A Survey on Industrial Applications of Oxygen Concentration Cells with Solid Electrolytes

By Kazuhiro S. GOTO**

1. A History of Investigations on Oxygen Concentration Cells at Elevated Temperatures

The oxygen concentration cell can be defined as a type of galvanic cells, whose electromotive force is generated by the difference in the chemical potential of oxygen, or in other words, in the oxygen concentration, at the two electrodes under isothermal and isobaric conditions.

As the electrolyte, used are the solid or liquid oxides with predominant ionic conductivity at elevated temperatures. This category of galvanic cells can be expressed by the following generic cell formula;

\[
P'_o \frac{p}{p'_o} \text{ Electrode I} \quad \text{Solid or liquid} \quad \frac{p}{p'_o} \text{ Electrode II} \quad \text{oxides with} \quad \text{ionic conduction}
\]

In 1908, Haber measured the electromotive force of this type of cell, using Thuringer hard glass as the electrolyte. Eight years later, Treadwell tried to use fused borates, silicates, or solid porcelain as the electrolyte and to control the oxygen pressure at the electrodes by using the two phase mixtures of Fe and FeO, or Cu2O and CuO. A similar study was independently reported by Baur, et al. After the extensive study by Treadwell, the oxygen concentration cells have been investigated in many countries. Among them, Esin in Russia has constructed various types of the oxygen concentration cells.

In 1957, Sanbongi, Ohtani and Omori reported a review including all reports after Treadwell, and hence the details will not be repeated here, except for the industrial applications.

The first industrial application of the oxygen concentration cells was reported by Onaka in 1944. To control the refining operation of steels, he tried to determine the oxidizing power of the slag of an acid open hearth furnace from the electromotive force of the following cell:

\[
\begin{align*}
Pt & \text{(I),} \quad \text{Slag I} \quad \text{SiO}_2 \quad \text{tube} \quad \text{Slag II} \quad \text{Pt (II),} \\
P'_o & \quad \text{P}_o
\end{align*}
\]

where the electrolyte was composed of solid silica containing iron oxide absorbed from slag I.

Onaka showed that the electromotive force is exclusively generated by the difference in the oxygen potential of the two slags or in the ratio of Fe\textsuperscript{3+} to Fe\textsuperscript{2+}-content.

Then, he tried to determine rapidly the oxygen concentration in molten steels from the electromotive force of the following cell:

\[
\begin{align*}
\text{Liquid} & \quad \text{Fe-O} \quad \text{Ag} \quad \text{Slag from acid open hearth furnace} \\
& \quad \text{Ag, H}_2 \text{ or O}_2 \text{ gas} \quad \text{(reference elect'd.)}
\end{align*}
\]

Figure 1 shows the structure of this cell and Fig. 2 the relation between the electromotive force and the oxygen content in steels determined by the conventional vacuum fusion method.

A similar experiment was made by Sanbongi and Ohtani supported by Fuji Iron and Steel Corp., using solid magnesia as the electrolyte in 1958.

In Japan, these two investigations played an important role in the development of the oxygen concentration cells for the rapid oxygen analysis of molten steels. The cells are now widely used in Japanese steel plants as described in the following section. All

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the investigations cited above are quite unique, but the following reasons limited their wider applications.

1. The electric conduction mechanism in the electrolytes was not clearly known. Virtual cell reactions were not definite accordingly.

2. Because solid oxides with large ionic conductivity were not yet found, the internal resistance of the cells was too large to have a reproducible electromotive force.

3. When liquid oxides are used instead of solid ones, the internal resistance of the cell can be reduced, but in many cases, the liquid electrolytes react with the electrode materials. Therefore, the stability of the electromotive force was not acceptable.

These difficulties could be covered to some extent by the art of the construction of the galvanic cells and the careful measurements of the electromotive forces. However, the difficulties limited the applications of the oxygen concentration cells only to specific experiments.

To solve these theoretical problems, C. Wagner\(^9\) reported two theoretical works in 1933 and 1966, which strictly related the conduction mechanism of the oxide electrolytes to the electromotive force at elevated temperatures.

Furthermore, Kiiukkola and Wagner\(^11\) discovered that zirconia or thoria base solid solutions can be used as the electrolyte to have very stable and reproducible electromotive forces, simply because of their very large oxygen ion conductivity above 500°C.

Thanks to this celebrated publication, high temperature electrochemistry has been extensively developed all over the world in the 1960's.

Two review papers have been published on this development in 1970 by Rapp and Shores\(^12\) and in 1972 by Goto and Pluschke\(^13\) documenting 242 and 295 publications, respectively. However, these review papers did not deal with the industrial applica-

\[ E = \frac{RT}{4F} \int_{P_{o_{1}}}^{P_{o_{2}}} (t_{a} + t_{b}) d \ln P_{o} \]

\[ = \frac{RT}{2F} \int_{a_{a}}^{a_{a'}} (1 - t_{a}) d \ln a_{a} \]

\[ = \frac{RT}{2F} \int_{a_{a}}^{a_{a'}} (1 - t_{a}) d \ln a_{a} \]

\[ \text{where,} \ E: \text{the electromotive force} \]

\[ F: \text{the Faraday constant} \]

\[ P_{o_{1}} \text{and} P_{o_{2}}: \text{the oxygen pressures at the two electrodes} \]

\[ a_{a} \text{and} a_{a'}: \text{the chemical activities of the metal at the two electrodes} \]

\[ t_{a}: \text{means the transference number of the charge carriers} \]

For zirconia base solid electrolytes, the transference number of oxygen is known to be unity at a higher oxygen pressure, and thus all other transference numbers become zero. Therefore, Eq. (5) gives simply

\[ E = \frac{RT}{4F} \ln \frac{P_{o_{1}}}{P_{o_{2}}} \]

At an oxygen pressure lower than that for chromium–chromium oxide equilibrium, the transference number of electrons cannot be neglected and is given as a

\[ E = \frac{RT}{4F} \ln \frac{P_{o_{1}}}{P_{o_{2}}} \]

\[ \text{II. The Conduction Mechanism in the Oxide Electrolytes and the Electromotive Force} \]

1. For the Case of the Oxide Electrolytes of Uniform Composition

The cell can be described as follows.

\[ P_{o_{1}} \]

Electrode I \ MO, of uniform composition \ P_{o_{2}} \]

Electrode II \ ...

The charge carriers in the oxide, MO, would be M\(^2+\), O\(^2-\), electrons or positive holes. Using the assumption of the local equilibrium in the electrolyte, Wagner\(^9\) obtained the Gibbs free energy change of the thin slice of the electrolyte, when the infinitesimal current was supplied to the cell under isobaric conditions. Then, this infinitesimal Gibbs free energy change was integrated from the leftmost to the rightmost side of the electrolyte to obtain the total free energy change of the virtual cell reaction. Using the relation, \(JG = -nFE\), one gets the following expression for the electromotive force:

\[ E = \frac{RT}{4F} \int_{P_{o_{1}}}^{P_{o_{2}}} (t_{a} + t_{b}) d \ln P_{o} \]

\[ = \frac{RT}{2F} \int_{a_{a}}^{a_{a'}} (1 - t_{a}) d \ln a_{a} \]

\[ \text{where,} \ E: \text{the electromotive force} \]

\[ F: \text{the Faraday constant} \]

\[ P_{o_{1}} \text{and} P_{o_{2}}: \text{the oxygen pressures at the two electrodes} \]

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\[ E = \frac{RT}{4F} \ln \frac{P_{o_{1}}}{P_{o_{2}}} \]

At an oxygen pressure lower than that for chromium–chromium oxide equilibrium, the transference number of electrons cannot be neglected and is given as a
function of oxygen pressure. In this case, Eq. (5) can be integrated to yield Eq. (12) in the following section.

2. For the Case of the Binary Oxide Electrolytes of Non-uniform Composition

Using AO-BO₂ as the binary oxides, the cell can be described by

\[ \eta_{\text{e}} \quad \text{AO-BO}_2 \text{ of non-uniform composition} \quad \eta_{\text{e}} \quad \text{Electrode I} \]

\[ \eta_{\text{a}} \quad \text{AO} \quad \text{Electrode II,} \quad \text{...}(7) \]

where \( \eta_{\text{e}} \) denotes the chemical potential of oxygen, and the possible charge carriers would be ionic species, \( \text{AO}^2+ \), \( \text{AO}^4+ \) and ionic species, and positive holes or electrons.

If the local equilibrium condition applies throughout the electrolyte, the Gibb's free energy change due to the migration of the carriers induced by the externally supplied current can be calculated, and the electromotive force can be expressed by the following equation:\(^{16}\)

\[ E = -\frac{1}{F} \left[ -\frac{1}{4} (\eta_{\text{e}} - \eta_{\text{a}}) + \frac{1}{2} \int \mu^{\text{e}} \, d\eta_{\text{AO}} \right. \]

\[ \left. + \frac{1}{4} \int \mu^{\text{e}} \, d\eta_{\text{AO}} + \frac{1}{4} \int t_i \, (\text{or } t_o) \, d\eta_{\text{PO}} \right] \quad ...(8) \]

where, \( t_i \) means the transference number of charge carrier \( i \), and \( \mu_i \) means the chemical potential of \( \text{O}_2 \), AO or BO₂.

The local equilibrium being assumed, the Bibbs-Duhelen relation will be satisfied throughout the electrolyte:

\[ d\eta_{\text{AO}} = -\frac{N_{\text{AO}}}{N_{\text{AO}}} \, d\eta_{\text{PO}} \quad \ldots \ldots \ldots \ldots (9) \]

where, \( N_{\text{AO}} \) and \( N_{\text{PO}} \) are the mole fraction of oxides, AO and BO₂. Inserting Eq. (9) and \( \eta_{\text{e}} = RT \ln P_{\text{O}} \) for \( \eta_{\text{e}} \) in Eq. (8), one has

\[ E = \frac{RT}{4F} \ln \frac{P_{\text{O}}^{\text{po}}}{P_{\text{O}}^{\text{e}}} - \frac{1}{2} \int \mu^{\text{e}} \, \frac{N_{\text{AO}}}{\text{AO}} \, d\eta_{\text{AO}} \]

\[ - \frac{RT}{4F} \int t_i \, d\ln P_{\text{PO}} \quad \ldots \ldots \ldots \ldots \ldots (10) \]

The first term in the right hand side of this equation is the same as \( E \) in Eq. (6), and the second term is the electromotive force induced by the difference between the diffusivities of the cation species. The third term, arising from the internal current, caused by the migration of electrons or positive holes in the electrolyte, means the decrease of the measureable electromotive force.

In the case of zirconia or thoria base solid solution, the transference numbers of the cation species are zero. Thus the second term becomes zero regardless of non-uniformity of the electrolyte composition. This is one of the reasons why these electrolytes give very stable and reproducible electromotive force.

In contrast, beta-alumina phases\(^{14,15}\) (\( A_2O-NM_2O_8 \)), where, A is Na, Rb, Ag, K, Li or Tl and M is Al, Ga or Fe\(^{3+}\) have a very large cationic conductivity even at lower temperatures. However, its use is very limited, because the second term can not be neglected due to easy vaporization of alkali metal oxides.\(^{16}\)

III. Industrial Production of Zirconia Base Solid Electrolytes and Thier Impurity Contents

In laboratory zirconia-lime solid solution can be made from the aqueous solution containing zirconium nitrate, \((\text{ZrO}_2)(\text{NO}_3)_2\) and calcium carbonate, CaCO₃. Slowly drying the solution, the compounds deposit in very fine powders. The decomposition of the nitrate and carbonate at 700° to 800° C gives the mixture of zirconia and lime. After pressing the powders in a desired shape, sintering at 1 500°C gives the solid solution of zirconia and lime with the fluorite type crystal structure with white color. However, commercial zirconia base solid electrolytes have yellowish color due to the impurities.

Table 1 is the flow sheet of the industrial production of the solid electrolyte reported\(^{17}\) from a Japanese company. Table 2 shows the impurity contents in the commercial electrolytes and their physical properties.\(^{17}\)

The users' claims are mostly the spalling of the electrolytes, the precision in size and shape of the electrolytes, and the effects of the impurities upon the electromotive force and the life time of the oxygen concentration cells for industrial uses. As Table 2 shows, the major impurities are SiO₂, TiO₂, Al₂O₃ and Fe₂O₃. However, the impurities would hardly affect the electromotive force in a short time because of the absence of the cationic conduction as explained in the above. In a long time, silica and ferric oxide would react with the electrode materials, decreasing the life time of the galvanic cells. Electromotive force observed at extremely low oxygen pressures would be influenced by ferric oxide impurity in the electrolyte, because ferric oxide decomposes to yield oxygen at such pressures and, if existing at grain boundaries, the ferric oxide provide the path for oxygen transfer.

Figure 3 shows the specific resistivity of commercial electrolytes.\(^{17}\) The electrolyte stabilized by \( Y_2O_3 \) has large conductivity even at lower tempera-

<table>
<thead>
<tr>
<th>Table 1. A flow sheet of manufacturing of ( \text{ZrO}_2 )-base solid solutions for the solid electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Mixing of raw materials for a fixed composition</td>
</tr>
<tr>
<td>(2) Crushing by ball mills</td>
</tr>
<tr>
<td>(3) Shurry with a fixed viscosity</td>
</tr>
<tr>
<td>(4) Casting of slurry</td>
</tr>
<tr>
<td>(5) Sintering at 1650°C for 60 hr</td>
</tr>
<tr>
<td>Testing of gas tightness, Chemical and X-ray analyses, Testing of physical properties</td>
</tr>
</tbody>
</table>
Review

Because chemical and physical properties are different for various electrolytes, careful selection is necessary to have long life and stable electromotive force of the galvanic cells for various industrial uses.

Table 2. Chemical composition and physical properties of a commercial stabilized zirconia for electrolyte use

<table>
<thead>
<tr>
<th>Chemical composition (%)</th>
<th>CaO (9mol%)</th>
<th>CaO (11mol%)</th>
<th>CaO (15mol%)</th>
<th>MgO (15mol%)</th>
<th>Y₂O₃ (15mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>1.63</td>
<td>1.58</td>
<td>1.66</td>
<td>0.6</td>
<td>0.49</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.28</td>
<td>0.24</td>
<td>0.27</td>
<td>0.24</td>
<td>0.26</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.69</td>
<td>0.71</td>
<td>0.67</td>
<td>0.29</td>
<td>0.27</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.16</td>
<td>0.17</td>
<td>0.18</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CaO</td>
<td>4.7</td>
<td>5.8</td>
<td>7.7</td>
<td>0.36</td>
<td>0.04</td>
</tr>
<tr>
<td>MgO</td>
<td>0.89</td>
<td>0.92</td>
<td>0.99</td>
<td>5.2</td>
<td>—</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>13.2</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.03</td>
<td>0.02</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>K₂O</td>
<td>tr.</td>
<td>tr.</td>
<td>tr.</td>
<td>tr.</td>
<td>tr.</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>91.62</td>
<td>90.55</td>
<td>88.5</td>
<td>93.27</td>
<td>85.67</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Max. water absorption (%)</th>
<th>Apparent porosity (%)</th>
<th>Apparent density</th>
<th>Degree of stabilization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.29</td>
<td>1.56</td>
<td>5.5</td>
<td>74</td>
</tr>
</tbody>
</table>

Figure 3. Reciprocal temperature and the specific resistivity of commercial zirconia base solid electrolyte\(^{17}\)

IV. On the Meters for Oxygen Analysis in the Waste Gases of Boilers and Various Furnaces

The first try to use the oxygen concentration cell with the solid electrolytes for gas analysis has been reported independently by Weissbart and Rukla\(^{18}\) in 1961 and by Goto and St. Pierre\(^{19}\) in 1962.

The cell\(^{19}\) can be expressed by

\[ \text{Gases for analysis, Pt} ZrO₂-CaO Fe, FeO mixture, \ldots (11) \]

Figure 4 shows the structure of this cell\(^{19}\). In steel industry, this cell was used by Matsushita, et al.\(^{20}\) to determine continuously the oxygen content in the waste gas of the open hearth furnace. As shown in Fig. 5, the waste gas was continuously sampled by the steam ejector and sent to the oxygen concentration cell. Figure 6 shows the change of the electromotive force with respect to time, when the standard electrode is made of a mixture of nickel and its oxide powders. During the use of No. 1 burner, the electromotive force gave the oxygen pressure in the waste gas but during the use of No. 2 burner, it gave the oxygen pressure in air used for the combustion of the fuel oil. From this measurement, an optimal amount of the secondary air for the combustion was determined. However, the life time of the cell was only 3 to 4 days for its continuous use, probably due to iron oxide powders generated by oxygen lancing.

After this study, Fischer and Janke\(^{21}\) made an extensive study on the behaviors of the galvanic cell as the oxygen analyzer for high temperature gases.

Toward the end of the 1960's, many companies manufacturing industrial instruments have started to make commercial oxygen meters using the solid electrolytes. Table 3\(^{22}\) includes five commercial oxygen meters. For the sakes of easy handling and long life time, air and platinum are used as the reference electrode in all meters in Table 3. The deterioration by
harmful elements of the platinum electrode during the gas analysis is always the problem of these meters, so that platinum is fixed to the electrolyte with various special techniques developed by each manufacturing companies. The oxygen meters in Table 3 can be used for the following purposes:

1) Continuous oxygen analysis of waste gases of boilers and various industrial furnaces
2) Oxygen analysis in various heat treatment furnaces in ferrous and nonferrous industry
3) Oxygen analysis in heating and decomposition furnaces in petroleum industry
4) Oxygen pressure determination of sintering bed in iron making industry
5) Permeability determination of moisture through the coating and mold materials for electronic parts.

Manufacturing of the oxygen meters was very much accelerated in Japan by a new law to prevent the pollution of air, effective since June, 1971. In this law, equations are proposed to estimate NO\textsubscript{x} content from the oxygen pressure in the industrial waste gases.

The lower limit of oxygen analysis was reported\textsuperscript{13} to be close to the equilibrium oxygen pressure of Cr and Cr\textsubscript{2}O\textsubscript{3} or about 10\textsuperscript{-28} atm at 800°C. However, in reality it is not so, particularly when the gas has no buffering capacity with respect to the leaked-in oxygen gas.

The flow rate dependency of the electromotive force for inert gas–oxygen mixtures has been reported by Etsell and Flengas,\textsuperscript{25} Iwase, Fujimura and Mori,\textsuperscript{26} and Sunayama, et al.\textsuperscript{27} Figures 7 and 8 show the relation between the determined oxygen pressure in argon and the linear velocity of the gas flow in the vicinity of the gas electrode made of a platinum wire. When the oxygen content was lowered, the larger flow rate was needed to have a constant and reproducible oxygen content in argon. The larger flow rate seems to be needed to exclude the effect of the oxygen leaked in from various parts of the gas train and through the solid electrolyte.
Table 3. The comparison of five commercial oxygen meters

<table>
<thead>
<tr>
<th>Specification</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell design*</td>
<td>OBE</td>
<td>COE</td>
<td>OBE</td>
<td>COE</td>
<td>COE</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>ZrO₂·CaO</td>
<td>ZrO₂·CaO</td>
<td>ZrO₂·CaO</td>
<td>ZrO₂·CaO</td>
<td>—</td>
</tr>
<tr>
<td>Cell temperature</td>
<td>850°C</td>
<td>815.6°C</td>
<td>850°C</td>
<td>850°C</td>
<td>815.6°C</td>
</tr>
<tr>
<td>Sample gas flow rate</td>
<td>200~300 ml/min</td>
<td>0.97~42.5 l/min</td>
<td>500 ml/min</td>
<td>250 ml/min</td>
<td>0.24~42.5 l/min</td>
</tr>
<tr>
<td>Flow sensitivity</td>
<td>Less than 0.1% per 50 ml/min</td>
<td>Less than 0.01% per 470 ml/min</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O₂ input ranges</td>
<td>1~100 ppm</td>
<td>0<del>1%, 0</del>5%</td>
<td>1~100 ppm</td>
<td>0.8~150 ppm</td>
<td>0<del>0.5%, 0</del>1%</td>
</tr>
<tr>
<td>Speed of response</td>
<td>1 sec for 63%</td>
<td>3 sec for 90% (250 ml/min)</td>
<td>1 sec for 63%</td>
<td>3 sec for 90% (250 ml/min)</td>
<td>3 sec for 63%</td>
</tr>
<tr>
<td>Temperature of sample gas</td>
<td>0~50°C</td>
<td>150°C</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Power requirements</td>
<td>AC 100 V, 300 W</td>
<td>AC 115 V, 300 W</td>
<td>AC 100 V, 130 W</td>
<td>—</td>
<td>AC 118 V, 120 W</td>
</tr>
</tbody>
</table>

* OBE means "open on both ends" and COE means "closed one end".

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Fig. 7. The linear velocity of argon gas and logarithm of oxygen pressure obtained from the EMF of the galvanic cell by Sunayama, et al.\(^{27}\)

Fig. 8. The linear velocity of argon gas at the vicinity of the gas electrode converted to 25°C and the obtained oxygen pressure\(^{27}\)

V. Determination of Total Oxygen Demand in Waste Water and NOₓ Control of Gasoline Engines

Two special applications of the above oxygen meters are the determination of total oxygen demand of polluted water and NOₓ control of vehicle engines.

The total oxygen demand, TOD, is recently used as an index of magnitude of pollution of water. Procedure of its determination is sampling a fixed quantity of polluted water, heating it to a high temperature with a catalyst and with excess of oxygen gas, and then, the quantity of oxygen consumed to combust organic compounds contained in the sampled water can be measured by an oxygen concentration cell with the solid electrolyte. Furthermore, the quantity
of carbon dioxide produced is determined by an infrared absorption gas analyzer to have total carbon, TC. Thus, the combination of an automatic water sampler, the oxygen concentration cell, and the infrared absorption gas analyzer makes it possible to check continuously TOD and TC in the industrial waste water. This combined set is now commercially available in Japan. The sample water of 10 g is intermittently taken, and TOD and TC can be determined in the range of 10 to 10,000 ppm and 5 to 500 ppm, respectively.

Another special application of the oxygen concentration cell is its use for vehicle engines to control the NO\textsubscript{x} content in the exhaust gas by measuring the oxygen content in the exhaust gas and feeding it back to the carburetor to control the ratio of air to fuel to minimize the NO\textsubscript{x} content. This unique study was reported in 1973 independently by Fleming, et al.\textsuperscript{30} and by Düker and Neidhard.\textsuperscript{29}

Later in 1975, Düker, et al.\textsuperscript{30} reported a detailed study on the relation of the life time to the quantities of stabilizers of CaO, Y\textsubscript{2}O\textsubscript{3}, and MgO, and to the structure of the oxygen concentration cell. The life time was reportedly corresponding to that for the vehicle running distance of 24,000 km. Figure 9 shows the relation between the contents of CO, NO\textsubscript{x}, and hydrocarbon in the exhaust gas and the ratio of air to fuel supplied to a reciprocating engine. In the figure, the curve of an isothermal electromotive force of the oxygen meter shown in Fig. 11 is also given to show its stepwise change at the quantity of air needed theoretically for a complete combustion. Figure 10 shows the principle how to automatically control the ratio of air to fuel to minimize the NO\textsubscript{x} content with the aid of the catalyst. Figure 11 shows the construction of the oxygen concentration cell used. The inner platinum electrode is fixed to the solid electrolyte with the coating technique of thick film. The outer one is made with the evaporation method and then covered by a magnesium spinel oxide layer sprayed by plasma flame. This spinel layer would protect the platinum electrode from compounds of P, S and Pb contained in the exhaust gas. The galvanic cell gives the electric signal at 300° to 900°C with a response time of 5 \times 10^{-3} sec and its internal resistance is 10^4\Omega at 400°C.

Düker, et al.\textsuperscript{31} reported that the electrical conductivity was large even at lower temperatures with zirconia stabilized by 8mol\% Y\textsubscript{2}O\textsubscript{3}, and that the mechanical strength of the electrolyte increases by the addition of 3% SiO\textsubscript{2} but at the sacrifice of the conductivity.

VI. Rapid Determination of Oxygen Content in Copper and Steels at Their Refining Plants

In 1965, Pluschke11 and Engell\textsuperscript{31} first reported on the oxygen content determination in molten copper by the electromotive force method using zirconia-lime solid electrolyte. Recently, Janke and Fischer\textsuperscript{32,33} studied on many copper alloys with this method.

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**Fig. 9.** Contents of CO, NO\textsubscript{x} and hydrocarbons in waste gas of a gasoline engine as a function of ratio air to fuel. The EMF curve is the values obtained by the oxygen concentration cell shown in Fig. 11 by Düker, et al.\textsuperscript{30}

**Fig. 10.** Principle to control the ratio of air to fuel based on the EMF of galvanic cell to minimize the contents of harmful gases in the waste gas\textsuperscript{30}
Kametani and Yamauchi\textsuperscript{34,35} have measured the oxygen potential change during vacuum treatment of molten copper and molten matte.

In parallel with these basic studies, Dompas and Lockyer have studied for 7 years on the application of the galvanic cell to copper refining industry and reported their results in 1972.\textsuperscript{36} They have continuously dipped the oxygen concentration cell in molten copper in the launders of wirebar casting, of an anode reverberatory furnace, and of continuous casting of tough pitch billets. In Fig. 12, the cell is dipped in copper at the connection of the launder and the continuous casting machine. From the obtained electromotive force, the quantities of the air to the burner to heat the launder and of the adding deoxidizer are controlled to maintain a constant oxygen content in copper for continuous casting. Figure 13 shows the measured electromotive force and the oxygen content determined by the conventional method. Until 1972, this new monitoring method has been used as the standard operation of the wirebar production of 300,000 t. The life time of the galvanic cell was about 70 hr in average. The details of the structure of the cells are given in Refs. 37 and 38).

On the applications of the galvanic cells to steel industry, more than twenty papers have been published\textsuperscript{13} between 1960 and 1970, because of the intense industrial needs of the rapid determination of oxygen content in steels.

The first try to use this method in steel plants in Japan was made by Ihida and Kawai\textsuperscript{39} which stimulated very much further development in other steel companies in Japan. Two groups of the steel plant metallurgists, the one represented by Saecki and Hiraoka\textsuperscript{40,41} and the other by Suzuki\textsuperscript{42} have made very extensive investigations to use the oxygen concentration cells on lines of steel refining, with co-operation with companies manufacturing the instruments for steel industry. Because of these investigations, the galvanic cell as shown in Fig. 14 is now commercially available in Japan. This cell has the reference elec-

![Fig. 11. Schematic diagram of the oxygen concentration cell to make the continuous analysis of the waste gas of the engine\textsuperscript{20}](image)

![Fig. 12. Backfeed control system for continuous casting of tough pitch copper billet using the oxygen concentration cell at the exit of the launder, by Dompas and Lockyer\textsuperscript{36}](image)

![Fig. 13. The EMF obtained by the method of Fig. 12 and the oxygen content in copper determined by vacuum fusion analysis\textsuperscript{46}](image)
to 3 000 ppm in 8 sec. Figure 15 shows the "combination lance" of the galvanic cell, a thermocouple to measure temperature, and another thermocouple to obtain the cooling curve to determine the carbon content. This combination lance can be used as the sub-lance of the basic oxygen furnace to refine steels without turning down the furnace until the end point of refining.

These Commercial galvanic cells are used in Japan in the following ways.30-42

1) Dipping the cell in steels in the converter during refining to control the final oxygen content
2) Dipping the cell in steels just before the deoxidation to determine the quantity of the deoxidizer to control the intensity of rimming action of rimmed and semi-killed steels
3) Dipping the cell in steels during treatments by RH and DH processes to find the end point of the treatments
4) Dipping the cell in steels in the tundish to measure the oxygen content change during the continuous casting

Figure 16 shows how to control the boiling intensity of silico-semi-killed steels or to control the content of the soluble aluminum in aluminum-silicon-killed steels.

Suzuki, et al.42 studied the effect of the long nozzle on the air oxidation of steels during pouring from the ladle to the tundish of the continuous casting. Figure 17 shows the changes of the flux composition and the oxygen content during the continuous casting of steels. The open circles are the results without the long nozzle and the filled circles are the results with the long nozzle to protect from the air oxidation. In the figure, [\%O], means the dissolved free oxygen determined by the galvanic cell and [\%O], means the oxygen content as the oxide inclusions.

The results of Fig. 17 suggest that the long nozzle is definitely necessary to protect the ultra-low carbon steels from the oxidation by air during pouring from the ladle to the tundish. In Japanese steel plants, the automatic dipping machines with different designs are used to dip the cell with the optimum speed. An instrument company in Japan had sold 21,000 gal-
vanic cells to steel plants during September, 1974 to March, 1974. \(^{43}\) The reproducibility is said very good, when the cells are used for the plain carbon steels containing more than 50 ppm oxygen. However, the results are not impressive, when they are used for steels with less than 50 ppm oxygen or for special steels.

Therefore, the recent studies are concerned to the determination of oxygen less than 50 ppm or in special steels.\(^ {44-48}\) When the oxygen content becomes extremely small, the electronic conduction in the zirconia–lime solution can not be neglected. For such a case, Pluschkell\(^ {49}\) integrated Eq. (5) and obtained the following expression for the standard electrode of Cr and Cr\(_2\)O\(_3\):

\[
a_0 = K \left[ a^{(P)}_1 \right] \left( a^{(P)}_{Cr/Fe} \right)^{1/4} + \left( a^{(P)}_{Cr/Fe} \right)^{1/4} \exp \left( \frac{-FE}{RT} \right) - \left( a^{(P)}_1 \right)^{1/4}
\]

where, \(a_0\) is the Henrian activity of oxygen in unit of wt\%, \(K\) is the equilibrium constant of 1/2O\(_2\) = O (%) in iron, and \(P_i\) is the oxygen pressure, at which the transference number of ions becomes equal to that of electrons. In zirconia–lime solid solution, \(P_i\) is about 10\(^{-15.8}\) atm at 1600\(^\circ\)C. \(P_{Cr/Fe}\) means the equilibrium oxygen pressure with chromium and its oxide. Inserting these constants, Pluschkell pointed out that no correction is necessary down to 10 ppm O in plain carbon steel, but it is needed for the range of 1 to 0.01 ppm O. Therefore, the galvanic cell can be used, in principle, at 1600\(^\circ\)C down to 0.01 ppm O according to Eq. (12). However, in reality, it would not be so. When the content becomes so low as 10 ppm, the buffering capacity of the iron–oxygen melt with respect to any small change of oxygen potential would be very small.

This means that the oxygen pressure at the interface between the solid electrolyte and molten iron would so easily deviate from the average oxygen potential in the bulk of the molten iron.

Further, when one considers the contents of ferric oxide and silica in the electrolyte given in Table 2, it is a very natural and sound question to ask about the magnitude of the deviation of the oxygen pressure due to the reduction of these unstable impurities. In this respect, Fischer and Janke\(^ {43}\) suggested an intense stirring of the molten iron to minimize the deviation.

VII. Continuous Determination of Oxygen Content in Liquid Sodium Used as Coolant of Fast Bleeder Reactors

For the safe operation of the atomic reactors, it is very important to check continuously the oxygen content in liquid sodium used as the coolant. Three papers in 1963 and 1968 have been already documented in Ref. 13. Recent two papers by Berkery and Read,\(^ {50}\) and by Roy,\(^ {51}\) reported the wide use of the following cells in the world for the fast bleeder reactors:

**Na–O (liquid) ThO\(_2\)–Y\(_2\)O\(_3\) Pt, air (reference) ... (13)**

\[ E \text{ (volts)} = K_1 - K_2 \log (\text{ppm O}) \ldots \ldots (14) \]

\(K_1\) and \(K_2\) are constants at a given temperature and are 1.828 and 0.075, respectively, at 483\(^\circ\)C. Yttria is used as the stabilizer to have a good conductivity at its service temperature of 350\(^\circ\)C to 500\(^\circ\)C. Because of the partial positive hole conduction at the oxygen pressure of higher than 10\(^{-6}\) atm, the electromotive force measured would be smaller by 5 to 10\% than that calculated according to Eq. (14).

When the thorium–yttria solid electrolyte was highly purified and then isostatically pressed, followed by complete homogenization by sintering, its corrosion resistance against liquid sodium increased very much and the life time became 5,000 hr under the continuous service.\(^ {51}\) The lower limit of the oxygen analysis was reported 0.1 ppm O in liquid sodium.

VIII. Concluding Remarks

Since a very celebrated paper by Kiukkola and Wagner in 1957, several hundred papers have been published throughout the world, all using zirconia or thoria base solid electrolytes. The reasons of this wide uses of the special solid oxides seem simply because of their excellent oxygen ion conductivity and their thermodynamic stability with high melting points. The former reason gives the very small internal resistance of the galvanic cells, which is very necessary to have a stable and reproducible electromotive force. In many colleges in Japan, the galvanic cells are constructed by students to learn one of the methods to determine the Gibbs free energy change of reactions at high temperatures. The latter reason is as well important to exclude any solid state reactions...
between the electrolyte and the electrode materials even at high temperatures. This means that the wide variation of combinations of electrode materials is possible to make very different types of galvanic cells with miscellaneous objectives.

Because two review papers\textsuperscript{12,13} have been published on the applications of the solid electrolytes to basic studies, the present survey was made on their industrial applications. The industrial applications have many difficulties as follows, which are quite different from the case of the applications to basic studies;

(1) The electrolytes must be made by mass production with constant and good qualities in chemical, physical and mechanical properties.

(2) The oxygen concentration cells are sometimes used continuously in the gas or liquid metals containing many harmful elements.

Thus, to have a long life time, special ways should be developed for each case to prevent the deterioration of the electrode and electrolyte.

(3) For the use of the galvanic cells in molten steels, a stable electromotive force should be obtained in less than 10 sec, because the molybdenum electrode dissolves quickly. Thus, the cells must be constructed in very small size but with good precision in many aspects.

(4) In the industrial applications, untrained employees use the cells in rough ways. Thus, the galvanic cells must be mechanically and thermally very strong.

The above difficulties will be eventually solved with the help of the art of peoples with different origins and traditions, because the principle of the galvanic cell is simple and universal.

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