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*Electrochemical methods for the in situ regeneration of active surface area of aged fuel cell type electrodes**

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One of the main reasons for the decay in performance of phosphoric acid fuel cells (150° C) is the decrease in surface area of the platinum catalyst with time. It was found that fast potentiostatic cycling ($50\,\mathrm{mV\,s^{-1}}$) could regenerate the surface area of the Pt and recover the performance. The mechanism of regeneration is likely to be charge injection, resulting in electrostatic repulsion of the platinum particles in the loosely held agglomerates.

1. Introduction

The sintering of Pt black electrodes in phosphoric acid fuel cells operating above 150° C is one of the major reasons for the decay of Pt/C electrodes. In the first 1000 h of operation, there is a 100 mV drop in cell potential at a current density of $100\,\mathrm{mA\,cm^{-2}}$ [1]. Various mechanisms for the sintering of Pt black have been proposed. Bett *et al.* [2] and Gruver *et al.* [3] are in favour of the surface migration mechanism where the Pt particles collide with each other, leading to coalescence. Tseung and Dhara [4] suggest that sintering occurs via a solution–reprecipitation process, similar to the liquid phase mechanism encountered in the sintering of pottery and cobalt–tungsten carbide cutting tools.

Various attempts have been made to reduce the rate of sintering of Pt black in phosphoric acid fuel cells. Blurton *et al.* [5] succeeded in reducing the rate of sintering of Pt black by pre-oxidation of the carbon support prior to being coated with platinum. Tseung and Dhara [6] used Sb-doped SnO_2 instead of graphite to reduce the rate of sintering. However, these methods do not provide long-term solutions.

From a thermodynamic point of view, all systems tend to the lowest possible free energy state. Thus, it is certain that at elevated temperatures and in corrosive environments, high surface area electrocatalysts will grow in size. Therefore, one practical long-term solution is to devise a method of periodic regeneration of electrochemical active surface area of aged electrodes. One possible approach is electrochemical regeneration, whereby the potential is increased and lowered repeatedly. In this way, the surface of the platinum may be roughened due to the repeated formation of platinum oxides and their reduction to platinum metal.

Kinoshita *et al.* [7] used a slow potential cycling method ($0.045\,\mathrm{V\,s^{-1}}$, 0.05–1.4 V/RHE) on Pt foil, Pt black and Pt/C electrodes in H_2SO_4 at room temperature and found that the surface area of Pt foil could be increased but that the surface area of Pt black and Pt/C was decreased. Untereker and Brunkenstein [8] investigated the fundamental roughening mechanism of Pt foil by using a

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rotating ring disc technique on smooth platinum electrodes. They used a higher potential cycling rate (90 V s^{-1}, 0.2–2.0 V/RHE). By monitoring the current on the ring electrodes, they were able to prove that the roughening process is due to solution and reprecipitation and it was also shown that lower rotation speeds gave greater surface roughening, since more soluble platinum species would be available at the platinum surface. In the case of Pt black and Pt/C electrodes studied by Kinoshita *et al.* [7], the concentration of soluble platinum species near the platinum surface should be high since these will be trapped inside the pores of the electrodes. The inability to achieve surface roughening in these cases may be due to the low potential cycling rate.

2. Experimental procedure

2.1. *General methodology*

In the present work, two electrochemical approaches were selected to attempt the periodic regeneration of the electrochemically active surface areas of aged electrodes. In one, the potential of the electrode was stepped up to a value at which a uniform oxide is formed and then the potential was lowered to reduce the oxide, with the expected roughening of the surface. In the second, the potential of the electrode was cycled at a fast rate in the desired potential range. It was expected that if the scan rate was fast enough, the platinum ions, formed at the anodic potentials, would be deposited in a pulse-plating mode as fine crystallites which would consequently roughen the surface.

For a quantitative evaluation of the method, the electrochemically active surface areas were determined prior to and after electrochemical treatment. In addition, some of the experiments also involved the measurement of oxygen reduction currents as a function of time in an effort to correlate the change in electrocatalytic activities with the change in electrochemically active surface areas. In the initial experiments, H_2SO_4 was used as the electrolyte with smooth and Pt black electrodes. However, for the more detailed studies unsupported and supported porous fuel cell type electrodes were used in 85% H_3PO_4. Electrodes were operated in the flooded mode for the surface area measurements and in the gas-fed mode for characterization of oxygen reduction performance.

2.2. *Cell–Electrodes–Electrolyte*

2.2.1. Cell. A special 9-compartment quartz cell consisting of 3 individual cells was fabricated. The working and reference compartments were connected by a Luggin capillary. This cell was used for the unsupported Teflon bonded Pt black electrodes. A Teflon beaker cell was used for carbon supported electrodes. The counter electrode was inserted into an open-ended quartz tube and the reference electrode into a quartz tube with a Luggin capillary. These cells were placed in a furnace and heated up to 150° C. Incoming gases were prehumidified to keep the concentration of the electrolyte constant.

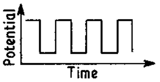
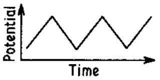
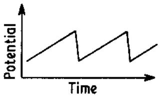
2.2.2. Electrodes. Unsupported electrodes were fabricated into thin film hydrophobic Teflon bonded electrodes, according to the method described by Vogel and Lundqvist [9]. The catalyst/dispersion ratio was 10:3. The thin film was pressed into a 52-mesh Pt current collector screen. The catalyst loading was 11.58 mg Pt cm^{-2}.

These electrodes were run in two modes, as gas-fed electrodes to monitor current variation with time and in the flooded mode to observe changes in surface area with time. The counter electrodes consisted of large cylindrical Pt screen Teflon bonded Pt black electrodes. Dynamic hydrogen electrodes or reversible hydrogen electrodes served as references.

The carbon supported platinum fuel cell electrodes were obtained from the Energy Research Corporation (ERC). The catalyst loading was 0.35 mg Pt cm^{-2}. The carbon backing paper of these electrodes was removed and the carbon catalyst layer was mounted onto 100-mesh gold screens, serving as current collectors.

Two of the electrodes were heat treated in 85% H_3PO_4 at 150° C for various lengths of time. This was done by placing them in sealed glass vials. One electrode was a fresh sample. (ERC heat treats the electrodes to improve wetting characteristics.) All three electrodes were run in the flooded mode to monitor surface area with time changes.

Table 1. Variation in techniques of electrochemical treatment of freshly prepared and aged porous electrodes

Number	*Treatment*	*Potential limit* (V/RHE)		*Wave form*	*Length of treatment* (min)
		Lower	*Upper*		
1	Potential step Pulse width 2 s–1 h	0.5 0	1.3 1.3		10–60
2	Triangular wave Sweep rate 1 V s^{-1}–100 V s^{-1}	0	1.3		10–60
3	Sawtooth wave Oxide formation/reduction at ramp of 10 s/1 s	0.5	1.3		10–60

2.2.3. Electrolyte. The electrolyte used was 85% H_3PO_4 from the Mallinckrodt Company. The electrolyte was cleaned by purifying it with 30% H_2O_2 at elevated temperatures. This procedure was followed by pre-electrolysis at + 1.3 V [10].

2.3. *Surface area measurements*

A cyclic voltammetry technique was used to determine the Pt surface areas. This method was extensively tested on high surface area electrodes in concentrated H_3PO_4 at elevated temperatures. The voltage envelope for measuring the hydrogen oxidation charge on porous electrodes was defined and it was found that the cathodic limit of the sweep range was not critical, since no molecular hydrogen in the vicinity of the electrode was oxidized at the anodic side of the sweep. These findings are contrary to planar electrodes, where about one-third of the molecular hydrogen, which is evolved at the cathodic side of the sweep, is oxidized anodically.

2.4. *Techniques attempted for* in situ *regeneration of the active surface area of the electrodes*

Three techniques were selected for *in situ* regeneration of the active surface areas of porous electrodes. These were: (a) potential step or square-wave; (b) triangular wave; and (c) sawtooth wave (see Table 1). All three methods were based on pulsing the electrodes between two potentials at various time intervals in order to induce oxide formation and the reduction or making and breaking the Pt–O bond. All three treatments described in Table 1 were attempted on fresh and aged Teflon bonded Pt black electrodes. Only the triangular wave treatment (also referred to as fast potential cycling) was successful in regenerating the active surface area of an aged porous electrode.

Table 2. Changes in surface area of an unsupported platinum catalysed porous electrode (10 mg Pt cm^{-2}) with time before and after electrochemical activation as measured using hydrogen desorption or the double-layer charging method

Time *Electrochemical treatment*	*H_2 desorption* (Coulombs)	*Change ratio* (C_s/C_0)	*Double-layer capacitance* (Farads)	*Change ratio* (F_s/F_0)
Initial	0.185	1.0	0.105	1.0
5 days later	0.15	0.81	0.0825	0.78
8 days later	0.13	0.70	0.0775	0.73
After treatment at 10 V s^{-1} for 60 min	0.178	0.96	0.1	0.95

No surface area changes were observed on the fresh electrodes with any of the above treatments.

3. Results

3.1. *Regeneration studies on unsupported platinum electrodes*

Two electrochemical methods were attempted for the periodic regeneration of the active surface area and hence of the electrocatalytic activity for the oxygen reduction reaction. In one, the potential of the electrode was stepped up to a value at which a uniform oxide layer was formed and then the potential was lowered to reduce the oxide. In the second, the potential of the electrode was cycled at a fast rate between 0 and 1.3 V versus the reversible hydrogen electrode. During this procedure it was expected that platinum dissolves and reprecipitates on the surface as fine particles. The changes in surface areas, if any, were ascertained by using the cyclic voltammetric techniques as described in the previous section. The electrodes were Teflon bonded Pt black applied to a Pt screen current collector. The first method, i.e. by stepping up the potential to 1.3 V and then lowering it to 0.5 V/RHE was not successful. However, the second method, i.e. fast potential cycling over the range 0 to 1.3 V/RHE had a beneficial effect (see Table 2).

A striking result was that none of the methods (potential cycling, potential step or sawtooth wave) tabulated in Table 1 produced any change in the surface area of freshly prepared, unsupported platinum fuel cell type electrodes. However, the behaviour was different with aged electrodes. The fast potential cycling method proved to be successful for the regeneration of active surface areas of these electrodes. For further investigation of this phenomenon, the time variation of the oxygen electrode performance was determined. This study required hydrophobic leak-free electrodes, which could be monitored in the gas fed mode. New Teflon bonded Pt black electrodes were prepared by the method of Vogel and Lundquist [9]. All the data were obtained in 85% H_3PO_4 at 150° C. The potentials were measured with respect to a DHE. The electrodes were utilized in three different configurations: a gas-fed floating electrode which was used only for monitoring the oxygen reduction performance; a flooded electrode used only for determining the change in surface area with time; and a gas-fed electrode with oxygen for monitoring oxygen reduction performance and with nitrogen for surface area determination. These electrodes were not pre-aged but were placed directly in 85% H_3PO_4 and brought up to 150° C in the furnace. The initial aging was carried out in the operating cell. The surface areas were determined *in situ* by the hydrogen desorption technique. In Fig. 1 the time dependence of the surface area is shown for completely immersed electrodes held at

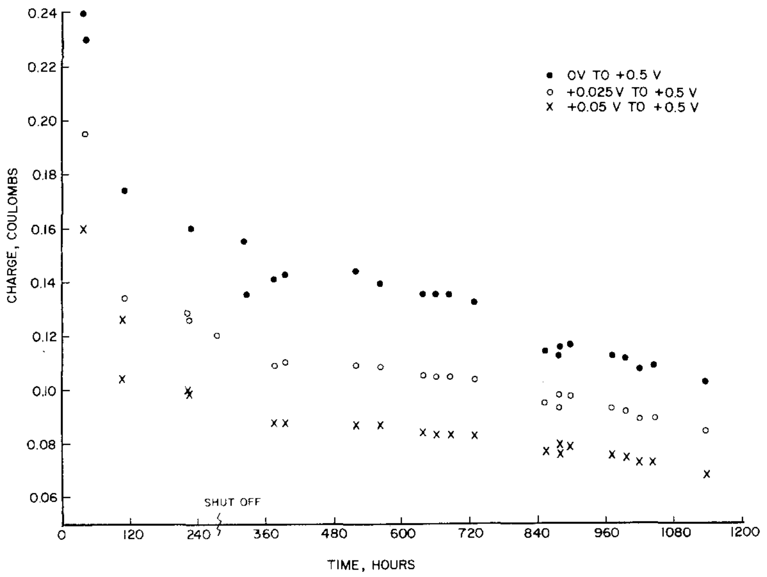


Fig. 1. Change of surface area of an unsupported platinum catalysed porous electrode (11.6 mg Pt cm^{-2}) with time in 85% H_3PO_4 at 150° C.

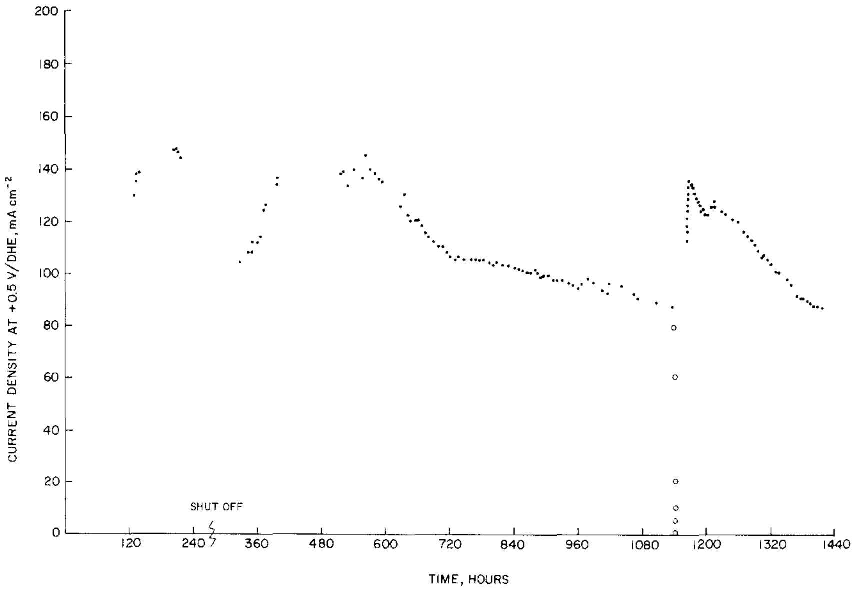


Fig. 2. Change in performance of an unsupported platinum catalysed porous electrode (11.6 mg Pt cm^{-2}) with time in 85% H_3PO_4 at 150° C.

0.6 V/DHE. The three curves show the dependence of the decrease in the amount of adsorbed hydrogen with time on the cathodic sweep limit, which is consistent with the loss of surface area shown by using both the capacitance and BET techniques. Fig. 2 shows the performance of the same type of electrode, run with O_2 in a fuel cell mode at 0.5 V/DHE. Initially, the current increased and then passed through a maximum. This behaviour is typical during the conditioning of a new hydrophobic electrode and is due to changes in the wetting characteristics of the electrode. After passing through a maximum, the performance decays at a rapid rate (5 mA day^{-1}) initially and after about 200 h, this rate of decay changed to 1 mA day^{-1} and remained constant for about 940 h. After the first 1140 h, there was a decrease of 40% from the initial current, which is consistent with the equivalent loss of surface area. The changes in surface area can be very clearly seen from the cyclic voltammograms in Figs 3 and 4. After this time, the porous electrode was cycled

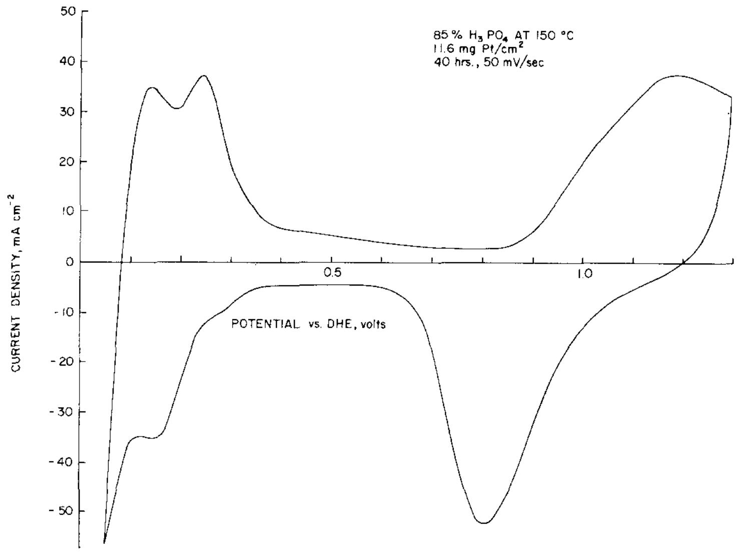


Fig. 3. Cyclic voltammogram of an unsupported platinum catalysed porous electrode (11.6 mg Pt cm^{-2}) after 40 h at + 0.6 V/DHE in 85% H_3PO_4 at 150° C.

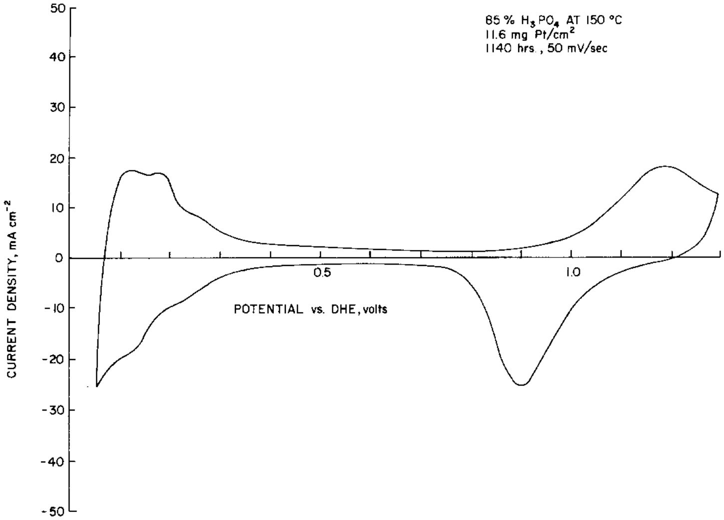


Fig. 4. Cyclic voltammogram of an unsupported platinum catalysed porous electrode (11.6 mg Pt cm^{-2}) after 1140 h at + 0.6 V/DHE in 85% H_3PO_4 at 150° C.

between 0 and 1.3 V at several different sweep rates and the surface area was determined following each of these treatments. The results of the fast potential cycling experiments are summarized in Table 3. The surface area increases with all fast cyclic treatments; however, there is a definite dependence on the sweep rate. A sweep rate of 100 V s^{-1} produced the largest increase in surface area which reaches a constant value after about 20 min of cycling. Overall, 95% of the original performance and surface area are regenerated by the fast cycling process. The rate of decay of oxygen reduction performance follows the same pattern as the decrease in electrochemically active surface area of the electrode.

Table 3. Dependence of increase in surface area of aged, unsupported platinum catalysed porous electrode (11.6 mg Pt cm^{-2}) on sweep rate and time using the fast potential cycling method

Potential cycling time, 0–1.3 V/DHE (min)	*Sweep rate* (V s^{-1})	*H_2 oxidation charge, 0–0.5 V/DHE* (Coulombs)	*Surface area increase factor*
0		0.11	1.0
60	10	0.13	1.18
60	50	0.148	1.35
20	100	0.154	1.40
15	100	0.155	1.41
15	100	0.155	1.41
15	100	0.155	1.41
15	100	0.155	1.41
10	100	0.155	1.41

3.2. *Regeneration studies on supported platinum electrodes*

The experimental studies on carbon supported platinum fuel cell type electrodes consisted of: (a) investigations of the effect of pre-aging; (b) *in situ* determinations of the decrease in electrocatalyst surface area with time; and (c) attempts to regenerate the active area of the electrocatalyst by the fast potential cycling technique in various voltage envelopes. The carbon supported platinum sheets were in the form of PTFE bonded sheets (0.015 inch, 0.38 mm thick). These electrodes furnished by ERC had a platinum loading of 0.35 mg cm^{-2}. The sheets were identical to standard fuel cell type electrodes, except that there was no carbon paper backing.

Three electrodes were tested. Electrodes 1 and 2 were pre-aged for 197 and 43 days, respectively, at 150° C in quartz vials. The three electrodes were then mounted in PTFE cells and aged for several thousand hours at 150° C in the flooded mode. The surface areas were determined by the hydrogen desorption method and are shown as a function of time in Fig. 5. The anodic sweep limit for cyclic voltammetry on supported electrodes for determination of surface areas was changed from 1.3 V (as with unsupported electrodes) to 0.8 V due to the expected carbon corrosion at higher potentials. Electrodes 1 and 2 showed a steady decrease in area with time of aging. Electrode 3 which had not been pre-aged, showed an initial increase in surface area due to wetting of

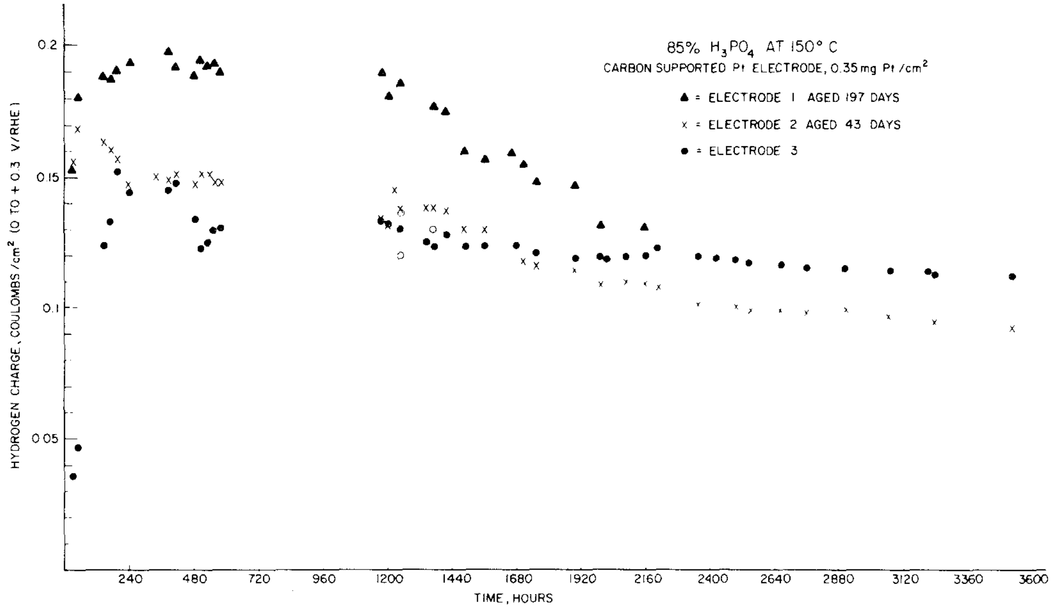


Fig. 5. Decrease of hydrogen desorption charge at carbon supported platinum catalysed porous electrodes with aging time in 85% H_3PO_4 at 150° C.

the electrode, followed by a sharper decrease up to 600 h. After 600 h, all electrodes exhibited the same behaviour, Figs 6 and 7 represent typical cyclic voltammograms after the stated aging times. In all three cases, the rate of decrease in electrochemically active surface area was much slower than previously observed for unsupported platinum electrodes.

The surface area loss was then monitored on two electrodes for a total period of 5112 h. By this time, Electrodes 2 and 3 had lost 51 and 27% of their original surface areas, respectively. Before an attempt was made to regenerate the surface areas of these electrodes electrochemically, investigations were carried out on other electrodes to determine the effect of various voltage cycling regimes on carbon oxidation. In these studies, fresh carbon supported platinum electrodes were mounted in a cell with an identical configuration to that used in the long-term study. The electrolyte used was 85% H_3PO_4 and the temperature was 150° C. The electrode surface area was monitored by cyclic voltammetry at 50 m V s^{-1} between 0 and

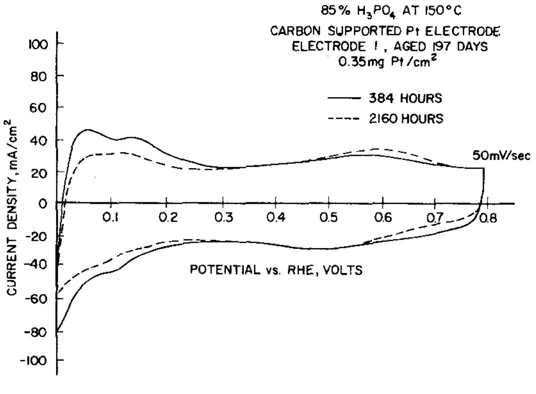


Fig. 6. Time dependence of cyclic voltammograms on the carbon supported platinum catalysed porous Electrode 1 in 85% H_3PO_4 at 150° C.

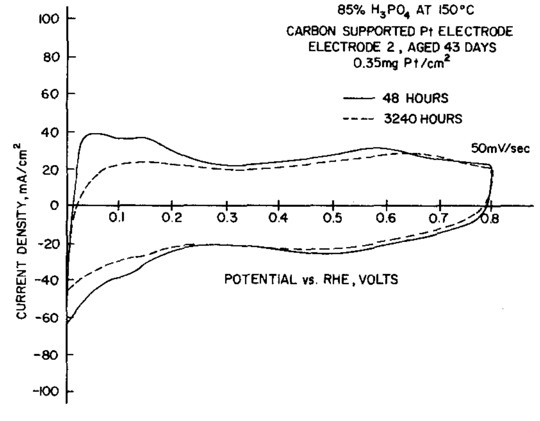


Fig. 7. Time dependence of cyclic voltammograms on the carbon supported platinum catalysed porous Electrode 2 in 85% H_3PO_4 at 150° C.

0.8 V/RHE until stable wetted behaviour was obtained. The electrode was subjected to fast potential cycling between 10 V s^{-1} and 1000 V s^{-1} in various voltage envelopes up to an anodic limit of 1.4 V/RHE. After each fast cycling treatment, the anodic sweep limit was reduced to 0.8 V/RHE and voltammograms were recorded at 50 mV s^{-1}. The hydrogen desorption charges were compared after each fast sweep treatment. At slow sweep rates (e.g. 50 mV s^{-1}), a carbon oxidation peak was observed when the electrodes were cycled above 1.0 V. There was a concomitant decrease in the hydrogen adsorption and desorption area. However, at fast sweep rates (e.g. 100 V s^{-1}) there was no carbon oxidation peak even when the electrode was anodized up to 1.4 V. Thus it was established that fast cycling treatments in the range 0–1.4 V did not damage the carbon support. Attempts were then made to regenerate the aged electrodes by fast potential sweeps extending into this anodic region.

The first attempt at regeneration was by fast cycling for 60 min at 100 V s^{-1} in the voltage range 0–1.4 V. This treatment resulted in a 20% increase in the area of Electrode 2 and a 9% increase in the area of Electrode 3. A second treatment at 200 V s^{-1} in the voltage range 0–1.4 V for 60 min resulted in a recovery of 77% of the surface area of Electrode 2 and a 97% recovery of the initial surface area of Electrode 3. Further treatments at 500 and 1000 V s^{-1} yielded no further improvement. The surface area recovery was stable over a period of 15 days. The cells were dismantled ater a total of 5616 h of running time.

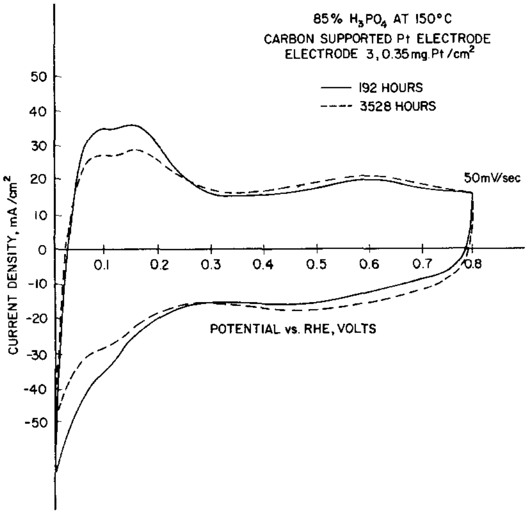


Fig. 8. Time dependence of cyclic voltammograms on the carbon supported platinum catalysed porous Electrode 3 in 85% H$_3$PO$_4$ at 150° C.

The results of these tests demonstrate that aged carbon supported electrocatalysts can be regenerated by fast potential cycling (200 V s^{-1}) in the potential range 0–1.4 V/RHE without any damage to the carbon structure. This treatment corresponds to a frequency of 71.5 Hz with a peak-to-peak voltage of 1.4 V. The results of the aging and regeneration of the supported catalysts are summarized in Table 4. The cyclic voltammograms at Electrodes 2 and 3 before and after fast cycling treatment are shown in Figs 9 and 10.

4. Discussion

4.1. *Comparison of electrochemical techniques used for surface area regeneration: fast potential cycling, the only successful method*

In the present work, two methods (potential step and fast potential cycling) were attempted for the periodic regeneration of the active surface areas of aged fuel cell type electrodes (unsupported and supported). Only the fast potential cycling method was successful. A very definite dependence of the extent of regeneration on the sweep rate, on the potential range and on the time of cycling was observed. With the unsupported platinum electrodes, a sweep rate of 100 V s^{-1} in the potential

Table 4. Changes in the electrochemically active surface area of carbon supported platinum catalysed porous electrode 0.35 mg Pt cm^{-2} with aging time and after fast potential cycling activation in 85% H$_3$PO$_4$ at 150° C

Aging time, time of activation at 150° C (h)	*Surface area, percentage loss (—) or gain (+) of initial area*		
	Electrode 1	*Electrode 2*	*Electrode 3*
504	− 3.0	− 10.5	− 12.4
1248	− 7.5	− 16.6	− 12.4
2160	− 33.9	− 35.4	− 20.6
3500	—	− 43.2	− 24.5
5112 (before treatment)	—	− 51.0	− 27.0
5112 (after treatment)	—	+ 77.0	+ 97.0

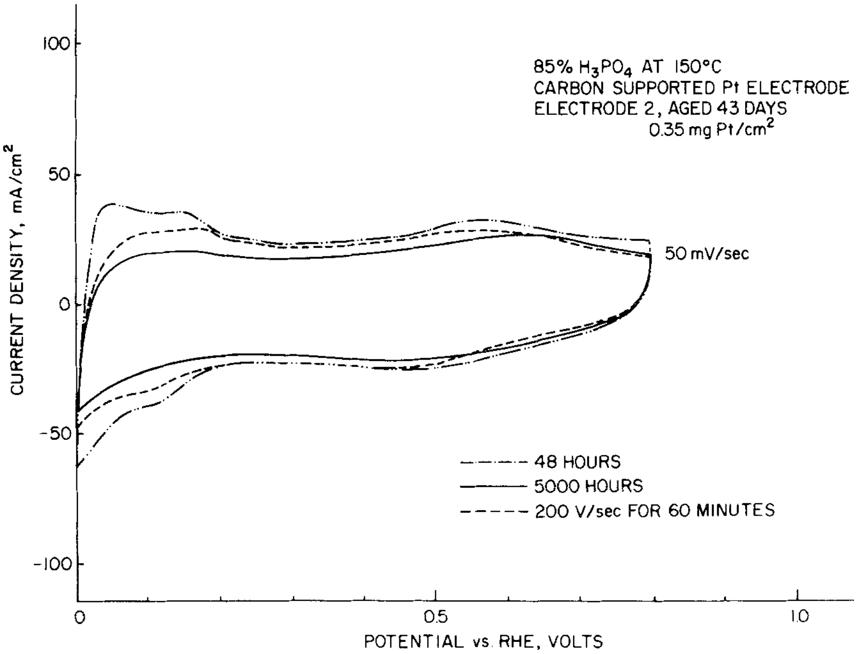


Fig. 9. Surface area loss with time and its regeneration by fast potential cycling on the carbon supported platinum catalysed porous Electrode 2 in 85% H_3PO_4 at 150° C.

range 0 to 1.3 V/DHE produced the largest increase in the surface areas. With the supported electrodes, it was necessary to double the sweep rate and extend the anodic potential limit to 1.4 V/DHE.

4.2. Comparison of the results for unsupported and supported platinum electrodes

In the course of these studies on aging and regeneration of unsupported and supported platinum

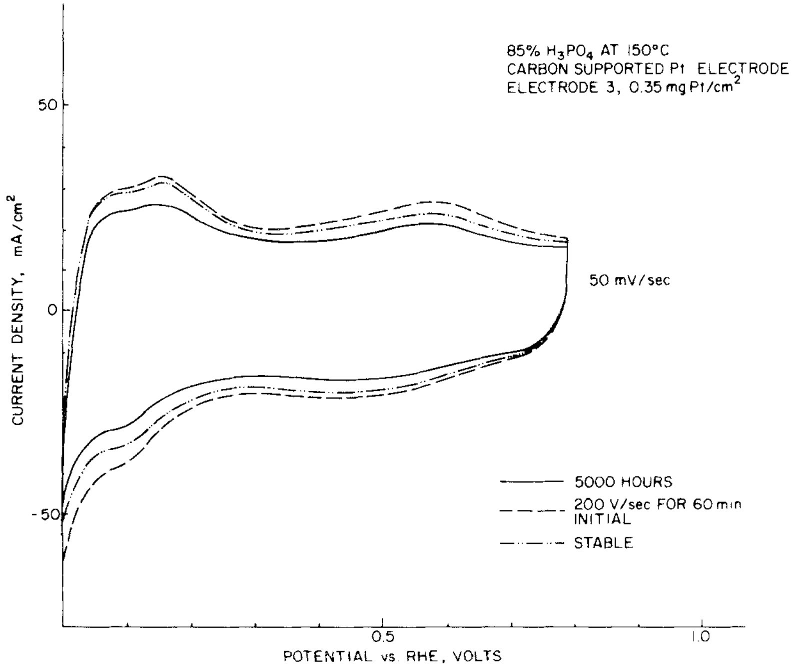


Fig. 10. Surface area loss with time and its regeneration by fast potential cycling on the carbon supported platinum catalysed porous Electrode 3 in 85% H_3PO_4 at 150° C.

electrocatalysts, the following phenomenology has been established:

(a) No treatment has been found that yields a surface area greater than the initial surface area of the electrocatalysts.

(b) Fast cycling treatments at 100 V s^{-1} between 0 and 1.3 V restores ~ 95% of the original surface area of sintered unsupported catalysts.

(c) Fast cycling treatments at 200 V s^{-1} between 0 and 1.4 V restores between 77 and 97% of the surface area of aged supported platinum catalysts.

(d) The rate of decay of both supported and unsupported catalysts proceeds rapidly at first and then continues at a slower rate.

(e) Dispersion of the platinum electrocatalysts on a carbon support decreases the rate of surface area loss by a factor of five.

4.3. *Possible mechanism for sintering fuel cell electrodes and regeneration of active surface area by fast potential cycling*

The observed phenomenon, that it is not possible to increase the surface area of a fresh electrode by the potential cycling treatment, has important implications regarding the mechanism of sintering. It certainly supports the particle agglomeration mechanism due to platinum migration as opposed to liquid phase sintering. The observed experimental data indicate that sintering may perhaps proceed in two steps. First there is the agglomeration of small particles to form clusters that can be broken up by fast cycling. These clusters may then form necks between the large agglomerates. If this occurs, it is unlikely that fast cycling would restore the original surface area.

From the present work, it is possible to exclude the dissolution–precipitation mechanism for the regeneration of the active surface areas of aged electrodes, using the fast potential cycling method, for the following reasons. Firstly, it is not possible to increase the surface areas of fresh electrodes using this treatment. Secondly, only the original surface areas can be regained by the fast potential cycling. On the contrary, increases over the original surface areas should be possible if the dissolution–precipitation mechanism was operative. On the basis of these results, the following scheme is proposed for the mechanism of regeneration by the fast cycling method: (a) injection of charge to agglomerated particles and consequently a change in double layer characteristics; (b) electrostatic repulsion of charged particles; and (c) dispersion of charged particles which leads to the original surface area.

4.4. *An assessment of the usefulness of the fast potential cycling method for the regeneration of electrochemically active surface areas*

The results obtained by the use of the fast potential cycling method on fresh and aged electrodes lend support to the view based on thermodynamic reasoning that small particles will grow in size by migration and agglomeration and not by the dissolution–precipitation mechanism. The agglomeration is a reversible phenomenon, i.e. the activity of aged electrodes can be regenerated by fast potential cycling which causes a dispersion of the loosely held agglomerates. There is a concomitant decrease of oxygen reduction performance with loss of surface area due to aging, and likewise, a similar correlation exists between the increase of performance and surface area by fast potential cycling. The incorporation of inert materials (eg. oxides, phosphorus) could slow down the aging phenomenon. This was confirmed by the observation that the aging is five times slower on supported than on unsupported electrodes. The rates of oxygen reduction and surface area decay on the rejuvenated electrode are the same as on a fresh electrode. One can envisage the periodic regeneration of initial activities of operating fuel cells by the fast potential cycling method. It will be necessary to make some detailed estimates of: (a) energy and auxiliary equipment requirements, (b) net performance gains, (c) effect of regeneration on cost of electricity produced, and (d) effect of repeated regeneration on the carbon support. At the present time, it appears that this method of rejunevation is more feasible for small fuel cell systems (e.g. less than 100 kW on site integrated energy systems), rather than megawatt size power plants.

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