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Electrophoretic deposition of doped ceria: Effect of solvents on deposition microstructure

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Abstract

Electrophoretic deposition of doped ceria has been carried out in non-aqueous solvent to prepare coatings on different substrates and free standing films. It has been found that uneven deposition occurred in ethanol, while in butanol deposition yield is low having very little variation with deposition time. On the other hand, good deposit obtained in acetyl acetone medium, but had a porous structure. The best result however was obtained in mixed solvent. Effect of adding charge modifying additives in the ceria suspension on the deposit microstructure has been studied. Mechanism of charging in the non-aqueous medium to modify the surface properties of the suspended particles has been discussed.

Keywords: Film (A); Suspension (A); Microstructure (B); Ceria (D); Electrophoretic deposition

1. Introduction

Ceria is known to be an intermediate temperature (500 °C) ionic conductor and by doping ceria with other lanthanides (of lower valency) such as Gd, Sm [1], ionic conductivity can be enhanced. As a result, ceria (doped/undoped) finds applications as electrodes in electrochemical cells, oxygen sensor, catalysts, etc. [2]. In many of these applications, it is required to prepare thin or thick coating/or free standing film of desired microstructure (dense or porous). Electrophoretic deposition (EPD) is one of the low cost film forming processes, where it is possible to control the film thickness, uniformity of deposition by simple control of process parameters [3]. In EPD process, charged ceramic powder particles dispersed in a liquid medium gets attracted and migrates towards an electrode of opposite charge and consequently gets deposited there under the influence of a DC electric field (electrophoresis), forming homogeneously compact films. It has its own advantages of short formation time, little restriction on the shape of the substrate, suitability for mass production and no requirement for binder burnout as the green coating contains few or no organics.

In general organic liquids are favoured compared to water, because it eliminates the electrode reaction and gas evolution commonly encountered in the latter case due to electrolysis of water on application of electric field. While the generally lower dielectric constant in organic liquids limits the charge on the particles as a result of the lower dissociating power, much higher field strength can be used since the problems of electrolytic gas evolution, joule heating and electrochemical attack of the electrodes are greatly reduced or non-existent. The organic liquids are also preferred due to their high density, good chemical stability and low conductivity. In EPD, the ionic concentration in the liquid must remain low; a condition favoured for low dielectric constant liquids, and is satisfied by organic liquids.

While choosing a solvent there are certain criteria also to be satisfied. The ceramic powder should be stable in the solvent, i.e. no reaction or agglomeration should be there. Solvent should be able to generate charge on the surface of the powder, i.e. a high zeta potential, since the mobility of the particles in an electric field depends on the surface charge. There should be minimum charge carrier (ionic species) in the solvent. Current should be carried mostly by the suspended particles. The surface of the deposit should have low surface tension and evaporation rate to prevent cracking during drying.

So a proper selection of suitable solvent and optimization of the operating parameters are necessary for obtaining depositions of desired thickness and microstructure by EPD.

The present paper presents preparation of coatings and free standing films of doped ceria by electrophoretic deposition on suitable substrates and study the effect of different organic

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Table 1
Physical properties of solvents.

Solvents	Density (g/cc)	Relative dielectric constant	Vapour pressure (mmHg)	Vapour density (Air = 1)	Evaporation rate (n-butylacetate = 1)
Ethanol	0.79	24.55	25	1.6	2
Butanol	0.81	17.51	6.7	2.6	0.46
Acetylacetone	0.97	25.7	6	3.5	0.75
Acetone	0.79	20.7	400	2	7.7

solvents, additives (to modify charges) on the microstructures of deposits.

2. Experimental

2.1. Materials

Ceria used in this investigation was obtained from M/s Indian Earth Ltd., Kochi, India. The product is a mixed metal oxides containing La, Nd, Pr, Gd other than the major constituent Ce. The particle size of the as received sample is quite large and unsuitable for EPD due to high settling rate, hence the comparatively bigger particles were screened and particles below 3 μm was used for further studies. Physical parameters of organic solvents used for EPD are given in Table 1. Other reagents employed, are of analytical grade and were used without any further purification.

2.2. Preparation of substrate

Graphite and stainless steel were used as substrate. Rectangular graphite strips of 2.0 cm × 3.0 cm cut from a large sheet (purchased from Alfa Aesar, USA) was first soaked in the solvent for sufficient time to allow wetting of the surface so as to make it solventphilic. This was necessary since graphite being solventphobic for most of the solvents, did not allow adhesion of the deposits on its surface. Stainless steel substrate was made by cutting rectangular sheet from a bigger sheet (316L). Stainless steel substrates were repeatedly washed in acetone to remove dust particles and the surface contaminants. Then these substrates were dried before deposition. The deposition was carried out on an area of 1.5 cm × 1.5 cm.

2.3. Preparation of suspension

The first step in electrophoretic deposition is to prepare a stable, agglomerate free colloidal suspension containing the ceramic particles. The ceramic particles are required to be dispersed in a suitable solvent so as to produce a stable suspension as well as maximum deposition yield and the deposit should be homogeneous and crack free.

Before adding to solvent, the ceria powder was initially dry ground to ensure exposure of fresh oxide surface layer. This is very important as the nature of the particle surface plays an important role in colloidal processes. The suspension was prepared by adding ceria powder to the solvent media. The suspension was magnetically stirred at moderate speed for 10 min followed by ultrasonication for 20 min by Vibronic Ultrasonic Processor (Model P2) at 200 V to break up the agglomerates and homogenize the suspension. Different solvents (listed in Table 1) and their mixture were used for deposition. In some cases, iodine, cerium nitrate were added to modify surface charges. Unless stated otherwise, a 5 wt.% slurry concentration was used in all the experiments.

2.4. Deposition procedure

The deposition experiments were conducted using an electrophoretic setup. It consists of two electrode holders made of L-shaped copper plate hung vertically from a rectangular horizontal wooden bar. They were movable and can slide along the wooden bar and can be fixed at the desired distance by tightening the screws provided. At the lower portion of each L-shaped holder, arrangements were made to attach the electrodes. Generally one electrode was kept fixed and by moving the other electrode, the distance was adjusted to the desired position. Unless otherwise mentioned, an electrode spacing of 15 mm was maintained in each of the EPD experiments. The electrodes hanging from the holders were dipped into the reservoir containing the suspension of ceria. Sedimentation of the particles was prevented by slow stirring by a magnetic bead stirrer. EPD experiments were carried out at constant dc voltage of 250 & 500 V using a high voltage dc power source (Keitheley model no. 2412) with a deposition time varying from 5 s to 5 min. In all the solvents used (along with additives), cathodic deposition of the particles was observed, showing that the particles were positively charged. After deposition, the electrodes were carefully taken out and the deposits were allowed to dry at room temperature. The suspension was replenished after every three deposits to keep the concentration of the suspension unchanged.

2.5. Drying & preparation of free standing film

A post-EPD processing step like firing or sintering is usually required in order to further densify the deposits and to eliminate porosity. The green deposits of ceria powder on steel substrate were first dried in air at room temperature for 24 h, and weighed to obtain the amount of deposit yield. Free standing film was obtained by heating the deposit on graphite substrate in air to 1000 °C at a rate of 4 °C/min and soaked for 2 h in a programmable furnace. The graphite sheets get burnt off during the heat treatment leaving behind a free standing film of ceria.

2.6. Microstructural characterization

The microstructure of the deposited films were characterized by SEM (Hitachi 3400N). Microstructure of top surface as well as the fractured surface was examined.

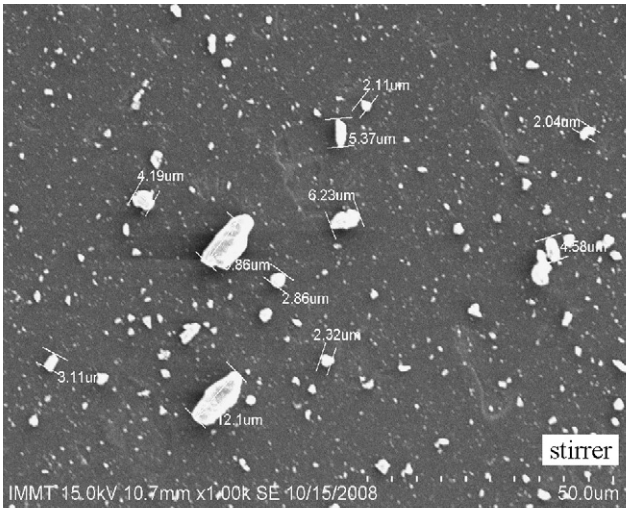


Fig. 1. SEM image of as received powder showing wide particle size distribution.

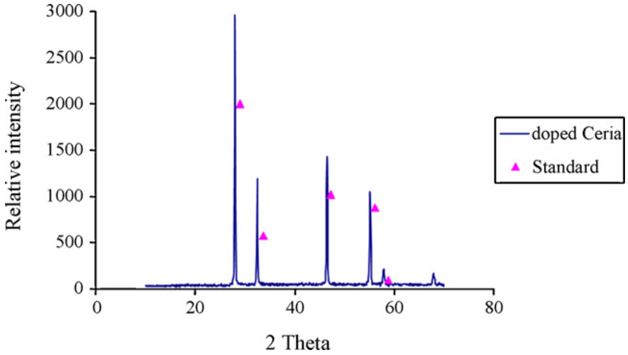


Fig. 2. XRD study of as received doped ceria powder.

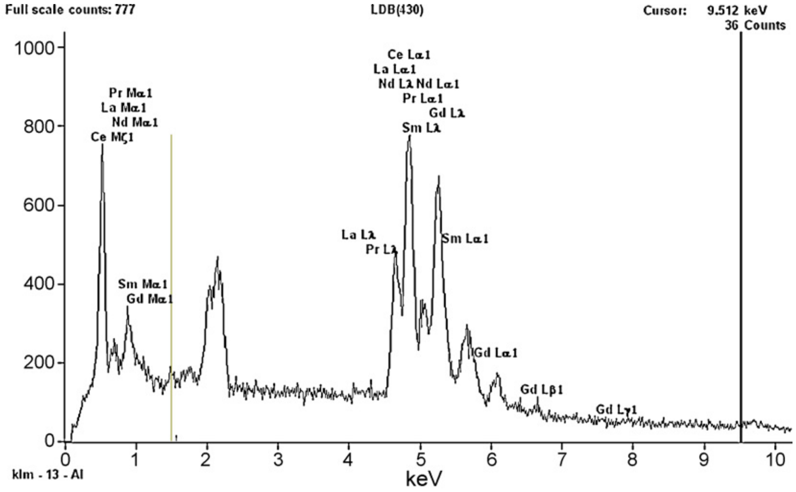
3. Results and discussion

3.1. Characterization of the powder

Fig. 1 shows the SEM of as received ceria powder, having fairly irregular and large particle size. XRD (Fig. 2) of as received sample confirmed that the structure corresponds to CeO_2 fluorite structure, however, there is shift of all diffraction peaks to lower 2θ values compared to pure ceria, indicating expansion of unit cell (Pure ceria—unit cell parameter: 0.54221 nm, doped ceria—unit cell parameter: 0.5451 nm). EDAX analysis of the powder revealed the presence of appreciable amount of lanthanum and neodymium with lesser amount of praseodymium and gadolinium (Fig. 3). Dissolution of larger size lanthanides in CeO_2 expands the unit cell. The particle size distribution of the as received powder was fairly broad (0.5–15 μm) with a BET surface area of 2.28 m^2/g. Hence, as mentioned earlier, the as received powder was screened at particles size below 3 μm and was used for further studies.

3.2. Mechanism of generation of charge

In EPD process, preparation of stable suspension and deposition of particles on the substrate are the two important steps. In preparing stable suspension, it is essential for the particle to have enough surface charges to impart sufficient repulsion between the particles to avoid aggregation. Surface charge is again related directly to the electrophoretic mobility, higher the



Element	Weight %	Formula
O	14.54S	
La	18.79	La2O3
Ce	40.87	Ce2O3
Pr	5.86	Pr2O3
Nd	17.62	Nd2O3
Sm	2.13	Sm2O3
Gd	0.19	Gd2O3
Total	100.00	

Fig. 3. EDAX study of as received powder.

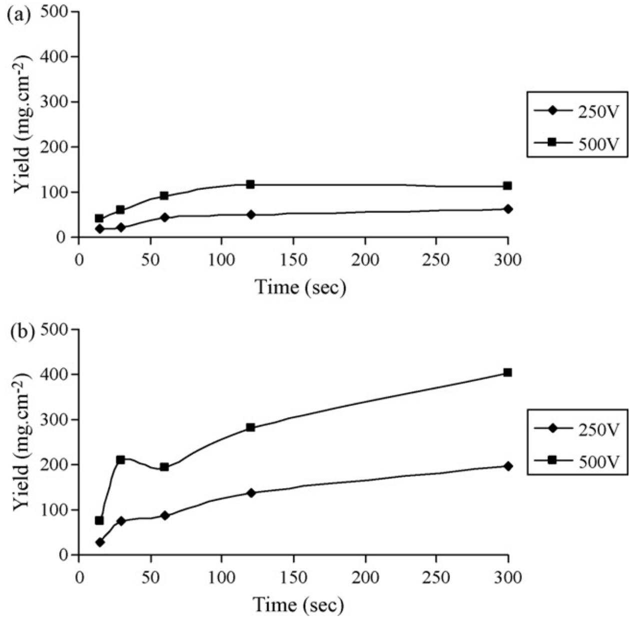


Fig. 4. Deposition yield of doped ceria at two different voltages (a) butanol and (b) acetyl acetone.

charges, higher is the mobility, hence higher the deposition. In case of highly polar solvent like water, which has high dissociating power (high relative dielectric constant ~80), oxide powder acquires surface charges by proton exchange reactions [4,5]. In contrast, non-aqueous solvents have much lower dielectric constant (Table 1), making them less attractive as a medium for generation of surface charges. But to avoid water electrolysis during EPD, non-aqueous solvents are preferred, and in this particular case ethanol, butanol, acetyl acetone and their mixture thereof were studied as solvent, whereas iodine and cerium nitrate were used as additives to enhance the charges on the surface.

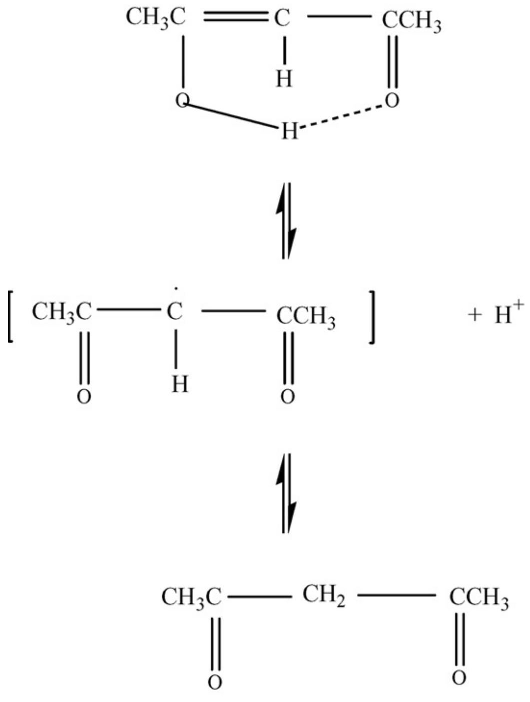
In case of alcohol, which is very hydrophilic, it is difficult to maintain it completely anhydrous. As a result, alcohol always contains some residual water. It has been proposed [6] that in alcohol medium, oxides surfaces acquire charges in a similar fashion to that in water, i.e. by proton exchange reactions. In this case mechanism of charging is based on the particle in the solvent functioning as a proton donor or acceptor. The sign of the charge depends on the direction of the transfer according to the following reaction

$$\mathrm{MOH_2}^+ + \mathrm{X}^- \leftrightarrow \mathrm{MOH} + \mathrm{XH} \leftrightarrow \mathrm{MO}^- + \mathrm{XH_2}^+$$

where MOH and XH are the surface groups of the particle and the solvent molecule, respectively. Several studies [7–10] have confirmed the mechanism, where it was shown that operational pH of the alcohol medium can be adjusted by adding acids like HCl or acetic acid or bases such as LiOH, thereby modifying the surface charges, in a similar way as in water.

For EPD of ceria, deposits obtained from its suspension in ethanol exhibited uneven surface, whereas smooth deposits were obtained from its suspension in butanol. Fig. 4a shows the deposit yield with time in butanol medium for two different voltage conditions. Though the deposit weight was small and varied slowly with deposition time, dried deposit surface was smooth and crack free. In acetyl acetone medium, the deposit yield was higher (Fig. 4b) compared to that for butanol, but at high deposition time (>1 min), the deposits were porous. It may be noted here that in all the three cases, cathodic deposition occurred, showing that the particles were positively charged.

Dissociative powers of ethanol and acetyl acetone are comparable as indicated by similar values of dielectric constant (Table 1) but butanol being higher alcohol, its dissociation is lower. Therefore, ionic concentration of ceria suspensions in ethanol and acetyl acetone is expected to be higher compared to butanol. This was confirmed by the conductivity measurement which revealed the conductivity of ceria suspension in butanol (0.2 μS/cm) was much lower than the ceria suspension in ethanol (12.2 μS/cm). This may lead to double layer compression, reducing the magnitude of zeta potential and consequently promoting agglomeration. Although we did not measure the zeta potential, it was a common phenomena observed for many systems in the literature. For example, when ionic concentration of titania in ethanol was increased from 10^{-3} to 10^{-2} M, zeta potential decreased from 40 to 15 mV [11]. Since ceria and titania are similar oxides, a similar reduction in zeta potential is expected. However, deposit characteristics are eventually controlled by the surface chemistry of the given powder and operational pH. It has been shown that [12] deposit yield was higher for acidic oxides such as hydroxyapatite (HAp) in alcohol medium, whereas basic oxide such as MgO exhibited better deposition from their suspension in ketone. For amphoteric oxide such as alumina, mixed solvent worked better. In the mixed solvent, protons are the intermediate by-products of the following keto–enol equilibrium reaction



Additionally, hydrophilicity of ethanol will result in supplying more protons through proton exchange reaction. The

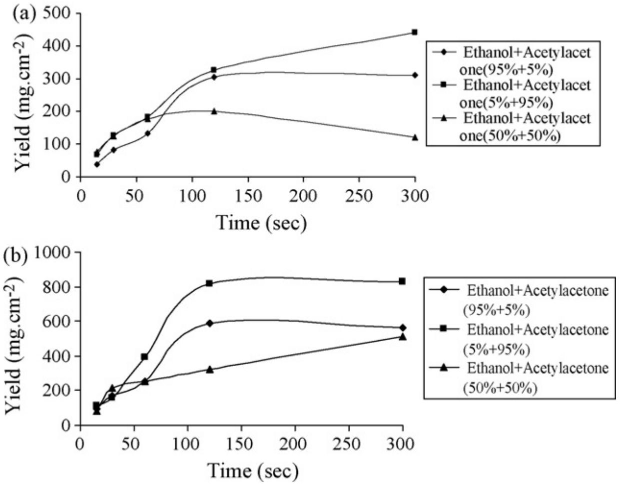


Fig. 5. Deposit yield of doped ceria in mixed solvent, without any additives at (a) 250 V and (b) 500 V.

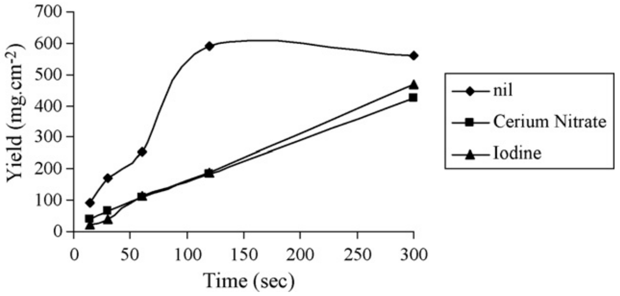


Fig. 6. Comparison of deposition yield of doped ceria in mixed solvent with & without additives.

protons get adsorbed onto the particle surfaces to modify the surface charges. But unlike pure ethanol suspension, addition of small amount of acetyl acetone in ethanol, modified the surface properties of ceria particles. Acetyl acetone acts as a non-ionic surfactant. Acetyl acetone has a strong tendency to form chelate or complex bonds with the metal atoms, thereby introducing a steric repulsion between the particles. In 5 vol.% acetyl acetone in ethanol medium, a very good deposition rate was obtained. Fig. 5a and b shows the deposit yield in mixed solvent. The deposition experiments were conducted with varying amount of ethanol and acetyl acetone. The results are tabulated in Table 2. For 5 vol.% acetyl acetone in ethanol deposit surfaces were smooth and crack free. However further increase in acetyl acetone in ethanol [50 vol.% acetyl acetone and 50 vol.% ethanol] resulted in decreased yield. Although deposition occurred in this case, the surface morphology was very uneven and surfaces of the deposits were porous. In extreme case of 5 vol.% ethanol in 95 vol.% acetyl acetone, the deposition yield increased but surface morphology remained uneven and porous indicating the presence of agglomerated powder. The above results suggest that when dispersion is good, the yield follows Hamaker's equation, i.e., deposit yields are proportional to the voltage (see Table 2). The Hamaker's equation is invalid for suspensions of poor dispersion (last 4 columns of Table 2).

3.3. Effect of additives on the microstructure

Iodine was added to improve the charging mechanism in non-aqueous solvent [13–15]. Experiments were conducted with addition of 1 mM iodine in the mixed solvent system (5 vol.% acetyl acetone in ethanol). The following are the proposed reactions of alcohol and ketone to generate proton on addition of iodine.

$$\begin{aligned} CH_3-CH_2-CH_2-CH_2-OH+I_2 \rightarrow \quad & CH_3-CH_2-CH_2-CHO+HI \\ & \qquad\qquad \downarrow +I_2 \\ & CH_3-CH_2-CH_2-CHO+H^{+}+I^{-} \end{aligned}$$

The protons released in the process are adsorbed on the surface of the suspended particles to enhance the particle charging and deposition yield. Similar protonation reaction occurs on addition of iodine in acetyl acetone:

$$CH_3\text{–}CO\text{–}CH_2\text{–}CO\text{–}CH_3{}^{+} + I_2$$
$$\rightarrow\ ICH_2\text{–}CO\text{–}CO\text{–}CH_2I\ +\ 2I^{-} + 2H^{+}$$

Adsorption of the formed protons onto the suspended particles will make them positively charged. Fig. 6 shows the deposit yield with the addition of 1 mM iodine in mixed solvent system. Though the deposition increased with time, yield was consistently lower than the mixed solvent system without any additive. Also at higher deposition time, the deposits were visibly porous. In this case, addition of I_2 increased the electrolyte concentration, so that effect of H^+ adsorption was more than offset by the double layer thickness decrease, that eventually led to agglomeration. At higher deposition time,

Table 2
Deposition yield of doped ceria (fine) in mixed solvent, without additives.

Yield (mg cm^{-2})						
Time	Ethanol + acetylacetone 95% + 5%		Ethanol + acetylacetone 5% + 95%		Ethanol + acetylacetone 50% + 50%	
	250 V	500 V	250 V	500 V	250 V	500 V
15 s	38	92	68	85	76	117
30 s	84	170	127	215	123	157
60 s	134	254	184	254	178	395
120 s	305	590	325	325	200	817
300 s	311	561	441	511	122	826

agglomerated particles were depositing, rendering the film highly porous.

EPD experiments were conducted with mixed solvent (5 vol.% acetyl acetone in ethanol) with the addition of 1 mM $Ce(NO_3)_3{\cdot}6H_2O$. It has been shown that [16] to achieve a high deposition rate, certain potential distribution in the cell need to be achieved to supply sufficient voltage at the electrode interface. This can be achieved by adding suitable electrolyte. In this case, cerium nitrate is added to modify the potential distribution, cerium ions are expected to deposit on cathode during EPD, which is not going to contaminate the deposit. Results are shown in Fig. 6. In contrast to the work carried by Zhitomirsky et al. [17], addition of cerium nitrate yielded no satisfactory results. The yield was almost identical with the results obtained with I_2. Addition of cerium nitrate also resulted in significant aggregation with high settling rate. At higher deposition time the film was highly porous.

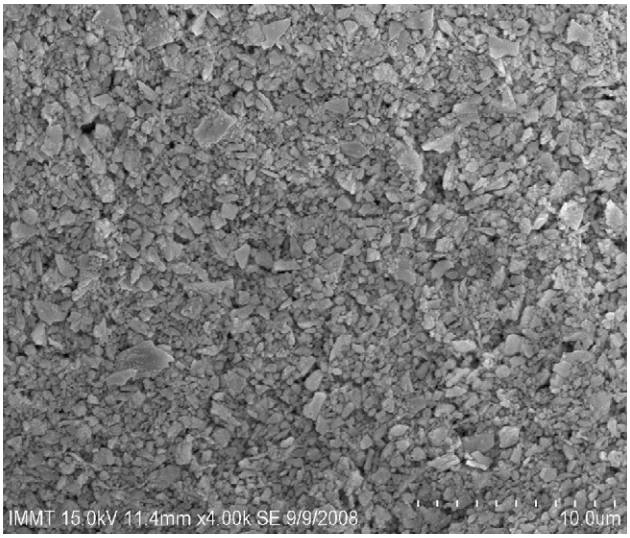


Fig. 7. Green deposit of doped ceria in butanol, at 500 V DC, 1 min deposition time.

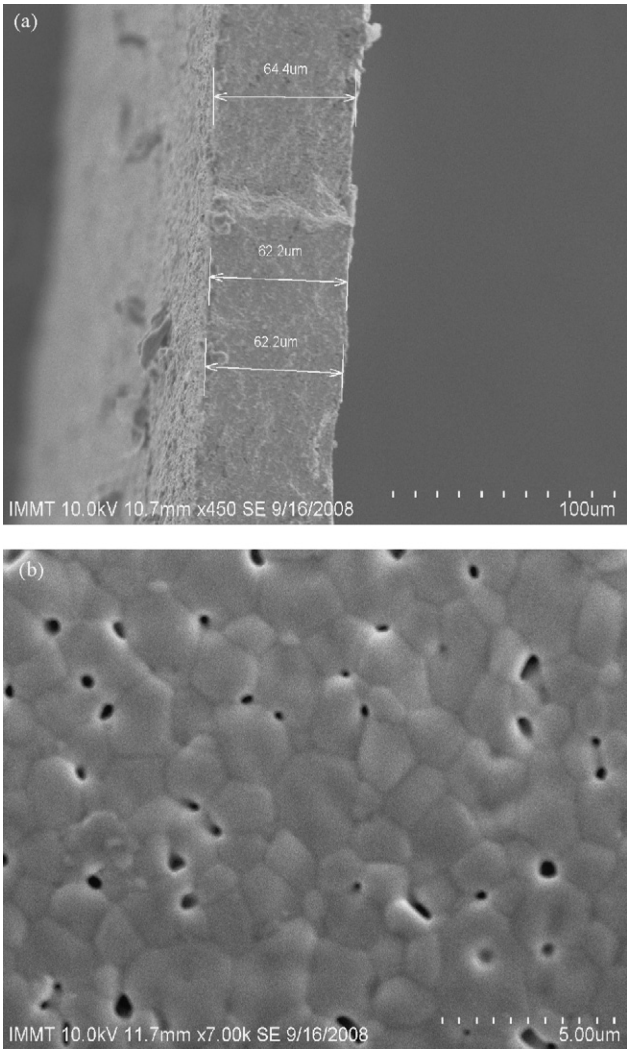


Fig. 8. (a) Thickness of the sintered films at 1400 °C/4 h for 15 s deposition time. (b) Surface microstructure of doped ceria film after sintering at 1400 °C/4 h.

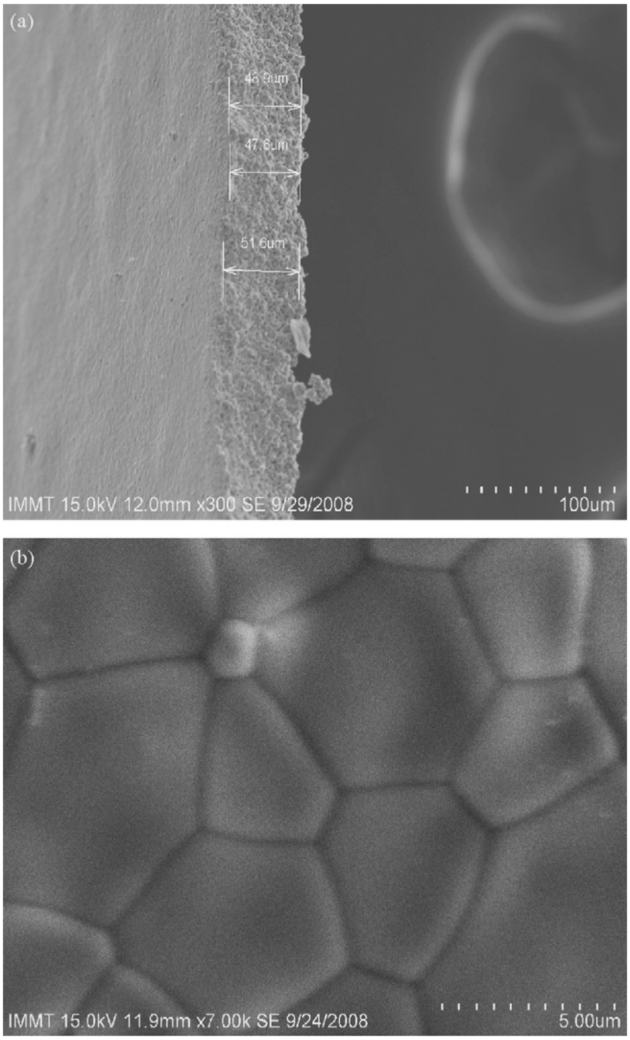


Fig. 9. (a) Thickness of sintered film at 1500 °C/4 h for 15 s deposition time. (b) Surface microstructure of doped ceria film after sintering at 1500 °C/4 h.

3.4. Characterization of deposits

Fig. 7 shows the typical SEM pictures of green deposits of doped ceria obtained in butanol, at 500 V DC, for 1 min deposition time. Fig. 8a and b shows the microstructure of free standing film after burning out of the graphite support followed by sintering at 1400 °C for 4 h. Thickness of the film was ∼60 μm after 15 s deposition. However, surface of the film showed presence of pinholes indicating incomplete sintering. Hence the films were sintered again at temperature 1500 °C for 4 h (Fig. 9a and b). After sintering at 1500 °C, the pin holes were reduced, but there was considerable grain growth (Fig. 9b), grain size almost doubled. Thickness of the film was also reduced from 60 to ∼50 μm for 15 s deposition time (Fig. 9a). The density of the films after sintering at 1500 °C was found out to be around 98% of the theoretical density.

4. Conclusions

Electrophoretic deposition of doped ceria was studied in various non-aqueous solvents. It was observed that deposition yield and the quality of deposit depends on the nature of solvent. In ethanol very uneven deposition occurred while in acetyl acetone deposition yield was good but the surface was uneven and porous, which showed that though the solvents able to charge the surface of the particles, but relatively higher ionic concentration led to agglomeration of particles so that deposition of agglomerated powder rendered the deposit uneven and porous. In case of butanol, deposition yield was much lower but the surface of deposit was smooth and crack free. Due to low dielectric constant of butanol, the surface charge generated on the particle surfaces was low as well as the ionic concentration. This explained low deposition yield due to low electrophoretic mobility, but fairly smooth deposition (less agglomeration). Deposition yield and the deposition quality were found to be best in mixed solvents, having 5 wt.% acetylacetone in ethanol medium. When a small amount of acetyl acetone was added to ethanol, it acted as a non-ionic surfactant. Acetyl acetone has a strong tendency to form chelate or complex bonds with the metal atoms, thereby introducing a steric repulsion between the particles, which stabilizes the suspension. On the other hand, the protons, which were the intermediate by-products of keto–enol reaction, get adsorbed on the particle surfaces to modify the surface charges. It has been possible to prepare a film of thickness 50 μm after sintering at 1500 °C for a deposition time of 15 s at 500 V potential. Deposition yield was found to vary quite linearly till 200 s.

Addition of surface charge modifiers such as iodine and cerium nitrate in mixed solvent system did not improve the result. Though the deposition increased with time, yield was consistently lower than the mixed solvent system without any additive. Also at higher deposition time, the deposits were visibly porous. In this case, addition of modifiers that released protons tend to increase the electrolyte concentration, so that effect of H^+ adsorption on the particle surfaces was more than offset by the double layer thickness decrease, that eventually led to agglomeration. At higher deposition time, agglomerated particles were depositing, rendering the film highly porous.

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