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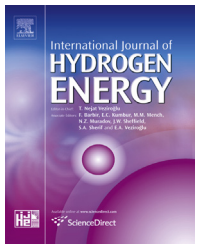

Development of PtGe and PtIn anodic catalysts supported on carbonaceous materials for DMFC

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ABSTRACT

Bimetallic PtGe and PtIn catalysts (Ge/Pt and In/Pt molar ratios = 0.33, 17 wt.% Pt loading) were prepared over carbonaceous supports (carbon Vulcan, carbon nanotubes and structured mesoporous carbon). The liquid phase deposition–reduction method by using 0.4 M sodium borohydride as a reducing agent was employed. The electrocatalytic activity for methanol oxidation was compared with a commercial Pt/CV E-TEK catalyst. The onset potential of the CO oxidation was shifted to less positive values for carbon Vulcan and carbon nanotubes supported catalysts and with a smaller effect in the case of mesoporous carbon supported ones. The best electrocatalytic performance was obtained by using carbon Vulcan as support of bimetallic catalysts, followed by carbon nanotubes. The performance of mesoporous carbon as a support was not adequate. PtGe/CV, PtGe/NT and PtIn/CV catalysts displayed the best performance in DMFC. The good performance of these catalysts could be due to the presence of small particle sizes with a narrow distribution, and to geometric effects (observed from different characterization techniques) related to a probable decoration of Ge or In around the small Pt particles.

1. Introduction

The objective of producing new and more efficient electrocatalysts is a very important goal in the development of low temperature fuel cells, mainly in the named direct conversion cells, which use organic molecules such as methanol, ethanol and formic acid. Direct methanol fuel cells (DMFC) are promising systems for energy conversion due to the high efficiency, low emission of contaminants and low operation temperatures [1,2]. Important efforts have been made in order to develop an adequate technology for the DMFC, mainly in the field of the development of very active catalysts for the electro-oxidation of methanol. Electrochemical studies show that CO, formic acid and formaldehyde are the intermediary compounds in the oxidation of methanol on Pt electrodes [3,4]. The electro-oxidation of methanol over Pt involves several intermediate steps such as dehydrogenation, CO chemisorption, adsorption of OH (or H_2O), chemical reaction between adsorbed CO and OH, and evolution of CO_2. One of them is the limiting step which depends on the temperature and the characteristics of the catalytic surface (crystallographic

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orientation, presence of defects) [5]. The electro-oxidation reactions of organic compounds of low molecular weight (methanol, ethanol, formaldehyde, formic acid) require a catalyst containing a noble metal like Pt. However, all these reactions produce CO, which is strongly adsorbed on Pt. Hence an important number of works try to modify the vicinity of Pt atoms by adding other elements [5].

One of the roles of the added elements to Pt/C is to facilitate the CO oxidation on the catalyst surface via a bifunctional mechanism or by a ligand effect or a combination of both effects. The bifunctional mechanism enhances the catalytic oxidation of CO through the presence of oxyhydride species dispersed on the catalytic surface. The effect of these groups is the diminution of the CO oxidation potential. Moreover, the addition of a second element modifies the water and oxygen adsorption properties [6].

Presently, PtRu catalysts have been extensively studied as anodic electrocatalysts for DMFC, since Pt is the responsible of the methanol activation to produce CO, while Ru is the responsible for the CO conversion into CO_2 [7].

Several authors studied PtRu catalysts with both metals forming alloys and these catalysts were compared with others which do not form alloys between Pt and Ru [5,8]. They observed that both catalyst types were active for the methanol oxidation, but the catalysts with the smaller amount of RuO_x, which display the smaller Ru–O bond energy (Pt–Ru alloys), showed the best results. In addition, the electrocatalysts for DMFC based on PtRu presented a higher activity than Pt alone or Pt doped with other metals. The state of Ru in these catalysts is under discussion up to now, since the alloy degree between Pt and Ru and the content of RuO_xH_y are the main factors to define the catalytic activity. Though for some authors, the catalyst containing Pt–RuO_x species is slightly more active than that with alloyed PtRu species, the last one appears to have a better stability [9]. Dubau et al. [10] reported that Ru appears to decorate the Pt, and presents a better tolerance to CO than the Pt–Ru alloys with the same Pt/Ru atomic ratio. Neto et al. [11] made a comparison of PtSn/C, PtRu/C and PtSnRu/C catalysts prepared by the ethylenglicol method for methanol and ethanol oxidations. The XRD spectra showed that PtRu/C catalyst displayed a fcc structure, typical of the alloyed Pt with Ru, while PtSn/C and PtSnRu/C catalysts showed not only alloyed compounds but also the presence of SnO_2 phase. By using amperometric measurements it was found that the PtSn/C catalysts were more active than PtRu/C and PtSnRu/C for the oxidation of methanol and ethanol at room temperature. The higher yield of the PtSn/C catalyst could be due to the fact that a fraction of Sn would be forming alloys with Pt, thus modifying the electronic properties of Pt. Hence, in this way the capacity of the metallic surface to adsorb methanol and ethanol and to dissociate the C–H bond is modified. Besides, it was found that SnO_2 species enhance the oxidation of the adsorbed oxidized intermediary (bifunctional mechanism).

With respect to the PtGe couple for fuel cells, few papers have been reported in the literature. Crabb et al. [12] found that when the catalyst was prepared by controlled surface reaction, there was a promotional effect of GeO_2 at low potentials, though this effect was not very important and it does not change with the Ge loading. By using CO stripping measurements on PtGe catalysts, it was observed a diminution of the total amount of CO, thus indicating that the Pt sites could be covered by Ge. In addition, the combination of Pt with Ge appears to have an incidence on the adsorption properties of CO on the Pt surface. With respect to PtIn couple for fuel cells, the literature only mentions one work about PtSnIn catalysts [13], finding a promoter effect of In on the ethanol electro-oxidation activity.

The development of more efficient electrocatalysts with lower affinity to CO is a very important point in order to achieve technological advances in DMFC. In conclusion, an ideal anodic catalyst would be such that it must be completely tolerant to CO, thus reaching a total oxidation of CO to CO_2 at very low potentials.

In this paper two few studied bimetallic systems are proposed: PtGe and PtIn supported on different carbonaceous materials (carbon Vulcan, carbon nanotubes and mesoporous carbon) which were compared with a commercial Pt/VC E-TEK catalyst. Taking into account that there is little information in the literature about these bimetallic couples in fuel cells, and that this literature reported that both Ge and In could be promising systems, the objective of this paper is the development of PtGe and PtIn anodic catalysts supported on carbonaceous materials to be used in direct methanol fuel cells. The proposed systems were characterized by temperature programmed reduction (TPR), H_2 chemisorption, benzene hydrogenation, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), CO stripping and transmission electron microscopy (TEM). Moreover, a laboratory cell (DMFC) was used for testing the catalysts under different temperature and pressure conditions.

2. Experimental

2.1. Preparation of the electrocatalysts

Electrocatalysts based on supported PtGe and PtIn were prepared by a deposition–reduction in liquid phase method, by using sodium borohydride 0.4 M (RB) as a reductive agent. The catalysts contained 17 wt.% Pt and the second metal were added maintaining a Ge/Pt or In/Pt molar ratio of 0.33. The metallic precursors were H_2PtCl_6, $GeCl_4$ and $In(NO_3)_3$. Three different supports were used: carbon Vulcan XC-72 (CV), multiwall carbon nanotubes (NT) and a structured mesoporous carbon from CNEA-Argentina (MC). Vulcan carbon XC-72 has a specific surface area (S_{BET}) of 240 $m^2\ g^{-1}$, a pore volume (V_{pore}) of 0.31 $cm^3\ g^{-1}$ and a mean particle size of 40 nm. Commercial multiwall carbon nanotubes (MWCN from Sunnano, purity >90%, diameter: 10–30 nm, length: 1–10 μm) with the following textural properties: $S_{BET} = 211\ m^2\ g^{-1}$, $V_{pore} = 0.46\ cm^3\ g^{-1}$, were used. The physical properties of the structured mesoporous carbon, were: $S_{BET} = 476\ m^2\ g^{-1}$, $V_{pore} = 0.35\ cm^3\ g^{-1}$. A maximum in the pore size distribution is found at around 9 nm. The micro- (<2 nm) and meso-porosity (between 2 and 50 nm) is attributed to the structure of the carbon, which consists of clusters of porous uniform spheres in a fairly regular array. Therefore, the obtained material has a hierarchical pore structure (micro- and meso-porosity) [14,15].

The liquid phase deposition–reduction was carried out at 50–60 °C. When the basic solution $NaBH_4$ 0.4 M was added in

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