Original Article

Application of lithium-silicate based oxynitrideglass into pH-responsive glass for improvement of responsibility and stability

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Abstract

A pH glass electrode is made of lithium-rich special glass, and the durability is often inferior in comparison with general hard glass. The glass electrode is often used under strong alkalinity or acidic conditions, wherein the electrode has an extremely short life. In recent years, oxynitrideglasses have been reported, in which a part of oxygen in the glass structure was replaced with nitrogen, for superior durability in strong acid and strong alkaline solutions. In this study, Li_2O-SiO_2-Si_3N_4 glass was prepared, and the possibility of the application as the pH responsive glass was checked. As a result, the new glass electrodes showed good response time for pH standard as short as ten seconds. Furthermore, its sensitivity between pH 4 and pH 9 was more than 97 % against theoretical value. The glass showed approximately half of silicon and lithium elution in alkaline solution for the chemical durability, compared with traditional pH responsive glass.

Key words
lithium-silicate based oxynitrideglass, pH-responsive glass, responsibility, stability, chemical durability

1. Introduction

The reliable and accurate measurement of the pH value in chemical, biological, clinical, industrial and environmental samples is of great importance (Ertürün et al., 2015). The pH measurements are generally performed by use of glass electrodes that are known very reliable, selective and have very wide dynamic range.

When the pH glass electrode is often used in the water samples with severe conditions containing strong or alkaline, its pH response and chemical durability are necessary for most satisfactory. For such examples, the improvement of a pH glass electrode has been needed (Cremer, 1906; Yuqing et al., 2005; Scholz, 2011).

However, there are extremely few studies to enhance pH response of the glasses by adding an ion. There seems to be no report to use the oxynitrideglasses which is replaced a part of oxygen with nitrogen as pH responsive glass. The oxynitrideglass was reported for the lithium silicate type by Sakka (1986), Unuma and others (1987; 1988), and the oxynitrideglasses provided the improvement for the chemical durability, physical strength and low resistance.

Because the oxynitrideglass composition is similar to pH responsive glass, these oxynitrideglasses can expect pH responsiveness. In other words, an extension of life of the pH electrode can be expected if the oxynitrideglasses as a pH glass electrode are used. Therefore, lithium silicate oxynitrideglasses were manufactured by fusion method, and pH-responsiveness and the chemical durability were evaluated for the glass specimens. Finally, the possibility of the application to a pH electrode was checked.

2. Experimental

2.1 Fabrication of the oxynitrideglasses

Firstly, oxynitrideglasses of Li_2O-SiO_2 having the possibility for the pH response were manufactured based on a report by Sakka et al. (1986). The pH responsive glasses was prepared by using normal fusion method. SiO_2, Li_2CO_3, $CsNO_3$, $BaCO_3$, and Y_2O_3 (Nacalai Tesque) were equally mixed with parchment paper. These powders were put in a platinum melting pot, melted at 1400 °C for three hours and stirred with a platinum stick hourly. The molten glass was cast as a metal board, and it was made caret materials of the pH responsive glass. After this was crushed thoroughly and mixed with powder of Si_3N_4 enough, these were put in a zirconia crucible. This was burnt in nitrogen atmosphere bottom, at a temperature of 1400-1450 °C during 1-3 hours and it was cast as an iron plate quickly and pressed. The glasses were cut, and the part in which surface nitrogen vaporized were removed and they were considered to be the glasses board of approximately 40 mm × 50 mm × 1 mm. The manufactured glass composition is shown in Table 1. The pH responsive glasses composition that was added with the rare-earth element was tried by adding nitrogen (Nishio, 2015). Content of nitrogen of those glasses were checked by the Kjeldahl method.

Table 1: Composition of starting materials

	SiO_2	Li_2O	Y_2O_3	La_2O_3	Cs_2O	BaO	Ta_2O_5	Si_3N_4
OX-1A	67.0	30.0	–	–	–	–	–	1.0
OX-2A	61.5	30.0	1.0	3.0	–	–	–	1.5
OX-3A	58.5	30.0	1.0	3.0	–	–	–	2.5
OX-3B	59.5	28.0	1.0	3.0	2.0	2.0	–	1.5
Y7	26.0	26.0	1.0	3.0	2.0	2.0	2.0	–

Note: The value is mole percent.

2.2 Performance evaluation of the pH responsive glasses

2.2.1 Sensitivity, Asymmetric potential, the responsive measurement

The oxynitride pH responsive glass, that was manufactured in this work, was glued together with epoxy based adhesive (Spar X made in Cemedine, Co., Ltd.) by a cell made by vinyl chloride such as in Figure 1. KCl solution of the silver saturation was poured into the cell inside and silver-argentic chloride inserted, and the working electrode was made. The reference electrode used double junction sleeve model #2565-10C (Horiba, Co., Ltd.) using the silver-argentic chloride pole. The pH standard solution (pH = 4, 7, 9) dissolved powder #150-4, #150-7, #150-9 (Horiba, Co., Ltd.) in high purity water. These standard solutions were kept with a constant temperature water at 25 °C. Those electrodes were connected to pH F-55 (Horiba, Co., Ltd.), and electric potential was measured.

The experiment system is as follows. Sensitivity:

Ag/AgCl, 3.3 mol/L KCl, Ag saturated solution | 3.3mol/L KCl | sample solution | pH responsive glass | 3.3 mol/L KCl, Ag saturated solution, neutrality phosphate, Ag/AgCl

Those electrodes were immersed in pH 4, pH 7 and pH 9 standard solutions, and sensitivity was calculated from the electromotive force after three minutes. Temperature of the solution reaches the theory electromotive force per 1 pH with 59.16 mV at the time of 25 °C than an expression of the Nernst. Furthermore, the sensitivity is defined as the following expressions when two kinds of standard solution a and b, respectively are assumed.

$$\text{Sensitivity}\,(\%) = \frac{-(E_b - E_a)}{(pH_b - pH_a) \times 2.3026\,(RT/F)} \times 100$$

Asymmetric potential: The asymmetric potential was assumed when the electromotive force was measured as standard solution 7. The coefficient of thermal expansion measurement was measured using a coefficient of thermal expansion meter (Rigaku, Co., Ltd. TDL-8411).

2.3 Chemical durable evaluation using the glass specimen

The durable test method of glass samples referred to the study of Sakka (1986). The caret specimens of OX-1A, OX-2A, OX-3A, OX-3B and Y7 were polished by #800, and the thickness was 0.5 mm. Furthermore, they were cut to 5 mm in square. One hundred ml of NaOH solution (0.1 mol/L) was poured into the container made of polypropylene. Next, those glass specimens were bound with a thread of PTFE, and fixed to the cover of the container. The glass specimens were immersed in a state of hanging in midair, and sealed (Figure 2). The containers were fixed in a constant temperature concussion water tank (product made in Waken Yaku, Co., Ltd.

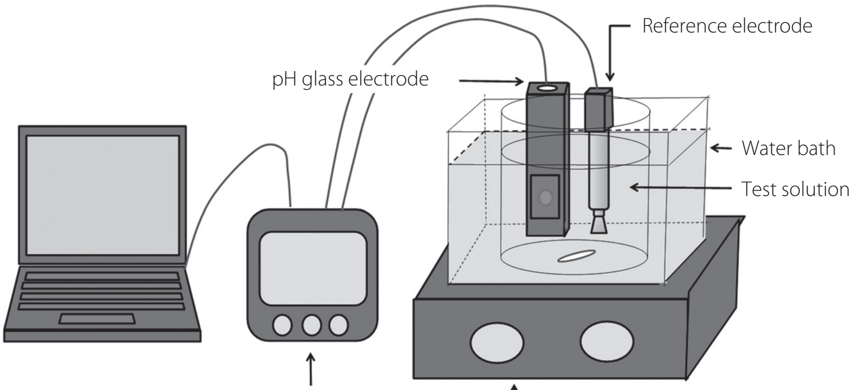


Figure 1: Potentiometric measurement system for pH responsive glasses

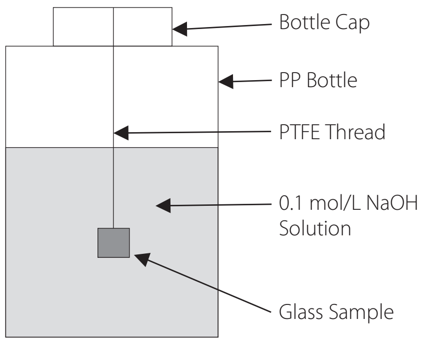


Figure 2: Experimental system for chemical durability

Petit bus shaker MODEL2220), and the samples were shaken at 40 °C for 20 days. The sample concentrations of Si and the Li were measured by ICP emission spectrometry (ULTIMA, Horiba, Ltd.) after a concussion examination of glass.

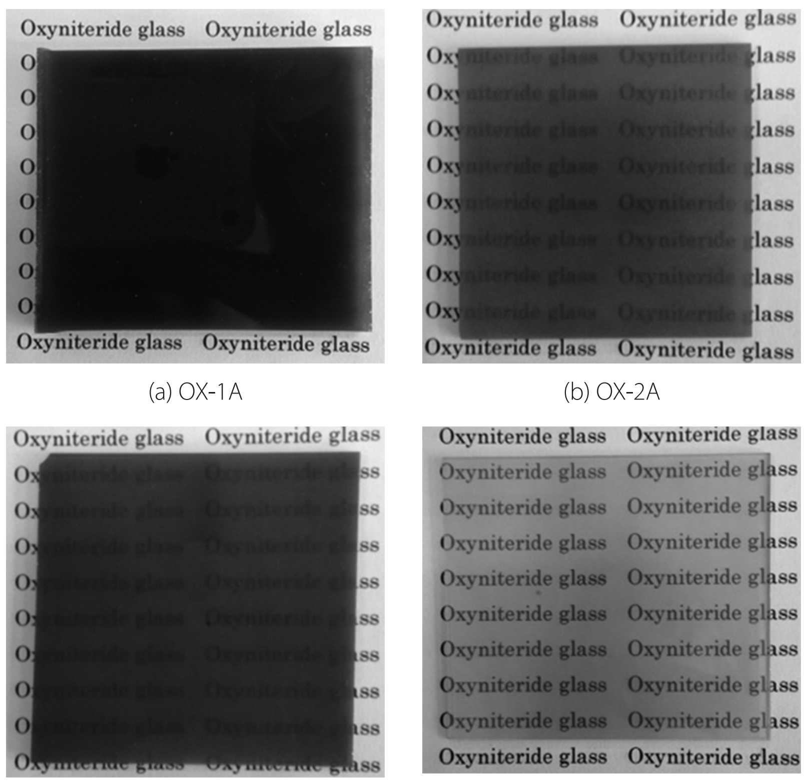
3. Result and discussion

3.1 Composition of the pH responsive glass

The photographs of OX-1A, OX-2A, OX-3A and the OX-3B samples for oxynitrideglasses are shown in Figure 3 (a)-(d). The glass samples produced experimentally were all gray glass, but OX3-B was almost transparent. It is reported in the coloration of glass samples by Messier and Deguire (1984). Similarly, it seems that it was colored by separation of silicon. The result of nitrogen content is shown in Table 2, which was checked by the Kjeldahl method. The content of N_2 was 0.88 mol% whereas training composition of Si_3N_4 was 1 mol% in OX-1A. Therefore, it is thought that the result was 0.12 mol% of N_2 in the case of fusion and the cast. The content of nitrogen of OX-2A, OX-3A and OX-3B was 1.28 mol%, 2.02 mol% and 1.06 mol%, respectively. A similar tendency was seen in these glasses. OX-3A contained nitrogen in the glass samples, and the content was 2.02 mol%. The glasses contained 0.88-2.02 mol% of nitrogen.

3.2 pH responsive evaluation

Sensitivity of each pH responsive glass, asymmetric potential, the results of the coefficient of thermal expansion are shown in Table 2. The sensitivity of each glass was more than 97.3 %. Particularly, not only sensitivity was more than 98.5 %, but also asymmetric electric potential was 11 mV. The OX-3B sample equalled a commercial glass electrode as a result of level. On the other hand, other glass samples occurred at more than 54.4 mV, and asymmetric electric potential was 78.3 mV in the case of OX-1A. It is thought that the degree of the color (quantity of silicon) is related with this reason. The silicon in glass is distributed heterogeneously so that the coloration is strong. It is thought that the asymmetry potential was produced by silicon. Therefore, as OX-3B was superior in transparency, it is thought that there became little asymmetric electric potential. The thermal expansion coefficient of glass samples was 95.4-100.3/°C, and it seems that it can be equalled to a lead-free glass tube such as commercial PS-94



(a) OX-1A (b) OX-2A

(c) OX-3A (d) OX-3B

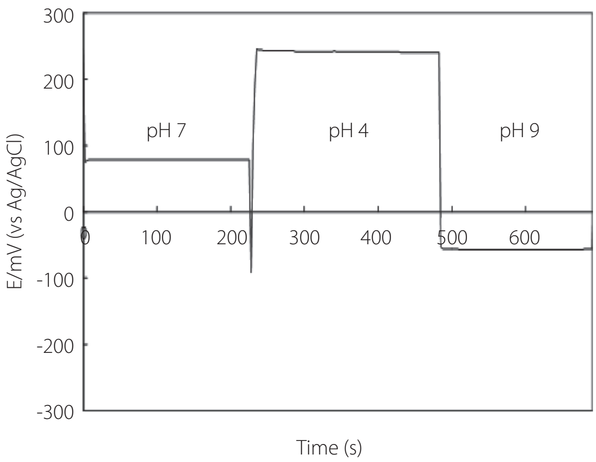
Figure 3: Photographs of oxynitrideglasses

Table 2: Nitrogen content and pH responsive performance

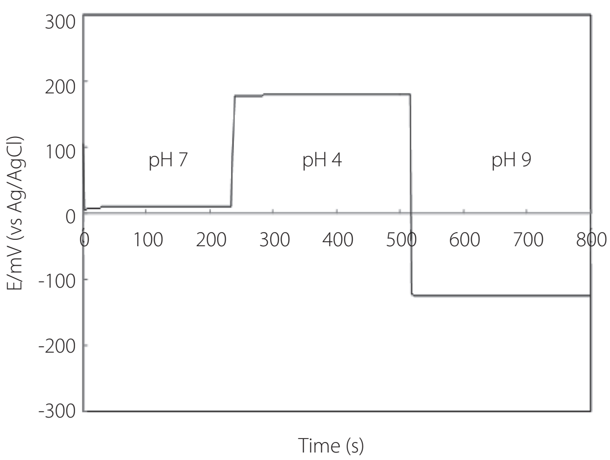
	N_2 mol%	Sensitivity (4-7) (%)	Sensitivity (7-9) (%)	Sensitivity (4-9) (%)	Asymmetry Potential (mV)	Coefficient of thermal expansion α
OX-1A	0.88	96.7	98.0	97.3	78.3	96.5
OX-2A	1.28	97.5	100.5	98.8	54.5	97.5
OX-3A	2.02	99.6	98.7	99.2	59.8	95.4
OX-3B	1.06	99.8	98.5	99.2	11.0	100.3

(Nippon Electric Glass, Ltd.) (Table 2).

Then, the pH responsiveness of the glass electrode using the OX-1 sample was measured. Figure 4 (a) is the responsiveness curve that was measured in order of standard solutions of pH 7, pH 4, and pH 9. For response time of each standard solution, the response time before reaching ±1.5 mV of the electric potential level after three minutes was less than ten seconds. This result showed the responsiveness was equal to commercial pH responsive glasses. In addition, for the glass electrode to each standard solution after the dipping, the electric potential change between 60 seconds and 180 seconds was less than ±3 mV. A drift could not been seen. Similarly, the responsive curve of the OX-3B sample is shown in Figure 4 (b). For OX-3B sample, the electric potential change between 60 sec and 180 sec was also less than ±3 mV. A drift was not seen. Therefore, the OX-3B sample was able to confirm that it is useful as pH responsive glass. From these results, it was suggested that the oxynitrideglasses were applicable to the pH responsive glass electrodes.



(a) OX-1A



(b) OX-3B

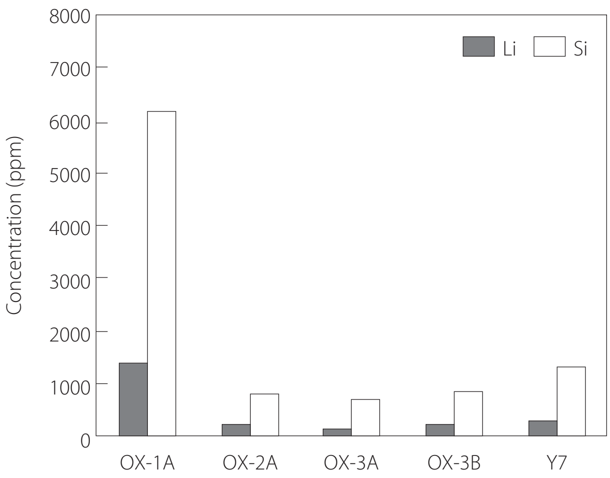
Figure 4: pH response curves

3.3 Chemical durable evaluation using the glass specimen

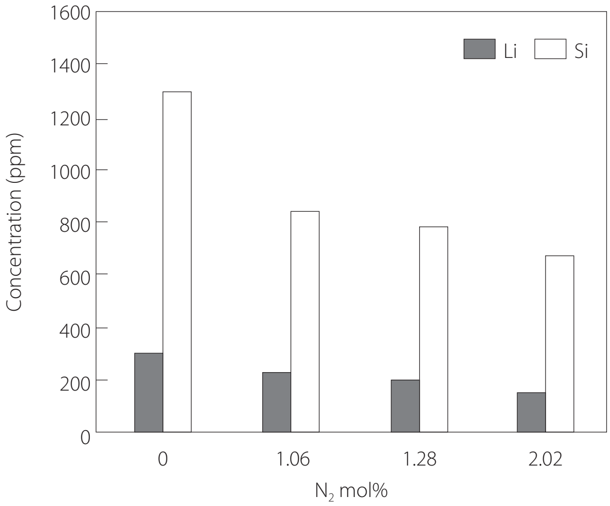
The glass specimens made in this study were immersed in a sodium hydroxide solution of 0.1 mol/L at 40 °C for 20 days. For the results of having measured the eluted metal ions by ICP, it is shown in Figure 5 (a). OX-2A, OX-3A and OX-3B were a little quantity of elution of Si and Li, compared with conventional pH responsive glass Y7. OX-1A was 6,200 ppm and a little less than 7 times concentration, whereas Si of other glass was 800-1500 ppm. As for the quantity of elution of the Li, OX-2A, OX-3A, OX-3B were 100-200 ppm likewise, but OX-1A was 1,300 ppm and a little less than 10 times concentration. It is reported that OX-1A includes alkali such as the La according to many composition ratios of SiO_2 and the report of Perley (1949) that water resistance increases. It seems that a difference occurred to the concentration by the durability alkali. The result that plotted N_2 content and OX-2A, OX-3A, OX-3B and Y7 elution amounts are shown in Figure 5 (b) except for OX-1A. As content of the N_2 increased, quantity of elution of Si and the Li was inversely proportional and decreased. In Glass Y7 which did not include N_2, the elution amounts of Si and Li were 1300 and 300 ppm, respectively. For OX-3A where approximately 2 mol% N_2 was included, the elution amounts of Si and Li were near 700 and 100 ppm, respectively. From the results, the glass frame is strengthened by including N_2, and it is thought that durability increased.

4. Conclusion

The oxynitrideglasses were manufactured for the purpose of pH resonsive glass. It was suggested that the oxynitrideglasses had pH response performance. In addition, not only sensitivity, and coefficient of thermal expansion were practical, but also, for the manufactured oxynitrideglasses, the re-



(a) Oxynitrideglasses and general glass



(b) Comparison between N_2 content and eluted content for Li and Si

Figure 5: Elution of Li and Si

sult showed responsiveness and the durability are practical. It was able to confirm that oxynitrideglass was useful as the pH glass membrane. It seems that oxynitrideglass contributes to the development of pH responsive glasses.

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