

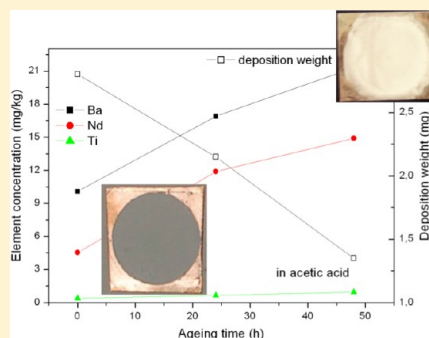
Critical Role of Suspension Media in Electrophoretic Deposition: The Example of Low Loss Dielectric $\text{BaNd}_2\text{Ti}_5\text{O}_{14}$ Thick Films

Paula M. Vilarinho,^{*,†} Zhi Fu,[†] Aiyong Wu,[†] and Angus I. Kingon[‡]

[†]Department of Materials & Ceramic Engineering, Centre for Research in Ceramics and Composite Materials, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

[‡]School of Engineering, Brown University, Providence, Rhode Island 02912, United States

ABSTRACT: The importance of electrophoretic deposition (EPD) is well recognized for thick film technology, but unfortunately there is no universal suspension medium for the EPD of oxides. Thus, the selection of the medium, the stability of the suspensions, and the control of the particle potentials, critical for a good deposition, need to be established for each new material being processed by EPD. In this article, we investigate the key parameters, studying the electrochemistry of $\text{BaNd}_2\text{Ti}_5\text{O}_{14}$ (BNT) suspensions, and establish relationships between suspension media, EPD process conditions, microstructure of the deposits, and resulting electrical properties of the BNT films. Suspension stability of water, ethanol, acetic acid, and acetone-based media was analyzed in terms of zeta potential, particle size distribution, UV transmittance, and inductively coupled plasma spectrometry. The highest absolute zeta potential values determined for acetone with I_2 and acetic acid media are in good agreement with the high stability, small and narrow particle size distribution, and low UV light transmittance measured for these suspensions. Very high quality thick deposits were consequently achieved. However, it was demonstrated that aging of the acetic acid-based suspension have serious negative effects on the EPD process for BNT materials, including leaching of the metallic elements with a consequent modification of the material stoichiometry, change of the conductivity of the suspension, and degradation of the films microstructure. These facts severely restrict the use of acetic acid. Our results clearly indicate that, besides the stability of the suspension, the electrochemistry and aging behavior are key aspects for the EPD of functional oxides. Our systematic approach could be viewed as providing a set of guidelines for the development of EPD of other oxides.



INTRODUCTION

Key trends in the communication industry include increased integration, higher frequencies, miniaturization, and drive to reduce costs. Consistent with these goals, the replacement of bulk ceramic dielectric components by thick films is under consideration.

Among the thick-film fabrication techniques, such as tape casting and screen printing, electrophoretic deposition (EPD) offers unique advantages that include conformal, defect-free deposition with high uniformity, along with excellent control over the film thickness and deposition rate.¹ The method can be implemented with low capital costs and is used (for example) in low cost polymer powder coating processes at an industrial scale. As a process controlled by the electric field, the conformal deposition of EPD allows uniform film deposition on substrates of complicated shapes, impregnation of porous substrates, and deposition on selected areas of the substrates.² The use of EPD has been reported for high dielectric constant ceramic thick films of various types, including BaTiO_3 , $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$, and $(\text{Pb}_{1-x}\text{Zr}_x)\text{TiO}_3$, among others.^{3–5} The present work is part of a comprehensive effort, using EPD processing, to develop low loss thick film devices for microwave circuit applications. The present authors have previously reported on the barium titanate bronzoid family^{6,7} and,

specifically, on low dielectric loss $\text{BaNd}_2\text{Ti}_5\text{O}_{14}$ (BNT) films. These previous reports focused on methods to control microstructure and properties, especially on the tailoring of the grain orientation and thereby the permittivity and the temperature dependence of the permittivity, while maintaining Q values approaching 2000.^{6,7} The present article reports on the complementary studies into the electrochemistry of the process and shows that careful attention needs to be paid to the chemistry of the suspension and deposition conditions in order to achieve reproducible, high quality thick films.

While the advantages of EPD are apparent, there is unfortunately no general or universal suspension medium for the EPD of oxides.⁸ Suspension media used for EPD can be classified in two main groups, aqueous and nonaqueous, in which the most common are acetone, acetylacetone, acetic acid, ethanol, methanol, *n*-propanol, iso-propanol, *n*-butanol, 2-methoxyethanol, ethylene glycol, tetraethoxysilane, and methyltriethoxysilane, with additives that may include acids (hydrochloric and nitric), dopamine, dolapix, hydroquinone,

Special Issue: Electrophoretic Deposition

Received: June 25, 2012

Revised: October 15, 2012

Published: November 6, 2012

iodine (I₂), nitrocellulose, polyetherimide (PEI), poly(acrylic acid), polyethylene glycol polyvinyl, and pyrrolidone triethanolamine (TEA), among others. A fundamental condition for performing EPD is the use of a stable suspension where particles are kept well dispersed in the liquid medium and can move toward the electrode without influencing or being influenced by other particles.⁹ However, in spite of the extensive studies that have been carried out on the suspension properties (conductivity, dielectric constant, viscosity, stability, particle size, transmittance, and zeta potential) to optimize the composition and the amount of additives to be added in order to obtain the required particle dispersion and high suspension stability, there is still a lack of a universal suspension media and guiding rules to optimize. It is known that, for a successful EPD, suspended particles must have an elevated electrophoretic mobility, but conductivity of the media (determined by the number of charge carriers (ions and/or particles)) also determines the viability of the process; in fact, a compromise between high particle mobility and low particle charge per unit weight should be considered; i.e., the ionic concentration in suspension should be low and the suspended particles the main current carriers.¹⁰ The key role of conductivity of the suspension media was made clear in previous systematic studies.¹¹ In general, there is a narrow band of conductivity range in which a deposit is formed; however, this optimal range is different for different systems.^{10,11}

The selection of the medium, the stability of the suspensions, and the control of the particle potentials are therefore critical^{2,12,13} and need to be established for each new material being processed by EPD. In this article, we investigate the key parameters, studying the electrochemistry of BNT suspensions, and establish relationships between suspension media, EPD process conditions, microstructure of the deposits, and resulting electrical properties of the BNT films. The same approach may be applied to the development of EPD of other oxides.

■ EXPERIMENTAL SECTION

BaNd₂Ti₅O₁₄ powders were synthesized by a solid-state reaction method. Reagent-grade powders of BaCO₃ (Aldrich, ref 513-77-9, >99.9%), Nd₂O₃ (Aldrich, ref 1313-97-9, >99.9%), and TiO₂ (Aldrich, ref 1317-80-2, >99.9%) were mixed in stoichiometric proportions in ethanol and ball-milled with ZrO₂ balls for 12 h. After drying, the ball-milled powders were calcined at 1200 °C for 3 h. The calcined powders were milled again to reduce the particle size to an average value of 0.4 μm.

EPD of BNT powders was conducted in four different suspension media: deionized water, acetone (>99.9%, Merck), ethanol (>99.9%, Merck), and glacial acetic acid (>99.9%, Merck), respectively. The concentration of the suspension was 10 g/L for all experiments. Prior to EPD, suspensions were ultrasonically dispersed and magnetically stirred for 5 and 10 min, respectively, followed by settling for 5 min in order to sediment the coarse particles. The platinum foil (11 × 11 × 0.025 mm, 99.95%, Goodfellow, U.K.) used as the working electrode (cathode) was separated 2 cm from the Pt counter electrode (anode) in a glass deposition container. For the case of acetone medium, I₂ (≥99.8%, Aldrich) dissolved in isopropanol (>99.9%, Merck) was used as an additive to adjust the pH value of BNT suspensions. This iodine solution consisted of 0.92 g of isopropanol containing 0.5 wt % dissolved I₂. The pH of water-based suspensions and the

operational pH values of the organic-based suspensions were measured by a pH meter. The operational pH is defined as¹⁴

$$p\alpha_H = \text{pH} - \frac{\Delta E_j}{0.05916} \text{ at } 25^\circ\text{C} \quad (1)$$

where $p\alpha_H$ stands for the negative logarithm of proton activity in the organic solvent, which is the real pH in nonaqueous media, and ΔE_j stands for the difference between the liquid-junction potentials and pH for the operational readings by a standard pH meter. Thus, for a given suspension medium, the $p\alpha_H$ can be calculated from the operational pH reading in the nonaqueous medium. However, for convenience the operational pH is used for the organic suspensions.

The electric current through the EPD cell was monitored by a digital multimeter (MY-64, MASTECH, Hong Kong) located in series with the EPD circuit, during the EPD process.

The effect of the suspension media on the BNT suspension stability was investigated in this work by means of particle size distribution, suspension UV light transmittance, and zeta potential. An electrophoretic light scattering (ELS) spectrophotometer (Delsa-440 SX, Beckman Coulter, Inc., USA) was used to determine the zeta potential of the BNT suspensions. The particle size in different suspension media was assessed by a nanosizer Malvern Dynamic Light Scattering instrument (Zetasizer nano ZS, Malvern, UK). The degree of dispersion of BNT powders in the different suspensions was evaluated by UV light transmittance using a UV spectrophotometer (UV-2101/3101PC, Shimadzu Scientific Instruments, Inc., USA). Inductively coupled plasma atomic emission spectrometry (ICP, Jobin Yvon Activa-M) analysis was employed to study the chemical composition of BNT suspensions, in particular the concentration of the metallic elements in the suspension supernatant to address the suspension aging.

As-deposited films were dried at 90 °C for 24 h. The dried films were then pressed under an isostatic pressure of 200 MPa to enhance the green density, and the films sintered in air at 1300 °C for 1 h. The thickness of unsintered and sintered films was evaluated by a micrometer and scanning electron microscopy (SEM). The structure of the sintered films was analyzed by X-ray diffraction (XRD) (Rigaku, Geigerflex D/Max-B) and the microstructure by SEM (Hitachi, S-4100).

The electrical measurements were undertaken via a metal–insulator–metal (MIM) configuration using Au as top electrodes, sputtered through a shadow mask of 0.6 mm diameter. BNT films with top electrodes were postannealed at 200 °C for 30 min to improve the interface between the metal and the film. The electrical properties were evaluated using an impedance bridge (HP 4284A) within the frequency range of 1 kHz to 1 MHz. The oscillation level of the applied voltage was set to 1.0 V. The analyzed electrical properties include the dielectric constant, loss tangent, temperature dependence of capacitance, and capacitance–voltage variation (C–V).

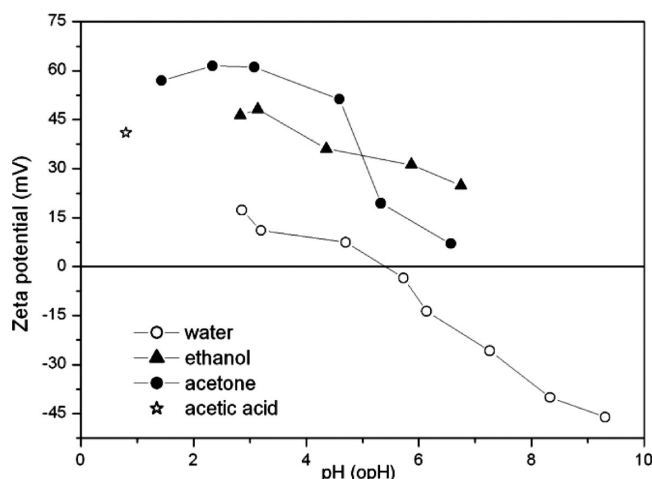
■ RESULTS AND DISCUSSION

Suspension Stability and EPD. The physical properties of the suspension media are summarized in Table 1. Figure 1 depicts the zeta potential of BNT particles in the different suspension media as a function of pH or operational pH in the case of the organic media.

The zeta potential analysis revealed that the surface of BNT particles is positively charged in acetic acid, pure ethanol, and acetone. Compared with the organic solvents, the zeta potential

Table 1. Physical Properties and EPD Performance of Used Suspension Media

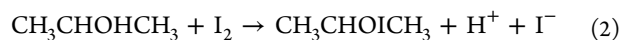
suspension media	dielectric constant	viscosity (cP)	EPD performance
water	80	0.89	No Deposition
ethanol	24.3	1.20	Poor
acetone	20.7	0.31	Good
acetic acid	6.2	1.22	Very Good

**Figure 1.** Zeta potential of different BNT suspensions. The water-based suspension displays the lowest zeta potential values.

of BNT particles in water is much lower, reaching the isoelectric point at $\text{pH} \approx 5$, and with negative values of zeta potential at higher values of pH. A positive zeta potential of 41 mV for BNT particles in glacial acetic acid has been measured at an operational pH of 0.8. For ethanol-based suspension, the zeta potential increases from 25 to 46 mV when the operational pH value is decreased from 6.7 to 2.8 by adding a dilute 10^{-2} M HCl solution.

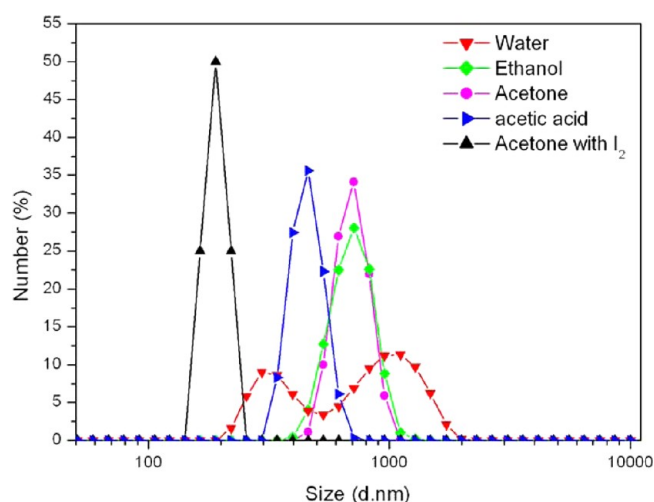
Iodine dissolved in isopropanol was used to adjust the operational pH value of acetone-based suspensions. The zeta potential increases from 7 to 61 mV by adding I_2 , accompanied with an operational pH change from 6.5 to 2.3, indicating that iodine is very effective in charging BNT powders in acetone-based suspensions. It has previously been shown to be an effective additive to disperse PZT, BST, YSZ, and YBCO ceramic powders for EPD process as well.^{15,16}

Iodine dissolves rapidly in isopropanol where it reacts producing positively and negatively charged ions, according to the following equation:¹⁷



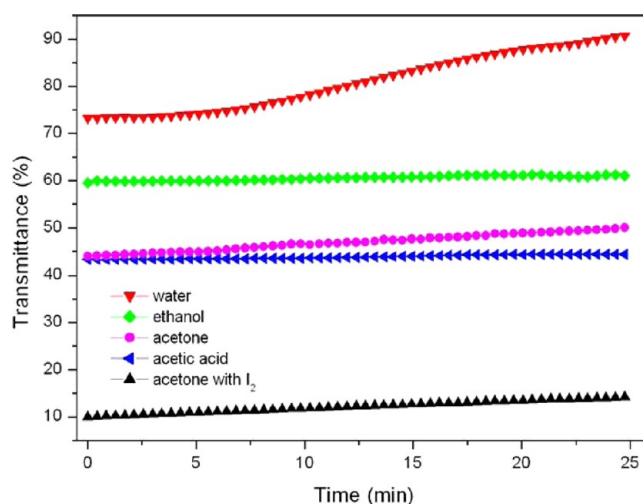
It is then suggested that the protons generated by the above reaction are adsorbed on the surface of the suspended BNT particles, making them positively charged and enhancing the electrostatic repulsion force (Figure 1). The increase of the zeta potential is considerable, rising from 7 to 61 mV. However, as more iodine is added to the suspension, i.e., when operational pH value decreases from 2.3 to 1.4, the large amount of free positive charge results in a decrease of the zeta potential to the value 51 mV. It is believed that the concomitant increase in the ion concentration in the solution increases screening of the surface charge by the double layer and hence reduces the zeta potential.

Figure 2 represents the particle size distribution of BNT powders in the different suspensions. As expected, BNT

**Figure 2.** Particle size distributions of the different BNT suspensions.

particles show dissimilar dispersion characteristics in the different suspension media. In the case of water-based suspension, a bimodal distribution of the particles was observed, which indicates the existence of particle agglomeration, but in organic media (acetone, ethanol, and acetic acid), BNT suspensions exhibit a narrow monomodal distribution of the particle size that peaks at approximately 0.7, 0.72, 0.45, and $0.2 \mu\text{m}$ for ethanol, pure acetone, acetic acid, and acetone with I_2 , respectively. To prepare a well-dispersed BNT suspension for EPD to obtain a dense BNT coating, a fine particle size powder suspension is required, and BNT suspensions in acetic acid and acetone solutions yield good results, in particular BNT acetone with I_2 -based suspension.

Transmittance of UV light was recorded for the different suspensions of BNT particles and is illustrated in Figure 3. Initial transmittance values of about 70%, 60%, 45%, and 10% were obtained for water, ethanol, acetone, acetic acid, and acetone with I_2 suspensions, respectively. As the time increases,

**Figure 3.** UV light transmittance versus time for the different BNT suspensions. Time zero corresponds to the instant just after the sonication.

the transmittance slightly increases for the organic-based suspensions. In contrast, this increase is very obvious for the water-based suspension. A small transmittance and small change in transmittance imply that the particles remain in a stable dispersed state for a long period of time, fulfilling the optimized suspension conditions to be used for EPD. In opposition, a high transmittance and a clear variation in the transmittance with time implies that more UV light is transmitted through the suspension because a fast and high degree of sedimentation is occurring. This is the case of water-based suspensions that, besides displaying the highest values, the transmittance increases constantly with time, and the majority of the particles sediment continuously. These results are consistent with the above analysis of particle size distribution and the zeta potential curves for the different suspension media.

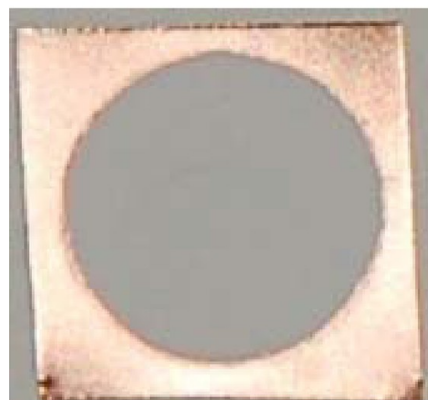
In terms of visible observations, acetic acid- and acetone with I_2 -based suspensions do not display a tendency to immediate coagulate, but instead settle slowly, forming a compact deposit at the bottom of the container. On the contrary, water- and ethanol-based suspensions, both showing high transmittance values, settle rapidly (minutes) and form low density and loose compacts.

On the basis of the above results, BNT powders suspended in acetic acid and acetone with I_2 display excellent suspension dispersibility and colloid stability with respect to flocculation. Both systems would be expected to be good candidates for EPD of BNT films. However, for comparison purposes, EPD was attempted using all four types of suspension (water, ethanol, acetic acid, and acetone with I_2).

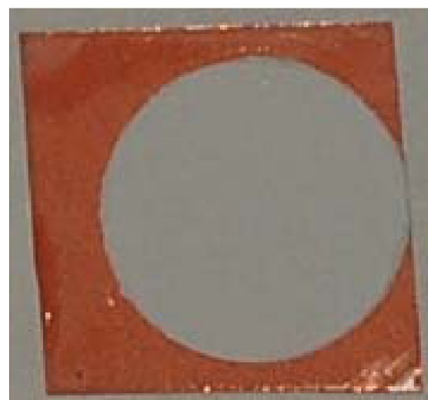
Because the particles are positively charged (Figure 1), cathodic deposition was performed. There was no deposition observed in water-based suspensions (for any pH value) or pure acetone suspensions. Surprisingly, in the case of ethanol-based suspensions, even at the highest zeta potential of 47 mV achieved by adjusting to the operational pH value of 2.8 (with the addition of HCl), there was still no continuous deposition, and the deposited layers obtained were quite heterogeneous. Indeed, suspensions in ethanol and water exhibit a rapid sedimentation when ultrasonic treatment is interrupted as evidenced by the suspension stability studies. In contrast, the expected good deposition performance was observed for acetic acid and acetone with I_2 suspensions (Table 1). Figure 4 illustrates the optical micrographs of BNT films derived from ethanol (Figure 4a), acetic acid (Figure 4b), and acetone with I_2 (Figure 4c), suspensions, respectively. In terms of unsintered microstructure, conformal and highly uniform BNT films were obtained from acetic acid- and acetone with I_2 -based suspensions. However, thin and fluffy layers with irregular edges were obtained from ethanol-based suspensions. The EPD performance in different suspension media is summarized in Table 1. It should be noted that the iodine content of the acetone/ I_2 suspensions should be well controlled in order to yield the maximum zeta potential. Too much or too little iodine, corresponding to lower zeta potentials, yields particle coagulation, sedimentation, and poor electrophoretic deposition. At high iodine concentrations (low operational pH), we deduce that it is the increased ion concentration that reduces the double layer thickness and thus particle–particle repulsion, and the result is a rapid coagulation and sedimentation. Taken together, the results described above indicate the sensitivity of deposition to the magnitude of the surface charge and the dispersion of the suspension.



(a)



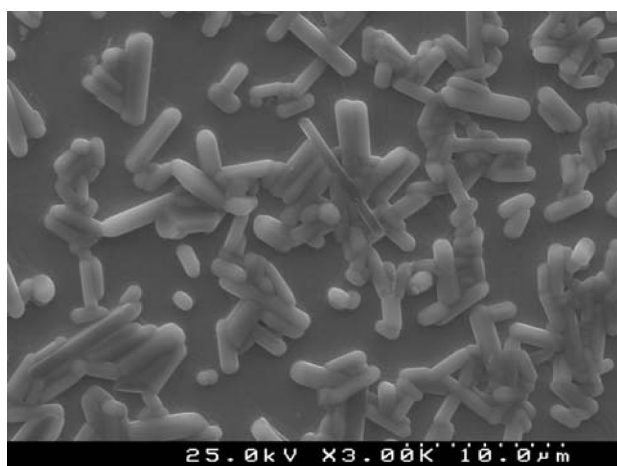
(b)



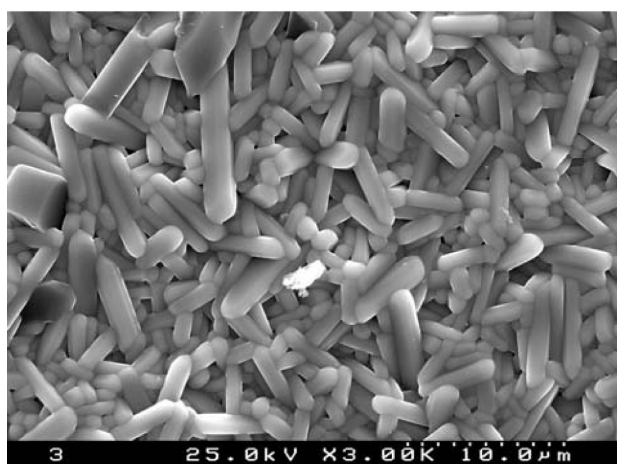
(c)

Figure 4. Optical micrographs of BNT films deposited from (a) ethanol, (b) acetic acid, and (c) acetone with I_2 suspensions, respectively. Conformal and highly uniform BNT films were obtained from acetic acid- and acetone with I_2 -based suspensions.

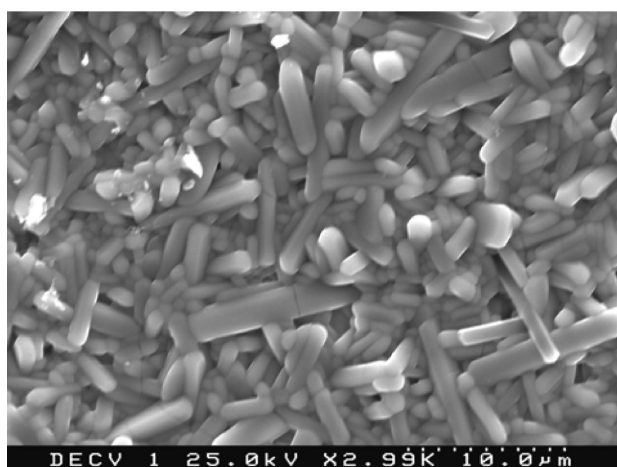
The effect of the suspension media on the microstructure of sintered BNT films was examined by SEM (Figure 5). For acetic acid- and acetone with I_2 -based suspensions, crack-free, dense, uniform, and homogeneous microstructures were obtained (Figure 5b,c), and in contrast, a quite porous microstructure was developed in ethanol-based films, where BNT does not cover the entire substrate (Figure 5a), consistent



(a)



(b)



(c)

Figure 5. SEM surface micrographs of sintered BNT thick films derived from (a) ethanol, (b) acetic acid, and (c) acetone with I_2 -based suspensions. Ethanol is not a suitable suspension medium for EPD of BNT powders.

with the unsintered microstructure shown in Figure 4. We conclude that ethanol is not a suitable suspension medium for EPD of BNT powders.

Because of the good deposition results, further studies were undertaken with acetic acid- and acetone with I_2 -based suspensions to investigate the reproducibility of the electro-phoretic deposition process for BNT.

Long-Term Stability and Reproducibility of Acetic Acid- and Acetone-Based BNT Suspensions and Films.

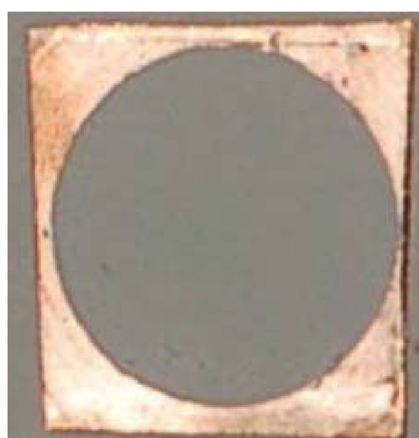
Both acetic acid- and acetone with I_2 -based suspensions can be used for EPD of BNT powders, and in terms of unsintered microstructure, there is little difference between the films derived from both fresh suspensions. However, the stability of the suspension is an important aspect in terms of the reproducibility of the process.

The first clues as to critical differences in the reproducibility of EPD with the two suspension media came from monitoring the current during deposition. It was observed that, in the case of acetic acid, the current increased during deposition but did not do so for the acetone/ I_2 case. In fact, the latter would typically be slightly lower after deposition, as expected from the increased resistance corresponding to the deposited insulation film. In contrast, during one deposition using acetic acid where the voltage was ramped up and back down over the course of several minutes, the current at 200 V was 33% higher on the down-ramp than the up-ramp.

We investigated this further by undertaking a series of repeated depositions at 200 V for 1 min. The experiments compare a single 1 min deposition with a sample deposited with four 1 min depositions and a further sample subjected to six 1 min deposition pulses. Optical microscope images of the unsintered films are shown in Figure 6. It is clear that the first deposition yielded conformal, uniform, and crack free layers (Figure 6a). However, for further depositions, the surface of the deposited films starts to become less smooth and uniform as observed for the sample subjected to four 1 min deposition pulses (Figure 6b), and if deposition cycles continue, the surface of the deposited films became more and more rough till a noncontinuous surface layer is formed, as shown in Figure 6c for the film subjected to six consecutive deposition cycles.

The deposition weight and electric current through the suspension were further examined against deposition cycles in order to track any changes occurring in the suspension and are illustrated in Figure 7. The deposition weights are 9, 6, and 1 mg for the first, fourth and sixth depositions, respectively, and meanwhile, the corresponding current values through the suspension were 0.05, 0.6, and 1.3 mA. The trend of decreasing deposition weight is consistent with the above microstructure observations. The deposition becomes more and more difficult as the current through the suspension increases and the quality of the suspension decreases with the increased number of consecutive deposition cycles. These results clearly show that the physical properties of the acetic acid-based suspension change along the course of EPD.

The origin of the problem became apparent with the results of ICP-AES analysis of the supernatant of fresh and aged suspensions (shelf time aging), as indicated in Figure 8 in which the concentration of Ba, Nd and Ti elements in the solution and the deposition weight are plotted against the aging time. The leaching of metallic elements from the solution is evident. After aging an acetic acid-based suspension for 48 h, severe Ba leaching occurs; the concentration of Ba in the solution increases from about 10 mg/kg to 21 mg/kg (Figure 8a). The concentration of Nd in the supernatant increases as well, following a similar trend but to a lower extent. The leaching of Ti ions is also observed but at a considerably reduced scale



(a)



(b)



(c)

Figure 6. Optical surface micrographs of unsintered BNT films after (a) a single deposition cycle, (b) four deposition cycles, and (c) six deposition cycles, in acetic acid-based suspensions. If deposition cycles continue, the surface of the deposited films became increasingly rough until a noncontinuous surface layer is formed as the number of deposition cycles increases.

when compared with the previous elements. At the same time, the deposition weight decreases with the aging time (Figure 8a).

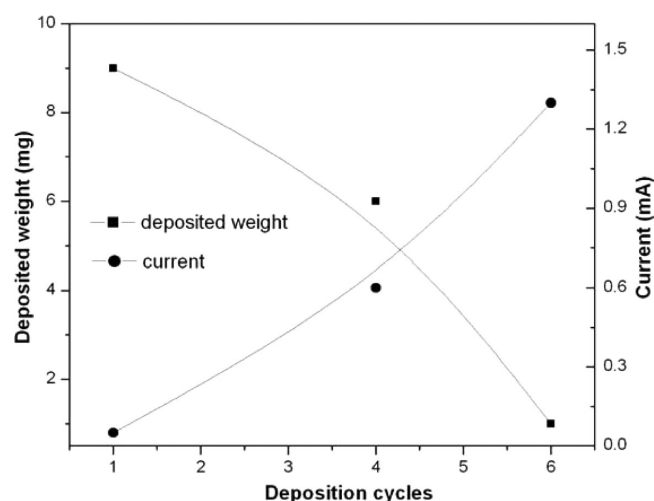


Figure 7. Deposition weight and electric current through the suspension in acetic acid-based suspension as a function of the deposition cycles. The quality of the suspension decreases with the increased number of consecutive deposition cycles.

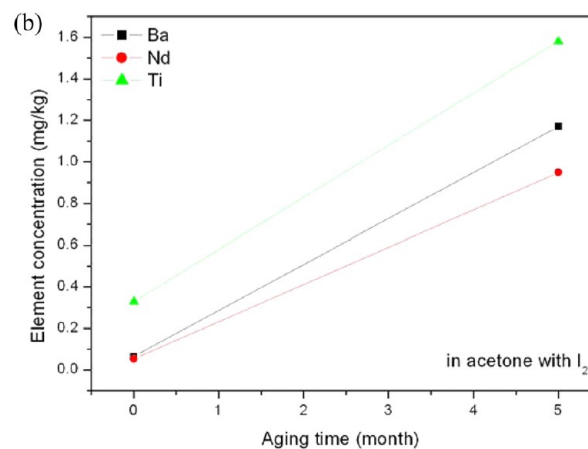
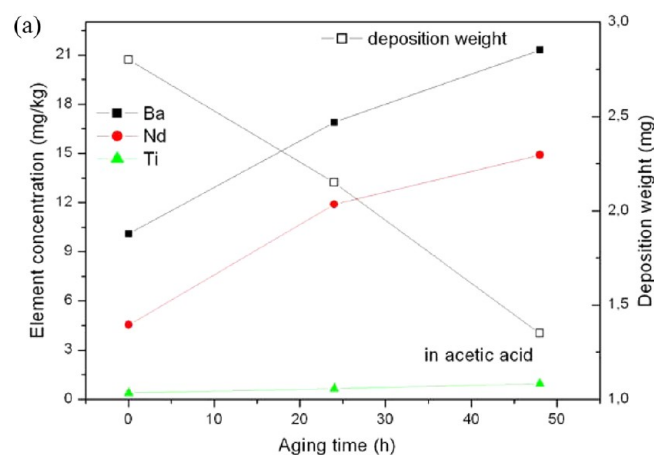
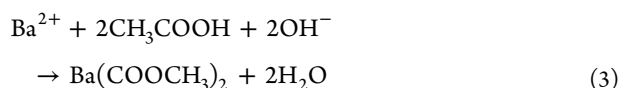


Figure 8. Elemental concentration in the suspensions of (a) acetic acid- and (b) acetone with I_2 -based suspensions as a function of the suspension aging time (note: at zero aging, the elemental concentrations are from the original pure suspension media). After aging an acetic acid-based suspension for 48 h, severe Ba leaching occurs. Minimal leaching is observed for the case of acetone/ I_2 suspensions.

Some leaching of ions was also observed in the supernatant of acetone with I_2 suspensions (Figure 8b), but it should be noted that the concentrations of Ba and Nd leached ions in this case are about *three orders* of magnitude lower. The highest concentration of metallic ions is, in this case, Ti followed by Ba and Nd that increased with the aging time. The concentration of titanium changed minimally from 0.329 to 1.58 mg/kg in the supernatant of acetone with I_2 -based suspensions after aging for 5 months (Figure 8b). Again emphasizing the differences between acetic acid and acetone/ I_2 , the Ba concentration in the supernatant is 14 times higher for 48 h of aging in acetic acid-based suspension than after 5 month of aging in acetone with I_2 -based suspension.

In the suspension of BNT powders dispersed in glacial acetic acid, barium ions on the surface of the BNT powder will react with the acid to form barium acetate and water, according to the following reaction:



Similar reactions occur between Nd^{2+} and Ti^{4+} ions and acetic acid. The increasing content of leached ions causes the increase of the content of free ionic species and the current flow in the suspension, as observed in Figure 7, and the quality of the deposited films is markedly degraded.

The likely cause for the degraded deposition behavior in the case of acetic acid is the increase in ion concentration, which decreases the thickness of the double layer, as described many years ago by DLVO theory.^{18,19} Below a certain thickness of the solvation layer, the attractive forces dominate at small interparticle distances, the energy barrier (repulsive) is overcome, and the particles coagulate.

At the initial stages of EPD, the double layer surrounding the dispersed particles is not greatly affected, and particles remain well dispersed. The current flow through the suspension is very small during EPD, and consequently, a uniform deposition with high deposition mass rate is observed for the first depositions (Figure 6). As the EPD cycles proceed and the concentration of free ionic species due to leaching into the suspension increases, the level of particle agglomeration increases, the rate of deposited mass decreases, and the quality of the deposited layers degrades.

According to the DLVO theory, the thickness of the double layer surrounding the particles characterized by the Debye length is very sensitive to the electrolyte concentration. It is demonstrated that the potential energy peak decreases as the electrolyte concentration increases, and as the energy barrier disappears, coagulation becomes favorable and the suspension unstable.²⁰ The same phenomenon was also reported for EPD of PZT in acetic acid and other systems.^{4,21,22}

The lower values of the current for the case of acetone with I_2 -based suspensions indicate the absence of excess free carriers in the suspension, as the EPD cycles proceed; as a consequence, there is no visible degradation of the EPD performance during deposition in acetone with I_2 -based suspensions when compared with that observed for the acetic acid-based suspensions.

Optimization of EPD Parameters in Acetone with I_2 -Based Suspension. Among the studied suspension media, acetone with I_2 presents the best performance for EPD of BNT powders. Because of that, the parameters, deposition time,

operational pH, and applied voltage were studied for the optimization of the EPD process.

The operational pH in acetone-based suspension was optimized based on the zeta potential curve (Figure 1). The surface of sintered BNT films deposited at 5.3, 2.3, and 1.4 operational pH is depicted in Figure 9. At high operational pH of 5.3, a quite porous microstructure is observed. As the operational pH value decreases to 2.3, much denser and homogeneous BNT films are obtained, as shown in Figure 9b. It is worthwhile to note that this operational pH value corresponds to the highest zeta potential (Figure 1). As the operational pH value continues to decrease to 1.3, accompanied by a drop in the zeta potential, a porous microstructure for the BNT films is again formed (Figure 9c). The results are summarized in Table 2. The deposition quality of the film is indeed consistent with the zeta potential of the suspension used in the preparation.

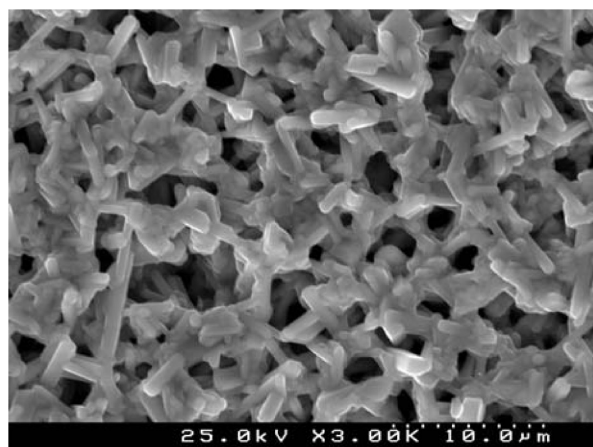
Figure 10 depicts the deposition thickness against the deposition time at a constant applied voltage of 200 V in which an asymptotic correlation occurs. A significant and linear increase in the deposition thickness is recorded for short deposition times (from 0.5 to 2.5 min) followed by a limited increase when the deposition time is increased from 2.5 to 3.5 min. Similar observations have been reported in the literature¹⁵ and attributed to the change in the deposition rate and particle concentration as the deposition continues. It is noted that, under constant voltage EPD, the potential-induced electrophoresis decreases with increasing deposition on the electrode. This voltage drop across the electrodes results in the decrease in the current density and hence in the deposition rate. This phenomenon under constant voltage is mainly due to the building up of an insulating layer on the electrode as the deposition progresses.^{14,23}

The other parameter that affects the mass deposition rate and that may change during the course of the deposition is the solid content of the suspension. If the solid content is not kept constant, for example, by a continuous inflow and outflow of the suspension, the decreasing powder concentration with time results in a decreasing deposition rate as well. From these results, it becomes obvious that EPD is an efficient method to produce thick deposits at short deposition times, and the deposit thickness can be simply controlled by the variation of the deposition time at constant applied voltage.

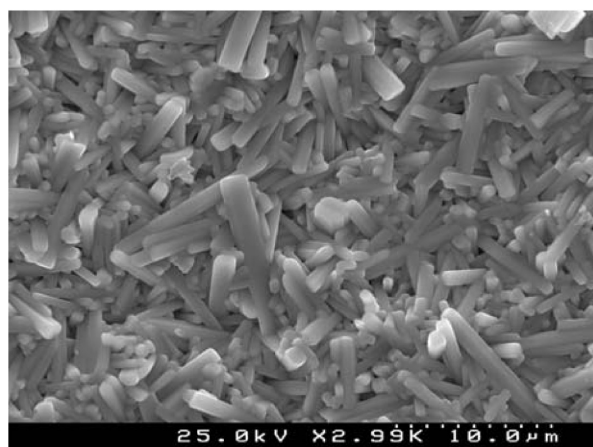
For the same initial powder concentration in the suspension, the yield of deposition is expected to increase linearly as the dc voltage and deposition time increases according to Hamaker's equation:²⁴

$$M = \int_0^t aAC\mu E dt \quad (4)$$

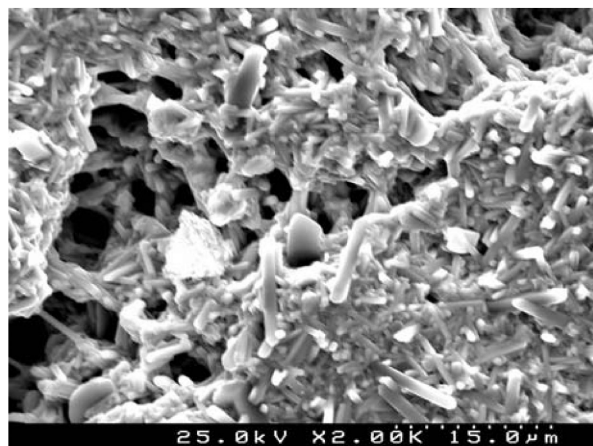
where M is the mass deposited in time t (s), C the particle concentration in the suspension (kg/m^3), E the electric field (V/m), A the electrode area (m^2), and m the electrophoretic mobility ($\text{m}^2/(\text{V s})$); a is a coefficient representing the fraction of particles deposited near the electrode. Figure 11 shows the measured deposition thickness of BNT films as a function of applied voltage in acetone/ I_2 suspensions. The expected linear increase is observed, except at high field, where a drop in thickness (and thus deposition rate) is a reproducible effect. An explanation for this effect is that it is due to the local turbulence in the suspension and interactions between the particles created under very high driving forces. Under these conditions, the highly mobile particles experience difficulty in moving



(a)



(b)



(c)

Figure 9. SEM micrographs of BNT films deposited at operational pH of (a) 5.33, (b) 2.34, and (c) 1.43 in acetone with I_2 -based suspension and sintered at 1300 °C/h. A degradation of the microstructure is observed as the operational pH value decreases to 1.3, accompanied by a drop in the zeta potential.

uniformly toward the counter electrode and to find a location on the substrate to form a close packed structure. Under these high electric fields, the green film was indeed visibly affected, a high level of nonuniformity developed, and porous deposits formed. Similar observations were reported for the deposition

Table 2. Deposition Qualities at Various Operational pH for Acetone-Based Suspensions

pH	zeta potential (mV)	deposition quality
<2	57	non uniform
3	61	uniform
4	51	uniform
>5	7	non uniform

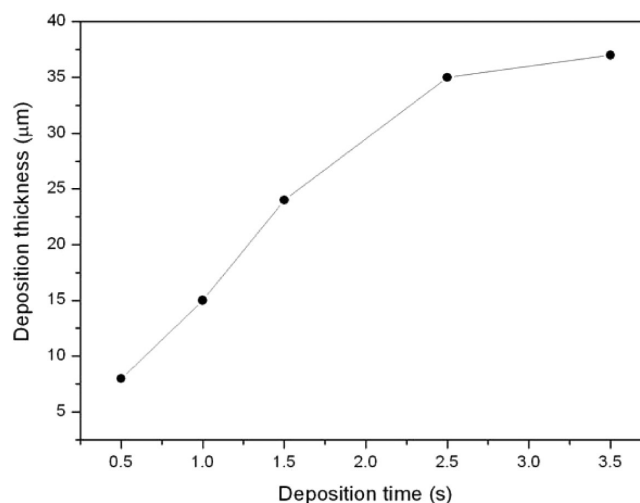


Figure 10. Deposition thickness versus deposition time for acetone with I_2 -based suspensions.

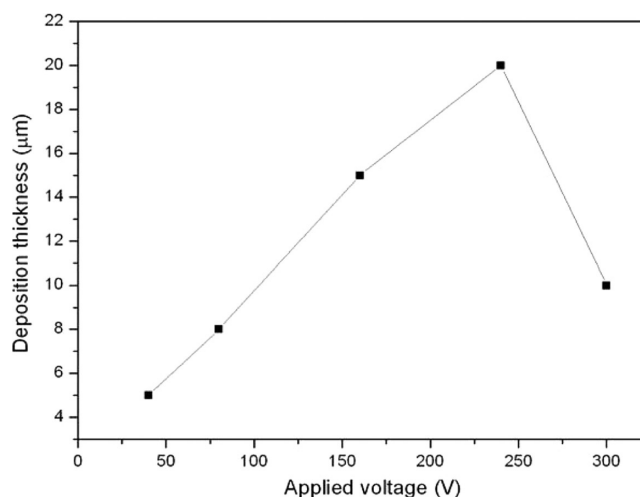


Figure 11. Deposition thickness of BNT films as a function of applied voltage in acetone with I_2 -based suspensions. The expected linear increase is observed at low fields.

of zirconia electrolyte films in acetic acid²⁵ and nanosized cordierite powders,²⁶ among others. However, at very low applied voltage (40 V), porous BNT films were obtained. For voltage <40 V, the adherence is poor, and the deposits are partially washed away as the cathode is being extracted from the cell. This very porous microstructure can be attributed to the weak adherence of the deposit to the electrode under very low voltages. In the current work, the adherence of the deposit to the cathode is adequate for voltages >80 V.

On the basis of this set of experimental results, the optimal conditions for EPD of BNT powders were identified as (i) suspension media, acetone with I_2 , at pH 2–3, and (ii) applied

voltage, 200 V. Using these parameters, high-quality, uniform BNT films on Pt foils were obtained, and a good dielectric response is therefore expected. The final section confirms the quality of the sintered films.

Characterization of BNT films. BNT films exhibit a well-crystallized orthorhombic structure, and all the diffraction peaks are identified as belonging to $\text{BaNd}_2\text{Ti}_5\text{O}_{14}$ as reported previously.^{6,7}

Figure 12 represents the frequency dependence of the relative permittivity and loss tangent of these BNT films, with

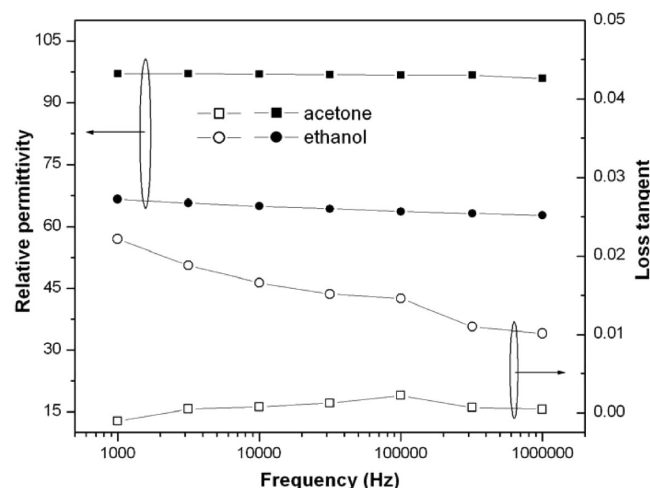


Figure 12. Relative permittivity and loss tangent as a function of frequency of BNT films deposited from ethanol- and acetone with I_2 -based suspensions and sintered at 1300 °C/h. Films derived from acetone with I_2 -based suspensions exhibit enhanced electrical performance.

the films prepared from ethanol suspensions included for comparison. At 1 MHz, the relative permittivities are 96 and 62, respectively, and the loss tangents 0.0005 and 0.01 for the films derived from acetone with I_2 - and ethanol-based suspensions, respectively. As expected, films derived from acetone with I_2 -based suspensions exhibit enhanced electrical performance, consistent with the denser and more homogeneous microstructure of these films when compared with those prepared from ethanol suspensions.

CONCLUSIONS

In this work, the role of the suspension media for the EPD of thick BNT films was assessed for water-, ethanol-, acetic acid-, and acetone-based media. The suspension stability was analyzed in terms of zeta potential, particle size distribution, and suspension transmittance. The quality of the deposits was evaluated by the microstructure and electrical response of the films. The highest absolute zeta potential values were determined to be 61, 48, 41, and 17 mV for acetone with I_2 , ethanol, acetic acid, and water suspensions, respectively, which are in agreement with the high stability and dispersibility, small particle size and narrow particle size distribution, and low UV light transmittance of acetone with I_2 suspensions. High quality thick deposits were achieved with acetic acid and acetone with I_2 . However, the reliability and reproducibility of the deposition was verified to be difficult to control for the case of acetic acid suspensions, limiting its utilization, due to aging of the suspensions through leaching of the metallic elements, with a consequent modification of the material stoichiometry,

increasing of the conductivity, loss of suspension stability, and degradation of the film compactness. These facts severely restrict the use of acetic acid for an industrial application. Among the studied suspensions, acetone with I_2 was found to be the most suitable suspension media for EPD of BNT thick films. Owing to the uniform, homogeneous, and dense microstructure, BNT films deposited from acetone with I_2 -based suspensions exhibit very good dielectric properties. This study clearly indicates that a high zeta potential is indeed a *sine qua non* condition for the deposition of good films, but the electrochemistry stability of the suspension against the time and electric field are also major factors. In the present case, acetone with I_2 suspensions possess a higher stability (with the highest zeta potential value) and a longer shelf time, which is of importance for industrial applications.

AUTHOR INFORMATION

Corresponding Author

*E-mail: paula.vilarinho@ua.pt.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the financial support from FEDER, QREN, COMPETE, and FCT. F.Z. is thankful to FCT for financial support under the scholarship SFRH/BD/19327/2004.

REFERENCES

- (1) Corni, I.; Ryan, M. P.; Boccaccini, A. R. *J. Eur. Ceram. Soc.* **2008**, *28* (7), 1353–1367.
- (2) Zhitomirsky, I.; Petric, A. *J. Mater. Sci.* **2004**, *39*, 825–831.
- (3) Louh, R. F.; Hsu, Y. H. *Mater. Chem. Phys.* **2003**, *79*, 226–229.
- (4) Wu, A.; Vilarinho, P. M.; Kingon, A. I. *J. Am. Ceram. Soc.* **2006**, *89*, 575–581.
- (5) Wu, A.; Vilarinho, P. M.; Kingon, A. I. *Acta Mater.* **2010**, *58*, 2282–2290.
- (6) Zhi, F.; Wu, A.; Vilarinho, P. M.; Kingon, A. I.; Wördenweber, R. *Appl. Phys. Lett.* **2007**, *90*, 052912–052914.
- (7) Wu, A.; Vilarinho, P. M.; Kingon, A. I. *Adv. Funct. Mater.* **2009**, *19*, 1–11.
- (8) Zarbov, M.; Brandon, D.; Cohen, N.; Shemesh, E. L. *J. Mater. Sci.* **2006**, *41*, 8115–8122.
- (9) De Riccardis, M. F. *Ceramic Coatings Obtained by Electro-phoretic Deposition: Fundamentals, Models, Post-Deposition Processes and Applications*. In *Ceramic Coatings: Applications in Engineering*; Shi, F., Ed.; InTech: New York, 2012.
- (10) Besra, L.; Liu, M. *Prog. Mater. Sci.* **2007**, *52*, 1–61.
- (11) Ferrari, B.; Moreno, R. *J. Eur. Ceram. Soc.* **2010**, *30*, 1069–1078.
- (12) Negishi, H.; Yamaji, K.; Sakai, N.; Hopita, T.; Yanagishita, H.; Yokokawa, H. *J. Mater. Sci.* **2004**, *39*, 833–838.
- (13) Xu, Z. G.; Rajaram, G.; Sankar, J.; Pai, D. *Surf. Coat. Technol.* **2006**, *201*, 4484–4488.
- (14) Sarkar, P.; Nicholson, P. S. *J. Am. Ceram. Soc.* **1996**, *79*, 1987–2002.
- (15) Nicholson, P. S.; Sarkar, P.; Huang, X. *J. Mater. Sci.* **1993**, *28*, 6274–6278.
- (16) Zhitomirsky, I. *J. Mater. Sci. Lett.* **1998**, *17*, 2101–2104.
- (17) Mathews, T.; Rabu, N.; Sellar, J. R.; Muddle, B. C. *Solid State Ionics* **2000**, *128*, 111–115.
- (18) Derjaguin, B. V.; Landau, L. *Acta Physicochim. USSR* **1941**, *14*, 633–662.
- (19) Verwey, E. J. W.; Overbeek, J. T. G. *Theory of the Stability of Lyophobic Colloids*; Elsevier: Amsterdam, The Netherlands, 1948.
- (20) Winslow, W. M. *J. Appl. Phys.* **1949**, *20*, 1137–1140.
- (21) Biesheuvel, P. M.; Verweij, H. *J. Am. Ceram. Soc.* **1999**, *82*, 1451–1455.

- (22) Tassel J. V. Ph.D. Dissertation, Pennsylvania State University, 2004.
- (23) Ma, J.; Cheng, W. *J. Am. Ceram. Soc.* **2002**, *85*, 1735–1737.
- (24) Hamaker, H. C. *Trans. Faraday Soc.* **1940**, *36*, 279–286.
- (25) Basu, R. N.; Randall, C. A.; Mayo, M. J. *J. Am. Ceram. Soc.* **2001**, *84*, 33–40.
- (26) Kaya, C.; Kaya, F.; Boccaccini, A. R. *J. Mater. Sci.* **2002**, *37*, 4145–4153.