Understanding the effects of different microstructural contributions in the electrochemical response of Nickel-based semiconductor electrodes with 3D hierarchical networks shapes

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Abstract

It is well known that exposed surface area, nanoparticles connectivity and its consolidation level in a nanostructure are key points in the enhancement of the electrochemical performance in energy storage devices. The design and optimization of different electrodes with specific microarchitectures (based on the arrangement manipulation of NiO nanoplatelets, used as building blocks), has allowed distinguishing the effects of each microstructural contribution in their final electrochemical responses, overpassing thermal and mechanical mismatches between the semiconductor ceramic structure and the metallic collector. In all cases, the same electroactive material and the same coating technique were used, preventing the interference of secondary phenomena in the EIS studies, and allowing argue over the contribution of the microstructural features incorporated to the electrode (nature and shape of the collector, degree of sintering and consolidation of the ceramic microstructure, incorporation of non-noble metallic nanoparticles and the macro/meso/microposity effect) in the effective profiting of the Faradaic phenomena observed during their cycling. The modification of the Ni-based electrodes allows understanding how microstructural features infer the electron transport and the ion diffusion through the consolidated structure. The EIS analysis proves that the design of the porous hierarchical network of our semiconductors electrodes resulted in a good rate capability (with capacitance values of 1000F g⁻¹ or 500 C g⁻¹), exhibiting a relaxation time constant (τ₀ = 18 ms), while a slight increase of the charge-transfer resistance (Rct = 3.65 Ω) is negligible if the exposed surface is high enough to maintain a high ion transport. The inclusion of non-noble nanoparticles, such as Ni NPs, in the NiO semiconductor microstructure and the optimum deposited mass and sintering treatment create a metal-ceramic electrode that enhances both the charge transfer resistance (1.55 Ω) showing relaxation time in the range (τ₀ = 11 ms) and maintaining an excellent capacitive behavior (750 F g⁻¹ or 375 C g⁻¹) at quick charge/discharge rate.

Introduction

Pseudocapacitive materials growing attention is due to their capacity to enhanced energy density, improving simultaneously cycling stability with high capacity retention in hybrid supercapacitors and outdistancing traditional electrical double-layer capacitors [1,2]. These storage devices have several advantages over batteries in terms of power density, long cycle life and efficiency and thermal stability [3–5]. For these reasons, pseudocapacitors (PC) are now strong candidates to be used in wearable electronic devices [6] or energy harvesters [7], as well as in electric vehicles [8] or storing of intermittent renewable energy sources such as wind and solar[9].

Semiconductor nanomaterials based on RuO$_2$, MnO$_2$, Fe$_3$O$_4$ and Co$_3$O$_4$ have been intensively studied as PC [10,11] while the electrochemical performance of new compositions, such as carbides, nitrides or mixed oxides, as well as 3D nanostructures are matter of study[12–14]. Among the electroactive materials, Ni-based nanostructured electrodes have been considered promising candidates due to the high theoretical specific capacitance and theoretical capacity of NiO (3750 F g$^{-1}$ or 718 mA h g$^{-1}$ respectively), its ready availability and low cost, and its good thermal and chemical stability [2,10,15].

Although Ni-based materials have been recently proposed as battery-type electrodes due to their electrochemical signature (e.g., cyclic voltammogram and charge/discharge curve) [16,17] is analogous to that of a “battery” material, they have been repeatedly treated as a pseudocapacitor by considering the identification of their charge storage mechanism [17,18].

Anyway, the full profiting of the Ni surface reactions to improve the electrochemical behavior and achieve higher capacity values is still a challenge since the electrochemical response of the semiconductor electrodes not only depends on the inherent properties of the selected material. They should have high surface area with plentiful reaction sites to achieve a successful electrolyte impregnation through the porous nanostructure, while conducting electrons through the metal oxide. Consequently, an optimal performance requires of a 3D nanostructure with mixed meso and macro interconnected pores to hold easily accessible redox active sites as well as reinforced charge transfer and ion diffusion capability.

Traditionally the fabrication of semiconductors electrodes, as NiO and Ni(OH)$_2$, lies on the formulation of a mixture of the electroactive material with binder additives like carbon black (CB), acetylene black, PVDF, PTFE, etc. which are used to improve contact between particles. The resulting pastes are directly applied and pressed onto conductive substrates such as

metallic or carbon [19–22]. Nevertheless, the poor electrical connectivity and the weakness of
the resulting electrodes lead the development of fabrication routes of alternative binder-free
electrodes where the electron transfer movement through the shaped microstructure is
favored. In this sense nanosized metal oxides such as Ni-based nanocompounds can be
consolidated by a sintering treatment at low temperature after synthesis and shaping [23–27],
leading to a stronger electrically connected electrodes, where the porous nanostructure
provides the structural tolerance needed to overpass the volume changes associated to the
faradaic reactions. It is well known that the formation of ceramic necks between particles
provides a better electron transport and improve the electrochemical response. Also the
electrical conductivity can be improved by including metal [28–30] or nonmetal impurities [31–
34] within the oxide nanostructure, generating donor or acceptor states in the bandgap and
thereby increasing the concentration of charge carriers.

The use of a simple, reliable, controllable, as well as green and cost-effective colloidal
technique such as EPD allows obtaining nanostructures tailoring and strengthening the control
over deposited mass onto the 3D metallic collector. Opposite to other coating techniques, the
EPD is able to cover difficult access surfaces in the 3D architectures. Moreover, significant
physical parameters such as the films thickness, the amount of the deposited electroactive
material as well as the particles packing can be easily tuned by EPD parameters like the
concentration of the suspension, the applied potential and/or the deposition time.

In previous works [27,30,35,36] the electrochemical response of synthesized NiO nanoplatelets
were evaluated. Resulting electrodes showed robust 3D electroactive electrodes with micro-,
meso- and macroporosity hierarchically ordered in different microarchitectures and achieved
specific capacitances up to 1000 F g\(^{-1}\) (500 C g\(^{-1}\)) at 2 A g\(^{-1}\). In these studies, the NiO
nanoplatelets surfaces were modified by either the alternative adsorption of polyanions and
poylcatons forming a polyelectrolyte multilayer or the in situ heterogeneous precipitation of
metallic Ni nanoparticles (NPs). The control on the processing parameters like the amount of
deposited mass, thickness, temperature and time of the thermal treatment of sintering, etc.,
resulted in different features of the Ni-based coatings which improve the film quality as well as
pseudocapacitor performance in many senses.

In this new paper the key role of tuning the microstructure of a shaped material (with different
pore-channel openness and interconnection) is presented as the light of the electrochemical
measurements. Electrochemical Impedance Spectroscopy (EIS) was herein performed as a
diagnostic tool to study the effects of i) the microstructural design of the two levels of porosity
achieved by the Layer-by-Layer (LbL) surface manipulation of Ni(OH)\(_2\) nanoplatelets and ii) the

connectivity level of the shaped nanoparticles achieved either by the optimization of the thermal treatment or the inclusion of a non-noble in the semiconductor structure. Microstructures were obtained by covering different collector substrates (2D and 3D structures), followed by sintering at 325 °C or 375 °C under Ar atmosphere during 15 or 60 minutes. EIS data were compared by using an appropriate equivalent circuit and analyzing the circuit parameters extracted from the experimental data.

**Experimental Section**

All chemicals were of reagent grade and used without any further purification. The Ni(OH)$_2$ nanoplatelets and NiO/Ni core-shell nanoparticles were synthesized by chemical precipitation and reduction reactions at room temperature under the ultrasound action as an external energy source (45 W/cm$^2$, 24 kHz, titanium T13 tip, Sonopuls HD 2200, Bandelin Electronic, Germany). The β-Ni(OH)$_2$ was synthesized by mixing 8 mmol of nickel nitrate hexahydrated (Ni(NO$_3$)$_2$, 99.9% purity; Panreac, Spain), and 40 mmol of ammonia (NH$_3$, PA 25%, Panreac, Spain) in a total volume of 80 ml of aqueous solution. The annealing of Ni(OH)$_2$ powder to obtain NiO was carried out in Ar at 325 °C during 15 minutes with a heating rate of 10°C /min. Metallic Ni nanoparticles (NPs) was synthesized onto the surface of the NiO nanoplatelets by heterogeneous reduction of a nickel precursor (Ni(NO$_3$)$_2$.6H$_2$O, 99.9% purity; Panreac, Spain). For that, a specific amount of NiO nanoplatelets was previously dispersed in deionized water where the nickel salt precursor was also dissolved. The pH value of the reaction medium was adjusted around 10 with tetramethylammonium hydroxide (TMAH 25%, Merck, Darmstadt, Germany) due to a better NiO nanoplatelets dispersion where their surfaces are chemically stable. The NPs were precipitated by the chemical reduction by adding a mixture of monohydrate Hydrazine (N$_2$H$_4$.H$_2$O, Sigma-Aldrich, Germany), with Potassium Hydroxide (KOH, Panreac, Spain), also sonicating with the same ultrasonic horn (Sonopuls HD2200). The temperature was controlled through the recirculation from a cryothermal bath. Both procedures have been previously described more in detail elsewhere [27,30,37].

The identification of the crystal phases of the synthesized powders was carried out with a X-ray diffractometer (D8 Advance, Bruker, Bremen, Germany) using Cu K radiation ($\lambda$= 1.5418 Å) at 40 kV and 30 mA and 2θ = 10–70). Crystallite size (L$_{hkl}$) and unit cell dimensions (c) were determined by using the following equations:

$$L_{hkl} = \frac{k \cdot \lambda}{FWHM \cdot \cos \theta}$$  \[Eq.1\]

$$C = \frac{\lambda \sqrt{h^2+k^2+l^2}}{2 \cdot \sin(\theta)}$$  \[Eq.2\]
Where \( L_{hkl} \) is the size of the crystallite; \( k \) is a dimensionless shape factor, with a value close to unity, \( \lambda \) is the X-ray wavelength; \( \text{FWHM} \), is the width of the peak at half height after subtracting the instrumental line broadening, in radians; and \( \theta \) is the Bragg angle in radians. And \( c \) is the unit cell dimension in Armstrong, and \( \theta \) is the Bragg angle in radians, \( \lambda \) is the X-ray wavelength; and \( hkl \) the Miller index for the family of lattice planes.

The \( N_2 \) adsorption/desorption isotherms and BET specific surface area (SSA) determination for the Ni(OH)_2, NiO and NiO/Ni nanoparticles were carried out with an accelerated surface area and porosimetry system (ASAP 2020, Micromeritics Instrument Corp., Atlanta, GA, USA). The nanoparticles morphologies were observed with a field emission scanning electron microscope (FESEM), (S-4700, Hitachi High-Technologies, Tokyo, Japan). High resolution transmission electron microscopy (HRTEM) images were recorded operating at 200 kV using a (Jeol JEM 2100F) electron microscope equipped with a CCD camera (Orius Gatan). To avoid degradation of the material, TEM images were recorded at low energy conditions.

After the synthesis, the resulting powder were separated from the reaction waters by centrifugation and washed several times with distilled water at pH 10, adjusted with TMAH. The washed precipitate, still wet, was re-diluted in a desired amount of water at pH 10 where the polyelectrolytes are sequentially added following the procedure described previously elsewher [38–40]. The polyelectrolyte used for the modification of nanoplatelets surfaces was branched Polyethylenimine (PEI, Mw 25000, Sigma Aldrich, Darmstadt, Germany). It confers a positive charge to the Ni(OH)_2 and NiO/Ni nanoparticles which stabilizes the suspension and allows the use of cathodic deposition.

Ni-based electrodes were prepared following the EPD method described previously elsewhere[30,36]. Ni foams, Ni foils, Cu foils and SS foils substrates were introduced in a 1g/L suspension of Ni-based nanoparticles in Ethanol:DI water 19:1, during the necessary time to deposit around 1 mg of electroactive material. This mass was optimized with further tests through FESEM pictures (not included herein). A mass below this value resulted in uncovered surfaces of the Ni foams whereas higher values produced coatings with critical thicknesses where the presence of relevant cracks and surface defects are attributable to the excess of the electroactive material. After drying the electrodes were sintered in air at different temperatures and dwell times (\( \leq 325^\circ\text{C} \) and \( \leq 60 \) minutes).

The electrochemical measurements were carried out in an electrochemical half-cell equipped with an Ag/AgCl (saturated KCl) reference electrode (CH instruments, Inc.) and a platinum-plate counter electrode. A KOH solution (1M) was used as electrolyte. The capacitive...
performance of the electrodes was tested under different conditions. Cyclic voltammetry (CV) tests were carried out with a Potenciostat/Galvanostat Auto-lab (PGSTAT204), 10 sequential cycles were programmed at a scan rates of 2, 5, 10, 20, 30 and 50 mV s\(^{-1}\) in a potential window of 0.0–0.5 V. 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. The charging/discharging measurement was carried out through chronopotentiometry analysis (CP) at a scan rate of 2 A g\(^{-1}\) during 1000 cycles using a multichannel potentiostat–galvanostat system (Arbin BT2000).

Finally, the Electrochemical Impedance Spectroscopy (EIS) measurements were performed in potentiostatic mode at room temperature employing an Autolab PGStat302 N instrument (Switzerland) in the frequency range 0.1 - 10\(^6\) Hz with an applied voltage of 50 mV.

The diffusion coefficients (D) were calculated by the Randles-Sevcik Equation:

\[
i_p = 268.6 \times n \times 2 \times A \times D^{1/2} \times C \times v^{1/2}
\]  

[Eq. 3]

where \(i_p\) is the current oxidation maximum in amperes, \(n\) is the number of electrons transferred in the redox reaction (2 e\(^-\) in our case). \(A\) is electrode area in cm\(^2\), \(D\) is the diffusion coefficient in cm\(^2\) s\(^{-1}\), \(C\) is the electrolyte molar concentration and \(v\) is scan rate in V s\(^{-1}\).

Results and Discussion

NiO nanoplatelets of Fig. 1a were obtained after annealing in Ar from the polymorph Ni(OH)\(_2\) nanopowders synthetized by a chemical precipitation with ammonium hydroxide as precipitating agent and free of any type of additive [27]. The precipitation reaction was carried out at basic pH, ranging from 9 to 10, at room temperature with the aids of ultrasound. Figure 1b shows the NiO/Ni powders obtained by reduction of Ni\(^{2+}\) with hydrazine directly as Ni NPs onto the surface of the NiO nanoplatelets [30]. Detailed process descriptions for syntheses, which were ultrasound aided, were previously published elsewhere[27],[30].

The surface of the bare NiO nanoplatelets of figure 1a is a completely flat plate with a size ranging 150-200 nm of diameter and 20-30 nm in thickness (inset shows the detail). The heterogeneous synthesis of smaller metallic Ni nanospheres, 30 nm in diameter, partially covers the NiO nanoplatelets resulting in NiO/Ni nanostructure core-shell like, as shown and illustrated on figure 1b.
A detailed physical characterization of the starting powders was made to monitor the changes before and after Ni NPs synthesis (Fig. 2). The XRD curves for the different species synthetized, Fig. 2a, indicate the presence of Ni(OH)$_2$ and two crystallographic phases after annealing, both with a face-centered cubic lattice (space group: Fm3m). According to the index card JCPDS No 47-1049, correspond to Ni, and No. 22-1189 corresponds to NiO. There are no other peaks, suggesting that the Ni(OH)$_2$ was mainly turned into NiO and Ni during the thermal annealing and the heterogeneous synthesis, respectively [30,36]. Crystallite size of NiO and Ni nanoparticles calculated from the Scherrer equation (Eq.1) were 9.54 and 16.33 nm respectively. The unit cell dimensions (calculated by Eq.2) were 4.20 and 3.53 Å and the interplanar distances were 2.43 and 1.80 Å respectively. The BET specific surface area (SSA), the total pore volume as well as the open SSA and the micropore volume determined by the t-plot method for the three nanopowders (the Ni(OH)$_2$ precursor of NiO, NiO nanoplatelets and NiO/Ni core-shells) are compiled in Table 1. Figure 2b (main and inset) show the N$_2$ adsorption/desorption isotherms and the pore size distribution of the hierarchical nanostructures, respectively. The shape of the isotherm indicates that the Ni(OH)$_2$ and NiO nanoplatelets have higher porosity than NiO/Ni and a small but representative population of micropores. The amount of N$_2$ adsorbed at high-relative pressure for NiO/Ni is very low.

indicating that the porosity of the NiO nanoplatelets changes because of the Ni nanospheres precipitation onto their surfaces. This could be also the main reason of the differences in BET SSA from 83.7 m² g⁻¹ for NiO to 16.1 m² g⁻¹ of NiO/Ni. Moreover, the pore-size distribution plot (Fig. 2b inset) confirms a significant region of mesopores in the NiO nanostructures, which correspond to the voids seen on the nanoplatelets surfaces in TEM image of figure 2c. This mesoporous distribution was not detected in the pore-size distribution plot corresponding to the NiO/Ni core-shells particles, which is due to the presence of the metallic phase onto the semiconductor material surfaces (see Figure 1b).

Differences in SSA and pore volume values can be correlated to the SSA and volume associated with the micropores (porosity below 2 nm in diameter). The analysis of the data in Table 1 summarizes the SSA and the micropores volume calculated by BET and t-plot methodologies. All micropore volumes are lower than 2% of the total pore volume and they don’t exceed the 18% of the total exposed surface, being microporosity the lowest representative fraction in NiO nanoplatelets where micropores are only 0.1% of the total porosity and 1.5% of the SSA. Focusing on the electrolyte impregnation, we can conclude that although all porosities (from macroporosity to microporosity through mesoporosity) are relevant the high specific surface area value of the NiO calcined at 325°C is mainly due to the mesoporosity (5-10 nm). On the other hand, the microporosity was recently related with electron transfer [14] and, although the volume of micropores is relatively low in both nanostructures, it is important to notice that the precipitation of metallic Ni NPs onto NiO nanoplatelets produces the decrease in the SSA while highlight the relevance of bare-NiO microporosity. These data also evidence the filling of macro and mesopores of NiO nanoplatelets with Ni NPs.
Fig. 2. a) XRD patterns of the β-Ni(OH)$_2$, NiO and NiO/Ni powders. b) N$_2$ gas adsorption-desorption isotherms and pore size distribution of as-prepared β-Ni(OH)$_2$, NiO calcined at 325 °C and NiO/Ni powders. And c) and d) HRTEM images of NiO/Ni powders (where different interplanar distance can be observed depending on the nanoparticle NiO and Ni respectively). Electron diffraction pattern of the sample was included at the inset.

Table 1. Textural properties of as-synthesized nanoparticles

<table>
<thead>
<tr>
<th></th>
<th>Ni(OH)$_2$</th>
<th>NiO</th>
<th>NiO/Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET SSA/ m$^2$ g$^{-1}$</td>
<td>74.1</td>
<td>83.7</td>
<td>16.1</td>
</tr>
<tr>
<td>Open SSA by t-plot/ m$^2$ g$^{-1}$</td>
<td>65.1</td>
<td>82.4</td>
<td>13.2</td>
</tr>
<tr>
<td>SSA contributed by micropores/ %</td>
<td>12.0</td>
<td>1.5</td>
<td>18.0</td>
</tr>
<tr>
<td>Total Pore Volume N$_2$/ cm$^3$ g$^{-1}$</td>
<td>0.481</td>
<td>0.457</td>
<td>0.064</td>
</tr>
<tr>
<td>Micropore Volume by t-plot/ cm$^3$ g$^{-1}$</td>
<td>0.004</td>
<td>0.000</td>
<td>0.001</td>
</tr>
<tr>
<td>Micropore on N$_2$ pore volume/ %</td>
<td>0.8</td>
<td>0.1</td>
<td>2.0</td>
</tr>
</tbody>
</table>

The HR-TEM micrographs of Fig. 2c and 2d corroborate the growth of metallic NPs onto the NiO nanoplatelets in NiO/Ni core-shell nanostructures as well as the presence of micropores (white arrows). The measurements of the interplanar distances at the c-axis confirmed the results seen by XRD where the presence of the Ni nanospheres was justified by the presence of the main peaks (111 and 200). The interplanar distances in the Fourier transform (FFT) (Fig. 2d) were 2.43 Å and 1.80 Å for the NiO nanostructures and Ni nanospheres respectively. Both distances match with that of the well-defined cubic phase of NiO and metallic Ni. The electron
diffraction pattern (also in Fig. 2d) shows diffraction effect with some bright spots that lay on the diffraction rings. Both the rings and spots confirm the polycrystallinity of the species, and also evidence the mixture of the NiO and Ni in NiO/Ni nanopowders. The metallic Ni nanoparticles are very unstable under the electron beam. The structure degrades as observed in the diffuse streaking appearing in the FFT. The rings were identified and assigned with the planes (220) and (111) which lattice distances corresponds to \( \sim 2.04 \) and \( 2.43 \) Å, respectively, at the SAED (Selected Area Diffraction) patterns of NiO. Additionally, the diffraction pattern of Ni was more difficult to be observed due to the mentioned liability and its lower crystallinity, but faint points corresponding to (200) lattice distance of Ni \( \sim 1.80 \) Å are also identified.

The surfaces of the bare NiO nanoplatelets were also modified with a polyelectrolytes multilayer to induce changes in their packing in the electrode microstructure, especially in the exposed specific surface and the porosity, when they were shaped by EPD. The multilayer was built up following the layer by layer methodology which consisted on the alternative adsorption of polyethilenimine and polyacrylic acid as polycation and polyanion respectively. The details of the process have been previously reported elsewhere[35,36]. The samples here analyzed were prepared with NiO nanoplatelets modified with a final polyelectrolyte multilayer of 5 layers, here labelled as NiO-5LbL.

A scheme of the nanostructures and PC electrode processing is shown in figure 3.

![Scheme of the processing of NiO, NiO/Ni and NiO-5LbL nanostructures and PC electrodes](image)

**Fig. 3.** Scheme of the processing of NiO, NiO/Ni and NiO-5LbL nanostructures and PC electrodes

The electrochemical response of Ni foams fully covered by NiO, NiO/Ni and NiO-5LbL nanostructures were firstly determined with comparative purposes. Figure 4 shows the results of these analyses.
The CVs were scanned for a potential window between 0.0−0.5 V, avoiding the effect of oxygen evolution reaction (OER) on the NiO surface evidenced at 0.6 V by other authors [41,42]. All CV curves of the figure 4a presented faradic profile with oxidation and reduction reversible peaks associated to the charge and discharge processes corresponding to the following redox reaction:

\[
\text{NiO} + y\text{OH}^- \leftrightarrow y\text{NiOOH} + e^-
\]

where, the NiOOH is formed at the surface of the NiO during the cycling in the KOH aqueous solutions [43].

Here the electrodes capacity is mainly caused by the redox contribution since the shape of the CVs is distinguished from that of EDLC, which is usually close to an ideal rectangle. However, various thermodynamic and/or ion transport barriers occurred during the faradaic reactions, which cause the non-ideal behavior of pseudocapacitance. Ohmic loss resulting from the electrolyte diffusion within the porous electrode or electrolyte concentration depletion can cause the irreversibility of the redox reaction [44]. In battery-type materials, the potentials separations (oxidation potential-reduction potential, EO-ER) obtained from the cyclic
Voltamograms are often with rather large potential separation (greater than 0.1 to 0.2 V) [45]. The potential separation of our three systems are in this range within values of 0.10, 0.11 and 0.14V for NiO, NiO/Ni and NiO-5LbL respectively, which indicates that NiO/Ni and NiO-5LbL could be treated with battery-type electrode whereas the NiO electrode could be more closed to a pseudocapacitor.

In addition, according to the voltammograms, the current density of the NiO-5LbL electrode is higher than at NiO electrode and it suggests a higher intercalation rate of electrolyte ions along the electrode free surface leading to a higher rate of hydroxide/oxide formation. Moreover, the larger area under the curve for the NiO-5LbL electrode indicates higher efficiency in the capacitive characteristics at the electrode/electrolyte interface. This suggests that the increase of the specific surface area, produced as a consequence of the electrode modification (by the adsorption of the polyelectrolyte multilayer), generates more active sites where reactions take place.

On the other hand, current density also increases when Ni nanospheres are deposited onto NiO nanoplatelets, and in all cases (NiO-5LbL and NiO/Ni electrodes) a significant shift of the potential window was found referred to the NiO electrode behavior. Both the center of the oxidation and reduction peaks shifted toward higher potentials. Such phenomena could be related to the increasing roughness on the electrode surface, as well as the fast ionic/electronic diffusion rates during the charge and discharge processes [28].

These results sustain that the capacitive properties of the NiO electrode can be improve both by the increase of porosity, and by the precipitation of metallic Ni onto the surface of the NiO nanoplatelets. This is also supported by the capacity vs scan rate curves. Figure 4b displays the variations of specific capacitance values (calculated by the integration of the cathodic peak areas) with the scan rate for the three types of electrodes. Similar tendencies with gradual decreases of the capacitance values were herein observed. In addition, the cycling stability of the electrodes was measured by galvanostatic charge/discharge curves. The three discharge profiles of the cycles tenth were plotted in figure 4c. All curves showed three similar processes. However, NiO-5LbL and NiO/Ni electrodes display prominent voltage plateaus, resulting from NiO/NiOOH phase transition (Faradaic contribution), followed by a sharp voltage drop by concentration polarization, corresponding to an Electric Double Layer Contribution (EDLC). Noting that NiO/Ni electrode exhibits the lower activation polarization which could be also associated to the fast reversibility of this electrode. The specific capacitance values were also calculated and plotted vs. the number of cycles in figure 4d leading to expected different results in values and retention capacity.
Table 2 collects the specific capacitance values corresponding to the 10th cycle, and also the energy density and power density values for the different NiO-based electrodes shaped by electrophoretic deposition (EPD) on Ni foams, and sintered at temperatures ≤ 375°C in Ar. These values of capacitance were considered with comparative proposes since the EIS graphs were also measured for the 10th cycle.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Substrate</th>
<th>Capacity/ F g⁻¹ of the 10th cycle at 2 A g⁻¹</th>
<th>Energy Density/ W h kg⁻¹</th>
<th>Power Density/ W kg⁻¹</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO/Ni</td>
<td>Ni foam</td>
<td>~750</td>
<td>375</td>
<td>52.4</td>
<td>1008</td>
</tr>
<tr>
<td>NiO</td>
<td>Ni foam</td>
<td>~250</td>
<td>125</td>
<td>17.4</td>
<td>1085</td>
</tr>
<tr>
<td>NiO-LbL</td>
<td>Ni foam</td>
<td>~1000</td>
<td>500</td>
<td>69.4</td>
<td>1176</td>
</tr>
</tbody>
</table>

EIS is a steady state method used to obtain electric response of an electrochemical cell to an applied AC potential over a range of frequencies. It is usually measured with a very small input signal, which does not perturb the system much [46]. It was herein used to discriminate the effects of each microstructural contribution and determine the electron charge-transfer resistance and the storage mechanisms of the different proposed electrodes microstructures. The influence of the type of substrate/collector was firstly analyzed by using the bare NiO films, considered as the initial reference film. Current collectors of SS foil, Cu foil, Ni foil and Ni foam were covered with ~1 mg of bare NiO deposited by EPD (50 μA/ cm² and 240 s for the SS foils and 1.5 mA cm⁻², 120 s for Ni and Cu Substrates) followed by a thermal treatment at 325°C during 60 minutes.

The results of these EIS measurements are included in table 3, where Rs is the resistance of electrolyte; Rct is the resistance of charge transfer; and CPE is the constant phase element of capacitance. Nyquist plots and bode phase plots are displayed in Fig. 5a and 5b respectively. The equivalent circuit used is included in Fig. 5c. All experimental data were fitted with errors below the 10%. Moreover, no significant differences were found among the three measurements carried out for each electrode. Typically, this kind of materials shows two differentiated parts on the Nyquist plot. In the high frequency range, the semicircle is related to the electronic resistance and the charge-transfer impedance. It is well-know that a big semicircle represents a large resistance in the electronic charge-transfer. Meanwhile, in the low frequency region, the nearly vertical straight lines correspond to the ion diffusion process within the electrodes structure. A vertical line of 90° phase angle indicates an ideal capacitor.

The deviation from the vertical line to phase angles < 90° can indicate pseudo-capacitive behavior. Additionally, the Bode plots allow comparing the maximum phase angle (Φ\textsubscript{max}) and relaxation time constant (τ\textsubscript{0}) of the prepared electrodes, which define the ideal capacitor for Φ\textsubscript{max} = 90° and the minimum time needed to discharge the stored energy with more than 50% efficiency respectively [47],[48]. To determine τ\textsubscript{0}, the corresponding frequency is inversely related to the relaxation time constant at which the phase angle (Φ) is −45° [49,50]. It represents a transition for the PC from a resistive to a capacitive behavior and is related to the cell power. A lower τ\textsubscript{0} indicates a higher power capability (fast charge-discharge) of a PC.

### Table 3. Fitted EIS parameters of the NiO films prepared onto different current collector.

<table>
<thead>
<tr>
<th>Collector</th>
<th>Film</th>
<th>Mass</th>
<th>Rs/Ω</th>
<th>Rct/Ω</th>
<th>CPE-P</th>
<th>τ\textsubscript{0}/ms</th>
<th>Φ\textsubscript{max}/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni foil</td>
<td>NiO</td>
<td>1.2</td>
<td>-</td>
<td>0.21</td>
<td>0.90</td>
<td>26.3</td>
<td>82</td>
</tr>
<tr>
<td>Cu foil</td>
<td>NiO</td>
<td>1.1</td>
<td>1.53</td>
<td>0.48</td>
<td>0.87</td>
<td>34.5</td>
<td>80</td>
</tr>
<tr>
<td>SS foil</td>
<td>NiO</td>
<td>1.6</td>
<td>1.17</td>
<td>2.14</td>
<td>0.77</td>
<td>83.3</td>
<td>74</td>
</tr>
<tr>
<td>Ni foam</td>
<td>NiO</td>
<td>1.1*</td>
<td>-</td>
<td>1.71</td>
<td>0.85</td>
<td>8.0</td>
<td>76</td>
</tr>
</tbody>
</table>

* This electrode is considered the reference and its characterization is also included in table 4 and 5.

Related to the collector nature, at the insert on figure 5a it can be seen that, both of the metallic Ni current collector, foil and foam (Fig 5d), do not show the arc corresponding to the electrolyte resistance at high frequencies, Rs. This resistance can disappear due to the faradic reactions of the collector which compete with those provide by the electroactive material. In this case, the absence of semicircles would indicate that a diffusion process is prevailing beyond a capacitive one [51]. The biggest single depressed semicircle in the high frequency region observed for SS substrate indicates that the resistance between the NiO films and the collector is higher than Cu and Ni substrates (table 3). This phenomenon was expected since it is tabulated that the stainless steel presents a lower percentage of conductivity than Cu and Ni. Thus, the trend attending to the nature and the shape of the substrate continues as follows: R\textsubscript{SS} > R\textsubscript{Cu} > R\textsubscript{Ni}. The Cu substrate is slightly more resistant than Ni, which can lie in the electronic configuration. Cu has the electrons in an energy state more stable (Ar, 3d\textsuperscript{10}, 4s\textsuperscript{1}) than Ni (Ar, 3d\textsuperscript{8}, 4s\textsuperscript{2}), what makes the electron sharing easier in Ni foils.

The NiO films onto Ni and Cu foil-shaped substrates exhibit the lower Rct values (0.21 and 0.48 Ω) while the NiO film made on SS substrate shows the highest one (2.14 Ω). The value of Rct corresponding to the coating on the Ni foam is higher than that of the Ni plate, increasing one order of magnitude, from 0.21 to 1.71 Ω. This can be explained because the electronic charge-transfer depends on the collector nature but also on the collector section. The section of a dense foil-collector is wider than the conductive section of the Ni foam, so the electronic...
transfer in foil-collectors is promoted [52] and a smaller arc is obtained in the Nyquist plot, which can be considered even negligible.

Nevertheless, the use of the 3D Ni substrates as collector, with an interconnected macroporosity of about 200 μm, is justified due to the increase of exposed surface that compensates the final electrochemical response [53]. In addition, the use of the EPD process allows distributing the same amount of electroactive material (~1 mg) onto the 3D foam instead over one side of the 2D foil, resulting in homogeneous and continuous films covering Ni threads of the foam skeleton with a controllable and lower thicknesses (as lower as 760 nm) [27]. Although the CPE-P values in table 3 does not reflect this fact, the 3D foam coatings should exhibit a more effective electrochemical performance of a determined deposited mass.

Bode plots of the four electrodes were also drawn in figure 5b to analyze the relaxation time constant (τ₀) for determining the discharge rates of the electrodes. Ni foam electrode shows a lower τ₀ (8 ms) than Ni and Cu foils (26.3 and 34.5 ms respectively) being the SS foil electrode which presents the highest value (83.3 ms). The rapid frequency response (low τ₀) as well as the shape and the phase angle of the Bode plot indicate that the NiO coating the Ni foam electrode has an improved rate capability and capacitance retention at high charging/discharging rate, which could be attributed to the higher accessible surface area in

the unique hierarchical porous network [50]. Additionally, the $\tau_0$ value is within the range of the electrochemical double layer capacitors (EDLC) and is lower than the commercial Carbon based EDLC ($\tau_0 = 10$ s) [54], which supports the presence of improved ion transport by the electrodes [33,34] when the porous structure of the Carbon is emulated.

However, the bode plot of the NiO deposited on Ni foams shows a protuberance in the resistive range, for phase angles ranging $-45^\circ < |\Phi| < 25^\circ$, not visible for NiO films deposited on 2D foil-collectors. This resistive effect decays the capacitive behavior evidenced by the lower values of CPE-P and $\Phi_{\max}$ collected in the table 3, which vary from 85 and 76° for the NiO film in Ni foam to 90 and 82° in the Ni foil. The slightly increase of the charge-transfer resistance in electrodes shaped on Ni foams reflects the presence of a large Ni-NiO interface due to the tridimensional structure of the NiO film. Although Ni-NiO interface area increases with the use of 3D foam-collectors, which promotes the increase of charge-transfer resistance, the increase of the active surface improves the capacitance retention at high charging/discharging rate. The 3D collectors deliver values of power density of 1085 W Kg$^{-1}$ for an accumulated energy of 17.4 W h Kg$^{-1}$.

The analysis of the current collectors promotes the testing of electrodes with a larger porous microstructure. In this sense, the electrochemical performance of the NiO-SLbL microarchitecture was also measured by EIS. The LbL surface modification of NiO nanoplatelets is a processing strategy addressed to enhance the electrode capacitance by increasing the macro- mesoporosity of the active material deposited by EPD in Ni foams. In fact, NiO-SLbL electrodes achieve specific capacitances above 600 F g$^{-1}$ at 2 A g$^{-1}$ (300 C g$^{-1}$) (figure 4). Figure 6a and 6b shows a comparative of the Niquist and Bode plots respectively for the NiO reference electrode and the NiO-SLbL electrode. Both electrodes have the same mass ($\approx 1$mg) and they were prepared under similar conditions of EPD by using Ni foam as collector. The modification on the surface of the NiO nanoplatelets by the polyelectrolyte multilayer modifies the packing in the deposited material which are also shown in the micrographs and in the schematic illustration of figure 6c.
Characteristic parameters of NiO and NiO-5LbL electrodes obtained from the adjustments with Z-view of these EIS curves are summarized in table 4.

**Table 4.** Comparative of the fitted EIS parameters of the NiO-5LbL and the NiO electrodes

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Coating</th>
<th>Mass</th>
<th>Rct/Ω</th>
<th>CPE-P</th>
<th>τ₀/s</th>
<th>Φₑ max/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni foam</td>
<td>NiO</td>
<td>1.1</td>
<td>1.71</td>
<td>0.85</td>
<td>8.0</td>
<td>76</td>
</tr>
<tr>
<td>NiO-5LbL</td>
<td>NiO</td>
<td>3.65</td>
<td>0.90</td>
<td>18.0</td>
<td>82</td>
<td></td>
</tr>
</tbody>
</table>

*This electrode is considered the reference and its characterization is also included in table 3 and 5

The CPE-P value of the NiO-5LbL electrode (0.90) is higher than the value of the NiO coating indicating that benefits of the exposed surface and the porosity increase in the electrode microstructure, which is especially relevant in the electrochemical response in spite of the significant increase of Rct value (3.65 Ω). Although there were no significant differences in the slope of both Niquist curves, the results seen in the bode plots (Figure 5b) showed a phase angle value of -82° for NiO-5LbL, which is closer to -90° than the phase angle of the NiO.
reference, 76°. It implies that the porous NiO-5LbL electrode has stronger capacitive behavior [8, 26] than the NiO reference electrode, maintaining a lower \( \tau_0 \) constant (18ms) that is a quick charge/discharge rate. Those electrodes are able to achieve a higher power density, 1176 W Kg\(^{-1}\) tripling the energy accumulation, 69.4 W h Kg\(^{-1}\), and demonstrating that exposed surface overdues the increment of charge-transfer resistances, improving the electrochemical performance of PC electrodes.

However, the main drawback of many ceramic semiconductor electrodes is the poor electron transport along their structure. Consequently, we propose the reduction of the Rct values of the NiO-based electrodes by including a non-noble metal, such as the Ni NPs, by synthesizing NiO/Ni core-shell nanostructures. Figures 7a and 7b compare the Niquist and Bode curves corresponding to the NiO/Ni electrode and the NiO reference electrode, also including the NiO-LbL coating results for comparative proposes. The data of the naked collector has also been included herein. The compared electrodes were also shaped by EPD under similar conditions up to achieve 1 mg coating on the Ni foam (15 mA cm\(^{-2}\) and times ranging from 30-90 s), followed by a thermal treatment at 325°C during 60 minutes in Ar atmosphere.

Since electronic transport is easier on metal than semiconductors, naked Ni foam exhibited a steeper slope and a smaller semicircle than those coated by NiO and NiO/Ni nanoparticles. Naked nickel foam has no depressed semicircle in the high frequency region due to the absence of coating. This reason could also explain why the NiO/Ni core-shell nanocomposite has a charge-transfer resistance lower than NiO, 1.55 and 1.71 \( \Omega \) respectively. The inclusion of the Ni NPs favors the electron transport through the semiconductor microstructure, reinforced by the contribution of the microporosity in the NiO/Ni core-shell (Figure 2).

![Fig. 7](image_url) (a)Nyquist and (b)Bode plots of Ni foam and NiO, NiO/Ni coatings onto Ni foam, also including
Moreover, the NiO/Ni electrode showed better capacitive response than the electrode without Ni NPs. The straight line in the low frequency region was steeper than the slope of the NiO/Ni electrode. The closer value to the unit means a best capacity which is also confirmed by the CPE-P value of table 5. These CPE-P values increased from 0.85 to 0.90 while \( \Phi_{\text{max}} \) also increased from -76° to -81°. In this case, the relaxation time constants obtained from Bode curves were similar (\( \tau_0 = 11 \text{ ms} \)), thus the variations of the capacitance retention at high charging/discharging rate were not significant if it is compared with NiO-5LbL electrodes, achieving a power density of 1008 W Kg\(^{-1}\) with an accumulated energy of 52.4 W h Kg\(^{-1}\).

In order to deepen into the behavior of the metal-ceramic system, the influence of the sintering treatment and the consolidation level of the ceramic microstructure were also investigated. Both the electron transport and the ion diffusion can be affected by the pathways or channels of connection inside of the semiconductor microarchitectures. If the film is continuous and too dense, the specific surface area and the porosity are reduced and part of the deposited mass of the active material is hidden to the faradaic reactions. Sintering times and/or temperatures should be optimized to form necks among nanoplatelets and NPs avoiding their complete densification so maintaining the meso and microporosity. For this purpose, 1 mg films of NiO/Ni core-shell nanostructures deposited on 3D foams were sintered at three different thermal treatments in Ar atmosphere. Table 5 summarizes the EIS data and the details the thermal conditions chosen for each electrode. The electrode annealed at 325 °C during 15 minutes exhibits a higher transfer charge resistance (\( R_{\text{ct}} = 2.43 \Omega \)) than the electrodes treated at a higher temperature, 375°C (\( R_{\text{ct}} = 1.64 \Omega \)), or for a longer time, 60 minutes (\( R_{\text{ct}} = 1.55 \Omega \)), indicating that the softest thermal conditions lead to a lower connected nanostructures[30].

**Table 5.** Fitted values of the as-prepared NiO/Ni electrodes with different coatings onto Ni foam.

<table>
<thead>
<tr>
<th>Collector</th>
<th>Film</th>
<th>Mass</th>
<th>Thermal Treatment</th>
<th>Rct / Ω</th>
<th>CPE-P</th>
<th>( \tau_0 )/ ms</th>
<th>( \Phi_{\text{max}}/° )</th>
</tr>
</thead>
<tbody>
<tr>
<td>bare</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>0.87</td>
<td>1</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>NiO</td>
<td>1.1*</td>
<td>325°C 60 min Ar</td>
<td>1.71</td>
<td>0.85</td>
<td>8</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>Ni foam</td>
<td>1.0</td>
<td>325°C 15 min Ar</td>
<td>2.43</td>
<td>0.84</td>
<td>6</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>NiO/Ni</td>
<td>1.1</td>
<td>325°C 60 min Ar</td>
<td>1.55</td>
<td>0.90</td>
<td>11</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>375°C 15 min Ar</td>
<td>1.64</td>
<td>0.90</td>
<td>11</td>
<td>81</td>
<td></td>
</tr>
</tbody>
</table>

In the Nyquist plot recorded for this NiO/Ni at different thermal conditions on figure 8a it can be observed that the electrode annealed at 325 °C during 15 minutes displayed less steep slope that the other two, which were very similar, confirming that its capacitive behavior can be improved by adjusting slightly the thermal treatment. The CPE-P value (0.84) of this poor sintered electrode, and then the maximum phase angle achieved at the Bode plot ($\Phi_{\text{max}} = -76$), were also lower than for the other sintering conditions, while the relaxing time decreases up to 6 ms. Those data evidence that the capacitive response could be deleterious when charge-transfer resistance increases and it is not compensated in the microstructure as occurs in the case of the NiO-5LbL electrodes.

Bode plot in figure 8b shows how the effect of the resistance decreases when the thermal treatment temperature and time increase in the sintering process. Similar improvements are shown for sintering at 325°C during 60 min and 375°C during 15 min. These plots displayed phase angle values of $-81^\circ$ at low frequency, corroborating that the increase of the time and temperature approach the electrochemical behavior of the electrodes to that of the ideal capacitor.
Additionally, the influence of the deposited mass in the charge transfer resistance was also evaluated. For this purpose, electrodes with less amount of electroactive mass, 0.6 mg, were prepared and sintered. The EIS measurements were compared with the obtained data for prior electrodes of ~1 mg of mass (table 5). Plots in figure 9a and 9b compare Nyquist curves at sintering conditions of 325 °C - 60 min and 375 °C - 15 min, respectively. For both, the higher is the deposited mass the steeper is the straight part of the Nyquist curve at lower frequencies, being the difference larger for the NiO/Ni electrodes annealed at 375 °C for 15 min. Also, the Rct values increases, being higher the charge-transfer resistance for the electrode treated at a higher temperature. The detriment of the whole electrochemical response determined for the lower deposited mass for both thermal treatments. Figure 9d evidences the presence of small naked surfaces on partially uncover Ni foams which limits the NiO/Ni nanostructure connectivity, confirming that a minimum amount of deposited mass is needed to fully cover the collector, which in our case is close to 1 mg.

Fig. 9. a) and b) Nyquist plot, and (c) Bodes plot of different NiO/Ni deposit mass onto Ni foams. d) FESEM image of a Ni foam partially coated with 0.6 mg of NiO/Ni nanoparticles

To reach a better understanding about the ionic and electronic charge carriers and their diffusion, the height of the current peaks of the CV (not showed here) as well as the diffusion coefficient (D) have been plotted in figure 10 as functions of the scanning rate.

![Graphs of figure 10](image)

**Fig. 10.** a) The relationship between \(I\) and scan rate, constructed from anodic peak of the corresponding CV, b) Diffusion coefficient calculated by the Randles–Sevcik equation vs scan rate and c) NiO-Ni 325-1h-Ar and d) NiO-5LbL electrodes microstructures, which includes schemes of their electronic transfer.

The relationship of peaks current versus scan rate of both electrodes, figure 10a, indicates a fast surface-controlled Faraday process for lower scan rates (around 5 mV/s), whereas final appreciable exponential regime evidences the battery-like behaviour of the electroactive material (at scanning above 10mV/s) [55]. The plateau of the diffusion limiting current is clearly achieved for both electrodes at a scan rate of 50 mV/s, being highly limited for the NiO-5LbL electrode since the mass transport rate is widely restricted by its porous microstructural feature. In fact, while the value of the diffusion coefficient, D, of the NiO-Ni electrode maintains partially stable with the scan rate, D decreases significantly for the NiO-5LbL electrodes (figure 10b). Consequently, the larger porosity of the NiO-5LbL limits the adsorption of the solvated ions and then the diffusion control.

It is also remarkable that the movement of the charge carriers is more favored in the NiO-Ni electrode than the NiO-5LbL electrode. This is directly related to the fact that the presence of metallic Ni nanoparticles in the semiconductor microstructure is benefiting the electron transfer, as the calculated $R_{ct}$ value ($1.55 \Omega$) confirmed in table 5. The schemes of figures 10c and 10d propose two alternatives conduction pathways due to the manipulation of dissimilar arrangement of the NiO nanoplatelets in the electrodes microstructures. The former shows a more linear route than the interrupted trajectory of the latter, where the electronic carriers find dislocated nanoplatelets with grains boundary sliding [56]. Despite of the $R_{ct}$ value ($3.64 \Omega$) and the $D$ value of the NiO-5LbL electrode were higher and lower respectively than the values of the NiO-Ni electrode, the specific capacitance value was higher for the NiO-5LbL, which means that the effect of a high exposed surface area is predominating over the effect of the connectivity among nanoparticles.

**Conclusions**

An extensive analysis of the physicochemical features (exposed SSA and nanoparticles connectivity by separately) of different Ni-based semiconductor 3D electrodes microarchitectures allowed to understand the contribution of the electron transport and the ion diffusion to the final electrochemical response.

The two different colloidal strategies followed allowed tuning the 3D electrodes microstructures in order to discriminate the effects produced by both electrochemical contributions. Firstly, increasing the SSA by the adsorption of a polyelectrolyte multilayer onto nanoplatelets surfaces (NiO-5LbL) and later enhancing the nanoparticles connectivity by the inclusion of a metallic phase in the semiconductor material (NiO/Ni). Moreover, the study about the influence of the collectors used minimized the additional resistances values due to the electrochemical performance of the NiO nanoplatelets.

Electrodes shaped by EPD depend on the electronic charge-transfer of collectors, mainly determined by its nature and conductive section. For a similar collector configuration, in Cu and Ni foils, differences in the charge-transfer resistance is a consequence of the electronic configuration. Considering Ni collectors, NiO nanostructured films on Ni foams improve rate capability and capacitance retention at high charging/discharging rate, exhibiting a relaxation time constant ($\tau_0 = 8 \text{ ms}$) in the same range of EDLC capacitors. However, the charge-transfer resistance of electrodes shaped in this configuration is relatively high ($R_{ct} = 1.71 \Omega$) due to the lower conductive section of the 3D collector (Ni foam) and the larger interface collector/ electroactive material (Ni/NiO), which is widely compensated by the high accessible

surface area which provides a rapid ion transport in the unique hierarchical porous 3D network.

The results obtained in EIS analysis are in concordance with the CV and CP curves and confirms the benefits of having a high exposed surface area and porosity increase in the NiO-5LbL electrode microstructure. This strengthen the capacitive contribution of the electrochemical response (CPE = 0.90 and $\Phi_{\text{max}} = 0.82^\circ$) and $\tau_0$ of 18 ms, in spite of the significant increase of $R_{\text{ct}}$ value (3.65 $\Omega$).

On the other hand, the precipitation of Ni NPs and micropores favor the electron transport through the semiconductor NiO microstructure, leading to a lower charge-transfer resistance (1.55 $\Omega$) for electrodes shaped by NiO/Ni core-shells deposition. Moreover, the NiO/Ni electrode maintains a high capacitive response with CPE = 0.90, $\Phi_{\text{max}} = 0.81^\circ$ and $\tau_0$ of 11 ms.

The deep study of the thermal consolidation of the ceramic microstructure of the active mass of the NiO/Ni electrodes demonstrates that the capacitive response can be deleterious when charge transfer resistance increases and it is not compensated in the microstructure by enough faster ion diffusion, like occurs in the case of the NiO-5LbL electrodes. Finally, a minimum amount of deposited mass is needed to fully cover the collector and enhance the capacitive response and limits the charge-transfer resistance.

Acknowledges
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References


Figure Captions

Fig. 1. FESEM micrographs and schematic illustration of the synthetized powders of a) NiO nanoplatelets and b) core-shell NiO/Ni.

Fig. 2. a) XRD patterns of the β-Ni(OH)₂, NiO and NiO/Ni powders. b) N₂ gas adsorption-desorption isotherms and pore size distribution of as-prepared β-Ni(OH)₂, NiO calcined at 325 °C and NiO/Ni powders. And c) and d) HRTEM images of NiO/Ni powders (where different interplanar distance can be observed depending on the nanoparticle NiO and Ni respectively). Electron diffraction pattern of the sample was included at the inset.

Fig. 3. Scheme of the processing of NiO, NiO/Ni and NiO-5LbL nanostructures and PC electrodes

Figure 4. Comparative of the electrochemical response of the three electrodes NiO, NiO/Ni and NiO-5LbL. a) Cyclic Voltammograms (CV) at a scan rate of 10mV/s, b) variation of the specific capacitance values with the scan rates, c) Galvanostatic discharge profiles and d) Cyclic Chronopotentiometric measurements made at a current density of 2A/g.

Fig. 5 Nyquist plot (a) and bode phase plot (b) of NiO coatings onto different substrate. Equivalent circuit used to adjust the data c) and images and detail of the NiO films on Ni foil and foam respectively d).

Fig. 6. (a) Nyquist plot, (b) Bodes plot of NiO and NiO5LbLcoatings and (c) FESEM images and schematic illustration of the coatings made with NiO and 5LbL nanoparticles onto Ni foams

Fig. 7. (a)Nyquist and (b)Bode plots of NiO and NiO/Ni coatings onto Ni foam

Fig. 8. (a) Nyquist plot, and (b) Bodes plot of NiO/Ni electrodes at different TT

Fig. 9. a) and b) Nyquist plot, and (c) Bodes plot of different NiO/Ni deposit mass onto Ni foams. d) FESEM image of a Ni foam partially coated with 0.6mg of NiO/Ni nanoparticles

Fig. 10. a) The relationship between I and scan rate, constructed from anodic peak of the corresponding CV, b) Diffusion coefficient calculated by the Randles–Sevcik equation vs scan rate and c) NiO-Ni 325-1h-Ar and d) NiO-5LbL electrodes microstructures, which includes schemes of their electronic transfer