

Review

Recent advances in activity and durability enhancement
of Pt/C catalytic cathode in PEMFC
Part I. Physico-chemical and electronic interaction between Pt
and carbon support, and activity enhancement of Pt/C catalyst

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Abstract

Carbon-supported platinum or platinum alloys are generally used as the cathodic electrocatalysts in polymer electrolyte membrane fuel cells (PEMFC) to enhance the oxygen reduction reaction (ORR). Main challenges to be addressed in this area are the high electrochemical activity and high stability maintenance for low-Pt-loading catalysts toward the feasibility for fuel cell operation and the reduction of the system cost. The interaction of Pt with carbon support, as well as the interaction of Pt precursor with carbon during the supported catalyst formation, are considered to be beneficial to the improvement of catalytic activity and durability of the electrocatalysts. This paper provides a review of recent advances related to the physico-chemical and electronic interactions at the catalyst–support interface and the catalyst activity enhancement through improved Pt–C interaction, especially focusing on the surface modification of the carbon support to form proper functional groups and chemical links at the Pt/C interface.

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Keywords: PEMFC; Pt/C cathodic catalyst; Interaction; Activity enhancement; Surface treatment

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1. Introduction

Among the various types of fuel cells, polymer electrolyte membrane fuel cells (PEMFC) is being in the forefront stage, and have drawn a great deal of attention in both fundamental and application in recent years [1–3]. From the 1960s to the present, great progress has been made in the research and development of PEM fuel cells in terms of membranes, anodic/cathodic catalysts, bipolar plate materials as well as the system design, etc. [3–6]. However, these progresses are still not enough to fulfil the requirement for successful large-scale commercialization of PEMFCs.

One of the big advantages of the PEMFC stack is its fitness in the automobile industry as the zero-emission power supply. The number of automobiles in the world is expected to exceed 1.5 billion in 2020 [7]. At the current level of the state-of-the-art technology (cathode Pt loading: 0.4 mg cm^{-2} ; anode: 0.05 mg cm^{-2}), the Pt storage in the earth would be short if each car that is powered by a 100 kW fuel cell stack needs 100 g Pt [8,9]. One and one-half billion cars would need 150,000 t of Pt. However, the total Pt resources in the world are estimated to be $\sim 28,000 \text{ t}$ [7], which could only supply $\sim 20\%$ of all automobiles. If there are 1.5 billion automobiles, all powered by a fuel cell stack by 2020, the Pt loading must be reduced by a factor of 10. According to the US Department of Energy (DOE) cost reduction targets [10], the total Pt catalyst loading in a membrane electrode assembly (MEA) must be reduced to $<0.03 \text{ mg cm}^{-2}$ [10]. At present, two approaches toward the reduction of Pt usage in the PEMFC catalysts are continuing to be very active: exploration of non-noble catalysts, and reduction of Pt loading through the usage of non-precious supports [4,11]. With respect to non-noble catalysts, there have been no significant breakthroughs in the areas of materials and technology.

The attractive features of high electrical conductivity, chemical stability and low cost lead the extensive applications of carbon materials for the precious metal catalyst supports [12–14]. In PEM fuel cell systems, the most common low-Pt-loading catalysts are platinum (or platinum alloys) supported by high surface carbon and used in both the cathode and anode [15]. Quite a lot of promising approaches and results have been reported for Pt loading reduction through supporting tactics recently [16–56]. However, it is very difficult to maintain or improve catalyst layer performance when the Pt catalyst loading is reduced. Furthermore, a series of aspects, such as effective Pt catalyst layer utilization, the durability and reliability of such a supported catalyst component, are still problematic [57,58]. In order to achieve high catalytic performance with the low Pt loading, great effort must be put on Pt utilization and the enhancement of catalyst activity. Of the several factors which

influence electrocatalytic activity of carbon-supported PEMFC catalysts, particle size, dispersion and structural effects, are of crucial importance [59–64].

The Pt–carbon support interaction has recently been paid more and more attention in the carbon support catalyst studies. This interaction has been considered to have the effects on the growth, the structure, and the dispersion of platinum particles on the carbon supports, thus providing the potential benefits to the improvement of catalytic properties and stability of the electrocatalyst [11,14,15,59,65–68]. However, these effects and mechanism of interaction, *vis-a-vis* overall performance, have been, at best, vaguely understood. This paper aims to provide a topical review on the interaction of platinum with the carbon support, as well as the interaction of Pt precursor with carbon during the supported catalyst formation, and the role of these interactions towards the catalytic activity improvement of the catalysts in PEMFCs. To this extent, this paper summarizes the fundamental aspects of the physico-chemical and electronic interactions at the catalyst–support interface, especially focusing on the interaction improvement through the surface modification of the carbon support to form proper functional groups and chemical links at the Pt/C interface.

In a PEMFC operation system, the kinetics of cathode oxygen reduction on Pt is relatively slow compared to that of anode hydrogen oxidation. Therefore, the large overpotential for the oxygen reduction reaction (ORR) has been a major issue in PEM fuel cell performance [69,70], and contributes about 80% portion of the total cell voltage losses [71–73]. Reducing the overpotential of ORR at the cathode is very critical to improvement of the efficiency of the PEM fuel cell performance [74,75]. The main focus of this paper will be on cathode oxygen reduction catalysis.

2. Pt/C and Pt(M)/C cathodic catalysts of PEMFC

This section gives a general introduction of the carbon-supported Pt or Pt alloys cathodic catalysts in PEMFC, including the Pt or Pt alloys active catalyst layer, carbon support materials and the techniques for the preparation of carbon-supported catalysts.

2.1. Pt and Pt(M) cathodic catalyst layer

Platinum supported on carbon is generally used as electrocatalyst for PEMFC cathodes, having Pt the highest catalytic activity for oxygen reduction reaction (ORR) of any of the pure metals [76]. Alloy catalysts of platinum with various transition metals were employed to improve the catalytic activity and to

reduce the cost. Many approaches have been reported for Pt catalytic activity enhancement towards ORRs in fuel cell applications [77–81]. In particular, the Pt–transition metal alloys have attracted much interest due to their enhanced catalytic activities towards ORR in PEM fuel cell developments. United Technologies Corporation (UTC) reported the first Pt alloying research on ORR catalysis for the phosphoric acid fuel cell in 1980 [78]. Mukerjee and Srinivasan [82] reported Pt alloy catalysts for PEM fuel cells in 1993. In these reports, the carbon-supported Pt/Cr, Pt/Co and Pt/Ni alloy catalysts showed a performance gain of 20–30 mV over Pt at low current density range. From 1995 to 1997, Johnson Matthey investigated carbon-supported Pt alloys (Pt/Fe, Pt/Mn, Pt/Ni, Pt/Ti, Pt/Cr and Pt/Cu) for PEM fuel cells [8,78], demonstrating that Pt/Ti, Pt/Mn and Pt/Fe catalysts could enhance fuel cell performance by 20–40 mV at a practical current density range. Tafel slopes of ca. 60 mV dec⁻¹ were found for Pt alloys, which are similar to that of pure Pt catalysts, suggesting that the ORR mechanisms may not be changed significantly. Recently, ternary Pt alloys together with binary Pt alloys have been developed. Tamizhmani and Capuano [83] reported that a carbon-supported Pt/Cr/Cu ternary alloy showed two times greater activity towards ORR than pure Pt. The mixture of Pt/Cr/Cu alloy with base metal oxides such as copper oxide and chromium oxide could enhance the activity by a factor of 6 compared to a pure Pt catalyst [83]. More recently, Toda et al. employed a sputtering method and successfully prepared the Pt/Ni, Pt/Co and Pt/Fe alloy catalysts [73]. Although the catalytic activities of these Pt alloys were not validated in a real fuel cell operating condition, the claimed increase in maximum activity could be 10, 15, and 20 times higher than a pure Pt catalyst when the Ni, Co and Fe contents in the Pt alloy catalysts were ca. 30, 40 and 50%, respectively. It is obvious that the approach of Pt alloying with non-noble transition metals can create some active alloy catalysts for catalytic activity enhancement towards ORR. However, there are many concerns about the long-term stability of these Pt-alloy catalysts due to the leaching issue of the non-noble metals under the cathode-operating environment [8,77].

2.2. Different forms of carbon supports

Carbon has been used for many years as a support for industrial precious metal catalysts [12], and activated carbon, carbon black, graphite and graphitized materials have all been applied in various catalytic processes [14]. However, in fuel cell area by

far, the application and studies on comparing different forms of carbon support for fuel cell electrocatalysts is quite sparse. Most scientists have tended to stay with just a few well-characterized forms of carbon black, even though it is recognized that the form of carbon can affect the dispersion of the Pt particles [84–87]. Two main types of carbon black have successfully been used as supports for Pt catalysts: oil-furnace blacks and acetylene blacks. Oil-furnace blacks are manufactured from aromatic residue oils from petroleum refineries, while acetylene blacks are made by thermal decomposition of acetylene (ethyne). In general, furnace blacks have surface areas ranging from 20 to 1500 m² g⁻¹, while acetylene blacks typically have areas below 100 m² g⁻¹, but developmental products are now available with areas up to 1000 m² g⁻¹. The common carbon black support materials, together with some properties are listed in Table 1 [88].

Recently, variety of novel carbon materials have been explored as the catalyst supports in PEM fuel cells. The materials in these studies include the modified graphite [89], modified diamond [90], mesoporous carbon materials [91–94], monodispersed hard carbon spherules [95], carbon cryogel [96], and carbon aerogel [97]. The carbon nanomaterials (such as nanotube or nanofiber) are also increasingly becoming proposed as catalyst supports [98–110].

2.3. Techniques for the preparation of Pt/C catalysts

Development of techniques in order to control the size (monodisperse nanoparticles are preferred) and composition of the supported catalyst has been a major area of research. Two main chemical methods are widely used to obtain carbon-supported fuel cell catalysts, impregnation method [111–118] and colloidal method [119–133].

In impregnation method, a solution of metal salt(s) is prepared and mixed with the carbon support. The resulting slurry is dried to remove the solvent and then usually heat-treated and/or reduced to decompose the salt to give the desired form of the catalyst. A variation of this method is incipient-wetness impregnation. Here the volume of the impregnating metal solution is chosen to match the pore volume of the carbon. This method has the advantage that metal is only deposited within the pore structure of the carbon. Colloidal method consists in the preparation of a platinum metal colloid, followed by adsorption on the carbon support, or in the formation of a Pt oxide colloid, followed by simultaneous reduction and adsorption, or adsorption followed by reduction. The development of colloidal methods

Table 1
Carbon blacks that have been used as support for Pt catalysts in PEMFCs [88]

Carbon	Supplier	Type of carbon	BET surface area (m ² g ⁻¹) ^a	DBP adsorption (units) ^b
Vulcan XC72	Cabot Corp.	Furnace black	250	190
Black Pearls 2000	Cabot Corp.	Furnace black	1500	330
Ketjen EC300J	Ketjen Black International	Furnace black	800	360
Ketjen EC600JD	Ketjen Black International	Furnace black	1270	495
Shawinigan	Chevron	Acetylene black	80	–
Denka black	Denka	Acetylene black	65	165

^a BET: Brunauer–Emmett–Teller method.

^b DBP: dibutyl phthalate number (measure of carbon void volume).

to prepare Pt-based fuel cell catalysts has received more attention. In particular, colloidal methods have been used to prepare bimetallic catalysts with narrow particle size distributions and alloy structures [134].

In addition to the impregnation and colloidal methods, many other methods have also been applied to the preparation of carbon-supported fuel cell catalysts, e.g. ion exchange method [135], vapor phase method [136], and recently, microemulsion methods [137–142].

Many fuel cell catalysts used in PEMFC are multi-component systems and alloying the components is necessary to give the maximum benefit. To achieve this with practical catalyst technology requires the use of flexible preparation routes. One straightforward way of preparing a bimetallic catalyst is to impregnate a second component on a preformed catalyst. Specific interactions can be induced by subsequent treatment of the catalyst. Component alloying can be induced by high-temperature heat treatment under either inert or reducing gas streams. This method has the disadvantage of particle sintering, thus lower catalyst active area [143–147]. Other methods involve the co-deposition of soluble metal salts using changes in pH or the addition of reducing agents. This has the advantage of forming bimetallic structures at low temperature and hence, at high dispersion [148]. However, this approach is generally restricted to components with similar precipitation chemistry and/or ease of reduction to metals. As noted above, colloid methods have also been applied to bimetallic catalysts. An alternative method of depositing a second metal on a preformed catalyst is the use of surface organometallic modification. In this approach, an organometallic precursor is reacted in a solvent with a preformed catalyst that has a layer of adsorbed H_2 . This approach has the advantage that the precursor only reacts with adsorbed hydride and therefore is only deposited on active catalyst sites. The technique has been reported to prepare Sn-, Ge-, and Mo-modified Pt catalysts [149–151].

3. Interaction of Pt with carbon support and its influence on the performance of the cathodic catalysts in PEMFC

3.1. Electronic interaction of Pt–carbon support

In a carbon-supported metal–catalyst system, carbon support is not mere inert materials. It alters the system's Galvani potential, raise the electronic density in the catalysts, and lower the Fermi level. These factors accelerate the electron transfer at the electrode–electrolyte interface, thus accelerating the electrode processes. In most cases, electrons are transferred from microdeposits to carbon [152]. In the carbon-supported platinum PEMFC catalyst, the interaction is attributed to the presence of a platinum–support electronic effect. The specific metal–support interaction is through electron transfer from platinum clusters to oxygen atoms of the surface of the support [153]. In many cases, chemical bonds are formed or charge transfer takes place between the contacting phases. The Pt–carbon support interaction is considered to be beneficial to the enhancement of catalytic properties [154] and to improve stability of the electrocatalyst

[155]. Bogotski and Snudkin [156] have attempted to account for the change in electrocatalytic activity due to catalyst support synergism on the basis of changes in the electronic state of Pt when deposited on the carbon support. According to them, the electrical double layer formed between the microdeposit (platinum) and the support is indicated, to a certain extent, by the difference in the electronic work functions of platinum (5.4 eV) and the carbon support (4.7 eV), thereby resulting in an increase of electron density on the platinum. However, the rise in electron density can be significant only if particle size of the microdeposit (platinum) is comparable to the thickness of the double layer. The dependence of particle size to thickness of the double layer had been illustrated by Kobelev et al. [157] who have shown that if the change in electron density is assumed to occur in a layer 0.3 nm thick and the platinum microdeposits are in the shape of a tetrahedron with edge 'a', the ratio of the double layer volume to the volume of the whole microdeposit amounts to 71, 42, 28, and 21% for 'a' equal to 0.6, 1.0, 1.5 and 2.0 nm, respectively. Hence, the particle size of the catalyst metal crystallite does influence the catalyst support interaction or synergism.

In addition to the interaction between the carbon support and Pt, the intra-alloy interaction also occurs in the carbon-supported PtM/C catalyst system. Alloying with other metals causes electronic effects on the Pt and changes the Pt electronic structure, thus affecting the catalysts' activity [158–162]. This interaction is not the main topic of this paper and will not be discussed in detail.

3.2. Study methodologies of Pt–C interaction

Electronic interaction effects between Pt catalyst and the carbon support have been studied by variety of conventional physical, spectroscopic and electrochemical methodologies. Electron-spin resonance (ESR) studies, for example, have demonstrated electron donation by platinum to the carbon support [163]. This is further supported by X-ray photoelectron spectroscopy (XPS) studies [164] showing the metal acting as an electron donor to the support, their interaction depending on the Fermi-level of electrons in both. In XPS studies, the Pt 4f signal has always provided the valuable information. For the carbon-supported pure Pt catalyst, the peak maximum for the Pt 4f_{7/2} shifted to higher values with respect to unsupported platinum due to the platinum–support electronic effects as shown in Fig. 1 [165,166]. There is also a small particle effect [167,168]: particles in the 1–2 nm range have not yet attained the normal bulk band structure, so the binding energy for the particles shifts to higher values, the full width at half maximum of the peak increases, and its intrinsic asymmetry decreases relative to the bulk metal. In carbon-supported PtRu catalyst study, Denis et al. [169] found the Pt 4f signal for unsupported PtRu in the atomic ratio 1:1 slightly shifted towards lower binding energies with respect to unsupported platinum. A work of Shukla et al. [170] on PtRu/C revealed no difference of Pt 4f_{7/2} peak with respect to pure Pt/C. A more recent work [171], instead, revealed a further shift to higher energy values for the Pt 4f_{7/2} of PtRu/C by 0.2–0.3 eV with respect to pure Pt/C. This further shift for PtRu/C was attributed to stronger platinum–support

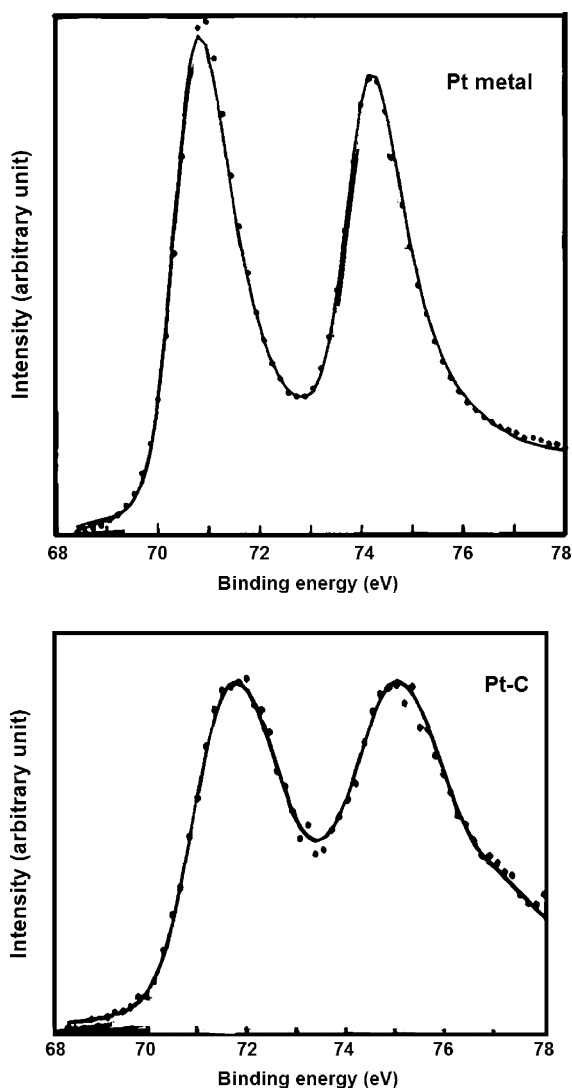


Fig. 1. Pt 4f X-ray photoelectron spectra of Pt metal and Pt/C catalyst [165].

interactions or small particle effect. The presence of Ru precursors and their decomposition could influence the acid–base properties of the carbon support. This effect should produce a strong metal–support interaction, which affects the electronic nature of the platinum sites. Goodenough and Manoharan [172] combined XPS, EXAFS and ESR measurements on carbon-supported PtRu, to conclude that synergistic catalytic effects result from an intra-alloy electron transfer from Ru to Pt. Pt XANES at 0.0, 0.24 and 0.54 V at the respective Pt L3 and L2 edge, performed by McBreen and Mukerjee [173] on Pt, Pt/C and PtRu/C catalysts, indicated that alloying with Ru causes electronic effect on the Pt. The calculated Pt d band vacancies in the double-layer region (0.54 V) were 0.397, compared with a value of 0.329 for a Pt/C catalyst. So, alloying with Ru causes an increase in the number of Pt d band vacancies. EXAFS analysis indicated a decrease in the Pt–Pt nearest-neighbor distance (2.72 Å) of PtRu/C with respect to Pt/C catalyst (2.77 Å). Also the Pt–Pt distance can be used to evaluate the degree of alloying.

From the discussion above, in the electronic interaction studies of the Pt/C catalysts, there are two different viewpoints on

the electron transfer between Pt and the carbon support. In most cases [152,153,163–168], electrons are proved to transfer from Pt microdeposits to carbon. However, according to the results of Bogotski and Snudkin [156], the electron density on the platinum is increased due to catalyst support synergism. More efforts need to be accomplished to further understand the mechanism of the electronic interaction between Pt and carbon support.

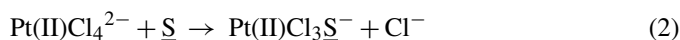
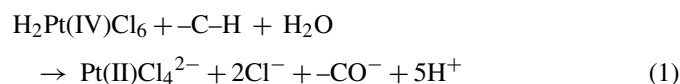
3.3. Effect of Pt–C interaction on the catalyst performance

Electronic structure change of platinum catalytic layer by the presence interaction between the platinum active phase and the carbon support phase leads to the change of the catalyst properties. Generally, this electronic interaction has the positive effects towards the enhancement of catalytic properties, and the improvement of the catalysts' stability. In fuel cell catalyst studies, it was found that metal–carbon support interactions do influence the oxidation of both CO and methanol [65,85]. However, the quantitative correlation between the metal–carbon support interaction and the oxygen reduction reaction (ORR) activity at the cathode was not yet established.

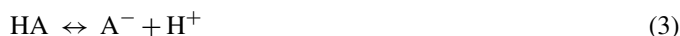
4. Interaction of Pt precursor with carbon support during Pt/C catalyst formation and the effects of carbon surface functional groups

4.1. Interaction models of Pt precursor with carbon support

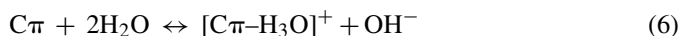
H_2PtCl_6 (in acid media) and $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ (in basic media) are always the precursor for Pt/C catalyst formation. In the impregnation catalyst formation method, Pt reduction during the impregnation step was observed by several authors [113–115]. According to De Miguel et al. [116], the interaction of H_2PtCl_6 with the carbon implies a redox process in which after impregnation and drying the metal complex is stabilized as Pt^{2+} on the carbon surface. As van dam and van Bekkum showed [114], a simple electrostatic mechanism cannot explain the adsorption process of H_2PtCl_6 on the different carbon supports. They proposed a model to describe the chemistry of the impregnation of hexachloroplatinic acid on carbon. First, carbon reduces the Pt(IV) complex to a Pt(II) complex, which is then coordinatively bound to the carrier, as:



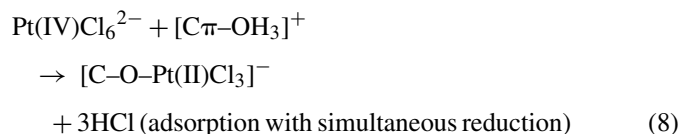
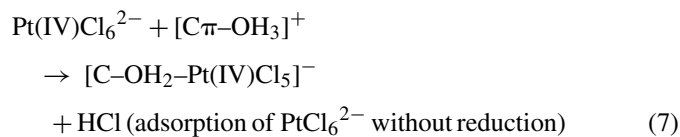
The ligand site S is assumed to be either a π -complex structure or an oxygen surface group. A model for an oxidized carbon surface would be based on independent acid and basic groups, which ionize according to the following equilibria:



where A and B denote sites of the carbon solid matrix or surface oxygen groups [174]. Thus, the combination of the model of van dam and van Bekkum with the model for the ionisation behaviour of the carbon surface based on independent acid and basic groups leads to the conclusion that the acid oxygen surface groups should be considered as weak anchoring sites. On this basis, carbon surface basic sites act as anchoring sites for the hexachloroplatinic anion and are responsible for the strong adsorption of platinum on carbon. The carbon surface basic sites are frequently associated with pyrone-like structure. Such structures which have a $pK_b > 11$ and which decompose thermally at 777–927 °C, generating CO [175,176], would present a strong electronic interaction with the surface carboxyl groups, which leads to their destruction by surface oxidation [175]. According to other authors [177–179], the surface basic sites are essentially of Lewis type and are associated with π -electron rich regions within the basal planes. According to Leon et al. [179], the protonation of such oxygen-free basic carbon sites would lead to an electron–donor–acceptor complex, as the following:



where $C\pi$ is probably a graphitized carbon surface platelet in which single π electron pairs may become partially localized as a result of the H_3O^+ addition. Lambert and Che [180] proposed an alternative formulation of the model for the strong adsorption of $PtCl_6^{2-}$, using the mechanism of inner-sphere adsorption, as described:



According to this model, surface groups would replace some of the original ligands (Cl^-) of the transition metal in solution. In the case of Eq. (7), an insertion of a water ligand takes place, while for that regarding Eq. (8) a C–O–Pt linkage would be formed. Being $C\pi-OH_3^+$ one of the basic surface groups of carbon, as shown in Eqs. (5) and (6), Eqs. (7) and (8) should not be taken as stoichiometric ones.

4.2. Investigation methods of carbon–Pt precursor interaction

X-ray photoelectron spectroscopy (XPS) was an effective way to probe the valent state change of Pt precursor under the interaction with carbon support. Early studies [113] indicated that after impregnation of carbon with H_2PtCl_6 and subsequent drying in air, the platinum was present as Pt^0 and Pt^{2+} . Van dam and Van Bekkum [114] showed that upon impregnation into activated carbon, H_2PtCl_6 is partly converted into a Pt^{2+}

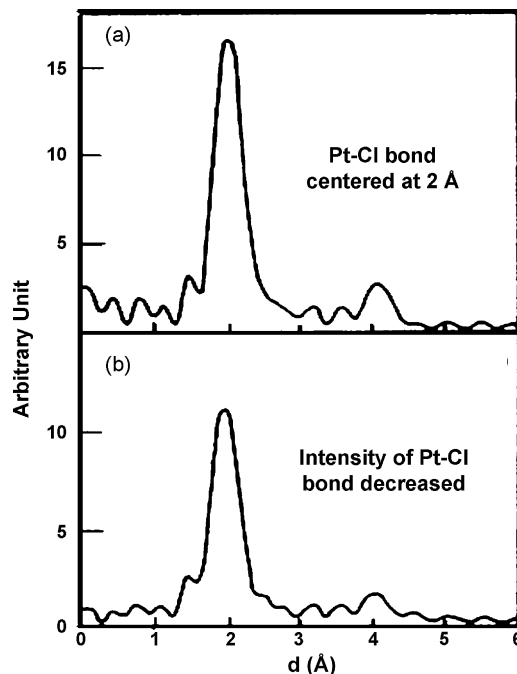


Fig. 2. EXAFS measurements of (a) H_2PtCl_6 and (b) Pt/C after impregnation step. The formation of Pt–O bonds (b) decreases the intensity of the Pt–Cl signal [116].

complex. The presence of divalent platinum in the catalyst after impregnation was observed also by Coloma et al. [115]. The amount of surface oxygen groups on carbon support has always been analyzed by temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) through the amount of CO or CO_2 evolving. Fourier transform extended X-ray absorption fine structure (FT-EXAFS) has been used to analyze the interaction of carbon and the Pt precursor, and indicated that for some Pt/C catalysts prepared by impregnation with H_2PtCl_6 the strong interaction between the Pt precursor and the support is associated with a change in the Pt coordination from Cl to O atoms (Fig. 2) [116,181].

5. Catalyst activity enhancement through proper surface treatment of carbon support

5.1. Effect of oxidative treatment of carbon

Surface oxygen functional groups on carbon materials are responsible both for the acid/base and the redox properties of the carbon [182], and are of great interest in the preparation of carbon-supported catalysts. The precise nature of carbon–oxygen structures is not entirely established. Some common types of oxygen functionals (e.g. carboxylic groups, phenolic groups, lactonic groups, etheric groups) are shown in Fig. 3.

The oxidative treatment of the carbon surface gives rise to the formation of surface acidic sites and to the destruction of surface basic sites. This treatment of carbon can be performed through chemical methods by different oxidants: HNO_3 , H_2SO_4 , H_3PO_4 , H_2O_2 , O_2 or O_3 , K_2ClO_3 , $KMnO_4$, etc. The effect

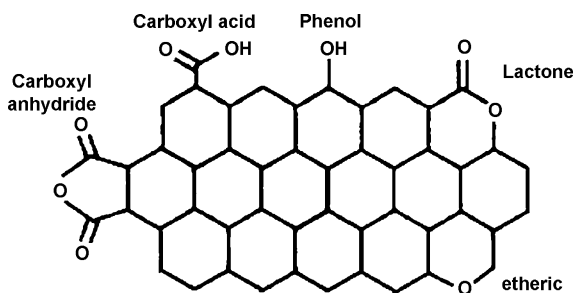


Fig. 3. Various types of surface oxygen functional groups on carbon.

of surface oxygen functional groups on platinum dispersion in carbon-supported catalyst has been extensively studied. One example for this study is provided here: Prado-Burguete et al. [183,184] examined and clarified the effect of oxygen surface groups on the dispersion and sintering of Pt/C catalysts. They used a high surface area carbon black, which was heat treated in hydrogen at 950 °C to reduce the oxygen surface groups to a minimum, and then oxidized it with solutions of H₂O₂. In this way, several supports with the same porosity but different proportion of oxygen surface groups were available. By maintaining all preparation variables fixed for all catalysts it was possible to analyze the effect of the oxygen surface groups. These authors concluded that the acidic groups (evolving as CO₂ upon temperature-programmed desorption (TPD) at relatively low temperature) introduced by treatment with H₂O₂, decreased the hydrophobicity of the carbon thus making the surface more accessible to the aqueous solution of the metal precursor. Fig. 4 shows that platinum dispersion increases with increasing amount of oxygen surface groups and this in turn shows that the oxygen surface groups of the carbon support play a major role in the final metal dispersion since all supports have the same porosity and the catalyst were prepared using the same experimental procedure [183]. Furthermore, the less acidic oxygen groups introduced (evolving as CO at high temperature upon TPD) increased the interaction of the metal precursor or the metal particle with the support and thus minimized the sintering propensity of the Pt/C catalysts. The more stable oxygen surface groups are more effective for the anchorage of platinum particles, thus enhancing the thermal stability of the platinum particles supported.

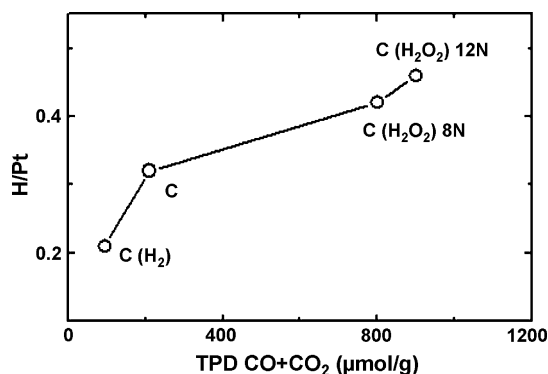


Fig. 4. Relationship between Pt dispersion and amount of oxygen surface groups (evolved as CO, and CO upon TPD) of the carbon support [183].

In most literatures [116,117,183,185], the dispersion increases with increasing the number of oxygen surface groups in the support. Torres et al. [117] showed that the effect of the different oxidants could be related to the nature of the functional groups on the carbon surface. HNO₃-treated carbon displays a high density of both strong and weak acid sites, while H₂O₂- and O₃-treated carbons show an important concentration of weak acid sites but a low concentration of strong acid sites. The H₂PtCl₆ isotherms in liquid phase at 25 °C showed a stronger interaction of the metallic precursor with the carbon of low acidity (like those treated with H₂O₂ or O₃) than with the most acidic carbon (treated with HNO₃). Carbons functionalised with weak oxidants, which develop acidic sites with moderate strength and show strong interaction with H₂PtCl₆ during impregnation, would favor the Pt dispersion on the carbon surface. According to Sepulveda-Escribano et al. [186], the presence of oxygen surface groups in the support favors the anchoring of [Pt(NH₃)₄]²⁺, but does not affect the amount of platinum retained by the support when H₂PtCl₆ is used as metal precursor. They also showed that the oxidized support hinders the reduction of the Pt precursor. Rodriguez-Reinoso summarized the interactions taking place between the sites on the carbon surface and the metal cation or anion, and indicated that maximum catalyst dispersion and resistance to sintering can be obtained by either: (i) oxidation of the carbon typically renders the carbon surface more acidic and thus negatively charged over a wide range of pH; this in turn results in electrostatic repulsion of the PtCl₆²⁻ anions and will favor electrostatic attraction of the [Pt(NH₃)₄]²⁺ cations, maximizing catalyst dispersion; (ii) increasing the basic Cπ sites on the basal plane surface of oxygen-free carbon will maximize the electrostatic attraction with the metal anion (e.g. Cπ-H₃O⁺-PtCl₆²⁻) and also will minimize the electrostatic repulsion (e.g. COO⁻PtCl₆²⁻), thus increasing the dispersion; and (iii) C=O groups acting as anchoring centers hinder agglomeration and surface diffusion of catalyst particles across the graphene layers [14].

An important point to be taken into account is that some oxygen surface groups may not be stable under the reduction conditions to which the catalysts are subjected to obtain the active phase, and their decomposition would favor the sintering of the metal species. Also, oxygen surface groups may influence other kinds of centers on the carbon surface. In this way the strength of the π sites may be diminished by the presence of oxygen groups, due to the electron-withdrawing effect exerted by the oxygen atom. Coloma et al. studied this effect [115], and the results indicate that the carbon-platinum precursor interaction is favored by the presence of oxygen surface groups, which make the carbon surface more hydrophilic, and thus, a better dispersion of the platinum precursor is achieved. However, after reduction in hydrogen at a high temperature, the main part of the less stable oxygen surface groups are decomposed, and those remaining affect the electron delocalization in the π sites, weakening their capability to act as anchoring centers. As a result of this a better platinum dispersion and an improved resistance to sintering are obtained when the pregraphitized carbon black support is free of oxygen surface groups. There are also some contradictory results about the effect of oxidative pre-treatment

of the carbon on platinum dispersion in literature data. Some authors [181,187,188], instead, reported that the presence of oxygen surface groups on carbon decreases the metal dispersion. Microcalorimetric measurements of CO adsorption performed by Guerriero-Ruiz et al. [188] evidenced that the presence of oxygen surface groups diminishes the metal–support interaction. According to the authors, the decrease in the dispersion with the increase in the total surface oxygen is due to the reduction of the number of surface basic sites, which are centers for the strong adsorption of PtCl_6^{2-} .

5.2. Effect of thermal treatment

Thermal treatment carbon blacks have been studied as catalyst support for platinum [189]. When a high surface area carbon black is subjected to heat treatment in an inert atmosphere at temperatures ranging from 1600 to 2200 °C there is not only a decrease in surface area, but also an increase in crystalline ordering and crystallite size. Furthermore, there is an increase in the basicity of the carbon, which cannot be explained by basic groups. The basicity of the carbon surface is explained in terms of the π sites of the carbon basal plane, which upon interaction with water lead to Eqs. (5) and (6). During the Pt/C catalyst formation, it is proved that the greater the difference between the pH of the impregnating solution and the isoelectric point of the carbon, the better the interaction between the surface and the anionic precursor will be. Furthermore, there is an increase in the resistance to sintering of the platinum crystallites with increasing degree of pregraphitization of the supports [189], because the interaction of the platinum particles with the support increases. This increasing metal–support interaction is related to the increasing strength of the π sites on the support upon pregraphitization, which act as anchoring centers for platinum. Recently, Cerro-Alarcon et al. indicate that thermal treatment of carbon black in N_2 atmosphere affects the distribution of the metal precursor over the support, and subsequently, the final dispersion of the metal particles [190].

5.3. Other novel surface treatment methods

In addition to the commonly studied surface oxidation treatment, recently, there have been some novel carbon surface treatment studies towards the improvement of Pt/C catalyst properties in PEMFC. These methods are summarized in Table 2.

As to using graphite as the catalyst support, relatively low surface area together with random and inert surface crystalline

orientations can limit Pt dispersion on the graphite surface as well as the adherence [195]. Therefore, surface treatment of graphite to form the functional groups is more of importance for the formation and properties of Pt/C catalyst. Novel surface treatment methods listed in Table 2 improved the electronic interaction between the Pt catalyst layer and carbon support, and subsequently, enhanced the electrocatalytic activity of the Pt/C catalyst.

5.4. Surface treatment of carbon nanotube (CNT) and nanofiber (CNF), and its effect on the property of Pt/CNT catalyst

Under the driving force of PEM fuel cell cost reduction and performance optimization, carbon nanotubes (CNTs) and nanofibers (CNFs), as the novel catalyst supports for increasing Pt utilization, have drawn a great deal of attention due to their unique surface structure, high electric conductivity and large surface areas. The main purposes for using CNT- and CNF-supported Pt catalysts are to reduce Pt loading through increasing the catalyst utilization, and improving the catalyst activity/performance. However, since CNT and CNF are relatively inert, it is necessary to modify the nature and concentration of surface functional groups in order to deposit Pt particles on their surface [196,197]. Therefore, their pretreatment process and Pt deposition methods could affect the Pt catalyst dispersion and catalytic activity for fuel cell reactions.

Surface treatment methodologies of CNT/CNF introduced in recent literatures are similar to that for the treatment of regular carbon materials, mainly on the chemical oxidation method [198–200]. Effect of oxidative pretreatment of CNT studied by Rajalakshmi et al. (chemical oxidation treatment with 70% HNO_3 at 110 °C) [198], Matsumoto et al. (chemical oxidation treatment with 14N HNO_3 at 423 K) [199] and Li and Hsing (chemical oxidation treatment with 70% HNO_3 at 90 °C, or 1:1 $\text{HNO}_3/\text{H}_2\text{SO}_4$ at 90 °C) [200] revealed that the electrocatalytic activity for ORR of Pt/CNT cathodic catalyst was enhanced by the presence of oxidation groups on CNT surface form by such chemical treatments (Fig. 5).

5.5. Sulfonation and phosphonation of carbon-supported catalysts

Instead of building a surface group on carbon materials prior to the formation of Pt/C catalyst, the chemical link between carbon support and Pt can also be developed for a ‘formed’

Table 2
Some novel surface treatment methods for carbon supports and their effects on the ORR at the Pt/C cathodic catalyst in PEMFC

Surface treatment	Carbon materials	Effect on catalyst activity	Reference
Chemical treatment with a tin–palladium chloride solution	Graphite	Pt dispersion and electrocatalytic activity is increased	[191]
C_2F_6 radio frequency plasma treatment	Carbon black	Catalytic activity of Pt/C for ORR is enhanced by the presence of CF_3 group	[192]
Chemical treatment with basic (NaOH), neutral (C_6H_6) agent	Carbon black	Electrocatalytic activity for ORR is enhanced	[193]
Intercalation of CuCl_2 and PdCl_2	Graphite	Catalytic activity for ORR is enormously improved when CuCl_2 is used as intercalate	[194]

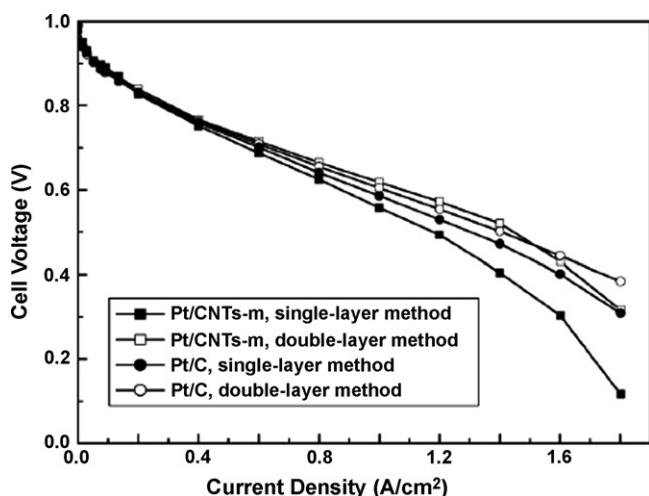
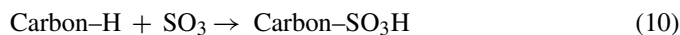
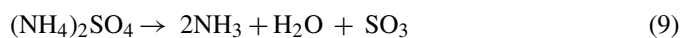


Fig. 5. Comparison of H_2O_2 fuel cell performance with Pt/CNTs-m and Pt/C cathode; operating condition: 70°C and 3 atm; anode Pt loading: 0.4 mg cm^{-2} (20 wt.% Pt/C, E-TEK); cathode Pt loading: 0.4 mg cm^{-2} . Pt/CNTs-m: CNT was treated with a mixture of sulfuric and nitric acids (1:1, v/v, 98% and 70%) prior to the Pt deposition [200].

Pt/C catalyst to improve the Pt–C interaction. This work has been reported by Xu et al. recently [201–203]. In their initial studies, Xu et al. chemically linked short chain sulfonic or phosphonic acid groups onto carbon-supported catalysts through diazonium salts formed by reacting 2-aminoethanesulfonic or 2-aminoethanephosphonic acid with isobutyl nitrite, and the resulting sulfonated catalysts showed much better performance than the untreated counterparts and less Nafion was required within the catalyst layers [201,202]. An easier and more effective sulfonation method has also been developed by them. In this new method, carbon-supported catalysts were sulfonated by decomposing $(\text{NH}_4)_2\text{SO}_4$ in the presence of the catalysts in two steps. First, $(\text{NH}_4)_2\text{SO}_4$ solution was mixed with a proper amount of catalyst based on a predetermined weight percentage of $(\text{NH}_4)_2\text{SO}_4$. Second, after the mixture was well agitated, it was heated at 235°C for 30 min. It is believed that at 235°C , $(\text{NH}_4)_2\text{SO}_4$ decomposes according to Eq. (9). Then the formed SO_3 reacts with carbon via its surface hydrogen atoms to have

– SO_3H groups linked onto it according to the following equation:



Electrodes made using such sulfonated catalysts need less Nafion in the catalyst layer and perform much better than those made using the unsulfonated counterpart (Fig. 6) [203].

6. Summaries

Carbon-supported Pt catalyst is a two-solid joining system. Interaction between the carbon support and the Pt plays an important role in the properties of the Pt/C catalyst. It has been demonstrated that this interaction is attributed to the electron transferring from platinum to carbon support. Electronic structure change of platinum catalytic layer by the presence of interaction leads to the change of the catalyst properties. Generally, this electronic interaction has the positive effects towards the enhancement of catalytic properties, and the improvement of the catalysts' stability in PEMFC operation.

During Pt/C catalyst formation, interaction of the Pt precursor with the carbon support is crucial and affects the Pt particle size, dispersion, adhesion properties. Surface functional groups on carbon materials play the major role in the Pt precursor–carbon interaction. Surface oxygen functional groups (SOFGs) are the most widely studied ones and can be formed by variety of oxidation treatment of carbon materials. In the procedure of Pt/C catalyst formation, the carbon–platinum precursor interaction is favored by the presence of the oxygen surface groups, which make the carbon surface more hydrophilic, and thus, a better dispersion of the platinum precursor is achieved. Also the interaction of the Pt precursor with the carbon of low acidic SOFGs is stronger than that with the carbon of high acidic SOFGs and would favor the Pt dispersion on the carbon surface. However, some oxygen surface groups may not be stable under the reduction conditions during catalyst formation, and their decomposition would cause a negative effect on catalysts.

In addition to the formation of SOFGs by oxidation treatment, novel recently developed carbon surface treatment methods towards the improvement of Pt/C catalyst properties in PEMFC are summarized. These novel methods including (i) chemical treatment with tin–palladium chloride solution, basic (NaOH), neutral (C_6H_6) agent; (ii) C_2F_6 radio frequency plasma treatment and (iii) intercalation of CuCl_2 and PdCl_2 in graphite, improved the electronic interaction between the Pt catalyst layer and carbon support, and subsequently, enhanced the electrocatalytic activity of the Pt/C catalyst.

Carbon nanotube (CNT) is novel support material for Pt catalyst in PEMFC. Due to its inert character, surface modification of CNT is necessary to develop the surface functional groups in order to deposit Pt particles on their surface. Surface treatment methodologies of CNT introduced in recent literatures are mainly on the chemical oxidation method. The results revealed

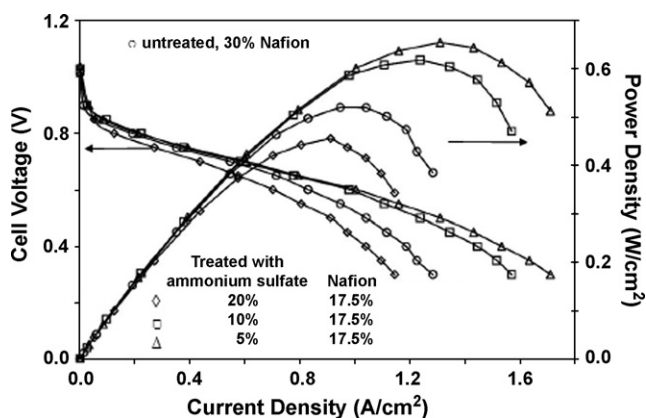


Fig. 6. Activity enhancement of Pt/C catalyst by sulfonation method. V – I curves for catalysts treated with 0, 5, 10, and 20% $(\text{NH}_4)_2\text{SO}_4$. Cell temperature, 35°C ; Pt loading, 0.3 mg cm^{-2} [203].

that in a PEMFC system, the electrocatalytic activity of Pt/CNT catalyst was enhanced by the presence of oxidation groups on CNT surface.

Interaction between carbon support and Pt can also be improved by developing a chemical link for a 'formed' Pt/C catalyst. Sulfonic acid groups and phosphonic acid groups have been successfully linked onto carbon particles supporting a catalyst by chemical methods. Electrodes made using such sulfonated or phosphonated catalysts need less Nafion in the catalyst layer and perform much better than those made using the unsulfonated counterpart in PEMFC.

References

- [1] P. Costamagna, S. Srinivasan, *J. Power Sources* 102 (2001) 242.
- [2] P. Costamagna, S. Srinivasan, *J. Power Sources* 102 (2001) 253.
- [3] K. Sopian, W.R. Wan Daud, *Renew. Energy* 31 (2006) 719.
- [4] L. Zhang, J. Zhang, D. Wilkinson, H. Wang, *J. Power Sources* 156 (2006) 171.
- [5] H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang, D. Wilkinson, *J. Power Sources* 155 (2006) 95.
- [6] J. Wee, K. Lee, S. Kim, *J. Power Sources* 165 (2007) 667.
- [7] N. Sato, *Oyo Buturi* 72 (2003) 857.
- [8] H. Gasteiger, S. Kocha, B. Sompalli, F. Wagner, *Appl. Catal. B: Environ.* 56 (2005) 9.
- [9] N.P. Brandon, S. Skinner, B.C.H. Steele, *Annu. Rev. Mater. Res.* 33 (2003) 183.
- [10] DOE FY 2002 & 2004 Annual Progress Reports.
- [11] E. Antolini, *J. Mater. Sci.* 38 (2003) 2995.
- [12] E. Auer, A. Freund, J. Pietsch, T. Tacke, *Appl. Catal. A: Gen.* 173 (1998) 259.
- [13] S. Litster, G. Mclean, *J. Power Sources* 130 (2004) 61.
- [14] F. Rodriguez-Reinoso, *Carbon* 36 (1998) 159.
- [15] E. Antolini, *Mater. Chem. Phys.* 78 (2003) 563.
- [16] A.S. Arico, S. Srinivasan, V. Antonucci, *Fuel Cells* 2 (2001) 133.
- [17] Y. Takasu, T. Kawaguchi, W. Sugimoto, Y. Murakami, *Electrochim. Acta* 48 (2003) 3861.
- [18] M. Uchida, Y. Fukuoka, Y. Sugawara, H. Ohara, A. Ohta, *J. Electrochem. Soc.* 145 (1998) 3708.
- [19] M.L. Anderson, R.M. Stroud, D.R. Rolison, *Nano Lett.* 2 (2002) 235.
- [20] G. Park, T. Yang, Y. Yoon, W. Lee, C. Kim, *Int. J. Hydrogen Energy* 28 (2003) 645.
- [21] M. Mastragostino, A. Mossioli, F. Soavi, *J. Electrochem. Soc.* 151 (2004) 1919.
- [22] V. Rao, P.A. Simonov, E.R. Savinova, G.V. Plaksin, S. Cherepanova, G. Kryukova, U. Stimming, *J. Power Sources* 145 (2005) 178.
- [23] Z. Wang, G. Yin, P. Shi, *Carbon* 44 (2005) 133.
- [24] Z. Liu, X. Lin, J.Y. Lee, W.S. Zhang, M. Han, L.M. Gan, *Langmuir* 18 (2002) 4054.
- [25] C. Wang, M. Waje, X. Wang, J.M. Tang, R.C. Haddon, Y. Yan, *Nano Lett.* 4 (2004) 345.
- [26] T. Matsumoto, T. Komatsu, K. Arai, T. Yamazaki, M. Kijima, H. Shimizu, Y. Takasawa, J. Nakamura, *Chem. Commun.* (2004) 840.
- [27] H. Tang, J.H. Chen, Z.P. Huang, D.Z. Wang, Z.F. Ren, L.H. Nie, Y.F. Kuang, S.Z. Yao, *Carbon* 42 (2004) 191.
- [28] W. Li, C. Liang, J. Qiu, W. Zhou, H. Han, Z. Wei, G. Sun, Q. Xin, *Carbon* 40 (2002) 791.
- [29] W. Li, C. Liang, J. Qiu, W. Zhou, A. Zhou, Z. Wei, G. Sun, Q. Xin, *J. Phys. Chem. B* 107 (2003) 6292.
- [30] W. Li, C. Liang, W. Zhou, J. Qiu, H. Li, G. Sun, Q. Xin, *Carbon* 42 (2004) 436.
- [31] G. Che, B.B. Lakshmi, C.R. Martin, E.R. Fisher, *Langmuir* 15 (1999) 750.
- [32] B. Rajesh, V. Karthik, S. Karthikeyan, K.R. Thampi, J.M. Bonard, B. Viswanathan, *Fuel* 81 (2002) 2177.
- [33] B. Rajesh, K.R. Thampi, J.M. Bonard, N.X. Xanthopoulos, H.J. Mathieu, B. Viswanathan, *J. Phys. Chem. B* 107 (2003) 2701.
- [34] G. Girishkumar, K. Vinodgopal, P. Kamat, *J. Phys. Chem. B* 108 (2004) 19960.
- [35] R.H. Baughman, A.A. Zakhidov, W.A. de Heer, *Science* 297 (2002) 787.
- [36] Z. Liu, J.Y. Lee, W. Chen, M. Han, L.M. Gan, *Langmuir* 20 (2004) 181.
- [37] Z. He, J. Chen, D. Liu, H. Tang, W. Deng, Y. Kuang, *Mater. Chem. Phys.* 85 (2004) 396.
- [38] Y. Lin, X. Cui, C. Yen, C.M. Wai, *J. Phys. Chem. B* 109 (2004) 14410.
- [39] R. Louh, H. Huang, F. Tsai, *Trans. ASME* 4 (2007) 72.
- [40] H.I. Han, J.S. Lee, S.O. Park, S.W. Lee, Y.W. Park, H. Kim, *Electrochim. Acta* 50 (2004) 791.
- [41] X. Sun, R. Li, B. Stansfield, J. Dodelet, S. Desilets, *Chem. Phys. Lett.* 394 (2004) 266.
- [42] X. Sun, R. Li, B. Stansfield, J.P. Dodelet, S. Desilets, *Int. J. Nanosci.* 1 (2002) 223.
- [43] C.A. Bessel, K. Laubernds, N.M. Rodriguez, R.T.K. Baker, *J. Phys. Chem.* 105 (2001) 1115.
- [44] E.S. Steigerwalt, G.A. Deluga, D.E. Cliffel, C.M. Lukehart, *J. Phys. Chem.* 105 (2001) 8097.
- [45] E.S. Steigerwalt, G.A. Deluga, C.M. Lukehart, *J. Phys. Chem.* 106 (2002) 760.
- [46] T. Heon, S. Han, Y. Sung, K. Park, Y. Kim, *Angew. Chem. Int. Ed.* 42 (2003) 4352.
- [47] K. Park, Y. Sung, S. Han, Y. Yun, T. Hyeon, *J. Phys. Chem.* 108 (2004) 939.
- [48] K. Vinodgopal, M. Haria, D. Meisel, P. Kamat, *Nano Lett.* 4 (2004) 415.
- [49] K.Y. Chan, J. Ding, J. Ren, S. Cheng, K.Y. Tsang, *J. Mater. Chem.* 14 (2004) 505.
- [50] J.S. Yu, S. Kang, S.B. Yoon, G. Chai, *J. Am. Chem. Soc.* 124 (2002) 9382.
- [51] G. Chai, S. Yoon, J. Yu, J. Choi, Y. Sung, *J. Phys. Chem. B* 108 (2004) 7074.
- [52] V. Raghuvver, A. Manthiram, *Electrochem. Solid-State Lett.* 7 (2004) 336.
- [53] V. Raghuvver, A. Manthiram, *J. Electrochem. Soc.* 152 (2005) 1504.
- [54] G.S. Chai, S.B. Yoon, J.H. Kim, J.S. Yu, *Chem. Commun.* (2004) 2766.
- [55] Y.C. Liu, X.P. Qiu, Y.Q. Huang, W.T. Zhu, *J. Power Sources* 111 (2002) 160.
- [56] Y.C. Liu, X.P. Qiu, Y.Q. Huang, W.T. Zhu, *Carbon* 40 (2002) 2375.
- [57] K. Lee, J. Zhang, H. Wang, D. Wilkinson, *J. Appl. Electrochem.* 36 (2006) 507.
- [58] H. Suzuki, M. Shintaku, T. Sato, M. Tamano, T. Matsuura, M. Hori, C. Kaito, *Jpn. J. Appl. Phys.* 44 (2005) L610.
- [59] S. Mukerjee, *J. Appl. Electrochem.* 20 (1990) 537.
- [60] O. Antoine, Y. Bultel, R. Durand, P. Ozil, *Electrochim. Acta* 43 (1998) 3681.
- [61] T. Hottinen, O. Himanen, P. Lund, *J. Power Sources* 138 (2004) 205.
- [62] Y. Verde, G. Alonso, V. Ramos, H. Zhang, A. Jacobson, A. Keer, *Appl. Catal. A: Gen.* 277 (2004) 201.
- [63] M. Chisaka, H. Daiguji, *Electrochim. Acta* 51 (2006) 4828.
- [64] L. Zhang, K. Lee, J. Zhang, *Electrochim. Acta* 52 (2007) 3088.
- [65] A. Dicks, *J. Power Sources* 156 (2006) 128.
- [66] P. Kim, H. Kim, J. Joo, W. Kim, I. Song, J. Yi, *J. Power Sources* 145 (2005) 139.
- [67] S. Hall, V. Subramaniana, G. Teeterb, B. Rambabu, *Solid State Ionics* 175 (2004) 809.
- [68] K. Kong, Y. Choi, B. Ryu, J. Lee, H. Chang, *Mater. Sci. Eng. C* 26 (2006) 1207.
- [69] K. Kinoshita, *Electrochemical Oxygen Technology*, John Wiley & Sons, New York, 1992, p. 19.
- [70] K. Kordesch, G. Simader, *Fuel Cells and Their Applications*, VCH, New York, 1996, pp. 3–93.
- [71] M. Arita, *Fuel Cells* 2 (2002) 10.
- [72] D.M. Bernardi, M.W. Verbrugge, *J. Electrochem. Soc.* 139 (1992) 2477.
- [73] T. Toda, H. Igarashi, H. Uchiada, M. Watanabe, *J. Electrochem. Soc.* 146 (1999) 3750.
- [74] R. Hiesgen, D. Eberhardt, E. Aleksandrova, K. Friedrich, *Fuel Cells* 6 (2006) 425.

- [75] T. Ralph, M. Hogarth, *Platinum Met. Rev.* 46 (2002) 3.
- [76] A.J. Appleby, in: R. Dudley, W. O'Grady, S. Srinivasan (Eds.), *The Electrochemical Society Softbound Proceedings Series, PV 79-2*, Princeton, NJ, 1979, p. 23.
- [77] G. Liu, H. Zhang, Y. Zhai, Y. Zhang, D. Xu, Z. Shao, *Electrochem. Commun.* 9 (2007) 135.
- [78] D. Thompsett, in: W. Vielstich, H.A. Gasteiger (Eds.), *Handbook of Fuel Cells—Fundamentals, Technology and Applications*, vol. III, John Wiley & Sons, New York, 2003, pp. 467–480.
- [79] O. Savadogo, P. Beck, *J. Electrochem. Soc.* 143 (1996) 3842.
- [80] J. Shim, C. Lee, H. Lee, J. Lee, E. Cairns, *J. Power Sources* 102 (2001) 172.
- [81] K. Ota, A. Ishihara, S. Mitsushima, K. Lee, Y. Suzuki, N. Horibe, T. Nakagawa, N. Kamiya, *J. New Mater. Electrochem. Syst.* 8 (2005) 25.
- [82] S. Mukerjee, S. Srinivasan, *J. Electroanal. Chem.* 357 (1993) 201.
- [83] G. Tamizhmani, G.A. Capuano, *J. Electrochem. Soc.* 141 (1994) 968.
- [84] T.R. Ralph, M.P. Hogarth, *Platinum Met. Rev.* 46 (2002) 117.
- [85] M. Kim, J. Park, H. Kim, S. Song, W. Lee, *J. Power Sources* 163 (2006) 93.
- [86] T. Van Nguyen, S. Wiley, M.V. Nguyen, *American Institute of Chemical Engineering Spring National Meeting*, New Orleans, LA, United States, 2002.
- [87] S. Hall, V. Subramanian, G. Teeter, B. Rambabu, *Solid State Ionics* 175 (2004) 809.
- [88] G. Hoogers, *Fuel Cell Technology Handbook*, CRC Press, Boca Raton, FL, 2003 (Chapter VI).
- [89] H. He, J. Klinowski, M. Forster, A. Lerf, *Chem. Phys. Lett.* 287 (1998) 53.
- [90] G. Salazar-Banda, K. Eguiluz, L. Avaca, *Electrochem. Commun.* 9 (2007) 59.
- [91] J. Ding, K. Chan, J. Ren, F. Xiao, *Electrochim. Acta* 50 (2005) 3131.
- [92] S. Joo, C. Pak, D. You, S. Lee, H. Lee, J. Kim, H. Chang, D. Seung, *Electrochim. Acta* 52 (2006) 1618.
- [93] S. Chen, X. Zhang, P. Shen, *Electrochem. Commun.* 8 (2006) 713.
- [94] J. Joo, P. Kim, W. Kim, J. Kim, J. Yi, *Catal. Today* 111 (2006) 171.
- [95] R. Yang, X. Qiu, H. Zhang, J. Li, W. Zhu, Z. Wang, X. Huang, L. Chen, *Carbon* 43 (2005) 11.
- [96] B.M. Babic, L.M. Vracar, V. Radmilovic, N.V. Krstajic, *Electrochim. Acta* 51 (2006) 3820.
- [97] A. Smirnova, X. Dong, H. Hara, A. Vasiliev, N. Sammes, *Int. J. Hydrogen Energy* 30 (2005) 149.
- [98] C. Li, Z. Yu, K. Yao, S. Ji, J. Liang, *J. Mol. Catal. A* 226 (2005) 101.
- [99] Y. Liu, B. Yi, Z. Shao, L. Wang, D. Xing, H. Zhang, *J. Power Sources* 163 (2007) 807.
- [100] Y. Xing, *J. Phys. Chem. B* 108 (2004) 19255.
- [101] X. Wang, W. Li, Z. Chen, M. Waje, Y. Yan, *J. Power Sources* 158 (2006) 154.
- [102] Z. Liu, L.M. Gan, L. Hong, W. Chen, J.Y. Lee, *J. Power Sources* 139 (2005) 73.
- [103] D.J. Guo, H.L. Li, *J. Electroanal. Chem.* 573 (2004) 197.
- [104] C.C. Chen, C.F. Chen, C.H. Hsu, I.H. Li, *Diamond Relat. Mater.* 14 (2005) 770.
- [105] S.D. Oh, B.K. So, S.H. Choi, A. Gopalan, K.P. Lee, K.R. Yoon, I.S. Choi, *Mater. Lett.* 59 (2005) 1121.
- [106] C.L. Lee, Y.C. Ju, P.T. Chou, Y.C. Huang, L.C. Kuo, J.C. Oung, *Electrochem. Commun.* 7 (2005) 453.
- [107] T. Yoshitake, Y. Shimakawa, S. Kuroshima, H. Kimura, T. Ichihashi, Y. Kudo, D. Kasuya, K. Takahashi, F. Kokai, M. Yudasaka, S. Iijima, *Physica B* 323 (2002) 124.
- [108] K. Sasaki, K. Shinya, S. Tanaka, A. Furukawa, K. Ando, T. Kuroki, H. Kusaba, Y. Teraoka, *Proceedings of the 11th FCDIC Fuel Cell Symposium*, Tokyo, Japan, 2003, p. 239.
- [109] A. Asami, S. Iinou, A. Ishihara, S. Mitsushima, N. Kamiya, K.I. S Ota, *Proceedings of the 24th Annual Meeting of Hydrogen Energy Systems Society of Japan*, Saitama, Japan, 2004, p. 16.
- [110] L. Zhang, B. Cheng, E.T. Samulski, *Chem. Phys. Lett.* 398 (2004) 505.
- [111] L. Okhlopova, A. Lisitsyn, V. Likhobolov, M. Gurrath, H. Boehm, *Appl. Catal. A* 204 (2000) 229.
- [112] M. Fraga, E. Jordao, M. Mendes, M. Freitas, J. Faria, J. Figueredo, *J. Catal.* 209 (2002) 355.
- [113] E. Czaran, J. Finster, K. Schnabel, *Z. Anorg. Allg. Chem.* 443 (1978) 175.
- [114] H. Van dam, H. Van Bekkum, *J. Catal.* 131 (1991) 335.
- [115] F. Coloma, A. Sepulveda-Escribano, J. Fierro, F. Rodriguez-Reinoso, *Langmuir* 10 (1994) 750.
- [116] S. De Miguel, O. Scelza, M. Romanmartinez, C. Salinas-Martinez, D. Cazorlaamoros, A. Linares-Solano, *Appl. Catal. A* 170 (1998) 93.
- [117] G. Torres, E. Iablonski, G. Baronetti, A. Castro, S. De Miguel, O. Scelza, M. Blanco, M. Pena Jimenez, J. Fierro, *Appl. Catal. A* 161 (1997) 213.
- [118] Y. Pai, J. Ke, C. Chou, J. Lin, J. Zen, F. Shieu, *J. Power Sources* 163 (2006) 398.
- [119] M. Watanabe, M. Uchida, S. Motoo, *J. Electroanal. Chem.* 229 (1987) 395.
- [120] H.G. Petrow, R.J. Allen, U.S. Patent 4,044,193 (1977).
- [121] J. Lobato, M. Rodrigo, J. Linares, K. Scott, *J. Power Sources* 157 (2006) 284.
- [122] N. Giordano, E. Passalacqua, L. Pino, A.S. Arico, V. Antonucci, M. Vivaldi, K. Kinoshita, *Electrochim. Acta* 36 (1991) 1979.
- [123] Y. Nakao, K. Kaeriyama, *J. Colloid Interf. Sci.* 110 (1986) 82.
- [124] D. Duff, T. Mallat, M. Schneider, A. Baiker, *Appl. Catal. A* 133 (1995) 133.
- [125] N. Toshima, K. Hirakawa, *Polym. J.* 31 (1999) 1127.
- [126] A. Honji, T. Mori, K. Tamura, Y. Hishinuma, *J. Electrochem. Soc.* 135 (1988) 355.
- [127] X. Wang, I.M. Hsing, *Electrochim. Acta* 47 (2002) 2981.
- [128] J. McBreen, H. Olender, S. Srinivasan, K. Kordesch, *J. Appl. Electrochem.* 11 (1981) 787.
- [129] M. Uchida, Y. Aoyama, M. Tanabe, N. Yanagihara, N. Eda, A. Ohta, *J. Electrochem. Soc.* 142 (1995) 2572.
- [130] M. Watanabe, H. Sei, P. Stonehart, *J. Electroanal. Chem.* 261 (1989) 375.
- [131] M. Watanabe, S. Saegusa, P. Stonehart, *Chem. Lett.* 9 (1989) 1487.
- [132] A. Honji, T. Mori, K. Tamura, Y. Hishinuma, *J. Electrochem. Soc.* 137 (1990) 2084.
- [133] H. Bonnemann, G. Braun, W. Brijoux, R. Brinkmann, A. Tilling, K. Seevogel, K. Siepen, *J. Organomet. Chem.* 520 (1996) 143.
- [134] T. Schmidt, *J. Electrochem. Soc.* 145 (1998) 925.
- [135] C. Huang, Z. Han, X. Li, Y. Chen, *Chin. J. Power Sources* 24 (2000) 243.
- [136] T. Kodas, U.S. Patent 6,103,392 (2000).
- [137] Z. Liu, J.Y. Lee, M. Han, W. Chen, L.M. Gan, *J. Mater. Chem.* 12 (2002) 2453.
- [138] Y. Liu, X. Qiu, Z. Chen, W. Zhu, *Electrochem. Commun.* 4 (2002) 550.
- [139] X. Zhang, K. Chan, *Chem. Mater.* 15 (2003) 451.
- [140] J. Solla-Gullon, F.J. Vidal-Iglesias, V. Montiel, A. Aldaz, *Electrochim. Acta* 49 (2004) 5079.
- [141] L. Xiong, A. Manthiram, *Solid State Ionics* 176 (2005) 385.
- [142] S. Rojas, F.J. Garcia, S. Jaras, M.V. Huerta, J.L.F. Fierro, M. Boutonnet, *Appl. Catal. A: Gen.* 285 (2005) 24–35.
- [143] V. Jalan, U.S. Patent 4,202,934 (1980).
- [144] V. Jalan, D. Landsman, U.S. Patent 4,186,110 (1980).
- [145] D. Landsman, F. Luczak, U.S. Patent 4,316,944 (1982).
- [146] F. Luczak, D. Landsman, U.S. Patent 4,677,092 (1987).
- [147] K. Kinoshita, P. Stonehart, in: J.O'M. Bockris, B.E. Conway (Eds.), *Modern Aspects of Electrochemistry*, vol. 12, Plenum Press, New York, 1977, p. 183.
- [148] X. Zhang, T. Wang, B. Xia, P. Qin, N. Xu, *J. Fuel Chem. Tech.* 31 (2003) 411.
- [149] E. Crabb, M. Ravikumar, *Electrochim. Acta* 46 (2001) 1033.
- [150] E. Crabb, R. Marshall, D. Thompsett, *J. Electrochem. Soc.* 147 (2000) 4440.
- [151] E. Crabb, *Electrochem. Solid State Lett.* 5 (2002) A5.
- [152] A.S. Fialkov, *Russ. J. Electrochem.* 36 (2000) 389.
- [153] J.J. Escard, C. Leclerc, J.P. Contour, *Catalysis* 29 (1973) 31.
- [154] C. Vedrine, M. Dufaux, C. Naccache, B. Imelik, *J. Chem. Soc., Faraday Trans. 74* (1978) 440.
- [155] A. Biloul, F. Coowar, O. Contamin, G. Scarbeck, M. Savy, D. van den Ham, J. Riga, J. Verbist, *J. Electroanal. Chem.* 289 (1990) 189.
- [156] V.S. Bogotski, A.M. Snudkin, *Electrochim. Acta* 29 (5) (1984) 757.

- [157] A.V. Koblelev, R.M. Kobleleva, V.F. Ukhov, *Dokl. Akad. Nank. (USSR)* 243 (1978) 692.
- [158] J. Bett, K. Kinoshita, P. Stonehart, *J. Catal.* 41 (1976) 124.
- [159] M. Watanabe, S. Motoo, *J. Electroanal. Chem.* 60 (1975) 275.
- [160] M. Krauzza, W. Vielstich, *J. Electroanal. Chem.* 379 (1994) 307.
- [161] T. Iwasita, F.C. Nart, W. Vielstich, *Ber. Bunsenges. Phys. Chem.* 94 (1990) 1030.
- [162] B. Beard, P.N. Ross, *J. Electrochem. Soc.* 137 (1990) 3368.
- [163] L.J. Hillenbrand, J.W. Lacksonen, *J. Electrochem. Soc.* 112 (1965) 249.
- [164] F. Coloma, A. Sepulveda, J. Fierro, F. Rodriguez-Reinoso, *Appl. Catal. A: Gen.* 148 (1996) 63.
- [165] A.K. Shukla, M.K. Ravikumar, A. Roy, S.R. Barman, D.D. Sarma, A.S. Aricò, V. Antonucci, L. Pino, N. Giordano, *J. Electrochem. Soc.* 141 (1994) 1517.
- [166] A. Shukla, K. Ramesh, R. Manoharan, P. Sarode, S. Vasudevan, *Ber. Bunsenges. Phys. Chem.* 89 (1985) 1261.
- [167] M.G. Mason, *Phys. Rev. B* 27 (1983) 748.
- [168] W. Eberhardt, P. Fayet, D.M. Cox, Z. Fu, A. Kaldor, R. Sherwood, D. Sondericker, *Phys. Rev. Lett.* 64 (1990) 780.
- [169] M.C. Denis, G. Lalonde, D. Guay, J.P. Dodelet, R. Schultz, *J. Appl. Electrochem.* 29 (1999) 951.
- [170] A.K. Shukla, A. Arico, K.M. El-Kathib, H. Kim, P.L. Antonucci, V. Antonucci, *Appl. Surf. Sci.* 137 (1999) 20.
- [171] E. Antolini, L. Giorgi, F. Cardellini, E. Passalacqua, *J. Solid State Electrochem.* 5 (2001) 131.
- [172] J.B. Goodenough, R. Manoharan, *Chem. Mater.* 1 (1989) 391.
- [173] J. McBreen, S. Mukerjee, *J. Electrochem. Soc.* 142 (1995) 3399.
- [174] P. Carott, M. Carott, A. Candeias, J. Ramalo, *J. Chem. Soc., Faraday Trans.* 91 (1995) 2179.
- [175] A. Polania, E. Papirer, J. Donnet, G. Dagois, *Carbon* 31 (1993) 473.
- [176] H. Boehm, *Carbon* 32 (1994) 759.
- [177] M. Lopez-Ramon, F. Stoekli, C. Morenocastilla, F. Carrasco-Marín, *Carbon* 37 (1999) 1215.
- [178] S. Barton, M. Evans, E. Halliop, J. Macdonald, *Carbon* 35 (1997) 1361.
- [179] C. Leon, Y. Leon, J. Solar, V. Calemma, L. Radovic, *Carbon* 30 (1992) 797.
- [180] J. Lambert, M. Che, *J. Mol. Catal. A* 162 (2000) 5.
- [181] M. Roman-Martinez, D. Cazorla-Amoros, A. Linares-Solano, C. Lecea, *Carbon* 33 (1995) 3.
- [182] D. Cameron, S. Cooper, I. Dodgson, B. Harrison, J. Jenkins, *Catal. Today* 7 (1990) 113.
- [183] C. Prado-Burguete, A. Linares-Solano, F. Rodriguez-Reinoso, C. Salinas-Martinez, *J. Catal.* 115 (1989) 98.
- [184] C. Prado-Burguete, A. Linares-Solano, F. Rodriguez-Reinoso, C. Salinas-Martinez, *J. Catal.* 128 (1991) 397.
- [185] D. Suh, T. Park, S. Ihm, *Carbon* 31 (1993) 427.
- [186] A. Sepulveda-Escribano, F. Coloma, F. Rodriguez-Reinoso, *Appl. Catal. A* 173 (1998) 247.
- [187] P. Ehrburger, O. Majahan, P. Walker, *J. Catal.* 43 (1976) 61.
- [188] A. Guerriero-Ruiz, P. Badenes, I. Rodriguez-Ramos, *Appl. Catal. A* 173 (1998) 313.
- [189] F. Coloma, A. Sepulveda, F. Reinoso, *J. Catal.* 154 (1995) 299.
- [190] M. Cerro-Alarcon, A. Maroto-Valiente, I. Rodriguez-Ramos, A. Guerrero-Ruiz, *Carbon* 43 (2005) 2711.
- [191] T. Tran, S. Langer, *Electrochim. Acta* 38 (1993) 1551.
- [192] H. Shioyama, K. Honjo, M. Kiuchi, Y. Yamada, A. Ueda, N. Kuriyama, T. Kobayashi, *J. Power Sources* 161 (2006) 836.
- [193] S. Kim, S. Park, *J. Power Sources* 159 (2006) 42.
- [194] H. Shioyama, Y. Yamada, A. Ueda, T. Kobayashi, *Carbon* 43 (2005) 2374.
- [195] K. Kinoshita, *Carbon, Electrochemical and Physicochemical Properties*, Wiley, New York, 1988, p. 10.
- [196] P. Serp, M. Corrias, P. Kalck, *Appl. Catal. A: Gen.* 253 (2003) 337.
- [197] N.M. Rodriguez, *J. Mater. Res.* 8 (1993) 3233.
- [198] N. Rajalakshmi, H. Ryu, M.M. Shaijumon, S. Ramaprabhu, *J. Power Sources* 140 (2005) 250.
- [199] T. Matsumoto, T. Komatsu, H. Nakano, K. Arai, Y. Nagashim, E. Yoo, T. Yamazaki, M. Kijima, H. Shimizu, Y. Takasawa, J. Nakamura, *Catal. Today* 90 (2004) 277.
- [200] X. Li, I. Hsing, *Electrochim. Acta* 51 (2006) 5250.
- [201] Z. Xu, Z. Qi, A. Kaufman, *Chem. Commun.* (2003) 878.
- [202] Z. Xu, Z. Qi, A. Kaufman, *Electrochem. Solid-State Lett.* 6 (2003) A171.
- [203] Z. Xu, Z. Qi, A. Kaufman, *Electrochem. Solid-State Lett.* 8 (2005) A313.