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Research Progress of Silicon Suboxide-Based Anodes for Lithium-Ion Batteries

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With unique advantages, such as high energy density, long lifespan and environmental friendliness, lithium-ion batteries (LIBs) have been widely used in various portable electronics, and placed great expectations on the application in electric vehicles. To meet the ever-increasing high-energy-density demand of the next-generation LIBs, silicon suboxide $SiO_x(0 < x < 2)$ has been considered as one of the most promising anode materials, due to its high mass specific capacity, good cycling performance, proper working potential, low cost, and environmental friendliness. However, there are still several drawbacks before the application of SiO_x, such as low intrinsic electronic conductivity and high irreversible capacity in the first cycle, which lead to low electrochemical activity and low initial coulombic efficiency (ICE). To tackle these issues, extensive efforts have been made and remarkable progresses have achieved in recent years. Here, latest developments of SiO_x-based anodes are briefly reviewed, especially on the subject of metal/metal oxide doping on SiO_x-based electrode materials, and the future application of SiO_x anodes in rechargeable LIBs is also prospected.

Keywords: silion suboxide, anode, composite, electrochemical performance, lithium-ion batteries

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INTRODUCTION

With unique advantages of high operating voltage, large energy density and long lifespan, LIBs have been widely used in various portable electronics, and placed great expectations on the application in electric vehicles (Li et al., 2020b; Liu et al., 2021). Graphite, which is relatively cheap, reliable and easy to manufacture into large electrodes by slurry coating process, has been extensively used as an active anode material for commercial LIBs. However, due to its low theoretical capacity of 372 $mAh{\cdot}g^{-1}$, graphite cannot meet the increasing actual requirements of the high-quality and fast-paced life for energy density, safety and service life in energy storage and supply devices (Yu et al., 2020a; Yu et al., 2020b; Zhou et al., 2020; Li et al., 2021), it is urgent to develop new anode materials with higher specific capacity (Etacheri et al., 2011; Zhou et al., 2019; Qu et al., 2020). With a theoretical capacity of 4,200 $mAh{\cdot}g^{-1}$, Si is expected as an ideal candidate anode material for the next-generation LIBs with high energy density. However, the drastic volume fluctuation (~300%) and the formation of unstable solid electrolyte interface (SEI) during lithiation/de-lithiation process always result in indisposed cycling efficiencies and capacity retention, which hinders the widespread application of Si-based electrodes (Bruce et al., 2008; An et al., 2019; Weng et al., 2020; Xiang et al., 2020). As a derivative of Si, SiO_x $(0 < x < 2)$ has attracted more and more attentions because of its abundant reserves, low cost,

easy synthesis, ideal gravimetric capacity and relatively small volume expansion compared with pure Si (Pan et al., 2019).

However, several crucial issues still need to be solved before the practical application of SiO_x-based anode materials. Its relatively low conductivity (6.7×10^{-4} S·cm^{-1}) (Kim et al., 2007) and large volume change (~200%) during cycling always results in poor rate performance and rapid capacity decline, respectively. Moreover, the large initial irreversible capacity of SiO_x hinders its practical application (Temkin, 1975). To tackle these issues, significant efforts have been devoted. Composing SiO_x with conductive carbonaceous materials, such as carbon layer, graphite and graphene sheets, can largely improve the charge transfer capability (Doh et al., 2008; Ren et al., 2011; Nguyen et al., 2013; Back et al., 2014; Yuan et al., 2015). Recently, researchers focused on creating nanostructures and limiting the size of the active material into the nanoscale range, which not only reduces the diffusion distance of Li^+, but also effectively adapts to the accommodation of volume change during cycling, resulting in the improvement of the high-rate and long-term-stability performance (Zhang et al., 2017a). Designing and constructing rational structures of SiO_x, such as porous structure, layered structure and so on, plays a very important role in the mitigation of the volume change during cycling and the improvement of the lithium-storage performance (Liu et al., 2009; Lee and Park, 2013; Chen et al., 2020). Up to now, there have been several reviews on SiO_x-based anode materials (Chen et al., 2017; Liu et al., 2019; Jiao et al., 2020), which mainly focus on reviewing the compositing SiO_x with carbon materials, and the selections and optimizations on electrolytes, additives or binders for the improvements of electrochemical properties for SiO_x-based electrodes. However few reviews have been published specifically on the subject of metal/metal oxide doping on SiO_x-based electrode materials, which is an easy industrialization of the research direction and of great significance for the development of SiO_x-based anode materials. In this review, the recent advances of SiO_x anode materials in lithium-storage mechanisms, modifications and electrochemical properties are also summarizes. At the end of this review, a general outlook is given for the application of SiO_x-based electrodes in LIBs.

LITHIATION PROCESS OF SILION SUBOXIDE

SiO_x ($0 < x < 2$) is a kind of amorphous material with relatively complex structure. Among the various silicon suboxide, SiO ($x \approx 1$), owning a relatively simple structure, has attracted most attentions as one of the most promising anode material for commercial use in next-generation LIBs. The atomic structure of SiO has been a subject of controversy since its discovery, where two main models were preferred. Philipp proposed a random-bonding model, which described that the Si-Si and Si-O bonds were statistically and randomly distributed throughout a continuous random network of single-phase SiO, hence implying a single-phase material (Philipp, 1971). Temkin suggested a random-mixture model, which assumed that SiO contained mixtures of small domains of Si and SiO_2, corresponding to a multi-phase mixture (Temkin, 1975).

Even so, it is very important to understand the lithiation/de-lithiation process of SiO_x materials in order to solve the inherent defects of materials in practical application. Considering the complex and indeterminate structure of SiO_x, the lithium-storage mechanism of SiO_x and the composition of its lithiated products are complex. For instance, the lithium-storage mechanism of SiO can be proposed as follows (Liu et al., 2019):

$$SiO + 2Li^+ + 2e^- \rightarrow Si + Li_2O \quad (1)$$

$$4SiO + 4Li^+ + 4e^- \rightarrow 3Si + Li_4SiO_4 \quad (2)$$

$$5SiO + 2Li^+ + 2e^- \rightarrow 3Si + Li_2Si_2O_5 \quad (3)$$

$$7SiO + 6Li^+ + 6e^- \rightarrow 5Si + Li_6Si_2O_7 \quad (4)$$

$$3SiO + 2Li^+ + 2e^- \rightarrow 2Si + Li_2SiO_3 \quad (5)$$

$$Si + xLi^+ + xe^- \leftrightarrow Li_xSi \quad (6)$$

At the initial stage during lithiation process, Si, lithium silicates and Li_2O are formed by the irreversible reaction of SiO with Li. And then, the lithiation/de-lithiation reactions between the formed Si and Li can proceed reversibly. When the formed Si from SiO is fully lithiated to form $Li_{4.4}Si$, a theoretical reversible capacity of 2,680 mAh·g^{-1} can be delivered for SiO (Pan et al., 2019). In a similar way, Li_2O and Li_4SiO_4 are produced during the lithiation of nonstoichiometric SiO_x, which can act efficiently as volume buffer zones, which is beneficial to the full lithiation and de-lithiation of the formed Si. However, the formed Li_2O and Li_4SiO_4 are both inert phases, which consume the Li irreversibly and further results in low initial coulombic efficiency (Kim et al., 2013).

IMPROVEMENTS IN LITHIUM-STORAGE ELECTROCHEMICAL PERFORMANCE OF SILION SUBOXIDE-BASED ANODES

The low intrinsic conductivity of SiO_x, large volume change during the lithiation/de-lithiation process, and the partially irreversible reaction of SiO_x with Li are the major stumbling blocks of SiO_x-based anodes for practical application. To tackle these issues, extensive efforts have been made. Reducing the particle sizes (Zhang et al., 2017a), constructing porous structures (Yu et al., 2014), combining with conductive carbonaceous materials, and/or composing with other heterogeneous metals or components can be taken to effectively improve lithium-storage electrochemical performance of SiO_x-based anodes.

Silion Suboxide/C Composite Materials

To improve electrical conductivity of SiO_x-based electrodes, combining SiO_x with conductive carbonaceous materials is an effective strategy. Owing to their unique properties of high conductivity, good ductility, readily accessibility, and ability to form stable SEI layers, carbonaceous materials are ideal additives for electrode materials (Choi et al., 2012; McDowell et al., 2013). Guo et al. developed a graphite-like SiO_x/C composite, in which the nano-sized SiO_x particles uniformly anchored in the carbon matrix (Xu et al., 2018a). Benefiting from the unique structure, when used as anode for LIBs, the obtained graphite-like SiO_x/C

derived high reversible capacity of 645 $mAh{\cdot}g^{-1}$ with a high capacity retention of 90% for 500 cycles. Wu and his co-workers designed a two-step manufacturing process to prepare SiO_x-C composite with a hierarchical structure (Wu et al., 2015). After 100 cycles, the SiOx-C anode delivered a reversible specific capacity of 674.8 $mAh{\cdot}g^{-1}$ and 83.5% capacity retention at 100 $mA{\cdot}g^{-1}$. Direct growth of vertical graphene nanosheets on SiO microparticles can remarkably improve the lithium-storage performance, which showed a high capacity retention up to 93% after 100 cycles (Shi et al., 2017). More recently, an integral interface containing Li polyacrylate (Li-PAA) and carbon nanotubes (CNTs) was constructed on the carbon-coated SiO_x by Guo et al. (Li et al., 2020). The flexible Li-PAA protective layer can not only adjust the volume change of SiO_x due to its high stretchability (up to 582%), but also provide uniform Li^+ transmission interface during charging and discharging. The embedded CNTs can provide fast electronic pathways in the Li-PAA layer, which ensures the superior electronic conductivity. Attributing to the dynamically stable interface (**Figure 1**), the obtained C-SiO_x/C anode showed a remarkably improved cycling ability for 500 cycles, and a high reversible specific capacity of 836 $mAh{\cdot}g^{-1}$ can be delivered. The pea-pod structure of SiO_x/C composite via combining electrospinning and high-temperature carbonization also showed the enhanced cycling stability and rate performance, attributing to its unique structure with carbon conductive network (Zheng et al., 2020).

Silion Suboxide/Metal or Silion Suboxide/Alloys Composite Materials

On account of favorable electrical conductivity and good flexibility, metals or alloys can be used to improve the lithium-storage electrochemical performance of SiO_x anode. The lithium-inactive metal of Fe, Ni or Ti was doped into SiO_x, respectively, via a co-deposition technique, which was conducive to the diffusion of Li^+ (Miyachi et al., 2007). The obtained Ni-doped SiO_x anode delivered a high ICE of 84% and a capacity retention rate of 82% after 400 cycles when matched with an manganese oxide cathode. Similarly, a mixture of SiO, Ni, and reduced graphene oxide was prepared by a hydrothermal mixing and sintering process, and showed an improved cycle performance (Liu et al., 2018). A SiO/Cu/expanded graphite composite was fabricated by a simple electroless plating combined with ultrasonication method, and delivered a markedly improved reversible capacity and cycling stability (Zhang et al., 2017b). In addition, Xu et al. developed a carbon-coated SiO/Cu composites via Cu deposition combined with carbon coating, which also demonstrated a good cycling performance with capacity retention of 88.3% (Xu et al., 2018b). More recently, by conducting a selective alcoholysis method, Kwon et al. synthesized a vanadium-doped SiO_x composites, which exhibited an excellent reversible capacity of 1,305 $mAh{\cdot}g^{-1}$ at 100 $mA{\cdot}g^{-1}$, attributing that the sluggish kinetics of the electrochemical reactions between SiO_x and lithium has been accelerated by metal doping (Kwon et al., 2020). The pre-lithiation strategy of SiO_x can also greatly improve its ICE (Kim et al., 2016).

The SiO_2 phase in SiO can be partially converted into other lithium inactive metal oxides and additional silicon through chemical reduction of SiO_2 with elemental metals, which would reduce the irreversible lithiation and improve the reversible specific capacities and ICEs of the electrodes. Based on this, Jeong and his colleagues converted the SiO_2 phases in SiO into lithium-inactive alumina and new formed nano-silicon through a mechanochemical process, during which the nanostructured $SiAl_{0.2}O$ material was *in situ* formed. The new formed silicon nanocrystallites in the matrix enhanced the ICE, while the lithium-inactive alumina improved the cycling performance (Jeong et al., 2010).

Beyond that, the electrochemically active metal can be also added into SiO_x for enhancing lithium-storage performance. For example, nanoscale Sn particles were mixed with SiO through a mechanical milling process, and the obtained hybrid delivered a significant improvement of both specific capacity by 50% and ICE from 66.5 to 85.5% (Fu et al., 2019). During the lithiation/de-lithiation process, Sn nanoparticles not only can boost reaction kinetics due to their excellent conductivity, but also play as a reagent revive intermediate

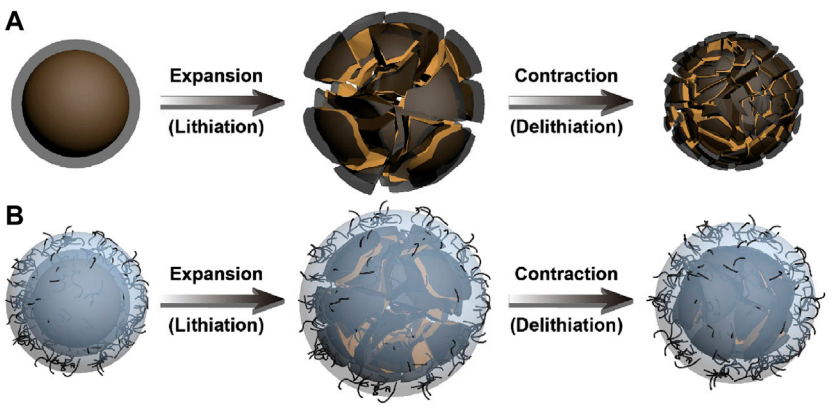

FIGURE 1 | Schematic illustration of the lithiation and delithiation of **(A)** SiO_x/C and **(B)** C-SiO_x/C (Li et al., 2020). Reproduced with permission from ref. (Li et al., 2020). Copyright 2020, Elsevier.

Li_2O interphase by the reaction of $Sn + xLi_2O \rightarrow SnO_x + xLi^+ + xe^-$, which benefits to the improvement of the lithium-storage performance. A submicron-sized hybrid SiO_x/Sn/C anode was prepared by Li et al., in which the 0D-Sn nanoparticles were reduced *in situ* in 2D-SiO_x inner layer and closely coated by carbon outer layer. With the introduction of Sn, the as-obtained SiO_x/Sn/C anode demonstrated a remarkable tap density of 0.74 $g{\cdot}cm^{-3}$ and an excellent long-cycle performance of 654 $mAh{\cdot}g^{-1}$ at a current density of 1 $A{\cdot}g^{-1}$ even after 500 cycles (Li et al., 2019).

In addition, alloys are also used as boosters for the electrochemical properties of SiO_x-based anodes. For instance, Abouimrane et al. prepared a SiO-$Sn_xCo_yC_z$ composite by high-energy mechanical milling using 50 wt% SiO and 50wt% $Sn_{30}Co_{30}C_{40}$ as raw materials. The as-obtained hybrid exhibited a remarkable improved specific capacity of 900 $mAh{\cdot}g^{-1}$ at 300 $mA{\cdot}g^{-1}$ (Liu et al., 2012) . A nanocrystal-FeSi-embedded Si/SiO_x anode was synthesized using Fe-Si alloy as the raw material (He et al., 2017). Using the amorphous SiO_x as a buffer layer and the self-conductive nanocrystal-FeSi as a robust skeleton, the as-prepared sample showed a reversible capacity of 616.6 $mAh{\cdot}g^{-1}$ even at a high current density of 500 $mA{\cdot}g^{-1}$. The retractable three-dimensional porous residual Al-doped Si/SiO_x composite was also prepared from 6-μm Al-Si alloy particles (Wang et al., 2020), which displayed an attractive application prospects with specific capacity of 899.7 $mAh{\cdot}g^{-1}$ even after 300 cycles. Recently, MXene/Si@SiO_x@C layer-by-layer superstructure with auto-adjustable function was successfully prepared by magnsiothermic reduction and pyrolytic carbon coating using two-dimensional MXene $Ti_3C_2T_x$ (Zhang et al., 2019b). The as-obtained nanohybrids provided a reversible specific capacity of 1,674 $mAh{\cdot}g^{-1}$ at 0.2 C with an initial coulombic efficiency of 81.3%, and superior stable lithium storage with 76.4% capacity retention even after 1,000 cycles. The superior lithium-storage performance can be attributed to the advantages of mechanical stability by the synergistic effect of SiO_x, MXene, and N-doped carbon coating, and excellent structural stability by the forming a strong Ti-N bond among the layers.

Silion Suboxide/Metal Oxides Composite Materials

In recent years, the strategy of combining SiO_x with metal oxides has been adopted to improve the electrochemical lithium-storage performance of SiO_x-based anodes. Among them, TiO_2 is usually considered as one of the best composition of electrode materials due to the high reversibility and conductivity of the lithiated product Li_xTiO_2 ($TiO_2 + nLi^+ + ne^- \leftrightarrow Li_nTiO_2$). Furthermore, the insertion/extraction process of lithium ions in TiO_2 layer is very rapid along (001) plane. A nano-scale and thin TiO_2 surface coating on SiO has been obtained by a facile sol–gel process (Jeong et al., 2012). According to the unique role of the TiO_2 coating, the obtained anode delivered significantly improved specific capacity, coulombic efficiency, rate capability and cycling performance, which are much higher than these of bare SiO electrode. Li et al. embedded ultrafine TiO_2 nanocrystals in SiO_x particles to form SiO_x-TiO_2 dual-phase core and then coated them with carbon shells (Li et al., 2018). The initial lithiation process of the as-obtained watermelon-like SiO_x-TiO_2@C nanoparticle is shown in **Figure 2**. The incorporation of TiO_2 effectively enhanced the lithium ionic and electrical conductivities, and released the structure stress during cycling. As a result, the as-obtained watermelon-like structured SiO_x-TiO_2@C nanocomposite could exhibit a high capacity of 910 $mAh{\cdot}g^{-1}$ for 200 cycles at a current density of 100 $mA{\cdot}g^{-1}$. Hu and his co-workers designed a nitrogen plasma-treated core-bishell structure, in which Si nanoparticles were encapsulated in SiO_x shell and N-doped $TiO_{2-\delta}$ shell (Hu et al., 2019). Both the SiO_x shell and N-doped $TiO_{2-\delta}$ shell acted as buffer components to adapt the volume change and stabilize the SEI films. In addition, increased oxygen vacancies and Ti^{3+} species can be obtained after the nitrogen plasma treatment, resulting in the improved diffusion kinetics and conductivity of Li^+. After 300 cycles in the half-cell, the Si@SiO_x@$TiO_{2-\delta}$ electrode showed excellent cycling stability with a reversible specific capacity of 650 $mAh{\cdot}g^{-1}$ at 200 $mA{\cdot}g^{-1}$.

Meanwhile, during the charge/discharge processes, corresponding metal nanoparticles can be *in situ* transformed from the added transition metal oxides, which are helpful to

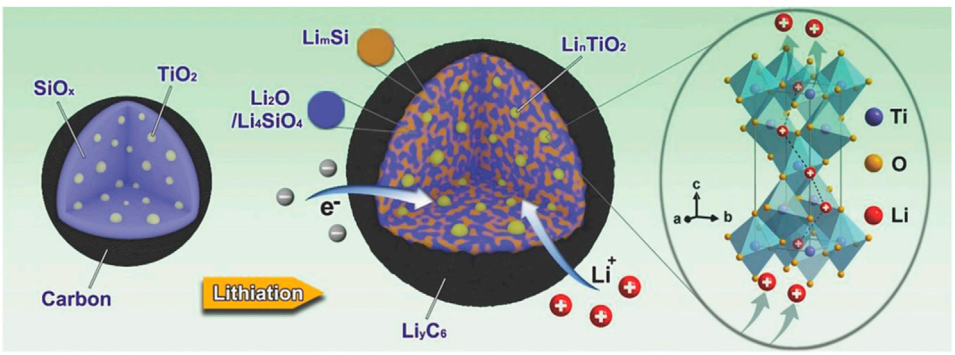

FIGURE 2 | Schematic illustration for first lithiation process of watermelon-like structured SiO_x-TiO_2@C nanoparticle (Li et al., 2018). Reproduced with permission from ref. (Li et al., 2018). Copyright 2018, Wiley Online Library.

increase the electrical conductivity of the composite materials. Zhou et al. successfully prepared a SiO/Fe_2O_3 composite via a mechanical grinding process (Zhou et al., 2013). The additional Fe_2O_3 phase can be lithiated to form metallic Fe during the discharge processes, which can improve the electrical conductivity, resulting to the enhanced reversible specific capacity and ICE from 59 to 68%. An egg-like few-layered graphene-wrapped and Fe_3O_4-pillared SiO_x anodes was established by Liao et al., which delivered a reversible specific capacity of 833.4 $mAh{\cdot}g^{-1}$ with a high ICE of 84.9% and capacity retention ratio of 81.8% even after 500 cycles at a current density of 500 $mA{\cdot}g^{-1}$ (Liao and Wu, 2019). The excellent performance was benefited from the comprehensive effects of integrated structure, enhanced Li^+-diffusion kinetics, and improved pseudocapacitance behavior.

Morover, metal oxides can react with SiO_x to form metal silicate compound at high temperature, which can increase the crystallinity of SiO_x, resulting in the improvement on the ICEs of SiO_x-based anodes. For instance, SiO was coated with a olivine structure Fe_2SiO_4 layer by heating Fe_2O_3 and SiO at a molar ratio of 1:0.2, which significantly improved ICE from 70 to 90% (Yamamura et al., 2013). Zhang et al. prepared carbon-coated C-SiO-$MgSiO_3$-Si composites by heating the mixture of SiO, MgO and Si (Zhang et al., 2019a). The *in situ* formation of the $MgSiO_3$ phase can consume the deleterious SiO_2 phase resulting from the disproportionation reaction of SiO at high temperatures, which helps to improve the ICE to 78.3% for lithium storage. Meanwhile, as an electrochemically inert phase, $MgSiO_3$ can also effectively buffer the volume change during cycling, which is beneficial to enhanceing the cycling stability.

DISCUSSION

Because of its high capacity, good cycling stability and appropriate operating voltage, silicon suboxide (SiO_x) has been regarded as one of the most promising anode materials for the next-generation LIBs. It is accepted that Li_2O and a series of lithium silicates are formed *in situ* during the initial lithiation of SiO_x, which not only insulates the inner active material from electrolyte, but also acts as a buffer for volume expansion. Therefore, SiO_x possesses high capacity and excellent cycling performance, but it suffers from unsatisfied initial coulombic efficiency and low intrinsic conductivity, which limit the practical application of SiO_x-based materials. In this mini review, the lithium-storage mechanism, modifications and electrochemical properties of SiO_x-based anode materials are reviewed briefly. Only by fully understanding the lithiation/de-lithiation mechanisms of materials, can they be targeted to solve their own drawbacks. In addition, this review emphasizes that metal/metal oxide doping into SiO_x electrode materials is effective to solve the issues before practical applications. Other strategies for improving electrochemical performance, such as pre-lithium technology through the *in-situ* formation of silicates, are also covered. Although some strategies have been proposed, large-scale practical applications of SiO_x-based anode still have a long way to go. As for future's research, more consideration should be given to the feasibility and cost of the batch production process, we look forward to seeing a breakthrough of SiO_x-based anode materials in the field of LIBs.

AUTHOR CONTRIBUTIONS

XZ: Conceptualization, Investigation, Formal analysis, Investigation, Validation, Visualization, Writing—original draft. ZQ: Writing—review and editing. QL: Supervision, Project administration. JT: Investigation, Validation. ML: Visualization. KD: Editing and Review. ZL: Review.

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