

Formation Mechanism of Carbon-Coated Amorphous Si Nanoparticles Synthesized by Induction Thermal Plasmas

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Abstract: Amorphous Si nanoparticles were synthesized with carbon-coated by CH₄ or C₂H₄ injection into the downstream induction thermal plasma. The difference of carbon source influences the characteristics of carbon coating. Analysis of STEM-EDS shows Si nanoparticles were covered by carbon coating with a thickness ranges from 4 to 8 nm. Induction thermal plasma enables to fabricate the Si nanoparticles as new anode materials in lithium-ion batteries.

Keywords: Thermal plasmas, lithium-ion battery, negative electrode

1. Introduction

Lithium-ion battery (LiB) has been used as light-weight and high-density rechargeable batteries for various portable devices and electric vehicles. Silicon is expected as a promising material which has high theoretical capacity of 4200 mAh/g, nearly 10 times higher than that of the conventionally used graphite. However, the problem of Si as an anode is a large volume change up to 400% associated with lithiation-delithiation during the charge/discharge cycle. This leads to pulverization of Si particles and formation of unfavourable solid electrolyte interphase (SEI), resulting in a drastic capacity decay in short recharge cycles [1].

Nanoparticulation, amorphization, and coating of the particle surface with electrically conductive material are the best ways to solve above-mentioned problems. Silicon nanoparticles can be lithiated without cracking when the diameter is less than 150 nm. Amorphous particles can prevent from cracking by a volume change. Coating of the particle surface by carbon is effective to inhibit the surface oxidation. Furthermore, carbon coating allows long charge/discharge cycle performance because of the proper SEI formation [2]. The techniques commonly employed in the fabrication of these Si materials are chemical vapor deposition, sol-gel, microemulsion, and spray pyrolysis. However, productivity of Si materials by these techniques are insufficient to be applied to LiB industry that is the biggest markets in the world.

Thermal plasmas have attracted a great attention to overcome current situation due to its high productivity at single step synthesis of many kinds of attractive nanomaterials such as core/shell structured nanomaterials including carbon-coated Si nanoparticles. This originates from unique advantages of thermal plasmas such as high enthalpy to enhance reaction kinetics, high chemical reactivity, selectivity of reaction atmosphere in accordance with required chemical reactions, and rapid quenching capability to synthesize metastable nanomaterials such as amorphous nanoparticles. In addition, induction thermal plasma can synthesize high-purity nanoparticles because it

can be generated in a plasma torch without internal electrodes.

The purpose of the present work is to synthesize carbon-coated amorphous Si nanoparticles by induction thermal plasma, and to investigate the formation mechanism.

2. Experiment methods

Figure 1 shows an experimental setup of the induction thermal plasma. This setup consists of a plasma torch, a synthesis chamber, a particle filter, and power supply with the frequency of 4MHz. Plasma is generated by applying high frequency power to the induction coil outside of the torch. Crystalline Si powder with 5 μ m of average diameter was injected from the powder feeder by Ar carrier gas. These raw materials were introduced into the top of the plasma torch and immediately evaporated in the high temperature region. In the tail region of the plasma, Si vapour nucleated and then condensed onto its nucleus

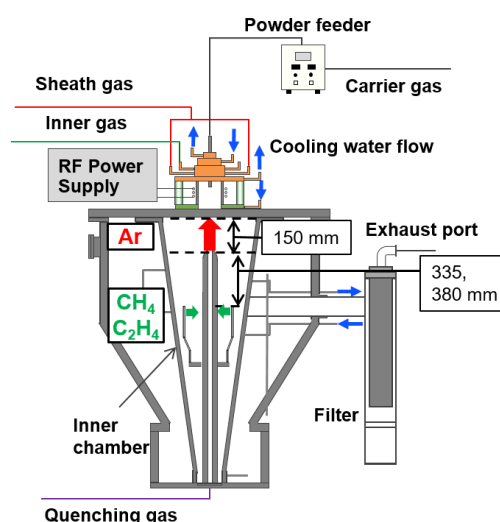


Fig. 1. Experimental setup of RF induction thermal plasma for preparation of nanoparticles.

Table 1. Experimental conditions for the induction thermal plasma system.

Input power [kW]	17.5
RF frequency [MHz]	4
Pressure [kPa]	101.3
Sheath gas rate [L/min]	60(Ar)
Inner gas rate [L/min]	5(Ar)
Carrier gas rate [L/min]	3(Ar)
Quenching gas rate [L/min]	20(Ar)
Discharge time [min]	5
Feed rate [g/min]	0.4
CH ₄ or C ₂ H ₄ gas rate [L/min]	0.96 or 0.48
C/Si	3
Carbon source injection positions	500-530 mm from the torch to carbon source injection position

forming Si nanoparticles. Ar quenching gas was introduced as a counter flow to enhance the quenching effect for the purpose of amorphization of Si. Hydrocarbon gas, CH₄ or C₂H₄, was also injected into the lower temperature region as a carbon source. Synthesized nanoparticles were collected at the filter.

Table 1 summarizes the experimental conditions. Ar was used as the sheath, carrier, and inner gases. The quenching gas was injected at flow rate of 20 L/min. In this work, carbon source was changed to investigate the formation mechanism of carbon-coated amorphous Si nanoparticles. CH₄ or C₂H₄ gas was injected at flow rate of 0.96, 0.48 L/min at the fixed C/Si of 3.0.

3. Analysis

The phase identification of the synthesized nanoparticles was determined through powders X-ray diffraction (XRD, Rigaku Multiflex), operating with a Cu K α source ($\lambda = 0.1541$ nm). The diffraction data was collected using the continuous scan mode at a speed of 2°/min in the region of 10–90° with a step of 0.04°. The accelerating voltage and applied current were 40 kV and 50 mA, respectively. The particle morphology was observed by transmission electron microscopy (TEM, JEOL JEM-2100HCKM) and size distributions were measured by counting approximately 200 different particles. Element mapping of nanoparticles was conducted by scanning STEM-energy dispersive X-ray spectrometry (STEM-EDS, JEOL JEM-ARM 200F). The chemical bonds were identified through Raman spectra measured using a microscopic laser Raman spectrometer (LabRAM ARAMIS) equipped with a 532 nm excitation laser.

4. Results

Figure 2 presents the XRD patterns of the synthesized nanoparticles at different carbon sources and injection positions. Only crystal Si peaks can be observed from the nanoparticles synthesized with the lower injection position of 530 mm from the plasma torch. However, SiC was generated with the higher injection position of 500 mm from the plasma torch. Mole fractions of the products are

summarized in **Fig. 3**. The amorphization degree was defined as shown in the following equation.

$$\text{Amorphization degree} = \frac{w_{\text{Si}(\alpha)}}{w_{\text{Si}(\alpha)} + w_{\text{Si}(\text{c})}} \quad (1)$$

where w indicates the mass fraction of the considered species in the prepared nanoparticles. The estimated amorphization degrees were in the range of 34–58%.

The obtained TEM images and size distributions of prepared Si nanoparticles are shown in **Figs. 4** and **5**. Most of the observed nanoparticles have spherical shapes, while some of the nanoparticles are in angular shape. In addition, nanowire was also observed, while similar phenomenon also was observed in previous research [3]. Number mean diameters of the prepared Si nanoparticles except nanowires were 43–48 nm.

Figures 6 and **7** show the STEM-EDS mappings of Si and C in the prepared nanoparticles. These images indicate

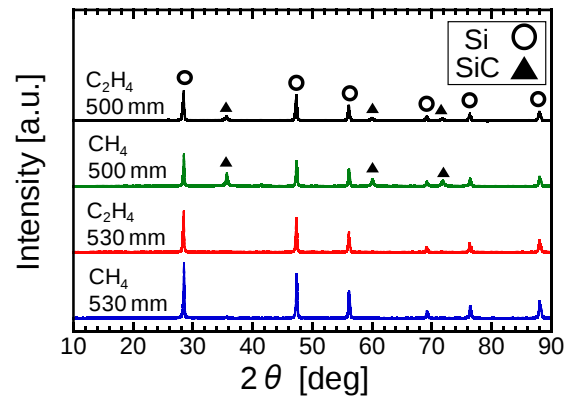


Fig. 2. XRD patterns of the synthesized Si nanoparticles with different carbon sources and injection positions.

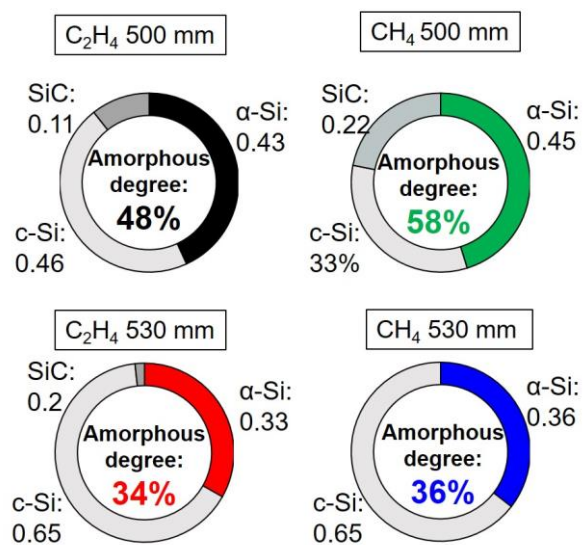


Fig. 3. Mole fractions of prepared nanoparticle with different carbon sources and injection positions.

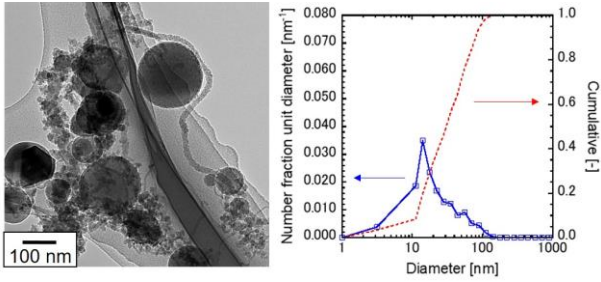


Fig. 4. TEM images and size distributions of prepared Si nanoparticles with carbon source of CH₄.

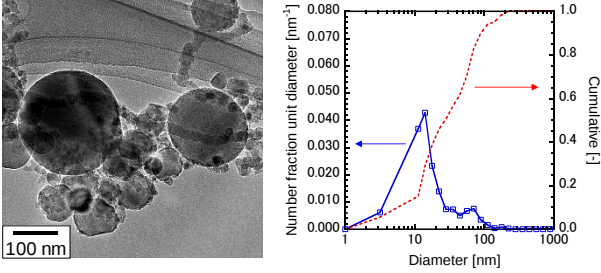


Fig. 5. TEM images and size distributions of prepared Si nanoparticles with carbon source of C₂H₄.

that the synthesized nanoparticles were coated by carbon. The angular shaped particles were SiC because the Si and C were clearly overlapped.

The Raman spectra (1100-1700 cm⁻¹) for the prepared products with injection of CH₄ and C₂H₄ are shown in **Fig. 8**. Both G band and D band were appeared. The G band and D band are associated with stretching vibrations in graphene layers and disorder, respectively. The electric conductivity of this coat was also confirmed. As a conclusion, the synthesized amorphous Si nanoparticles was successfully coated by DLC structure. The Raman spectra from 2800 to 3000 cm⁻¹ shown in **Fig. 9** present the difference of carbon sources. The peak related to -CH₃ was the highest in the case of CH₄ injection. In contrast, the peaks associated with -CH₂ and =CH₂ were dominated when C₂H₄ was used as the carbon source. These obtained results indicate that the kind of carbon source influences the composition of the synthesized coating.

Decomposition mechanisms of different carbon sources were discussed on the basis of the obtained results. CH₄ decomposes into CH₃ + H or CH₂ + H₂ at about 880 K [4]. Therefore, most of the carbon coating in the case of CH₄ consist of CH₃ and CH₂. On the other hand, two C₂H₄ molecules break down into C₂H₃ + C₂H₅ at about 780 K and these radicals bond to the surface of the Si particles [5]. For the difference of decomposition mechanism, the component of coating is determined.

5. Discussion

Homogeneous nucleation temperatures of Si considered in the present study were estimated based on nucleation theory considering non-dimensional surface tension [6]. The homogeneous nucleation rate J can be expressed as:

$$J = \frac{\beta_{ij} n_s^2 S}{12} \sqrt{\frac{\Theta}{2\pi}} \exp \left[\Theta - \frac{4\Theta}{27(\ln S)^2} \right] \quad (2)$$

where S is the saturation ratio and n_s is the equilibrium saturation monomer concentration at temperature T . β is the collision frequency function. The dimensionless surface tension Θ is given by the following equation:

$$\Theta = \frac{\sigma s_1}{kT} \quad (3)$$

where σ is the surface tension and s_1 is the monomer surface area. The surface tension and the saturation ratio

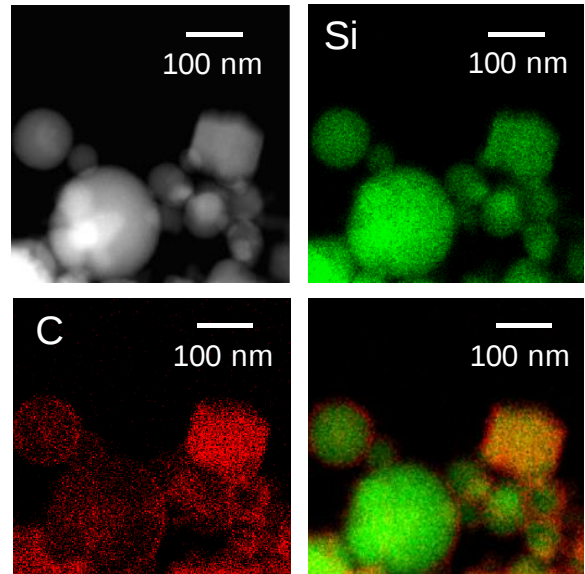


Fig. 6. STEM-EDS mapping of prepared Si nanoparticles with carbon source of CH₄.

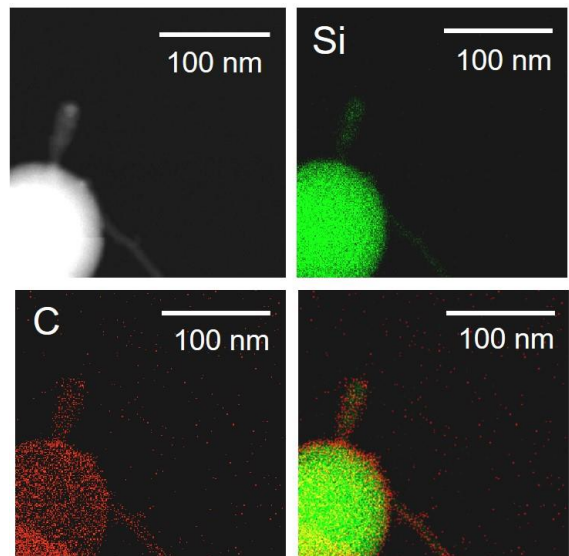


Fig. 7. STEM-EDS mapping of prepared Si nanoparticles with carbon source of C₂H₄.

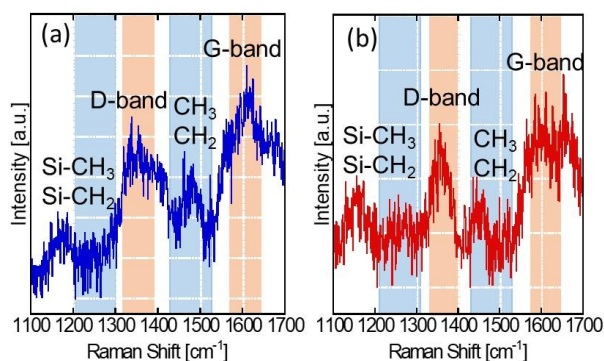


Fig. 8. Raman spectra (1100-1700 cm^{-1}) of prepared Si nanoparticles with carbon source of (a) CH_4 and (b) C_2H_4 .

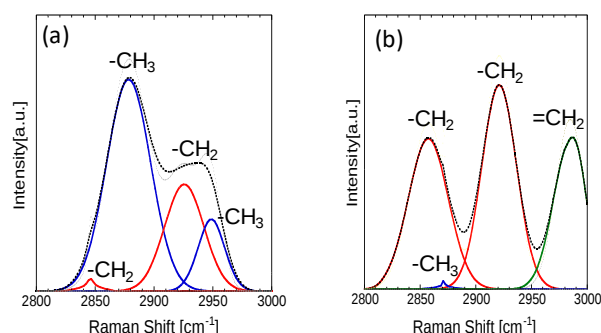


Fig. 9. Raman spectra (2800-3000 cm^{-1}) of prepared Si nanoparticles with carbon source of (a) CH_4 and (b) C_2H_4 .

have strong influences on determining the nucleation rate. A stable nucleation can be confirmed when the nucleation rate becomes higher than $1 \text{ cm}^{-3}\text{s}^{-1}$. The corresponding saturation ratio can be defined as critical saturation ratio at nucleation temperature. Therefore, calculated nucleation temperature at the condition of this experiment was 2410 K. Then the growth zones for the Si particles were determined, where the temperature is lower than the nucleation temperature at 2410 K and higher than the melting point at 1683 K. Furthermore, Gibbs free energy of SiC was calculated by thermodynamic calculation software FACT-WIN. It has a negative value when temperature is lower than 3400K, and indicates that SiC stably exists in this range.

The formation mechanism of carbon coated amorphous Si nanoparticles is shown in **Fig. 10**. The carbon source should be injected at the region where the temperature is

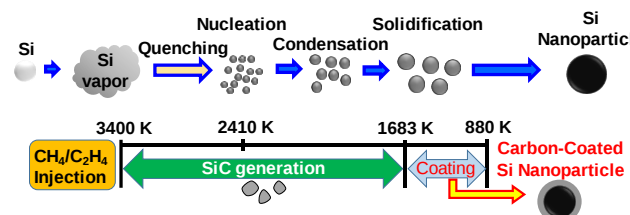


Fig. 10. Formation mechanism of carbon coated amorphous Si nanoparticles.

less than 1683 K to prevent the unfavourable formation of SiC. In addition, carbon source gases should also be decomposed sufficiently, therefore the carbon sources should be injected at the region where the temperature is higher than 880 K. In the present work, the carbon-coated amorphous Si nanoparticles were successfully synthesized even though the synthesis window is narrow.

6. Conclusion

Carbon-coated amorphous Si nanoparticles were successfully synthesized in a single step by induction thermal with additional quenching gas flow and carbon source injection at the downstream region. Si nanoparticles were covered with DLC. The difference of carbon source affects to the composition of synthesized carbon coating. Based on the above, this thermal plasma process allows us to synthesize carbon-coated Si nanoparticles.

7. References

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