Proceedings of CONF-FMCE 2026 Symposium: Smart City and Infrastructure Engineering
DOI: 10.54254/2755-2721/2026.CH37782

Recent Advances in the Preparation of Nickel Tungstate Electrode Materials for Supercapacitor Applications

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Abstract. As energy systems move toward more sustainable forms and the need for efficient energy storage increases, supercapacitors have drawn wide research interest because of their high power density, fast charge-discharge behavior, and good cycling stability. Their energy-storage performance is closely tied to the microstructure and electrochemical properties of the electrode materials. Nickel tungstate ($NiWO_4$) is a typical transition-metal tungstate with promising electrochemical properties. Because it is based on abundant resources, has relatively low cost, and shows multivalent blueox activity, it appears well suited for pseudocapacitive electrode materials. The energy-storage mechanisms of supercapacitors are discussed in this review. The main methods used to prepare $NiWO_4$-based electrode materials are also summarized, and the focus is placed on how different synthesis routes affect their morphology, electronic structure and electrochemical properties; $NiWO_4$-based electrode architectures are compared in terms of specific capacitance, rate capability, cycling stability, and energy density. Then their application prospects and the remaining challenges are considered, so a basis is provided for the rational design of high-performance tungstate-based electrode materials for advanced energy-storage applications.

Keywords: nickel tungstate, electrode material, supercapacitor

1. Introduction

As the global energy structure shifts toward green and low-carbon development, the advancement of efficient and clean energy storage technology has become a central research priority in the energy field. Fossil energy consumption has intensified the risk of resource depletion and caused severe environmental pollution, thereby accelerating the global transition toward renewable energy systems. Among various energy equipment, supercapacitors exhibit broad application prospects in smart grids, electric vehicles, and portable electronic equipment owing to their ultra-high power density, extremely fast charge and discharge speed, and excellent cycle stability. Consequently, they are regarded as one of the key technologies for promoting energy utilization [1]. Electrode materials play a decisive role in determining the performance of supercapacitors, as their microstructure and electrochemical characteristics directly influence the energy density and power output of the device. Currently, carbon materials, metal oxides, and conductive polymers constitute the principal categories of electrode materials under investigation [2]. However, carbon materials often face the problems of high preparation cost or difficult to control the structure, resulting in capacity and cycle

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DOI: 10.54254/2755-2721/2026.CH37782

life in practical applications far lower than the theoretical value. In recent years, transition metal tungstate, represented by nickel tungstate, has gradually become a hot spot in the research of pseudocapacitor electrode materials due to its advantages of abundant reserves, low cost, multivalent redox reaction and high theoretical specific capacity [3]. Nanostructured nickel tungstate electrode materials prepared by hydrothermal method exhibit excellent electrochemical energy storage potential [4]. In addition, different morphology control strategies and composite modification methods have a significant impact on the ion transport path and electronic conductivity of the material, which in turn determines its energy storage mechanism and device performance. At present, nickel tungstate-based materials have been widely used in the construction of nanoparticles, nanowires, nanosheets and heterocomposite structure [5]. Based on the above research background, this paper systematically combs the energy storage mechanism of supercapacitors, and summarizes and analyzes the preparation methods, morphology control, composite modification strategies and electrochemical properties of nickel tungstate electrode materials, aiming to provide theoretical reference for the design and application of high-performance transition metal tungstate-based energy storage materials.

2. Supercapacitor and energy storage device thereof

Supercapacitors, also referred to as electrochemical capacitors and gold capacitors, are energy-storage devices based on electric double-layer or pseudo-capacitance mechanisms. Their extremely high power density, extremely fast charge and discharge speed, and extremely long cycle life make them a key technology for integrating renewable energy into the grid.

2.1. Introduction to supercapacitors

Supercapacitor is a power-type energy storage device between capacitors and batteries. It has both the instantaneous response of capacitors and the large-capacity energy storage characteristics of batteries. It is an indispensable key in the modern high-efficiency and green energy technology system. component. Its working principle is to use physical adsorption or electrode surface chemical reaction to realize charge storage. This physics-based and chemistry-supplemented mechanism provides distinct advantages, including high power density, long cycle life, high charging and discharging efficiency, broad applicability, and high safety. Based on the energy storage mechanism, supercapacitors can be classified as electric double layer capacitors, pseudocapacitor capacitors, or hybrid capacitors that combine both characteristics [6]; According to the electrode materials employed, they can be categorized as metal oxide electrode capacitors, carbon electrode capacitors or conductive polymer capacitors. Among them, carbon-based materials dominate commercial use with high conductivity and structural designability, while composite material strategies are becoming both energy density and power density. mainstream optimization direction.

2.2. Energy storage device of supercapacitor

Supercapacitor is an efficient electrochemical energy storage device, and its charging and discharging function depends on the coordination of physical configuration and electrochemical system. The energy storage structure of the device does not present a single configuration, but a complete technical chain from micro materials to macro system integration, with obvious multi-level characteristics. At the mechanistic level, energy storage in supercapacitors primarily involves electrochemical double-layer capacitance and pseudo-capacitance. For electrochemical double-layer

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capacitance (EDLC), energy is stored through the oriented arrangement of charges at the interface between the electrodes and the electrolyte, resulting in the formation of electric double layers. This process does not involve chemical reactions, so it has extremely high charge and discharge reversibility and cycle stability, and the cycle can reach hundreds of thousands of times under actual working conditions; Pseudocapacitance effect: ts energy-storage behavior originates from the reversible redox reaction of the electrode surfactant. Compared with EDLC, it provides higher specific energy but exhibits a slightly lower cycle rate.

Supercapacitors are mainly composed of four key components: electrode material, electrolyte, diaphragm and current collector (as shown in Figure 1) [7]. Among these factors, the selection of electrode material and electrolyte directly determines the overall performance of the device [8].

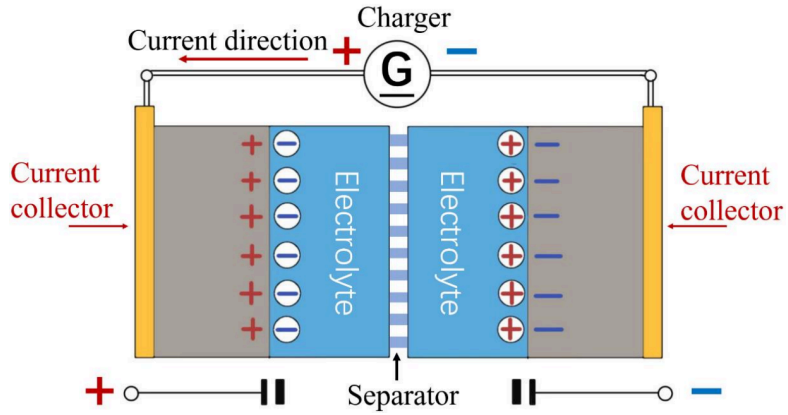


Figure 1. Diagram of supercapacitor device

3. The parts of supercapacitor device and its conduction mechanism and energy storage principle

Supercapacitor is a high-power energy storage device based on the principle of electrochemical double-layer, and its basic structure includes ionic conductor electrolyte, insulating diaphragm and high specific surface area electrode [9]. Its conduction mechanism originates from the physical separation of charges. Under an external electric field, positive and negative ions in the electrolyte migrate toward electrode surfaces of opposite polarities, while an equivalent amount of inverse charge is generated within the electrode through the compensatory flow of electrons or holes. Consequently, two charge layers with a potential difference are established at the solid–liquid two-phase interface, forming a "double electric layer" that enables physical energy storage [10]. Its energy-storage principle is described by the classical parallel plate capacitor model, in which the energy density is expressed as

$$E = \frac{1}{2} CV^2 \tag{1}$$

To increase the capacitance C, electrode materials with a high specific surface area and porous structure are commonly employed to enlarge the interfacial area between the electrode and the electrolyte [11]. Furthermore, the chemical composition of the electrolyte determines its withstand voltage performance and, consequently, the energy storage capacity of the system, enabling rapid charge and discharge while maintaining high power output [12].

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3.1. Principle of electric double layer energy storage

Double-layer energy storage is the most fundamental and widely applied mechanism in supercapacitors. It enables physical energy storage through electrostatic attraction between electrolyte ions and electrode materials with a high specific surface area. This mechanism stands out because the energy storage process is fully reversible. Storage depends only on ions adsorbing to and desorbing from the electrode surface, without any chemical reaction. When the porous electrode is immersed in the electrolyte, its surface attracts oppositely charged ions and forms a "double electric layer" at the solid–liquid interface(as shown in Figure 2). Because the separation between the positive and negative charge layers is on the nanometer scale, an extremely high capacitance can be achieved per unit area, with electrical energy stored between the oppositely charged layers in the form of an electrostatic field. At present, the research focuses on the improvement of micropore structure. Generally, biomass or polymer materials are used to prepare carbon skeletons with graded micropore structure and high porosity. This type of material enhances capacitive performance by increasing the effective specific surface area and provides transport channels for electrolyte ions through the regulation of pore size distribution and surface group types, thereby improving the energy density of the device while maintaining high power output.

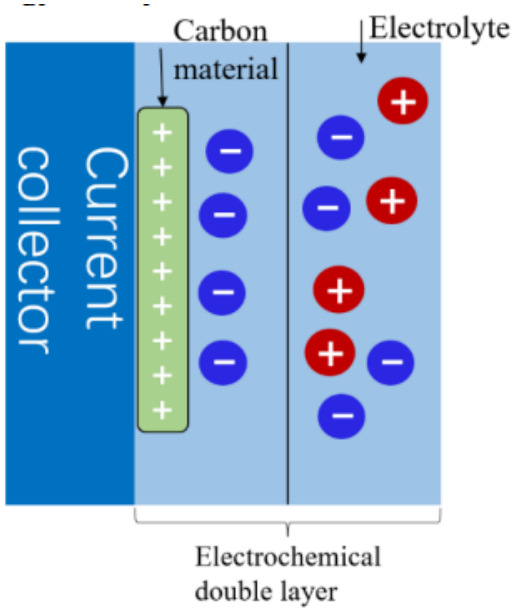


Figure 2. Schematic diagram of electric double layer energy storage

3.2. Principle of Pseudocapacitance Energy Storage

In recent years, pseudocapacitive energy storage has become a central topic in supercapacitor research. Its charge-storage mechanism lies between that of electric double-layer capacitors and secondary batteries. In contrast to the electrostatic ion adsorption and desorption involved in EDLC, pseudocapacitance stores energy through rapidly reversible redox reactions occurring on the surface of the electrode material (shown in Figure3). Typical pseudocapacitive materials include oxides and conducting polymers. In the process of charging and discharging, these materials realize the rapid storage and release of charges through electron transfer and ion intercalation and release. Compablue with carbon-based EDLCs, pseudocapacitors usually have much higher specific capacitance, often about 10 to 100 times greater. Because of this, energy density can be significantly

DOI: 10.54254/2755-2721/2026.CH37782

improved by them, and high power density is still kept. However, this process includes ion diffusion within the electrode, so the power density and cycle life are generally worse than those of a double-layer system that only relies on electrostatic interaction. Moreover, the structural degradation of some pseudo-capacitive materials under high voltage is still not solved. In recent years, research in this field has been moved to composites based on graphene or metal-organic frameworks, mainly because these materials can provide high energy density along with a longer cycle life.

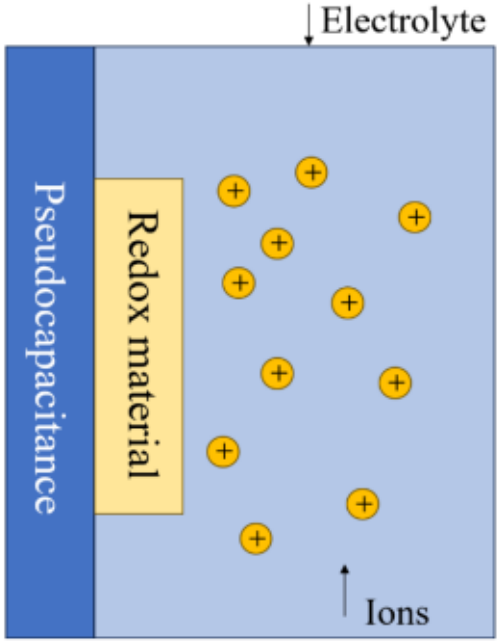


Figure 3. Schematic diagram of supercapacitor energy storage

4. Preparation method of nickel tungstate material

As an important transition metal tungstate, nickel tungstate ($NiWO_4$) has received considerable attention in supercapacitors, lithium-ion batteries, and electrocatalysis owing to its excellent conductivity, multivalent redox activity, and stable crystal structure. Because nickel tungstate has particular microstructural and functional requirements, several preparation methods have been developed, mainly around nanostructure control and composite design. At present, the preparation of nickel tungstate electrode materials mainly follows three directions. One is the controlled design of microscopic morphology, where crystal growth is adjusted to obtain nanostructures with high specific surface area and short ion transport paths. Another is multi-component composite and electrode structure design. In this approach, carbon-based materials or other metal compounds are introduced to build composite systems, which can reduce nanoparticle agglomeration and improve electronic conductivity. There is another common route. Self-supporting arrays are grown in situ on conductive substrates, so no binder or conductive agent is needed. This lowers interface resistance and can improve the utilization rate of active substances. The third direction is the regulation and modification of electronic structure. Here, blueox activity and cycle stability are improved through lattice-level electronic structure adjustment and the synergistic effect of polymetals. These three directions try to manage conductivity, structural stability and electrochemical activity at the same time, with the goal of improving the performance of nickel tungstate-based electrode materials in supercapacitors.

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Table 1. Nickel tungstate material type and preparation method

Serial number	Types of materials	Raw materials	Methods of preparation	References
1	Nickel tungstate nanomaterials	Nickel salt + tungsten source	Hydrothermal/solvothermal method, microwave-assisted hydrothermal method	[14]
2	Nickel tungstate/carbon-based composite materials	Nickel tungstate/carbon-based composite materials	In-situ growth method, co-precipitation method	[15]
3	Self-supported nickel tungstate electrodes	Nickel foam/carbon cloth + nickel salt + tungsten source	One-step hydrothermal method, two-step hydrothermal method	[16]
4	Nickel tungstate thin films	Electrolyte containing Ni^{2+} and WO_4^{2-}	Electrodeposition method	[17]
5	Metal-doped nickel tungstate	Nickel salt + tungsten source + doped metal salt (Co/Zn/Fe)	Hydrothermal/solvothermal doping method, high-temperature solid-state reaction method	[18]

DOI: 10.54254/2755-2721/2026.CH37782

Table 1. (continued)

6	Bulk nickel tungstate	Nickel oxide + tungsten oxide	High-temperature solid-state synthesis method	[19]

5. Study on the performance of nickel tungstate material used in supercapacitors

In supercapacitor research, nickel tungstate has attracted steady attention because its polyvalent blueox behavior and stable crystal structure make it a good candidate for electrode materials. Yet samples produced by different methods often differ clearly in specific capacitance, rate performance, and cycle life, and those differences largely determine their practical use and the limits that still remain. The hydrothermal method lets researchers adjust reaction time, temperature, and surfactant with reasonable flexibility, so nickel tungstate nanomaterials can be prepablue in several forms, including nanosheets, nanowires, and sea urchin-like microspheres. These structures usually have a high specific surface area, which shortens the diffusion path of electrolyte ions and helps electrochemical reactions proceed more quickly. Because of this, the material often shows better specific capacitance and rate performance, particularly under energy storage conditions that require fast charging and discharging. There is a clear weak point. Nickel tungstate has poor intrinsic electrical conductivity and limited electron transport ability. During use, its nanostructures may also agglomerate or lose their original morphology, and this often causes gradual capacity decay. For this reason, in-situ growth and co-precipitation methods have been used to build nickel tungstate/carbon-based composite electrodes by combining nickel tungstate with conductive skeletons such as graphene, carbon nanotubes, or MXene. The interconnected carbon network speeds up charge transfer,and its spatial barrier prevents the active particles from agglomerating,which improves rate performance and cycle stability. These composite materials can,to some extent,retain both energy density and cycle life,but uniform dispersion at multi-component interfaces is still difficult to achieve. Adding carbon components can also lower the electrode's compaction density and blueuce the device's volumetric energy density.Self-supporting nickel tungstate array electrodes can also be fabricated through the in-situ hydrothermal growth of nickel tungstate on nickel foam or carbon cloth substrates. This approach removes the binder and conductive agent used in the coating process, improves contact between the active materials and the current collector, blueuces interface resistance, and increases the utilization rate of active substances. This helps. Integrated electrodes of this kind have strong application potential in flexible and micro-energy-storage devices. However, the incorporation of current collectors lowers the energy density of the overall device, and the uniformity of large-area preparation still needs improvement. The electrodeposition method enables the controllable preparation of nickel tungstate films at room temperature. With precise control of film thickness and density, micro supercapacitors can better meet the needs of electrode miniaturization and integration. Even so, the film carries only a limited amount of active material, so the overall capacity stays relatively low. Element doping offers another route to improve performance at the lattice level. During preparation, metal ions such as cobalt, zinc, and iron are introduced to partially replace nickel sites. This alters the electronic structure of nickel tungstate and may produce synergistic effects among multiple metals, which then improve the reversibility of the blueox reaction and its charge storage capacity. Although this strategy improves material activity at the intrinsic level, the control of doping amount and its influence on crystal stability require systematic investigation. High-temperature solid-state synthesis is relatively simple and can be scaled up easily, but it often causes particle sintering and produces irregular particle shapes. As a result, these materials usually show poorer electrochemical performance than nanomaterials

DOI: 10.54254/2755-2721/2026.CH37782

prepablue by wet chemical methods; Therefore, this approach is more commonly used for fundamental comparative studies. Overall, nickel tungstate electrode materials prepared through different routes exhibit distinct advantages and limitations. Future work should focus on three issues: improving conductivity, designing multi-component interfaces more deliberately, and developing scalable preparation processes so these materials can be used more effectively in practical supercapacitor applications. The details are shown in Table 2.

Table 2. Properties of nickel tungstate used in supercapacitors

Serial number	Category of materials	Specific surface area (m^2/g)	Specific capacitance (F/g)	Power density (W/kg)	Energy density (Wh/kg)	Cycle stability (%)	References
1	Nickel tungstate nanomaterials	80-200	400-800	4000-6000	25-45	85-92	[20]
2	Nickel tungstate/carbon matrix composites	120-300	600-1200	5000-8000	35-60	90-96	[21,22]
3	nickel tungstate self-supporting array electrodes	100-250	500-1000	4500-7000	30-50	88-94	[23]
4	nickel tungstate film	60-120	60-120	3000-5000	15-30	85-90	[24]
5	Metal-doped nickel tungstate	90-180	500-1000	4500-7000	30-55	90-95	[25]
6	Bulk nickel tungstate (solid phase method)	10-40	10-40	2000-4000	10-20	75-85	[26]

6. Conclusion

Nickel tungstate has emerged as a research hotspot in pseudocapacitor electrode materials owing to its high-valence redox properties, high specific capacity, and abundant resources. Hydrothermal/solvothermal methods, in-situ growth, electrodeposition, and element doping can all be used to build different electrode architectures, including nano-powders, carbon-based composites, and self-supporting arrays. Current studies suggest that carbon-based composites and self-supporting arrays perform better in raising energy density and extending service life. Even so, some problems remain. Materials often still show limited intrinsic conductivity, nanostructures tend to lose stability during cycling, and the construction of multi-component interfaces is not yet controlled well enough.Defect engineering and ion doping technology should be used in further work to adjust the electronic structure and make the conductivity better. At the same time, when in-situ characterization is combined with theoretical calculation, it may help to make clear the reaction kinetics and the way that the structure evolves during energy storage. Furthermore, developing green and low-cost large-scale synthesis processes is a necessary thing, because it can promote the practical application of high-performance electrode materials in flexible, wearable, and miniature energy storage devices. A theoretical reference for designing high-performance nickel tungstate energy storage materials is provided by the systematic review and analysis in this paper. And core research directions are clarified, including making conductivity better, making structural stability stronger and large-scale

DOI: 10.54254/2755-2721/2026.CH37782

preparation. Also, data support and a theoretical basis are given for further study of methods such as defect engineering, in-situ characterization, and green synthesis.

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