



Low Pt content on the Pd₄₅Pt₅Sn₅₀ cathode catalyst for PEM fuel cells

J.J. Salvador-Pascual^a, V. Collins-Martínez^b, A. López-Ortíz^b, O. Solorza-Feria^{a,*}

^a Depto. Química, Centro de Investigación y de Estudios Avanzados del IPN, A. Postal 14-740, 07360 México D.F., Mexico

^b Centro de Investigación en Materiales Avanzados, Miguel de Cervantes 120, 31109 Chihuahua, Mexico

ARTICLE INFO

Article history:

Received 25 October 2009

Received in revised form

11 December 2009

Accepted 11 December 2009

Available online 21 December 2009

Keywords:

Oxygen reduction reaction

Pd₄₅Pt₅Sn₅₀ electrocatalyst

Electrocatalyst synthesis

PEMFC performance

ABSTRACT

Pd₄₅Pt₅Sn₅₀ electrocatalyst was prepared by a NaBH₄ reduction of PdCl₂, H₂PtCl₆ and SnCl₂ in THF at 0 °C. This catalyst was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS) microanalysis and hydrodynamic electrochemical technique. XRD, SEM and TEM results demonstrate that the borohydrate reduction methodology enable the synthesis of conglomerated particles nanometric in size ranging from 1 to 6 nm. Oxygen reduction reaction (ORR) activity was investigated on carbon dispersed catalyst by rotating disk electrode (RDE) technique in H₂SO₄ 0.5 M. The effect of temperature on the kinetics was analyzing resulting in an apparent activation energy of 42.54 ± 1 kJ mol⁻¹, value which is less than the obtained for the nanostructured bimetallic PdSn electrocatalyst under the same experimental condition. The Pd₄₅Pt₅Sn₅₀ electrocatalyst dispersed on a carbon powder was tested as cathode electrocatalyst in a membrane-electrode assembly (MEA) arriving to a power density of 210 mW cm⁻² at 0.35 V and 80 °C.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Fuel cells and metal-air batteries offer attractive alternative power source for stationary and portable applications in relation to traditional fossil-fuel energy production, conversion and storage. However, one critical issue to be addressed is the lack of effective electrocatalysts for multi-electron charge transfer processes of oxygen reduction at low overpotential. The cathodic overpotential is strongly influenced by several physical parameters such as electrocatalysts intrinsic properties, active catalysts surface area, concentration and diffusion coefficient of the oxygen and so on. The novel electrocatalysts are specially aimed to promote the dissociation of the O–O bond during the oxygen reduction reaction (ORR) mechanism, and to maintain reactivity and selectivity on the electrode surface [1–6]. Multi-metallic and alloy catalysts have been particularly active area of research because it has been established that for the cathode reaction, multi-metallic surfaces have superior activity to pure metal [7,8]. The enhanced reactivity of the catalysts surfaces is attributed to their electronic and geometric structure associated to the bi-functional effects, in which the unique catalytic properties of each of the elements in the catalytic compound combine in a synergetic manner to yield a surface which results more active than each of the elements alone. Also an electronic effect could modify the electronic properties of the alloy to enhance the active catalytic surface. Among the electrocatalysts

that have shown interesting electrochemical properties both in terms of tolerance to alcohol and high activity toward the ORR are Pd- and Pd-alloys [9,10]. Recently, we have shown that Pd [11] and Pd-based catalysts [12,13], such as PdSn of nanometric sizes exhibited an attractive catalytic activity for the ORR, but limited by the stability of the catalyst in acid media. The interest of this work in developing palladium thin bimetallic compound bearing low concentration of platinum atoms is to improve the stability and avoid the lixiviation of the bimetallic compound as well as to reinforce the electrocatalytic activity for the ORR through the synergistic effects of the three metals. The effect of temperature on the kinetics of the ORR study of the Pd₄₅Pt₅Sn₅₀ catalyst and the performance response of this cathode catalyst in a membrane-electrode assembly also constitutes part of this work.

2. Experimental

2.1. Physical and chemical characterizations

At present, there are several methods for synthesizing supported and unsupported nanomaterials based on nanoparticles catalysts of various controllable sizes. Pd₄₅Pt₅Sn₅₀ electrocatalyst with low content of Pt was prepared by a NaBH₄ (0.06 M) reduction of PdCl₂ (0.86 mM), H₂PtCl₄ (0.086 mM) and SnCl₂ (0.86 mM) in a 100 mL tetrahydrofuran solution, THF a 0 °C, following the methodology we have reported previously for the preparation of nanometric Pd-based electrocatalysts [11–13]. Briefly, a chemical reactor was charged with the reagents and vigorously stirred for the chemicals solvation. Afterwards, NaBH₄ (0.06 mM) solution

* Corresponding author. Tel.: +52 55 5747 3715; fax: +52 55 5747 3389.
E-mail address: osolorza@cinvestav.mx (O. Solorza-Feria).

was slowly added maintaining the stirred solution at 0 °C under N₂ atmosphere for 16 h. The reaction product was washed with distilled water to eliminate the sodium chloride formed during the reaction. After filtered, the powder was dried and weighted obtaining a 99% of yield. The powder was subject to thermal treatment under H₂ atmosphere (4 bar) at 573 K for 3 h following a procedure described for Sn-bimetallic alloys [14,15], in order to avoid Sn lixiviation in the alloy as observed previously during the electrochemical activation process. The afterward the resulted powder was cooled down obtaining a yield of 91% and maintained in a closed recipient prior to optical and electrochemical characterization.

2.2. Physical characterization

Phase identification of the powdered catalyst, after thermal treatment, was carried out with a MPD Phillips diffractometer equipped with Cu K α radiation and a graphite monochromator ($\lambda=0.1542$ nm). Scanning steps of 0.02° 2 θ were used in the range of 30–90° 2 θ . Particle size was determined from transmission electron microscopy (TEM) analyses, using a CM200 Phillips microscope, operated at 200 keV and equipped with energy dispersive spectroscopy (EDS) used to obtain an average and local chemical composition of the samples. For superficial studies, a Leica-Cambridge Stereoscan 440 SEM, at 20 kV, was used to analyze the morphology and distribution of the elements in the materials.

2.3. Electrochemical characterization

For electrochemical studies, experiments were carried out in a temperature controlled double compartment three-electrode test cell. A platinum mesh was used as the counter electrode and Hg/Hg₂SO₄/0.5 M H₂SO₄ (MSE = 0.680 V/NHE) as reference electrode. This electrode was outside the cell, kept at room temperature and connected by a porcelain Luggin capillary close to the surface of the working electrode. The electrode potentials were referred to NHE. The electrolyte was a 0.5 M H₂SO₄ solution prepared from double-distilled water which was degassed with N₂ for the working electrode activation and saturated with O₂ for 20 min before each ORR electrochemical measurements. Electrochemical studies were performed in a Voltalab potentiostat. Cell temperature was controlled by a Haake thermostat (model F3) from 308 to 333 K. Rotating disk electrode, RDE measurements were conducted on a thin film catalyst deposited on a glassy carbon disk electrode (0.196 cm²) mounted in a interchangeable RDE holder (Pine Instruments). The glassy carbon ink-type working electrode disk was prepared according to a method reported previously [16,17]. The thin film was deposited from a solution which was prepared by adding 5 μ L of a suspension resulting by mixing 45 μ L 2-propanol, 5 μ L Nafion® (5 wt.%, Du Pont 1000EW) and 1 mg Pd₄₅Pt₅Sn₅₀ (50 wt.%/C). The estimated amount of catalyst in the thin film was about 0.5 mg cm⁻². The rotation rate of the working electrode was in the range of 200 and 2500 rpm at 5 mV s⁻¹. During the ORR measurements an oxygen flux was maintained above the electrolyte surface.

2.4. Membrane-electrode assembly (MEA) preparation and characterization

The anodic catalysts layer was prepared by spraying a suspension of ink containing a mixture of a 20 wt.% Pt/C (E-Tek) electrocatalyst in one side of a Nafion 115 membrane. The catalytic ink was prepared by mixing 14 mL of Nafion 5 wt.% (Du Pont, 1100EW), 240 mL of isopropanol, 5 mg of the supported Pt/C and sonicated for 20 min. The resulting suspension was sprayed onto the 115 Nafion membrane by means of a home fabricated semiautomatic device. The anodic and cathodic loading in both catalyst

layers was about 1.0 mg cm⁻². The cathode catalytic ink was prepared following the same procedure as described for the anode side by mixing 5 mg of Pd₄₅Pt₅Sn₅₀ with 7.5 mg of Vulcan carbon XC-72 and the resulted suspension sprayed onto the cathodic side of the 115 Nafion membrane. The gas diffusion medium at the anode and cathode side was Teflon-treated carbon paper (Electrochem). The MEA was obtained by hot pressing (4.4 kg cm⁻²) at 120 °C for 1 min. The active surface area of the anode and cathode was 5 cm². PEMFC test was carried out in an Electrochem Fuel Cell Test System 890B operated with high purity hydrogen and oxygen at 400 cm³ min⁻¹. The fuel cell performance was measured at 40 °C, 60 °C and 80 °C without pressure of both gases. The fuel cell station was equipped with a humidifying system for the reactant gases and the humidified temperatures were fixed 5 °C higher than the fuel cell temperature.

3. Results and discussions

3.1. Characterization of the prepared Pd₄₅Pt₅Sn₅₀ catalyst

X-ray diffraction results of PdSn and Pd₄₅Pt₅Sn₅₀ compounds synthesized under the same experimental conditions are shown in Fig. 1. Synthesized PdSn [13] showed an orthorhombic structure Pnma, which experimental XRD pattern matches well the standard JCPDS card 03-065-2603. Narrow peaks in the PdSn XRD pattern indicate the presence of nanocrystallites which percentage, about 90%, was determined by MDI jade 5.0 software. The average size of the PdSn catalyst, about 8.6 nm (Rpw 10.3), was deduced by fitting the diffraction patterns using the academic Topas software. Low Pt concentration addition changes the bulk structure of the palladium thin bimetallic compound as shown in XRD and TEM results: XRD pattern of Pd₄₅Pt₅Sn₅₀ showed a reduced number of peaks in relation to obtained on PdSn, fitting in almost all the cases with structural Pd face-centered cubic (fcc) package (JCPDS card 046-1043), Pt (JCPDS card 04-0802) and Sn (JCPDS card 04-0673). However, crystalline faces positioned at 2 θ = 52°, 58° and 80° not correspond to the lattice phase of the three metals of the compound, revealing the alloy formation between Pd, Pt and Sn. These new phases are associated to strong interactions between the three metallic atoms which enhanced the stability of the Pd₄₅Pt₅Sn₅₀ compound in relation to that of Pd alone [11]. The average crystallite size of the PdSn catalyst, about 6.3 nm (Rpw 10.3), was

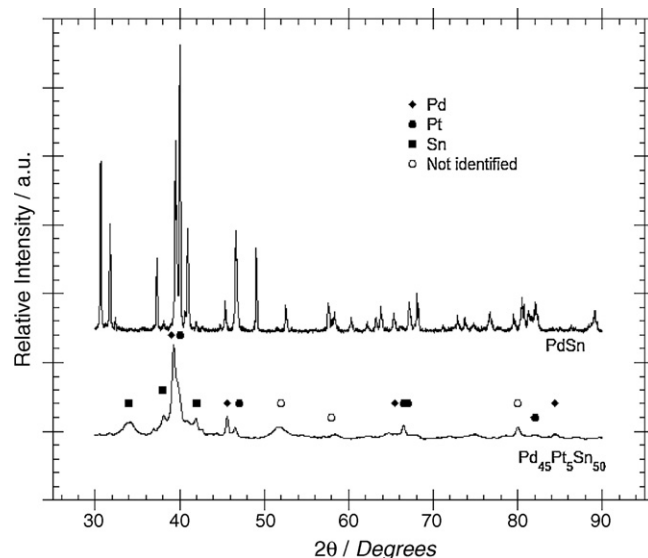


Fig. 1. XRD patterns of nanosized particles of PdSn and Pd₄₅Pt₅Sn₅₀ catalysts as-synthesized by the borohydride reduction method.

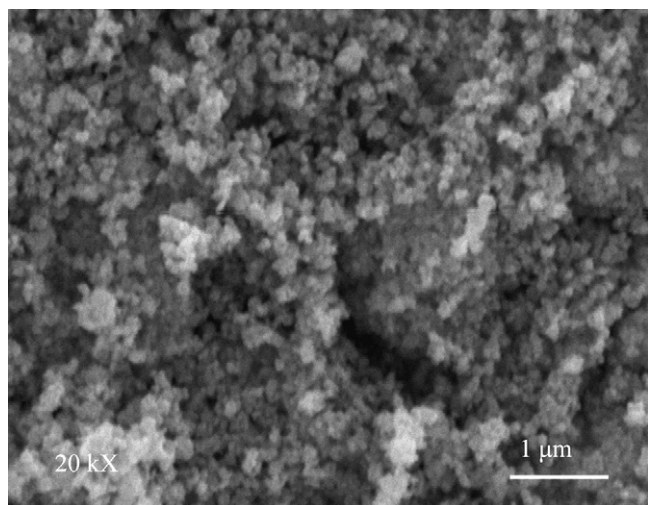


Fig. 2. SEM micrograph of Pd₄₅Pt₅Sn₅₀ catalyst synthesized by the NaBH₄ reduction method in THF at 0 °C.

deduced by fitting the diffraction patterns using the same academic Topas software mentioned above. Broad peaks in the Pd₄₅Pt₅Sn₅₀ diffraction peaks suggest low crystallinity which percentage about 30% was also determined by using the same software. Studies by SEM, Fig. 2, showed a homogenous distribution of spherical powder agglomerates composed of numerous powder particles having sizes less than 100 nm. Notice that these particle sizes are still much larger than the calculated crystallite size (~6 nm), indicating that the particles are nanocrystalline, a common feature reported for materials produced by the NaBH₄ reduction process [11]. The average composition of the as-synthesized powders, as determined by EDS, was approximately 45 at% Pd, 5 at% Pt and 50 at% Sn (Pd₄₅Pt₅Sn₅₀), in concordance with the started estimated composition of synthesis. The morphology of Pd₄₅Pt₅Sn₅₀ was analyzed by TEM and results exhibited spherical agglomerates which are built of fine particles. Fig. 3 shows a TEM micrograph of Pd₄₅Pt₅Sn₅₀ particle sizes catalyst of around 1–6 nm which are agglomerated in a greatest degree of clustering spherical particles in a range of 100 nm.

Fig. 4 shows mapping images for the Pd₄₅Pt₅Sn₅₀ sample where a uniform distribution of elemental palladium, platinum and tin

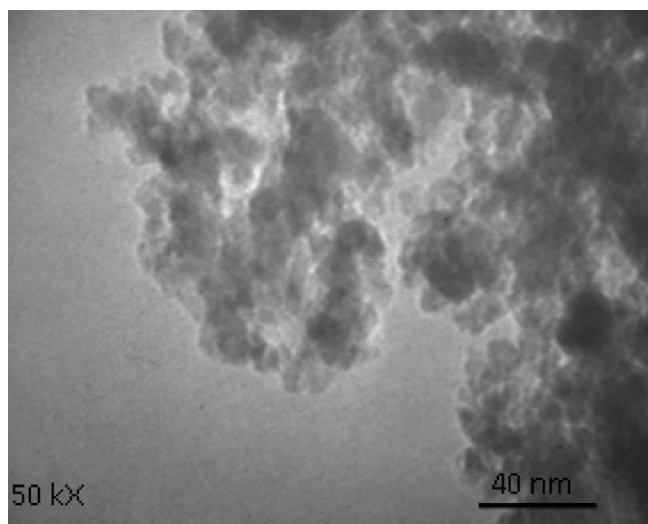


Fig. 3. TEM micrograph of Pd₄₅Pt₅Sn₅₀ catalyst synthesized by the borohydride reduction method.

throughout the particle with no evidence of metal segregation within the mapped area is observed.

These results of XRD, SEM-EDS and TEM indicate that the as-synthesized Pd₄₅Pt₅Sn₅₀ powder mixtures consist mostly of powder agglomerates in which palladium, platinum and tin particles are intimately mixed.

3.2. Electrochemical study of oxygen reduction

Fig. 5 presents the final cycle from a typical voltamperometric cyclic activation process for the PdSn and Pd₄₅Pt₅Sn₅₀ samples. These voltamperograms indicate the characteristic behavior of PdSn, showing that with the incorporation of Pt its electrochemical response is modified in the anodic and cathodic regions. Well-defined typical adsorption/desorption peaks are observed on the Pd₄₅Pt₅Sn₅₀ catalyst in the region of 0.0–0.35 V/NHE. In the region the 0.5–1.2 V/NHE the adsorption of H₂O at the electrode surface is notorious and shift of the onset potential for the cathodic reaction on the Pd₄₅Pt₅Sn₅₀ is detected. An increase in the obtained ORR current density can be observed, thus indicating that the Pd₄₅Pt₅Sn₅₀ catalyst possess a higher oxygen adsorption capacity than PdSn alone.

The oxygen reduction reaction is a complex combination of charge transfer and mass transport processes which by the low concentration of oxygen in acid environment, is usually studied under hydrodynamic conditions. Fig. 6 shows hydrodynamic behavior of the Pd₄₅Pt₅Sn₅₀ catalysts with Vulcan carbon powder dispersed into a Nafion film coated on a glassy carbon in oxygen saturated 0.5 M H₂SO₄ at 25 °C. The polarization curves were recorded from the open circuit potential to 0.2 V versus NHE. A charge transfer kinetics control with rotation rate-independent current is observed in the range of 0.75–0.90 V/NHE; at more cathodic potentials, mixed control became significant arriving to a well-defined mass transport-limited current as a function of the rotation rate. A different behavior was observed for Pd [11] and PdSn nanoparticles catalyst [13] where only mixed kinetic-diffusion control was clearly observed, regardless of the electrode rotation rates. It was considered that increases in the limiting current on high performance electrocatalysts are associated with the increase of molecular oxygen diffusion in the boundary-layer thickness through the electrode surface. The reduction reaction is fast enough at high cathodic overpotentials, associated in almost all the cases to a flat limiting plateau as described for a Pt/C electrode [18]. An explanation for the well-defined current plateau could be attributed to a distribution of electrocatalytic active sites on the electrode surface such as observed in the mapping of Fig. 4. In a film-coated electrode surface, the overall measured current, *i*, is related to the kinetic current, *i_k*, the boundary-layer diffusion-limited current, *i_d*, and film diffusion-limited current, *i_f* by [19]

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} + \frac{1}{i_f} \quad (1)$$

i_f represents the film diffusion-limited current controlled by reactant diffusion in the *i_f* Nafion® layer and is given by the following equation:

$$i_f = \frac{n_e F D_f C_f}{\delta_f} \quad (2)$$

In this equation, *D_f* and *C_f* are the diffusion coefficient and the concentration of O₂ in the film, respectively, and *δ_f* is the film thickness. The effect of the film diffusion is significant only in the case when the electrode is covered by a Nafion film [19,20] and can be neglected in the present study since the amount of Nafion (5 μL 5 wt.% in 45 μL of solution) in the prepared catalyst suspension is sufficiently small and hence not expected to be a factor in the limiting current density on the rotating electrode where only 5 μL of

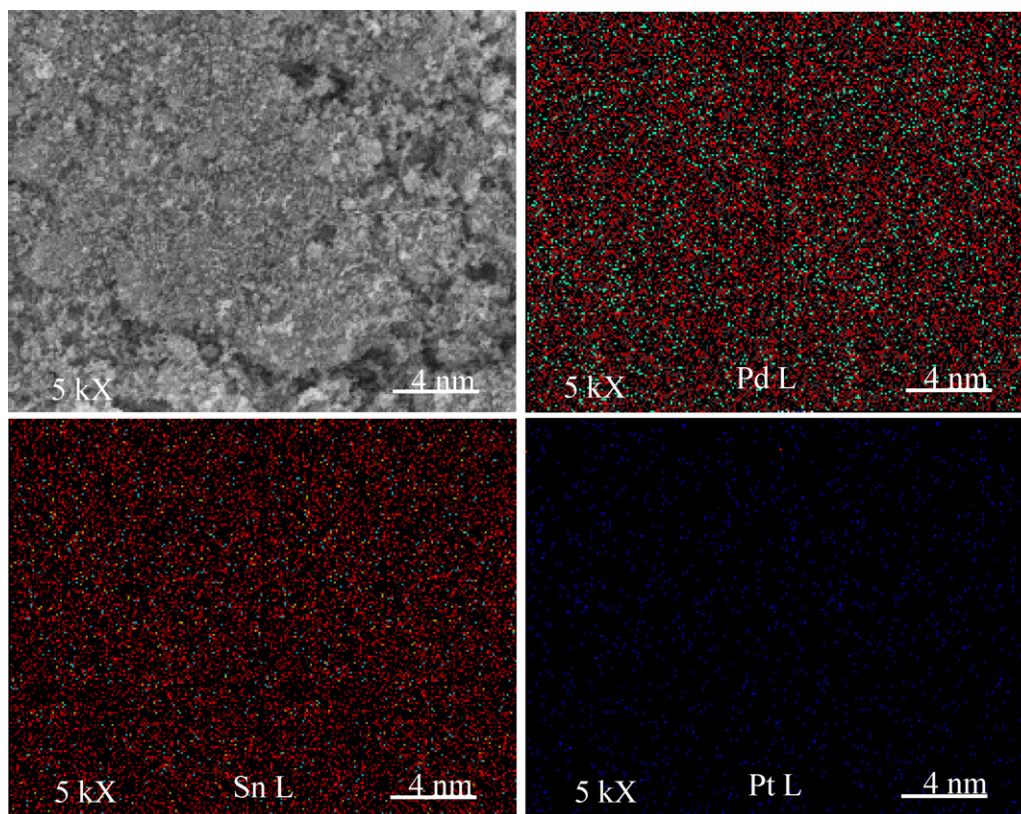


Fig. 4. Mapping images of the components of the Pd₄₅Pt₅Sn₅₀ catalyst.

catalyst ink is loaded. The boundary-layer diffusion-limited current can be expressed as

$$i_d = 0.2n_eFC_0D_0^{2/3}\nu^{-1/6}\omega^{1/2} = B\omega^{1/2} \quad (3)$$

where 0.2 is a constant used when ω is expressed in revolution per minute, n_e is the number of electrons transferred per molecule of O₂ in the overall reaction, F the Faraday constant, C_0 the concentration of oxygen dissolved (1.1×10^{-6} mol cm⁻³), D_0 the diffusion coefficient of oxygen in the solution (1.4×10^{-5} cm² s⁻¹), ν the kinematic viscosity of the sulfuric acid (1.0×10^{-2} cm² s⁻¹) [21] and B the Levich constant. The current of the oxygen reduction reaction can be written as dependent on the kinetic current and the diffusion-limited current as shown in the following equation:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} = \frac{1}{i_k} + \frac{1}{B\omega^{1/2}} \quad (4)$$

From the data of Fig. 6, the Koutecky–Levich plots (i^{-1} vs. $\omega^{-1/2}$) were drawn (figure not included). At all the rotation speeds, a series of essentially parallel straight lines in a broad potential range was observed, which indicates that the reaction order for the O₂ reduction at a Pd₄₅Pt₅Sn₅₀ catalyst electrode is unity, similar to observed and reported previously on PdSn [13]. Fig. 7 shows the mass transport corrected Tafel plots obtained for the Pd₄₅Pt₅Sn₅₀ catalyst ink-type electrode on which oxygen reduction kinetics studies were conducted in 0.5 M H₂SO₄ at 298 K. Electrochemical polarization curves on Pd, PdSn and Pt were also included in this figure for comparison. The Tafel plots were obtained after the measured currents were corrected for diffusion to give the kinetic currents in the mixed activation-diffusion region, calculated from Eq. (4):

$$i_k = \frac{i i_d}{i_d - i} \quad (5)$$

where $i_d/(i_d - i)$ is the mass transfer correction. The Tafel plots show a linear behavior in the mixed activation-diffusion region and a deviation of the kinetic current occurs with higher slope at high current density. A Tafel slope of -40 mV dec⁻¹, charge transfer coefficient of 0.68 and an exchange current density of 3.35×10^{-4} mA cm⁻² was determined on Pd₄₅Pt₅Sn₅₀ at 308 K. The kinetic parameters deduced for the oxygen reduction on all the catalysts ink-type electrodes at 308 K are presented in Table 1.

The effect of temperature on the kinetic parameters of the Pd₄₅Pt₅Sn₅₀ electrocatalyst is of paramount importance in the cathodic reaction of a fuel cell. The oxygen reduction was per-

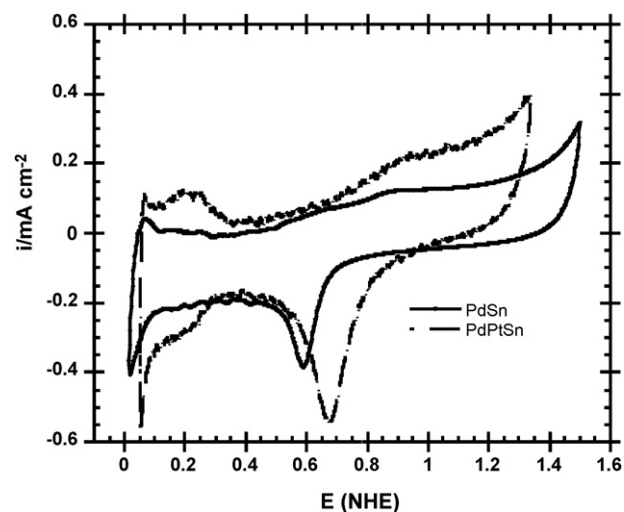


Fig. 5. Cyclic voltammetry of PdSn and Pd₄₅Pt₅Sn₅₀ catalysts in oxygen free 0.5 M H₂SO₄ solution at 298 K. Scan rate potential of 50 mV s⁻¹.

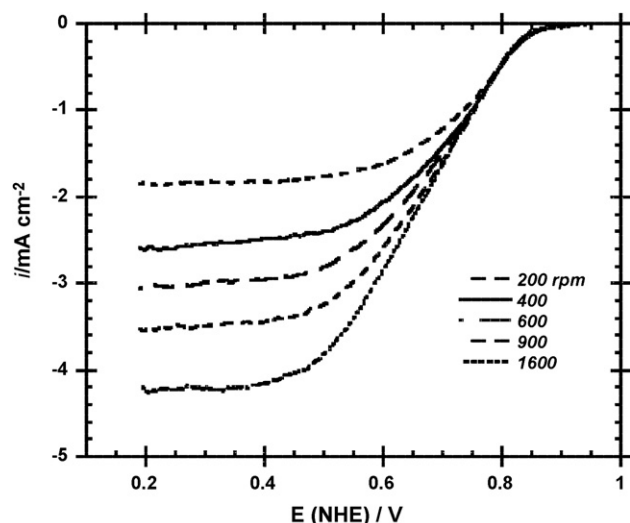


Fig. 6. Current–potential curves of ORR at Pd₄₅Pt₅Sn₅₀ catalyst in 0.5 M H₂SO₄ saturated with O₂ at 308 K, at different rotation rates. Current recorded at 5 mV s⁻¹.

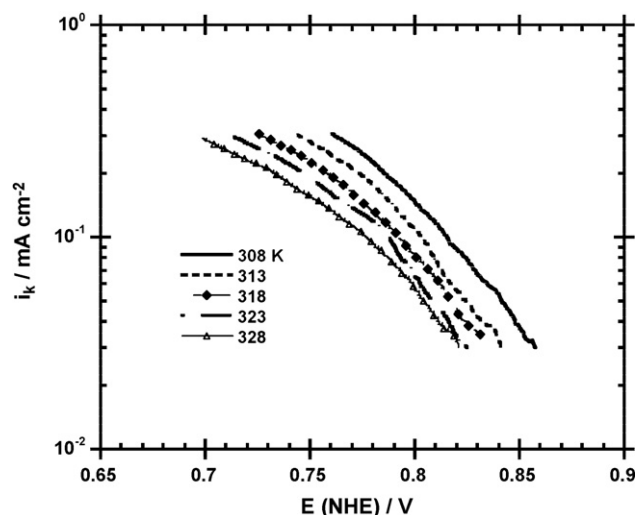


Fig. 8. Mass transfer corrected Tafel plots for the ORR on Pd₄₅Pt₅Sn₅₀ catalyst at different temperatures.

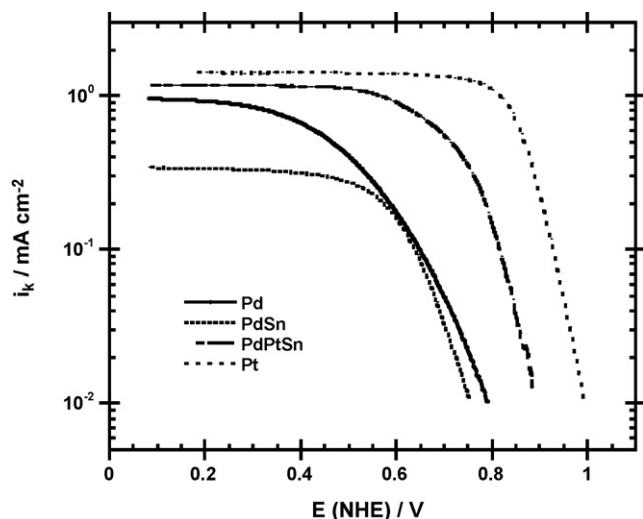


Fig. 7. Mass transfer corrected Tafel plots for ORR in O₂ saturated 0.5 M H₂SO₄ at 308 K of different Pd-based ink-type electrocatalysts deposited on glassy carbon. Pt is depicted as comparison.

Table 2

Variation of kinetic parameters with temperature for ORR on Pd₄₅Pt₅Sn₅₀ electrocatalyst in 0.5 M H₂SO₄.

T (K)	α	$-b$ (mV dec ⁻¹)	i_0 (mA cm ⁻²)
308	0.68	40.0	3.352×10^{-4}
313	0.62	43.0	4.390×10^{-4}
318	0.68	39.9	6.353×10^{-4}
323	0.68	40.7	5.720×10^{-4}
328	0.65	47.9	10.41×10^{-4}

[13] was evaluated using the value of ΔG° (H₂–O₂ cell) at each temperature using equations (6a) and (6b):

$$\Delta G_{(\text{H}_2/\text{O}_2)}^\circ = -296,658 - 33.6T \ln T + 389.8T, \quad (\text{J mol}^{-1}) \quad (6a)$$

$$E_r = \frac{-\Delta G_{(\text{H}_2/\text{O}_2)}^\circ}{2F} \quad (6b)$$

Tafel slopes and kinetic parameters deduced from the linear part at each temperature of Fig. 8, are presented in Table 2. One can see that Tafel slope is practically invariant with temperature, leading to a dependence of the transfer coefficient with temperature. Table 2 shows Tafel slopes are invariant with temperature and are closely equal to -120 mV at all temperatures, *i.e.* to $2.3 \times 2RT/(\alpha F)$.

The exchange current density corresponding to each Tafel slope was calculated by extrapolating the potential to the E_r value at the experimental operating cell temperature. The temperature dependence of the exchange current density in Table 2 can be analyzed via conventional Arrhenius plot (Fig. 9). The apparent activation energy, ΔE^\ddagger , for the oxygen reduction reaction on Pd₄₅Pt₅Sn₅₀ electrocatalyst was evaluated in the temperature range of 308–333 K, from a linear regression analysis of the slope of the Arrhenius equation represented by the relationship

$$\Delta E^\ddagger = -2.3R \left[\frac{d \log i_0}{d(1/T)} \right] \quad (7)$$

Table 1

Kinetic parameters deduced from the oxygen reduction reaction in 0.5 M H₂SO₄ at 298 K.

Electrocatalysts	E_{oc} (NHE V ⁻¹)	$-b$ (V dec ⁻¹)	α	i_0 (mA cm ⁻²)	Potential/V at $i = 0.1$ mA cm ⁻²	Ref.
Pd	0.78	0.131	0.46	6.6×10^{-6}	0.647	[11]
PdSn	0.80	0.056	0.46	1.606×10^{-6}	0.64	[13]
Pd ₄₅ Pt ₅ Sn ₅₀	0.90	0.068	0.40	3.352×10^{-4}	0.81	

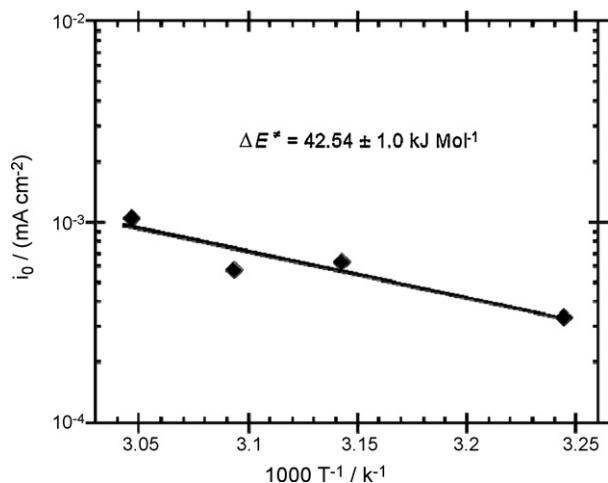


Fig. 9. Electrochemical Arrhenius plot deduced from the exchange current density of the corrected data of Fig. 8.

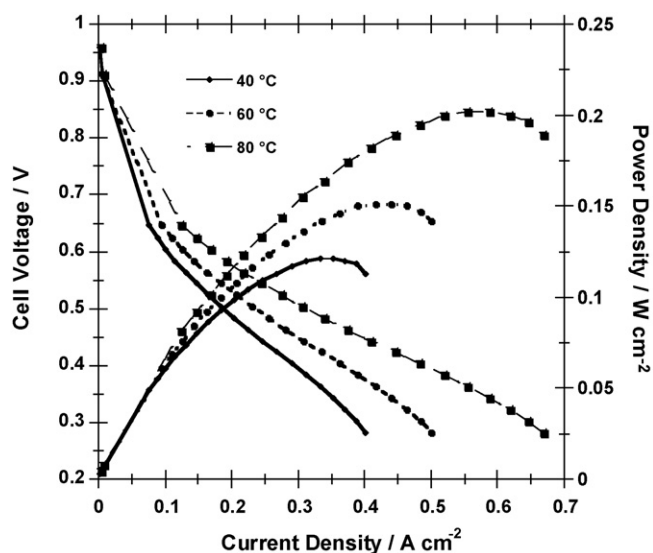


Fig. 10. Performance curve for Pt (20 wt.%) anode/Pd₄₅Pt₅Sn₅₀ (40 wt.%) cathode, operating on H₂/O₂ at 80 °C.

An average value of $\Delta E^* = 42.54 \pm 0.08 \text{ kJ mol}^{-1}$ was calculated. This value is lower in comparison to that of nanometric Pd (89.8 kJ mol^{-1}) [11] and PdSn ($53.18 \text{ kJ mol}^{-1}$) [13] electrocatalysts. This result indicates that the incorporation of low concentration of platinum to a palladium tin bimetallic compound improves the catalytic activity and selectivity of the Pd₄₅Pt₅Sn₅₀ electrocatalyst towards the reduction of molecular oxygen in acid medium to water formation. The performance of the Pd₄₅Pt₅Sn₅₀ (20 wt.%) carbon supported catalyst produced by NaBH₄ reduction, synthesized and used as cathode electrode in polymer membrane fuel cell will be the subject of forthcoming communications.

3.3. PEMFC performance

Fig. 10 shows result of the MEA performance of the anode, Pt 20 wt.%/C (E-tek) with a catalyst loading of 1.0 mg cm^{-2} , and cathode catalyst loading (1.0 mg cm^{-2}) of Pd₄₅Pt₅Sn₅₀ 20 wt.% dispersed on Vulcan carbon, tested at 40 °C, 60 °C and 80 °C. An increase of the power density was observed with temperature. The maximum performance obtained under this experimental con-

dition was 210 mW cm^{-2} at 0.35 V and 80 °C. The performance of Pd₄₅Pt₅Sn₅₀/Vulcan carbon was about 46% lower than MEA Pt performance reported by our group in Ref. [1]. This behavior is attributed to the low Pt content in the Pd₄₅Pt₅Sn₅₀ catalyst and by using the same catalyst loading on anodic and cathodic side, situation which could be improved by thorough loading study on the MEA cathodic side. Further study is carried out in our group of research in order to properly support the catalyst to improve the electrochemical behavior and to determine the long term stability of the Pd₄₅Pt₅Sn₅₀ as cathode in a PEMFC.

4. Conclusions

The borohydride reduction process has been proven to be a significant synthetic tool for the preparation of spherical powder agglomerates composed of Pd₄₅Pt₅Sn₅₀ catalyst, with particles less than 100 nm, containing crystallites of around than 6 nm in size. The electrocatalytic activity of this compound, for the oxygen reduction reaction in acid media, showed that the electrocatalyst allowed multi-electron charge transfer to water formation, with an apparent activation energy of $42.54 \pm 0.08 \text{ kJ mol}^{-1}$. The Pd₄₅Pt₅Sn₅₀ electrocatalyst has also demonstrated catalytic activity as cathode in a single PEMFC. The performance achieved with anodic and cathodic loading of 1.0 mg cm^{-2} was 210 mW cm^{-2} at 0.35 V and 80 °C. This value is about the half of the performance reported with Pt under the same experimental conditions.

Acknowledgements

This work was financially supported by Mexican Council of Science and Technology, CONACYT (Grant No. 101537) and Science and Technology Institute of Mexico City, ICYTDF (Grant OSF). JJSP thanks CONACYT for doctoral fellowship.

References

- [1] K. Suárez-Alcántara, O. Solorza-Feria, *Electrochim. Acta* 53 (2008) 4981.
- [2] J. Kim, T. Momma, T. Osaka, *J. Power Sources* 189 (2009) 909.
- [3] K. Suárez-Alcántara, O. Solorza-Feria, *J. Power Sources* 192 (2009) 165.
- [4] A. Sarkar, A.V. Murugan, A. Manthiram, *J. Mater. Chem.* 19 (2009) 159.
- [5] G. Vázquez, O. Solorza-Feria, *J. New Mater. Electrochem. Syst.* 12 (2009) 17.
- [6] V. Collins-Martínez, R.G. González-Huerta, A. López-Ortiz, D. Delgado-Vigil, O. Solorza-Feria, *J. New Mater. Electrochem. Syst.* 12 (2009) 63.
- [7] A. Gebert, N. Mattern, U. Kuehn, J. Eckert, L. Schultz, *Intermetallics* 15 (2007) 1183.
- [8] X. Wang, N. Kariuki, J.T. Vaughev, J. Goodpaster, R. Kumar, D.J. Myers, *J. Electrochem. Soc.* 155 (2008) B602.
- [9] A. Sarkar, A. Murugan, A. Manthiram, *J. Mater. Chem.* 19 (2009) 159.
- [10] F.P. Hu, Z. Wang, Y. Li, Ch. Li, X. Zang, P.K. Shen, *J. Power Sources* 177 (2008) 61.
- [11] J.J. Salvador-Pascual, S. Citalán-Cigarroa, O. Solorza-Feria, *J. Power Sources* 172 (2007) 229.
- [12] G. Ramos-Sánchez, H. Yee-Madeira, O. Solorza-Feria, *Int. J. Hydrogen Energy* 33 (2008) 3596.
- [13] J.J. Salvador-Pascual, A. Chávez-Carvayar, O. Solorza-Feria, *ECS Trans.* 15 (2008) 3.
- [14] L. Jiang, Z. Zhou, W. Li, W. Zhou, S. Song, H. Li, G. Sun, Q. Xin, *Energy Fuels* 18 (2004) 866.
- [15] A.C. Bernardes-Silva, A.F. De Mesquita, E. Moura, A.O. Porto, G.M. De Lima, J.D. Ardisson, F.S. Lameiras, *Solid State Commun.* 135 (2005) 687.
- [16] R.G. González-Huerta, R. González-Cruz, S. Citalán-Cigarroa, C. Montero-Ocampo, J. Chávez-Carvayar, O. Solorza-Feria, *J. New Mater. Electrochem. Syst.* 8 (2005) 15.
- [17] R.G. González-Huerta, J.A. Chávez-Carvayar, O. Solorza-Feria, *J. Power Sources* 153 (2006) 11.
- [18] U.A. Paulus, T.J. Schmidt, H.A. Gasteiger, R.J. Behm, *J. Electroanal. Chem.* 495 (2001) 134.
- [19] S.K. Zecevic, J.S. Wainright, M.H. Litt, S.L. Gojkovic, R.F. Savinell, *J. Electrochem. Soc.* 144 (1997) 2973–2982.
- [20] N.M. Marcovic, H.A. Gasteiger, P.N. Ross Jr., *J. Phys. Chem.* 99 (1995) 3411–3415.
- [21] C. Couteanceau, P. Crouigneau, J.-M. Léger, C. Lamy, *J. Electroanal. Chem.* 379 (1994) 389.