*A Sensor for Sulfur Gas Based on Silver β-Alumina

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ABSTRACT

EMF measurements were made with an electrochemical cell of the type

Pt/Ag(s)/Ag^+-beta alumina/Ag_2S(s), S_2(g), S(s or l)/Pt

at temperatures between 95 and 241°C. Silver β-alumina was prepared with the ion exchange technique. The patial pressure of diatomic gas obtained from cell voltages agreed with the literature data.

INTRODUCTION

A solid state galvanic sensor for gaseous sulfur ideally requires a sulfide ion conductor as the electrolyte /1/. At elevated temperatures, however, most metal sulfides are unstable in an oxygen-bearing atmosphere. A sulfur sensor was designed by using silver halide as the solid electrolyte and silver sulfide as an auxiliary electrode /2/. A disadvantage of such a sensor comes from the fact that silver halide forms a solid solution with silver sulfide at temperatures greater than 400°C /3/.

An alternate approach is to use Ag^+-beta alumina, which is predominantly an ag^+-ion conductor. The ionic domain or Ag^+-beta alumina was clearly delineated by Whittingham and Huggins /4/. In the present study, Ag^+-beta alumina was tested for its applicability as a solid electrolyte for a sulfur gas sensor. The electrochemical cell used in this study can be expressed as

Pt/Ag/Ag^+-beta alumina/Ag_2S(s), S_2(g), S(s or l)/Pt

Open-circuit cell voltage, E, of this cell reflects the chemical potential gradient for silver and is given by

$$E = -(RT/F)\ \ln a(Ag) \qquad (1)$$

where a(Ag) is the activity of silver at the $Ag_2S + S_2$ electrode fixed by the equilibrium reaction:

$$4\ Ag(s) + S_2(g) = 2\ Ag_2S(s) \qquad (2)$$

$$\Delta G^o(2) = RT \ln P(S_2) + 4\ RT \ln a(Ag) \qquad (3)$$

By combining equations (1) and (3), one obtains

$$\Delta E = -[\ G^o(2) - RT \ln P(S_2)\}/4F \qquad (4)$$

where $P(S_2)$ is the partial pressure of diatomic sulfur gas. By using the available literature data /5/ for $\Delta G^o(2)$, one obtains

$$\text{Log}\ \{P(S_2)/\text{atm}\} = \{20.16(E/\text{mV}) - 9{,}792\}/(T/K) + 4.831 \qquad 298 \le T \le 452\ K \qquad (5)$$

$$\text{Log}\ \{P(S_2)/\text{atm}\} = \{20.16(E/\text{mV}) - 9{,}175\}/(T/K) + 3.610 \qquad 452 \le T \le 1115\ K \qquad (6)$$

EXPERIMENTAL METHODS

Silver-β alumina was prepared by using the ion exchange technique described by Yao and Krummer /6/. A sodium β-alumina tube, containing about 20% Na_2O in excess of the stoichiometric composition $Na_2O.11Al_2O_3$, was immersed in molten silver nitrate and metallic silver at 250°C for 48 hours. The sodium-beta alumina tube, closed at one end with a flat bottom, had an outer diameter of 15mm, an inner diameter of 13mm and a length of 150mm. After removing from the silver nitrate, the tube was washed in methanol with an ultrasonic vibrator, dried and weighed. A weight increase of 22.6% was observed which corresponded to the formation of $Ag_2O{\cdot}7Al_2O_3$.

The experimental set-up is schematically shown in Fig. 1. A graphite crucible(A), which was contained in a graphite holder(B), was charged with elemental sulfur(C), which generates gaseous sulfur at elevated temperatures. The electrolyte tube(D), containing an Ag disk(E) in contact with its inner surface, was placed on the graphite holder. The outer surface of the tube was in contact with a disk of Ag_2S(F), which had been prepared by pressing Ag_2S powder in a steel die. The entire cell assembly was encased in a Pyrex tube(G). This pyrex tube was purged with flowing argon during emf measurement. The electrical contact to the electrodes were made with platinum wire(H). The temperature was measured with an alumel-chromel thermocouple(I) placed inside the silver-beta alumina tube.

All the emf measurements were based on four experimental runs and were conducted at temperatures between 95 and 241°C.

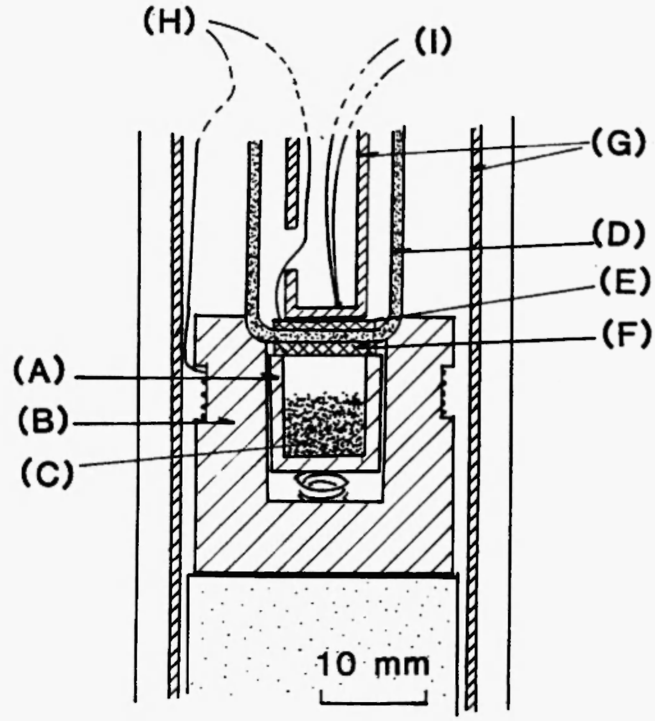

Fig. 1 Experimental set-up

(A) graphite crucible;
(B) graphite holder
(C) elemental sullfur;
(D) Ag^+-beta alumina tube;
(E) Ag disk;
(F) Ag_2S disk;
(G) pyrex tubes;
(H) platinum wires;
(I) alumel-chrome thermocouple

EXPERIMENTAL RESULTS

Fig. 2 shows the open-circuit emf as the function of time. Within a single experimental run, emfs were stable within ± 0.5 mV. Fig. 3 gives a summary of the experimental results based on four experimental runs. As shown in this figure, measured cell voltages were reproducible within ±2 mV and were in agreement with those reported by Kiukkola and Wagner /2/. These authors measured the potentials of the cell.

$Ag(s)/AgI(s)/Ag_2S(s)$, S(s or 1)

The relatively small scatter ± 2 mV could be attributed to errors in termperature measurement.

Values for $P(S_2)$ obtained from emf measurements are plotted against the recioprocal of absolute temoperature in Fig. 4. The results obtained in this study are in agreement with the data of Kiukkola and Wagner /2/. It is also worth

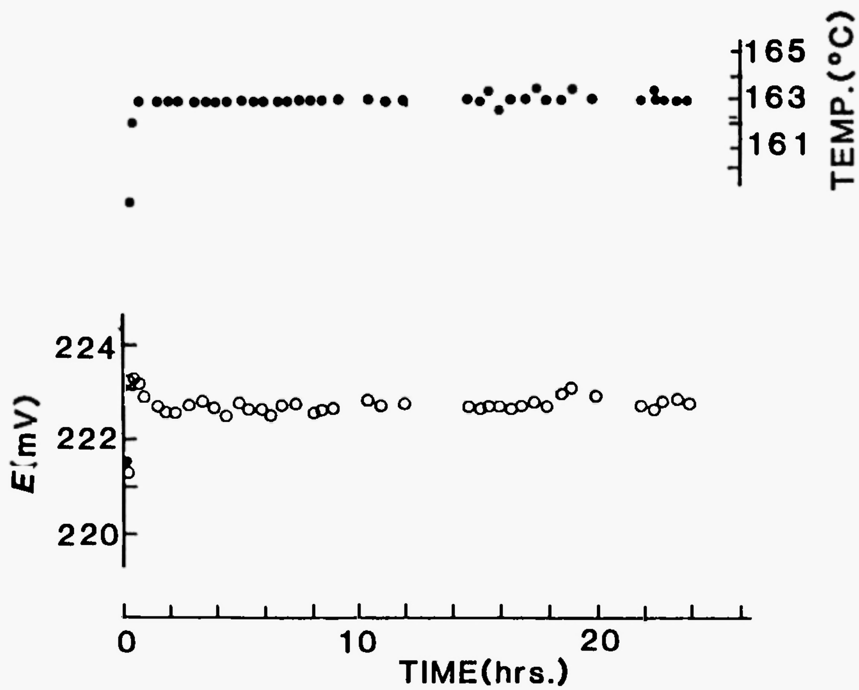

Fig. 2 Measured cell potentials as a function of time

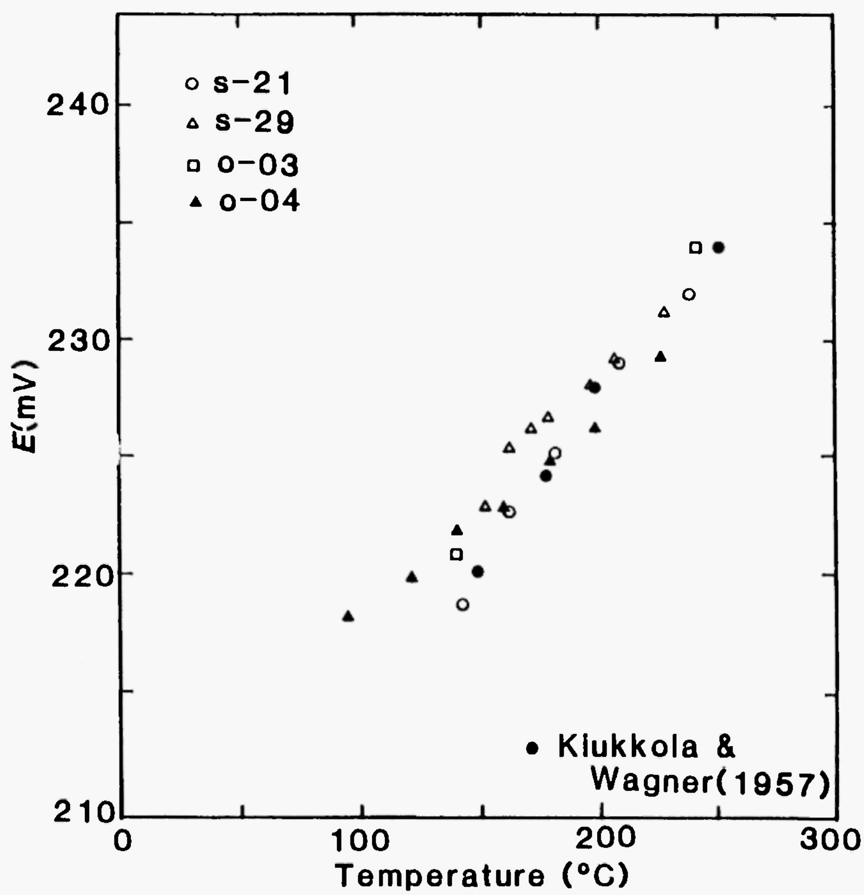

Fig. 3 Measured cell potentials as a function of temperature

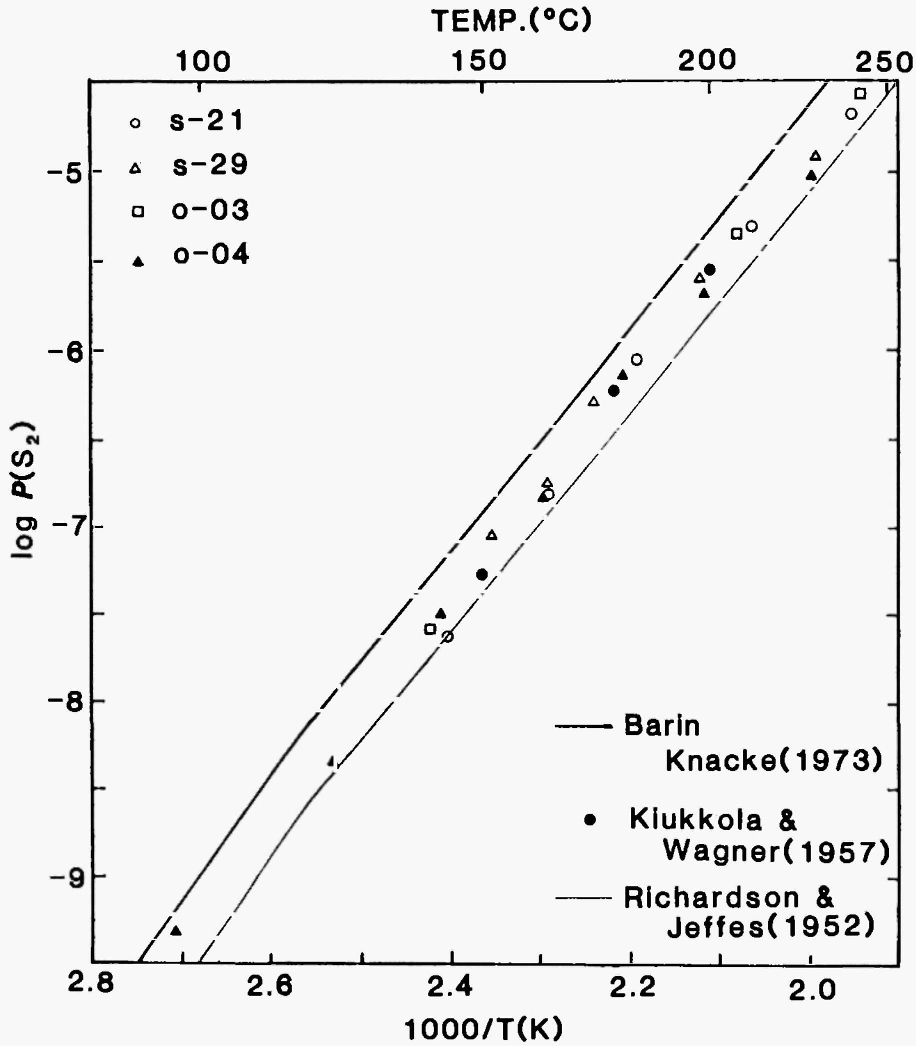

Fig. 4 The partial pressure of S_2 as the function of reciprocal temperature

mentioning that the present results are close to the average values for vapor pressure of sulfur obtained by Richardson and Jeffes /5/ and Barin and Knacke /7/.

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