Evaluation of voltammetric redox potential for $\text{Fe}^{3+}/\text{Fe}^{2+}$ in silicate liquids

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Redox potentials of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in silicate liquids measured by voltammetry were evaluated by comparison with those obtained by other analytical methods. Differential pulse voltammetry was carried out for $20\text{Na}_2\text{O}\cdot 80\text{SiO}_2$ and $18\text{K}_2\text{O}\cdot 82\text{SiO}_2$ (mol%) melts doped with 0.5 or 3 wt% Fe_2O_3 and $15\text{Na}_2\text{O}\cdot 9\text{CaO}\cdot 76\text{SiO}_2$ and $25\text{CaO}\cdot 16\text{MgO}\cdot 9\text{Al}_2\text{O}_3\cdot 50\text{SiO}_2$ melts doped with 1 wt% Fe_2O_3 . Observed half wave potentials ($E_{1/2}$) agreed with those of previous voltammetry experiments, however, systematically smaller than $E_{1/2}$ calculated from redox ratios measured by wet chemistry and Mössbauer spectroscopy and redox potentials estimated from calorimetric data by about 0.1–0.3 V. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios calculated from the $E_{1/2}$ by the voltammetry were always overestimated compared with those by other analytical methods. We could not explain the reason for discrepancy of the $E_{1/2}$. It is expected that at least the discrepancy can not result from reduction of oxygen in working electrode, ohmic drop effect and difference between diffusivities of Fe^{2+} and Fe^{3+} in the liquids.

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1. Introduction

Knowledge of redox behavior of polyvalent elements in glass melts is essential in understanding of fining and coloring or decoloring process in glass production. Redox ratios of polyvalent elements can be determined by various different techniques such as colorimetry, Mössbauer spectroscopy, Raman spectroscopy, EPS spectroscopy, XANES and voltammetry. In recent two decades, square wave voltammetry (SWV) and differential pulse voltammetry (DPV) have been frequently used, because redox reaction of small amount of polyvalent elements in melts can be detected sensitively and directly at high temperatures.^{1)–17)}

An experimental technique of voltammetry and redox potentials for various polyvalent elements in glass melts have reviewed by Rüssel.¹⁸⁾ He suggested that redox ratios of some polyvalents in waste glasses and redox potentials of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in $\text{Na}_2\text{O}\text{--}\text{SiO}_2$ liquids measured by voltammetry are obviously different from those obtained by other analytical methods. Rüssel¹⁸⁾ described that these discrepancies were probably caused by large analytical errors in wet chemistry, but no evidence was provided. Although, if true, this is critical in consideration of the redox behavior in glass melts, there is no detailed research about this problem.

The aim of the present study is to confirm the difference or agreement between redox ratios measured by voltammetry and by other analytical methods. Because many studies have been reported on the ferric-ferrous ratio of silicate liquids by wet chemistry (colorimetry) and Mössbauer spectroscopy,^{19)–30)} we measured redox potentials of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in liquids by differential pulse voltammetry.

2. Experimental procedure

The experiments were carried out in liquids with the compositions $20\text{Na}_2\text{O}\cdot 80\text{SiO}_2$ and $18\text{K}_2\text{O}\cdot 82\text{SiO}_2$ (mol%) doped with 0.5 or 3 wt% Fe_2O_3 and $15\text{Na}_2\text{O}\cdot 9\text{CaO}\cdot 76\text{SiO}_2$ and $25\text{CaO}\cdot 16\text{MgO}\cdot 9\text{Al}_2\text{O}_3\cdot 50\text{SiO}_2$ (mol%) doped with 1 wt% Fe_2O_3 . The last one is an eutectic composition of diopside ($\text{CaMgSi}_2\text{O}_6$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) ($\text{Di}_{58}\text{An}_{42}$, in wt%). We refer to these samples as soda-silica (SS), potassium-silica (PS), soda-lime-silica (SLS) and diopside-anorthite (DiAn), respectively. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios in liquids (quenched glasses) of SS, PS and DiAn compositions have already measured by means of wet chemical analysis and Mössbauer spectroscopy.^{20),25),28),30)}

Starting materials were prepared from appropriate proportions of reagent grade SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaCO_3 , Na_2CO_3 and K_2CO_3 powders. These reagents were ground in an agate mortar with ethanol for 30 min and were melted in platinum crucible at 1623 K.

The experimental method of differential pulse voltammetry is basically the same as that reported by New Glass Forum¹¹⁾ and Nishimura et al.¹²⁾ Schematic drawing of experimental set-up is shown in Fig. 1.

The glass batch of approximately 60 g was inserted into a platinum crucible with a diameter of 45 mm and a depth of 28 mm. Working electrode is made of straight platinum wire. Reference electrode is replicate platinum wire, and the lower half is immersed in the melt to accelerate oxygen reduction reaction. A diameter of both electrode wires is 0.6 mm. Platinum crucible is used as counter electrode.

The measurement cell was placed in the hot spot of the furnace using MoSi_2 as heating elements with a vertical alumina tube (100 mm diameter). The temperature was measured by two Pt–PtRh₁₃ thermocouples calibrated against melting point of gold, situated above and below the cell. The temperature gradient of

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Fig. 1. Schematic drawing of voltammetry cell and experimental set-up.

sample melt is estimated to be less than ± 3 K. The furnace is capable of operating at temperatures up to 1823 K and of controlling the oxygen fugacity by mixing of pure N_2 , O_2 and dry

air. Mixed gas was introduced with a flow rate between 250 and 500 ml/min from below. The oxygen fugacity was measured with a galvanic cell oxygen analyzer (Type OX61, Yokogawa Inc.).

Differential pulse voltammetry (DPV) was carried out using a potentiostat controlled by computer (ALS model 619, CH Instrument). The pulse amplitude and step time are 20 mV and 0.1 sec, respectively.

For the SS and PS samples, temperature dependence of half wave potential was measured between 1673 and 1423 K at oxygen fugacity of dry air ($f_{\text{O}_2} = 0.21$). For the SLS and DiAn samples, oxygen fugacity dependence of half wave potential was measured in the range from $f_{\text{O}_2} = 1$ to 0.02 at 1655 K (SLS) and 1680 K (DiAn). The sample was kept at constant temperature and f_{O_2} conditions for 8–12 h, then voltammogram was recorded at two hour intervals.

Chemical compositions of starting glass and glasses retrieved from surface, middle and bottom areas in glass batch after a series of measurements were measured with energy dispersive X-ray analyzer (EDX) (HORIBA, EX-200) in order to check the homogeneity and evaporation of element.

3. Thermodynamics of iron redox reaction in liquids

In the differential pulse voltammetry, the ferric iron is reduced to ferrous iron around the surface of working electrode by a cathodic scan. The reaction is given by

In the reference electrode, the reaction is generally assumed to be reduction of oxygen:

Table 1. Chemical Compositions (wt%) of Glasses Measured by EDX

Samples		SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
SS + 3 wt% Fe_2O_3	N	77.2		2.9			19.9	
	B	77.0 (0.1)		2.7 (0.1)			20.3 (0.0)	
	A	76.1 (0.6)		2.6 (0.1)			21.3 (0.6)	
SS + 0.5 wt% Fe_2O_3	N	79.1		0.5			20.4	
	B	80.1 (0.1)		0.4 (0.2)			19.5 (0.1)	
	A	80.7 (0.5)		0.5 (0.1)			18.8 (0.6)	
PS + 3 wt% Fe_2O_3	N	72.2		2.9				24.9
	B	72.4 (1.3)		2.6 (0.6)				25.0 (0.7)
	A	72.1 (0.2)		2.8 (0.3)				25.1 (0.2)
PS + 0.5 wt% Fe_2O_3	N	74.0		0.5				25.5
	B	72.0 (1.6)		0.5 (0.3)				27.5 (1.8)
	A	74.8 (0.6)		0.5 (0.2)				24.7 (0.6)
SLS + 1 wt% Fe_2O_3	N	75.3		1.0		8.3	15.3	
	B	74.5 (0.2)		1.2 (0.1)		8.7 (0.1)	15.6 (0.2)	
	A	75.3 (0.6)		1.1 (0.2)		8.1 (0.7)	15.4 (0.9)	
DiAn + 1 wt% Fe_2O_3	N	49.8	15.2	1.0	10.7	23.3		
	A	51.0 (2.2)	14.1 (0.4)	0.9 (0.1)	10.0 (0.8)	24.0 (1.8)		

N: Nominal compositions

B: Before voltammetry runs, averages of 3 measurements

A: After voltammetry runs, averages of 9 measurements for glasses retrieved from surface, middle and bottom areas in glass batch in Pt crucible

The number of parenthesis represents 1 sigma standard deviation

Thermodynamic relationships between potentials of the working electrode (E_1) or the reference electrode (E_2) and Gibbs energy of pure species (G^0) at temperature, T , are given by

$$-F(E_1 - \phi) = \left(G_{FeO}^0 + \frac{1}{2}G_{O^{2-}}^0 - G_{FeO_{1.5}}^0 - G_e^0 \right) + RT \ln \frac{X_{FeO}}{X_{FeO_{1.5}}} + RT \ln \frac{\gamma_{FeO}}{\gamma_{FeO_{1.5}}} + \frac{1}{2}RT \ln \alpha_{O^{2-}} \quad (3)$$

and

$$-F(E_2 - \phi) = \left(\frac{1}{2}G_{O^{2-}}^0 - \frac{1}{4}G_{O_2}^0 - G_e^0 \right) + \frac{1}{2}RT \ln \frac{\alpha_{O^{2-}}}{(f_{O_2})^{1/2}} \quad (4)$$

where ϕ , X and $\alpha_{O^{2-}}$ represent potential of melt, mole fraction and activity of O^{2-} , respectively. R is gas constant and F is faraday constant. Eliminating ϕ from the Eqs. (3) and (4) yields

$$E_1 - E_2 = -\frac{1}{F} \left(G_{FeO}^0 + \frac{1}{4}G_{O_2}^0 - G_{FeO_{1.5}}^0 \right) + \frac{RT}{F} \ln \frac{X_{FeO_{1.5}}}{X_{FeO}} + \frac{RT}{F} \ln \frac{\gamma_{FeO_{1.5}}}{\gamma_{FeO}} - \frac{1}{4} \frac{RT}{F} \ln f_{O_2}. \quad (5)$$

Nernst equation is obtained from the Eq. (5):

Fig. 2. Differential pulse voltammogram recorded in 20Na₂O-80SiO₂ melts doped with 3 wt% Fe₂O₃ at $f_{O_2} = 0.21$.

Fig. 3. Variation of peak potential with run duration observed in 20Na₂O-80SiO₂ melts doped with 3 wt% Fe₂O₃ at $f_{O_2} = 0.21$.

$$E_{redox} = E^{0'} + \frac{RT}{F} \ln \frac{X_{FeO_{1.5}}}{X_{FeO}} \quad (6)$$

where $E_{redox} = E_1 - E_2$ and $E^{0'}$ is standard reduction potential expressed by

$$E^{0'} = -\frac{1}{F} \left(G_{FeO}^0 + \frac{1}{4}G_{O_2}^0 - G_{FeO_{1.5}}^0 \right) + \frac{RT}{F} \ln \frac{\gamma_{FeO_{1.5}}}{\gamma_{FeO}} - \frac{1}{4} \frac{RT}{F} \ln f_{O_2}. \quad (7)$$

The Gibbs energy change of iron redox reaction has been determined by high temperature calorimetry³¹⁾:

$$G_{FeO}^0 + \frac{1}{4}G_{O_2}^0 - G_{FeO_{1.5}}^0 = 105200 - 49.1 \times T \text{ (J/mol)}. \quad (8)$$

The relationship between half wave potential ($E_{1/2}$) and the $E^{0'}$ is given by

$$E_{1/2} = E^{0'} + \frac{RT}{2F} \ln \left(\frac{D_{FeO}}{D_{FeO_{1.5}}} \right) \quad (9)$$

Table 2. Half Wave Potentials Measured by Differential Pulse Voltammetry

Basic compositions/mol%		20Na ₂ O-80SiO ₂		18K ₂ O-82SiO ₂	
Fe ₂ O ₃ /wt%		3	0.5	3	0.5
Number of measurements		2	1	3	2
T/K	log f_{O_2}	$E_{1/2}$ /mV	$E_{1/2}$ /mV	$E_{1/2}$ /mV	$E_{1/2}$ /mV
1405	-0.68	-645 ± 0	-590	-576 ± 2	-563 ± 7
1455	-0.68	-614 ± 2	-575	-569 ± 8	-541 ± 6
1505	-0.68	-589 ± 2	-551	-555 ± 14	-520 ± 6
1555	-0.68	-569 ± 2	-524	-530 ± 5	-498 ± 6
1605	-0.68	-550 ± 1	-506	-509 ± 10	-476 ± 4
1655	-0.68	-537 ± 6	-489	-490 ± 14	-457 ± 3

Basic compositions/mol%		15Na ₂ O-9CaO-76SiO ₂		25CaO-16MgO-9Al ₂ O ₃ -50SiO ₂	
Fe ₂ O ₃ /wt%		1		1	
T/K	log f_{O_2}	$E_{1/2}$ /mV	T/K	log f_{O_2}	$E_{1/2}$ /mV
1655	-0.68	-494	1680	-0.68	-423
1655	-1.92	-399	1680	-0.28	-448
1655	-1.72	-407	1680	0.00	-466
1655	-1.51	-416	1680	-0.27	-446
1655	-1.37	-425	1680	-0.68	-414
1655	-1.25	-431	1680	-0.93	-381
1655	-1.12	-439	1680	-1.19	-364
1655	-0.67	-469	1680	-1.46	-344
1655	0.00	-525	1680	-1.66	-322
1655	-0.67	-513	1680	-1.85	-303
1655	0.00	-530	1680	-1.68	-318
1655	-0.67	-494	1680	-1.44	-338
1655	-1.18	-442	1680	-1.19	-351
1655	-1.44	-420	1680	-0.93	-373
1655	-1.66	-402	1680	-0.68	-389
1655	-0.92	-450	1680	-0.29	-432
1655	-0.67	-476	1680	0.00	-451

where D is self diffusion coefficient.³²⁾ According to Christie et al.,³³⁾ the $E_{1/2}$ can be obtained from peak potential of voltammogram (E_p) and pulse amplitude (ΔE) by the equation:

$$E_{1/2} = E_p + \Delta E/2. \quad (10)$$

In the case of $E_1 - E_2 = 0$, thermodynamic equilibrium for the reaction

is expressed as follows:³¹⁾

$$\ln \frac{X_{\text{FeO}_{1.5}}}{X_{\text{FeO}}} = -\frac{1}{RT} \left(G_{\text{FeO}}^0 + \frac{1}{4}G_{\text{O}_2}^0 - G_{\text{FeO}_{1.5}}^0 \right) - \ln \frac{\gamma_{\text{FeO}_{1.5}}}{\gamma_{\text{FeO}}} + \frac{1}{4} \ln f_{\text{O}_2}. \quad (12)$$

Therefore, from the Eqs. (7), (9), (10) and (12), the ferric-ferrous ratio in liquids is given by

$$\ln \frac{X_{\text{FeO}_{1.5}}}{X_{\text{FeO}}} = -\frac{F}{RT} \left(E_p + \frac{\Delta E}{2} \right) + \frac{1}{2} \ln \left(\frac{D_{\text{FeO}}}{D_{\text{FeO}_{1.5}}} \right) \quad (13)$$

It is important to note that the $\text{Fe}^{3+}/\text{Fe}^{2+}$ can be calculated from

the E_p observed in voltammogram without any information of activity coefficients.

4. Results

Glass compositions measured by EDX are given in **Table 1**. In the glass samples after voltammetry run, compositional differences among glasses retrieved from three different area (surface, middle and bottom) are within analytical error. No significant difference between compositions before and after the measurements was observed. Thus, it was confirmed that the composition of liquids was homogeneous during voltammetry.

Example of voltammogram recorded for SS sample is shown in **Fig. 2**. **Figure 3** represents a plot of peak potential against run duration. When the temperature is dropped by 50 K, the E_p became almost constant until 8 h. Half wave potentials of all samples are summarized in **Table 2**.

Figures 4(a) and **5(a)** are comparisons of temperature dependence of half wave potentials for the SS and PS samples ($E_{1/2}(\text{SS})$ and $E_{1/2}(\text{PS})$) with the $E_{1/2}$ of previous voltammetry experiments, the $E_{1/2}$ calculated from Eqs. (10) and (13) using $\text{Fe}^{3+}/\text{Fe}^{2+}$ measured by wet chemistry ($E_{1/2}(\text{wet chemistry})$)^{20),25),28)} and the calculated using Eqs. (7)–(9) from calorimetric data ($E_{1/2}(\text{calorimetry})$).³¹⁾ Then $D_{\text{FeO}} = D_{\text{FeO}_{1.5}}$ in Eqs. (9) and (13) and $\gamma_{\text{FeO}} = \gamma_{\text{FeO}_{1.5}}$ in Eq.

Fig. 4. Half wave potentials (a) and $\text{Fe}^{3+}/\Sigma\text{Fe}$ (b) of soda-silicate melts ($f_{\text{O}_2} = 0.21$). Solid circles: $20\text{Na}_2\text{O}\cdot 80\text{SiO}_2 + 0.5 \text{ wt\% Fe}_2\text{O}_3$ (DPV, present study); Solid squares: $20\text{Na}_2\text{O}\cdot 80\text{SiO}_2 + 3 \text{ wt\% Fe}_2\text{O}_3$ (DPV, present study); Dotted line: $20\text{Na}_2\text{O}\cdot 80\text{SiO}_2 + 0.5 \text{ mol\% Fe}_2\text{O}_3$ (SWV⁴⁾); Dashed line: $16\text{Na}_2\text{O}\cdot 10\text{CaO}\cdot 74\text{SiO}_2 + 0.5 \text{ mol\% Fe}_2\text{O}_3$ (SWV⁴⁾); Open squares: $23\text{Na}_2\text{O}\cdot 77\text{SiO}_2 + 3.5 \text{ wt\% Fe}_2\text{O}_3$ (wet chemistry²⁵⁾); Open circles: $15\text{Na}_2\text{O}\cdot 85\text{SiO}_2$ and $20\text{Na}_2\text{O}\cdot 80\text{SiO}_2 + 0.4 \text{ wt\% Fe}$ (wet chemistry²⁰⁾); Solid line: calculated from Eqs. (7)–(9) (Calorimetry³¹⁾); The basic composition is in mol%.

Fig. 5. Half wave potentials (a) and $\text{Fe}^{3+}/\Sigma\text{Fe}$ (b) of potassium-silicate melts ($f_{\text{O}_2} = 0.21$). Solid circles: $18\text{K}_2\text{O}\cdot 82\text{SiO}_2 + 0.5 \text{ wt\% Fe}_2\text{O}_3$ (DPV, present study); Solid squares: $18\text{K}_2\text{O}\cdot 82\text{SiO}_2 + 3 \text{ wt\% Fe}_2\text{O}_3$ (DPV, present study); Dashed line: $15\text{K}_2\text{O}\cdot 10\text{CaO}\cdot 75\text{SiO}_2 + 0.5 \text{ mol\% Fe}_2\text{O}_3$ (SWV⁴⁾); Open squares: $15\text{K}_2\text{O}\cdot 85\text{SiO}_2 + 3 \text{ wt\% Fe}_2\text{O}_3$ (wet chemistry²⁸⁾); Open circles: $15\text{K}_2\text{O}\cdot 85\text{SiO}_2$ and $20\text{K}_2\text{O}\cdot 80\text{SiO}_2 + 0.4 \text{ wt\% Fe}$ (wet chemistry²⁰⁾); Solid line: calculated from Eqs. (7)–(9) (Calorimetry³¹⁾); The basic composition is in mol%.

Fig. 6. Half wave potentials of soda-lime-silica melts doped with 1 wt% Fe_2O_3 at 1655 K. Solid circles: DPV (present study); Dotted line: least-square fit for the DPV data of the present study; Open squares: DPV¹²⁾; Solid line: Calorimetric value³¹⁾ calculated from Eqs. (7)–(9).

(7) are assumed. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ calculated from Eq. (13) using the $E_{1/2}$ (SS) and $E_{1/2}$ (PS) and that by wet chemistry are shown in Figs. 4(b) and 5(b). The results can be summarized as follows:

(1) The $E_{1/2}$ (SS) is nearly consistent with that reported by previous voltammetry experiments.⁴⁾

(2) The $E_{1/2}$ (SS) and $E_{1/2}$ (PS) of melts including 0.5 wt% Fe_2O_3 are higher than those of SLS (16 $\text{Na}_2\text{O}\cdot 10\text{CaO}\cdot 74\text{SiO}_2$, mol%) and PLS (15 $\text{K}_2\text{O}\cdot 10\text{CaO}\cdot 75\text{SiO}_2$, mol%),⁴⁾ respectively, by about 0.01–0.03 V.

(3) The $E_{1/2}$ determined by voltammetry ($E_{1/2}$ (voltammetry)), $E_{1/2}$ (wet chemistry) and $E_{1/2}$ (calorimetry) all increase with increasing temperature, while the $E_{1/2}$ (voltammetry) are systematically smaller than the $E_{1/2}$ (wet chemistry) and $E_{1/2}$ (calorimetry) by about 0.1–0.3 V in both the SS and PS samples.

(4) Both of the $E_{1/2}$ (voltammetry) and $E_{1/2}$ (wet chemistry) increase with decreasing iron content.

Figures 6 and 7(a) are comparisons of oxygen fugacity dependence of half wave potentials for the SLS and DiAn samples ($E_{1/2}$ (SLS) and $E_{1/2}$ (DiAn)) with the $E_{1/2}$ of previous voltammetry experiments, the $E_{1/2}$ calculated from Eqs. (10) and (13) using $\text{Fe}^{3+}/\text{Fe}^{2+}$ measured by Mössbauer spectroscopy ($E_{1/2}$ (Mössbauer))³⁰⁾ and the $E_{1/2}$ (calorimetry). The $\text{Fe}^{3+}/\Sigma\text{Fe}$ calculated from Eq. (13) using the $E_{1/2}$ (DiAn) and that by Mössbauer spectroscopy is shown in Fig. 7(b).

(5) The $E_{1/2}$ (SLS) of the present study is agree with that reported by previous voltammetry measurement at $f_{\text{O}_2} = 1$ and 0.21.¹²⁾

(6) The $E_{1/2}$ (SLS) at 1655 K and $E_{1/2}$ (DiAn) at 1680 K can be approximated by equations

$$E_{1/2}(\text{SLS}) = -0.532 + 0.229 \left(-\frac{RT}{F} \ln f_{\text{O}_2} \right) \quad (14)$$

and

$$E_{1/2}(\text{DiAn}) = -0.463 + 0.258 \left(-\frac{RT}{F} \ln f_{\text{O}_2} \right), \quad (15)$$

respectively. The slopes of these relationships (0.229 and 0.258) are almost consistent with theoretical value given by the Eq. (7) (0.25).

(7) The $E_{1/2}$ (DiAn) are systematically smaller than the $E_{1/2}$ (Mössbauer) and $E_{1/2}$ (calorimetry) by about 0.2 V. The $E_{1/2}$ (Mössbauer) is close to the $E_{1/2}$ (calorimetry).

Fig. 7. Half wave potentials (a) and $\text{Fe}^{3+}/\Sigma\text{Fe}$ (b) of diopside-anorthite melts doped with 1 wt% Fe_2O_3 at 1680 K. Solid circles: DPV (present study); Dotted line: least-square fit for the DPV data; Open squares: Mössbauer spectroscopy³⁰⁾; Solid line: Calorimetric value³¹⁾ calculated from Eqs. (7)–(9).

5. Discussion

5.1 Reproducibility and reliability of voltammetry, wet chemistry and Mössbauer spectroscopy

As shown in Figs. 4–7, the systematic discrepancies between the half wave potentials by voltammetry and by other analytical methods are observed in not only $\text{Na}_2\text{O}\text{--}\text{SiO}_2$ melts described by Rüssel¹⁸⁾ but also $\text{K}_2\text{O}\text{--}\text{SiO}_2$ and Di–An melts. The $E_{1/2}$ (voltammetry) is reproducible and reliable because the values measured at different laboratories are consistent with each other (Figs. 4(a), 7(a)). On the other hand, it has been reported that $\text{Fe}^{3+}/\text{Fe}^{2+}$ of quenched glasses measured by colorimetry, Mössbauer spectroscopy and XANES agree with each other.^{23),24),34)} Magnien et al.³⁴⁾ carried out in-situ measurement of iron redox ratio in liquids with basic composition 5 $\text{Na}_2\text{O}\cdot 17\text{MgO}\cdot 17\text{CaO}\cdot 10\text{FeO}\cdot 51\text{SiO}_2$ (mol%) at 873–973 K by using XANES. They demonstrated that the $\text{Fe}^{3+}/\text{Fe}^{2+}$ of liquid is consistent with that by prediction equation deduced from the redox ratio of quenched glass measured by colorimetry.³⁵⁾ It has been also reported that, in $\text{H}_2\text{O}\text{--}\text{Na}_2\text{O}\text{--}\text{K}_2\text{O}\text{--}\text{CaO}\text{--}\text{Al}_2\text{O}_3\text{--}\text{SiO}_2$ glasses, the iron redox ratio is not dependent on the quench rate.^{29),36)} Thus, the redox ratio of iron in quenched glasses measured by wet chemistry and Mössbauer spectroscopy can be considered as that in melts at high temperature. The $E_{1/2}$ (calorimetry) is closer to the $E_{1/2}$ (wet chemistry) and $E_{1/2}$ (Mössbauer) than the $E_{1/2}$ (voltammetry) (Figs. 4(a), 5(a) and 7(a)), probably suggesting that the former values are closer to true value

defined by thermodynamic equilibrium of iron redox reaction. Therefore, it can be considered that the half wave potentials for iron redox reaction measured by voltammetry are systematically lower than the true value by about 0.1 to 0.3 V. Since this is significantly larger than the differences of $E_{1/2}$ (voltammetry) between the SS and SLS and between the PS and PLS (0.01–0.03 V), the discrepancy must be resolved when the compositional dependence of the iron redox reaction is discussed by using the voltammetry.

5.2 Homogeneity of ferric-ferrous ratio of liquid in voltammetry cell

Redox reactions in silicate liquids have long been assumed to be rate-limited by oxygen diffusion.^{37)–40)} If so, a gradient of $\text{Fe}^{3+}/\text{Fe}^{2+}$ would be formed in depth because of slow diffusivity of oxygen. This is attributable to heterogeneous electrode reaction in the working electrode. However, subsequent studies have reported that the rate-limiting step is diffusion of network-modifier cations along with a counter flux of electrons.^{34),41)–45)} Recently, by using micro-Raman spectroscopy, Roskosz et al.⁴⁵⁾ measured the redox profile of iron across partially oxidized glass samples heated for various durations. They demonstrated that redox ratio was constant in the whole sample and moved toward equilibrium value with time. Thus, it is considered that the ferric-ferrous ratio would be constant in whole melts in voltammetry cell.

5.3 Effect of assumptions on the $E_{1/2}$

In order to clear the reason of underestimation of the $E_{1/2}$ (voltammetry), we examine the effect of some assumptions on the half-wave potential.

It is generally assumed that the reaction in working electrode is only the reduction of polyvalent ions (Eq. 1). However, reduction of oxygen (Eq. 2) may also be occurred at an interface of working electrode and surface of sample melt. Assuming that electrons are consumed by the reactions 1 and 2 in the proportion of α to β , respectively, difference between the $E_{1/2}$ (voltammetry) and the true value determined by thermodynamic properties of liquid, $\Delta E_{1/2}$, is given by

$$\Delta E_{1/2} = \left(\frac{\beta}{\alpha + \beta} \right) E^{0'}. \quad (16)$$

The observed value of $\Delta E_{1/2}$ is the range from –0.1 to –0.3 V and is independent of T and f_{O_2} (Figs. 4(a), 5(a) and 7(a)). However, the Eq. (16) suggests that the $\Delta E_{1/2}$ depends on the T and f_{O_2} . Thus, the $\Delta E_{1/2}$ can not be explained by the reduction of oxygen in working electrode.

Strictly, peak potential observed in the voltammetry is affected by ohmic drop effect.³²⁾ When solution resistance between working electrode and reference electrode is $R_{\text{W-R}}$, the $E_{1/2}$ (voltammetry) is described by

$$E_{1/2} (\text{Voltammetry}) = E_{1/2} + IR_{\text{W-R}} \quad (17)$$

where $E_{1/2}$ is the true value determined by thermodynamic properties of liquid. Although the ohmic drop effects in glass melts are usually ignored, there is no evidence to support it. Effect of the ohmic drop on square wave voltammetry response has been examined theoretically⁴⁶⁾ and experimentally for low conductivity organic solvent.⁴⁷⁾ However, as demonstrated by these reported studies, the $E_{1/2}$ (voltammetry) become more positive relative to the $E_{1/2}$ by ohmic drop effect. The negative $\Delta E_{1/2}$ can not be explained by this effect.

In previous voltammetry studies for glass melts, it has been

assumed that diffusion coefficient of oxidized species (D_{Ox}) is the same as that of reduced species (D_{Red}), thus $E_{1/2} = E^{0'}$ in the Eq. (9).^{1)–17)} We also assumed $D_{\text{FeO}} = D_{\text{FeO}_{1.5}}$ in the calculations. However, diffusion of network modifier oxides may be faster than that of network former and intermediate oxides. According to the previous measurements,^{48),49)} divalent cation shows one order of magnitude higher diffusivity than trivalent cation in silicate liquids. Assuming that $D_{\text{FeO}} > D_{\text{FeO}_{1.5}}$, the half wave potential in the Eq. (9) increases. This is inconsistent with the negative $\Delta E_{1/2}$. Contrary to this, if the $D_{\text{FeO}_{1.5}}$ is one to two order of magnitude larger than the D_{FeO} , the $\Delta E_{1/2}$ agree with observed value, but this must be verified in further research.

6. Conclusion

The $E_{1/2}$ of iron in silicate liquids measured by voltammetry increases with increasing temperature and decreasing oxygen fugacity. This is consistent with thermodynamics theory, and thus it is clear that the voltammetry response represents redox reaction in liquids qualitatively. The $E_{1/2}$ obtained from voltammetry, however, is quantitatively underestimated by about 0.1 to 0.3 V, and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is overestimated compared with that measured by wet chemistry and Mössbauer spectroscopy.

The magnitude of discrepancy ($\Delta E_{1/2}$) depends on composition, while independent of T and f_{O_2} . The $\Delta E_{1/2}$ is significantly larger than values of differences between $E_{1/2}$ (voltammetry) for soda-silica and soda-lime-silica melts and between those for potassium-silica and potassium-lime-silica melts (0.01–0.03 V). Therefore, it must be noted that structural examination of iron redox reaction in glass melts based on the compositional dependence of the $E_{1/2}$ (voltammetry) may be unreliable, unless the reason for discrepancy is clear.

In this study, we could not explain why the $E_{1/2}$ (voltammetry) is underestimated. It is expected that at least the discrepancy can not result from reduction of oxygen in working electrode, ohmic drop effect and difference between diffusivities of Fe^{2+} and Fe^{3+} . Comparisons between voltammetry and other analytical methods should be also required for the other polyvalent elements in glass melts.

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