



Tailoring properties of platinum supported catalysts by irreversible adsorbed adatoms toward ethanol oxidation for direct ethanol fuel cells



Marta C. Figueiredo^a, Annukka Santasalo-Aarnio^a, Francisco J. Vidal-Iglesias^b, José Solla-Gullón^b, Juan M. Feliu^b, Kyosti Kontturi^a, Tanja Kallio^{a,*}

^a Fuel Cell Research Group, Department of Chemistry, School of Chemical Technology, Aalto University, FI-00076 AALTO, Finland

^b Instituto Universitario de Electroquímica, Universidad de Alicante, Apt 99, 03080 Alicante, Spain

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ABSTRACT

In this work ethanol oxidation on carbon supported Pt catalysts modified with irreversibly adsorbed adatoms is reported. This study concerns understanding of the effect of a second metal on real catalysts in conditions as close as possible to those applied in fuel cells systems. The results were acquired using cyclic voltammetry, chronoamperometry and *in situ* infra-red techniques always taking into account the future application of the electrocatalyst materials in fuel cells. Foreign adatoms, both Bi and Sb, irreversibly adsorbed on a Pt electrode were studied, and revealed to enhance catalytic activity toward a more efficient ethanol oxidation. The catalytic enhancement continuously increased with the coverage of the adatom on the surface up to coverages close to saturation. With these high coverages a decrease of the activity was observed suggesting that free platinum atoms are required to oxidize ethanol. The results suggest that the adatoms play a third body role avoiding the poisoning of the Pt sites that will then be free for oxidizing ethanol. However, electronic effects on Pt/C–Bi and bifunctional mechanism at Pt/C–Sb are also suggested. The oxidation products were identified by *in situ* FTIR and are mainly acetaldehyde and acetic acid for the three catalysts. CO₂ was also observed for the unmodified Pt/C and interestingly for the Pt/C–Sb electrodes.

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1. Introduction

The direct alcohol fuel cell (DAFC) has emerged in the last decades as a promising alternative power source for portable applications. The biggest advantages of the use of alcohols as fuels instead of hydrogen are their easy storage (liquid state) and high theoretical mass energy density [1,2]. The most studied alcohol for these applications has been methanol. However, ethanol offers an attractive alternative due to its lower toxicity and a possibility to be produced in large quantities from biomass. Nevertheless, the direct ethanol fuel cells (DEFCs) have also encountered some difficulties associated with their low efficiency due to the incomplete oxidation to CO₂.

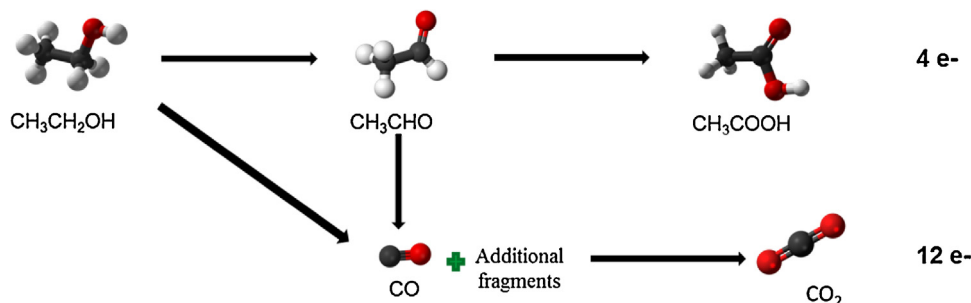
Electro-oxidation of ethanol can occur by different reaction pathways (Scheme 1). If the reaction is complete and CO₂ is the final product twelve electrons per molecule are produced, which is two times that produced by complete oxidation of methanol, for example. However, some pathways lead to the formation of

partially oxidized products (as acetaldehyde and acetic acid) due to the difficulty of breaking the C–C bond. These intermediates subsequently desorb from the surface and do not undergo further oxidation resulting in loss of efficiency.

Acetaldehyde and acetic acid have been found as the major products of ethanol oxidation in a wide range of catalysts [3] which limits the potential performance of the fuel cell. In addition, the formation of acetic acid is not desired in a fuel cell because it also causes local changes in the pH of the anode decreasing the membrane life time. By these reasons further investigation to understand the reaction mechanism and to find more efficient catalysts that can promote the total oxidation of ethanol to CO₂ are required.

One efficient way to induce new catalytic properties is the use of bimetallic surfaces. Materials, such as PtSn [4], PtRh [5], and PtRu [1,6,7], have been widely used for ethanol oxidation and in many cases the improvement of the reactivity is noticeable. One simple way to produce bimetallic surfaces is by irreversible adsorption of adatoms on the Pt surface. Many elements of the sp group can be spontaneously adsorbed on the Pt surface just by putting it in contact with a solution containing the respective salt. These surfaces are normally stable in a large potential range. A successful example

* Corresponding author. Tel.: +358 505637567; fax: +358 947022580.
E-mail address: Tanja.kallio@aalto.fi (T. Kallio).



Scheme 1. Proposed mechanisms for ethanol oxidation on Pt.

of the enhancement of the catalytic properties of platinum surfaces by the deposition of irreversible adsorbed adatoms was found on the oxidation of formic acid [8,9], methanol [10] and also ethanol [11–13] at Pt single crystals. These reactions also proceed through a dual-path mechanism. Adatom modification can affect each of these pathways independently, the effect normally sought being inhibition of the poisoning reaction and enhancement of the direct oxidation reaction.

In this work we report the use of carbon supported platinum nanoparticles modified by irreversible adsorption of Bi and Sb for ethanol oxidation. The experiments were performed and results obtained in very similar conditions to those that would be applied in fuel cell tests, aiming to obtain useful information about activity and durability of the catalyst for further *in situ* applications. Moreover, the reaction products and intermediates were examined by *in situ* infrared spectroscopy. The main products found on the modified electrodes were acetaldehyde and acetic acid. Although these are not the desirable products for fuel cell applications, here is demonstrated that platinum catalysts properties can be tailored by simple and easy to do methods, favoring the reaction toward one of the many possible paths. However, the lower poisoning rate was demonstrated for these catalysts in both the cases. This is definitely an advantage for fuel cells application. Nevertheless, the understanding of the reactions is one of the most important steps for the design of new catalysts.

2. Experimental

The synthesis of the nanoparticles supported on carbon (20 wt%) was done as described in a previous report [14]. Very briefly, sodium citrate, H₂PtCl₄ and sodium borohydride were used as stabilizer, metallic precursor and reducing agent, respectively. After the reduction step, the carbon Vulcan XC-72R was added under fast stirring, alternating both magnetic and ultrasonic for about 2 h, in order to properly disperse the hydrophobic carbon in the water solution, and also to favor the homogeneous adsorption of the nanoparticles on the solid surface. Once the nanoparticles were adsorbed on the carbon surface, some NaOH pellets were added to the mixture, in order to precipitate the solid, and the synthesis mixture was left to stay overnight. After complete precipitation, the sample was filtered and rinsed, at least 4–5 times, with ultra-pure water to make sure that a clean sample, without any reactant adsorbed on the surface, was obtained.

The mean size of the particles was about 2.2 ± 0.5 nm measured by transmission electron microscopy (TEM). These experiments were performed with a JEOL JEM-2010 microscope working at 200 kV (Fig. 1). The sample for TEM analysis was obtained by placing a drop of the dispersed solution onto a Formvar-covered copper grid and evaporating it in air at room temperature.

An ink for the electrochemical experiments was prepared using 5 mg of carbon supported Pt catalyst, 20 μ l of Nafion[®] solution (5 wt% Aldrich) and 200 μ l of ethanol (p.a., Altia) that were

carefully mixed with a magnetic stirrer and an ultrasonic bath. The experiments were performed in a classical three electrode cell at controlled temperature of 20 °C and under nitrogen purge (5.0 from AGA gases). A platinum coil was used as counter electrode and a reversible hydrogen electrode as a reference. The working electrode was prepared by deposition of 4 μ l of the ink onto a glassy carbon electrode (0.1963 cm² of geometric area) previously cleaned by polishing with an alumina solution and putting in the ultrasonic bath. The electrodes prepared with this procedure will have a Pt loading of ~ 0.02 mg. The experiments were performed with a potentiostat/galvanostat PGSTAT100 Autolab system and a rotating device from Pine Instruments.

The electrochemical characterization and cleaning of the carbon supported Pt nanoparticles was performed in a 0.1 M H₂SO₄ solution at room temperature. Following the procedure previously described [15], prior to the use of the nanoparticles for ethanol oxidation, they were cleaned by CO adsorption and stripping, after which the base voltammograms were recorded in 0.1 M H₂SO₄ not only to calculate the real surface area of the catalyst but also to assess the surface cleanliness by simple examination of the voltammograms [16]. The active surface area of the Pt nanoparticles was determined by the charge involved in the so-called hydrogen UPD region assuming 0.23 mC cm⁻² for the total charge after the subtraction of the conventional current attributed to double layer charging contribution [16].

The adatom layer was adsorbed on the electrode surfaces by putting it in contact with a 0.1 M H₂SO₄ solution containing 10⁻⁵ M of the correspondent salt (Bi₂O₃ or Sb₂O₃) at open circuit. The electrode was then rinsed with ultra-pure water and transferred to the cell containing the supporting electrolyte (0.1 M H₂SO₄) where the voltammogram was recorded.

The surface coverage of the adatoms was measured according with previously reported methods ([17] for Bi and [18] for Sb). Different coverages were obtained by different immersion times and different adatom concentrations on the acidic solution. Then the electrode was transferred to the electrochemical cell containing 1 M of ethanol in 0.1 M HClO₄ where the catalysis was evaluated. The stability of the modified electrode was achieved by comparing the blank CV after ethanol oxidation with the one obtained before (no significant differences were found for both Bi and Sb).

As usual [7,17] Fourier-transform infrared spectroscopy (FTIRS) experiments were performed with a Nicolet Magna 850 spectrometer, equipped with an MCT detector. The spectroelectrochemical cell was provided with a prismatic CaF₂ window beveled at 60°. Spectra shown are composed of 100 interferograms collected with a resolution of 8 cm⁻¹ and p-polarized light. They are presented as absorbance, according to $A = \log(R/R_0)$, where R and R_0 are the reflectance corresponding to the single beam spectra obtained at the sample and reference potentials, respectively. All the spectroelectrochemical experiments were conducted at room temperature, with a reversible hydrogen electrode (RHE) and a platinum wire used as the reference and counter

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