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Spectroelectrochemical Study of CO₂ Reduction on TiO₂ Electrodes in Acetonitrile.

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ABSTRACT

One of the main current goals of humanity is the CO₂ conversion into compounds with energetic value for facilitating both a diminution of the CO₂ atmospheric levels and the development of energy storage strategies. In many studies, TiO₂ has been successfully used as a photocatalyst for CO₂ reduction, but there is still a lack of understanding of its catalytic behavior. In this context, CO₂ reduction has been studied on nanoporous TiO₂ electrodes in acetonitrile media by means of (spectro)electrochemical methods (ATR-IR and UV-vis). Importantly, the onset of the cathodic Faradaic processes related with CO₂ reduction on TiO₂ electrodes is located at -0.81 V vs. SHE, which is less negative than that observed for metal electrodes under similar conditions. UV-vis spectroelectrochemical results indicate that the electrocatalytic behavior of TiO₂ is related to the generation of oxygen vacancies and Ti³⁺ sites at its surface, promoted by electrolytes with non-intercalating cations in agreement with recent results on WO₃ electrodes. ATR-IR spectroelectrochemical measurements allow for a monitoring of the TiO₂/solution interfacial state as reduction proceeds. Specifically, IR bands for carbon monoxide and carbonyl groups related with carbonate and oxalate are observed. Additionally, a chromatographic analysis shows CO and oxalate as main products. With controlled water addition (0.5 M), methanol and CO were found to be the main products. Based on these results, a mechanism for CO₂ reduction on TiO₂ electrodes is presented in which the regeneration of the TiO₂ surface by oxide electrodisolution/deposition is a critical step.

KEYWORDS: CO₂ reduction; TiO₂ electrodes; ATR-IR spectroelectrochemistry; UV-vis spectroelectrochemistry; electrochromism; electrocatalysis

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1. INTRODUCTION

The trend to increase the atmospheric carbon dioxide levels from 280 ppmv in preindustrial times to more than 400 ppmv today (a 43% increase, with half of it occurring since 1965), mainly because of the combustion of fossil fuels, is raising serious concerns about the ensuing rise in Earth's global temperature. This has motivated many research groups in the world to search for feasible ways to reduce CO₂ emissions and/or to reutilize it by conversion into other chemical compounds with energy value, leading to alternative energy storage strategies.^{1,2} Extensive reviews on catalytic reactions with the use of CO₂ as a feedstock source and on different approaches for CO₂ reduction have been published.^{3,4} Photocatalytic and homogeneous and heterogeneous electrocatalytic reduction processes seem to be effective ways for processing carbon dioxide.^{5,6} Many different products have been obtained depending on the specific reaction pathway and, obviously, on the number of transferred electrons, which determines the final oxidation state of the carbon atom.^{7,8} Factors such as the solvent (aqueous vs nonaqueous, protic vs aprotic, ionic liquids, supercritical CO₂), electrolyte, pH, temperature, concentration of CO₂, the choice of electrode material, its surface structure, electrode potential, among others can affect the reduction pathway.⁹⁻¹²

The carbon dioxide molecule is a very stable, linear molecule, with a closed-shell electronic configuration. The CO₂ reduction is an endergonic reaction, because of the low electron affinity of CO₂ (0.6 eV), related with the high energy level of its LUMO, and the increased repulsion between the free electron pairs in the oxygen atoms and the newly added electron in the carbon atom. Thus, the generation and stabilization of the CO₂^{•-} anion radical is key to achieving efficient CO₂ reduction. The CO₂ molecule can be activated over a solid-state catalyst, the role of which is to adsorb CO₂ molecules, facilitating electron transfer from the solid.¹³ In this respect, the formation of CO₂^{•-} over different metal oxides has been extensively reported.^{14–17}

In aqueous solution, different factors such as low solubility of CO₂ under ambient conditions, the existence of acid-base equilibria and hydrogen evolution occurring as a competitive process induce a loss of efficiency and selectivity. In this sense, non-aqueous aprotic solvents such as acetonitrile (ACN) have been used for studying CO₂ reduction. These solvents provide a wider electrochemical window to carry out reductions (down to -2.5 V vs Ag/Ag⁺ electrodes) due to the difficulty of breaking C-H bonds in ACN, in contrast with O-H bonds in water. Additionally, the solubility of CO₂ in ACN at 1 atm and room temperature is 280 mM, which is approximately 8 times that in water.^{18,19} The mechanism of CO₂ reduction on metal electrodes in nonaqueous solvents with low proton availability has been reported by Amatore and Saveant²⁰ and later by Gennaro et al.²¹ The CO₂^{•-} radical anion formed upon accepting the first electron is adsorbed, followed by oxalate formation (2 CO₂^{•-} → C₂O₄²⁻) or by CO and CO₃²⁻ formation (2 CO₂^{•-} → CO + CO₃²⁻). In all cases, the determining step of the process is the formation of the radical anion. It is important to note that different studies in aprotic solvents

show a strong dependence on water presence, even in trace amounts, inducing several changes in the pathway of the CO₂ reduction reaction.^{7,19}

An important tool for studying CO₂ reduction in ACN media has been infrared spectroelectrochemistry with either external (electrolyte thin layer)^{22–24} or internal²² (attenuated total reflection infrared, ATR-IR) configurations. Most of the reports have focused on Pt²⁵, Au and glassy carbon electrodes²⁶, and more recently on Cu, Pt, Pb, Au, Pd, Ag²⁷ and Sn²² electrodes. However, regarding the actual mechanism for CO₂ activation and reaction, there is no consensus about band assignment, particularly in the presence of water traces, and the pathway for CO₂ reduction is not fully understood yet. Such a pathway, has been reported to have a strong dependence on water content.^{27–29} For instance, with a low water content, IR bands related with the formation of CO have been reported at less negative potentials than those related to the formation of (bi)carbonates. There is thus a decoupling between (bi)carbonate and CO formation.

TiO₂ is one of the most extensively investigated photocatalyst for CO₂ reduction. Many authors have shown the appearance of different products of reduction as a proof of CO₂ photoreduction. However, isotope labeling studies have shown that ¹²C₁ products were generated even when ¹³CO₂ was used as a reactant.³⁰ This suggests that the interpretation of the photocatalytic results should be done with caution. On the other hand, the thermodynamic limitations of TiO₂ as a reductant should be kept in mind because the conduction band edge is located at a potential less negative (–0.5 V vs SHE at pH 7) than that required for the one-electron reduction of CO₂.

As in our previous work with WO₃,³¹ in order to explain the unusual electrochromic effect accompanying CO₂ reduction, the model of electrochromism with large cation-containing

electrolytes proposed by Hepel and coworkers³² is adopted, in which other processes such as lattice polarization, dissociative reduction and electrodisolution are taken into account.

EXPERIMENTAL SECTION

Electrodes for electrochemical studies were prepared on FTO substrates by a spin coating method with suspensions obtained by grinding 1 g of commercial TiO₂ powder (P25 Degussa) in 5 mL of distilled H₂O, followed by calcination at 450°C for 1 h in air, as previously reported.³³

All the electrochemical experiments were carried out under the same conditions in a conventional three-electrode glass cell. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAP) ($\geq 99.0\%$ from Sigma-Aldrich) in ACN (99.88% anhydrous from Scharlau, Multisolvant, HPLC grade), which was subjected to a drying procedure with a 3Å molecular sieve (rods from Sigma-Aldrich) following a reported procedure.³⁴ All the potentials in ACN solutions were measured against either a homemade Ag⁺/Ag reference electrode or an Ag/AgCl(s)/KCl(aq,sat) reference electrode. A Pt wire was used as a counter electrode in all the experiments. Unless otherwise stated, potentials are referred to the Ag⁺/Ag electrode. The measurements were performed with a computer-controlled micro-Autolab potentiostat. In all the experiments, the electrolyte was purged with either N₂ (Alphagaz 99.999%) or CO₂ (Air Liquid, 99.98%) for 30 min using an ACN trap to prevent solvent evaporation. Potentiostatic electrolysis experiments were carried out at -1.8 V for 3h in a closed and sealed glass cell with two compartments separated by a Nafion TM membrane NM-117 pretreated before use for the removal of organic impurities.³⁵

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3 In situ spectroelectrochemical UV/vis measurements were carried out by coupling an
4 electrochemical cell to an UV-vis spectrophotometer (UV-2401 PC Shimadzu). The cell
5 employed for the spectroelectrochemical measurements was equipped with a cuvette fitted at its
6 bottom and mounted on the support of the spectrophotometer sample chamber. To achieve
7 maximum contrast and high transparency, nanostructured TiO₂ were prepared in this case by
8 means of a chemical bath deposition method (see SI for details).
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18 ATR-IR experiments were carried out with a Nexus 8700 (Thermo Scientific) spectrometer
19 equipped with an MCT-A detector. In these experiments, a TiO₂ nanostructured layer was also
20 generated by chemical bath deposition on a gold-covered silicon prism beveled at 60 ° and used
21 as a working electrode (see SI for details). All the spectra were obtained with a resolution of 8
22 cm⁻¹. One hundred interferograms were collected at each potential using p-polarized light. The
23 resulting spectra, which are referred to the single beam spectrum collected at 0 V, are presented
24 in absorbance units. Thus, positive-going and negative-going bands correspond, respectively, to
25 a gain or loss of the responsible species in the sample spectrum with respect to the reference
26 spectrum.
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40 Finally, CO₂ reduction products were determined upon potentiostatic electrolysis at -1.8 V for
41 3h in 0.1 M TBAP/ACN and 0.1 M TBAP/ACN + 0.5 M H₂O solutions. A Hewlett Packard
42 5890 gas chromatograph equipped with a thermal conductivity detector (TCD) was employed to
43 measure gas samples produced from electrolysis. Methanol determination was carried out by
44 semiquantitative determination with an Agilent model 6890N gas chromatograph coupled to an
45 Agilent 5973 mass selective detector. Detailed information about additional analytic
46 determinations (ion chromatography, ICP-MS) are presented in the SI.
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RESULTS

3.1 Electrode characterization

Figure 1. (a) FE-SEM micrograph for an FTO/TiO₂ electrode. (b) Cyclic voltammograms for a TiO₂ electrode in aqueous 0.1 M HClO₄, purged with N₂. Scan rate: 50 mV s⁻¹.

Figure 1a shows a FE-SEM micrograph for a TiO₂ electrode, which shows nanoparticles with an average diameter of 20 nm, well distributed over the FTO substrate. Such a nanoparticulate morphology is expected when using slurries prepared from commercial powders. The electrode surface area of the thin film electrodes was assessed by using CV measurements in aqueous 0.1 M HClO₄ purged with N₂ (Figure 1b). The electrochemical response is characterized by a reversible charge accumulation region. This electron accumulation is accompanied by adsorption/insertion of protons for charge compensation and it is limited to the TiO₂ external layer (interfacial region), that is, to the TiO₂ region in close vicinity with the electrolyte.

Importantly, the charge integrated under the CV in the accumulation region has been shown to be proportional to the interfacial area.^{33,36,37}

3.2 Electrochemical studies

Figure 2. Electrochemical measurements for FTO/TiO₂ electrodes in 0.1 M TBAP/ACN; a) Cyclic voltammograms at 50 mV s⁻¹. Inset: Enlarged CV profile for an N₂-purged solution; b) Chronoamperograms at an applied potential of -1.7 V. Black and red curves correspond to the electrolyte purged with either N₂ or CO₂, respectively.

In Figure 2, both voltammetric and chronoamperometric profiles in the presence and absence of CO₂ are shown. First, the potential window for CO₂ reduction was determined by recording the corresponding CV in the nitrogen-purged supporting electrolyte. As shown in Figure 2a, a voltammetric signal appears at -1.3 V for the N₂-purged solution, corresponding to the beginning of the accumulation region and leading to reduction of Ti⁴⁺ to Ti³⁺ at the TiO₂ surface (filling of surface states) (the inset in Figure 2a shows a CV for an N₂-purged solution). In this respect, one should consider that tetrabutylammonium cations (TBA⁺) are more

voluminous than the cavity available in TiO_2 for intercalation. This fact is important because the formation of oxygen vacancies is favored when intercalation is not possible. This would entail a loss of mass, due to the electrodisolution of TiO_2 .³⁸

According to Eq. 1, the partial electroreduction of titanium lattice atoms from Ti^{4+} to Ti^{3+} induces the formation of oxygen deficient titanium dioxide (TiO_{2-x}) and probably the electrodisolution of TiO_3^{2-} or a similar titanium-containing species.

In CO_2 -purged solutions, an increase in the cathodic currents associated with CO_2 reduction, with an onset at -1.3 V vs Ag/Ag^+ (-0.81 V vs SHE),³⁹ is observed. Such an onset is close to the beginning of the TiO_2 accumulation region, which is, in turn, related to the location of the TiO_2 conduction band edge. In this way, the accumulation of charge in surface states through the formation of Ti^{3+} species, which act as electron-rich centers, plays in favor of CO_2 reduction. Interestingly, there is also an increase in the capacitive currents in the accumulation region, even at potentials for which CO_2 reduction does not proceed. This suggests important changes in the electrode state that may be associated with an increase in the surface density of Ti^{3+} species due to an enhancement of the oxygen vacancy generation. In addition, in Fig. 2b, the current versus time profiles at -1.7 V show an increase of the cathodic current densities from $-0.14\text{ mA}\cdot\text{cm}^{-2}$ in the N_2 -purged solution to values ranging from -0.27 to $-0.42\text{ mA}\cdot\text{cm}^{-2}$ in the CO_2 -purged solution, confirming that the increase in the cathodic currents in Fig. 2a does not correspond solely to capacitive processes. It is also apparent that the cathodic current grows over time.

Figure 3. Voltammograms for FTO/TiO₂ electrodes in a CO₂-purged 0.1 M TBAP/ACN solution; a) black and red curves correspond to solutions with and without water addition (0.5 M). Scan rate: 50 mV s⁻¹; b) LSV with addition of different amounts of water. Scan rate: 5 mV s⁻¹. The inset in panel (a) shows an enlarged portion of the CV in the water-containing solution.

In aprotic solvents, traces of water not only change the CO₂ reduction reaction path,^{19,28} but also may increase proton concentration, enhancing the intercalation of protons in the TiO₂ lattice. Figure 3a shows CV profiles for CO₂-purged solutions with both dry ACN and upon the addition of 0.5 M of water. In the presence of water, the onset of the cathodic currents shifts to less negative potentials, which could be associated to changes in the local pH because of the existence of an acid-base equilibrium between CO₂ and water. In addition, in the positive-going scan, the peak related with the oxidation of Ti(III) to Ti(IV) at around -1.5 V is clearly diminished. This reflects the stabilization of Ti³⁺ species, probably through the intercalation of protons in the TiO₂ lattice. Figure 3b presents linear sweep voltammograms for different water concentrations at a scan rate of 5 mV s⁻¹. Both an increase in the cathodic currents and a shift of their onset toward less negative potentials are observed. This supports the notion of a beneficial

effect of water on CO₂ reduction. Of course, the increase of the cathodic currents could be attributed to water reduction, but in the CV profiles, a new small peak at -0.25 V in the positive-going scan also appears, probably related with the oxidation of a CO₂ reduction product (see inset in Fig. 3a). Analogously, chronoamperometric curves confirm the substantial increase of the cathodic current upon the addition of water (see Fig. S1 in the Supporting Information, SI). Recent results from our laboratory on CO₂ reduction at WO₃ electrodes have shown that the presence of water change the reduction pathway to CO and formate generation, in contrast to the case of dry ACN, in which CO and carbonate were shown to be the main product.³¹

Figure 4. Cyclic voltammograms for an FTO/TiO₂ electrode in 0.1 M LiClO₄/ACN. Black and red curves correspond to the electrolyte purged with N₂ and CO₂, respectively. Scan rate: 50 mV/s

Figure 4 shows the voltammetric responses for a TiO₂ electrode in contact with 0.1 M LiClO₄ in ACN purged with either N₂ or CO₂. No Faradaic cathodic currents associated with CO₂ reduction are observed. This is a general trend reported for other electrode materials such as boron-doped diamond.¹⁰ These observations have been explained on the basis of Li⁺ inhibiting CO₂ reduction by adsorption at the working electrode and formation of hydrophobic layers.^{40,41} In our case, Li⁺ would not only block the adsorption of CO₂, precluding the activation of the molecule, but it would also facilitate the stabilization of Ti³⁺ sites by intercalation into the TiO₂ lattice, promoting titanium bronze formation instead of oxygen vacancy formation.

3.3 UV/vis spectroelectrochemical study

To follow the density of Ti³⁺ centers in the TiO₂ thin film electrode, in situ UV/vis spectroelectrochemical experiments were carried out. The electrode was first polarized at different potentials between -1.0 and -1.8 V for 300s, followed by 600 s at open circuit (OC). An interesting observation is the appearance of an intense blue coloration upon negative polarization in a CO₂-purged 0.1 M TBAP/ACN working solution. Figure S2 in the Supporting Information (SI) shows the absorption spectra in the visible for an FTO/TiO₂ electrode in a CO₂-purged solution at -0.3 V and -1.8 V and at -1.8 V in an N₂-purged solution. A relatively intense and stable broad band is observed at 700 nm due to electrons localized in surface states (reduction of Ti⁴⁺ to Ti³⁺ in surface states), which is not evident for the N₂-purged solution. Based on these observations, spectroelectrochemical experiments were performed at this wavelength.

Table TS1 in the SI gathers the absorbance values obtained after applying different potentials for 300 s for both N₂ and CO₂-purged solutions. Note that in all cases the absorbance

values in CO₂-purged solutions are significantly larger than in N₂-purged solutions. An enhancement of the electrochromic effect in CO₂-purged solutions was seemingly observed for Ramesha et al on TiO₂ electrodes under conditions comparable to those employed here.⁴² However, these authors only showed normalized values for absorbance and thus the significant difference existing between N₂ and CO₂-purged solutions was not dealt with. Electrocatalytic activity was attributed to the reduction of Ti⁴⁺ sites to Ti³⁺ according to:

However, the unusual electrochromic effect observed in CO₂-purged ACN solutions is not clarified through Eq. 2.

Figure 5. a-e) Absorbance at 700 nm as a function of time for an FTO/TiO₂ electrode in 0.1 M TBAP/ACN solution; the solution was purged with CO₂ for 30 min prior to the measurements. The indicated potentials were applied in the time window from 0 to 300 s.

Figure 5 shows spectroelectrochemical UV/vis experiments performed in CO₂-purged solutions. Not unexpectedly, as the applied potential becomes more negative, the Ti³⁺ density in TiO₂ increases and so do the absorbance values.

Figure 6. a) Absorbance at 680 nm vs time for FTO/TiO₂ electrodes in 0.1 M TBAP/ACN solutions purged for 30 min with either N₂ (red) or CO₂ (black). First, a potential of -1.8 V was applied for 300 s. Then, open circuit conditions were maintained for 600 s. Inset: normalized absorbance as a function of time. b) Logarithm of absorbance versus time at open circuit in CO₂-purged solution. The red line shows the linear regression for a pseudo-first order kinetics fit.

As observed in Figure 6a, the absorbance builds up after application of a potential of -1.8 V and subsequently decays at OC in the presence of either N₂ or CO₂. However, the maximum absorbance attained is 4 times larger in the presence of CO₂ and the bleaching kinetics is faster, revealing the ability of CO₂ to scavenge electrons accumulated in the oxide. In fact, at OC, the electrons accumulated in TiO₂ are transferred to CO₂ molecules and an exponential decay of

absorbance as a function of time is observed. In figure 6b, the logarithm of absorbance versus time for the OC period is plotted. A linear tendency indicates a pseudo-first order kinetics for Ti^{3+} consumption under CO_2 -purged solution with a constant equal to 0.0078 s^{-1} . This spectroelectrochemical behavior agrees with the results obtained by means of cyclic voltammetry, in which an increase in capacitance is evident when the electrolyte is saturated with CO_2 , even at potentials at which CO_2 reduction does not take place.

3.4 ATR-IR spectroelectrochemical study

Figure 7. ATR-IR spectra for TiO_2 thin film electrodes in an Ar-purged 0.1 M TBAP/ACN solution at different applied potentials; reference potential is 0.0 V vs Ag^+/Ag . Consecutive spectra are shifted upwards by a constant value for the sake of comparison.

The vibrational properties of interfacial species can be addressed by in situ ATR-IR spectroelectrochemical measurements. Figure 7 shows ATR-IR spectra from 3100 to 1500 cm^{-1} in an Ar-purged solution for TiO_2 (P25) electrodes in 0.1 M TBAP/ACN at different applied potentials from -0.2 V to -1.8 V (reference spectrum taken at 0.0 V). In these spectra, several bands related with the supporting electrolyte can be identified. A 2963/ 2875 cm^{-1} contribution from the CH asymmetric and symmetric stretching modes from CH_3 in TBA^+ and ACN can be distinguished.^{43,44} These bands consistently increase in intensity as more negative potentials are applied, reflecting the accumulation of TBA^+ cations by electrosorption. In addition, the spectra show a bipolar band centered at 2245 cm^{-1} , which is assigned to the $\nu(\text{CN})$ of adsorbed ACN.⁴⁴ The shape of this feature reflects the sensitivity of the corresponding band frequency to the electrode potential, and therefore it could be associated with adsorbed ACN. It has been proposed that chemisorbed ACN can present two different states, a donative state, bound through the free electron pair of the nitrogen atom, or an associative state, in which both carbon and nitrogen atoms are bound to the surface.⁴⁵ The negative contribution and the increase of band intensity with decreasing potentials could be tentatively related with a potential-dependent change of orientation of the adsorbed ACN molecule.

In addition, two bands appear at 2038 and 2090 cm^{-1} , whose intensities increase as potential decreases. It is known that acetonitrile may behave as a very weak Brønsted acid, which can interact with surface base sites in transition metal oxides, generating the adsorbed carbanion CH_2CN^- , which presents a $\nu(\text{CN})$ vibration at wavenumbers 150-200 cm^{-1} below that of the free molecule in liquid ACN (2265 cm^{-1})⁴⁶. In the case of TiO_2 in gas phase, the $\nu(\text{CN})$ band has been reported at 2073 cm^{-1} ⁴⁷. On the other hand, a spectroelectrochemical study on Pt

electrodes has provided evidence on the formation of the acetonitrile carbanion in cathodic reactions in acetonitrile/tetra-n-butylammonium tetrafluoroborate electrolytes⁴⁸. Based on these precedents, we assign the bands at 2038 and 2090 cm⁻¹ to the generation of adsorbed acetonitrile anions according to:

A reductive and dissociative adsorption of acetonitrile would occur, with adsorption/intercalation of the released proton. It is now understandable why the intensity of the band increases as the potential becomes more negative.

Figure 8a shows ATR-IR spectra between 2300 and 1150 cm⁻¹ for a TiO₂ electrode in contact with a CO₂-purged solution at different applied potentials (from -0.2 to -1.8 V). As the potential decreases, there is a shift of the baseline toward higher absorbance values at lower wavenumbers, being thus this effect most pronounced when the electrode is biased at -1.8 V. This behavior has been previously observed in (photo)electrochemical studies with TiO₂ thin films and is related to the accumulation of electrons in the oxide associated with the upward displacement of the Fermi level as potentials decrease.⁴⁹ Interestingly, the baseline shift observed in the presence of CO₂ for wavenumbers below ca. 1600 cm⁻¹ is minor in its absence (not shown in Figure 7). From a comparison of Figs. 2a and 8a, it is apparent that the enhancement in the capacitive voltammetric currents agrees well with an increase in the baseline shift.

Figure 8. **a)** ATR-IR spectra for TiO₂ thin film electrodes in CO₂-purged 0.1 M TBAP/ACN solutions at different potentials; reference potential is 0.0 V (vs Ag/Ag⁺); **b)** Enlarged ATR-IR spectra in the carboxyl region at times 0 and 20 min upon application of a potential of -1.80 V.

Fig. 8a shows a band at 1920 cm^{-1} probably related with the stretching vibration of adsorbed CO. This band appears at potentials more negative than -1.2 V in agreement with the onset potential for the appearance of Faradaic currents related with CO_2 reduction. FT-IR studies on gaseous CO adsorption on TiO_2 have shown bands at $2050\text{--}2110\text{ cm}^{-1}$ related with CO bound to Ti^{4+} .⁵⁰ However, the band at 1920 cm^{-1} related with the adsorption of CO in the electrochemical environment has a wavenumber lower than expected; revealing that CO bound to TiO_2 at negative applied potentials is likely affected by the presence of a high density of oxygen vacancies and Ti^{3+} sites. The C-O stretching frequency for CO adsorbed at Ti^{3+} sites on TiO_2 is expected to be lower than that of gaseous CO, due to an important electron donation from occupied d orbitals of the metal to empty O2p π -antibonding orbitals in the CO molecule⁵¹. Admittedly, and as far as we know, such a low value for the adsorbed CO stretching frequency has not been reported in published experimental studies. However, published theoretical results support our tentative assignment⁵². In this work, the authors calculate that in defective anatase surface, the $\nu(\text{CO})$ frequency would significantly redshift down to a value of 1936 cm^{-1} , particularly for adsorption on a Ti^{3+} site associated to a bridging oxygen vacancy. The electrochemical environment would be particularly prone to showing this adsorption mode as the negative applied potential and the presence of CO_2 would extraordinarily favor the attainment of a high density of oxygen vacancies. It is worth noting that the development of the CO band is paralleled by the observation of bands at ca. 2240 cm^{-1} (see Figure 8a). In contrast with the bipolar features in Figure 7, suggesting a potential-dependent reorientation of adsorbed CAN molecules (vide supra), the bands at ca. 2240 cm^{-1} in the CO_2 -containing ACN solution are negative, thus indicating the displacement of adsorbed CAN upon CO adsorption.

Figure 8b allows the comparison, in the spectral carboxyl region between 2100 and 1680 cm^{-1} , for ATR-IR spectra acquired in CO_2 -purged solutions immediately after applying a potential of -1.80 V and after 20 min of polarization. Both the band assigned to adsorbed CO at 1920 cm^{-1} and that at 1754 cm^{-1} associated with oxalic acid formation (due to residual water in solution), develop over time. In addition, a small band at 1705 cm^{-1} is clearly distinguished, in particular for a time of 20 min, and it is probably related with carbonate formation. Carbonate anions have an D_{3h} symmetry and are expected to have three active modes in IR; however, adsorbed carbonate can be associated to either a monodentate or a bidentate configuration, inducing a change in the symmetry and the vibrational modes of the carbonate species. In a recent study of CO_2 reduction on copper electrodes in ACN, tetraethylammonium carbonate, formate and oxalate salts were used as patrons for IR band assignment in the carbonyl group region. The C=O vibration exhibits two distinguishable bands at 1681 and 1641 cm^{-1} for (bi)carbonate species, but only one at 1586 and 1569 cm^{-1} for formate and oxalate, respectively.²⁷ In our ATR-IR spectra, a broad band at 1570 is observed. On this basis, we could tentatively assign this broad band at 1570 cm^{-1} to the C=O vibration of carbonyl groups in oxalate.

On the other hand, the fact that the band related with carbonate anion appears later than the CO band, can be related with the decoupling of CO and carbonate formation because of the presence of residual water in solution²⁷ or through TiO_2 regeneration, according to the model described below. This behavior is in contrast with the classic mechanism proposed for metal electrodes in aprotic solvents, in which the formation of CO and carbonate happen simultaneously.²⁰

3.5 Determination of CO_2 reduction products.

CO₂ reduction products were determined upon potentiostatic electrolysis at -1.8 V for 3h in both 0.1 M TBAP/ACN and 0.1 M TBAP/ACN + 0.5 M H₂O solutions. Figures S3 and S4 show potentiostatic electrolysis I-t and Q-t profiles for both dry ACN and ACN + 0.5 M H₂O solutions. In table 1, a summary of the products determined with different analytical techniques is presented.

Table 1. Summary of the CO₂ reduction products for potentiostatic electrolysis at -1.8V in 0.1 M TBAP/ACN and 0.1 M TBAP + 0.5 M H₂O/ACN solutions. N.D.: not detected.

Product	Faradaic efficiency		Technique
	dry acetonitrile	acetonitrile + 0.5 M H ₂ O	
Carbon monoxide	48%	12%	GC -TCD
Oxalate	12%	N.D.	IC
Methanol	N.D.	60%	GC-MS
Carbonate	N.D.	N.D.	ATR IR
Titanium	0.19%	N.D.	ICP-MS

Figure S5 in the SI shows the GC-TCD chromatograms for the injection of a CO patron and a 250 µL sample from the headspace of the working electrode compartment. Air and CO₂ patrons were injected and no signal were detected at the retention time of the CO patron. Figure S6 shows ion chromatograms (IC) for the injection of oxalate patrons as well as for the working solution after 1.5h of electrolysis. Figure S7 shows GC-MS chromatograms for the injection of both a methanol patron and sample from the catholyte solution after 75 min of electrolysis. ICP-MS results confirm the presence of titanium in the catholyte. Additional quantitative information is shown in tables TS2 and TS3 in the SI.

4. DISCUSSION

Based on the results presented above, a model for CO₂ reduction on TiO₂ electrodes with large-cation electrolytes has been developed. An analogous model was previously proposed for WO₃ electrodes in acetonitrile solutions, providing an explanation for the direct relationship existing between an enhanced electrochromic effect and CO₂ reduction.³¹ In this section, after some electrochemical considerations, a model for CO₂ reduction on TiO₂ electrodes is first presented, offering an explanation for both the catalytic behavior for CO₂ reduction and the concomitant enhanced electrochromic effect observed. Next, the UV-vis absorbance decay at open circuit potential is analyzed in detail and shown to include kinetic information for CO₂ reduction on TiO₂ electrodes. Finally, a brief discussion on the CO₂ reduction products in both dry and humid ACN is presented.

Faradaic currents appear with an onset potential of -1.3 V vs. Ag⁺/Ag (which corresponds to a potential value of -0.81 V vs SHE (see SI)) for CO₂ reduction on TiO₂ electrodes in dry ACN solutions. This reflects a decrease in the overpotential expected for the first electron transfer in CO₂ reduction, which requires, in principle, a potential more negative than -1.97 V (vs. SHE) in aprotic solvents (couple CO₂/CO₂^{•-}).⁵³ This decrease has been related to the activation of the CO₂ molecule by adsorption on TiO₂ with the formation of charged species (CO₂^{δ-}). The interaction of the CO₂ molecule with the surface induces several changes due to a bending of the linear geometry of the CO₂ molecule. Specifically, a diminution in the O-C-O bond angle, leads to a decrease of the CO₂ LUMO level through electron density donation. In particular, a decrease of 0.14 eV in the energy of the LUMO level with a change in the O-C-O angle from 180° to 170° has been reported.^{13,54}

The reduction of Ti^{4+} to Ti^{3+} sites is facilitated by the presence of CO_2 in solution. The enhancement of the capacitive currents in the CV profiles indicates an increase in the density of surface states located below the conduction band of TiO_2 . This fact can be rationalized by the formation of oxygen vacancies caused by the application of increasingly negative potentials. In this way, the chemisorption of CO_2 could not only induce the activation of the CO_2 molecule, but also the stabilization of electron-rich Ti^{3+} centers. Sorescu et al. found that oxygen vacancies considerably influence the adsorption properties of CO_2 on rutile (110) and anatase (101) surfaces, and they anticipated that these defects play an important role in the complex surface chemistry of the CO_2 reduction catalysis.⁵⁵ Consistently, studies on CO_2 reduction show that the activation energy for CO_2 desorption from Ti^{3+} sites is higher than that from Ti^{4+} sites.⁵⁶ This suggests that CO_2 is more strongly bound to Ti^{3+} than Ti^{4+} sites. In addition, it has been shown that reduced TiO_2 consistently has a higher catalytic activity for the reduction of CO_2 , as the presence of point defects provides a higher density of active sites.⁵⁷ In scheme 1, the adsorption of CO_2 on TiO_2 electrodes with i) a downshift of the LUMO level, ii) electron transfer from TiO_2 to the CO_2 molecule, and iii) the subsequent enhancement of the density of surface states are sketched.

Scheme 1. Schematic representation of the different processes associated with the adsorption of CO₂ molecules on TiO₂ and the application of a negative potential.

Based on the previously published dissociative model for the electroreduction of CO₂,³¹ one may explain the enhancement of the capacitive currents observed in the CV profiles (even at potentials at which CO₂ reduction does not proceed). In this way, CO₂ reduction begins with the electrosorption of CO₂ over TiO₂ according to:

In Eq. 4, the coefficient y is expected to be significantly larger than coefficient x in Eq. 1. It is worth noting that the electrosorption of the CO₂ molecule with concomitant partial oxide electrodisolution as TiO_3^{2-} is thought to be restricted to the interfacial region, without significant structural damage in the subsurface region of the TiO₂ film.³² Thus, the formation of

the adsorbate $\text{TiO}_{2-y}(\text{CO}_2)_y$ induces several modifications in the interface, which are reflected in the development of capacitive currents promoting the generation of non-stoichiometric TiO_{2-y} , together with the formation of TiO_3^{2-} species. This behavior would point to a synergistic effect between the CO_2 molecule and the surface: electrosorption triggers the activation of the CO_2 molecule together with the promotion of oxygen vacancies.

When the potential decreases below -1.3 V (-0.81 V vs SHE), the resulting high concentration of localized electrons (as Ti^{3+} sites) at the surface region plays in favor of electron transfer to adsorbed CO_2 molecules. Thus, the appearance of Faradaic currents related with the products of CO_2 reduction is observed. ATR-IR spectra show that the development of a broad band related with CO generation coincides with the onset potential of the Faradaic currents. Interestingly, the presence of a band at 1925 cm^{-1} assigned to the stretching vibration of CO adsorbed in a bridge configuration provides evidence for the generation of the adsorbed species $\text{TiO}_{2-y}(\text{CO})_y$. This process is accompanied by a depletion of ACN molecules in the interface, suggesting the substitution of ACN molecules by the CO_2 reduction products. The processes of CO adsorbate formation, CO generation and electrodisolution of TiO_3^{2-} would be described according to:

The global equation for CO_2 reduction (concomitant with electrodisolution of TiO_2) would result from the sum of Eqs. 4 to 6:

The partial electroreduction of TiO_2 in CO_2 -purged solutions induces several changes: i) a shift of the Fermi level, which approaches the conduction band edge, ii) an increase in the UV/vis absorbance values as shown by the spectroelectrochemical measurements and, iii) a displacement of the baseline in the ATR-IR spectroelectrochemical measurements. The partial electroreduction of TiO_2 implies that it suffers a corrosion (through TiO_3^{2-} formation) tantamount to CO_2 reduction (or CO generation) according to Eq. 7. The results shown in table TS4 in the SI for ICP-MS analysis confirm the presence of titanium in the working solution after electrolysis, supporting partial electrodisolution of the TiO_2 electrode. However, a concentration of titanium around 3 orders of magnitude lower than that expected based on Eq. (7) was detected. Importantly, the concentration of titanium in solution does not increase after 3 h of electrolysis. This suggests that TiO_2 is not a reactant and that TiO_3^{2-} species are recovered to TiO_2 in the presence of CO_2 in a process accompanied by carbonate formation according to:

This mechanism leads to a gradual renewal of the surface via electrodisolution/deposition of TiO_2 . An evaluation of the specific interfacial area of the TiO_2 electrodes using CV measurements in aqueous 0.1M HClO_4 solutions before and after the electrolysis of the CO_2 -purged solution was also carried out (Fig S8). Clearly, after electrolysis at -1.8 V for 3 h, the accumulation region is larger, specifically by a 46%, confirming an increase in interfacial electroactive area. The formation of TiO_3^{2-} from TiO_2 in the presence of CO_2 has been identified in molten carbonate fuel cells by means of XPS measurements.⁵⁸

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3 It is also worth noting that this model for the electrocatalytic reduction of CO₂ helps to
4 rationalize the growth of the reduction current over time (see Fig. 2b). It is likely that, as
5 electrolysis progresses, the density of surface oxygen vacancies increases. Taking into account
6 that these are considered to be the active sites for CO₂ reduction, this would lead to the
7 monotonous enhancement of the CO₂ reduction process.
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15 The model presented above rationalizes the electrocatalytic behavior of the TiO₂
16 electrodes. In addition, an enhanced electrochromic effect (higher absorbance values) is observed
17 in CO₂-purged solutions, which can be interpreted as a result of an increase in the density of Ti³⁺
18 centers and oxygen vacancies. However, when the electrode is maintained at open circuit the
19 absorbance decays in CO₂-purged solutions at a faster rate than in N₂-purged solutions (Fig. 6).
20 This confirms that the CO₂ molecule can act as an electron scavenger in nonstoichiometric TiO₂.
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41 It is worth noting that the exothermic dissociation of CO₂ with CO formation has been
42 observed by Lee et al. using scanning tunneling microscopy (STM). They have shown that
43 electron injection from the STM tip into adsorbed CO₂ induces the dissociation of CO₂ with CO
44 formation.⁵⁹ Importantly, the oxygen vacancy defect on TiO₂ anatase is healed by the oxygen
45 atom released during the dissociation process.
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53 A pseudo-first order reaction was determined for the decay of the species responsible for
54 coloration (Ti³⁺) when the FTO/TiO₂ electrode is first biased at -1.8 V and then maintained at
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OC (see Figure 6). In Fig. S9 in the SI, the logarithm of the absorbance is plotted against time for different initial potentials and the same polarization time. A linear behavior, corresponding to a pseudo-first order reaction, is consistently observed. Table 2 gathers the corresponding kinetic constant values.

Table 2. Rate constant values for the pseudo-first order reaction of consumption of TiO_{2-y} ; the corresponding plots are shown in Fig. S9.

Applied potential	Constant rate /s ⁻¹
-1.8 V	0.0078
-1.6 V	0.0057
-1.4 V	0.0045
-1.2 V	0.0043
-1.0 V	0.0041

The diminution of the constant values as applied potential becomes less negative indicates that there is a progressive decrease in trapped electron reactivity. This is expected as the electrons accumulated as Ti^{3+} species have different effective electrode potentials (positive to the applied potential). Obviously, only electrons with negative enough potentials can reduce CO_2 .

On the other hand, under controlled water addition, both methanol and CO are detected as the main products with Faradaic efficiencies close to 60% and 17% respectively. In the presence of water as a proton source, C-H coupling is achieved, and the reduction reaction proceeds via proton-electron coupled transfers.⁶⁰ The formation of thermodynamically favored C_1 products is feasible. Scheme 2 shows a representation of the TiO_2 conduction band position, the onset potential of the Faradaic currents obtained in this study under controlled water addition (-0.50 V

vs SHE) and the potentials versus SHE at pH 7 for some relevant redox couples. Reduction to methanol is thermodynamically feasible although the existence of a relative small overvoltage (understood as the difference in potential between those corresponding to the CB edge of TiO_2 and the $\text{CO}_2/\text{CH}_3\text{OH}$ redox couple, ~ 0.12 V in the present case) could hinder to some extent the process.

Scheme 2. A sketch showing the conduction band position for TiO_2 (vs SHE) and the onset of the Faradaic currents together with the potentials for some relevant redox couples.

5. CONCLUSIONS

The role of oxygen vacancies and Ti^{3+} species in the CO_2 reduction reaction on TiO_2 is key for reaching a fundamental understanding of the electrocatalytic activity of TiO_2 electrodes. The adsorption of the CO_2 molecule on TiO_2 not only seems to induce its activation, probably via adduct formation, but it also promotes the oxygen vacancy generation with the subsequent formation of electroreduced TiO_{2-y} species. This increase in the density of TiO_{2-y} species causes the development of capacitive currents, an enhancement in absorbance (electrochromic effect) and a displacement in the IR spectrum baseline at sufficiently negative applied potentials. At open circuit, the decay of TiO_{2-y} species, followed by UV/vis spectroelectrochemical measurements, shows that the corresponding rate constant is potential-dependent. Faradaic currents associated with CO_2 reduction appear with an onset at -0.81 V (vs SHE), being CO and oxalate the main detected products in dry acetonitrile. The pathway of CO formation has been related with a model for large-cation containing electrolytes that includes lattice polarization and partial electrodisolution of TiO_2 . Finally, an enhancement of CO_2 reduction has been observed when water is added as witnessed by a significant shift of the onset potential. The analysis of CO_2 reduction products shows methanol as the main product in such a case.

The fact that the mechanism proposed initially for WO_3 electrodes can be extended to TiO_2 electrodes suggests that it could be of general validity for transition metal oxide electrodes. Studies along these lines are underway in our laboratory.

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8. SUPPORTING INFORMATION

Additional experimental details. Conversion of measured potentials to the SHE scale. Supplementary figures: additional chronoamperometric and voltammetric curves, additional UV-vis spectra and absorbance vs. time curves, and different chromatograms. Supplementary tables: absorbance values and amounts of different species after electrolysis.

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