

High energy ball-milling: Synthesis of nanocrystalline Pt-Ru catalysts for PEMFC and DMFC

M.C. Denis, D. Guay, J.P. Dodelet
INRS-EMT, C.P. 1020, Varennes, QC, Canada, J3X 1S2
and

C. Bock, B. MacDougall
ICPET, NRC, Ottawa, ON, Canada, K1A 0R6

For recent years, Pt-Ru alloys have been used as anode catalysts for oxidation of hydrogen in the presence of CO in PEMFC and for oxidation of methanol in DMFC [1,2]. The high energy ball-milling technique is a relatively simple method of producing alloys and composites with a nanocrystalline or amorphous structure presenting interesting properties for a wide range of applications [3]. This technique can also be used to prepare unsupported electrocatalysts for fuel cells by implementing a subsequent leaching procedure devised to increase the specific area of the ball-milled materials [4].

Typical ball-milled Pt-Ru catalysts present a mixed structure of alloyed Pt nanocrystalline phase (3 nm) and of two unalloyed Ru phases, one with larger crystallites (35-50 nm) and one with nanocrystallites (3 nm). By varying the ball-milling parameters, such as the balls-to-powder weight ratio and the amount of dispersive agent, series of Pt-Ru catalysts were prepared. It was found that the amount of dispersive agent, used for the leaching procedure, mainly influences the specific area obtained by BET measurements of the final catalysts, with values ranging from 13 to 74 m²/g. The balls-to-powder weight ratio largely determines the structure of the Pt-Ru catalysts. Increasing this ratio, hence the intensity of the ball-milling, reduces the weight fraction of the unalloyed Ru phase of larger crystallites. Fig.1 presents XRD diagrams of two samples showing reduction of the intensity of the Ru(101) diffraction peak, associated with the Ru phase of larger crystallites due to its small FWHM.

All unsupported ball-milled Pt-Ru catalysts were evaluated for H₂ oxidation in presence of CO in a PEMFC with an anode loading of 1.0 mg/cm² Pt-Ru. The CO tolerance of these catalysts was evaluated by calculating the relative loss of performance due to the addition of 100 ppm CO in the H₂ feedstream, according to equation 1:

$$\text{Relative loss at } V = \frac{i_{\text{H}_2} - i_{\text{H}_2+\text{CO}}}{i_{\text{H}_2}} \times 100\% \quad (1)$$

Fig. 2 presents the relative loss curves after 20h under H₂ + 100 ppm CO as a function of the cell potential for selected samples demonstrating a large range of CO tolerance for ball-milled Pt-Ru catalysts.

In this work, we will attempt to understand the different fuel cell behaviors of the ball-milled Pt-Ru catalysts on the basis of their structure and of other physico-chemical properties (specific area, surface composition, bulk composition). At first, the influence of the structure of the ball-milled Pt-Ru catalysts on their CO tolerance can clearly be shown. Fig. 3 presents the relative loss of performance at 0.5V and the weight fraction of the crystalline Ru phase (large crystallites) as a function of the balls-to-powder weight ratio. It can be seen that the reduction of the weight fraction of the crystalline Ru phase, obtained by increasing the balls-to-powder weight ratio, leads to lower relative losses, hence an improved CO tolerance of the catalysts.

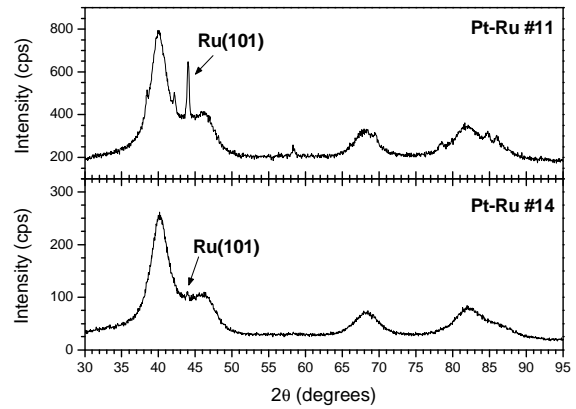


Fig. 1. XRD diagrams of two ball-milled Pt-Ru catalysts prepared with different balls-to-powder weight ratios showing reduction of the intensity of Ru(101) reflection.

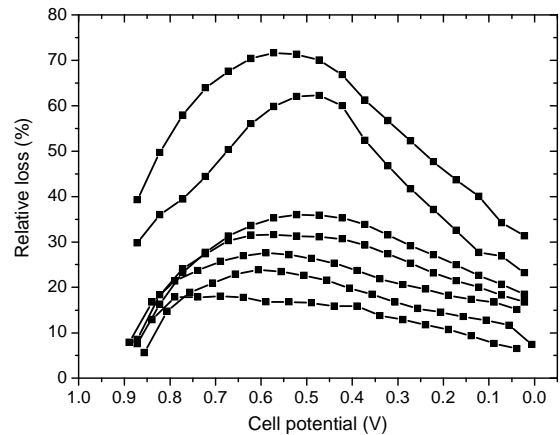


Fig. 2. Relative loss of performance in PEMFC after 20h under H₂ + 100 ppm CO at various cell potentials for selected ball-milled Pt-Ru catalysts.

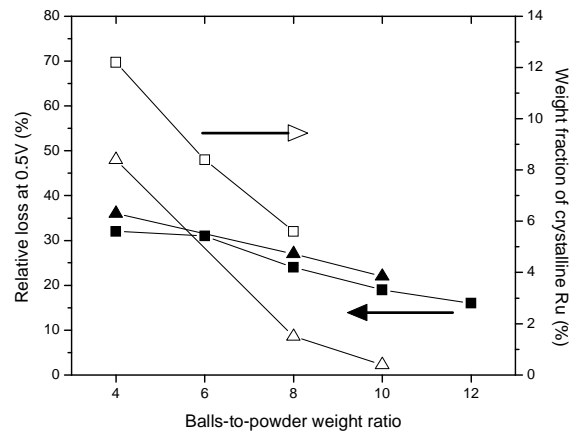


Fig. 3. Relation between the relative loss of performance at 0.5V (dark symbols) and the weight fraction of unalloyed crystalline Ru phase (open symbols) as a function of the balls-to-powder weight ratio for two series of ball-milled Pt-Ru catalysts (squares and triangles).

References:

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