Application of porous flow through electrodes: IV. Hydrogen evolution on packed bed electrodes of iron spheres in flowing alkaline solutions

B. E. EL-ANADOULI, M. M. KHADER, M. M. SALEH, B. G. ATEYA

Chemistry Department, Faculty of Science, Cairo University, Cairo, Egypt

Packed bed electrodes of small iron spheres have been used for the electrolytic production of hydrogen from alkaline solutions at different temperatures under conditions of electrolyte flow. The effects of temperature, electrolyte type, concentration and flow rate on the polarization behavior of the electrode were evaluated and analyzed. It was shown that increases in the conductivity of the electrolyte or the operating temperature decreases the potential required to support the reaction. The generated gas bubbles disperse in the pore electrolyte, resulting in an increase in its resistivity and, subsequently, an increase in the potential. It was shown that some gas bubbles are trapped within the porous electrode. The implications of the trapped gas bubbles on the behaviour of the electrode are discussed.

Nomenclature

A geometrical cross-sectional area (cm^2)
a empirical constant $(cm^3\,C^{-1})$
b RT/F in volt, with R the gas constant, T the absolute temperature
E_0 electrode potential at the entry face (V)
E_L electrode potential at the exit face (V)
F Faradays's constant
i_0 exchange current density of the electrode reaction $(A\,cm^{-2})$
i_L experimentally measured current density at the exist face $(A\,cm^{-2})$
L bed thickness (cm)

q tortuosity
Q electrolyte volume flow rate $(cm^3\,s^{-1})$
V electrolyte flow rate, $V = Q/A$ $(cm\,s^{-1})$
S specific surface area of the bed (cm^{-1})
x position in the electrode
α transfer coefficient
ε gas void fraction
η_0 polarization at the entry face (V)
η_L polarization at the exit face (V)
θ porosity
ρ pore electrolyte resistivity $(\Omega\,cm)$
ρ^0 resistivity of the bubble-free pore electrolyte $(\Omega\,cm)$
ρ_b^0 resistivity of the bulk electrolyte $(\Omega\,cm)$

1. Introduction

Water electrolysis has traditionally been the means of obtaining very pure hydrogen. It is a rather simple one step process, hence it became the basis of the most proven technology for hydrogen production. The literature pertaining to the subject is already quite vast. A good deal of this literature can be found in several review papers, chapters, books or symposium proceedings [1–6].

It is now well established that the power consumption in an electrolysis cell is used to activate the electron transfer reactions at the electrodes and to overcome the resistance of the electrolyte, within which gas bubbles are dispersed. Since electrochemical reactions are essentially surface processes, their rates increase with the surface area of the electrode and/or its catalytic properties. This led us previously [7, 8] to consider the application of porous flow through electrodes for the electrolysis of water in order to gain the benefit of their large internal surface area in reducing the activation polarization and hence the

power consumption of the cell. These measurements were performed on relatively noble bulk metals, i.e. Cu and Ag in H_2SO_4.

The aim of the present work is to test the feasibility of using a packed bed electrode of iron spheres, for the hydrogen evolution reaction (h.e.r.) from alkaline solutions under flow conditions. The effects of electrolyte concentration (and hence conductivity), flow rate and temperature on the current–potential $(i–E)$ relations were evaluated and analyzed.

2. Experimental details

Figure 1 is a schematic illustration of the cell and experimental arrangements. The electrochemical cell was in the form of a cylindrical glass tube with a cross-sectional area of $2.32\,cm^2$. The electrode was prepared from spheres of carbon steel having a mean diameter of 0.36 cm. It had a porosity of 0.45, a specific surface area of $10\,cm^{-1}$ and a thickness of 1.9 cm. It rested on a fritted glass disc. The cell was held upright and the electrolyte was fed from the bottom (entry face) of the
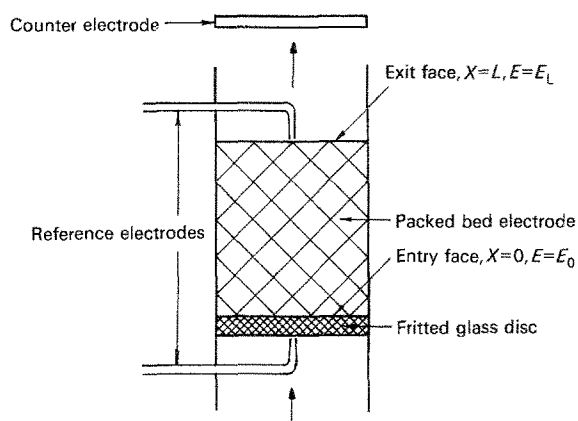
Fig. 1. Schematic of the cell and the experimental arrangements.

electrode, while the reacted electrolyte, along with the resulting gas bubbles, emerged from the top (exit) side of the electrode. The latter was polarized using a platinum counter electrode placed downstream. The potentials, E_0 and E_L, were measured using two Hg/HgO/1 M NaOH reference electrodes. The temperature was controlled to $\pm 2°$ C. The current density was calculated on the basis of the geometrical cross-sectional area of the electrode. Further details are reported elsewhere [7].

3. Results and discussion

3.1. Effects of electrolyte concentration and resistivity

Measurements were performed on solutions of either NaOH or KOH at various concentrations and temperatures. Figure 2 illustrates the effect of NaOH concentration on the i–E relations. The figure reveals some important features: (i) As the electrolyte concentration increases, E_L decreases as well as the ohmic potential drop through the pore electrolyte i.e. $\Delta E = E_L - E_0$. Note that the conductivities of NaOH solutions at 30°C are 0.11, 0.21, 0.40, and $0.40\,\Omega^{-1}\,\text{cm}^{-1}$ for the 0.5, 1.0, 3.0 and 5.0 M, respect-
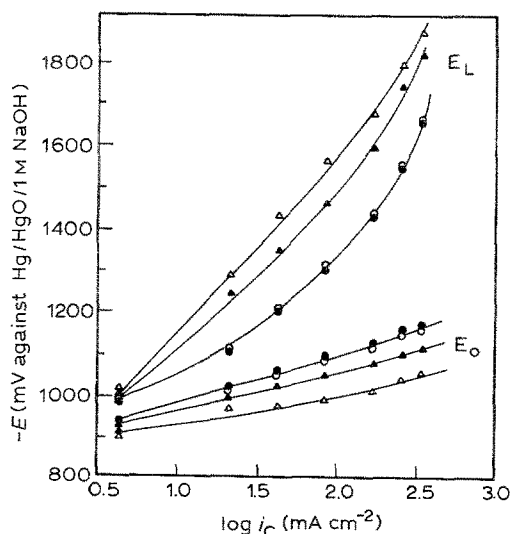

Fig. 2. Effect of electrolyte concentration on the i–E relations for the h.e.r. at 30°C: ($\triangle$) 0.5M, ($\blacktriangle$) 1.0M, (O) 3.0M and ($\bullet$) 5.0M NaOH.
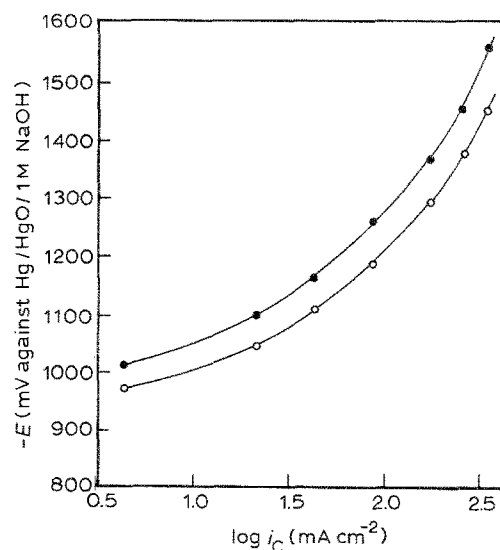

Fig. 3. Effect of alkali type on the i–E relations at 30°C: ($\bullet$) 6.0 M NaOH and (O) 6.0 M KOH.

ively [9]; (ii) The i–E relations for both 3.0 and 5.0 M NaOH solutions are essentially the same, despite the large difference in concentration. This is attributed to the fact that both solutions have the same conductivity. On the other hand, Fig. 3 shows a comparison between the i–E relations for both 6.0 M NaOH and 6.0 M KOH at 30° C. Clearly KOH requires lower potential than NaOH. Note also that the conductivity of 6.0 M KOH is $0.56\,\Omega^{-1}\,\text{cm}^{-1}$ while that of 6.0 M NaOH is $0.33\,\Omega^{-1}\,\text{cm}^{-1}$ at 30° C [9].

In view of the above results, it is concluded that the observed effect of alkali concentration on the i–E relations is indeed a conductivity effect. This conclusion is also supported by the fact that the h.e.r. in alkaline solutions results from the reduction of water, that is,

$$2H_2O + 2e^- = H_2 + 2OH^- \qquad (1)$$
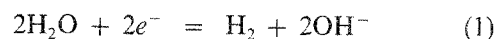
hence its rate is independent of the alkali concentration. Since water is always present in large excess even within the pores of the electrode, there is no possibility of any significant concentration polarization arising during the process.

3.2. Effect of flow rate

The operation of the electrode in a stationary mode leads to continuous increase in the potential as shown in Fig. 4. Ths is attributed to accumulation of the gas bubbles within the pores with simultaneous increase in the resistivity of the pore electrolyte and decrease in the internal surface area of the electrode in contact with the electrolyte. Both effects are detrimental to the behaviour of the electrode. The former increases the ohmic potential drop in the electrolyte, while the latter increases the activation polarization. As the electrolyte starts to flow, the potential decreases quickly indicating a decrease in the resistivity of the pore electrolyte, as a result of the removal of some accumulated gas bubbles.
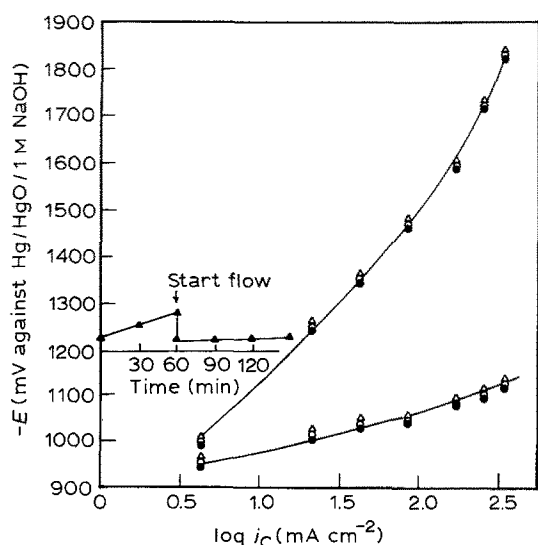
Fig. 4. Effect of electrolyte flow rate on the i-E relations for the h.e.r. in 1 M NaOH at 30° C. Inset: potential–time curve at a current density of 250 mA. Flow rate: ($\triangle$) 0.2 T, ($\bigcirc$) 0.89, ($\bullet$) 0.46 cm s^{-1}. ($\blacktriangle$) Effect of time on E.

Figure 4 shows the effect of flow rate on the i-E relations. Although the i-E relations are sensitive to the presence of electrolyte flow, they are not sensitive enough to variations in the flow rate over the tested range. This observation has two implications: (i) the rate of the process is independent of concentration or mass transfer effects. This is in agreement with the conclusion reached above; (ii) the flowing electrolyte does not sweep the bubbles fast enough to affect the pore electrolyte resistivity (see below).

3.3. Interpretation of the i-E relations

The results shown in Figs 2–4 indicate that the potential increases rather nonlinearly with the logarithm of the current output. The theory of operation of porous flow-through electrodes had been the subject of extensive mathematical modelling during the
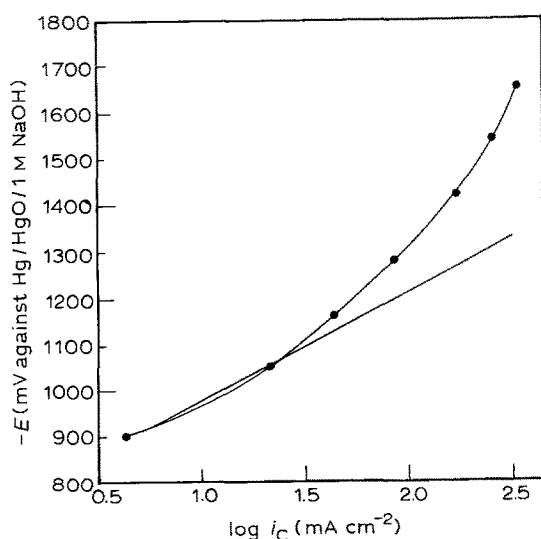

Fig. 5. Predicted and experimental i-E plots for the h.e.r. in 3 M NaOH at 30° C. ($\bullet$) Experimental, (———) theoretical (i = 2.3 × 10^{-4} A cm^{-2}).

last three decades [10–12]. Several analytical solutions for the equations of the proposed models, under various limiting conditions, were listed by Austin and Gagnon [13]. The existing mathematical theory of porous electrodes has no provisions for the effect of gas bubbles on the i-E relations. According to this theory [13] a linear relation is obtained between E and log i in the irreversible region with a slope of twice the normal Tafel slope, i.e.

$$\eta_L = E_L - E_{rev}$$
$$= (2b/\alpha) \ln i - (b/\alpha) \ln (2i_0 Sb/\alpha\rho) \qquad (2)$$

This equation predicts that the electrode potential increases as the pore electrolyte resistivity increases and/or the product $i_0 S$ decreases. A comparison between the experimental measurements and the predictions of Equation 2 is shown in Fig. 5 for 3 M NaOH at 30° C. The theoretical line is calculated using $\rho = 7.22\,\Omega\,\text{cm}$, $\alpha = 0.5$ and $S = 10\,\text{cm}^{-1}$. The best fit was found with a value of $i_0 = 2.3 \times 10^{-4}$ which is comparable to values reported in the literature [5].

In the present system, gas bubbles are generated profusely within the pores of the electrode. They are generated at much higher rates near the exit face of the electrode than near the entry face. Under these conditions, the conducting medium is a heterogeneous non-uniform mixture of three phases, i.e. solid iron spheres, liquid aqueous electrolyte and hydrogen gas bubbles. The geometry of the interfaces and the conducting medium within the porous electrode is difficult to predict. The electrical resistivity of such a medium is a complex function of the volume fractions and resistivities of the components [14]. Since the porosity is uniform throughout the packed bed, the variation in pore electrolyte resistivity is related to the variation in gas void fraction. There are several equations which describe the effect of gas bubbles on the resistivity of the electrolyte through which they are dispersed [14–16]. Of these, one might use the Bruggeman equation,

$$\rho(x) = \rho^0[1 - \varepsilon(x)]^{-3/2} \qquad (3)$$

Note that ρ^0 is related to the resistivity of the bulk electrolyte, ρ_b^0 by [17].

$$\rho^0 = \frac{\rho_b^0 q}{\theta} \qquad (4)$$

The local value of gas void fraction at any distance within the packed bed, ε, is related to the local current by [18].

$$\varepsilon(x) = \frac{ai(x)}{Q} \qquad (5)$$

For the h.e.r., $a = 0.127\,\text{cm}^3\,\text{C}^{-1}$ at 25° C and 1 atm. Substituting in Equation 3 yields,

$$\rho(x) = \rho^0 \left[1 - \frac{ai(x)}{Q} \right]^{-3/2} \qquad (6)$$

In view of Equation 6, the increase in current increases the potential by virtue of Equation 2, even for constant pore electrolyte resistivity. In the present

case the increase in current produces an additional increase in pore electrolyte resistivity, which is reflected in a greater increase in potential. Consequently, the increase in current produces a more progressive increase in potential in the presence, than in the absence, of the bubbles.

Some numerical calculations are useful at this point. Consider the case where $Q = 0.1\,cm^3\,s^{-1}$ and $a = 0.127\,cm^3\,C^{-1}$. At currents $i(x)$ of 50, 200 and 500 mA cm^{-2}, the values of $\rho(x)$ are $1.1\,\rho^0$, $1.6\,\rho^0$ and $4.5\,\rho^0$, respectively, i.e. the effective pore electrolyte resistivities are 1.1, 1.6 and 4.5 times greater than the value in the absence of gas bubbles. Clearly, as the pore electrolyte resistivity increases, the polarization increases.

This analysis does not preclude the possible masking effect of the trapped gas bubbles on the internal surface area of the porous electrode. The masked part does not support the reaction, hence progressively higher potentials are required.

3.4. Effect of temperature

Figure 6 shows the effect of temperature on the i–E relations for a packed bed electrode in 3 M NaOH. The results show that as the temperature increases, the potential (i.e. power consumption) decreases. This is attributed to two primary effects, i.e. to the effect of temperature on the kinetics of the electron transfer step and on the conductivity of the electrolyte. A third, secondary, effect may arise due to the effect of temperature on the surface tension and viscosity of the electrolyte and, hence, on the bubble size, which in turn affects the pore electrolyte resistivity.

4. Summary

From this study it may be concluded that:

(i) Packed bed electrodes, similar to those used here, may be used for the electrolytic production of hydrogen from flowing alkali solutions. With such systems,
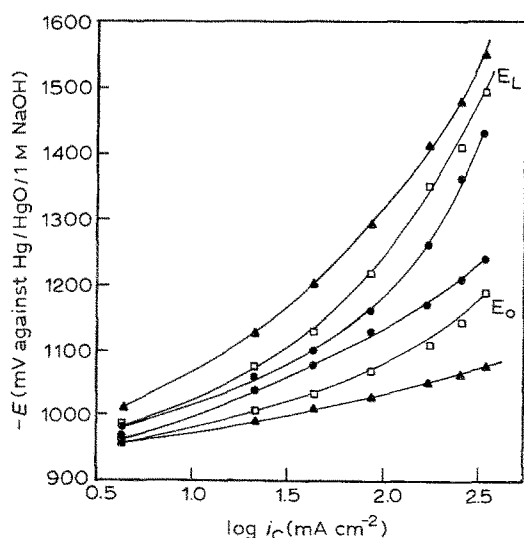
one gains the benefits of a large electrochemically active surface area in a small volume.

(ii) An increase in the electrolyte conductivity or temperature improves the behaviour of the electrode, i.e. decreases the potential and, hence, power consumption of the process.

(iii) Gas bubbles accumulate within the porous electrode with a resulting increase in potential. At higher currents, excessive potentials are obtained. This is attributed to the effects of trapped gas bubbles on the effective resistivity of pore electrolyte and on the internal surface area available for the electrochemical reaction. While their effect on the electrolyte resistivity was treated using Bruggeman's equation, their effect on the internal surface area is more difficult to analyze quantitatively. The subject is worthy of further analyses and measurements on the physicochemical and hydrodynamic aspects of the heterogeneous three-phase medium.

It is realized that a better-optimized electrode must be much thinner and of considerably larger specific surface area and exchange current density for h.e.r. than that used here. The present results confirm the feasibility and advantages of using such an electrode geometry and operating conditions.

References

[1]   T. Nejat Veziroglu (ed.), 'Hydrogen Energy', Plenum, New York (1975).
[2]   J. O. M. Bockris, 'Energy: The Solar Hydrogen Alternative', John Wiley & Sons, New York (1975).
[3]   D. Pletcher, 'Industrial Electrochemistry', Chapman and Hall, New York (1982), Chapter 5.
[4]   H. Wendt and G. Imarisio, J. Appl. Electrochem. 17 (1988) 1.
[5]   B. V. Tilak, B. W. T. Lin, I. E. Colman and S. Srinivasan, in 'Comprehensive Treatise of Electrochemistry', vol. 2 (edited by J. O'M. Bockris, B. E. Conway, E. Yeager and R. E. White), Plenum, New York (1981).
[6]   A. J. Appleby, M. Chemla, H. Kita and G. Bronoel, in 'Encyclopedia of the Electrochemistry of the Elements', (edited by Allen J. Bard), Marcel Dekker, New York (1982).
[7]   B. G. Ateya and E. S. Arafat, J. Electrochem. Soc. 130 (1983) 380.
[8]   B. G. Ateya, A. A. Ateya and M. E. El-Shakre, J. Appl. Electrochem. 14 (1984) 357.
[9]   D. Dobos, 'Electrochemical Data', Elsevier Scientific Publishing Company, New York (1975).
[10] J. Newman and C. W. Tobias, J. Electrochem. Soc. 109 (1962) 1183.
[11] J. S. Newman and W. Tiedman in 'Advances in Electrochemistry and Electrochemical Engineering', vol. 11, (edited by C. Tobias and H. Gerischer), Interscience, New York (1978).
[12] R. E. Sioda and K. B. Keating in 'Electroanalytical Chemistry', vol. 12 (edited by A. J. Bard), Marcel Dekker, New York (1982).
[13] L. G. Austin and E. G. Gagnon, AIChE J. 17 (1971) 1057.
[14] C. W. Tobias and R. E. Meredith in 'Advances in Electrochemistry and Electrochemical Engineering', vol. 2, Interscience, New York (1962).
[15] P. J. Sides, in 'Modern Aspects of Electrochemistry', No. 18, (edited by R. E. White, J. O'M. Bockris and B. E. Conway), Plenum, New York, 1986.
[16] H. Vogt, in 'Comprehensive Treatise of Electrochemistry', No. 6, Plenum, New York (1983).
[17] L. G. Austin in 'Handbook of Fuel Cell Technology', (edited by C. Berger), Prentice-Hall, New Jersey (1968).
[18] B. G. Ateya and B. E. El-Anadouli, 174th meeting of the J. Electrochem. Soc., Chicago, IL (1988).

Fig. 6. Effect of temperature on i–E relations for the h.e.r. in 3 M NaOH at iron spheres bed electrode. Temperatures: (▲) 50°C, (□) 50°C and (●) 80°C.