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Authors: Z. Gonzalez, J. Yus, A. Caballero, J. Morales, A.J. Sanchez-Herencia, B. Ferrari

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Electrochemical performance of pseudo-capacitor electrodes fabricated by Electrophoretic Deposition inducing Ni(OH)₂ nanoplatelets agglomeration by Layer-by-Layer

Z. Gonzalez¹, J. Yus¹, A. Caballero² and J. Morales², A.J. Sanchez-Herencia¹, B. Ferrari^{1*}

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

²I.U.R Fine Chemistry and Nanochemistry. Inorganic Chemistry and Chemical Engineering Department. University of Córdoba, Córdoba. Spain.

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

Abstract

The electrochemical behaviour of ceramic semiconductors not only depends on the characteristics of the electroactive material but also on the processing method, the nanoparticles arrangement and the consolidation degree of the formed microstructure. In this sense, the use of nanoparticles with plane morphologies (disc, platelets, etc.) results interesting due to the formation of conduction pathways produced as a consequence of their laminar structures. Electrophoretic Deposition (EPD) is a shaping methodology which allows achieving high degrees in nanoplatelets packing by controlling their alignment during the coating process specifically over 3D substrates. In this work, we have studied the effect of a moderate nanoplatelets

agglomeration, by tuning their surfaces with a polyelectrolyte multilayer following a Layer-by-Layer (LbL) methodology and fixing the electric conditions of the EPD process. Overcoming the destructive effects of the full agglomeration of nanoplatelets, NiO films with a stable and extremely open macroporous structure were processed to coat Ni foams, improving the capacitive performance of pseudocapacitors leading to values of specific capacitances of 650 F/g. Results collected in this work also evidence that an efficient ordering and orientation of nanoplatelets in EPD mainly depends on tuning the suspension parameters (solid contents, conductivity, electrophoretic mobility, etc.) to avoid the massive flux and interactions among interparticles and electrohydrodynamic forces, as well as the interference of collateral electrode phenomena.

Keywords: Nanoplatelets, Layer by Layer, Colloidal Processing, Electrophoretic Deposition, Ni-based materials and Pseudocapacitors

1. Introduction

Among a large variety of nonspherical colloids, nanodiscs or nanoplatelets are particularly interesting as they enable the bottom-up assembly of layered nanocomposites, which enhances the ionic/electronic conduction throughout the formation of crystallographic pathways, or combines unmatched strength and toughness in laminar structures. Advances in nanoplatelets applications imply mastering their manipulation, during their assembly, orientation, packing, and the film deposition [1]. In these structures, the spontaneous organization of nanoentities is the key challenge. The nanosheets of graphite and graphene [2,3], hydroxides and oxides [4,5], chalcogenides [1] or metallic nanoclusters [6], have a tendency to vertically stack in suspension, forming aggregates, due to strong Van der Waals interactions between

the basal planes of their lattices. Dissimilar surface charge density can be also used to force nanoplatelets arrangement by a layer-by-layer strategy (LbL, i.e. alternating negatively charged nanosheets and cationic polyelectrolytes), or their reorientation in a magnetic or electric field. Then the formulation of stable dispersions of nanoplatelets can be used as slurries or inks to prepare tailored thin films by drop casting, inkjet printing, or electrophoretic deposition (EPD) [7].

In the EPD process, charged nanoparticles move toward the electrode with the opposite charge under the influence of an electric field, and deposit forming a compact film. The EPD behaviour of a large variety of nanoplatelets in nature and dimensions was studied during the last decade for different applications (table 1). An example are the LbL assembly of alternate modified gibbsite nanoplatelets (100-200 nm in diameter) and polyelectrolyte multilayers, where the shaped smooth surfaces play a crucial role in the mechanical properties of the final lamellar structure [8] or the nanoplatelets alignment leads to optically transparent and flexible coatings [9]. In these works, Lin et al. [8][10] demonstrated how gibbsite can be oriented during EPD by the particular distribution of charges in their surfaces and edges, when they are electrostatically stabilised at pH 7 in a mixture of H₂O and EtOH. Further works of the same authors demonstrate that modified gibbsite-silica stabilised by the adsorption of high molecular weight Polyethylenimine (PEI) leads to crack-free coatings, but simultaneously nanoplatelets preferential alignment is slightly deteriorated. Those results suggest that the branched PEI molecule acts as flocculant disturbing the nanoplatelets ordering.

In a lower range of particle size [11,12,13], ZnO-based films made on aligned nanoparticles (20-35 nm in diameter) leads to high packing green density and room

transparency even previously to the sintering process [12]. In those publications, the difference in charge of ZnO basal planes determines the massive adsorption of the stabilizer (branched PEI) in one side of the nanoflake, setting their hydrodynamic behaviour and then fashioning deposition. In a low concentrated suspension (1 g/L), hydrodynamic, polarization and also interparticles forces govern the arrangement of flake-like dispersed nanoparticles at the electrode. When the solid concentration increases, a massive arrival of particles prevents this ordering effect. This clearly opens the possibility of controlling the nanoplatelets orientation by EPD tuning their electrokinetics by designing the stabilization system.

The mechanisms of the deposit formation of graphene sheets have been also recently described in the literature. Most of the studies describe the stabilization of graphene by an electrostatic mechanism, and argue that the charge neutralisation is the main cause of the deposit formation [14]. But in the EPD of graphene sheets, side reactions, such as GO reduction, aqueous electrolysis, composite clusters (ceramic or metallic nanoparticles / graphene) have to be considered. Although low solid loadings deserve the graphene sheets alignment [15], even moderately for the deposition of composite clusters (TiO₂ nanoparticles and graphene nanoplatelets) [3], side reactions can disturb the nanoplatelets arrangement.

Finally, most recent studies of the EPD of flakes-like clusters of Au and Cu [6], in the micronic range, also suggest that the key for governing the deposition efficiency is the lateral size of the sheets (the shape factor), inferring that the sheets with a large lateral size possess high electrophoretic mobility and strong face-to-face Van der Waals interactions, thus leading to high deposition efficiencies.

The experimental work described in those manuscripts (table 1) suggests that there

are several reasons that can explain the nanoplatelets alignment during EPD. Depending on the nanoflakes crystallography the charge distribution in basal planes is different than in the flake edges, or even different between both basal planes. That promotes strong Van der Waals interactions among the nanoplatelets and the electrode surface, but also among particles, during deposit growth. From the point of view of dispersion, the mechanism of stabilization (electrostatic/electrosteric) should promote the individual movement of dispersed nanoentities. However, it is necessary to consider that the yield rate prevail over other parameters, and the solid content, the electrophoretic mobility (zeta potential) and the conductivity should be adjusted to avoid the massive arrival of particles to the electrode, and also the premature agglomeration of nanoplatelets that can disturbs the contribution of the osmotic flow of the solvent to the nanoplatelets ordering, predicted by models [16,17,18]. Those premises should be considering in the fabrication by EPD of electrodes and structures based on nanoplatelets stacking.

On the other hand, in energy storage applications, electrodes based on NiO and Ni(OH)₂ nanostructures (3D and 2D nanoparticles) have demonstrated a high performance, especially when metallic foams were used as substrates of the active material or collectors [19, 20]. It is well known the viability of EPD to cover 3D substrates or complex shapes, so the number of publications dealing with the preparation of films by EPD for energy storage and generation devices, and the functionalization of biostructures, is increasing. EPD is also recognised as the available technique to achieve the highest degrees of nanoparticles packing, even using diluted suspensions or sols, where rheological requirements are lowered [21]. Consequently, there are a strong research interest to transfer packing and ordering of the coatings

achieved by EPD in flat substrates, to cover the skeleton of 3D structures, especially scaffolds or metal foams [22,23,24].

In this line, Wu et al. [25] described the EPD of synthetic Ni(OH)_2 nanoplatelets, with a specific surface area of $170 \text{ m}^2/\text{g}$ and a mayor diameters of 50-150 nm, in which nanoplatelets are stabilized by means an electrostatic mechanisms, adding water, acetone and iodine to Isopropyl alcohol. These suspensions had an elevated conductivity (provided by the iodine addition) and zeta potential. Nanoflakes coagulate at the electrode due to the increases of solid content and the neutralisation (reduction) of the ionic double layer, since the pH of the cathode is mainly basic. But significant hydrogen bubbling had also observed. These EPD conditions and an elevated solid loading of the suspension (10 g/L) result on a random deposition of Ni(OH)_2 nanoplatelets, which promotes the formation of the mesoporous microstructures after the coating aneling (300°C - 1h), achieving capacities of 1409 F/g at 1.0 A/g with 92% of capacity retention after 2500 cycles.

Ni(OH)_2 electrodes based on aligned nanoplatelets, and also built by a full yield EPD process on 3D substrates, have been recently reported in the literature for both pseudocapacitors and Li-Batteries (LIBS) [23,26]. Described results demonstrate the viability of the EPD process for replicate the nanoplatelets alignment in a dense and connected microstructure either in flat substrates or in 3D metallic foams. However, in those systems the high packing density limits the capacity performance of Ni(OH)_2 nanoplatelets. Consequently, in order to increases the open meso- and macroporosity in the semiconductor electrodes, evading the loss of connectivity, the surface modification of nanoplatelets by the Layer-by-Layer (LbL) approach has been proposed [22]. Recent results shown that in a porous microstructure shaped by EPD of Ni(OH)_2

modified by LbL adsorption of polyelectrolytes, the direct contact between the electrolyte ions and the semiconductor material is favoured leading to a specific capacitance of 400 F/g at 2 A/g with 100% retention. The use of LbL approach as porous template seemed to be limited to the 3 layers assembly of polyanions and polycations, due to side effect of agglomeration induced by the LbL modification of nanoplatelets, which impedes the homogeneous deposition by EPD.

This work is aimed to overcome this agglomeration effect, by tuning nanoplatelets surface modification and EPD conditions, to coat 3D electrodes with a stable and extremely open mesoporous structure, which will increase the capacitive performance of the pseudocapacitor electrode.

2. Experimental

β -Ni(OH)₂ nanoplatelets were synthesized following the procedure described in a previous work [27] which consist on a chemical precipitation from a salt of nickel, (Ni(NO₃)₂·6H₂O Panreac, Spain), with ammonium hydroxide addition (NH₃, PA 28%, Panreac, Spain). The reaction was carried out at room temperature using a high intensity ultrasonic horn (45 W/cm², 24 kHz, titanium T13 tip, Sonopuls HD 2200, Bandelin Electronic, Germany). The obtained green precipitate was washed several times and re-diluted in a desired amount of distilled water at pH~ 10 (adjusted with tetramethyl ammonium hydroxide, TMAH, Merck, Germany).

The surface of the synthesized nanoplatelets were directly functionalized in the aqueous media with a polyelectrolyte multilayer through LbL self-assembly methodology [22]. The polyelectrolytes used were branched Polyethylenimine (PEI, Mw 25,000, Sigma Aldrich, Germany) for odd layers, and Polyacrylic Acid (PAA in a 63 wt.% solution in water, Mw 2000, Across, USA) for even layers. The built-up of the

multilayer was evaluated in terms of zeta potential by adsorption of the specific amount of polyelectrolyte (PEI or PAA) which saturates either the surface of nanoplatelets in the first layer or the previous layer in the subsequent additions. To favour the adsorption of the following layer of opposite charge, the pH value of the suspension was adjusted. A pH value of 8 was selected for the adsorption of PEI in order to promote the protonation of the amino groups (NH_2^+), while a pH value of 10 was selected to promote the adsorption of the PAA layer with deprotonated carboxyl groups (COO^-). All zeta potential measurements were made with a Zetasizer Nano ZS (Malvern, UK) by laser Doppler velocimetry with suspensions at a concentration value of 0.1 g/L. The pH was adjusted by adding HNO_3 or TMAH and determined with a pH probe (Metrohm AG, Germany).

Cathodic EPD were used as shaping technique to prepare the $\beta\text{-Ni}(\text{OH})_2$ coatings. Considering the negative charge of the work electrode, suspensions of nanoplatelets modified with 1, 3 and 5 layers (charged positively) were only employed. After the polyanion adsorption suspensions was rinsed in order to eliminate the residual precursors, and then $\beta\text{-Ni}(\text{OH})_2$ aqueous suspensions were diluted in ethanol with a volume ratio of 19:1 of EtOH:DI-Water to a concentration of 1 g/L of solid contents. The modified nanoplatelets were deposited onto as-received stainless steel foils (AISI 316L) of 30x20x0.5 mm and onto nickel foams of 15x10x1mm with a specific surface at least 10 times higher than foils. The counter electrode was a platinum foil separated from the work electrode by a distance of 18 mm in the electrophoretic cell. Also, previous to the deposition, substrates (foils and foams) were washed following an industrial cleaning protocol. The experimental EPD kinetic curves were determined under galvanostatic/potenciostatic conditions using a high voltage power source (2611

System SourceMeter, Keithley Instruments Inc., USA), applying current densities from 50 to 100 μA with electric field values from 57 to 71 Vcm^{-1} , at deposition times from 0 to 900 seconds. In addition, the foams were coated under potentiostatic conditions applying a voltage closed to 200 V at times from 60 to 180 seconds in order to achieve the desired amount of deposition.

The most general equation [28] formulated up today was used to determine the theoretical deposition rate:

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

where, m (g), is the deposition mass, m_0 (g), is the initial amount of powder in suspension and τ (s) is the characteristic time, calculated by:

$$\tau = \frac{V}{fSEu_e} \quad \text{eq. 2}$$

where, V (cm^3), is the volume of suspension, S (cm^2), is the conducting area, E (V/cm), is the applied electric field, u_e , ($\text{m}^2/\text{V}\cdot\text{s}$), is the electrophoretic mobility of the nanoparticles, and f ($0 < f < 1$), is the sticking factor. The sticking factor represents the percentage of depositing particles among the arriving particles to the work electrode by electrophoresis.

After EPD, all green coatings were firstly left to dry at room conditions and then they were calcined and sintered in Ar, maintaining a dwell temperature at 325°C for 1 h, with heating and cooling rates of 10°C/min, resulting in consolidated NiO films. Pore size distributions were characterized with scratched powders from NiO films by Mercury Intrusion Porosimetry (MIP) using a Micromeritics AutoPore IV 9510 (USA). X-Ray Diffraction analysis (XRD) were determined with a Siemens D5000 diffractometer (Germany) with a Kristalloflex 710 generator ($K\alpha(\text{Cu})$ $\lambda = 1.5405 \text{ \AA}$; 40 kV; 30 mA; $2\theta =$

5–70), and microstructural observations were examined by field emission scanning electron microscopy (FE-SEM) in an S-4700 microscope (Hitachi, JAPAN).

The capacitive performance of the electrodes was tested under different conditions. For the cyclic voltammetry (CV) measurements carried out with a Potenciostat/Galvanostat Autolab (PGSTAT204), 5 sequential cycles were programmed at scan rates of 2, 5, 10, 20 and 50 mV/s in a potential window of 0.0-0.5 V. A three-electrode configuration consisting of Ni foam/NiO composite as working electrode, Ag/AgCl as reference electrode and a Pt foil as counter electrode, was used. The electrolyte employed was a 1 M KOH aqueous solution. The specific capacitance was determined from the charge value Q , proportional to the integral of the CV curve. Q represents the difference between the area under the charge curve and the area under discharge curve for the upper and lower limits of the potential window. Thus, the specific capacitance was obtained from the equations 3-5.

$$Q = \int I \cdot dt \quad ; \quad t = V/v \quad \text{eq. 3}$$

$$Q = \frac{1}{v} \int I \cdot dV \quad \text{eq. 4}$$

$$C = \frac{Q}{m \cdot \Delta V} \quad ; \quad C = \frac{\int I dV}{v \cdot m \cdot \Delta V} \quad \text{eq. 5}$$

where I is the current (A), t the time(s), V the voltage (V), v the scan rate, C the specific capacitance (F/g), m the mass (g) and Q the charge/discharge value (C).

The charging/discharging measurement was carried out through chronopotentiometry analysis (CP) at a scan rate of 2 A/g using a multichannel potentiostat–galvanostat system (Arbin BT2000). From CP measurements, the specific capacitance value was calculated according to the equation 4:

$$C = \frac{I \cdot \Delta t}{m \cdot \Delta V} \quad \text{eq. 6}$$

where C (F/g) is the specific capacitance, I (A) is the discharge current, Δt (s) is the charging/discharging time, ΔV (V) is the voltage window for discharge, and m (g) is the mass of the active NiO material in the electrode.

3. Results and Discussion

In this work, synthetic β -Ni(OH)₂ nanoplatelets superficially modified by a 1, 3 and 5 LbL organic shells were employed to manipulate the microstructure of the EPD coating. In a previous work, the successful assembling in a LbL system of PEI and PAA polyelectrolytes onto the surface of β -Ni(OH)₂ nanoparticles with platelet morphology was demonstrated [22]. Figure 1a shows schematically the β -Ni(OH)₂ nanoplatelets stacking when precipitates during their synthesis with the aid of ultrasound. This particular kind of synthesis modifies the morphology and crystallography of the nanostructure at several levels [27,29]. The unit cell of nickel hydroxide stacks in a layer by layer structure of OH⁻ and Ni along the c-axis. Ni atoms are superficially exposed when the nanoplatelets are fashioned thus the 2D nanostructures are negatively charge in aqueous media when the synthesis ends (pH > 8.5). So the branched polycation (PEI) added to the nanoplatelet suspension in the post-synthesis medium can be anchored to the hydrated Ni atoms in two different ways [12]. Depending on the pH, long PEI chains can acquire two different features as a function of their ionization state and the density of negative sites at the nanoplatelet surface (Figure 1a). Schematically, the PEI adsorbs onto the β -Ni(OH)₂ surface in a mono- or multipoint way, and due to their particular stereochemistry in each ionisation state, the branched chain adopts both conformations *tail* and *train*, respectively. For pH values higher than 8, we can consider that the PEI chain is completely ionized acquiring

an open and strongly positive charged structure surrounding both faces of the nanoplatelets, while for pH values lower than 10, the PEI chain is multipoint adsorbed and becomes retracted onto the nanoplatelet surface, and then the whole system maintains a slightly positive charge.

Once the first layer of the PEI was formed, pH was accommodated to favour the deposition of the polyanion PAA. In this way, the LbL deposition of layers of PEI and PAA onto the nanoplatelet surfaces leads to an organic/inorganic core-shell nanostructure, where the organic corona will act as template in the further formation of a porous NiO-based structure. The exactly amount of each polyelectrolyte can be determined in terms of zeta potential in an aqueous suspension, and this parameter was used to modify in situ and massively the surface of β -Ni(OH)₂ nanoplatelets after their synthesis. Figure 1b shows the zeta potential curve obtained after each polyanion and polycation addition. The plot also summarizes the amount of each polyelectrolyte added to the suspension in order to achieve a full covering or neutralization of the nanoplatelet surface or the previous polyelectrolyte layer, respectively.

When the nanoplatelet surfaces were massively modified in an aqueous suspension, they were diluted in EtOH up to achieve a EtOH:H₂O ratio of 19:1. Table 2 summarises the parameters which define the electrokinetics behaviour of the modified nanoplatelets or core-shell nanostructures (NH-1LbL, NH-3LbL and NH-5LbL). Suspensions used for EPD have conductivities, σ , below 1 μ S/cm, and the electrophoretic mobility, u_e , of the core-shells ranges from 0.82 to 0.71 $\times 10^{-4}$ cm²/V·s. The only current carriers in the suspension are the core-shells, which optimises the efficiency of the deposition process. Both electrokinetics properties results in different ratios of σ/u_e (from 1.02 to 0.70) and define the movement ability of the core-shells.

In this sense, EPD tests were carried out applying current densities of 40, 30 and 20 $\mu\text{A cm}^{-2}$, for the NH-1LbL (which implies electric fields ranging from 55 and 75 V/cm), and 40, 12 and 8 $\mu\text{A cm}^{-2}$, for the NH-1LbL, NH-3LbL and NH-5LbL core-shells respectively, in order to maintain the electric field between 75-80 V cm^{-1} and consider the decrease of σ/u_e values as the number of layers increases. Considering the starting conditions in the theoretical approach (eq. 1-2), then characteristic times of the kinetics were adjusted to 308-423 s^{-1} .

Plot in Figure 2a shows the deposition kinetics of NH-1LbL suspensions when different current densities were applied (20, 30 and 40 mA cm^{-2}). The straight line represents the theoretical kinetics of NH-1LbL suspensions, calculated considering the electrokinetics parameters listed in table 2 and a sticking factor of 1 (eq. 1-2), while dashed lines were used as eye guides for the experimental data plot. The increases of the applied electric field reasonably steps up the deposition process, and after 900 s the amount of deposited mass increases with the current density from the 25% to the 50% of the nanoplatelets in the suspension. However, in all cases the sticking factor of the NH-1LbL suspension barely achieves 0.1. Consequently, we can consider that nanoplatelets deposit discreetly under these conditions, compared to their electrokinetics ability of the dispersion. To determine the thickness range of the processed coatings, FE-SEM has been used to explore coatings in flat substrates. After the deposition of the 50% of powders (figure 2 a) in the NH-1LbL suspensions, 2.1 mg/cm^2 (4.6 mg) films with thicknesses of 5 μm are obtained.

Plots in Figure 2b, 2c and 2d show the kinetics of the deposition of the NH-1LbL, NH-3LbL and NH-5LbL core-shells respectively. Similarly to the plot in figure 2a, in all cases straight lines represent the theoretical kinetics of each system (following eq. 1-2 and

considering a sticking factor of 1 and starting conditions summarized in table 2), while dashed lines represent the evolution of collected experimental data. Two facts can be corroborated associated to the deposit growth: deposition reliability slightly decreases, since the data of the deposited mass are more dispersed, and the sticking factor, f , doubles (from 0.10 to 0.2). So the deposition kinetics step up with the number of layers.

The low value of the sticking factor calculated for some systems is still matter of controversy in the literature. Stable suspensions should collapse at the working electrode to form the coating. So regularly the deposition takes place due to chemical changes in the electrode surroundings (increase of solid content, changes in pH, the increase of the ionic strength, etc.) [28]. Low ionic strength of the suspensions prepared in the present work softens collateral electrochemical phenomena at the working electrodes and stability of the core-shells prevail. So, electrostatic attraction with the electrode, hydrogen bridges and hydrodynamic forces could be some of the driving forces for the core-shell assembly and deposition, while the moderate agglomeration of the nanoplatelets could be the cause of the step up of the sticking factor with the number of layers of the LbL system.

Figure 3 shows a detail of the NH-1LbL (Figure 3a), NH-2LbL (Figure 3c) and NH-5LbL (Figure 3e) as-deposited microstructures where differences in the nanoplatelets arrangement are evidenced. The 2D nanostructures lay parallel to the substrate surface for the NH-1LbL core-shells, while they seem to stack forming agglomerates deposited perpendicularly to the electrode in the case of the NH-5LbL system. In fact nanoplatelets agglomeration was pointed out as a reason of the deposition kinetics step up with the number of polyelectrolyte layers that form the core-shell. Figure 3b

schematise the nanoplatelets arrays as they can be imagine from the micrographs, while Figure 3d shows the XRD of as-synthesized β -Ni(OH)₂ platelets as well as those of NH-1LbL, NH-3LbL and NH-5LbL coatings. In the coating spectra we can realise the presence of peaks belonging to the stainless steel used as substrates (γ (111) and γ (200)), but also if we compare the signals we can observe the intensity growth of (101), (102) and (101) reflections with the number of layers of polyanios/polycations. This can be definitely considered as an indicative of the increasing disorder. Indeed, the LbL approach seems to promote the agglomeration and certainly it determines the stacking behaviour of β -Ni(OH)₂ nanoplatelets in the suspension (Figure 3b), and it affects to the core-shell arrangement during deposition.

As it is described in the introduction chapter, we should consider that the tendency of the β -Ni(OH)₂ platelets to align the (0 0 l) planes parallel to the substrate is due to the Van der Waals forces developed among particles and their interaction with the electro-hydrodynamic forces acting over them when approach to the substrate. Especially under smooth EPD conditions (for low current densities and low solid concentrations), their arrival to the working electrode slows down favouring nanoplatelets lying down. For LbL core-shell suspensions (NH-1LbL, NH-3LbL and NH-5LbL), the properties were adjusted not only to slow down the massive arrival of core-shells to the substrate (Table 2 and Figure 3b), but for reduce as much as possible the conductivity of the suspension and avoid collateral phenomena derived from the electrophoretic movement of contra and co-ions, and the presence of excessively charged nanostructures. On the other hand, low suspension conductivity relatively impedes the nanoplatelets flocculation in the suspension [29], and is enough to maintain a stable current density during EPD providing reliability to the mesostructures formation.

Under these conditions, the electrostatic contribution to the nanoplatelets stability was reduced to the minimum necessary to assure the electrophoretic movement and the highest deposit yield. Thus, the flocculation of the nanoplatelets at the substrate is due to the PEI neutralization (at the 1st, 3rd and 5th layer) under basic conditions at the electrode surroundings, and then nanoplatelets packing was favoured by the reduction of the interparticle depletion and the electrostatic repulsion among them [30]. Consequently, the adhesion of the film to the substrate as well as the own cohesion among the nanoplatelets, depends on the manipulation of the ionization and conformation of the surface modifiers at the organic corona of the core-shell system. Therefore, the decrement of the interparticles forces leads to that the electrohydrodynamic forces govern the nanoentities arrangement. In this sense, micrographs in figure 3 (a, c and e) show that the increase of the number of layers of the shell structure alters the hydrodynamics and promotes disorder under the reported smooth EPD conditions.

After β -Ni(OH)₂ nanoplatelets shaping, the EPD coatings were annealed by 1 h at 325°C to obtain a NiO consolidated structure, and then the surfaces of as-deposited hydroxide-based films as well as that of the consolidated oxide-based structures were inspected by SEM. Figure 4 shows the surface of NH-1LbL and NO-1LbL (a and b), NH-3LbL and NO-3LbL (c and d), and NH-5LbL and NO-5LbL (e and f) coatings. Low magnification micrographs evidence the uniform coatings built by EPD, and the increasing disorder promoted by the LbL modification of the nanoplatelets during deposition, even strikingly than those studied in a previous work for more intense EPD conditions [22]. However, a common factor of all of the LbL coatings is that their microstructures maintain their structural integrity after the thermal annealing.

To determine the microstructural sturdiness of the NO-5LbL coatings, NiO-based electrodes were electrochemically tested in terms of capacity, and the micro, meso and macroporosity of the consolidated microstructures after the thermal treatment was characterised.

First at all, micro and mesoporosity of the as-synthesized (unmodified) and calcined NiO powder was determined by N₂ adsorption/desorption isotherm. Main morphological properties, such as the specific surface area (SSA) and pore size distribution (PSD), were summarised in table 3, while PSD are plotted in figure 5a (straight line). Results reveal that the thermal annealing leads to powders with an open SSA of 83.71 m²/g, with a fraction of small mesopores with diameters ranging 4-10 nm, which corresponds to voids among nanoparticles forming the nanoplatelets [27], and a wide fraction of the large macro- mesoporosity (30-100 nm) that represents the inter-nanoplatelets spaces.

On the other hand, meso and macroporosity of the core-shells scrapped from the substrate after the EPD coating calcination was determined by Mercury Intrusion Porosimetry (MIP). Results of MIP are also shown in table 3 and Figure 5a (dashed line) and Figure 5b. The SSA of the core-shells decreases with the number of polyelectrolyte layers, as well as the volume of pores. Nevertheless, the PSD obtained by MIP for the analysis of NO-5L core-shells verifies the presence of a fraction of macro- mesoporosity (30-100 nm) in the NO-5LbL coating after the thermal treatment. The detail of the microstructure in the inset identifies the nanoplatelets stacking in the sintered microstructure of the NO-5LbL semiconductor film. Plot in figure 5b shows the population of mesopores and small macropores of NO-1LbL, NO-3LbL and NO-5LbL coatings after the thermal treatment. The plot quantifies the decrease of the porous

volume with the increase of the number polyelectrolyte layers in this range of porosity, and also it shows the increasing tendency of the size of the residual spaces among platelets formed during the coating sintering.

Those results evidence the consolidation of the nanoplatelets stacking during the thermal treatment, which confers the structural integrity to the porous coating, and also corroborate the presence of agglomerates (marked in the micrographs in Figure 3). In this sense, we can consider that the SSA of the nanoentities decreases from 83.71 m²/g for unmodified NiO powder to 10.25 m²/g of the NO-5LbL nanoplatelets staking, but it is still enough to favors electrolyte impregnation and ion diffusion. The decreasing of SSA and the volume of porous in the meso- macro-range (30-100 nm) is a consequence of the nanoplatelets agglomeration promoted by the LbL modification, and further sintering of the coating.

Consequently, for further characterization we should consider that the NO-5LbL coating exhibits a well consolidated and interconnected but also open macroporous microstructure, with a larger macroporosity in the range of 2-5 µm (Figure 4f) and a moderated mesoporosity of 30-100 nm.

Electrochemical performance of the sample NO-5LbL was evaluated by cyclic voltammograms (CV) and galvanostatic charge/discharge tests (CP). The results were compared with a NO-1LbL electrode with a similar deposited mass [21] in Figure 6. The CV curves for NO-5LbL were measured at different sweep rate 5, 10, 20 and 50 mV/s (Figure 6a). All plots present faradic profile with oxidation and reduction peaks associated to the charge and discharge processes, respectively. The redox reaction is identified with the following equation:

An increase of the window of potential (ΔV) was observed. The anodic peaks shifted to positive potentials and the cathodic peak to the negative potential with scan rate due to the polarization in the electrode material and the OH^- ions intercalated quickly at the interface of electrode/electrolyte at the high scan rate (50 mV/s). The values of peaks separation mean a high rate capability and a good reversibility, exhibiting a fast kinetic of the indicated faradaic reaction.

Figure 6b shows the variations of specific capacitance (calculated by the integration of the cathodic peak area shown in eq. 3-6 of the experimental section) with the scan rate for the two modified electrodes. Both curves show a gradual decrease of the capacitance values, however, the data of the sample NO-5LbL is above the sample NO-1LbL displaying a higher diffusion of alkali cations into the porous and disorganized microstructure, and thereby the access to a major fraction of active sites and a better contact of the electrolyte with the electroactive material.

On the other hand, the cycling stability of the NO-5LbL electrode was evaluated by galvanostatic charge/discharge curves at the current density of 2 A/g in the voltage range of 0-0.5V for 1000 cycles. The discharge plots (Figure 6c) are composed of three steps. The first two processes are assigned with the reduction of Ni^{+2} and are subdivided in a fast initial potential drop followed by a slow potential decay. Contrarily the third, which shows a faster voltage drop, corresponds to an Electric Double Layer Contribution (EDLC). Both electrodes presented similar slopes for the first and second step, and main differ in the discharge rate of the second step (slower in NO-5LbL coating), which indicates a higher redox contribution for the opener microstructure in the NO-5LbL electrode. The macroporous microstructure of the NO-5LbL results in the increases of the active surface leading to a higher specific capacitance. The high

density of macropores produced by the LbL surface modification generates new diffusion pathways which favor the electrolyte impregnation, while the ceramic microstructure connectivity maintains by sintering. The higher surface area exposed to the electrolyte solution maximize the insertion of the OH^- ions favoring the faradaic reaction.

In addition, Figure 6d shows the trend of the specific capacitance vs. the number of cycles. The specific capacitance increases with the number of organic layers, but also NO-5LbL electrode exhibits a significant increase of the specific capacitance, from 650 to 1000 F/g, between the first 50-100 cycles due to the activation and stabilization of the opener microstructure. The electrolyte ions have to go through every nook to favor the contact with all the active sites in the semiconductor structure. After 100 cycles, the specific capacitance value starts to decrease down to 650 F/g, stabilizing the capacitance retention (100%) after 1000 cycles.

4. Conclusions

Synthetic $\beta\text{-Ni}(\text{OH})_2$ nanoplatelets superficially modified by a 1, 3 and 5 LbL organic shells were employed to manipulate the microstructure of the EPD coating. In $\beta\text{-Ni}(\text{OH})_2$ deposition, we demonstrated that the new microstructural arrangement of nanoparticles with 2D morphology is a consequence of both processing strategies: (i) the LbL modification of their surfaces and (ii) their electrically-driven deposition.

The dispersion of core-shell structures was adjusted to slow down the massive arrival of modified nanoplatelets to the substrate, in order to reduce as much as possible the collateral phenomena derived from the electrophoretic movement of contra and co-ions. The electrostatic contribution to the nanoplatelets stability was also reduced to

the minimum necessary to assure the electrophoretic movement and the highest deposit yield, while smooth EPD conditions (for low current densities and low solid concentrations) favor nanoplatelets lying down. Nanoplatelets deposit discreetly compared to their electrokinetics ability (sticking factor of 0.1), and only a 50% of the nanoplatelets in the suspension can be deposited after 900 s.

Results demonstrate that under these conditions, the LbL modification of the nanoplatelets surfaces promotes a moderated agglomeration, and specifically determines their stacking behavior in the suspension and their arrangement during deposition. The increase of the number of layers at the shell structure alters the hydrodynamics and promotes disorder, and the formation of an open microstructure, even under the reported smooth EPD conditions. Achieved moderated agglomeration allows the full and homogeneous coating of 3D substrates.

NO-5LbL coatings of 2D Ni substrates exhibit a well consolidated and interconnected but also open macroporous microstructure with a larger macroporosity in the range of 2-5 μm and a moderated mesoporosity of 30-100 nm. **This extremely open porous microstructure can be reproduced in coatings of 3D Ni foams**, stabilizing a specific capacitance of 650 F/g measured at 2 A/g after 1000 cycles.

Once the stability conditions of the NH-5LbL suspensions were optimized for a successful EPD, the amount of deposited mass will depend on the deposition time and the electric field applied over the suspension. Further work should be done to study the electrochemical efficiency of the electrode as a function of the deposited mass and the free surface able to react with the electrolyte.

This clearly opens the possibility of controlling the nanoplatelets orientation by designing the stabilization system in EPD. The adhesion of the film to the substrate as

well as the own cohesion among the nanoplatelets, depend on the manipulation of the ionization and conformation of the surface modifiers at the organic corona of the core-shell system. The manipulation of the stability conditions promote the decrement of the interparticles forces and leads to that the electro-hydrodynamic forces govern the nanoentities arrangement. In this way, the 2D nanostructures lay parallel to the substrate surface for the NH-1LbL core-shells, while they stack forming agglomerates and deposit perpendicularly to the electrode in the case of the NH-5LbL system.

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Captions

Figure 1. Scheme of polycation adsorption onto the β -Ni(OH)₂ nanoplatelet adopting a tail or train conformation (a). Zeta potential evolution, core-shell scheme and added amount of polyelectrolyte in the LbL adsorption (b).

Figure 2. EPD Kinetics for NH-1LbL core-shell deposition for current densities from 20-40 $\mu\text{A}/\text{cm}^2$ (a), and for NH-1LbL (b), NH-3LbL (c) and NH-5LbL (d) at 10, 12, 8 $\mu\text{A}/\text{cm}^2$, respectively.

Figure 3. FE-SEM micrographs of as-deposited NH-1LbL (a), NH-3LbL (c) and NH-5LbL (e) coatings, scheme of NH-1LbL and NH-5LbL core-shells (b) and XRD patterns of as-synthesized β -Ni(OH)₂ nanoplatelets and NH-1LbL, NH-3LbL and NH-5LbL coatings.

Figure 4. FE-SEM micrographs of NH-1LbL and NO-1LbL (a and b), NH-3LbL and NO-3LbL (c and d), and NH-5LbL and NO-5LbL (e and f) coatings.

Figure 5. Pore size distribution of NiO powders and NO-5LbL core-shell determined by N₂ isotherms and MIP, respectively, and a detail of the NO-5LbL microstructure (a). Pore size distribution of NO-1LbL, NO-3LbL and NO-5LbL core-shells determined by MIP (b).

Figure 6. Comparative of the electrochemical tests between the samples NO-5LbL and NO-1LbL [22]. Cyclic voltametries of the sample NO-5LbL at different scan rates (a), variation of specific capacitance with scan rate (b), Galvanostatic discharge curves (c) and Cyclic Chronopotentiometric measurements at a current density of 2 A/g (d).

Table 1. Characteristic of nanoplatelets and thin films obtained by EPD described in the Literature

Material	Diameter (nm)	Solvent	Stabilization mechanism	Electrophoretic kinetics	Particle arrangement
Graphite [2]	1000	H ₂ O	Electro-steric (PEI + pH 9-10)	H ₂ bubbling	Random
Ni(OH) ₂ [24]	100	IPA	Electro-static (H ₂ O + I ₂)	High PZ (+30 mV) High solid content (10 g/L) H ₂ bubbling	Random
Gibbsite [9]	100-200	EtOH/H ₂ O	Electro-static (pH 7)	High PZ (+40 mV) Low electric field 11V/cm	Aligned
ZnO [12,13]	35	H ₂ O	Electro-Steric (PEI)	Solid content: 1-10 g/L ZP = +22 mV (PEI)	Aligned & Perpendicular
SiO ₂ -Gibbsite [8]	100-200	EtOH	Electro-steric (H ₂ O+ PEI pH 7)	High ZP (+28 mV) Low electric field 10V/cm PEI as binder	Moderately aligned
GO [15]		H ₂ O	Electrostatic	Low solid content (1.5 g/L) Low electric field 10V H ₂ bubbling	Aligned
GdOCl [5]	200-400	Cyclohexane IPA H ₂ O	Electro-Steric (TOPO synthesis modifier)	ZP = -66 mV (cyclohexane) ZP = +30, +48 mV (IPA, H ₂ O) Electric field 25-400 V	Aligned
TiO ₂ -Graphene [3]		IPA	Electrostatic (PVB-binder)	Low ZP (+10 mV) High solid content (>30 g/L) Composite clusters	Moderately aligned
Ni(OH) ₂ -CB [25]	200/10	H ₂ O	Electro-Steric (PVP, Igepal)	Solid content: 1 ZP mixture= +40 mV	Aligned
Au-Cu [8]	>1000	Chloroform+ Acetone	Electrostatic	Low solid content (<1 g/L) Electric field 200 V	Cu Aligned Au moderately Aligned
ZnO [11]	10	Acetonitrilo	Electrostatic	Low solid content (<1 g/L) Electric field 20-40 V	Aligned

Table 2 Summary of the electrokinetics parameters of NH-1LbL, NH-3LbL and NH-5LbL core-shells and the EPD electric conditions

Core-Shell Electrokinetics Parameters	NH-1L	NH-3L	NH-5L
Electrophoretic Mobility, u_e , ($\times 10^{-4}$ cm ² /V·s)	0.82	0.77	0.71
Suspension Conductivity, σ , (μ S/cm)	0.84	0.63	0.50
Ratio of Mobility, σ / u_e	1.02	0.82	0.70
Current Density (μ A/cm ²)	40	12	8
Electric Field (V/cm)	75	76	80
Characteristic Time for EPD* (eq. 2)	308	351	423

*calculated for a volume of suspension of 30 ml and a sticking factor 1

Table 3. Morphological properties of the NiO powders and NO-1LbL, NO-3LbL and NO-5LbL core-shells

Morphology of β -Ni(OH) ₂ and NiO nanoplatelets	NiO		
BET SSA (m ² /g)	83.71		
Open SSA by t-plot (m ² /g)	82.39		
Total Pore Volume N ₂ (cm ³ /g)	0.46		
Micropore Volume by t-plot (cm ³ /g)	1.32		
Morphology of the Core-Shell structures	NO-1L	NO-3L	NO-5L
SSA determined by MIP (m ² /g)	49.91	22.71	10.25
Total Pore Volume MIP (cm ³ /g)	1.27	1.37	0.79