

# How bimetallic electrocatalysts does work for reactions involved in fuel cells?

## Example of ethanol oxidation and comparison to methanol

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### Abstract

Carbon-supported Pt-based nanosized electrocatalysts can be synthesized for methanol and ethanol electrooxidation. The electrocatalytic activity of Pt can be greatly enhanced by using Pt-Ru/C for methanol oxidation or Pt-Sn/C for ethanol oxidation. In situ IR reflectance spectroscopy is a convenient tool to better understand the importance of the different adsorption steps involved in the mechanisms of electrooxidation. With Pt/C, it appears clearly that linearly adsorbed CO is the poisoning species formed during methanol and ethanol oxidation. In the case of methanol, even with Pt-Ru/C (the most active catalyst), adsorbed CO is also a reactive intermediate. The enhancement of activity observed in such a case is due to the possibility to activate water at lower potentials in the presence of Ru. With Pt-Sn/C, the mechanism of the electrooxidation of ethanol is strongly modified. If at low potentials, poisoning with adsorbed CO still exists (as with Pt/C), the oxidation of ethanol at potentials greater than 0.4 V versus RHE occurs through an adsorbed acetyl species which can lead to the formation of acetaldehyde and acetic acid as final products in addition to carbon dioxide.

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### 1. Introduction

While pure hydrogen or a hydrogen-rich gas as fuel in a Polymer Electrolyte Membrane Fuel Cell (PEMFC) allows to obtain higher electric efficiency than alcohols, its production, storage and distribution are still a strong limitation for the development of such techniques [1–2]. In this context, the use of hydrogen carrier like alcohols in a Direct Alcohol Fuel Cell (DAFC) appears then advantageous for two main reasons: they are liquids (easy storage) and their theoretical mass energy density is rather high, 6.1 and 8.0 kWh/kg for methanol and ethanol, respectively [3].

The improvement of the performances of DAFC needs a deep understanding of the mechanisms of the electrocatalytic reactions involved. The case of alcohols (mainly methanol and ethanol) have been often considered [4–10], but as the consequence of the acidic environment of the ionomeric conducting membrane, a rather poor kinetics of electrooxidation is observed with platinum, which is impossible to circumvent for its properties to initiate the C–H bond cleavage during the first adsorption steps. The increase of the overall kinetics can be obtained only by using at least bimetallic platinum-based electrocatalysts. Each component of the catalyst plays a key role during a specific step of the mechanism.

Methanol [11–14] and ethanol [15–17] are the most studied alcohols for DAFC application. Methanol is adsorbed with the formation of poisoning species (adsorbed carbon monoxide). On other hand, due to the chemical structure of

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ethanol, its electrooxidation is difficult because of the necessity of a cleavage of the C–C bond to form the final product (carbon dioxide). However, even if the breaking of the C–C bond is difficult, adsorbed CO is observed for example by in situ infrared reflectance spectroscopy. In both cases, the formation of such poisoning species leads to a poor activity, and the challenge is to enhance the activity of platinum. This is the aim of the use of bimetallic and plurimetallic electrocatalysts.

The aim of this paper is to show how it is possible to influence greatly the catalytic activity for alcohol electrooxidation. The choice of the second metal (to be added to platinum) is the key issue. This choice can be made only when the mechanism of the electrocatalytic reaction is sufficiently understood. This elucidation can be obtained only when a detailed study of the reaction is carried out mainly with spectroscopic methods under electrochemical conditions. When some key steps are identified, it is conceivable to propose the modification of platinum catalysts. However, the preparation of bimetallic electrocatalysts is also a key issue in relation to the necessary limitation of amount of platinum contained in electrodes. Synthesis of stable nanoparticles containing two metals is a hard work, depending greatly on the nature of the metals involved.

New results obtained mainly by IR in situ reflectance spectroscopy are discussed for the electrooxidation of ethanol on Pt/C, PtSn/C and PtRuSn/C. A reaction mechanism can be then proposed and compared to the case of the oxidation of methanol on Pt/C and PtRu/C. The importance of the modification of Pt electrocatalysts by at least a second metal will be emphasized.

## 2. Experimental

### 2.1. Preparation of carbon-supported Pt-based electrocatalysts

Pt and Pt-based particles were prepared from colloidal precursors and dispersed on carbon powder (Vulcan XC72). The technique used is based on the well known “Bönneman” method [17–19]. The colloid precursor is first synthesized under an inert atmosphere from anhydrous metallic salts in an organic solvent (THF) in the presence of a surfactant (typically a quaternary ammonium salt). The role of this surfactant is essential as it prevents the agglomeration of the metallic particles during the reduction step and allows the formation of particles in the nanometric size range.

The Pt-based nanoparticles are obtained by a similar technique using a co-reduction of the different metallic salts. The precursors are then adsorbed on the carbon powder and the surfactant is removed by thermal treatment. This step is important and the temperature used is crucial to avoid sintering of the metallic particles. Typically, 300 °C is the optimal temperature for such a process.

Electrodes were prepared from ink made from the carbon-supported catalyst and a Nafion<sup>®</sup> solution according to a method described elsewhere [20–22]. For cyclic voltammetry (CV) and in situ IR reflectance measurements, this ink is deposited on a vitreous carbon disk and, after evaporation of the solvent at room temperature for several hours; the electrode is ready to be used for the experiment.

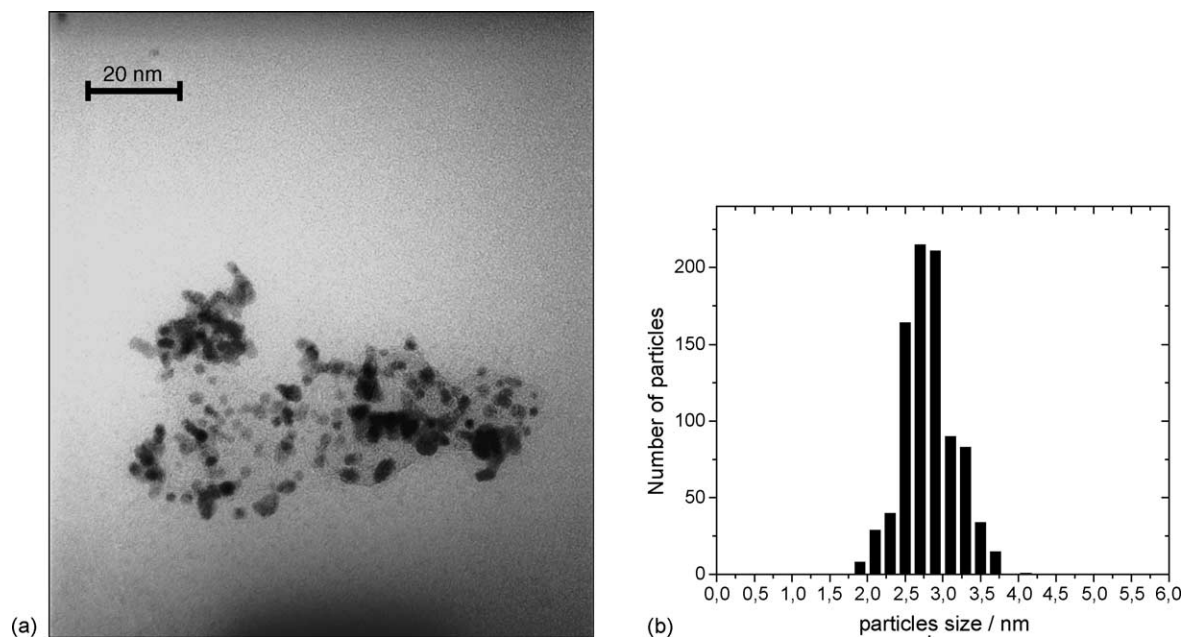


Fig. 1. Physical characterization of a 60% Pt-Sn (90:10)/C catalyst. (a) TEM image and (b) particle size distribution.

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