

Abstract

The request for electrode materials that exhibit satisfactory catalytic activity and high stability under particular conditions of potential and current density, has stimulated the synthesis of new devices, characterized by improved performances. Among these, electrodes based on RuO₂ and IrO₂ have found wide application in the field of DSA anodes[®] (*Dimensionally Stable Anodes*), thanks to their features of good electrocatalytic activity and high resistance to corrosion. An increase of the stability of materials can be obtained through the utilization of mixtures of oxides: along with the electrocatalytic oxide, other ones (TiO₂, SnO₂, *etc.*) are added, which have the double purpose of increasing the corrosion resistance of the electrode, while diluting the main oxide to minimize the production costs of the device.

As described in **Chapters 1 & 2**, the present research aims to the improvement of iridium-based electrodes, to be used for chlorine and oxygen evolution reactions, and to the development of “better” materials, which should be characterized by reduced costs of production and/or higher catalytic activity and stability. Their main uses concerns the chlor-alkali industry, where they are exploited as anodes for the chlorine production, and several electro-metallurgy processes, where the anodic process is represented by the oxygen evolution; a short review on these and others uses has been presented in **Chapter 3**. A not conventional preparative was chosen: the reactive sputtering, which belongs to the family of Physical Vapor Depositions (PVDs). The industrial preparative of DSA anodes[®] typically exploits the most common sol-gel technique, for reasons related to costs and operational simplicity; however, the sputtering synthesis may offer advantages, in terms of activity and reactivity of the final device, and, therefore, a specific investigation has been planned. Both preparation methods have been deeply discussed in **Chapter 4**.

Chapter 5 deals with the theoretical details on which nuclear techniques are based, because of the fact that their utilization for the characterization of this kind of materials is uncommon; a quite detailed review of theoretical notions about RBS and ERDA has been reported.

This work of thesis has been focused on films constituted by mixed oxides of iridium and titanium, prepared through the two different methods mentioned above (sol-gel and reactive sputtering), at 350 and 450 °C. Details on the preparation have been resumed in **Chapter 6**.

Structural and morphological analyses (AFM, RBS, ERDA, XRD, SEM-EDX, XPS) have been coupled to electrochemical studies (CV, PC, EIS), aiming to obtain a thorough description of the studied materials. All experimental details are included in **Chapter 7**. The

relationship between the structural and catalytic properties represents a key-step in the development of a new catalyst, and the information available in the literature is often unclear or contradictory, as in the case of the reaction mechanisms proposed for the chlorine evolution at noble-metal-oxide-based materials.

The *ex-situ* and *on-site* characterizations via XRD, RBS, AFM, CV and ERDA are discussed in **Chapter 8**. Preliminary studies on the behavior of the mixture, carried out via XRD, showed that for quantities exceeding 20 %mol in iridium, the crystallization of both components occurs in the rutile form (with reference to TiO₂, this phase is not kinetically favored under these experimental conditions) with partial formation of a solid solution, and the growth preferentially follows specific crystallographic directions (*e.g.*, the (110)). RBS, AFM, ERDA and CV analyses, carried out on samples prepared by sputtering, evidenced that films are more compact than those obtained by sol-gel, and constituted by columnar structures that are the source of a “meso/nano”-porosity; the latter can strongly affect the mass transport of reagents in the innermost portions of the electrode. Samples prepared by sol-gel, conversely, are characterized by a strongly wrinkled surface, which leads to an increase of the real active area of two orders of magnitude. The different structure of the materials greatly influences the stability of the devices: one of the causes of deactivation of DSA electrodes[®] consists on the passivation of the titanium metal at the interlayer: this event is plausibly more probable when the material exhibits cracks and macro-pores, which allow the permeation of the electrolyte solution, leading to device decommissioning. Moreover, a compactness of the deposit can also increase the resistance to dissolution of the electrocatalytic material, prolonging greatly the service life.

The mechanism of chlorine evolution reaction (ChIER) has been also investigated, and a detailed discussion can be found in **Chapter 9**. The investigation required a careful analysis using impedance spectroscopy and also the application of a mathematical model proposed by Conway in the early 90s. This approach has led to identify a sequence of stages in agreement with the so-called Volmer-Heyrovsky mechanism. The whole picture of experimental data becomes interpretable by assuming the involvement of a rather high coverage by reaction intermediates, which allows explaining the abnormalities occurred in terms of Tafel slopes and reaction orders. The impedance spectroscopy analysis pointed out an important contribution associated to the porosity for the samples prepared at 350 °C. Polarization experiments carried out at different temperatures provided information on the reactivity of the active site and on how this reactivity depends on both temperature and method of preparation. The high values of coverage involved in the process (around 0.7 - 0.8) have been confirmed by *ex-situ* measurements carried out on *ad hoc* samples, after heavy treatments of polarization

under ChLER conditions: RBS and XPS confirmed the presence of chlorine (radical anion) on sample surfaces (Chapter 10), and even in the bulk in the case of films fired at the lowest temperature. Moreover, **Chapter 10** included XRD tests on sample after strong polarizations under chlorine evolution and accelerated service life tests. Finally, **Chapter 11** collects the conclusions drawn on the basis of the whole picture of experimental results collected.