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Layered double hydroxides (LDHs) as promising electrode materials for commercial supercapacitors

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Introduction

The increasing environmental challenges such as the rise of global warming and depletion of fossil fuels have enthused the scientific community to dedicate tremendous effort to the development of various clean energy technologies in recent years [1-2]. Thus, most of the efficient, clean and sustainable energy production sources were successfully developed, such as solar cells, tidal power, wind energy, hydrogen fuel cells, geothermal energy, and so forth. However, most of these energy production sources are not able to generate electric power continually and thus they cannot meet human life practical requirements and industrial production. Therefore, to store the produced energy from those energy production sources, proper energy storage devices are required [3]. Besides, the electric and hybrid vehicles sector and the demand for energy in modern digital communications (i.e. 5G) also urge the development of the next generation of energy storage devices exhibiting high energy and power density.

Electrochemical capacitors also known as ultracapacitors or supercapacitors (SCs) are gaining tremendous momentum over batteries and becoming the centre of attention of a large number of studies owing to their superior capabilities, such as environmental friendliness, high efficiency, fast charge-discharge rates, high power density, safe operation, good cycling stability and lower maintenance cost [1-2]. They have also the ability to work under a wide voltage window, at relatively high temperatures and exhibit an exceptionally high number of the charge-discharge cycle ($> 500\,000$) [4]. Thus, supercapacitors have the merit to be one of the most effective energy storage devices.

In addition to the above-mentioned advantages, supercapacitors have found numerous applications, in memory backup systems, elevators, consumer electronics, bullet trains, electric & hybrid electric vehicles and military devices. It is also important to note that their remarkable properties make them key candidates for several applications where high power density is highly desired.

Supercapacitors are designed or manufactured like batteries (two electrodes, separator and electrolyte). However, unlike batteries, supercapacitors charge mechanisms operate entirely on the surface of electrodes, either for the electric double-layer capacitors (EDLC) or for pseudo-capacitors (PCs). Thus, electrodes with high specific surface area are greatly required to accommodate more electrolyte ions and optimize the performance of supercapacitors. To meet this goal, nanostructured electrodes are the best candidates [5].

Even though supercapacitors have been commercialized already and have several advantages over other energy storage devices; but in principle, they exhibit a major drawback that permanently limits their practical application. Generally, they have low energy density compared to batteries, which are globally the centre-topic of thousands of research reports yearly [6].

It should be reminded that the performances of supercapacitors are strongly dependent on the intrinsic fundamental physicochemical properties of electrode materials that they are made of [5]. Therefore, exploring electrodes interfacial properties to achieve high specific capacitance is one of the key tasks in order to successfully improve the energy density of supercapacitors. Nowadays, most of electrode materials used for supercapacitors are nanostructured.

Carbon-based materials are the main electrode materials used for most of the commercial supercapacitors because they are easy to be developed with good thermal stability and excellent corrosion resistance for a moderate cost [7]. In addition, they exhibit high specific surface area, have good cycling stability, controllable porosity, high maximum power density and good safety. However, their energy density is still unsatisfactory (below 10 Wh kg^{-1}) due to the reversible ion adsorption limitation at the electrode/electrolyte interface [8]. Thus, the pseudo-capacitive

materials can facilitate the achievement of that goal in improving the energy density of supercapacitors available on the market, including good rate capability, because their charge mechanism occurs through superficial faradaic reactions. Various pseudo-capacitive materials have been developed and tested for supercapacitor applications, such as conducting polymers, metal oxides/hydroxides, and layered double hydroxides (LDH).

To date, several pseudo-capacitive electrode materials for supercapacitor applications with excellent properties have been developed in academia arena; unfortunately, not all of them have reached the industry for practical applications; because most of them are developed via complicated synthesis procedures that involve high cost. Some are relatively toxic to humans and environment and others are not up scalable. Therefore, they cannot meet the industrial requirements.

Among many pseudo-capacitive materials developed in academia; layered double hydroxides (LDHs) proved to be the best candidates for commercial supercapacitors since most of their properties meet the industrial requirements, such as low production cost, high specific capacitance, facile synthesis, ability to be up-scaled [9-10], easy tunability, good chemical stability and the ability to intercalate diverse varieties of anions (inorganic, organic, biomolecules, and even genes) [11].

That is why this chapter presents Layered Double Hydroxides (LDHs) as promising electrode materials for commercial supercapacitors, it describes their structure, it displays different routes to synthesize them and some characterization techniques. Finally, it demonstrates some advantages that prove that LDHs are the best candidates to be applied as electrode materials for commercial supercapacitors.

Supercapacitors (Overview)

The popular energy storage devices are, on one hand, batteries which allow a relatively high energy density with a moderate specific power density, and on the other hand, capacitors known for their high specific power density, but not allowing sufficient operating energy density to supply applications that require a little energy. However, the versatile engineered configurations of supercapacitors enable them to deliver high power and energy density simultaneously. That is why supercapacitors are located between batteries and capacitors.

Supercapacitors are devices mainly composed of two electrodes of desired highly porous materials that are electrically isolated using a separator that prevents short-circuiting between electrodes commonly impregnated in a suitable electrolyte as displayed in figure 4.1.

Basically, supercapacitors function by storing charge through the adsorption of ions at the interface between the electrodes and electrolyte. In concrete, when a potential (V) is applied from an external source, an electrical field is created, then ions from the electrolyte with opposite charge are attracted onto the surface of each electrode and form an electric double-layer (EDCL) as shown in figure 4.1, which is considered as the first charge storage mechanism of supercapacitors, and it is free of any chemical reaction [12]. Devices that undergo electric double layer (EDLC) mechanism are called « Electric double layer capacitors »; their capacitance arises from the stored ions at the interface between electrodes and electrolyte. The capacitance for electric double-layer capacitors is proportional to the surface area and accessible pore of the electrode materials. That is why the electrode materials with the high surface area are greatly needed for EDLC capacitors. Nevertheless, the specific surface area can also be highly enhanced through the nanoarchitecture design of the electrode materials [13].

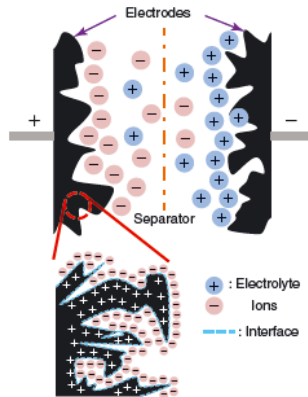


FIGURE 4.1
Supercapacitor structure [6].

Carbon-based materials are the mainly used electrode materials for electric-double layer capacitors because they exhibit high specific surface area, have good cycling stability, controllable porosity, high maximum power density, and safety. That is why carbon-based material in different forms have been tested and used as electrode materials for EDLC capacitors, including carbon nanotubes, graphene sheets, carbon onions, fibers, carbon blacks, carbide-derived carbons and activated carbons [14-17]. However, the reversible ion adsorption limitation at the electrode/electrolyte interface impedes carbon-based materials to have high specific capacitance [17]. This limitation is attributed to the decrease of the pore wall thickness of carbon with the increase of the specific surface area. This tightening of the distance between the pores reduces the screen effect of carbon, which increases the repulsive interactions between ions and decreases the attractive interactions between ions and carbon [18]. Thus, in order to prevent the above-highlighted challenge and improve the supercapacitors energy density, the use of other types of electrode materials such as conducting polymers, metal oxides/hydroxides was encouraged. However, metal oxides/hydroxides exhibit excellent charge storage abilities, good cycling stability than conducting polymers and high specific capacitance relative to carbon materials. Supercapacitors using metal oxides/hydroxides as electrode materials present simultaneously good energy density and high power ability [19]. In addition, most metal oxides/hydroxides exhibit pseudo-capacitance behaviour [20].

The pseudo-capacitance is the second charge storage mechanism of supercapacitors that involves a reversible faradaic reaction, which occurs on the surface of active materials during the charge/discharge process. Trasatti [21] introduced it. The corresponding devices are called "Pseudo-capacitors (PCs)" [12]. The expression pseudo-capacitance was used to describe the electrochemical behaviour of RuO₂ in 1971 [22]. Concretely, RuO₂ was reduced to lower oxidation state during the charge process resulting in the adsorption of electrolyte cations. During the discharge, the process was practically reversed [23,24], then, first pseudo-capacitors (PCs) were reported [20].

Overall, it can be concluded according to what is stated above that, on one hand, supercapacitors have two charge storage mechanisms, the electric double layer (EDLC) and the pseudo-capacitance. On the other hand, the performances of supercapacitors are strongly dependent on the intrinsic fundamental physicochemical properties of electrode materials that they are made of [5]. Reason

why exploring electrode materials with excellent properties to achieve high specific capacitance remains a goal to achieve in order to successfully improve the energy density of supercapacitors.

Electrode materials

High specific capacitance and long cycling life of supercapacitors belong to an ideal electrode material. Therefore, the selection and the preparation of electrode materials must be done with particular care. However, there are tremendous factors which determine the suitability of electrode material. (1) Since the charge is stored on the surface of the electrode material, the surface area is an important factor for selecting the appropriate electrode material [6]. (2) The power density is a crucial characteristic of supercapacitors and it is impeded by the presence of high series resistance (ESR). To avoid that and promote the power density, good electrical conductivity is highly desired for the electrode material [26]. (3) Since the lifetime of supercapacitors makes them the most assuring energy storage devices, the more stable electrode material is highly desirable because it yields also long cycle stability [6]. (4) Finally, the cost related to the synthesis procedure of the electrode material and the toxicity of components used should also be taken into consideration before selecting the electrode material.

Carbon-based materials, conducting polymers, and metal oxides/hydroxides are the main types of materials used as supercapacitors electrode materials. However, considering the unsatisfactory performance of carbon-based materials and conducting polymers; several metal oxides/hydroxides materials have been studied and confirmed to be promising pseudo-capacitive electrode materials for supercapacitors. Nevertheless, most of them are not used for commercial applications because they exhibit low specific capacitance, poor conductivity and low cyclic stability when used alone. That is why layered double hydroxides (LDHs) materials have proved to be excellent candidates for this purpose since their synthesis generally involves two or more components, resulting to enhancement of the performance of the material and boosts its electrochemical properties due to the synergetic effect of components within the material.

Layered double hydroxides (LDHs) electrode materials are gaining tremendous momentum and becoming the centre of attention of a large number of studies due to many advantages such as high specific capacitance, low-cost production, facile synthesis procedure, unique structure, unvarying distribution of diverse metal cations in the brucite layer, surface hydroxyl groups and the possibility to obtain through the synthesis, the compositions and the combinations of metal-anions [9].

Layered double hydroxides (LDHs)

Historical background

Layered double hydroxides (LDHs) are a class of ionic lamellar compounds, also known as anionic clays having $[M(II)_{1-x}M(III)_x(OH)_2](Y^{n-})_{x/n} \cdot yH_2O$ as a general formula; where M(II) and M(III) are divalent and trivalent metals, respectively, whereas Y^{n-} represents the anion between the layers. LDHs, are known for over 150 years since the discovery of hydrotalcite, which constitutes with sjogrenite, the typical compounds of this large class of minerals. However, the hydrotalcite stoichiometry ($[Mg_6Al_2(OH)_{16}][CO_3 \cdot 4H_2O]$) has been correctly determined for the first time in 1915 by professor E. Manasse from the University of Florence (Italy) [27]. Later in 1940, Feitknecht synthesizes the first LDHs via co-precipitation method. he called these compounds "doppelschichtstrukturen" (double layer structures) also called layered double hydroxides (LDHs),

considering the simple stacking of sheets of brucite $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ sheets [28]. In 1960, Almann and Taylor described the LDHs structure [29,30]. Then early in 1970, the hydrotalcite compounds were proposed for first applications in fields such as catalysis or ion exchange. Followed by the first reported works on hydrotalcite used as basic catalysts in 1971 [31]. However, beyond energy storage, LDHs are world widely acclaimed and applied in different technological applications due to their outstanding physicochemical properties, the cost-effectiveness, the facile synthesis procedure and the thermal stability. In addition, they effectively allow the use of transition metal atoms to achieve unique structural property [32,33].

Description of LDHs structure

The most interest part of LDHs among other materials in the field of energy storage is the structure. Many authors have demonstrated that during the faradaic redox charge transfer, the surface of LDHs is not the only part that participates; they have stated that the entire crystalline structure is also involved in the charge storage mechanism via intercalation/de-intercalation of electrolyte ions favouring LDHs to possess excellent energy storage capabilities [34-36].

The LDHs structure is settled on that of brucite $\text{Mg}(\text{OH})_2$, whereby a portion of divalent ions is randomly substituted by trivalent ions, giving to the octahedral units an excess of positive charge in order to ensure the overall electrical neutrality. This excess charge is compensated by the negative charges of anions intercalated in the interlayer space. The octahedral units comprise divalent and trivalent metallic cations and share their borders to form brucite-like layers $\text{Mg}(\text{OH})_2$ as displayed in figures 4.3. However, the entire LDHs structure is composed by stacking of layers made up of metal cations between which anionic species and water molecules are incorporated. Moreover, the principal layers are charged positively and the charge density is directly related to the arithmetical values of the trivalent metal ratio $x = \text{M}^{\text{III}}/(\text{M}^{\text{II}} + \text{M}^{\text{III}})$; thus, the chemical formula can be reduced as $[\text{M}^{\text{II}}-\text{M}^{\text{III}}-\text{X}]$ [37].

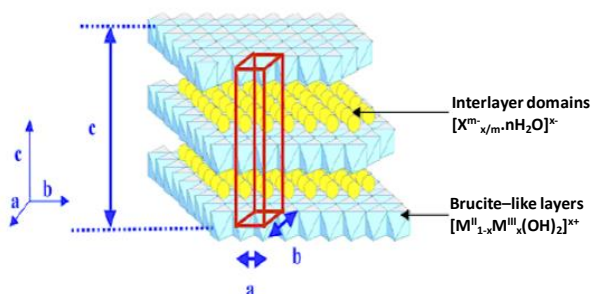


FIGURE 4.2

General structure of LDHs [38].

The hexagonal mesh of parameters “a, b and c” shown in figure 4.2, describe the hydrotalcite nature of LDHs. The parameter “a” corresponds to the distance between neighbouring metal cations within the same layer. Its value depends on the nature and the ionic radius of the interlayer cations, as well as the substitution rate within the layer. In contrast, the parameter “b” is the distance between metal and oxygen and finally, the parameter “c” is correlated with the nature, orientation, charge and hydration rate of compensation anions [38].

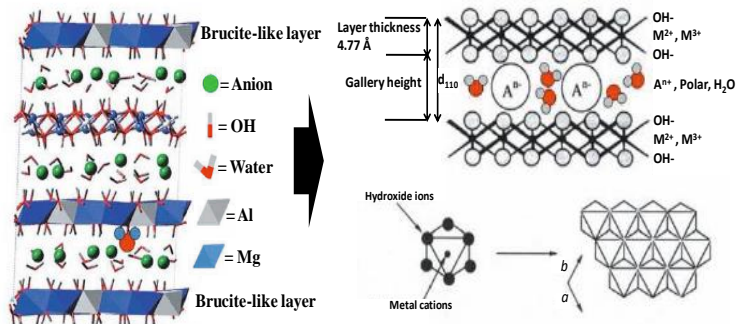


FIGURE 4.3
Detailed schematic representation of LDHs structure [39].

The interlayer domain of LDHs is described as a disordered environment (see figure 4.3); whereby, interactions between layers, oxygen and anions, as well as on the liaison of hydrogen bonds established between hydroxyl groups of the layers, anions and molecules of water within interlayer are weak electrostatic type liaison that favours the mobility of the intercalated species. The interlayer domain of LDHs is also a hydrophilic environment, because of the presence of water molecules. However, the hydrophilic status of LDHs structure is highly beneficial for their electrochemical performances, because it improves the ionic diffusion [40]. Furthermore, V. Rives reported that when in the brucite, a portion of M^{II+} is replaced; the anions located in the interlayer domain together with water molecules balance the positive charge of the layer [41]. Additionally, it was also reported that the incorporation of anions in the interlayer domain is always along with the molecules of water for the restoration of charge neutrality and stability [42]. In the same direction, Richetta *et al.*, reported that the presence of water within the LDHs structure contributes greatly to their spectacular characteristics [43].

The number of water molecules in the interlayer depends on the temperature and humidity conditions of the environment. Most of the divalent and trivalent metal cations discovered in LDHs are the property of the third and fourth periods of the periodic classification of elements [37]. Some of them are listed below.

Divalent cations: Mg^{2+} , Fe^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , Cu^{2+} , Ca^{2+} and Li^{2+} .

Trivalent cations: Fe^{3+} , Al^{3+} , Cr^{3+} , Co^{3+} , Mn^{3+} and Ni^{3+} .

The following anions can be located between the LDH layers:

- Simple anions: CO_3^{2-} , OH^- , Cl^- , Br^- , I^- , NO_3^- , ClO_4^- , SO_4^{2-} , CrO_4^{2-} ...
- Halo complexes: $(NiCl_4)^-$, $(COClO_4)^-$, $(IrCl_6)^{2-}$...Oxo-anions: carbonate, nitrate, sulphate, bromated,...
- Oxo complexes: $[MoO_2(O_2CC(S)Ph_2)_2]^{2-}$, $[MoO_2(O_2)C_4H_2O_6]^{4-}$...
- Polyoxo-metallates: chromate, dichromate, $(Mo_7O_{24})^{6-}$, $(V_{10}O_{28})^{6-}$,...
- Anionic complexes: ferro and ferricyanide, $(PdCl_4)^{2-}$, ...
- Organic polymer anions: carboxylates, phosphonates, alkyl sulphates, adipic, oxalic, malonic acids, or acrylate and polyacrylate, sulfonate...
- Macrocyclic ligands: metalloporphyrins, metallophthalocyanines...
- Heteropolyoxometallates: $(PMo_{12}O_{40})^{3-}$, $(PW_{12}O_{40})^{3-}$...

However, it should be noted that there is a close correlation between the size, charge, and layout of these interlayer anions species since they can lead to the modification of the basal spacings of layers. That is why a stringent selection should be done, either an inorganic or an organic anions species [44].

Different synthesis methods of LDHs

There are many methods to synthesize LDHs, the direct as well as the indirect method. However, the techniques applied to synthesize LDHs are generally quite simple and do not require any sophisticated apparatus, resulting in low cost. Furthermore, the synthesis conditions allow to determine the structural parameters of layers, while, their charge and composition depend directly on the composition of the solution of metal salts used. The commonly used methods to synthesize LDHs are: (1) the co-precipitation method considered as the direct synthesis method of LDHs. It is the most generally applied technique. In this method, the goal is to co-precipitate the metal hydroxides by a slow addition of a solution having targeted anions into a stirred solution of divalent and trivalent metal cations present into a container, while respecting an appropriate ratio. It is desired that the pH be increased during the operation by adding a base or urea for hydrolysis that contributes to the precipitation of the LDHs. The above-presented method is based on the condensation of hexa-aqua metal complexes in solution, allowing the brucite-like layers to be formed with a uniform distribution of metallic cation with solvated interlayer anions [45]. However, the working pH value of the reaction system must preferably be controlled, since it greatly impacts the morphology which indirectly influences the surface area [46]. In addition, the pH value selected must preferably suit the types of metals ions used, because, when several metal ions coexist in a solution, the co-precipitation pH value is different from the required pH values related to the precipitation of each metallic ion considered individually [46]. Most of LDHs involve urea as a reagent during the synthesis procedure, leading the solution to possess a pH 9, depending on the thermolysis temperature used. Nevertheless, the pH values ranging from 7 to 10 are generally selected for LDHs synthesis, because the acidic condition within the solution causes the brucite-like layer within the LDHs to collapse.

(2) The anion-exchange, also known as an indirect method. This is a frequently used synthesis method of LDHs composites. It appears to be a method of synthesis of great importance because it is sometimes a special route available to obtain new types of LDHs. Practically, the starting LDHs phase is dispersed into an aqueous solution containing excess anions to be exchanged. To carry out the exchange, you must put LDHs precursor generally containing chloride or nitrate ions suspended into a solution containing the anion to be inserted, and then bring the solution to the desired pH (preferably the pH must be kept at 4.0 or above 4.0 otherwise, the hydroxyl layers will be broken), while maintaining agitation and operating away from CO₂ in the air. Generally, the host-guest exchange is linked to the electrostatic forces based between the positively charged layers and the exchanging anions. Thus, as the electrostatic interaction with the layers is weak, the anions present in the interlayer can easily be replaced by those which possess high electrostatic interaction with layers, and then new materials can be obtained, in particular hybrids [41]. It should be noted that carbonate anions are generally more preferred than other anions by the LDHs systems. The reason why during the synthesis of LDHs, either through direct or indirect method, carbonate and carbon dioxide must be excluded from the system especially when there is excess water. Carbonate anions prevail more at higher pH [47].

(3) The hydrothermal method. This method is firstly aimed for further treatment of obtained precipitates after co-precipitation method. It is usually performed after the obtained precipitates are filtered, washed and dried to improve the crystalline of the particles [43]. Nevertheless, it is advantageous to be applied, when chlorides and nitrates precursors are not required to be intercalated as guest species with a low attraction for LDHs. Besides, it is also beneficial, when LDHs material must be synthesized using powders like starting reactants [48]. However, the hydrothermal temperature does not permit the control of the LDHs structure [49].

(4) LDHs can also be calcined for specific purposes [50], but this should be done with caution because the calcination of LDHs involves the decomposition of a part of their crystalline structure or in some cases the total crystalline structure; whereas the particular property that makes LDHs being promising electrode for energy storage is their unique crystalline structure which was demonstrated to be involved in the charge storage mechanism via intercalation/de-intercalation of electrolyte ions favouring the remarkable energy storage properties [36-37].

Different characterisation techniques of LDHs

The uniqueness about LDHs resides on their crystalline structure. Thus, the crystalline structure confirms the LDHs identity. It should be noted that all the LDHs have all most the same crystalline structure.

Nowadays, there are many techniques to characterize LDHs. However, since their identity can exactly be confirmed through the crystalline structure, X-rays Diffraction (XRD) is found to be more reliable and the most important characterization technique for LDHs, followed by the Fourier-Transform Infrared spectroscopy (FTIR) which identifies the nature of anions located between the interlayer. In addition, the surface morphology of the material also plays a great role on the performance. That is why is always advisable to analyze the morphology as well as the chemical distribution within the material.

The crystalline structure of LDHs and lattice parameters “*c*” are precisely identified by X-rays Diffraction (XRD) analysis. The lattice parameter “*c*” is equivalent to three times the spacing “*d*” between two consecutive layers (see figure 4.2).

Figure 4.4 shows a XRD patterns of NiCo-LDH@80°C, displaying peaks, which are, attributed to diffraction by planes (003), (006), (009), (012), (110). However, from this XRD result, the value of the lattice parameter “*c*” can simply be calculated by referring to the position of the peak by plane (003) (“ $c = 3d(003)$ ”), or by calculating the average of three harmonics peaks positioned by planes (003), (006), (009), (“ $c = d(003) + 2d(006) + 3d(009)$ ”). It should also be reminded that the peak by plane (009) is frequently overlapped with those assigned to other non-basal planes that are occasionally broad, due to the turbostratic disorder of anions and the water molecules within the interlayer space. The lattice parameter “*a*” is very dependent on the nature of cations composing the layers (ionic radii). Whereas, the value of the lattice parameter “*c*” relies on the nature and orientation of anions within the interlayer. Furthermore, the orientation of the interlayer anions is the results of the changes occurring in electronic interactions with layers due to the ratio of divalent and trivalent cations (M^{II+} , M^{III+}). Thus, the value of the diffraction peak by plane (110) is equivalent to one half of parameter “*a*” (with “ $a=2d(110)$ ”) [41].

The Fourier-Transform Infrared spectroscopy (FTIR) is a useful technique especially in the study of LDHs, because it has the ability to deliver the identity related to the interlayer anions present within the LDHs materials and follow their exchange reactions. In addition, the FTIR informs also about the presence of water molecules, the hydroxyl group as well as the metal-oxygen bending vibration that confirms the existence of metals used to prepare the LDHs [51].

Generally, the surface morphology of the material is characterized by the scanning electron microscopy (SEM), which is a powerful electron microscope instrument that provides images of material by scanning its surface. In practical, an electron column generates a beam of incident electrons that strike the targeted sample. Then, a given electron will interact with atoms in the material, generating several signals containing information related to the precise description of the surface morphology of the material [51].

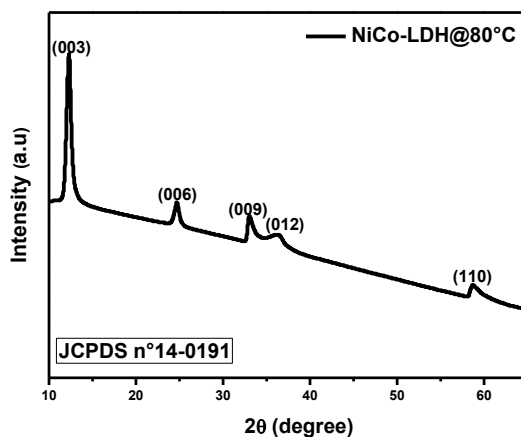


FIGURE 4.4

XRD pattern of NiCo-LDH@80°C [10].

The specific surface area is also an important factor to achieve high-performance supercapacitors; this applies also for LDHs materials. That is why the analysis of the specific surface area of LDHs is also very crucial. Brunauer-Emmett-Teller (BET) is generally used for this purpose.

However, It must be noted that the nitrogen adsorption-desorption isotherms shapes in the case of LDHs are strongly dependent on the size of interlayer anions. For LDHs containing small anions such as chloride, carbonate, nitrate, etc., the isotherms similar to type II in the IUPAC classification is recorded, although a narrow hysteresis loop is also reported most often, due to the lack of enough enlargement of layers to allow access to nitrogen molecules. However, for LDHs with large intercalated anions such as hexacyanoferrate, polyoxometalate, etc., the isotherms similar to type I is recorded, while the solids display micro-porosity corresponding to the interlayer space due to the size of anions that moves apart the layers and open good access for nitrogen molecules [41].

LDHs as promising electrode materials for commercial SCs

Electrode materials are the most important components of supercapacitors since the performance depend on them. This section presents some advantages of LDHs supporting them to be the best candidates for commercial supercapacitors.

The global market for supercapacitors is growing well and the growth is expected to double in the coming years. The total SCs market was evaluated at \$470 million in 2010 and shifted at \$1.2 billion in 2015. Since the demand continues to increase, it has anticipated that SCs market growth will reach \$5.0 billion in 2025 [52]. In addition, the SCs market devoted to memory protection in the electronic industry is estimated at \$1.34 billion/year [53-54]. The growth of the SCs market is triggered by the need to have them as a bridge upon the gap between conventional capacitors and

batteries in terms of power and energy density, because the combination of high energy and power density in one device is greatly needed since the electric vehicles, electric grids, hybrid vehicles, electric rail vehicles etc... are nowadays the potential market opportunities for SCs. The reason being, the energy density serves for a long-distance driving while the power density supports the acceleration. Unfortunately, the limit of the energy density of supercapacitors available in the market lies only up to 10 Wh/kg, while the common lead-acid batteries exhibit 35-40 Wh/kg and lithium-ion batteries go up to 100 Wh/kg [55]. That is why the energy density of commercial supercapacitors still needs to be optimised.

Electrode materials are considered as the most costly components of supercapacitors besides the electrolyte and separator. Therefore, improving the energy density of commercial supercapacitors while keeping the production cost low is an important goal to achieve in order to promote future market penetration for supercapacitors.

Layered double hydroxides (LDHs) have proved to be the best electrode materials to achieve the above-highlighted goal due to many of their advantages that meet the commercial requirements such as: high theoretical specific capacitance, high surface area, low production cost, facile synthesis, able to be up-scaled, easy tunability, good chemical stability and the ability to intercalate diverse varieties of anions (inorganic, organic, biomolecules, and even genes). Thus, the properties of commercial SCs can be improved by the use of LDHs, while the production cost remains low or even be lowered further.

LDHs advantages

LDHs materials possess countless advantages that make them promising electrode materials for commercial SCs. Some of them are presented here in more details.

As discussed earlier, current commercial SCs are made of carbon-based materials. Carbon-based materials undergo EDLC charge storage mechanism; thus, the high specific surface area to achieve high energy density is required. However, the increase of the specific surface area in carbon-based materials causes the decrease of the pore wall thicknesses that reduces the screen effect of carbon and increases the repulsive interactions between ions [18]. That is why carbon-based materials suffer low energy density and the commercial SCs as well.

The above situation displays clearly that the excellent electrochemical performance derives from the charge storage mechanism that the material undergoes and its physical properties.

The pseudo-capacitive charge storage mechanism is foreseen as the solution to the challenges that carbon-based materials are facing, because pseudo-capacitors (PCs) can deliver an excellent energy density than electric double layer capacitors (EDLC).

Xin Zhao *et al.*, reported that supercapacitors with nanostructured electrode materials that undergo pseudo-capacitive charge storage mechanism are able to exhibit simultaneously a battery like behavior (high energy density) and the power capability of electrostatic capacitors. However, the authors stated that their application in the industry is still hindered due to challenges such as: their durability, feasibility, production cost, as well as their environmental friendliness [56]. Contrarily to what Xin Zhao *et al.*, have stated, LDHs materials do not meet the above challenges because of their advantages. Therefore, their industrialization cannot be hindered.

The physicochemical properties of LDHs

LDHs materials store charge through the pseudo-capacitive charge mechanism as shown in figure 4.5 and most of them are nanostructured materials. The performances of supercapacitors depend

on the physicochemical properties of the electrode materials that they are made of. As for LDHs materials, their physicochemical properties rely on their crystalline structure. The LDHs crystalline structure is the important part that supports their remarkable energy storage capabilities [34-36]. It is settled on that of brucite-like layers that are formed out of the combination of two or more transition metals cation, resulting to improved redox activity, thus excellent electrochemical performance.

Interestingly, LDHs crystalline structure is easily tunable. The tunability ability of LDHs is a great advantage because it leaves a big room to their properties to be further optimized. LDHs crystalline structure can easily be adjusted or be tailored for a specific purpose. Countless factors can be applied to redesign the crystalline structure of LDHs and improve their performances. While, Mingifei Shao *et al.*, state that by controlling the pH of the reaction system, the morphology of LDHs can greatly be influenced and indirectly affect the surface area [46]; Bangqing Xiao *et al.*, have successfully tailored the morphology of CoNi-LDH via the process of cathodic electrodeposition, which was done by adding surfactants. As results, the electrochemical performances recorded were better than the untreated sample [57]. In the same direction, WenQiang Chen *et al.*, fabricated a high-performance supercapacitor made of NiCo₂O₄@Co-Fe LDH, developed by a mixture of various metal cation; the authors stated that NiCo₂O₄@Co-Fe LDH sample exhibited excellent performance compared to individual NiCo₂O₄ LDH and Co-Fe LDH samples [58]. Furthermore, Shuai Yu *et al.*, have developed an ultra performance hybrid nanoarchitecture electrode material that benefited from the synergetic effect between NiMn-LDH nanosheets and Ni₃S₂ nanorods and yielded superior specific capacitance [59]. Consecutively, Wenwen Zheng *et al.*, have developed two nanostructure LDHs composites (NiAl-LDH and NiFe-LDH) via a simple hydrothermal method. Afterwards, they have improved their electrochemical performances by loading MnO₂ particles on their surface through the redox reaction. Then the authors stated that even the surface areas of the composites were greatly increased [60]. Moreover, it should be noted that the hydrophilic status of LDHs structure improves the ionic diffusion [40]. This allows LDHs in most cases to exhibit low ionic diffusion resistance, as well as relatively low interfacial resistance in the system (see figure 4.6) and favours them not to compromise the power density. Furthermore, it was notice that whenever the LDHs electrochemical performance improves, it goes along with conductivity that greatly affects their internal resistances, making LDHs excellent materials that bridge the gap between supercapacitors and batteries in term of power and energy density. For more light, some other reported studies where the redesign of LDHs structure had improved their performance are displayed in Table 4.1.

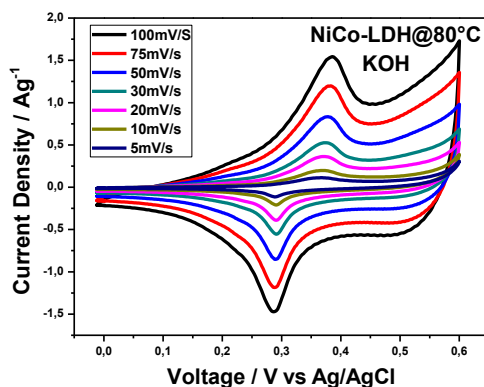


FIGURE 4.5

CV curves of NiCo-LDH@80°C at different scan rates 1 M KOH electrolyte [10].

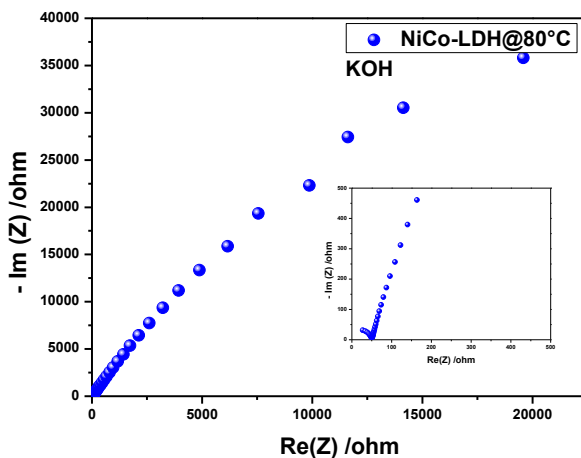


FIGURE 4.6
Nyquist plots of NiCo-LDH@80°C in 1 M KOH electrolyte.

TABLE 4.1

Some reported studies where the redesign of LDHs structure had improved their performances.

Authors	Experiments done	Journals
Yinyin Lin <i>et al.</i> ,	The authors have modified the LDH structure by intercalating sodium dodecylbenzene sulfonate (SDBS) into the LDH interlayer, resulting to the expansion of the interlayer space. Then, they have discovered that even though the obtained electrode material exhibited a relatively low specific surface area ($15.28 \text{ m}^2\text{g}^{-1}$), but a remarkable specific capacitance of 1094 Fg^{-1} at a scan rate of 5 A g^{-1} was recorded and a super long cycle life retention of 81% over 3000 cycles. They ascribed the performance enhancement to the structural feature of SDBS and the expansion of interlayer space.	ElectrochimicaActa 246 (2017) 406–414.
Feifei Wang <i>et al.</i>	The LDH was made of three metals along with carbon nanofibres (CNFs) in order to improve the crystallization of the LDH which promotes the stability of the material. Moreover, the addition of CNFs had promoted the easy transport of the interior voids and favoured the enhancements of LDH performance.	www.nature.com/scientificreports/2017

Xueqin Wang <i>et al.</i>	The crystalline structure, the morphology and the supercapacitive performance of LDH were systematically controlled by the effect of concentration rate. Thus, the obtained material has displayed small nanosheet size. Then the authors stated that the morphology and composition of the obtained material were highly depended on the molar ratios of the solution containing the divalent and trivalent. As Result, excellent specific capacitances of 2189.8 and 1908.8 Fg^{-1} at the current density of 1 and 30 Ag^{-1} were recorded, respectively. Furthermore, 70.3% of the initial capacitance was retained after 20000 charge and discharge at 50 A g^{-1} .	Electroanalysis, 29 (2017) 1286 – 1293
Teng Wang <i>et al.</i>	A structural disorder was caused into the LDH structure by using 2-methylimidazole as a base instead of urea. The structural disorder is generally the result of a low crystalline status of LDH. It helps to ease the structure distortion produced by the electrostatic force and promotes high capacitance at high current density, because it exposes a lot of active sites of the material. Thus, the authors stated that the LDH prepared with 2-methylimidazole exhibited excellent properties compared to the one prepared with urea.	Mater.interfaces, 9 (2017) 15510-15524.
Xiaoqing Cai <i>et al.</i>	A LDH composite made of Nickel, Cobalt and reduced grapheme Oxide (RGO) was tested as supercapacitor electrode. The material has exhibited excellent properties which were ascribed to the combination of components used to prepare the LDH. The addition of RGO has improved the conductivity within LDH, resulting to excellent properties.	http://dx.doi.org/10.1016/j.cej.2015.01.072

In terms of production procedure and cost

The synthesis procedure of electrode material is a very crucial step in the industry, since the

economical feasibility relies on it. Therefore, it must be simple, facile and cost-effective. However, many procedures applied to synthesize LDHs were simple, facile and in most cases they do not require sophisticated apparatus, resulting in low production cost. Moreover, even the components used are cost-effective and many of them are low toxic. Table 4.2 displays the list of some reported facile synthesis procedures for LDHs.

TABLE 4.2

Some reported facile synthesis procedures for LDHs.

Authors	Titles	Journals
Xi Cao <i>et al.</i>	Facile fabrication of the polyaniline/layered double hydroxide nanosheet composite for supercapacitors.	Applied Clay Science 168 (2019) 175–183.
Zeng Peng Diao <i>et al.</i>	Facile synthesis of CoAl-LDH/MnO ₂ hierarchical nanocomposites for high-performance supercapacitors	Ceramics International 40 (2014) 2115–2120.
Wenwen Zheng <i>et al.</i>	Facile synthesis of NiAl-LDH/MnO ₂ and NiFe-LDH/MnO ₂ composites for high-performance asymmetric supercapacitors.	Journal of Alloys and Compounds 768 (2018) 240–248.
Xiujiao Gao <i>et al.</i>	Low-cost and high-performance of a vertically grown 3D Ni-Fe layered double hydroxide/graphene aerogel supercapacitor electrode material.	RSC Adv., 2016, DOI: 10.1039/C6RA19495H.
Lei Li <i>et al.</i>	Facile synthesis of NiAl layered double hydroxide nanoplates for high-performance asymmetric supercapacitor.	Journal of Alloys and Compounds (2017), doi: 10.1016/j.jallcom.2017.06.062.

Large scale preparation

TABLE 4.3

some reported studies related to the scalable synthetic methods of LDHs.

Authors	Titles	Journals
G.E. Nyongombe <i>et al</i>	Up-scalable synthesis of highly crystalline electroactive Ni-Co LDH nanosheets for supercapacitor applications.	Int. J. Electrochem. Sci., 15 (2020) 4494 – 4502.
BebiPatil <i>et al</i>	Scalable nanohybrids of graphitic carbon nitride and layered NiCo hydroxide for high supercapacitive performance.	RSC Adv., 9 (2019) 33643.
Ruchun Li <i>et al</i>	Large Scale Synthesis of NiCo Layered Double Hydroxides for Superior Asymmetric Electrochemical Capacitor.	Sci. Rep. 6 (2016) 18737.

The development of cost-effective and large scale preparation methods of an electrode material for its industrialization is very important. This applies also for LDHs. Recently; many studies were devoted to the scalable preparation procedures of LDHs in order to promote their industrialization. Table 4.3 displays some of them.

In terms of energy density

Even though the assembly and the evaluation of supercapacitors performances in academia may differ to those in the industry, it can still be acknowledged that most of supercapacitors made of LDHs exhibit excellent properties; especially in terms of energy density compared to that reported for commercial SCs (10 Wh/kg [55]). Table 4.4 displays various supercapacitors made of LDHs and their properties.

TABLE 4.4
some supercapacitors made of LDHs and their properties.

Devices	Properties		Journals
	Energy density	Power density	
Mg-Co-Al-LDH//AC	13.09 Wh kg ⁻¹	149.49 W kg ⁻¹	Yuqing Zhang, J NanopartRes,21 (2019)14.
Co-Mn-LDH//AC	20.3 Wh kg ⁻¹	435 W kg ⁻¹	F.O.Ochai-Ejeh <i>et al.</i> , j.electacta. 08 (2017) 163.
CoAl-LDH/GF//AEG	28 W h kg ⁻¹	1420 W kg ⁻¹	Tshifhiwa M. <i>et al.</i> , RSC Adv., 6 (2016) 46723.
Ni ₅₀ Co ₅₀ -LDH// GOMC	33.7 Wh kg ⁻¹	5452 W kg ⁻¹	Ruchun Li <i>et al.</i> , Sci. Rep. 6 (2016) 18737.
LDH@CNP _s //AC	47.7 Wh kg ⁻¹	51 kW kg ⁻¹	Xiaoxi Liu <i>et al.</i> ,J. Mater. Chem. A, 2 (2014) 1682.
NiMn-LDH@Ni ₃ S ₂ //AC	57 Wh kg ⁻¹	738 W kg ⁻¹	ShuaiYu <i>et al.</i> , Scientific Reports, 8 (2018)5246.
NiCo-LDH/Mn ₃ O ₄ //AC	57.03 Whkg ⁻¹	765.8Wkg ⁻¹	Nan Zhao <i>et al.</i> ,Journal of Alloys and Compounds, 796 (2019) 111e119.
NiMn-LDH//AC	59 Wh kg ⁻¹	808 W kg ⁻¹	Zhao Yang <i>et al.</i> , ChemElectroChem, 6 (2019) 4456.
NiCo-LDH/CFC//AC	59.2 Whkg ⁻¹	34 kW kg ⁻¹	Teng Wang <i>et al.</i> , Mater. interfaces, 9 (2017)15510.
Ni _{0.76} Co _{0.24} LDH//AC	66 Whkg ⁻¹	7500 W kg ⁻¹	Xueqin Wang <i>et al.</i> , Electroanalysis, 29 (2017) 1286.
NiCo-LDH-S7.5//AC	73.54 Whkg ⁻¹	375 W kg ⁻¹	Zhicheng Shi <i>et al.</i> , ACS Appl. Energy Mater, https://dx.doi.org/10.1021/acsaem.0c02058

Conclusion

LDHs are types of materials that have attracted tremendous interests because of their uncommon physicochemical properties that are the results of their unique crystalline structure. They have been studied, tested and applied for various technologies. As for energy storage, LDHs proved to be

the excellent electrode materials. Although many pseudo-capacitive materials beside LDHs have been reported with superior performances in academia, the industry remains a bit skeptical for their penetration into the commercial arena due to some industrial requirements, such as: (1) the production cost must be moderate or low, (2) the production procedure must be simple and facile, (3) the product must preferably yield excellent properties, (4) the product must be environmental friendly, (5) finally, the product must be up-scalable. This chapter has demonstrated that among many pseudo-capacitive electrode materials developed in the academia, LDHs are the best candidates for commercial SCs because they meet the industrial requirements. Thus, some of the advantages that support them as promising electrode materials for commercial SCs were displayed in detail in this chapter. Their crystalline structure, synthesis methods and some characterization techniques were also discussed here. In the light of above discussions, we can easily conclude that LDHs are promising electrode materials for commercial supercapacitors.

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