

A Novel Sodium Silicate Fluoride Solution and a H₂ Gas Formed by a Reaction Between Si and an Aqueous Solution of NaOH and NaF

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Oxidation of Si in an alkali solution has attracted much attention to produce hydrogen gas from Si wastes. It was found that hydrogen gas was generated from Si in NaOH and NaF solution with more than 10 times reaction rate than in the NaOH solution. The reaction by-product was a sodium silicate fluoride, Na_{x+z}Si_yO_{2y+x/2}F_z solution, and it proved to transform to a glass foam by boiling. The Raman spectrum suggested that the silicon and oxygen atoms in the silicate anions were arranged in a sheet-like structure. This may affect the behavior to form the glass foam.

I. Introduction

REGENERATION of energy from waste products has attracted much attention, for example, thermal power generation utilizing the combustion heat of urban garbage, CH₄ generation by fermenting kitchen refuse as biomass. Amorphous silica fume and the waste of silicon wafers are emitted in large quantities from the semiconductor industry. The reaction between ferrosilicon and alkali solutions is well known since the early 20th century, and H₂ gas production has been proposed based on the following equation:¹



The ΔH_{298} and ΔG_{298} of Eq. (1) are -423.8 and -470.8 kJ/mol, respectively. Although the thermodynamic parameters showed that the reaction proceeds, the reaction rate of the Eq. (1) is slow and insufficient for practical use. Because the reaction occurs at the solid/liquid interface between silicon and sodium hydroxide solution, the reaction rate depends on the surface area of the silicon, i.e., grain size and the concentration of the sodium hydroxide. An early researcher reported that it took ca. 30 min to obtain the theoretical amount of hydrogen gas using a ferrosilicon (Si, 88%) ground to pass a 100-mesh screen in a 20 wt% NaOH solution at room temperature.¹ The other researchers reported that it took 40 h to obtain 38% of the theoretical amount of hydrogen gas using a silicon waste powder in an alkali solution of pH 11 at 80°C.² In the reaction system, it was necessary to grind the silicon to a fine powder to increase the reaction rate, and using a silicon lump or wafer without grinding was unrealistic. In the present study, the reaction rate proved to increase drastically by addition of NaF in the reaction system in Eq. (1). A highly efficient H₂ gas formation from Si, NaOH, and NaF, and a novel sodium silicate obtained as a by-product are presented here.

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II. Experimental Procedure

An aqueous solution of NaOH and NaF was prepared by dissolving 150 g of NaOH and 20 g of NaF in 1000 g of water. All the experiments were performed using this solution. Three types of silicon, namely, Si powder through 100 mesh with purity of over 98%, Si lump with purity of over 98%, and silica fume emitted as a waste material from the semiconductor industry with the composition of Si: 95.5%, O: 2.5%, and C: 0.1% were used for the reaction with the aqueous solution.

Emission rate of hydrogen gas was measured by a mass flow meter, and a detecting tube was used for checking whether the emitted gas contained hydrogen fluoride or the other fluorides. Viscosity of the byproduct was measured by a rotational rheometer at 60 rpm. Surface tension was measured by the Du Nouy ring method. Melting point was determined by the differential thermal analysis (DTA).

III. Results and Discussion

Ten grams of the Si powder were added into 117 g of the aqueous solution of NaOH and NaF. A vigorous reaction like bumping started about 2 min after the mixing, and 8.2 L of hydrogen gas corresponding to the half of the theoretical amount was emitted in 1 min. The vigorous reaction was initiated at over 35°C. Once the reaction was initiated, the reaction proceeded vigorously because the reaction accompanied heat generation. The reaction rate was improved more than tenfold by adding NaF in the reaction system compared with the conventional one. In addition, it was confirmed that hydrogen fluoride or the other fluorides were not contained in the emitted gas.

One hundred grams of Si lumps were added into 1170 g of the aqueous solution of NaOH and NaF. The reaction occurred gradually at over 35°C, and the formation of bubbles of hydrogen gas was observed at solid/liquid interfaces. The temperature of the solution was in the range of 40°–50°C without heating or cooling. The emission rate of hydrogen gas was in the range of 80–160 mL/min. The emission rate depended on the temperature and the amount of unreacted Si and NaOH, and it can be controlled by adjusting temperature of the solution. The reaction ceased after ca. 20 h, and about 5 g of Si lumps remained unreacted. The remained Si was found to react with a new NaOH and NaF solution of the same initial component. This indicates that the reaction ceased because of the shortage of NaOH or NaF, and thus all the Si can be converted to the theoretical amount of hydrogen gas by renewing the solution. The present reaction system is advantageous because the lumps as well as the powders can be used for the production of hydrogen gas. This is the first report on using Si lumps in alkali solution for hydrogen gas generation.

Ten grams of silica fume were added into 117 g of the aqueous solution of NaOH and NaF. A vigorous reaction started in the same way as the Si powder, and 7.9 L of hydrogen gas was obtained in 1 min. My result indicates that the waste silica fume can be recycled as a fuel source using this reaction system.

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It was demonstrated that the oxidation of Si in alkali solution is promoted to a great extent by NaF. The following equation is considered to be one of the elemental processes in the reaction:



The ΔH_{298} and ΔG_{298} of Eq. (2) are -26.8 and -62.7 kJ/mol, respectively. One of the reasons why the oxidation of Si is promoted by NaF may be that NaOH is generated as a reaction product of Eq. (2). From the thermodynamic point of view, however, the reaction in Eq. (2) does not appear to be a vigorous reaction because the ΔH_{298} and ΔG_{298} values of Eq. (2) are smaller than those in Eq. (1). It is considered that NaF acts as a catalyst and lowers the activation energy of the reaction between Si and NaOH. In other words, the presence of NaF mainly affects the kinetics of the reaction. In addition, the emitted hydrogen gas is expected to be filled in a gas cylinder without pressurization operation because it can be emitted with high pressure.

The reaction by-product in the liquid phase was a pale yellow basic solution with viscosity of $18.5 \text{ mPa} \cdot \text{s}$, pH 11.3, $\rho 1.31 \text{ g/cm}^3$ at 20°C . This liquid contained ca. 40 wt% of solute, which is assumed to be a sodium silicate fluoride, $\text{Na}_{x+z}\text{Si}_y\text{O}_{2y+x/2}\text{F}_z$ akin to the conventional sodium silicate, $\text{Na}_x\text{Si}_y\text{O}_{2y+x/2}$ (water glass). The sodium silicate fluoride solution was found to exhibit an anomalous behavior, which has not been observed for the conventional sodium silicate solutions. The sodium silicate fluoride solution transformed to a glass foam like polystyrene foam by heating over 100°C (Fig. 1 inset). The density of the glass foam was $0.1\text{--}0.2 \text{ g/cm}^3$, and its compressive strength was $1\text{--}2 \text{ N/mm}^2$. The vesicant was water vapor contained as a solvent in the sodium silicate fluoride. Bubbles of water vapor were formed in the solution by a boiling, and they were difficult to collapse around 100°C . After almost all of the solvent was vaporized, the solute forms the glass foam reflecting the bubbles in boiling. Furthermore, when the solution was sprayed into a hot wind ($160^\circ\text{--}180^\circ\text{C}$), microballoon ($10\text{--}100 \mu\text{m}$), or microfilm of sodium silicate fluoride was formed (Fig. 1). Stability of foam or balloons is generally due to high surface activity and low fluidity of liquids. The surface tension and the viscosity of the solution were 67.6 mN/m and $16.6 \text{ mPa} \cdot \text{s}$ at 25°C , and they changed to 50.4 mN/m and $8.0 \text{ mPa} \cdot \text{s}$ at 60°C , respectively. The behaviors to form a foam or balloons may be ascribed to the high viscosity and low fluidity of the concentrated solution after the evaporation of water. Figures 2(a) and 2(b) show the SEM images of the glass foam obtained by heating in an oven at 120°C and 180°C , respectively. The property of film formation is observed in Fig. 2(b), and their morphology is greatly different from the conventional sodium silicate. DTA analysis indicated that the

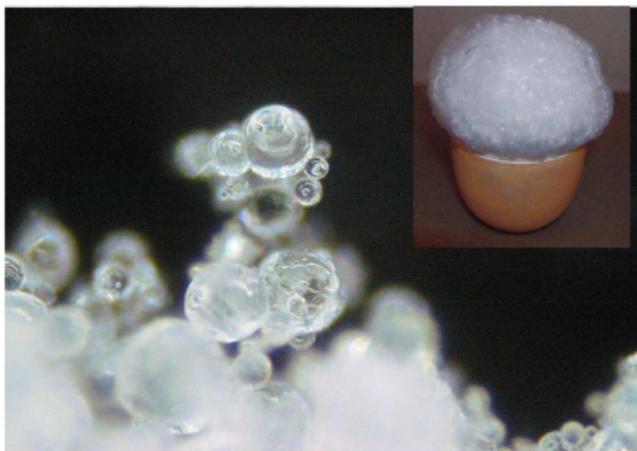


Fig. 1. Optical microscope image of microballoon obtained by spraying the sodium silicate fluoride into a hot wind, and appearance of glass foam obtained by heating the sodium silicate fluoride in an oven at 180°C (inset).

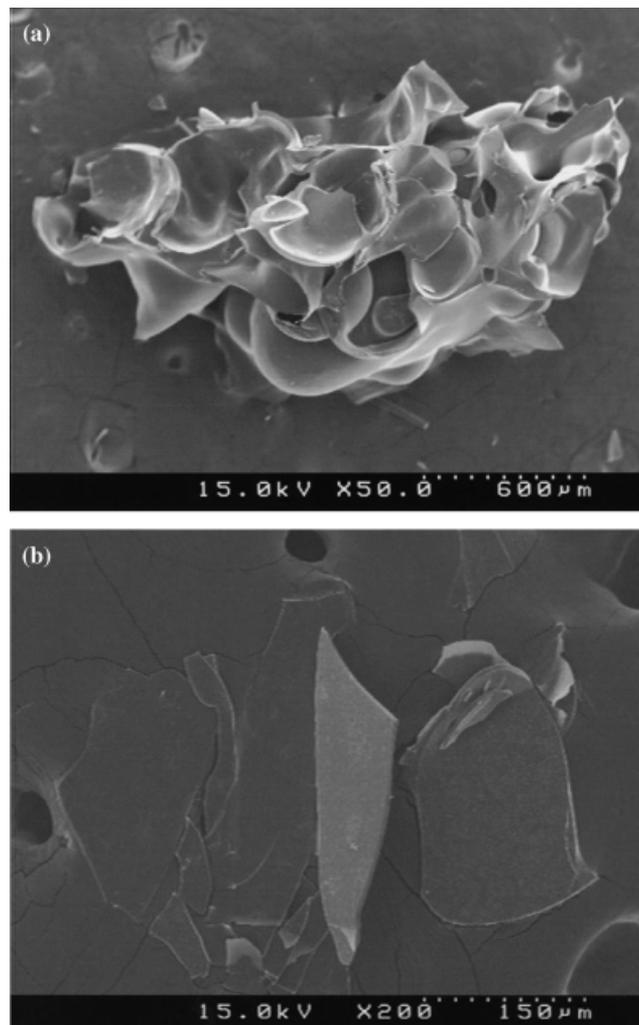


Fig. 2. SEM images of glass foam obtained by heating in an oven at (a) 120°C and (b) 180°C .

melting point of the glass foam was 790°C . The glass foam was soluble in hot water ($70^\circ\text{C} \sim$), and the solution transformed to the glass foam by heating again.

Raman spectrum of the sodium silicate fluoride is shown in Fig. 3. Peaks were observed at 600 , 786 , 1057 , and 1657 cm^{-1} . According to McMillan, the structural units in silicates glasses can be distinguished based on Si-O stretching frequencies in Raman spectra: four terminal oxygens (SiO_4^{4-}), $\sim 850 \text{ cm}^{-1}$; three terminal oxygens ($\text{Si}_2\text{O}_7^{6-}$), $\sim 900 \text{ cm}^{-1}$; two terminal oxygens ($\text{Si}_3\text{O}_9^{6-}$, chains), $950\text{--}1000 \text{ cm}^{-1}$; and one terminal oxygen

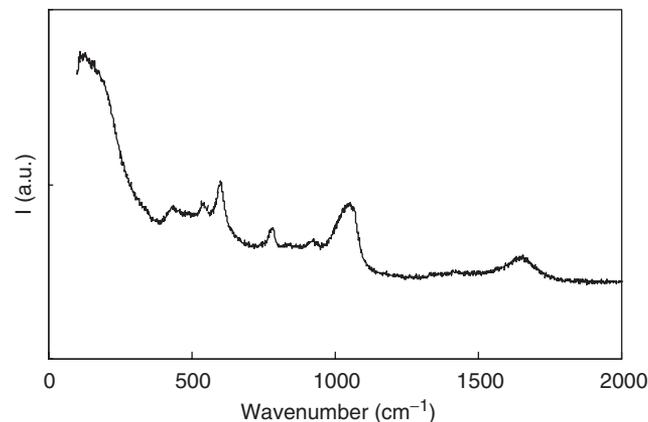


Fig. 3. Raman spectrum of the sodium silicate fluoride solution (38 wt%).

(sheets), $1050\text{--}1100\text{ cm}^{-1}$.^{3,4} The largest peak observed at 1057 cm^{-1} can be assigned to one terminal oxygens in sheets, and this suggests that the silicon and oxygen atoms in the present silicate anions are arranged in a sheet-like structure unlike the conventional sodium silicate. The anomalous behavior to form the stable glass foam may reflect the sheet-like structure of the silicate anions.

IV. Summary

Hydrogen gas was produced by oxidation of Si in NaOH and NaF solution with more than 10 times reaction rate than in the NaOH solution. The reaction by-product was a sodium silicate fluoride, $\text{Na}_{x+z}\text{Si}_y\text{O}_{2y+x/2}\text{F}_z$ solution with viscosity of $18.5\text{ mPa}\cdot\text{s}$, pH 11.3, $\rho\ 1.31\text{ g/cm}^3$ at 20°C . This solution transforms to a glass foam by boiling because the bubbles containing water vapor are difficult to collapse due to special property of the solute. The Raman spectrum suggests that the silicon and oxygen atoms in the silicate anions are arranged in a sheet-like structure. The behavior to form the glass foam may reflect the sheet-like structure of the anions. It is expected that silica fume and silicon waste will be recycled as hydrogen sources, and thus silicon will be an

intermediary between renewable energy and hydrogen based on the reaction. Furthermore, the sodium silicate fluoride obtained as a by-product can be used as a fire extinguisher and as a neutralizer for acidic gases in flues of incinerators of urban garbage.

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References

- ¹E. R. Weaver, "The Generation of Hydrogen by the Reaction Between Ferrosilicon and a Solution of Sodium Hydroxide," *J. Ind. Eng. Chem.*, **12**, 232–40 (1920).
- ²M. Terano, T. Sugino, and R. Muratsubaki, "Apparatus and Methods for Hydrogen Production," *Jpn. Kokai Tokkyo Koho JP*, **191303** (2000).
- ³K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part A, 5th edition; pp. 257–61. John Wiley & Sons, New York, 1997.
- ⁴P. McMillan, "Structural Studies of Silicate Glasses and Melts—Applications and Limitations of Raman Spectroscopy," *Am. Miner.*, **69**, 622–44 (1984). □