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

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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 tungstet 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.

Keywords: WO₃, Supercapacitor, Nanocomposite, Nanostructure, Electrochemical energy storage

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 (WO₃) 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 WO₃ structures have been reported. It could be used in optical and electrical applications because it has a high melting point, is photoelectrochemical, 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 WO₃, a polymorphous compound with trioxide that occurs when W⁶⁺ 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 WO₃·nH₂O, 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$^{2+} = 1.40 \text{ Å}$) 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$_{12}$O$_{64}$ and W$_2$O$_8$ have orthorhombic crystal structures; W$_{18}$O$_{46}$, W$_{17}$O$_{47}$,
W$_{20}$O$_{59}$ and W$_{25}$O$_{73}$ have monoclinic crystal structures; and W$_5$O$_{14}$ has tetragonal crystal structures. The Magnéli 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 Magnéli 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>
<thead>
<tr>
<th>Material</th>
<th>Synthesis method</th>
<th>Electrode coating substrate</th>
<th>Specific capacitance value</th>
<th>Electrolyte</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO$_3$</td>
<td>Hydrothermal method</td>
<td>carbon cloth</td>
<td>391 F g$^{-1}$</td>
<td>H$_2$SO$_4$</td>
<td>31</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>Hydrothermal method</td>
<td>Cu foil</td>
<td>436 F g$^{-1}$</td>
<td>Na$_2$SO$_4$</td>
<td>32</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>Hydrothermal method</td>
<td>carbon cloth</td>
<td>538 F g$^{-1}$</td>
<td>H$_2$SO$_4$</td>
<td>33</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>Precipitate and calcination</td>
<td>carbon cloth</td>
<td>148 F g$^{-1}$</td>
<td>H$_2$SO$_4$</td>
<td>34</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>Hydrothermal method</td>
<td>carbon cloth</td>
<td>605.5 F g$^{-1}$</td>
<td>H$_2$SO$_4$</td>
<td>35</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>Hydrothermal method</td>
<td>carbon cloth</td>
<td>474 F g$^{-1}$</td>
<td>H$_2$SO$_4$</td>
<td>36</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>Precipitation</td>
<td>lithium foil</td>
<td>1054 mA h g$^{-1}$</td>
<td>1M LiPF$_6$/EC: DMC</td>
<td>37</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>Hydrothermal and annealing process</td>
<td>lithium metal</td>
<td>749 mA h g$^{-1}$</td>
<td>1 M LiPF$_6$/EC: DEC: DMC</td>
<td>38</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>Solvothermal method</td>
<td>Lithium metal foil</td>
<td>1700 mA h g$^{-1}$</td>
<td>1 M LiPF$_6$/EC: DMC</td>
<td>39</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>Hydrothermal method</td>
<td>Nickel foam</td>
<td>218 mA h g$^{-1}$</td>
<td>1 M LiPF$_6$</td>
<td>40</td>
</tr>
</tbody>
</table>
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 WO₃ is also frequently employed. The closed system’s chemical reaction is aided by the use of high temperatures and pressures in this method. Different WO₃ 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 WO₃ microspheres had a specific capacitance of 797.05 F g⁻¹ and excellent cycling stability. When combined with the WO₃ 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 WO₃’s electrochemical performance was presented by Shinde et al. [27]. In comparison to WO₃ nanoplates and nanogranaules, WO₃ nanorods had an electrochemical performance of 694 F g⁻¹. These results are due in large part to the nanorod-like structure of WO₃, which facilitates charge transportation and provides an easy path for electrolyte ions to travel. WO₃ metastable hexagonal phase formation could only be achieved using the hydrothermal technique [28]. As Wu et al. reported, hydrothermal nanotube bundles of WO₃ were also created. As an anode material, WO₃ nanotube bundles provided an aerial capacitance of 2575 mF/cm² and an acyclic stability of 85.1 percent over 6000 cycles at a current density of 3 mA/cm² and a specific capacitance of 615.7 F/g. It has been found that WO₃ with a crystal structure has a volumetric capacitance of 66.7 C g⁻¹. The hydrothermal synthesis of hierarchical WO₃ 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 WO₃ 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 WO₃ 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 WO₃-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 WO₃’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 WO₃ 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.

References


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All the Authors equally contributed to this work.

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