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## **No Significant Effect of Phosphorous Doping on the Electrochemical Performance of Silicon-Carbon Composite Anodes for Li-ion Batteries**

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In this paper we demonstrate production of doped silicon nanoparticles and testing of the material in Li-ion battery half cells. Incorporation of 3 at% of phosphorous in the reactants of the free-space reactor used resulted in a doping level of 1.8 at%, a very high level of doping with regards to the standard in semiconductor silicon. However, even with this high level of doping, no significant effect was observed for cycling of silicon anodes using 60 wt% silicon. We propose that the benefit of doping silicon is masked by the effect of the conductive carbon and other additives used in preparation of the test cells.

### **Doped silicon as anode material for Li-ion batteries**

The use of silicon as part of the anode in Li-ion batteries (LIBs) enhances the potential storage capacity greatly. While the graphite anode used in standard Li-ion batteries has a theoretical capacity of 372 mAh/g, the theoretical capacity for Si is 3,572 mAh/g [1]. Unfortunately, the application of silicon in Li-ion battery anodes is not straight forward. The two primary challenges are related to the large volume expansion and material stress that silicon is exposed to when absorbing 4 Li ions per Si atom, and the low electrical conductivity of silicon itself. The first challenge is addressed by nanostructuring [2], while sufficient electrical conductivity of the anode can be achieved by mixing or coating the silicon with an electrically conductive material, normally carbon-based.

It has been suggested that a small amount of a dopant (normally boron or phosphorous) can be a strategy to overcome the challenge of low electrical conductivity in silicon. Doping of silicon is well-known from the semiconductor industry, and doping can change the conductivity of crystalline silicon by several orders of magnitude.

Ohara et al. [3] might have been the first experimental report on use of doped silicon in LIB anodes. Using thin-film anodes, a positive effect of doping was reported, although few details are provided in their proceedings.

Kong et al. [4] produced doped silicon nanoparticles (80-100 nm) by plasma arc discharge of a gas mixture of SiH<sub>4</sub> and PH<sub>3</sub> diluted in Ar (Ar:SiH<sub>4</sub>:PH<sub>3</sub> ratio 4:15:3). The resulting dopant concentration is not given in the paper, but the high PH<sub>3</sub> reactant concentration suggests high concentration of several percent. Kong et al. reported substantial effect of doping, also when using a carbon/silicon composite electrode. The cycle performance was substantially improved with respect to intrinsic silicon, although the first cycle capacities were reduced. Hülser et al. produced a similar, but boron-doped material and performed electrochemical testing, but the results were not benchmarked against pure intrinsic silicon [5].

Doped silicon for LIBs has also been investigated in the form of silicon nanowires (Si-NW) produced from SiH<sub>4</sub> and PH<sub>3</sub> deposited on stainless steel. Kang et al. [6] produced intrinsic and phosphorous-doped Si-NW with a low doping concentration of 10

ppm(at), and saw better capacity retention rates, especially at high C rates. Later, Kim et al. [7] showed similar results for Si-NWs, but also reported higher capacities, better coulombic performance and changes in the impedance spectrum. Kim et al. did not state the dopant concentration, but the  $\text{PH}_3$  to  $\text{SiH}_4$  concentration in the reactant gas was around 1:9, which should result in several percent phosphorous in the produced material. Kim et al. explains the improvement in the doped Si-NW not only by the reduced electrical resistance, but also suggest that phosphorus gives strengthened structural stability in the Si-NW.

Doped silicon by ball milling of silicon and dopant-containing precursors has been reported by two different authors, with diverging results: Yi et al. [8] ball milled  $\text{SiO}$  powder with  $\text{B}_2\text{O}_3$  powder and obtained a very high dopant concentration (4.1 at%). They reported up to 80% higher capacity retention rates for the boron doped samples as compared to intrinsic silicon at high C-rates, and relates the increased performance to the conductivity of doped samples. On the other hand, Rousselot et al. [9] saw no significant effect of boron doping in their similar experiment. They prepared samples by ball milling of pure silicon and boron with doping levels from 167 ppm(at) to 16.7 at% dopant. It is unclear from their results how well the boron atoms actually got incorporated in the Si particles by the ball milling process. Their conclusion is, however, that except of a change in the electrical resistivity of the material, there is no significant effect on the electrochemical cycling behavior, independent of the cycling method or C rate used.

Long et al. [10] has attempted to understand the role of n- and p-type doping in silicon in LIBs, focusing on the insertion of Li ions in crystalline silicon. Their work combines Raman studies on phosphorous and boron doped crystalline wafers with density functional theory calculations. Their results suggest that doping can be a way to spatially select where Li ions should be inserted in silicon, but to our knowledge this has never been followed up in any electrochemical study.

While the bulk of the studies done on the performance of Si particles in LIB anodes use a silicon-carbon composite electrode, a study of pure silicon with different levels of phosphorous doping up to 1000 ppm(at) was published recently by Domi et al. [11]. The production method of their materials is not disclosed, but there is reason to believe that the doped material is obtained from melts of doped silicon, and the dopant may be assumed to be evenly distributed. This study shows a consistent change in electrochemical behavior moving towards lower initial cycle capacity but substantially higher capacity retention as the doping level increases. The coulombic efficiency is also substantially better for samples doped with more than 50 ppm phosphorous.

There are a limited number of studies reporting electrochemical results on use of doped silicon in the LIB anodes. The studies also vary substantially in silicon material synthesis method, material morphology, doping levels and electrode preparation method, which makes them difficult to compare. In summary, however, there seems to be evidence that the introduction of dopants in silicon may be beneficial, especially when using electrodes without graphite constituents and for high cycling rates.

### **Synthesis of doped silicon nanoparticles**

In this work, we produced doped and intrinsic silicon particles by pyrolysis of  $\text{SiH}_4$  and  $\text{PH}_3$  diluted in He and  $\text{H}_2$  in a free-space reactor. The production method is described elsewhere [12]. For intrinsic particles, 5 standard liters per minute (SLM) of  $\text{SiH}_4$  and 5 SLM of He and 9 SLM of  $\text{H}_2$  was used. For doped particles, the He flow was

exchanged with a mixture of 3%  $\text{PH}_3$  in He. The corresponding Si to P atomic flow rate was thus 100:3.

Figure 1 shows scanning electron microscope images of the intrinsic and doped silicon particles obtained. The particle morphologies are similar; we see agglomerated particles with primary particles in the range of 50-500 nm in diameter. X-ray diffraction on the produced materials showed that they were amorphous. The composition of the materials was measured independently by energy dispersive X-ray spectroscopy (EDS) and inductively coupled plasma mass spectrometry (ICP-MS), which yielded a phosphorous content of  $1.9 \pm 0.5$  at% and  $1.8 \pm 0.4$  at%, respectively. The conductivity of the silicon particles was not measured, but observation of charging effects on the intrinsic silicon material suggested substantially higher electrical resistivity of this material with respect to the doped silicon particles.

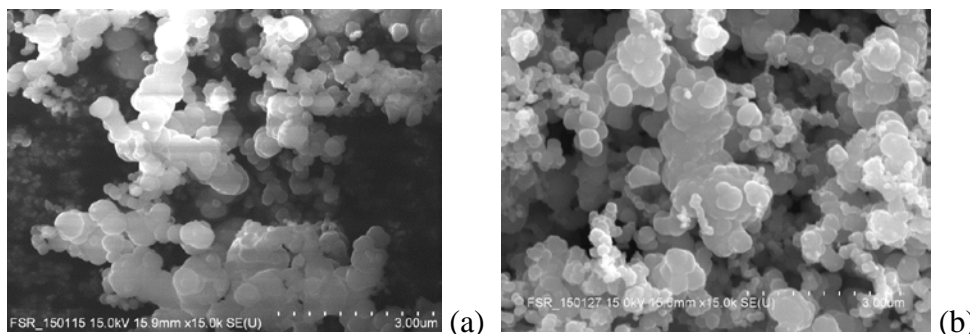


Figure 1. SEM images of (a) the intrinsic and (b) the doped silicon particles produced and tested in the current work.

### Electrochemical testing

Electrochemical tests were performed in a crimped 2032 coin cell with lithium metal used as a counter electrode, with a polymer separator (Celgard 3401) and 1 M  $\text{LiPF}_6$  in 1:1 EC/DMC electrolyte (LP30, BASF). 10 wt% fluoroethylene carbonate (FEC) was used as electrolyte additive. The slurry was prepared with 60% silicon, 10% graphite, 15% carbon black and 15% CMC binder. The cells were cycled at 25 °C between 1.0 and 0.05 V using a battery cycler from Arbin Instruments.

Figure 2 shows cycling results for an intrinsic and a phosphorous doped silicon electrode. As can be seen, there was no substantial difference in the performance of the materials. The small peak at cycle number 18 is due to an uncontrolled change in temperature during those cycles.

We also performed limited capacity cycling of 10 samples, 4 and 6 of respectively doped and intrinsic samples, to test the potential capacity when working at a design capacity of 1000 mAh per g of silicon. As can be seen in Figure 3, neither these results provided any difference between the doped and intrinsic materials.

Cycling at different C-rates neither provided any differences in performance between the doped and intrinsic silicon particles. As demonstrated in Figure 4, the cycling at different C-rates shows little difference in the capacity retention between samples. The difference that can be observed can anyway not be explained by doping effects, but rather by the difference in electrode loading, as shown in Figure 4b.

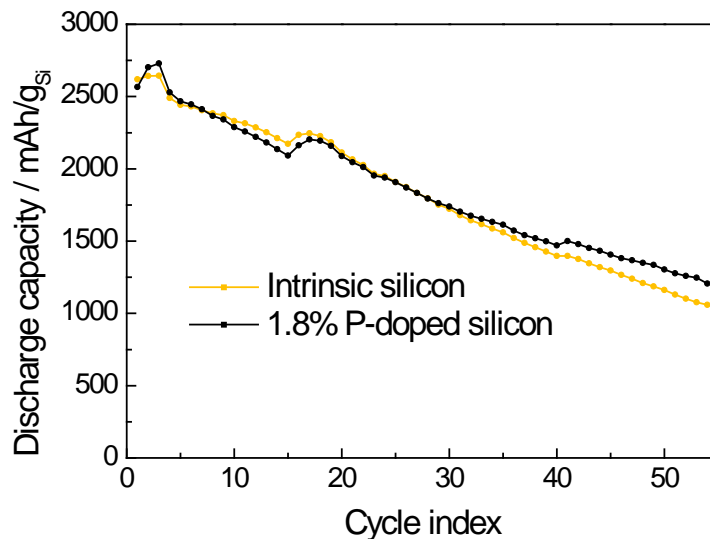


Figure 2. Discharge capacity of silicon based anodes with intrinsic and doped silicon particles.

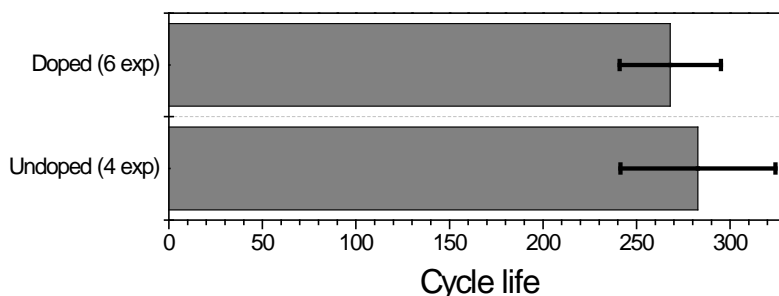


Figure 3. The average cycle life of doped and intrinsic silicon electrodes under limited cycling at 1000 mAh/g. The cycle life is defined as the number of cycles for which the electrode is able to maintain the designated capacity between 0.05 V and 1.20 V. The error bars represent the standard deviation of the data set of cycle life.

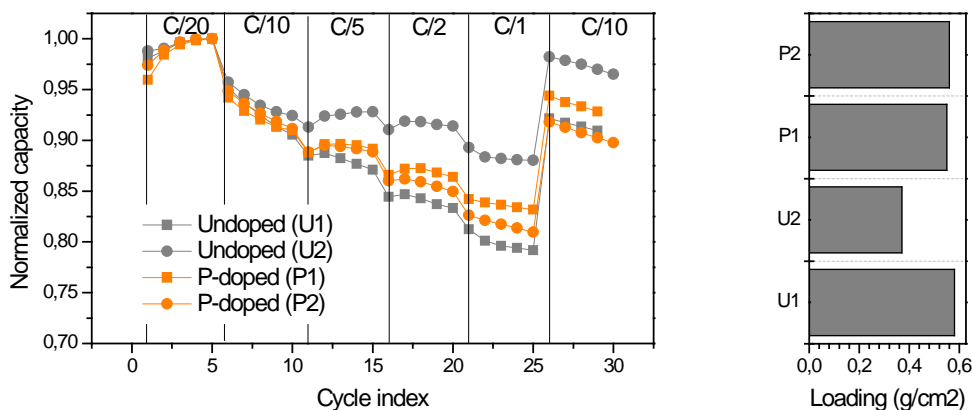


Figure 4. (a) Capacity retention at different C-rates and (b) the electrode loading ( $\text{g}_{\text{Si}}/\text{cm}^2$ ) of the corresponding samples.

## Discussion

Of the several papers cited in the introduction of this paper, only Rousselot et al. [9] seems to have observed the same as us, namely no significant effect of doping on the electrochemical performance of silicon-based anodes. All the other authors report that doping has been observed to be beneficial. None of the studies can be compared directly to ours, because of the difference in materials, doping levels and electrode preparation methods, but our results suggest that when using the standard state-of-the-art preparation method for silicon based anodes, the effect of doping the silicon material is minimal. This can partly be explained by the addition of conductive graphite to the electrode material, and partly by the use of FEC additive in the electrolyte. The graphite introduces electrical conductivity that may mask any effect of increased conductivity in the silicon, and the FEC controls the silicon-electrolyte interface and may mask any effect related to the interface as suggested by Long et al. [10]. Therefore, we cannot rule out that there indeed is a positive effect of doping of silicon materials when using other electrode and electrolyte chemistries than the current.

## Conclusion

We have demonstrated that there is no significant effect of 1.8 at% phosphorous doping on the electrochemical performance of amorphous silicon nanoparticles in Li-ion battery anodes. In our experience, there is no increased capacity and no enhancement in capacity retention at higher C-rates, contrary to what has been reported earlier by most other groups that have published on this topic. Our divergence may be explained by the preparation of silicon-graphite composite anodes and the use of electrolyte additives. The additives act as electronic conductors that mask any conductivity enhancement provided by the doping of the silicon itself. Even if we found no benefit of doping silicon, there may be benefits in other LIB cell designs, especially when using low or zero carbon content in the anode or with other electrolyte additives.

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