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# Electron and Ion Transport of Tin Dioxide in Secondary Batteries: Enhancement Approaches, Mechanisms, and Performance

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Secondary batteries have been important across several aspects of daily life and industrial manufacture. The electron and ion transport of electrodes significantly affects the energy-storage performance of batteries. Among many fascinating materials, transition metal oxides have been considered promising as candidate electrode materials of high-performance batteries owing to their high theoretical capacity and good stability. Herein, tin dioxide is chosen as a representative transition metal oxide to show the specific electron and ion transport in some types of secondary batteries including lithium-ion, lithium-sulfur, potassium-ion batteries, etc. The way to optimize the structure and the strategies to enhance electron and ion transport have been summarized. Recently, tin dioxide doping and the preparation of tin dioxide-based composites have been reported. In addition, the main challenges and possible prospects are also proposed, which provide important suggestions for researchers to develop high-performance energy-storage materials and to explore new physical science.

**Keywords: electron transfer, ion diffusion, transition metal oxide, composite, doping**

## INTRODUCTION

Depending on the rapid development of modern society, the production of clean, renewable energy has become an important direction [1–3] that is necessary to the development of energy storage systems. Secondary batteries have been considered the best choice. In the past few decades, apart from lithium-ion (Li-ion) batteries, some new types of batteries, such as lithium-sulfur (Li-S), sodium (Na)-ion, and potassium (K)-ion batteries, have been developed [4–7]. The energy-storage performance relies on the property of the electrode materials, and this is especially relevant when it comes to large theoretical capacity and good stability.

As a transition metal oxide, tin oxide ($SnO_2$) has a high theoretical capacity, good safety, and a low cost of production, which has attracted much attention [8–11]. However, $SnO_2$, as a semiconductor, has poor conductivity and ion diffusivity, which highly restricts its electrochemical performance [12, 13]. After many cycles, the electrode structure changes greatly, which results in capacity decay [14, 15]. It is important to improve the electron and ion transport of the $SnO_2$ electrodes, which is mainly achieved by constructing composites and doping [16–18]. In this

review, we focus on the main strategies to improve the electron transfer and ion diffusion of $SnO_2$ in batteries, which will be important for the broad researchers who are working on energy storage and related physical sciences.

## CHALLENGES FOR ELECTRON AND ION TRANSPORT

Even though $SnO_2$ has been widely studied for secondary batteries, it has several disadvantages that restrict its electrochemical performance and practical applications, such as low electronic conductivity and the poor ability of ion transport. For example, the conductivity of $SnO_2$ at room temperature reported by Park et al. was only $1.242 \times 10^{-8}$ S $cm^{-1}$ [12]. In addition, Xie et al. reported that the Li-ion diffusion coefficient of amorphous $SnO_2$ thin film was $10^{-15}$-$10^{-13}$ $cm^2$ $s^{-1}$ [13]. It greatly limits the overall capacity and rate-performance of $SnO_2$-based secondary batteries. Moreover, the $SnO_2$ exhibits a large volume change during the lithiation–delithiation, which makes the electrode gradually pulverize, resulting in a rapid capacity decay.

Recently, it was reported the physical properties of $SnO_2$ can be adjusted by controlling the morphology [2]. Many researchers have selectively focused on the adjustment of the morphology of nanostructured $SnO_2$ in secondary battery systems. It was reported the conductivity of a single $SnO_2$ nanowire was 0.1–0.9 S $cm^{-1}$[19]. Park et al. employed $SnO_2$ nanowires as anode materials for Li-ion batteries and compared the electrochemical performance with $SnO_2$ powders. $SnO_2$ nanowires showed a high lithium-storage performance [20]. The improvement of the electrochemical performance of $SnO_2$ nanowires was ascribed to the large surface area. Yin et al. indicated the electrochemical performance of $SnO_2$ nanosheets for Li-ion batteries was improved because the nanostructure increased the surface area, enhanced the structural stability, and shortened the diffusion distance of ions and electrons [21].

Compared to some morphologies such as 1D nanowires [22, 23], nanorods [24, 25], nanotubes [26], and two-dimensional (2D) nanosheets [27, 28], three-dimensional (3D) porous structures provide sufficient voids to buffer volume expansion. Since then, it has attracted great attention [29]. In 2017, Li et al. prepared a dumbbell hollow porous $SnO_2$ anode for a Li-ion battery, and it exhibited a high capacity [10]. There were nanopores in the porous shell, which promoted electrolyte transport and Li-ion diffusion; and the hollow porous structure provided space for buffer volume expansion. Zhang et al. prepared uniform multi-shell $SnO_2$ hollow microspheres through a continuous hard template method, which was used as the anode of the Li-ion battery [30]. Each shell of the multi-shell hollow structure could form parallel resistance to improve the conductivity.

Nanostructured $SnO_2$ can not only improve the electronic conductivity but also shorten the Li-ion diffusion pathway by improving the electrode–electrolyte interface properties [3, 31]. However, the electrochemical performance of the nanostructured $SnO_2$ hinders the application in large-scale secondary batteries. In some studies, it was found that surface coating and elemental doping improved the performance [3, 9, 32]. Researchers have developed several strategies to improve the electron and ion transport of $SnO_2$ to enhance the energy-storage performance, and these have potential for large-scale application.

## ELECTRON AND ION TRANSPORT OF $SnO_2$ COMPOSITES

### $SnO_2$@C Composites in Li-Ion Batteries

Carbonaceous materials have good electrical conductivity, exhibiting a synergistic effect with $SnO_2$ to improve the overall electronic conductivity [33]. Guo et al. prepared porous carbon-coated $SnO_2$ nanoparticles ($SnO_2$@PC) by using glucose as the carbon source [34]. Porous carbon provided a fast electron/ion transport pathway, which prevents the crushing and aggregation of $SnO_2$ nanoparticles and promotes the formation of stable solid electrolyte interface (SEI) films. Moreover, the highly specific surface area provided more active centers for Li storage and promoted ion/electron transport. When the carbon content was 14.1%, the discharge capacity was 1130.1 mAh $g^{-1}$ after 100 cycles at 0.2 A $g^{-1}$.

Since graphene was discovered by Andre and Konstantin Novoselov in 2004, it has attracted wide attention in many fields. Owing to its excellent mechanical properties and electrical conductivity, graphene has been used for energy storage [35]. Many studies have focused on combining graphene with a transition metal oxide like $SnO_2$. Chen et al. reported a $SnO_2$/graphene composite, which was beneficial to improve the electrochemical performance [36]. The green approach to prepare the $SnO_2$/graphene composites directly anchored $SnO_2$ nanoparticles on graphene nanosheets via Sn-O-C bonds. The prepared $SnO_2$/graphene composite exhibited a capacity of 1420 mAh $g^{-1}$ at 0.1 A $g^{-1}$ after 90 cycles and good cycling retention of 97% at 1 A $g^{-1}$ after 230 cycles.

Some investigations have indicated that the composites of $SnO_2$ with carbon materials often suffered from material loss during long-term cycles, which leads to the increase of resistance and the rapid decay of electrochemical performance. Therefore, researchers have prepared some multi-dimensional materials with a topological structure. A double-carbon confinement strategy was presented by Wu et al. to prepare double-carbon to confine $SnO_2$ hollow nanospheres (denoted as G@C@$SnO_2$), as shown in **Figure 1** [33]. The G@C@$SnO_2$ showed a highly reversible performance in Li-ion batteries. The enhancement was ascribed to the following advantages: (i) a 3D structure based on graphene increased the conductivity, avoided the aggregation of nanoparticles, and provided an open framework for the transmission of electrons and ions; (ii) hollow $SnO_2$ nanospheres shortened ion diffusion distance and buffered volume change; and (iii) a nitrogen-doped carbon shell can further accommodate volume change, ensuring structural integrity and improved conductivity.

### $SnO_2$@C Composites in Li-S Batteries

Li-S battery is considered an excellent candidate for energy-storage systems because of its high energy density. However, the sulfur cathode has the problem of low conductivity ($5 \times 10^{-30}$ S

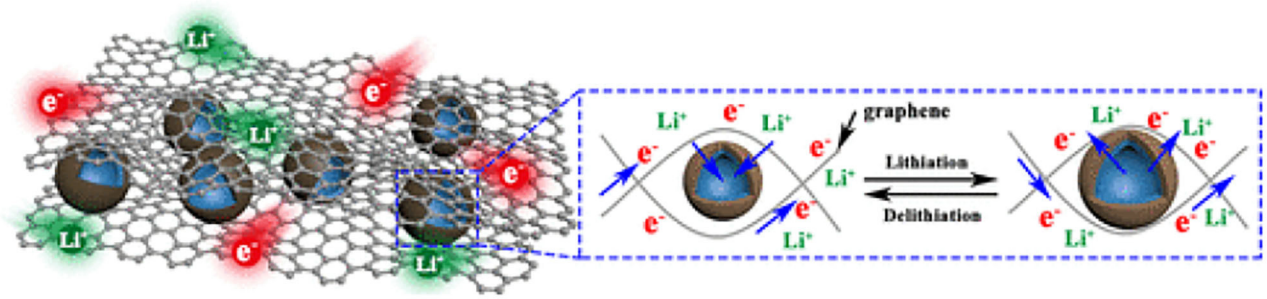


**FIGURE 1 |** Illustration of the reversible Li-ion storage in G@C@$SnO_2$. Reproduced from Wu et al. [33].

$cm^{-1}$) and the huge volume-change during cycling, resulting in a rapid capacity decay [7, 37]. In addition, polysulfide is easily soluble in electrolytes, leading to a shuttle effect [38]. Surface modification of sulfur cathodes and coating with conductive materials are common strategies to solve the problems [39]. Liu's group prepared a ternary composite of S/C@$SnO_2$, which could improve the conductivity of sulfur, adapt to the volume-change, and adsorb polysulfide [40]. Porous carbon could improve the conductivity, and the porous structure reserved space for the volume change of sulfur. In addition, the $SnO_2$ shell improved the mechanical strength of the whole structure, displayed strong adsorption toward polysulfide, and further reduced the shuttle effect.

Moreover, $SnO_2$/carbon composites, as functional interlayer materials used in Li-S batteries, weaken the shuttle effect by chemical adsorption. In the meantime, carbon materials in $SnO_2$/carbon composite can improve the overall conductivity of the composite. Hu et al. prepared a $SnO_2$/reduced graphene oxide (rGO) composite as dual-function interlayer cathode material for Li-S batteries [41]. The close interaction between rGO and $SnO_2$ nanoparticles not only reduced the resistance of the sulfur cathode but also averted the deformation of the electrode.

## $SnO_2$@TMO Composites in Secondary Batteries

Typical transition metal oxides (TMOs), including $SnO_2$, $TiO_2$, $MoO_2$, $Co_3O_4$, $V_2O_5$, NiO, CuO, ZnO, and $Fe_2O_3$, etc., commonly possess a high capacity compared to the graphite anode in Li-ion batteries [42, 43]. Researchers found that TMO composites are beneficial to the improvement of cycle stability, and they are attributed to the synergistic effect [44–46]. Recently, many studies have been conducted in developing composites of $SnO_2$ and TMOs. $SnO_2$@TMO composites are often used as anodes of Li-ion batteries, and they show good electrochemical performances. For example, $SnO_2$ is n-typed semiconductor with a wide band gap (3.6 eV), while α-$Fe_2O_3$ is a p-type semiconductor with a narrow band gap (2.2 eV). Electron transfer from the conduction band of $SnO_2$ to the conduction band of α-$Fe_2O_3$, crosses the heterojunction interface, and finally their Fermi levels reach an equilibrium. **Figure 2** schematically shows the energy band of lithium storage of a $SnO_2$/α-$Fe_2O_3$ heterostructure. The synergistic effect of $SnO_2$ and α-$Fe_2O_3$ effectively improved the conductivity, and the diffusion rate of lithium ion thus improved the rate performance of the battery [47].

$SnO_2$@TMO has been used in many secondary batteries, such as Li-ion and Li-S batteries, exhibiting good performance. Liu et al. indicated that the low conductivity of pure sulfur and shuttle effect seriously hindered the commercial development of Li-S batteries [48]. The results showed the resistance of the S@$SnO_2$@$MnO_2$ composite was $6.4 \times 10^7\ \Omega$, which was one order of magnitude lower than pure sulfur ($5.8 \times 10^8\ \Omega$). According to the first-principal calculation, $SnO_2$ and $MnO_2$ had a compact band gap structure and a good density of states (DOS), which are helpful to the reduction of the electron transfer barrier. It was indicated that $SnO_2$ and $MnO_2$ improve the electrical conductivity and accelerate the electron transfer of S@$SnO_2$@$MnO_2$ composite. The capacity of the Li-S battery with a S@$SnO_2$@$MnO_2$ composite as the cathode was 1,323 mAh $g^{-1}$ at 0.1 C, and the low capacity decay rate was 0.03% after 500 cycles, indicating great confinement of the shuttle effect. In addition, the battery also showed good rate-performance.

## ELECTRON TRANSFER AND ION DIFFUSION OF DOPED-$SnO_2$ FOR ENERGY-STORAGE

Doping technology is an economical, simple, and effective modification strategy that has been used broadly to improve the electronic properties of $SnO_2$ in secondary batteries. Several materials have been chosen as dopants, including the group IIIA element (Al, Ga, and In), the group VA elements Sb, and so on [49, 50]. It has been reported that doping transition metals can not only increase the conductivity of $SnO_2$ but also reduce the volume change in the process of circulation [51, 52]. Lübke et al. reported two categories of transition metal dopants in $SnO_2$ [53]. The first one are the elements without redox activity, including Zr [53], Ti [54], Nb [55], W [56], and Pb [57]. The doping of these elements will not change the capacity of $SnO_2$, but it can significantly increase the cycling life and rate performance [53]. Dominic et al. indicated that the improvement of the performance of doped $SnO_2$ depending on the increase

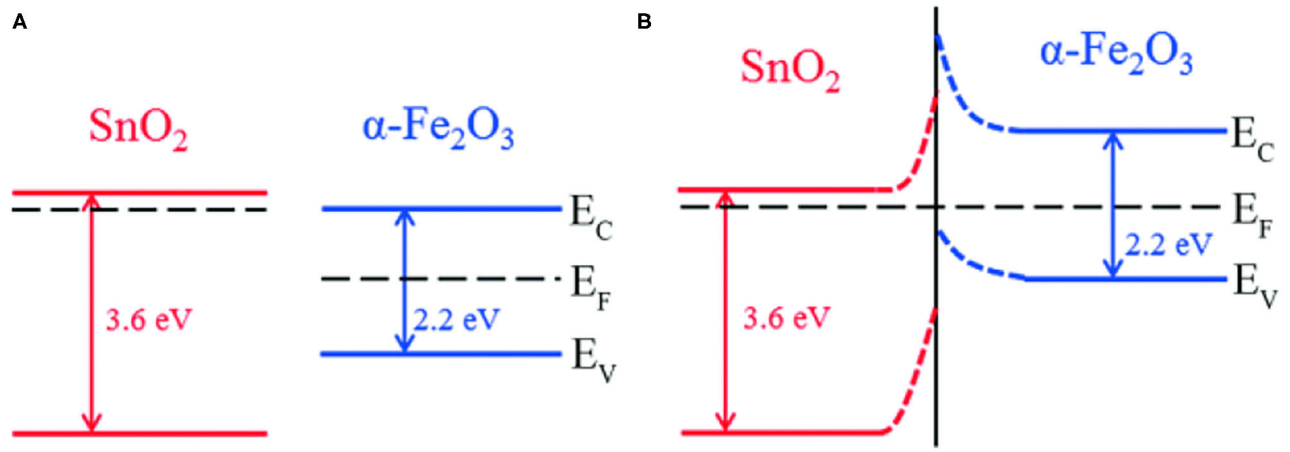


**FIGURE 2 | (A)** Schematic diagram of the energy band structures for $SnO_2$ and α-$Fe_2O_3$. **(B)** The energy band of $SnO_2$@α-$Fe_2O_3$ heterostructures. $E_C$, $E_F$, and $E_V$ stand for conduction band energy, Fermi energy, and valence band energy, respectively. Reproduced from Cui et al. [47].

of the electrical conductivity caused by the additional charge percolation path. Belonging to the second group elements of Cu [53], Mn [58], Fe [59], Co [60], Ni [61], Zn [62], Mo [63], and Sb [64], which showed redox activity, can ensure participation in the conversion reaction, leading to the increase of theoretical capacity. Among them, Mo is an interesting dopant, as it increased the concentration of free electrons in $SnO_2$. Chen et al. prepared ultrafine Mo-doped $SnO_2$ in which Mo uniformly distributed and banded to a $SnO_2$ lattice in the form of $Mo^{6+}$ [63]. The initial capacity was as high as 2751.4 mAh $g^{-1}$. Even at 0.5 A $g^{-1}$, the initial capacity was 1121.8 mAh $g^{-1}$, and the high capacity of 670.5 mAh $g^{-1}$ can be maintained after 700 cycles. Moreover, Sb-doped $SnO_2$ has also been studied widely. Wang et al. reported a Sb-doped $SnO_2$ hollow nanosphere that showed the capacity of 709 mAh $g^{-1}$ at 0.1 A $g^{-1}$ after 100 cycles [65].

In addition, doping and co-doping strategies by non-metallic elements are also reported, such as F [66–68], N [69], P [70], S/F [71], and Co/F [52]. It was reported that doping fluorine atoms in $SnO_2$ could increase the electrical conductivity to about $5 \times 10^3$ S $cm^{-1}$ [72]. In order to improve the Li-storage performance, Luo et al. chose active fluorine and sulfur atoms as dopants to prepare S and F co-doped $SnO_2$@graphene oxide binary composites [71]. On the one hand, fluorine atoms replaced $O^{2-}$ in $SnO_2$ to improve the electrical conductivity; on the other hand, S-doping enhanced Li-ion diffusion efficiency in the binary structure. The improvement of electronic conductivity can also be verified through the impedance spectra. Furthermore, the material can effectively reduce the volume expansion of electrode materials, thus reducing the capacity loss in the cycling process. It can be ascribed to the formation of the $SnS_x$ protective layer and C–F bond on the surface of $SnO_2$ and graphite oxide [71]. In addition, Ma et al. demonstrated the effect of doping ratio by comparing pure $SnO_2$ and cobalt-doped $SnO_2$ with the content of 5, 10, and 15%, respectively [73]. They found the size of the synthesized particles decreased with the increase in dopant concentration. Electrochemical tests showed a doping ratio of 10% ($Sn_{0.9}Co_{0.10}O_2$) possessed the best stability among the four samples.

## ELECTRON AND ION TRANSPORT IN Na- AND K-ION BATTERIES

### $SnO_2$ in Na-Ion Batteries

Because of the larger diameters of Na- and Li-ions than Li-ions ($K^+ > Na^+ > Li^+$, 1.38 Å>1.02 Å>0.76 Å), the problems caused by volume change during the cycling are extremely critical, resulting in rapid capacity decay. In order to solve this problem, researchers have developed many strategies, such as nanostructures, making composites with carbon, etc. For example, Chen et al. used the synergistic-induced ultra-fine $SnO_2$/graphene nanocomposite as the cathode for a K/Na-ion battery, which showed a highly reversible capacity [36]. Xu et al. prepared a sandwich structure (MWNTs@$SnO_2$@C) in which MWNTs were coated with thick $SnO_2$, $SnO_2$, thin $SnO_2$, and the carbon layer [74]. After removing the thick and thin $SnO_2$, the larger internal space could alleviate the problems caused by $SnO_2$ volume transformation, and the 1D MWNTs and carbon layer also improved the conductivity, which made the composite material have a better performance.

Ma et al. demonstrated the failure mechanism of the $SnO_2$ electrode in Na- and K-ion batteries and indicated that OVs could manipulate the energy band structure and carrier migration, thus adjusting the intrinsic properties of oxide semiconductors [75]. In addition, Wang et al. used layer-by-layer-assembled porphyrin derivatives as an interface linker to uniformly attach $SnO_2$ crystals to N and S co-doped graphene, achieving a high capacity and optimizing the electrochemical performance effectively [76].

### $SnO_2$ in K-Ion Batteries

Owing to the significant advantages, such as fast interface diffusion rate, low price, and wide distribution, K-ion batteries have become a possible candidate to replace Li-ion batteries.

Since 2015, research on K-ion batteries has become a hot spot. Some studies indicated that the use of $SnO_2$ in K-ion batteries can significantly alleviate the large volume change and the capacity decay.

Recently, Huang et al. reported the K-storage performance of $SnO_2$/carbon nanofibers [18]. Graphene was introduced through the electrospinning process, and the synergistic effect between $SnO_2$, rGO, and carbon was generated to improve the conductivity of the composites. Huang et al. doped $SnO_2$/rGO/C with phosphoric acid. The prepared composite showed an improved diffusion of $K^+$ ions after the modification by $H_3PO_4$ and an increased conductivity by rGO, which further improves the electrochemical performance [77]. Suo et al. prepared $SnS_2/SnO_2$ heterostructures to enhance the K-storage performance through a facile two-step hydrothermal method to fix $SnS_2/SnO_2$ heterostructures onto stainless steel mesh ($SnS_2/SnO_2$/SSM). The $SnS_2/SnO_2$/SSM anode displayed an enhanced electrochemical performance [78]. Li et al. used amorphous carbon to coat $SnO_2$ nanosheets, which exhibited good K-ion storage performance. The HCHS, as a stable carrier skeleton for $SnO_2$ nanosheets, is good at providing high electrical conductivity. Amorphous carbon wrapping solved the problems of volume expansion and provided surface-induced capacitance [79].

## CONCLUSION

In summary, the challenges for enhancing the electronic and ionic properties of $SnO_2$ electrodes reported recently have been introduced. The conductivity and ion diffusion of $SnO_2$ strongly depends on the structure and composition. Moreover, we indicated that the $SnO_2$ exhibited great potential as the electrode material with good volumetric and gravimetric capacities in many secondary batteries, including Li-ion, Li-S, Na-ion, and K-ion batteries, as displayed in **Supplementary Tables 1–6**. However, electrons and ions transport both require significant improvement. In order to address the issues and enable the application of $SnO_2$-based secondary batteries, some approaches have been demonstrated. It is expected that possible investigations in the future will be focused on the optimization of the $SnO_2$ structure, modifying this with some other functional dopants to seek ideal $SnO_2$-based composites through both theoretical modeling and experimental preparation.

## AUTHOR CONTRIBUTIONS

JL and CH supervised the mini-review. All authors prepared and approved the manuscript.

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## SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fphy.2021.669736/full#supplementary-material

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.