JOURNAL OF APPLIED ELECTROCHEMISTRY **27** (1997) 1304–1306

SHORT COMMUNICATION

# High-performance hydrogen anodes using a glass microfibre substrate

A. R. KUCERNAK*, G. T. BURSTEIN, C. J. BARNETT, K. R. WILLIAMS

*Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street,*
*Cambridge CB2 3QZ, Great Britain*

Received 14 February 1997; revised 22 April 1997

## 1. Introduction

Although anodes for hydrogen oxidation are made relatively easily to high performance, most acidic electrolytes demand a high corrosion resistance to maintain stability. Suitable membranes for these anodes are commercially available, and consist typically of carbon papers and carbon fabrics as a substrate for the catalyst as well as an electron conductor [1–4]. An alternative to this design is to use an insulating membrane, rendered conductive with an appropriate metal coating. Both porous polymers as well as ceramics are possible [5]. We present below a design employing a glass fibre membrane coated with gold to engender electronic conductance.

## 2. Experimental details

Electrodes were fabricated as follows. A thin film of gold ($< \sim 0.2\,\mu$m mean thickness) was evaporated on glass microfibre filters (Whatman type GF/A). This formed the electron-conducting substrate. The catalyst used was platinum/ruthenium on carbon (Johnson-Matthey type 87/86, noble metal content: 5% Pt, 5% Ru by weight). This was suspended in a solution of a polymer in a solvent. Two such combinations were tested: polyvinylidene difluoride (PVDF) in butan-2-one, and polyethylene (PE) in carbon tetrachloride. After thorough mixing the slurry was sprayed from an air-powered spray gun onto the gold-covered glass membrane to give a catalyst loading of $0.2\,\mathrm{mg\,cm^{-2}}$ of precious metal ($0.1\,\mathrm{mg\,cm^{-2}}$ Pt). The PVDF-bound catalyst layer contained 25% by weight binder, 75% carbon/catalyst. The polyethylene bound layer contained 22% by weight binder, 78% carbon/catalyst. The finished electrodes were circular, of overall diameter 2.5 cm with 2 cm diameter working surfaces. They were evacuated in a desiccator over night to evaporate the solvent fully.

The electrodes were tested in a three-electrode electrochemical cell constructed of polytetrafluoroethylene (PTFE) with a uniform cylindrical 2 cm internal diameter bore. The cell carried a coaxial facing platinum counter electrode of the same diameter. Electrical contact with the Pt/Ru hydrogen electrode was made via a gold ring surrounding the working surface. The catalyst faced outward from the electrolyte into a gas compartment through which hydrogen was fed at ambient pressure during a run. The cell was equipped with a Luggin capillary connected to an externally mounted saturated calomel reference electrode (SCE). The working electrolyte was 3 M $H_2SO_4$, of conductivity $\sigma = 0.7\,\mathrm{S\,cm^{-1}}$. Experiments were carried out galvanostatically, with the test electrode polarized by a Solartron 1286 electrochemical interface; they were performed at ambient temperature (19 ± 2 °C). The potential at each constant applied current was recorded for 200 s before the current was incremented. The results presented below are the as-recorded data; no correction for the ohmic potential drop has been made because at this preliminary stage of the work, the distribution of the various ohmic components is unknown. Although a portion of this lies across the working electrode/Luggin capillary tip displacement, some also clearly lies in the electrode structure itself, as well as in the contact between the electrode and the current collector, and in the thin-film gold conductor. Both electronic and ionic resistances are expected to be components in the working electrode structure. At this stage these components are not separable. However, with a Luggin capillary tip/working electrode displacement of 2 mm, the present cell geometry gives a resistance of 90 mΩ across this 'bulk' region of the electrolyte, giving an ohmic potential drop of 28 mV at a current density of $0.1\,\mathrm{A\,cm^{-2}}$.

## 3. Results and discussion

Galvanostatic potential–time traces for the anodic oxidation of hydrogen over one such electrode (bound with PE) is shown in Fig. 1. A small initial rise in potential indicates a small degree of deactivation, but the effect is insignificant after about 20 s, and is less than 1 mV. For the remaining period, the potential falls but only slightly, and the data describe the approximate steady state oxidation of hydrogen for each applied current. Repeat runs using the same anode showed a high degree of reproducibility.

Figure 2 shows the current density–potential characteristics obtained after 200 s of reaction at each applied current density. The results from electrodes made with both binders (PE and PVDF) are plotted. These electrodes show very high performance for the anodic oxidation of hydrogen: the better of the two

---

[*] Present address: Department of Chemistry, Imperial College of Science Technology and Medicine, London SW7 2AZ, Great Britain.

0021-891

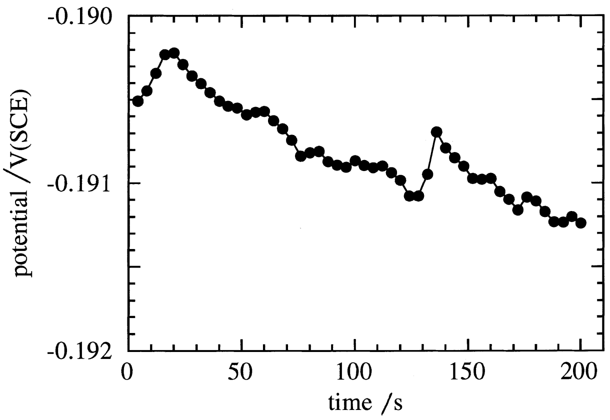

Fig. 1. The potential as a function of time under application of an anodic current density of 32 mA cm$^{-2}$ to polyethylene-bound anode fuelled with hydrogen at ambient temperature and pressure in 3 M $H_2SO_4$.

(PVDF-bound) gives an overpotential of 0.3 V (0.02 V vs SCE) at 0.27 A cm$^{-2}$, equivalent to 1.35 kA g$^{-1}$of precious metal (2.6 kA g$^{-1}$ Pt). The graphs are approximately linear over the first 0.25 A cm$^{-2}$, and curve very gently at higher current densities: most of the anodic overpotential is due to ohmic resistances. The observed ohmic limitation is due to a constant ohmic resistance up to about 0.25 A cm$^{-2}$, and it is believed that this ohmic resistance ceases to be constant at current densities greater than this. Such behaviour could arise, for example, by variation in the reactive surface area of the electrocatalyst with current density as the current density is raised. It could also arise from resistive heating of the porous electrode at high current density. Figure 2 shows that the ohmic resistance for the system, read as the gradient $\partial E/\partial i$ below 0.25 A cm$^{-2}$, is greater for the polyethylene-bound electrode (1.84 Ω cm$^2$) than for the PVDF-bound electrode (0.96 Ω cm$^2$). This implies that at least some of the ohmic resistance involved is in the electrode structure itself: the electrode bound with PVDF shows the lower resistance. It is also seen in Fig. 2 that whereas the PVDF-bound electrode tends towards higher resistance as the current density increases above 0.25 A cm$^{-2}$, the PE bound electrode tends towards lower resistance above the same current density. Since these two opposing deviations start at the same current density (0.25 A cm$^{-2}$), they are believed to be of the same origin, probably resistive heating. As the temperature rises because of resistive heating the conductivity of the electrolyte rises, lowering the overall ohmic potential drop. However, as the temperature rises, it would be expected that the polymer binder may swell slightly, lowering the diameter of the channels within the electrode structure through which the ionic current must flow, and perhaps shielding some catalyst from reaction. This latter effect would serve to increase the apparent resistance. Both of these effects are likely with the present system, with alternative domination of the two differently bound electrodes as shown in Fig. 2. It should be noted that the temperature rise is not large: at the end of one run, the temperature was measured as 25 °C compared with an ambient of 19 °C.

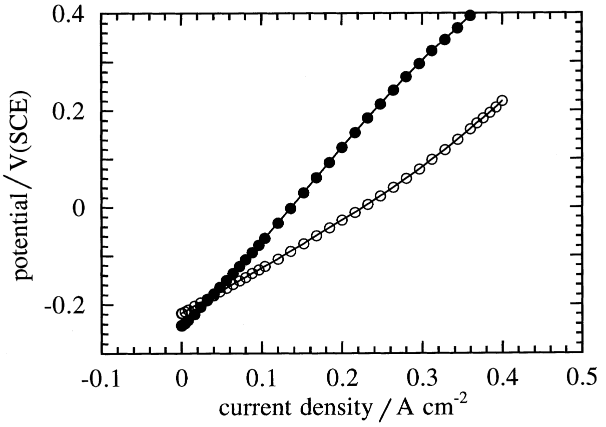

Fig. 2. Electrode potential as a function of the applied anodic current density measured after 200 s at each galvanostatic step. The fuel is hydrogen at ambient temperature and pressure in 3 M $H_2SO_4$. Open circles: electrode bound with polyvinylidene difluoride. Filled circles: electrode bound with polyethylene. The potentials are not compensated for the ohmic potential drop.

No attempt has yet been made to minimize the ohmic resistance of these electrode systems, although vast improvements are clearly possible (for example, by examining the ratio of catalyst to binder, and by increasing the thickness of the conductive layer). However, aside from the ohmic potential involved in the electrode performance described above, the measurements are consistent with those of other high performance hydrogen anodes [6, 7]. For example, Chen *et al.* achieved a hydrogen oxidation current at 80 °C of 1.3 A cm$^{-2}$ using a loading of 1.43 mg cm$^{-2}$ Pt [6] seven times that used in the present work. Hards *et al.* measured [7] about 0.5 A cm$^{-2}$ also at 80 °C, at an uncompensated overpotential estimated to be 0.3 V and a platinum loading of 0.5 mg cm$^{-2}$. These should be compared with our values of 0.27 A cm$^{-2}$ at an uncompensated overpotential of 0.3 V using a platinum loading of 0.2 mg cm$^{-2}$ at 19 °C. The glass microfibre membrane provides a cheap, clean and chemically durable gas electrode.

## 4. Conclusions

A gas diffusion electrode made using a gold-coated glass microfibre membrane has been fabricated. The electrode is chemically inert in hot strongly acidic solutions, and gives a high performance as a hydrogen anode when coated with a suitable electrocatalytic ink.

## Acknowledgements

We are grateful to the EPSRC for financial support of the programme under the Clean Technology Initiative, and to Johnson-Matthey for the provision of catalytic materials.

## References

[1] A. Hamnett and B. J. Kennedy, *Electrochim. Acta* **33** (1988) 1613.

[2] E. J. Taylor, E. B. Anderson and N. R. K. Vilambi, *J. Electrochem. Soc.* **139** (1992) L45.

[3] M. P. Hogarth, J. Munk, A. K. Shukla and A. Hamnett, *J. Appl. Electrochem.* **24** (1994) 85.

[4] X. Gang, L. Qingfeng, H. A. Hjuler and N. J. Bjerrum, *J. Electrochem. Soc.* **142** (1995) 2890.

[5] K. R. Williams (ed.) 'An Introduction to Fuel Cells' Elsevier, Amsterdam (1966), pp. 97–101.

[6] K. Y. Chen, P.K.Shen and A.C.C. Tseung, *J. Electrochem. Soc.* **142** (1995) L185.

[7] G. A. Hards, T. R. Ralph and S. J. Cooper, ETSU Report ETSU/FCR/002 (1992) Harwell, Oxon.