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Article

Investigation of the Surface Properties of an Oxide of Interest in the Field of a Conductive Oxide System: Influence of Precursor and Purification

Gilmar de Almeida Gomes[a*]***, and Julien Françoise Coleta Boodts***[a,b]

[a]*Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão*
Preto, Universidade de São Paulo, Av. Bandeirantes 3900,
14040-901 Ribeirão Preto - SP, Brazil
[b]*Departamento de Química, Universidade Federal de Uberlândia,*
Av. João Naves de Ávila 2160, 38400-902 Uberlândia - MG. Brazil

As propriedades superficiais de TiO_2 comercial e de amostras sintetizados por decomposição térmica, usando diferentes precursores, foram investigadas por microeletroforese. Os pie's obtidos em função da força iônica, controlada com KNO_3 ou KCl, revelaram que: 1) A amostra comercial e as sintetizadas a partir de precursor contendo cloreto dissolvido em HCl 1:1(v/v) apresentaram valores de pie muito baixos devido à inclusão de cloreto no óxido; 2) Os métodos de purificação explorados (suspensão do óxido em pH 12 e diálise) se mostraram ineficientes; 3) TiO_2 sintetizado a partir de um precursor orgânico e condições livres de cloreto forneceu um pie de 5,9 valor em excelente concordância com a literatura.; 4) Adsorção específica de cloreto em TiO_2 é fraca.

The surface properties of commercial TiO_2 and samples synthesized by the thermal decomposition procedure using several precursor salts were investigated by a microelectrophoresis technique. The iep was determined as a function of the ionic strength which was controlled with KNO_3 or KCl. The experimental results showed: 1) The commercial sample and the ones synthesized from the chloride salt dissolved in HCl 1:1 (v/v) show low iep's due to chloride inclusion; 2) The purification methods explored (oxide suspension at pH~12 and dialysis) are inefficient; 3) TiO_2 samples synthesized from an organic precursor salt under totally chloride-free conditions furnished an iep of 5.9 in excellent agreement with literature data; 4) Chloride specific adsorption on TiO_2 is weak.

Keywords: *electrocatalysis, surface properties, titanium dioxide, chloride specific adsorption*

Introduction

Conductive metallic oxide electrodes, known as Dimensionally Stable Anodes, DSA, are of outstanding technological importance due to their excellent catalytic properties for the chlorine and oxygen evolution reactions[1,2]. The basic composition of DSA is a mixture of $RuO_2(IrO_2)+TiO_2$, the first oxides providing the catalytic properties while TiO_2 promotes the mechanical stability and chemical inertness of the mixture. Frequently other oxides (modulators) are introduced into the mixture to modulate specific properties of the mixture. The overall electrocatalytic efficiency of an oxide electrode is influenced by both morphological (surface area) and synergistic (electronic) features. So, the overall response is a combination of the apparent (surface area effect) and real catalytic (synergistic) properties of the material. Unfortunately, absolute methods to determine the real surface area of these rugose materials are not available[3] making the separation of morphological and synergistic features a difficult matter. Therefore the investigation of an intensive property (area independent) such as the acidity (pK_a) or chloride specific adsorption of the oxide[4] are of interest to the field of electrocatalysis. However, more experimetal results are needed before a rationalization of the data can be attempted.

Freshly prepared oxides, obtained at relatively low temperatures (350-600 °C), are hydrophilic rapidly react-

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fax 55-16-6338151;
e-mail: gilmar@fisquim.ffclrp.usp.br

ing with atmospheric moisture. This process results in an oxide surface covered by OH groups capable of mediating the interactions between the surface and its surrounding. Electrocatalysis being a surface phenomenon makes the investigation of the oxide surface properties (pK_a, pCl), which in turn define the intermediates (MOH_2^+, MO^-, $MOCl^-$) existing at the oxide surface, of fundamental importance[5] for a better understanding of the catalytic properties with respect to the hydrogen, oxygen and chloride evolution reactions on these electrode materials. An excelent review of oxygen evolution at oxide electrodes and the correlation of electrocatalytic activity with the pzc of oxides was recently published by Ardizzone and Trasatti[6]. Due to the limited amount of data on acid/base surface properties and chloride specific adsorption available in the literature we initiated our investigation of oxides of interest to the field of electrocatalysis starting with TiO_2. Despite the fact this oxide in not an electrocatalyst we decided to start with this material since it is the most widely used oxide to stabilize electrocatalytic systems being frequently present in concentrations up to 70 mol %. Besides, the experimental procedure used to prepare oxide electrodes frequently causes synergistic effects making the investigation of the individual components of interest. TiO_2 is an intensively investigated oxide due to its industrial importance (*e.g.* paints). However, as far as we know the acid/base properties of TiO_2 synthesized using conditions as close as possible to electode preparation were only recently investigated by acid/base titration[7].

Experimental

Preparation of the oxides

In order to stay as close as possible to the established experimental conditions used in the preparation of DSA, oxides were synthesized by the thermal decomposition route using $TiCl_4$ (Ventron) and $Ti[O(CH_2)_3CH_3]_4$, $Ti(OBu)_4$, (Aldrich) as precursors. For comparison commercial TiO_2 (Ultrex brand from J. T. Baker) was also included in the investigation. In the case of $TiCl_4$ the precursor was dissolved in HCl 1:1 (v/v) (Merck) while with $Ti(OBu)_4$ 1:2 (v/v) HNO_3 (Merck) was used as a solvent in order to avoid any trace of Cl^-.

Initially, the solvent of the ~0.2 mol dm^{-3} precursor solution was evaporated at low temperature until dryness (~90 °C) and the residue calcinated at 450 °C for 1 h in an oven pre-heated at the desired temperature. The oxide was then suspended in 10^{-2} mol dm^{-3} KOH, (pH ~12), and stirred for 24 h. The pH of the oxide suspension was ajusted periodically. Next, the oxide was isolated by filtration using a Millipore HA ∅ 0.45 µm membrane and air-dried for 1 h at 120 °C. A final 1 h calcination at 450 °C completed the procedure.

The above described suspension, filtration and calcination (120 °C, 450 °C) sequence was repeated three times. The oxide obtained from $TiCl_4$, already three times purified, was divided in two portions, A and B, and each portion submitted to one more purification step. Portion A was purified by dialysis for 21 days while portion B purified once more by suspension in 10^{-2} mol dm^{-3} KOH (pH ~ 12).

Oxide characterization

Oxide structure was obtained by X-ray diffraction using a Siemens model D5000 diffractometer (40 kV, 40 mA). X-ray fluorescence spectra were recorded on a Sequential X-ray Fluorescence Spectrometer, model VRA 30, Carl Zeiss (40 kV, 30 mA.)

Zeta potential measurements

Approximately 0.1 g of TiO_2 was suspended in 1.0 dm^3 of the appropriate supporting electrolyte (KNO_3 or KCl) of the desired ionic strength and stirred for 24 h prior to use. While a commercial product was used as a source of KCl (Merck p.a.), KNO_3 was synthesized neutralizing HNO_3 (Merck p.a.) with KOH (Merck p.a.). The KNO_3 obtained after crystallization contained less then 5 ppm of chloride. Aliquots of the 0.01% TiO_2 suspension were adjusted to the desired pH values using HNO_3 or KOH. The pH of the suspension was considered constant when it remained for at least 30 min at the desired value. Ionic strengths investigated covered the $1 \times 10^{-2} - 1 \times 10^{-4}$ mol dm^{-3} range. Zeta potentials, ζ, were measured using a Zetasizer 4 equipment from Malvern (UK).

Results and Discussion

1 X-ray diffraction and fluorescence

Representative diffractograms of TiO_2 samples are shown in Fig. 1. Comparison of our spectra with published data[8] (ASTM Cards) revealed TiO_2 to be present in the rutile structure in both the commercial product and the sample synthesized from the $TiCl_4$ precursor dissolved in HCl 1:1 (v/v). In the later sample a small amount of the anatase form of TiO_2 was also identified by its characteristic peaks. The oxide obtained from the organic precursor was pure anatase. Judged by the width of the peaks, the commercial oxide and the TiO_2 sample obtained from $TiCl_4$ showed a higher degree of crystallinity than the oxide obtained from $Ti(OBu)_4$. Successive purification steps resulted in an increase in the degree of crystallinity of the oxides as a consequence of the extra calcination time (each successive purification sequence involves a 1 h calcination step at 450 °C).

Despite the experimental evidence obtained from zeta potential data (ζ-pH curves) pointing to the presence of chloride in the commercial product, this element was not detected by X-ray fluorescence suggesting its content falls

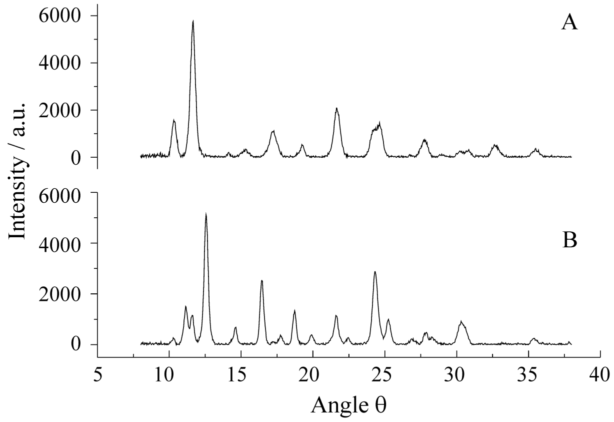

Figure 1. X-ray diffractograms of thermally prepared TiO_2 samples from: (A) $Ti(OBu)_4$ in 1:2 HNO_3; (B) $TiCl_4$ in 1:1 (v/v) HCl (3 purifications at pH ~12).

below the detection limit of the analytical technique. As expected, considering the experimental precautions taken during the synthesis of TiO_2 from $Ti(OBu)_4$ (any possible chloride source was excluded), no Cl^- was detected in this sample. The presence of Cl^- in the oxide synthesized from $TiCl_4$ was confirmed by X-ray fluorescence. This finding is consistent with the results of UHV analysis of TiO_2-containing oxide electrodes[9], prepared using similar experimental conditions, in which Cl^- was also detected. It is worthwhile to mention that once the electrode material was submitted to strong oxygen evolution from 1.0 mol dm^{-3} $HClO_4$ the presence of Cl^- in the outer 20-30 nm region of the oxide layer was no longer evidenced by XPS[9].

Acid/base surface properties

Figure 2 shows a series of ζ-pH curves obtained in 10^{-3} mol dm^{-3} KNO_3 as a function of the number of purifications for TiO_2 samples obtained from $TiCl_4$. A representative curve for the commercial sample is shown in Fig. 3.

All curves exhibit some common features: (1) no positive ζ-limit is observed in the curves and; (2) the iep's obtained (2.3-3.5 for TiO_2 samples prepared from $TiCl_4$ and 2.9 for the commercial product) are all significantly lower than the values published in the literature[7,10-12]. These results suggest an excess of negative charge of the oxide which could be due to either Cl^- specific adsorption or inclusion of Cl^- in the oxide bulk as supported by X-ray fluorescence and XPS[9] results. Substitution of O by Cl in the crystal lattice can be ruled out since this would lead to an excess positive charge. The results of the specific adsorption study (see Chloride specific adsorption section) and the inefficiency of extensive purification through suspension in 10^{-2} mol dm^{-3} KOH, expected to be efficient when dealing with a surface equilibrium process, all support the idea of chloride inclusion into the oxide to be the main source of the excess negative charge.

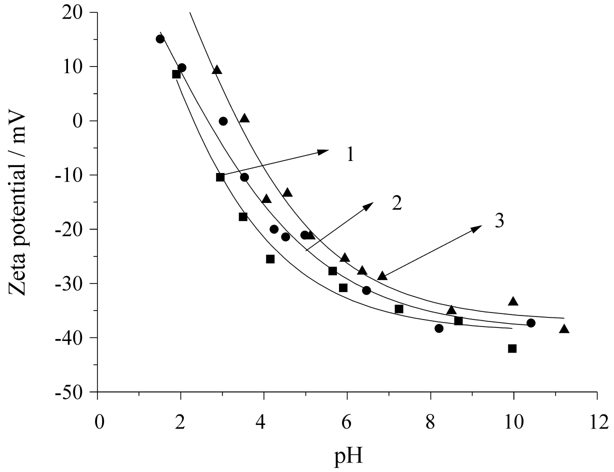

Figure 2. Zeta potential as a function of pH. Numbers on the curves represent the number of purification steps (pH ~12) the sample was submitted to. TiO_2 synthesized from $TiCl_4$ (Ventron). [KNO_3] = 1.0 x 10^{-3} mol dm^{-3}; [TiO_2 suspension] = 0.01%.

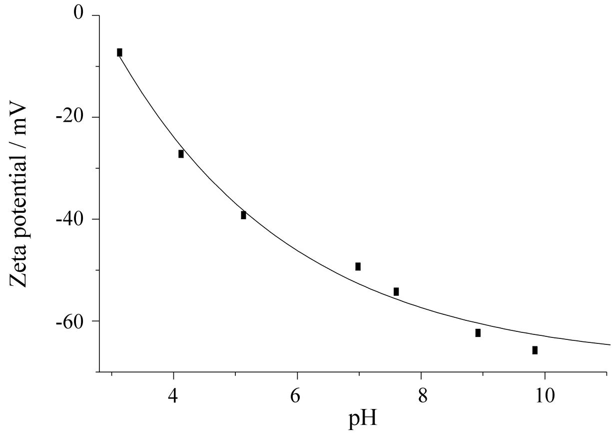

Figure 3. Zeta potential as a function of pH for commercial TiO_2 (Ultrex - J. T. Baker). [oxide suspension] = 0.01%; [KNO_3] = 1.0 x 10^{-3} mol dm^{-3}.

The ζ-pH curves (see Figs. 2 and 3) show the surface of TiO_2 suspended in 10^{-2} mol dm^{-3} KOH to be in the MO^- form. In the case where a surface adsorption process results in the low iep values, it is reasonable to presume that successive suspension steps would result in a displacement of the abnormally low iep values towards those of the literature. The purification procedure only caused a small increase of the iep from 2.3 to 3.5. This result not only supports chloride specific adsorption is of minor importance but also that oxide purification by suspension in basic medium is an inefficient method when inclusion is the main cause of chloride contamination of the oxide.

Representative ζ-pH curves obtained at different ionic strengths (KNO_3) of TiO_2 samples synthesized from $Ti(OBu)_4$ precursor in HNO_3 1:2 (v/v) are shown in Fig. 4. All curves are symmetrical showing a single intersection point at ζ = 0 while the positive and negative branches have almost identical ζ-values ($\zeta^{+}_{max} = \zeta^{-}_{min}$). An iep of 5.9 ± 0.2 was obtained. KNO_3 is known as a supporting electrolyte which is not subject to specific adsorption. This, together with the behavior of the ζ-pH curves as a function of ionic strength of the KNO_3 supporting electrolyte furnishes a pK_a-value of 5.9 ± 0.2 for TiO_2. This value is in excellent agreement with literature data[7,10-12]. A comparison with the value of 6.2 ± 0.1 obtained by Faria and Trasatti[7], who investigated by acid/base titration TiO_2 samples thermally prepared from $TiCl_4$ precursor dissolved in HCl 1:1 (v/v), is of interest. Despite the fact that thermal synthesis of TiO_2 from $TiCl_4$ leads to Cl-inclusion (see above) these authors obtained a pK_a-value which, within the experimental error, coincides with the value obtained for oxide samples synthesized under Cl-free conditions (from $Ti(OBu)_4$ in HNO_3). This can be understood considering the differences in the experimental procedures. While ζ-measurements are strongly affected by any phenomenon resulting in an excess charge at the oxide, acid/base titrations are less affected by them. Faria and Trasatti[7] worked with an oxide which was pre-equilibrated suspending it for 24 h in KNO_3. The experimental procedure used by these authors together with our finding that chloride specific adsorption on TiO_2 is weak (see Chloride specific adsorption item) explains the excellent agreement observed between the pKa-values obtained by the two independent experimental methods. It also supports the idea that Cl-inclusion is the main cause for the anomalous iep observed for TiO_2 samples synthesized from chloride containing precursors.

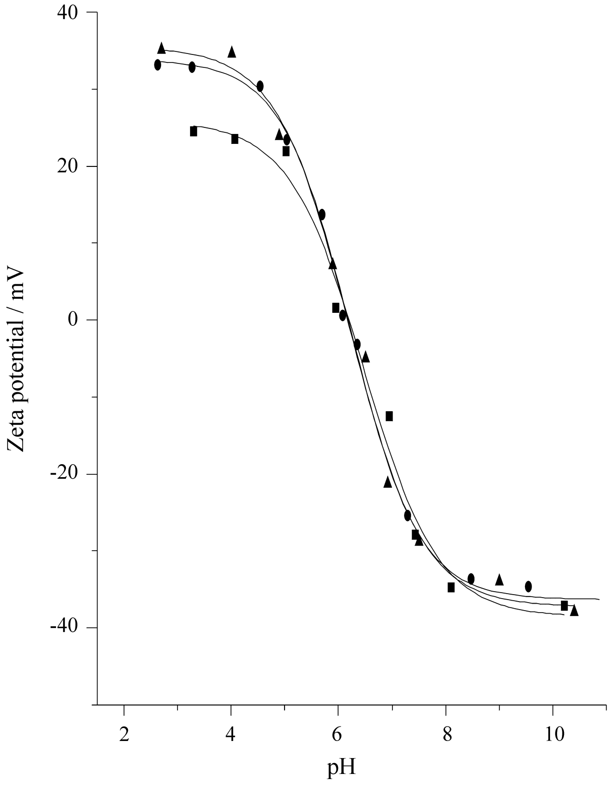

Figure 4. Zeta potential as a function of pH for different ionic strengths. [KNO_3]: (▲) 1.0 x10^{-4}; (•) 1.0 x 10^{-3}; (■) 1.0 x 10^{-2} mol dm^{-3}. TiO_2 sample prepared from $Ti(OBu)_4$ dissolved in 1:2 (v/v) HNO_3 ; [oxide suspension] = 0.01%; T_{calc}= 450 °C.

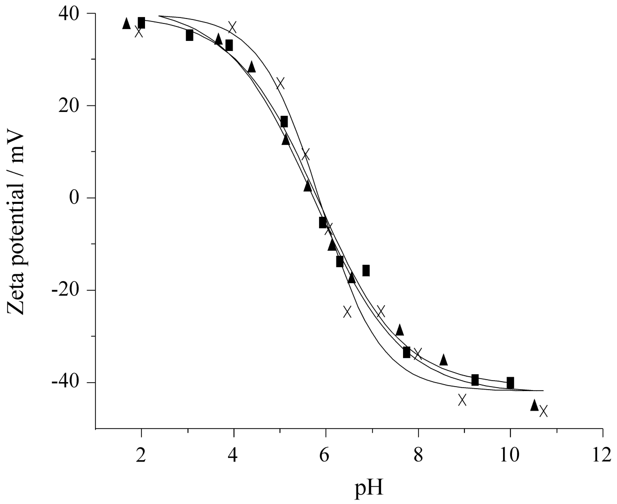

Figure 5. Zeta potential as a function of pH for different ionic strengths [KCl]: (▲) 5.0 x 10^{-4}; (x) 5.0 x 10^{-3} and (■) 1.0 x 10^{-2} mol dm^{-3}. TiO_2 sample prepared from $Ti(OBu)_4$ dissolved in 1:2 (v/v) HNO_3; [oxide suspension] = 0.01%; T_{calc}= 450 °C.

Chloride specific adsorption

Chloride specific adsorption on TiO_2 samples obtained from $Ti(OBu)_4$ was studied in KCl, changing the ionic strength between 10^{-2}-10^{-4} mol dm^{-3} KCl. Representative ζ-pH plots are shown in figure 5. The curves are slightly asymmetric with respect to the ζ-axis showing a single intersection at ζ = -10 mV from which an iep of 5.7 ± 0.2 was obtained. This result, together with the ζ-pH behavior, supports chloride specific adsorption on TiO_2 to be weak.

Conclusions

a- TiO_2 samples synthesized by the thermal decomposition route from chloride precursor dissolved in strongly acid medium (HCl 1:1 (v/v)) results in an oxide showing a much lower iep than the well established pK_a-value of ~6.1.

b- The iep, determined using a KNO_3 supporting electrolyte, of the oxide synthesized under Cl-free conditions (organic precursor; 1:2 (v/v) HNO_3], furnishes a pK_a = 5.9 ± 0.2 in good agreement with literature data.

c- The anomalous iep of TiO_2 sample synthesized from chloride containing precursor solution is due to chloride inclusion in the oxide and not to chloride specific adsorption.

d-The widely used techniques of suspending the oxide in alkaline solution and dialysis are inefficient purification methods when inclusion is the main source of excess charge at the oxide.

e- Chloride specific adsorption on TiO_2, as supported by ζ-pH data in KCl, is weak.

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