Pt-Ru catalysts prepared by high energy ball-milling for PEMFC and DMFC: Influence of the synthesis conditions

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Abstract

High energy ball-milling was used to prepare several unsupported Pt-Ru anode catalysts for PEM- and direct methanol fuel cells. Pt and Ru with a 50:50 nominal Pt/Ru ratio were ball-milled at various ball-to-powder weight ratios (from 4/1 to 12/1) and with various Pt:Ru:MgH_2 proportions (from 1:1:2 to 1:1:10), where MgH_2 is a leacheable dispersive agent. The presence of MgH_2 is necessary to obtain unsupported catalysts with a specific surface area of between 50 and 75 $m^2 g^{-1}$. The ball-milling parameters greatly affected the relative proportions of the three phases constituting the catalysts. These phases are: Pt(Ru) alloy nanocrystallites, unalloyed Ru crystallites and nanocrystallites. The best CO tolerant catalyst is obtained by using a 12/1 ball-to-powder ratio and a 1:1:8 Pt:Ru:MgH_2 proportion of dispersive agent. It is made of 57 at.% of a nanocrystalline (3 nm) $Pt_{80}Ru_{20}$ alloy, 42 at.% of a nanocrystalline (3 nm) Ru phase and 1 at.% of a crystalline (∼40 nm) Ru phase. This catalyst has the lowest Pt/Ru surface ratio (0.9), the highest content in nanocrystalline Ru, and the highest ratio of oxidized/metallic Ru (3.3). Both Pt-Ru alloy and nanocrystalline Ru participate to the CO tolerance. The best CO tolerant catalyst is, however, not the best catalyst in DMFC. The latter is obtained by using a 4/1 ball-to-powder ratio and a 1:1:6 Pt:Ru:MgH_2 proportion. Within the starting 50:50 Pt-Ru nominal atomic ratio, no specific correlation was found between catalyst performance in DMFC and atomic surface Pt/Ru ratio, nor nanocrystalline Ru content, nor oxidized/metallic Ru ratio. Performances of the best ball-milled catalysts are compared to those of commercial unsupported catalysts in PEMFC and DMFC.
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1. Introduction

Among the different types of fuel cells, proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) are being developed for transportation, portable and small stationary applications [1,2]. For PEMFC systems operating under reformate gas and for DMFC systems, a major problem is the poisoning of Pt catalysts by CO and CO-like species [1–5]. Pt-Ru catalysts are currently recognized as the most effective catalyst for H_2 oxidation in the presence of CO and for methanol oxidation in low temperature fuel cells applications [2,4–8]. Since the 1990s, extensive research has focused on gaining a better understanding of the catalytic activity enhancement for

CO oxidation and for methanol oxidation by Pt-Ru catalysts compared to Pt catalysts through electrochemical, spectroscopic and theoretical studies. These works have been reviewed, for instance, in references [2,3,8–11]. Two main effects are usually invoked to explain the role of Ru in promoting CO and methanol oxidation: (i) the bifunctional mechanism in which Ru provides OH groups necessary for oxidation of CO into CO_2 and (ii) the ligand model in which Ru alters the electronic properties of Pt and thus leads to a change in the binding energy of CO onto Pt [2,8,11,12].

The structure, the morphology and the surface composition of Pt-Ru catalysts have a strong influence on their performances in PEMFC and DMFC systems [2,4,5,13–15]. Despite several years of research, some aspects of the chemistry of the catalyst are still open to debate, such as the need to completely alloy Pt and Ru, the role of Ru oxides and the best surface oxidation state of Ru [2,8,13]. Some authors state that alloyed metallic Ru is the most active state for providing effective catalytic sites [15–17] while others argue that alloying of Ru is not necessary,

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as long as a strong interaction exists between Pt and Ru, due to the high surface mobility of CO [18–20]. Others believe that amorphous hydrated Ru oxides also play an important role due to their mixed proton–electron conductivity leading to co-catalytic activity with Pt-Ru [21,22]. Furthermore, recent works on the role of Ru adatoms deposited on Pt catalysts, where Ru is unalloyed but in a metallic state, bring new insight as these catalysts show excellent performances for CO and methanol oxidation [8,23,24]. Obviously, the physico-chemical properties of Pt-Ru catalysts strongly depend on the synthesis method and different approaches have been developed for their preparation, either as carbon-supported catalysts (see, for instance, the review by Liu et al. [7]) or unsupported catalysts [22,25–27].

Since the mid-1990s, we have been developing the high energy ball-milling technique combined with a leaching procedure to produce unsupported Pt-based catalysts [28–30]. The high energy ball-milling technique, also called mechanical alloying, is a solid-state method for the synthesis of metallic powders or ceramics. This technique was developed in the 1960s for the synthesis of oxide dispersion-strengthened nickel-based superalloys but it gained a renewed interest in the 1990s for the preparation of nanostructured and metastable materials [31,32]. In the ball-milling process, powder particles are submitted to high energy impacts from balls inside an air-tight crucible. During milling, materials are submitted to intense mechanical deformations, and solid-state reactions are induced at the atomic level. The powder particles are repetitively flattened, fractured and cold-welded until a balance between fragmentation (fracture) and agglomeration (cold-welding) is established [31,32]. Through this process, a structure refinement, a particle size reduction and a homogenous alloy formation are obtained. The resulting materials are strongly influenced by various factors such as the type of miller and crucible, the ball-milling parameters (size and density of balls, ball-to-powder weight ratio, miller speed, milling time), and the temperature and gas atmosphere during milling [31,32].

In the synthesis method implemented in our laboratory, the high energy ball-milling technique performed at or near room temperature has been combined with a leaching procedure in order to obtain unsupported Pt-Ru catalysts of high specific surface area. Hence, Pt and Ru powders are ball-milled along with a dispersive agent such as magnesium hydride or aluminium (with sodium fluoride) [28,29]. After completion of milling, subsequent removal of the dispersive agent by leaching in an acid or alkaline solution leads to a significant increase of the specific surface area from about $1 \, m^2 \, g^{-1}$ (without dispersive agent) up to more than $40 \, m^2 \, g^{-1}$ [29].

In the present investigation, three series of unsupported Pt-Ru catalysts were prepared with the same nominal Pt/Ru bulk atomic ratio of 50/50 but with different ball-milling parameters, such as the ball-to-powder weight ratio and the molecular proportion of dispersive agent added. These variations resulted in different physico-chemical properties, and the specific surface area, crystalline structure and Ru surface oxidation of the resulting materials were determined. Then, all ball-milled Pt-Ru catalysts were evaluated for H_2 oxidation in presence of CO in a PEMFC and for methanol oxidation in a DMFC. Doing

so, it was possible to draw correlations between the physico-chemical properties of the catalysts and their performances in fuel cells, and to determine which are the limiting factors controlling CO tolerance in PEMFC and methanol oxidation in DMFC systems. Finally, the performances of the best ball-milled Pt-Ru catalysts were compared to those obtained with commercial catalysts tested in our PEMFC and DMFC systems.

2. Experimental

2.1. Synthesis of ball-milled Pt-Ru catalysts

Three series of unsupported Pt-Ru catalysts were prepared by combining the high energy ball-milling technique with a leaching procedure implemented in our laboratory [28,29]. In this synthesis procedure, Pt powder (−200 mesh, 99.98% purity (metals basis), Laboratoire MAT) and Ru powder (−325 mesh, 99.95% purity (metals basis), Alfa AESAR) were ball-milled together along with MgH_2 powder (98% purity, ABCR GmbH & Co. KG). MgH_2 was added as a dispersive agent to increase the specific surface area of ball-milled material. It also prevents the sticking of the powders to the crucible walls and grinding balls during milling. Pt, Ru and MgH_2 powders were loaded in a $50 \, cm^3$ WC crucible inside a glovebox under an argon atmosphere. Then, 10 mm diameter WC balls were added in the crucible and it was sealed before being removed from the glove box to be installed in a SPEX 8000M mixer/mill (SPEX CertiPrep, Inc.). The powders were ball-milled for 40 h. The total amount of powders was always 5 g but the atomic/molecular ratio of the powders was varied and the number of balls was adjusted to obtain various ball-to-powder weight ratios. All catalysts were prepared with a Pt/Ru nominal atomic bulk ratio of 50/50. After the completion of milling, the ball-milled material was removed from the crucible and MgH_2 was leached in a 250 ml solution of 1 M HCl magnetically stirred for 4 h. After this step, the remaining material was allowed to settle at the bottom of the flask. The used acid solution was replaced with 250 ml of deionized H_2O for rinsing and was stirred for 20 h. Finally, the rinsed ball-milled Pt-Ru catalyst was recovered by filtering and drying for 1 h in a vacuum oven at $75 \, °C$.

The 1st series of Pt-Ru catalysts was prepared by varying the molecular proportion of MgH_2 while keeping a constant ball-to-powder weight ratio: $R = 4/1$. The various atomic/molecular proportions used were Pt:Ru:MgH_2 = 1:1:x where $x = 2$, 4, 6, 8 and 10. For the 2nd series, the ball-to-powder weight ratios were $R = 4/1$, 8/1, 10/1 and 12/1 for a constant atomic/molecular proportion of Pt:Ru:MgH_2 = 1:1:8. For the 3rd series, the ball-to-powder weight ratios were $R = 4/1$, 8/1 and 10/1 for a constant atomic/molecular proportion of Pt:Ru:MgH_2 = 1:1:6. The synthesis parameters of the three series of ball-milled Pt-Ru catalysts are given in Table 1.

2.2. Physico-chemical characterization of ball-milled Pt-Ru catalysts

Bulk chemical composition of the ball-milled Pt-Ru catalysts was obtained for Pt, Ru and Mg elements from neutron acti-