

Applications of nanomaterials in micro-supercapacitors and their performance enhancement mechanisms

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Abstract. With the development of flexible electronics and wearable devices, micro energy storage devices are subject to increasingly stringent requirements for high power output, rapid response, and long-term stable operation. Despite their advantages of rapid charge/discharge capability, high power density, and long cycling stability, Micro-Supercapacitors (MSCs) still face challenges in practical applications due to their limited energy density, sluggish ion transport, and insufficient structural stability. To address these challenges, nanomaterials can enhance MSC performance by enhancing electron transport, ion diffusion, and interfacial charge storage. Specifically, carbon materials build conductive networks and facilitate ion transport; metal oxides and conductive polymers boost charge storage via pseudocapacitive reactions; and two-dimensional materials such as MXene accelerate charge transfer and interfacial reactions due to their high conductivity and abundant active sites. This review summarizes the charge storage mechanisms and key challenges of MSCs, highlighting the performance optimization of carbon-based materials, metal oxides/conductive polymers, and MXene-based composites, and exploring the relationship between nanocomposite structure and MSC performance. The results show that nanomaterial structural and compositional optimization improves electron/ion transport and interfacial charge storage, thus leading to enhanced energy density, power performance, and cycling stability of MSCs.

Keywords: micro-supercapacitors, nanomaterials, pseudocapacitance, MXene, flexible energy storage

1. Introduction

To meet the demands of flexible electronic devices, wearable sensors, and Internet-of-Things (IoT) terminals, micro energy storage devices must provide high power output, rapid response, and long-term cycling stability [1-3]. In contrast, although conventional batteries offer relatively high energy density, their limited charge/discharge rates and cycle life hinder their ability to meet high-frequency energy demands. Micro-Supercapacitors (MSCs), owing to their fast charge/discharge capability, high power density, and long cycle life, are therefore more suitable for such applications [4-6]. However, device miniaturization reduces the loading of active electrode materials, limiting the energy density of MSCs. Meanwhile, electron transport resistance, ion diffusion efficiency, and electrode/electrolyte interface stability also impact their rate capability and cycling performance. Consequently, the design of electrode materials with efficient charge transport, high charge storage capacity, and structural stability has become a key strategy for improving MSC performance.

Importantly, nanomaterials can effectively enhance charge storage and transport processes due to their high specific surface area, abundant active sites, and tunable electron/ion transport structures [7]. Furthermore, nanocomposite structures combine the conductive, energy-storage, and structural-support properties of different components to improve the overall electrochemical performance of electrodes, mitigating the trade-offs among energy density, power density, and stability. This review highlights the applications of nanomaterials in MSCs, with emphasis on energy storage mechanisms, performance regulation, and composite structural design strategies. By summarizing recent advances in nanomaterial-based MSCs, it further elucidates the relationship between structural design and electrochemical performance.

2. Performance bottlenecks and mechanistic basis of micro-supercapacitors

2.1. Charge storage mechanisms and the essence of performance

The energy storage process of MSCs mainly occurs at the electrode/electrolyte interface, and their performance is governed by electron transport, ion diffusion, and interfacial charge storage processes. Based on differences in charge storage mechanisms, supercapacitors can be classified into three types: Electric Double-Layer Capacitors (EDLCs), pseudocapacitors, and hybrid capacitors.

Among these, electric double-layer capacitance mainly relies on the electrostatic adsorption and desorption of electrolyte ions at the electrode surface to store energy, without involving redox reactions, and therefore exhibits fast charge/discharge capability and excellent cycling stability. However, its energy storage capacity is limited by the effective interfacial adsorption area, resulting in relatively low energy density [8]. In contrast, pseudocapacitance stores charge through reversible redox reactions, ion intercalation, or surface adsorption processes at the electrode surface, providing more active sites and thereby increasing specific capacitance and energy density. However, the Faradaic reaction process may reduce the charge transfer rate and affect structural stability, thereby limiting rate capability and cycle life [9, 10]. Building on this, hybrid energy storage mechanisms combine the characteristics of electric double-layer capacitance and pseudocapacitance, achieving performance optimization through the combination of different energy storage mechanisms.

2.2. Multi-scale transport limitations and structural failure

The charge/discharge process of MSCs involves two key steps, electron transport and ion diffusion, both of which are influenced by the scale of the electrode structure. At the nanoscale, electron transport is primarily governed by the material conductivity and interfacial contact quality. At the mesoscale, ion diffusion is affected by pore size distribution, pore connectivity, and diffusion path length. Moreover, limited electron transport reduces the utilization of active sites, while unreasonable pore structures and excessively long ion diffusion pathways increase transport impedance, leading to degraded rate capability [11].

However, improving the transport process alone cannot fully guarantee the long-term stable operation of MSCs, as the continuous evolution of the electrode structure during cycling can also lead to performance degradation. In pseudocapacitive materials in particular, repeated redox reactions may induce volume changes and the accumulation of internal stress, further causing particle aggregation, structural collapse, and a reduction in active surface area. In addition, side reactions and mechanical deformation at the electrode/electrolyte interface can disrupt interfacial stability and accelerate capacity fading. Therefore, the synergistic regulation of electron/ion transport and structural stability can further enhance the overall electrochemical performance of MSCs.

2.3. Design strategies for nanocomposite materials

To overcome the limitations of poor electron transport, inefficient ion diffusion, and reduced cycling stability in MSCs, single-component materials often fail to simultaneously achieve high conductivity, large energy storage capacity, and long-term stability. Consequently, nanocomposite materials have emerged as a promising strategy for enhancing MSC performance. The key to composite design lies in utilizing the synergistic interactions between different components to achieve complementary properties through structural and interfacial engineering.

Specifically, carbon-based materials and metallic components are mainly employed to construct conductive networks and enhance electron transport, while metal oxides and conductive polymers provide additional charge storage via redox reactions, increasing the pseudocapacitive contribution. Moreover, two-dimensional nanomaterials utilize their high specific surface area and open structures to facilitate ion transport and boost electrode structural stability. Also, nanocomposite architectures can enlarge the electrode/electrolyte contact area, shorten ion diffusion pathways, and enhance active site utilization. Accordingly, by regulating material composition, interfacial structure, and nanoscale morphology, it is possible to match electron transport, ion diffusion, and charge storage processes, achieving a balance among conductivity, energy storage capacity, and cycling stability.

3. Functions of nanomaterials in MSCs and their performance enhancement mechanisms

3.1. Conductive structures and energy storage characteristics of carbon-based materials

To address the issues of limited electron transport and insufficient cycling stability in MSCs, carbon-based materials are widely used in electrode construction owing to their high conductivity, structural stability, and chemical stability. They store charge mainly via electric double-layer capacitance at the electrode/electrolyte interface, with ion adsorption/desorption enabling fast charge–discharge and stable cycling performance [12, 13].

Through the regulation of electron transport pathways and ion diffusion behavior, carbon materials with different structural types can enhance MSC performance. Among them, graphene, with its high specific surface area and excellent conductivity, provides abundant ion adsorption sites and reduces electron transport impedance, making it a commonly used carbon-based electrode material [14]. Carbon nanotubes, owing to their one-dimensional conductive structure and high aspect ratio, can construct continuous electron transport networks, improving the conductivity and structural stability of electrodes [15]. Porous carbon materials, with hierarchical pore structures composed of micropores, mesopores, and macropores, promote electrolyte wetting and ion diffusion, improving the utilization of active sites [16]. Thus, carbon-based materials primarily enhance electron transport, ion diffusion, and interfacial charge storage through the regulation of conductive networks, pore structures, and specific surface areas, thereby improving the rate capability and cycling stability of MSCs. However, the electric double-layer adsorption mechanism limits their energy density. The introduction of metal oxides and conductive polymers with pseudocapacitive characteristics provides additional charge storage through reversible Faradaic reactions, further increasing energy density and improving the balance between energy and power performance.

3.2. Pseudocapacitive mechanisms of metal oxides and conductive polymers

Unlike carbon-based materials that primarily store charge through electric double-layer capacitance, metal oxides and conductive polymers enable pseudocapacitive energy storage through fast and reversible redox reactions, resulting in higher charge storage capacity and energy density [17]. Metal oxides such as MnO_2 and NiO utilize multivalent ion redox processes to provide abundant Faradaic active sites, thus enhancing capacity and capacitance [18]. Meanwhile, conductive polymers such as Polyaniline (PANI) and Polypyrrole (PPy) achieve charge storage via reversible doping/de-doping processes while offering excellent flexibility and processability [19].

However, pseudocapacitive materials generally undergo ion intercalation/deintercalation or redox reactions during charge/discharge, which may cause volume variation, structural degradation, and active-site loss, thus resulting in decreased conductivity and cycling stability. Therefore, the balance between high energy storage capacity and long-term structural stability remains a key challenge for the application of pseudocapacitive materials in MSCs. To address this limitation, pseudocapacitive materials are often compounded with carbon-based materials, exploiting the excellent conductivity and structural stability of carbon materials to construct fast electron transport channels, while combining the high-capacity characteristics of metal oxides or conductive polymers to enhance charge storage capacity. This composite strategy can improve rate capability and cycling stability while simultaneously enhancing energy density.

3.3. Synergistic effects of two-dimensional materials and composite structures

With the increasing demand for high energy density, high power output, and long-term stability in MSCs, two-dimensional nanomaterials have attracted attention owing to their unique structural characteristics. Among them, MXene is widely used in MSC electrodes owing to its high conductivity, abundant surface functional groups, and layered structure. The layered structure enables fast electron transport, while surface active sites participate in redox reactions, allowing MXene to exhibit both electric double-layer capacitive and pseudocapacitive storage characteristics and enhancing charge storage capacity [20, 21].

However, strong van der Waals interactions between MXene layers cause sheet restacking, reducing active surface area and hindering ion diffusion and interfacial charge transport [22]. Thus, MXene-based nanocomposites with structural regulation boost electrode performance by mitigating restacking effects. For example, MXene/graphene composites form two-dimensional heterointerfaces that suppress sheet restacking and improve electron transport; MXene/carbon nanotube composites construct three-dimensional conductive networks that enhance structural stability and ion diffusion; and MXene/metal oxide or MXene/conductive polymer composites introduce additional redox-active sites, increasing pseudocapacitive contribution and charge storage capacity [23]. Consequently, MXene-based composite structures effectively optimize the electron transport, ion diffusion, and charge storage behavior of electrodes by regulating sheet arrangement, conductive networks, and active interfaces.

4. Performance factors of different material systems and composite structural design

4.1. Performance differences among different material systems

Performance variations across different material systems stem primarily from their distinct energy storage mechanisms and structural characteristics. As shown in Table 1, carbon-based materials store charge predominantly via the EDLC mechanism. While they exhibit rapid charge responses, high rate capabilities,

and excellent cycling stability, their energy density falls short due to a limited capacity for interfacial ion adsorption. Conversely, metal oxides and conductive polymers offer additional Faradaic charge storage through reversible redox reactions, which significantly enhances energy density. However, these materials are prone to structural degradation during the reaction process, leading to compromised cycling stability. In contrast, MXenes and their composites synergistically combine EDLC with surface pseudocapacitance. By providing both high electrical conductivity and abundant active sites, they achieve an optimal balance among energy density, power output, and long-term cycling stability.

Table 1. Mechanisms and performance of MSC materials

Material System	Dominant Energy Storage Mechanism	Energy Density	Power Density	Cycling Stability	Main Advantages and Limitations
Carbon-based materials	Electric Double-Layer Capacitance (EDLC); interfacial ion adsorption/desorption	Low	High	Excellent	Advantages: fast response, long cycle life Limitations: limited energy density
Metal oxides and conductive polymers	Pseudocapacitive redox reactions	High	Moderate	Weak	Advantages: high specific capacitance, high energy density Limitations: insufficient structural stability
MXene and its composites	Synergy of EDLC and surface pseudocapacitance	Moderate–High	High	Good	Advantages: balanced overall performance Limitations: sheet restacking issue

4.2. Synergistic enhancement mechanisms of nanocomposite materials

The better performance of nanocomposite materials originates from the functional complementarity between their components. Compared with single materials, composite structures combine the fast electron transport of conductive parts with the charge storage capacity of active elements, boosting charge transfer and storage inside the electrode.

In composite systems, highly conductive components such as carbon materials and MXene can serve as electron transport scaffolds, providing continuous conductive pathways for metal oxides or conductive polymers, reducing interfacial transport impedance, and improving the utilization of active materials. Meanwhile, the redox reactions introduced by metal oxides and conductive polymers can add extra charge storage, increasing the capacity of the composite electrode. By constructing hierarchical pore structures, three-dimensional conductive networks, and open interfaces, composite materials can enhance electrolyte wetting, speed up ion diffusion, shorten ion paths, and boost active site use. In addition, the composite scaffold can reduce volume changes and structural damage of active materials during cycling. Flexible carbon networks or two-dimensional supports limit the clumping and loss of active parts, maintaining electrode structure and boosting cycling stability.

4.3. Material design principles and implementation pathways

Based on these material traits and how composites improve them, designing MSC electrodes requires careful control of their parts, structures, and storage mechanisms. For high power output requirements, conductive scaffolds with high electron transport capability should be prioritized, and charge transport pathways should be

shortened by constructing composite conductive networks. For energy density enhancement requirements, components with redox activity need to be introduced, improving charge storage capacity via the synergy of electric double-layer capacitance and pseudocapacitance mechanisms.

In terms of structural design, regulating the interlayer structure, constructing heterointerfaces, and assembling multidimensional nanostructures can improve electrolyte wetting and ion transport, thereby improving the utilization of active sites. To address structural degradation during cycling, flexible carbon networks, interfacial bonding, and structural confinement can be used to mitigate the aggregation, detachment, and volume changes of active materials. Thus, the design of MSC electrodes needs to factor in material parts, interfaces, and paths to improve storage, rate, and stability.

5. Conclusion

MSCs, owing to their fast charge/discharge capability, high power density, and long cycle life, are suitable for micro energy storage scenarios such as flexible electronics, wearable devices, and IoT terminals. Carbon-based materials mainly achieve fast charge storage through the electric double-layer capacitance mechanism, while providing good electron transport and structural stability. In contrast, metal oxides and conductive polymers enhance charge storage capacity through redox reactions, while two-dimensional materials such as MXene combine high conductivity with abundant surface active sites to improve electron transport and interfacial charge storage processes. This review demonstrates that MSC performance depends not only on the intrinsic energy storage capability of the material itself, but is also jointly influenced by material structure, electron transport, ion diffusion, and interfacial stability. Accordingly, constructing conductive networks, regulating pore structures, and optimizing interfacial structures can improve the energy storage capacity, rate capability, and cycling stability of electrodes. In the future, two-dimensional materials, flexible composite structures, and multi-mechanism energy storage systems still require further optimization to meet the application requirements of MSCs in high-performance microelectronic devices.

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