On the role of surface functional groups in Pt carbon interaction

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The interaction between platinum crystallites and surface functional groups of carbon in a homologously prepared series of Pt/C catalysts for phosphoric acid fuel cell (PAFC) applications has been studied by X-ray photoelectron spectroscopy (XPS) and potentiometric titration techniques. It has been found that the platinum surface area depends on the amount of oxygenated groups on the carbon support. In addition, relationships between the platinum electroactive surface area and the acid–base nature of support functionalities have been found. The carbon support functional groups have been shown to affect the electronic nature of the platinum states.

1. Introduction

In the literature dealing with the properties of Pt/C electrocatalysts for the oxygen reduction reaction (ORR) in phosphoric acid fuel cells (PAFC), no unanimous consensus has been reached, for example, regarding particle size effects, valence states and stabilization of platinum and the nature of metal-support interactions on the electrocatalytic activity. In addition to an interest in the electrochemical and morphological aspects related to the electrode characteristics as a function of catalyst properties [1–5], previous studies related to PAFC catalysts have been focused on the acid–base properties of carbon supported platinum catalysts [6]. The acid–base properties constitute one of the driving parameters able to determine the level of metal-support interaction. Thus the activity and stability characteristics of the whole catalyst and electrode ensemble depend on these properties. In particular, the activation temperature strongly influences the amounts of acidic and basic surface functional groups of the catalyst which progressively pass, on activation from 110 to 900° C, from strongly acidic to basic behaviour. On the other hand, the varying role of oxygenated functionalities on the formation of the dispersed metal phase is well recognized [7, 8] but little understood. Under equal preparative conditions of metal precursor,

impregnation method and loading, the final catalyst properties of dispersion, sintering resistance, chemical nature of the supported metal and coupled metal-support interactions are affected by the interactions occurring between surface platinum crystallites and the oxygenated carbon support during treatment at a given T.

Recently, there is an increasing trend to use surface sensitive techniques such as X-ray photoelectron spectroscopy (XPS), in combination with other physical and electrochemical techniques, to characterize both catalysts [9–11] and electrodes [12–15]. This paper adds to previous investigations of PAFC related materials technology [1–6, 13], by correlating properties such as metal surface area, surface functional group concentration and acid–base characteristics of a homologously prepared Pt/C electrocatalyst series to the observed activity levels in the oxygen reduction reaction.

2. Experimental details

The electrocatalysts, prepared from a carbon black slurry in distilled water (10 g of carbon per litre of H_2O), consisted of platinum (20% w/w) supported on Ketjenblack EC from Akzo Chemie. The carbon black was 0.1% ash with BET surface area of $950\,m^2\,g^{-1}$. An aqueous solution of H_2PtCl_6 (Engel-

Table 1. Catalysts characteristics

Catalyst		1	2	3	4	5	6	7	8	9	10	11	12	13	14
Activation temperature °C		900	600	600	900	600	600	600	400	500	600	700	600	900	900
Dissociation constant	pK_a	n.d.	n.d.	n.d.	–	5.24	6.36	6.00	–	~	5.36	–	6.36	–	–
	pK_b	n.d.	n.d.	n.d.	3.48	–	8.56	–	–	3.84	–	–	–	3.6	3.4
Amount of functional groups by potentiometric titration	acid	n.d.	n.d.	n.d.	–	0.15	0.13	0.06	–	–	0.08	–	0.02	–	–
	basic	n.d.	n.d.	n.d.	0.12	0.01	0.10	–	0.02	0.06	–	0.02	–	0.15	0.28
MSA by CV/m^2 g^{-1}		42	50	30	22	88	77	75	54	78	85	88	58	110	8
Mass activity mA mg^{-1} Pt at 0.9 V in O_2		19	24	30	29	45	59	37	37	47	37	44	36	57	n.d.

hard, 99.9%) was added to the carbon black slurry. The carbon supported platinum was reduced at 45° C, by adding dropwise an excess amount of $Na_2S_2O_4$ solution. The electrocatalysts were repeatedly washed with distilled water, filtered and dried overnight at 70° C and thermally activated in a quartz tube with flowing nitrogen under reducing conditions at temperatures in the range 400–900° C (see Table 1).

The electrodes for electrochemical characterizations were manufactured according to a screen printing based procedure described elsewhere [4]. Cathodic polarizations were carried out in a half-cell apparatus with 90% w/w phosphoric acid at 170° C. The platinum surface area was determined by cyclic voltammetry at a sweep rate of 50 mV s^{-1}. The hydrogen adsorbed in the potential range 0.05–0.4 V vs RHE on flooded electrodes (10% PTFE) was measured in 50% w/w phosphoric acid at room temperature [4].

X-ray photoelectron spectroscopy (XPS) analyses were performed on a Perkin Elmer ESCA Lab. 2000 spectrometer. The excitation radiation was AlK_α generated at a source power of 300 W. The analyser was run at constant resolution with a pass energy of 89.5 eV. The powder samples were pressed into carbon steel sample holders from which no interfering signals were observed.

The catalysts acid–base properties were evaluated by potentiometric titration in aqueous suspension of Pt/C catalysts according to Parks *et al.* [16]. The apparatus [17] consisted of a Pyrex glass cell with an external jacket for circulation of thermostatic liquid, a glass electrode for pH measurement (Orion model 91–92) and a probe for temperature control (Orion ATC probe 917002). The two probes were connected to an Orion model 311 pH/mV meter. Titration of 500 ml 0.1 M KNO_3 electrolyte solution containing
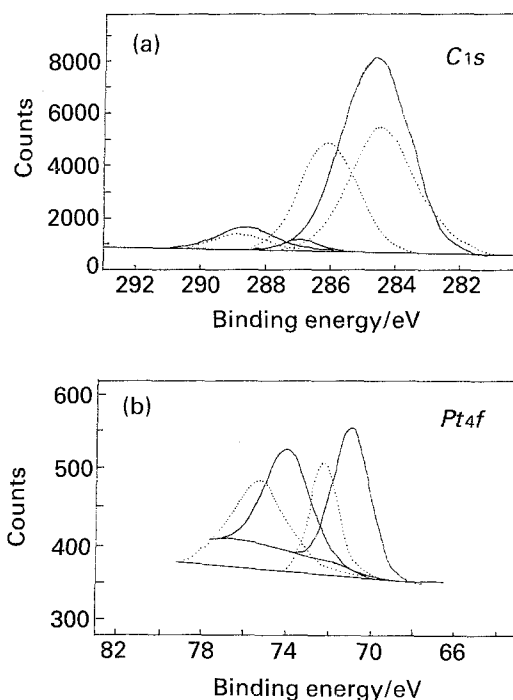
Fig. 1. XPS spectra of C 1s (a) and Pt 4f$_{7/2,5/2}$ (b) of samples 13 and 14.

the catalyst powder (2 g) was carried out under stirring. A 0.1 N HNO_3 solution was introduced (in increments of 5 ml to 20 ml) to the suspension in the electrolytic solution and the titrant (0.1 N KOH) was added with an automatic burette (analytical control method).

3. Surface analysis

The XPS binding energy data (referenced to C 1s at 284.6 eV shown in Fig. 1(a), solid curve) of the Pt/C

Table 2. XPS data of Pt/C catalysts

| Catalyst	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Pt 4f 7/2	72.1	72.3	72.2	72.2	71.9	71.8	71.6	71.9	71.7	71.7	71.6	71.8	70.9	72.7
Pt 4f 5/2	75.4	75.4	75.5	75.4	75.2	75.2	75.0	75.2	75.2	75.6	75.0	75.2	74.0	76.1
C 1s	285.4	285.4	285.3	285.3	284.6	284.6	284.6	284.5	284.6	284.6	284.6	284.6	284.5	284.4
	287.1	286.6	286.6	286.6	285.6	285.5	285.5	285.4	285.7	285.7	285.6	287.0	286.1	286.6
	289.2	288.7	288.4	288.4								288.7	288.9	289.1
O 1s	531.5	532.0	531.8	531.7	532.7	532.7	532.6	532.9	532.0	532.3	532.7	532.5	532.6	532.7
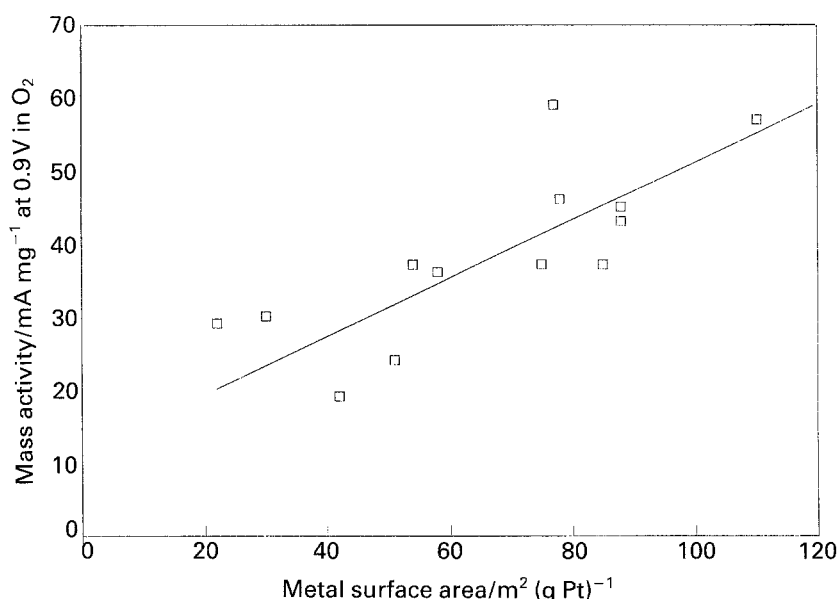
Fig. 2. Electrocatalytic mass activity against platinum surface area by CV.

catalysts are presented in Table 2. The general XPS scans show the Pt 4f, C 1s and O 1s as the major peaks. Figure 1(b) shows the Pt $4f_{7/2}$ and Pt $4f_{5/2}$ signals, which are asymmetrically shaped towards higher binding energies. The interaction of platinum with the support shifts the peak maxima from the expected 70.9 eV (Pt $4f_{7/2}$) and 74.0 eV (Pt $4f_{5/2}$) values to higher values by 0–1.8 eV for low oxygen (solid curve) and highest oxygen content (dotted curve), respectively. The carbon 1s signal is split by oxidation as seen in Fig. 1(a), dotted curve. The shift due to PtO has been reported to vary from 0.9 to 2.5 eV, and that caused by PtO_2 from 2.9 to 3.8 eV [18], but no Pt–O signal from either the Pt 4f or the O 1s has been discerned. This suggests the presence of a metal support electronic effect that accounts for the shifts. According to several authors [18–22], the shift can be taken as a measure of the presence of oxidized platinum species but in these samples the electronic metal-support effects must be accounted for first, since the expected Pt–O surface Pt $4f_{7/2}$ signal component will be only a few percentage points of the unoxidized Pt $4f_{7/2}$ signal. The C 1s signals are noticeably asymmetric at high binding energies. This is caused by several oxidized carbon species at the surface. These have been separated, identified by curve fitting and attributed to the specific species by making reference to Albers [22].

In addition to chemical state information from XPS, there is considerable information about the electronic properties of certain samples available, depending on the nature of the materials examined. Electronic effects associated with local and long range charge transfer phenomena can be inferred from the XPS spectra. In addition, differential charging and variations in electrical contact between the sample and sample components with the spectrometer may cause asymmetric peak broadening and peak shifts, from which more information can be drawn with careful analysis. The integral nature of the spectroscopy prevents differentiation

between spectral changes due to chemical and structural effects. Additional microscopic data is often needed to better interpret XPS spectral changes. Thus the present XPS data do not represent absolute values, but the comparison of observation on similarly prepared Pt–C catalysts has demonstrated significant differences.

4. Results

Figure 2 shows the electrocatalytic mass activity values of the samples against the corresponding platinum surface areas. As expected, a linear trend was observed in the platinum dispersion range (Fig. 2) in a manner similar to that reported by other authors [23, 24].

The role exerted by the oxygen concentration on the surface of the support on the catalyst dispersion is shown in Fig. 3. A decrease in the platinum surface area with an increasing amount of the carbon support's surface oxygenated functionalities, as detected by XPS, is seen. Since the carbon support has almost the same porosity characteristics and the catalysts have been prepared by the same experimental procedure (except for the final heat treatment temperature), it is clear that the decrease in dispersion may be attributed mainly to the presence of these oxygenated surface functional groups.

The platinum XPS binding energy shift has normally been directly related to the degree of platinum oxidation [18], but it may reflect the nature of the metal support interaction and the state of the support. This is shown in Fig. 4 where the platinum binding energy shift is correlated with the concentration of the oxygenated carbon functional groups. The trend may be accounted for by the presence of progressively more oxidized platinum species or by an indirect effect through the metal support interaction. The influence exerted by the concentration of such groups on metal dispersion, already shown in Fig. 3, is reflected in the behaviour shown in Fig. 5, where an
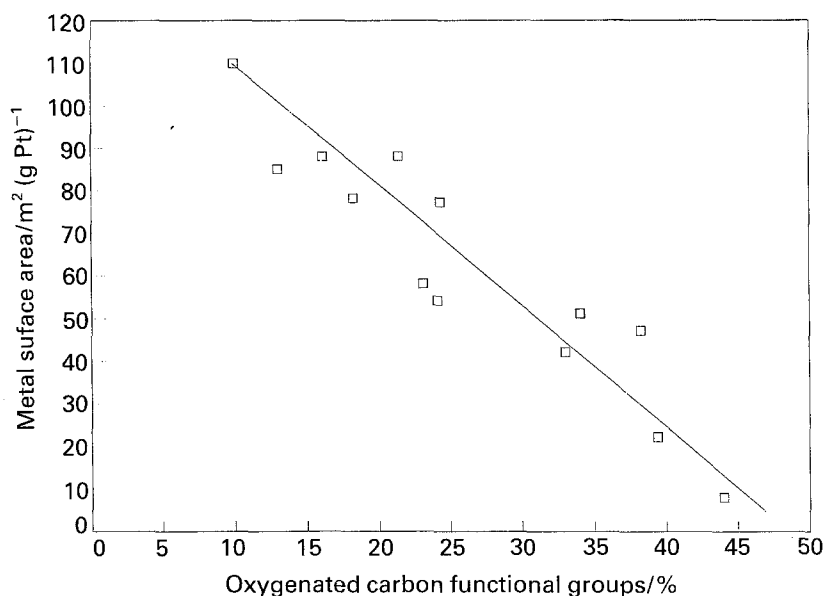
Fig. 3. Platinum surface area by CV against oxygenated carbon functional groups by XPS.

indirect correlation between the Pt 4f binding energy shift and metal surface areas (by CV) is shown. Assuming the Pt 4f binding energy shift to be affected by the nature of the chemical environment (i.e. surface functional groups) with which the platinum species interacts, it seems evident that as the extent of such interaction increases (due to the increase in the electronegativity of the neighbouring sites) a correspondingly apparent increase in the Pt 4f binding energy should result. This should occur irrespective of the platinum metal dispersion. Since the platinum metal surface area is lowered by the increase in oxygen on the carbon support, there appears to be a correlation between the Pt 4f binding energy and its dispersion, as shown in Fig. 5.

To gain a better insight into the nature of oxygenated functionalities, potentiometric titration experiments were carried out with the aim of discriminating the acid–base characteristics of the catalysts. Although unequivocal identification of surface groups is not feasible by the potentiometric technique

employed here, general information related with the acid-base properties of the carbons, as derived from known literature, suggests that the highly basic dissociation constants found for our catalysis (pK_b 3.4–3.8) probably account for the presence of C–π electron donor sites, or pyrone-type groups. Lower K_b values can be reasonably associated with hydroxyl groups bonded to an aliphatic- or to quinone- and/or lactone-functionalities. On the other hand, high values of acidic dissociation constant K_a warrant the presence of carboxylic groups, while lower values strongly suggest the presence of anhydrides or phenols. Furthermore, ketone complexes are presumed to be present in neutral or mildly acidic carbon materials [25, 26].

Thus the presence of increasing amounts of oxygenated species on the carbon surface decreases the platinum surface area. It is of interest to explore the detailed effect of the different types of oxygenated functionalities on the platinum surface area. Two different types of behaviour on the platinum dispersion
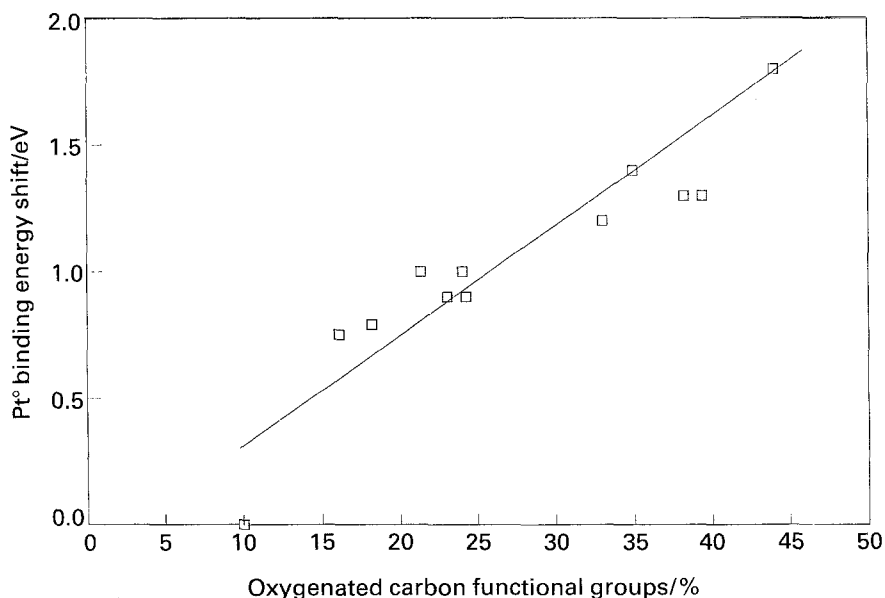

Fig. 4. Pt 4f$_{7/2}$ binding energy shift against oxygenated carbon functional groups.
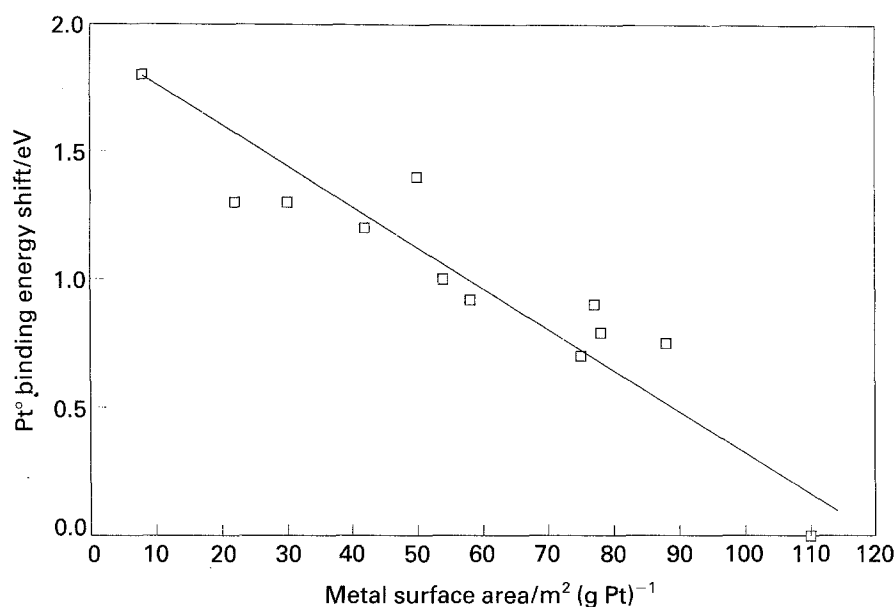
Fig. 5. Indirect correlation between Pt $4f_{7/2}$ binding energy shift and platinum surface area by CV.

were noticed as to the influence of the concentration of the acidic and basic functional groups (Figs 6 and 7).

The trend of the data shown in Fig. 6 suggests that an increasing population of mildly acidic functionalities (pK_a in the range 5.2–6.4) favours the metal dispersion as, on the other hand, expected on the basis of previous evidences [8]. A more complex behaviour is associated with the role of the basic functionalities (Fig. 7). Two distinct trends are observed, differentiated by (a) a decreasing or (b) an increasing concentration of oxygenated groups (detected by XPS) as the total amount of basic surface complexes (detected by ZPC) increases. In the former case (curve (a)), an increase in basic groups causes a corresponding increase in platinum surface area. On the other hand, curve (b) shows the opposite trend, denoting an inverse relationship between platinum dispersion and basic group concentrations. A distinguishing feature of such apparently anomalous behaviour may reside in the varying nature of these groups (i.e. C–π sites and pyrone type complexes). As their dissocia-

tion constants both fall in the same range (pK_b 3.4–3.8), no distinction is feasible by the potentiometric titration technique. On the other hand, XPS data appear to account for the observed different behaviour in the Pt–MSA dependence, as a consequence of the differing electron–donor character exerted by the dual nature of the surface functionalities (polar adsorption sites, Pt–O complex formation by pyrones and electron interactions by Lewis base-like carbon basal planes), encountered in the present examination.

5. Discussion

The results suggest that electrocatalytic activity is sensitive to changes in the physical and electronic structure of platinum deposited on carbon. Metal-support synergistic effects are largely established by catalytic and electrocatalytic studies [27] and revealed indirectly by XPS if crystallite size effects are taken into consideration. Thus, the crystallite size effects reported in a number of investigations [28, 29], deal-
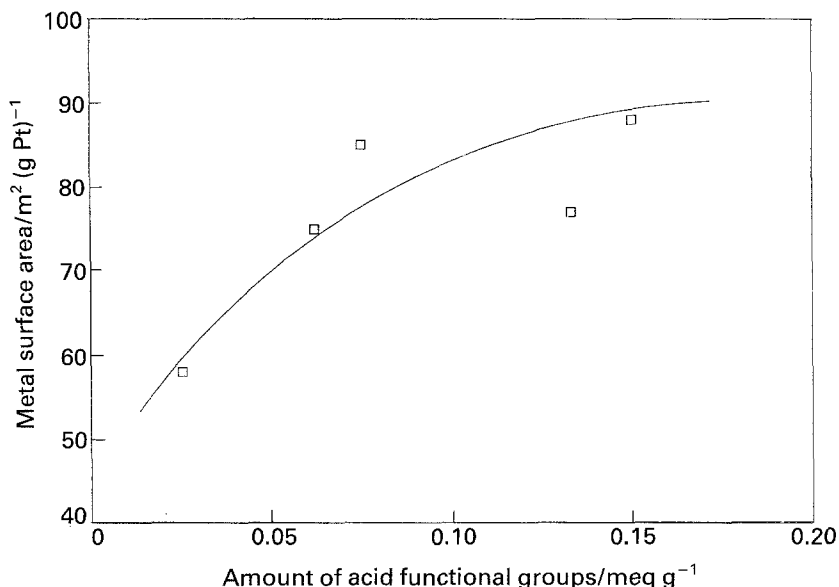

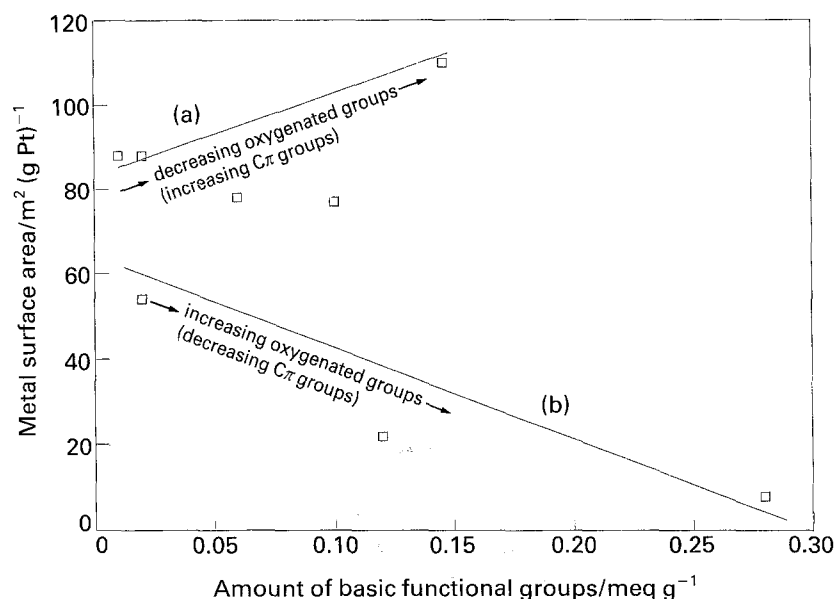Fig. 6. Platinum surface area by CV against amount of acid functional groups by potentiometric titration.

Fig. 7. Platinum surface area by CV against amount of basic functional groups by potentiometric titration.

ing with the oxygen reduction reaction in PAFC conditions must be differentiated from the metal-support synergistic effects which may, in part, be associated with the difference in electronic work function between the metal and the support material. It has been previously shown [30] that the dual nature of the carbon black surface (the basal plane of graphite-like structure and the polar sites) has an important influence on its surface behaviour.

Before individual functionalities are discussed, it is enlightening to consider the surface physical chemistry. Binary bonding energies of $-C=O$ ($749\,kJ\,mol^{-1}$), Pt–O ($389\,kJ\,mol^{-1}$) and Pt–C ($599\,kJ\,mol^{-1}$) [31, 32] indicate that: (a) platinum is capable of forming a strong bond to carbon, (b) the Pt–O bond is weaker than the Pt–C bond and (c) the interaction of oxygen will break the Pt–C bond by the high bond strength of the $-C=O$ bond and not by the Pt–O interaction. Therefore, it may be expected that preparation under proper conditions will produce platinum bound to carbon surface sites that will be destroyed by carbon oxidation which may be catalysed by the platinum.

Surface energy considerations are also important. The high Pt–C bond energy indicates that the Pt–C interfacial energy will promote the spreading of platinum on the carbon and thus enhances the dispersion particularly at edge sites. The relative surface energies of Pt, Pt–O and the functionalized carbon surfaces probably have the order Pt > Pt–O = C–OH (acidic or basic) or C–O– (basic) > C=O (electron donating) > C. Thus, the high surface energy of reduced platinum works against platinum dispersion. The lower surface energy Pt–O, if it spreads, could lower the total surface energy, but it is questionable if the total surface energy is lowered for basic surfaces. Thus, acidic surfaces and high energy basic surfaces should promote Pt-oxide dispersion to a higher degree than carbonyl surfaces.

The relationship connecting electroactive platinum area and total amount of oxygenated functionalities

indicates a general trend according to which platinum dispersion is negatively affected by an increasing concentration of the oxygen–carbon complexes (Fig. 3). This agrees with Yeung and Wolf [33]. They used scanning probe microscopy to study the changes in platinum morphology caused by nitric acid oxidative functionalization of supported platinum catalysts. The STM of the platinum crystallites showed them to be rough rectangular parallelepiped structures with rounded corners. These were shown to change size and morphology on functionalization of the graphite. The present results provide further insight into the effects of the different types of functionalities of carbon. Examination of the samples exhibiting surface acidic characteristics, accounts for an apparent positive role of the latter towards metal dispersion, in agreement with previous evidence [8], according to which mildly acidic oxygenated functionalities, such as phenols and quinones, are thought to be responsible for an enhanced platinum dispersion (according to the above discussion, possibly as the Pt-oxide).

XPS detected almost no differences in the total amount of oxygenated groups in the acidic samples shown in Fig. 6 where an apparent increase in platinum surface area is correlated with increasing concentration of acidic functional groups. Since the variations in MSA of acidic samples are restricted to a range between 60 and $90\,m^2\,g^{-1}$ Pt, evidence from potentiometric titration measurements does not contradict the conclusion that an increasing amount of oxygenated functionalities lowers the platinum surface area. On a more general basis, extended to 10–$110\,m^2\,g^{-1}$ Pt, the scatter in Fig. 3 is due to the different nature of the oxygenated functionalities. Thus there is a net decrease in platinum dispersion with increase in the total oxygen content, irrespective of the acid–base properties.

On the other hand, the formation of π-complexes with platinum, due to the electron releasing centre of the graphitic basal plane, was recently reported to
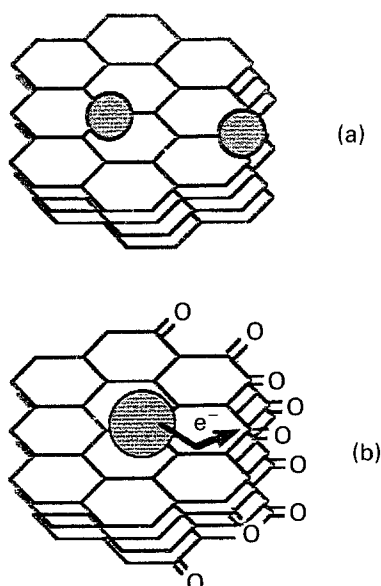
Fig. 8. Schematic representation of Pt–C–π and P–C edge interactions (a), and electronic interaction between platinum and oxygenated carbon functionalities (b).

give rise to high metal dispersions [34]; curve (a) in Fig. 7, marked by the progressively decreasing amount of oxygenated groups with a corresponding increase in the overall basic complex concentration, agrees with such evidence.

The opposite behaviour, exerted by the increasing presence of oxygenated basic groups (curve (b)), may be explained by the lower electron donating character of the carbon–oxygen complexes (in comparison with C edge and C–π functionalities shown in Fig. 8). In this case, the more electronegative oxygenated sites interact less with zero valent platinum. The stabilization of oxidized platinum states by basic oxygenated sites has been previously reported for γ-alumina [35], but, in that case, an increase in dispersion resulted. In the present investigation, an optimal level of interaction strength between the supported platinum crystallites and the carbon surface appears to be associated with carbon edge sites and C–π sites (Fig. 8). The lower electronegativity (with respect to oxygen groups) but high Pt–C bond strength and the stabilization by resonance on the aromatic ring of the electron pair seem to be sufficient to anchor the platinum particles without any concurrent deactivation effect, as observed for basic oxygenated groups.

Information from XPS indirectly shows the influence of the presence of oxygen–carbon complexes on the degree of platinum dispersion (Fig. 5). The binding energy shifts in the XPS Pt 4f signals appear to reflect the electron withdrawing nature of the neighbouring oxygenated carbon support. Detailed XPS studies are currently underway to explain these observations and to relate the results to electroactive surface area (Fig. 2).

The above considerations suggest that a significant structural (Pt-surface area) and electronic (positive Pt-surface) influence is exerted by the changing nature of the support functionalities. This has direct effects on the properties of platinum/carbon electrocatalysts for the oxygen reduction reaction in PAFC.

Strictly controlled preparation and activation conditions are necessary in order to manage the degree of interaction between the deposited metal and support, as it has been shown that (within a homologously prepared series of samples), the different acid–base characteristics of the surface functional groups, and their amount, are able to strongly affect the physical and electronic state of the supported platinum, with the observed consequences on its surface properties.

Acknowledgements

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