

Alessandro Minguzzi – GILDA Beamline Report 2008

Proposal number of the experiment/s:

08-01-769

Title of the experiment/s

The role of Ta reticular accommodation and speciation on the electrochemical properties of SnO₂-IrO₂-Ta₂O₅ nanostructured composites

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Date of measurements at GILDA

9 shifts on beamline BM08 from 16-APR-2007 to 20-APR-2007

We pointed out good quality beam with excellent signal/noise ratio.

Beamtime on other beamlines/facilities on the same research

None

Introduction.

A large variety of electrolytic processes (from electrometallurgy to water treatments, from chlor-alkali industry to hydrogen production by water electrolysis) becomes energetically significant only when it is combined with an efficient anodic process. The search for new materials for anodes in electrolyzers is restless as the oxygen evolution reaction, the more so in acid environment, represents a very severe test for the electrodic material. Only precious metal oxides are relatively stable. Among these, IrO₂ is, in principle, the most resistant. However the application of pure iridium oxide coatings is strongly restricted by high costs and limited electrode lifetime. Additives of non noble elements (e.g. Ta, Ti, Zr, Ce, Sb, Nb, Sn) are used to reduce the cost of the catalyst and/or to improve the coating properties [1-4]. Numerous binary and ternary oxide mixtures have been presented in the literature with respect to the anodic O₂ evolution in acidic media. In several cases the requirement of molar percentage of the expensive Ir component is still high (e.g. for IrO₂-ZrO₂ 80 mol % and for IrO₂-Ta₂O₅ mixtures, 70 mol % [5]). We have recently synthesized, by a common sol-gel route, composite-ternary SnO₂-IrO₂-Ta₂O₅

systems obtained both as powders and as films on Ti substrates. The composites, in any case composed by nanocrystalline particles, show superior electrochemical properties also with respect to the parallel SnO₂-IrO₂, systems. Tantalum, (even at low molar fraction) plays a key role in expanding the specific surface area, reducing the crystallite size and promoting the surface enrichment of iridium [6]. The combined effect of reducing the particle size and lowering the phase crystallinity produces an increase in surface defective sites which in turn increases the interfacial capacitance, thus doubling the capability of charge accumulation. The SnO₂-IrO₂-Ta₂O₅ samples XRPD patterns show only the peaks of the SnO₂ cassiterite structure but the general low degree of crystallinity reduces the possibility to either confirm or exclude, tassatively, the presence of minority phase components. The addition of Ta species to the mixture provokes, invariably, a decrease in crystallinity, and of crystallite dimension as testified by XRPD analysis. The pronounced effect of crystallinity reduction provoked by the addition of Ta is not related to a surface enrichment of these species. XPS data indicate, in fact, that the surface amount of Ta is more than one order of magnitude lower than the bulk one. The addition of Ta, instead, promotes the surface enrichment of Ir. The mechanisms leading to the final features of the composites need to be investigated in detail. Solid solutions are reported to form in the case of SnO₂-IrO₂ in all the range of compositions [1]; in the case of Ta₂O₅-IrO₂ composites Ta species are reported to substitute Ir in the lattice up to 30% molar fractions [2]. No data have been found in the literature concerning SnO₂-Ta₂O₅ solid solutions or the solubility of Ta species in the cassiterite lattice, but for (Co,Ta)-doped SnO₂ ceramics at extremely low (0.5 mol%) Ta₂O₅ content [7]. On the grounds of the similarity between Ir and Ta ionic radii it could be suggested that, in the ternary mixtures, Ta ions compete with Ir in the reticular substitution of Sn in the cassiterite lattice. In order to elucidate the role played by Ta species in promoting the electrocatalytic activity of the ternary mixtures, the local structures around the tantalum atom should be investigated by EXAFS spectroscopy. This approach which is particularly useful for investigating short-range pair-distribution functions in solids becomes essential in this special case in which the general degree of crystallinity is very low. Data concerning the coordination number around the absorbing atom and the bond length between the absorbing atom and its neighbouring atoms could be obtained.

Experiment.

In the case of binary oxides, spectra were obtained by recording the absorption coefficient of the sample after the L_{III} iridium absorption edge (11.215 keV). Otherwise, samples containing Ta were investigated only over L_{III} Ta absorption edge (9.881 keV). In the case of samples containing both elements, only Ta has been observed because L_{III} Ir edge is too close to L_I Ta edge (11.681 keV). Ir excitation could therefore partially overlap to Ta absorption region, thus causing the signal distortion. All the spectra were recorded at -193 °C (liquid nitrogen) in order to limit atomic vibrational motion thus increasing resolution.

For the two components samples, spectra were recorded in transmission mode. Otherwise, for samples containing tantalum, since the element content is low in all samples, spectra were recorded in fluorescence mode.

Results.

XANES and EXAFS spectra have been recorded on $\text{SnO}_2+\text{IrO}_2$ and on $\text{SnO}_2+\text{IrO}_2+\text{Ta}_2\text{O}_5$ samples, in order to highlight bulk structural features. In the case of $\text{SnO}_2+\text{IrO}_2$ mixtures (listed in table 1), samples have been analyzed in the L_{III} Ir absorption edge. The results are still under elaboration; nonetheless, some preliminary remarks can be given. Powders are synthesized by sol-gel method at 25°C , followed by drying at 80°C and calcination under O_2 flux. In the case of $\text{SnO}_2+\text{IrO}_2$ mixtures, three methods have been applied. In the case of the so-called “co-synthesis” (CS), the two precursors were mixed before the reaction. In the other cases, the sol-gel process involved only the Sn precursor. Ir precursor was then added by mechanical mixing (MM) or impregnation (Imp).

Sample number	Final composition	Precursor(s)	Precursors mixing method	$T_{\text{calcination}} / ^\circ\text{C}$
6	$\text{Sn}_{0.85}\text{Ir}_{0.15}\text{O}_2$	$\text{Sn}(\text{C}_4\text{H}_9\text{O})_4 + \text{IrCl}_3$	CS	450
7	$\text{Sn}_{0.85}\text{Ir}_{0.15}\text{O}_2$	$\text{Sn}(\text{C}_4\text{H}_9\text{O})_4 + \text{IrCl}_3$	CS	500
8	$\text{Sn}_{0.85}\text{Ir}_{0.15}\text{O}_2$	$\text{Sn}(\text{C}_4\text{H}_9\text{O})_4 + \text{IrCl}_3$	CS	550
10	$\text{Sn}_{0.85}\text{Ir}_{0.15}\text{O}_2$	$\text{Sn}(\text{C}_4\text{H}_9\text{O})_4 + \text{IrCl}_3$	MM	500
12 §	$\text{Sn}_{0.85}\text{Ir}_{0.15}\text{O}_2$	$\text{Sn}(\text{C}_4\text{H}_9\text{O})_4 + \text{IrCl}_3$	Imp	450
13	$\text{Sn}_{0.80}\text{Ir}_{0.2}\text{O}_2$	$\text{Sn}(\text{C}_4\text{H}_9\text{O})_4 + \text{IrCl}_3$	CS	500
14	$\text{Sn}_{0.93}\text{Ir}_{0.07}\text{O}_2$	$\text{Sn}(\text{C}_4\text{H}_9\text{O})_4 + \text{IrCl}_3$	CS	500
20	$\text{Sn}_{0.85}\text{Ir}_{0.15}\text{O}_2$	$\text{Sn}(\text{C}_4\text{H}_9\text{O})_4 + \text{IrCl}_3$	Imp	500
22 *	IrO_2	IrCl_3	-	500
24 +	$\text{Sn}_{0.85}\text{Ir}_{0.15}\text{O}_2$	$\text{SnCl}_4 + \text{IrCl}_3$	MM	500

§ In this case, only aqueous dilute HCl is used to dissolve IrCl_3

*Sample obtained as a standard by direct thermal decomposition

+ SnO_2 precursor obtained by precipitation from NH_4OH solution

Table 1: List of samples

XANES

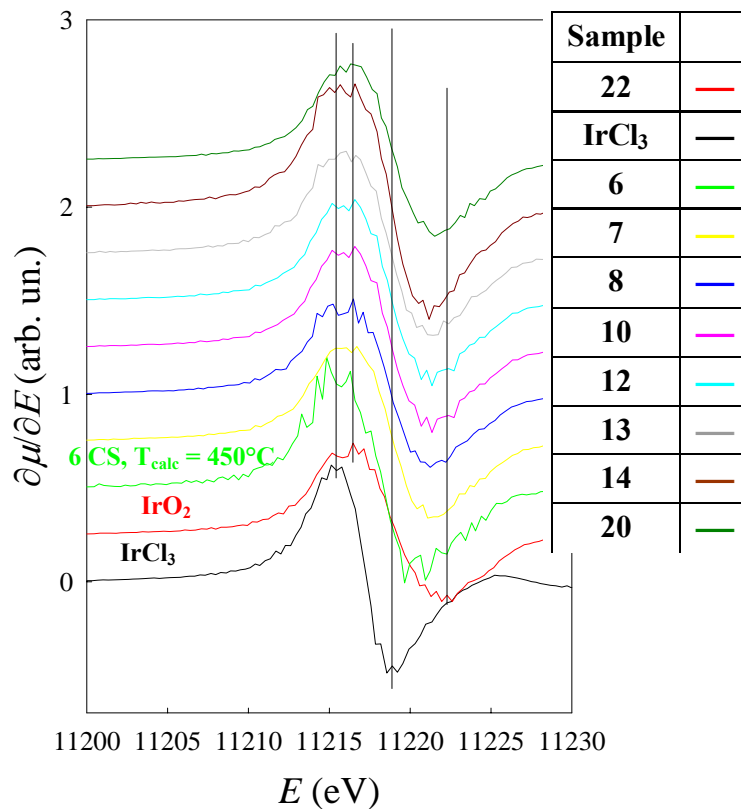


Figure 1. Derivative of XANES spectra recorded on IrO₂-SnO₂ binary mixtures and standards

Figure 1 shows the derivative of absorption coefficient on energy in dependence on the beam energy for all the samples analyzed in the energy range close to the Ir L_{III} absorption edge.

The comparison between spectra obtained on samples and on standards (IrO₂, sample 22, and IrCl₃) demonstrates the presence of mixed Ir III / IV in all the powders. This confirms the defective nature of the mixed oxide, as implied by the sol-gel preparation methodology, which, in turn, is at the basis of the pseudocapacitive currents observed by cyclic voltammetry.

Also the calcination temperature is observed to affect the final composition of the samples; for example, sample 6 (calcined at 450°C) signal has the highest similarities with the one obtained for IrCl₃ reference material, thus pointing to an incomplete decomposition of the iridium precursor salt, as already suggested by XPS analysis. Nonetheless, as evidenced by EXAFS analysis (see below), iridium oxide is still the main Ir component of this sample.

EXAFS

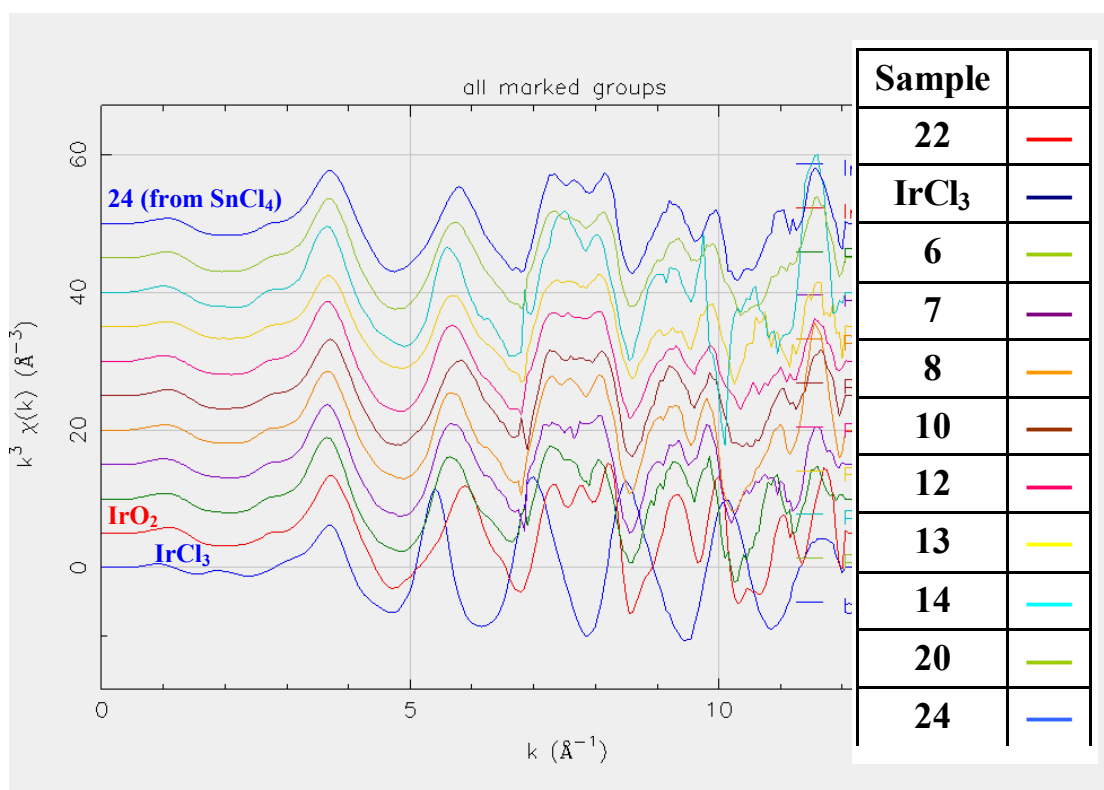


Figure 2. EXAFS spectra of IrO₂-SnO₂ binary mixtures and standards.

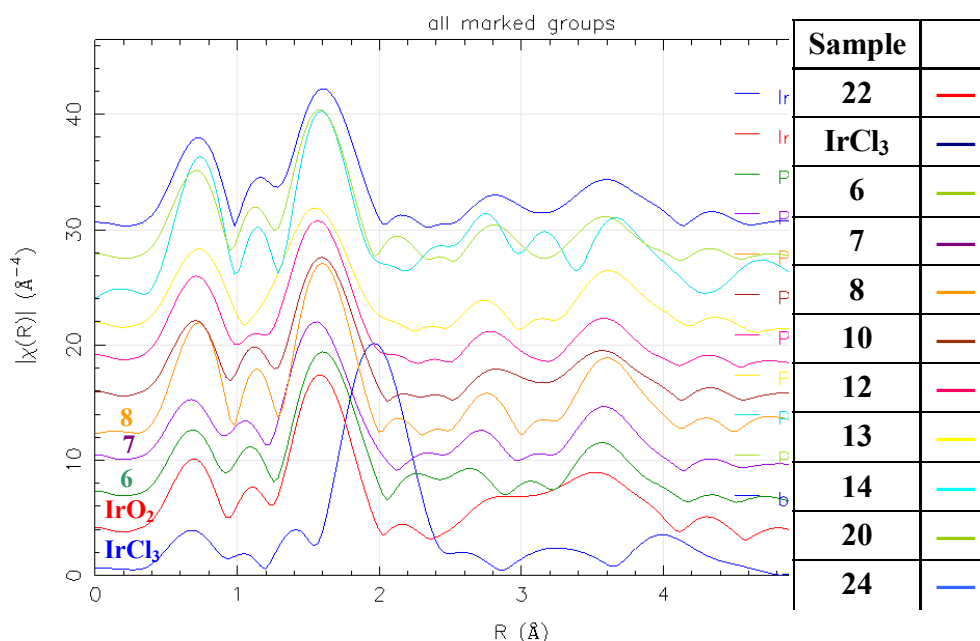


Figure 3. Fourier transforms EXAFS spectra of $\text{IrO}_2\text{-SnO}_2$ binary mixtures and standards.

Figure 2 represents EXAFS spectra obtained on $\text{SnO}_2 + \text{IrO}_2$ mixed oxide samples. After applying the Fourier transform on data reported in Fig 2, Fig 3 is obtained. All the spectra show good signal/noise ratio. All the characteristics, except for the one obtained on IrCl_3 standard, are rather similar. This means that the first coordination shell is represented by oxygen atoms, as in the case of IrO_2 standard. Nonetheless, some remarks can be given.

A difference is observable between samples 6, 7 and 8 (all obtained by co-synthesis of the precursors followed by calcination at 450, 500 and 550 °C respectively). Sample 8 is more ordered, as expected, because of the higher calcination temperature (higher crystallinity degree) and presents partial IrO_2 segregation, as highlighted by XRPD patterns. Sample 24 is the most similar to the IrO_2 standard; as can be noted in Fig 2, for both samples three small peaks are observable in the central region. Therefore in sample 24 IrO_2 is almost completely segregated, and its structure is independent on the host material (SnO_2). Interestingly, sample 24 is the only one obtained starting from SnCl_4 and by precipitation of the corresponding hydroxide by means of an NH_4OH solution. This emphasizes the role of the precursor nature and of the preparation technique on the final structure.

Data obtained on samples containing Ta are still under elaboration. However, at first sight, the expected Ta features are not observed.

Future Perspectives.

The research, focused on the synthesis and characterization of new mixed oxides as electrocatalysts for oxygen evolution reaction in acid media, will be devoted to the development of different Ir-based oxide mixtures and of their preparation methodologies (e.g. co-synthesis, impregnation, mechanical mixing, thermal, electrochemical). On the basis of the preliminary results obtained in the present project, XANES and EXAFS measurements provide key information on the structure of the samples, which are in complementary agreement with the electrochemical evidence. Therefore, a subsequent application will be presented for the prosecution of this research theme, to elucidate the role of synthetic pathway in relationship with the one of the dispersing matrix.

References.

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- 7) C. Wang, J. Wang, H. Chen, W. Wang, W. Su, G. Zang, P. Qi, *J. Phys. D: Appl. Phys.* 36 (2003) 3069.

Publications.

Alessandro Minguzzi, “*Advanced Oxygen Electrocatalysts for Energy Conversion Devices: Research and Development of Innovative Synthetic Paths and Investigation Methodologies*”. PhD thesis, 2007. Supervisor: Prof. S. Rondinini, co-tutor: Prof. S. Ardizzone, Dott. A. Vertova, University of Milan, Department of Physical Chemistry and Electrochemistry.

Conferences.

Some preliminary results will be shown during the conference: “GEI – ERA, Giornate dell’Elettrochimica Italiana – Elettrochimica per il Recupero Ambientale 2008”.