



Short communication

Assessing Si-based anodes for Ca-ion batteries: Electrochemical decalciation of CaSi₂



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ABSTRACT

Density functional theory (DFT) calculations are used to investigate the basic electrochemical characteristics of Si-based anodes in calcium ion batteries (CIBs). The calculated average voltage of Ca alloying with fcc-Si to form the intermetallic Ca_xSi phases (0.5 < x ≤ 2) is of 0.4 V, with a volume variation of 306%. Decalciation of the lower Ca content phase, CaSi₂, is predicted at an average voltage between 0.57 V (formation of Si-fcc, 65% volume variation) and 1.2 V (formation of metastable deinserted-Si phase, 29% volume variation). Experiments carried out in conventional alkyl carbonate electrolytes show evidence that electrochemical “decalciation” of CaSi₂ is possible at moderate temperatures. The decalciation of CaSi₂ is confirmed by different characterization techniques.

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1. Introduction

Concerns on Li availability have prompted the search for suitable alternatives to rechargeable lithium-ion battery (LIBs) technologies. Among these, batteries based on multivalent charge carriers (Mⁿ⁺) can exhibit advantages in terms of energy density since for a certain amount of M carriers the capacity is doubled ($n = 2$) or tripled ($n = 3$) when compared to single valent carriers like Li⁺ or Na⁺. Calcium is an attractive candidate [1,2,3] due to its low cost, natural abundance and low reduction potential. We have recently reported on the feasibility and reversibility of calcium plating in conventional alkyl carbonate electrolytes at moderate temperatures [4], which opens the way to the development of a new rechargeable battery technology using calcium anodes. Yet, the theoretical capacity of Ca is 1340 mAh/g, and the exploration of alternative anodes based on intercalation or alloy reactions with higher capacities is a must to open as many research avenues as possible for new calcium-based battery technologies (CIBs).

Alloying electrodes have exhibited large capacities with lithium [5] and are also starting to be investigated with sodium and magnesium [6,7]. A recent publication reported on a tin anode for a Ca-ion system utilizing manganese hexacyanoferrate as the cathode, although no detailed characterization was provided on the tin electrode reaction mechanism [8]. The electrochemical formation of Si-based alloys with calcium has, to the best of our knowledge, not been investigated to date. Yet, in light of the existing knowledge on the Ca–Si phase diagram

[9], it seems that it could be feasible. Table 1 lists the theoretical specific capacity for Ca_xSi alloys; a maximum theoretical capacity of 3818 mAh/g could be achieved reacting one mole of Si with two moles of Ca ions. The lower Ca content phase, CaSi₂ with a theoretical specific capacity of 557 mAh/g, is commercially available and thus an interesting starting point to investigate the possibilities of Si-based anodes for Ca batteries. In this work, we perform first principles calculations at the density functional theory (DFT) level to extract basic electrochemical characteristics of Si-based anodes in CIBs. Encouraged by the DFT results, the intermetallic CaSi₂ is tested in Ca cells.

2. Methodology

2.1. Computational

Total energies of Ca, fcc-Si, deinserted-Si, Ca₂Si, Ca₅Si₃, CaSi and CaSi₂ (see Table 1) have been calculated using VASP program Vienna Ab-initio Simulation Program. [12] Density functional theory (DFT) calculations were performed within the General Gradient Approximation (GGA), with the exchange and correlation functional form developed by Perdew, Burke and Ernzerhof (PBE) [13]. The energy cutoff for the plane wave basis set was fixed at a constant value of 500 eV throughout the calculations. The integration in the Brillouin zone was done on an appropriate set of *k*-points determined by the Monkhorst–Pack scheme. All crystal structures were fully relaxed and the final energies of the optimized geometries were recalculated to correct the changes in the basis set of wave functions during relaxation.

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Table 1
Theoretical specific capacity and crystallographic information of Ca–Si compounds.

Phase	Molar mass (g/mol)	Theoretical specific capacity (mAh/g initial phase)	S.G.	Experimental lattice parameters (Å) [9,10]	Calculated lattice parameters (Å)
fcc-Si	28.086	3818	<i>Fd-3 m</i>	$a = 5.43^*$	$a = 5.468$
Deinserted Si	28.086	–	<i>R-3 m</i> [§]	–	$a = 3.86$ $c = 24.36$
CaSi ₂ (Ca _{0.5} Si)	96.250	557	<i>R-3 m</i>	$a = 3.86$ $c = 30.07$	$a = 3.84$ $c = 31.68$
CaSi	68.164	787	<i>Cmcm</i>	$a = 4.56$ $b = 10.73$ $c = 3.89$	$a = 4.54$ $b = 10.74$ $c = 3.90$
Ca ₅ Si ₃ (Ca _{5/3} Si)	314.65	852	<i>I4/mcm</i>	$a = 7.64$ $c = 14.87$	$a = 7.63$ $c = 14.79$
Ca ₂ Si	108.24	991	<i>Pnma</i>	$a = 7.69$ $b = 4.82$ $c = 9.03$	$a = 7.60$ $b = 4.82$ $c = 9.04$

[§] Symmetry analysis was performed with the PLATON software [11].

2.2. Experimental

Two-electrode Swagelok cells were assembled in an Ar-filled glove box. The working electrode consisted of a powder mixture of CaSi₂ (Aldrich), with 30% of carbon black (Super P, Timcal Switzerland) on an aluminium current collector. The electrolyte used was 0.45 M Ca(BF₄)₂ in EC:PC (50/50 wt.%), which enables Ca plating/stripping at moderate temperatures [4]. When compared to standard redox potential of the Ca²⁺/Ca⁰ vs. NHE, a negative potential shift was recorded and found to be close to 0.8 V [4,14]. For the sake of clarity, all potentials reported are denoted as V vs. Ca²⁺/Ca_{passivated} in the manuscript. Potentiostatic intermittent titration technique (PITT) measurements were performed with potential steps of 5 mV, the potential being stepped to the next value when the current dropped below a rate of C/200 (1C being one Ca²⁺ inserted in one hour), and cyclic voltammetry (CV, 0.05 mV/s, between 2 and 3.5 V vs. Ca²⁺/Ca_{passivated}) were carried out at 100 °C using a Bio-Logic VMP3 potentiostat. After testing, the electrochemical cell was dismantled inside an Ar-filled glove box, the powder was scratched from the working electrode and introduced in a borosilicate glass capillary ($\phi = 0.3$ mm) for Synchrotron X-ray powder diffraction (SXRPD) at MSPD beamline (Mythen detector, $\lambda = 0.61971$ Å) at ALBA synchrotron. [15] Scanning electron microscopy (SEM) studies on CaSi₂ powder electrodes before and after electrochemical testing were performed using a Quanta 200 ESEM FEG FEI microscope equipped with an energy-dispersive X-ray spectrometer (EDS). Average particle sizes were estimated from SEM images as a mean over 90 randomly chosen particles.

3. Results and discussion

Table 1 lists crystallographic details of the calculated Ca_xSi alloys and fcc-Si (the thermodynamically stable form of Si at 25 °C). Fig. 1 shows the calculated voltage–composition curve for fcc-Si alloying with Ca. The total volume variation when going from fcc-Si to Ca₂Si is of 306% at an average voltage of 0.37 V. In short, the calculated voltage profile and volume variation follow the same characteristics encountered in the Li–Si system [16]. This makes the exploration of Si anodes for calcium-based batteries appealing. While in-depth investigations of the Si anode are underway, in this communication, we focus on the possible decalciation of CaSi₂. The dealloying process of CaSi₂ to produce fcc-Si is predicted at 0.57 V, with a volume contraction of 65% (see Fig. 1). With this large volume variation, it is reasonable to think that decalciation of CaSi₂ at moderate temperatures could originate a metastable-Si phase, rather than the fcc-Si.

The crystal structure of the layered intermetallic CaSi₂ (S.G. *R-3 m*) is shown in Fig. 1. We have calculated the energy of the related deinserted

Si phase. The deinsertion of all Ca ions from CaSi₂ would occur at an average voltage of 1.2 V (Fig. 1, blue) with volume variation of 29% due to a contraction along the *c* axis of the Si layers (see Table 1). The deinserted-Si structure is notoriously less stable (0.62 eV/atom.) than the fcc-Si. Therefore, even if Ca deinsertion from CaSi₂ would be achieved during the first charge of the Ca//CaSi₂ cell, there would be a strongly driven force for the unstable “deinserted-Si framework” to transform to a more stable fcc-Si phase upon cycling.

In summary, DFT calculations indicate that the decalciation of CaSi₂ to form a Si phase is possible at a maximum voltage of 1.2 V (formation of metastable deinserted-Si framework) and at a minimum voltage of 0.57 V (formation of the most stable form, fcc-Si). Voltages between 1.2 V and 0.57 V would represent a situation where the decalciation process has produced a Si phase less stable than fcc-Si but more stable than the deinserted framework.

The electrochemical performance of CaSi₂ was investigated by PITT and the results are shown in Fig. 2e. Signatures of electrochemical activity (specific capacity of about 240 mAh/g (or ca. 340 mAh/(g of CaSi₂)) considering that the pristine powder is a mixture of 70% of CaSi₂ and 30% of Si, see below) can be observed, with a pseudo plateau centred at ca. 2.75 V vs. Ca²⁺/Ca_{passivated} upon oxidation and at ca. 0.88 V vs. Ca²⁺/Ca_{passivated} upon reduction. A voltage hysteresis ranging from 1.7 up to 2.3 V is observed, thus indicating the existence of a notorious overpotential in the system, which is enhanced on further oxidation thereby limiting the achievable

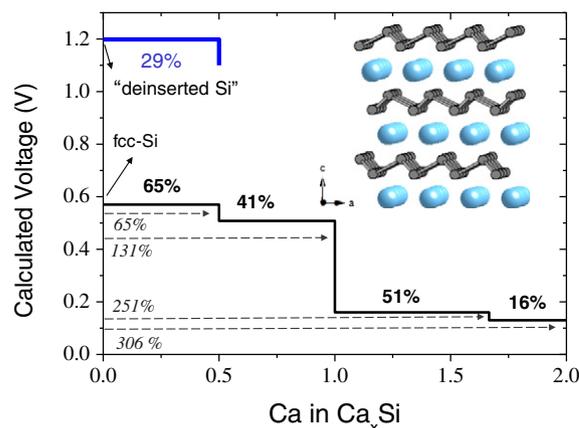


Fig. 1. Calculated composition–voltage profiles. The black line corresponds to the calculation of fcc-Si following an alloying mechanism in which intermetallics Ca_xSi are formed. The blue line accounts for the deinsertion of Ca ions from the layered CaSi₂. The inset shows the schematic crystal structure of CaSi₂ (Si in grey, Ca in blue). The calculated volume expansions are given as a percentage, either associated to each voltage step (in bold) or referred to the Si phase (in italic).

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