

# Research progress on hydroxide fluoride-based electrode materials for supercapacitors

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**ABSTRACT:** Supercapacitors have attracted much attention due to their high-power density and long cycle life, making them a potential substitute for traditional batteries. Research on hydroxide fluorides as electrode materials for supercapacitors has been increasing. Hydroxide fluorides exhibit higher specific capacitance due to the redox reactions between transition metal elements in different oxidation states. However, their high resistance limits their rate performance and cycling stability, which hinders their large-scale application. This article summarizes the main synthesis methods of hydroxide fluorides, and by controlling the reaction conditions, hydroxide fluorides with different morphologies and structures can be obtained to meet various application requirements. In addition, considering the limitations of hydroxide fluorides, this article systematically introduces the main approaches to improving their electrode performance and summarizes the electrochemical characteristics and latest research progress of hydroxide fluorides.

**KEYWORDS:** supercapacitors; hydroxide fluoride; electrode materials; elemental doping

## 1. Introduction

As global energy demand continues to grow, the depletion of fossil fuels and the worsening environmental pollution highlight the increasing importance of developing sustainable and renewable energy sources<sup>[1-3]</sup>. New energy sources such as solar power, wind energy, and tidal energy have been developed as alternatives to traditional fossil fuels. However, these energy sources are intermittent in their availability. To ensure a continuous energy supply, there is an urgent need to develop efficient energy storage devices<sup>[4,5]</sup>. Supercapacitors have the potential to serve as an alternative electrochemical energy storage technology, replacing widely commercialized rechargeable batteries<sup>[3,6,7]</sup>.

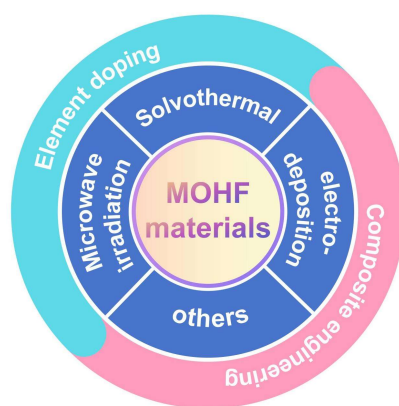
According to energy storage principles, supercapacitors can be divided into three main categories: double-layer capacitors, pseudocapacitors, and hybrid capacitors<sup>[8-11]</sup>. Double-layer supercapacitors store energy based on the adsorption of ions in the electrolyte onto the positive and negative charges on the electrode surface<sup>[12-16]</sup>. Pseudocapacitors store energy based on the adsorption resulting from redox reactions between ions in the electrolyte and the electrode material<sup>[17-20]</sup>. Hybrid capacitors are composed of carbon materials that can form a double layer as the negative electrode and metal oxides/hydroxides, conductive polymers, or traditional battery materials as the positive electrode<sup>[21-26]</sup>. Compared to double-layer capacitors and pseudocapacitors, hybrid capacitors can meet higher power density and energy density requirements, making them more widely used<sup>[27-31]</sup>. Supercapacitors possess higher capacitance

compared to conventional electrochemical capacitors, but they have a lower energy density than batteries<sup>[32-37]</sup>. However, supercapacitors have gained significant research attention due to their favorable characteristics, including excellent cycling stability and lifespan, high power density, wide operating temperature range, relatively lower cost, enhanced safety, and environmental friendliness, when compared to batteries<sup>[38,39]</sup>. However, the construction of high-performance supercapacitors with both high energy density and high power density remains a challenging task<sup>[40]</sup>. Therefore, the continuous exploration of high-energy-density materials has been a primary objective in the development of supercapacitors<sup>[41-44]</sup>.

Hydroxide fluorides have been extensively studied as electrode materials for supercapacitors due to their simple and versatile synthesis methods, high specific surface area, high theoretical capacitance, and excellent electronic transport capabilities. However, the high resistance of hydroxide fluorides has limited their widespread application. Therefore, strategies such as doping and compositing have been employed to improve the performance of hydroxide fluorides. Although there have been reports on the use of hydroxide fluorides in energy storage applications such as lithium batteries<sup>[45-48]</sup> and supercapacitors<sup>[49-52]</sup>, their current performance is not sufficient to support large-scale energy storage applications. There is a wide variety of hydroxide fluorides, and common metal cations found in hydroxide fluorides include Mg, Co, Ni, Cu, Zn, and Cd, among others<sup>[53-56]</sup>. Metal hydroxide fluorides, due to their simple synthesis routes, controllable morphology, strong oxidation resistance, stability in air, and unique electronic band structures, have been widely applied in the development of new functional materials. Low-dimensional nanostructures can self-assemble to form materials with a high specific surface area and abundant pore structures. Mixed transition metal oxides and their derivatives exhibit reversible valence state transitions during charge and discharge processes, offering advantages of high specific capacitance and structural stability. In particular, mixed transition metal hydroxide fluorides, composed of two individual transition metal hydroxide fluorides, exhibit higher conductivity due to the lower activation energy for electron transfer. The strong synergistic effect also enables them to demonstrate characteristics that are difficult to achieve with single-metal hydroxide fluorides. Therefore, hydroxide fluorides hold promising potential as electrode materials for supercapacitors, capable of meeting the energy storage demands of supercapacitor electrodes<sup>[57]</sup>.

According to the factors influencing the performance of electrode materials for supercapacitors, the performance of hydroxide fluoride electrode materials can be influenced by the following factors: 1) specific surface area; 2) electronic transport capability; 3) conductivity; and 4) unique nanostructures. Different nanostructures, such as nanorods, nanowires, and nanoplate arrays, can result in different performances of hydroxide fluorides. As long as the dispersion is uniform, the electronic transport performance will be better. However, if the distribution is too aggregated or too dispersed, it can lead to a decrease in electrochemical performance. The high specific surface area of hollow nanostructures allows for sufficient contact between the electrode material and the electrolyte, thereby enhancing electrochemical performance. The anisotropy of hydroxide fluorides also contributes to their large specific surface area, exposure to low-energy surfaces, significant size effects, and good electronic transport capability. Rapid electron transfer in electrode materials enhances their conductivity. Moreover, improving the specific surface area by controlling the nanostructure of the electrode can further enhance the performance of supercapacitors, facilitating fast redox reactions and ion/electron transfer at the electrode/electrolyte interface. Activated materials with nanowire structures can provide a higher spectral surface area, accelerating ion diffusion and electron transfer, resulting in higher specific capacitance.

This review provides a comprehensive overview of the synthesis methods of hydroxide fluorides and strategies to enhance their performance as electrode materials for supercapacitors, aiming to facilitate their more effective application. Firstly, the article summarizes the main synthesis methods of hydroxide fluorides, emphasizing the ability to obtain hydroxide fluorides with diverse morphologies and structures by controlling reaction conditions to meet various application requirements. Secondly, addressing the limitations of hydroxide fluorides, the article systematically introduces key methods to improve their electrode performance and summarizes the electrochemical characteristics and latest research progress of hydroxide fluorides. These insights provide a more comprehensive understanding of the potential applications of hydroxide fluorides in fields such as supercapacitors, offering practical guidance and inspiration for related research. This article's exposition enables readers to better grasp the potential applications of hydroxide fluorides in the realm of supercapacitors, providing important references and inspiration for future research (**Figure 1**).



**Figure 1.** The challenges and strategies for promising hydroxide fluorides as the next-generation energy storage materials.

## 2. Synthesis strategies of hydroxide fluoride

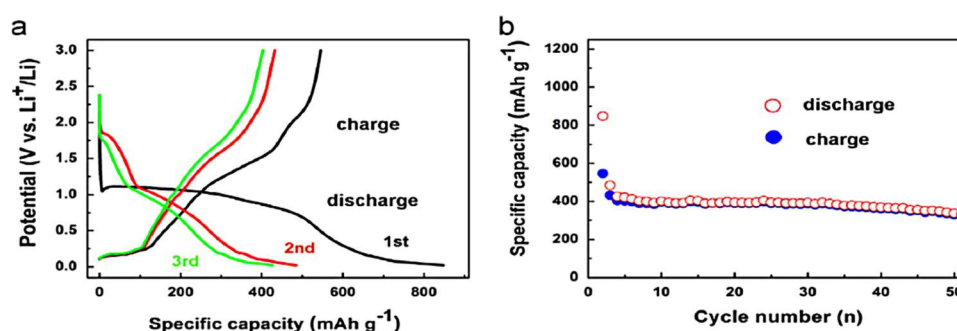
There are several methods commonly used for the preparation of hydroxide fluorides, including hydrothermal synthesis, solvothermal synthesis, microwave-assisted synthesis, and electrodeposition. These methods are relatively simple and offer flexibility to control reaction conditions for synthesizing materials with different morphologies and properties. Hydrothermal synthesis is a commonly used method for preparing hydroxide fluorides. It involves a reaction in a high-temperature and high-pressure water environment, utilizing water's solubility and thermal stability to facilitate the reaction. In hydrothermal synthesis, fluoride and metal ions are commonly used as reactants, and by reacting at specific temperatures and pressures for a certain period of time, hydroxide fluorides can be obtained. Solvothermal synthesis is another commonly used method for preparing hydroxide fluorides. It utilizes the thermal stability and solubility of organic solvents to facilitate the reaction. In solvothermal synthesis, fluoride and metal salts are dissolved in an organic solvent, and the reaction mixture is heated to induce the reaction. By controlling the temperature and reaction time, hydroxide fluorides can be obtained. Microwave-assisted synthesis is a method developed in recent years for preparing hydroxide fluorides. It utilizes the heating effect of microwaves to rapidly and uniformly heat the reaction system, promoting the reaction. This method offers advantages such as fast reaction rates and low energy consumption, allowing for the synthesis of hydroxide fluorides in a shorter time period. Electrodeposition is a method that utilizes electrochemical principles to prepare hydroxide fluorides. By applying a current in an electrolyte solution, metal ions are reduced to metal at the electrode, simultaneously reacting with fluorides to form hydroxide fluorides. Electrodeposition enables control over the reaction rate and

morphology, allowing for the preparation of materials with different properties at different current densities. In summary, the preparation methods for hydroxide fluorides are relatively simple, and suitable methods can be chosen depending on the specific requirements. By adjusting the reaction conditions, materials with different morphologies and properties can be synthesized. These methods hold broad application prospects in the fields of materials science and chemistry.

## 2.1. Solvothermal method

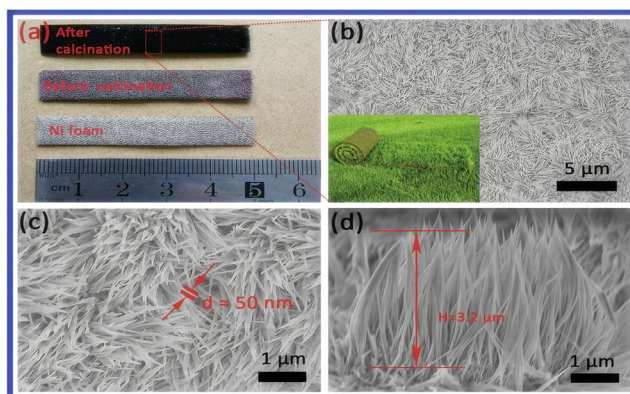
Hydrothermal synthesis involves using a water-based solution as the medium and heating the reaction vessel, typically a high-pressure autoclave lined with polytetrafluoroethylene (PTFE), to create a high-temperature and high-pressure environment. This allows for the dissolution and recrystallization of substances that are typically insoluble or difficult to dissolve. The morphology and size of the resulting product can be controlled by adjusting factors such as solvent ratios, pH, temperature, pressure, reaction time, and solvent concentration. In contrast, solvothermal synthesis uses solvents other than water. While water is the solvent in hydrothermal synthesis, some solutes are sensitive to water, necessitating the use of non-aqueous solvents such as methanol or ethanol.

Ni et al.<sup>[48]</sup> prepared rod-shaped Co(OH)F samples by conducting a 24-hour hydrothermal reaction at 120 °C, utilizing sodium fluoride, hexamethylenetetramine, and cobalt acetate tetrahydrate as raw materials. Excess sodium fluoride in the solution acted as a capping agent, inducing the oriented growth of Co(OH)F. Subsequently, the Co(OH)F was combined with natural graphite, acetylene black, and polyvinylidene fluoride (PVDF). The resulting mixture was coated onto a copper foil to produce a disk electrode. Charge-discharge tests were performed at a current density of 0.1 mA cm<sup>-2</sup>, as illustrated in **Figure 2(a)**, demonstrating the initial discharge and charge capacities of the Co(OH)F electrode at 847.9 mAh g<sup>-1</sup> and 546.2 mAh g<sup>-1</sup>, respectively. The cycling performance of the Co(OH)F electrode, as shown in **Figure 2(b)**, gradually reached a stable value after 50 cycles, maintaining capacities of 332.6 mAh g<sup>-1</sup> and 329 mAh g<sup>-1</sup>, respectively.



**Figure 2.** (a) Initial three charge-discharge curves; (b) cycle performance of Co(OH)F as anode for Li-ion batteries<sup>[48]</sup>.

Jiang et al.<sup>[49]</sup> employed Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O as starting materials and then introduced ammonium fluoride and urea to form a uniform solution. The homogeneous solution was subsequently subjected to high-pressure autoclave heating at 120 °C for a duration of 10 h, leading to the formation of three-dimensional (3D) lawn-like Co-Zn(OH)F nanoneedle arrays directly on nickel foam. The microscopic structure of the material is depicted in **Figure 3**. The highly active ordered nanoneedles, featuring a tip diameter of approximately 50 nm, contributed to the exceptional specific capacitance of 1970 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup> achieved by this 3D electrode structure. Additionally, it demonstrated remarkable cycling stability, retaining 105% of its initial capacity after 5000 cycles of cyclic voltammetry testing.



**Figure 3.** (a) Optical images of Ni foam substrate, Co-Zn(OH)F precursor grown directly on Ni foam and Co-Zn(OH)F nanoneedles on Ni foam. (b, c) The high-magnification SEM image of the region highlighted by a red rectangle in (a), the photo of lawn in the inset of (b). (d) Cross-section SEM images of Co-Zn(OH)F nanoneedles<sup>[49]</sup>.

Zhang et al.<sup>[51]</sup> utilized a one-pot solvothermal synthesis approach to create a novel and distinct nickel-cobalt hydroxide fluoride (NiCo-HF) nanowire material. The research explored the impact of varying hydrothermal temperatures on the formation mechanism. Findings suggested that  $\text{Ni}^{2+}$  tended to form nanospheres, while  $\text{Co}^{2+}$  favored nanowire formation. With increasing temperature, a greater number of  $\text{Co}^{2+}$  ions engaged in the reaction, promoting increased nanowire formation. NiCo-HF synthesized at 140 °C exhibited a higher specific surface area compared to NiCo-HF prepared at other temperatures. This, combined with its mesoporous structure, not only accelerated the ion/electron transfer rate, but also provided abundant active sites during electrochemical reactions. The prepared NiCo-HF electrode displayed a high specific capacitance of  $3372.6 \text{ F g}^{-1}$  and maintained a capacitance retention of 94.3% after 10,000 cycles at a high current density of  $200 \text{ A g}^{-1}$ . The outstanding electrochemical performance of the electrode can be attributed to the synergistic effects of the nanowire morphology and the complex redox process of the active material.

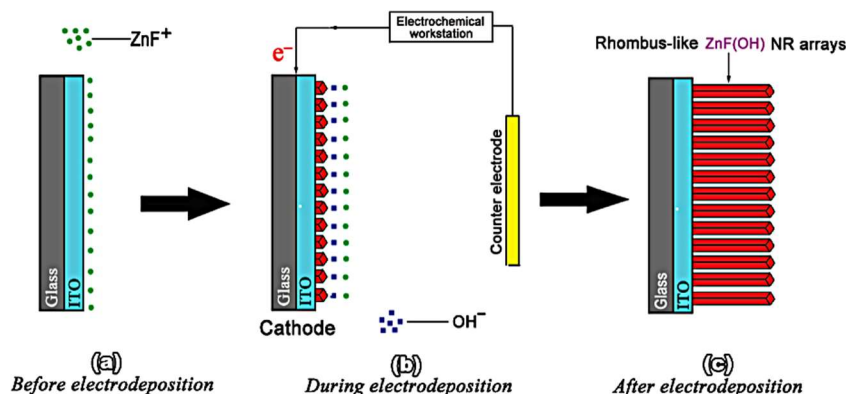
The solvothermal method has the ability to dissolve a wide range of substances, allowing reactions that are not feasible or are slow under normal conditions to occur or proceed at an accelerated rate. Solvents can control the growth of crystals, and using different solvents can result in products with different shapes. Additionally, this method offers advantages such as low energy consumption, reduced aggregation, and controllable particle shapes. However, a disadvantage of this method is its relatively low yield and insufficient product purity. Moreover, the method may not always yield satisfactory uniformity in terms of the size and morphology of the products.

## 2.2. Electrochemical deposition method

Electrochemical deposition refers to the technique where positive and negative ions in an electrolyte continuously migrate under the influence of an external electric field and undergo oxidation-reduction reactions to form a coating on the electrode. Electrodeposition is typically conducted at low operating temperatures, often in aqueous solutions, allowing the reactants to retain their individual characteristics and resulting in products with enhanced performance.

Xu et al.<sup>[58]</sup> documented the electrochemical deposition of rhombic ZnOHF nanorod (NR) arrays in an aqueous electrolyte containing  $\text{Zn}(\text{NO}_3)_2$  and sodium fluoride (NaF). The growth of the ZnOHF NR arrays was facilitated by spin-coating a zinc oxide (ZnO) nanocrystal seed layer on an ITO substrate (Figure 4). The study elucidated the electrochemical deposition mechanism of ZnOHF, where the preferential chemical combination of  $\text{ZnF}^+$  complexes with the electrogenerated  $\text{OH}^-$  ions hindered the binding of free  $\text{Zn}^{2+}$  ions with  $\text{OH}^-$  ions and the formation of zinc hydroxide ( $\text{Zn}(\text{OH})_2$ ). The presence

of fluoride ions effectively interfered with the formation of zinc oxide. Therefore, the process was designated as fluoride ion-mediated ZnOHF electrochemical deposition. Previous reports on the synthesis of ZnOHF samples via dissolution-based synthetic routes did not yield ordered one-dimensional nanostructures. Electrochemical deposition easily achieved this objective in the present study.



**Figure 4.** Schematic illustration of the electrodeposition process of the rhombus-like ZnFOH NR arrays on ITO glass substrates<sup>[58]</sup>.

### 2.3. Microwave irradiation method

The microwave irradiation method involves placing the reactants in a reaction vessel and heating them in a microwave oven (a household microwave oven is sufficient). After complete cooling of the reaction vessel, the product is washed, centrifuged, and dried for subsequent testing.

Zhu et al.<sup>[59]</sup> initially utilized  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  as the raw material to synthesize  $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , and subsequently produced Zn(OH)F nanorods for utilization in solar cells. The work demonstrated the capability of the unique microwave irradiation strategy for constructing nanostructured hydroxide fluorides. Song et al.<sup>[60]</sup> employed the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ( $[\text{Bmim}]\text{BF}_4$ ) as both the reactant and template to synthesize novel flower-like Zn(OH)F through a simple and rapid microwave-assisted approach. In this study, Zn(OH)F also acted as a precursor for the creation of porous ZnO nanostructures. The introduction of the ionic liquid and microwave irradiation played vital roles in shaping the unique structure of Zn(OH)F. Microwave irradiation notably reduced the heating time and enhanced heating efficiency. Ionic liquids, comprising inorganic anions and organic cations, possess high polarization and conductivity. Their ionic nature makes them exceptional solvents for absorbing microwave radiation. Farshad Barzegar et al.<sup>[61]</sup> examined the influence of microwave irradiation on the performance of carbon-based electrode supercapacitors. The results showed significant changes in the specific surface area of the materials, leading to increased storage capacity of the electrode materials. By enhancing the active surface area during microwave irradiation, the specific capacitance also exhibited stability compared to before irradiation.

### 2.4. Other methods

Peng et al.<sup>[62]</sup> synthesized ZnOHF using a method without any additives in their study titled "Synthesis, characterization, and photocatalytic activity of Zn(OH)F hierarchical nanofibers prepared by a simple solution-based method." Shahzad Ahmad et al.<sup>[63]</sup> used a simple and environmentally friendly method to synthesize zinc hydroxide fluoride (Zn(OH)F) by hydrolyzing  $\text{KZnF}_3$ , a single-source precursor, with potassium iodate at 120 °C in their work. The process was harmless, straightforward, and scalable. Lemoine et al.<sup>[64]</sup> reported the synthesis and electrochemical properties of open-framework

iron hydroxyfluorides prepared by the thermal decomposition of  $\text{Fe}^{2+}\text{Fe}^{3+}\text{F}_5(\text{H}_2\text{O})_2$  and  $\text{Fe}^{2+}\text{Fe}^{3+}2\text{F}_8(\text{H}_2\text{O})_2$  under ambient air in their study titled “Synthesis by Thermal Decomposition of Two Iron Hydroxyfluorides: Structural Effects of Li Insertion.” The combination of thermogravimetric analysis, X-ray thermal diffraction (XRD), and infrared spectroscopy confirmed the rapid conversion of the two unstable porous oxyfluorides into hydroxyfluorides in ambient air, resulting in  $\text{Fe}^{3+}\text{F}_{2.5}(\text{OH})_{0.5}$  and HTB-structured  $\text{Fe}^{3+}\text{F}_{2.66}(\text{OH})_{0.34}$ . In the case of defluoridation, partial substitution of iron cations by other transition metals such as manganese, cobalt, or nickel could also have a positive impact on the electrochemical properties and identify a promising chemical composition with high capacity associated with long-term cycling ability as a cathode material.

In summary, the current synthesis methods often utilize solvothermal synthesis, typically using water as the solvent. This method is relatively simple, without the need for additives or templates, and allows for control over the morphology and structure of the samples by adjusting synthesis conditions such as temperature and time. However, the yield of this method is relatively low. Electrodeposition can produce pure samples with reduced impurities and operates at lower experimental temperatures. Microwave irradiation has a significant impact on the specific surface area of materials, thereby increasing the storage capacity of electrode materials. By enhancing the active surface area of the electrode material through microwave irradiation, the stability of discharge capacitance before irradiation is improved. Microwave irradiation is a promising technique as it can be conducted at room temperature in a short period of time with minimal energy consumption. Additionally, solution-based methods and hydrolysis methods for the synthesis of zinc hydroxide fluoride were introduced, which have lower environmental requirements and lower production costs compared to solvothermal synthesis. Furthermore, thermal decomposition was mentioned as a method to obtain hydroxyfluoride by decomposing mixed-valence iron fluorides at high temperatures.

### **3. Supercapacitor applications of hydroxide fluoride**

Hydroxide fluorides exhibit characteristics such as high specific surface area, exposure to low-energy surfaces, size effects, excellent electronic transport capability, and high theoretical capacitance. As a result, they are considered electrode materials with potential for developing supercapacitors capable of meeting the energy storage demands of supercapacitor electrodes. However, compared to the currently used electrode materials for supercapacitors, hydroxide fluorides may face challenges regarding rate performance and cycling stability. To further enhance the performance of hydroxide fluoride electrode materials, researchers have explored various methods. These include doping with a certain number of other metals or compounds, as well as the fabrication of composite electrode materials through the combination of metal oxides or hydroxides. These composite electrode materials are then assembled with carbon electrodes to form supercapacitors, allowing for the evaluation of their electrochemical performance.

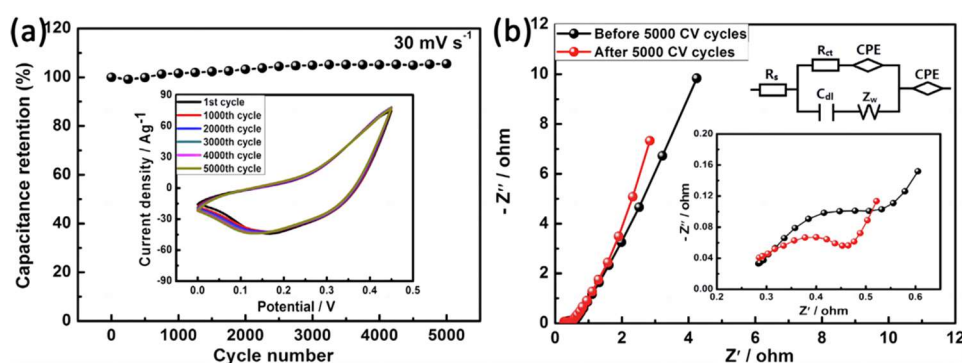
#### **3.1. Elemental doping**

Doping is a commonly used method to improve the performance of materials or substances. It involves intentionally introducing small amounts of other elements or compounds into the material or substrate to regulate its electronic properties, thus giving it specific value or utility. Doping can generally be categorized into two types: impurity doping and ion doping. Impurity doping refers to introducing small amounts of other elements into the material, which often have different atomic sizes, electronic structures, or chemical properties. By impurity doping, the material’s conductivity, optical properties, mechanical performance, etc., can be altered. Ion doping refers to introducing small amounts

of ions (usually metal ions) into the material, which can substitute for atomic positions in the material. Through ion doping, the material's lattice structure, stability, and electronic band structure can be adjusted, thus affecting its conductivity, thermal conductivity, optical properties, etc. In summary, the purpose of doping is to give materials specific properties or functionalities to meet specific application needs. Doping is an effective method for improving the performance of materials or substances. By purposefully introducing small amounts of other elements or compounds, the material's electronic properties can be regulated, giving it specific value or utility. Doping technology has broad prospects in the fields of materials science and engineering.

Lv et al.<sup>[65]</sup> employed a one-step hydrothermal method to synthesize nitrogen-doped Co(OH)F. The raw materials used included  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , sodium fluoride, and urea. The CFP (2 cm × 3 cm × 0.01 cm) was immersed in the reaction vessel with the mixed solution, and the resulting product was subsequently filtered, washed, and dried. The introduction of the halide anion F and heteroatom N led to the generation of a large number of oxygen vacancies, thus enhancing the OER (oxygen evolution reaction) activity. The prepared N-doped Co(OH)F-CFP (N:Co(OH)F-CFP) displayed favorable hydrophilicity, promoting interaction with the electrolyte and expediting the reversible electron transfer between the material surface and the electrolyte.

Jiang et al.<sup>[49]</sup> employed a hydrothermal approach to directly cultivate doped Co element Zn(OH)F three-dimensional nano-edge arrays on a Ni foam substrate. The resulting Zn(OH)F electrode, featuring a three-dimensional structure, attained an exceptionally high specific capacitance of 1970 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup>. In **Figure 5(a)**, a cycling stability test was performed on this electrode, revealing 105% initial capacity retention after 5000 charge-discharge cycles, thus confirming its outstanding cycling stability. Additionally, **Figure 5(b)** illustrates that the impedance spectra before and after 5000 CV cycles are nearly indistinguishable. As a result of the electrode's electroactivation process, it demonstrated reduced resistance, in line with the findings of the aforementioned cycling stability test. Furthermore, an asymmetric supercapacitor (ASC) was constructed using Co-Zn(OH)F as the positive electrode and activated carbon as the negative electrode. When compared to ASCs assembled with other cobalt-based electrode materials, the Co-Zn(OH)F//AC configuration exhibited higher energy density and power density. At a power density of 285.1 W kg<sup>-1</sup>, it achieved a maximum energy density of 86.2 Wh kg<sup>-1</sup>, comparable to lithium-ion batteries. Even at a high power density of 5062 W kg<sup>-1</sup>, the device's energy density could still be maintained at 18.8 Wh kg<sup>-1</sup>.



**Figure 5.** (a) The cycle performance of Co-Zn(OH)F electrode at a scan rate of 30 mV s<sup>-1</sup>. Inset: the CV curves of the different cycles; (b) The electrochemical impedance spectra of Co-Zn(OH)F electrode before and after 5000 cycling tests. Inset: the electrical equivalent circuit used for fitting impedance spectra<sup>[49]</sup>.



Shi et al.<sup>[57]</sup> successfully synthesized a series of Co<sup>2+</sup>-doped nickel hydroxyfluorides using a one-pot solvothermal method, and the excellent conductivity resulting from Co<sup>2+</sup> doping was confirmed through density of states calculations and experimental validation. Building upon a larger surface area and more defects compared to pure Ni<sub>4</sub>OHF<sub>7</sub>, the material achieved an ultra-high specific capacitance of 3380.2 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup>, while maintaining a capacitance retention of 78.4% at a high current density of 20 A g<sup>-1</sup>, demonstrating remarkable rate performance. To address the challenges of smaller interlayer spacing and lower conductivity in cobalt hydroxyfluoride, Hao et al.<sup>[66]</sup> modified it by doping with Fe. By incorporating Fe atoms with a slightly larger atomic radius, the interplanar spacing was increased, thereby enhancing ion storage capacity and significantly improving the conductivity of cobalt hydroxyfluoride. The optimized sample, CoOHF-0.06Fe, exhibited a high specific capacitance of 85.8 F g<sup>-1</sup> and achieved a high energy density of 37.2 Wh kg<sup>-1</sup> at a power density of 1600 W kg<sup>-1</sup> in an asymmetric supercapacitor composed of activated carbon.

### 3.2. Material composite

Materials composite is a method of combining two or more material components with different chemical or physical properties together in a pre-designed structure, proportion, and distribution to obtain materials with excellent performance. This method has the advantage of structural designability, allowing for the preservation of the individual properties of each component material and achieving comprehensive performance that cannot be achieved by a single component material. For materials such as hydroxyfluorides with high resistance, their conductivity can be optimized by composites with other materials, such as carbon materials. Carbon materials have good electrical conductivity and can enhance the conductivity of composite materials. By mixing or compositing hydroxyfluorides with carbon materials in certain proportions, composite materials with lower resistance and good rate performance can be formed.

Composite materials can be achieved through various methods, such as physical mixing, chemical reactions, deposition, and impregnation. When preparing hydroxyfluoride composite materials, appropriate methods can be chosen to mix or composite hydroxyfluorides with carbon materials. By controlling the composition ratio, distribution, and structure of the composite materials, their conductivity can be adjusted, thereby optimizing their performance. By selecting suitable composite components and optimizing the composite structure, the electrochemical performance of hydroxyfluorides can be regulated and enhanced. In conclusion, material composites are an effective method for optimizing material performance. For materials such as hydroxyfluorides with high resistance, their conductivity can be optimized by composites with carbon materials, leading to enhanced comprehensive performance. Materials composite technology has broad prospects in the fields of materials science and engineering.

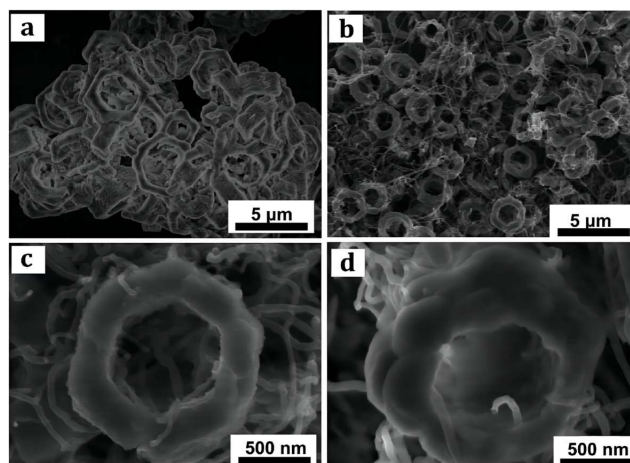
Zhu et al.<sup>[45]</sup> prepared Zn(OH)F/N-C (nitrogen-doped carbon) composite material using a hydrothermal method and utilized it as a new anode material for lithium-ion batteries (LIBs), as depicted in **Figure 6**. The Zn(OH)F/N-C electrode features a distinct porous structure, a high Li<sup>+</sup> diffusion coefficient, and a large specific surface area. This unique structure effectively facilitates electrolyte penetration, improves electronic conductivity, and accelerates lithium-ion diffusion. The small grain size of the Zn(OH)F/N-C material indicates its ability to form numerous grain boundaries, shortening the diffusion path of Li<sup>+</sup> ions, facilitating Li<sup>+</sup> transport, and enhancing the ion conductivity and rate performance of the battery. Additionally, the sample displays numerous surface defects, offering more

active sites for ion storage and contributing to increased specific capacity. The presence of oxygen defects significantly enhances the electrode and ion conductivity. Structures with various pore sizes provide ample space to accommodate the phase change of the active material, ensuring full contact between the electrolyte and the electrode and preventing electrode fracture, thereby enhancing the cyclic stability of the battery. As a result, the Zn(OH)F/N-C composite material demonstrates a good initial discharge capacity ( $946.8 \text{ mAh g}^{-1}$ ), high coulombic efficiency (87.3%), excellent cyclic stability ( $1050.2 \text{ mAh g}^{-1}$  after 430 cycles), and outstanding rate capability.



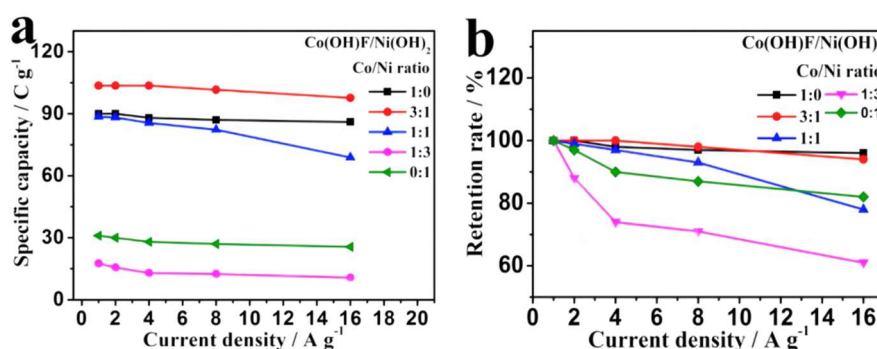
**Figure 6.** Schematic of the synthesis routes of ZnOHF-embedded N-doped porous carbon nanocomposite<sup>[45]</sup>.

Chen et al.<sup>[46]</sup> engineered a composite material consisting of Ni<sub>0.33</sub>Co<sub>0.66</sub>(OH)F hollow hexagons interwoven with multi-walled carbon nanotubes (MWCNTs), demonstrating outstanding electrochemical performance characterized by high reversible capacity and stable cycling performance. Illustrated in **Figure 7**, the addition of carbon nanotubes resulted in the Ni<sub>0.33</sub>Co<sub>0.66</sub>(OH)F hollow hexagons becoming smaller, well-dispersed, more uniform in size, and exhibiting a more regular shape. Simultaneously, the carbon nanotubes were seamlessly interconnected with the Ni<sub>0.33</sub>Co<sub>0.66</sub>(OH)F hollow hexagons, forming a distinctive woven network structure that significantly enhanced the conductivity of the composite material. Leveraging this unique composite structure, the Ni<sub>0.33</sub>Co<sub>0.66</sub>(OH)F/CNTs electrode showcased a high reversible capacity of  $1014 \text{ mAh g}^{-1}$  after 100 charge-discharge cycles (at a current density of  $100 \text{ mA g}^{-1}$ ), and it also achieved a high capacity of  $585 \text{ mAh g}^{-1}$  at a current density of  $1000 \text{ mA g}^{-1}$ . The exceptional electrochemical performance of the Ni<sub>0.33</sub>Co<sub>0.66</sub>(OH)F/CNTs electrode can be attributed to its three-dimensional interconnected hollow structure and the synergistic effect of each component. Firstly, the MWCNTs prevented the aggregation of Ni<sub>0.33</sub>Co<sub>0.66</sub>(OH)F, thereby increasing the surface area and greatly reducing the pressure caused by volume changes during cycling. Secondly, the MWCNTs network connected the separated Ni<sub>0.33</sub>Co<sub>0.66</sub>(OH)F hollow hexagons into a three-dimensional structure, thereby improving the conductivity of the composite material. The interconnected hollow structure not only increased the contact area between the active material and the electrolyte but also provided a network for charge and ion conversion. Lastly, due to the high ionic nature of metal fluoride bonds, the formation of fluoride derivatives resulted in higher redox voltages.



**Figure 7.** SEM images of (a)  $\text{Ni}_{0.33}\text{Co}_{0.66}(\text{OH})\text{F}$  and (b–d) hollow hexagon  $\text{Ni}_{0.33}\text{Co}_{0.66}(\text{OH})\text{F}/\text{CNTs}$  at different magnifications<sup>[46]</sup>.

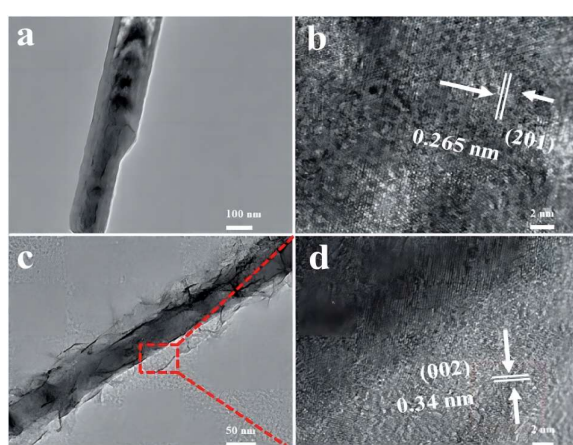
Li et al.<sup>[50]</sup> produced a  $\text{Co}(\text{OH})\text{F}/\text{Ni}(\text{OH})_2$  (Co/Ni = 3:1) hybrid material for supercapacitor electrodes using a straightforward one-pot hydrothermal method. In **Figure 8**, the specific capacitance variation of different candidate materials with varying  $\text{Co}(\text{OH})\text{F}/\text{Ni}(\text{OH})_2$  composite ratios at different current densities is illustrated. Compared to the pre-composites and other composite ratios (Co/Ni = 1:0, 1:1, 1:3, 0:1), the  $\text{Co}(\text{OH})\text{F}/\text{Ni}(\text{OH})_2$  (Co/Ni = 3:1) electrode demonstrated significantly enhanced specific capacitance and rate performance. Furthermore, the  $\text{Co}(\text{OH})\text{F}/\text{Ni}(\text{OH})_2$  (Co/Ni = 3:1) electrode was subjected to a 5000-cycle stability test, retaining 116% of its capacity at a current density of  $6 \text{ A g}^{-1}$ , showcasing its exceptional cycling stability. As a result of the optimal synergistic effect between Co and Ni redox species, the material displayed high specific capacitance, rate capability, and excellent cyclic performance. Additionally, the designed AC// $\text{Co}(\text{OH})\text{F}/\text{Ni}(\text{OH})_2$  (Co/Ni = 3:1) asymmetric supercapacitor exhibited higher energy density, power density, and longer cycle life compared to other  $\text{Co}(\text{OH})\text{F}/\text{Ni}(\text{OH})_2$  candidate materials (Co/Ni = 1:0, 1:1, 1:3, 0:1).



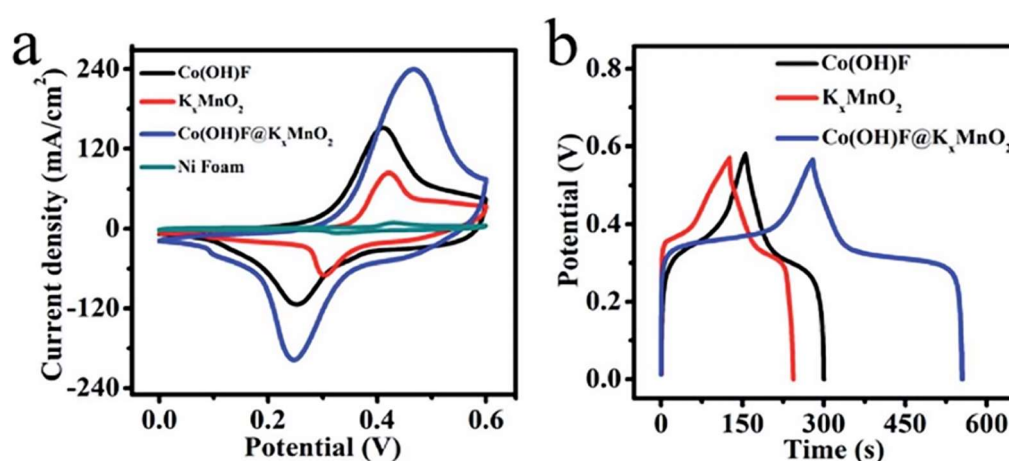
**Figure 8.** Specific capacity (a) and retention rate (b) as a function of current density of  $\text{Co}(\text{OH})\text{F}/\text{Ni}(\text{OH})_2$  electrodes (Co/Ni = 1:0, 3:1, 1:1, 1:3, 0:1)<sup>[50]</sup>.

Creating electrodes with unique structures can also enhance the electrochemical performance of materials. Chen et al.<sup>[67]</sup> created a core-shell structure array of  $\text{Co}(\text{OH})\text{F}$  nanorods coated with  $\text{K}_x\text{MnO}_2$  using electrodeposition. The electrochemical performance was assessed using  $\text{Co}(\text{OH})\text{F}$  nanorods as the working electrode in a 0.02 M manganese acetate and 0.2 M potassium sulfate electrolyte. In **Figure 9(a)**, the transmission electron microscopy image of individual  $\text{Co}(\text{OH})\text{F}$  nanorods obtained in ethanol through ultrasound reveals the relatively smooth surfaces of the nanorods. The transmission electron microscopy image of the  $\text{Co}(\text{OH})\text{F}@K_x\text{MnO}_2$  core-shell structure (**Figure 9(c)**) illustrates that the surface

of the Co(OH)F nanorods (dark region) is encompassed by  $K_xMnO_2$  nanosheets (light region). Additionally, the high-resolution projection image (**Figure 9(d)**) corresponds well to the interplanar spacing of the (002) plane of  $MnO_2$ , further confirming the successful synthesis of the structure. Compared to Co(OH)F nanorods and  $K_xMnO_2$  nanosheets, the core-shell structure demonstrates a larger integrated area in cyclic voltammetry, indicating higher areal capacity and suggesting the additional contribution of  $K_xMnO_2$  as the shell to the overall value (**Figure 10(a)**). In the galvanostatic charge-discharge curves (**Figure 10(b)**), the Co(OH)F@ $K_xMnO_2$  core-shell structure sample exhibits the longest discharge time among the three samples, indicating the highest capacitance. Calculations demonstrate a high areal capacitance of  $1046 \text{ mF cm}^{-2}$  at  $1 \text{ mA cm}^{-2}$ , and after 3000 cycles at a constant current density of  $10 \text{ mA cm}^{-2}$ , it shows a high capacitance retention of 118%. These results indicate that the core-shell array nano-composite material displays improved electrochemical performance and substantial energy storage potential.



**Figure 9.** (a) TEM image of Co(OH)F nanorods; (b) HRTEM images of the Co(OH)F nanorods; (c) TEM image of Co(OH)F@ $K_xMnO_2$  core-shell structure; (d) HRTEM images of the Co(OH)F@ $K_xMnO_2$  core-shell structure<sup>[67]</sup>.



**Figure 10.** (a) CV curves of the Co(OH)F nanorods electrode, the  $K_xMnO_2$  nanosheets electrode, the Co(OH)F@ $K_xMnO_2$  core-shell structure electrode and the pure Ni foam at a scan rate of  $100 \text{ mV s}^{-1}$ ; (b) galvanostatic charge-discharge curves of the Co(OH)F nanorods electrode, the  $K_xMnO_2$  nanosheets electrode and the Co(OH)F@ $K_xMnO_2$  core-shell structure electrode at a current density of  $2 \text{ mA cm}^{-2}$ <sup>[67]</sup>.

In this novel non-uniform core-shell structure, both the electrochemical materials serving as the “core” and “shell” are fully utilized and exhibit excellent synergistic effects. Importantly, the direct growth on a conductive substrate avoids the resistance introduced by binders, facilitating rapid electron transfer to the conductive substrate and enhancing the electrochemical performance of the electrode.

## **4. Conclusions and outlook**

By doping with other metal elements and utilizing synergistic effects, mixed transition metal hydroxyfluorides exhibit higher conductivity. Composites retain the advantages of each component material and achieve more comprehensive performance than single-component materials. The unique electrode structure enhances the material's electrochemical performance. Modified hydroxyfluoride electrode materials demonstrate improved conductivity, cycling stability, and the lifespan of supercapacitors. However, the large-scale application of hydroxyfluoride electrode materials still faces significant challenges, necessitating further development and exploration of higher-performance hydroxyfluorides and the adoption of more reasonable modification measures to promote their use.

Research has demonstrated that, due to their high specific surface area, theoretical capacitance, and fast electron transfer rate, hydroxyfluorides perform well in electrochemical tests. Consequently, an increasing amount of research is applying hydroxyfluorides in electrode materials for supercapacitors and lithium-ion batteries, which is crucial for enhancing energy storage capabilities. With their straightforward and cost-effective preparation methods, hydroxyfluorides have the potential for large-scale applications in the future. However, hydroxyfluoride materials themselves suffer from poor rate performance and stability, necessitating improvement through modification measures. Additionally, further refinement of hydroxyfluoride preparation methods is needed to optimize product structure and properties. Furthermore, research on hydroxyfluorides is still relatively limited, and continued exploration of the preparation of other transition metal hydroxyfluorides and their application in supercapacitor electrode materials requires significant effort.

Despite the potential of hydroxyfluorides as efficient catalysts, they still face significant challenges in both fundamental and practical aspects. This includes: 1) developing advanced scaling-up methods that are simple, convenient, and cost-effective, in addition to refining synthesis strategies; 2) precise control of the composition, size, morphology, pore structure, phase, and impurities in the nanostructures of efficient catalysts to improve the utilization of active sites; 3) comprehensive characterization techniques for structure and composition information; 4) high-throughput methods for characterizing composition, configuration, microstructure, and catalytic performance to identify unexplored core catalysis within a vast combination of elements; 5) computational models with high accuracy, generality, and simplicity to provide a time- and cost-efficient approach for optimizing the composition and surface structure of hydroxyfluoride-based materials; 6) collaborative efforts between experimental and theoretical approaches to determine active sites and structure-performance relationships.

In conclusion, while hydroxyfluorides hold significant development potential as electrode materials for energy storage devices, addressing challenges related to rate performance and stability is essential. With continued technological advancements and further research, hydroxyfluorides are expected to play a crucial role in energy storage and contribute to efficient and sustainable energy storage solutions.

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## **Conflict of interest**

The authors declare that they have no conflict of interest.

## References

1. Shi W, Meng Z, Xu Z, et al. Controllable vacancy strategy mediated by organic ligands of nickel fluoride alkoxides for high-performance aqueous energy storage. *Journal of Materials Chemistry A*. 2023, 11(3): 1369-1379. doi: 10.1039/d2ta08004d
2. Meng Z, Gong X, Xu J, et al. A general strategy for preparing hollow spherical multilayer structures of Oxygen-Rich vacancy transition metal Oxides, especially high entropy perovskite oxides. *Chemical Engineering Journal*. 2023, 457: 141242. doi: 10.1016/j.cej.2022.141242
3. Wang F, Wu X, Yuan X, et al. Latest advances in supercapacitors: from new electrode materials to novel device designs. *Chemical Society Reviews*. 2017, 46(22): 6816-6854. doi: 10.1039/c7cs00205j
4. Wang Y, Du Z, Xu J, et al. Improved Catalytic Activity and Stability of Co<sub>9</sub>S<sub>8</sub> by Se Incorporation for Efficient Oxygen Evolution Reaction. *Inorganic Chemistry*. 2022, 61(51): 21139-21147. doi: 10.1021/acs.inorgchem.2c03805
5. Sun X, Meng Z, Hao Z, et al. Efficient fabrication of flower-like core-shell nanochip arrays of lanthanum manganate and nickel cobaltate for high-performance supercapacitors. *Journal of Colloid and Interface Science*. 2023, 630: 618-628. doi: 10.1016/j.jcis.2022.10.035
6. Olabi AG, Abbas Q, Al Makky A, et al. Supercapacitors as next generation energy storage devices: Properties and applications. *Energy*. 2022, 248: 123617. doi: 10.1016/j.energy.2022.123617
7. Salanne M, Rotenberg B, Naoi K, et al. Efficient storage mechanisms for building better supercapacitors. *Nature Energy*. 2016, 1(6). doi: 10.1038/nenergy.2016.70
8. Simon P, Gogotsi Y. Materials for electrochemical capacitors. *Nature Materials*. 2008, 7(11): 845-854. doi: 10.1038/nmat2297
9. Aricò AS, Bruce P, Scrosati B, et al. Nanostructured materials for advanced energy conversion and storage devices. *Nature Materials*. 2005, 4(5): 366-377. doi: 10.1038/nmat1368
10. Wang G, Zhang L, Zhang J. A review of electrode materials for electrochemical supercapacitors. *Chemical Society Reviews*. 2012, 41(2): 797-828. doi: 10.1039/c1cs15060j
11. Chhowalla M, Shin HS, Eda G, et al. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nature Chemistry*. 2013, 5(4): 263-275. doi: 10.1038/nchem.1589
12. Zhang LL, Zhao XS. Carbon-based materials as supercapacitor electrodes. *Chemical Society Reviews*. 2009, 38(9): 2520. doi: 10.1039/b813846j
13. Zhu Y, Murali S, Stoller MD, et al. Carbon-Based Supercapacitors Produced by Activation of Graphene. *Science*. 2011, 332(6037): 1537-1541. doi: 10.1126/science.1200770
14. Kötz R, Carlen M. Principles and applications of electrochemical capacitors. *Electrochimica Acta*. 2000, 45(15-16): 2483-2498. doi: 10.1016/s0013-4686(00)00354-6
15. Frackowiak E, Béguin F. Carbon materials for the electrochemical storage of energy in capacitors. *Carbon*. 2001, 39(6): 937-950. doi: 10.1016/s0008-6223(00)00183-4
16. Chen LF, Zhang XD, Liang HW, et al. Synthesis of Nitrogen-Doped Porous Carbon Nanofibers as an Efficient Electrode Material for Supercapacitors. *ACS Nano*. 2012, 6(8): 7092-7102. doi: 10.1021/nn302147s
17. Augustyn V, Simon P, Dunn B. Pseudocapacitive oxide materials for high-rate electrochemical energy storage. *Energy & Environmental Science*. 2014, 7(5): 1597. doi: 10.1039/c3ee44164d
18. Pandolfo AG, Hollenkamp AF. Carbon properties and their role in supercapacitors. *Journal of Power Sources*. 2006, 157(1): 11-27. doi: 10.1016/j.jpowsour.2006.02.065
19. Snook GA, Kao P, Best AS. Conducting-polymer-based supercapacitor devices and electrodes. *Journal of Power Sources*. 2011, 196(1): 1-12. doi: 10.1016/j.jpowsour.2010.06.084
20. Bonaccorso F, Colombo L, Yu G, et al. Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage. *Science*. 2015, 347(6217). doi: 10.1126/science.1246501
21. Liu C, Yu Z, Neff D, et al. Graphene-Based Supercapacitor with an Ultrahigh Energy Density. *Nano Letters*. 2010, 10(12): 4863-4868. doi: 10.1021/nl102661q
22. Zhai Y, Dou Y, Zhao D, et al. Carbon Materials for Chemical Capacitive Energy Storage. *Advanced Materials*. 2011, 23(42): 4828-4850. doi: 10.1002/adma.201100984
23. Chen H, Cong TN, Yang W, et al. Progress in electrical energy storage system: A critical review. *Progress in Natural Science*. 2009, 19(3): 291-312. doi: 10.1016/j.pnsc.2008.07.014
24. Zhong C, Deng Y, Hu W, et al. A review of electrolyte materials and compositions for electrochemical supercapacitors. *Chemical Society Reviews*. 2015, 44(21): 7484-7539. doi: 10.1039/c5cs00303b
25. Luo X, Wang J, Dooner M, et al. Overview of current development in electrical energy storage technologies and the application potential in power system operation. *Applied Energy*. 2015, 137: 511-536. doi: 10.1016/j.apenergy.2014.09.081
26. Wang Y, Shi Z, Huang Y, et al. Supercapacitor Devices Based on Graphene Materials. *The Journal of Physical Chemistry C*. 2009, 113(30): 13103-13107. doi: 10.1021/jp902214f

27. Wei W, Cui X, Chen W, et al. Manganese oxide-based materials as electrochemical supercapacitor electrodes. *Chemical Society Reviews*. 2011, 40(3): 1697-1721. doi: 10.1039/c0cs00127a
28. Wan F, Wang X, Tang C, et al. Metallic 1T-MoS<sub>2</sub> coupled with MXene towards ultra-high rate-capabilities for supercapacitors. *Journal of Materials Chemistry A*. 2022, 10(22): 12258-12268. doi: 10.1039/d2ta01908f
29. Yu J, Xie F, Wu Z, et al. Flexible metallic fabric supercapacitor based on graphene/polyaniline composites. *Electrochimica Acta*. 2018, 259: 968-974. doi: 10.1016/j.electacta.2017.11.008
30. Yu Z, Tetard L, Zhai L, et al. Supercapacitor electrode materials: nanostructures from 0 to 3 dimensions. *Energy & Environmental Science*. 2015, 8(3): 702-730. doi: 10.1039/c4ee03229b
31. Ling Z, Ren CE, Zhao MQ, et al. Flexible and conductive MXene films and nanocomposites with high capacitance. *Proceedings of the National Academy of Sciences*. 2014, 111(47): 16676-16681. doi: 10.1073/pnas.1414215111
32. Zhang K, Zhang LL, Zhao XS, et al. Graphene/Polyaniline Nanofiber Composites as Supercapacitor Electrodes. *Chemistry of Materials*. 2010, 22(4): 1392-1401. doi: 10.1021/cm902876u
33. González A, Goikolea E, Barrena JA, et al. Review on supercapacitors: Technologies and materials. *Renewable and Sustainable Energy Reviews*. 2016, 58: 1189-1206. doi: 10.1016/j.rser.2015.12.249
34. Yan J, Wang Q, Wei T, et al. Recent Advances in Design and Fabrication of Electrochemical Supercapacitors with High Energy Densities. *Advanced Energy Materials*. 2013, 4(4). doi: 10.1002/aenm.201300816
35. Wang H, Casalongue HS, Liang Y, et al. Ni(OH)<sub>2</sub> Nanoplates Grown on Graphene as Advanced Electrochemical Pseudocapacitor Materials. *Journal of the American Chemical Society*. 2010, 132(21): 7472-7477. doi: 10.1021/ja102267j
36. Yan J, Fan Z, Sun W, et al. Advanced Asymmetric Supercapacitors Based on Ni(OH)<sub>2</sub>/Graphene and Porous Graphene Electrodes with High Energy Density. *Advanced Functional Materials*. 2012, 22(12): 2632-2641. doi: 10.1002/adfm.201102839
37. Fan Z, Yan J, Wei T, et al. Asymmetric Supercapacitors Based on Graphene/MnO<sub>2</sub> and Activated Carbon Nanofiber Electrodes with High Power and Energy Density. *Advanced Functional Materials*. 2011, 21(12): 2366-2375. doi: 10.1002/adfm.201100058
38. Pershaanaa M, Bashir S, Ramesh S, et al. Every bite of Supercap: A brief review on construction and enhancement of supercapacitor. *Journal of Energy Storage*. 2022, 50: 104599. doi: 10.1016/j.est.2022.104599
39. Zhang J, Gong X, Li X, et al. Electron-ion conjugation sites co-constructed by defects and heteroatoms assisted carbon electrodes for high-performance aqueous energy storage. *Journal of Colloid and Interface Science*. 2023, 640: 600-609. doi: 10.1016/j.jcis.2023.02.147
40. Zeng F, Meng Z, Xu Z, et al. Biomass-derived porous activated carbon for ultra-high performance supercapacitor applications and high flux removal of pollutants from water. *Ceramics International*. 2023, 49(10): 15377-15386. doi: 10.1016/j.ceramint.2023.01.122
41. Zhi M, Xiang C, Li J, et al. Nanostructured carbon-metal oxide composite electrodes for supercapacitors: A review. *Nanoscale*. 2013, 5(1): 72-88. doi: 10.1039/c2nr32040a
42. Futaba DN, Hata K, Yamada T, et al. Shape-engineerable and highly densely packed single-walled carbon nanotubes and their application as super-capacitor electrodes. *Nature Materials*. 2006, 5(12): 987-994. doi: 10.1038/nmat1782
43. Lin T, Chen IW, Liu F, et al. Nitrogen-doped mesoporous carbon of extraordinary capacitance for electrochemical energy storage. *Science*. 2015, 350(6267): 1508-1513. doi: 10.1126/science.aab3798
44. Frackowiak E. Carbon materials for supercapacitor application. *Physical Chemistry Chemical Physics*. 2007, 9(15): 1774. doi: 10.1039/b618139m
45. Zhu B, Liu Y, Zhao H, et al. ZnOHF/N-doped carbon hybrids as a novel anode material for enhanced lithium storage. *Journal of Alloys and Compounds*. 2021, 889: 161705. doi: 10.1016/j.jallcom.2021.161705
46. Chen H, Zhang Y, Yang J, et al. Ni<sub>0.33</sub>Co<sub>0.66</sub>(OH)F hollow hexagons woven by MWCNTs for high-performance lithium-ion batteries. *Journal of Materials Chemistry A*. 2015, 3(41): 20690-20697. doi: 10.1039/c5ta05143f
47. Wu F, Ma X, Feng J, et al. 3D Co<sub>3</sub>O<sub>4</sub> and CoO@C wall arrays: morphology control, formation mechanism, and lithium-storage properties. *Journal of Materials Chemistry A*. 2014, 2(30): 11597. doi: 10.1039/c4ta01676a
48. Ni S, Ma J, Zhang J, et al. Facile synthesis of Co(OH)F micro-rods and its application as anode for lithium ion batteries. *Materials Letters*. 2015, 139: 138-140. doi: 10.1016/j.matlet.2014.10.035
49. Jiang S, Pang M, Zhao J, et al. Superior performance asymmetric supercapacitors based on a directly grown three-dimensional lawn-like cobalt-zinc hydroxyfluorides nanoneedle arrays electrode. *Chemical Engineering Journal*. 2017, 326: 1048-1057. doi: 10.1016/j.cej.2017.06.017
50. Li X, Ding R, Shi W, et al. Hierarchical porous Co(OH)F/Ni(OH)<sub>2</sub>: A new hybrid for supercapacitors. *Electrochimica Acta*. 2018, 265: 455-473. doi: 10.1016/j.electacta.2018.01.194

51. Zhang JF, Wang Y, Shu X, et al. One-pot synthesis of nickel-cobalt hydroxyfluorides nanowires with ultrahigh energy density for an asymmetric supercapacitor. *Science Bulletin*. 2018, 63(5): 322-330. doi: 10.1016/j.scib.2018.01.024
52. Chen S, Zhou X, Ma X, et al. Asymmetric supercapacitors with excellent rate performance by integrating Co(OH)F nanorods and layered  $Ti_3C_2T_x$  paper. *RSC Advances*. 2019, 9(53): 30957-30963. doi: 10.1039/c9ra06393e
53. Dong Q, Su T, Ge W, et al. Atomic Doping and Anion Reconstructed  $CoF_2$  Electrocatalyst for Oxygen Evolution Reaction. *Advanced Materials Interfaces*. 2020, 7(7). doi: 10.1002/admi.201901939
54. Zhang B, Jiang K, Wang H, et al. Fluoride-Induced Dynamic Surface Self-Reconstruction Produces Unexpectedly Efficient Oxygen-Evolution Catalyst. *Nano Letters*. 2018, 19(1): 530-537. doi: 10.1021/acs.nanolett.8b04466
55. Roger I, Shipman MA, Symes MD. Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting. *Nature Reviews Chemistry*. 2017, 1(1). doi: 10.1038/s41570-016-0003
56. Zhang L, Wang W, Xu G, et al. Facile synthesis of  $Co_xFe_{1-x}P$  microcubes derived from metal-organic frameworks for efficient oxygen evolution reaction. *Journal of Colloid and Interface Science*. 2019, 554: 202-209. doi: 10.1016/j.jcis.2019.07.008
57. Shi W, Jiang C, Meng Z, et al. Novel Co-doped nickel hydroxyfluorides with rapid electron transfer for high-performance supercapacitors. *Journal of Alloys and Compounds*. 2023, 959: 170558. doi: 10.1016/j.jallcom.2023.170558
58. Xu F, Sun L, Dai M, et al. Fluorine-Ion-Mediated Electrodeposition of Rhombus-Like ZnFOH Nanorod Arrays: An Intermediate Route to Novel ZnO Nanoarchitectures. *The Journal of Physical Chemistry C*. 2010, 114(36): 15377-15382. doi: 10.1021/jp1066082
59. Zhu L, Zheng Y, Hao T, et al. Synthesis of hierarchical ZnO nanobelts via Zn(OH)F intermediate using ionic liquid-assistant microwave irradiation method. *Materials Letters*. 2009, 63(28): 2405-2408. doi: 10.1016/j.matlet.2009.07.062
60. Song J kui, Zheng M bo, Yang Z jiang, et al. Synthesis of Novel Flower-Like Zn(OH)F via a Microwave-Assisted Ionic Liquid Route and Transformation into Nanoporous ZnO by Heat Treatment. *Nanoscale Research Letters*. 2009, 4(12). doi: 10.1007/s11671-009-9428-1
61. Barzegar F, Bello A, Momodu DY, et al. Effect of radiation on the performance of activated carbon base supercapacitor: Part I. Influence of microwave irradiation exposure on electrodes material. *Energy Procedia*. 2019, 158: 4554-4559. doi: 10.1016/j.egypro.2019.01.754
62. Peng Y, Zhou HY, Wang ZH. Synthesis, characterization and photocatalytic activity of Zn(OH)F hierarchical nanofibers prepared by a simple solution-based method. *CrystEngComm*. 2012, 14(8): 2812. doi: 10.1039/c2ce06389a
63. Ahmad S, Rawat P, Nagarajan R. Facile green synthesis of Zn(OH)F from the single source precursor  $KZnF_3$ . *Materials Letters*. 2015, 139: 86-88. doi: 10.1016/j.matlet.2014.10.037
64. Lemoine K, Zhang L, Dambournet D, et al. Synthesis by Thermal Decomposition of Two Iron Hydroxyfluorides: Structural Effects of Li Insertion. *Chemistry of Materials*. 2019, 31(11): 4246-4257. doi: 10.1021/acs.chemmater.9b01252
65. Lv J, Yang X, Zang HY, et al. Ultralong needle-like N-doped Co(OH)F on carbon fiber paper with abundant oxygen vacancies as an efficient oxygen evolution reaction catalyst. *Materials Chemistry Frontiers*. 2018, 2(11): 2045-2053. doi: 10.1039/c8qm00405f
66. Hao Z, Jiang C, Xu Z, et al. Reasonably optimized structure of iron-doped cobalt hydroxylfluoride for high-performance supercapacitors. *Journal of Colloid and Interface Science*. 2023, 644: 64-72. doi: 10.1016/j.jcis.2023.04.061
67. Chen S, Song Y, Zhou X, et al. Co(OH)F nanorods@ $K_xMnO_2$  nanosheet core-shell structured arrays for pseudocapacitor application. *RSC Advances*. 2019, 9(62): 36208-36212. doi: 10.1039/c9ra07024a