



A novel sputtered Pd mesh architecture as an advanced electrocatalyst for highly efficient hydrogen production



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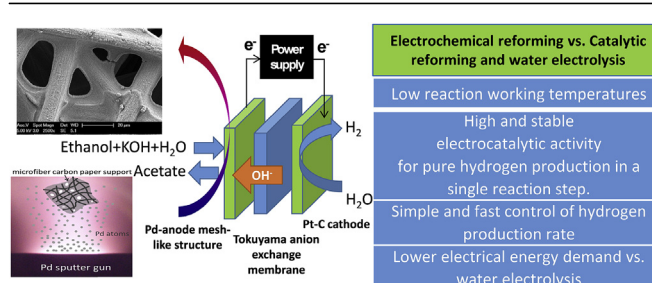
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HIGHLIGHTS

- AEM electrochemical reforming of ethanol was developed for pure H₂ production.
- A novel sputtered Pd mesh-like anode was used as an advanced electrocatalyst.
- Large H₂ production rates were obtained with low energy requirement.
- The system was stable for long working times.
- Potassium acetate was the main anodic product.

GRAPHICAL ABSTRACT



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ABSTRACT

This study reports the preparation, characterization and testing of a sputtered Pd mesh-like anode as an advanced electrocatalyst for H₂ production from alkaline ethanol solutions in an Alkaline Membrane Electrolyzer (AEM). Pd anodic catalyst is prepared by magnetron sputtering technique onto a microfiber carbon paper support. Scanning Electron Microscopy images reveal that the used preparation technique enables to cover the surface of the carbon microfibers exposed to the Pd target, leading to a continuous network that also maintains part of the original carbon paper macroporosity. Such novel anodic architecture (organic binder free) presents an excellent electro-chemical performance, with a maximum current density of 700 mA cm⁻² at 1.3 V, and, concomitantly, a large H₂ production rate with low energy requirement compared to water electrolysis. Potassium hydroxide emerges as the best electrolyte, whereas temperature exerts the expected promotional effect up to 90 °C. On the other hand, a 1 mol L⁻¹ ethanol solution is enough to guarantee an efficient fuel supply without any mass transfer limitation. The proposed system also demonstrates to remain stable over 150 h of operation along five consecutive cycles, producing highly pure H₂ (99.999%) at the cathode and potassium acetate as the main anodic product.

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1. Introduction

The need to expand the supply of domestically produced energy is a strategic issue because fossil fuels, the main energy source, are often imported. In such a domestic production scenario, hydrogen

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is considered to be an excellent energy carrier for renewable and sustainable-based energy systems via fuel cells utilization [1]. Traditional large-scale production of hydrogen is mainly based on methane reforming process. However, this pathway produces other carbon-derived products such as carbon monoxide and carbon dioxide, together with hydrogen, which requires several reaction and purification steps in order to clean the reformer gas stream before entering the fuel cell. In this sense, there is a growing interest in developing effective alternatives to produce hydrogen, especially for on-site applications by more simple and compact production processes [2]. In this sense, the electrolysis process has gained much attention due to the production of pure hydrogen at high rates in a single reaction step. Thus, a lot of scientific interest has been focused on water electrolysis due to its advantages for the production of clean hydrogen [3]. However, although water electrolysis is a well-established commercial technology, its practical application is limited by the electrical energy consumption due to the high overvoltage required for producing large amounts of hydrogen.

In the last years, the electrolysis of alcohols has demonstrated to be a promising alternative to decrease the energy demand ascribed to the electrolytic production of hydrogen [4]. The high energy contained in these fuels supplies part of the energy requirements, thus reducing the external energy demands, and enables obtaining higher current density values at lower anode potential (below 1.3 V) than required for water electrolysis. In this way, it is possible to produce H_2 with a lower electrical energy requirement (as shown later on, 30 kWh kg H_2^{-1} after deactivation) in comparison with commercial PEM water electrolyzer stacks (50 kWh kg H_2^{-1}) [5]. This process of water alcohols mixture electrolysis has been also named Electrochemical Reforming or Electro-Reforming, and is based on the use of electrical power to split water molecule and transform it into H_2 by the electro-oxidation of the alcohol fuel.

Previous works have already demonstrated the interest of this technique for the production of high purity hydrogen by electrochemical reforming of methanol [4,6–8], glycerol [9–11], ethanol [5,12], bioethanol [13,14] and ethylene glycol [15]. However, most of these previous works have been carried out in Proton Exchange Membrane (PEM) cells and, hence, expensive anodic catalyst typically based on Pt-Ru/C of high metal loadings have been used. Possible utilization of alkaline environment presents the advantage of improved electro-oxidation kinetics with non-precious metal catalysts. In this sense, a previous communication of Chen et al. [14] has demonstrated the interest of using Pd nanoparticles deposited on titania nanotubes for alkaline electrochemical reforming of ethanol, ethylene glycol, glycerol and 1,2-propanediol using an Anion Exchange Membrane (AEM) based electrolysis cell. The authors report polarization curves recorded at 10 mV s^{-1} , showing high electro-catalytic activity for H_2 production, comparable with that of conventional PEM water electrolysis. However, further experiments should be performed in order to address several technological demands, especially the level of purity of the produced H_2 , sub-products formation, influence of the main operation conditions, system durability and anodic catalyst stability under such alkaline conditions.

This study presents, for the first time in literature, the preparation, characterization and testing of a self-standing sputtered Pd mesh-like anode structure of high electro-catalytic activity and stability for alkaline electro-chemical reforming of ethanol-water solutions in alkaline media. Synthesis of self-standing metallic membranes generally involves the conformal deposition of a metal layer on a support followed by local dissolution of the support. This approach has been successfully employed to produce microporous Pd/Au alloy membranes using sputtering as a metal deposition method [16]. The strategy reported in this work is radically

different as it involves the self-formation of a metallic mesh-like structure during deposition on a carbon paper with the carbon microfibers acting as anchorage lines for the Pd mesh-like structure. For that purpose, magnetron sputtering method has been used since it can be easily scaled-up. Moreover, porous films can be produced for conditions associated to a low mobility of the ad-atoms [17], which qualifies it for the synthesis of metal catalysts of large developed surface area. Compared to supported catalysts, self-supported ones offer the possibility to maximize the surface in contact with the reactive medium and, thereby, represent an interesting possibility to improve the electro-catalytic efficiency.

2. Experimental

2.1. Synthesis and characterization of the anodic Pd mesh-like architecture

Magnetron sputtering was used to produce macroporous Pd mesh-like structure by deposition on a microfiber Carbon Paper (Fuel Cell Earth) substrate. A 2" diameter Pd target positioned at a target–substrate distance of 70 mm was sputtered in a pure Argon atmosphere of 11 Pa using a discharge current of 0.3 A. The target was placed off-axis relative to the rotating substrate-holder axis, which enables ensuring a good lateral homogeneity of the flux of deposited material [18]. The overall film density was calculated by weighing the carbon microfiber paper before and after deposition, and measuring the film thickness obtained by deposition on a glass slide. The mass of Pd supported on the carbon paper was also measured before and after experiments by Atomic Absorption Spectrophotometry on a SPECTRA 220FS analyzer. The Pd film structure was also characterized before and after electrocatalytic experiments by X-Ray Diffraction (XRD) analysis using a Philips PW-1710 instrument with Cu K_α radiation ($\lambda = 1.5404 \text{ \AA}$). Surface morphology was imaged with a Scanning Electron Microscope (SEM) Philips XL30S FEG equipped with a field emission gun using an acceleration voltage of 15 kV and through lens detector. Chemical analysis was performed via an Energy-Dispersive Spectrometer (EDS) coupled to the SEM apparatus.

2.2. Preparation of the membrane electrode assembly (MEA)

The prepared sputtered Pd mesh-like structure was used as anode, while standard Pt supported on carbon (20 wt % Pt/C- Alfa Aesar) was adopted as cathode catalyst in the electrochemical reforming unit. Both electrodes were deposited on Carbon Paper substrates (Fuel Cell Earth) with a metal loading of 1.93 mg cm^{-2} (measured by Atomic Absorption Spectrophotometry) for the anode and 0.5 mg cm^{-2} for the cathode. Geometric surface area was 6.25 cm^2 . Membrane electrode assembly (MEA) was prepared by pressing together anode (Pd), cathode (Pt/C) and a Tokuyama A901 Alkaline Exchange Membrane, applying a load of 1 ton at 120 °C for 3 min. Prior to use, the AEM was pretreated by successive immersion in boiling deionized water for 1 h, and subsequently in 1 mol L^{-1} KOH for 24 h.

2.3. Electrochemical reforming activity measurements

Experimental tests were carried out in an electrolysis unit described in detail elsewhere [5]. The MEA was introduced between two Teflon gaskets to ensure sealing between anode and cathode compartments (0.2608 cm^3 per chamber). Graphitic bipolar plates of 2 cm thickness and 36 cm^2 area were placed on both sides of the MEA. Parallel grooves were drilled in the graphite plates, with a total surface area of 6.25 cm^2 , which served as flow channels. All the above items were finally placed between two

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