JOURNAL OF APPLIED ELECTROCHEMISTRY 15 (1985) 575–580

*Gas evolution on porous electrodes**

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Received 26 October 1984

The factors governing the choice and strength of electrocatalyst aggregates in Teflon (PTFE) bonded electrodes are discussed in terms of their preparation routes. For electrocatalysts prepared via physical routes, the aggregates are very weak while those prepared via chemical routes are strong enough to withstand the pressures generated inside the pores during gas evolution reactions. Effectiveness factor and catalyst loading investigations show conclusively that the existence of dry PTFE channels provide a convenient pathway for the gas bubbles to escape, thereby ensuring the interior of the electrode will not be completely denuded of electrolyte, thus allowing more of the electrocatalyst surface to be utilized.

1. Introduction

Gas evolution reactions are one of the most common types of electrode reaction in the electrochemical industry. Though a significant number of studies have been made on the effect of Teflon bonded electrode structures on the performance of fuel cells [1–3], comparatively few studies have been made on their use in gas evolution reactions. Most of the commercial Teflon bonded fuel cell electrodes are based on precious metal–carbon electrocatalyst and such electrodes invariably disintegrate on gas evolution. However, work on high surface area semiconducting oxide electrocatalysts [4–6] have necessitated the use of Teflon bonded electrode structures and the experience gained from such studies have resulted in a better understanding of the factors affecting the strength, performance and stability of such electrodes in gas evolution reactions. This paper briefly reviews the work done in this field.

2. Fabrication and structure of Teflon bonded electrodes

Basically, Teflon bonded electrodes are prepared by mixing an aqueous dispersion of polytetrafluoroethylene (PTFE) with electrocatalyst powder in a suitable proportion and then applying the resultant mixture to a current collector, usually a metallic mesh, followed by curing at about 300° C for 1 h to remove the Trixton X-100 wetting agent from the PTFE surfaces and to bond the electrocatalyst together [1–2]. Electron microscopic studies showed that the electrode is composed of two porous, continuous phases intimately intermingled together – the porous electrocatalyst phase is hydrophillic and is filled with electrolyte when in use; the porous hydrophobic PTFE phase remains dry and allows rapid diffusion of gas in and out of the flooded electrocatalyst aggregates. Provided the size of the aggregates are relatively small (2–3 μm), the concentration polarization can be greatly reduced even at 1 A cm^{-2} [3]. This 'flooded aggregate model' has become the basic model for the optimization of Teflon bonded electrodes used for gas dissolution reactions [7].

3. Factors governing the strength of Teflon bonded electrodes

3.1. *Pressure generated inside catalyst pores during gas evolution*

At low current densities, the amount of gas pro-

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* Paper presented at the International Meeting on Electrolytic Bubbles organized by the Electrochemical Technology Group of the Society of Chemical Industry, and held at Imperial College, London, 13–14 September 1984.

0021-891X/85 $03.00 + .12

duced is low enough for it to dissolve in the electrolyte and diffuse out of the pores without the formation of bubbles. However, as the current density increases, the rate of diffusion of gas through the electrolyte is no longer fast enough and bubbles are formed. In order for these bubbles to escape, the gas pressure in the pore must exceed the value given by

$$P = 2\gamma\cos\theta/r \qquad (1)$$

where P is the gas pressure; γ is the surface tension of the electrolyte; r is the pore radius; and θ is the contact angle. If we assume that the contact angle is zero, then the maximum pressure which can be developed in a pore of radius r is $2\gamma/r$. This pressure is of the order of 1000 atm for a 2 nm pore and 100 atm for a 20 nm pore.

Since the pore size of the catalyst aggregates is usually in the region of 2–5 nm, it is important to use catalyst aggregates which have sufficient mechanical strength to withstand the relatively high gas pressures generated during gas evolution reactions.

3.2. *Effect of preparation methods on the strength of catalyst aggregates*

There are many methods for the preparation of high surface area catalysts, but they essentially follow two distinct routes [8]:

(a) Physical route. This route involves the breaking up of solid–solid bonds in a solid by physical means, e.g. grinding or arc vaporization. The resultant fine powders may still form aggregates but the strength of the aggregates is likely to be low since there are no solid–solid bonds between the particles.

(b) Chemical route. This route involves the formation of particles by joining ions and atoms together to form particles of metals or compounds and in the process, the particles are joined together at contact points by solid–solid bonds, e.g. chemical precipitation, followed by thermal decomposition to form mixed oxides; *in situ* chemical reduction of metallic salts to form metallic blacks, etc. Therefore, catalysts prepared by a chemical route should have stronger aggregates.

3.3. *Theoretical strength of a pore* [9]

Let us consider the pore as a thin walled cylinder of wall thickness h and inside radius r, subject to a uniform internal pressure, p. To determine the circumferential stress, S_c consider a section of the cylinder of length l. Figs. 1a and b show the forces (F) acting on a cross section of the cylinder. The components of the radial pressure orthogonal to line ab cancel one another by virtue of symmetry about this line. In the direction ab, the equilibrium equation is

$$\Sigma F_V = -2S_c hl + \int_0^\pi pr(\mathrm{d}\theta)(\sin\theta) = 0. \qquad (2)$$

Integration gives

$$2S_c h = -prl\,[\cos\theta]_0^\pi \qquad (3)$$

Therefore,

$$S_c = \frac{pr}{h} \qquad (4)$$

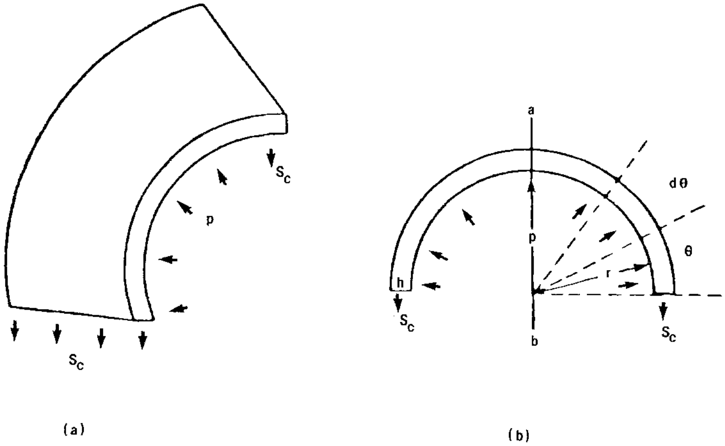

Fig. 1. The strength of a model pore.

The tensile strength of annealed platinum is 20 000 psi [10] and if h is 10^{-6} cm and r is 2×10^{-7} cm, then p for platinum black is 6×10^3 atm. This calculation indicates that even pores of radius greater than 1 nm could be stable. On the other hand, graphite particles are only bonded to each other by weak Van der Waal's bonds and would not be strong enough to withstand the pressure generated.

3.4. *Electrochemical evaluation of aggregate strength [11]*

Electrocatalysts produced by physical and chemical routes were evaluated for mechanical stability as a function of current density. In the case of graphite and tungsten carbide, both produced by physical routes, disintegration set in at about 40 mA cm^{-2} on hydrogen evolution. The same electrodes disintegrate above 15 mA cm^{-2} on oxygen evolution. For electrodes made from electrocatalysts produced via chemical routes, e.g. platinum black, $NiCo_2O_4$, there was no deterioration even at 1 A cm^{-2}. Thus, the above hypothesis has been validated. Since hydrogen has a similar solubility and greater diffusivity than oxygen (about 3 times greater), it is not surprising that the critical cathodic current density for the disintegration of Teflon bonded electrodes based on catalysts produced by physical routes is also significantly higher, despite the fact that the volume of hydrogen produced per Faraday is twice that of oxygen.

4. Comparison of gas evolution performance from non-Teflon bonded and Teflon bonded electrodes [12–14]

In the case of non-Teflon bonded porous electrodes, such as those prepared by thermal decomposition of metallic salts onto metal meshes, only a small part of the available electrocatalyst area is expected to participate in hydrogen or oxygen evolution reactions. Since the gas bubbles produced inside the pores push the electrolyte out of the pores, rendering the bulk of electrodes inactive, the electrochemical reaction will be concentrated at the uppermost layers of the electrode. For Teflon bonded electrodes, the dry PTFE channels offer rapid escape avenues for the gas bubbles and hence the interior of the electrodes will not be completely denuded of electrolyte, thus allowing greater utilization of the available electrocatalyst area. In order to test the above hypothesis, two different evaluation techniques were used:

(a) Effectiveness factor. This is defined as steady state performance × transient performance. The transient performance is measured by a potentiostatic pulse method [11]. Since the transient current represents the maximum attainable current in the absence of mass transfer effects, all the available electrocatalyst area is utilized. The steady state performance, however, gives the current output from the electrocatalyst area which has not been denuded of electrolyte. An efficient electrode structure should therefore have a high effectiveness factor. Table 1 gives the effectiveness factor of Teflon bonded and platinized platinum electrodes [13]. The results clearly indicated the superiority of Teflon bonded electrodes over non-Teflon bonded electrodes. It is worth noting that the use of effectiveness factor to evaluate different electrode structures is independent of the catalyst loading or area.

(b) Performance as a function of catalyst loading [14]. A good electrode structure should allow more of the electrocatalyst surface to be utilized. In addition, the performance should increase proportionately with increased catalyst loading. Fig. 2 shows that for Teflon bonded $NiCo_2O_4$, the anodic performance between 1650–1720 mV increases almost linearly with loading. Beyond 20 mg cm^{-2}, there is no further increase in performance. However, the performance

Table 1. Comparison of H_2 evolution current on Teflon bonded and platinized platinum electrodes, 5N H_2SO_4 25° C

	Teflon bonded electrode cd at 50 mV overvoltage (mA cm^{-2})	Platinized electrode cd at 50 mV overvoltage (mA cm^{-2})
Pulse current i_p (after 100 μs)	500	110
steady state current, i_s	265	19
Effectiveness factor, i_s/i_p	0.53	0.17

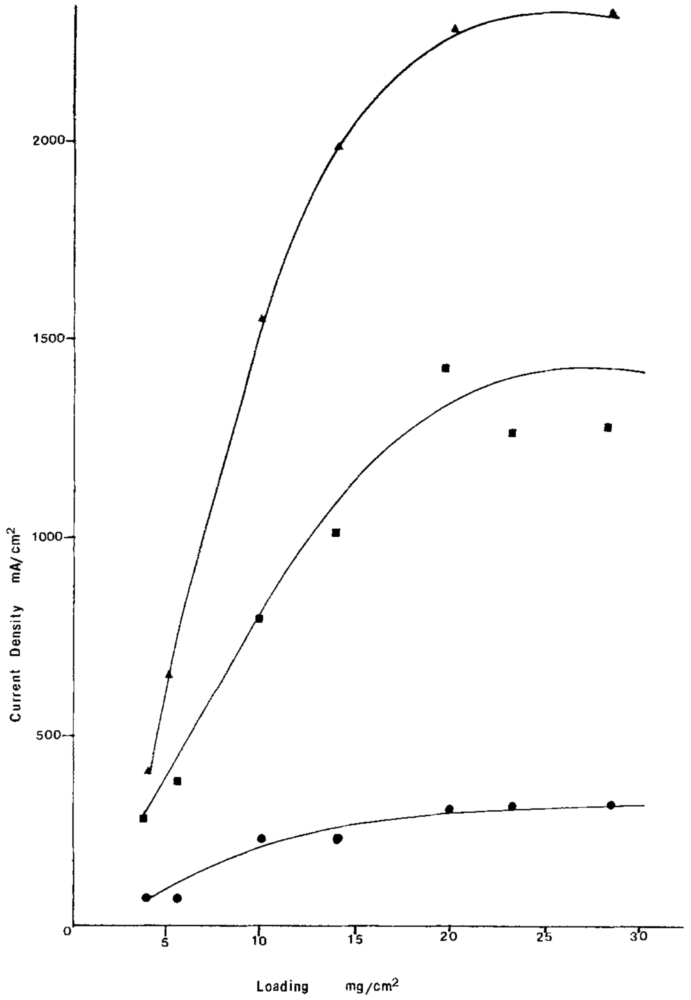

Fig. 2. Oxygen evolution on Teflon-bonded $NiCo_2O_4$ ● 165 mV vs DHE; ■ 1700 mV vs DHE; ▲ 1720 mV vs DHE 5 N KOH, 25° C, *iR* corrected.

of non-Teflon bonded porous $NiCo_2O_4$ (Fig. 3) is lower and except within a limited range of loadings, 4–6 mg cm^{-2}, the anodic performance actually decreases with increasing loading, indicating that the utilization of the electrocatalyst surface is lower at increased loading. Visual observation of the porous $NiCo_2O_4$ electrodes showed that at low loadings, up to 10 mg $NiCo_2O_4/cm^{-2}$, the nickel screen is not completely covered by the porous $NiCo_2O_4$ layer. The catalyst coats the nickel wires but there are still holes left at the centre of each mesh opening. As the loading is increased further, the holes are completely covered and the coating is much denser.

On the other hand, Teflon bonded $NiCo_2O_4$ electrodes, because of the additional volume of Teflon, cover the nickel mesh completely even at 5 mg $NiCo_2O_4/cm^{-2}$ loading. For the non-Teflon bonded $NiCo_2O_4$ electrode containing low catalyst loading, the total top surface of the $NiCo_2O_4$ layer will be higher than for the case where the nickel mesh is completely covered. Furthermore, since the higher $NiCo_2O_4$ loadings are prepared by repeated impregnation of nickel cobalt nitrates, the resultant $NiCo_2O_4$ structure is denser, again leading to reduced performance. Teflon bonded electrode structures, however, do not have similar problems since a significant part of the interior of the catalyst area is used and is therefore not dependent on the area of the top surface; hence the performance increases linearly with catalyst loading over a wide range of loadings.

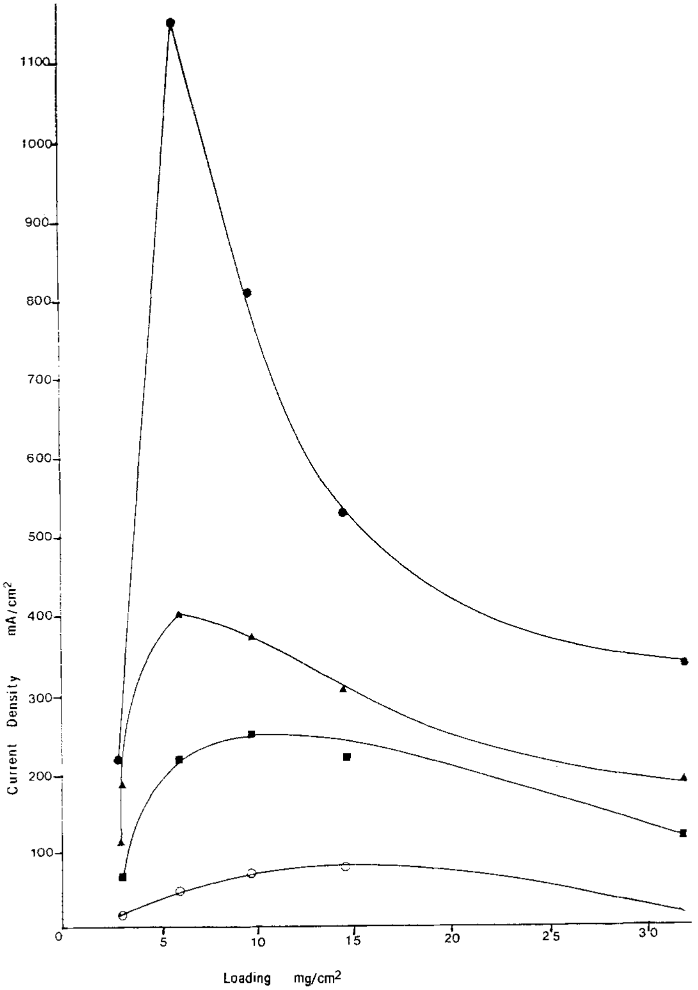

Fig. 3. Oxygen evolution on non-Teflon bonded porous $NiCo_2O_4$ electrodes, 5N KOH 25° C, *iR* corrected. ○ 1650 mV vs DHE; ■ 1700 mV vs DHE; ▲ 1720 mV vs DHE; ● 1750 mV vs DHE.

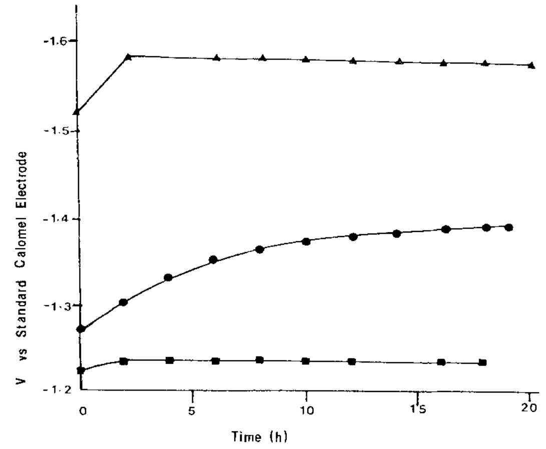

Fig. 4. H_2 evolution performance as a function of time in saturated $FeSO_4$, 10% NaOH, 0.3 A cm^{-2}, room temperature. ■-■ Teflon bonded Pt black; ●-● electroplated Pt black; ▲-▲ Ni screen.

5. Scale-up, durability, poisoning, effect of mesh size

Teflon bonded electrodes have been scaled up to 1 sq ft in size by Dams *et al.* [15], and the performance compared favourably with laboratory size electrodes. Teflon bonded lithium doped Co_3O_4 electrodes have been tested at 1 A cm^{-2} 45% KOH, 85° C for 6000 h with only 40 mV increase in overvoltage [16]. Since Teflon bonded electrodes utilize more of the available electrocatalyst area in the interior of the electrode, they should be less susceptible to poisoning by impurities. Fig. 4 shows that the presence of Fe ions does not affect the hydrogen evolution performance of Teflon bonded platinum black electrodes but has a significant effect on nickel mesh and platinized platinum electrodes [17]. Recent studies [18] have shown that it is necessary to take into account the current collection efficiency of various current collector mesh sizes since incorrect choice could lead to drastic reduction in performance.

6. Conclusion and suggestions for further work

The results clearly indicate the effectiveness of Teflon bonding in achieving better utilization of the electrocatalyst surfaces. Furthermore, since the curing temperature is only 300 to 350° C, higher surface area electrocatalyst could be used with less likelihood of sintering. The existence of a hydrophobic, non conductive PTFE components at the electrode surface has an adverse effect on bubble size and detachment. Further fundamental studies on this aspect should prove fruitful.

7. Acknowledgement

The above studies have been supported by the Ministry of Defence, the SERC and the EEC.

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