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Lithium Alloying Potentials of Silicon as Anode of Lithium Secondary Batteries†

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Using first principles density functional theory, formation energies of lithium silicides were calculated. The formation of lithium silicides such as Li_1Si_1, $Li_{12}Si_7$, Li_2Si_1, Li_7Si_2, $Li_{15}Si_4$ and $Li_{22}Si_5$ were energetically favourable with potential decreasing. $Li_{15}Si_4$ calculated to be more stable than Li_7Si_2. Differences of Si-Si bond distances between 2.383 Å of $Li_{3.5}Si$ as relatively good reversible range and 4.548 Å of $Li_{3.75}Si$ as relatively low reversibility can be correlated to reversible lithiation range. Silicon is not only electron semi-conductor but also not good lithium ion conductor. Therefore during lithiation(delithiation) silicon has multi-level lithiated silicides to show broad and complicated XRD pattern.

Key Words: Lithium battery, Anode, Silicides, First principle, Vienna *ab initio* simulation package.

INTRODUCTION

Carbonacious materials including graphite have been used as active anode materials of rechargeable lithium ion batteries[1,2]. The specific capacity (capacity density) of graphite is 372 mAh/g (840 mAh/mL) assuming the density of graphite as 2.26 g/mL. The volume expansion (*ca.* 10.5 %) of Li_1C_6 is relatively small compared to other anode materials, such as silicon and tin. Recently, many efforts were devoted to develop lithium-silicon alloy anode for the application to commercial lithium secondary battery. A Japanese company reported 4 Ah cylindrical 18650 battery[3] with the weight of 54 g to be the specific energy of 253 Wh/kg. This battery used silicon based anode instead of graphite. Although its's successive application, silicon material have intrinsically low electronic conductivity and large volumetric expansion during lithium insertion/desertion to diminish cycle performance. Therefore technologies to enhance cycle performance are currently required. Silicon can be accommodated by 22 lithium atoms [3]per 5 silicon atoms ($Li_{22}Si_5$)[4,5], according to the equilibrium phase diagrams. The theoretical specific capacities of silicon and tin are 4200 mAh/g-Si and 993 mAh/g-Sn, respectively. However the high specific capacity of silicon (and tin) could not be adapted yet as anode materials for the commercial lithium secondary batteries. It is the reason that the lithium secondary battery adapting silicon as the anode material has poor cycle performances due to the micro-cracking[6,7], of particle. The crystal strain induced by the large volumetric changes and the heterogeneous multi-phase changes during the lithium insertion and desertion to the silicon host caused the micro-cracking of particle. $Li_{22}Si_5$ as a lithium intercalated compounds has the volume of *ca.* 400 % compared to that of silicon[8]. Yoshio *et al.*[9] described that the reasonable cycling performance of silicon could be achieved working with the lithium content alloy to $Li_{1.71}Si$ or $Li_{2.33}Si$. Obrovac *et al.*[10] studied that the reversibility of the lithiation to the silicon compounds is better for the limit potential of insertion to 50 mV (Li/Li^+) than for that of 0 mV(Li/Li^+) avoiding the amorphous-to-crystalline change and the fully lithiated compound at 0 mV (Li/Li^+) by the electrochemical reaction at the room temperature is $Li_{15}Si_4$ ($Li_{3.75}Si$) not $Li_{21}Si_5$ ($Li_{4.2}Si$). Grey[11] studied on the phase changes of the lithium silicides and found that intensity of the characteristic XRD peaks of silicon were reduced by the lithium to be amorphous phase. Bond distances of Si-Si and Li-Si were 4.6 Å and 2.6-2.9 Å for $Li_{22}Si_5$, Li_7Si_3 and $Li_{15}Si_4$. Weydanz *et al.*[12] also published that the electrochemically reversible insertion/desertion ranges of lithium to silicon to form lithium silicides is until $Li_{13}Si_4$ ($Li_{3.25}Si$). Recently, Dahn *et al.*[13] performed the first principles calculations on the lithiation of amorphous silicon using Abinit program with the PAW data. The structure of amorphous silicon was obtained through the full structural relaxation of a silicon structure of

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TABLE-1
STRUCTURAL PARAMETERS FOR SILICON AND LITHIUM SILICIDE COMPOUNDS

Materials		Space group	Structural parameter (Å,?)	Unit cell volume (Å^3)	Density (g/mL)	Z (atom)	Bond length of Si-Si; Li-Si; Li-Li (Å)
Si	(Li_0Si_1)	Fd-3m (227)	a = 5.42979 α = 90	160.08	2.331	8	2.351 - -
Li_1Si_1	(Li_1Si_1)	$I4_1/a$ (88)	a = 9.35300 α = 90	502.39	1.852	16	2.417 2.609 2.725
$Li_{12}Si_7$	($Li_{1.71}Si_1$)	Pnma (62)	a = 8.566 b = 19.701 c = 14.299 α = 90	2413.08	1.541	8	2.359 2.589 2.546
Li_2Si	(Li_2Si_1)	C2/m (12)	a = 7.700 b = 4.410 c = 6.560 α = 90 β = 113.4 γ = 90	204.44	1.364	4	2.372 2.590 2.920
Li_7Si_2	($Li_{3.5}Si_1$)	Pbam (55)	a = 7.990 b = 15.210 c = 4.430 α = 90	538.37	1.292	4	2.383 2.308 2.492
$Li_{15}Si_4$	($Li_{3.75}Si_1$)	I-43 d (220)	a = 10.6852 α = 90	1219.97	1.179	3	4.548 2.652 2.706
$Li_{22}Si_5$	($Li_{4.40}Si_1$)	F-43 m (216)	a = 18.75 α = 90	6591.8	1.181	16	4.556 2.573 2.696
Li	(Li_1Si_0)	Im-3 m (229)	a = 3.43879 α = 90	40.66	0.567	2	- - 2.978

F-43 m (216) eliminating several Si atoms. Lithium was filled the appropriate sites in the level of 0-4 for x in Li_xSi in steps of one Li atom. The lithiation to silicon has a fixed increase of 14.7 Å^3 in volume for every lithium atom. The reaction potentials to form Li_xSi for x = 0-4 were calculated as 0.6-0.1 V(Li/Li$^+$).

In this article the structures and the reaction potentials of the lithiated silicides were considered using the first principles calculations of VASP. The reaction potentials of lithium silicides were calculated and found that $Li_{4.4}Si$ ($Li_{22}Si_5$) can also be formed above of 0 mV (Li/Li$^+$). The structures of $Li_{4.4}Si$ as the highest lithium content silicides and $Li_{3.75}Si$ as the reversible lithium content silicides were discussed.

EXPERIMENTAL

Calculation: The total-energy calculation and full structural optimization were performed using the Vienna *ab initio* simulation package (VASP)[14]. Projector augmented-wave pseudo potentials were used[15]. The exchange and correlation were treated within the generalized gradient approximation (GGA)[16]. The size of the k-mesh was appropriately chosen considering the size of unit cell as shown at Table-2 for the conventional cell. To assure convergence of the energy, a cutoff value of 500 eV was used. 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.

The reaction potentials were calculated from the total energies of reactants and products using eqn. (6)[17,18].

$$V(x) = \frac{\mu_{Li}^{cathode}(x) - \mu_{Li}^{anode}(x)}{-nF} \quad (6)$$

RESULTS AND DISCUSSION

Structures and potentials of the lithium silicides: Silicon has the *sp*^{3} hybrid atomic orbital, the space group of Fd-3 m (227) and the short Si-Si distance of 2.3541 Å. Silicon react lithium to form lithium silicides. Nine compositions and six structures of the lithium silicides were known as shown in Table-1. The short Si-Si bond lengths were below 2.4 Å between the compositions of Si and Li_7Si_2 indicating the existence of the direct Si-Si bonding. The short Si-Si bond length of $Li_{22}Si_5$ and $Li_{15}Si_4$ were 4.556 Å and 4.548 Å, respectively. Indicating the absence of the direct Si-Si bonding. The short Si-Li bond length of Li_xSi inter-metallic compounds were ~2.6 Å which was longer than 2.3541 Å of the short Si-Si bond length in silicon and shorter than 2.98 Å of the short Li-Li bond length of metallic lithium. Weydanz *et al.*[19] studied on the electro-chemical reaction of the binary lithium-silicon materials.

The total energies of each structures of Li_xSi were evaluated using VASP calculations with the fixed atomic position and with the full relaxation of atomic position. Reaction energies and potentials were calculated using the total energies as shown in Table-2. The potentials in the condition of the fixed atomic position and the full relaxation of atomic position were similar not so different. The reaction enthalpies were shown at Fig. 1

TABLE-2
FORMATION ENTHALPY, REACTION ENTHALPY AND REACTION POTENTIAL OF THE LITHIUM SILICIDE FORMATION

Material	Unit reaction	KPOINTS	Calculation by fixed atomic position			Calculation by full relaxation of atomic position		
			Formation enthalpy[1] (eV)	Reaction enthalpy[2] (meV)	Reaction potential[3] (mV)	Formation enthalpy[1] (eV)	Reaction enthalpy[2] (meV)	Reaction potential[3] (mV)
(Li_0Si_1)	-	-	-5.378	-	-	-5.378	-	-
(Li_1Si_0)	-	-	-1.901	-	-	-1.901	-	-
(Li_1Si_1)	$Li + Si = Li_1Si_1$	4,4,4	-7.714	-435	435	-7.714	-435	435
($Li_{1.71}Si_1$)	$12Li + 7Si = Li_{12}Si_7$	4,2,2	-65.523	-5,059	422	-65.523	-5,059	422
(Li_2Si_1)	$2Li + Si = Li_2Si$	4,6,3	-9.860	-679	340	-9.877	-696	348
($Li_{2.63}Si_1$)[4]	$21Li + 8Si = Li_{21}Si_8$	-	-	-	-	-	-	-
($Li_{3.25}Si_1$)[4]	$13Li + 4Si = Li_{13}Si_4$	-	-	-	-	-	-	-
($Li_{3.5}Si_1$)	$7Li + 2Si = Li_7Si_2$	4,2,6	-26.051	-1986	284	-26.086	-2020	289
($Li_{3.75}Si_1$)	$15Li + 4Si = Li_{15}Si_4$	4,4,4	-54.618	-4586	306	-54.727	-4695	313
($Li_{4.20}Si_1$)[4]	$21Li + 5Si = Li_{21}Si_5$	-						
($Li_{4.40}Si_1$)	$22Li + 5Si = Li_{22}Si_5$	4,4,4	-74.290	-5571	253	-74.336	-5617	255

[1]Formation enthalpy were evaluated based on the product of unit reaction. VASP calculation were performed by the condition of the full relaxation of atomic positions and the fixed atomic positions using PAW_PBE potential codes; [2]Reaction enthalpy wase evaluated based on the unit reaction. [3]Reaction potential were evaluated based on reaction enthalpy; [4]Crystallographic data were not available.

to be -435 to -465 meV for Li_1Si_1. Reaction enthalpy was proportional to lithiated content and can be converted to reaction potential dividing by electron-enriched content which is just same to lithiated content. The reaction potentials were plotted as Fig. 2. Increasing the lithium content in the lithium silicides the potentials were gradually and continuously decreased. Li_1Si_1 has the potential of +435 mV. $Li_{22}Si_5$ as the highest lithium accommodation has the potential of +253 mV. Obeying the calculated results of the positive reaction potentials all compositions of the lithium silicides including $Li_{22}Si_5$ could be formed by the electrochemical reaction. The reaction potentials of Li_1Si_1, $Li_{12}Si_7$, Li_2Si_1, Li_7Si_2, $Li_{15}Si_4$ and $Li_{22}Si_5$ were +435, +422, +340, +284, +306 and +253 mV respectively with the continuous decreasing of the potentials except Li_7Si_2. $Li_{15}Si_4$ had higher potential than Li_7Si_2 to lead the thermodynamically favourable formation of $Li_{15}Si_4$ instead of Li_7Si_2. This speculation suggests that $Li_{15}Si_4$ ($Li_{3.75}Si$) was the favourable material by the electrochemical reaction to 0 V (Li/Li^+) at the room temperature. Weydanz *et al.*[19] reported that the good reversible range of the lithium insertion/desertion to silicon by electrochemical reaction was until $Li_{13}Si_4$ ($Li_{3.25}Si$). For $Li_{12}Si_7$, Li_7Si_3 and $Li_{13}Si_4$ phases the potential plateaus were 582, 520 and 428 mV (Li/Li^+), respectively.

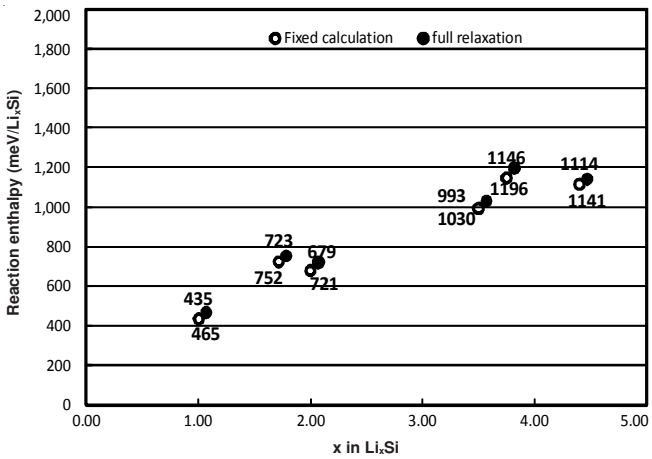

Fig. 1. Reaction enthalpies of the lithium silicide formation

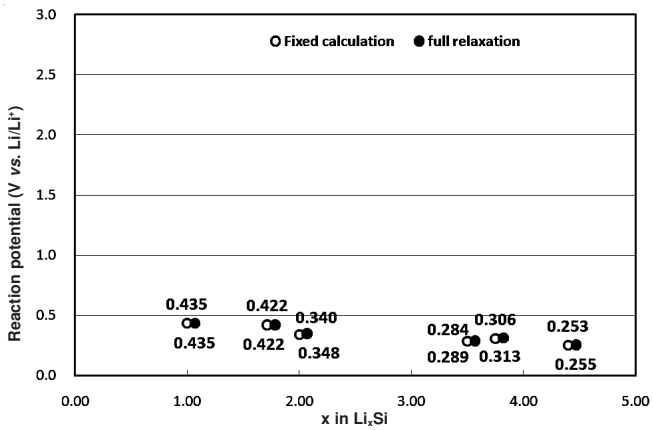

Fig. 2. Reaction potentials of the lithium silicide formation

By the load of current at the closed circuit the overpotential will not be zero. The overpotential at high current may lead lowering the reaction potential of lithium silicides below 0 V (Li/Li^+) during the lithium insertion. In which condition lithium metal may be deposited to the surface of lithium silicide particles. This phenomenon might be eminent for silicon to have low electronic conductivity and high volumetric change during lithiation.

Crystal structures of $Li_{22}Si_5$ ($Li_{4.4}Si$) and $Li_{15}Si_4$ ($Li_{3.75}Si$): $Li_{4.4}Si$ has the richest lithium content among the lithium silicide compounds and the space group of F-43 m (216) with the lattice parameters of a as 18.75 Å. The formula of the conventional unit cell is $Li_{352}Si_{80}$ (Fig. 3a). The primitive cell of $Li_{352}Si_{80}$ has 16 coordinates of lithium and 4 coordinates of silicon (Fig. 3b). Symmetrical multiplicity, Wyckoff symbol, coordination and occupancy of each atom were presented at Table-3. Wyckoff sequences were 8 kinds of a, b, c, d, e, f, g and h. The symmetrical multiplicities of each occupation site of lithium and silicon were summarized as shown in Table-4. Occupancy of each coordinates of lithium and silicon is one.

The inter-atomic distances of Li-Li, Li-Si and Si-Si of $Li_{22}Si_5$ were collected as shown in Table-5. The Li-Si distances were various to be 2.573 Å as the shortest case and 2.634 Å as a next case. The Li-Li distances were also varies to be 2.695 Å

as the shortest case and 2.706 Å, 2.717 Å, 2.728 Å as next cases. The next short Li-Li distances was 3.112 Å to be comparatively long distance compared to the shorter 4 cases. The short Li-Li distances of 2.695~2.728 Å in $Li_{22}Si_5$ were shorter than that of 2.978 Å in lithium metal. The shortest Si-Si distance of 4.360 Å in $Li_{22}Si_5$ corresponds 185 % of that of 2.351 Å in silicon. The Li-Si distances were shorter than the Li-Li distances as the results of the strong chemical bonding for Li-Si.

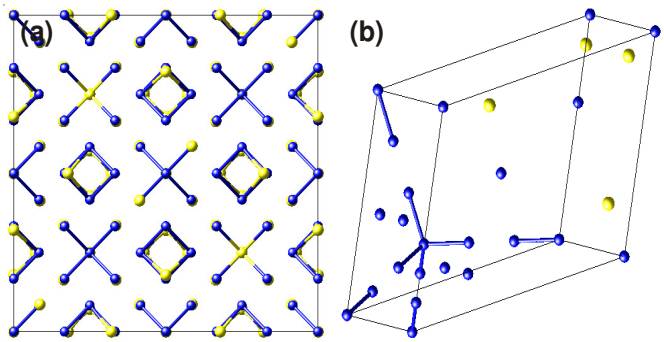

Fig. 3. (a) conventional cell and (b) primitive cell of $Li_{352}Si_{80}$($Li_{22}Si_5$; $Li_{4.4}Si$)

TABLE-3
INFORMATIONS OF THE CRYSTAL STRUCTURE OF $Li_{22}Si_5$

Position label	Symmetry multiplicity	Wyckoff symbol	Coordination X-axis	Coordination Y-axis	Coordination Z-axis	Occupancy
Si1	16	e	0.9141	0.9141	0.9141	1
Si2	16	e	0.6641	0.6641	0.6641	1
Si3	24	f	0.3211	0	0	1
Si4	24	g	0.0711	0.25	0.25	1
Li1	4	a	0	0	0	1
Li2	4	b	0.5	0.5	0.5	1
Li3	4	c	0.25	0.25	0.25	1
Li4	4	d	0.75	0.75	0.75	1
Li5	16	e	0.083	0.083	0.083	1
Li6	16	e	0.167	0.167	0.167	1
Li7	16	e	0.333	0.333	0.333	1
Li8	16	e	0.417	0.417	0.417	1
Li9	16	e	0.583	0.583	0.583	1
Li10	16	e	0.833	0.833	0.833	1
Li11	24	f	0.167	0	0	1
Li12	24	g	0.583	0.25	0.25	1
Li13	48	h	0.833	0.167	0	1
Li14	48	h	0.667	0.167	0	1
Li15	48	h	0.25	0.083	0.083	1
Li16	48	h	0.75	0.083	0.083	1
	(432)					

Therefore, the silicon as a host material for the lithium insertion experienced the large volume expansion/shrinkage during lithium insertion and desertion accompanying the mechanical stresses which is known as the cause of the cracking of particles and as the capacity fading during the prolonged cycling.

$Li_{15}Si_4$ ($Li_{3.75}Si$) which is known as the final product[20] of the electrochemical lithiation to silicon has the space group of I-43d (220, cubic) with the lattice parameters of a as 10.6852 Å and cell volume as 1220 $Å^3$. The formula of the conventional unit cell is $Li_{60}Si_{16}$ as shown at Fig. 4a. The primitive cell of $Li_{60}Si_{16}$ has 1 coordinate of silicon and 2 coordinates of lithium (Fig. 4b).

TABLE-4
WYCKOFF SYMBOLS AND WYCKOFF MULTIPLICITIES OF $Li_{22}Si_5$

Atom	Wyckoff symbol	Position label (symmetry multiplicity)	Wyckoff multiplicity
Si (80)	e	Si1(16), Si2(16)	32
	f	Si3(24)	24
	g	Si4(24)	24
Li(352)	a	Li1(4)	4
	b	Li2(4)	4
	c	Li3(4)	4
	d	Li4(4)	4
	e	Li5(16), Li6(16), Li7(16), Li8(16), Li9(16), Li10(16)	96
	f	Li11(24)	24
	g	Li12(24)	24
	h	Li13(48), Li14(48), Li15(48), Li16(48)	192

TABLE-5
INTER-ATOMIC LENGTHS OF Li-Li, Li-Si and Si-Si IN $Li_{22}Si_5$

Inter-atomic bond length (Å)		
Li-Si	Li-Li	Si-Si
2.573	2.695	4.360
2.573	2.706	4.556
2.634	2.717	4.744
2.687	2.728	4.963
2.842	3.112	–
2.889	3.131	–
3.078	–	–
3.139	–	–
3.168	–	–

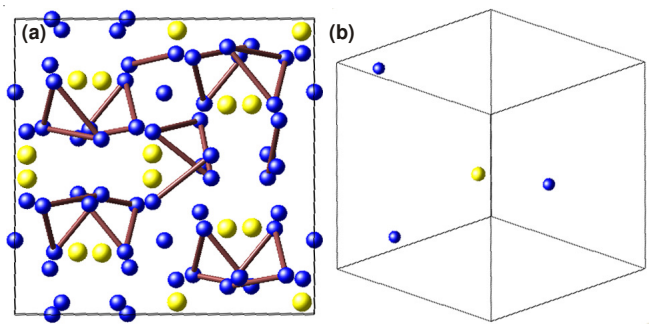

Fig. 4. (a) conventional cell and (b) primitive cell of $Li_{60}Si_{16}$($Li_{15}Si_4$; $Li_{3.75}Si$)

Symmetrical multiplicity, Wyckoff symbol, coordination and occupancy of each atoms were presented in Table-6. The inter-atomic distances of Li-Li, Li-Si and Si-Si of $Li_{15}Si_4$ were listed as shown in Table-7. The Li-Si distances varies to be 2.652 Å as the shortest case and 2.708 Å as a next case. The Li-Li distances were also varies to be 2.706 Å as the shortest case and 2.764 Å, 2.805 Å, 2.928 Å, 2.941 Å as next cases. The next short Li-Li distances was 3.224 Å to be comparatively long distance compared to the shorter 5 cases. The short Li-Li distances of 2.706-2.941 Å in $Li_{15}Si_4$ were shorter than that of 2.9780 Å in lithium metal. The shortest Si-Si distance of 4.548 Å in $Li_{15}Si_4$ corresponded 193 % of that of 2.351 Å in silicon. The distances of Li-Si and Li-Li were similar.

Comparing the structures of $Li_{15}Si_4$ ($Li_{4.4}Si$) and $Li_{22}Si_5$ ($Li_{3.75}Si$) the bond distances of Li-Si and Li-Li in $Li_{15}Si_4$ were shorter than that of in $Li_{22}Si_5$. Nevertheless the bond distances of Si-Si in $Li_{15}Si_4$ were also shorter than that of in $Li_{22}Si_5$. The

densities of $Li_{15}Si_4$ and $Li_{22}Si_5$ were similar as shown in Table-1 indicating similar average bond distances. Therefore the differences of the bond distances in $Li_{22}Si_5$ were larger than that in $Li_{15}Si_4$. The formation of the tightly bounded Li-Si and Li-Li bonding are relatively difficult compared to the loosely bounded Li-Si and Li-Li bonding. The difficulty of the formation of the tightly bounded Li-Si and Li-Li bonding in $Li_{22}Si_5$ might be a reason limiting the reversibility as a composition of $Li_{15}Si_4$.

TABLE-6
INFORMATION OF THE CRYSTAL STRUCTURE OF $Li_{15}Si_4$

Position label	Symmetry multiplicity	Wyckoff symbol	Coordination			Occupancy
			X-axe	Y-axe	Z-axe	
Si1	16	c	0.4588	0.4588	0.4588	1
Li1	12	a	0.375	0.0000	0.2500	1
Li2	48	e	0.118	0156	0.961	1

TABLE-7
INTER-ATOMIC LENGTHS OF Li-Li, Li-Si AND Si-Si IN $Li_{15}Si_4$

Inter-atomic bond length (Å)		
Li-Si	Li-Li	Si-Si
2.652	2.706	4.548
2.708	2.764	4.627
2.876	2.805	4.791
2.885	2.928	
4.197	2.941	
4.548	3.224	
4.614	3.299	
4.949	3.968	
4.952	4.456	

XRD pattern of known Li_xSi (x = 0 ~ 4.4): XRD pattern of $Li_{4.4}Si$, $Li_{3.75}Si$, $Li_{3.5}Si$, Li_2Si, $Li_{1.71}Si$, Li_1Si and Si were depicted as Fig. 5. Compositional mixture of Li_xSi' was produced by the equivalent accumulation of seven Li_xSi compositions as a comparative model.

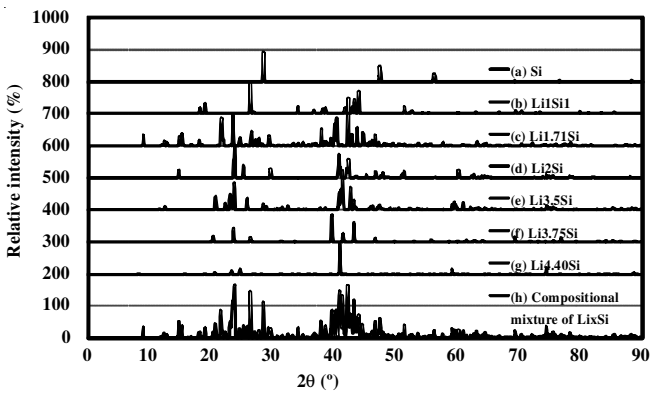

Fig. 5. Simulated XRD pattern of (a) Si, (b) LiSi, (c) $Li_{1.71}Si$, (d) Li_2Si, (e) $Li_{3.5}Si$, (f) $Li_{3.75}Si$, (g) $Li_{4.4}Si$ and (h) $Li_{4.4}Si$

$Li_{4.4}Si$, $Li_{3.75}Si$, Li_2Si and Li_1Si have clear XRD pattern compared to that of $Li_{3.5}Si$ and $Li_{1.71}Si$. XRD pattern of $Li_{3.5}Si$ and $Li_{1.71}Si$ are already complicated peak distribution as anticipated from crystal structural data. Silicon is not only so good electron conductor but also good lithium conducting host. Therefore during lithiation and delithiation silicon has multi-level lithiated silicides to show broad and complicated XRD pattern as shown at Fig. 5(h).

Conclusion

The first principles calculations using VASP and the structural studies of lithium silicides were carried out to get information of total energy, reaction energy and reaction potential. The reaction potentials of Li_1Si_1, $Li_{12}Si_7$, Li_2Si_1, Li_7Si_2, $Li_{15}Si_4$ and $Li_{22}Si_5$ were +435, +422, +340, +284, +306 and +253 mV, respectively, with continuous decreasing of potential except Li_7Si_2. $Li_{15}Si_4$ had higher potential than Li_7Si_2 to lead thermodynamically favourable formation of $Li_{15}Si_4$ instead of Li_7Si_2. The crystal structures of $Li_{22}Si_5$ and $Li_{15}Si_4$ were compared together. In $Li_{22}Si_5$ the short chemical bond distances were 2.695 Å as Li-Li bonding, 4.360 Å as Si-Si bonding and 2.573 Å as Li-Si bonding. The Li-Li distances of 2.695 Å, 2.706 Å, 2.717 Å and 2.728 Å in $Li_{22}Si_5$ were shorter than the Li-Li distance of 2.978 Å in lithium metal to be strong Li-Li bonding in $Li_{22}Si_5$. The bond distances of Li-Si and Li-Li in $Li_{22}Si_5$ were shorter than that in $Li_{15}Si_4$. Moreover the bond distances of Si-Si in $Li_{22}Si_5$ were also shorter than that in $Li_{15}Si_4$. The differences of bond distances in $Li_{22}Si_5$ were larger than that in $Li_{15}Si_4$. Inter-atomic bond lengths of lithium silicides were compared using crystal structures. Differences of Si-Si bond distances between 2.383 Å of $Li_{3.5}Si$ as relatively good reversible range and 4.548 Å of $Li_{3.75}Si$ as relatively low reversibility can be correlated to reversible lithiation range. Silicon is not only electron semi-conductor but also not good lithium ion conducting host.

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