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Energetics of compounds related to Mg_2Si as an anode material for lithium-ion batteries using first principle calculations

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ABSTRACT

Electronic energy calculations of (1) Li-intercalated Mg_2Si assuming 4*b* sites occupancy by Li and (2) the formation of $MgSiLi_2$ with the assumed structures by Wengert et al. and Herbst and Meyer have been performed by a density-functional theory. The calculated energy changes for intercalation reactions of $Mg_8Si_4 + nLi \rightarrow Mg_8Si_4Li_n$ are +0.349 eV, +0.822 eV, +1.178 eV, and +1.741 eV for n = 1–4, respectively, and the energy change for $Mg_8Si_4 + 8Li \rightarrow Mg_4Si_4Li_8 + 4Mg$ is −1.95 eV when Mg is in the metallic state, while +4.12 eV when Mg is in the state of an isolated atom. If we can retard the growth of metallic Mg from Mg_2Si by some methods, undesirable structural change of the Mg_2Si into $MgSiLi_2$ during charge–discharge cycles would be prevented and intercalation/disintercalation reaction of Li into/from Mg_2SiLi_n (n = 0–1.0) would proceed reversibly by applied electric field.

1. Introduction

Most of researches on development of anode materials for rechargeable lithium (Li)-ion batteries have been devoted to Li–graphite intercalation compounds since carbon materials are still the only commercially viable anode material for Li-ion batteries [1].

However, several binary Li alloys (e.g. Li–Al, Li–Si, and Li–Sn) and intermetallic systems have been investigated as possible replacement for graphite which may offer larger capacities than graphite. One of the examples is Mg_2Si. Since this is composed of light metals, it is favorable particulary for mobile applications. It is also ecologically friendly because both of Mg and Si are naturally abundant and relatively harmless to the environment.

As for the reaction mechanism of Mg_2Si and Li, there have been two conflicting schemes: (1) intercalation of Li into Mg_2Si [2] and (2) a formation of a ternary phase of $MgSiLi_2$ [3]. From the detailed X-ray diffraction experiments, it is now considered that Li intercalation into Mg_2Si proceeds at the first stage, followed by formation of $MgSiLi_2$ accompanied by a discharge of Mg from Mg_2Si. After that, conversion of $MgSiLi_2$ into binary Li–Mg and Li–Si alloys proceeds [4].

This mechanism seems reasonable but there has been no thermodynamic evaluation of the compounds related to these processes due to the lack in thermodynamic data for Li–Mg–Si system except for enthalpy values at high temperatures [5].

In the present paper, we tried to evaluate the energetic formulation of related compounds using first-principle calculations based on the density-functional theory (DFT) with GGA, the generalized gradient corrected local density approximation. It is generally admitted that DFT calculation based on the local density approximation underestimate the lattice constants, reflecting overestimation of binding energy. However, it is also known that one can expect GGA to predict correctly trends of energy value. Therefore, we believe results described here will give proper prediction on the energetic relations among related compounds. We describe the results of energetic consideration on reactions between Mg_2Si and Li.

2. Calculation method

The calculation methods are the same as those used in previous studies on the electronic energy calculations of anode materials for rechargeable Li-ion batteries, Li–graphite [6] and Li–$La_3Ni_2Sn_7$ [7]. That is, calculations have been performed using CASTEP (Cambridge Serial Total Energy Package) developed by Payne et al. [8]. This is a first-principle pseudopotential method based on DFT in describing the electron–electron interaction, a pseudopotential description of the electron–core interaction, and a plane-wave expansion of the wavefunctions. The pseudopotential used is the ultrasoft pseudopotential generated by the scheme of Vanderbilt [9] which is bundled in the Cerius2[1] graphical user interface.

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[1] Cerius2 is a trademark of Accelrys Inc.

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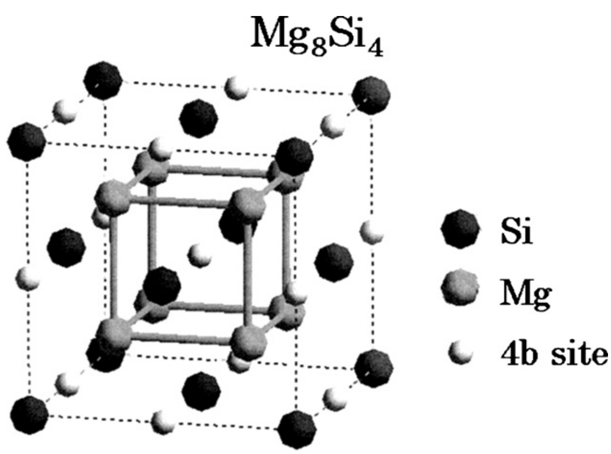

Fig. 1. Unit cell of Mg_2Si and the possible intercalation 4*b* sites by Li.

As for the method of approximation to the exchange-correlation term of the DFT, we used local density approximation with the Perdew–Wang generalized gradient correction (GGA) [10]. Total one-electron band-structure energy can be obtained by integration of the DOS, multiplied by band energy, with the energy from the bottom of the band to the Fermi level. The kinetic cutoff energy for the plane wave expansion of the wavefunctions was set at 380 eV and the Monkhorst–Packe scheme [11] was used for the *k*-points sampling for the total energy calculations with the spacing of 0.4 nm^{-1} in the reciprocal space, corresponding to the mesh parameters of $4 \times 4 \times 4$ which produced 32 points sampled from the irreducible part of the Brillouin zone in the cases of $Mg_8Si_4Li_n$ and $Mg_4Si_4Li_8$.

3. Compounds considered

Mg_2Si is known to have an antifluorite structure, belongs to the space group of $F_{m-3\,m}$. In the unit cell of Mg_2Si, Mg occupies 8*c* sites (Wyckoff notation) and Si occupies 4*a* sites. Thus, the unit cell of Mg_2Si contains four formula units. As for the possible inserted sites by Li, we assumed vacant 4*b* sites which are surrounded octahedrally by eight Mg atoms, though there has been no experimental study on the sites of Li intercalation to our knowledge. The unit cell of Mg_2Si and the assumed intercalation sites are shown in Fig. 1. If Li atoms occupy all the 4*b* sites, the chemical composition can be described as $Mg_8Si_4Li_4$. We cannot exclude the possibility that other sites will be favorably inserted by Li, but we leave this possibility for future study.

As for $MgSiLi_2$, Wengert et al. proposed two possible structure models [12]. One belongs to the space group $P_{-4\,3}$ with the unit cell composition of $Li_8Mg_4Si_4$ (Wengert et al.'s 'model m1′, which will be referred to as the 'model 1′ in the present paper) and other belongs to $F_{m-3\,m}$ with the unit cell composition of $Li_{64}Mg_{32}Si_{32}$ (Wengert et al.'s 'model m2′, which will be referred to as 'model 2′).

Recently, Herbst and Meyer proposed another crystal structure belonging to $P_{-4\,3\,m}$ [13], which will be referred to as 'model 3′ in the present paper, and claimed that their structure is energetically more favorable than other models, based on the calculations using the Vienna Ab initio Simulation Package (VASP). Therefore, we tried to confirm their claim using the program described in Section 2.

All the present calculations on the electronic energies have been performed on the optimized structure obtained by a full relaxation of each structure. A geometrical optimization using total energy minimization algorithm was performed so as to determine the lattice parameters and atomic arrangements. They are changed using the Broyden–Fletcher–Goldfarb–Shannon optimization procedure under the constraint condition of the assumed space groups. Convergence of an optimization mode was controlled by the following criteria: The energy change between two steps, the root-mean-square (rms) residual force on movable atoms, the rms displacement of atoms during the geometrical optimization process, and the rms residual bulk stress must be smaller than 1 meV, 10^{-9} N, 10^{-4} nm, and 0.1 GPa, respectively.

4. Results and discussion

The calculated values of electronic energies for Li-intercalated Mg_2Si, $Mg_8Si_4Li_n$ (n = 0–4), along with their optimized lattice constants are shown in Table 1. Those of pure Li and Mg are also given in Table 1.

The energy of Mg was calculated not only for metallic state but also for an isolated single atom state. For the calculation of the energy of Mg in an isolated single atom state, we adopted the array of Mg atoms arranged in the simple cubic structure with the lattice constant of 1.000 nm, which is much larger than the interatomic distance of the equilibrium metallic state of Mg, 0.3197 nm. The calculated energy difference of Mg_1 between metallic state (=−1957.0512 eV/2) and the isolated state of a single atom (=−977.0081 eV) was 1.517 eV per one Mg atom. This value corresponds to 146.4 kJ/mol, which gave a close approximation to the observed sublimation enthalpy of 147.1 kJ/mol.

It should be noted that calculations here have been performed for possible Li insertion sites which are apparently different but really equivalent to each other. For example, in the case of $Mg_8Si_4Li_1$, there seem to be two possible cases: (1) one of the edge center sites of Mg_8Si_4 is inserted by a Li atom and (2) the body center site of Mg_8Si_4 is inserted by a Li atom. These two cases may look inequivalent but are equivalent from the crystallographic space group viewpoint for $F_{m-3\,m}$. The purpose of overlapped calculations here is to evaluate the possible error margin for the present calculations. Though there seems to be some scattering of the calculated values for the same crystallographic sites insertion, this is considered to be within the error caused by the assumed self-consistency convergence criterion.[2]

As shown in Table 1, predicted lattice constant of Li (a = 0.2993 nm: α = 109.471°, which corresponds to the lattice constant of the conventional body-centered-cubic lattice of 0.3457 nm) is 1.5% smaller than the observed one (=0.3509 nm), as is often experienced. One of the predicted lattice constants of Mg (a = 0.3229 nm) is 0.6% larger than observed one (a = 0.3209 nm), while predicted c = 0.5179 nm was 0.6% smaller than the observed one (c = 0.5211 nm). The predicted lattice constant of Mg_8Si_4, 0.6339 nm, is 0.2% smaller than the observed value (=0.6351 nm). However, these errors seem to be small enough for the purpose of the present study.

Li insertion into Mg_8Si_4 causes cell volume expansion, as expected. However, we would like to mention that interatomic distances between Mg atoms where a Li atom is inserted between them are sometimes smaller than those where a Li atom is not inserted. For example, in the case of $Mg_8Si_4Li_2$, value of a and b (=corresponding to the interatomic distances between Mg atoms where Li atoms are inserted into (0.5 0 0) and (0 0.5 0)) are 0.6349 nm while c is 0.6658 nm, though both of them are larger than that of the optimized Mg_8Si_4 (=0.6339 nm). Thus, Li insertion will cause the extension of the lattice constants, as would be expected, but this effect is more remarkable for the interatomic distance between Mg atoms where Li is not inserted. This appar-

[2] In the present calculations, we adopted the value of 0.001 eV/atom as the self-consistency convergence criterion. Therefore, the numerical values of calculated energy may have errors *ca.* ±0.012–0.0016 eV per formula unit.

Table 1
Optimized lattice constants and electronic energy of Mg_8Si_4 with and without Li intercalation into 4*b* sites and those of Li and Mg.

Composition of the cell	Fractional coordinates of intercalated sites by Li	Optimized lattice constants (nm or deg)	Cell volume (nm^3)	Calculated energy (eV)
Mg_8Si_4	–	$a=b=c=0.6339$	0.2546	−8265.0859
$Mg_8Si_4Li_1$	(0.5 0 0)	$a=b=c=0.6381$	0.2598	−8454.9978
	(0.5 0.5 0.5)	$a=b=c=0.6390$	0.2609	−8455.0054
$Mg_8Si_4Li_2$	(0.5 0 0) (0 0.5 0)	$a=b=0.6349$	0.2683	−8644.8009
		$c=0.6658$		
	(0.5 0 0) (0.5 0.5 0.5)	$a=0.6522$	0.2699	−8644.7849
		$b=0.6419$		
		$c=0.6446$		
$Mg_8Si_4Li_3$	(0.5 0 0) (0 0.5 0) (0 0 0.5)	$a=b=c=0.6522$	0.2774	−8834.6392
	(0.5 0 0) (0 0.5 0)	$a=b=0.6418$	0.2774	−8834.7623
	(0.5 0.5 0.5)	$c=0.6735$		
$Mg_8Si_4Li_4$	(0.5 0 0) (0 0.5 0) (0 0 0.5) (0.5 0.5 0.5)	$a=b=c=0.6603$	0.2878	−9024.4027
Li_1 (body center cubic)	–	$a=0.2993$: $\alpha=109.471°$	0.02066	−190.2644
Mg_2 (hexagonal)	–	$a=b=0.3229$	0.04676	−1957.0512
		$c=0.5179$		
Mg_1 (isolated)	–	–	–	−977.0081

Table 2
Optimized lattice constant and fractional coordinates of $MgSiLi_2$.

Name of model	Cell composition	Space group	Optimized lattice parameter (nm)	Atoms with multiplicity and Wyckoff letter	Optimized fractional coordinates			Calculated total energy per $Mg_4Si_4Li_8$ for the optimized structure (eV)
Model 1	$Mg_4Si_4Li_8$	215 ($P_{-4\,3\,m}$)	$a=0.6324$	$Si^{(1)}$ (1a)	0	0	0	−5874.8785
				$Si^{(2)}$ (3c)	0.5	0.5	0.5	
				$Li^{(3)}$ (1b)	0.5	0.5	0.5	
				$Li^{(4)}$ (3d)	0.5	0	0	
				$Li^{(5)}$ (4e)	0.25	0.25	0.25	
				$Mg^{(6)}$ (4e)	0.75	0.75	0.75	
Model 2	$Mg_{32}Si_{32}Li_{64}$	225 ($F_{m-3\,m}$)	$a=1.2661$	$Si^{(1)}$ (4a)	0	0	0	−5874.7726
				$Si^{(2)}$ (4b)	0.5	0.5	0.5	
				$Si^{(3)}$ (24d)	0.5	0.25	0.25	
				$Li^{(4)}$ (8c)	0.25	0.25	0.25	
				$Li^{(5)}$ (24e)	0	0	0.21784	
				$Li^{(6)}$ (32f)	0.125	0.125	0.125	
				$Mg^{(7)}$ (32f)	0.37403	0.37403	0.37403	
Model 3	$Mg_4Si_4Li_8$	215 ($P_{-4\,3\,m}$)	$a=0.6305$	$Si^{(1)}$ (4e)	0.25476	0.25476	0.25476	−5875.0439
				$Li^{(2)}$ (1b)	0.5	0.5	0.5	
				$Li^{(3)}$ (3c)	0	0.5	0.5	
				$Li^{(4)}$ (4e)	0.72793	0.72793	0.72793	
				$Mg^{(5)}$ (1a)	0	0	0	
				$Mg^{(6)}$ (3d)	0.5	0	0	

Models 1 and 2 are based on Wengert et al. [12] and model 3 is based on Herbst and Meyer [13].

ently strange effect would be caused by a strong chemical affinity of Li with Mg, as suggested by a strong negative deviation of lattice constants of Li–Mg system from Vegard's law [14].

From the values in Table 1, we can evaluate energy change of the following insertion reaction so as to judge if the insertion reactions will proceed spontaneously.

$$Mg_8Si_4 + nLi \rightarrow Mg_8Si_4Li_n \quad (1)$$

The calculated energy changes for (1) are +0.349 eV, +0.822 eV, +1.178 eV, and +1.741 eV for $n=1$–4.

Therefore, spontaneous insertion of Li into the Mg_2Si lattice will not proceed but applied electric field of several hundred millivolts *vs.* Li/Li^+ electrode will make one or two Li atoms per Mg_8Si_4 intercalate into the Mg_2Si lattice.[3]

However, it was found that the energy change for

$$Mg_8Si_4 + 8Li \rightarrow Mg_4Si_4Li_8 + 4Mg$$

is negative, as shown below, and this reaction will proceed with no applied electric voltage *vs.* Li/Li^+ electrode.

Table 2 shows the optimized crystal structures and the energies for assumed models 1–3 of $Mg_4Si_4Li_8$ above stated. Among three structures assumed here, the model 3 structure by Herbst and Meyer has the most negative energies, which is in accordance with their previous energy calculations using VASP code, though there are small disagreements in the lattice parameter.[4]

Energy change for

$$Mg_8Si_4 + 8Li \ \ (\text{metal}) \rightarrow Mg_4Si_4Li_8 + 4Mg \ \ (\text{metal})$$

is $(-5875.0439)+2\times(-1957.0512)-(-8265.0859)-8\times(-190.2644)=-1.95$ eV.

Therefore, this reaction will proceed spontaneously. Though entropy effect is not considered here, the following reaction:

$$Mg_8Si_4 + 8Li^+ + 8e^- \rightarrow Mg_4Si_4Li_8 + 4Mg \ \ (\text{metal})$$

[3] It should be noted that the electrochemical energy change of $Mg_8Si_4 + nLi^+ + ne^- \rightarrow Mg_8Si_4Li_n$ can be regarded as the same with that of Eq. (1) since electrochemical energy change of $Li^+ + ne^- \rightarrow Li$ is regarded as 0 eV in the conventional electrochemical definition where Li/Li+ electrode is used as a reference. However, contribution of the entropy change of the reaction is not considered here.

[4] Herbst and Meyer stated that optimized lattice constants are 0.64 nm, 1.28 nm, and 0.6387 nm for models 1–3, respectively, while those of our results are 0.6324 nm, 1.2661 nm, and 0.6305 nm. Their fractional coordinates of the atoms of the optimized structures for model 3 are relatively close to ours.

will also proceed, even if there is no applied electric voltage *vs.* Li/Li+ electrode, in parallel with above intercalation reactions. However, if the growth of metallic Mg from discharged Mg atoms is slow, the term of $2\times(-1957.0512)$ should be changed to $4\times(-977.0081)$ and the energy change for

$$Mg_8Si_4 + 8Li \quad (metal) \rightarrow Mg_4Si_4Li_8 + 4Mg \quad (atom)$$

is +4.12 eV, which means this reaction will not proceed.

Thus, formation of metallic Mg from discharged Mg atoms is of vital importance in the competitive intercalation reactions of Li into Mg_2Si and the formation of $MgSiLi_2$.

If there are some methods to retard the growth of metallic Mg from Mg_2Si lattice, for example, by adding some reagents in the electrolyte, we will be able to obstruct the proceeding of this reaction and the undesirable structural change of the Mg_2Si electrode during charge–discharge cycles would be prevented.

5. Conclusion

We have performed energetic consideration of Li-intercalation into the Mg_2Si lattice and the formation of $MgSiLi_2$ by calculations based on a density-functional theory.

The calculated energy changes for $Mg_8Si_4 + nLi \rightarrow Mg_8Si_4Li_n$ are +0.349 eV, +0.822 eV, +1.178 eV, and +1.741 eV for $n = 1–4$, respectively, and the energy change for

$$Mg_8Si_4 + 8Li \rightarrow Mg4Si_4Li_8 + 4Mg$$

is −1.95 eV when Mg is in the metallic state, while +4.12 eV when Mg is in the state of an isolated atom. Therefore, if we can find some methods to retard the growth of metallic Mg, undesirable structural change of the Mg_2Si into $MgSiLi_2$ during charge–discharge cycles would be prevented and intercalation/disintercalation reaction of Li into/from Mg_2Si would proceed reversibly by applied electric field.

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