Carbon supports for phosphoric acid fuel cell electrocatalysts: alternative materials and methods of evaluation[+]

J. McBREEN, H. OLENDER, S. SRINIVASAN [‡]
Department of Energy and Environment, Brookhaven National Laboratory, Upton, New York 11973, USA

K. V. KORDESCH
Technischen Universitat Graz, A-8013 Graz, Austria

In early development of the phosphoric acid fuel cell, the most common carbon support material for the platinum catalyst was a Cabot Corporation furnace black called Vulcan XC-72R. Even though use of this material facilitates dispersion of platinum and electrode fabrication, it is unstable at elevated temperatures and high electrode potentials. At present the main approach to the problem is to heat-treat the Vulcan material or use acetylene black. The present study is an evaluation of five Cabot Corporation furnace blacks of widely varying physical and chemical properties, including Vulcan XC-72R. These studies include an investigation of wetting characteristics, oxygen reduction on platinum supported on these carbons, and a determination of carbon stability using a cyclic voltammetric technique. Carbons with high volatile content and acid pH (Cabot Corporation Mogul 1300, CSX 98 and Mogul L) were hydrophobic and inhibited platinum dispersion. Platinum dispersion was good on Vulcan XC-72R but the platinum sintering rate was high. One carbon (Regal 660R) with a low volatile content and a neutral pH had high platinum dispersion, good electrode performance, a negligible platinum sintering rate and a high resistance to corrosion. It appears to be a potentially useful substitute for Vulcan XC-72R.

1. Introduction

One of the main causes of deterioration in performance with time in a phosphoric acid fuel cell is degradation of the carbon support for the platinum electrocatalyst. Other causes of the performance decay are poisoning of the fuel electrode by carbon monoxide or sulphur impurities and sintering of the fuel cell electrocatalyst particles. The problem of carbon corrosion is more severe at or close to open-circuit potentials, as may be expected on thermodynamic reasoning. The trend towards operation of phosphoric acid fuel cells at higher temperatures and pressures, from the point of view of improving power plant efficiencies, has resulted in a search for more stable carbons [1–3].

Hitherto, a furnace black, Vulcan XC-72R from Cabot Corporation, has been used as the support for anode and cathode platinum electrocatalysts in phosphoric acid fuel cells. Several studies are in progress, either to pretreat this carbon or to find alternative materials in order to improve the stability of the carbon support. It is worthwhile at this stage to briefly review the progress that has been made in these directions.

The potential sweep method was used by Kinoshita and Bett [4, 5] to analyse the oxidation products of carbon subjected to heat treatment, electrochemical oxidation or gas-phase oxidation. An analysis of the current–voltage curves revealed that the observed anodic and cathodic peaks at about 600 mV/RHE are due to the quinone–hydroquinone redox couple and that the surface concentration of the redox species is of the order of 10^{-11}–10^{-10} mol cm^{-2}. The oxidation treatments (air, chromic acid or nitric acid) increased

the surface oxide concentration, whereas the heat pretreatment decreased it. A second oxidation peak at about 1200 mV was observed and this was attributed to a second type of species.

In efforts to inhibit sintering of the platinum electrocatalyst particles, Pan et al. [6] evaluated different types of carbons (as well as conductive oxides), adion (e.g., Al^{3+}, Th^{4+}) effects, and the addition of potentially stable components such as refractory metals (W, Mo, Re). These workers found that a phosphorous-containing activated charcoal (North American P100) retards the sintering of the supported platinum, possibly by interaction of the platinum with the phosphorous. The electronic conductivity of this material is not high enough and it was necessary in these studies to add conductive, uncatalysed graphon carbon to electrode structures. One of the conclusions reached from this study was that it is preferable to use a single carbon component for fabrication of fuel cell electrodes.

A systematic study of the development of electrocatalysts and conductive substrates for cathodes in phosphoric acid fuel cells is being carried out by Stonehart [3]. Several types of carbon, containing different loadings of platinum, have been examined. It was found that the surface area of the platinum deposited on the carbon support is proportional to the BET surface area of the support. The electrochemical characteristics of these carbons have been correlated with their structural parameters, as reflected by the lattice parameters. The Tafel slopes of the corrosion reactions on these carbons are dependent on the heat-treatment temperatures. Two types of surfaces, ordered and disordered, contribute to the observed Tafel slope. As

the extent of ordering increases, the Tafel slope approaches that for graphitized carbon.

It is essential to find stable supports for platinum fuel cell electrocatalysts (the goals are that the electrochemical cell stack, and hence the electrodes, in a fuel cell power plant should last 40 000 hours). A method is also needed for the rapid evaluation of the stability of the carbon supports. Thus the present study was undertaken to determine the effects of alternative carbon supports on the electrode kinetics of oxygen reduction and on the electrode stability.

2. Experimental

2.1. Properties of the carbon materials

Five furnace blacks covering a wide range of physical and chemical properties were obtained from Cabot Corporation. The following properties were considered: surface area, particle size, electrical resistivity, volatile content, pH and apparent density. The data for the five carbons are summarized in Table 1.

2.2. Determination of wetting characteristics of carbon materials

The wetting characteristics of the carbon materials in 85% H_3PO_4 were evaluated using a simple flotation test. An aliquot of the carbon was added to 85% H_3PO_4 at 25° C and the solution heated slowly to 120° C. The amount of carbon still afloat was monitored as the temperature was increased.

Table 1. Physical and chemical properties of selected Cabot carbons

Cabot carbon type	Surface area (m² g⁻¹)	Particle size (nm)	Electrical resistivity (dry)	Volatile content (%)	pH	Apparent density (kg m⁻³)
Monarch 1300	560	13	Medium	9.5	3.3	289
CSX 98	Similar to Monarch 1300					
Mogul L	138	24	High	5.0	3.4	240
Vulcan XC-72R	254	30	Lowest	2.0	5.0	96
Regal 660R	112	24	Low	1.0	7.5	240

2.3. Electrode fabrication, electrochemical cells and electrolyte pretreatment

The electrodes were made as follows. The carbon was mixed with a Teflon T-30 suspension to yield a 12 wt% PTFE content. The mixture was rolled on to a carbon substrate paper (obtained from Energy Research Corporation) with an average carbon/PTFE layer thickness of 0.076 mm. The samples were pressed at 0.02 ton cm^{-2} and dried in an oven at 315° C for 15 min. The samples were catalysed by brushing on a layer of 1% chloroplatinic acid until a loading of 1 mg cm^{-2} was obtained. The samples were dried again at 150° C for 15 min and then dipped in a 1% solution of sodium borohydride to reduce the platinum oxide. The electrodes were then mounted on gold grid current collectors.

All electrodes were mounted in PTFE beaker cells with large platinum screen counter and dynamic or reversible hydrogen reference electrodes. The electrolyte was 85% H$_3$PO$_4$, which was purified by a combined hydrogen peroxide/pre-electrolysis treatment. It is believed that the phosphorous component of orthophosphoric acid causes problems during electrode reactions, such as increased peroxide production and activity decay. Therefore, this impurity in the electrolyte was oxidized using 10 wt% H$_2$O$_2$. The electrolyte was then heated to 100° C for 10 hours and to 160 ° C for 24 hours. After the heat treatment, triple-distilled water was added to attain the desired concentration of H$_3$PO$_4$. Thereafter the electrolyte was pre-electrolysed at 1.3 V for 30 hours.

2.4. Electrochemical techniques

The Princeton Applied Research Company potentiostat, universal programmer and digital coulometer were used in the experimental work for the following electrochemical studies.

2.4.1. Surface area measurements using cyclic voltammetry. Cyclic voltammograms were recorded in the voltage range 0 to + 0.7 V/RHE at 50 mV s^{-1}. The hydrogen desorption charge was measured in the range 0 to + 0.3 V using a coulometer. Assuming one hydrogen atom is adsorbed on each Pt surface atom and the area required per Pt atom is 0.089 nm^2 for a polycrystalline surface,

the charge required for monolayer adsorption or desorption of hydrogen is 210 μC cm^{-2}. The electrolyte was purged with nitrogen prior to cyclic voltammetry. Measurements of the surface area were made at 25° C and 135° C on the fresh electrodes. These measurements were then repeated at the higher temperature after several hundred hours of ageing.

2.4.2. Oxygen reduction kinetics. The samples were polarized potentiostatically from a high overpotential for oxygen reduction (0.4 V/RHE) to the oxygen reversible potential (or open-circuit potential) and back to 0.4 V/RHE at 25° C and 135° C. The kinetic parameters (Tafel slopes, exchange current densities and transfer coefficients) were then calculated from the Tafel lines.

2.4.3. Carbon stability determination using cyclic voltammetry. On completion of the oxygen reduction studies, the corrosion resistance of the carbons was evaluated at 138° C using cyclic voltammetry at a sweep rate of 50 mV s^{-1}. In all cases, the negative end of the voltage envelope was 0 V/RHE. The positive limit was stepped up in 0.1 V increments from 0.7 to 1.4 V/RHE. With each increment, a cyclic voltammogram was recorded in order to measure the hydrogen charge changes with increasing anodic sweep limits.

3. Results

3.1. Wetting characteristics of carbon materials

The observations on the wetting characteristics are summarized in Table 2. The CSX 98 carbon displayed the most hydrophobic characteristics. The Vulcan XC-72R material remained suspended in the acid. However, on cooling, the material sank to the bottom. Its behaviour is probably due to gas-filled internal pores rather than any hydrophobic quality.

3.2. Surface area data from hydrogen desorption charge

The data on the electrochemically active surface area, as determined from the hydrogen desorption charge at 25° C and 135° C before polarization and at the higher temperature after polarization,

Table 2. Floating tests on Cabot carbon black samples

Temperature (° C)	Observations on settling rate of various carbons: location of majority of particles				
	Monarch 1300	*CSX 98*	*Mogul L*	*Vulcan XC-72R*	*Regal 660R*
27	T	T	S	T	T
33	B	T	B	S	B
48	B	T	B	S	B
57	B	T	B	S	B
63	B	T	B	S	B
75	B	T	B	S	B
98	B	B	B	S	B
120	B	B	B	S	B

T, Afloat on top of electrolyte;
S, suspended in the electrolyte;
B, at the bottom.

are shown in Table 3. The changes in surface area with time are also indicated in the table. As seen from this table, the surface area of the Regal 660R sample is stable with increasing temperature as well as after polarization. However, with the Vulcan XC-72R sample, a decrease of surface area is observed with the above mentioned change in conditions. A typical cyclic voltammogram from which the electrochemically active surface area is calculated is shown in Fig. 1. The charge includes the double-layer contribution. This was not subtracted since its absolute value could not be unequivocally determined. Nevertheless, trends in surface area changes could be determined.

3.3. *Oxygen reduction kinetics*

Tafel lines for oxygen reduction at platinum supported on the five types of carbons in 85% phosphoric acid at 25 and 135° C revealed some differences. The kinetic parameters for oxygen reduction are summarized in Table 4. Typical Tafel plots on two of the sample electrodes are shown in Fig. 2.

Table 3. Surface area data for platinum on various Cabot carbons

| Sample	Initial surface area at 25° C	Surface area at 135° C		Surface area after polarization at 135° C		
	(Coulombs, 0 to + 0.3 V/RHE)	*Time* (h)	(Coulombs, 0 to + 0.3 V/RHE)	*Time* (h)	(Coulombs, 0 to + 0.3 V/RHE	*Change*
Monarch 1300	1.92×10^{-2}	168	2.2×10^{-2}	1638	2.75×10^{-2}	Increase at elevated temperature
CSX 98	2.34×10^{-2}	624	3.1×10^{-2}	1656	3.15×10^{-2}	No change at elevated temperature
Mogul L	2.78×10^{-2}	192	2.75×10^{-2}	1624	3.65×10^{-2}	Increase at elevated temperature
Vulcan XC-72R	7.4×10^{-2}	624	4.85×10^{-2}	1632	3.9×10^{-2}	47% overall decrease
Regal 660R	4.1×10^{-2}	168	4.4×10^{-2}	1660	4.42×10^{-2}	Very stable
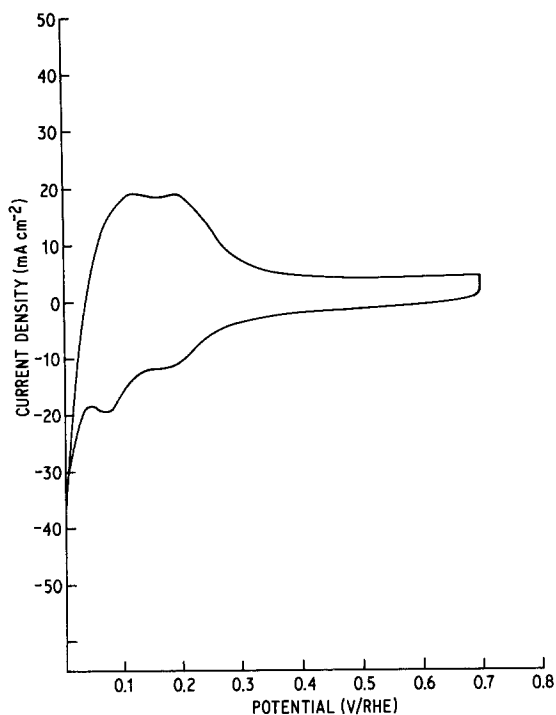
Fig. 1. Cyclic voltammogram of platinum-catalysed Vulcan XC-72R (1 mg Pt cm⁻²) in 85% H_3PO_4 at 25° C. Sweep rate: 50 mV s⁻¹.

3.4. Carbon stability determination using cyclic voltammetry

The cyclic voltammograms (sweep rate 50 mV s⁻¹) at platinum supported on the five types of carbon at 138° C provided valuable information on the stability of the carbon materials when the negative end of the voltage envelope was at 0 V/RHE and the positive end was stepped up in 0.1 V incre-

ments from 0.7 to 1.4 V/RHE. For platinum supported on the carbon Monarch 1300, there was a slight increase in the hydrogen desorption charge on increasing the positive end of the voltage envelope up to 1.2 V/RHE. However, on increasing the limit to 1.3 V/RHE, there was a considerable decrease in hydrogen desorption (Fig. 3). When the limit was extended to 1.4 V/RHE, the electrode displayed a redox behaviour with a reduction peak at 1.05 V. Hydrogen desorption was completely eliminated and a broad oxidation peak appeared at 0.65 V. With further cycling, the reduction peak at 1.05 V shifted to lower potentials (0.95 V) and a new reduction peak appeared at 1.25 V (Fig. 4). With continued cycling, both reduction peaks shifted around an isobestic point at 1.15 V. Platinum supported on CSX 98 carbon exhibited better redox behaviour than on the Monarch 1300 material. However, the poisoning of the electrode in the hydrogen region was less. The Pt/Mogul L carbon also exhibited a redox behaviour, but to a lesser extent than either the Pt/Monarch 1300 or Pt/CSX 98 materials. The results for the Pt/Vulcan XC-72R material are shown in Fig. 5. At 1.3 V there was considerable redox behaviour. On sweeping to 1.4 V, the hydrogen desorption charge decreased by 29%. The results on the Pt/Regal 660R electrode were unique in that there was no redox behaviour even when the sweeps were extended to 1.4 V (Fig. 6). Furthermore the reduction in the degree of hydrogen desorption was only 15%.

Fig. 7 summarizes the effect of increasing the positive limit of the voltage envelope on the hydrogen desorption charge. In some cases, (e.g., Pt/ Mogul L and Pt/Monarch 1300) there was an

Table 4. Kinetic parameters for oxygen reduction on flooded, carbon-supported platinum electrodes (1 mg Pt cm⁻²) in 85% H_3PO_4

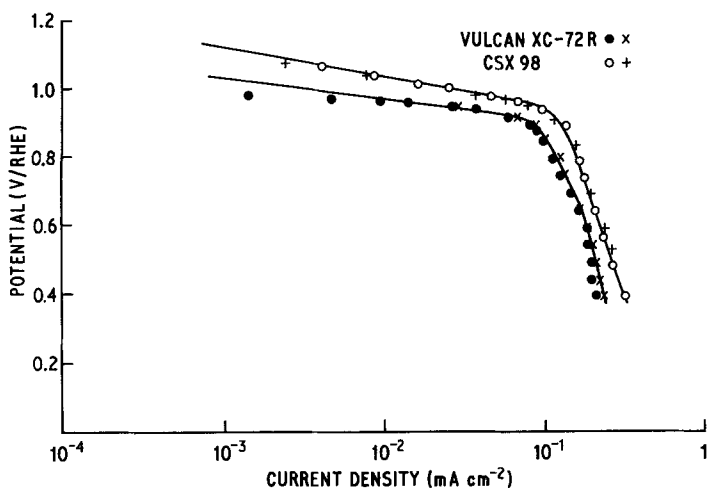| Sample	Tafel slope b (V)		Exchange current density, i_o (A cm⁻²)		Transfer coefficient		Potential at 10^{-4} A cm⁻² (V)	
	25° C	135° C	25° C	135° C	25° C	135° C	25° C	135° C
Monarch 1300	0.105	0.085	5×10^{-10}	2×10^{-7}	0.56	0.95	–	0.87
CSX 98	0.110	0.085	5×10^{-9}	5×10^{-7}	0.54	0.95	–	0.92
Mogul L	–	0.080	–	2×10^{-7}	–	1.0	–	0.82
Vulcan XC-72R	0.080	0.060	3×10^{-9}	2×10^{-8}	0.74	1.35	–	0.85
Regal 660R	0.070	0.070	5×10^{-11}	1×10^{-7}	0.84	1.16	0.46	0.91

Fig. 2. Potential–current density relationship for platinum-catalysed Vulcan XC-72R and CSX 98 (1 mg Pt cm^{-2}) in 85% H_3PO_4 at 135° C.

initial increase up to 1.2 V. This was presumably due to desorption of impurities or to a surface roughening of the platinum in the oxide region. Above 1.2 V, there was a decrease in the hydrogen desorption on platinum for all carbons.

4. Discussion

4.1. *Oxygen reduction kinetics: dependence on carbon support*

The carbon support affects the initial performance and the change of electrode performance with time. The initial performance depends on the degree of dispersion of the platinum and the access of electrolyte to the electrocatalyst. The degree of dispersion of the catalyst was best on the Vulcan XC-72R and Regal 660R materials. The low degree of dispersion on the other materials is presumably due to the hydrophobic character of the other carbons, which is attributed to the large volatile content. This hydrophobic character was evident in the wetting tests, particularly in the case of the
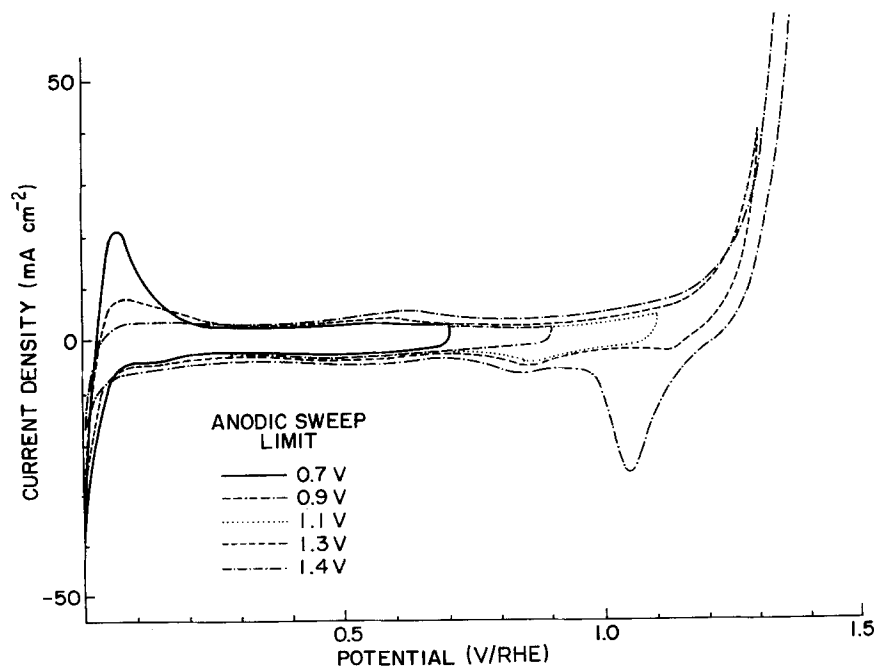

Fig. 3. Cyclic voltammograms on Monarch 1300 carbon (1 mg Pt cm^{-2}) with increasing anodic sweep limits; 85% H_3PO_4 at 138° C. Sweep rate: 50 mV s^{-1}.
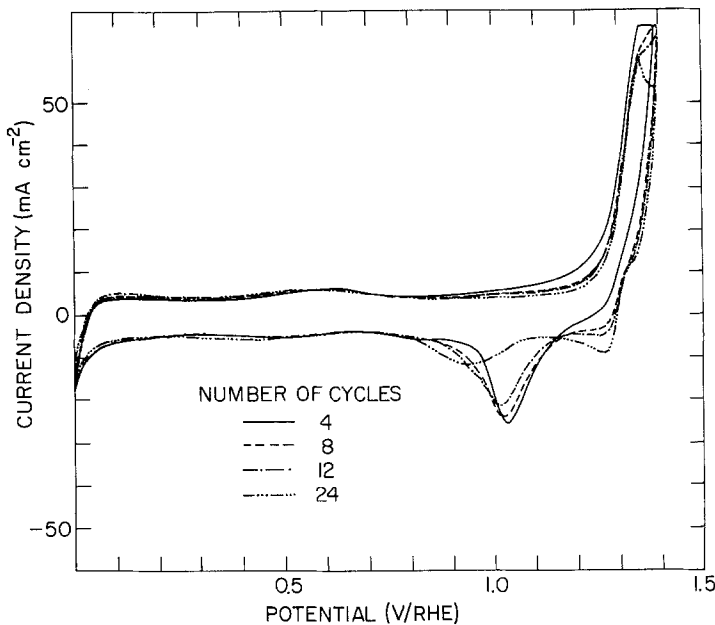
Fig. 4. Changes in cyclic voltammogram on Monarch 1300 carbon (1 mg Pt cm^{-2}) with cycling between 0 V and 1.4 V in 85% H_3PO_4 at 138° C. Sweep rate: 50 mV s^{-1}.

CSX 98 material, and in the poor electrode performance at 25° C. In addition to the wetting characteristics, internal porosity appears to be important and probably contributes to the higher degree of dispersion on Vulcan XC-72R. Correlations have been made between the degree of dispersion and the surface area of the carbon support [3, 7]. However, this work and the results of Ehrburger and Walker [8] indicate that a high degree of dispersion can be obtained on a low-surface-area material if it has the proper surface properties.

Since, at 25° C, not all the supported platinum electrocatalysts were wetted, it is best to compare oxygen reduction kinetics at 135° C. The Tafel slope on the Vulcan XC-72R and on the Regal 660R was low (60–70 mV). On the other materials the Tafel slope was somewhat higher. This may be due to adsorption of impurities from
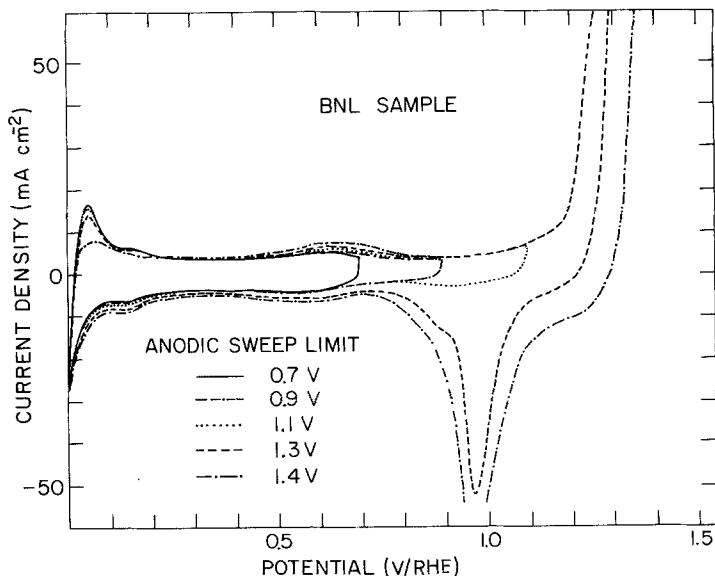
Fig. 5. Cyclic voltammograms on Vulcan XC-72R carbon (1 mg Pt cm^{-2}) in 85% H_3PO_4 at 138° C. Sweep rate: 50 mV s^{-1}.
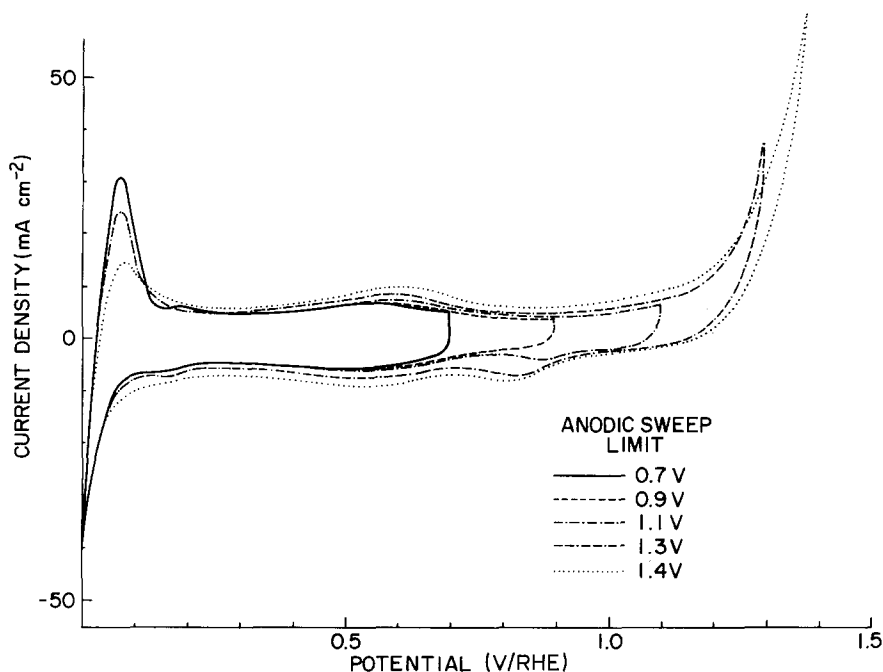
Fig. 6. Cyclic voltammograms on Regal 660R carbon (1 mg Pt cm^{-2}) in 85% H_3PO_4 at 138° C. Sweep rate: 50 mV s^{-1}.

the volatile component of the carbon. Oxidation of these impurities on platinum on Mogul L and Monarch 1300 carbon could account for the

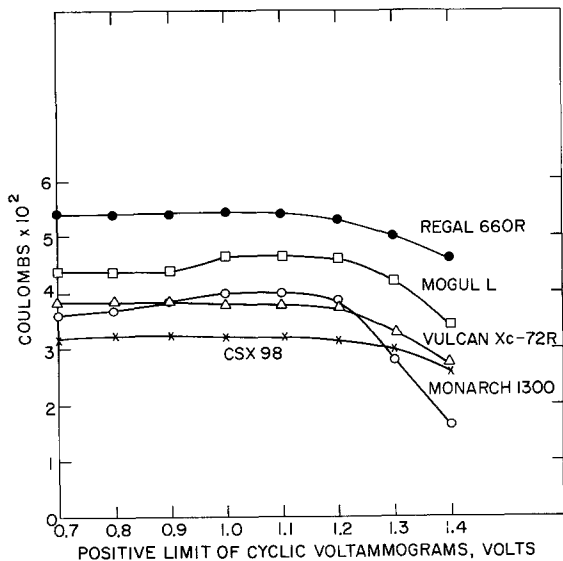increase in hydrogen desorption on extending the linear sweeps to 1.0 V (Fig. 7).

There is a general consensus in recent work [9, 10] that the Tafel slope for oxygen reduction is about 65 mV/decade for potentials more positive than ~ 0.8 V. In the normal operating region of fuel cells (0.6 V to 0.8 V) the Tafel slope is ~ 120 mV/decade. Because the electrodes were operated in the flooded mode, Tafel behaviour occurred only in the potential region 0.9 V to 1.1 V. At more negative potentials the slope increased because of mass transfer limitations. The low Tafel slope and a transfer coefficient close to unity has been ascribed to oxygen reduction with adsorption of oxygen under Temkin conditions [11]. Even though the low Tafel slope extends over a very small potential region (0.9–1.1 V) it could be reproduced repeatedly at 135° C in these tests and in other work on electrodes operated in the gas-diffusion mode [12]. At 25° C, the only carbon support that yielded a transfer coefficient close to unity was the Regal 660R carbon. However, it was the only carbon that gave stable performance at 25° C. The other lower values for the Monarch 1300 and the CSX 98 carbons may be due to impurities from the high volatile content of these carbons.

Fig. 7. Dependence of hydrogen desorption charge on the positive limit of the linear sweep rate in 85% H_3PO_4 at 138° C. Carbon supports as indicated on figure with 1 mg Pt cm^{-2}.

4.2. *Dependence of platinum sintering on carbon support*

Even though the degree of dispersion on Vulcan XC-72R was good the sintering rate was rapid. This behaviour is in agreement with other results on sintering of platinum supported on Vulcan XC-72R carbon where an initial rapid sintering was observed followed by a slower overall rate of decrease in surface area [13]. After about 1600 h the platinum surface area decreased by 47.3% where, over a similar time period, no decrease in surface area was observed in the case of the Regal 660R support. The difference may be due to the fact that the degree of dispersion of platinum on Vulcan XC-72R is due to the high internal porosity which disperses the chloroplatinic acid, whereas the dispersion of platinum on the Regal 660R is due to the surface properties of the carbon which results in a strong carbon–platinum interaction. This concept has been invoked to explain the remarkable stability of platinum at elevated temperatures on activated carbon supports [8].

4.3. *Cyclic voltammetry: a useful technique for assessing stabilities of carbon supports for platinum electrocatalysts*

The present study demonstrates the usefulness of the cyclic voltammetric technique, with progressive increase of the anodic sweep limits, to gain information on the stability of carbon supports for platinum electrocatalysts. Assessment of the carbon stability can be made from two observations on the cyclic voltammograms. Firstly, by increasing the anodic sweep limit above 1.2 V/RHE: the anodic currents increase significantly and a new cathodic peak for reduction of the oxidized carbon is visible. Secondly, the hydrogen desorption charge is decreased. It is very probable that some of the carbon corrosion products at the high anodic potentials remain adsorbed on the electrode surface, even at the more cathodic potentials and inhibit the hydrogen absorption reaction. The method can be used *in situ* to correlate performance decay with carbon degradation.

In the case of Monarch 1300, the carbon with the highest volatile content, an isobestic point was observed on the cathodic sweep at 1.15 V. It has been shown that isobestic points can occur when an electrode is cycled repeatedly in the same potential envelope [14]. This has been ascribed to the fact that there is at least one adsorbed species on the electrode and the initial amount of adsorbed species is different for each potential sweep [15]. In this case it could be due to oxidation of quinone groups to carbon dioxide.

4.4. *An assessment of the usefulness of the tested carbon materials*

Of the four types of Cabot carbon materials (Monarch 1300, CSX 98, Modul L and Regal 660R), in addition to Vulcan XC-72R, which were tested as support materials for platinum electrocatalysts, only the Pt/Regal 660R electrode exhibited a stable oxygen reduction performance at 25° C and 135° C. At the higher temperature, the experiments were carried out over a 2000 h period. The cyclic voltammetric studies on this electrode indicated a marked resistance to corrosion. The Regal 660R carbon sample has a low internal porosity, low volatile content and neutral pH. This furnace black, without any further heat treatment, shows prospects of being a suitable substitute for Vulcan XC-72R as the carbon support for platinum fuel cell electrocatalysts. A more detailed, long-term evaluation in single and multicell phosphoric acid fuel cells is essential before a final assessment can be made of the usefulness of Regal 660R as a support material for platinum electrocatalysts.

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