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Effects of Additives in Electrospraying for Materials Preparation

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Abstract

TiO_2 thin films and ZrO_2 fine powders were prepared by electrostatic spray deposition (ESD). The morphology of the thin films and the particle size of the powders can be varied considerably by adding well-chosen additives to the precursor solutions. Acetic acid (HOAc) and ammonia nitrate (NH_4NO_3) were used as a solution chemistry modifier and a conductivity enhancement additive, respectively. It is found that by adding HOAc in an alcoholic precursor solution of $Ti(OPr^i)_4$, the structure of the deposited TiO_2 films changes from severely cracked to crack-free reticular. In the ZrO_2 powder preparation, the particle size of ZrO_2 decreases substantially, i.e. from 3·5 μm down to 1 μm upon adding NH_4NO_3 in the precursor solution of zirconium acetylacetonate. Quantitative analysis of the impedance spectroscopy data of their precursor solutions has supported this result. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

By applying a potential difference of a few thousands of volts between a plate and the end of a capillary through which a liquid is allowed to flow, one can generate a very fine spray, or aerosol, of the liquid. Although this spraying phenomenon, referred to as electrospraying, was already studied early this century,[1,2] it has received renewed attention in the last decade[3–7] owing to its applications in chemical analysis and materials synthesis. With regard to materials synthesis, the aerosol technique was modified to deposit thin films,[8–16] and has reached a high level of sophistication in powder production.[17]

It is known that many physical properties of the liquid, including electrical conductivity, viscosity, surface tension and density, influence the functioning of the spray. Hence they are expected to influence the structures and properties of thus-prepared materials as well. Therefore, the structure and properties of a material can be tailored by using additives in its precursor solution in order to modify above-mentioned solution properties. In addition to varying the physical properties, some additives may also change the chemical properties of the precursor solution, which also determine the structures of the final product. It should be stressed that the additives normally should not introduce impurities into the synthesized materials. Therefore, additives like lithium chloride, which was used as dopant by other authors[18,19] cannot be used for materials preparation.

In this work, we have chosen acetic acid (CH_3COOH, HOAc) and ammonium nitrate (NH_4NO_3) as additives to modify the chemical properties and electrical conductivity of the precursor solutions for TiO_2 thin-film deposition and ZrO_2 powder production, respectively. The results indeed demonstrate a significant role of the additives to the structure, making it possible to tailor products.

2 Experimental

2.1 ESD set-up

Both TiO_2 thin films and ZrO_2 powders were prepared by using a home-built Electrostatic Spray Deposition (ESD) equipment. Its structure and working principles have been described in details elsewhere.[11,13] In this study, a peristaltic pump (Watson Marlow 101U) was used to transfer

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precursor solutions with constant and proper flow rates from a glass container to the metal nozzle at which a potential was applied in the range of 8 to 15 kV. The exact value to generate a stable spray depended on the physical properties of the precursor solutions, and was obtained by trial and error.

2.2 TiO_2 thin-film deposition

Titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$ or $Ti(O\text{-}Pr^i)_4$) was quickly transferred into and dissolved in absolute ethanol (100%) to obtain a solution (0·01 M). In order to prevent the hydrolysis during a prolonged storage time, the solution was diluted to 0·005 M by adding an equal volume of butyl carbitol (BC, $CH_3(CH_2)_3O(CH_2)_2O(CH_2)_2OH$). This solution was also used to study the deposition of films with a unique porous morphology.[11] To the above-mentioned solution, proper amounts of acetic acid (CH_3COOH or HOAc) were added as an additive. Three precursor solutions (0·005 M) were prepared in this way containing 0, 20, and 30 vol% HOAc. During deposition, the liquid flow rate was kept at 1·6 ml h^{-1}. Aluminum discs (0·2 mm thick, 14 mm in diameter) were used as substrate; the nozzle-to-substrate distance was 3 cm. According to our previous study,[11] the substrate temperature was maintained at 240°C. The DC voltage applied in order to obtain a stable spray was found to be 9·2 kV

2.3 ZrO_2 powder production

Proper amount of zirconium acetylacetonate ($Zr[CH_3COCH=C(O-)CH_3]_4$ or $Zr(AcAc)_4$) was dissolved in ethanol to obtain a precursor solution (0·05 M). Another solution was prepared containing ammonium nitrate (NH_4NO_3), which is very soluble and dissociates easily in ethanol, in order to increase the conductivity. The actual ethanol solution consists of 0·045 M $Zr(AcAc)_4$ and 0·03 M NH_4NO_3. Aluminium foil (0·2 mm thick) heated at 340°C was used to collect the powders. The flow rate of the precursor solutions was kept at 0·8 ml h^{-1}. The DC voltage applied in order to obtain a stable spray in this case was found to be 11 kV.

2.4 Characterization

A scanning electron microscope (JEOL JSM-35) was used to observe the morphologies of the TiO_2 thin films, and to measure the particle sizes of the ZrO_2 powders prepared here. The conductivities of the zirconium precursor solutions were obtained by measuring the impedance spectra with a frequency response analyzer (Solartron 1260). The measured solutions were put in a cell consisting of two parallel platinum plates ($8\times10\,mm^2$, at a distance of 8 mm). The measurements were conducted at 25°C by applying an AC voltage of 50 mV in the frequency range from 0·01 Hz to 10 MHz.

3 Results and Discussion

3.1 TiO_2 thin-film deposition and solution chemistry modifier

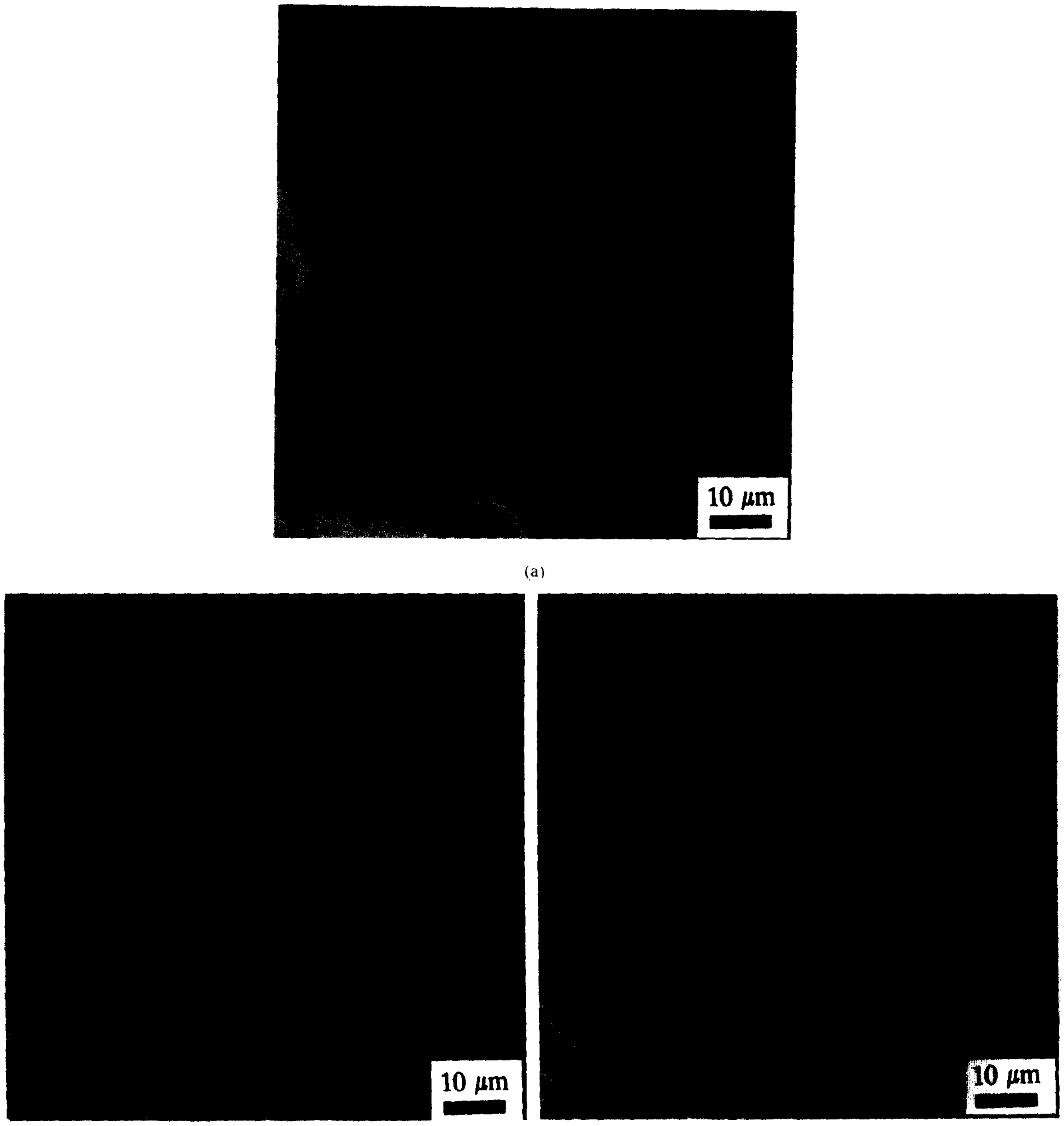
It is found that addition of butyl carbitol decreases the hydrolysability of $Ti(OPr^i)_4$. This is probably due to the following alcohol interchange reactions:[18]

$$\begin{aligned} &Ti(OPr^i)_4 + xBu^nO(CH_2)_2O(CH_2)_2OH \\ &\quad \rightleftarrows Ti(OPr^i)_{4-x}[O(CH_2)_2O(CH_2)_2OBu^n]_x \\ &\quad + xPr^iOH (x = 0-4) \end{aligned}$$

The alkoxy group $-O(CH_2)_2O(CH_2)_2OBu^n$ has larger steric hindrance than $-OPr^i$, leading to a markedly decreased hydrolysability of $Ti(OPr^i)_{4-x}[O(CH_2)_2O(CH_2)_2OBu^n]_x$. Of course, alcohol interchange reactions may also take place when $Ti(OPr^i)_4$ is dissolved solely in ethanol.

The scanning electron micrographs of *TiO_2* thin films resulting from the precursor solutions containing different amounts of AcOH are shown in Fig. 1. It can be seen that introducing AcOH has made a significant difference in their surface morphologies. From the precursor solution without AcOH present, a severely cracked film was formed [Fig. 1(a)]. The crack formation may be ascribed to the stress resulted from the drying process during the film deposition. Since the deposition was performed at 240°C, which is close to the boiling point of a solvent component BC (231°C), the solvent evaporation of spray droplets is incomplete when they arrive at the substrate surface. Therefore, a very thin and wet top layer is always present in the film during deposition. The too fast drying of this wet top layer may easily result in stress and cause severe cracking

On the other hand, upon introducing AcOH in the precursor solutions, TiO_2 films were formed with a reticular structure and minor or no cracking [Fig. 1(b) and (c)]. This is mainly due to the fact that the chemical properties of the precursor solution have changed. In a polymeric sol–gel process, AcOH is usually added to decrease the hydrolysability of alkoxides.[18] In our case, less hydrolysable and, what is more important, less soluble alkoxides $Ti(OPr^i)_{3-y}[O(CH_2)_2\ O(CH_2)_2OBu^n]_y(OAc)$ $(y = 0-3)$ are probably obtained when adding AcOH. From these less soluble acetates, a reticular structure is obtained as was the case in



(a)

(b)

(c)

Fig. 1. Scanning electron micrographs of TiO_2 thin films deposited from 0·01 M $Ti(OPr^i)_4$ precursor solutions containing (a) 0, (b) 20 vol%, and (c) 30 vol% HOAc.

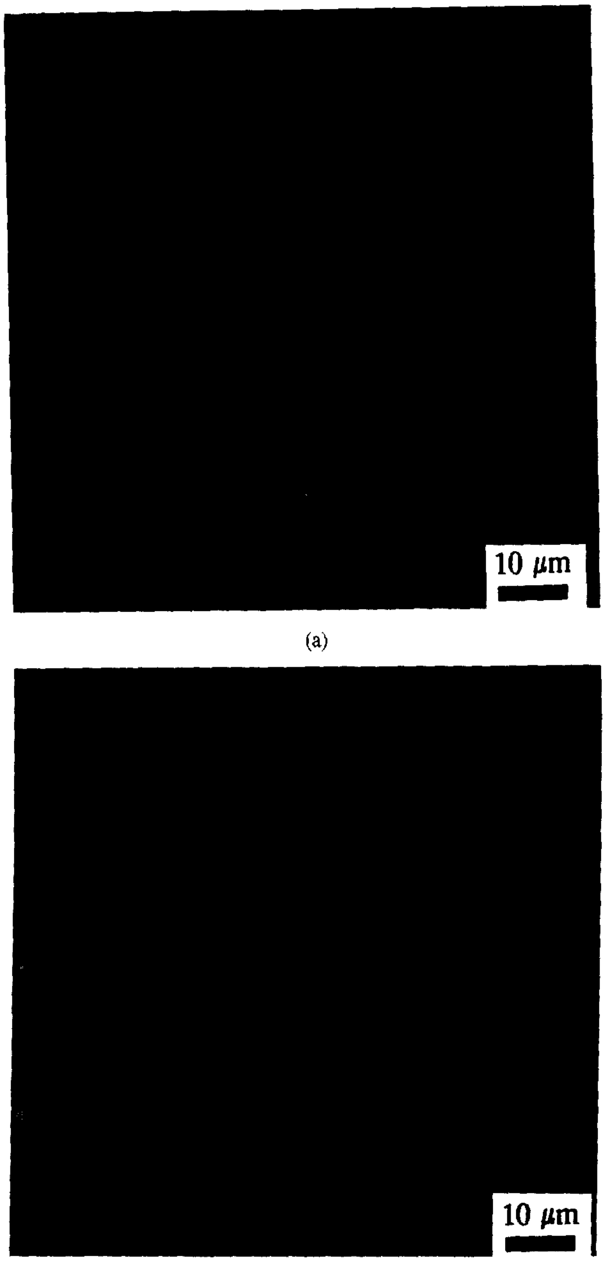
$LiCoO_2$ film formation.[11] The drying process of this reticular structure yields no cracks.

The difference between Fig. 1(b) and (c) may be due to the difference in the sizes of spray droplets. Upon adding more HOAc in the precursor solution, its conductivity increases and this leads to the generation of smaller spray droplets (see next section). Owing to a larger specific surface area, more solvent has evaporated from smaller droplets when they reach the substrate surface. This means that less solvent evaporation is involved in the drying process, and hence reduced cracking.

In addition to drying, hydrolysis may also contribute to crack formation. Therefore, compared with $Ti(OPr^i)_4$, the less hydrolysable $Ti(OPr^i)_{3-y}[O(CH_2)_2O(CH_2)_2OBu^n]_y(OAc)$, which is presumably of bidentated bridging structure as that of $Ti(OPr^i)_3(OAc)$,[18] would also give rise to a less extent of cracking.

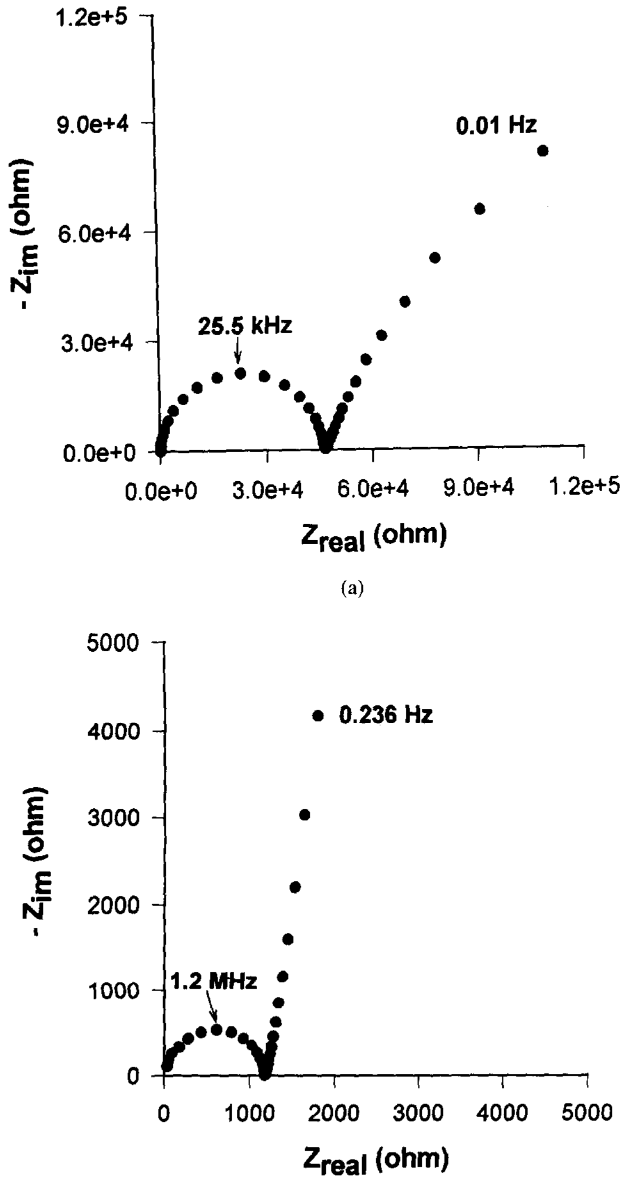
3.2 ZrO_2 powder production and conductivity enhancement additive

NH_4NO_3 used in this work is to enhance the electrical conductivity of the precursor solution, as it is highly soluble and dissociates in a polar solvent. In addition, it can be removed easily upon heating during deposition. As shown in Fig. 2, the Zr precursor solutions with and without NH_4NO_3 give rise to ZrO_2 powders with different particle sizes. Obviously, upon using NH_4NO_3, ZrO_2 particle sizes drop from about 3·5 μm to 1 μm. Since the addition of NH_4NO_3 increases the conductivity of the precursor solution, a decrease in droplet size occurs as is indicated by the relation:



(b)

Fig. 2. Scanning electron micrographs of ZrO_2 thin films deposited from precursor solutions: (a) 0·05 M $Zr(AcAc)_4$ in ethanol and (b) 0·045 M $Zr(AcAc)_4$ + 0·03 M NH_4NO_3 in ethanol.



(b)

Fig. 3. Impedance spectra of precursor solutions: (a) 0·05 M $Zr(AcAc)_4$ in ethanol and (b) 0·045 M $Zr(AcAc)_4$ + 0·03 M NH_4NO_3 in ethanol.

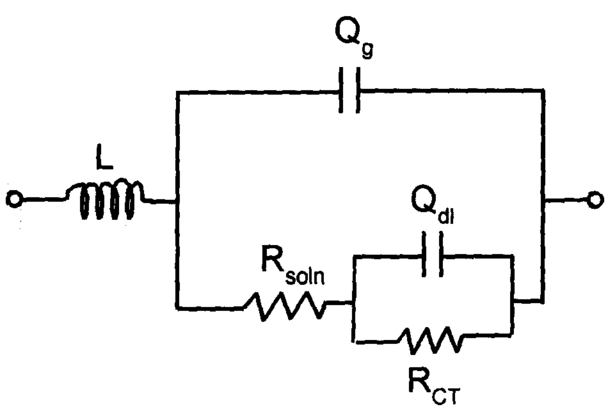


Fig. 4. The equivalent circuit for the impedance spectra shown in Fig. 3.

$d \propto (\varepsilon Q/k)^{1/3}$, where d is the diameter of the spray droplets arriving at the substrate surface, ε, Q, and k are the dielectric constant, the flow rate, and the electrical conductivity of the precursor solution, respectively.[19]

The impedance spectra of the precursor solutions, as shown in Fig. 3, provide a quantitative understanding of the above results. Both spectra reveal two well-separated semicircles, and can be fitted to an equivalent circuit as given in Fig. 4, which in the Boukamp representation is $L(Q[R(RQ)])$.[20] In this equivalent circuit, L arises probably from the cell lead inductance, Q_g from geometric capacitance, R_{soln} from the resistance of the bulk solution, while R_{CT} and Q_{dl} are the charge transfer resistance and double layer capacitance at the interfaces between the solution and the electrodes, respectively. The fitting results using a non-linear least squares (NLLS) fitting programme[20] are listed in Table 1. The orders of magnitude of

Table 1. Fitting results of impedance spectra with the equivalent circuit $L(Q[R(RQ)])$ (Fig. 4)

Precursor solution	L (μH)	Q_g		R_{soln} *(ohm)*	R_{CT} *(ohm)*	Q_{dl}	
		Y_0 *(F)*	n			Y_0 *(F)*	n
Without NH_4NO_3	0·782 (±5%)	2·54e-10 (±2·86%)	0·947 (±0·20%)	4·64e4 (±0·34%)	2·86e5 (±9·45%)	7·94e-5 (±2·15%)	0·779 (±1·6%)
With NH_4NO_3	0·767 (±12%)	2·43e-10 (±14·9%)	0·950 (±0·92%)	1·18e3 (±0·73%)	7·14e5 (±33·3%)	1·62e-4 (±1·25%)	0·913 (±0·7%)

Q_g and Q_{dl}, 10^{-10} F and 10^{-4} F, respectively, indicate that this proposed equivalent circuit is justified. It is clear that after adding NH_4NO_3, R_{soln} decreases from 46·4 to 1·18 kohm, corresponding to a conductivity change from $2{\cdot}16\times10^{-5}\,S\,cm^{-1}$ to $8{\cdot}47\times10^{-4}\,S\,cm^{-1}$, while the dielectric constant ε remains almost unchanged since Q_gs have almost the same value. Therefore, the ratio between droplet diameters can be calculated as $d_1/d_2=(46{\cdot}4/1{\cdot}18)^{1/3}=3{\cdot}4$. This agrees extremely well with our experimental results of the SEM-derived particle sizes as these were found to be about 3·5 and 1 μm for d_1 and d_2, respectively.

4 Conclusions

The recently developed ESD technique[8] has been used to prepare TiO_2 thin films and ZrO_2 fine powders. We have shown that the morphology of thin films and the particle size of the powders can be changed considerably by adding additives to the precursor solutions. In this study, HoAc was used as a solution chemistry modifier to obtain a crack-free reticular structure. By adding HOAc to the precursor solution, the deposited TiO_2 films revealed a change from a severely cracked structure to a less cracked, and even a crack-free reticular structure. In addition, in the ZrO_2 preparation, by adding NH_4NO_3 as a solution conductivity enhancement additive, the particle size of ZrO_2 powders decreases from 3·5 to 1 μm. Impedance spectroscopy analysis of the used precursor solutions has supported this result.

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