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ELECTROCHEMICAL SO_x AND NO_x SENSORS WITH Ag^+-BETA"-ALUMINA AS SOLID ELECTROLYTE AND Ag AS SOLID REFERENCE ELECTRODE

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ABSTRACT

Polycrystalline Ag^+-ß"-Alumina tubes and pellets were prepared from Na^+-ß"-Alumina by ion exchange and characterized by XRD, DTA, TGA, SEM and EDAX analysis. Applying Ag^+-ß"-Al_2O_3 as solid electrolyte, metal Ag as solid reference electrode and porous Pt as working electrode, fully solid galvanic cells were constructed as SO_x and NO_x electrochemical sensors:

Pt, Ag/Ag^+-ß"-Al_2O_3/Ag_2SO_4/porous Pt, SO_2-SO_3-O_2, Pt
Pt, Ag/Ag^+-ß"-Al_2O_3/$AgNO_3$/porous Pt, NO_2-NO-O_2, Pt

The Nernst EMF response of the SO_x sensor to the SO_2 partial pressure is fairly consistent with the theoretical prediction in the working temperature region of 500-700°C and the PSO_2 range of 10 ppm to 1000 ppm. The response time is usually about 5-10 mins. The experimental results indicate the potential of this SO_x sensor in practical use. A primary investigation of NO_x sensors shows that the sensor has promissing EMF response to the change of NO partial pressure from 500 ppm to 1000 ppm in the operating temperature range of 150-220°C, but the response time is as long as a few hours, which might be shortened by improving the properties of Pt working electrode.

1. INTRODUCTION

It is of great importance to develop a reliable and rapid method for the continuous measurement of the SO_x (x=2,3) and NO_x (x=1,2) concentrations in the atmosphere and gaseous environments of industrial processes. For these measurements, solid state electrochemical sensors with solid electrolytes have advantages over other detection methods.

Since the first SO_x sensor with solid electrolyte was reported by Gauthier et al[1,2], many attempts have been made to use alkali sulfates including K_2SO_4[1,2], Na_2SO_4[3] and Li_2SO_4-Ag_2SO_4 two phases solid solution[4] as solid electrolytes for SO_x sensors. However, these alkali metal sulfates undergo phase transition with volume change on heating and have poor sinterability. This would result in micro cracks and pores. In recent years, some Na^+ ion conductors such as Nasicon[5], ß,ß"-Alumina[6] were employed to avoid the above problems because no structural phase transition takes place during heating from room temperature to the melting point of these materials. But, a standard gas reference with a known SO_2 partial pressure is necessary when a galvanic cell with a Na^+ conductor is used as an SO_x sensor. Considering the ion exchangability of Na^+-ß"-Alumina by other ions, in our previous work[7], we prepared polycrystalline Ag^+-ß"-Alumina and used it as the solid electrolyte. In this case, metal Ag is a good choice as the stable solid reference for a fully solid SO_x sensor. Itoh et al[8] also published the similar work on the Ag^+-ß-Al_2O_3 sensor disks. The present paper is focused on our recent experimental results for the SO_2 sensor with a tubular Ag^+-ß"-alumina solid electrolyte.

Regarding NO_x sensors, two types of material were applied, one is semiconductor, such as metal oxides[9,10,11] and phthalocyanines [12], the other is solid electrolyte, e.g. nitrates[13] and Na-ß/ß"-Al_2O_3[14]. Semiconductor sensors usually have the problem of selectivity. For the solid electrolyte sensors being developed, there is also a problem of choosing a good solid reference. In this work, a primary study on NO_x sensors with Ag-ß"-alumina as solid electrolyte, metal Ag as solid reference and porous Pt as working electrode is being carried out.

2.EXPERIMENTAL

Polycrystalline Na^+-ß"-Alumina tubes(ϕ11x1.5x40) and pellets (ϕ16x1.5, ϕ10x1) used in this work were supplied by Shanghai Institute of Ceramics, Academia Sinica. To obtain Ag^+-ß"-Alumina, Na^+-ß"-Alumina samples were dipped into a molten $AgNO_3$ at 300°C to undergo ion exchange reaction for 30 hrs. The ion exchange completeness of the Na^+ by Ag^+ was examined with the weight increase of the samples, Na^+ content of the samples after ion exchange was detected by EDAX.

The XRD patterns of the specimens were taken on a D/max-ra 12kw Diffractometer (Rikadenki, Japan) over the 2θ range from 20° to 70°. An X-650 SEM (Hitachi, Japan) was used to obtain the surface morphology of the sensor material. DTA and TG were employed to investigate the thermal stability of the materials by a DF-30 Thermoanalyzer (Shimadsu, Japan).

Using Ag^+-ß"-Alumina as solid electrolyte, metal Ag as solid reference electrode and porous Pt as working electrode, the tubular SO_X and both planar and tubular NO_X sensors were fabricated. Figure 1 shows the SO_X sensor tube and the electrodes, the SO_X sensors were tested in a system shown in figure 2. The sample gas with different SO_X partial pressure was made by mixing air and SO_2 in N_2. As can be seen, two mass flow meters were employed to control the gas flow rate and the SO_2 partial pressure on the working electrode. NO_X sensor device has a similar construction. The Nernst EMF response and working temperature of the SO_X and NO_X sensors were collected by an HP 85B PC or a recorder, then analysed using Supercalc 4 program. EMF response as a function of operating time, SO_2, NO and O_2 partial pressure and working temperature were tested respectively.

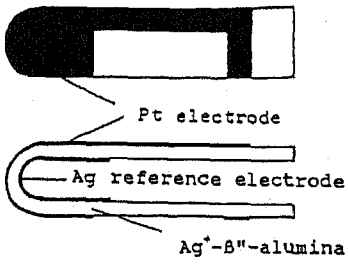

Fig.1 Ag^+-ß"-alumina SO_2 sensor tube and electrodes.

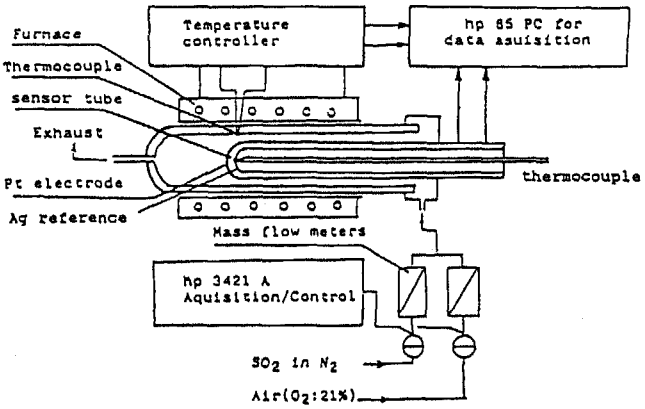

Fig.2 System for the testing of Ag^+-ß"-alumina SO_2 sensors.

3.RESULTS AND DISCUSSION

3.1 Preparation and characterization of Ag^+-ß"-Alumina

The measurement on the weight increase of the Na^+-ß"-alumina samples after ion exchange showed that at 300°C in $AgNO_3$ melt, the complete ion exchange of Na^+ by Ag^+ in ß"-alumina could be accomplished in less than 30 hrs. XPS, EPMA and X-ray fluoroscopy analysis all indicated that no Na^+ ion could be detected in the sample after 30 hrs of ion exchange.

Figure 3 gives an SEM photo showing a typical microstructure of the polycrystalline Ag^+-ß"-Al_2O_3. XRD pattern indicated that Ag^+-ß"-Al_2O_3 has the same lattice structure as Na^+-ß"-Al_2O_3. Ag^+-ß"-Alumina exhibits good thermal stability as Na^+-ß"-alumina, there is no phase transition from room temperature to 1200°C. Furthermore, Na^+-ß"-Alumina is easily corroded by CO_2 and/or H_2O, forming Na_2CO_3 or $NaHCO_3$ while Ag^+-ß"-Alumina is quite stable in moist air. Even when the Ag^+-ß"-Alumina samples were put into water for 10 hrs and then analylized, no considerable changes were observed in their structure and properties. The good chemical

stability of Ag^+-ß"-alumina makes it easy to be used in practical environment.

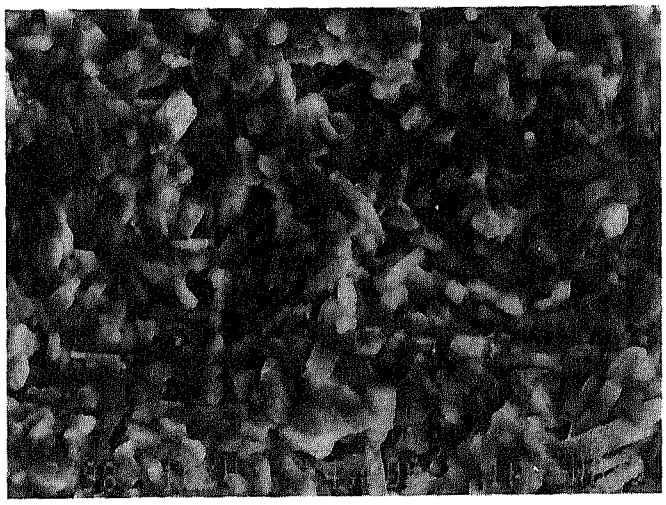

Fig.3 SEM photo showing a typical microstructure of Ag^+-ß"-aluumina

3.2 EMF expression for the Ag^+-ß"-Al_2O_3 SO_x and NO_x sensors
For the following galvanic cell

$$Pt,Ag/Ag^+\text{-ß"-Alumina}/SO_2,SO_3,O_2,Pt \quad (1)$$

The theoretical EMF of this cell can be expressed as

$$EMF=-\delta G^\circ(T)/2F+(RT/2F)*\ln[KPO_2/(1+KPO_2^{1/2})]+(RT/2F)*\ln PSO_2 \quad (2)$$

where $\delta G^\circ(T)$ is the standard free energy of the cell reaction

$$2Ag + SO_3 + 1/2\ O_2 == Ag_2SO_4 \quad (3)$$

and K is the equilibrium constant for the reaction

$$SO_2 + 1/2\ O_2 == SO_3 \quad (4)$$

$\delta G^\circ(T)$ and K can be calculated from the thermodynamic data:

$$\delta G^{\circ}(600K<T<703K) = -312148+227.36T \quad (J/mol) \tag{5}$$

$$\delta G^{\circ}(703K<T<933K) = -290016+196.10T \quad (J/mol) \tag{6}$$

$$\delta G^{\circ}(933K<T<1100K) = -261600+165.52T \quad (J/mol) \tag{7}$$

and

$$\ln K(600K<T<1100K) = -11.15+11783/T \tag{8}$$

In equation (2), PSO_2 is the initial SO_x (x=2,3) partial pressure in the gas mixture introduced into the sensor system. If PO_2 is known (Say, 0.21 atm for atmosphere), PSO_2 could be calculated from the measured EMF of the sensor cell. Figure 4 and 5 show the theoretical EMF as a function of SO_2 concentration and temeprature, respectively. We can see that EMF increases with SO_2 partial pressure but decreases with temperature. When temperature is rather high and SO_3 concentration is very small, for instance, at the fixed temperature, PSO_3 is below its decomposition partial pressure for reaction(3), the theoretical EMF calculation will give negative values, and it implies that the electrochemical reaction is stopped.

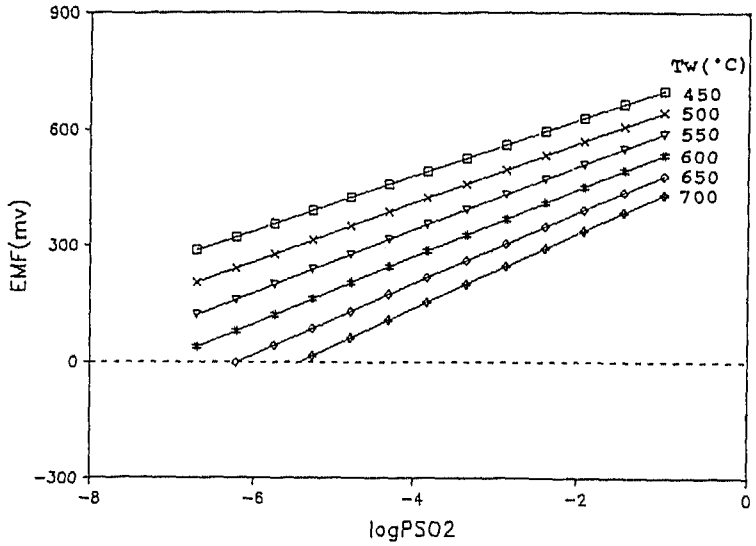

Fig.4 Theoretical EMF of the Ag^{+}-β"-alumina as a function of SO_2 partial pressure when PO_2=0.21atm.

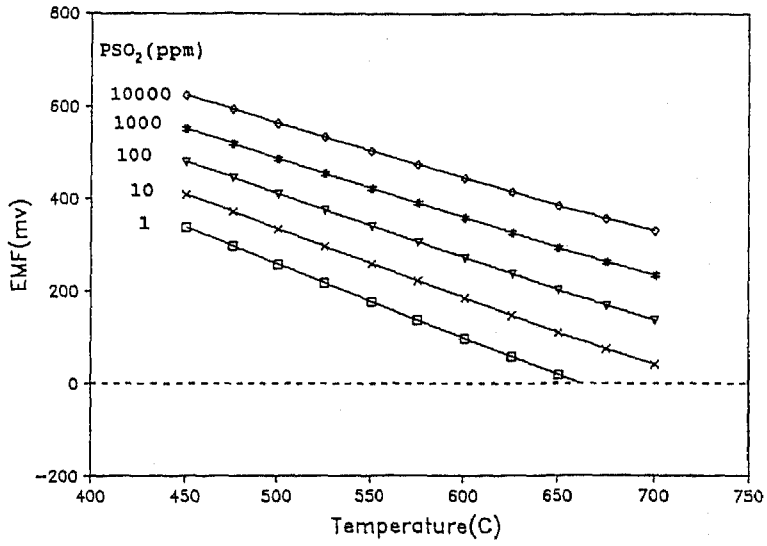

Fig.5 Theoretical EMF of the Ag^+-β"-alumina SO_2 sensor as a function of temperature when PO_2=0.21atm.

In this case, the formed Ag_2SO_4 on the working electrode will completely decompose to silver metal, SO_3 and O_2 gas, and this sensor cell cannot work anymore, the EMF output of this sensor should become zero. Therefore, in practical measurements, the working temperature should be controlled to avoid the decomposition of Ag_2SO_4.

For NO_x sensors, a similar theoretical discussion can be given and theoretical EMF can be prodicted by the equations below

$$EMF=-\delta G^\circ(T)/F+RT/F*\ln[KP(O_2)/(1+KP(O_2)^{1/2})]+RT/F*\ln P(NO) \quad (9)$$

$$\delta G^\circ(298K<T<433K) = -152130+239.6T \quad (J/mol) \quad (10)$$

$$\delta G^\circ(433K<T<483K) = -145578+224.5T \quad (J/mol) \quad (11)$$

$$\delta G^\circ(483K<T<600K) = -131871+196.4T \quad (J/mol) \quad (12)$$

and

$$\ln(K) = -9.15 + 6993/T \quad (13)$$

3.3 EMF response to SO_2 partial pressure

Figure 6(a) shows the sensor EMF response to the change of SO_2 partial pressure from 30ppm to 140ppm at the working temperature of 615°C. We can see that the response time is about 5-10 mins, at low SO_2 partial pressure, the response time is longer and the EMF

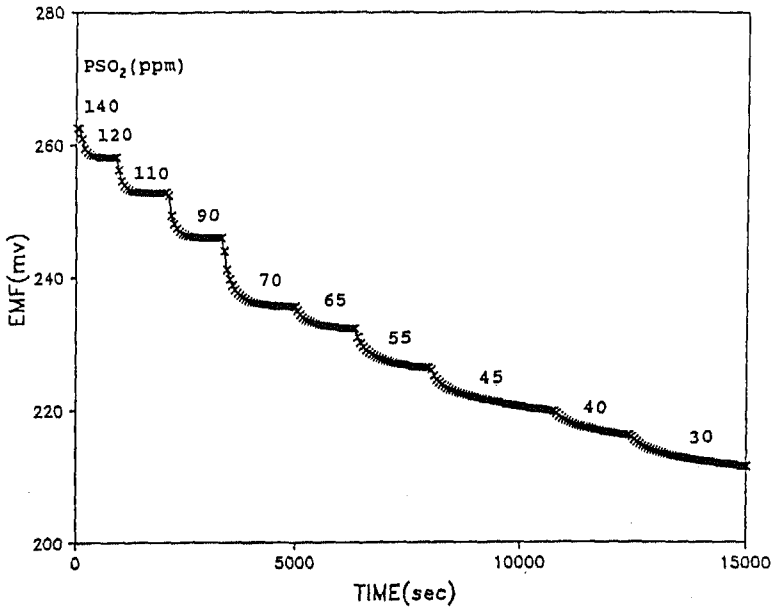

Fig.6(a) Sensor EMF response to the change of SO_2 concentration when Tw=615°C.

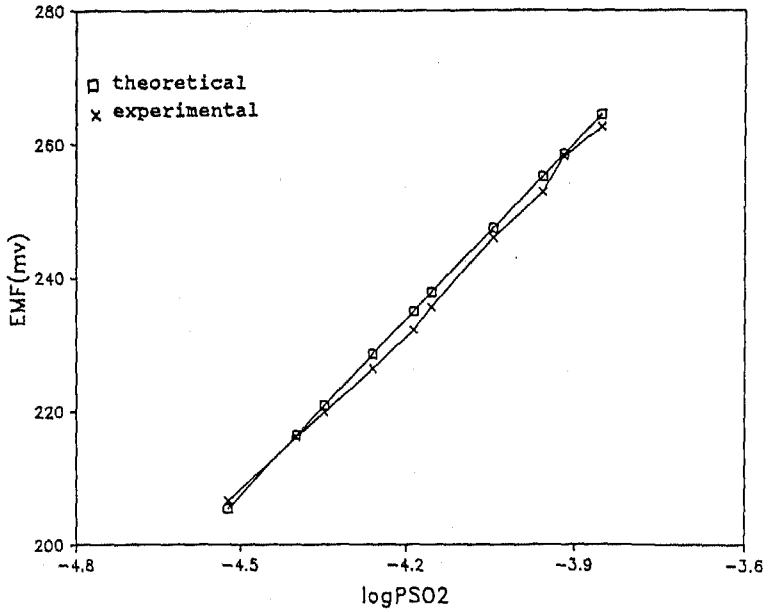

Fig.6(b) EMF response as a function of SO_2 concentration when Tw=615°C.

value decreases slightly. Figure 6(b) gives the EMF response as a function of SO_2 partial pressure calaulated from Figure 6(a). It can be seen that the EMF values are essentially consistent with the theoretical prediction from equation (2), a little negative deviation of the experimental results from the theoretical values could be attributed to the lack of the catalytic activity of the Pt electrode for reaction (4). An SO_3 partial pressure smaller than the equilibrium value certainly leads to a lower EMF response of the sensor.

Figure 7(a) shows an EMF response curve similar to figure 6(a) at the same working temperature but higher SO_2 partial pressure. A sharp increase of the EMF response can be observed when the SO_2 concentration increases, but when the SO_2 concentration changes to a smaller value, the EMF response is slower. It might be caused by the difficulty of the SO_2/SO_3 gas escape from the Pt electrode. Figure 7(b) shows the SO_2 dependence of the sensor EMF response calculated from figure 7(a). Here we also see the experimental EMF in good agreement with the predicted value.

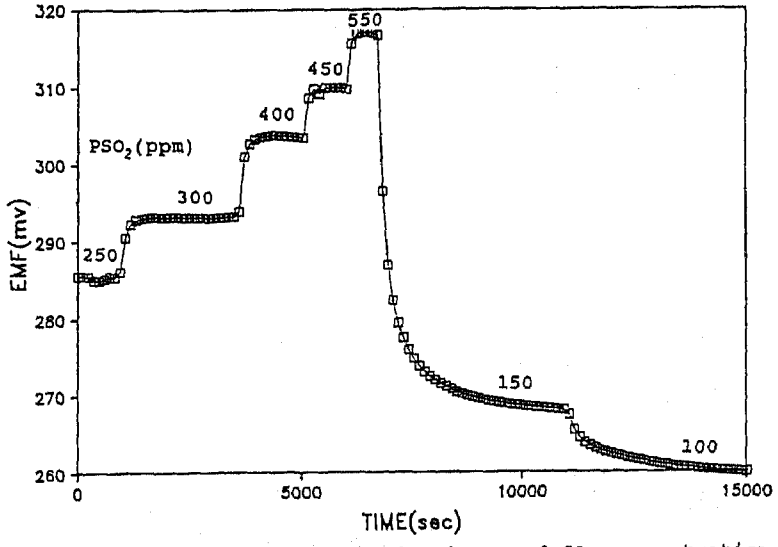

Fig.7(a) Sensor EMF response to the change of SO_2 concentration when Tw=615°C.

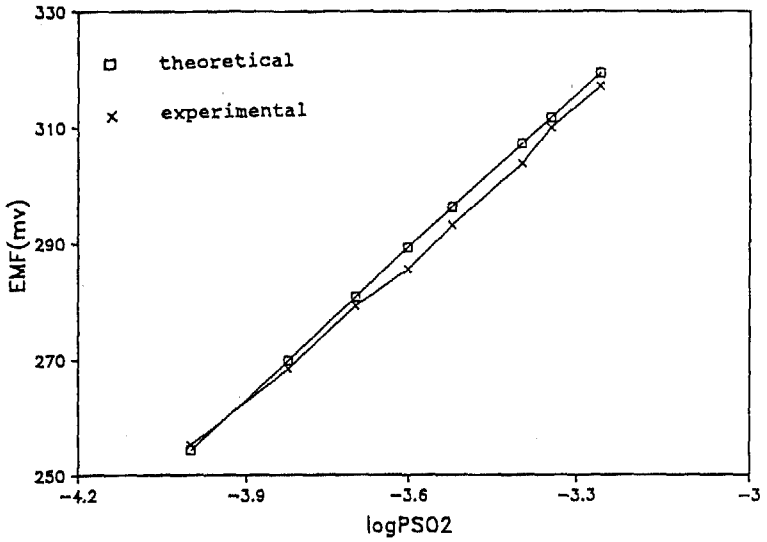

Fig.7(b) EMF response as a function of PSO_2 when Tw=615°C.

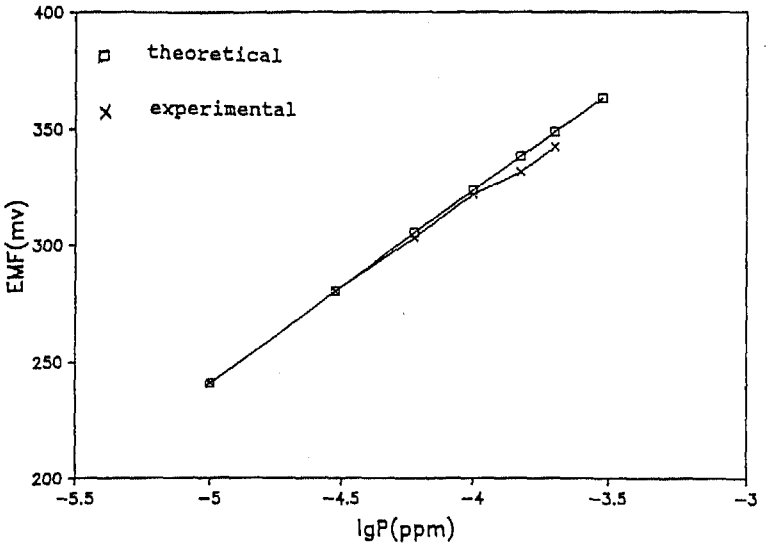

Fig.8 EMF response as a function of SO_2 partial pressure when Tw=565°C

Figure 8 gives another EMF response as a function of SO_2 partial pressure at the working temperature of 565°C. As is seen, the experimental EMF value fits the theoretical value quite well in the low SO_2 concentration range, however, a negative deviation was observed at high SO_2 concentration.

3.4 Temperature dependence of sensor response

The curves shown in figure 9 are the theoretical and experimental temperature dependence of the sensor EMF response when PSO_2=10ppm. Obviously, from 500°C to 700°C, the experimental EMF values are in excellent agreement with the theoretical ones at higher temperatures, while in the low temperature range, a negative deviation of the EMF output was observed. It may be because that the porous Pt electrode as catalyst is not enough for the equilibrium of SO_2 oxidation. If some other catalyst such as V_2O_5 can be used upstream in the gas system, the sensor response at low temperature could be improved.

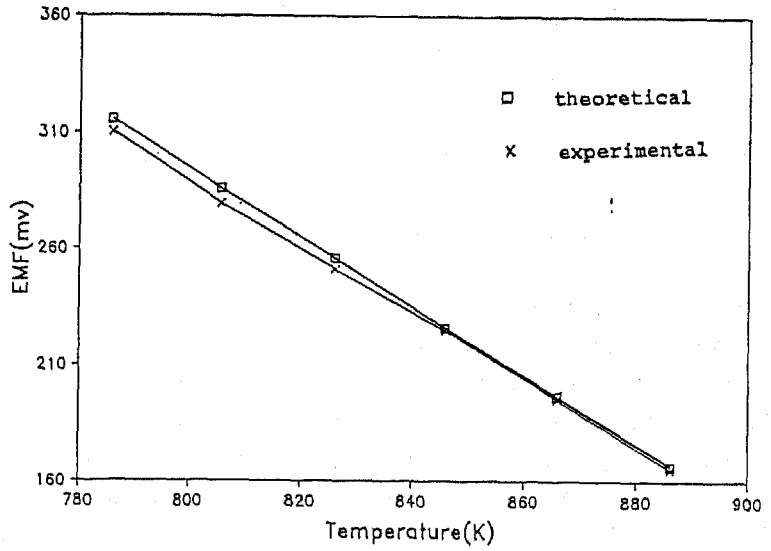

Fig.9 Temperature dependence of the sensor response when PSO_2=10ppm.

Figure 10 shows another example of temperature dependence of the sensor EMF response when PSO_2=100ppm. We can see that the experimental EMF fits the theoretical value quite well. Similar results were also obtained for other SO_2 concentrations in the range of PSO_2=10-1000 ppm.

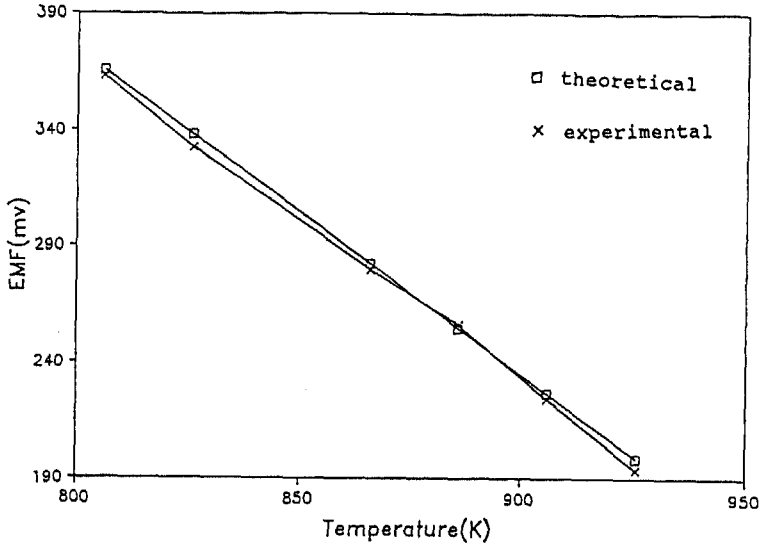

Fig.10 EMF response as a function of temperature when PSO_2=100ppm.

3.5 NO_x sensors EMF response

Two planar Ag-ß"-alumina NO_x sensors are being tested. it took a few hours to form a $AgNO_3$ layer in pure NO_2 and after that a constant EMF signal of about 420 mv was obtained at 150°C. Then a gas mixture of Ar, O_2 and NO was introduced into the system and it has been seen that EMF signal sensitively increases when NO concentration is higher. At 200°C, when NO concentration is around 500-1000 ppm and O_2 partial presure is about 15%, an EMF response within 300 mv can be observed. However, it takes as long as a couple of hours to get a stable response which may result from the low operating temperature. Two tubular NO_x sensors are also to be tested.

Based on the above results, it is clear that this Ag^+-ß"-alumina SO_X sensor could be developed by improving the catalytic activity of the porous Pt working electrode and it has prospect of commercial use. However, for NO_X sensors, the study has been just started and further efforts should be made to get improvement.

4.CONCLUSIONS

(1) Ag^+-ß"-Alummina polycrystalline materials were prepared from Na^+-ß"-Alumina by ion exchange reaction at 300°C in tha $AgNO_3$ melt. It has a typical polycrystalline surface morphology and the same lattice structure as Na^+-ß"-Al_2O_3. Its chemical stability is better than Na^+-ß"-Al_2O_3 which will make it easily used in practical measurements.

(2) Fully solid state SO_X sensor with a tubular Ag^+-ß"-alumina as solid electrolyte, silver metal as solid reference electrode and porous Pt as working electrode was fabricated in gas flowing system. When the temperature is higher than 500°C and the SO_2 concentration is in the range of 10-1000 ppm, the EMF output of the sensor shows a good Nernst response consistent with the theoretical prodiction, and the response time is usually about 5-10 mins. The experimental results indicate the potential of this SO_2 sensor in practical use.

(3) A preliminary study on planar and tubular Ag-ß"-alumina NO_X sensors has been started.

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