JOURNAL OF APPLIED ELECTROCHEMISTRY 9 (1979) 765–775

The role of electrode structure and surface texture in the performance of gas evolving electrodes

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Received 7 January 1979

The literature on gas-evolving electrodes is reviewed. Cell voltage measurements are reported for an undivided cell in NaOH at 70° C in which the cathode was mild steel plate, mild steel mesh or composites of both these materials. The anode was Ni-plated mild steel sheet or mesh. Variation in the structure of one electrode, leaving the other unchanged allowed changes in overvoltage to be measured. It is shown that substantial voltage reductions can be obtained using multiplex electrode structures and that these are mainly explicable in terms of specific surface areas. Sheet electrodes are seen to be more efficient than mesh ones on this basis however. It is shown that sheet electrodes with very high specific surface areas show significantly higher overvoltages than electrodes of low specific area and this surprising result is interpreted in terms of bubble entrapment.

1. Introduction

Problems relating to gas-evolving electrodes resolve themselves into three distinct areas. Firstly there is the problem of micro-release of bubbles from an electrode surface. This is an effect which is important at approximately the 1 mm scale, and is concerned with the adherence of bubbles to the electrode surface immediately following their generation. There is a whole body of literature (much of which has been summarised in [1, 2]) dealing with contact angles of bubbles immediately prior to their release, and the effect of the obvious parameters such as the metal used, the form and texture of that metal, the current density and the particular gas evolved (which has been shown to relate to the rational potential at which it forms). However these studies were not concerned with overvoltage measurements.

Secondly, there are the problems on the macroscale, that is to say the design of electrode structures which facilitate the discharge of a large volume of gas, with minimal electrode 'blinding' effects.

Finally, there is the totally different 'porous electrode' technology which has been derived from the reverse-sense operation of gas–liquid porous fuel cell electrodes.

In this paper, a brief review of these three areas is given, and experimental results are presented to show the effect of both micro-texture (electrode roughness) and structural effects on the much larger scale.

Cells with planar (or quasi-planar) vertical electrodes are prone to inequality of current distribution from top to bottom of the cell [3], mainly because the electrolyte at the lower part of the electrodes is virtually free from gas bubbles, while the liquid at the upper end of the electrodes is populated with the total gas evolved from the system [4].

A second problem concerning gas-evolving electrodes relates to their surface texture or roughness. It is widely believed that it is beneficial to increase the surface area of electrodes used on an industrial scale since this decreases the true current density and thus the electrode overvoltage. To what extent this philosophy is vitiated by the obscuration of the greater surface area by small bubbles which can lodge in the rugiosities characteristic of such surfaces appears as yet, to be undetermined.

The present work concerns itself with a

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preliminary examination of these two separate and yet related phenomena.

2. Structure and geometry of gas-evolving electrodes

The quantitative treatment of unequal current distribution in vertical cells due to differences of electrolyte medium resistivity has been considered by various authors [5–7].

Recognition of the importance of gas release in this context is reflected more by patents than by scientific publications. In metal-winning, shaped anodes [8] were introduced in which the anode–cathode gap increased as the height of the cell increased. This minimized the effects due to increasing gas-void fraction with cell height and also promoted more even mass-transport conditions as between top and bottom of the cell.

In chlor-alkali technology, and latterly in design of water electrolysers, a rather different approach has been adopted and a range of patents described means of venting gases formed at the front (i.e. facing the counter-electrode) of the electrode to its rear side. Thus German Patent DOS 2419 204 (1974 to Kureha) shows a series of baffles placed across the electrodes and inclined upwards to deflect the bubbles away from the electrode face; the voltage is thus reduced from 3·46 to 3·26 V at 15 A dm^{-2}. The stated intention of this patent is not so much a reduction of the volume of gas in the inter-electrode gap as the prevention of a 'gas-blanket' formation on the electrode surface. In another Japanese patent (German Auslege 2059 868 of 1970 to Nippon Soda) vertical electrodes fitted either with louvres or with slots ('cheesegrater') or similar apertures is described. Impressive voltage reductions in the examples are valueless since a precious metal oxide anode conforming to the patent is compared with a graphite one thus incorporating elements of genuine electro-catalysis effects in the data. In DOS 2527 873 (1976 to Olin Corp) steel mesh cathodes are provided with inclined ramps at regular intervals behind the mesh to facilitate bubble disengagement. Though no electrochemical data is quoted, tables show how, using compressed air to simulate bubble evolution, a very high percentage of the gas can be led away along the ramps. DOS 2430 444 (1975 to Oronzio de Nora) again features louvred mesh electrodes. French Patent 947 057 stresses the importance of open-structured meshes, while 2029 723 features a double-skinned cathode structure where gas escape takes place between the two. Both are quoted in French Patent 2303 093 (1976 to Rhone Poulenc) which also features perforated cathodes with a rear chamber for gas escape. DOS 2609 212 is a close equivalent to the French patent. Four patents which mention the problems of gas release in relation to 'finger' type mesh cathodes are DOS 2353 583 (1974 to Solvay) and three patents all similar and all assigned to Hooker–French Brevet 1530 541 (1968); DOS 2430 384 (1975) and US Patent 3871 988 (1975). German Offen Patent 2419 204 (1974 to Kureha), describes cells with gas-bubble guiding plates. Louvred anodes are disclosed in US Patent (4121 990) (1977 to ICI) and a similar, but much earlier version of the same idea is due to Baier [British Patent 730 649 (1955)].

One very different approach is featured in DOS 2344 647 (1975 to Metallgesellschaft). While gas release is also the aim here, the end is achieved by laying down, on vertical flat sheet anodes, vertical zones so treated to achieve a hydrophobic condition. The intention is that the bubbles shall spill over onto these zones and thus travel upwards. A voltage gain of 0·3 V is claimed at 1·2 kA m^{-2} on an 80 cm high cathode.

US Patent 3880 721, recognizes that bubbles are more easily detached from surfaces with a small radius of curvature, and describes an electrode consisting of very fine (2–10 'thou') wires mounted on a supporting/conductive element, which is itself masked-off from the electrolyte by means of a resin coating. German Patent 2735 237 (1976 to ICI) also uses wire anodes on a Ti back-plate. Not only the diameter of the wires but also their spacing one from another, is important, a spacing of about 8 mm seems to be the minimum for best performance.

In addition to the patents cited above, there are others, some of which are cited in [9–12] which suggest that gas release has been considered in their design, though the problem is not specifically mentioned.

This brief review of concepts of gas-release in industrial electrolysers would not be complete without mentioning the totally different approach of using a porous electrode structure and venting the gases at the rear of the electrode. By exploring the variables of pore size, or using a coarse and fine pore duplex structure, together with total or partial wet-proofing of the structure, some interesting effects can be obtained and these are described in the patents listed in [13–20]. Apart from the scientific publications [21–25] it would appear that this whole area of technology has been largely neglected by researchers, as opposed to inventors.

3. Surface treatment of electrodes

It is clear from the literature that many attempts have been made to maximize the specific activity of industrial electrodes. Broadly, we can subdivide these into attempts at creating on the one hand, the greatest possible surface area on a massive metal electrode (usually mild steel) by etching, rusting or sandblasting the surface prior to use. The accepted view on such procedures is that the initial benefit (at least at the cathode) is rapidly eroded by the deposition of metallic impurities such as iron, which is difficult to exclude at the ppm level from industrial plants. The alternative approach, which is scarcely less free from the same objection, is to deposit on the surface a coating intrinsically more electro-active than the basis metal on which it is formed. [26–38] contain a selection of patents and publications in this area in which the two main themes appear to be Raney-type leaching and flame/plasma arc spraying of metals to create a high surface area.

4. Basis of the present work

In this paper, we present results of two separate investigations. In the first section we present current–voltage data for electrodes (Ni and Fe) structures in which we have attempted to maximize the 'macro' surface area and also improve the means of gas-release. In the second part, an investigation of the effect of surface area treatment is given.

The effects described in the following sections pertain to the 'hour' timescale. During the experimental work, it was seen that current–voltage data required up to one hour to stabilize. On the other hand we are well aware of reports in the literature [39–43] of longer-term (days) effects occurring both at mild steel cathodes (ascribed to hydrogen permeation) and at Ni anodes (ascribed to changes of oxide stoichiometry). These effects fall outside the remit we have considered here.

5. Experimental

An extremely simple experimental rig was employed, and should be considered as a laboratory analogue of the widely used 'Tank' type water electrolyser [44]. Electrodes were mounted on stems of 25 cm length, these stems being sealed into glass tubing. An anode–cathode assembly was then made by mounting the two electrodes by their stems in a perspex block. The entire assembly was then rested on top of a 2 litre beaker, so that the electrodes themselves were well below the surface when the beaker was filled with liquid. The beaker itself was placed on a hotplate held at 70° C ± 2° C, and the temperature gradient from top to bottom of the inter-electrode gap was found to be less than $0{\cdot}2^\circ$ C, no doubt as a result of the vigorous stirring effects due to gassing. In all the work, an electrolyte of 5 M NaOH was used (GP grade). The sodium hydroxide was covered with a thin layer of paraffin, to prevent carbonation. No reference electrode was used, and all voltages are cell voltages. Since the electrolyte conditions were constant, and the anode-type was unchanged in all experiments where cathodes were studies and vice versa, the effect of electrode design can be unequivocally assessed. The inter-electrode gap remained the same within each set of experiments and in the case of electrodes with a finite thickness, the constant gap was maintained based on the separation from the front face of the structure. Current was supplied by a Farnell C2 constant current unit for low current (up to 2 A) and from a Westinghouse cinema-arc rectifier for larger currents (up to 100 A). The results reported relate to small electrodes ($4{\cdot}5$ cm^2 projected area) and larger electrodes (100 cm^2 projected area).

6. Electrode construction

The small ($4{\cdot}5$ cm^2) electrodes are seen in Fig. 1. The larger electrodes can be seen in Fig. 2. The small electrodes were simply sheets of mild steel or Ni-plated mild steel using the conditions described in [45]. Alternatively, mesh electrodes were used. Following this, composite electrode structures were assembled by spot-welding. Two meshes were superimposed and welded together, or even three layers. Alternatively, layers of mesh were superimposed on a sheet substrate. In one experiment, a 'sachet' of mesh was filled with wire wool. Finally, a series of duplex or triplex electrode structures was evaluated in which vertical spacer rods separated the layers. The effect of various rod thickness (i.e. separation of one layer from another) was explored. Much the same procedure was followed for the larger electrodes (100 cm^2). However, whereas epoxy resin, was satisfactorily used to mask off the rear of the small electrodes, it was found that this peeled off when attempts were made to mask the rear face of the larger electrodes. These were therefore mounted in a perspex 'picture-frame' as seen in Fig. 2, and fitted with a rear face of the same material. Electrodes were sealed into this with silcoset moulding compound. However it will be noticed that the top beading of the 'picture-frame' has been omitted to allow unimpeded escape of gas in the upward direction. Fig. 2 also shows that three stems were fitted to these larger electrodes (again cased in glass tubing). The outer two were connected together and power was fed to them. The inner one carried no current and was used solely for the measurement of potential (Keithley 4½ type 179 DVM). The data for these large electrodes shown in the figures is thus equivalent to 'voltage measured at terminal' in industrial parlance.

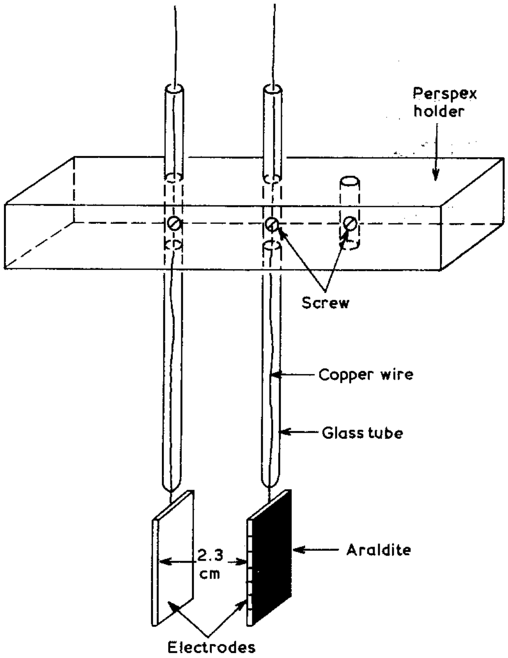

Fig. 1. Electrodes and mounting arrangement used for 4·5 cm^2 electrode testing.

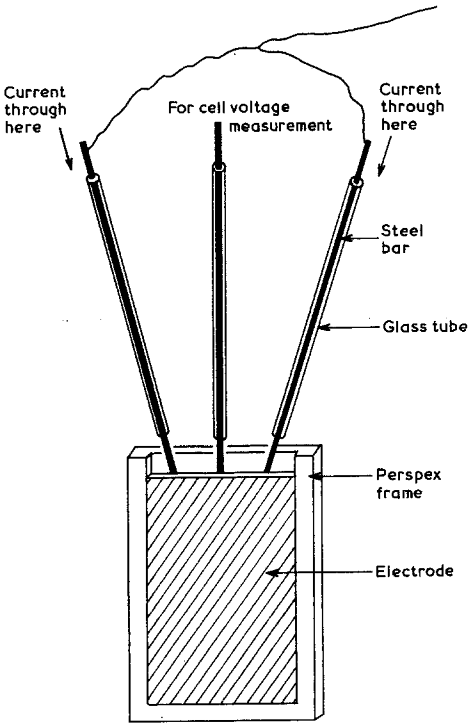

Fig. 2. Electrode configuration for 100 cm^2 electrodes.

7. Results

The data obtained is presented in graphic form in Figs. 3–10. The reproducibility of data from the same electrode in two successive runs was better than 5 mV. Data plotted is the mean of three (in some cases more) sets of results based on different electrodes made to the same specifications. The scatter here was somewhat wider; up to 20 mV in some cases, and this is understandable bearing in mind the non-uniformities of industrially-manufactured mesh material. The lines in all figures are drawn for best fit. The legends are self-explanatory except that a code is used to describe the electrode structures themselves. MSS denotes the mild steel sheet basis. Where spacers were used,

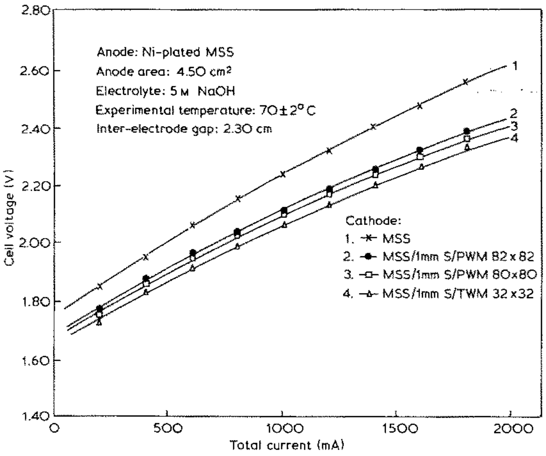

Fig. 3. Total impressed current versus measured cell voltage showing the effects of cathode structure using an identical anode (see text for structure code).

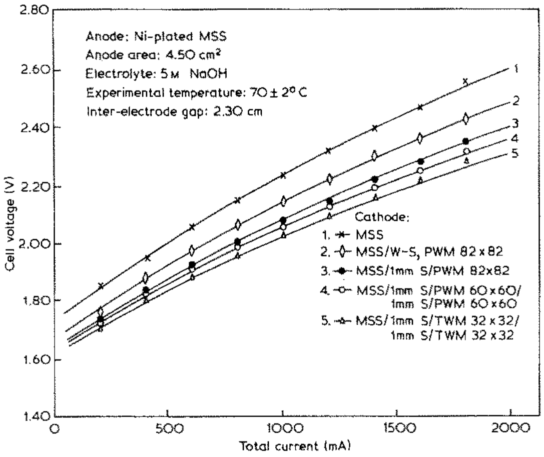

Fig. 4. Total impressed current versus measured cell voltage showing the effects of cathode structure using an identical anode (see text for structure code).

these are denoted by 1S (1 mm spacer). On top of this, one or more meshes were used. These were either plain weave (PWM) mesh or twill-weave (TWM) mesh. The following numbers, e.g. 60 x 60, indicates the wire gauge in the mesh and the denseness of the weave. These are standard terminologies in the wire-mesh weaving industry.

8. Discussion

Although mesh electrodes are widely used in industry, not least as cathodes in chlor-alkali cells, only single layers appear to have been used, and these are normally large-apertured slitted metal ('Expanded Metal' or 'Expamet') rather than the much closer-textured woven meshes discussed in this paper. The latter possess much greater specific surface areas than the former. Only one publication appears to treat gas evolution at mesh electrodes, including multiply stacked meshes, and this is the paper by Fouad *et al.* [46]. However the emphasis here is on gas bubbles to enhance mass-transfer and no reference at all is made to reduction in overvoltage, indeed no voltage measurements are reported here.

The current–voltage data is shown in Figs. 3–10. Although it is clear that large voltage reductions can be obtained by use of multiple mesh screens (and this does not appear to have been previously examined) the shape of the curves and their relation one to another, is not easy to interpret. In the majority of cases, visual inspection shows that $\mathrm{d}V/\mathrm{d}i \neq$ const, indeed, rather, it appears that $\mathrm{d}(\Delta V)/\mathrm{d}i \approx 0$, thereby implying that

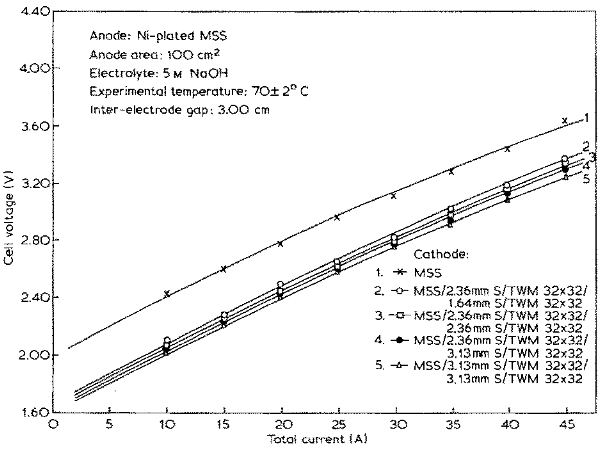

Fig. 5. Total impressed current versus measured cell voltage showing the effects of cathode structure using an identical anode (see text for structure code).

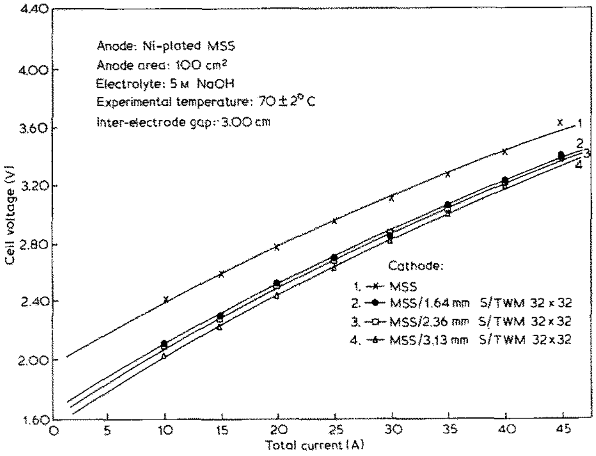

Fig. 6. Total impressed current versus measured cell voltage showing the effects of cathode structure using an identical anode (see text for structure code).

the resistance of the inter-electrode medium remains constant. To the slight extent this is not true, it would signify that bubbles (in the case of duplex structures) had escaped behind the electrode rather than in front of it, and presumably the data could be analysed on the basis. But the major trend is a simple and current density-independent reduction in E, the cell potential and the only immediate explanation of this lies in terms of a reduction, in the case of the composite electrodes, in the fraction of surface obscured by bubbles. More exact analysis of this situation must be extremely difficult. On the one hand, as Matov and other authors have shown, bubble release is favoured by using as electrodes, wires of small radius. However if too fine a mesh is used, surface tension forces will allow bridging of bubbles from one wire to an adjacent one so making release more difficult again. Presumably the optimum (with surface area as a further parameter) is struck in some intermediate position.

The above data was recalculated in terms of current density–voltage data. To do this, the area of each mesh was calculated by taking the surface area of the wires of which the mesh was made but subtracting the area of each hemi-cylinder of wire of diameter d hidden behind each crossing of the weave (Fig. 11). The resulting data is shown in Figs. 12–17. From these five plots, a number of facts become clear. In the first place (Fig. 12) it is seen that in the case of a duplex electrode structure, the reductions in cell voltage seen in Figs.

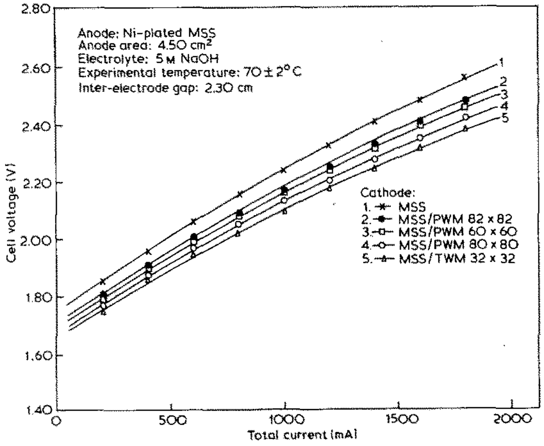

Fig. 7. Total impressed current versus measured cell voltage showing the effects of cathode structure using an identical anode (see text for structure code).

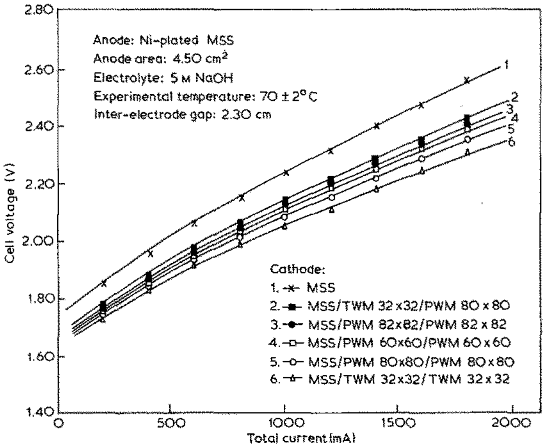

Fig. 8. Total impressed current versus measured cell voltage showing the effects of cathode structure using an identical anode (see text for structure code).

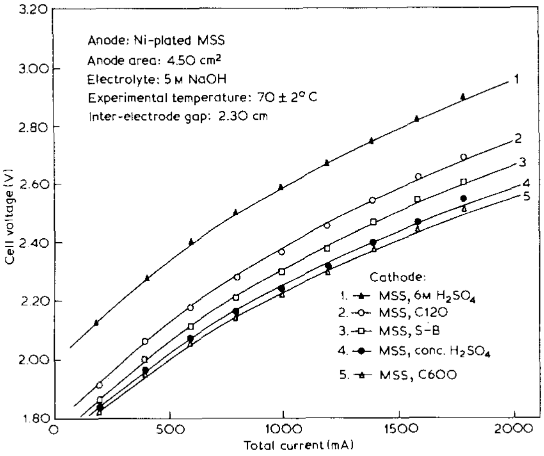

Fig. 9. Total impressed current versus measured cell voltage showing the effects of cathode surface treatment using an identical anode (see text for structure code).

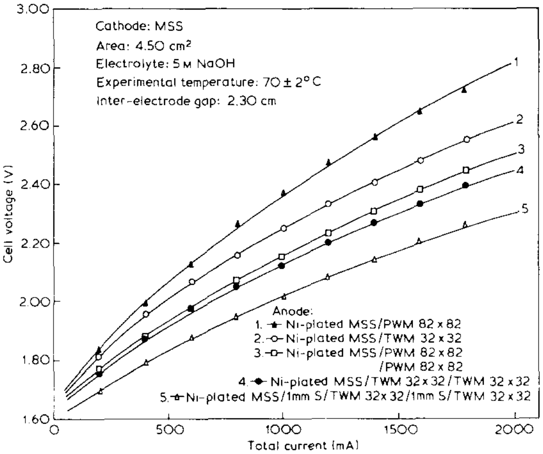

Fig. 10. Total impressed current versus measured cell voltage showing the effects of anode structure using an identical cathode (see text for structure code).

3–10 are simply due to an increase in macrosurface area, and when re-plotted against current density, these disappear. The notable exception to this is the simplest electrode of mild steel sheet and here it is seen that this electrode shows very much lower (Fig. 14) overvoltages at the same current densities than the corresponding mesh composites, and that the divergence becomes progressively greater as current density increases. This shows the effect to be one of bubble release and in no way connected with any uncorrected surface area effects. In Fig. 13, the same approach has been applied to duplex electrodes with spacers and (though the scatter is slightly larger) the effects are again seen to be due to simple differences of surface area. In Figs. 15 and 16 which relate to triplex structures, the scatter is even greater. The data can best be surveyed when a collection of single, duplex and triplex structures are plotted simultaneously as in Fig. 14. It now becomes clear that as an extra electrode surface is created by adding further layers of mesh, the electrode area is increased but diminishingly so. This we must attribute not so much to the increasing inter-electrode gap of the rear layers, since calculation readily shows that in a medium of high conductivity and with relatively small additional distances, this effect is small, but rather to the much higher resistance created by the curtain of gas bubbles formed at the forward electrode screens. The effect is seen (Fig. 10) to apply equally to anodes. The question thus arises as to what extent one can maximize the effective depth of what is a three-dimensional gas-evolving electrode structure. We believe the answer is not readily susceptible to cal-

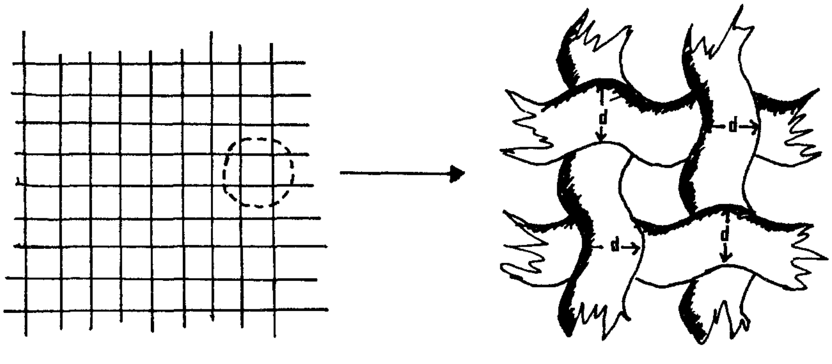

Fig. 11. Close-up view of mesh, showing 'obscured' area subtracted from calculated total surface area.

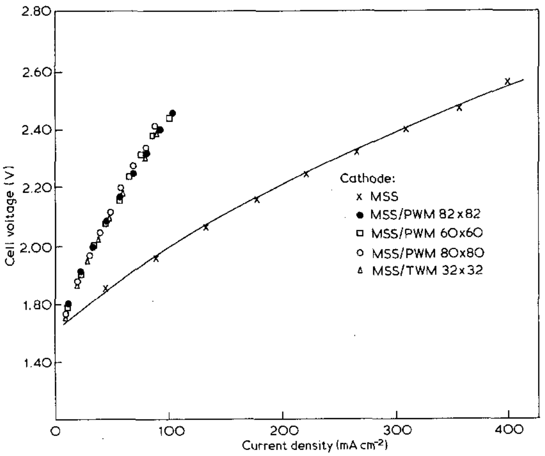

Fig. 12. Current density (calculated on the basis of exposed geometric area) versus cell voltage (see text for structure code).

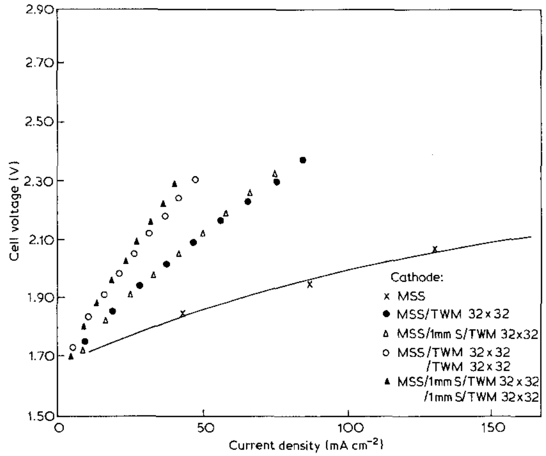

Fig. 14. Current density (calculated on the basis of exposed geometric area) versus cell voltage (see text for structure code).

culation, and that an interactive situation will develop where the fraction of current passed at the rear electrodes depends on the rate of gas-release at the forward ones; in particular the rate of release at the rear face of the forward members. It may be asked why the 'macro-surface' area cannot be extended by corrugation or pleating of the sort of structure described here. Such ideas have been advanced in [47] while several recent publications have devoted themselves to calculation of current distribution in such structures [48–51] in which various parts of the electrode are closer or further from the counter. These papers do not consider gas-evolving electrodes which represent a far more complex situation, since the propensity of gas bubbles to lodge in recessed areas of the electrode will even further increase the resistive path to that area and so lower the current fraction there even further. Electrode effects of this kind must therefore be further investigated on an empirical basis in order to explore the relationship between the parameters involved and to optimize the structure. It is broadly true to say that the size of the mesh apertures used in this work is of the same order as the mean bubble size for wire electrodes of the diameter in question [52, 53]. In terms of a single mesh, one might consider a bubble-release model where up to four bubbles

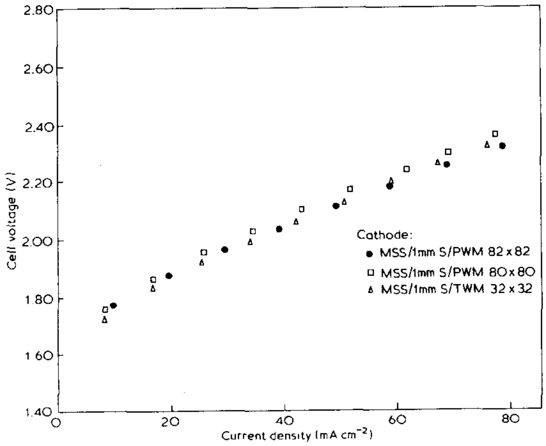

Fig. 13. Current density (calculated on the basis of exposed geometric area) versus cell voltage (see text for structure code).

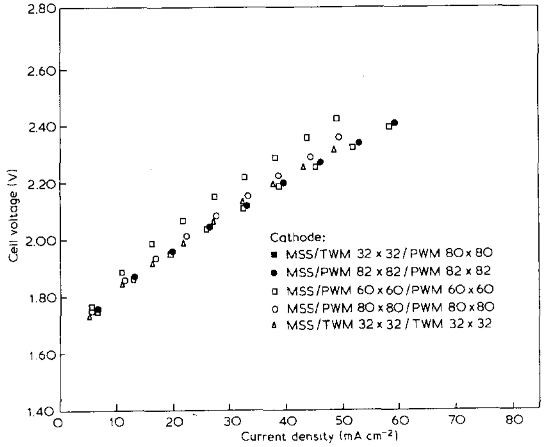

Fig. 15. Current density (calculated on the basis of exposed geometric area) versus cell voltage (see text for structure code).

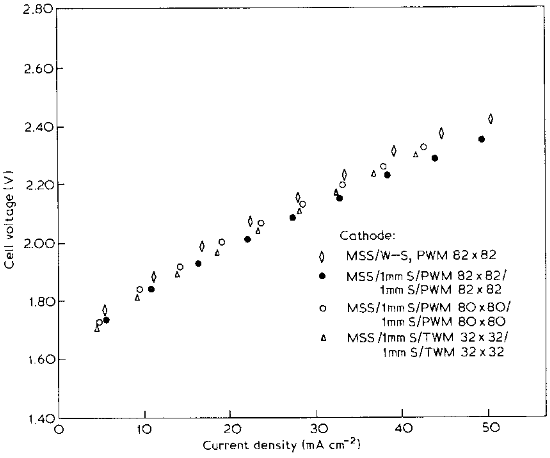

Fig. 16. Current density (calculated on the basis of exposed geometric area) versus cell voltage (see text for structure code).

(one on each side of the square aperture) formed and then coalesced. In terms of duplex structures, there might be an additional dimension to this situation in which bubbles were 'caged' between the two parallel meshes. The importance of such processes calls for further analysis both with respect to the approach to steady state and the final condition itself, and these matters are being studied.

9. Surface treatment of electrodes

Fig. 9 shows how the pre-treatment of a mild steel sheet cathode can drastically affect the current-voltage performance. The five lines relate to chemical etching in 6 M sulphuric acid (1) or in concentrated (BDH GP grade) sulphuric acid (4), to surface treatment with 120 or 600 grade emery paper (2 and 5) or bead-blasting (3) using glass beads. The effect of such treatments on the surface is seen in the SEM photographs (Fig. 18) A–E. There appears to be an inverse correlation between the perceived roughness and the measured current–voltage behaviour, and the highly damaged and deeply cratered structure of the bead-blasted surface, though it must have intrinsically a very high surface area, could well harbour bubbles over a large fraction of its surface and thus effectively become a low-surface area electrode after a short time on load. This trend seemed so surprising to us that one of us (P.H.) repeated the work to confirm the earlier findings. Fig. 18F shows a bead-blasted (4 'thou' glass beads in a Honermaster SH 100-217 airbrasive machine) which gave cell voltages of about 25 mV higher than those obtained with the electrode treated with 600 grade emery paper. The voltage reduction is less than that seen in Fig. 9, and the surface is correspondingly less contoured, thereby confirming the finding. At the relatively smooth surface achieved by fine-grade emery polishing, bubble-release is clearly much easier, and the population at any one instant might thus be smaller.

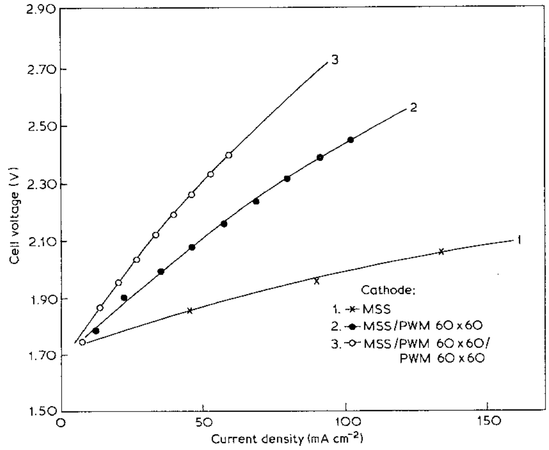

Fig. 17. Current density (calculated on the basis of exposed geometric area) versus cell voltage (see text for structure code).

We have searched for other studies in this area, but apart from the work of Smith [54, 55] who considered bubble effects on smooth electrodes, and papers by Thonstad [56] relating to bubble effects at horizontal or inclined electrodes and Ibl [59], there is only the work of Kitano [57] which is not available in translation. The latter investigation concerns bubble effects at mercury cell anodes.

10. Conclusion

We submit that even in an apparently well-defined electrode–electrolyte system such as mild steel–alkali, there is much scope for maximizing the performance of a gas-evolving electrode structure. The fate of the gas bubbles in determining the overvoltage is clearly of very great importance. In this connection, and with DOS 2344 647 very much in mind, the question must be asked to what extent the claims made for novel electro-catalysts as gas-evolving electrodes rest on the catalysts

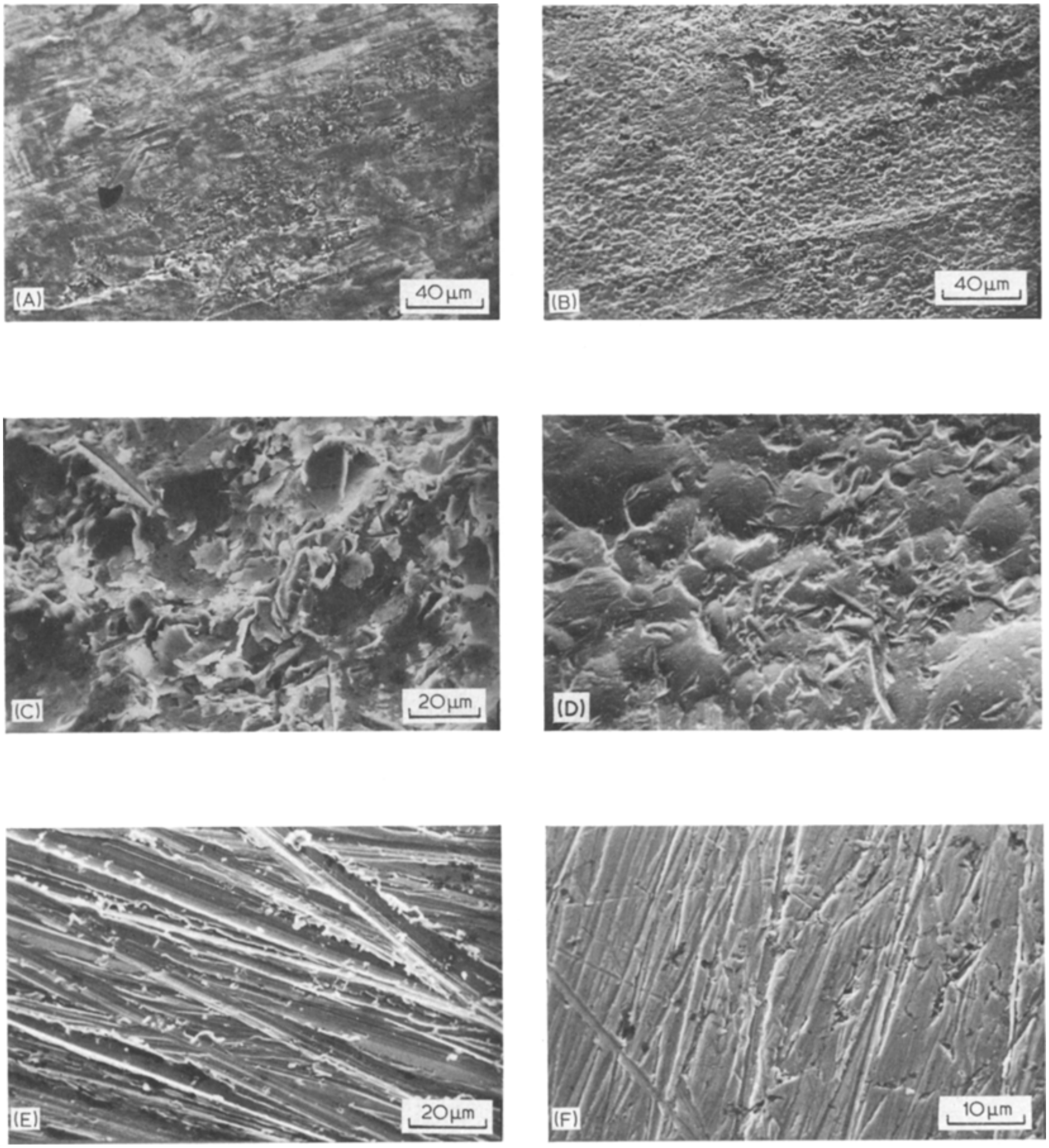

Fig. 18. SEM photomicrographs of mild steel sheet treated as follows: A, etched for 5 min in 6 M sulphuric acid; B, etched for 5 min in concentrated H_2SO_4; C, bead-blasted (about 3 min); D, bead-blasted (about 1 min) (X 850); E, polished, C120 grade emery paper; F, polished, C600 grade emery paper.

themselves, and to what extent the p.t.f.e. or other hydrophobic material used as binder confers advantages over straightforward metallic electrodes and is responsible for their frequently superior performance. Further research in progress will, it is hoped, shed light on this question.

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