

The control of platinum impregnation by PZC alteration of oxides and carbon

X. Hao, L. Quach, J. Korah, W.A. Spieker¹, John R. Regalbuto*

Chemical Engineering Department, University of Illinois at Chicago, 810 S. Clinton Street, Chicago, IL 60607, USA

Received 20 February 2004; received in revised form 13 April 2004; accepted 13 April 2004

Available online 7 June 2004

Abstract

In this paper, we examine the influence of two methods of PZC alteration, ion-doping of oxides and oxidation of carbon, on the control of Pt uptake, using both anionic and cationic Pt complexes. The former method was found to be unsuccessful and the latter successful for ‘engineering’ the impregnation of catalyst support materials. We use the latter approach to suggest a simple, effective way to synthesize highly loaded, highly dispersed Pt/carbon materials that have applications as fuel cell electrocatalysts.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Catalyst preparation; Impregnation; Adsorption; Carbon; Platinum; Point of zero charge; Fuel cell electrocatalyst

1. Introduction

Much recent progress in the ‘transformation of the art of heterogeneous catalyst preparation into a science’ has been made through fundamental studies of the adsorption phenomena that occur during catalyst impregnation. A landmark in this transformation is the postulation of Brunelle that the adsorption of noble metal complexes onto common oxides supports was essentially coulombic in nature [1]. The hydroxyl groups that populate oxide surfaces become protonated and so positively charged below, or deprotonated and negatively charged above, a characteristic pH value. This pH, at which the surface is neutral, is termed the point of zero charge (PZC). Brunelle cited many instances in which oxides placed in solutions at pH values below their PZC would adsorb anions such as hexachloroplatinate $[\text{PtCl}_6]^{-2}$, while at pH values above their PZC would adsorb cations such as platinum tetraammine (PTA), $[\text{Pt}(\text{NH}_3)_4]^{+2}$. This electrostatic mechanism was semi-quantitatively developed by another landmark work, that of Contescu and Vass [2], who studied the adsorption of $[\text{PdCl}_4]^{-2}$ and $[(\text{NH}_3)_4\text{Pd}]^{+2}$ over alumina at low and high pH, respectively, and was soon

followed by the comprehensive series of Heise and Schwarz for anionic Pt chloride adsorption over positively charged alumina at low pH [3–6].

Much more work on the experimental verification and quantification of this ‘physical’ adsorption process has been conducted in our own laboratory, beginning with the chloroplatinic acid (H_2PtCl_6 or CPA)/alumina system [7–10]. In this system, anionic chloride and oxy-chloride complexes adsorb over a positively charged alumina surface in the low pH range. The revised physical adsorption (RPA) model [9] has also been extended to the PTA/silica system at high pH [11,12], in which case, cationic complexes adsorb over negatively charged surfaces. The latter two works especially demonstrate the practical consequence that when ‘strongly adsorbed’ at the optimal pH, the monolayer of adsorbed coordination complexes retains its high dispersion through the catalyst pretreatment process.

An intriguing extension of this accrued knowledge of catalyst preparation fundamentals is the possibility of controlling the adsorptive properties of the solid substrate by changing its point of zero charge. The potential of this control is illustrated in Fig. 1, in which the uptake of charged complexes is simulated over surfaces of various PZCs using the RPA model. In Fig. 1a, anionic platinum hexachloride, $[\text{PtCl}_6]^{-2}$, is taken as the adsorbate, while in Fig. 1b, the cationic platinum tetraammine complex, $[(\text{NH}_3)_4\text{Pt}]^{+2}$, is assumed. Curves representative of silica (PZC near 4) and

* Corresponding author. Tel.: +1 312 9960288; fax: +1 312 9960808.

E-mail address: jrr@uic.edu (J.R. Regalbuto).

¹ Present address: UOP Research Center, 50 E. Algonquin Road, Des Plaines, IL 60017, USA

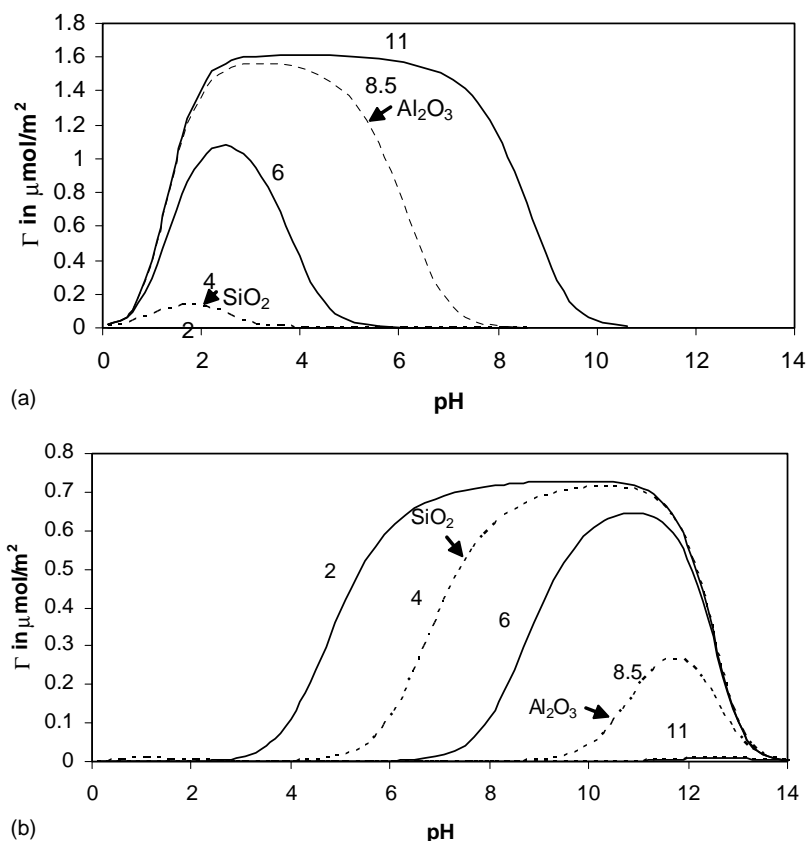


Fig. 1. (a) RPA prediction of CPA adsorption over oxides of various PZC surfaces: (a) CPA; (b) PTA. PZCs representative of silica and alumina are indicated.

alumina (PZC near 8.5) are indicated by the dashed lines in Fig. 1. For CPA, Fig. 1a, Pt uptake increases as the pH falls from the PZC of each material, as the surface charges increase. At the low pH extreme, adsorption is inhibited over all surfaces by high ionic strength [7–10]. The materials with the highest PZC can attain the highest surface charge before the onset of high ionic strength inhibition, and so, adsorb the highest density of Pt. Analogously, it is the lowest PZC materials that adsorb the greatest amounts of the cationic Pt complex at high pH (Fig. 1b). High ionic strength inhibition also occurs at the high pH extreme [11]. The maximum Pt uptake of both complexes appears to be dictated by a steric maximum, which can be calculated as a close packed monolayer of complexes that retain either one hydration sheath in the case of the anionic chloride complexes, or two sheaths in the case of the cationic amine complexes [9,13]. On an areal basis, the maximum loading of CPA is about 1.6 mmol/m² or about 1 complex/nm² and of PTA is about 0.86 mmol/m² or 1 complex/2 nm². The absolute weight loadings of Pt that can be achieved by strong electrostatic adsorption are thus directly proportional to the substrate specific surface area (m²/gm).

Fig. 1 shows that pure silica has almost no attraction for CPA, and pure alumina has little attraction for PTA. The idea of PZC-altered supports is to open up or extend the pH range over which a support is capable of adsorbing a

particular metal complex, with the ultimate goal of being able to generate small, well dispersed, highly active metal particles with a variety of metal complexes.

To attempt this molecular-level control, various means can be used to alter the PZC of solid surfaces. Several papers have indicated that the PZC of alumina can be decreased by several pH units through doping with an anion such as chloride or fluoride, and the PZC of silica can be significantly raised by doping with cations such as Na⁺ or K⁺ [14–19]. In a previous work, we have increased the PZC of silica from a pure value of about 4 to values as high as 8.8 by doping with potassium and decreased the PZC of alumina from pure values of 8.5 to as low as 4.8 by chloride doping [19].

With carbon, controlled oxidation of the surface at mild or rigorous conditions leads to a lesser or greater amount of oxygen functional groups on the surface [20–24]. Pure carbon surfaces such as graphite or washed activated carbon generally have a neutral or slightly basic point of zero charge. The modification of carbon surfaces can be achieved through different oxidative treatments in both liquid and gas phase. Generally speaking, PZC is inversely proportional to the weight percent of O, though it is also a function of the type of the oxygen groups; these are commonly characterized using infrared [22].

In this paper, we examine the influence of both methods of PZC alteration, ion-doping of oxides and oxidation of

carbon on the control of Pt uptake, using both anionic and cationic Pt complexes. The former method was found to be unsuccessful and the latter successful for ‘engineering’ the impregnation of catalyst support materials. We use the latter approach to suggest a simple, effective way to synthesize highly loaded, highly dispersed Pt/carbon materials that have applications as fuel cell electrocatalysts.

2. Experimental

Amorphous precipitated silica (Degussa VN 3S) with a surface area of 160 m²/g and a γ -alumina (LaRouche VGL15) with a surface area of 147 m²/g were used. Ion-doped silicas and aluminas were prepared by dry impregnation of the oxide support with solutions of potassium nitrate (for silica) and ammonium chloride (for γ -alumina). The amount of liquid required to fill the pore volume of the supports was about 1.2 ml/g alumina and 2.5 ml/g silica. The concentration of the solutions were adjusted so as to achieve a dopant loadings of one chloride ion per 4.6–24 surface hydroxyl groups on the alumina surface (8 OH/nm² assumed) and one potassium ion per 1.9–20 hydroxyl groups on the silica surface (5 OH/nm² assumed) [19]. A complete list of all alumina and silica samples is given in Table 1. After impregnation, the samples were dried in a muffle furnace in air at 110 °C for 3 h following drying over night under ambient conditions and were then calcined for 5 h at 500 °C in a muffle furnace in air.

The PZCs were determined by the method of Park and Regalbuto (equilibrium pH at high loading, EpHL) [25]. Using a special spear-tip semi-solid electrode, the equilibrium pH of a thick slurry of the oxide at incipient wetness is measured over a wide range of initial pH values. In this simple, accurate method, the PZC is manifested by a wide plateau in the plot of pH (final) versus pH (initial). Data for pure and doped silica and alumina is shown in Fig. 2a. The PZC plateaus of 4 and 8.5 for the pure silica and alumina are clearly seen (closed circles and squares, respectively). Doping with 0.94 wt.% K⁺ brings the PZC of silica up past that of the pure alumina (open circles), while Cl⁻ doping at

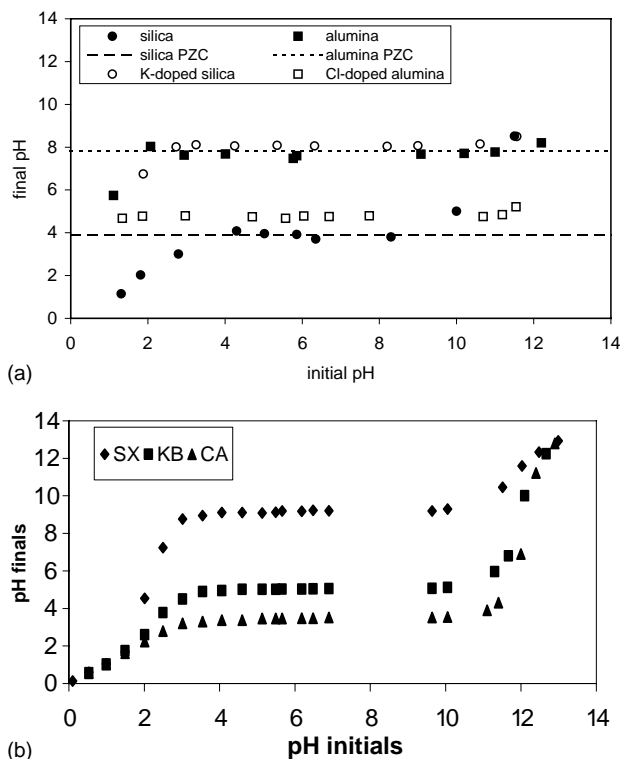


Fig. 2. PZC determinations of (a) pure and doped alumina and silica, (b) activated carbons.

1.49 wt.% (open squares) brings the PZC of alumina down almost to that of pure silica. The PZC values of all doped samples are given in Table 1.

The pertinent properties of the carbon materials employed are shown in Table 2. The types of carbons ranged from high surface area activated carbon to lower surface area carbon black and graphite. The wide range of PZCs of the activated carbon samples came from the supplier’s different pretreatment conditions. The measurement of this wide range of PZC values is illustrated in Fig. 2b.

The effect on oxide and carbon PZC of washing with acidic, neutral and basic solutions was determined. For the washing procedure, a volume of solution about 10 times in excess of the pore volume was employed, and after contacting the mixtures were shaken for 1 h, and then filtered. The filtered samples were dried overnight and calcined for 6 h at 500 °C in air. A first set of each sample was washed three times with deionized water with a pH of about 5.8. Second sets were also washed three times with an acidic HNO₃ solution at a pH of 2. The third set was washed with a basic solution of NH₄OH at a pH of about 9 (silica), or a pH 12 NaOH solution for those samples with the highest PZCs (alumina, carbon).

For the adsorption experiments, CPA (99.9%) and PTA (99.0%) were obtained from Aldrich. The pH values of various Pt dilutions were adjusted using HCl or NaOH. Most of the adsorption experiments were carried out in an excess of liquid to enable the measurement of solution pH and to

Table 1
Ion loading and PZC values of the pure and modified silica and alumina

Support	OH sites/ion ^a (wt.%)	Dopant (mmol)	Dopant/g support.	Solution (mol/l)	PZC
Alumina	–	–	–	–	7.7
Alumina	24	0.29	0.08	0.06	6.2
Alumina	20	0.35	0.09	0.08	5.9
Alumina	4.6	1.49	0.42	0.35	4.8
Silica	–	–	–	–	3.0
Silica	20.2	0.26	0.06	0.01	7.0
Silica	8.2	0.63	0.16	0.03	7.8
Silica	5.5	0.94	0.24	0.04	8.0
Silica	1.9	2.68	0.70	0.11	8.8

^a Assumes 8 OH/nm² for alumina, 5 OH/nm² for silica.

Table 2
Carbon specifications

Carbon name	Carbon type	Abbreviation	Surface area (m ² /g)	Measured PZC
Norit CA1	Activated carbon	CA	1400	2.5
Darco KB-B	Activated carbon	KB	1500	5.0
Norit SX-ULTRA	Activated carbon	SX	1200	8.1
Asbury Grade 4827	Graphite	AS	115	5.0
Cabot Vulcan XC-72	Carbon black	V-XC	254	8.6

prevent large shifts in it from the ‘oxide buffering’ effect [25]. The parameter of ‘surface loading’ is convenient to indicate the amount of oxide surface in solution. For example, 0.313 g of 160 m²/gm silica in 50 ml of solution yields 1000 m²/l. Both silica and alumina were used at this surface loading with 120 ppm CPA or PTA so as to try to compare ion-doped silica and alumina head-to-head. With carbon, 200 ppm CPA solutions were employed over all carbons at 500 m²/l, while 312 ppm PTA was used at 2000 m²/l. These amounts of Pt correspond to about 10% excess of the maximum coverage at these surface loadings. Contacted slurries in 50 ml bottles were placed on a rotary shaker for 1 h, after which 3–4 ml was withdrawn and filtered for ICP analysis. Previous work with silica and alumina has shown that 1 h is more than sufficient to achieve adsorption equilibrium over these surfaces [7,11]. Platinum uptake was determined as the difference in Pt concentrations in the precontacted and postcontacted solutions.

EXAFS measurements were performed at the Materials Research Collaborative Access Team (MRCAT) undulator beam-line equipped with a double-crystal Si (111) monochromator with a resolution better than 4 eV at 11.5 keV (PtL₃ edge). A Rh-coated mirror was used to minimize the presence of harmonics. Spectra of the Pt solutions were taken in fluorescence mode using the stern and Heald configuration with a 0.1-mm high-purity Zn foil filter. The resulting signal-to-background ratio was approximately 0.8 from a 1-cm 200 ppm Pt solution.

3. Results and discussion

3.1. Ion-doped silica and alumina

Silica doped with potassium at 8.2 OH groups per ion yielded a PZC of 7.8 (Table 1). The RPA model calculations shown in Fig. 1 suggests that the uptake of CPA over the PZC 8 silica might be greatly enhanced, and the uptake of PTA over a PZC 8 silica might be greatly retarded if the doped samples obey an electrostatic mechanism. A comparison of Pt uptake of the undoped and doped silicas at 1 h contact time is shown in Fig. 3 for both CPA at low pH (Fig. 3a) and PTA at high pH (Fig. 3b). In both cases, the doped silicas behave identically to the pure samples. Platinum hexachloride could not be made to adsorb over silica at low pH, nor was platinum tetraammine uptake retarded at high pH. The RPA model for

pure silica also simulates adsorption over the doped support in both pH ranges.

Analogous results were seen with alumina. Doping with 0.35 wt.% Cl⁻ yielded an alumina with a PZC of 5.9 (Table 1). The RPA calculations of Fig. 1 suggest that the uptake of CPA over the doped alumina at low pH should be retarded, while the uptake of PTA at high pH should be enhanced. The comparison of the doped and undoped samples is shown in Fig. 4. Once again, the doped samples behave as if pure in both pH ranges with the respective Pt complexes. The RPA model for the pure surface applies also to the doped surface.

In an attempt to understand the failure of ion dopants to influence Pt uptake, detailed experiments were conducted to examine the reversibility of the ion-doping process [19] and a summary of this work is presented here. The doped silicas and aluminas were washed in acid, neutral and basic solutions after which PZCs were remeasured. Typical pH shifts for a set of silica samples from an abbreviated range of initial pHs are given in Fig. 5a. The PZC of each sample is taken as the average of the final pH values. These results are summarized in Fig. 5b, which more clearly indicates the effect of the first two washing treatments on the silica PZC. The high PZC of the doped sample is unaltered after repeated washes in either DIW or basic solutions and ICP analysis of the wash solutions does not show K⁺. This suggests that in the mid to upper pH range the dopant remains somehow anchored to the silica surface and effects the deprotonation chemistry of surrounding OH groups, rather than existing as K₂O and dissolving as K₂O + H₂O → 2K⁺ + 2OH⁻. After an initial wash with acid solution (0.01 M HNO₃); however, the PZC drops back almost to that of pure silica. A second wash brings the PZC fully back to the pure oxide value. A third wash results not in a further lowering of the PZC, but the pure oxide PZC again. Qualitative analysis by ICP revealed significant amounts of K⁺ in the initial acid wash solution.

It appears then that the K⁺ dopant is redissolved in the low pH range, and this can explain the failure of the doped sample to adsorb anionic Pt. In the basic pH range, however, the similarity of PTA uptake over the doped and undoped sample cannot be explained by a loss of the dopant in a caustic solution. In this case, we postulate, that the K⁺ ions are removed from the surface by the divalent Pt cations which compete more strongly for the surface layer than the K⁺. Thus, potassium ions might be removed from the silica surface either by high concentrations of protons in the

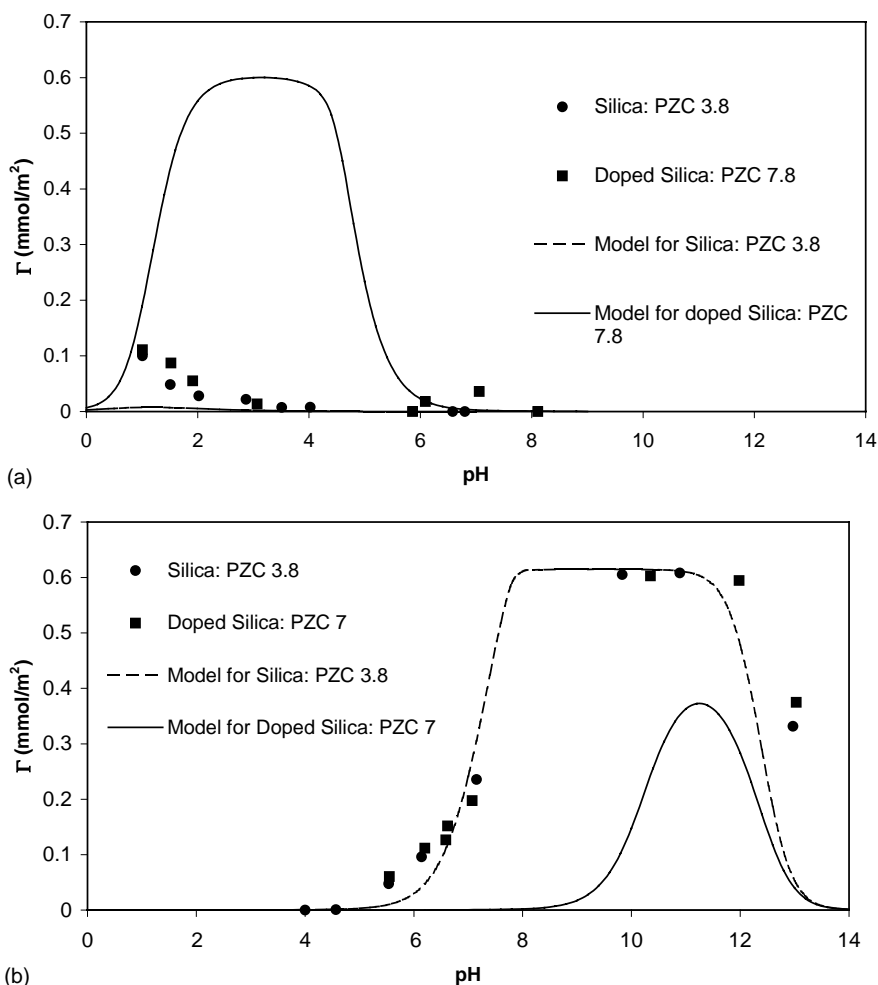


Fig. 3. Experimental and simulated platinum adsorption over ion-doped and pure silica vs final pH: (a) from CPA solution; (b) from PTA solution.

bulk liquid phase (low pH) or by high local concentrations of cationic PTA (at high pH). In neither case does the presence of the dopant seem to affect the Pt–silica interaction. Along practical lines, this means that the RPA model has application even to silica surfaces that contain significant impurities. Precipitated silicas, for example, contain significant amounts of Na⁺ impurities. The PZCs of this material as-received is often about six [11], and acid washing brings it down to the value of pure silica at about four. The present results reveal that the adsorptive properties of the impure silica should be the same as the purified; the washing of the silica need not be done if the impurity has no adverse effect on catalyst activity.

Turning now to alumina, a similar series of washes was conducted with the highly doped sample; the results are summarized in Fig. 6. In this case, it is the base wash that brings the PZC back to that of pure alumina. The initial wash in pH 12 NaOH brought the PZC all the way up to that of pure alumina; subsequent washing did not alter the PZC any further. The PZCs are virtually unchanged after repeated washes in acidic and neutral solutions suggesting that the dopant remains fixed to the surface under these conditions.

The interpretation is again analogous to that for silica; Cl[−] might be removed from the alumina surface either by high concentrations of OH[−] in the bulk (high pH) or by high local concentration of divalent Pt anions (CPA at low pH). This notion is consistent with a previous study in which chloride was shown not to compete with CPA for the alumina surface at low pH [7]. And like silica, alumina surfaces containing univalent ionic impurities can be treated as pure for the estimation of Pt adsorption properties via the RPA model.

3.2. Surface oxidation of carbon

In acid or base washes, the PZCs of silica and alumina either remained at their original value or virtually returned to the value of the pure oxide. The influence of acidic and basic solutions on carbon is more complicated. Fig. 7 gives the variation of PZC of three activated carbons with as-received PZCs of 2.5 (CA), 5.0 (KB) and 8.1 (SX) (Table 2). The changes of the acidic CA carbon with washing are shown in Fig. 7a. Washing in the acid solutions results in an increase in the PZC of up to about one pH unit, a neutral wash does nothing, while a base wash moved the PZC up almost two

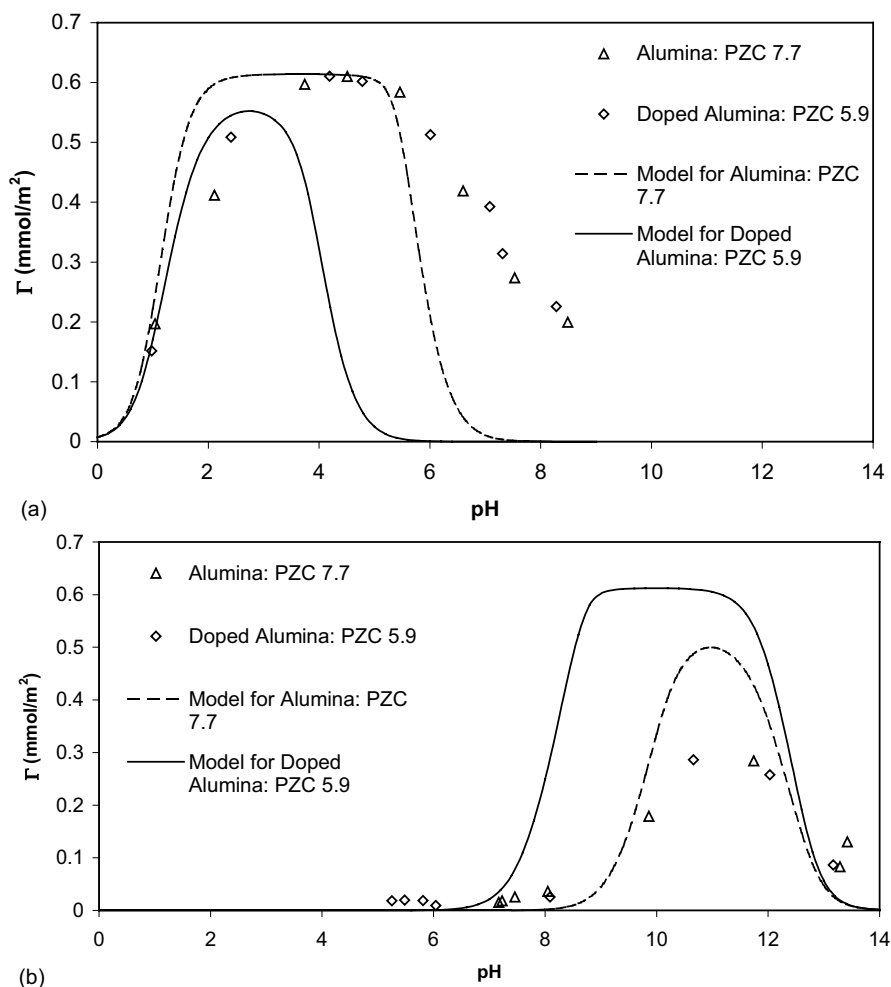


Fig. 4. Experimental and simulated platinum adsorption over ion-doped and pure alumina vs final pH: (a) from CPA solution, (b) from PTA solution.

units to a value of 4.0. The upward PZC shift in an acid solution can be explained by the previous history of the CA sample. In the supplier's preparation the strong acidity of the CA sample was created by prolonged exposure to concentrated phosphoric acid. The nitric acid used for the wash was relatively dilute. Qualitative analysis by ICP showed that some phosphorus had been removed during the wash; thus the surface became less acidic by loss of some phosphoric acid during the acid wash. The neutral deionized water solution does not wash off the phosphoric acid and so the PZC remains stable.

KB carbon, shown in Fig. 8b, has an as-received PZC of 5.0. The KB PZC remains the same after a neutral wash, drops about 2 pH units in an acid wash, and increases about two units after a base wash. We conclude that the conditions used are sufficient to either create or destroy a portion of the surface oxygen.

SX carbon, which initially contains only mildly acidic OH groups and has an as-received PZC of 8.1, is little affected by either neutral or base washes. Apparently there are no highly reactive surface oxygen groups to neutralize. In acid solutions, however, the PZC becomes more acidic by about

2 pH units. The acidity of the wash solutions was again sufficient to induce oxidation of the carbon surface. This is commonly reported [21,23,24] when nitric acid is used as the oxidation agent.

In contrast to silica and alumina, carbons of varying PZC differ markedly in their capacity to adsorb Pt complexes. The uptake of CPA over the three activated carbons is shown in Fig. 8a. In the set of data, the qualitative trend predicted by the RPA model in Fig. 1a is observed; at any pH the carbon with the highest PZC adsorbs the most CPA, that with the lowest PZC adsorbs the least, and that with an in-between PZC adsorbs intermediate amount of Pt. Quantitatively, uptake is higher over the CA carbon (PZC:2.5) than predicted by the RPA model. Revisions to the RPA model for carbon will be presented in a future work.

At high pH the uptake of PTA complexes, shown in Fig. 8b, also varies systematically with the carbon PZC and is qualitatively in agreement with Fig. 1b. The carbon with the lowest PZC adsorbs the most PTA, that with the highest PZC adsorbs the least, and that with an in-between PZC adsorbs an intermediate amount. In the two highest surface area carbons (CA and KB), however, uptake is about half

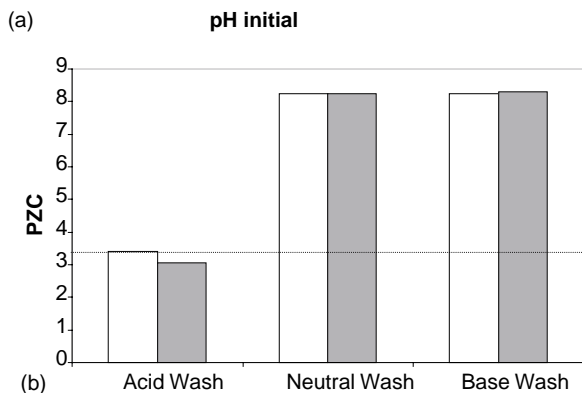
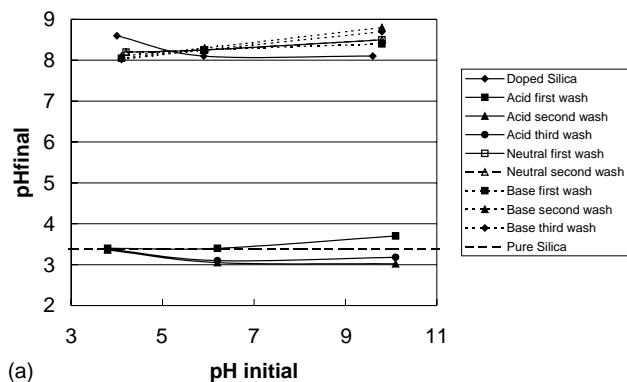


Fig. 5. PZC determinations for silica washed in acidic, neutral and basic solutions: (a) raw data, simplified results.

that predicted by the RPA model. We hypothesize that the discrepancy can be explained simply by steric exclusion of the large Pt ammine complexes, which are believed to retain two hydration sheaths, from the smallest micropores of the high surface area activated carbon. To test the theory of pore exclusion, we performed another uptake experiment at the same surface loading with a lower surface area, larger

pore size carbon (AS, shown in Table 2). This carbon has a PZC similar to that of KB. Over this carbon, as seen in Fig. 9, the maximum surface density is closer to a steric monolayer and as high as would be expected for a PZC 5 material (Fig. 1b).

The trends in anionic and cationic Pt adsorption with carbon PZC seen here are consistent with the adsorption of other ionic metal complexes reported in the literature. For example, Cu^{2+} uptake has been observed to be significantly enhanced by surface oxidation [26], along the lines of Fig. 8b. Similarly, surface oxygen has been shown to favor the anchoring of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ on carbon black [20], and oxidized carbon fibers exhibited enhanced Ag^+ adsorption [27]. Finally, over a series of activated carbons oxidized with nitric acid, it was demonstrated that the lower the PZC, the greater the uptake of cobalt cations at the same solution pH [28].

Many reports of anionic complex adsorption also appear to be consistent with an electrostatic mechanism; less severe or no oxidation (and correspondingly higher PZCs) leads to greater uptake of anionic complexes. This has been demonstrated in several papers for CPA adsorption over various forms of carbon [24,29–31]. Heat-treated carbons, with presumably less surface oxygen and higher PZCs, adsorb more CPA than oxidized carbon [29,30]. Molybdate adsorption also appears to follow an electrostatic adsorption mechanism, if the equilibrium adsorption method is followed [21,32].

There appears to be a good amount of literature in qualitative agreement with an electrostatic mechanism of adsorption. Up to now, however, the effect of solution pH on metal uptake has not been systematically studied. The current results reveal that there exists an optimal pH for each type of complex (anionic or cationic) for a carbon of a given PZC at which the Pt uptake is highest and the metal-support

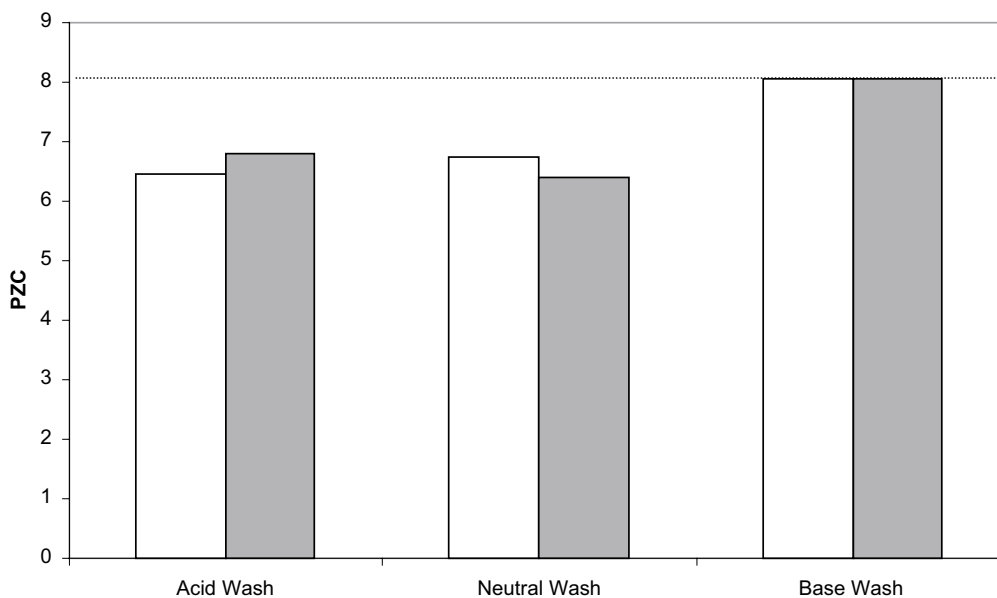


Fig. 6. PZC determinations for alumina washed in acidic, neutral and basic solutions.

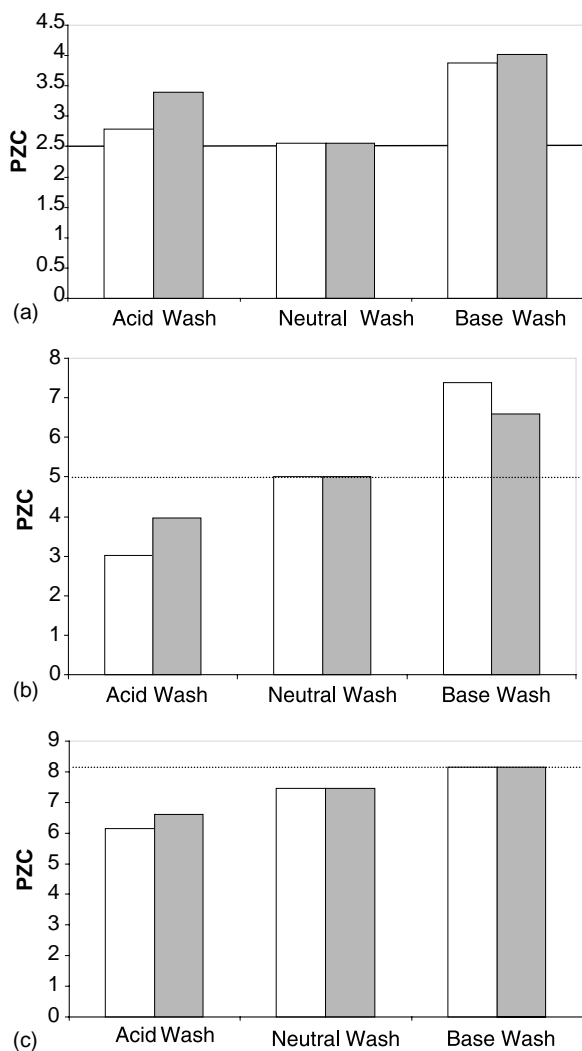


Fig. 7. PZC determinations for activated carbons washed in acidic, neutral and basic solutions: (a) CA, pure PZC = 2.5; (b) KB, pure PZC = 5.0, c) SX, pure PZC = 8.1.

interaction is the strongest (Figs. 8 and 9). This range appears to be quite narrow for the anionic chloride complexes. The current results also suggest that the easily measured PZC values are accurate indicators of surface oxidation and the adsorptive capacity.

3.3. Fuel cell electrocatalyst fabrication

Our results for Pt adsorption onto carbon have application in the synthesis of Pt/C fuel cell electrocatalysts, which typically consist of a high weight loading of Pt on a conductive carbon black support. The key component of any fuel cell is the electrode stack; in proton exchange membrane (PEM)-based fuel cells, which are among the most prevalent, the anodes and cathodes are comprised of noble metals on carbon.

Published methods for the synthesis of Pt/carbon fuel cell electrodes are rather complex, involving many steps

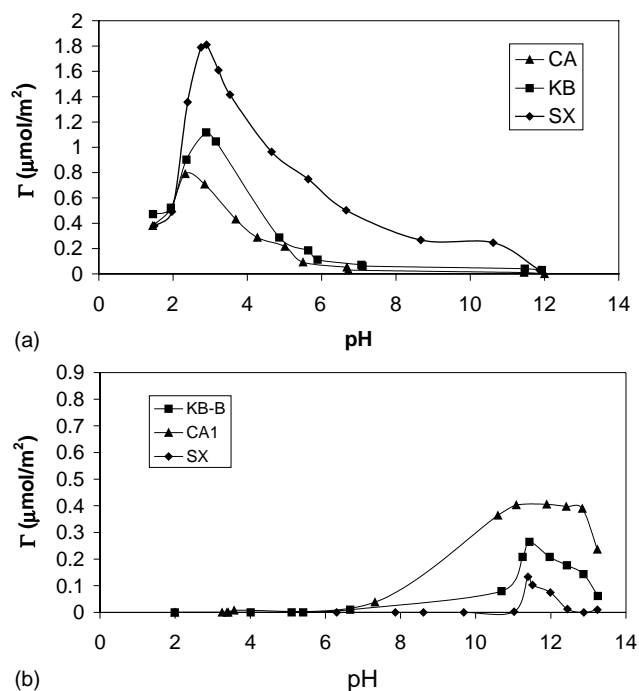


Fig. 8. Uptake results (1-hr contact time) vs final pH over activated SX, KB and CA: (a) CPA; (b) PTA.

and chemical reagents [33,34]. For example, the procedure begins with dissolved CPA, which is then converted to a sulphite complex and ultimately to a mixture of platinum oxides by a number of liquid phase reductions, decompositions and oxidations.

The current results suggest a simpler procedure to obtain a high loading of highly dispersed Pt, provided that the carbon black support obeys an electrostatic adsorption mechanism. To obtain the highest possible Pt loading in a single adsorption step, the PZC of the carbon should be as high as possible so that the Pt chloride complex can be used. As mentioned above, this complex appears to retain only one hydration sheath and not two, and so can be adsorbed at twice the surface density as the Pt ammine complex. The adsorption should be conducted at the acidic pH that yields the strongest electrostatic interaction of the carbon surface

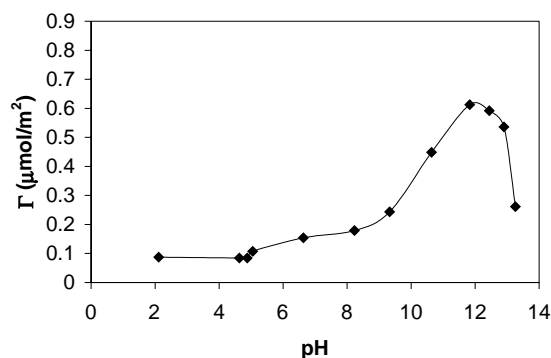


Fig. 9. PTA uptake (1-hr contact time) vs final pH over large-pore graphitic carbon (Asbury).

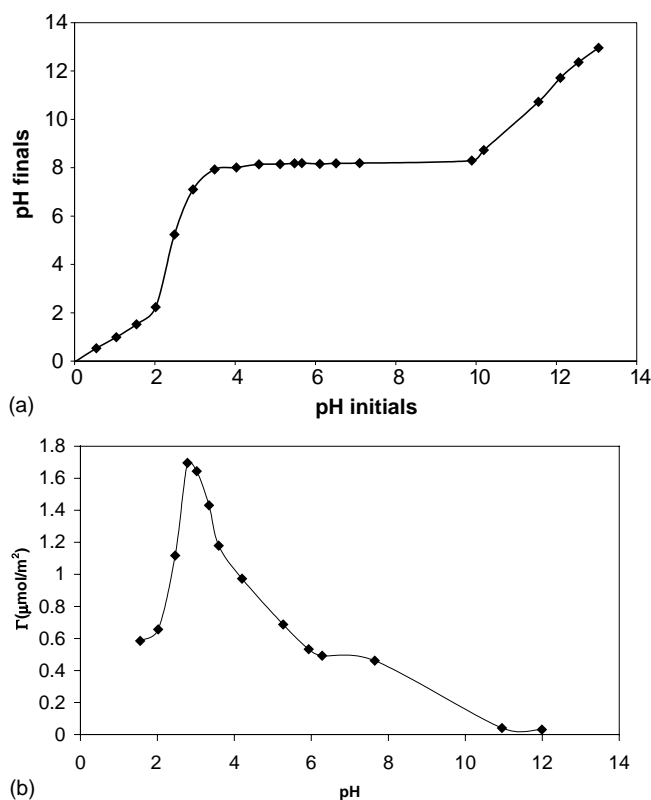


Fig. 10. PZC and adsorption measurements with Vulcan XC-72 carbon black: (a) PZC determination; (b) CPA uptake.

with CPA. This pH can be identified and the electrostatic adsorption mechanism verified by an uptake versus pH survey as shown in Fig. 8 for the activated carbons, and the PZC can be measured in the manner of the pH shift experiments of Fig. 2.

These experiments were performed with Vulcan XC-72 (V-XC), currently the industrial standard carbon black for fuel cell electrodes. Shown in Fig. 10a, the PZC of as-received Vulcan XC-72 is 8.5. This as-received PZC is ideal for our purpose. Should the PZC have been too acidic, it would be possible to increase the PZC by annealing.

Employing the same surface loading of 500 m²/l as used for the activated carbons, the uptake of CPA versus pH was

recorded and is shown in Fig. 10b. A sharp maximum is seen in the narrow pH range of 2.9–3.0, similar to the high PZC activated carbon sample (Fig. 8a). Compared to alumina at low pH, the narrowness of the strong adsorption range probably stems from a much lower density of surface OH groups, typically cited in the range 1–3 OH/nm² [35] compared to 8 OH/nm² for alumina [9]. At the adsorption maximum, the ‘strong adsorption’ condition, the uptake of 1.75 mmol CPA/m² corresponds to a Pt weight loading of 9.4 wt.%.

The Pt dispersion of the 9.4 wt.% Pt/Vulcan material prepared by strong adsorption (at the optimal final pH of 2.9) was estimated using the Pt–Pt coordination number obtained from EXAFS. The solid was filtered from the solution, dried at room temperature overnight, and was reduced in flowing hydrogen at 250 °C for 1 h and sealed in H₂ at room temperature during EXAFS analysis. For the sake of comparison, a 9.4 wt.% sample prepared by pore filling or incipient wetness impregnation (IWI) was also prepared and pretreated in the same manner. The pH of this solution, which would not be expected to change appreciably during impregnation (see Fig. 2b) was 1.1. The Pt oxidation state and coordination numbers obtained from XANES and EXAFS for the dried and reduced samples are given in Table 3. Fourier transforms of the EXAFS spectra of the reduced samples are shown in Fig. 11. Pt crystallites prepared by strong adsorption are significantly smaller than those prepared by IWI. The 9.4% Pt sample had a CN of 7.9 (a dispersion of about 50% based on a hydrogen chemisorption versus Pt–Pt coordination number correlation developed previously [12]). The corresponding particle size, about 2.0 nm, is as good or a bit better than catalysts prepared by the more complex Pt sulphite acid route [33,34]. The particles by IWI were much larger, with a Pt–Pt coordination number of 10.9 and a dispersion of about 10%. XANES revealed further differences in the impregnation chemistry: after adsorption but before reduction, the CPA complexes adsorbed at pH 2.9 remained as Pt(IV) with six ligands (about 4.5 Pt–O and 1.5 Pt–Cl), while the CPA deposited by IWI was about 90% reduced to Pt(II) with 4.2 Cl ligands. The exchange of O ligands for Cl ligands during adsorption of dilute CPA solutions is similar to that seen previously over alumina [36]. A detailed

Table 3
XANES and EXAFS fits of H₂PtCl₆ on Vulcan carbon

Sample	Fraction Pt ²⁺	Fraction Pt ⁴⁺	Pt–O CN 2.05 Å	Pt–Cl CN 2.32 Å	Total CN	
Pt (9.4 wt.%), dried samples						
Incipient wetness, pH 1.1	0.9	0.1	–	4.2	4.2	
Strong adsorption, pH 2.9	–	1.0	4.5	1.5	6.0	
Reduced at 250 °C						
	Estimated dispersion	Fraction Pt ⁰	Pt–Pt CN	R (Å)	DWF (×10 ³)	E _o (eV)
IWI	0.1	1.0	10.9	2.75	1.5	–2.9
Strong adsorption	0.5	1.0	7.9	2.75	1.5	–1.9

Dispersions estimated from hydrogen chemisorption vs Pt–Pt coordination numbers for Pt/silica [12].

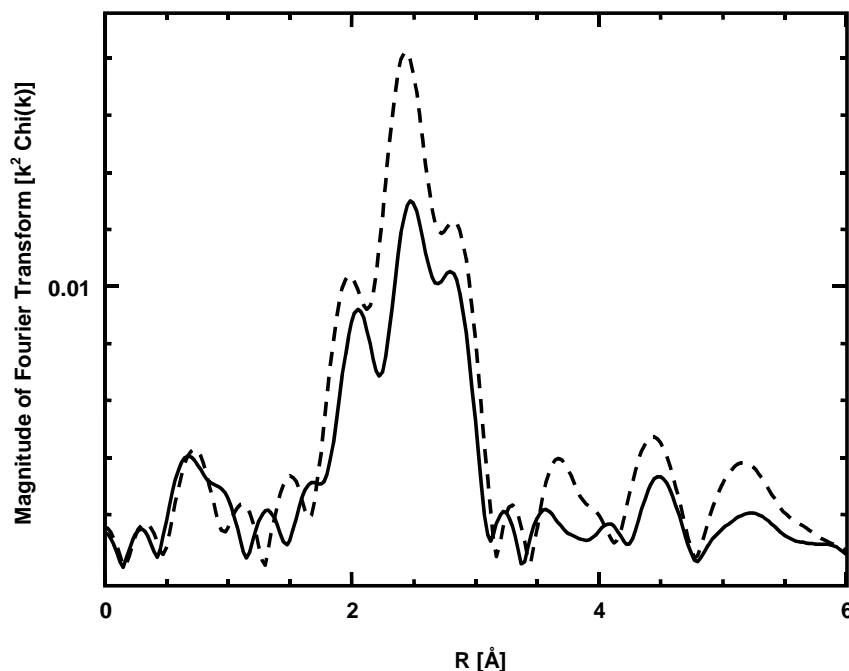


Fig. 11. EXAFS: magnitude of Fourier transform of reduced H_2PtCl_6 on Vulcan Carbon (k^2 ; Δk : 2.75–13.20 \AA^{-1}). Solid: strong adsorption at final pH 2.9. Dashed: IW1 at final pH 1.1.

EXAFS and XANES study of the reduction of CPA by various carbons at various impregnation conditions is currently being conducted.

4. Conclusions

Even though ion-doping can alter the PZC of the alumina and silica, there appears to be no concomitant effect on platinum adsorption. We suggest that potassium ions might be removed from the silica surface either by high concentrations of protons in the bulk liquid phase (low pH) or by high local concentrations of cationic PTA (at high pH). Analogously for alumina, doped chloride ions might be removed by either high concentration of hydroxide in the bulk (high pH) or high local concentration of anionic CPA (at low pH). The metal uptake is virtually the same for the doped and undoped materials, and while ion-doping cannot be used to influence uptake, modeling the metal uptake is simplified in that only the PZC of the pure material need be known.

On the other hand, the oxidation of carbon surfaces can irreversibly alter the PZC and influences the adsorption of Pt complexes in a way that is systematic and controllable. Following the trend predicted by RPA model, the highest-PZC carbons adsorb the most anions $[\text{PtCl}_6]^{-2}$ and least cations $[\text{Pt}(\text{NH}_3)_4]^{+2}$ while the lowest-PZC carbon adsorb the least anions and the most cations. Metal uptake attains a maximum with respect to pH for a given metal precursor and carbon PZC. For PTA, there appears to be some pore exclusion from the highest surface area materials because of the larger size of the cationic adsorbents.

The current results of CPA over carbon provides a simple procedure to obtain a high loading of highly dispersed Pt over the industrial standard carbon black for fuel cell electrodes, Vulcan XC-72. In a preliminary trial, the Pt dispersion resulting from a strong adsorption preparation was much higher than that from incipient wetness impregnation and was very near that in commercial electrocatalysts.

Acknowledgements

The support of the National Science Foundation (CTS 99-08181 and 02-43210) is gratefully acknowledged. We also thank Dr. Jeff Miller of the BP Naperville Complex and Dr. Jeremy Kropf of Argonne National Laboratory for the XANES and EXAFS analysis.

References

- [1] J.P. Brunelle, *Pure Appl. Chem.* 50 (1978) 1211.
- [2] C. Contescu, M.I. Vass, *Appl. Catal.* 33 (1987) 259.
- [3] M.S. Heise, J.A. Schwarz, *J. Colloid Interface Sci.* 107 (1985) 237.
- [4] M.S. Heise, J.A. Schwarz, *J. Colloid Interface Sci.* 113 (1986) 55.
- [5] M.S. Heise, J.A. Schwarz, *J. Colloid Interface Sci.* 123 (1988) 51.
- [6] M.S. Heise, J.A. Schwarz, *J. Colloid Interface Sci.* 135 (1990) 461.
- [7] J.R. Regalbuto, A. Navada, S. Shadid, M.L. Bricker, Q. Chen., *J. Catal.* 184 (1999) 335.
- [8] W.A. Spieker, J.R. Regalbuto, *Stud. Surf. Sci. Catal.* 130 (2000) 203.
- [9] W.A. Spieker, J.R. Regalbuto, *Chem. Eng. Sci.* 56 (2001) 214.
- [10] X. Hao, J.R. Regalbuto, *J. Colloid Interface Sci.* 267 (2003) 259.
- [11] M. Schreier, J.R. Regalbuto, *J. Catal.* 255 (2004) 190.

- [12] J.T. Miller, M. Schreier, A.J. Kropf, J.R. Regalbuto, *J. Catal.* 225 (2004) 203.
- [13] N. Santhanam, T.A. Conforti, W.A. Spieker, J.R. Regalbuto, *Catal. Today* 21 (1994) 141.
- [14] L. Vordonis, P.G. Koutsoukos, A. Lycourghiotis, *J. Catal.* 98 (1986) 296.
- [15] L. Vordonis, P.G. Koutsoukos, A. Lycourghiotis, *J. Catal.* 101 (1986) 186.
- [16] K.C. Akrapopulu, L. Vordonis, A. Lycourghiotis, *J. Catal.* 109 (1988) 41.
- [17] L. Vordonis, A. Akrapopulu, P.G. Koutsoukos, *Stud. Surf. Sci. Catal.* 31 (1987) 309.
- [18] J.A. Mieth, J.A. Schwarz, Y.-J. Huang, S.C. Fung, *J. Catal.* 122 (1990) 202.
- [19] J. Korah, W.A. Spieker, J.R. Regalbuto, *Catal. Lett.* 85 (2003) 123.
- [20] A. Sepúlveda-Escribano, F. Coloma, F. Rodríguez-Reinoso, *Appl. Catal. A: Gen.* 173 (1998) 247–257.
- [21] C.A. Leon, Y. Leon, J.M. Solar, V. Calemma, L.R. Radovic, *Carbon* 30 (1992) 797.
- [22] J.L. Figueiredo, M.F. Pereira, M.M.A. Freitas, J.J.M. Orfao, *Carbon* 37 (1999) 1379.
- [23] M.A. Fraga, E. Jordao, M.J. Mendes, M.M.A. Freitas, J.L. Faria, J.L. Figueiredo, *J. Catal.* 209 (2002) 355.
- [24] H.E. Van Dam, H. van Bekkum, *J. Catal.* 131 (1991) 335.
- [25] J. Park, J.R. Regalbuto, *J. Colloid Interface Sci.* 175 (1995) 239.
- [26] C.A. Toles, W.E. Marshall, M.M. Johns, *Carbon* 35 (1997) 1407.
- [27] Z.R. Yue, W. Jiang, L. Wang, S.D. Gardner, C.U. Pittman, *Carbon* 37 (1999) 1785.
- [28] J. Rivera-Utrilla, M.A. Ferro-García, *Carbon* 25 (1987) 645.
- [29] F. Coloma, A. Sepúlveda-Escribano, J.L. Fierro, F. Rodríguez-Reinoso, *Langmuir* 10 (1994) 750.
- [30] F. Coloma, A. Sepúlveda-Escribano, F. Rodríguez-Reinoso, *J. Catal.* 154 (1995) 299.
- [31] G.C. Torres, E.L. Jablonski, G.T. Baronetti, A.A. Castro, S.R. de Miguel, O.A. Scelza, M.D. Blanco, M.A. Pena Jimenez, J.L.G. Fierro, *Appl. Catal. A: Gen.* 161 (1997) 213.
- [32] J.M. Solar, F.J. Derbyshire, V.H.J. De Beer, L.R. Radovic, *J. Catal.* 129 (1991) 330.
- [33] M. Watanabe, M. Uchida, S. Motoo, *J. Electroanal. Chem.* 229 (1987) 395.
- [34] H. G. Petrow, R. J. Allen, US Patent 4,044,193.
- [35] H.P. Boehm, *Adv. Catal.* 16 (1966) 179.
- [36] W.A. Spieker, J. Liu, X. Hao, J.T. Miller, A.J. Kropf, J.R. Regalbuto, *Appl. Catal. A: Gen.* 243 (2003) 53.