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Ag-nanoparticles improving the electrocatalytic activity of glycerol oxidation reaction in alkaline media

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The development of greener and more sustainable energy sources has become a key focus of research in the technology and environmental sectors, driven primarily by concerns over climate change caused by fossil fuel combustion [1]. Therefore, the use of biofuels, such as glycerol (a byproduct of biodiesel production, generated in excess in Brazil), presents an attractive alternative for applications in fuel cells and for producing higher value-added products [2]. Glycerol electrocatalysis processes are commonly conducted using electrocatalysts based on noble metals, such as Pt and Pd, emphasizing the need for development of cheaper and more abundant materials that exhibit high activity and selectivity in electrocatalytic processes. In this context, the present study investigates the role of oxophilic metals, such as silver (Ag), in the composition of nanoparticulate electrocatalysts containing small amounts of Pd and Au, focusing on glycerol oxidation reactions in alkaline media [3]. Ag/C, AgPd/C, AgAu/C and AgPdAu/C electrocatalysts were synthesized using the chemical reduction method via sodium borohydride [4]. The electrocatalysts were prepared with a metallic load of 45% by mass, with 35–40% consisting of Ag nanoparticles to more significantly evaluate the contribution of silver; and 55% by mass of Vulcan XC-72 carbon. The composition of the electrocatalysts was confirmed through thermogravimetric analysis (TGA) and energy-dispersive spectrometry (EDS). The high-cost metal load (Pd and Au) was verified by ICP-MS, showing values close to the nominal mass ratio of 5%. The diffractograms displayed a broad peak at approximately 25°, attributed to the Vulcan XC-72 support, along with the planes (111), (200), (220), (311), and (222), characteristic of the face-centered cubic (fcc) structure. The mean particle size histograms were generated based on transmission electron microscopy (TEM) images, yielding nanoparticles with sizes of 11.5 ± 6.4 nm for Ag/C, 14.8 ± 4.9 nm for AgAu/C, 8.1 ± 3.2 nm for AgPd/C, and 9.7 ± 8.0 nm for AgPdAu/C. The electrochemical profiles exhibited characteristic Ag peaks, attributed to AgOH as well as a larger and more compact outer hydrous oxide layer [5,6]. The GOR results in KOH (1 mol L^{-1}) showed competitive current densities and less positive oxidation onset potentials for the AgPd/C and AgPdAu/C electrocatalysts compared to the commercial Pd/C, which has a notably higher high-cost metal loading (20% Pd). Furthermore, the best-performing electrocatalyst in the chronoamperometry experiments for GOR was AgPdAu/C, achieving 9 mA cm^{-2}, compared to 7 mA cm^{-2} obtained with the commercial material. Mechanistic studies of GOR using *in situ* FTIR technique revealed that, at potentials of 0.50 V (*vs.* ERH), several bands being developed for all electrocatalysts. The most intense band, centered at 1580 cm^{-1}, is likely associated with the production of formate and/or glycerate, while a very broad band centered at 1400 cm^{-1} corresponds to the generation of CO_3^{2-}, suggesting the cleavage of the C–C bond [7]. Therefore, the contribution of Ag-nanoparticles may be assigned to its oxophilic characteristics, similar to those of Au, which enhance CO tolerance and improve the electrocatalytic activity of the materials through synergistic and electronic mechanisms [3,5].

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