JOURNAL OF MATERIALS SCIENCE 38 (2003) 4307 – 4317

Development of a selective gas sensor utilizing a perm-selective zeolite membrane

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Reported here is a novel sensor that utilizes a zeolite film to selectively limit gas exposure of the sensing surface. A unique amperometric sensor design based on a non-porous mixed conducting sensing electrode enables the formation of a continuous zeolite film covering the entire sensor surface. The sensor was tested in a variety of oxygen containing gases. The sensor without a zeolite film responded strongly to both oxygen and carbon dioxide at a bias of 1.8 V. In contrast, the sensor coated with a zeolite film showed a discernable, but diminished response to oxygen, and a more marked drop in response to CO_2 indicating that the diffusion of oxygen through the zeolite film is preferential to that of CO_2. The response of the zeolite coated sensor to a mixture of oxygen and carbon dioxide gases is attributed primarily to the oxygen content. Expanding this concept using a variety of different zeolite structures covering an array of sensors, complete analyses of complex gaseous mixtures could be performed in a very small device. *© 2003 Kluwer Academic Publishers*

1. Introduction

The automotive market relies on gas sensors for the control of combustion to attain increased fuel efficiency, reduced emissions, and adequate power [1]. This is particularly important in these times of diminishing oil supplies and global warming. Lean-burn combustion [2] holds promises to reduce CO_2, a necessary by-product from hydrocarbon fuels, where the amount of fuel is limited to no more than the stoichiometric amount for combustion. Efficiencies improve significantly and the amount of CO_2 emitted is decreased based on similar power consumption. The drawback to lean burn engines is that they produce high levels of NO_x [3]. It is supposed that rigorous control of the engine could find a fine line where both high fuel efficiency with minimal CO_2 output and low levels of NO_x emissions is possible, but current oxygen sensors are not sensitive enough in the lean-burn range [4].

Many sensor designs rely on a response based on the reduction or oxidation of the gas present near the sensor surface. While some sensors have enhanced selectivity based on surface treatments [5–7], few can claim to have true gas selectivity. Selectivity allows the distinction between reducing gases such as nitric oxide from others such as hydrocarbons. Ideally, a sensor, or array of sensors, would make it possible to quantify all or nearly all gases in a complex gas mixture as would be seen in many combustion processes.

To achieve this goal, sensors of high selectivity are needed. Among many approaches that have been tried, one very promising one is the combination of electrochemical and molecular sieving effects to effectively separate gaseous species. The success of this approach depends not only on the development of a high sensitivity amperometric oxygen sensor based on mixed conducting membranes but also on fabrication of a full-coverage zeolite perm-selective membrane for gas filtering. To this end, an amperometric sensor has been developed which is composed of an oxygen-transporting zirconia electrolyte and a mixed conducting electrode system. The sensing electrode is produced from a zirconia-platinum composite that is still electrochemically active when polished to a smooth surface. This surface accommodates the deposition and growth of a zeolite membrane that provides selectivity of the gaseous species to which the sensor is exposed.

Creating the proper interaction zone in the electrode is of prime importance. The electrode must have sufficient contact between both ionic and electronic conductors, for it is only where these phases meet that reactions can readily occur. The region where the ionic conducting and electronic conducting phases meet the chemical environment is known as the triple phase boundary. In a typical electrochemical system, including sensors, fuel cells, and batteries, the triple phase boundaries are expanded in two ways. The first is the use of highly porous electrode materials to maximize the contact with the chemical environment. The second method is the utilization of mixed conducting materials.

In this case, the triple phase boundary cannot be expanded through the use of high porosity, since the surface must be smooth to be best suited to zeolite application. In fact, the exact opposite happens in the smooth electrode, the triple phase boundary is minimized. If a typical metallic electrode were used, the triple phase boundary would go to zero. The mixed-conducting

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electrode is then, the only way to introduce ionic and electronic conducting elements into contact with the chemical environment to allow the sensor to operate. The processing conditions for the zeolite and the operating environment limit the usefulness of traditional mixed-conducting single-phase ceramics and lead to a composite of two very durable materials. The composite used is composed of platinum and yttria stabilized zirconia (YSZ). The platinum is an electronic conductor and the YSZ phase conducts oxygen anions from the electrochemical reaction sites at the surface. This composite material suits the need for high chemical durability, smooth surface, and process compatibility with the zeolite.

Zeolite is a naturally occurring mineral with the unique property of having a molecularly uniform porous structure. Their general form is that of aluminosilicates with many variants being developed since the early days of synthetic zeolite. In the specific case of zeolite A, the crystals are grown in a hydrothermal synthesis process that involves dissolved aluminum and silica sol. Sodium hydroxide is necessary as the basic templating agent around which the zeolites assemble. In typical processing, the crystals are near perfect cubes, well under 1 micron in width. Under conditions of added growth medium or nucleation deterrents, larger crystals can be formed since the growth of crystals follows the laws of thermodynamics as they apply to crystal growth [8]. Under the right conditions, crystals as large as 50 microns can be grown on earth or up to 85 microns in low earth orbit micro-gravity [9].

Several other research groups have worked with zeolites to create selective gas sensors. One interesting approach was the measurement of dielectric constant of zeolite crystals with selectively adsorbed gases within the channels [10]. Another approach [11] used a zeolite membrane to selectively limit gases involved in a controlled combustion to determine concentration of various hydrocarbons. Similar to the latter approach, our sensor uses the concept of gas flow through a selective zeolite membrane, but utilizes the direct measurement of an amperometric sensor.

Amperometric sensor designs have not yet seen as widespread use as either potentiometric electrochemical sensors or sensors based on semi-conducting oxides in spite of their marked advantages. Most designs are based on yttria-stabilized zirconia used as an oxygen anion conductor. As such, oxygen-containing species that encounter the electrode surface of the sensor may dissociate and allow the oxygen anions to permeate through the YSZ electrolyte. This permeation is slow at room temperature and only becomes significant at temperatures above 400°C. Electrons freed in the transition from oxygen molecule to oxygen anion then travel from the electrode through an external circuit where they may be counted and attributed to the gas interaction at the sensor surface. To facilitate that all gaseous species of interest that encounter the sensor surface do dissociate and get counted, an electrical bias is placed across the two sides of the cell which drives the oxygen through.

The amplitude of the applied voltage depends on the energy required to dissociate the specific oxygen containing gaseous species. By choosing a set voltage or sweeping the voltage applied, the response to a single oxygen-containing component can be determined. The signal measured is a current, which is proportionally linear to the number of gaseous species dissociated into oxygen anions. The measurement, however, must be performed under the conditions that the current passing through the cell is limited by mass transfer, hence the name, diffusion limiting sensor.

This requires that the gas contacting the sensor be of low partial pressure for the species of interest and others that may interfere. To accomplish this, two approaches have been used. The first is to utilize a diffusion-limiting hole in a solid membrane, which sits above the active electrode of the sensor. This allows the cell to pump away oxygen faster than it can diffuse through the hole. The second approach is to use a two-chambered cell. Gas entering the first chamber is pumped at a constant rate to reduce the amount of oxygen or interfering gas species. The remaining gas then enters the second chamber where the gas partial pressure is measured. Both of these approaches will prolong response time and produce complex responses as the gas composition changes.

A new approach has been realized through the utilization of a mixed conducting membrane that serves not only as the electrode, but also as the diffusion barrier, eliminating diffusion holes or secondary pumping chambers [12]. In this case, the sensing electrode is a mixed conducting composite consisting of platinum and YSZ. The composite is developed to have connectivity of both phases in three dimensions, allowing for the simultaneous transport of both electrons and oxygen anions as is required at the electrode of an electrochemical cell. The gas interactions will only be viable if they occur near the phase boundaries on the surface of the electrode.

2. Experimental

2.1. Amperometric sensor fabrication

The creation of a new sensor begins with new materials. Many of the materials used in the sensor were created expressly for this application using novel synthesis techniques to obtain uniquely tailored properties. Schematically shown in Fig. 1 is the sensor developed in this study. The basic amperometric sensor is composed

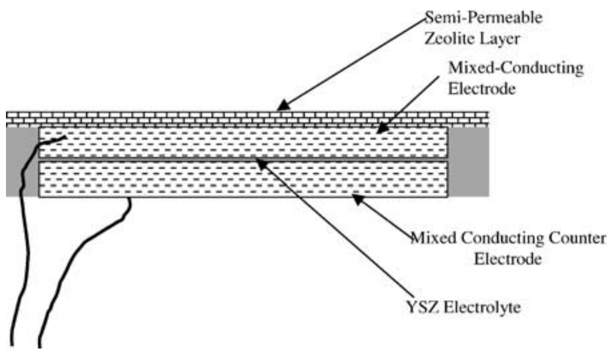

Figure 1 Schematic of amperometric sensor design with perm-selective zeolite membrane.

of a concentrically layered and uniaxially pressed tri-layered structure containing yttria-stabilized zirconia (YSZ) and platinum. The YSZ was derived from two sources. The first source is Tosoh spray dried zirconia (TZY8) and the second is a finely synthesized zirconia produced using a proprietary precipitation/glycine-nitrate process. Similarly, the platinum was also produced as a fine, nanometer powder using the glycine nitrate process.

Upon producing the necessary precursor powders for the sensor, electrodes containing an YSZ-platinum composite were pressed into thin (0.2 mm thick) pellets using a 10 mm die. The electrolyte layer of the amperometric cell was produced by pressing YSZ powder into the center of a 13 mm die. By carefully removing the punch from one end of the die, the pre-pressed 10 mm composite electrode was placed on top of the electrolyte and the remaining circumference of the die was filled with YSZ. Repeating the process for the opposite side yielded the structural basis for the amperometric sensor. The sensor pellets were fired to a temperature of 1500°C for 4 h. The surface of the pellets were polished to provide a smooth surface for zeolite deposition and to expose the back of the sensing electrode for wire attachment.

2.2. Zeolite synthesis

Zeolite crystals were grown by hydrothermal synthesis, beginning from aluminum flake (Aldrich), sodium hydroxide (Baker), tetramethylammonium hydroxide (TMA, Aldrich) and HS40, a colloidal silicate solution. Silicate and aluminate solutions were combined to form the crystallization solution similar to the method employed by Tsapatsis and Boudreau [13]. This solution was immediately placed in a Teflon container inside a pre-heated stainless steel pressure vessel (Parr 200 cc) with a magnetic stir bar and sealed. The vessel was then placed in an oil bath on a hot plate modified to control the oil temperature. The oil bath was controlled at 80°C and the solution was stirred continuously inside the sealed pressure vessel via a magnetic stirring bar.

The solution was recovered from the pressure vessel after 2 to 3 days and separated by centrifuge. The centrifuge separated the zeolite crystals from the remaining growth solution, which was then discarded. Distilled water was added to the zeolite crystals, which were put into suspension with the aid of an ultrasonic probe. The separation and dilution process continued until the suspended solution had a pH between 10.0 and 10.5.

2.3. Zeolite deposition

The zeolite solutions produced are diluted to a level of 1 g of zeolite per 150 g of distilled water. The dilute zeolite solutions were placed on the active sensor surface by the use of a dropper. Typically, a 1 cm diameter sample received 1 to 1.5 g of dilute solution to create near monolayer zeolite coverage.

The sensor with the solution covering its surface was placed in a covered petri dish for a period of 3 days to allow slow settling of the particles on the surface. The dish was opened for 30 min each morning then resealed. On the third morning, the dish was opened and the remaining solution was allowed to air dry. On the fourth day, the dry sample was rinsed with de-ionized water from a wash bottle for about one minute.

2.4. Zeolite film growth

The zeolite regrowth solution is similar to the original growth solution except that it contains more silica and water. The solution is 4.1 $(TMA)_2O$:0.35 Na_2O:1 Al_2O_3:4.4 SiO_2:706 H_2O. The solution was prepared in a manner similar to that used to grow the crystals, first producing a sodium aluminate solution to which a silicate solution is added.

The sensor substrates, which have already undergone the deposition of a zeolite seed layer, are placed in the bottom of the pressure vessel with their zeolite side up. About 75 grams of regrowth solution was added to the vessel. The pressure vessel was then sealed and placed in an oven for 2 days at 80°C. After 2 days, the growth solution was replaced with fresh growth solution and the vessel was sealed and heated another two days. Sensor samples were rinsed thoroughly with deionized water before adding silver lead wire extensions and testing.

2.5. Characterization

A variety of characterization techniques were used throughout the sensor fabrication to assure that the final product was a viable sensor. X-ray diffraction was carried out using a Philips PW 1800 on the precursor powders used for the base sensor as well as the zeolite crystals, before and after deposition. A Hitachi S-800 field emission microscope was crucial to the analysis of the zeolite crystals, depositions and films produced and was also used for analysis of the sensor microstructures.

2.6. Performance testing

Sensors were evaluated for sensitivity to gaseous species and selectivity. The apparatus for testing contained mass flow controllers for portioning the gaseous mixtures and a tube furnace to maintain the sensor temperature in a uniform atmosphere. The sensor sample was placed in the furnace and heated to a stable 600°C.

The atmosphere was controlled through three mass flow controllers and switching valves which allow various gases to flow to each mass flow controller. The nominal scale on two of the mass flow controllers was 0 to 200 sccm and 0 to 20 sccm for the third. The gases available for use included high purity (Air Products UHP, 99.995% purity) oxygen, nitrogen, and argon. Also used were 1% oxygen in nitrogen, air, 1000 ppm NO in argon and CO_2. All gases were supplied at 40 psi, and were calibrated in each mass flow control before experimentation started.

Lead wires from the sensor exited the sealed tube and were attached to an EG&G 273A potentiostat. The potentiostat was used to apply a bias to the cell while measuring the current flow, the basic amperometric sensor measuring technique. A bias of 1.8 V was used for all measurements sited herein since this potential is suitable for dissociation of most species without causing damage to the cell itself.

3. Results and discussion

This complex and unusual mating of materials requires in depth explanation of each component in order to understand the overall function of the sensor developed. In fact, successful fabrication of each component is in itself a milestone. Three distinct materials systems are combined to produce the final sensor. The mixed ionic-electronic conducting (MIEC) electrode and zeolite layers are discussed in depth to better understand their functionality in the system. Finally, the testing of the sensor system with and without the zeolite membrane is discussed.

3.1. Sensor fabrication

Complications in producing uniform compactions were prevalent, particularly when producing the composite layers, which consisted of a platinum-YSZ disk surrounded by YSZ. The platinum containing powder had a very high density compared with the YSZ powder and compacted in a very different manner. The platinum-YSZ composite powder would easily compact and densify, often leading to a low-density annular YSZ ring around the electrode. If the pellet would stay together, shrinkage differences would cause delamination during the firing process. Pressing difficulties only enhanced already existing problems due to difference in thermal expansion and firing shrinkages inherent in the material systems.

During the polishing process, one edge was ground at a steep angle from the backside to allow attachment of the platinum wire to the back of the front-side electrode thereby preventing interference on the active sensor surface, where the zeolite was yet to be applied. The final amperometric sensors are seen in Fig. 2. Short wire sections allow the cell to be placed in the pressure vessel for subsequent zeolite growth.

3.2. Composite MIEC electrode

In electrochemical systems, most activities occur at the electrode surface. It is where electrons are injected or collected to drive the electrochemical reactions. The use of extremely fine powders produced a very fine-scaled platinum-YSZ composite with large amounts of triple phase boundary, which was required in order to maximize the signal available from the sensor. The fired and polished surface of a platinum-YSZ composite electrode is seen in Fig. 3.

3.3. Zeolite film

The zeolite film was produced in three steps beginning with the growth of zeolite crystals. In subsequent steps, the zeolite crystals were deposited onto the surface of the sensor and the zeolite film was grown around the deposited crystals.

3.3.1. Zeolite crystal growth

Since the goal is to prepare a membrane less than 1 micron thick, the experimentation took place without the use of nucleation deterrents. Many batches of zeolite

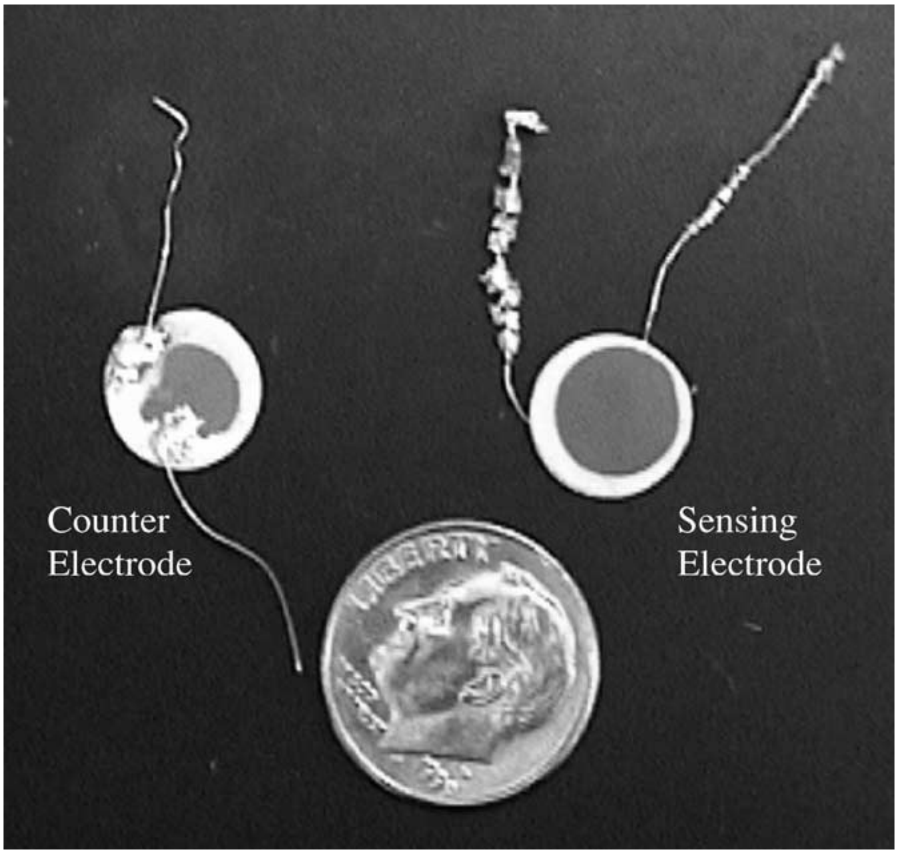

Figure 2 Front and back of finished amperometric sensors.

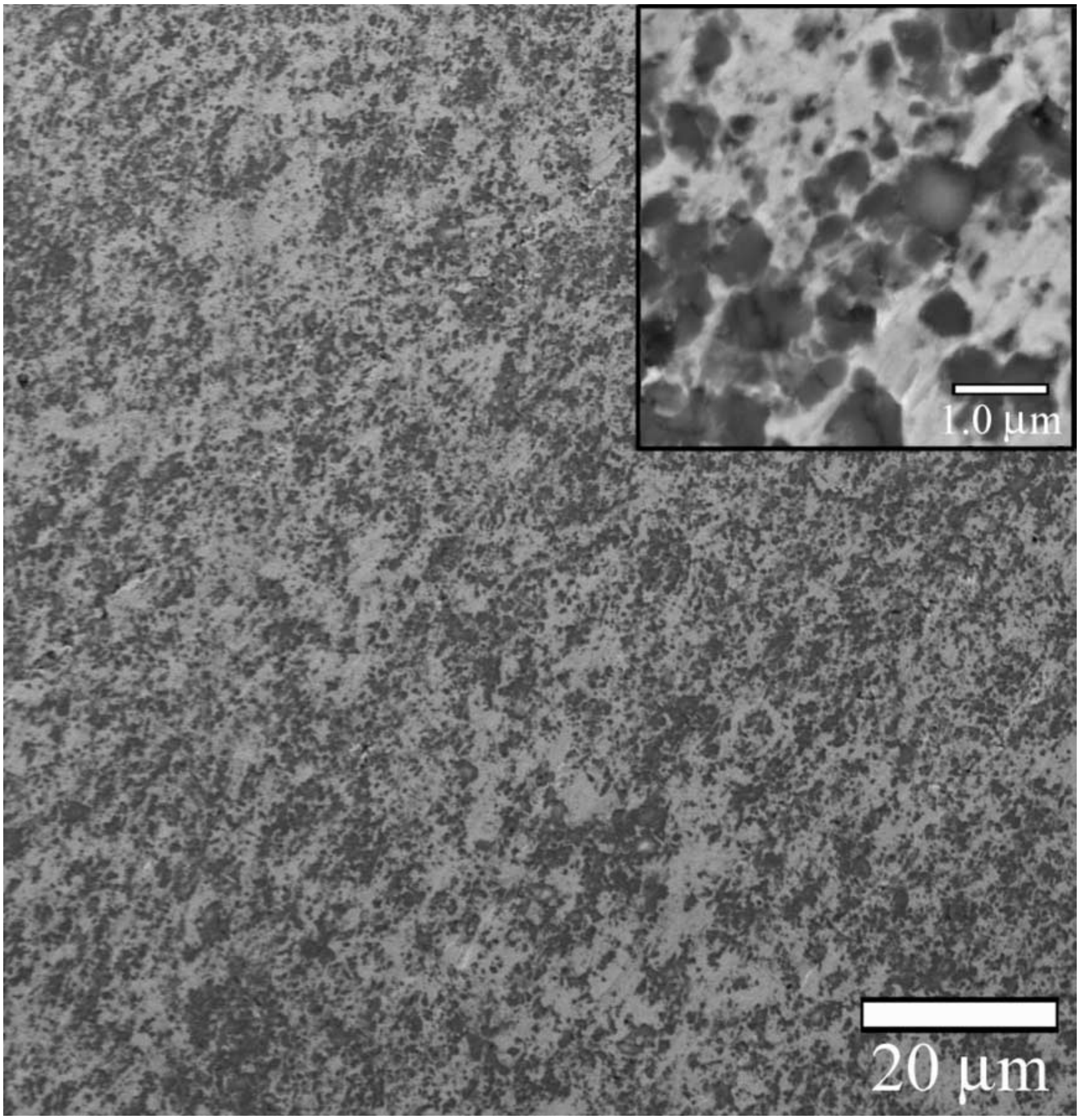

Figure 3 Surface of platinum-YSZ composite MIEC electrode that has been polished for zeolite membrane application.

crystals were grown to develop a technique suitable to this application. Reproducibility was good given careful lab technique. The best method found involved pre-cleaning the glassware with tetramethylamonium hydroxide.

In a given range of chemistry, the crystallite size was generally constant. The growth process was controlled by an initial nucleation stage, which determines the number of crystals to be produced and a secondary growth phase that determines the final size of crystals grown [14]. In this case, a clear dilute solution technique [15] was chosen as it appeared to be slower to nucleate and more controllable. The processing conditions could be varied to produce a final product of the zeolite as small as 20 nm and as large as 500 nm. The uniformity of the distribution was achieved only under the conditions of constant stirring.

3.3.2. Zeolite deposition

The zeolites were deposited by creating an aqueous suspension in the concentration range to allow a monolayer to be produced over the area of a drop placed on the sensor. The work at this stage involved much trial and error since the drop size is related to surface tension between the drop and the sensor surface, and concentrations are extremely low. For the samples produced, the concentrations were estimated from the area of the sensor and the weight of a drop placed on its surface. The zeolite suspensions are relatively stable given the inherent surface charge associated with zeolites [16]. At the extremely low concentrations used, no notable settling was observed for two to three days. The key to this process was a controlled drying process. The probability of success was high if a low concentration was used in conjunction with a long settling period and slow drying.

The technique was developed as a replacement for the dip coating/Langmuir Blodgett films produced by Boudreau and Tsapatsis [17]. This technique requires minimal equipment and produces suitable results. The films which were going to be regrown later could not be observed under an SEM, since the zeolites require gold coating for SEM observation, which would interfere

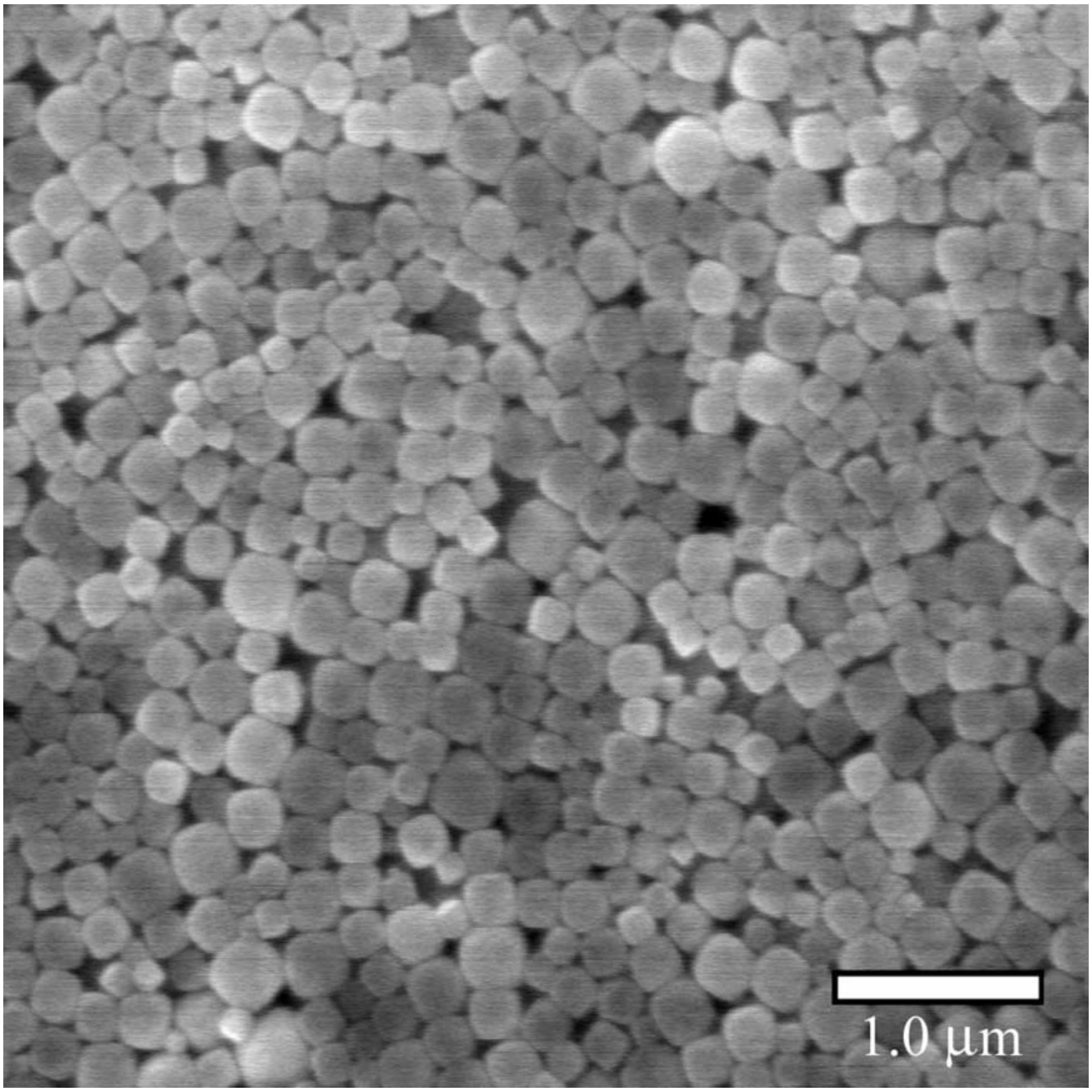

Figure 4 Alignment and close packing of zeolite crystals deposited on sensor surface.

with the subsequent regrowth process. The sensors were coated with zeolite at the same time as a glass slide and handled in an identical manner. The films on the glass slides were evaluated to determine if the procedure went as planned or if the coating was to be removed from the sensor and started again. Shown in Fig. 4 is the deposition achieved in the early stages of the process.

As a test for ordering, the deposited films were tested by X-ray diffraction. In the case of highly ordered samples, the diffraction pattern simplifies as some crystallographic planes are missing due to orientation. These samples show very few peaks in the XRD pattern from the diffractometer, as seen in Fig. 5, where the deposited film creates a high level of orientation in the ⟨100⟩ direction. These results are also in good agreement with others who have made similar depositions [13].

3.3.3. Membrane formation

The procedure used to create the completed membrane was a secondary growth procedure similar to that developed by Boudreau, Kuck, and Tsapatsis [13]. In this procedure, a growth solution was produced, similar to the one by which the original zeolite A crystals were produced. This solution, however, is richer in silicates, to eliminate the ability of the solution to nucleate. This solution then can only add to the size of already formed crystallites.

With a highly dense clustering of crystals already deposited, the process was developed to bridge the deposited crystals and grow into a complete membrane. Developed by working with depositions on glass slides, the procedure is only complicated in that the original crystals must not be disturbed by the growth solution. In cases where the original seed crystal depositions were multi-level in thickness, the seeds dislodged and zeolites were grown in large volumes away from the substrate. At this stage, the only information to follow was produced from the surrogate glass substrates. After a single day in the growth solution, it was clear that the growth was occurring as needed (Fig. 6), but more than one day would be required. In total, 4 days of growth were used for the films deposited on sensors.

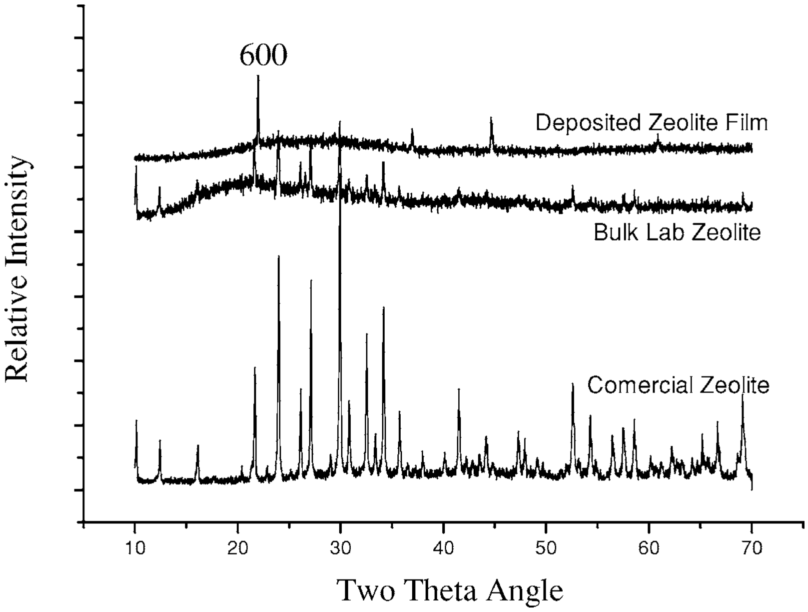

Figure 5 Diffraction patterns comparing deposited zeolite with preferred orientation to that of crystallites in bulk form.

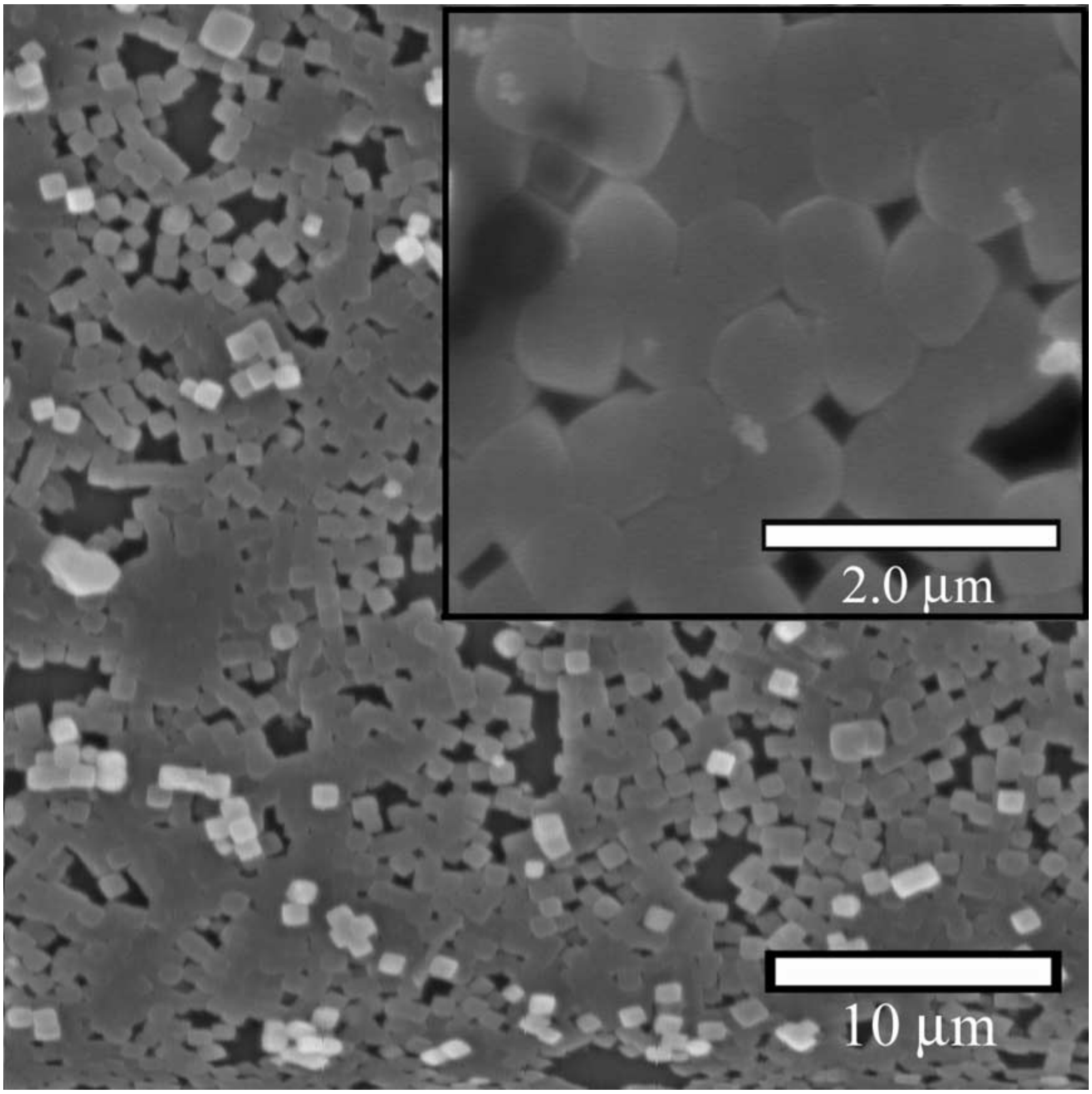

Figure 6 Film growth demonstrated after a single day of regrowth.

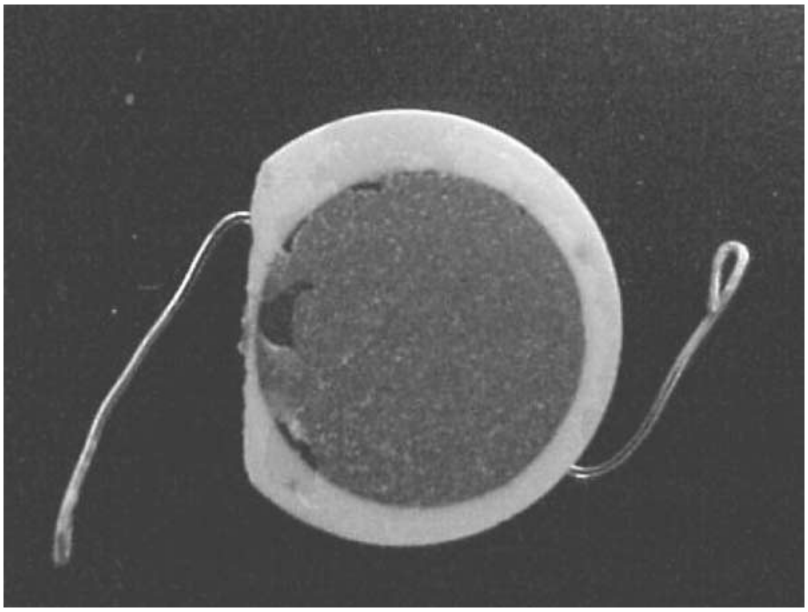

Figure 7 Finished sensor with zeolite membrane over an active electrode.

3.4. Sensor testing

The initial sensor testing was performed using a specific sensor specimen, which did not have the added zeolite gas-selective membrane. This same sensor then had the zeolite film grown over its working electrode to run the final tests with the membrane in tact. This sensor with its zeolite membrane is seen in Fig. 7. A typical run of four hours is seen for the uncoated sensor in Fig. 8. In this run, oxygen and carbon dioxide were added individually and together into an inert gas stream. The sensor responded positively when either gas was present, and more strongly when both were added simultaneously.

For oxygen containing gases, the sensor response was linear at lower oxygen content and showed a diminishing response at higher oxygen content. This is illustrated in Fig. 9. Our experience with these sensors that utilize solid composite electrodes is that coarsening the microstructure of the composite and providing a less active and more current limiting electrode can expand the linear region. In this case, the electrode was intentionally produced to be highly active since the zeolite layer was anticipated to limit gas diffusion.

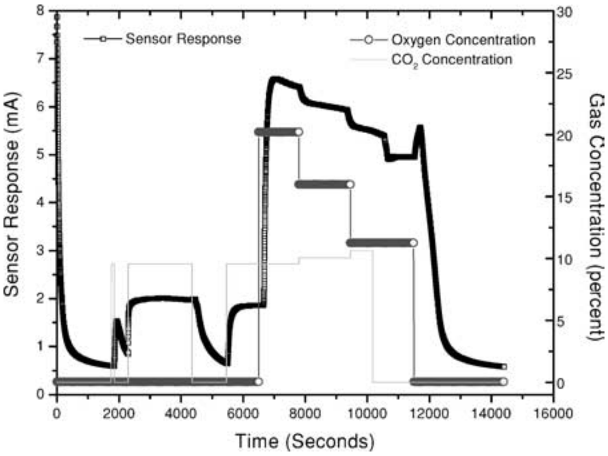

Figure 8 Sensor response to oxygen and CO$_2$ in a four-hour test run.

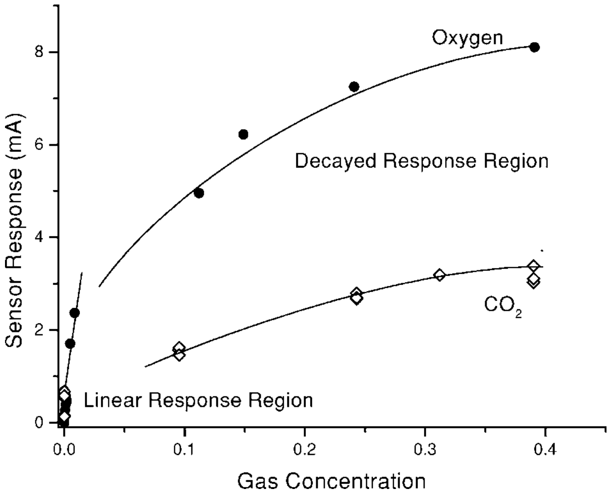

Figure 9 Response of the basic amperometric sensor to a range of oxygen and carbon dioxide concentrations.

A similar test using oxygen and carbon dioxide was performed on the sensor after zeolite coating. Fig. 10 shows the response of the zeolite-coated sensor to various atmospheres. The sensor is highly sensitive to even small concentrations of oxygen, showing a 0.32 mA response when changing from nitrogen ($P_{\mathrm{O}_2} = 1\,E^{-4}$), to 3 percent oxygen, seen at the 1100 s mark in Fig. 10. In contrast to the previous tests, the sensor showed virtually no response to changes in carbon dioxide content of 30 percent (at 3000 s and again at 5000 s), while giving a marked response to as little as 3 percent of oxygen. So the initial appearance is that the zeolite film effectively blocks carbon dioxide from the sensor surface.

3.4.1. *Zeolite selectivity*

The theoretical selectivity of zeolites is very specific. Add to this, the fact that our estimated 1 micron layer

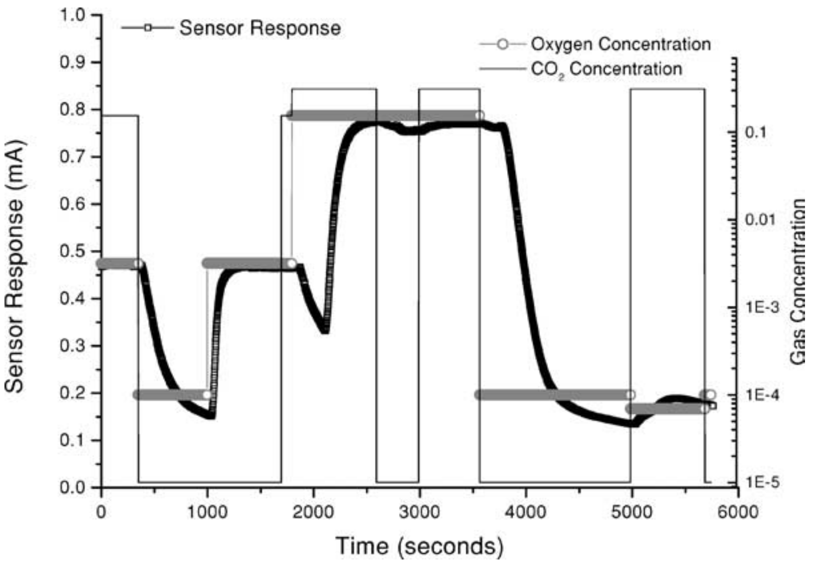

Figure 10 Response of the zeolite coated sensor to oxygen and CO_2 containing gases.

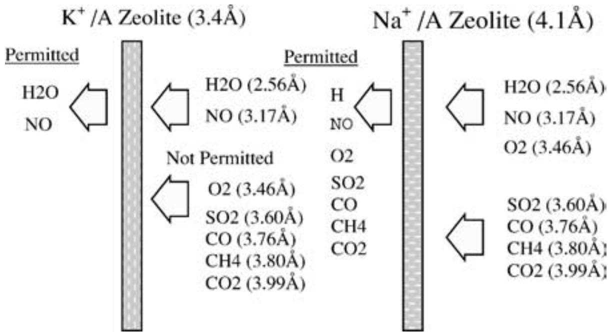

Figure 11 Anticipated selectivity of potassium and sodium zeolite-A membranes.

would repeatedly filter any gas passing through more than 300 times before a molecule could pass completely through. The selectivity expected for two of the A-type zeolites is as shown in Fig. 11. It can clearly be seen that no absolute selectivity is expected within the gases tested if the layer consists of zeolite Na^+-A, which is indeed the case here.

But selectivity can also be achieved by near size effects. When the porosity is on the order of the length of the mean free path of a gas molecule, selectivity is according to Knudson diffusion, wherein the permeation is proportional to the square root of the reciprocal of the molecular weight. This would indicate that CO_2 would have about one-third lower permeation than oxygen or NO, which would be essentially the same. In the case where the pore size is smaller than the mean free path, but large enough to admit the molecule, the situation is difficult to predict. In this case, the affinity of the gas molecule for specific sites within the zeolite may aid in surface diffusion through the pores. Limited data was taken before the sensor failed, and there is no clear answer on the mechanism for diminished sensor response to CO_2, but it is clear that some limiting of the CO_2 gas interaction with the sensor has occurred.

Quantifying the selectivity attained is based on limited experimentation and some difficulties. Ideally more, and better planned experiments were to have taken place, but the data shows the uncoated sensor with an average response of 0.43 mA/percent of oxygen and 0.22 mA/percent of CO_2. This yields a selectivity of about 2 for oxygen over CO_2. This is anticipated since the reduction potential for CO_2 is -1.6 V and the reduction potential for O_2 is -0.67 V. At the surface of the amperometric sensor, oxygen is more likely to dissociate and traces of oxygen were always present in the gas mixtures. For the zeolite coated sensor, the response to all gases was diminished. The response to oxygen by the coated sensor was one tenth that of the uncoated sensor (0.041 mA/percent) and even more diminished for CO_2 at 0.001 mA/percent. The selectivity of the coated sensor for oxygen was 40 times greater than for CO_2.

3.5. Film analysis

As stated earlier, analysis of the zeolite film by SEM is generally not practical for samples to be used as sensors. After failure of the sensor, a careful analysis of the zeolite film was performed. Images of the surface, shown in Fig. 12, indicate that the zeolite had developed cracks at some unknown time. The nature of the cracks, permeating across the individual zeolite grains, suggests that the crack evolved from the sensor, thereby splitting a previously intact zeolite film. This also indicates that the film was likely to be well attached to the sensor given that it did not spall away from the sensor under stress and that the film itself was coherently bonded together.

As estimated during analysis of glass slides processed along side the sensor, the film formed was indeed on the order of 1 micron in thickness as shown in the cross-sectional view shown in Fig. 13. The film showed significant surface roughness, but no apparent open pores through the surface other than the cracks. The point during testing at which the cracks appeared is unknown, so their influence on the data is left to experimental replication. The dimensions of the crack were sufficiently large to produce no selectivity based on their gross scale.

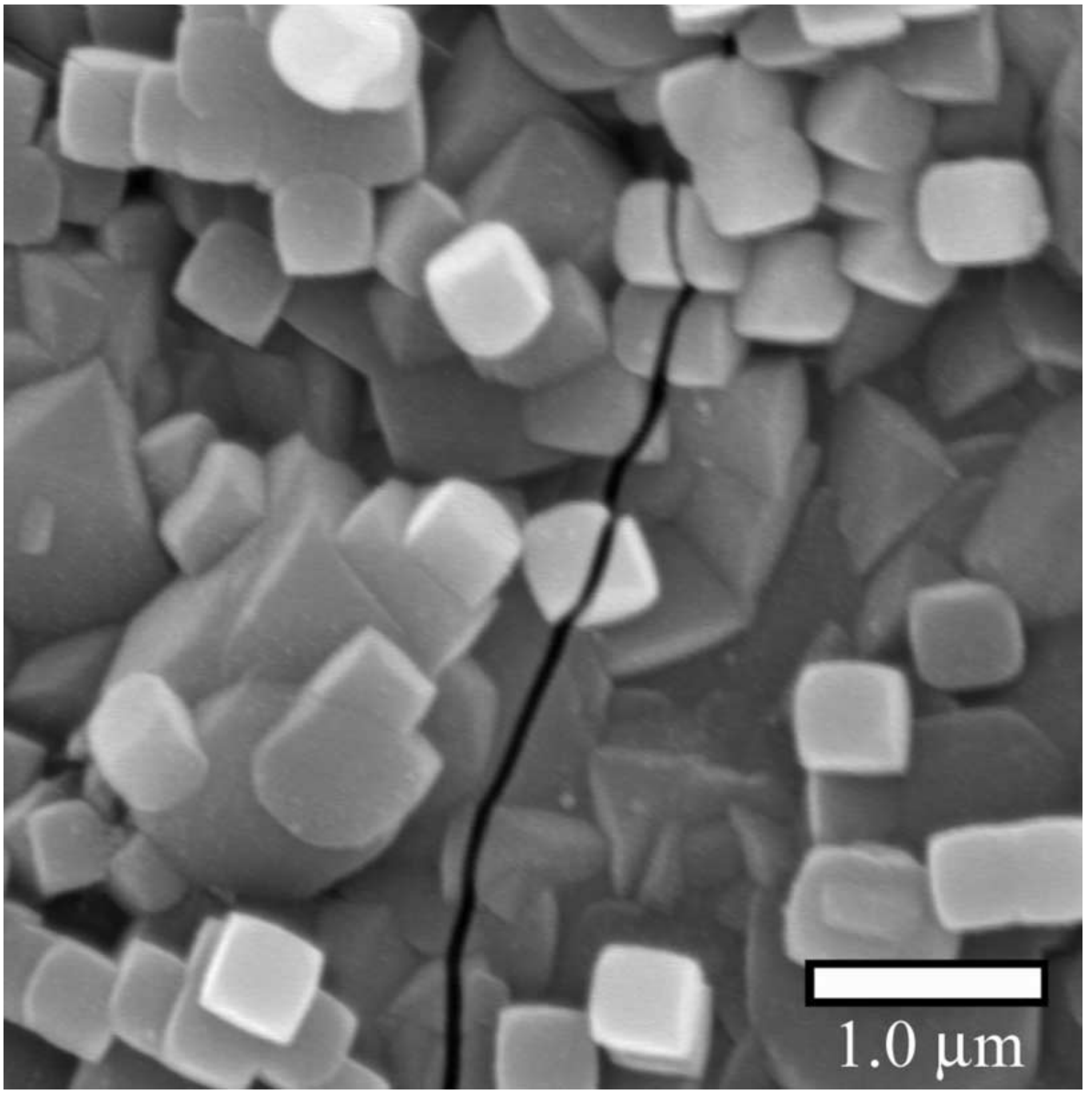

Figure 12 Surface of zeolite film showing cracks through the film permeating the grains.

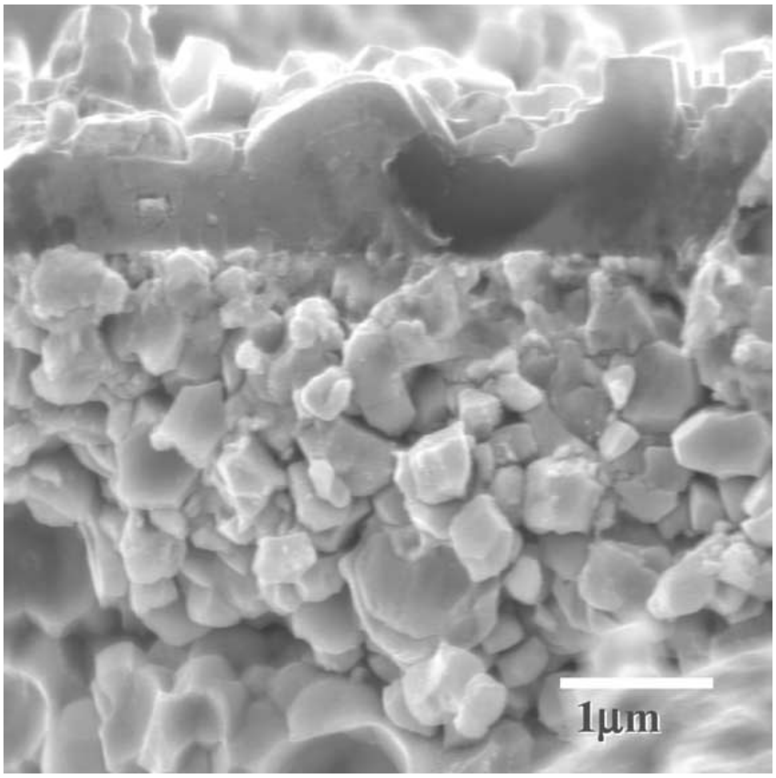

Figure 13 Cross-section of sensing electrode and zeolite membrane.

4. Conclusions

The primary goal of showing that zeolite can add selectivity to a sensor has been achieved. The unique new sensor design provides a suitable substrate for the application of zeolites and their subsequent regrowth to form a solid dense film. The zeolite Na^+-A film produced was shown to limit the response of the amperometric sensor to carbon dioxide while maintaining high sensitivity to oxygen. Although it is unlikely that true molecular sieving occurred, based on the size of the gas molecule versus the pore dimensions of the zeolite, a level of selectivity of 40 was achieved and may be due to limitations based on Knudsen diffusion. The ability to produce specific zeolite films on sensor substrates generates new possibilities for increasing the selectivity of many types of gas sensors for a wide range of practical applications.

Acknowledgements

The authors wish to thank Gary Hunter from the NASA Glenn Research Center and Mark White (Georgia Tech) for their participation and the funding provided through NASA-GSRP.

References

1. J. BINDER, *Sens. Actuators* A **31** (1992) 60.
2. N. KOTO, Y. HAMADA and K. KURACHI, in "Automotive Electronics Series: Sensors and Transducers," edited by Ronald K. Jurgen (Soc. of Automotive Engineers Inc. Warrendale, PA, 1997) p. 5.
3. Y. NAKANONCHI, H. KAROSOMA, M. HASEI, Y. YAN and A. KUNIMOTO, in "Automotive Electronics Series: Sensors and Transducers," edited by Ronald K. Jurgen (Soc. of Automotive Engineers Inc. Warrendale, PA, 1997) p. 157.
4. AI QUOC PHOM and ROBERT S. GLASS, *J. Electrochem. Soc.* **144**(11) (1997) 3929.
5. A. MENNE and W. WEPPNER, *Solid State Ion.* **40/41** (1990) 468.
6. I. KOCEMBA and T. PARYJCZAK, *Thin Solid Films* **272** (1996) 15.
7. I. SAYAGO, J. FUTIERREZ and J. AGAPITO, *Sens. Actuators* B **26/27** (1995) 19.
8. F. DI RENZO, F. FAJULA, F. FIGUERAS, S. NICOLAS and T. DES COURIERS, in "Zeolites: Facts, Figure, Future," edited by P. A. Jacobs and R. A. van Santen (Elsevier Science Publications, Amsterdam, 1989) p. 119.
9. JULIUSZ WARZYWODA, NURCAN BAC, JACOBUS C. JANSEN and ALBERT SACCO, JR., *J. Cryst. Growth* **220** (2000) 140.
10. HAAS, *et al.* US patent no. 5,143,696.
11. TAKAHASHI, *et al.* US patent no. 5,948,966.
12. ZUOYAN PENG, MEILIN LIU and ED BALKO, *Sens. Actuators* B **3598** (2000) 1.
13. LAURA C. BOUDREAU, JULIA A. KUCK and MICHAEL TSAPATSIS, *J. Membr. Sci.* **152** (1999) 41.
14. PETER M. BUDD, GRAHAM J. MYATT, COLIN PRICE and STUART W. CARR, *Zeolites* **14** (1994) 198.
15. B. J. SCHOEMAN, J. STERTE and J. E. OTTERSTEDT, *ibid.* **14** (1994) 110.
16. B. J. SCHOEMAN, J. STERTE and J. E. OTTERSTEDT, *ibid.* **14** (1994) 208.
17. LAURA C. BOUDREAU and MICHAEL TSAPATSIS, *Chem. Mater.* **9**(8) (1997) 1705.

Received 16 April
and accepted 1 August 2003