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TiO₂-CeO₂ Nanometric Powders Prepared by Sol-Gel Method

Maria Zaharescu^[a], Alexandra Wittmar^[a,b], Valentin Teodorescu^[c], Cristian Andronesu^[a], Matthias Wittmar^[b], Michael Veith^{[b]*}

Dedicated to Professor Martin Jansen on the Occasion of His 65th Birthday

Abstract. Nanometric powders in the TiO₂-CeO₂ system were synthesized using sol-gel methods aiming at corrosion inhibitor preparation. The precursors employed were Ti(OiPr)₄ as TiO₂ source and Ce(NO₃)₃·6H₂O or (CH₃CO₂)₃Ce·xH₂O as CeO₂ source. Several parameters were varied, like the cerium precursor (cerium nitrate or cerium acetate) and the TiO₂:CeO₂ molar ratios. For both cerium sources binary powders with TiO₂:CeO₂ = 4:1 or 1:1 molar ratios were prepared. The obtained materials were dried overnight in the oven at 100 °C and then thermally treated for 1 h at 400 °C with a heating rate of 1 °C/min in order to eliminate the water and organic residues. In all cases, nanometric – predominantly amorphous – powders have been obtained which crystallized after the 1 h thermal treatment at 400 °C. The only exception was recorded for the TiO₂:CeO₂ = 4:1 composition prepared from the Ce(NO₃)₃·6H₂O precursor which remained amorphous after the thermal treatment. Even though the primary particle sizes were ~ 4 – 5 nm, the material is constituted from aggregates larger than 50 nm. The desired presence of cerium in two valence states, necessary in active corrosion protection, was achieved and it was put into evidence by XPS and DTA/TGA for the TiO₂:CeO₂ = 4:1 binary compositions. Future studies have to be done in order to reduce the agglomeration of the material.

Keywords: Sol-gel processes; Titanates; Rare earth compounds; Nanostructures; Inhibitors

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3 Metal oxides play an important role in many fields such as electrochemistry, catalysis, gas
4 sensing, corrosion protection, etc. In the last years, titanium dioxide (TiO_2) has raised a large
5 interest due to its non-toxicity, chemical stability and low cost. Recently, applications of TiO_2
6 films for cathodic protection of metals under ultraviolet (UV) illumination have been reported
7 [1,2]. Unfortunately, pure TiO_2 coating cannot be used under dark conditions due to its charge
8 recombination. On the other hand, the rare earth metal oxides and especially cerium dioxide
9 (CeO_2), possess a relatively high reactivity and find applications in different fields including
10 corrosion protection. This is due to the fact that cerium has an affinity to oxygen, and bonding
11 between cerium and oxygen is unlikely to be broken by applied cathodic potentials.
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27 According to the literature data, TiO_2 - CeO_2 powders and films were prepared for use as
28 catalysts [3-7], electrochromic device materials [8-13], oxygen sensors [14] and several other
29 applications [15-28]. Even though TiO_2 , CeO_2 and their binary powders are mostly discussed
30 in the literature due to their catalytic behaviour, in recent years, these oxides have found new
31 applications as corrosion inhibition dopants for silica based sol-gel corrosion protection
32 coatings which are considered environmentally friendly by comparison with the traditional
33 chromate conversion coatings.
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46 Light materials with high weight/strength ratios gain in importance in the fields of automotive
47 and aeronautical industries due to the new concerns regarding low CO_2 emissions. As a
48 consequence, the use of magnesium, aluminium and their alloys is continuously increasing
49 and the need to prevent and retard their natural deterioration process using environmentally
50 compliant methods has become more and more evident. The replacement of hazardous
51 chromate conversion coatings constituted the object of many studies in the last period of time
52 [29-39].
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One of the most promising alternatives for the corrosion protection pretreatments is offered by the sol-gel technology which is environmentally unproblematic and compatible with the organic paints used in most of the applications. Within the sol-gel family, hybrid films are the most promising but unfortunately they are able to offer only a barrier protection as long as they are crack free and pore free. To extend the protection offered by those materials in an active corrosion protection, the use of inhibitors which can induce the “self healing” effect is required. Rare earth elements like cerium and lanthanum are versatile inhibitors. The corrosion protection mechanism offered by the cerium ions was widely studied and it is generally accepted that cerium ions lead to precipitation of cerium oxides and hydroxides which hinder the cathodic reduction reaction. On the other hand, Ce^{3+} can be oxidized to Ce^{4+} . These Ce^{4+} ions due to their high oxidizing potential are able to promote the superficial oxidation of the aluminium alloy to aluminium oxides conferring a natural protection layer [40-44].

The mostly preferred precursors for binary oxide materials were $\text{Ti}(\text{OiPr})_4$ as TiO_2 source and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ [5-7,15,16,27,28] or $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ [9,45] as CeO_2 source. The literature data suggest that the binary powders in the TiO_2 - CeO_2 system may be realized in any proportion of the two oxides from 100% TiO_2 – 0% CeO_2 to 0% TiO_2 – 100% CeO_2 . In the present work, binary powders in the TiO_2 - CeO_2 system were prepared by sol-gel method using two cerium sources ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $(\text{CH}_3\text{CO}_2)_3\text{Ce} \cdot x\text{H}_2\text{O}$). For all binary materials, two different oxide molar ratios were taken into consideration, $\text{TiO}_2:\text{CeO}_2 = 4:1$ or $1:1$. The sol-gel method allows the preparation of some special mixed oxides in the system TiO_2 - CeO_2 and the most significant steps can be summarized by the following reactions (equations 1 – 4):

In basic conditions, the hydrolysis step takes place according to the following mechanism:

In the presence of a cerium salt, the basic hydrolysis can take place after the following reactions:

In the sol-gel method, when the two precursors react simultaneously, some chemical bonds are expected to be formed between them:

This study is mainly focused on the preparation of new cerium containing inhibitors, which can act both as reinforcing agents for the hybrid matrix which help obtaining a pore free and crack free material and also can promote the “self healing” effect by the presence of the cerium ions in two valence states Ce^{3+} and Ce^{4+} . For the success of the protection offered, it was desired to obtain nanometric, amorphous and non-aggregated powders which can form good suspensions in water and/or alcohol media without the use of surfactants.

Results and Discussion

Under the experimental conditions presented above, light yellow, highly dispersed powders were obtained. In the case of binary powder preparation, the hydrolysis – condensation reactions went differently depending on the cerium source. In the case of the cerium nitrate precursor, which is totally soluble in alcohol, a mixture at molecular level of the two precursors was possible allowing, as will be discussed later, the entrapment of cerium ions in the TiO_2 structure. Cerium acetate, which is only partially soluble in ethanol, was not completely dispersed and its conversion to CeO_2 took place most probably later, after the complete precipitation of TiO_2 .

The thermal behaviour of the binary powders was determined by DTA/TGA and is presented in Table 1; for exemplification, two graphs are presented in Figures 1 and 2.

Table 1 DTA/TGA results for the TiO₂-CeO₂ powders.

Sample	Temperature range [°C]	Effects [°C]		Weight loss [%]	Assignment
		endo	exo		
TiO ₂ Ti(O-iC ₃ H ₇) ₄	20-200	98	-	18.85	Adsorbed water and ROH evolution
	150-1000	-	410		Burning out of the organic residues
	20-1000			18.85	
CeO ₂ , from Ce(NO ₃) ₃ ·6H ₂ O	20-200	108	-	4.17	Adsorbed water and ROH evolution
	200-500	-	-	3.57	Structural OH evolution
	100-1000	-	-	1.30	
	20-1000			9.04	
CeO ₂ (CH ₃ CO ₂) ₃ Ce·xH ₂ O	20-200	98	-	5.11	Adsorbed water and ROH evolution
	200-400	253	-	8.74	Acetates decomposition and the organic residues evolution
	400-600	513	-	3.66	Structural OH evolution
	600-1000	-	-	1.61	
	20-1000			19.12	
TiO ₂ :CeO ₂ 80:20 Ti(O-iC ₃ H ₇) ₄ Ce(NO ₃) ₃ ·6H ₂ O	20-200	86	-	14.16	Adsorbed water and ROH evolution
	200-500	268	-	3.084	Structural OH evolution
	500-1000	-	655	+0.238	Ce ³⁺ oxidation to Ce ⁴⁺
	20-1000			17.01	
TiO ₂ :CeO ₂ 50:50 Ti(O-iC ₃ H ₇) ₄ Ce(NO ₃) ₃ ·6H ₂ O	20-200	93	-	8.90	Adsorbed water and ROH evolution
	200-500	261 419	- -	4.87	Structural OH evolution
	500-1000	-	698	0.29	Ce ³⁺ oxidation to Ce ⁴⁺
	20-1000			14.05	
TiO ₂ :CeO ₂ 80:20 Ti(O-iC ₃ H ₇) ₄ (CH ₃ CO ₂) ₃ Ce·xH ₂ O	20-200	84	-	11.64	Adsorbed water and ROH evolution
	200-500	-	278	13.74	Acetates decomposition and burning out of the organic residues
	500-1000	-	700	+0.2346	Ce ³⁺ oxidation to Ce ⁴⁺
	20-1000			25.27	
TiO ₂ :CeO ₂ 50:50 Ti(O-iC ₃ H ₇) ₄ (CH ₃ CO ₂) ₃ Ce·xH ₂ O	20-200	98	-	7.03	Adsorbed water and ROH evolution
	200-500	-	265	19.57	Acetates decomposition and burning out of the organic residues
	500-1000	-	800	-	Ce ³⁺ oxidation to Ce ⁴⁺
	20-1000			26.70

Figure 1 DTA/DTG curves for the $\text{TiO}_2\text{:CeO}_2$ (80:20) sample prepared from $\text{Ti}(\text{OiPr})_4$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

Figure 2 DTA/DTG curves for the $\text{TiO}_2\text{:CeO}_2$ (80:20) sample prepared from $\text{Ti}(\text{OiPr})_4$ and $(\text{CH}_3\text{CO}_2)_3\text{Ce} \cdot x\text{H}_2\text{O}$.

According to the recorded DTA/TGA curves, differences could be noticed in the thermal

behaviour of the prepared powders starting with different cerium precursors. In the case of the binary powders obtained starting with cerium nitrate, three thermal effects could be noticed. The large endothermal effect at 88 °C could be assigned to the dehydration of the binary powders followed by a smaller endothermal effect at about 290 °C assigned to structural OH evolution. At 655 °C an increase of the weight was noticed accompanied by an exothermal effect that could be assigned to Ce^{3+} to Ce^{4+} oxidation. Based on the results obtained by thermal analysis one may conclude that in this case powders with composition of titanium-cerium oxy-hydroxide were obtained.

In the case of the binary powders obtained starting with cerium acetate, the endothermal effect at 84 °C could be assigned to the dehydration of the powders. The endothermal effect at 264 °C followed by the exothermal one at 278 °C could be assigned to the decomposition of the acetates kept in the composition of the prepared powders and the subsequent oxidation of CO resulted from the acetate decomposition to CO_2 . At about 700 °C, a weight increase is noticed due to the oxidation of Ce^{3+} to Ce^{4+} . Based on the data obtained by DTA/TGA, one may conclude that when cerium was introduced in the reaction, a titanium-cerium hydrated acetate complex was formed, as in the case of cerium acetate. In both cases, in the initial powders as well as in the powders thermally treated at temperatures lower than 650 °C at least a part of cerium occurs in the valence form Ce^{3+} . Differences in the composition of the initial powders are supposed to determine differences in their structure and properties.

Based on the results of the DTA/TG analysis, all the powders further investigated were thermally treated at 400 °C for one hour, with a heating rate of 1 °C/minute.

The XRD diffraction patterns for the $\text{TiO}_2\text{:CeO}_2$ (80:20) binary materials prepared with the two different cerium sources thermally treated as mentioned above are presented in Figures 3 and 4.

Figure 3 The XRD diffraction pattern for the $\text{TiO}_2\text{:CeO}_2$ (80:20) powder obtained from $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, thermally treated at 400 °C.

Figure 4 The XRD diffraction pattern of the $\text{TiO}_2\text{:CeO}_2$ (80:20) powder obtained from $(\text{CH}_3\text{CO}_2)_3\text{Ce} \cdot x\text{H}_2\text{O}$ thermally treated at 400 °C (lines are from anatase and cerianite).

The $\text{TiO}_2\text{:CeO}_2$ (80:20) powder obtained from $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Figure 3) could be considered amorphous, the characteristic diffraction patterns for crystalline TiO_2 , CeO_2 and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ being absent. The two broad bands recorded in the spectra are characteristic

for an amorphous state or for an early stage of crystallization. In the case of the $\text{TiO}_2\text{:CeO}_2$ (80:20) powder obtained from $(\text{CH}_3\text{CO}_2)_3\text{Ce}\cdot x\text{H}_2\text{O}$ the presence of quasi-crystalline anatase and cerianite was noticed. The structural parameters calculated based on the XRD investigation are summarized in Table 2. According to the XRD data, all of the thermally treated powders present a low crystallisation, with one exception: the $\text{TiO}_2\text{:CeO}_2$ (80:20) prepared from $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ which is predominantly amorphous.

Table 2 Crystallite size, cell parameters and crystalline phases as determined from XRD diffraction patterns.

Probe	Crystallite size (nm)	a (Å)	c (Å)	Phase name
TiO_2	19	3.7876(3)	9.5038(6)	anatase
CeO_2 ¹	9	5.4167(4)	-	cerianite
CeO_2 ²	9	5.4151(4)	-	cerianite
$\text{TiO}_2\text{:CeO}_2$ (80:20) ¹	-	-	-	amorphous
$\text{TiO}_2\text{:CeO}_2$ (80:20) ²	18	3.7922(3)	9.5173(6)	anatase
	8	5.4163(4)	-	cerianite
$\text{TiO}_2\text{:CeO}_2$ (50:50) ¹	-	-	-	Anatase
				cerianite
$\text{TiO}_2\text{:CeO}_2$ (50:50) ²	16	3.7961(3)	9.5173(6)	anatase
	4	5.4161(4)	-	cerianite

Note: 1 - from $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$; 2 - from $(\text{CH}_3\text{CO}_2)_3\text{Ce}\cdot x\text{H}_2\text{O}$

All samples were also investigated by transmission electron microscopy.

The mono-phase as prepared powders are constituted of aggregates which turn after the thermal treatment at 400 °C into crystallites of 4 - 5 nm. The as prepared binary powders are predominantly amorphous and the particle size decreases with the increase of cerium quantity for both types of precursors used. They are presented in Figures 5 and 6.

Figure 5 TEM micrographs for the as prepared binary powders in the $\text{TiO}_2\text{-CeO}_2$ system from $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$; a) $\text{Ti}:\text{Ce} = 80:20$ and b) $\text{Ti}:\text{Ce} = 50:50$.

Figure 6 TEM micrographs for the as prepared binary powders in the $\text{TiO}_2\text{-CeO}_2$ system from $(\text{CH}_3\text{CO}_2)_3\text{Ce}\cdot x\text{H}_2\text{O}$; a) $\text{Ti}:\text{Ce} = 80:20$ and b) $\text{Ti}:\text{Ce} = 50:50$.

Figures 7 and 8 present the TEM micrographs for the 400 °C thermally treated bi-component powders with two oxide compositions $\text{TiO}_2:\text{CeO}_2 = 80:20$ and $50:50$, prepared from $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (Figure 7) and from $(\text{CH}_3\text{CO}_2)_3\text{Ce}\cdot x\text{H}_2\text{O}$ (Figure 8).

Figure 7 TEM micrographs for the 400 °C thermally treated binary powders from $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, a) $\text{TiO}_2:\text{CeO}_2 = 80:20$ and b) $\text{TiO}_2:\text{CeO}_2 = 50:50$.

Figure 8 TEM micrographs for the 400 °C thermally treated binary powders from $(\text{CH}_3\text{COO})_3\text{Ce} \cdot x\text{H}_2\text{O}$, a) $\text{TiO}_2:\text{CeO}_2 = 80:20$ and b) $\text{TiO}_2:\text{CeO}_2 = 50:50$.

Regardless of the cerium salt used as precursor, the tendency of agglomeration is decreasing with the increase of cerium amount in the composition, the tendency to crystallize increasing at the same time. The bi-component powders thermally treated at 400 °C are formed from predominantly amorphous phases for the sample prepared from $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in the $\text{TiO}_2:\text{CeO}_2 = 80:20$ molar ratio and contain some crystallite of ~ 5 nm. A more detailed microscopic investigation of the material obtained from $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in the $\text{TiO}_2:\text{CeO}_2 = 80:20$ revealed the fact that the material is actually constituted from two phases: a predominant one that is amorphous and another crystalline one of pure anatase, proven by

EDAX, with crystallite sizes ranging between 50 and 100 nm as can be seen in Figure 9.

Figure 9 TEM micrographs of the two phases from the $\text{TiO}_2\text{:CeO}_2 = 80\text{:}20$ thermally treated at 400 °C obtained from $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. a) Predominant amorphous $\text{TiO}_2 \cdot \text{CeO}_2$ phase and b) TiO_2 crystalline phase.

The formation of the two different solid composites with different microscopic aspects may occur for two reasons: firstly, during the synthesis in the ammonia precipitation step due to the higher reactivity of the titanium alkoxide and its higher amount in the solution, TiO_2 seems to precipitate in the first place. Secondly, after thermal treatment, when the crystallization process is about to start, it is expected that this process will lead to the formation of the same stable compounds consisting in a $-\text{Ti}-\text{O}-\text{Ce}-$ network. As most of the TiO_2 is not engaged in the network formation, it is supposed to crystallize independently. However, the amount of crystalline TiO_2 phase seems to be negligible, compared to the amorphous phase, being not evidenced in the XRD record.

The XPS spectra for the binary powders prepared starting with cerium nitrate are presented in Figure 10, while the spectra for the samples starting with cerium acetate are presented in Figure 11. The surface composition as resulted from XPS is presented in Table 3. The

obtained results suggest that regardless of the cerium precursor employed, in the $\text{TiO}_2\text{:CeO}_2$ samples 80:20 thermally treated at 400 °C, the titanium is present in the Ti^{4+} valence state while cerium is present in the two valence states Ce^{3+} and Ce^{4+} .

Figure 10 The XPS spectra for the $\text{TiO}_2\text{:CeO}_2$ (80:20) sample from $\text{Ti}(\text{O-}i\text{C}_3\text{H}_7)_4$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, thermally treated at 400 °C. The lines represent electronic configurations which suggest the presence of titanium in one valence state (left) and of cerium in two valence states as may be deduced from the “doublets” (right).

Figure 11 The XPS spectra for the $\text{TiO}_2\text{:CeO}_2$ (80:20) sample from $\text{Ti}(\text{O-}i\text{C}_3\text{H}_7)_4$ (left) and $(\text{CH}_3\text{CO}_2)_3\text{Ce} \cdot x\text{H}_2\text{O}$ (right), thermally treated at 400 °C.

In literature [27] it is mentioned that pure cerium oxides are more likely to have cerium in Ce^{4+} oxidation state without excluding the presence of Ce^{3+} to some extent. In the $\text{TiO}_2\text{-CeO}_2$ binary system, at low cerium doping levels, it was found that cerium’s preferred valence state

is Ce^{3+} . With the increase of the cerium content in the sample, the presence of the Ce^{4+} species gradually increases [27]. In our results, the peaks obtained after the deconvolution of the XPS spectra sustain this hypothesis: the peaks of ~ 884.5 and 902.5 eV can be attributed to the photoemissions of the cerium (III) cations while the peak at ~ 898 eV corresponds to the photoemissions of the Ce(IV) cations. The peak at ~ 880.5 eV suggests that the sample contains some oxygen vacancies and is to some extent in a reduced state.

Table 3 Surface composition as determined from XPS (%at)

Sample/Element	C	O	Ti	Ce
$\text{TiO}_2\text{:CeO}_2$ (80:20) nitrate	44.72	41.11	10.90	3.26
$\text{TiO}_2\text{:CeO}_2$ (80:20) acetate	53.14	35.24	8.93	2.69

The XPS investigations confirm and extend the results of the DTA/TGA that have shown the presence of Ce^{3+} in the powders by its oxidation at temperature higher than 650°C .

The FT-Raman spectra of the mono-component powders have shown all the characteristic peaks mentioned in the literature for TiO_2 or CeO_2 [25, 26].

Figure 12 FT-Raman spectra for the $\text{TiO}_2\text{-CeO}_2$ (80:20) samples, thermally treated at 400°C , a) prepared from cerium nitrate and b) prepared from cerium acetate.

Figure 12 presents the Raman spectra for the $\text{TiO}_2\text{:CeO}_2$ (80:20) samples, thermally treated at 400 °C. In the case of the $(\text{CH}_3\text{CO}_2)_3\text{Ce}\cdot x\text{H}_2\text{O}$ precursor, there are a number of bands observed at 140, 395, 514 and 635 cm^{-1} which are in agreement with the anatase spectra reported by Ocana [47] and a peak at 460 cm^{-1} corresponding to the cerium oxide. For all the peaks, a shift of $\sim 4 \text{ cm}^{-1}$ was observed. In this case the Raman spectrum of the binary powder is composed by the characteristic peaks of the both mono-component constituent oxides suggesting that a mechanical mixture of oxides was formed. When the $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ precursor was employed, some new Raman bands appeared at 164, 193, 268, 328, 364, 433, 565 and 608 cm^{-1} . Several of these bands were previously reported in the literature by Luo [48] and they were assigned to a new compound obtained by substitution of Ce atoms in the TiO_2 lattice. The mixing of TiO_2 and CeO_2 is probably more efficient at smaller scale in such a way that even Ti-O-Ce arrangements have to be envisaged. The small intensity of these bands confirmed once again the XRD results which indicate that the material is still predominantly amorphous.

Based on the Raman investigations, the following reaction mechanism (equation 8) can be imagined for the preparation of binary powders when cerium nitrate source is used:

(8)

BET surface area determinations showed that all the samples had relatively high surface areas, the highest values being recorded for CeO_2 samples prepared from the cerium acetate precursor ($146 \text{ m}^2/\text{g}$). The binary powders prepared with the same cerium precursor have also a higher specific surface area as the corresponding samples prepared with cerium nitrate. This fact could be explained by the higher porosity of the particles determined by acetate evolution from the composition of initial powders obtained with cerium acetate. The results for the BET measurements are presented in Table 4.

Table 4 BET surface area for mono- and bicomponent powders thermally treated at 400°C .

Sample	Monocomponent powders			Binary powders			
	TiO_2	$\text{CeO}_2^{(1)}$	$\text{CeO}_2^{(2)}$	Starting with $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$		Starting with $(\text{CH}_3\text{CO}_2)_3\text{Ce} \cdot x\text{H}_2\text{O}$	
				$\text{TiO}_2:\text{CeO}_2$ (80:20)	$\text{TiO}_2:\text{CeO}_2$ (50:50)	$\text{TiO}_2:\text{CeO}_2$ (80:20)	$\text{TiO}_2:\text{CeO}_2$ (50:50)
S_{BET} [m^2/g]	67	111	146	79	85	122	99

Note: (1) starting with $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, (2) $(\text{CH}_3\text{CO}_2)_3\text{Ce} \cdot x\text{H}_2\text{O}$

Conclusions

Mono component single phase and binary phase powders in the TiO_2 - CeO_2 system were successfully prepared by sol-gel method. All prepared powders are in the nanometric range and the dried material is constituted of amorphous aggregates of particles while the 400°C thermally treated samples are formed of crystallites of 4 - 5 nm. Only the thermally treated $\text{TiO}_2:\text{CeO}_2$ (80:20) prepared from the $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ precursor makes an exception and is predominantly amorphous.

According to the recorded DTA/TGA curves, differences could be noticed in the thermal behaviour of the prepared powders starting with different cerium precursors. Based on DTA/TG analysis data when cerium nitrate was used as cerium source, a titanium-cerium

oxy-hydroxide powder was obtained, while in the case of cerium acetate, a titanium-cerium hydrated acetate complex was formed.

The XPS measurements on the thermally treated $\text{TiO}_2\text{:CeO}_2$ (80:20) samples reveal that regardless of the cerium source used, the titanium is present in the Ti^{4+} state while cerium is presented in the two valence states Ce^{3+} and Ce^{4+} , in almost equivalent amounts.

The FT-Raman results suggest the formation of a Ti-O-Ce type bonding in the case of bi-component thermally treated samples prepared from cerium nitrate.

All materials were investigated by transmission electron microscopy and confirmed by XRD results. A more detailed microscopic investigation of the material obtained from $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in the $\text{TiO}_2\text{:CeO}_2 = 80:20$ reveal that the material is actually constituted from two phases: one predominant that is amorphous constituted from $\text{TiO}_2\text{:CeO}_2$ ($\sim 2:1$) and another one crystalline composed from TiO_2 with crystallite sizes ranging between 50 and 100 nm.

The results obtained have shown that the cerium precursor as well as the cerium ratio in the mixture have played a very important role to the properties of the resulted materials. When cerium nitrate, which is totally soluble in the reaction medium, was employed, a mixture of the precursors at molecular level was achieved and differences were induced by the different speed of hydrolysis-condensation reactions of the two starting materials. At $\text{TiO}_2\text{:CeO}_2$ (80:20) ratio, it was observed that cerium ions were entrapped in TiO_2 network, hindering the crystallization when thermally treated at 400 °C. At $\text{TiO}_2\text{:CeO}_2$ (50:50) ratio, it was observed that some of the cerium precursor remained still unreacted when titanium alkoxide was totally transformed and it reacted to CeO_2 . When the cerium acetate precursor which is only partially soluble in reaction medium, was used, regardless of its amount, it was found that cerium precursor reacts after the complete precipitation of the TiO_2 leading to CeO_2 . When TiO_2 and CeO_2 are only physically mixed, the crystallization was found to start earlier.

Future work will include the testing of the powders in the $\text{TiO}_2\text{-CeO}_2$ system as inhibitors for metals corrosion protection.

Experimental

The $\text{TiO}_2\text{-CeO}_2$ powders were prepared by the sol-gel method at ratios of $\text{TiO}_2\text{:CeO}_2$ of 4:1 and 1:1 using $\text{Ti}(\text{O-iC}_3\text{H}_7)_4$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $(\text{CH}_3\text{CO}_2)_3\text{Ce} \cdot x\text{H}_2\text{O}$ as starting precursors in ethanol. The metal oxide precipitation was achieved by use of NH_4OH (NH_3 25% aqueous solution). The molar ratio of the reagents was the following: precursors: $\text{C}_2\text{H}_5\text{OH}$: $\text{EtOH:H}_2\text{O:NH}_4\text{OH}$ = 1:36,5:3:3, when cerium nitrate was used as cerium source, or 1:36,5:3:6, when cerium acetate was used as cerium source. The obtained reaction mixture was homogenized at 80 °C, for 2 hours. The resulted precipitate was filtered, carefully washed with distilled water and dried in the oven for 48 h and then (based on the results of DTA/TGA) annealed for 1 h at 400 °C with a heating rate of 1 °C/min in order to eliminate the water and organic residues.

The $\text{TiO}_2\text{-CeO}_2$ powders obtained in the conditions mentioned above were characterized by differential thermal analysis and thermo-gravimetric analysis using a Mettler Toledo TGA/SDTA 851e equipment with a heating rate of 5°C/min., XRD with a Bruker D8 equipment with Lynxeye detector, measuring time of 1sec for each step and wavelength of Cu - $\text{K}_{\alpha 1} + \text{K}_{\alpha 2}$. Visible laser Raman spectra were recorded on a HORIBA Jobin Yvon LabRAM ARAMIS Raman microscope and the laser lines at 632 nm and 785 nm were used as excitation source. The chemical composition of the powders prepared as described before was examined by X-ray photoelectron Spectroscopy (XPS). A VG ESCA 3 MkII-EUROSCAN Instr. Spectrometer was used in the following conditions: the X-ray source: an emission tube with a dual anode of Mg/Al (energy: $P \approx 10^{-9}$ torr; $U_{\text{me}} = 3$ kV; RX: $U = 12.5$ kV, $I = 20$ mA, $P = 250$ W; Alk_{α} ($E = 1486.6$ eV); Flood gun: $U = 3$ V, $I = 0.2$ mA). The spectra were analyzed with

the *S-PROBE* and *SDP-32* programmes. Transmission electron microscopy (TEM) involved a JEOL 200 CX microscope and a Topcon 00B and instrument. BET specific surface area determinations were realized using the nitrogen adsorption method at liquid nitrogen temperature.

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References

- [1] R. Subarsi, T. Shinohara, K. Mori, *Sci. & Technol. Of Adv. Mater.* **2005**, 6, 501.
- [2] J. Li, H. Yun, C. J. Lin, *J. Electrochem. Soc.* **2007**, 154[11], C631.
- [3] S. Pavasupree, Y. Suzuki, S. Pivsa-Art, S. Yoshikawa, *J. Solid State Chem.* **2005**, 178, 128.
- [4] J. Rynkowski, J. Farbotko, R. Touroude, L. Hilaire, *Appl. Catal. A: Gen.* **2000**, 203, 335.
- [5] S. Yang, W. Zhu, Z. Jiang, X. Chen, J. Wang, *Appl. Surf. Sci.* **2006**, 252, 8499.
- [6] Z. Liu, B. Guo, L. Hong, H. Jiang, *J. Phys. Chem. Solids* **2005**, 66, 161.
- [7] P. Periyat, K. V. Baiju, P. Mukundan, P. Krishna Pillai, K. G. K. Warrier, *J. Sol-Gel Sci. & Technol.* **2007**, 43, 299.
- [8] C. O. Avellaneda, L. O. S. Bulhoes, A. Pawlika, *Thin Solid Films* **2005**, 471, 100.
- [9] A. Verma, S. B. Samanta, A. K. Bakhshi, S. A. Agnihotry, *Solid State Ionics* **2004**, 171,

81.

[10] D. L. Sun, S. Heusing, J. Puetz, M. A. Aegerter, *Solid State Ionics* **2003**, 165, 181.

[11] F. E. Ghodsi, F. Z. Tepehan, G. G. Tepehan, *Electrochim. Acta* **1999**, 44, 3127.

[12] C. O. Avellaneda, A. Pawlika, *Thin Solid Films* **1998**, 335, 245.

[13] D. Keomany, J. P. Petit, D. Deroo, *Sol. Energ. Mat. Sol. C.* **1995**, 36, 397.

[14] A. Trinchì, Y. X. Li, W. Wlodarsky, S. Kaciulis, L. Pandolfi, S. Viticoli, E. Comini, G. Sberveglirieri, *Sensor Actuat. B-Chem.* **2003**, B95, 145.

[15] T. Lopez, F. Rojas, R. Alexander-Katz, F. Galindo, A. Balankin, A. Buljan, *J. Solid State Chem.* **2004**, 177, 1873.

[16] H. Zhu, Z. Qin, W. Shan, W. Shen, J. Wang, *J. Catal.* **2004**, 225, 267.

[17] Z. Mei, W. Xidong, W. Fuming, L. Wenchao, *Sensor Actuat. B-Chem.* **2003**, B92, 167.

[18] F. E. Ghodsi, F. Z. Tepehan, G. G. Tepehan, *Sol. Energ. Mat. Sol. C.* **2001**, 68, 355.

[19] P. Knauth, H. L. Tuller, *Solid State Ionics* **2000**, 136-137, 1215.

[20] G. Tavcar, K. Kalcher, B. Ogoreve, *Analyst* **1997**, 122, 371.

[21] D. Camino, D. Deroo, J. Salardenne, N. Treuil, *Sol. Energ. Mat. Sol. C.* **1995**, 39, 349.

[22] D. Keomany, C. Poinsignon, D. Deroo, *Sol. Energ. Mat. Sol. C.* **1994**, 33, 429.

[23] A. Makishima, M. Asami, K. Wada, *J. Non-Cryst. Solids* **1990**, 121, 310.

[24] A. Makishima, M. Asami, K. Wada, , *J. Non-Cryst. Solids* **1988**, 100, 321.

[25] D. Bersani, G. Antonioli, P. P. Lottici, T. Lopez, *J. Non-Cryst. Solids* **1998**, 232-234, 175.

[26] F. Zhang, S. W. Chan, J. E. Spanier, E. Apak, Q. Jin, R. D. Robinson, I. P. Herman, *Appl. Phys. Lett.* **2002**, 80[1], 127.

[27] J. Fang, X. Bi, D. Si, Z. Jiang, W. Huang, *Appl. Surf. Sci.* **2007**, 253, 8952.

[28] Q. Z. Yan, T. S. Su, Z. Y. Huang, C. C. Ge, *J. Eur. Ceram. Soc.* **2006**, 26, 915.

[29] Y. Liu, D. Sun, H. You, J. S. Chung, *Appl. Surf. Sci.* **2005**, 246, 82.

[30] H. Wang, R. Akid, *Corr. Sci.* **2007**, 49, 4491.

- [31] D. G. Shuchkin, S. V. Lamaka, K. A. Yasakau, M. L. Zheludkevich, M. S. G. Ferreira, H. Möhwald, *J. Phys. Chem.* **2008**, *C 112*, 958.
- [32] T. Lampke, S. Darwich, B. Wielage, S. Steinhäuser, *Mat.-wiss u. Werkstofftech.* **2008**, *39*, 460.
- [33] M. Quinet, B. Neveu, V. Moutarlier, P. Audebert, L. Ricq, *Progr. Org. Coat.* **2007**, *58*, 46.
- [34] S. K. Poznyak, M. L. Zheludkevich, D. Raps, F. Gammel, K. A. Yasakau, M. G. S. Ferreira, *Progr. Org. Coat.* **2008**, *62*, 226.
- [35] A. Tiwari, J. Zhu, L. H. Hihara, *Surf. & Coat. Technol.* **2008**, *202*, 4620.
- [36] K. H. Wu, C. M. Chao, T. F. Yeh, T. C. Chang, *Surf. & Coat. Technol.* **2007**, *201*, 5782.
- [37] J. A. Vreugdenhil, V. J. Gelling, M. E. Woods, J. R. Schmelz, B. P. Enderson, *Thin Solid Films* **2008**, *517*, 538.
- [38] T. L. Metroke, O. Kachurina, E. T. Knobbe, *Progr. Org. Coat.* **2002**, *44*, 185.
- [39] A. S. Hamdy, *Mat. Lett.* **2006**, *60*, 2633.
- [40] K. A. Yakasau, M. L. Zheludkevich, O. V. Karavai, M. G. S. Ferreira, *Progr. Org. Coat.* **2008**, *63*, 352.
- [41] V. Moutarlier, B. Neveu, M. P. Gigandet, *Surf. & Coat. Technol.* **2008**, *202*, 2052.
- [42] A. Pepe, M. Aparicio, S. Cere, A. Duran, *J. Non-Cryst. Solids* **2004**, *348*, 162.
- [43] L. S. Kasten, J. T. Grant, N. Grebasch, N. Voevodin, F. E. Arnold, M. S. Donley, *Surf. & Coat. Technol.* **2001**, *140*, 11.
- [44] A. M. Cabral, W. Trabelsi, R. Serra, M. F. Montemor, M. L. Zheludkevich, M. G. S. Ferreira, *Cor. Sci.* **2006**, *48*, 3740.
- [45] A. Dauscher, P. Wehrer, and L. Hilaire, *Catal. Lett.* **1992**, *14*, 171.
- [46] M. Crisan, A. Jitianu, M. Zaharescu, F. Mizukami, S. Niwa, *J. Disper. Sci. Technol.* **2003**, *24*, 129.

[47] M. Ocana, J. V. Garcia-Ramos, C. J. Serna, *J. Am. Ceram. Soc.* **1992**, 75, 2010.

[48] M. Luo, J. Chen, J. Lu, Z. Feng, C. Li, *Chem. Mater.* **2001**, 13, 197.