

Novel Gas Sensors for High-Temperature Fossil Fuel Applications

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ABSTRACT

SRI is developing ceramic-based microsensors for detection of exhaust gases such as NO, NO₂, and CO in advanced combustion and gasification systems. The sensors detect the electrochemical activity of the exhaust gas species on catalytic electrodes and are designed to operate at high temperatures, elevated pressures, and corrosive environments typical of large power generation exhausts. Under this research project we are developing sensors for multiple gas detection in a single package along with data acquisition and control software and hardware. The sensor package can be easily integrated into online monitoring systems for active emission control. This report details the research activities performed from October 2003 to April 2004.

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EXECUTIVE SUMMARY

To address the critical need for on-line emission monitoring in advanced fossil fuel energy production systems, SRI is developing an array of miniature solid-state electrochemical sensors that are reliable, rugged, and inexpensive. These sensors are based on solid-state ionic conducting materials and catalytic materials and could be used for on-line, real-time detection of O₂, NO_x, SO_x, 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 will consist 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. Selective detection of gases is further accomplished 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 also critical to obtain the best sensor response. Thus, our research work included selection and synthesis of suitable catalytic materials for detection of 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 in a simulated exhaust environment.

Based on literature and our previous experiments, we selected CdMnO₄ and NiCrO₄ as potential candidates for NO and NO₂ detection. These materials were prepared by solid-state synthetic routes, and their structures were confirmed by x-ray diffraction. The materials were ball-milled for 12-24 hours to obtain fine particle sizes. For electrode fabrication we used nanoparticles, which we separated from the powder by preparing slurries in terpinol and letting the larger particles settle down.

YSZ membranes for the electrolyte were prepared by tape casting, a procedure similar to one used in commercial fabrication of multilayer capacitors. A slip of YSZ powder in an organic liquid mixture was prepared with added dispersants, binders, plasticizer, and release agents. The slip was then cast into a tape on a glass plate using a doctor blade. Once the tape was dry, required cell geometries were cut with a laser and sintered at 1400°C to obtain ceramic membranes. The catalytic electrodes were painted on the membranes using terpinol as the vehicle. The counter and reference electrodes were prepared using commercial platinum ink. The sensor was heated to 750°C to sinter the electrode material.

To run the pulse voltammetry waveforms on sensors, we developed software using Microsoft Visual Basic. We interfaced PAR 283 to a computer and tested the functionality of the software using known aqueous solutions of Cd²⁺ and Pb²⁺. Both the applied waveform and resulting currents were carefully examined to confirm the operation of the software package.

We have built a sensor test station with multiple mass flow controllers and a programmable furnace. We have begun testing sensors using this setup at temperatures from 500° to 900°C and will present the results of these tests in the next semi-annual report.

We are conducting this microsensors research program in two phases. Phase I includes the proof of concept and preliminary demonstration of a package with multiple sensors. Phase II involves in-depth analysis and testing of sensor arrays for stability, sensitivity, and selectivity; prototype development and testing; and identifying pathways for use of integrated sensor systems in fossil fuel energy conversion systems. The research activities in this report were performed as part of the Phase I effort.

INTRODUCTION

The use of sensors can provide the electrical power industry with increased operational efficiency, reduced emissions, and lower operating costs. Advancements in robust sensing and control algorithms can accelerate the time to full-scale commercial implementation of novel power generation technologies such as advanced combustion, gasification, and turbines. While the monitoring of oxygen content is the primary method of optimization of the combustion process, emission control 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 proposed to develop an array of miniature solid-state electrochemical sensors that are reliable, rugged, and inexpensive. These sensors are based on solid-state ionic conducting materials and catalytic materials and 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 proposed sensors in this research project measure potential (potentiometric) and/or current (amperometric and voltammetric) in a solid-state electrochemical cell. The sensor array will consist 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. It is also of great significance that the sensor materials are stable in the operational environment for a period up to one 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 to obtain the best sensor response. Thus, the research work reported here included fabrication of ceramic electrochemical cell components with controlled microstructure, which would increase the selectivity, sensitivity, and response time of the sensor.

We are conducting this research program in two phases. Phase I, which is the focus of this report, includes the proof of concept and preliminary demonstration of multiple sensors. Phase II involves in-depth analysis and testing of sensor arrays for stability, sensitivity, and selectivity; prototype development and testing; and identifying pathways for use of integrated sensor systems in fossil fuel energy conversion systems. Successful completion of this proposed research program will provide an economical method to monitor 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 to reach the goals of the DOE NETL Instrumentation Sensor and Control Systems Program.

EXPERIMENTAL

For initial evaluation, we selected three materials, CdMn_2O_4 , NiCr_2O_4 , and LaCuO_4 based on literature and our previous experience. In this reporting period, we made CdMn_2O_4 and NiCr_2O_4 by solid-state synthesis methods as explained below.

Synthesis of CdMn_2O_4

To synthesize cadmium manganate, CdO powder (6.4 g) and MnO_2 powder (8.7 g) were mixed and ball milled for 12 hours. The powder was pressed to 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 to a pellet and sintered again at 1000°C for 6 hours. The powder was analyzed by x-ray diffraction (XRD) to confirm the compound.

Synthesis of NiCrO_4

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

Fabrication of Yttria-Stabilized Zirconia Membranes

The sensors were fabricated on YSZ membranes, which serve as the electrolyte. The base zirconia discs (electrolyte) were prepared by tape casting. The procedure is similar to the one used in the commercial fabrication of multi-layer capacitors. In brief, 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 the 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 to obtain defect-free, flat zirconia discs. Approximately 30% shrinkage occurs in the dimensions of the cells during sintering.

Fabrication of Sensors

We fabricated the sensor on a zirconia disc (50 μm thick and 1 cm diameter) as shown in Figure 1. The membrane was painted one side with platinum ink (counter and reference electrodes) and on the other side with the catalytic working electrode (e.g., cadmium manganate) and fired at 850°C for 1 hour. The electrical contacts to the electrodes were made with fine Pt wires (0.1 mm). The sensor element was mounted to an alumina tube using a high-temperature cement (Aremco) as shown in Figure 2. The sensor element end of the tube was placed in a high-temperature furnace. The initial tests were performed at a temperature range of 500° to 700°C .

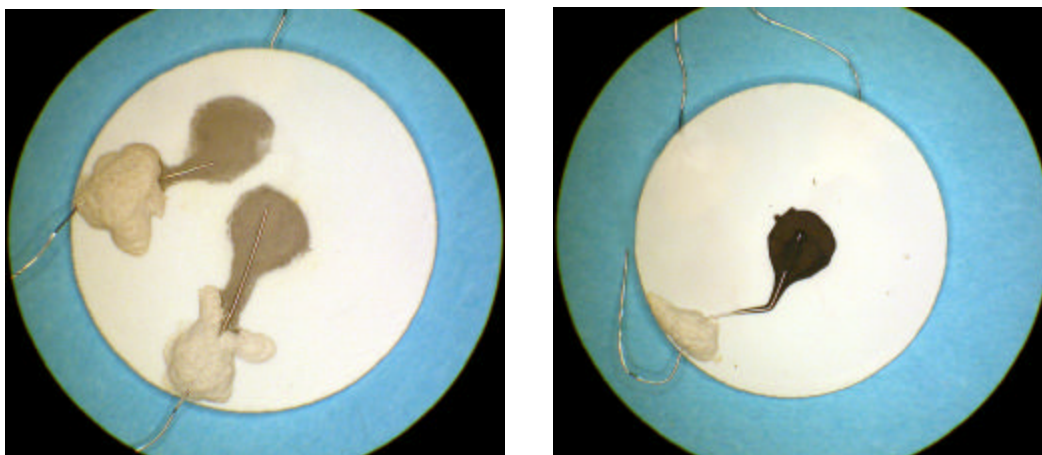


Figure 1. Photographs of a single sensor, Pt counter and reference electrodes (left) and catalytic working electrode (right).

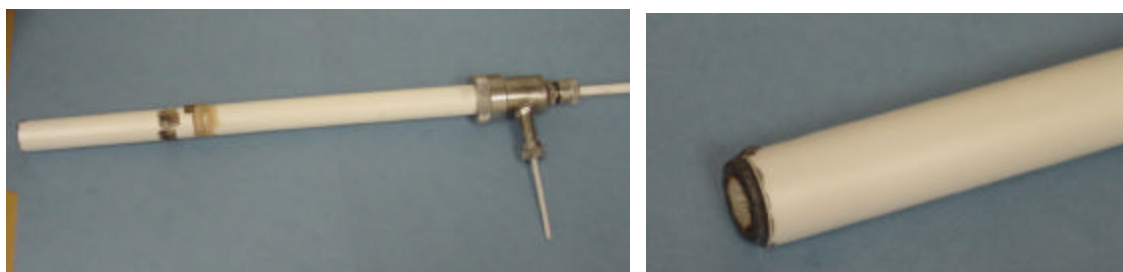


Figure 2. Photographs of the sensor assembly (left) and the sensor element (right).

Sensor Test Station

Figure 3 shows the experimental setup that we built to test the sensors. The gas flow to the sensor assembly is controlled by four mass flow meters. The gas compositions can be accurately varied by setting the mass flow controllers to deliver the necessary flow. The mass flow controller unit (Aalborg) is interfaced to the computer via RS 232 serial communication port. The potentiostat is interfaced to a computer with a National Instruments GPIB card. 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.

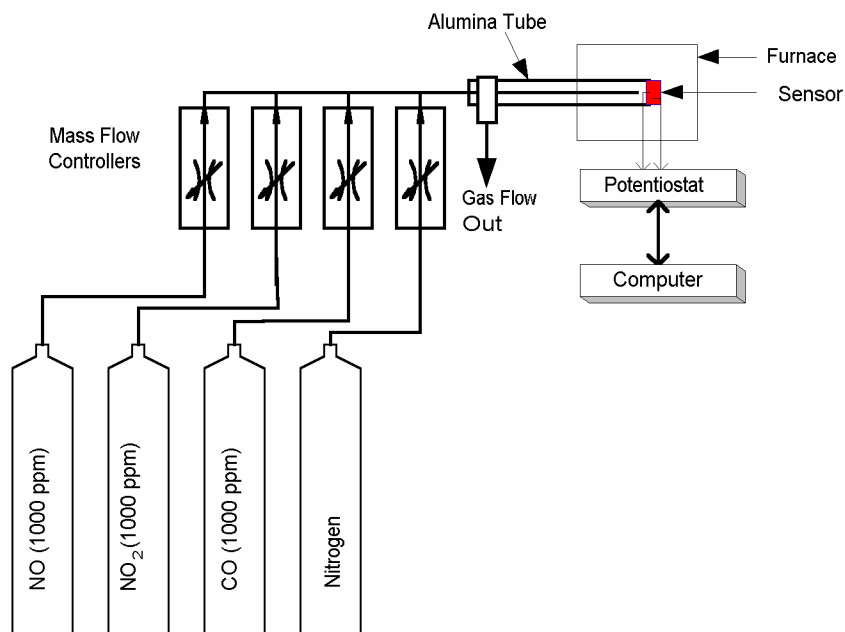


Figure 3. Experimental setup for testing sensors.

Computer Program Development

For the first phase of the project, we are using a commercial potentiostat (PAR Model 283) for waveform generation and data acquisition. Since the commercial software package we bought with the instrument did not provide the flexibility for the type of experiments planned, we wrote the data acquisition and experimental software in our laboratory. Initial codes for square wave voltammetry were developed with Microsoft Visual Basic. The main control and data acquisition computer program development was completed during this reporting period.

RESULTS AND DISCUSSION

In potentiometric measurements, CdMnO_4 has shown selectivity to NO at 600°C (1), and NiCrO_4 has shown to be selective for NO_2 at 650°C (2). Both of these compounds are insensitive to CO , CO_2 , HC , and O_2 according to published literature (1-3). In this reporting period, we prepared CdMn_2O_4 and NiCr_2O_4 by solid-state synthesis methods.

Electrode Materials

Figure 4 shows the XRD spectrum of the synthesized CdMn_2O_4 . It matches well with the library spectrum of CdMn_2O_4 , confirming the formation of the compound by the selected synthetic route. Figure 5 shows the XRD spectrum of the synthesized NiCrO_4 compound, which matches well with the library spectrum of NiCr_2O_4 , indicating the presence of the required oxide phases in the synthesized compound.

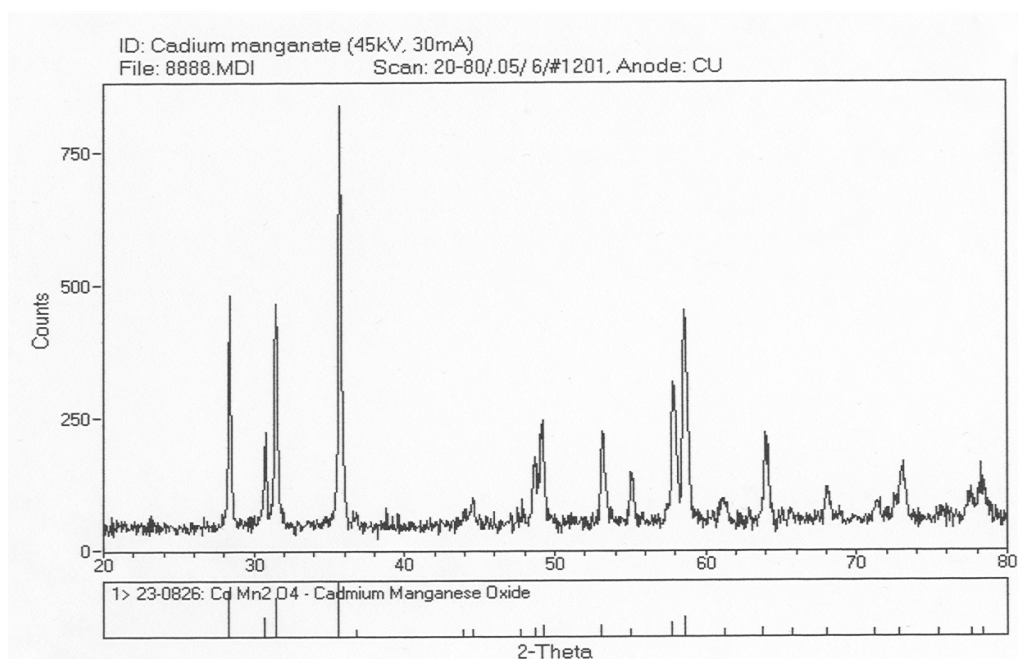


Figure 4. XRD spectrum of cadmium manganate (top: synthesized, bottom: library)

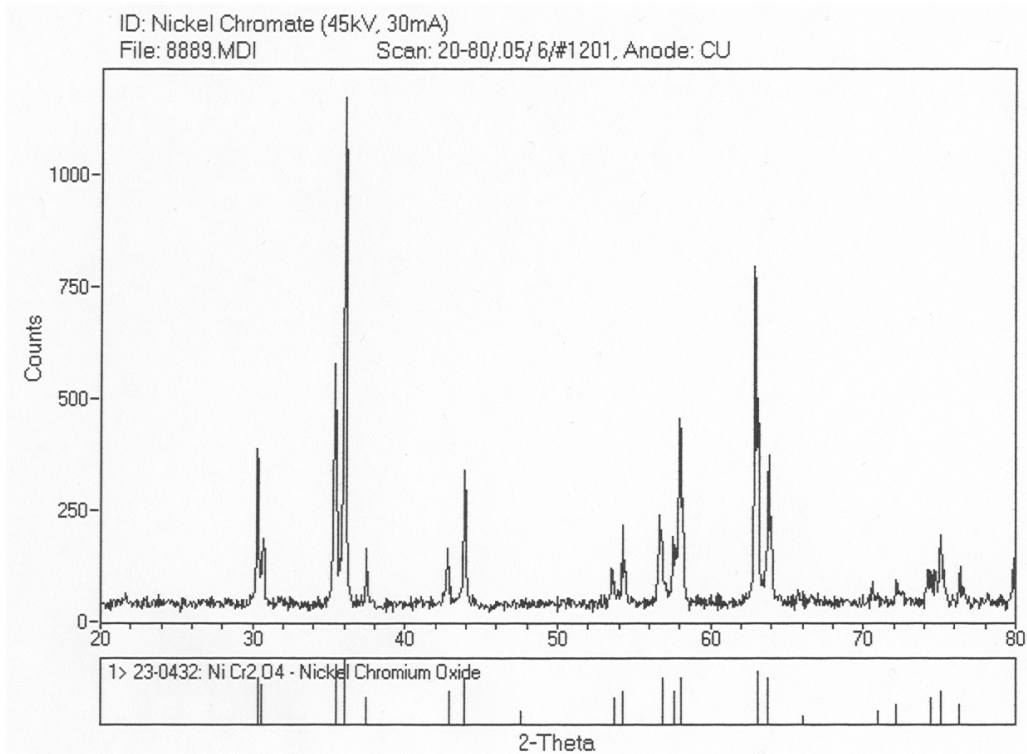


Figure 5. XRD spectrum of nickel chromate (top: synthesized, bottom: library)

YSZ Membrane Fabrication

In this reporting period, we experienced an abnormally high rate of failure during the sintering of ceramic membranes, such as cracking and delamination of the membrane. Thus, we performed thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies to develop an optimum heating profile to control the sintering of the ceramic assembly that would not develop cracks. It is common knowledge that the binder removal is an important processing operation in the fabrication of ceramic components. The selection of heating rates, hold temperatures, and hold times for binder burnout is critical to maximize the yield of final product with minimum furnace time.

During heating, the organic binder (PVB), plasticizer (BBP), and release agent (PEG) either vaporize, decompose, or oxidize 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 6). 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 very low (0.087 kJ/mole), and the heat released during decomposition of PPG was moderate (2.2 kJ/mole). Both these compounds vaporized over a narrow temperature range.

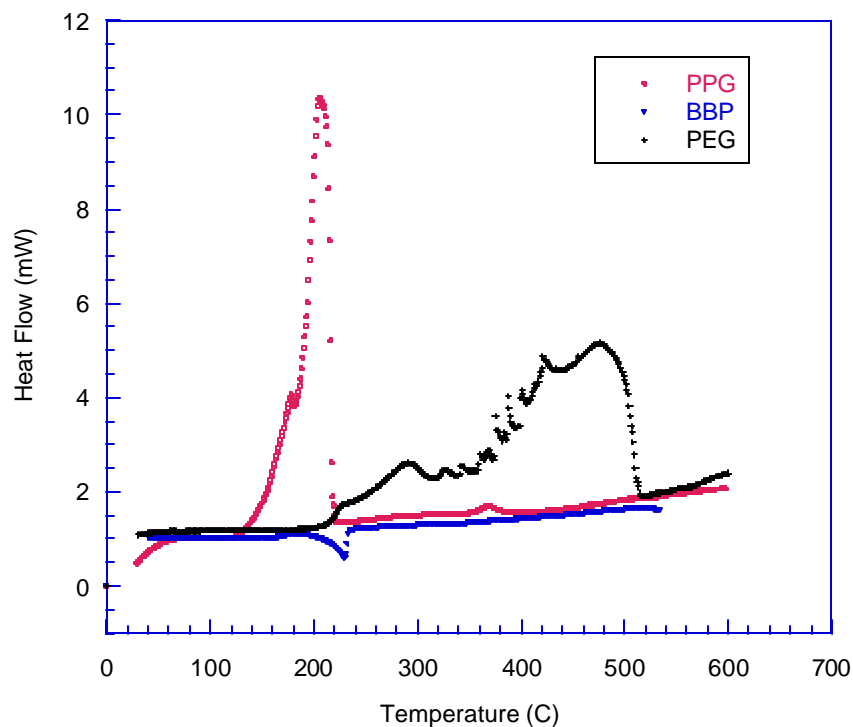


Figure 6. DSC trace of the vaporization of PPG, BBP, and PVB during heating (3°C/min)

Figure 7 shows the mass loss that occurred during heating of these organic chemicals. The TGA results can be used to determine the decomposition kinetics. However, they can be used as a guide, and adjustments must be made to account for mass transfer limitations that may be present in thick and large samples.

The TGA and DSC data showed that the organic chemicals in the tape begin to vaporize in the temperature range 150° to 270°C; the PEG and the PVB vaporize before the PVB is removed. The mass loss connected with BBP and PPG occur over a narrow temperature range, while that of PVB is 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 (4). Hence, the data obtained with pure compounds must be modified in the presence of zirconia particles.

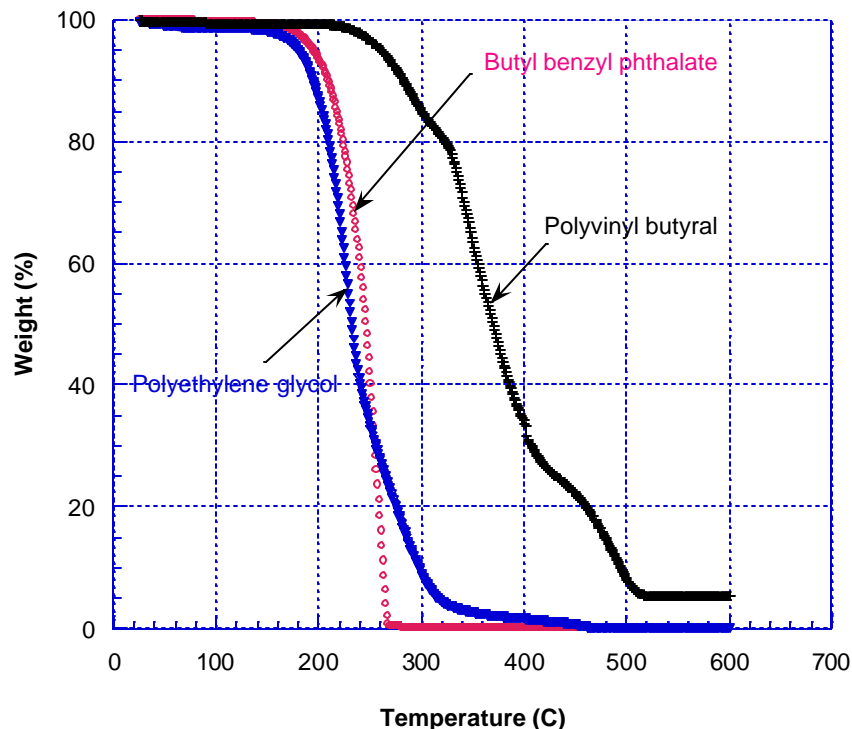


Figure 7. TGA profile of plasticizer, release agent, and binder during heating (3°C/mi).

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 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. The heating profile was adjusted so that the mass loss rate will be in the range 0.5 to 1 wt% per minute. At this rate, the binder burnout phase will be about 10 h.

Electrode Fabrication

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

Software Development and Testing

The software for experiment control and data acquisition was written in Microsoft VisualBasic. Figure 8 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 data acquisition process. Upon completion of potential scans, data are downloaded to the control computer and displayed and saved for further analysis. Figure 9 shows a typical data output window of the program.

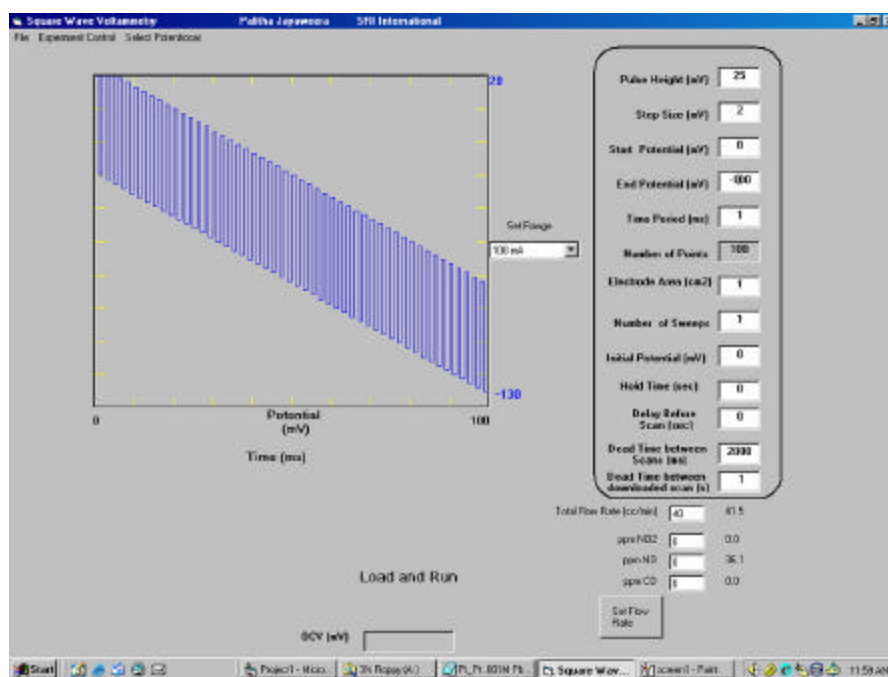


Figure 8. Graphical user interface window of the control program.

Since our gas phase electrochemical cell was not well defined at this stage, we performed a calibration/system check 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 10 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.

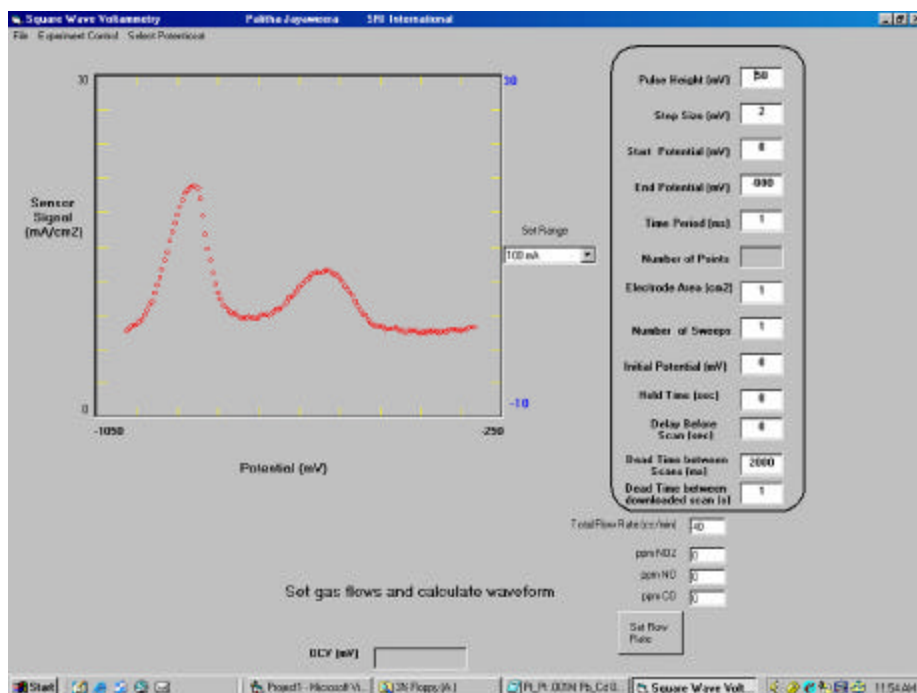


Figure 9. Data output window of the program.

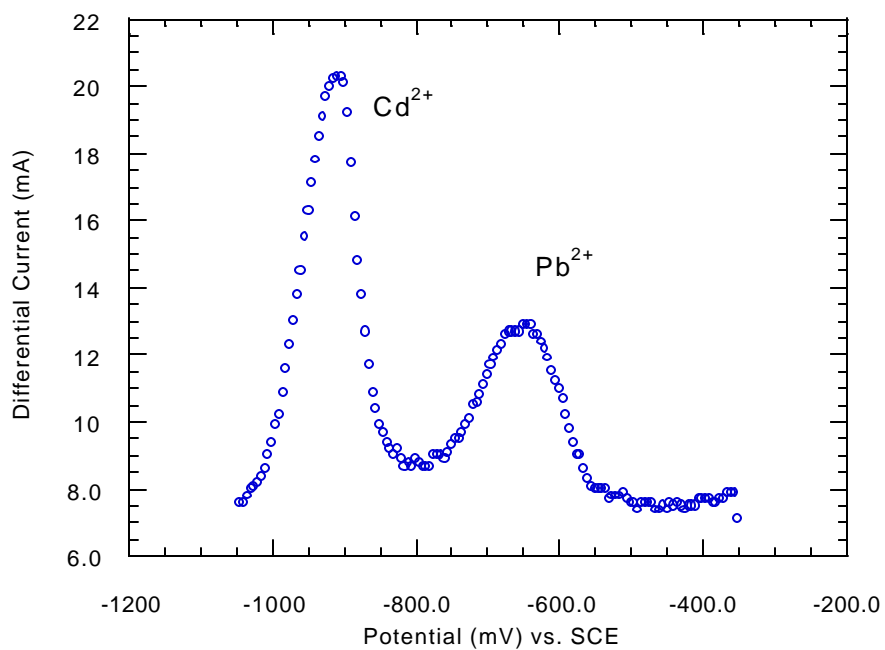


Figure 10. Square wave voltammogram for 10^{-3} M Cd^{2+} and Pb^{2+} solution obtained with the new software.

CONCLUSIONS

We have completed preliminary selection of materials for catalytic electrodes NO and NO₂. The catalytic electrodes have been fabricated with CdMn₂O₄ and NiCr₂O₄. A test station for evaluation of sensor performance has been built. We have optimized sintering profiles of YSZ membrane to yield pinhole-free thin electrolytes. The typical electrolyte thickness is about 100 to 200 μm. We have found the sintering conditions to attach the catalytic electrode material to the electrolyte.

We have completed software development and instrument interfacing for sensor testing. We confirmed the operation of the software using a well-known aqueous electrochemical cell containing Cd²⁺ and Pb²⁺. We have just begun testing of various sensor designs. We plan to vary the geometry, methods of fabrication of electrodes, and the potential scan parameters to optimize the selectivity and sensitivity of sensors. We will report our findings in the next semi-annual report.

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