



Special Feature: Nanomaterials and Processing

Research Report

A Facile and Scalable Synthetic Method for Si-based and Silicide-based Nanomaterials towards Energy-related Applications

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■ABSTRACT■ Silicon (Si) and silicides (i.e., Si-based intermetallic compounds) are attractive material systems in the context of functional materials composed of ubiquitous elements. Nanomaterials, which have a large surface or interface to exhibit various functions, have the desired morphology for use as energy storage or energy conversion materials. However, nanomaterials of Si and silicides can hardly be produced by conventional synthetic methods. In contrast, we have found that the solid-state reaction of layered CaSi_2 and transition metal chlorides gives a nanocomposite-containing material with slit-like nanopores (termed here as Ca_xSi_2). We verified that the Ca_xSi_2 material is formed by extracting Ca from CaSi_2 , thereby exfoliating the layered structure of CaSi_2 , while the formation of CaCl_2 is the driving force of the reaction between CaSi_2 and metal chlorides. The reaction is one type of solid-state metathesis (element substitution) reaction, in which stable salt formation is the driving force of the reaction. We named our method the ‘solid-state exfoliation reaction’ method. As one possible application, we demonstrated that the Ca_xSi_2 /nickel silicide nanocomposites, which were prepared using CaSi_2 and NiCl_2 , exhibited excellent performance as a Li ion battery anode. We also confirmed that fine particles of $\text{MnSi}_{1.73}$ (a semiconducting material with thermoelectric properties), a novel Ca-bridged siloxene (a material with a controllable direct optical band gap and is capable of storing Li) and Mg_2Si (a semiconducting material with thermoelectric properties and capable of storing Li) were prepared using the exfoliation and/or metathesis reaction.

■KEYWORDS■ Silicon, Silicide, Fine Particles, Nanocomposites, Semiconductor, Li Ion Battery, Energy Conversion

1. Introduction

Si and silicides (i.e., Si-based intermetallic compounds) are attractive material systems because they are composed of non-toxic and abundant (ubiquitous) elements. In order to use these materials as energy storage or energy conversion materials, it is essential to enlarge their surface or interface exhibiting a specific function. Porous or hollow particles and nanotubes, i.e., nanomaterials with free nano-spaces, have a large surface-to-volume ratio. Thus, they are expected to be used in applications such as secondary batteries, catalyst supports, photovoltaics and hydrogen storage.⁽¹⁾ A typical example of Si-based nanocomposites that have been reported are hollow Si nanotubes coated with SiO_2 . The nanotubes exhibited stable cycle performance even during rapid charge-discharge cycles.⁽²⁾ Nanomaterials with free nano-spaces are commonly fabricated using templates such as anodized Al_2O_3 ,⁽³⁾ polymer fibers,^(2,4) and SiO_2 fine particles.⁽⁵⁻⁷⁾ The composite Si and

template material is prepared, after which the template is removed by calcination or chemical etching.⁽¹⁾ However, the high complexity and production cost due to the sacrificing of templates may prevent practical applications.

We have developed a facile and scalable synthetic method that uses layered CaSi_2 and transition metal chlorides as raw materials for the fabrication of nanomaterials with slit-like nanopores. The nanomaterial consists of agglomerates of nano-flakes assembled with a small gap between them. We verified that the formation of the nanomaterials is based on the following reaction: extraction of Ca from the layered CaSi_2 and simultaneous exfoliation of the layered structure with CaCl_2 formation (Sec. 2).⁽⁸⁾ Hereafter, the fabricated nanomaterial with slit-like nanopores is referred to as Ca_xSi_2 because the material is derived from CaSi_2 . We termed the synthetic method the ‘solid-state exfoliation reaction’ method. The reaction belongs to the category of solid-state metathesis (element exchange) reactions,⁽⁹⁾ wherein the formation

of a stable salt is the driving force.

We then demonstrated that the solid-state exfoliation reaction using CaSi_2 and NiCl_2 provided Ca_xSi_2 /nickel silicide nanocomposites with various mixing ratios and that the nanocomposites showed excellent anode performance as Li ion batteries (Sec. 3).⁽¹⁰⁾

Furthermore, we found that the exfoliation reaction and/or the metathesis reaction are/is applicable to form fine particles of semiconducting silicides such as $\text{MnSi}_{1.73}$ and $\text{Mg}_2\text{Si}^{(11)}$ (Sec. 4).

This report introduces the synthetic methods used to obtain the nanocomposites and fine particles mentioned above.

2. Synthesis and Formation Mechanism of Nanocomposites Containing Ca_xSi_2 with Slit-like Nanopores⁽⁸⁾

This section introduces how Ca_xSi_2 materials with slit-like nanopores are formed. We used a mixture of layered CaSi_2 and NiCl_2 as the model system. In an Ar atmosphere glove box, a mixed powder of ca. 200 mg of CaSi_2 and NiCl_2 was loaded in a BN crucible, after which the crucible was placed inside a stainless-steel cell (inner volume of ca. 10 cm^3). The molar ratio of CaSi_2 : NiCl_2 was fixed at 1:2. Then, the mixture was heated to between 250 and 400°C (heating rate of 100 °C/h) for 5 h and cooled to room temperature.

The raw material, CaSi_2 , included a trace amount of Si, as shown in the X-ray diffraction (XRD) in Fig. 1. At synthesis temperatures below 200°C, CaSi_2 and NiCl_2 did not react. The powder XRD patterns for the samples prepared at 250°C and 300°C exhibited clear peaks assigned to CaCl_2 and Ni (patterns A and B in Fig. 1). The patterns for the samples prepared at 350°C and 400°C (patterns C and D in Fig. 1) have peaks assigned to CaCl_2 and nickel silicide (i.e., Ni_3Si , $\text{Ni}_{31}\text{Si}_{12}$ and/or Ni_2Si).

Here, we show the microstructure of the sample prepared at 350°C as a typical result. The sample was obtained after removing CaCl_2 by washing with anhydrous dimethylformamide and vacuum drying at 80°C overnight. The scanning transmission electron microscopy (STEM) images show regions of dark contrast ca. 100 nm in length and widespread regions of brighter contrast with a streak-like pattern, as shown in Figs. 2(a) and (b). STEM-EDX analysis (Figs. 2(c)-(e)) suggests that the former is nickel silicide and the latter is Ca_xSi_2 with a composition close

to Si (Ca:Si = 0.07:2). The obtained N_2 adsorption isotherm (Fig. 2(f)) shows a clear IUPAC H3 type hysteresis loop,⁽¹²⁾ which is typically observed for materials containing slit-like pores. The average pore size deduced from the isotherm was 3-4 nm. These results indicate that the regions of brighter contrast (streak-like pattern) correspond to the agglomerates of Ca_xSi_2 nano-flakes with a thickness of ca. 10 nm, and that the Ca_xSi_2 nano-flakes are assembled with a gap of 3-4 nm between each flake, thereby absorbing N_2 as a material with slit-like pores.

For as-prepared samples (i.e., without washing), the XRD peaks corresponding to the layered CaSi_2 get smaller, while those corresponding to CaCl_2 get stronger with increasing synthesis temperature (patterns (B)-(C) in Fig. 1). All as-prepared samples exhibited N_2 adsorption isotherms with similar shapes, and the size of the hysteresis loop got larger with increasing synthesis temperature. In this study, the

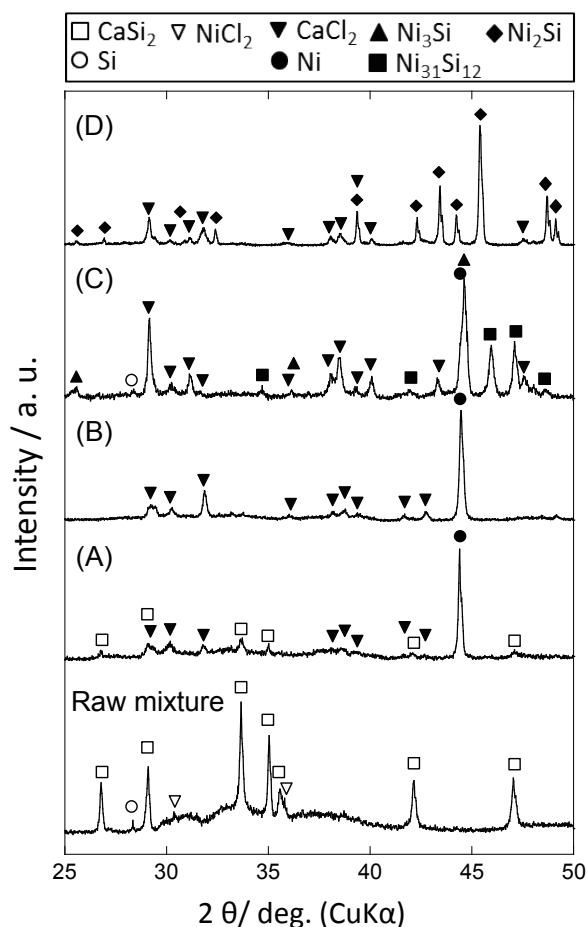


Fig. 1 Powder XRD patterns for raw mixture of NiCl_2 and CaSi_2 , and as-prepared samples synthesized at 250 (A), 300 (B), 350 (C) and 400°C (D).

shape of the isotherm was unchanged for the samples before and after washing. These results suggest that the formation of CaCl_2 promotes the extraction of Ca from layered CaSi_2 , thereby exfoliating the layered structure to form Ca_xSi_2 with slit-like pores (Fig. 3). In addition, nickel silicide is considered to be formed by a reaction between Si in Ca_xSi_2 and Ni in NiCl_2 at high synthesis temperatures.

We confirmed that a solid-state exfoliation

reaction method using CaSi_2 provides Ca_xSi_2 with CaCl_2 formation when FeCl_2 or MnCl_2 was used instead of NiCl_2 as a raw material. Depending on the synthesis conditions, Ca_xSi_2 /iron silicide nanocomposites^(10,13) and Ca_xSi_2 /manganese silicide nanocomposites⁽¹⁰⁾ were formed with various mixing ratio. Thermodynamically, CaCl_2 (standard enthalpy of formation at 600°C ⁽¹⁴⁾: -750 kJ/mol) is more stable than NiCl_2 (-260 kJ/mol), FeCl_2 (-280 kJ/mol) or

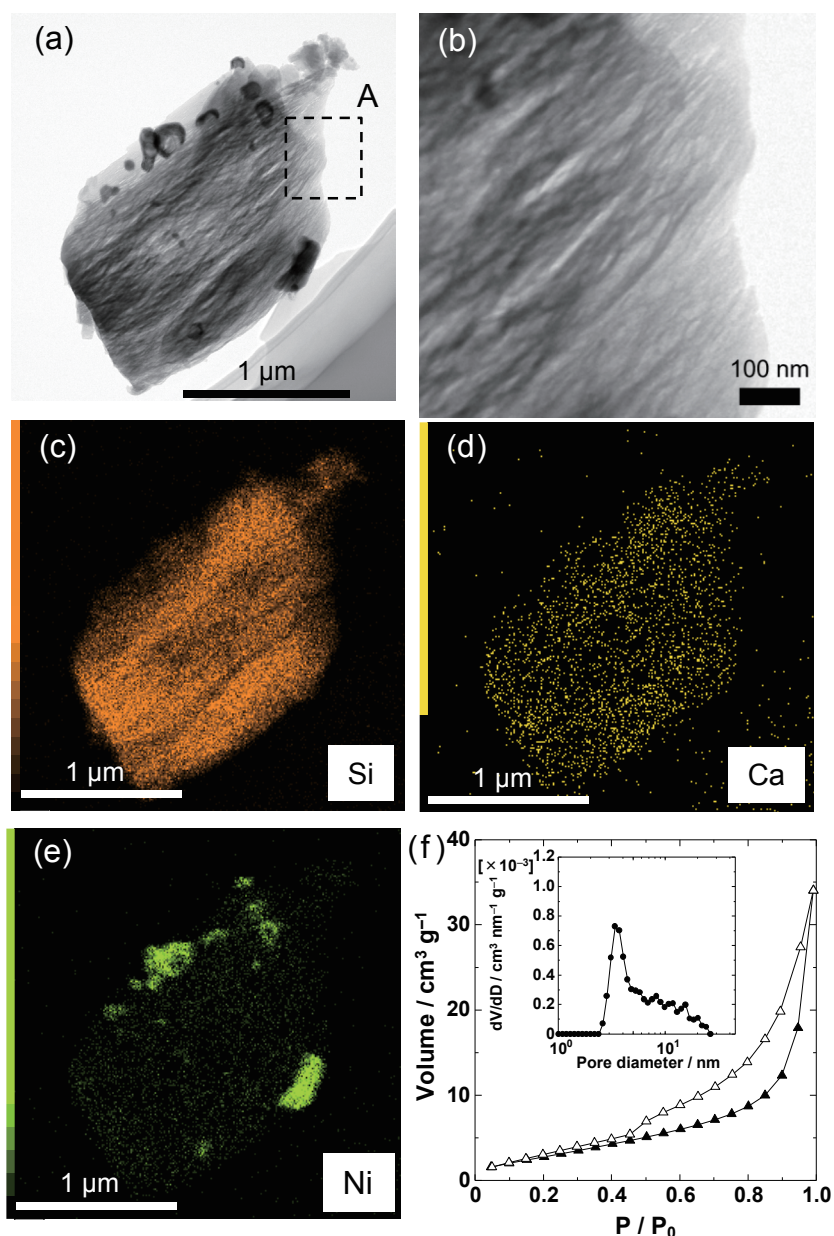


Fig. 2 STEM-EDX analysis results (a)-(e) and N_2 -adsorption isotherm (f) for DMF-washed sample synthesized at 350°C . (a) BF-STEM image, (b) high-magnification BF-STEM image of area A (dotted square in (a)). (c)-(e) Elemental mapping of BF-STEM image (a) for Si, Ca and Ni, respectively. Open and closed symbols in (f) indicate results for the adsorption and desorption processes, respectively. The inset in (f) shows the pore size distribution.

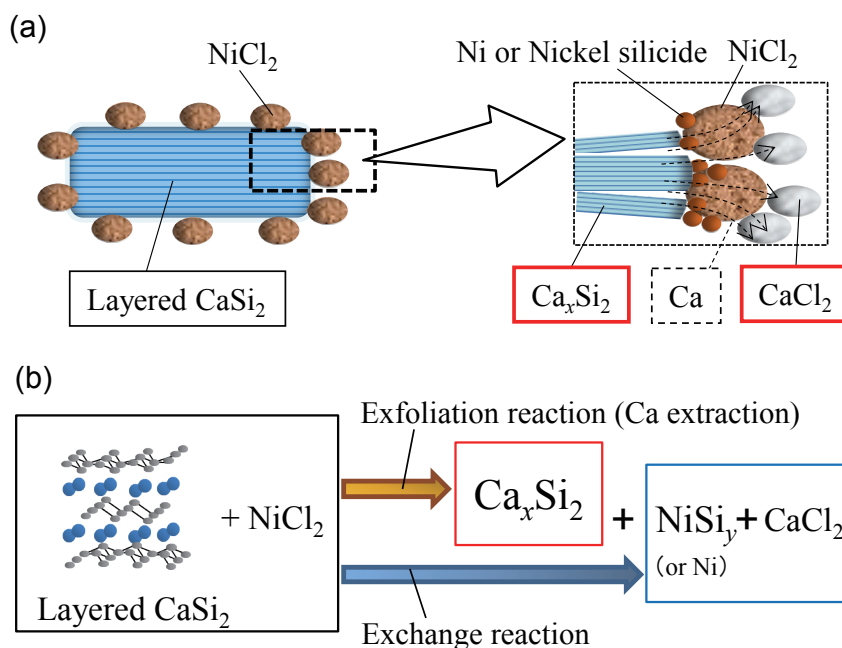


Fig. 3 Schematic illustration for possible reaction mechanism. (a) Solid-state exfoliation reaction model for layered-structure of CaSi_2 . (b) Formation model of nanocomposite consisting of Ca_xSi_2 and Ni (or NiSi_y).

MnCl_2 (-430 kJ/mol). Additionally, the synthesis temperatures were lower than the melting points of all substances that appeared in the reaction. Therefore, our solid-state exfoliation reaction method belongs to the category of solid-state metathesis (element substitution) reactions,⁽⁹⁾ where stable salt formation is the driving force of the reaction. There are many reports of liquid phase reactions involving the immersion of exfoliation agents into the layered compounds or mechanical exfoliation by applying shear stress to the layered compounds.⁽¹⁵⁾ However, the Ca_xSi_2 formation described here is the first example of exfoliation of layered compounds for a solid-state reaction. We have therefore termed this reaction a ‘solid-state exfoliation reaction’.

3. Synthesis and Application of Ca_xSi_2 /nickel Silicide Nanocomposites as an Anode for Li Ion Batteries⁽¹⁰⁾

Nanocomposites composed of Li storable materials such as Si and conductive media such as conductive silicides^(1,16) or other conductive materials (e.g., carbon, TiN, and SiC)^(1,2) are being energetically investigated, with the aim of finding anode materials for Li ion batteries that provide stable cycle performance. In this section, we discuss the anode performance of

Ca_xSi_2 /nickel silicide nanocomposites in terms of one possible application of our solid-state exfoliation reaction method.

As described in Sec. 2, the samples were prepared using NiCl_2 and layered CaSi_2 mixed powders (ca. 200 mg) under the synthetic conditions shown in **Table 1**. Here, all of the samples were obtained after removing byproduct CaCl_2 by washing with dimethylformamide and vacuum drying (80°C , overnight). Nanocomposites with various compositions were obtained.

For the samples prepared with $\alpha = 2.0$ (α : nominal molar ratio of NiCl_2 and CaSi_2), Ni/ Ca_xSi_2 nanocomposites were obtained at a synthetic temperature of 250°C (sample T1) and 300°C (T2). At higher synthesis temperatures, nanocomposites composed of nickel silicide were obtained. Nickel silicide phases with higher Si content were formed with increasing synthesis temperature (350°C (sample T3) < 400°C (T4) < 500°C (T5) < 600°C (T6(A1))). Nickel silicides were considered to be formed from the reaction of the Si in Ca_xSi_2 and the Ni in NiCl_2 . Thus, an increase in the amount of nickel silicide resulted in a decrease of Ca_xSi_2 .

For the samples prepared at 600°C , some of the raw CaSi_2 remained unreacted when the nominal amount of NiCl_2 was small (i.e., samples A7 ($\alpha = 0.5$) and

Table 1 Synthetic conditions and components comprising the nanocomposites prepared by $\alpha\text{NiCl}_2/\text{CaSi}_2$ systems.

Sample	$T_{\text{syn}} / ^\circ\text{C}$	$\alpha^{(a)} / -$	Reaction products					CaSi_2 (Raw material)	
			$\text{Ca}_x\text{Si}_2^{(b)}$	$\text{NiSi}^{(c)}$	$\text{Ni}_3\text{Si}_2^{(c)}$	$\text{Ni}_2\text{Si}^{(c)}$	$\text{Ni}_3\text{Si}^{(c)}$		$\text{Ni}^{(c)}$
T1	250	2.0	Major					Major	Minor
T2	300		Major					Major	
T3	350		Minor	Major					Minor
T4	400		Major						
T5	500				Minor	Major			
T6(A1)					Major		Major		
A2			1.6		Minor	Major		Minor	
A3		1.3		Major		Major		Minor	
A4	600	1.1	Minor	Major		Minor			
A5		1.0	Major			Major			
A6		0.7	Major			Major			Minor
A7		0.5	Major			Major			Major

Note: (a) is the molar ratio of ($\text{NiCl}_2/\text{CaSi}_2$). (b) and (c) were identified by SEM-EDX and powder XRD analyses, respectively. The NiCl_2 (raw material) contained in as-prepared sample T1 (before washing) was subjected to powder XRD analysis. CaCl_2 in all as-prepared samples was removed by washing with DMF.

A6 ($\alpha = 0.7$)). This is because the amount of CaCl_2 formed was small, thereby forming a small amount of Ca_xSi_2 . The samples prepared with a higher nominal amount of NiCl_2 ($1.0 \leq \alpha$) had no unreacted CaSi_2 . The nanocomposite containing Ni was obtained for sample A5 ($\alpha = 1.0$) and the nanocomposites containing nickel silicides were obtained for samples A4 ($\alpha = 1.1$), A3 ($\alpha = 1.3$) and A2 ($\alpha = 1.6$). The syntheses involving a higher amount of NiCl_2 (i.e., larger α value) had a higher amount of Ni in the reaction system. Thus, the amount of Ni and/or nickel silicide in the reaction products was increased and that of Ca_xSi_2 was decreased.

As typical samples, the microstructures of samples A5 and A3 are shown in the scanning electron microscopy (SEM) images in **Fig. 4**. Sample A5 is a nanocomposite composed of Ca_xSi_2 with a diameter of 10-20 μm (aggregate of many nano-flakes) and Ni particles with diameters of ca. 1 μm . Sample A3 is an agglomerated powder of nickel silicide particles with diameters of ca. 1 μm and contains little Ca_xSi_2 .

Figure 5 shows the relationship between the initial discharge capacity and potential for samples A5, A4, and A3 (synthesis temperature = 600 $^\circ\text{C}$, $\alpha = 1.0$, 1.1, and 1.3, respectively). The anode capacity was evaluated using electrodes prepared by mixing the

samples and carbon black (nominal weight ratio of 70 to 30), followed by pressing onto a nickel foam (current collector) at 10 MPa. Here, a Li foil was used as the counter/reference electrode and a 1 M LiPF_6 solution (solvent: 50/50 v/v ethylene carbonate/diethyl carbonate mixture) was used as the electrolyte solution. A constant current of 100 mA/g was applied with a voltage window of 1.5-0.02 V (vs. Li/Li^+). As shown in **Fig. 5**, the discharge capacity increased at potentials between 0.3 and 0.6 V, and this behavior is similar to that for a Si anode. In addition, the capacity of sample A5 was about 3 times larger than that of conventional graphite. Ni and nickel silicides are materials that absorb only small amounts of Li (**Fig. 5** and **Ref. (17)**); thus, the discharge capacity values are considered to correspond to the amount of Ca_xSi_2 in the samples. On the other hand, Ni and nickel silicides act as conductive media to enhance the electron transport from Ca_xSi_2 (Li storage sites) to the current corrector, as shown in **Fig. 6**.

Figure 6 shows the relationship between the electrical conductivity and initial discharge capacity for Ca_xSi_2 /nickel silicide nanocomposite samples. The electrical conductivity was measured using the two-probe method, while the powder samples were uniaxially pressed at 2 MPa or 10 MPa inside the

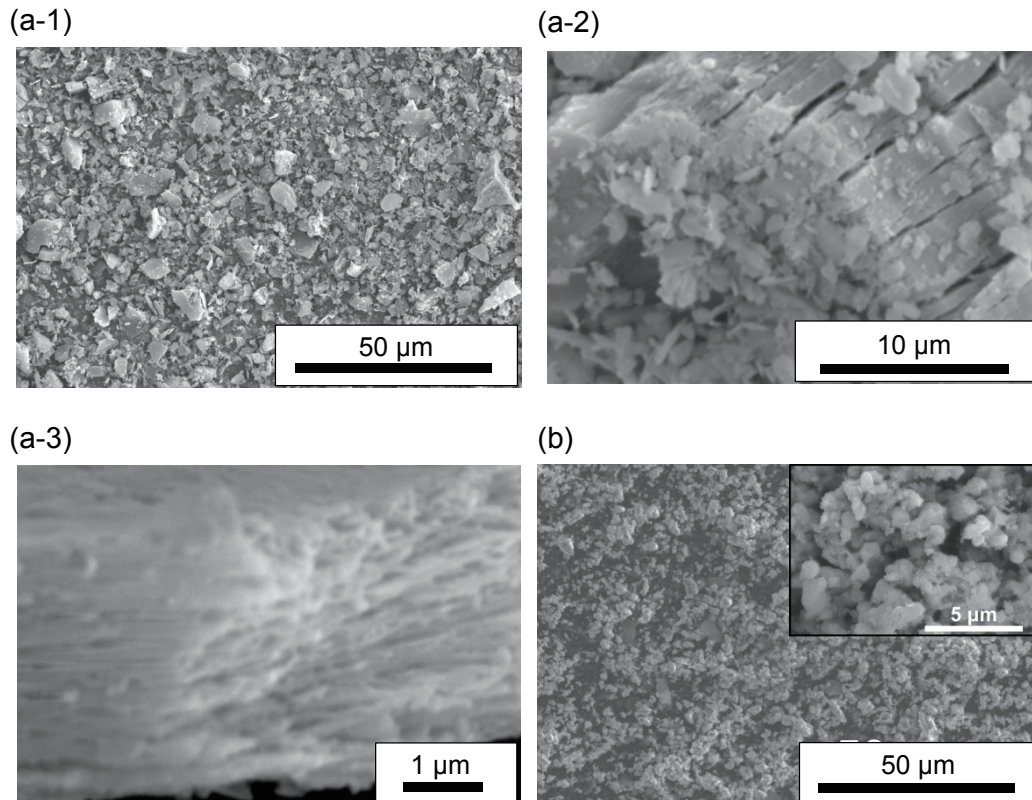


Fig. 4 SEM images of DMF-washed samples synthesized at 600°C. (a) and (b) show samples A5 ($\alpha = 1.0$) and A3 ($\alpha = 1.3$), respectively. The inset of (b) is a higher magnification image. (a-2) and (a-3) show SEM images of Ca_xSi_2 particles of sample A5.

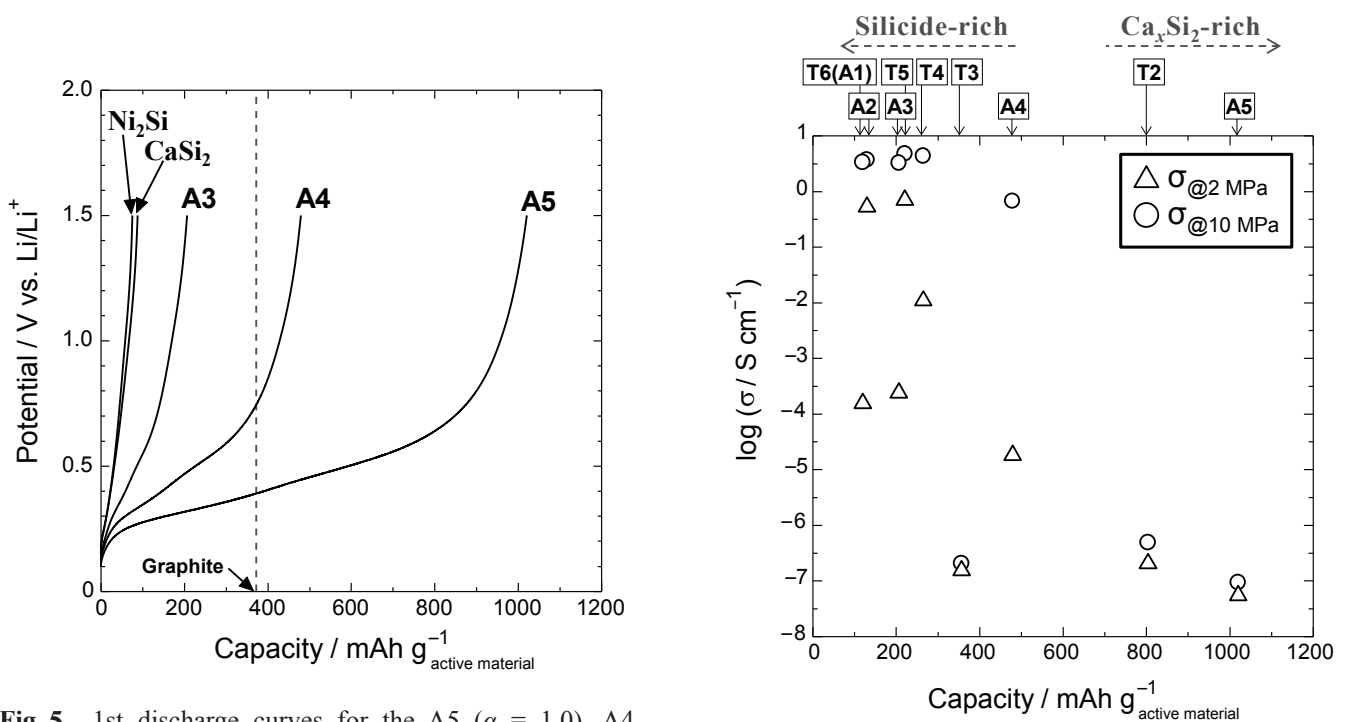


Fig. 5 1st discharge curves for the A5 ($\alpha = 1.0$), A4 ($\alpha = 1.1$) and A3 ($\alpha = 1.3$) samples synthesized at 600°C. The curves for CaSi_2 and Ni_2Si reagents are also presented for comparison.

Fig. 6 Correlation between electrical conductivity and 1st discharge capacity for samples of Ca_xSi_2 /nickel silicide nanocomposites.

insulator mold. The samples with a larger amount of Ca_xSi_2 exhibited higher capacity while the samples with a larger amount of nickel silicides exhibited higher electrical conductivity. These results suggest that a solid-state exfoliation reaction method would be a facile synthetic method to fabricate materials with diverse characteristics by adjusting the synthesis conditions such as temperature and nominal compositions.

4. Application of the Synthetic Strategy to Other Si- or Silicide-based Systems

In this section, we introduce other materials developed using the exfoliation and/or metathesis reaction. First, depending on the synthesis conditions, a raw mixture of 'CaSi₂ and FeCl₂' or 'CaSi₂ and MnCl₂' gave Ca_xSi₂/iron silicide nanocomposites^(10,13) and Ca_xSi₂/manganese silicide nanocomposites⁽¹⁰⁾ with various mixing ratios. These nanocomposites exhibited excellent performance as Li ion battery anodes. Then, we confirmed that single phase MnSi_{1.73} (semiconducting phase with thermoelectric properties) fine particles were formed under the particular conditions in which all of the Si and Mn in the reaction system stoichiometrically reacted. Furthermore, we found that the solid-state exfoliation reaction method using CaSi₂ and TaCl₅ formed a novel material, a Ca-bridged siloxene.⁽¹⁸⁾ The material was amorphous and the local structure was thought to be stacked Si layer sheets bridged by Ca atoms, where the Si sheet layer is composed of Si six-membered rings connected via Si-O-Si bonds. We also found that the material exhibited excellent cycle performance as a Li ion battery anode and had a controllable direct optical band gap.

We have also developed a novel metathesis reaction route to obtain surface-oxidation-free Mg₂Si fine particles,⁽¹¹⁾ where NaSi and MgCl₂ were used as raw materials. Although Mg₂Si is an easily-oxidizable material, the method provides surface-oxidation-free Mg₂Si fine particles. As a result, the anode prepared using the Mg₂Si fine particles exhibited one of the best cycle performances in a Li ion battery among previous reports on Mg₂Si anodes. Mg₂Si fine particles would be useful also as raw materials for the production of nanostructured bulk thermoelectric materials⁽¹⁹⁾ similar to MnSi_{1.73} fine particles. As described above, a solid-state exfoliation reaction method using layered

CaSi₂ and a metathesis reaction method using NaSi are novel synthetic methods to obtain silicon-based and silicide-based functional nanomaterials, which can hardly be produced by conventional synthetic methods.

5. Summary

We have developed a novel synthetic method, termed a 'solid-state exfoliation reaction' method, which forms silicon-based nanocomposites with slit-like nanopores or silicide (Si-based intermetallic compound) fine particles. In general, the method uses layered CaSi₂ and transition metal chlorides as raw materials for solid-state reactions. We verified that the formation mechanism of the Ca_xSi₂ material with slit-like nanopores is based on the extraction of Ca from CaSi₂ and exfoliation of the layered structure, wherein the formation of a stable salt CaCl₂ promotes the reaction of CaSi₂ and metal chlorides. The synthetic method provides Ca_xSi₂-containing nanocomposites with various compositions. As one of the possible applications, we demonstrated that the Ca_xSi₂ (Li storage sites)/nickel silicide (conductive media) nanocomposites exhibited excellent performance as a Li ion battery anode. Depending on the synthesis conditions, a solid-state exfoliation reaction method also forms semiconducting silicide fine particles (such as MnSi_{1.73}, the phase showing thermoelectric properties) and a novel material, Ca-bridged siloxene (a material with a controllable direct optical band gap and is capable of storing Li). Conventional synthetic methods can hardly be used to produce the nanomaterials described above. Thus, our developed solid-state exfoliation reaction method opens a new possibility to obtain silicon-based and silicide-based nanomaterials, which are applicable as energy storage or energy conversion materials.

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Figs. 1-3

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Figs. 4-6 and Table 1

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