

Titania-Based Miniature Potentiometric Carbon Monoxide Gas Sensors with High Sensitivity

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Miniature, potentiometric, solid-state, carbon monoxide (CO) sensors with semiconducting oxide electrodes were investigated over the temperature range 500°–700°C. The effects of the electrochemical properties of the semiconducting oxides, after the addition of a catalyst and an alkaline metal oxide were evaluated in terms of the improvement in selectivity and response time. A sensor with high sensitivity and reversibility was obtained using a combination of an *n*- (titania) and *p*-type (composite titania with yttria and palladium) electrode to form a difference in the electrode equilibria. The device was able to measure a wide range of CO concentrations (10–16 000 ppm) with a high sensitivity to CO. A low-cost, rugged device could be fabricated because the sensing and reference electrodes were exposed to the same gaseous atmosphere. The results presented herein were attributed to the differential electrode equilibria mechanism, which comprises both semiconducting response and heterogeneous electrocatalysis contributions to the potentiometric sensor response.

I. Introduction

(1) *Electrochemical, Solid-State, Potentiometric Carbon Monoxide (CO) Gas Sensors*

Electrochemical, solid-state, potentiometric sensors convert gas concentration directly to an electrical signal for detecting specific species in gas streams. These gas sensors can be used for the detection of ambient levels of environmental pollutants. There is presently a critical need for simple, rugged, and reliable sensing devices to monitor and control industrial and pollutant gases in the air such as nitrogen oxides (NO_x), hydrocarbons, sulfur oxides, CO, and volatile organic compounds in combustion exhaust and in flammable and toxic gases.^{1,2} These gases need to be monitored and their concentrations should be controlled at the ppm levels.³ Among the toxic gases, CO is one of the primary reducing gases that must be controlled in combustion, automobiles exhaust, and hydrocarbon fuel manufacture.^{4,5}

There are three major types of gas sensors in current use—solid electrolyte gas sensors, catalytic combustion gas sensors, and resistive-type semiconductor gas sensors.^{2,6} Among these, potentiometric solid-electrolyte zirconia sensors with noble metal (Pt, Au) electrodes are the best known and most thoroughly investigated type of sensor for CO detection in combustion processes.^{6,7} Compared with other types of sensors, the important advantages of this type are that they are simple, rugged, cheap, durable over wide CO detection range, and have a wide-sensing temperature range.^{6–9} CO oxidizes catalytically in the presence of O₂, reaching thermodynamic equilibrium in the Pt electrode but not the Au electrode. The CO oxidation consumes O₂ at the Pt electrode, resulting in a lower P_{O₂} relative to the Au electrode, thereby generating a non-Nernstian potential across the YSZ electrolytes.^{10,11} However, these sensors showed poor sensing performance due to the inherent characteristics of the noble metal-sensing electrodes. As Pt is an active oxidation catalyst, CO is oxidized completely by Pt at high temperatures, before the gas molecules can reach the triple-phase boundary.¹² Furthermore, due to its low melting point, Au electrodes densify rapidly at high temperature resulting in decreased TPB and limited, long-term operational stability.¹³

One of the sensing mechanisms proposed to explain the non-Nernstian potential behavior observed with two different metal oxide electrodes, which has received much attention in the literature is the “mixed potential.”^{11–15} This theory is based on the Tafel-type behavior for two redox reactions occurring on two different electrodes. The difference in potential between each electrode is due to the difference in the kinetic rates between the two redox reactions occurring at each electrode.^{1,16} However, one of the problems in applying the mixed potential theory to gas sensors (e.g., NO_x) is that NO is not in thermodynamic equilibrium with O₂ and N₂ at either electrode at sensor-operating temperatures.¹⁷ Furthermore, in actual exhaust gas, there are numerous additional gaseous species and reactions that can occur, resulting in non-Nernstian behavior.^{9,17} In addition, when semiconducting oxides are used as sensing electrodes, the voltage response depends on the surface morphology, adsorption–desorption behavior, and particle size—which cannot be explained by the mixed potential theory.^{13,17}

To explain these phenomena, Wachsman *et al.*¹⁷ proposed a more comprehensive mechanism “differential electrode equilibria.” This explanation for potentiometric sensor response includes the contribution of differences in electrocatalytic activity and adsorption–desorption behavior between two different electrodes exposed to the same environment.^{9,17–24} Differential

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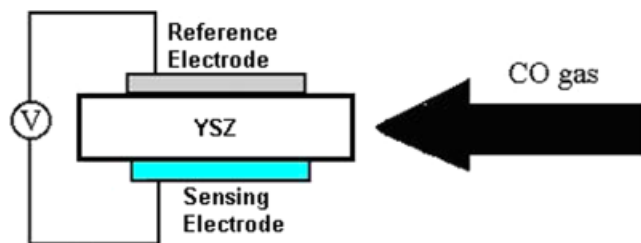


Fig. 1. Potentiometric sensor using differential electrode equilibria, which are a difference in electrochemical potential between two electrodes exposed to the same environment.

electrode equilibria arise out of the difference in electrochemical potential (η) caused by differences in heterogeneous kinetics between two electrodes in the same gas stream (Fig. 1). The electrochemical potential of the semiconducting electrode is equivalent to the Fermi level of the electrons in that electrode in electrochemistry fields. Because the Fermi level of a semiconducting oxide electrode (e.g., TiO_2) will be different from the energy of electrons in the metal electrode (e.g., Pt), a voltage difference is generated between the two electrodes even when both electrodes are exposed to the same atmosphere. Moreover, because the Fermi level of semiconducting oxides change with gas adsorption while the electron energy of metals is unaffected by the same changes in gas concentration, this mechanism provides an approach for both sensitive and selective response to certain gasses (e.g., NO_x and CO).

In addition, a simple, miniaturized and inexpensive device can be fabricated because the sensing and reference electrodes are exposed at the same gaseous atmosphere. This approach is extended in this paper to the development of sensitive and selective potentiometric CO sensors using electrodes based on previously studied semiconducting resistive sensor elements.

(2) Strategy for Development of CO Sensors

Novel technological development and materials research has led to the development of solid-state gas sensors using semiconducting oxides (e.g., SnO_2 , TiO_2) as resistive sensor elements for CO detection.^{25–28} The adsorption and reaction of gas species on semiconducting surfaces alters their electrical properties due to defect formation in the band gap.^{4,6,29} This modification in semiconducting properties is used to determine the concentration of the reactive gas being measured. However, even the most recent advances have not resulted in sufficient selectivity (cross-sensitivity), response time, sensitivity, reversibility, size, and cost necessary for wide-spread commercialization.

Based on the differential electrode equilibria approach, solid-state potentiometric YSZ sensors with semiconducting oxide electrodes for CO detection were developed. Solid-state, tape cast YSZ substrates were chosen due to their compatibility to the conventional oxygen sensor design and favorable mechanical properties.^{30,31} In addition, because the tape-casting process is inexpensive and scalable, simple and inexpensive devices can be fabricated that are suitable for mass production with further technological progress. Our strategy for developing potentiometric sensors includes (a) selection of an oxide with a semiconducting response to CO, (b) addition of other semiconducting materials, (c) addition of a catalyst (Pd), (d) utilization of combined *p*- and *n*-type electrodes in one sensor configuration, and (e) optimization of operating temperatures.

Firstly, among semiconducting oxides, materials with energy band gaps between 3 and 4 eV show resistivity changes due to defect formation in the band gap upon adsorption of gaseous species.^{28,32} As an example, in the case of an *n*-type semiconductor (e.g., SnO_2), surface defect states are formed by chemisorption of oxygen from ambient air (Eq. (1)). With increasing CO concentrations, CO reacts with the surface-adsorbed oxygen, releasing the trapped electron to the conduction band (Eq. (2)). This increases the Fermi level of electrons in the semiconducting oxides, and consequently the resistance decreases.

Hence, measurable sensitivity could be achieved in the various semiconducting oxides due to band-gap energy criterion:



As well as the band-gap energy criterion, material properties such as electrocatalytic activity and thermal stability (sintering temperature) are important factors for selection of semiconducting oxide electrodes for highly sensitive detection of CO with long-term operational stability.^{2,6,33} Based on these criterions, among the semiconducting oxides, *n*-type TiO_2 (anatase)-sensing electrodes have been found to be very effective for CO detection at $400^\circ\text{--}700^\circ\text{C}$.^{4,27,28}

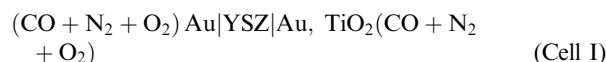
Secondly, doping is a well-accepted method to enhance sensitivity and selectivity in resistive sensors, because the addition of dopants can enhance or suppress specific chemical reactions by altering the morphology of the adsorption sites for the gas molecules and by changing the electrical properties of the semiconducting oxides.^{34,35} That is, the resistive response of the sensor can be changed by suitable selection of the donor or acceptor. The electrical properties in the semiconducting oxides are modified by varying the Fermi level through doping. Changing the Fermi level by doping affects the voltage response of the potentiometric sensor through “differential electrode equilibria,” in the same way as it does in the resistive sensor. Thus, in order to significantly improve selectivity to CO in reducing gas mixtures, we added other oxide materials (e.g., Y_2O_3) to the TiO_2 . In addition, selective CO detection with a fast response time has been reported in several studies,^{36,37} using a semiconducting oxide mixed with a noble metal as a catalyst on potentiometric sensors. The addition of a small amount of noble metal (Pd) is useful not only to activate the reactive gas by enhancing its spillover, but also to improve its catalytic activity, so that gas molecules react with the oxygen adsorbates more easily.³⁴ In this work, 5 wt% Pd was added to the composite TiO_2 and Y_2O_3 to improve the sensitivity and response time of solid-state potentiometric CO sensors.

Thirdly, the electrical behavior of semiconducting oxide electrodes can be modified from *n*- to *p*-type or vice versa by addition of other semiconducting oxides (donor or acceptor).^{33,38–40} When potentiometric sensors are fabricated using *n*-type electrodes on one side and *p*-type electrodes on the other, the resulting response will be additive.⁴¹ In other words, it will be the algebraic sum of the magnitude of the negative and positive voltages, thereby enabling an even higher CO sensitivity to be achieved. Furthermore, because adsorption–desorption are thermally activated processes, the response and recovery time of the sensors depend on temperature.^{4,9,42} In addition, changes of the chemical (surface coverage, chemical reaction), physical (geometry, morphology), and electrical (charge-carrier concentration, Fermi energy) properties of the semiconducting oxides are temperature dependent, and thus result in different voltage responses with diverse sensing mechanisms.²² Hence, dependence on operating temperature is one of the most significant factors in determining sensor performance in terms of sensitivity, response time, and reversibility. In this study, the sensing performance of YSZ potentiometric sensors with titania-based materials was tested in the temperature range between $500^\circ\text{--}700^\circ\text{C}$. The dependence of specific sensing mechanisms on the temperature is presented.

II. Experimental Procedure

(1) Preparation of Potentiometric Sensors with Titania-Based Electrodes

Three potentiometric sensors in the following cell design (Fig. 2(a)) were studied,



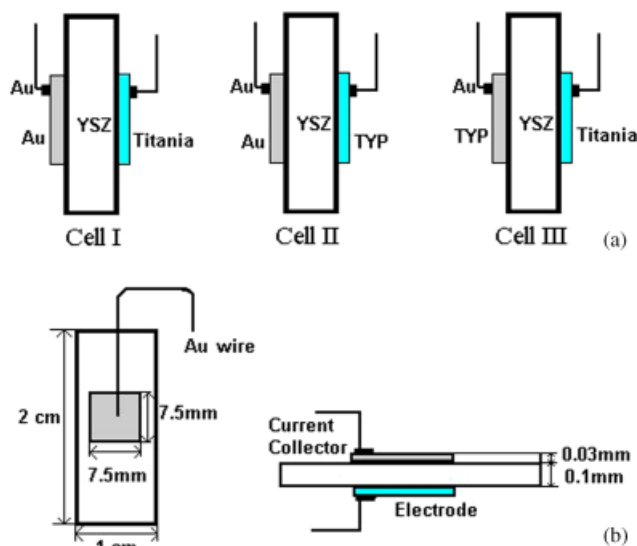
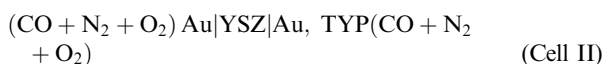


Fig. 2. The (a) cell configuration and (b) device structure of potentiometric sensors using titania-based sensing electrodes with Au current collector.



where TYP is a composite electrode of TiO_2 , Y_2O_3 , and Pd. Thin, tape cast, 8% YSZ substrates ($1 \text{ cm} \times 2 \text{ cm} \times 0.1 \text{ mm}$ thick) were procured from Marketech International (Ceraflex, Port Townsend, WA). Figure 2(b) shows the simple design of the YSZ potentiometric sensor using differential electrode equilibria.

In Cell I, TiO_2 powder (anatase 99.9%, Alfa Aesar, Ward Hill, MA) was mixed with ethanol using a mortar and pestle after adding solvent (α -terpineol), plasticizer (dibutyl phthalate), and binder (polyvinyl butyral) to impart good adhesion between the YSZ and electrode. Cell II was tested to study the effect of the addition of both an additional semiconducting oxide (Y_2O_3) and a catalyst (Pd). The composite electrode (TYP) was prepared with TiO_2 , Y_2O_3 (99.99%, Alfa Aesar), and Pd (99.99%, Alfa Aesar) in a weight ratio of 85:10:5 and was thoroughly mixed in an agate mortar, similar to Cell I. TiO_2 and TYP slurries were screen printed ($7.5 \text{ mm} \times 7.5 \text{ mm}$ electrodes) on either side of YSZ, dried by heating at 125°C for 30 min, and finally sintered at 700°C for 4 h. The opposite side of the YSZ substrates was covered with an Au electrode (HC1105, Engelhard, Florham Park, NJ).

In addition, the sensing performance of the combination of these two semiconducting oxide electrodes was investigated in Cell III, using TiO_2 on one side and TYP on the other. Au wires were then attached to the sintered surfaces of both electrodes with Au paint for Cells I, II, and III. These leads were dried and sintered under the same conditions as the electrodes.

The phases of the starting raw materials were identified using X-ray diffraction (XRD, Philips APD 3720, Westborough, MA). The surface area of the semiconducting oxide powders was characterized using the Brunauer–Emmett–Teller equation (Quantachrome Corporation, Boynton Beach, FL). The microstructure and chemical composition of the electrodes before and after the sensing test were investigated using a scanning electron microscope (SEM, JSM-35CF JEOL, Peabody, MA) and energy dispersive X-ray spectroscopy (EDX), respectively.

(2) Preparation of Resistive-Type Sensors with Semiconducting Electrodes

Thick-film electrodes of TYP (Cell IV) were prepared on YSZ substrates by screen printing and calcined at 700°C for 4 h. The thick films had surface dimensions of $7.5 \text{ mm} \times 7.5 \text{ mm}$ and a thickness of around $30 \mu\text{m}$. Figure 3 shows the fabricated, re-

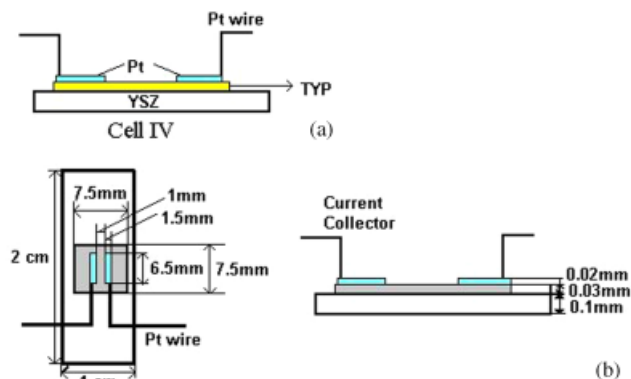


Fig. 3. The (a) sensor configuration and (b) device structure with composite TYP (Cell IV) electrodes for resistive measurements.

sistive-type, sensor configuration with both contacts on the same face of the semiconducting element placed side-by-side. Two parallel Pt layers, 1 mm apart, were painted over the semiconducting oxide electrodes, connected with Pt wires using Pt paint (CL11-5349, Heraeus, West Conshohocken, PA) for electrical resistivity measurements, and sintered under similar conditions, as described above to ensure good contact between the electrodes and current collectors. The resistivity of Cell IV was examined at various temperatures (500°C – 700°C) and CO gas concentrations (10–16000 ppm) in a nitrogen stream.

(3) Measurement of Gas-Sensing Characteristics

The selectivity, sensitivity, response time, and reversibility of these sensors for CO were investigated as a function of temperature and CO concentration. In order to examine the sensitivity and reproducibility of the sensing elements, investigations in Cell I and II were carried out with three different devices fabricated using the same procedures as described above. Combination sensors of Cell III were tested with more than five samples to prove whether the overall sensor signal is the sum of the voltage generated individually in each electrode. In addition, measurements were performed as a function of time in both increasing and decreasing steps of CO concentration to examine the response time and reversibility of the sensors. In order to explore selectivity to CO against O_2 , high-purity nitrogen with varying concentrations (1%–21%) of oxygen was used as a carrier gas with varying CO concentrations at a total flow rate of 250 sccm, as shown in Table I. In order to simulate exhaust environments, 3% H_2O was added.

The sensor was placed in a quartz tube, positioned within a furnace. The flow rates of CO and other carrier gases were precisely controlled with mass flow controllers (1605, BOC Edwards, Tewksbury, MA). The sensor signal was monitored with a high-precision digital multimeter (Keithley 2000, Cleveland, OH) and automatically acquired by a computer through a Lab-View program.

III. Results

(1) Microstructure Analysis of Semiconducting Oxide Films

The semiconducting response relies on the adsorption–desorption behavior of gas molecules. Higher sensitivity is expected

Table I. Gas Composition with Step Change of Carbon Monoxide (CO) Concentration with O_2 , N_2 , and 3% H_2O as Carrier Gases

Gases	Concentration (total flow rate: 250 sccm)
N_2	Base gas
H_2O	Moisture saturated (3%)
O_2	1%, 3%, 5%, 10%, 21%
CO	0–16000 ppm (0, 16, 32, 48, 64, 80, 160, 320, 480, 640, 800, 1000, 2000, 4000, 8000, 12000, 16000)

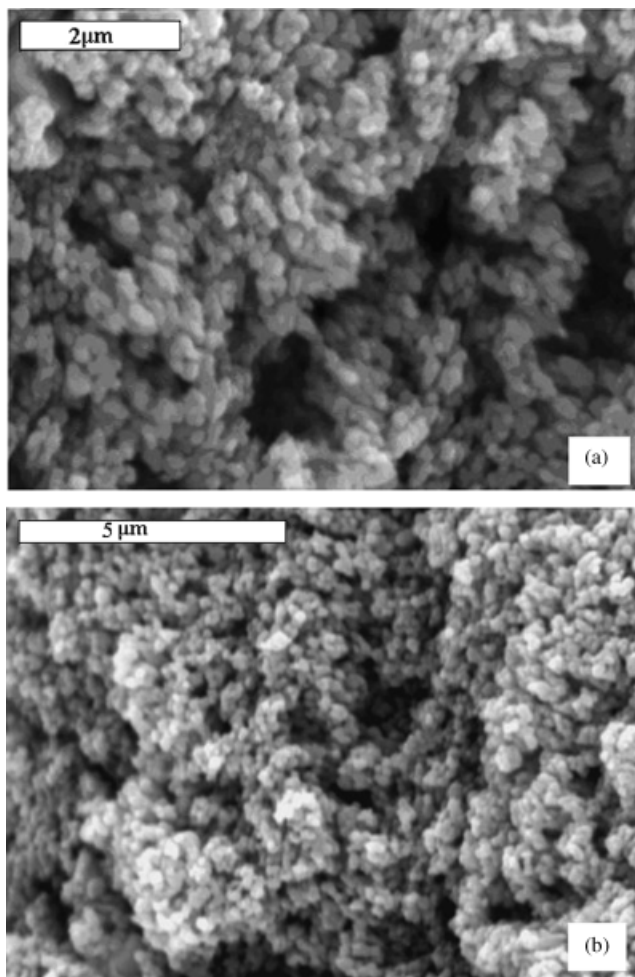


Fig. 4. Scanning electron micrographs showing the surface morphology of the screen-printed sensor elements of (a) TiO_2 and (b) TYP composite electrodes.

with electrodes having high-surface area and small pores.³⁶ In order to investigate the dependence of sensor response with the morphology of sensor elements, the SEM microstructure of the CO sensor elements was investigated and two micrographs are presented in Fig. 4. The average size and surface area of the starting oxide powders were 0.1–0.4 μm and 5 m^2/g , respectively. The small particle size of the starting raw materials was transformed into sintered sensing elements with submicron grains and a very porous structure. Addition of Y_2O_3 and Pd to TiO_2 did not have a significant effect on the particle size, surface area, and morphology of the thick-oxide films.

A cross-sectional SEM micrograph of the titania-based potentiometric sensors is shown in Fig. 5. The thickness of the oxide films (TiO_2 and TYP) was $<30 \mu\text{m}$. The SEM image also reveals the good adherence of the thick-oxide film to the YSZ substrates. Unfavorable solid-state reaction and interdiffusion of the two phases were not detected by EDX.

(2) Performance of TiO_2 Potentiometric Sensors (Cell I)

Figure 6 shows the voltage response of Cell I as a function of CO concentration (100–1000 ppm) at 500°–700°C. The slope of the voltage response versus the logarithmic CO concentration is the sensor sensitivity. The sensitivity was linear throughout the measurement range and decreased with increasing temperature. The sensitivity values evaluated from Fig. 6 are presented in Table II and decreased in magnitude from -70 to $-36 \text{ mV}/\log [\text{CO}, \text{ppm}]$ with increasing temperature.

The response/recovery time and reversibility behavior of Cell I can be estimated from Fig. 7. Even though cell I showed a fast

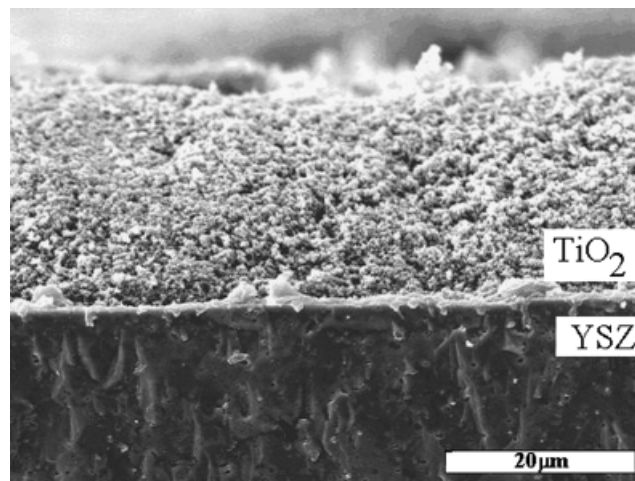


Fig. 5. Cross-sectional scanning electron micrograph of the titania film prepared on the dense YSZ substrate via screen printing.

response time with high reversibility in high CO concentrations (160–800 ppm) at 500°C, a poor sensing performance at low CO concentration was exhibited due to kinetically limited adsorption–desorption rate.

(3) Performance of Composite TYP Potentiometric Sensors (Cell II)

The sensor voltage developed in Cell II as a function of CO concentration at 500°–650°C is shown in Fig. 8. As with Cell I, a high sensitivity was observed. As shown in Table II, the slope decreased from 85 to 25 $\text{mV}/\log [\text{CO}, \text{ppm}]$ with increasing temperature. A relative improvement in sensitivity was observed in Cell II through the addition of Y_2O_3 and Pd catalysts, compared with that of Cell I. The value of the slope for Cell II at 500°C was 85 $\text{mV}/\log [\text{CO}, \text{ppm}]$, while that of Cell I was $-70 \text{ mV}/\log [\text{CO}, \text{ppm}]$ at the same conditions.

While Cell I exhibited a negative response due to the *n*-type characteristics of its electrodes,^{40,43} Cell II showed a positive response due to its *p*-type electrodes. In other words, the electrical behavior (voltage signal) of the TiO_2 -semiconducting oxides changed from *n*- to *p*-type by addition of Y_2O_3 and Pd. Mizsei³⁸ demonstrated through thermoelectric power measurements that even though SnO_2 is an inherently *n*-type semiconducting oxide, partial agglomeration of Pd in SnO_2 -Pd systems changes it to *p*-type by catalytic oxidation of Pd, even in reducing atmospheres. We considered similar phenomena to

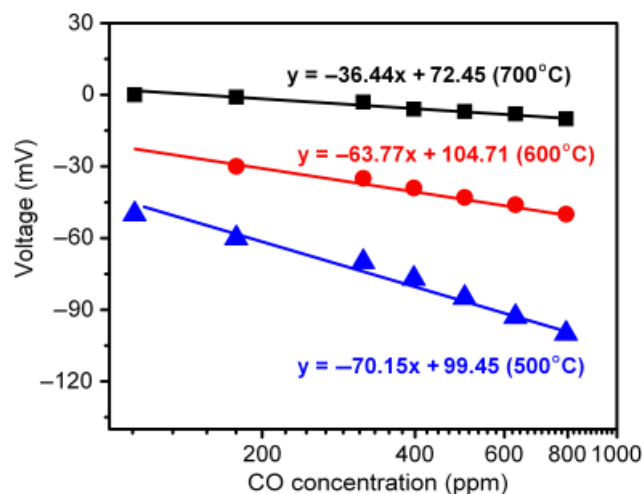


Fig. 6. Dependence of voltage response as a function of carbon monoxide (CO) concentration (base gas: $\text{N}_2+3\% \text{O}_2$ in wet condition) for Cell I using the TiO_2 (anatase) electrode.

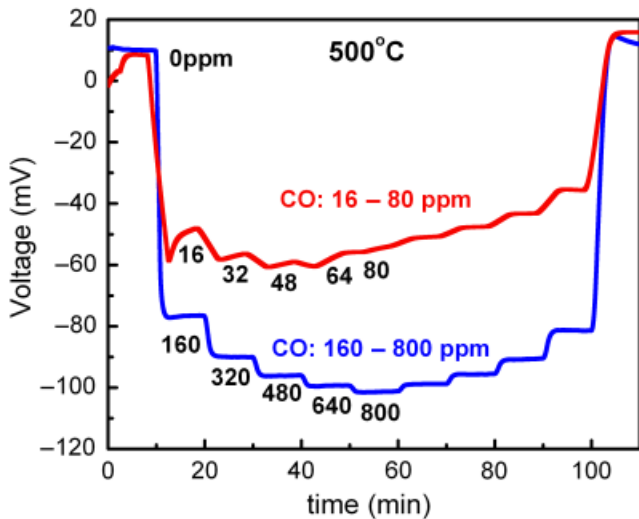


Fig. 7. Voltage response as a function of carbon monoxide (CO) concentration (base gas: $N_2+3\% O_2$ in wet condition) at $500^\circ C$ in Cell I.

have occurred in our TYP system, which changed it from *n*- to *p*-type, thus resulting in a change from negative to positive sensor sensitivity.

(4) Performance of Resistive-Type Sensors with TYP Electrodes (Cell IV)

In order to verify the electrical transition of TiO_2 semiconducting oxides from *n*- to *p*-type by addition of Y_2O_3 and Pd, the variation in the resistivity of the TYP sensors (Cell IV) was measured as a function of CO concentration and temperature. The relative resistance was defined as the ratio of the original resistance in the absence of CO gas (R_0) to the resistance while exposed in CO environments (R). The dependence of the resistance of the TYP sensors on the CO concentration and temperature is presented in Fig. 9. The resistance of the TYP film increased with increasing CO concentration up to a CO concentration of 500 ppm at all measurement temperatures. This indicates that TYP acts as a *p*-type electrode at ≤ 500 ppm CO, which is the concentration range used in our potentiometric sensor measurements.

However, at higher CO concentrations (beyond ~ 500 ppm), the resistance decreased rapidly with increasing CO concentration, indicating the onset of *n*-type behavior in this range of

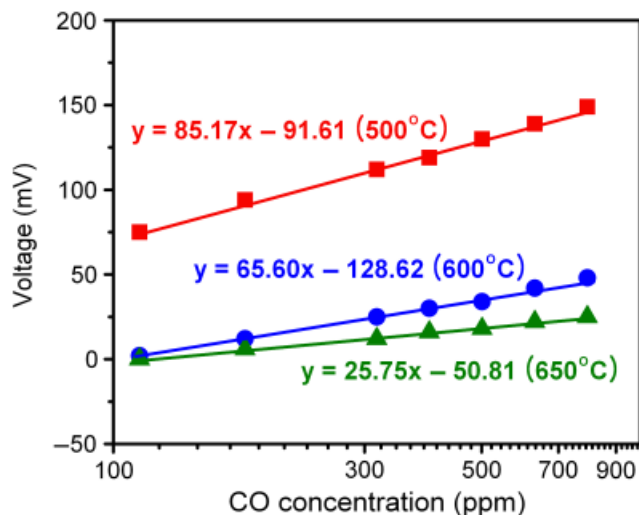


Fig. 8. Voltage response as a function of carbon monoxide (CO) concentration (base gas: $N_2+3\% O_2$ in wet condition) in Cell II using the composite TYP electrode.

Table II. Performance of Potentiometric Sensors with Titania-Based Sensing Electrodes, in Terms of their Sensitivity (Slope of Voltage and Log CO Concentration)

Cell	Electrodes	Sensitivity graph (mV/log [CO, ppm])	Detection range (ppm)	Oxygen content (%)	Temperature ($^\circ C$)		
I	TiO_2/Au	-70.15	100–1000	3	500		
		-63.77			600		
		-36.44			700		
II	TYP/Au	85.17	100–1000	3	500		
		69.60			600		
		25.75			650		
III	TiO_2/TYP	-43.56	10–100	1	500		
		-41.84			500		
		-28.37	10–1000	3	500		
		-6.89			500		
		-6.57	10–1000	1	600		
		-5.73			600		
		Linear range slope		9.58	10–1000	1	700
				35.92			1000–16000
2.85	10–1000			3			700
0.78	10–1000			5			700

CO, carbon monoxide.

operation. While the relative resistance was independent of temperature at lower concentration, at high CO concentration, it was significantly affected by temperature due to the different sensing mechanism. Therefore, the upper limit of operation of the potentiometric sensor is limited to below the range of CO concentration where the sensing element changes to *n*-type, and consequently a reduction in sensitivity is observed.

(5) Performance of Combination of *n*- (TiO_2)+*p*- (TYP) Type Sensors (Cell III)

Cell III was fabricated using one electrode (TiO_2) inherently having a negative response on one hand, and another electrode (TYP) having a positive response on the other, so as to achieve an even higher CO sensitivity, as described in Section I. Figure 10 shows a relatively linear dependence of voltage response as a function of CO concentration at $500^\circ C$ – $700^\circ C$ in Cell III. Because Cell III is essentially the combination of the first (Cell I) and second (Cell II) cells, the overall sensitivity of the potentiometric CO sensor should effectively be the sum of the voltage generated individually in each electrode on opposite sides of the cell.

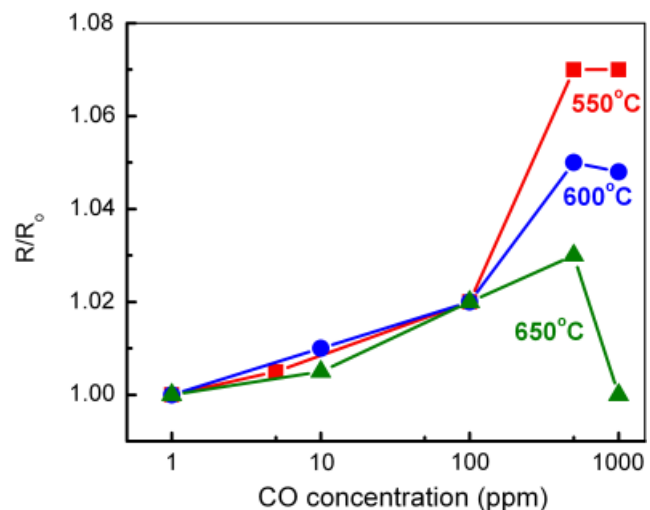


Fig. 9. Relative resistance of composite TYP electrodes in Cell IV as a function of carbon monoxide (CO) concentration at $550^\circ C$ – $650^\circ C$.

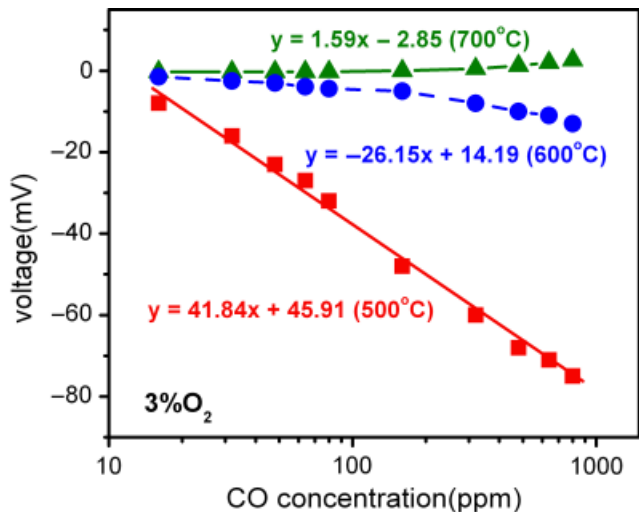


Fig. 10. Voltage response as a function of carbon monoxide (CO) concentration (base gas: $N_2+3\% O_2$ in moist condition) in Cell III using the TiO_2 electrode on one side and the composite TYP electrode on the other.

However, this linear improvement of sensitivity was not observed for Cell III using a noncatalytic current collector (Au). Further research needs to be conducted to make feasible the linear improvement of sensitivity in Cell III.

The sensitivities obtained for various combinations of semi-conducting oxide electrodes are summarized in Table II. The high slopes of voltage versus log CO curves for Cells I, II, and III produced sufficient sensitivity in the potentiometric mode of operation. Among the three, Cell III was highly sensitive to CO over a relatively wide detection range and a capability to resolve a 10 ppm variation in CO concentration. As presented in Section III(2), Cell I showed a poor sensing performance at low CO concentrations, but was highly sensitive for high CO concentration ranges at 500°C.

The temperature dependence of the CO sensitivity was tested for Cell III and is presented in Fig. 11. The voltage signal was highly reproducible and steady-state voltage was achieved quickly at each CO concentration in either direction. The response time (the time required to reach 90% of the stable value) at each temperature was <2 min for each CO step change, and was further improved with increasing temperature and CO concentration.

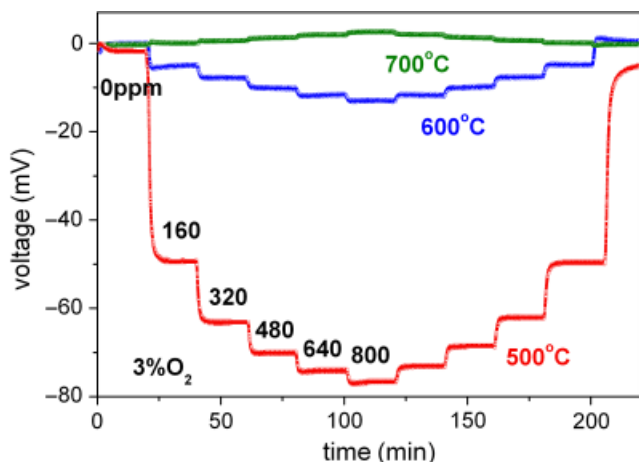


Fig. 11. Plot of response voltage as a function of time over the temperature range 500°–700°C in Cell III indicating the effect of response time, reversibility, and sensitivity.

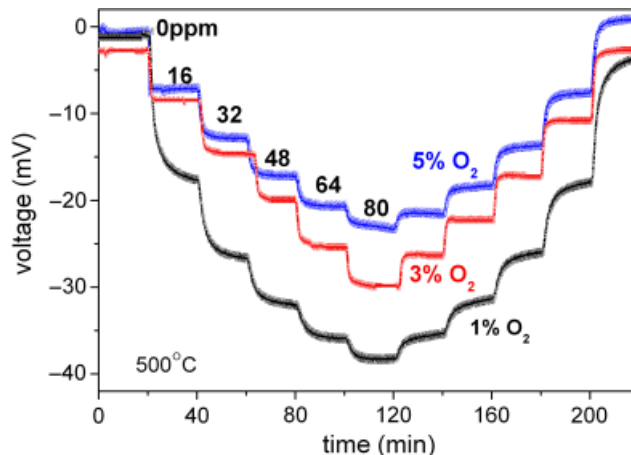


Fig. 12. Plot of immediate voltage response with varying carbon monoxide (CO) concentration at different ranges of O_2 concentration as a function of time at 500°C for Cell III fabricated with both *n*-type TiO_2 and composite TYP electrodes.

Figure 12 shows the variation in sensor signal at 500°C, when Cell III was exposed to 0–800 ppm of CO with an oxygen concentration of 1%–5%. The selectivity of CO against O_2 of Cell III at 500°C is presented in Fig. 13. The sensor was extremely selective to CO versus O_2 at the low CO and high O_2 concentrations that are typical of fuel-lean combustion. However, further improvement remains necessary for fuel-rich combustion conditions.

Another important observation is the overall sensor voltage switched from negative to positive response with increasing operating temperature (Fig. 14). This transition occurred because the effect of the electrodes was subtractive in generating the overall response, and the dependence of the mechanism on temperature caused one electrode to be the major contributor to the response voltage at one temperature range while the other was dominant at other temperature range.

IV. Discussion

With increasing temperature, the overall response was significantly decreased (Figs. 6, 8, 10, and 14), and for Cell III switched from a negative to a positive response (Figs. 10 and 14) due to the temperature-dependent change in mechanism at both electrodes. This result is in good agreement with the sensing properties of an YSZ-based potentiometric sensor with La_2CuO_4

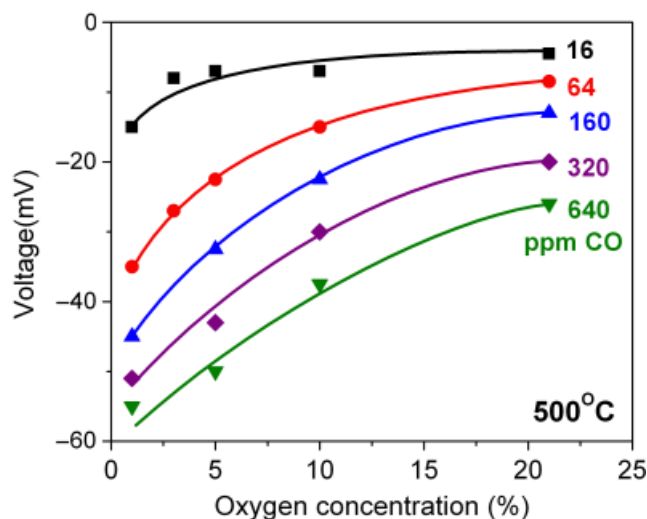


Fig. 13. Selectivity of the carbon monoxide (CO) sensor according to O_2 concentration at 500°C in Cell III.

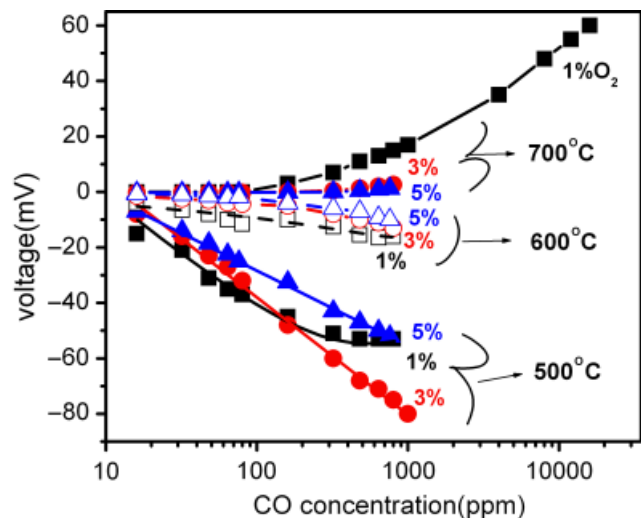
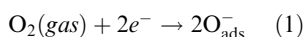
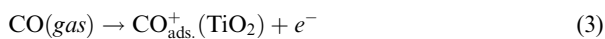


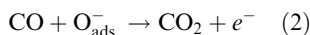
Fig. 14. Sensor response with varying O₂ concentrations as a function of carbon monoxide (CO) concentration at 500°–700°C in Cell III fabricated with both *n*-type TiO₂ and *p*-type composite TYP electrodes.

semiconducting electrodes [La₂CuO₄|YSZ|Pt] in prior literature.^{9,19,22–24} The CO sensitivity of the potentiometric sensor with La₂CuO₄ electrodes decreased with increasing temperature from 300° to 550°C.⁹ Based on temperature-programmed desorption (TPD) and electrochemical impedance spectroscopy (EIS) results, it was determined that the CO response of this sensor was related to adsorption/desorption phenomena and its effect on the semiconducting behavior of the La₂CuO₄ electrode at lower temperatures,^{9,19,21–24} while at higher temperature, the catalytic behavior dominated, because gas adsorption was negligible due to fast desorption kinetics, and the gas sensitivity relied strongly on the P_{O₂} change.^{9,22–24,44,45}

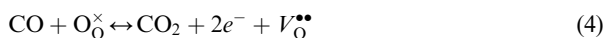
This mechanistic understanding can be extended to the titania-based electrode potentiometric sensors to understand temperature-dependent change in mechanism in this work. That is, at lower temperatures ($T \leq 500^\circ\text{C}$), the selective adsorption of CO molecules at the semiconducting oxide electrode (TiO₂) surface might be dominant over O₂ due to facilitated CO adsorption kinetics. This induces a voltage response owing to increased surface defect concentrations in the donor levels of the semiconducting oxide, as described in Section I(2):



In contrast, increased catalytic oxidation of CO at higher temperature ($T \geq 600^\circ\text{C}$) dominates reducing the magnitude of the voltage response:



In addition, differential electrocatalytic reactions such as Eq. (4) might also contribute to the sensing performance because bulk defect equilibrium processes can occur at high temperature:



Consequently, at lower temperature, the dominant sensing mechanism is due to the change of electrical properties through the adsorption–desorption behavior of the semiconducting electrode surface, while the differential heterogeneous catalytic activity for CO oxidation dominates the sensor signal at higher temperatures.

These results confirm the “differential electrode equilibria” mechanism, in which the sensing mechanism shifts from a semiconducting response, through adsorption–desorption phenom-

ena, to heterogeneous catalysis with increasing temperature.^{9,21–24} However, the various contributions to response of titania-based potentiometric sensors, such as adsorption/desorption behavior, electrode catalytic activity, and effect of surface morphology, need further investigation to increase our understanding of the fundamental sensing mechanism. Therefore, TPD/reaction, EIS, and transient isotope exchange experiments of these electrode materials (as was previously performed for La₂CuO₄^{9,22–24}) are necessary to verify the gas-sensing mechanism of titania-based solid-state potentiometric sensors.

Another possible reason for the change in the magnitude of the sensor signal is the structural change of TiO₂ from anatase to rutile. In the case of rutile TiO₂, the resistance increased with increasing CO concentration (*p*-type behavior), but decreased for anatase (*n*-type behavior).⁴⁰ CO reacts with the surface-adsorbed oxygen, releasing electrons and consequently increasing conductivity for anatase TiO₂. However, as the majority carriers in the rutile phase are holes, the injected electrons recombine with the holes, thereby decreasing conductivity. The behavior of switching from *n*- to *p*-type (and vice versa) as a function of oxygen partial pressure is well reported in the literature.⁴³ Transitions between *n*- and *p*-type behavior in TiO₂ are dependent on temperature, oxygen partial pressure, and impurity concentrations.^{39,40,43} However, in the current study, no structural change from anatase to rutile phase was observed by XRD (not shown).

An attractive feature of the sensors is that while the voltage at 0 ppm CO concentrations in Cells I and II was dependent on the operating temperature that of Cell III was relatively independent of temperature. Even at zero CO concentration, a differential equilibrium exists between the semiconducting oxide and metal electrodes, so that a temperature-dependent voltage difference is generated. However, in the case of Cell III, because the Fermi level for both electrodes was similar in the absence of CO gas, there was no voltage difference in the absence of CO.

The high sensitivity, selectivity, reversibility, and fast-response time in Cell III were achieved through the use of different semiconducting oxides, the addition of a noble metal as a sensing electrode, and the utilization of combined *p*- and *n*-type electrode in series. Cell III was able to resolve a 10 ppm variation in CO gas concentration and had a CO concentration range up to 1000 ppm.

V. Conclusions

A solid-state, YSZ-based potentiometric sensor was developed using semiconducting oxide electrodes. In order to increase the CO sensitivity, the sensors were fabricated using *n*-type electrodes (TiO₂) on one side and *p*-type electrodes (TYP) on the other. This potentiometric sensor was highly sensitive to CO over a relatively wide detection range and a capability to resolve a 10 ppm variation in CO concentration. The voltage signal of this sensor was highly reproducible and a fast response/recovery time was observed for each CO step change. Compared with other traditional, potentiometric CO sensors, a simple, miniaturized, rugged, and low-cost device could be fabricated because the sensor’s sensing and reference electrodes were exposed to the same gaseous atmosphere. With increasing temperature, the sensing mechanism was shifted from a semiconducting response by adsorption–desorption behavior to a heterogeneous catalysis phenomenon. The results confirmed the mechanism of “differential electrode equilibria,” which include both the semiconducting response and heterogeneous electrocatalysis.

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