

Test of vanadium pentoxide as anode for the electrooxidation of toluene

A theoretical approach of the electrode process

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Abstract

Vanadium pentoxide (V_2O_5) films were prepared by electrochemical and thermal decomposition of vanadyl sulphate on titanium dioxide covered titanium plates and glassy carbon discs. The prepared material by thermal decomposition showed high surface area and good physical stability; while the electrodeposited films, although being homogeneous, showed poor adhesion. The V_2O_5 electrodes were chemically and electrochemically stable in aqueous (1 M H_2SO_4 + 1 M NaOH, pH 3) and organic (0.1 M But_4NPF_6 + CH_3CN) solutions. In both cases, a well defined electrochemical response was observed. At the experimental conditions, the prepared materials were not active for the electrooxidation of toluene. The theoretical modeling suggests that the lack of activity is due to the weak interaction between toluene and the V_2O_5 surface.

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1. Introduction

The electrocatalytic activity of some metal oxides has been evaluated by using the oxidation of organic compounds in aqueous solutions as a test reaction [1–3]. How this reaction occurs is still a topic of discussion, but two general mechanisms have been accepted [4]: (i) preadsorption of the organic compound and its reaction with generated OH radical during water discharge, and (ii) reaction of the organic substance in solution with generated OH radical during water discharge. The relevance of this reaction is mainly based on its use for the treatment of industrial wastewater streams [5].

Metal oxides and their mixtures have been extensively used as anodes in direct methanol fuel cell (DMFC) [6], solid

oxide fuel cells (SOFC), in which liquid and gaseous hydrocarbons are utilized as fuels [7,8], and other applications.

Titanium dioxide (TiO_2) has been employed as a support due to its high surface area and stability [9]; furthermore, it shows activity for some electrochemical and non-electrochemical reactions: oxygen reduction [10] and photocatalytic and photoelectrocatalytic oxidation of organic molecules [11,12]. On the other side, it has been developed important applications of vanadium pentoxide (V_2O_5) as principal component for cathodes in lithium insertion batteries [13,14]. Also it is a well-known catalyst for the hydrocarbon oxidation at high temperatures, due to its high oxygen lability [15,16].

In this work, V_2O_5 films were prepared by electrochemical and thermal decomposition techniques on titanium dioxide covered titanium plates and glassy carbon discs. Exploring the electrochemical properties of V_2O_5 , in aqueous and organic electrolytes, its activity for the electrooxidation of toluene at ambient temperature was evaluated. The theoretical modeling reinforced the experimental results,

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since the adsorption interactions between molecular orbitals of the aromatic compound and the valence and conduction bands of the metal oxides were also quantified.

2. Experimental and computational method

2.1. Cells and electrodes

The electrochemical deposition of vanadium pentoxide was carried out on glassy carbon (GC) discs (Carbone Lorraine, geometric area: 0.78 cm^2) and titanium dioxide covered titanium plates (TiO_2/Ti) in a two compartment cell. The counter electrode (platinum gauze Aldrich, 99.99%) was separated by a glass frit from the working electrode compartment. A Ag/AgCl (KCl saturated) reference electrode was utilized for all the experiments.

For the electrochemical response of the films and the oxidation of toluene, a two compartment cell was employed. The reference electrode was separated from the working electrode compartment by a Luggin capillary. For all these tests three working electrodes were used: $\text{V}_2\text{O}_5/\text{GC}$ (geometric area: 0.78 cm^2), bare GC discs (geometric area: 0.78 cm^2) and $\text{V}_2\text{O}_5/\text{TiO}_2/\text{Ti}$ plates (geometric area: 1 cm^2).

2.2. Electrochemical preparation of V_2O_5 on GC and TiO_2/Ti

Electrodeposition of V_2O_5 was carried out by repetitive potential cycling from 0 to 2000 mV in 0.1 M vanadyl sulphate (VOSO_4) solutions at pH 1.8. The vanadium salt ($\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, Merck, 99.9%) was dissolved in 1 M H_2SO_4 (Riedel de Haën, 95–97% aqueous solution) and pH was adjusted to 1.8 with 4 M NaOH (Merck, 99%) [17].

Just prior to the deposition, the GC discs were polished using different grades of Al_2O_3 powder. Electrodes were rinsed with ultrapure water ($18\text{ M}\Omega\text{ cm}^{-1}$) and ultrasonically cleaned in water for 10 min.

2.3. Preparation of V_2O_5 films by thermal decomposition on TiO_2/Ti plates

Before any use, titanium plates (Aldrich, 99.99%) were abraded with silicon carbide paper, grades P600A and P1200A (E.A. & C.L.). The plates were washed with ultrapure water, etched in 8 M HCl (Riedel de Haën, 37%) at 30°C for 10 min and then rinsed again with ultrapure water. The TiO_2/Ti support was prepared by thermal oxidation of a titanium plate (geometric area, 1.0 cm^2) in a muffle furnace (Lindberg Blue) under oxygen atmosphere following the temperature program: (i) the temperature was scanned from 25 to 450°C at a rate of 2°C min^{-1} ; (ii) maintained at 450°C for 6 h; and (iii) scanned from 450 to 25°C at a rate of 2°C min^{-1} .

The amount of V_2O_5 did not exceed about 10% of the weight of the pretreated titanium plate ($\approx 0.6\text{ g}$), since higher

percentages lead to high electrical resistances. The V_2O_5 films were prepared as follows: (i) 0.0193 g of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ were dissolved in $5\ \mu\text{l}$ of ultrapure water; (ii) the prepared solution was spread out drop wise on the TiO_2 surface until all of it was wet; (iii) the wet plate was introduced in the muffle furnace under oxygen atmosphere, and the same temperature program used for the TiO_2/Ti support preparation was applied. Steps (ii) and (iii) were done repetitively until total consumption of the solution.

2.4. Characterization of V_2O_5 films

Films morphology and chemical analyses were determined using a scanning electron microscope (Philips Model XL30) coupled with an energy dispersive X-ray detector (EDX, Model IDX4).

X-ray photoelectron spectroscopy (XPS) analyses were carried out employing a spectrometer (Leybold Heraeus) with a non-monochromatic aluminum (Al) radiation (Model LH-1, 1486.6 eV) operating at 370 W. The analyses chamber pressure was maintained at about 5×10^{-8} mbar during all measurements. Binding energy values were corrected using the signal located at 284.6 eV, which is assigned to carbon (C) contamination.

2.5. Electrochemical response of V_2O_5

Electrochemical measurements were carried out with an Autolab 20 potentiostat, controlled with a General Purpose Electrochemical System software (GPES) version 4.8.

Two electrolytes were used: aqueous (1 M H_2SO_4 + 1 M NaOH, pH 3) and organic (0.1 M But_4NPF_6 (Aldrich, 99.9%) + CH_3CN (Aldrich, HPLC grade)). The electrooxidation of toluene was performed in both electrolytic media.

2.6. Computational method

The band structure calculation and the density of states (DOS) of the metal oxide surface were obtained using the computational program YAeHMOP; Bind 3.0 [18]. The crystal structure data for the program was obtained from Retrieve, Powder Diffraction Files and Diamond 2002 [19–21]. The parameters used in the calculations are standard literature values and are shown in Table 1 [18].

3. Results and discussions

3.1. Electrodeposited V_2O_5 films on GC discs

3.1.1. Electrodeposition and morphological details of V_2O_5 films

According to Pourbaix diagrams a variety of vanadium species could be produced at different pH values [22]. From these diagrams, there are two possible mechanisms of V_2O_5

Table 1
Hückel atomic parameter used in the calculations

| Atoms | Orbital | H_{ii}^a (eV) | ζ_1^b | C_1^c | ζ_2 | C_2 |
|-------|---------|-----------------|-------------|---------|-----------|-------|
| H | 1s | -13.600 | 1.300 | — | — | — |
| C | 2s | -21.400 | 1.625 | — | — | — |
| | 2p | -11.400 | 1.025 | — | — | — |
| O | 2s | -32.300 | 2.275 | — | — | — |
| | 2p | -14.800 | 2.275 | — | — | — |
| V | 4s | -8.810 | 1.300 | — | — | — |
| | 4p | -5.520 | 1.300 | — | — | — |
| | 4d | -11.000 | 4.750 | 0.476 | 1.700 | 0.701 |

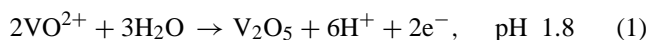
^a Orbital ionization potential.

^b Orbital exponent.

^c Orbital coefficient.

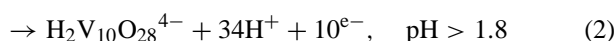
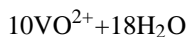
deposition from vanadyl species (VO^{2+}), which depend on the pH values [17]:

Direct step

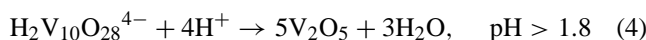


Indirect step

Formation of soluble products



Precipitation on the surface electrode



Cyclic voltammograms of a GC disc in a $\text{VOSO}_4 + 1 \text{ M H}_2\text{SO}_4 + 4 \text{ M NaOH}$ (pH 1.8) solution, show significant differences when the positive limits were changed from 1000 to 2000 mV (Fig. 1). After fifty cycles, when the positive limits

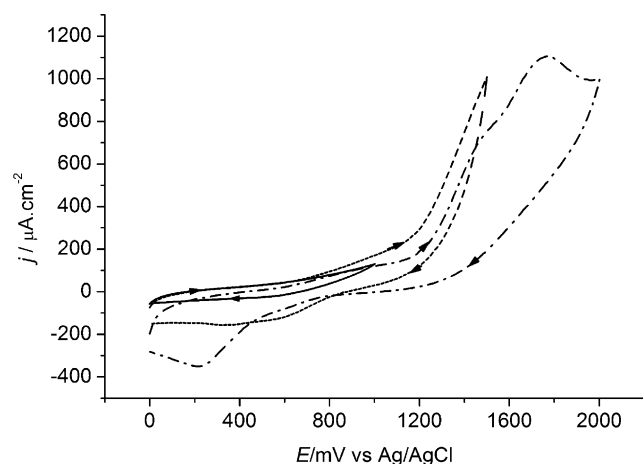


Fig. 1. Cyclic voltammograms of a GC rod in N_2 saturated 0.1 M $\text{VOSO}_4 + 1 \text{ M H}_2\text{SO}_4 + 4 \text{ M NaOH}$ (pH 1.8). Anodic limits: (—) 1000 mV, (---) 1500 mV, (-·-·-) 2000 mV. Sweep rate, 50 mV s^{-1} . Geometric area of the electrode: 0.78 cm^2 .

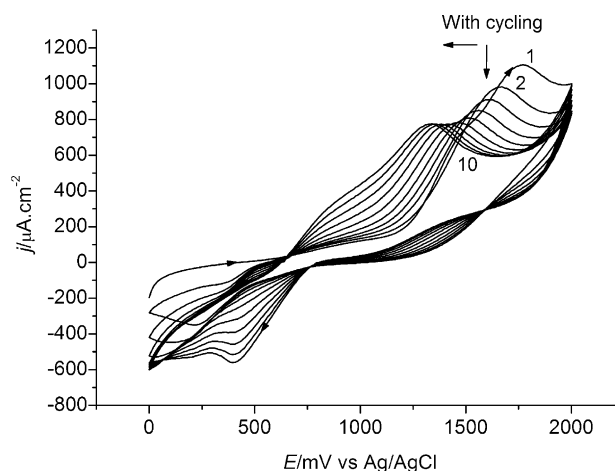


Fig. 2. Repetitive cyclic voltammograms of a GC rod in N_2 saturated 0.1 M $\text{VOSO}_4 + 1 \text{ M H}_2\text{SO}_4 + 4 \text{ M NaOH}$ (pH 1.8) between 0 and 2000 mV. Sweep rate, 50 mV s^{-1} . Geometric area of the electrode: 0.78 cm^2 .

where 1000 and 1500 mV, non V_2O_5 was detected on the GC surface. A positive limit of 2000 mV was required for V_2O_5 deposition.

The anodic limit dependence is explained taking into account the water discharge reaction (WDR). Potentials higher than 1500 mV are required to oxidize $\text{V}^{\text{IV}}-\text{V}^{\text{V}}$, and the oxidation of water occurs concomitantly at these potential. These observations are supported by Eqs. (1) to (5), which clearly suggest that the oxidation of water must occur for V_2O_5 electrodeposition.

Fig. 2 shows that with repetitive potential cycling of a GC rod in a vanadyl solution between 0 and 2000 mV, both the current density and the peak potential of the anodic peak initially located at 1800 mV decrease. The current decay is due to the consumption of VO^{2+} with formation of V_2O_5 on the GC surface.

The SEM picture shows that the deposit is homogeneous and thin (Fig. 3(a)), while the EDX spectrum (Fig. 3(b)) shows the presence of elements from the electrolytic medium (sodium, chloride, sulphur and others), as it is expected. The XPS spectrum (Fig. 3(c)) is quite similar to that reported [23]; however, the binding energy values are slightly shifted compared to the reported values for V_2O_5 [23]. This energy displacement is due to the presence of ions from the electrolytic medium.

The electrochemical deposition of V_2O_5 on TiO_2/Ti substrates at similar conditions could not be detected; which is explained considering that TiO_2/Ti is less active than GC for WDR [24].

3.1.2. Electrooxidation of toluene on electrodeposited V_2O_5 films

Fig. 4 unequivocally shows that V_2O_5 strongly inhibits the activity of GC in the organic medium ($0.1 \text{ M But}_4\text{NPF}_6 + \text{CH}_3\text{CN}$); the peak current of the toluene electrooxidation on $\text{V}_2\text{O}_5/\text{GC}$ is only 12% compared to that registered on GC.

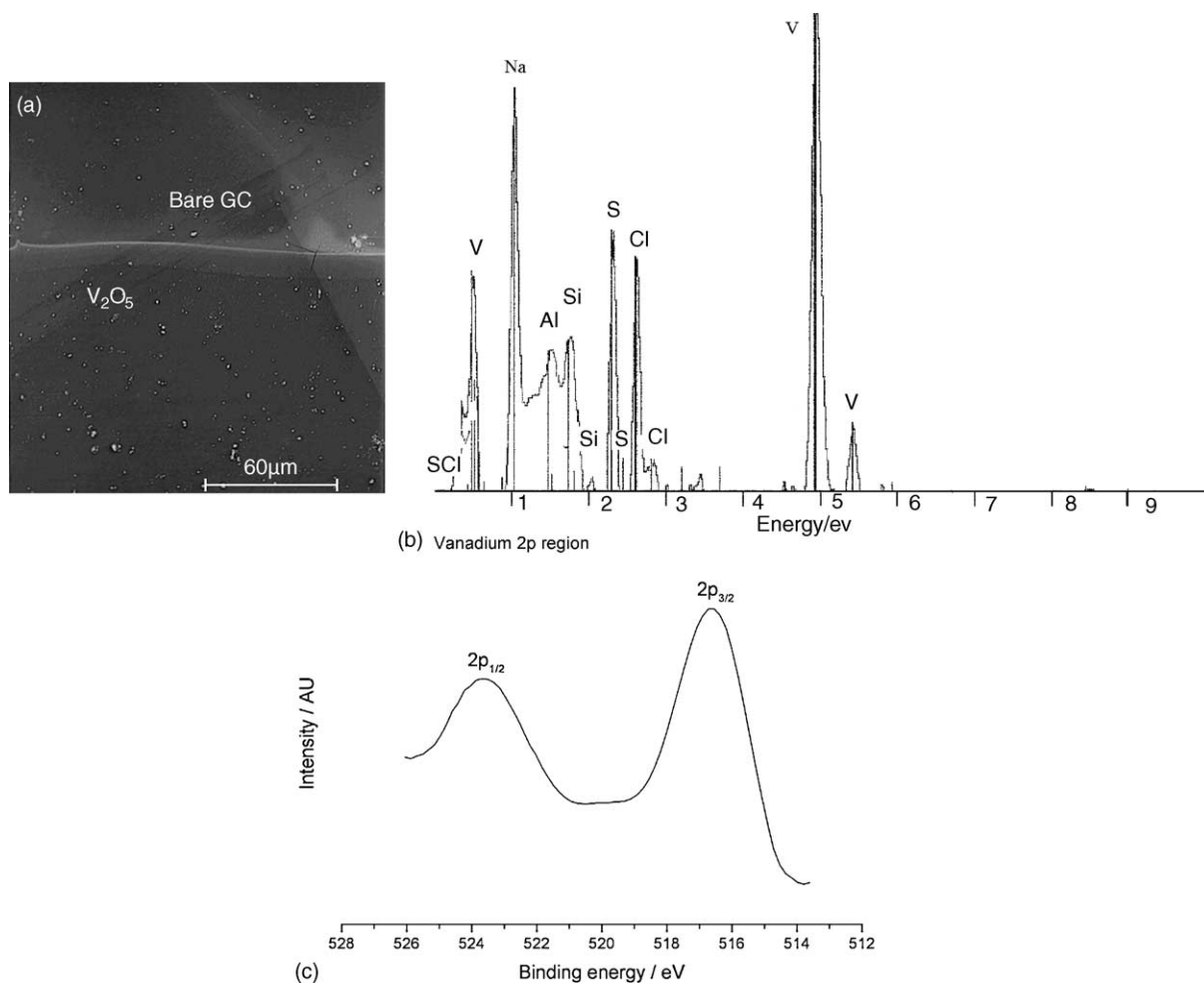


Fig. 3. Morphological and chemical characteristics of the electrodeposited V_2O_5 films on GC after consecutive cycling (50 cycles): (a) scanning electron microphotograph; (b) EDX spectrum; (c) XPS spectrum.

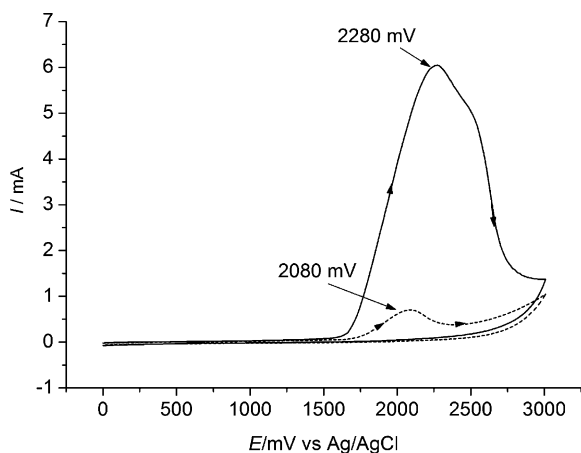


Fig. 4. Cyclic voltammograms of different electrodes in N_2 saturated 50 mM toluene + 0.1 M But_4NPF_6 + CH_3CN : (—) GC, (---) V_2O_5/GC . Sweep rate, $100 mV s^{-1}$. Geometric area of the electrodes: $0.78 cm^2$.

The active sites of GC would be completely blocked by the metal oxide film.

In order to detect if V_2O_5 has some activity for toluene electrooxidation, a less active support than GC was used (i.e., TiO_2/Ti). In previous reports, we have shown that TiO_2/Ti is slightly active for toluene electrooxidation in organic and aqueous media [24].

3.2. Preparation of V_2O_5 by thermal decomposition of $VOSO_4$ on GC and TiO_2/Ti

3.2.1. Electrochemical and morphological details of the films

V_2O_5 films prepared on GC did not show a good adhesion, reason for what we did not carry out experimental work using this material.

In contrast, V_2O_5 obtained by thermal decomposition TiO_2/Ti showed good physical stability, high porosity and high surface area (Fig. 5(a)). It can be seen from Fig. 5(b) and (c) that pure and high quality vanadium pentoxide deposits are obtained by this technique [23].

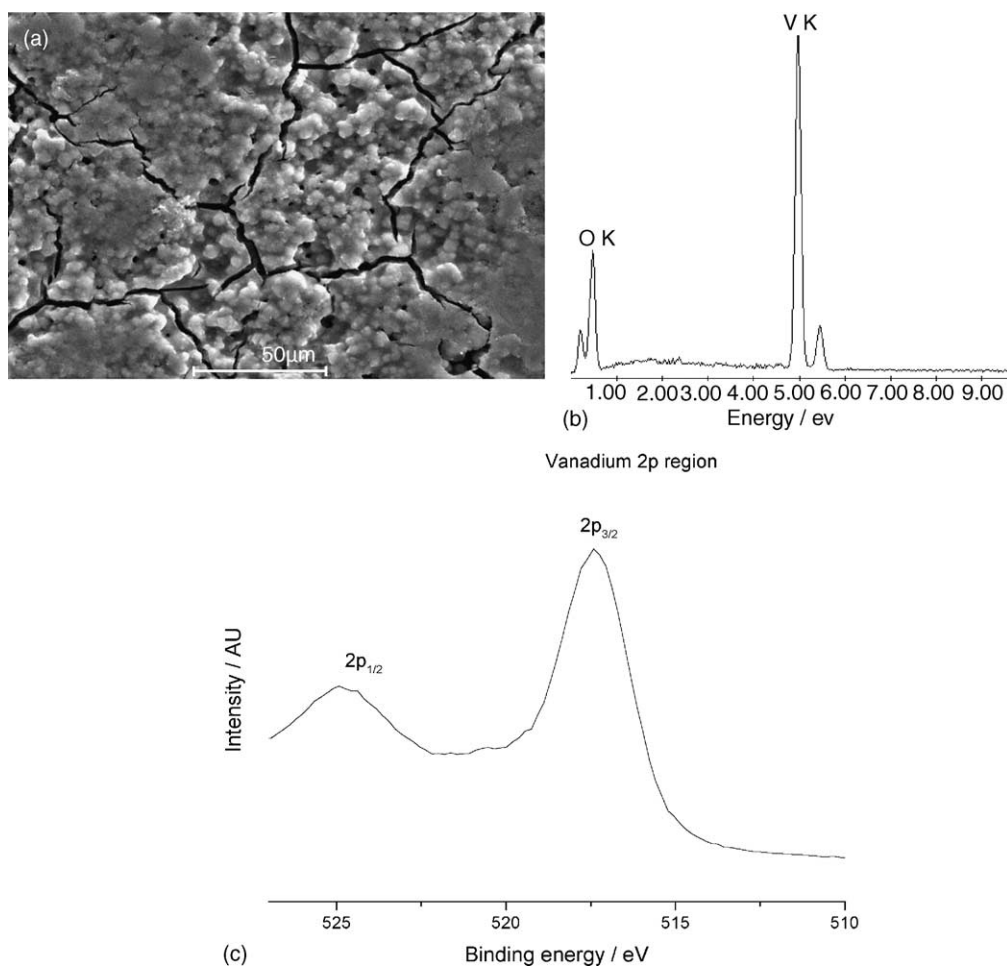
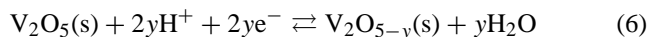


Fig. 5. Morphological and chemical characteristics of V_2O_5 films prepared by thermal decomposition of $VOSO_4$ on TiO_2/Ti : (a) scanning electron microphotograph; (b) EDX spectrum; (c) XPS spectrum.

According to the vanadium Pourbaix diagram, V_2O_5 is stable at potentials between -500 mV and 2000 mV versus NHE and pH range between 1 and 3. Repetitive cyclic voltammograms for a $V_2O_5/TiO_2/Ti$ electrode in aqueous media (pH 3) showed a very stable film between these potentials (Fig. 6).

At the initial potential (-500 mV) the oxide film is in its reduced form. When the potential is scanned into the positive direction, a wave (A) appeared around 1250 mV due to the surface oxidation (V_2O_5 formation). During the cathodic sweep, two new bands (B, C) at 250 mV and -250 mV were respectively observed, which can be explained taking into account the V_2O_4 and V_2O_3 formation according to the Pourbaix diagrams and the following scheme reaction:



The anodic peak current (A) varies linearly with the sweep rate (see inset in Fig. 6), which suggests that a surface redox reaction is involved at these potentials values [25]. For peaks B and C, it was not possible to study the peak current versus sweep rate relation, since it was difficult to obtain accurate peak current values from the cyclic voltammograms. Color

changes were easily observed on the surface electrode when the applied potential was scanned in both directions (anodic and cathodic); from orange (V_2O_5 formation) going through blue (V_2O_4) and finally pale green (V_2O_3 generation).

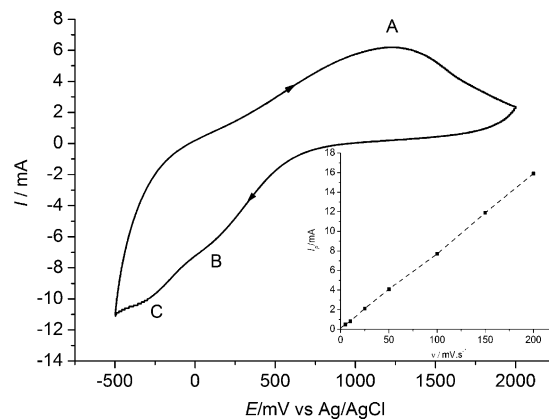


Fig. 6. Cyclic voltammogram of $V_2O_5/TiO_2/Ti$ in N_2 saturated $1 M H_2SO_4 + 0.1 M NaOH$ (pH 3). Sweep rate, $50 mV s^{-1}$. Geometric area of the electrode: $1 cm^2$. Inset: anodic peak current (peak A)–sweep rate relationship.

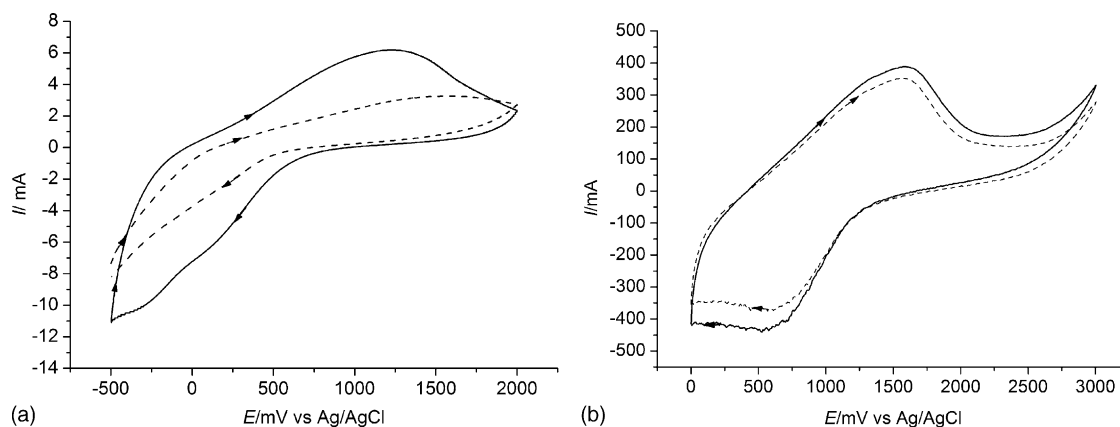


Fig. 7. Cyclic voltammograms of $V_2O_5/TiO_2/Ti$ in N_2 saturated solution: (a) 1 M H_2SO_4 + 0.1 M NaOH (pH 3); (b) 0.1 M $But_4NPF_6 + CH_3CN$. (—) Absence of toluene, (---) presence of toluene. Sweep rate, 50 mV s^{-1} . Geometric area of the electrode: 1 cm^2 .

3.3. Electrochemical activity of $V_2O_5/TiO_2/Ti$ films towards toluene oxidation

Fig. 7(a) (solid line) shows the typical behavior for a $V_2O_5/TiO_2/Ti$ electrode in a 0.1 M But_4NPF_6/CH_3CN electrolyte. Depending on the applied potential the electrolyte's cations diffuse in or out the V_2O_5 film; a sort of doping or undoping process takes place in the oxide film.

We have already found that toluene is electrooxidized about 2280 mV in organic medium, on bare and modified GC electrodes. The cyclic voltammogram (dash line, in Fig. 7(a) and (b)) did not show any oxidation wave attributed to the toluene transformation. This means that V_2O_5 is not an active surface for the electrooxidation under the experimental conditions.

Toluene additions to the electrolyte medium, organic and aqueous solutions, produced a current decaying (respect to the blank solution) due to the possible irreversible absorption of toluene on the surface (Fig. 7(a) and (b)). In aqueous medium, even at high overpotentials (water electrooxidation occurs), no toluene electrooxidation was detected.

3.4. Theoretical consideration of the electrode process at the metal oxide surface

Any electrochemical process involves three fundamental steps [25]: (a) diffusion of the electroactive species from the bulk solution to the electrode surface; (b) charge transfer reaction; (c) diffusion of products from the surface electrode to the bulk solution. The nature of the electrode reaction depends on the intrinsic characteristics of the electroactive species and the surface electrode.

Definitely, interactions of the electroactive species with the electrode surface control the charge transfer reaction. Absence of any sort of interaction that modifies the energy levels of the system does not lead to any electrochemical reaction.

Based on the crystallographic data of the material, YAeHMOP [18] allowed the estimation of DOS of the ex-

tended surface [26,27]. It was also possible to calculate the theoretical energy interactions between V_2O_5 surface and the molecular orbitals of a molecule of toluene placed at 2 \AA from the surface with three different geometrical arrangements of the oxygen and vanadium atoms, as shown in Fig. 8. In this figure, the first four atomic layers of the metal oxide surface are illustrated.

As is well-known the Extended Hückel method is not reliable for geometry optimization [27,28]. Thus, a significant orbital interaction criteria, based on overlap population, was used to select 2 \AA as the appropriate interaction distance between toluene and metal oxide surface. However, due to limitations of Extended Hückel methods, our conclusion is not qualitatively change under small variation of the interaction distance.

The calculated band gap value (Table 2) suggests that the free V_2O_5 is a semiconductor [29]. In general, an electrode process involves interactions between bands close to the Fermi level (E_F) of the materials and the frontier orbitals (highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO)) of the electroactive

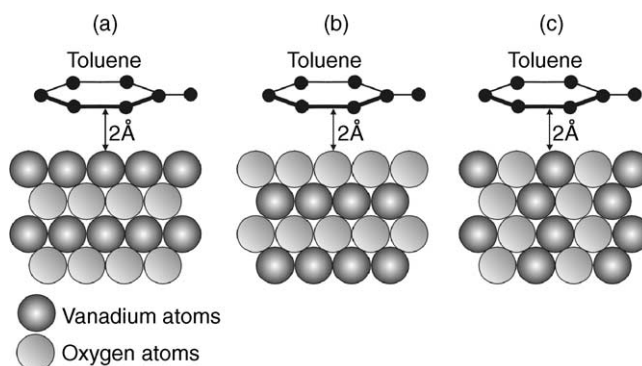


Fig. 8. Different geometrical configuration of a molecule of toluene interacting with the four slabs vanadium oxide surface: (a) only vanadium atoms are exposed; (b) only oxygen atoms are exposed; (c) both, vanadium and oxygen atoms, are exposed.

Table 2
Calculated energy values for V₂O₅

| Metal oxide | Band gap (eV) | Fermi energy level (E_F), (eV) |
|-------------------------------|---------------|------------------------------------|
| V ₂ O ₅ | 2.43 | −14.3328 |

species [24]. Comparing the frontier energy values of toluene (HOMO, −12.5048 eV; LUMO −8.6927 eV) and E_F of V₂O₅ (Table 2), we conclude that toluene should be oxidized at the oxide surface without many complications. However, we have experimentally shown that this is not the fact at all, so other factors must be considered.

Fig. 9 shows the energy values (ΔE) of toluene–vanadium atoms and toluene–oxygen atoms (O) interactions. In the figure, toluene- n Me means that a molecule of toluene is interacting with n metallic atoms (n could be 1 or 2) while toluene- n O means that a molecule of toluene is interacting with n oxygen atoms (n could be 1 or 2); the number of neighbor atoms respect to the center of a toluene molecule were changed moving the toluene molecule over the oxide surface. Negative values of ΔE mean stabilization while positive values reflect repulsive interaction or destabilization; this is compared to the system toluene-surface oxide without interaction. It is necessary to consider that the calculated energy values show the real qualitative tendency; however, these are slightly over-estimated.

It may be noted that attracting interactions increase with the numbers of vanadium atoms involved; however, interactions via atoms of oxygen are generally repulsive and stronger. Attractive interactions do not lead to important changes in the Fermi level energy value of V₂O₅. It must be also highlighted that V₂O₅ films were prepared under oxygen atmosphere (thermal decomposition method) and aqueous media (electrochemical method); for these reasons the V/O surface relation should be extremely small. As a result, the repulsive interactions become more important than the attractive ones.

On the other hand, if V/O surface relation is experimentally increased, using another method of preparation, the sta-

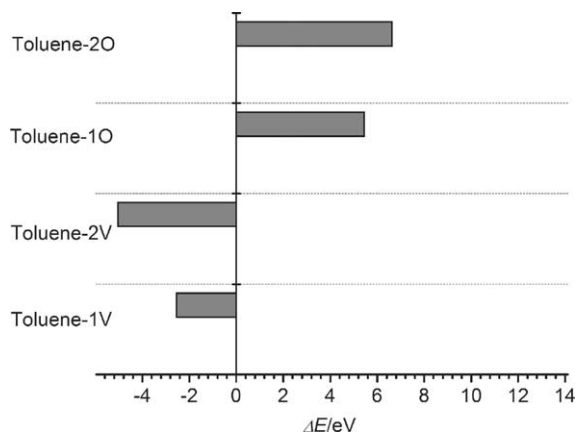


Fig. 9. Theoretical values of toluene-vanadium atoms (V) and toluene-oxygen atoms (O) interactions.

bilizing interactions will be stronger and the charge transfer reaction would be favored. At the experimental conditions, toluene does not interact with the oxide surface so the electron transfer reaction does not take place.

YAcHMOP, as the majority of the molecular orbital calculation methods, does not consider solvent effects, since calculations are done in vacuum. Toluene showed the same electrochemical behavior in supporting electrolytes with very different chemical and physical properties (1 M H₂SO₄ + 1 M NaOH (pH 3) and 0.1 M But₄NPF₆ + CH₃CN); which drive us to suppose that solvent is not an important parameter to be considered.

4. Conclusions

V₂O₅ electrodeposition could be achieved from acid solutions at experimental conditions where water discharge reaction is kinetically favored. When the electrodeposition was carried out on TiO₂/Ti there was non-evidence of V₂O₅ formation; however, a thin, homogeneous and impure V₂O₅ film is obtained on GC. The anodic limit potential and the nature of the substrate are two very important variables to be considered.

V₂O₅ films obtained by thermal decomposition of VOSO₄ showed very good mechanical and physical properties; good adherence, high porosity and high purity. In aqueous medium, V₂O₅ films showed a well defined surface redox process and an evident electrochromism effect.

The electrochemical activity of V₂O₅ towards toluene electrooxidation could be theoretically supported considering two important aspects: (i) the attractive interactions, between toluene and the metal oxide surface do not have important effects in the E_F value; (ii) preparation of V₂O₅ by thermal decomposition and electrochemical methods yields a metal oxide with a very small V/O surface relation; which makes repulsive interactions more important than the attractive ones.

At the experimental conditions, interactions do not have any positive effect in the energy parameters of V₂O₅; the repulsive interactions predominate over stabilization.

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