Controlling Oxidation of Kerf Loss Silicon Waste Enabling Stable Battery Anode

Yan Jiang, Sitong He, Siqi Ma, Fengshuo Xi, Ilya M. Gavrilin, Zhongqiu Tong, Jijun Lu, Neng Wan, Wenhui Ma, Yunpeng Zhu, Pingkeng Wu and Shaoyuan Li

Abstract: The recovery of massive kerf loss silicon waste into silicon anodes is an attractive approach to efficiently utilizing resources and protect the environment. Tens-of-nanometers-scale-thickness Si waste particles enable the high feasibility of high-rate Li-ion storage, but continuous oxidation leads to a gradual loss of electrochemical activity. Understanding the relationship between this oxidation and Li-ion storage properties is key to efficiently recovering silicon wastes into silicon anodes. However, corresponding research is rare. Herein, a series of silicon waste samples with different oxidation states were synthesized and their Li-ion storage characters were investigated. By analyzing their Li-ion storage properties and kinetics, we found that oxidation has absolutely detrimental effects on Li-ion storage performance, which is different to previously reported results of nano-silicon materials. The 2.5 wt.% Si provides a substantial initial discharge capacity of 3519 mAh/g at 0.5 A/g. The capacity retention of 2.5 wt.% Si is almost 70% after 500 cycles at 1 A/g. However, the 35.8 wt.% Si presents a modest initial discharge capacity of merely 170 mAh/g. Additionally, oxidation leads the Li-ion storage kinetics to transform from Li-ion diffusion-controlled to charge transfer-controlled behaviors. For kerf loss silicon waste with an oxygen content over 35.8 wt.%, Li-ion storage capability is lost due to a high charge transfer resistance and a low Li-ion diffusion coefficient.

Keywords: kerf loss silicon waste; Si anodes; oxidization; Li-ion storage kinetics

1. Introduction

To promote the sustainable development of human society, efficiently recovering industrial wastes into valuable materials is an important and efficient approach [1]. Accompanying the rapidly growing photovoltaic silicon industry, hundreds of thousand tons of kerf loss silicon (Si) waste are produced during the wire-saw cutting process of Si ingots [2,3]. Recovery of this waste into valuable materials is important to efficiently utilize resources and protect the environment. The transformation of kerf loss Si waste into Si anodes is an attractive approach with high economic profit [4–7]. Benefiting from an intrinsic tens-of-nanometers-scale thickness, Si waste-derived anodes can demonstrate a high-rate capacity and high cycling stability [8–10]. For example, by reconstructing the surface oxidation status and downsizing the diameter of Si waste via a simple ball milling process, Liao et al. have prepared a sub-micron silicon particle anode with an impressive cycling stability [11]. Even after 200 cycles at 0.5 A/g, it maintained a capacity of 913 mAh/g. Zhang et al. have employed a DC thermal plasma approach to simultaneously remove...
silicon oxide impurities and shape Si waste into nano-spherical silicon materials, which demonstrate a high cycling stability with a retained capacity of 1000 mAh/g over 200 cycles at 0.5 A/g [12]. Lu et al. have treated the Si waste via an electrothermal shock method to produce a Si nano-wire anode with a high capacity of 2381 mAh/g over 500 cycles at 1.0 A/g [13]. These results confirm that Si waste is an ideal candidate to prepare Si anodes.

However, the small size-derived inevitable oxidation of nano-silicon leads to gradual Li-ion storage performance degradation [14]. For instance, Si dense film demonstrated an inverted U relationship between oxygen content and Li-ion storage capacity, with a maximum capacity of 1760 mAh/g at an oxygen content of 13 at. % [15]. Spherical silicon nanoparticles of 200 nanometers in diameter demonstrate a similar oxygen content and Li-ion storage relationship to the dense film, while their maximum Li-ion storage capacity occurs when the oxygen content is 18 at. % [16]. For mesoporous silicon microparticle anode, the maximum Li-ion storage capacity occurs at an oxygen content of 39 at. % [17]. Meanwhile, high- (4–5 N) and low-purity (2–3 N) nano-silicon samples prepared by chemical vapor deposition [18] and magnesiothermic reaction, respectively [19], demonstrate different oxygen content-dependent Li-ion storage properties. The former loses Li-ion storage capability at 23 at. % oxygen content, while the oxygen content that leads to Li-ion storage performance failure in the low-purity magnesiothermic sample is 46 at. %. These works clearly indicate that the oxygen content threshold that leads to the Li-ion storage failure of nano-Si anodes highly depends on morphology and purity.

Given the high purity (>5 N) and the unique twisted nanosheet morphology of the tens-of-nanometers-scale thickness [20], it is reasonable to deduce that kerf loss silicon waste should demonstrate unique oxidation-dependent Li-ion storage behaviors. In fact, our previous works indeed imply that silicon waste demonstrates different oxidation behaviors to the reported nano-silicon materials, and Li-ion storage properties are highly dependent on oxidation status [21–26]. However, the relationship between the oxidation status and Li-ion storage properties of kerf loss silicon waste is still unclear. Herein, this work is performed to fill this gap. By designing a series of silicon waste samples with various oxidation contents, oxidation-dependent Li-ion storage capabilities, charge transfer resistances, Li$^+$ diffusion coefficients, and Li-ion diffusion activation energies were systematically studied. We found that oxidation has absolutely detrimental effects on Li-ion storage performance. Additionally, oxidation leads the Li-ion storage behaviors to transform from a Li-ion diffusion-controlled state to a charge transfer-controlled state, with an oxygen content threshold of ca. 13.5 wt.%. Kerf loss silicon waste samples with an oxygen content over 35.8 wt.% show negligible Li-ion storage properties.

2. Experimental

2.1. Material Preparation

To better study the influence of oxidation-dependent Li-ion storage properties and kinetics, the impurities of kerf loss silicon waste need to be wiped off. Silicon waste was treated with a 5 wt.% HF solution to remove the original oxide layer. After 1 h of HF solution treatment, plenty of anhydrous ethanol was added. The mixture underwent several rounds of filtering and washing. Subsequently, in order to remove any remaining moisture in the filtered sample, we placed it in a constant temperature environment at 60 °C and subjected it to vacuum technology for a drying treatment lasting 12 h. Elemental analysis showed that the prepared sample had an oxygen content of 2.5 wt.%. This sample was denoted as 2.5 wt.% O-Si. Samples with various oxygen contents were prepared by annealing the purified kerf loss silicon waste in air at 100 °C for different times of 3, 15, 40, and 80 days. These produced samples possessed oxygen contents of 6.4, 13.5, 22.2, and 35.8 wt.%, respectively. The corresponding samples were denoted as 6.4 wt.% O-Si, 13.5 wt.% O-Si, 22.2 wt.% O-Si, and 35.8 wt.% O-Si, respectively. Figure S1 shows a graph of the relationship between annealing time at 100 °C and oxygen content.
2.2. Material Characterization

The pertinent data concerning oxygen content were ascertained through the utilization of a nitrogen–hydrogen–oxygen analyzer (ONH-800, Science, Chengdu, China). The morphology and phase information of the samples with various oxygen contents were observed using a field emission scanning electron microscope (FESEM, FEI Quanta200, FEI, Hillsboro, OR, USA), high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 TF30S-Twin, 300 KV, FEI, Hillsboro, OR, USA), and X-ray diffraction (XRD, D8 Venture, Bruker AXS, Karlsruhe, Germany), respectively. The specific surface area of the samples was analyzed using the static volume method (BET, UltraSorb X800, Guo Yi Quantum, Hefei, China). The particle size distributions of the samples with various oxygen levels were tested by using a particle size analyzer (Nano ZS90, Malvern Panalytical, Malvern, UK). An analysis of the silicon oxidation states in the samples was conducted by using X-ray photoelectron spectroscopy (XPS, K-alpha+, Thermo Scientific Nexsa G2, Thermo Fisher Scientific, Shanghai, China). In conducting a detailed analysis of the silicon elements within the samples, Raman spectroscopy can provide insights into their crystalline structure, defects, and other properties. Renishaw apparatus was set up with the excitation source at a wavelength of 532 nanometers. During data acquisition, our focus was directed to a precise micro-area measuring 50 µm × 50 µm, ensuring a thorough examination of specific portions of the samples. Simultaneously, to mitigate potential thermal damage to the samples, we rigorously controlled the laser power, setting it to 8 milliwatts. Subsequently, specialized Omnic V8.2 software was utilized for in-depth analysis and processing of the collected Raman spectral data, extracting crucial information regarding the distribution and state of the silicon elements within the samples.

2.3. Electrochemical Measurement

The preparation of the electrodes for lithium storage testing involved finely mixing the silicon samples with a conductive additive (Super P) and an efficient binder (sodium alginate) in a mass ratio of 6:2:2. The dried electrodes were transferred to an argon gas atmosphere glove box (O2 < 0.01 ppm, H2O < 0.01 ppm) and assembled into CR2025 coin cells with an electrolyte of 1 mol/L LiPF6-DMC/EC solution (volume ratio DMC:EC = 1:1). During the preparation process, the electrode was precisely cut into discs with a radius of approximately 7 mm. To remove residual moisture and solvents, ensuring the electrode’s dryness and stability, we placed it in a vacuum oven at 60 °C for a thorough drying process lasting 4 h. Throughout this procedure, we rigorously controlled the mass loading of the active materials, ensuring it remained within the range of 1.2 to 1.5 milligrams to optimize the electrode’s performance and efficiency. The specific capacity was calculated based on 60% of the mass of the active material in the loading level. Electrochemical impedance spectroscopy (EIS) curves were measured using an electrochemical workstation (CHI 660E) with a test frequency ranging from 0.01 to 100,000 Hz. In the evaluation of battery performance, constant current cycling tests were conducted using a battery testing system (model CT-4008Q, Neware, Shenzhen, China) maintained at a temperature of 30 °C. Additionally, to delve deeper into the electrochemical characteristics of the battery, cyclic voltammetry (CV) measurements were performed using a PARSTAT MC electrochemical workstation (Parstat MC, Princeton Instruments, Trenton, NJ, USA). For the CV measurements, a wide scan range of 0.1 to 1.5 V was set, with a precise scan rate of 0.5 mV/s. To compare the differences in lithium storage properties among the samples with different oxygen contents, further evaluation of their capacity and cycling stability was conducted using a Neware battery testing system.

3. Results and Discussion

SEM images of the kerf loss silicon waste are shown in Figure 1a. As shown in the figure, the sample demonstrates a typical sawdust morphology with a thin and micron-level curved nanosheet character. HRTEM images of the samples with various oxygen contents are displayed in Figure 1b–f. As shown in the figure, the increase in time under
100 °C in air gives rise to a continuous increase in oxygen content and in the thickness of the SiOₓ surface layer. The HRTEM examination indicates that the SiOₓ surface layers are amorphous. As shown in Figure 1b, the as-prepared Si waste sample exhibits an intrinsic SiOₓ layer with a thickness of ca. 2.3 nm. By regulating the duration of oxidation at 100 °C, the thicknesses of the amorphous layers are controlled. Furthermore, the 6.4 wt.% O-Si, 13.5 wt.% O-Si, 22.2 wt.% O-Si, and 35.8 wt.% O-Si samples possess surface layers of 5.4, 8.1, 14.1, and 19.5 nm, respectively (Figure 1c–f). Additionally, the almost unchanged morphology of all the oxidized samples indicates that the oxidation only occurs on the surface of Si NPs (Figure S2).

The particle sizes of the various oxidized materials range from 405 to 430 nanometers (Figure S3a,c,e,g,i), respectively. The average diameter of all the particles is larger than 400 nm. The specific surface area values of the different oxidation states do not differ significantly, all ranging from around 27.8146 m²/g to 32.6874 m²/g (Figure S3b,d,f,h,j). The disparities they exhibit are not particularly substantial, and the primary divergence resides in the thickness of the oxide layer. Thus, these are microparticles which have similar surface areas. There is no effect of the increase in oxygen content on the morphology of kerf loss silicon waste.

Figure 2a demonstrates the XRD patterns of the samples with various oxygen contents. The broad peak located around 20.1-25.8° is assigned to amorphous SiOₓ [29,30]. The diffraction peaks located at 2θ = ca. 28.4, 47.3, 56.1, 69.1, 76.4, and 88.0° correspond to the (111), (220), (311), (400), (331), and (422) planes of the cubic silicon phase [27,28]. Furthermore, the amorphous peak intensity increases along with the increase in thermal-treatment time, which is in accordance with the HRTEM examination results. To further detect the oxidation status of the samples, Raman spectroscopy examinations were conducted. As shown in Figure 2b, compared to silicon wafer [31,32], the red shift of the Raman peak occurs for all the silicon waste samples. This phenomenon can be ascribed to the altered lattice structure of crystalline Si induced by the wire-saw cutting process. [33]. This phenomenon may originate from the strong optical phonon mode exhibited by the Si crystal confined in the SiOₓ matrix. This pronounced phonon mode further influences the lattice vibration mode of...
Si, leading to time-dependent variations in the samples during the oxidation process. Thus, we speculate that there exists a close relationship between the specific optical properties of the confined Si crystal in the SiO$_x$ matrix and the oxidation behavior of the samples.

![Figure 2.](image_url) (a) XRD patterns. (b) Raman spectra of kerf loss silicon waste samples with different oxidation contents.

Further insights into the chemical composition of the samples were revealed through XPS analysis, and their Si 2p signals were detected. The corresponding data are shown in Figure 3a–e. Before fitting, the Si 2p peak was adjusted using the C 1s peak at 284.8 eV as a reference. Shirley background subtraction was used during the fitting process, and the ratio of Si 2p1/2 to Si 2p3/2 peak areas was set at 1:2, which is the theoretical value. The XPS spectra shown in Figure 3 also demonstrate that the peaks at binding energies of 98.9 eV and 99.5 eV correspond to the Si 2p3/2 and Si 2p1/2 peaks. The broad peaks are fitted into four peaks of Si$^{1+}$, Si$^{2+}$, Si$^{3+}$ and Si$^{4+}$, corresponding to its position 102.8 eV, 103.5 eV, 104.0 eV, 104.7 eV [34–36]. The low and weak signal intensities of the positive Si cations in the 2.5wt.% O-Si sample around 103 eV are consistent with their low oxidation status due to the thinner natural oxide layer enveloping the silicon core. Additionally, along with the increase in annealing time, the signal intensity of this broad peak increases, further confirming the increased oxidation contents. The atomic percentages of Si$^0$, Si$^{1+}$, Si$^{2+}$, Si$^{3+}$ and Si$^{4+}$ are summarized in Figure 3f. With the prolonged thermal treatment duration, the concentrations of Si$^{3+}$ and Si$^{4+}$ increased, implying a continuous decrease in Li-ion storage activity [24,30].

The lithium storage performances of the samples with different oxygen contents were investigated, as shown in Figure 4. Evidently, the initial five cycles of 2.5 wt.% O-Si overlapped well, suggesting good stability during cycling (Figure 4a). We found that the 2.5 wt.% O-Si with minimal oxygen content demonstrated superiorities in Li-ion storage capacity at 0.5 A/g (Figure 4b,c). Its initial discharge capacity was 3519 mAh/g, with a higher ICE of 86.04%, Figure 4h and Table S1 (Supporting Information) compare our work with recently reported silicon oxide composite electrode materials, demonstrating that kerf loss silicon waste is an ideal candidate for preparing Si-based anodes. Additionally, an impressive capacity of 2082 mAh/g was still maintained after 100 cycles. Furthermore, the 2.5 wt.% O-Si sample also demonstrated reasonable cycling performance at 1 A/g. After 500 cycles, a high capacity of 1107 mAh/g was still maintained (Figure 4g). Alternatively, the continuous degradation of Li$^+$ storage capacity and ICE for all the thermal treatment samples with the increasing oxygen contents clearly indicates the absolutely harmful effects of oxidation on Li-ion storage performance. The samples with oxygen contents of 6.4,
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13.5, and 22.2 wt.%, respectively, demonstrate initial discharge capacities of 2612, 2230, and 1824 mAh/g with ICE values of 84.65%, 80.71%, and 80.13%, and they, respectively, remain at capacities of 1482, 634, and 438 mAh/g after 100 cycles. The sample with an oxygen content of 35.8 wt.% only delivers an initial discharge capacity of 170 mAh/g with the lowest ICE of 64.02%, and it remains to have the worst capacity of 59 mAh/g after 100 cycles. The comparatively greater concentrations of $\text{Si}^{3+}$ and $\text{Si}^{4+}$ in the outer oxide layer most likely cause this phenomenon. $\text{Si}^{3+}$ and $\text{Si}^{4+}$ have a great propensity to react with lithium ions during a battery’s lithiation process, generating lithium silicates. This reaction lowers the battery’s reversible capacity during charge–discharge cycles, which has an impact on the battery’s overall performance. It is important to note that there is a notable volume expansion associated with the formation of lithium silicates, with an expansion ratio of up to 200%. An anode’s structural stability is seriously threatened by this sudden shift in volume, which frequently results in the development of cracks or even fractures. The solid electrolyte interphase (SEI) grows abnormally faster when the oxide layer cracks because new silicon material is exposed to the electrolyte directly. The anode’s polarization phenomenon is made worse by the excessive growth of the SEI, which also causes a major reduction in battery capacity.

Figure 3. (a–e) Si 2p (XPS) spectra of the samples with different oxygen contents, 2.5 wt.% O-Si (a), 6.4 wt.% O-Si (b), 13.5 wt.% O-Si (c), 22.2 wt.% O-Si (d), and 35.8 wt.% O-Si (e). (f) The molar ratios of $\text{Si}^0$, $\text{Si}^{1+}$, $\text{Si}^{2+}$, $\text{Si}^{3+}$ and $\text{Si}^{4+}$.

Figure 4d illustrates the rate performance of samples with various oxygen contents across a range from 0.1 A/g to 2 A/g. It shows that the sample with minimal oxygen content (2.5 wt.% O-Si) demonstrates a highest rate performance (Figure 4e). The discharge capacity gradually decreases from 3298 mAh/g to 1959 mAh/g as the current density ranges from 0.1 A/g to 2 A/g. Upon returning the current density to 0.1 A/g, the capacity rebounds to 2453 mAh/g. The discharge capacity from 0.1 A/g to 2 A/g of the 6.4 wt.% O-Si, 13.5 wt.% O-Si, 22.2 wt.% O-Si, and 35.8 wt.% O-Si are decreased from 2645 to 1223 mAh/g, 1842 to 548 mAh/g, 1614 to 428 mAh/g, and 198 to 34 mAh/g, respectively. In comparison, the samples with an oxygen content of 6.4 wt.%, 13.5 wt.%, 22.2 wt.%, (Figure S4b–d) and 35.8 wt.% (Figure 4f) exhibit unsatisfied rate capabilities compared to the 2.5 wt.% O-Si.
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Figure 4. Li-ion storage properties of samples with different oxygen contents. (a) The first 5 cycles’ lithium extraction curves of the 2.5 wt.% O-Si at 0.5 A/g. (b) Discharge capacity. (c) Coulombic efficiency. (d) Rate capabilities. (e) Lithium extraction curves of 2.5 wt.% O-Si at all cycling rates. (f) Lithium extraction curves of 35.8 wt.% O-Si at all cycling rates. (g) Cycling performance of the 2.5 wt.% O-Si at 1.0 A/g. (h) Comparison of the ICE of this work, standard silicon oxide material, and other SiO_x for LIBs.

Figure 5a displays the cyclic voltammetry (CV) curves of the 2.5 wt.% O-Si anode, recorded at a scan rate of 0.5 mV/s. A distinct reduction peak at approximately 0.7 V is evident during the first cycle, progressively diminishing in 2–3 cycles. This unique behavior is not limited to the 2.5 wt.% O-Si anode but is also observed in the other four anodes of samples with various oxygen contents (6.4, 13.5, 22.2, and 35.8 wt.%), as depicted in Figure 5b–e. Upon deeper analysis, we unveiled that the reduction peak was significantly associated with irreversible interactions between active species and the electrolyte [37], alongside the formation of the solid electrolyte interface (SEI) film [38–40]. A significant cathodic peak appears at about 0.2 V, indicating the lithiation process of silicon creating Li_xSi. Two oxidation peaks were detected at 0.25 V and 0.6 V, indicating the transformation of Li_xSi into amorphous silicon [37]. The cyclic voltammetry curves of the successive cycles, except for the first one, almost completely overlap, suggesting a high reversibility of the 2.5 wt.% O-Si anode. Furthermore, it is noted that the oxidation current density decreased with increasing oxygen content. This trend can be attributed to the greater involvement of SiO_y in capacity, coupled with the shift in silicon oxidation states from lower (e.g., Si^{1+}, Si^{2+}) to higher (e.g., Si^{3+}, Si^{4+}) levels.
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The depressed semicircle region mainly represents the charge transfer impedance ($R_t$) process of lithium ions [45–47].

Figure 5. (a–e) The first 3 cycles CV at 0.5 mV/s rate of samples with different oxygen contents, the 2.5 wt.% O-Si anode (a), the 6.4 wt.% O-Si anode (b), the 13.5 wt.% O-Si anode (c), the 22.2 wt.% O-Si anode (d), the 35.8 wt.% O-Si anode (e). (f) Comparisons of the $dQ/dV$ plots of samples with different oxygen contents.

In Figure 5f, we conducted a detailed comparison of the differential capacity ($dQ/dV$) curves of the samples with varying oxygen contents during their initial charge–discharge cycles. Through this comparison, we found that these samples exhibit similar variations in overpotential, indicating the crucial role of the oxide layer in surface activation. Within the observed sample series, we identified a cathodic peak attributed to Si lithiation, located around 0.07 V, accompanied by two distinct anodic peaks during delithiation. These curves also clearly depict the formation process of the SEI film and the lithiation behavior of the SiO$_x$ region. It is worth noting that, after the first charge–discharge cycle, all the electrodes experienced irreversible capacity loss, primarily due to the formation of irreversible components such as SEI, Li$_2$O, and lithium silicates [41–43]. The variation in oxygen levels and the distribution of silicon valence states among the samples led to variations in SEI formation and surface kinetics. Specifically, we observed that the Li ion intercalation potential, SEI formation, and lithiation potential of the 2.5 wt.% O-Si sample were more noticeable compared to the other four samples with higher oxygen contents, possibly due to its thinner surface oxide layer and lower silicon valence states. However, the cathodic peak of the 35.8 wt.% O-Si sample was weaker and broader, likely due to severe polarization from a 19.5 nm thick surface oxide layer and a greater concentration of Si$^{3+}$ and Si$^{4+}$. This finding provides a new perspective for understanding the influence of various oxygen contents on silicon-based electrodes.

The Li-ion storage kinetics of all the samples were detected to understand the relationship between oxidation and Li-ion storage properties [44]. After the second cycle of charging, we conducted a thorough EIS measurement. The frequency range of this test spans a broad spectrum from 100 kHz to 10 mHz, aiming to delve into the electrode’s electrochemical response under different frequencies. Figure 6a displays the EIS Nyquist plots of samples, and the shape of this curve gives important information about how electric charge is transferred between the electrode and the interface with the electrolyte. The depressed semicircle region mainly represents the charge transfer impedance ($R_t$) at the electrode–electrolyte interface, whereas the sloping tail is associated with the diffusion process of lithium ions [45–47].
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Figure 6. (a) EIS spectra of samples with different oxygen contents. (b) Bar chart model depicting the numerical relationship between oxygen content and \( R_{ct} \). (c) Warburg coefficients for samples with different oxygen contents. (d) Bar chart model depicting the numerical relationship between oxygen content and lithium-ion diffusion coefficient. (e) Logarithm of the slope from \( \ln(D_{\text{Li-ion}}) \) versus the inverse temperature for Li-ion uptake in samples with different oxygen contents. (f) Bar chart model depicting the numerical relationship between oxygen content and activation energy.
The equivalent circuit elements were incorporated to analyze the EIS data, such as contact resistance (R_{sol}), charge transfer impedance (R_{ct}), constant phase element capacitance (CPE_{ct}), and Warburg impedance (W_{diff}) [48,49]. Figure 6b displays the charge transfer impedance (R_{ct}) values of the samples with varying oxygen contents, facilitating a direct comparison and investigation of the discrepancies in charge transfer efficiency among the samples. A low R_{ct} value of 163.5 Ω was observed in the sample with a minimal oxygen content of 2.5 wt.% O-Si. Additionally, there was a significant rise in R_{ct} from 215 to 500 Ω for the 13.5 wt.% O-Si sample to 35.8 wt.% O-Si, indicating that Li-ion storage kinetics might be charge transfer-controlled with high oxygen contents.

To further study the oxidation-dependent Li-ion storage kinetics, the Li diffusion characteristics were further examined using electrochemical impedance spectroscopy. As depicted in Figure 6c, the Li^+ diffusion coefficient was determined using the following formula:

\[
D = R^2 T^2 / 2 A n^4 F^4 C^2 \sigma^2 \tag{1}
\]

where A represent the electrode surface area with a value of 1.54 \times 10^{-4} \text{ m}^2, and n denotes the number of electrons involved in the electronic transfer reaction per molecule. F represents the Faraday constant, measured at 9.65 \times 10^4 \text{ C/mol}, C is the concentration of lithium ions in the electrode, R symbolizes the gas constant, valued at 8.314 J/K mol, and T signifies the experimental room temperature. \sigma corresponds to the slope of the line Z\sim\omega^{-1/2} [50–53], which is inversely proportional to the lithium-ion diffusion coefficient \(D_{Li-ion}\). It is observed that the sample with a minimal oxygen content (2.5 wt.% O-Si) demonstrates the highest Li-ion diffusion coefficient of 7.67 \times 10^{-12} \text{ cm}^2/s (Figure 6d), which might be attributed to a thinner amorphous layer facilitating the diffusion of lithium ions. A slight increase in oxygen content to 6.4 wt.% leads to a significant decrease in the Li-ion diffusion coefficient to 2.51 \times 10^{-12} \text{ cm}^2/s. Furthermore, the increase in the thickness of its outer amorphous layer is unfavorable for the transmission of lithium ions, and all the studied samples with oxygen content over 6.4 wt.% demonstrate similar Li-ion diffusion coefficients. The improved electrochemical performance of the anode can be imputed to both the increased Li^+ diffusion coefficient and the reduced distance for Li-ion transfer. This observation further supports the notion that the Li^+ storage kinetics of the 2.5 wt.% O-Si are controlled by diffusion transfer processes.

By determining the \(D_{Li-ion}\) of the samples under different temperatures, the activation energy for Li-ion uptake can be obtained as follows:

\[
D_{Li-ion} = D_0 e^{-E_a/kT} \tag{2}
\]

\(D_0\) is the pre-exponential factor (the specific method for calculating \(D_0\), please refer to the supporting information), \(E_a\) is the activation energy, \(k\) is the Boltzmann constant, and \(T\) is the absolute temperature [47]. The methodology used for measuring activation energy involves experimental techniques such as Arrhenius plotting; plotting the natural logarithm of the rate constant against the reciprocal of the temperature can help determine activation energy, which is temperature-dependent. Figure 6e shows the logarithm of the \(D_{Li-ion}\) versus \(T^{-1}\), and the corresponding normalized activation energy for lithium-ion insertion is plotted in Figure 6f. The sample with the lowest oxygen content demonstrates the lowest activation energy. Benefited by the low \(R_{ct}\), the high \(D_{Li-ion}\), and the low \(E_a\), the 2.5 wt.% O-Si demonstrates high capacity and high-rate performance. The samples with oxygen contents ranging from 13.5 wt.% to 35.8 wt.% demonstrate relatively similar \(E_a\) values. Considering that these three samples demonstrate similar \(D_{Li-ion}\) values and obvious changes in \(R_{ct}\), we conclude that the Li-ion storage kinetics of these samples is charge transfer-resistance controlled. In the case of the 35.8 wt.% O-Si, its high \(E_a\) and \(R_{ct}\) values and low \(D_{Li-ion}\) lead to the absolute loss of Li-ion storage properties.

To elucidate the structural stability of the electrodes of the samples with various oxygen levels, cross-sections of the electrodes of the samples before and after 100 charge/discharge cycles at 0.5 A/g were analyzed by using SEM examination [48]. The initial thicknesses
of the 2.5 wt.% O-Si, 6.4 wt.% O-Si, 13.5 wt.% O-Si, 22.2 wt.% O-Si, and 35.8 wt.% O-Si electrodes were 13.8, 12.7, 14.1, 18.4, and 12.3 μm (Figure 7a,c,e,g,i). After 100 cycles, the thickness of the 2.5 wt.% O-Si electrode was 17.2 μm, and electrode cross-sectional expansion rate was only 24.6% (Figure 7b). While the thicknesses of the 6.4 wt.% O-Si, 13.5 wt.% O-Si, 22.2 wt.% O-Si, and 35.8 wt.% O-Si electrodes were 19.7, 28.7, 37.9, and 39.7 μm, the electrode cross-sectional expansion rates were, respectively, 55.1%, 103.5%, 106.0%, and 222.7% (Figure 7d,f,h,j). The structural changes in the 2.5 wt.% O-Si electrode material was not conspicuous, implying that to some extent, its thinner oxide layer inhibited the occurrence of expansion and side reactions induced by volume effects. As shown in Figure 7k, the gradual increase in expanded thickness along with the increase in oxygen contents further confirms the absolutely detrimental effects on the Li-ion storage performance of silicon waste samples.

4. Conclusions

In summary, a series of silicon samples with various oxygen contents were primed to investigate the impact of oxidation on the Li⁺ storage properties of kerf loss silicon waste materials. By systematically studying the Li-ion storage properties and kinetics, it was found that oxidation plays an absolutely detrimental effect on the Li-ion storage performance, which is different to previous results about the oxidation of other nano-silicon materials. Additionally, oxidation leads the Li-ion storage kinetics to transform from a Li-ion diffusion-controlled to a charge transfer-controlled state. The results presented in this work might be helpful for supporting the exploration techniques used to transform kerf loss silicon waste into silicon anodes.

Figure 7. SEM images of the cross-sectional expansion changes in electrodes from samples with various oxygen contents before and after 100 charge/discharge cycles: (a,b) 2.5 wt.% O-Si, (c,d) 6.4 wt.% O-Si, (e,f) 13.5 wt.% O-Si, (g,h) 22.2 wt.% O-Si, (i,j) 35.8 wt.% O-Si, (k) Cross-sectional expansion rates corresponding to samples with various oxygen contents.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/ article/10.3390/pr12061173/s1. Figure S1: The graph of the relationship between annealing time at 100 °C of the purified kerf loss silicon waste in air at different time intervals and oxygen contents. Figure S2: SEM images of images of the samples with different oxygen contents. (a) 2.5 wt.% O-Si, (b) 6.4 wt.% O-Si, (c) 13.5 wt.% O-Si, (d) 22.2 wt.% O-Si, (e) 35.8 wt.% O-Si. Figure S3: The particle sizes and specific surface areas of samples with different oxygen contents. (a,b) 2.5 wt.% O-Si, (c,d) 6.4 wt.% O-Si, (e,f) 13.5 wt.% O-Si, (g,h) 22.2 wt.% O-Si, (i,j) 35.8 wt.% O-Si. Figure S4: Charge–discharge curves of samples with different oxygen contents at all cycling rates. (a) 2.5 wt.% O-Si, (b) 6.4 wt.% O-Si, (c) 13.5 wt.% O-Si, (d) 22.2 wt.% O-Si, (e) 35.8 wt.% O-Si. Table S1: Comparison of research on standard silicon oxide material, SiO$_2$-based anodes, and kerf loss Si in recent years. Refs. [14,43,56–59] are cited in Table S1.

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