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Experimental Study on Electrical Conductivity of Fe_xO-CaO-SiO_2-Al_2O_3 System at Various Oxygen Potentials

DOI 10.1515/htmp-2016-0102
Received May 31, 2016; accepted December 23, 2016

Abstract: The electrical conductivity of Fe_xO-CaO-SiO_2-Al_2O_3 slags was measured by a four terminal method. The results show that the temperature dependences of total, electronic and ionic conductivity for different compositions obey the Arrhenius law and all of them increase as increasing the temperature. For all the studied slags, as increasing CO/CO_2 ratio which is used to controlled the oxygen potential, both the total electrical conductivity and electronic conductivity increase, but the ionic conductivity decreases. It was also found that the electronic transference number exhibits a strong correlation with oxygen potential, but is independent of temperature. Under the condition of constant Fe_xO content, the higher the basicity of slags is, the higher the total electrical conductivity and ionic/electronic conductivity will be, which is resulted from the increase of free oxygen ion.

Keywords: Fe_xO-CaO-SiO_2-Al_2O_3 slags, electrical conductivity, electronic transference number

Introduction

The electrochemical properties of the iron oxide bearing molten slags have attracted more and more attention because of their significant importances for understanding the structures of molten slags and operating the electric smelting furnace during the production of ferroalloys [1–7]. In recent years, molten oxide electrolysis [8–10] (MOE) as a carbon-neutral electrochemical technique to decompose iron oxide directly into liquid iron and oxygen gas upon use of an inert anode was proposed. For an efficient electrolysis, the melt must be predominantly an ionic conductor. Knowledge of the electrical conductivity of slags can help in designing and selecting the proper slags for electrolysis. Some related literatures of electrical conductivity, for instance Fe_xO-CaO-SiO_2 [11–13], Fe_xO-CaO-MgO-SiO_2 [14], Fe_xO-CaO-SiO_2-Al_2O_3 [15, 16] slags, had been reported in the past few decades. However, relative to viscosity, the available data of electrical conductivity of Fe_xO-bearing slags are far more enough, considering their widely applications in the pyrometallurgical processes. The electrical conductivity of Fe_xO-bearing slags includes two parts, ionic conductance and electronic conductance. Because temperature, oxygen partial pressure and composition can greatly affect the value of electronic/ionic conductivity, experimental conditions should be accurately controlled during the measurement process. The aim of the present work was to study the influence of Fe_xO content on the electrical conductivity of Fe_xO-CaO-SiO_2-Al_2O_3 slags at different temperatures and oxygen potentials controlled by CO-CO_2 gas mixtures.

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Experiments

In this study, a four terminal method was employed to accomplish the electrical conductivity measurements. The detailed descriptions of device and experimental principle have already been introduced in our previous study [16, 17]. The oxygen partial pressure was controlled by the ratio of CO to CO_2 in the experimental process. The stepped potential chronoamperometry (SPC) method [18–20] was applied to measure the transference numbers, and the electronic conductivity and ionic conductivity can be calculated by total electrical conductivity and electronic transference numbers.

The initial slag compositions are provided in Table 1. In each group, the molar ratio of CaO, SiO_2 and Al_2O_3 remain constant (CaO: SiO_2: Al_2O_3 = 6: 1: 3), but the content of FeO gradually increases. Slag samples were prepared using reagent grade Fe_2O_3, Al_2O_3, SiO_2 and $CaCO_3$

Table 1: Compositions of slag samples (mole percent).

FeO	CaO	SiO_2	Al_2O_3	B (Optical basicity except FeO)
30	42	7	21	0.73
	28	28	14	0.64
20	48	8	24	0.73
	32	32	16	0.64
10	54	9	27	0.73
	36	36	18	0.64
5	57	9.5	28.5	0.73
	38	38	19	0.64
2.5	58.5	9.75	29.25	0.73
	39	39	19.5	0.64
0	60	10	30	0.73
	40	40	20	0.64

powders (analytically pure, Sinopharm Chemical Reagent Co., Ltd, China), all of which were calcined at 1,273 K (1,000 °C) for 10 h in a muffle furnace to decompose any carbonate and hydroxide before use. The pure FeO was obtained by calcining Fe and Fe_2O_3 powder in CO/CO_2 atmosphere at 1,373 K (1,100 °C) for 24 h. Then 12 g mixtures were used in each experiment.

All the measurements are completed using a CHI 660a electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.). The resistance was found to be independent of the frequency, over the range 0.5 kHz to 100 kHz. All of the measurements were carried out at 20 kHz.

Results and discussion

Effect of temperature

It can be known that the temperature dependence of electrical conductivity can be expressed by the Arrhenius law as:

$$\sigma = A\exp(-E/RT) \quad (1)$$

or

$$\ln\sigma = \ln A - E/RT \quad (2)$$

where σ is electrical conductivity, Ω^{-1} cm^{-1}; A is pre-exponent factor; E is activation energy, J/(mol•K); R is the gas constant, 8.314 J/(mol•K); T is the absolute temperature, K. The temperature dependence of electrical conductivity was measured at $CO/CO_2 = 1$ for all slags. The effect of temperature on total electrical conductivity was shown in Figure 1. It can be seen that the temperature dependence of total electrical conductivity obeys the Arrhenius law very well and the total electrical conductivity increases as increasing the temperature.

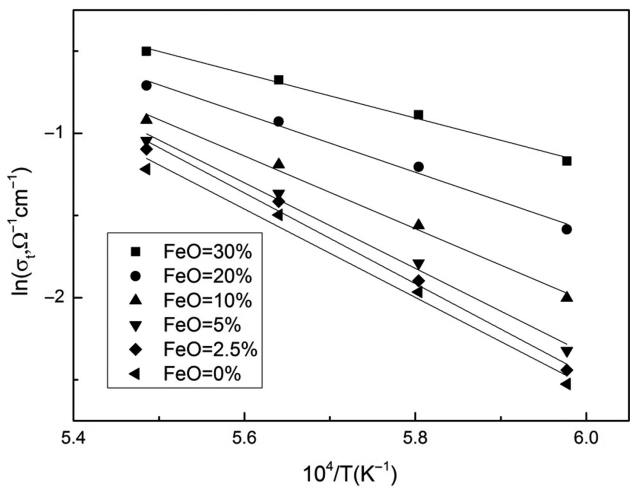

Figure 1: The effect of temperature on total electrical conductivity, at $CO/CO_2 = 1$.

Figure 2 shows the changes of the electronic transference number as functions of temperature for different slags, at $CO/CO_2 = 1$. As seen in this figure, the electronic transference number increases with increasing Fe_xO content. It also obviously shows that the electronic transference number is essentially independent of the temperature in the range of experimental conditions. The negligible effect of temperature on the transference number has also been reported by other authors. [16, 21, 22]

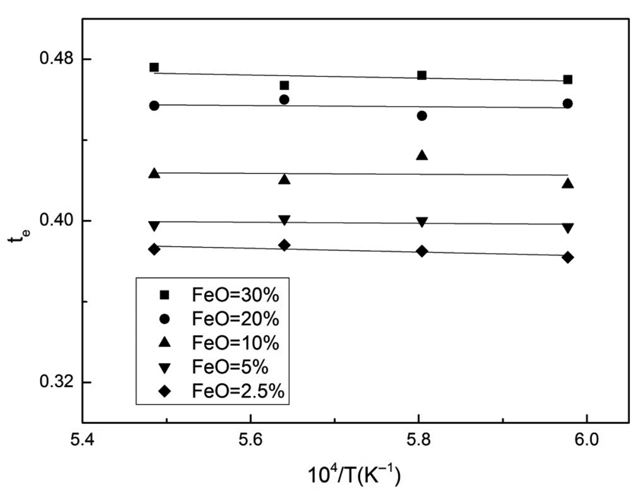

Figure 2: The changes of the electronic transference number as functions of temperature for different slags, at $CO/CO_2 = 1$.

Figures 3 and 4 show the effect of temperature on the ionic conductivity and electronic conductivity, at CO/

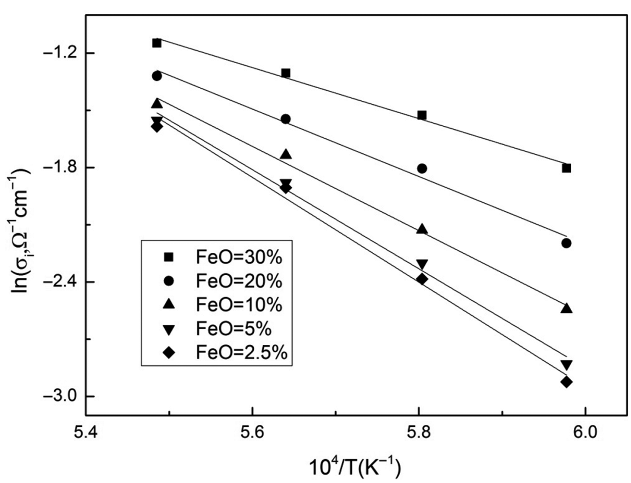

Figure 3: The effect of temperature on the ionic conductivity at $CO/CO_2 = 1$.

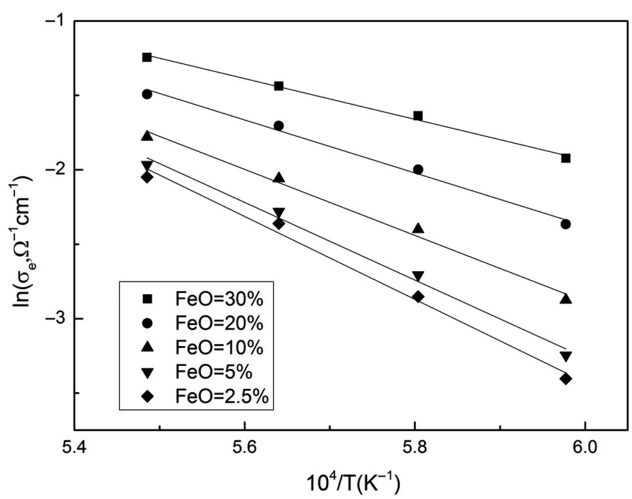

Figure 4: The effect of temperature on the electronic conductivity at $CO/CO_2 = 1$.

$CO_2 = 1$. Just liking the total conductivity, the relationships between temperature and both ionic conductivity and electronic conductivity follow the Arrhenius law.

Effect of equilibrium oxygen potential

Figure 5 shows the total electrical conductivity for different compositions at 1,823 K (1,550 °C) as a function of CO/CO_2 ratio. In Figure 5, the data of B = 0.64 (B was defined as the optical basicity value of the composition excluding Fe_xO) was cited from our previous research [23]. As seen, for slags with various Fe_xO contents, increasing the CO/CO_2 ratio will decrease the total electrical conductivity. In addition, at a fixed CO/CO_2 ratio, the total electrical

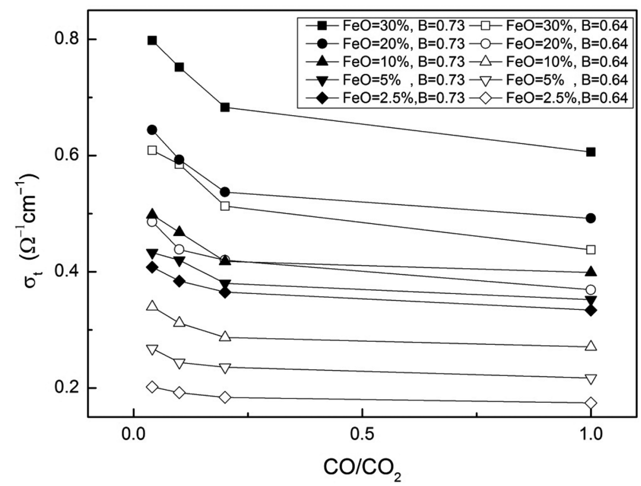

Figure 5: The total electrical conductivity for different compositions at 1,823 K (1,550 °C) as a function of CO/CO_2 ratio. (B: Optical basicity).

conductivity increases as increasing Fe_xO content, because of the increase of ferrous ion acting as the main conductor.

The CO/CO_2 dependence of electronic transference number for different slags at 1,823 K (1,550 °C) is shown in Figure 6. It is evident from Figure 6 that the electronic transference numbers vary from about 37 % to 73 % under the present experimental conditions. Moreover, Electronic transference number decreases as increasing CO/CO_2 ratio but increases slightly as increasing the Fe_xO content.

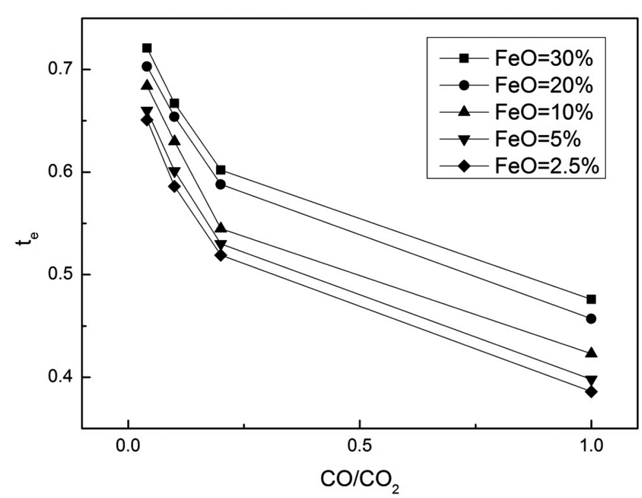

Figure 6: The CO/CO_2 dependence of electronic transference number for different slags at 1,823 K (1,550 °C).

In the iron-bearing molten slags, the tendency of the ferric ion toward covalent binding with oxygen is strong enough to stimulate the formation of highly covalent anions (FeO_4^{5-}) instead of an isolated Fe^{3+} cation. Therefore, the reaction among ferrous ion, ferric ion and gas is shown as follows:

$$4FeO_4^{5-} = 4Fe^{2+} + O_2 + 14O^{2+} \tag{3}$$

Figure 7 shows the effect of the CO/CO_2 ratio on ionic conductivity at 1,823 K (1,550 °C). It can be seen that for all slags, the ionic conductivity increases as increasing the CO/CO_2 ratio and Fe_xO content, which because of the increase of ferrous ions according to eq. (3). Fe^{2+} and Ca^{2+} ions are the main charge carriers in the Fe_xO-CaO-SiO_2-Al_2O_3 slags, however, the highly covalent anions (FeO_4^{5-}) have weaker mobility compared with Fe^{2+} ion. As increasing the CO/CO_2 and Fe_xO content, the Fe^{2+} will increase, which will lead to increase of the ionic conductivity.

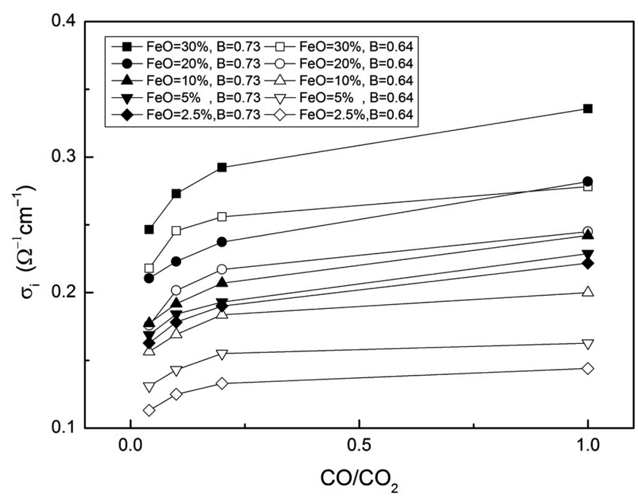

Figure 7: The effect of the CO/CO_2 ratio on ionic conductivity at 1,823 K (1,550 °C) (B: Optical basicity).

The electronic conductivity of all slags as a function of CO/CO_2 is shown in Figure 8. From Figure 8, the electronic conductivity of all slags decreases as increasing the CO/CO_2 ratio and decreasing the Fe_xO content. According to the diffusion-assisted charge transfer model proposed by Barati and Coley, [24] charge transfer between divalent and trivalent iron ions can be regarded as a bimolecular reaction. Before the electron hopping, the ions should travel to reach sufficiently short separation distance, that is to say, this model requires neighboring divalent and trivalent iron ions to interact. According to the Barati and Coley's study, when the content of iron oxide is fixed, the electronic conductivity is proportional to $y*(1-y)$, where y is the ratio of ferrous ion to the total iron. So, the electronic conductivity should first increase

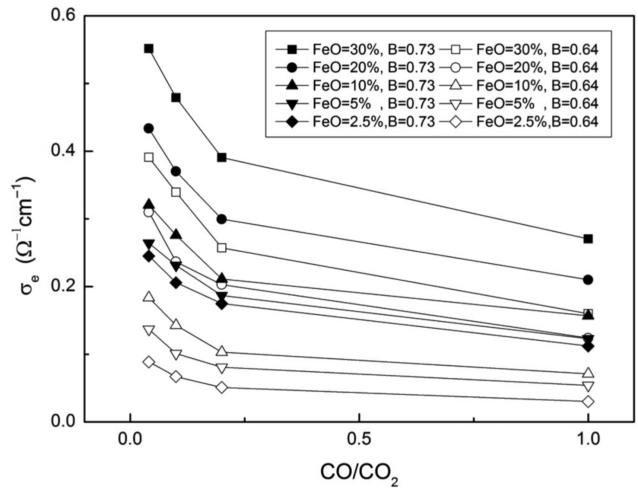

Figure 8: The effect of the CO/CO_2 ratio on electronic conductivity at 1,823 K (1,550 °C) (B: Optical basicity).

and then decrease as decreasing the oxygen potential (or increasing CO/CO_2 ratio) because of the monotonous increase of ferrous ion, and there should be a maximum when $Fe^{3+}/Fe^{2+} = 1$. In our results, it was found the electronic conductivity always decrease as increasing CO/CO_2 ratio. The reason for the absence of maximum may be that all the used oxygen potentials controlled by CO/CO_2 in the present study are not high enough, and even in the case of the lowest CO/CO_2 ratio, the y is still larger than 0.5. If y increases in the range of 0.5 to 1 as increasing CO/CO_2, there will be a monotonous decrease of electronic conductivity. In the present studied compositions, there are high content of Al_2O_3, which may also lead to the larger value of y. In other words, Al_2O_3 is beneficial for the increase of ferrous ion concentration, but harmful to ferric ion. This point can be interpreted from eq. (3), it can be seen that the increase of free oxygen ion concentration is beneficial for the increase of ferric ion concentration. However, Al_2O_3 can decrease the free oxygen concentration by the charge compensation effect of Al^{3+} ion which consumes the basic oxide such as CaO. So, the increase in Al_2O_3 content will lead to the equilibium of eq. (3) moves toward right to increase the concentration of ferrous ion. So, in the present oxygen potential and composition ranges, the ferrous ion proportion y may be so large (higher than 0.5) that the maximum of electronic conductivity could not occur.

Effect of basicity

The electrical conductivity of metallurgical slag is closely related to the optical basicity of slag [25], and it is meanful to study the influence of optical basicity of slag (except FeO) on electrical conductivity of Fe_xO-CaO-SiO_2-Al_2O_3. From Figures 5, 7 and 8, it is obvious that under the condition of constant Fe_xO content, the higher the optical basicity of slags is (the compositions with the optical basicity of 0.64 are also given in Table 1), the higher the total electrical conductivity and ionic/electronic conductivity will be. When the optical basicity of slag is high, there will be more free oxygen ion. From eq. (3), increasing of free oxygen ion will lead to the decrease of Fe^{2+} and increase of Fe^{3+}, which will result in increasing of the product of the concentrations of Fe^{3+} and Fe^{2+} ions, since as stated above the value of y is in the range of 0.5 to 1. So, the electronic conductivity of the slag with a high optical basicity is higher. From the variation tendencies of ionic and electronic conductivity with optical basicity, it can be concluded that the total electrical conductivity increases as increasing the optical basicity, as shown in Figure 5.

Conclusions

In this study, the composition dependences of electrical conductivity of Fe_xO-CaO-SiO_2-Al_2O_3 slags at different oxygen potentials and temperatures have been studied experimentally. For all slags, the total electrical conductivity and electronic conductivity decrease as increasing CO/CO_2 ratio from about 0 to 1. As increasing Fe_xO content, the total electrical conductivity and electronic conductivity increase at a fixed CO/CO_2 ratio. The results also show that the ionic conductivity increases with increasing the CO/CO_2 ratio, which is resulted from the increase of Fe^{2+} ion concentration. In the present experimental conditions, a higher optical basicity will promote the total electrical conductivity, ionic conductivity and electronic conductivity. The electronic transference number exhibits a strong relationship with oxygen potential, but is independent of temperature. In addition, the temperature dependences of ionic, electronic and total conductivity for different compositions obey the Arrhenius law.

Funding: Thanks are given to the National Natural Science Foundation of China (51304018 and 51474141).

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