Journal of Power Sources 196 (2011) 4242–4250

Contents lists available at ScienceDirect

Journal of Power Sources

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

Physico-chemical study of the degradation of membrane-electrode assemblies in a proton exchange membrane fuel cell stack

P. Ferreira-Aparicio [a,*], B. Gallardo-López [a], A.M. Chaparro [a], L. Daza [a,b]

[a] Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Avda. Complutense, 22, E-28040 Madrid, Spain
[b] Instituto de Catálisis y Petroleoquímica (CSIC), C/Marie Curie, 2, Campus de Cantoblanco, E-28049 Madrid, Spain

ARTICLE INFO

Article history:
Received 28 July 2010
Received in revised form 19 October 2010
Accepted 19 October 2010
Available online 28 October 2010

Keywords:
PEMFC stack
Membrane-electrode assembly (MEA) degradation
Postmortem analysis
Ultramicrotome-sectioned samples for TEM
XPS analysis

ABSTRACT

A proton exchange membrane fuel cell stack integrated by 8-elements has been evaluated in an accelerated stress test. The application of techniques such as TEM analyses of ultramicrotome-sliced sections of some samples and XRD, XPS and TGA of spent electrodes reveal the effects of several degradation processes contributing to reduce the cells performance. The reduction of the Pt surface area at the cathode is favored by the oxidation of carbon black agglomerates in the catalytic layer, the agglomeration of Pt particles and by the partial dissolution of Pt, which migrates towards the anode and precipitates within the membrane. In the light of the TEM, EDAX and XPS results, two combined effects are probably responsible of the increase of the internal resistance of the stack cells: (i) a lower proton conductivity of the membranes due to the high affinity of the sulfonic acid groups for ions originated from Pt crystallites and other peripherical elements such as the silicone elastomeric gaskets and (ii) the increment of electrically isolated islands in the cathode gas diffusion electrodes resulting from carbon corrosion and the degradation of the perfluorinated polymers. Water accumulation and inhomogeneous gas distribution throughout the stack cells originate different degradation rates in them.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The analysis of the degradation mechanisms affecting the life and the long-term performance of proton exchange membrane fuel cells (PEMFC) is a subject of growing interest [1]. Extensive recent reviews concerning the durability of catalysts [2–6], membrane-electrode assemblies (MEAs) [7], and PEMFC performance [8,9] identify numerous stressors and degradation mechanisms. However, much more effort is needed to analyze the ageing of the several PEMFC components, establish mitigation strategies and extend their useful life. The use of accelerated stress tests has been proved to be a useful tool to assess the durability of the PEMFC components. Using this strategy, performance losses and component damages can be more efficiently analyzed under specific working conditions than applying costly and time-consuming steady-state lifetime tests [5,7].

The main degradation processes in MEAs include Pt sintering, agglomeration and redistribution, corrosion of the carbon support in the electrodes, chemical and structural degradation of the membrane, and poisonous effects aroused by contaminants from external components. As demonstrated by many researchers, agglomeration and particle growth of nanostructured Pt is the most dominant mechanism for catalyst degradation in PEM fuel cells. Virkar and Zhou [10] have explained that Ostwald ripening, involving coupled transport of electrically charged species, is the main reason for particle growth in Pt/C catalysts, where the Pt is transported through the liquid and/or through the ionomer and the electrons through the carbon support. Other groups [11,12] believe that two other mechanisms are predominately responsible for degradation: Pt particles detaching from the support and dissolving into the electrolyte without re-deposition, and/or a combination of Pt particle coalescence and Pt solution/re-precipitation within the solid ionomer. Whatever mechanism the particle growth follows, dissolution of Pt is an important step during the catalyst degradation process.

Many groups have reported the presence of Pt particles inside the PEM as well as enrichment of Pt in the catalytic layer-membrane interface under different conditions [13–19]. These Pt particles originate from the dissolved Pt species, which diffuse in the ionomer phase and subsequently precipitate in the ionomer phase of the electrode or in the membrane. The precipitation probably occurs via the reduction of Pt ions by hydrogen that has crossed over from the anode. Concerning the direction and degree of the Pt particle migration and redistribution, the results presented in current literature are not always consistent. Bi and Fuller [20], Fer-

* Corresponding author. Tel.: +34 91 3460897; fax: +34 91 3466269.
E-mail address: paloma.ferreira@ciemat.es (P. Ferreira-Aparicio).

0378-7753/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2010.10.059