Enhancement of Electrode Stability using Platinum-Cobalt Nanocrystals on a Novel Composite SiCTiC Support

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Abstract

PtCo alloy catalysts for high temperature PEMFCs (Protonic Exchange Membrane Fuel Cells) were synthesized on a novel non-carbonaceous support (SiCTiC) using the impregnation method with NaBH₄ as the reducing agent at different synthesis temperatures to evaluate the effect of this variable on their physicochemical and electrochemical properties. The catalysts were characterized by inductively coupled plasma optical emission spectrometry (ICP-OES), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), X-ray diffraction (XRD), transmission electron microscope-energy dispersive X-ray (TEM) and temperature programmed reduction (TPR). In addition, the electrochemical characterization (i.e., cyclic voltammetry (CV), oxygen reduction reaction (ORR) and chronoamperometry) was carried out with a rotating disk electrode (RDE). For the cyclic voltammetry investigation, 400 cycles were performed in hot phosphoric acid and a half-cell to evaluate the stability

of the synthesized catalysts. The catalyst synthesized on SiCTiC exhibited excellent durability compared to the catalyst synthesized on a Vulcan support. In addition, all synthesized catalysts exhibited better catalytic activity than that of the PtCo/C catalysts. The best results were observed for the catalyst synthesized at 80 °C due to its shorter Pt-Pt nearest-neighbor and higher alloy degree. Finally, a preliminary stability test was conducted in an HT-PEMFC, and promising results in terms of stability and performance were observed.

1. Introduction

The increasing concerns surrounding global warming, the energy crisis and air pollution have increased research efforts on new alternative energy sources¹⁻². Polymer electrolyte membrane fuel cells (PEMFCs) are a promising device for the conversion of chemical energy from a fuel, such as hydrogen, directly into electricity with high energy efficiency, high power density and low environmental impact³⁻⁴. Among the PEM fuel cells, the cells that operate at a high temperature are very promising. The use of this cell significantly increases the CO tolerance, enhances the oxygen reduction reaction kinetics and decreases the thermal and water management of the system⁵⁻⁹. However, durability issues, cost reduction and fuel cell performance improvements are the main challenges for the widespread application of this technology in the market.

Several catalyst supports have been studied for application as anode and cathode electrodes in PEMFCs by Sharma et al.¹⁰. The numerous material supports can be classified as carbonaceous and non-carbonaceous. Carbon black is commonly used as a support in PEM fuel cells. However, this carbonaceous support exhibits high corrosion. Therefore, the development of new materials that decrease the corrosion degree while maintaining good conductivity is necessary¹⁰. Recently, several novel ceramic materials,

such as tungsten carbide¹¹, titanium-based materials¹²⁻¹⁴ and silicon carbide¹⁵⁻¹⁸, have been evaluated as catalyst supports to improve the service lifetime of the catalytic layer. The use of a non-carbonaceous support, such a SiCTiC, resulted in better thermal and electrochemical resistance than the carbon material under the same operating conditions¹⁹.

In regards to the metal catalyst, platinum has been the most used metal in this type of fuel cells. Nevertheless, the scarcity and high cost of this metal is a hindrance, and new materials that decrease the cost without compromising the catalytic activity would be beneficial²⁰⁻²². Therefore, binary and ternary Pt-alloys that exhibit a higher activity than Pt alone have been developed²³⁻²⁵. The use of alloys results in an improvement in the oxygen reduction reaction (ORR) due to different structural changes caused by alloying (i.e., modifications in the geometrical²⁶ (decrease in the Pt-Pt bond distance) or electronic²⁷ (increase in the Pt d-electron vacancy) structure of platinum metal). Therefore, PtM alloys could increase the rate of the oxygen reduction reaction, which is one of the main challenges in this type of fuel cell²⁸. Furthermore, the catalytic activity of the Pt-based catalysts is influenced by their structure, metal particle size and shape and the supporting material used on the electrode²⁹⁻³².

In this study, binary PtCo alloy catalysts supported on a novel non-carbonaceous support (SiCTiC) have been synthesized using an impregnation method with NaBH₄ as the reducing agent. The effect of temperature (30, 50 and 80 °C) during the synthesis was investigated. All obtained samples were physically and chemically characterized using ICP, XRD, SEM, TEM and TPR. In addition, a rotating disk electrode (RDE) was used to gain insight into the kinetics and mechanism of the O₂ reduction reaction and the electrochemical active surface area of the catalysts. Furthermore, the electrodes were prepared to evaluate their stability in a half-cell with catalysts synthesized at different

temperatures. Finally, electrodes for the high temperature PEMFC were prepared for use as a cathode in this type of fuel cell, and the experiments were performed with phosphoric acid-doped PBI membranes, which are good electrolytes for this type of technology^{8,33}.

2. Experimental

2.1. Synthesis of Pt-Co catalysts

PtCo nanocrystal catalysts were prepared using two different methods. The first approach employed the formic acid method (FAM), which consists of deposition of precursor salts using formic acid as a reducing agent¹⁹. The second approach employed an impregnation method using NaBH₄ as the reducing agent. SiCTiC (90:10 mol ratio) was used as a support (provided by SICAT, Paris; France), and H₂PtCl₆·6H₂O and Cl₂Co·6H₂O were employed as precursor salts (Sigma-Aldrich). The mixture was suspended in deionized water and stirred at different temperatures to evaluate the influence of this variable on the physicochemical and electrochemical properties. Once the set temperature was reached, 20 ml of NaBH₄ per gram of metal were added to the suspension. The amount of the metal precursor was adjusted to achieve a Pt:Co molar ratio of 1:1, and the total metal content in the catalysts was 40 wt%. The resulting black precipitate was filtered and washed with deionized water at 80 °C. Finally, the solid was dried in a vacuum oven at 90 °C for 12 h.

2.2. Characterization

The metal loading and molar ratio of both metals were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Varian Liberty RL spectrometer. The X-ray diffraction (XRD) measurements were carried out on a Philips PW-1700 diffractometer using Cu K α radiation. The 2 θ angular regions between 20° and 90° were explored at a scan rate of 0.1 ° s⁻¹. In addition, the samples were characterized

by SEM-EDX using a Jeol 6490LV. The morphology and particle size distribution of the PtCo catalysts were determined using a Joel 2100 transmission electron microscope (TEM). Furthermore, the presence of surface oxides was evaluated by temperature programmed reduction analysis. The reduction of the catalyst was carried out under a stream of hydrogen (5 vol%) diluted with Ar at a flow rate of 20 mL min⁻¹. The temperature was increased at a heating rate of 5 °C min⁻¹ up to 900 °C.

2.3. Preparation of inks

Different catalyst inks were prepared to investigate the catalytic stability. The first ink was prepared for use in an RDE, and the second ink was employed for preparing electrodes that were used in the half-cell and single cell.

The catalyst inks for the RDE were prepared by sonicating the catalyst and Nafion in a water-propanol mixture. 2 mg of the catalyst and 8 µL of Nafion (Sigma-Aldrich, 5 wt. %) were mixed and stirred for 1 min. Then, 200 µL of isopropanol and 800 µL of deionized water were added and sonicated for 30 min. The working electrode consisted of a glassy-carbon rotating disk electrode (0.196 cm²). 20 µL of the catalyst ink was dropped onto the working electrode and dried in a N₂ flow.

Next, electrodes with 0.3 mg Pt-Co cm⁻² and 0.6 mg Pt-Co cm⁻² were prepared for use in a half-cell and single cell, respectively. The inks were prepared using N, N' - dimethylacetamide (DMAc (1-20 PBI/support ratio)) as a dispersing solvent and polybenzimidazole (PBI, 1.5 wt. %) as a binder. The first ink was spread over 4 cm² on the surface of carbon paper for the half-cell test and heated at 190 °C for 2 h to eliminate any remaining solvent.

2.4. MEA preparation

A catalyst layer was deposited by spraying the catalyst ink over the commercial electrodes (Freudenberg Vliesstoffe, H23C2). The catalyst ink for the cathode and anode electrodes was prepared from the 40% wt. PtCo/SiCTiC and PtCo/Vulcan catalysts synthesized at 80 °C and a commercial 40% wt. Pt/C catalyst, respectively. This metal amount on the catalyst powder was fixed based on the optimization results for the catalyst layer in HT-PEMFCs, which was previous reported by our research group³³ and in agreement with the ratios employed in previously reported studies³⁴. In all cases, the Pt and PtCo loading on the two electrodes (anode and cathode) was 0.6 mg_{Pt} cm⁻². After deposition of the catalyst layer, the electrodes were dried at 190 °C for 2 h to remove the remaining DMAc. Then, a 10 wt. % phosphoric acid solution was dropped on the electrode surface to dope the PBI into the catalytic layer. The electrodes were left to absorb the acid for one day. To prepare the MEA, a PBI membrane was doped in 85 wt. % PA at room temperature for 5 days to achieve good proton conductivity. The doping level acquired by the membrane was approximately 9 molecules of acid per polymer repeating unit. The corresponding thickness of the doped membrane was 83.2 μm. The superficial acid on the membrane was thoroughly wiped off with filter paper, and the membrane was used to prepare the MEA. To fabricate the MEA, the doped membrane was sandwiched between a couple of electrodes, and the whole system was hot-pressed at 130 °C and 1 MPa for 15 min. The completed MEA was inserted into the cell between bipolar plates of graphite (with a five serpentine channels frame in each plate). The geometric area of each electrode was 25 cm².

2.5. Electrochemical measurements

All electrochemical measurements were carried out on an Autolab potentiostat/galvanostat (PGSTAT-302N). Pure Au foil and Ag/AgCl electrodes were used as the counter and reference electrode, respectively, in the RDE and half-cell tests.

2.5.1. Rotating disk electrode tests

To evaluate the ECSA (electrochemical surface area)^{33, 35-36}, cyclic voltammetry was performed between -0.2 and 1 V at a scan rate of 50 mV s⁻¹. The rotation rate was 1500 rpm, and the system was maintained in an inert atmosphere containing N₂. Then, the oxygen reduction reactions were performed using different rotation rates (400, 800, 1200 and 1600 rpm) to evaluate the activity and kinetics of this reaction. In this case, the system was saturated in O₂, and the ORR was performed between 0.1 and 0.9 V using a scan rate of 4 mV s⁻¹. Finally, a chronoamperometric analysis was carried out to assess the degradation suffered by the catalysts at a constant potential (0.55 V) and 1000 rpm. The analyses were performed in 0.5 M H₂SO₄, which was used as a proton generator.

2.5.2. Half-cell tests

To evaluate the electrochemical stability of the catalysts, various 1.5 cm² diameter electrodes were prepared using the same method as that employed during the MEA electrode preparation with a targeted Pt loading of 0.3 mg cm⁻². Then, 400 cycles were performed in 2 M phosphoric acid media to approximate the conditions of the HT-PEM fuel cell environment between -0.2-1 V vs Ag/AgCl at 50 mV s⁻¹. The system was maintained under an inert atmosphere containing N₂. In addition, the medium was heated at 50 °C to approximate to the cell conditions and simultaneously promote catalyst degradation. A schematic diagram of the half-cell that was used to perform the electrochemical tests has been reported elsewhere³⁷.

2.5.3. Fuel cell characterization

The MEAs that prepared with thermally cured PBI membranes were mounted and characterized in a commercially available cell compression unit (CCU) that was provided by Baltic fuel cells GmbH (Germany). The break-in procedure consisted of operating at 0.1 A cm⁻² and a λ (H₂ / O₂ ratio) of 1.5/9.5 for 60 h. A preliminary stability test was conducted by increasing the current density to 0.2 A cm⁻² (160 °C) while working at constant stoichiometric coefficients (λ_{H_2} of 1.5 and λ_{O_2} of 9.5). For further characterization, galvanostatic polarization curves were recorded every 48 h since the final step of the break-in procedure according to a previously reported³⁸. These tests were performed from the OCV to 0.4 V with air at a constant λ_{H_2/O_2} of 1.5/2 and then with oxygen at a constant λ_{H_2/O_2} of 1.5/9.5. Therefore, this preliminary life test was performed under accelerate stress conditions.

3. Results and discussion

3.1. Physicochemical characterization

The synthesized catalysts were physicochemically characterized using previously reported techniques. First, the formic method was used to produce the electrocatalysts to evaluate the effect of the addition of Co to Pt/SiCTiC because this method was previously used by our research group¹⁹. However, this method cannot reduce the cobalt precursor salt. Therefore, this method does not allow us to prepare PtCo catalysts. Then, the impregnation method using sodium borohydride as a reducing agent was performed as stated in the experimental section. Initially, the ICP measurements were carried out to evaluate the amount of metal deposited on the support. Table 1 shows the weight percentages of Pt and Co and the obtained molar ratios for the samples synthesized at different temperatures using the NaBH₄ method based on the ICP and EDX-SEM analyses. The experimental Pt/Co molar ratio was double the desired nominal rate. To evaluate the influence of the catalytic support on the metal loading and alloy composition,

an additional 1:1 PtCo-based catalyst was prepared using Vulcan XC72 as the catalyst support. 34.9 and 5.7 wt. % Pt and Co, respectively, were obtained in an atomic ratio of approximately 2. Therefore, the PtCo atomic ratio was not influenced by the catalytic support. Next, the differences between the theoretical and observed PtCo atomic ratios may be due to a competitive effect during the reduction process. Co^{2+} ions may not have an equal chance of being reduced when the process occurs in the presence of PtCl_6^{2-} ions in solution³⁹. Furthermore, Figure 1 shows the SEM images and the EDX spectra of the PtCo(1:1)/SiCTiC catalysts synthesized at different temperatures. Based on the SEM analysis, the obtained atomic ratios were similar to those obtained from ICP, as shown in Table 1.

Table 1. Data obtained from ICP and EDX-SEM analyses.

Synthesis temperature	ICP results			SEM results		
	wt. % Pt	wt. % Co	Pt/Co atomic	wt. % Pt	wt. % Co	Pt/Co atomic
30 °C	38.6	5.6	68:32	38.2	5.5	68:32
50 °C	34.8	5.3	66:34	34.8	5.3	66:34
80 °C	34.6	5.3	66:34	34.6	5.2	67:33

Figure 1. EDX-SEM spectra of PtCo (1:1)/SiCTiC catalysts that were prepared using different synthesis temperatures: a) 30 °C, b) 50 °C and c) 80 °C.

The temperature has a strong influence on the dispersion of the metallic particles. As the temperature increases, the agglomeration of the metallic particles increases, which is most likely due to a faster reduction reaction at high temperatures. Therefore, optimal distribution of the PtCo particles is prevented. Figure 2 shows the XRD patterns of Pt and PtCo on SiCTiC and the support. First, the platinum catalyst was successfully deposited on the support because the main peaks corresponding to the platinum crystals were observed. The Pt peaks located at 40°, 47°, 68° and 82° correspond to the (111), (200), (220) and (311) planes, respectively, of face-centered cubic (fcc) Pt. Based on a

comparison of the XRD patterns for Pt/SiCTiC and PtCo/SiCTiC, the peaks shifted to higher angle values when Co was added⁴⁰. Figure 3 shows the XRD patterns of PtCo/SiCTiC prepared at different synthesis temperatures. No obvious peaks that correspond to the presence of free Co or Co and Pt oxides were observed in the XRD patterns. Based on the results in Figures 2 and 3, the particle size was evaluated using the Scherrer equation⁴¹⁻⁴², and the alloy degree was evaluated using the Vegard law^{40, 43}. First, Bragg's law along with the Pt lattice geometry and the Miller indices (equation (1)) to calculate the lattice parameters.

$$a(200) = \frac{\lambda_{k\alpha}}{\sin \theta_{max}} \quad (1)$$

where $a_{(200)}$ is the lattice parameter for the PtCo alloy corresponding to the (200) peak, $\lambda_{k\alpha}$ is the wavelength of Cu K α radiation ($\lambda_{k\alpha} = 0.15418$ nm) and θ_{max} is the angle corresponding to the maximum intensity of the (200) Pt peak.

The cobalt atomic fraction in the alloy and the alloying degree parameters were calculated from equations (2) and (3):

$$a_{PtCo} = a_{Pt} - k \cdot x_{Co} \quad (2)$$

$$\text{Alloying degree} = \frac{x_{Co}}{[(1 - x_{Co}) \cdot (Co/Pt)_{real}]} \quad (3)$$

where a_i are the lattices parameters corresponding to Pt and the PtCo alloy, k is the copper constant ($k=0.124$ Å), x_{Co} is the cobalt atomic fraction and $(Co/Pt)_{real}$ is the real atomic ratio.

Figure 2. XRD patterns for the support and the Pt/SiCTiC and PtCo/SiCTiC catalysts.

Figure 3. XRD patterns for the PtCo/SiCTiC catalysts that were prepared using different synthesis temperatures.

Table 2 shows the crystal and particle sizes, which were obtained from the XRD patterns and TEM images, respectively, as well as the lattice parameters and alloy degrees of each sample. The obtained crystallite sizes of PtCo/SiCTiC were smaller than those of

the Pt/SiCTiC catalyst synthesized using the same method at 80 °C (7.08 nm) and the formic acid method at 80 °C (7.67 nm¹⁹). A substantial effect of the temperature on the crystal size was observed. As the synthesis temperature increased, the crystallite size increased, which may be due to enhanced reduction efficiency of the Pt precursor salt during the synthesis process due to the higher temperature. This effect may also increase the agglomeration of the metallic particles on the SiCTiC surface due to the low BET area of this material compared to that of carbon black ($BET_{SiCTiC} = 99.5 \text{ m}^2 \text{ g}^{-1}$ and $BET_{VulcanXC72} = 268 \text{ m}^2 \text{ g}^{-1}$).

Moreover, the addition of smaller cobalt atoms into the Pt lattice resulted in a reduction in the Pt-Pt bond distance, which contracted the crystallite net of the Pt particles due to generation of a PtCo alloy⁴⁴⁻⁴⁵. The obtained lattice parameters differ from lattice parameter of pure Pt ($a_{Pt} = 0.391 \text{ nm}$) due to the solubility of Co in the face-centered cubic Pt lattice⁴⁶. Taking into account the different atomic sizes ($R_{Pt} = 0.139 \text{ nm}$ and $R_{Co} = 0.125 \text{ nm}$), the inclusion of the smaller atoms results in contraction of the Pt crystallite net, which changes the alloy lattice parameter compared to that of Pt⁴⁷. Furthermore, smaller lattice parameters correspond to high alloying degrees⁴⁴, which is consistent with the obtained result. The shorter Pt-Pt nearest-neighbor distance in the alloys compared to that of pure Pt results in easier oxygen reduction and enhanced kinetics, increasing the overall fuel cell performance⁴⁶. The influence of the temperature on the synthesis results in two different effects. Therefore, an increase in the temperature increases the alloying degree but results in a larger crystal size.

Figure 4 shows the TEM images of the PtCo/SiCTiC powders synthesized at two different temperatures and of the PtCo/Vulcan powder synthesized at 80 °C. For all catalysts, the PtCo particles were uniformly dispersed over the entire non-carbonaceous support. However, some agglomeration was observed due to the high content of metal

deposited on the support and the low BET surface of SiCTiC ($\approx 100 \text{ m}^2 \text{ g}^{-1}$) compared to those of others carbonaceous supports, such as Vulcan carbon ($250 \text{ m}^2 \text{ g}^{-1}$). The particle size distributions of the PtCo catalysts were measured for more than 200 particles in each sample. The obtained values were slightly higher than those obtained from XRD data.

Table 2. Crystal sizes and alloying degrees.

Sample	Crystal size	Particle size	Lattice	X_{Co}	Alloying
	XRD (nm)	TEM (nm)	parameter		degree (%)
PtCo/SiCTiC 30 °C	5.0 ± 0.6	5.6	0.3876	0.27	17.6
PtCo/SiCTiC 50 °C	5.2 ± 1.1	-	0.3867	0.35	27.5
PtCo/SiCTiC 80 °C	6.3 ± 1.5	7.1	0.3864	0.37	29.3
PtCo/Vulcan 80 °C	6.2 ± 0.7	7.5	0.3861	0.39	33.1

Figure 4. TEM images at different magnifications for the PtCo/SiCTiC catalysts synthesized at 30 °C (a, b) and 80 °C (c, d) and for the PtCo/Vulcan catalyst synthesized at 80 °C (e,f).

3.2. Electrochemical characterization using an RDE

The rotating disk electrode (RDE) technique has been extensively used as a screening tool to estimate the activity of lab-scale (mg) quantities of novel PEMFC electrocatalysts⁴⁸.

ECSA was evaluated by integrating the hydrogen adsorption-desorption regions in the CV curves using equation 1:

$$ECSA = \frac{A}{v \cdot C} \cdot \frac{1}{Le} \quad (1)$$

where A is the peak area (AV cm^{-2}), v is the scan rate (V s^{-1}), C is the charge required to reduce the proton monolayer of the active platinum (0.21 mC cm^{-2}) and Le is the platinum load in the catalysts (0.016 and 0.3 mg cm^{-2} for the RDE and electrode, respectively).

Figure 5 shows the voltammograms of PtCo (1:1) / SiCTiC prepared using different synthesis temperatures. The adsorption and desorption regions typically contain two peaks, which are related to the (100) and (111) crystal face planes of Pt¹⁹. Occasionally, both peaks overlap generating a single peak that corresponds to the more active one, which is the (100) crystal face due to its higher activity²⁴. The ECSA values were obtained from cycle 10 to determine the value after stabilization of the system. During the first cycles, the H₂ desorption peak area increased due to hydration of the Nafion ionomer, which was used as a binder, by the electrolyte, which improves the three-phase boundary. However, larger amounts of Nafion may exert a negative effect on the calculation of the ECSA because the close interaction between Pt and Nafion may affect to the H₂ absorption-desorption processes. After the total saturation of the Nafion ionomer with the electrolyte, the ECSA began to decrease due to both the Pt-Nafion interactions and the electrochemical degradation of the catalyst, which was caused by the electrochemical test²⁴. The ECSA values were 9.91 and $13.47 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ for the $30 \text{ }^\circ\text{C}$ and $80 \text{ }^\circ\text{C}$ synthesized catalysts, respectively. The catalyst synthesized at $50 \text{ }^\circ\text{C}$ exhibited a very small desorption peak, and the ECSA value could not be calculated. The obtained ECSA values were lower than that of the catalyst without Co ($ECSA_{\text{Pt/SiCTiC}} = 18.13 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$). Yang et al.⁴⁹ obtained ECSA values of $20 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ for a Pt catalyst on a novel TiC

support. The higher ECSA values obtained by Yang et al. may be due to its smaller particle size (2.2 nm). However, ECSA values of approximately 4-6 m² g_{Pt}⁻¹ were also reported for Pt/TiC, which was obtained using different synthesis methods. These values are much lower than the one reported in this study. The high ECSA values are directly related to the availability of the active centers on the electrocatalysts. Therefore, a higher synthesis temperature results in a PtCo catalyst with enhanced activity, which is most likely due to high efficiency during reduction of the metallic precursors²⁰.

Figure 5. Cyclic voltammetry curves for PtCo (1:1) / SiCTiC prepared using different synthesis temperatures, which were recorded at room temperature in N₂-purged 0.5 M H₂SO₄ solutions at a sweep rate of 50 mV s⁻¹.

The observed electrochemical surface area decreased with the addition of a second metal since the presence of cobalt oxide could increase the contribution to the double layer, which would decrease the observed H₂ desorption peak region. Furthermore, the cobalt oxide could block the Pt active centers, which would decrease the electrochemical active area of the PtCo-based catalyst^{40,50}. The increase in the current density in the high

potential region may be due to oxygen evolution, which decreased resulting from the presence of more oxides due to the cobalt species. To confirm this hypothesis, TPR analyses of the catalysts PtCo/SiCTiC synthesized at different temperatures were performed. Figure 6 shows the TPR profiles for all the synthesized catalysts. The H_2 adsorption peaks were 154, 198 and 130 $\mu\text{mol g}_{H_2}^{-1}$ for the catalysts synthesized at 30, 50 and 80 °C, respectively. The sample synthesized at 50 °C exhibited the highest H_2 adsorption area, which indicates the highest oxide content. This result explains this sample possessing the lowest ECSA value, as shown in Figure 5. Based on comparison of these results to the Co and Pt wt%, the catalyst synthesized at 80 °C possessed a lower ECSA due to the higher Co content in the catalyst. In addition, a large crystal size and low dispersion decreased the active area of the catalyst⁴⁴, which explains the obtained results.

Figure 6. TPR profile of the different catalysts prepared under flowing gas consisting of 5 vol.% H_2 /Ar. Heating rate: 5 °C min^{-1} .

Figure 7 shows the evolution of the mass activity as a function of time for the different catalysts at 0.55 V, and the experiment was performed at room temperature in 0.5 M H₂SO₄ saturated in O₂. Table 3 shows the percent degradation suffered by the different catalysts. The PtCo/SiCTiC samples demonstrated lower currents than Pt alone. However, the PtCo-based catalysts exhibited higher stability than the pure Pt catalysts in terms of current density drops, which indicates that the presence of the non-precious metal may prevent migration of the platinum particles on the support^{4, 28}. Moreover, when the SiCTiC and Vulcan XC72 supports were compared, the carbonaceous-supported catalysts exhibited more degradation than the non-carbonaceous one, as expected. Furthermore, the PtCo alloys with large particle sizes (synthesized at higher temperatures) were more stable⁵¹⁻⁵².

Figure 7. Chronoamperometric results for different catalysts at 0.55 V in 0.5 M H₂SO₄ (rotation disk electrode, ω = 1000 rpm).

Table 3. Degradation after chronoamperometric analysis

Catalyst	Degradation / mA g _{Pt} ⁻¹ s ⁻¹
PtCo/SiCTiC 30 °C	7.382E-5
PtCo/SiCTiC 50 °C	4.790E-5
PtCo/SiCTiC 80 °C	6.534E-5
Pt/SiCTiC 80 °C	1.508E-4
PtCo/Vulcan 80 °C	3.278E-4
Pt/Vulcan 80 °C	3.701E-4

The oxygen reduction reactions were performed to evaluate the catalytic activity using the Tafel plot and the electron transfer number from the Koutecky-Levich equation. Table 4 shows the Tafel values and the limiting current density values at different rotation rates and temperatures. Tafel slopes of 60 mV dec⁻¹ correspond to an oxygen reduction mechanism that involves an initial fast charge transfer step followed by a chemical step, which is determined under Langmuir conditions⁵³⁻⁵⁴. The result indicates Tafel values higher than 60 mV dec⁻¹, which may be result from a low O₂ concentration in the background due to a mixed activation/mass transport control⁵⁵. Liu et al.⁶ obtained Tafel plot values in H₃PO₄ of the same order of magnitude (98 mV dec⁻¹) as the results obtained in the current study. The results do not show any relationship between the kinetic reaction and the synthesis temperature. However, an increase in the kinetic reaction and limit current density was observed as a function of the rotation rate due to the increase in the rotation rate decreasing the mass transfer resistance. The low activity of the ORR in the PtCo/SiCTiC catalyst synthesized at 80 °C may be related to the oxide content on the catalyst surface. It is important to note that the lower H₂ adsorption areas may explain the higher ORR activity achieved by the catalysts synthesized at 30 and 80 °C because the oxide content on the catalyst surface was lower than that on the catalyst synthesized at 50 °C. Low crystal sizes increase the metallic surface exposed to the media, which increases the oxide formation, blocks the active site for oxygen adsorption and decreases the ORR activity. Furthermore, as previously mentioned, the lower synthesis temperature may

prevent complete metallic reduction, which is consistent with the lower alloying degree, and decrease the catalytic activity of the resulting PtCo catalyst⁵⁶.

Table 4. Tafel slope and limit current density at different rotation rates.

ω (rpm)	Tafel slope (mV dec ⁻¹)			Limiting current density (A cm ⁻²)		
	30 °C	50 °C	80 °C	30 °C	50 °C	80 °C
400	88.5	124.9	109.4	0.00166	0.00195	0.00235
800	86.9	122.3	108.3	0.00214	0.0027	0.00319
1200	84.6	121.4	106.5	0.00243	0.00299	0.00384
1600	82.2	121.1	106	0.00262	0.00332	0.00435

Figure 8 shows the Koutecky-Levich plot for the synthesized catalysts. The parallelism and linearity observed in this plot indicates first order kinetics with respect to molecular oxygen⁵⁷⁻⁵⁸. Based on these results, the transferred electron number in the oxygen reduction reaction was calculated to be 3.18, 3.30 and 3.58 for the PtCo/SiCTiC catalysts synthesized at 30, 50 and 80 °C, respectively. A lower n value may indicate the production of H₂O₂. This fact may be related to the presence of oxides on the catalytic surface and the Co oxide presence, which may cause non-complete reduction of the oxygen to H₂O³⁹. Moreover, these values are higher than other previously reported values for PtCo-based catalysts. Hyun K. et al. obtained n values of approximately 2.8 for PtCo/C catalysts prepared using the same method⁴⁰, which is smaller than the results for these catalysts.

Figure 8. Plot of $1/j$ as a function of $1/\sqrt{\omega}$ from the experimental data for H_2O_2 reduction on Pt in 0.5 M H_2SO_4 at 25 °C.

3.3. Electrochemical characterization using a half-cell

To achieve complete ex situ characterization after the RDE evaluation, electrodes were prepared using the catalysts, and electrochemical activity was exhibited (catalysts synthesized at 30 °C and 80 °C) in the half-cell test. The ECSA and its loss was evaluated in a H_3PO_4 medium, which was closer to the fuel cell conditions.

Figure 9 shows the evolution of the voltammograms of the PtCo/Vulcan catalysts synthesized at 80 °C and the PtCo/SiCTiC catalysts synthesized at 30 and 80 °C. The measurements were recorded at 50 °C in N_2 -purged 2 M H_3PO_4 solutions at a sweep rate of 50 mV s^{-1} . The oxidation of the carbon surface on carbon black in aqueous acid electrolytes occurs at a potential close to 0.6 V (vs. RHE)^{4, 59}. In this case, the steep hydroquinone-quinone (HQ-Q) peak at approximately 0.4 V (vs Ag/AgCl) that was observed in the PtCo/Vulcan CV curve after 400 cycles indicated surface oxidation. This difference between the carbonaceous and non-carbonaceous supports confirms the poorer

degree of electrochemical stability of the carbonaceous supports^{38, 60}. In contrast to the cyclic voltammetry curves of the PtCo/SiCTiC catalysts in the RDE, the half-cell CV curves display more differentiated (100) and (111) Pt crystal faces. However, an overlap continues to be observed. Both peaks are observed in the adsorption and desorption regions. The obtained ECSA values of the PtCo/SiCTiC catalysts synthesized at 30 and 80 °C were 10.6 and 11.3 m² g_{Pt}⁻¹, respectively. The higher double layer contribution for the PtCo/SiCTiC catalyst synthesized at 30 °C can mask a portion of the H₂ absorption/desorption peak, reducing the observed active area⁶¹. Double layer changes were not shown after 400 cycles, which indicates that these materials do not exhibit important structural or chemical changes during the experiments. Moreover, a higher electrochemical stability was observed for the PtCo/SiCTiC catalyst synthesized at 80 °C (17% ECSA loss compared to 21% ECSA loss for the PtCo/SiCTiC catalyst synthesized at 30°C). The larger crystallite size of this catalyst may improve the electrochemical resistance of the catalyst, which may prevent agglomeration and catalyst migration processes. Furthermore, the higher alloying degree reached by the catalyst prepared at the highest temperature may be beneficial for achieving higher stability. The ECSA losses may be due to polarization of the catalysts in acid media and corrosion of the carbon support²⁴. In a previous study, the electrochemical activity of the Pt/SiCTiC catalysts was evaluated, and an ECSA value of 7.93 m² g_{Pt}⁻¹ was reported¹⁹. Although the addition of a second metal could decrease the ECSA, the crystal size reduction due to formation of the PtCo alloy increases the availability of active centers for oxygen adsorption, which results in an increase in the ECSA⁵³.

Figure 9. Cyclic voltammograms of different catalysts recorded at 50 °C in N₂-purged 2 M H₃PO₄ solutions at a sweep rate of 50 mV s⁻¹.

3.4. Tests in a single HT-PEMFC

Finally, taking into account that this technology is close to entering the market, the novel prepared and characterized materials were tested in a single fuel cell operating at 160 °C to gain insight into the performance of the PtCo-based catalyst in a real HT-PEMFC system. The best bimetallic catalyst based on the ex situ characterization (PtCo/SiCTiC synthesized at 80 °C) and a PtCo/Vulcan catalyst were used as a cathode catalyst to prepare an MEA according to the procedure described in section 2.4, and this system was tested according to the conditions described in section 2.5.3. Figures 10A and 10B show the polarization curves recorded at different times with oxygen and air, respectively. The evolution of the voltage as a function of time at a constant j of 0.3 A cm⁻² for the evaluated MEA and other MEA prepared with Vulcan as the catalyst support is shown in Figure 10C.

Figure 10. Polarization curves as a function of time with (a) air and (b) oxygen. (c) Evolution of the fuel cell voltage as a function of time at a constant load for the MEAs prepared with PtCo/SiCTiC and PtCo/Vulcan catalysts on the cathode side. Black points indicate the time at which the polarization curves were recorded.

As shown in Figure 10C, both PtCo-based catalysts exhibit similar potential values during the first 100 hours of the preliminary short test. However, PtCo/SiCTiC exhibits much better stability ($-119 \mu\text{V/h}$ vs $-472 \mu\text{V/h}$ reached by the carbonaceous-based catalyst), which indicates that the SiCTiC support avoids degradation of the metallic electrocatalyst particles better than Vulcan carbon XC72. Regarding the polarization curves, the obtained values are closer to the other values found in the literature for PtCo-based catalysts in smaller HT-PEMFC systems⁶². Table 5 compares the power density per mg Pt and the voltages achieved by the PtCo-based MEAs after a 48 hour test. By comparing to the same parameters obtained for a standard Pt/C MEA under the same conditions⁶¹, the ECSA and ORR activity during the ex situ characterization were slightly lower than the Pt-based catalysts. Both PtCo-based MEAs exhibited slightly higher power density values (8% lower than PtCo/SiCTiC and 4% lower than PtCo/C-based MEAs, respectively) per mg of Pt. However, the performance in terms of the voltage was lower (i.e., approximately 30 mV lower than that for the Pt/C-based MEA, as expected from the real Pt loading being lower, and the bimetallic catalyst manufacturing method is not fully optimized, which indicates that this values could be improved. Figure 11 shows TEM images at different magnifications for PtCo/Vulcan and PtCo/SiCTiC electrodes after electrochemical tests. The particles size were calculated to evaluate their change. The PtCo/Vulcan particles size increased from 7.5 to 15.1 nm (100 %) and from 7.1 to 12.4 nm (75 %) for the PtCo/SiCTiC catalyst. These results mean that the alloy supported on non-carbonaceous support suffered of a lower agglomeration effect. On the other hand, it can be also observed, in Figure 11, how in the case of the PtCo on Vulcan samples some areas are empty whereas other areas show high agglomeration (dark black zones in Figure 11.b). This could be explained by the Ostwald ripening which is a well-known degradation mechanism of catalyst of electrodes of PEMFCs^{63, 64}.

Table 5. Comparison between the voltage and power density values at same current densities for different MEAs.

	PtCo (2:1)/SiCTiC		40% Pt/Vulcan commercial		40% PtCo (2:1)/Vulcan	
Current density (mA cm ⁻²)	Voltage (V)	Power density (W cm ⁻² mg ⁻¹ Pt)	Voltage (V)	Power density (W cm ⁻² mg ⁻¹ Pt)	Voltage (V)	Power density (W cm ⁻² mg ⁻¹ Pt)
100	0.64	0.124	0.684	0.114	0.631	0.119
200	0.58	0.223	0.619	0.206	0.561	0.213

Figure 11. TEM images at different magnifications for PtCo/Vulcan catalyst (a,b) and PtCo/SiCTiC catalyst (c,d).

4. Conclusions

Considering our results, the main conclusions are as follows:

- PtCo-based catalysts on a novel SiCTiC support were successfully synthesized. The support has a strong influence on the final properties of the catalysts, especially in terms of stability.
- Temperature affects the properties of the PtCo/SiCTiC catalysts, and the best results in terms of durability and performance were obtained with the PtCo catalysts synthesized at 80 °C, which was most likely due to the higher alloying degree.
- The PtCo nanocatalyst exhibited a slightly better performance per mg of Pt than the pure Pt-based catalysts under the same operation conditions. In addition, the PtCo/SiCTiC catalyst exhibited promising performance and stability for use in HT-PEMFC technology. Further studies must be performed to optimize the synthesis method and electrode composition to increase the performance of this novel catalyst.

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Graphical Abstract