Int. J. Electrochem. Sci., 7 **(2012)** 1079 - 1092

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Evaluation of a Cr_3C_2(NiCr) Coating Deposited on s4400 by Means of an HVOF Process and Used for Flow Plates of PEM Fuel

M. Rendón-Belmonte[1]*,J. T. Pérez-Quiroz*[1]*,J. Terán-Guillén*[1]*,J. Porcayo-Calderón*[2]*,A. Torres-Acosta*[1]*,*

G. Orozco-Gamboa[3]

[1] Instituto Mexicano del Transporte, Sanfandila Pedro Escobedo Querétaro, C.P 76703 México.
[2] Instituto de Investigaciones Eléctricas, Av. Reforma 113, Palmira, CP 62490, Cuernavaca, Morelos, México.
[3] Centro de Investigación y Desarrollo Tecnológico en Electroquímica, S. C. Parque Sanfandila S/N, Pedro, Escobedo, CP. 76703, Querétaro, México.
[*]E-mail: mbelmonte@imt.mx

Received: 2 December 2011 / *Accepted:* 15 January 2012 / *Published:* 1 February 2012

In this research the electrochemical behavior of a Cr_3C_2(NiCr) coating deposited on S4400 through the use of an HVOF (high velocity oxygen-fuel) thermal spraying process was studied. The electrolyte used was a solution of H_2SO_4 0.5 M + 2 ppm F^- used at environment temperature. As a reference electrode a mercurous sulfate (Hg_2SO_4) was used and a graphite bar as a counter electrode. The morphological aspect of the coating evaluated was analyzed by SEM (Scanning Electron Microscopy) before and after the electrochemical evaluation. The coating electrochemical values obtained for a period of 576 hrs fulfilled the corrosion resistance criteria required by USDOE (US Department of Energy). As a starting point, this coating could be considered in flow plates for PEM-based (Proton Exchange Membrane) fuel cells. Nevertheless, the loss of coating during this period may limit its application.

Keywords: Coating, HVOF, PEM fuel, Corrosion

1. INTRODUCTION

Hydrogen is an excellent source of energy for its unique properties. It is more efficient and clean than fossil fuels. It can also generate, through electrochemical process, electricity by means of fuel cells that at the end have a better efficiency than fossil fuels (Figure 1).

$$H_2 \rightarrow 2H^+ + 2e^- \qquad 1/2O_2 + 2e^- + 2H^+ \rightarrow H_2O$$

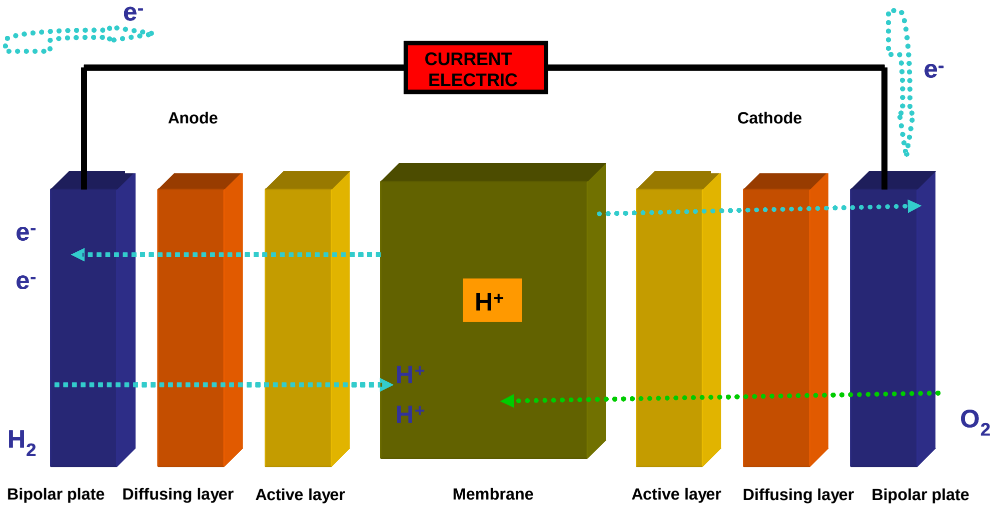


Figure 1. Elements of a PEM fuel cell.

This study is focused on the research of new materials for flow plates in PEM-based (Proton Exchange Membrane) fuel cells, taking into consideration that these plates are elements that represents the biggest part of the cell. These materials can develop functions such as: mechanical bearing of the membrane/electrode assembling (MEA): flow plate/diffuser layer, diffuser layer/active layer, and active layer/membrane; connect electrically adjacent cells in a stack simultaneously, distribute gases in the electrodes through flow channels and, at the same time, drain the water generated in the cathode. To perform these functions, they should have the following characteristics: high corrosion resistance ($\leq$ 0.016 mA/cm^2), good electrical conductivity ($\geq$ 10 S/cm), good thermal conductivity ($\geq$20 W/cm K), compressive strength higher than 22 lb/in^2, light, easy to machine in a minimum thickness, and cheap [1].

The first criterion that should be considered to evaluate the coating is its corrosion resistance, because if the system does not have a high corrosion resistance, it is not important to determine the other parameters, such as the interface contact resistance (ICR) value and the humidifying capacity. The main cause that produces corrosion in the flow plate is the progressive degradation of the polymeric membrane (electrolyte) during the electrochemical process that generates electric current in the fuel cell. This process produces ions such as: F^-, SO_4^{2-}, SO_3^{2-}, HSO^-_4, HSO^-_3, and HCO^-_3 as well as water, developing an acid solution with pH values between 1 and 4 which in turns induce corrosion problems in the flow plates. As a consequence, the efficiency of the cell decreases [2]. One possibility to diminish this problem is the use of noble metals (i.e. stainless steels and its alloys) and coatings with high chromium, nickel, nitrides, and carbide content, keeping at all time a balanced relation between cost and performance [1,3,4,5].

Different kinds of steels have been studied and it has been determined that flow plates made with stainless steel allow to have an acceptable electric power which can be used in commercial cells [6-12]. Therefore, it is considered that steels with high chromium content (i.e. 316, 349 etc.) are the most feasible ones to be used in the fabrication of flow plates. Nevertheless, to obtain a better performance of the flow plates, it is necessary to coat them with a conductive material, because typical passive coatings that protect these plates against corrosion, may present high electrical resistance. Therefore, this research evaluates a Cr_3C_2(NiCr) coating deposited on S4400 ferritic stainless steel by means of a HVOF (high velocity oxygen-fuel) thermal spraying process.

2.-EXPERIMENTAL CONDITIONS

A Cr_3C_2(NiCr) alloy coating (see Tables 1 and 2 for chemical composition) was applied on S4400 stainless steel, 10x10x3 cm, plates (Table III) with the help of a HVOF (High Velocity Oxygen-Fuel) system using a Sulzer-Metco metallizing equipment (model Dj2700), with an oxygen-propane mixture flame. Prior to the application of the coating, the surface of the plate was prepared by means of a ceramic granulated metal burst, according with NACE No. 1/ SSPC-SP 5 standard [13]. The plates were then cleaned with acetone and afterwards the coating was applied to them.

Table 1. Cr_3C_2(NiCr) alloy chemical composition

Alloy	Cr_3C_2	NiCr
Cr_3C_2(NiCr)	80	20

Table 2. Cr_3C_2(NiCr) coating chemical phase composition

Alloy	Cr	Ni	C	Fe	Others
Cr_3C_2	86.16	-	13.3	0.3	0.24
NiCr	20.4	78	-	0.2	1.05

Table 3. Chemical composition of S4400

Steel	Designation	C	Cr	Mn	Si	Ti	Nb
441	S4400	0.03	17.5	1.0	1.00	0.5	0.39

The electrolyte used was a solution of H_2SO_4 0.5 M + 2 ppm F^-. A custom made electrochemical cell was used in the experimental program, and includes a sulfate mercorous (Hg_2SO_4) electrode as the reference, and a graphite bar as the counter-electrode.

The experiments were made at laboratory temperature (25±3 ºC) with the existing oxygen in the atmosphere (Figure 2).

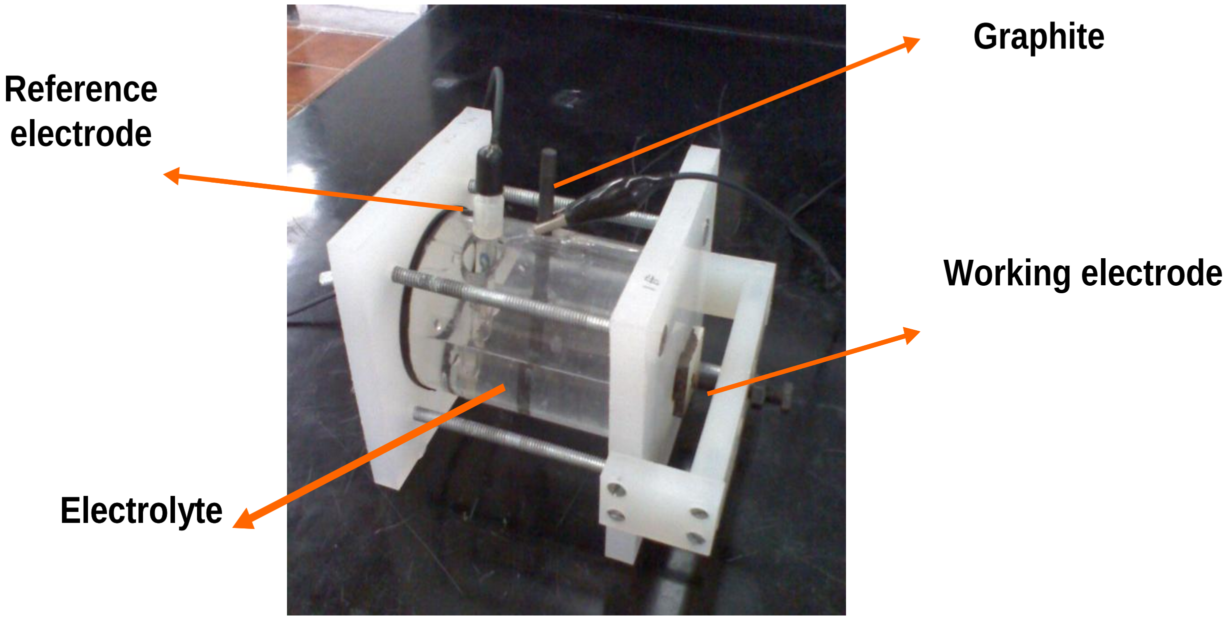


Figure 2. Cell used for the electrochemical evaluation of the Cr_3C_2(NiCr) coating

Tafel extrapolation technique, using a Gamry potentiostat (model PC4 in carrying case), was used to study the electrochemical behavior with a scan rate of 0.15 mV/s in agreement with standards ASTM G5 and ASTM G59 [14-15]. Prior to the Tafel tests, the E_{corr} was measured with a high impedance (10^6 Ω) multimeter.

The coating surface morphology was analyzed by SEM (scanning electron microscopy) before and after the electrochemical tests was performed, and the alloy composition was determined by atomic absorption spectroscopy (ABS).

3. RESULTS AND DISCUSSION

Table 4 shows the current densities (i_{corr}) and the corrosion rates (V_{corr}) obtained from the Tafel curves for the coating tested (S4400 coated with a Cr_3C_2(NiCr)) and exposed to an environment that simulates the operation conditions of the collector side, where oxygen is supplied into the fuel cell.

Table 4. Results of S4400 coated with the Cr_3C_2(NiCr) alloy

Time (hrs)	E_{corr} vs SHE (V)	i_{corr} (mA/cm^2)	V_{corr} (mm/year)
24	0.48	1.73 e-4	8.46 e-3
144	0.49	2.12 e-4	0.010
336	0.51	1.68 e-4	8.21e-3
384	0.52	2.95 e-4	0.014
576	0.57	2.20 e-4	0.010

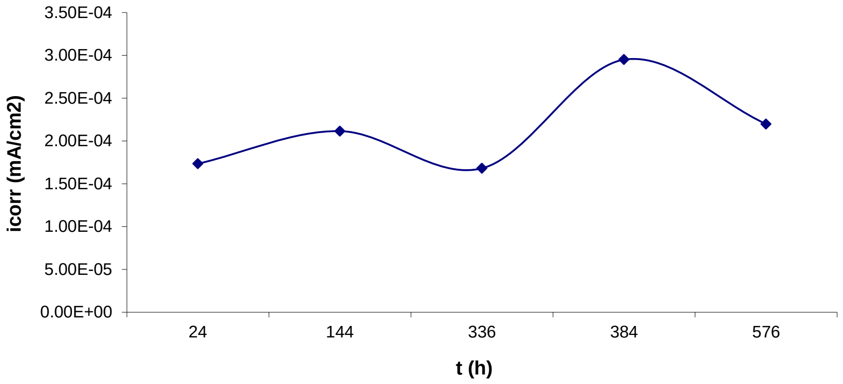
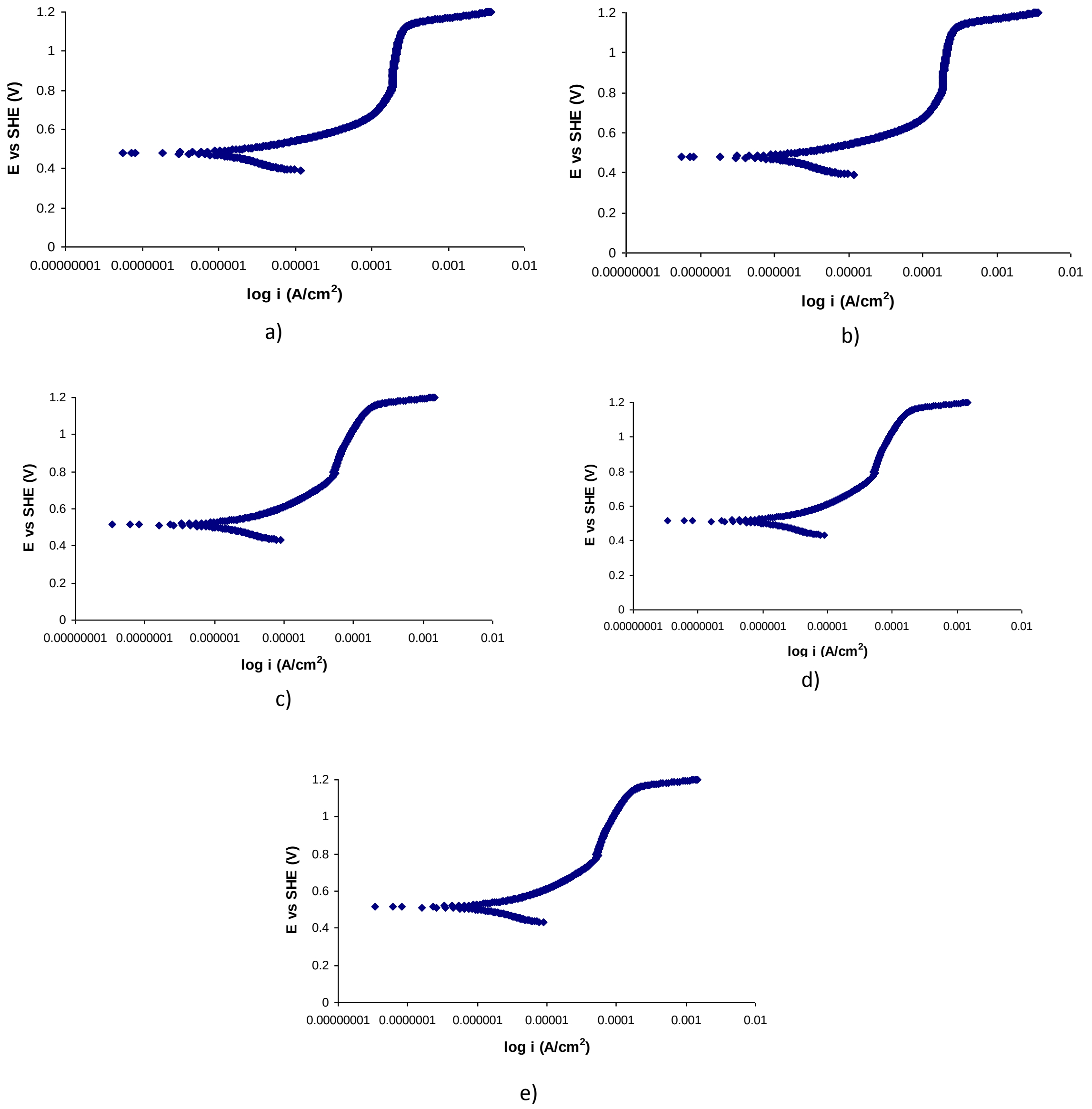


Figure 3. i_{corr} performance of S4400 coated with the Cr_3C_2(NiCr) coating in H_2SO_4 0.5 M + 2 ppm F^-



a)

b)

c)

d)

e)

Figure 4. Polarization curves of S 4400 coated with a Cr_3C_2(NiCr) alloy exposed to H_2SO_4 0.5 M + 2 ppm de F after a) 0.08 hrs., b) 144 hrs., c) 336 hrs., d) 384 hrs and e) 576 hrs.

Based on Table 4 and Figure 3, i_{corr} values obtained were between 1.7 and 2.95 10^{-4} mA/cm^2, until 576 hrs (24 days). Comparing these values with the ones shown in previous investigations [1-16], this material fulfills the $i_{corr} \leq 0.016$ mA/cm^2 criterion established by the USDOE (US Department of Energy) [12].

Tafel curves, shown in Figure 4, presented a passive zone between 0.7 to 1.1 V (vs. SHE). It is important to mention that in this research the membrane/electrode pack interface is only formed by the membrane and the bipolar plate (see figure 5), simulating a sever situation for the flow collector due to critical degradation of the membrane.

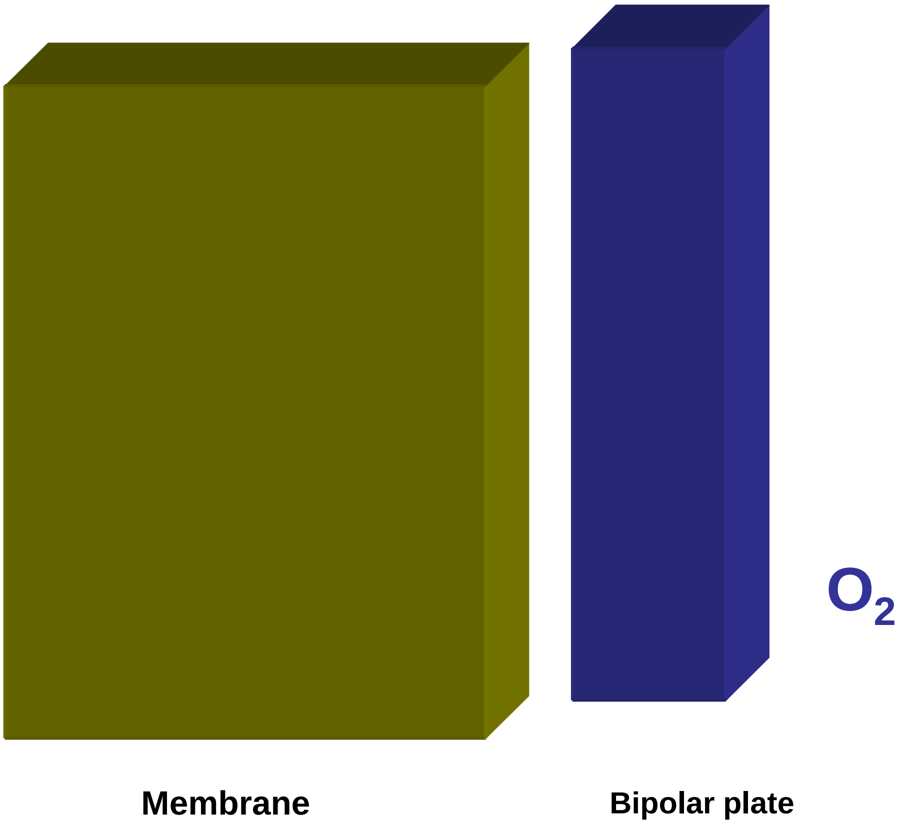


Figure 5. Representation of the studied interface

Shores determined experimentally [17] (see Figure 6) the optimal potential of a fuel cell in service, or the reactions that are carried out on the oxygen flow collector side (cathode), and on the hydrogen flow collector side (anode) in relation to a reference electrode. Nevertheless, it is important to mention that in the experimental determination of the potential of the cell made by Shores, the potential drop by the interface is included: flow plate/diffuser layer, diffuser layer/active layer, and active layer/membrane (see Figure 7). The potential values of passivation obtained in the stainless steel plate coated with Cr_3C_2(NiCr) in this investigation, are in accordance with the oxygen collector side as determined by Shores.

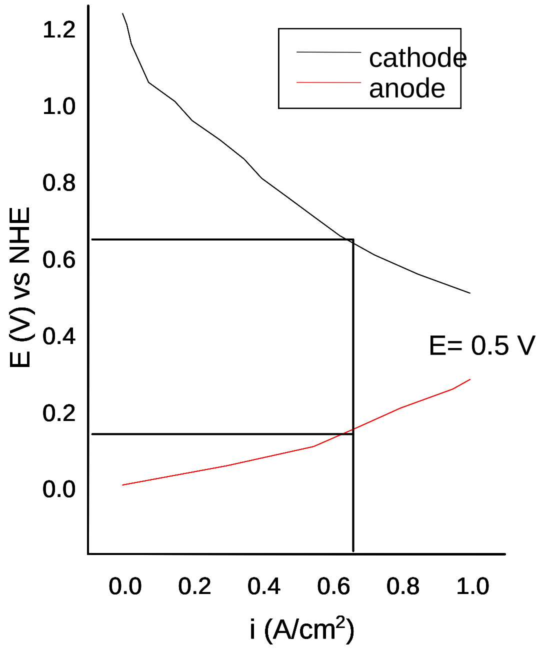


Figure 6. Approximate representation of the potential of each electrode of a PEM cell determined by Shores [17]

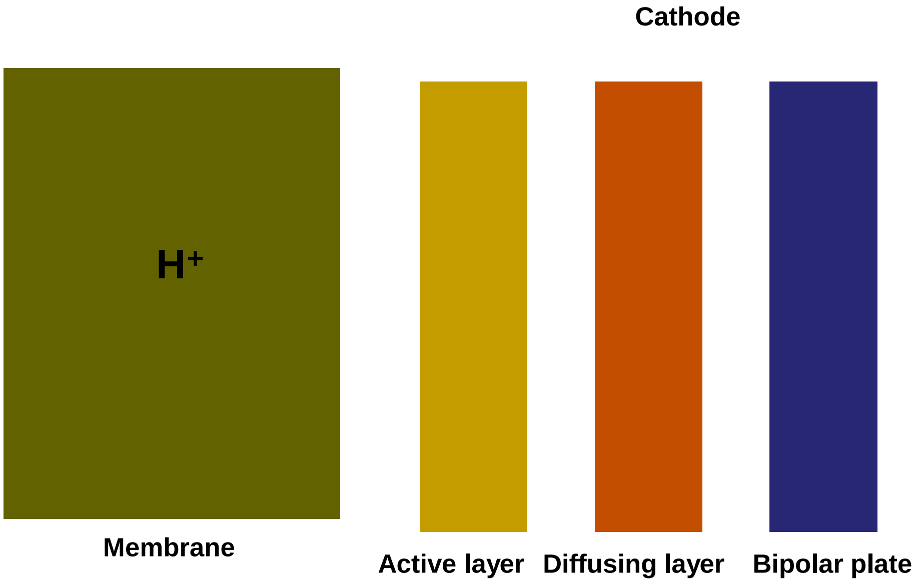


Figure 7. Approximate representation of the potential of the flow collector where oxygen is supplied and determined by Shores [17]

The surface finish of the Cr_3C_2(NiCr) coating applied on the S4400 is shown in Figure 8. The surface appearance corresponds to a typical coating deposited by a HVOF process with a surface rugosity similar to the particle size used for deposition (~ 37 µm) [18]. The surface rugosity is an important variable during electrochemical characterization, because the real coating surface area is much larger than the one used to calculate the corrosion rate.

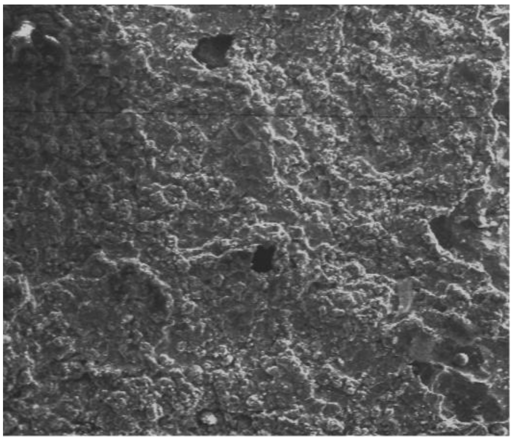


Figure 8. Micrograph of the surface of the Cr_3C_2(NiCr) coating deposited on steel S4400 (200X).

Figure 9 shows a transverse section micrograph of the same coating deposited by a HVOF process. Due to the characteristics of this process, the coatings have a high density and a porosity of less than 1% [18]. High density and low porosity coatings are produced due to particle sprayed rate is higher than 500 m/s, and high kinetic energy generated at the impact moment of the particles on the substrate. The apparent porosity seen in the Figure 9 is due to the detachment of chrome carbide particles during the process of metallographic preparation of the sample. The coating adherence to the substrate is due mainly to the mechanical bonding forces produced by the incrustation of particles that are deformed during impact on the superficial roughness of the substrate. The thickness of the obtained coating was approximately 223 μm (average of 7 measurements).

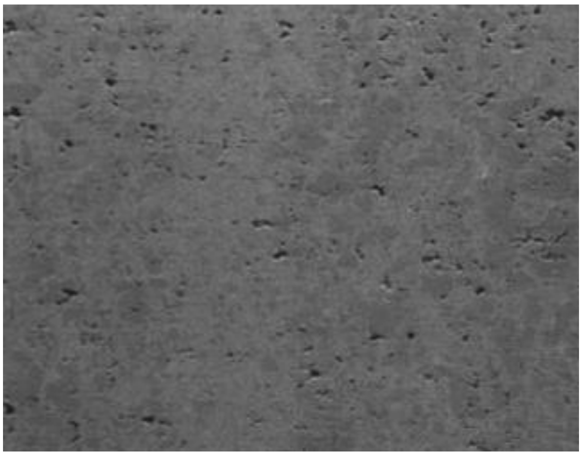


Figure 9. Micrograph of the appearance in transversal section of the Cr_3C_2(NiCr) coating deposited on S4400 steel (500X).

Hung et al. [19] studied aluminum plates coated with a carbide alloy and graphite compound plates used as collector dishes for PEM cells. These plates were evaluated in a cell at a 70 ºC temperature using bubbling oxygen and hydrogen during 1,000 hrs. The investigation by Hung et al.

shows that the cell made with aluminum flow plates, coated with carbide, consumed less hydrogen per Watt as compared with graphite compound flow plates (22% savings).

According with a SEM and an X-ray diffraction analysis made by Hung et al. to the carbide coated bipolar plates, they determined that chromium was present in high quantities. The X-ray diffraction analysis of MEA (membrane-electrode assembly) showed a presence of Platinum, and Carbon and small quantities of chromium in the MEA analysis in the cathode location. Nevertheless, according to the results obtained, chromium in the electrocatalyst process did not react to form PtCr. The water generated during the cell operation was also analyzed using the mass emission spectroscopy technique which showed the presence of aluminum, chromium, Platinum, iron and nickel in very low levels (less than 1 ppm). These concentrations are lower to the ones noticed between 5-10 ppm of metallic ions that exist when there is a considerable contamination in the membrane [19]. Hung et al. did not study the use of a coating application method, but concludes that this carbide alloy is a candidate to be used in flow or collector plates.

In the experimental development of this investigation the HVOF technique was used due to its versatility [20, 21] to obtain the Cr_3C_2 (NiCr) coating and low cost compared to other techniques such as PVD (Phase Vapor Deposition). With the basis on the results obtained in this research, it is considered that the application of carbide coatings to bipolar plates could be a promising option.

To determine the composition of the coating applied on S4400, a localized composition analysis was made using SEM and ABS in five different points of the evaluated Cr_3C_2(NiCr) coating: three points outside the immersion area (Figure 10) and two points at the immersed area (Figure 11).

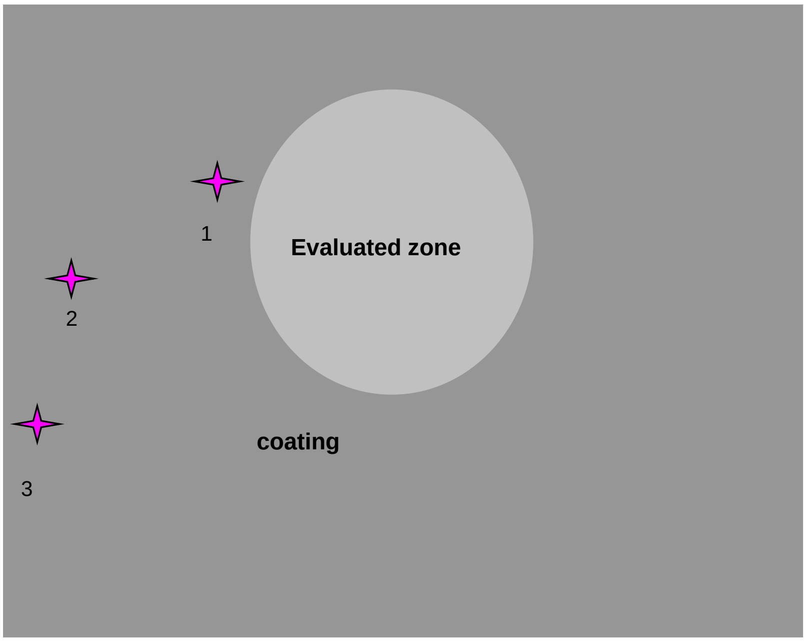


Figure 10 .Localization of the analyzed points of the coating (not immersed in the electrolyte)

Results are shown in Tables 5 and 6 for virgin coating and for immersed coating, respectively.

Table 5. Composition in three different points of the Cr_3C_2(NiCr) coating, applied on the S4400 plate, tested in the surface with no previous electrolyte immersion.

	Element	Weight %
Point 1	Carbon	11.894
	Aluminum	2.508
	Silicon	0.228
	Titanium	0.539
	Chromium	59.678
	Iron	12.078
	Nickel	13.074
Point 2	Carbon	10.827
	Aluminum	0.239
	Silicon	0.212
	Chromium	69.018
	Nickel	19.704
Point 3	Carbon	10.605
	Aluminum	0.151
	Silicon	0.156
	Chromium	70.812
	Nickel	18.276

In agreement with the data shown in Table 5 (virgin coating), there was small composition variability between the points evaluated, which indicates that the application of the coating by HVOF technique was homogeneous.

The chromium content differences obtained in the virgin coating (Table 5) were probably due to the fact that in a point near the interface exists a contact with the electrolyte by effect of capillarity, which produced these differences. It is also noticed that the bigger is the distance from the interface, the higher is the chromium quantity.

On other side, considering the composition of the virgin coating (Table 5), it can be concluded that the deposited coating had a chromium content between 60-70%, nickel content between 13-20% and carbon content between 10 -11%.

On the other hand, the immersed section of the coating showed (by SEM visual inspection) a metallic grey color, which could be an area without coating. To confirm this observation, an accurate quantification was made in two different points of the test area using SEM with ABS. The results are shown in Table 6.

Table 6. Composition in two different points of the Cr_3C_2(NiCr) coating, applied on the S4400 plate, tested in the surface with previous electrolyte immersion.

Element		Weight %
Point 1	Chromium	19.830
	Iron	79.581
	Nickel	0.590
Point 2	Aluminum	0.355
	Silicon	0.523
	Phosphorus	0.457
	Chromium	19.859
	Iron	78.444
	Nickel	0.361

In Figure 11, the analyzed points are represented.

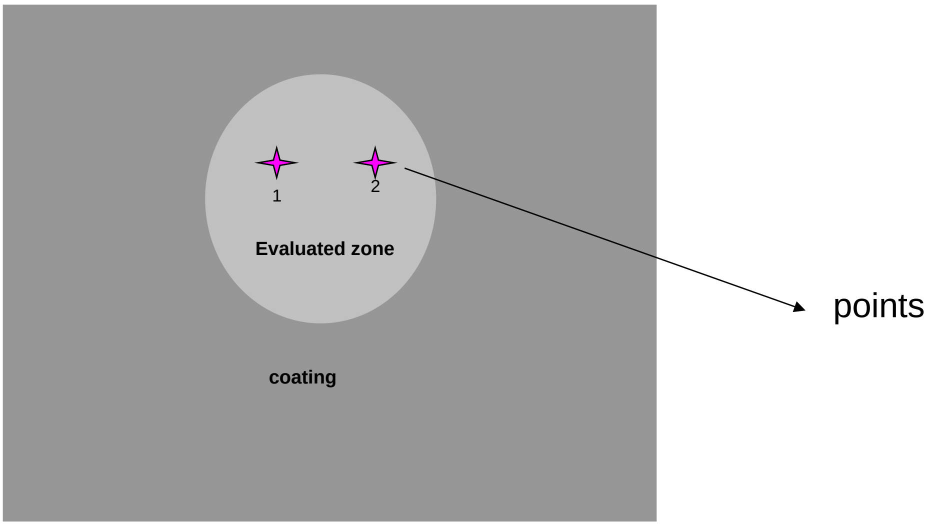


Figure 11. Localization of the analyzed points of the evaluated area immersed in the electrolyte

According to the composition shown in Table 6, the relation of chromium-iron-nickel is very similar between the two points analyzed. Nevertheless, point 2 composition presented other elements such as aluminum, silicon, and phosphorous. The presence of silicon is justified because it is present in the S4400 substrate composition (See Table 5) and the presence of small quantities of aluminum and phosphorous is attributed to the composition of the coating, which although it is not taken into account in the composition of the applied alloy (Table 5 and 6), it is still present in very small quantities in the form of agglutinants.

Considering the chromium contents in Tables 3 and 5 (substrate = 17.5% and non-immersed coating = 60-70%), there is a considerable difference. On the other hand, Tables 3 and 6 (substrate = 17% and immersed coating = 19.8%)) show similar values. This indicates that the chromium content in the immersed zone corresponded to the percentage of chromium contained in the steel plate. This indicates the chromium present in the coating was consumed during the electrochemical evaluation.

In addition, the nickel content in the immersed zone (Table 6) was attributed to the one present in the coating, because in the composition of the substrate (Table 3) there is no nickel present, although the percentage of nickel was significantly less than the one found in the coating (Table 2).

The third zone of analysis was the virgin coating-immersed coating interface (see Figure 12). A SEM with ABS composition analysis was made, and the data is shown in Table 7.

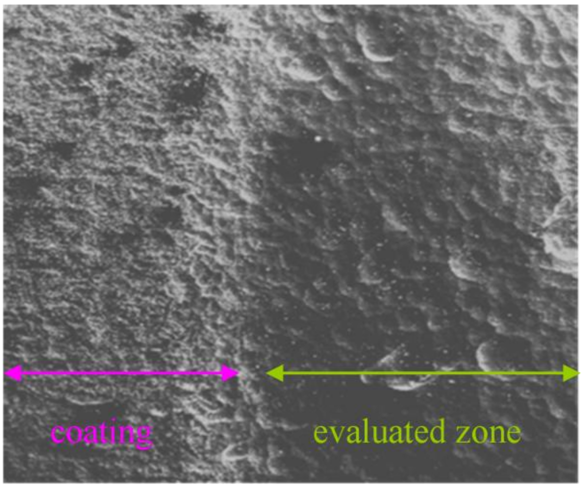


Figure 12. SEM of the evaluated coating-area interface (20X).

Considering the data shown in Tables 5 and 6, and comparing them with Table 7, it is noticed that values in Tables 6 and 7 are very similar, which means that the degradation of the coating started at the interface and expanded to the rest of the test area.

Table 7. Composition of the virgin coating-immersed coating interface

Element	Weight %
Carbon	7.423
Oxygen	4.912
Aluminum	1.824
Silicon	0.582
Sulfur	0.670
Chromium	17.541
Iron	66.587
Nickel	0.460

Considering the physical damage noticed in the plate (Figure 12) and the SEM with ABS quantification of the S4400 plate coated with Cr_3C_2(NiCr), it was determined after an evaluation of 576 hrs (24 days) in a solution of H_2SO_4 0.5 M + 2 ppm F^- that the chromium and nickel content considerably decreases in relation to the content determined in the plate before the electrochemical evaluation.

4. CONCLUSIONS

The Cr_3C_2(NiCr) coating showed a good performance probably due to its high content of chromium. With basis on the results obtained, we can assert that this coating, if applied on the oxygen flow collector side (cathode), fulfills the established criterion for corrosion resistance, being this as one of the most important criterion to consider in the case of flow plates. Nevertheless, although the encouraging results, when an analysis of the surface of the plate was made after the evaluation, it was noticed coating depleting, which in turn reduced the life expectancy in a fuel cell environment. It is worth mentioning that the evaluation conditions simulated the direct contact of the flow collector with the membrane, the most critical case to which a collector flow plate can be submitted as a consequence of the degradation of the membrane.

ACKNOWLEDGEMENTS

The corresponding author acknowledges CIDETEQ (Centro de Investigación y Desarrollo Tecnológico en Electoquímica) for its economic support by a MScE scholarship. Also to the Instituto Mexicano del Transporte (IMT) for allowing to make the experimental part of the research in its facilities; and to Dr. J.T. Pérez Quiroz, for all his support during the development of this research.

References

1. Allen Hermann, Tapas Chaudhuri, Priscila Spagnol. *J. Hydrogen Energy* 30 (2005) 1297-1302.
2. Tian Rujin, SUN Juncai and Wang Jianli. *Rare Metals* 25, (2006) 229.
3. H. Tawfik, Y. Hung, D.Mahajan. *J. Power Sources* 163, (2007)755-767.
4. J. Wind, R. Spah, W. Kaiser, G. Bohm. *J. Power Sources* 114, (2003) 181.
5. Neil Aukland, Abdellah Boudina, David S. Eddy, Joseph V. *J. Mater. Res. Soc.* 1723 (2004) .
6. Sandra Virginia Rivas Gándara. Tesis de Maestría, "Diseño y Construcción de una Stack de Celdas de Combustible de Membrana de Intercambio de Protones", CIDETEQ México Querétaro. 2004.
7. S. V. Rivas, M. E. Hernández, A. A. Ortiz, E. Castaño, H. Ruiz, G. Orozco, "Desarrollo de platos bipolares de acero inoxidable para una celda de combustible tipo PEM", Memorias del XIX Congreso de la Sociedad Mexicana de Electroquímica 2004.
8. Sandra Rivas Gándara, Merith Esperanza Hernández, Alondra Anahí Ortiz, Germán Orozco, "Platos bipolares de acero inoxidable para una celda de combustible tipo PEM", Memorias del IV Congreso Nacional de la Sociedad Mexicana del Hidrógeno. México 2004.
9. Sandra V. Rivas Gandara, Edgar Cuara Díaz, Federico Manríquez Guerrero, Iván R. Terol Villalobos, Germán Orozco Gamboa, "Evaluación de aceros como materiales para construir Platos Bipolares", Memorias del VI Congreso de la Sociedad Mexicana del Hidrógeno. México 2006.

10. Edgar Cuara Díaz. Tesis de maestría, “Evaluación de aceros e encóneles como materiales para construir platos bipolares”, CIDETEQ México Querétaro 2006.
11. S. Rivas, E. Cuara, F. Manríquez, I. R. Terol, G. Orozco. Corrosion , “Performance of Stainless Steel and Inconel in Simulated Fuel-Cell Media”, XXI Congreso de la Sociedad Mexicana de Electroquímica. México 2006.
12. DOE Hydrogen Program. Next Generation Bipolar Plates for Automotive PEM Fuel Cells. (2007) 722-725.
13. Joint Surface Preparation Standard NACE No. 1/SSPC-SP 5. White Metal Blast Clearing
14. ASTM G5 – 94 (2004), Standard reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements.
15. ASTM G59 – 94 (2004), Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements.
16. K. RoBberg, V. Trapp. “Graphite-based bipolar plates”, in Handbook of fuel Cells- Fundamentals, Technology and Applications, Edited by wolf Vielstich, Hubert A. Gasteiger, Arnold Lamm A (2003), John Wiley & sons, England, Chapter 26, Volume 3.
17. D. A. Shores, G. A. Deluga. “Basic materials corrosion issues”, in Handbook of fuel cells-Fundamentals, Technology and Applications, Edited by wolf Vielstich, Hubert A. Gasteiger, Arnold Lamm A (2003), John Wiley & sons, England, Chapter 23, Volume 3, 556 pp.
18. Lech Pawlowski. “The Science and Engineering of Thermal Spray Coatings”. John Wiley & Sons Ltd, (Second edition) 2008.
19. Y. Hung, H. Tawfik , D. Majan. *J. Powers Sources* (2008).
20. V. Higuera, F.J. Belzunce, J.A Carriles. Boletín Español de Cerámicos 43, (2004) 307-310.
21. M. Rendón Belmonte Tesis de Maestría, “Evaluación de aceros inoxidables recubiertos para platos bipolares”, CIDETEQ, México Querétaro 2009.