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Electrochemical study of platinum deposited by electron beam evaporation for application as fuel cell electrodes

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ABSTRACT

Platinum is the most used catalyst in electrodes for fuel cells due to its high catalytic activity. Polymer electrolyte and direct methanol fuel cells usually include Pt as catalyst in their electrodes. In order to diminish the cost of such electrodes, different Pt deposition methods that permit lowering the metal load whilst maintaining their electroactivity, are being investigated. In this work, the behaviour of electron beam Pt (e-beam Pt) deposited electrodes for fuel cells is studied. Three different Pt loadings have been investigated. The electrochemical behaviour by cyclic voltammetry in H_2SO_4, $HClO_4$ and in $HClO_4$ + MeOH before and after the Pt deposition on carbon cloth has been analysed. The Pt improves the electrochemical properties of the carbon support used. The electrochemical performance of e-beam Pt deposited electrodes was finally studied in a single direct methanol fuel cell (DMFC) and the obtained results indicate that this is a promising and adequate method to prepare fuel cell electrodes.

1. Introduction

Two of the major challenges that low temperature fuel cells (PEM H_2/O_2 and DMFC) must address to attain viable commercial use and the subsequent mass production stage are cost and durability. In addition to the transportation industry, other important energy dependent fields such as residential, back-up and portable power supply face the high cost of these fuel cells as the main barrier to their widespread applications in these areas.

One of the primary drivers of cost in a fuel cell is due to the MEA [1] which consists of the membrane, plus the anode and cathode electrodes which are integrated by the diffusion media and catalyst layers, typically wearing platinum-based (Pt-based) catalysts. Regarding PEM and DMFC costs, the

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electrodes represent about 40% of the total cost of PEMFC [2], with the Pt cost share being 1.7%. For mass production, the catalyst ink cost is approximately 34% of the total stack cost [3]. For DMFC, Pt is until now the most effective metal for methanol oxidation, though pure Pt is not efficient and Pt-based bimetallic catalysts are used instead [4–6]. In any case, Pt is the most common catalyst for oxygen reduction in PEMFC and DMFC.

There are several approaches to reduce the cost of PEMFC stacks, where a number of MEAs must be created to obtain significant power values. This feature becomes especially important in DMFC for two main reasons: these fuel cells are mainly used for portable power devices, and methanol electrooxidation requires higher Pt quantities than hydrogen, so its electrodes require greater amounts of catalyst than PEM fuel cells do [7]. The Pt loading has been reduced by two orders of magnitude in the past decade and there is still room for further reductions [1]. One possible approach to lower PEMFC and DMFC cost is to investigate alternative electrocatalysts to Pt including non-noble metals [1,8]. Another important option consists in lowering the Pt content in the catalyst layer, either by using alloys or by improving electrode or catalyst preparation methods with higher control for Pt particle deposition [2,8–14]. In summary, Pt and its alloys are commonly used as electrocatalysts and a variety of deposition methods have been used with this purpose. With regards to the fabrication of electrodes for fuel cells, low Pt loading is being achieved fusing of a variety of procedures such as thin-film, vacuum deposition or electrodeposition methods [10].

Vapour deposition methods include, among others, sputtering and electron beam physical vapour deposition, also called electron beam evaporation or e-beam evaporation [15]. Physical preparation methods offer the advantage over chemical ones of being one-step processes [13] leading to the formation of thin films of metal nanoparticles, thus giving rise to lower Pt loading electrodes. Both methods allow the obtention of thin catalyst layers ejecting atoms from a given material (target) which are deposited on the surface of a near-placed substrate. The sputtering technique does not cause the target to evaporate so it remains in a solid state, but atoms are dragged away from the target. With the e-beam evaporation method, the target melts and releases gas phase atoms that then precipitate on the substrate. Whereas sputtering allows metal and insulating materials deposition, e-beam evaporation can only be used with metals. Also, high melting point metals can be deposited more easily by sputtering than by e-beam evaporation. Moreover, in general, sputtering targets are bigger and more costly than e-beam ones. Besides, if an alloy is to be deposited, a target with a specified composition must be prepared and such target must be discarded if another composition is to be investigated. By using an e-beam evaporator equipped with various heads and controlling the evaporation rates of the diverse metals, deposition and further study of different alloys can be easily implemented. Then, bearing in mind the possibility of investigating bi- or tri-metallic catalyst layers with different atomic ratios for fuel cell electrode preparation, the e-beam evaporation technique is seen as a highly controllable and cost-effective deposition method.

Although a number of works have been devoted to study Pt sputtering to be used as electrodes in H_2/O_2 PEMFC or even in

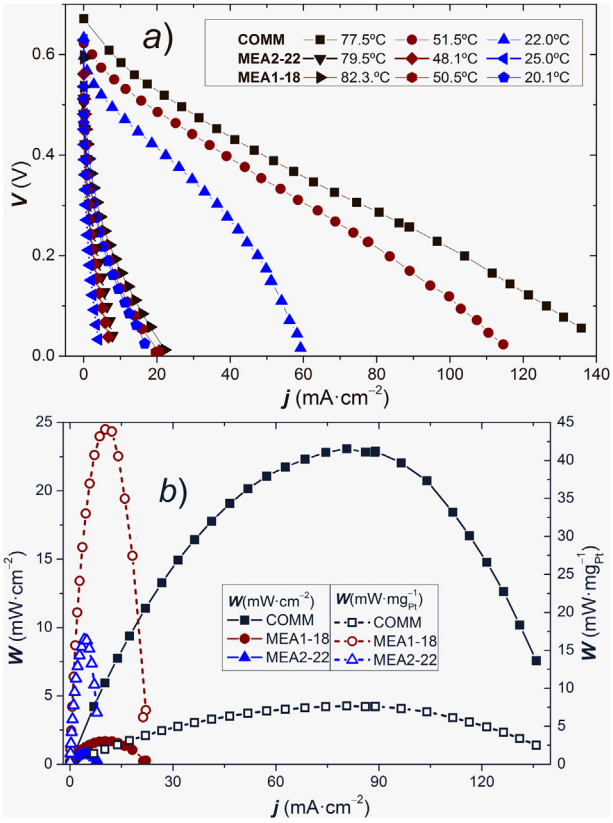

Fig. 1 – *a*) DMFC polarisation curves of three MEAs: one of them prepared with commercial electrodes (COMM) and the other two, MEA1-18 and MEA2-22 are custom MEAs with low Pt loading cathodes deposited by e-beam on GDL2 and GDL1 carbon cloths at 80 °C, 50 °C and 20 °C; *b*) power output per surface unit and per unit Pt mass curves at 80 °C. (See Subsection 2.5 for nomenclature).

DMFC [16–23], studies on e-beam evaporation as a Pt deposition technique for such purpose are very scarce [24,25] and no use for DMFC has been found. In one study [25] e-beam Pt deposited electrodes are used in a microbial fuel to investigate

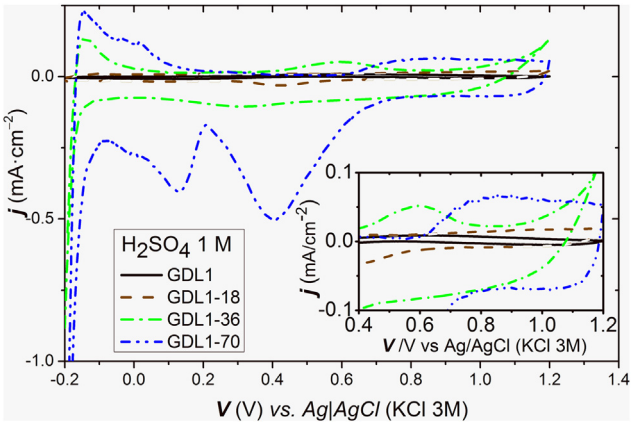

Fig. 2 – Cyclic voltammograms of samples GDL1 (—), GDL1-18 – –, GDL1-36 ·-· and GDL1-70 –·–· in 1 M H_2SO_4. (See Subsection 2.1 for nomenclature).