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High-performance carbon electrodes for acid methanol–air fuel cells

RAMASAMY MANOHARAN, JOHN B. GOODENOUGH,
ANDREW HAMNETT

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK

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High-performance, Teflon-bonded carbon electrodes, catalysed with highly dispersed platinum metal, have been developed for oxygen reduction in H_2SO_4. Surface-treated Vulcan XC-72 carbon has been used as the substrate material. The electrodes can be loaded with current densities of $1.1\,A\,cm^{-2}$ intermittently and $900\,mA\,cm^{-2}$ for extended periods without serious degradation. The performance of these electrodes in the presence of methanol has also been examined.

1. Introduction

The long-range goal of fuel-cell research is the development of fuel-cell batteries that operate on inexpensive fuels and have air as the oxidant. These batteries must convert chemical energy to electric power with high efficiency at practical current densities; they must also have long operational life – or a low cost of replacement of ageing parts – if they are to compete with present forms of power generation from the same inexpensive fuels.

A primary impediment to the commercial realization of fuel-cell technology is failure to identify suitable catalytic electrodes having a long operational life in acidic electrolytes. Alkaline electrolytes react with carbon dioxide to form carbonates that foul the electrodes, so direct conversion of a hydrocarbon fuel such as methanol requires an acidic electrolyte. Although fouling by CO_2 from the air can be slowed to nearly tolerable rates for low-cost, exchangeable alkaline air electrodes in a pure hydrogen–air fuel cell, an acidic electrolyte has great advantages even in this case. One option for the use of liquid fuels in fuel cells is to convert the fuel to hydrogen with a reformer, though this adds considerably to the complexity and cost of the power unit and represents a far from optimal situation. A direct methanol fuel cell is therefore a prime technical target, and for this cell an acid electrolyte is mandatory. This paper reports the development of a carbon-based air electrode that operates with high performance in an acidic electrolyte and in the presence of methanol.

High performance requires fabrication of a porous electrode substrate of high surface area on which a suitable catalyst is effectively dispersed; moreover, the effective surface area must not be degraded by normal operating conditions. Degradation may be caused by (i) chemical attack from the product of an unwanted side reaction, (ii) poisoning, (iii) mechanical collapse, or (iv) sintering due to heat from internal losses. Therefore attention must be directed to the choice of substrate material and catalyst as well as to the method of electrode fabrication and catalyst dispersion.

Selection of a suitable substrate material is dictated by at least six factors: cost, inertness in the operating medium, ease of fabrication into colloidal-size particles, high electrical conductivity, effectiveness as a substrate for a highly dispersed catalyst, and inertness to unwanted side reactions. Various types of active (high surface area) carbon have been examined as supports for platinum-metal catalysts in electrodes used for both oxygen reduction and methanol oxidation in acid solution [1–4]. The present study shows that Vulcan XC-72 carbon, which has a low ash content, functions as an excellent air

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electrode substrate in acid if its surface is suitably pretreated and platinum is uniformly dispersed onto it. Such a Teflon-bonded electrode appears to reduce dioxygen to water in 2.5 M H_2SO_4 with no detectable formation of hydrogen peroxide and to be able to sustain load currents of about 900 mA cm^{-2} for long periods without serious degradation; moreover, this performance is not significantly reduced in the presence of methanol. The performance of these electrodes as the anode in direct methanol conversion is also reported.

2. Experimental details

High-surface-area Vulcan XC-72 carbon was obtained from the Cabot Corp., Billerica, MA. The ash content of this carbon was found to be about 0.05%, which is significantly lower than the values of 1.5–6% reported for several other carbons [2, 5, 6]. The other physical and chemical parameters of this carbon are as follows:

surface area	254 $m^2 g^{-1}$
mean particle size	30 nm
apparent density	96 kg m^{-3}
pH	5

This carbon was subjected to mechanical grinding and then gas-activated by heating in a CO_2 atmosphere at 900° C for 1 h. Gas activation [4] rather than continued grinding was chosen to minimize particle agglomeration; it produced a 27% weight loss of the carbon, increased the effective surface area and modified the surface.

The desired quantity of platinum was dispersed into the gas-activated carbon by reducing chloroplatinic acid with sodium formate solution as described elsewhere [3, 7]. This procedure yields fine platinum particles of uniform size (about 63 Å in diameter) on carbon substrate. Chloroplatinic acid solution containing the required weight of platinum was taken from a 2 wt % stock solution, mixed with half of its volume of isopropanol and neutralized with a dilute solution of sodium carbonate. The isopropanol acts as a surfactant for the otherwise hydrophobic carbon particles ensuring preferential deposition of the platinum salts [4]. An appropriate quantity of gas-activated Vulcan XC-72 carbon was added, and the entire mixture was dried in an air oven before it was added, with vigorous stirring, to an excess of boiling, 5 wt % sodium formate solution to reduce the chlorophatinic acid to platinum metal. The resulting mass was filtered and washed repeatedly with hot, distilled water before being dried in an air oven.

In this study Teflon-bonded electrodes were prepared for electrochemical measurements under gas-fed conditions. The Teflon binder provides the necessary mechanical strength to prevent electrode collapse under the gas pressure required for gas-electrolyte interface control in a gas diffusion electrode, and it does so while retaining the necessary electrode porosity.

Our Teflon-bonded electrodes were made as follows. Tetrahydrofuran (THF) was added to a measured quantity of catalysed substrate powder in a beaker, and the mixture was agitated in an ultrasonic bath for about 30 min before a few millilitres of a dilute suspension of a Teflon emulsion (ICI GP2 Fluon dispersion, particle size 0.1–0.2 μm) was added to the mixture without interruption of the agitation. The product material was centrifuged repeatedly with THF and finally spread on a platinum expanded-metal (Exmet) screen (0.76 mm diameter wire, 1024 mesh cm^{-2}). The coated screen was air-dried for about 15 min before it was cold-pressed at 125 kg cm^{-2} for 5 min. The pressed mass was dried for 2 h at 110° C and then cured in air at 360° C for 30 min. The Teflon content of the electrodes was optimal at 25 to 35% by weight depending on the surface area of the substrate. Typically the total weight of electrode material was 25 mg cm^{-2}. The resistivity of an optimized electrode is about 0.001 Ω cm, and its thickness is about 0.5 mm.

A cell for measuring electrochemical performance parameters was set up as described elsewhere [3]. It consisted of a thermostatted liquid-phase compartment and a gas-phase compartment interfaced with a working porous electrode placed between them. The liquid compartment contained a 2.5 M H_2SO_4 solution in doubly distilled water as the electrolyte, a high surface area, flat-bed counter electrode, a Hg/Hg_2SO_4, H_2SO_4 reference electrode, and a magnetic

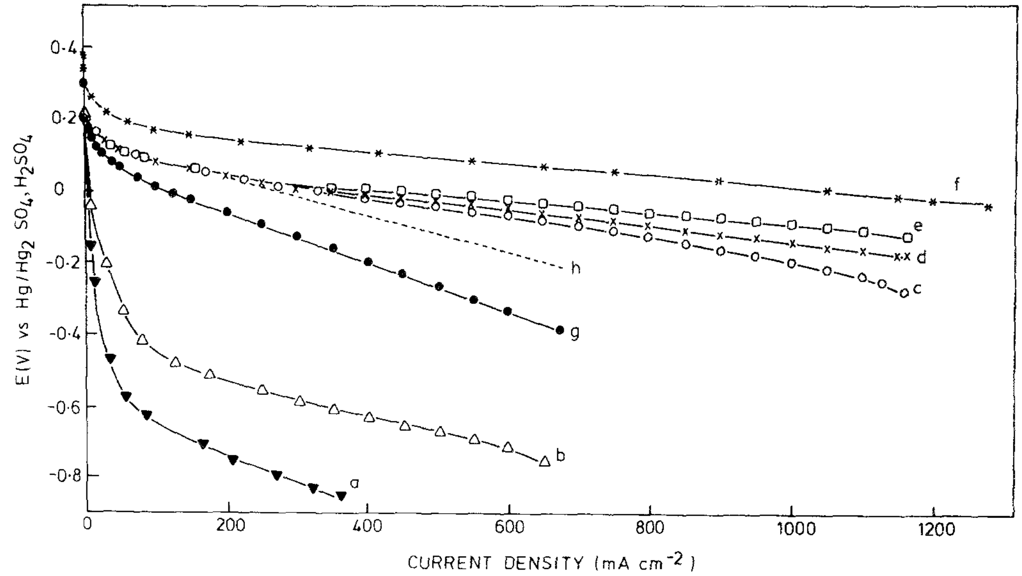

Fig. 1. Performance curves for oxygen reduction in 2.5 M H_2SO_4 on untreated Vulcan XC-72 carbon electrodes at 20° C with (a) 35% Teflon and (b) 25% Teflon, and on 30% Teflon-bonded 7% Pt/CO_2-treated Vulcan XC-72 carbon electrodes at the gas pressure of (c) 5, (d) 20 and (e) 50 mm Hg all at 20° C, and (f) at 60° C with the gas pressure of 50 nm Hg. Performance curves for 10% Pt/coconut-shell charcoal at 30° C (curve g) and 60° C (curve h) in 2.5 M H_2SO_4 [3] are also shown for comparison.

stirrer. The gas compartment contained dioxygen at a pressure regulated to force gas into the pores of the electrode where it dissolved in the electrolyte permeating through the electrode from the liquid compartment. The current-collecting lead was a platinum O-ring that was pressed tightly against the gas compartment side of the electrode. Temperature was controlled by regulating the current through a metal coil heater.

The reported current–potential curves were obtained galvanostatically; they were not *I–R* corrected. The galvanostatic polarization studies were carried out with a regulated d.c. power supply and a high-power-rated rheostat in series with the electrochemical cell. The experiments were repeated with a minimum of two different electrodes and were found to be fairly reproducible from one electrode to another.

Life-time measurements were made by loading the electrodes with various current densities over a period of time and recording the corresponding changes in the electrode potential.

3. Results and discussion

The short-term polarization curves obtained for dioxygen reduction in 2.5 M H_2SO_4 solution on various Vulcan XC-72 carbon electrodes are shown in Fig. 1 for 20° C and 60° C. Curves (a) and (b) are the polarization curves obtained at 20° C for unplatinized carbon electrodes that were not gas activated. Although the electrodes function at current densities of 400 to 600 mA cm^{-2}, their polarization values are high. These curves also show the effect of reducing the effective surface area by increasing the Teflon content. An optimal Teflon content for these electrodes was found to be 25% by weight. However, after the surface area had been increased by activating with a CO_2 anneal, adequate mechanical strength was only achieved by increasing the Teflon content to 30%.

Curves (c) to (f) were obtained on gas-activated Vulcan XC-72 substrates impregnated with 7 wt % dispersed platinum metal and loaded with 30% Teflon. Curves (c) to (e), taken at 20° C, are polarization curves for a range of gas pressures (5–50 mm Hg). The data clearly show a sufficiently reduced mass-transfer polarization to allow loading of the electrodes to high current densities. These electrodes could be loaded intermittently at current densities of 1.1 A cm^{-2} for periods of several minutes. It is

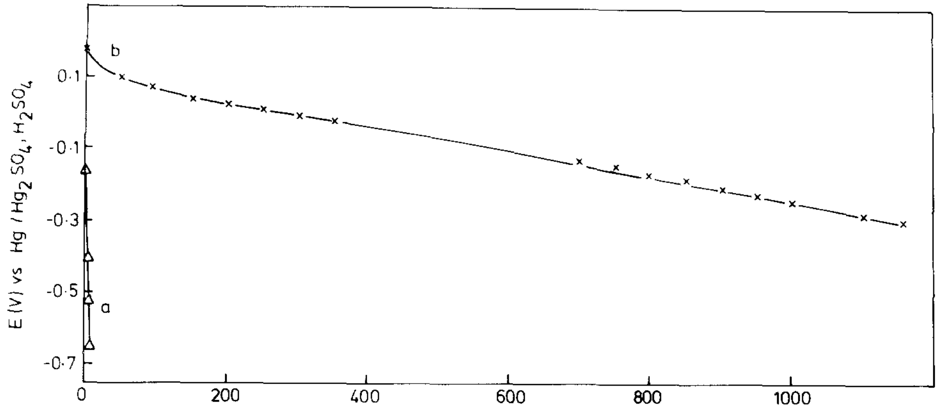

Fig. 2. Performance curves for oxygen reduction in 2.5 M H_2SO_4, 1 M CH_3OH at 20° C on 7% Pt/CO_2-treated Vulcan XC-72 carbon electrodes in (a) the absence of oxygen and (b) the presence of oxygen.

evident from our results that both gas activation and optimized electrode structure are important, and considerable effort has been devoted in recent years to improve our understanding of the phenomenon. The two commonly used gases are CO_2 and steam, which both cause loss of carbon:

$$CO_2 + C \longrightarrow 2CO$$

$$H_2O + C \longrightarrow CO + H_2$$

However, it is clear from *FT–IR* data on carbon powders [8] that substantial chemical modification of the surface also takes place. Electron micrographs show not only a reduction in the mean particle size, but also a marked decrease in agglomeration, suggesting that the surface structure is significantly more stable. This is also borne out by earlier catalytic studies [9] and by observations by ourselves and earlier workers [3, 10, 11] that such treatments lead to a high activity for H_2O_2 decomposition — so much so in our case that no H_2O_2 can be detected even at the level of 0.001% in the catholyte. The origin of this surface stability in not clear: gas activation appears to remove certain oxygen-containing groups that are normally present on the surface [8, 12, 13], and it is possible that these groups are easily oxidized, providing 'weak sites' for electrode decomposition [14].

Another role for gas activation may be to alter the internal structure of the carbon particles. It has been suggested [15], on the basis of electron micrographs, that both steam and CO_2 activation may give rise to shell-like structures that have internal suface area. However, we have found it far from straightforward to verify this hypothesis from our own micrographs.

The effect of temperature is quite significant, as can be seen from the performance curve at 60° C, curve (f).

Fig. 1 includes for comparison the data of Ramesh and Shukla [3] for a coconut-shell charcoal electrode catalysed with 10 wt % platinum, curves (g) and (h). The Vulcan XC-72 carbon is a better substrate material for oxygen reduction in acid medium; the reverse is true in alkali medium [16].

Addition of 1 M of methanol to the acid electrolyte gave the performance shown in Fig. 2, curve (b). The open-circuit voltage is reduced by about 200 mV from its value in the absence of methanol, and the overall performance is slightly reduced. The drop in open-circuit voltage may be due to the formation of a mixed potential of the reactions of methanol oxidation and oxygen reduction. Curve (a) of Fig. 2 is the polarizaton curve obtained in the presence of methanol but with no oxygen. Polarization of the electrode at very low current density ($\sim 5\,mA\,cm^{-2}$) indicates that the methanol has a negligible effect on the reduction of oxygen on the catalysed carbon electrode. However, its effect on mass transfer polarization cannot be ignored completely. The kinetic data for the electrodes are shown in Table 1. A decrease in Tafel slope and exchange-current density in the

Table 1. Kinetic parameters for oxygen reduction on platinized Vulcan XC-72 carbon electrodes

Electrolyte	*Tafel slope (V)*	*Exchange current density ($A\,cm^{-2}$)*
2.5 M H_2SO_4	0.085 at 20° C	1.0×10^{-7} at 20° C
	0.088 at 60° C	8.42×10^{-7} at 60° C
2.5 M H_2SO_4, 1 M CH_3OH	0.07 at 20° C	9.44×10^{-9} at 20° C

presence of methanol indicates an increase in both the ohmic and the charge transfer polarization components.

The feasibility of direct oxidation of methanol in acid electrolyte at our platinum-catalysed carbon electrodes was also examined. The anodic activities at 20° and 60° C are shown as curves (a) and (b), respectively, in Fig. 3. The highly active form of platinum chemisorbed via a platinum–carbon bond may be responsible for the much better performance of these electrodes; poisoning of the platinum by CO or COH residues is normally a much more serious problem [17].

Fig. 4 shows a stability test on a platinum-catalysed electrode during oxygen reduction. The applied current density was increased in a series of steps from an initial value of 100 mA cm^{-2} until breakdown was observed 120 h later at a current density of 1 A cm^{-2}. The electrode was quite stable up to a current density of 500 mA cm^{-2}; above this the electrode started deteriorating slowly, but in this test breakdown of the electrodes occurred only after the current density was raised to 1 A cm^{-2}. This performance is quite remarkable.

Hydrogen peroxide concentration in the electrode was monitored after loading electrodes at current densities of 100 mA cm^{-2} for 17 h, 200 mA cm^{-2} for 12 h, and 300 mA cm^{-2} for 12 h. No hydrogen peroxide was detected, which indicates either that the electrodes reduce dioxygen directly to water without forming hydrogen peroxide as an intermediate or that any H_2O_2 that is formed is rapidly and effectively decomposed to water and dioxygen, the latter being recycled.

Finally, high-resolution scanning electron micrographs of these gas diffusion electrodes were obtained prior to and after service in a cell. Before service the micrographs indicate that the interpore structure in the electrodes is homogenous, i.e. the pores are uniformly distributed throughout the electrode. They also confirm that the platinum is thoroughly dispersed on the support. After the electrodes have been loaded with higher current densities for long periods of time, the porous structure of the electrode is almost

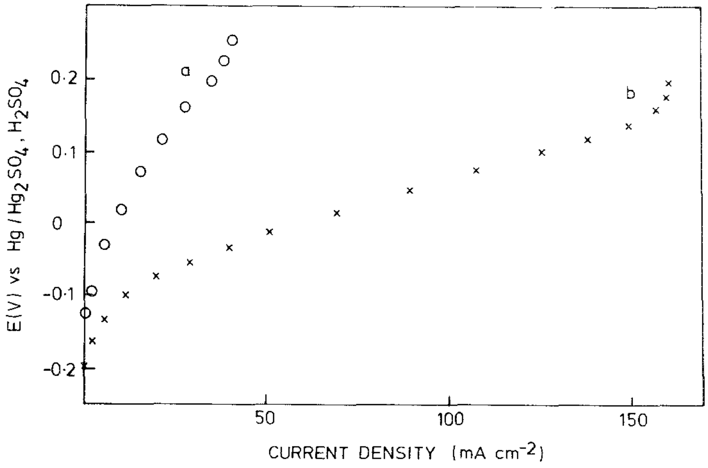

Fig. 3. Catalytic activity of 7% Pt/CO_2-treated Vulcan XC-72 carbon electrodes for methanol oxidation at (a) 20 and (b) 60° C.

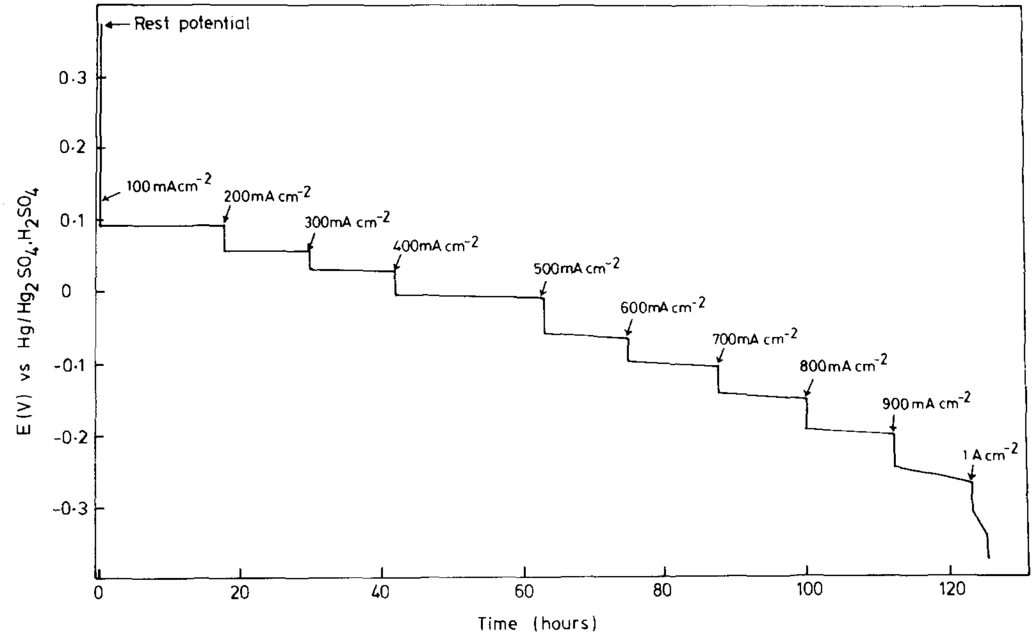

Fig. 4. Operational lifetime curves for 7% Pt/CO$_2$-treated Vulcan XC/72 carbon electrode at room temperature.

unchanged; however, the platinum particles have formed rather bigger aggregates and the pore distribution is slightly altered. This aggregation suggests that some sintering of the platinum particles occurs as a result of zonal heating.

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