An investigation into factors affecting the stability of carbons and carbon supported platinum and platinum/cobalt alloy catalysts during 1.2 V potentiostatic hold regimes at a range of temperatures

S.C. Ball, S.L. Hudson*, D. Thompsett, B. Theobald

Johnson Matthey Technology Centre, Reading, RG4 9NH, UK

Abstract

To meet automotive targets for fuel cell operation and allow higher temperature operation an understanding of the factors affecting carbon and platinum stability is critical. The stability of both carbons and carbon supported platinum and platinum/cobalt alloy catalysts was studied during 1.2 V versus RHE potentiostatic hold tests using carbon and catalyst coated electrodes in a three-chamber wet electrolyte cell at a range of temperatures. At 80 °C the wt% of carbon corroded increases with increasing BET area. Surface oxidation was followed electrochemically using the quinone/hydroquinone redox couple. Increasing temperature, time at 1.2 V and wt% platinum on the carbon increases surface oxidation. Although increasing temperature was shown to increase the extent of carbon corrosion, catalysing the carbon did not significantly change how much carbon was corroded. Platinum stability was investigated by electrochemical metal area loss (ECA). Platinum catalysts on commercial carbons lost more ECA with increasing temperature. A platinum/cobalt alloy on a low surface area carbon was demonstrated to be more stable to both carbon corrosion and metal area loss at temperatures up to 80 °C than platinum catalysts on commercial carbons, making this material an excellent candidate for higher temperature automotive operation.
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Keywords: Corrosion; Platinum; Cobalt; Catalyst; Fuel cell

1. Introduction

The stability of carbon as a catalyst support in fuel cells has previously been widely investigated for phosphoric acid fuel cell applications [1–3]. More recently, challenging durability targets for catalysts, and hence carbon supports, have been proposed for PEMFCs for automotive applications. Catalysts must survive repeated potential cycling and exposure to high potentials during idle/open circuit potential conditions [4]. During a typical automotive stack lifetime of 5000 h, excursion to high potentials (e.g., 1.2 V versus RHE) on start up and shut down can be expected to occur 30,000 times. This has been equated to an accelerated durability test of 100 h at 1.2 V [5]. As a first step to this target, this work reports the findings of potentiostatic hold tests at 1.2 V versus RHE for up to 24 h using carbon and catalyst coated electrodes in three-chamber wet electrolyte cell.

A number of groups [1,2,4,6,7] have studied carbon corrosion using potentiostatically controlled experiments. Antonucci et al. subjected screen-printed carbon black electrodes to 100 min at 1 V versus RHE under phosphoric acid fuel cell operating conditions. By monitoring the corrosion currents with time, they concluded that log (corrosion current) was directly related to log (time on stream) for the duration of the test and the surface area of the carbon related linearly to the measured corrosion currents [2]. For PEMFC applications Mathias et al. report findings of a 100 h 1.2 V hold MEA test with periodic evaluation of the samples under proton exchange membrane fuel cell operating conditions. Standard carbon catalysts experienced unacceptably high performance loss during the test as a result of carbon corrosion. Platinum alloy catalysts, on a corrosion resistant carbon, showed no decrease in performance after 100 h at 1.2 V. However, the initial performance of these catalysts did not meet the activity requirements for fuel cell commercialisation [4].

* Corresponding author. Tel.: +44 118 924 2035; fax: +44 118 924 2254.
  E-mail address: hudsos@matthey.com (S.L. Hudson).

In acid electrolytes the mechanism of electrochemical carbon corrosion is generally thought to proceed via a three-step process involving four electrons [8]. In the first step the carbon is oxidised (Step 1). This allows the formation of oxidised carbon intermediates by two electron partial oxidation (Step 2). The intermediates may be electro active such as the quinone/hydroquinone redox couple and can be studied by cyclic voltammetry [9–11] or other species such as hydroxides and carboxylates that can be studied by X-ray photoelectron spectroscopy or infrared spectrometry [6,12,13]. The final step of corrosion process (Step 3) is the formation of carbon dioxide.

Step 1   Oxidation of the carbon lattice $C_s \rightarrow C_s^+ + e^-$
Step 2   Hydrolysis $C_s + 1/2\,H_2O \rightarrow C_sO + H^+$
Step 3   Gasification to carbon dioxide: $2C_sO + H_2O \rightarrow C_sO + CO_2 + 2H^+ + 2e^-$

$$Net: C + H_2O \rightarrow CO_2 + 4H^+ + 4e^-, \qquad E = 0.207\,V_{RHE}$$

Thus, at 1.2 V carbon corrosion is thermodynamically favourable and has been studied by measuring the evolved CO_2 by volumetric analysis [1], mass spectrometry [4,8] or, as in this work, by monitoring the corrosion current with time.

Loss of electrochemically active metal area results in loss of fuel cell performance. A comprehensive discussion on the instability of Pt/C electrocatalysts has been recently published by Ferreira et al. [14] the processes relevant to this study in acid electrolyte are:

(i) Platinum particle agglomeration triggered by corrosion of the carbon support
(ii) Platinum dissolution and redeposition as a nanoscale Ostwald-ripening process. This dissolution may be electrochemical $Pt \rightarrow Pt^{2+} + 2e^-$ or chemical via platinum oxide film formation $PtO + 2H^+ \rightarrow Pt^{2+} + H_2O$ [15].

In order to meet automotive performance targets [16] there has been a recent focus on platinum alloy catalysts for PEMFC applications. Currently Pt/Co alloy catalysts have been reported to be twice as active as commercially available platinum supported catalysts for oxygen reduction in PEM fuel cells [17–19] and under 0.6–1.0 V cycling regimes [18] and holds at potentials up to 0.9 V [20,21] alloying has been shown to have a beneficial effect on platinum stability.

It has yet to be shown whether these materials can survive in an operating PEMFC environment at higher temperatures of up to 120 °C. Under these conditions thermal management of the system is improved and benefits in terms of reaction kinetics and tolerance to impurities, such as CO, are achieved [22,23]. The lack of suitable ionomer materials is currently limiting the progression to high temperature operation, however, it is important to determine how the other membrane electrode assembly components will perform at these higher temperatures.

This work therefore, not only aims to determine which factors affect the stability of carbons and carbon supported platinum and platinum/cobalt alloy catalysts during 1.2 V potentiostatic hold regimes at 80 °C and discusses the mechanisms by which they

occur, but will also allow prediction of consequences on MEA performance at 120 °C.

2. Experimental

2.1. Carbons

Commercial carbons and heat treated carbons with BET surface areas in the range of 60–1500 $m^2\,g^{-1}$ were studied. A selection of carbons, C01, (850 $m^2\,g^{-1}$), C02, (250 $m^2\,g^{-1}$), both commercial carbons and a heat treated carbon C03, (130 $m^2\,g^{-1}$) were used as catalyst supports.

2.2. Catalyst preparation & characterisation

Catalysts were prepared as summarised in Table 1. Catalysts b, c and d are the commercially available materials, HISPEC 4100, 11100 and 4000, respectively. The other catalysts were prepared using methods that have previously been described [24–26]. Briefly, the carbon is slurred in weakly basic water before addition of the metal salts. On complete deposition of the metal, the metal was reduced either by chemical methods or by heat treatment. Alloying of the Pt/Co catalysts was confirmed by the presence of a Pt_3Co phase using XRD analysis with a BrukerAXS D-500 Diffractometer. XRD crystallite sizes were determined for each catalyst. Measurement of electrochemical surface area (ECA) was determined from cyclic voltammetry using the hydride adsorption/desorption (HAD) areas (using a correction factor of 210 $\mu C/cm^2$ Pt [11]).

2.3. Electrode fabrication

Electrodes were fabricated by coating aqueous nafion inks of carbon or catalyst/carbon, onto Toray TGP060 paper. Carbon loadings ranged from 0.70 to 0.9 mgC/cm^2 and Pt loadings 0.3–0.5 mgPt/cm^2 depending on the wt% of metal. Before testing, the electrodes were cut into 3.14 cm^2 buttons, heat treated and fully flooded in acidified deionised water to ensure the entire electrode was fully wetted with the test electrolyte.

2.4. Potentiostatic corrosion measurements on catalysts & carbons

Measurement of carbon corrosion rate on carbon and catalyst samples was carried out from 20 to 80 °C in 1 M H_2SO_4 in

Table 1
Characterisation of catalysts by XRD and ECA

Code	Catalyst	XRD crystallite sizes (nm)	ECA ($m^2\,g^{-1}$)
a	10%Pt/C01	<2	89
b	40%Pt/C01	<2	118
c	70%Pt/C01	2.6	70
d	40%Pt/C02	3.0	53
e	40%Pt/C03	4.5	27
f	40%Pt/Co/C01	5.9	24
g	30%Pt/Co/C03	7.6	26

a three-chamber wet electrolyte cell using a potentiostatic hold at 1.2 V for 24 h, whilst logging current with time. The electrolyte was initially purged with N_2, the system was then sealed for the duration of the corrosion test. Cyclic voltammetry was measured at the start and end of the test to observe changes in double layer capacitance and the appearance of any new features such as the quinone/hydroquinone couple at 0.6 V. Measurement of electrochemical surface area was determined from the cyclic voltammetry using the hydride adsorption/desorption areas (using a correction factor of 210 $\mu C/cm^2$ Pt [11]).

The wt% of carbon corroded was calculated for each material via integration of the corrosion current over time, assuming a four-electron process [8], and disregarding the charging current during the first 60 s of the experiment as this was assumed to represent double layer charging and Pt-oxide layer growth processes. The values determined by this method correlate well to values determined by CO_2 measurement reported elsewhere [27]. The area specific carbon corrosion rate of each carbon was determined by calculating the number of surface atoms on the carbon from the BET surface area and assuming 3.79×10^{19} C atoms m^{-2} of carbon [6]. Using this figure and assuming a four-electron process the maximum charge required to remove one monolayer of carbon was determined. The experimentally determined charge associated with carbon corrosion was then expressed as a percentage of a monolayer, giving the specific corrosion rate.

The rate of carbon corrosion was determined at different temperatures to characterise the Arrhenius behaviour of the materials. Current time plots were integrated and the gradient of the line determined in the linear region, after 5 h at 1.2 V.

Transmission electron microscopy (TEM) using a Tecnai F20 Microscope was carried out on the electrode buttons pre and post 1.2 V hold to determine changes in metal particle size. Energy dispersive X-ray analysis (EDX) analysis was used to confirm the elemental compositions of the different components.

2.4.1. Potentiostatic pulsed hold protocol at 80 °C

The effect of the duration of the 1.2 V hold on both platinum and carbon stability was investigated using a pulsed hold protocol where the electrode was repeatedly stepped up from 0.6 to 1.2 V and held at 1.2 V sequentially for 1, 5, 10, 30, 60, 180 min. The total duration at 1.2 V during this test was 5 h. A cyclic voltammogram was recorded before the start of each new hold.

3. Results & discussion

3.1. The effect of carbon surface area on carbon corrosion rate at 80 °C

A series of commercially available and heat treated carbon blacks were evaluated for electrochemical stability. Fig. 1 shows the calculated cumulative carbon corrosion expressed as maximum weight loss in wt%. The higher the carbon BET surface area the more carbon weight loss occurs for the commercial carbons and the log (corrosion current) is proportional to the log (time) at 1.2 V, as reported by Antonucci under phosphoric acid
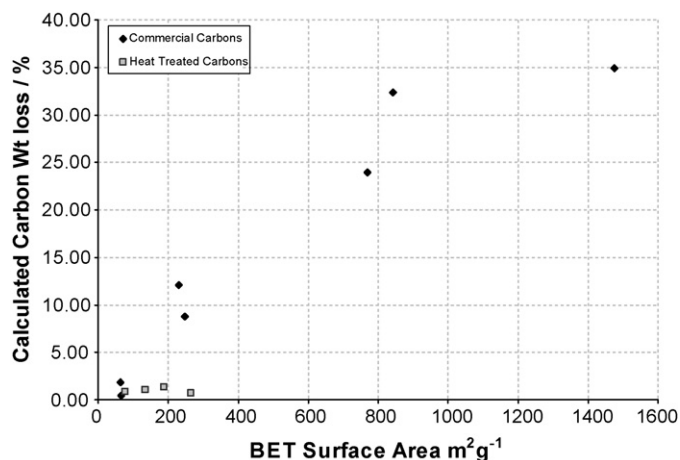

Fig. 1. Comparison of BET surface area and cumulative carbon corrosion following a 24 h 1.2 V potentiostatic hold at 80 °C in 1 M H_2SO_4 for different carbons.

conditions [2]. Low area and heat-treated carbons show up to 25 times less corrosion than the high area carbons that are typically used today as supports for commercial platinum catalysts. Heat treated carbons do not show a correlation with BET surface area.

The specific carbon corrosion for the same set of carbons expressed in terms of percentage monolayer of carbon removed during the test is shown in Fig. 2. If the carbon corrosion process depended only on the number of surface sites for reaction, the specific carbon corrosion would be independent of BET surface area. Fig. 2 shows that for the commercial carbons this is generally true as each material loses on average the equivalent of 40% of a monolayer of carbon during the test. One outlier lost 70% of a monolayer and another, the commercial carbon with a similar surface area to the heat treated carbons, had a similar specific corrosion rate to the heat treated carbons. Differences in these materials may be due to the materials having fewer or more sites susceptible to oxidation. All of the heat treated carbons fall into a band with low specific corrosion in the region of 10% of a monolayer removed during the corrosion test. This
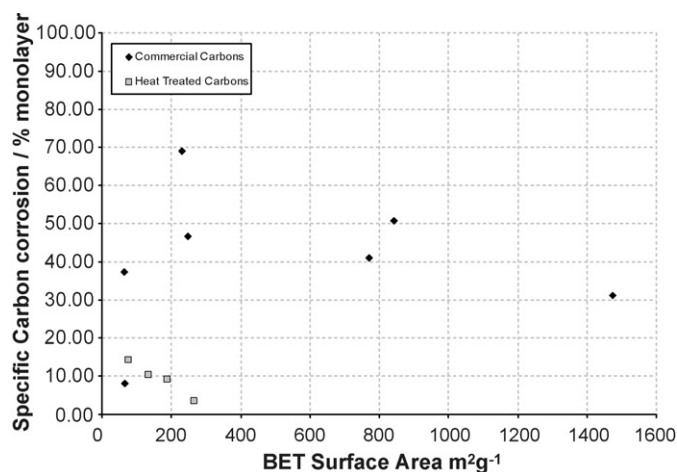

Fig. 2. Comparison of BET surface area and specific carbon corrosion following a 24 h 1.2 V potentiostatic hold at 80 °C in 1 M H_2SO_4 for different carbons.
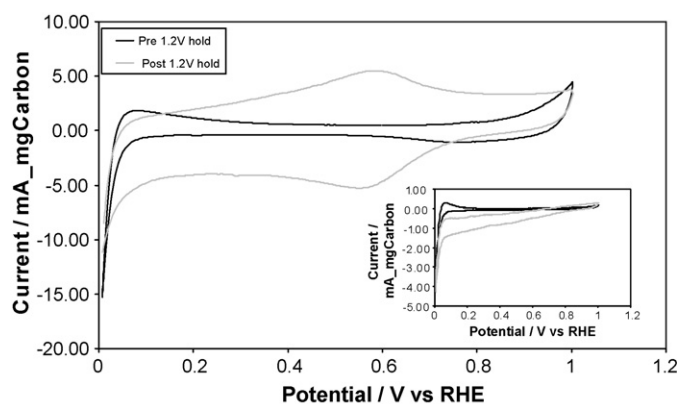
Fig. 3. Comparison of the cyclic voltammetry before and after a 24 h 1.2 V potentiostatic hold at 80 °C in 1 M H_2SO_4 for a high surface area carbon black and low surface area carbon black (Inset).

Fig. 4. Comparison of the cumulative carbon corrosion following a 24 h 1.2 V potentiostatic hold at 80 °C in 1 M H_2SO_4 for carbons C01, 2 and 3 and platinum and Pt/Co alloy catalysts on these carbons.

would suggest either heat treated carbons and commercial carbons corrode via different mechanisms, or that the mechanism is the same for both sets of carbons but heat treated ones have fewer sites available/able to be corroded.

The cyclic voltammetry of the commercial and heat treated carbons was measured before and after the corrosion test. In general after the 1.2 V hold the high surface area commercial carbons showed an increase in double layer capacitance and the appearance of a quinone/hydroquinone redox couple at 0.6 V (Fig. 3). This phenomenon has also been reported in the literature [9–11] and supports the theory that one pathway for carbon oxidation is via a two electron partial oxidation step. For low surface area carbons, while a slight increase in double layer capacitance was observed, the voltammetry showed no evidence of quinone formation (Inset Fig. 3). The formation of electro active oxidised species is therefore, not necessarily required for carbon corrosion.

3.2. The effect of catalysing the carbon surface on carbon corrosion at 80 °C

Two commercial carbons, C01 and C02, and one heat treated carbon, C03, were catalysed with platinum and the carbon corrosion occurring during the 1.2 V hold at 80 °C was compared to the uncatalysed carbons. Fig. 4 shows the calculated cumulative carbon corrosion as expressed as maximum weight loss in wt%. Catalysing the carbon with platinum does not significantly change the amount of carbon corroded during the 24 h steady state hold. Lowde et al. also report that platinum does not influence the catalytic oxidation of carbon [11]. C01 and C03 were also catalysed to make a Pt/Co alloy. These materials show a slightly lower corrosion compared to the uncatalysed carbon but again this difference is not significant. These results are contrary to work published by a number of groups [8,28] where platinum is shown to catalyse carbon corrosion. Jarvi and co-workers investigated the effect of platinum on the stability of Vulcan XC72R by mass spectrometry in MEAs [8]. When platinum was present the rate of CO_2 evolution was higher than in the carbon only electrodes. Using differential electrochemical mass spectroscopy (DEMS) Willsau and Heitbaum showed that
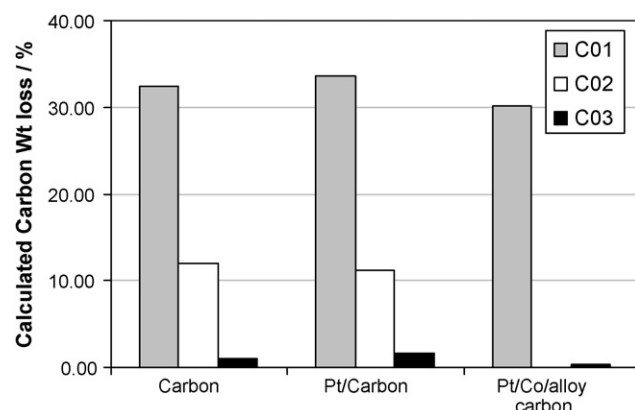
carbon is oxidised at lower potentials in the presence of platinum [28].

3.2.1. The effect of %Pt on carbon corrosion at 80 °C

Jarvi and co-workers showed that the higher the mass fraction of platinum the higher the generation rate of CO_2 [8]. Fig. 5 shows that the %Pt on the carbon does not significantly change the amount of corrosion occurring suggesting that the main contribution to the process of carbon corrosion is dominated by the carbon rather than the metal. The amount of quinone observed after the 1.2 V hold does increase with increasing wt% platinum loading suggesting that the $2e^-$ oxidation of carbon to quinone is catalysed by platinum and with increasing interfacial sites. Jarvi and co-workers measured the amount of electrochemically active species and determined quinone to be a minor fraction (3%) of the total surface oxides generated during a 1.2 V hold [6], so even though more electro active species are generated with increased metal loading, in this instance no direct correlation with the total amount of carbon corroded is observed.
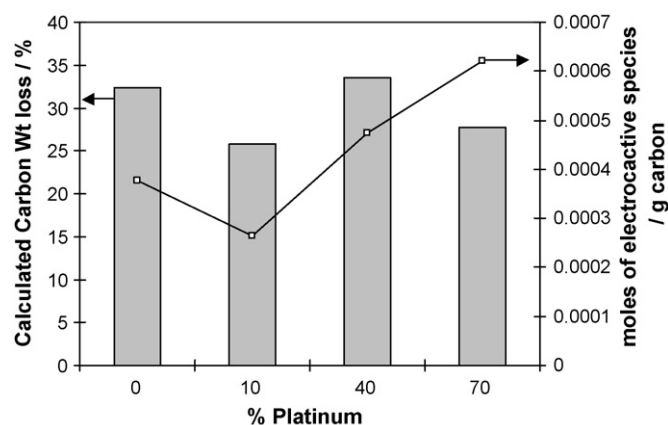

Fig. 5. Comparison of the cumulative carbon corrosion following a 24 h 1.2 V potentiostatic hold at 80 °C in 1 M H_2SO_4 for platinum catalysts on C01 at a range of metal loadings (bars) and a comparison of the no. of moles of electroactive species following a 24 h 1.2 V potentiostatic hold at 80 °C in 1 M H_2SO_4 for the same set of catalysts.
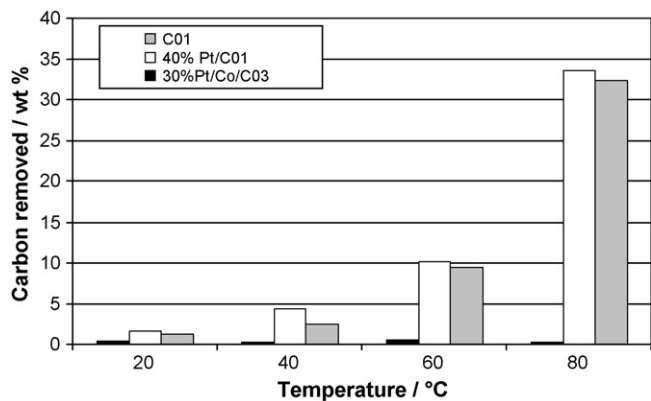
Fig. 6. Comparison of the cumulative carbon corrosion following a 24 h 1.2 V potentiostatic hold at 80 °C in 1 M H_2SO_4 for H_2SO_4 for C01, 40%Pt/C01 and 30%Pt/Co/C03.

3.3. The effect of temperature on carbon corrosion of C01, 40%Pt/C01 & 30%Pt/Co/C03

The effect of temperature on carbon corrosion was investigated for C01, 40%Pt/C01 and 30%Pt/Co/C03. Higher temperatures gave increased carbon corrosion for C01 and 40%Pt/C01 however, the low corrosion of 30%Pt/Co/C03 showed no temperature dependence (Fig. 6).

The voltammetry of all C01 and 40%Pt/C01 shows increasing amounts of quinone/hydroquinone with temperature and an increase in double layer capacitance compared to before the 1.2 V hold. 30%Pt/Co/C03 shows little change in the quinone/hydroquinone region with temperature (Figs. 7 and 8).

The Arrhenius behaviour of the three materials is shown in Fig. 9. C01 and 40%Pt/C01 show very similar behaviour, the activation energy for carbon corrosion is 49 and 45 KJ mol^{-1}, respectively. This supports the view that catalysing the carbon has little effect on the corrosion behaviour. On extrapolating to 120 °C, a five-fold increase in the rate of corrosion would be predicted. The corrosion rate of 30%Pt/Co/C03 is 100 times lower than C01 at 80 °C, indicating that low surface area car-
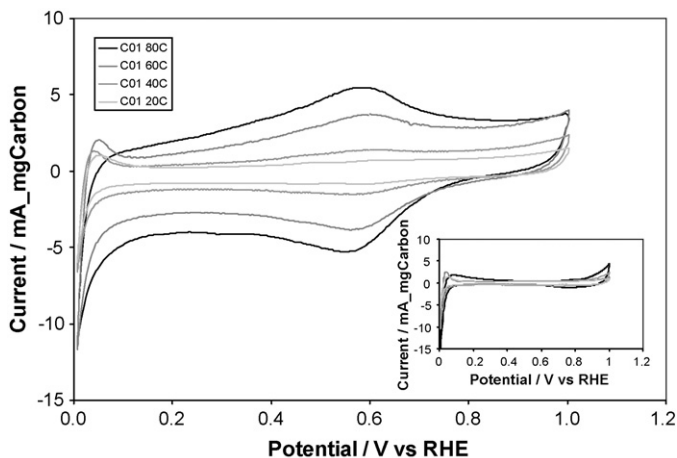

Fig. 7. Comparison of the effect of temperature on the cyclic voltammetry of C01 before (inset) and after a 24 h 1.2 V potentiostatic hold at a range of temperatures in 1 M H_2SO_4.
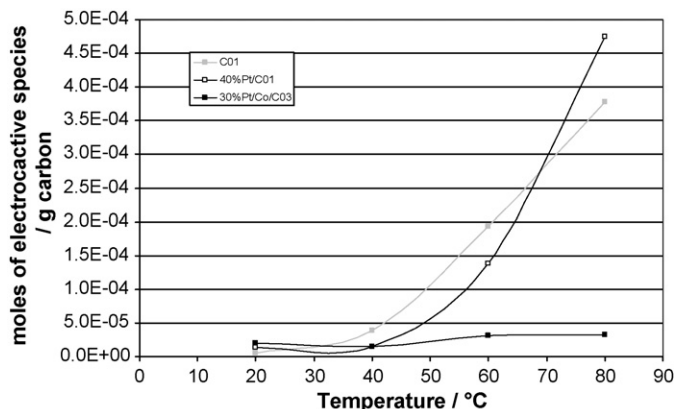

Fig. 8. Comparison of the number of moles of electroactive species after a 24 h 1.2 V potentiostatic hold at a range of temperatures in 1 M H_2SO_4 for C01, 40%Pt/C01 and 30%Pt/Co/C03.

bons of this type are suitable as catalyst support materials at higher temperatures. The rate has been found to be independent of temperature. This result is unexpected and may indicate that the very low corrosion currents measured for this material are on the limit of what can be detected by the sensitivity of the measurement. An alternative way of measuring carbon corrosion, such as monitoring CO_2 evolution by mass spectrometry, is required to confirm this result. The data does however, provide an upper limit for the rate of carbon corrosion of this catalyst at 80 °C.

3.4. The effect of 1.2 V potentiostatic hold on platinum stability at a range of temperatures

The electrochemical platinum area was measured before and after the 24 h 1.2 V potentiostatic hold test. At 80 °C platinum catalysts on commercial carbons lost up to 35% of initial metal area during the 1.2 V hold.

The mechanism of metal area loss for platinum catalysts was investigated by comparing the cyclic voltammetry before and after the 1.2 V hold (Fig. 10), and TEM analysis. The voltammetry shows no sharpening or changes to the position of hydride features, suggesting that the metal particle surface has not significantly reconstructed during the hold [29,30], although significant carbon corrosion has occurred shown by
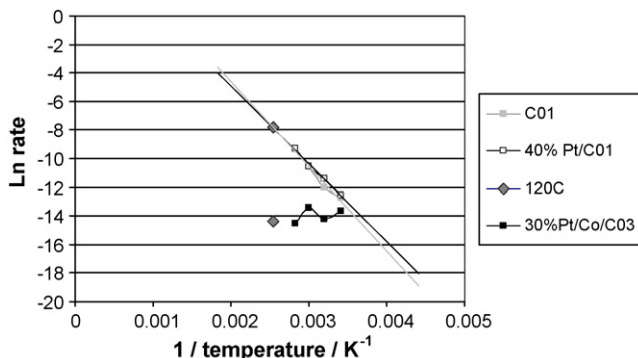

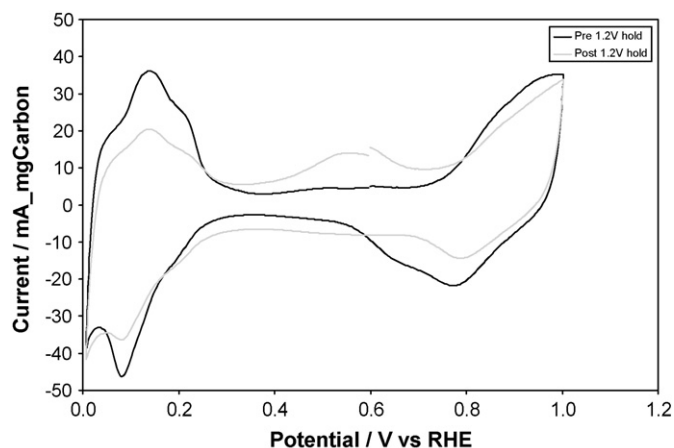Fig. 9. Arrhenius plots for C01, 40%Pt/C01 and 30%Pt/Co/C03.

Fig. 10. Comparison of the cyclic voltammetry before and after a 24 h 1.2 V potentiostatic hold at 80°.

Fig. 11. Comparison of the ECA loss for 40%Pt/C01 after a 24 h 1.2 V potentiostatic hold at a range of temperatures in 1 M H_2SO_4.

the increase double layer capacitance and the appearance of the quinone/hydroquinone redox couple.

TEM analysis showed evidence of particle agglomeration with a change in the platinum particle size from 2 to 8 nm with clusters up to 55 nm for 40%Pt/C01 and the appearance of bare areas of carbon support. Therefore, small platinum particles (ca. 2 nm) are susceptible to agglomeration under steady state voltage holds at 1.2 V. Since carbon support corrosion has occurred particle agglomeration as a result of corrosion of the carbon support and dissolution/re-precipitation are possible mechanisms for ECA loss.

Pt/Co/C01 lost no ECA during the hold. Metal surface area was retained despite the fact that a similar amount of carbon to 40%Pt/C01 is corroded over 24 h. This implies that metal area loss by particle agglomeration triggered by corrosion of the carbon support does not occur for Pt/Co/C01. It seems likely that both the larger particle sizes (5–6 nm) and the alloying itself is responsible for the excellent stability shown by these materials. When compared to platinum alone, Pt/Co [16,18] Pt/Ni [21] and Pt/Fe [20] catalysts have been reported to stabilise the platinum to sintering under both cycling regimes between 0.6 and 1.0 V [18] and potential holds at 0.9 V [20,21]. Catalysts prepared on C03 did not lose any metal area during the 1.2 V hold.

The effect of temperature on ECA loss was studied for 40%Pt/C01. The rate of ECA loss was found to be temperature dependant. The higher the temperature the more ECA loss occurred during the 1.2 V potentiostatic hold test (Fig. 11). The metal area loss at 120 °C will be significant and would result in significant cell performance loss during operation. Under these conditions based on the results seen at 80 °C, a Pt/Co alloy on a heat treated carbon such as C03 would be more resistant to metal area loss during high temperature operation.

3.5. The effect of testing protocol on platinum and carbon stability at 80 °C

The effect of the duration of the 1.2 V hold on platinum and carbon stability was investigated using a pulsed hold protocol on 40%Pt/C01 (Fig. 12). The amount of quinone increases through-
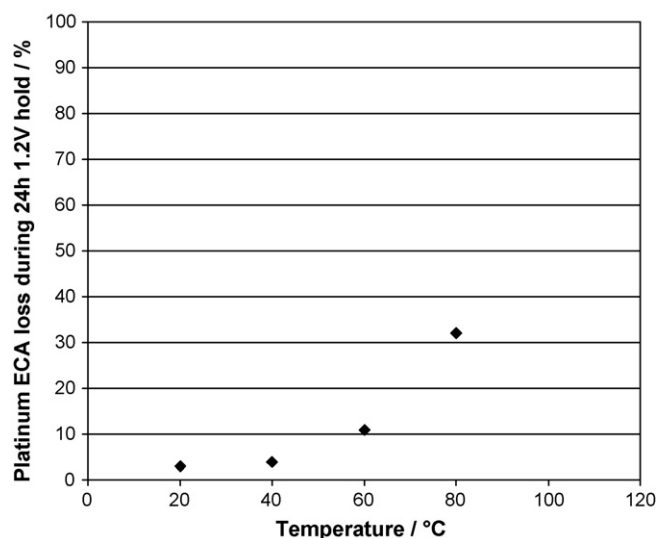
out the pulsed test and after 5 h, accounts for half the amount of quinone seen after the 24 h continuous hold (Fig. 13). During the pulsed test 33% of the initial metal area is lost, this is equivalent to the metal area lost after the 24 h 1.2 V continuous hold. Fig. 12 compares the charge/time plots for the pulsed and continuous hold. It can be seen that the corrosion current of the pulsed test reaches the same value at a shorter time than in the continuous hold test (i.e., the corrosion current at 10 000 s in the pulsed test is the same at the current after 100 000 s in the continuous hold.) The rate of carbon corrosion is therefore, increased in the pulsed hold test compared to the continuous hold. In terms of both metal area loss and carbon corrosion, the pulsed test is more aggressive than continuous hold. Under operational automotive fuel cell conditions the MEA will experience many repeated short excursions at 1.2 V more similar to the pulsed test than the continuous hold protocol and at higher operating temperatures. A material that survives a continuous 1.2 V hold test at 80 °C for 100 h, therefore, may not survive in an operating fuel cell.
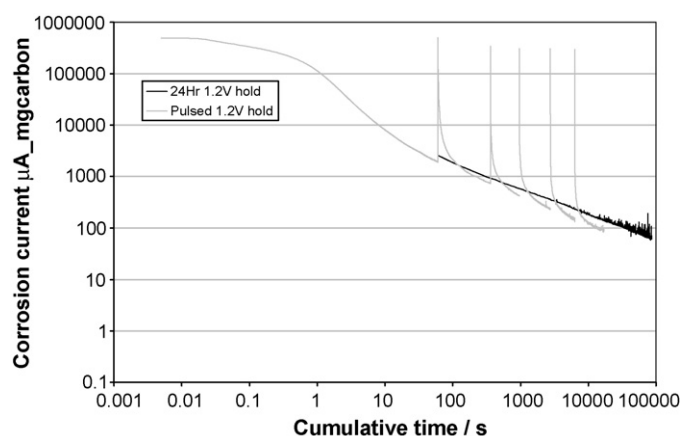

Fig. 12. Comparison of corrosion current during the pulsed hold 1.2 V potentiostatic hold and 24 h continuous hold at a 80 °C in 1 M H_2SO_4 for 40%Pt/C01.
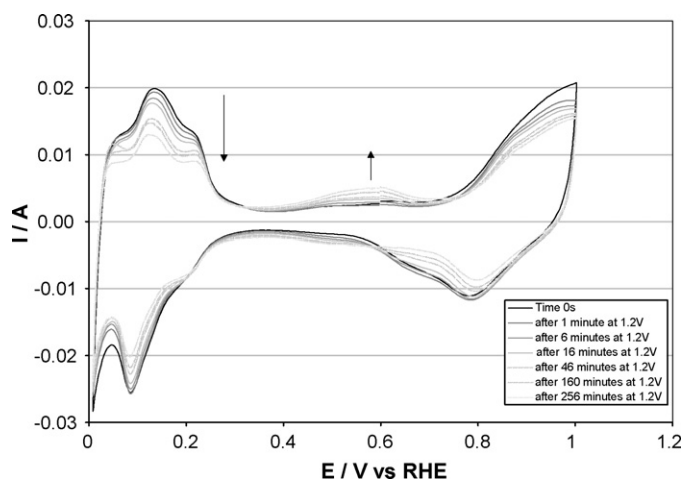
Fig. 13. Comparison of the cyclic voltammetry during the pulsed 1.2 V potentiostatic hold at 80 °C in 1 M H_2SO_4 for 40%Pt/C01.

4. Conclusions

The stability of both carbons and carbon supported platinum and Pt/Co alloy catalysts has been investigated during 1.2 V versus RHE potentiostatic hold tests using carbon and catalyst coated electrodes in three-chamber wet electrolyte cell at a range of temperatures. At 80 °C the higher the BET surface area of the commercial carbons the more corrosion was observed. However, since the specific corrosion rates of the carbons were very similar, this suggests the mechanism of corrosion for different carbons was the same with differences in amounts of corrosion being explained by the number of available sites to corrode. The extent of carbon corrosion occurring has been quantified electrochemically using the quinone/hydroquinone redox couple. Catalysing the carbon has been shown not to significantly increase the rate of carbon corrosion. However, with higher metal loadings more quinone/hydroquinone redox couple was observed. The commercial carbons tested showed increased carbon corrosion with increasing temperature, irrespective of the BET area of the carbon. Higher temperatures also resulted in more platinum metal area loss for catalysts prepared on these carbons. A Pt/Co/alloy on a heat treated carbon has been shown to be more stable to both carbon corrosion and metal area loss at temperatures up to 80 °C. The effect of changing the testing protocol on the carbon and metal particle stability has been demonstrated by comparing a series of short 1.2 V potentiostatic holds to a continuous hold. Recent DoE targets suggest 100 h at 1.2 V are equivalent to 30 000 potential excursions to 1.2 V during start-up and shut down. This work suggests that brief potential excursions to high potential are much more damaging than a continuous steady state hold.

These results clearly indicate that platinum catalysts on commercial carbons will not be durable in a PEMFC operating at 120 °C. The carbon corrosion experienced is predicted to be five times greater than at 80 °C and the metal surface area loss will also be significant. This will result in problems with water handling in the layer and low active surface area for reaction, hence MEA performance loss. Enhanced stability to carbon corrosion and no metal area loss had been demonstrated for a Pt/Co/alloy on a heat treated carbon, making this an excellent candidate for higher temperature automotive operation.

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