Structural evolution and degradation of Si anodes:
Insights from first-principle calculations

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Abstract

Due to its high mass-specific capacity for Li storage and its abundance, Si is one of the most desirable anode materials for Li-ion batteries. However, rapid capacity fading has so far hindered successful commercialization [1]. Numerous experimental investigations have been conducted since the 1980s in order to improve on the cyclability of Si and, recently, Si nanowires (SiNW) with lifetimes of more than 1000 cycles have been synthesized [2]. Despite these achievements a detailed understanding of degradation mechanisms in Si anodes is still lacking. Atomistic modelling may help in revealing and eventually switching off relevant mechanisms. Here we demonstrate how density functional theory (DFT) calculations can help understanding (i) internal degradation of Si anodes and (ii) anisotropic swelling of SiNWs observed during first-cycle lithiation [3].

Bulk amorphous Li_xSi [4]

Model geometries of amorphous lithiated Si are created by an iterative insertion/extraction algorithm using a five-fold replication scheme. Starting with crystalline Si (c-Si), Li is inserted homogeneously into replicas at positions with large free volume. All replicas are equilibrated and optimized and the lowest-energy replica is used for further insertion. Extraction is done correspondingly.
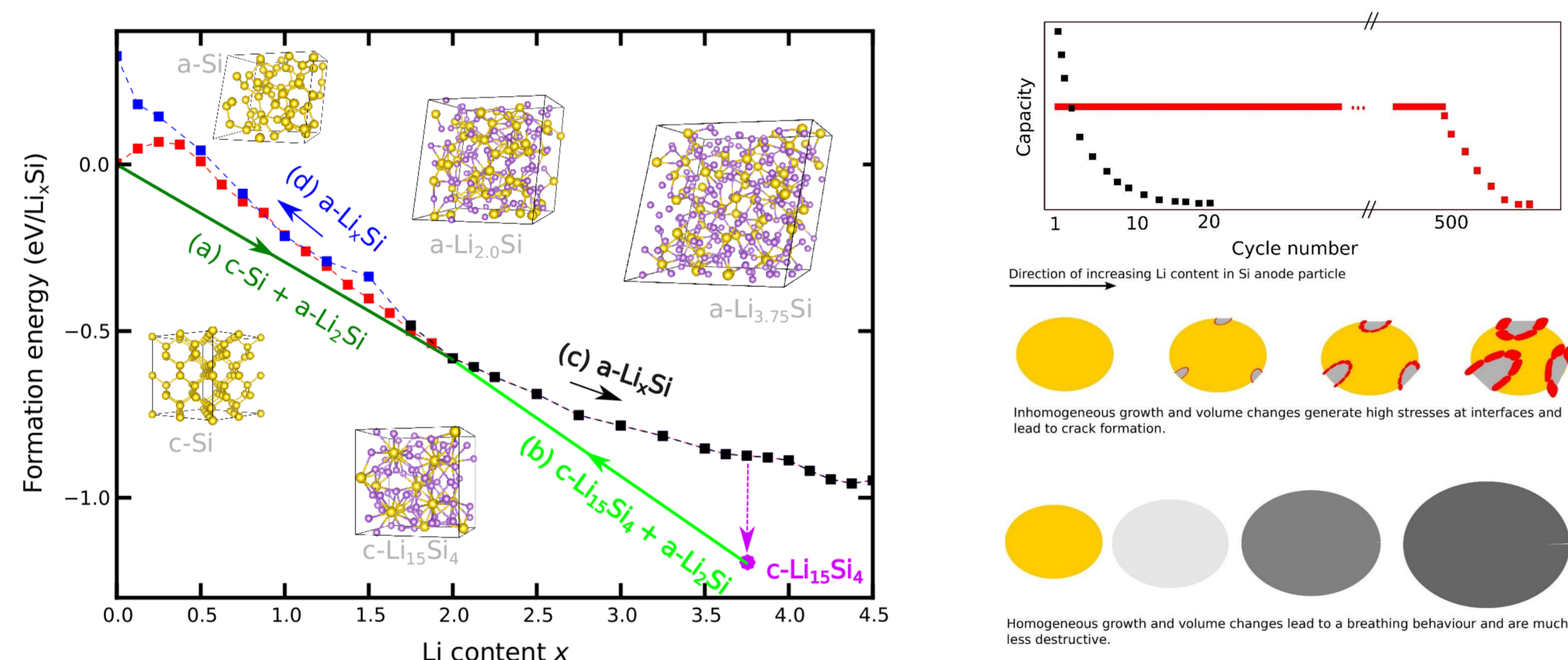
Formation energies suggest presence of various one- and two-phase regions during cycling. (a) Lithiation of c-Si leads to a c-Si/a-Li$_2$Si two-phase region with highly destructive inhomogeneous volume changes. (b) Delithiation of Li$_{15}$Si$_4$ (after crystallization) leads to a Li$_{15}$Si$_4$/a-Li$_2$Si two-phase region with highly destructive inhomogeneous volume changes. (c) Lithiation of amorphous Si proceeds *homogeneously* and is therefore less destructive. (d) Similarly, delithiation of a-Li$_x$Si with x<<3.75 also proceeds homogeneously. This could *explain extended lifetimes of a-Si anodes under capacity-limited cycling.*
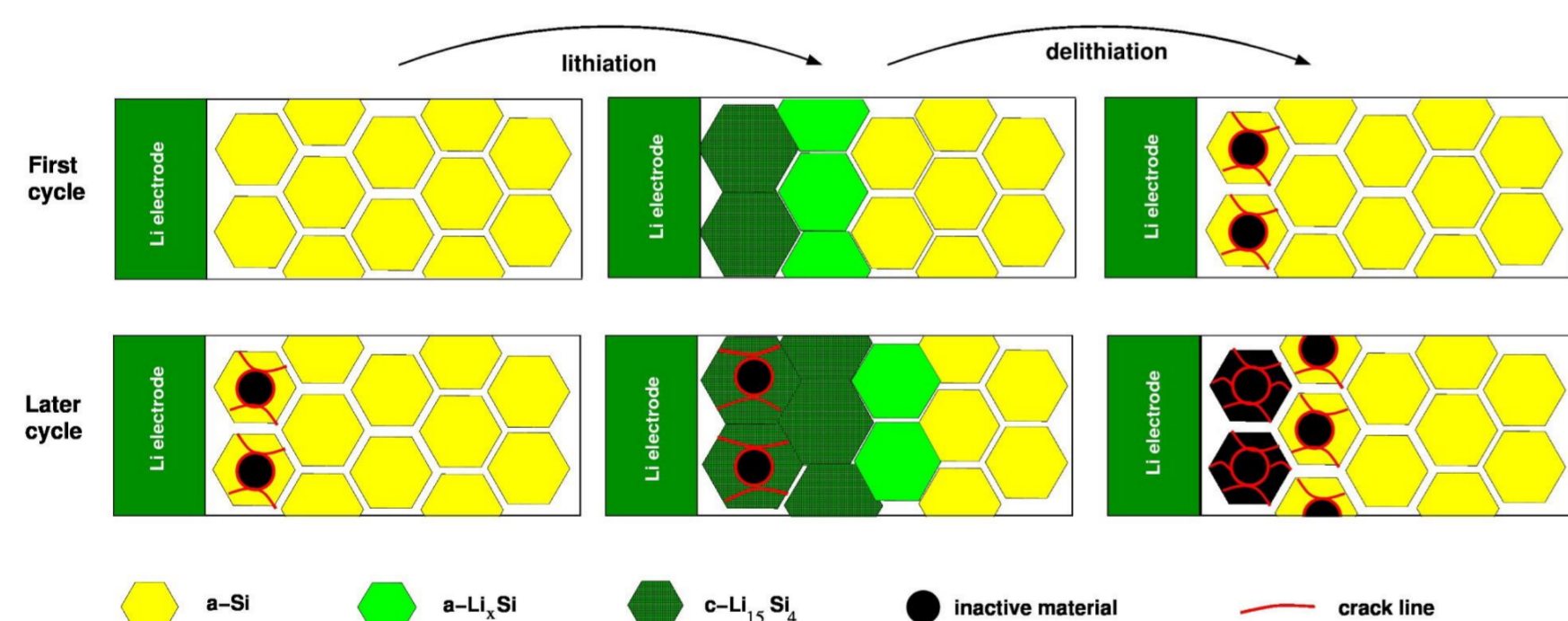
Globally inhomogeneous lithiation of anode particles could explain rapid fading after hundreds of cycles. In each cycle some particles would degrade heavily during delithiation due to crystallization of Li$_{15}$Si$_4$ during previous lithiation. Once only few particles are left, rapid capacity fading sets on.
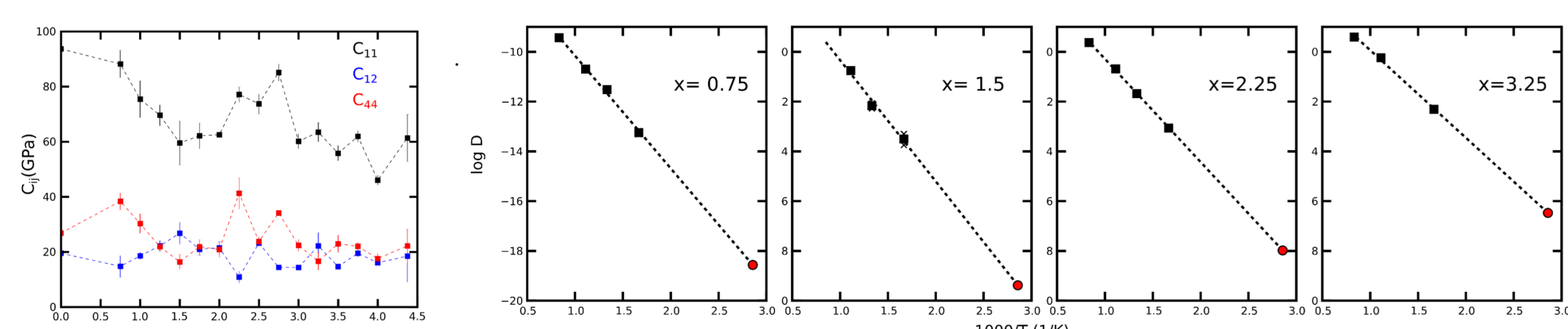
Calculated elastic and kinetic properties may be valuable input for mesoscopic simulations of Si anodes.

Energetics and Li kinetics at surfaces and interfaces [5]

Energetics and Li intercalation barriers at Si surfaces.
(i) Li/Si(111) is most stable followed by Li/Si(100) and Li/Si(110). Adsorption is most favoured and thus fastest at Si(110).
(ii) Li intercalation is favoured at Si(110), at least at high coverages.

Initially Si(110) facets are covered and intercalation takes place along <110>.

Energetics and Li intercalation barriers at Li$_2$Si/Si interfaces.
(i) Li$_2$Si/Si(111) is most stable followed by Li$_2$Si/Si(100) and Li$_2$Si/Si(110).
(ii) Li intercalation barriers are independent of orientation.

Kinetics of Li atoms does no longer determine the fastest direction of lithiation. However, …

Orientation-dependence of interface energies govern orientation-dependent lithiation. Nuclei that propagate a high-energy Li$_x$Si/Si(110) interface generates low-energy Li$_x$Si/Si(111) interfaces and vice versa. Propagating high-energy Li$_x$Si/Si(110) interfaces is therefore energetically more favourable than propagating low-energy Li$_x$Si/Si(110) interfaces. High-energy Li$_x$Si/Si(110) interfaces are thus more mobile and the experimentally observed orientation-dependent swelling of SiNWs can be understood as a consequence of the orientation-dependence of interface energies.

Summary & Conclusions

Atomistic model structures of lithiated Silicon were generated by iterative insertion and extraction of Li. Formation energies, elastic moduli and Li diffusion constants were extracted as functions of the Li content using density functional theory calculations. Interfaces between lithiated and unlithiated Si were constructed and optimized in order to study energetics and Li kinetics.

Improved performance of amorphous vs. crystalline Si anodes can be explained by the absence of two-phase regions during lithiation in the former case. Improved performance under capacity-limited cycling can be associated to suppressing crystallization of Li$_{15}$Si$_4$ that would otherwise lead to a two-phase region during delithiation. Rapid capacity fading after several hundreds of cycles could be due to globally inhomogeneous lithiation which has recently also been reported experimentally [6].

Orientation-dependent swelling of SiNWs is explained on the basis of interface energies and not on the basis of Li diffusion barriers, as was previously reported using smaller model systems for lithiated Si surfaces [7]. These models show a high degree of ordering and are therefore similar to Li-covered surfaces.

Finally, physical properties of Li$_x$Si might by useful for further investigating Si anodes on a mesoscopic scale.

References

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