Cu(II)/Cu(I)/Cu Redox in Alkali Borate Melts

Takafumi Sakurada , Hideki Maekawa
and Toshio Yokokawa

Faculty of Science, Hokkaido University,
Sapporo 060, Japan (tel. 011-706-2706)

ABSTRACT

Electrochemical method was applied to the redox study of copper oxides in alkali borate melts in a wide range of the basicity,where Li to Cs borates were employed. Comparison was also made of various metal working electrodes besides Pt. The two peak waves of the linear sweep cyclic voltammetry were assigned to Cu(II)/Cu(I) and Cu(I)/Cu redoxes. The extraordinary nature of copper oxides has been reported; thus, Cu(II) is easier reduced in more basic melt. The present experimental results seem to suggest that there is a boundary beyond which Cu(I) behaves differently. In the highly basic melts, Cu(I) ion is considered to be associated with O^{2-} ions and functions as an acidic solute than the higher valent Cu^{2+} ion. The results were compared with our old data with sodium borates with various compositions. The two sets of data are consistent with each other when the alkali borates are given the appropriate indices of the basicity.

1. INTRODUCTION

It is well known that the redoxes of multi-valent ions in high temperature melts as well as in aqueous solutions depend on the solvent basicity. While its oxygen pressure dependence obeys strictly what the valence difference predicts, its ordinary dependence on the solvent basicity is qualitative, that is,"the higher valent cation is the more stabilized in the increasing basicity". Moreover this is not a strict rule but there are many exceptions, the present Cu(II)/Cu(I) redox being one of them. The highly oxidized cation is naturally smaller in the ionic size than the counter cation, and the former exerts greater coulombic force upon the surrounding anions and can be said to behave more acidic. Therefore, the exceptional stability of Cu(I) ion in the basic solvent implies Cu(I)-O^{2-} bond is stronger than Cu(II)-O^{2-} bond to our interest.

Quite a number of the experimental data of this redox has been reported, in which this extraordinary nature of the redox couple is noticed. However, the data are not necessarily consistent and the rationalization is not established at all. This is somehow related with the experimental difficulties. The chemical analysis of quenched glasses assumes quenching of valencies, which is not guaranteed, and nonexistence of zero-valent Cu in the oxide phase. A small shift of d-d transition of Cu(II) (9d) as a function of the basicity is usually observed. This may be or not may be the effect of quench, or the energy and then the activity coefficient of that ions do not stay constant independent of the basicity, when the equilibrium constant changes with the basicity.

Since the basicity itself has not systematically been studied in the borate melts, the basicity dependence of the redox of Cu(II)/Cu(I) pair has not been clarified yet, but some reports will be mentioned below. Johnston and Chelko[1] have measured $K= [Cu^{3+}]/[Cu^{+}]\bullet p(O_2)^{-1/2}$ at $Na_2O\bullet 2SiO_2$. Banerjee and Paul[2] measured the same quantities at $30Na_2O\bullet 70B_2O_3$ and $25Na_2O\bullet 10Al_2O_3\bullet 65B_2O_3$. Sakka et at.[3] found that the equilibrium constant decreases with increase of the temperature and decreases with the series of $Li_20<Na_2O<K_2O<Cs_2O$ in $30Alk_2O\bullet 70SiO_2$. The latter means the more basic the solvent is the more the deduced species becomes stabilized. Duran and Valle[4] found maximum of Cu(II)/Cu(I) value at around 18 mole % of alkaline oxide in sodium and potassium borates, and the equilibrium constant decreased with alkali content and their slope decreasing in the order Li>Na>K>Cs. They confirmed the experimental finding by Lee and Bruckner.[5] The maximum of the equilibrium constant seems to be related to the boron anomaly as they suggest. Miura and Takahashi,[6] and Russel and Freude,[7] applied voltammetry to sodium borate($28.7Na_2O\bullet 71.3B_2O_3$) and soda-lime-silica ($16Na_2O \bullet 10CaO\bullet 74SiO_2$) melts respectively and they found that Cu(II) is reduced in two steps,

$$Cu^{2+} + e = Cu^{+} \qquad (1)$$

$$Cu^{+} + e = Cu. \qquad (2)$$

The former authors did not conclude as to the second step, mentioning that the step is irreversible because the oxidation current is not observable, but it may be either eq.(2) or direct reduction,

$$Cu^{2+}\ 2e\ = Cu. \qquad (3)$$

In the laboratory of the present authours[8], the redox equilibria of several multi-valent metal oxides in sodium borate melt have been studied and a minimum of the redox potential (corresponding to maximum stability of Cu(II) in the intermediate composition.

Xu et al.[9] investigated EXAFS and XANES of Cu in borate glasses and found a minimum of the redox in a intermediate composition at dilute (l mole %) copper content. They also found a minimum of Cu-O bond length at around 30 mole % of Na_2O. This may occur on the quenching process. It seems also possible that the boron anomaly, that first addition of Na_2O in B_2O_3 generates BO_4 unit in the network up to 30 mole % Na_2O and the network is not destroyed but reinforced, comes into play in the network structure. Cu(II)/Cu(I) equilibrium ratio will be influenced, because the generation of the non-bonding oxygen, BO^-, is essential of solubilization of Cu(II) and Cu(I) ions. Later, Baucke and Duffy[10] studied the effect of basicity on redox in borate and silicate glasses, in which they sucseeded to correlate basicity vs Cu(II)/Cu(I) redox in $CaO\text{-}M_2O\text{-}SiO_2$, where M_2O denotes Na_2O or K_2O. Recently, Denzumi and Suzuki and others[11,12] introduced a new basicity scale determined from the redox of Cr(VI)/Cr(III) in alkali and alkaline earth silicate melts, respectively.

In the present paper, Cu(II)/Cu(I)/Cu equilibria were investigated in alkali borate melts for the second time. Both of Cu(II)/Cu(I) and Cu(I)/Cu redoxes were analyzed to clarify the stability of Cu(I) ion as a function of the basicity.

2. EXPERIMENTAL

2.1 Cell and redox measurement

Voltammetry was employed to measure the redox potential, from which the equilibrium oxygen pressure can be evaluated. A three-electrode cell was constructed from platinum crucible and three platinum electrodes which are shown in Fig. 1. The working electrode of platinum wire was immersed in the melt. The immersed part was folded in a ring form in order to have relatively big surface area compared with the gas-metal-melt coexisting area (mostly in one atmospheric oxygen). The platinum crucible functioned as the counter electrode. The reference electrode is made of platinum wire and its folded end was located just in contact with the melt surface in order to have wide area of gas-melt-metal coexisting zone and to respond to the electrochemical reaction,

$$1/2O_2\,(g) + 2e = O^{2-}. \qquad (4)$$

Two voltammetric methods, linear sweep voltammmetry (LSV) and differential pulse voltammetry (DPV) were applied. The details are given in text books[13] and will be described briefly. In LSV the potential is swept linearly negative and then positive,

$$E = E_i - vt \qquad (0<t<\lambda) \qquad (5)$$

$$E = E_i - v\lambda + vt, \quad (\lambda<t<2) \qquad (6)$$

where E_i is the initial potential (usually 0V), v is the sweep rate, and λ is a half period of the one cycle and then positive directions so as to return to the original starting potential, while the electrochemical current is measured as a function of time. When no solute is dissolved, the solvent cation like Na^+, Si^{4+} and/or B^{3+} is reduced at certain potentials and the big current is observed. If the redox potential E of a solute oxide is located between zero (eq.(1)) and the potentials of the solvent cations, we observe an additional current peak due to its reduction (and oxidation in the return of the cycle), when the cation M^{m+} is reduced to $M^{(m-n)+}$,

$$M^{m+} + ne = M^{(m-n)+}. \qquad (7)$$

The potential is the standard redox potential of $M^{m+}/M^{(m-n)+}$ pair referred to the potential of the reference electrode of O_2/O^{2-} pair of one atmospheric oxygen and O^{2-} ion of the sample solvent, and is related to the free energy change for the reaction,

$$M^{m+} + n/2\,O^{2-} = M^{(m-n)+} + n/4\,O_2 \qquad (8)$$

$$-nE^0F = \Delta G^0. \qquad (9)$$

The current is so related to the potential as to adjust the concentration ratio (of the red. and ox. ions on the surface) consistent with the changing potential,

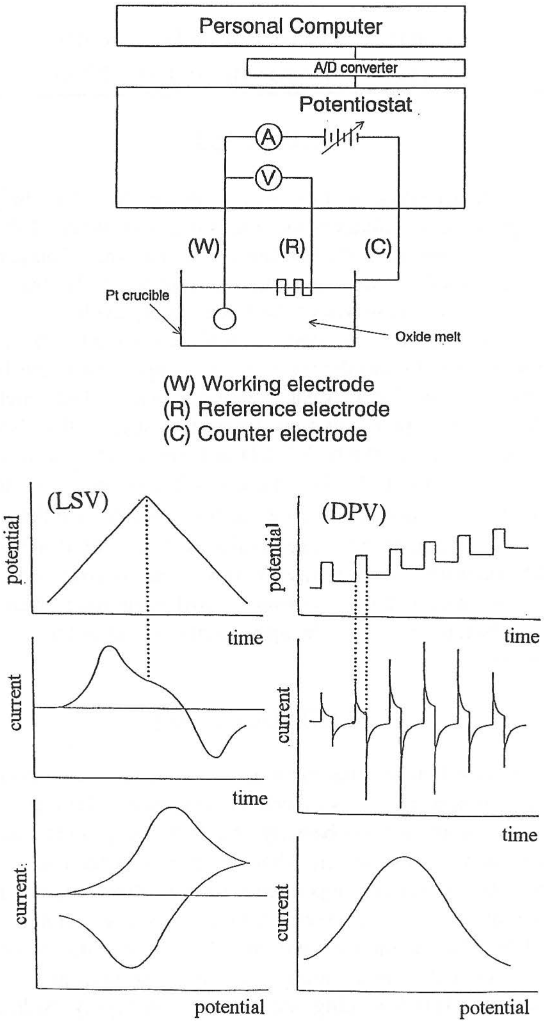

Fig.1. Cell assmbly and schematic current vs. potential curves of LSV and DPV.

$$E = E^0 + RT/nF \ln a(M^{m+})/a(M^{(m-n)+})a(O^{2-})^{n/2}/p(O_2)^{n/4}$$
$$= E^{0'} + RT/nF \ln [M^{m+}]/[M^{(m-n)+}], \qquad (10)$$

where $E^{0'}$ is the formal potential,

$$E^{0'} = E^0 + RT/nF \ln f(M^{m+})/f(M^{(m-n)+})$$
$$+ RT/F \ln a(O^{2-})^{1/2}/p(O_2)^{1/4}. \qquad (11)$$

Since the current is measured naturally off equilibrium at steadily swept potential, the evaluated potential is not $E^{0'}$ but $E_{1/2}$ associated with the diffusivity of the approaching reactant ions and leaving product ions,

$$E_{1/2} = E^{0'} + RT/nF \ ln\{D(\text{Red})/D(\text{Ox})\}^{1/2}, \quad (12)$$

where $E_{1/2}$ is called the polarographic half wave potential. However, the diffusion coefficient ratio, D(Red)/D(Ox), is usually not far from 1, and $E_{1/2}$ is used in the discussion of the equilibrium properties. The potential ranged 0 to -1500mV and the sweep rate was 50 to 1000mV/s.

In DPV, the potential is swept in a staircase type and a pulse of a certain width is superposed on the each step of the former sweep potential. Because of the extra current due to charging the double layer we sample the currents just before the pulse and at the end of the pulse. The difference of the two current gives much higher sensitivity compared with that of LSV. The LSV is employed to grasp the general profile and test the reversibility of the reaction and DPV was used for quantitative evaluation of the equilibrium potential. The peak potential E_p is corrected for the pulse height, ΔE, to evaluate the polarographic half wave potential $E_{1/2}$,

$$E_p = E_{1/2} + \Delta E/2. \quad (13)$$

The sweep rate of the potential in DPV was 5, 10 and 20 mV/s and the pulse height was 25 to 100 mV. Most measurements were performed in oxygen atmosphere (at the flow rate of 500ml/min) but some were also performed in ambient and argon atmosphere ($1 \cdot 10^{-4}$ atom O_2). Pt working electrode was tried to be replaced by other metals to test reversibility or effect of alloying and so on. Alkali oxides were exchanged to see the effect of the basicity of the melts. Comparison was made between the basicity sequence brought out by alkali species on one hand and by the concentration of Na_2O of Na_2O-B_2O_3 melts on the other hand.

2.2 Sample melts

Binary alkali borate melts of $0.3R_2O \bullet 0.7B_2O_3$ were prepared from heating powder mixture of nominal weights of boric acid H_3BO_3 and the corresponding alkali carbonate and 0.5 mole % CuO, all of the guaranteed reagent grade. They were kept at around 1123 to1223 K in ambient atmosphere in order to expel water and carbon dioxide.

3. RESULTS

3.1 LSV Experiment

LSV curve of the system without copper oxide (Fig. 2) is reproduced to show the potential range where the solute cations can be reduced. The general current-potential in LSV is shown in Fig. 3. The first peak with the corresponding anodic peak on return is a typical redox curve with reversible electrode reaction of both soluble red. and ox. solutes. The current increases with the sweep rate, just as it should be proportional to square root of the rate. It is quite natural to assign the following reaction to this peak,

$$\text{Cu(II)} + e = \text{Cu(I)}. \quad (1)$$

The second peak without the corresponding oxidation peak on return seems attributable to,

$$\text{Cu(I)} + e = \text{Cu}. \quad (2)$$

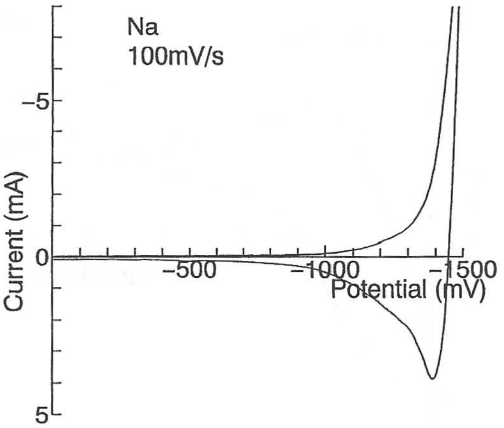

Fig.2. Current-potential curve of Cu-free solvent.

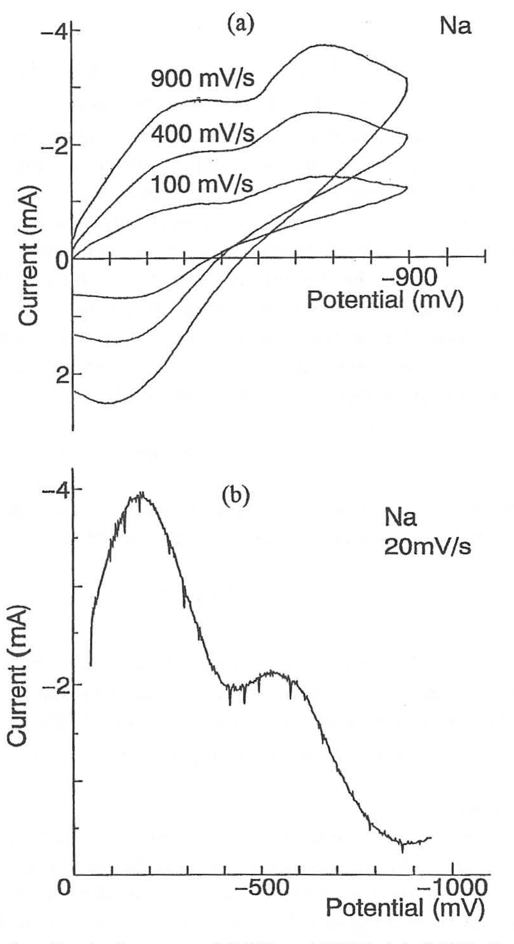

Fig.3. Typical curves of LSV and DPV. (a); LSV, Pt electrode, at 1123K at $p(O_2)$ =0.2atm. (b); DPV, in the same condition.

3.2 Effect of the electrode materials on the second peak

A couple of different materials were tried instead of Pt in order to clarify the electrochemical reaction of the second peak.

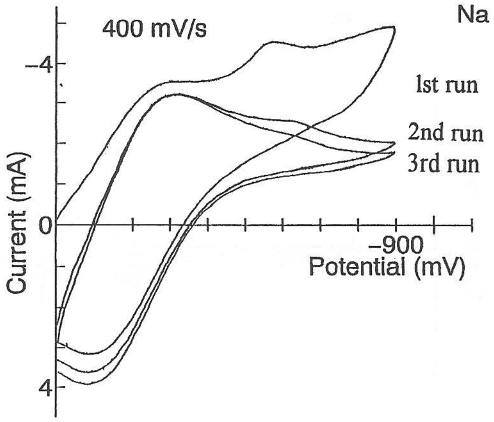

Fig. 4 LSV curves with Au electrode at 1123K at $p(O_2) = 0.2$atm

Au electrode

Fig. 4 shows LSV of the system, $0.3Na_2O \bullet 0.7B_2O_3$ + 0.5 mole% CuO in p_{O2}=0.2. The first cycle was not so reproducible. The second peak is disappearing sweep by sweep. The peak height increased in proportion with the sweep rate. Disappearance of the second peak is not understood well. Aside a small potential due to the difference of the material of the reference and the working electrode, only difference will be the activity or solubility on Cu in the electrode metal. If Cu is so well soluble in Au, the underpotential deposit with low activity Cu may affect the reaction (2) to shift to the left and even pile up on that of the reaction (1). In the latter case, the peak should be,

$$\mathrm{Cu(II)} + 2e = \mathrm{Cu(in\ Au)}. \qquad (14)$$

The peak profile is predicted if both of the red and ox species are soluble and their flow rates are controlled by diffusion,

$$E_{p/2} - E_p = 1.76RT/nF, \qquad (15)$$

where E_p and $E_{p/2}$ are the peak potential and the potential where the current is one half of the peak current respectively. The sharpness of peak is bigger with Au electrode than with Pt electrode, where n=1, but not so big as to lead to n=2.

Cu electrode

Figs. 5 shows the LSV curves of redox of CuO with Cu electrode. With repeating the cycle (1) the first peak tended to disappear and (2) current vs. potential became a straight line, showing that the reactants do not need to diffuse onto or from the electrode. Also the open circuit potential, about -600mV, is just what can be expected when Cu electrode is in equilibrium with the residual oxygen (or a local cell reaction between the working electrode parts near the melt surface and bulk) and Cu(I) ion. As the time goes on, the concentration of copper ion in the melt increases little by little and the redox potential is not quantitative any more. Iridium metal was also tried to replace platinum electrode. However, probable oxidation of the metal generated complex current-potential curves and did not produce any meaningful information.

With this additional evidence from replacing the electrode material, the electrode reactions in Pt working electrode were concluded to be eqs.(1) and (2) as have been concluded in the previous studies. Unit activity of copper deposit was tentatively assumed in the following discussion, although alloying with Pt was suspected.

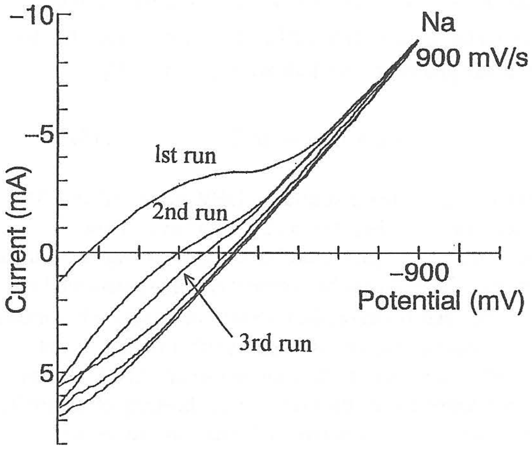

Fig. 5. LSV curves with Cu electrode at 1123K at $p(O_2)$ =0.2atm

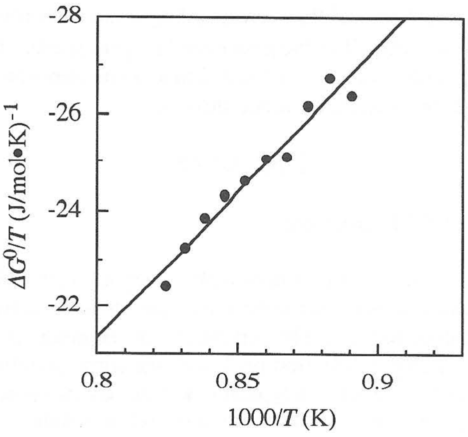

Fig. 6. Temperature dependence of the standard free energy of redox reaction obtained from the potential with Au electrode.

3.3 Dependencies on temperature and solvent basicity

The temperature dependence of the first reaction was evaluated from the measurement from 1123 to 1223K, which is shown in Fig.6, where $-E_{1/2}F = \Delta G^0$ is assumed as for the reaction,

$$Cu^{2+} + 1/2\ O^{2-} = Cu^{+} + 1/4O_2. \qquad (16)$$

ΔH^0 was calculated to be 61.2kJ/mol. It is to be noted that since the standard state of O^{2-} here is that of the solvent, ΔH^0 is not ΔH^0 of $CuO = 1/2Cu_2O + 1/4O_2$. The original data are listed in Table I.

Replacement of Na_2O of the solvent melt with other alkali oxides was carried out and the results are shown in Fig.7, where the potentials are plotted as functions of the optical basicity of the solvent borates calculated along the formulae suggested by Duffy and Ingram.[10] In Fig.7, the previous data in sodium borate melts are also plotted. The optical basicities of the melts were evaluated with in the same way. The potentials and assigned basicity are listed in Table II.

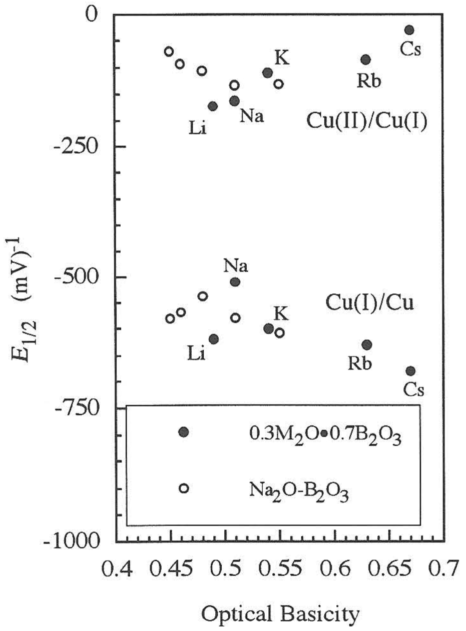

Fig. 7 Potentials of two reactions vs. the basicity of the solvent, from the various alkali borates in the present work and from sodium borates of various composition (ref.8).

Table I. Cu(II)/Cu(I) redox potentials with Au electrode (Fig. 6).

T (°C)	$E_{1/2}$ (mv)	T (°C)	$E_{1/2}$ (mv)
850	-307	900	-299
860	-314	910	-298
870	-310	920	-295
880	-300	930	-290
890	-302	940	-282

Table II. The potentials, $E_{1/2}$, of Cu(II)/Cu(I) and Cu(I)/Cu redoxes in the solvents of various basicities, at 1173K, pO_2=1atm.

Composition	$E_{1/2}$ {Cu(II)/Cu(I)} (mv)	$E_{1/2}$ {Cu(I)/Cu} (mv)	Optical Basicity
$0.3M_2O•0.7B_2O_3$			
M=Li	-172	-620	0.49
M=Na	-162	-510	0.51
M=K	-110	-600	0.54
M=Rb	-83	-630	(0.63)
M=Cs	-30	-680	(0.67)
$xNa_2O•(1-x)B_2O_3$			
x=0.10	-70	-581	0.45
x=0.15	-93	-569	0.46
x=0.20	-106	-538	0.48
x=0.30	-133	-580	0.51
x=0.40	-131	-608	0.55

4. DISCUSSIONS

From the various evidences described above, the first peak and the second peak with Pt electrode can be attributed to the reaction (1) and (2) respectively. The following discussion will be based on this assumption. Since the dependencies on the oxygen pressure have been established, attention will be paid more on the basicity dependencies . The basicities of alkali silicates have been quantitatively compared in the laboratory of the present authors.[11,12] Although such thing has not been carried out as for the borates, the optical basicity[12] would be employed instead. Therefore apparently different two sets of data, e.g. the data in various alkali borates on one hand and in sodium borate of various composition on the other hand, are brought out in one figure in Fig.7.

As is shown in Fig. 7, reaction (1) tends to have a minimum and the second reaction (2) shows a maximum, although the consistency as for the reaction (1) is quite poor. It will be natural that the inflections of the both potential-basicity curves are attributed to the stability change of Cu(I) state with the basicity, because the two curves show opposite inflections at around the same basicity. If we assume that Cu(II) does not change much in the whole basicity range, Cu(I) should change its entity from Cu^+ to CuO^- beyond an intermediate basicity, when the combination of eq.(4) with eqs.(1) and (2) should be replaced by,

$$2Cu^{2+} + 3O^{2-} = 2CuO^{-} + 1/2O_2 \qquad (17)$$

$$2CuO^{-} = 2Cu + O^{2-} + 1/2O_2. \qquad (18)$$

On the other hand, such inflection does not occur but Cu(I) is steadily more stabilized than Cu(II) with increasing basicity in alkali silicates.[10] Therefore, the tendency below some basicity limit (0.5) will be interpreted by either the boron anomaly or the basicity alone. Thus, B_2O_3 network respond to the basicity change in its own way, in which the B-O- end is not produced, and CuO- is not produced. The number of O^{2-} ions to associate one Cu(I) ion is not definitely one, although it is small.

5. CONCLUSION

The redox equilibria of copper oxide in alkali borate melts were investigated by voltammetry. The results were studied assuming two step reduction of Cu(II) to Cu(I) and Cu(I) to Cu metal. The inflections of the redox potential vs. basicity curves in intermediate basicity were found, suggesting formation of CuO- ion in highly basic melts. It is not conclusive whether non-existence of CuO- entity is matter of basicity range of the solvent or the boron anomaly.

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