

# Electrophoretic deposition of electrolyte materials for solid oxide fuel cells

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Electrophoretic deposition of electrolyte materials for solid oxide fuel cells, including  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.875}\text{Mg}_{0.125}\text{O}_{3-x}$ , yttria stabilized zirconia and  $(\text{Ce}_{0.8}\text{Gd}_{0.2})\text{O}_{1.9}$ , was studied under various experimental conditions. The use of phosphate ester as a dispersant and poly (vinyl butyral) as a binder enabled high deposition rate and formation of crack-free, adherent deposits. Electrodeposition rates were quantified in experiments performed at constant current and constant voltage modes from suspensions in ethanol, isopropanol and mixed ethanol–isopropanol solvents. The microstructure of as prepared and sintered deposits was studied by electron microscopy. The bath composition was optimized to enable formation of dense deposits. © 2004 Kluwer Academic Publishers

## 1. Introduction

Electrophoretic deposition (EPD) is increasingly being used for the preparation of ceramic coatings for various applications [1–5]. Significant interest has been recently generated in applications of this method for solid oxide fuel cells (SOFC) [6–15]. EPD offers important advantages such as simple and low cost equipment, rigid control of coating thickness and deposition rate. The method enables uniform deposition on substrates of complex shape [16].

The success in EPD is intimately related to a careful choice of bath composition and deposition conditions. Organic solvents are preferable to water since EPD in water is accompanied by significant gas evolution and results in porous deposits. However, some organic solvents are toxic and cause environmental and health concerns. The solvent must dissolve inorganic and organic additives. Recent studies highlighted the importance of chemical compatibility of solvent, powder and other bath components [13, 17].

Ceramic particles must be electrically charged to permit transport by EPD. It should be noted that cathodic EPD is preferable to anodic EPD, because of problems related to anodic dissolution, oxidation of substrates and deposit contamination. Therefore, the important task is to find effective additives for charging particles positively. It is also important to have the capability to deposit laminates of different SOFC materials, including cathode and anode materials, electrolytes and intermediate layers. Such laminates must be deposited cathodically using similar bath compositions. Indeed, changing the direction of electric field as well as changing solvent or additives for deposition of certain materials could result in stripping off the previously deposited layers of other materials.

EPD of submicrometre powders enables dense packing, good sinterability and homogeneous microstruc-

ture [18]. However, due to the high surface area, the submicrometre particles have a strong tendency to agglomeration. Agglomeration of fine ceramic particles can be enhanced by the electric field [19]. Well-dispersed and stable suspensions of fine particles may be obtained by selection of an effective dispersant. It is important to note that the use of fine particles promotes deposit cracking during drying, which could be prevented by the use of a binder. The optimal amount of binder depends on particle size and particle surface area.

In a previous investigation [13] we demonstrated that using ethanol as a solvent, polyvinyl butyral (PVB) as a binder and phosphate ester as a dispersant, advanced materials for SOFCs could be deposited cathodically. Phosphate ester is an effective electrostatic stabilizer, which charges the particles positively, thus allowing cathodic deposition. Moreover, phosphate ester acts as a steric dispersant by anchoring the long-chain molecules to the particle surfaces. PVB is an advanced binder material, which acts also as a dispersant. Important advantages of the solvent–binder–dispersant system are chemical compatibility of the bath components, non-toxic nature of the solvent, effective dispersant and binder and relatively high deposition rate.

In order to utilize the advantages of the approach developed in the previous study, a number of processing parameters must be established. It is important to clarify how the additives affect the deposition rate and deposit morphology. Further investigations are necessary for optimization of bath composition in order to minimize the amount of additives and obtain adherent and uniform deposits of controlled thickness, prevent pinholes, cracks and other defects. In this work we present experimental data on electrophoretic deposition of advanced electrolyte materials for SOFC, including  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.875}\text{Mg}_{0.125}\text{O}_{3-x}$  (LSGM), yttria stabilized zirconia (YSZ) and  $(\text{Ce}_{0.8}\text{Gd}_{0.2})\text{O}_{1.9}$  (CGO).

## 2. Experimental procedures

$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.875}\text{Mg}_{0.125}\text{O}_{3-x}$  (Praxair Surface Technologies), yttria stabilized zirconia (TZ-8Y, Tosoh) and  $(\text{Ce}_{0.8}\text{Gd}_{0.2})\text{O}_{1.9}$  (NexTech Materials) were used for preparation of suspensions in ethanol, isopropanol and mixed ethanol-isopropanol solvents. Poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVB, average  $M_w = 50,000\text{--}80,000$ , Aldrich), and phosphate ester (Emphos PS-21A, Witco) were used as binder and dispersant, respectively. Concentration of ceramic powders in the solvents was 100 g/l.

Ni foils ( $60 \times 30 \times 0.1$  mm) and Ni-yttria stabilized zirconia cermet ( $40 \times 50 \times 1$  mm) were used as substrates for electrophoretic deposition. Cermet substrates were prepared by tape casting technology [13]. The electrophoretic cell was configured with the cathodic substrate centered between two parallel counter-electrodes. The distance between the cathode and anode was 1.5 cm. The suspensions were ultrasonically treated immediately before EPD. EPD experiments were performed at constant current ( $0.05\text{--}1$  mA/cm<sup>2</sup>) or constant voltage (50–200 V) regimes. Deposit mass was obtained by weighing the Ni substrates before and after deposition experiments and drying at room temperature for 15 h. Deposits produced on cermet substrates were sintered in air at 1300°C in a programmable furnace and then thermally treated at 1000°C in forming gas (Ar-7%H<sub>2</sub>). The microstructures of the deposited films were studied by a Philips 515 scanning electron microscope (SEM).

## 3. Experimental results

### 3.1. Effect of dispersant

Suspensions of LSGM, YSZ and CGO in ethanol and isopropanol solvents generally exhibit the problem of rapid sedimentation when ultrasonic treatment is interrupted. EPD experiments have not yielded noticeable deposition from such suspensions at deposition voltages of 50–200 V. The addition of phosphate ester (PE) stabilizes the suspensions from settling allowing one to obtain cathodic deposits.

Fig. 1 shows deposit weight versus PE concentration ( $C_{pe}$ ) for YSZ suspensions at a constant deposition voltage

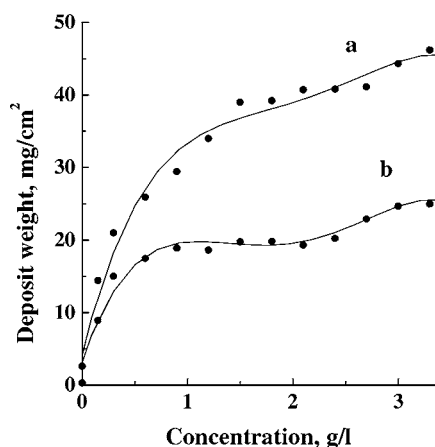


Figure 1 Deposit weight versus  $C_{pe}$  for 100 g/l YSZ suspensions in ethanol (a) and isopropanol (b) at constant deposition voltage of 75 V and deposition time of 3 min.

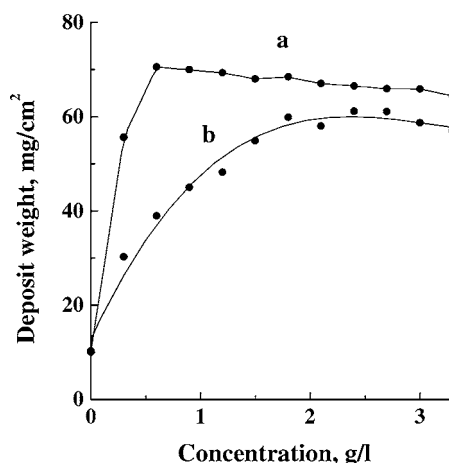


Figure 2 Deposit weight versus  $C_{pe}$  for 100 g/l LSGM suspensions in ethanol (a) and isopropanol (b) at constant deposition voltage of 75 V and deposition time of 3 min.

of 75 V and deposition time of 3 min. Experiments performed with YSZ suspensions in ethanol exhibited higher deposition rates than suspensions in isopropanol. A remarkable increase in the deposit weight was observed when  $C_{pe}$  was increased to the range of 1 g/l. Above 1 g/l, the deposition rate becomes less sensitive to the  $C_{pe}$ . Indeed, the amount of deposit increases more slowly with increasing  $C_{pe}$  in ethanol, and no appreciable change in deposit weight was observed for isopropanol suspensions when  $C_{pe}$  increased from 1 to 2.5 g/l.

Similar experiments performed with LSGM suspensions showed higher deposition rates for ethanol compared to isopropanol solvent (Fig. 2). For suspensions in ethanol a steep increase in deposit weight with increasing  $C_{pe}$  was observed in the range up to 0.6 g/l, but at higher  $C_{pe}$  the addition of PE resulted in slight decrease of the deposition rate. For LSGM suspensions in isopropanol the amount of the deposited material increased with increasing  $C_{pe}$  up to 2.5 g/l and slightly decreased at higher  $C_{pe}$ .

The deposition results from CGO suspensions are shown in Fig. 3. No deposition was observed from ethanol suspensions for  $C_{pe}$  in the range up to 0.6 g/l;

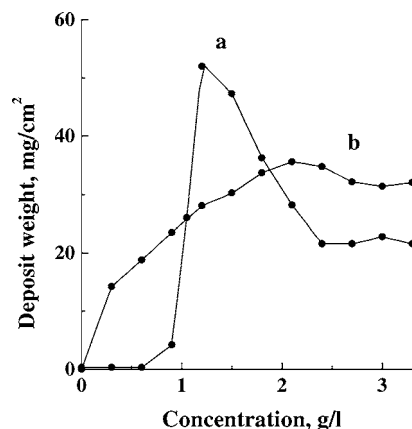


Figure 3 Deposit weight versus  $C_{pe}$  for 100 g/l CGO suspensions in ethanol (a) and isopropanol (b) at constant deposition voltage of 75 V and deposition time of 3 min.

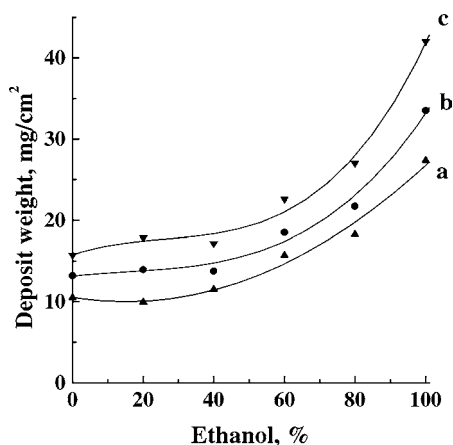


Figure 4 Deposit weight versus ethanol content for 100 g/l YSZ suspensions in mixed ethanol-isopropanol solvent, containing 1.5 g/l PE at deposition voltage of 50 (a), 75 (b) and 100 V (c) and deposition time of 2 min.

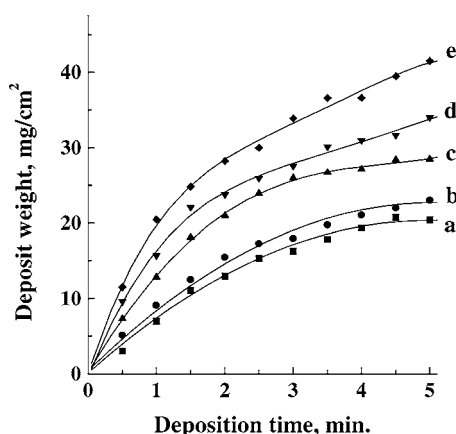


Figure 5 Deposit weight versus deposition time for 100 g/l suspensions of YSZ in mixed ethanol-isopropanol solvent, containing 0 (a), 40 (b), 60 (c), 80 (d) and 100% (e) ethanol and 1.5 g/l PE at constant deposition voltage of 75 V.

at higher  $C_{pe}$ , the deposit weight increased abruptly to a maximum at  $C_{pe} \sim 1.2$  g/l. Further addition of PE resulted in decreasing deposition weight. In contrast, for CGO suspensions in isopropanol, the deposit weight increased gradually with  $C_{pe}$  in the range 0–2.2 g/l, then decreased slightly. However, for  $C_{pe}$  below 0.6 g/l and in the range 2–3.3 g/l, isopropanol was a better vehicle for deposition of CGO, yielding higher rates than ethanol.

The deposition process was also studied in mixed solvents. The experimental data for YSZ suspensions presented in Figs 4 and 5 indicate that the deposit weight increases with increasing content of ethanol in mixed ethanol-isopropanol solvent. Deposit weight increases with increasing voltage and time, thus allowing deposition of layers of variable thickness. Similar dependences were obtained for LSGM suspensions.

### 3.2. Effect of binder

The effect of PVB binder on the deposition rate is illustrated in Fig. 6. The addition of 1 g/l PVB to YSZ suspension containing 1 g/l PE yielded no noticeable change in the deposition rate. However, further addi-

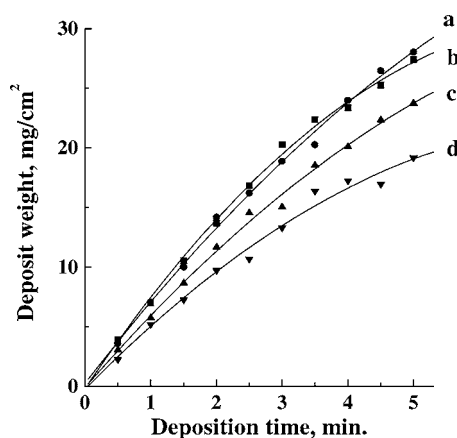


Figure 6 Deposit weight versus deposition time for 100 g/l suspension of YSZ in ethanol containing 1 g/l PE and 0 (a), 1 (b), 2 (c) and 3 g/l (d) of PVB at constant current density of 0.25 mA/cm².

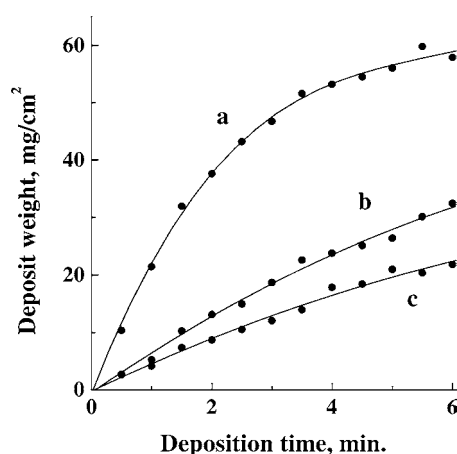


Figure 7 Deposit weight versus deposition time for 100 g/l suspension of LSGM in ethanol solvent, containing 1 g/l PE, without binder (a,b) and with 2 g/l PVB (c) at constant deposition voltage of 50 V (a) and constant current density 0.02 mA/cm² (b,c).

tion of PVB resulted in decreasing deposition rate, as shown in Fig. 6.

Fig. 7 compares the deposit weight—time dependences for LSGM suspensions in the constant voltage and constant current modes. For constant voltage conditions, the amount of material deposited increases with time in a decelerating manner. On the other hand, nearly linear deposit weight—time dependence was observed for the constant current mode. Similar to experiments performed with YSZ suspensions, the addition of binder to LSGM suspensions resulted in decreased deposition rate when deposition was performed in constant current mode (Fig. 7). However, examination of the dependence of deposit weight versus binder concentration ( $C_{pvb}$ ) in YSZ, LSGM and CGO suspensions exhibited different behavior at constant current and constant voltage modes. Experimental results for CGO suspensions, shown in Fig. 8, indicate that deposit weight is nearly independent of  $C_{pvb}$  at constant levels of PE and constant voltage. In contrast, the constant current regime yields a decreasing deposition rate with increasing  $C_{pvb}$ . Constant current experiments performed with YSZ, LSGM and CGO suspensions showed that the measured cell voltage decreased with increasing  $C_{pvb}$ .

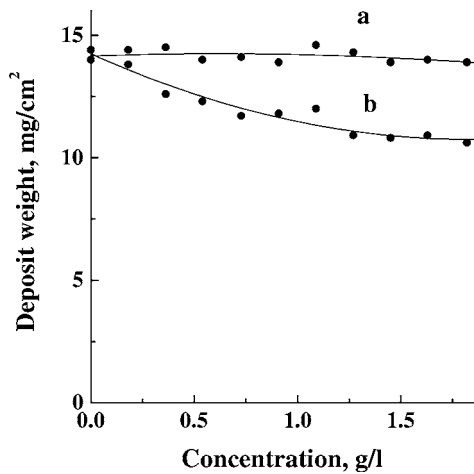


Figure 8 Deposit weight versus  $C_{pvb}$  in 100 g/l suspension of CGO in isopropanol containing 3.3 g/l PE at constant deposition voltage of 75 V (a) and constant current density of 0.015 mA/cm<sup>2</sup> (b), deposition time 2 min.

3.3. Optimization of bath composition

Morphologies of deposits prepared under various experimental conditions were studied by SEM. YSZ and LSGM deposits were non-uniform at  $C_{pe}$  below ~0.5–0.7 g/l and exhibited significant cracking after drying. Further addition of PE resulted in uniform deposits and reduced cracking when deposition was performed at voltages up to ~100 V. Pinholes were observed in the deposits when  $C_{pe}$  was higher than ~2–2.5 g/l or deposition voltage was higher than 150–200 V. Addition of binder resulted in improved deposit adhesion. The thickness of crack free deposits increased with increasing  $C_{pvb}$ . Crack-free, adherent and uniform YSZ and LSGM deposits with thickness up to 100 μm were obtained from suspensions in ethanol containing 1–1.5 g/l PE and 1–2 g/l PVB. In the case of CGO suspensions in ethanol, the binder and dispersant concentrations were in the range  $C_{pe} = 1.5–2$  g/l and  $C_{pvb} = 1.5–2$  g/l. For

CGO suspensions in isopropanol optimal concentrations of binder and dispersant were in the range  $C_{pe} = 1–1.5$  g/l and  $C_{pvb} = 1–1.5$  g/l.

Fig. 9 shows the cross section of a YSZ deposit on a cermet substrate after sintering in air at 1300°C for 2 h and reducing the sample at 1000°C for 1 h. The deposit was relatively dense and adhered well to the substrate.

4. Discussion

4.1. Deposition rate

The deposition rate  $w$  in the EPD process can be described by the relation:

$$w = C\mu U/d \tag{1}$$

where  $C$  and  $\mu$  are particle concentration and mobility, respectively,  $U = U_{app} - U_{dep}$ , where  $U_{app}$  is applied voltage,  $U_{dep}$  is voltage drop in the deposit, and  $d$  is the distance between electrodes.  $U_{dep}$  is proportional to deposit resistivity, which, in turn, increases with deposit thickness.

When particle radius is large compared to the Debye length,  $1/\kappa$ , the electrophoretic mobility is given [20] by Smoluchowski’s formula:

$$\mu = \epsilon\epsilon_0\zeta/\eta \tag{2}$$

where  $\zeta$  is zeta potential,  $\eta$  and  $\epsilon$  are, respectively, the viscosity and the relative permittivity of the liquid and  $\epsilon_0$  is the permittivity of vacuum.

For particles that are much smaller than  $1/\kappa$ , the electrophoretic mobility is given [20] by Hückel’s formula:

$$\mu = 2\epsilon\epsilon_0\zeta/3\eta \tag{3}$$

The use of PE for particle charging enables formation of stable suspensions and prevents particle

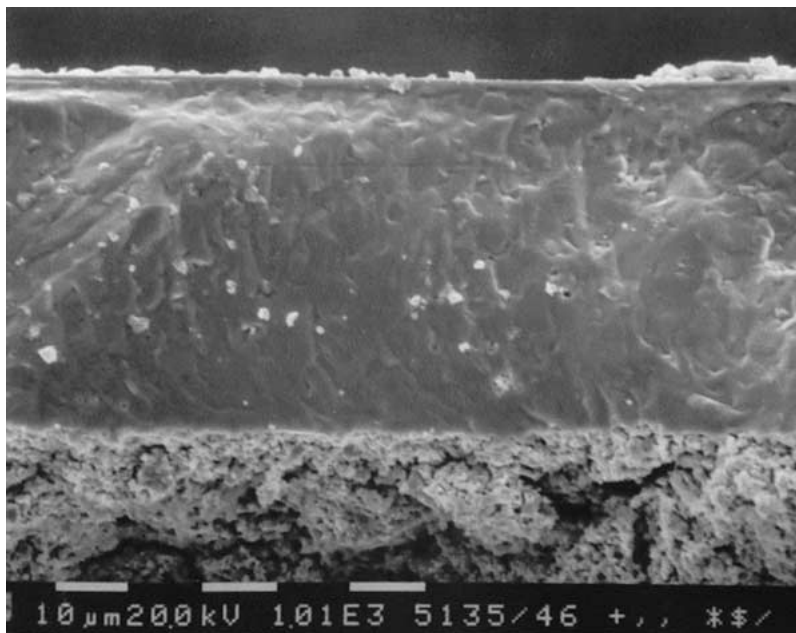


Figure 9 SEM picture of YSZ deposit on a porous Ni-YSZ cermet substrate sintered at 1300°C in air during 2 h and reduced in forming gas (Ar-7%H<sub>2</sub>) at 1000°C during 1 h.

agglomeration. Relatively high deposition rates were observed for all ceramic materials in this study (Figs 1–3). The amount of deposited material can be controlled by variation of bath composition, deposition time, current density or applied voltage (Figs 1–8). The mechanism of particle charging using PE (Emphos PS-21A) was discussed in several papers [21–24]. According to the mechanism proposed by Mickeska and Cannon, PE adsorbs as a neutral molecule on ceramic particles, followed by proton transfer to basic sites and creation of a positively charged surface [22]. It should be noted that the most common methods for particle charging in EPD are based on the use of additives. The dissociation of additives in the solvent, followed by ion adsorption on the particle surface results in particle charging. However, it is suggested that only a fraction of the ions is adsorbed on the particle surface. On the other hand, the dissociation of additives increases the ionic strength of suspensions, resulting in reduced thickness of the electrical double layer of ceramic particles, which, in turn, results in particle coagulation and sedimentation. Due to particle sedimentation, the concentration of ceramic particles in suspension decreases during deposition. According to Equation 1, the decrease in particle concentration leads to decreasing deposition rate. On the other hand particle coagulation could result in deposits of low green density and poor sinterability. Therefore, the important task is to find a possibility of particle charging at low ionic strength of suspensions.

#### 4.2. Particle charging and stabilization using PE

The combination of electrostatic and steric stabilization provided by PE is advantageous for electrophoretic deposition. Indeed, steric stabilization is less sensitive to increased ionic strength [25]. It is important to note that in the case of PE the increase in ionic strength can be diminished, as dissociation of the additive is achieved mainly on the particle surface. Conductivity measurements performed in refs. 22 and 26 indicate that ionization of PE is relatively slight in the pure solvent while ionization is appreciable in the presence of BaTiO<sub>3</sub> powder. It was concluded that ceramic powders promote PE dissociation. In a recent investigation [27], experimental results were obtained supporting a suggestion of Cannon *et al.* [26] that the powder surface acts as a catalyst for dissociation of PE. Conductivity measurements were performed for YSZ suspensions in ethanol and isopropanol and compared with conductivities of the pure solvents, containing the same amounts of PE [27]. Relatively small changes in conductivity were observed with increasing PE content in ethanol and isopropanol solvents. However, conductivity increased significantly in the presence of YSZ particles.

Successful utilization of PE in EPD requires an understanding of the mechanism of dispersant adsorption on particle surfaces and particle charging. Recent studies showed that particle—PE, solvent—PE and particle—solvent interactions must be considered [24, 28]. It is in this regard that much higher conductivities

were obtained for YSZ suspensions in ethanol compared to YSZ suspensions in isopropanol solvent [27]. The experimental data presented in Figs 4 and 5 are in line with these results. Indeed, higher deposition rates in ethanol suspensions (Figs 4 and 5) could be attributed to enhanced dissociation of PE on the particle surfaces in ethanol, which in turn resulted in increasing particle charge and increasing conductivity. However, it should be noted that some difference in deposition rate could also result from different mass transport conditions. Indeed, electrophoretic mobility (Equations 2 and 3) should be higher in ethanol compared to that in isopropanol owing to higher dielectric constant and lower viscosity of ethanol [29]. It was also established that surface properties of the particles [27] and acid—base interactions between particles and PE [28] are important factors controlling particle charging.

In a previous investigation [13], deposition rate was traced as a function of  $C_{pe}$  in ethanol suspensions. For all ceramic compositions studied, the measurements yielded a maximum in deposit weight versus  $C_{pe}$  dependences. Note, that in previous investigations, deposit weights were compared at constant current density. The increase in  $C_{pe}$  provides better stability of suspensions and increases the particle charge and deposition rate. However, it was demonstrated that the increase in  $C_{pe}$  also resulted in an increase of suspension conductivity [27].

Turning again to the experimental data presented in ref. 13 it is suggested that when  $C_{pe}$  increases, the increase in suspension conductivity can result in a lower voltage drop at the same current density. In accordance with Equation 1, the deposition rate decreases with decreasing voltage, resulting in observed [13] maximum in  $w = w(C_{pe})$  dependences. When EPD is performed in the constant voltage mode, the initial electric field is the same for suspensions with different  $C_{pe}$ . Some changes in electric field could be expected during deposition due to the voltage drop in the deposit. In this work we analyze deposition rates obtained at a constant voltage mode and different  $C_{pe}$  (Figs 1–3).

Constant voltage data showed deposit weight versus  $C_{pe}$  dependence (Figs 1 and 2) different from that observed for constant current experiments [13]. Indeed, a continuous increase in deposit weight with  $C_{pe}$  was observed for YSZ suspensions (Fig. 1). For LSGM suspensions deposit weight increased with  $C_{pe}$  at low dispersant concentrations. Only a slight decrease in  $w$  was observed for LSGM suspensions (Fig. 2) at relatively high  $C_{pe}$ . In contrast, a maximum followed by a significant decrease in deposition rate was observed in the  $w = w(C_{pe})$  dependence for LSGM in constant current experiments [13]. The difference in  $w = w(C_{pe})$  dependence obtained in this work and in previous investigations for YSZ and LSGM can be attributed to higher conductivity of suspensions at higher  $C_{pe}$  which resulted in lower electric fields when  $w = w(C_{pe})$  dependences were acquired at constant current modes.

For CGO suspensions,  $w = w(C_{pe})$  behavior in ethanol and isopropanol was different. When  $C_{pe}$  was varied in the low range of 0–0.6 g/l, deposition was achieved only from suspensions in isopropanol. For

CGO suspensions in ethanol a sharp maximum was observed in  $w = w(C_{pe})$  dependence in the constant voltage mode (Fig. 3), similar to that obtained in constant current experiments [13]. The experimental data indicate that isopropanol is a preferred solvent for CGO suspensions, as deposition can be achieved at lower  $C_{pe}$  and the deposition rate is not so sensitive to small changes in  $C_{pe}$ . It should be noted that the deposition rate in the electrophoretic process depends on various factors, discussed above. Therefore, more detailed investigation, currently under way, is necessary to explain the experimental results obtained for CGO suspensions.

Another point to be considered is the possibility of PE intercalation into the ceramic deposits. It should be noted that PE was found to leave a certain amount of residual phosphorus in BaTiO<sub>3</sub> ceramics prepared by tape casting, modifying the sintering behavior, structure and properties of the ceramic material [30]. However, it was shown that suspensions of ceramic particles for tape casting could be stabilized at low  $C_{pe}$ , with PE content in green bodies of <100 ppm. Moreover, a significant part of the PE is pyrolyzed during sintering [26]. Experimental results of this work indicate that suspensions for electrophoretic deposition can be stabilized at much lower  $C_{pe}$ , compared to tape casting technology [31]. This is not surprising, as in suspensions for EPD, particle concentrations are much lower and interparticle distances are larger, compared to suspensions used for tape casting. It is suggested that ceramic particles in the EPD process transport adsorbed PE molecules to the electrode surface. Therefore, only adsorbed PE molecules are included in EPD deposits. In contrast, the entire PE from suspensions is included in the product after drying of the tapes prepared by tape casting technology. Therefore, the risk of PE intercalation in ceramic deposits is much lower in EPD. Taking into account the industrial importance of PE for tape casting, we can suggest that PE will also find increasing application in EPD.

### 4.3. PVB binder in EPD

PVB binder was added to the suspensions in order to increase the adherence and strength of the deposited material and prevent cracking. The polymer can provide steric stabilization of suspensions of ceramic particles and reduce viscosity of the suspensions. In EPD processing, charged ceramic particles transport adsorbed polymer to the electrode surface, thus allowing the polymer binder to be included in the deposit. This is in contrast to some other ceramic techniques, where the entire dissolved polymer is included in green bodies after solvent evaporation. Therefore, the control of polymer adsorption is of paramount importance for electrophoretic deposition. The amount of adsorbed polymer depends on polymer concentration in suspension and specific polymer-particle, polymer-solvent, particle-solvent and particle-dispersant interactions. Good solvents are necessary to dissolve polymers. However, the polymer can be adsorbed on the surface of ceramic particles when its solubility in the dispersion medium is low. Adsorption of polymer on ceramic particles in a poor solvent can result in bridging flocculation.

In contrast, good solvents are important to achieve steric stabilization. Polymer stabilizing moieties, which extend out from the particle surface must be well solvated in a good solvent. Therefore, for electrophoretic deposition it could be advantageous to use copolymers of a block or graft type. Indeed, insoluble polymers serve to anchor copolymer molecules to the particle surface, whereas chains of soluble polymers enable steric stabilization.

Polyvinyl butyral is an important binder material in ceramic processing due to its good adhesion to oxide particles and easy burnout properties. It is advantageous to use this binder material, which also acts as a dispersant [32–34]. In this work PVB was used for EPD. Polyvinyl alcohol functional groups are important for adsorption of PVB on ceramic particles. It is suggested that these functional groups form hydrogen bonds with hydroxyl groups on the particle surface [32–36]. In contrast, butyral segments can be directed toward the suspension, providing steric stabilization [35, 36]. Our experiments indicate that the use of PVB improved adhesion of deposits and prevented cracking.

Polymers could be utilized to induce steric stabilization where the polymers are attached to the particle surface, or depletion stabilization in which the polymers are free in suspension. However, increasing polymer concentration can induce bridging or depletion flocculation [37] and particle sedimentation. Particle sedimentation results in decreasing particle concentration, which in turn results in decreasing deposition rate (Equation 1). Moreover, competitive adsorption of PE and polymer could result in decreasing particle charge. Therefore it is important to study the deposition process at various  $C_{pvb}$ .

For application in SOFCs it is important to deposit gas-tight electrolyte layers. However, sintered deposits obtained in ref. 13 were porous. Presented experimental data are important for the optimization of suspension compositions and deposition conditions in order to obtain the proper microstructure for the deposits. Dense deposits were obtained in current investigations. Further experiments will be focused on testing of fuel cells prepared by EPD.

## 5. Conclusions

Electrophoretic deposition of La<sub>0.8</sub>Sr<sub>0.2</sub>Ga<sub>0.875</sub>Mg<sub>0.125</sub>O<sub>3-x</sub>, yttria stabilized zirconia and (Ce<sub>0.8</sub>Gd<sub>0.2</sub>)O<sub>1.9</sub> was achieved from suspensions in ethanol, isopropanol and mixed ethanol–isopropanol solvent. The use of phosphate ester as a dispersant enabled the formation of cathodic deposits from stable suspensions. Crack free and adherent deposits were obtained using poly(vinyl butyral) additive as a binder. The electrodeposition process has been quantified in experiments performed at constant current and constant voltage modes, while varying the solvent content and concentration of the additives. For La<sub>0.8</sub>Sr<sub>0.2</sub>Ga<sub>0.875</sub>Mg<sub>0.125</sub>O<sub>3-x</sub> and yttria stabilized zirconia suspensions, higher deposition rate was observed in ethanol compared to that in isopropanol solvent, whereas isopropanol is the preferred solvent for deposition of (Ce<sub>0.8</sub>Gd<sub>0.2</sub>)O<sub>1.9</sub>. It was shown that the increase in concentration of dispersant and binder

could result in a decreasing deposition rate in the constant voltage mode due to an increase in suspension conductivity. These results were utilized for optimization of bath composition and deposit morphology and allowed formation of dense sintered coatings.

## References

1. M. S. J. GANI, *Industr. Ceram.* **14** (1994) 163.
2. P. SARKAR and P. S. NICHOLSON, *J. Amer. Ceram. Soc.* **79** (1996) 1987.
3. R. MORENO and B. FERRARI, *Bull. Amer. Ceram. Soc.* **79** (2000) 44.
4. A. R. BOCCACCINI, P. A. TRUSTY, D. M. R. TAPLIN and C. B. PONTON, *J. Europ. Ceram. Soc.* **16** (1996) 1319.
5. C. KAYA, A. R. BOCCACCINI and K. K. CHAWLA, *J. Amer. Ceram. Soc.* **83** (2000) 1885.
6. T. ISHIHARA, K. SATO and Y. TAKITA, *ibid.* **79** (1996) 913.
7. T. ISHIHARA, K. SHIMOSE, T. KUDO, H. NISHIGUCHI, T. AKBAY and Y. TAKITA, *ibid.* **83** (2000) 1921.
8. H. NEGISHI, N. SAKAI, K. YAMAJI, T. HORITA and H. YOKOKAWA, *J. Electrochem. Soc.* **147** (2000) 1682.
9. Z. PENG and M. LIU, *J. Amer. Ceram. Soc.* **84** (2001) 283.
10. F. CHEN and M. LIU, *J. Europ. Ceram. Soc.* **21** (2001) 127.
11. R. N. BASU, C. A. RANDALL and M. J. MAYO, *J. Amer. Ceram. Soc.* **84** (2001) 33.
12. J. WILL, M. K. M. HRUSCHKA, L. GUBLER and L. J. GAUCKLER, *ibid.* **84** (2001) 328.
13. I. ZHITOMIRSKY and A. PETRIC, *J. Europ. Ceram. Soc.* **20** (2000) 2055.
14. *Idem.*, *JOM, The Miner. Met. Mater. Soc. J.* **53** (2001) 48.
15. T. MATHEWS, N. RABU, J. R. SELLAR and B. C. MUDDLE, *Solid State Ion.* **128** (2000) 111.
16. I. ZHITOMIRSKY, *J. Europ. Ceram. Soc.* **18** (1998) 849.
17. J. VAN TASSEL and C. A. RANDALL, *ibid.* **19** (1999) 955.
18. I. ZHITOMIRSKY and L. GAL-OR, *J. Mater. Sci.: Mater. Med.* **8** (1997) 213.
19. W. M. WINSLOW, *J. Appl. Phys.* **20** (1949) 1137.
20. H. OHSHIMA, *Coll. Surf. A: Physicochem. Engin. Asp.* **103** (1995) 249.
21. K. MIKESKA and W. R. CANNON, in "Advances in Ceramics. Forming of Ceramics," edited by J. A. Mangels and G. L. Messing (American Ceramic Society, Columbus, OH, 1984) Vol. 9, p. 164.
22. *Idem.*, *Coll. Surf.* **29** (1988) 305.
23. T. CHARTIER, E. STREICHER and P. BOCH, *Bull. Amer. Ceram. Soc.* **66** (1987) 1653.
24. U. PAIK, V. A. HACKLEY, S.-C. CHOI and Y.-G. JUNG, *Coll. Surf. A: Physicochem. Engin. Asp.* **135** (1998) 77.
25. D. H. NAPPER, "Polymeric Stabilization of Colloidal Dispersions," (Academic Press, London, 1983) p. 20.
26. W. R. CANNON, R. BECKER and K. R. MIKESKA, in "Advances in Ceramics. Ceramic Substrates and Packages for Electronic Applications," edited by M. F. Yan, K. Niwa, H. M. O'Bryan, Jr. and W. S. Young (American Ceramic Society, Westerville, OH, 1989) Vol. 26, p. 525.
27. I. ZHITOMIRSKY and A. PETRIC, in Proceedings of the 1st International Conference on Electrophoretic Deposition, Banff, Canada, 2002, p. 222.
28. G. F. HUDSON, M. M. ANDREWS and S. RAGHAVAN, *Coll. Polym. Sci.* **271** (1993) 56.
29. R. MORENO, *Bull. Amer. Ceram. Soc.* **71** (1992) 1521.
30. A. C. CABALLERO, J. F. FERNÁNDEZ, C. MOURE and P. DURÁN, *Mater. Res. Bull.* **32** (1997) 221.
31. W. R. CANNON, J. R. MORRIS and K. R. MIKESKA in "Advances in Ceramics. Multilayer Ceramic Devices," edited by J. B. Blum and W. R. Cannon (American Ceramic Society, Westerville, OH, 1986) Vol. 19, p. 161.
32. J. H. JEAN, S. F. YEH and C. J. CHEN, *J. Mater. Res.* **12** (1997) 1062.
33. S. BHATTACHARJEE, M. K. PARIA and H. S. MAITI, *J. Mater. Sci.* **28** (1993) 6490.
34. M. D. SACKS and G. W. SCHEIFFELE in "Advances in Ceramics. Multilayer Ceramic Devices," edited by J. B. Blum and W. R. Cannon (American Ceramic Society, Westerville, OH, 1986) Vol. 19, p. 175.
35. M. D. SACKS, C. S. KHADILKAR, G. W. SCHEIFFELE, A. V. SHENOY, J. H. DOW and R. S. SHEU, in "Advances in Ceramics. Ceramic Powder Science," edited by G. L. Messing, K. S. Mazdizyani, J. W. McCauley and R. A. Haber (American Ceramic Society, Westerville, OH, 1987) Vol. 21, p. 495.
36. K. NAKAMAE, K. SUMIYA, T. TAIH and T. MATSUMOTO, *J. Polym. Sci.: Polym. Simp.* **71** (1984) 109.
37. E. DICKINSON and L. ERIKSSON, *Adv. Coll. Interf. Sci.* **34** (1991) 1.

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