



Design of nanohybrids based on layered double hydroxides and electrochemically reduced graphene oxide for energy applications

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ABSTRACT

An innovative electrosynthesis method recently developed by our research group for the composite Ni/Al layered double hydroxide (LDH) intercalated with electrochemically reduced graphene oxide (ERGO) has been successfully applied to the deposition of Co/Al LDH ERGO on Grafoil sheets, demonstrating the high versatility of the procedure. Four materials have been electrosynthesized and characterized structurally and morphologically: Ni/Al LDH, Ni/Al LDH ERGO, Co/Al LDH, and Co/Al LDH ERGO. A deep investigation of their electrical and electrochemical properties in terms of Faradaic processes involving the redox active metal centers has been carried out. The effect of the presence of ERGO in the composite materials has been studied, highlighting an improvement of the electrical conductivity and the Faradaic process kinetics only for the Ni based LDH. The Co/Al LDH ERGO modified Grafoil was investigated as positive electrode in an asymmetric supercapacitor in solution and its performance compared with the one exhibited by the pure LDH. Also in such a case, the intercalation of ERGO inside the Co/Al LDH has not affected significantly its properties in terms of capacitance, but only has shown a positive effect on the material stability.

1. Introduction

Layered Double Hydroxides (LDHs) are very promising materials for electrochemistry, as demonstrated by their wide use in several applications that span from energy storage and conversion to sensing [1–4]. Although LDHs are widely described in the literature, they are not employed yet for the production of commercial devices, as they do not satisfy the high specifications required in terms of electrical conductivity [5] and stability [6], under operating conditions. The synthesis of composite materials is a successful approach to overcome these limitations. To this aim LDHs are combined with carbonaceous nanomaterials, such as nanotubes and graphene, to produce LDH hybrid composites with boosted performances that are maintained under operative conditions for a long time [7–9]. However, further research efforts are needed to identify guidelines necessary for a rational design of these materials.

LDHs general formula is $M(II)_{1-x}M(III)_x(OH)_2]^{x+} (A_n^{x/n-}) \cdot mH_2O$, where M(II) and M(III) are the metal cations that are bivalent and trivalent, respectively. The cations exhibit an octahedral coordination,

which is the same as brucite $[Mg(OH)_2]$, but the excess of positive charge, due to the presence of trivalent cations in the 2D hydroxide layers, requires the intercalation of anions in the interlayer region to maintain the electroneutrality [10,11]. Due to tunable chemical composition, relatively low cost, environmentally friendly features, ion-exchangeability and large surface area, LDHs have been found to be extraordinary materials for a great number of applications, ranging from electrochemistry [12–14] to industrial catalysis [15], environmental decontamination [16] and drug delivery systems [17]. If M(II) is redox active, LDHs become somewhat electrically conductive and could be employed for the development of electrochemical technologies, for instance as pseudo capacitive materials for energy storage devices [18], as electrode coatings for amperometric or potentiometric sensors [19] and as catalysts for the water splitting reaction [20].

However, the LDHs electrical conductivity is still low and does not allow the flow of the high current density required by the most performant devices [5,6]. As already stated above, this drawback can be overcome synthesizing composites made of LDHs and carbon

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nanomaterials.

Our research group has recently developed a protocol to electro-synthesize materials based on Ni/Al LDH and reduced graphene oxide [21]. The application of a cathodic potential scan allows to get in a single synthetic step both the production of the OH⁻ necessary for the precipitation of the hydroxide on the conductive support, and the electrochemical graphene oxide (GO) reduction to obtain electrochemically-reduced graphene oxide (ERGO). This procedure is very fast (it takes a few minutes) and simple if compared with bulk synthesis which requires: i) at least a few hours to be completed; ii) a further modification step that often needs the use of additional reagents (for example binders).

The electrodes modified with Ni/Al LDH ERGO have been assembled to fabricate a hybrid supercapacitor, which exhibited faster charge and discharge processes than the LDH as such and maintained a high performance even after prolonged use [21].

Taking into account graphene (G) as the nanomaterial capable to increase the electrical conductivity of LDHs, we can state that it has complementary properties with LDHs, from both a structural and electrochemical point of view [19,21]. It is an excellent conductor [22], but at the same time, it does not possess a sufficient number of active sites to give significant Faradaic processes [23]. Since the formulation of composite materials is helped by the complementarity of the involved chemical structures, GO is more commonly employed due to its easier processability related to the water solubility [24]. Several synthetic routes exploit GO as starting material, and its subsequent reduction restores almost completely the peculiar characteristics of graphene. Furthermore, graphene oxide exhibits negatively charged oxygenated groups that can strongly interact with positively charged hydroxide sheets. For these reasons, several LDH/graphene composite materials were synthesized by bulk chemical synthesis [25] exploiting the above cited interaction [26,27]. The idea, which underpins these materials, is that the electron charge transport easily occurs through carbon skeleton, while the redox active hydroxides undergo the Faradaic processes required to display high pseudo capacitance or electrocatalytic properties. In addition, the graphene layers also represent a steric hindrance that slows down the LDH reorganization processes that take place during the operativity of the LDHs based electrochemical devices, and thus the relevant composite materials generally display a high stability in their performance [19].

In this work, we have optimized the electrosynthesis of composite materials based on different LDHs (Ni/Al and Co/Al) and ERGO. Ni/Al LDH was chosen as a benchmark of a robust synthesis that ensures a repeatable and reproducible redox behavior. The oxidation process of Ni/Al LDH leads to a distortion of the crystal lattice due to a transition from the α to the γ phases [28]. The Faradaic process involving the Ni (III)/Ni(II) couple is not fully reversible, even if it is characterized by a sharp electrochemical wave. Conversely, the Co/Al LDH exhibits a more complex electrochemical behavior, characterized by a first anodic irreversible process, in which a partial oxidation of the cobalt centers occurs. The electrochemical response of the composite LDH is pseudo-capacitive, with very broad redox peaks. The electrodes obtained after modification with the two LDHs/ ERGO were extensively characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and electrical measurements to determine their conductivities, and compared with the electrodes modified with the two LDHs as such, in order to highlight the effect of the presence of the carbon nanomaterial. Finally, the storage charge capabilities of the composite Co/Al LDH ERGO were investigated and compared with those exhibited by the pure LDH, and a hybrid asymmetric super capacitor (SC) was tested in solution, employing poly(3,4-ethylenedioxythiophene-poly(styrene sulfonate)) as the anodic component and the Co/Al LDH or Co/Al LDH ERGO as the cathodic counterpart.

2. Material and methods

2.1. Chemicals

Nickel (II) nitrate hexahydrate, aluminum nitrate nonahydrate, cobalt (II) nitrate hexahydrate, graphene oxide (4 mg/mL, in water dispersion), polystyrene-sulfonate sodium salt (PSS), ethanol, and 3,4-Ethylenedioxythiophene (EDOT) were obtained from Sigma-Aldrich. Sodium hydroxide and potassium hydroxide were purchased from Merck. All the reagents were analytical reagent grade and used as received. The supporting electrolytes for the electrochemical experiments were 0.1 or 6 M KOH. The salt solutions were prepared with distilled water. Grafoil GTJ (Graphite > 99.8 %) was used as the support and purchased from VED (<https://www.ved.it>). It possessed the following properties: the bulk density was 1.12 g/mL, the resistivity $7.33 \cdot 10^{-4} \Omega \text{ cm}^{-1}$ and the carbon content was estimated at 99.5 %, while the ash content at 0.5 %.

2.2. Apparatus

The majority of the electrochemical experiments were carried out using a single compartment, three electrode cell. Electrode potentials were measured with respect to an aqueous saturated calomel electrode (SCE) or with respect to a mercury/mercury oxide electrode (Hg/HgO). A Pt wire or gauze was used as the counter electrode. The electrochemical deposition and characterization were performed by using a CH Instrument Mod. 660 C, controlled by a personal computer via CH Instrument software. Galvanostatic cycling with potential limitation in constant current mode was performed by using a battery cycler (Neware Battery Testing System). The capacitance of the four investigated materials was estimated from the galvanostatic charge-discharge (GC-D) curves recorded at 20 mA cm^{-2} in 6 M KOH. EIS tests were performed on Grafoil supports modified with LDHs or LDHs ERGO materials in 0.1 M NaOH, at the potential of 0 V at which no Faradaic reaction occurs, and at 0.5 V, at which the response is ruled by Ni or Co redox behavior, in order to learn more about the ERGO effects on the charge transfer processes.

An Autolab PGSTAT20 (Ecochemie, Utrecht, The Netherlands) potentiostat/galvanostat interfaced with a personal computer was used in the electrochemical quartz crystal microbalance (EQCM) experiments, which were performed with a MAXTEK PM-710 device, equipped with 5 MHz-AT cut quartz crystal coated with sputtered Pt (surface area 1.37 cm^2). From EQCM data it was possible to estimate the mass of the electrodeposited LDHs and, therefore, calculate the specific capacitance per gram [29].

Powder X-ray diffraction (PXRD) was performed by means of an X'Pert PANalytical diffractometer equipped with a copper source ($K\alpha$ radiation, $\lambda = 0.15418 \text{ nm}$), operating in reflection mode. The 2θ interval from 5° to 60° was explored (step of 0.066° and counting time of 300 s/point) with a fast X'Celerator detector. The length of coherent domains perpendicular to 003 plane was calculated by Scherrer equation [30]. The morphology of the LDH films was investigated by Field Emission-Scanning Electron Microscopy (FE-SEM) using a LEO 1530 ZEISS instrument equipped with Schottky emitter, operated at an acceleration voltage variable from 5 to 15 keV, and Everhart-Thornley and Inlens detectors for secondary electrons imaging. Energy Dispersive X-ray Spectroscopy (EDS) measurements were performed with an Oxford INCA system equipped with a 30 mm^2 Silicon Drift Detector in order to investigate the chemical compositions.

2.3. Electrodeposition of LDHs

For the electrodeposition of LDHs and LDHs ERGO, Pt or Grafoil supports were employed. Preliminarily, the supports were cleaned to improve the adhesion of the modifier. For Pt electrodes, the surface was first polished to a mirror-like surface by a mechanical cleaning, using

sand-paper, and then the electrode was submitted to an electrochemical treatment consisting in 250 voltammetric cycles between -0.25 V and $+1.30$ V in 0.1 M H_2SO_4 at a scan rate of 1 V s^{-1} . For Grafoil, the surface was rinsed in ethanol for 10 min and then dried to constant weight. The LDH films were deposited on the conductive surface immersed into a freshly prepared solution, containing 0.03 M Ni or Co and Al (from nitrate salts) at a molar ratio of 3:1, by applying four segments of CV between 0 and -1.3 V, vs SCE, at a scan rate of 25 mV s^{-1} for the Ni based material and of 30 mV s^{-1} for the Co based LDH. The co-deposition of LDH and ERGO was carried out using the same parameters adopted for the synthesis of the pure LDH, but an amount of GO into the starting solution equal to 0.05 mg/mL was added. At the end of the synthetic procedure, all the electrodes were gently washed with distilled water, and dried.

The Grafoil modified with LDH, acting as the cathode of the SC, must be prepared the same day when the device is tested, since we have proved that the efficiency of LDHs or LDHs ERGO materials is still high only if they are employed within 24 h since the electrosynthesis.

2.4. Electrodeposition of PEDOT:PSS

As to the anode, poly(3,4-ethylenedioxythiophene-poly(styrene sulfonate)), PEDOT:PSS, has been chosen as the active material. It was electrodeposited on Grafoil starting from a solution containing 0.1 mM PSS and 10 mM EDOT. The mixture of EDOT and PSS was stirred for 45 min until complete dissolution. The deposition was carried out by means of 50 cycles of CV from 0.0 V to $+1.2$ V at 100 mV s^{-1} . At the end of the electrodeposition, the modified electrode was gently washed with distilled water, and dried. The anode of the SC is stable and can be prepared some days before the investigation of the performances in solution.

2.5. In solution set-up of the hybrid supercapacitor

The asymmetric hybrid supercapacitor was composed of two electrodes: the cathode was made of Grafoil modified with Co/Al LDH or Co/Al LDH ERGO, the anode of Grafoil modified with PEDOT:PSS. It was tested in solution in a glass cell containing 6 M KOH, under nitrogen.

All the CVs display a nearly capacitive behavior in the potential range investigated, thus evidencing the charge storage capabilities of the device, when operating in solution.

3. Results and discussion

3.1. Electrochemical synthesis and material characterization

The Grafoil electrode has been directly modified through an electrochemical synthesis, recently optimized by our group for the production of the LDH ERGO material. Briefly, the synthesis was carried out by performing two cycles of cyclic voltammetry in the potential range from 0.0 V to a cathodic value (-1.3 V vs SCE) which was applied to the electrodes immersed in a solution of graphene oxide and the nitrate salts of the divalent and trivalent cations. The cathodic potential induces: i) the water and nitrates reduction, which leads to a pH increase, and thus to the precipitation of the hydroxide sheets on the Grafoil electrode; ii) the partial reduction of graphene oxide for partly restoring the electrical conductivity of graphene sheets.

The thin films were characterized by PXRD to investigate the structure of the electrodeposited materials. All diffractograms exhibit the two typical reflections ascribed to the formation of a layered structure, indexed as 003 and 006, highlighting the formation of the expected LDH. The reflexes are quite broad as usually occurs for electro-synthesized LDHs, as they are poorly crystalline materials.

The interlayer distances (d) have been calculated from the 003 reflections and resulted 0.88 and 0.90 nm for Ni/Al and Co/Al LDH, respectively. They are longer than those usually reported for LDHs

prepared simply by precipitation, likely because greater swelling and disorder are present, as confirmed by larger peaks. However, interlayer distances are comparable with those of samples prepared by electrodeposition in nitrate environment [21,31]. The d values shift toward lower values for the LDH/ERGO composites, i.e. 0.81 and 0.85 nm for Ni/Al and Co/Al, respectively. The displacements support the formation of LDHs where ERGO is intercalated among the hydroxide sheets. In fact, the literature reports that LDH materials wherein the ERGO sheets are alternated with hydroxide layers exhibit d values that are lower than the same LDHs synthesized with nitrate as the counter ion [31].

The peak width of the patterns is different, and since it is in relation with the mean length of the crystal domains in the direction perpendicular to $00l$ planes, it was estimated with Scherrer formula and gave 36 nm for Ni/Al LDH, 31 nm for Ni/Al LDH ERGO, 66 nm for Co/Al LDH and 47 nm for Co/Al LDH ERGO. They are in the same scale range, but Ni containing samples show smaller crystal size as compared to the Co ones, and in both systems the LDH ERGO materials are less ordered than the respective LDHs.

The surface of the LDH films was investigated by FE-SEM (Figs 1 and 2). The Ni/Al LDH exhibits a homogeneous and compact layer with a nanostructured surface due to the very small LDH crystallites (around 40 nm) that appear well interconnected. On the other hand, the Co/Al LDH appears less compact than the Ni/Al LDH, and the crystallites are well visible in Fig. 2 A and look smaller (around 20 nm) than the ones observed for Ni/Al LDH. In the materials synthesized in the presence of GO, the morphology is different for both LDHs. The structure due to ERGO sheets is well evident in Fig. 2 B and D, even if the LDH crystallites are visible in the picture. The bulky ERGO layers, which are bigger than the LDH crystallites, act as a framework in the LDH ERGO material and thus they determine the dimensions which are in the range of 100 nm. EDX analysis has been performed to check the ratio between divalent and trivalent cations in the hydroxide layers. Our previous studies have demonstrated that the potentiodynamic synthesis here adopted allows to synthesize LDHs with almost the same molar ratio $\text{Me}^{2+}/\text{Me}^{3+}$ as the one of the deposition bath (3:1). In fact, the Co/Al values are 2.81 and 2.66 for Co/Al LDH and Co/Al LDH ERGO, respectively, while the Ni/Al ratios are 2.43 and 2.61 for Ni/Al LDH and Ni/Al LDH ERGO.

Summarizing PXRD data, morphological observations and chemical analysis suggest the formation of materials wherein the LDH layers and ERGO sheets alternate in the composites. The morphology of such materials follows the framework determined by the ERGO sheets, that are well visible in SEM images. Finally, EDX analysis confirms that the $\text{Me}^{2+}/\text{Me}^{3+}$ ratio is rather close to 3 for all the synthesized materials.

3.2. Electrical characterization of LDH thin films

In order to underpin a rational design of composite materials based on LDHs and ERGO, we also investigated their electrical conductivity. The resistance of Co/Al LDH, Co/Al LDH ERGO, Ni/Al LDH, and Ni/Al LDH ERGO films was investigated by two-terminal measurements and EIS in order to highlight the differences in the behavior of the two LDH materials.

The thin LDH films were deposited on a Pt electrode. After drying, the modified surface was pressed on a soft Grafoil electrode. The resistance was estimated by measuring the current flowing in the LDH, when a difference of voltage was applied between the two extremity of the film. In order to evaluate the resistivity (ρ), the thicknesses of the films were measured by scanning electron microscopy. The ρ values are reported in Tables 1 and 2. It is worthy noting that Co/Al LDH exhibits a ρ equal to 1.3 K Ω cm^{-1} . On the other hand, in the case of Ni/Al LDH ρ is one order of magnitude higher with a value of 17 K Ω cm^{-1} [32]. The measured values are in fair agreement with the literature that reports a ρ value for Co/Al LDH of 9 K Ω cm^{-1} . The ρ values for Co/Al LDH ERGO and Ni/Al LDH ERGO are 1.5 and 1.2 K Ω cm^{-1} , respectively.

Fig. 3 shows the Nyquist plots recorded at 0 and 0.5 V for Co/Al LDH, Ni/Al LDH, Co/Al LDH ERGO, and Ni/Al LDH ERGO to gain further

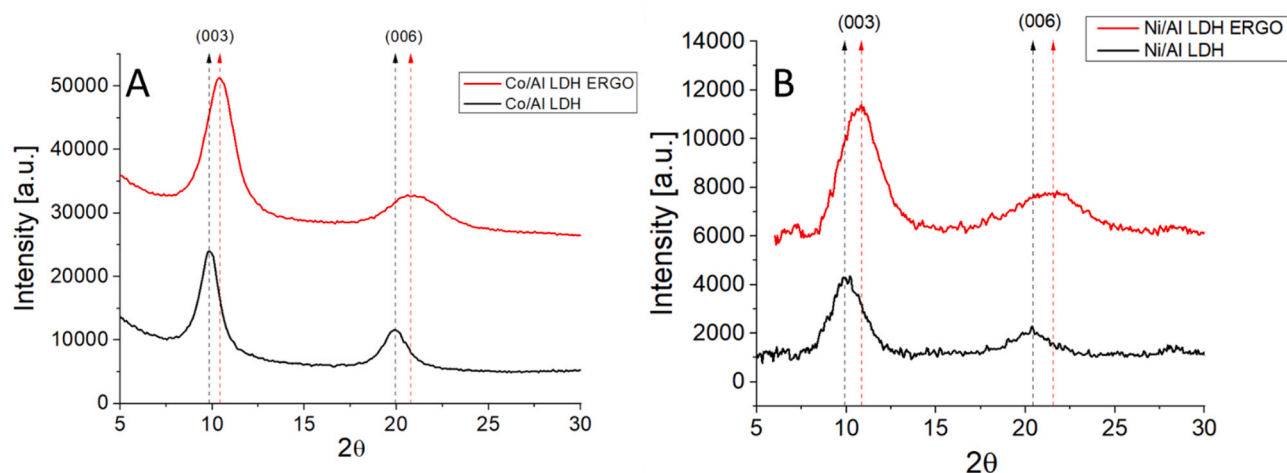


Fig. 1. PXRD recorded on Grafoil electrodes modified with a thin film of Co/Al LDH or Co/Al LDH ERGO (A) or of Ni/Al LDH or Ni/Al LDH ERGO (B).

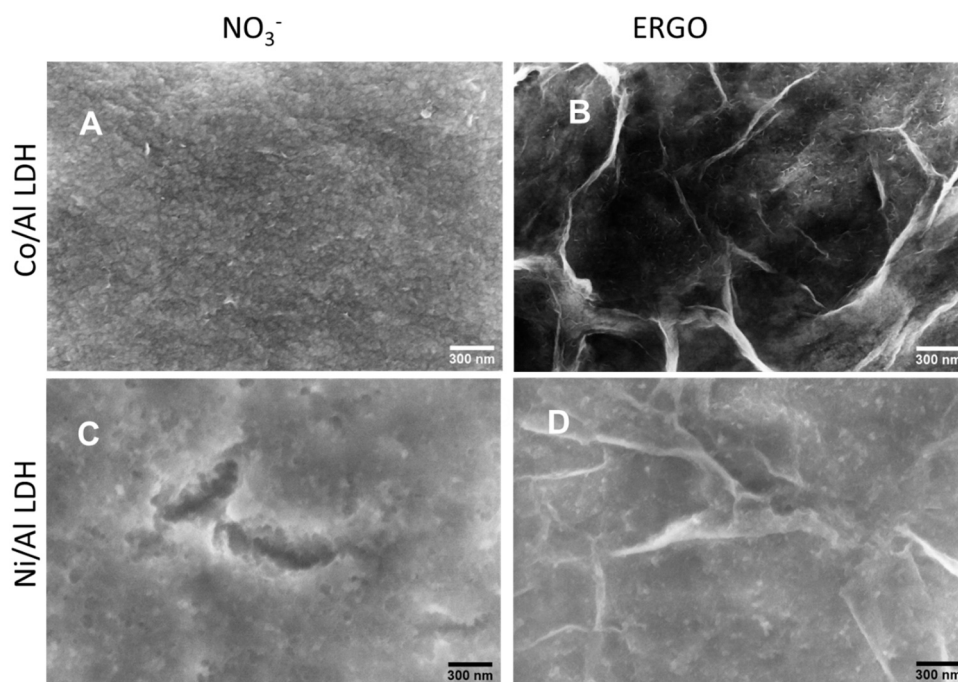


Fig. 2. SEM images of Co/Al LDH (A), Co/Al LDH ERGO (B), Ni/Al LDH (C) and Ni/Al LDH ERGO (D).

Table 1
Thickness and resistance properties of the electrosynthesized materials.

	Co/Al LDH	Co/Al LDH ERGO	Ni/Al LDH	Ni/Al LDH ERGO
Thickness (μm)	1.0 ± 0.2	1.2 ± 0.2	1.3 ± 0.2	1.6 ± 0.3
Resistance (Ω)	4.0 ± 0.1	5.8 ± 0.7	$(7 \pm 1) \cdot 10$	5.8 ± 0.4
Resistivity ($\text{k}\Omega \text{ cm}^{-1}$)	1.3 ± 0.3	1.5 ± 0.3	17 ± 4	1.2 ± 0.2

information on the conductivity of the various electrode modifiers, and to compare the results with those obtained by the two-electrode system. The EIS spectra have been fit with an equivalent circuit containing two resistances, a capacitance and a Warburg element to simulate the diffusion in the LDH layer. The graph recorded at 0 V shows lower impedance values for Co/Al LDH and Co/Al LDH ERGO, highlighting a higher conductivity of the Co containing materials. Surprisingly, at 0 V

Table 2
Parameters of the equivalent circuit fitting the EIS spectra.

	R_1 (Ω)	R_2 ($\text{k}\Omega$)	C (mF)	Warburg $\text{mMho s}^{-1/2}$
E = 0 V				
Co/Al LDH	92.5	29.8	0.0301	0.265
Co/Al LDH ERGO	77.3	10.5	0.135	0.232
Ni/Al LDH	99.4	65.7	0.0272	0.198
Ni/Al LDH ERGO	94.1	255	0.0290	0.0445
E = 0.5 V				
Co/Al LDH	94.2	4.16	10.0	2.28
Co/Al LDH ERGO	76.1	1.22	8.32	15.5
Ni/Al LDH	100	4.39	2.23	2.60
Ni/Al LDH ERGO	99.7	2.71	7.67	9.47

the Ni/Al LDH ERGO presents the curve with the highest impedance values, for most the examined frequencies. The fitting circuit highlights this effect in the resistance R_2 , that represents the charge transport

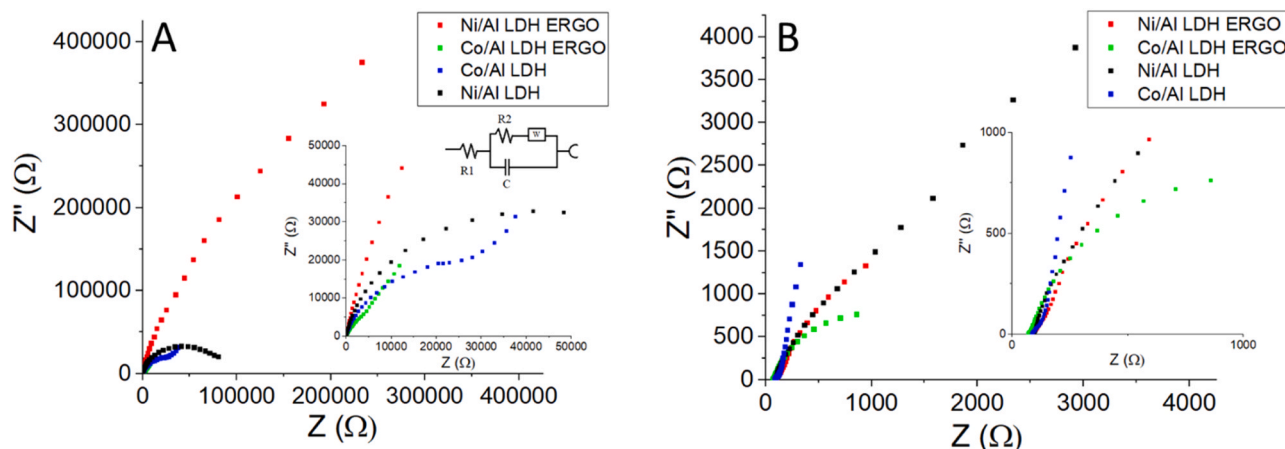


Fig. 3. Nyquist plot recorded on Grafoil electrodes modified with a thin film of the investigated materials at 0 V (A) and 0.5 V (B). The insets show the equivalent circuit and the magnifications of Nyquist plot.

inside the LDH film. The intersection of the curve with the abscissa axis can be used to evaluate the overall resistance of the device, which is given by the combination of the ionic resistance, the intrinsic resistance of the material and the contact resistance [33]. The obtained values are 68.9, 77.8, 86.1 and 93.5 Ω for Co/Al LDH ERGO, Ni/Al LDH ERGO, Co/Al LDH and Ni/Al LDH, respectively. These values are close to the one of resistance R_1 fitted in the equivalent circuit. The data confirm the role of ERGO in increasing the intrinsic conductivity of the material, and at the same time highlight the higher conductivity of Co/Al based materials. Finally, the capacitance values obtained by the simulation are comprised between 0.0272 mF and 0.135 mF.

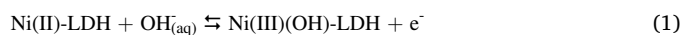
Impedance spectra were also recorded under conditions in which LDHs are partially oxidized. Fig. 3 shows a lower impedance for all the materials analyzed, and this result affects the capacitance and the resistances fitted by the equivalent circuit. R_2 values are one order of magnitude lower than the values recorded at 0 V, suggesting a higher conductivity of oxidized materials. On the other hand, the capacitance values increase due to the redox processes occurring at the potential employed for the characterization. Also in this case, the overall resistance values of the system were evaluated through the intersection with the axes of the impedance curves. The values obtained are 72.7, 94.4, 89.7, and 93.7 Ω for Co/Al LDH ERGO, Ni/Al LDH ERGO, Co/Al LDH and Ni/Al LDH, respectively. Summarizing, the EIS spectra recorded at 0.5 V highlight: i) the higher conductivities of oxidized materials due to

a higher concentration of charge carriers (i.e., the oxidized sites in LDH); ii) the higher capacitances of oxidized LDHs due to the occurrence of a redox Faradaic process at the examined potential.

Finally, the obtained results show that the electro synthesized Co/Al LDH exhibits low resistance, at least one order of magnitude lower than that of Ni/Al LDH. The intercalation of ERGO does not lead to an improvement in the conductivity of Co/Al LDH, while this effect is evident for Ni/Al LDH. Consequently, it can be assumed that ERGO simply acts as a diluent for the Co/Al LDH, so decreasing the concentration of the redox sites that generate the pseudo capacitive behavior.

3.3. Electrochemical characterizations

In Fig. 4 A are shown the characterization CVs obtained in the potential range from 0.25 to 0.70 V in 0.1 M KOH solution for the films of Ni/Al LDH and Ni/Al LDH ERGO, and in Fig. 4 B those recorded in the potential window from 0 to 0.55 V for Co/Al LDH with and without ERGO. The typical peaks, observed in the range between +0.35 and +0.60 V are related to the quasi reversible redox couple Ni(III)/Ni(II), involved in the reaction:



The partial irreversibility is due to the oxidation of the Ni(II) centers to Ni(III), characterized by the formation of the γ phase, which could

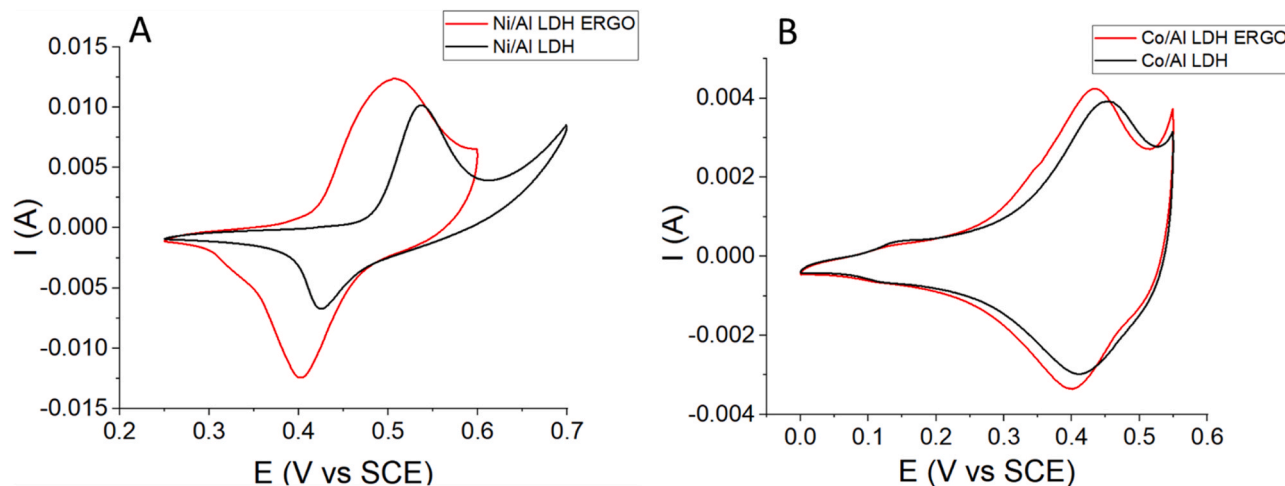
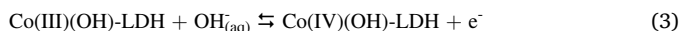
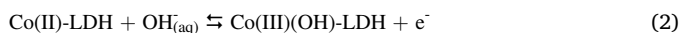


Fig. 4. Characterization CVs recorded in 0.1 M KOH at 10 mV s^{-1} for Grafoil electrodes modified with Ni/Al LDH and Ni/Al LDH ERGO (A) and Co/Al LDH and Co/Al LDH ERGO (B).

induce a chemical/structural instability [28].

For the composite material, it is immediately evident that in the presence of ERGO the CV trace shifts at less anodic potentials, and, in particular, the anodic peak potential occurs at 0.48 V vs 0.52 V, which is recorded for the pure LDH.

The Co based LDH coating displays a broad feature between 0.25 and 0.48 V, which is supposed to be related to the reactions 2 and 3.



Such reactions possess formal potentials close to each other; for this reason the resolution of the two peaks is strongly hindered. Anyway, the behavior can be considered quasi reversible since the ratio of the anodic to the cathodic charge of the feature is very close to 1. Furthermore, when the bivalent cation is Co the anodic peak potential is highly anticipated with respect to the value displayed by the Ni/Al LDH, and this confirms the greater ease by which Co is involved in the oxidation reaction. In such a case, the CV recorded for the Co/Al LDH ERGO is practically coincident with the one displayed by the pure LDH; therefore, the presence of ERGO does not affect significantly the redox behavior of the Co based LDH.

Besides the Faradaic processes above discussed, the charge storage characteristics of the electrodeposited films were investigated in order to check their possible application in hybrid electrochemical capacitors. Fig. 5A shows the galvanostatic charge-discharge curves recorded at 10 A g^{-1} in 6 M KOH for Ni/Al LDH and Ni/Al LDH ERGO, in the potential range of 0.25–0.45 V. The potential window was selected to highlight the typical behavior of the Faradaic process involving the LDH redox centers. There is an obvious deviation of the charge/discharge curves from a straight line, which confirms that the capacitance mainly comes from the Ni redox activity. As can be seen, in the case of Ni/Al LDH the charge curve consists of two clear voltage stages: a fast potential raise (from 0.25 to 0.40 V) followed by a slow potential growth (from 0.40 to 0.45 V). The former might result from the internal resistance of the LDH and the latter represents the pseudocapacitive feature of the electrode material. When ERGO is present the potential increases more gradually, with a consequent extension of the charging time which is due to the higher electrical conductivity of the composite and to the faster kinetics of the Ni(II) to Ni(III) oxidation. When the current is reversed from charge to discharge, an ohmic drop occurs due to the internal resistance. The IR drop is slightly decreased in the case of Ni/Al LDH ERGO. The discharge time is slightly higher in the presence of ERGO, so supporting that the capacitive performance of the electrode is effectively improved.

For Co/Al LDH and Co/Al LDH ERGO the GC-D curves were recorded in the potential window from -0.10 – 0.40 V. In both cases, the charging curves are somewhat mirror-symmetrical to their discharging counterparts, and do not differ significantly between the pure and the composite LDH. The only difference is related to the slightly longer times of charge and discharge when LDH only is present. Furthermore, for the Co based materials it can be noticed a smoother trend of the potential during the charging and discharging processes. The results were expected due to the intrinsic higher electrical conductivity of Co/Al LDH, which is not significantly favored by the presence of ERGO, as well as the redox process involving the Co centers (see characterization CVs). Therefore, it is possible to affirm that the electrical conductivity and capacitive properties of Ni/Al LDH are effectively improved by the presence of ERGO, whereas that does not occur for the Co/Al LDH. The specific capacitance per gram of the various materials was determined with an electrochemical quartz crystal microbalance (EQCM) equipped with a Pt electrode. LDH thin films were electrodeposited, and the occurred mass variations were measured. The charging and discharging curves were recorded by setting a current equal to 2.5 A/g . The specific capacity (C_s) values were 418, 345, 550 and 650 F/g for Co/Al LDH, Co/Al LDH ERGO, Ni/Al LDH and Ni/Al LDH ERGO, respectively. These results show that the Ni based LDHs possess a higher specific capacity than the Co containing materials; in particular Ni/Al LDH ERGO displays a greater C_s than Ni/Al LDH, while for Co/Al LDH ERGO the calculated C_s value is lower if compared with the pure Co/Al LDH. Also the literature reports excellent performance for composite materials based on Ni/Al LDH and graphene, whose intercalation in the interlayer region underpins an improvement of specific capacitance with respect to the pristine LDH. Differently, the effect of the presence of graphene in Co/Al LDH based composites is debated in literature. The first examples refer to materials where LDH crystallites were synthesized on the surface of graphene sheets, which showed a clear advantage in terms of specific capacity [34–36]. The study of materials in which graphene was intercalated in the LDH interlayers has led to contrasting results. On one side, some papers reported good performance [37–39], on the other, the recent literature suggests that the composites in which graphene is intercalated inside the Co/Al LDH do not display an improvement in their outputs [40]. When different layered structures with intercalated graphene were investigated, Co/Al LDH and layered CoOOH showed the worst performances. The values of specific capacitance obtained from that study were close to those reported in this work. The authors explained the Co/Al LDH better performance considering that the presence of the intercalated ERGO hindered the OH^- diffusion during the redox processes. However, this effect was not observed for Ni/Al LDH ERGO.

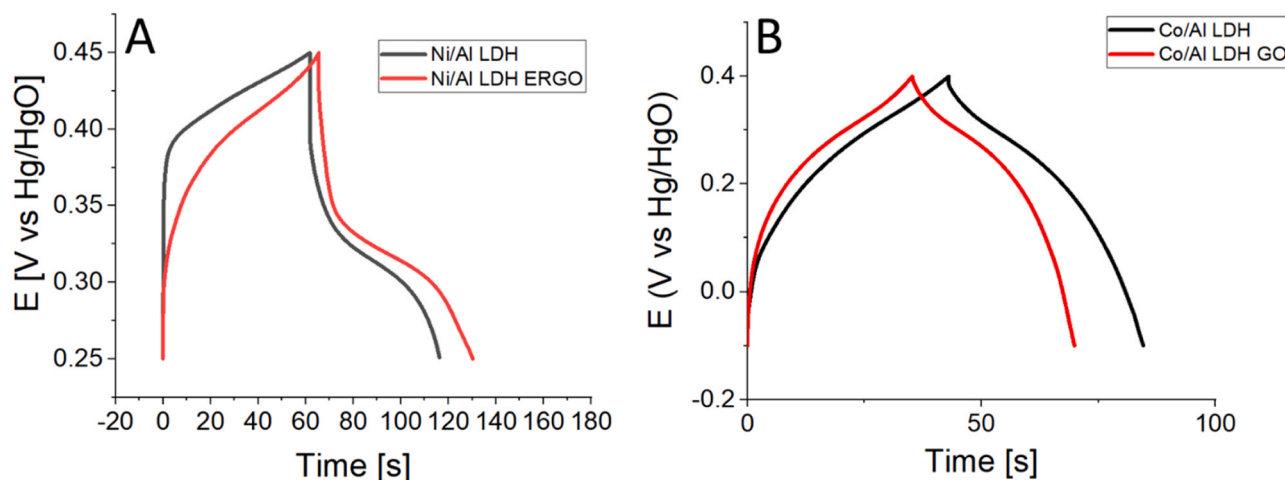


Fig. 5. Galvanostatic charge-discharge curves of Grafoil electrodes modified with Ni/Al LDH and Ni/Al LDH ERGO (A) and Co/Al LDH and Co/Al LDH ERGO (B) recorded in 6 M KOH, at the current density of 10 A g^{-1} .

3.4. Performance of the asymmetric supercapacitors

Since the charge storage capabilities of the pure Ni/Al LDH and of Ni/Al LDH ERGO had been already investigated in a previous paper [21], in this work only the performance of the Co based materials has been taken into account. In particular, our interest was aimed to verify if the presence of ERGO intercalated inside the LDH would increase the stability and the performances of the SC with respect to the device where the cathode was made of the pure LDH, since the results above reported on the capacitance had demonstrated that, differently from Ni based LDHs, the Co/Al LDH did not display an increased performance in the presence of ERGO.

As far as Grafoil modified with PEDOT:PSS is concerned, both the recorded characterization CVs and the GC-D curves displayed a purely capacitive behavior in the potential range investigated, thus evidencing the charge storage capabilities also of the anodic component.

PEDOT:PSS electrodeposition was carried out by means of 50 cycles of CV. Actually, also 25 CVs have been tried, but the SC specific capacitance per square centimeter was higher employing 50 CVs. For this reason, this number of cycles was selected to prepare the anode, when studying the capacitance of the SC in solution. The GC-D curves were recorded using the same experimental conditions as for the single electrodes, but the potential window was from 0 to 1.50 V. In Fig. 6 A, two C-D cycles recorded at 1 mA cm^{-2} are shown. It is evident that ERGO containing LDH displays a slightly better performance since both the charge and discharge times are little longer.

Long-term cycling stability was investigated carrying out at least 5000 cycles at a current density of 1 mA cm^{-2} .

The supercapacitor based on the Co/Al LDH ERGO had a starting discharge C_s of 52 mF cm^{-2} which decreased in the first cycles, and, after a fluctuating trend, stabilized at 47 mF cm^{-2} after about 1700 cycles. The supercapacitor employing the pure Co/Al LDH possessed an initial discharge C_s of 46 mF cm^{-2} , which after a slight increase during the first 500 cycles, maybe related to the activation of the Co redox centers and the swelling of the LDH structure, displayed unstable values even after 5000 cycles.

In Fig. 6B the percentage of the specific discharge capacitance retention is plotted against the cycle number by using the Co/Al LDH or the Co/Al LDH ERGO at one terminal side. From the results of the specific capacitances per square centimeter just reported, we can state that Co/Al LDH ERGO displays a slightly higher value than Co/Al LDH. On the other hand, the specific capacity per gram above reported was higher for Co/Al LDH than for Co/Al LDH ERGO, highlighting that the intercalation of ERGO does not lead to an increase in performance. We

decided to consider more reliable the results referred to the mass since the amount of active materials on Grafoil can be different in dependence on the electro-synthesis conditions of the electrode modifier. Therefore, we can state that the intercalation of ERGO inside the Co/Al LDH does not affect significantly its properties in terms of capacitance, but surely affects positively the material stability when used as cathode in a SC. This conclusion is supported by the literature [6], which has demonstrated that the presence of graphene sheets slows down the LDH reorganization that occurs during the operativity of the LDHs based electrochemical devices.

4. Conclusions

Ni/Al and Co/Al LDHs electro-synthesized on Grafoil, as such and intercalating ERGO inside their structure, have been morphologically and structurally characterized. Furthermore, their electrical and electrochemical properties have been deeply investigated to verify if they are affected in a similar way by the ERGO presence.

The electrical resistance of Co/Al LDH, Co/Al LDH ERGO, Ni/Al LDH and Ni/Al LDH ERGO films was investigated by EIS and two-terminal measurements, and the results obtained showed that the Co/Al LDH exhibits a low resistance, at least one order of magnitude lower than that of Ni/Al LDH. The intercalation of ERGO does not lead to an improvement in the conductivity of Co/Al LDH, while conductivity is significantly higher for the Ni/Al LDH. As to the electrochemical behavior of the redox active Ni and Co centers, the presence of ERGO in the Ni based LDH has a significantly favorable effect as it shifts at less anodic potentials the redox process, whereas the effect is insignificant for the Co containing LDH. Besides the Faradaic processes, the charge storage characteristics of the electrodeposited films were investigated, again with the aim to verify the effect of the ERGO presence on the pseudo-capacitive properties. The result was that the intercalation of ERGO inside the Co/Al LDH does not affect positively its properties in terms of capacitance (differently from the behavior of Ni/Al LDH), but only increases the material stability when used as cathode in a SC.

Summarizing, this research highlights that the synthesis of composites based on LDHs and nanocarbon materials, such as ERGO, does not necessarily lead to a better performance in the field of energy storage. Therefore, the design of new materials must consider the peculiar characteristics of the LDH used as pseudo-capacitive material.

Furthermore, it is important to underline that the electrochemical synthesis leads to the formation of materials strongly adherent to the electrode and, therefore, displaying a better charge transfer at the electrode/modifier interface compared to the chemically synthesized

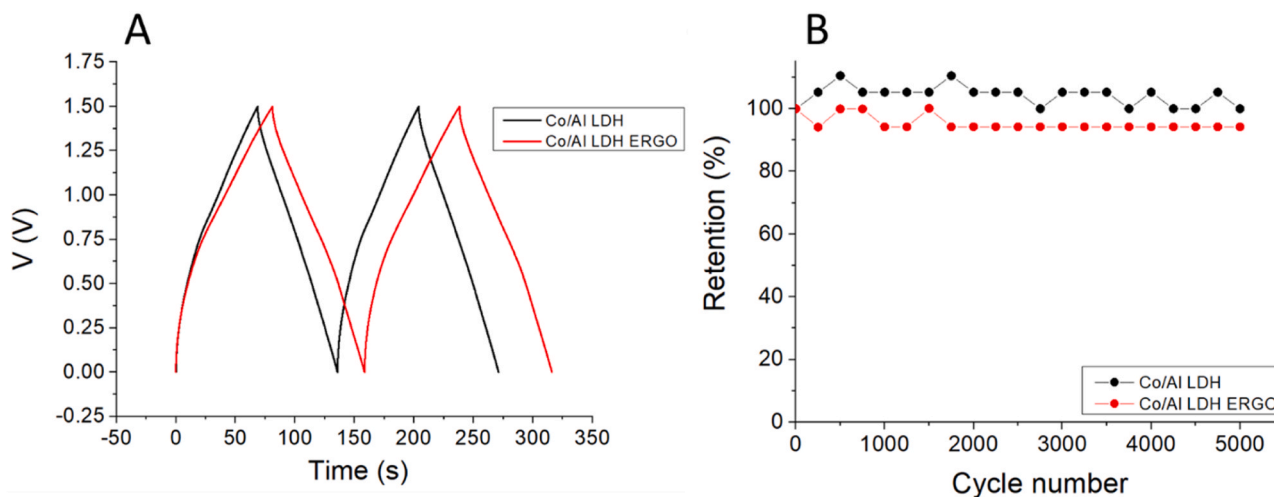


Fig. 6. Galvanostatic charge-discharge curves of the hybrid supercapacitor recorded in 6 M KOH, at the current density of 1 mA cm^{-2} (A) and percentage of the specific discharge capacitance retention for 5000 cycles (B).

LDHs, which require more complex electrode preparations and the use of binders. Therefore, the electrochemical approach plays a key role on the technological performance of the final device.

CRedit authorship contribution statement

D.Tonelli and I. Gualandi: design of the Project, discussion of results and writing the MS; E. Musella and I. Gualandi: experimental electrochemical work and treatment of data; E. Scavetta: fund acquisition and supervision; M. Gazzano: execution of X ray diffractometry and discussion of the relevant results; V. Morandi and M. Christian: execution of FE-SEM characterization and discussion of the relevant results; V. Morandi: fund acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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