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## FLUORINATED ORGANOTINS AS PRECURSORS OF F-DOPED TIN DIOXIDE

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### ABSTRACT

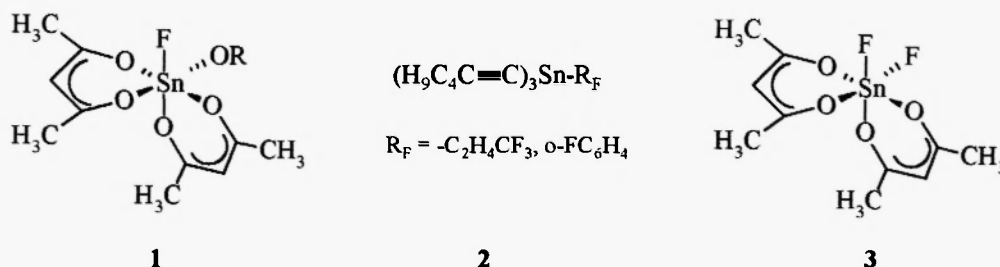
Alkoxyfluorodi( $\beta$ -diketonato)tins **1**, trialkynyl(fluoroorgano)tins **2** and difluorodi( $\beta$ -diketonato)tin **3** have been synthesised in order to prepare F-doped tin dioxide materials by the sol-gel route. After hydrolysis and densification in air at 550°C, these compounds lead to nanocrystalline tin dioxide powders containing the required amount of doping fluorine (4-8 at%) and exhibiting a resistivity at least two times lower than that reported for similar tin dioxide materials. In the case of **2**, thermally induced  $\beta$ - or  $\gamma$ -elimination reactions were evidenced by TG/MS, allowing the insertion of fluorine into the oxide network and the clean removal of the undesirable organics. The characterisation of sol-gel thin films prepared from **1** and **3** are also described. They exhibit excellent optical transparencies but resistivities ( $\rho > 7 \cdot 10^{-2} \Omega \cdot \text{cm}$ ) lower than those of thin layers prepared by pyrosol deposition from  $\text{SnCl}_4\text{-NH}_4\text{F}$  mixtures ( $\rho < 10^{-3} \Omega \cdot \text{cm}$ ). The presence of polluting carbon and the porosity of the sol-gel films are thought to be responsible for these resistivities.

### INTRODUCTION

Transparent conducting oxides deposited on glass substrates find wide spread applications in energy-efficient windows and, in photovoltaic or flat panel displays, as transparent electrodes.<sup>1</sup> Among these oxides, fluorine-doped tin dioxide (F:SnO<sub>2</sub>) exhibits the best mechanical and chemical durabilities, the best thermal stability, the least toxicity and the lowest cost.<sup>2</sup> F-doped tin dioxide is therefore of peculiar interest for architecture and environment applications. Furthermore, doped tin dioxide powder are used as conductive and antistatic agents in photographic films and paints.<sup>3</sup>

F:SnO<sub>2</sub> thin films have been prepared by many different techniques including r.f. sputtering,<sup>4</sup> chemical vapor deposition (CVD),<sup>5,6,7,8</sup> spray pyrolysis,<sup>9,10,11</sup> pyrosol deposition<sup>12</sup> and liquid vapor deposition (LPD).<sup>13</sup> Sol-gel process combined with deposition by spin- or dip-coating is a simple and low-cost route to produce oxide thin films.<sup>14</sup> It involves hydrolysis and condensation of metal alkoxides under mild conditions, performing a soluble oxide network which is then deposited on a substrate by spin- or dip-coating. A subsequent thermal treatment gives the desired thin films.<sup>15</sup> The preparation of undoped or antimony-doped SnO<sub>2</sub> films by the sol-gel method is rather well-documented.<sup>16,17</sup> Most of the sols have been prepared from tin(II) chloride,<sup>18</sup> tin(IV) alkoxide<sup>19</sup> or tin(II) carboxylate<sup>20</sup> and from antimony chloride<sup>21</sup> or alkoxide<sup>22</sup> as dopant source. However, very few reports have been addressed to the preparation of sol-gel F:SnO<sub>2</sub> materials,<sup>21</sup> likely due to a lack of a suitable precursor. Indeed, the hydrolysis step in the sol-gel method would lead to the release of the fluorine if the unimolecular precursors previously described, for instance tin(II) di(trifluoroacetate)<sup>5</sup> and tetra(hexafluoroisopropoxy)tin(IV),<sup>7</sup> were used. To circumvent this inconvenience, we have designed two new families of tin compounds. First of all, we have chosen to synthesise alkoxyfluorobis( $\beta$ -diketonato)stannanes **1** including a covalent tin-fluorine bond, which was expected to be stable upon mild hydrolysis conditions, and bearing, on one hand, alkoxide groups (known for their fast hydrolysis kinetics) and, on the other hand,  $\beta$ -diketonato ligands (known for their chelating properties which diminish hydrolysis rates) to prevent precipitation during the hydrolysis stage.<sup>22</sup> Our second approach exploited thermally-induced elimination reactions to create Sn-F bonds during the thermal treatment used to densify the final materials. Trialkynyltin derivatives being suitable starting materials to yield soluble condensed species upon hydrolysis,<sup>23</sup> we have prepared trialkynyltin compounds **2** possessing a trifluoropropyl or a *o*-fluorophenyl group.<sup>24</sup> After hydrolysis and thermal treatment, both families have led to nanocrystalline conductive F-doped tin dioxide powders.<sup>24,25</sup> Semiconducting fluorine containing tin dioxide thin films have also been prepared by spin-coating and spray-pyrolysis from alkoxyfluorobis( $\beta$ -diketonato)tins **1**.<sup>26</sup>

In this paper, we report a comparison of the properties of the various sol-gel materials prepared from these two precursor families and we also describe the optical and electrical properties of tin dioxide thin films prepared by spin-coating from difluorodi(pentan-2,4-dionato)tin(IV) **3**.<sup>27</sup>



**Scheme 1:** Sol-gel precursors used in this study.

## MATERIALS AND METHODS

Precursors **1-3** were synthesised as previously reported.<sup>22,24,27</sup> Hydrolysis of **1** (resp. **2**) with 2 eq. of water (resp. 8 eq.) in  $\text{CH}_3\text{CN}$  (resp.  $\text{PrOH}$ ) was carried out as previously described,<sup>22,24</sup> yielding xerosol  $\text{X}_2^1$  (resp.  $\text{X}_8^2$ ) after drying. Compound **3** was hydrolyzed as follows. In a Schlenk tube, water (0.41 g, 23 mmol) in 2,2,2-trifluoroethanol (0.9 mL) was added dropwise to a solution of **3** (3.55 g, 10 mmol) in  $\text{CF}_3\text{CH}_2\text{OH}$  (36 mL). After the reaction mixture was stirred at room temperature for 1 hour, the volatile products were removed under reduced pressure. The resulting powder was washed with *n*-hexane ( $2 \times 30$  mL) and dried under vacuum at  $70^\circ\text{C}$  for 6 hours to yield 2.6 g of a white xerosol  $\text{X}_2^3$ .

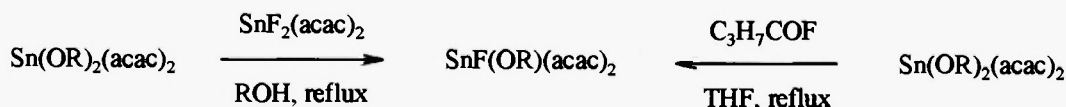
Elemental analyses were performed in the Center of Chemical Analysis of CNRS, Vernaison, France. IR spectra (KBr pellets) were recorded on a FTIR Perkin-Elmer spectrophotometer. The thermogravimetry analysis was carried out with a Netzsch STA 409 under helium flow at a heating rate of  $5^\circ\text{C}\cdot\text{min}^{-1}$ , coupled to a Thermostar (Balzers Instruments) mass spectrometer. The resistivity of the thermolysed xerosols were estimated according to a previously described method.<sup>25</sup>

The spin-coated films prepared from  $\text{X}_2^1$  in  $\text{CH}_3\text{CN}$  were obtained as previously reported.<sup>26</sup> For  $\text{X}_2^3$ , the deposition solutions ( $C = 0.27$  and  $0.37$  M) were prepared by dissolving the previous xerosol in the suitable amount of  $\text{CF}_3\text{CH}_2\text{OH}$  and they were, if necessary, filtered before use. They were then deposited by spin-coating over commercially available glass microslides with a TR110 apparatus from Karl Suss operating at 1500 rpm. Multilayer deposition was necessary to obtain films of sufficient thickness. After each deposit, the film was dried at  $150^\circ\text{C}$  for 30 min and then sintered in air in a furnace ( $550^\circ\text{C}$  for 15 min).

Film composition was determined by Electron Probe Microanalysis (EPMA) and by Auger Photoelectron Spectroscopy. The film morphology was studied by Scanning Electron Microscopy (SEM) with a JEOL-JEM-820 apparatus. The film optical transmission was determined thanks to a HP 8453 spectrophotometer in the 300-800 nm spectral range. Sheet resistances were measured with a four probe technique and film resistivities were obtained by the Van der Pauw method.

## RESULTS AND DISCUSSION

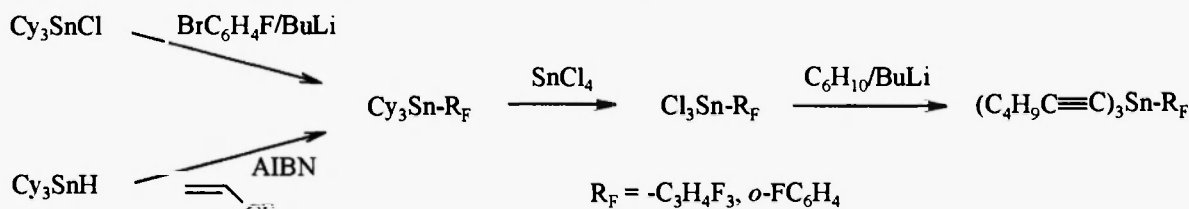
The detailed syntheses of the precursors investigated in this study have been previously published.<sup>22,24</sup> Two synthetic pathways can be used to get alkoxyfluoro( $\beta$ -diketonato)tin complexes **1** (Scheme 1). The first one consists in a conproportionation reaction between a dialkoxy( $\beta$ -diketonato)tin complex and the difluoro( $\beta$ -diketonato)tin compound **3**, giving the desired precursor in 60-90% conversion rates depending on the nature of the alkoxy group. Another possible route is the direct fluorination of the dialkoxy( $\beta$ -diketonato)tin complex with butanoyl fluoride. In both cases, six-fold coordinated complexes of  $C_1$  symmetry were obtained as shown by solution multinuclear NMR analyses.



**Scheme 2 :** Synthesis of alkoxyfluoro( $\beta$ -diketonato)tin complexes **1**

Trialkynyl(fluoroorgano)tins **2** were prepared in three steps from tricyclohexyltin hydride or chloride in an overall 40% yield (Scheme 3). A hydrostannation or a nucleophilic substitution reaction gave the tricyclohexyl(fluoroorgano)tins. The selective electrophilic cleavage of the tin-primary alkyl or tin-phenyl

bond with tin tetrachloride yielded the corresponding tin trichloride which was finally converted into the trialkynyl(fluoroorgano)tins by reaction with 3 eq. of hexynyllithium.



**Scheme 3** : Synthesis of trialkynyl(fluoroorgano)tins **2**.

The hydrolytic behaviour of molecules **1-3** in low boiling point solvents was studied in order to prepare materials by the sol-gel route. Qualitative data for different hydrolysis ratios  $h = [\text{H}_2\text{O}]/[\text{precursor}]$  are reported in Table 1. Stable sols in  $\text{CH}_3\text{CN}$  and  $\text{CF}_3\text{CH}_2\text{OH}$  were obtained for  $h$  up to 2 in the case of **1** and **3**, respectively. For the trialkynyltin precursor **2**, soluble species were prepared for  $h$  up to 8.

Precursor	Solvent	$h = 0.5$	$h = 1$	$h = 2$	$h = 3$	$h = 8$
<b>1</b> $\text{R} = ^i\text{Am}$	$\text{CH}_3\text{CN}$	S	S	S	G	-
<b>2</b> $\text{R}_F = \text{C}_3\text{H}_4\text{F}_3$	$^i\text{PrOH}$	-	-	-	-	S
<b>3</b>	$\text{CF}_3\text{CH}_2\text{OH}$	S	-	S	S + P	-

**Table 1**: Hydrolytic behaviour of precursors **1-3**. S: sol, G: gel, P: precipitate.

By evaporation of the solvent, these sols furnished xerosols, labeled  $\text{X}_2^1$  (**1**,  $h = 2$ ),  $\text{X}_8^2$  (**2**,  $h = 8$ ) and  $\text{X}_2^3$  (**3**,  $h = 2$ ). Xerosol  $\text{X}_2^1$  likely contained stannic fluorinated oxo-oligomeric or -polymeric species bearing  $\beta$ -diketonate ligands with a F/Sn atomic ratio equal to 1.<sup>22</sup> As expected, the Sn-F bond remained unaffected by the hydrolysis stage. Upon thermal treatment,  $\beta$ -diketonate ligands pyrolyzed in two steps at 200 and 320°C and fluorine was continuously lost as fluorhydric acid from 230 to 550°C.<sup>25</sup> Xerosol  $\text{X}_8^2$  included oxo-hydroxoorganotin oligomers where each tin atom is bounded to a 3,3,3-trifluoropropyl chain. During thermolysis, the latter was released as 3,3,3-trifluoropropene and 1,1-difluorocyclopropane which indicated that  $\beta$ - and  $\gamma$ -elimination reactions have occurred.<sup>24</sup> This afforded the insertion of fluorine in the oxide network and the removal of the organics. Xerosol  $\text{X}_2^3$  was characterized by elemental analysis, IR spectroscopy and TG/MS. By IR spectroscopy, bands due to acetylacetonato ligands coordinated to tin were observed at 1583, 1545 and 1360  $\text{cm}^{-1}$  (respectively  $\nu_{\text{sym}}(\text{C-O}) + \nu_{\text{asym}}(\text{C-C})$  and  $\delta(\text{CH}_3)$ ). A strong resonance at 1253  $\text{cm}^{-1}$  accounted for the presence of trapped  $\text{CF}_3\text{CH}_2\text{OH}$ . Broad bands between 700 and 500  $\text{cm}^{-1}$  were in favour of the formation of Sn-O-Sn and Sn-OH bonds. Furthermore, elemental analysis of  $\text{X}_2^3$  gave an atomic ratio F/Sn = 1.6. The nature of the remaining organics was confirmed by TG/MS analyses. Four mass losses were observed on TG curves between 50 and 650°C and the main molecules detected by MS measurements were  $\text{H}_2\text{O}$ , HF, acetone, trifluoroethanol and traces of acetic acid. The various pyrolysis stages can be rationalized as follows: (1) departure of adsorbed water (87°C, 5% mass loss); (2) elimination of trifluoroethanol and first step of acetone release (197°C, 8% mass loss); (3) loss of structural water, part of fluorine, traces of acetic acid and second step of the acetone removal (330°C, 11% mass loss); (4) subsequent loss of fluorine and remaining carbon as  $\text{CO}_2$  (495°C, 6% mass loss). The chelating groups were presumably lost via retro-Claisen reaction.<sup>28</sup> As previously found in the case of  $\text{X}_2^1$ ,<sup>25</sup> the Sn-F bond cleavage in the presence of traces of water led to the fluorine release. To summarise, xerosol  $\text{X}_2^3$  is mainly formed of fluorinated stannic oxo-hydroxopolymeric species including remaining  $\beta$ -diketonato ligands and trifluoroethanol molecules. However, in contrast to  $\text{X}_2^1$ , the F/Sn ratio has decreased upon hydrolysis which indicated that the Sn-F bond in **3** was more sensitive towards hydrolysis than it was in **1**.

As thermal treatment at 500°C removed most of the fluorine and the organics, the previous xerosols were thermolyzed in air at 550°C for 15 minutes. Powder X-ray diffraction measurements confirmed the formation of nanocrystalline cassiterite  $\text{SnO}_2$  materials.<sup>24,25</sup> In each case, the fluorine content (4-8 at%) fell into the range of doping amount and the resistivities of the powders were noticeably lower than these found

for undoped or Sb-doped SnO<sub>2</sub> powders (Table 2). The main difference between the two families of precursor herein studied lies in the carbon amount in the final material. The fluorodi( $\beta$ -diketonato)tin complexes **1** and **3** indeed led to carbon-rich samples with slightly lower conductivities. These results demonstrated that thermally-induced  $\gamma$ -elimination reaction is a very efficient way to include fluorine in SnO<sub>2</sub> and to remove cleanly the organics in sol-gel materials.

Xerosol	Solvent	$\rho$ ( $\Omega$ .cm)	F/Sn (at%)	C/Sn (at%)	Ref.
X <sub>5</sub> <sup>1</sup>	CH <sub>3</sub> CN	0.7	4-6	10-12	25
X <sub>8</sub> <sup>2</sup>	<sup>1</sup> PrOH	0.3	5	< 2.5	24
X <sub>2</sub> <sup>3</sup>	CF <sub>3</sub> CH <sub>2</sub> OH	1	8	12-16	this study
SnO <sub>2</sub> Aldrich		2 10 <sup>3</sup>			25
SnO <sub>2</sub> :Sb		2			3

**Table 2:** Properties of the F-doped tin dioxide powders prepared from precursors **1-3**.

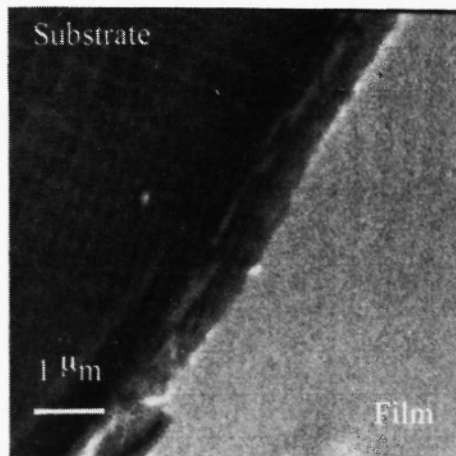
Thin films were prepared by spin-coating from xerosol X<sub>2</sub><sup>3</sup>. Multilayer deposition and thermal treatment after each deposit were necessary to obtain films with good optical properties. As pointed out above by TG/MS measurements, a heat treatment above 450°C removed most of the fluorine and of the organics. In addition, it was found that within the temperature range 450-550°C, there was no noteworthy difference in the film properties. Results described hereafter therefore refer to films annealed at 550°C in air.

Concentration (M)	Number of deposits	Thickness t (nm)	Transmittance T (%)	Sheet Resistance R (k $\Omega$ )
0.27	3	210	95	9000
	7	450	90	1000
	9	530	85	40
	11	600	85	20
0.37	3	310	95	6000
	7	520	85	200
	9	670	85	5
	11	820	85	0.9

**Table 3:** Thickness, optical transmission and sheet resistance of the spin-coating thin films prepared from two different concentrations of X<sub>2</sub><sup>3</sup>.

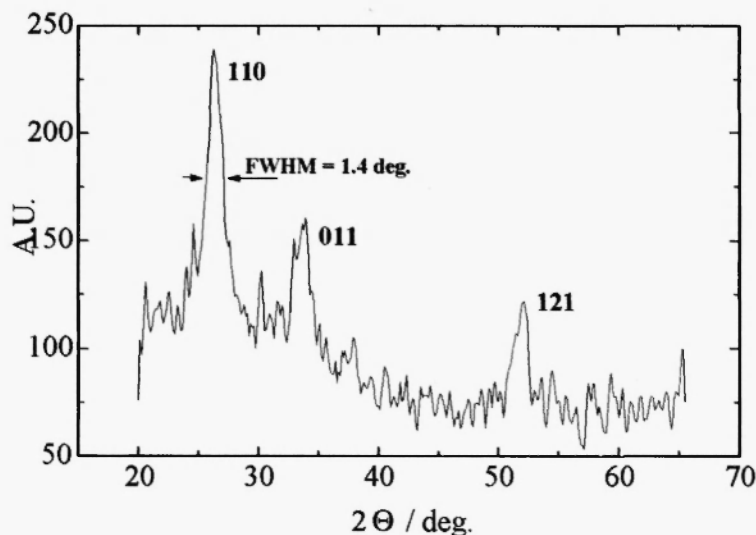
Whatever the preparation conditions of the films, the optical transparency was higher than 85% (Table 3). The thickness of the thin films increases linearly with the number of coatings with a concomitant decrease of the sheet resistance. The thicker films were prepared from the most concentrated solution and exhibited the lower sheet resistances. However, solutions more concentrated than 0.4 M gave thicker films but with very poor optical transmittances. The lowest value of sheet resistance was 900  $\Omega$  /  $\blacksquare$  for a thickness of 820 nm which corresponds to a resistivity value of 7.4 10<sup>-2</sup>  $\Omega$ .cm.

The surface morphology was studied by Scanning Electron Microscopy. As for films prepared from xerosol X<sub>2</sub><sup>1,26</sup>, cracks were observed for film thickness below 400 nm. As the number of deposits was increased, cracks progressively disappeared even if few localized defects were still present on the surface. For more than ten layers, the surface is smooth with no conspicuously coarseness at the microscope magnification used. In addition, the thicker films were rather homogeneous as depicted by the cross-section exhibited Figure 1.



**Figure 1:** SEM cross-section micrograph of a 820 nm spin-coated F:SnO<sub>2</sub> film heat treated at 550°C for 15 minutes in a furnace

The nature and the chemical composition of the most conductive films were determined. The XRD pattern of an eleven coating film prepared from a 0.37 M solution is consistent with the formation of a crystallised SnO<sub>2</sub> thin film with cassiterite structure (Figure 2). The crystallite size, calculated from the line width by using the conventional Laue-Scherrer formula,<sup>21</sup> was about 6 nm, a lower value than those (50 nm) reported for highly conductive films prepared from CVD.<sup>30</sup>



**Figure 2:** X-ray diffraction pattern (Cu K<sub>α</sub>) of a 820 nm spin-coated F:SnO<sub>2</sub> film sintered at 550°C for 15 minutes in a furnace

The fluorine and the carbon contents, measured by EPMA, was found to be F/Sn = 7 at% and C/Sn = 12 at%. Auger analysis as a function of the depth indicated that the most of the carbon was localized at the very near surface and that the C/Sn atomic ratio reached a plateau value of 3% for an etching level of 10% of the whole film thickness. As previously found in the case of thin films prepared from X<sub>2</sub><sup>1,26</sup> the fluorine

amount was higher than it is actually required for doping (# 1 at%) and the layer was polluted by undesirable carbon.

The spin-coated films prepared from  $X_2^3$  are two orders of magnitude more conductive than those made from  $X_2^1$  (Table 4). The lower carbon content of the films prepared from  $X_2^3$  was likely at the origin of the lower resistivities observed. The latter however remained three times and two orders of magnitude higher than the best values reported for F:SnO<sub>2</sub> films prepared by dip-coating<sup>21</sup> and pyrosol deposition,<sup>12</sup> respectively. On the other hand, the optical transmittances were appreciably better than these described for dip-coating films.<sup>21</sup> It is worthwhile to mention that the spray deposition technique has allowed to decrease notably the thin film resistivities in the case of  $X_2^1$ . Nonetheless, this could not be generalized with each precursor. For instance, the sprayed films prepared at 500°C from a 0.2 M solution of **3** in CF<sub>3</sub>CH<sub>2</sub>OH (thickness: 90-350 nm; F/Sn = 4.5-5.5 at%) indeed show resistivities in the range 0.07-0.13 Ω.cm<sup>31</sup>, similar to those found by spin-coating from  $X_2^3$ .

Precursor	Method	t (nm)	ρ (Ω.cm)	%T	Ref.
$X_2^1$	Spin-coating	450	20	80-90	26
	Spray	290	1 10 <sup>-2</sup>	85	26
$X_2^3$	Spin-coating	850	7.4 10 <sup>-2</sup>	80	this study
	Dip-coating	2960	2.4 10 <sup>-2</sup>	50-60	21
	Pyrosol deposition	600	6 10 <sup>-4</sup>	85	12

**Table 4:** Physical properties of the thin films prepared. t: thickness; ρ: resistivity; T: optical transmittance.

The origin of these rather poor electrical properties still remains unclear due to the number of factors acting upon the thin film resistivity. The low conductivities of the spin-coated and, to a less extent, of the sprayed films prepared from the precursors investigated in this study are presumably due to the combination of: 1) fluorine excess and carbon pollution, leading to structural defects; 2) porosity arising from the removal of the remaining organics during the thermal treatment.<sup>26</sup> These factors strongly affect the macroscopic mobility of the charge carriers and, therefore, the electronic conductivity. In view of these results, xerosol  $X_2^3$  ought to be a promising precursor of spin-coated films owing to its low carbon content. However, it was available in too low amount to be investigated so far.

Finally, it is worthwhile to mention that the presence of carbon in nanocrystalline F:SnO<sub>2</sub> materials seems to be an asset for electrochemical applications. Indeed, the carbon-rich F:SnO<sub>2</sub> powder obtained from  $X_2^1$  was recently used as an efficient electroactive material to study chloride oxidation in aqueous media.<sup>32</sup> Furthermore, preliminary studies have showed that the electrochemical behaviour of carbon-rich F:SnO<sub>2</sub> films prepared from  $X_2^1$  by spray-pyrolysis was similar to this of carbonaceous thin film electrode materials.<sup>33</sup>

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