

Ceramic materials as supports for low-temperature fuel cell catalysts

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ABSTRACT

The performance and durability of low-temperature fuel cells seriously depend on catalyst support materials. Catalysts supported on high surface area carbons are widely used in low temperature fuel cells. However, the corrosion of carbonaceous catalyst-support materials such as carbon black has been recognized as one of the causes of performance degradation of low-temperature fuel cells, in particular under repeated start-stop cycles or high-potential conditions. To improve the stability of the carbon support, materials with a higher graphitic character such as carbon nanotubes and carbon nanofibers have been tested in fuel cell conditions. These nanostructured carbons show a several-fold lower intrinsic corrosion rate, however, do not prevent carbon oxidation, but rather simply decrease the rate. Due their high stability in fuel cell environment, ceramic materials (oxides and carbides) have been investigated as carbon-substitute supports for fuel cell catalysts. Moreover, the higher specific electrocatalytic activity of some ceramic supported metals than unsupported and carbon supported ones, suggests the possibility of a synergistic effect by supporting metal catalyst on ceramic supports. This paper presents an overview of ceramic materials tested as a support for fuel cell catalysts, with particular attention addressed to the electrochemical activity and stability of the supported catalysts.

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1. Introduction

Fuel cell technology offers an attractive combination of highly efficient fuel utilisation and environmentally-friendly operations [1]. Fuel flexibility is an important characteristic of the fuel cells: the ideal fuel for optimum fuel cell operation is hydrogen, although various materials, such as low molecular weight alcohols, that can undergo an oxidation reaction, can be used as fuels for a fuel cell system [2]. In order to obtain sufficient electrical output from a fuel cell, the electrochemical reaction must occur at a sufficient rate. In low temperature fuel cells (such as polymer electrolyte membrane fuel cells (PEMFCs) and phosphoric acid fuel cells (PAFCs), operating at temperature <200 °C), this is achieved using platinum-based catalysts [3]. It has to be promptly pointed out, however, that the acid environment in the PEMFCs is different from that of PAFCs. The PEMFCs operate at less than 100 °C, as compared with the PAFCs, which operate at twice this temperature. Furthermore, the anions of the perfluorinated sulfonic acid polymer are only weakly adsorbed on Pt, in contrast to the phosphoric anions, which are strongly adsorbed.

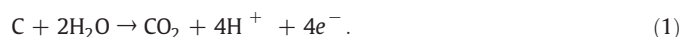
The importance of the metal support in fuel cell catalysis is well recognized. Typically, the support provides a physical surface for dispersion of small metal particles, which is necessary for achieving high surface area. Carbon is a common choice for supporting

nanosized electrocatalyst particles in low temperature fuel cells because of its large surface area, high electrical conductivity, and pore structures [4]. However, porous electrically conductive carbon blacks do not always exhibit adequate resistance to corrosion caused by electrochemical oxidation in the fuel cell. The problem of the electrode stability, particularly of cathode stability, is well known. Universally, oxygen reduction is a slow reaction, and good catalysts have been very difficult to find. As reported by Couper et al. [5], the problems of finding a good electrocatalyst (and a stable, inert substrate) are compounded by the instability of most materials to corrosion close to the reversible potential for the O₂/H₂O couple. Corrosion can be accelerated by the presence of trace hydrogen peroxide, and the lifetimes of potential candidate catalysts can be reduced by poisoning and sintering. Substrate corrosion is as difficult to avoid as dissolution of the catalyst. Catalyst support corrosion has been predominantly observed in phosphoric acid fuel cells. Indeed, thermodynamically, carbon as a material is unstable at the cathode potential in hot phosphoric acid present in PAFCs. Carbon is lost from the system through oxidation leading to significant losses of carbon over a short period of time. The stability of carbon support affects the loss of platinum surface area following both platinum particle sintering and platinum release from the carbon support [6–8]. Kangasniemi et al. [9] reported that the surface of carbon Vulcan XC-72 is oxidized under conditions simulating the cathode environment of a PEMFC (0.8–1.2 V vs. RHE in 1 M H₂SO₄ at 65 °C). During single PEMFC durability testing, Borup et al. [10] found that carbon corrosion of the cathode catalyst layer increases with increasing

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potential and decreasing humidity. Wang et al. [11] investigated the durability of Pt/C catalysts with different carbon black supports under simulated PEMFC conditions. They found that carbon support with high surface area in PEMFC electrode is susceptible to corrosive conditions. If the support is oxidized to CO₂/CO, Pt may be lost from the support, so the more the carbon support is oxidized, the more Pt is lost. If the support is partially oxidized to surface oxide, it may accelerate the increase of Pt particle size, because the presence of surface oxides may weaken the platinum–support interaction, leading to a lower resistance to surface migration of Pt particles. Accordingly, corrosion of the cathode catalyst support may affect the durability of the PEMFC. On the other hand, the anode catalyst could also be exposed to much more oxidative conditions than the cathode during the cell voltage reversal caused by fuel starvation [12]. Summarizing, high-surface-area carbon supports in PAFC and PEMFC electrodes are susceptible to corrosive conditions, which include high water content, low pH, high temperature, high potential, and high oxygen concentration. In addition, Pt catalysts seem to accelerate the rate of carbon corrosion [13]. Two different reaction pathways for carbon oxidation have been distinguished, reversible oxidation to oxygenated surface carbon species and irreversible oxidation to CO₂. If the carbon is partly oxidized to oxygenated surface carbon species, the conductivity at the contact between the carbon support and the catalyst nanoparticles may decrease. If the carbon is oxidized to CO₂, catalyst nanoparticles may be lost from the support, resulting in a significant decrease of the catalyst active surface area, which in turn reduces the performance and operation lifetime of the PEMFC. Typically, CO₂ formation is generalized as given by the following equation [14]:



The standard potential for the electrochemical oxidation of carbon to carbon dioxide is 0.207 V vs. RHE at 25 °C [15]. Therefore, under typical PEMFC cathode operation conditions, carbon corrosion is not only thermodynamically feasible due to the high potentials (0.6–1.2 V) and high O₂ concentrations, but also kinetically enhanced by the elevated temperatures (50–90 °C).

Therefore, various alternatives of electrocatalyst supports are being searched. Due their high surface area and high amount of mesopores, which allow high metal dispersion and good reactant flux, ordered mesoporous carbons and carbon gels have been receiving attention as fuel cell catalyst supports. Catalysts supported on these carbons showed higher catalytic activity than the same catalysts supported on carbon black. Their thermal stability, however, is almost the same to that of carbon blacks [4]. In view of their high thermal stability, boron-doped diamonds (BDDs) have been tested as catalyst supports. The results indicated that the anchoring of metal atoms on BDD surface in a stable way has to be improved. The use of Nafion as the binder seems to enhance the stability of BDD supported catalysts [4]. Recently, nanostructured carbon materials with graphitic structure, such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs) were investigated as catalyst supports in fuel cells [4]. The higher catalytic activity of Pt and Pt–M catalysts supported on CNTs and CNFs than that of the same catalysts supported on carbon blacks was ascribed to their unique structure and properties such as high surface area, good electronic conductivity and chemical stability [4]. Tests carried out in PEM fuel cell conditions indicated that these materials can be more durable and can outlast the lifetime of conventional Vulcan XC-72 [16–18]. By comparing carbon nanotubes and mesoporous carbons, taking into account of the cost of the materials, the complexity of the synthesis methods, and the versatility in pore size and pore distribution tailoring, the mesoporous carbons seem to have more changes to substitute carbon blacks as fuel cell catalyst substrates. The stability in fuel cell conditions of mesoporous carbons is lower than that of CNTs, but can be increased by graphitization [4].

However, these alternative materials do not prevent carbon oxidation, but rather simply decrease the rate. For this reason non-carbon materials have been investigated as catalyst support. Conducting oxides are emerging candidates for oxidation resistant catalyst supports. In addition to their high stability in fuel cell environment, unlike carbon, which does not help electrocatalytic activities, but serves only as a mechanical support, many metal oxide supports can act as co-catalysts. Indeed, it is well known that metal oxides such as RuO₂, SnO₂ and WO₃ enhance the catalytic activity of platinum for methanol and ethanol oxidation [19–24].

The main requirements of a suitable fuel cell catalyst support are the following:

- high surface area, to obtain high metal dispersion;
- suitable porosity, to boost gas flow;
- high electrical conductivity;
- high stability under fuel cell conditions.

It has to be remarked that, frequently, in the literature the difference between catalyst-metal oxide dispersion and metal oxide supported catalyst is not adequately taken into account. In the former case the metal oxide only acts as a cocatalyst, not as a support, and the size of metal and metal oxide particles are not correlated, while in the latter metal particle size depends on, and is considerably lower than the metal oxide particle size.

This paper presents an overview of some metal oxides and carbides, which could substitute carbon as fuel cell catalyst support. Particular attention has been addressed to the electrochemical activity and stability of the supported catalysts.

2. Inorganic metal oxides

Inorganic metal oxides have been studied to determine whether they can serve as good corrosion-resistant supports. Unfortunately, replacing carbon with traditional metal-oxides is difficult, due to their electrical-insulating properties at temperatures below 200 °C. However, sub-stoichiometric metal oxides, such as reduced oxidation state titania (e.g., Ti₄O₇ and Ebonex), doped metal oxides, such as doped TiO₂ and SnO₂, and nanostructured metal oxides, such as TiO₂ nanotubes and WO₃ nanorods, have been proposed as electrically conductive support materials with high corrosion-resistant properties.

2.1. Ti-based oxides

Among the inorganic metal oxides, titanium dioxide, TiO₂, is used in many applications that depend on its photoelectrochemical and catalytic properties and its excellent resistance to corrosion in various electrolytic media [25,26]. Titania exists in three main crystallographic forms e.g., anatase, rutile, and brookite. Each structure exhibits different physical properties, which lead to their different applications. It is generally accepted that anatase titania is more efficient as photocatalyst than rutile titania. Regarding the application in fuel cells, Gustavsson et al [27] investigated thin film of Pt and stoichiometric TiO₂ in a polymer electrolyte electrochemical cell. Individual thin films of Pt and TiO₂ were deposited directly on Nafion membranes by thermal evaporation. Oxygen reduction reaction polarization plots showed that the presence of a thin TiO₂ layer between the platinum and the Nafion increases the performance compared to a Pt film deposited directly on Nafion. They attributed this improvement to a better dispersion of Pt on TiO₂ compared to on Nafion and in addition, substantial proton conduction through the thin TiO₂ layer.

Stoichiometric rutile is an insulator with a band gap of 3.06 eV at room temperature. Bulk transport measurements show that for very slightly nonstoichiometric TiO₂, with a carrier concentration in the range below 2.0 10²⁰ cm^{−3}, the low-temperature activation energy for conduction is about 0.028 eV [26]. *n*-type dopants for TiO₂, as

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