



Thermally Pretreated 46% Pt/Vulcan XC72: Characterisation by TGA/DSC/TEM and Cyclic Voltammetry

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Received December 5, 2008; accepted March 12, 2009

Abstract

We report a study of thermal stability and impact of thermal pretreatment procedures for 46% Pt/Vulcan XC72 (Tanaka) fuel cell catalyst. Stability in air and in inert gas (nitrogen, argon, helium) has been investigated by thermal gravimetric analysis (TGA), TGA-mass spectrometry (TGA-MS) and differential scanning calorimetry (DSC). Two distinct low temperature mass loss processes (100–200 and 285–300 °C) were observed, each exhibiting unique pretreatment temperature dependencies. TGA-MS data in helium show fragment ions that suggest the thermal degradation processes are associated with decomposition of materials such as processing aids. Transmission electron microscopy (TEM) reveals a modest increase in average Pt nanoparticle size upon ther-

mal pretreatment. After a pretreatment protocol based on TEM and thermal characterisation (300 °C/15 min, N₂), the electrochemically active surface area did not increase. At the kinetically controlled potential region ($E > 0.8$ V) there was a small drop in current density for treated 46% Pt/C in comparison with as-received catalyst. The slowing in ORR kinetics is significant. Apparently, the removal of organic components, which would improve mass transport, is negated by increased nanoparticle size.

Keywords: Carbon-supported platinum catalyst, Platinum nanoparticles, Pretreatment, thermal stability, Vulcan XC72

1 Introduction

For proton exchange membrane (PEM) fuel cells longevity is determined by the thermal stability of PEM fuel cell materials and particularly of the catalysts [1, 2]. Carbon-supported platinum is the standard electrocatalyst for low temperature PEM fuel cells because platinum and platinum-based catalysts are catalytically active at low temperature. In addition to longevity, economic considerations have generated interest in lowering platinum loading of the catalyst layer, with a current engineering target of 0.05 mg cm⁻². Development of optimum protocols for composition, dispersity and initial electrochemical activity has therefore been vital in catalyst research and development.

Table 1 shows representative synthesis procedures, stabilisers and thermal pretreatment protocols for the synthesis of carbon-supported nanoparticles. Thermal protocols play an integral role in determining the catalytic activity of platinum-based catalysts [3–9]. Most reports show that after thermal treatment, the spatial distribution of nanoparticles remains unchanged but particle size gradually increases with increased pretreatment temperatures.

Investigations such as those described by Bönnemann [3] and Luo [10] stress the importance of thermal pretreatment protocol on catalyst electrochemical availability and state of

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Table 1 Different stabilisers and pretreatment protocols for preparation of metal nanoparticle/carbon catalysts

Particles	Stabiliser	Reductant	Size ^{a)} , nm	Pretreatment T, °C	Gas	Time, h	Size ^{b)} , nm
Pt [12]	1-hexanethiol	LiBEt ₃ H	2.0	200	Ar	4	2.6
				400			4.5
			2.1	200			2.8
				400			4.6
Pt [22]	D400(EI) ₂₀ ^{c)}	NaBH ₄	2.4–2.7	360	N ₂	10	3.0–3.6
Pt [7]	C ₁₂ (EI) ₇ ^{d)}	NaBH ₄	2.5	280	N ₂	5	3.8
PtRu [5]	SB12 ^{e)}	CH ₃ OH	2.0	300	Ar	2	2.4
				700			3.4
Pt [11]	Citric acid	NaBH ₄	3.8	400	N ₂	2	3.9
Pt [23]	SPA ^{f)}	H ₂	10.7	260	N ₂	1	9.1
PtRu [3]	QAS ^{g)}	QAS ^{g)}	1.6	250–300	Ar ⁱ⁾	0.5	2.0
					10% O ₂ in Ar	0.5	
					H ₂	0.5	
					20% O ₂ in N ₂ ^{j)}	1.5	
PtVFe [10]	Oleylamine and oleic acid	C ₁₆ H ₃₄ O ₂ ^{h)}	2.3	300	7% H ₂ in N ₂	2	2.5
				400			

^{a)} Average particle size before heat treatment.

^{b)} Average particle size after heat treatment.

^{c)} Pseudo-dendritic polyethyleniminated poly(oxypropylene)diamine.

^{d)} Pseudo-dendritic polyethylenimine.

^{e)} 3-(N,N-dimethyldodecylammonio) propanesulphonate.

^{f)} Sodium polyacrylate.

^{g)} N(Oct)₄[B(Et)₃H].

^{h)} 1,2-Hexadecanediol.

ⁱ⁾ Sequential treatment under three gases (Ar, O₂, H₂).

^{j)} Sequential treatment under two gases (O₂, H₂).

results from a concomitant elimination of stabiliser originally present in the catalyst synthesis/preparation.

Bönnemann has demonstrated the value of TGA in the development of catalyst thermal protocols [3]. There are a number of processes that can be responsible for catalyst mass changes at temperatures higher than 100 °C, including combustion of carbon, adsorption of gases into microporous carbon and/or degradation of volatile non-carbon components [13]. In our previous work, we used TGA to study the thermal behaviour of 46% Pt/Vulcan XC72 (Tanaka K) [14]. The nature of a low-temperature mass loss process (100–200 °C) was analysed, as this temperature range is important for PEM fuel cell applications. The purpose of the present research was to study 46% Pt/Vulcan XC72 (Tanaka K) further so as to evaluate pretreatment protocols using TGA, TGA-MS and DSC. In this report, striking differences are found for thermal behaviour in air *versus* inert atmosphere. TEM measurements are used to evaluate particle aggregation under pretreatment conditions suggested by thermal analysis.

aggregation. Bönnemann described a method for activating fuel cell catalysts in which the tetraalkylammonium protecting shell is removed from the metal surface in three steps, *viz.* sequential, 30 min annealing under a flow of argon, oxygen and hydrogen, respectively, at 250–300 °C [3]. Luo described the preparation of Pt₃₂V₁₄Fe₅₄/C catalysts and a final thermal treatment (H₂/N₂) at 400 °C [10]. The Pt₃₂V₁₄Fe₅₄/C catalyst after the protocol shown in Table 1 exhibited the highest electrocatalytic activity for the oxygen reduction reaction (ORR). Guo reported the preparation of Pt/C catalysts by borohydride reduction of hexachloroplatinic (IV) acid using citric acid (CA) as a stabilising agent (electrostatic stabilisation) [11]. For this Pt/C catalyst a relatively simple thermal pretreatment (2 h/400 °C/N₂) optimised the electrochemical active surface area.

Varied outcomes have been reported after subjecting Pt catalysts to thermal pretreatment (Table 1). Sen analysed the anodic part of cyclic voltammograms for a thiol-stabilised platinum catalyst after thermal treatment [12]. Here, increased treatment temperature resulted in increased platinum particle size and decreased catalytic activity for methanol oxidation. Others report that Pt/C [6] or Pt/Ru [3] were more active than as-prepared catalysts after specific thermal protocols. The latter authors concluded that increased activity

2 Experimental

2.1 Materials

45.5% Pt/Vulcan XC72 (Pt/V, TEC10V50E) was obtained from Tanaka K, Japan. Vulcan XC72R was obtained from Cabot Company. Ethanol (HPLC) and Nafion[®] 5% solutions in a mixture of lower aliphatic alcohols and water were obtained from Aldrich. Perchloric acid, double distilled, 70% was purchased from GRS Chemicals, inc. Isopropanol (HPLC, 99.9%) was purchased from ECROS Co. Millipore[®] NanoPure water was used with 18 MΩ cm⁻¹ resistance.

2.2 Measurements

2.2.1 Thermal Analysis

Thermogravimetric analyses were performed with Q5000 TGA (TA Instruments-Waters, LLC). Platinum pans were used in all measurements. The balance gas was inert (nitrogen, argon or helium) with purge rate 10 mL min⁻¹. The sample gas was either an inert gas (nitrogen, argon or helium, purge rate 25 mL min⁻¹) or dry air (purge rate 90 mL min⁻¹). Heating rates were in the range from 2.5 to 10 K min⁻¹. Sample masses were 3 ± 1 mg.

DSC measurements were performed using differential scanning calorimeter Q1000 (TA Instruments-Waters, LLC). Purge gas was nitrogen at 50 mL min⁻¹; heating rate was 10 K min⁻¹. Sample mass was 2.5 ± 0.5 mg.

TGA (TA Instruments Q5000) coupled with mass spectrometry (Pfeiffer Vacuum Thermostar quadrupole mass spectrometer) was used to analyse the degradation products of Pt/Vulcan XC72 when heated in helium. The heating rate in these measurements was 2.5 K min⁻¹. Mass spectra were collected in the range from 10 to 150 mass-to-charge (*m/e*).

2.2.2 Data Deconvolution

After pretreatment (at 200 °C for 1 h in air) DTG data for 46% Pt/Vulcan consisted of a main peak and a broad, mass loss from 200 to 350 °C. The DTG data for XC72 were deconvoluted into two curves according to Eq. (1) using Origin 7.5 software. The deconvolution is in the form of two superposed Lorentz curves [Eq. (1)]

$$y = \frac{2A_1}{\pi} \times \frac{w_1}{4(x - x_{c1})^2 + w_1^2} + \frac{2A_2}{\pi} \times \frac{w_2}{4(x - x_{c2})^2 + w_2^2} \quad (1)$$

where parameters x_{c1} , x_{c2} were fixed; parameters A_1 , A_2 , w_1 and w_2 were varied to get the best fit.

2.2.3 Transmission Electron Microscopy

The catalysts were examined using a JEOL 1010 transmission electron microscope (TEM). Suspensions of the catalyst powders were prepared in an aqueous ethanol solution using an ultrasonic bath. These suspensions were dropped onto copper grids coated with carbon or polymer films. Excess solution was removed by adsorbent paper and the samples were dried in air.

2.2.4 Electrochemical Measurements

Electrocatalytic activity of ORR was studied at ambient temperature with a rotating disc electrode (RDE) technique described in detail by Gasteiger et al. [15]. We used a PARSTAT 2263 potentiostat equipped with Pine Instruments modulated speed rotator and the glass cell. The counter electrode was platinum mesh and the reference electrode was the double junction Ag/AgCl electrode (4 mol L⁻¹ KCl). All data are presented with the potentials referenced to the reversible hydrogen electrode (RHE).

Catalyst dispersions or inks, were prepared by ultrasonically dispersing 10 mg of carbon-supported catalyst in a 10 mL of aqueous isopropanol/Nafion solution. This solution contained 20–30 mL of isopropanol, 0.4 mL of 5% Nafion solution and nanopure water added to give 100 mL total volume. For thin-film RDE measurements the catalyst dispersion (ink) was placed onto a polished glassy-carbon disc and dried in air at room temperature. The mass of the catalyst loaded was typically 23 µg. An aqueous solution of perchloric acid (0.1 mol L⁻¹) was used as the electrolyte. To remove any re-

sidual impurities on the catalyst surface the potential was scanned 20 times between 0.05 and 1.2 V at a scan rate 200 mV s⁻¹ in deaerated perchloric acid. The final cyclic voltammogram for the catalyst layer was recorded at a scan rate of 20 mV s⁻¹. Current-potential curves were obtained in an O₂-saturated aqueous solution of HClO₄ with a rotation speed of 1,600 rpm and a scan rate of 20 mV s⁻¹. Current density was calculated using the geometric surface area of the glassy carbon disc (0.196 cm²).

3 Results and Discussion

3.1 TGA analysis

3.1.1 As-Received Thermal Analysis in Air

Previously we showed by TGA and TGA-MS that the degradation in air of 46% Pt/Vulcan XC72 catalyst (Tanaka K) occurs in two steps: a low temperature mass loss between 100 and 200 °C and a second major mass loss between 200 and 500 °C [14]. In this initial study the utility of TGA and TGA-MS for studying the thermal stability of carbon-supported platinum catalysts was established. Below, we describe several pretreatment protocols along with TGA and TGA-MS results that modify previous conclusions [14] and provide a basis for pretreatment options.

3.1.2 Pretreatment in Air/Thermal Analysis in Air

To further evaluate mass loss processes for Tanaka catalysts, pretreatment in air, above the 100–200 °C low temperature mass loss previously reported [14], was investigated. Figure 1 shows TGA (Figure 1a) and DTG (Figure 1b) in air for 46% Pt/Vulcan XC72. Data are presented for as-received catalyst (Figure 1, a-1 and b-1) and samples pretreated for 1 h in air at 200 °C (Figure 1, a-2 and b-2). Without pretreatment the low temperature mass loss (100–200 °C) was 3.5%, while none was observed after pretreatment. Previously the low temperature mass loss was ascribed to Pt catalysed oxidation of the carbon support [14]. However, the absence of a low temperature mass loss after 200 °C pretreatment in air indicates that a different process, namely thermal desorption of residual constituents is responsible rather than oxidation of the carbon support. Thermal desorption rather than oxidation is suggested by the observation of a similar percent mass loss in inert gas (3.4%, Section 3.1.3).

Although, the mass loss below 200 °C is absent after thermal treatment in air at 200 °C, there is a gradual mass loss above 200 °C that merges with the Pt catalysed oxidation of the carbon support. The maximum rate of mass loss for oxidation of the carbon support occurs at 413 °C. The DTG curve for 46% Pt/Vulcan XC72 after pretreatment exhibits a low, broad shoulder from 200 to 375 °C (Figure 1, b-2). The DTG data were fitted by superposing two Lorentz curves according to Eq. (1) as described in the Experimental section (Figure 1c). The following fit parameters were obtained: $A_1 = 43.6\%$; $w_1 = 22.8$ °C; $x_{c1} = 409$ °C; $A_2 = 16.1\%$;

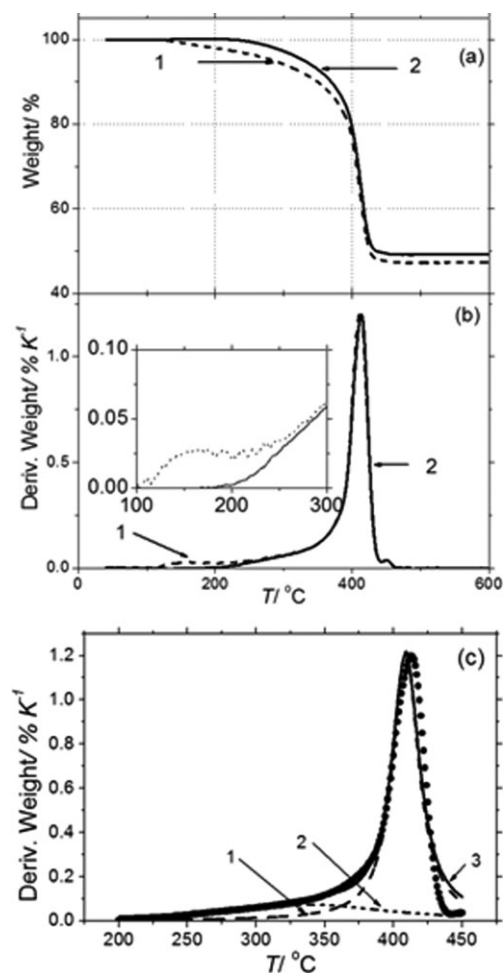


Fig. 1 (a) TGA and (b) DTG in air (2.5 K min^{-1}) for 46% Pt/Vulcan XC72 catalyst (Tanaka K): (1) as-received, (2) pretreated for 1 h at 200°C in air; (c) Fit of DTG data after pretreatment by superposition of two Lorentz curves; (1) the first Lorentz curve; (2) the second Lorentz curve; (3) resulting curve; (●) DTG data.

$w_2 = 140^\circ\text{C}$; $x_{c2} = 340^\circ\text{C}$. A mass loss of 12% (from 200 to 375°C) was estimated from the deconvoluted curves, while the TGA gave 11%.

To summarise, the following mass losses in air are found for 46% Pt/Vulcan XC72: (i) 2% during 1 h pretreatment in air at 200°C ; (ii) 11% during heating from 200 to 375°C at $2.5^\circ\text{C min}^{-1}$. In total, the low temperature mass loss for (i) and (ii) is 13%. Of course, this combination of pretreatment times and temperatures is arbitrary. However, the chosen combination gives a useful measure of oxidative stability.

3.1.3 As-Received Thermal Analysis in Inert Gas

To compare with TGA in air, 46% Pt/Vulcan XC72 was examined using TGA ($40\text{--}600^\circ\text{C}$) in inert gases (nitrogen, argon and helium). Within experimental error, the same results were obtained independent of inert gas. Typical TGA and DTG in nitrogen are shown in Figure 2. The DTG curve exhibits two maxima. The first mass loss maximum is low and broad ($100\text{--}210^\circ\text{C}$, 3.4%) and similar to that observed in

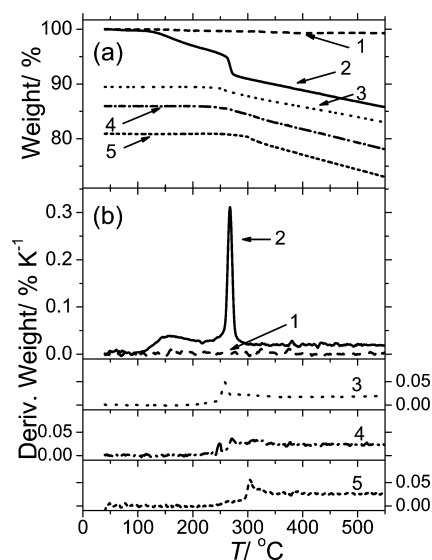


Fig. 2 TGA (a) and DTG (b) in nitrogen (2.5 K min^{-1}) for: as-received Vulcan XC72 carbon 1; 46% Pt/Vulcan XC72 catalyst (Tanaka K): as-received 2, pretreated for 30 min in N_2 at 300°C , 3, 30 min at 325°C , 4, and 30 min at 350°C , 5.

air. Unlike TGA in air, the second mass loss occurs over a narrow temperature range with a maximum at 268°C (5.7%). The total mass loss up to 300°C is 9.1%. At temperatures over 300°C , the sample mass decreases at a constant rate. The slow mass loss above 300°C is assigned to Pt catalysed carbon oxidation due to traces of oxygen in the TGA gas stream. The surprising sharp mass loss at 268°C indicates a different thermal process in nitrogen compared to air and prompted a more detailed investigation of thermal stability.

3.1.4 Pretreatment in N_2 /Thermal Analysis in Inert Gas

The mass loss at $\sim 270^\circ\text{C}$ in inert gas led to the study of pretreatment in nitrogen at 300, 325 and 350°C for 30 min (Figure 2). Not surprisingly, after this pretreatment the $100\text{--}210^\circ\text{C}$ mass loss is no longer detected. Approximately 270°C DTG maximum is barely detectable in the range $250\text{--}310^\circ\text{C}$. Both the $100\text{--}210^\circ\text{C}$ and the 270°C mass losses (in inert gas) are attributed to thermal decomposition of stabilisers/additives included in the proprietary catalyst compositions.

Because thermal pretreatment results in mass loss (Figure 2), the platinum concentration in the remaining catalyst is increased. Table 2 summarises results for various pretreatment temperatures for 46% Pt/Vulcan XC72. For example, after 30 min in nitrogen at 300°C , the concentration of platinum in Pt/Vulcan XC72 increases to 51%.

3.1.5 Pretreatment in Air/Thermal Analysis in Inert Gas

Most organic materials decompose differently in air and inert gases. The same trend is expected for catalyst stabilisers and/or additives. For example, alkyl polyethylene oxide surfactants have precipitous mass losses that are much lower in

Table 2 Mass loss for 46% Pt/Vulcan XC72 after different pretreatment protocols and percent platinum remaining after pretreatment

TGA sample gas	Pretreatment condition		Mass loss, %	Concentration of Pt after treatment, % (± 0.5) ^{a)}
	Gas	T, °C		
Air	air	200	60	48
Air	N ₂	300	30	10
N ₂	N ₂	300	30	11
N ₂	N ₂	325	30	14
N ₂	N ₂	350	30	19

^{a)} The concentration of platinum at the remaining material was estimated by multiplying the original Pt percentage by $100/(100 - \text{mass loss}\%)$.

air (200 °C) compared to nitrogen (400 °C) [16]. For comparison, the effect of thermal pretreatment in air followed by thermal behaviour in inert atmosphere was examined. TGA and DTG data in argon for 46% Pt/Vulcan XC72 after pretreatment (2 h at 200 °C in air) are shown in Figure 3. After the pretreatment in air, TGA in inert gas shows that, as observed for TGA in air, the low temperature mass loss (100–200 °C) is no longer observed. Surprisingly, unlike TGA in air, a distinct maximum accounting for 7% mass loss is observed at 306 °C. That is, the sharp mass loss peak at 268 °C in inert gas for the as-received catalyst shifts about 38 °C higher after the 2 h pretreatment in air at 200 °C. The cause of the 38 °C increase may be due to partial oxidation of stabilisers/additives that survived the pretreatment in air. That is, partial oxidation may create materials that are then more thermally stable. After cooling to 40 °C and reheating (Figure 3, curve 2) the maximum at 300 °C is barely observed.

In summary, as expected, pretreatment in air at 200 °C eliminates the 100–200 °C TGA mass loss whether run in air (Section 3.1.2) or in inert gas. If analysed by TGA in air, mass loss over a broad temperature range is observed below the combustion temperature for carbon (400 °C) but if analysed in inert gas, a sharp mass loss peak (7%) is observed at 306 °C.

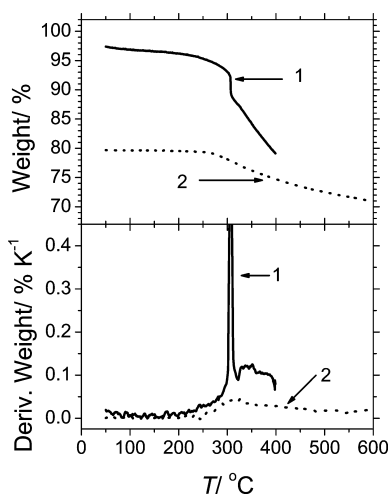


Fig. 3 TGA and DTG in argon (2.5 K min^{-1}) for 46% Pt/Vulcan XC72 catalyst (Tanaka K) pretreated for 2 h in air at 200 °C; (1) first scan; (2) second scan.

3.2 DSC Analysis

DSC for 46% Pt/Vulcan XC72 was carried out in nitrogen from 25 to 350 °C (Figure 4). The heat flow curve for the first scan has two exothermic maxima: a broad one centred at 200 °C and a narrow one at 273 °C. The exotherm at 280 °C is barely observed in the second scan.

Comparison of DSC and TGA data shows strong correlation. The TGA curve for as-received 46% Pt/Vulcan XC72 has two maxima at similar temperatures and only one small maximum was detected after pretreatment. The agreement of DSC and TGA thermal analyses is rationalised by the assumption that at least two residual materials are present and thermally decompose in air at 200 and 273 °C, respectively. Guided by this result (and TEM) a pretreatment protocol was used that consisted of heating in a nitrogen atmosphere for 15 min at 300 °C. The effect of this, a heating protocol on electrochemical behaviour, is addressed further below.

3.3 TGA-Mass Spectrometry

TGA-MS measurements were obtained on 46% Pt/Vulcan XC72 (Figure 5). As a control, Vulcan XC72 was also investigated by TGA-MS in helium. No significant ion current was observed below 500 °C.

In a TGA experiment run in inert gas, traces of air have negligible impact on mass loss because traces of air are overwhelmed by the quantity of material lost through decomposition or volatilisation. However, due to high sensitivity, only a small fraction of the material vapourised by TGA is admitted into the mass spectrometer. It is not possible to exclude traces of air when obtaining mass spectrometric data, and because such traces of air constitute masses that are comparable to the mass of material 'bled' into the spectrometer, ion currents from nitrogen and oxygen are always observed. Thus, ion current curves at 28 (N₂) and 32 (O₂) are associated with air [17]. Inspection shows that the ratio of the N₂/O₂ ion current at 50 °C is 3.2 while at the highest temperature (400 °C) the ratio increases to 4.6. The ratio changes abruptly at the shoulder (175 °C) and peak (270 °C) mass losses but remains high above these inflections. The higher value at the upper

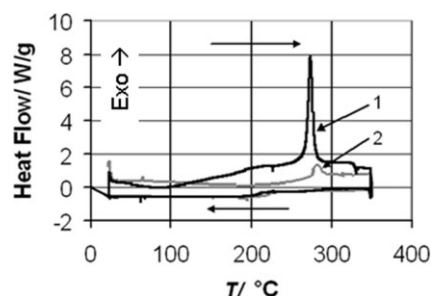


Fig. 4 Thermogram (10 K min^{-1}) for 46% Pt/Vulcan XC72 catalyst (Tanaka K) in nitrogen: (1) first scan, (2) second scan.

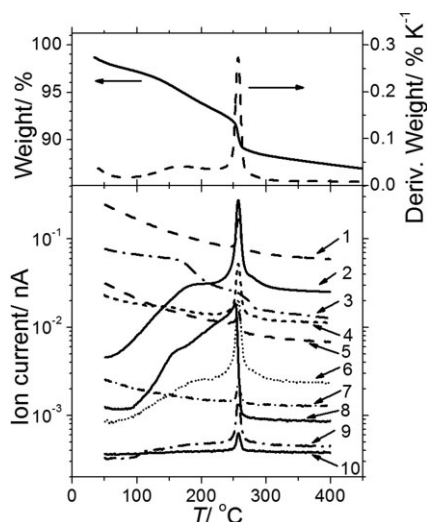


Fig. 5 (a) TGA and DTG and (b) TGA-MS (2.5 K min^{-1}) in helium for 46% Pt/Vulcan XC72 catalyst (Tanaka K) for m/e : (1) 28, (2) 44, (3) 32, (4) 16, (5) 14, (6) 12, (7) 29, (8) 30, (9) 46, (10) 22.

temperature range is due to consumption of trace oxygen by Pt catalysed oxidation of the support [13, 18]. Such a process that occurs readily is separately confirmed by TGA data in air at atmospheric pressure (Figure 1).

The ion current curves for m/e 12, 30, 44 and 46 exhibit shoulders in the temperature interval of 100–225 °C, which correspond to the first maximum on the DTG mass loss (3.4%, Figure 5a). Ion current shoulders are coincident with the drop in O_2 ion current (32) signalling oxidation of volatilised species, in large part to CO_2 (44). Considering the oxidising environment, the next most prominent ion current at m/e 30 is assigned to CH_2O or NO .

Ion current–temperature curves with m/e 12, 14, 16, 22, 28, 29, 30, 44 and 46 exhibit maxima at 270 °C which correspond to the second maximum for DTG in inert gas (5.7%, Figure 5a). The drop in O_2 ion current (32) matches the DTG peak for mass loss.

The TGA-MS curves fall into two categories. One set (12, 30, 44 and 46) have low temperature shoulders that merge into the high temperature peak. These peaks are assigned to carbon (12), oxygen (16) and oxidised carbon species (CO_2 (44) CH_2O (30)). The origin of the small (ion current $< 3 \times 10^{-4} \text{ nA}$) m/e 46 peak is not clear.

The other set (14, 16, 28, 29, 22) has no low temperature shoulders. Thus, the component that decomposes at high temperature has a unique set of peaks some of which overlap those of the component that decomposes at lower temperature. The high temperature peaks at 14 and 28 have relatively high ion currents. Because of the oxidising atmosphere noted above, the peak at m/e 28, superposed on the N_2^+ ion current curve is assigned to CO^+ . The small peak at m/e 14 superposed on the N^+ curve from nitrogen leakage indicates a nitrogen component in the higher temperature decomposition products. Nitrogen in the form of an alkylammonium detergent may be the source. The origin of the m/e peak

could also be CH_2^+ from the breakdown of formaldehyde, CH_2O . The peak at m/e 22 is superposed to CO_2^{++} , [19] while the remaining peak at m/e 29 might be due to CHO^+ .

The ion current curve at m/e 30 is unique; in that, the intensity follows the two thermal decompositions and then falls off to a level below that observed initially (at $T < 100$ °C). When the carbon source from processing aids is exhausted ($T > 280$ °C), the m/e current falls to $9 \times 10^{-4} \text{ nA}$, which is nevertheless above the background current ($< 3 \times 10^{-4} \text{ nA}$). Above ca. 280 °C the m/e peak at 30 is assigned to NO , as the ratio of $\text{N}_2^+/\text{N}^+/\text{NO}^+$ ion current (74/9/1) is close to that observed for the carbon control (100/8/1). As noted above, nitrogen is mostly from traces of air. CH_2O could also contribute to m/e 30. In addition to CO_2 , fragments such as $(\text{CH}_3)_2\text{N}$, CONH_2 may contribute to m/e 44 [20, 21]. Thus, signals at m/e 30 and 44 could be due in part to degradation of aliphatic amines, aliphatic amides or some nitro compounds from surfactants or stabilisers [20].

3.4 Transmission Electron Microscope Characterisation

TEM micrographs of as-received 46% Pt/ Vulcan XC 72 and samples after pretreatment (15 min, 300 °C in nitrogen, 30 min at 325 °C in argon) are compared in Figure 6. The TEM images show that the pretreatments lead to a modest increase in nanoparticle size. The particle shapes are irregular so that post-treatment particle size measurement has low accuracy. Using conventional Scion Image software for image processing, the average particle size of as-received Pt/Vulcan XC72 is found to be 2.2 nm in agreement with Tanaka Catalyst Specification (2.3 nm). Modest aggregation is observed with treated catalysts. The average Pt particle size after 15 min pretreatment at 300 °C (N_2) is 3.3 nm, whereas after pretreatment for 30 min at 325 °C (Ar), the nanoparticle size increases to 4.4 nm. This size increase confirms information provided by Tanaka Catalyst Specification. According to the latter document, the average Pt/Vulcan XC72 particle size after pretreatment (30 min, 300 °C in argon) increases from 2.3 to 5.1 nm (XRD Measurement), respectively. Similar results have been reported previously [5, 7, 8, 12, 22]. For example, investigations described by Li [5] showed that after a 2-h pretreatment, 2.0 nm particles increased to 2.4 (300 °C), 2.8 (500 °C) and 3.4 nm (700 °C).

3.5 Rotating Disc Electrode Measurements

For Tanaka 46% Pt/C, TGA and DSC analysis indicates that thermal decomposition amounting to 6% occurs below 300 °C. TGA-MS is consistent with the loss of organic materials. TEM micrographs of as-received 46% Pt/Vulcan XC 72 and treated samples (15 min at 300 °C in nitrogen and 30 min at 325 °C in argon) confirmed an increase in platinum particle size after pretreatment. In view of these results a pretreatment protocol of 300 °C/15 min/ N_2) was selected prior to rotating disc electrode measurements. The selected temperature is at the threshold for nanoparticle agglomeration but

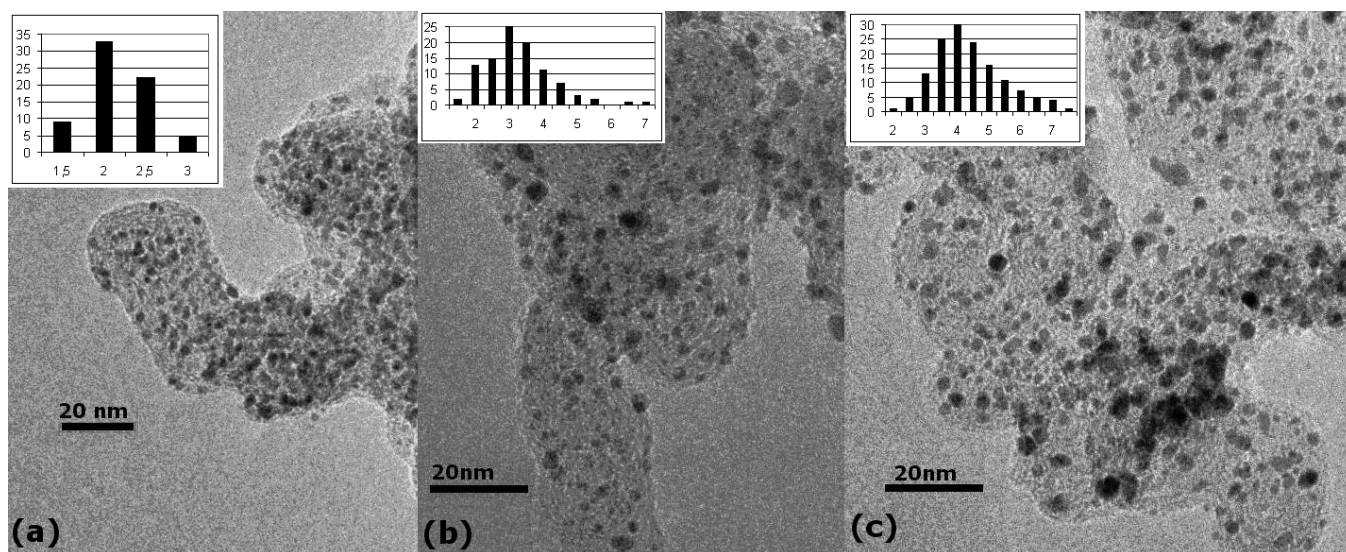


Fig. 6 TEM micrographs and histograms of 46% Pt/Vulcan XC72 catalyst (Tanaka K): (a) as-received, (b) after pretreatment for 15 min at 300 °C in nitrogen and (c) after pretreatment for 30 min at 325 °C in argon.

above the mass loss temperature. Fifteen minutes (rather than 30 min) were selected to minimise nanoparticle agglomeration. The objective was to carry out preliminary experiments to ascertain whether electrochemical changes accompanied the 300 °C/15 min/N₂ pretreatment protocol.

Figure 7 shows cyclic voltammograms of the Pt/Vulcan XC72 catalyst as-received and after pretreatment. It is well known that electrochemically active surface area reflects the changing nanoparticles size [15]. Most reports show that catalyst particle size increases with high temperature pretreatments using *ex-situ* techniques such as TEM [3]. For Pt/Vulcan XC72, the electrochemically active surface areas for both as-received and treated samples are similar, showing that the pretreatment protocol did not measurably decrease the active platinum surface area. This can be explained due to compensating effects of activity gain by removing the impurities such as surfactants and stabilisers and activity loss by agglomeration of nanoparticles.

ORR rotating disc measurements for 46% Pt/C catalysts in 0.1 mol L⁻¹ HClO₄ at 1,600 rpm are shown in Figure 8. The

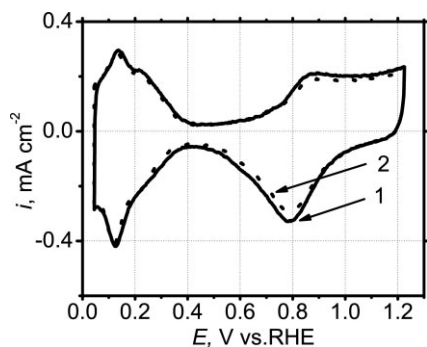


Fig. 7 Cyclic voltammograms of Pt/Vulcan XC72 catalyst (Tanaka K): (1) as-received and (2) after pretreatment 15 min at 300 °C in nitrogen; scan rate 20 mV s⁻¹.

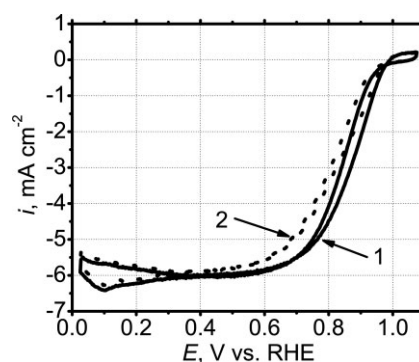


Fig. 8 Oxygen reduction current densities of Pt/Vulcan XC72 catalyst (Tanaka K): (1) as-received and (2) after pretreatment 15 min at 300 °C in nitrogen; speed 1,600 rpm; scan rate 20 mV s⁻¹.

O₂-reduction current density–voltage curves for as-received and post-pretreatment, exhibit differences in *i*–*E* profiles. At the kinetically controlled potential region (*E* > 0.8 V), there is a small drop (~1 mA cm⁻² at 0.8 V) at the current density for treated 46% Pt/C in comparison with the as-received catalyst. Even though the active surface area of the catalyst remains almost the same (Figure 7), the slowing in ORR kinetics is significant. The latter is attributed to the reduction in dispersity of the Pt nanoparticles and the increase in nanoparticle size (TEM). Some compensation may be gained from removing organic components, which would improve mass transport by opening more paths for the reactants and the products.

4 Conclusion

TGA, TGA-MS and DSC are useful methods for studying the thermal stability of Pt/C catalysts and the influence that additional components (e.g. stabilisers) may have on thermal

stability. For 46% Pt/Vulcan XC72 (Tanaka K), thermal processes were observed in inert gas between 100 and 300 °C that accounted for a 13% loss of organic component(s). A particularly sharp mass loss (TGA) accompanied by an equally sharp exotherm (DSC) was observed at 270 °C.

Thermal pretreatment can result in two basic processes: decreasing the electrochemically active platinum surface area by increasing nanoparticle size and increasing the electrochemically available surface area after removal of constituents such as stabilisers. Our results show that after 300 °C/15 min (N₂) pretreatment described above, 46% Pt/Vulcan XC72 (Tanaka K) particle size (2.3 nm) increased modestly to 3.3 nm.

Our evaluation of catalyst performance is limited to cyclic voltammetry. After pretreatment (300 °C/15 min, N₂) the electrochemically active surface area did not increase despite removal of 13% organic material. At the kinetically controlled potential region ($E > 0.8$ V), there is a small drop in current density for treated 46% Pt/C in comparison with as-received catalyst. The slowing in ORR kinetics is significant. The latter is attributed to the increase in average nanoparticle size (TEM). Apparently, the removal of organic components, which would improve mass transport, is negated by increased nanoparticle size.

Acknowledgements

Support from the NASA Space Science Office (Grant Number NNC04GB13G) is gratefully acknowledged.

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