

# A room temperature study of the binary lithium–silicon and the ternary lithium–chromium–silicon system for use in rechargeable lithium batteries

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## Abstract

Several binary lithium–silicon and ternary lithium–chromium–silicon samples were produced and then characterized by X-ray diffraction, as well as electrochemical methods at room temperature. The known lithium–silicon phases, as well as silicon–chromium phases, were found, but no ternary phases. The electrochemical characterization of the materials yielded behavior differing from that predicted from high temperature experiments. Experiments on highly lithiated samples yielded charge potentials in the realm of 300–650 mV vs. Li/Li<sup>+</sup> and discharge potentials of about 20–300 mV vs. Li/Li<sup>+</sup>. The binary lithium–silicon materials showed reversible capacities of up to 550 mA h/g. The ternary materials showed higher reversible capacity of up to 800 mA h/g. The capacity is dependent on the initial stoichiometry of the material with Li:Si ratios of about 1:3.5 showing the highest reversible capacities. Good cycling performance could also be achieved. © 1999 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

Lithium alloys possess considerably higher energy densities than the commonly used anode materials for rechargeable lithium batteries, carbons (see Table 1). Graphitic carbons show reversible capacities of up to 372 mA h/g. Following the over 200 patents of Fujifilm on lithium metal oxides [1,2], this area has again gained worldwide interest.

The binary lithium–silicon system shows the highest energy densities per weight. It shows four different phases Li<sub>12</sub>Si<sub>7</sub>, Li<sub>7</sub>Si<sub>3</sub>, Li<sub>13</sub>Si<sub>4</sub> and Li<sub>21</sub>Si<sub>5</sub> [3,4]. The total theoretical capacity for the reaction of lithium and silicon to Li<sub>21</sub>Si<sub>5</sub> is 1967 mA h/g (corresponding to 4.2 mol lithium per mol silicon). This is the highest capacity obtainable from any of the lithium alloys studied to date. The binary system has not yet been investigated at temperatures around 25°C. The prior literature only contained a characterization at 415°C by Wen and Huggins [5]. Thus, we studied this

binary system at room temperature to form a basis for theoretical calculations on further ternary lithium–silicon metal systems.

As can be seen from Table 1, the lithium–magnesium–silicon system shows high capacities and fewer reactions steps, as reported by Huang et al. [6]. The lithium–chromium–silicon system was chosen here as a second system for investigation due to its very high theoretical capacity for a ternary system of 996 mA h/g or 1197 mA h/g, corresponding to the proposed reaction of CrSi<sub>2</sub> with lithium to form Cr<sub>3</sub>Si and Li<sub>13</sub>Si<sub>4</sub> or Li<sub>21</sub>Si<sub>5</sub>, respectively.

This work deals with the preparation, characterization and electrochemical evaluation of the binary lithium–silicon and the ternary lithium–chromium–silicon systems at 25°C.

## 2. Experimental

The electrochemical lithium uptake of the unlithiated starting materials is very low at 25°C. Thus, only chemically lithiated materials were used in the experiments. Lithium silicides and lithium chromium silicides were

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Table 1

Calculated equilibrium potentials and capacities for some lithium alloys at 420°C from Anani and Huggins [7], A = 'lithium – silicon'

System	Starting material	Phases in equilibrium	Potential [mV vs. Li/Li <sup>+</sup> ]	Ratio [Li/Si]	Lithium per gram in 10 <sup>3</sup>
A	Silicon	Li <sub>12</sub> Si <sub>7</sub> –Li <sub>7</sub> Si <sub>3</sub>	288	2.33	82.9
	Silicon	Li <sub>13</sub> Si <sub>4</sub> –Li <sub>21</sub> Si <sub>5</sub>	44	4.20	149.5
A–Mg	Mg <sub>2</sub> Si	Mg <sub>2</sub> Si–Mg–Li <sub>13</sub> Si <sub>4</sub>	60	3.25	32.7
A–Cr	CrSi <sub>2</sub>	CrSi <sub>2</sub> –CrSi–Li <sub>7</sub> Si <sub>3</sub>	223	1.17	18.8
	CrSi	CrSi–Cr <sub>5</sub> Si <sub>3</sub> –Li <sub>7</sub> Si <sub>3</sub>	205	0.93	10.8
	Cr <sub>5</sub> Si <sub>3</sub>	Cr <sub>5</sub> Si <sub>3</sub> –Cr <sub>3</sub> Si–Li <sub>13</sub> Si <sub>4</sub>	138	1.44	11.6

produced by reacting silicon (Heraeus, 99.9%, < 160 μm) or chromium disilicide, CrSi<sub>2</sub> (CERAC, 99.9%, – 325 mesh), with lithium (Aldrich, 99.9%) in an oven within a glove box under argon. All samples were annealed at 360°C for 15 h.

All materials were characterized by X-ray diffraction using a Siemens D5000 series diffractometer in theta–theta geometry. The scans from 38 to 80° were performed in a special X-ray holder under argon atmosphere using a mylar foil window that allowed X-ray penetration.

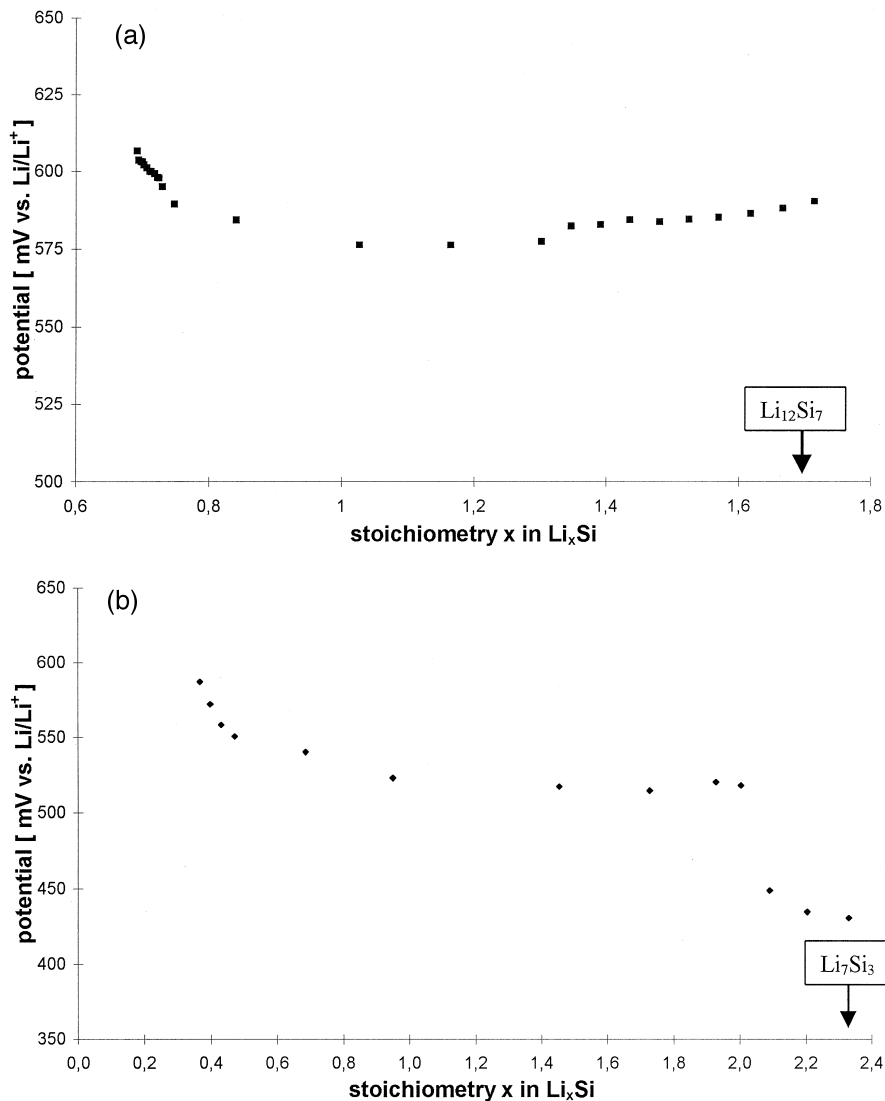


Fig. 1. (a) Electrochemical equilibrium potential values for lithium removal from the binary phase Li<sub>12</sub>Si<sub>7</sub>. (b) Electrochemical equilibrium potential values for lithium removal from the binary phase Li<sub>7</sub>Si<sub>3</sub>. (c) Electrochemical equilibrium potential values for lithium removal from the binary phase Li<sub>13</sub>Si<sub>4</sub>. (d) Electrochemical equilibrium potential values for lithium removal from the binary phase Li<sub>21</sub>Si<sub>5</sub>. For comparison, a curve with C/180-rate current is shown for this material.

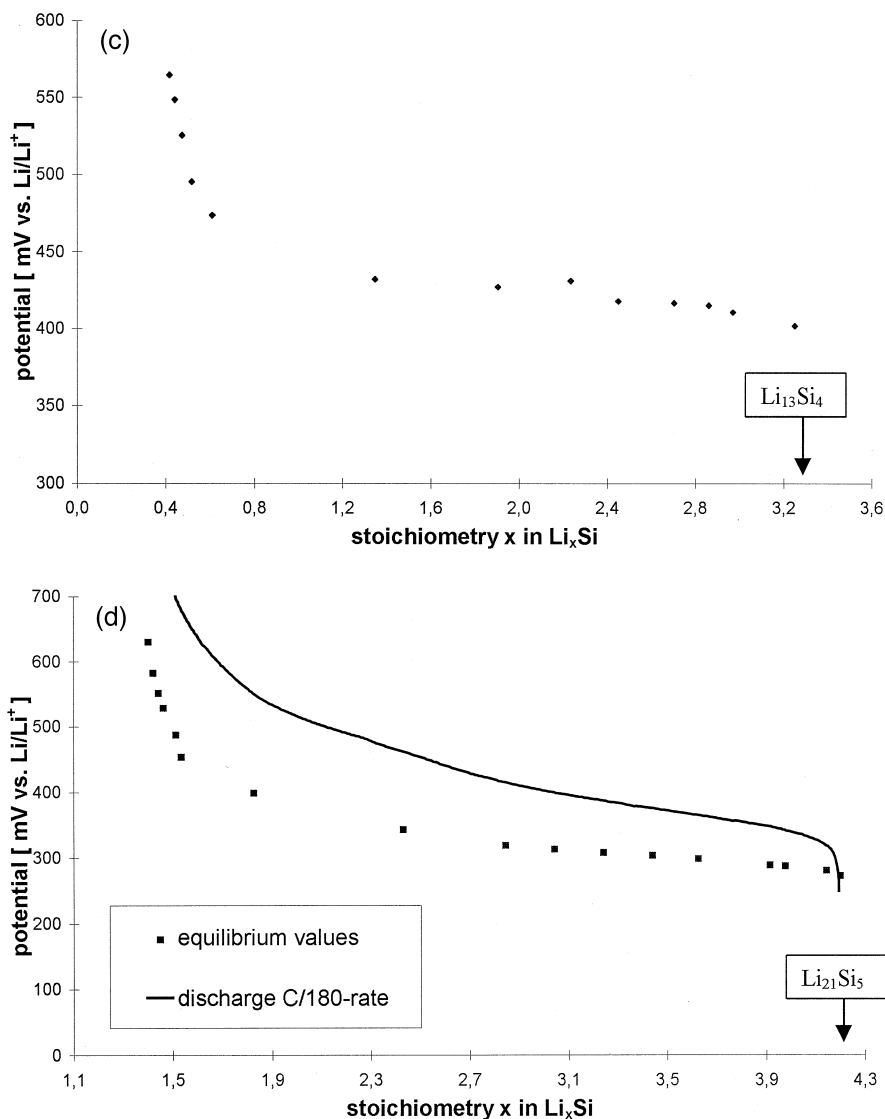


Fig. 1 (continued).

The active materials were pressed into thin tablets of 10 mm diameter using dendritic copper powder (Aldrich, 99.7%) in a ratio of about 1:1 with pressures of about 8–9 Torr [8]. These tablets were then pressed into a nickel net for electrical contact and mechanical stability. The electrochemical measurements were conducted using a computer-controlled test set-up. All coulometric titration experiments were conducted galvanostatically with lithium as reference and counter electrodes using LP30 (Merck, PC:EC:DMC, 1:1:3, 1 molar LiPF<sub>6</sub>) as the electrolyte. C-rates are specified with respect to the theoretical capacity of the electrodes.

### 3. Results and discussion

#### 3.1. The binary lithium–silicon system

A total of 22 binary samples were prepared and characterized. All four phases of the binary systems, Li<sub>12</sub>Si<sub>7</sub>,

Li<sub>7</sub>Si<sub>3</sub>, Li<sub>13</sub>Si<sub>4</sub> and Li<sub>21</sub>Si<sub>5</sub>, could be produced as pure materials. A theoretical diffraction pattern for the phase Li<sub>7</sub>Si<sub>3</sub> was calculated which matched the experimental data completely and uniquely. Further, samples with stoichiometries between the pure phases were made. They could be characterized fully and uniquely as mixtures of the two respective neighboring phases.

##### 3.1.1. Equilibrium potential values

Fig. 1a to d show equilibrium potential values for the first lithium removal of the four pure binary phases. The stoichiometry axes refer to the nominal compositions of the samples. Due to the kinetic hindrance of the reconstitution reactions expected under equilibrium conditions different samples of nominally equal stoichiometry cannot be considered equal in their phase composition.

For the phases Li<sub>12</sub>Si<sub>7</sub>, Li<sub>7</sub>Si<sub>3</sub> and Li<sub>13</sub>Si<sub>4</sub> the curves show indications of two-phase plateaus at 582, 520 and 428 mV vs. Li/Li<sup>+</sup>, respectively. However, most of the

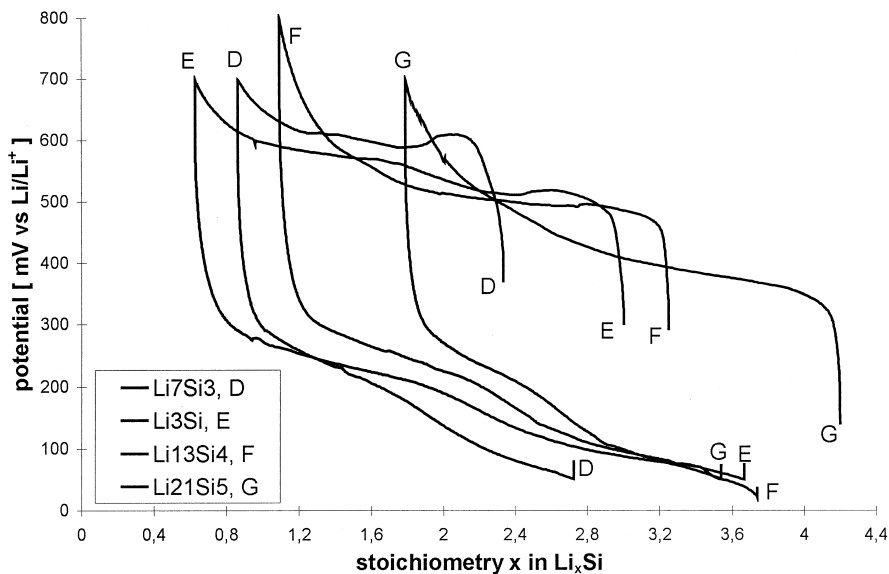


Fig. 2. Comparison of the first cycle for electrodes of materials  $\text{Li}_7\text{Si}_3$ ,  $\text{Li}_{3,0}\text{Si}$ ,  $\text{Li}_{13}\text{Si}_4$  and  $\text{Li}_{21}\text{Si}_5$ , current:  $C/90$ -rate.

expected reconstitution reactions were kinetically hindered. This situation is characterized by equilibrium in the lithium atom sublattice, but not the silicon sublattice.

### 3.1.2. Cycling behavior

Different first-cycle potential composition behavior was found for the different starting materials, as shown in Fig. 2. The materials also have different delithiation capacities. The following lithiation behavior is characterized by similar curve shapes with two pseudo-plateau-like regions around 240 and 100 mV vs.  $\text{Li}/\text{Li}^+$  for all materials but with significant differences in their capacities.

The only binary sample that showed evidence of two plateaus in potential on delithiation was the one with the initial stoichiometry  $\text{Li}_{3,0}\text{Si}$ . Here, two different phases were present in the starting material.

Cycling experiments were performed on a sample with initial composition  $\text{Li}_{21}\text{Si}_5$ . The results are shown in Fig. 3. A loss per cycle of 4% was found, which is very low for unoptimized lithium alloy electrodes. It was further shown by measurements on electrodes that were repressed after cycling that the capacity loss is not a property of the active material. It is evidently due to the reduction of electronic contact in the electrodes as the result of cycling.

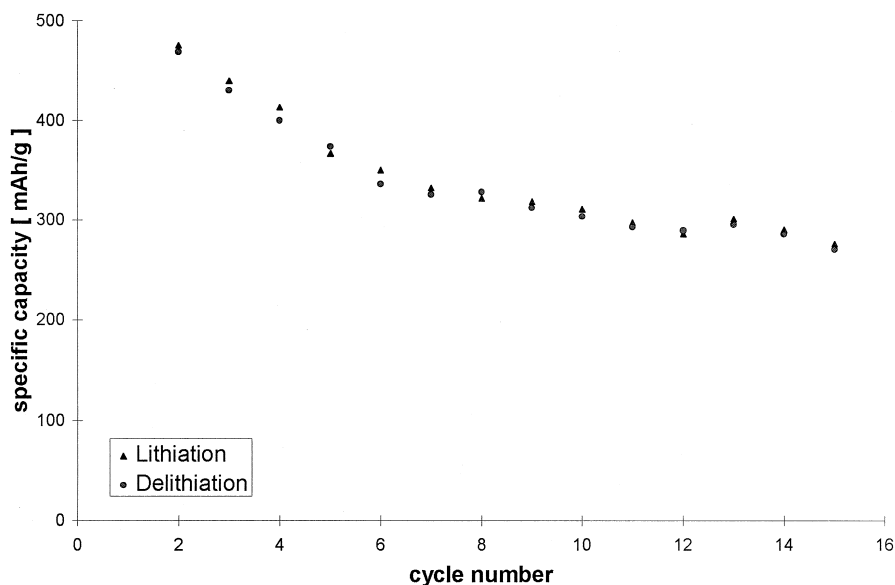


Fig. 3. Cycle test of an electrode from the material of phase  $\text{Li}_{21}\text{Si}_5$  over 15 cycles, current:  $C/60$ -rate.

Table 2

Summary of the reconstitution reactions as found from X-ray diffraction measurements after the chemical lithiation of  $\text{CrSi}_2$ 

Assumed chemical reactions	Found for initial stoichiometry ratio of $\text{Li}:\text{CrSi}_2$	Calculated capacity (mA h/g)	Experimental delithiation capacity (mA h/g)
Lithium intercalation into $\text{CrSi}_2$	up to 60:40	–	–
$15 \text{CrSi}_2 + 49 \text{Li} \rightarrow 3 \text{Cr}_5\text{Si}_3 + 7 \text{Li}_7\text{Si}_3$	75:25	669	–
$9 \text{CrSi}_2 + 35 \text{Li} \rightarrow 3 \text{Cr}_3\text{Si} + 5 \text{Li}_7\text{Si}_3$	80:20	771	496
$12 \text{CrSi}_2 + 65 \text{Li} \rightarrow 4 \text{Cr}_3\text{Si} + 5 \text{Li}_{13}\text{Si}_4$	85:15	996	682
$3 \text{CrSi}_2 + 21 \text{Li} \rightarrow \text{Cr}_3\text{Si} + \text{Li}_{21}\text{Si}_5$	88:12	1197	836

Also included are the nominal initial composition ratios of  $\text{Li}:\text{CrSi}_2$ .

Experimentally measured capacities are also listed.

### 3.2. The ternary lithium–chromium–silicon system

#### 3.2.1. Characterization of the materials

Lithium intercalation was found in the  $\text{CrSi}_2$  phase. The host  $\text{CrSi}_2$  diffraction pattern was still found up to a ratio of  $\text{Li}:\text{CrSi}_2$  of 60:40. A total of 10 samples in the composition range from  $\text{Li}:\text{CrSi}_2$  of 0:100 to 60:40 were prepared and a reproducible change of lattice constant of the  $\text{CrSi}_2$  substructure was observed. The lattice grows in the  $a$ -direction by about 0.15% and shrinks in the  $c$ -direction by the same amount. This is a typical behavior for an intercalation material.

For higher  $\text{Li}:\text{CrSi}_2$  ratios reconstitution reactions take place and evidence was found for the formation of the phases  $\text{Li}_7\text{Si}_3$  and  $\text{Cr}_5\text{Si}_3$ . The phase  $\text{Li}_{12}\text{Si}_7$  was not formed. This can be understood from the ternary phase diagram.  $\text{CrSi}_2$  first reacts to  $\text{Cr}_5\text{Si}_3$ . The phase  $\text{CrSi}$  was not found, as theoretically predicted. With increasing lithium content, the phase  $\text{Li}_{13}\text{Si}_4$  was formed. Then,  $\text{Cr}_5\text{Si}_3$  transforms to  $\text{Cr}_3\text{Si}$  and finally,  $\text{Li}_{21}\text{Si}_5$  is observed

at the highest lithium content. Ternary phases were not found in any of the samples. Table 2 summarizes the reconstitution reactions as found from the X-ray diffraction measurements. Included also are the nominal composition ratios of  $\text{Li}:\text{CrSi}_2$  at which the respective phases were observed.

Table 2 also showed theoretically calculated, as well as experimental capacities. The experimentally measured delithiation capacity of the highly lithiated ternary materials is about 2/3 of the theoretical capacity predicted from the assumed reconstitution reactions in all cases.

#### 3.2.2. Cycling behavior

The discharge capacities were dependent on the initial lithium content. This can be seen from Fig. 4 for highly lithiated samples. The discharge capacities here were between 661 and 811 mA h/g. It is interesting that the material with the highest initial lithium content did not show the highest capacity. Instead, the sample containing  $\text{Li}_{13}\text{Si}_4$  ( $\text{Li}:\text{CrSi}_2$ ; 85:15) showed the highest discharge

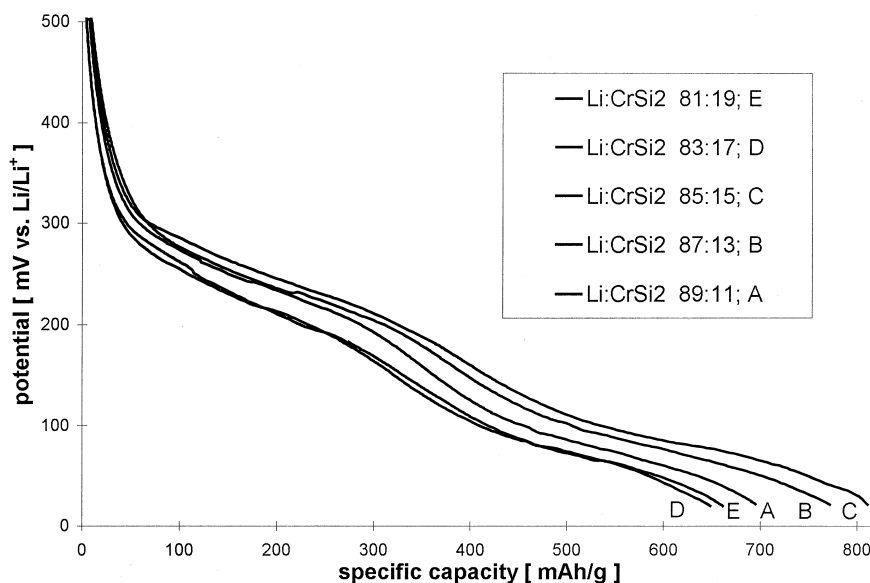


Fig. 4. Comparison of first lithiation curves for materials with  $\text{Li}:\text{CrSi}_2$  ratios between 81:19 and 89:11, measured at the  $C/60$ -rate.

capacity. The structure of the phase  $\text{Li}_{13}\text{Si}_4$  is evidently more stable than that of  $\text{Li}_{21}\text{Si}_5$ . Thus, loading and unloading of  $\text{Li}_{13}\text{Si}_4$  is easier while the structure of  $\text{Li}_{21}\text{Si}_5$  tends to fall apart on deintercalation of lithium.

The experimentally obtained reversible capacities of ternary samples were higher than for the binary lithium–silicon samples, although the theoretical capacities were much smaller. We propose that this is due to the  $\text{Cr}_x\text{Si}$  phases acting as a stabilizing conductive matrix in the electrodes. The reversible capacity for lithium being only due to the lithium–silicon phases in the samples. The chromium–silicon phases are electrochemically mostly inactive after the initial chemical lithiation process.

#### 4. Summary

Samples of the binary lithium–silicon and the ternary lithium–chromium–silicon systems were prepared. All four binary lithium–silicon-phases could be synthesized. All binary and ternary samples could be uniquely characterized by binary lithium–silicon and binary chromium–silicon phases. No ternary phases were observed.

Electrochemical experiments showed lithium intercalation behavior in the case of  $\text{CrSi}_2$ . The expected reconstitution reactions were only partly observed. The phases  $\text{Li}_{21}\text{Si}_5$  and  $\text{Li}_{13}\text{Si}_4$  showed intercalation behavior at 25°C, i.e., lithium is deintercalated from the host lattice of the silicon atoms. Equilibrium was found only in the sublattice of the lithium atoms.

Reversible capacities of up to 500 mA h/g were measured for highly lithiated binary materials. The area of initial stoichiometry which proved most reversible was between the stoichiometries  $\text{Li}_{1.0}\text{Si}$  and  $\text{Li}_{3.5}\text{Si}$ . The binary phase with the highest reversible capacity was  $\text{Li}_{13}\text{Si}_4$  and not  $\text{Li}_{21}\text{Si}_5$ , probably due to structural stability considerations. For ternary materials, reversible capacities of over 800 mA h/g were measured on materials containing  $\text{Li}_{13}\text{Si}_4$  as the active binary lithium–silicon phase. The higher reversible capacities for the ternary materials may be due to the  $\text{Cr}_x\text{Si}$  phases acting as a stabilizing conductive matrix in the electrodes.

The relatively good cycle stability can still be improved by using other electrode preparation techniques. Cycle life is apparently not limited by the reactive materials themselves but by changes in the microstructure of the materials.

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