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Analysis on the Formation of Li_4SiO_4 and Li_2SiO_3 through First Principle Calculations and Comparing with Experimental Data Related to Lithium Battery

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ABSTRACT

The formation of Li-Si-O phases, Li_4SiO_4 and Li_2SiO_3 from the starting materials SiO and Li_2O are analyzed using Vienna Ab-initio Simulation (VASP) package and the total energies of Li-Si-O compounds are evaluated using Projector Augmented Wave (PAW) method and correlated the structural characteristics of the binary system $SiO-Li_2O$ with experimental data from electrochemical method. Despite Li_2SiO_3 becomes stable phase by virtue of lowest formation energy calculated through VASP, the experimental method shows presence of Li_4SiO_4 as the only product formed when SiO and Li_2O reacts during slow heating to reach 550°C and found no evidence for the formation of Li_2SiO_3. Also, higher density of Li_4SiO_4(2.42 g ml^{-1}) compared to the compositional mixture $1SiO_2$-$2Li_2O$ (2.226 g ml^{-1}) and better cycle capacity observed through experiment proves that Li_4SiO_4 as the most stable anode supported by better cycleabilityfor lithium ion battery remains as paradox from the point of view of VASP calculations.

1. Introduction

The search for high specific capacity anode alternative to the low capacity graphite (372 mAh/g) of lithium ion battery has opened up new area of research based on tin and silicon which have specific capacity values of 4190 and 990 mAh/g corresponding to $Li_{22}Si_5$ and $Li_{22}Sn_5$ alloys respectively.[1-2] Despite exhibiting high initial capacities, the crystallographic volume changes of these electrodes during cycling cause premature cell failure. In the case of silicon based composite a reasonable level of cycle capacity has been achieved employing dual composites comprising of Si or SiO with graphite. Improvements in performance have been reported by incorporating

metal powders,[3] silicon alloys,[4] silicon compounds[5] and carbon coatings to the composites.[6-7] The silicon oxide based composite anodes perform better over silicon based ones as the former generates a buffer component Li_2O along with possibly nanoslicon during the first cycling which reduces electrode strain during cycling process.[8] Later, Miyachi *et al.*[9] explained that high performance of SiO based composite is due to silicate formation in the electrode which acts both as volume buffer and electroactive species. Even though different mechanisms are reported to explain the high cycleability of SiO, a report by Schulmeister and Mader[10] states that the commercially produced SiO is not a single phase compound but a mixture of amorphous SiO_2 and amorphous Si. Such findings could explain the complicated chemistry of SiO based anode comprising duringcharge/discharge process. Further improvement in electrode performance was made by

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incorporating/generating inert material such as Li_2O,[11,12] Al_2O_3,[13] SiO_2[14] during synthesis and first lithiation process. Interdependency of sustainable reversible capacity and initial irreversible capacity (Li_2O) of the electrode materials has also been reported for the SiO/C composite.[15] The composite material consisting of nano-sized silicon, Li_4SiO_4[16] and Li-doped SiO-negative material (LixSiO)[17] are capable of delivering high capacity with a flat plateau in the cycle life performance.

SiO is generally prepared by rapid condensation of vapor (gaseous SiO) formed when pure Si and pure quartz (SiO_2) are reacted in a vacuum at high temperatures[18] or reduction of SiO_2 with H_2 or CO at high temperatures[19] as shown by the reactions (1) and (2) respectively. Silicon monoxide could be trapped in an argon matrix cooled by helium[20] which eventually decomposes into SiO_2 and Si.[21]

$$SiO_2 + Si \rightarrow 2SiO \qquad (1)$$
$$SiO_2 + H_2(\text{or CO}) \rightarrow 2SiO + H_2O \text{ (or } CO_2) \qquad (2)$$
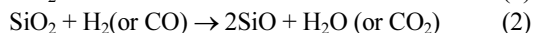
This paper compares the electrochemical and structural data obtained for the experimentally synthesized compound from the starting materials SiO and Li_2O with the possible compound that could be expected from the first principle calculations using VASP. The paradox that underlies in formation of the product is analyzed by considering the data such as formation energies, density values and electrochemical data.

2. Methodology

2.1. Experimental

Equimolecular quantities of lithium hydroxide monohydrate (LiOH·H_2O, Aldrich) and SiO (~325 mesh, LTS Chemicals Inc.) were mixed in a mortar and then heated to 550°C for 3 h in an argon atmosphere. Graphite was then added to maintain the weight ratio of C and SiO at 1 : 1 and ball-milled for 15 h. The composite was named as 'A'. In order to understand the behavior of the new composite 'A' another composite 'B' was prepared by just ball milling SiO and graphite in a weight ratio of 1 : 1 for 15 h.

The composite powders 'A' and 'B' were then examined by means of a Philips 1830 X-ray diffractometer with nickel-filtered Cu Ká radiation at a scan rate of 0.04°s⁻¹ over a 2θ range of 10~80°. The composite 'A' material was used to prepare a composite electrode named as (A) and its electrochemical properties were compared with electrode (B) prepared by using the composite

'B'. Conditions of the electrode and cell preparation were described elsewhere.[22-23] The coin cell of anodes of (A) and (B) with lithium counter electrode were cycled between 0 and 1.5 V versus Li^+/Li^0 at a constant current of 0.253 mAcm⁻² (1/10 C rate based on the theoretical capacity of graphite) using a charge-discharge analyzer (Toyo System Co., Ltd. Japan).

2.2. Computational

The crystallographic data of Li-Si-O phases are obtained from inorganic materials database and published papers. The total-energy calculation and full structural optimization of Li-Si-O compounds were performed using the Vienna *ab initio* Simulation Package (VASP).[24-25] Projector augmented-wave pseudopotentials were used.[26] The exchange and correlation were treated within the generalized gradient approximation (GGA-PBE).[27] The size of the k-mesh was chosen appropriately as shown in Table 2 through KPOINTS convergence test. The result of KPOINTS convergence was shown in Fig. 4. The value of x-axis means the multiplicity of KPOINTS as shown in Table 2. When the multiplicity of KPOINTS was changed in the range of 1/2, 1, 2 and 3, the formation energy differences of different multiplicity of 1, 2 and 3 were lower than 1 meV/unit reactant except that of 1/2. In INCAR, ISMEAR of 1, EDIFF(electronic accuracy) of 1×10^{-5} eV, EDIFFG(ionic accuracy) of −0.02 eV were used. A cutoff value of 400eV was used to assure convergence of the energy. It was found that the convergence in the total energy was better than 1 meV/atom using this cutoff energy and k-mesh grid. Total-energy minimization via a lattice parameter optimization and atomic position relaxation in a conjugate gradient routine was obtained by calculating the Hellmann-Feynman forces which are reduced to within the 0.01 eV/Å for each atom. Other computational and structural details are available in references.[28]

3. Results and discussion

3.1. Reaction and theoretical specific capacity

The formation of L_4SiO_4 phase by the reaction of SiO and Li_2O around 550°C has been reported earlier[29] as shown in Fig. 1. The stable compositions of Li-Si-O ternary material are described in Fig. 2. Li-Si-O ternary materials could be treated as pseudobinary materials of Li_2O and SiO_2.

The structure of SiO is reported to follow interface clusters mixture model (ICM model)[30] composed of
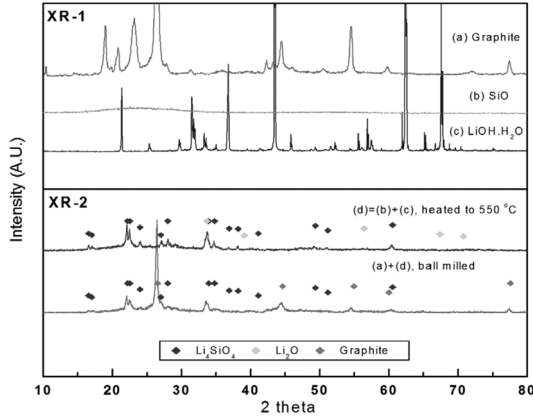
Fig. 1. XR-1 represents XRD pattern of (a) graphite (b) SiO, (c) LiOH·H$_2$O, XR-2 represents d = (b) + (c) material heated at 550ºC in argon atmosphere and (a) + (d) ball milled composite material.
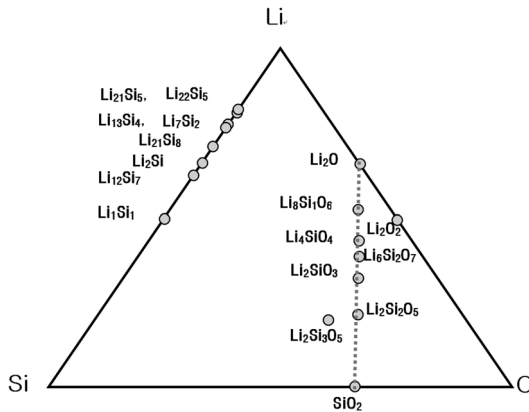
Fig. 2. A phase diagram of Li-Si-O ternary and Li$_2$O-SiO$_2$ pseudobinary materials.

nanometric domains of Si and SiO$_2$. Following ICM model, chemical reaction of SiO and Li$_2$O is expected to produce products based on Li-Si-O arrangements. Confining Li-Si-O compounds as Li$_4$SiO$_4$ the chemical reaction is represented as follows,

$$2SiO \rightarrow Si + SiO_2$$
$$SiO_2 + 2Li_2O \rightarrow Li_4SiO_4$$
$$2SiO + 2Li_2O \rightarrow 2Li_4SiO_4 + Si \quad (3)$$
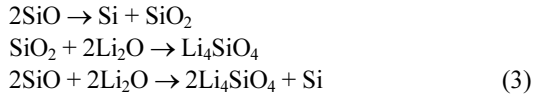
Reaction (3) is a disproportionation reaction, changed the oxidation state of silicon in SiO from +2 to 0 in the case of nano Si and +4 oxidation state in SiO$_2$ and Li$_4$SiO$_4$. Silicon compounds having +4 oxidation state is inert to

electrochemical reaction with lithium. Reaction (3) shows that a half of SiO gets converted into Li$_4$SiO$_4$, which possibly remains as an electrochemically inactive species (ΔG$^o_{298K}$ = −2366 kJ/mole)[31] in the composite similar to that reported by Yang et al.[32] The fully lithiated silicon was known as Li$_{22}$Si$_5$ (Eq. 4). However, Li$_{15}$Si$_4$ phase was known as a fully lithiated silicon compound under electrochemical condition at room temperature.[33-34]

$$22Li + 5Si \rightarrow 2Li_{22}Si_5 \quad (4)$$

By combining the reactions (3) and (4), the theoretical specific capacity of SiO and (Si- Li$_4$SiO$_4$) will be 1337 mAh/g-SiO (Eq. 5) and 797 mAh/g-(Si-Li$_4$SiO$_4$) (Eq. 6), respectively. Formula ratio of SiO and Li$_2$O materials used in this experiment was 4 and 2 leading to theoretical specific capacity of 999 mAh/g-(2Si-SiO$_2$-Li$_4$SiO$_4$) (Eq. 7).

26800 mAh/eq.-Li × (22/5)eq.-Li/eq.-Six (1/2)eq.-Si/eq.-SiO × (1/44.0849)eq./g-SiO = 1337 mAh/g-SiO   (5)

26800 mAh/eq.-Li × (22/5)eq.-Li/eq.-Si × 1eq.-Si/eq.-(Si-Li$_4$SiO$_4$) × (1/147.9326)eq./g-(Si-Li$_4$SiO$_4$) = 797 mAh/g-(Si-Li$_4$SiO$_4$)   (6)

26800 mAh/eq.-Li × (22/5)eq.-Li/eq.-Si × 2eq.-Si/eq.-(2Si-SiO$_2$-Li$_4$SiO$_4$) × (1/236.1024)eq./g-(2Si-SiO$_2$-Li$_4$SiO$_4$) = 999 mAh/g-(2Si-SiO$_2$-Li$_4$SiO$_4$)   (7)

3.2. Specific capacity and cycle behavior

Variation of specific capacity with cycle number for the heat treated-(SiO+Li$_2$O)/C electrode (A) and SiO/C electrode (B) are shown as Fig. 3.[35] The first lithiation specific capacity of electrode (A) is 862 mAh/g which gets reduced to 521 mAh/g in the second cycle and simi-
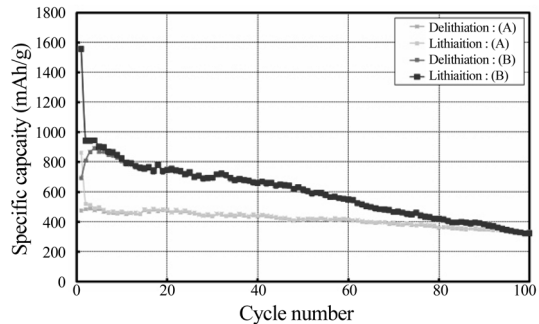
Fig. 3. Cycle life curves of electrode (A) : heat treated-(SiO + LiOH. H$_2$O)/Graphite and electrode (B) : SiO/Graphite. Potential range 0~1.5 V vs. Li/Li$^+$, current density 0.253 mAh/cm^2.
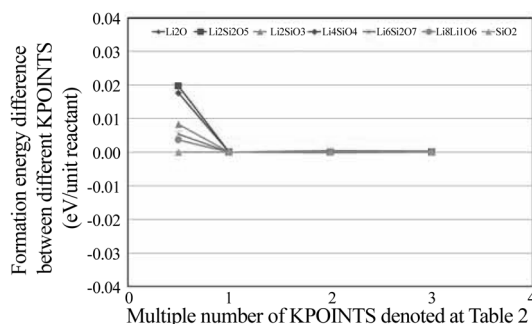
Fig. 4. KPOINTS convergence results.

larly for the electrode SiO/C (B) the value1556 mAh/g is reduced to 950 mAh/g.Theoretical specific capacity of $(2Si-SiO_2-Li_4SiO_4)/C$ (1 : 1) electrode (A) and SiO/ C (1 : 1) electrode (B) will be 685.5 mAh/g-$(2Si-SiO_2-Li_4SiO_4/C(1 : 1)$, Eq. 8) and 854.5 mAh/g-(SiO/C(1 : 1), Eq. 9), respectively.Capacity retentions of $(2Si-SiO_2-Li_4SiO_4)/C(1 : 1)$ electrode (A) and SiO/C(1 : 1) electrode (B) were 67% and 36% at 100th cycle against the maximum capacity, respectively, showing better cycle performance for Li_4SiO_4 based electrode.

999 mAh/g-$(2Si-SiO_2-Li_4SiO_4) \times 50\%$ + 372 mAh/g-C $\times$ 50% = 685.5 mAh/g-$(2Si-SiO_2-Li_4SiO_4)/C(1 : 1)$
(8)

1337 mAh/g-SiO x 50% + 372 mAh/g-C × 50% = 854.5 mAh/g--SiO/C(1 : 1)
(9)

3.3. Structural properties and densities of Li-Si-O phases

Possibilities of the formation of Li_4SiO_4could beunderstood from the first principle calculations. Phase diagram for Li-Si-O ternary materials has been drawn with the aid of datafrom JCPDSis represented as Fig. 2. Stable phases of Li-Si binary system denote the favorable electrochemical reactions of Li with Si host material.Stable Li-Si-O ternary phases could be encountered as pseudo-binary materials of Li_2O andSiO_2.Structural information of stable Li-Si-O phases is summarized in Table 1.

Total energiesof stable Li-Si-O ternary materials evaluatedby VASP (Vienna Ab-initio Simulation Package)are shown in the Table 2.

Stable Li-Si-O phases can be formed by reaction of Li_2O and SiO_2 as shown in reaction (10)

$$x\ Li_2O + ySiO_2 \rightarrow Li_{2x}Si_yO_{x+2y}$$
(10)

Formation energy = $E_0(Li_{2x}Si_yO_{x+2y}) - (xE_0(Li_2O) + yE_0(SiO_2))$
(11)
(ΔH, eV/unit(x + y))

In Fig. 5 the formation energies of the stable Li-Si-O

**Table 1.** The structural information of the stable Li-Si-O phases

Material	Space group	ICSD no.	Mole content of Li_2O (%)		Lattice parameters						Density (g/ml)
					a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	
Li_2O	Fm3-m	60431	100	ICSD	4.619	4.619	4.619	90	90	90	2.014
				Calculated	4.619	4.619	4.619	90	90	90	
$Li_2Si_2O_5$	CCG2	52157	100/3	ICSD	5.778	7.840	4.755	90	90	68.4	2.466
				calculated	5.767	7.842	4.748	90	90	68.4	
Li_2SiO_3	Cmc21	853	50	ICSD	9.325	5.374	4.644	90	90	29.8	2.529
				calculated	9.311	5.365	4.638	90	90	29.8	
Li_4SiO_4	P21/m	8222	200/3	ICSD	11.405	6.040	16.680	90	99	90	2.420
				calculated	11.405	6.040	16.600	90	99.4	90	
$Li_6Si_2O_7$	P4-21m	25752	60	ICSD	7.671	7.671	4.798	90	90	90	2.413
				calculated	7.671	7.671	4.798	90	90	90	
$Li_8Si_1O_6$	P63cm	65176	80	ICSD	5.379	5.379	10.561	90	90	120	2.203
				calculated	5.369	5.369	10.544	90	90	120	
SiO_2-á	P3₁21	67117	0	ICSD	4.831	4.831	5.353	90	90	120	2.650
				calculated	4.830	4.830	5.353	90	90	120	

Table 2. The total energies and the formation energies of the stable Li-Si-O phases

| Material	KPOINTS	Total energy (eV/formula)	Mole ratio of reactants[a]		Formation energy
			x (Li_2O)	y (SiO_2)	(eV/unit reactant)[b]
Li_2O	10,10,10	−14.327	1	0	0.00
$Li_2Si_2O_5$	6 ,4, 6	−63.207	1	2	−0.49
Li_2SiO_3	6,10,6	−39.404	1	1	−0.68
Li_4SiO_4	4,6,2	−54.294	2	1	−0.64
$Li_6Si_2O_7$	4,4,6	−93.506	3	2	−0.62
$Li_8Si_1O_6$	6,6,4	−83.084	4	1	−0.41
SiO_2-α	6,6,6	−23.711	0	1	0.00

[a]x and y are described in Eq. (10)
[b]based on unit reactant having unity of (x+y) in Eq. (10)
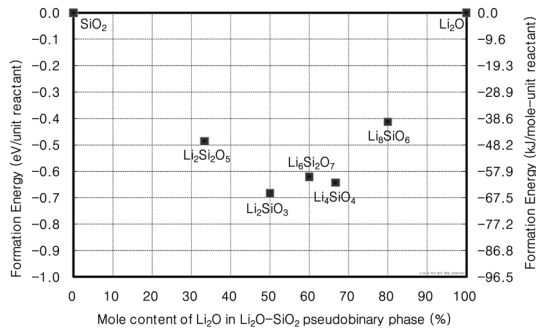
Fig. 5. The formation energies of stable Li-Si-O phases based on unit reactant.

phases are presented based on unit reactant and the corresponding values are listed in Table 2. Interpretations of the formation energies per unit product are difficult as the unit product has different content of Li_2O and SiO_2. The meaning of unit reactant was used as unity of (x + y) in Eq. (10). Li_2SiO_3 has the lowest formation energy ~ −0.68 eV based on unit reactant of Li_2O and SiO_2 which is supposed to be the most stable phase material. Even though Li_4SiO_4 has some higher value of formation energy of −0.64 eV, it remain as the only dominant product from the experiment rather than Li_2SiO_3, which shows that only Li_4SiO_4 is kinetically favored product. At higher temperature 1000ºC[36-37)] it is reported that Li_4SiO_4 is transformed into Li_2SiO_3.

Densities of Li-Si-O ternary materials are presented in Table 1, Fig. 6 shows densities of the compounds along with corresponding densities of the compositional mixtures
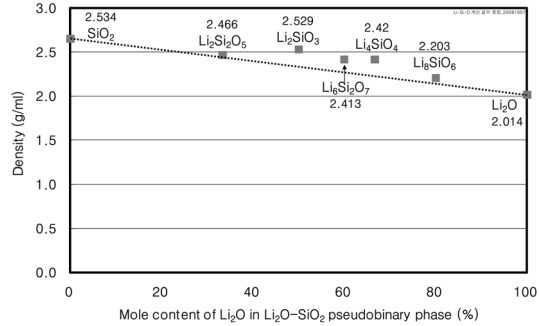
Fig. 6. Densities of Li-Si-O ternary materials.

of Li_2O and SiO_2. All ternary compositions have higher density than that of compositionally mixed materials. Density of Li_4SiO_4(2.42 g/ml) is higher than that of 1SiO_2-2Li_2O (2.226 g/ml) as a compositional mixture. Lithium insertion to silicon host accompanies volume expansion. This volume expansion is mitigated by buffer matrix. Buffering property of Li_4SiO_4 is considered to be better than that of material containing 1SiO_2-2Li_2O from the consideration of densities. Therefore an improved cycle performance could be obtained from the improved buffer matrix.

Electronic conductivities of Li_4SiO_4 and SiO_2 are 10^{-8}~10^{-10} S/cm at 100ºC[38)] and 10^{-14}~10^{-18} S/cm at room temperature, respectively. So, high conductivity of Li_4SiO_4 could contribute better to deliver high rate capability. Presence of Li_4SiO_4 acts as a buffer as wellas provides favorable lithium environment foreasy lithium ion diffusion and easy electron conduction.

4. Conclusion

Formation of Li-Si-O phases from SiO and Li_2O has been discussed by first principle calculations through VASP. From the calculations it is expected that Li_2SiO_3 with its lowest formation energy ~−0.68 eV has to be most stable phase. Contrary to this the experimental results showed the compound formed during slow heating of Li_2O and SiO_2 to reach 550ºC is Li_4SiO_4 which has slightly higher formation energy of −0.64 eV than Li_2SiO_3. Synthesized material contained only Li_4SiO_4 and there is no evidence to the formation of Li_2SiO_3. This paradox could be explained by invoking the kinetics which favors only the formation Li_4SiO_4 at those particular experimental conditions. The higher density value, 2.42 g/ml of Li_4SiO_4 than the compositional mixture 1SiO_2-2Li_2O (2.226 g/ml) and the ability to deliver sustainable long cycle life during charge-

discharge as lithium anode material further confirms the stability of Li_4SiO_4 compound.

Acknowledgement

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