Review Article

Nanostructured and nanocomposite Tungsten Oxide electrodes for electrochemical energy storage: A Short Review

M. Gowtham [a,*], N. Senthil Kumar [a], Chandrasekar Sivakumar [b], K. Mohanraj [c]

[a] Department of Physics, Kongunadu Arts and Science College, Coimbatore-641029, Tamil Nadu, India.
[b] Department of Physics, National Chung Hsing University, Taichung 40227, Taiwan.
[c] Department of Environmental Engineering and Management, Chaoyang University, of Technology, Taichung 41349, Taiwan
*Corresponding author Email: gowthampsix@gmail.com

Abstract: The stable and efficient supercapacitor investigation synthesized tungsten-based oxides using many approaches. The impact of the tungsten precursor on the product was significant in this research, and the most important consequences are highlighted. Supercapacitors and other energy storage devices have been using tungstate metal oxide because of its high electrical conductivity as well as low manufacturing costs. This article is mostly about how tungsten oxide-based electrodes for supercapacitors (SCs) and batteries have changed in recent years. Electrodes for energy storage devices made of nanostructured materials can benefit from a variety of features, including high surface-to-volume ratios, excellent charge transport capabilities, as well as excellent physical-chemical properties. Nanostructures and nanocomposites for supercapacitors and storage applications will be summarized in this paper.

1. Introduction

The nanoparticles are small particles that range People are becoming more aware of renewable energy sources as the world's population grows and energy demand increases. Energy storage is needed because of the inability to control or predict the nature of these sources. Devices that use electrochemical materials, electrolytes, and electrodes can store or change energy [1]. Tungsten oxide (WO_3) has stimulated researchers' interest because it is an n-type wide bandgap semiconductor. 2.65 to 3.05 eV is the range of its electronic bandgap. Orthorhombic, cubic, triclinic, monoclinic, tetragonal, hexagonal, and orthorhombic WO_3 structures have been reported. It could be used in optical and electrical applications because it has a high melting point, is photo-electrochemical, is hard, and has good mechanical properties [2]. When compared to sulphides, selenides, or halides, metal oxides appear to be especially attractive due to their lower molecular weight and/or toxicity. The dominance of metal oxide-based cathodes in the primary and secondary battery markets confirms their importance [3]. Metal oxides in various forms are common in tungsten due to its transitional nature and the fact that Oxidation states 2, 3, 4, 5, and 6 are all possible. The most widely used form of tungsten oxide

is the nanostructure of WO_3, a polymorphous compound with trioxide that occurs when W^{6+} is fully oxidised. According to what has been said so far, the unique nanostructure of tungsten trioxide has influenced the scientists and engineers who use this material in a variety of ways. There are numerous tungsten oxides and their corresponding hydrates, which can be identified by the formula WO_3nH_2O, where the n is an integer [4]. Supercapacitors have gotten a lot of attention in the field of energy storage because they can be charged and drained quickly, have a high-power density, stay stable over time, and could be used safely [5, 6]. Compared to rechargeable batteries, supercapacitors have faster charge-discharge properties and greater energy storage capacity [7–10]. Because of their high tensile strain resistance, supercapacitors are also better for flexible and wearable electronic devices. On the other hand, supercapacitors are more suitable for flexible and wearable electronic devices because of their high tensile strain tolerance [11, 12]. Supercapacitors have several advantages over batteries, but their lower energy density limits their use in portable electronic devices. This means that new nanomaterials with better performance that have been changed chemically at the nanoscale level are needed. When making

electrodes for energy storage devices, it is essential to consider the cost and safety of these nanomaterials. tungsten oxide (WO_3)-based composite materials for energy storage applications such as SCs and Li-ion batteries are reviewed in this article. The stoichiometric and non-stoichiometric crystal structures of tungsten oxide are briefly discussed. WO_3 nanostructured electrodes and their electrochemical performance are thoroughly summarised for various fabrication methods.

2　Overview of Tungsten Oxide compounds

2.1　Crystal structure of Tungsten Oxide

Due to the fact that WO_3 has a wide range of crystal structures, such as monoclinic, tetragonal, orthorhombic, cubic, and hexagonal stoichiometric WO_3 as well as non-stoichiometric WO_3 [2], it is a very complex material. Thermal treatment also has an effect on the structural properties of the WO_3 compounds prepared by various methods. In the past few years, researchers have paid a lot of attention to sub stoichiometric phase transitions and structural changes in WO_3. This has led to a greater focus on finding uses for the material.

2.2　Stoichiometric Tungsten Oxide

At various temperatures, the stoichiometric WO_3 exhibits various structural polymorphs and phase transitions. A cubic perovskite-like (ReO_3) structure is the ideal WO_3 crystal structure. Distortion of the cubic ReO_3 structure creates the various WO_3 polymorphs [13–14]. WO_6 octahedra share their corner faces, resulting in a three-dimensional network of hexagons, and their arrangement results in a simple cubic symmetry. This structure is formed by an oxygen-encircled cation. It has an eight-sided shape, and its centre is made up entirely of tungsten, with four corners made up entirely of oxygen [15]. Alternating the placement of O and WO_2 planes helps to form the network of crystals. The symmetry of the WO_3 structure is lower than that of the ideal ReO_3 structure because of the tilting of the WO_6 octahedra and the translation of the W atom from the centre of the octahedra. Different crystal structures of WO_3 are also affected by temperature.

In each unit cell, tungsten atoms are separated by 0.375 nm, making WO_3 monoclinic crystals an octahedral WO_6 structure [16]. When heated to a higher annealing temperature, monoclinic WO_3 crystallises (orthorhombic and tetragonal). However, when it returns to room temperature, it cannot return to these alternate states. As the W–O bond displacement decreases along the (001) direction during the change from the monoclinic to the orthorhombic phase, it is possible that the W atoms can be moved by tilting the WO_6 octahedra. There have been previous reports that WO_3 can undergo a minimum of eight phase transitions between 0 and 1200 K. At lower temperatures, there are two most common transformations of WO_3: triclinic and monoclinic. The physico-chemical properties of these two phases are distinct and thermodynamically stable.

A pseudocubic ReO_3 structure with corner-sharing distorted WO_6 octahedra can be seen in the atomic arrangement of triclinic WO_3. Tilting octahedra are skewed toward each other as a result of the three coordination axes acting on one of the tilting components. There are two W atoms that are off-center in the O octahedron. In the end, there are three short separations and three long separations between the W–O bond. In WO_6 octahedra, the main ionic bond is displayed for long bonds while the equilibrium bond distance significantly alters the properties of the W–O bond. The sum of the ionic radii (W^{6+} = 0.64, O^{2+} = 1.40 Å) determines the W–O bond distance.

The hexagonal phase WO_3 (h-WO_3) has also been observed and is a stable phase. The hexagonal phase isn't formed during structural transformation, which is surprising. An aqueous medium must be present for the dehydration of tungsten oxide hydrate to produce the hexagonal phase [17]. The first synthesis of hWO_3 was reported by Gerand et al. in 1979. There are two metastable states of WO_3, one of them being h-WO_3. Electrochemical applications benefit most from h-WO_3 and its various crystal structures of WO_3 [18-19]. Octahedra with three to six members share corner oxygen in the (001) plane when they are arranged in a ring. The W–O framework made by these WO_6 octahedra that share a corner has three different kinds of tunnels: triangular and hexagonal holes in the ab plane, and square windows along the c axis. During electrochemical processes, a large number of cations can be accommodated in these tunnels.

2.3　Non-stoichiometric Tungsten Oxide

Glemser and Sauer were the first to report on non-stoichiometric tungsten oxide, claiming that oxygen vacancies can transform a pure WO_3 phase structure into $WO_{2.9}$ [20]. $W_{32}O_{84}$ and W_3O_8 have orthorhombic crystal structures; $W_{18}O_{49}$, $W_{17}O_{47}$,

$W_{20}O_{58}$, and $W_{25}O_{73}$ have monoclinic crystal structures; and W_5O_{14} has tetragonal crystal structures. The Magneli phases are formed when monoclinic WO_3 is reduced. As the number of oxygen vacancies increases, octahedra in the crystal structure shift from corner-sharing to edge-sharing positions, which are split by shear planes [21]. They also form pentagonal columns and hexagonal tunnels because the WO_6 octahedra with channels share an edge. W^{5+} species are reduced in the lattice structure of WO_x, which maintains substantial oxygen deficiency. With increasing suboxide non-stoichiometry, they become even more metallic. Oxygen vacancies change everything about the tungsten oxide lattice, including the position of the Fermi level and the size of the energy gap. The Magneli phases are made up of WO_7 pentagonal bipyramids surrounded by WO_6 octahedron corners [22]. The electrical conductivity and crystal structure of tungsten oxides with slightly different stoichiometry are altered by non-stoichiometry. These factors make non-stoichiometric WO_{3-x} an attractive energy storage material. The oxygen vacancies on the surface of WO_{3-x} cause a strong adsorption affinity for electrolyte ions, ii) the high electrical conductivity of WO_{3-x} is due to the free surface electrons offered by the oxygen vacancies, and iii) oxygen vacancies significantly reduce the material's band gap [23-25].

3 Importance of Tungsten Oxide-based materials in electrochemical energy storage

Consumer electronics, hybrid electric vehicles, and memory storage systems have all made significant strides forward in the last two years, increasing the demand for energy storage devices.

Table 1. Tungsten Oxide comparison of synthesis, electrode substrate, specific capacitance value, and electrolyte

Material	Synthesis method	Electrode coating substrate	Specific capacitance value	Electrolyte	Reference
WO_3	Hydrothermal method	carbon cloth	391 F g^{-1}	H_2SO_4	31
WO_3	Hydrothermal method	Cu foil	436 F g^{-1}	Na_2SO_4	32
WO_3	Hydrothermal method	carbon cloth	538 F g^{-1}	H_2SO_4	33
WO_3	Precipitate and calcination	carbon cloth	148 F g^{-1}	H_2SO_4	34
WO_3	Hydrothermal method	carbon cloth	605.5 F g^{-1}	H_2SO_4	35
WO_3	Hydrothermal method	carbon cloth	474 F g^{-1}	H_2SO_4	36
WO_3	Precipitation	lithium foil	1054 mA h g^{-1}	1M LiPF$_6$/EC: DMC	37
WO_3	Hydrothermal and annealing process	lithium metal	749 mA h g^{-1}	1 M LiPF$_6$ /EC: DEC: DMC	38
WO_3	Solvothermal method	Lithium metal foil	1700 mA h g^{-1}	1M LiPF$_6$/EC: DMC	39
WO_3	Hydrothermal method	Nickel foam	218 mA h g^{-1}	1 M LiPF$_6$	40

On the other hand, as non-renewable energy sources like fossil fuels are depleted due to human use and environmental consequences, scientists are scrambling to find alternatives and environmentally friendly materials for energy storage. Compared to other common electrode materials, tungsten oxides are an important class of transition metal oxides with high specific capacities and electrical conductivity values [26].

In addition to the aforementioned methods, hydrothermal synthesis of WO_3 is also frequently employed. The closed system's chemical reaction is aided by the use of high temperatures and pressures in this method. Different WO_3 morphologies, including nanorods, nanowires, nanoflowers, and nanoparticles, have been obtained using the hydrothermal method in previous studies. Consider the work of Xu et al. At a current density of 0.5 A g^{-1}, the WO_3 microspheres had a specific capacitance of 797.05 F g^{-1} and excellent cycling stability. When combined with the WO_3 microspheres, the intertwined nanofibers provided an enormous effective surface for electrolyte access and quick electrochemical reactions, resulting in improved SC performance, as demonstrated by the authors. Another example of the morphological dependence of WO_3's electrochemical performance was presented by Shinde et al. [27]. In comparison to WO_3 nanoplates and nanogranules, WO_3 nanorods had an electrochemical performance of 694 F g^{-1}. These results are due in large part to the nanorod-like structure of WO_3, which facilitates charge transportation and provides an easy path for electrolyte ions to travel. WO_3 metastable hexagonal phase formation could only be achieved using the hydrothermal technique [28]. As Wu et al. reported, hydrothermal nanotube bundles of WO_3 were also created. As an anode material, WO_3 nanotube bundles provided an aerial capacitance of 2575 mF/cm^2 and an acyclic stability of 85.1 percent over 6000 cycles at a current density of 3 mA/cm^2 and a specific capacitance of 615.7 F/g^1. It has been found that WO_3 with a crystal structure has a volumetric capacitance of 66.7 C g^1. The hydrothermal synthesis of hierarchical WO_3 nanofibers was reported by Yao et al. [29].

The as-prepared electrode had a capacitance of 1716.92 mF cm^{-2} and good cycling stability (20.9 percent capacitance decrease over 6000 cycles) at a scan rate of 2 mA cm^{-2} [30] presented an easy hydrothermal method for the preparation of WO_3 nanorods, nanoplates, and 3D microspheres, among others. Investigations were made into how the morphology affected electrochemical performance. At the scan rate of 10 millivolts per second (mV/s), microspheres, with their 536.72 specific capacitance and 751.40 mF cm^{-2} areaal capacitance, outperformed the WO_3 nanorods and nanoplates, respectively, in terms of specific capacitance and areaal capacitance. The microspheres' cyclic stability was 92.3 percent over 2000 cycles. Table 1 shows that Tungsten Oxide comparison of synthesis, electrode substrate, specific capacitance value, and electrolyte.

4. Conclusion

The stoichiometric and non-stoichiometric crystal structures of tungsten oxide were thoroughly covered in this review. Future approaches to fabricating WO_3-based materials and hybrid composites, as well as the most recent developments in this field, were discussed. Tungsten oxide-based materials have shown promising electrochemical performance and energy storage applications in supercapacitors and batteries, and we anticipate further progress in this area. There are many obstacles to WO_3's further development, even though it has been used as a superior anode for energy storage devices. Finally, energy storage systems relying on SCs and batteries are expected to meet society's energy needs and overcome environmental concerns raised by fossil fuel use in the near future. Recent improvements to WO_3 and electrodes made from their composites have made it possible to make and sell great energy storage devices that don't harm the environment, work safely, and store a lot of energy and power.

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