

Electrophoretic deposition of ceramic materials for fuel cell applications

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Abstract

La_{0.8}Sr_{0.2}Ga_{0.875}Mg_{0.125}O_{3-x} (LSGM), La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF), yttria stabilized zirconia (YSZ) and (Ce_{0.8}Gd_{0.2})O_{1.9} (CGO) were electrophoretically deposited on Ni foils and Ni-yttria stabilized zirconia substrates prepared by tape casting. It was demonstrated that the ethyl alcohol–phosphate ester–polyvinyl butyral system is an effective solvent–dispersant–binder system for electrophoretic deposition of these materials. The influence of dispersant, binder and current density on deposition efficiency and deposit morphology was studied. The microstructure of the deposits was examined by electron microscopy. The proposed solvent–dispersant–binder medium for electrophoretic deposition of LSGM, LSCF, YSZ and CGO has important advantages and implications in fuel cell design. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Electrodeposition of ceramic films has become an attractive alternative for the fabrication of solid oxide fuel cells (SOFC),^{1–7} due to the need to reduce layer thickness to the order of microns. Electrodeposition is especially attractive for SOFC applications owing to simple, low cost equipment and ease of deposition of multilayer films of controlled thickness on substrates of complex shape. Two processes are commonly used to prepare ceramic coatings by electrodeposition: the electrophoretic process that is based on the use of suspensions of ceramic particles⁸ and the electrolytic process that starts from solutions of metal salts.^{9,10} Electrophoretic deposition (EPD) allows preparation of thick films and laminates of complex oxides^{11–14} with film thickness from a few microns to mm. Cathode and anode supported fuel cells have been produced this way.^{1–3}

Electrophoresis is achieved by the motion of charged particles towards an electrode under an applied electric field. Cathodic or anodic deposits can be obtained depending on the nature of the particle charge. According to Ref. 8, particle/electrode reactions are not involved in

EPD and ceramic particles do not lose their charge on being deposited. The reversal of the electric field results in stripping off the deposited layer. Therefore, for formation of laminates of ceramic materials it is important to use suspensions of similarly charged particles. Moreover, for better control of film thickness, it is important to perform deposition of consecutive layers of different ceramic materials from suspensions of similar compositions.

A suspension for EPD is a complex system in which each component has a substantial effect on deposition efficiency. Success in the electrophoretic processing is intimately related to a careful choice of solvent and additives. It is very important to obtain well-dispersed and stable suspensions. In general, suspensions can be dispersed by electrostatic, steric, or electrosteric stabilization mechanisms. Ceramic particles must be electrically charged to permit forming by EPD. The charge on a colloidal particle could originate from various sources, such as from adsorbed simple inorganic ions or from dispersants. A binder is also added to the suspension to increase the adherence and strength of the deposited material and prevent cracking. Important factors to consider when selecting a binder-dispersant-solvent system are: chemical compatibility of components, solubility of binder and additives, viscosity and electric resistivity of the suspension.

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In this paper experimental results are presented on EPD of important materials used for fuel cell applications: $(\text{Ce}_{0.8}\text{Gd}_{0.2})\text{O}_{1.9}$, yttria stabilized zirconia (anode, electrolyte¹⁵), $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.875}\text{Mg}_{0.125}\text{O}_{3-x}$ (electrolyte^{16,17}) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (cathode²). The goal of this work involves the finding of a common solvent–binder–dispersant system for cathodic EPD of these materials.

2. Experimental procedures

2.1. Materials for electrophoretic deposition

$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.875}\text{Mg}_{0.125}\text{O}_{3-x}$, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (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 as ceramic powders for electrophoretic deposition. Poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (average $M_w = 50,000$ – $80,000$, Aldrich), and phosphate ester (Emphos PS-21A, Witco) were used as binder and dispersant, respectively. Concentration of ceramic powders in ethyl alcohol, used as a solvent, was 100 g/l.

2.2. Substrates for electrophoretic deposition

Ni foils ($60 \times 60 \times 0.1$ mm) and Ni-yttria stabilized zirconia cermet ($40 \times 55 \times 1$ mm) were used as substrates for electrophoretic deposition. Cermet substrates were prepared by tape casting technology.

2.3. Tape casting procedure

The slurry composition for tape casting of nickel oxide (Inco, F-grade) and yttria stabilized zirconia YSZ (TZ-8Y, Tosoh) has been developed as given in Table 1. A mixture of toluene and ethyl alcohol was used as a solvent. To obtain well-dispersed slurry, Z-3 Blown Menhadeh fish oil was chosen as a dispersant. The binder used is a polyvinyl butyral (Butvar, B79) and the plasticizer is a butyl benzyl phthalate (S-160). The carrier film was silicone coated mylar. Z-3 Blown Menhadeh fish oil, polyvinyl butyral, butyl benzyl phthalate and mylar were purchased from Richard E. Mistler, Inc. The milling was done in two stages. First, the dispersant

Table 1
Slurry composition for tape casting of Ni–YSZ cermet

Material	Function	Wt. %	Vol. %
NiO	Powder	36.1	10.5
YSZ	Powder	27.2	9.0
Ethyl alcohol	Solvent	10.5	25.9
Toluene	Solvent	15.7	35.4
Fish oil	Dispersant	1.0	1.9
PVB	Binder	3.3	6.5
Butyl benzyl phthalate	Plasticizer	6.2	10.8

was added to the solvent, followed by nickel oxide and YSZ powders. This slurry was ball milled for 24 h in order to break up weak agglomerates. Then binder and plasticizer were added to the above suspension and the resulting slurry was milled for 24 h.

Tape casting was performed using a laboratory tape casting unit. This device enables the production of tapes of 16 cm width and maximum length 150 cm, by moving a container with 2 blades along a fixed support. The gap between the doctor blade and the casting surface was 400 μm . Tape drying was carried out at room temperature in the air. After drying, the tapes peeled easily off the substrate. The tapes were sectioned along both directions and laminated with the casting direction alternating between layers. The laminates (70×50 mm) were die pressed for 5 min at a pressure of 10 MPa at room temperature. The laminates were slowly heated to 1200°C at a heating rate of 0.3°C/min with three dwells at 185°C (3 h), 400°C (4 h), and 600°C (3 h) to burn out the organic components, then held 5 h at 1200°C. The NiO was then reduced to metallic nickel at a temperature of 1000°C in reducing atmosphere (7% H_2 in Ar).

2.4. Electrophoretic deposition

The electrophoretic cell included the cathodic substrate centered between two parallel counterelectrodes. 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 (0.05–1 mA/cm²) regimes. Deposit weights were obtained by weighing the Ni substrates before and after deposition experiments followed by drying at room temperature for 15 h. Deposits obtained on cermet substrates were sintered in air in a programmable furnace and then thermally treated at 1000°C in a reducing atmosphere. The microstructures of the deposited films were studied by a Philips 515 scanning electron microscope (SEM).

3. Experimental results

Experiments performed with suspensions of $(\text{Ce}_{0.8}\text{Gd}_{0.2})\text{O}_{1.9}$ (CGO), yttria stabilized zirconia (YSZ) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.875}\text{Mg}_{0.125}\text{O}_{3-x}$ (LSGM) in ethyl alcohol have not yielded noticeable deposition. However, after addition of phosphate ester (PE) to the suspensions, cathodic deposits were obtained. Fig. 1 shows the weight of cathodic deposits on Ni substrates versus PE concentration for constant deposition time and current density. For LSGM suspensions, the deposit weight increased abruptly with increasing dispersant concentration in the range up to 0.5 g/l. However, these deposits were non-uniform. The deposit uniformity could be improved by further addition of dispersant,

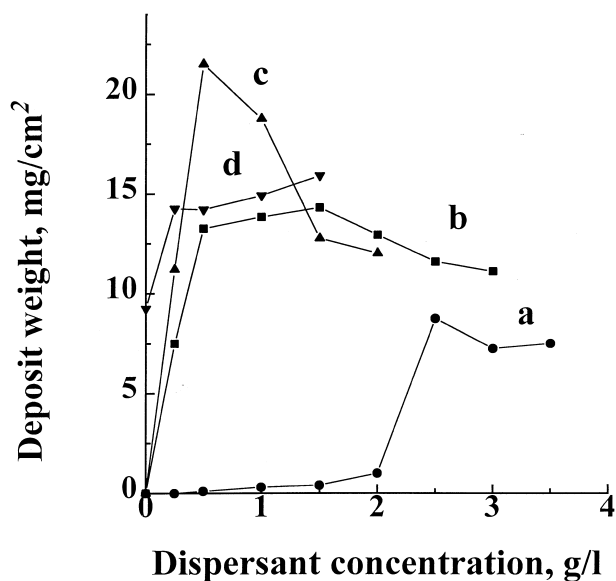


Fig. 1. Deposit weight versus PE concentration in 100 g/l suspensions of (a) CGO, (b) YSZ, (c) LSGM and (d) LSCF in ethyl alcohol, current density 0.1 (a) 0.3(b) 0.2(c) and 1.0 (d) mA/cm², deposition time 3 (a,b,d) and 0.5 (c) min, Ni substrate.

but deposit weight decreased when dispersant concentration was higher than 0.5 g/l. For CGO suspensions, appreciable deposition rates were obtained when dispersant concentration was higher than 2 g/l. In contrast, La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) deposits could be obtained from suspensions in ethyl alcohol without additives. However, deposits obtained without the dispersant were highly agglomerated and non-uniform. The data presented in Fig. 1 indicate that the weight of LSCF deposits increased with increasing dispersant concentration. However, significant deposit spalling was observed when dispersant concentration was higher than 1.5 g/l and deposition times higher than 1.5 min. In contrast, no deposit spalling was observed during 10 min at the same current density when 2 g/l poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVB) was added to the suspension. Sedimentation experiments have shown that the addition of PE up to 2–3.5 g/l resulted in increasing stability of CGO, YSZ, LSGM and LSCF suspensions in ethyl alcohol, but electric conductivity of the suspensions also increased. Addition of PVB binder up to 2.5–3 g/l resulted in better adhesion of the electrophoretic deposits. Further experiments were performed using both PE and PVB additives.

Fig. 2 shows deposit weight of the CGO coating per unit surface area as a function of deposition time. It can be seen that the deposit weight increases with deposition time at constant current density, as well as with current density at fixed deposition time. Nearly linear deposit weight–time dependencies were recorded. Similar dependencies were obtained for YSZ, LSCF and LSGM (Fig. 3). The experimental data presented in Figs. 2 and 3 illustrate the way in which the amount of deposit can be controlled.

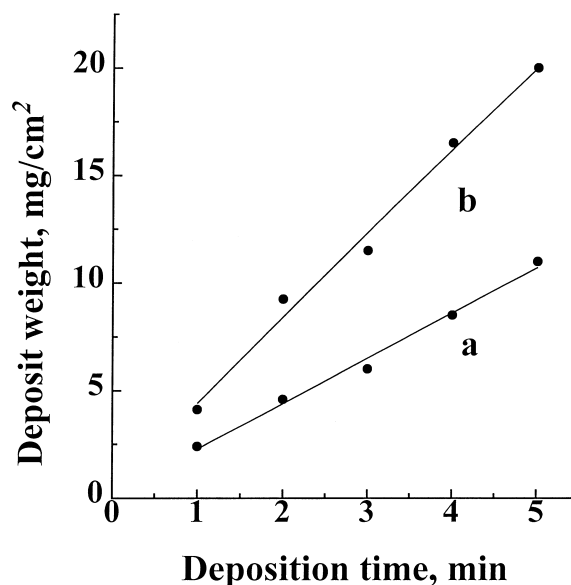


Fig. 2. Deposit weight versus deposition time for 100 g/l suspensions of CGO in ethyl alcohol, contained 3.5 g/l PE + 3 g/l PVB, current density 0.05 (a) and 0.1 (b) mA/cm², Ni substrate.

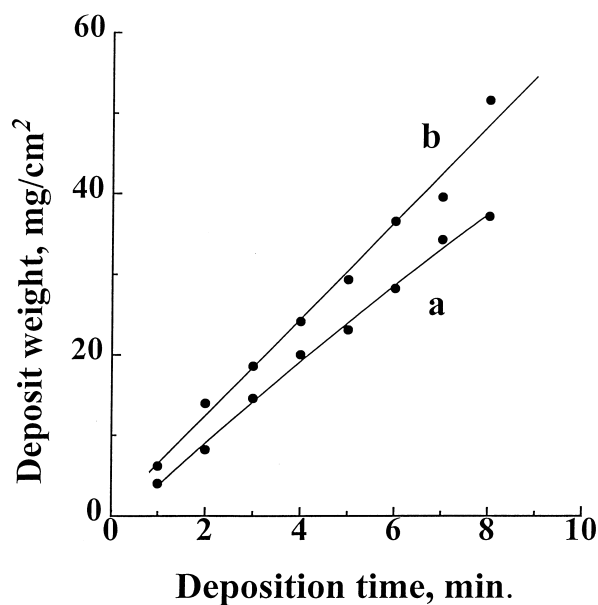


Fig. 3. Deposit weight versus deposition time for suspensions in ethyl alcohol: 100 g/l YSZ + 2.5 g/l PE + 2.5 g/l PVB, current density 0.3 mA/cm² (a) and 100 g/l LSCF + 2.5 g/l PE + 2.5 g/l PVB, current density 1.0 mA/cm² (b), Ni substrate.

In deposition experiments performed without binder, the deposits were prone to poor adhesion. Cracking was observed in the coatings after solvent evaporation when deposit thickness exceeded 50–100 μm. The cracking was more obvious in YSZ coatings when the powder consisted of submicron particles. In contrast, deposits obtained from suspensions containing PVB adhered well to the substrates and were crack free for deposit thickness in the range of 150–200 μm.

In addition to Ni substrates, electrophoretic deposition of CGO and YSZ was also performed on tape cast Ni-YSZ cermet. Fig. 4 shows the surface of the cermet sintered at 1200°C in air for 4 h and then thermally treated in reducing atmosphere at 1000°C for 1 h to convert NiO to Ni. This process, accompanied by oxygen loss and volume change, increases the porosity of the cermet.

CGO and YSZ films of 10–40 microns thickness have been found to exhibit good bonding to the substrate. Fig. 5 shows SEM photos of CGO deposits on the cermet substrate. The green deposit (Fig. 5a) contained particles of various dimensions ranging up to ~1–2 µm. SEM observations showed relatively dense packing of the particles. Observed microporosity could be attributed to flaws in particle packing. CGO (Fig. 5b) and YSZ (Fig. 6) deposits on the cermet substrate, sintered at 1400°C for 5 h in air and then thermally treated in reducing atmosphere at 1000°C for 1 h have undergone densification, as indicated by particle coalescence and interparticle neck formation. However, the deposits exhibited a high level of porosity.

4. Discussion

In this work, the suspensions for EPD contained ethyl alcohol, PE and PVB as solvent, dispersant and binder, respectively. This selection has been motivated by several reasons. There are two principal types of solvents used for electrophoretic deposition, water and organic liquids. Organic liquids are superior to water as a suspension medium. The use of water-based suspensions causes gas formation from the hydrolysis of water, preventing the deposition of a uniform adherent layer and yielding pin holes. However, some organic solvents used for EPD, such as dichloromethane,¹⁸ acetone,^{3,19–21} acetylacetone,^{1,3,22} and trichloroethylene²³ are toxic and

cause environmental and health concerns. The main advantage of ethyl alcohol as solvent is that health and environmental risks are reduced.

Solvent and additives should be inert with respect to the powder. A wide variety of additives can be used to control particle charge, so as to produce well-dispersed suspensions. A mixture of acetylacetone or acetone, iodine and water was found to be effective for particle charging.^{1,3,19} Particle charging was achieved via adsorption of protons, which were formed by the keto-enol reaction catalyzed by I₂ and H₂O. Experimental data presented in²⁴ indicate that suspensions of particles in acetone containing iodine exhibited significant settling. It was established that more stable suspensions could be obtained in isopropyl alcohol solvent when a small I₂-H₂O-acetone additive is used for particle charging.²⁴ Acids were used as solvents²⁵ or additives^{20,21,26,27} for charging of ceramic particles. However, acids can react with powders^{21,25} and bring

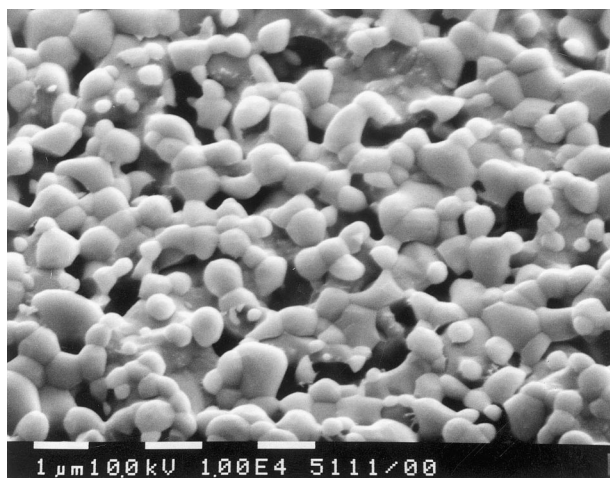
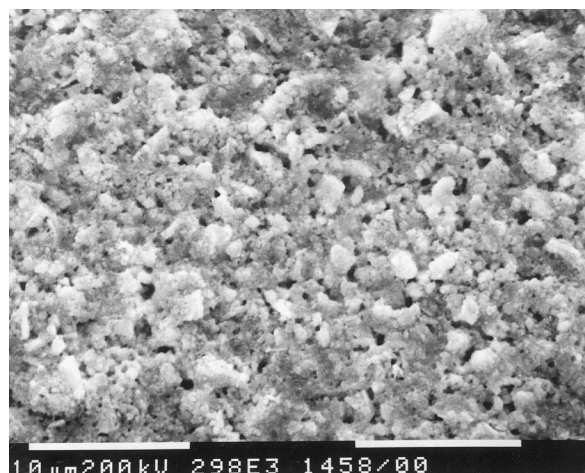
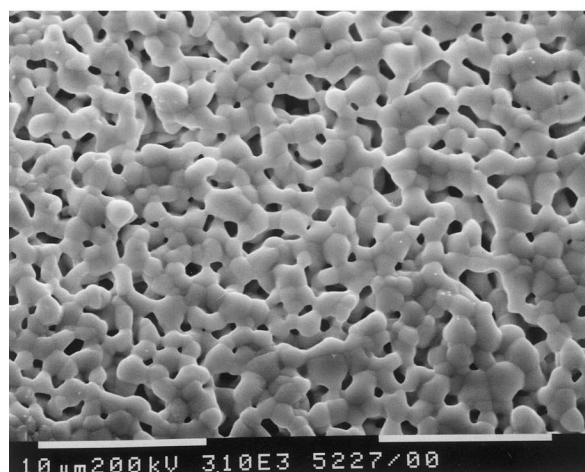


Fig. 4. SEM picture of Ni-YSZ cermet prepared by tape casting, sintered at 1200°C for 4 h in air and thermally treated at 1000°C in reducing atmosphere for 1 h.



(a)



(b)

Fig. 5. SEM pictures of green CGO deposit (a) and CGO deposit sintered at 1400°C in air and thermally treated in reducing atmosphere at 1000°C (b), Ni-YSZ substrate.

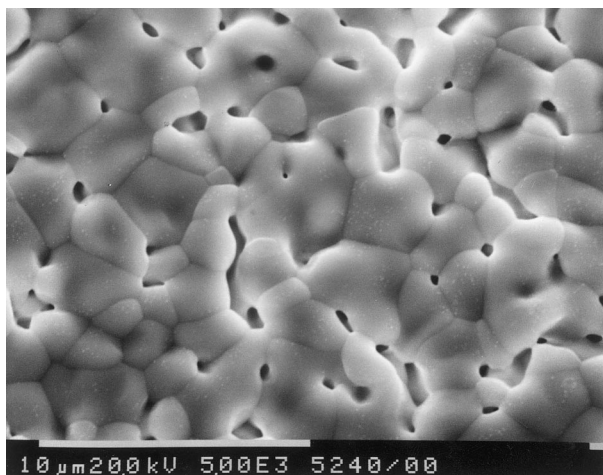


Fig. 6. SEM picture of YSZ deposit on Ni-YSZ substrate, sintered at 1400°C in air and thermally treated in reducing atmosphere at 1000°C.

about corrosion of electrodes. The charging of ceramic particles could be achieved by the adsorption of inorganic cations of Mg^{2+} , Ca^{2+} , Al^{3+} , etc.^{28–30} However, for applications in fuel cells, it is important to prevent deposit contamination, which could result in changing conductivity of the deposited layer.

Mikeska and Cannon³¹ studied the stability of barium titanate in mixed ethanol–methyl ethyl ketone solvent using about 70 commercial dispersants. It was concluded that the most effective are phosphate ester, menhaden fish oil and ethoxylate. Phosphate ester is successfully used as a dispersant in tape casting technology.^{32,33} An important finding³¹ was that phosphate ester imparted a large positive charge to the surface of barium titanate particles. The phosphate ester is an effective electrostatic stabilizer, which charges the particles positively in organic liquids by donating protons to the surface.^{32,33} Moreover, phosphate ester acts as a steric dispersant by anchoring the long chain molecules to the particle surfaces.

Experimental results of this work indicate that phosphate ester improves stability of CGO, YSZ, LSGM and LSCF suspensions in ethyl alcohol solvent and provides a positive charge to CGO, YSZ, and LSGM particles. As a result, cathodic deposits are obtained. In the case of LSCF suspensions, the addition of the phosphate ester resulted in an increase of the deposition rate. Addition of PE resulted in higher conductivity of the suspensions. Current data indicate that deposit uniformity can be improved by addition of small amounts of PE. At this point, it is important to note that a certain potential distribution should be achieved in the electrophoretic cell in order to supply sufficient voltage at the electrode interface.²⁰ Such potential distribution was realized by adding an electrolyte which increases the suspension conductivity.²⁰ As pointed out in Ref. 30 the addition of an electrolyte resulted in improved deposit uniformity.

In the EPD process, the electric field drives ceramic particles toward the electrode. Therefore, it is desirable to maintain a high potential difference between the anode and the cathode. It is suggested that the PE additive accounts for charging and dispersion of ceramic particles. As a result, the deposit weight increases with PE concentration at low PE levels (Fig. 1). However, further addition of PE resulted in higher conductivity, lower voltage drop and, therefore, lower electric field in the electrophoretic bath. As a result, the deposition rate decreased at higher PE concentration when current density was constant (Fig. 1). Increasing the current density increases the voltage drop and higher deposition rates can be achieved (Fig. 2). On the other hand, high current flow with resultant deposit porosity and suspension heating is not desirable.

PVB binder was added to suspensions in order to enhance the strength and adhesion of the deposit and prevent cracking. Present experimental data indicate that the maximum thickness of the deposited material could be increased by binder addition. PVB is an important binder material for non-aqueous tape casting³⁴ and electrophoretic deposition.³⁰ Moreover, PVB was found to improve the dispersion of ceramic powders.^{31,35,36} In EPD experiments performed in Ref. 30, significant increases in deposition rate were observed after addition of PVB to the suspension of $CaO-SiO_2-P_2O_5$. As pointed out in Ref. 36, it is advantageous to use this binder material, which also acts as a dispersant. In this work submicron YSZ particles were used for deposition. Electrophoretic deposition of submicron particles^{37,38} offers advantages in fabrication of uniform ceramic coatings with dense packing and good sinterability. Ceramic structures made from fine particles can be densified at lower sintering temperatures. However, the use of fine particles initiates deposit cracking, which could be prevented by the use of binder. The optimal amount of binder depends on particle size and particle surface area.

In the constant current regime, the electric field in the suspension remains constant,⁸ resulting in constant deposition rate. Indeed, nearly linear deposit weight–time dependencies were obtained (Figs. 2 and 3). Therefore, thickness of individual layers could be controlled by variation of deposition time.

Presented results indicate that the ethyl alcohol–PE–PVB system is an effective system for deposition of advanced ceramic materials for SOFC applications. Problems, related to application of toxic materials, particle–additive interactions and corrosion of electrodes could be eliminated or diminished. Prepared suspensions exhibited high stability and relatively high deposition rate can be achieved. Due to the use of an effective binder, the deposits obtained adhered well to the substrates and exhibited enhanced stability against cracking. All the materials were deposited via cathodic deposition

using similar bath compositions. This is important for deposition of consecutive ceramic layers of controlled thickness. The CGO and YSZ deposits obtained on cermet substrates were porous. It should be noted that porosity in the substrate as well as its surface roughness can initiate defects in the coatings. As pointed out in Ref. 39, gadolinium doped ceria reacts with YSZ at 1300°C resulting in porosity at the interface. Therefore, further optimization of the deposition process and thermal treatment procedures are necessary in order to obtain dense deposits for application as electrolyte layers in fuel cells. Control of porosity of CGO deposits is important for their application as anodes as well as interlayers.^{40–42}

5. Conclusions

This investigation has shown that advanced ceramic materials for fuel cell applications, such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.875}\text{Mg}_{0.125}\text{O}_{3-x}$, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, yttrium stabilized zirconia and $(\text{Ce}_{0.8}\text{Gd}_{0.2})\text{O}_{1.9}$ could be deposited via cathodic electrophoretic deposition from an electrophoretic bath containing ethyl alcohol, phosphate ester and polyvinyl butyral as solvent, dispersant and binder, respectively. Phosphate ester provides good dispersion and charging of ceramic particles, whereas polyvinyl butyral prevents cracking and improves adhesion of the deposits. The deposit yield has been quantified with respect to dispersant concentration, deposition duration and current density. A procedure has been developed for tape casting of Ni-yttria stabilized zirconia cermet to be used as a substrate for electrophoretic deposition. SEM observations revealed that additives and powder characteristics influence deposit morphologies. The proposed solvent–dispersant–binder system has important advantages for electrophoretic processing of ceramic laminates for fuel cell applications.

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