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Investigation of Pd-based electrocatalysts for oxygen reduction in PEMFCs operating under automotive conditions

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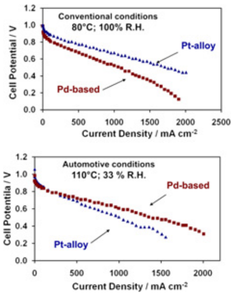
HIGHLIGHTS

- ► Pd-based electrocatalysts are prepared by using a sulphite-complex route.
- ► Structure, morphology and surface characteristics are investigated.
- ► Better surface characteristics are recorded with the two-step Pd catalyst.
- ► Pd-based catalyst shows a significant increase of performance at 110 °C.
- ► Pd-based composite catalysts get advantage of operation under automotive conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Composite Pd-based electrocatalysts consisting of a surface layer of Pt (5% wt.) supported on a core Pd_3Co_1 alloy were prepared. Two preparation approaches were investigated. One consisting of a single-step reduction procedure; in the second method, preparation of the PdCo alloy and deposition of a Pt overlayer occurred in two distinct steps. The catalyst prepared by a one-step process showed oxidised Pt species on the surface even if characterized by a smaller crystallite size with respect to the two-step Pd-based catalyst (4 nm vs. 6 nm). Moreover, the two-step process showed an enrichment of Pt on the surface and a smaller content of Co in the outermost layers. The enhanced surface characteristics of the two-step Pd catalyst resulted in a better performance. At 80 °C, the mass activity was lower than a Pt_3Co_1 alloy catalyst with the same crystallographic structure. Interestingly, the composite PtPdCo catalyst showed a significant increase of performance as the temperature was increased to 110 °C whereas the Pt_3Co_1 showed a decrease due to a prevailing effect of ionomer dry-out in the catalytic layer. The composite catalyst appeared sufficiently stable after 10^4 electrochemical cycles between 0.6 and 0.9 V at 110 °C and 33% R.H.

1. Introduction

Highly dispersed carbon-supported nanosized Pt particles are presently the benchmark electrocatalyst for polymer electrolyte fuel cells (PEMFCs) [1–7]. The rate determining step is the oxygen reduction reaction which occurs at large cathodic overpotentials, e.g. overpotentials greater than 0.4 V for current densities of practical interest, e.g. 1 A cm^{-2} and with Pt loadings as high as 0.4 mg cm^{-2} [2,7]. Large efforts have been made in the last decades to significantly reduce the Pt loading while maintaining suitable performance essentially by increasing Pt utilization. Novel approaches to form nanostructured materials or thin film nanostructured catalyst layers with an extension of the triple phase boundary have provided promising results [8–11]. At the same time, the development of

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suitable binary and ternary Pt-alloys, e.g. PtCo, PtNi, PtCoCr, PtCoMn has allowed to increase considerably the mass activity with respect to the conventional Pt/C providing a basis for Pt content reduction [2,6,9–13]. Yet, the continuous increase of the cost of Pt has made less effective such progresses. Moreover, an increase in mass activity using Pt-alloys or nanostructured catalysts, as observed under rotating disc configuration, often does not correspond to a proportional increase of power density in fuel cells at practical cell voltages, e.g. 0.65 V, of interest for automotive applications. This is because the contribution of other effects such as ohmic constraints and mass transfer polarizations becomes more relevant as the fuel cell current density increases. As alternative to Pt, pyrolized cobalt or iron porphyrins [14,15], non-precious metals/heteroatomic polymers [16], transition metal chalcogenides [17] have been actively investigated. Although the recently achieved performances appear very promising, the main drawbacks regard a poor stability during fuel cell operation at relevant current densities and a low voltage efficiency. In the transition process from Pt to cheaper non Pt-group (NPG) metals or non-precious catalysts, Pd-based electrocatalysts appear as a proper compromise. Pd shows a suitable electrocatalytic activity for the oxygen reduction reaction, even though lower than Pt, whereas its cost is at present significantly lower than Pt and its reserves much wider [18]. Several attempts have been made to develop Pt–Pd catalysts especially with the aim to take advantage of a possible synergistic effect; however, the ORR activity for Pd-based electrocatalysts is generally lower than that of Pt-rich electrocatalysts [19–23]. However, stable and highly performing Pt-alloys are characterized by large excess of Pt content (e.g. formulations such as Pt_3Co_1), thus providing limited perspectives to reduce consistently the Pt content. On the other hand Pt-alloys, such as PtCu, with large non-noble metal content give rise to significant dealloying during practical operation. This may cause performance degradation due to the poisoning of membrane sulphonic groups as a consequence of an ion-exchange process between protons and the dissolved transition metal ions. A controlled electrochemical dealloying approach during the fuel cell conditioning process and subsequent purification in acid solutions of the MEA containing the de-alloyed catalyst has been suggested [6]. Although this approach is interesting to increase the mass activity, it appears not easily applicable to stack manufacturing.

Pd-based electrodes may represent a consistent way to reduce the Pt content in PEMFCs [18] and provide a performance that is not significantly lower than Pt/C [24,25]. One interesting approach to reduce the Pt loading while maintaining proper activity and stability is to form a Pt monolayer on Pd or Pd-alloys [26–28]. In the case of a Pt monolayer coated on annealed-Pd_3Fe single crystals, two positive effects were observed: (i) a downshift of the Pd d-band center relative to pure Pd caused by the alloying with Fe, and (ii) a suitable interaction between the segregated Pt layer and Pd. In particular, the first effect caused a decreased interaction of oxygen species (e.g. OH) with Pd favouring oxygen molecules adsorption and dissociation [26–28].

Various procedures have been used for preparing Pt and Pd fuel cell catalysts. These include polyol or borohydride reduction, microemulsion method, formic acid reduction of Pt and Pd precursors, electroless deposition of Pt on Pd, etc.[18,24,25,29–39]. One of the main drawback is the increase of particle size passing from Pt-rich to Pd-rich catalysts. Nanodendrites and core-shell type Pd electrocatalysts appear useful to increase the ORR activity [29,40,41].

The approach pursued in this work is based on the synthesis of an inorganic salt of Pd (Pd–sulphite complex) which is then decomposed on the surface of a carbon black support in solution forming colloidal amorphous nanoparticles which are easily impregnated by a Co precursor. After a thermal treatment, PdCo nanoparticles surface-enriched in Pd are obtained. These are successively covered by a Pt layer using a colloidal solution obtained from a similar Pt–sulphite complex.

A commonly used technique to investigate Pt nanoparticles engineering, in particular the occurrence of a surface segregation of Pt (Pt skin layer, Pt skeleton layer, percolated and core-shell structures, etc. [6,12,13]), is based on the use of aberration-corrected high-angle annular dark-field in the scanning transmission electron microscope in combination with energy dispersion spectroscopy [13]. This technique while providing useful information on a local basis appears more accurate for nanoparticles of dimensions in the range of 10 nm. Moreover, it provides an information concerning with a few selected nanoparticles that may not be a representative of the overall sample. The approach used in this work involves low-energy ion scattering spectroscopy (LE-ISS) using $3He^+$ ions at low accelerating voltage (1 kV). The kinetic energy of the reflected $3He^+$ is analysed to get information on the chemistry of the outermost layer. Depth profiling in this work is carried out by combining LE-ISS with X-ray photoelectron spectroscopy (XPS) and X-ray fluorescence (XRF).

Another aspect concerns with the effect of temperature. Most of the recently investigated Pd-based catalysts have been studied in rotating disc configuration at room temperature or under PEMFC at the conventional temperature of 80 °C. Whereas, for automotive applications, operation at intermediate temperatures such as 110–130 °C can mitigate the constraints concerning with thermal and water management simplifying the fuel cell system, reducing its volume inside the car with a strong impact on costs and reliability [42]. The pre-requisites of an electrolyte for automotive applications are a good capability of operation in the intermediate temperature range as well as at conventional and low temperatures as required by a rapid or cold start-up. Recent progresses include short side chain perfluorosulfonic electrolyte membranes, composite membranes and novel electrolyte polymers [42–45]. However, since the aim of this study is concerned with the assessment of the Pd-based catalysts at both conventional and intermediate temperatures, we have preferred to work with conventional Nafion membranes under pressurised mode thus avoiding complete membrane dehydration above 100 °C [7].

In order to assess the performance of Pd-rich catalysts with respect to benchmark Pt-based catalysts, a comparison with a Pt_3Co_1/C catalyst characterised by the same crystallographic structure which has been shown previously to perform better than Pt/C [42] is made.

2. Experimental

2.1. Catalyst preparation

Cathodic Pd-based catalysts consisted of 5% wt. Pt and 95% wt. Pd–Co. The nominal core alloy atomic composition was Pd_3Co_1. The total metal fraction on carbon was 50% wt. Ketjenblack EC (KB) carbon black with BET surface area of 850 $m^2 g^{-1}$ was used as conductive support.

Two preparation procedures were used for the Pd-based catalysts. In both procedures $Na_6Pt(SO_3)_4$ and $Na_6Pd(SO_3)_4$ salts were prepared by reaction of H_2PtCl_6 and $PdCl_4$ with sodium dithionite. The Pd–sulphite salt was first dissolved in acidic solution and subsequently decomposed with H_2O_2 to form a colloidal dispersion that was impregnated on the carbon black. Co was deposited by incipient wetness of cobalt nitrate on the amorphous PdOx/C catalyst previously obtained. The concentration of $Co(NO_3)_2$ was adjusted to achieve a Pd/Co atomic ratio of 3:1 in the final catalyst. The obtained amorphous catalyst was thus thermal treated in Ar atmosphere at 500 °C to form PdCo alloy nanoparticles (carbothermal reduction). To achieve a Pd surface enrichment, the treated