

A Comparative Computational Study of Structures, Diffusion, and Dopant Interactions between Li and Na Insertion into Si

To cite this article: Oleksandr I. Malyi *et al* 2013 *Appl. Phys. Express* **6** 027301

View the [article online](#) for updates and enhancements.

You may also like

- [Electron tomography: a short overview with an emphasis on the absorption potential model for the forward problem](#)
D Fanelli and O Öktem
- [Photoelastic Constants of Strontium Titanate](#)
Koichi Aso
- [Comment on Paper: On Determining the Sign of Structure Factors of "Forbidden Reflections", by H. J. Juretschke and Z. Barnea, \(Physica Scripta: 33, 167 \(1986\)\)](#)
Roberto Colella

A Comparative Computational Study of Structures, Diffusion, and Dopant Interactions between Li and Na Insertion into Si

Oleksandr I. Malyi^{1*}, Teck L. Tan², and Sergei Manzhos^{1*}

¹Department of Mechanical Engineering, National University of Singapore, Singapore 117576, Singapore

²Institute of High Performance Computing, Agency for Science, Technology and Research, Singapore 138632, Singapore

E-mail: mpeom@nus.edu.sg; mpemanzh@nus.edu.sg

Received November 28, 2012; accepted December 20, 2012; published online January 16, 2013

We present a comparative computational study of sodiated vs lithiated bulk Si, including the effects of Li–Li and Na–Na interactions on dopant mobility. Both Na and Li prefer to act as interstitial defects located at the tetragonal sites of the Si matrix. The migration barrier between tetragonal sites is 0.54 eV larger for Na than for Li, which is expected to result in a drastically lower diffusion rate. The interdopant interactions reduce the barrier for Li and Na diffusion by 0.16 and 0.28 eV, respectively, providing ab initio evidence that finite ion concentrations may improve the battery charge/discharge rate. © 2013 The Japan Society of Applied Physics

Energy storage devices with high density and durability are needed to utilize fully the potential of renewable and clean sources of electricity (e.g., to enable a widespread use of electric vehicles). Lithium batteries deliver today the highest energy density over hundreds of cycles.¹⁾ The growing share of intermittent sources of electricity, such as solar or wind, means a growing need for bulk storage.²⁾ Here, the use of widely available materials, e.g., Na rather than Li, becomes the priority.³⁾ Na is abundant and inexpensive.³⁾ While much progress has been made in the rational design of electrode materials for Li batteries,^{4–6)} much less is known about Na batteries. While effective Na-reservoir cathode materials have been proposed,^{7–9)} much less progress has been made in designing high-capacity anodes for Na-ion batteries. This is, however, becoming an area of active research.¹⁰⁾ Specifically, for Na batteries, very little is known about the performance of promising electrode materials proposed for Li batteries. Proposed anodes for Li batteries include Si, Ge, and Sn, TiO₂ and titanates, and metal oxides (e.g., Fe₂O₃, NiO, and CuO), and they have shown rates or/and specific capacities that could exceed those of carbon anodes by an order of magnitude. Carbon has been shown to provide Na *intercalation* capacities comparable to Li.¹¹⁾ Yet the larger atomic radius of Na and differences in electronic structure are expected to result in a significantly different *alloying* and *conversion* dynamics vs Li.¹²⁾

Silicon is abundant and inexpensive. As an anode, Si offers an extremely high theoretical Li capacity of about 4200 mAh/g. The capacity fading issues that plagued the development of Si anodes are being effectively resolved.^{13,14)} Yet with Na, Si has been known to form bulk alloys of Na_xSi with $0 < x < 1$ only,¹⁵⁾ while in Li-based alloys (Li_xSi), x could go up to 4.4.¹⁶⁾ Hence, the theoretical Na capacity is expected to be lower. Recent experimental studies confirm this.¹⁰⁾ For bulk storage applications, capacity might not be critical as long as charging and discharging are done at a high rate.¹⁷⁾ Can Si be a good anode also for Na ion batteries? The answer thus depends on the dynamics of sodiation/desodiation. In particular, comparative studies of the ion diffusion barriers would guide the development of high-performance Na batteries. Recently, via molecular dynamics simulations using a simple pairwise potential energy surface, it was shown that concerted motion of Li ions in a cathode material has a significant effect on

diffusion, possibly leading to orders of magnitude changes in the diffusion coefficient.¹⁸⁾ Hence, in this work, we go beyond the conventional single-ion diffusion barrier ab initio calculations and take into account effects arising from dopant-dopant interactions.

We present a comparative computational study of Na vs Li doping (alloying) of Si. We compare the crystal and electronic structures, energetics, and diffusion of these two types of atoms in bulk Si. We also study how dopant-dopant interactions affect diffusion in both systems, shedding light on possible differences arising from cooperative effects.

All calculations are done using density functional theory (DFT) and the Perdew–Burke–Ernzerhof (PBE)¹⁹⁾ functional using the Quantum Espresso package.²⁰⁾ Ultrasoft pseudopotentials were used with configurations 1s²2s¹, 1s²2s²2p⁶3s¹, and 3s²3p² for Li, Na, and Si, respectively. Convergence tests were performed initially to determine the plane-wave kinetic energy and charge density cutoffs used for all subsequent calculations, 40 and 400 Ry, respectively. Atoms were relaxed until the internal forces are within 0.01 eV/Å. To predict the minimum energy pathways for Na and Li diffusion, the Nudged Elastic Band (NEB) method²¹⁾ was used (with nine images). To minimize interactions between the defects and their periodic images, a large supercell with 64 Si atoms was used. The volume of the simulation cell could be held fixed due to its large size. We verified that at the dopant concentrations considered here, the effects of supercell relaxation are negligible and no crystal phase instability is induced. The Brillouin-zone integrations were performed using Monkhorst–Pack grids: an 8 × 8 × 8 mesh for Si bulk structure (with an eight-atom cell), an 4 × 4 × 4 mesh for predictions of density of states (DOS), and a 2 × 2 × 2 mesh for all other calculations. The computed Si lattice constant is 5.46 Å, in good agreement with the experimental value (5.43 Å).²²⁾ To elucidate the effect of dopant-dopant interactions, migration barriers were also studied as a function of Na–Na (and Li–Li) distances.

We first predict the stability of interstitial Na and Li defects in Si by calculating their defect formation energies, $E_f = E_{\text{Si}-nX} - E_{\text{Si}} - nE_X$, with X representing Na or Li; $E_{\text{Si}-nX}$, E_{Si} , and E_X are the energies of Si–(Li)Na supercell, Si supercell, and a single Li(Na) atom within a 10.92 × 10.92 × 10.92 Å vacuum supercell, respectively. Interstitial defects were limited to hexagonal (H) and tetragonal (T) defects, as only T sites are likely to be occupied at the

Table I. Defect formation energies (in eV) of Li and Na defects in bulk Si.

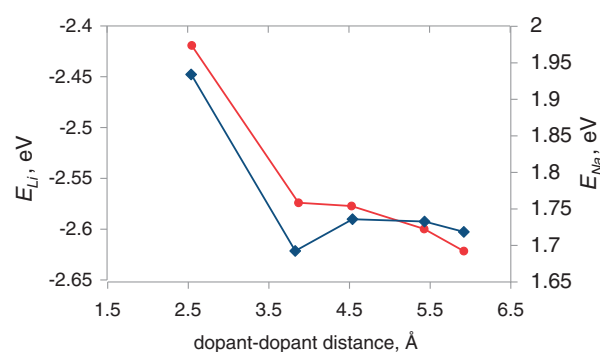
	Li	Na
T	-1.42	0.75
H	-0.81	1.88
S	1.17	2.66

Table II. Optimized distances (Å) between Na/Li and surrounding Si atoms. M-Si^{1st} and M-Si^{2nd} correspond to M-Si average distances (where M is Li or Na) for first and second coordination spheres, respectively. Na/Li are either in the tetragonal (T) or the hexagonal (H) sites.

	Relaxed		Unrelaxed
	Li/Si	Na/Si	Na(Li)/Si
(T) M-Si ^{1st}	2.44	2.50	2.35
(T) M-Si ^{2nd}	2.74	2.77	2.71
(H) M-Si ^{1st}	2.36	2.46	2.22
(H) M-Si ^{2nd}	3.49	3.44	3.53

concentrations considered here.²³⁾ We also consider the formation of a substitutional defect (S)—where Li or Na replaces Si on a lattice site. In the presence of Si vacancies, occupation of the vacant sites is thermodynamically favoured for both Li and Na, with defect formation energies of -0.61 and -2.10 eV for Na and Li, respectively. However, the high formation energy of Si vacancies (3.27 eV computed here) implies that the formation of Li or Na substitutional defects is much less likely than the formation of the interstitial defects. The analysis of the defect formation energies, listed in Table I, suggests that the formation of Li interstitial defects is thermodynamically favorable (the defect formation energy is negative). By contrast, the formation energies of all Na defects are positive. Na(Li) insertion leads to relaxations of the surrounding Si atoms. Because Na has a larger atomic radius than Li, Na insertion induces a larger relaxation of the surrounding Si atoms than Li, but the directions of atomic displacements are similar (see Table II). For instance, a Na(Li) dopant at the T site has six second nearest-neighbor and four nearest-neighbor Si atoms with Na(Li)-Si distances of 2.77 (2.74) and 2.50 (2.44) Å, respectively. The Na(Li)-Si distances before and after relaxation suggest that Na(Li) insertion causes the neighbouring Si atoms to displace outwards, away from the inserted Na(Li) atom. The larger displacement in the case of Na is largely responsible for the positive defect formation energy.

Although the insertion of Li/Na does not alter the overall DOS significantly, the Fermi level is shifted to the bottom of the conduction band. The insertion will therefore lead to improved electron conductance of the anode and possibly to a semiconductor-metal transition. This is caused by a charge transfer from the metal atoms to the host lattice. For instance, a Bader charge analysis shows the charges of +0.83|e| and +0.75|e| on Li and Na, respectively. For both systems, transferred electrons fill the antibonding sp^3 states of neighboring Si atoms weakening the corresponding Si-Si bonds. Assuming that the weakening of Si-Si interactions is the reason for Si amorphization,²⁴⁾ the larger extent of charge transfer into the antibonding orbitals of Si from Li implies that the chemistry of Li-Si interactions is more conducive to the amorphization of the Si matrix compared

**Fig. 1.** Formation energies of two defects as functions of Li-Li (red circles, left scale) and Na-Na (blue rhombs, right scale) distance in Si. The connecting lines are to guide the eye.

to Na even as Na insertion induces a larger strain due to its size.¹⁵⁾ Indeed, Na only forms Na₁Si at maximum sodiation (vs Li_{4.4}Si), and there is no destruction of the crystal structure like that happening at high Li concentrations, where Si undergoes amorphization.²⁴⁾

Recent investigations by Hwang and co-workers concluded that Li/Si interaction has a polar covalent nature.²⁵⁾ In our calculations, the charge density difference for the Si matrix with a single Na atom on the T site is similar to that for the Li/Si system, suggesting similar bonding mechanisms for the two systems. Nevertheless, the smaller amount of charge transferred from Na to Si indicates that the Na-Si bond has lower ionicity than the Li-Si bond.

As the defect concentration of Li/Na increases, the interaction between the inserted atoms becomes important and will in fact determine the performance of anodes under real operating conditions. At concentrations below 0.125, the Na/Li atoms prefer the T sites in the Si matrix.²³⁾ However, due to dopant-dopant interactions, the T sites are not equivalent. The predicted formation energy of two Li defects is a function of the Li-Li distance. Figure 1 suggests that Li atoms do not cluster. These results agree well with previous investigations.^{23,25)} The Na-Na interaction is complicated by the fact that the equilibrium distance between Na atoms in bulk Na (~3.7 Å) is close to the distance between T sites located in the second coordination sphere of each other. We obtained the lowest formation energy of two Na defects with the distance between Na atoms of 3.83 Å (see Fig. 1); this is not surprising as Na atomic configurations close to the bulk positions are energetically favoured. Nevertheless, since the above calculations are performed at 0 K and the difference in the formation energies between Na placed in the second and third coordination spheres is 0.05 eV, Na clustering is not expected to be significant.

An analysis of the migration pathways shows that both Li and Na atoms migrate between two T sites through the H configurations (Fig. 2). Despite similarities in the lowest energy and saddle point configurations, the diffusion rate of a single Na is expected to be much lower than that of Li; the computed migration barrier of Na is 0.54 eV higher than that for Li diffusion. Dopant-dopant interaction has a significant effect on diffusion of Li and Na atoms. When the distance between the dopants is ~2.6–3.9 Å, the dopant-dopant interaction modifies the migration pathway (see Fig. 3). The dopant still migrates through the H configurations;

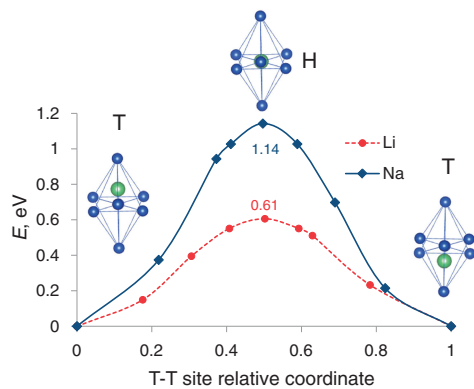


Fig. 2. Shape of the energy barriers of Na (blue rhombs) and Li (red circles) in bulk Si. The points correspond to the nine images used in the NEB calculations, the lines are to guide the eye. The configurations of the initial, final states (T), and the saddle points (H) are shown in the inserts.

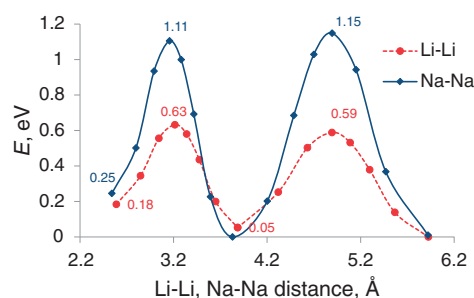


Fig. 3. Migration barriers of Li (red circles) and Na (blue rhombs) in bulk Si vs Li-Li and Na-Na distance in Si. The symbols correspond to the images in the NEB calculations, the lines are to guide the eye.

however, the lattice distortion (see Table II) caused by the presence of another dopant atom modifies the barrier, which is now a function of both the Na-Na (Li-Li) distance and direction. When the distance between dopant atoms is ~ 2.6 Å, an inserted atom has three equivalent pathways for migration. The barrier along these paths for Na (Li) is 0.28 (0.16) eV smaller than that for single-atom diffusion. At ~ 3.8 Å, the migrating atom has three (two of four migration pathways are equivalent to each other) different migration pathways available. Out of these three possible paths, the lowest Na(Li) energy pathway ends with a dopant-dopant distance of ~ 5.9 Å, similar to those for single atoms. The reduction of migration barriers is caused by the additional relaxation of surrounding Si atoms induced by the second dopant atom. In fact, even small lattice reconstruction can noticeably change the migration barrier.²⁶⁾ It is the destabilization of the Si matrix and of the initial state for migration caused by dopant-dopant interaction that causes an asymmetry for migration pathway (see Fig. 3) and ultimately reduces the migration barrier. A similar mechanism of improved mobility via higher Li concentration has been suggested for a cathode material.²⁷⁾ Due to the local nature of lattice distortions caused by dopant insertion, the effect of dopant-dopant interaction quickly diminishes with the distance between the dopants. Still, all neighbouring T sites will be filled at Li/Na concentrations as low as 0.125, and the effect reported here is expected to affect significantly the kinetics during the charging and discharging of the batteries.

In summary, based on a single-atom diffusion model, one would deduce that bulk Si is not a promising anode material for Na batteries in that both the capacity (uptake of 1 Na per Si atom vs up to $\text{Li}_{4.4}\text{Si}$) and the rate are expected to be much lower than in Li batteries. However, in the presence of a second dopant in the nearest T site, the diffusion barrier is reduced, and to a larger extent for Na than for Li: by 0.28 and 0.16 eV, respectively. This ab initio evidence that an increased dopant concentration can increase the rate of charge/discharge corroborates the recent findings in Ref. 18 for cathode materials. Therefore, it is important to account for the effect of dopant concentration on the diffusion rates of ions in the batteries.

Acknowledgments This work was supported by the Tier 1 AcRF Grant from the Ministry of Education of Singapore (R-265-000-430-133). We gratefully acknowledge the use of supercomputers in A-STAR Computational Resource Center (ACRC) and support from the Institute of High Performance Computing of A-STAR Singapore.

- 1) M. M. Thackeray, C. Wolverton, and E. D. Isaacs: *Energy Environ. Sci.* **5** (2012) 7854.
- 2) J. Rugolo and M. J. Aziz: *Energy Environ. Sci.* **5** (2012) 7151.
- 3) V. Palomares, P. Serras, I. Villaluenga, K. B. Hueso, J. Carretero-Gonzalez, and T. Rojo: *Energy Environ. Sci.* **5** (2012) 5884.
- 4) B. Scrosati and J. Garche: *J. Power Sources* **195** (2010) 2419.
- 5) H. Li, Z. X. Wang, L. Q. Chen, and X. J. Huang: *Adv. Mater.* **21** (2009) 4593.
- 6) S. C. Chung, P. Barpanda, S. Nishimura, Y. Yamada, and A. Yamada: *Phys. Chem. Chem. Phys.* **14** (2012) 8678.
- 7) B. L. Ellis, W. R. M. Makahnouk, Y. Makimura, K. Toghill, and L. F. Nazar: *Nat. Mater.* **6** (2007) 749.
- 8) H. Kim, D. J. Kim, D. H. Seo, M. S. Yeom, K. Kang, D. K. Kim, and Y. Jung: *Chem. Mater.* **24** (2012) 1205.
- 9) P. Barpanda, T. Ye, S. Nishimura, S. C. Chung, Y. Yamada, M. Okubo, H. Zhou, and A. Yamada: *Electrochem. Commun.* **24** (2012) 116.
- 10) S. Komaba, Y. Matsuura, T. Ishikawa, N. Yabuuchi, W. Murata, and S. Kuze: *Electrochem. Commun.* **21** (2012) 65.
- 11) S. Komaba, W. Murata, T. Ishikawa, N. Yabuuchi, T. Ozeki, T. Nakayama, A. Ogata, K. Gotoh, and K. Fujiwara: *Adv. Funct. Mater.* **21** (2011) 3859.
- 12) V. Milman, M. C. Payne, V. Heine, R. J. Needs, J. S. Lin, and M. H. Lee: *Phys. Rev. Lett.* **70** (1993) 2928.
- 13) M. Y. Ge, J. P. Rong, X. Fang, and C. W. Zhou: *Nano Lett.* **12** (2012) 2318.
- 14) N. Liu, H. Wu, M. T. McDowell, Y. Yao, C. M. Wang, and Y. Cui: *Nano Lett.* **12** (2012) 3315.
- 15) V. L. Chevrier and G. Ceder: *J. Electrochem. Soc.* **158** (2011) A1011.
- 16) T. T. Tran and M. N. Obrovac: *J. Electrochem. Soc.* **158** (2011) A1411.
- 17) E. Barbour, I. A. G. Wilson, I. G. Bryden, P. G. McGregor, P. A. Mulheran, and P. J. Hall: *Energy Environ. Sci.* **5** (2012) 5425.
- 18) M. Salanne, D. Marrocchelli, and G. W. Watson: *J. Phys. Chem. C* **116** (2012) 18618.
- 19) J. P. Perdew, K. Burke, and M. Ernzerhof: *Phys. Rev. Lett.* **77** (1996) 3865.
- 20) P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougousis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolò, G. Sciauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch: *J. Phys.: Condens. Matter* **21** (2009) 395502.
- 21) G. Henkelman, B. P. Uberuaga, and H. Jonsson: *J. Chem. Phys.* **113** (2000) 9901.
- 22) G. Celotti, D. Nobili, and P. Ostoja: *J. Mater. Sci.* **9** (1974) 821.
- 23) W. H. Wan, Q. F. Zhang, Y. Cui, and E. G. Wang: *J. Phys.: Condens. Matter* **22** (2010) 415501.
- 24) K. Zhao, G. A. Tritsarlis, M. Pharr, W. L. Wang, O. Okeke, Z. Suo, J. J. Vlassak, and E. Kaxiras: *Nano Lett.* **12** (2012) 4397.
- 25) H. Kim, K. E. Kweon, C.-Y. Chou, J. G. Ekerdt, and G. S. Hwang: *J. Phys. Chem. C* **114** (2010) 17942.
- 26) M. Nakayama, M. Kaneko, and M. Wakihara: *Phys. Chem. Chem. Phys.* **14** (2012) 13963.
- 27) M. P. O'Callaghan and E. J. Cussen: *Chem. Commun.* (2007) 2048.