Supplementary Information for

Metathesis Reaction Route to Mg_2Si Fine Particles

H. Itahara [a], T. Yamada [b], S.-Y. Oh [a], R. Asahi [a], H. Imagawa [a] and H. Yamane [b]

[a] Toyota Central Research & Development Labs., Inc., 41-1 Yokomichi Nagakute, Aichi 480-1192, Japan, E-mail: h-itahara@mosk.tytlabs.co.jp
[b] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan.

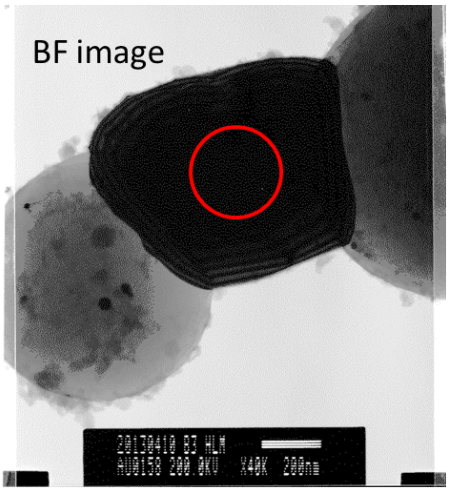
Synthesis and characterization:

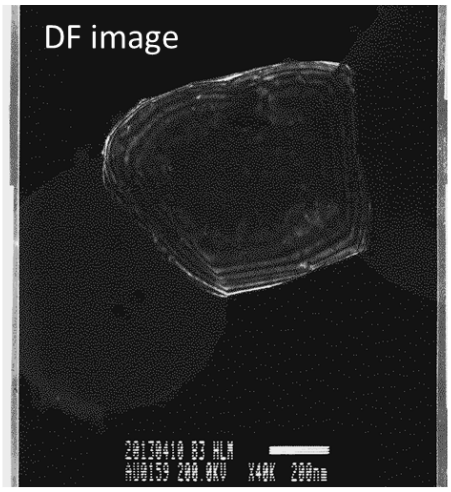
NaSi was prepared by heating a mixture of Na and Si at 850 °C for 6 h in a boron nitride (BN) crucible sealed in a stainless steel tube. Predetermined amounts of $MgCl_2$, NaSi, and Na (total amount of ca. 150 mg) were loaded into a BN crucible. Each BN crucible was then placed under an Ar atmosphere within a stainless steel cell (inner volume of ca. 10 cm^3). Table 1 lists the nominal amounts of $MgCl_2$, NaSi, and Na for samples A, B, and C. The molar ratio of Mg:Si was set as 2:1 for all samples to produce the target Mg_2Si. Heat treatment was conducted at 650 °C for 10 h (heating rate of ca. 325 °C/h). Sample C product powder was washed using two different methods. Sample C-1 powder was washed with 2-propanol, dimethylformamide, and then formamide under a N2 atmosphere. Sample C-2 powder was washed with 2-propanol, ethanol, and then water in air. Both powders were dried in vacuum at 80 °C for 5 h after washing.

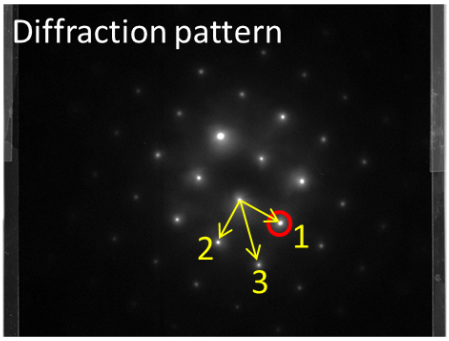
Evaluation of anode performance in a Li ion battery:

The Mg_2Si electrode was prepared using a mixture of the synthesized powders (sample C-1 or C-2, 66.7 wt%) and carbon black (33.3 wt%). The mixture (ca. 5 mg) was uniaxially pressed (10 MPa) onto nickel foam (ca. 80 mg, ca. 5×5 mm^2). 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 of Mg_2Si and the particle size of Mg_2Si on anode performance. We focus here on the proof that the surface of Mg_2Si particles is not oxidized, by showing the anode performance.

Another electrode was prepared in the same manner using commercial Mg_2Si powder (Koujundo Chemical Labs. Co. Ltd., diameter less than 53 μm) for comparison. For half-cell tests, Li foil was used as a counter/reference electrode, and 1 M $LiPF_6$ 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^+.







	d (nm)	Mg_2Si (a=0.635nm Fm3m)	
		d_calc. (nm)	Plane index
1	0.318	0.318	002
2	0.316	0.318	200
3	0.223	0.225	202

Incident along [010] direction

Figure S1. TEM images and Electron diffraction pattern for the sample C-1 obtained after washing formamide in N_2 (scale bar = 200 nm): The diffraction pattern corresponds to the Mg_2Si crystal structure.

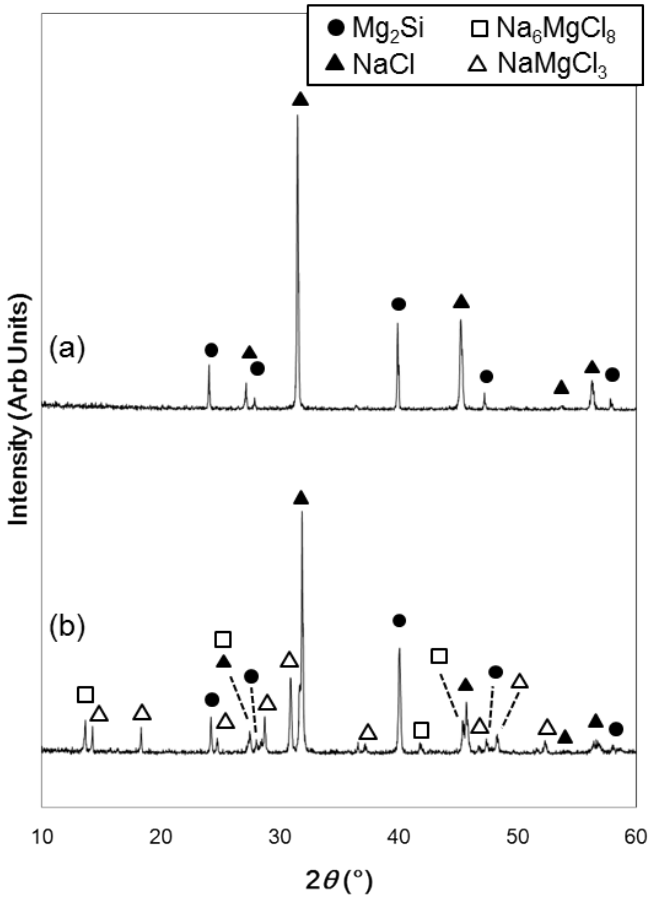


Figure S2. Powder XRD patterns for (a) sample C prepared at 650 °C and (b) sample prepared at 450 °C, both with the same nominal composition as sample C.

Table S1. Crystalline phases detected from powder XRD measurements

Sample	$MgCl_2$	$NaMgCl_3$	Na_6MgCl_8	NaCl	Mg_2Si
C (650 °C)	–	–	–	Major	Major
C (450 °C)	–	Major	Major	Major	Major

As shown in Fig. S2 and Table S1., sample C (450 °C) included $NaMgCl_3$, Na_6MgCl_8, NaCl, and Mg_2Si, while sample C (650 °C) included only NaCl and Mg_2Si.

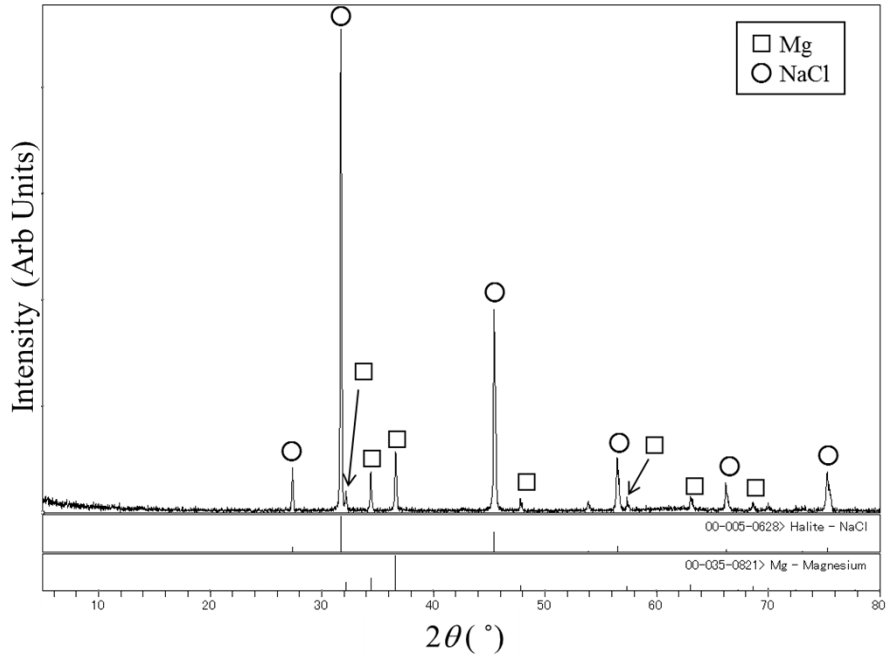


Figure S3. Powder XRD pattern for the product obtained by heating a mixture of $MgCl_2$ and Na at 650 °C. The pattern corresponds to a mixture of Mg and NaCl.

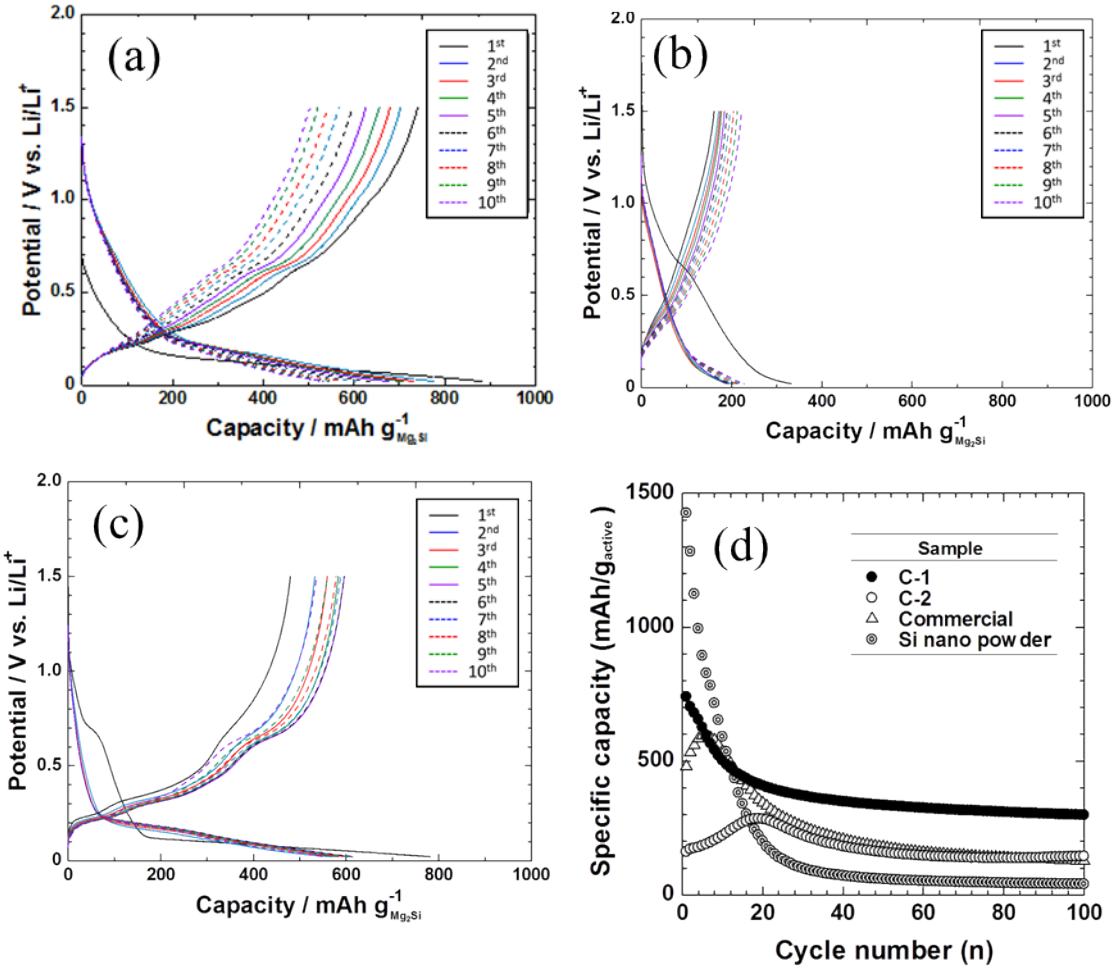


Figure S4. Voltage profiles for charge and discharge process for (a) Sample C-1, (b) Sample C-2 and (c) commercial sample. (d) Comparison of cycle performance for Mg_2Si samples and Si nanoparticles (reagent from Sigma-Aldrich Co. LLT., diameter < 100 nm)

Theoretical capacity of Mg_2Si is 1,136 mAh g^{-1} under the hypothesis of the reaction of $13Li + 4Mg_2Si \rightarrow 8Mg + Li_{13}Si_4$（ref : A. Anani and R. A. Huggins, "Multinary alloy electrodes for solid state batteries I. A phase diagram approach for the selection and storage properties determination of candidate electrode materials," Journal of Power Sources, vol. 38, pp. 351-362, (1992). Initial capacity of 740 mAh $g^{-1}$for sample C-1 would be reasonable value at the relatively high discharge rate of 100mA/g.

At least, two steps are observed for the voltage profiles of Mg_2Si samples. One step would correspond to the reaction between Li and Si. The reaction usually occur around 0.4 V (vs. Li/Li^+). The origin of the other step was not investigated in the current paper.

Under the current evaluation conditions, fine Mg_2Si particles showed higher cyclability than commercical Si nanoparticles (The electrode was prepared in a same manner for that of Mg_2Si). For consideration of a practical application, however, further refinement of preparation conditions of electrodes would be necessary in order to derive maximum performance.