Journal of Power Sources 293 (2015) 823–830

Contents lists available at ScienceDirect

Journal of Power Sources

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

Binary and ternary palladium based electrocatalysts for alkaline direct glycerol fuel cell

Adriana Napoleão Geraldes [a], Dionisio Furtunato da Silva [b], Leonardo Gondim de Andrade e Silva [b], Estevam Vitório Spinacé [b], Almir Oliveira Neto [b], Mauro Coelho dos Santos [a, *]

[a] Laboratório de Eletroquímica e Materiais Nanoestruturados, Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Rua Santa Adélia, 166, 09210-170, Santo André-SP, Brazil
[b] Instituto de Pesquisas Energéticas e Nucleares-Comissão Nacional de Energia Nuclear (IPEN-CNEN), Av. Prof. Lineu Prestes, 2242, 05508-900, São Paulo-SP, Brazil

HIGHLIGHTS

- Palladium based electrocatalysts.
- Electron beam irradiation reduction process.
- Single alkaline direct glycerol fuel cell.
- PdAuSn/C 50:40:10 electrocatalyst show the higher power density.

ARTICLE INFO

Article history:
Received 3 April 2015
Received in revised form
18 May 2015
Accepted 2 June 2015
Available online

Keywords:
Alkaline direct glycerol fuel cell
Palladium-based
Durability tests
Electron beam irradiation
Glycerol electro-oxidation

ABSTRACT

Pd/C, PdAu/C 50:50, PdSn/C 50:50, PdAuSn/C 50:40:10 and PdAuSn/C 50:10:40 electrocatalysts are prepared using an electron beam irradiation reduction method and tested for glycerol electro-oxidation in alkaline medium. X-Ray diffraction (XRD), Energy dispersive X-ray analysis (EDX), Transmission electron Microscopy (TEM) and Cyclic Voltammetry (CV) are used to characterize the resulting materials. The activity for glycerol electro-oxidation is tested in alkaline medium at room temperature using Cyclic Voltammetry and Chronoamperometry (CA) and in a single alkaline direct glycerol fuel cell (ADGFC) at temperature range of 60–90 °C. EDX analysis demonstrate that Pd:Au:Sn atomic ratios are very similar to the nominal ones. X-ray diffractograms of PdAuSn/C electrocatalysts evidence the presence of Pd (fcc), Au (fcc) and SnO_2 phases. TEM analysis demonstrates a good dispersion of the nanoparticles on the carbon support with some agglomerates. Cyclic Voltammetry experiments suggest that PdAuSn/C electrocatalysts demonstrate better results. In single fuel cell tests, at 85 °C, using 2.0 mol L^{-1} glycerol in 2.0 mol L^{-1} KOH solutions, the electrocatalyst PdAuSn/C 50:40:10 demonstrate highest power density (51 mW cm^{-2}) and the 120 h durability tests demonstrate a 210 μV h^{-1} degradation rate.

1. Introduction

In the current situation, where world's energy system needs to be changed radically in the next decades, researches on materials, processes and systems are provided as a critical aspect for the development of a clean and more efficient energy system. The environmental problems and the global demand for energy have stimulated the scientific community to research clean and renewable energy sources [1–3].

Due to their high energy efficiency, convenient operation, and friendly environmental characteristics, polymer electrolyte membrane fuel cells (PEMFC) are considered one of the most promising fuel cell technologies for both stationary and mobile applications. Significant progress has been achieved over the past few decades. However, durability and cost have been identified as the most important issues in PEMFC technology. Durability is one of the major difficults to have polymer electrolyte membrane fuel cells

* Corresponding author.
E-mail addresses: drinager@ig.com.br (A.N. Geraldes), dfsilva@ipen.br (D.F. da Silva), lgasilva@ipen.br (L.G.A. e Silva), espinace@ipen.br (E.V. Spinacé), aolivei@ipen.br (A.O. Neto), pdrmcsa@gmail.com (M.C. dos Santos).

http://dx.doi.org/10.1016/j.jpowsour.2015.06.010
0378-7753/

(PEMFC), accepted as a viable commercial product. Electrocatalyst degradation mechanisms depend on factors such as potential, temperature, humidity, contaminants, and carbon support stability [4].

In this context, fuel cells appear to be an appropriate technology for generating electricity through the electro-oxidation of alcohols [5–9].

When compared to hydrogen-fed fuel cells the direct alcohol fuel cell, (DAFC) is more interesting because the use of liquid fuels simplifies the fuel delivery system [5,6,10–12]. Primary alcohols such as ethanol, 1-propanol, ethylene glycol, and glycerol have demonstrated to be interesting as fuels in DAFC for several reasons, such as, their low toxicity, high boiling point, high specific energy and less prominent crossover due to their larger molecular size [13].

Recently, the electro-oxidation of glycerol in fuel cells to add value to the large amount of this alcohol - generated as a byproduct of biodiesel used as fuel in internal combustion engines of fleets of large cities - have been studied. The glycerol electro-oxidation could bring environmental benefits and economic feasibility to biodiesel production. Although the complete electro-oxidation of glycerol to CO_2, is hard due to the need of C–C bond breaking. The use of glycerol - a non-valued residue of biodiesel production - as fuel may be an interesting alternative, because it is less toxic than methanol and displays relatively lower theoretical energy density, 5.0 kWh kg^{-1}, *versus* 6.1 kWh kg^{-1} for methanol [14]. Alkaline medium should be preferred to acid medium since the electrochemical reaction kinetics occurring at fuel cell electrodes - fuel oxidation [15] and oxygen reduction [15,16] – are favored and lower platinum loadings or platinum-free electrocatalysts could be used [17].

It has been reported that palladium is an active metal for glycerol and/or ethanol electro-oxidation [14,18–21]. On the other hand, gold is generally considered as a poor electrocatalyst in acid medium; however, its activity in alkaline medium is slightly greater. The reactivity of glycerol and ethanol on gold, in alkaline medium, is related to the fact that, practically, no poisoning species (CO-like species) may be formed and adsorbed on the surface [22], however tin is also studied in the literature.

Pd/C and PdSn/C were studied by Liu et al. [23] as catalysts for formic acid oxidation. PdSn/C has higher electrocatalytic activity for formic acid electro-oxidation than a comparative Pd/C catalyst and it shows great potential as a less expensive electrocatalyst for formic acid electro-oxidation in direct formic acid fuel cells (DFAFC). Du et al. [24] studied a series of carbon-supported Pd–Sn binary alloyed catalysts, as anode electrocatalysts, for direct ethanol fuel cell reactions in an alkaline medium. Among various Pd–Sn catalysts, $Pd_{86}Sn_{14}$/C catalysts showed a great deal of enhanced current densities in cyclic voltammetric and chronoamperometric measurements, compared to commercial Pd/C (Johnson Matthey). The overall rate law of ethanol oxidation reaction, for both $Pd_{86}Sn_{14}$/C and commercial Pd/C, was also determined, showing that $Pd_{86}Sn_{14}$/C was more favorable in high ethanol concentration and/or high pH environment.

The nature, structure, and composition of multi-metallic catalysts have an important effect on the alcohol electro-oxidation in terms of activity (energy generation) and selectivity. Considering that the chemical and physical characteristics of these electrocatalysts depend on the preparation procedure, this becomes a key factor regarding their electrochemical activity [12]. In our studies, the carbon-supported metal nanoparticles have been prepared for fuel cell applications using radiation-induced reduction of precursors of metal ions [25]. Silva et al. prepared PtRu/C electrocatalysts for methanol electro-oxidation, in acid medium, using gamma irradiation and electron beam irradiation [26–28]. Silva et al. [25] also prepared $PtSnO_2$/C electrocatalysts for ethanol electro-oxidation, in acid medium, using electron beam irradiation. Moreover, Silva et al. [28] studied the activity of the electrocatalysts for alcohol oxidation in alkaline medium and the results showed that PtAu/C electrocatalysts had a better performance for methanol electro-oxidation when compared to other electrocatalysts prepared. PtAuBi/C (50:40:10) indicated a superior performance for ethanol electro-oxidation in alkaline medium [28]. Geraldes et al. [29,30] prepared carbon-supported Pd, Au and bimetallic PdAu (Pd:Au 90:10, 50:50 and 30:70 atomic ratios) electrocatalysts using electron beam irradiation for ethanol and glycerol electro-oxidation. In ethanol electro-oxidation [29], chronoamperometry (CA) experiments, at room temperature, demonstrated that PdAu/C electrocatalysts with Pd:Au ratios of 90:10 and 50:50, presented superior activity. Using *in-situ* ATR-FTIR spectroscopy measurements it was observed that the mechanism for ethanol electro-oxidation is dependent on catalyst composition, leading to different reaction products such as acetaldehyde and acetate, depending on the number of electrons transferred. Experiments on a single alkaline direct ethanol fuel cell (ADEFC) were conducted between 50 and 90 °C, and the best performance of 44 mW cm^{-2} in 2.0 mol L^{-1} ethanol was obtained at 85 °C for Pd:Au with Pd:Au atomic ratio 90:10 electrocatalyst. Geraldes et al. [30] also studied the glycerol electro-oxidation in single alkaline direct glycerol fuel cell (ADGFC). Cyclic voltammetry (CV) and chronoamperometry showed that PdAu/C electrocatalyst with Pd:Au atomic ratio of 50:50 indicated superior activity for glycerol electro-oxidation at room temperature. Using *in-situ* ATR-FTIR spectroscopy experiments it was identified oxalate, glycerate oxalate, glycerate ion, 1,3-dihydroxy-2-propanone, glyceraldehyde and glycolate as products of glycerol electro-oxidation. Experiments with single ADGFC were carried out from 50 to 90 °C, using Pd/C electrocatalyst: the best performance was obtained at 80 °C. In another study [31], Pd and PdSn (Pd:Sn atomic ratios of 90:10), supported on Multi Wall Carbon Nanotubes (MWCNT) or Carbon (C), were prepared. CV analysis finds that Pd/MWCNT and PdSn/MWCNT present onset potentials changing to negative values and high current values, compared to Pd/C and PdSn/C electrocatalysts. In-situ ATR-FTIR analysis identified acetate and acetaldehyde as principal products formed during the ethanol electro-oxidation with low conversion to CO_2. In single fuel cell tests, at 85 °C, using 2.0 mol L^{-1} ethanol in 2.0 mol L^{-1} KOH solutions, the electrocatalysts supported on MWCNT, showed higher power densities, compared to the materials supported on carbon: PdSn/MWCNT presented the best result (36 mW cm^{-2}). The results demonstrated that the use of MWCNT improves the electrocatalytic activity for Ethanol Oxidation Reaction (EOR).

In our laboratory, we have prepared electrocatalysts for electron beam irradiation reduction process [25–31]. Considering that binary PdAu/C and PdSn/C electrocatalysts prepared according to this methodology showed good activity for glycerol and ethanol electro-oxidation in alkaline medium [28–31], we proposed a study of ternary electrocatalysts. In this regard, the aim of this paper is focused on the preparation of ternary PdAuSn/C electrocatalysts and test of these materials for glycerol electro-oxidation in an alkaline medium at room temperature using electrochemical techniques and in a single ADGFC at 60–90 °C.

2. Experimental

Pd/C, PdAuSn/C50:40:10, PdAuSn/C 50:10:40, PdAu/C 50:50 and PdSn/C 50:50 electrocatalysts (20 wt% metal loading), were prepared using $Pd(NO_3)_2.2H_2O$ (Fluka), $HAuCl_4$ $3H_2O$ (Fluka), and $SnCl_2$ (Fluka) as metal sources, dissolved in 50/50 (v/v) water/2-propanol. Carbon Vulcan® XC72R used as a support, was, then, dispersed in the solution using an ultrasonic bath. The resulting mixtures were