Instantaneous formation of SiO$_x$ nanocomposite for high capacity lithium ion batteries by enhanced disproportionation reaction during plasma spray physical vapor deposition

Tohru Tashiro$^a$, Masashi Dougakiuchi$^b$ and Makoto Kambara$^a$

$^a$Department of Materials Engineering, The University of Tokyo, Hongo, Japan
$^b$Shimane Institute for Industrial Technology, Matsue, Japan

ABSTRACT
Nanocomposite SiO$_x$ particles have been produced by a single step plasma spray physical vapor deposition (PS-PVD) through rapid condensation of SiO vapors and the subsequent disproportionation reaction. Core-shell nanoparticles, in which 15 nm crystalline Si is embedded within the amorphous SiO$_x$ matrix, form under typical PS-PVD conditions, while 10 nm amorphous particles are formed when processed with an increased degree of non-equilibrium effect. Addition of CH$_4$ promotes reduction in the oxygen content $x$ of SiO$_x$, and thereby increases the Si volume in a nanocomposite particle. As a result, core-shell nanoparticles with $x = 0.46$ as anode exhibit increased initial efficiency and the capacity of lithium ion batteries while maintaining cyclability. Furthermore, it is revealed that the disproportionation reaction of SiO is promoted in nanosized particles attaining increased Si diffusivity by two orders of magnitude compared to that in bulk, which facilitates instantaneous composite nanoparticle formation during PS-PVD.

1. Introduction
Silicon is a strong candidate for anodes in high density lithium ion batteries (LIB) owing to its 10-fold higher theoretical gravimetric and volumetric capacities than those of the conventional carbonous material. To make the best of its potential, however, structuring the material is necessary to cope with fracturing associated with a huge volume change as a result of (de)lithiation during (dis)charge reaction. Various structures have been reported to be effective in maintaining high cycle capacity:[1–10] decreasing the size of the material improves the capacity at longer cycles,[1–3] and in particular sizes smaller than 150 nm are reported to be free from fracturing.[4] However, smaller particles could reduce the initial efficiency as a result of the increased solid electrolyte interphase (SEI) formation on the increased specific surface area. Coating the silicon materials with carbonous materials works to improve the cyclability, possibly due to more stable SEI formation.[5,6] Composites including porous and nanotube structures are also effective in accommodating the Si dilation during lithiation and maintaining the contacts between particles and current collector after delithiation.[7–10] Another approach is to use SiO as active material.[11–21] Using the characteristic disproportionation reaction of SiO, nanosized Si can be dispersed within a SiO$_x$ matrix that is expected to reinforce the Si crystalline precipitates and attain stable
cyclability for long cycles.[12–14] Amorphous Si (a-Si) could also form by disproportionation reaction at temperatures lower than 800°C,[22] such that more stable cyclability can be anticipated,[23–25] although a-Si formation requires in general an annealing time longer than several hours. In addition, the presence of oxygen in this material becomes a source of irreversible capacity and the large initial capacity drop is a critical issue of this material when designing the battery structure.[20] Reduction of SiO is thus important not only to improve the initial efficiency but also to increase the volumetric capacity as a result of the increased relative volume of the Si active material. However, conventional annealing under a reducing atmosphere is not effective enough to attain reduction uniformly in a bulk SiO.

Plasma spray physical vapor deposition (PS-PVD) is a potential approach in producing composite SiO nanoparticles (SiO-NP) and reducing the oxygen content at the same time. The elemental process of SiO-NP formation in PS-PVD is evaporation of SiO raw powders and the subsequent condensation of these vapors. Therefore, addition of CH$_4$ to SiO at the vapor state promotes removal of oxygen from the vapor mixture owing to preferable formation of CO than SiO$_2$ vapor state promotes removal of oxygen from the vapor at temperatures higher than 1900 K,[26] and the oxygen content of the SiO-NP so produced after condensation is expected to decrease accordingly. In addition, SiO-NP undergoes disproportionation reaction immediately after condensation to form crystalline Si core structure. SiO-NP produced by PS-PVD in industry compatible high-throughput production using metallurgy grade SiO raw powders have shown a clear increase in capacity while maintaining cyclability.[27] This characteristic process of PS-PVD further implies that the SiO-NP structure can be modified by tuning the cooling history during co-condensation of SiO-CH$_4$ vapor mixtures. Especially with large non-equilibrium effect by rapid gas quenching, together with CH$_4$ addition, a-Si core structure is expected to form by low temperature disproportionation reaction in smaller SiO-NP with reduced oxygen content. In this article, we report the advantages and uniqueness of PS-PVD SiO-NP as anode for an increase in the capacity and cyclability of LIB, and also the fundamental path of composite formation during PS-PVD with particular emphasis on the enhanced disproportionation reaction in nanosized particles.

### 2. Experimental details

PS-PVD has been carried out with a hybrid PS system. Compared with the conventional PS systems, a greater degree of complete evaporation of coarse raw powders is anticipated due to a direct injection of powders into the highest temperature region of the direct-current (DC) plasma jet superimposing the radio-frequency (RF) plasma flame, which is advantageous for higher production throughputs.[28,29] Metallurgical grade SiO powders are used as raw materials and are injected into the plasma jet generated with Ar and H$_2$. A water-cooled gas-quenching vessel is placed underneath the plasma torch so that the plasma gas including the evaporated SiO vapors is immediately cooled and the nanoparticles so formed after condensation are attached on the vessel walls. Schematics of the system can be found elsewhere.[30] To modify the nanoparticle structures, two plasma conditions, at which different powder heating and cooling histories are expected, are employed; condition [A] as the typical PS-PVD and [B] for an increased quenching capability. The detailed plasma conditions are listed in Table 1. In brief, for case [B], plasma is generated at slightly higher pressure of 500 Torr with an increased RF input power in a smaller plasma torch tube. Under this condition, according to the fluid dynamics simulation,[31] the high temperature gas jet is confined axially and the cooler surrounding gas is caught more significantly at the tail flame in the gas-quenching vessel, resulting in a rather rapid gas cooling speed especially near the nucleation and growth temperature of SiO. For comparison, CH$_4$ gas is also added at a fixed molar ratio of C/Si = 0.25, at which no SiC phase was detected in the previous work.[27]

The PS-PVD particles collected from the vessel are ground in a mortar and sieved with a 20 μm mesh to remove greatly agglomerated particles. The existing phases are analyzed by X-ray diffraction (XRD) with Cu Kα irradiation. The XRD patterns are also used for Rietveld analysis to evaluate the crystallite size and the relative amount of the phases involved in the particles. Raman scattering is used to identify the presence of the amorphous structure in the PS-PVD particles. The nanostructure of the particles is observed by scanning transmission electron microscopy (STEM) and field-emission scanning electron microscopy (FE-SEM). The oxygen content of the PS-PVD particles is evaluated from the peak area fraction of XRD patterns after Rietveld analysis, assuming that the broad peak is attributed to SiO$_2$ phase. For the particles with no crystalline structure, thermogravimetry (TG) is employed and the residual oxygen amount is estimated by the increased weight.

### Table 1. PS-PVD conditions.

| Parameter | Case [A] | Case [B] |
|-----------|----------|----------|
| DC power (kW) | 8 | 9 |
| RF power (kW) | 90 | 100 |
| Pressure (Torr) | 400 | 500 |
| DC Ar flow rate (slm) | 10 | |
| Radial Ar flow rate (slm) | 140 | |
| Tangential Ar flow rate (slm) | 30 | |
| Powder carrier Ar flow rate (slm) | 3.6 | |
| Radial H$_2$ flow rate (slm) | 30 | |
| CH$_4$ addition (CH$_4$/SiO molar ratio) | 0, 0.25 | |
| ICP torch dia. and length (mm) | 60, 150 | 40, 100 |
| SiO powder average size (μm) | 165 | 15 |
| Powder feeding rate (g min$^{-1}$) | 8.0 | 2.2 |
| Processing time (min) | 10 | |

Abbreviations: ICP, inductively coupled plasma; slm, standard liter per minute.
after annealing under oxygen flow atmosphere with an assumption of complete oxidation to form SiO₂.

The PS-PVD particles after sieving are mixed with a conducting regent and polyimide binder at a fixed weight ratio of 60:15:25 to form a slurry and they are applied to a Cu foil current collector with a thickness of 40 μm. After roll-pressing and drying in Ar flow at 110 °C for 2 h, a 15 mm diameter anode is prepared. A half-coin cell using lithium metal as counter electrode is assembled with the electrolyte of LiPF₆ dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) mixture solvent with EC:DEC = 1:1 vol. The battery cycle test is carried out at a fixed temperature of 23 °C under a constant current mode with 0.1 mA (corresponding to 0.02 C rate) for the first three cycles and 0.5 mA (0.1 C) for the remaining cycles.

3. Results and discussion

3.1. Characteristics of Si/SiOₓ nanoparticles and battery performance

Figure 1 shows the XRD patterns of the SiO nanoparticles processed at different PS-PVD conditions. The raw SiO powder shows only a broad pattern, indicating the presence of only the non-crystalline structure. Once this powder is processed under the condition [A], sharp peaks corresponding to the crystalline Si appear along with a broad pattern with slightly reduced intensity. With an addition of CH₄, the diffraction patterns become sharper while the broad peak intensity decreases. For the case [B], in contrast, no diffraction patterns associated with the crystalline Si is observed and only the broad pattern is present for [B] without CH₄. When CH₄ is introduced during PS-PVD, crystalline Si phase is confirmed although the peak becomes rather broad, compared to that of the case [A], suggesting that Si particles become finer or partly amorphous.

Raman scattering spectra of these particles are shown in Figure 2. The peak associated with crystalline Si (c-Si) appears around 520 cm⁻¹ for condition [A] while the corresponding peak for condition [B] seems to shift toward the lower wave number and become wider especially to the low wave number direction. Defining the crystallinity as the area fraction of a peak centered at 520 cm⁻¹ (Ic) with respect to the sum of Ic and the peak at 480 cm⁻¹ (Ia) associated with amorphous, quantitative analysis after peak separation reveals that the crystallinity for particles [A] is 60% (without CH₄) and increases to 70% by addition of CH₄, whereas that of the particle [B] is as little as 32% (without CH₄) and reaches only 52% with CH₄. These suggest that the condition [B] tends fundamentally to suppress crystallization and CH₄ addition promotes crystallization for both conditions.

The structure of these particles processed without CH₄ is shown in Figure 3. From the SEM image, the particles at both [A] and [B] conditions are seen to form agglomerates of several 100 nm that are composed of smaller primary particles. In fact, TEM images (insets of Figure 3) show that the size of the primary particles is approximately 20 nm for case [A], whereas that for [B] looks slightly smaller, i.e. 10 nm on average. A major difference between these conditions is that a crystalline structure is surrounded by the amorphous shell for [A] while no lattice image is observed for [B]. This observation reasonably agrees with the presence/absence of the peaks in the XRD pattern shown in Figure 1.

The core-shell structure of [A] is suggestive of the occurrence of disproportionation reaction in a nanoparticle SiOₓ.[27] Therefore, given that the XRD sharp and broad peaks are attributed to Si and SiO₂, respectively, formed after disproportionation reaction of SiO, the degree of reduction of SiO can be quantified as the...
relative amount of oxygen, $x$, in the overall SiO$_x$ representation by the phase content evaluation with the Rietveld analysis. Note that the value $x$ so estimated is the maximum and may become even smaller if the shell is also partially reduced. As a result, $x$ for the particles [A] are estimated to be 0.87 (with CH$_4$) and 0.58 (without CH$_4$), suggesting that the reduction of SiO powders is enhanced by an addition of CH$_4$ during PS-PVD. In contrast, $x$ of the particles [B] with CH$_4$ is further reduced to be 0.46 compared to that of [A]. For the particles [B] without CH$_4$, in which no appreciable Si peaks are observed in the XRD, $x$ is estimated to be $x = 0.63$ by thermogravimetry analysis. This can be reasonably explained by the fact that the plasma gas temperature at condition [B] is expected to be higher than that at [A] and also that the CO(g) formation becomes more preferential to SiO at elevated temperatures.[26]. Therefore, the condition [B] works to promote reduction of SiO appreciably without CH$_4$ as well as to make c-Si finer or to suppress crystalline phase formation. Unfortunately, it was hard to identify clearly the state of Si from electron energy loss spectra (EELS) and distinguish a-Si from a-SiO in this particle. Even so, as will be discussed in the next section, considering that the disproportionation reaction is promoted in a nanoparticle, it is plausible that the a-Si forms at the core at least partly as a result of disproportionation reaction at low temperature.[22]

The half coin cells are assembled using these PS-PVD particles as anode and the cycle capacities and coulombic efficiencies are compared in Figure 4. As a general tendency, all the cells show a large capacity drop at the initial stage of the cycles but the capacities are stabilized after five cycles. For both cells with [A] and [B] particles, addition of CH$_4$ is seen to increase the average capacity, and the initial capacity increases from 51.6% (without CH$_4$) to 54.0% (with CH$_4$) for [A] and 45.3% (without CH$_4$) to 60.1% (with CH$_4$) for [B]. In addition, irrespective of CH$_4$ addition, the cells with the particles [B] show higher average capacity than that with [A] particles. These are reasonably explained by the increased degree of reduction, i.e. the increased Si relative volume. Moreover, considering also the fact that the fraction of

![Figure 3](image1.png)

**Figure 3.** SEM images of the SiO particles processed by PS-PVD without CH$_4$ addition under (a) [A] and (b) [B] condition. Inset is the STEM image of the primary particles. Circle and arrow are guide-to-eye for crystalline part and the primary particle, respectively.

![Figure 4](image2.png)

**Figure 4.** Comparison of the cycle capacity (a) and coulombic efficiency (b) of the PS-PVD SiO$_x$ particles. Parenthesis in (b) shows the initial efficiency.
c-Si in the [A] particles is relatively higher than that in [B], the reduction in the oxygen content has greater contributions to the increase in the capacity compared to the difference in the Si structure. Even so, it is interesting to note that the cell involving potentially a-Si (B) without CH\textsubscript{4} attains higher coulombic efficiency compared to other cells, and the a-Si structure at the pristine particle is therefore considered to be less vulnerable to the structural change in the repeated (de)lithiation. Nevertheless, the reduction during PS-PVD works effectively to compensate or even increase the inevitable low initial efficiency for nanosized particles.

### 3.2. Formation path of nanocomposite particles

#### 3.2.1. SiO nanoparticle growth

The premise of nanoparticle formation in PS-PVD is evaporation of the injected raw powders and the successive rapid condensation of the vapors so produced. Considering the fact that several 10 nm particles have been produced from 165 μm SiO powders under the condition [A] and also that the thermal load of powders at condition [B] is 0.275 of that at [A], the SiO vapor is potentially attained in the plasma under both conditions. The calculated equilibrium plasma chemistries also predict that SiO(g) is the most stable phase containing a Si atom and the relative amount of SiO(g) is somewhat constant at temperatures ranging from 2200 to 3500 K. Si(g) also forms because of decomposition of SiO but its relative amount is approximately smaller by 1/17 times than that of SiO(g) when no CH\textsubscript{4} is added in the system.[27] Therefore, SiO(g) is considered to present as a major gas species in the plasma jet.

Girshick et al. [32] have suggested that nucleation from alloy vapors could be treated similarly to gas with a single element as long as the relevant chemical reactions are completed before the nucleation event. SiO(s) is considered to form from SiO(g) vapor with no additional reactions during condensation. Therefore, homogeneous nucleation temperature of SiO(s) is estimated by the Becker-Döring classical nucleation model, taking into account the Lothe-Pound conception accordingly.[33,34] In the estimation, condensation of SiO(g) with constant gas partial pressure at 2500 K is assumed. Saturation vapor pressure of SiO reported by Ferguson and Nuth [35] and the temperature dependent specific surface energy of SiO(s) derived based on the scaled nucleation theory by Hale et al. [36] are also used. For the critical nucleation frequency, 10\textsuperscript{17} m\textsuperscript{-3}s\textsuperscript{-1} is employed as is introduced in estimation of the surface energy.[36] As a result, homogeneous nucleation temperature of SiO (T\textsubscript{N(SiO)}) under [A] and [B] conditions is calculated to be 1584 and 1494 K, respectively, both of which are approximately 0.7–0.8 of the sublimation temperature of SiO (2070 K).[37]

Nanoparticle growth after homogeneous nucleation has been extensively discussed, and several models are widely known to predict quite nicely the experimental evidence.[32,38–40] In the present work, we employ rather simple model proposed by Ulrich,[40] which is confirmed to reproduce at least the growth of Si nanoparticles in PS-PVD.[30] Compared to the growth of Si, collision between SiO and H\textsubscript{2} molecules in the plasma gas would become important as is found experimentally in the reduction of SiO in the Ar + H\textsubscript{2} plasma. Therefore, the growth inhibition factor, which is the ratio of the collision frequency of SiO particles with respect to that between SiO and H\textsubscript{2}, is introduced in the SiO particle number density evolution, assuming that the SiO molecule that collides with H\textsubscript{2} does not participate in the SiO growth. Moreover, the SiO particle would nucleate and grow along the gas stream in the vessel. Therefore, a typical gas streamline is selected from the simulated temperature and gas velocity distributions within the gas quenching vessel reported elsewhere,[31] and the SiO particle growth is calculated accordingly, as shown in Figure 5. The cooling curves below the estimated SiO homogeneous nucleation point are only shown in the figure. Not only the nucleation temperature but also the temperature of the gas stream within the vessel is lower for case [B]. Averaged cooling speed after nucleation for [B] is 4.5 × 10\textsuperscript{3} K s\textsuperscript{-1}, which is slightly greater than 3.4 × 10\textsuperscript{3} K s\textsuperscript{-1} for [A]. With these ‘increased degrees of non-equilibrium effect’, the growth of SiO particle at condition [B] is suppressed although the particle is seen to grow monotonically for both conditions.

Meanwhile, fluid flow simulation has predicted that the surface of the vessel wall is at 1100 K for [A] and 1000 K for [B] on average, thus the nanoparticles attached on the wall would be exposed to the high temperature gases at this temperature for the processing time of 10 min at the longest. However, if one compares the calculated SiO particle size with the experimentally observed average particle size shown in Figure 3, i.e. 20 nm for [A] and 8 nm for [B], the SiO growth is expected to terminate at temperature around 1200–1300 K irrespective of
the plasma conditions. That is, the SiO growth finishes during flight and the nanoparticles attached on the wall are readily subject to the disproportionation reaction at the wall temperature for the remaining PS-PVD time.

### 3.2.2. Disproportionation reaction in a nanoparticle

It is known that SiO undergoes disproportionation reaction to form Si precipitates in SiO matrix when exposed to high temperature, and the size of precipitates varies significantly with annealing temperature and duration. [14,22,41,42] Generally, high temperature and long annealing time is required to form large Si precipitates: For instance, to attain crystalline Si precipitates as large as 10 nm, 4 h at 1423 K [41] or 24 min at 1573 K [14] is necessary. When the annealing temperature is lowered below 1073 K, structure of the precipitates is primarily amorphous.[22,42] In this case, also, an annealing time as long as 18 h is required to produce 4.5 nm amorphous Si at 1073 K.

Formation of crystalline clusters through disproportionation reaction is considered to proceed by Si diffusion-controlled growth.[42] Although Nesbit [42] assumes that the diffusion coefficient is independent of the O/Si ratio, in the present work, adopting the diffusion-controlled disproportionation reaction model, oxygen content dependent diffusion coefficient, $D(x)$, is introduced and estimated for bulk SiO using the data reported in the reference. In this approach, the size of the precipitate $d(x)$ is expressed as a function of annealing time $t$ and temperature $T$:[41,43]

$$d(x)^2 - d_0^2 = t D_0 (x) \exp \left( \frac{-E_a}{kT} \right)$$

(1)

where $d_0$ is the initial precipitate size, $E_a$ the activation energy for diffusion, and $k$ the Boltzmann constant. $D_0(x)$ is the $x$ dependent pre-factor of diffusivity, i.e. $D(x)=D_0(x)\exp(-E_a/kT)$. Using the values $d_0 = 0.5$ nm, $E_a = 1.9 \text{ eV/atom}$ and the Si precipitate size at a certain $x$ and $T$, which are all reported by Nesbit, $D_0(x)$ is obtained as $D_0(x) = (4.35 - 2.36x) \times 10^{-9} \text{ [cm}^2/\text{s}]$.

Meanwhile, with Equation (1), one can calculate the precipitate growth size $\Delta d$ during an infinitesimal time $\Delta t$ at a certain temperature $T$: the final Si precipitate size as a result of an annealing is thus given by summing $\Delta d$ for the entire thermal history of PS-PVD. Since the crystalline Si is potential to precipitate and grow at temperature higher than 1073 K below which amorphous Si is to form,[22] the disproportionation reaction in PS-PVD is assumed to start immediately after SiO nucleation and continue until PS-PVD finishes in 10 min. It is, therefore, noted that the size of the Si precipitate so estimated corresponds to the maximum size. Also, from Figure 3, the crystalline Si precipitate size $d$ of the particles processed by PS-PVD is 20 nm on average and is much larger than $d_0$ yielding $(d_0^2/d^2) < 10^{-4}$. This reasonably allows us to ignore the term $d_0$ in Equation (1). With these assumptions and the reported $E_a$ of 1.9 eV/atom, Si precipitate size along the cooling history shown in Figure 5 is calculated to be approximately 0.5 nm, which is much smaller than the size observed in TEM shown in Figure 3. This large discrepancy is presumably due to the value $E_a$ used which is derived for the bulk SiO not for nanoparticle.

To elucidate the characteristics of the disproportionation reaction in a nanosized SiO, the continuous-cooling-transformation (CCT) diagram is considered for formation of crystalline precipitates during cooling in PS-PVD. The nose of Si precipitates can be expressed by rearranging the equation (1):

$$T = \frac{E_a}{k} \left[ \ln \left( \frac{t D_0 (x) \exp(-E_a/kT)}{d_0 (x)^2} \right) \right]^{-1}$$

(2)

The critical precipitate size for crystallization $d_{cr}(x)$ and $E_a$ can be uniquely determined by satisfying the experimental evidence that crystalline Si precipitate forms under condition [A] without CH$_4$. That is, the cooling curve of [A] should intersect with the CCT nose of $x = 0.87$ and the c-Si core size $d$ after cooling reaches as large as 15 nm, as is observed in Figure 3(a). To meet these conditions, $d_{cr}(x)$ is estimated to be 0.4 nm, which would be reasonable as the nucleation threshold for nanometer sized particle. Also, $E_a$ is calculated to be 1.43 eV/atom, indicating that the less activation energy is required for diffusion in nanoparticle than bulk SiO.

The CCT nose estimated for nanoparticle SiO$_x$ with $x = 0.87$ is shown in Figure 6 and compared with that of bulk, along with the cooling curves after the nucleation point of SiO for the cases [A] and [B]. It is seen that the CCT nose for bulk SiO intersects with the cooling curve of [A] only very close to the end of the processing (5 × 10$^3$ ms). This implies that the c-Si hardly grows in a

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Figure 6. CCT diagram describing the nose of the disproportionation reaction of formation of crystalline Si precipitates (dotted line) both in bulk (black) and nanosized SiO$_x$ (green) with $x = 0.87$. Cooling curves of case [A] and [B] are also shown for comparison.
between the initial SiO\(_x\) and the a-SiO\(_2\) and a-Si/c-Si mixture as a driving force. It is therefore expected that greater driving force is attained for the nanoparticle and tends to promote the reaction. Also, this tendency should be further pronounced for SiO\(_x\) with smaller \(x\) due to the increased energy at \(x < 1\). However, as seen in Figure 1, the nanoparticles processed under condition [B] (blue circle) include a small amount of c-Si (with CH\(_4\)) or no c-Si (without CH\(_4\)), suggesting that the corresponding energies of these nanoparticles are not necessarily on the same balanced energy line of the particles [A] (green circle). This readily supports that the disproportionation reaction is kinetically controlled, and the structure of the nanoparticle can be designed by the processing accordingly.

By adopting the same approach to the a-Si formation in bulk SiO reported in [22], the activation energy for amorphous phase formation \(E_{\text{a,amo}}\) is estimated to be 0.14 eV/atom for \(x = 1\), which is much smaller than 1.9 eV/atom for the c-Si in a bulk SiO. It is understood that a-Si formation proceeds with less energy because of lack of necessity of atomic alignment. In the case of [B], on the other hand, despite that the CCT nose intersects with cooling curve at around \(1 \times 10^4\) ms, since the temperature drops immediately below 1073 K in \(2 \times 10^2\) ms, a-Si is expected to form before c-Si precipitates.

The estimated diffusivity \(D(x)\) is also plotted in Figure 7 as a function of temperature. It is clearly seen that diffusivity in nanoparticles increases by approximately two orders of magnitude than that for the bulk SiO within the temperature range considered in the present work. Also, diffusivity increases with decreasing the oxygen content \(x\), although its effect is rather small compared to the particle size.

Considering the phase and relative amount after disproportionation reaction of SiO\(_x\) with different \(x\), the Gibbs energy–composition diagram for the Si-O system is drawn schematically in Figure 8. The Gibbs energy of amorphous SiO\(_x\) phase exists supposedly over a wide area of \(x\) having the local minimum at \(x = 1\) as no other stable phase is reported in this system. Also, the Gibbs energy of SiO\(_x\) nanoparticle phase should be larger than that of bulk SiO\(_x\) phase as a result of the Gibbs–Thomson effect.

Under this relationship, when a-SiO\(_x\) is annealed at a certain temperature and disproportionation reaction takes place, the Gibbs energy of SiO\(_x\) phase with any \(x\) is dropped to the balanced energy of a mixture of a-SiO\(_2\) and either c-Si or a-Si, having the energy difference between the initial SiO\(_x\) and the a-SiO\(_2\) and a-Si/c-Si mixture as a driving force. It is therefore expected that greater driving force is attained for the nanoparticle and tends to promote the reaction. Also, this tendency should be further pronounced for SiO\(_x\) with smaller \(x\) due to the increased energy at \(x < 1\). However, as seen in Figure 1, the nanoparticles processed under condition [B] (blue circle) include a small amount of c-Si (with CH\(_4\)) or no c-Si (without CH\(_4\)), suggesting that the corresponding energies of these nanoparticles are not necessarily on the same balanced energy line of the particles [A] (green circle). This readily supports that the disproportionation reaction is kinetically controlled, and the structure of the nanoparticle can be designed by the processing accordingly.

4. Conclusions

Nanocomposite SiO\(_x\) particles 10–20 nm in diameter have been produced by PS-PVD. Addition of CH\(_4\) during PS-PVD is found to be effective in reducing SiO, which
is further pronounced under the condition of less powder-feeding rate with greater gas-quenching degrees during PS-PVD. Under such environments, SiO particles are cooled rapidly to attain smaller size and the subsequent disproportionation reaction is also influenced to alter the particle structure from crystalline to amorphous. Batteries using these nanocomposites produced at the rapid-cooling condition with CH$_4$ have exhibited increased cycle capacity and initial efficiency while maintaining stable cyclability. In addition, it is identified that Si diffusion during the disproportionation reaction is significantly enhanced in the nanosized particle, attaining greater diffusivity by two orders of magnitude than that in a bulk SiO, which facilitates instantaneous nanoparticle and composite structure formation in PS-PVD.

**Funding**

This work is partly supported by the Grant-in-Aid for Scientific Research [(B) 15H04152].

**References**

[1] Graetz J, Ahn CC, Yazami R, et al. Highly reversible lithium storage in nanostructured silicon. Electrochem Solid-State Lett. 2003;6:A194–A197.

[2] Kasavajjula U, Wang C, Appleby AJ. Nano- and bulk-silicon-based insertion anodes for lithium-ion secondary cells. J. Power Sources. 2007;163:1003–1039.

[3] Zhao K, Pharr M, Classak JJ, et al. Fracture of electrodes in lithium-ion batteries caused by fast charging. J Appl Phys. 2010;108:073517.

[4] Liu XH, Zhong L, Huang S, et al. Size-dependent fracture of silicon nanoparticles during lithiation. ACS Nano. 2012;6:1522–1531.

[5] Yoshio M, Wang H, Fukuda K, et al. Carbon-coated Si as a lithium-ion battery anode material. J Electrochem Soc. 2002;149:A1598–A1603.

[6] Ng SH, Wang J, Wexler D, et al. Amorphous carbon-coated silicon nanoparticles: a low-temperature synthesis via spray pyrolysis and their application as high-capacity anodes for lithium-ion batteries. J Phys Chem. 2007;111:11311–11318.

[7] Chan CK, Peng H, Liu G, et al. High-performance lithium battery anodes using silicon nanowires. Nat Nanotechnol. 2008;3:31–35.

[8] Liu N, Lu Z, Zhao J, et al. A pomegranate-inspired nanoscale design for large-volume-change lithium battery anodes. Nat Nanotechnol. 2014;9:187–192.

[9] Wu H, Chan G, Choi JW, et al. Stable cycling of double-walled silicon nanotube battery anodes through solid-electrolyte interphase control. Nat Nanotechnol. 2012;7:310–315.

[10] Magasinski A, Dixon P, Hertzberg B, et al. High-performance lithium-ion anodes using a hierarchical bottom-up approach. Nat Mater. 2010;9:353–358.

[11] Miyachi M, Yamamoto H, Kawai H, et al. Analysis of SiO anodes for lithium-ion batteries. J Electrochem Soc. 2005;152:A2089–A2091.

[12] Morita T, Takami N, Nano Si cluster-SiOx-C composite material as high-capacity anode material for rechargeable lithium batteries. J Electrochem Soc. 2006;153:A425–A430.

[13] Park CM, Choi W, Hwa Y, et al. Characterizations and electrochemical behaviors of disproportionated SiO and its composite for rechargeable Li-ion batteries. J Mater Chem. 2010;20:4854–4860.

[14] Mamiya M, Takei H, Kikuchi M, et al. Preparation of fine silicon particles from amorphous silicon monoxide by the disproportionation reaction. J Cryst Growth. 2001;229:457–461.

[15] Doh CH, Shin HM, Kim DH, et al. Improved anode performance of thermally treated SiO/C composite with an organic solution mixture. Electrochem Soc. 2008;10:233–237.

[16] Kim JH, Sohn HJ, Kim H, et al. Enhance cycle performance of SiO-C composite anode for lithium-ion batteries. J Power Sources. 2007;170:456–459.

[17] Kim JH, Park CM, Kim H, et al. Electrochemical behavior of SiO anode for Li secondary batteries. J Electroanal Chem. 2011;661:245–249.

[18] Kim T, Park S, Oh SM. Solid-state NMR and electrochemical dilatometry study on Li+ uptake/extraction mechanism in SiO electrode. J Electrochem Soc. 2007;154:A1112–A1117.

[19] Wang J, Zhao H, He J, et al. Nano-sized SiOx/C composite anode for lithium ion batteries. J Power Sources. 2011;196:4811–4815.

[20] Al-Maghribi MA, Suzuki J, Sanderson RJ, et al. Combinatorial studies of Si1-xOx as a potential negative electrode material for Li-ion battery applications. J Electrochem Soc. 2013;160:A1587–A1593.

[21] Park E, Yoo H, Lee J, Park MS, et al. Dual-size silicon nanocystal-embedded SiO$_x$ nanocomposite as a high capacity lithium storage material. ACS Nano. 2015;9:7690–7696.

[22] Wang J, Wang XF, Li Q, et al. The microstructure of SiO thin films: from nanoclusters to nanocrystals. Philos Mag. 2007;87:11–27.

[23] Baranchugov V, Markevich E, Pollak E, et al. Amorphous silicon thin films as a high capacity anodes for lithium batteries in ionic liquid electrolytes. Electrochem Comm. 2007;9:796–800.

[24] Bourderau S, Brousse T, Schleich DM. Amorphous silicon as a possible anode material for Li-ion batteries. J Power Sources. 1999;81–82:233–236.

[25] Maranchi JP, Hepp AF, Kunta PN. High capacity, reversible silicon thin-film anodes for lithium-ion batteries. Electrochem Solid-State Lett. 2003;6:A198–A201.

[26] Elliott JJ, Gleiser M. Thermochemistry for Steelmaking. Reading (MA): Addison-Wesley; 1960.

[27] Homma K, Kambara M, Yoshida T. High throughput production of nanocomposite SiO$_x$ powders by plasma spray physical vapor deposition for negative electrode of Li-ion batteries. J Power Sources. 2011;196:4811–4815.

[28] Yoshida T, Tani T, Nishimura H, et al. Characterization of a hybrid plasma and its application to a chemical synthesis. J Appl Phys. 1983;54:640–646.

[29] Huang H, Eguchi K, Kambara M, et al. Ultrafast thermal plasma physical vapor deposition of yttria-stabilized zirconia for novel thermal barrier coatings. J Thermal Spray Technol. 2006;15:83–91.

[30] Kambara M, Kitayama A, Homma K, et al. Nano-composite Si particle formation by plasma spraying for negative electrode of Li ion batteries. J Appl Phys. 2014;115:143302.

[31] Kambara M, Hideshima T, Kaga M, et al. Plasma Spray PVD: High throughput production of powders. Encyclopedia of Plasma Technol. In press.
[32] Girshick SL, Chiu CP, McMurry PH. Modelling particle formation and growth in a plasma synthesis reactor. Plasma Chem Plasma Process. 1988;8:145–157.
[33] Abraham FF. Homogeneous nucleation theory. New York (NY): Academic Press; 1974.
[34] Lothe J, Pound GM. Reconsiderations of nucleation theory. J Chem Phys. 1962;36:2080–2085.
[35] Ferguson FT, Nuth III JA. Vapor pressure of silicon monoxide. J Chem Eng Data. 2008;53:2824–2832.
[36] Hale BN, Kemper P, Nuth JA. Analysis of experimental nucleation data for silver and SiO using scaled nucleation theory. J Chem Phys. 1989;91:4314–4317.
[37] Schnurre SM, Gröbner J, Schmid-Fetzer R. Thermodynamics and phase stability in the Si-O system. J Non-Cryst Solids. 2004;336:1–25.
[38] Girshick SL, Chiu CP, McMurry PH. Time-dependent aerosol models and homogeneous nucleation rates. Aerosol Sci Technol. 1990;13:465–477.
[39] Shigeta M, Watanabe T. Growth model of binary alloy nanopowders for thermal plasma synthesis. J Appl Phys. 2010;108:043306.
[40] Ulrich GD. Theory of particle formation and growth in oxide synthesis flames. Comb Sci Technol. 1971;4:47–57.
[41] Ke W, Feng X, Huang Y. Annealing effects on the size of Si-nanocrystals embedded in bulk SiO. J Cryst Growth. 2011;316:191–195.
[42] Nesbit LA. Annealing characteristics of Si-rich SiO$_2$ films. Appl Phys Lett. 1985;46:38–40.
[43] Burke JE, Turnbull D. Recrystallization and grain growth. Prog Metall Phys. 1952;3:220–292.