

ナノ構造エネルギー変換貯蔵デバイスの非平衡電気化学プロセッシング

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Non-equilibrium Electrochemical Processing of Nano-structured Energy Conversion & Storage Devices

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ABSTRACT: Non-equilibrium electrochemical processing of ZnO nanowire arrays is engaged in Kyoto University. The gravitational level effect has been recognized in the uniformity of PL characteristics of electrodeposited ZnO nanowire arrays. Amorphous Si thin film has been also electrodeposited in ionic liquid(TMHA TFSI-0.1MSiCl₄) as well as PC organic electrolyte. Based on these achievements, the electrodeposition of Si nanowire is now challenging. Amorphous SiO₂ powder refined from diatomaceous earth (DE-SiO₂, 5N in purity) are pressed into pellets, and the electrolytic reduction of them is investigated in molten CaCl₂ at 1123 K. DE-SiO₂ pellets are successfully reduced to Si at 1.00 and 1.20 V vs. Ca²⁺/Ca. Rod-like nanostructure is observed in SEM of reduced Si sample. Furthermore, the reduction rate of DE-SiO₂ pellet is higher than that for fumed-SiO₂ pellet. DE-SiO₂ will be one of the most promising Si sources in the industrial-scale electrolytic reduction in both aspects of the reduction rate and the abundance of the resources.

Key words: Direct electrolytic reduction, Amorphous SiO₂ powder, Diatomaceous earth, Molten salts, Low-cost Si production

Introduction

The non-equilibrium electrochemical interfacial phenomena have been the good subjects to examine the gravitational effects on the materials tailoring. Many papers have been published in the international journal of electrochemical science and technology based on the experiments with JAMIC drop tower. That is, the electrodeposition and electrochemical dissolution of metals like Cu or Ag in aqueous electrolyte solution over 8

seconds are described as well as alkaline water electrolysis. Kyoto university research team is especially focusing the charging and discharging operation of advanced secondary battery installed in EV (electric vehicle) technology, because such operations indispensably correspond to the electrodeposition and electrochemical dissolution of metal negative electrodes. Surely, JAMIC is essentially good facilities to pursue or clarify the effects of gravitational level to the non equilibrium

electrochemical interfacial phenomena including nucleation and growth.

Now that, the nanotechnology is a key driving force in the advanced materials processing. It is essentially important to control the nucleation phenomena completely separated from the growth process. The electrochemical reaction is ideal to introduce such a situation, because the electronic circuit can control the reaction mechanism or rate by changing the electrode potential or current. Thus, the non equilibrium electrochemical processing of nanostructured devices is designed in the international space station to provide longer duration of microgravity environment.

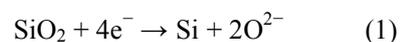
Moreover, the global environmental issue is the largest research subjects for modern scientists and engineers. Green energy technology must be supported by a possible materials tailoring technology to guarantee the huge production rate of Si solar cell backed up by stable and low cost supply system of natural resources. We have proposed a new electrochemical processing route stemming from the purification of diatomaceous earth (5N in purity). The electrochemical processing of Si is now focused in trimethyl-*n*-hexylammonium bis(trifluoromethylsulfonyl)imide (TMHATFSI).

This ionic liquid is one of the most popular hydrophobic room-temperature molten salts with high stability against the reduction reaction. Nonpolar tetrahedral symmetric SiCl₄ molecule as a Si precursor might be dissolved into this ionic liquid by van der Waals force acting between the hexyl group in TMHA⁺ cation and SiCl₄. Actually, 0.1 mol L⁻¹ SiCl₄ appears to be

completely dissolved in TMHATFSI. Moreover, the hydrophobic property of TMHATFSI is advantageous to hinder the hydrolysis of SiCl₄. Tetrachlorosilane (SiCl₄) is nonflammable, differently from hydride silanes such as SiH₄ and SiHCl₃. Therefore, SiCl₄ is selected as an appropriate Si source for Si electrodeposition.

A possible way to electrodeposit Si has been studied in trimethyl-*n*-hexylammonium bis(trifluoromethylsulfonyl)imide containing 0.1 mol L⁻¹ SiCl₄. Cyclic voltammetry suggests that SiCl₄ should be reduced to form Si around -2.0 V. Potentiostatic electrolysis at this potential forms a yellowish-brown film on a Ni substrate. X-ray photoelectron spectroscopy and Raman spectroscopy reveal that the electrodeposited film contains amorphous Si. It is also found from SEM observation and EDS analysis that highly uniform and dense thin film can be obtained in the initial stage of electrodeposition and that the electrodeposited Si film becomes rougher and thicker with the progress of electrolysis.

Now, we have proposed a novel reduction process of SiO₂,¹⁻³ based on our achievements. Solid-state SiO₂ is then electrochemically reduced to Si directly in higher temperature molten salt, as represented by



At 1123 K, Si behaves as an electric conductor. Hence, the electrochemical reaction in Eq. (1) continuously proceeds as far as the produced O²⁻ is removed from the reaction sites. More importantly, the Si produced in this process is expected to have the same purity as the starting SiO₂. So far, we have clarified the reduction

mechanism.¹⁻³ Fumed SiO₂ powder was investigated as a starting material.⁴ We also reported that solar grade SiO₂ (SOG-SiO₂) powder can be easily obtained by refining SiO₂ from diatomaceous earth in acidic and basic solution processes^{5,6} Diatomaceous earth originally contained high-purity amorphous SiO₂ in the frustules of fossil diatoms, which has been concentrated through a long-term decomposition process of organic substances in the diatoms. Its resource is abundantly distributed throughout the world, differently from the high-purity silica stones as a current SiO₂ resource. Other important features on the SiO₂ powder refined from diatomaceous earth (DE-SiO₂) are that it is amorphous, which may invoke the high reduction rate of SiO₂.

2. EXPERIMENTAL

CaCl₂ (300 g, 99.9%, Kojundo Chemical Laboratory Co., Ltd.) was used as an electrolytic bath. It was placed in a graphite crucible (90 mm in diameter and 100 mm in height, Tokai Carbon Co., Ltd.) and dried at a pressure less than 0.1 Pa at 473 K for 72 hours, subsequently at 773 K for 24 hours. All experiments were carried out at 1123 K under an Ar atmosphere in a sealed stainless steel holder and flange, which was sufficiently dried before installing the graphite crucible containing CaCl₂. The working electrode was made of a SiO₂ pellet and a Mo wire (0.2 mm in diameter, 99.95%, Nilaco Corp.) as an electron-conducting material. A SiO₂ pellet was prepared by compressing SiO₂ powder and sintering in a vacuum at 1273 K for 10 minutes in a high-frequency induction furnace (MU-1700, Sekisui Chemical Co., Ltd.).

Electric contacts were then formed by winding a Mo wire around the SiO₂ pellet. Two types of amorphous SiO₂ powders were used and compared: DE-SiO₂ (99.999%) and amorphous fumed-SiO₂ powder (99.999%, Kojundo Chemical Laboratory Co., Ltd.). All potentials reported in this paper were set with reference to that of the Ca²⁺/Ca electrode.

Samples were prepared by electrolysis at 1.00 or 1.20 V based on the previous cyclic voltammetric studies.^{1,4} Electrolysis was preformed with a potentiostat-galvanostat (HZ-3000, Hokuto Denko Co., Ltd.).

3. RESULTS AND DISCUSSION

Fig.1 shows XRD patterns of a pellet made of DE-SiO₂ (a) before and (b) after the electrolysis at 1.00 V for 60 minutes. The reference pattern of crystalline Si is also indicated in this figure as pattern (A). DE-SiO₂ is electrochemically reduced to form crystalline Si in molten CaCl₂.

Fig.2 compares SEM micrographs of pellets made of DE-SiO₂ and fumed-SiO₂ before and after the electrolysis at 1.00 V for 10 minutes. Fig.2 (a) and (b) depict the original pellets made of DE-SiO₂ and fumed-SiO₂, respectively. Fig.2 (c) and (d) show the electrochemically formed Si from DE-SiO₂ and fumed-SiO₂, respectively. In the case of DE-SiO₂, the electrochemically produced Si has a rod-like structure. Meanwhile, a plate-like Si is observed for the fumed-SiO₂. The structural difference observed in these two SiO₂ pellets is explained as follows. The reaction rate for electrolytic reduction of SiO₂ has been reported to be controlled by the diffusion of O²⁻ anions from the reaction

interface as far as electrons are successfully supplied to the interface.³ As seen in Fig.2 (a) and (b), the DE-SiO₂ pellet has larger and more definite pores than the fumed-SiO₂ pellet. In fact, the porosity [= 1 - (filling rate)] was higher for the DE-SiO₂ pellet than the fumed-SiO₂ pellet. As a result, the more porous SiO₂ pellet produces the more porous and lower density Si. Then, the reduction rate is expected to be higher for the DE-SiO₂ pellet due to the more favorable diffusion paths of O²⁻ anions. The combination of the higher reduction rate and the lower Si density suppresses the aggregation of the produced Si, which results in the formation of rod-like nanostructure.

From the above discussion, it is considered that the porosity of a SiO₂ pellet and the microstructure of SiO₂ powder are key factors in

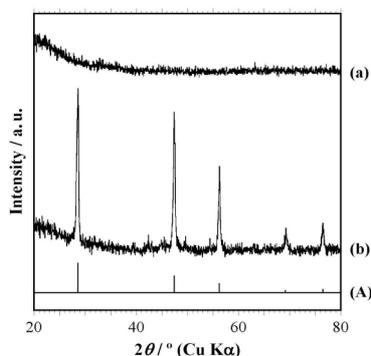


Fig.1 XRD patterns of a pellet made of DE-SiO₂ (a) before and (b) after the electrolysis at 1.00 V for 60 minutes in molten CaCl₂ at 1123 K. The reference XRD pattern of (A) Si (JCPDS no. 27-1402) is also shown for comparison.

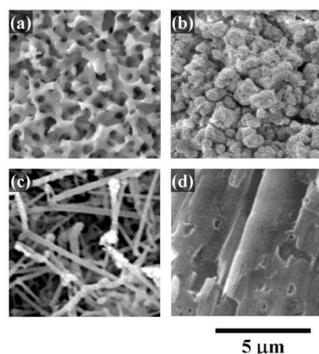


Fig.2 SEM images of pellets before and after the electrolysis at 1.00 V for 10 minutes in molten CaCl₂ at 1123 K. (a) Original DE-SiO₂, (b) original fumed-SiO₂, (c) electrolyzed DE-SiO₂, and (d) electrolyzed fumed-SiO₂.

improving the reduction rate and tailoring the microstructure of the produced Si for the electrolytic reduction of SiO₂ powders.

4. CONCLUSIONS

Direct electrolytic reduction has been successfully accomplished for pellets made of amorphous SiO₂ powders refined from diatomaceous earth in molten CaCl₂ at 1123 K. XRD and SEM analyses confirmed that DE-SiO₂ is electrochemically reduced to form crystalline Si having rod-like nanostructure. The reduction rate for the DE-SiO₂ pellet is accelerated by changing the electrode potential more negative. Furthermore, the reduction rate for the DE-SiO₂ pellet is higher than that for the fumed-SiO₂ pellet. The high reactivity of DE-SiO₂ and the evolution of rod-like structure are considered to be derived from its unique porous structure. DE-SiO₂ is regarded as a promising SiO₂ source in both aspects of the high reduction rate and the abundance of the resources when the industrial-scale electrolytic reduction is realized.

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