Electrophoretic Deposition of Ni(OH)₂ Nanoplatelets modified by polyelectrolyte multilayers. Study of the Coatings Formation in a Laminar Flow Cell

Z. Gonzalez^{1, *}, C. Filiatre², C.C. Buron², A.J. Sanchez-Herencia¹ and B. Ferrari¹

1) Institute for Ceramic and Glass, CSIC, Madrid, Spain.

2) Institute UTINAM-UMR 6213, University of Bourgogne - Franche-Comté, Besançon, France

(*corresponding author: zgonzalez@icv.csic.es)

Abstract

The electrophoretic deposition (EPD) of semiconductor ceramic nanoplatelets functionalized by self-assembled polyelectrolyte multilayers has been investigated. The influence of particle surface modification in the packing of the nanostructured film on a nickel cathode has been determined for different electrical conditions. A polymer multilayer shell has been fashioned onto β -Ni(OH)₂ nanoplatelets surfaces by alternating the adsorption of Polyethylenimine (PEI) and Polyacrylic Acid (PAA). Two different core-shell systems with 1, 3 and 5 layers were considered using either linear or branched PEI as polycation to alternate with the anionic polyelectrolyte (PAA). The Layer by layer, (LbL) build-up of polyanions and polycations was characterized both in terms of particle zeta potential measurements and *in situ* measurements of polyelectrolyte adsorption onto a flat substrate by optical fixed-angle reflectometry. The amount of polyelectrolyte required to build up each layer was determined from zeta potential measurements. Both data allowed the design of the *in situ* formation of the core-shell nanostructures as well as the shaping of the particulated coatings following the one-pot procedure, avoiding intermediate steps of drying or washing. The movement of the core-shell particles, their aggregation state and the coating growth during electrophoretic deposition were studied *in situ* using a laminar flow cell coupled to an optical microscope. The particle flux was calculated from the surface coverage of the cathode and compared to the values estimated by the EPD electrokinetic model, demonstrating the strong impact of the steric interaction between the core-shell particles in both the deposition rate of nanoplatelets and the coating morphology.

Keywords: Polyelectrolyte Multilayer, Layer-by-layer adsorption, Electrophoretic Deposition, Nickel Hydroxide, Optical fixed-angle reflectometry

1. Introduction

Since last decades the nanoparticle fashioning (0D, 1D, 2D and 3D nanostructures) has receive a remarkable attention, and their processing as coatings is still challenging to achieve higher performances. The design of assembled nanoparticles as thin films on a conductive surface is used into a large variety of applications such as electrochemical devices, photonic material, magnetic data storage, biosensors, protective coatings, etc. Dimensionally controlled nanoparticles are synthesized and employed for different functional applications, where their small size and their elevated specific surface area enhance the electrochemical properties or provides new ones¹⁻⁷.

In energy storage devices, semiconductor metal oxides/hydroxides in general and Ni-based materials in particular are commonly used as electroactive material due to their well-defined electrochemical redox activity and their high theoretical values of specific capacitance or energy/power density (2584 and 2082 F/g for NiO and Ni(OH)₂ in pseudocapacitors and 718 and 578 mAh/g for NiO and Ni(OH)₂ in batteries respectively)⁸⁻¹⁰.

In addition to the physicochemical parameters of the raw powder (morphology, crystallinity, size, etc.), the in use properties strongly depends on the features of the after packing characteristics (active surface area, conductivity, pore-size distribution, etc.). That evidences the need to address the research towards the development of new methods to tune the arrangement of nanoparticles to finally improve the overall behavior of the devices.

In this sense, the processing of ceramic films through the use of the colloidal techniques allow to tailor these nanostructures and strengthen the control over specific properties. In a suspension of nanoparticles, the manipulation of the colloidal chemistry and the adjustment of interaction forces (liquid-solid and/or solid-solid) results in a higher uniformity of the material. Besides, the adsorption of ionizable organic molecules onto inorganic particles extends the design possibilities due to the modification of the surface chemistry^{11,12}. Under this approach, the adsorption of a polyelectrolyte multilayer onto the surface of ceramic particles could be an alternative

66 strategy to vary the particle packing in a final microstructure. The assembly (LbL) is a
67 technique based on the sequential adsorption of polyelectrolytes via electrostatic and
68 non-electrostatic interactions (e.g. hydrophobic interactions, hydrogen bonding,
69 charge-transfer interactions, host-guest interactions, biologically specific interactions,
70 coordination chemistry interactions, covalent bonding, stereo complexation, surface
71 sol-gel process)^{13,14}. The versatility of the LbL approach allows the assembling of a
72 broad range of materials such as polymers, nanoparticles, lipids, proteins, dye
73 molecules, etc. The properties of LbL films like composition, thickness, density and/or
74 functionality, can be tuned by simply varying the type of adsorbed species, the number
75 of deposited layers and the conditions employed during the assembly process¹⁵. Thus,
76 the couple polyethylenimine (PEI) and poly(acrylic acid) (PAA) was already used in
77 several studies¹⁶⁻¹⁸, where large variations of the shell thickness, ranging from 90 nm
78 to 4.7 μm , can be promoted by changing the pH¹⁶.

79 On the other hand, Electrophoretic Deposition (EPD) is a simple and a reliable colloidal
80 technique which can be employed for shaping films as alternative to other methods
81 based on solvent evaporation such as dipping, spinning or spraying. In EPD a DC
82 voltage is applied between two electrodes in a parallel plate configuration immersed in
83 a suspension. The charged particles suspended in the polar solvent are attracted by
84 the Coulomb forces to the electrode of opposite charge where they assemble forming
85 a film. The EPD process offers several advantages: short formation time, simple setup,
86 low cost, suitability for mass production and above all, any kind of particle/entity can
87 be deposited by EPD, independently of its nature, morphology and size.

88 In EPD, both the thickness of the films and the amount of the deposited mass can be
89 controlled varying the concentration of the suspension, the applied potential or/and
90 the deposition time^{19,20}. Moreover the coating performance strongly depends on the
91 particle surface chemistry, the behavior of the surface-liquid interfaces under the
92 electric field and the development of particle-particle and particle-substrate networks
93 during particle assembly²¹. In this sense, the deposition yield and the particle packing
94 in EPD also depends on the aggregation and the arrangement of the nanoparticles on
95 the electrode surface, since during deposition fluid-solid interactions modify particles
96 adhesion and directly influence on the deposit morphology and hence on its
97 microstructure.

Up to now, several kinetics models have been proposed based only on the electrophoresis movement of suspended particles, but the particle arrangement in a cohesive deposit is not so well-understood and the EPD process is still a matter of controversy. The debate dealing with both particle aggregation and their arrangement at the electrode surface is still open to further detailed research in different systems²¹.

Some authors have predicted the movement of particles and its aggregation through the analysis of the images obtained with cells coupled to optical microscopes which allow monitoring the deposition process under different conditions. Adamczyk et al.²² demonstrated the influence of flow intensity on adsorption kinetics of polystyrene latex particles and more recently they have determined in situ the coverage of colloids particles directly adsorbed in the streaming potential cell under diffusion conditions^{23–25}. Semmler et al.²⁶ compared the radial distribution functions with theoretical calculations performed according to the random sequential modeling considering the polydispersity of a latex suspension. Hosseini et al.²⁷ have recently studied the effect of electrostatic field on the aggregation rate and aggregate size of asphaltene particles using a horizontally oriented glass micro-model, with a pair of opposing electrodes inserted within the model and a microscopic camera. Filiâtre et al.^{28–30} have reported studies with polystyrene particles modified with surfactant and/or polyelectrolytes using a specific laminar flow cell. In fact, her group has recently reported the electrophoretic deposition of polystyrene particles pre-coated with chitosan–alginate multilayer³¹.

Following this line, the aim of this work is the study of the deposition behavior of β -Ni(OH)₂ nanoplatelets modified by the Layer-by-Layer adsorption of PEI and PAA onto their surfaces in aqueous medium. Linear and branched PEI (L-PEI and B-PEI) were used resulting in (PEI/PAA)/ β -Ni(OH)₂ core-shell structures. In a previous work³², the high specific capacitance of Ni-based electrodes modified with polyelectrolyte multilayers was successfully measured in a supercapacitor configuration. Herein we determine the growth of both (PEI/PAA) multilayer systems, describing the formation of the inorganic/organic core-shell structures and the implication of the polyelectrolyte multilayer in the electro-driven movement of nanoplatelets and their aggregation on the cathode. For this purpose, the core-shell particle flux was directly calculated from the substrate coverage and related to data extracted from the well-known Sarkar and

130 Nicholson EPD kinetics models³³.

131

132 2. Experimental

133

134 2.1 Particles synthesis

135 All chemicals were of reagent grade and used without any further purification. The
136 synthesis of β -Ni(OH)₂ was described in detail in previous works.^{34,35} It consists in a
137 chemical precipitation at room temperature using a high intensity ultrasonic horn (170
138 W/cm², 20 kHz, titanium tip of 19mm, Labsonic U, B. Braun, Germany). The
139 identification of the crystal phases of the synthesized powders was carried out by X-ray
140 diffraction (XRD) with a Siemens D5000 diffractometer (Germany) with a Kristalloflex
141 710 generator ($K\alpha(\text{Cu}) \lambda = 1.5405 \text{ \AA}$; 40 KV; 30 mA; $2\theta = 5-70$). After the synthesis, the
142 remaining chemicals were eliminated by filtration and the particles were washed
143 several times with distilled water at pH ~ 10 (adjusted with tetramethyl ammonium
144 hydroxide (TMAH, Merck, Germany). The cleaned precipitate, still wet, was re-diluted
145 up to 10 g/L in water at pH ~ 10 for nanoplatelets surface functionalization(Core-shell
146 formation).

147

148 2.2 Build-up of the LbL shell on β -Ni(OH)₂ nanoplatelets

149 The procedure for the elaboration of self-assembled multilayers has consisted in the
150 successive and alternate deposition of polyelectrolytes of opposite charge on a flat
151 (wafer) or colloidal substrate. The polyelectrolytes used for the functionalization of β -
152 Ni(OH)₂ nanoplatelets were Branched and linear Polyethylenimines (B-PEI, Mw 25000,
153 and L-PEI, Mw 2000, respectively, Sigma Aldrich, Germany) and Polyacrylic Acid (PAA in
154 a 63 wt.% solution in water, Mw 2000, Acros Organics, USA).

155 All multilayers were formed using the LbL technique according to the procedure
156 described as follow: the formation of each polyelectrolyte layer was carried out by
157 adsorption of the specific amount of polyelectrolyte which saturates the previous
158 layer. This amount is different for each layer and type of polyelectrolyte (B-PEI, L-PEI or
159 PAA) and it was determined by zeta potential measurements as it will be later

described. After the polyelectrolyte addition, the suspension having a particle concentration of 10 g/L was stirred during a minimum of 2 hours.

Core/shell particles were labelled depending on the number of polyelectrolyte adsorption steps and the type of PEI used (Table 1). Odd numbers correspond to PEI as outer layer.

Table 1. Sample labels

Polyelectrolytes	Number of layer	Labelled
Branched PEI / PAA	1	1B-PEI
	3	3B-PEI
	5	5B-PEI
Linear PEI / PAA	1	1L-PEI
	3	3L-PEI
	5	5L-PEI

To favor the adsorption of the next layer of the polyelectrolyte with opposite charge, the pH value of the suspension was adjusted before each polyelectrolyte addition. A pH value of 8 was selected for the adsorption of B-PEI and L-PEI in order to favor the total/partial protonation of the amino groups (pKa 8.6 for B-PEI and 7.1 for L-PEI), while a pH value of 10 was selected to promote the adsorption of the PAA layer with deprotonated carboxylic groups (pKa 4.2). The pH was adjusted by adding HNO₃ or TMAH and determined with a pH probe (Metrohm AG, Germany).

In all cases, the adsorption of polyelectrolytes onto the β -Ni(OH)₂ nanoplatelets surface at each step of the multilayer build up was evaluated in terms of zeta potential. A Zetasizer Nano ZS (Malvern, UK) was used to measure the electrophoretic mobility of core-shell particles in diluted suspensions (0.1 g/L) and the zeta potential was calculated using the Smoluchowski relation.

To evaluate the interaction between the two couples of polyelectrolytes and thus the formation of the multilayer, optical fixed-angle reflectometry was used as complementary analysis. For all experiments, the reflectometry measurements started with the injection of DI-water free of polyelectrolyte during 2-6 min. The pH value of the water was adjusted to 10 to induce the negative charge on the surface of the oxidized silicon substrate. Then it continued with the addition of the cationic polyelectrolyte (L-PEI or B-PEI) solution (first layer) and subsequently the PAA solution

188 (second layer), and so on. For reflectometry experiments, the polyelectrolyte solutions
189 were prepared at 0.1g/L at pH 8 and 10 for B-PEI/L-PEI and PAA, respectively, and were
190 injected during 10 min. No rinsing was made between each adsorption step. The
191 influence of the size and the type of counterions of the basic specie was also studied
192 by adding two different bases: NaOH or TMAH.

193 Figure 1a shows a diagram of the home-made equipment. The reflectometry is based
194 on the measurement of the relative change of parallel (p) and perpendicular (s) light
195 intensities of a polarized reflected laser beam when polyelectrolyte adsorbed onto the
196 substrate (oxidized silicon wafer). The relative variation of the reflectometry output S -
197 $S_0/S_0=\Delta S/S_0$ is based on the combination of the outputs when the substrate is free of
198 polymer (S_0) and when a polymer layer is adsorbed (S). The variation of the
199 reflectometry output is due to the change of the thickness and/or refractive index of
200 the deposited film and is linked to the adsorbed polyelectrolyte amount^{36,37}.

201

202 2.2 EPD of core/shell β -Ni(OH)₂ nanoplatelets

203 All suspensions used in EPD process were prepared following a one-pot route to avoid
204 nanoparticles agglomeration during drying. The modification of β -Ni(OH)₂ particles
205 with the polyelectrolyte multilayers were carried out in a 10 g/L aqueous suspension
206 and then suspensions were diluted in ethanol with a volume ratio of 19:1 of EtOH:DI-
207 Water to a concentration of 0.25 g/L of solid contents. We demonstrated in a previous
208 work that this is an appropriated solvent for EPD, that stepped up the deposition of
209 homogeneous β -Ni(OH)₂ films³⁵.

210 Electrophoretic deposition experiments were performed at room temperature using a
211 home-made apparatus, figure 1b, equipped with a laminar flow cell comprising three
212 electrodes and a video setup, which was formerly described elsewhere²⁸.

213 The particle suspension flows in a rectangular channel between two parallel
214 poly(methyl methacrylate) plates (PMMA). Steady flow was maintained by gravity
215 between two vessels. A peristaltic pump allowed recycling in order to maintain a
216 constant liquid level, therefore the particles move several times through the cell. In
217 one plate is inserted a removable cathode plug comprising a circular nickel electrode
218 acting as the working electrode and a treated silver wire serving as the reference
219 electrode (Ag/AgCl). The other facing plate contains a conductive glass coated with a

tin oxide film acting both as a window and the counter electrode. The electric potential was applied using a potentiostat–galvanostat PAR model 363. The optical and measurement setup, allowing observation of 1–100 μm particles between the two facing electrodes, contained a microscope (Olympus BH2-UMA) equipped with a 20 $\times$ long working distance objective, a 3.3 $\times$ intermediate lens, a video tube, a lighting system, a CCD camera(DXC-ISIP, Sony), an image monitor (SONY PVM 1450). An image analysis package was used for image capture and analysis. The coated $\text{Ni}(\text{OH})_2$ particles were electrodeposited onto metallic nickel disks having a diameter of 1.2 cm. Just before electrophoretic deposition experiment, the electrodes were mechanically polished with SiC emery paper and then with diamond slurry down to 1 μm . Between each step, electrodes were sonicated in ethanol. The deposition experiments were performed at room temperature and at a constant flow rate (2 mL/min). The potential and the time of application were -5V and -20V (versus the reference electrode) and from 1 to 10 min.

Also, the morphology and shape of the particles and the film microstructure were examined by a field emission scanning electron microscope (FE-SEM Hitachi S-4700, Japan). Finally, the percentages of surface coverage of the electrodes were calculated from the analysis of the micrographs using the Image J software.

238

239 3. Results and Discussion

240 3.1. XRD and SEM characterization of $\beta\text{-Ni}(\text{OH})_2$ nanoplatelets

Figure 2a shows the XRD pattern of the synthesized $\beta\text{-Ni}(\text{OH})_2$ powders. The diffraction peaks were indexed according to the XRD pattern (JCPDS Card file No 140117) as the hexagonal phase of the polymorph beta ($\beta\text{-Ni}(\text{OH})_2$) of $\text{Ni}(\text{OH})_2$. Crystallite size calculated from the Scherrer equation was 7.7 nm and unit cell dimensions were $a = 0.303\text{ nm}$ and $c = 0.450\text{ nm}$. Morphology and size of the as-synthesized particles is shown in the FE-SEM micrographs in figure 2b. Aggregates of orientated two-dimensional nanoparticles (circled by white and dash lines) were observed after a washing process several times with DI water at pH 10. The detail of the micrograph showed that each aggregate of 400-500 nm was formed by nanoplatelets of 100-150 nm in diameter and 15-20nm in thickness. Moreover nanoplatelets can be composed

of several crystalline regions (of 7.7 nm) such as the β -Ni(OH)₂ powder obtained under similar US conditions in previous works³⁸.

3.2. Polyelectrolytes Multilayer build up on flat substrates.

Before functionalization of the particle surface by applying LbL technique, reflectometry analyses were carried out to study the growth of the (PEI/PAA) multilayers. Although all reflectometry experiments were made onto an oxidized silicon wafer, this method was used to study the effect of pH (8 and 10) and the size and the type of ions of the basic species (NaOH and TMAH) on the growth of multilayer films. Figure 3 presents the results of the successive (PEI/PAA) depositions from 0.1 g/L polyelectrolyte solutions in DI water: (L-PEI/PAA) multilayers built up with polyelectrolyte solutions having the same pH (pH 10 adjusted with NaOH or TMAH and pH 8 adjusted with TMAH). The last two reflectometry experiments were performed under similar conditions that the β -Ni(OH)₂ modification to simulate and to compare the growth of the multilayer on an oxidized silicon wafer and on β -Ni(OH)₂ nanoplatelets. Results are shown on Figures 3d and 3e. In all cases, the addition of a new layer (either polycation or polyanion) produced an increase of the reflectometry output, which indicated the build-up of the multilayer. In the figure 3b, where the pH of the polyelectrolyte solutions was adjusted to 10 with TMAH, the reflectometry output presented a higher variation than in plots in figures 3a and 3c, where the pH was adjusted to 10 with NaOH or to 8 with TMAH, respectively. The changes of the reflectometry output can be produced by the variations of the refractive index (n) of each polyelectrolyte solution. Therefore the refractive index value of $n=1.5290\pm0.001$ for PEI and $n=1.5080\pm0.001$ for PAA solutions were measured and no significant difference was found for polyelectrolyte solutions taking account of both the two pHs values (8 and 10) and the two types of basic species (NaOH and TMAH). Thus the variations in the obtained outputs were due to the adsorbed amount and not to a change of the refractive index of the solution output.

Following the general trend of the three outputs, it is very important to notice that the addition of both types of polyelectrolytes does not form common rectangular steps, but rather peaks (overshoots) whose the origin is still debated in the literature

283 between a change in the thickness of the polyelectrolyte multilayer due to a
284 rearrangement of the functional groups or a partial desorption of them^{39,40}. The
285 variation of the pH values promotes changes on the ionization state of PEI and PAA
286 and consequently in the conformation of the polymer chains ("tail" or "train") on the
287 particle surface^{11,12}. The constant value of zeta potential after each addition, shown in
288 figure 4f, corroborates a change of conformation of polyelectrolytes with probably an
289 exchange of ions instead of the possible polyelectrolyte desorption.

290 According to this, we can conclude that the optical fixed-angle reflectometry
291 confirmed qualitatively the growth of polyelectrolyte multilayers formed by the
292 couples B-PEI/PAA and L-PEI/PAA onto an oxidized silicon substrate.

293

294 3.3. Polyelectrolytes Multilayers Adsorption onto β -Ni(OH)₂ nanoplatelets

295

296 Additionally, to confirm the polyelectrolytes self-assembly in a multilayer shell system
297 onto β -Ni(OH)₂ nanoplatelets, complementary zeta potential measurements were
298 carried out. In a previous work³⁵, the colloidal stability of β -Ni(OH)₂ nanoplatelets was
299 studied resulting that uncovered nanoparticles had a zeta potential value of about -20
300 mV and were well dispersed in aqueous medium at pH 10. Consequently, β -Ni(OH)₂
301 nanoplatelets were kept in aqueous suspension at pH 10 at room temperature to avoid
302 full drying and agglomeration.

303 In contrast to the qualitative character of the reflectometry analysis, the
304 determination of the evolution of zeta potential with the polyelectrolyte addition
305 allows to quantify the exact concentration of PEI or PAA required to fully cover the
306 surface of the nanoplatelets. The addition of an exact amount of polyelectrolyte to
307 build each layer allows the *in situ* formation of the core-shell nanostructures and their
308 further shaping following an one-pot procedure without any drying or washing
309 intermediate step. Figures 4a-e represent the evolution of the zeta potential as a
310 function of the amount of added polyelectrolytes. In all cases, zeta potential (in
311 absolute value) decreases with the increase of polyelectrolyte concentration. Then,
312 according to the last adsorbed outer layer, a reverse to a positive or negative value is
313 observed up to a maximum value which determines the saturation point and
314 correspond to the amount of polyelectrolyte needed to saturate the previous layer.

Plot in figure 4f shows zeta potential values at the saturation point for each layer (PEI at pH8 and PAA at pH10) in a LbL core-shell structure, while the values of the polyelectrolyte concentrations at the saturation point are summarized in Table 2. The saturation curves of the multilayer made with the pair B-PEI/PAA were reported in a previous work ³². Results are also included in figure 4f and table 2 for comparison.

Table 2. Amount of polyelectrolytes (polyelectrolyte weight/particle weight) and sign of zeta potential after each layer addition

Layer	Charge	pH	% L-PEI/PAA	% B-PEI/PAA ³²
1 (PEI)	+	8	2.5	2.5
2 (PAA)	-	10	5.5	10
3 (PEI)	+	8	9.5	8.5
4 (PAA)	-	10	8.5	7
5 (PEI)	+	8	15	8.5

The L-PEI and B-PEI adsorption for the first layer necessary to reach the saturation point of the core-shell β -Ni(OH)₂ nanoplatelets was the same, 2.5 wt.%. However, from the adsorption of the second layer, a large amount of PAA (10 wt.%) was required to neutralize the positive charge of the first B-PEI layer, while only a 5.5 wt.% of PAA was absorbed in the multilayer built with L-PEI. The B-PEI polycation has a branched conformation and a molecular weight of 25000, so it has a large number of protonated groups (amine) which should be neutralized by the next layer of the polyanion. However, although the greatest length and ionization capacity of B-PEI, its particular stereochemistry ⁴¹ makes that the amount of B-PEI needed in the neutralization of 10 wt.% of PAA was slightly lower than that of the L-PEI used to neutralize the 5.5 wt.% PAA (8.5 wt.% of B-PEI versus 9.5 wt.% of L-PEI). Same effect can be observed in the construction of the fourth PAA and fifth PEI layers. Accordingly, the thickness of the organic shell may be expected to be greater with B-PEI than with the L-PEI, although the zeta potential are similar in both cases (figure 4f). Results demonstrate the LbL build-up by optical fixed-angle reflectometry and that colloidal β -Ni(OH)₂ nanoplatelets were coated by a multilayer shell after the sequential

addition of an exact amount of each polyelectrolyte.. Moreover, it evidences the formation of two kind of inorganic-organic core-shell structures depending on the PEI type (linear or branched).

344

3.4. Effect of Polyelectrolyte Multilayers on EPD process.

346

Following the LbL procedure, different suspensions of as-synthesized β -Ni(OH)₂ nanoplatelets were modified with the multilayers of B-PEI/PAA and L-PEI/PAA (1, 3 and 5 layers). Then core-shell particles were dispersed in EtOH until reaching a final solid loading (C) of 0.25 g/L at a solvent volume ratio of 19:1 (EtOH: DI-Water). Moreover, they were characterized to define the initial conditions of the process. Table 3 summarizes the main electrophoretic parameters (zeta potential (ZP), electrophoretic mobility (μ_e) and conductivity (σ)) of the suspension of as-synthesized β -Ni(OH)₂ nanoplatelets after their surface modification in aqueous media (DI-water) and after the dilution with EtOH (EtOH:DI-water (19:1)

356

Table 3. Zeta potential (ZP), Electrophoretic mobility (μ_e) and conductivity (σ) of the β -Ni(OH)₂ nanoplatelets after their surface modification in aqueous suspension and after dilution in EtOH:DI-water

360

Sample	DI-water			EtOH:DI-water (19:1)		
	ZP (mV) $\epsilon = \pm 5$	μ_e ($\times 10^{-4}$ cm ² V ⁻¹ s ⁻¹) $\epsilon = \pm 0.2$	σ (μ S/cm ²) $\epsilon = \pm 5$	ZP (mV) $\epsilon = \pm 5$	μ_e ($\times 10^{-4}$ cm ² V ⁻¹ s ⁻¹) $\epsilon = \pm 0.2$	σ (μ S/cm ²) $\epsilon = \pm 5$
1L-PEI/PAA	30	2.10	127	29	0.58	9
3L-PEI/PAA	30	2.16	125	30	0.62	20
5L-PEI/PAA	22	1.56	126	30	0.61	47
1B-PEI/PAA	41	2.33	93	38	1.45	<10
3B-PEI/PAA	29	2.03	45	30	0.80	<10
5B-PEI/PAA	15	1.65	46	36	0.71	<10

361

362

The dilution of suspensions in an organic media like ethanol not only reduces the water hydrolysis during EPD process (> -4V) but both electrophoretic mobility and conductivity also decrease due to the lower polarity of the EtOH.

According to these values, the zeta potential values in the organic solvent are similar for all suspensions. However there are differences of electrophoretic mobility and

367

conductivity values between particles functionalized with linear or branched PEI, which could affect the deposition phenomena.

Suspensions diluted in ethanol were used to study the kinetics of the EPD process with nanoparticles superficially modified with a polyelectrolyte multilayer. The β -Ni(OH)₂ coatings were shaped by EPD on metallic Ni substrates applying an electric field of -5 and -20V for times up to 600 s. EPD tests were performed under potentiostatic conditions in order to neglect differences in conductivity between formulated suspensions. The deposition kinetic was studied applying the general model proposed by Sarkar and Nicholson³³ where the exponential growth of the coatings is related to the characteristic time, τ through the equations 1 and 2.

$$m = m_0(1 - e^{-\tau/t}) \quad (1)$$

$$m = m_0(1 - e^{-\tau/t}) \quad (2)$$

where m is the deposited mass (g), $m_0 = \frac{V}{f\mu_e SE}$ total mass (g), t is the time (s), τ is the characteristic time (s), V is the geometric volume of the electrophoretic cell (7.27 ml), f is the sticking factor or the probability of the particles to be deposited on the substrate, μ_e is the electrophoretic mobility ($\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$), S is the surface (1.13 cm^2) and E is the electric field (100 V cm^{-1}). This value corresponds to the applied voltage (-20V) in the EPD cell. Once the EPD conditions were fixed, the characteristic time (τ) determines the speed of the process and it can be calculated assuming a 100% deposition yield ($f = 1$). Table 4 summarizes the values of the electrophoretic mobility of the suspensions and the characteristic time of their EPD kinetics.

390

391 **Table 4. Electrophoretic Mobility and Characteristic Time values of the suspensions corresponding to**
392 **the theoretical approximation.**

	1L-PEI	3L-PEI	5L-PEI	1B-PEI	3B-PEI	5B-PEI
$\mu_e (\times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1})$ $\varepsilon = \pm 0.2$	0.58	0.62	0.61	1.45	0.80	0.71
$\tau (\text{s})$	1103	1044	1055	443	803	905

393

394 The theoretical values of characteristic time range from 1103 to 1044 s for the
395 suspensions modified with 1, 3 and 5 layers of B-PEI/PAA and from 905 to 443 s for the

suspensions modified with 1, 3 and 5 layers of L-PEI/PAA. Using these data, the theoretical curves of the EPD kinetics for suspension modified with 1, 3 and 5 shells were calculated and plotted in figure 5. It is important to note that the lower is the characteristic time the faster is the deposition process. Therefore the shape of the theoretical curves and their associated electrophoretic mobility values (table 3) indicate that the kinetics of the suspensions dispersed by the addition of the couple B-PEI/PAA is faster than that of the suspensions dispersed with the couple L-PEI/PAA. This effect could be also expected from differences in the conductivities of the suspensions (table 3). Moreover, differences in the electrophoretic mobility of the core-shell structures built with B-PEI result on a strong variation of the EPD kinetics with the number of layers. Contrarily, from the point of view of the movement of particles under the influence of the applied electric field, the increase of layers for the L-PEI based core-shell systems has no influence in the kinetics of deposition.

Figure 5. Theoretical Approximation of the EPD kinetics for different suspensions of modified β -Ni(OH)₂ nanoplatelets deposited on a Ni foil substrate.

The deposition of particles in EPD consists in the movement of particles toward the electrode of the opposite charge and their deposition onto the electrode. The particle transport is governed by both hydrodynamic and electrophoretic forces which determine their flux toward the electrode. Moreover, those forces also interfere over

416 the surface coverage. The deposition of particles is controlled by the inter-particle and
 417 particle-electrode interactions comprising changes in the polyelectrolyte configuration
 418 and ionization, the electrostatic double-layer constrain and finally the ability of
 419 overtake the dispersion forces described by the DLVO theory³³. However, specific
 420 interactions such as electro-hydrodynamic, osmotic, hydrophobic and hydration forces
 421 plays a main role in the particle arrangement^{21,42}. So inter-particle networks modify
 422 the particle deposition and impact the film morphology. To understand the effect of
 423 the polyelectrolyte multilayer on the last step of the EPD process, the image analyses
 424 of the pictures taken in situ during the coating were carried out. As an example, Figure
 425 6 shows pictures of 3B-PEI and 3L-PEI layers after 600s of deposition.
 426 Figure 7 represents the surface coverage, defined as the fraction of electrode surface
 427 area occupied by deposited particles as a function of time at two different applied
 428 voltages of -5 and -20 V, flow rate of 2 ml/min and for 1 layer (Figure 7a) and 3 layers
 429 (Figure 7b) core-shell particles.
 430 Several authors have described previously the occurrence of adsorption regime in
 431 barrier-less transport conditions was linear at the beginning of EPD process³⁰. That
 432 means, all particles that reach the electrode surface remain attached and thus, the
 433 deposition rates are only controlled by transport conditions and by attractive particle-
 434 surface interactions. In our systems, the deposition rate was considered as a linear
 435 function of time up to 4 minutes deposition, achieving coverages up to 60%. The
 436 linearity is maintained for shorter times that in systems described in other works²⁸⁻³⁰,
 437 but the percentages of covering are beyond the values reported in the literature. So,
 438 results indicate that we have adjusted EPD conditions for faster systems than those
 439 previously reported, where deposition maintains its electrokinetic dependence for
 440 wider coverages. But also the core-shell particle deposition is strongly affected by the
 441 type of cationic polyelectrolyte (linear or branched PEI) and the number of the
 442 polyelectrolyte layers. Since the colloidal conditions of the suspensions (determined by
 443 zeta potential values of particles with an odd outer layer, figure 4f) set a similar
 444 electrostatic barrier, deposition depends on the steric interaction among core-shell
 445 particles.
 446 Indeed for deposition of one-layer core-shell particles (figure 7a) under both applied
 447 electric fields the percentage of surface coverage by 1B-PEI particles was higher than

the percentage corresponding to nanoplatelets modified with 1L-PEI, as it is predicted by the theoretical curves and zeta potential values (table 2 and figure 5). Moreover the 3L-PEI system deposits faster than the 3B-PEI core-shell particles for the strongest electric conditions (-20 V) and leads to a higher surface coverage. However, for 3 layers core-shell particles (figure 7b) there is no deposition under the lower electric field (-5 V). That corroborates the influence of other factors than electrokinetic forces (matched by the stabilization system and the electrophoretic mobility) acting over deposition in the 3 layers systems. Thus, we can conclude that when suspensions are prepared with -3 layers modified particles, the effect of the length of the cationic polyelectrolyte predominates over the deposition.

To determine the effect of the polycation length, we considered the normalized flux calculated from the coverage parameters. The initial particle flux $j_{\perp}$ (number of deposited particles per unit area per unit time) and the normalized particle flux $\bar{j}$ (particle flux normalized by the bulk concentration) were determined directly as:

$$j_{\perp} = \frac{N_s}{t} = \frac{1}{\pi a^2} \frac{\theta}{t} \quad (3)$$

$$\bar{j} = \frac{j_{\perp}}{n_b} \quad (4)$$

where, N_s is the number of particles deposited on an unit electrode area, t is the time, a is the particle radius, θ is the surface coverage ($\theta = \pi a^2 N_s$), and n_b is the particle concentration in the bulk.

Figure 8 shows the dependence of the normal particle flux on the electrophoretic mobility of core-shells (1L-PEI, 3L-PEI, 3B-PEI and 1B-PEI) for different electric fields (-5 V and -20 V) at a similar deposition time 240 s.

The normalized particle flux was lower when the applied electric field was lower (-5 V) and even close to zero for 3 layers core-shell particles. For higher electric fields (-20 V) flux values range was from 8 and 15 $\mu\text{m/s}$. In all cases, flux doesn't follow any trend with the evolution of the electrophoretic mobility, being the flux of the 3B-PEI core-shells lower than that of the 3L-PEI system. According to these data, the steric impediment provided by the branched PEI chain seems to be higher than that of the linear chain in the 3-layers system. However, when electric forces are higher enough to overtake the electrosteric barrier, the 3L-PEI and 1B-PEI core-shells result in the fastest systems.

479

480

481 A general view of the coating surface of 1L-PEI and 3L-PEI core-shells at -20V is shown
482 at the FE-SEM micrographs in Figure 9a and 9b, respectively. Those micrographs
483 evidence the coverage of the Ni substrate by a dense and well packing structure of β -
484 $\text{Ni}(\text{OH})_2$ nanoplatelets, displaying a more disordered arrangement in the 3 layers core-
485 shell particle films. In order to better analyze the organization and the packing level of
486 β - $\text{Ni}(\text{OH})_2$ nanoplatelets at the electrode surface, coatings were also examined at
487 higher magnifications. Figure 9c and 9d display a detail of the nanoplatelets arrays at
488 the 1L-PEI and 3L-PEI films, respectively, supporting significant differences in the
489 orientation of nanoplatelets. An increasing disorder is evident when the number of
490 layers of polyelectrolyte increases, as corroborate the detail of the microstructures of
491 the 1B-PEI (E) and 3B-PEI (f) films. In view of the microstructural analysis, particles of
492 the samples 1L-PEI and 1B-PEI presented a flat arrangement, where nanoplatelets lied
493 parallel to the substrate, while particles of the 3L-PEI and 3B-PEI films showed higher
494 disorder degree, shaping a denser structure with the linear polycation. Details of the
495 different nanoplatelets arrangements evidence the influence of the steric barrier
496 promoted by organic shells on the electrophoretic deposition of β - $\text{Ni}(\text{OH})_2$
497 nanoplatelets.

498 4. Conclusions

499 Two types of polyelectrolyte multilayers, B-PEI/PAA and L-PEI/PAA, were successfully
500 assembled in a LbL system onto the surface of β - $\text{Ni}(\text{OH})_2$ nanoparticles with platelet
501 morphology, resulting in different organic/inorganic core-shell nanostructures. The
502 formation of multilayers was confirmed by zeta potential and optical angle
503 reflectometry measurements. The characteristics of the PEI chain (linear or branched)
504 determine the exact amount of each polyelectrolyte needed to build the multilayer
505 system, leading to a higher concentration of polyelectrolytes when L-PEI was used. As
506 consequence of the multilayer formation, the EPD parameters of core-shell structures
507 differ. According to the electrokinetic model the deposition of the suspensions of B-PEI
508 core-shells was faster than that of the L-PEI structures.

509 In all cases, the obtained surface coverage are beyond the values described in the

510 literature for analogous systems. The normalized flux varies between 8 and 15 $\mu\text{m}\cdot\text{s}^{-1}$
511 for the different polyelectrolyte multilayers.
512 From the data of coverage, the core-shell **particle** flux and deposition **are** mainly
513 governed by the interactions among particles and not **only** by their electrophoretic
514 mobility. Moreover, it is important to notice that the effect of the length of the
515 cationic polyelectrolyte **(linear or branched PEI)** strongly determines not only the
516 kinetics but also the nanoplatelets arrangement.

517

518 **Acknowledges**

519 The authors acknowledge the support to the European Ceramic Society through JECS
520 Trust funding. Also they acknowledge the support to the project S2013/MIT-2862 and
521 MAT2015-70780-C4-1.

522

523 **References**

- 524 1. G. R. Patzke, Y. Zhou, R. Kontic, and F. Conrad, *Angew. Chemie-International Ed.*, 50,
525 826–859 (2011).
- 526 2. L. Qi, *Coord. Chem. Rev.*, 254, 1054–1071 (2010)
- 527 3. H. Goesmann and C. Feldmann, *Angew. Chemie International Ed.*, 49, 1362–1395
528 (2010).
- 529 4. J. J. Licari, *Coating materials for electronic applications : polymers, processes,*
530 *reliability, testing*, p. 547, Noyes Publications, (2003).
- 531 5. Y.-G. Guo, J.-S. Hu, and L.-J. Wan, *Adv. Mater.*, 20, 2878–2887 (2008).
- 532 6. R. A. Caruso and M. Antonietti, *Chem. Mater.*, 13, 3272–3282 (2001).
- 533 7. A. A. Abrashov, N. S. Grigoryan, T. A. Vagramyan, A. V Kolesnikov, and D. Y. Zhilenko,
534 *Glas. Ceram.*, 71, 392–395 (2015).
- 535 8. C. D. Lokhande, D. P. Dubal, and O.-S. Joo, *Curr. Appl. Phys.*, 11, 255–270 (2011).
- 536 9. J. Yan et al., *Adv. Funct. Mater.*, 22, 2632–2641 (2012).
- 537 10. C. Yuan, X. Zhang, L. Su, B. Gao, and L. Shen, *J. Mater. Chem.*, 19, 5772–5777
538 (2009).
- 539 11. W. M. Sigmund, N. S. Bell, and L. Bergstrom, *J. Am. Ceram. Soc.*, 83, 1557–1574
540 (2000).

- 541 12. J. A. Lewis, *J. Am. Ceram. Soc.*, 83, 2341–2359 (2000).
- 542 13. K. Ariga, Q. Ji, W. Nakanishi, and J. P. Hill, *J. Inorg. Organomet. Polym. Mater.*, 25,
543 466–479 (2015).
- 544 14. J. Borges, L. C. Rodrigues, R. L. Reis, and J. F. Mano, *Adv. Funct. Mater.*, 24, 5624–
545 5648 (2014).
- 546 15. Y. Wang, A. S. Angelatos, and F. Caruso, *Chem. Mater.*, 20, 848–858 (2008).
- 547 16. Y.-H. Yang, M. Haile, Y. T. Park, F. A. Malek, and J. C. Grunlan, *Macromolecules*, 44,
548 1450–1459 (2011).
- 549 17. Y. Song, P. Tzeng, and J. C. Grunlan, *Macromol. Rapid Commun.*, 37, 963–968
550 (2016).
- 551 18. M. Haile, S. Fomete, I. D. Lopez, and J. C. Grunlan, *J. Mater. Sci.*, 51, 375–381
552 (2016).
- 553 19. L. Besra and M. Liu, *Prog. Mater. Sci.*, 52, 1–61 (2007).
- 554 20. I. Corni, M. P. Ryan, and A. R. Boccaccini, *J. Eur. Ceram. Soc.*, 28, 1353–1367 (2008).
- 555 21. B. Ferrari and R. Moreno, *J. Eur. Ceram. Soc.*, 30, 1069–1078 (2010).
- 556 22. Z. Adamczyk, B. Siwek, and L. Szyk, *J. Colloid Interface Sci.*, 174, 130–141 (1995)
- 557 23. M. Nattich-Rak, Z. Adamczyk, and M. Kujda, *Colloids Surfaces B Biointerfaces*, 137,
558 176–182 (2016)
- 559 24. M. Zembala, Z. Adamczyk, and P. Warszynski, *Colloids Surfaces A-Physicochemical*
560 *Eng. Asp.*, 195, 3–15 (2001).
- 561 25. M. Ocwieja, M. Morga, and Z. Adamczyk, *J. Nanoparticle Res.*, 15 (2013).
- 562 26. M. Semmler, J. Rička, and M. Borkovec, *Colloids Surfaces A Physicochem. Eng. Asp.*,
563 165, 79–93 (2000)
- 564 27. A. Hosseini et al., *Fuel*, 178, 234–242 (2016).
- 565 28. C. Pignolet, C. Filiatre, and A. Foissy, *Langmuir*, 24, 10181–10186 (2008).
- 566 29. C. Pignolet, M. Euvrard, A. Foissy, and C. Filiatre, *J. Colloid Interface Sci.*, 349, 41–48
567 (2010).
- 568 30. C. Filiatre, C. Pignolet, A. Foissy, M. Zembala, and P. Warszynski, *Colloids Surfaces*
569 *A-Physicochemical Eng. Asp.*, 222, 55–63 (2003).
- 570 31. C. Dange-Delbaere, C. C. Buron, M. Euvrard, and C. Filiâtre, *Colloids Surfaces A*
571 *Physicochem. Eng. Asp.*, 493, 1–8 (2016)
- 572 32. Z. Gonzalez, B. Ferrari, A. J. Sanchez-Herencia, A. Caballero, and J. Morales,
573 *Electrochim. Acta*, 211, 110–118 (2016)

- 574 33. P. Sarkar and P. S. Nicholson, *J. Am. Ceram. Soc.*, 79, 1987–2002 (1996).
- 575 34. S. Cabanas-Polo, K. S. Suslick, and A. J. Sanchez-Herencia, *Ultrason. Sonochem.*, 18,
576 901–906 (2011).
- 577 35. Z. Gonzalez, B. Ferrari, A. J. Sanchez-Herencia, A. Caballero, and J. Morales, *J.*
578 *Electrochem. Soc.*, 162, D3001–D3012 (2015).
- 579 36. D. Kovacevic, S. van der Burgh, A. de Keizer, and M. A. C. Stuart, *Langmuir*, 18,
580 5607–5612 (2002).
- 581 37. C. C. Buron, F. Membrey, C. Filiatre, and A. Foissy, *Colloids Surfaces A-*
582 *Physicochemical Eng. Asp.*, 289, 163–171 (2006).
- 583 38. S. Cabanas-Polo et al., *J. Eur. Ceram. Soc.*, 35, 573–584 (2015).
- 584 39. L. Wagberg, G. Pettersson, and S. Notley, *J. Colloid Interface Sci.*, 274, 480–488
585 (2004).
- 586 40. C. C. Buron and C. Filiatre, *J. Colloid Interface Sci.*, 413, 147–153 (2014).
- 587 41. M. Verde, M. Peiteado, A. C. Caballero, M. Villegas, and B. Ferrari, *J. Colloid*
588 *Interface Sci.*, 373, 27–33 (2012)
- 589 42. B. Giera, L. A. Zepeda-Ruiz, A. J. Pascall, and T. H. Weisgraber, *Langmuir*, 33, 652–
590 661 (2017).
- 591

a) **b)**

Figure Captions

Figure 1. Optical fixed-angle reflectometer (SP stagnation point, P prism, $D_{1,2}$ photodiodes and CS polarizing beamsplitter cube) and b) Schematic diagram of the EPD cell (upper view).

Figure 2. DRX analysis (a) and FESEM images (b) of the as-synthesized $\text{Ni}(\text{OH})_2$

Figure 3. Reflectometry outputs of the successive depositions of PEI/PAA layers from 0.1 g/L polyelectrolyte solutions in DI water, for the linear PEI and PAA (L-PEI/PAA) multilayer system at pH 10 adding NaOH (a) or TMAH (b), at pH 8 adding TMAH (c), L-PEI at pH 8 (TMAH) and PAA at pH 10 (TMAH) (d) and B-PEI at pH 8 (TMAH) and PAA at pH 10 (TMAH) (e)

Figure 4. Zeta Potential of $\beta\text{-Ni}(\text{OH})_2$ nanoplatelets as a function of the amount of added polyelectrolytes: plots in (a), (c) and (e) correspond to the first, third and fifth layers of adsorbed L-PEI, and plots in (b) and (d) correspond to the second and fourth layers of adsorbed PAA. Plot in (f) corresponds to zeta potential as a function of number of adsorbed polyelectrolytes layers (L-PEI or B-PEI at pH8/ PAA at pH10) in LbL core-shell structures.

Figure 5. Theoretical Approximation of the EPD kinetics for different suspensions of modified $\beta\text{-Ni}(\text{OH})_2$ nanoplatelets deposited on a Ni foil substrate.

Figure 6. Pictures of the 3L-PEI and 3B-PEI coatings after 600 s for an applied voltage of -20 V

Figure 7. Evolution of the surface coverage of $\beta\text{-Ni}(\text{OH})_2$ core-shells (B-PEI/PAA and L-PEI/PAA) of Ni electrodes, observed under laminar flow at two applied voltages (-5V and -20V) and a fluid flow of 2ml/min, for (a) 1 layer core-shells and (b) 3 layers core-shells.

Figure 8. Dependence of the normal particle flux on the electrophoretic mobility of core-shell particles at (a) different voltages (-5 and -20 V) at a similar deposition time of 240 s

Figure 9. FE-SEM images of a general view of the 1L-PEI (a) and 3L-PEI (b) coatings out of the flow cell and images of the detail of the nanoplatelets arrangement for 1L-PEI (c) and 3L-PEI (d) coatings compared with that of the 1B-PEI (e) and 3B-PEI (f) films.