Influence of the nature of the electrode material and process variables on the kinetics of the chlorine evolution reaction. The case of IrO$_2$-based electrocatalysts

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ABSTRACT

Kinetic studies on the chlorine evolution reaction (ChlER) on oxide-based materials have been the subject of a number of papers since the seventies, following the introduction of DSAs (*Dimensionally Stable Anodes*) in chlor-alkali plants. On the basis of experimental data, different pathways have been proposed for the reaction over the years. Actually, specific experimental conditions and different approaches in sample preparation may lead to conflicting explanations. In the present paper, the ChlER kinetics has been studied at four electrode materials based on iridium and titanium oxides (with a 1:2 molar ratio). Electrodes were synthetized at two temperatures (350 and 450 °C) and by two different preparation methods: physical vapor deposition (rf-magnetron sputtering) and a conventional sol-gel technique, using special precursors developed in our laboratory. Both methodologies guarantee a high level of reproducibility. As also observed by other authors, experimental data have shown a lack of linearity in Tafel plots, high *b* slopes and reaction orders with respect to chloride ≤ 1, which have been justified on the basis of a Volmer-Heyrovsky pathway, by considering a model proposed by Tilak and Conway in 1992. This approach highlighted the role of the adsorbed intermediates, also at low overpotentials, for all electrode materials. To analyze further the kinetics, Langmuir and Frumkin models for intermediates adsorption were considered. Values for the lateral interaction parameter *g* were estimated, which ranged between 1 and 10, in all cases. Concerning the effect of pH, its influence on the ChlER rate seems to be related only with electrode surface modifications, without any involvement of protons in the *rate determining step* of the process. A slight inhibiting effect was assessed, by increasing the protons concentration. Eventually, impedance spectroscopy analysis did not appear sensitive to intermediate adsorption, plausibly because of the low variation of the coverage within the Tafel region; a poorly resolved contribution related to porosity was found in the case of samples prepared at 350 °C.

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1. Introduction

The introduction of mixed-oxide film-electrodes (the so-called DSAs, *Dimensionally Stable Anodes*) in the chlor-alkali technology has represented a fundamental progress in industrial electrochemistry, leading to enormous energy saving and cleaner processes, through a continuous progress in cell and electrode engineering. The impressive industrial impact of the original invention [1–5], further enhanced by the extension of DSA applications to the oxygen evolution reaction (relevant to aqueous electrometallurgy and hydrogen production), has obviously prompted the fundamental research, mainly addressed to DSA-coating synthesis and characterization.

In fact, papers have been published on the subject as early as 1972-1974, already quite well focused on preparation technique and microstructural properties of RuO$_2$ coatings [6,7]. The further development of research has been more and more concerned with the latter themes, while what could have been the main target, the chlorine evolution reaction (ChlER), has been relatively less studied. On the other hand, the first of the two themes is quite rich and complex. The methodology of preparation of active coatings, with the wide variety of parameters involved (*i.e.*, the quality and quantity of precursors, the choice of the path leading from precursor mixture to final mixed-oxide coating), has attracted, and attracts so far, a number of research works. In comparison, the study of a "facile" electrochemical reaction, namely the electrochemical oxidation of chlorides, has been considered a bit obvious.

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Nevertheless, in close temporal continuity with papers on the kinetics of chloride discharge at graphite [8,9], the first reports and papers on chloride discharge [10–12] at Ti-supported RuO_2-IrO_2-TiO_2 electrodes appeared essentially in conjunction with first fundamental papers on DSA preparation and characterization. The apparent "simplicity" of the reaction has favored more or less straightforward application of mechanisms of typical gas-phase reactions catalyzed by solid surfaces, like the Langmuir-Hinshelwood and Eley-Rideal ones, to chloride discharge. Their electrochemical equivalents, Volmer-Tafel and Volmer-Heyrovsky mechanisms, had previously found application in the formally similar case of hydrogen evolution reaction (HER), further justifying such extension. However, the study of the literature of this period, reviewed by Trasatti at the ending of the '80s [13], clearly shows all the difficulty of a mechanistic hypothesis for the reaction. A basic problem is that, quite often, results have been obtained under different conditions: consequently, the lack of a sufficiently rich and homogenous experimental database makes generalizing attempts quite difficult. A considerable number of papers deeply discussed in ref. [13] have been devoted to ChlER from concentrated chloride solutions (*e.g.* 5 M), under different acidities and sometimes at high temperatures (around 60-80 °C). In solutions with a so high ionic strength, assuming solvation numbers of 6 for both, Na^+ and Cl^- [14], the number of "free" molecules of solvent is negligible. Even though these features of the working solution resemble those of the industrial chlor-alkali process, and because of that may supply useful information for the latter, they definitely make the system more complex than required by a classical study in electrochemical kinetics. One more complication, unknown for the "sister" hydrogen evolution reaction, is the electrode material. While in the case of HER the electrode material is a metal, exposing polycrystalline surface or a well-defined single-crystal face, for which reproducibility of features is guaranteed, in the case of ChlER, the electrode material is an oxide, or better an oxide mixture (for reasons of stability), one of the components being RuO_2, or IrO_2, or a combination of the two oxides. As well established by the literature, the electrochemical performance of these electrodes is conditioned by a number of variables hardly reproducible, sometimes even within one and the same laboratory. "Benchmark" electrodes are not easily available either.

From a strictly mechanistic point of view, the fact that inevitably chloride discharge has to happen at metal-oxide, oxygen-terminated surfaces (theoretical studies on single-crystal faces of IrO_2 and RuO_2 have confirmed the existence of a surface fully covered by oxygen under typical chlorine evolution conditions, see e.g. refs. [15,16]), implies that the nature of adsorbed reaction intermediate(s) and activated complexes have to reflect the chemistry of Ru-O, Ir-O, Cl-O and do not exclude *a priori* also Ru-Cl and Ir-Cl chemistry. The not small number of reaction mechanisms proposed, despite stoichiometric simplicity and the substantial difficulty to adapt mechanisms to experimental kinetic evidence, is also related with this inescapable obstacle. A recent paper by Over [17] has thoroughly discussed these aspects, proposing unifying views of heterogeneous catalysis and electrocatalysis.

In the present paper, a comparison has been made of the electrocatalytic properties of electrode materials of the same composition: 33 mol% IrO_2 - 66 mol% TiO_2, synthesized by both a sol-gel method and Physical Vapor Deposition (PVD) (magnetron reactive sputtering). The active mixed-oxide coatings were deposited on Ti metal at two different temperatures: 350 and 450 °C. The oversimplification of the electrodes composition, compared with industrial benchmarks, has been chosen in order to try to isolate the contribution of components. The generalized higher stability of IrO_2-based electrodes and consequent higher reproducibility of experimental results has also been taken into consideration. On the basis of the experimental acquired evidence, mechanistic considerations have been developed.

2. Experimental

Titanium supports with a geometric surface area of 4 cm^2 were purchased from Titanium Consulting & Trading (Italy) and preliminary electro-polished, as described in ref. [18]. Oxide films were grown by a sol-gel method (SG) [19] and through physical vapor deposition (PVD). Electrode samples were synthesized at 350 and 450 °C; further details on the preparation of samples have been given in ref. [20]. In the case of sol-gel samples, 0.76 M Ir-HAC and 2 M Ti-HAC solutions were mixed in such a way to obtain an Ir/Ti molar ratio close to 1:2. The precursor solution was deposited on the Ti support by brushing; each precursor layer was first dried in oven at a temperature of 100 °C for 5 minutes, then calcined at 350 or 450 °C, for 10 minutes. The final mixed-oxide loading (about 1 μm of thickness) was attained with three successive precursor depositions. Sputter depositions were performed in a custom-built rf-magnetron sputtering system (13.56 MHz), equipped with three independent 2" sources and an rf-biased sample holder. The base pressure of the chamber was about 2×10^{-10} bar; targets materials were 2" diameter Ir (99.9%) and Ti (99.995%) metallic disks. Before starting the depositions, sources were conditioned for 15 min. at the operating conditions. Pure (99.9995%) Ar and a 20% mixture of O_2 in Ar gases were used at a working pressure of 6×10^{-6} bar. Power applied at sources were of 25 and 300 W for Ir and Ti targets, respectively; films have been prepared with a thickness of 1 μm.

For the sake of brevity, throughout this paper, sol-gel samples will be indicated as SG350 and SG450, while the acronyms PV350 and PV450 will be used in the case of sputtered specimens.

The surface morphology of the samples was investigated by Atomic Force Microscopy (AFM), making use of a NT-MDT microscope equipped with a NSG10 golden silicon tip. Analyses were carried out in semi-contact mode; the tapping frequency was varied from 0.8 to 0.9 Hz, depending on the sample analyzed, and was adjusted before each test for optimizing the resolution of obtained images.

The electrochemical *in situ* characterization of the samples was carried out by the traditional cyclic voltammetric technique, using an Autolab PGSTAT20 digital apparatus, equipped with a SCANGEN module that allows the applications of linear sweeps. A three-electrode cell with a Luggin capillary was used, and measurements were carried out in different solutions in dependence of the experiment. A double junction, saturated calomel electrode (SCE), with an intermediate $NaNO_3$ saturated solution, and a large-area Pt mesh were chosen as reference and counter electrodes, respectively. Experiments were carried out by varying the scan rate from 10 to 1000 mV s^{-1} (10, 25, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000 mV s^{-1}) in 1 M perchloric acid.

A limited surface area (1 cm^2) of each sample was used for electrochemical experiments; the remaining electrode surface was protected by wrapping it with a Teflon tape.

The investigation of the ChlER involved different chloride solutions, saturated with Cl_2; a pH <2 was employed for minimizing the parasitic contribution due to oxygen evolution reaction (OER) [21,22]; gaseous chlorine was electrochemically synthesized in a secondary cell, and bubbled into the working cell by means of a silicone pipe connected to a glass frit. A triple-body measuring cell was adopted, in which the working and counter electrode (WE and CE, respectively) compartments were divided by a Nafion® membrane. The two compartments were kept at 25 °C through a circulating bath thermostat. The reference electrode (RE) was placed in a