Evaluation of the Nickel Titanate-Modified Pt Nanostructured Catalyst for the ORR in Alkaline Media

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The electrocatalytic performance of novel Pt-NiTiO3/C catalyst for the oxygen reduction reaction (ORR) is investigated for the first time. The cathode has been synthesized in a two-step procedure. Firstly, the NiTiO3 co-catalyst is obtained via a wet-chemical method. Then, 20% Pt-NiTiO3/C electrocatalysts (Pt: NiTiO3 ratio of 1:1 at. %) is prepared by irradiating a mixture of NiTiO3, Vulcan and Pt precursor for 4 min in a microwave apparatus. As a reference, a 20% Pt/C catalyst has been synthesized by the same procedure. XRD analysis confirmed a crystalline NiTiO3 with particle size between 25–40 nm. It also indicates the formation of nanostructured Pt-NiTiO3/C having a Pt particle size of less than 2 nm. TEM results show the formation of homogenously dispersed Pt nanoparticles, with particle size of 2.3 nm. The linear scan voltammograms show a performance for the ORR of Pt-NiTiO3/C as high as that of Pt/C in KOH. The results suggest that the reaction proceeds following a four-electron transfer mechanism. Moreover, the mass and specific activities of Pt-NiTiO3/C are the same as those of Pt/C, demonstrating good performance with less Pt. Furthermore, ORR selectivity tests show an enhanced tolerance of Pt-NiTiO3/C to 0.1 M methanol, compared to Pt/C.

Polymer Electrolyte Membrane (PEMFCs) and Direct Alcohol Fuel Cells (DAFCs) are energy-producing devices with high conversion efficiency and zero or very low emission of greenhouse gases.1–2 Due to the feasibility of using H2 as sustainable fuel or the alternative use of low-molecular weight liquid fuels with high energy density (for example CH3OH and C2H5OH), fuel cell systems have called the attention of research groups worldwide.1–5 Because of these energetic advantages compared to traditional heat engines, PEMFCs and DAFCs are promising as power sources for transportation, as well as portable and stationary applications.3–5

Over the last decades, mostly acid membranes have been used during the development of PEM fuel cells.5 However, recent advances in the synthesis of chemically stable anion-exchange membranes have open the opportunity for the development of Alkaline Fuel Cells (AFCs) as compared to PEM fuel cells, which have been called to attract attention due to their environmental advantages.4 AFCs are also of technical interest because their atmosphere is less corrosive than the operating conditions found in PEM fuel cells, theoretically ensuring a longer life-cycle.11–15

Even more, the kinetics of the cathode reaction is faster in alkaline media than the analogous reaction in acid environment.16,17

Nevertheless, the use of noble metals is highly relevant in the progress of A-PEMFCs and A-DAFCs, where electrocatalyst based on Pt are still widely used.10,16–21 This is particularly important in the case of the ORR, several orders of magnitude slower than the hydrogen oxidation reaction. In order to reduce the costs of cathode electrocatalysts, the amount of noble metal must be decreased, yet sustaining a high catalytic activity for the ORR. In addition to such issues, another key drawback arising in the case of A-DAFCs is the efficiency losses due to the crossover effect. Therefore, the cathode electrocatalysts in this type of fuel cells must also show a high tolerance to the presence of organic substances. Even though the crossover phenomenon is less important in A-DAFCs than in acid fuel cells because of the reversed electro-osmotic drag, high fuel concentrations may cause a decrease in catalytic activity of Pt/C electrocatalysts for the ORR.11,17,22

Pt-alloys and Pt-oxides have been developed for A-PEMFCs and A-DAFCs as a successful strategy to develop high-performance and tolerant cathodes, with lesser amount of Pt than monometallic Pt/C electrocatalysts.23–27 A correlation of activity and composition has been found for AuPt alloys by Zhong’s group, as they report a higher mass activity for the ORR for AuPt alloys having 60–80% Au, compared to Pt/C and Au/C in alkaline electrolyte.25 Adzic et al. have reported the excellent performance of Pt-containing cathodes in alkaline solutions. The Volcano plots indicate a catalytic activity of the Pt/Pd(111) system for the ORR higher than that of Pt(111).22 Meanwhile, the work by Liu et al. demonstrates the enhanced catalytic activity of Pt-Ni alloys compared to Pt toward the ORR in alkaline and acid media. They found the maximum catalytic activity for the ORR at alloys containing ca. 50 atom % Ni.26 Rodriguez-Varela et al. have demonstrated a high catalytic activity for the ORR and enhanced tolerance to organic molecules of Pt- CeO2 cathodes, related to comparable Pt and Pt-Pd electrocatalysts in alkaline and acid electrolytes.27–28

Therefore, it is important to evaluate the use of composite cathodes in A-PEMFCs and A-DAFCs which may give electrocatalytic advantages over monometallic Pt/C. Even though the use metal oxides such as CeO2 has been encouraging, further research on alternative catalytic oxides may provide an insight on the development of Pt-based fuel cell cathodes. As an example, metatitanates having a general formula MTOx, where M is a divalent metal, have shown excellent properties as photocatalytic materials.25–34 Particularly, nanosized NiTiO3 has been evaluated in photocatalytic systems for the degradation of nitrobenzene and methylene blue in the visible-light range, with positive results.32–35

Early research carried out by Manoharan and Goodenough has demonstrated that when a passivated oxide layer having thickness lesser than 2 nm is deposited as a film on an ordered NiTi alloy, can catalyze the methanol oxidation reaction for fuel cells.35 This catalytic activity promoted us to examine NiTiO3 nanoparticles as electrocatalysts materials for the methanol oxidation reaction (MOR, results not shown in this work) and the ORR. In this context, this study focuses on the use of NiTiO3 as co-catalyst for the ORR. It is worth emphasizing this important feature, because the support in the systems presented in this research is Vulcan. To the best of the authors’ knowledge, this is the first time that the use of titanates in fuel cell cathode electrocatalysts is reported. The novel Pt-NiTiO3/C cathode has been synthesized in a two-step procedure. NiTiO3 is first obtained via a wet-chemical method. Afterwards, 20% Pt-NiTiO3/C nanosized

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electrocatalysts having a Pt: NiTiO₃ ratio of 1:1 (at. %) is obtained by the microwave-assisted polyol method. The electrocatalyst has been tested for the ORR in alkaline media. Moreover, its tolerance behavior to methanol and ethanol has been evaluated. The performance of Pt-NiTiO₃/C is compared to that of a 20% Pt/C cathode.

Experimental

Reactants and gases.— The following high purity reagents and gases were used in this work: Ni(OOCCH₃)₂·4H₂O, Ti(OCH(CH₃)₂)₄, H₂PtCl₆·6H₂O, ethylene glycol (EG), KOH, 2-propanol, CH₃OH and C₂H₅OH (ACS grade purchased from Aldrich); UHP grade O₂ and N₂ (acquired from Infra); Vulcan XC-72 obtained from Cabot Corp.

Physicochemical characterization.— X-ray diffraction analysis was performed in an Philips X’Pert (PANalytical) apparatus with a Ni-filtered Cu Kα radiation. Diffraction patterns were collected in the range of 10° to 80° (2θ) for NiTiO₃ powders and from 10° to 100° (2θ) for the Pt-NiTiO₃ electrocatalysts. Chemical composition by EDS was obtained in a Philips XL30 SEM apparatus having an accelerating voltage of 20 kV. TEM images were obtained in a JEOL 2100 microscope with 200 kV accelerating voltage. The particle size distribution of the supported electrocatalysts was determined by measuring approximately 300 nanoparticles using the Image-Pro Plus software.

Synthesis of NiTiO₃ nanoparticles and Pt-NiTiO₃/C catalysts.— NiTiO₃ nanoparticles were obtained by a wet-chemical procedure. The stoichiometric amounts of Ni(OOCCH₃)₂·4H₂O and Ti(OCH(CH₃)₂)₄ were separately dissolved in methanol, maintaining a Ni:Ti cationic ratio = 1:1. Citric acid was added to the titanium solution under magnetic stirring until a transparent phase was achieved. To this mixture, the nickel solution was added. Then, the solution containing Ti and Ni precursors was heated at 90°C for 12 h, followed by calcination in air atmosphere for 3 h at 700°C. After cooling down to room temperature, the NiTiO₃ nanoparticles were filtered and recovered.

The 20% Pt-NiTiO₃/C nanocatalyst with Pt: NiTiO₃ nominal ratio 1:1 (at. %) was synthesized by the microwave assisted polyol method. H₂PtCl₆·H₂O in water, as well as NiTiO₃ and Vulcan powders in ethylene glycol (EG) were separately dispersed by ultrasound for 30 min. Then, the solutions were put together and introduced in a modified domestic microwave to be magnetically stirred. Then, an EG solution of NaOH was added to adjust the pH to 11, followed by on/off pulses of irradiation of the sample for 4 min. After cooling down to room temperature, H₂SO₄ in EG was used to adjust the pH to 2, maintaining stirring for 1 h. The product was then filtered and dried in a dessicator overnight. A 20% Pt/C electrocatalyst was synthesized under the same on/off microwave irradiation and pH variation for comparison purposes, only avoiding the addition of the titinate.

Electrode preparation and electrochemical set-up.— The catalytic ink of each electrocatalyst was prepared separately. 10 mg of the powder material were mixed by ultrasound for 30 min with 1 mL 2-propanol and 5 μL Nafion solution. To form the working electrode, an aliquot of 10 μL of the ink were dispersed on a glassy carbon substrate (5 mm in diameter), which is placed in a rotating disc set-up (Pine Inst.). The catalyst layer deposition was performed by drop evaporation, forming an homogeneous film over the glassy carbon support. Catalytic activity measurements were carried out in an electrochemical three-electrode cell using a potentiostat (both from Pine Inst.). A Pt wire was used as the counter electrode, with an Ag/AgCl (sat. KCl) employed as the reference electrode. Attention was paid to avoid any electrolyte anion contamination, placing it in a separate reservoir with a salt bridge that ended up in a Luggin capillary closed to the working electrode. All the potentials have been reported in this work with respect to the Reversible Hydrogen Electrode (RHE), using the Nernst equation:

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \, pH + \frac{E^{0}_{\text{Ag/AgCl}}}{2} \]

where \( E_{\text{RHE}} \) is the potential converted with respect to RHE, \( E^{0}_{\text{Ag/AgCl}} \) is 0.197 V (i.e., the potential of the reference electrode used in the experiments), and \( E_{\text{Ag/AgCl}} \) is the potential measured against the Ag/AgCl reference electrode in the experiments.

Cyclic voltammograms (CVs) were obtained in N₂-satured 0.5 M KOH solution, in the 0.05 to 1.2 V range (vs. RHE) at a scan rate of 20 mV s⁻¹. To evaluate the catalytic activity of the synthesized electrocatalysts for the ORR, background current-subtracted polarization curves were built. First, CVs were obtained in N₂-saturated electrolyte at 5 mV s⁻¹ in the 0.05 to 1.2 V interval (vs. RHE) at a rotation rate (ω) of 2000 rpm. Afterwards, CVs were acquired in O₂-saturated electrolyte at ω = 400, 800, 1200, 1600 and 2000 rpm, scan rate = 5 mV s⁻¹ and same potential range. Then, the background current density was subtracted from the ORR current densities. In this work, only the cathodic sweeps of the ORR voltammograms have been shown. The selectivity behavior of the nanomaterials was studied obtaining polarization curves at 2000 rpm in the presence of 0.1 and 0.5 M CH₃OH, or 0.1 and 0.5 M C₂H₅OH, under O₂ atmosphere. Also, CVs of the oxidation of methanol and ethanol in N₂ atmosphere were acquired at 2000 rpm.

The current density in the electrochemical characterization has been given mainly in terms of the geometrical area of the working electrode. Mass and specific plots were built, taking into account the Pt loading and real area of the catalysts, respectively.

Results and Discussion

Physicochemical characterization.— The XRD patterns of NiTiO₃, Pt/C and Pt-NiTiO₃/C are shown in Figure 1. The high crystallinity of the titane can be confirmed in Figure 1a, where all reflections can be assigned to pure NiTiO₃ having rhombohedral structure (PDF 33-0960). No evidence of secondary phases such as NiO or anatase TiO₂ has been observed. EDS analysis of the titane has indicated a composition (wt%) of Ni: 38.29, Ti: 31.56, O: 30.14, which basically gives a Ni:Ti atomic ratio of 1:1. Figure 1b shows the diffraction patterns of the Pt/C and Pt-NiTiO₃/C catalysts, with characteristic features of crystalline fcc Pt. The peaks located at around 25° (2θ) are due to the Vulcan support and are attributed to the graphite (002) plane. Reflections at ca. 20° = 40, 67 and 81 can be ascribed to Pt (111), (220) and (311), respectively. In the diffractionogram of Pt-NiTiO₃/C, besides the Pt reflections, narrow peaks at 20 around 33, 35, 49, 53, 62 and 64, corresponding to the nickel titane planes (104), (110), (024), (116), (214) and (300) are clearly detectable. Figure 1c depicts a zooming of the (311) reflections. No significant shift to higher or lower angles is observed when comparing the peaks of Pt-NiTiO₃/C and Pt/C, as reported elsewhere for Pt-based alloys, metal-metal oxides and core-shell nanostructures. This structural characteristic may be related to the fact that the Pt precursor is reduced to metallic nanoparticles in the presence of already formed NiTiO₃ particles. Nevertheless, the Pt lattice parameter calculated from the (311) reflection is slightly modified, from 0.391 nm of Pt/C to 0.396 nm of Pt-NiTiO₃/C (Table 1).

The data of the wide Pt (311) peak has been used to estimate the crystallite size of the catalysts using the Scherrer equation. This reflection is chosen in order to avoid any interference of the NiTiO₃ peaks observed at the (220) reflection in Figure 1b. Sizes of 1.4 and 1.7 nm have been calculated for Pt/C and Pt-NiTiO₃/C, respectively (Table 1). Moreover, the results of the EDS analysis are shown in Table 1. The data is the average of the analyses over 5 different regions of the catalysts. The real chemical composition of Pt-NiTiO₃/C is very close to the one expected from nominal calculations. The Pt: NiTiO₃ ratio is 0.95:1 (at. %) and the total catalyst content is roughly 20 wt%. In the case of Pt/C, the metal content is around 16 wt%, which approaches the expected value.

The TEM image in Figure 2a shows the quasi-spherical morphology of the NiTiO₃ material. Its particle size has been determined to
Figure 1. XRD patterns of a) NiTiO$_3$ and b) Pt/C and Pt-NiTiO$_3$/C catalysts.

**Table I. Physical and chemical characteristics of Pt/C and Pt-NiTiO$_3$/C.**

| Catalyst       | Lattice parameter (nm) | Particle size, XRD (nm) | Particle size, TEM (nm) | Chemical composition (wt%) | Pt: NiTiO$_3$ ratio |
|----------------|------------------------|-------------------------|-------------------------|-----------------------------|---------------------|
| Pt/C           | 0.391                  | 1.4                     | 2.2                     | 16.39                       | -                   |
| Pt-NiTiO$_3$/C | 0.396                  | 1.7                     | 2.3                     | 10.37 8.65 80.98            | 0.95:1              |

be in the 15–40 nm range. The NiTiO$_3$ co-catalyst shows highly crystalline characteristics, as seen in the selected area electron diffraction (SAED) pattern inserted, in good agreement with the XRD results.

Figure 2. TEM (a) and HRTEM (b) images of the NiTiO$_3$ co-catalyst. SAED patterns are shown in the inserts.

Figure 2b shows the HRTEM micrograph of a NiTiO$_3$ nanoparticle having around 20 nm in diameter. A SAED pattern showing its crystalline features can be seen in the insert.

The morphology and particle size distribution of Pt/C (Figures 3a-3c) and Pt-NiTiO$_3$/C (Figures 3d-3f) have been analyzed by TEM and HRTEM. The images show the highly homogenous dispersion and nanosized characteristics of both Vulcan-supported electrocatalysts. The insert in Figure 3b is the SAED corresponding to the region specified by the red square. A distance between lattice fringes of 0.22 nm, attributed to the Pt (111) plane, has been determined. The SAED pattern in Figure 3d illustrates different rings of Pt-NiTiO$_3$/C (labeled 1 to 4) with interplanar distances of 0.39, 0.28, 0.22, 0.18 nm, ascribed to the NiTiO$_3$ (012) and (104) and the Pt (111) and (200) planes, respectively. Meanwhile, distances between planes of 0.39 and 0.22 nm (NiTiO$_3$ (012) and Pt (111) planes) have been calculated from the SAED pattern shown in the insert of Figure 3e, which corresponds to the area highlighted by the red square. This analysis confirms that Pt and NiTiO$_3$ nanoparticles are present in the catalysts, supported on Vulcan. The histograms of Pt/C and and Pt-NiTiO$_3$/C (Figures 3c and 3f, respectively) show the narrow particle size distribution of the
Figure 3. TEM and HRTEM micrographs of Pt/C (a-b) and Pt-NiTiO3/C (d-e). The histograms of the catalysts are shown in (c) and (f), respectively. A schematic representation of the Pt nanoparticles dispersion at Pt-NiTiO3/C is presented (g).

electrocatalysts. The average particle size of Pt/C is 2.2 nm, while that of Pt-NiTiO3/C is 2.3 nm. These values are larger than those obtained from XRD calculations (see Table I). However, it can be concluded that the two analyses indicate a very small particle size of the cathodes.

Due to the physical characteristics of Vulcan and NiTiO3, it is not feasible to distinguish them only by color contrast in the TEM images. Thus, it is not straightforward to visualize where the Pt nanoparticles sit. Nevertheless, the high distribution observed in Figure 3d gives evidence that Pt is supported on Vulcan, while some nanoparticles may probably also be dispersed on titanate sites, as proposed schematically in Figure 3g.

Catalytic activity for the ORR.—The CVs of Pt/C and Pt-NiTiO3/C are shown in Figure 4. The curves in the full potential scan (Figure 4a) show the characteristic regions expected for Pt-based electrocatalysts, i.e., the hydrogen adsorption/desorption (Hads/des), double layer and Pt-oxides formation/reduction regions. The Pt/C catalyst shows higher current densities than Pt-NiTiO3/C. The peaks corresponding to the Hads/des region at Pt-NiTiO3/C are well defined indicating a high Pt participation during the potential scan, but the intensity observed is lower compared to the monometallic. The behavior of Pt-NiTiO3/C indicates that there is no noticeable detrimental effect of the titanate on the Hads/des features of the cathode. Also, in the oxides region, which in alkaline media is mostly due to the specific adsorption of hydroxide anions, the onset potentials of Pt-OH formation are practically the same. A noticeable difference is that the typical peak at the beginning of the Pt-OH formation is more flat at Pt-NiTiO3/C. Figure 4b shows a comparison of the Pt-oxides reduction peaks. A very small shift of 3 mV to lower potentials is observed for the Pt-NiTiO3/C (719 mV/RHE) compared to Pt/C (722 mV/RHE) at the peak maximum. Therefore, it can be concluded that the adsorption strength of oxygen species on the Pt sites at the titanate-containing catalysts is roughly the same as that in the monometallic. This means that the reduction of intermediates should proceed similarly on both catalysts.

The polarization curves of the ORR at Pt/C and Pt-NiTiO3/C (cathodic sweep) at rotation rates of 400, 800, 1200, 1600 and 2000 rpm are shown in Figures 5a and 5b, respectively. The curves have been built after background current subtraction (see Experimental section). The insert in each Figure shows the CVs obtained in N2 and O2-saturated electrolyte before current density correction. From the curves, the onset potential of the ORR (Eonset) at Pt/C (~1.03 V/RHE)
is roughly the same as that of Pt-NiTiO3/C (~1.04 V/RHE), see Table II. Meanwhile, the current density at 0.2 V/RHE and \( \omega = 2000 \) rpm is ~4.40 mA cm\(^{-2}\) for Pt/C, very close to the value of ~4.38 mA cm\(^{-2}\) at Pt-NiTiO3/C under the same conditions. The polarization curves show that the titanate-containing material has fundamentally the same catalytic activity for the ORR, compared to that of the monometallic cathode.

It is well known that the Levich Equation (1) applies when RDE measurements of the ORR are collected:

\[
\frac{1}{j} = \frac{1}{j_e} + \frac{1}{j_d} = \frac{1}{j_e} + \frac{1}{B \omega^{1/2}} \quad [1]
\]

where the disk current density \( j \) correlates with the kinetic \( j_e \) and the diffusion limited \( j_d \) current densities. Nafion layer diffusion parameters have no effect in the behavior of the catalysts for the ORR curves because the amount of Nafion used in this study is very small.\(^{47} \)

The measured ORR current densities in the mixed-controlled region (see Figures 5a and 5b) can be expressed as a function of the rotation rate as follows:

\[
B = 0.2nF D^{2/3}v^{-1/6}C_{O_2} \quad [2]
\]

where \( B \) is the Levich constant, the constant 0.2 applies when \( \omega \) is expressed in rpm, \( n \) is the number of electrons transferred, \( F \) is the Faraday constant (96,500 C), \( D \) is the diffusion coefficient of molecular \( O_2 \) in the electrolyte (1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}), \( v \) is the kinematic viscosity of the electrolyte (1 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}), and \( C_{O_2} \) is the concentration of \( O_2 \) (1.2 \times 10^{-6} \text{ mol cm}^{-3}).\(^{48} \) Koutecky-Levich plots of Pt/C and Pt-NiTiO3/C at different potentials are shown in Figures 6a and 6b, respectively. The plots show linearity and parallelism, indicating first-order kinetics with respect to \( O_2 \).\(^{49,50} \)

In both cases, the lines fall close to that corresponding to a theoretical 4 e\(^{-} \) transfer slope, also included in the Figure and calculated from Equation 2. The slope of a 2 e\(^{-} \) mechanism is shown for comparison too. From the experimental data, \( n \) has been calculated as 3.8. This result suggests that the ORR at the novel home-developed Pt-NiTiO3/C may proceed via a mechanism according to the reaction in alkaline media:

\[
O_2 + H_2O + 4e^{-} \rightarrow 4OH^- \quad [3]
\]

Mass and specific activity plots of the ORR at both catalysts are shown in Figure 7, calculated from the data of Figure 5 using the mass-transport correction:\(^{1} \)

\[
i_k = \frac{i_{dl}}{i_d - i} \quad [4]
\]

where \( i \) is the experimental current collected at the working electrode, \( i_{dl} \) is the diffusion-limited current and \( i_k \) is the kinetic current corrected for mass transport. The mass activity curves in Figure 7a have been normalized with respect to the Pt mass content deposited in the thin porous electrodes taking into account the EDS results (Table I). Meanwhile the specific activity plots in Figure 7b have been built taking into account the Pt real surface area \( (A_{Ft}, \text{ in cm}^2) \), calculated by measuring the charge in the Hdes region \( (Q_{Hd}, \text{ in } \mu \text{C}) \) after double layer correction in the CVs of Figure 4. The following relationship has been used:

\[
A_{Ft} = \frac{Q_H}{Q_{Hd}} \quad [5]
\]

where \( Q_{Hd} \) is the theoretical charge needed for the oxidation of a monolayer of hydrogen on smooth Pt, taking here as 210 \( \mu \text{C cm}^{-2} \). The calculated values of \( Q_H \) and \( A_{Ft} \) are presented in Table II.

### Table II. Electrochemical parameters at Pt/C and Pt-NiTiO3/C.

| Catalyst          | \( E_{onset} \) (V) | \( Q_H \) (\( \mu \)C) | \( A_{Ft} \) (cm\(^2\)) | \( b \) at hop (mV dec\(^{-1}\)) | \( b \) at hop (mV dec\(^{-1}\)) | \( \Delta E_{onset} \) with 0.1 M fuel (mV) |
|-------------------|---------------------|------------------------|--------------------------|--------------------------------|--------------------------------|------------------------------------------|
| Pt/C              | 1.03                | 2947.2                 | 14.03                    | 77                             | 116                            | 60                                        |
| Pt-NiTiO3/C       | 1.04                | 1549.6                 | 7.37                     | 67                             | 112                            | 60                                        |
| Pt-NiTiO3/C       |                     |                        |                          |                                |                                |                                          |

Two regions with distinct Tafel slopes \((b)\) can be observed. The first one is at low overpotentials \((lop)\), i.e., potentials between 0.95 and 0.85 V (vs. RHE). At high overpotentials \((hop)\), i.e. 0.85 V and lower, there is a change into higher slopes in good agreement with the behavior reported in several references, beginning with those of Damjanovic et al.\(^{50-52} \) The change in Tafel slope is attributed to an effect of the adsorbed oxygen-containing species such as reaction intermediates from the ORR, or chemisorbed hydroxyl groups \((OH_{ad})\) from the electrolyte.\(^{53} \) The smaller \( b \) at low overpotentials is associated to a Temkin adsorption mechanism at a higher coverage of O-like species, while the slope at high overpotentials is ascribed to a Langmuir adsorption due to the first electron transfer of the reaction (rate determining step).\(^{53,54} \) Tafel slopes of 60 and 120 mV dec\(^{-1}\) at low and high overpotentials, respectively, have been reported for the ORR in alkaline media.\(^{55} \)
Figure 6. Koutecky-Levich plots of the ORR at different electrode potentials on Pt/C (a) and Pt-NiTiO3/C (b).

The $b$ values under Langmuir adsorption mechanism are 112 mV dec$^{-1}$ at the Pt-NiTiO3/C catalyst and 116 mV dec$^{-1}$ at Pt/C, slightly lower than 120 mV dec$^{-1}$. Meanwhile, the values of $b$ at log are 67 and 77 mV dec$^{-1}$ for Pt-NiTiO3/C and Pt/C, respectively. These values are higher than the theoretical 60 mV dec$^{-1}$, particularly in the case of the monometallic. The behavior of the catalysts may be related to the participation of the carbon support on the ORR in alkaline media, which has an important effect on the kinetics of the reaction as has been reported previously. Overall, the approximation in Tafel slopes in Figures 7a and 7b indicates that the reaction mechanism of the ORR at Pt-NiTiO3/C is the same as the mechanistic pathway on Pt/C in the KOH electrolyte.

However, it should be noticed that the mass catalytic activity of Pt-NiTiO3/C surpasses that of Pt/C at potentials of ca. 0.91 V/RHE and below (Figure 7a). Likewise, the specific activity of Pt-NiTiO3/C is higher at potentials of ca. 0.94 V/RHE and below compared to Pt/C in Figure 7b. These results suggest a positive effect of using the titanate as co-catalyst to for the ORR in the alkaline electrolyte.

Tolerance to the presence of methanol and ethanol.— It is well known that Pt/C cathodes become rapidly depolarized by the presence of organic molecules, with a reduction in catalytic activity for the ORR and therefore in the fuel cell efficiency. The loss of catalytic activity of Pt-NiTiO3/C has been observed for a wide variety of liquid fuels such as methanol, ethanol, ethylene glycol and 2-propanol. For example, the shift in potential with respect to $E_{\text{onset}}$ toward more negative values ($\Delta E_{\text{onset}}$) can be as high as 620 mV in the presence of 0.125 M ethylene glycol, when Pt/C is used in acid media. A loss in performance of Pt/C has also been demonstrated in alkaline media in the presence of methanol. Therefore, a key feature of candidate catalysts to be used in A-DAFC cathodes is their selectivity toward the ORR and tolerance to organic substances.

Figure 8 shows the polarization curves of the ORR on Pt/C (8a) and Pt-NiTiO3/C (8b) in the absence (with data from Figure 5, $\omega = 2000$) and presence of 0.5 and 0.1 M CH$_3$OH or C$_2$H$_5$OH. At the high concentration, both catalysts show a preference for the oxidation of both of the fuels, with Pt/C delivering higher peak current densities. At the low concentration, the Pt/C catalyst shows higher current densities associated to the oxidation of the molecules, with peak maximums due to the oxidation of 0.1 M MeOH and EtOH of 3.3 and 20.5 mA cm$^{-2}$, respectively. The corresponding values at Pt-NiTiO3/C are $-1.65$ and $2.5$ mA cm$^{-2}$, respectively. A zoom of the polarization curves, taking into account only the 0.1 M concentration of the fuels is shown for Pt/C in Figure 8c and Pt-NiTiO3/C in Figure 8d. The higher tolerance in terms of oxidation current densities of each of the fuels is more evident at Pt-NiTiO3/C. Moreover, the $\Delta E_{\text{onset}}$ values with MeOH and EtOH are the same at both catalysts (see Table II). The behavior of the catalysts in Figures 8c and 8d indicates that the higher selectivity toward the ORR is obtained with Pt-NiTiO3/C in the presence of 0.1 M methanol. The inserts in Figure 8 show the catalytic activity of Pt/C and Pt-NiTiO3/C for the oxidation of (0.5 and 0.1) M CH$_3$OH and (0.5 and 0.1) M C$_2$H$_5$OH in N$_2$ atmosphere. The Pt/C catalyst shows higher current densities at both concentrations of the two fuels, a behavior that can be correlated with its lower degree of tolerance, compared to the titatate-containing cathode. Meanwhile, Pt-NiTiO3/C shows a higher catalytic activity for the oxidation of ethanol, as indicated by a significantly lower on-set potential related to the MOR, at any of the fuels concentrations. Such performance explains its lower tolerance to EtOH in Figure 8d.

Figure 7. (a) Mass and (b) specific activity plots of the ORR on Pt/C and Pt-NiTiO3/C catalysts. Electrolyte: 0.5 M KOH saturated with O$_2$, $\omega = 2000$ rpm.
Figure 8. Polarization curves of the ORR at (a) Pt/C and (b) Pt-NiTiO₃/C in the absence and presence of (0.5, 0.1) M CH₃OH or (0.5, 0.1) M C₂H₅OH. A zoom only with 0.1 M MeOH and EtOH is shown for Pt/C (c) and Pt-NiTiO₃/C (d). Electrolyte: 0.5 M KOH. Scan rate: 5 mV s⁻¹, ω = 2000 rpm. The inserts show the CVs of the oxidation of (0.5, 0.1) M MeOH and (0.5, 0.1) M EtOH in N₂-saturated 0.5 M KOH at the scan rate of 20 mV s⁻¹.

Even though a full tolerance to the organic molecules has not been reached, from the catalytic behavior in Figure 8, the presence of the titanate increases the catalyst’s selectivity toward oxygen reduction, over methanol and ethanol oxidation. Interestingly, one of the reasons of the enhanced selectivity toward the ORR can be the larger Pt-Pt distance related to the modification of lattice parameter at Pt-NiTiO₃/C (Table I). The lattice strain may inhibit the dissociative chemisorption of the organic fuels that requires three neighboring Pt atoms to be activated.⁵⁷

Moreover, it has been reported that by Goodenough et al. that at oxide materials, the ORR in alkaline media occurs by exchange of surface OH⁻.⁵⁹ For NiTiO₃ nanoparticles of 15–40 nm, the O-site present in the NiTiO₃-x(OH)x phase may be functioning as the reaction site for the ORR. The reaction in Equation 3 occurs by exchange of surface OH⁻ species present in the surface of NiTiO₃-x(OH)x·H₂O. This can explain why mass and specific activities of Pt-NiTiO₃/C are the same and at some potentials better than those of Pt/C. Also, the surface OH⁻ species may be a positive issue increasing the tolerance behavior of Pt-NiTiO₃/C for low concentration MeOH and EtOH. Another factor promoting the tolerance may be that O₂ is more strongly adsorbed than alcohols at Pt sites in Pt-NiTiO₃/C (due to the presence of the titanate), compared to the Pt-alone catalyst.

Even though this may not be the optimized chemical composition of Pt-NiTiO₃/C, its catalytic activity and enhanced selectivity for the ORR (especially in the case of MeOH) make it potential cathode material for A-DAPCs. Active research in our laboratories includes the variation of the Pt:NiTiO₃ ratio in order to evaluate the effects of the chemical composition on the electrocatalytic behavior of the novel cathode, with the aim of sustaining or even improving the high catalytic activity of Pt-NiTiO₃/C for the ORR with respect to Pt/C, yet keeping a high selectivity performance.

Polyol continues to be the method of choice since NiTiO₃ has proven to be a suitable co-catalyst in 0.5 M H₂SO₄ solution for the oxidation of methanol.⁶₀ Therefore, the modification of pH during the synthesis should not have a negative effect on the titanate structure and thus on its loading at the final chemical composition of the catalysts. Figure 1b shows that the (104), (110), (024), (116), (214) and (300) reflections of NiTiO₃ are detectable, suggesting that the structure of the material remains stable. Moreover, no peaks corresponding to the TiO₂ phase are observed. However, it is of interest to further evaluate the stability of the titanate, in order to discard any structural modification, or leaching of Ni in the acid media.

NiTiO₃ samples have been submitted to 500 cycles between 50 and 1200 mV/RHE, in 0.5 M H₂SO₄. Post-mortem TEM analysis has been carried out. Figure 9a shows a HRTEM image of a NiTiO₃ nanoparticle after electrochemical cycling, with its SAED pattern shown in Figure 9b. It can be observed that the morphology and crystallinity

Figure 9. (a) TEM image of NiTiO₃ nanoparticles after electrochemical cycling (500 cycles between 50 and 1200 mV/RHE) in 0.5 M H₂SO₄. (b) Corresponding SAED pattern.
are not significantly changed after electrochemical tests, compared to its characteristics in Figure 2b, i.e., before cycling.

EDS analysis shows that after electrochemical testing, NiTiO₃ preserves high Ni and Ti contents (35.64 and 47.78 wt%, respectively). Even though this result may not be conclusive, it suggests that leaching of Ni is not occurring, or at least not significantly. Table III shows a comparison of chemical composition of as-synthesized NiTiO₃ and after electrochemical cycling.

Furthermore, in order to evaluate the effects of strong acid solution on the structural characteristics of the titanate, a NiTiO₃ sample has been soaked in 1 M H₂SO₄ for 24 h. Figure 10 shows the XRD pattern after acid treatment, demonstrating that there are no significant structural changes when compared with the pattern before treatment (Figure 1a). The relative intensity of the reflections is only slightly modified, while no shifts in the peaks maximum has been observed. Furthermore, the chemical composition of the sample after acid treatment is shown in Table III. No major differences are observed with respect to the composition before soaking. Overall, the results suggest that nanostructured NiTiO₃ is stable in acidic media.

Table III. Chemical composition of as-synthesized NiTiO₃ after electrochemical cycling in 0.5 M H₂SO₄ and after treatment in 1 M H₂SO₄.

| NiTiO₃ sample                  | Ti     | Ni     | O      |
|-------------------------------|--------|--------|--------|
| As-synthesized                | 31.536 | 38.29  | 30.174 |
| After cycling                 | 35.64  | 47.78  | 16.58  |
| After acid treatment          | 32.08  | 33.03  | 34.89  |

Figure 10. XRD pattern of NiTiO₃ after acid treatment in 1 M H₂SO₄ for 24 h.

Conclusions

Nanostructured Pt-NiTiO₃/C catalyst (Pt:NiTiO₃ ratio of 0.95:1 at. %) was successfully synthesized by the microwave-assisted polyol method. The catalyst showed homogeneously dispersed nanoparticles on the support. It was proposed that some Pt may also be dispersed on the support. It was proposed that some Pt may also be dispersed on the support. It was proposed that some Pt may also be dispersed on the support.

Moreover, the studies indicate that NiTiO₃ is stable in H₂SO₄, which opens the interest to study Pt-NiTiO₃/C as catalyst in acid fuel cells.

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