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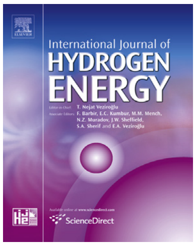

Modification of palladium surfaces by bismuth adatoms or clusters: Effect on electrochemical activity and selectivity towards polyol electrooxidation

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ABSTRACT

The syntheses of Bi-modified Pd catalysts with a controlled size distribution are presented as well as the characterizations of their structures and of their surfaces. Effects of the modification either of non-supported Pd nanospheres by spontaneous deposition of Bi or of carbon-supported Pd-based nanomaterials by decoration with bismuth clusters on the electrocatalytic activity towards glycerol electrooxidation were evaluated and compared in alkaline medium. The method of bismuth deposition has a dramatic effect on the activity of the palladium based catalysts: spontaneous deposition of Bi on non-supported Pd nanoparticles leads to relatively low activity enhancement, whereas decoration of carbon-supported Pd nanoparticles by Bi_2O_3 and $Bi(OH)_3$ clusters leads to very high activity increase at low overpotentials. *In situ* infrared spectroscopy indicated that the modification of Pd by Bi did not affect the selectivity of glycerol oxidation, whereas in the case of Pt containing catalyst, a dramatic change in selectivity occurred at low potentials.

Introduction

The recent environmental and energy challenges faced by society could be addressed by envisaging the production of electricity using hydrogen/air solid polymer electrolyte fuel cells (SPEFC). However hydrogen, which is the most abundant element in the universe, does not exist as dihydrogen molecule on earth, but is mainly combined with carbon (hydrocarbon) or oxygen (water), so that molecular hydrogen has to be produced. The most common method for hydrogen production consists in the reforming of fossil hydrocarbons. But the reforming process of such compounds, although less expensive than other hydrogen production methods, produces significant amount of carbon monoxide which is detrimental for the proton exchange membrane fuel cell (PEMFC) performances [1], so that complicated and costly hydrogen purification processes have to be implemented in parallel. Water electrolysis is also being developed, leading to high purity hydrogen, suitable to feed a low temperature fuel cell, such as a PEMFC or an alkaline fuel cell (AFC) [2–4]. In water electrolysis liquid or gaseous water is fed to the anodic

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compartment where it is oxidized producing oxygen and protons:

$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^- \quad (1)$$

Oxygen evolves in the gaseous phase, whereas the electrons circulate in the external circuit and protons cross-over the membrane, reaching the cathodic compartment where they are reduced by the electrons coming from the external circuit, thus producing hydrogen, as follows:

$$2H^+ + 2e^- \rightarrow H_2 \quad (2)$$

This corresponds to the overall decomposition of water into hydrogen and oxygen:

$$H_2O \rightarrow H_2 + 1/2O_2 \quad (3)$$

with $\Delta H = 286$ kJ and $\Delta G = 237$ kJ $(\text{mole } H_2)^{-1}$ under standard conditions.

The corresponding theoretical cell voltage can be calculated from ΔG, i.e. $E_{cell} = \Delta G/2F$, giving $E_{cell} = 1.23$ V. But the overvoltage of the oxygen evolution reaction (OER) is hardly decreased below 0.5 V (i.e. a cell voltage of at least 1.7–1.8 V at 1 A cm^{-2}) [5], so that the energy yield between both systems, water electrolysis and fuel cell, is lower than 40% (considering a H_2/air PEMFC performance of 1 A cm^{-2} at 0.7 V). An alternative can be the use of compounds produced from biomass as hydrogen source since the theoretical cell voltage for their electrochemical decomposition with hydrogen production is lower than the theoretical cell voltage of water electrolysis (1.23 V under standard conditions) [6,7]. For example, glycerol can be oxidized in the anodic compartment of the electrolysis cell instead of water, producing carbon dioxide and protons:

$$CH_2OH{-}CHOH{-}CH_2OH + 3H_2O \rightarrow 3CO_2 + 14H^+ + 14e^- \quad (4)$$

The protons are reduced to hydrogen in the cathodic compartment according to Eq. (2). The overall electrochemical decomposition reaction of glycerol into hydrogen and carbon dioxide is:

$$CH_2OH{-}CHOH{-}CH_2OH + 3H_2O \rightarrow 3\,CO_2 + 7H_2 \quad (5)$$

with $\Delta G_r = 3.9$ kJ $mol^{-1}{}_{glycerol}$, giving $E_{cell} = 0.003$ V [8].

The thermodynamic data point out that the use of alcohols, and particularly of glycerol, as anodic reactants in an electrolysis cell could be energetically more interesting than water for the production of hydrogen.

Despite their promising thermodynamics properties, the main limitation in using alcohols as hydrogen source in an electrolysis cell is the slow kinetics of their oxidation reaction. For this reason, alkaline medium has to be preferred to acid medium: the electrochemical reaction kinetics of fuel oxidation is faster [9], and both reactions (alcohol oxidation reaction at the anode and hydrogen evolution reaction at the cathode) can be performed on low platinum loaded electrodes or platinum-free catalysts [10,11].

Now, the question could be: what is the best alcohol to be used as hydrogen source in an alkaline electrolysis cell. Methanol is the simplest and more reactive alcohol, but it is mainly produced from petrochemical industries and it is a toxic compound. Ethanol is less toxic and is an attractive compound because it can be produced from biomass. But, because the breaking of the C–C bond is very difficult to realize at low temperature, in alkaline medium as well as in acidic one, the main reaction products are acetaldehyde and acetate [12,13] which are non-value added compounds, with only two hydrogen molecules produced from one molecule of ethanol oxidized into acetate. The use of polyols as hydrogen sources can be an interesting alternative. Polyols such as ethylene glycol and glycerol are less toxic than methanol. Each carbon of these compounds carries an alcohol group and as a consequence their partial oxidation without C–C bond breaking and CO_3^{2-} production leads to the simultaneous production of hydrogen and high value added products, with higher amount of hydrogen than in the case of mono-alcohol when oxalate (Eq. (6)), tartronate (Eq. (7)) and mesoxalate (Eq. (8)) are produced:

$$CH_2OH{-}CH_2OH + 2OH^- \rightarrow COO^-{-}COO^- + 4H_2 \quad (6)$$

$$CH_2OH{-}CHOH{-}CH_2OH + 2OH^- \rightarrow COO^-{-}CHOH{-}COO^- + 4H_2 \quad (7)$$

$$CH_2OH{-}CHOH{-}CH_2OH + 2OH^- \rightarrow COO^-{-}CO{-}COO^- + 5H_2 \quad (8)$$

But again, ethylene glycol is a product from the petrochemical industry, whereas glycerol is a by-product of the biofuel industry which has to be valorised to make this sector profitable. Therefore, the present contribution will focus on glycerol electrooxidation process.

The problem of catalysis is of paramount importance for the selective oxidation of polyols. Palladium is an active material for alcohol electrooxidation in alkaline medium [14], and particularly for glycerol oxidation [15]. It is also known that the modification of palladium by oxophilic metal from the p-group affects dramatically the electrocatalytic behaviour [16], particularly bismuth [17]. But, the role of bismuth in the changes of the catalytic behaviour is not yet really understood. The aim of the present paper is to study the activity and selectivity of Pd nano-catalysts modified by either Bi-adatoms or Bi-clusters toward glycerol electrooxidation. The catalyst composition and structure are indeed very important in electrocatalysis. For example, it has recently been shown on self-supported PdBi materials prepared by a sacrificial support method that the microporous structure of the catalysts influenced its catalytic behaviours, activity as well as selectivity, towards glycerol electrooxidation [18]. The oxidation reactions of alcohols involve several elementary steps: adsorption process, alcohol dehydrogenation reaction, electron transfer, reaction with adsorbed OH and product desorption [19]. And each step can limit the anode performance.