Advances in Nickel-cobalt Electrode Materials for Supercapacitors

Linkun Sun¹, a, Yuxuan Zhang², b

¹ University of Shanghai for Science and Technology, Shanghai 200082, China;
² University of Shanghai for Science and Technology, Shanghai 200082, China.

a2107025762@qq.com, b392452000@qq.com

Abstract. With the rapid development of society, supercapacitors have been widely studied in energy storage devices for their unique advantages of high energy density, good cycle stability, fast charge and discharge speed. However, the development of supercapacitors is limited by low energy density. To address this challenge, it is important to develop and prepare electrode materials with excellent electrochemical properties for supercapacitors. To improve the energy density of supercapacitors, nickel-cobalt electrode materials have been widely studied due to their advantages of high energy density, high safety and long life. In this review, the research progress in material morphology and microstructure of supercapacitors prepared from nickel-cobalt metal oxides/hydroxides, sulfides, selenides and phosphates in recent years is summarized and prospected.

Keywords: Supercapacitor; nickel cobalt electrode material; material morphology; microstructure.

1. Introduction

1.1 Background

With the development of the social economy, people's demand for energy is increasing, at the same time, the rapid change in society has brought the phenomenon of energy shortage to the circulation system of nature and caused serious damage to the natural environment, so it has been unable to meet the sustainable development of human beings [1, 2]. People are gradually shifting electricity production from fossil fuel sources to green energy sources such as solar, water, wind, and other green clean energy sources.

The most widely used energy storage devices are supercapacitors and lithium-ion batteries [3, 4], but the high cost and shortage of lithium-ion batteries have a negative impact on the production and research of lithium-ion batteries [5].

Supercapacitors are energy storage devices with fast charge and discharge rates and high energy density[6]. Lithium-ion secondary batteries have the advantages of high energy density and high safety[7]. The organic combination of supercapacitors and lithium-ion batteries shows the synergistic effect of the two, making them to a large extent improve the performance defects of a single type of energy storage device, and have been significantly applied in mobile energy storage devices [8].

1.2 Introduction to Capacitors

The supercapacitor is a kind of electrochemical energy storage device based on double-layer electrostatic adsorption/Faraday reaction. The charge is mainly stored at the interface between the electrolyte and electrode/near the surface of the electrode. Compared to batteries, supercapacitors store electrical energy through double-layer adsorption/Faraday reaction near the surface of the surface, giving supercapacitors both high power density and high capacity [9, 10].

1.2.1 Capacitor structure

The structure of the supercapacitor is shown in Figure 1. Assembly process in the middle of the diaphragm to prevent the positive and negative electrode material short circuit phenomenon, the middle part is the electrolyte, one end of the positive electrode material, one end of the negative electrode material.
1.3 Transition metal compounds

As a typical pseudocapacitive electrode material [11], transition metal compounds need to meet the following conditions: First, metal elements have multiple valence states, and their oxides/hydroxides have certain chemical stability; Then, a semiconductor metal with certain conductivity is selected; Second, when a chemical reaction occurs, protons can quickly be freely inserted and removed from the lattice of the metal compound [12]. Common metal materials are mostly transition metal compounds (Mn, Ni, Co, Fe, etc.) [11]. However, due to the shortcomings of transition metal compounds such as poor electrical conductivity and slow chemical reaction rate, their development in supercapacitors has been affected. In recent years, people have improved the performance of capacitors by developing transition metal sulfides [13], transition metal phosphides [14], transition metal hydroxides [15], etc.

1.2.1 Transition metal sulfides

Transition metal sulfide is widely regarded as a potential electrode active material due to its abundant reserves, high electrochemical activity, ideal specific capacitance, etc. [16] A NiCo2S4/CuCo2S4 heterostructured three-dimensional nanocomposite was designed. Due to the new heterogeneous structure, the mass transfer kinetics of nanocomposites has been significantly improved.

1.2.2 Transition metal oxides/hydroxides

Transition metal oxides/hydroxides are also widely used as electrode materials with great potential due to their low cost and abundant oxidation states. Compared with metal oxides, metal hydroxides have their unique advantages, among which layered bimetallic hydroxides [17] (LDHs) are considered to be more promising energy storage materials because of their rapid REDOX kinetics and unique layered structure. In this study, in 2021, Nguyen, TT [18] used a simple solvothermal method to grow nickel-cobalt LDH (Ni-Co LDHs) nanosheets in layers on the surface of nickel foam. Interconnect nanosheets with a thickness of about 25 nm were grown uniformly on nickel foam and good performance was obtained.

1.2.3 Transition metal phosphide

Because sulfur is a non-metallic main group element like hydrogen and oxygen, it has a larger atomic radius and electronegativity, resulting in its excellent electrical conductivity and excellent REDOX properties in the electrode material has been widely concerned. Among them, transition
metal phosphates have been used as electrochemically active materials in electrochemical energy storage due to their abundant natural resources and low price. In 2021, Cheng, YH [19] designed a new layered transition metal sulfide and transition metal phosphide composite electrode material, in which CoNi2S4/Ni3P (CNSP-500) nanocomposite material was prepared by a two-step anion exchange method. This structure has a unique sugar-coated nanostructure. As an electrode material, it has excellent electrochemical properties. The optimized CNSP-500 electrode material obtained an extremely high area-specific capacitance of 8.86 F cm\(^{-2}\) and a mass-specific capacitance of 3100 F g\(^{-1}\), about 7 times that of the cobalt carbonate nickel-metal hydride (CN) precursor.

1.2.4 Transition metal selenides

Transition metal selenides have been widely used in the field of electrochemical energy storage due to their excellent electrical conductivity and remarkable electrochemical activity. It shows good adjustable characteristics in various electrochemical applications. Basically, the chemical properties of selenides and sulfides are very similar, which has led researchers to explore different applications for these materials [20]. In 2019, Wang, YH [21] team developed a simple hydrothermal method for the synthesis of nickel-cobalt selenide nanoparticles, and the optimized Ni\(_{0.6}\)Co\(_{0.4}\)Se\(_2\) electrode had a specific capacity of 602.6 C g\(^{-1}\) at 1 A g\(^{-1}\) and a specific capacity of 468.5 C g\(^{-1}\) at 20 A g\(^{-1}\). Using BNPC material as negative electrode and Ni\(_{0.6}\)Co\(_{0.4}\)Se\(_2\) sample as positive electrode, an all-solid-state asymmetric supercapacitor is constructed. In KOH/PVA gel electrolyte, the energy density is as high as 42.1 Wh kg\(^{-1}\), and the capacity maintenance rate is 91.0% after 5000 cycles.

2. Material morphology and microstructure

2.1 Key factors affecting the electrochemical properties of transition metals

Through the analysis of high-quality papers published in the past, we concluded that the excellent cycle stability of transition metal oxides/hydroxides, sulfides, selenides, and phosphates is inextricably related to the material morphology and microstructure of the electrode materials.

The morphology and microstructure of electrode materials greatly affect the reachable region, diffusion path, and structural stability of electrolyte ions, thus determining the permittivity and cycle performance of supercapacitors. Highly active transition metal electrode materials are usually composed of particles with sizes ranging from tens of nanometers to several microns. This is based on consideration of the trade-off between high surface area and reduced electrochemical stability of small particle sizes [22]. Small nanoparticles usually have a high surface energy and therefore tend to cluster together, which reduces the stability of the material and the specific surface area of the electrochemical reaction. By constructing nanostructures to increase structural stability and electroactive sites, and reduce the diffusion distance of electrolyte ions, the methods to improve the performance of supercapacitors have aroused extensive research interest. Promising structures such as three-dimensional micro-nano structures, porous structures, and hollow structures have been reported to improve the performance of supercapacitors. Nickel-cobalt materials have been widely studied in terms of morphology and microstructure because of their high energy density and long life.

2.2 Electrode materials

2.2.1 Three-dimensional micro-nano structure

Three-dimensional micronano structures can integrate a large number of nano components into a microscale structure while maintaining the component's unique properties at the nanoscale, and different microstructure often results in different supercapacitor properties with different performance [23].
2.2.1.1 Nickel-cobalt metal sulfide

Tuo, YX [24] synthesized coral-like CoFeS$_2$ nanomaterials by organic solvothermal method. Due to its large specific surface area and unique coral-like structure, CoFeS$_2$ electrode material has a specific capacity of 1457.1 F g$^{-1}$ at 2 A g$^{-1}$ in 2M KOH aqueous solution. The asymmetric CoFeS$_2$ AC supercapacitor has an energy density of 66.4 Wh kg$^{-1}$ when the power density is 790 W kg$^{-1}$, and a specific capacitance retention rate of 97.6% after 10000 cycles at 10 A g$^{-1}$ current density. Meanwhile, Hu, Y [25] synthesized a sea urchin-like NiCo$_2$S$_4$ material by a one-step solvothermal method. Polyethylene glycol (PEG) 200 and thiourea were used as control agents and sulfur sources for in-situ vulcanization, respectively. The prepared NiCo$_2$S$_4$ has an ion diffusion structure, a high specific capacitance (1334 F g$^{-1}$ at 0.5 A g$^{-1}$), and an excellent rate capacity (78.1% of the original capacity at 0.5 to 20 A g$^{-1}$) in 6 M KOH aqueous solution. In addition, an asymmetric supercapacitor is assembled with NiCo$_2$S$_4$ as the positive electrode and activated carbon (AC) as the negative electrode. Under the power density of 317.8 W kg$^{-1}$, the energy density of NiCo$_2$S$_4$/AC device is as high as 37.32 Wh kg$^{-1}$, the capacity retention rate is 91.9%, and the number of charge and discharge cycles can reach 2000 times under the condition of 3 A g$^{-1}$.

2.2.1.2 Nickel-cobalt metal oxide/hydroxide

In terms of nickel-cobalt metal oxides, Huang, LJ [26] prepared a novel sea urchin-like Zinc-nickel-cobalt oxide (ZNCO) microsphere with spinel cubic structure by a simple hydrothermal method. This structure provides a larger surface area, and polynickelatic species can enhance electrical conductivity, introduce external defects, and improve their electrochemical properties. The results show that the specific capacity of ZNCO prepared under 1 A g$^{-1}$ condition is 766 C g$^{-1}$, and the capacity retention under 20 A g$^{-1}$ condition is 93.21%. The assembled device exhibits a high specific energy of 41.4 Wh kg$^{-1}$ at 850 W kg$^{-1}$ and a cycle stability of nearly 90% after 20,000 charge and discharge cycles. In addition, Zhu YY [27] prepared ternary aluminum-nickel-cobalt oxide (AlNiCo-O) based on the hot blast stove method and carried out subsequent calcination. AlNiCo-O presents a floral network. AlNiCo-O electrode has a specific capacity of 1008.5 C g$^{-1}$ at 1 A g$^{-1}$, and has good charge storage performance. In addition, hybrid supercapacitors based on AlNiCo-O electrodes have a high energy density of 63.3 Wh kg$^{-1}$ at a power density of 881.4 W kg$^{-1}$ and a good magnification capability of 41.6 Wh kg$^{-1}$ at 13.3 kW kg$^{-1}$. It has 84.27% cycle performance after 5000 cycles.

In terms of transition metal hydroxides, Zhang, D [28] prepared honeycomb Te Ni-Co layered double hydroxides (HS-Te-NiCo-LDHs) by controlled anode electrodeposition with the help of dynamic oxygen bubble template method (DOBT). The HS-Te-NiCo-LDH/NiO/NF electrode was designed as an OER electrocatalyst with an ultra-low overpotential of 221 mV at 10 mA cm$^{-2}$. It has long stability over 24 hours in 1 mol L$^{-1}$ KOH solution (maintained at a high specific capacity similar to 90 mA cm$^{-2}$) and 650 C g$^{-1}$. Wang, JR [29] prepared a flower-like TMC-LDH (Ni$_{0.75}$Co$_{0.25}$(CO$_3$)$_{0.125}$(OH)$_2$, NCCO) material by hydrothermal method. It has a high specific capacity of 306.8 mAh g$^{-1}$ (0.52 mAh cm$^{-2}$ at 0.5 A g$^{-1}$ and a capacity retention rate of 70.5% after 2000 cycles. The solid-state hybrid supercapacitor device NCCO//PVA/KOH//IHPC based on the prepared NCCO material and interconnecting Laminated porous carbon (IHPC) provides high specific energy of 50.96 Wh kg$^{-1}$ at 1.06 kW kg$^{-1}$ specific power. A high specific energy of 36.39 Wh kg$^{-1}$ can still be provided at a high specific power of 10.49 kW kg$^{-1}$. After 12,000 cycles, more than 181.2% of the initial specific capacity is retained. In addition, Jiao, ZC [30] proposed a new 3D/3D composite structure in which three-dimensional hollow NiCo LDH were fixed on three-dimensional sea urchin-like CoO microspheres through a multi-step process (Fig. 2). The results show that three-dimensional CoO provides efficient and stable channels for ion diffusion, while hollow NiCo LDH provides abundant REDOX active sites. The results show that the area-specific capacity of CoO@NiCo LDH electrode is 4.71C cm$^{-2}$ when the current density is 3 mA cm$^{-2}$(440.19C g$^{-1}$ when 0.28 A g$^{-1}$), and the initial capacitance can still maintain 88.76% after 5000 cycles.
2.2.1.3 Nickel-cobalt metal phosphide

Jingzhou Ling [31] team combined highly conductive materials with transition metal phosphide and prepared NiCo materials with sea urchin structure on carbon cloth substrate by solvothermal method. In addition, it was found that the NiCo material was composed of one-dimensional nanoneedles and two-dimensional nanosheets, which grew uniformly on the carbon cloth and formed a good conductive network. On this basis, the carbon-coated material remained intact after phosphating, and the pore size distribution was more concentrated and the specific surface area was larger. The assembled NiCoP@C-ULAs//AC all-solid-state device has a specific capacity of up to 168.5 C g\(^{-1}\), excellent rate performance, and long cycle life, and exhibits a high energy density of 37.1 Wh kg\(^{-1}\) at 792.8 W kg\(^{-1}\). Ma, SQ [32] prepared nickel-cobalt ammonium phosphate (NH\(_4\)(Ni, Co)PO\(_4\))/carbon fiber (CFs) electrode material by hydrothermal method. Nickel-cobalamin phosphate has a nanoflower-like structure, uniformly distributed on the surface of carbon fiber. The capacitance retention rate of the electrode material was 89.1% after 2000 cycles. The maximum energy density of NCCF-3 is 20.28 Wh kg\(^{-1}\), and the power density is 189.17 W kg\(^{-1}\). It is proposed that the combination of the double electric layer of conductive carbon fiber and the pseudocapacitance of NH\(_4\)(Ni, Co)PO\(_4\) can improve its electrochemical performance.

2.2.1.4 Nickel-cobalt selenides

Han Qu [33] added silica microspheres as a template to synthesize a new type of porous tremella nickel cobalt selenide by a simple two-step hydrothermal method. The new thin sheet morphology and porous structure provide a large number of electrochemically active sites and improve the reaction kinetics. Tests have also proved that the electrochemical-specific surface area of the material is greatly increased, and the electrical conductivity of the nickel-cobalt-based material after selenization is also greatly improved compared with its hydroxide. The single electrode of the new silver-shaped nickel-cobalt selenide can reach 636.2 C g\(^{-1}\) at 1 A g\(^{-1}\), showing high capacity, good magnification performance (20 A g\(^{-1}\), 66.1%), and electrical conductivity.

2.2.2 Porous structure

Porous structures [34] have also been extensively explored to improve the properties of materials due to several advantages, such as providing abundant free space to buffer changes in the amount of activity of materials under high current density cyclic testing; The inner material can be effectively exposed to the electrolyte, which can shorten the electrolyte ion diffusion path. It can greatly increase the specific surface area, provide rich active sites for electrochemical charge storage processes, and so on, so it is a kind of electrode material suitable for supercapacitors.
2.2.2.1 Nickel-cobalt metal sulfide

Lu, ZW \cite{35} prepared porous hollow nickel-cobalt sulfides by a simple water bath and anion exchange. The newly designed porous hollow structure provides more active sites, a chamber to store electrolytes, and an optimized electron/ion diffusion pathway. Then, the Ni-Co ratio and NCDs doping quality were optimized. The specific capacity of prepared NCDs/Ni$_2$Co$_1$S-50 at 1 A g$^{-1}$ is 764.1 C g$^{-1}$. Hybrid supercapacitors based on NCDs/Ni$_2$Co$_1$S-50 have excellent energy/power density (73 mWh cm$^{-2}$/1.39 W cm$^{-2}$) and good cycle performance (96.5% hold 10000 times).

2.2.2.2 Nickel-cobalt metal oxide/hydroxide

In terms of nickel cobalt metal oxides Dang, SQ \cite{36} prepared porous rod-like NiCo$_2$O$_4$ nanostructures by water-ethylene glycol mixed solvothermal method and calcined them. The prepared NiCo$_2$O$_4$ electrode material has a high specific capacitance of 417.1 C g$^{-1}$ at 1 A g$^{-1}$ and a high capacitance retention of 73.4% in the range of 1 ~ 10 A g$^{-1}$. It has excellent cyclic stability of 130% (340.9 C g$^{-1}$ at 10 A g$^{-1}$) after 10,000 cycles. In terms of nickel-cobalt metal hydroxide, Gao, MY \cite{37} reported a nickel-cobalt (oxygen) hydroxide composite with a three-dimensional layered porous structure, which triggered the active site and structural rearrangement by in-situ electrochemical activation method (Fig. 3). By systematically adjusting the pore size in the layered structure, the optimal composite can provide a high area capacity of 34.8 mAh cm$^{-2}$ and an energy density of 19.1 mWh cm$^{-2}$ at mass loads up to 230 mg cm$^{-2}$. The team of Qingsong Liu \cite{38} prepared NiCo-LDH by electrodeposition and converted hydroxide into phosphide by one-step phosphating. The obtained NiCoP has a 3D porous nanosheet stack structure, and its electrochemical properties are significantly improved compared with nickel-cobalt mono-metals. The prepared NiCoP electrode has high specific capacitance (1142.84 F g$^{-1}$ at 1 A g$^{-1}$), good magnification performance (62.07% initial specific capacitance at 10 A g$^{-1}$), and excellent cycle stability (74.5% initial capacitance maintained after 5000 cycles at 10 A g$^{-1}$).

![Fig. 3 Two-step process for preparing a three-dimensional layered porous composite structure](image)

2.2.2.3 Nickel-cobalt metal phosphide

Zhang, XY \cite{39} prepared a new electrode material by surfactant-assisted self-assembly method. The prepared transition metal phosphate (SDBS-Ni$_2$Co$_1$PO$_4$) had mesoporous morphology and showed excellent electrochemical capacitance. At the same time, the material has excellent cyclic stability, a 77% retention rate after 2000 charge and discharge at 10 A g$^{-1}$.

2.2.2.4 Nickel-cobalt selenides

Yuan, Y \cite{40} designed a carbon-coated mixed metal selenide with carbon nanotubes as roots using nickel-cobalt bimetallic organic frameworks as raw materials (Ni-Co-Se@C-CNT). Due to the unique porous structure, the synergistic effect of bimetallic selenides and the in-situ growth of carbon nanotubes, the composite has good electrical conductivity, high structural stability and abundant REDOX active sites. The results show that Ni-Co-Se@C-CNT exhibits a high specific capacity of
554.1 \text{ F g}^{-1} (1108.2 \text{ F g}^{-1}) at 1 \text{ A g}^{-1}, and has excellent cycling performance, that is, 96.4\% of the initial capacity is still maintained after 5000 cycles at 10 \text{ A g}^{-1}. In addition, Zhou, TL \cite{41} synthesized \((\text{Ni}_{0.85}\text{Se})_3(\text{Co}_{0.85}\text{Se})/\text{rGO}\) composites by simple and efficient microwave heating and solvothermal method. It can be observed that \((\text{Ni}_{0.85}\text{Se})_3(\text{Co}_{0.85}\text{Se})/\text{rGO}\) presents a three-dimensional porous structure composed of stacked nanorods. The synthesized \((\text{Ni}_{0.85}\text{Se})_3(\text{Co}_{0.85}\text{Se})/\text{rGO}\) has an excellent specific capacitance of 2009 \text{ F g}^{-1} at current density of 2 \text{ A g}^{-1}, and 83\% ultra-high power performance when the current density increases from 2 \text{ A g}^{-1} to 30 \text{ A g}^{-1}. It has 79.7\% capacity retention after 5000 cycles at 30 \text{ A g}^{-1}.

2.2.3 Hollow structure

Hollow structures have also been investigated as promising structures for improving the properties of transition metal-based materials \cite{42}. The interior of the space exposes more atoms to the surface of the electrode material to better contact with the electrolyte and shorten the diffusion distance of electrolyte ions. At the same time, the hollow structure can stabilize the packaged electroactive material and effectively alleviate the volume strain during the charge-discharge cycle. Single-shell hollow structures \cite{43} have been reported to be combined with a range of transition metal compounds to obtain high electrochemical properties. During the study, hollow structures with more complex characteristics were prepared to further improve the capacitive properties of the electrode materials \cite{44}. Multi-shell hollow structures have been reported to have better electrochemical properties than single-shell hollow structures. This is because it can expose more inner surface active sites, with higher packing density and structural stability.

2.2.3.1 Nickel-cobalt metal sulfide

Gong, JX \cite{45} synthesized nickel-cobalt sulfide (Ni-CoS) hollow spheres by using the hard template method and hydrothermal method in two steps (Fig. 4). Ni-Co-S has an optimally sized hollow spherical structure and mesoporous surface with an excellent specific capacity of 819.9 \text{ C g}^{-1}. The energy density of the prepared Ni-Co-S//CS asymmetric supercapacitor is 65 \text{ Wh kg}^{-1} at 850 \text{ W kg}^{-1} power density, and the capacity retention rate is 82.8\% after 10,000 cycles. In addition, Ding, MJ \cite{46} studied the preparation of three-dimensional NiCo_{2}S_{4} and NiCo_{2}S_{4}/rGO composites by a two-step hydrothermal method as electrode materials for high-performance supercapacitors. The results show that pure NiCo_{2}S_{4} has a three-dimensional flower-like structure. The ultra-pasteurized NiCo_{2}S_{4} nanospheres were then successfully inserted into the graphene surface by hydrothermal method. During the experiment, when the current density is 1 \text{ A g}^{-1}, the specific capacitance of the NiCo_{2}S_{4}/rGO electrode reaches 1002.9 \text{ F g}^{-1}. After 2000 cycles at 5 \text{ A g}^{-1}, the capacitance retention of NiCo_{2}S_{4}/rGO composite electrode material was increased by 59.6\% to 88.5\% compared with NiCo2S4. Electrochemical independent spectroscopy (EIS) shows that NiCo_{2}S_{4}/rGO electrode materials have higher ion diffusion rates and lower solution resistance.

Chen, LA \cite{47} reported the synthesis of a novel hollow structure of ternary metal sulfide, namely nickel cobalt sulfide hollow cube, by a simple ion exchange method and hydrothermal treatment. A homogeneous ZIF-67 (Zeolitic Imidazolate Framework-67) cube was synthesized as a precursor, and then the CoNi_{2}S_{4} hollow polyhedron was successfully realized by chemical conversion without annealing. The hollow cube CoNi_{2}S_{4} has a specific capacitance of 2448 \text{ F g}^{-1} at a current density of 1.0 \text{ A g}^{-1}. In addition, an asymmetric supercapacitor (ASC) device based on the CoNi_{2}S_{4} hollow cube has been assembled. The asymmetric supercapacitor has a high energy density of 62.19 \text{ Wh kg}^{-1} at a power density of 775 \text{ W kg}^{-1}. However, building layered hollow structures remains a challenge. Here, Shi, ZQ \cite{48} report a simple template-free method to prepare a novel hollow nickel cobalt sulfide (NiCo_{2}S_{4}) in the form of sea urchins. The experiment shows that the capacitance of 1398 \text{ F g}^{-1} exhibited by the hollow NiCo_{2}S_{4} sphere at 1 \text{ A g}^{-1} is maintained at 1110 \text{ F g}^{-1} at high current density of 10 \text{ A g}^{-1}. The hybrid supercapacitor prepared from NiCo_{2}S_{4} and activated carbon has an energy density of 39.3 \text{ Wh kg}^{-1} at a power density of 749.6 \text{ W kg}^{-1} and maintains a cycle stability of 74.4\% after 5000 cycles.
2.2.3.2 Nickel-Cobalt metal oxide/hydroxide

Liu, L [49] developed a simple one-step self-template method for manufacturing Ni$_2$Co(CO$_3$)$_2$(OH)$_2$ hollow microspheres (NiCoHSs) as high-performance hybrid supercapacitor electrodes. Good morphology with large specific surface area, suitable pore size, and good electrical conductivity gives high specific capacity (890.8 C g$^{-1}$ at 0.5 A g$^{-1}$) and excellent retention rate (700.8 C g$^{-1}$ at 50 A g$^{-1}$) and high stability (87.5% over 5000 cycles), Superior to most nickel-cobalt oxide/hydroxide based electrodes. Du, YQ [50] reported the results of reasonable design and synthesis of porous hollow nickel-cobalt-manganese hydroxide (NiCoMn-OH) polyhedra using zeolite imidazole acid skeleton-67 (ZIF-67) as a template. The edge-to-side superposition of the ultra-thin nanosheets forms a three-dimensional multi-stage hollow polyhedron structure with internal nanopore channels that facilitate electron/ion transfer (Fig. 5). In terms of supercapacitor applications, NiCoMn-OH electrodes show excellent capacitance performance (up to 1654.5 F g$^{-1}$ at 1 A g$^{-1}$) and excellent magnification performance (up to 58.5% at 30 A g$^{-1}$) in three-electrode alkaline systems.

2.2.3.3 Nickel-cobalt metal phosphide

Zhang, HX [51] reported a simple strategy for the preparation of porous hollow nanostructured cobalt-Zinc-nickel phosphor/carbon (CoZnNiP/C) composites using Zn/Co zeolite imidazole acid framework (ZIF) as a precursor through solvothermal reaction and subsequent phosphorylation. The optimized CoZnNiP/C-2 electrode has a high specific capacity of 760 C g$^{-1}$ and a good magnification
performance of 603 C g⁻¹ (20 A g⁻¹). In addition, Gao, M [52] adopted a mild hydrothermal method to prepare sea urchin-shaped nickel-cobalt phosphide hollow spheres, considering the advantages of polycrystalline reoxidation reduction center and excellent electrical conductivity of term-based nickel-cobalt phosphide for improving the performance of supercapacitors. The prepared material exhibits an excellent capacity of 761 C g⁻¹ at 1 A g⁻¹ current density, and maintains 693 C g⁻¹ even at 20 A g⁻¹ current density, showing a high magnification capacity with an initial capacity retention rate of about 91.1%.

2.2.3.4 Nickel-cobalt selenides

Tan, LC [53] successfully assembled nickel-cobalt selenide (H-Ni-Co-Se) nanoarrays with hollow structures on foam nickel using sequential chemical etching and selenization strategies. The hollow structure growing on the surface of nickel foam can provide an abundant electroactive region, shorten charge/ion diffusion length and enhance mass/electron transfer. The prepared H-Ni-Co-Se has good specific capacitance, which can reach 1175 F g⁻¹ at 1 A g⁻¹, and the charging and discharging speed is fast. Quan, L [54] successfully synthesized the unique layered (Ni₀.₃₃Co₀.₆₇)Se₂ composite hollow spheres (CHSs) starting from metal-organic frameworks (MOFs). The layered (Ni₀.₃₃Co₀.₆₇)Se₂ CHSs show a high specific capacitance of 827.9 F g⁻¹ at a current density of 1 A g⁻¹ and can still maintain 646.2 F g⁻¹ at a current density of 30 A g⁻¹. In addition, after 2000 cycles at 6 A g⁻¹, a high capacitance of 865.8 F g⁻¹ was obtained, indicating good cycle stability.

2.2.4 Core-shell structure

The core-shell structure [55] is also considered to be a structure that can improve the performance of capacitors, and the core-shell structure can provide more electroactive sites, higher conductivity, and faster ion electron transfer, which may lead to unprecedented electrochemical performance. In principle, a core material with a higher conductivity can optimize charge transport paths, while a shell material with a larger accessible surface area can facilitate ion transport and buffer volume changes during electrochemical tests.

2.2.4.1 Nickel-cobalt metal sulfide

Gong, JX [56] prepared NiCo₂S₄ with core-shell and microporous structure on nickel foam by hydrothermal method and co-vulcanization method as an efficient anode material for asymmetric supercapacitors (Fig. 6). The NiCo₂S₄ electrode has a specific capacitance of 850.2 C g⁻¹ at 1 A g⁻¹ and retains 93.6% of its original capacitance after 5000 cycles. In addition, the NiCo₂S₄ electrode also has excellent electrochemical performance as the anode of the asymmetric NiCo₂S₄/ activated carbon (AC) supercapacitor, with an energy density of 38.1 Wh kg⁻¹ at 700 W kg⁻¹ and a capacity retention rate of 84.3% after 5000 cycles.

2.2.4.2 Nickel-cobalt metal oxide/hydroxide

In terms of nickel-cobalt hydroxide, Acharya, J [57] used soluble hydrothermal and metal-organic framework (MOF) assisted co-precipitation method to prepare three-dimensional porous layered ZNCO@Co-Ni-LDH core-shell nanostructures on nickel foam. In a three-electrode system,
ZNCO@Co-Ni-LDH-2 The electrode material has excellent electrochemical properties, with a specific capacitance of 2866 F g\(^{-1}\) at 1 A g\(^{-1}\), an ultra-high capacitance retention of 68.35% at a high current density of 10 A g\(^{-1}\), and an excellent lifetime of 89% after 8000 cycles. Zhu, ML\(^{[58]}\) used a simple method to synthesize Zn/Co MOF derived Zn-Co oxide/nickel-Co layered double hydroxide (Zn-Co-O/NiCo-LDH) layered core/shell nanostructures on the surface of nickel foam (NF). The prepared Zn-Co-O/NiCo-LDH battery-type electrode has an excellent specific capacitance of 2275.2 F g\(^{-1}\) at 1 A g\(^{-1}\) and a cycle stability of 82.4% after 5000 cycles. In addition, a hybrid supercapacitor (HSC) device was assembled using the prepared Zn-Co-O/NiCo-LDH as a positive electrode, which obtained a significant energy density of 44.5 W h/kg at a power density of 800 W kg\(^{-1}\) and a retention rate of 71.5% after 5000 cycles of the device.

2.2.4.3 Nickel-cobalt metal phosphide

In the study of YL Zhu\(^{[59]}\), a self-supported three-dimensional layered core-shell NiCoP@NiCoP@CC electrode was prepared by a two-step hydrothermal method and phosphating method. The electrode integrates the advantages of a one-dimensional core that provides a "hyper channel" for electron transport, a two-dimensional shell on the core that reduces the diffusion distance of ions and charges while improving cyclic stability, and the flexibility of a three-dimensional networked substrate. The prepared electrodes exhibited excellent electrochemical properties, with a high specific capacity of 1125 C g\(^{-1}\) (312 mAh g\(^{-1}\)) at 1 A g\(^{-1}\) and a retention rate of 78.0% at 10 A g\(^{-1}\). 808 C g\(^{-1}\) (224 mAh g\(^{-1}\)) was maintained after 2000 cycles (71.8% retention rate).

2.2.4.4 Nickel-cobalt selenides

RM Luo\(^{[60]}\) synthesized a novel nanocluster consisting of NiCoO\(_4\)Se\(_3\) (represented as NCOSe) nanowire core and Ni\(_2\)Co\(_2\)-LDH nanosheet shell on carbon fiber (CF@NCOSe/Ni\(_2\)Co\(_2\)-LDH) for the first time (Fig. 7). This core-shell structure can improve the stability of the material and further stimulate the REDOX reactivity of the inner nanowires. Due to the synergistic action of NCOSe and Ni\(_2\)Co\(_2\)-LDH, the nanocluster CF@NCOSe/Ni\(_2\)Co\(_2\)-LDH has a capacity of 3270 F g\(^{-1}\) (454.17 mAh g\(^{-1}\)) at 1 A g\(^{-1}\). The prepared CF@NCOSe/Ni\(_2\)Co\(_2\)-LDH//AC hybrid supercapacitor (HSC) has an energy density of 89.7 Wh kg\(^{-1}\) when the power density is 800 W kg\(^{-1}\). In addition, HSC has a capacitance retention rate of 95.6% after 10,000 charge and discharge cycles. In addition, Si qi Li\(^{[61]}\) team grew cobalt-nickel bimetallic selenide nanotubes on Ni foam by two-step hydrothermal method, and coated the surface of cobalt-nickel bimetallic selenide nanotubes with a layer of polypyrrole (PPy) shell by potentiostatic deposition method to form a core-shell structure, and obtained cobalt-nickel bimetallic selenide - polypyrrole composite electrode material grown on Ni foam. The electrode has a high area-specific capacitance of 13.27 F cm\(^{-2}\) at a current density of 5 mA cm\(^{-2}\), and still maintains 92.63% of the initial specific capacitance after 1000 cycles at a current density of 30 mA cm\(^{-2}\).
3. Summary

In summary, this paper reviews the latest research progress of nickel-cobalt metal sulfides, oxides/hydroxides, sulfides, phosphates and selenides in terms of material morphology and microstructure regulation to improve the magnification capacity and cycle stability of supercapacitors. Through the analysis of these electrode materials, it is concluded that the construction of nanostructured materials with controllable morphology is a necessary condition to obtain good capacitor performance. The optimized material structure can provide a larger surface area, shorten the diffusion path of electrolyte ions and electrons, and provide sufficient free space for buffering large volume changes in the active material during charge and discharge.

Although many promising approaches have been demonstrated to achieve high performance in supercapacitors using nickel-cobalt metal sulfides, oxides/hydroxides, sulfides, phosphide and selenides, there are still many challenges and research questions to be addressed in this area. In addition to the materials discussed in this paper, other recently developed transition metal-based materials, such as transition metal carbides \cite{62}, carbonitriles \cite{63}, and nitrides \cite{64}, also have great potential in terms of material morphology and microstructure.

Current research on transition metal compounds in terms of material morphology and microstructure is still very limited, which is critical for designing capacitor materials with high electrochemical properties. So further research to fill this knowledge gap is urgently needed and should be a focus in the future.

References


Sari HMK, Li X. Controllable Cathode–Electrolyte Interface of Li[0.8Co0.1Mn0.1]O2 for Lithium Ion Batteries: A Review. Advanced Energy Materials. 2019;9(39).


[55] Lin J, HenanLiang, HaoyanChen, ShulinCai, YifeiQi, JunleiQu, ChaoqunCao, JianFei, WeidongFeng, Jicai. Hierarchical CuCo2S4@NiMn-layered double hydroxide core-shell hybrid arrays as electrodes for supercapacitors. Chemical engineering journal. 2018;336.


[59] Zhu Y, QuanZhang, QilongYang, HuiWang, QianqianWang, Huiying. Three-dimensional core-shell NiCoP@NiCoP array on carbon cloth for high performance flexible asymmetric supercapacitor. Electrochimica Acta. 2019;299.


