A solid state amperometric humidity sensor

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The behaviour of cells of the form $Ag(s) \mid Ag_7I_4AsO_4(s) \mid M(s)$, where $Ag_7I_4AsO_4$ is a vitreous solid electrolyte with high silver ion conductivity and M is an inert anode such as platinum or stainless steel, has been investigated under different levels of d.c. polarisation. It has been shown that electrolytes of this type are not readily electrolysed, even under applications of large fields (despite the negligible impedance of the cathode). On the other hand, the anode is readily depolarised by water vapour, and the resulting cell current is related to the humidity of the gas in contact with it. The applicability of such cells for quantitative humidity determination by amperometry has been assessed.

1. Introduction

Significant electrolysis of a molten salt or solid electrolyte to give gaseous products occurs when the potential applied across a cell is sufficient to ensure a *continuous* evolution of gas. In practice, when an increasing voltage is applied, a region of potential corresponding to an initial low residual current is generally followed by a more or less sharp break called the 'decomposition potential' where the partial pressures of the liberated gases exceed one atmosphere. In some cases this value is simply related to the standard free energy change corresponding to the decomposition reaction; in others it may be very significantly affected by overvoltage. For solid electrolytes, behaviour of such cells under d.c. polarisation may be further complicated by the presence of electronic conductivity which often results in currents which increase exponentially with applied voltage due to voltage-dependent hole or electron generation. Nevertheless for many simple solid silver ion conductors, such as α-AgI, it is straightforward to undertake quantitative electrolysis, here to elemental silver and iodine, at potentials only slightly greater than those calculated from the standard free energy of formation. Similarly, *reversible* solid state cells of the form

$$Ag(s) \mid AgI(s) \mid I_2-D(s)$$
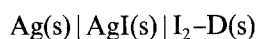
where I_2-D represents either iodine or an iodine source such as a charge transfer complex, have theoretical e.m.f. values [1].

Some twenty years ago a number of more complex silver ion-conducting phases were reported which, unlike silver iodide which reverts to the poorly conducting β-phase below 149° C, could sustain high silver ion conductivity at room temperature and below [2, 3]. These were two types. The first, consisting of $RbAg_4I_5$ and related compounds showed similar electrolysis behaviour to AgI, forming iodine quantitatively at the anode. The second was prepared by

the reaction of silver iodide with one of a number of silver oxosalts to form either crystalline or vitreous phases. Ten years ago, Scrosati and one of the present authors studied a number of glasses in order to establish the potential range over which they were stable [4]. In general a practical decomposition potential of around 700 mV was found for cells of the type

$$Ag \mid vitreous\ electrolyte \mid M$$
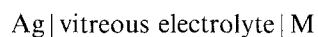
where M represents an inert electronic conductor. What was surprising was that for a number of these vitreous phases, no iodine could be detected at the anode, even after prolonged electrolysis. (The absence of significant electronic conductivity was proved by the quantitative formation of silver at the cathode). In the case of silver iodoarsenate glass of composition $Ag_4I_7AsO_4$ a yellow reaction product, later shown to contain crystalline silver iodide was found. The absence of iodine led to speculation that the anodic electrolysis product might be oxygen. More recently an attempt was made to verify this suggestion by polarising similar cells in which the anode was maintained under vacuum in order to detect any oxygen produced. It was noted, however, that immediately vacuum was applied to a polarised cell, the current fell from a value of say 5 mA, effectively to zero. Clearly the cell was being depolarised not by oxidation of the electrolyte, but by the oxidation of a component in the laboratory atmosphere. It was soon established that only residual currents of a few hundreds of nanoamps flowed when the anode was bathed in a dry inert gas or in air which had been equilibrated with P_2O_5, and that the agent responsible for depolarising the cell was water vapour. We have now studied this process in more detail and assessed its applicability for quantitative humidity determination by ampereometry.

2. Experimental details

Silver iodoarsenate glass was prepared as described

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previously [5, 6] by co-melting under nitrogen finely ground AgI and Ag_3AsO_4 in a molar ratio of 4 : 1, followed by quenching in liquid nitrogen. The glass was then ground and sieved to produce a grain size of between 100 and 125 μm. Because of the light-sensitive nature of this electrolyte, all work was undertaken in subdued illumination.

Cells were prepared by pressing the glass powder to form 13 mm diameter cylinders using a stainless steel die and hydraulic press. In order to minimise the interfacial impedance of the silver cathode, a composite region was fabricated in which 0.15 g of a finely ground miture of silver powder and silver iodoarsenate glass in a ratio of 1 : 2 by weight was first pressed at 0.05 MPa. 0.50 g of pure glass powder was then added to the die, and the two–layer structure was then pressed at 0.3 MPa for 5 min. The anode usually consisted of a fine mesh of platinum, nickel or stainless steel. Carbon fibre and carbon felt were also studied. The mesh was either pressed against the electrolyte face by the cell-holder shown in Fig. 1, or, in other experiments, semi-embedded in the electrolyte using the die. When required, a silver wire reference electrode could be screwed up against the face of the electrolyte.

All experiments were carried out with the cell enclosed in a glass chamber which was attached to a standard vacuum line. Electrical contacts were established by means of tungsten wires through the chamber wall. Atmospheres of accurately known humidity were generated using either carefully thermostatted ice or $CuSO_4 \cdot 5H_2O$ with large surface area, for which water vapour pressures are known, together with oxygen, nitrogen or air.

D.c. and pulse polarisation experiments were carried out using a Solartron 1286 potentiostat; impedance spectroscopy was undertaken with a Solartron 1250 frequency response analyser interfaced to the cell through the potentiostat.

3. Results and dicsussion
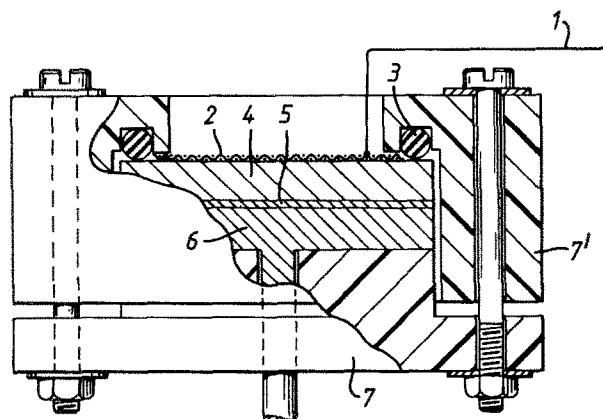
The first polarisation of a newly formed cell in

Fig. 1. Cell and cell holder: 1. anode current collector; 2. anode mesh; 3. O–ring; 4. silver iodarsenate glass; 5. silver powder/silver iodoarsenate cathode; 6. cathode current collector; 7. 'Macor' ceramic cell holder.
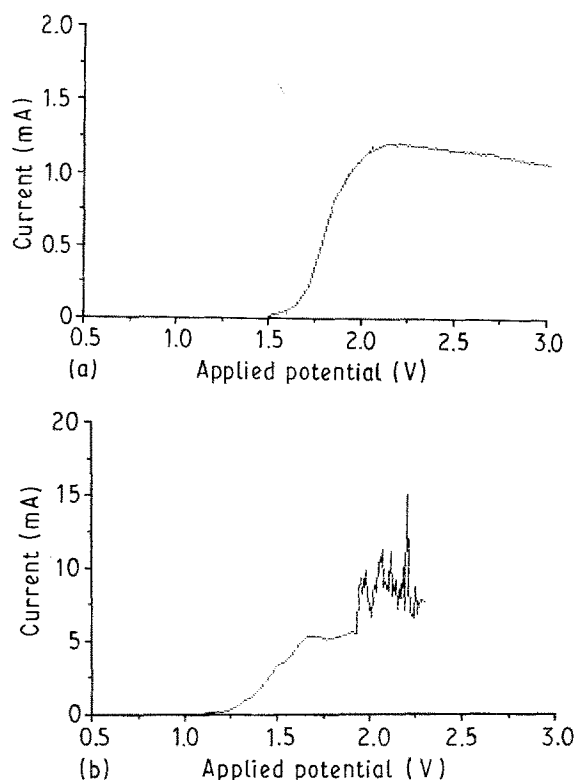

Fig. 2. Polarisation curves for cells exposed to air with water vapour partial pressure of (a) 50 Pa and (b) 500 Pa.

vacuum, produced transient currents which were dependent on the nature of the anode material and its pretreatment. Details of this process which are thought to involve oxide layers on the metal are not considered here. Following an initial polarisation in vacuum during which the anode was held at 3.0 V for 15 min (or scanned slowly to this voltage), residual currents at applied potentials between 0 and 3.0 V with respect to the silver reference electrode were typically 200 nA or less. Indeed it was possible to scan the voltage to 5.0 V without passing significant current.

Figure 2(a) shows the current flowing following the introduction of air with a comparatively low humidity (a water vapour partial pressure of 50 Pa) to the cell chamber. Here as the potential was slowly scanned from 0.5 V to 3.0 V, a 5000–fold increase in the current to over 1 mA was observed. For atmosphere with a water vapour pressure of 500 Pa, currents of over 10 mA were recorded, but these were now erratic, as seen in Fig. 2b. Information was also obtained by carrying out a.c. impedance analysis on cells in which the anode was subjected to varying degrees of d.c. bias. In Fig. 3, complex plane plots are shown for a pre-polarised cell which was maintained under high vacuum. The high frequency intercept on the real axis corresponds to uncompensated electrolyte resistance while the curves are consistent with an electrode impedance showing incomplete blocking behaviour – i.e. a double layer (probably best represented as a constant phase element because of the surface roughness generally detected in cells of this nature) shunted by a very large resistor. A very different response was observed when the anode was exposed to air with a
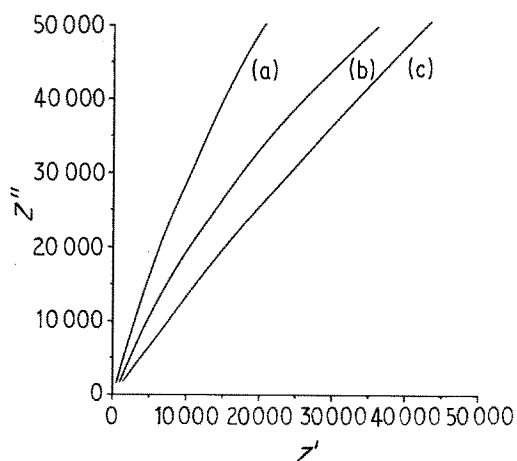
Fig. 3. Complex plane plots over a frequency range of 100 Hz–65 kHz for a cell in vacuum, polarised at potentials of (a) 2.0 V, (b) 1.5 V, (c) 1.0 V.

humidity corresponding to 500 Pa of water vapour pressure (Fig. 4). As the applied d.c. potential was increased anodically from 1.10 V, the low frequency end of the curve was depressed progressively to produce, at 1.5 V a semicircle followed by a straight line, and at higher voltages by a second semicircle with the cell impedance returning to the real axis at the lowest frequencies. It is not yet possible to identify unequivocally the basis of these two series circuit elements. Non-linear regression analyses showed that the RC values of the high frequency semicircle were consistent with a double layer capacitance shunted by a charge transfer resistance which reduces to about 20 Ω at high values of applied potential. The lower frequency semicircle exhibits very high capacitance or pseudocapacitance values of the type often noted with the quasi-steady state concentration waves associated with diffusional impedance at low frequencies.

Prolonged d.c. polarisation of cells in the presence of water vapour resulted in the formation of a reaction product which was first seen as a yellow discolouration at the points where the anode mesh made contact with the electrolyte. Further electrolysis caused these regions to grow and merge, so that finally a
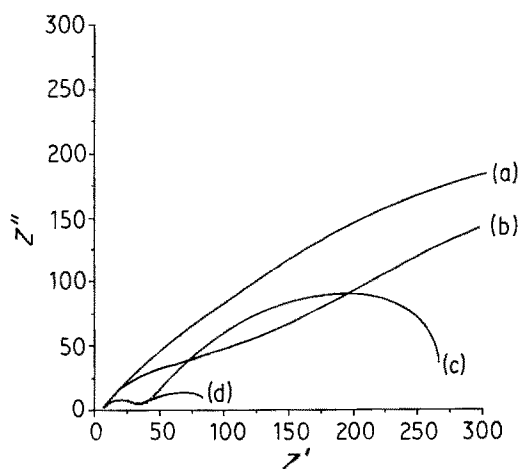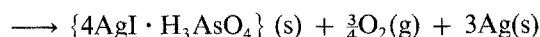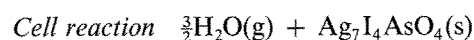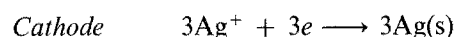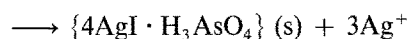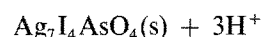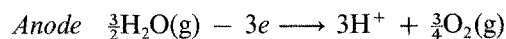

Fig. 4. Complex plane plots over a frequency range of 100 Hz–65 kHz for a cell in air with a water vapour potential pressure of 500 Pa, polarised at potentials of (a) 1.10 V, (b) 1.15 V, (c) 1.20 V, (d) 1.30 V.

reaction front was formed. By sectioning cells after several days of polarisation, it was possible to monitor the front penetrating the electrolyte layer and moving slowly towards the cathode. The yellow product was analysed by X-ray powder diffraction and shown to contain crystalline silver iodide (γ–phase). We propose that the cell reaction may be written as follows:

$$Anode \quad \tfrac{3}{2}H_2O(g) - 3e \longrightarrow 3H^+ + \tfrac{3}{4}O_2(g)$$

$$Ag_7I_4AsO_4(s) + 3H^+$$

$$\longrightarrow \{4AgI \cdot H_3AsO_4\} \, (s) + 3Ag^+$$

$$Cathode \quad 3Ag^+ + 3e \longrightarrow 3Ag(s)$$

$$Cell \ reaction \quad \tfrac{3}{2}H_2O(g) + Ag_7I_4AsO_4(s)$$

$$\longrightarrow \{4AgI \cdot H_3AsO_4\} \, (s) + \tfrac{3}{4}O_2(g) + 3Ag(s)$$

The reaction product is similar to the material produced when the glass is attacked by aqueous acids. The exact nature of the As(V) species is unknown, but is clearly some hydrate of As_2O_5. The product has sufficient ionic conductivity (probably mainly protonic) to allow the cell reaction to proceed past the stage of a simple surface process. We have made a preliminary study of the effect of this product on the electrolyte conductivity, as discussed below. Since the cell current is limited at least initially by the first step of the anodic reaction, small changes in the electrolyte conductivity have little effect on the cell response.

An electrochemical study was also undertaken to verify the proposed reaction scheme. A cell was fabricated in which the electrolyte layer consisted of three separate discs which were weighed before and after the passage of a known quantity of charge. No weight change was expected or observed with the central disc. According to the reaction scheme, the effect of current flow is to replace silver ions by protons in the electrolyte layer adjacent to the anode. A theoretical weight change of $q/F(M_{Ag} - M_H)$ is expected in this layer, where q is the total charge passed, and M_{Ag} and M_H are the relative atomic masses of silver and hydrogen respectively. The results of the study are shown in Table 1, which are seen to be in agreement with the proposed reaction scheme to well within experimental error.

4. Application as a humidity sensor

It was considered that the cell described might form

Table 1. q = total charge passed; $\{q/F(M_{Ag} - M_H)\}$ = theoretical mass change of anode layer using proposed reaction scheme; Δm = actual mass change of anode layer.

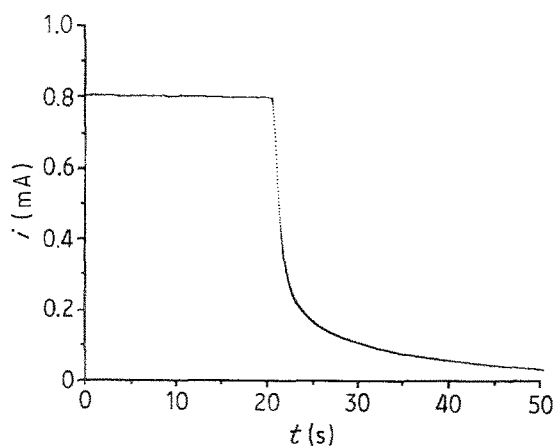| q (C)	$\{q/F(M_{Ag} - M_H)\} \times 10^3$ (g)	$\Delta m \times 10^3$ (g)
0.111	0.123	0.133
1.014	1.123	1.115
2.638	2.922	2.909

Fig. 5. Current response following application of a pump to a cell exposed to laboratory air.

the basis of a practical humidity sensor [7]. The response of the system was found to be fast, especially in situations where the water vapour was removed by pumping (Fig. 5): indeed the apparent response was probably determined here by the efficiency of the pumps. Figure 6 shows the reproducibility and the response of the system during a sequence in which the cell, held at a potential of 2.0 V, was subject to alternate 100 s exposure to 500 and 50 Pa levels of humidity. Here the reproducibility is seen to be excellent, but the response to the higher water vapour pressure seems slow. Much faster response was observed for lower values of the latter, but we are not yet able to confirm whether or not part of the response is determined by slow water vapour diffusion within the vacuum layer.

Current values at voltages in excess of about 0.70 V were dependent on the water vapour pressure. On polarisation up to potentials of around 2.0 V the current rose very rapidly with increasing applied potential, so that small variations in the latter gave rise to large current fluctuations, making in difficult to determine the effect of varying the water vapour pressure. For fixed values of the latter, different forms of time dependence were noted for the current, as shown in Fig. 7. Below 1.20 V, the current fell rapidly to a more or less constant value; for higher values of applied potential, a slow increase in current with time
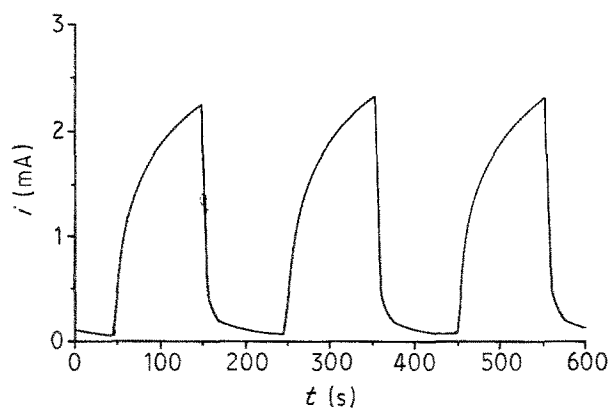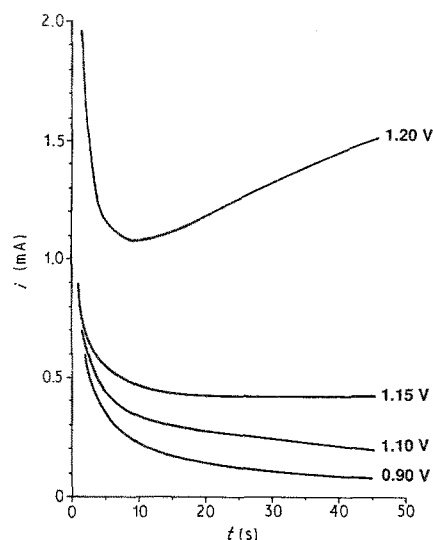

Fig. 7. Time dependence of the current following stepped potential changes for a constant water vapour pressure.

was seen. Above 2.0 V the current became much less dependent on potential or time, but remained very sensitive to water vapour pressure.

The absolute values of the current were found to be dependent on (i) the glass and anode metal used, (ii) cell design and fabrication and (iii) and cell history. The first of these variables is easily fixed, while the second is a technical problem which can be solved at least in principle (e.g. by use of photolithography to produce a consistent anode grid). From the point of view of developing a practical sensor the third is more serious. After long passage of high currents and the consequent accumulation of anodic product, the response of the cell changed. The ionic conductivity of the product phase was sufficient to enable the oxidation at the anode to continue, but the current response eventually began to vary, becoming less sensitive to variations in applied potential or water vapour pressure. The reasons for this are not fully understood: from the results of variable frequency impedance measurements it did not appear that reduction in the ionic conductivity of the electrolyte was primarily responsible. Rather, it seemed that the
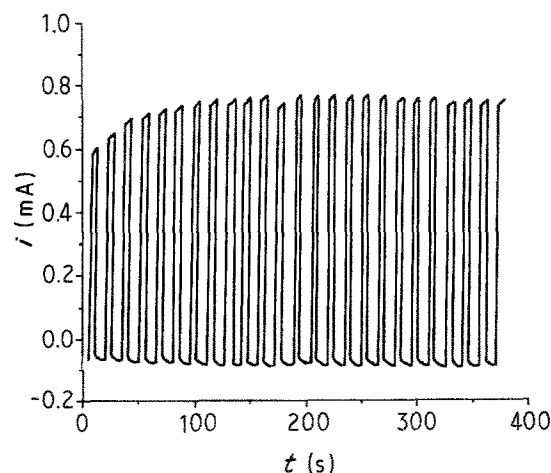

Fig. 6. Current response of cell subjected to 100 s alternate levels of 50 Pa and 500 Pa partial pressure of water vapour.

Fig. 8. Current response during a sequence of 2 V polarisation pulses (5 s ON; 10 s OFF) for a cell exposed to air with a water vapour partial pressure of approximately 250 Pa.
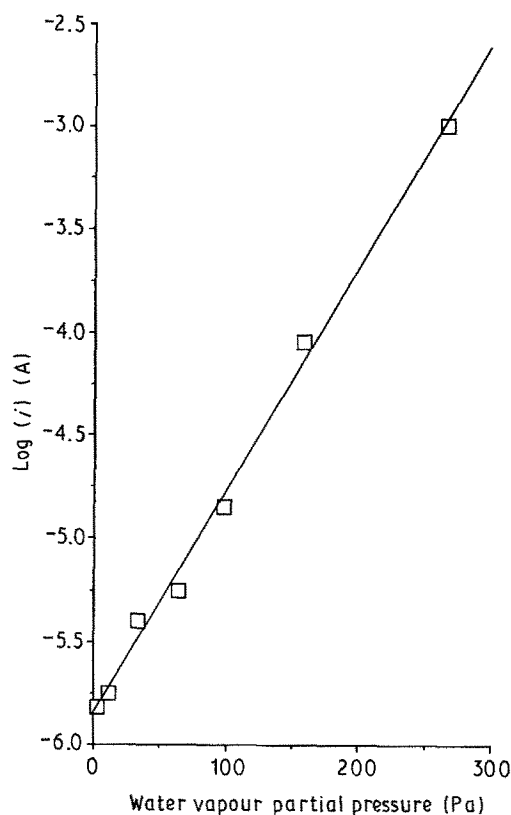
Fig. 9. Plot of $\log_{10}(i)$ against water vapour partial pressure, where the current is the 'steady state' value determined using the pulse technique illustrated in Fig. 8.

nature of the anodic process became altered. It was, however, possible to minimise this problem and extend the useful lifetime of the device. First, it proved unnecessary to polarise the cell for long periods in order to obtain analytical information; for example, voltage pulse sequences could be used, with a variety of mark/space ratios, as illustrated in Fig. 8. Second, if application of the cell as a sensor was confined to low water levels ($\leqslant 100$ Pa), then advantage could be taken of the very high sensitivity of the device without producing significant chemical change. The current response of a cell in this range is shown in Fig. 9.

5. Other work

We have found similar behaviour with cells based on ·

borate– and tungstate–based silver ion conducting glasses, and with cells constructed with splat-formed glass films. Preliminary studies have been made where the anode was immersed in organic liquids containing trace amounts of water. In the gas phase the cell is found to respond to other sources of acidic hydrogen such as methanol, but not to methane or molecular hydrogen.

6. Conclusions

Cells based on viterous $Ag_7I_4As_5O_4$ and certain other silver ion–conducting glasses have been shown to be depolarised at an inert anode by water vapour, rather than by electrolysis of the glass. The currents flowing at high values of polarisation potential were found to be dependent on the humidity of the gas surrounding the anode, so that cells of the form $Ag(s)|Ag_7I_4 \, AsO_4(s)|M(s)$ may find application as amperometric humidity sensors. Because of irreversible changes in the electrolyte brought about by the current flow, practical application of such cells is limited to low levels of humidity. The restriction would not apply to cells of the form $M'(s)|HX(s)|M(s)$ where HX is a solid state proton conductor and $M'(s)$ is a metal at which proton reduction takes place easily.

Acknowledgements

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