Scientific Research Publishing

World Journal of Nano Science and Engineering, 2026, 16(3), 163-204
https://www.scirp.org/journal/wjnse
ISSN Online: 2161-4962
ISSN Print: 2161-4954

Advancements in Synthesis Methods and Nanostructure Designing of SiO_x-Based Anode for High-Capacity Li-Ion Batteries

Ila Prasad

Faculty of Physics, Department of Physics and Engineering, University of St Thomas, Houston, TX, USA
Email: prasadi@stthom.edu

How to cite this paper: Prasad, I. (2026) Advancements in Synthesis Methods and Nanostructure Designing of SiO_x-Based Anode for High-Capacity Li-Ion Batteries. *World Journal of Nano Science and Engineering*, **16**, 163-204.
https://doi.org/10.4236/wjnse.2026.163008

Received: June 30, 2026
Accepted: September 25, 2026
Published: September 28, 2026

Abstract

Lithium-ion batteries (LIBs) provide the highest energy and power densities. They have a longer cycle life compared to all other batteries in commercial use. They are, therefore, preferable ones in electronic products and electric vehicles (EVs). The graphite anodes used in LIBs have low specific capacity and therefore limited efficiency for high energy density applications. In the last decade, due to its ubiquitous nature, extremely high theoretical specific capacity and low cost, silicon-based anode materials have emerged as a potential candidate to replace the graphite anode of LIBs. However, the large volume expansion of silicon during cycling causes deformation of the electrode and loss of electrical contact resulting in significantly low performance. To alleviate this issue, SiO_x ($0 \le x \le 2$) and its composites with structural modifications are under extensive investigation. This review evaluates the main synthetic methodologies of SiO_x anodes with nanostructure designing and hybridizing. The paper includes the most recent developments in this direction and summarizes the main results. Limitations and challenges in improving the energy storage capabilities and commercialization of SiO_x-based anode material for high energy density applications are discussed with future research trends.

Keywords

Li-Ion Batteries (LIBs), Solid Electrolyte Interface (SEI), Initial Coulomb Interface (ICE), Silicon Nanoparticles (SiNP)

1. Introduction

Li-ion batteries (LIBs) are an established technology for high energy storage. They provide the highest energy and power densities, fast charging capability, longer

cycle life, minimal self-discharge and no memory effect [1]. They are, therefore, extensively used in electronic products, like computers and cell-phones [2], electric vehicles (EVs) [3] [4] and aerospace [5]. Lithium Cobalt Oxide-based ($LiCoO_2$) cathode and graphite as the anode have controlled the Li ion batteries since their inception and commercialization by Soni Co. in 1990s [6] [7]. Graphite has been the most popular anode material in commercial LIBs due to its excellent cycling stability and fast charging capability [8]. However, the theoretical specific capacity of graphite is 372 $mAhg^{-1}$ limiting its capability for high energy density applications. To achieve higher energy density, the intercalation chemistry of graphite must be replaced with another anode material which is capable of electrochemically alloying lithium. Various anode materials including transition metal oxides, transition metal sulfides and alloys, with different structural designs have been under investigation [9]-[15]. In the last decade, silicon has emerged as the most promising candidate for anode material. Silicon is ubiquitous, has a low production cost, and the theoretical specific capacity of silicon is extremely high, 4212 $mAhg^{-1}$ ($Li_{22}Si_5$) which is ten times higher than the specific capacity of graphite (LiC_6) 372 $mAhg^{-1}$ [16]. The average voltage platform of Si (0.4 V vs Li/Li^+) is also higher than that of graphite electrode (0.125 vs Li/Li^+) which helps it avoid dendritic lithium formation and lithium plating on the anode material surface during the lithiation process, leading to improvement in safety performance of the LIB [16] [17]. While silicon shows many advantages including lower working potential and high specific capacity, it has poor electrical conductivity contributing to its hysteretic Li^+-ion reaction dynamics. In addition, high Li-storage capacity means a large amount of Li^+ can be alloyed with silicon resulting in large volume expansion of silicon (more than 300%) after full lithiation [18] [19]. This large volume expansion causes high mechanical strain leading to the deformation of the electrode, pulverization of the Si particles, and loss of electrical contact with the current collector. Meanwhile, fresh unstable solid electrolyte interface (SEI) films are continuously generated on the fracture surfaces [19]-[21]. Studies reveal that the formation of the unstable solid electrolyte interphase (SEI) consumes a significant amount of lithium ions, which reduces the initial Coulombic efficiency (ICE) of the cell, eventually depleting the electrolyte and reducing the energy density of the cell [21]. Oxides of silicon have been widely investigated in recent years to circumvent this issue. SiO_x ($0 < x < 2$) has gained considerable interest as a potential alternative to Si due to its enhanced cycling stability and smaller volume variation. Compared to bulk silicon, SiO and SiO_2, the non-stoichiometric silicon oxide (SiO_x, $0 < x < 1$ and $1 < x < 2$) anode material has high specific capacity and long cycling stability [22] [23]. Studies reveal an overly complex amorphous structure of SiO_x. Angstrom beam electron diffraction (ABED) and synchrotron high energy XRD (HEXRD) patterns exhibit the presence of amorphous Si clusters and amorphous SiO_2 with SiO [24]. SiO_x inherits the high capacity of Si-based materials (2100 $mAhg^{-1}$), but less severe volumetric expansion/shrinkage during lithiation/prelithiation, resulting in extended cycling life [25]. However, this non-neg-

ligible volume change, confirmed by imaging techniques and recording of various Li-Si phases [16] [21] [23] [26], remains the main challenge due to the irreversible conversion of active lithium. Especially in the current situation, where the specific capacity of commercially used cathodes is low (<300 $mAhg^{-1}$), low ICE of SiO_x anode causes a substantial portion of the cathode capacity to be consumed in full cell, reducing the energy density of it [26]. Various optimized structure designs and surface modifications, namely C/SiOx, carbon coating on the SiO_x surface, doping, alloying with other metals, SiO_x-carbon nanocomposites, etc. have been extensively studied and used in recent years with significant improvement in cycling stability of SiO_x-based anodes [22] [23] [27]-[34]. One group has suggested that soft carbon may prove to be a more suitable match for SiO_x and therefore capable of replacing the graphite anode in LIBs [35]. However, some other groups promote hard carbon coating and its composites with SiO_x. Pouch cells with SiO_x/biomass carbon anodes exhibit enhanced electrochemical performance [36] [37].

Strategies to enhance the electrochemical performance, safety, and stability of LIBs with SiO_x based anodes for industrial scale applications are based on synthetic methodologies, structural modification and surface engineering of silicon, hybridization with other materials [36]-[40] and pre-lithiation [41] [42]. Recent investigations report a more design dependent relationship between the physical parameters and electrochemical performance of the SiO_x based anode in Li-ion batteries. An initial size of 4 - 6 nm for Si nanodomains influenced the pulverization of Si domains in SiO_x [43] [44]. Pulverization of SiO_2 matrix in SiO anodes has been detected during cycling due to the irreversible formation of lithium silicate. The authors propose an initial optimum Si nanodomain size of 4 - 6 nm to prevent the pulverization [44]. Si-rich SiO_x with smart design has been found beneficial for volume change accommodation. It is therefore more suitable for commercialization [45] [46]. Several research groups have discussed Si-based anodes for LIB in general. However, not many research groups have focused on SiO_x-based anodes. SiO_x is a promising replacement to elemental silicon due to its easy synthesis, low cost, and lower volume expansion (~118%) [46] [47]. Research groups have also expressed their concern over most of the studies conducted on half cells. A complete scenario of research progress on SiO_x-anode with full lithium-ion batteries, is discussed by not many authors [45]-[49].

In this paper, recent progress in performance enhancement of the SiO_x-based anode material for LIBs has been investigated and discussed based on the synthetic methodologies and structural designing. A comparative analysis of the synthesis methods has been presented. Electrochemical performance of the SiO_x based anodes was evaluated after structural modifications. Finally, suggestions proposed by various research groups, based on recent studies, have been discussed for further enhancing the knowledge and understanding of the underlying mechanism of operation of LIBs with SiO_x anodes. Challenges remaining towards the commercialization of SiO_x-based LIBs have been summarized.

2. SiO_x: Structure and Electrode Mechanism

According to oxygen content, SiO_x based anode material can be SiO_2 (x = 2), SiO (x = 1) and non-stoichiometric SiO_x. Oxygen content in the silicon directly affects the electrical conductivity, structural stability, and reversible/irreversible capacity of the Si-based electrode [49]. Depending on the method of preparation, reaction condition and time, exact composition of the oxidation layer may change, affecting the electrochemical properties of the electrode. Manipulating the oxygen content in SiO_x can result in excellent electrochemical properties of the SiO_x electrode in terms of cyclic stability, Coulombic efficiency, and rate capability. It is accepted that silicon rich SiO_x possesses high capacity but poor cycling performance, whereas O-rich SiO_x is favorable for volume change accommodation [50]. Physical parameters like particle size, shape, and film thickness also significantly affect the electrochemical performance of silicon-based anodes [24] [25] [35] [36] [43] [44] [47] [48].

It is important to know that SiO_x is not a naturally stable phase structure. It has an overly complex, amorphous structure. According to the widely accepted heterostructure model of amorphous SiO_x, SiO_x exists in the interface region between Si and SiO_2 [24]. It has poor electrical conductivity. Nevertheless, SiO_x ($0 < x \leq 2$) has emerged as a promising candidate to replace elemental Si due to easy synthesis, mild volume expansion (~118% for SiO compared to ≥300% for Si) and low cost. The SiO_x family includes SiO, SiO_2, non-stoichiometric SiO_x and Si-O-C based anode materials [45].

The Li^+ intercalation mechanism of SiO_x has been discussed by various research groups [25]-[27] [39] [41] [42] [45]. It is understood that during the first cycle of lithiation, SiO_x reacts with Li to produce mixture of Si, Li_2O and silicates of lithium (Li_4SiO_4, $Li_6Si_2O_7$, $Li_2Si_2O_5$, etc.). An electrochemically inert mixture of Li_2O and Li_4SiO_4 produced during the first lithium-ion process together with $Li_{15}Si_4$, can be used to form a buffer matrix to form a stable SEI layer [25] [45]. During the subsequent cycles, Si will further lithify and form $Li_{15}Si_4$ alloy which is reversible, and it occurs at a favorable low potential relative to the lithium electrode [26] [46]. However, the main reaction products of SiO_x material are still unclear, though the Li^+ intercalation mechanism has been clarified. The specific reaction mechanism of each component in SiO_x, the type and content of products after Li^+ intercalation, and its effective factors need to be explored. The presence of these compounds enhances hysteresis, and the Li consumed in the formation of these compounds and alloys are not electrochemically reversible [26] [27] [46].

The relationship between film thickness and electrochemical performance of SiO_x anodes was studied with SEM images and electrochemical impedance spectroscopy (EIS) data. Evidence confirms that an optimum film thickness of SiO_x (450 nm) results in low charge transfer resistance, formation of reduced SEI and good electrode integrity upon cycling [48].

The value of x in SiO_x also influences its performance for practical applications. Several groups have studied the effect of oxygen content on the electrochemical

performance of SiO_x anodes. The oxygen content affects the specific capacity, voltage hysteresis (voltage hysteresis refers to the voltage difference between the charge and discharge profiles) and cycle life [50]-[53]. A detailed study of the influence of oxygen content on electrochemical behavior of SiO_x@C anodes revealed that a rational O/Si ratio can acquire a balance between the cycling stability and the ICE of SiO_x anodes. The oxygen content in SiO was precisely controlled by adjusting the molar ratio of Mg:SiO@C in magnesiothermal reduction. Different O/Si ratios of SiO_x@C (x = 0.95, 0.81, 0.71, 0.61) were investivated. Out of all the O/Si ratio, $SiO_{0.81}$ @C exhibited proper oxygen content and porous structure. It displayed the best electrochemical performance with an initial reversible capacity of 1374 $mAhg^{-1}$ and an ICE of 73%. The composite exhibited a reversible capacity of 1230 $mAhg^{-1}$ after 200 cycles with a retention rate of ~90% at a high current density of 1 Ag^{-1}. The study provides a path to achieve balance between cycling stability and ICE of SiO_x anodes with a rational ratio of O/Si [49].

Another study investigated the role of oxygen in lithiation/delithiation cycle and the formation process of solid electrolyte interface (SEI) in Si and SiO_x electrodes were investigated. Both, Si and SiO_x electrodes were synthesized via magnetron sputtering technique. Co-sputtering Si target and SiO_2 target, SiO_x anodes were prepared. To vary the oxygen content, different combination of power was applied to the Si and SiO_2 target. SiO_x with differing ratios of Si:O ($SiO_{0.2}$ and $SiO_{0.6}$) were synthesized and CR 2032 coin cell with 14 mm diameter was used to evaluate these thin film electrodes [50]. Excluding the effect of carbon additives and binders, SiO_x anodes with higher oxygen content displayed less volume change and formed a thinner and more stable SEI's during cycling. Accomodation of volume change during cycling can be attributed to the formation of internal porous structure. However, it had a nonreversible and longer plateau around 0.7V during the first lithiation, exhibiting the reduction of Si-oxide, leading to lower ICE, unwanted for practical applications [50]. Annealing-etching procedures also control the oxygen distribution in SiO_x with an improved electrochemical performance [51]. On the other hand, with a decrease in oxygen content, reversible capacity and the ICE increase were observed leading to poor cycle life. It shows that all SiO_x films undergo significant chemical changes during cycling. They can restructure after a long cycling time. This implies that tuning the surface oxygen content can control the SEI performance [52].

For practical applications, porous structures with good stoichiometry enhance the performance of SiO_x anodes. Effective designing and low-cost synthesis methods need to be explored.

3. Synthesis of SiO_x

In this section, the most common physical/chemical methodologies to produce nanostructured SiO_x anodes for LIB are discussed. The advantages and disadvantages of each synthetic strategy with suggested modifications by various reviewers are summarized.

Based on the wide range of research reported, synthesis of SiO_x can be grouped in three main categories: i) thermal evaporation ii) high energy mechanical milling (HEMM) and iii) wet chemistry. The raw material for preparation of SiO_x can be i) pure silicon, ii) SiO iii) SiO/SiO_2 or iv) Silicon compounds [23] [53] [54].

3.1. Thermal Evaporation

a) Thermal evaporation method is the most widely adopted method for synthesis of various nanostructured SiO_x by thermal evaporation in practice. The starting material can be pure Si powder [55] a mixture of Si and SiO_2 [22] or Si grains [56]. In 2001, *in-situ* SiO_x was produced by heating pure Si powder to 1373 K under Ar flow. Due to various vapor concentrations, substrate surface condition and temperature gradients, SiO_x powder with various morphologies were achieved [55]. Presently, one of the widely adopted methods on the industrial scale for preparation of SiO_x has been the thermal evaporation method. SiO_x powder is produced by sublimating and condensing a mixture of Si and SiO_2 at elevated temperatures. The silicon/oxygen ratio is controlled by manipulating the process conditions and ratio of raw materials [22].

In another study, a-SiO_x films were synthesized by reactive evaporation of Si grain with oxygen gas in vacuum. The chemical reaction is

$$\mathrm{Si(g)}+(x/2)\ \mathrm{O_2} \rightarrow \mathrm{SiO}_x\mathrm{(s)}.$$

By controlling the process parameters such as oxygen flow rate and evaporative silicon, ultrafine powder of SiO_x or film with different ratios of silicon oxygen content in SiO_x (x = 0.17, 0.51, 1.02, and 1.34) were obtained. The effect of total oxygen content on the electrochemical reactions of a-SiO_x with Li was investigated. The reaction products were determined by x ray photoelectron spectroscopy (XPS). The initial charge (lithiation) and discharge (delithiation) capacities were found to be strongly related to the value of x in SiO_x. The a-SiO_x (for x = 1.02, 1.34) displayed excellent cyclability at a range of 0.0005 - 1.05 V vs Li/Li^+. Absence of peaks at 0.45 V in differential capacity vs voltage (dQ/dV) profiles demonstrates the suppression of crystallization of lithiated a-Si even under deep cycle conditions [56].

The synthesis methods yield *in-situ* SiO_x of high quality. When combined with ball milling, porous structures could be achieved for SiO_x anodes. Reactive ion evaporation method needs much higher temperature.

b) PVD (physical vapor deposition) includes vacuum evaporation, magnetron sputtering, electron beam evaporation, and ion plating. In one study, researchers synthesized SiO_x@C by PVD method at two different temperatures 200˚C and 400˚C followed by carbonization at 950˚C. Pyrolysis fuel oil was the carbon precursor and PVD was performed on pristine SiO_x. SiO_x@C-200 exhibited excellent cycling stability with a capacity retention of 90.2% after 80 cycles at 1.0 C confirming suppressed volume expansion of SiO_x [57]. In another study, metallurgical grade raw a-SiO powder was utilized to obtain Si/SiO_x nanocomposite powder by Plasma spray physical vapor deposition (PS-PVD). The procedure consisted of

complete evaporation of raw SiO powder and subsequent condensation of high temperature SiO_x vapor, followed by disproportionation reaction of nucleated SiO_x nanoparticles. Half-cell batteries constructed with PS-PVD SiO_x powder with C/Si = 0.25 exhibited improved initial efficiency and maintenance of high capacity as high as 1000 $mAhg^{-1}$ after 100 cycles at the same time [58]. Undoped silicon target was RF sputtered to obtain Li-active, nanoporous SiO_x layer for coating of a-Si thin film [59]. Infrared nanosecond laser ablation method has also been in practice to produce ultrafine nanoparticles of SiO_x. When synthesized ultrafine nanoparticles of SiO_x were utilized as anode material for LIBs, it showed excellent cycling stability and a capacity comparable to commercialized graphite [60]. Another research group employed Infrared nanosecond laser ablation technique to synthesize silicon oxide films of various stoichiometry at different partial pressures of oxygen. The SiO_x films with varying oxygen content were analyzed by three different characterization techniques. It was observed that the composition of the film could be controlled by varying the inert gas pressure at the constant pressure of the active component in the ambient mixture [61].

PVD is conducted at a lower temperature compared to thermal evaporation. The films generally exhibit highly adaptable stoichiometry though compared to thermal oxides; deposited oxides are often sub-stoichiometric (oxygen deficient). Magnetron sputtering has the advantage of high precision over film thickness and density. It has fast deposition rate and low substrate temperature but high equipment complexity and high cost.

PSPVD and Infrared nanosecond laser ablation are higher temperature, complex processes with limited precision though both have high deposition rates.

c) CVD (chemical vapor deposition) is another deposition technique in which a thin film is formed by a chemical reaction on the surface of a substrate. It is primarily used in modification of SiO_x anode material while SiO_x is fabricated via disproportionation (d-SiO_x) or thermal reduction methods. Recently, the chemical vapor deposition (CVD) method was utilized to enhance the conductivity of SiO_x by preparing SiO_x@C composites. C_2H_2 was used as carbon source in a rotating CVD furnace to produce hard carbon coated SiO_x (SiO_x@C). At the rate of 0.5 C (1 C = 2.1 Ag^{-1}), the discharge specific capacity stayed at 1116.8 $mAhg^{-1}$ after 140 cycles, which is 539.8 $mAhg^{-1}$ higher than pristine SiO_x. The carbon coating suppressed the volume expansion leading to good electrical conductivity. It also avoided the agglomeration of SiO_x. The SiO_x @C anode exhibited excellent performance in both cycling and rate performance tests [36].

Recent studies confirm the significance of carbon precursors and deposition temperatures. Methane based carbon coating of SiO_x via CVD at 1000˚C exhibited excellent electrochemical performance. A high capacity of 778 $mAhg^{-1}$ at 0.75 Ag^{-1} and a remarkable capacity retention of 92.8% after 100 cycles was observed. At industrial scale production of SiO_x, this optimized CVD method is of much use [37].

PECVD has also yielded reliable results for d-SiO_x/CN (carbon nanosheet) an-

odes material. The d-SiO_x@CNs composite exhibited high reversible capacity (first charge/discharge capacity of 1456.7 and 1794.4 $mAhg^{-1}$, respectively) and excellent cycling stability (capacity retention of 87.2% after 200 cycles at a current density of 0.4 Ag^{-1}). The electrochemical performance of the anode (d-SiO_x@CNs15/G||NCM811) in full cell with commercial NCM811 cathode was noteworthy with capacity retention of 76.3% after 200 cycles at 1C and a high energy density of 424.2 $Whkg^{-1}$ [62].

Thermal evaporation methods are vapor phase synthesis methods used to deposit nanostructured silicon oxide material for SiO_x anodes. The powder material obtained has excellent coating uniformity for line of sight but fails on complex 3D particles. Oxygen content is very homogenous and tunable in the dense film structure but requires ultra-high vacuum control. Besides the harsh experimental conditions such as elevated temperature and pressure, these methods are extremely expensive due to the need for large equipment, low productivity, and high energy consumption [23] [54]-[62]. Standard thermal evaporation, PVD and CVD usually yield relatively dense, continuous films rather than inherently porous SiO_x networks.

3.2. High Energy Ball Milling

Mechanical milling is a facile, low-cost technique for nanosizing advanced materials and has been in use for the last fifty years [63]. High energy ball milling (HEMM) is usually employed to synthesize SiO_x with or without other synthesis processes like CVD, metal reduction, thermal evaporation and so on [53]. The starting material can be Si powder [64] [65], commercial SiO_x powder [66] or a mixture of Si and SiO_2 powders [67]. One group of researchers have synthesized, high purity, with good cycling stability, amorphous SiO_x negative electrode material by high energy ball milling silicon powder in air or Ar [64]. The oxygen content in SiO_x was controlled by adjusting the exposure time of silicon powder to air or Ar. Samples were high energy balled milled for a total time of 20 hr. SiO_x with x between $0 \leq x \leq 0.6$ were obtained. XRD, XPS, SEM and TEM analysis of the structure of SiO_x displayed nanosized Si embedded in a-SiO_x matrix. SiO_x with $x < 0.6$ displayed lower ICE and higher reversible capacity compared to commercial SiO_x sample [64]. Another group investigated SiO_x with various oxygen content synthesized from Si powder by reactive gas milling [65]. A mixture of Si and SiO_2 powder milling was also carried out to produce SiO_x for comparison. XRD, XPS and TEM revealed nano a-Si dispersed in a-SiO_x matrics. All samples had the same morphology. After annealing in Ar atmosphere at temperature between 300˚C - 800˚C, the SiO_x anode material exhibited improved cycling performance. The 1st irreversible capacity of the synthesized samples reduced after high temperature annealing due to mitigating the defects, while the high reversible capacity (1500 - 2000 $mAhg^{-1}$ or 1600 - 1800 Ahg^{-1}), was well maintained. Study of the electrochemistry and thermal behavior of SiO_x prepared by reactive gas milling revealed $SiO_{0.37}$ to be thermally stable up to 800˚C with improved cycling performance after

annealing [65]. Recently, SiOx with controlled oxygen content was obtained by ball milling crystalline silicon powder in an oxidizing medium using two different ball milling techniques. The total synthesis time extended to 30 hours. The SiO_x powder thus obtained had a large surface area [68]. A "dry powder micro granulation" procedure reported by other groups [69] has been suggested by the authors to reduce the surface area and improve the electrochemical performance of the ball milled SiO_x electrode material. Reaction-ball milling surface coating strategy also involves HEMM. The technique involves high energy milling of partially prelithiated and pristine Si microparticle samples in CO_2 atmosphere for different durations and pressures. A multicomponent amorphous layer coating of SiO_x, C, SiC and Li_2SiO_3 was observed. The four-fold coating layer successfully suppressed the pulverization of partially prelithiated Si microparticle anodes during cycling due to a stable SEI film formation on the electrode surface. The reversible capacity remained at 1439 $mAhg^{-1}$ at 100 mAg^{-1} after 100 cycles. It is four times higher than that of pristine Si microparticle anode [70].

Ball milling strategy, a top-down synthesis method, is, at present, the main route for mass production of nanosized SiO_x. High-energy ball milling physically reduces the particle size to micron and nanosized silicon. It can also be used to combine various materials, but the energy supplied by grinding can also stimulate reduction processes [63]. Large surface area is created by ball milling, leading to higher consumption of Li^+ ions during initial cycle to form SEI layer. This lowers the ICE [68]. On the other hand, HEMM may cause secondary agglomeration and impurities can be incorporated from the ball milling chamber. The method requires long synthesis time extending to many hours [24] [54] [63]-[70]. High heat is generated which would oxidize the silicon. High energy ball milling conducted in an inert atmosphere can be more productive [71] [72].

3.3. Wet Chemistry

The hydrothermal method, Metal reduction method, and the sol-gel method are the three most widely used wet-chemical methods to prepare Si/SiO_x nanoparticles. The morphology and electrochemical properties differ depending on the reaction conditions and the starting material. All these methods are often preceded by ball milling. Rice husks are the most common raw materials used [24] [71] [72].

a) Hydrothermal method is one of the most used methods to prepare Si/SiO_x nanoparticles which serve as the precursor to obtain SiO_x/C after carbon coating. By controlling both the physical and chemical conditions in the hydrothermal reactor, high purity nanoparticles of Si/SiO_x can be obtained. Quite a few research groups have extensively used the hydrothermal method to prepare Si/SiO_x nano particles and applied carbon/graphene coating to obtain the desired SiO_x/C anode material. The hydrothermal method is often preceded by ball milling. Nanocomposites thus produced show improved electrochemical properties [71]-[75]. One group fabricated SiO_x/C nanocomposites with controllable oxidation of silicon

under mild hydrothermal conditions and synchronous carbon coating. The researchers report a high reversible capacity of 1133 $mAhg^{-1}$ at 0.5 Ag^{-1} with 89.1% capacity retention after 200 cycles for the fabricated SiO_x/C nanocomposites. With 15 wt.% SiO_x/C composite, graphite-SiO_x/C hybrid electrode, a high reversible specific capacity of 496 $mAhg^{-1}$ and stable electrochemical cycling with a capacity retention of 90.1% for 100 cycles was observed [75].

The microwave hydrothermal method has also been reported for delicate construction of Si/SiO_x which avoids the long reaction time and elevated temperature conditions needed for the hydrothermal process [76].

The wet chemical reduction in hydrothermal methods provides a facile and homogenous liquid environment and applicable for production of nanostructured, or/and porous structures. Carbon coating is excellent for solution-based core/shell wraps. However, the need for high-cost solvents, high toxicity and air sensitive chemicals limits its applicability for commercial scale production and application in LIB [71]-[76].

b) Metal reduction methods

Metal reduction utilizes suitable metals with low melting point and suitable reduction potential to reduce silicon to SiO_x. Mg, Zn and Al are the most used metals to synthesize SiO_x [54] [77]-[79]. Compared to traditional carbothermal reduction [80], the reduction temperature is lower, and the reaction conditions are mild.

Magnesiothermic reduction provides an efficient and economic method to synthesize SiO_x nanoparticles with low-cost silicates, silica, and minerals of silicon as raw materials [81]-[86]. In industry, SiO_x is manufactured using vapor deposition techniques under harsh conditions at extremely elevated temperatures.

$$x\mathrm{SiO_2} + (2-x)\ \mathrm{Si} \rightarrow 2\mathrm{SiO}_x\ (0 < x < 2)$$

The elevated temperature, pressure and variation in synthesis parameters affect the electrochemical performance of SiO_x. Magnesio-mechanochemical reduction of natural SiO_2 resulted in highly porous SiO_x with excellent cyclic stability up to 2000 cycles under a high current density of 4 Ag^{-1} Blending with graphite further improved the performance. [81] In another investigation, solid SiO_2 and porous SiO_2 were utilized separately to produce porous SiO(p-SiO) with carbon shell by magnesiothermic reduction at low temperature(650˚C). The p-SiO@C displayed good cycling stability (777.1 $mAhg^{-1}$, at 500 mAg^{-1} after 300 cycles) and excellent rate capability (977 $mAhg^{-1}$, at 1000 mAg^{-1}) [82]. Talc has also been utilized to obtain a mixture of Si and SiO_x by magnesio-thermal reduction and acid etching processes. A porous network structure of Si/SiO_x was obtained. Finally, carbonization of Si/SiO_x produced C@Si/SiO_x with particularly good cycling stability. Si/SiO_x nanoparticles thus obtained delivered initial discharge capacity of 842 $mAhg^{-1}$ at current density of 1C (1500 mAg^{-1}), and 470 $mAhg^{-1}$ after 300 cycles could be maintained. The superior performance was attributed to the porous network structure capable of mitigating the volume stress [83].

Another research group reported production of Si/SiO_x powder by magnesium thermal reduction of silica in an argon atmosphere for two hours at elevated tem-

perature. The temperature varied from 675˚C to 825˚C followed by acid leaching for 24 hours and drying. Si/SiO_x with various oxygen content were obtained. The samples thus produced were analyzed using XPS and compared with empirical results. The optimum Si/SiO_x anode not only showed high specific capacity with acceptable ICE but also improved cycling performance [84]. Other groups have also studied the Si/SiO_x network and reported good cycling stability and rate capability utilizing magnesiothermic reduction of Si/SiO_2 mixture or SiO_2 to obtain Si/SiO_x, SiO and their nano composites [53] [80]-[86].

Utilization of a combination of microwave and magnesiothermic reduction for the fabrication of ultrafast Si@SiO_x core/shell structures is the most recent approach. By adjusting the microwave assisted hydrothermal process at 50˚C, 150˚C and 250˚C thickness of the SiO_x shell layer on the Si core surface was controlled and Si@SiO_x amorphous shell thickness was optimized. After magnesiothermic reduction, oxygen vacancies developed due to the etching process of MgO. It contributed to the lithium-ion diffusion kinetics leading to high electrochemical performance [87].

Zinc has a lower boiling point (907˚C) and melting point (419.5˚C). Zinco thermic reduction is therefore in practice to obtain SiO_x and their nanocomposites [23] [53] [88]. One research group prepared Zn and SiO composite by HEMM and subjected to heat treatment at 900˚C. Evaporated Zn induced mesopores in the composite material. The boiling temperature of zinc leads to partial reduction of SiO. Carbon incorporation in the porous SiO_x further improved the electrochemical performance of the SiO_x/C composite electrode. The porous structure was conducive to improving cycling stability [88].

Aluminum is another active metal in use to prepare SiNP and its composites. Aluminum acts as a reducing agent for amorphous silica. The reaction time and temperature (600˚C - 900˚C) are carefully controlled that SiO_2 is only partially reduced to yield SiO_x and Si core embedded in a carbon framework. The basic reaction is

$$3SiO_2 + 4Al \rightarrow 3Si + 2Al_2O_3$$

Porous SiO_x@C Composites have been synthesized from rice husk by aluminothermic reduction at 700˚C in 2016 [89]. In another investigation aluminothermic reduction was combined with hydrolytic polymerization and carbon coating to obtain SiO_x/Si/C nanocomposites. The SiO_x/Si/C anode material displayed a high specific capacity and excellent cyclability (1355 $mAhg^{-1}$ at 0.2 Ag^{-1} after 350 cycles). The nanocomposite had excellent structural stability. It could preserve 78.11% of its original structure after 350 cycles [90].

The carbothermic reduction process has often been combined with sol-gel process and the reduction process is carried out at high temperatures. Spherical SiO_2 powder was synthesized using TEOS as the starting material to obtain SiO_x powder in one study [91]. Homogenously dispersed micro/nano structure of SiO_x/C has been reported by another group after carbothermic reduction of silica-carbon binary xerogel. The synthesized SiO_x/C anodes have high electrochemical perfor-

mance [92].

Chemical reduction processes-magnesiothermal and carbothermic reduction are elevated temperature processes, 600˚C - 900˚C and 800˚C - 1500˚C, compared to hydrothermal, alumino assisted zincothermal and aluminothermic processes. However, it often involves carbonization which is another high temperature process. All these reduction processes have slow reaction kinetics, and the energy consumption is high. Occurrence of side reaction, large amount of heat generation during the reaction process and long synthesis time are other negative aspects. The resulting elevated temperature leads to agglomeration, disappearance of pores and formation of impurities [53] [54] [71] [72].

c) Sol-Gel method

The Sol-Gel method is comparatively mild method for preparing silicon oxides. The reaction conditions are mild, and synthesis can be executed at low temperature in solvents. Silicon organic compounds are disseminated in solvents as precursors. It is then hydrolyzed and polymerized to generate gels with certain spatial structures [53]. SiO_x can be produced directly in the solution by hydrolytic condensation of orthosilicate easters such as tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS) [71] [72]. Improved electrochemical performance of the LIB has been reported with the electrode prepared by sol-gel method [93]-[97]. A 30% improvement in the capacity of LIB was demonstrated by incorporating a C/SiO_x nanocomposite electrode having a SiO_x nanoparticle loading of 15 wt%. The synthesized C/SiO_x electrode had a reversible capacity of 383 $mAhg^{-1}$, and the charge discharge cycle exhibited 84% capacity retention after 100 cycles [93]. Unique structures can also be prepared using the sol-gel method [93]-[97]. In one study, a solvent-free, mass producible strategy was developed to prepare carbon encapsulated $SiO_x/C@C$ nanocomposites utilizing sol-gel, ball milling, and CVD processes. The nanocomposites thus formed exhibited superior performance as LIB anodes [97].

Sol Gel process yields porous SiO_x allowing precise control on pore size and volume. Exceptional *in-situ* molecular carbon blending and flawless carbon wrapping are possible. The main constraints are the expensive raw materials used in the sol-gel process, some of the organic compounds in use are harmful to health. Long synthesis time is another constraint. The reaction conditions require strict regulation to attain the required composition and structure of SiO_x. When combined with the ball milling process, additional complexities associated with ball milling arise [93]-[97].

3.4. Other Methods

Other methods-Chemical etching [53] [98]-[100], disproportionation [69] [101]-[103], and electrochemical methods [104] have also been employed by several research groups to achieve SiO_x and their composites.

Acid or Alkaline leaching of rice husk by NaOH or KOH for extraction of silica is reported by several authors [24] [53] [98]-[100]. Heat treatment of rice husk

followed by alkaline/acid leaching has been reported as another effective method to prepare C/SiO_x anodes. In one study, C/SiO_x was produced by heating rice husk in a tubular furnace at 600˚C for one hour under N_2 gas flow at 1 L·min^{-1} and then immersing the pre-carbonized rice husk in NaOH solution. By adjusting the immersion temperature and time, different SiO_x content were achieved for C/SiO_x anodes of LIB. Half coin cell studies indicated initial CE decreased with decreasing SiO_x content. More experiments with different SiO_x content proved that the SiO_x is helpful for increasing the specific capacity of C/SiO_x active material. Prelithiating the C/SiO_x anode displayed a stable anodic operation. Full cells consisting of prelithiated C/SiO_x anode and a Li ($Ni_{0.5}Co_{0.2}Mn_{0.3}$) O_2 cathode exhibited high ICE (initial coulombic efficiency (~85%)) and high discharge specific capacity displaying the maximum performance of the cathode (~150 $mAhg^{-1}$). The specific capacity retention increased with higher SiO_x content at increased current density. This is another elevated temperature method and needs long processing time [99]. Recently NF3 flourination has been reported to design yolk shell structured CNT/SiO_xF_y/C composites for Si-based anodes [100].

Disproportion reactions have an edge over other processes due to facile, and large-scale synthesis of SiO_x/C composites. The low electrical conductivity, low (ICE) and volume expansion issues have been successfully addressed with prelithiation, carbon coating and nanostructure designing. Porous, ultrapure SiO_x NP with good control on morphology has been produced by this method. A high reversible capacity and excellent electrochemical performance of the SiO_x/C anode have been reported by researchers [69] [101]-[103].

However, disproportionation reactions are very high temperature, complex processes. It is often combined with HEMM and CVD for large scale production of SiO_x/C [53].

A facile synthesis of SiO_x NP (nanoparticles) for mass production has been proposed by electrochemical anodization of Si electrodes with an adjustable oxygen content. The process involves the application of a strong electric field near the surface of Si electrode to directly convert the Si electrode to SiO_x NP. The study is focused on analysis of SiO_x NP oxygen content and size. Application of the SiO_x NP in LIB is proposed, not investigated [104].

To avoid toxic organic solvents and reduce the long processing time, laser induced SiO_x (LI-SiO_x) layer derived from commercial adhesive tape has been studied by one group. The homogenous, porous SiO_x layer was directly deposited over the current collector electrode. They report an improved performance with the SiO_x coating in lithium metal batteries with a zero-excess ("anode free") configuration and verified 100% improved performance [105].

HEMM, metallothermic reduction and metal assisted chemical etching (MACE) are cost-effective and scale to mass manufacturing. However, these methods have less control on particle size distribution, internal uniformity and oxygen distribution in SiO_x.

Thermal Disproportionation, CVD, PECVD and sol-gel reactions have excellent control on particle morphology and uniform nano silicon dispersion within

the oxide matrix. Carbon coating is very uniform. Thermal Disproportionation has high yield also. Production of high-quality material at large scale makes them suitable for industry.

Presently, thermal disproportionation, combined with mechanical milling and CVD carbon coating is the main synthesis route for SiO_x in industry. By vaporization and condensation of a mixture of raw Si and SiO_2 powder in vacuum reactor at 1400˚C, crude condensate is produced. Mechanical milling is the next step for pulverizing the crude condensate followed by CVD for carbon coating [45] [53].

Each synthesis method has its own characteristics as presented in **Table 1**. Choices are made based on the specific experimental environment and requirements. For mass production, high yield of high-quality material is the first and foremost requirement with affordable cost and safety concerns.

Table 1. Synthesis methodologies.

Synthesis Methods	Temperature	Advantages	Challenges	References
Thermal Evaporation	Elevated temperature and pressure	Good morphology, dense, continuous films of nanometer precision, oxygen content is highly homogenous.	Expensive, slow process, coating uniformity fails on complex, 3D structures, requires ultra-high vacuum control.	[22] [45] [53]-[56] [71] [72]
Mechanical Ball Milling	Room temperature	Facile and scalable synthesis, submicron scaling, conductivity enhanced via composite blending, Low cost and high efficiency. High yield.	Very slow process, high energy consumption, agglomeration and heat generation. Patchy to non conformal layers of carbon coating. Less control over internal uniformity and specific oxygen distribution in SiO_x.	[22] [45] [53] [54] [63]-[72] [97]
PVD	Low Temperature	Low cost, porous structure, good morphology, 1D nanoscale thin film of SiO_x with precise thickness control, uniform carbon coating, enhanced structural integrity, tunable suboxides, high purity.	Slow deposition rates, high equipment costs. Agglomeration possible, Poor conformal coating on 3D, Intrinsic bulk remains insulating, Film thickness is limited.	[22] [45] [53] [54] [57]-[61] [71] [72]
CVD	High temperature	Good control on film properties, high purity, high nano structure precision, uniform nano silicon dispersion within the oxide matrix, very uniform carbon coating.	Expensive complex equipment. High production costs. Lower production throughput, higher energy consumption.	[22] [37] [45] [53] [54] [62] [71] [72]
PS-PVD	Very High Temperature, High pressure.	High deposition rate. 0D-3D structures, good control on film density and thickness, good stoichiometry. Excellent self-assembling core-shell structures.	Complex process, strong secondary particle aggregation, high sensitivity to gas flows and local oxidation.	[22] [45] [53] [54] [58] [71] [72]

Continued

Chemical etching	Low temperature	Temperature and precise structure control, micro size with internal nano pores, highly reactive surfaces for coating, excellent ion diffusion, surface level oxygen tunability.	Localized fracturing and brittle structure, high SEI resistance, High risk of runaway native air oxidation.	[22] [53] [54] [71] [72] [98]-[100]
Disproportionation	Very High temperature	Facile, cost effective, large-scale synthesis, high yield, Excellent control on particle morphology, uniform nano silicon dispersion within the oxide matrix, Sub-10 nm active clusters of Si, oxygen content and conductivity excellent, stable structure.	unwanted reaction byproducts. Over sintering and domain growth at >1100˚C Low ICE due to large irreversible Li^+ consumption, capacity fading.	[22] [29] [53] [54] [69] [71] [72] [101]-[103]
Hydrothermal	Low temperature process (180˚C)	Facile process and nanoscale controllable morphology, excellent carbon coating and oxygen tuning for solution-based core shell wraps.	Severe agglomeration during drying, Invisible, slow preparation process, requires separate calcination for good conductivity, trapped -OH impurities cause Low ICE, Low yield.	[22] [53] [54] [71]-[76]
Magnesio-thermal	650˚C and above	Low cost, scalable, porous matrix, 1D, 2D and 3D nanostructured architectures of SiO_x.	Inhomogeneous product, Violent heat process, high SEI resistance, poor surface conductivity, rapid capacity fading, less control on particle size distribution, internal uniformity and oxygen distribution in SiO_x.	[22] [53] [54] [71] [72] [77] [80]-[87] [103]
Alumino-thermic	Low temperature (300˚C)	Low cost, scalable, facile synthesis, ultrathin,2D hierarchical porous structure.	slow process, high energy consumption, less control on particle size distribution, internal uniformity and oxygen distribution in SiO_x.	[22] [53] [54] [71] [72] [89] [90]
Zinc-thermic	Low temperature	Porous structure	Slow reaction kinetics, High energy consumption. less control on particle size distribution, internal uniformity and oxygen distribution in SiO_x.	[20] [22] [53] [54] [71] [72] [78] [88]
Sol-Gel	Low temperature, 180˚C	Homogenous, facile liquid environment, fine particle size, particle shape control, High yield. Carbon coating is very uniform. High safety.	Toxic, high-cost solvents, solvent waste and shrinkage during drying.	[20] [22] [26] [53] [54] [71] [93]-[98]
Electrochemical anodization	Room temperature process	Highly controlled method.	High-Cost, complex process.	[104]

4. Strategies to Enhance the Electrochemical Performance of SiO_x Anodes

Structural modifications and Surface Engineering

SiO_x is a mixture of Si and SiO_2 and some metastable silicon oxides, so the specific capacity of SiO_x is also between the specific capacity of SiO_2 (1600 $mAhg^{-1}$) and Si (4200 $mAhg^{-1}$) [53]. The volume expansion of SiO_x is much lower than elemental silicon due to the different lithium intercalation mechanism attributable to the change of silicon species [72]. However, it still has a volume expansion of more than 160% and the addition of oxides end up in poor electrical conductivity. Structural variation during cycling limits its electrochemical performance [106]. Particle crushing and pulverization during cycling are the issues that remain to be addressed. Good material design is required to effectively enhance performance [106]-[109]. Quite a few *in-situ* and *ex-situ* measurements and characterization techniques (e.g., XRD, XPS, TEM, NMR, SEM, etc.) have been employed to understand the structural changes and reaction kinetics during the lithiation-delithiation process [110]-[112].

Various strategies have been employed to improve the electrical conductivity of SiO_x to enhance the cycling stability and electrode capacity. To mitigate the volume expansion and improve the conductivity, coatings such as carbon, graphene, carbon nanotubes (CNT), Titanium dioxide (TiO_2), SnO_2 and polymers have been in practice. Hollow structures and multilayers with coating, structural confinement, and embedded structures have been designed [101] [106] [113]-[119]. Carbon coating, doping and composite formation have been effective approaches and are often combined with nanostructure designing and surface engineering of anode material [114]. Carbon coating slows down the volume expansion of Si based electrode and improves electrochemical performance by forming a stable SEI [53] [59] [106] [114]-[116]. Structural modifications with coating [94] [117] [118] and doping [30] [120] [121] have been, therefore, the most effective approach to enhance the electrochemical performance of Si-based anodes. The designing strategies, advanced characterization techniques and approaches to identify and circumvent capacity decay mechanisms have been well documented and discussed by many research groups [110]-[112] [114]-[121].

4.1. SiO_x/C Composites

4.1.1. Role of Carbon Coating

The formation of Li_2O and lithium silicates counteract volume expansion of SiO_x. However, it lowers the ICE of SiO_x, leading to poor electrochemical performance. Incorporation of carbon is an effective strategy to mitigate the large volume expansion of SiO_x and improve the electrochemical properties. Carbon is an ideal coating material that has high conductivity with controlled morphology and easy synthesis [114]. The combination of carbon is the most common modification method to improve the electrochemical properties of SiO_x based anodes. However, carbon is unstable at high temperature and forms silicon carbide. The difference

in morphology between SiO_x and carbon also results in poor contact [53]. Extensive research has been carried out to resolve these issues. Currently, carbon coated SiO_x/C composites [29] [31] [33] [95] [97] [106] [122]-[125], embedded SiO_x/C composites [126] hybrid SiO_x/C composite [127]-[129] and micro/nanosized SiO_x/C composite [89] [90] [99] [102] [106] [125] [126] [130] [131] anodes are in practice.

Coated SiO_x/C refers to composites where the SiO_x particles are coated with a protective carbon layer. Carbon reduces direct contact between electrolyte and active substances. It buffers the volume expansion of lithium intercalation, thereby inducing a stable SEI film. Depending on the various designs, porous, core shell [17] [87] [95] [130], yolk shell [79] [132], carbon nanotubes (CNT) [100] [101] [118] [132]-[134] etc. an improved cycling performance has been reported [17] [53] [54] [72] [86] [87] [115] [122]. It is noteworthy that co-doping with heteroatoms of greater electronegativity and electron affinity, such as C, N, F, SP, B further improves the stability and efficiency of the SiO_x anode [31] [72] [100] [101] [113] [114] [121]. Doped carbon coated SiO_x [135]-[140] and carbon coated doped SiO_x [141] [142] material are the two approaches leading to improved electrochemical performance of the anode material.

Doped carbon layers enhance the electrical conductivity of SiO_x buffering the volume variation of SiO_x thus preventing the structural degradation of the composite material. Nitrogen doping has been most extensively applied. In one study, the SiO_x@NC displayed high reversible capacity (774 $mAhg^{-1}$), ideal rate capability, and long-term durability (112% capacity retention over 500 cycles) [135]. Recent studies report enhanced lithium storage performance of nitrogen enriched lignin carbon/SiO_x composites. The anode material was synthesized via a novel co-precipitation and selectively etching approach. The prepared NEC@LC-SiO_x exhibited excellent performance. A high reversible specific capacity of 802 $mAhg^{-1}$ and outstanding rate capability was observed [136]. Recent study has been conducted on Si/SiO_x structures with fluorine doped carbon. The Si/SiO_x@F-C electrode delivered promising electrochemical performance [137].

Co doping with multiple heteroatoms further enhanced the electrochemical performance of the composite anode. Co-doping into the C matrix provides additional active sites and defects leading to improved reactivity, rate capacity conductivity, and Li^+ storage capacity of the material [138]-[140]. Synthesized from rice husk through a simple calcination approach, the as-fabricated SN@C/SiO_x demonstrated high reversible capacity (1150 $mAhg^{-1}$ at 0.1 Ag^{-1}), improved initial coulombic efficiency (CE) of 70.4%, outstanding rate capacity, and long-life cycling stability (632 $mAhg^{-1}$ under 1.0 Ag^{-1} over 1200 cycles) [138]. In another study micron sized SiO_x encapsulated in B, N co doped carbon nanotubes exhibited ultra-high capacity [139].

However, carbon coating is beneficial if the layer is thin. The addition of too much carbon reduces the specific capacity of the material. Therefore, introducing as little carbon as possible that matches the material particle size and gives a uni-

form morphology is especially important. Other negative aspects are the requirement of complicated, multistep high temperature processes [53].

Embedded and hybrid SiO_x/C composites.

Embedded SiO_x/C composites and hybrid SiO_x/C composites embed the amorphous SiO_x nanoparticles in a carbon matrix. The highly dispersed SiO_x offers plentiful active sites for Li^+ storage. The carbon matrix provides a transport network for Li^+ and electrons and buffers for volume expansion. SiO_x/C composites exhibit better electrochemical performance and fast Li^+ diffusion kinetics. Recent investigations carried out on embedded SiO_x/C composites demonstrate excellent electrochemical performance, low charge resistance with fast diffusion kinetics [114] [131]-[134] [139]. Researchers emphasize that encapsulation of micron sized SiO_x particles into 3D B, N co doped carbon nanotube via metal-cation assisted carbonization guaranteed slight volume variation during cycling, fast Li ion and electron transfer and electrolyte diffusion [139]. The authors report further enhancement of the lithium storage capacity when heteroatomic active sites were introduced with Sn, B, N carbon nanotubes. When the silicon sub oxide co-doped boron, carbon nanotube (SSBCN) composite material was utilized as anodes in LIB half cells, it displayed ultrahigh reversible capacities of 2072.8 $mAhg^{-1}$ at 0.1 Ag^{-1}, a very high-rate performance of 501.8 $mAhg^{-1}$ at 10 Ag^{-1} and excellent long-term cycle stability of 400 and 1000 cycles at 1 and 5 Ag^{-1}, respectively. Moreover, SSBCN/$LiFePO_4$ (LFP) full batteries exhibited remarkable cycle durability with a 92.72% capacity retention after 600 cycles at 1 C [139].

Nanosized SiO_x/C composites

Nanosized SiO_x/C composites are beneficial offering more space to accommodate the volume stress due to their unique size. However, they would create more interparticle space and surfaces leading to low tap density and low volumetric capacity, not suitable for high density LIB [53] [54]. To address these issues micro sized SiO_x based materials with nanostructure characteristics have been investigated. The micro-nano sized SiO_x/C composite material could be synthesized by integrating nano SiO_x with micro-sized carbon matrix [140]-[144]. Studies revealed that it effectively alleviated the inherently low electron/Li^+ conductivity and improved the structural integrity of SiO_x. The assembled SiO_x/NC-2/$LiFePO_4$ full cell exhibited a capacity retention of 89% after 350 cycles at 2 C [140]. In another investigation, micro-nano structured SiO_x/C composites were synthesized by carbothermal reduction of silica carbon binary xerogel. The micron sized SiO_x/C spheres were found to be composed of many near spherical nanoparticles. The structures exhibited a high reversible capacity of 830 $mAhg^{-1}$ for 100 cycles and excellent rate capability [92]. In another investigation sub nanoscopic SiO_x/C composites prepared by heating precursor liquid in a sealed vessel at high temperature exhibited excellent performance. The SiO_x/C consisted of homogenously dispersed SiO_x and free carbon in SiO_x/C spheres. The structure exhibited 96.1% capacity retention after 400 cycles, outstanding rate performance (146.2 $mAhg^{-1}$ at 10 Ag^{-1}) and high specific capacity of 1667.3 $mAhg^{-1}$. A high areal capacity of

2.6 - 2.0 mAh·cm^{-2} during cycling promises practical applications [143].

Homogenous dispersion of spherical SiO_x and free C components on the atomic scale is the key requirement for preparation of SiO_x@C microspheres with nano structures or sub nanoscopic structures. Such dispersion accommodates the volume change and ensures high electrical conductivity. It could be an effective strategy for implementation of micrometer size electrode materials in practical battery systems. The commercial scale production aspect is being explored as well [53] [115] [139] [140] [143]-[146].

4.1.2. Metal Doped; Carbon Coated Structures

As discussed in the previous section, doped carbon materials enhance the electronic conductivity of SiO_x/C composites. Co-doping with heteroatoms of N, P, B, and S has already been discussed in the previous section. Doping SiO_x or carbon with metals is also in practice. Metals like Mg, Sn, Fe, Ni, Mn, Ti have been reported to enhance the electrochemical performance and structural integrity of SiO_x/C anodes materials and reviewed [147]-[153]. SiO_x/iron/nitrogen co-doped carbon (Fe-N-C) microspheres were synthesized using electrospray-carbonization strategy. Studies indicated that Fe doping contributed to advanced electrochemical reaction and storage reversibility of the anodes [151]. Recent studies establish the superiority of Mg doped carbon coated SiO_x anodes over the carbon coated SiO_x without Mg doping. Researchers utilized magnesio-thermic reduction to prepare Mg doped carbon coated SiO_x anode material. The capacity of SiO_x was improved to 1477 mAhg^{-1} with a minimal compromise in the ICE (83.77%). The enhanced electrochemical performance was attributed to the synergistical modification of both Mg doping and prelithiation [148]. High ICE, high specific capacity and cycling stability of premagnesiated anodes, C@M-SiO_x has been reported by another group with its commercialization aspects [150].

An extensive study of the role of carbon material on the electrochemical performance of SiO_x/C composites indicates a dual role of carbon. It enhances the conductivity of the SiO_x/C composite and helps retain the integrity of the SiO_x/C anode during lithiation/delithiation process. The lithium storage capacity differs based on the carbon morphology, architecture, and properties. Researchers have established that carbon nanostructure differs based on the carbon source and type [114] [115] [145] [154].

4.2. Porous Structures

Carbon cladding provides an attractive option to alleviate volume expansion and low electrical conductivity of SiO_x. Research shows that the effectiveness of carbon encapsulation is limited. 0D, 1D, 2D nanoscale SiO_x/C structures mitigate the issues of low electrical conductivity and high-volume expansion [30] [39] [53] [54] [72]. However, these structures have an adverse effect on mass transfer processes within the electrode after prolonged cycling due to accumulation of the material. 3D SiO_x/C porous structures are designed to circumvent this issue [145] [146]. Porous structures provide plenty of space to buffer the volumetric stress during

the cycling of SiO_x/C anodes [72] [88] [98] [100] [128] [146] [155]-[165]. A nanoporous material has pore size ranging from 1nm to 100nm or smaller according to IUPAC. Following IUPAC, porous materials can be divided into microporous (pore size < 2 nm), mesoporous (pore size between 2 - 50 nm) and macroporous (pore size > 50 nm) material depending on the size of the pores. Porous SiO_x/C structure can be porous SiO_x, Si/SiO_x/C or combination of SiO_x and a porous framework, mostly porous carbon [72] [154]-[167].

3D-ordered honeycombs like macroporous SiO_x/C structures have been extensively investigated by researchers. [156] [157] Unlike the 0D - 2D structures, these 3D honeycomb like structures offer plenty of active sites for lithiation/delithiation process for a stable SEI after prolonged cycling. Carbon coating alleviates volume expansion and enhances electrical conductivity. It alleviates electrode pulverization. The synthesis process of 3D honeycomb structure is also simple, based on wet chemistry and CVD. Quite a few studies are carried out on full cell structures [154] [156] [157].

The most recent study proposes encapsulation of SiO_x in a joint structure of carbon shell and carbon nanotube with excellent electrochemical performance. LPCVD and spray drying were employed to construct the composite anode material. On half cells, the anode SiO_x@C@CNTs exhibited excellent cycling stability (624.7 $mAhg^{-1}$ after 1000 cycles at 2 Ag^{-1}) and rate performance (790.3 $mAhg^{-1}$ reversible lithium storage capacity at 4 Ag^{-1}). Full cell study with SiO_x@C@CNTs anode and NCM 811 cathode material provided a substantial energy density of 401.8 $Whkg^{-1}$ with excellent cycling stability of 134.8 $mAhg^{-1}$ after 100 cycles at a rate of 1C. The capacity retention rate was 80.7% [161].

The porous SiO_x/C structures-macroporous, mesoporous, and nanoporous SiO_x/C structures, provide large surface area with an abundant number of pores for Li^+ transportation leading to improved rate performance and cycling stability. Other than pore size, various other pore properties, such as pore structure, pore alignment, specific surface area, symbiosis, and defects influence the performance of the porous SiO_x/C anodes [156]-[170].

Material cost and tap density are the two main concerns for commercialization. Though nanosized porous structures have the advantage of mitigating the volume expansion, excessive specific surface area and side reactions result in low ICE of the anode. The low tap density is another disadvantage limiting practical applications. Micro sized porous material with nano characteristics is therefore best suited for production of composite anodes [171].

Recent research proposes a novel SiO_x/G/C composite with SiO_x nanoparticles, graphite, and carbon nanotube. The structure was achieved by a simple ball milling and annealing process [169]. The dual carbon framework connection with SiO_x via C-O-Si bonds offered enhanced reaction kinetics with reduced volume fluctuations. Excellent cycling stability and performance rate were demonstrated by the composite anode. A capacity retention of ~700 $mAhg^{-1}$ over 500 cycles at 1.0 Ag^{-1} was observed. In a full-cell configuration (SiO_x/G/C//$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$),

this system exhibited a reversible capacity of 113 $mAhg^{-1}$ over 100 cycles at 1.0 $mA{\cdot}cm^{-2}$ emphasizing its superior performance.

Another group recently reported fabrication of porous Si/SiO_x assembled microspheres interweaving CNT network (CNT/SFDP-Si/SiO_x@C microspheres) utilizing bottom-up inverse water-in-oil microemulsion method and magnesiothermic reduction. Silica fume (SF), an industrial byproduct or solid waste of the manufacture of silicon metal and ferrosilicon alloys was added as the precursor to form nano-Si. The particle size of SF ranged from 50 nm to 250 nm. N doped outer carbon shell improved the electronic conductivity and induced the formation of stable SEI to enhance the overall structural integrity [170]. The approach was facile compared to yolk-shell or core-shell structure fabrication methods. The structure had an excellent electrochemical performance. A long cycling lifespan with a reversible capacity of 675.8 $mAhg^{-1}$ after 1000 cycles at 2 Ag^{-1} was achieved. A very small decay rate per cycle of 0.018% was observed with a high-rate performance. The prelithiated $LiFePO_4$||CNT/SFDP-Si/SiO_x@C full cell performance was also analyzed. It exhibited the reversible capacity of 129.4 mAh g at 0.2 C.

Synthesis of porous structures:

Porous SiO_x-based structures can be either porous SiO_x or SiO_x with a porous carbon shell. The synthesis of porous SiO_x can be divided into two groups. The top-down type of porous SiO_x prepared by etching technology and the bottom-up type of porous SiO_x formed by weak interaction self-assembly according to the different construction strategies. Therefore, there are different preparation processes such as etching, template-assisted method, chemical exfoliation and treatments etc. [53] [54]. Most of the synthesis methods to prepare porous SiO_x are based on magnesiothermic reduction methods. Recently, low temperature zincthermal reduction has been utilized to fabricate porous SiO_x@C (pSiO_x@C) composites. When the pSiO_x@C composite material is used as an anode in LIB, it displayed stable cyclic stability even after 1300 charge/discharge cycles at 0.3 Ag^{-1}, and superior rate capability even at a high current density of 3.0 Ag^{-1}. Full cells exhibited superior Li-ion storage attaining a high reversible capacity of 147 $mAhg^{-1}$ at 0.2 Ag^{-1} [171].

These synthesis methods have been discussed earlier in Section 2.3.

Porous 3D SiO_x/C structures successfully mitigate large volume expansion and have long cycle life. However, there are challenges at industrial scale production as wet processes like magnesiothermic reduction, hydrothermal reduction, Aluminothermic or zinc thermic reduction have achieved small scale production.

Another porous structure is SiO_x encapsulated in a porous carbon shell [139] [155] [156] [160] [162] [172]. Biomass carbon is the potential source for large scale synthesis [77] [128] [138] [140] [173]. Researchers have successfully utilized bamboo charcoal to produce porous carbon shell embedded SiO_x composite anode for LIB. The synthesis followed a top-down route [70] [152] [159] [160]. Catkins derived, N, P co doped, SiO_x/C nanosheets (N/P-SiO_x/C-Nss) architecture

exhibit ultra long cycle life with about 340 $mAhg^{-1}$ and almost no capacity decay after 10,000 cycles at 10 Ag^{-1}. The studies utilized chemical exfoliation and treatments to fabricate the anodes [172]. In the most recent work, mesoporous SiO_x@C spheres (m-SiO_x@CS) were encapsulated in a three-dimensional ordered macroporous carbon (3DOMC) framework. Sol-gel and soft templating methods were utilized to obtain the nanocomposite (3DOMC/m-SiO_x@CS). The anode thus prepared displayed excellent structural stability, electrochemical performance, and cycling stability. A comparison with some other SiO_x/C anodes has been presented by the authors in Tab. S4 and Tab. S5 [173] presented here as in **Table 2** and **Table 3**.

Table 2. Comparison of the rate performances of the 3DOMC/*m*-SiO_x@CS electrode with previously reported SiO_x-based electrodes.

Electrode	Rate capability	
3DOMC/*m*-SiO_x@CS (this work)	861.5 mAh· at 0.1 Ag^{-1}	121.1 $mAhg^{-1}$ at 5 Ag^{-1}
SiO_x/C[4]	670 $mAhg^{-1}$ at 0.05 Ag^{-1}	69 $mAhg^{-1}$ at 5 Ag^{-1}
(SiO_x/G/SnO_2)@C[5]	490 $mAhg^{-1}$ at 0.1 Ag^{-1}	100 $mAhg^{-1}$ at 2 Ag^{-1}
SiO_x/C[6]	642 $mAhg^{-1}$ at 0.05 Ag^{-1}	299 $mAhg^{-1}$ at 1.5 Ag^{-1}
SiO_x/graphite[7]	430 $mAhg^{-1}$ at 0.1 Ag^{-1}	150 mAg^{-1} at 1.2 Ag^{-1}
SiO_x/C[8]	610 $mAhg^{-1}$ at 0.1 Ag^{-1}	238 $mAhg^{-1}$ at 1.2 Ag^{-1}
SiO_x/C-rGO[9]	676.9 $mAhg^{-1}$ at 0.1 Ag^{-1}	234.4 $mAhg^{-1}$ at 1 Ag^{-1}
TiO_2/SiO_x/C[10]	510 $mAhg^{-1}$ at 0.0335 Ag^{-1}	61 $mAhg^{-1}$ at 3.35 Ag^{-1}

Table 3. Electrochemical performance comparison of the 3DOMC/*m*-SiO_x@CS electrode with previously reported SiO_x-based electrodes.

Electrode	Current density (Ag^{-1})	Cycle	Capacity after cycles ($mAhg^{-1}$)
3DOMC/*m*-SiO_x@CS (this work)	1	2000	488.1
SiO_x/C HSs[11]	1	1000	469.2
SiO_x/G/C[12]	0.1	500	487
SiO_x/BNCNTs[13]	0.2	100	660.6
YSG-SiO_x/C@C[14]	0.2	150	680
SiO_x/C@CNTs[15]	0.1	200	702
MRH-SiO_x/C[16]	0.5	150	392.91
SiO_x@ZrO_2@C[17]	0.5	500	412.9
SiO_x@C[18]	1	400	506.9
B-SiO_x/CNT@LBO[19]	1	300	532.3

Reproduced from Ref. [173] with permission from American Chemical Society.

Ongoing research on porous structures based SiO_x anodes establishes their superiority over other anodes. However, the etching methods involve expensive toxic chemicals. On the other hand, the sacrificial template approach remains a challenge for industrial scale production due to the complex processes involved and high production cost [53] [54] [113].

Recently, solvent free approaches to developing SiO_x/C anodes have also been explored [97] [174] [175]. Though the approach offers reduced cost and less en-

vironmental impact, inhomogeneous mixing of SiO_x nanoparticles within the carbon matrix, limited control on the particle size of SiO_x nanoparticles, and controlling the morphology of SiO_x/C composites remains the key challenges [53] [97] [169] [176].

4.3. Surface Modification with Metal Oxides

Carbon coating buffers the volume change of SiO_x, improves the conductivity of the material as well as its electrochemical performance. However, carbon layer diffusion to Li^+ is limited, hindering the formation of stable SEI [107] [113]. The surface modification with metal oxides reduces the direct contact of the SiO_x core and the electrolyte, thereby reducing the consumption of Li^+ ion to form stable SEI [23] [72] [107] [153] [167]. Therefore a promising surface modification strategy is to combine hybrid coating with transition metal oxides [96] [119] [153] [174] [177]-[184] or other metal oxides [185]-[190]. Nanostructured transition metal compounds with high specific surface area and appropriate pore size distribution display high ion diffusion coefficients suitable for Li^+ diffusion in SiO_x leading to improved electrochemical performance [174]. One group synthesized a 3D hierarchical SiO_x@C@CoO mosaic structure nanosheets via high energy ball milling and hydrothermal reduction process. The electrode material displayed good cyclic performance with a reversible discharge capacity of 1079 $mAhg^{-1}$ over 250 cycles at a current density of 1 Ag^{-1}. It also exhibited an excellent rate capability (with an average specific reversible discharge capacity of 777.8 $mAhg^{-1}$ at 2000 mAg^{-1} and 480 $mAhg^{-1}$ at 5000 mAg^{-1}). The improved performance is attributed to the specific structure and the synergistic effect between the two materials [177]. In another study, sponge-like structures of SiO_x@C@CoO, were synthesized via spray drying and electrostatic self-assembly strategy. The novel design containing ultrathin nanosheets of CoO on SiO_x@C improved the conductivity of SiO_x, shortened the diffusion length and provided large surface area for enhanced Li^+ diffusion. Moreover, the sponge like structure successfully accommodated the large volume change of SiO_x. An improved and stable electrochemical performance was observed during the charging/discharging process with the multifunctional composite anode. When employed in half cells, a reversible specific capacity of up to 1287 $mAhg^{-1}$ at a current density of 0.1 Ag^{-1} and retaining 714 $mAhg^{-1}$ after 750 cycles at 1 Ag^{-1} with a capacity retention of 98.9% was observed. The full pouch-type cells, employing $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM 811) as the cathode, exhibited an excellent reversible capacity of 206 $mAhg^{-1}$ and a long-term cycling stability with a capacity retention of 85.9% after 200 cycles [178]. Similarly, TiO_2 coating has been an efficient and feasible strategy to effectively improve the electrochemical performance of SiO_x based anodes. TiO_2 has strong mechanical stability, favorable electronic conductivity and ionic conductivity properties contributing to efficient charge transport within the material leading to small volume change in SiO_x electrode after lithium insertion. Synthesis routes ranged from sol-gel deposition/carbonization methods, ball-milling and surface coating during electrospinning to

CVD [96] [119] [174] [179]-[181] [184]. Hierarchical mesoporous structures with hybrid MnO-SiO_x@C microspheres, obtained via spray pyrolysis and subsequent annealing, proved to effectively enhance the cyclic stability and rate performance of SiO_x anode. Researchers concluded that the Mn_2SiO_4 phase was attributed to the improvement of structural stability [182]. It is crucial to highlight that multi-layer coatings are more effective in mitigating the volume change of SiO_x. A double-coated composite structure exhibited improved cycling performance. Synthesized by elevated temperature heat treatment, the double layer composite SiO_x/C/Cu_2O exhibited excellent long-cycle ultra-high stability [183]. Similarly, dual-shell SiO_x/C@Sn@NC anode exhibited excellent lithium storage ability. A combination of the hydrolysis method and polymer coating technology was utilized to synthesize the hybrid material. SEM and TEM analysis confirmed the uniformly layered, coated structure with clear lattice stripes of Sn and N-doped amorphous carbon on the outermost layer [185]. Ternary composites with Tin (IV)oxide, SiO_x@SnO_2@C [187] and (SiO_x/G/SnO_2)@C [188] displayed high lithium-ion diffusivity and lower volume expansion. In a comparative study of dry coated SiO_x/C with metal oxides, Al_2O_3-coated SiO_x/C anodes also displayed improved electrochemical properties [186]. Researchers have obtained SiO_x/MgO/Mg_2SiO_4/C composite anode material after magnesium thermal reduction and carbonization. The material effectively maintained structural integrity during cycling leading to improved electrochemical performance of the SiO_x anode [189]. Double layered SiO_x/Mg_2SiO_4/SiO_x composites also displayed enhanced ICE and good control on volume expansion [190].

Single layer carbon coating of the SiO_x material is always beneficial and universally accepted practice. Adding multiple layers gives rise to additional complexities at manufacturing level affecting the cost-effective processes.

4.4. Doped SiO_x

To counteract the volume expansion problem of SiO_x anode, there are two widely studied approaches 1) Nanosizing SiO_x particles [23] [24] [45] [53] [54] [72] [113] [120]; 2) Doping with heteroatoms, metals, and carbon [31] [140] [147] [148] [150] [173]. The first approach uses the internal void space to Si and SiO_x structures to expand and contract without disrupting the connection between the particles. The second approach helps achieve better conductivity than SiO_x as the atoms replace some of the silicon atoms in the structure or occupy interstitial positions in the material. It modifies the physical and chemical properties of the material and establishes a stronger skeleton structure [176] [191]. Non-metallic doping as well as metal atom doping improve the performance of SiO_x material. Non-metallic dopants significantly alter the surface chemistry of SiO_x making it more stable during charge/discharge cycles. A finer control over the chemical and electronic properties of SiO_x can be achieved with non-metallic dopants without the fear of unwanted metal oxide formation [153]. On the other hand, certain metal dopants, like Ni, Ti, Fe, or Mg can enhance the Li^+ diffusion kinetics and mechan-

ical stability of the 3D doped SiO_x framework [147] [148] [152]. Studies carried on Al doped 3D Si/SiO_x porous structures confirm good structural stability, buffered volume change, and increased cycling life of the anodes [191]. In another investigation, porous $SiO_x@Li_2SiO_3/C$ composites were synthesized by one pot carbonization method. The hierarchical porous structure displayed improved electrochemical performance [192]. Co-modification with carbon and lithium borate hybrid coating simultaneously improved the electronic and ionic conductivity of SiO_x. The alloy type anode structure $SiO_x@C@Li_3BO_3$ displayed superior cycling performance (81% capacity retention after 500 cycles at 1 Ag^{-1}). The enhanced electrochemical performance is attributed to the synergistic effect of carbon and Li_3BO_3 [193]. The most recent investigation reports high ICE of 85.4% and relatively stable cycling performance of 759.2 $mAhg^{-1}$ after 100 cycles at 0.5 C with the capacity retention of 59.8% for $MgSiO_3$ doped SiO_x carbon coated, $MgSiO_3$-SiO_x@C nano architectures [194].

Structural modification due to dopant insertion in the various 3D structures such as porous and pomegranate structures may prove crucial as it increases Li^+ diffusivity resulting in more homogenous lithiation across the material. It also mitigates volume expansion, improving the ICE of the SiO_x anode. However, due to the different element ratios in SiO_x, exploration of the microscopic mechanism of Si, O, Li, and doping elements in the battery reaction process is very much required for industrial applications. Simulation of the process is a good option as it saves the cost of trial and error [195].

Recent development of "Nanoskeleton" Si-SiO_x/C anode supported by CNTs has exhibited enormous potential for improved cycling stability in full cells [196]. Another recent approach has been uniform nano-Si dispersion to achieve Si-rich SiO_x materials. Electrochemical analysis revealed silicon sub oxides achieved through high energy mechanical milling demonstrated a higher reversible capacity of 2558 $mAhg^{-1}$ and an ICE of 89%. Carbon incorporation further enhanced the cycling stability [197].

5. Conclusions

Contemporary research trends establish surface modified SiO_x/C anodes as the most promising candidate for the higher energy storage option in Li-ion batteries. They offer higher cycle stability and rate capacity compared to silicon or graphite anodes. Combination of carbon improves the overall efficiency supporting structural integrity and the conductivity of high-capacity SiO_x. Prelithiation has proved crucial to the electrochemical performance of the end product [198].

Better electrochemical performance of a battery requires a uniform carbon coat, evenly dispersed Si particles and a flexible buffer phase. All together these attributes stop pulverization, speed up ion flow and keep the battery stable over many cycles. Uniform carbon coat lowers the resistance and helps electrons speed up. A smooth, complete layer of carbon also prevents the liquid electrolyte from touching the inner silicon and causing bad side reactions. Buffer phase creation forms

specific silicates absorbing the swelling stress of charging [53] [114] [150] [184] [197]. Industrial application of SiO_x anodes for LIB requires high tap density, uniform SEI formation, chemical and structural stability, high conductivity and high purity leading to high ICE, high specific capacity and high cycling stability with high-rate capability of the SiO_x anodes in full cells. Synthetic methodologies which are highly controllable with high yield, low cost and eco-friendly, are therefore required. Structural designing of SiO_x anodes is based on these considerations. An open, porous, or well-spaced design letting Li-ions travel faster through the anode is the preferred one.

Present day synthesis methodologies at the industrial level utilize thermal disproportionation, mechanical milling and CVD carbon coating. This is a complex process with high yield and highly pure SiO_x material with the required morphology. It is considered cost effective compared to pure nano silicon alternatives and moderately expensive relative to graphite anodes. Wet chemistry-mostly magnesiothermic reduction with HEMM and CVD is also in use due to high yield. It is considered comparatively greener technology though it generates chemical by-products and large energy consumption. A third methodology is Spray drying. It is often combined with carbonization. HEMM, sintering and LPCVD. It is another highly scalable method with high production yields, though a complex high temperature process [161] [182] [188] [199] [200].

Structurally modified, three-dimensional, porous structured SiO_x anode material with single layer of carbon coating has an edge over other types of anodes. The effectiveness of SiO_x/C stems from several factors. SiO_x has a high specific capacity and smaller volume fluctuation due to the formation of Li_2O and silicates of lithium counteracting the volume expansion. Carbon matrix promotes electron and ion transportation. It contributes to SEI layer formation, establishing the structural integrity of SiO_x. Incorporation of non-carbonaceous materials, such as metals and metal oxides, improves mechanical robustness and stability, contributing to efficient electron and Li^+ transport. However, the intrinsic formation of Li_2O and lithium silicates lowers the ICE of SiO_x-based materials, demanding novel material design strategies.

Porous SiO_x/C nano particles buffer the volume expansion, structural stability and enhanced electrochemical performance have been reported. However, mass production of porous SiO_x/C is an expensive and complex manufacturing process. Therefore, excellent performance in all performance metrics (high specific capacity, ICE, capacity retention, stability, tap density and rate capacity) along with reproducibility, safety strategies and acceptable production cost are yet to be attained at industrial scale [201].

Future research should therefore be directed toward eco-friendly, scalable synthesis of SiO_x/C nanostructures with precise control on process parameters to produce required morphologies towards specific applications. Simulation of the processes and parameters can provide cost-effective solutions. Testing under real world conditions can address the safety concerns of the device. Optimized pre lithiation

strategies and innovative technologies need to be combined with the factors mentioned above for system level integration. This may bridge the gap between academia and industry.

Data Availability

No new data was created or analyzed in this study. Data sharing is not applicable to this article.

Acknowledgements

Logistic and material support from UST is acknowledged.

Conflicts of Interest

Author declares no conflicts of interest.

References

[1] Brandt, K. (1994) Historical Development of Secondary Lithium Batteries. *Solid State Ionics*, **69**, 173-183. https://doi.org/10.1016/0167-2738(94)90408-1

[2] Nagai, R., Kita, F., Yamada, M. and Katayama, H. (2011) Development of Highly Reliable High-Capacity Batteries for Mobile Devices and Small- to Medium-Sized Batteries for Industrial Applications. https://www.hitachihyoron.com/rev/pdf/2011/r2011_01_105.pdf

[3] Kennedy, B., Patterson, D. and Camilleri, S. (2000) Use of Lithium-Ion Batteries in Electric Vehicles. *Journal of Power Sources*, **90**, 156-162. https://doi.org/10.1016/s0378-7753(00)00402-x

[4] Ghafari, A., Bayat, V., Akbari, V.S. and Ghasemi Yeklangi, A. (2023) Current and Future Prospects of Li-Ion Batteries: A Review. *Journal of NanoScience Technology*, **8**, 22-43. https://doi.org/10.52319/j.nanoscitec.2023.21

[5] Evshchik, E.Y., Shikhovtseva, A.V., Kolmakov, V.G., Bugaev, V.I., Valeev, R.L., Voropaev, V.S., *et al.* (2026) Lithium-Ion Batteries for Space Applications in Low Earth Orbits: Promising Technologies and Testing Methods. *Applied Energy*, **406**, Article 127266. https://doi.org/10.1016/j.apenergy.2025.127266

[6] Ribeiro, J.F., Silva, M.F., Carmo, J.P., Gonçalves, L.M., Silva, M.M. and Correia, J.H. (2013) Solid-State Thin-Film Lithium Batteries for Integration in Microsystems. In: Bhushan, B., Ed., *NanoScience and Technology*, Springer, 575-619. https://doi.org/10.1007/978-3-642-25414-7_20

[7] Opitz, A., Badami, P., Shen, L., Vignarooban, K. and Kannan, A.M. (2017) Can Li-Ion Batteries Be the Panacea for Automotive Applications? *Renewable and Sustainable Energy Reviews*, **68**, 685-692. https://doi.org/10.1016/j.rser.2016.10.019

[8] Zhao, L., Ding, B., Qin, X., Wang, Z., Lv, W., He, Y., *et al.* (2022) Revisiting the Roles of Natural Graphite in Ongoing Lithium-Ion Batteries. *Advanced Materials*, **34**, Article 2106704. https://doi.org/10.1002/adma.202106704

[9] Zhang, H., Li, C., Eshetu, G.G., Laruelle, S., Grugeon, S., Zaghib, K., *et al.* (2019) From Solid-Solution Electrodes and the Rocking-Chair Concept to Today's Batteries. *Angewandte Chemie*, **132**, 542-546. https://doi.org/10.1002/ange.201913923

[10] Salvatierra, R.V., Raji, A.O., Lee, S., Ji, Y., Li, L. and Tour, J.M. (2016) Silicon Nanowires and Lithium Cobalt Oxide Nanowires in Graphene Nanoribbon Papers for

Full Lithium Ion Battery. *Advanced Energy Materials*, **6**, Article 1600918. https://doi.org/10.1002/aenm.201600918

[11] Lv, L., Peng, M., Wu, L., Dong, Y., You, G., Duan, Y., *et al.* (2021) Progress in Iron Oxides Based Nanostructures for Applications in Energy Storage. *Nanoscale Research Letters*, **16**, Article No. 138. https://doi.org/10.1186/s11671-021-03594-z

[12] Etrini, A., Elomrani, A., Oukahou, S., Maymoun, M., Sbiaai, K. and Hasnaoui, A. (2023) Two-Dimensional Dirac Tib_2C_2 as a Potential Anode Material for Li-Ion Batteries: A First-Principles Study. *Physical Chemistry Chemical Physics*, **25**, 21699-21707. https://doi.org/10.1039/d3cp02724d

[13] Li, Y., Duan, C.N., Jiang, Z., bin Zhou, X. and Wang, Y. (2021) Cuo/Rgo Nanocomposite as an Anode Material for High-Performance Lithium-Ion Batteries. *Materials Research Express*, **8**, Article 055505. https://doi.org/10.1088/2053-1591/abfe2f

[14] Cao, Z., Yang, Y., Qin, J. and Su, Z. (2021) A Core-Shell Porous MnO_2/Carbon Nanosphere Composite as the Anode of Lithium-Ion Batteries. *Journal of Power Sources*, **491**, Article 229577. https://doi.org/10.1016/j.jpowsour.2021.229577

[15] Wang, S., Qu, C., Wen, J., Wang, C., Ma, X., Yang, Y., *et al.* (2023) Progress of Transition Metal Sulfides Used as Lithium-Ion Battery Anodes. *Materials Chemistry Frontiers*, **7**, 2779-2808. https://doi.org/10.1039/d2qm01200f

[16] Zhang, J.-G., Wang, W., Xiao, J., Xu, W., Graff, G.L., Yang, G., *et al.* (2012) Silicon-Based Anodes for Li-Ion Batteries. In: Meyers, R.A., Ed., *Encyclopedia of Sustainability Science and Technology*, Springer New York, 9293-9316. https://doi.org/10.1007/978-1-4419-0851-3_496

[17] Obrovac, M.N. and Chevrier, V.L. (2014) Alloy Negative Electrodes for Li-Ion Batteries. *Chemical Reviews*, **114**, 11444-11502. https://doi.org/10.1021/cr500207g

[18] Nitta, N. and Yushin, G. (2013) High-Capacity Anode Materials for Lithium-Ion Batteries: Choice of Elements and Structures for Active Particles. *Particle & Particle Systems Characterization*, **31**, 317-336. https://doi.org/10.1002/ppsc.201300231

[19] Feng, K., Li, M., Liu, W., Kashkooli, A.G., Xiao, X., Cai, M., *et al.* (2018) Silicon-Based Anodes for Lithium-Ion Batteries: From Fundamentals to Practical Applications. *Small*, **14**, Article 1702737. https://doi.org/10.1002/smll.201702737

[20] Lu, Y., Zhang, Q. and Chen, J. (2019) Recent Progress on Lithium-Ion Batteries with High Electrochemical Performance. *Science China Chemistry*, **62**, 533-548. https://doi.org/10.1007/s11426-018-9410-0

[21] Li, J. and Dahn, J.R. (2007) An *in Situ* X-Ray Diffraction Study of the Reaction of Li with Crystalline Si. *Journal of the Electrochemical Society*, **154**, A156-A161.

[22] Li, Z., Du, M., Guo, X., Zhang, D., Wang, Q., Sun, H., *et al.* (2023) Research Progress of SiO-Based Anode Materials for Lithium-Ion Batteries. *Chemical Engineering Journal*, **473**, Article 145294. https://doi.org/10.1016/j.cej.2023.145294

[23] Jiao, M., Wang, Y., Ye, C., Wang, C., Zhang, W. and Liang, C. (2020) High-Capacity SiO ($0 \le x \le 2$) as Promising Anode Materials for Next-Generation Lithium-Ion Batteries. *Journal of Alloys and Compounds*, **842**, Article 155774. https://doi.org/10.1016/j.jallcom.2020.155774

[24] Hirata, A., Kohara, S., Asada, T., Arao, M., Yogi, C., Imai, H., *et al.* (2016) Atomic-Scale Disproportionation in Amorphous Silicon Monoxide. *Nature Communications*, **7**, Article No. 11591. https://doi.org/10.1038/ncomms11591

[25] Wang, F., Wang, B., Yu, Z., Zhu, C., Liu, P., Li, J., *et al.* (2022) Construction of Air-Stable Pre-Lithiated SiO_x Anodes for Next-Generation High-Energy-Density Lithium-Ion Batteries. *Cell Reports Physical Science*, **3**, Article 100872.

https://doi.org/10.1016/j.xcrp.2022.100872

[26] Pender, J.P., Jha, G., Youn, D.H., Ziegler, J.M., Andoni, I., Choi, E.J., *et al.* (2020) Electrode Degradation in Lithium-Ion Batteries. *ACS Nano*, **14**, 1243-1295. https://doi.org/10.1021/acsnano.9b04365

[27] Zhang, H., Liu, K., Liu, Y., Lang, Z., He, W., Ma, L., *et al.* (2020) Observably Improving Initial Coulombic Efficiency of C/SiOx Anode Using -C-O-PO_3Li_2 Groups in Lithium Ion Batteries. *Journal of Power Sources*, **447**, Article 227400. https://doi.org/10.1016/j.jpowsour.2019.227400

[28] Li, W., Zhou, L. and Liao, W. (2021) Synthesis of Carbon Coated Silicon Monoxide with Double Carbon Source and Its Application as Anode for Lithium Ion Battery. *International Journal of Electrochemical Science*, **16**, Article 211013. https://doi.org/10.20964/2021.10.04

[29] Li, G., Li, J.-Y., Yue, F.-S., Xu, Q., Zuo, T.-T., Yin, Y.-X. and Guo, Y.-G. (2019) Reducing the Volume Deformation of High Capacity SiO_x/G/C Anode toward Industrial Application in High Energy Density Lithium-Ion Batteries. *Nano Energy*, **60**, 485-492. https://doi.org/10.1016/j.nanoen.2019.03.077

[30] Jin, C., Dan, J., Zou, Y., Xu, G., Yue, Z., Li, X., *et al.* (2021) Carbon-Coated Nitrogen Doped SiO_x Anode Material for High Stability Lithium Ion Batteries. *Ceramics International*, **47**, 29443-29450. https://doi.org/10.1016/j.ceramint.2021.07.112

[31] Mukhan, O., Umirov, N., Lee, B., Yun, J., Choi, J. and Kim, S. (2022) A Facile Carbon Coating on Mg-Embedded SiO_x Alloy for Fabrication of High-Energy Lithium-Ion Batteries. *Advanced Materials Interfaces*, **9**, Article 2201426. https://doi.org/10.1002/admi.202201426

[32] Ouyang, P., Jin, C., Xu, G., Yang, X., Kong, K., Liu, B., *et al.* (2020) Lithium Ion Batteries with Enhanced Electrochemical Performance by Using Carbon-Coated SiO_x/Ag Composites as Anode Material. *Ceramics International*, **47**, 1086-1094. https://doi.org/10.1016/j.ceramint.2020.08.224

[33] Li, Z., Jin, J., Yuan, Z. and Yang, W. (2020) Surface Modification of SiO_x Film Anodes by Laser Annealing and Improvement of Cyclability for Lithium-Ion Batteries. *Materials Science in Semiconductor Processing*, **121**, Article 105300. https://doi.org/10.1016/j.mssp.2020.105300

[34] Ge, J., Shen, H., Zhou, F., Li, Y., Yuan, N., Yang, W., *et al.* (2022) Oxygen-Tailoring in Sio_x/C with a Covalent Interface for High-Performance Lithium Storage. *Journal of Materials Chemistry A*, **10**, 1928-1939. https://doi.org/10.1039/d1ta07965d

[35] Sun, Q., Zeng, G., Li, J., Wang, S., Botifoll, M., Wang, H., *et al.* (2023) Is Soft Carbon a More Suitable Match for SiO_x in Li-Ion Battery Anodes? *Small*, **19**, Article 302644. https://doi.org/10.1002/smll.202302644

[36] Chen, H., Xu, G., Jin, C., Wu, J., Xiong, L., Li, X., *et al.* (2023) Preparation of SiO_x@C via CVD Method as Anode Materials for High-Performance Lithium-Ion Batteries. *Materials Letters*, **341**, Article 134192. https://doi.org/10.1016/j.matlet.2023.134192

[37] Kwak, W., Kim, R., Lee, J., Park, H., Ha, J. and Choi, J. (2025) Chemical Vapor Deposition Carbon Coating of SiO_x Anode for Li-Ion Batteries: Significance of Carbon Precursor Selection and Deposition Temperature. *ACS Omega*, **10**, 2553-2560. https://doi.org/10.1021/acsomega.4c06951

[38] Brydson, R., Yang, J., Gregory, D.H. and Liu, W. (2026) SiO_x/Hard Carbon Composite Derived from Pineapples as Potential Anode Materials for Li Ion Batteries. *Surface and Coatings Technology*, **525**, Article 133298. https://doi.org/10.1016/j.surfcoat.2026.133298

[39] Kong, X., Xi, Z., Wang, L., Zhou, Y., Liu, Y., Wang, L., *et al.* (2023) Recent Progress in Silicon-Based Materials for Performance-Enhanced Lithium-Ion Batteries. *Molecules*, **28**, Article 2079. https://doi.org/10.3390/molecules28052079

[40] Peng, J., Li, W., Wu, Z., Li, H., Zeng, P., Yang, J., *et al.* (2022) Engineering Si-Based Anode Materials with Homogeneous Distribution of SiO_x and Carbon for Lithium-Ion Batteries. *Energy & Fuels*, **36**, 5465-5474. https://doi.org/10.1021/acs.energyfuels.2c00693

[41] Yan, M., Li, G., Zhang, J., Tian, Y., Yin, Y., Zhang, C., *et al.* (2020) Enabling SiO_x/C Anode with High Initial Coulombic Efficiency through a Chemical Pre-Lithiation Strategy for High-Energy-Density Lithium-Ion Batteries. *ACS Applied Materials & Interfaces*, **12**, 27202-27209. https://doi.org/10.1021/acsami.0c05153

[42] Meng, Q., Li, G., Yue, J., Xu, Q., Yin, Y. and Guo, Y. (2019) High-Performance Lithiated SiO_x Anode Obtained by a Controllable and Efficient Prelithiation Strategy. *ACS Applied Materials & Interfaces*, **11**, 32062-32068. https://doi.org/10.1021/acsami.9b12086

[43] Zhu, G., Wang, Y., Yang, S., Qu, Q. and Zheng, H. (2019) Correlation between the Physical Parameters and the Electrochemical Performance of a Silicon Anode in Lithium-Ion Batteries. *Journal of Materiomics*, **5**, 164-175. https://doi.org/10.1016/j.jmat.2019.03.005

[44] Wang, J., Wang, X., Liu, B., Lu, H., Chu, G., Liu, J., *et al.* (2020) Size Effect on the Growth and Pulverization Behavior of Si Nanodomains in SiO Anode. *Nano Energy*, **78**, Article 105101. https://doi.org/10.1016/j.nanoen.2020.105101

[45] Liu, Z., Yu, Q., Zhao, Y., He, R., Xu, M., Feng, S., *et al.* (2018) Silicon Oxides: A Promising Family of Anode Materials for Lithium-Ion Batteries. *Chemical Society Reviews*, **48**, 285-309. https://doi.org/10.1039/c8cs00441b

[46] Eshetu, G.G., Zhang, H., Judez, X., Adenusi, H., Armand, M., Passerini, S., *et al.* (2021) Production of High-Energy Li-Ion Batteries Comprising Silicon-Containing Anodes and Insertion-Type Cathodes. *Nature Communications*, **12**, Article No. 5459. https://doi.org/10.1038/s41467-021-25334-8

[47] Eshetu, G.G., Zhang, H., Judez, X., Adenusi, H., Armand, M., Passerini, S., *et al.* (2023) Silicon-Containing Anodes for High-Energy Density Lithium-Ion Batteries. *ECS Meeting Abstracts*, **2023**, 522-522. https://doi.org/10.1149/ma2023-012522mtgabs

[48] Xiang-Lu, M., Han-Yu, H., Xiang-Xin, G. and Shao-Ming, D. (2018) Influence of Film Thickness on the Electrochemical Performance of α-SiO_x Thin-Film Anodes. *Journal of Inorganic Materials*, **33**, Article 1141. https://doi.org/10.15541/jim20180227

[49] Tang, J., Hou, L., Hu, T., Fan, S., Zhou, X. and Yang, J. (2021) Influence of Oxygen Content on the Electrochemical Behavior of SiO_x@C Anodes for Li-Ion Battery. *Composites Communications*, **23**, Article 100544. https://doi.org/10.1016/j.coco.2020.100544

[50] Li, Z., Stetson, C., Frisco, S., Harvey, S., Huey, Z., Teeter, G., *et al.* (2022) The Role of Oxygen in Lithiation and Solid Electrolyte Interphase Formation Processes in Silicon-Based Anodes. *Journal of the Electrochemical Society*, **169**, Article 120512. https://doi.org/10.1149/1945-7111/aca833

[51] Fan, S., Zhou, X., Tang, J., Ma, Y. and Yang, J. (2021) Insights to the Variation of Oxygen Content and Reasons for Improved Electrochemical Performance of Annealing SiO_x Anodes for Li-Ion Battery. *Applied Surface Science*, **579**, Article 152179. https://doi.org/10.1016/j.apsusc.2021.152179

[52] Cho, J.H., Xiao, X., Verbrugge, M.W. and Sheldon, B.W. (2022) Influence of Oxygen

Content on the Structural Evolution of SiO_x Thin-Film Electrodes with Subsequent Lithiation/Delithiation Cycles. *ACS Applied Energy Materials*, **5**, 13293-13306. https://doi.org/10.1021/acsaem.2c01903

[53] Zhang, M., Liang, N., Hao, D., Chen, Z., Zhang, F., Yin, J., *et al.* (2023) Recent Advances of SiO_x-Based Anodes for Sustainable Lithium-Ion Batteries. *Nano Research Energy*, **2**, e9120077. https://doi.org/10.26599/nre.2023.9120077

[54] Yao, N., Zhang, Y., Rao, X., Yang, Z., Zheng, K., Świerczek, K., *et al.* (2022) A Review on the Critical Challenges and Progress of SiO_x-Based Anodes for Lithium-Ion Batteries. *International Journal of Minerals, Metallurgy and Materials*, **29**, 876-895. https://doi.org/10.1007/s12613-022-2422-7

[55] Chen, Y.-J., Li, J.-B. and Dai, J.-H. (2001) Si and Sio Nanostructures Formed via Thermal Evaporation. *Chemical Physics Letters*, **344**, 450-456. https://doi.org/10.1016/s0009-2614(01)00742-4

[56] Takezawa, H., Iwamoto, K., Ito, S. and Yoshizawa, H. (2013) Electrochemical Behaviors of Nonstoichiometric Silicon Suboxides (SiO_x) Film Prepared by Reactive Evaporation for Lithium Rechargeable Batteries. *Journal of Power Sources*, **244**, 149-157. https://doi.org/10.1016/j.jpowsour.2013.02.077

[57] Kim, D., Kim, K.H., Lim, C. and Lee, Y. (2022) Carbon-Coated SiO_x Anode Materials via PVD and Pyrolyzed Fuel Oil to Achieve Lithium-Ion Batteries with High Cycling Stability. *Carbon Letters*, **32**, 321-328. https://doi.org/10.1007/s42823-021-00314-6

[58] Homma, K., Kambara, M. and Yoshida, T. (2014) High Throughput Production of Nanocomposite SiO_x Powders by Plasma Spray Physical Vapor Deposition for Negative Electrode of Lithium Ion Batteries. *Science and Technology of Advanced Materials*, **15**, Article 025006. https://doi.org/10.1088/1468-6996/15/2/025006

[59] Sitinamaluwa, H.S., Li, H., Wasalathilake, K.C., Wolff, A., Tesfamichael, T., Zhang, S., *et al.* (2019) Nanoporous Sio Coated Amorphous Silicon Anode Material with Robust Mechanical Behavior for High-Performance Rechargeable Li-Ion Batteries. *Nano Materials Science*, **1**, 70-76. https://doi.org/10.1016/j.nanoms.2019.02.005

[60] Qiang, W., Huanhuan, H., Jian, W. and Zhurui, S. (2017) Fabrication of SiO_x Ultra-Fine Nanoparticles by IR Nanosecond Laser Ablation as Anode Materials for Lithium Ion Battery. *Applied Surface Science*, **422**, 155-161. https://doi.org/10.1016/j.apsusc.2017.06.002

[61] Rodionov, A.A., Starinskiy, S.V., Shukhov, Y.G. and Bulgakov, A.V. (2021) Deposition of Oxide Nanostructures by Nanosecond Laser Ablation of Silicon in an Oxygen-Containing Background Gas. *Thermophysics and Aeromechanics*, **28**, 549-554. https://doi.org/10.1134/s0869864321040089

[62] Zhou, H.P., Yang, B., Zhang, Z.D., Zhang, H., Zhang, S., Feng, T.T., *et al.* (2022) Fastly PECVD-Grown Vertical Carbon Nanosheets for a Composite SiO_x-C Anode Material. *Applied Surface Science*, **605**, Article 154627. https://doi.org/10.1016/j.apsusc.2022.154627

[63] El-Eskandarany, M.S., Al-Hazza, A., Al-Hajji, L.A., Ali, N., Al-Duweesh, A.A., Banyan, M., *et al.* (2021) Mechanical Milling: A Superior Nanotechnological Tool for Fabrication of Nanocrystalline and Nanocomposite Materials. *Nanomaterials*, **11**, Article 2484. https://doi.org/10.3390/nano11102484

[64] Cao, Y., Bennett, J.C., Dunlap, R.A. and Obrovac, M.N. (2018) A Simple Synthesis Route for High-Capacity SiO_x Anode Materials with Tunable Oxygen Content for Lithium-Ion Batteries. *Chemistry of Materials*, **30**, 7418-7422. https://doi.org/10.1021/acs.chemmater.8b02977

[65] Cao, Y., Dunlap, R.A. and Obrovac, M.N. (2020) Electrochemistry and Thermal Behavior of SiO_x Made by Reactive Gas Milling. *Journal of the Electrochemical Society*, **167**, Article 110501. https://doi.org/10.1149/1945-7111/ab9e83

[66] Zhang, J., Zhang, C., Liu, Z., Zheng, J., Zuo, Y., Xue, C., *et al.* (2017) High-Performance Ball-Milled SiO_x Anodes for Lithium Ion Batteries. *Journal of Power Sources*, **339**, 86-92. https://doi.org/10.1016/j.jpowsour.2016.11.044

[67] Hwang, J., Kim, K., Jung, W., Choi, H. and Kim, J. (2019) Facile and Scalable Synthesis of SiO_x Materials for Li-Ion Negative Electrodes. *Journal of Power Sources*, **436**, Article 226883. https://doi.org/10.1016/j.jpowsour.2019.226883

[68] Dressler, R.A. and Dahn, J.R. (2023) Simple Synthesis and Characterization of Ball Milled SiO_x for Use as a Negative Electrode Material. *Journal of the Electrochemical Society*, **170**, Article 080505. https://doi.org/10.1149/1945-7111/aceb8e

[69] Zhou, H., Liu, J., Guo, L., Zhang, J., Feng, S. and Zhang, X. (2022) Disproportionated SiO_x/C Composite Anode Materials for Lithium-Ion Batteries. *Colloids and Surfaces A*: *Physicochemical and Engineering Aspects*, **648**, Article 129386. https://doi.org/10.1016/j.colsurfa.2022.129386

[70] Yang, Y., Qu, X., Zhang, L., Gao, M., Liu, Y. and Pan, H. (2018) Reaction-Ball-Milling-Driven Surface Coating Strategy to Suppress Pulverization of Microparticle Si Anodes. *ACS Applied Materials & Interfaces*, **10**, 20591-20598. https://doi.org/10.1021/acsami.8b05609

[71] Zhou, J. and Lin, N. (2022) Synthetic Methodologies for Si-Containing Li-Storage Electrode Materials. *Advanced Energy and Sustainability Research*, **3**.

[72] Yu, G., Jing, J., Li, C., Li, Q., Yang, Z., Yao, S., *et al.* (2023) A Review on Recent Progress of Non-Stoichiometric SiO_x Anodes Based on Lithium Ion Batteries. *Progress in Natural Science*: *Materials International*, **33**, 47-54. https://doi.org/10.1016/j.pnsc.2023.02.003

[73] Zhang, J., Ma, P., Hou, Z., Zhang, X. and Li, C. (2020) One-Step Synthesis of SiO_x@Graphene Composite Material by a Hydrothermal Method for Lithium-Ion Battery Anodes. *Energy & Fuels*, **34**, 3895-3900. https://doi.org/10.1021/acs.energyfuels.9b04242

[74] Wei, H., Xu, D., Chen, W., Liu, X., Zhang, Z., Dai, L., *et al.* (2022) Low-Temperature Hydrothermal Activation-Catalytic Carbonation Boosting Porous Si/SiO_x@C Composites Derived from Bamboo Leaves for Superior Lithium Storage Performance. *Applied Surface Science*, **584**, Article 152580. https://doi.org/10.1016/j.apsusc.2022.152580

[75] Ge, G., Li, G., Wang, X., Chen, X., Fu, L., Liu, X., *et al.* (2021) Manipulating Oxidation of Silicon with Fresh Surface Enabling Stable Battery Anode. *Nano Letters*, **21**, 3127-3133. https://doi.org/10.1021/acs.nanolett.1c00317

[76] Zhang, J., Hou, Z., Zhang, X., Zhang, L. and Li, C. (2020) Delicate Construction of Si@SiO_x Composite Materials by Microwave Hydrothermal for Lithium-Ion Battery Anodes. *Ionics*, **26**, 69-74. https://doi.org/10.1007/s11581-019-03204-0

[77] Chu, H., Wu, Q. and Huang, J. (2018) Rice Husk Derived Silicon/Carbon and Silica/Carbon Nanocomposites as Anodic Materials for Lithium-Ion Batteries. *Colloids and Surfaces A*: *Physicochemical and Engineering Aspects*, **558**, 495-503. https://doi.org/10.1016/j.colsurfa.2018.09.020

[78] Wang, S., Wu, Q., Cai, Z., Lei, Q., Ahsan, Z., Li, J., *et al.* (2023) Significantly Enhanced Performance of Li-Storage via *In-Situ* Oxidation of Silicon Particles by Zinc Oxide. *Materials Today Communications*, **36**, Article 106504. https://doi.org/10.1016/j.mtcomm.2023.106504

[79] Chen, W., Kuang, S., Wei, H., Wu, P., Tang, T., Li, H., *et al.* (2022) Dual Carbon and Void Space Confined SiO_x/C@Void@Si/C Yolk-Shell Nanospheres with High-Rate Performances and Outstanding Cyclability for Lithium-Ion Batteries Anodes. *Journal of Colloid and Interface Science*, **610**, 583-591. https://doi.org/10.1016/j.jcis.2021.11.099

[80] Liu, Y., Ruan, J., Liu, F., Fan, Y. and Wang, P. (2019) Synthesis of SiO_x/C Composite with Dual Interface as Li-Ion Battery Anode Material. *Journal of Alloys and Compounds*, **802**, 704-711. https://doi.org/10.1016/j.jallcom.2019.06.072

[81] Wu, W., Wang, M., Wang, R., Xu, D., Zeng, H., Wang, C., *et al.* (2018) Magnesio-Mechanochemical Reduced Sio for High-Performance Lithium Ion Batteries. *Journal of Power Sources*, **407**, 112-122. https://doi.org/10.1016/j.jpowsour.2018.10.065

[82] Ge, J., Tang, Q., Shen, H., Zhou, F., Zhou, H., Yang, W., *et al.* (2020) Low-Temperature Fabrication of Porous SiO with Carbon Shell for High-Stability Lithium Ion Battery. *Ceramics International*, **46**, 12507-12516. https://doi.org/10.1016/j.ceramint.2020.02.013

[83] Park, Y.-K., Boyer, M., Hwang, G. S. and Lee, J.-W. (2018) Synthesis of Si/SiO_x from Talc and Its Characteristics as an Anode for Lithium-Ion Batteries. *Journal of Electroanalytical Chemistry*, **833**, 552-559. https://doi.org/10.1016/j.jelechem.2018.12.037

[84] Lee, J., Han, S.A., Lee, S., Park, M. and Kim, J.H. (2019) Electrochemical Properties of Nonstoichiometric Silicon Suboxide Anode Materials with Controlled Oxygen Concentration. *Composites Part B: Engineering*, **174**, Article 107024. https://doi.org/10.1016/j.compositesb.2019.107024

[85] Liu, S.-F., Kuo, C.-H., Lin, C.-C., Lin, H.-Y., Lu, C.-Z., Kang, J.-W., Fey, G. T.-K. and Chen, H.-Y. (2022) Biowaste-Derived Si@SiO_x/C Anodes for Sustainable Lithium-Ion Batteries. *Electrochimica Acta*, **403**, Article 139580. https://doi.org/10.1016/j.electacta.2021.139580

[86] Zhou, C., Liu, J., Gong, X. and Wang, Z. (2021) Optimizing the Function of SiO_x in the Porous Si/SiO_x Network via a Controllable Magnesiothermic Reduction for Enhanced Lithium Storage. *Journal of Alloys and Compounds*, **874**, Article 159914. https://doi.org/10.1016/j.jallcom.2021.159914

[87] Moon, D.B., Jo, M.H. and Ahn, H.J. (2026) Tuning Si@SiO_x Core/Shell Structures by Controlling the Microwave Heating Temperature for Ultrafast Lithium-Ion Battery Anodes. *Applied Surface Science*, **719**, Article 165077. https://doi.org/10.1016/j.apsusc.2025.165077

[88] Kim, H., Cho, W., Park, D., Kim, K., Jung, W., Choi, H., *et al.* (2019) Zn-Induced Synthesis of Porous SiO_x Materials as Negative Electrodes for Li Secondary Batteries. *Journal of Alloys and Compounds*, **803**, 325-331. https://doi.org/10.1016/j.jallcom.2019.06.270

[89] Cui, J., Cui, Y., Li, S., Sun, H., Wen, Z. and Sun, J. (2016) Microsized Porous SiO_x@C Composites Synthesized through Aluminothermic Reduction from Rice Husks and Used as Anode for Lithium-Ion Batteries. *ACS Applied Materials & Interfaces*, **8**, 30239-30247. https://doi.org/10.1021/acsami.6b10260

[90] Wei, H., Niu, L., Zhou, X., Zhang, Y., Zhong, L., Yang, Y., *et al.* (2023) Nanostructured SiO_x/Si Composite Confined by Carbon Layer as Anode Materials for High-Performance Lithium-Ion Battery. *Journal of Alloys and Compounds*, **969**, Article 172462. https://doi.org/10.1016/j.jallcom.2023.172462

[91] Kwon, J.C., Oh, B.H. and Lee, S.J. (2023) Fabrication of SiO_x Anode Active Materials Using Spherical Silica Powder and Shape Control Technology. *Korean Journal of Ma-*

terials Research, **33**, 530-536. https://doi.org/10.3740/mrsk.2023.33.12.530

[92] Li, X., Shi, H., Zhang, L., Chen, J. and Lü, P. (2020) Novel Synthesis of SiO/C Composite as High-Capacity Lithium-Ion Battery Anode from Silica-Carbon Binary Xerogel. *Chinese Journal of Chemical Engineering*, **28**, 579-583. https://doi.org/10.1016/j.cjche.2019.11.003

[93] Izawa, T., Arif, A.F., Taniguchi, S., Kamikubo, K., Iwasaki, H. and Ogi, T. (2018) Improving the Performance of Li-Ion Battery Carbon Anodes by *In-Situ* Immobilization of SiO_x Nanoparticles. *Materials Research Bulletin*, **112**, 16-21. https://doi.org/10.1016/j.materresbull.2018.11.044

[94] Ling, Y., Peng, Y. and Guan, S. (2023) Facile Synthesis of SiO_X/C Composite with Homogeneous Distribution of SiO_x and Carbon as Anodes for Superior Lithium-Ion Batteries. *ChemistrySelect*, **8**, e202300233. https://doi.org/10.1002/slct.202300233

[95] Anh Cao, K.L., Arif, A.F., Kamikubo, K., Izawa, T., Iwasaki, H. and Ogi, T. (2019) Controllable Synthesis of Carbon-Coated SiO_x Particles through a Simultaneous Reaction between the Hydrolysis-Condensation of Tetramethyl Orthosilicate and the Polymerization of 3-Aminophenol. *Langmuir*, **35**, 13681-13692. https://doi.org/10.1021/acs.langmuir.9b02599

[96] Li, J., Li, Y., Shi, J., Liu, H., Wang, D., Zhai, W., *et al.* (2021) A Nanotubular TiO_2/SiO_x/Si Composite Derived from Cellulosic Cotton as an Anode Material for Lithium-Ion Batteries with Enhanced Electrochemical Performance. *Colloids and Surfaces A*: *Physicochemical and Engineering Aspects*, **625**, Article 126870. https://doi.org/10.1016/j.colsurfa.2021.126870

[97] Wang, Z., Zhang, H., Zhang, X., Wang, X. and Zhang, X. (2022) Solvent-Free and Large-Scale Synthesis of SiO/C Nanocomposite with Carbon Encapsulation for High-Performance Lithium-Ion Battery Anodes. *Composites Part B*: *Engineering*, **247**, Article 110308. https://doi.org/10.1016/j.compositesb.2022.110308

[98] Zhang, S., Zhang, N., Zhao, W., Lan, D., Hao, G., Yi, X., *et al.* (2021) Green Preparation of Hierarchical Porous C/SiO_x Composites from Coal Gangue as Anodes for Li-Ion Batteries. *Solid State Ionics*, **371**, Article 115772. https://doi.org/10.1016/j.ssi.2021.115772

[99] Abe, Y., Tomioka, M., Kabir, M. and Kumagai, S. (2022) Role of SiO_x in Rice-Husk-Derived Anodes for Li-Ion Batteries. *Scientific Reports*, **12**, Article No. 975. https://doi.org/10.1038/s41598-022-04979-5

[100] Myeong, S., Lim, C., Cheon, S., Lee, I.W., Huang, Z., Lv, R., *et al.* (2026) Structurally and Chemically Tailored CNT/SiOxFy/C Composites by Precise NF3 Fluorination for Advanced Si-Based Anodes. *Chemical Engineering Journal*, **528**, Article 172230. https://doi.org/10.1016/j.cej.2025.172230

[101] Li, B., Xie, H., Tian, H., Chang, K., Xu, H., Zhang, L., Hou, J., Wang, X., Wang, B.P., Lu, H., Yang, S. and Hou, C. (2026) Designing Hierarchical D-SiO_x@NC/C@CNTs/rGO Composites via Thermal Disproportionation and Interfacial Reconstruction for High-Performance Lithium-Ion Batteries. *Journal of Power Sources*, **690**, Article 240821.

[102] Li, J., Zeng, G., Horta, S., Martínez-Alanis, P.R., Jacas Biendicho, J., Ibáñez, M., *et al.* (2025) Crystallographic Engineering in Micron-Sized SiO_x Anode Material toward Stable High-Energy-Density Lithium-Ion Batteries. *ACS Nano*, **19**, 16096-16109. https://doi.org/10.1021/acsnano.5c03074

[103] Ge, J., Tang, Q., Shen, H., Zhou, F., Zhou, H., Yang, W., *et al.* (2021) Controllable Preparation of Disproportionated SiO_x/C Sheets with 3D Network as High-Performance Anode Materials of Lithium Ion Battery. *Applied Surface Science*, **552**, Article 149446. https://doi.org/10.1016/j.apsusc.2021.149446

[104] Lee, J., Lee, S.Y., Jeong, H.Y. and Cho, S.O. (2020) Oxygen Content-Controllable Synthesis of Non-Stoichiometric Silicon Suboxide Nanoparticles by Electrochemical Anodization. *Nanomaterials*, **10**, Article 2137. https://doi.org/10.3390/nano10112137

[105] Chen, W., Salvatierra, R.V., Ren, M., Chen, J., Stanford, M.G. and Tour, J.M. (2020) Laser-Induced Silicon Oxide for Anode-Free Lithium Metal Batteries. *Advanced Materials*, **32**, Article 2002850. https://doi.org/10.1002/adma.202002850

[106] Li, G., Huang, L., Yan, M., Li, J., Jiang, K., Yin, Y., *et al.* (2020) An Integral Interface with Dynamically Stable Evolution on Micron-Sized SiO_x Particle Anode. *Nano Energy*, **74**, Article 104890. https://doi.org/10.1016/j.nanoen.2020.104890

[107] Li, H., Li, H., Yang, Z., Yang, L., Gong, J., Liu, Y., *et al.* (2021) SiO_x Anode: From Fundamental Mechanism toward Industrial Application. *Small*, **17**, Article 2102641. https://doi.org/10.1002/smll.202102641

[108] Li, Y., Qian, Y., Zhou, J., Lin, N. and Qian, Y. (2021) Molten-Licl Induced Thermochemical Prelithiation of SiO_x: Regulating the Active Si/o Ratio for High Initial Coulombic Efficiency. *Nano Research*, **15**, 230-237. https://doi.org/10.1007/s12274-021-3464-2

[109] Kim, M., Yang, Z. and Bloom, I. (2020) Review—The Lithiation/Delithiation Behavior of Si-Based Electrodes: A Connection between Electrochemistry and Mechanics. *Journal of the Electrochemical Society*, **168**, Article 010523. https://doi.org/10.1149/1945-7111/abd56f

[110] Pan, K., Zou, F., Canova, M., Zhu, Y. and Kim, J. (2019) Systematic Electrochemical Characterizations of Si and Sio Anodes for High-Capacity Li-Ion Batteries. *Journal of Power Sources*, **413**, 20-28. https://doi.org/10.1016/j.jpowsour.2018.12.010

[111] Liu, D., Shadike, Z., Lin, R., Qian, K., Li, H., Li, K., *et al.* (2019) Review of Recent Development of *in Situ*/Operando Characterization Techniques for Lithium Battery Research. *Advanced Materials*, **31**, Article 1806620. https://doi.org/10.1002/adma.201806620

[112] Xiang, Y., Li, X., Cheng, Y., Sun, X. and Yang, Y. (2020) Advanced Characterization Techniques for Solid State Lithium Battery Research. *Materials Today*, **36**, 139-157. https://doi.org/10.1016/j.mattod.2020.01.018

[113] Yang, Y., Liu, Y., Jiang, X., Zhao, L., Wang, P. and Zhang, Y. (2024) Rational Design of SiO_x Based Anode Materials for Next Generation Lithium-Ion Batteries. *Materials Advances*, **5**, 896-919. https://doi.org/10.1039/d3ma00859b

[114] Yang, H.-W. and Kim, S.-J. (2019) SiO_x as a Potential Anode Material for Li-Ion Batteries: Role of Carbon Coating, Doping, and Structural Modifications. In: Demirkan, M.T. and Attia, A., Eds., *Energy Storage Devices*, IntechOpen. https://doi.org/10.5772/intechopen.82379

[115] Lee, J., Oh, G., Jung, H.Y. and Hwang, J.Y. (2023) Silicon Anode: A Perspective on Fast Charging Lithium-Ion Battery. *Inorganics*, **11**, Article 182. https://doi.org/10.3390/inorganics11050182

[116] Rehnlund, D., Wang, Z. and Nyholm, L. (2022) Lithium-Diffusion Induced Capacity Losses in Lithium-Based Batteries. *Advanced Materials*, **34**, Article 2108827. https://doi.org/10.1002/adma.202108827

[117] Tian, H., Tian, H., Yang, W., Zhang, F., Yang, W., Zhang, Q., *et al.* (2021) Stable Hollow-Structured Silicon Suboxide-Based Anodes toward High-Performance Lithium-Ion Batteries. *Advanced Functional Materials*, **31**, Article 2101796. https://doi.org/10.1002/adfm.202101796

[118] Lee, R., Choi, J., Choi, S., Choi, A.R., Lee, J.H., Kim, J.H., *et al.* (2026) Structural Con-

finement Engineering of Current Collectors Enables the Development of Durable SiO_x Anodes for Lithium-Ion Batteries. *Nanoscale Horizons*, **11**, 1636-1650. https://doi.org/10.1039/d5nh00822k

[119] Zhao, X., Liu, M., He, H., Wang, F. and Zhong, S. (2026) A Ternary TiO_2/SiO_x/C Composite with Different Crystalline Phases of TiO_2 as an Anode Material for High Performance Lithium-Ion Batteries. *Journal of Electroanalytical Chemistry*, **1006**, Article 119831. https://doi.org/10.1016/j.jelechem.2026.119831

[120] Yao, Y., Xu, X., Zhao, H., Tong, Y. and Li, Y. (2022) Multilayer Si@SiO_x@Void@C Anode Materials Synthesized via Simultaneously Carbonization and Redox for Li-Ion Batteries. *Ceramics International*, **48**, 12217-12227. https://doi.org/10.1016/j.ceramint.2022.01.082

[121] Xu, S., Tu, W., Xu, Z., Zhang, D., Sun, S., Pan, H., *et al.* (2024) Enhanced Lithium-Ion Diffusion Kinetics and Inhibition Volume Expansion via Sn-Bridged N-Doped Carbon and SiO_x for Highly Reversible Lithium-Ion Storage. *Energy & Fuels*, **38**, 23114-23125. https://doi.org/10.1021/acs.energyfuels.4c04545

[122] Li, Q., Wang, S., Li, Y., Huang, N., He, X., Gao, L., *et al.* (2023) Carbon-Coated Sio for Libs with Superior Capacity and Cycle Stability. *Materials Letters*, **351**, Article 135057. https://doi.org/10.1016/j.matlet.2023.135057

[123] Wan, Y., Jin, C., Xu, G., Chen, H., Sun, F., Li, Y., *et al.* (2024) Preparation of SiO_x@C via Wet Carbon Coating for High Performance Lithium-Ion Batteries. *Solid State Ionics*, **411**, Article 116534. https://doi.org/10.1016/j.ssi.2024.116534

[124] Guo, J., Zhao, G., Xie, T., Dong, D., Ma, C., Su, L., *et al.* (2020) Carbon/Polymer Bilayer-Coated Si-SiO_x Electrodes with Enhanced Electrical Conductivity and Structural Stability. *ACS Applied Materials & Interfaces*, **12**, 19023-19032. https://doi.org/10.1021/acsami.0c02445

[125] Xiao, Z., Yu, C., Lin, X., Chen, X., Zhang, C. and Wei, F. (2019) Uniform Coating of Nano-Carbon Layer on SiO_x in Aggregated Fluidized Bed as High-Performance Anode Material. *Carbon*, **149**, 462-470. https://doi.org/10.1016/j.carbon.2019.04.051

[126] Nulu, A., Nulu, V. and Sohn, K.Y. (2020) Si/SiO_x Nanoparticles Embedded in a Conductive and Durable Carbon Nanoflake Matrix as an Efficient Anode for Lithium-Ion Batteries. *ChemElectroChem*, **7**, 4055-4065. https://doi.org/10.1002/celc.202001130

[127] Zhang, B., Wu, L., Tang, M., Yang, X., Chen, R., Liu, Y., *et al.* (2026) Carbon-Coated Porous Copper-Loaded SiO_x Architecture for High-Performance and Volume-Stable Anode Design in Lithium-Ion Batteries. *Journal of Power Sources*, **663**, Article 238828. https://doi.org/10.1016/j.jpowsour.2025.238828

[128] Xu, M., Ma, J., Niu, G., Yang, H., Sun, M., Zhao, X., *et al.* (2020) A Low-Cost and High-Capacity SiO_x/C@Graphite Hybrid as an Advanced Anode for High-Power Lithium-Ion Batteries. *ACS Omega*, **5**, 16440-16447. https://doi.org/10.1021/acsomega.0c00686

[129] Sun, S., Wu, Y., Wang, Z., Zhang, Y., Chen, D. and Chen, J. (2023) Plasma Enabled *In-Situ* Deposition of Hybrid Structured SiO_x/C on Polymorphous Carbon Hosts for Superior Lithium Storage. *Carbon*, **205**, 253-261. https://doi.org/10.1016/j.carbon.2023.01.045

[130] Ren, Z., Liu, S., Chen, J., Yu, Y., Shang, Q., Fakudze, S., *et al.* (2022) One-Step Synthesis of Interface-Coupled Si@SiO_x@C from Whole Rice-Husks for High-Performance Lithium Storage. *Electrochimica Acta*, **402**, Article 139556. https://doi.org/10.1016/j.electacta.2021.139556

[131] Hwang, S.W. (2024) SiO_x/C Composite Anode for Lithium-Ion Battery with Improved Performance Using Graphene Quantum Dots and Carbon Nanoparticles. *Mol-*

ecules, **29**, Article 2578. https://doi.org/10.3390/molecules29112578

[132] Wang, H., Que, X., Liu, Y., Wu, X., Yuan, Q., Lu, J., *et al.* (2021) Facile Synthesis of Yolk-Shell Structured SiO_x/C@Void@C Nanospheres as Anode for Lithium-Ion Batteries. *Journal of Alloys and Compounds*, **874**, Article 159913. https://doi.org/10.1016/j.jallcom.2021.159913

[133] Wang, Z., Kong, L., Guo, Z., Zhang, X., Wang, X. and Zhang, X. (2022) Bamboo-Like SiO_x/C Nanotubes with Carbon Coating as a Durable and High-Performance Anode for Lithium-Ion Battery. *Chemical Engineering Journal*, **428**, Article 131060. https://doi.org/10.1016/j.cej.2021.131060

[134] Guo, W., Yan, X., Hou, F., Wen, L., Dai, Y., Yang, D., *et al.* (2019) Flexible and Free-Standing SiO_x/CNT Composite Films for High Capacity and Durable Lithium Ion Batteries. *Carbon*, **152**, 888-897. https://doi.org/10.1016/j.carbon.2019.06.088

[135] Hu, G., Zhong, K., Yu, R., Liu, Z., Zhang, Y., Wu, J., *et al.* (2020) Enveloping SiO_x in N-Doped Carbon for Durable Lithium Storage *via* an Eco-Friendly Solvent-Free Approach. *Journal of Materials Chemistry A*, **8**, 13285-13291. https://doi.org/10.1039/d0ta00540a

[136] Qiu, S., Huang, Z. and Fu, F. (2024) Enhancing Lithium Storage Performance of Carbon/SiO_x Composite via Coating Edge-Nitrogen-Enriched Carbon. *International Journal of Hydrogen Energy*, **91**, 1355-1364. https://doi.org/10.1016/j.ijhydene.2024.10.231

[137] You, Z., Lin, C., Zheng, P., Li, J., Feng, Q., Tao, J., *et al.* (2024) Fluorine-Doping Carbon-Modified Si/SiO_x to Effectively Achieve High-Performance Anode. *Small*, **21**, Article 2407215. https://doi.org/10.1002/smll.202407215

[138] Cui, J., Qiu, Y., Zhang, H., Yao, Z., Zhao, W., Liu, Y., *et al.* (2021) Sulfur- and Nitrogen-Doped Rice Husk-Derived C/SiO_x Composites as High-Performance Lithium-Ion Battery Anodes. *Solid State Ionics*, **361**, Article 115548. https://doi.org/10.1016/j.ssi.2021.115548

[139] Shen, B., Fu, N., Chen, Y., Shao, W., Yan, Y., Huang, J., *et al.* (2022) Micron SiO_x Encapsulated into Amorphous B, N Co-Doped Carbon Nanotube Network for High-Capacity and Long-Durable Li-Ion Half/Full Batteries. *Chemical Engineering Journal*, **455**, Article 140820. https://doi.org/10.1016/j.cej.2022.140820

[140] Liu, D., Jiang, Z., Zhang, W., Ma, J. and Xie, J. (2020) Micron-Sized SiO_x/N-Doped Carbon Composite Spheres Fabricated with Biomass Chitosan for High-Performance Lithium-Ion Battery Anodes. *RSC Advances*, **10**, 38524-38531. https://doi.org/10.1039/d0ra07029g

[141] Chen, Q., Tan, L., Wang, S., Liu, B., Peng, Q., Luo, H., *et al.* (2021) A Facile Synthesis of Phosphorus Doped Si/SiO_2/C with High Coulombic Efficiency and Good Stability as an Anode Material for Lithium Ion Batteries. *Electrochimica Acta*, **385**, Article 138385. https://doi.org/10.1016/j.electacta.2021.138385

[142] Xie, H., Hou, C., Yue, Z., Zhai, L., Sun, H., Lu, H., *et al.* (2023) Facile Synthesis of C, N, P Co-Doped Sio as Anode Material for Lithium-Ion Batteries with Excellent Rate Performance. *Journal of Energy Storage*, **64**, Article 107147. https://doi.org/10.1016/j.est.2023.107147

[143] Han, M. and Yu, J. (2019) Subnanoscopically and Homogeneously Dispersed SiO_x/C Composite Spheres for High-Performance Lithium Ion Battery Anodes. *Journal of Power Sources*, **414**, 435-443. https://doi.org/10.1016/j.jpowsour.2019.01.030

[144] Gao, X., Gao, Y., Li, Q., Wang, Y., Zhao, D., Xu, G., *et al.* (2022) Scalable Synthesis of High-Performance Anode Material SiO_x/C for Lithium-Ion Batteries by Employing the Rochow Reaction Process. *Journal of Alloys and Compounds*, **902**, Article 163668.

https://doi.org/10.1016/j.jallcom.2022.163668

[145] Cui, S., Zhang, J., Fan, S., Xing, X., Deng, L. and Gong, Y. (2022) SiO_xC_y Microspheres with Homogeneous Atom Distribution for a High-Performance Li-Ion Battery. *Nano Letters*, **22**, 9559-9565. https://doi.org/10.1021/acs.nanolett.2c03699

[146] Choi, T., Jo, S., Pervez, A., Kim, J., Chang, D.R., Oh, P., *et al.* (2025) Optimal Structural Design to Improve Cycling Stability of SiO_x-Spherical Porous CNTs Composite Anode for Lithium-Ion Battery. *ACS Applied Materials & Interfaces*, **17**, 66696-66706. https://doi.org/10.1021/acsami.5c18771

[147] Han, J., Jo, S., Na, I., Oh, S., Jeon, Y., Park, J., *et al.* (2021) Homogenizing Silicon Domains in SiO_x Anode during Cycling and Enhancing Battery Performance via Magnesium Doping. *ACS Applied Materials & Interfaces*, **13**, 52202-52214. https://doi.org/10.1021/acsami.1c14121

[148] Liu, B., Liu, J., Zhong, C. and Hu, W. (2023) Mg-Doped, Carbon-Coated, and Prelithiated SiO_x as Anode Materials with Improved Initial Coulombic Efficiency for Lithium-Ion Batteries. *Carbon Energy*, **6**, e421. https://doi.org/10.1002/cey2.421

[149] Li, M., Qiu, J., Ming, H., Zhao, P., Jin, Z., Zhang, S., *et al.* (2019) A SiO_x/Sn/C Hybrid Anode for Lithium-Ion Batteries with High Volumetric Capacity and Long Cyclability. *Journal of Alloys and Compounds*, **809**, Article 151659. https://doi.org/10.1016/j.jallcom.2019.151659

[150] Li, J., Xin, G., Song, J., Zhang, B. and Li, X. (2026) Preparation and Electrochemical Performance of Different Premagnesiated SiO_x Anodes. *Vacuum*, **246**, Article 115055. https://doi.org/10.1016/j.vacuum.2025.115055

[151] Guo, X., Xu, H., Li, W., Liu, Y., Shi, Y., Li, Q., *et al.* (2022) Embedding Atomically Dispersed Iron Sites in Nitrogen-Doped Carbon Frameworks-Wrapped Silicon Suboxide for Superior Lithium Storage. *Advanced Science*, **10**, Article 2206084. https://doi.org/10.1002/advs.202206084

[152] Guo, X., Zhang, Y., Zhang, F., Li, Q., Anjum, D.H., Liang, H., *et al.* (2019) A Novel Strategy for the Synthesis of Highly Stable Ternary SiO_x Composites for Li-Ion-Battery Anodes. *Journal of Materials Chemistry A*, **7**, 15969-15974. https://doi.org/10.1039/c9ta04062e

[153] Kim, T., Li, H., Gervasone, R., Kim, J.M. and Lee, J.Y. (2023) Review on Improving the Performance of SiO_x Anodes for a Lithium-Ion Battery through Insertion of Heteroatoms: State of the Art and Outlook. *Energy & Fuels*, **37**, 13563-13578. https://doi.org/10.1021/acs.energyfuels.3c00785

[154] Ling, Y., Zeng, P., Wang, B., Zhang, L. and Wang, J. (2024) Influence of Carbon Sources on Silicon Oxides for Lithium-Ion Batteries: A Review. *Journal of Materials Chemistry A*, **12**, 14957-14974. https://doi.org/10.1039/d4ta02708f

[155] Hong, F., Zhou, R., Gao, C., Liu, Y., Sun, Z. and Jiang, Y. (2023) Fabrication of Porous SiO_x/NanoSi@C Composites with Homogeneous Silicon Distribution for High-Performance Li-Ion Battery Anodes. *Journal of Alloys and Compounds*, **947**, Article 169511. https://doi.org/10.1016/j.jallcom.2023.169511

[156] Sun, X., Wang, Z., Zhang, H., Si, K., Wang, X. and Zhang, X. (2023) Honeycomb-Like 3D Ordered Macroporous SiO/C Nanoarchitectures with Carbon Coating for High-Performance Lithium Storage. *Journal of Colloid and Interface Science*, **651**, 394-403. https://doi.org/10.1016/j.jcis.2023.07.199

[157] Song, J., Guo, S., Kou, L., Kajiyoshi, K., Su, J., Huang, W., *et al.* (2021) Controllable Synthesis Honeycomb-Like Structure SiO_x/C Composites as Anode for High-Performance Lithium-Ion Batteries. *Vacuum*, **186**, Article 110044. https://doi.org/10.1016/j.vacuum.2021.110044

[158] Song, J., Kou, L., Wang, Y., Ai, T., Kajiyoshi, K. and Wattanapaphawong, P. (2023) A Three-Dimensional Porous Si/SiO_x Decorated by Nitrogen-Doped Carbon as Anode Materials for Lithium-Ion Batteries. *Colloids and Surfaces A*: *Physicochemical and Engineering Aspects*, **673**, Article 131821. https://doi.org/10.1016/j.colsurfa.2023.131821

[159] Kuang, S., Xu, D., Chen, W., Huang, X., Sun, L., Cai, X., *et al.* (2020) In Situ Construction of Bamboo Charcoal Derived SiO_x Embedded in Hierarchical Porous Carbon Framework as Stable Anode Material for Superior Lithium Storage. *Applied Surface Science*, **521**, Article 146497. https://doi.org/10.1016/j.apsusc.2020.146497

[160] Hui, X., Lin, Y., Mo, H., Zha, Z., Ma, Z., Chen, Z., *et al.* (2024) Facile Synthesis of SiO/C as High-Performance Anodes for Lithium-Ion Batteries. *Chemical Physics Letters*, **848**, Article 141388. https://doi.org/10.1016/j.cplett.2024.141388

[161] Zhou, H., Yang, B., Zhou, H., Liu, C., Zhang, S., Feng, T., *et al.* (2024) Carbon Shells and Carbon Nanotubes Jointly Modified SiO_x Anodes for Superior Lithium Storage. *ACS Applied Energy Materials*, **7**, 10307-10316. https://doi.org/10.1021/acsaem.4c01513

[162] Peng, J., Luo, J., Li, W., Zeng, P., Wu, Z., Wang, Y., *et al.* (2021) Insight into the Performance of the Mesoporous Structure SiO_x Nanoparticles Anchored on Carbon Fibers as Anode Material of Lithium-Ion Batteries. *Journal of Electroanalytical Chemistry*, **880**, Article 114798. https://doi.org/10.1016/j.jelechem.2020.114798

[163] Liu, D., Fang, K., You, X., Tang, H., Xie, Z., Li, J., *et al.* (2019) Formation of Thin Layer Graphite Wrapped Meso-Porous SiO_x and Its Lithium Storage Application. *Ceramics International*, **45**, 24707-24716. https://doi.org/10.1016/j.ceramint.2019.08.210

[164] Li, Z., Zhao, H. and Wang, J. (2019) Dandelion-Like Mesoporous SiO_x@C Nanoparticles for High-Capacity and Ultralong Lifespan Lithium-Ion Battery Anode. *ECS Meeting Abstracts*, **2019**, 319-319. https://doi.org/10.1149/ma2019-01/2/319

[165] Chen, W., Liu, H., Kuang, S., Huang, H., Tang, T., Zheng, M., *et al.* (2021) *In-Situ* Low-Temperature Strategy from Waste Sugarcane Leaves towards Micro/Meso-Porous Carbon Network Embedded Nano Si-SiO_x@C Boosting High Performances for Lithium-Ion Batteries. *Carbon*, **179**, 377-386. https://doi.org/10.1016/j.carbon.2021.04.043

[166] Sun, Q., Li, J., Yang, M., Wang, S., Zeng, G., Liu, H., *et al.* (2023) Carbon Microstructure Dependent Li-Ion Storage Behaviors in SiO_x/C Anodes. *Small*, **19**, Article 2300759. https://doi.org/10.1002/smll.202300759

[167] Deng, W., Zhou, Y., Hu, N., Ni, S., Zhang, W. and Li, C.M. (2024) Recent Advances of High-Performance SiO ($0 < x < 2$) Anodes. *Materials Reports*: *Energy*, **4**, Article 100270. *https://doi.org/10.1016/j.matre.2024.100270</x*

[168] Gong, S., Lee, Y., Choi, J., Lee, M., Chung, K.Y., Jung, H., *et al.* (2023) *In Situ* Mesopore Formation in SiO_x Nanoparticles by Chemically Reinforced Heterointerface and Use of Chemical Prelithiation for Highly Reversible Lithium-Ion Battery Anode. *Small*, **19**, Article 2206238. https://doi.org/10.1002/smll.202206238

[169] Zhang, K., Xing, J., Peng, H., Gao, J., Ai, S., Zhou, Q., *et al.* (2024) Modulation of Physical and Chemical Connections between SiO_x and Carbon for High-Performance Lithium-Ion Batteries. *Energy Materials*, **4**, Article 400043. https://doi.org/10.20517/energymater.2023.102

[170] He, D., Li, P., Wang, T., Wan, Q., Zhou, H., Wu, M., *et al.* (2024) A Novel Approach to Synthesize Micrometer-Sized Porous Si/SiO_x@C with Internally and Externally Interweaved CNTs as a High Performance Anode for Lithium-Ion Batteries. *Journal of*

Power Sources, **621**, Article 235309. https://doi.org/10.1016/j.jpowsour.2024.235309

[171] Sun, L., Jiang, X. and Jin, Z. (2023) Interfacial Engineering of Porous SiO_x@C Composite Anodes toward High-Performance Lithium-Ion Batteries. *Chemical Engineering Journal*, **474**, Article 145960. https://doi.org/10.1016/j.cej.2023.145960

[172] Song, L., Zhao, T., Tan, X., Mao, D., Su, S., Fan, Z., *et al.* (2022) Biomass-Derived Hierarchically Porous (Nitrogen, Phosphorus) Co-Doped SiO_x/C Composite Nanosheet Architectures for Superior Lithium Storage and Ultra-Long Cycle Performance. *Batteries & Supercaps*, **5**, e202100350. https://doi.org/10.1002/batt.202100350

[173] Qiao, Y., Pan, H., Gao, M., Jin, G., Guo, Q., Tolochko, O.V., *et al.* (2026) Confining Mesoporous SiO_x@C Spheres into 3D Ordered Macroporous Carbon as an Anode with Long-Cycling Performance for Lithium-Ion Batteries. *ACS Applied Nano Materials*, **9**, 11084-11096. https://doi.org/10.1021/acsanm.6c01784

[174] Kaize S., Wang, Z., Zhang, H., Sun, X., Zong., Wang, X. and Zhang, X. (2024) Green Synthesis of SiO_x/C-TiO_2 with Continuous Conductive Network towards Enhancing Lithium Storage Performance. *Journal of Energy Storage*, **104**, Article 114493. https://doi.org/10.1016/j.est.2024.114493

[175] Cheng, M., Tan, J., Zhou, H., Cai, X., Zhang, Y., Liu, Y., *et al.* (2026) Sustainable Production of SiO_x Anodes from Quartz Waste via Solvent-Free Mechanochemical Synthesis. *Ionics*, **32**, 5077-5090. https://doi.org/10.1007/s11581-026-07078-x

[176] Xie, G., Tan, X., Shi, Z., Peng, Y., Ma, Y., Zhong, Y., *et al.* (2024) SiO_x Based Anodes for Advanced Li-Ion Batteries: Recent Progress and Perspectives. *Advanced Functional Materials*, **35**, Article 2414714. https://doi.org/10.1002/adfm.202414714

[177] Wang, P., Hou, S., Pang, F., Liu, M., Li, Y., Liu, T., *et al.* (2019) SiO_x/C-Decorated Coo Nanosheets as a Long-Life Anode for Lithium-Ion Batteries. *ChemElectroChem*, **6**, 1574-1581. https://doi.org/10.1002/celc.201801900

[178] Wang, P., Sun, Z., Liu, H., Gao, Z., Hu, J., Yin, W., *et al.* (2021) Strategic Synthesis of Sponge-Like Structured SiO_x@C@CoO Multifunctional Composites for High-Performance and Stable Lithium-Ion Batteries. *Journal of Materials Chemistry A*, **9**, 18440-18453. https://doi.org/10.1039/d1ta02880d

[179] Tan, F., Guo, H., Wang, Z., Niu, X., Li, X., Yan, G., *et al.* (2021) Electrospinning-Enabled SiO @TiO_2/C Fibers as Anode Materials for Lithium-Ion Batteries. *Journal of Alloys and Compounds*, **888**, Article 161635. https://doi.org/10.1016/j.jallcom.2021.161635

[180] Wang, X., Xia, Y., Zuo, X., Schaper, S.J., Yin, S., Ji, Q., *et al.* (2019) Synergistic Effects from Super-Small Sized TiO_2 and SiO_x Nanoparticles within TiO_2/SiO_x/Carbon Nanohybrid Lithium-Ion Battery Anode. *Ceramics International*, **45**, 14327-14337. https://doi.org/10.1016/j.ceramint.2019.04.147

[181] Xiao, Z., Yu, C., Lin, X., Chen, X., Zhang, C., Jiang, H., *et al.* (2020) TiO_2 as a Multifunction Coating Layer to Enhance the Electrochemical Performance of SiO_x@ TiO_2@C Composite as Anode Material. *Nano Energy*, **77**, Article 105082. https://doi.org/10.1016/j.nanoen.2020.105082

[182] Wang, T., Chen, Z., Chen, D. and Zhao, R. (2021) Hybrid MnO-SiO_x@C Microspheres with a Hierarchical Mesoporous Structure for Advanced Lithium-Ion Battery Anodes. *Journal of Alloys and Compounds*, **899**, Article 163251. https://doi.org/10.1016/j.jallcom.2021.163251

[183] Wu, J., Jin, C., Xu, G., Chen, H., Lu, B., Li, X., *et al.* (2023) A Novel Double-Coated Anode Material SiO_x/C/Cu_2O for Lithium Ion Batteries. *Solid State Ionics*, **394**, Article 116211. https://doi.org/10.1016/j.ssi.2023.116211

[184] Wei, B., Zhang, B., Yue, C., Zhang, J., Chen, J., Hua, L., *et al.* (2026) One-Pot Synthesis of SiO_x@C@TiO_2 Precursor for Lithium-Ion Battery Anodes with High Electrochemical Performance. *Journal of Energy Storage*, **162**, Article 121969. https://doi.org/10.1016/j.est.2026.121969

[185] Li, H., Peng, J., Wu, Z., Liu, X., Liu, P., Chang, B., *et al.* (2023) Constructing Novel SiO_x Hybridization Materials by a Double-Layer Interface Engineering for High-Performance Lithium-Ion Batteries. *Chemical Engineering Journal*, **462**, Article 142172. https://doi.org/10.1016/j.cej.2023.142172

[186] Costa, A.L.A., Liebertseder, M., Gambaryan-Roisman, T., Esken, D. and Menzel, F. (2025) A Comparative Study of Dry-Coated Fumed Metal Oxides for Enhanced Cycling Performance of SiO_x/C Anodes in Lithium-Ion Batteries. *Electrochemistry Communications*, **177**, Article 107941. https://doi.org/10.1016/j.elecom.2025.107941

[187] Gu, Z., Li, W., Chen, Y., Xia, X. and Liu, H. (2020) Synthesis of the Microspherical Structure of Ternary SiO_x@SnO_2@C by a Hydrothermal Method as the Anode for High-Performance Lithium-Ion Batteries. *Sustainable Energy & Fuels*, **4**, 2333-2341. https://doi.org/10.1039/d0se00053a

[188] Yuan, T., Tang, R., Xiao, F., Zuo, S., Wang, Y. and Liu, J. (2023) Modifying Sio as a Ternary Composite Anode Material((SiO_x/G/SnO_2)@C) for Lithium Battery with High Li-Ion Diffusion and Lower Volume Expansion. *Electrochimica Acta*, **439**, Article 141655. https://doi.org/10.1016/j.electacta.2022.141655

[189] Xu, B., Shen, H., Ge, J. and Tang, Q. (2021) Improved Cycling Performance of SiO_x/MgO/Mg_2SiO_4/C Composite Anode Materials for Lithium-Ion Battery. *Applied Surface Science*, **546**, Article 148814. https://doi.org/10.1016/j.apsusc.2020.148814

[190] Raza, A., Jung, J.Y., Lee, C., Kim, B.G., Choi, J., Park, M., *et al.* (2021) Swelling-Controlled Double-Layered SiO_x/MgO/Mg_2SiO_4 Composite with Enhanced Initial Coulombic Efficiency for Lithium-Ion Battery. *ACS Applied Materials & Interfaces*, **13**, 7161-7170. https://doi.org/10.1021/acsami.0c19975

[191] Wang, K., Tan, Y., Li, P. and Sun, J. (2020) Scalable 3D Porous Residual Al-Doped Si/SiO_x Composites for High Performance Anodes: Coupling Effects of Porosity, Conductive Sites and Oxide Layer. *Electrochimica Acta*, **353**, Article 136538. https://doi.org/10.1016/j.electacta.2020.136538

[192] Yi, X., Cai, C., Hao, G., Yang, Z., Liu, H., Huang, J., *et al.* (2022) Facile One-Pot Preparation of Porous SiO_x@Li_2SiO_3/C Composite from Rice Husks for High Initial Coulomb Efficiency Lithium-Ion Battery Anodes. *Journal of Electroanalytical Chemistry*, **912**, Article 116265. https://doi.org/10.1016/j.jelechem.2022.116265

[193] Su, M., Song, Y., Cai, L., Gao, T., Zhou, Y., Dou, A., *et al.* (2023) Carbon and Li_3bo_3 Co-Modified SiO_x as Anode for High-Performance Lithium-Ion Batteries. *Energy Technology*, **11**, Article 2300019. https://doi.org/10.1002/ente.202300019

[194] Song, R., Yang, L., Luan, J., Yuan, H., Ji, S., Wan, D., *et al.* (2025) Mgsio3 Doped, Carbon-Coated SiO_x Anode with Enhanced Initial Coulombic Efficiency for Lithium-Ion Battery. *Journal of Energy Storage*, **105**, Article 114687. https://doi.org/10.1016/j.est.2024.114687

[195] Zhu, X., Liu, B., Shao, J., Zhang, Q., Wan, Y., Zhong, C., *et al.* (2023) Fundamental Mechanisms and Promising Strategies for the Industrial Application of SiO_x Anode. *Advanced Functional Materials*, **33**, Article 2213363. https://doi.org/10.1002/adfm.202213363

[196] Guan, X., Zhang, Y., Kinloch, I.A. and Bissett, M.A. (2025) "Nanoskeleton" Si-SiO_x/C Anodes toward Highly Stable Lithium-Ion Batteries. *ACS Applied Materials & Interfaces*, **17**, 10580-10592. https://doi.org/10.1021/acsami.4c18254

[197] Jang, S. and Kim, J. (2025) SiO_x-Based Anode Materials with High Si Content Achieved through Uniform Nano-Si Dispersion for Li-Ion Batteries. *Materials*, **18**, Article 3272. https://doi.org/10.3390/ma18143272

[198] Chen, H.X., Xu, D.X., Li, G., Xiao, S.H., Lu, Z.Y., Wang, W.L., Wang, W.P., Shi, J.L., Zhang, J. and Guo, Y.G. (2026) Phase Engineering of Lithium Silicate in SiO_x Anodes for Fast-Charging Lithium-Ion Batteries. *ACS Applied Materials & Interfaces*, **18**, 1854-1864.

[199] Yang, X., Zhan, C., Xu, D., Nan, D., Lv, R., Shen, W., *et al.* (2022) SiO_x@Si-Graphite Microspheres for High-Stable Anode of Lithium-Ion Batteries. *Electrochimica Acta*, **426**, Article 140795. https://doi.org/10.1016/j.electacta.2022.140795

[200] Hsiao, Y.S., Huang, J.H., Hsieh, T.H., Weng, L.Y., Liao, S.W., Yen, Y.C., *et al.* (2026) Spray-Dried Nanoarchitectonics of SiO_x/C Composite as a High-Performance Anode Material for Lithium-Ion Batteries. **184**, Article 106243. https://doi.org/10.1016/j.jtice.2025.106243

[201] Khan, M., Yan, S., Ali, M., Mahmood, F., Zheng, Y., Li, G., *et al.* (2024) Innovative Solutions for High-Performance Silicon Anodes in Lithium-Ion Batteries: Overcoming Challenges and Real-World Applications. *Nano-Micro Letters*, **16**, Article No. 179. https://doi.org/10.1007/s40820-024-01388-3