Some Evidences on the Instability of Cr-Cr₂O₃ Electrode in the Electrochemical Oxygen Sensors at Steelmaking Temperatures*

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Synopsis

Anomalies are observed in measurements of electromotive force and electric conductivity measurements of solid oxide electrolyte cells involving Cr(s)-Cr₂O₃(s) electrode. Transformation in Cr(s)-Cr₂O₃(s) system at about 1 653 K is suggested to explain the anomalies mentioned above on the basis of measured temperature dependencies of electromotive force and total and electronic conductivities of the cells.

I. Introduction

It is well known that one of the most important applications of the solid oxide electrolytes is their use in galvanic cells, for example, as is shown below,

which is used for monitoring of oxygen activity in steelmaking processes.

In order to obtain a correct measure it is of great significance to know behaviour of reference electrode as well as the electrolyte domain of the solid electrolyte utilized. In fact, unless both of these aspects mentioned above are considered, they may cause errors because of the following reasons:

(1) Any physico-chemical transformation in the reference electrode materials could strongly change its own oxygen chemical potential, μ'_{O_2} ; its electrical potential changes with EMF of cell I.

(2) To calculate EMF of cell I, the Wagner's equation¹⁾

$$EMF = (1/4F) \int_{\mu'_{O_2}}^{\mu''_{O_2}} t_{ion} d\mu_{O_2} \dots\dots\dots(1)$$

is applied, however, integration by Eq. (1) cannot be carried out because the ionic transport number, $t_{ion} = f(\mu_{O_2})$, is not always known as a function of oxygen chemical potential. The Nernst's equation

$$EMF = (RT/4F) \ln (P''_{O_2}/P'_{O_2}) \dots\dots\dots(2)$$

is used only when t_{ion} is unity within a range of μ_{O_2} from μ'_{O_2} to μ''_{O_2} , which, respectively, corresponds to P'_{O_2} and P''_{O_2} . This means that for a given solid oxide electrolyte it is necessary to set both of μ'_{O_2} and μ''_{O_2} inside the electrolyte domain,²⁾ in which t_{ion} is guaranteed to be equal to unity.

If this restriction is not satisfied measured EMF will be always less than the value calculated by Eq. (2).

Therefore, these two effects derive changes in value of measured EMF of cell I and accordingly an error on calculated value of the oxygen activity in liquid steel; the difference between values of measured and true EMF is principally indeterminate in the first case and always less than the true value in the second one, though, in the latter case, the magnitude of the error can be sometimes evaluated by Schmalzried's equation.³⁾

Concerning the effect of the electronic conductivity of solid electrolytes on the EMF of galvanic cells, several papers have been published⁴⁻¹⁰⁾ in which the criteria to avoid or to minimize errors caused by partial short circuit generating through the electrolyte is suggested.

An aim of this paper is to put questions to the stability of the Cr(s)-Cr₂O₃(s) system, at least when it acts as reference electrode in galvanic cells used for monitoring of oxygen activity in liquid steel. The anomalous behaviour of Cr(s)-Cr₂O₃(s) electrode is systematically shown through electrochemical measurements independently carried out at the Centro Sperimentale Metallurgico, SpA, Rome, and at the Istituto di Chimica Fisica, Università di Roma. The electrolytic properties of solid electrolytes such as YDT (yttria doped thoria), CSZ (calcia stabilized zirconia) at the equilibrium oxygen partial pressure of Cr(s)-Cr₂O₃(s) mixture are also derived by taking the anomalies of Cr(s)-Cr₂O₃(s) system into account.

II. Experimental

1. Measurements in Liquid Iron

The measurements were carried out in a Tamman or in a Balzers furnaces; the Balzers furnace was appropriately modified to accept the glavanic cell without any oxygen contamination by introducing inert atmosphere.

Iron baths were prepared by melting suitable quantities of Armco iron in alumina (Tamman furnace) or magnesia (Balzers furnace) crucibles under inert atmosphere (flowing high purity argon).

Magnesia stabilized zirconia (MSZ) tubes with 3 w/o of MgO content were used as solid electrolytes and their dimensions were 12.7 mm O.D.×9.5 mm I.D.×45.6 mm length, as supplied from Zircoa (USA). An MSZ sample was chemically analysed and its purity was found to be of 99.3 w/o with an

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Fe₂O₃ content of 0.15 w/o.

The electrolyte tubes were filled with Cr(s)-Cr₂O₃-(s) mixture for a length of about 3 cm, which was covered with alumina powder. The mixture containing 2 w/o of Cr₂O₃ was prepared by dry mixing of 325 mesh powders. Purity of Cr and Cr₂O₃ powders, purchased from Cerac (USA) was, respectively, 99.95 % and 99.7 %. The reference electrode and the iron bath were connected to a high impedance digital electrometer (precision ±1 mV) by molybdenum leads. A Metamic sheath was used to encase Mo lead wire to be dipped in iron bath, which caused thermal EMF against Mo less than 1 mV at 1 873 K.

Samples taken from iron bath by a home-made quartz sampler were chemically analysed.

2. EMF and Conductivity Measurements

EMF measurements were carried out on the following cells:

in which ThO₂ discs doped with 10 w/o of Y₂O₃ supplied from Zircoa or Sfec Corporations were used as the solid electrolyte. The differences between electrolyte discs were only in dimensions and in impurity level of the electrolytes: In electrolyte discs made by Zircoa with diameter of 9.27 mm and thickness of 5.08 mm, iron oxide (0.6 w/o) was detected by chemical analysis whereas in discs made by Sfec (4.5 mm dia. and 4.5 mm in thickness) iron oxide was not detected.

The electrode discs were prepared by cold pressing (1.4 GPa) suitable amount of the mixture, prepared by dry mixing of 325 mesh powders of the metal and its oxide in the weight ratio 10:1. Powders of Ta and Ta₂O₅ were purchased from Cerac both with stated purity of 99.9 %. Both the Cr-Cr₂O₃ and Ta-Ta₂O₅ discs were separately sintered and treated as described in literature,¹¹⁾ whose final dimensions were 6 mm dia. and 3~5 mm in thickness.

Both total and partial electronic conductivity measurements were simultaneously carried out, respec-

tively, on the cell

Mo/Cr(s)-Cr₂O₃(s)/CSZ/Cr(s)-Cr₂O₃(s)/Mo ...IV

by the alternating current method and on cell

(+) Mo/Cr(s)-Cr₂O₃(s)/CSZ/Pt/Mo (-)V

by the blocking electrode technique.

Detailed informations on assembly of these cells and on measured results have been reported previously by the present authors.¹¹⁾

III. Results

1. EMF Measurements of Liquid Iron

On Fig. 1 are shown typical EMF curves for cell I with an aim to monitor activity of oxygen in iron bath containing various amounts of dissolved oxygen.

Curves of type *a* were observed in a range of oxygen activity from 50 to about 400 ppm, whereas, above the latter value a new trend of type *b* was noticed.

Measured EMF values at,

1) Immediately after immersion of the probe,
2) 4 min after immersion of the probe,

are, respectively, given in Table 1, column Nos. 3 and 6 and oxygen content of liquid steel determined by chemical analysis is also given in column No. 9.

EMF curves changing stepwise may be explained by the hypothesis that a transformation in Cr(s)-Cr₂O₃(s) reference electrode may take place at about 20 sec after immersion of the cell, as will be given in the discussion.

Oxygen activities were calculated for two cases according to assumptions as follows:

Fig. 1. EMF trends of cell I depending on activity of oxygen, a_O, in liquid iron.

Table 1. Oxygen activity, a_{O} , in liquid iron measured by cell I. (Cr-Cr₂O₃ reference mixture with 2 w/o of Cr₂O₃)

No.	Temp. of the bath (K)	Immediately after immersion			4 min after immersion			Chemical analysis $\bar{O}$ (ppm)
		EMF (mV)	$a_{\bar{O}}$ (ppm)		EMF (mV)	$a_{\bar{O}}$ (ppm)		
			Cr-Cr ₂ O ₃ Ref.	Cr-Cr ₃ O ₄ Ref.		Cr-Cr ₂ O ₃	Cr-Cr ₃ O ₄	
1	2	3	4	5	6	7	8	9
1	1 823	100	59	(191)	14	(17)	56	70
2		134	80	(259)	52	(28)	90	—
3		178	141	(454)	97	(50)	160	140
4		218	235	(756)	134	(80)	260	260
5		228	267	(858)	134	(80)	260	250
6		225	257	(826)	143	(90)	290	—
7		258	391	(1 258)	168	(124)	400	—
8		263	416	(1 341)	168	(124)	400	—
9		280	517	(1 665)	188	(160)	516	—
10		278	504	(1 623)	192	(169)	543	—
11		287	565	(1 820)	201	(189)	609	560
12		298	650	(2 094)	209	(209)	674	690
13		304	702	(2 260)	215	(226)	727	—
14	1 873	191	247	(792)	85	(66)	212	—
15		239	447	(1 436)	145	(136)	448	420
16		254	539	(1 730)	164	(176)	567	530
17		268	641	(2 057)	178	(210)	674	—
18		269	649	(2 083)	182	(220)	708	—
19		301	965	(3 097)	210	(312)	1 002	950
20		312	1 105	(3 550)	227	(385)	1 237	—
21		327	1 331	(4 275)	236	(431)	1 384	1 360
22	1 923	100	119	(382)	15	(43)	137	120
23		137	187	(598)	34	(54)	172	—
24		184	329	(1 054)	94	(112)	355	300
25		207	435	(1 392)	119	(150)	480	500
26		283	1 088	(3 483)	189	(350)	1 120	1 050

(b) Cr(s)-Cr₃O₄(s) equilibria:
 $3\text{Cr(s)} + 2\text{O}_2\text{(g)} = \text{Cr}_3\text{O}_4\text{(s)}$ (7)
 $\Delta G^\circ = -1503.31 + 0.378T \text{ kJ/mol}$(8)
(Danilovich *et al.*, cited in the paper of Gasik *et al.*¹³⁾)*
 $\log P_{\text{O}_2} \text{(ref.)} = -39\,275.6/T + 9.87$ (9)
 $\log a_{\text{O}} = 5.0866 + (10\,083E - 13\,519)/T$ (10)

The calculated values of a_{O} are given in columns Nos. 4, 5, 7 and 8 of Table 1; the values in columns Nos. 4, 8 are compared with oxygen contents determined by chemical analysis (column No. 9 in Table 1) in Fig. 2.

2. Analysis of Cr(s)-Cr₂O₃(s) Electrode after EMF Measurements

At the end of measurements lasting more than 20 min zirconia tube was chilled in water. Reference electrode mixture in a chilled specimen was treated by Br₂-CH₃OH solution and successively by H₂SO₄. A rough determination of metallic, bivalent, and trivalent chromium becomes possible by these two treatments. From data given in Table 2, content of Cr-

(II) in the reference electrode dipped in an iron bath at higher oxygen activity is higher than that dipped at lower oxygen activity.

X-ray diffraction applied on powder obtained after the Br₂-CH₃OH treatment gave diffraction pattern corresponding to Cr₂O₃ and that for another hexagonal phase with $a=0.279 \text{ nm}$ and $c=0.446 \text{ nm}$. According to the diffraction tables,¹⁴⁾ these parameters might be attributed to Cr₂C, however, carbon was not detected by chemical analysis of the specimen. Hansen¹⁵⁾ and Pearson¹⁶⁾ attributed the diffraction pattern of the hexagonal structure to “CrO” and some authors^{17,18)} to Cr₃O₄ (CrO·Cr₂O₃) or “twisted spinels”.

Reference electrode mixture suffers immediate oxidation if it is cooled in air after use: therefore, it is difficult, if not impossible, to confirm whether divalent Cr ion have been present just before cooling or not.

3. Effect of Iron Oxide Contained in YDT on EMF

During EMF measurements of cell II to determine standard free energy change of Cr₂O₃(s), marked dif-

* Applicable temperature range of Eq. (8) is not given in that paper. Consequently, the applicable temperature range of Eqs. (9) and (10) cannot be given.

Fig. 2. Comparison between activity of oxygen calculated by Eq. 6 (Cr-Cr₂O₃ as reference mixture—Table 1, column No. 4) and that by Eq. 10 (Cr-Cr₃O₄ as reference mixture—Table 1, column No. 8). In brackets oxygen contents determined by chemical analysis are shown.

Table 2. Chemical analysis of Cr-Cr₂O₃ reference mixture (2 w/o of Cr₂O₃) used for EMF measurements of 1 hr at two activity values of the dissolved oxygen in liquid iron.

a_{O} (ppm)	Colour after chilling	% Cr soluble in Br ₂ -CH ₃ OH sol. -Cr(0)-	% Cr soluble in H ₂ SO ₄ (1+1)v/v sol. -Cr(II)-	% Cr in the residual -Cr(III)-
200	bright	92.3	3.2 (4.1)	2.3 (2.6)
1 000	dark	83.2	13.2 (17.0)	1.5 (1.7)

Values in brackets denotes concentrations as oxides.

ference was observed between EMF *vs.* temperature curves obtained for cells II and III as were shown in Figs. 3 and 4.

Photograph 1 shows SEM analysis on the Cr(s)-Cr₂O₃(s) disc surface in contact with the electrolyte of cell II before and after the experiments. In the latter case contamination of Cr(s)-Cr₂O₃(s) with iron oxide in an electrolyte disc is clearly observed, which suggests existence of compounds such as Fe₂O₃·Cr₂O₃ or FeO·Cr₂O₃ at the interface between Cr(s)-Cr₂O₃(s) electrode and electrolyte.

What is important to emphasize is in the difference in shape of EMF *vs.* temperature curves. The interaction of Cr(s)-Cr₂O₃(s) electrode with small amount of iron compounds in the electrolyte disc may shift the break point from 1 653 K (Fig. 4) to 1 327 K (Fig. 3) because the principal difference between cells II and III is in iron oxide content in electrolyte disc used. While the fact that temperature dependence of EMF of cell II becomes negative at $T < 1\,327\text{ K}$

Fig. 3. Temperature dependence of EMF for cell II.

and cell III at $T > 1\,653\text{ K}$, suggests that cell reaction with negative entropy change takes place other than reaction,

Fig. 4. Temperature dependence of EMF for cell III.

which should have positive temperature dependency of EMF. At a temperature range higher than 1 327 K, temperature dependence of EMF well agrees with the theoretical one for cell II calculated by using appropriate thermochemical data in JANAF Table.¹⁹⁾ As are shown in Photo. 2 (X-ray selective diffraction patterns on surfaces of Cr(s)–Cr₂O₃(s) electrode discs before and after an experiment), chromium oxide phase is consumed at the surface of disc after EMF measurement. If the cell worked in an ideally open circuit, change in chemical composition of the electrode surface should not be detected, however, the electronic conduction through the electrolyte promotes the most electrokinetically activated reaction among those thermodynamically possible. From temperature dependency of EMF and change in surface composition the reaction (11) seems to take place in cell II in the direction to consume away Cr₂O₃ phase.

Through we observe a diffraction pattern quite similar to those shown in Photo. 2 temperature dependency of EMF of cell III is very far from the theoretical one.

Above 1 327 K for cell II (see Fig. 3), EMF values do not depend on the thermal cycle and they begin to have a linear and reproducible behaviour as the temperature reached for the first time about 1 327 K as one can see by following the sequence of the experimental points. Besides, the similar behaviour is also observed on EMF of cell III at a temperature range lower than 1 653 K (Fig. 4).

Photo. 1. Results of analysis on Cr–Cr₂O₃ electrode surface by using SEM.

Photo. 2. Selective X-ray diffraction spectra on surfaces of Cr–Cr₂O₃ electrode discs.

4. Measurements of Ionic and n-type Conductivity of 15 m/o CSZ Electrolyte

On relation to the anomalies in EMF *vs.* temperature curves, some aspects of conductivity measure-

ments made by the authors¹¹⁾ is summarized, which is closely related to the transformation phenomena in Cr(s)-Cr₂O₃(s) electrodes of cells IV and V mentioned above:

- (a) $A \log \sigma_{ion}$ vs. T^{-1} curve shows a break point at 1 658 K (cell IV, see Fig. 5).
- (b) Total conductivity, σ_t , depends on the frequency in the range of 50~300 Hz and the trend is a function of temperature. At about 1 663 K, this trend changes in sign (cell IV, see Fig. 6).
- (c) Arrhenius plot of n -type conductivity, σ_n^2 , also shows a break point at about 1 623 K (cell V, see Fig. 5).
- (d) The transport number of oxygen ion, $t_{O^{2-}}$ vs. T curves has a sharp decrease at about 1 653 K (see Fig. 7).

It is important to emphasize that the experimental observations, have been derived by various experimental devices applied on cells IV and V. For example, to evaluate ionic transport number, $t_{O^{2-}}$, two different methods have been adopted;

- 1) By using data of σ_t and σ_n^2 , respectively, measured by cells IV and V through equation $t_{ion}=(\sigma_t -$

- $\sigma_n^2)/\sigma_t$ (Fig. 7(A)),
- 2) By oscillographic detection of the current peak obtained by very sudden polarization steps (1 000 V/sec, Fig. 7(B), and 50 V/sec, Fig. 7(C)) applied to cell V.

In this case the peak and the stationary current values, respectively, represent the total current crossing the cell and the current due to the migration of excess electrons, e' , in the solid electrolyte. Accordingly, observation, (d), can be considered as another independent information supporting the instability of the Cr(s)-Cr₂O₃(s) electrodes.

From Photo. 3, one can easily understand that the melting of the Cr(s)-Cr₂O₃(s) disc occurred. In this case, the highest temperature reached was 1 917 K, melting of Cr(s)-Cr₂O₃(s) mixture might occur at a temperature lower than 1 917 K as was observed previously.^{10,23,26)}

Fig. 5. Relations among ionic conductivity, n -type conductivity, absolute temperature, and oxygen partial pressure. Dashed straight-line denotes oxygen partial pressure of mixture Cr(s)-Cr₂O₃(s) calculated according to JANAF Tables.¹⁹⁾

Fig. 6. Evaluation of the transition temperature by the function of $(d \log \sigma_t / df)_{f=0}$ obtained by cell IV.

Curve A: $(\sigma_t - \sigma_n^2) / \sigma_t$
Curves B and C: $I_\infty / I_p(1000)$ and $I_\infty / I_p(50)$ ratios, respectively.

I_∞ stands for stationary current and I_p for the peak current. Bracketed numbers refer to sweep voltage rate values in V/sec.

Fig. 7. Relations between ionic transport number, t_{ion} and temperature.

- A: An electrolyte disc after the experiment
 B: An electrolyte disc before the experiment
 C: Alumina container of the cell
 D: Molybdenum lead
 E: Cr-Cr₂O₃ electrode

Photo. 3. A typical example of cell V after an experiment.

IV. Discussion

In the experimental results mentioned above it undoubtedly seems that Cr(s)-Cr₂O₃(s) electrode is the principal cause of the observed discrepancies. In fact, apart from the results in liquid iron, some phenomena occurs at a temperature very close to 1 653 K which gives a break point in EMF *vs.* temperature curves and concerns other than the electrolyte itself utilized. (Exceptionally, the reaction of iron oxide impurities in the electrolyte with Cr(s)-Cr₂O₃(s) electrode are probably responsible for the different behaviour observed in the temperature range lower than 1 327 K, Fig. 3).

Concerning the role of iron in the Cr-O system, literatures seem to agree with the stabilizing effect of iron on Cr₃O₄ phase^{18,20-22}; therefore the different trends in Figs. 3 and 4 observed in the temperature range lower than about 1 300 K might be attributed to the properties of Fe-Cr-O system.

Because EMF is markedly influenced by the electronic conduction within the electrolyte, anomalies observed in Figs. 3 and 4 should be discussed with oxygen flux rising from Cr(s)-Cr₂O₃(s) electrode to Ta(s)-Ta₂O₅(s) electrode and *vice versa* for electrons, rather than thermodynamic data on Cr(s)-Cr₂O₃(s) system. This phenomena practically corresponds to an internal discharge of the cell which reduces Cr₂O₃ and oxidizes tantalum.

It is very difficult to identify the products of these two processes probably because their quantities are too small for analysis by X-ray and/or they are stable only at high temperature. For instance, according to Hilty *et al.*,¹⁸ Cr₃O₄ disproportionate to Cr and Cr₂O₃ upon slow cooling or reheating. The suggestion given by Hilty *et al.* well explains the disappearance of Cr₂O₃ from the surface of the Cr(s)-Cr₂O₃(s) electrode (Fig. 6).

A possible reaction scheme can be deduced by con-

sidering the results obtained at measurements in liquid iron (Table 1) where the oxygen chemical potential of the bath is higher than that of Cr(s)-Cr₂O₃(s) mixture. The equilibrium reaction which determines EMF in cell I after 30 sec (see Fig. 1) cannot be the oxidation of Cr to Cr₂O₃ unless ΔG° for formation of Cr₂O₃(s) is affected by a large error.

The experimental results, however, agree well with the case when one assumes formation of Cr₃O₄(s). Therefore, decrease in EMF observed at about 20 sec after the immersion of cell I (Fig. 1) might be attributed to a reaction of the following type

which necessarily involves an electronic conduction through the electrolyte. This agrees with a higher Cr(II) content in the electrode dipped in liquid steel with a higher activity of oxygen as found by chemical analysis (see Table 2). When the equilibrium between Cr(s) and Cr₃O₄(s) is reached at the Cr(s)-Cr₂O₃(s) electrode/electrolyte interface, a stationary trend of EMF is observed for several min as is shown in Fig. 1. A further decrease of EMF noticed in case of curve *b* in Fig. 1, can be again explained in terms of the complete depletion of Cr at Cr(s)-Cr₂O₃(s) electrode/electrolyte interface by reaction (12). Obviously, this change occurs more rapidly at higher gradient of oxygen activity because the gradient is the driving force of the reaction (12).

When the cell I works in iron baths with oxygen activity lower than that of the reference electrode, EMF of cell I calculated by assuming Cr(s)-Cr₃O₄(s) equilibrium gave too high oxygen activity in comparison with those derived from soluble aluminum content given by the chemical analysis and Al-O equilibria. So, for killed baths, we suggest the presence of CrO in the reference mixture as already supposed by Healy and Schotmiller²³ in the study of the Cr-Si-O system.

Since thermochemical data do not exist on CrO(s), we approximately evaluated ΔG° for CrO by using Gasik *et al.*'s, data on CrO(l)¹³ by taking the Cr(l)→Cr(s) transformation into account.

As a result of thermochemical calculations, the standard free energy change of CrO formation has been derived in the temperature range from 1 873 to 2 153 K as follows:

$$\Delta G^\circ = -516.306 + 0.038T^{(13)} \text{ kJ/mol} \\ (1\,873 \sim 2\,153 \text{ K}) \quad \dots\dots\dots(14)$$

$$\Delta G^\circ = -41.84 + 0.0188T^{(12)} \text{ kJ/mol} \\ (1\,873 \sim 2\,153 \text{ K}) \quad \dots\dots\dots(16)$$

$$\Delta G^\circ \cong 0 \text{ kJ/mol} \quad \dots\dots\dots(18)$$

$$\Delta G^\circ = 474.47 + 0.019T \text{ kJ/mol} \\ (1\,873 \sim 2\,153 \text{ K}) \quad \dots\dots\dots(20)$$

According to Healy and Schottmiller the melting temperature of CrO is close to 1 873 K, consequently, $4G^\circ$ of reaction (17) can be considered negligibly small when compared with the uncertainty of Eq. (14). Oxygen partial pressure calculated by Eq. (20) is 5.7×10^{-13} atm at 1 873 K not far from that for Cr(s)–Cr₂O₃(s) electrode (7.8×10^{-13} atm).¹²⁾

Discussions mentioned above do not claim to show a true stoichiometry but they only mean that the formation of compounds or solid solutions different from Cr₂O₃(s) may be possible. In any case activity of oxygen according to Eq. (10) (Cr(s)–Cr₃O₄(s) reference) well agrees with our experimental points and with those of Foerster and Richter.²⁴⁾ Similar results have also been obtained by Iwase.²⁵⁾

Finally, the conductivity measurements represent a further confirmation of the anomalous behaviour of the Cr(s)–Cr₂O₃(s) electrode, since the break points observed in the Arrhenius plots should not be attributed to electrolyte characteristics but to changes in the electrolyte/electrode interface.

Obviously, these changes entail physical and chemical effects on the electrode properties which are detected with different sensitivity according to the experimental technique utilized. Therefore, the total conductivity measurements is considered to be the most suitable method to follow the physical displays of these changes, whereas, the measurement of the electronic conductivity is the most suitable device to follow the chemical ones. In fact, the break points in the total conductivity is mostly caused by a change in the bulk resistance of Cr(s)–Cr₂O₃(s) electrodes (cell IV) and the break point in the electronic conductivity mostly by a change in oxygen partial pressure at the electrode/electrolyte interface which modifies the electrolyte behaviour.

V. Conclusions

The instability of the Cr–O system at temperature lower than that of the steelmaking processes are deduced to explain the anomalies found in different and independent measurements on electrochemical cells, involving Cr(s)–Cr₂O₃(s) electrodes, carried out in two different laboratories and in dissimilar experimental conditions.

Such a standpoint agrees with some authors^{18,20–22)} on the Cr–O system at high temperatures, however, it could not be exactly defined by any devices applicable at present.

The authors hope that this paper may contribute to question this problem by a critical revision of the Cr(s)–Cr₂O₃(s) system as reference electrode in the oxygen sensors at steelmaking temperatures especially when activity of oxygen in liquid steel is monitored in a long period.

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