SRI International

Novel Gas Sensors for High-Temperature Fossil Fuel Applications

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ABSTRACT

SRI International (SRI) is developing ceramic-based microsensors to detect exhaust gases such as NO, NO₂, and CO in advanced combustion and gasification systems under this DOE NETL-sponsored research project. The sensors detect the electrochemical activity of the exhaust gas species on catalytic electrodes attached to a solid state electrolyte and are designed to operate at the high temperatures, elevated pressures, and corrosive environments typical of large power generation exhausts. The sensors can be easily integrated into online monitoring systems for active emission control. The ultimate objective is to develop sensors for multiple gas detection in a single package, along with data acquisition and control software and hardware, so that the information can be used for closed-loop control in novel advanced power generation systems.

This report details the Phase I Proof-of-Concept, research activities performed from October 2003 to March 2005. SRI's research work includes synthesis of catalytic materials, sensor design and fabrication, software development, and demonstration of pulse voltammetric analysis of NO, NO₂, and CO gases on catalytic electrodes.

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EXECUTIVE SUMMARY

To address the critical need for on-line emission monitoring in advanced fossil fuel energy production systems, SRI International (SRI) is developing an array of miniature solid-state electrochemical sensors that are reliable, rugged, and inexpensive. We are conducting this sensor research program in two phases: Phase I includes the proof of concept and preliminary demonstration of a sensor package with multiple elements. Phase II involves in-depth analysis and testing of sensor arrays for stability, sensitivity, and selectivity; prototype development and testing; and identification of pathways for use in integrated sensor systems in fossil fuel energy conversion systems. The research activities discussed in this report were performed as part of the Phase I effort.

The high-temperature gas sensors being developed in this research program are based on solid-state ionic conducting and catalytic materials and could be used for on-line, real-time detection of O_2 , NO_x , SO_x , hydrocarbons (HC), and CO in exhaust gases. The sensors measure potential (potentiometric) and/or current (amperometric and voltammetric) in a solid-state electrochemical cell. The sensor array consists of a number of electrochemical cells fabricated with yttria-stabilized zirconia (YSZ) solid-state electrolyte and catalytic working electrodes. Each working electrode material is designed to be selective to a specific gas in the gas mixture. Selective detection of gases is enhanced by applying fast-pulse voltammetric techniques to the specific catalytic electrode, which is optimized for the gas of interest. The configuration and geometry of the electrode are also critical for obtaining the best sensor response. Thus, SRI's Phase I research work included selection and synthesis of suitable catalytic materials for detection of NO, NO_2 , and CO; fabrication of YSZ ceramic membranes with controlled microstructure; preparation of catalytic electrodes; electrochemical cell design; software development for pulse voltammetry; and testing of sensors in a simulated exhaust environment.

We have successfully demonstrated that NO, NO_2 , and CO can be detected in the presence of excess O_2 in a solid-state electrochemical cell using pulse voltammetric techniques on a catalytic electrode. The voltammograms show high sensitivity and selectivity as shown in Figure E1, thus the sensors show tremendous potential in online emission monitoring applications. The specific research activities performed in Phase I follow.

- Drawing on literature findings and our experience, we selected $CdMn_2O_4$ and $NiCr_2O_4$ as candidates for NO and NO_2 detection, and $LaSrFeO_3$ (LSF) for CO and NO detection. These catalytic materials were prepared by solid-state synthetic routes, and their phase structures were confirmed by X-ray diffraction.
- Paintable slurries of catalytic electrode materials were prepared with nanoparticles of the synthesized materials. The sensor electrodes were fabricated by painting the solid YSZ electrolyte with slurries made of appropriate materials and sintering at $750^\circ C$. The adhesion of the catalytic electrode to the solid electrolyte was improved by optimizing the sintering program and the slurry composition. The counter and reference electrodes were prepared by painting with commercial Pt ink, followed by sintering.
- YSZ solid-state electrolyte was prepared by tape casting. The required cell geometries were cut with a laser from the "green" tape and sintered at $1400^\circ C$ to obtain solid-state

electrolyte membranes. For novel cell designs, solid/porous YSZ membranes were prepared by laminating “green” tapes with and without pore formers, followed by sintering.

- To run the pulse voltammetry scans on sensors, we developed software using Microsoft Visual Basic[®]. We interfaced a potentiostat (EG&G PAR 283) with a computer for data acquisition and experiment control. Software operation was verified with known electrochemical systems. The software is highly versatile and easily upgradeable to control the prototype sensor designs.
- We designed and fabricated a number of sensors with different electrode configurations. We tested these sensor designs with emission gas species to determine their sensitivity and selectivity in the presence of 1 to 5% oxygen. The tests were performed at temperatures from 500° to 900°C.

Figure E1. A photograph of a sensor with multiple elements (a), schematic diagram (b), response of the LSF sensor to NO (0–200 ppm) and CO (0–125 ppm) (c), and the calibration plot (d).

- We have successfully demonstrated that pollutant gases such as NO, NO₂, and CO can be detected in the presence of excess O₂ in a solid-state electrochemical cell using pulse voltammetric techniques on a catalytic electrode. NO₂ and NO can be detected on either CdMn₂O₄ or NiCr₂O₄ electrodes in a diffusion-restricted cell. CO and NO can be detected on an LSF electrode as shown in Figure E1. Because the potentials that peaks appear are different, the species can be easily identified in the voltammogram. The calibration plots obtained for each of these gases on the respective electrodes showed excellent linearity, indicating that the technique can be used reliably to monitor exhaust gas streams.
- The solid-state electrochemical cell and the electrode design were critical for obtaining sensitivity and selectivity. As the diffusion of gases to the catalytic electrode must be restricted to obtain mass transfer control in the electrochemical reactions, a simple cell design with a catalytic electrode did not provide adequate sensitivity or selectivity for the detection of emission gases. Because mass transfer rate is quite high in the gas phase, the charge transfer rate was not sufficient to establish a mass transfer-controlled reaction, and thus the cell current did not reach a plateau as would be the case in typical aqueous solutions.
- We have proposed a mechanism for selectivity of the species, based on mixed potential at the electrochemical interface. From pulse electrochemical measurements and AC impedance analysis, we believe that the species are preferentially adsorbed on the catalyst-electrolyte interface, and thus change the response of the electrode to the voltage waveform. Depending on the bias of the electrode, the activities of the species adsorbed are different, and thus multiple species can be detected on a single electrode.

INTRODUCTION

Purpose of the Project and Project Objectives

Sensors can provide the electrical power industry with increased operational efficiency, reduced emissions, and lower operating costs. Advances in robust sensing and control algorithms can accelerate the time to the full-scale commercial implementation of novel power generation technologies such as advanced combustion, gasification, and turbines. Whereas the monitoring of oxygen content is the primary method of optimization of the combustion process, emission control also requires monitoring of NO_x, SO_x, CO, and hydrocarbons (HC). For closed-loop control, fast-response, reliable sensors are needed near the combustion zone. However, the harsh conditions prevalent in the conversion of fossil fuel to energy create a barrier to making many of the desired measurements. These conditions include high temperatures (up to 1000°C), elevated pressures (up to 500 psi), corrosive environments, and high particulate loading.

To address the critical need of on-line emission monitoring in advanced fossil fuel energy production systems, SRI International (SRI) is developing an array of miniature solid-state electrochemical sensors that are reliable, rugged, and inexpensive. These sensors, which are based on solid-state ionic conducting materials and catalytic materials, could be used for on-line, real-time detection of O₂, NO_x, SO_x, HC, and CO in exhaust gases.

In general, most high-temperature gas sensors operate on the principle that change in gas composition is related to a corresponding change in property such as potential, current, capacitance, or resistance. The sensors being developed in this research project measure potential (potentiometric) and/or current (amperometric and voltammetric) in a solid-state electrochemical cell. The sensor array consists of a series of electrochemical cells fabricated with yttria-stabilized zirconia (YSZ) solid-state electrolyte and catalytic working electrodes. Each working electrode material is designed to be selective to a specific gas in the gas mixture, and the sensor materials must also be stable in the operational environment for a period up to 1 year. Gases are selectively detected by application of fast-pulse voltammetric techniques on the specific catalytic electrodes optimized for the gas of interest. The configuration and geometry of the electrode are critical for obtaining the best sensor response. Thus, the research work reported here has included fabrication of ceramic electrochemical cell components with controlled microstructure to increase the selectivity, sensitivity, and response time of the sensor.

The research program consists of two phases. Phase I, which is the focus of this report, includes the proof of concept and preliminary demonstration of multiple sensors. Phase II will involve in-depth analysis and testing of sensor arrays for stability, sensitivity, and selectivity; prototype development and testing; and identification of pathways for use of integrated sensor systems in fossil fuel energy conversion systems. Successful completion of this research program will provide an economical method for monitoring emission gas in fossil energy applications. The ability to manufacture and install reliable sensor systems with high stability, high reliability, and long service life at a low cost will significantly improve clean energy generation technology and will help reach the goals of the DOE NETL Instrumentation Sensor and Control Systems Program—real-time monitoring, diagnostics, and control, which are critical for the safe and efficient operation of energy conversion systems.

Current State of Knowledge and Technology

Advanced coal combustion systems such as pressurized fluidized-bed combustors (PFBCs) are capable of producing electricity at significantly higher efficiencies than conventional coal-fired boilers. Although the fluidized bed combustor reduces the generation of thermal NO_x , it produces nitrogen oxides (~ 200 ppm) because of the conversion of fuel-bound nitrogen. Oxides of sulfur (SO_2 and SO_3) are also produced during the combustion processes, and they can be as high as 0.5% of the combustion gases, depending on the sulfur level of the coal.

In a PFBC, coal and air are introduced into a high-pressure reactor along with sulfur-capture agents such as dolomite. The ash and hot gases leaving the reactor are passed through cyclones and ceramic filters to remove the ash. The hot gases are then sent to a gas turbine to produce electricity. In second-generation PFBC systems, coal is pyrolyzed initially to produce a fuel gas, and the char is then sent to the combustor. The fuel gas is burnt in a gas turbine to produce additional electricity.

Emission gases can be monitored on line after most of the ash particulates have been removed by the cyclones and barrier filters. Advanced ceramic barrier filters have been demonstrated to operate at about 500°C , and they could operate at even higher temperatures with continued research and development of the filter technology. No significant changes in the concentration of nitrogen and sulfur oxides are expected during passage through the ceramic barrier filters. Recent developments in high-temperature gas sensing mostly concern sensors that measure potential (potentiometric) and/or current (amperometric and voltammetric) in a solid-state electrochemical cell; thus, the discussion below focuses on current knowledge about such devices.

Potentiometric Gas Sensors. One early development in the field of high-temperature gas sensing technology was the potentiometric oxygen sensor used in the automotive industry; that sensor measures the open-circuit potential generated by the difference in the exhaust-gas oxygen partial pressure relative to a reference gas, which is usually air (1-3). Yttria-stabilized zirconia (YSZ) has been the electrolyte of choice because it is an oxygen ion conductor. Pt has been used as the working electrode material in many designs because it yields nearly reversible oxygen chemistry and catalyzes the oxidation of many gaseous species. The simple potentiometric cell used for oxygen sensing is $\text{O}_2(P_{\text{O}_2'})$, Pt/ZrO₂(Y₂O₃)/Pt, $\text{O}_2(P_{\text{O}_2''})$, where $P_{\text{O}_2'}$ and $P_{\text{O}_2''}$ represent two different partial pressures of oxygen. Oxygen molecules acquire electrons at the electrode-electrolyte boundary and migrate into the electrolyte as oxide anions to occupy the vacant lattice sites, which gives rise to an electrochemical (ΔE) potential given by

$$\Delta E = (RT/nF) \ln (P_{\text{O}_2'}/P_{\text{O}_2''})$$

where R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K), n is number of electrons per mol, and F is the Faraday constant (96480 C mol^{-1}).

When the electrolyte is impermeable to oxygen molecules and when conduction through YSZ is totally ionic, the electrodes behave in a reversible manner, and each electrode is in a thermodynamic equilibrium with the adjacent electrolyte and gas (3). Such sensors, with some modifications, are used for the control of the air/fuel ratio of combustion engines and can be operated at temperatures above 600°C (4).

Potentiometric devices for high-temperature gas sensing have advanced beyond their initial application for O₂ detection. Catalytic metal oxides have been tested as sensor electrodes for gas sensing in different environments under potentiometric conditions using the YSZ electrolyte. Limited selectivity has been achieved by selection of a proper oxide for the application desired. For instance, the differences in *emf* responses for 200 ppm NO and 200 ppm NO₂ in air at 700°C at sensors based on the oxides CrMn₂O₄, ZnCr₂O₄, NiCr₂O₄, and ZnFe₂O₄ are approximately 3, 8, 14, and 43 mV, respectively. In the absence of any metal oxide, the two gases showed similar *emf* values at the Pt electrode, suggesting the necessity of a modifier for preferential detection. The *emf* values associated with metal oxides indicate that ZnFe₂O₄ is best at differentiating NO₂ and NO among many other spinel-type oxides (5). Using impedance measurements, a ZnCr₂O₄-based electrode has been used to detect the total NO_x content at 700°C (6).

Among other potentiometric devices, CuO/ZnO layers deposited on Pt electrodes are able to detect CO at temperatures around 500°C (7). The MnO₂-added In₂O₃ electrode has shown larger mixed potentials for hydrocarbons and smaller values for H₂ and CO, showing preferential detection of hydrocarbons (8). Addition of SrCe_{0.95}Yb_{0.05}O_{3-α} (SCY), an ionic conductor, to the Pt sensing electrode has further improved the sensitivity for hydrocarbons over other reducing gases (9).

Although individual gas detection with metal oxide-based potentiometric sensors has been possible, their use has not improved selectivity significantly, despite the many modifications discussed above. Thus, it is not possible to simultaneously detect a combination of gases using potentiometric approaches. Furthermore, adsorption of the gas under investigation and the kinetics of the electrode reaction are relatively complex because of the presence of the modified electrode/electrolyte/gas multiple phase boundaries. Consequently, gases are not necessarily in thermodynamic equilibrium (i.e., they do not obey the Nernstian relationship) at the electrode surface and at the other interfaces, resulting in mixed potentials. Mixed potentials depend strongly on catalytic and electrocatalytic properties. These complications, together with sintering effects and surface poisoning problems, cause the sensor signal to drift, resulting in erroneous results. Therefore, more accurate, sensitive, and selective analytical devices are needed for the simultaneous detection of gases under harsh conditions such as those in fossil fuel energy conversion systems.

Amperometric Gas Sensors. Another aspect of electrochemical detection entails monitoring electrochemical activity of different analytes at selective operational potentials by measuring the resulting current (i.e., amperometric detection). NO and NO₂, both at 200 ppm and in the presence of O₂, showed mixed potentials at –15 mV and +45 mV, respectively, for a CdCr₂O₄/Pt potentiometric device at 550°C, indicating that the oxidation of NO and the reduction of NO₂, as given below, can be detected at two different potentials (10).

However, NO sensitivity is much less than that of NO₂ even at CdCr₂O₄-attached Pt electrodes, making it impossible to detect the two gases selectively in a gas mixture using potentiometric devices (11, 12). This drawback has been overcome by amperometric detection, where the preferential reduction of NO₂ has been possible at –60 mV, while the preferential oxidation of NO is performed at +100 mV on a single CdCr₂O₄/Pt electrode. It should be noted that common amperometric sensors operate in the diffusion-limited mode and that each molecule

passing the diffusion barrier reaches the interface for immediate reaction, generating a current given by the following relationship.

$$I_{lim} = [nFD_G P_{tot} A / RTL] \ln(1-x_G)$$

where I_{lim} is the diffusion-limited current; n is the number of electrons associated with the electrochemical reaction; F is Faraday's constant; D_G is the diffusion coefficient of the gas, G; A is the surface area of the electrode; R is the gas constant; T is the temperature of detection; L is the diffusion length; and x_G is the mole fraction of G. This relationship clearly indicates the analytical utility of amperometry.

The presence of CdCr₂O₄ has been crucial for enhancing NO selectivity, provided that a suitable anodic potential is selected for its detection. At the NO detecting potential, interference effects from CO₂, CH₄, H₂, and CO were found to be negligible, whereas at the NO₂ detecting potential, interference from CO₂, CH₄, and H₂ was negligible. However, the use of oxide-modified electrodes in amperometric detection is still in its early stages and has not received widespread attention to date.

Interference of Oxygen with Analyte Sensitivity. The effect of oxygen on the detection of other gases was recently investigated, and dual-electrode configurations have been reported for the determination of nitrogen oxides or other emission gases, in the presence of O₂, at high temperatures (12,13). In all the configurations designed to date, it has been necessary to reduce O₂ completely at the first electrode, but prevent the reduction of the second species. The gas reaching the second electrode is therefore free of O₂. As such, the most crucial part of this arrangement is the first electrode. The dual-electrode configuration is more sensitive than the single-electrode amperometric sensor, and the application improves the selectivity. As the interfering gas components are removed at the first electrode by electrochemical filtering, selectivity and sensitivity are considerably improved. However, this design does not provide a means of independent detection of multiple emission gases (e.g., NO_x and SO_x). In addition, interference with detecting one analyte from the other constituents in the sample has been detected when some constituents are present above a certain threshold concentration.

SRI's Innovative Approach

We are designing sensors based on a combination of amperometric and fast, differential pulse voltammetric techniques, and on an array of electrocatalytic electrodes. These techniques offer higher sensitivity than other electrochemical techniques, as shown in Table 1. Figure 1 presents a conceptual design for the sensor array. The sensors are designed with a diffusion channel and, if necessary, with a relatively large first electrode so that oxygen can be electrochemically filtered. Subsequent sensor electrodes will be designed to provide high selectivity and sensitivity for a specific gas in the combustion exhaust.

Figure 2 depicts a typical waveform and the resulting current signal of a fast differential pulse voltammetric experiment. The entire waveform is applied on a sensor electrode in less than a second, and thus multiple sweeps are possible for signal averaging to increase the signal-to-noise ratio. If the interested components in the gas mixture have enough separation in their redox potentials, theoretically they can be resolved in a single electrode. However, in most applications, the complexity of gas mixtures precludes a complete analysis using a single device. Therefore, multiple electrodes, each with unique catalytic properties for a particular component,

are used to resolve and determine the concentration of individual components. For example, for a mixture of gases A, B, and C, the first sensor element may resolve A from B and C, whereas the second sensor element resolves B from A and C, and so on as shown in Figure 2b. Selectivity and sensitivity for specific gases are achieved by proper selection of potential program parameters and electrocatalytic material for the sensor element.

Table 1: Typical levels of detection of electrochemical methods.

Method	Level of detection, M
Potentiometry	10^{-3}
Voltammetry (linear sweep)	10^{-3} – 10^{-4}
Amperometry (steady state)	10^{-5} – 10^{-6}
Amperometry (flow injection mode)	10^{-7} – 10^{-9}
Pulse voltammetry	10^{-8}
Differential pulse voltammetry	10^{-9}

Figure 1. Conceptual design of a sensor array for simultaneous multicomponent gas analysis.

Figure 2. A typical differential pulse voltammetry waveform (a) and sensor response (b).

Selection of materials for sensor elements and fabrication techniques are of utmost importance for achieving the desired selectivity and sensitivity. The sensitivity and selectivity of an electrode material depends not only on the type of material, but also on the electrode's microstructure, configuration, and geometry. The ionic conductivity of the electrolyte is also important for achieving fast device response. Thus, our Phase I research work focused on selection and synthesis of suitable catalytic materials for detecting NO, NO₂, and CO; fabrication of YSZ ceramic membranes with controlled microstructure; preparation of catalytic electrodes; electrochemical cell design; software development for pulse voltammetry; and testing of sensors for their sensitivity and selectivity to emission gases.

EXPERIMENTAL

For initial evaluation, drawing on literature findings and our experience, we selected three materials, LSF, CdMn_2O_4 and NiCr_2O_4 . We prepared CdMn_2O_4 and NiCr_2O_4 by solid-state synthesis methods; we purchased LSF as a ready-made paintable ink from Nextech, Inc.

We fabricated test sensors on zirconia membranes (50-150 μm thick and 1.5 cm in diameter) with these materials as the catalytic electrodes. Sensor fabrication involved preparation of YSZ membranes, deposition of auxiliary electrodes, deposition of catalytic electrodes and electrical contacts, and mounting of the cell in the test housing. The sensors were then tested under a variety of conditions for their sensitivity and selectivity to NO , NO_2 , and CO gases.

Synthesis of CdMn_2O_4

To synthesize CdMn_2O_4 , CdO powder (6.4 g) and MnO_2 powder (8.7 g) were mixed and ball milled for 12 hours. The powder was pressed into a pellet and sintered at 1000°C for 6 hours in a high-temperature furnace. After sintering, the pellet was crushed, ball milled for 12 hours, and pressed into a pellet and sintered again at 1000°C for 6 hours. The powder was analyzed by X-ray diffraction (XRD) to confirm the phase structure.

Synthesis of NiCr_2O_4

To synthesize NiCr_2O_4 , 3.75 g of NiO and 7.6 g of Cr_2O_3 were mixed, ball milled for 12 hours, and pressed into a pellet. The pellet was sintered at 1400°C for 6 hours in a high-temperature furnace. The process was repeated two times. The phase identification of the compound was confirmed by XRD analysis.

Fabrication of YSZ Membranes

The sensors were fabricated on YSZ membranes, which serve as the electrolyte. The base zirconia discs (electrolyte) were prepared by tape casting. That procedure is similar to the one used in the commercial fabrication of multilayer capacitors. Briefly, a slip of YSZ powder in an organic liquid mixture of xylene and ethanol was prepared with a small amount of LCP Menhaden oil as a dispersant, polyvinyl butyral (PVB) as a binder, benzyl butyl phthalate (BBP) as a plasticizer, and polyethylene glycol (PEG) as a release agent. The slip was then cast into a tape using a doctor blade. To obtain porous ceramic layers, the slips were prepared with added pore formers, such as spherical carbon and graphite particles.

Xylene and ethanol solvents vaporized from the cast tape at ambient temperature, yielding a flexible dry tape that can be handled (“green” tape). For some sensor designs, we laminated a dense YSZ layer to a porous layer. The cells were cut from the green tape using a laser and heated in air at a controlled rate to 1400°C . The temperature program involved several steps for solvent evaporation, binder burnout, and sintering. The temperature program of the furnace is critical for obtaining defect-free, flat zirconia discs. Approximately 30% shrinkage occurs in the dimensions of the cells during sintering.

Fabrication of Sensors

The sensors were fabricated on YSZ membranes, which served as the electrolyte. The base zirconia membranes (electrolyte) were prepared by tape casting. The electrolyte was painted on one side with Pt ink and on the other side with the catalytic material (e.g., CdMn_2O_4) and fired at 850°C for 1 hour. Some sensors were made with all Pt electrodes. In the latter part of Phase I, the catalytic electrode sintering temperature was reduced to 750°C , and the sintering time was increased to 3 hours. The electrical contacts to the electrodes were made with fine Pt wires (0.1 mm). The contact wires were held in place by small amount of high-temperature cement (Aremco). Figures 3 and 4 show the single and multielectrode sensor designs, respectively, that we used in most experiments. In both cases, the counter electrode was painted to be about the same size as the catalytic electrode, and it was placed on exactly the opposite side of the catalytic electrode. The reference electrode was offset from the counter electrode by at least 3 times the thickness of the electrolyte. We fabricated numerous variations of this basic design to optimize the selectivity and sensitivity of the sensors. The sensors were mounted to an alumina tube using Aremco cement as shown in Figure 5. The sensor element end of the tube was placed in a high-temperature furnace. We performed the initial testing at between 500° and 800°C .

Figure 3. Photographs of a single sensor, Pt counter and reference electrodes (left) and catalytic working electrode (right). The contact wires are held in place with a dab of cement.

Figure 4. Photographs of a multielectrode design; Pt counter electrodes and the reference electrode in the center (left), and catalytic electrodes (right). Catalytic electrodes: 1- NiCr_2O_4 , 2-LSF, 3-Pt, and 4- CdMn_2O_4 .

Figure 5. Photographs of the sensor housing assembly (left) and the sensor element end (right).

Sensor Test Station

Figure 6 shows a schematic diagram of the experimental setup that we used to test the sensors. The gas flow to the sensor assembly is controlled by four mass flow meters. The gas compositions can be varied by setting the mass flow controllers to the necessary flow. The mass flow controller unit (Aalborg) is interfaced with the computer via a RS 232 serial communication port. The potentiostat (EG&G-PAR283) is interfaced with a computer with a GPIB card (National Instruments). The furnace is controlled by a programmable temperature controller (Eurotherm). The sensors to be tested are mounted on the tip of an alumina tube (16 mm). A second alumina tube (6 mm) is mounted inside the large tube for the inlet gas flow to the sensor. The gases enter the sensor chamber through the inside alumina tube (6 mm) and exit through the outer tube and the T-joint.

Figure 6. Experimental setup for testing sensors.

Computer Program Development

For Phase I, we used a potentiostat (EG&G PAR Model 283) for waveform generation and data acquisition. Because the commercial software package we bought with the potentiostat did not provide sufficient flexibility for the planned experiments, we wrote the data acquisition and experiment control software in our laboratory. The computer codes for square wave voltammetry and data acquisition were developed with Microsoft Visual Basic[®]. The main control and data acquisition computer program development was completed during Phase I.

AC Impedance Analysis.

AC impedance of sensors was determined using a phase sensitive detector (EG&G PAR Model 1025) coupled to a potentiostat (EG&G PAR 283). The experiments and data acquisition were performed using a commercial software package (EG&G EIS Software Model 398). Typically, a 10 mV perturbation in the frequency range of 10 kHz to 0.01Hz was applied to the cell at the open circuit potential, and the resulting current was measured with its phase information. Measurements were performed with and without analyte in a 2% O₂ (balance N₂) gas stream.

RESULTS AND DISCUSSION

Electrode Materials

In potentiometric measurements, CdMnO_4 has shown selectivity to NO at 600°C (10), and NiCr_2O_4 has shown selectivity to NO_2 at 650°C (11). Both compounds are insensitive to CO , CO_2 , HC , and O_2 according to published literature (10-12). Therefore, we selected these compounds as candidate electrode materials for the voltammetric cell. We prepared CdMn_2O_4 and NiCr_2O_4 by solid-state synthesis methods. Figure 7 shows the XRD spectrum of the synthesized CdMn_2O_4 . The XRD pattern matches well with the library spectrum of CdMn_2O_4 , confirming the oxide phase structure in the compound. Figure 8 shows the XRD spectrum of the synthesized NiCr_2O_4 compound, which also matches well with the library spectrum of NiCr_2O_4 , indicating the presence of the oxide phases in the synthesized compound.

Figure 7. XRD spectrum of CdMn_2O_4 (top: synthesized, bottom: library)

Figure 8. XRD spectrum of NiCr_2O_4 (top: synthesized, bottom: library)

YSZ Membrane Fabrication

Initially, we experienced an abnormally high rate of failure during the sintering of ceramic membranes (e.g., cracking and delamination of the membrane when we tried to fabricate multilayer membranes with porous/dense structure). Consequently, we performed thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies to develop an optimum heating profile to control the sintering of ceramic assemblies that would not develop cracks. Binder removal is an important processing operation in the fabrication of ceramic components, and the selection of heating rates, hold temperatures, and hold times for binder burnout is critical for maximizing the yield of final product with minimum furnace time.

During heating, the organic binder (PVB), plasticizer (BBP), and release agent (PEG) either vaporized, decomposed, or oxidized in air. The DSC experiments showed that while BBP vaporized endothermically, PEG and PVB produced an exotherm, presumably due to oxidation or decomposition of these organic chemicals (Figure 9). The heat released during the oxidation of PVB was somewhat high (9.9 kJ/mole) but not excessive, and it occurred over a wide range of temperature. The heat of vaporization of BBP was quite low (0.087 kJ/mole), and the heat released during PPG decomposition was moderate (2.2 kJ/mole); both of these compounds vaporized over a narrow temperature range.

Figure 9. DSC trace of the vaporization of PPG, BBP, and PVB during heating (3°C/min)

Figure 10 shows the mass loss that occurred during heating of these organic chemicals. The TGA results can be used to determine decomposition kinetics. Although, the results vary in the presence of YSZ, they can be used as a guide for the heating profile, and adjustments must be made to account for mass transfer limitations present in thick and large samples.

The TGA and DSC data showed that the organic chemicals in the tape began to vaporize in the temperature range 150° to 270°C; the PEG and the PVB vaporized before the PVB was removed. The mass loss connected with BBP and PPG occurred over a narrow temperature range, whereas that of PVB extended over a broad range of temperatures. Studies have shown that the surfaces of ceramic particles may play a catalytic role in the binder burnout (14). Hence, the data obtained with pure compounds must be modified in the presence of zirconia particles.

Figure 10. TGA profile of plasticizer, release agent, and binder during heating (3°C/min).

The TGA data obtained with our tape cast samples showed a complex mass loss profile because PPG and BBP were being removed in the same temperature range and because the decomposition of PVB occurred in more than one step. However, we used the data as a guide to develop a preliminary heating profile. If the vaporizing gases in the multilayer tape are not allowed to escape slowly, blisters and bubbles could appear during binder burnout. They occur especially when the volume fraction of the binder is sufficiently high to form a continuous film. We adjusted the heating profile so that the mass loss rate would be in the range 0.5 to 1 wt%/min. At that rate, the binder burnout would be completed in about 10 h.

Electrode Fabrication

Initially, we observed that the electrode material delaminated from the YSZ electrolyte surface during the electrode sintering process. This delamination was due to a thermal expansion coefficient mismatch of electrode/electrolyte materials. The problem was aggravated by the need for higher sintering temperatures for the electrode materials with large particle size. To address this problem, we lowered the sintering temperature requirements by reducing the particle size. Nanoparticles sinter at 100° to 200°C lower than the typical sintering temperature of the same material of micron size. We started sintering all electrodes at 750°C for 3 hours, which appeared to produce strongly bonded catalytic electrodes.

Software Development and Testing

We wrote the software for experimental control and data acquisition in Microsoft Visual Basic[®]. The software was written with prototype development in mind so that it could be easily upgradeable for prototype and commercial use. Figure 11 shows the graphical user interface window of the program. All experimental parameters are entered from this window, and the pulse waveform is calculated for downloading to the potentiostat. The waveform is displayed to visually confirm the expected potential range, pulse height, and time base. Once the operator is satisfied, the waveform codes are downloaded to the potentiostat, and the potential scan is performed. The downloaded waveform codes reside in the potentiostat memory so that fast multiple scans can be performed for signal averaging. The resulting current data are stored in the potentiostat during the scan. On completion of potential scans, data are downloaded to the control computer and displayed and saved for further analysis. Figure 12 shows a typical data output window of the program during the experiment.

Figure 11. Graphical user interface window of the control program.

We performed a calibration/system check of the software with an aqueous electrochemical cell. We prepared an electrolyte solution of 1 M KCl with 10^{-3} M Cd^{2+} and Pb^{2+} . The solution was purged with nitrogen for 30 min and square wave voltammetry was performed using the software and experimental setup described above. Figure 13 shows the resulting voltammogram for the 10^{-3} M Cd^{2+} and Pb^{2+} solution. The position of peaks and sensitivity were as expected, and thus this test confirmed the operation of software and computer interfaces.

Figure 12. Data output window of the program.

Figure 13. Square wave voltammogram for 10^{-3} M Cd^{2+} and Pb^{2+} solution obtained with the new software.

Sensor Designs

We fabricated and tested a number of sensor designs with CdMn_2O_4 , NiCr_2O_4 , and LSF catalytic electrodes. The sensor designs that we tested are shown in Figures 14 through 18. In the sensor design shown in Figure 14, all electrodes are in the emission gas stream. The

advantage of this design is that the sensor does not need to be sealed to the housing, and only the electrical connections are fed through the alumina walls of the housing. In addition, the ceramic sensor elements are not attached to the housing and thus the difference in thermal expansion of materials does not result in any stress on the elements, thereby minimizing sensor failure due to thermal shock.

For pulse voltammetric measurements, a reference electrode is needed for proper operation of the electrochemical cell. The reference electrode is placed on the surface of the inactive area of the electrolyte, some distance away from the edge of the active electrodes. The only difference in designs A1 and A2 is the placement of the reference electrode. In A1, the reference electrode is placed on the counter electrode side, and in A2, it is placed on the working electrode side. We found that both designs yielded similar results, provided that the reference electrode was placed at a distance more than 3 times the electrolyte thickness away from the edge of the active electrodes. The reference electrode measures the electrolyte potential along the equipotential surface somewhere between the two active electrodes. After more than three times the electrolyte thickness away from the edge of the active electrodes, the potential measured is essentially the potential at the center of the electrolyte regardless of the placement side of the reference electrode. However, the disadvantage of this design is that the reference electrode potential can vary depending on the gas composition nearby the electrode and thus peak positions can move around, leading to difficulty in species identification.

Figure 14. Two sensor designs (A1 and A2). In both designs, the catalytic electrode and auxiliary electrodes are in the emission gas stream. Only the placement of reference electrode is different.

Figures 15 and 16 show the response of the sensor A1 with a NiCr_2O_4 catalytic electrode to 1000 ppm NO, and 1000 ppm NO_2 in 1% O_2 (10,000 ppm) at 700°C, respectively. Although the peaks were broader than expected and the sensitivity was low, the results clearly demonstrated the applicability of pulse voltammetric techniques for the detection of emission gases. The peaks' broadening and low sensitivity can be ascribed to high diffusion coefficient and low activation energy of electroactive species in the gas phase at 700°C. Because of the high diffusion rate, it was difficult to establish mass transfer control during the potential scan. The sensitivity and the resolution can be increased by better electrode design and better electrode fabrication. However, uncertainty about the reference electrode potential in this design made it difficult to establish peak positions, and thus we decided to continue further work with sensor designs that had a Pt/air reference electrode.

Figure 15. Square wave voltammogram for NO at 700°C on NiCr_2O_4 electrodes.

Figure 16. Square wave voltammogram for NO_2 at 700°C on NiCr_2O_4 electrodes.

The sensor design shown in Figure 17 has both working and counter electrodes in the emission gas side, but the reference electrode is placed outside in ambient air. The electrode chambers were formed by sealing the cell to the alumina tube housing. Because the reference electrode is in equilibrium with the ambient air, its potential is determined by the Nernst potential according to the concentration of oxygen in the atmosphere. The placement of the electrode is also reasonably good in this design as it measures an equipotential surface between the two active surfaces. However, the cell current flows laterally through the membrane, and thus the cell resistance is significantly higher than in the previous design. This increased resistance poses a problem in pulse voltammetric techniques where high double layer charging and faradaic currents need to flow through the cell during pulsing. At lower temperatures ($\sim 600^\circ\text{C}$) where the response of species to the catalytic electrodes is at its best, the electronics became unstable because of the cell's high impedance. Therefore, we determined that this design was not suitable for pulse voltammetric techniques in which a significant amount of current is passed during the measurements. However, in potentiometric measurements, this sensor design would work well because no appreciable current is passed through the cell.

Figure 18 shows sensor design C, the design we studied the most intensively in Phase I. In this design, only the catalytic electrode is in the emission gas stream. Both the reference and counter electrodes are placed outside in ambient air, and thus the reference electrode potential is fixed by the oxygen in air similar to the previous design. Similar to design B, in cell design C the electrolyte is sealed to the cell housing (alumina tube), separating anodic and cathodic chambers.

Figure 17. Sensor design (B) with a Pt/air reference electrode. The catalytic electrode and the counter electrode are in the emission gas stream.

The cell resistance of design C is relatively small because the electrolyte is thin (50–200 μm), and thus we were able to perform voltammetric potential scans in this cell without making it electronically unstable. For low-temperature measurements (500°C), the cell was further stabilized by capacitively coupling the reference and counter electrodes. We used the smallest capacitor that provided the stable cell circuit without compromising the response speed. The typical capacitors were in the 0.001 to 0.1 μF range.

Figure 18. Sensor design (C) with a Pt/air reference electrode. The catalytic electrode is in the emission gas stream. The counter electrode and the reference electrode are in the air-side.

Figure 19 shows the response of sensor design C with a CdMn_2O_4 electrode to NO in 2% O_2 at 700°C. The differential current peak was broad and the background current was high, indicating fast mass transfer at the electrode. It was difficult to obtain accurate calibration curves for low concentrations with this cell design. To improve the cell response in pulse voltammetric measurements, it is critical to establish mass transfer control of the electrochemical reaction. We used porous YSZ membranes to control the gas diffusion to the sensing electrode.

Figure 19. CdMn_2O_4 sensor response to NO in 2% O_2 at 700°C

Sensor design D shown in Figure 20 is a modification of design C, with gas flow to the catalytic electrode restricted with a porous YSZ membrane. Sensor D was fabricated by attaching the porous YSZ to the sensor C with Aremco cement. Restricting the diffusion of gases to the electrode improved the performance of the sensor significantly. Figure 21 shows the response of the NiCr_2O_4 electrode to NO_2 in 2% O_2 at 700°C. The sensor response is clearly improved over that of design C, and thus the detection limit significantly improved as well. The peak appeared at 0.4 V, indicating that the peak corresponds to the second stage electron transfer reaction of NO_2 reduction to N_2 . The first stage electron transfer (NO_2 to NO) is apparently buried with the oxygen reduction around 0.0 V, given that the selectivity is low at high temperatures.

To further optimize the sensor response, we decided to use a highly restricted flow design. Sensor design E shown in Figure 22 is another modification of C, with gas diffusion to the catalytic electrode severely restricted with a porous/dense YSZ membrane. The gases are allowed to reach the catalytic electrode through the small pinhole and the porous layer. Sensor E is fabricated by attaching the porous/dense YSZ to sensor C with Aremco cement, and then piercing a fine hole in the top dense layer with a microdrill. By restricting the diffusion of gases to the electrode, we significantly improved the sensitivity and the selectivity of the sensor.

Figure 23 shows the response of sensor E with a CdMn_2O_4 electrode to NO_2 in 5% O_2 at 500°C. The high background current is due to oxygen in the gas stream. Clearly, the electrode responded well to the changes in the concentration of NO_2 . The noise level in the current signals is somewhat higher than that at high temperature due to high cell resistance at low operating temperature (500°C). The signal-to-noise ratio can be significantly improved by signal

averaging of potential scans. Figure 24 shows the calibration curve obtained from the plots in Figure 23, indicating excellent linearity of the sensor response in the tested NO concentration range.

Figure 20. Sensor design (D) with a Pt/air reference electrode. The catalytic electrode is underneath a porous YSZ membrane in the emission gas chamber. The counter and the reference electrodes are in the air side.

Figure 21. NiCr_2O_4 sensor (D) response to NO in 2% O_2 at 700°C.

Figure 22. Sensor design (E) with a Pt/air reference electrode. The catalytic electrode is underneath a porous-dense YSZ membrane in the emission gas chamber. The counter and the reference electrodes are in the air side.

Figure 23. Response of sensor design E with CdMn_2O_4 to NO_2 in 5% O_2 at 500°C

Figure 24. Calibration plot of sensor E with CdMn₂O₄ for NO₂ in 5% O₂ at 500°C.

Figure 25 shows the response of sensor E with a CdMn₂O₄ electrode to NO₂ in 2% O₂ at 700°C. The peak position is shifted because the concentration of oxygen in the gas stream and the temperature is different from the previous experiment. Nevertheless, the electrode responded well to the changes in the concentration of NO₂. The noise level in the response signal was lower at high temperature because the resistance is low in the electrochemical cell. Figure 26 shows the calibration curve obtained from these plots, which indicates excellent linearity in the tested NO₂ concentration range.

Figure 27 shows the response of sensor E with an LSF electrode to NO and CO in 2% O₂ at 700°C. The peak at 50 mV corresponds to CO and that at -250 mV corresponds to NO. The peaks in the voltammogram are well resolved, and thus species can be readily identified from their peak potentials. This experiment clearly demonstrates that the use of pulse voltammetric techniques for multicomponent detection is feasible on a single electrode. The calibration curve obtained from these plots in Figure 28 indicates excellent linearity in the tested NO and CO concentration ranges.

Figure 25. Response of sensor design E with CdMn_2O_4 to NO_2 in 2% O_2 at 700°C.

Figure 26. Calibration plot of sensor design E with CdMn_2O_4 for NO_2 in 2% O_2 at 700°C.

Figure 27. Response of sensor design E with an LSF electrode to NO and CO in 2% O₂ at 700°C.

Figure 28. Calibration plot of sensor design E with an LSF electrode for NO and CO in 2% O₂ at 700°C.

AC Impedance Analysis

The AC impedance analysis of the sensor provides a wealth of information such as frequency response, electrode kinetics, ionic and electronic conductivities, and capacitance of the electrochemical interface. Figure 29 shows AC impedance Nyquist plots for sensor design E with a CdMn_2O_4 in 2% O_2 at 600°C with and without 100 ppm NO_2 . The Bode plots (impedance, phase vs. frequency) of the same data are presented in Figures 30 and 31.

In the complex plane Nyquist plots, it is evident that the polarization resistance of the electrode decreases with introduction of NO_2 . The decrease stems from the low frequency response of the electrode, indicating that the mass transfer rate of the electrochemical reaction is affected by the presence of NO_2 . We believe that NO_2 is preferentially adsorbed in the porous catalytic electrode and thus is more readily available than oxygen to migrate to an active site for reduction. The phase angles in two frequency scans shown in Figure 31 indicate that reduction in interfacial capacitance in the 10 to 1000 Hz frequency range. This effect is most likely due to a combination of slight differences in charge transfer and diffusion of two active species.

Figure 29. Nyquist plots for sensor design E with CdMn_2O_4 in 2% O_2 at 600°C with and without 100 ppm NO_2 .

Figure 30. Bode plots (impedance-frequency) for sensor design E with CdMn_2O_4 in 2% O_2 at 600°C with and without 100 ppm NO_2 .

Figure 31. Bode plots (phase-frequency) for sensor design E with CdMn_2O_4 in 2% O_2 at 600°C with and without 100 ppm NO_2 .

Proposed Sensor Mechanism

The electrochemical reactions occurring at the three-phase boundary of the solid electrolyte, electrode, and the gas phase can be expressed as follows.

Reduction:

Oxidation:

These reactions give rise to the mixed potential at the sensor electrode in the emission gas phase. By proper selection of catalytic material, a specific reaction can be forced to occur preferentially at the sensor electrode. The number of oxygen ions accumulated at the interface can be strongly influenced by the electrode material, its surface morphology, and its catalytic activity. The porous layer and chemical properties of semiconducting oxide enhance the adsorption of gas molecules and hence promote reduction or oxidation of reactions of NO, NO₂, or CO over that of O₂. Therefore, under some polarization, the cell current changes with the exposure of the electrolyte/oxide interface to the pollutant gases. However, sensitivity of the sensor is quite low in a large excess of oxygen, which always competes at the electrode. Hence, the mixed potential theory reasonably explains the low sensitivity in both potentiometric and amperometric measurements.

In the pulse voltammetric measurements, the electrode interface is perturbed and thus larger transient signals are generated, thereby improving the sensitivity of the electrode. To obtain the maximum benefit of this technique, the gas diffusion to the electrode must also be restricted because the charge transfer rate at the electrode is comparable with the gas phase mass transfer rate at high temperature. We observed significant improvement of the sensor response in sensor designs with a porous YSZ layer on the catalytic electrode that restricted the mass transfer to the electrode surface.

Temperature and Oxygen Concentration Limits

The catalytic advantage of the materials used in the current sensor designs begins to fade above 800°C resulting in loss of selectivity between oxygen and analytes. At these temperatures, the current increased linearly with voltage due to the reduction of O₂ and thus, disappearing the peaks in the differential voltammogram. The operational temperature may be raised above 800°C with different catalytic materials that have selectivity at higher temperatures.

The upper limit of the oxygen concentration was about 10% where the sensor was saturated and stopped responding to changes in the concentration of the analyte. To operate sensors above 10% O₂, the oxygen must be removed by auxiliary electrodes as shown in the conceptual design

in Figure 1. If the prototype sensors are to be used in a high O₂ environment, we will be able to incorporate the auxiliary electrodes into the final design.

Other Combustion Gas Monitoring Technologies

Other popular gas sensing technologies mainly include optical methods, where the chromophore of the pollutant species is measured to detect and quantify the species. Among these techniques, tunable diode laser sensing in combustion environments has attracted attention for detection of trace species such as CO, NO and CO₂. Although these sensors work well at low temperatures, high temperature *in situ* detection has been a major challenge. In the near-IR overtone region between 1.31 and 1.65 μm , high temperature measurements of ppm levels of pollutants are complicated by interferences from poorly understood high temperature transitions of water vapor, a major combustion species. Thus, fast extractive sampling combined with gas cooling and drying has been used to demonstrate the optical technique for pollutant concentration measurements. These requirements, other instrumentation needs, and the cost are major impediments for the widespread use of these optical techniques.

CONCLUSIONS

We have completed preliminary selection of materials for catalytic electrodes to detect NO, NO₂, and CO in emission gas environment using pulse voltammetry in a solid-state electrochemical cell. For the electrolyte, we used thin YSZ membranes that were fabricated by tape casting and sintering, with the electrodes painted on the electrolyte using slurries of the catalytic materials. We optimized the sintering profiles to obtain pinhole-free thin YSZ electrolytes and to attach the catalytic electrode. The typical thickness of the electrolyte is about 50 to 200 μm, and that of the electrodes is about 20 to 30 μm.

We have tested sensor electrodes made of three catalytic materials—CdMn₂O₄, NiCr₂O₄, and LSF—for their selectivity and sensitivity for emission gases. We fabricated a number of sensor designs and tested them for performance at temperatures from 500° to 800°C in a flow-through cell. We varied the geometry, methods of electrode fabrication, and the potential scan parameters to optimize sensor performance.

We have developed software and interfaced a potentiostat with a computer for pulse waveform generation and data acquisition. We wrote the custom software for the sensor so that it could be easily incorporated into on-line exhaust monitoring systems. We confirmed the operation of the software using a known aqueous electrochemical cell containing Cd²⁺ and Pb²⁺.

We have successfully demonstrated that emission gases such as NO, NO₂, and CO can be detected in the presence of excess O₂ in a solid-state electrochemical cell using pulse voltammetric techniques on a catalytic electrode. NO₂ and NO can be detected on either CdMn₂O₄ or NiCr₂O₄ electrodes in a diffusion-restricted cell. CO and NO can be detected on an LSF electrode. Because the peak potentials are different, the species can be easily identified in the voltammogram. The calibration plots that we obtained for each of these gases on the respective electrodes show excellent linearity, indicating that the technique can be used reliably to monitor exhaust gas streams.

The solid-state electrochemical cell and the electrode design have been critical for obtaining sensitivity and selectivity. As the diffusion of gases to the catalytic electrode must be restricted to obtain mass transfer control in electrochemical reactions, a simple cell design with a catalytic electrode does not provide adequate sensitivity or selectivity for the detection of emission gases. Because the mass transfer rate is very high in the gas phase, the charge transfer rate would not be sufficient to establish a mass transfer controlled reaction and thus the cell current would not reach a plateau as in the case in typical aqueous solutions.

We have proposed a mechanism for selectivity of the species based on mixed potential at the electrochemical interface. From pulse electrochemical measurements and AC impedance analysis, we believe that the species are preferentially adsorbed on the catalyst-electrolyte interface, and thus change the response of the electrode to the voltage waveform. Depending on the bias of the electrode, the activities of the species adsorbed are different, and thus multiple species can be detected on a single electrode.

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