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Methodology for selection of charging agents for electrophoretic deposition of ceramic particles

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The zeta potential of particles is a key factor in the electrophoretic deposition process. It plays a role in the stabilization of the suspension by determining the intensity of repulsive interactions as well as in determining the direction and velocity of particle migration.

The zeta potential can be controlled by addition of charging agents such as acids, bases, and specifically adsorbed ions or polyelectrolytes, to the suspension. Thus there exist a variety of additives that affect the charge magnitude and its polarity. These additives act by different mechanisms.

The main criteria for the selection of a charging agent are the preferred polarity and deposition rate of the particles. While the deposition rate is directly dependent on the zeta potential, which is determined by the charging additive, the influence of such an additive is exerted also by its effect on the ionic conductivity of the suspension. The latter determines the potential drop in the bulk of the suspension, which constitutes the driving force for the transfer of the particles to the electrodes.

The present work will describe the methodology developed at Cerel for the selection of a charging agent based on its effect on the zeta potential/pH curve, on the isoelectric point and on the ionic conductivity of the suspension. © *2004 Kluwer Academic Publishers*

1. Introduction

The importance of electrophoretic deposition (EPD) rose in the last decade, because it allows products with complex geometries, and films of variable thickness to be processed in a low cost and simple setup. This advantage has made EPD more economical than conventional methods such as CVD, sol-gel deposition and sputtering for producing both thick and thin ceramic deposits to be used for superconductors, laminar components, multichip modules, fuel cells and etc. [1].

The zeta potential of particles is a key factor in the electrophoretic deposition process. It plays role in stabilization of the suspension as well as in the deposition stage. The zeta potential can be controlled by addition of charging agents such as acids, bases and specifically adsorbed ions or polyelectrolytes, to the suspension [2]. Thus there exist a variety of additives that affect the charge magnitude and its polarity. These additives act by different mechanisms [3].

The objective of the present work is to develop a methodology for selection of a charging agent for a specific powder to be deposited by EPD. The methodology presented in this work is based on data obtained from zeta potential/pH curves and from conductivity measurements [4, 5]. It is demonstrated on a barium titanate suspension in aqueous medium based on a mixture of water and ethanol. Barium titanate is the key material in one of the promising applications of EPD: the deposition of dielectric materials for electronic purposes such as production of multilayer capacitors.

In aqueous media barium titanate may undergo leaching of Ba^{2+} ions from the particle surface at pH values lower than 9. This may change the ratio of Ba/Ti and affect the dielectric properties of the material. Treatment with oxalic acid results in passivation of the particle surface by formation of an insoluble barium oxalate layer. Subsequent washing of the powder removes the excess of Ba^{2+} ions and reduces the conductivity of the suspension [6].

2. Experimental

2.1. Materials and methods

The ceramic powder studied was barium titanate produced by Degussa with D_{50} of 0.97 μm. The powder was suspended in a mixture of absolute ethanol ("Riedel de Haen") and water (HPLC grade "Merck") at a ratio of 30:70 vol%. The charging agents studied are presented in Table I. In this work we concentrate on polyelectrolytes since they are expected to exert the strongest effect on the zeta potential. In addition they may create an electrosteric effect due to the organic component thus enhancing suspension stability.

2.2. Suspension preparation and zeta potential measurements

The suspension was prepared by dispersion of $BaTiO_3$ particles (solid phase concentration 500 g/l) in the ethanol water mixture (30:70 vol%). The powder was suspended by an ultrasound treatment of 5 min ("Fisher Scientific 550" dismembrator) while maintaining a

TABLE I Chemical name and supplier of tested additives

Additive, supplier
Polydiallyl dimethyl ammonium chloride PDADMAC, 20 wt%. Solution in water, "Aldrich Chemical Company, Inc."
Polyethylene imine (PEI), "Aldrich Chemical Company, Inc."
Polyethyleneimine epychlorohydin modified (Co-polymer), 17 wt%. Solution in water, "Aldrich Chemical Company, Inc."
Poly [bis(2-chloroethyl) ether-alt-1,3-bis [3-(dimethylamino)propyl] urea], quaternized(Polyquaterium-2), 62 wt%. Solution in water, "Aldrich Chemical Company, Inc."
Polyacrilic acid, PAA "Aldrich Chemical Company, Inc."
OROTAN's, "Rohm and Haas UK Limited OROTAN-681 (Na salt of Polyacrilic acid), 850E (NH4 salt) and 731 K (K salt)
Polyethylene glycol-400, PEG-400, "Aldrich Chemical Company, Inc."

constant temperature of the suspension using a water bath. The charging agents were added in most experiments at a concentration of 150 μl/100 ml. This concentration was chosen based on numerous previous experiments. In later experiments the concentration was varied in order to determine the optimal concentration.

The zeta potential of the particles at different pH values was measured using a zeta potential analyzer (ESA-8000, Matec Applied Sciences). The pH was adjusted using nitric acid and ammonium chloride for the acidic and the alkaline range, respectively. Conductivity measurements were made using a conductivity meter (WTW-LF 330).

3. Results and discussion

3.1. Standard zeta potential curves

Zeta potential curves in the absence of additives (standard zeta potential curves) were prepared for three suspensions: non-treated powder washed powder and passivated powder. The powder was washed repeatedly with an ethanol water mixture 30:70 vol%, until the conductivity of the suspension of powder in washing liquid is constant. Passivation of the powder was performed by dispersing it in a solution of 0.1 M oxalic acid (5 ml for 10 g powder) and maintaining the dispersion until its conductivity reaches 2 μS/cm. Fig. 1 shows the curves obtained.

The washing reduced the zeta potential of the powder in the positive range and the passivation with oxalic acid practically nullified the zeta in whole pH range. These phenomena can be explained as follows: In the non-washed powder a positive particle charge is obtained by adsorption of Ba^{2+} ions leached out of the $BaTiO_3$ in the acidic pH range. The passivation process results in a thermodynamically stable surface layer of barium oxalate rendering the particle not charged in the entire pH range. In order to decide which surface treatment should be applied to the powder prior to the charging experiments, the effect of PEI on powder with and without treatment was studied. Fig. 2 shows that the effect is practically the same for the three tested powders and therefore further experiments were carried out on untreated powder, referred to further as "standard" powder.

3.2. Effect of cationic agents on standard zeta curve of $BaTiO_3$

The cationic polymers used in this work are divided in two groups: polyethylene imines and polyamines.

Polyethylene imine (PEI) is a highly branched aliphatic polyamine characterized by the repeating chemical unit denoted as $-(CH_2-CH_2-NH)-$. The amine groups in PEI exist in primary, secondary and tertiary form in the approximate ratio 1:2:1. Primary amine groups, which are the chain terminating units, are the most basic and reactive. PEI's function as weak Lewis bases in aqueous media. The high degree of branching is thought to be due to the chain transfer reaction of amine groups with the quaternary ammonium ion. As the molecular weight of PEI increases, the polymer structure assumes a characteristic spherical configuration. The viscosity of PEI is directly proportional to its concentration and molecular weight. PEI is soluble in most polar materials including water and alcohols. PEI

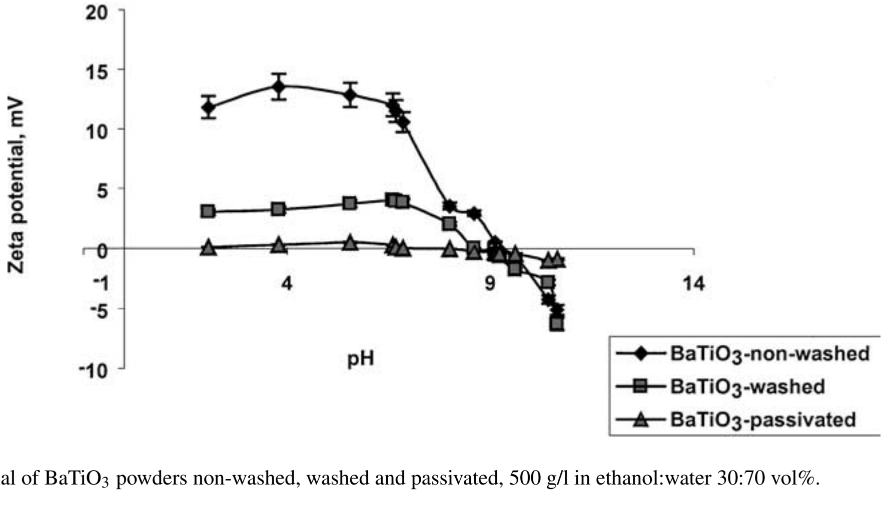

Figure 1 Zeta potential of $BaTiO_3$ powders non-washed, washed and passivated, 500 g/l in ethanol:water 30:70 vol%.

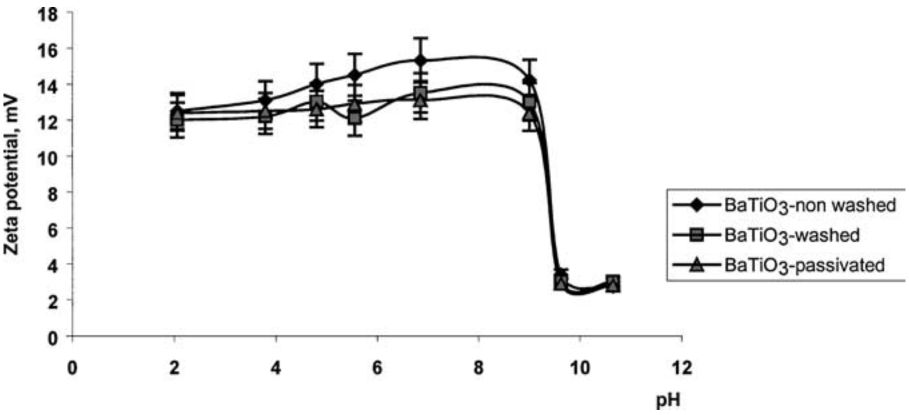

Figure 2 Effect of PEI 150 μl/100 ml on zeta potential of $BaTiO_3$ powders; washed, non-washed and passivated, 500 g/l in ethanol:water 30:70 vol%.

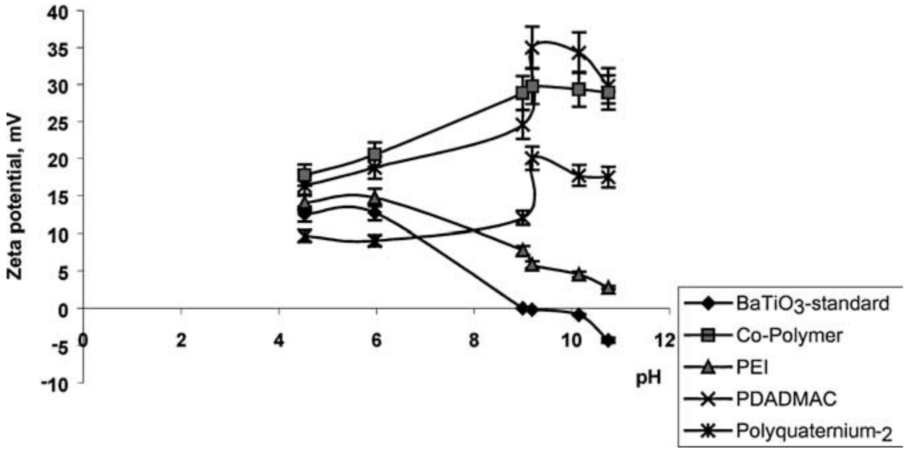

Figure 3 Comparison of effects of cationic additives at 150 μl/100 ml on zeta potential of $BaTiO_3$ powder, 500 g/l in ethanol:water 30:70 vol%.

does not contain an appreciable amount of quaternary groups; it achieves its cationicity trough protonation of the amine groups from the surrounding medium. This leads to correlation between pH and cationic charge density.

Polyamines are most often referred to a series of copolymers of dimethylamine and epichlorohydrin. The repeating unit of the linear form of the copolymers is $-CH_2-CHOH-CH_2-N^+(CH_3)_2-$. The presence of a quaternary ammonium group in these molecules ensures that it maintains its very strong cationic charge throughout the variable pH range.

Fig. 3 shows the effect of four cationic chargers: two polyimines (PEI and Co-polymer) and two quaternary ammonium salts (PDADMAC and Polyquaternium-2) at concentration of 150 μl/100 ml each. The particles are rendered positive in the whole pH range studied with a very convenient stable zeta potential in the pH range 6–9. An interesting observation is the steep falls in the zeta potential near the isoelectric point (IEP). The quaternary ammonium salts provide a higher charge particularly around pH 9. This is attributed to the presence of quaternary ammonium groups throughout the whole pH range. In case of PEI's protonation of amine groups depends on the pH of the media. Therefore it is preferable to use quaternary ammonium salts, because of the higher zeta and its lower dependence on pH. An increase of zeta up to 35 mV is obtained in the pH range 9–10 for PDADMAC at a concentration of 150 μl/100 ml.

3.3. Effect of anionic charging agents on the zeta curve of $BaTiO_3$

Fig. 4 shows the behavior of anionic charging agents based on polyacrylic acid (PAA) the active group being —COOH and named Orotans (see Table I). The IEP is shifted to a more acidic value (pH 6), the positive charge is reduced and quite efficient negative charging is obtained at pH 10 with the zeta reaching −35 mV for one of the Orotans. As with cationic chargers, these too are most effective in the 9–10-pH range. This pH range is close to the IEP, which could mean that the charging by an additive is more effective at a pH where the "native" charge of the surface is minimal.

3.4. Effect of additives on conductivity and deposition rate of $BaTiO_3$

The effect of the charging agents on the conductivity of the suspension is an important criterion for the selection process. The reason is that higher conductivities reduce the effective electric field exerted on the particles in the suspension. Therefore, the mobility of the particles is reduced and so is the deposition rate.

In numerous previous experiments we found that a conductivity of up to 10 μS/cm was acceptable. As can be seen in Fig. 5, at least two of the additives, including the most efficient charging agent (PDADMAC) result in a conductivity which is lower than that for concentrations which, as we shall see later, are sufficient to cause effective charging. Hence, conductivity curves as function of additive concentration must be

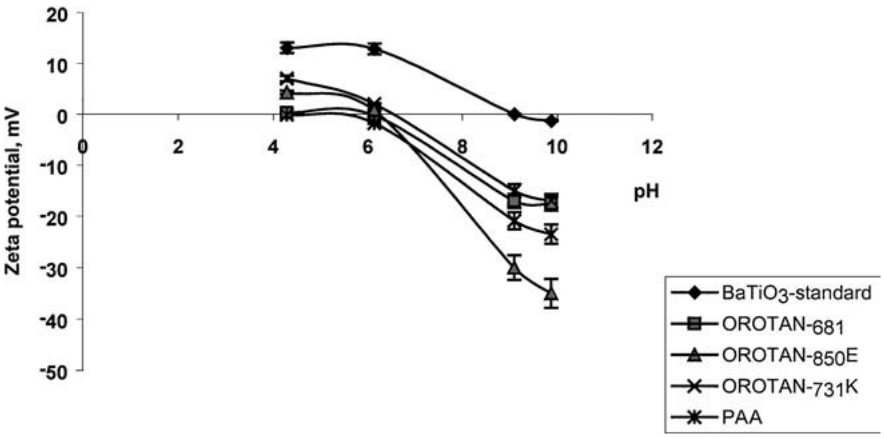

Figure 4 Comparison of effects of anionic additives at 150 μl/100 ml on zeta potential of $BaTiO_3$ powder, 500 g/l in ethanol:water 30:70 vol%.

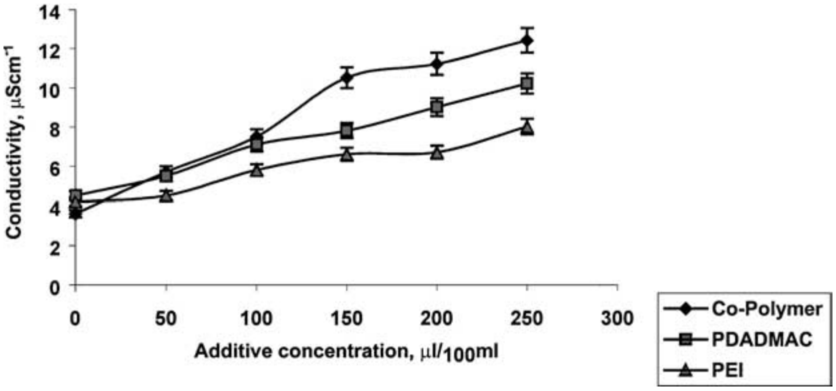

Figure 5 Conductivity of $BaTiO_3$ suspension, 500 g/l in ethanol:water 30:70 vol%, as function of cationic additives concentration.

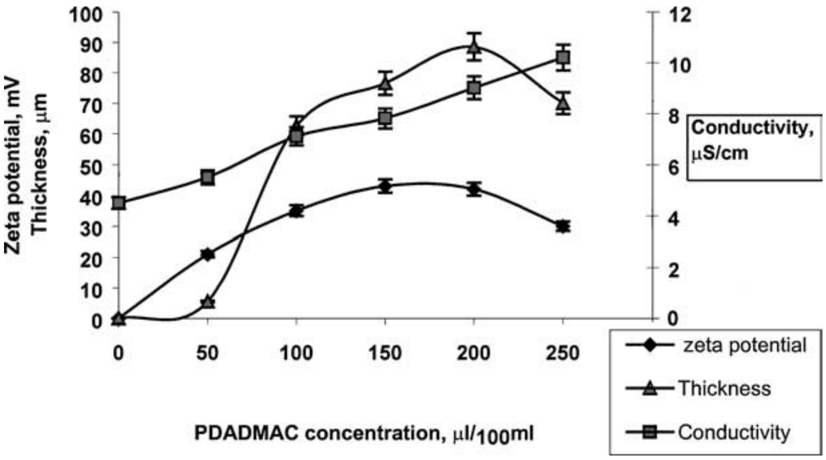

Figure 6 Influence of concentration of PDADMAC on zeta potential conductivity and thickness of $BaTiO_3$ deposit, 500 g/l in ethanol:water 30:70 vol%.

part of the selection process. Fig. 6 concentrates on the effect of PDADMAC on the three important criteria in the selection of a charging agent: zeta potential, conductivity and deposition rate. The deposition rate, expressed as deposit thickness, was measured on a deposit obtained in a cell with a cylindrical geometry at 100 V/cm for 3 min. A graphite cathode with 7 mm diameter and stainless steel anode with 6 cm diameter were used. The deposition rate exhibits a maximum at a concentration of about 200 μl/100 ml that coincides with the higher end of the effective range for the zeta potential. The reduction in deposition rate with a further increase in concentration can be explained by the resulting increase in conductivity of the suspension.

3.5. Effect of binders (PEG-400) on standard zeta curve of $BaTiO_3$ powder

Binders are added in order to improve the density and strength of the deposits. PEG is frequently used as a binder and therefore 150 μl/100 ml of PEG were added to suspensions used to determine the standard zeta/pH curve. As seen in the Fig. 7 no effect of PEG on the zeta exists in the positive range. The addition of binders to the suspension in the presence of charging agents

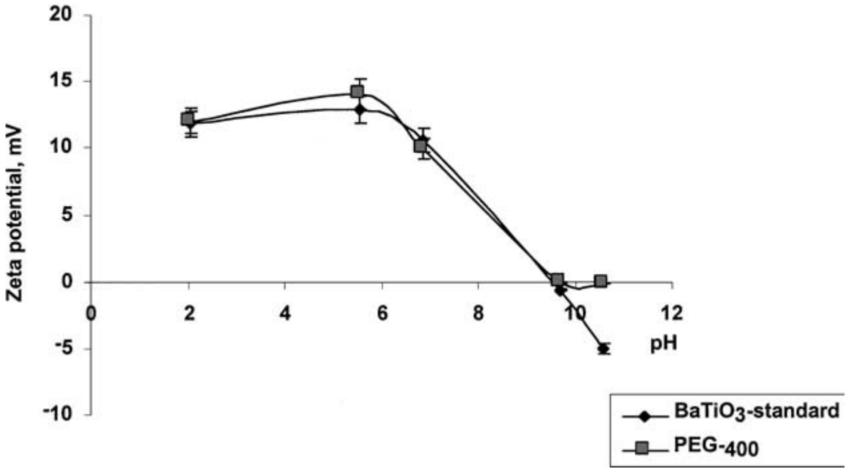

Figure 7 Effect of PEG-400 on zeta potential of $BaTiO_3$ powder, 500 g/l in ethanol:water 30:70 vol%.

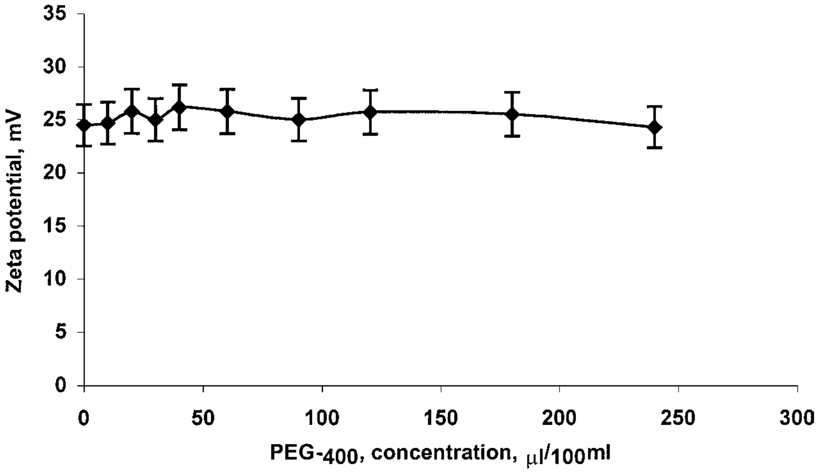

Figure 8 Effect of PEG-400 on zeta potential of $BaTiO_3$ powder, 500 g/l in ethanol:water 30:70 vol%; in presence of PDADMAC 150 μl/100 ml.

is addressed in Fig. 8. It is seen that the zeta, which was raised to 25 mV by the addition of PDADMAC, is not influenced by PEG-400 in the whole range of concentration studied. It can be deduced that PEG-400 does not interfere with the adsorption of PDADMAC on the particles and neither with the protonation of the amine groups.

4. Summary

Based on the above-mentioned experiments we have deduced the following methodology for the selection of a charging agent:

Obtain zeta potential/pH standard curve for powder in chosen solvent in absence of additives.

Perform zeta potential measurement in three points in presence of charging agents:

- at pH of IEP
- $\mathrm{pH} \sim \mathrm{pH}_{\mathrm{iep}} - 1$
- $\mathrm{pH} \sim \mathrm{pH}_{\mathrm{iep}} + 1$

Compare the values of the zeta potential measured at these three pH values with those of the standard curve (no additive).

From this comparison the following can be deduced:

- the charging agent is specifically adsorbed if there is a shift in the IEP, or it is indifferent or inactive if the IEP is not changed.
- the specifically adsorbed agent is preferred because of its potency.
- if the difference in the zeta potential values in the presence of the charging agents is significant (at least 10 mV), obtain a full zeta potential pH curve to select the optimal pH range
- obtain zeta potential/concentration curve to select concentration of the charging agent
- measure conductivity at this concentration (should be less than 10 μS/cm)
- obtain thickness/concentration curve to determine optimal concentration for deposition rate
- if a binder is needed check it's effect on zeta potential at optimal conditions for the specific charging agent.

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