

NiCo-LDH Based Electrode Materials for Supercapacitors: Modification Strategies and Recent Advances

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Abstract. As global demand grows for efficient, supercapacitors are widely studied on account of their excellent power density and prolonged cycle lifespan. Among the many electrode materials available, NiCo-LDH offers a high theoretical specific capacitance, yet it suffers from poor conductivity, few exposed active sites, and poor structural stability. This paper systematically summarizes recent modification strategies for NiCo-LDH through a literature review, including morphology control (e.g., 2D nanosheets and 3D hierarchical structures), heterostructure construction, and element doping (e.g., rare earth doping and anion phosphorization/nitridation). These strategies effectively enhance the electrochemical properties of NiCo-LDH by improving conductivity, increasing active sites, and buffering volume expansion. However, quantitative comparisons among different modification approaches remain insufficient, and practical device applications are underexplored. This review provides valuable guidance for designing high-performance NiCo-LDH-based supercapacitor electrodes.

Keywords: NiCo-layered double hydroxide, supercapacitors, modification strategies, electrochemical performance

1. Introduction

Given the global decline of fossil fuel reserves, it has become critical to develop energy storage and conversion systems that are efficient, clean, and environmentally friendly. Supercapacitors show strong promise for applications including electric vehicle start-stop, mobile communications, aerospace, and smart grids. This is due to their high power density, fast charge/discharge rates, ultra-long cycling stability, and superior safety. They bridge the performance gap between conventional capacitors and batteries [1].

Supercapacitors are divided into two main types according to their energy storage mechanism. Electric double-layer capacitors (EDLCs) store energy by physical adsorption of ions at the electrode-electrolyte interface. Representative materials include activated carbon, carbon nanotubes, and graphene, etc. [2]. Pseudocapacitors store energy via rapid, reversible redox reactions occurring at or near the electrode surface. They generally achieve a higher specific capacitance than double-layer capacitors [3]. Layered double hydroxides (LDHs) have attracted considerable interest among pseudocapacitive materials because of their distinctive layered structure, tunable composition, and high theoretical capacitance, which can be generally represented as

$[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}[A_{x/n}^{n-} \cdot m\text{H}_2\text{O}]^{x-}$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, and A^{n-} is the interlayer anion. By changing the types and ratios of M^{2+} and M^{3+} , the physical and chemical properties of LDHs can be regulated [4]. Common LHD systems include NiAl-LHD (good structural stability [5]), CoAl-LDH (excellent redox activity [6]), and NiFe-LDH (widely studied in both electrocatalysis and energy storage). These materials can provide abundant active sites through the exchange of interlayer anions and the valence transition of metal cations in layered sheets.

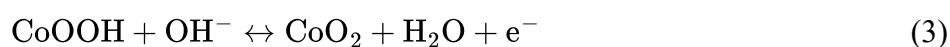
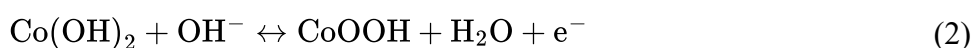
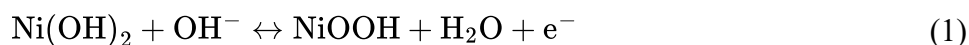
Among various bimetallic LDHs, NiCo-LDH has shown more significant synergistic effects by combining the prominent capacitive property of nickel and high electron conductivity and electrochemical activity of cobalt [7]. Nevertheless, NiCo-LDH encounters three main practical issues. Its inherently low conductivity restricts rate capability under high current; large volume change during charge/discharge degrades cycling stability; and few active sites are exposed, causing a large mismatch between actual and theoretical capacitance [8].

The goal of this review is to systematically summarize the modification strategies for NiCo-LDH in recent years, focusing on the enhancement mechanisms of electrochemical performance through morphology control, heterostructure construction, and element doping (such as rare earth element doping, anion phosphorization or nitridation treatment). By comparing the energy storage performance of different systems, this paper further outlines the future development direction of high-performance supercapacitors based on NiCo-LDH.

2. Energy storage mechanism of NiCo-LDH

2.1. Electrochemical energy storage mechanism

NiCo-LDH behaves as a typical pseudocapacitive material. Its charge storage arises primarily from fast, reversible redox reactions of Ni and Co ions in alkaline media such as KOH. The main redox reactions can be expressed as follows:



During charge and discharge, OH^- ions in the electrolyte enter interlayer of LDH or attach to its surface, where they undergo electron exchange with the active sites of Ni and Co. Due to the bimetallic synergy effect of NiCo-LDH, its redox peaks are often wider than those of single-metal hydroxides, which enables NiCo-LDH to achieve a higher capacitive capacity [9].

2.2. Key physical parameters affecting electrochemical performance

NiCo-LDH's real electrochemical behavior is strongly associated with its microscopic structure. Three core indicators can illustrate this correlation: specific surface area, pore size distribution and electrical conductivity.

2.2.1. Specific surface area

A high specific surface area allows the electrode material to better contact the electrolyte and to expose more active sites. Typically, 2D nanosheets or 3D hierarchical flower-like morphologies are used to prevent stacking of the electrode nanosheets, effectively enhancing the charge storage capacity [10]. The ultra-thin two-dimensional nanosheet morphology can maximize the exposure of redox active sites on the NiCo-LDH electrode plates, improving the capacitance calculated per unit mass of the material. Yang et al. reported a method for precisely preparing ultra-thin and curved NiCo-LDH nanosheets through a GO surface confinement strategy. The measured thickness of the prepared NiCo-LDH nanosheets is only 1.7-1.8 nm. The extremely thin design significantly facilitates sufficient effective contact for the electrode material and the electrolyte. As a result, this material exhibits a charge storage capacity of up to 1489 F/g (at 1 A/g) when used as a supercapacitor electrode. Furthermore, this structure with large specific surface area offers plenty of catalytic active sites, resulting in a low overpotential of only 0.337 V for the oxygen evolution reaction (OER).

2.2.2. Pore size distribution

A reasonable pore structure (a multi-scale pore structure consisting of micropores, mesopores and macropores) is crucial for ion transport. Zhao et al. used ZIF-67 metal-organic frameworks as templates and synthesized NiCo-LDH hollow nanocages with hierarchical pore structures via a hydrothermal method. The study showed that this hollow mesoporous porous microstructure greatly facilitated rapid ionic diffusion throughout the electrode interior, which endows the material with superior capacitive performance of 2203.6 F g⁻¹ at 2 A/g [11].

2.2.3. Electrical conductivity

Although the theoretical capacitive value of NiCo-LDH is high, its semiconductor properties result in low intrinsic electrical conductivity, which limits the transmission of electrons. In practical research, methods such as introducing conductive carbon materials, constructing heterojunctions, or performing anion doping treatments (e.g., phosphorization and nitridation) are commonly used to optimize the kinetics of electron transfer and thereby reduce the internal resistance (ESR). Wang et al. successfully synthesized cabbage-like P@NiCo-LDH spheres via a moderate co-precipitation strategy and later phosphorization treatment. Compared with NiCo-LDH (285.8 C g⁻¹), P@NiCo-LDHs achieve a significantly enhanced specific capacitance of 536 C g⁻¹ at 1 A g⁻¹, representing a 1.88-fold increase [12].

3. Morphology-controlled synthesis of NiCo-LDH

To address the intrinsic poor electrical conductivity and prominent stacking behavior of NiCo-LDH, researchers have developed various synthesis strategies to optimize its electrochemical activity through dimensional design and morphology control.

3.1. Main synthesis methods

Currently, the synthesis methods of NiCo-LDH mainly include hydrothermal, solvothermal, and co-precipitation methods, each of which has different control over the morphology and crystallinity of the material:

3.1.1. Hydrothermal/solvothermal method

Hydrothermal/solvothermal synthesis is the most widely adopted approach. Through tuning the synthetic temperature, pressure, and time in a high-pressure autoclave, the crystal growth of LDH can be precisely controlled. The advantage of this method is that the product has high crystallinity, uniform morphology, and can be easily grown in situ upon an electrically conductive support [13]. Chen et al. [14] successfully synthesized the CoFeSi/NiCo-LDH heterostructure in situ on the surface of fly ash-based silicate (CoFeSi) using a two-step solvothermal method. In this study, by optimizing the proportion of ethanol versus water in the secondary solvothermal process, the structural uniformity of the material was greatly enhanced. The establishment of the heterointerface not only introduced abundant active sites but also promoted charge transfer By rebuilding the electric field at the interface. Experimental results showed that this heterostructure had excellent specific capacitance of 1419 F/g at 1 A/g and a capacity retention rate of 89.35% after 10,000 cycles. Chen et al. [15] prepared a Using a facile one-step hydrothermal approach, researchers fabricated a NiCo-LDH@N-GH/NF composite that features a 3D hierarchical architecture, grown directly on nickel foam that had been pre-loaded with 3D porous nitrogen-doped graphene hydrogel. This hydrothermal growth method ensured the close contact between LDH and the 3D conductive network. The 3D hierarchical structure played an active role in promoting comprehensive electrochemical properties, achieving a specific capacitance of 1393 F/g. The fabricated asymmetric supercapacitor (ASC) delivered an energy density of 63.33 Wh/kg when operating at a power density of 260 W/kg.

3.1.2. Co-precipitation method

During the synthesis with controlled morphology of NiCo-LDH, the coprecipitation approach has gained considerable interest because of its straightforward procedures and potential for industrial scale-up.. By adjusting the types of precipitating agents, pH value, and the introduction of surface surfactants, the size and stacking behavior of NiCo-LDH layers can be effectively controlled. This is mainly achieved by adding an alkaline precipitant to the solution containing metal salts, where Ni^{2+} and Co^{2+} simultaneously hydrolyze and co-precipitate to form a layered structure. This method has significant advantages in regulating the types of interlayer anions and constructing multi-component composite materials [16]. Ghadimi et al. [16] successfully prepared a TMOs/rGO/NiCo-LDH nanocomposite on the surface of foam nickel (NF) loaded with hierarchical nickel-cobalt-copper transition metal oxides (TMOs) and reduced graphene oxide (rGO) using the co-precipitation method. In this system, the presence of rGO provided abundant sites for crystal nucleation and subsequent growth of LDH and produced a significant synergistic effect. At 1 A/g, the composite electrode delivered a specific capacitance of 2763 F/g. Even after 3000 GCD cycles at a high current density (24 A/g), its capacitance retention remained 85%. This indicates that the co-precipitation method is highly effective when combined with a highly conductive carrier to surmount the inferior inherent conductivity of NiCo-LDH.

3.1.3. Electrodeposition method

The electrodeposition method, as a low-cost, high-efficiency synthesis technique that does not require binders, enables the direct in situ growth of NiCo-LDH on conductive substrates, significantly reducing the interface contact resistance. However, traditional direct electrodeposition often leads to disordered stacking of nanosheets, limiting the emergence of active centers. He et al.

[17] reported a new strategy to assist electrodeposition by introducing positively charged carbon dots (p-CDs). In this study, p-CDs adsorbed NO_3^- from the electrolyte and acted as inducers, successfully guiding the ordered growth of ultrathin NiCo-LDH layered nanostructures on carbon cloth (CC).

3.2. Dimension design and morphology evolution

With meticulous control over structural sizes, the effective surface area and ion moving paths of NiCo-LDH may be modulated effectively.

3.2.1. 2D nanosheet structure

The 2D nanosheet structure is the most basic form of NiCo-LDH. Ultrathin nanosheet structures contribute to more exposed active sites and shorter transmission routes for ions. A large specific surface area allows electrolyte ions to reach the metal redox centers more readily, which shortens the ion diffusion path from the surface into the bulk material and consequently boosts the rate capability. Liu et al. [18] directly grew ultrathin nanosheet arrays of NiCo-LDH on foam nickel (NF). This layered interlayer porous network derived from cross-linked 2D nanosheets nanosheets achieved a current density of 10 mA/cm^2 at 1.66 V, demonstrating the core role of the 2D structure in enhancing electrochemical activity.

3.2.2. 3D hierarchical structure

To further address the severe stacking problem of 2D nanosheets during drying or cycling, researchers constructed 3D hierarchical structures through assembly methods.

Assembled from a large number of 2D nanosheets that are cross-linked with each other. This open structure not only prevents plate stacking but also abundant mesoporous channels are formed, facilitating the infiltration of the electrolyte. Jiang et al. [19] synthesized 3D flower-like hierarchical NiCo-LDH microspheres using NiCo-MOF as the precursor through a simple alkaline hydrolysis strategy. This structure retains the regular pore architecture and large specific surface area of the precursor material and shows a large specific capacitance of 1750.0 F/g at 1 A/g , and still maintains excellent durability after 5000 cycles, with 92.3% capacitance retention.

Hollow polyhedra and core-shell architectures are typical examples. Their internal cavities can accommodate volume expansion during extended cycling, which markedly enhances the material's structural durability and cycling stability. Moreover, both the inner and outer surfaces can participate in the reaction, further improving the specific capacitance. Zou et al. [20] synthesized 3D hollow NiCo-LDH nanocages decorated with porous bio-carbon using ZIF-67 as the precursor template. This 3D hollow structure has a larger effective surface area and faster electron transfer capability, enabling simultaneous ultra-sensitive detection based on electrochemistry of Cu^{2+} and Hg^{2+} . This result demonstrates the stability of the hollow hierarchical structure in complex electrochemical environments.

4. Modification strategies for improving electrochemical performance (electrochemical performance enhancement strategies)

Although NiCo-LDH possesses an ultra-high theoretical specific capacitance, its intrinsic low electrical conductivity and inferior cycling stability restrict its practical use. To address these

shortcomings, scholars have developed various modification approaches from macroscopic composite materials down to microscale atomic-level modulation.

4.1. Incorporation of conductive substrates

In situ growing NiCo-LDH on a three-dimensional conductive network is the most direct means to enhance the charge transmission efficiency. The three-dimensional pore structure of nickel foam can not only offer outstanding mechanical backing, but also greatly lower the contact resistance between electrode constituent materials and current collecting electrodes [21]. Graphene and CNTs: Introducing graphene or carbon nanotubes can construct efficient electron transport pathways. Utilizing great conductivity of carbon materials and the high capacity of LDH, it is possible to achieve a dual improvement in energy density and power density [22].

4.2. Element doping

Introducing exogenous atoms into the LDH lattice can fundamentally modify the electronic structure and chemical environment. Cation doping: In addition to single metal ion doping (e.g., Ce, Fe, Al), dual metal co-doping can significantly optimize catalytic activity by synergistically regulating electron orbital filling. Ma et al. proposed a Ru and Mn dual-metal co-doping strategy and successfully prepared modified NiCo-LDH (RMNCL). It was found that the well-dispersed Ru atoms provided abundant active centers. Meanwhile, the incorporation of Mn altered the occupancy of antibonding orbitals in the catalyst, which in turn modulated the adsorption of reactants onto the surface [23]. Anion doping/conversion: Through phosphorization (P), nitridation (N), or sulfidation (S) treatment, the hydroxides can be partially or completely converted into corresponding phosphides, nitrides, or sulfides. Such derivatives usually have metallic conductive characteristics and can significantly reduce electrochemical polarization and enhance ion migration rates [24-26].

4.3. Heterostructure construction

Constructing heterointerfaces is an effective way to utilize synergistic effects to enhance performance. Combining NiCo-LDH with other active materials (e.g., NiCoP, Co_3O_4) forms a heterostructure with a well-defined interface. A built-in electric field arises from the charge redistribution at the heterointerface, which accelerates charge transfer. Moreover, the cooperative interaction among the constituents can notably alleviate mechanical stress upon repeated cycling, thereby extending the cycling durability [27].

5. Conclusion

This paper systematically reviews recent modification strategies for NiCo-LDH supercapacitor electrodes, including morphology control, heterostructure construction, and element doping. These strategies effectively enhance electrochemical performance by improving conductivity, exposing more active sites, and buffering volume expansion, thereby overcoming the inherent limitations of NiCo-LDH. This review provides a structured synthesis of enhancement mechanisms and highlights the need for quantitative comparisons among different approaches (e.g., rare earth doping vs. anion phosphorization). However, this study relies on published literature, which may miss recent advances. Inconsistent testing conditions across studies hinder systematic quantitative comparisons, and practical device issues such as long-term stability, packaging, and cost efficiency remain underexplored. Future research should adopt in-situ characterization, establish standardized

performance evaluation protocols, and leverage machine learning to optimize modification routes. Additionally, more attention should be given to the cycle life and industrialization feasibility of NiCo-LDH-based electrodes to facilitate their transition from laboratory to practical applications.

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