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Research Paper

Effect of glass former (B_2O_3, SiO_2, GeO_2 and P_2O_5) addition to Fe_2O_3-Bi_2O_3 glass on pH responsivity

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ABSTRACT

The effect of glass former (constituent capable to vitrify by itself such as B_2O_3, SiO_2, GeO_2 and P_2O_5) addition to Fe_2O_3-Bi_2O_3 (FeBi) glass on pH responsivity (pH sensitivity and pH response time) was investigated in order to develop novel pH responsive, hydrophobic glasses. Additionally, the effect of glass composition on pH sensitivity of Fe_2O_3-Bi_2O_3 glasses was investigated in order to develop contaminant-free reference electrodes with very low pH sensitivity. A small amount of B_2O_3 and SiO_2 drastically increased the pH sensitivity. The addition of glass formers of 20 mol% provided high pH sensitivity (>90%) in any of the glass formers. Although all glass formers increased their contact angle with water for Fe_2O_3-Bi_2O_3 glass, the addition of GeO_2 was most effective. Most of the Fe_2O_3-Bi_2O_3-GeO_2 (FeBiGe) glasses with 20–30 mol% GeO_2, which serve as a working electrode, had compatibility between high pH sensitivity and a high contact angle with water (100°). However, certain Fe_2O_3-Bi_2O_3 glasses with approximately 20 mol% Fe_2O_3 showed low pH sensitivity (<10%). These FeBi glasses are considered to serve as contaminant-free reference electrodes, whereas KCl aqueous solution, as a contaminant, gradually leaks in commercial reference electrodes (Ag/AgCl immersed in KCl aqueous solution). Since the novel pH complex glass electrodes, consisting of a FeBiGe working electrode and a FeBi reference electrode, resist fouling of itself and serve as contaminant-free glass electrodes, these electrodes are expected to be highly useful in biological systems and drug development.

1. Introduction

Important customer issues with pH measurement are a decrease in pH sensitivity and an increase in pH response time, which primarily arise from the contamination of the responsive glass membrane and liquid junction and from the change in concentration of the internal liquid [1]. To avoid these issues, customers should maintain their pH glass electrodes. This maintenance is troublesome and requires significant cost, specifically in industrial uses because it is not easy to remove the accumulated stain from pH glass electrodes. For this reason, we have developed novel pH glass electrodes, such as a TiO_2-coated commercial pH glass electrode [2,3] and Ti^{3+}-containing TiO_2-P_2O_5 (TP) glasses [4–7], with a self-cleaning property based on photocatalytic activity and photoinduced hydrophilicity [8].

Alternatively, Bi_2O_3-B_2O_3 (BiB) glasses are relatively hydrophobic and are expected to show an anti-fouling effect [9]. However, BiB glasses were unsuitable for pH responsive glasses because they have high electrical resistivity. Accordingly, Fe_2O_3-Bi_2O_3-B_2O_3 (FeBiB) glasses were developed as novel pH responsive glasses with an anti-fouling property that was based on their hydrophobicity [10]. FeBiB glasses showed a pH sensitivity close to that of commercial pH responsive glass and a shorter pH response time (10 s) compared to that of a commercial glass (30 s). This quick pH response of FeBiB glasses is based on "electronic conduction" that is different from the "ionic conduction" present in commercial lithium silicate glasses. Fe_2O_3 and Bi_2O_3 in FeBiB glasses play an important role in electrical conduction in the bulk glass and in the pH response and hydrophobicity, respectively. Furthermore, we reported that the pH sensitivity of Fe_2O_3-Bi_2O_3 (FeBi) glass was very low, and FeBiB glasses drastically increased with increasing B_2O_3 content [11]. A moderate amount of Fe_2O_3 and a small amount of B_2O_3 produced bulk electronic conduction and a pH response on glass surfaces. Since the remaining components of the glass can be selected freely, this discovery could prove to be highly useful

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in developing novel pH glass electrodes that are self-cleaning and resist fouling. Thus, a small amount of so-called "glass formers" may strongly affect pH sensitivity. However, the influence of other glass formers on pH sensitivity and the effect of the composition on pH sensitivity of FeBi glasses besides 20Fe80Bi glass have not been clarified. Very recently, we have developed 3d-block metal oxide-coated, stainless-steel electrodes for disposable pH sensors as another approach to maintain clean pH electrodes [12].

Our previous studies on working electrodes has been described above; however, there still remains a problem for reference electrodes. Common commercial reference electrodes consist of an Ag/AgCl electrode as an internal electrode and KCl aqueous solution as an internal solution. Proper functioning of the electrode requires leakage of the KCl aqueous solution to allow for electrical contact between the internal solution and test solution. As a result, a small amount of the internal KCl aqueous solution becomes contaminant for the test solution, and a refill of the KCl aqueous solution is necessary.

In the present study, the effect of glass former (B_2O_3, SiO_2, GeO_2 and P_2O_5) addition to FeBi glass on pH responsivity (pH sensitivity and pH response time) was investigated in order to develop novel pH responsive hydrophobic glasses. Specifically, compatibility between high pH sensitivity and high contact angle with water for Fe_2O_3-Bi_2O_3-GeO_2 (FeBiGe) glasses were the primary focus. Additionally, the composition effect on the pH sensitivity of FeBi glasses was investigated in order to develop contaminant-free reference electrodes with very low pH sensitivity.

2. Experimental

$20Fe_2O_3\cdot(80\text{-}y)Bi_2O_3\cdot yM_aO_b$ (20Fe(80-*y*)Bi*y*M, M = B, Si, Ge and P, *y* = 0–20 mol%), $xFe_2O_3\cdot(100\text{-}x\text{-}y)Bi_2O_3\cdot yGeO_2$ (*x*Fe(100-*x*-*y*)Bi*y*Ge, *x* = 10–25 mol%, *y* = 0–40 mol%) and $xFe_2O_3\cdot(100\text{-}x)Bi_2O_3$ (*x*Fe(100-*x*)Bi, *x* = 15–25 mol%) glasses were produced by a conventional melt-quenching method. The following reagents were used as received; Fe_2O_3 (99.9%, Kojundo Chemical Lab. Co., Ltd., Sakado, Japan), Bi_2O_3 (99.9%, Kojundo Chemical Lab. Co., Ltd., Sakado, Japan), B_2O_3 (99.9%, Kojundo Chemical Lab. Co., Ltd., Sakado, Japan), SiO_2 (99.9%, Kojundo Chemical Lab. Co., Ltd., Sakado, Japan), GeO_2 (99.995%, Kojundo Chemical Lab. Co., Ltd., Sakado, Japan) and $NH_4H_2PO_4$ (99.0%, guaranteed reagent grade, Nacalai Tesque, Inc., Kyoto, Japan). 30 g batches in alumina crucible with cap were directly heated at 1100 °C for 1 h without mixing of melts. The melts obtained were pressed by stainless steel heated at 100 °C and then annealed at 350 °C for 1 h. For example, $20Fe_2O_3\cdot50Bi_2O_3\cdot30GeO_2$ glass was abbreviated to 20Fe50Bi30Ge as a sample name.

Potentiometric measurement for the *x*Fe(100-*x*-*y*)Bi*y*M glasses was carried out at 25 °C and, at time intervals of 3 s and 0.5 s using a pH meter F-73 (HORIBA, Ltd., Kyoto, Japan) and a portable multi-logger ZR-RX20 (OMRON Corp., Kyoto, Japan) equipped with a handmade cell with a glass plate of 1 mm thickness (Fig. 1). An *x*Fe(100-*x*-*y*)Bi*y*M pH glass electrode with Ag/AgCl electrode as an internal electrode and with KCl buffer solution as an internal solution was used as a working electrode. Electrode 2565 (HORIBA, Ltd., Kyoto, Japan) consisting of Ag/AgCl electrode as an internal electrode and KCl aqueous solution as an internal solution was used as a reference electrode. Potentiometric measurement of three cycles was run in order of pH 6.86 (150-7, monopotassium phosphate and disodium phosphate, HORIBA, Ltd., Kyoto, Japan, abbreviated as pH 7), pH 4.01 (150-4, potassium hydrogen phthalate, HORIBA, Ltd., Kyoto, Japan, abbreviated as pH 4) and pH 9.18 (150-9, sodium borate, HORIBA, Ltd., Kyoto, Japan, abbreviated as pH 9) according to JIS Z 8805. Potentials after 3 min in the third cycle at pH 7, pH 4 and pH 9 were read out as a stable one. In this case (25 °C), potential decreases ideally by 59.16 mV/pH with increasing pH according to Nernst equation.

The pH responsivity (pH sensitivity and pH response time) was determined as follows. Then, pH a–b sensitivity between pH a and pH b was estimated from potentials, E_a and E_b by the following equation,

$$\text{pHa–bsensitivity}(\%) = -100F(E_a\text{-}E_b)/2.3026RT(\text{pHa-pHb}) \quad (1)$$

where E_a, E_b, R, T and F are the potential of working electrode (prepared glass) versus reference electrode (Ag/AgCl) at pHa and pHb, the gas constant (8.3145 J/K mol), the absolute temperature and the Faraday constant (96485C/mol), respectively. In addition, pH response time was defined as average time required for coming to a constant potential with fluctuation less than ±0.5 mV/s for pH 4, 7 and 9 measured at time interval of 3 s using pH meter F-73.

In addition, influence of interfering ions (Na^+, K^+ and Cl^-) on the potential of 15Fe65Bi20Ge glass, as an example, and commercial glass (HORIBA) was investigated using pH 4 buffer solutions (150-4) adding NaCl (99.5%, guaranteed reagent grade, Nacalai Tesque, Inc., Kyoto, Japan) of 0–171 mmol/L corresponding to 0–1 g/L and pH 9 buffer solutions (150-9) adding KCl (99.5%, guaranteed reagent grade, Wako Pure Chemical Industries, Ltd., Osaka, Japan) of 0–134 mmol/L corresponding to 0–1 g/L. Each buffer solution was selected, as one does not include additive cations (Na^+ and K^+). The potential after 3 min was used as a stable one in all potentiometric measurements.

The DC electrical resistivity of 20Fe(80-*y*)Bi*y*M (M = B, Si, Ge and P) glasses with ~1 mm thickness and an Ag electrode of 6 mm ϕ on both sides was measured at 25 °C using a super megohm meter SM-8215 (HIOKI E. E. Corp., Ueda, Japan). The contact angle with ~2 μL of water for 20Fe(80-*y*)Bi*y*M, *x*Fe(100-*x*-*y*)Bi*y*Ge and *x*Fe(100-*x*)Bi glasses was measured at 25 °C using a mobile contact angle meter PG-3 (Matsubo Corp., Tokyo, Japan) as a measure of hydrophobicity. FT-IR absorption spectra of *x*Fe(100-*x*-*y*)Bi*y*Ge glasses with ~1 mm thickness, polished to optical grade, were recorded from 2000–6000 cm^{-1} using an FT-IR spectrometer IRAffinity-1 (Shimadzu Corp., Kyoto, Japan) and the peak position of approximately 3200–3500 cm^{-1} was estimated as a measure of OH content related to contact angle with water for the glasses.

3. Results and discussion

Fig. 2 indicates the change in potential with measurement time for 20Fe(80-*y*)Bi*y*Ge (*y* = 10–30 mol%) glasses in pH 7, pH 4 and pH 9 buffer solutions. All 20Fe(80-*y*)Bi*y*Ge glasses showed a large change in potential, resulting in high pH sensitivity (>90%). The dependence of pH 4–9 sensitivity between this range on M_aO_b content for 20Fe(80-*y*)Bi*y*M (M = B, Si, Ge and P, *y* = 0–20 mol%) glasses is shown in Fig. 3. pH sensitivity of 20Fe(80-*y*)Bi*y*Si glasses drastically increased with a small increase of the amount of SiO_2 content, as in the B_2O_3 of 20Fe(80-*y*)Bi*y*B glasses [11]. Conversely, pH sensitivity of 20Fe(80-*y*)Bi*y*Ge and 20Fe(80-*y*)Bi*y*P glasses gradually increased with increasing GeO_2 and P_2O_5 content, respectively. All 20Fe(80-*y*)Bi*y*M glasses showed high pH sensitivity when a M_aO_b of 20 mol% was added.

Fig. 4 presents the change in potential with measurement time for *x*Fe(100-*x*)Bi (*x* = 15–25 mol%) glasses in pH 7, pH 4 and pH 9 buffer solutions. *x*Fe(100-*x*)Bi glasses, except the 25Fe75Bi glass, showed a relatively small change in potential, resulting in a relatively low pH sensitivity (<20%) in contrast to 20Fe(80-*y*)Bi*y*Ge glasses (Fig. 2). The dependence of pH 4–9 sensitivity in this range on Fe_2O_3 content for *x*Fe(100-*x*)Bi (*x* = 15–25 mol%) glasses is represented in Fig. 5. *x*Fe(100-*x*)Bi glasses yielded low pH sensitivity (<10%), approximately 20 mol% Fe_2O_3, which is favorable as a ref-