JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 321–327

Water electrolysis and pressure drop behaviour in a three-dimensional electrode*

V. D. STANKOVIĆ, R. GRUJIĆ

Technical Faculty Bor, University of Belgrade, VJ 12, 19210 Bor, Yugoslavia

A. A. WRAGG

School of Engineering, University of Exeter, Exeter, EX4 4QF, Great Britain

Received 17 February 1997; revised 28 May 1997

Water electrolysis from acidified solution was used as a model system to investigate the net contribution of hydrogen bubbles to the pressure drop increase in a three-dimensional electrode. A bed of silvered glass beads in both fixed and fluidized state was used, assuming an unchanging particle surface during the experiments. Pressure drop behaviour with time was measured for different experimental conditions and presented relative to the pressure drop determined for a bubble free bed. Parameters, such as current density, electrolyte velocity and particle size, greatly influence the relative pressure drop behaviour in the three-dimensional electrode. A sudden increase in the pressure drop occurs with the appearance of a gas phase in the bed, reaching a constant value (plateau) after a certain time; this plateau corresponds to steady state conditions. The pressure drop increases with increasing current density. This increase is in the range 40–150% relative to the bubble free electrolyte flow through the bed. Electrolyte flow-rate also strongly influences the pressure drop in the hydrogen evolving fixed bed electrode. It was observed that the relative pressure drop decreases with increasing electrolyte velocity. At higher flow rates, peaks occur on the pressure drop–time curves, indicating the existence of channeling inside the bed in which spouting occurs. The time to reach the pressure drop plateau decreases with increasing electrolyte velocity as do the time intervals corresponding to maximum pressure drop values. At the minimum fluidization velocity the peaks disappear and the relative pressure drop decreases with time, tending to approach a constant value. For hydrogen evolution in the fluidized bed, the pressure drop is lower than that measured in the absence of gas, and reason for this decrease being the gas hold-up in the bed.

Keywords: *3D electrode*, *water electrolysis*, *hydrogen bubbles*, *pressure drop*, *gas bubbles*, *fixed bed*

1. Introduction

Electrochemical cells with three-dimensional electrodes have been investigated extensively for use in the electrochemical treatment of dilute solutions containing heavy or noble metal ions. Using three dimensional cathodes, it is possible to reduce metal concentration in a treated solution down to less than 1 ppm [1–6]. Under galvanostatic operation, the appearance of gas bubbles within the cathode is possible due to hydrogen evolution occurring simultaneously with metal electrodeposition. Hydrogen evolution will also take place, together with metal deposition, when the depositing metal is less noble than hydrogen, such as in the case of Zn and Cd. The presence of a gas phase in the cathode compartment contributes to mass transfer enhancement, especially at low electrolyte flow rates [7, 8], but hydrogen bubbles in an electrolyte change its physical properties, among which increased resistivity is the most important characteristic [9, 10], giving increased specific energy consumption, as described by Stanković and Wragg [11]. Beside these two effects, the evolution of hydrogen bubbles in a fixed bed electrode also causes increased obstruction to electrolyte flow through a bed, as observed by Stanković and Milanov [12]. The increased resistance to electrolyte flow, monitored as a pressure drop increase, was first demonstrated by Millinger and Simonsson [13]. They observed an increase in pressure drop during long-term copper deposition experiments and this increase was attributed to a decrease in bed voidage due to the deposition of metal on the particles, thus producing local agglomeration leading to increased energy loss of the electrolyte.

Pressure drop behaviour in fixed and fluidized bed cells, in the presence of gas bubbles in the cathode has not been studied in detail [12, 14, 15] in spite of extensive investigations of three-phase fluidized or fixed beds [16–20]. Two effects contributing to the pressure

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* This paper was presented at the Fourth European Symposium on Electrochemical Engineering, Prague, 28–30 August 1996.

0021-891X

drop increase during simultaneous metal deposition and hydrogen evolution processes, are present [14]: a change in the particle surface roughness, due to progressive copper deposition and gas bubbles evolving on the particles producing a two phase gas–electrolyte mixture.

The aim of this work is to investigate the net contribution of hydrogen evolution to the pressure drop increase in a fixed bed electrode using water electrolysis as a model-reaction system, while a bed of silvered, monodispersed, glass beads served as the three-dimensional cathode.

2. Experimental details

Experiments were carried out using the cell schematically presented in Fig. 1. The cell was of rectangular geometry and made of plexiglass, with dimensions 55 mm × 100 mm and 300 mm in height. The cell was separated vertically by a diaphragm of porous plastic, which prevented passage of bubbles. Side taps were connected to a differential U-tube manometer, as shown in Fig. 1. The other components of the hydraulic flow circuits were centrifugal pumps, flowmeter, valves and electrolyte reservoirs.

A stainless steel sheet (100 mm × 145 mm) was used as a current feeder while the counter electrode was a lead sheet of the same dimensions. Silvered glass particles were used as the conductive dispersed phase, constituting the fixed bed. Two sets of particles, with nominal size 2 mm and 3 mm were used separately. Silvering of the particles was carried out in two stages: firstly chemically and, subsequently, electrochemically. Electroless deposition of silver onto the particles was realized using the classical method of silver ion reduction by means of glucose solution. Since this silver deposit is not mechanically stable and can easily be removed, electrolytic deposition was carried out in a second metallization step using the conventional silver cyanide plating electrolyte containing 40 g dm^{-3} Ag ions. The applied current density was in the range 50–100 A m^{-2}, and silvering was carried out in a shallow bed in a separate cell. In such a way adherent and dense silver deposits were obtained, on top of the initial layer. This electrochemically deposited layer had good mechanical characteristics. The fixed bed height was 150 mm in all experiments.

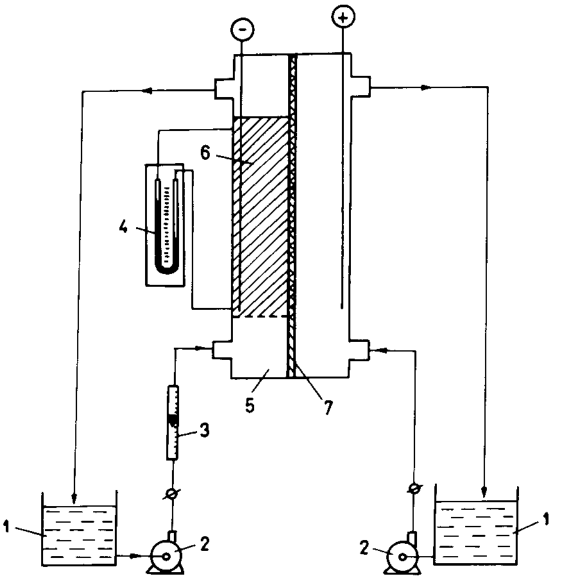

Fig. 1. Experimental setup: (1) reservoirs, (2) centrifugal pumps, (3) flowmeter, (4) U-tube manometer, (5) three-dimensional electrode cell, (6) fixed bed electrode, (7) diaphragm.

A 0.5 M solution of sulphuric acid in distilled water was used; both reservoirs contained 10 dm^3 of this solution.

Pressure drop in the cell was monitored using the U-tube manometer with carbon tetrachloride as manometer liquid. Experiments were carried out under galvanostatic conditions at different current densities and for different electrolyte flow rates. Experiments were conducted at ambient temperature.

Before switching on the cell the pressure drop, ΔP_0, was measured for a given electrolyte flow rate, as a reference value in the absence of a gas phase in the bed. After current switch-on electrolysis of water began and the change in pressure drop with time was measured. After termination of the experiment electrolyte flow was continued to remove residual gas from the bed. To reduce the time necessary the electrolyte flow rate was increased, so that fluidization occurred: the flow rate was then slowly decreased, to settle the bed back to the fixed bed form. The pressure drop registered at the beginning of the experiment, ΔP_0, should be equal to that obtained after removal of gas bubbles from the bed. Deviations from equality of these two pressure drop values, could be attributed to changes in particle packing before and after fluidization. To overcome this discrepancy in ΔP_0, from one experiment to another, for identical initial conditions, a relative pressure drop was used which is a ratio of any measured instantaneous pressure drop ΔP, to the initial pressure drop, that is $\Delta P/\Delta P_0$.

3. Results and discussion

A typical plot of pressure drop per unit bed height, against time, is presented in Fig. 2. The pressure drop increases steeply, following cell switch-on, and then tends to a constant value after a certain time. The value of the pressure drop plateau depends on the applied current density and the hydrodynamic conditions in the bed, that is: the interstitial velocity, the particle size and the bed voidage. The curve in Fig. 2, implies the existence of two process periods in which the pressure drop behaves differently, namely, in the initial unsteady period, where there is a strong dependence of $\Delta P/L$ with time and the second period, when steady conditions are established.

The pressure drop increase is caused by the presence of bubbles in the bed, especially coalesced bubbles bridging between particles, thus reducing the free cross sectional area for electrolyte flow. Detached gas

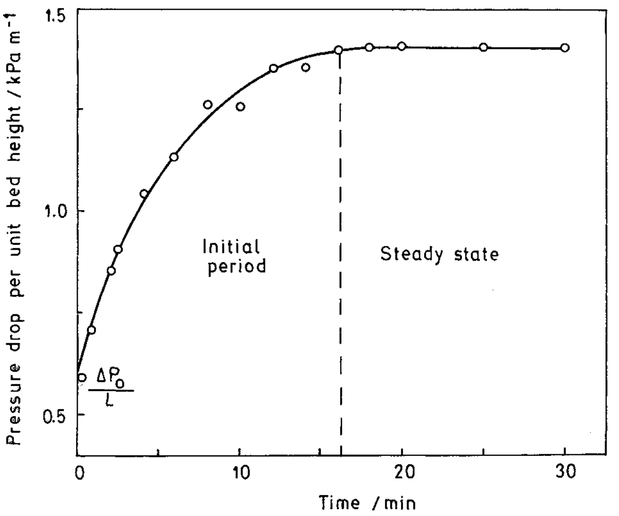

Fig. 2. Change of the pressure drop per unit bed length, with time: $i = 350\,\mathrm{A\,m^{-2}}$, $u = 0.8\,\mathrm{cm\,s^{-1}}$, $d_p = 2\,\mathrm{mm}$.

bubbles flow with the liquid phase forming a two-phase flow within the bed. Figure 3, illustrates the gas bubble behaviour in the bed. Since the gas hold-up, ε_g, which is defined as the ratio of gas volume, V_g, and bed volume, V_b, that is, V_g/V_b, increases with process time, it is clear that the pressure drop will consequently increase. The pressure drop plateau, in Fig. 2 corresponds to a maximum gas hold-up, $\varepsilon_{g,\max}$, in the bed for given experimental conditions. An equilibrium between the amount of generated gas per unit time and the gas removal rate per unit time is then established.

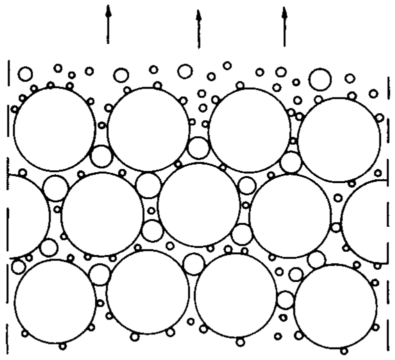

Fig. 3. Schematic of particles and bubbles in the bed.

3.1. *Effect of current density*

Figure 4 shows the relative pressure drop against time for a number of current densities. The pressure drop increases with increasing current density and this increase is in the range 40–150% relative to the bubble free electrolyte for current densities used in these experiments. Increase in the relative pressure drop with increasing current density is caused, by the higher hydrogen discharge rate. Increased gas content in the bed increases its resistivity to the electrolyte flow, thus increasing the pressure drop. The surface density of bubble sites, bubble detachment frequency and coalescence rate, all increase with increasing current density thus contributing integrally to the enhancement of the pressure drop. However, the net contribution of each factor cannot be estimated separately. The periods to reach steady state are longer

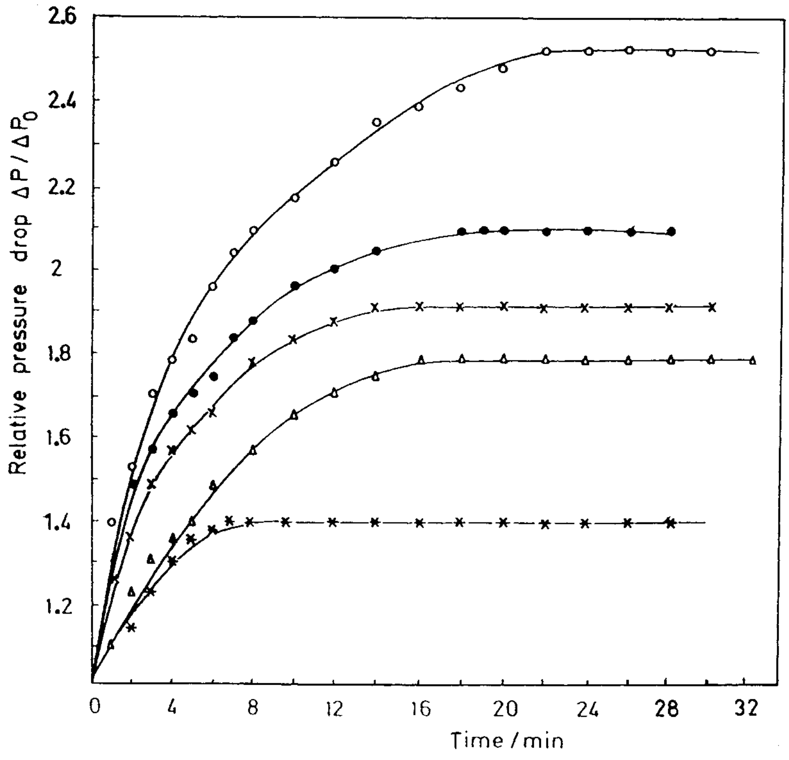

Fig. 4. Effect of current density on pressure drop against time. Current density: (*) 140, (△) 210, (×) 350, (●) 480 and, (○) 630 A m^{-2}. $d_p = 2\,\mathrm{mm}$, $u = 1.5\,\mathrm{cm\,s^{-1}}$.

with higher current density which may be attributed to the hydrogen evolution rate. Considering the initial periods of pressure drop rise, a linear region occurs at the beginning of the process, and the curves are steeper for higher current densities, indicating more rapid gas hold-up increase. Plotting the rate of pressure drop change in the initial period, against the current density, a linear relationship is obtained as shown in Fig. 5. This linearity implies a direct relationship between the gas evolution rate and the rate of pressure drop increase.

3.2. *Effect of electrolyte flow rate*

The electrolyte velocity strongly influences the relative pressure drop in the fixed bed as shown in Fig. 6. Three effects of flow rate on the pressure drop are evident. The first is the appearance of peaks on the curves at the higher electrolyte velocities. Namely, at low velocities (lower than $2.5\,\mathrm{cm\,s^{-1}}$ for the case presented in Fig. 6(a) there are no peaks on the curves. At moderate electrolyte velocities (higher than $2.5\,\mathrm{cm\,s^{-1}}$ in the case considered), peaks appear and are less prominent at the beginning tending to be higher and sharper with increase in electrolyte velocity as shown in Fig. 6(b). Such pressure drop behaviour may be attributed to channeling in some parts of the fixed bed closer to the diaphragm, where the bed is more active. During gas evolution spouting of the particles occurs here and there in the bed, forming small channels in which particles float upwards. Channels are not observed in the case of the pressure drop measurement in the bed in which bubble-free electrolyte flows at the same flow rate. An explanation for the existence of channeling in the fixed bed, resulting in the peaks on the relative pressure drop curves, is that the particles with bubbles attached to their surface have lower overall density and so that a lower upwards electrolyte flow is necessary to transform some parts of the bed from the fixed to the fluidized state. Bubbles which coalesce to a larger size and are captured in the bed, have a higher buoyancy effect, and such locations in the bed, containing larger bubbles, are potential sites for spouting. Recent data concerning the behaviour of gas bubbles, introduced concurrently with a liquid phase in a fixed bed, show an increase in bubble diameter with bed height due to coalescence, leading to varying hydrodynamics [18]. Entrainment of some particles with adjoining bubbles, due to an increased bubble buoyancy force supported by upwards liquid flow was also observed.

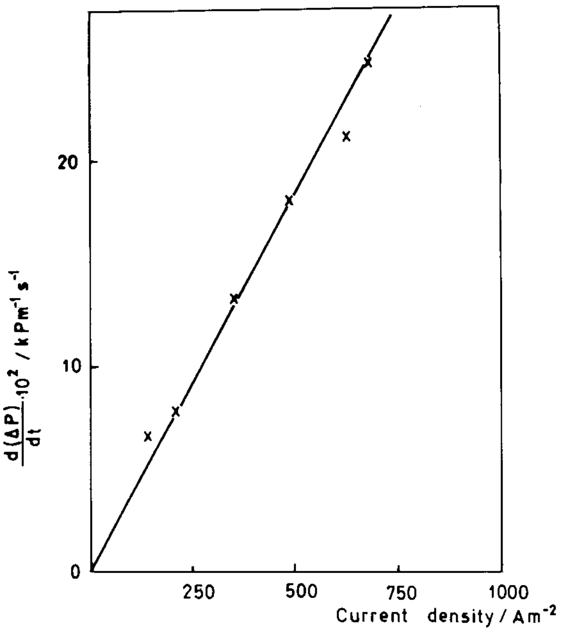

Fig. 5. Plot of relative pressure drop change, $d(\Delta P)/dt$, against current density

The decrease in the relative pressure drop plateau values $\Delta P_{\mathrm{pl}}/\Delta P_0$ with increase in the electrolyte velocity is the second notable effect in these investigations. Moreover, when the bed becomes fluidized, the absolute value of the plateau pressure drop, ΔP_{pl}, is less than that obtained in the bubble free bed (Fig. 6(b), the lowest curve). Based on three phase fluidized bed behaviour (Epstein [16] and Fan [17, 18]), it is possible to compare the pressure drop in a two- and three-phase fluidized bed. For a two-phase fluidized bed the pressure drop is defined by the well known equation:

$$\Delta P_0 = Ig(\rho_s - \rho_l)\varepsilon_s \tag{1}$$

where $\varepsilon_s = 1 - \varepsilon_l$ represents the hold-up of solids in the bed, L is the bed height, ρ_l and ρ_s are electrolyte and particle density, respectively and g is gravity constant.

For a three-phase fluidized bed an integral equation describing the pressure drop is

$$\Delta P = Ig(\varepsilon_s\rho_s + \varepsilon_l\rho_l + \varepsilon_g\rho_g) \tag{2}$$

where ε_l and ε_g are the hold-up of liquid and gas phase, respectively, and ρ_g is the gas density. Taking into account the relationship between phase fractions in the bed:

$$\varepsilon_s + \varepsilon_l + \varepsilon_g = 1 \tag{3}$$

and eliminating ε_l from Equation 2 gives:

$$\Delta P = Ig\left[\varepsilon_s(\rho_s - \rho_l) - \varepsilon_g\rho_l\right] \tag{4}$$

Subtracting Equation 4 from Equation 1 gives:

$$\Delta P_0 - \Delta P = Ig\ \rho_l\varepsilon_g \tag{5}$$

or in rearranged form, suitable for considering together with Fig. 6:

$$\frac{\Delta P}{\Delta P_0} = 1 - Ig\ \varepsilon_g\rho_l \tag{6}$$

Equation 6 clearly shows that the relative pressure drop in a three phase fluidized bed is less than unity as experimentally shown in Figs 6 and 7. The relationship between the relative pressure drop at steady state, $\Delta P_{\mathrm{pl}}/\Delta P_0$, and electrolyte velocity is given in Fig. 7. The pressure drop at steady state, ΔP_{pl}, decreases linearly with electrolyte velocity for both particle fractions used in these experiments. The

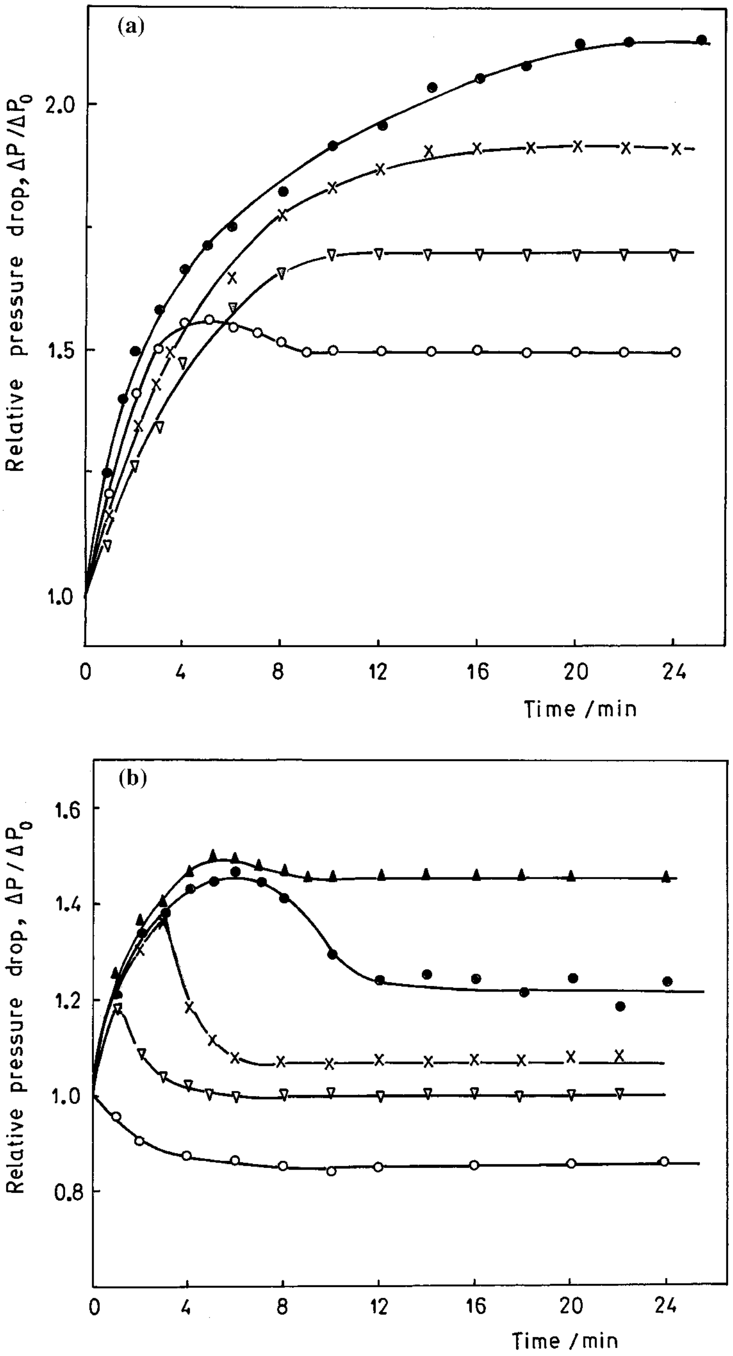

Fig. 6. Relative pressure drop behaviour with time for different electrolyte velocities. (a) At lower velocities (cm s^{-1}): (●) 0.8, (×) 1.5, (▽) 2.4, (○) 2.7; (b) at higher velocities when channels exist (cm s^{-1}): (+) 3.0, (△) 3.3, (▼) 3.8, (∗) 4.3, (▲) 5.3. $d_p = 2$ mm, $i = 350$ A m^{-2}.

decrease in $\Delta P_{pl}/\Delta P_0$ with increased electrolyte velocity is a result of reduced gas hold-up. The velocity increase complements the electrolyte buoyancy force that promotes the detachment of gas bubbles from the particles and their removal from the bed.

The time to reach the pressure drop plateau, as well as the corresponding peak values, become shorter with increase in electrolyte flow rate, as shown in Fig. 8, reaching zero value for minimum fluidization velocity. For the fluidized state, the peaks disappear and the relative pressure drop starts to decrease with time just after cell switch-on, tending to a constant value.

4. Conclusion

The presence of an electrogenerated bubble phase in a three-dimensional fixed bed electrode, causes an enhanced pressure drop in the cell. A sudden increase in the pressure drop occurs simultaneously with the appearance of hydrogen bubbles on the particle surface; the pressure drop reaches a constant value after a certain time. The pressure drop increases with increasing current density and this increase is in the range 40 to 150% relative to the bubble-free electrolyte in the current density range used in these experiments. This pressure drop increase is attributable

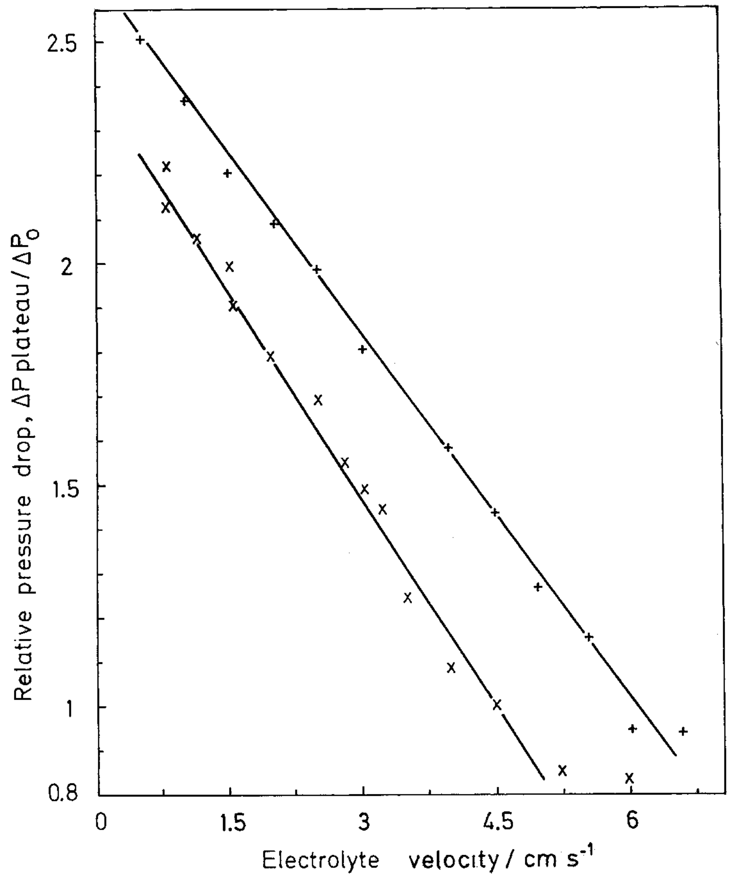

Fig. 7. Plot of relative pressure drop against electrolyte velocity at steady state: (×) $d_p = 2\,\text{mm}$, (+) $d_p = 3\,\text{mm}$. $i = 350\,\text{A m}^{-2}$.

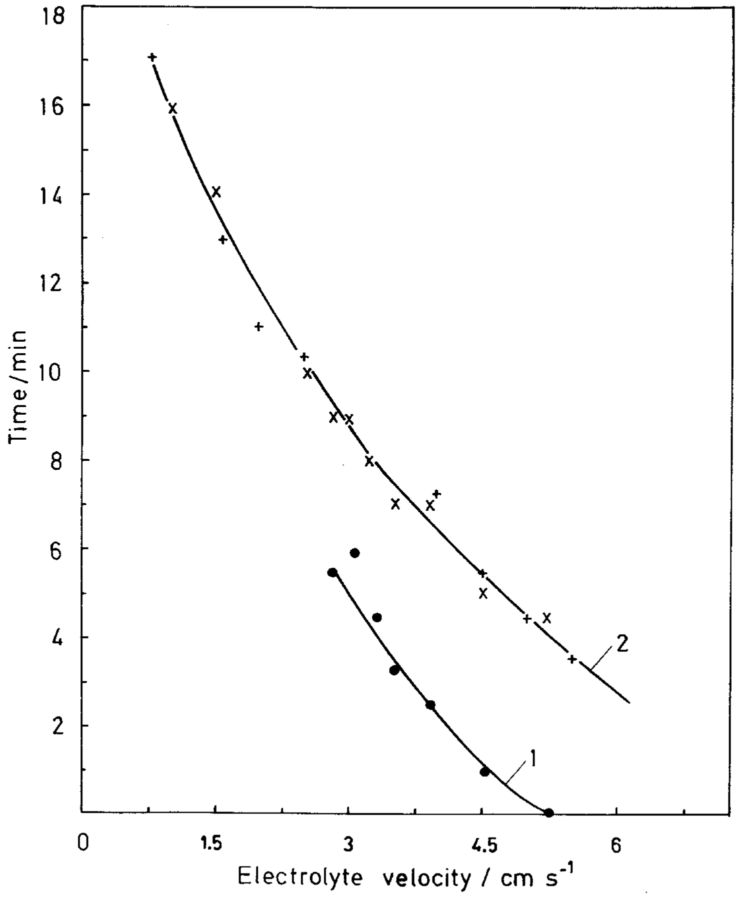

Fig. 8. Time to reach the pressure drop peak $\Delta P_{\max}$ (curve 1) and to reach steady state ΔP_{pl} (curve 2), against electrolyte velocity: $i = 350\,\text{A m}^{-2}$, (●, ×) $d_p = 2\,\text{mm}$, (+) $d_p = 3\,\text{mm}$.

to a change in the gas hold-up in the bed due to faster hydrogen evolution at higher current densities.

Electrolyte flow rate is the second parameter strongly influencing the pressure drop in the three dimensional cathode. The relative pressure drop at steady state decreases linearly with increasing electrolyte velocity. At higher velocities, peaks on the pressure drop against time curves appear before a steady state is reached. The peaks are more pronounced for higher flow rates. Times to reach a steady state decrease with increasing electrolyte flow rate, as do the times corresponding to maximum pressure drop.

Relative pressure drop in the fluidized state is lower in the presence of gas bubbles, compared to the electrolyte alone and the difference is proportional to the gas hold-up in the fluidized bed.

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