



Electrochemical growth of platinum nanostructures for enhanced ethanol oxidation



L.Q. Wang^{a,b}, M. Bevilacqua^a, J. Filippi^a, P. Fornasiero^b, M. Innocenti^{a,c}, A. Lavacchi^{a,*}, A. Marchionni^a, H.A. Miller^a, F. Vizza^{a,**}

^a ICCOM-CNR, Via Madonna del Piano 10, 50019 Sesto Fiorentino (FI), Italy

^b Department of Chemical and Pharmaceutical Sciences, University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy

^c Dipartimento di Chimica, Università di Firenze, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy

ARTICLE INFO

Article history:

Received 18 June 2014

Received in revised form

24 September 2014

Accepted 3 October 2014

Available online 14 October 2014

Keywords:

Platinum nanostructures

Ethanol oxidation

Electrocatalysis

Biomass

In situ spectroelectrochemistry

ABSTRACT

The catalytic activation of polycrystalline platinum toward ethanol electro-oxidation in alkaline environment has been obtained by a square wave potential treatment.

A detailed analysis that explores the effect of the period of the square wave on the evolution of the catalytic properties of the Pt surface is reported. The catalytic behavior of the treated and untreated surfaces has been interpreted both in terms of real surface area and surface structure evolution.

The most active surface has been produced with a treating period time of 120 min. Interestingly the maximum stability has been obtained with the sample produced with square wave potential with a period of 360 min with slightly lower initial performance.

We have also found that the treated samples limit C–C cleavage, as compared to bare Pt, offering an effective strategy to minimize the formation of CO. Via in situ FTIR we have demonstrated that the major oxidation product is acetate. These findings are especially important in view of the application of Pt as a catalyst in alkaline direct ethanol fuel cells.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

To date platinum is still the most commonly exploited material in electrocatalysis. This is because of its good catalytic activity in a variety of energy related electrochemical reactions together with outstanding corrosion resistance in both alkaline and acidic environments [1–4]. Indeed polymer electrolyte membrane fuel cell (PEMFCs) technology, often considered as the ultimate solution to automotive powering, heavily relies on platinum for catalyzing both hydrogen oxidation and oxygen reduction [5].

Platinum has also been proved to be effective for the catalysis of electrochemical oxidation of a variety of small organic molecules (SOMs) [6–9]. For this reason it has been applied as active phase at the anode and cathode of alcohol fed fuel cells with the main target of building a new generation of power sources for portable applications. Among these alcohols, methanol has certainly been the most widely explored [8,10,11]. Despite decades of research methanol

fuel cells are not yet a well-established commercial technology, mainly due to the instability of these devices and the relatively poor performance as compared to PEMFCs. More recently ethanol has entered onto the scene. It has the advantage over methanol of being easily produced with well-established technology from biomasses [12]. Furthermore ethanol is less volatile and far less toxic than methanol, also being easy to store, handle and transport. For all of these promising aspects, ethanol electro-oxidation in fuel cells is an issue of outstanding importance, being at the same time an extraordinarily challenging research topic [7,9,12,13]. Platinum and PtRu have been shown to be effective catalysts for alcohol electrooxidation [7,9,14,15]. Recently PtSn alloys have been proved to be even more performing exhibiting good activity in complete direct ethanol fuel cells tests [16–19]. Nevertheless the use of platinum raises two main concerns related to its practical exploitation: (i) the need for high metal loadings [8,20] and (ii) CO poisoning [21,22]. The need for high Pt loadings poses severe limitations, as the scarcity of platinum resources limits its use to applications where it is absolutely unavoidable. Recently the European Union has classified platinum among the so-called “critical raw materials”, stressing both on its technological relevance and rarity [23,24]. The US Department of Energy periodically publishes reports on future technology targets [25]. Lately a platinum

* Corresponding author. Tel.: +61 390555225250; fax: +39 0555225203.

** Corresponding author. Tel.: +61 390555225286; fax: +39 0555225203.

E-mail addresses: alessandro.lavacchi@iccom.cnr.it (A. Lavacchi), francesco.vizza@iccom.cnr.it (F. Vizza).

content of 0.125 mg cm^{-2} for automotive PEMFCs has been fixed as an objective to be achieved by 2017. This figure is believed to be reasonably good to guarantee the sustainability of platinum supply in the case of a full technological and commercial exploitation. Remarkably for PEMFCs no conventional supported high surface area platinum material has yet met such a target [26]. At present only nano structured thin films (NSTF) have been shown to be active enough to meet the requirements. CO poisoning is critical for PEMFCs and even more for direct alcohol fuel cells (DAFCs). It is well known that the electro-oxidation of ethanol may result in the production of CH_3CHO (unstable in alkali), CH_3COOH (CH_3COO^- in alkali) and CO_2 (CO_3^{2-} in alkali). CO, as an intermediate product may occur in case of C–C cleavage. The addition of ruthenium to platinum promotes CO oxidation and elimination, but CO poisoning is still an issue [27–33].

In order to overcome the problem of CO production it has been demonstrated, at least with Pd catalysts [34], that it is convenient to operate in alkaline conditions, where the C–C cleavage of ethanol has been shown to be hampered resulting in negligible production of C_1 fragments. While this could appear a limitation, in principle, as only four electrons are transferred, it is worth mentioning that to date the most energy efficient direct ethanol fuel cells are those operating in alkaline conditions resulting in the production of acetate. This is because no catalyst that produces effective C–C cleavage is actually known. Indeed the complete oxidation of ethanol to CO_2 or carbonate has very sluggish kinetics [35–39]. These kinetic drawbacks lower fuel cell performance despite the fact of having, in principle up to 12 exchanged electrons.

In the present work we introduce a new approach to the activation of platinum surfaces for application in ethanol electro-oxidation in alkaline environment. Inspiration was taken from a previous paper reporting an analogous procedure for Pd. In that work a square wave potential with fixed frequency was chosen to activate the Pd surface. The procedure was successful in generating nanostructured highly active Pd electrocatalysts [40,41]. Here we show that Pt requires different treatment conditions as compared to Pd. Particularly the dependence on the frequency of the square wave treatment in ethanol electro-oxidation activity in alkaline environment is reported here for the first time.

2. Materials and methods

In all the electrochemical experiments, a polycrystalline Pt disk with a geometric surface area of 0.1963 cm^2 was used as working electrode. The counter electrode was a platinum wire (0.5 mm diameter) while the reference electrode was a KCl saturated Ag/AgCl electrode. All potentials are reported against the reference hydrogen electrode (RHE). RHE potentials were calculated accounting for the hydrogen ion activity in the investigated electrolyte.

The treatment of the polycrystalline Pt foil was performed with a fixed duration of 360 min. through a repetitive square wave potential bounded between 4.55 V and -1.95 V (RHE) in 2 M KOH electrolyte. Wave periods of 6 min (60 full waves), 60 min (6 full waves), 120 min (3 full waves), 180 min (2 full waves), 360 min (1 full wave) were selected for the synthesis of the samples.

Electrochemical measurements were performed with a PAR-STAT 2273 potentiostat/galvanostat (Princeton Applied Research, USA) in a three-electrode cell arrangement at room temperature. All the solutions were purged with N_2 for 15 min before any electrochemical experiment. Before each square wave treatment the Pt electrode surface was mechanically polished with polycrystalline diamond suspension down to $1 \mu\text{m}$. Electrodes were subsequently washed in a FALC ultra-sonic bath for 15 min. At the end of each

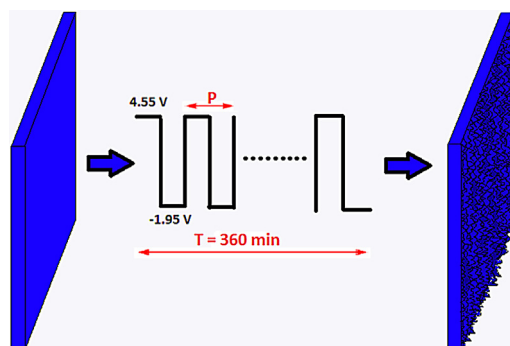


Fig. 1. Schematics of the square wave treatment. Roughness is enhanced by the application of the square wave potential. All the treatments applied had a duration of 360 min. The period (P) of the square wave was varied between 6 min (60 full wave) and 360 min (1 full wave).

square wave potential treatment, the electrode was cleaned with doubly distilled-deionized water.

The electrochemically active surface area (EASA) of this electrode was determined by integration of the charge in the hydrogen region of the cyclic voltammograms (CVs) between 0.05 and 0.4 V in 0.5 M H_2SO_4 solution [42]. The activity for ethanol oxidation was investigated in 2 M ethanol + 2 M KOH by cyclic voltammetry between 0.05 and 0.70 V. All of the CVs were repeated until curves were obtained with high stabilization. The reported CVs were acquired at a scan rate of 50 mV/s. Chronoamperometry was performed at 0.5 V vs. RHE for 3600 s.

Electrochemical in situ FTIR reflection spectroscopy was performed on a Nicolet 6700 spectrometer equipped with a DTGS detector. Prior to the acquisition of the reference spectrum the electrode has been cleaned in 0.1 M HClO_4 in the 0.0–1.0 V RHE potential window. The electrode has been then introduced in the FTIR cell imposing a 0.0 V RHE potential. The reference spectrum has been collected after 2 min from the electrode immersion for both the treated and the untreated Pt. Spectra have been acquired at the same potential values and with the same acquisition time for both samples to allow a direct comparison.

The spectro-electrochemical cell was designed to have the Pt electrode supported by a CaF_2 window. Such configuration allows only a thin film of electrolyte (10 μm range) to be in the gap between the electrode and the window. Each spectrum was determined averaging 128 interferograms acquired with a resolution of 4 cm^{-1} . The reference spectrum (R_{ref}) was collected at 0 V vs. RHE. Potential steps were set to 0.1 V until 1.2 V has been reached. Spectra were normalized according to Eq. (1) [43].

$$\frac{\Delta R}{R} = \frac{R_s - R_{ref}}{R_{ref}} \quad (1)$$

Under such a representation scheme, negative and positive bands correspond to produced and consumed species respectively.

Electron microscopy was performed with a field emission scanning electron microscopes Zeiss Gemini 1530, capable of a spatial resolution 2.1 nm at 1.0 kV.

3. Results and discussion

The platinum activation with square wave potential is performed according to the treatment schematized in Fig. 1.

Inspiration was taken from our previous studies on the application of a square wave potential to activate the surface of Pd leading to very active nanostructured electrocatalysts [40,41]. Nevertheless, the nature of Pt oxidation is different from that of Pd, so major adaptation has been required to accomplish the task of enhancing electrocatalytic activity for Pt. Indeed it has been previously

Download English Version:

<https://daneshyari.com/en/article/45548>

Download Persian Version:

<https://daneshyari.com/article/45548>

[Daneshyari.com](https://daneshyari.com)