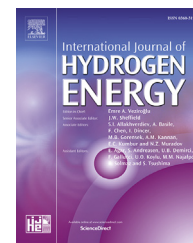


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# Bimetallic Pt-M electrocatalysts supported on single-wall carbon nanotubes for hydrogen and methanol electrooxidation in fuel cells applications

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## ABSTRACT

A series of Pt–Ru and Pt–Mo bimetallic catalysts were prepared via a chemical reduction method by bubbling CO to form carbonyl compounds as metal precursors. In both cases the Pt–Ru and Pt–Mo bimetallic electrocatalysts achieved the maximum activity when the amount of Ru and Mo in the material was 50%wt. The physicochemical characterization of the electrocatalytic materials through X-ray diffraction (XRD) and transmission electron microscopy (TEM) has determined the presence of bimetallic structures. The electrochemical characterization using cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and polarization curves in Proton Exchange Membrane Fuel Cells (PEMFC) and Direct Methanol Fuel Cell (DMFC) allowed to systematically investigate the electrocatalytic activity of the synthesized materials for the electrooxidation of hydrogen and methanol. The Pt–Ru/SWCNT electrocatalysts showed a higher current density at least 7-fold and 3-fold compared with Pt/SWCNT and Pt–Mo/SWCNT electrocatalysts, respectively. Besides, the Pt50%–Ru50%/SWCNT exhibited a shifting to negative values in the onset potential reaction for the electrooxidation of methanol of 200 mV in comparison with Pt100%/SWCNT and Pt50%–Mo50%/SWCNT electrocatalysts. The experimental and simulated polarization curves obtained from DMFC show that Pt–Ru/SWCNT and Pt–Mo/SWCNT electrocatalysts exhibited higher power and current densities values compared with the Pt/SWCNT electrocatalyst. The membrane-electrode assembly (MEA) with Nafion<sup>®</sup> and the Pt–Ru/SWCNT electrocatalysts showed an open-circuit voltage value of 0.730 V, significantly higher than that the values for the MEAs with Pt/SWCNT (0.663 V) and Pt–Mo/SWCNT (0.633 V), respectively.

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## Introduction

Proton-exchange membrane fuel cells (PEMFCs) are electrochemistry systems that convert chemical energy to electrical

energy by means of the combustion of hydrogen, alcohols, hydrocarbons, etc., through the anodic reaction that is catalyzed at the anode where the fuel is inserted, while the oxygen is inserted into the cathode to complete the reaction [1].

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Electrodes are generally porous gas diffusion electrodes to ensure the supply of reactant gases to active zones where the catalyst is in contact with the protonic membrane and the electronic (carbon) conductor. In the cathode, oxygen reduction reaction is normally catalyzed by platinum (Pt), where Pt dispersed on carbon exhibits a good performance. The oxidation reaction depends on the fuel, and the platinum is, in general, a good catalyst for this reaction. The platinum is important for oxidation of pure hydrogen. However, the presence of certain traces of gases such as CO, SO<sub>2</sub>, H<sub>2</sub>S, NO<sub>2</sub>, NH<sub>3</sub> can poison the catalyst, which is particularly relevant in the case of CO for low temperature fuel cells. The CO molecules are prone to be adsorbed on the Pt catalyst surface, causing severe poisoning at low temperatures [2,3]. Several strategies have been used to avoid CO contamination. Previous elimination of CO can be done by water-gas shift conversion of CO into CO<sub>2</sub> hereby producing more hydrogen. This conversion is favored at high temperature, but the equilibrium decreases with the H<sub>2</sub>/CO ratio [3]. A similar strategy is the oxidation of CO by small amounts of air or oxygen, but the presence of the oxidant leads to a decrease in the fuel cell efficiency and raises a safety problem. The purification of the hydrogen before its insertion into fuel cells involves a great energetic cost for fuel cells. Stepwise reforming of hydrocarbons has been proposed for production of CO-free hydrogen for fuel cell applications [4]. The use of Pt alloys or ternary Pt-based catalysts have been widely studied to enhance CO tolerance.

The ability to dissociate the molecule of water at lowest potentials has been associated to ruthenium [5], in consequence, an anode that uses ruthenium can work at low potentials to obtain higher cell voltages only by re-formulating the Pt-based electrocatalysts [5]. Also, the use of a second metal as molybdenum has been reported to reduce the drawbacks associated to the CO adsorption on platinum electrocatalytic sites [6], because the effect of molybdenum is similar to that of ruthenium concerning the dissociation of water to produce OH<sup>-</sup> anions on their surface. These OH<sup>-</sup> anions contribute to the oxidation of adsorbed species like CO carrying out their oxidation to CO<sub>2</sub> [7–9]. Some authors have proposed that the increase in the tolerance for CO poisoning in the Pt–Mo electrocatalyst is due to the oxygenated species formed by the molybdenum (MoO(OH)<sub>2</sub>) [10,11]. This species promotes the CO oxidation, which suggests that the increase in CO tolerance is achieved through a bifunctional mechanism [12]. Thus, there is a great interest in the study of Pt–M electrocatalysts, and the compositions studied include Pt–Ru [13–16], Pt–Mo [11,17,18], Pt–Ru–Mo [19] or Pt–Ru–X (X = Mo, Nb, Ta) [20]. Pt–Ru catalysts have been extensively used in direct methanol fuel cells (DMFC) [21]. CO is an intermediate specie in the methanol electro-oxidation and can occupy the active sites of the catalyst, resulting in slow reaction kinetics. With the use of ruthenium-platinum alloys the oxidation kinetics of methanol has improved significantly reaching a practicable level.

The majority of experimental studies focus the preparation of the electrocatalysts using carbon as support though of colloid based or different methods of impregnation [22,23]. However the use of surfactant remains on the surface of the method colloid and hinders the fuel access to the catalyst sites [24]. The physics of carbon nanotubes have evolved rapidly

since their discovery in 1991 of multi-wall carbon nanotubes and two years later the single-wall by Iijima [25]. Since then experimental studies have focused on different fields such as mechanics, optics and electronics due to excellent physical properties in various applications [25,26]. From then carbon nanotube (CNT) based materials are been intensively studied due to a number of novel and unique properties that make them potentially useful in a wide range of applications. CNT layers offer outstanding properties like excellent flexibility, optical transparency, high electrical conductivity, extremely small weight, and low processing cost [27]. Single-walled carbon nanotubes can be described as a sheet of graphite that is rolled generating a cylindrical figure resulting in a structure in one dimension with axial symmetry. The diameters of single-walled carbon nanotubes lie in a range of 0.7–10.0 nm [28]. The structure of the CNT depends on the orientation of the hexagons in the cylinder with respect to the axis of the tube. As consequence of the orientation CNT have attracted much interest because they can former essentially one-dimensional periodic structures with electronic characteristics (metallic or semiconductor) and could be interesting to prepare MEAs using appropriate inks for fuel cells applications.

For their application, the catalysts are deposited on Gas Diffusion Layer (GDL), which permit the access of the combustion reactants to the catalysts and the electronic conduction. GDL are normally carbon. The proton-exchange membrane is placed between the anode and the cathode and is used as an electrolyte. Nafion<sup>®</sup> is the most studied and operated electrolyte for PEMFC's at low temperatures, having a sulfonated poly-tetrafluoroethylene polymeric structure. This membrane usually has a small temperature range in which it is stable. The upper limit of temperature is dictated by the humidification of the membrane, as water is a prerequisite for proton conduction.

In this work, we report the synthesis of Pt–Ru and Pt–Mo electrocatalysts supported on single-wall carbon nanotubes (SWCNT) for the electrooxidation of methanol and hydrogen in a proton-exchange membrane fuel cell (PEMFC). The characterization of the electrocatalytic materials was carried out by X-ray diffraction (XRD) and transmission electron microscopy (TEM) in order to determine the presence of a bimetallic structure. The electrochemical characterization was achieved using cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and polarization curves in PEMFC and DMFC in order to systematically investigate the electrocatalytic activity of the synthesized materials for the electrooxidation of hydrogen and methanol.

Furthermore, the experimental results obtained in PEMFC and DMFC were compared with the theoretically calculated parameters obtained by the use of the thermodynamic equations describing the behavior of the system and the resistance in the fuel cell arrangement.

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## Experimental

### Synthesis of Pt–M bimetallic electrocatalysts

Metallic platinum was obtained from a precursor of H<sub>2</sub>PtCl<sub>6</sub> that after weighing the desired amount was dissolved in 20 mL

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