Journal of Power Sources 196 (2011) 2513–2518

Contents lists available at ScienceDirect

Journal of Power Sources

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

Study of a proton exchange membrane fuel cells catalyst subjected to anodic operating conditions, by synchrotron-based scanning photoelectron microscopy (SPEM) and high lateral-resolution X-ray photoelectron spectroscopy

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ARTICLE INFO

Article history:
Received 12 August 2010
Received in revised form 29 October 2010
Accepted 7 November 2010
Available online 12 November 2010

Keywords:
SPEM
XPS
Electrocatalyst
Degradation
MEA

ABSTRACT

In this paper we report an investigation of the degradation of the Pt/C electrocatalyst of an anodic membrane-electrode assembly (MEA) after 1000 h of operation in a laboratory single-cell PEMFC, using synchrotron-based space-resolved photoelectron spectroscopy. This study is complemented by the analysis of a pristine MEA and reference materials, as well as by electrochemical measurements, SEM imaging and energy-dispersive X-ray fluorescence spectroscopy (EDX). Catalyst ageing correlates with a corrugation of morphology, as observed by SEM and scanning photoelectron microscopy (SPEM), corresponding to Pt nanoparticle agglomeration. Moreover – on the basis of high lateral resolution SPEM, X-ray photoelectron spectroscopy (XPS) and EDX analyses, – we found that, after operation, Pt is transported onto the fibres of the gas-diffusion layer (GDL). Space-resolved XPS shows a peak shift of the Pt $4f_{7/2}$ level to higher and lower binding energies with respect to Pt(1 1 1) and pristine Pt black, respectively, corresponding to nanocrystallinity in the first case and agglomeration in the second one. No oxidised Pt was found in any location of the anodically used MEA.

1. Introduction

One of the most critical barriers to the widespread commercial application of proton exchange membrane fuel cells (PEMFCs) is their durability, crucially impaired by catalyst stability. In fact, not only the well-known CO-poisoning problems impact the reliability of these systems, but also: (i) Pt dissolution from the cathode and recrystallisation in the PEM [1–3]; (ii) nanoparticle (NP) degradation, agglomeration and Pt surface-transport [4–10] and (iii) carbon-support corrosion and poisoning by corrosion products released by structural materials [11–15] affect the operation of fuel cells (FC) of both laboratory and commercial scales. In fact, Pt and Pt-alloy NPs, typically dispersed on high surface-area carbon black substrates, are extensively used as cathodic and anodic catalysts. The performance of catalysts degrades via complex – so far poorly understood – pathways, including: reduction of active surface due to agglomeration, clustering and sintering on one side and dissolution of Pt and corrosion of the carbon black on the other one.

The parameters empirically known to affect the morphological stability of Pt-based NP electrocatalysts – and consequently their efficiency – include: adsorption of oxidation intermediates, electrochemical polarisation and operating time. The topography of real solid surfaces plays an important role in defining the electronic energy distribution at surface sites, particularly when irregularities at the atomic level are taken into account. Likewise, surface irregularities at the nanometric level determine the electrocatalytic properties. In fact, the reactivity of small metal clusters has been found to vary by orders of magnitude when the cluster size is changed by only a few atoms [16] or monoatomic metallic layers are adsorbed onto the surfaces of NPs [17].

In the literature, frequent use is made of X-ray photoelectron spectroscopy (XPS) in order to characterise electrocatalysts, typically in the as-fabricated conditions. Nevertheless, the number of investigations on Pt/C-based materials after prolonged electrochemical polarisation is rather limited (see below for further details). Moreover, use of space-dependent XPS and photoelectron imaging is completely absent, to the best of the authors' knowledge. Wang et al. [15] report XPS measurements of Pt/C electrocatalysts before and after 10,000 potential cycles between 0.6 and 1.2 V_{RHE}: an increase of the relative amount of Pt(0) to Pt(II) has been found, interpreted in terms of Pt dissolution and redeposition, result-

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doi:10.1016/j.jpowsour.2010.11.039

ing in Ostwald's ripening. Shao et al. [8] investigated by XPS the effects of repeated application of potential steps (from 0.60 or 0.85 to 1.4 V_{RHE}) and prolonged potentiostatic polarisation (at 1.2 and 1.4 V_{RHE}) on the degradation of Pt/C:O and C were found to increase and the C peak has been shown to shift towards the formation of oxidised C species. Similar conclusions have been reached in [18] that applied 800 potentiodynamic cycles between 0 and 1.5 V_{RHE}.

XPS work on real membrane-electrode assemblies (MEAs) has been reported in [19,20]. The former investigation – involving a commercial MEA and one fabricated by the authors – was based on potential cycling in an aqueous solution and concentrated on quantitative elemental analysis in view of performance optimisation. The latter paper reports on the degradation of a Pt–Ru catalyst implemented in a MEA, caused by cell reversal during starvation. Quantitative elemental analysis carried out by XPS measurements of a fragment from the MEA disclosed changes in C and O content and, in particular, highlighted the decrease of Pt content in the catalyst alloy.

In the present investigation, we mean to address the point of the space-dependent chemical state of Pt, through synchrotron-based X-ray spectromicroscopy approaches: scanning photoelectron microscopy (SPEM) and XPS with nanometric lateral resolution. In this work, we compare catalyst materials in their pristine state and after 1000 h of anodic operation in a simple laboratory scale single-cell PEMFC. Our choice of focussing on the anodic side of the MEA is dictated by the fact that this system – facing far less critical operating conditions than the cathodic side – has received less attention in terms of materials degradation. Notwithstanding the fact that anodic operation results in a lower damage rate, still important degradation phenomena are observed and, in particular, new kinds of phenomenology are found, worth addressing and rationalising in view of material optimisation. This kind of relatively fundamental investigation is expected to have a bearing on the synthesis and management of nanocrystalline electrocatalyst materials, since an insightful understanding of these stability issues is strongly required for the design of fuel-cell MEAs as well as MEA-GDL assemblies for applications in real-scale systems.

2. Materials and methods

In this research, we have concentrated on the anodic side of the MEA of a single-cell laboratory PEMFC with electrochemically active dimensions 5 cm × 5 cm, purchased from Materials Mates Italia S.r.l. (Milano). The commercial C-supported Pt catalyst exhibited the following properties: dimensions of Pt nanoparticles: ca. 6 nm, Pt loading: 1 mg cm^{-2}, composition of catalyst layer: 70 wt.% Pt/C, 30 wt.% PTFE. This catalyst was applied to the Nafion sheet, pretreated as described in [21]. The gas diffusion layers (GDLs) were carbon paper containing TiO_2 as stiffener. The end-plates were fabricated by punching AISI 304 foils of thickness 0.2 mm. The cell was run for a 1000 h run: operating details of this very experiment have been published in [22], where bipolar plate corrosion was studied. For reference purposes, we have considered the following materials: (i) Pt(1 1 1) disk (diameter: 10 mm, thickness 2 mm, roughness <30 nm, orientation accuracy better than 0.1°) from Mateck and (ii) Pt-black (Aldrich 205915).

The scanning electron microscopy (SEM) images and energy dispersive X-ray fluorescence spectroscopy (EDX) data of the samples have been recorded using a Jeol JSM 6480-LV microscope equipped with a SphinX 130 IXRF Systems energy dispersive X-ray spectrometer.

Compositional mapping and high lateral-resolution XPS measurements were carried out by using the scanning photoelectron microscope (SPEM) at the ESCA microscopy beamline at the ELETTRA synchrotron radiation facility located in Trieste, Italy where a synchrotron source X-ray beam is focused on the sample into a spot with a diameter of around 150 nm using Fresnel zone plate optics. In SPEM the sample can be raster scanned with respect to the microprobe. The microscope operates in imaging and spectroscopic modes. The imaging mode maps the lateral distribution of elements by collecting photoelectrons with a selected kinetic energy window while scanning the specimen with respect to the microprobe. When the element under consideration is present in a single chemical state, the spatial variation in the contrast of the images reflects the variation of the photoelectron yield, which is a measure of the local concentration of the element. The microspot mode is identical to the conventional XPS. Spatially resolved photoemission spectra of selected regions and chemical maps were acquired with 200 meV energy resolution by using 670 eV photon energy. More details on this microscope and on the beamline are provided in [23]. Before SPEM and XPS measurements, the Pt(1 1 1) single-crystal has been subjected to a sequence of sputtering and annealing processes, until a perfect low energy electron diffraction (LEED) pattern has been found. All the other samples were subjected to a light Ar-ion sputtering and checked for surface cleanliness by Auger electron spectroscopy (AES).

3. Results and discussion

3.1. SEM and EDX of the MEA in pristine and used conditions

After operation in the above-described conditions, the PEMFC was opened in view of analysing the catalyst layer of the MEA. It proved impossible to separate the MEA from the GDL without breaking off some fragments of the latter that were strongly sticking to the MEA itself. The exposed surface of the samples we

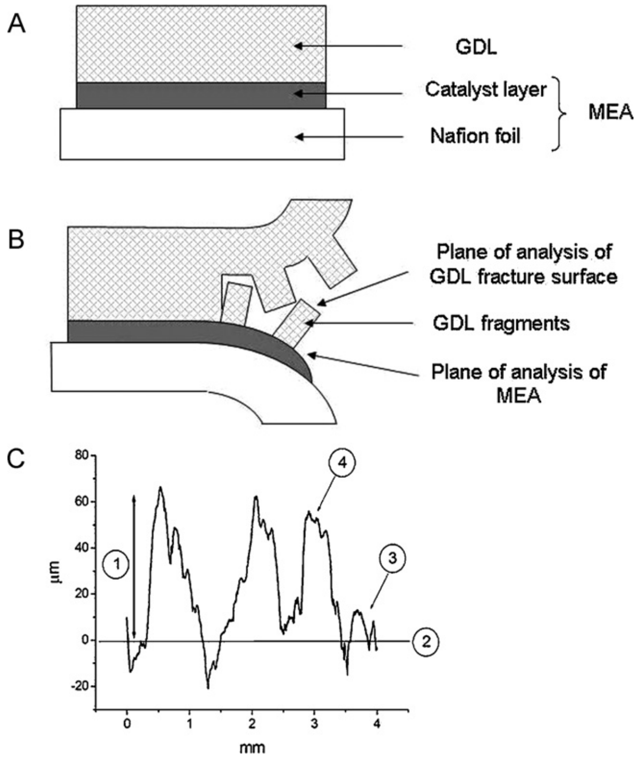

Fig. 1. Description of the analysed sample. (A) Schematic layout of the anodic MEA and GDL in pristine conditions. (B) Same, after operation and separation of MEA and GDL, leaving behind some GDL fragments, adhering to the MEA. (C) Typical Talystep line profile showing the dimensions of the GDL fragments and the locations of the analysed areas: (1) typical thickness of the GDL fragments, (2) nominal MEA/GDL interface, (3) plane of analysis of MEA, and (4) plane of analysis of GDL fracture surface.