ISSN: 2688-8645

Recent Advancement on Preparation and Electrochemical Performance Study of Metal-based Porous Electrodes

Ke Lv, Shuai Li, Yu Yang, Jiangyong Liu, Ran Zhang *

School of Materials and Chemical Engineering, Xuzhou University of Technology, Xuzhou, Jiangsu, 221018, China

* Corresponding author: Ran Zhang

Abstract

With the rapid growth of renewable energy and electrochemical energy storage and conversion technologies, the need for high-performance electrode materials is growing increasingly strong. Because of their large specific surface area, tunable three-dimensional pore structure, and effective mass transfer characteristics, porous electrodes are now essential for improving the performance of electrochemical energy devices. However, there are still many fundamental obstacles in the way of the development of porous electrodes: First, the stability of microstructures during preparation and cycling processes; second, the complex fabrication processes, high costs, and difficulties in large-scale production resulting from intricate pore structures; third, uneven reactions and reduced utilization efficiency caused by internally constrained transport kinetics; fourth, the multi-parameter coupling that makes performance optimization and precise characterization extremely difficult. Recent advancements in the field's study are methodically summarized in this overview. It initially discusses preparation methods for metal-based porous electrodes using standard metal salt systems, such as nickel, cobalt, manganese, copper, iron, and zinc, as precursors. Second, it analyzes the microstructural properties and electrochemical performance of metal-based porous electrodes created through diverse preparation processes. Finally, it discusses future research trends toward green, low-cost preparation technologies, precise creation of multi-level pore structures, and the application of improved in-situ characterization tools to disclose structural evolution principles during working conditions. This will encourage the practical use of next-generation metal-based porous electrodes that are high-performing, long-lasting, and inexpensive.

Keywords

Metal-based Porous Electrodes; Preparation Methods; Structural Regulation; Electrochemical Performance; Energy Devices.

1. Introduction

Global demand for renewable energy keeps rising as conventional fossil fuels run out and greenhouse gas emissions lead to environmental crises [1]. Due to their advantages of large energy storage capacity, fast response, and flexible configuration, supercapacitors and lithium-ion batteries, two significant types of electrochemical energy storage devices, have shown broad application prospects in areas like power grid frequency regulation, load control, and portable electronic devices[2]. Supercapacitors have a long cycle life and a high power density, but their energy density is often lower than that of lithium-ion batteries, which somewhat limits its continued use and promotion. Researchers have tackled the problem from several perspectives, such as electrolyte optimization, active material creation, and device structure design, in order to get around this bottleneck. Among these, creating electrode materials with porous architectures is thought to be one of the best approaches to raise the devices' overall performance. Porous electrodes can greatly increase the exposure of active sites, shorten ion diffusion pathways, and reduce volume strain on electrode materials during cycling because of their high specific surface area, tunable pore structure, and effective mass transfer features. This enhances the structural stability and response kinetics of the electrode[3]. Because of their rich valence states, high redox activity, and controllable electronic structures, metal-based porous electrodes—particularly those based on transition metals like nickel, cobalt, manganese, copper, iron, zinc, and their compounds—have attracted a lot of interest in energy conversion and storage fields, such as supercapacitors, lithium-ion batteries, and water electrolysis catalysis. However, contemporary research still faces problems such as complex preparation processes, expensive prices, and poor microstructural stability. Therefore, this work seeks to carefully analyze the preparation methods of metal-based porous electrodes and their performance in electrochemical energy devices. It focuses on porous electrode materials using metal salts such as nickel, cobalt, manganese, copper, iron, and zinc as precursors, investigates the impact of different preparation procedures on their microstructure, and describes their electrochemical behavior in energy storage and catalysis.

2. Method for Preparing Metal-based Porous Electrodes

2.1. Template-mediated Assembly Method

While the synthesis of materials with porous architectures can be finished in multiple steps, template-mediated assembly techniques usually employ self-templating or sacrificial templates[4]. One significant feature of the template-mediated technique is its capacity to utilize numerous templates and modify their layering sequence, enabling precise control over the size and morphology of the channels[5]. Additionally, the composition and porosity structure of transition metal (TM)-based porous electrode materials can be effectively constructed and regulated by adding co-templates or other functional atoms. These elements have a major impact on electron/ion transport processes, which results in the creation of TM-based electrodes with stable interfaces, optimal crystalline phases, programmable microstructures, and changeable chemical compositions. This makes it easier for supercapacitors to obtain better energy storage performance[6]. Self-template assembly and sacrificial template techniques are the two main categories into which template-mediated assembly strategies can be divided based on the features of the templates employed.

2.1.1. Self-template Assembly Method

The use of particular organic/inorganic hybrid combinations and reactive precursors, achieved by highly customizable synthetic methods, is the fundamental component of self-templated assembly systems. Solvent-based self-templated assembly methods constitute a widely employed technology primarily for producing porous TM-based electrodes. The micromorphology, porous structure, and pore size distribution of materials can all be precisely controlled using this technique[7]. The key to template-based techniques rests in the creation of pores and flaws inside precursor crystals. These can be broadly divided into three types based on their production mechanisms: non-uniform shrinkage, outward diffusion, and selective etching. Selective etching leverages the differential in chemical stability between the inside and exterior of the precursor crystal to selectively etch the template, thereby producing pores. This approach usually maintains the original size and porous nature of the template[8]. Internal materials move toward external areas during outward diffusion, creating a porous morphology. Phase changes within the solvent or crystal formation typically accompany this process[9]. During non-equilibrium heat treatment, solid materials can develop pores as a result of mass or volume loss, a process known as non-uniform shrinkage[10].

2.1.2. Sacrifice Template Strategy

The hard template method and the soft template method are two examples of sacrificial template strategies that are currently thought to be the most straightforward way to create porous structures[11]. The sacrificial template technique offers a noticeable advantage in that it allows for very uncomplicated customization of the size and shape of porous products by selecting alternative templates and managing the coating process. Additionally, the goods' porous structure and content can be directionally tailored using the right templates. Porous nanostructures' ion/electron transport characteristics and Faradaic reaction processes are strongly influenced by their form and chemical makeup. Thus, controlling morphology and chemical composition is essential to enhancing materials' electrochemical performance[12].

Carbon-based materials frequently develop a large number of pores as a result of thermal decomposition and gas evolution brought on by thermal conversion during the carbonization process of polymer counterparts[13]. In order to create structurally controlled porosity architectures, crystal formation can be guided simultaneously by soft and hard templates. In the manufacture of porous TM-based electrodes, inorganic salts such as sodium chloride and potassium chloride are also often utilized as templates. These templates can be easily removed by simple water cleaning, considerably simplifying the total preparation process[14].

2.2. In-situ Gas Foaming Method

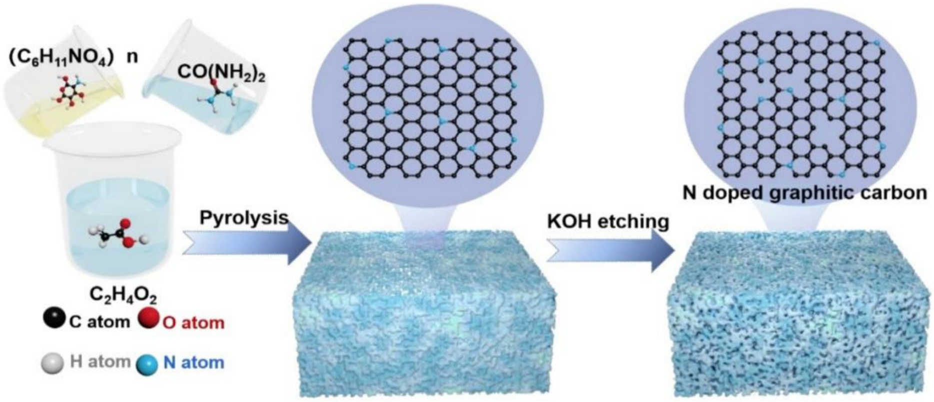

Fig 1. Schematic diagram of the synthesis route for NCS-K1[16]

The procedure of subjecting precursors to high-temperature treatment during thermal conversion is known as the "in-situ gas foaming method." Many pores form in the final crystal structure as a result of this treatment's gas escape caused by heat breakdown or surfactant removal. Additionally, high-temperature thermal conversion improves the crystallinity of porous TM-based electrodes, consequently boosting the cycling stability of the produced materials[15]. For instance, Xiatin Jia[16] used high-temperature gas-phase pyrolysis to successfully create nitrogen-doped porous carbon materials utilizing urea as the nitrogen source and structural regulator and chitosan as the carbon source. A dense blocky structure with a specific surface area of only 89.4 $m^2 g^{-1}$ is produced by pure chitosan carbonization, according to research. However, adding urea alters the material shape into a three-dimensional network porous structure. The resultant sample NCS(1:3), which included active nitrogen species such as pyridine nitrogen and pyrrole nitrogen, showed a markedly increased specific surface area of 343.9 $m^2 g^{-1}$ at a chitin-to-urea mass ratio of 1:3. Nitrogen doping adds more pseudocapacitive active sites, and this porous structure promotes electrolyte ion penetration and transport. Electrochemical testing found that NCS(1:3) attained a specific capacitance of 365 F g^{-1} at a current density of 1 A g^{-1} in 6 M KOH electrolyte, greatly exceeding that of the undoped sample (51 F g^{-1}). Further KOH chemical activation generated abundant intrinsic carbon defects into the material, raising the specific surface area to 642.9 $m^2 g^{-1}$ while keeping the porous structure. The modified sample NCS-K1 displayed higher electrochemical performance, with its specific capacitance increasing to 410 F g^{-1}. After 300 cycles at 200 mA g^{-1}, it reached a specific capacity of 283.7 mAh g^{-1} when utilized as a negative electrode for lithium-ion batteries. These findings show that nitrogen doping and KOH activation work in concert to enhance the pore structure and surface chemistry of carbon materials, greatly enhancing their double-layer capacitance and pseudocapacitive contributions.

2.3. Hydrothermal/Solvent-thermal Method

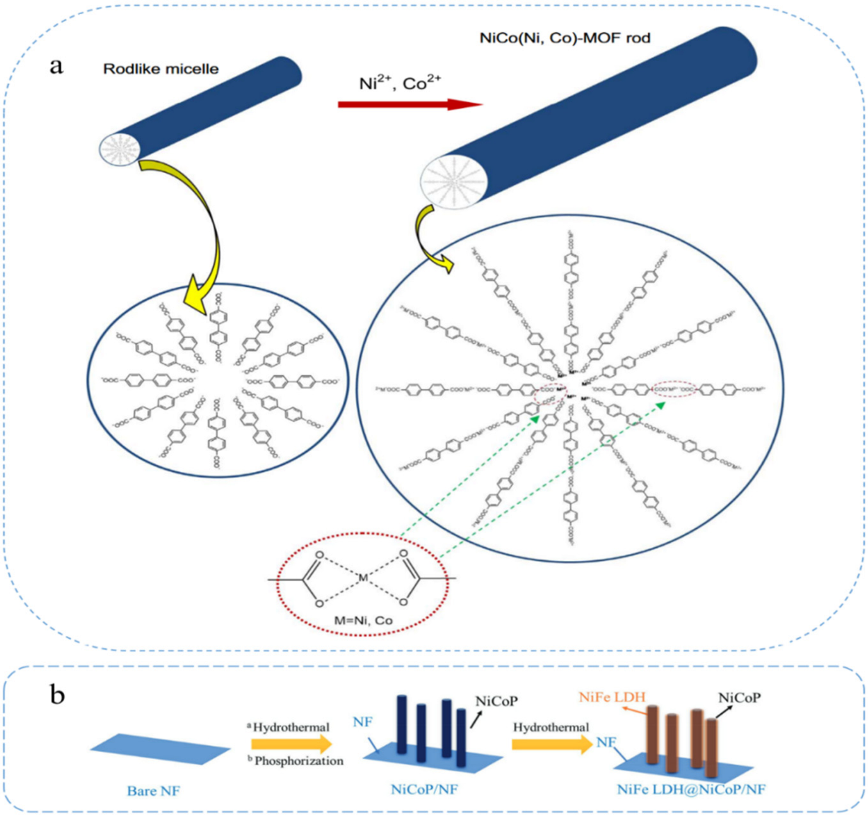

Fig 2. (a)Schematic diagram of the growth process of NiCo (Ni, Co)-MOF rods[17]; (b)Schematic diagram of synthesizing the three-dimensional hierarchical NiFe layered double hydroxide@NiCoP/foam nickel (NF) electrode[18]

In order to facilitate the reaction and crystallization processes of precursors, the fundamental idea behind the solvothermal approach is to alter the physical and chemical characteristics of solvents at high temperatures and pressures. This technology is widely used to model crystal formation environments, considerably enhancing reaction speeds under initial high-temperature and high-pressure circumstances while enabling control over the final products. In order to facilitate the creation of different porous structures, water is frequently chosen as the solvent. By precisely regulating crystal microstructures and nanostructures, solvothermal conversion technology may efficiently manage the physical phase and composition of goods, improving their electrochemical performance[15]. Additionally, the solvothermal approach is also commonly utilized to inject metal ions from solvents into porous TM-based electrode materials. Using 4,4'-biphenyldicarboxylic acid (BPDC) as the ligand, Wang et al.[17] effectively created a NiCo-based bimetallic metal-organic framework (NiCo-MOF) by a hydrothermal process. They constructed one-dimensional micro-nanorods into a three-dimensional cubic structure by varying the reaction temperature and duration. In this structure, nickel and cobalt ions establish stable coordination bonds with BPDC ligands, displaying high thermal stability below 300°C. Electrochemical testing demonstrated that following activation, the inherent resistance, charge transfer resistance, and ionic diffusion impedance of NiCo-MOF were dramatically reduced. Consequently, its specific capacitance grew from 156.5 F/g to 990.7 F/g at 1 A/g and maintained 405 F/g at a high current density of 20 A/g, yielding a coulombic efficiency of 98%. Zhang et al.[18] created a heterostructure (NiFe LDH@NiCoP/NF) on nickel foam using a three-step hydrothermal-phosphating-hydrothermal procedure that included NiFe layered double hydroxide nanosheets and NiCoP nanowires. This structure completely utilizes the three-dimensional porous features of the substrate, enabling uniform development and robust adherence of the active materials, generating a core-shell heterostructure morphology where nanowires support nanosheets. The homogeneous distribution of Ni, Co, Fe, and P with strong electronic interactions at interfaces was confirmed by elemental mapping and transmission electron microscopy. This self-supporting porous structure dramatically boosted exposed active sites while providing ample ion/electron transport channels. The layered porous 2D nanosheets generated a nanoflower-like shape, allowing electrolyte permeability and further increasing electrochemical performance.

2.4. Electrochemical Deposition Method

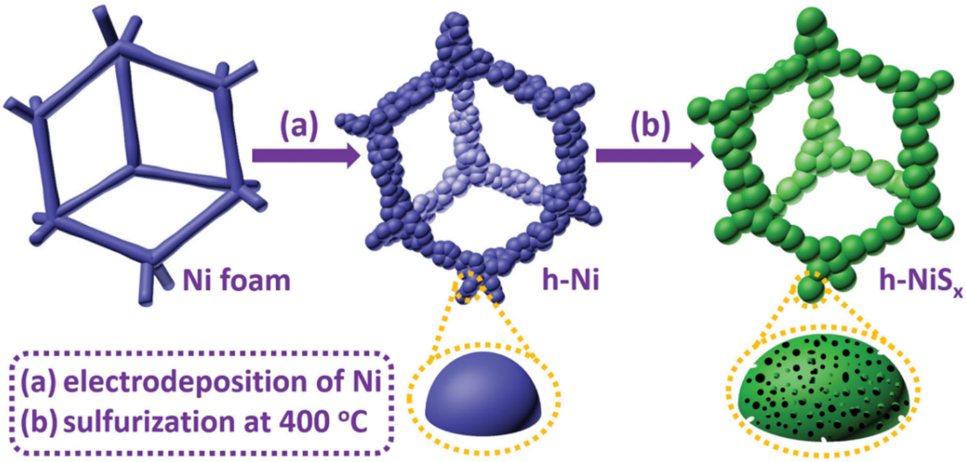

Fig 3. Schematic diagram for the preparation of h-NiS$_x$[20]. (a)Template-free electrodeposition of metallic Ni microsphere arrays and (b) sulfurization.

By depositing metallized sheets onto a variety of substrates, electrochemical deposition is an effective method for creating self-supporting electrodes. This approach directly coats active compounds onto electrode surfaces through cathodic or anodic electrolysis in suitably complex or salt solutions. Bubbles created in situ under polarization circumstances during electrodeposition aid in the development of a porous structure within the metal sheet. By manipulating electrochemical deposition parameters such as current density, solvent, deposition potential, and duration, the shape and thickness of the metal layer can be precisely managed. Since this approach eliminates the requirement for binders in electrode production, such modifications efficiently boost the electrode's active surface area, conductivity, and overall electrochemical performance[19]. For instance, Sun et al.[20] created hierarchical porous nickel sulfide superstructures (h-NiS_x) on nickel foam using a low-temperature vulcanization technique in conjunction with template-free electrodeposition. This method first created an array of porous metallic nickel microspheres on nickel foam by electrodeposition, with hydrogen gas bubbles serving as dynamic templates to direct the construction of the porous structure. The nickel microspheres were then converted into nickel sulfide by low-temperature sulfidation, which produced h-NiS_x material with a hierarchical macroporous structure and three-dimensional interconnected framework. Structural studies revealed that this material possesses both macro- and mesopores, demonstrating a high specific surface area and many active sites. In alkaline electrolytes, h-NiS_x displays remarkable bifunctional electrocatalytic activity, demonstrating overpotentials of -60 mV and 180 mV for HER and OER, respectively, at a current density of 10 mA cm^{-2}. Alkaline water electrolysers built with this material achieve 10 mA cm^{-2} at a cell potential of only 1.47 V, exceeding most documented non-precious metal catalysts. Additionally, h-NiS_x shows good cycle stability and a high surface capacitance of 6104 mF cm^{-2} when used as a supercapacitor electrode.

3. Study on the Electrochemical Properties of Metal-Based Porous Electrodes

3.1. Nickel Salt

Because of their unique electrochemical properties, high cost-effectiveness, and relatively available resources, nickel salts have a pivotal place among porous electrode materials in energy storage and conversion. The kind of anion and physicochemical features of nickel salts directly impact the choice of synthesis pathways, reaction kinetics, and the microstructure and performance of the final products. Additionally, the resultant porous materials typically show good catalytic activity and high specific capacity, which makes them perfect for creating high-performance electrodes[21]. Research focuses on enhancing materials' specific capacitance, energy density, and cycle stability in the direction of supercapacitors. For example, Jingmin Wang et al.[22] developed $NiCo_2O_4$/porous carbon composites by a hydrothermal-calcination process, attaining a specific capacitance of 497 F/g at 1 A/g. Shunxiang Wang[23] further developed a composite material with eggshell-structured $CuCo_2S_4$ and nano-grass-like $NiCo_2O_4$@NiCo-LDH through multi-metal synergistic effects and morphology control. This performance improvement was mainly due to the synergistic effect between the high specific surface area of porous carbon and the good conductivity of $NiCo_2O_4$. This increased the specific capacitance to 1658 F/g and produced an energy density of 73 Wh/kg, demonstrating the benefits of multi-metal components and intricate morphological design in enhancing pseudocapacitive effects. Yimin Wang[24] focused on the enhancement of material properties through electrochemical restructuring, reporting that the NiCoO/NiCoOOH heterostructure displayed a sevenfold increase in specific capacity after cyclic voltammetric activation. This shows that defect engineering and surface restoration are useful methods for increasing electrode material activity.

Additionally, nickel-based porous electrodes are being employed to develop innovative fuel cell devices. Using Co3O4 3DrGO/NiF as the anode and N/Fe-doped biochar as the cathode, Purkait et al.[25] created a membrane-free glucose fuel cell with a power output of 12.81 $\mu W/cm^2$. Its open-circuit voltage, however, was comparatively low (0.442 V), suggesting that long-term stability and voltage output may be improved. All of these investigations show that surface modification, composite material design, and morphological control can greatly improve the performance of nickel-based electrodes in a variety of energy conversion scenarios. However, more research is needed to determine their cost-effectiveness in real-world applications, long-term stability, and environmental adaptability.

3.2. Cobalt Salt

Ni et al.[26] creatively employed phosphorus-containing ionic liquids as a phosphorus source in their study on the pyrolysis of cobalt-based composites for oxygen reduction processes. They effectively created a composite of cobalt phosphide nanoparticles with nitrogen-, phosphorus-, and fluorine-co-doped mesoporous carbon by one-step pyrolysis using zeolite imidazolium framework materials and dicyandiamide. According to characterization, the material has a homogeneous multi-element doping, a high specific surface area, and a mesoporous structure. In alkaline environments, this composite displayed remarkable oxygen reduction catalytic activity with a half-wave potential of 0.86 V, beating standard platinum-carbon catalysts while following an efficient four-electron reaction pathway. Researchers attribute this superiority to synergistic effects between cobalt phosphide active sites and multi-heteroatom-doped carbon carriers. The latter modifies the electrical structure of the carbon skeleton in addition to enhancing conductivity and mass transfer. Additionally, the material exhibits significant power density and discharge potential when used in zinc-air batteries, underscoring its potential for practical use. This study emphasizes the effectiveness of generating metal compound-functionalized carbon matrix composites through precursor design and pyrolysis process control.

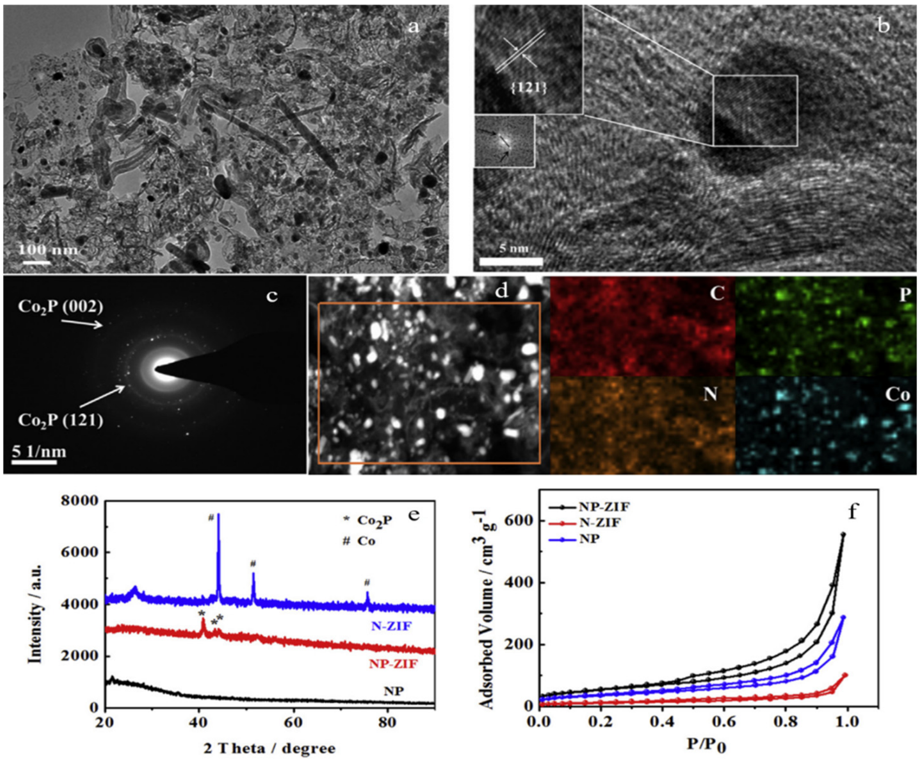

Fig 4. (a)TEM image of NP - ZIF; (b)HRTEM image of NP - ZIF; (c)The sead spectrum of NP - ZIF; (d)TEM image of NP - ZIF and corresponding distribution map of C, N, P and co elements; (e)XRD patterns of NP, N - ZIF and NP - ZIF; (f)N ɑ adsorption isotherms of NP, N - ZIF and NP – ZIF [26]

Direct development of cobalt-based nanoarrays on conductive substrates using hydrothermal deposition provides another essential technique for creating high-performance self-supporting electrodes. Wang et al.[27] achieved in situ synthesis of co-doped cobalt carbonate nanosheet arrays on nickel foam by adjusting the precursor ratios of molybdenum, vanadium, and cobalt. This material exhibits a vertically developed porous nanosheet structure with a significant electrochemically active surface area. Research shows that doping cobalt active centers with vanadium and molybdenum efficiently modifies their electronic structure, maximizing the adsorption free energy of chemical intermediates. In alkaline water hydrogenation tests, the material concurrently displays outstanding hydrogen evolution and oxygen evolution catalytic activity, permitting high current density at low voltages with good stability.

For supercapacitor electrode materials, a large specific surface area and plentiful pore structure are crucial to producing high specific capacitance. Cobalt precursors on foam nickel were initially transformed into porous arrays of cobalt sulfide nanoparticle needle bundles by Peng Sun et al.[28] via an ion exchange technique. This material kept the precursor's array architecture while generating a loose porous structure formed of nanoparticles on its surface, considerably enhancing both specific surface area and electrolyte wettability. According to electrochemical testing, the electrode mainly uses pseudocapacitive mechanisms to store energy. It maintains a high specific capacitance, good rate performance, and great cycling stability even at high current densities. Researchers attribute the porous structure creation to the Kirkendall effect during ion exchange, which improves quick ion transport and alleviates volume variations during cycling. This work shows that building porous metal sulfide arrays on conductive substrates as high-performance, binder-free supercapacitor electrodes is feasible.

3.3. Manganese Salt

The composite design approach of "conductive substrate + active material" is currently the main approach used in manganese-based porous electrode research. This technique boosts the overall electrochemical performance of the electrodes by developing multi-level pore architectures, introducing highly conductive networks, and combining synergistic active components[29-31].

Research on lithium-ion battery anode materials focuses on loading MnO_2 with porous carbon materials to reduce its volume expansion and enhance conductivity. Zeng et al.[32] exploited coal tar pitch as a precursor and synthesized porous graphite carbon (PGC) with an interconnected nanoporous structure via template-assisted synthesis. They next uniformly loaded MnO_2 nanoparticles or nanorods onto the PGC skeleton using an in-situ precipitation technique. With no effect on the porous framework from MnO_2 incorporation, microstructural analysis showed that the composite retained a high specific surface area and a mesoporous-dominated pore structure. Electrochemical tests found that the ideal sample MnO_2/PGC-36 displayed a reversible specific capacity of up to 1516 mAh/g at 0.05 A/g, sustaining 399 mAh/g even at a high rate of 5 A/g, with a capacity retention of 90% after 400 cycles. The study attributes this exceptional performance to the three-dimensional conductive network and buffer space supplied by PGC, which efficiently enables electron/ion transport and accommodates the volume expansion of MnO_2.

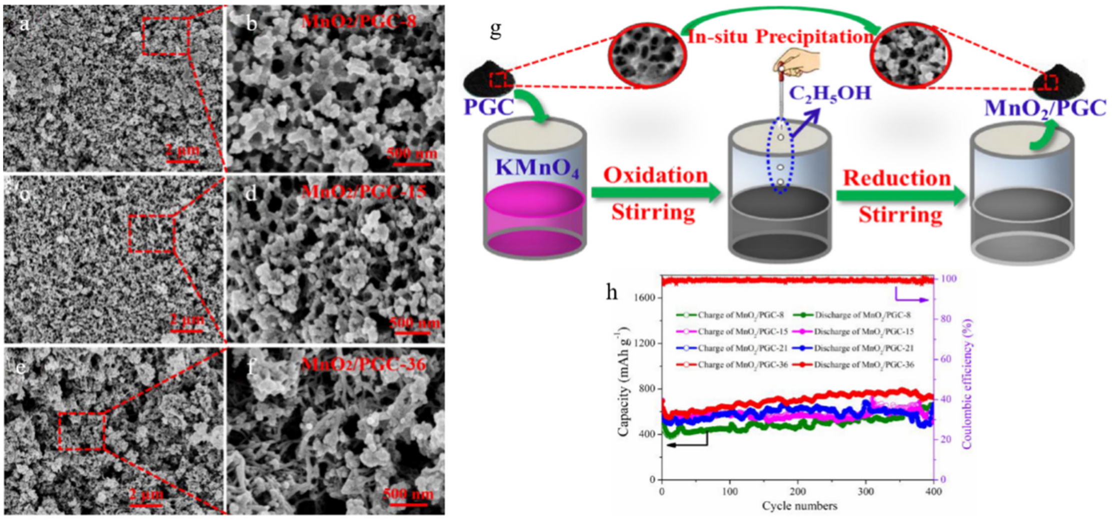

Fig 5. SEM images of MnO_2/PGC composites: MnO_2/PGC-8 (a) and (b); MnO_2/PGC-15 (c) and (d); MnO_2/PGC-36 (e) and (f); (g)Schematic flowchart of in situ synthesis of MnO_2/PGC composites; (h)Cycling performance and coulombic efficiency after 400 cycles[32]

In the field of supercapacitor electrode materials, research has taken several technical approaches aiming at merging double-layer capacitance with pseudo-capacitance, while extending applications to flexible wearables. There are other subdivisions based on variations in substrates and preparation techniques. One method is to use rigid or porous carbon frameworks to build high-performance electrodes. For instance, Sun et al.[33] used jujube shells as a biomass precursor in a two-step carbonization and activation process to create manganese-doped porous carbon, which they then mixed with Ti_3C_2Tx MXene. This work innovatively demonstrated that employing acetone instead of water as the composite medium considerably increased the interfacial wettability between MXene and porous carbon. This maintained a specific capacitance of 58.17 F/g at a high current density of 10 A/g while increasing the pseudo-capacitance contribution ratio from 10.1% to 30.7%. This underscores the necessity of interfacial engineering in generating material synergistic effects. Zuo et al.[34] in situ grew composite nanosheets of MnO_2 and $Ni_xCo_{2-x}(OH)_2$ on three-dimensional carbon felt using a one-step hydrothermal process. An electrode with a high areal capacitance of 1018.6 mF/cm^2 was produced by adjusting the Ni/Co ratio to 8:2. After 10,000 cycles, the built asymmetric supercapacitor retained 70.2% of its capacity. Although the device has a very low energy density, this approach cleverly uses carbon felt as a reducing agent, skeleton, and current collector, simplifying the electrode fabrication process. Second, it entails creating electrodes that are moldable and bendable for flexible electrical devices. Zhou et al.[35] created a hierarchical composite structure by developing vertical graphene nanosheets (VGNs) on nickel wires by plasma-enhanced chemical vapor deposition (PECVD), followed by electrodeposition of MnO_2. This electrode obtained an areal capacitance of 162 mF/cm^2 at a scan rate below 5 mV/s. The built filamentary supercapacitor demonstrated exceptional mechanical flexibility by maintaining a capacitance retention exceeding 80% after bending and twisting, thanks to the ductility of the nickel wire and the stability of the VGNs-MnO_2 composite structure. Third, nanocomposite thin-film electrodes were created using sophisticated laser processing methods. Reduced graphene oxide, multi-walled carbon nanotubes, CeO_2, and manganese oxide were co-deposited in a single step by Garcia Lebiere et al.[36] using reverse matrix-assisted pulsed laser ablation. The resultant composite electrode showed outstanding cycle stability and a high volumetric capacitance of 140 F/cm^3. Although the procedure is still somewhat complicated and expensive, this technology makes it possible to efficiently build composites and deposit numerous components under non-equilibrium conditions.

3.4. Copper Salt

Regarding three-dimensional nanostructured composite electrodes, Van et al.[37] adopted a hydrothermal self-assembly approach to mix one-dimensional copper oxide nanowires with two-dimensional reduced graphene oxide, building a three-dimensional porous network composite electrode. This material utilizes chemical interaction between ethylenediamine functional groups on the CuO nanowire surface and oxygen-containing functional groups on graphene layers to produce stable structural connectivity. Microscopic analysis showed that this three-dimensional structure had a large amount of porosity and a specific surface area of 184 m^2/g. With a capacitance retention rate of 91.2% after 5000 cycles, electrochemical testing revealed a specific capacitance of 364 F/g in 2 M KOH electrolyte—a 1.6-fold improvement over pure graphene electrodes. This study underlines the advantages of three-dimensional interconnected structures in enhancing electron conduction, ion diffusion, and buffering volume variations. However, it also implies that performance under high power density situations requires more research.

Composite electrodes made from MOFs provide novel methods for creating materials based on copper. Juni et al.[38] employed copper-based MOFs as precursors to create $Cu/Cu_2O/C$ composites through pyrolysis at different temperatures. The CM-900 sample developed at 900°C has a porous morphology and a Cu/Cu_2O heterostructure, displaying a specific capacitance of 249 C/g in 1 M KOH. It reaches an energy density of 30 Wh/kg when put together into an asymmetric supercapacitor. The conductive network and numerous active sites created during pyrolysis are mainly responsible for this material's improved performance. However, its comparatively low specific surface area (12.3 m^2/g) and the probable rise in preparation costs due to the high-temperature procedure hinder the full usage of its double-layer capacitance.

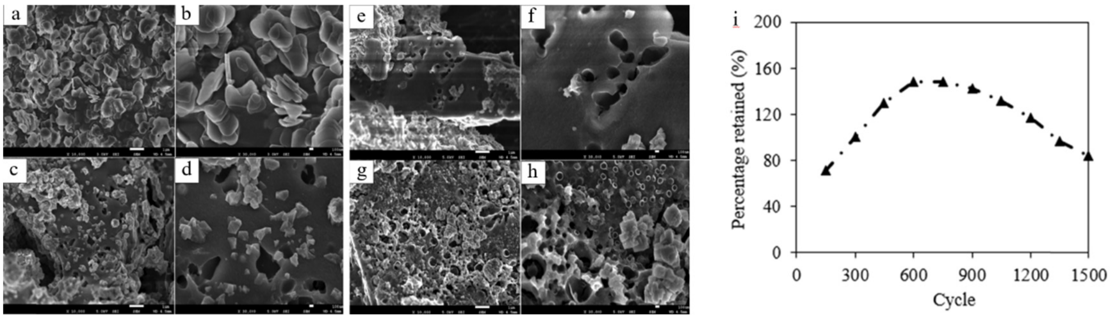

Fig 6. (a) (b)FESEM images of CM-RT; (c) (d)FESEM images of CM-700; (e) (f)FESEM images of CM-800; (g) (h)FESEM images of CM-900; (i)Capacity retention after 1500 cycles at a current density of 0.1 A g^{-1}[38]

Xie et al.[39] created a chemical copper plating method combined with in-situ growth for electrode production in small and flexible devices. Cu current collectors were directly printed on polyimide substrates, and Cu(OH)$_2$@FeOOH nanotube arrays were grown by immersion in solution. This structure has good interface contact and a high specific surface area of 224 m^2/g. The produced micro-supercapacitors maintained consistent performance under bending conditions, achieving an energy density of 18.07 μWh/cm^2 and an areal capacitance of 58.0 mF/cm^2. Although the preparation procedure is somewhat complicated and necessitates strict process control, this work shows the useful potential of copper-based materials in integrated, flexible energy storage systems.

3.5. Iron Salt

Recent studies on the production of graphitized porous carbon materials utilizing iron-based catalytic systems have demonstrated a tendency toward complex structural design and a variety of approaches[40,41].

Research focuses on obtaining low-temperature, quick, and structurally customizable carbon material preparation employing specialized solvent systems in synthetic routes controlled by ionic liquids or deep eutectic solvents. Using FeCl$_3$/BmimCl ionic liquid as the medium, Baccour et al.[42] methodically investigated an approach including ionothermal carbonization followed by pyrolysis of several polysaccharide precursors. This study demonstrated the crucial role that ionic liquid composition (e.g., FeCl$_3$/BmimCl molar ratio) plays in controlling nanopores in carbon materials: a lower molar ratio encourages denser, thermally more stable ionic nanostructures, which in turn cause higher specific surface area and external pore volume during carbonization. Importantly, by varying the washing processes, the study examined how residual iron species affected the microstructure and characteristics of the material. Samples with a higher iron content (4.5 at.%) showed noticeably better graphitization in carbon materials generated from chitosan (Raman ID/IG ratio decreased to 0.34). They outperformed the control sample, where the majority of the iron was eliminated by acid washing, and their reversible specific capacity (about 550 mAh g^{-1}) met or even exceeded that of high-surface-area samples. This shows that leftover Fe$_3$C/Fe species may favorably contribute to electrochemical capacity by engaging in conversion events or facilitating charge transfer, while also highlighting the synergistic impact of nitrogen doping (produced from the chitosan precursor) in increasing capacity. In a similar vein, Chen et al.[43] created a quick synthesis technique based on deep eutectic solvent (DES, which is made up of EG, FeCl$_3$, and ChCl). They obtained coordinated control over the crystallinity and porosity structure of carbon dry gels by adding water as a cosolvent to modify the DES/H2O ratio. The material displays a distinctive "biphasic" structure at an ideal water content (RFCA-70): numerous micropores coexist with well-developed graphitic nano-regions, allowing it to maintain good graphitization while having a high specific surface area (566 m^2/g). As a lithium-ion battery anode, this material demonstrates excellent rate performance (205 mAh g^{-1} @5 A g^{-1}) and high reversible capacity (633 mAh g^{-1} @0.1 A g^{-1}), attributed to the rapid electron conduction pathways provided by the graphitic nanostructure and the efficient ion diffusion ensured by the porous structure. Together, these investigations show that various elements of carbon material texture, graphitization, and chemical composition can be regulated under relatively mild conditions by customizing solvent composition and reaction conditions. However, the practicality of large-scale production and solvent recovery costs requires additional research.

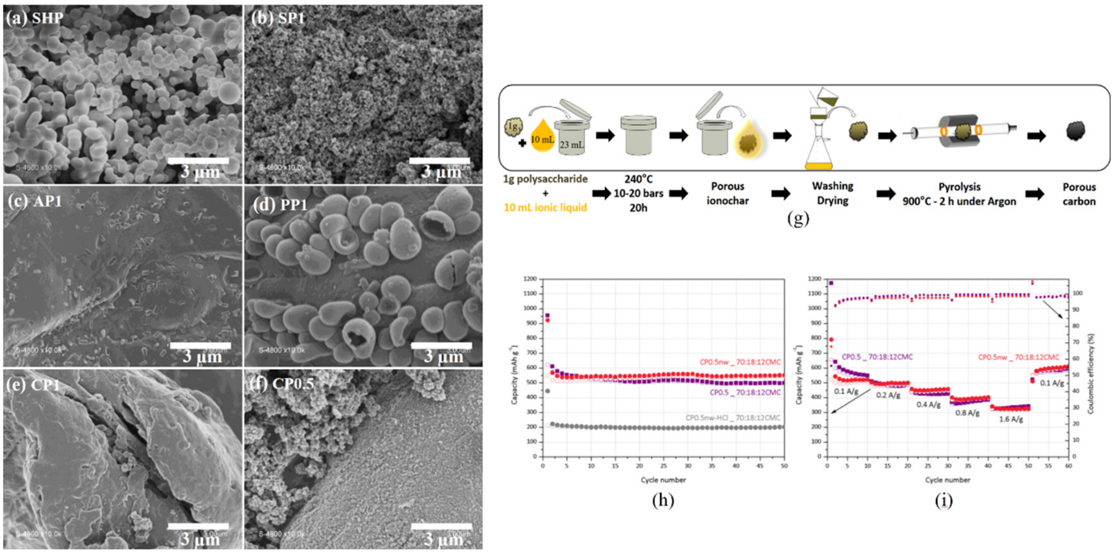

Fig 7. SEM images of carbon materials obtained via HTC of starch (SHP), and via ITC in a 1:1 FeCl3/BmimCl IL of starch (SP1), alginic acid (AP1), pectin (PP1), chitosan (CP1) and in a 0.5:1 FeCl3/BmimCl IL of chitosan (CP0.5); (g)Schematic representation of the procedure employed to prepare porous carbonaceous materials from the ionothermal carbonization of polysaccharides; (h) Cycling test of CP0.5 (0.17 at.% Fe)‡, CP0.5nw (4.5 at.% Fe)‡ and CP0.5nw-HCl (1.0 at.% Fe)‡; (i) rate capability test and Coulombic efficiency of CP0.5 (0.17 at.% Fe)‡ and CP0.5nw (4.5 at.% Fe)‡[42]. The specific capacities were calculated based on the mass of active material. ‡According to SEM-EDX

A more flexible and effective preparation pathway is provided by the molten salt pyrolysis approach, which allows for the simultaneous improvement of high graphitization and high specific surface area at lower temperatures. By pyrolyzing iron-containing organometallic precursors ($Fe(acac)_3$) using molten $ZnCl_2$ as a medium, Deng et al.[41] reported a one-step synthesis of hierarchically porous highly graphitized carbon (HPCHG). In this process, the molten salt not only works as a homogeneous heating medium and soft template but also corrodes the carbon surface to inhibit particle aggregation. In situ graphitization of carbon is catalyzed by atomically distributed iron. The resultant material has substantial graphite domains, hierarchical porosity, and a high specific surface area (1134 m^2/g). It has exceptional performance in sodium-ion batteries (322 mAh g^{-1} @0.1 A g^{-1}) and supercapacitors (248 F g^{-1} @0.5 A g^{-1}), demonstrating its versatility across energy storage systems. Its exceptional high-rate performance is caused by a capacitance-dominated sodium storage mechanism, according to kinetics studies. This is assisted by plentiful adsorption sites offered by the high specific surface area and quick electron transfer ensured by the high graphitization degree. The strategy's low cost, easy structural control, and very straightforward process are its main features. Nevertheless, further clarification is still required about the precise chemical characteristics of defect sites and their functions in energy storage.

3.6. Zinc Salt

Research on zinc-based transition metal oxides has mostly concentrated on spinel-type compounds such as zinc ferrite ($ZnFe_2O_4$) and zinc cobalt oxide ($ZnCo_2O_4$). The impact of various zinc salt precursors ($ZnCl_2$, $Zn(NO_3)_2$, and $ZnSO_4$) on the morphology and electrochemical performance of $ZnFe_2O_4$ films via chemical bath deposition was carefully studied by Shinde et al.[44]. They discovered that samples made with $ZnCl_2$ as the precursor showed a high specific capacity of 544 mA h/g in 1 M Na_2SO_4 electrolyte, as well as a porous peanut-shaped nanosheet structure with high specific surface area and ion transport channels. With this material and a MnO_2 cathode, the hybrid supercapacitor demonstrated good cycling stability and an energy density of 55.72 Wh/kg. However, Chen et al.[45] used a solvothermal technique in conjunction with heat treatment to successfully synthesize porous $ZnCo_2O_4$ with a quasi-cubic structure. This material exhibits a high specific surface area of 83.9 m^2/g and a pore distribution dominated by mesopores. It attained a high specific capacitance of 804 F/g in 2 M KOH electrolyte, with a capacity retention rate of 79.2% after 3000 cycles. According to these findings, zinc-based oxides' structural stability and energy storage capacity can be greatly improved by creating porous nanostructures under carefully regulated synthesis conditions.

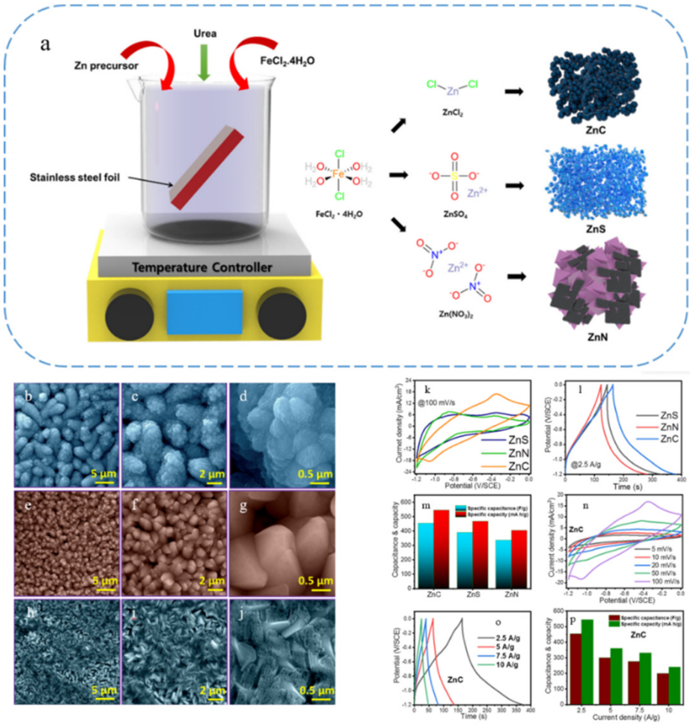

Fig 8. (a)Schematic illustration of the method for preparing zinc ferrite films on stainless steel substrates using different zinc metal precursors; SEM images of ZnC (b-d), ZnS (e-g), and ZnN (h-j) materials at three different magnifications; Electrochemical behavior of ZnC, ZnS, and ZnN electrodes in 1 M Na_2SO_4 electrolyte, including cyclic voltammetry (CV) curves (k) obtained at the same scan rate (100 mV/s) and constant current discharge (GCD) curves (l) obtained at the same current density (2.5 A/g); (m)Specific capacitance and specific capacity plots of ZnC, ZnS, and ZnN electrodes at a current density of 2.5 A/g; CV curves of the optimized ZnC electrode at different scan rates (n) and GCD curves at different current densities (o); Specific capacity of the ZnC electrode at different current densities [44]

Excellent electrochemical performance is also demonstrated by nitrogen-doped porous carbon made from zinc salts as precursors, in addition to metal oxides and pure zinc electrodes. Zinc disodium ethylenediaminetetraacetate ($EDTANa_2Zn$) was used as a multifunctional precursor by Wang et al.[46] and Yu et al.[47] to create hierarchical porous carbon materials using self-templating and self-activation techniques. Wang et al.[46] used high-temperature pyrolysis (950°C) to produce nitrogen-doped carbon with a specific surface area as high as 2160 m^2/g. This material demonstrated exceptional rate performance by maintaining a specific capacitance of 191 F/g in 6 M KOH even when the current density was increased to 300 A/g. Yu et al.[47] synthesized porous carbon with a nitrogen concentration of 6.71 at% by direct pyrolysis of $EDTANa_2Zn$ at 700°C, demonstrating a specific capacitance of 207 F/g at 100 A/g. Both investigations show that during pyrolysis, $EDTANa_2Zn$ concurrently serves as a carbon supply, nitrogen source, template agent, and activator. This greatly increases the charge storage capacity of carbon materials by enabling synergistic manipulation of pore structure and surface chemistry. Nevertheless, these techniques still struggle to achieve large-scale production, depend on high-temperature treatment, and have comparatively high process costs.

4. Conclusion and Perspectives

Because of their large specific surface area, adjustable pore structure, and effective mass and charge transport characteristics, metal-based porous electrodes have become a crucial material system for enhancing the performance of electrochemical energy devices. This work systematically analyzes research advancements in preparing porous electrodes employing conventional metal salts such as nickel, cobalt, manganese, copper, iron, and zinc as precursors. It includes a range of preparation techniques such as electrochemical deposition, hydrothermal/solvothermal procedures, in-situ gas foaming, and template-mediated assembly. Different metal-based porous electrodes show different performance advantages and research objectives. Hydrothermal/solvothermal synthesis encourages crystal growth and component incorporation under high temperature and pressure, making it suitable for synthesizing MOF-based and heterostructure electrodes; template-mediated assembly allows precise control over pore size and morphology; in situ gas foaming creates pores through precursor thermal decomposition, offering a straightforward process that improves crystallinity; and electrochemical deposition allows direct fabrication of self-supporting porous films on substrates, achieving precise control over morphology and thickness through parameter tuning, offering special benefits for integrated and flexible electrode fabrication. Even while each approach has unique qualities, they all have drawbacks like complicated processes, increased expenses, or trouble scaling up.

Although metal-based porous electrodes have been fully explored, additional deepening and expansion are still required. First, green, low-cost macro-scale manufacturing processes should be developed to promote the transition of materials from the laboratory to industrialization. Second, in order to accomplish synergistic optimization of pore distribution, pore size, and surface chemistry, it is necessary to improve the exact design and control of multilayer pore structures. This will improve the electrodes' volume energy density and power density. Additionally, developing more improved in-situ characterisation techniques would enable real-time observation of microstructural evolution and reaction kinetics during electrode operation, thereby establishing better quantitative “structure-property” connections. Through ongoing investigation in these areas, metal-based porous electrodes hold potential to play an increasingly crucial role in efficient, stable, and low-cost electrochemical energy storage and conversion systems.

Declaration of Competing Interest

The authors declare no competing financial interests.

Acknowledgments

This work was financially supported by the Undergraduate Innovation Training Program Project of Xuzhou University of Technology (No. xcx2025004).

References

[1] Ghosh S, Withanage S S, Chamlagain B, et al. Low pressure sulfurization and characterization of multilayer MoS2 for potential applications in supercapacitors[J]. Energy, 2020, 203: 117918.

[2] Zhang H, Nai J, Yu L, et al. Metal-Organic-Framework-Based Materials as Platforms for Renewable Energy and Environmental Applications[J]. Joule, 2017, 1(1): 77-107.

[3] Wenhong Wang, Min Guo, Jianling Li, et al. A study on the electrochemical behavior of the transition metal ion modified porous electrodes in vanadium redox cell system[C]//The 13th National Conference on Electrochemistry. Guangzhou, Guangdong, China, 2005: 831-832.

[4] Wang X, Feng J, Bai Y, et al. Synthesis, Properties, and Applications of Hollow Micro-/ Nanostructures [J]. Chemical Reviews, 2016, 116(18): 10983-11060.

[5] Miele E, Raj S, Baraissov Z, et al. Dynamics of Templated Assembly of Nanoparticle Filaments within Nanochannels[J]. Advanced Materials, 2017, 29(37): 1702682.

[6] He F, Chen G, Miao J, et al. Sulfur-Mediated Self-Templating Synthesis of Tapered C-PAN/g-C_3 N_4 Composite Nanotubes toward Efficient Photocatalytic H_2 Evolution[J]. ACS Energy Letters, 2016, 1(5): 969-975.

[7] Yu X, Yu L, Lou X W (David). Metal Sulfide Hollow Nanostructures for Electrochemical Energy Storage[J]. Advanced Energy Materials, 2016, 6(3): 1501333.

[8] Yu L, Wu H B, Lou X W D. Self-Templated Formation of Hollow Structures for Electrochemical Energy Applications[J]. Accounts of Chemical Research, 2017, 50(2): 293-301.

[9] Fang Y, Lindner B D, Destoop I, et al. Stereospecific Epitaxial Growth of Bilayered Porous Molecular Networks[J]. Journal of the American Chemical Society, 2020, 142(19): 8662-8671.

[10] Wang W, Yan H, Anand U, et al. Visualizing the Conversion of Metal–Organic Framework Nanoparticles into Hollow Layered Double Hydroxide Nanocages[J]. Journal of the American Chemical Society, 2021, 143(4): 1854-1862.

[11] Hedayat N, Du Y, Ilkhani H. Review on fabrication techniques for porous electrodes of solid oxide fuel cells by sacrificial template methods[J]. Renewable and Sustainable Energy Reviews, 2017, 77: 1221-1239.

[12] Kim M, Xin R, Earnshaw J, et al. MOF-derived nanoporous carbons with diverse tunable nanoarchitectures[J]. Nature Protocols, 2022, 17(12): 2990-3027.

[13] Huang J, Liu C, Jin Y, et al. Hierarchical porous carbon synthesis by carbonized polymer dots-based sacrificial template for high-performance supercapacitors[J]. Chemical Engineering Journal, 2023, 461: 141930.

[14] Meng T, Zheng L, Qin J, et al. A three-dimensional hierarchically porous Mo_2 C architecture: salt-template synthesis of a robust electrocatalyst and anode material towards the hydrogen evolution reaction and lithium storage[J]. Journal of Materials Chemistry A, 2017, 5(38): 20228-20238.

[15] Yang Y, Li L, Ruan G, et al. Hydrothermally Formed Three-Dimensional Nanoporous $Ni(OH)_2$ Thin-Film Supercapacitors[J]. ACS Nano, 2014, 8(9): 9622-9628.

[16] Xiatin Jia. Preparation of Porous Carbon Materials Modified by N/S/P Dopants for Supercapacitors and Lithium Storage [D]. Hunan Institute of Science and Technology, 2025.

[17] Wang X, Li Q, Yang N, et al. Hydrothermal synthesis of NiCo-based bimetal-organic frameworks as electrode materials for supercapacitors[J]. Journal of Solid State Chemistry, 2019, 270: 370-378.

[18] Zhang H, Li X, Hähnel A, et al. Bifunctional Heterostructure Assembly of NiFe LDH Nanosheets on NiCoP Nanowires for Highly Efficient and Stable Overall Water Splitting[J]. Advanced Functional Materials, 2018, 28(14): 1706847.

[19] Yang L, Zhang L. N-enriched porous carbon encapsulated bimetallic phosphides with hierarchical structure derived from controlled electrodepositing multilayer ZIFs for electrochemical overall water splitting[J]. Applied Catalysis B: Environmental, 2019, 259: 118053.

[20] You B, Sun Y. Hierarchically Porous Nickel Sulfide Multifunctional Superstructures[J]. Advanced Energy Materials, 2016, 6(7): 1502333.

[21] Mingyuan Gao. Structural design and supercapacitor performance of high mass loading nickel-based nanocomposites [D]. Tongji University, 2024.

[22] Jingmin Wang, Hong Bi. Synthesis and supercapacitance of cobalt nickel/porous carbon composite electrode material [J]. Electronic components and materials, 2017, 36(8): 45-49.

[23] Shunxiang Wang. Preparation of transition metal electrode materials and study on supercapacitor performance [D]. Guilin university of electronic technology, 2023.

[24] Yimin Wang. Preparation and electrochemical performance study of nickel-cobalt-based multi-metallic compound electrode materials[D]. Beijing University Of Chemical Technology, 2025.

[25] Purkait T, Dey R S. Fabrication of a membrane-less non-enzymatic glucose-air fuel cell with graphene-cobalt oxide nanocomposite anode and Fe, N-doped biomass carbon cathode[J]. Journal of Electroanalytical Chemistry, 2020, 874.

[26] Ni W, Liu S, Du C, et al. Ionic liquids as phosphorus sources for preparation of cobalt phosphide and multiple heteroatom-doped mesoporous carbon with high electrocatalytic activity toward oxygen reduction reaction[J]. International Journal of Hydrogen Energy, 2017, 42(30): 19019-19027.

[27] Wang W, Xu L, Ye R, et al. Molybdenum and Vanadium-Codoped Cobalt Carbonate Nanosheets Deposited on Nickel Foam as a High-Efficient Bifunctional Catalyst for Overall Alkaline Water Splitting[J]. Molecules, 2024, 29(15).

[28] Peng Sun, Jicai Liang, Guangyi Chen, et al. In-situ Synthesis and Properties of Porous Cobalt Sulfide Nanoneedle Bundles Arrays on Nickel Foam as Electrodes for Supercapacitors [J]. Rare Metal Materials and Engineering, 2018, 47(5): 1359-1364.

[29] Yinghui Shi. Preparation and Electrochemical Properties of Ni-Mn Based Supercapacitor Electrode Materials [D]. Dalian Jiaotong University, 2025.

[30] Siyu Jiang. Preparation and Electrochemical Properties of High Performance Manganese Based Cathode Materials for Aqueous Zinc Ion Batteries [D]. Jilin Normal University, 2025.

[31] Yang Wang. Mechanism Study of the Lithiation/Delithiation and the Structural Failure of the Porous Li-rich Mn-based Electrode for Lithium Extraction from Brine [D]. Tianjin University Of Science& technology, 2025.

[32] Zeng H, Xing B, Zhang C, et al. In Situ Synthesis of MnO2/Porous Graphitic Carbon Composites as High-Capacity Anode Materials for Lithium-Ion Batteries[J]. Energy & Fuels, 2020, 34(2): 2480-2491.

[33] Sun X, Fan Q, Yin X. Jujube Shell Based-Porous Carbon Composites Double-Doped by MnO2 and Ti3C2Tx: The Effect of Double Pseudocapacitive Doping on Electrochemical Properties[J]. Materials, 2022, 15(21).

[34] Zuo W, Yang C, Zang L, et al. One-step hydrothermal synthesis of flower-like MnO2-NixCo1-x(OH)2</ sub>@carbon felt positive electrodes with 3D open porous structure for high-performance asymmetric supercapacitors[J]. Journal of Materials Science, 2021, 56(7): 4797-4809.

[35] Zhou Y, Cheng X, Huang F, et al. Hierarchically structured electrodes for moldable supercapacitors by synergistically hybridizing vertical graphene nanosheets and MnO2[J]. Carbon, 2021, 172: 272-282.

[36] Garcia Lebiere P, Perez del Pino A, Domenech Domingo G, et al. Laser fabrication of hybrid electrodes composed of nanocarbons mixed with cerium and manganese oxides for supercapacitive energy storage[J]. Journal of Materials Chemistry A, 2021, 9(2): 1192-1206.

[37] Van H L, Han J H, Kang H W, et al. Highly porous and capacitive copper oxide nanowire/graphene hybrid carbon nanostructure for high-performance supercapacitor electrodes[J]. Composites Part B-Engineering, 2019, 178.

[38] Juni F J, Majid S R, Yusuf S N F, et al. Electrochemical characteristics of Cu/Cu2O/C composite electrode for supercapacitor application[J]. Microchemical Journal, 2021, 164.

[39] Xie J Q, Ji Y Q, Kang J H, et al. In situ growth of Cu(OH)2@FeOOH nanotube arrays on catalytically deposited Cu current collector patterns for high-performance flexible in-plane micro-sized energy storage devices[J]. Energy & Environmental Science, 2019, 12(1): 194-205.

[40] Zhang Q, Liu N N, Sun C Z, et al. Ultrasmall Iron Fluoride Nanoparticles Embedded in Graphitized Porous Carbon Derived from Fe-Based Metal Organic Frameworks as High-Performance Cathode Materials for Li Batteries[J]. Chemelectrochem, 2019, 6(8): 2189-2194.

[41] Deng X, Shi W, Zhong Y, et al. Facile Strategy to Low-Cost Synthesis of Hierarchically Porous, Active Carbon of High Graphitization for Energy Storage[J]. Acs Applied Materials & Interfaces, 2018, 10(25): 21573-21581.

[42] Baccour M, Louvain N, Alauzun J G, et al. Carbonization of polysaccharides in FeCl3/BmimCl ionic liquids: Breaking the capacity barrier of carbon negative electrodes in lithium ion batteries[J]. Journal of Power Sources, 2020, 474.

[43] Chen L, Deng J, Hong S, et al. Rapid, tunable synthesis of porous carbon xerogels with expanded graphite and their application as anodes for Li-ion batteries[J]. Journal of Colloid and Interface Science, 2020, 565: 368-377.

[44] Shinde A, Patil S J, Hwang S K, et al. Surface modified zinc ferrite as a carbon-alternative negative electrode for high-energy hybrid supercapacitor[J]. Ceramics International, 2021, 47(11): 16333-16341.

[45] Chen H, Du X, Sun J, et al. Simple preparation of ZnCo2O4 porous quasi-cubes for high performance asymmetric supercapacitors[J]. Applied Surface Science, 2020, 515.

[46] Wang L, Zhu Q, Zhao J, et al. Nitrogen-doped hierarchical porous carbon for supercapacitors with high rate performance[J]. Microporous and Mesoporous Materials, 2019, 279: 439-445.

[47] Yu S, Sun N, Hu L, et al. Self-template and self-activation synthesis of nitrogen-doped hierarchical porous carbon for supercapacitors[J]. Journal of Power Sources, 2018, 405: 132-141.