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Nernstian behaviour of zirconia oxygen sensors incorporating composite electrodes

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The Nernstian behaviour of zirconia oxygen sensors incorporating composite electrodes has been described in the low temperature ($<600^\circ$ C) range. The composite electrodes consisting of a semiconducting metal oxide and platinum lower the operating temperature of oxygen sensors to about 300–350° C, well below that achievable with conventional metal or metal oxide electrodes. Complex impedance measurements made as a function of Pt/metal oxide ratio show that both the electrode resistance and the time constant go through a minimum when plotted against Pt content in the composite.

1. Introduction

The potentiometric or Nernst sensor consists of an oxygen ion conducting membrane of a solid electrolyte (with negligible electronic conductivity) such as fully or partially stabilized zirconia and two electrodes reversible to the O_2/O^{2-} redox equilibria. If both electrodes of such a cell are exposed to different oxygen partial pressures an e.m.f. is established across the cell which with respect to air as the reference atmosphere is given by the Nernst equation:

$$E(\mathrm{mV}) = 0.0496T\log(0.21/pO_2) \qquad (1)$$

where pO_2 is the unknown oxygen partial pressure and T is the absolute temperature. The e.m.f. is measured by making electrical contacts to the electrodes.

The most commonly used form of the sensor body is that of a tube closed at one end and made entirely from the solid electrolyte. In other designs the solid electrolyte is used as a disc or pellet hermetically sealed in one end of the metal or ceramic supporting tube. In most cases the reference gas (usually air) is maintained on one side of the tube (commonly on the inside) and the other side of the tube is exposed to the test environment. Such cells provided with noble metal or metal oxide electrodes obey the Nernst equation only above about 600° C. Below this temperature they suffer from significantly large e.m.f. errors. These sensors therefore cannot be used to accurately monitor and control oxygen levels in fuel lean environments.

Several oxygen sensors based on the Nernstian principle are commercially available for high temperature ($>600^\circ$ C) operation [1–4]. Porous platinum electrodes are normally used in these sensors. Recently with the use of urania-based electrodes it has become possible to reduce the operating temperature of the sensor down to 300° C in relatively clean laboratory environments and to 400° C in the more demanding industrial environments [5, 6].

This paper investigates several materials as alternative electrodes for use in oxygen sensors at low temperatures. These new electrodes are composites consisting of finely divided platinum and one or more semiconducting metal oxides. Laboratory tests on sensors incorporating these composite electrodes have been reported in the 300–600° C temperature range. In addition the electrode kinetic behaviour of some metal oxide-only electrodes has been compared with composites containing that metal oxide and platinum.

Table 1. Composition of various semiconducting metal oxides tested and the total resistance of sensors at 600° C incorporating either metal oxide only or a composite electrode consisting of 75 wt % metal oxide + 25 wt % platinum dioxide

Composition of the metal oxide	*Total sensor resistance* (kΩ)*		*No*
	With metal oxide electrodes	*With composite electrodes*	
PrO_{2-y}	5.5	5.1	1
TbO_{2-y}	–	–	2
CeO_{2-x}	1918	73.2	3
NiO	37.9	4.9	4
$Fe_2O_3 + Fe_3O_4$	239	10.1	5
ZnO	307	111	6
MnO_2	1.7	1.8	7
SnO_2	439	46.9	8
V_2O_5	7.8	4.3	9
In_2O_3	70	2.1	10
$CrVO_4$	13.2	1.5	11
$CrNbO_4$	214	0.72	12
$(ZnO)_{0.97}(Al_2O_3)_{0.03}$	†	34.0	13
Sn doped In_2O_3	578	2.6	14
$LaNiO_3$	25.3	1.7	15
$(La_{0.8}Sr_{0.2})CrO_{3-x}$	15.1	1.3	16
$(Nd_{0.9}Sr_{0.1})CoO_{3-x}$	3.57	1.08	17
$(Pr_{0.7}Gd_{0.3})O_{2-x}$	14.2	3.8	18

The subscript x indicates a small departure and y indicates a large departure from the ideal oxygen/metal atom ratio for the oxide in question.

* Electrolyte resistance at 600° C is about 0.60–1.20 kΩ.

† Resistance too high for accurate measurements.

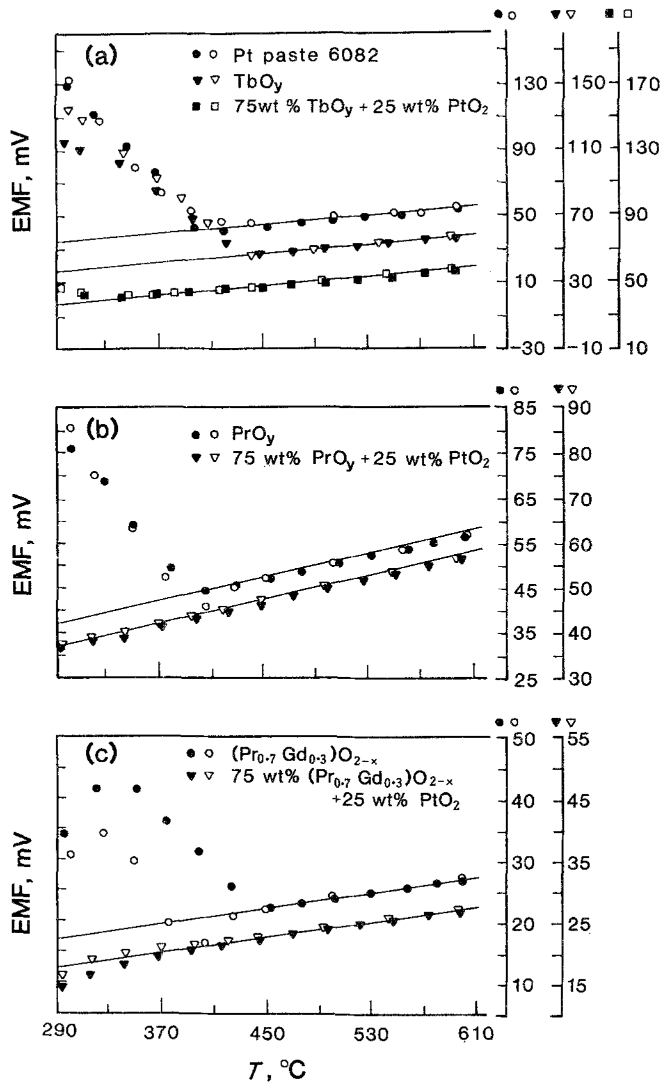

Fig. 1. E.m.f. versus temperature plots for oxygen sensors provided with composite electrodes including comparative results for sensors provided with either individual platinum or metal oxide constituting the composite electrodes. (a) and (b) Air versus 1% O_2 in N_2; (c) air versus 5% O_2 in N_2. ●▲■ cooling; ○△□ heating cycle.

2. Experimental details

The simple transition metal and rare earth oxides were obtained from chemical manufacturing companies. Solid solutions and compounds between two or more metal oxides were prepared by one of the following methods:

(i) Metal salts to give the required composition were dissolved in aqueous media followed by coprecipitation with aqueous ammonia solution. The coprecipitated powder was dried and calcined at high temperatures to complete the reaction.

(ii) The second method involved dissolving the metal nitrates (in the desired quantity) in water and carefully drying the solution. This was followed by grinding the dried material and firing at high temperatures.

Table 2. Composition and nomenclature of composite electrodes consisting of platinum dioxide and $CrNbO_4$

Nomenclature	*Electrode composition*
CN1	0 wt% PtO_2 + 100 wt% $CrNbO_4$
CN2	10 wt% PtO_2 + 90 wt% $CrNbO_4$
CN3	25 wt% PtO_2 + 75 wt% $CrNbO_4$
CN4	50 wt% PtO_2 + 50 wt% $CrNbO_4$
CN5	75 wt% PtO_2 + 25 wt% $CrNbO_4$
CN6	100 wt% PtO_2 + 0 wt% $CrNbO_4$

(iii) The metal oxides were mixed thoroughly with ethanol, dried and heated at high temperatures. In many cases it was necessary to grind and refire the powder several times to complete the reaction.

The completion of the reaction between metal oxides was detected by taking X-ray diffractograms of the fired powders and comparing the results with the literature data. Various metal oxides tested and which formed a component of the composite electrode are listed in Table 1. Fine pastes of various oxides listed in Table 1 in triethylene glycol were prepared by grinding the powdered oxide with a 25% solution of triethylene glycol in ethanol until the ethanol had evaporated. The procedure was repeated several times until a uniform and consistent paste was obtained. Fine pastes of composite electrodes comprising a mixture in triethylene glycol of 25 wt% platinum dioxide and 75 wt% of the metal oxide were prepared by the procedure described above. A number of pastes of platinum dioxide and a semiconducting metal oxide ($CrNbO_4$) in varying ratio were also prepared in a similar fashion in order to study the effect of platinum

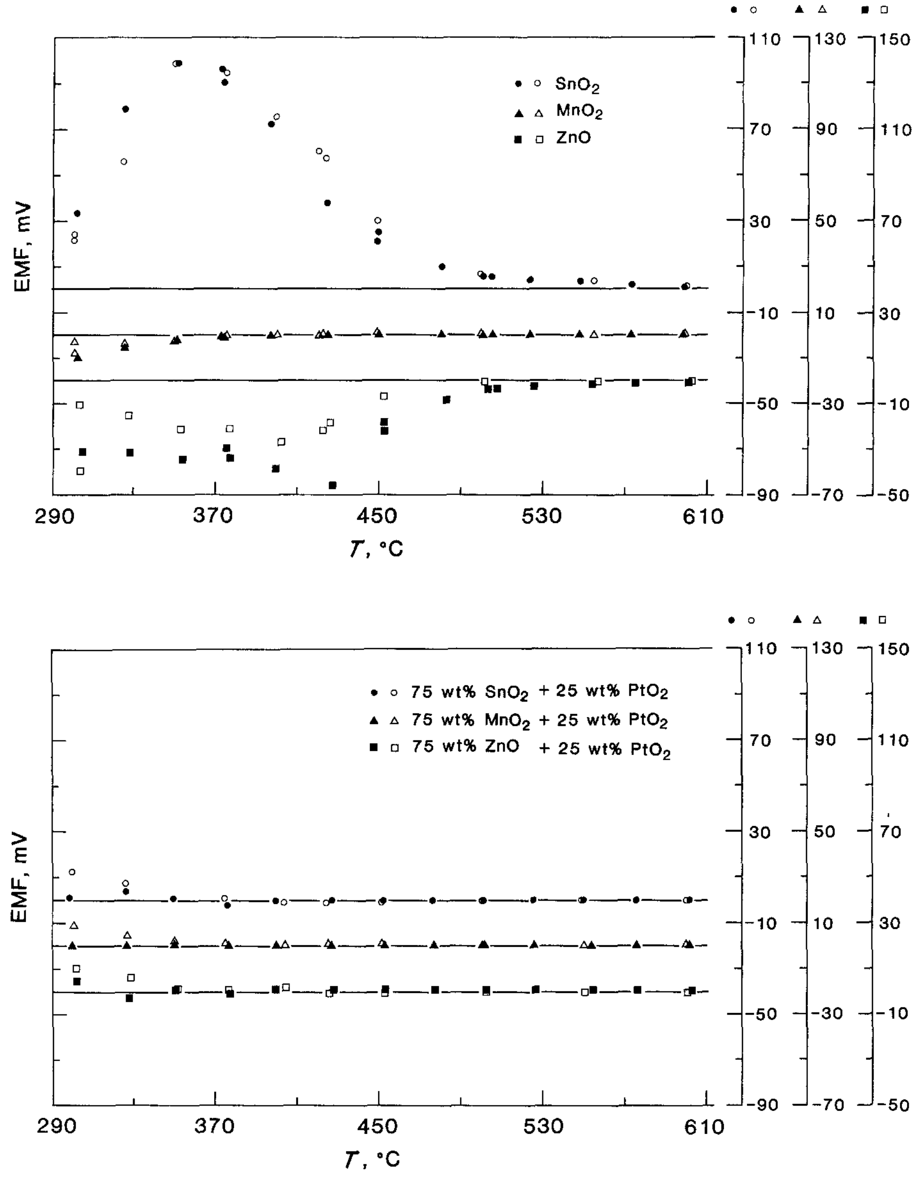

Fig. 2. E.m.f. versus temperature plots for sensors provided with composite and individual metal oxide electrodes in air versus air. ●▲■ cooling; ○△□ heating cycle.

content on the sensor performance and the electrode kinetic parameters. Table 2 gives the various platinum dioxide and $CrNbO_4$ compositions investigated.

Several composite electrodes were heated at 600° C for 10–15 h in air. The X-ray diffractograms of the heated electrodes showed that the platinum dioxide had decomposed to platinum without reacting with the metal oxide. In all the tests performed on composite electrodes to determine their electrode and Nernstian behaviour they were given preheat-treatment at 600° C to decompose the platinum dioxide to platinum. Although in all the sensor tests and electrode kinetic experiments, the composite electrodes consisted of *platinum* and the metal oxide but for convenience they will be referred to as consisting of a metal oxide and *platinum dioxide*. The final weight ratio of Pt/metal oxide differs only slightly from that of PtO_2/metal oxide.

The sensor bodies were prepared by high temperature eutectic welding of a solid electrolyte disc on to an alumina tube [6]. The solid electrolyte disc comprised a sintered mixture of 50 wt % alumina and 50 wt % of a zirconia-scandia solid solution containing 4.7 mol % Sc_2O_3. Complete sensors were prepared by painting the electrode under test (Pt, metal oxide or a composite consisting of platinum dioxide and the metal oxide) on both flat sides of the welded electrolyte disc. The sensor assemblies were slowly heated to 600° C to burn off the triethylene glycol and, in the case of composite electrodes, also to decompose platinum dioxide to platinum. The details of the sensor assembly are given elsewhere [5].

Sensor performance tests were carried out between 300° C and 600° C. These tests comprised (i) the determination of the cell voltage (E) with air at both electrodes and with air at the inner electrode and oxygen-nitrogen mixtures (1 to 100% oxygen) at the outer electrode; (ii) the effect of the cell voltage of varying the internal air flow rate by an order of magnitude and (iii) sensor resistance measurements with air at both the electrodes. Most tests were performed at temperature intervals of 25–50° C during both a heating

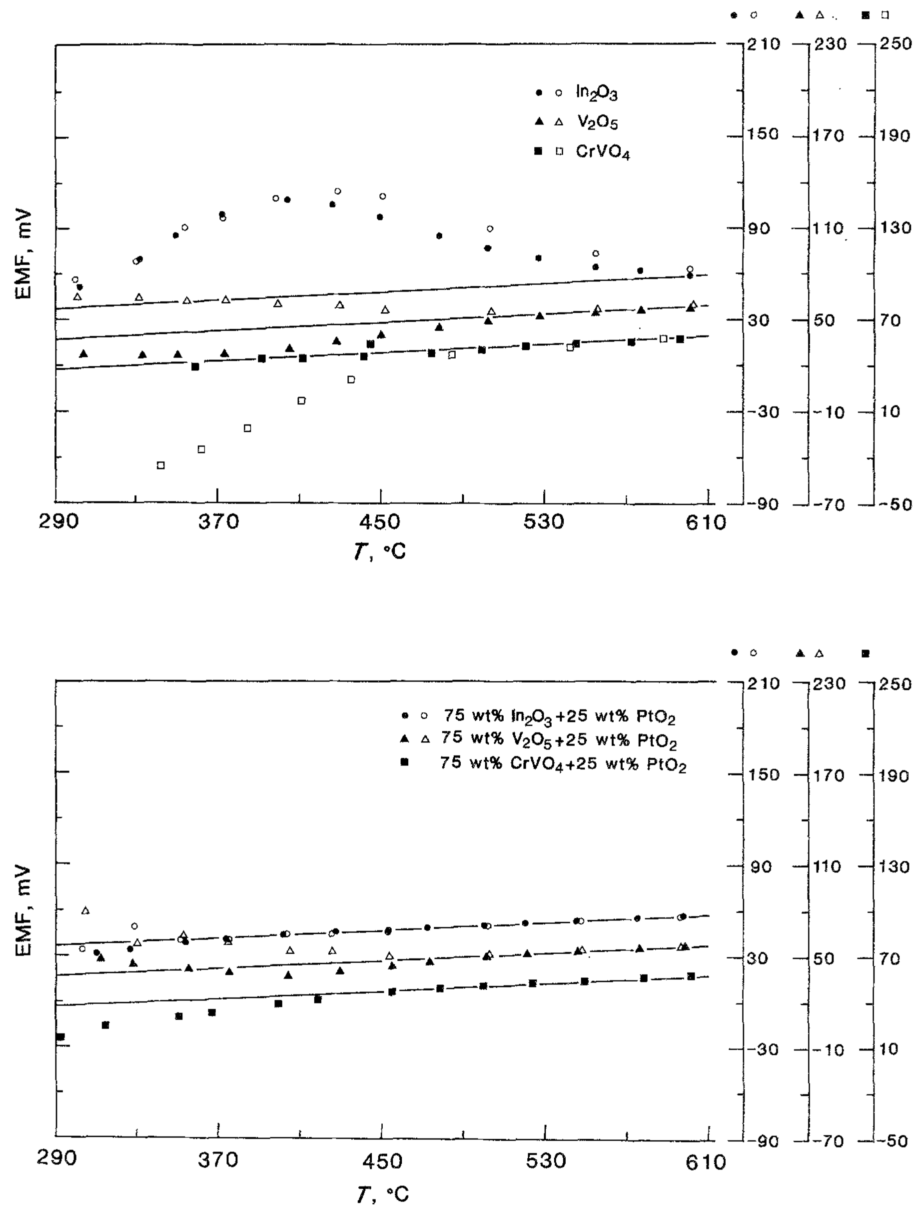

Fig. 3. E.m.f. versus temperature plots for sensors provided with composite and individual metal oxide electrodes in air versus 1% O_2 in N_2. ●▲■ cooling; ○△□ heating cycle.

and a cooling cycle. In all more than 60 sensors were tested including all the electrodes described in Tables 1 and 2 to show the superior characteristics of composite electrodes over their individual constituents.

In order to compare the response of metal oxide + platinum dioxide composite electrodes with metal oxide only or platinum electrodes to sudden changes in the oxygen concentration in the gas stream one flat side of a 10 mol% Y_2O_3 + 90 mol% ZrO_2 (YSZ10) sintered disc (diameter 9.3–9.4 mm, thickness ~2.6 mm and density ~98% of theoretical for the electrolyte discs) was painted with the metal oxide only or platinum and the other side with the metal oxide + platinum dioxide. Both electrodes of the cell were simultaneously exposed to a sudden change in the oxygen concentration. If both electrodes of the cell respond differently, a voltage signal is developed. The sign and shape of the voltage-time curves provide information on the relative speed of response of both electrodes [7]. These measurements were made on several couples at temperatures between 300° and 500° C.

In order to study the kinetic behaviour as a function of Pt content, the electrodes of Table 2 were painted on both flat faces of sintered discs of 10 mol% Y_2O_3 + 90 mol% ZrO_2 (YSZ10) electrolyte and heated to 600° C for 15 h in air. The CNX/YSZ10/CNX (X = 1, 2, 3, 4, 5 or 6) cells were then subjected to complex impedance measurements in air over the temperature and frequency ranges of 450–600° C and 0.5 mHz–1 MHz respectively. Impedance measurements were made with a Solartron 1174 frequency response analyser.

In order to determine current-potential characteristics, two cells, one provided with metal oxide only ($CrNbO_4$) and the second cell with a composite electrode consisting of 75 wt% of $CrNbO_4$ + 25 wt% platinum dioxide were prepared by painting the respective electrode on both flat sides of sintered discs of 10 mol% yttria + 90 mol% zirconia electrolyte.

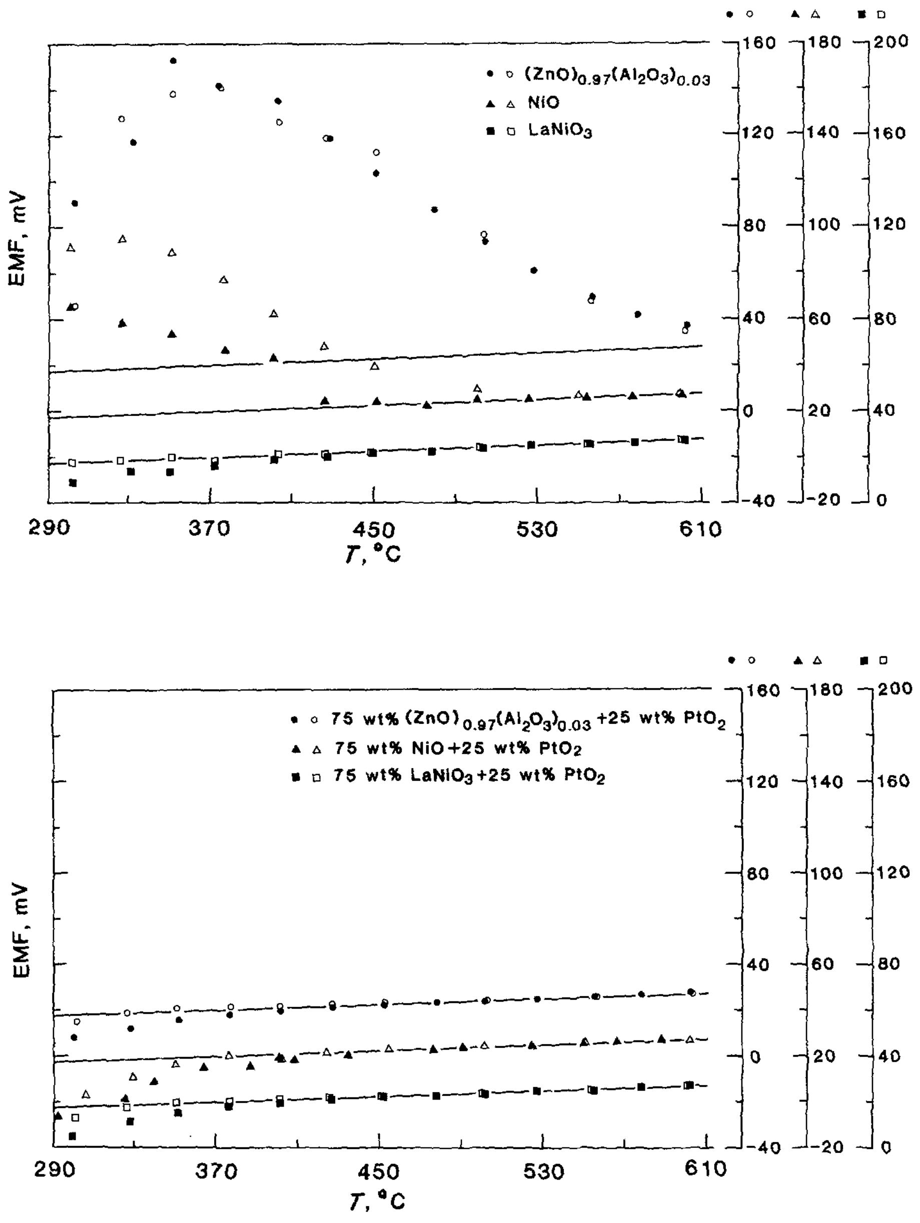

Fig. 4. E.m.f. versus temperature plots for sensors provided with composite and individual metal oxide electrodes in air versus 5% O_2 in N_2. ●▲■ cooling; ○△□ heating cycle.

Only a two electrode cell arrangement was used. The temperature of each cell was raised to 700° C in air and the cell left to equilibrate for several hours with the surroundings before making measurements on that cell. The current-potential characteristics were recorded over several temperatures between 500° and 700° C with a galvanostatic current interruption technique. In this method a constant current was passed through the working electrode-electrolyte-counter electrode until a steady state potential was reached. The current was then interrupted using a fast electronic switch (switching time $< 0.1\,\mu$sec) and the potential as a function of time ($10\,\mu$sec after the current switch-off) was recorded with a transient recorder. The analysis of the data for each current value gives the potential drop across the solid electrolyte (ohmic drop) and across both electrode/electrolyte interfaces (overpotential).

3. Results and discussion

3.1. *Nernstian behaviour*

Almost all sensors with oxide only or platinum electrodes gave significant zero errors (with air at both electrodes) and showed large deviations from Nernstian relationship (with air at the inner and oxygen–nitrogen mixtures at the outer electrode) at temperatures below about 450–500° C. In contrast the addition of platinum (in the form of platinum dioxide) considerably improved the low temperature behaviour. In fact most of the sensors provided with composite electrodes performed satisfactorily down to 350° C or below. Figs 1–5 compare the sensor performance of porous platinum (paste No. 6082, Engelhard Industries Inc.) and individual semiconducting metal oxide electrodes with those of composites constituting the

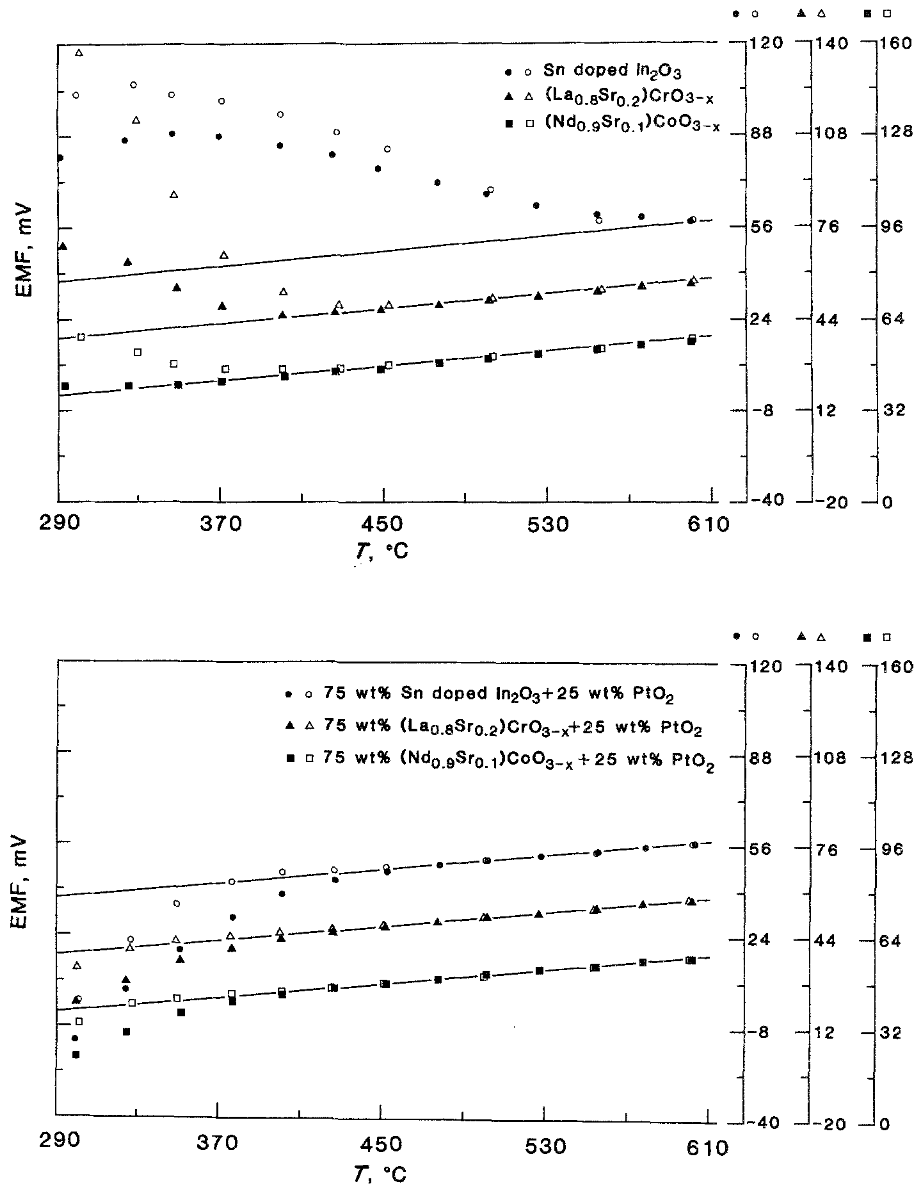

Fig. 5. E.m.f. versus temperature plots for sensors provided with composite and individual metal oxide electrodes in air versus 1% O_2 in N_2. ●▲■ cooling; ○△□ heating cycle.

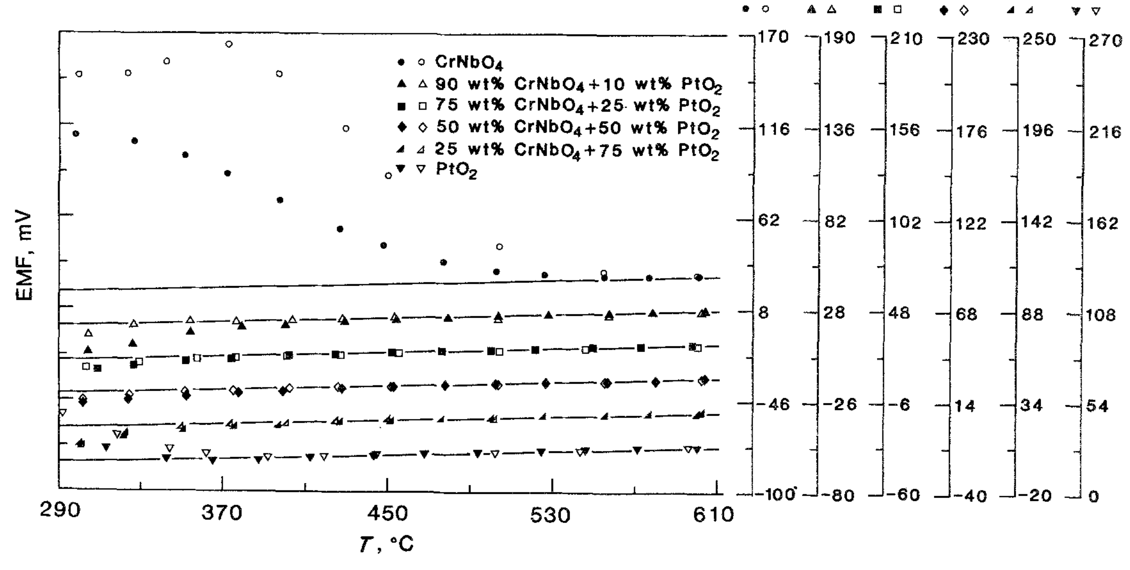

Fig. 6. E.m.f. versus temperature plots comparing the individual performance of $CrNbO_2$ and PtO_2 with composite electrodes consisting of the two materials in various ratios in air versus 5% O_2 in N_2. ●▲■◆◢▼ cooling; ○△□◇◺▽ heating cycle.

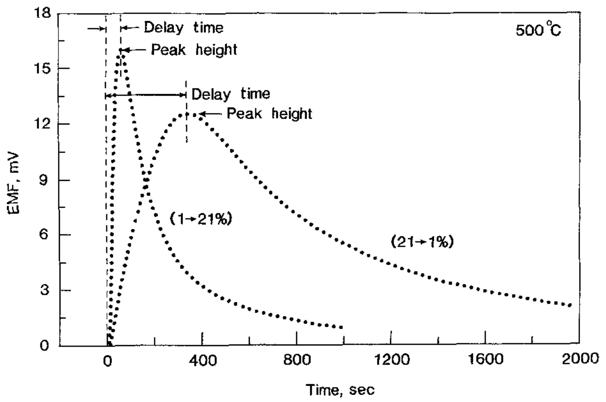

Fig. 7. Differential responses of a $CrNbO_4$/YSZ10/75 wt % $CrNbO_4$ + 25 wt % PtO_2 cell at 500° C subjected to oxygen concentration changes from 21 to 1% and 1 to 21%. Only the magnitude of the voltage signal is shown.

metal oxide and platinum. In Figs 1 to 5 and 6, the solid lines represent the theoretical response and the symbols show the measured responses. In the interest of clarity, the vertical scales in these figures have been offset for each set of data, as shown by the scale bars at the right of each figure.

In general, the sensors with metal oxide only or platinum electrodes exhibited much higher sensitivity to changes in the gas flow rate than those provided with metal oxide + platinum electrodes.

Table 1 compares the resistance of sensors provided with composite electrodes with those provided with individual metal oxide only electrodes at 600° C.

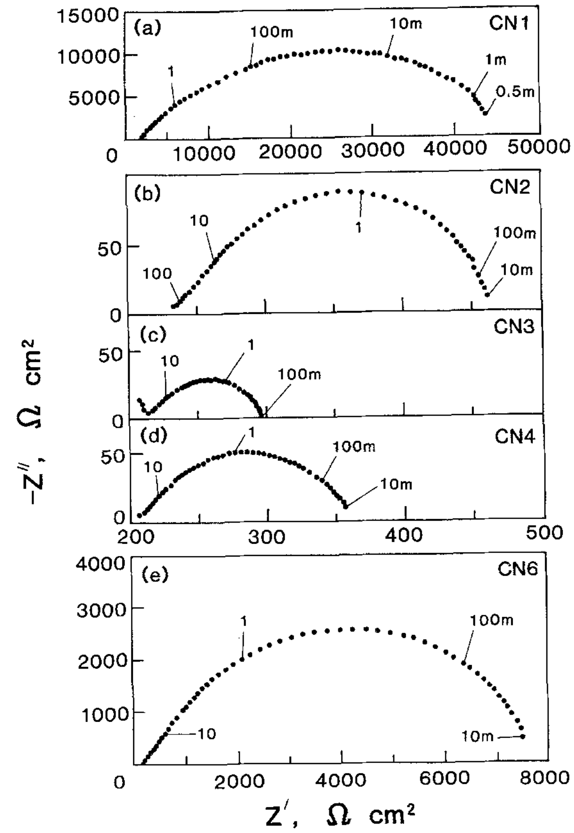

Fig. 8. Impedance diagrams in air at 550° C showing the electrode arc for $CrNbO_4$, PtO_2 and composite electrodes consisting of the two materials in various ratios. The numbers on the arc are frequencies in Hz.

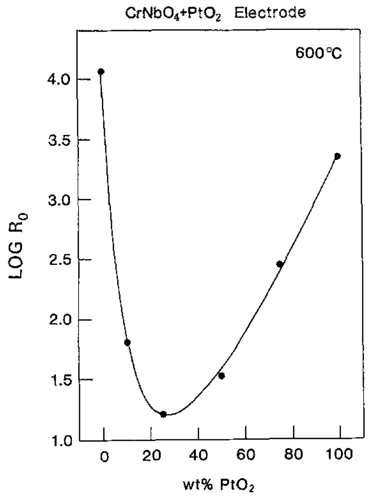

Fig. 9. A plot of the electrode resistance (R_0, Ωcm^2) versus composite electrode ($CrNbO_4$ and PtO_2) composition at 600° C.

These values of resistance also include the electrolyte resistance which (as determined by impedance dispersion analysis of a number of cells) is around 0.6–1.20 kΩ at 600° C. The resistance of sensors provided with composite electrodes is invariably much lower than those provided with semiconducting metal oxide only electrodes. Because of the much higher resistance of sensors provided with metal oxide only electrodes, they were extremely sensitive to electrical noise pickup at temperatures below 400–500° C. By contrast sensors with composite electrodes showed no such sensitivity even at temperatures as low as 350° C.

These results clearly demonstrate the superior low temperature performance of the composite electrodes over conventional metal oxide only or porous platinum electrodes on solid electrolyte oxygen sensors. In particular, several composite electrode materials enable oxygen sensors to operate reliably at temperatures as low as 300° C, well below the limit of similar sensors fitted with porous platinum or metal oxide electrodes.

Fig. 6 compares the individual performance of $CrNbO_4$ and platinum dioxide electrodes with composite electrodes consisting of the two materials in various ratios for air versus 5% oxygen in nitrogen. The best performance was observed for sensors provided with composite electrodes containing 25 and 50 wt % platinum dioxide. The deviations from the theoretical values increased for compositions on either side of this range.

3.2. *Differential response rates*

Typical experimental voltage response curves are shown in Fig. 7 for step changes in oxygen concentration from 1–21% and 21–1%. The voltage-time curves are characterized by the peak height which is mainly determined by the ratio of the response times of the two electrodes and a delay time. The sign of the voltage signal determines which of the two electrodes is responding faster. Three metal oxide electrodes from Table 1 (Nos 7, 12 and 17) were compared with the composites containing 75 wt % of the metal

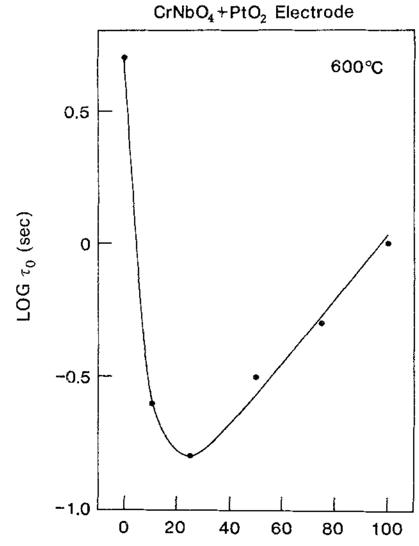

Fig. 10. A plot of the electrode time constant (τ_0) versus composite electrode ($CrNbO_4$ and PtO_2) composition.

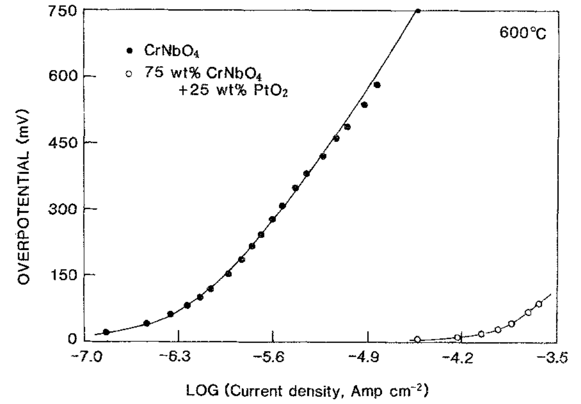

Fig. 11. Plots comparing the current-potential characteristics of a metal oxide ($CrNbO_4$) electrode with the composite electrode constituting 75 wt % $CrNbO_4$ + 25 wt % PtO_2 at 600° C in air.

oxide + 25 wt % platinum dioxide. In all cases the metal oxide only electrode responded slower to oxygen concentration changes compared with the corresponding composite electrode.

3.3. *Electrode kinetic studies*

Impedance curves obtained at 500° C for several composite electrodes consisting of platinum dioxide and $CrNbO_4$ along with those for platinum dioxide and $CrNbO_4$ are shown in Fig. 8. Only the electrode arc is shown for clarity. The electrode resistance (R_0) was determined from the difference of the intercept of this arc on the real impedance axis. The relaxation time (τ_0) was determined as the inverse of the peak frequency from imaginary impedance versus log (frequency) plots. Fig. 9 shows a plot of electrode resistance and Fig. 10 a plot of the time constant (τ_0) versus wt % of platinum dioxide. These graphs show a minimum in the values of the time constant and the electrode resistance around 25 wt % PtO_2. The time constant and the electrode resistance of composite electrodes containing about 25 wt % platinum dioxide are at least an order of magnitude lower than those for either constituent of the composite. Somewhat similar behaviour was also observed for mixtures of $(U_{0.38}Sc_{0.62})O_{2\pm x}$ and platinum [8].

In Fig. 11, the overpotential, current density (current normalized to 1 cm^2 of the electrode/electrolyte contact area) relationship for the composite electrode (75 wt % $CrNbO_4$ + 25 wt %) platinum dioxide is compared with the corresponding metal oxide only electrode. Although in obtaining current-potential data a two electrode arrangement was used for convenience and the overpotential values plotted in Fig. 11 include contributions from both electrodes, the results nevertheless clearly show that the overpotential losses at the composite electrode/electrolyte interface are much lower than those at the corresponding metal oxide only electrode/electrolyte interface.

These results clearly indicate that the oxygen exchange reaction at the composite-electrode/electrolyte interface is much faster than that at either the Pt/electrolyte or the metal oxide/electrolyte interface.

4. Conclusions

With the use of composite electrodes it is possible to reduce the operating temperature of oxygen sensors down to 300–350° C. Industrial trials of sensors incorporating these new electrodes are underway.

All the metal oxides investigated, on the addition of platinum, do not show similar improvements in their electrode behaviour. Some composite electrodes, however, showed major improvements over platinum but they were only marginally better than the corresponding metal oxide electrode. While investigations to understand this unusual behaviour are continuing, we believe that the faster kinetics at the composite-electrode/electrolyte interface and better low temperature performance of oxygen sensors incorporating these electrodes is due to both constituents of the composite participating in the oxygen exchange reactions.

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