The effect of dose rate on the preparation of PtRu/C electrocatalysts using electron beam irradiation

Dionísio Fortunato da Silva, Almir Oliveira Neto, Eddy Segura Pino, Marcelo Linardi and Estevam Vitorio Spinacé
Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, Av. Prof. Lineu Prestes, 2242, Cidade Universitária, São Paulo – SP, CEP 05508-900
e-mail: dfsilva@ipen.br, espinace@ipen.br

Fuel cells employing alcohols directly as combustible (Direct Alcohol Fuel Cell – DAFC) are attractive as power sources for mobile and portable applications. Methanol has been considered the most promising alcohol and carbon-supported PtRu nanoparticles (PtRu/C electrocatalyst) the best electrocatalyst. In this work the effect of dose rate on the preparation of PtRu/C electrocatalysts using electron beam irradiation was evaluated. PtRu/C electrocatalysts (20wt%, Pt:Ru atomic ratio of 50:50) were prepared using $H_2PtCl_6.6H_2O$ and $RuCl_3.xH_2O$ as metal sources, which were dissolved in water/2-propanol solution 75/25 (v/v). After this, the carbon support (Vulcan XC72R) was dispersed in the solution using an ultrasonic bath. The resulting mixture was submitted under stirring to electron source (Electron Accelerator's Dynamitron Job 188) and the following dose ratios were used: 8 kGy s^{-1} (time of irradiation of 54 s), 16 kGy s^{-1} (time of irradiation of 27 s) and 32 kGy s^{-1} (time of irradiation of 13.5 s), being a total dose of 432 kGy applied. After the irradiation the mixture was filtered and the solid (PtRu/C electrocatalyst) was washed with water and dried. The electrocatalysts were characterized by energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD) and cyclic voltammetry (CV). The electro-oxidation of methanol was studied by chronoamperomety using the thin porous coating technique. In the preparation of PtRu/C electrocatalysts the electron beam irradiation causes the ionization of the water of the reaction medium leading to the formation of species like, aqueous electron (e^-_{aq}) and $H^{\cdot}$ atoms that are strong reducing agents and reduce metal ions to the zero-valent state. On the other hand, $OH^{\cdot}$ radicals are also formed and they could oxidized the ions or the atoms in to a higher oxidation state. Thus, an $OH^{\cdot}$ scavenger was added to the solution, in this case 2-propanol, which reacts with these radicals leading to the formation of radicals with reducing power that are also able to reduced metal ions. The atoms produced by the reduction of metals ions progressively coalesce, leading to the formation of carbon supported PtRu nanoparticles. The Pt:Ru atomic ratio of the produced electrocatalysts determined by EDX were similar to the nominal ones. For all electrocatalysts XRD patterns showed a broad peak at about 25^o, which was associated to the Vulcan XC72R support material, and five diffraction peaks at about $2\theta = 40^o$, 47^o, 67^o, 82^o e 87^o that are associated to the (111), (200), (220), (311) e (222) planes, respectively, of the fcc structure of platinum and platinum alloys. The electrocatalysts also showed similar crystallite sizes of ca. 2.5-3.0 nm. The PtRu/C electrocatalysts prepared with different dose rates showed similar performance for methanol electro-oxidation. This indicates that even at low dose ratio used in this work, it was sufficiently to reduce all metal ions present in the reaction medium in a short period of time.

Acknowledgments: MCT-FINEP Pro-H_2, CNPq and FAPESP