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Aluminum doping improves the energetics of lithium, sodium, and magnesium storage in silicon: A first-principles study

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HIGHLIGHTS

- Al doping of Si improves insertion energies of Li, Na, Mg.
- Binding energy (E_b) of Li in Al–Si stronger than Li cohesive energy (E_{coh}).
- E_b of Mg in Al–Si similar to Mg cohesive energy.
- E_b of Na in Al–Si favors insertion vs vacuum state but weaker than Na E_{coh}.
- Barriers for diffusion of Li, Na, Mg similar in Al-doped and pure Si.

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ABSTRACT

While Si is an effective negative electrode material for Li-ion batteries, crystalline Si has been shown to be unsuitable for Na and Mg storage due, in particular, to insufficient binding strength. It has recently been reported that Si nanowires could be synthesized with high-concentration (several atomic %) and dispersed Al doping. Here we show based on density functional theory calculations that Al doping significantly improves the energetics for Na and Mg insertion, specifically, making it thermodynamically favored versus vacuum reference states. For high Al concentrations, the energy of Mg in Al-doped Si approaches the cohesive energy of Mg. However, the migration barriers for the diffusion of Li (0.57–0.70 eV), Na (1.07–1.19 eV) and Mg (0.97–1.18 eV) in Al-doped Si are found to remain about as high as in pure Si, likely preventing effective electrochemical sodiation and magnesiation.

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1. Introduction

The progress towards renewable but intermittent sources of electricity as well as the development of electrical vehicles calls for efficient energy storage systems [1]. Electrochemical batteries which offer relatively high energy densities have been attracting renewed interest [2]. Among them, the Li-ion batteries are already of widespread use, especially for portable electronics. However, because of safety issues and the limited lithium resources, alternatives are needed [3]. Na and Mg, which are abundant, cheap, and benign, have recently attracted much scientific attention as candidates for post-Li storage systems [4–6]. Among the remaining issues for their commercialization, a suitable negative electrode material, enabling the insertion/de-insertion of the metal ions at a reasonable rate, is still highly demanded. Si, which provides relatively high theoretical specific capacities for Na (~950 mAh g^{-1}) and Mg (~3820 mAh g^{-1}) storage and which was already shown to be practical for Li (theoretical capacity of ~4200 mAh g^{-1} and demonstrated capacities of >1000 mAh g^{-1} for thousands of cycles [7]), was an obvious candidate. But, as other good negative electrode materials for Li (e.g. graphite [8]), diamond Si was found to not work for Na and Mg [9–11]. First-principles calculations have shown that while the final states of charge (NaSi and Mg_2Si) have negative heats of formation [12–15], the insertion of Na and Mg in pure Si is thermodynamically unfavored (for small Na and Mg concentrations) [16–19].

DFT (density functional theory) calculations have also shown that modification of the ideal pure crystalline Si, especially amorphization [17,20], could make Si suitable for the insertion of Na and Mg. Specifically, Al is a promising dopant to improve the performance of battery electrodes. For example, Al–C nanoclustered [21] and Al-doped $Li_4Ti_5O_{12}$ [22] negative electrodes have

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been shown to exhibit significantly better cyclability and capacity compared to pure host materials. Similarly, experiments on Al-doped Si [23,24] and eutectic Al–Si (~88:12 wt%) [25] have also been reported, and have shown enhanced cyclability and capacity over pure Si and Al negative electrodes, respectively.

Moutanabbir et al. have reported that Al concentrations which exceed by orders of magnitude the equilibrium solid solubility, with average Al concentrations across samples as high as 4.3 at. %, are achievable by growing Si nanowires on a catalyst [26]. In this work, we show that doping Si with Al at concentrations of this magnitude improves significantly the energetics for Na and Mg (as well as Li) storage in Si.

We present a density functional theory study of the effects of Al doping of Si on the thermodynamics and kinetics of Li, Na, and Mg insertion. We find a significant improvement of the storage energetics and provide a mechanistic explanation of its mechanism. Our findings therefore show a possible way of making Si suitable not only for Li but also for Na and Mg storage.

2. Methods

A 64 atom cell was used to model Si and Al-doped Si. The electronic structure was computed using DFT [27] and the SIESTA code [28]. The PBE exchange-correlation functional [29] and the DZP basis set (double-ξ polarized orbitals) were used. A cutoff of 100 Ry was used for the Fourier expansion of the density. Core electrons were modeled with Trouiller–Martins pseudopotentials [30]. The basis sets of Si, Al, Li, Na and Mg were tuned to reproduce their cohesive energies (see Supporting information). The calculated and (vs.) the experimental values of E_{coh} (adjusted for the effect of zero-point motion, ZPE, where for Li, Na and Mg, the ZPE corrections are computed to be 0.034 eV, 0.016 eV and 0.029 eV, respectively) give for Si: 4.66 vs. 4.68 eV by using a ZPE correction of 0.06 eV [31,32], Al: 3.51 vs. 3.43 eV [33], Li: 1.67 vs. 1.66 [34], Na: 1.14 vs. 1.13 eV [34], Mg: 1.55 vs. 1.54 eV [34]). Geometries were optimized until forces on all atoms were below 0.01 eV Å^{-1} and stresses below 0.1 GPa. Brillouin-zone integrations were done with a 3 × 3 × 3 k-point Monkhorst–Pack mesh [35]. Unrestricted spin-polarized calculations were performed, but spin polarization was found to be insignificant in bulk.

The insertion energetics of Al in Si and of Li/Na/Mg in pure and Al-doped Si were analyzed by computing the defect formation energies associated with the following reactions:

$$m\mathrm{Si} + n_{\mathrm{Al}}\mathrm{Al} \rightarrow \mathrm{Si}_m\mathrm{Al}_{n_{\mathrm{Al}}}$$

$$X + n_M M \rightarrow X M_{n_M}$$

where mSi designates m Si atoms in an ideal Si cell, n_{Al} is the number of Al atoms inserted, $\mathrm{Si}_m\mathrm{Al}_{n_{\mathrm{Al}}}$ represents the Al-doped Si structure, X designates the host structure for Li/Na/Mg insertion which can be pure or Al-doped Si (i.e. $X = \mathrm{Si}_m\mathrm{Al}_{n_{\mathrm{Al}}}$), n_M is the number of Li/Na/Mg atoms inserted, M represents Li/Na/Mg, and XM_{n_M} the Li/Na/Mg-doped (and possibly Al-doped) Si structure.

To compute the defect formation energies (either for Li/Na/Mg insertion or for Al doping), one should subtract from the total energy the energy of the ideal supercell and the energy of the dopant atom. However, the energy of reference for the dopant can be the energy of one dopant atom either in vacuum (modeled as a single atom in a supercell of size ~11 × 11 × 11 Å^3) or in bulk metal (modeled as the *ccp* structure for Al, the *bcc* structure for Li and Na, and the *hcp* structure for Mg). The defect formation energies computed versus vacuum or bulk reference states have different meaning. A negative (positive) defect formation energy versus vacuum indicates that the insertion of a single dopant (considered without interaction with its surroundings) is favored (unfavored) while negative (positive) defect formation energy versus bulk indicates that the insertion of the dopant is favored (unfavored) versus segregation of the dopant atoms. The defect formation energies (E_f) are computed as follows:

$$E_f = \left(E_{m\mathrm{Si}/n\mathrm{Al}} - mE_{\mathrm{Si}} - n_{\mathrm{Al}}E_{\mathrm{Al}}\right)/n_{\mathrm{Al}}$$

for Al doping and

$$E_f = \left(E_{X/nM} - E_X - n_M E_M\right)/n_M$$

for Li, Na, and Mg insertion, where $E_{m\mathrm{Si}/n\mathrm{Al}}$ is the total energy of the simulation cell consisting of m Si atoms and n_{Al} Al atoms; E_{Si} is the energy of a Si atom in pure Si (i.e. Si bulk); E_{Al} is the energy of an Al atom in vacuum (Al bulk) for a vacuum (bulk) reference state; $E_{x/nM}$ is the total energy of the simulation cell with n_M metal atoms M (M = Li/Na/Mg) inserted; E_x is the energy of the cell X without alkali metal atoms (X designating Si_{64}, $\mathrm{Al}_1\mathrm{Si}_{63}$, $\mathrm{Al}_2\mathrm{Si}_{62}$, $\mathrm{A}_4\mathrm{Si}_{60}$ or $\mathrm{Al}_8\mathrm{Si}_{56}$); E_M is the energy of a metal atom M in vacuum or bulk, giving the defect formation energies versus vacuum (V) or bulk (B) reference states, respectively.

Diffusion barriers were computed for one Li, Na, and Mg atom in the supercell by constrained optimization, in which the dopant atom's projection on the line connecting the initial and the final sites of the diffusion step was fixed and stepped. A step of 0.3 Bohr (~0.16 Å) was used, which corresponds to 15 images per diffusion path. The atoms farther than 5 Å from the initial and final sites were fixed in the diffusion direction to avoid translation of all atoms. The cell was fixed. All other degrees of freedom were relaxed.

3. Results and discussion

We first study the insertion of Al in diamond Si and the three following insertion sites are considered: the substitutional (S), and the tetrahedral (T) and hexagonal (H) interstitial sites (see Fig. 1(a)–(c), respectively). For one Al dopant in a 64 Si atom cell (corresponding to an Al concentration of ~1.6 at. %), the corresponding defect formation energies are given in Table 1. For all insertion sites, the defect formation energies are found to be positive versus the bulk reference state, i.e. relative to the cohesive energy of Al. This means that at this concentration, the insertion of Al in Si is unfavored compared to Al clustering, which is expected given the lower value of solid solubility of Al in Si [36]. Among the three sites considered, the substitutional site is found the most preferred by more than 2 eV. At a concentration of ~1.6 at. % the S site is therefore predominant and Al atoms are mainly located at Si sites. The insertion of 2, 4 and 8 Al dopants, corresponding to a concentration of ~3.1, ~6.2 and ~12.5 at. %, respectively, is also considered, and the Al atoms are inserted by maximizing the inter-dopant distances (see Fig. 1(d)). The ~3.1 at. % Al concentration is practically achievable, as it is of the same order of magnitude as the one observed in the Al-doped nanowires synthesized by Moutanabbir et al. (~4.3 at. %) [26] while the ~6.2 and ~12.5 at. % Al concentrations help extract a general trend of the effects of Al doping on Li/Na/Mg insertion in Si. The well-separated Al configurations are chosen because in Refs. [26], the Al impurities were found to be homogeneously distributed in the nanowire and to not form precipitates or clusters. The computed defect formation energies (Table 2) show that the tetrahedral interstitial site starts (slightly) to be favored only when 8 Al dopants are inserted, but that the substitutional site remains preferred up to a concentration of 4 atoms per simulation cell, which includes the concentration reported by Moutanabbir et al. (~4.3 at. %). We considered

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