Electrochimica Acta 111 (2013) 152–159

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

The impact of iridium on the stability of platinum on carbon thin-film model electrodes

Maria Wesselmark[a,2], Björn Wickman[b], Carina Lagergren[a,*,1], Göran Lindbergh[a,1]

[a] *Applied Electrochemistry, School of Chemical Science and Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden*
[b] *Department of Applied Physics, Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden*

ARTICLE INFO

Article history:
Received 7 March 2013
Received in revised form 11 July 2013
Accepted 13 July 2013
Available online 26 July 2013

Keywords:
Fuel cell
PEMFC
Oxygen reduction
Iridium oxide
Platinum

ABSTRACT

Increasing the stability and lifetime of the electrodes is one of the most important factors in order to realise a large scale use of polymer electrolyte membrane fuel cells (PEMFC). By using well-defined thin-film model electrodes, the stability of Pt and Pt on Ir were examined as cathode catalysts in a single cell PEMFC setup. The electrodes were fabricated by evaporating thin layers of Pt and Pt on Ir onto the microporous layer of a gas diffusion layer. The amount of Pt deposited was equivalent to 3 nm (about 6.3 μg cm^{-2}) and the amount of Ir was varied between 1.5 nm and 20 nm (between 3.4 μg cm^{-2} and 45.3 μg cm^{-2}). All samples with Ir showed an increased stability over samples with sole Pt during cyclic corrosion test between 0.6 V and 1.2 V vs. the reversible hydrogen electrode. For thin layers of Ir, the initial activity for the oxygen reduction reaction was equal to or superior to that of sole Pt but for thicker Ir films it was somewhat lower. Hydrogen underpotential deposition and CO stripping were used to estimate the electrochemical surface area during the experiments and physical characterisation using scanning electron microscopy and X-ray photoelectron spectroscopy were used to determine the structure of the samples. The results suggest that Ir can stabilise Pt in the cathode electrode.

1. Introduction

Today, high amounts of Pt catalyst are needed on the cathode in the polymer electrolyte fuel cell due to the sluggish oxygen reduction reaction. In addition, the loss of electrochemically active surface area in the catalyst layer causes a considerable performance loss over time. The degradation is more severe on the cathode than on the anode, partly due to carbon corrosion, and it is therefore important to find a way to improve the activity and stability of the cathode catalyst layer [1].

By using alternative materials as support for Pt, an enhanced activity and stability may be obtained [2–8]. An increased ORR activity of a non-alloy, or catalyst on support, can be explained by a spill-over mechanism of reactants or intermediates between the two materials or by the adlineation mechanism, where new sites with enhanced activity is created in the interfacial area between the two materials [2,3,6]. The difference between Pt on a support and a Pt alloy are sometimes subtle and the effects of Pt on a support could be similar to the ones of an alloy. Recently there has been a strong development of Pt monolayer catalysts, with a very good Pt utilisation, improved activity and good stability [4]. The improved activity may be related to a change in the Pt–Pt distance, changes in the electron structure or an increased repulsion of OH$_{ad}$ on Pt [4,7,8]. Metal oxides are generally rather stable in the fuel cell environment and have been investigated both as support and combined with Pt in the catalyst layer in order to increase the stability of the electrode and the activity for ORR [9–18]. The advantage of using a metal oxide as catalyst support instead of carbon is a higher oxidation resistance, but additional effects such as better adhesion of the Pt and higher ORR activity on the alternative support material could also be achieved.

Ir (or Ir oxide) is a very good catalyst for the oxygen evolution reaction (OER) in acidic solution [19] and is therefore often added to the Pt catalyst of the cathode in unitised regenerative fuel cells [20–30]. Higher Ir content improves the OER whereas too high amounts of Ir have a negative effect on the ORR [26,27]. Due to the high potentials obtained during electrolysis of water in the regenerative mode it is important with an electrode which is stable at those potentials. With Ti and Ir oxide as gas diffusion layer, an improved stability of the catalyst layer has been achieved [30]. Improved stability as well as higher activity for oxygen reduction was predicted in DFT calculations by Balbuena et al. [31] of ternary alloys with Pt, Ir and Co or Cr. The improvements were

---

* Corresponding author.
E-mail address: carinal@kth.se (C. Lagergren).

[1] ISE member.

[2] Present adress: Intertek Semko AB, Torhamnsgatan 43, Box 1103, SE-164 22 Kista, Sweden.

0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.07.108

ascribed to the stability of Ir and a lower binding energy of OH. IrO_2 as well as Ir dendrites were shown by Oh et al. to inhibit carbon corrosion in the catalyst layer by eliminating water around the carbon support [32]. Pt–Ir alloys [33–36] or mixed monolayers of Pt–Ir on Pd nanoparticles [37] have also shown enhanced catalytic activity for oxygen reduction. The Ir was also in those studies suggested to weaken the adsorption strength of OH, which lowers the OH-coverage and facilitates the ORR [34,35,37]. Pt deposited on Ir oxide has shown enhanced catalytic activity for ORR compared to Pt [10]. Furthermore, Ir oxide alone has shown some activity for oxygen reduction when deposited as nanoparticles on a carbon support in the cathode of a polymer electrolyte fuel cell [38,39]. The studies mentioned above have all shown various beneficial effects on the cathode when Ir is included. Nevertheless, Ir is a noble metal, almost as expensive as Pt, and the improvements need to be extensive in order to motivate the use of Ir in fuel cell catalysts.

In a previous study, thin-film model electrodes were used for investigating the impact of different metal oxides on the stability and activity of Pt in the cathode in a PEMFC [40]. This type of model electrode can be seen as a two-dimensional, thin slice of a porous electrode with a three-phase interface of catalyst, support material and Nafion. The model electrodes are well defined and fast to fabricate, in contrast to conventional porous electrodes which need synthesising of supported catalyst particles as well as optimisation of the electrode structure before the catalytic activity can be tested in a fuel cell. In addition, it is very difficult to keep the structure of porous electrodes constant when examining different materials. The heterogeneous and complex structures of the porous electrodes also make it difficult to assess the true catalytic activity without including effects from local mass transport, potential and humidity conditions. Another advantage of the model electrode is the low catalyst loading, resulting in low currents, which give low iR-losses, and limited water and heat production.

In the present study, the interaction between Pt and Ir is examined. Model thin film electrodes with Pt deposited on a thin metallic layer of Ir was prepared. It is however well known that Ir can form irreversible thick layers of Ir oxides when cycled to higher potentials [41,42], which may influence the properties. The impact of different amounts of Ir on the activity and long-term stability of these electrodes is examined in a fuel cell.

2. Experimental

2.1. Model electrode preparation

CARBEL CL gas diffusion layers (GDL) were purchased from Gore Technologies and the surface was cleaned with flowing nitrogen gas prior to film deposition. Thin catalyst films were deposited by thermal evaporation in vacuum (AVAC HVC600, at about 10^{-6} mbar). Ir and Pt were evaporated on to the GDL at controlled thicknesses, measured with a quartz crystal microbalance sensor located in the chamber. The amount of Pt deposited was equivalent to 3 nm (about 6.3 $\mu g\,cm^{-2}$) and the amount of Ir was varied between 1.5 nm and 20 nm (between 3.4 $\mu g\,cm^{-2}$ and 45.3 $\mu g\,cm^{-2}$). The samples are named according to the amount of material in the following way; yPtzIr, represents a sample with *y* nm of Pt deposited on top of *z* nm of Ir, which in turn was deposited on GDL.

2.2. Electrode morphology and chemistry characterisation

The thin film catalysts morphology was characterised by scanning electron microscopy (SEM, Leo Ultra 55 FEG) operating at 10 kV in the secondary electron mode. Chemical characterisation was performed using X-ray photoelectron spectroscopy (XPS, Perkin Elmer PHI 5000 C ESCA system) using monochromatic Al Kα radiation and a 45° take-off angle [43].

2.3. Electrochemical evaluation

Circular disks with a diameter of 14 mm were punched out from the thin film electrodes and used as working electrodes (WE) in electrochemical evaluation in fuel cell measurements. Before the preparation of the membrane electrode assembly (MEA) some of the samples were sprayed with a Nafion solution. This was done with 2% Nafion in isopropanol and approximately ten times with drying in between until the surface became shiny of a thin layer of Nafion. In order to prepare MEAs, the thin model electrode disks were placed onto 45 × 45 mm pieces of Nafion^{TM} 115 membranes (Nafion 115, Aldrich). The membranes had previously been cleaned by boiling in 3% H_2O_2 for 1 h, in 0.1 M H_2SO_4 for 1 h and finally in three successive baths of Milli-Q water for 1 h each after which the membranes were dried in an oven at 80 °C overnight. Commercial porous ELAT electrodes (30% Pt on Vulcan XC-72) with a loading of 0.5 mg Pt cm^{-2} were placed on the counter side of the membrane and used as combined counter and reference electrode (CE/RE). The MEAs (thin film electrode on GDL + membrane + ELAT electrode) were hot pressed at 135 °C for 30 s at 1 MPa. The MEA was mounted in a laboratory PEEK (polyether–etherketone) fuel cell, described elsewhere [44], with cylindrical, 30 mm in diameter, graphite current collector with spirally formed gas channels and a clamping force over the current collectors of 380 N.

For the standard case, if nothing else is mentioned, the gases were humidified in heated humidifiers (Fuel Cell Technologies Inc.) held at 77 °C, resulting in 90% relative humidity (RH) in the fuel cell with a cell temperature of 80 °C. Cyclic sweeps were performed with O_2 or N_2 on the WE and 5% H_2 in Ar at the CE/RE fed in excess at 1 ml s^{-1}. The very low loading on the WE, compared to the porous CE/RE, made it possible to use 5% H_2 in Ar which avoids crossover of hydrogen to the WE. The CE/RE was also assumed not to be polarised due to the low current density. All measured potentials from the fuel cell tests are referred to the reversible hydrogen electrode (RHE) and the potentials have therefore been corrected for the 45.5 mV shift due to the lower hydrogen partial pressure (5% H_2 in Ar).

After 2 h of constant gas flow at the correct temperature, the electrochemical measurements always started with cyclic sweeps in nitrogen to get a description of the surface processes on the electrode. This was followed by an activation procedure by 2000 cycles at 20 mV s^{-1} between 0.6 V and 0.9 V vs. RHE in oxygen after which further measurements were performed.

CO-stripping curves were recorded in the potential window between 0.05 V and 1.2 V, at a sweep rate of 20 mV s^{-1}. After a cycle in humidified N_2 gas, the potential scan was stopped at 0.15 V and the gas flow shifted to CO-containing gas (2% CO balanced with Ar) for CO adsorption during 2 min. Thereafter the inlet gas was shifted back to nitrogen for 5 min, to flush out remaining CO in the cell, before subsequent stripping.

3. Results and discussion

3.1. Materials characterisation

SEM and XPS were employed to characterise the structure of the thin-film model electrodes prior to the electrochemical evaluation. Fig. 1 shows SEM images of 3Pt, 3Ir, 3Pt3Ir, 3Pt20Ir, and 3Pt1.5Ir evaporated on GDL. In agreement with what has been shown before, evaporating 3 nm of Pt results in a non-continuous Pt film of separated nanoparticles, roughly 3–6 nm in size on the exposed area of the GDL [39]. The structure of 3 nm Ir film on GDL is