THICK-FILM GAS MICROSENSORS USING CERMET MATERIALS, CYCLIC VOLTAMMETRY AND NEURAL NETWORKS.

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ABSTRACT

The sensing characteristics of a thick-film cermet cell, expressed as $MeO_x/Pt/solid\ electrolyte/Pt$ were investigated by applying cyclic voltammetry across the Pt electrodes and measuring changes in ionic current through the solid electrolyte. The sensors were fabricated using thick-film screen printing techniques with high-temperature ceramic-metallic (cermet) materials. In the presence of the cyclic applied voltage, gases react at the three phase, gas/solid electrolyte/electrode boundary (tpb), and cause a change in measured ionic current flow through the sensor. These changes resulted in distinct current-voltage envelopes (voltammograms) for different gases. Neural signal processing was used to characterize and analyze the sampled voltammetry signatures.

INTRODUCTION

In recent years, the need for improved, affordable gas microsenors in the fields of safety, environmental/emissions monitoring, process control, and other applications has grown tremendously. Argonne National Laboratory (ANL) has been developing an economical new type of gas microsensor to evaluate and demonstrate a unique gas sensing technology. The device has demonstrated the potential to address the needs for many industrial, safety, and environmental applications.

The technology involved applying cyclic voltammetry to sandwiched thick-film layers of cermet materials and identifying and quantifying the generated electrical signatures using neural signal processing. The cyclic voltammetry techniques produced complete, broad-spectrum responses. Early attempts at applying voltammetry to electrochemical cells found no elegant way to quantify the responses, but computational neural networks (CNN's) treat the complex sampled voltammetry signatures as simple 1-D patterns and allow training, recognition, quantification, and classification of the signatures.

THEORY

The cell: $Me-MeO_x(p(O_2))/Pt/solid\ electrolyte/Pt$ was used in this study, with $Me-MeO_x$, a metal/metal-oxide mixture in thermodynamic equilibrium with oxygen gas (O_2), providing a reference oxygen partial pressure, $p(O_2)$. When a cyclic voltage was superimposed across the galvanic cell, ions at the tpb were forced through the solid electrolyte. When the applied potential was negative, oxygen was pumped into the $Me-MeO_x$ reference. When the applied potential was positive, oxygen was driven out of the $Me-MeO_x$ reference [1]. The number of oxygen ions available at the tpb was greatly reduced for solid-electrolyte systems as compared to aqueous electrolytes. In this cell, only a fraction of the electrode surface was part of the tpb and was electrocatalytically active. The largest portion of the

electrode was not in contact with the solid electrolyte and was only catalytically active [2].

The response of the solid-electrolyte sensor studied was primarily dependent on the amount of oxygen anions (O^-) available at the tpb. In this cell, the porous platinum electrodes catalyzed the charge transfer reactions:

The oxygen anions were supplied to the solid electrolyte and measured as electronic current through the sensor. The catalytic reactions of gases exposed to the surface of the electrodes either add or remove the oxygen available for transport at the tpb. Different types of reactions were possible. The gas exposed to the electrode could react catalytically, creating oxygen at the tpb as in the reaction:

In addition, adsorbed gases could react with the electrode, freeing bound oxygen as in the reaction:

Other unreactive gases could hinder the oxygen at the tpb by blanketing the electrode.

The sensors consist of four overlapping thick-film layers (Figure 1) deposited on an aluminum oxide substrate with a platinum heating element on the back. The four layers are two porous catalytic electrodes, an oxygen-ion-conducting solid-electrolyte layer, and a metal oxide oxygen pressure reference layer. The two catalytic electrodes sandwich the solid electrolyte layer. The metal oxide reference layer is deposited beneath the lower electrode. These four layers serve three major functions.

Figure 1. Sensor Micrograph Profile of $Al_2O_3/Ni-NiO/Pt/YSZ/Pt$ Cell at 1500X

The catalytic electrodes promoted electrochemical reactions on their surfaces. In the driven mode, the catalytic electrodes conducted electrons created by the charge-transfer reactions at the tpb. The current measured between the lower and upper electrodes during a voltage scan provided quantitative and

qualitative signature information about specific gases. The catalytic electrodes contain glass frit to keep the layer porous to promote gas migration to the solid electrolyte, forming the tpb.

The solid-electrolyte layer was an oxygen-ion conductor. The current measured through the solid electrolyte was a direct measure of the amount of oxygen anions at the tpb.

The metal oxide reference layer provides a constant partial pressure of oxygen to the tpb. This metal oxide combination provides an oxygen sink/source reservoir described by the equilibrium equation:

where $p(O_2)$ was the oxygen partial pressure. Equilibrium was achieved when $p(O_2)$ has penetrated the metal and oxide. Homogeneity of $p(O_2)$ is maintained at the electrode/electrolyte interface by oxygen anion migration in the electrolyte and electron activity in the metal phase of the Me/MeO system. The electron activity reaction is described by:

In the driven mode of operating the gas sensor (applying a cyclic voltage), the preferred metal oxide reference serves as a constant oxygen source which stabilized the sensor response even in oxygen deficient environments.

CNNs function by interconnecting a number of separate computational "neurons." These artificial neurons are the building blocks for the network. Each neuron is modeled in two stages (Figure 2), the summation stage and the activation stage. The summation stage, quite simply, multiplies each input signal by its associated weight and sums them all together. The activation stage uses a squashing function (input $\pm \infty$, output approximately 0 or 1 only) and a threshold value to determine what the output from the neuron will be. This type of processing effectively makes a small decision on the basis of weighted variables. A collection of these small weighted decisions represents a powerful tool for pattern recognition and decision control.

Figure 2. Model computational neuron.

The CNNs can be used simply to recognize and classify the signatures that are sampled, but they also have the capability to approximate the functional response of the sensor signature changes. This can produce an interpolated value attached to the shape change of a signature. Qualitatively, different gases dissociate at characteristic voltages. This manifests itself as a "peak" or "valley" showing up along the voltage axis of a CV signature. An increase in concentration of a given gas increases the probability that that gas will react, and broadening and increasing the peak or valley at the characteristic voltage. The reactions are complex with obvious

covariant parameters and many hidden univariant parameters. This complexity normally limits voltammetry to a qualitative measurement technique; it also illustrates the value of being able to identify, and quantify, the univariant parameters with CNNs. The interpolation quality of a network is a function of the completeness of the training and validation sets used. If the signatures for a given gas are smooth and continuous, a relatively simple network and limited set of training samples can produce interpolation errors of only a few percent.

EXPERIMENTAL DETAILS

The sensors were screened onto 0.5 in. x 0.5 in. x .025 in. alumina substrates. The substrates were laser scored into ten 0.1 in. x 0.25 in. individual substrates. After all layers were deposited and fired, the substrates were separated into ten individual devices. This process insured reproducibility from sensor to sensor within each group of ten on a single substrate. NiO was used as the $Me-MeO_x$ reference material. Two oxygen-ion-conducting solid electrolytes, yttria stabilized zirconia (YSZ) (8 mol% Y_2O_3) and tungsten stabilized bismuth oxide (WBO) ($WO_3 - Bi_2O_3$) (0.25 mol% WO_3), were used. The NiO and solid electrolyte powders were pulverized to pass through a 325 mesh screen and mixed with Heraeus Cermalloy Electronic organic vehicle RV-025 (ethyl cellulose and terpineol) in a 1:3 ratio to form a thick paste. Commercial platinum oxygen sensor paste (Heraeus Cermalloy OS1) was used for the upper and lower catalytic electrodes and the heating element. The prepared platinum paste was thinned with 20 wt% organic vehicle. Each layer was screen-printed separately onto the aluminum oxide substrates by using a Presco™ industrial screen printer with photolithographically stenciled 325 mesh stainless steel screens. The films were fired separately after each screening. The sensors made with the WBO solid electrolyte required a YSZ "buffer" layer between the electrolyte and the upper Pt electrode to keep the Pt from migrating into the WBO layer and shorting the electrodes. The YSZ sensors were fired at 1350°C in air in a controlled cycle to prevent film blistering between screenings. The $WO_3-Bi_2O_3$ sensors were fired at 850°C in the same way. The film thickness ranged from 3-4 μm for the NiO, 20 μm for the solid electrolyte, and 10 μm for the Pt electrodes and Pt heating element.

The chamber used for gas testing was constructed from a 500-ml bell flask with one sealed spherical end. The stopper that sealed the chamber was channeled, and two, 8-mm stainless steel tubes were inserted to act as feed-throughs for the test and measurement leads. A gap was left in both feed-throughs to allow the incoming gas to escape and to maintain a small positive pressure of the test gas in the chamber so that no ambient air intruded during a test. The sensor was held by a spring-loaded test clip with gold-plated fingers. A micro-mass K-type thermocouple was used to measure the surface temperature of the sensor.

Once the sensor reached the set-point operating temperature in the range of 225°-300°C, the input voltage was applied and the sensor sampled. Three, -1 to +1 to -1 V DC, 30-second long, triangular waveforms were applied to the sensor in succession, and the current passing through the sensor was sampled at approximately 100 points/waveform. These triple (3 X 100 points) voltage-current curves were used to produce the voltammograms that were used in later analyses.

Gas standards of O₂, CO, CO₂, and a variety of hydrocarbons in a balance of N₂ were introduced to the test chamber via a gas-line manifold. A precision flowmeter was used to control the gas entering the chamber in two flushing stages. For gas mixture tests, a two-line gas proportioner was used. In the first stage, the test chamber was flushed with approximately 50 chamber volumes at approximately 5 L/min. for 5 min. In the second stage, the flow rate was lowered to 50 ml/min. to create a stable environment and allow the sensor to attain a predetermined operating temperature. This flow rate was maintained during sensor sampling. Temperature dependence of the sensor was studied by stabilizing the sensor in air and increasing the temperature by 25° increments in the range of 175° - 325°C before sampling.

The neural signal processing of the voltammograms involved introducing the 1-D sampled array to a neural algorithm and producing a resultant value that was an measurement of a particular gas in a mixture. The neural network was developed using NASA NETS3.0 software. The network was "trained" by presenting it with successive sets of known input signatures and algorithmically adjusting the network interconnections until the produced error was minimized. Typical training sets consisted of (3) samples each of (6) gas concentrations. Two of the three samples were presented to the network as training vectors, with the third sample being used for validation. This process typically produced errors of < 5% full scale value across the concentration range.

RESULTS

The dependence of the YSZ sensor on temperature is shown in Figure 3. As the temperature increases, the amplitude and sharpness of the peak current increase with the conductivity of the electrolyte.

Figure 3. Sensor (YSZ electrolyte) response to temperature.

A plot of peak current vs. temperature shows a similar relationship to the typical conductivity dependence for an oxygen-ion-conducting solid-electrolyte (Figure 4). The conducting range for the driven solid-electrolyte cell is in a much lower temperature range (200-300°C) as compared to a typical non-driven solid electrolyte cell (500-1100°C). The lower temperature range is possible because of the presence of the applied voltage, which forces the ions through the

electrolyte, as opposed to a strictly diffusion-controlled process in the non-driven cell.

Figure 5 shows a YSZ sensor response at 250°C to various concentrations of O₂ in a balance of N₂. The anodic and cathodic peaks increase with oxygen concentration. Since response is directly related to the amount of oxygen available at the tpb, increased peak magnitude was expected as higher oxygen concentrations directly supply more oxygen for transport through the solid electrolyte. The small O₂ peaks in the 100% N₂ voltammogram are due to the partial pressure of oxygen supplied to the tpb by the metal oxide reference layer.

Figure 4. Log of peak current vs. inverse temperature.

Figure 5. YSZ sensor response to oxygen.

Figure 6 shows a WBO sensor response at 250°C to various O₂ concentrations. The WBO sensor shows a greater sensitivity to change in O₂ concentrations than did the YSZ sensor. At higher O₂ concentrations, the voltammogram changes shape as the current increases significantly. The sensitivity to change in concentration does not increase with temperature for either sensor type. Although the magnitude of the peak current increased with temperature, the relative change in peak current with gas concentration did not increase with temperature:

$$\frac{\partial \left(\frac{dI}{d[c]} \right)}{\partial T} = 0 \quad (3)$$

The sensors appear to operate best in a window of about 225°-300°C. Above the "ideal" temperature range, the sensitivity to concentration change decreased.

Figure 7 shows the WBO sensor response to various concentrations of CO₂ in a balance of N₂. As expected, the voltammogram for CO₂ in N₂ was significantly different than that of O₂ in N₂. A unique CO₂ peak was formed that increased with concentration.

Figure 6. WBO sensor response to oxygen.

Figure 7. WBO sensor response to carbon dioxide.

Figure 8. YSZ sensor response to hydrocarbons.

This response implied that catalytic CO₂ reactions were occurring with a subsequent increase in O²⁻ ionic current through the bismuth oxide solid electrolyte as described by equation (6).

The YSZ sensor response to a variety of hydrocarbons is represented by the voltammograms in Figure 8. Between testing the gases, a standard of 20% O₂ in N₂ was run to bring the sensor back to an equilibrated state so that mixed responses

were avoided. The voltammogram for each gas at 100 ppm was distinct. A change in size and shape of the voltammograms was exhibited for each gas tested.

The typical analog CV sweep was 30 seconds long and subsequent voltammograms decreased in peak measured current when this was shortened. The reactions observable from the analog CV were clear and illustrated the reproducibility of the applied CV technique. The first discrete CV waveforms, used for the neural signal processing, modeled the analog and used a large number of steps and similar 30 s sweeps. Later changes were made to reduce the number of steps and shorten the sweep duration to only a few seconds.

The CNN algorithms allowed training of simple 24 input-5 hidden-1 output node networks in about (10) minutes. The networks were typically trained to $\pm 5\%$ FSV error and produced acceptable error from the validation vectors. The network algorithms for all the gases in this work were identical. They differed only by a table of interconnection weight values. This allowed very generic and optimized algorithms to be written for "gas analysis", with only table values changed to alter what gases were being analyzed "for". These algorithms were coded and implemented on microcomputers and single-chip microcontrollers.

CONCLUSIONS

Cyclic voltammetry applied to a thick-film electrochemical cell using cermet materials were used as a new class of active gas microsensors. The microsensors detected a variety of gases, including O₂, CO₂, CO, and hydrocarbons, and showed potential to distinguish individual gases in a mixture. The sensors exhibited a temperature dependence similar to that of typical oxygen-ion-conducting solid-electrolytes but at significantly lower temperatures due to the applied voltage. Advantages of thick-film cermet sensors include low cost, small size, versatility, and high-integrity materials and construction. The rugged materials allows them to withstand considerable mechanical, chemical, and thermal stress. Thick-film technology provides simple, low-cost fabrication without the need for exotic equipment or production methods. The ability of the CNNs to identify gas signatures without dissecting them gave the system the ability to be trained to recognize thresholds of simple mixtures, and the potential existed for recognition of very complex mixtures. This capability made the sensors attractive for applications that require multi-gas/mixture monitoring. Areas of future development include reducing the sensors' power consumption, improving their sensitivity, further improving the signal processing, and miniaturizing the support electronics.

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