

Fundamental and applied aspects of ethanol electro-oxidation

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Over the last 2 decades much effort has been done in order to develop the technology necessary to ensure an efficient use of energy sources specially that deriving from the renewable ones. Fuel cells are intended to be a clean source of energy. Direct Alcohol Fuel Cells (DAFC) have called the attention of researchers all over the world in the last years, due to the possibility of using alcohols obtained from the fermentation of different sources of biomass, such as ethanol (e.g. from sugar cane juice fermentation). Ethanol is an interesting candidate to operate a DAFC due to its low toxicity and the higher electron efficiency that could be achieved if C–C bond breaking route is followed. Unfortunately, direct ethanol fuel cells (DEFCs) are still presenting power densities and efficiencies below the required for commercialization. This is, basically, because of the complexity of the oxidation reaction network and the high energy barrier for C–C bond breaking, a reaction step that is important for achieving the maximum number of electrons per alcohol molecule (12 e⁻). In order to provide some insight into fundamental aspects of electro-oxidation mechanism of ethanol and applied aspects of fuel cells, different model surfaces will be discussed in this communication.

In terms of fundamentals aspects, the ethanol electro-oxidation reaction will be discussed on platinum single crystals and on modified polycrystalline gold surface by sub-monolayer of platinum. This modified Au surfaces serve as model that allow the understanding of the behavior of core-shell nanoparticles.

Another important point to be focused in this presentation is the influence of the acetic acid formed in the course of the ethanol electro-oxidation reaction. Using cyclic voltammetry, chronoamperometry and in-situ FTIR it was demonstrated that an inhibition of the ethanol oxidation occurs for bulk acetic acid concentration as low as 0.1 μmol L⁻¹. This effect is related to the decrease of CO₂ and acetaldehyde production due to a blocking of the platinum active sites and/or to the decrease in the number of oxygen containing species available for further oxidation of adsorbed residues that become from the dissociative chemisorptions of ethanol.

The applied aspects of direct ethanol fuel cells (DEFC) will be also discussed. Binary PtSn and ternary PtSnM (M = Ir, Mo, W, etc) electrocatalysts on carbon Vulcan XC-72 in various compositions will be focused. These catalysts, characterized by TEM, XRD, EDS, EXAFS, etc, consist of a solid solution formed between the constituting elements. Moreover, the increases of Sn loading promote phase separation and form the characteristic peaks of cubic Pt₃Sn. FTIR and HPLC were used to determine the oxidation reaction intermediates and products. The ethanol oxidation on these catalysts led mainly to acetaldehyde, acetic acid and small amounts of CO₂. Adsorbed intermediate as CO_L and CO₂ were also observed by FTIR. The presence of CO and CO₂ species in small amounts suggest the possible rupture of the C–C bond during the ethanol oxidation on this class of catalysts.

Pt_{0.9}Sn_{0.1}/C composition produced the largest

power density in a complete fuel cell. Single DEFC tests carried out using a membrane electrode assembly (MEA) with electrode geometric area of 5 cm², prepared by hot pressing a pre-treated Nafion® 117 membrane, allowed to produce a power density of *ca.* 72 mW cm⁻² at 110 °C. In general, the presence of tin was necessary to activate the catalyst and convert CO to CO₂ at lower potentials than those observed on Pt-alone.

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