

# Methods for functionalization of microsized polystyrene beads with titania nanoparticles for cathodic electrophoretic deposition

S. Radice <sup>a,\*</sup>, P. Kern <sup>a,1</sup>, H. Dietsch <sup>b</sup>, S. Mischler <sup>c</sup>, J. Michler <sup>a</sup>

<sup>a</sup> EMPA, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Mechanics of Materials and Nanostructures, Feuerwerkerstrasse 39, CH 3602 Thun, Switzerland

<sup>b</sup> Fribourg Center for Nanomaterials (FriMat), Department of Physics, Pérolles, CH 1700 Fribourg, Switzerland

<sup>c</sup> Ecole Polytechnique Fédérale de Lausanne (EPFL), Lab. for Metallurgical Chem., CH 1015 Lausanne, Switzerland

## Abstract

Functionalization of colloidal particles based on the use of polyelectrolytes and heterocoagulation was combined with electrophoretic deposition (EPD), with the aim of depositing titania–polystyrene ( $\text{TiO}_2$ –PS) composite particles on Ti6Al4V substrates. The composite particles were obtained by heterocoagulation of  $\text{TiO}_2$  nanoparticles on the surface of monosized polystyrene beads of  $4.6\ \mu\text{m}$  in diameter. Two alternative methods were developed for the preparation of the  $\text{TiO}_2$ –PS suspensions in organic fluids for cathodic electrodeposition. The first method was carried out in alkaline aqueous medium with the use of polyelectrolytes and intermediate control measurements of zeta potential, conductivity, and pH; the second one was carried out directly in the organic solvent used for EPD, typically isopropanol. Examples of deposits obtained by EPD in both suspensions and a comparative analysis between the two methods are presented.

**Keywords:** Heterocoagulation; Coating; Macroporosity; Template; Polyelectrolyte

## 1. Introduction

In the present work, particle functionalization is considered for subsequent electrophoretic deposition (EPD), a simple and flexible technique for producing coatings and thick films [1]. In particular, cathodic EPD is interesting because it avoids uncontrolled anodization (oxidation) of the metallic substrate. EPD of polystyrene (PS) beads has mostly been investigated within the research fields of colloidal crystals and photonic stop-band materials, utilizing only nanosized or submicrometer PS beads [2–7]. Polystyrene beads can also be used as spacers in combination with inorganic particles, leading to porous coatings or materials after removal of the PS spacers by heat treatment. For example, Jia et al. prepared green samples by slip casting of aqueous suspensions of nano- $\text{ZrO}_2$ -coated PS spheres

( $\varnothing 1\ \mu\text{m}$ ) and sintered them at 1000 and  $1400\ ^\circ\text{C}$  for 2 h [8]. Hamagami et al. prepared ethanol suspensions with hydroxyapatite nanoparticles mixed with PS beads ( $\varnothing 3\ \mu\text{m}$ ) and used electrophoretic deposition to prepare macroporous coatings on titanium substrates [9]. The electrophoretic co-deposition of microsized PS beads combined with nanosized inorganic particles such as  $\text{TiO}_2$  has great potentiality in the preparation of coatings with micropatterned surfaces combined with nanotopography, where the micropatterning is left by the microsized template and the nanotopography is given by the sintered inorganic nanoparticles. Such scale-resolved surface structuring is particularly relevant for biomedical applications, where specific combinations of micro- and nano-roughness were found to control cell adhesion and osteointegration of implant surfaces [10]. The fabrication of coatings with scale-resolved structuring by EPD starting from well-controlled particle functionalization remains a challenge.

Research activities on the functionalization of polystyrene beads include the use of polyelectrolytes and the concept of heterocoagulation (coagulation between oppositely charged par-

\* Corresponding author. Fax: +41 33 228 44 90.

E-mail address: simona.radice@empa.ch (S. Radice).

<sup>1</sup> Current address: Hoffmann Neopac AG, Burgdorfstrasse 22, CH 3672 Oberdiessbach, Switzerland.

ticles or species due to electrostatic attraction). PS beads and polyelectrolytes have been widely investigated for the preparation of hollow particles [11–15] and functionalized particles in the field of biosystems and drug delivery [16,17]. Additionally, F. Caruso and co-workers have extensively reported on the functionalization of PS beads using polyelectrolytes and a layer-by-layer deposition process [18–23]. In particular, they compared the layer-by-layer coating procedure of PS beads using titania ( $\text{TiO}_2$ ) precursors with that using  $\text{TiO}_2$  colloidal nanoparticles [19], pointing out the advantages of the latter. The procedure using  $\text{TiO}_2$  colloidal nanoparticles involved of PS particles as templates, on which layers of nanoparticles were deposited by the alternate adsorption of oppositely charged polyelectrolytes and nanoparticles, resulting in nanoparticle multilayer shells surrounding the template core. The authors used a variety of materials with the aim of producing hollow spheres. In particular,  $\text{TiO}_2$  nanoparticles ranging from 5 to 50 nm and PS beads from 210 to 640 nm in diameter were used.

In this context, we report on the controlled functionalization and EPD of bigger particles (microsized instead of the nanosized particles commonly found in the literature). In particular, suspensions of  $\text{TiO}_2$ -functionalized PS microbeads were prepared and used for cathodic EPD. The preparation of functionalized particles for cathodic EPD is constrained by specific requirements, such as the charge of the particles (positive, with the cathodic substrate negatively charged) and the suspension medium (organic solvent, avoiding the problem of gas evolution). Two parallel methods for the preparation of functionalized particles were developed and compared. In the first method, particles are mixed in ethanol and composite particles form by heterocoagulation; the second approach relies on the intermediate adsorption of polyelectrolytes in an alkaline aqueous suspension. In both cases, the suspensions obtained can be used for a controlled cathodic EPD of the composite particles alone, without any excess of  $\text{TiO}_2$  nanoparticles.

## 2. Materials and methods

### 2.1. Preparation of suspensions

Carboxylate-modified polystyrene beads of 4.6  $\mu\text{m}$  in diameter (<2% CV—coefficient of variation expressed as the standard deviation as a percentage of the mean diameter) in 4 wt% (3.8 vol%) water suspensions were purchased from Duke Scientific Corporation.  $\text{TiO}_2$  spherical nanoparticles were available from a flame-synthesis process [24]. Polydiallyl dimethyl ammonium chloride (PDADMAC) solution with very low molecular weight ( $M_w < 100,000$ ), 35 wt% in water, was purchased from Sigma-Aldrich Chemie GmbH. The solvents used were isopropanol puriss. p.a. (Fluka Chemie GmbH), deionized water 18.2  $\text{M}\Omega \text{ cm}$  (Milli-Q), and ammonium hydroxide solution puriss. p.a.  $\text{NH}_4\text{OH}$ , ≥25% in water (Fluka Chemie GmbH).

In the procedures for preparation of the suspensions for cathodic EPD, control measurements and analysis techniques were employed: zeta potential and electrical conductivity measurements (ZetaSizer Nano Z, Malvern Instruments Ltd.); pH monitoring (color-fixed indicator sticks from Roth); particle-

size distribution analysis by dynamic light scattering at an angle of 90° (Alv 5000L, laser Coherent Inc., Nd: YVO<sub>4</sub>, 532 nm); and scanning electron microscope analysis (SEM Hitachi S-4800). Intervals of 20 to 30 min were used between two sequential steps of a procedure. Zeta potential, conductivity, and pH were measured at the end of each interval. Intermediate centrifugation steps of 10 min were carried out in a Hermle Z 300 centrifuge at 2000 rpm (equivalent to 560g).

### 2.2. Electrophoretic deposition

As substrates for EPD, Ti6Al4V disks of 18 mm in diameter and 2 mm thickness were used. The substrates were previously HF-etched to a surface roughness of  $R_a = 0.1 \mu\text{m}$ , cleaned in an ultrasonic bath with water and ethanol, and, just before EPD, ultrasonicated with a piranha solution ( $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 3:1$ ) rinsed away by water and isopropanol. As counter electrode, a stainless-steel (316L) disk with an exposed area of ~0.4  $\text{cm}^2$  polished with a 600 grit SiC paper delimited by a mask of Araldit was used. A special electrochemical cell of 5-ml volume was constructed in our laboratory for a controlled withdrawal of the sample from the suspension. The exposed area of the working electrode was ≈0.12  $\text{cm}^2$ . The counter electrode was held at a fixed distance of 4 mm from the working electrode. Before the EPD, the cell was rotated to a vertical position so that the electrodes were immersed in the suspension. During the last 10 s of the EPD, the cell was turned back to the horizontal position so that the suspension was gradually removed from the exposed area of the sample. The rotation of the cell was achieved by means of an electric motor with a shaft rotating with a constant angular velocity of approximately 1 rpm (under load).

EPD experiments were performed at constant voltage supplied by a Xantrex XDC 300-20 Digital DC Power Supply. The applied voltages ranged from 100 to 300 V (from 250 to 750  $\text{V cm}^{-1}$ ), and the deposition time from 120 to 600 s. The current was measured by an ampere meter integrated into the circuit. The deposits were characterized by SEM.

## 3. Results

### 3.1. Preparation of $\text{TiO}_2$ -PS composite particles in suspension

Two parallel procedures for the preparation of suspensions in isopropanol with PS-TiO<sub>2</sub> composite particles are presented. The first procedure is based on the use of the cationic polyelectrolyte PDADMAC in water as preliminary medium and will be referred to as the PDADMAC procedure; the other one, carried out directly in isopropanol without the use of any polyelectrolyte, will be referred to as ISOPR procedure. A flow diagram summarizing both procedures is given in Fig. 1.

The first three steps of the PDADMAC procedure are: (1) 10-times dilution of a given volume of as-received PS suspension in deionized water; (2) addition of NH<sub>3</sub> to a final molarity of 3 mM NH<sub>3</sub>; (3) addition of PDADMAC from a 1 mM KCl solution to a final molarity of 0.1 mM PDADMAC. The initial dilution was required for zeta potential measurements with

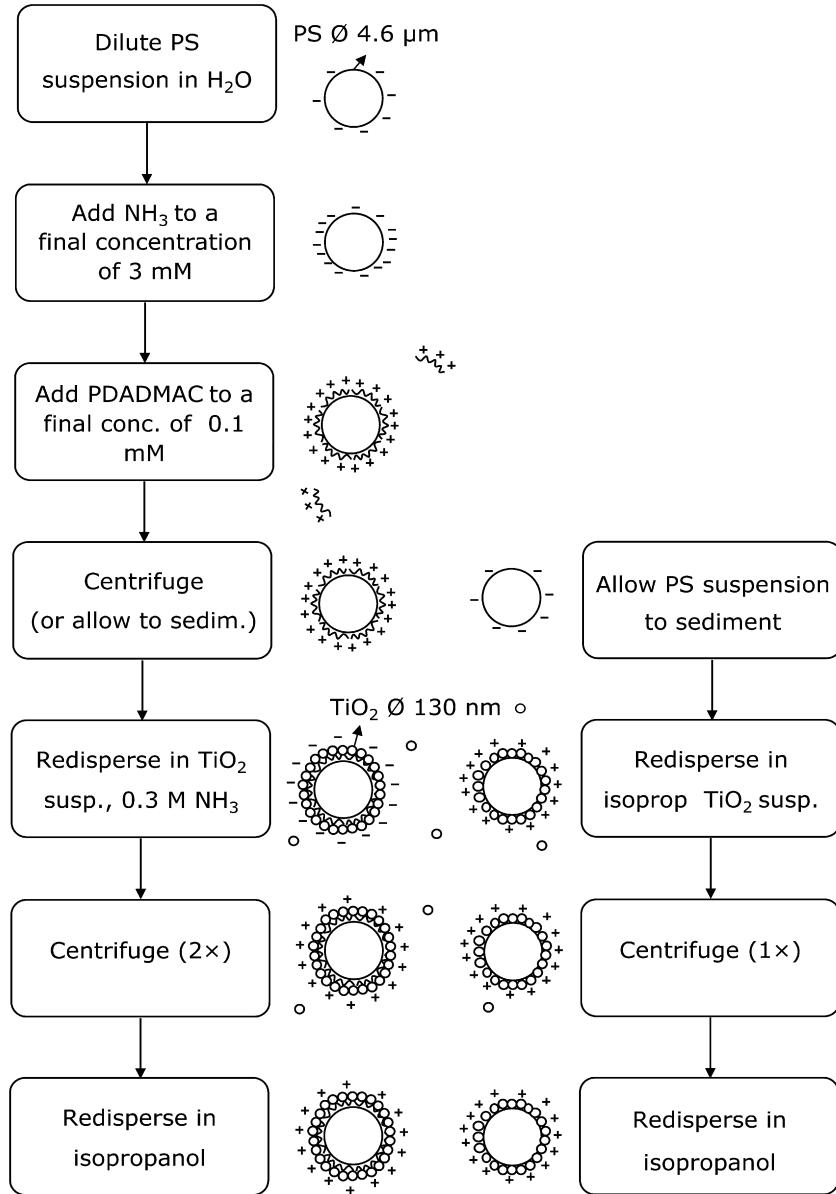


Fig. 1. Flow diagram explaining the two methods developed for the preparation of suspensions for cathodic EPD of TiO<sub>2</sub>-PS composite particles. (Left) Method in water with the use of polyelectrolyte (PDADMAC procedure); (right) method directly in isopropanol without polyelectrolyte (ISOPR procedure).

Table 1  
Zeta potential  $\zeta$ , conductivity  $\sigma$ , and pH measured 20–30 min after each of the initial three steps of the PDADMAC procedure

Procedure step	After PS dilution	After NH <sub>3</sub>	After PDADMAC
$\zeta$ (mV)	$-51.7 \pm 1.6$	$-51.3 \pm 0.8$	$+15.7 \pm 0.7$
$\sigma$ (mS cm <sup>-1</sup> )	$0.023 \pm 0.008$	$0.067 \pm 0.004$	$0.120 \pm 0.010$
pH	6.5–7.0	9.0	9.0

Note. The average values and standard deviations were calculated from three independent preparation processes where each measurement was repeated three times.

the ZetaSizer, which relies on light scattering (laser Doppler velocimetry) to measure the velocity of the particles and to calculate the zeta potential from the Henry equation with the Smoluchowski approximation [25]. The results of zeta potential  $\zeta$ , conductivity  $\sigma$ , and pH measurements after each step are

reported in Table 1. Procedures starting from higher dilutions (100 and 1000 times) were tried, but were abandoned because no EPD deposits could finally be achieved. The optimal NH<sub>3</sub> concentration, corresponding to the maximum negative value of the zeta potential, was previously identified by a series of zeta potential measurements with increasing amounts of NH<sub>3</sub>, as shown in Fig. 2. Similarly, the optimal concentration of PDADMAC was previously identified by a series of  $\zeta$  measurements with increasing amounts of PDADMAC (see Fig. 3). The range of PDADMAC concentration was derived from simple theoretical considerations of the available surface of PS beads and estimated dimensions of a PDADMAC monomer. According to these calculations a theoretical full coverage of PDADMAC linear macromolecules on the surface of one PS bead corresponds to  $2.16 \times 10^{-13}$  g of PDADMAC. These calculations led to the definition of a “factor of full coverage,” used to plot the results.

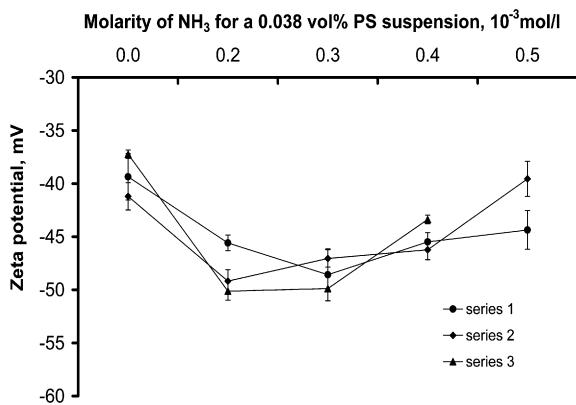


Fig. 2. Measurements of zeta potentials for the determination of the optimal NH<sub>3</sub> concentration corresponding to a maximum ratio of deprotonated negatively charged carboxyl groups on the surface of PS beads.

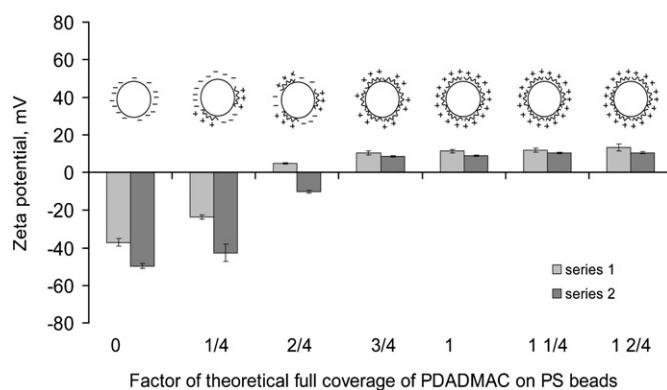


Fig. 3. Measurements of zeta potentials for the determination of the optimal PDADMAC concentration. The definition of a factor of theoretical full coverage of PDADMAC on PS beads was derived from simple theoretical considerations about the available surface of PS beads and estimated dimensions of a PDADMAC monomer. The factor “1” corresponds to 0.1 mM PDADMAC in the prepared suspensions.

The factor 1, assumed to be the optimal concentration, corresponds to a final PDADMAC concentration of 0.099 mM. The optimization experiments were carried out with PS, NH<sub>3</sub>, and PDADMAC concentrations 10 times less than the concentrations used for the first three steps of the procedure described above.

The resulting suspension of positively charged PDADMAC-PS beads was centrifuged and the sediment was redispersed in an alkaline suspension with negatively charged TiO<sub>2</sub> particles. The characterization of the TiO<sub>2</sub> alkaline suspension is reported in Table 2. The isoelectric point of TiO<sub>2</sub> (anatase) is known to be around pH 6. Theoretical calculations led to the volume of TiO<sub>2</sub> needed to achieve a full coverage of TiO<sub>2</sub> particles on the PS beads in a given volume of PS suspension: by dividing the spherical surface of a bead ( $\varnothing$  4.6 μm) by the projected area of TiO<sub>2</sub> particles ( $\varnothing$  130 nm) it can be estimated, that approx. 5000 TiO<sub>2</sub> particles are needed to cover the surface of 1 PS bead. The corresponding total volume of 5000 TiO<sub>2</sub> particles and of 1 PS bead are, respectively,  $5.8 \times 10^{-12}$  and  $5.1 \times 10^{-11} \text{ cm}^3$ . By keeping this TiO<sub>2</sub>-PS volume ratio, when considering a volume of suspension  $V$  of 6 ml and with

Table 2  
Characterization of the TiO<sub>2</sub> suspensions used in the PDADMAC and ISOPR procedure

TiO <sub>2</sub> suspension	Alkaline suspension (PDADMAC procedure)	Isopropanol suspension (ISOPR procedure)
Vol%	0.213	0.213
Medium	0.3 M NH <sub>3</sub>	Isopropanol
pH	10.5	6.5–7.0
$\zeta$ (mV)	$-39.9 \pm 3.0$	<0 (cathodic EPD)
$\sigma$ (mS cm <sup>-1</sup> )	$0.033 \pm 0.01$	—
Mean diameter (nm)	$119.4 \pm 1.0$	$149.0 \pm 2.1$

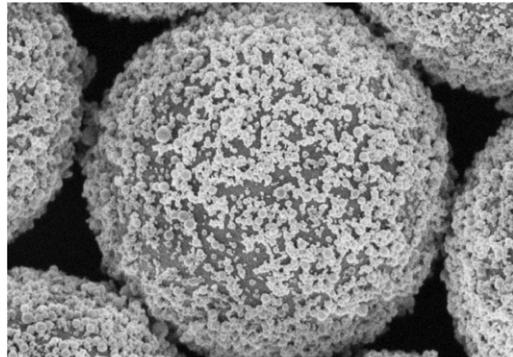
3.8 vol% PS, the same volume  $V$  with 0.427 vol% TiO<sub>2</sub> is needed for a theoretical complete coverage of the PS beads by the TiO<sub>2</sub> particles. In this work, a volume  $2 \cdot V$  of a 0.213 vol% TiO<sub>2</sub> suspension was mixed with a volume  $V$  of a 3.8 vol% PS suspension. Experimentally this concentration ratio led to an excess of TiO<sub>2</sub>. Consequently, two additional centrifugation steps with redispersion in isopropanol were needed at the end of the procedure. The composite particles gained a negative charge in isopropanol, thanks to the TiO<sub>2</sub> particles covering their surface.

The procedure for preparation of TiO<sub>2</sub>-PS composite particles without polyelectrolyte in isopropanol (ISOPR procedure) is much simpler (see Fig. 1). For comparison, the same volume ratio between PS and TiO<sub>2</sub> particles was used. In preliminary zeta potential measurements, the standard deviations were too large due to the low dielectric constant of isopropanol. The low mobility of particles in organic dispersants compared to water and the difficulty of producing a stable, homogeneous field in the capillary cell (DTS1060) caused great uncertainty in the measurements. For this reason, no control  $\zeta$  measurements were performed in the ISOPR procedure. The characterization of the TiO<sub>2</sub> suspension in isopropanol is reported in Table 2.

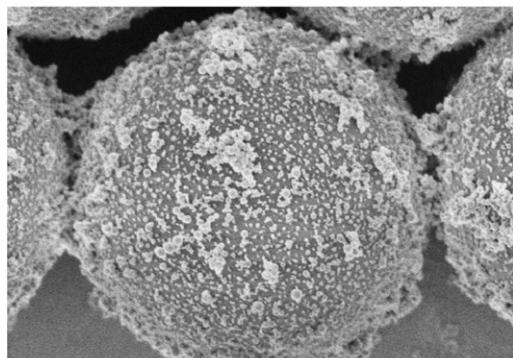
Considering all steps of preparation for either the PDADMAC or the ISOPR procedure, the obtained final suspensions for cathodic EPD had about 2.2 vol% of composite TiO<sub>2</sub>-PS particles in isopropanol with the rest of water (1–3 vol%). High magnification SEM micrographs of dried drops of suspensions are shown in Fig. 4. The TiO<sub>2</sub>-PS composite particles prepared by the PDADMAC procedure show a more complete and uniform TiO<sub>2</sub> coverage than the ones prepared by the ISOPR procedure.

### 3.2. Electrophoretic deposition

Deposits by electrophoretic depositions were obtained under different parameters (applied voltage and deposition times). The removal of the sample from suspension was found to be critical for the integrity of the deposit over the whole substrate. Fig. 5 illustrates an example of deposit obtained by EPD at 300 V for 600 s from a suspension prepared with the PDADMAC procedure. The deposited particles consist of TiO<sub>2</sub>-coated PS beads, without loose TiO<sub>2</sub> nanoparticles. No ordered structure built up by the TiO<sub>2</sub>-PS beads is observed. During the EPD process, the current monotonically decreased from 25 to 13  $\mu\text{A cm}^{-2}$ . The thickness of the deposit, estimated

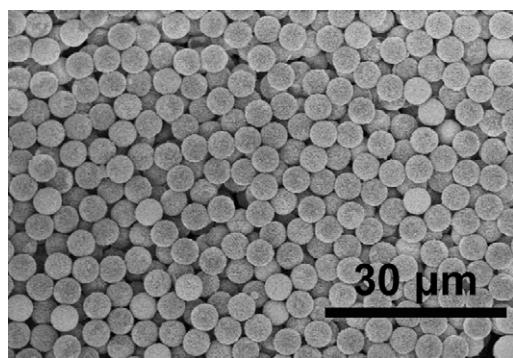


PDADMAC-procedure

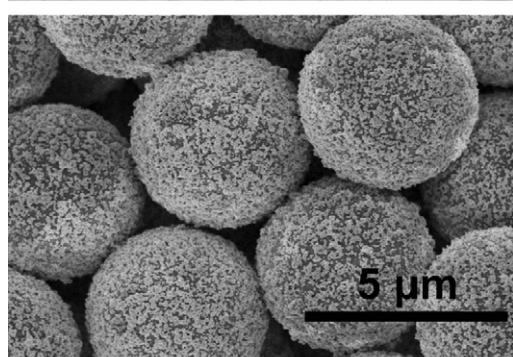


ISOPR-procedure

Fig. 4. High magnification SEM micrographs of dried drops of suspensions with 4.6  $\mu\text{m}$  PS beads functionalized with  $\text{TiO}_2$  nanoparticles prepared with the PDADMAC procedure (top) and the ISOPR procedure (bottom).

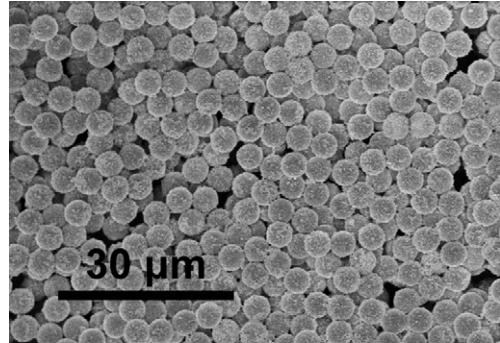


30  $\mu\text{m}$

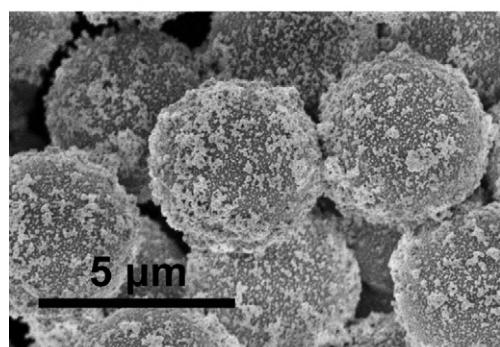


5  $\mu\text{m}$

Fig. 5. Secondary electron SEM micrograph at different magnifications of a coating obtained by EPD at 300 V (equivalent to  $750 \text{ V cm}^{-1}$ ) for 600 s from a suspension with 4.6  $\mu\text{m}$  PS beads functionalized with  $\text{TiO}_2$  nanoparticles prepared with the PDADMAC procedure.



30  $\mu\text{m}$



5  $\mu\text{m}$

Fig. 6. Secondary electron SEM micrograph at different magnifications of a coating obtained by EPD at 300 V (equivalent to  $750 \text{ V cm}^{-1}$ ) for 600 s from a suspension with 4.6  $\mu\text{m}$  PS beads functionalized with  $\text{TiO}_2$  nanoparticles prepared with the ISOPR procedure.

by the number of particle layers observed under SEM, was 10–15  $\mu\text{m}$  (two to three layers). Fig. 6 is a SEM micrograph of a deposit obtained under the same EPD parameters from a suspension prepared with the ISOPR procedure. The deposit looks similar to the one obtained from the PDADMAC procedure, but the single composite beads look different, as already pointed out in the SEM analysis of drops of suspensions (Fig. 4). The current showed an initial decrease from 103 to 87  $\mu\text{A cm}^{-2}$  followed by an irregular current increase up to 111  $\mu\text{A cm}^{-2}$ . The number of deposited particles layers observed under the SEM was also between two and three.

#### 4. Discussion

Explanatory drawings illustrating step by step both procedures are presented in Fig. 1. In the PDADMAC procedure, the addition of  $\text{NH}_3$  was carried out in order to maximize the amount of negatively charged carboxyl groups at the surface of the carboxyl-modified PS beads ( $pK_a$  approx. 5) and to start the process under well-defined conditions. The minimum in the measured  $\zeta$  (see Fig. 2) was assumed to correspond to the maximum amount of deprotonated carboxyl groups before a further increase of  $\text{NH}_3$  would lead to a thinning of the double layer due to increased ionic strength. However, it can be seen from the values reported in Table 1 referring to the 0.38 vol% PS suspensions (10 times less diluted than the suspensions used for the optimization experiments), that the measured  $\zeta$  value practically did not change when the ionic strength ( $\sigma$ ) increased after addition of  $\text{NH}_3$ . This was probably due to an increase in the negative surface charge of the particles according to

the diffuse double-layer model in the Gouy–Chapman theory and the Debye–Hückel approximation [25]. In fact, an increase in ionic concentration is typically related to a decrease in the measured  $\zeta$ . Since this was not the case, the effect of the increased ionic concentration was assumed to be compensated by a higher charge density of the particles. Regarding the third step of the procedure, the optimal concentration of PDADMAC was supposed to cause a full inversion of surface charge from negative to positive, while avoiding the formation of loops and tails in the polyelectrolyte chains and without leaving a significant excess of polyelectrolyte in suspension [26]. Among the polycations commonly found in the literature for particle functionalization, PDADMAC was chosen because it is a strong polyelectrolyte. Thanks to its quaternary ammonium group, the degree of dissociation of the ionic groups is nearly pH independent over a wide pH range. In contrast, weak polyelectrolytes such as, for example, polyethylenimine have a pH-dependent degree of ionization [27].

By comparing the composite particles derived from both procedures, two conclusions can be drawn. First, the surface coverage of the PS beads is smaller for the ISOPR procedure. Second, a difference in the agglomeration level of the TiO<sub>2</sub> nanoparticles adsorbed on the surface of the PS beads appears evident (see Fig. 4): the TiO<sub>2</sub> particles directly mixed from the isopropanol suspension in the ISOPR procedure seem to have a higher agglomeration level when adsorbed on the surface of the PS beads, in comparison to the particles suspended in 0.3 M NH<sub>3</sub> for the PDADMAC procedure. On the one hand, this could be explained by the different agglomeration levels of the TiO<sub>2</sub> starting suspensions. As can be seen in Table 2, the TiO<sub>2</sub> particles dispersed in the alkaline suspension have a smaller average size than those dispersed in isopropanol. In our interpretation, this is due to the different surface charge obtained in the two TiO<sub>2</sub> suspensions. The charge of the particles in isopropanol is attributed to a small amount of H<sub>2</sub>O included in commercially available organic solvents [28]: H<sup>+</sup> and OH<sup>-</sup> ions are generated by electrolytic dissociation; the generated H<sup>+</sup> ions adsorb on the amphoteric hydroxyl groups at the surface of the TiO<sub>2</sub> particles and are responsible for the positive surface charge of TiO<sub>2</sub> (like other ceramic particles like ZrO<sub>2</sub>) in organic solvents. However, the charge of the particles in the alkaline solution is negative, since the amphoteric hydroxyl groups get deprotonated above the isoelectric point of TiO<sub>2</sub>. The same behavior is observed for the carboxyl-modified PS beads with the addition of NH<sub>3</sub>. The electrostatic stability of the particles in suspension and thus their dispersion level are assumed to be more favorable for the particles in the alkaline suspension. On the other hand, the lower surface coverage of PS beads found in the ISOPR procedure might also be attributed to a lower density of negatively charged carboxyl groups on the PS surface. In fact, in the PDADMAC procedure the PS particles are first treated with a very small amount of NH<sub>3</sub> for a maximum deprotonation of the carboxyl groups. In the ISOPR procedure the negative charge of the PS particles relies on the residual amount of H<sub>2</sub>O remaining entrapped in the PS sediment. Because of these factors, the PDADMAC procedure is preferred despite its higher complexity. Moreover, it would be possible

to extend this procedure further by alternating PDADMAC and TiO<sub>2</sub> layers, so that the total thickness of TiO<sub>2</sub> around the PS beads could be increased layer by layer. This is one basic idea of our current research activities, aimed at EPD coatings with a controlled porosity obtained after sintering and burning out of the PS beads.

Both procedures presented here led to the preparation of TiO<sub>2</sub>–PS composite particles in isopropanol suspensions, which could be cathodically deposited by EPD. The suspensions were characterized by sedimentation times of about 10 min. The stability of the suspensions was sufficient for the EPD. Nevertheless, it needs to be improved in order to obtain more uniform coatings with lower applied voltages and shorter EPD times. For example, intermediate centrifugation and redispersion steps could be introduced within the PDADMAC procedure. This would lead to a higher positive zeta potential without a significant increase in ionic concentration. The optimization of the PDADMAC procedure is the subject of ongoing research.

The methods of preparation of the TiO<sub>2</sub>–PS suspensions were constrained by four main conditions dictated by the cathodic EPD process: (1) particles positively charged; (2) organic medium; (3) no excess of TiO<sub>2</sub> nanoparticles; (4) sufficiently high concentration. These four conditions are discussed next. In cathodic deposition the substrate is the negatively charged cathodic electrode, at the interface of which a reduction reaction of hydrogen occurs. The risk of Ti-alloy embrittlement due to hydrogen adsorption and diffusion into the substrate can be neglected, as discussed in our previous work [29]. On the other hand, an anodic deposition on metallic substrates is generally associated with uncontrolled oxidation and pitting reactions. For this reason, cathodic deposition was preferred and the particle functionalization required a final positive charge. The EPD process required the particles to be suspended in an organic medium, in this case isopropanol. Organic solvents are preferred to aqueous media for EPD because the problem of gas evolution and bubble formation is significantly reduced [1]. An excess of TiO<sub>2</sub> nanoparticles, experimentally related to an insufficient number of centrifugation steps, led to preferential deposition of TiO<sub>2</sub> nanoparticles due to their smaller size. The resulting coatings contained prevalently only TiO<sub>2</sub> particles: the predominant deposition of TiO<sub>2</sub> raised the ohmic resistance of the electrochemical circuit, apparently causing a decrease in the electrophoretic force acting on the bigger TiO<sub>2</sub>–PS particles. Only a few TiO<sub>2</sub>–PS particles could be deposited when using suspensions with an excess of TiO<sub>2</sub>. Finally, the concentration of particles in suspension was identified as a critical factor for a successful EPD. The reason why EPD coatings could not be achieved with suspensions with volume concentrations of 0.2 vol% or lower is not clear. The role of the solid contents in the EPD process was treated by Sarkar and Nicholson [30]. In a recent work, Ferrari et al. derived a generalized resistivity model for electrophoretic deposition from the Hamaker equation [31]. Both studies explain variations in the deposited weight with time due to changes in the concentration of the suspension during the EPD process. An investigation on different starting concentrations for fixed EPD parameters would lead to

the definition of a critical starting concentration for the given system, above which EPD is possible.

## 5. Conclusions

Two methods for the preparation of suspensions with TiO<sub>2</sub>-PS composite particles in isopropanol were developed, where nanosized TiO<sub>2</sub> particles covered the surface of microsized PS beads. The suspensions could be used for cathodic EPD onto metallic substrates, with all the related advantages of the EPD technique and the cathodic (rather than anodic) reaction at the substrate. The method based on the use of a polyelectrolyte was found to be superior in terms of more complete adsorption of the TiO<sub>2</sub> particles on the PS beads.

## Acknowledgments

We thank Dr. Rainer Dittmann from the EMPA Laboratory for High Performance Ceramics (headed by Dr. T. Graule) for the production and provision of the TiO<sub>2</sub> nanoparticles; Martin Elsener (ETHZ), Anton Böll, and Christian Kauer (EMPA Thun) for help in the experimental setup; Gerhard Bürki (EMPA Thun) for great patience and competence at the high resolution SEM; Dr. James Whitby for help in the preparation of the manuscript; Camille Dagallier, Mathias Reufer, Dr. Veronique Trappe, and all the Soft Condensed Matter group of Fribourg (Department of Physics, headed by Prof. P. Schurtenberger) for the use of the ZetaSizer and the Centrifuge.

## References

- [1] I. Zhitomirsky, JOM 52 (2000).
- [2] N.V. Dziomkina, G.J. Vancso, Soft Matter 1 (2005) 265–279.
- [3] P.C. Lewis, E. Kumacheva, M. Allard, E.H. Sargent, J. Dispersion Sci. Technol. 26 (2005) 259–265.
- [4] R.C. Hayward, D.A. Saville, I.A. Aksay, Nature 404 (2000) 56–59.
- [5] L.Q. Wu, K. Lee, X. Wang, D.S. English, W. Losert, G.F. Payne, Langmuir 21 (2005) 3641–3646.
- [6] N.V. Dziomkina, M.A. Hempenius, G.J. Vancso, Adv. Mater. 17 (2005) 237–240.
- [7] K. Kanamura, J. Hamagami, Solid State Ionics 172 (2004) 303–308.
- [8] Y. Jia, C. Duran, Y. Hotta, K. Sato, K. Watari, J. Colloid Interface Sci. 291 (2005) 292–295.
- [9] J. Hamagami, Y. Ato, K. Kanamura, Solid State Ionics 172 (2004) 331–334.
- [10] G. Zhao, O. Zinger, Z. Schwartz, M. Wieland, D. Landolt, B.D. Boyan, Clin. Oral Implants Res. 17 (2006) 258–264.
- [11] Y.Z. Li, T. Kunitake, S. Fujikawa, J. Phys. Chem. B 110 (2006) 13000–13004.
- [12] P. Wang, D. Chen, F.Q. Tang, Langmuir 22 (2006) 4832–4835.
- [13] X.J. Cheng, M. Chen, L.M. Wu, G.X. Gu, Langmuir 22 (2006) 3858–3863.
- [14] I.B. Jang, J.H. Sung, H.J. Choi, I. Chin, Synth. Met. 152 (2005) 9–12.
- [15] M. Zhang, G. Gao, C.Q. Li, F.Q. Liu, Langmuir 20 (2004) 1420–1424.
- [16] A.S. Angelatos, K. Katagiri, F. Caruso, Soft Matter 2 (2006) 18–23.
- [17] F. Caruso, H. Mohwald, J. Am. Chem. Soc. 121 (1999) 6039–6046.
- [18] F. Caruso, H. Mohwald, Langmuir 15 (1999) 8276–8281.
- [19] R.A. Caruso, A. Susha, F. Caruso, Chem. Mater. 13 (2001) 400–409.
- [20] M.K. Park, C.J. Xia, R.C. Advincula, P. Schutz, F. Caruso, Langmuir 17 (2001) 7670–7674.
- [21] G.B. Sukhorukov, E. Donath, S. Davis, H. Lichtenfeld, F. Caruso, V.I. Popov, H. Mohwald, Polym. Adv. Technol. 9 (1998) 759–767.
- [22] D.Y. Wang, F. Caruso, Chem. Mater. 14 (2002) 1909–1913.
- [23] D.Y. Wang, R.A. Caruso, F. Caruso, Chem. Mater. 13 (2001) 364–371.
- [24] R. Dittmann, J. Richter, A. Vital, D. Piazza, C. Aneziris, T. Graule, Adv. Eng. Mater. 7 (2005) 354–360.
- [25] B. Dobias, Coagulation and Flocculation: Theory and Applications, vol. 47, Dekker, New York, 1993.
- [26] R. Rehmet, E. Killmann, Colloids Surf. A 149 (1999) 323–328.
- [27] I. Zhitomirsky, J. Appl. Electrochem. 34 (2004) 235–240.
- [28] H. Negishi, K. Yamaji, T. Imura, D. Kitamoto, T. Ikegami, H. Yanagishita, J. Electrochem. Soc. 152 (2005) J16–J22.
- [29] S. Radice, P. Kern, G. Bürki, J. Michler, M. Textor, J. Biomed. Mater. Res. Part A 82A (2007) 436–444.
- [30] P. Sarkar, P.S. Nicholson, J. Am. Ceram. Soc. 79 (1996) 1987–2002.
- [31] B. Ferrari, R. Moreno, J.A. Cuesta, Key Eng. Mater. 314 (2006) 175–180.