



High selectivity of ethanol electrooxidation to carbon dioxide on platinum nanoparticles in low temperature polymer electrolyte membrane direct ethanol fuel cell

Jakub Seweryn, Adam Lewera*

Department of Chemistry, University of Warsaw, ul. Pasteura 1, 02-093 Warsaw, Poland

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ABSTRACT

Products of ethanol oxidation on Pt/C nanoparticles in low temperature, polymer electrolyte membrane direct ethanol fuel cell are determined qualitatively and quantitatively in broad range of cell voltages and temperatures. Despite the fact that platinum is one of the most popular anode systems studied, comparable literature data are severely limited due to the broad unawareness of the oxygen permeation process occurring in fuel cells. Correction for oxygen crossover from cathode compartment allowed us also to correlate our results to general mechanism of ethanol electrooxidation, determined based on ex situ spectroscopic analysis, as available in literature. We also determined that for certain conditions on platinum anode, in low temperature polymer–electrolyte membrane direct ethanol fuel cell, ethanol is oxidized to carbon dioxide with very high (ca. 82%) selectivity. Conditions required for obtaining the reported selectivity are presented and discussed.

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1. Introduction

Process of electrocatalytic oxidation of ethanol on platinum and platinum-group metals has long attracted the attention of many research groups [1–17]. Several approaches have been used to understand the mechanism of electrocatalytic oxidation of ethanol, using broad array of methods, such as IR [6,7,8,15], Raman [18,19] and sum-frequency generation spectroscopy [20–23], mass spectrometry [4,7,13,15] or radiometric [17,22] usually with control of electrode potential. Also in situ tests in working direct ethanol fuel cells (DEFC) were performed [24–31]. Still, the results obtained in fuel cell tests are to some point contrary in regards to distribution of products of ethanol oxidation.

It is generally accepted, that for complete oxidation of ethanol, adsorbed OH groups are needed [1], although they cannot be formed on Pt surface at low electrode potentials to the extend sufficient for creating the significant amount of acetic acid and carbon dioxide. Consequently at low electrode potential virtually no acetic acid (or adsorbed acetyl groups) was found using spectroelectrochemical methods [8,23].

But in case of DEFC experiments with platinum anode there are numerous observations of presence of acetic acid in anode outlet stream, which is contrary to the published ex situ data

[8,23]. We have previously provided evidence that this discrepancy can be attributed to chemical oxidation of ethanol by oxygen permeating from cathode side [32,33]. Those preliminary results were focused on oxygen permeation process thus were limited to three distinct temperatures and cell voltage equal or higher than 300 mV. To the best of our knowledge to this time only Nakagawa et al. have presented oxygen-permeation corrected distribution of products of ethanol electrooxidation for Pt/C, PtRu/C and PtRuRh/C DEFC anodes, but limited to 80 °C and cell voltages lower than 200 mV [34]. Here we show a much broader range of both, cell voltage and temperature, covering the common conditions of working DEFC, and limited only by the intrinsic properties of the system studied, which allowed us to comment on distribution of products of ethanol electrooxidation on platinum in working DEFC.

We have also determined the conditions required to oxidize ethanol in DEFC mainly to carbon dioxide, which is an important factor for improvement of efficiency of DEFC. Carbon dioxide is a product of total, 12-electrons oxidation of ethanol, and selective oxidation to carbon dioxide is a prerequisite for construction of highly-effective direct ethanol fuel cell.

2. Experimental

All chemicals were of analytical grade and were used without further purification. MilliQ (18 MΩ cm) water was used in preparation of electrolytes for electrochemical experiments and ethanol

* Corresponding author. Tel.: +48 22 822 0211x524; fax: +48 22 822 0211x524.
E-mail address: alewera@chem.uw.edu.pl (A. Lewera).

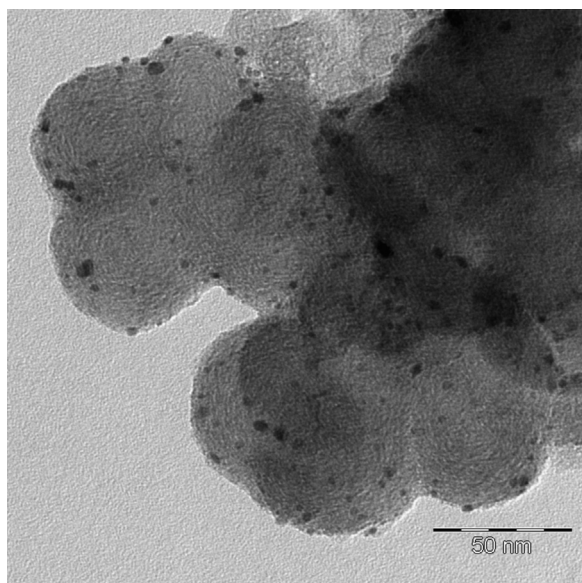


Fig. 1. TEM image of Pt/C catalysts prepared using impregnation–reduction method. Average particle size: 4 nm, metal loading: ca. 18 wt.%.

solution. High purity (N5.2) gases from Air Products were used to deaerate ethanol solutions (Ar) and as a cathode gas (O₂).

2.1. Catalyst preparation and morphology analysis

Pt/C catalyst has been prepared using impregnation–reduction method; detailed description can be found elsewhere [35]. In short, after treatment in aqua regia carbon sample has been mixed with H₂PtCl₆ solution to obtain desired metal loading and reduced in flow of hydrogen/argon mixture at 150 °C. Metal content was ca. 18% by weight. This procedure resulted in uniformly distributed Pt nanoparticles (size ca. 4 nm) on carbon substrate (Fig. 1). Transmission electron microscopy (TEM) imaging was performed using TEM Libra 120 (Zeiss).

2.2. Electrochemical investigation

For electrochemical experiments 10 μl of Pt/C catalyst's suspension in mixture of ethanol, water and Nafion® was placed on gold disk (diameter 3.6 mm), left to dry and used as a working electrode [35]. Catalyst's suspension used consisted of 4.5 mg of catalyst, 280 μl of water, 200 μl of ethanol and 20 μl of 5% Nafion solution in ethanol. Mass of dried deposit was about 120 μg. Cyclic voltammetry experiments were performed in aqueous solutions of: (a) sulfuric acid (0.5 mol dm⁻³) and (b) ethanol in sulfuric acid, (both 0.5 mol dm⁻³). All electrode potentials were registered versus Hg/Hg₂SO₄/0.5 M H₂SO₄ reference electrode and later recalculated versus RHE. PINE Instrument AFRDE5 bipotentiostat was used with National Instruments NI DAQ 6211 data acquisition card. Voltammograms have been normalized using the charge associated with hydrogen adsorption, assuming the charge of 210 μC cm⁻².

2.3. Fuel cell experiments

For fuel cell experiments, Nafion® 117 membrane was painted in the center with prepared catalysts' suspension on one side as anode, and 40% Pt/C (BASF/ETEK) on the other side as cathode, to obtain a square (area 10 cm²). Loading of anode and cathode side was approximately 1 mg(metal)cm⁻². When dry, each side was covered with pre-cut carbon paper squares and hot-pressed. Fuel cell hardware from Fuel Cell Technologies INC, consisting of two

graphite plates with single serpentine flow pattern (10 cm² active area) was used. The flow of oxygen at cathode side was maintained at 15 sccm s⁻¹ while fuel (0.2 mol dm⁻³ of ethanol in water) was fed at approximately 1 cm³ min⁻¹ rate. Fuel flow rate used has been pre-optimized to obtain: (i) relatively high concentration of products of ethanol oxidation in anode outlet stream, which increases the precision of determination of acetaldehyde and acetic acid concentration, (ii) to avoid fuel starvation conditions. In general the fuel utilization at this flow rate was not exceeding 10%. Flow rate has been kept stable to allow for assessing the carbon dioxide production rate from charge balance.

Ethanol solution was thoroughly deaerated (purged with Ar gas) before and during introducing it to the fuel cell. Fuel cell was operated at 60, 70, 80 and 90 °C and numerous cell voltages (from OCV to 100 mV, separated by 50 mV). Cell voltage and current were controlled using EG&G Princeton Applied Research 362 Scanning Potentiostat with National Instruments NI DAQ 6009 data acquisition card. More details can be found elsewhere [35].

To avoid misunderstanding, electrode (anode, cathode or working electrode) potential is always referred to as “anode potential”, “electrode potential” etc. Fuel cell voltage is always referred to as “cell voltage”.

Products of ethanol oxidation were sampled from the port, located directly at the anode outlet, then introduced to Hewlett Packard 5890 Series II Gas Chromatograph (GC) equipped with Flame Ionization (FID) and Mass Selective detectors, which allowed for separation and qualitative and quantitative determination of the components of the mixture leaving fuel cell. GC setup has been calibrated prior to the experiment. The response of FID detector to different concentration of ethanol, acetaldehyde and acetic acid in test samples has been determined and used to minimize the possible errors in quantitative analysis. The overall error of quantitative determination of ethanol, acetaldehyde and acetic acid has been well below 1%. Acetic acid and acetaldehyde formation rate was calculated from gas chromatography results, geometric fuel cell active area and fuel flow rate. Amount of CO₂ has been calculated from charge balance using the registered concentration of acetic acid, acetaldehyde, fuel cell active area and the fuel flow rate, as FID detector is insensitive to carbon dioxide.

Data have been corrected for the amount of acetaldehyde and acetic acid produced due to oxygen permeation by subtracting the amounts obtained in currentless conditions [32,33,35]. The contribution of oxygen permeation to the total amounts of products observed changes from 100% at OCV, ca. 20% at 300 mV and ca. 10% at 100 mV. It is worth to note that the ethanol oxidation products observed in currentless conditions are formed as a result of catalytic oxidation of ethanol by the oxygen permeating from the cathode side. Thus the observed amounts of products in currentless conditions are estimates of the lowest possible rate of oxygen permeation.

3. Results and discussion

3.1. Electrochemical investigation

Voltammetric responses of Pt/C catalyst deposited on gold substrate were registered in supporting electrolyte (0.5 mol dm⁻³ sulfuric acid) and in 0.5 mol dm⁻³ ethanol in 0.5 mol dm⁻³ sulfuric acid (Fig. 2A and B, respectively). The registered response is typical for metallic platinum: hydrogen adsorption/desorption signals at electrode potentials lower than 200 mV and Pt oxide formation (anodic scan, E > 700 mV) and their reduction (cathodic scan, E ca. 700 mV) are observed (Fig. 2A).

Voltammogram registered in H₂SO₄/ethanol solution (Fig. 2B) is typical for ethanol electrooxidation on platinum at those conditions

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