



Title	Study on the Structure and Composition of Electrochemically Prepared Li-Si Alloys in Organic Solvents [an abstract of dissertation and a summary of dissertation review]
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Citation	北海道大学. 博士(理学) 甲第13365号
Issue Date	2018-09-25
Doc URL	<a href="http://hdl.handle.net/2115/71833">http://hdl.handle.net/2115/71833</a>
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Type	theses (doctoral - abstract and summary of review)
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# 学位論文内容の要旨

博士の専攻分野の名称

博士 (理学)

氏名 林 恵文

## 学位論文題名

Study on the Structure and Composition of Electrochemically Prepared Li-Si Alloys in Organic Solvents

(電気化学的に作製したLi-Si合金の有機溶媒における構造と組成に関する研究)

Si is one of the most promising candidates among all the studied anode materials for Li based secondary batteries due to its high theoretical capacity of  $3600 \text{ mAh}\cdot\text{g}^{-1}$  when a fully alloyed  $\text{Li}_{15}\text{Si}_4$  phase forms at room temperature. This capacity is almost ten times higher than that of graphite. It is important to study the structure and composition of the Li-Si alloys after Si alloying with Li, because they determine the battery performance such as the energy capacity and cycle life. Electrolyte solutions are considered as key factors that affect the structures and compositions of the Li-Si alloys, which then affect the energy capacity and cycle life of the Li based secondary batteries. Some electrolyte solvents enhance the Si based secondary battery performance. Therefore, it is important to make clear the effects of the solvents on the structure and composition of the Li-Si alloys.

The objective of this thesis is to determine the structures and compositions of Li-Si alloys prepared in different solvents using scanning electron microscopy (SEM), windowless energy dispersive spectroscopy (EDS) and soft X-ray emission spectroscopy (SXES). The windowless EDS was used to determine the Li distribution in Li-Si alloys and study the Si lithiation process. By using these techniques, the solvent effects on the Si lithiation were determined and discussed.

In Chapter 1, the backgrounds of the Li based secondary batteries, the anode materials and the Si anode are given. The structures and compositions of Li-Si alloys after Si electrochemical lithiation are briefly reviewed. The electrolytes used in Li based secondary battery are also reviewed for Si anode.

In Chapter 2, the experimental details are given, including the materials, electrochemical measurements, and Li-Si alloys preparation and characterization techniques.

In Chapter 3, the composition of the Li-Si alloy was studied using the high-energy resolution analysis of SXES and high spatial resolution analysis of windowless EDS. The Li  $\text{K}\alpha$ , Si  $\text{L}_{2,3}$  and Si  $\text{K}\alpha$  intensity changes determined by windowless EDS were analyzed to obtain the specific thicknesses and composition for the Li-Si alloy layers. The Li-Si alloy prepared after a charge density of  $1000 \text{ mC}\cdot\text{cm}^{-2}$  in  $1.0 \text{ M LiPF}_6$  in

DMC consist of an approximately 1.0  $\mu\text{m}$  thick crystalline  $\text{Li}_{15}\text{Si}_4$  alloy layer, a 1.5  $\mu\text{m}$  thick amorphous  $\text{Li}_{13}\text{Si}_4$  alloy layer, and a 2.2  $\mu\text{m}$  thick Li diffused  $\text{Li}_x\text{Si}$  alloy layer. The Li distribution in diffused  $\text{Li}_x\text{Si}$  alloy layer was determined by windowless EDS measurements.

In Chapter 4, the Si lithiation was studied. The structures and compositions of five Li-Si alloys (the charge densities are 20, 50, 120, 500 and 1000  $\text{mC}\cdot\text{cm}^{-2}$ ) were determined by using SEM, SXES and windowless EDS to study the Si lithiation process. Combined with in-situ synchrotron XRD measurements, the Si lithiation process was declared. Under potentiostatic charging, the cathodic current due to lithiation increased to a maximum value, and then decreased to a constant value. The crystalline  $\text{Li}_{15}\text{Si}_4$  layer started to grow along with the Li diffused  $\text{Li}_x\text{Si}$  layer until the lithiation current reached its peak. Thereafter the amorphous  $\text{Li}_{13}\text{Si}_4$  alloy started to grow.

In Chapter 5, the effects of FEC and HF on the structures and compositions of the Li-Si alloys were studied. The HF were found to be adsorbed on the Si surface. F adsorption made the surface potential more negative and was expected to increase the  $\text{Li}^+$  ion concentration on the surface, resulting in more pyramid nuclei formation on the surface. More pyramid nuclei formation resulted in smaller pyramid that covered the Si surface, i.e., thinner crystalline  $\text{Li}_{15}\text{Si}_4$  alloy layer. This explained the reason of FEC to improve the battery performance, since FEC can decompose to generate large amount of HF which can make the pyramid smaller.

In Chapter 6, the solvent effects on the structures and compositions of the Li-Si alloys were studied. The solvents (DMSO, TMS, TEGDME, EA, DMC, PC) were used to prepare the electrolytes of 1.0 M  $\text{LiPF}_6$  in different solvents. It already determined the Li-Si alloys consist of crystalline  $\text{Li}_{15}\text{Si}_4$ , amorphous  $\text{Li}_{13}\text{Si}_4$  and Li diffused  $\text{Li}_x\text{Si}$  alloy phases. The thickness of crystalline  $\text{Li}_{15}\text{Si}_4$  alloy layer in the Li-Si alloy decreased by the solvent order  $\text{DMSO} > \text{TMS} > \text{EA} > \text{TEGDME} > \text{DMC} > \text{PC}$ . However, the amorphous  $\text{Li}_{13}\text{Si}_4$  alloy layer increased by the above solvent order. Through the analysis on the relationship of the nuclei number density and the overpotential and the solvents, it was considered that the desolvation ability of the solvents played a significant role on the pyramid nucleation on the Si surface. The easier the solvated Li ion desolvate, the more pyramid nuclei formed. More pyramid nuclei formation resulted in smaller pyramid that covered the Si surface, i.e., thinner crystalline  $\text{Li}_{15}\text{Si}_4$  alloy layer.

In Chapter 7, the general conclusion of this thesis and future prospects are given.