C. R. Chimie 17 (2014) 760–769

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

Full paper/Mémoire

Dimethoxymethane (DMM) electrooxidation on carbon-supported Pt-based nanosized catalysts for PEMFC☆

Gwénaëlle Kéranguéven [a,*], Éric Sibert [b], Françoise Hahn [c], Jean-Michel Léger [c]

[a] Institut de chimie et procédés pour l'environnement, l'énergie et la santé (ICPEES), UMR 75 15, CNRS UdS, 25, rue Becquerel, 67087 Strasbourg cedex 2, France
[b] LEPMI, UMR 5279, CNRS, Grenoble INP, université de Savoie, université Joseph-Fourier, 1130, rue de la Piscine, BP 75, 38402 Saint-Martin-d'Hères cedex, France
[c] Institut de chimie des milieux et matériaux de Poitiers (IC2MP), UMR 7285 CNRS, université de Poitiers, bâtiment B27, 4, rue Michel-Brunet, France

ARTICLE INFO

Article history:
Received 16 September 2013
Accepted after revision 17 December 2013
Available online 12 March 2014

Keywords:
Dimethoxymethane
Proton exchange membrane fuel cell
Nanosized PtM/C electrocatalysts
Voltammetry
In situ FTIR spectroscopy

ABSTRACT

Previous studies on dimethoxymethane (DMM: $CH_3–O–CH_2–O–CH_3$) on platinum poly- and single crystals allowed us to propose a general mechanism of DMM electrooxidation. At the time, making electrodes for proton exchange membrane fuel cells (PEMFC) with nanoparticles (based on Pt) was encouraged. It is well known that the improvement of Pt activity for electrocatalysis is possible by modifying platinum with other metals able to increase the kinetics of specific steps of the reaction (activation of water for example). Nanosized PtM/C electrocatalysts have been synthesized by the Bönneman method and characterized for DMM electrooxidation. Voltammetry, *in situ* IRTF spectroscopy and fuel cell tests were carried out to better understand DMM oxidation reaction. Voltammetry and fuel cell tests showed that PtRuMo and PtRu are the most active catalysts at high potential, whereas PtSn and PtMo have a best activity at low potentials. *In situ* IR experiments allowed the observation of CO_{ads} and CO_2 bands.

1. Introduction

Direct alcohol fuel cells operating at low temperature have attracted interest as power sources for numerous applications. Among several alcohols, which can be used in a direct fuel cell, methanol and ethanol are the most promising ones [1–4]. As a liquid they are easier to store and to handle compared to hydrogen. However methanol is toxic and the C–C bond of ethanol leads to an incomplete oxidation into CO_2. The use of ethers such as dimethylether (DME: $CH_3–O–CH_3$) and dimethoxymethane (DMM: $CH_3–O–CH_2–O–CH_3$) as fuels appears to be a good alternative to the utilization of alcohols because they do not have C–C bonds [5–9]. Unlike methanol, DME and DMM have a low toxicity; however DME is a gas at room temperature, which makes its handling and storage more difficult than for a liquid. According to the thermodynamic data ($\Delta rH^\circ = -1945.9$ kJ mol^{-1}, $\Delta rG^\circ = -1903.2$ kJ mol^{-1}, $\Delta rS^\circ = -143.4$ kJ mol^{-1} K^{-1}) related to DMM, the equilibrium potential is 1.23 V for its complete oxidation into CO_2, with $n = 16$ electrons.

DMM electrooxidation has been previously investigated [8–14]. The acetal reaction indicates that the acid hydrolysis of DMM gives two molecules of methanol and one molecule of formaldehyde. Previous works of the authors, obtained at room temperature, carried out on platinum poly- [8] and single-crystal [9] electrodes, demonstrated a complex mechanism, and excluding the direct hydrolysis of DMM in the operating conditions used.

☆ Thematic issue devoted to François Garin.

* Corresponding author.
E-mail addresses: kerangueven@unistra.fr (G. Kéranguéven), Eric.Sibert@lepmi.grenoble-inp.fr (É. Sibert), jean-michel.leger@univ-poitiers.fr (J.-M. Léger).

1631-0748/$ – see front matter © 2014 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.
http://dx.doi.org/10.1016/j.crci.2013.12.010

The use of platinum-based nanoparticle electrodes (Pt, PtRu, PtMo, PtSn, PtRuMo) completes the studies made on poly- and single-crystal platinum electrodes. The main advantage to associate the second and the third metals to metallic Pt is their ability to activate water at lower potentials (formation of OH_{ads}) and consequently to improve CO_{ads} oxidation. Electrode nanoparticles based on platinum with other metals such as ruthenium, molybdenum, and tin have been thoroughly studied for the electrooxidation of small organic molecules [15–18], like methanol which is an intermediate during DMM electrooxidation.

In this work, electrochemical results, fuel cell experiments and *in situ* infrared (IR) reflectance spectroscopy measurements during DMM adsorption and electrooxidation on PtRuMo/C, PtM/C (M = Ru, Sn, Mo) and Pt/C electrocatalysts are carried out in order to:

- evaluate the behavior of this fuel at monometallic and plurimetallic electrodes in terms of reactivity;
- provide results on activity and mechanism observed in previous studies done on poly- and single-crystal electrodes.

2. Experimental

2.1. Electrochemical measurements

The electrochemical material and experimental conditions were described previously [8]. The electrolytic solutions were prepared from 70% $HClO_4$ (Suprapur, Merck) in ultra-pure water (MilliQ, Millipore, 18 MΩ cm). The working electrode was a rotating glassy carbon disc (0.071 cm^2 geometric surface area) on which the catalytic powder was deposited, the counter electrode was a glassy carbon plate and the reference electrode was a Reversible Hydrogen Electrode (RHE). All potentials are referred to RHE. Electrochemical characterizations were performed at 50 mV s^{-1}, and in order to avoid the formation of unwanted oxides of Mo, Sn and Ru, the upper potential limit is set at 300 mV vs. RHE for PtMo(90–10)/C and PtSn(90–10)/C catalysts, and 500 mV vs. RHE for PtRu(80–20)/C and PtRuMo(85–15–5)/C catalysts. In this way, the electroactivity of the different catalysts are compared for the DMM electrooxidation.

2.2. Synthesis of the colloidal precursors of PtM/C and Pt/C electrocatalysts and characterizations

Pt and Pt-based particles [Pt/C, PtMo(90–10)/C, PtSn(89.3–10.7)/C, PtRu(82.9–17.1)/C, PtRuMo(80.2–13.2–6.6)/C] with 40% metal loading, were prepared from colloidal precursors and dispersed on carbon powder (Vulcan XC72). The technique used is based on the Bönneman method [19]. The synthesis is carried out under controlled atmosphere (argon) free of oxygen and water, with non-hydrated metal salts in an organic solvent (THF). The first step consists of the preparation under stirring of a tetra-alkyl triethylborohydride reducing agent $(Nalk_4)^+(Bet_3H)^-$, which will also act as a surfactant after metal reduction, preventing any agglomeration of the metallic particles:

$$MeCl_n + n(Nalk_4)^+(BEt_3H)^- \rightarrow Me\left[(Nalk_4)^+Cl^-\right]_n + nBEt_3 + (n/2)H_2$$

The colloidal precursors are then dispersed on a carbon support (carbon black, Vulcan XC72). The mixture is sonicated under atmospheric conditions then calcined at 300 °C for 1 h under the ambient atmosphere to remove the organic surfactant.

The Bönneman method allows several approaches for the synthesis of multimetallic supported catalysts.

The synthesis under stirring of catalysts with controlled atomic ratio occurs by co-reduction of different metal salts before the reduction step and formation of the precursor colloid:

$$xPtCl_2 + yMCl_n + (2x+ny)\left[(Nalk_4)^+(BEt_3H)^-\right] \rightarrow Pt_2M_y\left[(Nalk_4)^+Cl^-\right]_{2x+ny} + (2x+ny)BEt_3H + [2x+ny/2]H_2$$

This method was used for the preparation of PtRu/C, PtMo/C and PtRuMo/C.

The synthesis of catalysts with controlled atomic ratios occurs by co-deposition of different metal colloids before the calcination step and formation of the catalytic powder:

$$xPt\left[(Nalk_4)^+Cl^-\right] + yMe\left[(Nalk_4)^+Cl^-\right]_n \rightarrow Pt_x + Me_y/C$$

This method was used for the preparation of PtSn/C.

Then electrodes were prepared using ink made from the carbon-supported catalyst and a Nafion® solution according to a method described previously [20].

For voltammetry and *in situ* IR reflectance measurements, this ink is deposited on a vitreous carbon disk and after evaporation of the solvent at 40 °C (30 min), the electrode is ready to be used for the experiment.

Characterizations of the catalyst nanoparticles were carried out by different physical techniques: transmission electron microscopy (TEM) for a morphological observation of their surface with estimation of the particle size by X-ray energy dispersive analysis (EDX) with a Philips CM 120 microscope/EDX analyser equipped with a LaB_6 filament with a nanoprobe (5 nm). X-ray diffraction (XRD) is used to determine the catalyst's structure. Powder diffraction patterns are recorded on a Bruker D5005 Bragg–Brentano diffractometer operated with a powered copper tube (40 kV and 40 mA) at ambient temperature with 2θ ranging from 30° to 90° by 0.02° steps. The metallic composition of the catalyst was determined by TG-DTA experiments using a SDT Q 600 TA Instruments. The temperature ranged from 0 to 600 °C at a rate of 5 °C min^{-1}, under ambient atmosphere and in a platinum crucible.

2.3. In situ *infrared reflectance spectroscopy*

In order to better understand the overall mechanism of the oxidation of dimethoxymethane on the different electrocatalysts, an *in situ* IR reflectance spectroscopic study was performed. With this technique, it is possible to observe the adsorbed species at the electrode surface. In the case of dimethoxymethane, it was previously seen that