sensibly constant during the observation period, about 30 min after this. Slight hydrogen leakage from the cell at the highest temperatures was indicated by an experiment in which the temperature was held constant at 180°C for 16 h. A decrease in cell potential of 1·25 mV per h was noted. For this reason, e.m.f. values, although measured up to 220°C, are not considered reliable beyond 200°C.

From 20°C to 140°C the cell potential varied almost linearly with temperature, the coefficient dE/dT being $-0{\cdot}25$ mV/°C in both 0·1 M and 1·0 M sodium hydroxide solutions.

Fig. 5(a) shows clearly that the solubility of mercuric oxide in molar sodium hydroxide at 210°C is sufficient to cause contamination problems. The presence of mercury is clearly indicated by the dissolution and deposition current peaks close to the reference electrode potential. The dissolution peak is very characteristic falling away rapidly when the mercury on the electrode becomes depleted. Also characteristic is the absence of hydrogen evolution at the expected potential (about −850 mV w.r.t. Hg/HgO).

Contamination is suppressed, however, by the insertion of a porous p.t.f.e. plug in the interelectrode passage. Fig. 5(b) shows that this results in complete absence of mercury deposition/dissolution peaks and that hydrogen evolution/oxidation occurs reversibly in the expected potential region.

Subsequent experience with the mercury/mercuric oxide electrode with a porous separating plug in polarization experiments has shown that it appears to be stable, and not to contaminate the working electrode compartment at temperatures up to 250°C and solution concentrations up to 5 M sodium hydroxide. The oxide appears to sinter in 5 M solution at the higher temperatures, and the mercury which had been ground up with it is expelled, but there is no evidence of any deterioration of performance caused by this.

Summarizing, the mercury/mercuric oxide electrode is a well-behaved, practical electrode for high temperature alkaline solutions.

5. Acknowledgments

The work reported here was carried out at the Central Electricity Research Laboratories and is published by permission of the Central Electricity Generating Board.

6. Addendum

Workers using this electrode must realize that should leaks develop in the autoclave a serious toxic hazard can result. The maximum permissible concentration of mercury vapour in the laboratory atmosphere [13] is $100\,\mu\mathrm{g\,m^{-3}}$ whereas the vapour pressure of mercury at 200°C is 0·028 bar (equivalent to $213\ \mathrm{g\,m^{-3}}$). It is recommended therefore that scrupulous pressure testing procedures be adopted, that experiments be performed in a well-ventilated laboratory or in a fume cupboard, and that the mercury vapour level in the laboratory be monitored.

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