

The Electrocatalytic Oxidation of Ethanol in a Proton Exchange Membrane Electrolysis Cell (PEMEC): a way to produce clean hydrogen

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Ethanol, which is easily produced by the fermentation of biomass products (sugar cane, corn, grain, beetroot, ligno-cellulosic wastes, etc.) is an alternative fuel to feed a fuel cell [1, 2]. Its liquid state (which allows an easy storage) with a low toxicity and its large availability in many countries (Brazil, USA, Spain, France, etc.), together with its high energy density for complete oxidation to CO₂ (8 kWh kg⁻¹ compared to 11 kWh kg⁻¹ for gasoline) are important positive points for its use as a fuel [3].

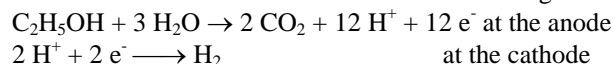
The direct oxidation of ethanol in a Polymer Electrolyte Fuel Cell (PEFC) is more difficult to realize than that of methanol with the necessity of breaking the C-C bond to obtain its complete oxidation to CO₂. The electrocatalytic reaction has been the subject of numerous studies on several Pt-based electrodes, including Pt-X alloys (with X = Ru, Sn, Mo, etc.) and dispersed nanoparticles [4, 5]. From these studies it appears that breaking the C-C bond at relatively low temperatures (80 to 120°C) is still a challenge, since the main reaction products are acetaldehyde and acetic acid together with a small amount of CO₂. Besides, particularly on smooth Pt electrodes, some adsorbed CO species are formed, which block the active sites, as shown by "in situ" IR reflectance spectroscopy [6]. It turns out that a Direct Ethanol Fuel Cell (DEFC) gives electrical performance one order of magnitude lower ($P_{\max} < 0.1 \text{ W cm}^{-2}$) than that obtained with a Proton Exchange Membrane Fuel Cell (PEMFC) fed with pure hydrogen ($P_{\max} \approx 1 \text{ W cm}^{-2}$).

Therefore another approach is the electrochemical decomposition of biomass compounds (instead of water) to produce very clean hydrogen and to feed a PEMFC. This seems to be very promising, since the theoretical cell voltage for the electrochemical decomposition of such compounds with hydrogen production is lower than the theoretical cell voltage of water electrolysis (1.23 V under standard conditions). Several organic feedstocks from biomass resource, like alcohols, carboxylic acids, sugars, etc., have been considered as sources of hydrogen, but relatively few works could be found in the literature on the electrochemical decomposition of organic compounds [7]. In particular, methanol [8, 9], ethanol [10], and formic acid [11] have been considered for hydrogen production through their electrolysis.

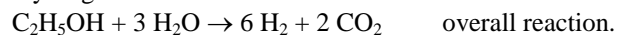
If most of the electrochemical decomposition reactions of these compounds have a low cell voltage (under standard conditions) which may lead to lower energy consumption (compared to water electrolysis at 1.23 V, i.e. 33 kW/kg under standard conditions) they lead usually to larger cell voltages, under working conditions, due to high anodic overvoltages. Thus the challenge is to

develop very active electrocatalysts able to work under the acidic condition of a PEMEC.

In an electrolysis cell based on a Proton Exchange Membrane Fuel Cell (PEMFC) and fed with ethanol the electrochemical reactions involved are the following :



leading to the electrochemical decomposition of ethanol to hydrogen :



In this communication we will discuss the feasibility of the production with high rate of clean hydrogen by the electrolysis of ethanol in a Proton Exchange Membrane Electrolysis Cell (PEMEC). Different Pt-based catalysts have been investigated for the anodic oxidation of ethanol leading to high reaction rates at relatively low overvoltages, of the order of 0.8 to 0.9 V at 100 mA cm⁻², as experienced in a Direct Ethanol Fuel Cell [12]. Similar Pt-based electrocatalysts were prepared according to a way derived from the Bönemann method [13] and were used for the electrochemical decomposition of ethanol in a PEMEC: monometallic Pt/C, bimetallic Pt₉₀Sn₁₀/C and trimetallic Pt₈₆Sn₁₀Ru₄/C catalysts. After their characterization by physicochemical methods (TEM, HRTEM, EDX, XRD, etc.), the electrochemical activity of these catalysts towards the electro-oxidation of ethanol was investigated by cyclic voltammetry.

Then membrane electrode assemblies (MEAs) were prepared with these anodic catalysts using a Nafion 117 membrane, and a Pt/C cathode (40% Pt loading on Vulcan XC-72). MEAs were mounted in a PEMFC structure and the electrolysis cell was operated at room temperature, ambient pressure and under controlled constant applied electrical currents. The cell voltage vs. current density curves were recorded and the exhaust gas from the cathode was analysed. The hydrogen evolving rate was measured simply by gas replacement in a graduated test tube containing initially water.

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