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Electrochemical reforming of alcohols on nanostructured platinum-tin catalyst-electrodes

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ABSTRACT

This study reports the feasibility of high purity H_2 production by means of the electrochemical reforming of biomass derived organic alcohols (methanol, ethanol and ethylene glycol)-water solutions in a proton exchange membrane (PEM) electrolysis cell. For that purpose, a nanostructured bimetallic carbon-supported Pt–Sn catalyst, with nominal Pt/Sn atomic ratios of 70/30, was synthesized by a modified polyol reduction method and characterized by means of TEM, XRD and XPS analysis. The resulting Pt_7–Sn_3/C catalyst consists of a bi-phase Pt/SnO_x structure and presents a narrow particle size distribution with size predominantly in the order of 4.5 nm, showing high dispersion on carbon support (20 wt.% metal loading). During electrochemical reforming tests, the influence of reaction temperature and the electrocatalytic stability of the system were verified for mild working operation times. Synthesized 20 wt.% Pt_7–Sn_3/C anodic catalyst provided a promising electro-catalytic activity, comparable to that of commercial 60 wt.% Pt–Ru/C and required lower amounts of Pt in order to produce the same amount of hydrogen. Proposed system allowed to produce H_2 with a lower electrical energy requirement (26 kWh $kg_{H_2}{}^{-1}$ even after deactivation), in comparison with commercial PEM water electrolyser stacks (50 kWh $kg_{H_2}{}^{-1}$). In addition, obtained H_2 purity was very high (99.938%) and only few ppm of CO and CO_2 were detected at the cathode chamber. These results demonstrated the potential interest of Pt_7–Sn_3/C anodic catalyst, synthesized via the polyol method, for production of pure hydrogen from biomass-derived compounds via electrochemical reforming at low temperatures.

1. Introduction

Hydrogen has attracted great interest as a future clean fuel for combustion engines and fuel cells [1]. It can be obtained by different processes and from a wide variety of materials (water, biomass, or hydrocarbons). Among them, the catalytic steam reforming of methane is currently being the most used in industry. However, this process required several reaction steps, such as reforming, water gas-shift and preferential oxidation (PROX) or methanation, in order to clean the reformer gas stream from CO before entering the fuel cell. Therefore, due to its practical use, especially for on-site applications, more efficient and compact processes for hydrogen production should be considered [2]. Electrolysis of water can generate highly pure hydrogen, in a fast single step process, and hence it can be considered as the most promising technology for small scale H_2 production [3]. The drawback of this process is the high-energy requirement. Theoretically, an energy consumption of 39.4 kWh kg^{-1} or 3.54 kWh/Nm^3 is required for the production of H_2. However, commercial electrolyzes require up to 50–55 kWh kg^{-1} or 4.5–5 kWh/Nm^3 [4]. In the last years, the electrolysis of alcohols (also called Electrochemical Reforming) have shown to be a promising method to decrease the energy demand ascribed to the electrolytic production of hydrogen [5]. An electrochemical reformer may operate in a similar way to a proton exchange membrane (PEM) water electrolysis cell. However, instead of water, an aqueous solution of the organic compound is electro-oxidized at the anodic side leading to the formation of other organic compounds, protons and electrons. The external circuit provides the electrical potential to drive the reaction, while protons migrate through the proton exchange membrane to the cathode side, where they recombine with electrons, which have passed through the external circuit to form pure hydrogen gas. In

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Table 1
Advantages and drawbacks of electrochemical reforming vs. catalytic steam reforming.

	Electrochemical reforming of alcohols	Catalytic steam reforming
Advantages	• Lower reaction temperatures (<100 °C) making possible a rapid startup • Low toxicity • Direct pure hydrogen production, separated from other reaction products • Easier and fast control of hydrogen production rate • Compact unit combining both reaction and hydrogen purification with a consequent capital costs reduction • High renewable energy integration • Reduced environmental impact • Seasonal energy storage without energy losses • Capability to handle power fluctuations by H_2 production • Lower power demands than water electrolysis, since part of the energy required is provided by the organic molecule	• Mature technology • Adequate legislature framework • Practical experience in plant operations • Safety of power and energy supply
Drawbacks	• Immature technology • Limited practical experience • Required development of more active catalysts and more stable membranes • High cost anodic catalyst typically based on Pt–Ru/C	• Higher reaction temperatures (200–1000 °C) • Poor hydrogen purity by production of H_2/CO mixtures, CO_2 and CH_4 • Required purification stages (multistep process) affecting negatively the overall process in terms of costs and efficiency • Pollutant emissions • Application of non-renewable resources • Catalyst deactivation due to coking

this context, recent studies have shown that the electrochemical reforming of water–alcohol mixtures, i.e., methanol [5–8], glycerol [9,10], ethanol [11,12], bioethanol [13,14] and ethylene glycol [15] has a great potential for H_2 production at atmospheric pressure. The use of such compounds allows electrolysis at potentials lower than 1.2 V, leading to electrical power savings if compared to conventional electrolytic water splitting. Table 1 also summarizes some interesting advantages of electrochemical reforming of alcohols vs. their catalytic conversion for H_2 production. In addition, similar energy requirements can be found for electrochemical reforming of alcohols (149–193 kJ/mol H_2, this work) compared to those obtained in a thermodynamic study of conventional steam reforming of ethanol (100–260 kJ/mol H_2 for 1000–400 °C) [16].

While undoubtedly promising, the electrochemical reforming approach suffers the limitation of delivering low current densities that must be improved for the technological exploitation of this kind of systems. Pt is known to be the best active and stable noble metal for alcohol oxidation, particularly in acid media [17]. However, the limitation of the usage of Pt-based catalysts comes from its high cost, limited resources and tendency for surface poisoning that could be mitigated by adding a second metal. Hence, the use of a bimetallic catalyst involving the addition of Ru, Sn, Os among others, has been reported to promote alcohol electro-oxidation in both acid an basic media [18–25]. Pt–Sn nanocomposites have been extensively studied as catalysts for the electro-oxidation of hydrogen/carbon monoxide, methanol and ethanol for electricity production in PEM fuel cells. A good CO tolerance during H_2 oxidation has been proved but regarding the methanol or ethanol electro-oxidation, controversial results depending on the phase of Sn [26] and Pt/Sn atomic ratio [23,27] have been described. Furthermore, alcohol oxidation reactions are well known to be structure sensitive, therefore particle size, dispersion, morphology and agglomeration degree, as well as surface and bulk structure, which strongly depends on the preparation method, have to be considered [23,28]. It is established that the electrocatalyst performance depends substantially on the atomic ratios of elements present, and the optimal composition of Pt–Sn/C for ethanol oxidation varies depending on the synthesis procedure and the reaction conditions. Lamy et al. [27] studied Pt/Sn compositions ranging from 4/1 to 9/1 and found that the addition of Sn always promoted the ethanol electro-oxidation compared to Pt. Even more, the presence of 10–20 at.% Sn resulted in the best resistance to catalyst poisoning or deactivation. Zhou et al. [29] published that the Pt–Sn composition of 33–40 at.% Sn provides the best ethanol electro-oxidation current densities for fuel cell applications. Recently, carbon supported Pt–Sn/C electro-catalysts with 30 at.% Sn (Pt_7–Sn_3/C), synthesized by the modified polyol method, were reported to have high catalytic activity for ethanol electro-oxidation in acid [30] and alkaline [31] solutions. According to the latter studies, the aim and contribution of the present work was to evaluate for the first time the application of these Pt_7–Sn_3/C nanoparticles with average particle size of 4.5 nm to the electrochemical reforming of ethanol, ethylene glycol and methanol for pure H_2 production in a PEM membrane fuel cell type reactor. In addition, a mild term stability study was developed in order to evaluate the real energy requirements of produced H_2, and hence, the practical feasibility of the proposed catalytic system, in comparison with a commercial PEM water electrolyzer.

2. Experimental

2.1. Preparation of the carbon-supported Pt_7–Sn_3/C catalyst

Colloidal Pt–Sn nanoparticles were synthesized using modified polyol reduction method [32,33], using ethylene glycol (EG) as a stabilizing and reducing agent. EG also acted as a surfactant after precursor metal salt reduction, preventing any particle agglomeration after the formation of colloidal particles. The detailed synthesis procedure of Pt–Sn nanoparticles with the atomic ratio of Pt to Sn of 70/30 at.% is described in details elsewhere [30]. In short: 19.8 mg of tin (II) chloride anhydrous (ACROS Organics, 98% Anhydrous) and 82.2 mg platinum (IV) chloride (Alfa Aesar, 99.9% metal basis, Pt (57.75%)) were used as precursors. First, those salts were dissolved in 50 mL of EG (anhydrous 99.8% Sigma-Aldrich) containing 0.2 M of NaOH (EM Science, ACS grade), pH 11. The solution was stirred for 1 hour at room temperature and then refluxed at 190 °C for 2 h. The dark brown colloidal solution containing Pt_7–Sn_3 nanoparticles (concentration of colloids in EG is 1.2 mg/mL) was cooled down to room temperature. The colloidal solution was then dispersed on a carbon support (Vulcan XC 72, Cabot) by mixing in a large beaker an appropriate amount of colloidal solution and carbon for up to 24 h, resulting in 20 wt.% metal loading. Carbon-supported Pt_7–Sn_3 catalyst was extensively washed with DI water (18 MΩ cm) and then