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Energy conversion using Pd-based catalysts in direct ethanol fuel cell

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Abstract.

Direct Ethanol Fuel Cells DEFCs are considered one of the promising renewable energy sources, as they can produce electrical energy directly from the ethanol electrooxidation reaction. The efficiency of ethanol electrooxidation is a big question from research point of view. In this work, Pd is used as catalyst for the electrooxidation in alkaline media aiming to improve the catalytic activity for ethanol electrooxidation reaction, and consequently the DEFC performance, more than using a Pt-based catalyst. In this research, Pd was used as an alternative for Pt-based catalyst. Additionally, it can be recorded that the alloying of Pd with Sn will enhance the efficiency through increasing the surface area of the PdSn catalysts.

Key words

Ethanol electrooxidation, Pd catalyst, alkaline media

1. Introduction

Direct Ethanol fuel cell is an electrochemical device which converts the energy through chemical reactions; electrooxidation of ethanol, into electrical energy. The demand for energy, coupled with concerns about environmental pollution and growing fossil fuel costs have created a great need for clean and efficient power sources [1]. Both direct methanol fuel cells (DMFCs) and direct ethanol fuel cells (DEFCs) have been projected to be strong candidates to compete with advanced batteries for powering mobile and portable electronic devices owing to their uniquely high specific energy [2]. Ethanol is more attractive than methanol because of its lower toxicity [2]. Moreover, direct alcohol fuel cells (DAFCs) that directly convert the chemical energy stored in the alcohol into electricity are promising as power sources for auxiliary power in transportation, portable electronics, and other contemporary applications [3-6]. Although DEFCs have a lower theoretical potential (1.15 V vs. 1.23 V for H_2 -fuel cells at the standard condition) their thermodynamic efficiency of 97% is higher than that for H_2 - fuel cells (83%) [7]. Ethanol has a volume energy capacity of 6.3 kWh/L, which is higher than hydrogen (2.6 kWh/L) and methanol (4.8 kWh/L) [7].

A significant challenge in the development of DEFC technologies is the need for highly active catalysts for the ethanol oxidation reaction (EOR) that takes place at the negative electrode (anode) [2]. It has been reported that PtSn-based catalysts have higher activity than other Pt-M (M ¼ Ru, Pd, W, etc) catalysts for ethanol oxidation in acid electrolyte [8-11]. Unfortunately, it was also found that in acid electrolyte, the kinetics of EOR remains sluggish (low activity) and the majority of the product of EOR is acetic acid (CH_3COOH), not CO_2 , which means that PtSn-based catalysts present low catalyst selectivity [4,12]. Recently, with the emergence of alkaline membranes that conduct hydroxide ions (OH−), alkaline direct alcohol fuel cells (DAFCs) have attracted interest [2]. The most significant advantage associated with the change in the electrolyte membrane from acid to base is that the kinetic reaction of both the alcohol anodic oxidation and the oxygen cathodic reduction in alkaline media become faster than in acidic media, thus making possible the reduction of catalyst loading [13-15].

Recently, much more attention has been directed to the use of Pd as base metal for a catalyst for DAFCs in alkaline media. The abundance of Pd on the Earth's crust is 200 times higher than Pt (0.6 ppb vs. 0.003 ppb), the comparatively low price of Pd (only 30%-40% compared to Pt) makes it attractive for large-scale fuel cell applications [16-18]. Although Pd is nearly inert to EOR in acid electrolytes, it has demonstrated competitive EOR activity [19-20], and slightly better ability to break C-C bonds of ethanol in high pH media, as compared to Pt-based catalysts [21]. In this regard, Pd and Pd-based catalysts are emerging as alternatives to Pt-based catalysts for the alcohol oxidation reaction, and especially for the EOR in alkaline media [22-25]. Metal oxides (CeO_2, NiO, Co_3O_4, and Mn_3O_4) were added to Pd catalyst [17, 18] and it was proved that NiO has given the best results in alkaline solutions. Although Pt−Sn has been considered as one of the best catalysts for the EOR in acidic electrolytes, its Pd-based counterpart (Pd−Sn) has not been well studied for the EOR in alkaline media [1]. Wenxin Du, have shown that the Pd-Sn/C catalysts have peak current densities two times higher than that of Pd/C [1]. In the study of Zhiyong Zhang, Le Xin, Kai Sun, Wenzhen Li, the addition of Ni to the Pd base catalyst proved to improve the performance of the EOR in alkaline media, increasing the current densities 33 times more than Pd/C [7].

In this work, a binary catalyst (Pd-Sn) was used aiming to enhance the performance of the DEFC by improving its EOR in alkaline media. The impregnation/reduction method was used to obtain the catalysts with different distribution of Pd, and Sn supported on Vulcan carbon due to the ease of its preparation [26]. X-ray Diffraction (XRD) and Transmission Electron Microcopy (TEM) tests were used to characterize the electrocatalysts. The Chronoamperometry (CA) and Cyclic Voltammetry (CV) tests were used to evaluate the performance of DEFC having PdNiSn/C catalysts in alkaline media.

2. Experimental

2.1 Catalysts preparation

The impregnation/reduction method was used to prepare the Pd based catalysts supported on Vulcan carbon (XC-72) functionalized with HNO_3; the compositions are described in table 1. This method is a famous method used to prepare nano-catalyst materials [27, 28]. The ethylene glycol was used as the reducing agent. A solution containing the salts $PdCl_2$, $SnCl_2.2H_2O$ was prepared with ethylene glycol and deionized water. After the carbon support was added and the solution was agitated in ultrasonic bath in order to dissolute the metallic elements from their corresponding salts. The pH solution was adjusted in alkaline media of NaOH (about pH 12) and heated at 130 °C, under agitation to enable the metals reduction. The samples passed through a centrifugation process and, after that, the samples were dried.

Table 1 Nominal composition of the synthesised alloys

Alloy	Nominal composition	Pd/Sn ration
Pd/C-HNO3	Pd-100%	-
PdSn/C- HNO3	Pd-SN 86:14	6

2.2 Catalyst characterization

X-ray diffraction test was performed to characterize the structure of the catalyst and to define the chemical composition, this was possible using a BRUKER-AXS-SIEMENS diffractometer, model D5000 with a Cu-Ka radiation generated at 40 kV and 25 mA.

2.3 Performance and activity evaluation

The catalysts activity was measured in a 1.0 M ethanol and 1,0 M NaOH solution. The cyclic voltammetry technique was used for this purpose and a three-electrode cell was used also. The three electrode cell consists in a working electrode (graphite disc) with an exposed area of 0.29 cm^2 covered by a mixture prepared as follows: 5 mg of catalyst was mixed with 2 mL of ethanol (Merck) and 25 mL of Nafion (5%, Aldrich) solution. The mixture was ultrasonically suspended to obtain ink slurry. Then, 136 mL of the slurry was spread on the working electrode to form a thin layer. The reference and counter electrodes were SCE and platinum respectively.

3. Results and Discussion

3.1 XRD Analysis

The X-ray diffraction (Fig. 1) shows a crystal structure of Pd base catalyst composed mostly by a *fcc* Pd crystalline structure.

It is clear from fig.1, that the noticeable peakes can be observed at the angles of 2Θ = 40, 47, 68, and 82 due to the planes (111), (200), (220), and (311) of Pd crystal structure. These results are in agreement with other results [1] about the crystal structure characterization of the Pd-based catalysts.

From fig. 1, it is clear the PdSn/C-HNO3 peaks have been shifted a little below the Pd/C-HNO3 peaks. And consequently, it can be revealed that an alloy of Pd and Sn has been formed, as similar expansion of the lattice structure reported previously, by other authors, for PdSn [28]. .

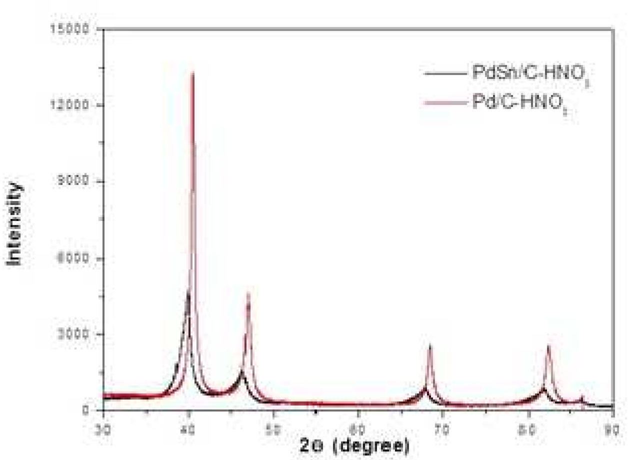

Fig.1 The XRD patterns of PdSn/C-HNO3 and Pd/C-HNO3

An estimative of lattice parameter was calculated from Equation (1):

$$n\lambda = 2d_{hkl} \sin \Theta \qquad \text{Equation (1)}$$

Where n represents the reflection order, l is the wavelength (in nanometers), d*hkl* is interplanar distance between two planes with Miller indices *hkl*, and q is the incident angle of X-rays.

The distance magnitude between two adjacent and parallel atom plans is a function of Miller indices (*hkl*), as well as lattice parameter a. For the crystalline cubic symmetry, the equation (2) is valid [29]:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad \text{Equation (2)}$$

The distance between the planes was determined from the equation (1) and the lattice parameter was estimated from equation (2). It was considered n ¼ 1 (first order reflection), l ¼ 1.5418 (Cu-Ka radiation), and Θ the half of 2Θ of the four peaks (111), (200), (220) and (311). For each plan, it was determined a lattice parameter value, and the average value is shown in Table 2.

The crystallite size, is estimated from the half-height width of the diffraction peak (222) using the Scherrer equation (3) [30] to avoid the effect of the agglomerations of individual nanoparticles would greatly impair the reliability of the particle size distribution.

$$\tau = \frac{(k\lambda)}{(\beta \cos \theta)} \qquad (3)$$

Where τ is the crystallite size nm, λ is the wave length (nm), β is the full width at half-maximum (FWHM) (in radians), k is a constant (0.94 to spherical crystallites) and θ is the diffraction angle. The crystallite size values are shown in Table 2.

Table 2 - *Crystallite size and lattice parameter calculated*.

Electrocatalysts	Crystallite size (nm)	Lattice Parameter(Å)
Pd/C-HNO_3	27.90	3. 87
PdSn/C-HNO_3	11.91	3.90

From table 2, attention should be given to the big reduction in the crystallite size from Pd to PdSn alloy although the lattice parameter did not change significantly. The crystallite size of Pd has been reduced from 27.90 to 11.91 (nanometers) after alloying with Sn. the big reduction in the crystallite size means that the surface area of Pd has been increased highly after alloying with Pd.

3.2 Cyclic Voltammetry

The cyclic voltammetry (CV) for the PdSn/C-HNO_3 and Pd/C-HNO_3 are shown in fig. 2. The CV was carried out to analyze the activity of the synthesized catalyst towards ethanol electrooxidation in alkaline media and to analyze the effect of Sn addition to Pd catalyst. The anodic oxidation behaviors on PdSn/C-HNO_3 and Pd/C-HNO_3 indicate that the Pd surface has changed after alloying with Sn.

It should be recorded here that the using of Pd to catalyze the EOR has proved better performance than using pure Pt. It is clear from the CV results obtained in this paper and the previous research efforts that using a family of Pd/C is better than a family of Pt/C for catalyzing the electro-oxidation of ethanol in DEFC [28].

Considering that the cyclic voltammetry analyses were obtained in alkaline medium of 1.0 mol L^{-1} of NaOH + 1.0 mol L^{-1} of ethanol, , it could be noticed from fig.2 that the onset potential for ethanol electro-oxidation of in alkaline medium using the catalyst Pd/C was about 550 mV. On the other hand, using PdSn/C catalyst the onset potential for electro-oxidation of ethanol in alkaline medium was 450 mV. Therefore the onset potential has decreased 100 mV after Sn addition. The change of onset potentials could be associated to the structure change after Pd was alloyed with Sn.

Additionally, the current density values have been increased in case of PdSn/C-HNO_3 more than Pd/C-HNO_3 due to the decrease in crystallite size and consequently the increase in active electrochemical surface area as happened with the reduction in the onset potential.

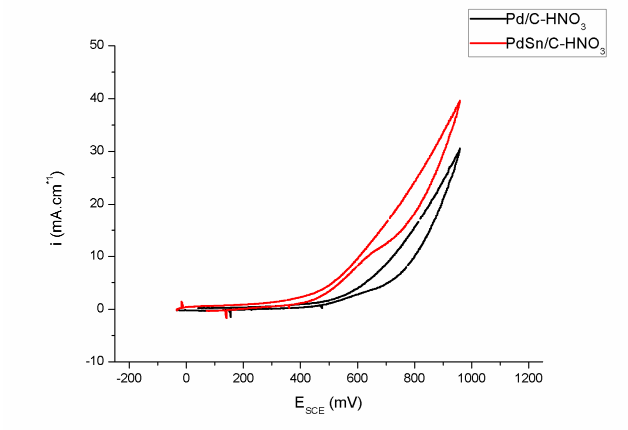

Fig.2 – (a) cyclic voltammograms CVs of Pd/C-HNO3 and PdSn/C-HNO_3 nano-catalysts in 1.0M NaOH containing 1.0M of ethanol with sweep rate 50 mV/s

4. Conclusion

Based on the obtained results and discussion, it is concluded that Pd based catalyst shows good promises to improve the activity of EOR of ethanol in alkaline media additionally, the impregnation/reduction method was used to synthesis the Pd based catalysts successfully. And finally, alloying Pd with a little of Sn will increase the EOR efficiency in alkaline medium and improve the DEFC performance.

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