

Electrochemical Measurements of Ni / Graphene based Nanohybrids for Electrochemical Energy Storage “Supercapacitors”

Ikram Djebablia, Ouanassa Guellati, Naima Habib, Aicha Harat, Fahima Djefafliya, Aissa Nait-Merzoug,

Izabela Janowska and Mohamed Guerioune

Abstract– Given the issues related to the use of fossil fuels and water pollution, the development and the application of new smart nanomaterials for supercapacitors and biosensors has become a vital issue for human and industrial societies. Therefore, nanotechnology has given more interest to these areas via micro/nanosystems or nanohybrids characterized by interesting composition, significant porosity and texture at nanoscale. In this work, we have produced electroactive nanohybrids based on in-situ Ni mono-hydroxide few layers Graphene oxide "GO" using a simple and low cost hydrothermal technique under well-studied thermodynamic conditions (120 and 180 °C growth temperature), for performant supercapacitor devices. We have carried out the structural, morphological, textural and optical characterization of these products and consequently we have specified the relationship between their physico-chemical characteristics and their electrochemical properties for ulterior application. Thus, we have carried out various electrochemical measurements through Cyclic Voltammetry tests and we have marked the important electrochemical properties of these Ni/Graphene nanohybrids in two NaOH electrolyte concentrations (0.1 and 1 M) in order to improve the performance of supercapacitors, which have become a socio-economic issue with this nanotechnological development. Consequently, these obtained Ni/Graphene nanohybrids have shown a very interesting electrochemical results with specific capacities 1863 and 253 F.g⁻¹ for the case of nanohybrid obtained at 6h/120°C in NaOH aqueous electrolyte with two different concentrations (1 and 0.1M), respectively. However, for a fixed electrolyte concentration of 1M NaOH, both nanohybrids obtained at 120 and 180°C gave specific capacity values around 1863 and 2981 F.g⁻¹, respectively.

Keywords– Energy storage, Supercapacitors, Nanohybrid, Ni Hydroxide, Graphene Oxide, Electrochemical measurement.

I. INTRODUCTION

The rapid development of human society has led to an ever-growing demand for energy and serious problems like global warming and environmental pollution [1, 2]. At the same time, the dependence of modern societies on fossil fuels and the rapid strides made in various areas such as industrialization has contributed also to these growing energy requirements. Reducing these issues is an increasingly important goal that can be achieved through developing other low-cost, clean and sustainable energy sources/storage technologies. Thus,

renewable sources (RSs) such as solar, hydro and wind energy have become widely endorsed solutions for addressing these concerns [3].

However, due to the large fluctuations in their generation, produced electricity from these renewable energy sources must be efficiently stored to supply the world with energy on demand. Energy storage systems (ESSs) are the key to deal with the intermittent nature of renewable energy sources and increase the power transmitted into the grid from systems such as wind and solar power. In this context, considerable efforts have been put into researching and developing most effective and practical technologies for more efficient electrochemical energy storage devices like: batteries, fuel cells and supercapacitors (SCs) [4, 5].

Manuscript received October 9, 2022; revised April 22, 2023.

I. Djebablia is with Mohamed Chérif Messaadia University, BP. 1553, Souk-Ahras 41000, ALGERIA. (e-mail: ikramdjebablia@gmail.com)

N. Habib, F. Djefafliya, A. Nait-Merzoug and O. Guellati are with Mohamed Chérif Messaadia University, BP. 1553, Souk-Ahras 41000, ALGERIA and LEREC Laboratory, Physic Department, Badji Mokhtar University of Annaba, BP. 12, Annaba 23000, ALGERIA. (e-mail: habib.naima23@yahoo.fr, djefafliyaahima@gmail.com, abenlala@yahoo.fr, guellati23@yahoo.fr)

A. Harat and M. Guerioune are with LEREC Laboratory, Physic Department, Badji Mokhtar University of Annaba, BP. 12, Annaba 23000, ALGERIA. (e-mail: harat_aicha@yahoo.fr and mguerioune@yahoo.fr)

I. Janowska is with ICPEES Institute, ECPM - CNRS, UdS, 25 Rue Becquerel, 67087 Strasbourg, FRANCE. (email: janowskai@unistra.fr)

In recent years, SCs also referred to electrochemical capacitor or ultracapacitor [5, 6] have attracted significant attention, mainly due to their high power density, long life cycle and higher charging/discharging rate capability [7]. While the energy density of supercapacitors is very high compared to conventional dielectric capacitors but it is still significantly lower than batteries, which limits their adoption to those applications that require high life cycle and power density [8]. Coupling with batteries (or another power source) is still required for supplying energy to longer periods of use. Thus, there is a strong interest for increasing this supercapacitors energy density to be closer to those of batteries.

In order to overcome this low energy density obstacle, different nanomaterials including carbonaceous nanomaterials [6], mixed metal oxides/hydroxides [9, 10] and

Digital Object Identifier (DOI): 10.53907/enpesj.v3i1.158

conducting polymers [11-13] have been used as supercapacitor electroactive functional materials. Carbon, in its various forms like Single (SWNTs) and Multi (MWNTs) Walled Carbon NanoTubes [14], activated carbon fibers (ACFs) [15, 16] and carbide derived carbons (CDCs) [17], owing to a unique properties combination, such as: high surface area, lightweight, good electrical conductivity and high temperature stability [6]. However, the application of these individual carbonaceous nanomaterials in supercapacitors is limited by their high cost and unsatisfactory electrochemical performance [18]. Due to their superior electrical conductivity, high theoretical surface area of over $2600 \text{ m}^2 \cdot \text{g}^{-1}$, optical and mechanical important properties [19, 20], Graphene as monolayer of graphite is expected to play a crucial role for energy applications in many fields especially in elastic and flexible electronic devices [21] as well as photovoltaics [22]. Recently, it has been proposed that this kind of nanomaterial should be a competitive electroactive material for supercapacitors application [23]. Unfortunately, due to the unavoidable aggregation of Graphene films, their surface area is usually much lower than the theoretical value and its capacitance is generally in the range [100–200 F] [24, 25]. In addition, they suggest the Graphene oxide which is a single sheet of Graphite oxide but it possesses less p-p stacking stability, poor conductivity and thus it has been theoretically claimed that it is not able to directly serve as the electrode material for supercapacitors [26]. Thereby, numerous studies have been focused on investigating earth-abundant alternatives transition metal oxides (Mn, Ni, Fe and Co) [27, 28] and transition metal layered double hydroxides (LDH) [29] as pseudo-capacitance storage materials. Among these alternatives, Ni compounds have captured in recent years tremendous research attention due to their high speed reversible surface redox reactions [30]. In particular, $\text{Ni}(\text{OH})_2$ possesses a specific properties like high power density, excellent cyclability, high specific energy and low toxicity [31]. Nevertheless, their relatively low conductivity and limited surface area restricts their further application.

Furthermore, carbon with metal oxides or hydroxides based nanocomposites/nanohybrids have attracted great interest with high capacitances and good cycling performances [32, 33]. Recently, nanocomposites based on $\text{Ni}(\text{OH})_2$ and carbon materials have been prepared and used as supercapacitors electrode. For instance, $\text{Ni}(\text{OH})_2/3\text{D}$ Graphene nanohybrid were prepared by C. Jiang's group via atmospheric pressure chemical vapor deposition (APCVD) and shows high specific capacitance around $1450 \text{ F} \cdot \text{g}^{-1}$ at a current density of $5 \text{ A} \cdot \text{g}^{-1}$ [34]. H. Wang et al. obtained 3D $\text{Ni}(\text{OH})_2/\text{GO}$ hybrid through a two-step process and their specific capacitance have shown 90% retention after 10000 charge/discharge cycles [35]. Additionally, J. Liu et al. have synthesized using a brief and facile hydrothermal method a 3D rose-like $\text{Ni}(\text{OH})_2/\text{rGO}$ nanohybrid with specific capacity around $802 \text{ F} \cdot \text{g}^{-1}$ at $2 \text{ A} \cdot \text{g}^{-1}$ [36].

Consequently in this paper, we present the successful synthesis of $\text{Ni}(\text{HCO}_3)_2$, $\alpha\text{-}3\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ and their nanohybrids with Graphene oxide using a facile and low cost urea based free template hydrothermal method at different optimized conditions. The new kind of Ni hydroxide based nanohybrids which are different than those obtained in literature have shown very interesting structural, optical and electrochemical properties for performant supercapacitor devices. Their electrochemical measurements through Cyclic Voltammetry (CV) tests in two different NaOH electrolyte concentrations (0.1 and 1 M) show a very interesting specific capacities of 253 and $1863 \text{ F} \cdot \text{g}^{-1}$, respectively, for the case of nanohybrid obtained at 6h/120°C. However, for a fixed 1M

NaOH electrolyte concentration, both nanohybrids obtained at 120 and 180°C hydrothermal growth temperature process gave specific capacity values around 1863 and $2981 \text{ F} \cdot \text{g}^{-1}$, respectively.

II. EXPERIMENTAL PROCEDURE

All the chemicals, urea (Merck, purity $\geq 98\%$), Ni chloride (Sigma-Aldrich, purity $\geq 99,99\%$), were of analytical grade and were used without further purification. Ni Foam (NiF) was purchased from (Alantum, Munich, Germany) with areal density of $420 \text{ g} \cdot \text{m}^{-2}$ as well as a diameter and a thickness of 16 mm and 0.2 mm, respectively.

A. *Ni and Ni/Graphene nanohybrids synthesis*

0.1M Ni (II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) with and without Graphene was dissolved in deionized water for 5 min at room temperature. After that, 0.5 M urea ($\text{CH}_4\text{N}_2\text{O}$), which is highly soluble in water, was added into the solution and ultrasonicated for 15 min until a green transparent or black green solution was obtained. The last dispersed solution was transferred into a 40 mL Teflon-lined hydrothermal autoclave system. The autoclave was sealed, maintained at two different growth temperatures (120 and 180°C) during 6 hours and then allowed to cool down naturally to room temperature. The obtained products with distinct colors were filtered and washed several times with distilled water and ethanol before drying in an oven at 80°C overnight.

B. *Working electrode preparation*

The working electrodes for electrochemical performance evaluation of Ni/Graphene nanohybrid material were prepared as follows: firstly, a mixture containing 80 wt.% of Ni or Ni/GO based electroactive materials, 10 wt.% of carbon black (CB) and 10 wt.% of PVdF binder with some drop of NMP solvent was well mixed in an agate mortar to form a paste. This was spread onto a $1 \times 1 \text{ cm}^2$ area of pre-treated NiF and dried at 80°C in an oven for 24 h to ensure complete evaporation of the NMP.

C. *Characterization techniques*

Detailed physico-chemical properties of these samples were examined by using various analysis tools :

The structural characterization of these nanohybrid products were investigated using powder X-ray diffraction (XRD) via an XRD D8 ADVANCE-BRUKER AXS diffractometer equipped with a copper anticathode tube "Cu K α radiation" ($\lambda = 1.5406 \text{ \AA}$), operating at 40 kV and 40 mA with a scanning rate of $0.2^\circ \cdot \text{s}^{-1}$. In addition, their Fourier-Transform Infra-red (FTIR) spectra were recorded using a Bruker Vertex 77v spectrometer in the wave number range [from 400 to 4000 cm^{-1}] with 4 cm^{-1} resolution and analyzed with an Opus software.

Moreover, the thermal stability of these products were measured using a Thermo Gravimetric Analysis technique, which was carried out using TA Instruments Q5000 Simultaneous (DSC/TG) analyzer which allows the measurements of the weight change in the products as a function of temperature under air atmosphere from 30°C to 1000°C with $10^\circ\text{C}/\text{min}$ heating rate.

However, the products morphology were analyzed using a Field Emission Scanning Electron Microscopy (JEOL 6700-FEG microscope) operating at 3 kV.

The absorbance spectra of the samples were obtained using UV-Vis spectrophotometer to investigate the optical properties of these nanoparticles. The spectral absorption were recorded using ThermoScientific™ GENESYS 10S UV-Visible spectrometer in the wave length range [100 to 1100 nm] using quartz cuvettes at room temperature.

The electrochemical measurements were carried out using a Gamry R600 potentiostat (USA) under ambient temperature in a three-electrode cell setup using NaOH aqueous electrolyte (with two different molarities 0.1 and 1 M) with Pt (platinum) and Hg/HgO (mercuric oxide) counter and reference electrode, respectively.

III. RESULTS AND DISCUSSION

The purity and the crystallinity of as-synthesized products were examined by powder XRD diffraction. Figure 1 illustrates the synthesized Ni mono-hydroxide and their nanohybrid with Graphene using free template hydrothermal growth technique at optimized conditions.

For the case of 6h/120°C synthesis condition, four peaks are observed at 12.06°, 33.84°, 35.52° and 59.80° assigned to the (001), (110), (111) and (300) crystal planes, respectively; characterizing the hexagonal structure " α - $3\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ " formation according to JCPDS card number [00-022-0444] with P-31m symmetry and $a = 5.29352 \text{ \AA}$ / $c = 7.32841 \text{ \AA}$ estimated crystalline parameters which are similar to the reported values in the literature [37, 38]. Additionally, no impurity peaks can be found in these XRD patterns.

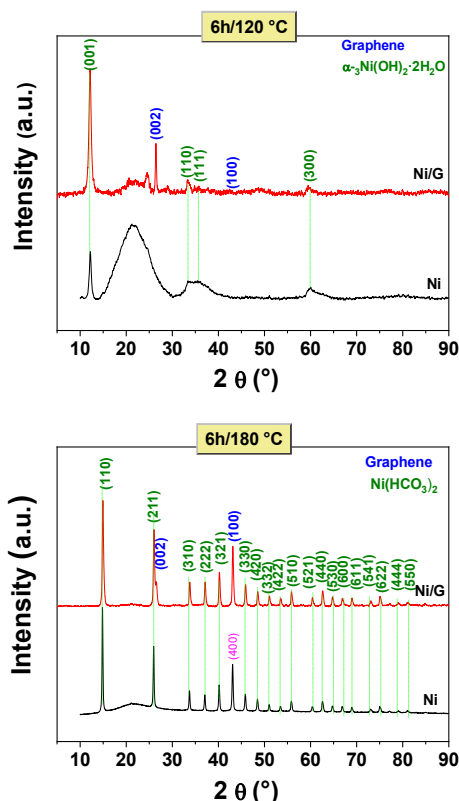


Fig. 1: XRD diffractograms of Ni mono-hydroxide and their Ni/Graphene nanohybrid synthesized by hydrothermal process at two different growth temperatures (120 and 180°C).

On the other hand, a second phase proving the existence of Graphene was found with its two characteristic peaks located at 26.45° and 43.02° corresponding, respectively, to the crystal planes (002) and (100) which in accord with the literature [39, 40]. However, in the second 6h/180°C synthesis condition, we notice a radical change on the formed structure

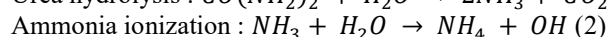
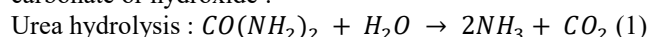
of these products due to the effect of growth temperature. So, we obtained a well crystallized phase with narrow peaks of Ni hydrogen carbonate " $\text{Ni}(\text{HCO}_3)_2$ " with a centered cubic structure according to JCPDS card number [00-015-0782] [41, 42]. This structure is recognized through its most intense peaks located at 14.80°, 26.1°, 33.70°, 37.02°, 40.34° corresponding to the crystalline planes (110), (211), (310), (222) and (321), respectively (Table I). Moreover, in the same way for their nanohybrids, we found Graphene with his two characteristic peaks at 26.54° (002) and 43.16° (100) [43]

Table. I
CALCULATED CRYSTALLINE PARAMETERS FOR NI MONO-HYDROXIDE AND THEIR NI/GRAPHENE NANOHYBRID.

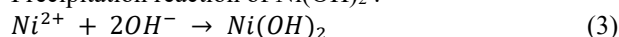
Phase/Ref	Crystalline parameters		
	a (Å)	b (Å)	c (Å)
α - $3\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$	5.29352	5.29352	7.32841
22-0444	5.34000	5.34000	7.50000
$\text{Ni}(\text{HCO}_3)_2$	8.45699	8.45699	8.45699
15-0782	8.38300	8.38300	8.38300

confirming thus the nanohybrid formation as in the previous growth condition.

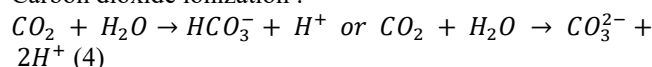
Consequently, we suggest the following main reactions of the urea homogeneous hydrolysis method for the synthesis of Ni carbonate or hydroxide :



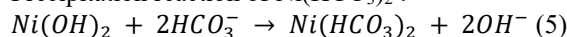
Precipitation reaction of $\text{Ni}(\text{OH})_2$:



Carbon dioxide ionization :



Precipitation reaction of $\text{Ni}(\text{HCO}_3)_2$:



For further composition study of these products based of Ni mono-hydroxide and their (Ni/Graphene) nanohybrids, the FT-IR spectra of samples are investigated and shown in figure 2 (a & b). Common vibration bands are observed in the first case of 120°C at 3633 cm^{-1} , [2358-2363 cm^{-1}], 2231 cm^{-1} , 1363 cm^{-1} , 631 cm^{-1} and 641 cm^{-1} . The narrow absorption located at around 3645 cm^{-1} is ascribed to the -OH in the brucite-like structure [44]. The band around [2358-2363 cm^{-1}] corresponds to the bending mode of water molecules [44, 45]. The strong absorption band at 2231 cm^{-1} indicates the presence of impurities $\text{C}\equiv\text{N}$ due to the used urea [46]. Two narrow peaks, which appear at 641 and 631 cm^{-1} in the low wave number region, correspond to the bending of Ni-OH due to the elongation vibration of $\text{Ni}(\text{OH})_2$ existing in this synthesized Ni mono-hydroxide with and without Graphene oxide [44-46]. Same peaks are observed also in the case of 180 °C, beyond a narrow peak at 3260 cm^{-1} which is ascribed to rise from hydrogen-bonded OH stretching [4] and C=O elongation vibration peaks which are observed at 1553 and 2358 cm^{-1} [44, 45]. Beside the existence of peaks in the range of [1365 – 1380 cm^{-1}] that are attributed to C-O vibration band of carbonate anions and Graphene network [39].

Furthermore, the thermal decomposition behavior investigation using TGA and DTG analyses is shown in figure 3. Four to three distinct regions of weight loss were observed in the TGA curves between 200-800°C, afterwards the sample remains stable, depending on the nanocomposite component phases.

The corresponding weight loss between [27-230 °C] at around 12 wt.% is attributed to the evaporation of inter-layered water molecules in Ni hydroxides (for 6h/120°C) [44]. Meanwhile, the corresponding weight loss between [230 – 500 °C] around 23 wt.% was derived from the transformation of hydroxide to their oxide [44]. Finally, the 7 wt.% weight loss found between [500 – 800 °C] is due to the oxidation of nanostructured basic carbon type graphene to CO₂.

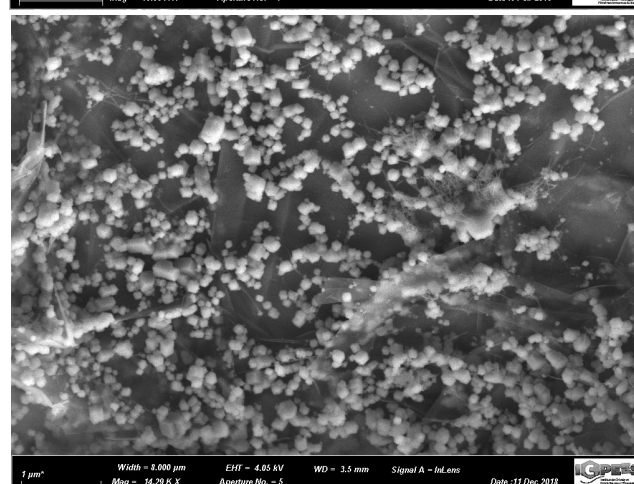
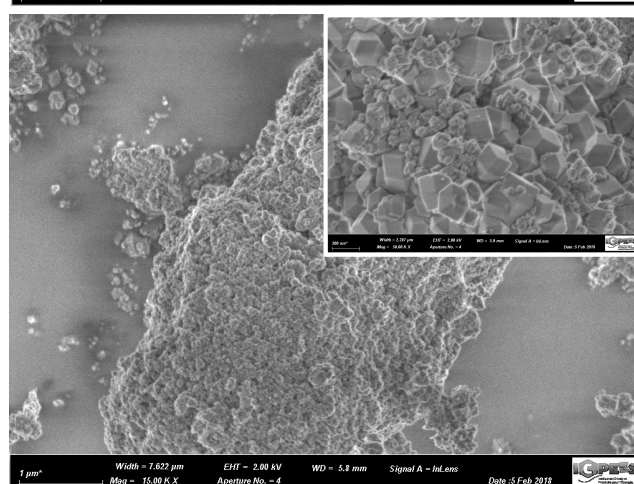
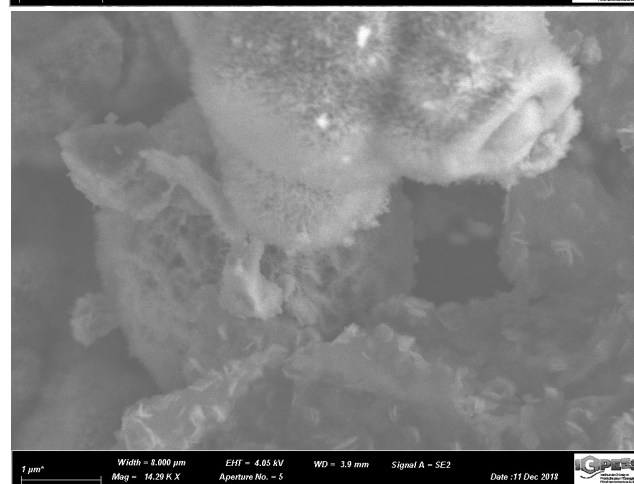
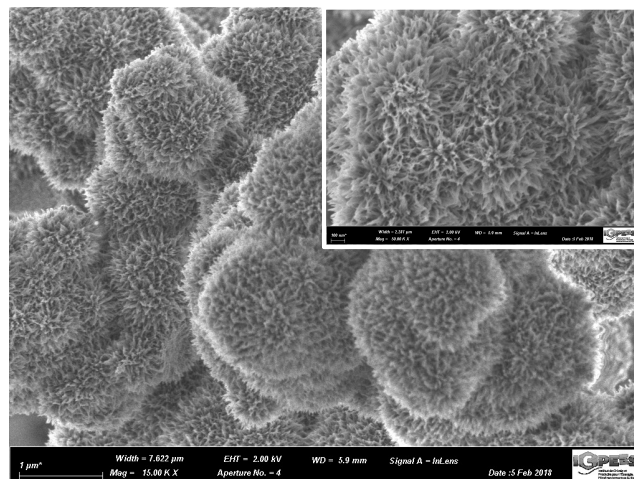
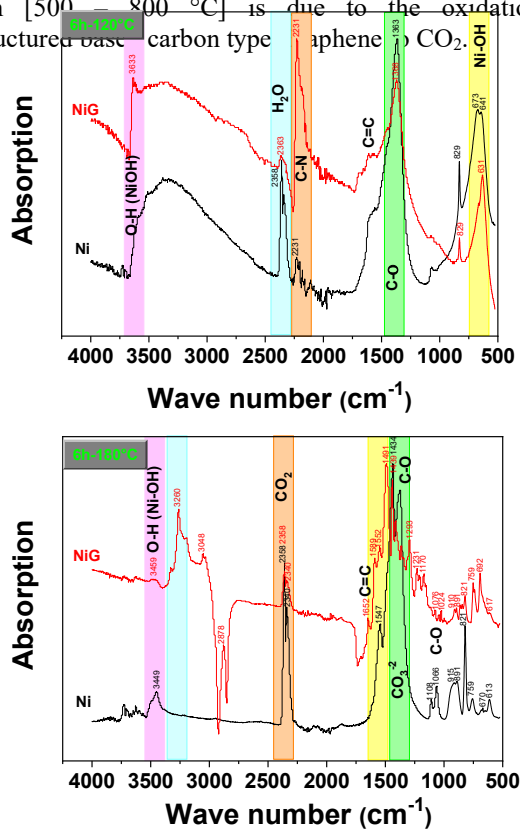


Fig. 2: FT-IR spectra of Ni mono-hydroxide and their Ni/Graphene based nanohybrid synthesized by hydrothermal process at two different conditions (6h/120°C and 6h/180°C).

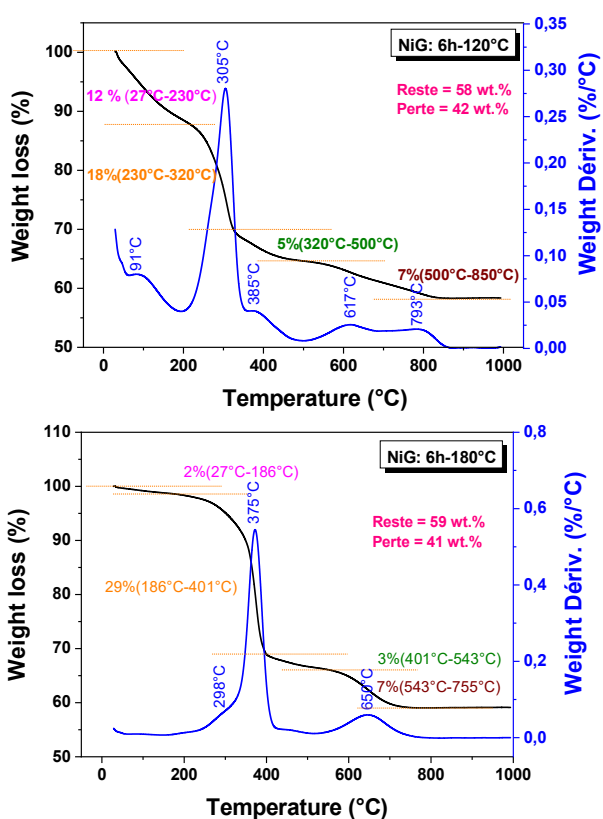


Fig. 3: TGA/DTA results of Ni hydroxide/Graphene based nanohybrid synthesized by hydrothermal process at two different conditions (6h/120°C and 6h/180°C).

Fig. 4: FESEM micrographs of synthesized Ni based mono-hydroxide (a, c) and their nanohybrids (Ni hydroxide/Graphene) (b, d) : 6h/120°C (a, b) and 6h/180°C (c, d).

Similarly, for the nanohybrid synthesized at 6h/180°C, the mass losses are 2, 29, 3 and 7 wt.% at oxidation temperatures found in the ranges: [27-186 °C], [186-401 °C], [401-543 °C] and [543-755 °C] confirming also the existence of water evaporation due to the presence of -OH radicals, oxidation of carbonate to CO₂ and transformation of Ni hydroxide to oxide without forgetting the Graphene oxidation [44]. At the end, the overall mass loss of these nanohybrid products synthesized at 6h/120°C and 6h/180°C is around 42 and 41 wt.%, respectively. From these thermal results, we can estimate the nanohybrid composition to be metal/carbon = 90/10 wt.% which may have surely a benefic effect on the electrochemical behavior.

In order to follow the morphological and textural aspect of these produced nanomaterials, FESEM microscopy was carried out on these samples of Ni based mono-hydroxide and their nanohybrid (Ni/Graphene) hydrothermally synthesized at 120 and 180°C during 6 hours (Fig. 4). Firstly, we can clearly observe in the case of 6h/120°C (pure Ni mono-hydroxide), a formation of quasi micro-nanospheres at 3D with a porous texture and with well dispersed porosity due to an organized assembly of nano-needles (Fig. 4 a) [47]. These quasi micro-nanospheres with a porous texture have diameters around 2.5 µm. On the other hand, the micrograph represented in figure 4(b) confirms the formation of two nanostructures in the form of well dispersed last micro-nanospheres supported by Graphene nanosheets. However, for products of 6h/180°C (pure hydrogen carbonate Ni), we have obtained nanostructured particles (nanospheres, nanocubs, ...) (Fig. 4c) which are different than that of the previous condition product confirming thus the effect of growth temperature on the products morphology which affect therefore their ulterior properties. In addition, figure 4(d) shows these nanostructured particles supported by Graphene oxide sheets forming consequently the in-situ nanocomposites.

Optical Properties

Another spectroscopic analysis technique has been used in order to determine the optical properties that allow us to deduce the gap energies of these synthesized products [48]. The optical absorption spectra are shown in figure 5.

They show an absorption threshold at about 938-1010 nm in the case 6h/120°C which can be attributed to a transition of electrons from the valence to the conduction band. Further, in the case of 6h/180°C, a continuous absorption spectrum is observed from 200 to 1100 nm with a slight adsorption in the same range.

Table. II

ESTIMATED GAP ENERGY E_G FOR NI MONO-HYDROXIDE AND THEIR GRAPHENE/NI NANOHYBRID

Products	Gap optique E _g (eV)			
	Direct		Indirect	
	120 °C	180 °C	120 °C	180 °C
α-Ni(OH) ₂	5.10	4.44	4.54	4.12
Graphene/ α-Ni(OH) ₂	4.90	3.50	4.35	3.21

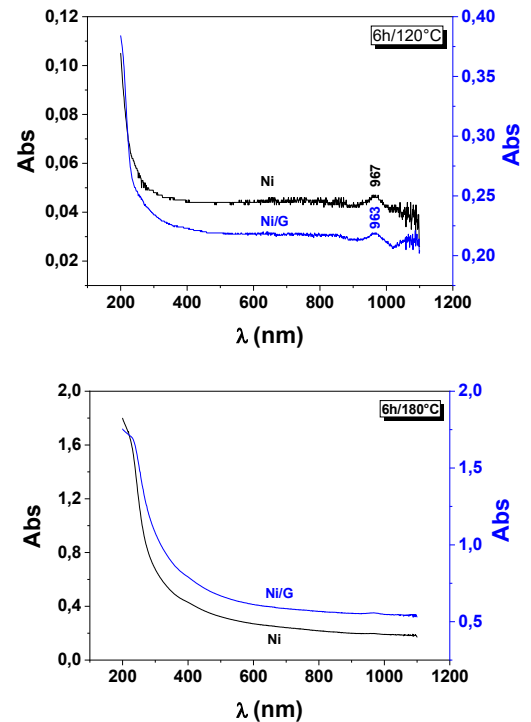


Fig. 5: Adsorption spectra of these products for two cases: 6h/120°C (a) and 6h/180°C (b).

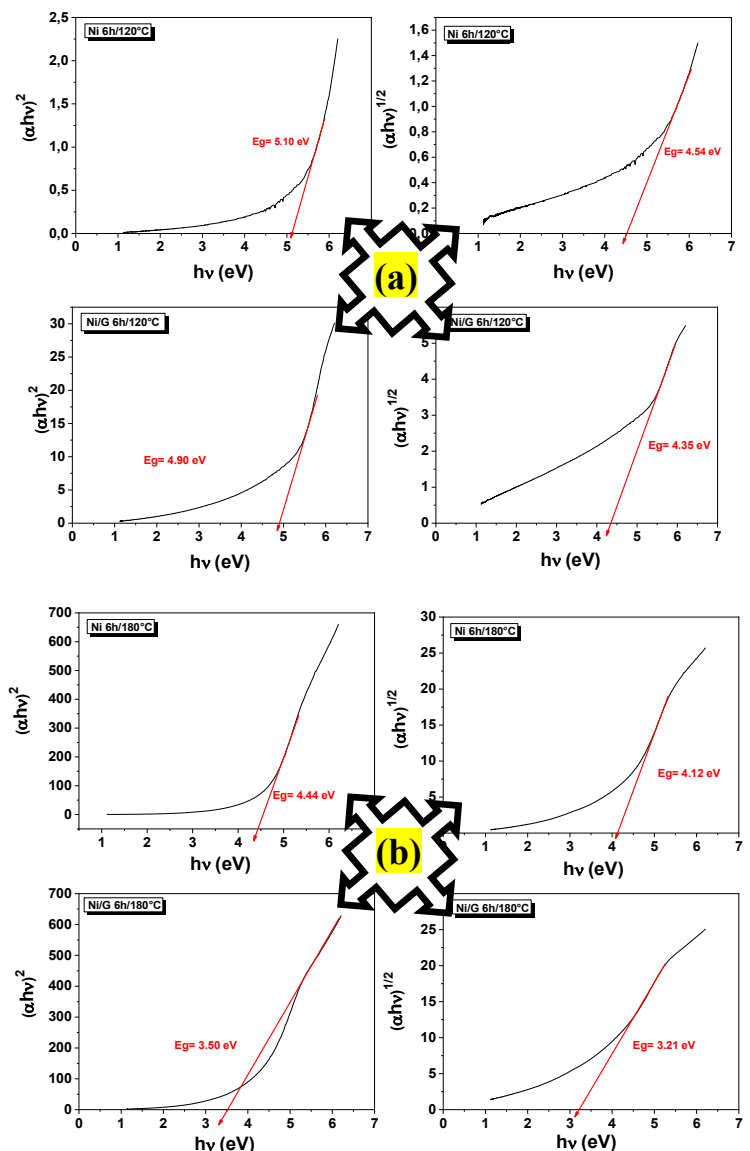


Fig. 6: E_g values for these synthesized products at two hydrothermal conditions: 6h/120°C (a) and 6h/180°C (b).

The gap band energy value (E_g) was calculated by using the following standard Tauc expression [45]: $(\alpha hv) = k(hv - E_g)$

where α is the absorption coefficient, k is a constant, hv is the incident photon energy, E_g is the gap band energy of the material. The value of n is $1/2$ or 2 depending upon whether the transition from valence to conduction band is direct or indirect.

The extrapolation of the linear part in figure 6 that meets the abscissa gives the values of the gap energy E_g of these products between 3.21 and 5.10 eV as are listed above in the table II. The best values were found with nanohybrid of 180°C growth temperature with nanostructured particles cubes and spheres shape composed of $\text{Ni}(\text{HCO}_3)_2/\text{Graphene}$ composition.

Electrochemical Properties

The cyclic voltammetry (CV) tests were carried out in the potential range 0 to 0.65 V at increasing scan rates ranging from 5 to 100 $\text{mV}\cdot\text{s}^{-1}$. Figure 7 shows the obtained CV voltammograms at a scan rate 5 $\text{mV}\cdot\text{s}^{-1}$ in this investigation where we have the current density measured as a function of the applied voltage via Hg/HgO reference electrode.

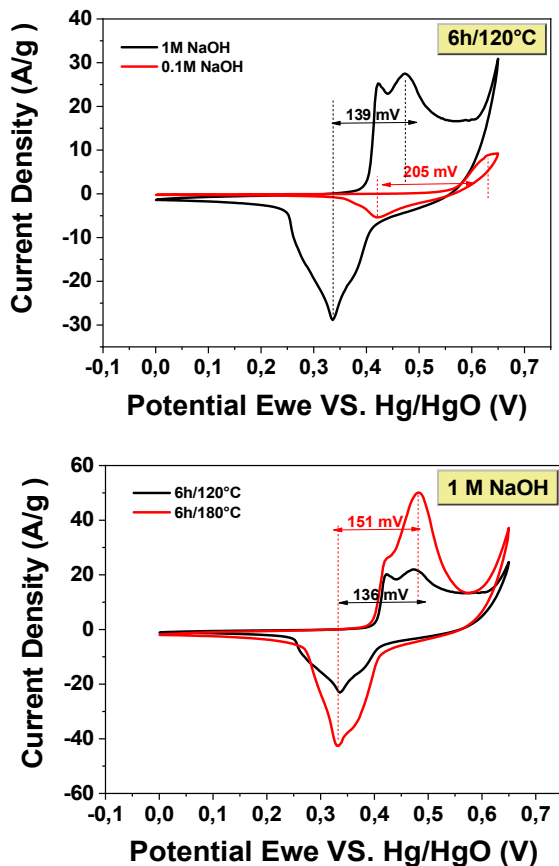
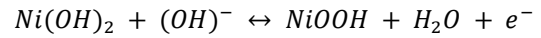


Fig. 7: Voltammograms (CV) of Ni/Graphene nanohybrid synthesized using hydrothermal method at two different conditions: electrolyte concentration and growth temperature effect.

These cyclic voltammetry curves clearly show a quasi-symmetric electrical response with $\Delta E_p = 136$ mV and 151 mV for obtained nanohybrids of 6h/120°C and 6h/180°C hydrothermal condition, respectively, thus proving the reversibility ($\Delta E_p < 200$ mV) of the electrochemical phenomenon in this potential range for both samples in 1M NaOH as generally reported in the literature [41]. The shape of these CV curves allows distinguishing the electrochemical mechanism involving these nanoproductions during the charge shift in the used aqueous electrolyte. Accordingly, they

represent cathodic peaks for the reduction process (bottom) and anodic peaks for the oxidation process (top); which consequently confirm an oxidation-reduction (Redox) mechanism. This confirms so a pseudo-capacitive or Faradic mechanism specific to transition metal electroactive materials, as reported in the storage energy literature [41]. Moreover, we confirm this mechanism via the peaks existence of the following redox reaction:



In addition, with increasing scan rate, we clearly can see also similar CV responses shape where anodic peaks shift positively, while their cathodic peaks shift negatively due to the internal resistance of the electrode that arises from the diffusion of the electrolyte ions within the electrode [49]. This phenomena was be accompanied with increasing current densities revealing higher charge storage; but this low shifting indicate the excellent EC reversibility and outstanding high-rate performance as found generally in literature.

The gravimetric specific capacitance (C_s in $\text{F}\cdot\text{g}^{-1}$) values were calculated according to the following equation [44] :

$$C_s = \frac{\int I dV}{m v \Delta V}$$

where m is the mass of the loaded active material (in g), n represents the scan rate (in $\text{mV}\cdot\text{s}^{-1}$), ΔV ($V_c - V_a$) refer to the potential window between high and low potential limit of the CV curve, $\int I dV$ is the integrated area under the curve for the cathodic current of the CV curve (in $\text{mA}\cdot\text{V}$)

Finally, these electrochemical CV results were also used to estimate the very interesting specific capacity values for each product that is around 1863 and 253 $\text{F}\cdot\text{g}^{-1}$ for nanohybrid obtained at 6h/120°C in two different NaOH electrolyte concentrations 1 and 0.1 M, respectively. However, for a fixed 1 M NaOH aqueous electrolyte concentration, these two nanohybrids obtained at 120°C and 180°C gave specific capacity values around 1863 and 2981 $\text{F}\cdot\text{g}^{-1}$, respectively. Consequently, they show very attractive specific capacity more in the case of $\text{Ni}(\text{HCO}_3)_2/\text{Graphene}$ nanohybrid based nanostructured cubes or spheres particles with low gap energy proved by previous optical properties. This experient has proved the efficiency of carbonate ions as well as the nanohybrid composition basing on transition metal and carbon at nanoscale.

IV. CONCLUSION

Simple and low cost hydrothermal method was employed to synthesize Ni hydroxide and Ni hydrogen carbonate and their nanohybrids based on Graphene nanosheets. The as-prepared products are studied by different characterization techniques to determine their physico-chemical properties. The results of the crystallographic analysis using XRD technique showed that these nanomaterials have quasi-amorphous nanostructures type hydroxide and carbonate at 6h/120°C and 6h/180°C, respectively. Then, this structural information is confirmed through their FTIR spectra by indicating the existence of the characteristic bonds such as Ni-OH and -OH groups linked to the existence of water in the case of the product with pure Ni mono-hydroxide kind, as well as added bonds of carbonate CO_3^{2-} in Ni hydrogen carbonate with C=O in the case of their nanohybrids basing on the Graphene existence (precisely Graphene oxide GO).

Moreover, the electrochemical measurements through their CV tests in two different NaOH aqueous electrolyte concentrations (1 and 0.1 M) show a very interesting specific capacities around 1863 and 253 F.g⁻¹ for nanohybrid obtained at 6h/120°C, respectively. However, at fixed 1 M NaOH electrolyte concentration, both nanohybrids obtained at 120°C and 180°C gave specific capacity values around 1863 F.g⁻¹ and 2981 F.g⁻¹, respectively, proving in consequence the role added of CO₃²⁻ and OH ions in electrochemical performance improvement besides metal transition nanocubes and Graphene conductivity.

ACKNOWLEDGMENT

We express our gratitude and sincere thanks to Prof. D. BEGIN and Prof. I. Janowska group's (ICPEES, Strasbourg) for performing the characterization experiment. The authors also thank the Algerian minister program and Directorate General for Scientific Research and Technological Development (DGRSDT) from Algeria for financial support.

REFERENCES

- [1] M.S. Dresselhaus, I. Thomas, "Alternative energy technologies", *Nature*, vol. 414, pp. 332-337, 2001. [doi: 10.1038/35104599](https://doi.org/10.1038/35104599)
- [2] D.A. Lashof, D.R. Ahuja, "Relative contributions of greenhouse gas emissions to global warming", *Nature*, vol. 344, pp. 529-531, 1990. <https://doi.org/10.1038/344529a0>
- [3] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, "Dye-sensitized solar cells", *Chemical reviews*, vol. 110 (11), pp. 6595-6663, 2010. <https://doi.org/10.1021/cr900356p>
- [4] C. An, Y. Zhang, H. Guo, Y. Wang, "Metal oxide-based supercapacitors: progress and perspectives", *Nanoscale Advances*, vol. 1, pp. 4644-4658, 2019. <https://doi.org/10.1039/C9NA00543A>
- [5] M. Winter, R.J. Brodd, "What are batteries, fuel cells, and supercapacitors?", *Chemical reviews*, vol. 104, pp. 4245-4270, 2004. <https://doi.org/10.1021/cr020730k>
- [6] A.G. Pandolfo, A.F. Hollenkamp, "Carbon properties and their role in supercapacitors", *Journal of power sources*, vol. 157, pp. 11-27, 2006. <https://doi.org/10.1016/j.jpowsour.2006.02.065>
- [7] P.J. Hall, M. Mirzaei, S.I. Fletcher, F.B. Sillars, A.J. Rennie, G.O. Shitta-Bey, G. Wilson, A. Cruden, R. Carter, "Energy storage in electrochemical capacitors: designing functional materials to improve performance", *Energy & Environmental Science*, vol. 3, pp. 1238-1251, 2010. <https://doi.org/10.1039/C0EE00004C>
- [8] Y. Zhu, S. Murali, M.D. Stoller, K.J. Ganesh, W. Cai, P.J. Ferreira, A. Pirkle, R.M. Wallace, K.A. Cychosz, M. Thommes, "Carbon-based supercapacitors produced by activation of graphene", *science*, vol. 332, pp. 1537-1541, 2011. [doi: 10.1126/science.1200770](https://doi.org/10.1126/science.1200770)
- [9] G. Santhosh, G. Nayaka, A.S. Bhatt, "Ultrahigh capacitance of NiCo₂O₄/CeO₂ mixed metal oxide material for supercapacitor applications", *Journal of Alloys and Compounds*, vol. 899, pp. 163312, 2022. <https://doi.org/10.1016/j.jallcom.2021.163312>
- [10] Y. Zhang, L. Li, H. Su, W. Huang, X. Dong, "Binary metal oxide: advanced energy storage materials in supercapacitors", *Journal of Materials Chemistry A*, vol. 3, pp. 43-59, 2015. <https://doi.org/10.1039/C4TA04996A>
- [11] A. Rudge, J. Davey, I. Raistrick, S. Gottesfeld, J.P. Ferraris, "Conducting polymers as active materials in electrochemical capacitors", *Journal of power sources*, vol. 47, no 1-2, pp. 89-107, 1994. [https://doi.org/10.1016/0378-7753\(94\)80053-7](https://doi.org/10.1016/0378-7753(94)80053-7)
- [12] A. Eftekhari, L. Li, Y. Yang, "Polyaniline supercapacitors", *Journal of Power Sources*, vol. 347, pp. 86-107, 2017. <https://doi.org/10.1016/j.jpowsour.2017.02.054>
- [13] H. Dai, R. Li, S. Su, Y. Cui, Y. Lin, L. Zhang, X. Zhu, "Preparation and characterization of PANI/MWCNT/RGO ternary composites as electrode materials for supercapacitors", *Journal of Electronic Materials*, vol. 51, no 3, pp. 1409-1420, 2022. <https://doi.org/10.1007/s11664-021-09421-6>
- [14] B. De, S. Banerjee, K.D. Verma, T. Pal, P. Manna, K.K. Kar, Carbon nanotube as electrode materials for supercapacitors, in: *Handbook of nanocomposites supercapacitor materials II*, Springer, pp. 229-243, 2020. https://doi.org/10.1007/978-3-030-52359-6_9
- [15] S. Hu, S. Zhang, N. Pan, Y.-L. Hsieh, "High energy density supercapacitors from lignin derived submicron activated carbon fibers in aqueous electrolytes", *Journal of Power Sources*, vol. 270, pp. 106-112, 2014. <https://doi.org/10.1016/j.jpowsour.2014.07.063>
- [16] J. Chen, J. Xie, C.Q. Jia, C. Song, J. Hu, H. Li, "Economic preparation of high-performance activated carbon fiber papers as self-supporting supercapacitor electrodes", *Chemical Engineering Journal*, vol. 450, pp. 137938, 2022. <https://doi.org/10.1016/j.cej.2022.137938>
- [17] R. Kötz, M. Carlen, "Principles and applications of electrochemical capacitors", *Electrochimica Acta*, vol. 45, no 15-16, pp. 2483-2498, 2000. [https://doi.org/10.1016/S0013-4686\(00\)00354-6](https://doi.org/10.1016/S0013-4686(00)00354-6)
- [18] T. Nguyen, M.d.F. Montemor, "Metal oxide and hydroxide-based aqueous supercapacitors: from charge storage mechanisms and functional electrode engineering to need-tailored devices", *Advanced Science*, vol. 6, no 9, pp. 1801797, 2019. <https://doi.org/10.1002/advs.201801797>
- [19] C. Lee, X. Wei, J.W. Kysar, J. Hone, "Measurement of the elastic properties and intrinsic strength of monolayer graphene", *science*, vol. 321, no 5887, pp. 385-388, 2008. <https://doi.org/10.1126/science.1157996>
- [20] X. Huang, X. Qi, F. Boey, H. Zhang, "Graphene-based composites", *Chemical Society Reviews*, vol. 41, no 2, pp. 666-686, 2012. <https://doi.org/10.1039/C1CS15078B>
- [21] G. Eda, G. Fanchini, M. Chhowalla, "Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material", *Nature nanotechnology*, vol. 3, no 5, pp. 270-274, 2008. <https://doi.org/10.1038/nnano.2008.83>
- [22] L. Gomez De Arco, Y. Zhang, C.W. Schlenker, K. Ryu, M.E. Thompson, C. Zhou, "Continuous, highly flexible, and transparent graphene films by chemical vapor deposition for organic photovoltaics", *ACS nano*, vol. 4, no 5, pp. 2865-2873, 2010. <https://doi.org/10.1021/nn901587x>
- [23] R. Raccichini, A. Varzi, S. Passerini, B. Scrosati, "The role of graphene for electrochemical energy storage", *Nature materials*, vol. 14, no 3, pp. 271-279, 2015. <https://doi.org/10.1038/nmat4170>
- [24] S. Vivekchand, C.S. Rout, K. Subrahmanyam, A. Govindaraj, C.N.R. Rao, "Graphene-based electrochemical supercapacitors", *Journal of Chemical Sciences*, vol. 120, no 1, pp. 9-13, 2008. <https://doi.org/10.1007/s12039-008-0002-7>
- [25] M.D. Stoller, S. Park, Y. Zhu, J. An, R.S. Ruoff, "Graphene-based ultracapacitors", *Nano letters*, vol. 8, no 10, pp. 3498-3502, 2008. <https://doi.org/10.1021/nl802558y>
- [26] S. Vazquez, S.M. Lukic, E. Galvan, L.G. Franquelo, J.M. Carrasco, "Energy storage systems for transport and grid applications", *IEEE Transactions on industrial electronics*, vol. 57, no 12, pp. 3881-3895, 2010. <https://doi.org/10.1109/TIE.2010.2076414>
- [27] G. Zhang, X. Xiao, B. Li, P. Gu, H. Xue, H. Pang, "Transition metal oxides with one-dimensional/one-dimensional-analogue nanostructures for advanced supercapacitors", *Journal of Materials Chemistry A*, vol. 5, no 18, pp. 8155-8186, 2017. <https://doi.org/10.1039/C7TA02454A>
- [28] R. Liang, Y. Du, P. Xiao, J. Cheng, S. Yuan, Y. Chen, J. Yuan, J. Chen, "Transition metal oxide electrode materials for supercapacitors: a review of recent developments", *Nanomaterials*, vol. 11, no 5, pp. 1248, 2021. <https://doi.org/10.3390/nano11051248>
- [29] X. Li, D. Du, Y. Zhang, W. Xing, Q. Xue, Z. Yan, "Layered double hydroxides toward high-performance supercapacitors", *Journal of Materials Chemistry A*, vol. 5, no 30, pp. 15460-15485, 2017. <https://doi.org/10.1039/C7TA04001F>
- [30] L. Zhang, D. Shi, T. Liu, M. Jaroniec, J. Yu, "Nickel-based materials for supercapacitors", *Materials Today*, vol. 25, pp. 35-65, 2019. <https://doi.org/10.1016/j.mattod.2018.11.002>
- [31] M. Aghazadeh, M. Ghaemi, B. Sabour, S. Dalvand, "Electrochemical preparation of α-Ni(OH)₂ ultrafine nanoparticles for high-performance supercapacitors", *Journal of Solid State Electrochemistry*, vol. 18, no 6, pp. 1569-1584, 2014. <https://doi.org/10.1007/s10008-014-2381-7>
- [32] C. An, Y. Zhang, H. Guo, Y. Wang, "Metal oxide-based supercapacitors: progress and perspectives", *Nanoscale Advances*, vol. 1, no 12, pp. 4644-4658, 2019. <https://doi.org/10.1039/C9NA00543A>
- [33] T. Nguyen, M. D. F. Montemor, "Metal oxide and hydroxide-based aqueous supercapacitors: from charge storage mechanisms and functional electrode engineering to need-tailored devices". *Advanced Science*, vol. 6, no 9, pp. 1801797, 2019. <https://doi.org/10.1002/advs.201801797>
- [34] C. Jiang, B. Zhao, J. Cheng, J. Li, H. Zhang, Z. Tang, J. Yang, "Hydrothermal synthesis of Ni(OH)₂ nanoflakes on 3D graphene foam for high-performance supercapacitors", *Electrochimica Acta*, vol. 173, pp. 399-407, 2015. <https://doi.org/10.1016/j.electacta.2015.05.081>
- [35] H. Wang, Y. Song, W. Liu, L. Yan, "Three dimensional Ni(OH)₂/rGO hydrogel as binder-free electrode for asymmetric supercapacitor", *Journal of Alloys and Compounds*, vol. 735, pp. 2428-2435, 2018. <https://doi.org/10.1016/j.jallcom.2017.11.358>
- [36] J. Liu, Y. Wang, R. Hu, H.A. Munir, H. Liu, "High-performance supercapacitor electrode based on 3D rose-like β-Ni(OH)₂/rGO nanohybrid", *Journal of Physics and Chemistry of Solids*, vol. 138, pp. 109297, 2020. <https://doi.org/10.1016/j.jpcs.2019.109297>
- [37] P.G. Choi, K. Kim, Y. Masuda, "Porous NiO Nanosheet Based High Sensitivity Acetone Gas Sensor Capable of Parts-Per-Billion Level Detection", <https://dx.doi.org/10.2139/ssrn.4077548>
- [38] A.K. Patra, S.K. Kundu, D. Kim, A. Bhaumik, "Controlled Synthesis of a Hexagonal-Shaped NiO Nanocatalyst with Highly Reactive Facets

- (110) and Its Catalytic Activity”, *Chem. Cat. Chem.*, vol. 7, no 5, pp. 791-798, 2015. <https://doi.org/10.1002/cctc.201402871>
- [39] Z. Gao, Z. Wang, J. Chang, L. Chen, D. Wu, F. Xu, X. Wang, K. Jiang, “Micelles directed preparation of ternary cobalt hydroxide carbonate nickel hydroxide-reduced graphene oxide composite porous nanowire arrays with superior faradic capacitance performance”, *Journal of Colloid and Interface Science*, Vol. 534, pp. 563–573, 2019. <https://doi.org/10.1016/j.jcis.2018.09.068>
- [40] R. Thangappan, S. Kalaiselvam, A. Elayaperumal, R. Jayavel, “Synthesis of graphene oxide/vanadium pentoxide composite nanofibers by electrospinning for supercapacitor applications”, *Solid State Ionics*, Vol. 268, pp. 321–325, 2014. <http://dx.doi.org/10.1016/j.ssi.2014.10.025>
- [41] X. Wu, X. Pang, X. An, X. Xie, “Kinetics and mechanism of formation of benzoin ethyl ether from benzaldehyde and ethanol using heterogeneous Ni(HCO₃)₂ as catalyst”, *Progress in Reaction Kinetics and Mechanism*, vol. 39, no 3, pp. 299-307, 2014. <https://doi.org/10.3184/146867814X14043731662783>
- [42] F. Kong, X. He, J. Chen, S. Tao, B. Qian, X. Jiang, H. Luo, “Hierarchical Ni(HCO₃)₂ Nanosheets Anchored on Carbon Nanofibers as Binder-Free Anodes for Lithium-Ion Batteries”, *Energy Technology*, vol. 7, no 6, pp. 1900094, 2019. <https://doi.org/10.1002/ente.201900094>
- [43] R. Siburian, H. Sihotang, S. Lumban Raja, M. Supeno And C. Simanjuntak, “New Route to Synthesize of Graphene Nano Sheets”, *Orient. J. Chem.*, Vol. 34(1), 182-187 (2018). DOI: [10.13005/ojc/340120](https://doi.org/10.13005/ojc/340120).
- [44] O. Guellati, A. Harat, D. Momodu, J. Dangbegnon, T. Romero, D. Begin, C. Pham-Huu, N. Manyala, M. Guerioune, “Electrochemical measurements of 1D/2D/3D Ni-Co bi-phase mesoporousnanohybrids synthesized using free-template hydrothermal method”, *Electrochimica Acta*, vol. 275, pp. 155-171, 2018. <https://doi.org/10.1016/j.electacta.2018.04.112>
- [45] Z. Liu, R. Ma, M. Osada, K. Takada, T. Sasaki, “Selective and controlled synthesis of α - and β -cobalt hydroxides in highly developed hexagonal platelets”, *Journal of the American Chemical Society*, vol. 127, no 40, pp. 13869-13874, 2005. <https://doi.org/10.1021/ja0523338>
- [46] P. Lokhande, U. Chavan, “Nanostructured Ni(OH)₂/rGO composite chemically deposited on Ni foam for high performance of supercapacitor applications”, *Materials Science for Energy Technologies*, vol. 2, no 1, pp. 52-56, 2019. <https://doi.org/10.1016/j.msct.2018.10.003>
- [47] N. Habib, O. Guellati, A. Harat, A. Nait-Merzoug, J. El Haskouri, D. Momodu, N. Manyala, D. Begin, M. Guerioune, “Ni–Zn hydroxide-based bi-phase multiscale porous nanohybrids: physico-chemical properties”, *Applied Nanoscience*, vol. 10, no 8, pp. 2467-2477, 2020. <https://doi.org/10.1007/s13204-019-01062-w>
- [48] J. Tauc, Optical properties and electronic structure of amorphous Ge and Si, *Materials research bulletin*, vol. 3, no 1, pp. 37-46, 1968. [https://doi.org/10.1016/0025-5408\(68\)90023-8](https://doi.org/10.1016/0025-5408(68)90023-8)
- [49] M.M.M. Mohammed, A.G. Abd-Elrahim, D.-M. Chun, One-step deposition of a Ni(OH)₂-graphene hybrid prepared by vacuum kinetic spray for high energy density hybrid supercapacitor, *Materials Chemistry and Physics*, vol. 244, pp. 122701, 2020. <https://doi.org/10.1016/j.matchemphys.2020.122701>



Ikram DJEBABLIA Phd in Applied physics, Domain of research : Energy storage (experimental and theoretical).



Ouanassa GUELLATI, researcher in LEREC laboratory in Algeria and Teacher at Souk-Ahras University, has completed her PhD from Badji-Mokhtar University of Annaba 2013, Algeria on production of Carbon nanotube (CNTs) using CCVD technique and their functionalization and macronisation. She has published 23 papers in reputed journals with high impact factor. She has presented in september 2020 her university habilitation at Annaba University. She is current reviewer in *Nanoscale Research Letters* and *Materials Science and Engineering B – Journal Elsevier*. Actually, she is working on the production of smart nanomaterials like transition metal hydroxides, oxides and nanostructured polyaniline and their nanocomposites / nanohybrids with CNTs and/or Graphene as well as mesoporous Biochars for energy storage, environment and Biosensing application. She is working in collaboration with ICPEES at ECPM, Strasbourg – France, IMS at University of Valencia – Spain, CES at Namur University, SARChI Chair in Carbon Technology and Materials at Pretoria University, South Africa and DISAT - Politecnico di Torino, Italy.