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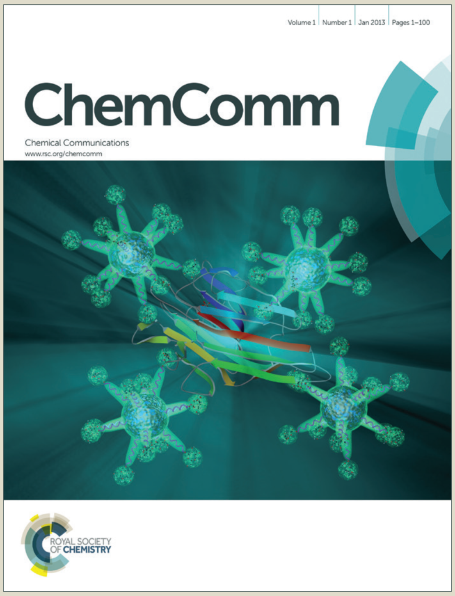

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Metathesis Reaction Route to Mg_2Si Fine Particles

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We have developed a novel synthetic route for the production of fine Mg_2Si particles (< 1 μm) using NaSi, $MgCl_2$, and Na. Mg_2Si was suggested to be formed by a solid-state metathesis reaction, in which $MgCl_2$ reacts with Na to form Mg and NaCl, and then Mg reacts with NaSi.

Mg_2Si is a semiconducting material that exhibits Li storage[1] and/or thermoelectric properties[2]. Mg_2Si has benefits in that it is composed of elements with plentiful resources and low toxicity. Mg_2Si has additional benefit as lightweight material (ca. 2 g/cm^3) when applied it to the moving vehicle. Fine Mg_2Si particles are expected to be used as a raw material for the anode of Li-ion batteries and for nanostructured bulk thermoelectric elements. Fine Mg_2Si particles or nanomaterials are considered to exhibit stable charge/discharge reaction[3], thereby enhancing the cyclability of batteries. In addition, a theoretical study reported that thermopower would be enhanced by a quantum confinement effect[4] for the nanostructured thermoelectric bulk material comprising grains with diameter in the nanometer range.

Conventional solution chemistry synthesis routes are useful for the production of fine particles of various noble metals or oxides; however, this route is not applicable, in principle, for the synthesis of fine Mg_2Si particles, because Mg^{2+} ions cannot be reduced in solution. Ball-milling or mechanical alloying tends to give an insufficient atomization effect or leads to the inclusion of undesirable impurities[1]. In contrast, it was recently reported that fine Mg_2Si particles with diameters of 1–2 μm were obtained by heating a ball-milled mixture of MgH_2 and Si powders[5]. The Mg_2Si particles showed an improved Li-ion storage ability[5]. Another group reported that Mg_2Si particles with diameters of ca. 100 nm were prepared by microwave heating of a powder mixture ball-milled from Mg and Si lumps[6]. However, insulating oxides formed at the grain boundaries[7] during sintering of the Mg_2Si particles. Such oxides generally decrease thermoelectric performance of the sintered bodies. Thus, the development of oxide phase-free fine Mg_2Si particles remains a challenging issue.

Yamada et al. reported[8] that a hollow structured polycrystalline Mg_2Si bulk was synthesized by heating a compact mixture of Mg and NaSi powders at 700 °C under an Ar atmosphere. The Mg_2Si particles comprising the polycrystalline bulk had diameters of 50–200 μm; therefore, fine Mg_2Si particles were not formed by this synthesis method. It was expected that Mg_2Si was formed at the boundary of Mg and Na-Si melts, thereby inducing the grain growth of Mg_2Si. Itahara et al. reported[9] that solid-state metathesis reaction[10] using layered $CaSi_2$ and $FeCl_2$ as starting materials gave nanocomposites containing iron silicides (*e.g.*, FeSi and Fe_3Si) and Si.

The present study shows that Mg_2Si fine particles with diameters of less than 1 μm can be successfully prepared through a metathesis reaction route using NaSi, $MgCl_2$, and Na as starting materials. The formation mechanism of fine Mg_2Si particles has been clarified and the synthetic conditions for high yield Mg_2Si formation with oxidation avoided have been determined. The synthesized fine Mg_2Si particles exhibit enhanced discharge capacity compared with that for fine oxidized Mg_2Si particles with similar diameter. In addition, the capacity after 10 cycles was 68% of the initial capacity, which is comparable to the highest value of 60% reported for Mg_2Si powder prepared by a hydrogen-driven reaction of MgH_2 and Si powders[5].

Table 1 summarizes the mixing ratio of the NaSi, $MgCl_2$, and Na starting materials. Mixtures with various compositions (total amount of ca. 150 mg) were loaded into BN crucibles. The Mg:Si molar ratio was fixed at 2:1, while the Na content was varied (see conditions A–C, Table 1). Each crucible was placed under an Ar atmosphere within a sealed stainless-steel cell (inner volume of ca. 10 cm^3). The cells were heated at 650 °C for 10 h. The samples obtained after heating were agglomerates that were then easily pulverized using a mortar and pestle.

Table 1. Synthesis conditions using NaSi, $MgCl_2$, and Na as source materials

Sample	NaSi (mmol)	Na (mmol)	$MgCl_2$ (mmol)	Molar ratio Mg:Si	Molar ratio Na:Si
A	0.77	0.023	1.5	2.0:1.0	1.0:1.0
B	0.59	0.29	1.2	2.0:1.0	1.5:1.0
C	0.60	1.9	1.2	2.0:1.0	4.1:1.0

Figure 1 and Table 2 show powder X-ray diffraction (XRD) patterns for the as-prepared samples and the assigned crystalline phases, respectively. Different reaction products were obtained according to the nominal Na/Si molar ratios as follows (the ratio was increased in the order of sample A < B < C). Sample A (Na:Si = 1.0:1.0) contained $MgCl_2$ (unreacted starting material) and $Na_2Mg_3Cl_8$[11] as major components and trace amounts of $NaMgCl_3$[11], NaCl, and Mg_2Si (Fig. 1(a)). Sample B (Na:Si = 1.5:1.0) included $NaMgCl_3$ and trace amounts of NaCl and Mg_2Si (Fig. 1(b)). In contrast, sample C (Na:Si = 4.1:1.0) included only NaCl and Mg_2Si (Fig. 1(c)). When $MgCl_2$ reacts with NaSi and Na to form Mg_2Si, the reaction formula is expressed as

$$NaSi + 2\ MgCl_2 + 3\ Na \rightarrow Mg_2Si + 4\ NaCl \qquad (1)$$

Equation (1) corresponds to the nominal compositions and the observed reaction products for sample C (Tables 1 and 2).

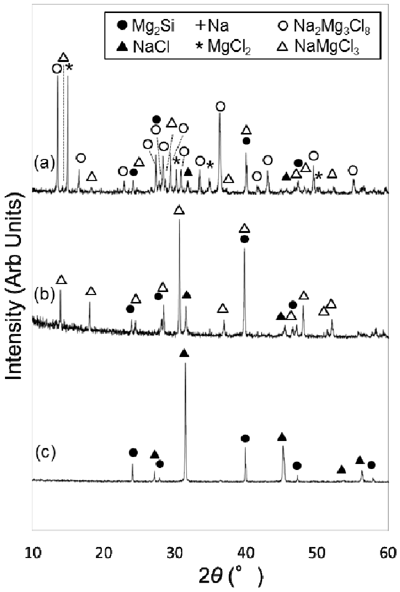

Figure 1. Powder XRD patterns for as-prepared (a) sample A, (b) sample B, and (c) sample C.

Table 2. Crystalline phases detected in the as-prepared samples using powder XRD.

Sample	$MgCl_2$	$Na_2Mg_3Cl_8$	$NaMgCl_3$	NaCl	Mg_2Si
A	Major	Major	Minor	Minor	Minor
B	–	–	Major	Minor	Minor
C	–	–	–	Major	Major

For sample C, the powder of pulverized agglomerates was washed using two different methods to remove by-product NaCl: sample C-1 was washed under a N_2 atmosphere with 2-propanol and then with solvents with high solubility for NaCl (dimethylformamide and formamide), and sample C-2 was washed under an air atmosphere using 2-propanol and then with other solvents with high solubility for NaCl (ethanol and water). XRD peaks assigned to NaCl in the as-prepared sample C (Fig. 1(c)) were not observed in the patterns for washed samples C-1 and C-2 (Fig. 2(a)). SEM images (Fig. 2(b)) of samples C-1 and C-2 indicated that the powders were composed of primary particles with diameters less than 1 μm. Na and Cl were not detected by energy-dispersive X-ray spectroscopy (EDX) measured in the 8 μm square region shown in Fig. 2(b). In addition, the primary particles for both samples were considered to be Mg_2Si with high crystallinity according to the clear electron diffraction pattern obtained (see the Supplementary Information (SI), Fig. S1). The infrared (IR) spectrum for sample C-2 measured in air atmosphere has peaks that correspond to Si-OH (ca. 3,200 cm^{-1}) and Si-O-Si stretching modes (ca. 1,000 cm^{-1}) (see Fig. 2(c)). However, these peaks were absent in the IR spectrum for sample C-1, which suggests that the washing conditions without air or moisture to remove NaCl are effective to prevent oxidation (probably surface oxidation) of the fine Mg_2Si particles.

The major chloride salt phases included in the powders synthesized at 650 °C changed with the increase in the Na/Si molar ratio (sample A < B < C) of the starting materials: $MgCl_2$ and $Na_2Mg_3Cl_8$ for sample A, $NaMgCl_3$ for sample B, and NaCl for sample C (Table 2). The powder synthesized at 450 °C, which had the same nominal composition of starting materials as sample C, contained Na_6MgCl_8[11] and $NaMgCl_3$ together with NaCl (see SI, Figure S2 and Table S1). These results suggest that Na-rich chlorides would tend to form under conditions with an increased nominal amount of Na or increased synthesis temperature. When $MgCl_2$ or Na-Mg complex chlorides are present, the corresponding amount of NaSi should remain without forming Mg_2Si. NaSi or the other chlorides observed can be also removed with solvents such as dimethylformamide, formamide, ethanol, and water, as with Na and NaCl. However, the synthesis condition for sample C, in which Mg and Si, and Na and Cl react in stoichiometric ratios (Formula (1)), is the optimal condition for the highest yield of Mg_2Si.

The synthesis condition for sample A (*i.e.*, NaSi + 2 $MgCl_2$ + 0.03 Na, 650 °C) resulted in almost no Mg_2Si formation from the mixture of $MgCl_2$ and NaSi. However, Yamada et al. reported that Mg reacted with NaSi to form Mg_2Si and Na at 700 °C[8]. In addition, Mg and NaCl were formed by heating a mixture of MgCl and Na at 650 °C (see SI, Figure S3). These results suggest that the metathesis reaction, in which a reaction of $MgCl_2$ and Na forms Mg and NaCl after which Mg reacts with NaSi, would be the fundamental reaction for the formation of Mg_2Si (*i.e.*, condition C: NaSi + 2 $MgCl_2$ + 3.1 Na, 650 °C).

It should be noted that the diameters of Mg_2Si primary particles reported by Yamada et al.[8] (reaction of NaSi and Mg) and those in the present study (condition C: NaSi + 2 $MgCl_2$ + 3.1 Na） were 50–200 μm and less than 1 μm, respectively. For the former synthesis conditions[8], it was suggested that a Na-rich Na-Si melt would be formed[12] during the formation of Mg_2Si and that Mg_2Si grain growth would occur at the boundary between the Na-Si and Mg melts, thereby forming coarse Mg_2Si particles. For condition C in the present study, NaCl and Mg were formed by the reaction between $MgCl_2$ and Na, and the Mg formed then reacted with NaSi to form Mg_2Si. No melt (liquid) phases would be formed because the melting points of NaCl, Mg, and NaSi are higher than the synthesis temperature of 650 °C.

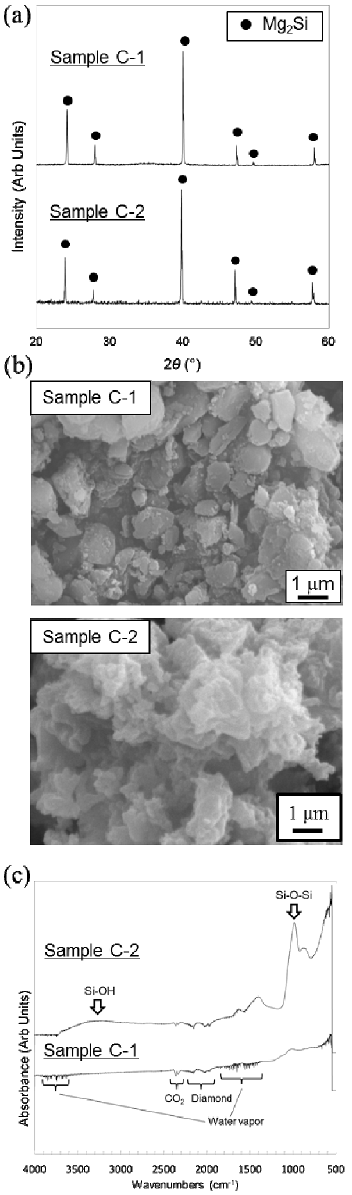

Figure 2. (a) Powder XRD patterns for samples C-1 and C-2 obtained after washing sample C with formamide under a N_2 atmosphere and with water in an air atmosphere, respectively. (b) SEM images of samples C-1 and C-2. (c) IR spectra for samples C-1 and C-2 measured in air with the attenuated total reflectance (ATR) method.

Electrodes were prepared to evaluate the charge/discharge properties by mixing the synthesized fine Mg_2Si particles and carbon black (mixing ratio of 66.7/33.3 wt%, sample weight ca. 5 mg), and then pressing the mixture onto Ni foam (ca. 80 mg, ca. 5×5 mm^2). Another electrode was prepared using coarse Mg_2Si particles (Koujundo Chemical Labs., Co. Ltd., particle diameter <53 μm) for comparison. In this study, sufficient amount of carbon was added so that all particles are electrically connected to the current collector. Thus, we are able to compare reasonably the effect of the extent of surface-oxidation and the particle size of Mg_2Si on anode performance. Li foil was used as a counter/reference electrode and $LiPF_6$ (1 M) dissolved in a mixture of ethylene carbonate/diethyl carbonate (50/50 v/v) was used as the electrolyte. A constant current of 100 mA/g was applied with a voltage window of 0.02–1.5 V (vs. Li/Li^+). Figure 3 shows the change in the discharge capacity over 100 cycles. (Voltage profiles for charge and discharge processes are shown in Figure S4). For sample C-1, the initial discharge capacity was 740 mAh/g, which is approximately twice that of conventional carbon. The capacity for sample C-1 after the 100th cycle was approximately twice that for sample C-2. The capacity for the commercial Mg_2Si sample from the 1st to the 20th cycle was comparable to that of sample C-1. However, after the 100th cycle, sample C-1 retained a much higher capacity compared to that of the commercial Mg_2Si sample.

The coulombic efficiency (defined as the ratio of discharge to charge capacity) of sample C-1 for the 1st cycle was 83.7% (Table 3), while the efficiency after the 2nd cycle was more than 95%. The low coulombic efficiency for the 1st cycle is due to decomposition of the electrolyte to form a solid electrolyte interphase (SEI) at carbon black contained in the electrode[13]. For sample C-2, the coulombic efficiency for the 1st cycle was 43.5% (Table 3), which is approximately half of that for sample C-1. Li-O compounds, which cannot reversibly release Li, would form during the charge and discharge processes of sample C-2. The formation of Li-O compounds is expected because the C-1 and C-2 samples powders had similar particle diameters, while only sample C-2 would contain oxide phases, as suggested in Fig. 2(c).

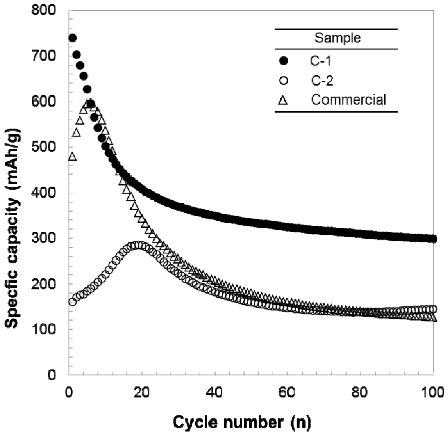

Figure 3. (a) Discharge capacity for samples C-1 and C-2 over 100 cycles evaluated at a constant current of 100 mA/g with a voltage window of 0.02–1.5 V (vs. Li/Li^+). The commercial sample is Mg_2Si reagent powder with particle diameters less than 53 μm.

Table 3. Initial coulombic efficiency

Sample	Coulombic efficiency (%)
C-1	83.7
C-2	43.5
Commercial	61.4

The commercial coarse Mg_2Si particles (diameter <53 μm) showed much faster capacity fade with cycling than sample C-1 (diameter <1 μm). For Si or Si family materials[3], capacity fade is attributed to a large volume change of the electrode that accompanies Li insertion and extraction, where the electrode particles are broken down and detached from the current collector. The difference in the expansion rates between the inner and outer parts of the particles would be less for particles with smaller diameters. For the C-1 sample, the breaking down of particles would occur less than that for the commercial coarse particles. Therefore, the C-1 sample retained a capacity that was twice that of the commercial coarse powders. Furthermore, it is noted that the capacity for C-1 sample after 10 cycles was 68% of the initial capacity. This capacity retention is comparable to the highest value of 60% reported for fine Mg_2Si particles (1–2 μm diameter) prepared by the reaction of MgH_2 and Si (evaluation conditions: Mg_2Si/acetylene black = 66.6/33.3 wt%, constant current of 100 mA/g at 0.01–3.0 V vs. Li/Li^+)[5].

Conclusions

Fine Mg_2Si particles (diameter <1 μm) were successfully prepared through a novel reaction route using NaSi, $MgCl_2$, and Na as starting materials. The formation of Mg_2Si fine particles was based on a metathesis reaction, in which $MgCl_2$ reacts with Na to form Mg and NaCl, and then Mg reacts with NaSi to form Mg_2Si. No liquid phases, which would induce grain growth of Mg_2Si, were present during the reaction, because the melting points of NaCl, Mg, and NaSi are higher than the synthesis temperature of 650 °C. We specified the conditions to produce the highest yield of Mg_2Si without oxidation. The prepared fine Mg_2Si particles exhibit enhanced capacity and cyclability compared with those for fine oxidized Mg_2Si particles with similar diameter. These results suggest that a metathesis reaction using Na or sodium compounds may provide a versatile strategy to synthesize fine particles of various functional materials that conventional synthesis techniques are not applicable.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental procedures, TEM images and Electron diffraction pattern for the prepared fine Mg_2Si and powder XRD patterns for the sample prepared different conditions]. See DOI: 10.1039/c000000x/

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