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Nicholas A. Wagner,^[a] Rahul Raghavan,^[a] Ran Zhao,^[b] Qun Wei,^[c, d] Xihong Peng,^[c] and Candace K. Chan^{*[a]}

Due to their high charge-storage capacity (i.e. > 3000 mA h g⁻¹), there has been much research activity in the development of silicon-based anodes for high-energy-density lithium-ion batteries. In recent years, there has been immense interest in understanding the electrochemical,^[1,2] structural,^[3-5] and mechanical properties^[6-8] of both diamond cubic (c-Si) and amorphous silicon (a-Si) under reaction with lithium. Silicon with a clathrate or cage-like structure has been recently investigated as a potential anode, with both theoretical^[9] and experimental verification by Langer et al.^[10] that lithiation is feasible. Since prior studies on silicon clathrates have focused predominately on their superconducting^[11-18] and thermoelectric^[19-24] properties, this is a potentially new and exciting application for this class of materials. Type-I clathrates of the form M₈Si₄₆, where M is a guest atom intercalated into the structure, are made of two pentagonal dodecahedra (Si₂₀) cages and six tetrakaidecahedra (Si $_{\rm 24}$ cages) per unit cell and crystallize in the $Pm\bar{3}n$ space group (Figure 1 a). Type-II clathrates^[25] of the form $M_x Si_{136}$ (0 < x < 24), are made of sixteen pentagonal dodecahedra plus eight hexakaidecahedra (Si₂₈ cages) per unit cell and crystallize in the $Fd\bar{3}m$ space group (Figure 1 b). Detailed X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) studies of the lithiation process into practically guest free type-II clathrate $Na_{1.3}Si_{136}^{[10]}$ showed that the clathrate structure could be maintained until insertion of 24 Li per formula unit. Upon insertion of more Li, the clathrate structure became amorphous and eventually transformed into crystalline Li15Si4 (c-Li₁₅Si₄), much like is observed during lithiation of c-Si. However, no delithiation behavior was shown in this previous work, and no extended cycling data were shown. To this end, we have conducted an extended electrochemical, structural, and theoretical study of sodium-filled silicon clathrate to better understand its properties as an anode for lithium-ion batteries.

Sodium-filled silicon clathrate was synthesized from the decomposition of Zintl phase NaSi.^[26-28] XRD patterns of the as-

[a]	N. A. Wagner, R. Raghavan, Prof. C. K. Chan Materials Science and Engineering School for Engineering of Matter, Transport and Energy Arizona State University, Tempe, AZ 85287 (USA) E-mail: candace.chan@asu.edu
[b]	R. Zhao Department of Chemistry and Biochemistry Arizona State University, Tempe, AZ 85287 (USA)
[c]	Dr. Q. Wei, Prof. X. Peng School of Letters and Sciences Arizona State University, Mesa, AZ 85212 (USA)
[d]	Dr. Q. Wei School of Science, Xidian University, Xi' an, 710071 (PR China)
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made samples showed that the product was a mixture of both type-I and type-II clathrate, as well as c-Si. The presence of c-Si in the product may be due to evaporation loss of Na during the synthesis, which has been counteracted through addition of excess Na in other reports.^[28,29] Although Horie et al.^[29] observed pure-phase type-II clathrate at decomposition temperatures below 440 °C, we obtained a mixture of products using similar conditions. Figure 1 c shows the powder XRD pattern of the as-made product along with reference patterns for Na₈Si₄₆^[26] and Na₂₄Si₁₃₆^[30] from the literature. After treatment with NaOH, the c-Si peaks were absent from the XRD pattern (Figure S1, Supporting Information), leaving only the peaks from the clathrates. The phase fraction, as determined by Rietveld analysis, showed that the powder was composed of about 80% type-II clathrate and 20% type-I clathrate.

Scanning electron microscopy (SEM) imaging revealed that the particles were approximately 1–5 μ m in diameter (Figure S2a). Energy-dispersive X-ray spectroscopy (EDS) analysis showed an average composition of 14.4 at% Na and 85.6 at% Si, with a standard deviation of 3.2%. This corresponds to a Na:Si ratio of 0.169, which is in close agreement with the ratios in Na₈Si₄₆ and Na₂₄Si₁₃₆, suggesting that the Na sites in the clathrates were almost fully occupied. The powders were mixed into slurries with carbon black and polyvinylidene difluoride (PVDF) binder, then coated onto Cu foil. SEM images of the coated films showed that the carbon black formed a conducting network around the clathrate particles (Figure S2b).

Potentiodynamic cycling of the clathrate films was performed to understand the basic electrochemical processes occurring in the electrodes during lithium insertion (charge) and de-insertion (discharge) in half-cells with Li metal counter electrodes. The cycling results using a 25 µA mg⁻¹ threshold current are shown in Figure 2a. The first charge was characterized by a flat plateau at around 0.120 V (vs. Li/Li⁺), similar to the plateau observed during lithiation of c-Si.^[1] However, since the XRD patterns showed that c-Si was etched away, and no features consistent with lithiation of a-Si were observed, these electrochemical features are likely from the reaction of Li with the clathrates. The discharge curve showed a flat plateau at 0.425 V and had a similar shape to that observed in the delithiation of c-Li₁₅Si₄,^[1] although at a slightly lower voltage. The first charge capacity was 2431 mAhg $^{-1}$, and the discharge capacity was 1213 mAhg⁻¹, resulting in a Coulombic efficiency (CE) of about 50% (Figure 2b). A prior study on lithiation of Na_{1.3}Si₁₃₆ by Langer et al.^[10] did not report any discharge curves, and the lithiation capacities presented in that work were only 1300–1600 mA h g^{-1} . Our results show that discharge of lithiated clathrate is possible, although subsequent cycling revealed drastic decreases in capacity to about 171 mAhg⁻¹ at the fifth cycle. The charge profiles also became sloped starting with the second cycle, although the discharge profiles remained flat. The low CE, even at the fifth cycle (only about 80%), could be due to pulverization from phase transformations or volume changes, since similar CE are observed in micron-sized Si particles^[31] whereas nanostructured Si anodes,^[32, 33] which do not pulverize, show much higher CE.



Figure 2. a) Voltage versus capacity determined by potentiodynamic cycling with a 25 μ Amg⁻¹ threshold current. b) Capacity and Coulombic efficiency.

On the other hand, such low CE could also be due to poorly passivated surfaces and solid electrolyte interphase (SEI) formation, which is not yet understood for silicon bonded in the clathrate structure.

To better understand the lithiation and delithiation features of Na-filled silicon clathrate, differential charge (dQ) versus potential plots were obtained for this system and compared to the results obtained for c-Si. Figures 3a and 3b show the first and second cycles, respectively, for an electrode cycled using a 25 μ A mg⁻¹ threshold current. Due to the differences in the observed capacities, the values of the dQ were scaled to clearly distinguish the differences between the two materials. The absolute, un-scaled plots for the clathrates are shown in Figure S3. Overall, the dQ plots of the clathrates look very similar to those for c-Si. Lithiation of c-Si is characterized by a transformation to amorphous LixSi in a two-phase reaction in the first charge, followed by conversion to c-Li₁₅Si₄ at voltages below 50 mV (vs. Li/Li⁺).^[1] Delithiation of c-Li₁₅Si₄ occurs as a twophase reaction to form amorphous Si (a-Si) at the end of the discharge. These two-phase reactions are observed as peaks in the dQ versus potential plots.

The similar shape of the dQ plots for the clathrates suggests a similar reaction mechanism. Prior XRD and NMR analyses

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Figure 3. Differential charge plots of clathrate compared to c-Si and a-Si using a 25 μ Amg⁻¹ (a,b) and a 5 μ Amg⁻¹ (c,d) threshold current. (a) and (c) are the first cycle and (b) and (d) are the second cycle. The values of the differential charge were scaled to facilitate comparison.

showing an amorphization and formation of c-Li₁₅Si₄ upon lithiation of Na_{1.3}Si₁₃₆^[10] are consistent with these observations. Another key difference between the clathrate dQ plots and those for delithiation of c-Li₁₅Si₄ is that the discharge was observed over a broader range of potentials for the clathrate. There is also a notable peak at 0.3 V (vs. Li/Li⁺) in the discharge, which is not seen in delithiation of c-Li₁₅Si₄. The second charge of the clathrate (Figure 3 b) showed two broad peaks, which are similar to those seen in lithiation of a-Si, although at slightly lower potentials. When performing cycling with a 5 μ Amg⁻¹ threshold current (Figure 3 c–Figure 3 d), the voltage hysteresis between the charge and discharge decreased from 0.28 V when using 25 μ Amg⁻¹ to 0.25 V, but the other features remained largely the same.

In the results reported by Langer,^[10] a plateau at 0.3 V (vs. Li/ Li⁺) was observed in the initial stage of the charge, with a capacity of about 100 mA hg⁻¹. Since in their work the starting clathrate material was Na_{1.3}Si₁₃₄, this feature was attributed to the insertion of about 24 Li per unit cell of type-II clathrate to form Li₂₄Si₁₃₆. Insertion of more Li was found to result in a lower reaction potential of about 0.25 V, which corresponded to the amorphization of the material in a similar process as what occurs in c-Si. However, the charge curve was notably sloped, suggesting a single-phase reaction mechanism. We did not observe this 0.3 V lithiation feature in our case and our lithiation potentials were much lower and not sloped in the first charge. This can possibly be explained by the fact that our type-II clathrate has a higher occupancy by Na, which can decrease the observed voltage and change the reaction mechanism in the first charge to a two-phase reaction. We also have a larger fraction of type-I clathrate in our sample, but currently it is unclear what role the Na₈Si₄₆ clathrate plays in the observed electrochemical characteristics.

To confirm the amorphization process, ex situ XRD measurements were performed on the cells after galvanostatic cycling using a current of $25 \,\mu\text{Amg}^{-1}$. The peaks attributed to the unlithiated clathrate (Figure 4a) were observed to decrease in intensity after lithiation to about 1300 mAhg⁻¹ (Figure 4b), confirming the amorphization process. This capacity corresponds to about 184 Li inserted into the clathrate (or ~1.6 Li/Si), assuming a composite anode of type-I and type-II clathrate with a total molecular weight of approximately 3790 g mol⁻¹, based

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Figure 4. XRD patterns of clathrate films on Cu: a) prior to cycling, b) after lithiation, and c) after lithiation and delithiation. The insets in (b) and (c) show the corresponding galvanostatic cycling curves.

on the phase fraction obtained from the Rietveld analysis. Several reflections corresponding to $c-Li_{15}Si_4$ were also observed (Figure 4 b).

For a sample that was lithiated to 1770 mAhg^{-1} and then partially discharged, the c-Li₁₅Si₄ peaks disappeared and no new reflections were observed (Figure 4 c), indicating that the material transformed into an amorphous phase during delithiation of c-Li₁₅Si₄. These results are consistent with the observed electrochemical characteristics. SEM imaging of the samples after ten cycles showed that the clathrate particles were cov-

ered with an SEI layer, but no obvious pulverization or cracks were observed in the particles (Figure S2c-d).

To better understand the amorphization process, first-principles density functional theory (DFT) was applied to calculate the lattice constant and energy of formation for several structures using the Vienna Ab initio Simulations Package (VASP) code.^[34,35] The results for Si₁₃₆, Na₂₄Si₁₃₆, Na₈Si₄₆, Li₂₄Si₁₃₆, Li₁₆Na₂₄Si₁₃₆, and Li₁₅Si₄ are shown in Table 1. Although the cal-

Table 1. Calculated properties, determined by DFT.			
Compound	Lattice constant [Å]	Formation energy [eV per atom]	
Si ₁₃₆	14.74	0.052	
Na ₈ Si ₄₆	10.24	0.002	
Na ₂₄ Si ₁₃₆	14.78	-0.005	
Li ₂₄ Si ₁₃₆	14.68	0.030	
Li ₁₆ Na ₂₄ Si ₁₃₆	14.95	0.012	
Li ₁₆ Na ₂₄ Si ₁₃₆ '	14.90	-0.002	
Li ₁₆ Na ₂₄ Si ₁₃₆ "	14.90	-0.003	
Li ₁₅ Si ₄	10.54	-0.239	

culated formation energies for Na $_8Si_{46}$ and empty Si₁₃₆ were slightly positive, both structures have been experimentally synthesized. Note that the calculated formation energies are based on the total energies predicted by DFT at the ground state, that is, 0 K, so the calculated values are reasonable. The formation energy for fully filled Na₂₄Si₁₃₆ was -0.005 eV per atom, suggesting it is the more stable structure compared to empty Si₁₃₆.

To model lithiated clathrate, the type-II structure was considered since our synthesized powders were predominately this phase. Type-II clathrate crystallizes in the $Fd\bar{3}m$ space group, with Si occupying the 8a, 32e, and 96 g sites and Na in the 8b and 16c sites, as described with Wyckoff symmetry notation. Replacing the Na with Li to form Li₂₄Si₁₃₆ resulted in a formation energy of 0.030 eV per atom, which is higher than that for Na₂₄Si₁₃₆. This is likely due to the ability of Na to better stabilize the clathrate structure due to its larger size. Despite this slightly positive formation energy, electrochemical Li insertion into the empty Na sites of type-II clathrate has been confirmed by NMR,^[10] as previously described.

Lithiation of Na-filled type-II clathrate was first modeled by placing Li into the 16d sites, which are typically unoccupied in type-II clathrate, to form Li₁₆Na₂₄Si₁₃₆ (Figure 5 a). The Si₂₈ polyhedra in type-II clathrate are composed of 12 pentagonal and four hexagonal faces. Occupancy of the 16d sites by Li places them on the faces of the hexagons, equidistant from each Si, such that they are bisected and shared by neighboring Si₂₈ clusters (Figure 5 b). In this configuration, the Li species are located in channels along the <110 > directions parallel to the rows of Na ions occupying the 16c sites. The Li–Si and Na–Li bond lengths were 2.454 and 3.237 Å, respectively, in this structure. The formation energy for this structure was 0.012 eV per atom, lower than that for Li₂₄Si₁₃₆. These results suggest that lithiation into Na-filled clathrate is not less favorable than lithiation into empty clathrate.

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Figure 5. Structures of Li₁₆Na₂₄Si₁₃₆ calculated by DFT: a,b) Li₁₆Na₂₄Si₁₃₆ with Li in the 16d sites. b) Unit cell for Li₁₆Na₂₄Si₁₃₆ showing the arrangement of Li atoms on the hexagon faces separating the Si₂₈ cages. Several cages were deleted for clarity. c) Unit cell for Li₁₆Na₂₄Si₁₃₆' and d) Li₁₆Na₂₄Si₁₃₆'' showing all eight Si₂₈ cages. The Si₂₀ cages were deleted for clarity. The Na atoms are labeled and the Na–Li bonds are indicated by red dashed lines.

Next, the positions of the Li species were displaced slightly from the 16d sites so that they were no longer sitting in the hexagonal faces, but rather inside the Si polyhedra. In the first structure, which we call $Li_{16}Na_{24}Si_{136}$, two Li atoms were placed inside the Si₂₈ cages so that they shared the interstitial space with the Na atoms (Figure 5 c). The second structure, which we call $\text{Li}_{16}\text{Na}_{24}\text{Si}_{136}{}^{\prime\prime}\text{,}$ had the Li atoms distributed amongst the eight Si_{28} cages of the unit cell in the following manner: two cages had one Li, two cages had three Li, and the remaining four cages had two Li sharing the cage volume with the Na (Figure 5 d). The calculated Na atomic coordinates for both structures showed that the Na positions were shifted away from the centers of the cages to accommodate the Li atoms. Both structures had negative formation energies (Table 1) and shorter bond lengths than in the original Li₁₆Na₂₄Si₁₃₆ structure, with the shortest bond length of 2.837 Å calculated in Li₁₆Na₂₄Si₁₃₆" (Table S1).

Importantly, these results suggest that it is energetically feasibly for more than one guest atom to occupy the space inside the Si₂₈ cage of type-II clathrate while maintaining the overall Si clathrate framework structure. The lattice constants for all of the lithiated type-II clathrate structures increased very slightly compared to the empty Si₁₃₆. This suggests that at the initial stages of Li insertion, the clathrate structure may be maintained. However, with more Li insertion, the experimental results show that transformation into an amorphous lithium and sodium containing silicide is more favorable. The formation energy of c-Li₁₅Si₄ was calculated to be -0.239 eV per atom. The very low energy for this phase can explain why lithiation of both empty^[10] and Na-filled (this work) clathrate eventually result in transformation to c-Li₁₅Si₄.

In summary, electrochemical and XRD analyses of lithium insertion into a mixture of Na-filled type-I and type-II clathrates showed a similar reaction mechanism in these materials as is found in diamond cubic silicon. Upon electrochemical lithiation, the clathrates became amorphous and transformed into c-Li₁₅Si₄ at low potentials, then remained an amorphous silicide after delithiation. The low Coulombic efficiencies and poor capacity retention observed are likely due to pulverization from the phase transformation and volume changes during lithiation of the amorphous silicide, which is also typically observed in micron-sized Si particles. However, low CE from poorly passivating SEI layers cannot be ruled out, and this will be investigated further in future studies. DFT was applied to calculate the lattice constants and formation energies for various type-II clathrate structures. The results showed that 16 Li atoms could be inserted per unit cell with very little increase in lattice constant. The DFT-predicted structures for Li₁₆Na₂₄Si₁₃₆ containing multiple-guest atoms inside the larger Si₂₈ cages shows that these configurations are energetically favorable and suggests that such lithiation processes can occur without significant changes in lattice constant or clathrate structure. Future work will focus on understanding the phase transformations in the clathrate structures during the initial stages of lithiation. The formation of clathrate structures with multiple guest atoms within the same cage may also yield materials with interesting and novel electronic properties for other applications.

Experimental Section

Synthesis

The synthesis of Na-filled clathrate was performed by thermal decomposition of the Zintl compound NaSi.^[26-28] NaSi was purchased from SiGNa Chemistry and dried at 100 °C to remove adsorbed moisture. NaSi was loaded into a h-BN crucible, then placed in a quartz tube and heated in a tube furnace under continuous vacuum evacuation (~10⁻⁴ Torr). The sample was heated to 340 °C (ramp rate of 10.5 °Cmin⁻¹) and held for 30 min, then ramped using the same rate to 420 °C and held for 18 h. After 18 h, the furnace was turned off while the sample remained under continuous vacuum for 6 h to remove Na vapor and enable the formation of more type-II clathrate.^[28] After the synthesis, the powder was quenched successively with toluene, isopropanol, ethanol, and water to remove any unreacted Na. To remove unreacted silicon, the powder was treated with 1 \bowtie NaOH for 8 h.

Characterization

Powder X-ray diffraction (XRD) was performed using CuK radiation on a PANalytical X'Pert Pro diffractometer. Structure refine-

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ment of the XRD data was performed using Bruker-AXS Topas 4.2. XRD patterns were indexed to structures for type-I and type-II clathrate from the literature.^[26,30] XRD measurements on electrodes after electrochemical cycling were performed by washing the electrode with hexanes after cell disassembly. Peak positions and intensities were normalized to the reflections originating from the Cu foil substrate. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were performed on a FEI XL30 ESEM-FEG. EDS was performed on 14 different particles to obtain an average composition.

Electrochemical Testing

Clathrate powder was mixed with carbon black (Timcal Super C45) and polyvinylidene difluoride (PVDF) in an 80:10:10 weight ratio and dissolved in N-methyl-2-pyrrolidone. This slurry was coated onto a copper foil with a Meyer rod and dried at 100 °C. The mass of the coating was determined using a microbalance (Mettler-Toledo, UMX2). Pouch cells were assembled in an Ar-filled glove-box using a Li metal foil as the counter electrode, a Celgard 3401 separator, and 1 \mbox{MiP}_6 in a 1:1 mixture of ethylene carbonate and diethylcarbonate (Novolyte). The cells were tested by potentiody-namic cycling to perform electrochemical potential spectroscopy^[36] from 2–0.01 V (vs. Li/Li⁺) with a 5 mV potential step amplitude and threshold current of either 5 or 25 $\mbox{\mu}$ Amg⁻¹ based on the mass of the clathrate. For preparing samples for ex situ XRD analysis after lithiation and delithiation, galvanostatic testing using a 25 $\mbox{\mu}$ Amg⁻¹ current density was performed.

Computational Methods

First-principles density functional theory (DFT) was applied to calculate the lattice constants and energies of the clathrate structures employing the VASP code.^[34,35] The Perdew–Burke–Ernzerhof (PBE) functional^[37] and projector-augmented wave (PAW)^[37] potentials were used along with the plane-wave basis sets. The energy cutoff for the plane-wave basis set was 300 eV. The convergence criteria for energy and forces were set to be 0.01 and 0.1 meV respectively. The Si 3 s3p, Na 2p3s, Li 1 s2s electrons were treated as valence electrons. The formation energies were calculated by subtracting the total energies of the elements from the energy of the structure, then dividing by the total number of atoms. For example, the formation energy for Si₁₃₆ was calculated using [Eq. (1)] and that for Li₁₆Na₂₄Si₁₃₆ was calculated using [Eq. (2)], where E(Si), E(Li) and E(Na) are the energies per atom for c-Si, Li and Na metals, respectively:

$$E_{\rm form} = \frac{E(Si_{136}) - 136E(Si)}{136} \tag{1}$$

$$E_{\text{form}} = \frac{E(Li_{16}Na_{24}Si_{136}) - 16E(Li) - 24E(Na) - 136E(Si)}{176}$$
(2)

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