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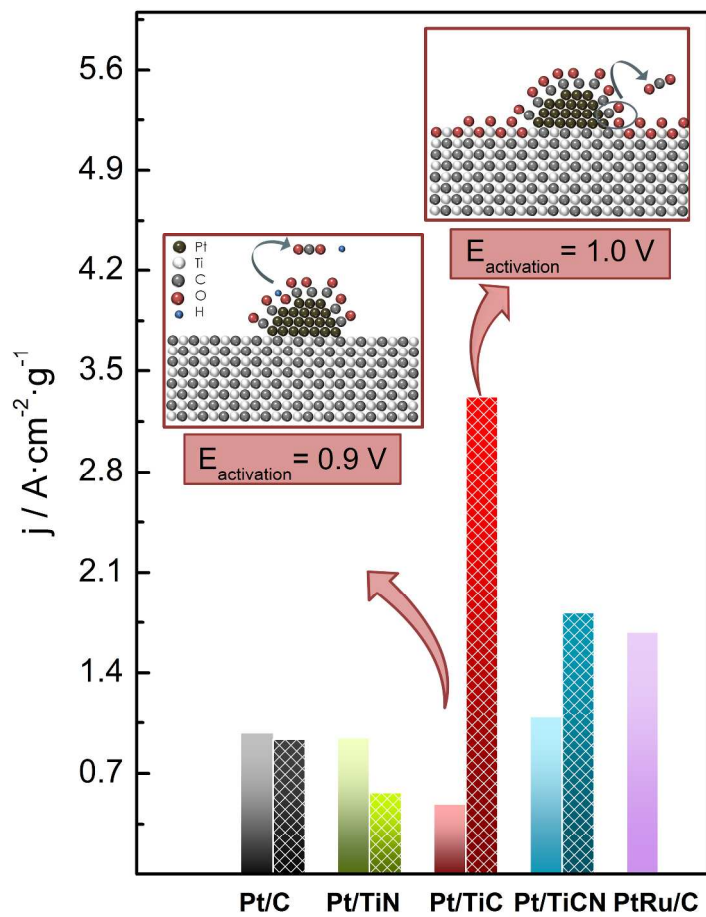


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COMMUNICATION

Titanium Carbide and Carbonitride Electrocatalyst Supports: Modifying Pt-Ti Interface Properties by Electrochemical Potential Cycling

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Titanium carbide and carbonitride are expected to be good materials to replace carbon as electrocatalytic support, since they are chemically stable in acidic media and possess high electrical conductivity. However, they eventually can be transformed to the titanium oxide, which is a thermodynamically stable compound, at potentials higher than 0.9 V (vs RHE) in acidic media. In this communication, we report an enhanced catalytic activity towards the CO and methanol electrooxidation on TiC and TiCN materials induced by surface oxides at the Pt/support interface. In particular, the current density obtained for Pt/TiC, activated up to 1.0 V, is 2-fold higher to that achieved with the commercial PtRu/C catalyst, which is accepted to be one of the best catalysts for methanol oxidation reaction.

Polymer electrolyte membrane fuel cells (PEMFCs), including direct methanol fuel cells (DMFCs), are emerging as promising candidates for the automobile industries and portable electronics due to their high power density and portability¹⁻³. However, the high cost due to noble metal based catalyst (e.g. Pt and Ru), and the low stability owing to corrosion of conventional carbon supports under chemical and electrochemical oxidation conditions have seriously hindered the commercialization of fuel cell technology⁴. Therefore, elaborate exploration and rational design of new materials of low cost, high efficiency and durability will have a significant impact on making these promising energy technologies commercially viable.

Transition metal carbides and nitrides have attracted increasing research interest during the past decade in the context of their potential applications as electrocatalysts, catalyst supports, lithium-ion battery materials, and solar cells components⁵⁻⁷. Particularly, these materials are expected to be suitable materials to replace carbon as electrocatalytic support, since they are chemically stable in acidic media and resistant to poisoning, have excellent mechanical durability and possess high

electrical conductivity^{8,9}. Additionally, some transition metal carbides and nitrides possess an electronic structure near the Fermi's level similar to Pt, which favors the electrical interaction between support and active phase⁹. Within this group of materials, Ti carbides and nitrides have emerged as an excellent alternative to carbon-based electrocatalyst supports¹⁰⁻¹⁴. From our previous work, a significant promoting effect of the support on Pt nanoparticles supported on TiC, TiCN and TiN was observed for 2 of the reactions involved in fuel cells, electrooxidation of CO and methanol, both in acidic and alkaline media¹⁵. XPS analysis revealed an enhanced catalytic activity of catalysts induced by an important charge transfer from the titanium-based supports to the metal nanoparticles, and especially those containing nitrogen. Moreover, catalyst supports influence the surface morphology of platinum nanoparticles creating different densities of surface defects, which strongly affect the reactivity.

Despite the advantages, one of the drawbacks of carbides and nitrides may be their thermodynamic instability under oxidative environments as present in a PEMFC. These materials are generally assumed to be "stable", though are eventually transformed to the transition metal oxide, which for most metals is the only thermodynamically stable compound under these conditions¹⁶⁻¹⁸. Therefore, on the basis of thermodynamic and electrochemical stabilities, conducting (transition) metal oxides appear to be potentially suitable as electrocatalyst supports^{1,9,19}. However, group 4 and 5 metal oxides are almost insulators, and therefore become necessary to appropriately modify their nature to produce catalysts with suitable conductivity and reactivity. In this context, it is well known that TiO₂ bulk resistivity is high and therefore needs to be reduced or doped to be suitable as an electrocatalyst support^{20,21}.

Herein, we report an enhanced catalytic activity towards the CO and methanol electrooxidation on carbides-based materials induced by surface oxides at the catalyst/support interface, which are produced by a simple methodology. Indeed, the performance

towards both reactions greatly increases at TiC and TiCN supported Pt nanoparticles after modifying the catalyst surface by electrochemical potential cycling. The last effect was not observed at carbon and titanium nitride supported platinum catalysts.

The details of the synthesis process and the results of the characterization of the catalysts are described elsewhere¹⁵. Briefly, 15% wt. Pt nanoparticles supported on carbon black (C), TiC, TiCN and TiN were synthesized following the ethylene glycol method²². The size of platinum particles was similar in all catalysts (between 2.8 and 4.5 nm average) being slightly higher for those containing titanium-based supports.

The electrochemical response of each catalyst support compared with the signal of the glassy carbon recorded before the deposition of the catalyst support ink is showed in Fig.1. Carbon Vulcan (C) exhibits the typical voltammetric profile of carbon black²³. TiN and glassy carbon profiles are similar, indicating the high electrical conductivity and low capacitance of the former. On the other hand, TiC and TiCN show an irreversible anodic peak at c.a. 1.15 V, which starts around 0.7 V at both materials. It is remarkable that in the subsequent cycles, the anodic contribution falls. The latter suggests an irreversible oxidation during the first anodic excursion, producing a stable surface.

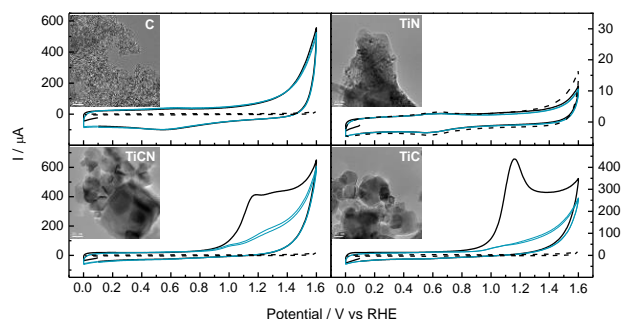
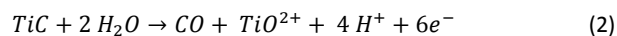
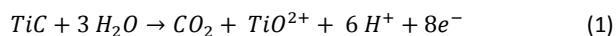


Fig. 1. TEM images and cyclic voltammograms of C, TiN, TiCN and TiC supports recorded in 0.5 M H₂SO₄. Scan rate: 20 mV·s⁻¹. First cycle: black solid lines; second and third cycles: blue solid lines; glassy carbon signal: dashed line.

To find out the electrochemical reactions associated with the anodic peak developed on TiC and TiCN at 1.15 V, in-situ Fourier Transform Infrared Spectroscopy (FTIRS) was employed (Fig. 2). Spectra were recorded by applying single potential steps from a reference potential ($E^0=0.1$ V) in the positive-going direction up to 1 V. Left panel of Fig. 2 shows the spectra achieved at all catalyst supports, in which only TiC and TiCN reveal significant signals at 2045 and 2343 cm⁻¹ associated to CO and CO₂ formation²⁴. Therefore, the anodic faradaic current developed on TiC and TiCN at higher potentials than 0.7 V is associated to catalyst support corrosion, i.e. oxygenated species formation.

The results obtained for TiC nanoparticles are similar to those obtained by Cowling and Hintermann^{18, 25}. They found that the electrochemical behavior of chemical vapour deposited TiC corresponds well with the Pourbaix diagram of Ti/TiO₂ in aqueous media and propose the following oxidation process:



Consequently, C and TiN supports do not corrode at lower potentials than 1 V, while TiC and TiCN produces oxygenated species. These species are the result of water dissociation on carbide based materials and therefore, adsorbed OH or H₂O may form on the catalyst support surface and presumably oxycarbides are formed. The oxidized support surface is not reduced during the backward scan (see Fig. 1) in addition to their insolubility in the electrolyte (with the exception of CO₂), as can be deduced by the absence of the anodic peak during the subsequent scans. As was described above, this behaviour suggests surface oxidation, which avoids further corrosion and keeps high conductivity (Fig. 1). The right panels of Fig. 2 show analogous infrared experiments but realized at supported Pt catalysts, in which similar results to those obtained at catalyst supports are achieved, i.e. Pt/C and Pt/TiN do not develop a change in their IR signals, while Pt/TiC and Pt/TiCN form CO₂ (2343 cm⁻¹) and adsorbed CO is also produced on Pt/TiC (bipolar band at ca. 2050 cm⁻¹).

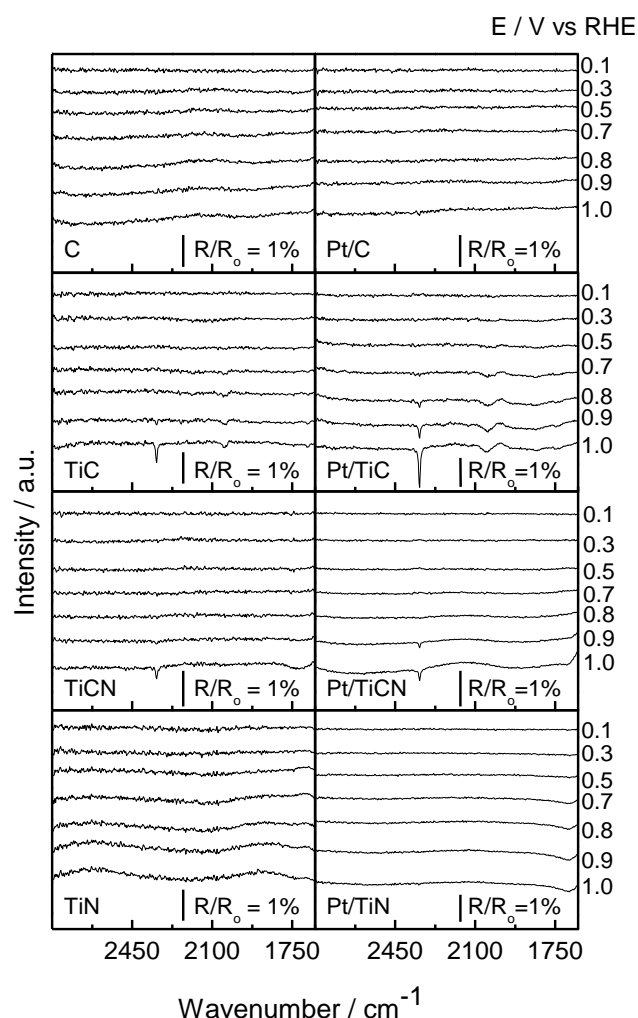


Fig. 2. In-situ FTIRS spectra of catalyst supports (left panels) and supported platinum catalysts (right panels) recorded in 0.5 M H₂SO₄. A reference spectrum, R₀, was recorded at 0.1 V and different sample spectra, R, were recorded increasing the potential by 0.1 V steps up to 1.0 V.

Main difference between catalysts and supports is the onset potential for CO and CO₂ formation, which is lower for Pt-based materials. These results agree with previous report of XPS experiments of same catalysts¹⁵, in which a shift towards lower binding energies of the 4f Pt peak was observed for titanium-based supported catalysts. The latter was associated to an electronic transfer from the support to the platinum nanoparticles that facilitates the surface oxidation of titanium-based supports. Therefore, Pt supported on TiC and TiCN promotes water dissociation, formation of oxygenated groups, and consequently surface oxidation.

In order to evaluate the role of the oxidized support surface in electrochemical reactions of fuel cell importance (CO and methanol electrooxidation), catalysts were activated using several potentiodynamic cycles between i) 0.05 and 0.9 V, and ii) 0.05 and 1.0 V. Upper potentials limits were chosen to produce different amount of oxygenated species, avoid platinum surface modifications and completely oxidize an adsorbed CO monolayer (CO stripping).

Fig. 3 shows the CO stripping (red line) and subsequent voltammograms (black line) performed at the four activated catalysts using the 2 activation procedures. Second voltammograms show the typical profiles of supported Pt catalysts, which change with the catalyst support but are independent of the upper potential limit. The latter indicates similar platinum surface modification with different activation treatments. Indeed, CO stripping on Pt/C and Pt/TiN develop equal onset and peak potential with both activation approaches, which indicate similar catalytic surface structure. However, the CO oxidation reaction is quite different at Pt/TiC and Pt/TiCN electrodes with different activation treatments.

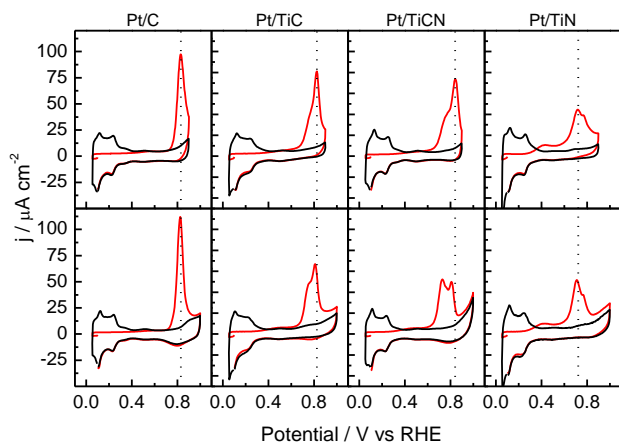


Fig. 3. CO stripping (red line) and subsequent voltammograms (black line) of Pt/C, Pt/TiC, Pt/TiCN and Pt/TiN recorded in 0.5 M H₂SO₄. E_{ad} = 0.1 V. Scan rate: 20 mV·s⁻¹. Upper panel: catalysts activated up to 0.9 V. Lower panel: catalysts activated up to 1.0 V.

A great enhancement towards the CO tolerance is achieved after applying the activation step at 1.0 V, in which an anodic charge increment at lower potentials is clear. The latter must be ascribed to different densities of oxygenated species on the oxidized support surface (e.g. OH_{ad}) as was established by

FTIRS experiments. Thus, catalyst activation up to 1.0 V produces high density of adsorbed oxygenated species on carbide-based support, and those close or in the Pt-support interface are especially active for the CO oxidation reaction.

Potentiodynamic electrooxidation of methanol on Pt/C and Pt/TiN show similar activity in both activation cases, whereas the performance of Pt/TiC and Pt/TiCN is greatly enhanced when are activated up to 1.0 V (Fig. 2S). This effect is much more visible by current transient experiments recorded at 0.55 V (Fig. 3S) and even more clear in Fig. 4, in which the current density recorded at 400s from Fig. 2S is depicted. The activity of commercial PtRu/C (30 wt.% Johnson Matthey) catalyst, which is activated up 0.8 V to avoid Ru dissolution, is also included for comparison purposes. Current densities for Pt/TiCN and Pt/TiC activated up to 1.0 V are 1.7 and 7 fold higher than those achieved with activation up to 0.9 V. On the other hand, a small decrease in activity for Pt/C material is observed, which is principally due to a higher kinetic of carbon corrosion at 1.0 V⁴. Pt/TiN loss the activity with the activation process up to 1.0 V due to surface oxygen passivation by cycling potential in acidic media¹⁷.

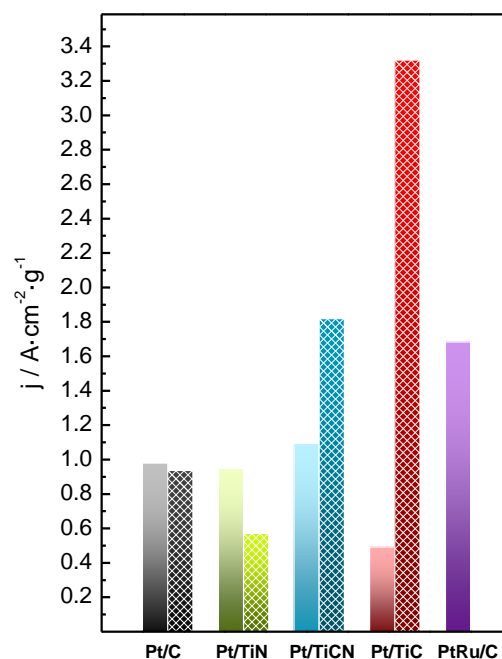


Fig. 4. Current density of Pt/C, Pt/TiC, Pt/TiCN, Pt/TiN and PtRu/C (Johnson Matthey) recorded at 10 min in 2M CH₃OH + 0.5 M H₂SO₄. E_r = 0.55 V. Solid color: catalysts activated up to 0.9 V. PtRu/C activated up to 0.8 V. Stripped color: catalysts activated up to 1.0 V.

It is remarkable that the current density obtained for Pt/TiC activated up to 1.0 V is 2-fold higher to that achieved with the commercial PtRu/C catalyst, which is accepted to be one of the best catalysts for methanol oxidation reaction²⁶. Moreover, noble metal loading at Pt/TiC is the half in weight that at the commercial material. Furthermore, it is well known that potential increase occurs during start-up or shutdown sequences, fuel starvation or reverse

current situations in low temperature fuel cells. These elevated potentials can result in an electrode potential larger than 1.0 V_{RHE}, which increases the reaction rates and causes a significant carbon corrosion and Ru dissolution, and consequently loss of fuel cell performance^{4, 27}. However, carbide-based catalysts have beneficial effect with this strong potential increment.

To explain all the results obtained, a synergetic effect of the oxygenated titanium species can be proposed by means of a bifunctional mechanism^{28, 29}. Oxygenated titanium species are able to supply oxygenated species (OH) at lower potentials than platinum, resulting in an enhancement of CO and methanol electrooxidation reactions. In this sense, the reaction seems to take place in the interface between platinum nanoparticles and TiC or TiCN supports, being an interparticular reaction³⁰, in which oxygenated species forms at the support while CO adsorbs on Pt and diffuses towards the interface and oxidizes. In addition to the bifunctional mechanism, quantum mechanical calculations suggested that TiO₂ increases the electron density on Pt and changes its chemisorptive properties for the reaction intermediates, decreasing the energy of the Pt-CO bonding and the activation energy for the CO_{ad} surface mobility³¹. In this context, previous XPS analysis demonstrated a charge transfer from Ti-based support to Pt nanoparticles¹⁵. Consequently, electronic and bifunctional effects are the responsible for the enhancement towards both reactions.

Conclusions

Ti-based materials were electrochemically modified to obtain a surface rich in oxygenated species. In this sense, it is well known that Ti oxides promote oxidation reaction in the gas phase, but the poor electric conductivity is not appropriate as electrode³². However, the electrical conductivity is not affected for the modified TiC and TiCN supports, as no electrical resistance or significant double layer modifications were observed. Pt/TiCN, and especially Pt/TiC, deliver great catalytic activity towards methanol oxidation reaction after being activated up to 1.0 V. The present work demonstrates that the electrochemically activated TiC and TiCN materials can be potential candidates for replacing carbon supports in conventional low temperature fuel cells.

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Notes and references

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