

# *Applications of porous flow-through electrodes.*

## *III. Effect of gas evolution on the pore electrolyte resistance*

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Gas evolution, within the pores of porous flow-through electrodes, was found to have significant effects on the pore electrolyte resistance. An electrical circuit was used whereby the pore electrolyte resistance was measured during hydrogen evolution *in situ* within the porous electrode. The resistance was measured for packed bed electrodes of Cu turnings, Cu wool and Ag wool at various rates of hydrogen evolution. The pore electrolyte resistance increased with the rate of hydrogen evolution in the order Cu turnings > Cu wool (shreds) > Ag wool (hair-like fibres). The gas void fraction was calculated, using Bruggeman's equations at various rates of hydrogen evolution. It was shown that the mode of variation of pore electrolyte resistance with the rate of hydrogen evolution can be explained on the basis of the variations in the gas void fraction. In all cases, it was found that the volume of gas retained within the porous bed depends on the rate of gas evolution rather nonlinearly.

### 1. Introduction

The evolution of gases at planar electrode surfaces has been known to affect the rate and mechanism of mass transfer [1-4], to influence the electrolyte resistance and current distribution at the electrode surface [5-9] and to disturb the hydrodynamic conditions near the electrode surface [7, 10].

The corresponding measurements at porous electrodes, although equally important, are clearly lacking. There are many systems where gas-electrolyte mixtures exist in porous electrodes [11-19]; the evolved gas may be a result of the main reaction or of a parasitic (side) reaction.

In this paper we have studied the effect of gas evolution on the resistance of the pore electrolyte within a porous flow-through electrode. The corresponding measurements on the mass transfer coefficient will be reported later. The importance of such measurements stems from the fact that the mass transfer coefficient affects concentration polarization whereas the pore electrolyte resistance affects the ohmic potential drop through the porous electrode. Adequate knowledge of these

effects is essential for a satisfactory understanding of the behaviour of such systems.

### 2. Experimental details

Packed bed electrodes were made from Ag wool, Cu wool and Cu turnings. Figs. 1*a, b* are SEM micrographs of some packed Ag wool and Cu wool, respectively. The Cu turnings were rather nonuniform, ranging from about 1-3 mm in dimension. The values of the specific surface areas of the packed wool electrodes ( $S$ ) were calculated from the dimensions of the fibres and the apparent density of the packed wool bed;  $S = 48 \text{ cm}^3 \text{ cm}^{-2}$  for Cu wool and  $S = 76 \text{ cm}^2 \text{ cm}^{-3}$  for Ag wool. The porosity ( $\theta$ ) and tortuosity ( $q$ ) were calculated as before [20]. The values were:  $\theta = 0.64, 0.93$  and  $0.94$ ; and  $q = 1.38, 1.23$  and  $1.12$  for Cu turnings, Cu wool and Ag wool, respectively. The packed electrode had a geometrical cross-sectional area of about  $3 \text{ cm}^2$  and a thickness of  $2.1 \text{ cm}$  (see Fig. 2). The electrode was packed by adding small amounts of the packing material, distributing them evenly, pressing gently with a glass rod and finally

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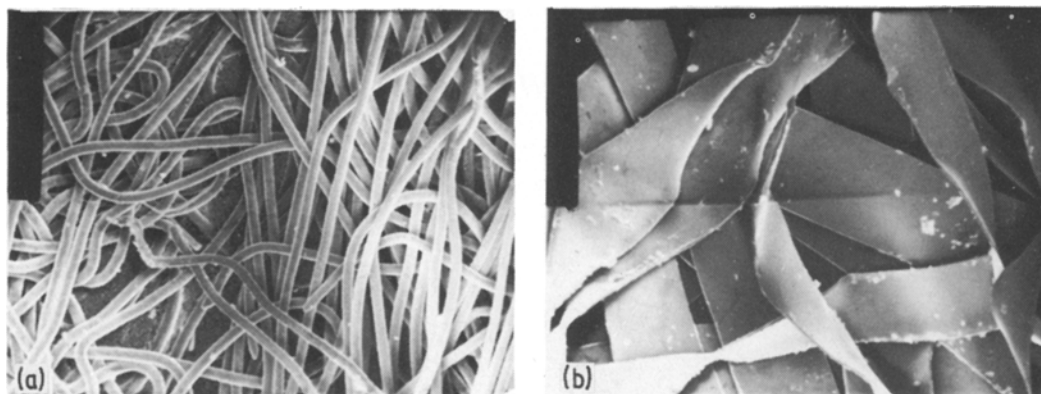


Fig. 1. (a) SEM micrograph of some randomly packed silver wool (50X). (b) SEM micrograph of some randomly packed copper wool (50X).

covering with a Cu screen to prevent floating of the packed bed.

The electrolyte was  $3 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . Its resistance, at various rates of hydrogen evolution, was measured using the flow cell and the circuits shown in Fig. 2. Two Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrodes ( $R_1$  and  $R_2$ ) were used to measure the electrode potentials at the entry ( $E_0$ ) and exit ( $E_L$ ) faces of the electrode. The cell has two counter electrodes,  $C_1$  and  $C_2$ , on either side of the packed bed electrode. The top counter electrode  $C_1$  is used to polarize the upper (exit) face of the electrode, i.e. it completes the circuit

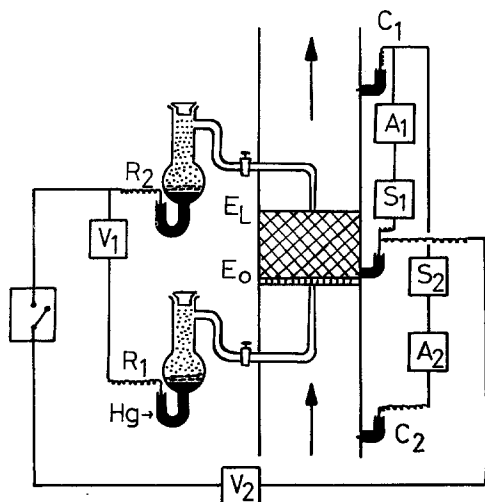


Fig. 2. A diagrammatic representation of the circuit used in measuring the pore electrolyte resistance with gas bubbles.  $S_1$  and  $S_2$  are d.c. power sources;  $A_1$  and  $A_2$  are ammeters;  $V_1$  and  $V_2$  are voltmeters;  $R_1$  and  $R_2$  are reference electrodes and  $C_1$  and  $C_2$  are counter electrodes.

$S_1$  &  $A_1$ , with the packed bed electrode. The Faradaic (hydrogen evolution) current  $i_c$  passes through this circuit. It also completes, with the bottom counter electrode  $C_2$ , a second circuit  $S_2$  &  $A_2$  through which the current  $i_r$  passes (see below).

The electrolyte was made to flow at about  $0.05 \text{ cm s}^{-1}$  from bottom to top, as shown in Fig. 2 to sweep out the bubbles. In this mode the current flow and reactant flow are opposite [18] to each other. The electrolytes were maintained at  $23 \pm 2^\circ \text{ C}$ . Note that since the resistance of the packed metal is very low, the potential through the metal is constant and hence the potential difference between  $E_L$  and  $E_0$  is due to ohmic potential drop through the pore electrolyte. With this in mind, the difference between  $E_L$  and  $E_0$  must, in all cases, be equal to the difference between the potentials at the points where the two reference electrodes are located, i.e.  $E_{R_1} - E_{R_2} = E(R_1, R_2)$ . This has been amply confirmed experimentally.

After steady electrolyte flow was reached, circuit  $S_1$  &  $A_1$  was closed. The desired rate of hydrogen evolution,  $i_c$ , was impressed on the packed wool electrode thus resulting in changes in the potentials  $E_L$  and  $E_0$ . After steady potential readings were reached, circuit  $S_2$  &  $A_2$  was closed. A fixed value of current ( $i_r$ ) was allowed to flow between the two counter electrodes,  $C_1$  and  $C_2$ . The flow of this current across the pore electrolyte generates an additional change in the values of the potential differences ( $E_L - E_0$ ) and ( $E_{R_1} - E_{R_2}$ ). According to Ohm's law, a plot of  $\Delta E = (E_{R_1} - E_{R_2})$  vs  $i_r$  should give a straight line with a slope

equal to the resistance of the current path, i.e. the resistance of the gas-electrolyte mixture in the packed bed. The intercept on the potential coordinate corresponds to  $\Delta E$  at  $i_r = 0$ , i.e. in the absence of current flow between  $C_1$  and  $C_2$ . The pore electrolyte resistance without Faradaic current flow was measured using the same circuit but without polarizing the packed bed electrode, i.e. at  $i_c = 0$ .

### 3. Results and discussion

#### 3.1. Pore electrolyte resistance

Fig. 3 shows some plots of  $\Delta E$  vs  $i_r$  for a few selected conditions. Clearly the plots give satisfactory straight lines; the slope of each equals the resistance of the column of pore electrolyte under the specified conditions. For a simple reaction where no gas bubbles are evolved, the pore electrolyte resistance is independent of current assuming the electrolyte is highly supported. This has been confirmed for the cathodic deposition of copper ions from an acid copper sulphate solution ( $0.001 \text{ mol dm}^{-3} \text{ Cu}^{2+}$  in  $3 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  at electrodes of packed Cu wool and Cu turnings).

Fig. 4 shows the measured pore electrolyte

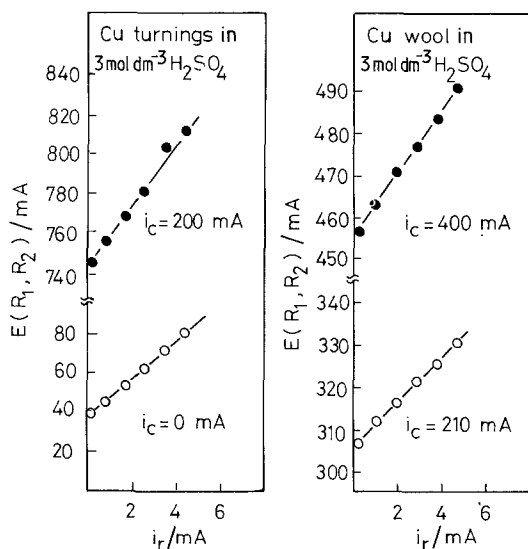


Fig. 3. A plot of the potential difference between the two reference electrodes  $E(R_1, R_2)$  against the magnitude of current  $i_r$  for Cu turnings in  $3 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  in the absence ( $i_c = 0$ ) and in the presence of hydrogen evolution at various rates, and for Cu wool at 210 and 400 mA.

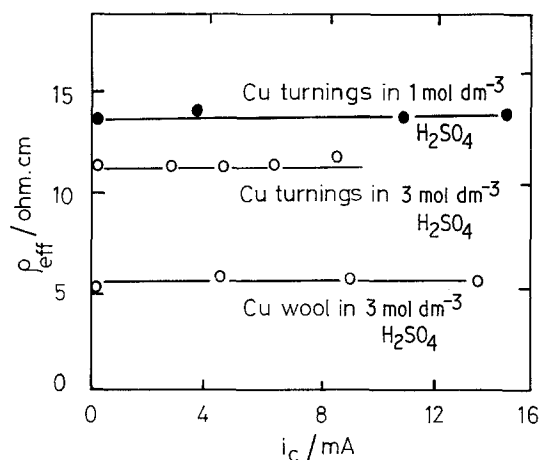


Fig. 4. The relation between the pore electrolyte resistance and the cathodic current for a redox reaction at currents below the limiting current  $i_L$ .

resistance at various cathodic currents (for currents less than or approaching the limiting current,  $i_L$ ). It is clear that the pore electrolyte resistance is independent of the cathodic current.

The pore electrolyte resistance was subsequently measured during hydrogen evolution at various rates. The variation of the pore electrolyte resistance with the rate of hydrogen evolution is shown in Fig. 5. Clearly the evolution of hydrogen increases the pore electrolyte resistance by up to two-fold. This is due to the reduction of the electrolyte-filled cross-sectional area of the porous electrode caused by both the continuous evolution (rising) and the retention (trapping) of gas bubbles inside the porous medium.

It is to be noted that this increase in resistance is only apparent; the true increase being significantly greater especially at high currents. This is because at the high currents employed, current flow through the pore electrolyte generates considerable local heating which decreases the resistance of the electrolyte and hence, also, the effective resistance of the gas-electrolyte mixture inside the pores. This is more so for electrodes of Cu turnings as they have the highest effective pore electrolyte resistance (Fig. 5). In comparing the results obtained on Cu turnings, Cu wool and Ag wool, two significant observations are made:

(a) The pore electrolyte resistance of the packed Ag wool electrode begins to increase with

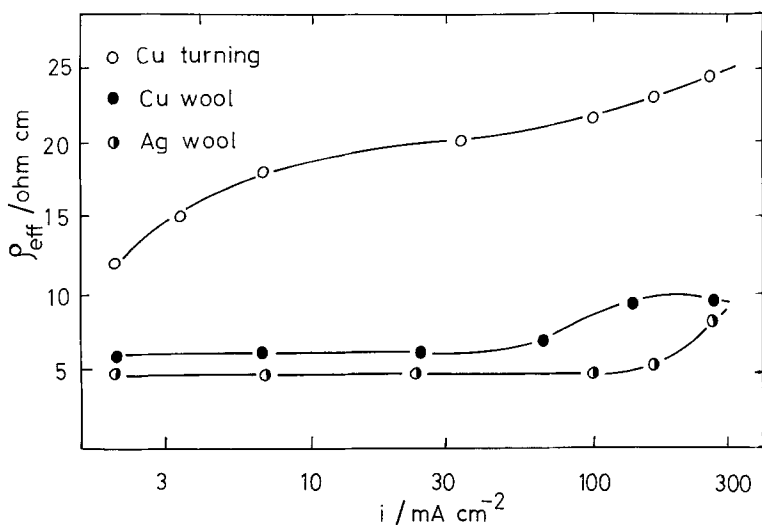


Fig. 5. Effect of the rate of hydrogen evolution on the pore electrolyte resistance for packed beds of Cu turnings, Cu wool and Ag wool.

current at much higher currents than for Cu wool and Cu turnings

(b) At the same rate of hydrogen evolution, the increase in pore electrolyte resistance is in the order: Cu turnings > Cu wool > Ag wool

These observations can be caused by differences in the growth and release mechanisms of hydrogen bubbles on the different metal surfaces and/or differences in the ability of the various packing materials to retain (trap) hydrogen bubbles. It appears that the shape of the packing materials is the principal factor in determining the mode of variation of pore electrolyte resistance with the rate of hydrogen evolution. This conclusion is based on the following arguments:

1. There is more resemblance between the curves of Cu and Ag wool than between those of Cu turnings and Cu wool.
2. Although we have no details of comparative studies on the kinetics of growth and release of gas bubbles on Ag and Cu, the available evidence does not point to significant differences, e.g. the adsorption energy of hydrogen on Ag and on Cu is about equal [21], and the sizes of the evolved hydrogen gas bubbles on both metals are of the same order of magnitude [3]. Therefore, the difference between the behaviour of the various packing materials is attributed to the differences in their ability to retain (trap) gas bubbles. Note from Figs. 1a and b that Ag wool is in the form of thin (hair-like) fibres while the Cu wool is in the form of shreads (which are long and thin) whereas

the Cu turnings are rather odd-shaped (compare also the differences in porosity and tortuosity).

### 3.2. Gas void fraction

There are several equations which express the effect of gas bubbles on the resistivity of the electrolyte through which they are dispersed [5, 7, 8]. Of these, the Bruggeman equation is rather simple

$$\rho/\rho^0 = (1 - \epsilon)^{-3/2} \quad (1)$$

where  $\rho$  and  $\rho^0$  are the resistivities of the electrolyte with and without gas bubbles, respectively, and  $\epsilon$  is the volume void fraction of the gas. This equation has been repeatedly used to evaluate the effect of gas bubbles on the resistance of the electrolyte in the gap between parallel plate electrodes in water electrolysis or chlor-alkali cells [5, 7]. It is used here to estimate an average apparent value of the volume fraction of pore electrolyte occupied by gas bubbles.

The calculated value of  $\epsilon$  is considered to be an average value since the (gas evolution) reaction is nonuniformly distributed within the electrode, and an apparent value because of the effect of local heating on the resistivity (see below). It refers to the volume fraction of pore electrolyte which is occupied by the gas bubbles. Thus, if the bed porosity is  $\theta = 0.5$  and  $\epsilon = 0.3$ , then the volume fraction of the gas in the packed bed is  $(1 - \theta)\epsilon = 0.15$ , i.e. 15% of the volume of the bed is filled with gas while 50% is filled with the packing material.

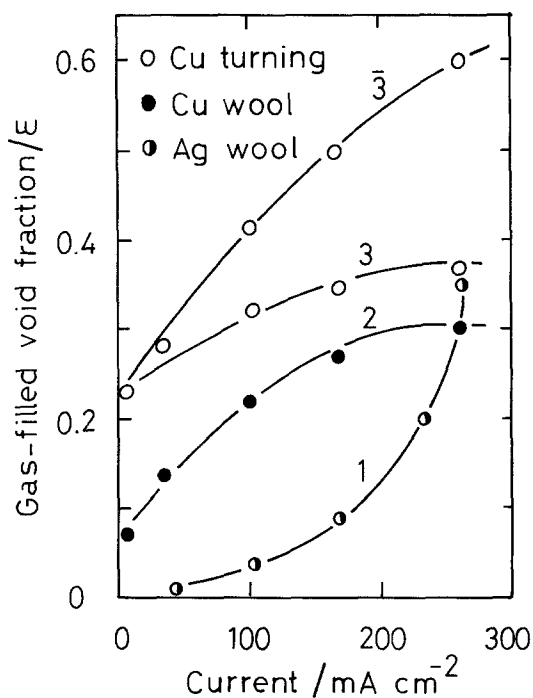


Fig. 6. Effect of the rate of hydrogen evolution on the volume void fraction of gas bubbles retained in packed beds. Curves 1–3 are for Ag wool, Cu wool and Cu turnings, respectively. Curve 3̄ illustrates the effect of local heating on Curve 3.

Fig. 6 shows the effect of the rate of hydrogen evolution on the volume void fraction,  $\epsilon$ , as calculated from Bruggeman's equation. As the current increases,  $\epsilon$  increases in the order Cu turnings > Cu wool > Ag wool. At the same rate of hydrogen evolution, the packed bed of Cu turnings retains (traps) a greater amount of gas than the Cu wool which in turn retains more gas than the Ag wool. This is compatible with the structural features of the packed beds (see Figs. 1a and b) and with the measured values of tortuosity (1.38, 1.23 and 1.12 for Cu turnings, Cu wool and Ag wool, respectively).

Consideration of the effect of local heating leads to a modification of the shape of Curves 1–3 in Fig. 6, although to varying extents. Thus, the curve representing the packed bed of Cu turnings will be affected most since it has the highest resistance and hence is heated most, whereas that for Ag wool will be least affected. A simple approximate numerical example illustrates this effect. Let us assume that the flow of 800 mA through the packed bed of Cu turnings causes local heating

which decreases the electrolyte resistance such that the measured value is actually half the true value. At lower currents, the extent of heating will be less; we take the resistance to be 2/3 of its measured value at 500 mA and 4/5 at 300 mA. We then calculate the (approximate) corrected value of  $\epsilon$ . Curve 3̄ in Fig. 6 shows the variation of  $\epsilon$  with current when we take into account the effect of local heating. The true curve would be quantitatively different from Curves 3 and 3̄ but closer in shape to that of Curve 3̄ than Curve 3. Curve 2 will be affected less than Curve 3, but more than Curve 1. Therefore, the marked effect of gas evolution on the resistance of pore electrolyte for packed Cu turnings as compared to Cu wool and Ag wool is attributed to a larger volume void fraction of gas being retained (trapped) within the packed Cu turnings as compared to Cu wool and Ag wool.

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